DENDRIMER LIGHT-EMITTING DIODES

Stuart G. Stevenson

A Thesis Submitted for the Degree of PhD at the University of St Andrews

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Dendrimer Light-Emitting Diodes

Stuart G. Stevenson

A thesis submitted to the School of Physics and Astronomy, University of St Andrews in application for the degree of Doctor of Philosophy

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Abstract

The electronics industry today is one that stands as a multi-billion dollar industry that is increasingly incorporating more and more products that have ever escalating applications in our everyday life. One of the main sectors of this industry, and one that is likely to continue expanding for a considerable number of years are flat-panel displays. Traditionally, the displays market has been dominated by cathode ray tube (CRT) and liquid crystal displays (LCDs) display types. The drawback of such display displays is that they can be bulky, heavy and/or expensive and so there is considerable room for an alternative and superior technology. One possibility is organic semiconductor displays where light-emitting molecules can be dissolved in common solvents before being inkjet printed, spin-coated or even painted onto any surface giving the benefits of simple and cost effective processing. Organic light-emitting diodes (OLEDs) have recently become ever more evident as a major display type.

This thesis focuses on the advancement of light-emitting dendrimers towards flat-panel display applications. The particular interest in dendrimers arises because it has been found they are capable of giving solution-processed phosphorescent devices with high efficiency. Throughout the thesis the benefits of the dendrimer concept are repeatedly shown revealing why this could become the ideal organic material for display applications.

The thesis introduces various techniques of electroluminescence and photoluminescence measurements before applying such methods to study a large number of light-emitting dendrimers in order to explore the role of intermolecular interactions, how they are related to molecular structure, and how this determines photophysical and charge transporting properties of the dendrimers. By such studies a number of highly efficient solution-processed phosphorescent light-emitting dendrimers have been identified while the efficiency of devices made from these dendrimers has been improved. This has been demonstrated in each of the three primary display colours of red, green and blue. The work detailed thus brings closer the prospect of dendrimer light-emitting diodes being the future flat-panel display type of choice.
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Declaration

I, Stuart G. Stevenson, hereby certify that this thesis, which is approximately 80,000 words in length, has been written by me and it is the record of work carried out by me and has not been submitted in any previous application for a higher degree.

Stuart G. Stevenson July 25, 2008

I was admitted as a research student in September 2004 and as a candidate for the degree of Doctor of Philosophy in September 2004; the higher study for which this is a record was carried out in the University of St Andrews between 2004 and 2008.

Stuart G. Stevenson July 25, 2008

I hereby certify that the candidate has fulfilled the conditions of the Resolution and Regulations appropriate for the degree of Doctor of Philosophy in the University of St Andrews and that the candidate is qualified to submit this thesis in application for that degree.

Emargo

The following is an agreed request by candidate and supervisor regarding the electronic publication of this thesis:

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Stuart G. Stevenson July 25, 2008

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Stuart G. Stevenson

July 25, 2008
Acknowledgements

While my name appears on the front of this thesis it is only there because of the help and support of a number of people who have in many ways contributed to the success of this project, and for that I thank them.

To begin with there is my supervisor Professor Ifor Samuel. Many thanks are given to you firstly for an interesting, stimulating and exciting project (did I really say that) and secondly for giving me the help, support, assistance, interest, enthusiasm and advice whenever required, and of course the facilities, space and freedom in which to do my PhD.

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for your deep knowledge, kind patience and studious approach to device fabrication and the lessons this taught me. Your contribution of a number of measurements presented in this thesis is also acknowledged.

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And finally leaving St Andrews I head back over the bridge to Dundee where I meet up with some old friends and my family; thanks are given for your help and support throughout my PhD.
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Chapter 1

Introduction

Through time humans through their ingenuity have added to the vast range of natural resources our planet provides for us to give us an extensive array of materials many of which we now take for granted. One such family of materials are inorganic semiconductors, consisting of mainly silicon and germanium. The discovery that these essentially insulating materials could under certain circumstances conduct electricity has over the last sixty years spawned a revolution in electronics that today reaches into all aspects of our lives: from mobile phones, to digital audio players, to computers, and the internet; without this discovery it is unlikely any of this would be now possible. Electronics today form a multi-billion dollar industry incorporating more and more products that have ever increasing applications in our everyday life. One of the main sectors of this industry, and one that is likely to continue expanding for a considerable number of years, is that of the displays market.

Regardless of the display type the functional requirements are the same; to convert electronic information to visual information and then convey this information such that it can be seen and understood by a viewing human. Without a display to output the information any electronic device is effectively useless. Thus, the manner in which the information is conveyed through a display device is extremely important.

Traditionally, the displays market has been dominated by cathode ray tube (CRT) displays. CRTs operate by the principle of thermionic emission, which although effective, requires the use of high vacuum, and very high and potentially dangerous voltages for operation. As a result the display can be very heavy, cumbersome and bulky due to the large size and weight of all the required components. Nevertheless, for many years there was no alternative display commercially available with a number of small but effective
improvements and innovations keeping this display type dominant. As a result the CRT is a very reliable,
durable and robust display medium and is able to produce an image of very high contrast that is viewable
in high levels of illumination, and furthermore is able to accept a wide variety of video frequencies and
resolutions.

Over recent times the supremacy of the CRT display type has been effectively eradicated by the
emergence of flat-panel displays (FPDs) of which liquid crystal displays (LCDs) and plasma displays
currently predominate. LCDs are a non-emissive digital type display that have found an almost universal
application as laptop computer screens, where the flat, light display form more than compensates for the
limited brightness and contrast of such display types. On the other hand plasmas are an emissive display
type. The main advantage of this display type is that it offers a thin, light display with large viewing
angles, that gives high picture quality. It does however suffer from a short display lifetime in comparison
to both LCD and particularly CRT displays. Both these flat-panel display types are capable of producing
large area displays, but this is generally at high cost.

A further flat-panel display type are light-emitting diode (LED) displays that operate by utilising
the properties of semiconductors. Operation is by the direct conversion of electrical energy to visible
light, the colour of the light emitted determined by the choice of semiconductor used to provide the
emission. Solid state semiconductors are typically used for this and consequently LEDs have typically
long lifetimes. The main disadvantages of such a display type are that an LED although small and durable
is not very bright, giving perhaps a luminous power of 3 lumens/watt, and thus are only really suitable
for low brightness applications. Where high brightness is needed a number of LEDs are required to be
bundled together, this leading to heat generation and dissipation problems. Furthermore, LEDs are grown
from the epitaxial growth of sequential layers of semiconductor, one on top of the other, and therefore
the quality of the final emitted light will strongly depend on the purity and structural precision of each
layer used.

Alternatively, more recent research has focused on LEDs constructed from organic semiconductors
with some very exciting results so far obtained. These organic materials can have plastic-like properties.
Plastics are found in applications as diverse as piping, compact discs, packaging, and electrical equip-
ment. In each case its use extending from its unique abilities and properties: it can be synthesised into
any shape or form; it is able to provide rigidity or strength if required, or malleability if not; while it can,
depending on the requirements, be amongst many other things transparent, heat resistant and insulating,
or as will be discussed in this thesis semiconducting. Just as we have had periods of history termed the Stone and Iron Ages, perhaps in centuries to come, this time at the end of 20\textsuperscript{th} century and beginning of the 21\textsuperscript{st} century will become to be known as the Plastic Age.

Plastics are synthetic long chains of atoms that are more correctly termed polymers, as in reality they are constructed from a large number of small repeating molecular groups or monomers. In general the atoms that form the main atom chain (or backbone) are carbon, to which principally hydrogen atoms are bonded with small amounts of other atoms such as nitrogen and oxygen also present. In some cases the arrangement of this bonding is such that the organic material is capable of demonstrating the characteristics of a semiconductor, and thus forms an alternative type of semiconductor to the traditional inorganics. The attraction of a semiconducting or conjugated polymer is immediately apparent: the inherent simplicity of manufacture allied with the ability to deposit from solution the semiconducting layer means cheap and simple processing with large area deposition, and even flexible substrates become possible.

Furthermore, such conjugated polymers are capable of emitting light across, and indeed beyond, the visible range, and can thus be used to form electroluminescent organic light-emitting diodes (OLEDs). This effect has been known since 1960s, where by subjecting thick films of crystalline anthracene to high voltages very unstable electroluminescence was found \cite{1,2}. This and subsequent work by others identified the main processes required for electroluminescence, namely the injection of electrons from one electrode and holes from the other, the capture of holes by electrons, and the radiative decay of the excited state produced by this recombination process. However, the short lifetimes and very low efficiencies of the organics considered meant electroluminescent organic devices were not overly successful at this stage.

Some years later in 1977 groups led by Heeger, MacDiarmid and Shirakawa \cite{3}, discovered that after doping conjugated polymers could be found to possess semiconducting properties. This discovery heralding a birth of a new field of research at the boundary of chemistry and physics. The importance of their discovery was recognised by the award to each of The Nobel Prize for Chemistry in 2000 \cite{4,5}.

In 1987 the first structure capable of effective and reasonably efficient electroluminescence in a thin film device was realised by a group at Kodak led by Tang and VanSlyke \cite{7}, thereby effectively creating the dawn of the organic semiconductor display industry. These initial OLED devices employed evaporated organic layers sandwiched between two electrodes to provide the required charge injection
and recombination to allow the electroluminescence to occur.

In 1990 the first report of electroluminescence from a conjugated polymer was recorded by a group at Cambridge led by Friend, this giving the second seminal publication of the field \[8\]. Their devices, based on a soluble polymer, poly(\textit{para}-phenylene vinylene), demonstrated that cheap, easy to process devices were possible using light-emitting polymers; this discovery leading to the creation of the spin-out company Cambridge Display Technology (CDT) that today is a world leading company in such organic displays. While light-emitting displays are currently the main application for conjugated polymers, these materials are also increasingly being used for solar cells, field effect transistors and organic lasers amongst many other applications due to the inherent advantages such materials bring.

Although great steps have so far been taken towards fully understanding the physics underpinning the behaviour of organic semiconductors there still remains much unknown. In particular, the effect of the conjugated polymer’s photophysical properties on its electrical behaviour has so far not been fully explained. In part this is due to the complicated nature of the disordered structure of the organic that is found to be strongly dependent on both the nature and effect of the processing conditions of the polymer.

The focus of this thesis was the advancement of a new class of organic semiconductor. These novel molecules termed dendrimers, shaped like a snowflake in three dimensions, are made up of branches which control the molecules behaviour. Similar to polymers they are completely soluble in a wide range of solvents so can be easily painted, printed or more commonly spin-coated from solution. This work concentrates on the use of use of dendrimers as a source of light emission for flat-panel display applications. In particular this thesis details work undertaken to further advance the current knowledge of dendrimer OLED device physics through electroluminescence and photoluminescence measurements. The materials chosen to be investigated are studied in order to explore the role of intermolecular interactions, how they are related to molecular structure, and how this determines photophysical and charge transporting properties of the dendrimers.

The thesis begins in Chapter 2 with an introduction to the basic organic physics of conjugated semiconductors, their uses and current problems in displays, before presenting the possible solution to those problems with the class of organic semiconductor known as the conjugated dendrimer. The chapter concludes with a description of how such organic semiconductors can be made into devices capable of emitting light - the organic light-emitting diode (OLED). Chapter 3 details the methods and techniques used to make such devices and characterise these materials both photophysically and electrically.
The experimental results sections of the thesis begin in Chapter 4. This chapter details an introduction and overview of the standard solution-processable light-emitting iridium(III) cored dendrimers and how some of the problems of these materials have been overcome to enable the fabrication of highly efficient OLEDs. In Chapters 5 and 6 the fundamental benefits of the dendrimer system were demonstrated. In particular it was investigated how by careful choice of the organic structure the dendrimer properties can be modified to change the hole or electron charge carrier transport properties.

In Chapter 7 the process of hole-carrier charge transport was again considered within dendrimers. In this chapter a number of devices were deliberately constructed so as to only contain one type of charge carrier and thus were non- emissive. In this way the charge transport of the carrier could be determined and subsequently through modelling allow a better understanding of the charge transport behaviour within the device to be determined.

The versatility of the dendrimer approach was again demonstrated in Chapter 8 where by simply changing the surface groups - the parts that infer the solubility to the dendrimer - the dendrimer could be made to behave so that it no longer became solution-processable after deposition, such that it could not be washed subsequently away. The use of such photo cross-linkable dendrimers allowed the previously unattainable possibility of multi-layer solution-processable dendrimer devices to be realised, where each layer could, as in those made solely by evaporation, be individually optimised to maximise the device performance.

The concluding experimental chapter, Chapter 9, considered an advanced class of organic semiconductor, that of the double dendron dendrimer. The chapter details that by careful choice of the chemical structure the colour of emitted light could be changed from the standard green to give either red or blue coloured light emission. The thesis concludes with Chapter 10 in which main results and ideas of the previous chapters are discussed and brought together.
Chapter 2

Organic semiconductors

2.1 Introduction

The majority of integrated circuits and devices that rely on semiconductors for their operation are currently made from inorganic materials such as silicon. Consequently, they are neither simple nor cheap to produce and offer little possibility of flexible electronics. Solutions to these problems are presented with the use of organic semiconductors, including conjugated polymers. Surprisingly the semiconducting behaviour of certain organic materials although relatively new to electronic applications is actually all around us and has always been here; without the conjugated molecule chlorophyll, photosynthesis, the basis for sustaining the life processes of all plants, would not be possible. The replication and synthesis of such conjugated organic materials has allowed many applications to become possible including displays.

This chapter describes the operation of an organic light-emitting diode (OLED) device from application of bias voltage to create a field across the organic layer enabling charge injection, transport, capture and subsequent light emission. The requirements of the organic materials that will allow this process to occur are detailed, introducing the concepts of how conjugation allows certain organics to act as semiconductors and emit light. The photophysical behaviour including the absorption and emission processes of organics are described. Material design and synthesis is considered and it is shown how knowledge of this combined with photophysical information can be used to maximise the performance of an OLED device. The phenomenon of triplet emission is detailed illustrating why this is vital for efficient light emission in devices. The chapter continues with the introduction of the dendrimer concept explaining
why dendrimers are often said to be an ideal organic semiconductor for light emission. The chapter concludes with some performance measures that are standardly used to evaluate device operation.

2.2 Plastics and Polymers

Organic chemistry derives its name from the original thought that it related to the study of chemical compounds related to life processes. Now it is applied to the chemistry of carbon, so making this study grouping one of the largest and most important in the world today. Oil is the lifeblood of modern industry yielding products such as petrochemicals and fuels, from kerosene to bitumen to petrol that almost all of transport and industry today relies on for energy. Paints, explosives, fertilisers, drugs and plastics are just some more of the many diverse products that can be yielded from oil. Although such materials are all very different they share many similarities in particular they are all organic; that is they all based on arrangements of carbon atoms. Simply put carbon is the backbone of all organic life - bonded with hydrogen it forms flammable compounds required for the production of fossil fuels; bonded with oxygen it gives the carbon dioxide essential for plant growth.

In a pure form carbon can exist in one of three distinct forms. The first is graphite, a flat sheet-like structure capable of acting as both a lubricant and a electrical conductor. The second is the well known form of diamond - lasts forever, a Girl’s Best Friend... a transparent crystal of tetrahedrally bonded carbon atoms highly priced and desired due to its exceptional physical properties, the most obvious being its lustre and high dispersion index giving its widespread use for jewelry. Of equal importance are its high thermal conductivity, its ability to conduct in some forms and most importantly its extreme hardness making it an excellent abrasive. Finally there are the fullerenes - a newer form of carbon where the atoms are arranged in a ball or tube shape. This from of carbon may perhaps in the future become the most important due to the potential such materials have for applications in electronics and in particular nanotechnology.

The fact that these same carbon atoms can lead to such diversity is due simply to the effect that the bonding arrangement of the large chains of carbon atoms can have on the chemical and physical properties of the molecule. In this work the arrangements of bonded carbon, with hydrogen, and often also with oxygen and nitrogen atoms also present, are through a conjugated bond system. With such conjugated bonds polymers are formed.
2.2.1 Conjugated Polymers

Polymers that possess arrangements of alternating single and double bonds between the carbon atoms are termed conjugated polymers; it is this arrangement that enables the organic molecule to exhibit semiconducting behaviour. Carbon (C) is found in group four of the periodic table and thus for a stable bonding arrangement requires the addition or removal of four valence electrons. To achieve this when more than one carbon atom is present in a chain single, double and triple bonds are possible. This is true as carbon with atomic number 6 has six electrons and hence an electronic groundstate configuration of \(1s^22s^22p^2\). That is two of the six electrons are contained in the inner 1s shell or orbital with the remaining four electrons in the outer orbitals. Hence it could be expected that two of these outer electrons occupy the inner s shell and the remaining two the outer p shell formed by three p orbitals, yet this arrangement does not give a stable electronic arrangement. In fact bonding arises from the 2s orbitals mixing with the unpaired outer orbitals (say \(p_x\) and \(p_y\)) to form four hybrid orbitals. These hybridised orbitals are in the configuration \(sp^2\). The new orbital arrangement is shown in Figure 2.1 which reveals that three hybrid \(sp^2\) orbitals each lie in the xy plane at an angle of 120° to each other. The remaining unhybridised p orbital (\(p_z\)) lies perpendicular to the plane of the \(sp^2\) orbitals sharing the remaining two electrons between the 2p orbitals and extending above and below the bonded carbons. This bond is termed a pi (\(\pi\)) bond. This new arrangement gives four covalently bonded orbitals each containing one valence electron, in this way the carbon-carbon double bond is formed.

Consider the bonding arrangement shown in Figure 2.1 which enables the bonding found in conjugated organic semiconductors to be more easily understood and explained. For example, the most simple case is the two carbon atom chain of ethene shown in Figure 2.2. This molecule, with four valence electrons for each carbon atom, has three \(sp^2\) bonds for each one of the carbon atoms; all contain one electron and can combine and bond with the carbon and hydrogen atoms to share electron pairs between them, in this way all the \(sp^2\) orbitals are filled. This type of bond is a single covalent bond commonly termed a sigma (\(\sigma\)) bond and gives for ethene the arrangement shown in Figure 2.3. The double bond in molecules such as ethene is formed from the additional contribution of the remaining 2p orbital, the (\(\pi\)) bond. A double bond always consists of a \(\sigma\) and \(\pi\) bond such as shown in Figure 2.4.

As the \(\sigma\) bond is between two carbon atoms and has no free electrons to conduct, the \(\pi\) orbital is said to be localised between the two carbon atoms. This strong bonding is essential for holding the molecule together. In contrast due to the weak overlap of \(p_z\)-atom orbitals the other electron in the \(\pi\) orbital is
more delocalised. Such electrons are much more free to move or conduct. By adding more carbon atoms to ethene, regularly alternated double and single bonds can be formed. A conjugated polymer is thus made up from a large arrangement of double bonds and hence the the number of \( \pi \) orbitals will also very be large. The smallest example of such a molecule is a 1,3-butadiene while Figure 2.5 shows a longer chain version of such a polymer. As the number of the \( \pi \) bonds increases both the number of anti-bonding states (empty energy levels) and bonding states also increase. Such states form two pseudo continua of energy levels separated by an energy gap. This energy gap decreasing in size as the splitting of both states becomes smaller. The repeated alternation of bonding type, i.e. conjugation, on which the \( \pi \)-electrons are delocalised will provide extended conductivity. Electrons are free to move up and down the carbon-carbon chain until the conjugation is broken either by intent (the inclusion of other atoms or groups in the chain) or by accident (kinks, twists and contortions in the chain) \[11\]. The distance along the chain over which the conjugation occurs is termed the conjugation length.

As noted above, a polymer, such as that shown in Figure 2.5 is simply a long chain of conjugated lengths or molecules bonded together to allow the electron delocalisation cloud to extend along the en-
CHAPTER 2: ORGANIC SEMICONDUCTORS

Figure 2.5: A long chain polymer showing the overlapping $p_z$ orbitals forming a delocalised cloud of electrons [14]

Figure 2.6: The benzene ring shown in (a) with its full structure representation and in (b) as a simplified structural representation

tire chain. This is possible due to the overlapping orbitals - the overlap being equal in both directions along the chain allowing the electrons to be delocalised along the entire chain. Subsequently, there is one $\pi$-electron per carbon atom which would be expected to give a half-filled band and hence metallic like conduction behaviour. However, it is found that the preferential energy state for this material is the formation of alternating single and double bonds. Hence, if one electron is added to the end of the chain it is able to move anywhere along the orbital - the conjugated molecule is capable of conduction of both positive and negative charges along its entire length. Semiconducting properties are thus possible as the overlapping orbitals give rise to bands - the linear combination of atomic orbitals (LCAO) theory. This behaviour is similar to that which applies in the inorganic semiconductor silicon. Conjugated polymers behave not as one dimensional metals but in the same way as silicon; both are wide bandgap semiconductors.

In the classic case of the six carbon atom chain, the circular $C_6H_6$ structure is formed. This structure, termed the benzene ring and shown in Figure 2.6, is the basis from which many polymers are constructed. In the structure each of the six carbon atoms are bonded to two other carbon atoms in the ring through an arrangement of three double bonds and three single bonds in an alternating pattern. This arrangement allows electron delocalisation throughout the entire ring structure.

10
2.2.2 Energy levels and bonding

Despite the large differences found between organic semiconductors and the classic inorganic semiconductors such as silicon, they have many of the same basic principles describing their behaviour. As a result some models (e.g. Reference [15]) have tried to adapt the inorganic picture to organics, translating the top of the inorganic semiconductor valence band into the polymer ionisation energy which is usually referred to as the energy of the Highest Occupied Molecular Orbital (HOMO). Similarly, the bottom of the inorganic semiconductor conduction band is equated to be the Lowest Unoccupied Molecular Orbital (LUMO) which is the polymers electron affinity energy. Such models were able to describe some simple structures but in general it was clear such a model was not sufficient.

In contrast, other models such as in Reference [16], introduced the concept of an exciton and were found to be more successful describing a wide range of polymers. In such models the oppositely charged holes and electrons are attracted to each other and then together held by Coulombic forces to form a bound state termed an exciton. This bonding is not a strong form of bond, but is sufficient to hold the hole and electron together as the exciton moves through the polymer chain without restriction, so enabling the exciton to find and occupy low energy locations from which they can emit.

Previously the molecule of ethene shown in Figure 2.2 was described as having two electrons within the \(\pi\) bond located above and below the C-C \(\sigma\) bond. Reconsidering this arrangement it is noted that in order to completely fill the electron shell a further two electrons are required; that is the \(\pi\) bond has four energy levels which electrons can occupy, only two of which are occupied in ethene. These four energy levels are termed \(1\pi\), \(2\pi\), \(3\pi^*\) and \(4\pi^*\).

Figure 2.7 shows how such states are located in a molecule of 1,3-butadiene. In this case \(*\) refers to anti-bonding states with no star implying bonding states. In this arrangement the HOMO is the \(2\pi\) state below which all states are completely occupied whilst the LUMO is the \(3\pi^*\) state above which all energy levels are free. As both energy levels are within the \(\pi\) orbitals transitions between them are termed \(\pi \rightarrow \pi^*\) transitions. The location of the \(\pi\) electrons in the higher occupied orbitals means they are most easily excited into the \(\pi^*\) state. As in conjugated molecules there are a large number (N) of bonding (\(\pi\)) and anti-bonding (\(\pi^*\)) orbitals, then the HOMO and LUMO can be thought of as analogous to the valence and conduction bands in the classic inorganic semiconductors.
2.2.3 Absorption and emission

The analysis of the absorption and emission properties of a conjugated semiconductor is a simple way to determine its electronic characteristics. Typically this is achieved through the use of a one-dimensional plot termed a configuration diagram such as shown in Figure 2.8. This figure gives the molecular potential energy plotted against the molecular co-ordinate [16], the lower part of the figure also shows the corresponding absorption and emission spectra.
2.2.3.1 Absorption

The process of absorption is shown in the left hand side of Figure 2.8. In the configuration plot in the upper part of the diagram, an excited ($S_1$) and a ground state ($S_0$) are shown. The plot shows these energy levels to be deliberately offset from each other, this is because the nuclear configuration coordinates of the ground and excited states are offset.

At room temperature the spacing of the energy levels is such that only the lowest energy level of the ground state is populated. The absorption of a photon then causes the excitation of an electron from this energy level to a higher vibrational level of the excited state. The ground state sub-level excited depends on the energy of the incident photon. The overlap of the ground and excited state wavefunctions determine the probability of excitation to a particular vibronic sub-level of the excited state. The transitions occur according to the Franck-Condon principle, which states that as the time of an electronic transition is much less than that for a nuclear rearrangement, the transition will be completed before the nuclei can change itself. Consequently in the configuration diagram, transitions are drawn as vertical lines.

2.2.3.2 Emission

The process of light emission, or luminescence, is shown in the right hand side of Figure 2.8. Simply put, this is the reverse case or mirror image of the absorption process, that is electrons excited to higher energy levels decay to the ground state with the emission of a photon. This process occurs because when an electron is raised to the excited state energy levels, the electron will eventually decay to the lowest energy excited energy level state by non-radiative processes such as phonon or heat emission. Some time later this electron then decays radiatively down to any of the ground state energy levels with the emission of a photon. The energy level the decay terminates in determines the energy of the emitted photon and leads to the emission spectrum shown in the lower part of the right hand side of Figure 2.8. Finally some time later electrons in higher ground state energy levels will decay non-radiatively to the lowest ground state energy level. As energy has been lost as heat, the emitted photon will be of longer wavelength than that of the excitation photon. The difference in the peak of the fundamental absorption and fluorescence bands is known as the Stokes shift. The effect of which is shown in Figure 2.8.

Of course not all the electrons excited to higher energy levels on photon absorption will result in the
emissive decay of a photon on returning to the lower energy level state, both non-radiative and radiative
paths are possible. The relative rates of these processes determine the efficiency of the light emission. For
efficient light emission non-radiative processes should be minimised and radiative paths maximised. The
standard measure of the luminescence efficiency of a material is the ratio of photons absorbed to photons
emitted - often termed the photoluminescence quantum yield (abbreviated PLQY or \( \Phi_{PL} \)). Hence for
maximum efficiency high PLQY is desired.

2.2.4 Singlet and triplet emission

Electrons are known to possess the property of spin \([9]\) that can only be in one of two states: spin up \( (+\frac{1}{2}) \)
or spin down \( (-\frac{1}{2}) \), and as orbitals or energy levels can only contain two electrons, these two electrons
must be of opposite spin to maintain the Pauli Principle. Hence, the result of an excitation will depend
crucially upon the spin of the excited electron and hole. Two types of excitation are possible: singlet
and triplet. The singlet is defined using a spin-asymmetric (total spin \( S = 0 \)) wavefunction, whereas the
triplet emission is a spin-symmetric transition \( (S = 1) \). Through elementary statistics it is apparent that
two electrons can at least theoretically be in any one of four combinations. Three of these lead to triplet
states (Equations 2.1 to 2.3 below), with one leading to a singlet state (Equation 2.4).

\[
S = |\uparrow\uparrow| \quad (2.1)
\]

\[
S = |\downarrow\downarrow| \quad (2.2)
\]

\[
S = (1/\sqrt{2})(|\uparrow\downarrow + \downarrow\uparrow|) \quad (2.3)
\]

\[
S = (1/\sqrt{2})(|\uparrow\downarrow - \downarrow\uparrow|) \quad (2.4)
\]

In singlet emission due to the inherent asymmetric ground state, the spins are never aligned and the
transition is always capable of producing a radiative decay through optical (photoluminescence) processes as shown in part (a) of Figure 2.9. This is termed fluorescence and can occur within nanoseconds of the original excitation.

### 2.2.4.1 Phosphorescence

Figure 2.9 also shows the process of triplet emission. As part (b) of the figure shows, triplets are located at a lower energy than the singlet state. Subsequently, electrons originally in the singlet state are also able to decay into the triplet state - intersystem crossing - before being emitted from the triplet state. This is termed phosphorescence and because of the spin forbidden nature of this process is significantly slower, and in most cases very inefficient. However, with careful design of the chemical structure through the inclusion of heavy metal atoms such as iridium or platinum efficient phosphorescence is possible.
2.2.4.2 Electroluminescence

For electroluminescence, that is electrical excitation, all four electron spin combinations are possible. For every three triplet excitons only one singlet exciton is produced - only one quarter of the excitons generated are capable of emitting light efficiently as all the triplets will be wasted. This further implies the maximum efficiency of any organic electroluminescence device will be limited to a maximum of 25 % [17, 18]. This ratio has long been accepted and confirmed by experimental evidence for small molecules [19, 20]. For conjugated polymers there is some debate about the ratio [21–24], but it is clear that the triplet formation is a substantial loss mechanism.

As a result research is focused into systems that allow such triplet emission to be utilised through the conversion of the triplets into singlet states prior to emission by, for example, the use of heavy metal cored small molecules [21, 25], organic semiconducting materials capable of direct phosphorescent emission such as dendrimers [26, 27], the incorporation of electron transporting materials into the emissive layer or device structure [22], and the the inclusion of fluorescent dyes into the emissive organic layer [21, 23, 24].

2.2.5 Intermolecular Interactions

Obtaining the PLQY of an organic semiconductor is an important measurement that enables a direct determination of the effectiveness of the material. The results of such measurements will be strongly dependent on the environment in which the material is measured. This arises as neighbouring atom interactions can have a strong effect on the material enhancing or quenching its luminescence efficiency. As a result PLQY values measured from solutions, where atoms are more isolated and such interactions are minimised, can be greatly different from those found in the bulk material. This is because in the bulk material the formation of excimers (excited state dimers) and aggregates (physical dimers) are highly probable. This leads to a quenching of the luminescence and a reduction in the PLQY of the organic material [16].

2.2.5.1 Physical Dimers

In chemistry the term dimer is used to describe a molecule consisting of two identical monomers bonded together. In contrast a physical dimer describes the case where although two identical molecules are very close together they are not in fact bonded together. In a conjugated polymer where a number of identical
Figure 2.10: Exciton splitting in dimers with the two extreme geometries. The short arrows represent the orientations of the monomer transition dipoles, dotted lines present dipole forbidden transitions. Adapted from [16]

molecules are packed in close proximity physical dimers (or aggregates) can readily result. This occurs when the wavefunctions of two identical closely spaced molecules overlap. This leads to a modification of both ground and excited state wavefunctions which results in a change in the absorption and emission spectrum.

The luminescence from aggregate states tends to be broad and featureless, and can, depending upon the orientation of the interacting molecules, result in a blue or red-shift in the absorption or emission spectrum. Figure 2.10 explains the reason for this in an absorption spectrum. In comparison to a monomer state the presence of a dipole results in the splitting of the energy levels, with the emission normally occurring from the lower energy site. Organic molecules possess dipoles that act to affect the interaction between individual molecules (and light). The orientation of the dipole determines as shown in the figure the relative contributions of each of the two lines of the doublet.

At their extreme the dipoles align in one of two positions. For dipoles aligned in parallel, the lower energy level becomes dipole forbidden and a blue-shift in the emission results. In the other extreme case for where the dipoles are aligned head-to-tail, a red-shift in the emission results as the higher energy level is forbidden. Of course in reality, the dipoles are likely to orientate at some angle to each other resulting in a splitting of the bands with both lines of the doublet contributing. In this case a simple vector addition is used to describe the behaviour [16].

By their very nature the effect of physical dimers increases as the molecular packing increases. Thus in a dilute solution where molecules are very able to adapt any position and space themselves apart the effects of physical dimers are minimal. In contrast on moving to a thin film the close packed molecules mean there will often be a significant contribution from physical dimers in any given spectrum [16].
2.2.5.2 Excimers

Excimers, or more correctly excited state dimers, also lead to unwanted contributions to the emissive spectrum of organic molecules. As for physical dimers their presence leads to broad and featureless luminescence. Excimers require an excited molecule to exist and thus are only present in an excited state. They are formed between two molecules that would otherwise not bond if both were in the ground state, in fact in the ground state they dissociate and the force between them is repulsive. The emission wavelength of an excimer is longer than that of the excited monomer and thus can be measured by fluorescence emissions [16].

Due to the nature of its excited state the lifetime of an excimer is very short. Similarly as it is formed by a bimolecular interaction, is only really observed at high monomer densities. At low density it is more probable that the excited monomers will decay to the ground state before they are able to interact with an unexcited monomer to form an excimer.

The reactions that give rise to excimer formation can be summarised as:

\[ S_1^* \rightarrow S_0 + h\nu_M \]  
(2.5)

\[ S_1^* + S_0 \rightarrow E_1^* \]  
(2.6)

\[ E_1^* \rightarrow S_0 + S_0 + h\nu_E \]  
(2.7)

In Equation 2.5 the excited state decays to the ground state to give monomer emission that is normal fluorescence. Alternatively in Equation 2.6 the excited state \( S_1^* \) can undergo collisional quenching with the ground state \( S_0 \) to give the excimer state \( E_1^* \). Finally in Equation 2.7 the excimer decays radiatively to the ground state, giving two ground state molecules and the emitted photon [16] with energy \( h\nu_E \).
2.3 Small Molecules

An alternate class of semiconducting organic materials to conjugated polymers are the small molecules. An example of this class of material is the 8-hydroxyquinoline aluminium (Alq$_3$) complex with structure shown in Figure 2.11 that was used by Tang and VanSlyke [7] in the first OLEDs. Since then it has perhaps become one of the most widely understood organic semiconductor due to the large number of studies presented on it.

Small molecular materials such as Alq$_3$, offer an attractive prospect as an organic semiconductor because their simple and highly defined exact molecular structure makes their synthesis and purification relatively simple compared to that of a conjugated polymer. The main disadvantage of such semiconductors are they are not soluble and so must be deposited through expensive high vacuum thermal or vapour phase deposition evaporation techniques [24, 28–30]. In common with conjugated polymers small molecules also possess the problems typical to any organic such as aggregation and excimers.

![Figure 2.11: Molecular structure of 8-hydroxyquinoline aluminium (Alq$_3$)](image)

2.3.1 Iridium Complexes

A major advance in small molecular OLEDs was the use of phosphorescent materials as this enabled efficiencies far in excess of those obtainable with conjugated polymers to be achieved. Initially phosphorescence in small molecules was only observed with the inclusion of phosphorescent dyes that allowed emission from both singlet and triplet states [21, 31]. In these initial materials low photoluminescence efficiencies prevented high efficiency devices being made. In later materials these problems were able to be overcome by considering only those that possessed both reasonable photoluminescence efficiency and short triplet lifetimes, such as the classic small molecular green electroluminescent iridium(III) complex fac tris(2-phenylpyridyl) iridium [Ir(ppy)$_3$] with structure shown in Figure 2.12 [25, 32].
Small molecular materials such as Ir(ppy)$_3$ are able to show phosphorescence because of the heavy metal atom at the core, in this case iridium, that is capable of emission via a metal-ligand charge transfer (MLCT) state [32, 33]. The presence of such atoms is found to induce strong spin-orbit coupling leading to mixing of the singlet and triplet states. This acts to reduce the triplet lifetime by increasing the transfer rate of the triplet states to the singlet state through Dexter energy transfer processes. As a result both singlets and triplets can contribute to the emission overcoming the limitations imposed by spin statistics and allowing internal quantum efficiencies of up to 100 % to be realised [26, 33, 34].

2.4 Conjugated Dendrimers

The possibility of solution-processable organic materials is for industry a very attractive prospect as it would allow such materials to be deposited using standard printing techniques, thereby leading to significant cost advantages for mass production. Conjugated polymers offer this solution-processable possibility but are often harder to synthesise and purify than small organic materials. This is due in part to the inherent polydispersity resulting from their synthesis meaning there can be large batch-to-batch variation in properties.

Dendrimers, or more precisely conjugated dendrimers, are often said to be the perfect organic semiconductor for display applications combining the advantages of conjugated polymers with those of small molecules whilst maintaining none of the drawbacks of either. Such materials are, in common with conjugated polymers, readily solution-processable and thus have simple and cost-effective processing. In addition being based on small molecules they also have the potential for 100 % internal quantum efficiency through the ability to harvest triplet states. In contrast to conjugated polymers and small molecules dendrimers are a much newer class of organic semiconductors. Hence, although considerable knowledge
has thus far been gained about such semiconductors, there is still much to be learnt and discovered regarding their physics, an issue this thesis addresses in regards to their application for light-emitting diode displays.

2.4.1 The dendrimer concept

Conjugated dendrimers consist of three components such as shown in the schematic of Figure 2.13: a luminescent core, dendrons or conjugated branches, and surface groups [35–40]. These three components can be individually varied to tune the electronic and processing properties as required. The core controls the electronic properties such as the colour of the emitted light; the surface groups control the solubility; and the conjugated dendrons control the intermolecular interactions of the core. A particular advantage of the dendrimer design is that the choice of dendron attached to the core will have no effect on the electronic properties of the core, that is the core and dendron can be electrically independent.

Consequently, the electronic control of a dendrimer is possible at three levels [41]: the nature of the dendron that is attached to the core; the number of such dendrons that are attached to the core; and the number of branching levels from the core - the generation of the dendron. Through careful variation of the dendron and its generation number, charge migration from the dendrons to core and subsequent trapping of charge at the core becomes possible. This means properties such as the majority carrier (hole) mobility can be varied with no influence on the other properties such as the solubility or emission colour [42, 43].
2.4.2 Light-emitting dendrimers

The use of dendrimers for light-emission in organic LEDs is a relatively new application. After the twin discoveries of Tang and VanSlyke [7] and Burroughes [8] of electroluminescence in small molecules and conjugated polymers respectively, work into all areas of organic semiconductors was energised. As time advanced and the knowledge of the field increased some new and important discoveries were gradually made eventually leading to the invention and subsequently patenting of the use of conjugated dendrimers to give red, green and blue light from organic light-emitting diodes [35–40].

Despite their successful operation these initial studies on dendrimers based on anthracene, porphyrin or distyrylbenzene cores with stilbene dendrons were unable to give devices with external quantum efficiencies greater than even 0.1 % [38, 44–48]. Such efficiencies although reasonable at the beginnings of this new field were not sufficient for display applications and thus considerable further research was required to find a more efficient light-emitting dendrimer that could be used for displays [49].

In 2002 this research finally bore fruit with the discovery of what is still one of the highest ever reported device efficiencies for a solution-processed organic light-emitting semiconductor. This new dendritic material reported in the two seminal publications of Reference [26] and Reference [27], utilised the recently discovered triplet harvesting highly electroluminescent small molecular iridium(III) complex fac-tris(2-phenylpyridyl) iridium(III) [Ir(ppy)₃] discussed previously. This building on an idea first suggested in the original report of this material that the future for efficient organic semiconducting materials “may be transition-metal complexes with aromatic ligands” [25]. As such, efficient dendrimer OLED devices were created through the attachment to the iridium(III) complex at the core conjugated dendrons and surface groups. In this way conferring to the molecule both the advantages of conjugated polymers and those only obtainable through the now dendritic nature of the molecule. The resulting dendrimer (G1-Ir or IrppyD) thus consisted of the Ir(ppy)₃ core, phenylene (biphenyl) dendrons attached meta (or para) to the branching phenyl ring relative to the pyridine ring, and 2-ethylhexyloxy surface groups (denoted OR). This giving for the first generation meta linked structure, G1-meta-Ir(ppy)₃ (G1mIr), the structure as shown in Figure 2.14(a), or as a simplified one dimensional structure as in Figure 2.14(b).

Since the initial publications on such dendrimers research has continued into the further optimisation of their device properties by increasing the understanding of the physics of their operation and the chemistry of the synthesis. While the understanding of dendrimers has greatly increased over their short lifetime there still remains much to be discovered and learnt.
This thesis details efforts to further investigate and explore the physics of conjugated light-emitting dendrimers through photoluminescence and more predominantly electroluminescence measurements. The results show how careful choice of the core chromophore, dendrons, surface groups, and the device structure can influence the properties of the materials and lead to efficient solution-processed dendrimer OLEDs.

2.5 Organic Light-Emitting Diodes (OLEDs)

The previous sections have introduced the concepts of conjugated polymers and dendrimers detailing how photoluminescence is produced in such materials. In this and the remaining sections of this chapter the process of electroluminescence in organic semiconductors that allows the creation of organic light-emitting diodes (OLEDs) will be described.

Historically organic semiconductors have been known and researched since the 1960s [1, 2], but it was not until groups led by Heeger, MacDiarmid and Shirakawa made in 1977 [3] the discovery that by doping conjugated polymers they could be found to possess semiconducting properties that the potential of such materials for future display applications was realised. Then in 1987 Tang and VanSlyke [7] working at Kodak using a double organic layer structure made the first operational OLED. In this first organic device the organic semiconductor layer was the small molecule of the metal chelate complex 8-hydroxyquinoline aluminium (Alq3) with structure shown previously in Figure 2.12. A second layer of an aromatic diamine was also used to improve charge injection and increase the device efficiency. This
structure gave green electroluminescence and at that time a very respectable external quantum efficiency of about 1% which equated to a luminous power efficiency of around 1.5 lm/W.

In 1990 three years after Tang and VanSlyke reported their work, the first report of electroluminescence from a conjugated polymer was recorded by a group at Cambridge led by Friend giving the second seminal publication of the field [8]. This work used a derivative of the polymer poly(para-phenylene vinylene) (PPV) made by a precursor route to overcome the solubility problems of such materials. As a result the first solution-processable OLED was constructed, which although was only able to show very low quantum efficiencies of up to 0.05%, it nevertheless demonstrated that cheap, easy to process devices were possible from such materials.

### 2.5.1 OLED Design and Construction

The most basic structure of a working OLED appears as shown in Figure 2.15. In this simple structure a single organic electroluminescent layer is sandwiched between the two injecting electrodes, usually termed the anode and cathode. An OLED operates through the injection of holes from the anode into the HOMO of the organic semiconductor, while electrons are injected from the metal cathode layer into the LUMO level of the material. To produce efficient OLEDs it is vital that the electrode materials chosen are highly conductive and possess work functions that are well matched in energy to the energy levels of the organic emissive layer. By doing so efficient charge injection is possible, and drive voltages and currents are become as low as possible thereby maximising display lifetime. The ideal electrode choice should be such that the injection of holes into the anode is at the same rate as that of the electron injection from the cathode, while ensuring there are no leakage currents through the device.

Moreover, the choice of anode and cathode contacts is greatly limited by the requirements of the
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Figure 2.17: The structure of a bilayer OLED

...device: it must be able to emit light. As such one contact must be able to allow the generated photons of light to escape: it must be transparent whilst still being able to inject carriers. Typically a layer of the optically transparent and highly conductive indium tin oxide (ITO) is coated over a transparent glass layer to provide such a suitable contact for hole injection into the anode and a large barrier for electron injection. In order to be effective, ITO must be cleaned to remove surface defects and contaminants prior to organic deposition so as to maximise the hole injection whilst creating a large barrier to electron injection at this contact. Generally it is believed [51, 52], a small amount of solution cleaning prior to a short plasma ash is sufficient and this has been used throughout for all devices made for this thesis. Untreated ITO tends to have a workfunction of around 4.7 eV [53] which can, depending on the treatment method, be increased to values as high as 5.1 eV [54], although this may be still someway below the HOMO level of the organic semiconductor. Fortunately, such differences are able to be overcome through the use of hole injecting polymer layers such as polyaniline [55], or more commonly a spin-cast layer of PEDOT/PSS [56]; such layers also decrease the oxidation of the organic by the ITO, thereby increasing the device lifetime.

With the hole injecting contact fixed as ITO the other contact must then be chosen to facilitate efficient electron injection into the LUMO of the organic semiconductor. This necessitates the use of a low work function metal and hence reactive metals such as magnesium [7, 21, 24] or calcium [18, 26, 57] are commonly used as the cathode layer. To overcome the reactivity of these materials with the ambient air these layers are normally capped with more stable higher work function metals such as aluminium, gold [58], or copper [59] to complete the device structure.

In reality such simple ITO anode/organic semiconductor/metal cathode sandwich structures are unable to fully realise the 100 % internal quantum efficiency possible from phosphorescent organic semiconductors such as dendrimers. This arises because the hole dominated nature of typical organic semi-
conductive materials means that such simple structures are unable to give balanced injection and transport of opposite charges. To improve device efficiencies the number of holes present in the organic layer must be reduced. This can be achieved through the use of additional organic layers that are not predominantly hole transporting materials, instead such materials are able to strongly limit the hole current without diminishing the electron current, these materials forming what is termed a Hole Blocking Layer (HBL) or Electron Transporting Layer (ETL). The use of such materials give a second organic layer within the device structure, and hence what is termed a bilayer structure. The ETL/HBL material used for the devices considered in this thesis was 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene (TPBI) with structure shown in Figure 2.16. A further change in going to the bilayer structure was made in the material choice of the cathode layer. For the single layer device a calcium layer was used, whereas in the bilayer device the cathode was formed from a very thin layer of an insulting large bandgap dielectric material such as caesium fluoride [60], or more commonly lithium fluoride (LiF) [61,72]. This was done to facilitate better electron injection into the organic layers. The resulting bilayer structure of the devices used in this report is shown in Figure 2.17.

2.5.2 OLED Operation

The processes of luminescence from photo and electrical excitation in organic semiconductors are shown diagrammatically in Figure 2.18. Electron-hole pairs (excitons) are either generated by photoexcitation by light of sufficient energy, or via the recombination of oppositely charged injected carriers. These
processes lead to emission spectra that are closely alike reflecting that the emissive species are similar in both cases.

The process of light emission in organic light-emitting diodes arises from four key steps: charge injection, charge transport, charge recombination, and radiative decay to give light emission. This process is summarised in Figure 2.19. The steps are considered in detail below.

2.5.2.1 Charge injection

The process of charge injection has been found to the the dominant factor in the performance of OLEDs having the greatest influence on the resultant device efficiency [75]. Despite this, the physics of charge injection (and transport) into organics remains poorly understood. Difficulties relate to the fact that organic semiconductors do not behave as conventional semiconductors, charge transport is by hopping and not free propagation in extended states for example, and thus standard models are often not applicable. The structure of an OLED also complicates any description: an addition of a electron transport layer will improve electron injection into the organic layer but will also modify the hole extraction of the device [76].

In the ideal case when a metal-organic semiconductor junction is formed an Ohmic contact results, that is a contact with a voltage independent resistance. This happens when the barrier to charge injection at the contact is zero or negative. Consequently the carriers are free to flow in or out of the semiconductor, there is a minimal resistance across the contact, and the current is dominated by the motion of free electrons. The resultant current (charge) density is given by Ohm’s Law, $J = V/R$, with the current density-voltage (J-V) curve of the device being linear and symmetric as shown in Figure 2.20.

Figure 2.19: The operation of a simple OLED structure (adapted from [74])
As the voltage is increased beyond a threshold voltage, $V_0$, the current-voltage relationship is no longer linear as the number of injected electrons becomes greater than that initially present within the organic semiconductor. This is termed a space charge limited current (SCLC). For both inorganic and organic semiconductors a model based on SCLC has been repeatedly shown to be successful in describing the charge transport behaviour \[77\]–\[82\]. The best models assume an exponential distribution of traps around the conduction band, which agrees with predictions also made by other models based on disorder formulations \[77\]–\[83\].

The single-carrier current density due to (trap-free) space-charge effects occurs as a voltage rather than a field dependence of the current. This is expressed in the form of a power law, typically using the voltage squared dependence of the current density as given by Child’s Law,

$$J_{SCLC} = \left(\frac{9V^2}{8L^3}\right)(\epsilon\mu) \tag{2.8}$$

where $L$ is the organic layer thickness, $\epsilon = \epsilon_0 \epsilon_r$ is the dielectric permittivity (generally assumed that $\epsilon_r = 3$ for organic semiconductors), and $\mu$ is single carrier (hole or electron) mobility within the organic layer.

Both ohmic and space-charge currents assume that there is no limitation to current flow placed on the organic semiconductor by the injecting contact. That is they are bulk-limited currents. In most situations the contact does present a barrier to injection, the current becomes injection-limited, as Figure 2.20 shows this current is less than that of the bulk-limited current \[76\]. The exact form of the current depends on the method of injection. In general injection into the organic semiconductor can be described as occurring by one of two methods: quantum tunneling (field emission theory), or thermionic emission. Depending upon both the device structure and what regime the device is operating in, one or both methods may dominate.

The thermally activated process of thermionic emission has been used to describe the behaviour of a number of OLEDs, in particular those made with organic layers of the precursor PPV as the emission layer \[84\]–\[85\].

In thermionic emission the current density $J_{TI}$ through the device is of the exponential form,

$$J_{TI} = q\nu N[\exp(-\frac{\phi_B}{V_t})][\exp\left(\frac{V_a}{V_t}\right) - 1] \tag{2.9}$$
where \( J_0 \) is a constant that depends on both the temperature (T) and the effective electron mass, V is the applied voltage, and \( \nu \) is the velocity termed the Richardson velocity.

In the alternative process of quantum tunneling the field emission theory is used to describe the device behaviour. This uses the Fowler-Nordheim (FN) model, first applied to OLEDs by Parker [57]. In such cases when the barrier to majority charge carrier injection is overcome by tunneling through the barrier - the current density is given by the Fowler-Nordheim (FN) equation,

\[
J_{FN} = \left( \frac{AE^2}{\phi t^2(y)} \right) \exp\left[ -B \frac{\phi^{3/2}}{E \nu(y)} \right]
\]

(2.10)

where \( E \) is the electric field; A and B are constants; \( \phi \) is the barrier height in electron volts; \( y \) is the image force lowering contribution of the barrier given by \( 3.79 \times 10^4 E^{1/2} / \phi \); \( t^2(y) = 1 \) is a field dependent factor; and \( \nu(y) = 0.95 - y^2 \) is a correction factor. Simplifying, approximating and rewriting the FN equation gives,

\[
(\ln\left[ \frac{1}{E^2} \right]) = (\ln\left[ \frac{A\alpha\beta^2}{\phi} \right]) - (\frac{B\phi^{3/2}\nu(y)}{\beta E}) \left( \frac{1}{E} \right)
\]

(2.11)

From which it becomes clear that a material that undergoes field emission will exhibit a current-voltage relationship which when plotted as \( \ln\left[ \frac{1}{E^2} \right] \) against \( \left[ \frac{1}{E} \right] \) will give a linear relationship.

Since Parker’s application [57] of the FN equation to describe hole tunneling in devices based on a structure of ITO anode/PPV/metal cathode this equation has been widely employed to describe similar systems. However, its validity for all organic devices is the source of much debate in the literature since
it was found to be unable to describe the behaviour in thin ITO/PPV/Al devices [77]. Furthermore, using this model the fits to experimental data are generally poor deviating at low fields and giving lower than would be expected barrier heights [77, 78].

### 2.5.2.2 Charge transport

Once charges have been injected from the electrodes into the organic layer they must be transported through this layer so that they can subsequently meet and recombine. Charge moves through organic layers by hopping mechanisms. Thus the resultant mobility is heavily dependent on the hopping distances and is greatly affected by defects and impurity sites within the organic. Consequently, the mobility of an organic semiconductor is significantly lower than that of a typical inorganic semiconductor. A typical mobility in a conjugated polymers is in the order of $10^{-6} \text{ cm}^2/\text{Vs}$ [80, 86, 87], with mobility strongly depending on the chemical purity and morphology of the organic. In addition, the hole mobility in organic semiconductors is usually orders of magnitude greater than that of the electron mobility due to the larger number of trapping sites for electrons at defects [88], thus most organic semiconductors are found to be hole transporting [89–91].

Charge transport in organics is therefore very different to the case of inorganic materials and new models have had to be made to describe the behaviour in such systems. In organics the bands are generally very narrow, but with such a large degree of inherent disorder there is a broad distribution of energy levels, thus greatly complicating the processes of charge carrier injection and transport in such materials.

### 2.5.2.3 The Gaussian disorder model

One model that is widely used to describe the behaviour of charges in organic semiconductors is Bässler’s Gaussian disorder model developed through Monte Carlo simulations [83]. In this model, a Miller-Abraham formalisation [92], charge transport is described as a hopping process via tunneling between an initial state and a target state where the mobility has an exponential square root dependence on the electric field. Conceptually this is similar to the Poole-Frenkel effect and so is often termed a ‘pseudo’ Poole-Frenkel effect. This effect, first described in 1938, has been observed in mobility measurements on polymers and other organic materials.

Often in order to simplify the analysis of organic semiconductors it is assumed the mobility has an electric field dependence [81, 82]. In this way the current density through the device can be determined
from Equation 2.8 where the mobility, $\mu$, which is found from,

$$\mu = \mu_0 \exp \left( \sqrt{\frac{E}{E_0}} \right)$$

(2.12)

where $E$ is the electric field, $\mu_0$ the field independent zero-field mobility, and $E_0$ parameter that determines the field dependence on the mobility. Using Equation 2.8 to plot the current density against electric field ($J$-$E$ curve) both $\mu_0$ and $E_0$ can be obtained. From Equation 2.12 a plot of the log of the mobility against $\sqrt{E}$ would be expected to show a linear relationship where the mobility of the material considered has an electric field dependence.

2.5.3 Single carrier devices

Through careful choice of the electrodes used in OLED device structures charges can be deliberately prevented from entering into the organic semiconducting layer from one of the electrodes through the use of large injection barriers. In such a structure no light emission is possible due to the predominance of one carrier over the other; the device is said to be a single carrier device. From such devices important device measurements such as the mobility of the injected carriers involved in the charge transport in the device become possible which otherwise in the presence of two carriers would be very difficult to perform.

Accordingly, for the standard device geometry to contain only hole carriers the efficient electron injecting calcium cathode is not used; the injection barrier from the aluminium to the LUMO level of the organic becomes too great and holes injected from the ITO, or preferably a gold or platinum anode, dominate in the device. For an electron-only device the ITO anode would be replaced by a low work function metal such as calcium thereby increasing the barrier to hole injection ensuring only electrons injected from the anode into the organic layer [57].

2.5.4 Other device models

In the previous modelling studies undertaken within the group [93] the model of Davids et al. [94] was used to describe the behaviour of dendrimer OLEDs. This simple model used a combined treatment of thermionic emission over a barrier and tunneling to describe the injection of charge into the organic semiconductor. By solving the coupled Poisson, drift, and continuity equations and with the Poole-Frenkel
form of mobility given by Equation 2.12, the charge-carrier density at the electrode can be determined.

However, since these studies it has become clear the inorganic formalism of this model is not best suited when applied to organic semiconductors due to their inherent disordered structure. Consequently, for the modeling used in Chapter 7 of this thesis the models as first proposed by Scott et al. [95], and also more recently used by Barker et al. [96], where the molecular nature of the semiconductor is explicitly included have been followed. Injection, transport and recombination of charges is simulated with an electric field-dependent carrier mobility given by Equation 2.12.

Using finite element simulations experimental data can be fitted using the methodology of Reference [97] for the current magnitude by fitting the barrier height to charge injection into the device. The use of this method allows a test of whether the injection barrier height can be deduced from the values of the the dendrimer HOMO and LUMO levels and the vacuum measured metal work functions given in the literature. Improvements of the fits to the current-voltage characteristics can be obtained by the method of including a series resistance, $R_I$ [98]. Further details of this are given in Chapter 7.

2.6 Electroluminescence Quantum Efficiency

To provide a valid comparison of the device and material properties it is important to establish a consistent level of performance measure. For OLEDs to be successful they will have to either match and exceed the performance of current display types or offer an alternative advantage that cannot otherwise be obtained. As such OLEDs in common with all display types have many ways of quoting their performance taking in many of the important parameters: device efficiency; power consumption; lifetime; cost; brightness or luminance; colour depth representation and contrast; viewing angle; display area, thickness and weight; and substrate choice. This section details a small number of measures to determine the performance of such parameters that are subsequently used to establish the performance of all the OLEDs reported within this thesis.

2.6.1 OLED Efficiency concepts

Whatever combination of materials are used within an OLED structure they will all tend to have high refractive indices thereby creating in effect a high index slab which causes much of the generated light to become trapped in waveguided modes. This can reduce device efficiency and change the emission
spectrum. Furthermore the ideal OLED emission spectrum of an Lambertian isotropic emitter with equal radiance in all solid angles in the forward viewing hemisphere can become modified by the stacked structure \[99\]. Thus, efficient light extraction from OLEDs can prove difficult. Moreover, as OLEDs are a display device viewed by humans, some measure of the eye response must be taken into account in describing the performance of a display.

The standard method of measuring and comparing the performance of an OLED is through its external quantum efficiency (EQE). The EQE is defined as the ratio of photons emitted by the OLED in the viewing direction to the number of injected charges \[99\]. Equally valid would be a measure of photons emitted in all directions, however as this is harder to measure, and by design OLEDs only emit in one direction, the first definition has become standard.

Due to waveguiding and edge emission the majority of the light generated within an OLED is not emitted into the viewing direction but is instead wasted or trapped within the device. A measure of the absolute device performance is given by the internal quantum efficiency, defined as the ratio of photons generated within the OLED to the number of injected charges \[99\]. The internal and external quantum efficiencies thus differ by the fraction of the light that can escape in the viewing direction. A simple analysis using Lambertian emission \[100\], suggests this fraction is equal to \[\frac{1}{2n^2}\] of the produced light, where \(n\) is the refractive index of the material. For a typical organic semiconductor the refractive index is around 2, implying a maximum external quantum efficiency of only \[\frac{1}{8}\] of that of the internal quantum efficiency.

As described previously the operation of an OLED is a four-stage process, consequently the quantum efficiency effectively equates to being equal to the product of the individual efficiencies of each of the stages involved in the device operation, these stages are shown diagrammatically in Figure 2.21. Therefore,

\[
\Phi_{\text{EXT}} = \Phi_{\text{CAPTURE}} \Phi_{\text{RADIATIVE}} \Phi_{\text{SPIN}} \Phi_{\text{ESCAPE}}
\]  

(2.13)

Hence, for maximum efficiency each parameter should be optimised. For maximum \(\Phi_{\text{CAPTURE}}\), the fraction of injected charges that meet to form an exciton, balanced charge injection of holes and electrons are required; this is obtained through the use of a bilayer structure. By using highly photoluminescent materials (high PLQY) \(\Phi_{\text{RADIATIVE}}\), that is the fraction of excitations that decay radiatively, becomes
as large as possible. By maximising the number of photons that can escape the device a large $\Phi_{ESCAPE}$ factor is obtained, typically this requires the use of waveguides and other novel structures within the device geometry. Finally, to obtain a large $\Phi_{SPIN}$ factor, which will be fixed at $\frac{1}{4}$ if only singlets are harvested, triplet emission must be harnessed; for this phosphorescent emitters are needed, so creating the possibility of 100 % internal efficiencies \[26, 33, 34\].

### 2.6.2 Experimental measurement of OLED efficiency

To give a measure of both the internal and external efficiencies of an OLED it is required that a measurement be made of number of photons exciting the device, standardly a photodiode is used to do this. This means that due to the broad emission spectrum of the measured OLED there will be large errors in the efficiency calculated unless the variation in the response of the photodiode with wavelength is accounted for. Consequently the calculation process of the efficiency requires multiplication by the detector response correction factor.

Consider the process of light generation schematically as shown in Figure 2.22 where $\eta_{EX}$, $\eta_{CAP}$ and $\eta_{DET}$ are the fractions of photons escaping the device, photons captured by the detector and photons
converted to electrons (the detector quantum efficiency) respectively. Accordingly,

\[ N_{OUT}^{e} = \eta_{EX} \eta_{CAP} \eta_{DET} N_{IN}^{e} \]  
\[ (2.14) \]

and so

\[ EQE = \frac{N_{OUT}^{p}}{N_{IN}^{e}} = \frac{1}{\eta_{CAP} \eta_{DET}} \frac{N_{OUT}^{e}}{N_{IN}^{e}} \]  
\[ (2.15) \]

By measuring the current the number of electrons (e) in the detector per unit time is found, thus

\[ N_{OUT}^{e} = \frac{I_{DET}}{e} \]  
\[ (2.16) \]

and

\[ N_{IN}^{e} = \frac{I_{DEVICE}}{e} \]  
\[ (2.17) \]

so

\[ EQE = \frac{N_{OUT}^{p}}{N_{IN}^{e}} = \frac{1}{\eta_{CAP} \eta_{DET}} \frac{I_{DET}}{I_{DEVICE}} \]  
\[ (2.18) \]

The process thus reduces to finding the values of \( \eta_{CAP} \) and \( \eta_{DET} \). Assuming then that the detector captures all photons incident on it and the OLED is a Lambertian emitter, then for a circular photodiode with radius \( r \), the fraction of light incident on the detector is given by

\[ \eta_{DET} = \sin^2(\alpha) \approx \frac{r^2}{d^2} \]  
\[ (2.19) \]

where \( \alpha \) is the cone angle given by the detector area, and \( d \) is the distance of the detector from the device.

Assume then output current of the detector, \( I_{DET} \), is a linear function of the incident flux, \( F_{INCIDENT} \) where the responsivity of the detector, \( R \) is the coefficient of proportionality, therefore

\[ I_{DET} = RF_{INCIDENT} \]  
\[ (2.20) \]
or

\[ R = \frac{I_{DET}}{F_{INCIDENT}} \]  \hspace{1cm} (2.21)

The spectral shape of the detector responsivity is a known function \( \delta(\lambda) \) normalised on the interval \([0,1]\), and the peak monochromatic responsivity is \( D \) in units of amps per watt (A/W). Assume then the spectral shape of the emission is a known function \( \beta(\lambda) \) normalised on the interval \([0,1]\) with peak power \( B \). Thus,

\[ F_{INCIDENT} = B \int \beta(\lambda) d\lambda \]  \hspace{1cm} (2.22)

\[ I_{DET} = BD \int \delta(\lambda) \beta(\lambda) d\lambda \]  \hspace{1cm} (2.23)

Then the total responsivity, (over all wavelengths) is given by:

\[ R_{TOTAL} = \frac{BD \int \delta(\lambda) \beta(\lambda) d\lambda}{B \int \beta(\lambda) d\lambda} = \frac{D \int \delta(\lambda) \beta(\lambda) d\lambda}{B \int \beta(\lambda) d\lambda} \]  \hspace{1cm} (2.24)

For a single wavelength monochromatic responsivity is given by:

\[ R^\lambda = \frac{I^\lambda_{DET}}{F_{INCIDENT}^\lambda} \]  \hspace{1cm} (2.25)

The quantisation of the current and flux to give the number of electrons and photons then gives monochromatic quantum efficiency of detector as

\[ \eta_{DET}^\lambda = \frac{hcR^\lambda}{e\lambda} = \frac{hcD\delta}{e\lambda} \]  \hspace{1cm} (2.26)

and so the total quantum efficiency over all wavelengths is then

\[ \eta_{DET} = \frac{\int hcD\delta(\lambda) \beta(\lambda) d\lambda}{\int e\lambda \beta(\lambda) d\lambda} = \frac{hcD}{e} \int \frac{\delta(\lambda) \beta(\lambda) d\lambda}{\lambda \beta(\lambda) d\lambda} \]  \hspace{1cm} (2.27)

Therefore, for a photodiode output of voltage \( V_{DET} \) for a reference resistor of value \( R_{REF} \), the equation
giving the EQE is given as,

$$\eta_{EX} = \left[ \frac{1}{\sin^2(\alpha)} \right] \left[ \frac{e}{hcD} \right] \left[ \frac{\int \lambda \beta(\lambda) d\lambda}{\int \delta(\lambda) \beta(\lambda) d\lambda} \right] \left[ \frac{V_{DET}}{R_{REF} I_{DEVICE}} \right]$$  \hspace{1cm} (2.28)

2.6.3 Visual response parameters

To correctly characterise a display some measure of the response of the human eye (photopic response) must be included in any analysis. To do this the response of a standard human eye is used and all display parameters weighted against this to enable the display response to the correctly described. The base unit in all photometric calculations is the SI unit of luminous intensity measured in candelas - one candela is defined as the luminous intensity emitted by a monochromatic light source of frequency 540x10^{12} hertz and that has a radiant intensity in that direction of 1/683 watt per steradian. From this definition the brightness of a display is defined as the luminance in candelas per meter squared (cd/m^2). A typical CRT display has a brightness value of 100 cd/m^2 at normal operating conditions, and therefore in most cases all display values are quoted at this luminance to allow consistent comparisons and those to the standard CRT display to be made.

Another important parameter in photometric measurements is the power or luminous flux. This quantity, measured in lumens (units lm), records the amount of light that falls on a unit area at unit distance from a source of one candela. In particular, it is the energy radiated over wavelengths sensitive to the human eye (around 330 - 780 nm). Therefore, luminous flux is a weighted average of the radiant flux in the visible spectrum. It is a weighted average because the human eye does not respond equally to all visible wavelengths.

It follows then that the luminous efficiency is the measure of the proportion of the energy supplied to a source that is converted into light energy. This is calculated by dividing the luminous flux of the source in lumens, by the power consumption, measured in watts (units lm/W). Similarly, a further measure of display efficiency that is also commonly used is the luminous intensity per current consumed (cd/A).

2.6.4 Display Colour

A further issue of concern in displays is a quantification of the emission colour. The detection of colour by the human eyes is via millions of photosensitive cells termed rods and cones. These are located in the retina and act to convert incident light energy into signals that are carried to the brain through the
optic nerve. The rods are much more numerous and sensitive than the cones performing in very bright light to very dim light but have no colour sensitivity, this is provided solely by the six to seven million cones located in the retina. There are three types of cones: the first sensitive to short wavelengths; the second sensitive to medium wavelengths; and finally one sensitive to long wavelengths. It follows that as all colours can be determined by the stimulus of these three detectors then visible colour can be reproduced in terms of three numbers called tristimulus values. This means that there can be many different combinations of light wavelengths that can act to produce the same perception of one color.

An international standard method of describing all possible colours that could be made by mixing red, green and blue light sources was established in 1931 by the Commission Internationale d’Eclairage (CIE) [101]. By studying test observers the response of a standard human eye was established in terms of three mathematical functions \( \bar{x}(\lambda) \), \( \bar{y}(\lambda) \) and \( \bar{z}(\lambda) \), where \( \bar{y}(\lambda) \) is equal to the photopic response of the eye. By using these functions as a weighting multiplication factor for the measured spectral power at each wavelength, \( S(\lambda) \), and summing over the entire wavelength range the tristimulus values of X, Y, and Z are obtained can can be used to calculate the CIE chromaticity coordinates. The values of the X, Y and Z primaries are thus given by

\[
X = k \int S(\lambda) \bar{x}(\lambda) d\lambda \\
Y = k \int S(\lambda) \bar{y}(\lambda) d\lambda \\
Z = k \int S(\lambda) \bar{z}(\lambda) d\lambda
\]

(2.29)  
(2.30)  
(2.31)

These values are chosen such that they can represent any given colour, they always produce a positive tristimulus value, and with equal values of each primary the colour produced is white. Moreover, the single parameter Y can be used to determine the luminance of the colour.

Colour is then specified in terms of the three variables x, y and z which are obtained from the the X,
Y and Z primaries according to the equations

\[ x = \frac{X}{(X + Y + Z)} \]  
\[ y = \frac{Y}{(X + Y + Z)} \]  
\[ z = \frac{Z}{(X + Y + Z)} \]

(2.32)  
(2.33)  
(2.34)

Therefore, if the x and y coordinates are known, the z coordinate can be calculated from \( z = 1 - x - y \). With these two x and y chromaticity coordinates and the Y brightness parameter all visible colours can be represented as a two dimensional plot termed the CIE Chromaticity Diagram such as in the example plot of Figure 2.23. The plot shows both the hue (colour) and chroma (saturation or strength of colour). Luminance is represented by the third dimension but is not shown in the simple diagram. Each point on the edge denotes a pure colour of a specific wavelength with white located at the center. Mixing the colours of any two light sources allows any colour that falls on the line joining their chromaticity coordinates to be created. For three colours the resulting gamut of available colours forms a triangle - it is thus possible to generate all the visible colours using only the three pixel colours of red, green and blue used in a display. The plot shown in Figure 2.23 is the 1931 CIE standard version. Although subsequent revisions to this version were made in 1960 and 1976, the 1931 version remains the most widely used version, and thus all colour coordinates quoted in this thesis correspond to this version.

2.6.4.1 Television Standards

The television and video standards committees of both the USA (NTSC) and Europe (PAL) have each created their own colour gamuts in which all displays used in these geographical locations should operate. The red, green and blue CIE coordinates which all displays must strive to approach are thus: for NTSC \((0.67, 0.33), (0.21, 0.71)\) and \((0.14, 0.08)\); and for PAL \((0.64, 0.33), (0.29, 0.60)\) and \((0.15, 0.06)\). In general within this report comparisons of experimentally obtained emission spectra are made to the
standard reference points of the PAL system.

### 2.7 Summary

This chapter has introduced the basic theory governing the behaviour of organic semiconductors. The concepts of conjugation were discussed revealing how this conveys semiconducting properties to organic molecules. The photophysical behaviour including the absorption and emission processes of organic semiconductors were also specified leading into the phenomenon of triplet emission showing why this is vital for efficient light emission in devices. The dendrimer concept was presented, and it was explained why phosphorescent conjugated dendrimers could well in the future become the ideal organic semiconductor for light emission. The chapter also briefly described the operation of organic light-emitting diode (OLED) devices, with a brief study given of the models used to describe charge transport within OLEDs and organics in general, before concluding by introducing some standard methods of measuring OLED performance parameters.
Chapter 3

Experimental techniques

3.1 Introduction

This chapter describes the basic photoluminescence and electroluminescence experimental methods and techniques used throughout this thesis. As introduced in Chapter 2 the class of organic semiconductor used exclusively within this thesis was the dendrimer. Consequently all the advantages of this material were conveyed to the experimental processing - films could be spin-coated from solution easily and quickly with most dendrimers being readily or even instantly soluble; various substrates both from thick to thin glass to plastic substrates could be coated if desired; and material consumption was low, using only a few milligrams per solution. A highly efficient dendrimer light-emitting diode could thus be fabricated very quickly through the spin coating of thin layer of dendrimer onto an etched ITO substrate, followed by vacuum evaporation of a metal cathode, before encapsulation and ultimately device testing.

3.2 Soluble Dendrimers

All dendrimers used in this thesis were synthesised by the Advanced Organic Materials Group of Paul Burn at the University of Oxford and thus could be used as received on arrival. When not being used all dendrimers were stored in a nitrogen glovebox. On removal they could immediately be dissolved in common solvents and used to make films.

In general dendrimers have attached at their periphery solubilising surface groups that impart solubility to the entire dendrimer molecule. Typically 2-ethylhexyloxy surface groups or tert-butyl surface
groups are used. Dendrimers are thus soluble in almost all solvents, including those such as chlorobenzene (C₆H₅Cl), tetrahydrofuran (THF - C₄H₈O), toluene (C₇H₈), and those most typically used for the devices presented this thesis: chloroform (CHCl₃), and dichloromethane (CH₂Cl₂). The high solubility of dendrimers means they can be deposited directly from solution, with for simplicity and speed the technique of spin-coating, as applied also standardly to polymers, used throughout.

In contrast to long chain polymers, dendrimers have lower molecular weights and thus to produce spin-coated films of good quality and smoothness for photoluminescence or device measurements film concentrations of around 20 mg/ml were required. Solutions were usually made so as to give either a neat dendrimer film (100 % by weight of dendrimer), or as has been found previously to be optimum, a 20:80 weight percentage blend of dendrimer and a host [102], with on occasion other blend ratios investigated. In all cases, unless otherwise specified, spin-coating was performed in air.

The host materials used in this thesis were restricted to a choice of 4,4'-N,N'-dicarbazolyl-biphenyl (CBP) and 4,4',4''-tris(N-carbazolyl)triphenylamine (TCTA) for green emitting materials, and N,N'-dicarbazolyl-3-5-benzene (mCP) for blue emitting materials, the structures of these hosts are shown in Figure 3.1.

3.3 Photophysical Measurements

The photophysical measurements considered were absorption and fluorescence measurements, and measurements of the Photoluminescence Quantum Yield (PLQY).

3.3.1 Absorption and Fluorescence Emission Spectra

The absorption spectra of dendrimer films and solutions presented in this thesis were all obtained using a Cary Varian 300 UV-Vis absorption spectrometer. This equipment was capable of measuring both the
wavelength and intensity of absorption of visible to ultraviolet light in the wavelength range of 800 nm to 200 nm for both films and solutions.

In both cases the design of the spectrometer was such as to allow the sample to be scanned in one chamber while a clean, blank reference sample was held in an adjacent chamber. This design allows the removal of any absorption effect of the solvent and the quartz glass disk (in the case of spin-coated films) or cuvette (for solutions).

Absorbance (optical density) was calculated through the comparison of the reference to the measurement beam with both samples illuminated with the same intensity. For an absorbent sample the beam will be dimmer than the reference so allowing the transmission \((T)\) to be determined by the ratio of the two intensities. Absorbance \((A)\) is then given by the relation

\[
A = -\log(T)
\]  

(3.1)

The fluorescence of organic material, that is its emission spectrum, for both films and solutions was measured using a Jobin-Yvon Fluoromax 2 spectrometer. In this apparatus one monochromatic excitation wavelength is selected from the xenon lamp source at which the sample is excited at an angle of 45°. The excitation wavelength was 360 nm, with a band pass of 1 nm used for both excitation and detection. The resulting emission was collected at each wavelength over a specified range through an emission monochromator by a photomultiplier tube in the photon counting mode. After correction for the quantum efficiency of the photomultiplier tube within the spectrometer (correction supplied by Jobin-Yvon), the PL emission spectra of the sample over the required range was found.

### 3.3.2 Photoluminescence quantum yield (PLQY)

Knowledge of a material’s photoluminescence quantum yield (PLQY) is a vital material parameter for determining its effectiveness for efficient light emission. PLQY is defined [103] as,

\[
\Phi_{PLQY} = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}
\]  

(3.2)

PLQY measurements were made either in a low concentration solution of the organic semiconductor dissolved in an organic solvent such as toluene or THF (solution PLQY), or as a spin-coated film on a
quartz disc (film PLQY).

For film PLQY measurements a thin dendrimer film was spin-coated onto a quartz disc before being held in an integrating sphere and subjected to the 325 nm line of a Kimmon Helium-Cadmium CW laser under flowing nitrogen. The integrating sphere was a hollow sphere coated on the inside with a diffusely reflecting material such that all the emitted light from a sample held at the center of the sphere could be collected. The sphere was designed so as to have a small entrance hole at one side to permit the laser light to enter the sphere and become incident on the sample. A further hole was located at the top of the integrating sphere to which a large area photodiode was attached to allow the luminescence to be measured. The light output at any aperture of the sphere was proportional to the total light produced by a sample within the sphere. For a measurement of the transmitted power of the laser through the sample an exit port on the integrating sphere was opened at the opposite side to that of the incident light. Light was thus able to pass completely through the sphere and the sample held within it before becoming incident on a power meter located outside the sphere thereby giving a value for the reduced laser power. With the sample removed from the sphere the full laser power could be similarly measured. Also required was the sample reflectivity; this was obtained in a separate measurement where the sample was held outside the sphere and the power of the reflected laser light of the sample measured.

For the measurement of solution PLQY the standard approach of a relative measurement of the emission spectra of a degassed solution of the organic semiconductor in comparison to a standard solution with a known quantum yield was used. Solutions were made in quartz degassing cuvettes, and degassed by three freeze-pump-thaw cycles, sealed under vacuum and warmed to room temperature by submerging in a bath of tepid water. The standard solution used was quinine sulphate dissolved in 0.5 molar concentration H$_2$SO$_4$ which has a quantum yield of 0.51 at an excitation wavelength of 360 nm \cite{104}. Both sample and reference solution had an optical density close to 0.1. The error in this method is estimated to be approximately 10%.

\section{3.4 OLED Fabrication}

One of the main benefits of organic electroluminescence (EL) is the ease with which devices can be prepared. All devices reported were fabricated in St Andrews in a Class 10,000 cleanroom. Device fabrication is a multi-step process with the main stages being: substrate (anode) preparation; active layer
3.4.1 Substrate (anode) preparation

In a standard OLED structure the anode is Indium Tin Oxide (ITO) coated glass. Throughout the work detailed in this thesis two types of ITO were considered and evaluated. Both ITO types were purchased from Merck (batch codes 300 735 X0 and 800 735 X0) in large sheets which were then cut to the required size of 12 mm x 12 mm squares.

Anodes were defined by selectively etching away the ITO from all but a 4 mm wide strip down the center of the square. In all cases a common anode configuration as shown in Figure 3.2 was used yielding four devices (pixels) per substrate. To do this electrical tape extending beyond the edges of the substrate was used to mask the ITO over the required area, while over the remaining ITO a thin layer of zinc powder was sprinkled before a few drops of concentrated hydrochloric acid (HCl, 37 %) were pipetted onto the zinc. The resulting reaction between the zinc, acid and ITO acted to remove the ITO from all but the protected area below the tape. After etching the samples were rinsed in IPA and/or deionised water to remove the acid before the tape was removed. Substrates were then dried in nitrogen.

For solution cleaning the substrates were placed sequentially in ultrasonic baths of acetone (which also dissolves any varnish present on the ITO), the spinning solvent, and IPA for around fifteen minutes in each solvent, with the samples dried in nitrogen after each of the three solution washes. After initial investigation of the solvent washing order there was found to be no resultant difference in device performance on adopting a different order or procedure, and hence the above order of solvent washing was used throughout. Plasma ashing was undertaken using an Emitech K-1050X in which the samples were subjected to an oxygen plasma treatment at a power of 100 W for five minutes.

3.4.2 Active layer preparation and deposition

After cleaning, the dendrimer layer was spin-coated directly onto the ITO (or glass) substrate. In general a spin speed of 2000 rpm was used for a duration of 60 seconds to yield a film of around 100 nm in thickness (on spinning in air). Film concentrations of 20 mg/ml were standardly used for both neat and blend films. As discussed in Chapter 4 host materials were predissolved prior to adding the dendrimer due to the differing degrees of solubility in these materials.
On occasion a hole injecting layer of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT/PSS or also denoted just as PEDOT) was also used in the device structures to provide a smoother interface and lower workfunction for the injection of holes into the HOMO of the organic semiconductor. PEDOT/PSS was water soluble and spun directly from stock solution at speed of 2200 rpm to yield a film approximately 100 nm thick. In order to remove excess water a drying process of heating the substrate on a hotplate at 200°C for 5 minutes was used. After annealing the PEDOT/PSS formed an insoluble layer onto which subsequent organic layers could be deposited.

### 3.4.3 Cathode evaporation

Immediately after spinning the films, samples were transferred to an evaporator thus minimising degradation as much as possible. The remaining layers were all then evaporated under high vacuum conditions of less than 1x10^{-6} mbar. When used, the organic TPBI layer was thermally evaporated at a rate of around 0.5 nm/minute for a thickness of 60 nm or as desired. The metal anode layers were evaporated through resistive heating - calcium and lithium fluoride from molybdenum boats and aluminium from a tungsten coil filament. For calcium and lithium fluoride an evaporation rate of around 0.1 - 0.2 nm/second was used to give thicknesses of 20 nm and 1.2 nm respectively. For aluminium the same low rate was used initially for the first 20 nm before being gradually increased to rates of 0.5 - 1.0 nm/second to complete a layer thickness in excess of 100 nm. Other contacts such as gold and platinum were also investigated using the same procedure as aluminium.

After evaporation the devices were removed from the evaporator and immediately electrically char-
acterised. In some cases where a longer lifetime of device was needed a simple encapsulation technique of covering the device with an epoxy glued microscope slide under inert conditions was used. In both cases it was found devices could be stored in a nitrogen glove box for a number of weeks with little loss of efficiency, however, unless specified testing was carried out immediately after completion of the fabrication process.

3.5 Electrical Characterisation

The standard testing setup for devices is shown in Figure 3.3. The arrangement allowed the devices to be tested under vacuum. For electrical connection inside the vacuum chamber the entire ITO substrate was held securely in a holder with the four device cathodes connected via sharp sprung gold pins, and the common central anode connected at the top and bottom to further pins. It has been found that for the best contact sharp pins were essential and thus care must be taken on loading and unloading the sample so as to not scratch and damage the thin cathode layers.

For testing a positive voltage bias was applied to the ITO electrode by a Keithley 2400 Sourcemeter. A second connection to the aluminium electrode of the pixel under test allowed the circuit to be completed the corresponding current through that device to be measured. Simultaneously, the output light emitted by the device was collected through a window in the vacuum chamber by a large area (1 cm\(^2\)) silicon photodiode that was subsequently amplified and then measured by a Keithley 2000 Multimeter.
Control of the applied bias voltage (V) and measurement of the resultant current (I) and photodiode voltage (L) was by a fully automated process using a computer and a Labview software program.

Alternatively, the photodiode was replaced by a fibre optic cable connected to a CCD spectrograph calibrated to give the number of photons in a set wavelength interval thereby allowing the emission spectrum of the output light of the OLED to be determined. This emission spectrum along with the I-V-L data were used to determine the resultant OLED efficiency according to procedure outlined in Section 2.6.2.

3.6 Time-Of-Flight (TOF) measurements

The measurement of the mobility of organic semiconductors is an important parameter to obtain to aid in the understanding of any system. Such details can be obtained from the time-of-flight (TOF) experimental technique.

3.6.1 The time-of-flight technique

As discussed in Chapter 2 to enable the production of efficient OLEDs the role of charge injection and transport is vital. Maximum efficiency occurs when charge recombination is maximised, that is when an equal number of hole and electrons combine and emit radiatively. In reality this is of course unlikely to occur, but through careful choice of material the carrier mobility can be made to be better balanced so leading to great improvements in device performance. The measurement of charge carrier mobility is therefore vital for the understanding and development of improved materials and device structures.

The high degree of disorder present in organic semiconductors normally means such materials have low mobilities [93, 105-107]. A problem particularly found in organics deposited by solution-processing techniques is that the film is unable to assume an ordered morphology on deposition, unlike in an evaporated case. This problem is further accentuated as the degree of disorder inherent in the material increases. Fortunately, all the materials studied in this thesis were dendrimers and so posses regular standard structures of fixed molecular weight. Therefore the ability to determine and describe the dominant processes in the charge transport behaviour of these materials was somewhat simplified.

Usually a description of the charge transport behaviour in organic semiconductors starts from a determination of the carrier mobility. The standard method of obtaining such mobility measurements is by the
time-of-flight (TOF) technique. Since its inception [108], a number of changes and advancements [109–111] have been made, but the principle remains the same: an optically generated sheet of charge is swept across the sample under test under an applied electric field, the time taken for the charge to traverse the sample is the experimentally obtained parameter known as the transit time ($t_T$). During the transit of the charge carriers across the sample thickness, a constant current is measured through the sample under test provided the waiting time distribution of the charge carriers on transport sites is narrow. When the charges arrive at the other side the measured current will then decrease due to the reduction in the number of free carriers in the film. Changes in the polarity of the bias applied to the device structure allow both hole and electron currents to be measured so enabling the mobilities of both carriers to be determined.

In the normal technique a thick (micrometres) organic film is sandwiched between two conductive electrodes, one of which must be transparent to allow the laser light to become incident on the organic layer, typically ITO is used as this electrode. Thick films are needed to ensure absorption depth is small compared with the film thickness; to give such a thick film the organic semiconductor would be required to be drop-cast. As a result the morphology between these thick TOF films and the thin ($\sim 100$ nm) films used in devices can be quite different, and as the morphology of organic systems is found to have a large dependence on the charge transport behaviour [112], this approach means comparisons between the two cases are not always simple.

### 3.6.2 CGL TOF

A solution to the problem was found in Reference [111] through the inclusion within the OLED structure of an additional charge generation layer (CGL) of an evaporated absorptive dye. This layer enabled a definite charge generation point even for thin organic layers, meaning that films of only a few hundred nanometers, easily obtainable by spin-coating techniques and much nearer to the thickness of those used in device applications, could be used. In all cases the mobility measurements presented in this thesis used this technique, with the CGL formed from a thin layer of the absorptive perylene dye Lumogen Red purchased from BASF.

### 3.6.3 TOF setup

To perform TOF measurements the setup shown in Figure 3.4 was used. In this configuration the dye pumped nitrogen laser wavelength was chosen so as to pass through the ITO and organic dendrimer
layers and be absorbed by the CGL. This optically generates a sheet of charge that under an applied field was swept across the device from the ITO contact to the aluminium contact. The time taken for the charge to traverse the sample was the experimentally obtained parameter known as the transit time ($t_T$).

Through variation of the bias polarity applied to the ITO contact both hole and electron currents could be measured to allow the mobilities of both carriers to be determined if so desired.

### 3.6.4 Non-dispersive and dispersive transport

In the ideal case a sheet of charge carriers move across the sample under the drift limit, but many materials are found not to obey this. Transport in organics is classed as either dispersive or non-dispersive in nature [113][114].

In the case of non-dispersive transport the one-dimensional law of diffusion is true and hence a Gaussian distribution of the charge carrier density in space applies. In this case the Einstein equation also then applies and the diffusion can then be said to be proportional to the mobility; the spread of the Gaussian distribution depends on the field applied to the sample. A resultant non-dispersive transient appears as shown in Figure 3.5 where the presence of a clear plateau region is evident. Such a plateau only forms if a dynamic equilibrium can be formed in a time short compared to the mean transit time. The initial spike at $t = 0$ is due to the presence of capacitive effects within the sample under test. From
such a transient, the transit time can be found through the intersection of asymptotes of the photocurrent in the power law regions either side of the transit time.

Figure 3.5: A plot of photocurrent against time for a typical non-dispersive transient [115]

In the alternate dispersive transport case there is no plateau region seen in the transient; the mean transit time is too short to allow the formation of a dynamic equilibrium; here the charge carrier packet becomes wider, more spread out, as the distribution of waiting times on carrier transport sites increases. This occurs when there is a high degree of disorder present in the organic and thus the Gaussian assumption is no longer valid. To describe dispersive transport a waiting time transport site distribution in the form of a power law dependency of the current is used [113, 114]. As a consequence of the model the transit time is found to depend on both the applied field and the film thickness. This underlining the importance of the fact that for meaningful comparisons, films for mobility and device measurements should be of comparable thickness.

The definition of the transit time in dispersive transport is also different, here it is defined as the intersection of the two power law regions of the transient either side of transit time. Therefore, the mobility (in cm²/Vs) of the charges is given as,

\[ \mu = \frac{d^2}{Vt_T} \]  

(3.3)
where $d$ is the film thickness under the applied bias $V$ and $t_T$ the transit time.

In the case of CGL-TOF measurements made on films of comparable thickness to those used in a standard OLED, the mobility from Equation 3.5 provides an excellent method of comparison to the mobility obtained from the modeled current-voltage characteristics. In such cases the Poole-Frenkel mobility, given by Equation 2.12 in Section 2.5.2.3, obtained by solving the coupled Poisson, drift, and continuity equations, are often used to give good fits to experimental data [93].

### 3.7 Summary

This chapter has described the basics underlying all the experimental procedures used to obtain the results presented in the remainder of the thesis. The photoluminescence and electroluminescence experimental methods used were detailed, with particular attention given to the details of the dendrimer preparation. Details of the device fabrication process and how such devices are electrically tested were also outlined.
Chapter 4

Highly efficient solution-processable dendrimer OLEDs

4.1 Introduction

This chapter describes the work that has taken place to improve the performance of devices made with neat films of iridium(III) cored dendrimers as the electroluminescent layer. The prospect of solution-processable organics, where intermolecular interactions can be controlled and important properties such as the emission colour be easily tuned, means that dendrimers are thought to be promising materials for OLEDs. The initial OLEDs fabricated from dendrimers had efficiencies restricted by the low intrinsic PLQY of the dendrimer. On replacement of these dendrimers with those containing iridium(III) cores the promise of efficient dendrimer OLEDs was finally realised with the best device quickly giving a maximum external quantum efficiency (EQE) of 16 \% [26]. This device was made using a bilayer structure of a host blended film of the first generation iridium(III) cored dendrimer fac-tris(2-phenylpyridyl) iridium [Ir(ppy)_3] or Ir-G1, the structure of which was shown in Figure 2.14 and is repeated as Figure 4.1. This dendrimer had an Oxford batch code of SVS01-34F.

The improvement in device performance outlined was realised purely through increased material development and knowledge gained through physical measurements. Reconsider Equation 2.13 reproduced below,

\[ \Phi_{\text{EXT}} = \Phi_{\text{CAPTURE}} \Phi_{\text{RADIATIVE}} \Phi_{\text{SPIN}} \Phi_{\text{ESCAPE}} \]  

(4.1)
In particular the increase in device performance was found from the improvement of the first three terms of Equation 4.1 where by using iridium(III)-cored dendrimers all could be simultaneously increased. Iridium(III) complexes are phosphorescent and thus highly photoluminescent; they are capable of 100% internal quantum efficiencies as both singlet and triplet emission is possible \([21, 23, 33]\), and so have \(\Phi_{\text{SPIN}} \) and \(\Phi_{\text{RADIATIVE}} \) close to unity. If used in a bilayer structure they can give balanced charge injection giving a very high \(\Phi_{\text{CAPTURE}} \) term as well. In these initial highly efficient devices no work was done on the \(\Phi_{\text{ESCAPE}} \) term to fully optimise the device performance.

Following this approach the modular nature of the dendrimer synthesis was again illustrated in the development of phosphorescent dendrimers capable of red \([116]\) and light or sky-blue \([117]\) emission. Although such colours have been successfully produced the resulting devices were not overly efficient in the case of the red emitting dendrimer, or for blue did not give a deep enough emission to be suitable for use in displays. These issues are addressed in subsequent chapters.

In many cases further efficiency improvements in OLEDs based on iridium(III) complexes were limited by effects of concentration quenching of the phosphorescence \([34, 118–120]\). Concentration quenching is the process where a molecule quenches its own fluorescence at high concentration. The mechanism can be through radiationless energy transfer between identical molecules, or through the formation or presence of aggregates and/or dimers as discussed in Section 2.2.5. Due to the longer excited state lifetime, quenching effects are more pronounced in phosphorescent than in fluorescent OLEDs. Nonetheless, the fact that both singlet and triplet excitons can be harvested for light emission in phosphorescent OLEDs means high efficiency in phosphorescent OLEDs becomes possible.
An example of this concentration quenching is that the neat film PLQY of the non-dendronised \text{Ir}(ppy)\textsubscript{3} is only 12 \% \textsuperscript{[119]}, but when dispersed in a CBP host matrix this can rise to nearly 100 \% depending on the concentrations used \textsuperscript{[34]}. The host acted to increase phosphorescent chromophore spacing thereby reducing the effects of the quenching. Therefore, in order to realise the high device efficiencies reported for OLEDs made from these materials it was normally the case that the electroluminescent layer was formed from a blend of a phosphorescent guest widely dispersed in a host material. The host was chosen so as to have a wider energy gap than the guest, in order that the guest sits within the host energy levels thereby ensuring efficient energy transfer from host to guest. Alternatively using dendrimers and with careful choice of the dendrons used, the intermolecular interactions could be equally controlled. Early work on green phosphorescent dendrimers showed the dendrimer generation had a significant effect on the resulting OLED efficiency, which was in part explained through the reduction in the intermolecular interactions between emissive species as the dendrimer generation increased. In more recent work, the standard iridium(III) dendrimer was synthesised such that it possessed an extra dendron on each ligand \textsuperscript{[121]}. In this double dendron approach, the core was given additional protection over the standard case by six first generation dendrons with one attached to each of the aromatic rings bonded to the \text{Ir}(ppy)\textsubscript{3} core. The resulting structure was that of Dendrimer \textsuperscript{2}, \text{Ir-G1}_2 (SVS02-41B), shown in Figure 4.2. In this way the rigidity of the dendrimer structure increased due to steric constraints \textsuperscript{[122]} and the encapsulation of the core was improved to such an extent that the control of intermolecular interactions was sufficient enough to enable devices to made with this dendrimer that had a maximum efficiency of 13.6 \% \textsuperscript{[121]} without the need for host blending. This approach will be subsequently seen in later chapters to be applied to other other dendrimers to improve the efficiency of red and blue-light emitting OLEDs.

This chapter instead studies the effect of the film preparation procedure used to make solution-processable OLEDs with iridium(III) cored dendrimers. To begin with, these studies were focused on the photophysical properties of films prepared from solutions of these dendrimers. The effects of varying the solvent used to dissolve the dendrimers, the time the solute is left in the solvent prior to spin-coating, and the storage conditions of the solution prior to spin-coating were all investigated. The effect on neat and host blended films for both Dendrimers \textsuperscript{1} and \textsuperscript{2} were considered. The results show that given certain processing and storage conditions, the solutions can undergo photodegradation that can have dramatic effects on the photoluminescence efficiency of the dendrimer, but given the correct processing conditions such effects can be greatly minimised. Using such conditions the efficiency of a neat film first generation
iridium(III) cored dendrimer OLED was shown to be dramatically increased without the need for host blending. A result which could have a significant positive impact for the advancement of dendrimers into use for commercial displays. The chapter continues with the application of this new spin-coating protocol to a number of other dendrimers, and in this way enabling the further optimisation of device performance. The results in all subsequent chapters were from measurements made using this new protocol unless otherwise stated.

In obtaining the measurements and results presented in this chapter I would thank and acknowledge the contributions of Dr Jean-Charles Ribierre and Dr Ruth Harding for the measurement of some of the photophysical results. The dendrimers reported in this chapter were all synthesised in the Advanced Organic Materials Group of Dr Paul Burn at the University of Oxford by Sarah Staton, Dr Zehua Liu, Dr Kevin Knights, Dr Homar Barcena, and Dr Shih-Chun Lo.

4.2 Iridium cored dendrimers

In almost all previous dendrimer device publications by the group it has been found that in order to obtain the best OLED device efficiency the dendrimer used was required to be first blended in a carbazole containing host prior to spin-coating. The common host used was CBP. Unfortunately, CBP and dendrimers have widely varying degrees of solubility: the majority of dendrimers dissolve instantly and even those less soluble within a couple of minutes; CBP on the other hand is only found to be soluble in CHCl₃ and CH₂Cl₂, with in both cases up to two hours on a stirring plate required for it to be fully dissolved.

It thus seemed early dendrimer researchers aware of this made a mixture containing CBP and dendrimer then added the solvent (always CHCl₃) and left this stirring in ambient lab conditions until all was completely dissolved, perhaps for a few hours, before then using this solution for device or photophysical measurements. In this way a value for the film PLQY of Dendrimer 1 was found to be 22 %, and for the double dendron Dendrimer 2 a value of 69 %, while the best neat film Dendrimer 1 devices gave an EQE of around 0.2 % [27, 93] in a single layer device, with and EQE of 4.8 % for a bilayer device [93]. In contrast on blending Dendrimer 1 with a TCTA host, devices were able to show remarkably high external quantum efficiencies of 16 % in a 20:80 wt % blend in a bilayer structure [26], and EQE of 8.1 % in a single layer structure [27] with a 20:80 wt % CBP blend. In a single layer device structure the EQE was further increased to greater than 10 % on using a 20:52:28 wt % three component blend with CBP.
and TPBI [123]. These greater device efficiencies arose in part from an increased PLQY of 78 % and 64 % respectively of these dendrimer-host blends [27]. The photoluminescence spectra from films of Dendrimer 1 and Dendrimer 2 are shown in Figure 4.5 along with those of Dendrimer 3 (KK-1-86A) and Dendrimer 4 (ZHL4-72). Dendrimer 3 was a second generation dendrimer of the original iridium(III) cored dendrimer of Figure 4.1. Dendrimer 4, similar to Dendrimer 2, was a double dendron dendrimer, but in this case the additional dendron was attached via a non-conjugated link, the effect of which will be subsequently discussed.

As the figure reveals all dendrimers showed a very similar shape of emission curve, albeit in Dendrimer 2 this spectrum was considerably redshifted in comparison to the other three dendrimers, all of which had an emission peak around 520 nm. All four dendrimers gave phosphorescent emission by the radiative decay to the ground state from the triplet state. The increase in dendrimer generation between Dendrimers 1 and 3 was found in accordance with Reference [119] only to give a very small change in the PL spectrum in that it narrowed slightly. In contrast the addition of a further dendron in moving from Dendrimer 1 to Dendrimer 2, where the first phenyl ring of each dendron was attached to a pyridyl ring so increasing in the conjugation length of the ligand involved in the metal-to-ligand charge transfer state, lead to a 27 nm red-shift in the emission peak [32, 43]. To reduce this red-shift, but still provide the reduced quenching effects of the double dendron approach for greater PL and EL efficiency, in Dendrimer 4 the conjugation was broken with the use of non-conjugated linkages to attach the dendron. By breaking this conjugation, the conjugation length of the ligand was shortened thereby reducing the red-shift of the ligand, a technique now commonly used in blue dendrimers to lead to deeper blue emission [117].

Figure 4.3: Structure of Dendrimer 3, Ir-G2

Figure 4.4: Structure of the double dendron Ir-DDG1, Dendrimer 4
4.3 The new solution-protocol

Section 4.2 introduced the main material, Dendrimer 1, that was used in this thesis and some other similar related molecules detailing some of the device and PL results previously published for these dendrimers. Since these publications more recent work to replicate these dendrimer results both in EL and PL seemed to indicate that these results were not in fact as previously believed optimised; they could in most cases be greatly exceeded through simple changes and improvements in the solution-processing technique.

These new results subsequently led to work by Dr Jean-Charles Ribierre to investigate whether aged solutions caused reductions in the photoluminescence efficiency of dendrimers [124]. For this study solutions of Dendrimer 1 and Dendrimer 2 were prepared at a 20 mg/ml concentration in chloroform before being left to dissolve prior to spin-coating. The storage conditions were in the ambient atmosphere and under normal room light illumination. The effect of photodegradation is clear in Figure 4.6, with in particular for Dendrimer 1 very little time in solution required to significantly reduce the PLQY. Intriguing for films made immediately after dissolving, the PLQY was exceeding high; 65 % for Dendrimer 1, and 81 % for Dendrimer 2, values close to those of degassed solutions of the same materials [119] and much greater than those previously reported for films of these dendrimers. The results, repeated in subsequent measurements, imply that through reducing the photodegradation by minimising the time spent in solution and under illumination prior to spin-coating the dendrimers, the effects of concentration quenching could be greatly reduced. The improvement in these results over those previously published shows the importance of correct solution preparation in order to achieve maximum efficiency. Furthermore, it is
noted the effect the additional dendron has on the rate of photodegradation. Dendrimer 2 shows a less dramatic decay than that of Dendrimer 1: the greater encapsulation has clearly acted to slow the decay kinetics of photodegradation, thus showing a further benefit of core encapsulation.

The effects of photodegradation were not found to be accelerated with the storage of solutions in the dark. The age, that is the time since opening to actual use, of the chloroform used to dissolve the dendrimer did not affect the PLQY. The grade of solvent used (spectrophotometric or HPLC) and the stabilisers (ethanol or amylenes) were found to affect the speed of photodegradation, however all start from the same initial value. It was thus apparent that provided films were made immediately after dissolving the dendrimer the solvent used had little effect, but for subsequent films made some time after dissolving it was best to use HPLC grade solvents and keep the solution stored in the dark until required.

4.3.1 New solution-protocol device characteristics

To elucidate the effect on the resultant device properties of this new solution preparation protocol where films were made immediately after dissolving, a set of bilayer devices were made. The devices used an electron transport/hole blocking layer of TPBI, with the electroluminescence layer made from one of three neat solutions of Dendrimer 1. The first film, made from solution A, was made from a solution spun immediately after dissolving whereas the other films, Film B and Film C, were made from solutions kept for 3 and 24 hours respectively under normal room light illumination prior to spin-coating. The resulting

Figure 4.6: Film PLQY as a function of time the dendrimer spent in solution prior to spin-coating [124]
current-voltage and luminance-voltage plots of the three devices are shown in Figure 4.7 and Figure 4.8 respectively. At any given applied bias voltage there was found to be a corresponding increase in light output with a decrease in current as the illumination time in solution was decreased. This was explained by a corresponding decrease in the film PLQY that Dr Ribierre measured for the same solutions; film A had a PLQY of 65 %, but after 3 hours in solution this fell to 35 % for a film made from solution B, falling to only 10 % after 24 hours in solution for the film made from solution C. The results are summarised in Table 4.1. There was also found to be an increase in the device current with photodegradation. This may have been due to the modification of the electrical properties by ionic species generated during photodegradation, or more probably from doping by oxygen. However, as the turn-on voltages for all the devices were similar, 2.7 V for devices A and B, and 2.9 V for device C, its clear that photodegradation did not significantly modify the charge injection into the device structure.

As Figure 4.10 shows, there was almost no change in the emission spectra caused by photodegradation. For all three devices the resulting emission spectrum was the same and did not change with applied bias voltage. The spectra shown were all taken at 8 V, with these and all other spectra taken at other applied voltages gave a CIE coordinate of (0.34, 0.61). The increase in quenching sites that arose as the photodegradation increased did not change the emissive properties of the device; these results were consistent with PL data (not included), and indicated the quenchers were non-emissive [125].

Plots of resulting external quantum efficiencies against applied bias voltages for devices A, B and C are shown in Figure 4.9. As the figure shows the EQE strongly decreased as the time in solution prior to spin-coating increased, which follows because the external quantum efficiency of a device is directly related to the PLQY of the emissive layer. The maximum EQE for device A was 9.8 % corresponding to power efficiencies of 16.6 lm/W or 34.8 cd/A, this maximum occurring at a luminance of 1700 cd/m$^2$
for an applied voltage of 6.6 V. For device B the maximum EQE was 7.4 % for 5.8 V applied voltage. Finally for device C the maximum EQE occurred at the lowest applied voltage of 5.0 V to give 2.2 % at 139 cd/m². Alternatively, at a standard brightness of 100 cd/m² the EQEs of devices A, B, C were 7.6 % (4.2 V); 6.6 % (4.2 V); and 2.1 % (4.8 V) respectively.

A summary of the device results is given in Table 4.1 alongside the PLQY values of the same solution to allow the direct comparison between them. The results show that for maximum efficiency the solution-processing technique must be optimised to ensure the concentration of quenchers were minimised. Previously under the old solution-processing protocol with neat dendrimer films, a PLQY of 22 % and bilayer device efficiency of 4.8 % were the best possible. Now by adopting the new solution-processing protocol these values have been increased by nearly three times in PL to a PLQY of 65 %, and over double in devices to give an EQE of 9.8 %. It was evident that the new protocol was very beneficial in achieving maximum performance and should be adopted in all cases. The presence of other factors in devices mean the drop in efficiency in devices was more pronounced than that seen purely in PL measurements, which in part was indicated by the changes in the current-voltage characteristics previously discussed and shown in Figures 4.7 and 4.8.

4.3.2 Effect of non-chlorinated solvents

Before the new solution-processing protocol had been developed, the effect of solvent was investigated for the solution-processing of Dendrimer 1 for single layer devices. For this a number of solvents were chosen, namely the aromatic solvents chlorobenzene and toluene; the moderately polar solvent tetrahydrofuran (THF); and the chlorinated solvents dichloromethane and chloroform. Other than the change
CHAPTER 4: HIGHLY EFFICIENT SOLUTION-PROCESSABLE DENDRIMER OLEDs

<table>
<thead>
<tr>
<th>Film</th>
<th>Film PLQY (%)</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>65</td>
<td>9.8 % (6.6 V, 16.6 lm/W, 34.8 cd/A)</td>
<td>7.6 % (4.2 V, 23.9 lm/W, 32.0 cd/A)</td>
<td>(0.342, 0.614)</td>
</tr>
<tr>
<td>B</td>
<td>35</td>
<td>7.4 % (5.8 V, 14.6 lm/W, 26.0 cd/A)</td>
<td>6.6 % (4.2 V, 19.6 lm/W, 26.1 cd/A)</td>
<td>(0.347, 0.610)</td>
</tr>
<tr>
<td>C</td>
<td>10</td>
<td>2.2 % (5.0 V, 4.8 lm/W, 7.7 cd/A)</td>
<td>2.1 % (4.8 V, 4.9 lm/W, 7.5 cd/A)</td>
<td>(0.344, 0.614)</td>
</tr>
</tbody>
</table>

Table 4.1: Summary of the PL and bilayer neat film EL data for neat films of Dendrimer 1

in solvent used to dissolve and spin-coat the electroluminescent dendrimer layer, all other aspects of the device were the same. The resulting device characteristics are shown in Figure 4.11 and summarised in Table 4.2.

The plot shows that the greatest device efficiency was obtained from the two chlorinated solvents with the other solvents resulted in devices with much lower device efficiencies. It was clear a change in solvent had a considerable effect on the device properties, possibly due to a change in film thickness resulting from the different vapour pressure of the solvents.

After establishing the new solution-processing protocol where the time of the dendrimer in solution was minimised, and all solvents kept in the dark prior to use, the above analysis of solvents was repeated. However in this case, for greater device performance, bilayer devices with a TPBI electron injection/hole blocking layer were used, and the solvent choice was limited to just one chlorinated solvent (chloroform) and one non-chlorinated solvent (toluene) the results of these devices are shown in Figure 4.12 and summarised in Table 4.3. For the chlorinated solvent the device curve is simply that of Figure 4.9 reproduced to compare with the performance of a new device made using toluene solution. In this latter case the device attained a maximum EQE of 8.4 % at 8.5 V, down from a maximum of 9.8 % at a much lower bias voltage of 6.6 V for when a chlorinated solvent was used. At the standard 100 cd/m² brightness the chlorinated solvent device was actually 0.2 % less efficient than the 7.8 % EQE found for the toluene device case, however this was severely countered by the fact that this improvement in efficiency required a 0.8 V increase in the driving voltage to 5.0 V. Furthermore, the PLQY measured under the new solution-processing protocol using toluene as the solvent was approximately equal to that found using chloroform as the solvent, and does not show the same level of degradation. The resulting difference in device performance was thus clearly related to changes in the electrical properties of the
devices caused by the presence of the aromatic rings in the toluene solvent case, which when not present in the chlorinated solvents case lead to superior device performance.

It was thus apparent, as found under the old solution-processing protocol, that chlorinated solvents were superior to non-chlorinated solvents for device manufacture. Moreover, this suggested that the generation of the quenchers responsible for the photodegradation in chlorinated solvents, that caused the decrease found in the film PLQY, were closely related to the strong photoactivity of cyclometalated iridium(III) complexes in chlorinated solvents. This has been previously observed for dichloromethane [126]. Finally, although the efficiency of neat film EL and PL has dramatically increased through the adoption of the new solution-processing protocol the resulting devices were still less efficient than the best devices using dendrimer-host blended films. Nonetheless, the obtainment of a device with an EQE of almost 10 % using a neat film emissive layer in such a simple structure was a considerable achievement for any organic semiconductor.
Table 4.2: Summary of device characteristics of single layer devices with various solvents prepared under the old protocol

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>0.36 % (10.0 V, 0.4 lm/W, 1.2 cd/A)</td>
<td>0.27 % (9.0 V, 0.3 lm/W, 1.2 cd/A)</td>
<td>(0.352, 0.605)</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>0.45 % (12.0 V, 0.4 lm/W, 1.5 cd/A)</td>
<td>0.13 % (9.2 V, 0.1 lm/W, 0.4 cd/A)</td>
<td>(0.353, 0.603)</td>
</tr>
<tr>
<td>chlorobenzene</td>
<td>0.15 % (9.4 V, 0.2 lm/W, 0.5 cd/A)</td>
<td>0.04 % (5.0 V, 0.1 lm/W, 0.1 cd/A)</td>
<td>(0.313, 0.629)</td>
</tr>
<tr>
<td>toluene</td>
<td>0.09 % (8.0 V, 0.1 lm/W, 0.3 cd/A)</td>
<td>0.04 % (5.4 V, 0.1 lm/W, 0.1 cd/A)</td>
<td>(0.309, 0.624)</td>
</tr>
<tr>
<td>THF</td>
<td>0.36 % (12.0 V, 0.3 lm/W, 1.2 cd/A)</td>
<td>0.12 % (7.4 V, 0.2 lm/W, 0.4 cd/A)</td>
<td>(0.345, 0.612)</td>
</tr>
</tbody>
</table>

Table 4.3: Summary of device characteristics of bilayer devices with various solvents prepared under the new protocol

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>chloroform</td>
<td>9.8 % (6.6 V, 16.6 lm/W, 34.8 cd/A)</td>
<td>7.6 % (4.2 V, 23.9 lm/W, 32.0 cd/A)</td>
<td>(0.342, 0.614)</td>
</tr>
<tr>
<td>toluene</td>
<td>8.4 % (8.5 V, 11.2 lm/W, 30.4 cd/A)</td>
<td>7.8 % (5.0 V, 15.8 lm/W, 25.1 cd/A)</td>
<td>(0.337, 0.620)</td>
</tr>
</tbody>
</table>

4.4 ITO Comparison

The adoption of a new solution-processing protocol as detailed in the previous section was found to lead to considerable enhancements in the device efficiency. Having optimised the performance of the electroluminescence layer, there remains many other parts of a standard device structure that could be considered for further device improvements. For example ITO, the standard anode choice for devices, due to its high conductivity and transparency, is normally a major limitation in device performance.

Indium tin oxide (ITO) is a polycrystalline single phase solid solution of a highly degenerate n type semiconductor with a wide band gap. It is formed by the sputtering together onto a glass substrate of a layer of a stoichiometric ratio of two metals to form an oxide layer. Unsurprisingly there can be a great variation in quality between manufactures and even between batches. The science of ITO deposition, cleaning, preparation and characterisation is vast and beyond the scope of this thesis, yet the importance of the careful choice of the quality of this layer can not be understated.

Throughout the duration of the thesis only two types of ITO glass were used. Both ITO types were purchased from Merck and both were of high grade quality. The first batch, ITO type A (with Merck
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Figure 4.12: Device characteristics of bilayer devices with various solvents prepared under the new protocol

batch code 300 735 XO), was used predominantly in the early stages of the project when throughout this time it became apparent that a better quality product could be purchased with little additional cost. The claimed literature advantage of this second batch, ITO type B (batch code 800 735 X0), was an improved surface roughness for the same transparency (≥ 80%), sheet resistance (∼ 20 Ω/□), and work function (∼ 4.7 eV without further surface treatment). In this case roughness was quoted as a density of the number of spikes per µm²; for ITO type A this was 2/µm², with a ten-fold improvement to 0.2/µm² for ITO type B. The advantage of a low surface roughness is the reduction of variations in the electric field within the OLED structure that would be caused by the spikes in the ITO piercing the organic layer deposited above and could lead to leakage currents and short circuits. For this reason often planarising techniques, or additional layers, are used to give a smoother ITO surface, for example see References [51, 127].

To determine whether there was any difference between the two ITO types used in this thesis, single layer neat film devices of structure ITO/dendrimer/Ca-Al were made in the same evaporation for both ITO types, the resulting device characteristics are shown in Figure 4.13 and summarised in Table 4.4.
As the figure shows, with the reduction in surface roughness there was a marginal improvement in the resulting device performance. With ITO type A the device attained a maximum EQE of 0.55 %, whereas with ITO type B the maximum EQE of the device increased to 0.64 % at a lower applied voltage of 10.8 V. Both devices gave a luminance in excess of 100 cd/m$^2$ at 6.6 V, for ITO type A this was 144 cd/m$^2$ for an EQE of 0.16 %, whereas at a lower luminance of 127 cd/m$^2$ ITO type B gave an EQE of 0.15 %.

It was accepted that batch-to-batch variability may account for some of the difference between the results, however similar device efficiencies were obtained using other batches of each ITO for the same device structure. Therefore the small change in the device efficiency results, prompted the question as to whether there was indeed any real differences between the ITO types. To assess this both types of ITO were analysed under an atomic force microscope (AFM) by Elizabeth Thomsen. For this 2 cm x 2 cm pieces of both types of ITO were cut before a number of 5 µm and 10 µm scans were taken across a number of points across the sample area. A sample of the resulting AFM scans are shown in Figure 4.14 for ITO type A, and in Figure 4.15 for ITO type B. The figures show that there was little apparent difference in the ITO types that could be determined through AFM measurements. Nevertheless, it is noted that any improvement in device performance, however minor, is welcome and strived for in industry, and thus the superior ITO type B was used unless otherwise stated for the remainder of the devices presented in this thesis.
4.5 PEDOT/PSS in iridium(III) cored dendrimer devices

No matter the quality of ITO used as the anode in devices, the use of ITO will still present a number of issues. Poor surface morphology, adsorption of impurities that affect its work-function, and batch-to-batch variations often lead to non-reproducible device performance and short lifetimes. To improve the performance of such devices and reduce the detrimental effects of ITO, numerous surface treatments and techniques have been investigated, for example see References [51, 53, 127–133].

The most successful method so far discovered, that leads to hole injection, efficiency and lifetime improvements, has been the simple coating of the ITO layer with the conjugated water-soluble polymer PEDOT/PSS. The extensive use of this layer has arisen from its insolubility after processing which allows other layers to be deposited onto it, making simple but efficient multi-layer devices possible. PEDOT/PSS has a HOMO level of \( \approx 5.1 \text{ eV} \) and so acts to reduce the energy barrier between the ITO
and organic layer. In addition, it acts as planarising layer on the ITO presenting a much smoother surface for the subsequent deposition of organic layers. In this way the contact area for charge injection into the organic is improved by the reduction of the possibility of electrical shorts that can be subsequently developing during operation.

Unfortunately PEDOT/PSS is very acidic and was apparently found to be detrimental to the efficiency of the iridium(III) cored devices studied previously on following the old solution-processing protocol [102], and thus was not commonly used within the device structure. Consequently these devices were likely to suffer from poor hole injection, and the lifetime of these early devices would have been limited.

Having adopted the new solution-processing protocol it seemed prudent to elucidate whether the same problems with the use of PEDOT/PSS layers remained present. For this study, neat and CBP host blend film bilayer devices with an electron transport/hole blocking layer of TPBI were fabricated, with all devices being made in the same evaporation. In all cases the electroluminescent layer was the standard iridium(III) cored dendrimer, Dendrimer 1. The resulting device structures were thus:

- Device structure A: ITO/100 wt % Dendrimer 1/TPBI/LiF/Al
- Device structure B: ITO/PEDOT/100 wt % Dendrimer 1/TPBI/LiF/Al
- Device structure C: ITO/20:80 wt % Dendrimer 1:CBD/TPBI/LiF/Al
- Device structure D: ITO/PEDOT/20:80 wt % Dendrimer 1:CBD/TPBI/LiF/Al

The resulting device characteristics are shown in Figure 4.16 and summarised in Table 4.5. From which it can be observed that for the neat film device without a PEDOT/PSS layer (Device structure A) the device was very efficient. In particular a maximum external quantum efficiency (EQE) of 8.5 % at 5.8 V was found. At the standard brightness of 100 cd/m$^2$ the EQE was 4.9 % at a bias of 4.0 V. The Dendrimer 1 device emitted light in the green corresponding to a CIE coordinate of (0.331, 0.626).

The inclusion of an additional PEDOT/PSS layer on the ITO (Device structure B) was found to slightly reduce the current through the device with little loss in light output. The current-light output was in this case better balanced causing the resulting device efficiency to increase slightly to obtain a maximum EQE of 9.4 % at 5.2 V, and at a brightness of 100 cd/m$^2$ an EQE of 8.6 % at 3.8 V. There was almost no colour shift in the emission spectra, this gave a CIE coordinate of (0.335, 0.623).

In the blend film of a 20:80 wt % ratio of Dendrimer 1 to a CBP host in device structure C, both the current through the device and the light output were considerably less than that of the neat film device.
case. Nonetheless the charge balance of current and light was still maintained which meant the resulting device efficiency was not affected. In fact the maximum EQE in the blend film device was slightly greater than that of the neat film case, albeit this required a higher driving voltage. For device structure C the maximum EQE achieved was 11.1 % at 7.0 V, and at a brightness of 100 cd/m$^2$ the EQE was 11.0 % at 6.6 V. Similarly, as seen in the neat film device case, the use of the additional PEDOT/PSS layer in device structure D gave a small decrease in the current and light output of the device. However in this case, unlike in the neat film case where this improved the device performance by assisting in charge balance, this decrease in light output and current caused a greater charge imbalance so causing a drop in efficiency compared to when no PEDOT/PSS layer was used. For device structure D the maximum EQE fell to 9.6 % at 7.4 V, and at a brightness of 100 cd/m$^2$ the EQE was 9.6 % at 7.6 V.

It was concluded that even when PEDOT/PSS layers were included within the device structure with iridium(III) cored dendrimers as the emission layer, it was still possible to make successful and efficient devices. Albeit it appeared, particularly in the neat film device case, to be giving no great benefit to the device efficiency.
Table 4.5: Summary of the EQE results for neat and blend film devices with and without PEDOT/PSS

<table>
<thead>
<tr>
<th>Device</th>
<th>Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ITO/100 wt % Dendrimer 1/TPBI/LiF/Al</td>
<td>8.5 % (5.8 V, 20.5 lm/W, 37.9 cd/A)</td>
<td>4.9 % (4.0 V, 14.4 lm/W, 18.3 cd/A)</td>
<td>(0.331, 0.626)</td>
</tr>
<tr>
<td>B</td>
<td>ITO/PEDOT/100 wt % Dendrimer 1/TPBI/LiF/Al</td>
<td>9.4 % (5.2 V, 20.8 lm/W, 34.4 cd/A)</td>
<td>8.6 % (3.8 V, 25.9 lm/W, 31.3 cd/A)</td>
<td>(0.335, 0.623)</td>
</tr>
<tr>
<td>C</td>
<td>ITO/20:80 wt % Dendrimer 1:CBP/TPBI/LiF/Al</td>
<td>11.1 % (7.0 V, 17.9 lm/W, 39.9 cd/A)</td>
<td>11.0 % (6.6 V, 21.9 lm/W, 39.6 cd/A)</td>
<td>(0.331, 0.622)</td>
</tr>
<tr>
<td>D</td>
<td>ITO/PEDOT/20:80 wt % Dendrimer 1:CBP/TPBI/LiF/Al</td>
<td>9.6 % (7.4 V, 14.9 lm/W, 35.1 cd/A)</td>
<td>9.6 % (7.6 V, 14.5 lm/W, 35.1 cd/A)</td>
<td>(0.313, 0.637)</td>
</tr>
</tbody>
</table>

4.5.1 Device lifetime comparisons

The previous section established that the use of PEDOT/PSS layers within the device structure give minimal improvement in device efficiency. However, the results presented were from one device run up to a maximum of a 10 V applied bias and thus in no way can show the real benefit of the use of a PEDOT/PSS layer - lifetime improvements.

To determine whether indeed PEDOT/PSS did give such lifetime improvements a different experiment was set up in which a simple measure of the device lifetime was made. An unencapsulated device was applied with a constant applied current with the required driving voltage to maintain this current and the light output of the device measured. The measurement was performed in air. In this experiment lifetime was defined as the time taken for the light output to fall to the background level; that is, the time taken for the device to stop emitting light due to degradation processes causing the growth of black spots across the entire emission area. The degradation may be caused by moisture, oxidation or electrical faults. Unlike the accelerated lifetime tests used in industry, which typically measure a time to half-brightness on driving at high brightness and then extrapolating, this is a simple and quantitative test that gives a measure of the device lifetime without the need for further mathematical analysis.

For this test single layer devices (ITO/Dendrimer/Ca/Al) were made with and without PEDOT/PSS layers included in the device structure. The electroluminescent layer was formed from a blended film of Dendrimer 1 in CBP at a 20:80 wt % ratio made at a concentration of 20 mg/ml with dichloromethane used as the solvent. For the device structure that included PEDOT/PSS a current of 1 mA was applied to the device of area 5.5 x10⁻⁶ cm². As Figure 4.17 shows the device was able to sustain this current by
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Figure 4.17: Lifetime plots for single layer blend film devices for Dendrimer 1 with and without PEDOT/PSS layers included within the device structure

<table>
<thead>
<tr>
<th>Structure</th>
<th>Applied Current</th>
<th>Lifetime (minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>With PEDOT/PSS</td>
<td>1 mA</td>
<td>281</td>
</tr>
<tr>
<td>No PEDOT/PSS</td>
<td>2 mA</td>
<td>51</td>
</tr>
</tbody>
</table>

Table 4.6: Lifetime summary for single layer blend film devices for Dendrimer 1 with and without PEDOT/PSS layers included within the device structure

Applying a constantly increasing voltage rising from an initial 15 V to 28 V. The increasing voltage, as the figure shows, was required to sustain an approximately constant light output at a photodiode voltage of around 0.12 V (corresponding to a brightness of around 100 cd/m²) that the specified current produced. Eventually the voltage applied to sustain the 1 mA current became too great and the device broke down and stopped emitting light and the experiment was stopped. In this case the device lasted 281 minutes or 4.6 hours before breakdown. In comparison a device of the same area but without a PEDOT/PSS layer lasted only 51 minutes when driven to produce the same initial brightness, this also required a higher applied current of 2 mA to give this brightness. The results are summarised in Table 4.6.

Of course using the same 1 mA applied current for both devices would have been possible, acting to prolong the lifetime of the non-PEDOT containing device, but without both devices starting at the same brightness this would not have been an accurate comparison. Instead the comparison has clearly shown that PEDOT/PSS did improve the lifetime of iridium(III) cored devices and thus such a layer could be readily used in future where such an effect was desired. For further improvements in device lifetime encapsulation layers could also be incorporated into the device structure and the testing could be performed under the normal vacuum conditions.
4.6 Dendrimer 1 batch analysis and optimisation

As noted before all dendrimers discussed in this thesis were synthesised in Oxford, all in varying quantities. Consequently it was often the case that a popular dendrimer was used to completion. In this case a second version (or batch) of the same dendrimer was required to be made. Before dispatch extensive comparison measurements between the batches were made in Oxford using techniques of TLC, NMR and MALDI mass spectroscopy to ascertain the equivalence of the two batches. However it was still necessary to check whether photophysical and device properties were the same.

All the devices discussed thus far in the thesis have used the same batch of Dendrimer 1 (Oxford batch code SVS01-3F) as the electroluminescent layer. In later cases a second batch (ZHL4-35) of this dendrimer was also used. This section briefly establishes the complete equivalence of these two batches through device and PL measurements. Consequently in subsequent chapters of the thesis no determination of the exact batch will be given unless particularly relevant, with all batches just referred to as Dendrimer 1.

4.6.1 Photoluminescence of Dendrimer 1

The resulting solution and film absorption and emission spectra for the two batches of Dendrimer 1 are shown in Figure 4.18. As can be seen both batches had effectively the same characteristics as previously found for Dendrimer 1 [119]. That is, in both solution and film, the absorption spectra consisted of two components: the absorption of the phenylene dendrons causing the large peak around 272 nm, and the absorption of the fac-tris(2-phenylpyridyl) iridium core between 325 and 475 nm. While in the emission spectra the peak for solution and film was around 520 nm as previously found. The similarity in emission spectra of the two dendrimers was reflected in the CIE coordinates: for the solution emission spectrum of batch A (SVS01-34F) a CIE coordinate of (0.335, 0.582) was calculated, with almost no change in batch B (ZHL4-35) which gave a CIE coordinate of (0.334, 0.582). Moving from solution to film gave a slight red-shift in the emission spectra leading to a CIE coordinate of (0.341, 0.617) for batch A, and (0.347, 0.614) for batch B. In both cases the equivalence of spectra confirmed that both dendrimer batches A and B were the same. Further chemistry analysis techniques also confirmed this [134].

The solution and film PLQY were measured for both batches of Dendrimer 1 and were found to be the same. In film a value of 62 % was found for both batches, well within the error of the 65 % measurement.
Figure 4.18: Solution and film absorption and emission plots showing the equivalence of the two batches of Dendrimer 1 used in the thesis, left hand plot shows solution results, right hand plot shows film results

<table>
<thead>
<tr>
<th>Dendrimer 1 Batch</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch A</td>
<td>11.6 %</td>
<td>9.6 %</td>
<td>(0.341, 0.616)</td>
</tr>
<tr>
<td></td>
<td>(4.8 V, 27.7 lm/W, 41.7 cd/A)</td>
<td>(3.6 V, 34.1 lm/W, 33.8 cd/A)</td>
<td></td>
</tr>
<tr>
<td>Batch B</td>
<td>12.1 %</td>
<td>12.1 %</td>
<td>(0.331, 0.623)</td>
</tr>
<tr>
<td></td>
<td>(6.0 V, 22.9 lm/W, 43.9 cd/A)</td>
<td>(6.0 V, 22.9 lm/W, 43.9 cd/A)</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.7: Summary of bilayer device characteristics of Dendrimer 1 for various batches

reported previously by Dr Jean-Charles Ribierre [124] (note this was for batch A). In solution a value of around 80 % was obtained for each dendrimer, which although was slightly higher than the published value [119], was within the experimental error of ± 10 %. The similarity in the results of the two batches of Dendrimer 1 reflected one of the main advantages of dendrimers; they are monodispersive and thus excellent batch-to-batch reproducibility is possible even for small batches.

4.6.2 Dendrimer 1 devices

To complete the characterisation studies of Dendrimer 1 to confirm the equivalence between the two batches a set of bilayer devices was made. For this the device structure was ITO/dendrimer/TPBI/LiF/Al where neat film layers of batch A and B of Dendrimer 1 formed the electroluminescent layer. The resulting emission spectra are shown in Figure 4.19. As in photoluminescence the EL emission spectra are equivalent; both peak at around 520 nm with batch A giving a CIE coordinate of (0.341, 0.616) close to that found for PL, while for batch B there was a slight shift in the CIE coordinate to give (0.331, 0.623).
In order to fully compare batches of dendrimers in devices an optimised device structure was required. By using neat films of Dendrimer 1 from the two different batches this was attempted using the standard bilayer structure with a TPBI layer included within the device structure as an ETL/HBL.

For batch A of Dendrimer 1 a number of device runs were made (data not shown) where the thickness of the TPBI layer was varied. This involved attempting layer thicknesses in the range 30 to 80 nm, with the optimum thickness for maximum device efficiency found to be 70 nm. The resulting maximum EQE achieved for this device was 11.6 % at 4.8 V. At the standard brightness of 100 cd/m$^2$ the EQE was 9.6 % at 3.6 V, an improvement of almost 2% on that reported previously for this dendrimer. A plot of the EQE versus applied voltage for this device is shown in Figure 4.19.

For batch B of Dendrimer 1, the same device structure with a 70 nm layer of TPBI as found for batch A was attempted, but in this case this was found to be no more successful. For an additional improvement on this device performance it was found necessary to change the solvent used for solution-processing of the film from chloroform to dichloromethane. Dichloromethane has a lower boiling point (40 °C) in comparison to chloroform (61 °C) which means it has a higher vapour pressure (290 mm Hg at 20 °C, against 159 mm Hg at 20 °C in chloroform). Consequently dichloromethane is a more volatile solvent than chloroform and so will evaporate more quickly during spin-coating leading to slightly thinner films. A film thickness of approximately 100 nm has been found to be standard. The resulting bilayer device using this dendrimer layer in combination with the 70 nm thick TPBI layer, an ITO anode (Merck 800 735 X0), and a cathode of 1.2 nm LiF capped with 100 nm of Al, gave a maximum EQE of 12.1 % at 6.0 V which also corresponded to the efficiency at the standard brightness of 100 cd/m$^2$. The effi-
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Efficiency curve against the applied voltage for this device is shown in Figure 4.19 in comparison to the best performing device obtained using batch A of the same dendrimer.

This efficiency of this device was very high, higher in fact than has been previously seen using CBP host blended films of this dendrimer [135]. These results showed firstly the importance of adopting the correct solution protocol for device fabrication, but more importantly indicated that for efficient devices hosts were not always required. The significance of this can not be overestimated. Reconsider Equation 4.1 in the standard bilayer structure there is nothing done to increase the $\Phi_{ESCAPE}$ term - in this device due to the large refractive index contrast with surrounding air a lot of emitted light becomes trapped in various waveguided modes, where it may be reabsorbed or emitted from the edges of the device. Lateral emission is not in the intended and useful forward direction and hence is regarded as a loss. A simplistic analysis gives the fraction of power coupling to leaky air modes as $\frac{1}{4n^2}$, or $\frac{1}{2n^2}$ if as done here a metal cathode is used to reflect light emitted backwards back out of the device (where n is the refractive index of the active layer) [100, 136, 137]. In general organic semiconductors have refractive indices of around 1.6, hence $\Phi_{ESCAPE}$ will be equal around 0.2; up to 80% of the light generated within a device remains trapped within the device. Consequently in Equation 4.1 the maximum theoretical $\Phi_{EXT}$ is limited to only 20% assuming all other terms are, as can be possible using dendrimers, equal to 1.

For Dendrimer 1 the neat film PLQY was measured to be 65%, therefore for devices with this dendrimer, from Equation 4.1 the maximum theoretical external quantum efficiency was limited to only 13%. The device shown in Figure 4.19 gave a maximum EQE of 12.1% and was thus almost as efficient as the maximum theoretically possible using this dendrimer. It is recalled that Dendrimer 1 was a single dendron first generation dendrimer where the effect of intermolecular interactions would be greatest. The results implied that with higher generations of dendrimer where the effect of such emission quenching interactions were reduced leading to higher PLQYs, the device performance could be further improved over those values so far reported.

4.7 New protocol results on other dendrimers

This chapter has already introduced Dendrimers 1 to 4 detailing the improved device results for Dendrimer 1 obtained using the new solution-processing protocol for film preparation. In this section the effects of applying the new solution-processing protocol to Dendrimers 2, 3 and 4 were investigated.
in order to see if these dendrimers could also undergo efficiency improvements on adopting this new protocol.

### 4.7.1 Dendrimer 2 new protocol results

The structure of Dendrimer 2 (SVS02-41B) was shown previously in Figure 4.2. Following measurements performed under the old solution-processing protocol for spin-coating this double dendron dendrimer was previously studied and published in Reference [121]. Now having adopted the new solution-processing protocol where the time of the dendrimer in solution prior to spin-coating was minimised to as close to zero as possible, and all solutions are kept in the dark, Dendrimer 2 was remeasured (by Dr Jean-Charles Ribierre) to have an increased film PLQY of 81 %. In comparison, under the old protocol, this same measurement yielded a value of only 70 % for this dendrimer. Although only marginal, there was still an improvement in the film PLQY for this dendrimer on following the new protocol. Furthermore, as the presence of the second dendron acted to reduce the photodegradation effects seen in Dendrimer 1 through increased encapsulation and thus protection of the core, Dendrimer 2 was more efficient than the single dendron Dendrimer 1. The photodegradation process was shown to depend on the macromolecular structure of the dendrimer and decreased as the complexity of this increased, and hence could be tuned as desired [124].

Due to a shortage of material only one set of devices were able to be attempted using Dendrimer 2. For this device set the standard bilayer structure with an electron transport/hole blocking layer of TPBI was used. A neat film of Dendrimer 2 acted as the emission layer. Unfortunately in this small device set no device optimisation was possible. The characteristics of the resulting device are shown in Figure 4.20 and are summarised in Table 4.8. Here a maximum EQE of 12.9 % at 5.2 V was able to be achieved following the new protocol, with at the standard brightness of 100 cd/m² the EQE falling to 11.4 % at 3.8 V. The figure also shows the electroluminescence emission spectrum from which the CIE coordinate was (0.466, 0.529). The yellow-greenness of the Dendrimer 2 emission showed the small improvement in PL and EL efficiency with this dendrimer, through the use of the second dendron, was only achieved by sacrificing the vibrant green emission colour seen in Dendrimer 1.

A comparison of these Dendrimer 2 device results to those obtained and published previously by following the old solution-processing protocol used at that time, shows they were comparable but were not any more efficient. It was perhaps unsurprising that the published maximum device external quantum
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Figure 4.20: Device characteristics of bilayer devices for Dendrimer 2

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Film PLQY (%)</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 2</td>
<td>81</td>
<td>12.9 %  (5.2 V, 25.8 lm/W, 42.6 cd/A)</td>
<td>11.4 %  (3.8 V, 30.1 lm/W, 29.7 cd/A)</td>
<td>(0.466, 0.529)</td>
</tr>
</tbody>
</table>

Table 4.8: Summary of bilayer device characteristics of Dendrimer 2

efficiency of 13.6 % (at 110 cd/m², 4.8 V) [121] turns out to be a little higher as this device was able to be optimised, unlike the new device results reported here on following the new solution-processing protocol for spin-coating. The results did however again show that efficient host-free dendrimers OLEDs were possible.

4.7.2 Dendrimer 3 new protocol results

As shown previously in Figure 4.3, Dendrimer 3 (KK-1-86A) was a second generation iridium(III) cored dendrimer (Ir-G2) and thus will have greater core-to-core spacing and undergo less quenching interactions than the first generation dendrimer. Previous measurements have found the addition of a second generation of dendrons to give an increase in the PLQY over that of the first generation Dendrimer 1. For Dendrimer 3 a PLQY of 31 % in a neat film [27], and 69 % in solution [119] were previously found. This result giving a 10 % improvement in PLQY efficiency in moving from the old solution-processing protocol result of the first generation iridium(III) dendrimer, Ir-G1, to the second generation. It has already been shown that Ir-G1 (Dendrimer 1) benefitted greatly in terms of improvements in its PL and EL efficiency as the photodegradation effects were minimised by adopting the new solution-processing protocol, and thus it was considered if Dendrimer 3 would too benefit in the same way.

On measuring the neat film PLQY using the new solution-processing protocol this was indeed found to be true; a new neat film PLQY value of 71 % was obtained for Dendrimer 3. The result was in-
triguing as firstly it implied the improvement in moving to the second generation dendrimer was not as
pronounced as first thought; and secondly a second dendron on the core, rather than a second generation
of dendrons, appeared to be more effective in reducing the effects of photodegradation on the dendrimer.

To further study these effects neat film bilayer devices were made using Dendrimer 3 as the emission
layer. As before TPBI was used as the electron transport/hole blocking layer with ITO and LiF-Al as the
anode and cathode respectively. Also as previously, due to the lack of material, no device optimisation
was possible with this dendrimer. The resulting device characteristics are shown in Figure 4.21 and
summarised in Table 4.9.

As the figure shows a Dendrimer 3 device emitted in the green with a corresponding CIE coordinate
of (0.320, 0.616). This coordinate was approximately equal to that found for a device of similar structure
for the first generation Ir-G1 dendrimer (Dendrimer 1) indicating that, as shown for the photolumines-
cence spectra in Figure 4.5 there was little discernable change in the emission spectra caused by the
increase in dendrimer generation.

In contrast, the increase in dendrimer generation was found to lead to improvements in the device
efficiency. For a bilayer neat film of Ir-G2, the maximum external quantum efficiency of the device
was 15.2 % at 5.2 V which happened also to occur at the standard brightness of 100 cd/m². There was
almost a doubling of the maximum efficiency previously found for this dendrimer [93], with the value
now obtained also greater than the 10 % obtained from a host blend device with this dendrimer [135].
Furthermore, the maximum efficiency of the device was around 2 % more efficient than the maximum
efficiency found for the double dendron Ir-G1₂ (Dendrimer 2) device, and 3 % more efficient than that
of the optimised first generation iridium(III) dendrimer device. It was evident that, as has been found
previously, there was a clear advantage in increasing the dendrimer generation due to the improvement
in charge carrier balance that arose from the increased core-to-core spacing reducing the hole mobility in
the higher generations of dendrimer [93]. The results showed that highly efficient devices could be made
using higher generations of dendrimer where there are less interactions acting to quench the emission.
With further layer optimisation this device performance could perhaps be further improved.

4.7.3 Dendrimer 4 new protocol results

The structure of the double dendron dendrimer Dendrimer 4 (ZHL4-72) was shown previously in Fig-
ure 4.4. This dendrimer has a break in the conjugation in the linkage connecting the dendron to the
pyridine off the iridium core. This non-conjugated links acts to reduce the conjugation length of the ligand in order to eradicate the red-shift that is normally present in such double dendron dendrimers (e.g. as in Dendrimer 2). This approach although applied to blue dendrimers [117] has never previously been used for green(-yellow) emitters.

This dendrimer was measured by Dr Ruth Harding to have astonishingly high PLQY value of 93 % in solution, the highest ever efficiency so far found for a dendrimer, and well in excess of those recorded for Dendrimers 1 to 3. However, the neat film PLQY of Dendrimer 4 was only 63 %. A value comparable to that of Dendrimer 1, but less than that of Dendrimers 2 and 3. Dendrimer 4 unlike in all these other dendrimers showed a considerable decrease in PLQY from the solution PLQY value indicating it suffered more from quenching effects than the other dendrimers. Considering the structure this was not surprising - it contains a non-conjugated linkage and thus does not have the strength of the dendrons normally used: the dendrons are said to be floppy. As a result Dendrimer 4 unlike the others was very hard to synthesise into the form of a final solid state and so it was a sticky oil that was used for film making. For the same 20 mg/ml solution concentration as used for the previous dendrimers, a film of Dendrimer 4 at this concentration was be thinner and softer.

The absorption and emission spectra of Dendrimer 4 are shown in Figure 4.22. For both film and solution the absorption spectra were very similar - both contained absorption from the iridium(III) core and the phenylene dendrons, and showed little change from the standard first generation iridium(III)
dendrimer. Consequently, the emission spectra as already shown (for film) in Figure 4.5, also showed little shift in the position of the peak from that of the first generation iridium(III) dendrimer, in contrast to the double dendron dendrimer Dendrimer 2 with conjugated dendrons. By breaking the conjugation to attach the dendron the emission colour, as can be determined from the spectra, remained green and gave a CIE coordinate of (0.332, 0.622) in solution, which slightly broadened in film to give a CIE coordinate of (0.371, 0.587).

Bilayer devices were also attempted with Dendrimer 4 using a structure of ITO/dendrimer/TPBI/LiF-Al where TPBI was the electron transport/hole blocking layer. The resulting device characteristics are shown in Figure 4.23. The figure shows that the device gave a maximum external quantum efficiency of 6.4% at 5.4 V, with at the standard brightness of 100 cd/m² the efficiency was 5.5% at 9.2 V. Table 4.10 summarises these results with the characteristics plotted in Figure 4.23.

The emission spectrum of the device is also shown in the figure. As shown in the figure the device emission in addition to a clear peak at 515 nm had a large hump in the red region of the spectrum around 640 nm which was not observed in the solution or film spectra. This result, repeated in a second device set of this dendrimer, suggested that in this device structure there was an additional emission from some charge transfer state, impurity or exciton that has contributed to the total device emission. As a result of this contribution the resultant device emission was not as green as found for the photoluminescence spectra in both solution and film. Nevertheless, the emission colour was still much more green than the conjugated double dendrimer (Dendrimer 2) device corresponding to a CIE coordinate of (0.398, 0.622).
0.539). Intriguing on moving to a 20:80 wt % Dendrimer 4:CBP blend film the green colour of the PL was maintained as shown in the figure. The red contribution was no longer found to be present in the device emission spectrum, and the device yielded a CIE coordinate of (0.352, 0.606). Unfortunately by blending this dendrimer with the charge transporting host the charge balance is modified and the efficiency dropped to a maximum of 3 %.

The neat film Dendrimer 4 device was thus significantly less efficient than any of the devices made using Dendrimers 1 to 3. It was clear that in this double dendron dendrimer maintaining some of the green colour of a single dendron dendrimer has come at the detriment of the device efficiency. The reasons for this are not as yet fully clear, but may be related to the presence of a charge transfer state causing the red contribution seen in the emission spectra, or an impurity in the dendrimer that was not noticeable in the PL measurements. Alternatively, or in addition, the floppy dendrons used in Dendrimer 4 may have collapsed in the film producing a poorer film quality than would normally be possible when other dendrons were used.

![Figure 4.23: Device characteristics of bilayer devices for Dendrimer 4](image)

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Film PLQY (%)</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 4</td>
<td>63</td>
<td>6.4 % (5.4 V, 6.5 lm/W, 11.2 cd/A)</td>
<td>5.5 % (9.2 V, 3.3 lm/W, 9.7 cd/A)</td>
<td>(0.398, 0.539)</td>
</tr>
</tbody>
</table>

Table 4.10: Summary of bilayer device characteristics of Dendrimer 4

### 4.8 Soluble hosts

The device results reported thus far in this thesis have shown that very efficient devices could be made from neat film devices where no host materials were required. In this case the device fabrication process...
was simplified and problems such as phase separation were not an issue. Yet for further efficiency improvements in devices, and in particular to obtain efficient devices of other emissive colours, it may be that in some cases that host blending could still be required.

Traditionally the host used was the small molecule CBP which has been found only to be soluble in chlorinated solvents after a couple of hours on a stirring plate. Therefore for host blending under the new solution-processing protocol it would require the pre-dissolving of the host before the dendrimer was added some time later just before spin-coating. In many cases this procedure was followed leading to the successful fabrication of many high efficiency devices as detailed in this and subsequent chapters. This process however was not ideal and it would be infinitely better if the host and dendrimer could be dissolved together at the same time; that is, the host was as readily soluble as the dendrimer. After considerable efforts to synthesise such a host, two soluble hosts became available late in the project. The structure of these hosts are shown in Figure 4.24.

In soluble host A (SCL18-67) the structure is that of a CBP host molecule with the addition of extra phenyl rings of the carbazole C3 and C6 positions onto which solubilising 2-ethylhexyloxy surface groups were attached. In soluble host B (HB03-29B) a similar approach for the attachment of surface groups was used, with in this case the central two phenyl groups between the end carbazole groups replaced by a fluorene molecule, an approach that has also been used elsewhere [138–141].

### 4.8.1 Photoluminescence of soluble hosts

To determine the effectiveness of these new hosts PL measurements were performed by Dr Jean-Charles Ribierre on these new hosts alongside the standard CBP host. For this the standard first generation iridium(III) cored dendrimer (Ir-G1), Dendrimer 1, was blended as a 20:80 weight percentage ratio of dendrimer to host in each of the three hosts.
The absorption and emission spectra of the three hosts blended with Dendrimer 1 are shown in Figure 4.25. As the figure shows the change in surface groups from CBP to soluble host A caused slight change in the resultant absorption spectra. The spectra of soluble hosts A and B were very similar but the CBP blend spectra had a pronounced peak at 237 nm that was not present in either of the other two cases which instead gave larger peaks around 264 nm caused by the absorption of the additional phenyl groups in these molecules. In all three blends the resultant emission spectra was dominated by the guest emission showing only very weak host emission, which indicated that for all three hosts there was sufficient host to guest energy transfer for efficient emission.

In the standard case with a CBP blend the film PLQY was measured to be around 80 %, similar to the value found and published previously in Reference [27]. On adding the soluble surface groups for soluble host A there was found to be no loss in PL efficiency, with a value of around 80 % also found. In soluble host B the use of fluorene central group was found to lead to a small if insignificant drop in the film PLQY to give a value of around 75 %. It appeared that the new soluble hosts could give similar advantages to CBP such as improved chromophore spacing and reduced triplet-triplet annihilation leading to high PL efficiencies, but with the additional and important advantage of high solubility.
CHAPTER 4: HIGHLY EFFICIENT SOLUTION-PROCESSABLE DENDRIMER OLEDs

4.8.2 Soluble host devices

To ascertain whether the similarity in performance demonstrated by the new hosts in PL could be replicated in EL, bilayer devices were made using each of the three hosts. For this a blend of a 20:80 weight percentage ratio of Dendrimer 1 in each host was used. For this films were made at a concentration of 20 mg/ml in dichloromethane with the solvent added to the host-dendrimer blend immediately prior to spin-coating except in the CBP case which was required to be predissolved two hours in advance. A 60 nm layer of TPBI was used as the electron transport/hole blocking layer. In all cases devices were able to be successfully made, thereby for the first time ever demonstrating emission from a phosphorescent dendrimer-soluble host blend. The resulting device characteristics are shown in Figure 4.26 and summarised in Table 4.11.

In the standard case with a CBP host the resulting device was extremely efficient achieving a maximum EQE of 19.2 % at 19.8 V, falling to 16.4 % at a brightness of 100 cd/m$^2$ for an applied voltage of 12.0 V. The spectral colour of emission as shown in the figure corresponded to a CIE coordinate of (0.352, 0.605). This coordinate was close to the value found in a neat film device of the same dendrimer in a similar device structure, emphasising as in PL the host played no role in the emission.
### Table 4.11: Summary table of device characteristics of bilayer devices for Dendrimer 1 host blends

<table>
<thead>
<tr>
<th>Host</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m² or Max Luminance</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>CBP</td>
<td>19.2 % (19.8 V, 10.9 lm/W, 68.8 cd/A)</td>
<td>16.4 % (12.0 V, 15.4 lm/W, 58.7 cd/A)</td>
<td>(0.352, 0.605)</td>
</tr>
<tr>
<td>Soluble host A</td>
<td>13.4 % (15.4 V, 9.7 lm/W, 47.5 cd/A)</td>
<td>13.3 % (10.6 V, 13.9 lm/W, 47.1 cd/A)</td>
<td>(0.326, 0.624)</td>
</tr>
<tr>
<td>Soluble host B</td>
<td>11.5 % (5.8 V, 22.1 lm/W, 40.9 cd/A)</td>
<td>0.55 % (70 cd/m², 20.0 V, 0.3 lm/W, 1.9 cd/A)</td>
<td>(0.315, 0.627)</td>
</tr>
</tbody>
</table>

For both soluble hosts A and B, as the figure shows, there was a slight narrowing of the emission spectra with the pronounced shoulder seen at 550 nm in CBP found to be almost discernable. This difference, not seen in photoluminescence, reflected the different ways in which the excitation occurs in these processes. For soluble host A the resulting CIE coordinate was (0.326, 0.624), which shifted marginally to (0.315, 0.627) for soluble host B.

For soluble host A both the resulting current through the device and the light output were considerably greater than those measured when a CBP host was used. Consequently the charge balance was not as effective as for a CBP blend and so the resulting maximum EQE was lower peaking at 13.4 % for a lower applied voltage of 15.4 V. At the standard brightness of 100 cd/m² the efficiency was 13.3 % at 10.6 V. Both the current and light output in the soluble host A device were the greatest recorded in any of the three device cases, which additionally appear from the flatness of the EQE curve for this device to be well balanced across the bias voltage range investigated. Consequently for this device the maximum voltage was obtained at a much lower voltage than with a CBP host, with in fact this soluble host giving more efficient devices than with CBP at all biases below 9 V.

Despite the apparent similarity of soluble host B to the other hosts in PL, the resulting devices using this host were considerably worse than when either of the other two hosts were used. The current through the soluble host B device was greater than that through a CBP host device but the light output of this device was over an order of magnitude less at any applied voltage. Consequently the resultant efficiency of the device was in comparison very low, only 11.5 %, peaking at a low bias of 5.8 V before quickly tailing off as the charge imbalance became more marked as the applied bias increased. The low light output also meant the maximum luminance recorded occurred at the maximum applied bias of 20 V giving only 70 cd/m² for an EQE of 0.55 %. Therefore the inclusion of the fluorene molecule in the host structure was found to be detrimental to device performance despite the apparent similarity in the PL.
behaviour of this host in comparison to the others considered. The reasons for this remain not obvious, but one factor may relate to the shorter radiative lifetime in this host \[125\], or its slightly poorer film forming ability.

**4.8.3 Soluble host devices - molar ratio blends**

One possible reason for the loss in efficiency at high applied bias voltages between the CBP host and the two soluble hosts may be because the blend ratios were not equivalent. Previously a ratio of 20:80 dendrimer to host by weight percentage was used as this ratio has been found to be optimum for a blend of Dendrimer 1 with CBP \[102\]. However as the soluble hosts have different structures to that of CBP, they will have a different molecular weight and thus this ratio is unlikely to be optimum. Consequently as a fairer comparison between the host materials a second bilayer device set was made but now with a blending ratio equivalent to the 20:80 wt % Dendrimer 1:CBP host blend. For soluble host 1 this was found to be a ratio of 8.5:91.5 wt % Dendrimer 1:soluble host A. Due to the inferior previously detailed performance of soluble host B no further devices were chosen to be made with using this host. The resulting device characteristic of the new soluble host A device are compared to that of the previously detailed CBP host device in Figure 4.27 and are summarised in Table 4.12.

In this case the device performance was found to be very similar up to about 8 V after which the CBP host device again started to become more efficient. The maximum device efficiency with a CBP host was 19.2 %, whereas with soluble host A this EQE maximum was some 5 % less at 14.2 %, but obtained at voltage of 15.0 V nearly 5 V less than of the maximum for the CBP host. At a brightness of 100 cd/m\(^2\), the EQE of the soluble host device was also less at 13.8 % (11.2 V), in comparison to the 16.4 % found previously for the CBP host device. There was also found to be little change in the emission spectra; with CBP the CIE coordinate was (0.352, 0.605), whereas with soluble host A this shifted slightly to give a CIE coordinate of (0.338, 0.609).

The high efficiencies found with soluble host A particularly at low applied bias voltages nevertheless showed that this host has great promise as a suitable replacement for the insoluble CBP host in future devices. CBP, the blend ratios of which are already optimised, has been shown to be capable of giving very efficient devices, but there is no reason why soluble host A can not likewise be optimised in its blending ratio to improve the efficiency of devices using this material. In this way it would possess the advantages over CBP of both solubility and efficiency, so making its future use in devices, particularly
4.9 Summary

This chapter has described the efforts to further improve the efficiency (and lifetime) of thin films of solution-processable light-emitting fac-tris(2-phenylpyridyl) iridium(III) [Ir(ppy)$_3$] cored dendrimers. In particular, it was shown that by careful control of the film preparation procedure used to make dendrimer...
films, the photodegradation processes present in solutions of such dendrimers can be minimised. This was an important result as in past publications regarding devices made from dendrimers it was found that for maximum efficiency the dendrimer used was required to be first blended in a carbazole containing CBP host prior to spin-coating \[26, 27\]. Unfortunately, CBP and dendrimers have large differences in their solubility; while CBP is only slightly slightly soluble in a small number of solvents, dendrimers dissolve instantly in almost all solvents. By modifying the solution-processing technique such that the time of the dendrimer in solution was minimised, it was found that a first generation iridium(III) cored dendrimer could in fact be used to give a highly efficient host-free green-emitting dendrimer OLED. In a simple neat film bilayer device structure the maximum efficiency recorded was 9.8 % at a brightness of 1700 cd/m\(^2\). This improvement in neat film device performance was established to arise from a corresponding improvement in the photoluminescence efficiency of the dendrimer through the reduction of the photoactivated degradation processes. It was found that this degradation was particularly extenuated when solutions of the dendrimer were prepared from chloroform and kept under illumination for a significant length of time prior to spin-coating.

The established new film solution-processing protocol was then applied to other solution-processed phosphorescent iridium(III) cored dendrimers and found to be equally successful. It was then shown that by combining this technique with optimisation of the entire device structure external quantum efficiencies greater than 10 % for green-emitting OLEDs were possible without the need for host blending. In fact, with the first generation iridium(III) dendrimer for a neat film bilayer device an EQE of over 12 % at a brightness of 110 cd/m\(^2\) was obtained. For a second generation iridium(III) dendrimer that benefited from greater core-to-core spacing and thus underwent less quenching interactions than the first generation dendrimer and had a lower hole mobility \[93\], the efficiency of a neat film bilayer device was found to as high as 15.2 % at a brightness of 100 cd/m\(^2\). The results clearly showed that highly efficient green-emitting OLEDs could be made in simple device structures without the need for host blending.

The adoption of the new protocol was also shown to lead to improvements in the lifetime of dendrimer OLEDs through the ability to incorporate PEDOT/PSS into the device structure which previously has not proved possible. The chapter also successfully identified and solved other areas of possible device efficiency limitations, for example the ITO anode layer, and introduced new soluble host materials that potentially could have major benefits in obtaining efficient devices and in particular those with a non-green emissive colours.
Chapter 5

Hole-transporting dendrimers - the carbazoles

5.1 Introduction

The aim of this chapter is to describe investigations into a new set of dendrimers that were deliberately synthesised to contain the hole transporting moieties that would normally be found in common host molecules. These dendrimers form the carbazole family.

As discussed in Chapter 4, for optimum device performance it has been found that the phosphorescent material must be doped (blended) into a semiconducting organic host [21, 25–27, 116, 123, 135, 142–145]. Normally the host material contained rigid carbazole groups and the molecules were often insoluble in standard solvents. As discussed previously, one of the main functions of the host was to increase the phosphorescent chromophore spacing, thereby reducing the number of intermolecular interactions that would otherwise act to quench the luminescence. This arrangement also allowed excitons to be readily trapped on the dendrimer, leading to increased device efficiencies. To work effectively as the host, the material chosen must not undergo phase separation when blended with the dendrimer, and must have suitable HOMO, LUMO and triplet energy levels to ensure efficient charge transfer within devices and minimise back energy transfer between the dendrimer and the host molecule [146]. Yet while the guest-host mixture may be well defined, it was much more difficult to determine what were the combination and arrangement of the two components in the as-deposited film.
Dendrimers have been shown to provide an ideal method of controlling the intermolecular interactions of iridium(III) complexes in the solid state \[147-152\], but they have still required to be host blended for maximum device performance. To overcome these problems, and the inherent complexity in the fabrication of a guest-host system, this chapter investigated a conjugated dendrimer family that negated the need for the host material. Such dendrimers were deliberately synthesised to have the carbazole units, that would be normally found in small molecule hosts, incorporated directly into the dendrons of an iridium(III) cored dendrimer structure to form a covalently linked guest-host system. In this way, the ratio of carbazole to emissive units was precisely known and the intermolecular interactions that govern the luminescence properties were able to be controlled at a molecular level by the dendrimer generation \[153-157\].

In this past this approach has received little attention due mainly to the problems in the synthesis of higher generation dendrons as well as poor reaction yields. More recently with improvements and advancements in the synthesis techniques, the approach has been reconsidered with the creation of some highly luminescent dendrimers \[138, 156-159\], including those considered in this thesis. The synthesis of the dendrimers studied was completed by Dr Kevin Knights at University of Oxford and is described in more detail in Reference \[160\].

In addition, the fact that the carbazole dendrons were included with the structure opened up a new direction which has not been considered previously; carbazole moieties capable of charge transport used within the dendrons. In prior work in other dendrimer systems the phenylene dendrons used were found to play no role in the charge transport \[42, 93, 161, 162\]. The effect of this change of dendron will be subsequently considered.

Dendrimers with charge transporting carbazole units as the dendrons have been synthesised and their electrochemical properties studied before \[157\]. In common with these first and second generation carbazole dendrimers the dendrimer family discussed in this chapter were solution-processable phosphorescent green-emitting dendrimers comprised of a fac-tris(2-phenylpyridine) iridium(III) \[Ir(ppy)_3\] core and covalently attached dendrons. The dendrimers were designed such that that the carbazole molecule was connected via its 9 (nitrogen) position to the first phenyl ring branching of the phenyl pyridine ligand bonded to the iridium core. Surface groups were attached to the carbazole from its C3 and C6 positions as this has been shown to lead to the best control of the resultant HOMO energy \[138\].

This new family of dendrimers differed from those studied previously in the replacement of the 2-
ethylhexyloxy groups at the distal ends of the dendrons with 9,9-di-n-propylfluorenyl surface groups (denoted Pr in the structures) to provide the required solubility to the dendrimer. A change in surface groups although simple can lead to improvements in solubility and hence improved film formation and thus is not trivial in its effect. Unlike previously, where only a first and second generation iridium(III) carbazole dendrimer were synthesised, this new family extended to the third generation dendrimer [160].

Further to this, the first ever iridium(III) double dendron carbazole dendrimers were also synthesised for both the first and second generation. The resulting structures of the first (Ir-CarbG1) (Oxford batch code KK-3-6E), second (Ir-CarbG2) (KK-3-51F), and third generation (Ir-CarbG3) (KK-4-25A) carbazole dendrimer, and the first (KK-3-29D), and second generation (KK-3-52A) double dendron (Ir-CarbDDG1 and Ir-CarbDDG2) carbazole dendrimers are shown in Figure 5.1 to Figure 5.5.

This chapter consists of a study of these charge transporting dendrimers. To begin these studies the results of molecular orbital calculations on the carbazole dendrimers were reported, the photophysical properties of each family member were then determined from both solution and film measurements. Direct measurements of the charge transport of a number of family members were then made via mobility measurements from the time-of-flight technique. The remainder of the chapter was devoted to the considerable amount of device studies undertaken using all members of the carbazole family.

As in previous chapters I would thank and acknowledge the contributions of Dr Jean-Charles Ribierre and Dr Ruth Harding in obtaining a number of the photophysical results. The time-of-flight mobility measurements detailed were undertaken when working in collaboration with Dr Salvatore Gambino, his help and assistance with this is acknowledged and much thanked. The molecular orbital calculations presented were performed by Dr Chris Shipley at the University of Oxford and Dr Seth Olsen at the University of Queensland.

### 5.2 Molecular orbital calculations

For the first generation dendrimer with biphenyl-based dendrons (Ir-G1) the LUMO and HOMO energy levels have been calculated to be 2.5 eV and 5.6 eV respectively. In all the carbazole dendrimers while the LUMO energy has also been found to be 2.5 eV, the HOMO energy was at 5.7 eV slightly greater than that of the biphenyl dendronised dendrimer. While knowledge of such numbers was important, of more interest was how these energy levels were distributed across the dendrimer structure.
CHAPTER 5: HOLE-TRANSPORTING DENDRIMERS - THE CARBAZoles

Figure 5.1: Structure of the first generation carbazole, Dendrimer 5, Ir-CarbG1

Figure 5.2: Structure of the second generation carbazole, Dendrimer 6, Ir-CarbG2

Figure 5.3: Structure of the third generation carbazole, Dendrimer 7, Ir-CarbG3

Figure 5.4: Structure of the first generation double dendron carbazole, Dendrimer 8, Ir-CarbDDG1
Density functional theory calculations are a useful tool in explaining the optical and electrical properties of organic molecules particularly when complementary experimental results are available. Previously such calculations have been performed on both the first generation \textit{fac}-tris(2-phenylpyridyl) iridium [Ir(ppy)$_3$] (Ir-G1) dendrimer with phenylene based dendrons, and a dendrimer with carbazole dendrons [157]. The calculations allowed the determination of the distribution and relative energies of the highest occupied (HOMO) and lowest unoccupied molecular orbitals (LUMO). These studies found that for Ir-G1, both the HOMO and LUMO energies of the dendrimer were strongly localised on the [Ir(ppy)$_3$] core. This result reflected the fact that the second generation phenylene dendronised dendrimer was more photoluminescent in the solid state, and had lower hole mobility than the first generation version of this dendrimer. These two properties were consistent with the optically and electronically active cores being on average held further apart by the larger dendrons in the second generation dendrimer [93]. In contrast for the dendrimer with carbazole dendrons the calculations showed that while the LUMO also resided on the core, the HOMO density was not only found on the [Ir(ppy)$_3$] core, but was also heavily located on the carbazole units at the dendrons.

In order to determine the effect on the molecular orbital distribution of the higher generation carbazole dendrimers a further set of calculations were performed on these carbazole dendrimers by Dr Chris Shipley at the University of Oxford and Dr Seth Olsen at the University of Queensland. The results of these calculations are summarised in Table 5.1 and those for the first generation biphenyl (Ir-G1)
and carbazole (Ir-CarbG1) dendronised dendrimers are shown as target diagrams in Figure 5.6, further details can be found in Reference [160]. For the carbazole dendrimer the fluorenyl surface groups were omitted to enable a simpler calculation. The angles between different aromatic units in the dendrons and their attachment points to the core were, also for simplicity, fixed in the calculation to an angle of 30° to take into account the interactions between neighbouring aromatic units. It is highly probable that the different generation of dendrimer could cause deviations from this structural arrangement due to differences in the steric interactions that occur. If for example, such steric interactions caused larger twisting in the dendrons than used in the calculations, then the calculated energy gap for the orbitals may be less than would be observed experimentally. Therefore while the technique is a powerful one it only allows general trends to be drawn from the results [160].

For the first generation dendrimer with biphenyl dendrons almost all (97.4 %) of the LUMO density was calculated to reside on the 2-phenylpyridyl ligand. Only around 2 % was found on the iridium and the remainder on the dendron. In each of the three generations of the carbazole dendrimers, as the table shows, the LUMO distribution was very similar, which indicated that the carbazole units did not strongly affect the LUMO energy density distributions.

As the data in Table 5.1 shows, the main difference between the dendrimers lay in the differing
Table 5.1: Mulliken populations of the frontier molecular orbitals of the first generation biphenyl based dendrimer and the three generations of carbazolyl dendronised dendrimers. Ir = iridium(III), ppy = 2-phenylpyridyl ligand, Layer 1 = first level of carbazole or phenyl branching units, Layer 2 = second level of carbazole branching units, and Layer 3 = final level of carbazole units [160].

HOMO distributions. For Ir-G1 the HOMO distribution was such that nearly all of the HOMO orbital density was on the central iridium metal core complex, 52.6 % of the density lay here, with 41.2 % on the ppy ligand, and the remaining 6.2 % on the biphenyl dendron [160].

In contrast moving to the Ir-CarbG1 dendrimer with carbazole dendrons, the amount of HOMO density on the iridium at 24.8 % was less than half of that found in the biphenyl dendron dendrimer. There was a similar percentage of the HOMO density on the ligand: 34.3 % in Ir-CarbG1. The remaining 40.4 % was found on the first layer of the carbazole units of the dendron, a large increase over the 6.2 % found on the biphenyl dendron for Ir-G1. In the second-generation carbazole dendrimer (Ir-CarbG2), the HOMO orbital density on the iridium atom fell further to 9.7 %, with 21.5 % on the ligand. Most of the density was found to reside on the first (41.5 %) and second (27.3 %) layers of carbazole units. A further dilution of the HOMO density on the iridium(III) complex continued with the third generation carbazole dendrimer where only 2.1 % was found on the iridium, and 6.7 % was found on the ppy ligand. The remaining HOMO orbital density was distributed between the first (22.3 %), second (37.8 %), and third (31.1 %) carbazole layers [160].

In the biphenyl dendronised dendrimers, in which the HOMOs on adjacent cores are effectively isolated from one another, the hole transport is known to be via core-to-core hopping, with hole transport found to increase with dendrimer generation [42, 93]. The fact that the HOMO was distributed over the whole of the carbazole dendronised dendrimers, as opposed to being localised on the core complex, indicates the hole transport in the two types of dendrimer could be very different, an issue that was considered further in subsequent sections of this chapter.
5.3 Photophysical Properties

The absorption and emission spectra of all members of the carbazole family were measured and are shown for solutions of these dendrimers in Figure 5.7 and for the corresponding films in Figure 5.8. In both cases the spectra of non-carbazole dendrimer iridium(III) cored dendrimer Ir-G1 (Dendrimer 1) has also been included for ease of comparison.

As the figures show, in all cases the absorption spectra consisted of two components: a short wavelength component due to the π-π* absorptions of the dendrons and ligand, and longer weak absorptions due to the metal-to-ligand charge transfer (MLCT) states. Both dendrimer types had the same core, but the slightly lower HOMO-LUMO energy gap of the carbazole units meant the carbazole dendrimers had stronger π-π* absorption at longer wavelengths in both solution and film. Also noticeable was the effect of the change in dendron on the absorption spectra - the carbazole spectra all produced a large peak at 320 nm, a characteristic of the carbazole unit. In contrast, the phenylene dendrons of Ir-G1 showed a peak at 273 nm that was not observed in the carbazole spectra. Although not shown here, on the non-normalised spectra the carbazole peak at 320 nm was found to increase in magnitude with dendrimer generation as the number of carbazole units was increased, albeit the general spectral shape was found to be independent of dendrimer generation [160].

Figure 5.7 and Figure 5.8 also compare the emission spectra of the carbazole dendrimers with that of Ir-G1. In all cases the emission arose from iridium(III) complexes with similar excited states and energies. In common with phenylene dendrons, for the carbazole dendrons, in both solution and film, no emission was seen from the dendrons indicating efficient energy transfer from the dendrons to the core. It was found that in both solution and film the spectra of the first to third generation carbazole dendrimers were very similar to that of Ir-G1, that is all emit green light. With increasing generation it might be predicted that the HOMO becomes more delocalised, this leading to a strong red-shift in the emission spectra in moving from the phenylene dendron Dendrimer 1 (Ir-G1) to the third generation carbazole dendrimer (Ir-CarbG3). The figure shows however that this was not the case here, which suggested the ground and excited state molecular orbital distributions between the two dendrimer types were different - with carbazole dendrons the excited state orbitals were likely to be strongly localised on the core of the dendrimer. The similarity in decay rates between the carbazole dendrimers and Ir-G1 lends further strength to this argument [119, 120].

On moving from the solution to the film spectra there was found to be a red-shift in the emission
spectra, with the magnitude of the shift decreasing with dendrimer generation. For the third generation carbazole dendrimer the shift from solution to film actually caused a 4 nm blue-shift. A blue-shift was also seen in both solution and film with increasing dendrimer generation. In both the double dendron dendrimers the presence of the additional dendron was found to lead to a red-shift in the emission spectra from their equivalent single dendron dendrimer. A similar red-shift was observed for the double dendron dendrimer Dendrimer 2 considered in Chapter 4. The role of the additional dendron is to improve the core encapsulation in order to decrease the number of intermolecular interactions. The drawback of this technique is that it increases the conjugation length of the ligand involved in the metal-to-ligand charge transfer state of the dendrimer, and so gives a red-shift in the emission colour [32, 43, 119].

For a further photophysical analysis of the carbazole dendrimer family, solution and film measurements of the photoluminescence quantum yield were made and the results are summarised in Table 5.2. As the table shows Ir-CarbG1, Ir-CarbG2 and Ir-CarbG3 were measured to have solution PLQYs of 75 %, 68 % and 66 % respectively, these latter two measurements were performed by Dr Ruth Harding. In comparison, the first generation Ir-G1 dendrimer was found, as discussed in Chapter 4, to have a solution PLQY of around 80 %, while the second generation (Ir-G2) dendrimer, Dendrimer 3 has been previously measured to give a solution PLQY of 69 % [119]. The similarity between these numbers, and
those of the carbazole dendrimers, clearly shows carbazole dendrons did not in any way significantly effect the luminescence efficiency of the dendrimer in solution. Similarly high solution PLQY values were also found for the two double dendron dendrimers, 74 % for Ir-CarbDDG1 and 66 % for Ir-CarbDDG2, these measurements also being performed by Dr Ruth Harding.

Table 5.2 also shows the values obtained for film PLQY measurements for each carbazole dendrimer. In this case, unlike for in solution, the values obtained were not similar but covered a range of values from 31 % for Ir-CarbDDG2 to 80 % for Ir-CarbDDG1. For the first generation carbazole dendrimer (Ir-CarbG1), a significantly lower film PLQY of 37 % was found in comparison to the second and third generation dendrimers which both gave a value of 65 % (the third generation dendrimer was measured by Dr Jean-Charles Ribierre). Ir-CarbDDG2 has a greater amount of carbazole units than the second generation carbazole dendrimer (Ir-CarbG2), and thus it was not clear why it would have such a low PLQY. Nonetheless, the large variations in all these film PLQY values did suggest that carbazole dendrimers underwent varying amounts of quenching in a neat film, the amount of quenching present depending, if not linearly, on the number of carbazole units present [163].

The similarity of the solution PLQYs across the carbazole family was again reflected when a solid solution PLQY measurement was made on the dendrimers. In this case by blending with a small molecule host the intermolecular spacing and thus the core separation was increased. For this a 20:80 wt % blend
of dendrimer to a CBP or TCTA host was used. In all cases, as detailed in Table 5.2, the PLQY found was in the range 70 - 88 %, close to that of the value found in solution. This confirming that even despite the presence of the carbazole groups, almost all of the carbazole dendrimers suffered some concentration quenching effects in neat films.

The blended film PLQY values found for the entire carbazole family were not only very similar to each other but also to that measured for a CBP host blend of a standard iridium(III) cored dendrimer with phenylene dendrons [27]. The neat film PLQY for Ir-CarbG1 was also comparable, while for Ir-CarbG2 it was greater, than those obtained for the previous carbazole dendrimers [157]. This may have related to the change in surface groups between these carbazole dendrimer families, or by the improved and simplified synthesis with which these new carbazole dendrimers can now be made [160]. In any case, once again dendrimers capable of incorporating the functions of a host material within their structure, without the loss of photoluminescence efficiency, have been successfully designed.

The results also implied that there was an optimum amount of hole transporting character that can be incorporated into the structure; Ir-CarbG1 which has the least amount of carbazole units within the dendrimer structure, suffered greatest from the effects of concentration quenching on moving from solution to film. In this low generation dendrimer, the carbazole units were not present in sufficient quantity to give the required chromophore spacing and hence the PLQY measured in the film fell. In the second and third generation dendrimers where the quantity of carbazole present in the molecule was much greater, the luminescence efficiencies in solution and film were similar. In these higher generation dendrimers which were more sterically demanding, the effects of concentration quenching were not as significant. In Ir-CarbDDG2, despite the large amount of carbazole units present in the dendrimer structure the film PLQY was very low. The reasons why this occurred are not clear, but may have been related to impurities

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Film PLQY (%)</th>
<th>Film PLQY (%) 20:80 wt % with CBP</th>
<th>Film PLQY (%) 20:80 wt % with TCTA</th>
<th>Solution PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>37</td>
<td>82</td>
<td>78</td>
<td>75</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>65</td>
<td>75</td>
<td>82</td>
<td>68</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>65</td>
<td>70</td>
<td>87</td>
<td>66</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-CarbDDG1</td>
<td>80</td>
<td>80</td>
<td>88</td>
<td>74</td>
</tr>
<tr>
<td>Dendrimer 9, Ir-CarbDDG2</td>
<td>31</td>
<td>-</td>
<td>-</td>
<td>66</td>
</tr>
</tbody>
</table>

Table 5.2: Summary of the photoluminescence properties of all members of the carbazole dendrimer family
in this dendrimer structure.

Finally, $^1$H NMR analysis of the carbazole dendrimers was performed by Dr Kevin Knights at the University of Oxford. The results of this indicated the spectra of the carbazole dendrimers were more complex than those of dendrimers with phenylene dendrons such as Dendrimer 1. More precisely, the aromatic region was found to be complex with some of the signals, even for the first generation Ir-CarbG1 dendrimer, being broad. This possibly indicated hindered rotation due to steric encumbrance. The hydrodynamic radii of the dendrimers were also calculated using the technique of gel permeation chromatography. For Ir-CarbG1 the hydrodynamic radius was $10.3 \, \text{Å}$ which meant it was similar to that measured for the first generation phenylene dendrimer, Dendrimer 1, reported in Reference [43]. It was interesting to note that despite the fact that the carbazole dendrons were significantly larger than in the phenylene dendrons the hydrodynamic radii were similar. The implication is that for the phenylene-based dendrons, the 2-ethylhexyloxy groups play an important role in controlling the intermolecular interactions of the emissive core. The second generation and third generation carbazole dendrimers had hydrodynamic radii of $14.0 \, \text{Å}$ and $18 \, \text{Å}$ respectively. The third generation carbazole is thus found to have a hydrodynamic radius of almost twice that of the first [160].

### 5.4 Time-of-flight mobility measurements

Section 5.3 demonstrated the minimal effect in photoluminescence on changing from phenylene dendrons to carbazole dendrons. This was despite the fact that in Section 5.2 the dendrons were found to have widely different HOMO distributions. This result emphasises one of the major benefits of dendrimer concept; separate components of a dendrimer can be independently varied without affecting other properties of that dendrimer. In this section it was considered whether the change in dendrons gave a change in the charge transport behaviour as indicated by the molecular orbital calculations. The investigations were by mobility measurements through the time-of-flight technique.

#### 5.4.1 Carbazole TOF measurements

As described in Chapter 3, the standard time-of-flight technique is ideally suited only for measurements on thick films. To allow measurements on film thicknesses comparable with those used in device studies, the charge transport properties of films of carbazole dendrimers were studied using the CGL TOF technique.
The charge transport between the first three carbazole dendrimer generations were considered, as was that of the first generation double dendron dendrimer (Ir-CarbDDG1). For this dendrimer the hole mobility was found to be among the highest reported in literature for a time-of-flight measurement for any soluble organic material.

In all cases samples were made for CGL TOF measurements using solutions of dendrimer made to concentrations of 40 mg/ml in chloroform. Films were spun onto an ITO substrate at speeds of 700-800 rpm to obtain films around 200-300 nm thick. The samples were then transferred to an evaporator where under high vacuum a 10 nm thick layer of the absorptive perylene dye, Lumogen Red (BASF Lumogen® F Red 305), followed by 100 nm of aluminium was deposited through a shadow mask to define the active area. Testing was undertaken using the setup previously shown in Figure 3.4, where the charge generation layer was excited through the ITO and dendrimer layer by a laser pulse of wavelength 580 nm. The aluminium electrode was biased positively and the photocurrent signal detected from the ITO by an oscilloscope.

5.4.2 Room temperature measurements

The room temperature hole current transients were measured for the first three generations (Ir-CarbG1, Ir-CarbG2 and Ir-CarbG3) of the carbazole dendrimers. These are plotted using a double log scale in Figure 5.9 with the corresponding linear scale plots shown in Figure 5.10. All data shown was obtained at the same applied field (E) of $5 \times 10^4$ V/cm.

As the figure shows the effect of generation on the photocurrent transients was immediately apparent: all had a different shape while their duration decreased with generation (from 4.95 $\mu$s for Ir-CarbG1 to 2.58 $\mu$s for Ir-CarbG3, for a field of $1 \times 10^5$ V/cm) - by changing the dendrimer generation the charge transport behaviour was changed. Consider for example the magnitude of the photocurrent transient, in the second and third generation dendrimer this was quite similar but the magnitude for the first generation carbazole dendrimer was nearly three orders of magnitude greater. It was not immediately clear as to why this change would have such a dramatic effect.

Considering further Figure 5.10 it was seen that only the second generation carbazole dendrimer (Ir-CarbG2) displayed any form of a current plateau consistent with non-dispersive hole transport behaviour. In contrast the other two generations of carbazole dendrimer (Ir-CarbG1 and Ir-CarbG3), showed no clear plateau, but did show an inflection point in the current transient when plotted on the double log scale.
Hence, transport in these dendrimers was dispersive, with a drift velocity that would decrease continually with time.

For all three generations of dendrimer, measurement of the hole current transients were repeated at a range of applied fields, and from each transient the transit time extracted as detailed previously. Taking the transit times and using Equation 3.3, the hole mobility was calculated. This allowed a Poole-Frenkel plot of mobility against the square root of the applied field to be determined for each dendrimer generation, this plot is shown in Figure 5.11.

The hole mobility against field plot showed that for each dendrimer, an increase in magnitude of the applied field resulted in a corresponding increase in the hole mobility. Also notable was that the hole mobility of Ir-CarbG1 was $6 \times 10^{-5}$ cm$^2$/Vs at a field of $20 \times 10^{-5}$ cm$^2$/Vs. In contrast for Ir-G1 at the same field, the hole mobility has been measured as $4 \times 10^{-6}$ cm$^2$/Vs [93]. It was evident that the change from phenylene to carbazole dendrons improved the hole mobility and thus enhanced the hole transport within the dendrimer. Moreover, an increase in the dendrimer generation was found to cause an increase in the hole mobility; there was a clear relationship between the degree of dendron branching and charge carrier mobility. For the three generations of dendrimer under an applied electric field in the range $(7.3 - 20) \times 10^4$ V/cm the mobility values found were $(3 - 6) \times 10^{-5}$ cm$^2$/Vs for Ir-CarbG1; $(4.6 - 10^{-5})$ cm$^2$/Vs for Ir-CarbG2; and $(5 - 8) \times 10^{-5}$ cm$^2$/Vs for Ir-CarbG3.

Figure 5.9: Room temperature hole current transient in double log scale for Ir-CarbG1, Ir-CarbG2 and Ir-CarbG3, all taken at $E = 5 \times 10^4$ V/cm
Figure 5.10: Room temperature hole current transient in linear scale for Ir-CarbG2 and Ir-CarbG3, inset shows data for Ir-CarbG1, all data taken at $E = 5 \times 10^4 \text{ V/cm}$

$9) \times 10^{-5} \text{ cm}^2/\text{Vs}$ for Ir-CarbG2; and $(7.3 - 12) \times 10^{-5} \text{ cm}^2/\text{Vs}$ for Ir-CarbG3. These measurements were taken with the assistance of Dr Salvatore Gambino.

The increase in hole mobility with dendrimer generation was in complete contrast to the decrease in mobility with generation seen previously in dendrimers with non-charge transporting phenylene dendrons [42, 93]. Previously hole charge transport was described as being by hopping between the dendrimer cores. The hole charge transport behaviour found for the carbazole dendrimers implied that with carbazole dendrons this was no longer true; here the role of the dendrons was not to slow the carrier packet through increased separation of the core regions. Instead it appeared that, by employing carbazole units within the dendrimer structure, the dendrons were able to play an active role in the charge transport. This result further supports those of the molecular orbital calculations detailed in Section 5.2, where the two different dendron types were found to have widely different HOMO distributions.

5.4.3 Ir-CarbDDG1 TOF

The effect of dendrimer generation on the charge transport behaviour of the carbazole dendrimers was determined in the previous section. Also relevant would be whether this charge transport behaviour could
be changed by the addition of a second dendron to the molecular structure. Measurements of mobility were thus made on the first generation double dendron carbazole dendrimer (Ir-CarbDDG1) to determine whether it had different charge transport behaviour from that of the standard first generation carbazole dendrimer (Ir-CarbG1).

As before measurements of the photocurrent were taken at a number of temperatures across a range of applied fields. Equation 3.3 was then used to calculate the mobility. The resulting Poole-Frenkel mobility-field plot is shown in Figure 5.12 for fields applied at both room temperature (295 K), and at a temperature of 77 K. Also included in the figure is the room temperature mobility of Ir-CarbG1 shown previously in Figure 5.11.

The figure showed that the decrease in temperature lead to a reduction in the hole mobility of the Ir-CarbDDG1 dendrimer. Under an applied electric field in the range (7.3 - 21) x10^4 V/cm the mobility values found were (3.9 - 9.7) x10^{-5} cm^2/ Vs at 77 K; and at 295 K the mobilities were much greater covering the range (0.75 - 1.1) x10^{-3} cm^2/ Vs. Once again the contribution and assistance of Dr Salvatore Gambino in obtaining this data are acknowledged. Also noticeable was that at a temperature of 77 K the Ir-CarbDDG1 dendrimer showed a mobility-field relationship.

An increase in field leading to an increase in mobility was observed in the first three generations of the
single dendron dendrimer, but was not observed for Ir-CarbDDG1 at 295 K. Instead the slope of the curve was in the opposite direction, where an increase in field gave a reduction in hole mobility. Moreover, there was a large increase of over one order in magnitude in mobility found in moving from Ir-CarbG1 to the double dendron Ir-CarbDDG1 dendrimer. The mobility of Ir-CarbDDG1 was also considerably greater, over one order of magnitude, than for Ir-CarbG2 and Ir-CarbG3, despite the increased number of dendron branches present in these higher generation dendrimers.

To understand this better, a hole-current photocurrent transient for Ir-CarbDDG1 obtained at 77 K was plotted in a linear scale as shown in Figure 5.13. From the plot, even at this very low measurement temperature the presence of a clear plateau region in the transient was evident - the hole transport was highly non-dispersive. In fact no transition temperature from non-dispersive to dispersive charge transport was revealed across the temperature range investigated for this dendrimer [164].

The highly non-dispersive TOF measurements obtained at 77 K indicated the presence of a more highly ordered system (a less amorphous film), in comparison to the other dendrimers. In Bässler’s disorder model [83], the two central parameters of the formalism are the energy width of the hopping site manifold (σ), and the positional disorder (Σ) due to a distribution of intersite distances. It was proposed that the highly ordered system present in this case gave a low value of the energetic disorder parameter [164].
In addition, the experimentally derived width of the density of states (DOS), $\sigma$, can be used to determine the Gaussian width of the density of states via Equation 5.1, where $k$ is the Boltzmann constant.

\[
\tilde{\sigma} = \frac{\sigma}{kT}
\]

Then according to Bässler’s disorder model developed through Monte Carlo simulations of the hopping mechanism within a Gaussian DOS [83], a non-dispersive photocurrent transient should be shown for $\tilde{\sigma} \leq 3.5$. For Ir-CarbDDG1 at a temperature of 77 K using Equation 5.1 the width of the DOS is calculated to be $\sigma \leq 20$ meV. Comparing this value to that obtained for a biphenyl based dendrimer in [93] where a value of 103 meV was obtained it is found to be considerably smaller. Similar values in the range 80 - 100 meV have also been found in molecularly doped polymers [165]. It is then interesting to note that a similar analysis of the non-dispersive nature of charge transport found in the second generation carbazole (Ir-CarbG2) yielded a value of $\sigma \leq 95$ meV [164] and is thus much closer to what has been found elsewhere. It is thus unclear whether with such a low value of $\sigma$ whether the Gaussian model is fully applicable for Ir-CarbDDG1.

Charge transport in the Ir-CarbDDG1 was found to resemble hopping between isoenergetic sites, or at least within a narrow distribution of energetic hopping sites. This accounted for the increase in mobility seen with field at large values of applied field at 77 K. By extension, at 295 K where, as commented
Table 5.3: Summary table of room temperature mobility values obtained for the carbazole dendrimers

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Mobility (cm²/Vs)</th>
<th>Field (V/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>(3 - 6) x10⁻³</td>
<td>(7.3 - 20) x10⁴</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>(4.6 - 9) x10⁻⁵</td>
<td>(7.3 - 20) x10²</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>(7.3 - 12) x10⁻⁵</td>
<td>(7.3 - 20) x10⁴</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-CarbDDG1</td>
<td>(6.6 - 8.6) x10⁻⁴</td>
<td>(8.5 - 21) x10¹</td>
</tr>
</tbody>
</table>

previously, in contrast to the behaviour seen at 77 K and for all the other carbazole dendrimers considered, an increase in field was found to give a reduction in hole mobility, this could be accounted for by the saturation of the drift velocity with the field in a hopping system with isoenergetic sites in which the field does not affect intersite jump rates [83, 87, 106, 164, 166].

Finally it is commented that the mobility of the Ir-CarbDDG1 dendrimer was higher than has been previously found in dendrimer systems. The mobility was comparable to those obtained for small molecules where mobilities in the range of 1x10⁻³ cm²/Vs have been reported [110]. It may be possible that an even higher mobility could be found in the second generation double dendron, Ir-CarbDDG2, however unfortunately the lack of sufficient quantity of this dendrimer made this impossible to test.

5.4.4 Carbazole TOF mobility summary

This sections introduced and described the TOF mobility measurement before the results of this technique were presented when applied to the family of carbazole dendrimers. The results showed that there was an increase in hole mobility with dendrimer generation when carbazole dendrimers were used, contrasting behaviour to that seen previously for dendrimers with biphenyl dendrons. This behaviour, when combined with knowledge of the differing HOMO density locations with the two dendrimer types, gave strong evidence that for carbazole dendrons the charge transport was not via core-to-core hopping but via the dendrons. Furthermore, by moving to a double dendron carbazole there was found to be over an order of magnitude increase in the hole mobility. The resulting room temperature mobility values are summarised in Table 5.3 Therefore, unlike in photoluminescence, where the change to carbazole dendrons and the increase in generation lead to minimal differences, such changes have been found to lead to large changes in the charge transporting properties of the dendrimers.
5.5 Electrical Characterisation

To determine whether the control of charge transport found in the carbazole dendrimers could also be used to understand the processes involved in the operation of OLEDs, and also to assess whether the high photoluminescence efficiency found in solution and films for the carbazole dendrimer family could lead to efficient OLEDs, a number of device structures were fabricated. This section presents the results of these devices.

5.5.1 Single layer devices

In the first simple tests, single layer devices were fabricated using neat films of the carbazole dendrimers as the electroluminescent layer sandwiched between an ITO anode and a cathode of calcium-aluminium. For these devices the old solution-processing protocol was used, where the time left for the dendrimer in solvent to dissolve prior to spin-coating was not minimised, unlike for all other subsequent devices which followed the solution-processing protocol as described in Chapter 4, where the time of the dendrimer in solution was minimised. The resulting device characteristics are shown in Figure 5.14, and are summarised in Table 5.4.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>0.35 % (8.9 V, 0.3 lm/W, 0.8 cd/A)</td>
<td>0.28 % (0.36 lm/W, 0.6 cd/A, 6.9 V)</td>
<td>(0.376, 0.575)</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>0.04 % (10.8 V, 0.02 lm/W, 0.07 cd/A)</td>
<td>0.04 % (10.8 V, 0.02 lm/W, 0.07 cd/A)</td>
<td>(0.359, 0.568)</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>0.04 % (10.9 V, 0.04 lm/W, 0.13 cd/A)</td>
<td>0.04 % (10.1 V, 0.04 lm/W, 0.13 cd/A)</td>
<td>(0.319, 0.595)</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-DDCarbG1</td>
<td>0.75 % (7.6 V, 0.9 lm/W, 2.2 cd/A)</td>
<td>0.51 % (5.4 V, 0.9 lm/W, 1.5 cd/A)</td>
<td>(0.470, 0.521)</td>
</tr>
</tbody>
</table>

Table 5.4: Summary of device characteristics of single layer devices for the carbazole family

For all these dendrimers the turn-on voltage was found to be around 3-6 V, well in excess of the organic bandgap and nearer to the work function difference of the two electrodes which is typical to most organic materials. A comparison of the device curves showed that the first to third generation carbazole dendrimers all drew a similar current through the device, with the double dendron device giving much more current and light output. The light output of the second and third generation carbazole devices were similar but the first generation carbazole device was capable of giving out slightly more
light, consequently this device was considerably more efficient. In fact for the device with Ir-CarbG1, the maximum external quantum efficiency (EQE) was 0.35 % at 8.9 V. At the standard display brightness of 100 cd/m$^2$, the EQE was 0.28 % at 6.9 V, this corresponded to a power efficiency of 0.29 lm/W or 0.63 cd/A. Despite the greater photoluminescence efficiency of both Ir-CarbG2 and Ir-CarbG3 in comparison to Ir-CarbG1, for both these higher generation dendrimers, the device performance was in fact worse. The slight reduction in current and large drop in luminance meant that both dendrimers were only capable of attaining a maximum EQE of around 0.04 %.

It is recalled from Section 5.4 that in the carbazole dendrimers the hole mobility increased with dendrimer generation, yet in these device structures the current was found to decrease with generation. The reduction in current with dendrimer generation was the same as has been observed previously in dendrimers with non-charge transporting phenylene dendrons [27, 93]. In this case the behaviour was explained by the enlarged distance between cores on increasing the dendrimer generation. This resulted in a reduction in charge mobility, because with an increased hopping distance between the cores the probability of hopping between the cores decreased resulting in a slowing of the charge carriers. However, in
the case of the carbazole dendrimers, where the hole mobility increased with dendrimer generation this cannot be the case. For these dendrimers, as shown in Figure 5.9 the photocurrent was reduced with dendrimer generation, although as shown in Figure 5.11 the hole mobility increased with dendrimer generation. While the change in dendron resulted in a change in the hole charge transport properties, the similarity of the LUMO distributions in both dendron types [160], suggested that the electron charge transport behaviour was the same. That is, electron transport remains via the cores in the carbazole dendrimers; electrons and holes are thus widely spaced and so the probability of exciton formation decreases in these dendrimers [163].

The best single layer device performance from a carbazole dendrimer was found for the double dendron dendrimer Ir-CarbDDG1. This device gave a maximum efficiency of 0.75 %, and at a brightness of 100 cd/m² the EQE was 0.51 %. Unfortunately, once again the lack of a sufficient quantity of the Ir-CarbDDG2 dendrimer prevented devices from being attempted with this dendrimer to test whether further efficiency improvements were possible.

The high single layer device efficiency with the double dendron Ir-CarbDDG1 carbazole dendrimer was found despite this dendrimer showing the highest hole mobility, and thus by intuition would be predicted to have the most unbalanced charge transport. Despite the possible charge transport imbalance problems within Ir-CarbDDG1 the light output was greater in the Ir-CarbDDG1 device than in any of the devices from the other carbazole dendrimers. Also in Section 5.4.3 it was discovered that Ir-CarbDDG1 gave hole transport behaviour that indicated a more ordered system than found for the other carbazole dendrimers. The fact that this was still able to give an efficient device may have arose from increased electron transport within this ordered dendrimer system due to the smaller core-to-core separation compared to the higher generations of carbazole dendrimer.

A further reason for the high device efficiency may be the higher neat film photoluminescence quantum yield of Ir-CarbDDG1, but a 15 % improvement in film PLQY over that of Ir-CarbG2 and Ir-CarbG3 can not fully account for the nearly 20 times improvement in the device efficiency. Of course, as a final explanation, as has been seen previously with double dendron dendrimers, Ir-CarbDDG1 may have suffered less photodegradation effects in comparison to the other dendrimers considered here where all were prepared under the old protocol solution-processing technique.

The corresponding emission spectra for each of the three generations of dendrimer are also shown in Figure 5.14 from which it can be seen they were very close to their PL counterparts with CIE co-
ordinates of (0.376, 0.575), (0.359, 0.568) and (0.319, 0.595) for Ir-CarbG1, Ir-CarbG2 and Ir-CarbG3 respectively. For Ir-CarbDDG1 the CIE coordinate was (0.470, 0.521), and thus again showed a red-shift from that of the single dendron dendrimer. This gave a coordinate and spectrum close to that found in the photoluminescence measurement. In all cases the EL spectra remained unchanged as the bias voltage was varied across the device operational range.

5.5.2 Single layer devices under the new solution-processing protocol

In an attempt to improve on the single layer device performance of the carbazole dendrimers detailed in the previous section a further set of devices were fabricated but following the new solution-processing protocol discussed in Chapter 4. In the same single layer device structure, a neat film and a 20:80 wt % dendrimer-CBP host blended film were used as the emissive layers. In this case only the first generation dendrimer, Ir-CarbG1, was investigated. The resulting characteristics of these devices are shown in Figure 5.15 and summarised in Table 5.5.

The change in solution-processing protocol was found to bring a marginal benefit in device performance; for the neat film device the same maximum EQE of 0.35 % was obtained, albeit this was at a greater bias voltage of 10.4 V. At a brightness of 100 cd/m$^2$ the EQE was slightly improved to 0.28 %, again requiring a greater bias, now a voltage of 7.2 V. For the 20:80 wt % CBP host blend film device the maximum EQE was 1.5 %, and at a 100 cd/m$^2$ brightness the EQE as 1.0 %. The improvement in the blend film device performance over that of the neat film device reflected the fact that, as detailed in Table 5.2, the film PLQY of the blend film was over double that of the neat film. This improvement in film PLQY was attributed to an increased core separation on blending with CBP which acted to the decrease concentration quenching effects that were observed in the neat film.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m$^2$</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 5</td>
<td>0.35 % (10.4 V, 0.4 lm/W, 1.2 cd/A)</td>
<td>0.24 % (7.2 V, 0.4 lm/W, 0.9 cd/A)</td>
<td>(0.378, 0.594)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 5:CBP</td>
<td>1.5 % (15.0 V, 1.1 lm/W, 5.4 cd/A)</td>
<td>1.0 % (9.8 V, 1.1 lm/W, 3.5 cd/A)</td>
<td>(0.347, 0.611)</td>
</tr>
</tbody>
</table>

Table 5.5: Summary of device characteristics of single layer devices for the first generation carbazole, Ir-CarbG1, made following the new protocol.

The fact that working OLEDs could be produced from all the carbazole dendrimers considered, using a single layer device structure, where there was no control or optimisation of charge injection
Figure 5.15: Device characteristics of single layer neat and dendrimer-CBP blend film devices for the first generation carbazole dendrimer, Ir-CarbG1. Devices were made following the new solution-processing protocol and transport, showed a particular advantage of the dendrimer concept; a simple change of the dendron allowed the dendrimer behaviour to be changed, or indeed tuned, as desired. In this case, it has been shown that successful devices could be fabricated by incorporating carbazole host units directly into the dendrimer structure as the dendron. By doing so, the dendron became hole transporting, and the hole charge transport behaviour, as discussed in Section 5.4, was found to be changed from the core-to-core hopping found for phenylene dendrons [93].

The HOMO and LUMO energy levels of all the members of the carbazole family were measured to be the same, and all were roughly comparable within error to those of a standard iridium(III) dendrimer with phenylene dendrons. Changing the dendrons of the dendrimer therefore provides an elegant way of tuning the mobility without significantly changing the energy gap of the material. A energy level diagram of a standard device is shown in Figure 5.16 whereby it can be seen, as for the standard phenylene dendron dendrimer, there were large barriers to both hole and electron injection in a single layer structure and thus inefficient charge injection. The improvement in film PLQY, as discussed above, gave an improvement in the efficiency of the blend film device over that of the neat film. Also contributing to
this efficiency improvement was, as revealed by the figure, the benefits gained in energy transfer to the dendrimer with the inclusion of the CBP host.

In the case of Ir-G1, a dendrimer with phenylene dendrons, the resultant single layer devices were found to be very efficient only when blended with a CBP host, these devices attaining a maximum efficiency of 8.1 % [27]. Comparing this device efficiency value to those obtained for the single layer carbazole dendrimer devices, it can be seen that all the carbazole devices were much less efficient. In these single layer device structures, the current through the Ir-G1 dendrimer device was also considerably greater than those through the carbazole dendrimer devices, Chapter 7 considers this comparison further. Furthermore as has been noted, the hole mobility of Ir-G1 was less than that of Ir-G1Carb. The single layer devices with Ir-G1Carb were inefficient in comparison to those of Ir-G1: mobility is important for devices; with knowledge of the mobility, better devices can be made with balanced charge transport.

### 5.5.3 Bilayer neat film devices

The previous section considered single layer devices with the carbazole dendrimers, which although successful in that they were able to produce devices capable of light emission, it was found the simple nature of the single layer device structure, and the large hole mobility of the dendrimers, meant the resultant devices were strongly hole dominated. To further improve the understanding of the device behaviour it was thought intuitive to introduce a hole blocking layer into the device structure in an attempt to limit the hole current. To do this the electron transport/hole blocking organic material TPBI was evaporated onto ITO anodes spin-coated with a neat film dendrimer layer. The device structure was completed with the evaporation of a lithium fluoride and aluminium cathode layer. The energy band
CHAPTER 5: HOLE-TRANSPORTING DENDRIMERS - THE CARBAZOLES

Figure 5.17: Device characteristics of bilayer neat film devices for the carbazole dendrimer family

diagram of this device layer structure is also shown in Figure 5.16. The figure shows the deep lying HOMO of TPBI, indicating how this layer is able to act as a hole blocking layer. The resulting bilayer neat film device characteristics are plotted in Figure 5.17 and summarised in Table 5.6.

As the figure and table reveal, in all cases the efficiency of the bilayer devices increased over the single layer device with the inclusion of a TPBI layer within the device structure. The maximum device efficiency recorded for the Ir-CarbG1 device was 5.5 %, while at the standard brightness of 100 cd/m$^2$ the EQE was 4.8 %. EQE values of 3.2 % and 3.5 % were found for the Ir-CarbG2 and Ir-CarbG3 devices respectively at this same brightness. For the Ir-CarbDDG1 dendrimer the maximum efficiency of the device was 3.6 %, while at a brightness of 100 cd/m$^2$ the EQE was 3.5 %.

The corresponding emission spectra of all the devices are shown in Figure 5.17, from which the CIE coordinates were determined as (0.359, 0.605), (0.302, 0.626), (0.296, 0.618) and (0.448, 0.543) for Ir-CarbG1, Ir-CarbG2, Ir-CarbG3 and Ir-CarbDDG1. As in the single layer device case, the emission spectrum for each dendrimer did not vary with applied voltage. Comparing the bilayer device emission spectra and CIE coordinates to those obtained for the single layer devices, it can be noticed there was a slight shift in the emission spectra. This indicated that the use of the additional layers in the bilayer
device structure gave, through presumably micro-cavity effects, minor changes to the emission of the device.

Since the function of the TPBI layer was to reduce the hole current, it would be expected that the total current measured through the bilayer device would be less than that through the equivalent single layer device. In fact on comparing the current-voltage plots of Figure 5.17 and Figure 5.14 this was observed to be the opposite of what occurs - the current was greatest in the bilayer device structure for the first to third generation carbazole dendrimers, only in Ir-CarbDDG1 was the current less in a bilayer structure than in the single layer device. Also noticeable, was that in the bilayer structure the current through the first to third generation carbazole devices were all very similar, which was unlike in the single layer device case where the current decreased with generation. Evidently the presence of the TPBI increased the current, and did not act as hole blocking layer. The fact that with this layer high device efficiencies were possible suggests the role of the TPBI in this case was an electron injection layer which helped improve the charge balance. The TPBI layer may also have acted as a blocking layer to prevent excitons from reaching and thus quenching on the metal cathode layer. The increase in current in the bilayer structure was combined with in all cases an increased luminance over that of the single layer structure thereby leading to the improvements in the device efficiency.

In the single layer device case, Ir-CarbDDG1 gave the most efficient device, but in the bilayer structure, this dendrimer was actually less efficient than both Ir-CarbG1 and Ir-CarbG3. It was apparent that the modification of charge balance in the bilayer structure was less effective on Ir-CarbDDG1 than for the other carbazole dendrimers. Alternatively, it may have been that the better core encapsulation of the double dendron dendrimer meant that Ir-CarbDDG1 suffered less than the single dendron carbazole dendrimers when prepared, as was done for the single layer devices, under the old solution-processing
The method of including a TPBI layer in the device structure was proven to be effective in increasing the device efficiency. However comparing the efficiency values obtained to a neat film device with a standard iridium(III) dendrimer with phenylene dendrons these values are lower than the maximum efficiency 9.8 % published thus far \[124\]. Figure 5.18 shows that the current through the neat film bilayer device of Dendrimer 5 (Ir-CarbG1) was much greater than that through the equivalent bilayer device with a neat film of Dendrimer 1 (Ir-G1) (this data corresponds to same device that was previously detailed in Figure 4.19). The results showed that, although the bilayer structure improved the charge balance somewhat and thus the efficiency over a single layer device, the high hole mobility, and thus the current in the carbazole dendrimer bilayer devices, in comparison to that of the phenylene dendrimer device, still limited the device efficiency. For a full realisation of the high internal quantum efficiency of the carbazole dendrimers further device structural modifications were seemingly required.

### 5.5.4 Bilayer blend film devices with CBP

The previous sections have showed that good charge balance is important to give efficient devices. Therefore, in order obtain a better charge balance with the carbazole dendrimer devices it was desired to reduce the hole charge mobility. To do so, the carbazole dendrimers were each blended with the small molecule host material CBP. A CBP host has been found previously on blending with an iridium(III) dendrimer with phenylene dendrons to play no role in charge transport, instead it acted merely to modify the spacing.
of the dendrimer cores. It was found that as the concentration of CBP in the blend increased the mobility decreased \[102, 167\]. With lower mobility, the recombination of opposite charge carriers before they reach, and are annihilated at the cathode, was improved and the efficiency of electroluminescence increased \[102, 167, 168\].

In this case, for blending with the carbazole dendrimers the CBP host was doped at a blend ratio of 20:80 wt % dendrimer to host. The device structure was ITO/dendrimer blend/TPBI/LiF-Al. The corresponding device results are shown in Figure 5.19 and are summarised in Table 5.7. Comparing across the device set, as revealed in the table, shows that for Ir-CarbG1, at a brightness of 100 cd/m\(^2\), the EQE of the device was 9.5 % at 4.8 V. At the same brightness for the device with Ir-CarbG2, the EQE was 6.0 % at 4.6 V; while for Ir-CarbG3 the EQE was 7.8 %; and finally for Ir-CarbDDG1 at this brightness, the EQE was 7.0 %.

The bilayer carbazole dendrimer-CBP blend devices all showed high efficiencies, with in the best device an EQE of almost 11 % found for Ir-CarbG1. In general the EQEs obtained were more than double those of the neat film bilayer OLEDs, and over one order of magnitude greater than found in the
CHAPTER 5: HOLE-TRANSPORTING DENDRIMERS - THE CARBAZoles

Table 5.7: Summary table of device characteristics of 20:80 wt % dendrimer-CBP host blended bilayer devices for the carbazole dendrimer family

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>10.9 % (6.6 V, 19.9 lm/W, 41.9 cd/A)</td>
<td>9.5 % (4.8 V, 25.5 lm/W, 38.9 cd/A)</td>
<td>(0.321, 0.627)</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>7.0 % (6.0 V, 12.7 lm/W, 24.4 cd/A)</td>
<td>6.0 % (4.6 V, 16.2 lm/W or 23.7 cd/A)</td>
<td>(0.301, 0.622)</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>7.9 % (7.2 V, 11.1 lm/W, 25.5 cd/A)</td>
<td>7.8 % (7.2 V, 11.1 lm/W, 25.5 cd/A)</td>
<td>(0.275, 0.613)</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-DDCarbG1</td>
<td>10.3 % (7.0 V, 16.3 lm/W, 36.2 cd/A)</td>
<td>7.0 % (4.6 V, 16.7 lm/W, 24.5 cd/A)</td>
<td>(0.427, 0.561)</td>
</tr>
</tbody>
</table>

neat film single layer devices. The efficiency improvement arose from the improved balance of holes and electrons in this structure where holes were transported via the carbazole-based dendrons. This advantage was further accentuated by the fact that in the bilayer device with a TPBI layer there was a better degree of charge carrier confinement within the device structure. This reduced the number of hole carriers that were able to reach the cathode and thus quench the luminescence. For example, a consideration of the current through each of the devices to those obtained previously, shows that with a dendrimer-CBP blended film the device currents were considerably reduced. For the Ir-CarbG1 devices this reduction in current was in excess of ten times. Also noticeable, was that the Ir-CarbG2 device, with the highest current of all the CBP blend devices, had the lowest device efficiency. This again confirmed the importance of careful control of charge transport and recombination for maximum device performance.

It is noted that both Ir-CarbG1 and Ir-CarbG3 were made from dendrimer solutions at the same 20 mg/ml concentration, whereas both Ir-CarbG2 and Ir-CarbDDG1 used a slightly lower solution concentration of 16 mg/ml. This was because, only in this CBP host blended case, the slightly reduced concentration was found to give a better quality film layer. For these 20:80 wt % dendrimer-CBP blend devices the resulting CIE coordinates were (0.321, 0.627), (0.301, 0.622), (0.275, 0.613), and (0.427, 0.561) for Ir-CarbG1, Ir-CarbG2, Ir-CarbG3, and Ir-CarbDDG1 respectively. A comparison of these coordinates to those found for the equivalent neat film dendrimer devices reveals that in each case to be little change. Blending lead to no colour change; the host played no role in the emission process of the device.

The results again showed that the carbazole dendrimer generation had a large effect on the performance of the devices. Here, although the Ir-CarbG2 device showed a lower EQE than the Ir-CarbG1
device, the difference in efficiency was smaller than in the single layer device case. This may have implied that even within the bilayer structure, the poor inherent electron mobility of the dendrimers limited the device performance. Furthermore, although the carbazole dendrimer devices were very efficient and indeed more efficient than those obtained elsewhere with similar types of dendrimer structures [169], there remained still room further efficiency enhancements. One possible way to achieve this could be through increasing the electron transport within the dendrimer to further improve the charge balance, an issue that is considered further in Chapter 6.

5.5.5 Bilayer devices with CBP molar mass ratio blends

To further determine the role and effect of the carbazole groups in the dendrimer, as oppose to those in the carbazole containing CBP host in a carbazole dendrimer-CBP blended film, a new blend ratio of carbazole to host was required that accounted for the total carbazole content of the blend. Previously the blend used was a ratio of dendrimer to host, but the dendrimer also contained carbazole groups. For example, at the same blending ratio the third generation carbazole dendrimer did not have an equal amount of total carbazole content present to that of a blend of the first generation carbazole dendrimer at the same dendrimer to host blend ratio. Thus another set of devices were fabricated where the blend concentration was fixed at a 20:80 molar mass ratio of dendrimer (that is all non carbazole parts) to the total carbazole content in the blend. For the Ir-CarbG1 blend with CBP, a 20:80 molar mass ratio of dendrimer to host equated to a 27:73 wt % ratio for Ir-CarbG1:CBP. To give the same molar mass ratio blends of Ir-CarbG2, Ir-CarbG3 and Ir-CarbDDG1 with CBP the blending percentage in terms of weight were calculated as 35:65, 40:60 and 29:71 wt % respectively.

The resulting device characteristics are shown in Figure 5.20 and summarised in Table 5.8. The results show that the highest device current was observed in the Ir-CarbG2 and Ir-CarbDDG1 devices, with Ir-CarbG3 giving the lowest device current, and Ir-CarbG1 gave a current between these extremities. The light output of the Ir-CarbG3 device was also low, consequently this device was the least efficient; at a brightness of 100 cd/m$^2$ the EQE was 5.3 %. The high currents in the Ir-CarbG2 and Ir-CarbDDG1 devices also corresponded with a high luminance at low voltage, consequently at a brightness of 100 cd/m$^2$, the EQE of Ir-CarbG2 was 6.3 %, and for Ir-CarbDDG1 the EQE was 6.7 %. The most efficient device however was that with Ir-CarbG1, which showed neither high current nor high light output at low voltage. For Ir-CarbG1, at a brightness of 100 cd/m$^2$ the EQE was 13.1 %. In this case the balance of charge
was proposed to be superior to other devices to account for its high efficiency; in this way the EQE of this device was over twice that of the lower generation dendrimers at any given voltage.

For the three generations of carbazole dendrimer by equating the carbazole content for each blending ratio there was, in the ideal case, a comparable number of hole charge transporting moieties in each emissive layer and thus a comparable charge balance in each of the devices. Assuming this to be true, the effects observed in the devices can thus be accounted for by the differing hole mobilities between the carbazole dendrimer generations; an increase in dendrimer generation has been previously been found to give an increase in the hole mobility [102, 167]. In this case, the best device was found using a CBP blended film in a bilayer device structure was that of the lowest mobility carbazole dendrimer, that of the first generation Ir-CarbG1. This gives evidence of the strong correlation of the dendrimer generation to the device efficiency via the hole mobility. Of course, in reality the situation is more complex as the hole mobility will also influence the charge balance within the device. Nevertheless, the results of these devices once again emphasise the importance having a balanced charge mobility for maximum device efficiency.
Table 5.8: Summary table of device characteristics of 20:80 molar mass ratio of dendrimer to CBP host bilayer blend devices for the carbazole dendrimer family

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>13.2 % (4.8 V, 29.2 lm/W, 44.6 cd/A)</td>
<td>13.1 % (5.2 V, 31.8 lm/W, 52.6 cd/A)</td>
<td>(0.331, 0.625)</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>7.2 % (5.8 V, 13.7 lm/W, 25.3 cd/A)</td>
<td>6.3 % (4.4 V, 17.4 lm/W or 24.4 cd/A)</td>
<td>(0.287, 0.638)</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>5.9 % (10.0 V, 6.1 lm/W, 19.5 cd/A)</td>
<td>5.3 % (8.4 V, 6.6 lm/W, 17.6 cd/A)</td>
<td>(0.292, 0.611)</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-DDCarbG1</td>
<td>10.9 % (5.8 V, 21.1 lm/W, 38.9 cd/A)</td>
<td>6.7 % (3.8 V, 38.1 lm/W, 46.1 cd/A)</td>
<td>(0.420, 0.569)</td>
</tr>
</tbody>
</table>

5.5.6 Bilayer blend film devices with TCTA

In the final set of bilayer devices with the carbazole dendrimers a further set of blend film devices were investigated but this time using a TCTA host. The structure of TCTA was shown in Figure 3.1. The triphenylamine center of TCTA is considered to impart greater hole-transport character than the biphenyl units in CBP. Also the dendritic nature of TCTA has been found previously to lead to improved film quality on blending with phosphorescent dendrimers and optimum device efficiency [26].

Films of a 20:80 wt % dendrimer-TCTA blend for each of the carbazoles were first measured for PLQY; the numbers obtained, as shown in Table 5.2, were similar to those of both the solution measurement and the solid solution film measurement on the dendrimers. While blending with TCTA was not found to be any more beneficial in reducing the concentration quenching effects in the dendrimer films than a CBP host, it does have the additional advantage of better aligned energy levels to the dendrimer than CBP. The HOMO and LUMO energy levels of CBP are, as plotted in Figure 5.16, located at 5.9 eV and 2.3 eV respectively, and thus both holes and electrons would be trapped on the dendrimer in a dendrimer-CBP blend. In contrast TCTA has HOMO and LUMO energies of 5.7 eV and 2.0 eV respectively [26]. The HOMO energy of TCTA is therefore equal to that of all the carbazole dendrimers. As a result the hole density should be more evenly distributed across the blended layer, charge trapping on the dendrimer will be minimised, and charge transport between these materials is optimised, and thus the device efficiency is improved [26].

Using the TCTA host with the dendrimer doped at a 20:80 wt % dendrimer-TCTA blend for each of the carbazole dendrimers, devices were fabricated using a structure of ITO/dendrimer/TPBI/LiF-Al, where TPBI was the electron transport/hole blocking layer. The resulting device characteristics are given
Figure 5.21: Device characteristics of 20:80 wt % dendrimer-TCTA host blended bilayer devices for the carbazole dendrimer family

As the results show for the Ir-CarbG1-TCTA blend device the maximum EQE was 14.4 % at 7.8 V, and a brightness of 3140 cd/m², with an emission spectrum corresponding to a CIE coordinate of (0.310, 0.637). At a brightness of 100 cd/m², the EQE was 11.9 % at 4.4 V. Very efficient devices were thus made with Ir-CarbG1 dendrimer, which strongly realised the TCTA blend film PLQY of 78 % detailed in Table 5.2 for this dendrimer.

Using a TCTA host was also found to improve the performance of the Ir-CarbG2 dendrimer over that obtained with a CBP host, although the resulting device efficiency was still some way short of the maximum theoretically possible given that a film PLQY of 82 % has been measured for the Ir-CarbG2-TCTA blend film. For the Ir-CarbG2 device, the maximum EQE was 9.3 % (at 7.0 V), and at a brightness of 100 cd/m² the EQE was 8.2 % (4.8 V). This device gave an emission spectrum corresponding to a CIE coordinate of (0.273, 0.632).

For the Ir-CarbDDG1 device, at a brightness of 100 cd/m² the EQE was 3.6 % (4.6 V), with the emission spectrum corresponding to a CIE coordinate of (0.406, 0.579). A comparison of the current-voltage
Table 5.9: Summary table of device characteristics of 20:80 wt % dendrimer-TCTA host blended bilayer devices for the carbazole dendrimer family

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 5, Ir-CarbG1</td>
<td>14.4 % (7.8 V, 21.3 lm/W, 52.9 cd/A)</td>
<td>11.9 % (4.4 V, 39.7 lm/W, 55.6 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 6, Ir-CarbG2</td>
<td>9.3 % (7.0 V, 14.4 lm/W, 32.0 cd/A)</td>
<td>8.1 % (4.8 V, 20.2 lm/W, 30.9 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 7, Ir-CarbG3</td>
<td>15.1 % (5.8 V, 27.9 lm/W, 51.5 cd/A)</td>
<td>15.0 % (6.0 V, 31.8 lm/W, 60.6 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 8, Ir-DDCarbG1</td>
<td>4.2 % (6.2 V, 7.8 lm/W, 15.3 cd/A)</td>
<td>3.6 % (4.6 V, 8.9 lm/W, 13.1 cd/A)</td>
</tr>
</tbody>
</table>

and EQE-voltage characteristics for all the devices that used an emissive layer containing Ir-CarbDDG1 is shown in Figure 5.22. As the figure shows the current in the neat film device was greatest but the efficiency of this device was least. For the low currents in the CBP blend devices the corresponding efficiency was the greatest, with the TCTA blended device between these two situations. It has been shown before with a phenylene dendronised dendrimer that a blend with a TCTA host gave higher hole mobility than a blend with a CBP host [102]. In this way it was concluded that with a CBP host holes preferentially hopped between dendrimer cores, whereas with a TCTA host both the host and the dendrimer played a role in the hole charge transport [102]. Ir-CarbDDG1 has been found to have a high hole mobility, and hence the device has a large current. On blending with CBP the lower device current suggested the mobility was reduced, and with CBP not participating in the charge transport, the device efficiency increased. In contrast, on blending with a TCTA host, the higher current indicated both the dendrimer and host transported the hole charges; the charge balance was modified and the efficiency of the device was reduced. A reason for the differences was proposed to be related the formation of excitons. Excitons, required for efficient radiative light emission, form when electrons and holes are in close proximity - in the double dendron dendrimer, the hole charge transporting dendrons, particularly in a blended film are widely spaced apart, and can be far from the electrons residing on the core; the probability of exciton formation was low and hence the dendrimer was inefficient [163].

Finally, for the third generation carbazole dendrimer, as found for both the first and second generation dendrimer, the use of a TCTA host gave the most efficient devices that have been able to be produced for the dendrimer. In this case for Ir-CarbG3 at the standard 100 cd/m² brightness the device gave an EQE of 15.0 % (6.0 V), and the maximum EQE of the device was 15.1 % (5.8 V), a high efficiency that finally was able to realise the high photoluminescent quantum yield of this dendrimer. The CIE
The coordinates of the emission spectrum of this device were (0.280, 0.623). The performance of this device placed it amongst the highest ever recorded for a solution-processed device. Furthermore, as it used a non-optimised device structure, further device efficiency improvements could be possible, through, for example, modification of the blend ratio for maximum charge balance. The results thus clearly show the significant advantage of the carbazole dendrimer structure.

5.5.7 Carbazole devices summary

In the previous sections the device performance of the carbazole dendrimer family was studied. The results have shown that devices made with emissive layers of dendrimers with carbazole dendrons perform very differently from those made from blend of a non-carbazole containing dendrimer and carbazole containing hosts. In both cases the dendrimer generation was found to have a large effect on the device performance. An increase in dendrimer generation caused an increase in device efficiency with non-carbazole dendrons, and a decrease with carbazole dendrons both with neat dendrimer layers and when blended such that there was an equivalent amount of carbazole content in each blend. Despite this, in both cases efficient devices were made, but for maximum efficiency it was found that both types of dendrimer needed to be blended with a carbazole-containing TCTA host.
5.6 Summary

This chapter has investigated a family of conjugated dendrimers that contained charge transporting moieties in the form of carbazole dendrons. It was shown that the design of the dendrimers was successful, whereby it was possible to incorporate the functions of a host material within the dendrimer structure without the loss of photoluminescence efficiency. The inclusion of carbazole dendrons was demonstrated to have significant effects on the electroluminescence and charge transporting properties of the dendrimers [160].

The effect of changing from standard phenylene dendrons to the carbazole dendron was considered through a calculation of the molecular orbital densities. This revealed that while both dendron types gave the same LUMO distribution, the majority of the HOMO density in a biphenyl dendronised dendrimer was located on the core, whereas in carbazole dendronised dendrimers the majority of the HOMO density resided on the dendron, and as the dendrimer generation was increased the amount remaining on the core became increasingly smaller [160]. This indicated that the change in dendron lead to a modification of the hole charge transporting of the dendrons. To test this hypothesis measurements were made of the hole mobility in the carbazole dendrimers. From such measurements it was discovered that for the carbazole dendrimers the hole mobility was found to increase with dendrimer generation, which contrasted with the behaviour in the biphenyl dendronised dendrimer. It was concluded the change in dendrons had modified the hole charge transport behaviour from the core-to-core hopping found with the phenylene dendronised dendrimers to hole charge transport via the carbazole dendrons [164].

The dendrimer generation was shown to have a large effect on the performance of devices; an increase in dendrimer generation caused an increase in device efficiency with non-carbazole dendrons, and a decrease with carbazole dendrons. The change in device behaviour with change of dendron was proposed to be related to the change in the hole transport behaviour, and the modification this caused in charge balance and recombination. While hole transport was modified on changing the dendron, the similarity of the LUMO distribution with either dendron type [160], indicated that electron transport remained via the core. In this way, and particularly with the higher dendrimer generations where the molecular size was larger, the hole and electron were widely spaced apart; recombination for exciton formation was low, and thus the device efficiency was low.

Despite this, in both cases efficient neat film devices could be made, but for maximum efficiency it was found that both types of dendrimer needed to be blended with a carbazole-containing host material.
On blending with a TCTA host, very efficient devices were possible: the first generation carbazole dendrimer gave a very high maximum EQE of 13.2 %. This result indicated that on host blending a more even distribution of hole density occurred, and charge trapping on the dendrimer was minimised due to the close energy matching; the blending improved the charge transport, and the most efficient devices of each of the three single dendron dendrimer generations were possible. Albeit the efficiency of this device was still less than the best value of 16.6 % reported for an alternative carbazole containing dendrimer system [156] that was based on the original carbazole dendrimer work performed in the group reported in Reference [157]. Although to achieve the high efficiency reported in Reference [156] both host blending and an optimised device structure were required. This remains no reason, given the high film PLQYs of the carbazole dendrimers reported here, that these dendrimers on similar device optimisation could not be as equally efficient as the best reports in the current literature.

For the double dendron dendrimer, Ir-DDCarbG1, which had a hole mobility much greater than all the single dendron carbazole dendrimers, there was found to be no benefit from host blending with TCTA. With a TCTA host, both the dendrimer and host transport the hole charges [102]. Consequently the charge balance of Ir-DDCarbG1 was upset and the probability of successful exciton formation was reduced [163]; and in this way the high efficiency found with a CBP host blended device, where the CBP played no role in the charge transport, was lost.

This chapter has thus considered a new family of dendrimers and showed that by simple modification of the dendron type the hole charge transport of the dendrimer could be modified. The results revealed that good charge balance rather than simply high hole mobility was the main parameter in achieving highly efficient devices. Knowledge of the effect of the carrier mobility on device performance remains important, as with such information, improvements in the understanding of the behaviour of dendrimer OLED devices can be gained, and this way better devices can be made.
Chapter 6

Dendrimers for electron transport

6.1 Introduction

The development of high efficiency organic electroluminescent devices requires various materials that perform different roles. Chapter 5 considered dendrimers capable of hole transport via carbazole dendrons. In general most organic molecules [89–91], including the dendrimers so far considered, were hole transporting, yet the nature of the dendrimer concept is such that by the simple adjustment of the dendron it could equally become capable of electron transport.

Typically it has been the case that in order to obtain high efficiencies in organic devices the large hole mobility of the organic layers has been required to be limited or reduced. To do so additional layers such as the hole blocking/electron transport layer TPBI have had to be included within the device structure. However, fabrication of such multi-layer devices is often tedious, difficult and more expensive than single layer devices. In this respect, one of the key challenges on the path of developing the next generation of high-performance OLEDs is the design and synthesis of molecules that are capable of functioning as efficient emitters as well as charge-transport materials. Consequently, for organic semiconductors to be used as the emission layer in future devices they must meet the requirement that their energy levels match the injection and transport of both holes and electrons, and hence should desirably possess bipolar character to permit the formation of both stable cation and anion radicals. To endow a single organic material with both electron and hole transporting abilities, which generally have to be realised by at least two kinds of molecules, and make the resultant molecule air-stable, although possible [170–171], has proved very hard to achieve.
In this chapter it was explored whether dendrimers incorporating moieties intended for electron transport as the dendrons could make the dendrimer suitable for electron transport, while still acting as the solution-processed electroluminescent layer in an OLED structure. If successful it was then ultimately hoped that dendrons capable of electron transport when combined with hole transporting dendrons would be able to give multi-functional dendrimers capable of bipolar charge transport.

The dendrimers considered in this Chapter were all synthesised in Oxford by Fumiaki Ito, the details of which are beyond the scope of this thesis. However it is commented that on many occasions it proved difficult if not impossible to synthesise the exact structure required. In all cases, as has been used throughout so far, the dendrimer was formed from a \( \text{fac-tris(2-phenylpyridyl) iridium(III)} \) \([\text{Ir(ppy)}_3]\) core, to which the dendrons were attached to give the required properties. The resulting dendrimers were divided into two groups. In the first group electron transport ability was attempted to be conveyed to the dendrimer through the use of triazine groups, whereas in the second group benzimidazole groups were used to provide this function.

The chapter thus consists of a study of these dendrimers. To begin with the triazine dendrimers were studied through photophysical studies and then through device measurements, before the benzimidazole dendrimers were similarly considered. The chapter concludes with a study on devices made from blends of electron and hole transporting dendrimers.

As in previous chapters I would thank and acknowledge the contribution of Dr Ruth Harding in obtaining a number of the photophysical results.

### 6.2 Triazine dendrimers

In the first set of dendrimers synthesised all shared the common functionality in that all possessed triazine containing groups within the dendrimer structure. The structure of a triazine ring is shown in Figure 6.1. The approach of using groups containing triazine rings in an attempt to impart electron transport behaviour to a molecule is common in the literature [172][174]. This is because triazine is well known as an electron-accepting unit, it possess a large electron affinity well in excess of other electron-deficient heteroaromatic compounds such as pyridine, and thus is able to easily prevent the fast movement of electrons. The high electron affinity arises due to the presence of the three electron withdrawing carbon-nitrogen double bond or imine \((-\text{C}=\text{N}-)\) bonds in each triazine ring. Traditionally such units have been
used to create materials suitable for use as host materials or as electron transport layers within a device, but only rarely, as was attempted here, as an actual part of the light-emitting molecule.

The desired structure of a light-emitting dendrimer containing functionalities capable of electron transport based on triazine dendrons is shown in Figure 6.2. In this structure the triazine group was connected to the first phenyl ring branching off the phenyl pyridine ligand bonded to the iridium core via the nitrogen atom. Surface groups are attached to the triazine from its C4 and C6 positions, with in this case carbazole groups, the same as those studied in Chapter 5, connected via the nitrogen used. In this way both hole and electron transport character were attempted to be conveyed to the dendrimer.

Unfortunately the structure shown in Figure 6.2 proved problematic to synthesise and thus instead the structure of Dendrimer 10 (Oxford batch code Fl02-97B) shown in Figure 6.3 was made. Unlike all the previous cases considered, this dendrimer was asymmetric containing only two dendronised 2-phenyl-pyridyl ligands. In the third dendron position was a leftover product of the reaction which in the usual case would be removed during the synthesis with the final dendron.

To form a symmetric triazine dendrimer with three dendrons containing carbazole groups it was found that the connection between the triazine ring and the first phenyl ring branched off the phenyl
Chapter 6: Dendrimers for Electron Transport

Figure 6.4: Structure of a triazine dendrimer, Dendrimer 11
Figure 6.5: Structure of a triazine dendrimer, Dendrimer 12

pyridine ligand must be via an interconnecting nitrogen atom. The third bond of the nitrogen atom in this position was to an alkyl chain. The resulting dendrimer structure was that of Dendrimer 11 (FI03-83C) shown in Figure 6.3 or with an increased length of alkyl chain as for Dendrimer 12 (FI05-58B) in Figure 6.5.

6.2.1 Photophysical properties of triazine dendrimers

The absorption and emission spectra of solutions in degassed THF of Dendrimers 10, 11 and 12 were measured (Dendrimer 11 measured by Dr Ruth Harding) with the resulting spectra plotted in Figure 6.6. As the figure shows the main features of the absorption spectra of the dendrimers were that each had a maximum in the spectra around 232 nm with a secondary peak at 283 nm. The absorption spectra of each of these three dendrimers were thus very similar, and quite different to those obtained previously in this thesis. Firstly despite the presence of the carbazole dendrons in the dendrimer structure there was no characteristic carbazole peak in the spectra around 320 nm as observed in each of the carbazole dendrimers considered in Chapter 5. Instead the peak was formed at 283 nm, this caused by the presence of the triazine ring. It was evident the increase in the alkyl chain length from Dendrimer 11 to Dendrimer 12 gave no change in the spectra. Similarly the additional nitrogen atom required to connect the triazine ring in Dendrimer 11 and Dendrimer 12 gave no contribution to the absorption, as observed from the similarity of their spectra to that of Dendrimer 10 where this atom was not used within the dendrimer structure.
Figure 6.6 also plots the emission spectra of the three dendrimers. From the spectra it can be noted that Dendrimer 10 showed a peak in the emission spectra at 504 nm, whereas Dendrimers 11 and 12 gave a peak at 512 nm. This 8 nm red-shift resulted from the increased conjugation length of these dendrimers with the inclusion of the interconnecting nitrogen atom between the branching phenyl ring and the triazine dendron. The shoulder of Dendrimers 11 and 12 was also much more pronounced than that of Dendrimer 10 reflecting the slightly different structures of these dendrimers.

The preparation of neat thin films was severely hampered by the limited solubility of some of the dendrimers. Generally to give a film of suitable thickness for photophysical measurements a film concentration of 10 to 20 mg/ml was needed, in contrast to the $10^{-6}$ mg/ml concentrations used typically in chemistry characterisation processes undertaken in Oxford on these dendrimers. Consequently for Dendrimer 10 where the surface groups were unable to synthesised onto the dendrimer structure there was insufficient solubility to allow suitable films to be made. A similar problem was also found for Dendrimer 11 despite the presence of the alkyl chain. Perhaps surprisingly, by increasing the length of the alkyl chain the solubility in Dendrimer 12 was considerably improved, albeit it was still not possible to completely dissolve the dendrimer even after heating and stirring on a hotplate. The resulting films were thus cloudy in nature. This is shown in the film absorption plot of Figure 6.7 where the high absorption across the measured range in comparison to that of the dilute solution was due to scattering effects caused the poor quality of the film.
Figure 6.7 also shows the emission spectrum of a film of Dendrimer 12. Comparing this spectrum to that of the solution emission spectra for this dendrimer shown in Figure 6.6 it can be observed that they were very similar in shape, differing only in the greater pronouncement of the shoulder at 530 nm in the film spectra. There was no significant red or blue-shift in moving from film to solution. In solution the resulting CIE coordinate of the emission spectra was (0.311, 0.617), which shifted slightly in film to a CIE coordinate of (0.299, 0.613).

The photophysical analysis of the three dendrimers was extended by the measurement of the photoluminescence quantum yield in solution, and for Dendrimer 12 in film also. The results of these measurements and all the other dendrimers that will be subsequently discussed in this Chapter are presented in Table 6.1.

Dendrimer 10 was measured to have a solution PLQY value of 35 %, with no film value able to be measured for this dendrimer. On adding the additional nitrogen atom to connect the triazine dendrons the solution PLQY was found by Dr Ruth Harding to have dramatically increased to 60 % in Dendrimer 11, again no film measurement was able to be made for this dendrimer. In contrast for Dendrimer 12 with an increased length alkyl chain a measurement of the film PLQY was possible, but the very poor quality cloudy film meant this value was only 25 %. Two measurements of the solution PLQY of this dendrimer were also made, where despite its structural similarity to Dendrimer 11 the value measured was only 15 %. It believed that this difference would not have resulted from the change in alkyl chain length but from differences in the chemical purity between these dendrimers.
### Table 6.1: Summary of the photoluminescence quantum yields of all the dendrimers considered within this chapter, where * indicates a cloudy film, and # denotes films made under the old solution-processing protocol (as defined in Chapter 4). The table also includes estimates of the HOMO level energies

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Solution PLQY (%)</th>
<th>Solution CIE coordinate</th>
<th>Film PLQY (%)</th>
<th>Film CIE coordinate</th>
<th>HOMO (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 10</td>
<td>35</td>
<td>(0.234, 0.612)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dendrimer 11</td>
<td>60</td>
<td>(0.311, 0.615)</td>
<td>Insoluble</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Dendrimer 12</td>
<td>15</td>
<td>(0.311, 0.617)</td>
<td>25*</td>
<td>(0.299, 0.613)</td>
<td>5.72</td>
</tr>
<tr>
<td>Dendrimer 13</td>
<td>73</td>
<td>(0.335, 0.607)</td>
<td>60</td>
<td>(0.347, 0.613)</td>
<td>5.69</td>
</tr>
<tr>
<td>Dendrimer 14</td>
<td>69</td>
<td>(0.382, 0.590)</td>
<td>20</td>
<td>(0.452, 0.533)</td>
<td>5.52</td>
</tr>
<tr>
<td>Dendrimer 15</td>
<td>46</td>
<td>(0.313, 0.605)</td>
<td>Insoluble</td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>Dendrimer 16</td>
<td>83</td>
<td>(0.263, 0.607)</td>
<td>&lt;7#</td>
<td>(0.350, 0.564)</td>
<td>5.72</td>
</tr>
<tr>
<td>Dendrimer 17</td>
<td>73</td>
<td>(0.266, 0.610)</td>
<td>&lt;8#</td>
<td>(0.346, 0.582)</td>
<td>-</td>
</tr>
</tbody>
</table>

#### 6.2.2 Soluble triazine dendrimers

The difficulty in obtaining suitable films for photoluminescence measurements of Dendrimers 10, 11 and 12 due to their limited solubility was because none of these dendrimers contained solubilising surface groups. Having established a method for synthesising dendrimers with moieties for electron transport within the dendrimer structure the next step was the design and synthesis of such a dendrimer that was highly soluble and thus could be used to produce light-emitting devices. The result was Dendrimer 13 (FI05-33B) with structure shown in Figure 6.8. In this dendrimer, to the carbazole units 2-ethylhexyloxy surface groups were attached in an attempt to improve the solubility to a level that it could be dissolved at suitable concentrations in all standard solvents.

The consequence of the inclusion of these surface groups was that the dendrimer became sufficiently soluble for film making, enabling film photoluminescence measurements and devices to be made from this dendrimer. The resulting absorption and emission spectra of a neat film of Dendrimer 13 made at a concentration of 20 mg/ml in dichloromethane, and the solution spectra from degassed THF are shown in Figure 6.9. As the figure shows the absorption spectra in both film and solution was very similar with both yielding a maxima at around 265 nm and minimal absorption at wavelengths greater than 400 nm. Similarly, there was little difference between the emission spectra in moving from film to solution. The film spectra yielded a CIE coordinate of (0.347, 0.613), which was shifted slightly from the value in solution which gave a CIE coordinate of (0.335, 0.607). In film the spectra peaked at 524 nm, a red-shift of 5 nm from the peak of the solution spectra.

The photoluminescence quantum yield of solution and films of Dendrimer 13 were measured and
found to be 73% in solution and 60% in a neat film. These high values show a highly photoluminescent dendrimer had been made. The values were also very close to those obtained for the standard iridium cored first generation dendrimer, Dendrimer 1, indicating the use of triazine rings in the dendrimer structure had little detrimental effect on the photoluminescence efficiency of the device. It was interesting to note that the photoluminescence efficiency of a film of Dendrimer 13 was considerably greater than that of the hole transporting first generation dendrimer with carbazole dendrons (Dendrimer 5), despite both having a similar solution PLQY. Evidently a change of the dendrons can be used to modify the dendrimer properties as desired.

6.2.3 Single layer devices with soluble triazine dendrimers

The previous section established that films of triazine containing dendrimers were efficient in photoluminescence. It was thus relevant to assess whether such efficiencies could be translated to electroluminescence through the successful fabrication of devices. In the first instance, single layer devices were fabricated using neat and host blended films of Dendrimer 13 in a simple ITO/dendrimer/LiF-Al device structure. Blend films were made as a 20:80 weight ratio of dendrimer to a CBP host. The resulting device characteristics are shown in Figure 6.10 and summarised in Table 6.2.

The figure shows successful devices were possible using just a single layer of a dendrimer that contained moieties capable of electron transport. The dendrimer was usable as the electroluminescent layer.
in an OLED and not just as a transport and/or blocking layer, a result that thus far has not been obtained elsewhere. In particular the neat film device of Dendrimer 13 was able to obtain a maximum efficiency of 0.71 % at 19.4 V, and at a brightness of 100 cd/m$^2$ the EQE was 0.58 % at 16.0 V. In the 20:80 wt % Dendrimer 13:CBP blend film device the maximum efficiency obtained was higher at 0.82 % (20.0 V), and at a brightness of 100 cd/m$^2$ the EQE was 0.76 % (19.6 V).

A further consideration of these device results showed that the neat film device efficiency was greater than that of the blend film at all but high (> 19 V) applied bias voltages. Beyond this voltage the neat film device efficiency started to tail-off whereas in the blend film the efficiency continued to increase with voltage. This arose as both the current and light output through the neat film device were considerably greater at any applied bias than that of the blend film.

The corresponding emission spectra of the devices are also shown in Figure 6.10. As the figure details there was minimal change in the spectra after host blending. The neat film device spectra produced a CIE coordinate of (0.353, 0.598) while the blend film device gave a CIE coordinate of (0.322, 0.621). The spectral difference arose from the greater pronouncement of the shoulder area in the blend film located around 535 nm in comparison to the neat film. In both cases the emission spectra remained unchanged as the bias voltage was varied across the device operational range.

The current and light output through the triazine dendrimer device is compared in Figure 6.11 to that of the corresponding neat film single layer devices made with dendrimers with phenylene dendrons (Dendrimer 1, Ir-G1) and carbazole dendrons (Dendrimer 5, Ir-CarbG1). As the figures detail, plotted on
Figure 6.10: Single layer device characteristics for neat and CBP blend films of Dendrimer 13

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 13</td>
<td>0.71 % (19.4 V, 0.4 lm/W, 2.4 cd/A)</td>
<td>0.58 % (16.0 V, 0.4 lm/W, 1.9 cd/A)</td>
<td>(0.353, 0.598)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 13:CBP</td>
<td>0.82 % (20.0 V, 0.5 lm/W, 2.9 cd/A)</td>
<td>0.76 % (19.6 V, 0.4 lm/W, 2.7 cd/A)</td>
<td>(0.322, 0.621)</td>
</tr>
</tbody>
</table>

Table 6.2: Summary of device characteristics of single layer devices for Dendrimer 13

a log scale to clearly show the difference, both the current and light output with Dendrimer 1 and Dendrimer 5 devices were similar (at operational voltages > 5 V), but both were over an order of magnitude greater than the Dendrimer 13 device.

The poor device performance with efficiencies < 1 % in comparison to the other dendrimer devices reported, either those with carbazole hole transporting dendrons or those with non-charge transporting phenylene dendrons, indicated clearly that in Dendrimer 13 the charge transport was greatly modified by the presence of the triazine electron-accepting ring within the molecular structure. Despite this, successful light emission was still obtained from a dendrimer that contained moieties with electron transporting functionality. This device was able to achieve in the neat film case a brightness in excess of 500 cd/m²
6.2.4 Bilayer devices with soluble triazine dendrimers

Having considered a simple single layer device structure with Dendrimer 13 the effect of incorporating a layer of TPBI in the device structure was investigated. In previous chapters TPBI was used as an electron transport/hole blocking layer and thus the effect such a layer would have on an emission layer that was potentially capable of electron transport was interesting to consider. The device structure chosen was ITO/Dendrimer 13/TPBI/LiF-Al, with both neat dendrimer and 20:80 wt % CBP host blended films considered as the emissive dendrimer layer. The resulting device characteristics are shown in Figure 6.12 and summarised in Table 6.3.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 13</td>
<td>1.8 % (12.2 V, 1.6 lm/W, 6.3 cd/A)</td>
<td>1.6 % (13.8 V, 1.3 lm/W, 5.7 cd/A)</td>
<td>(0.341, 0.613)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 13:CBP</td>
<td>1.0 % (15.4 V, 0.7 lm/W, 3.6 cd/A)</td>
<td>0.94 % (18.6 V, 0.6 lm/W, 3.2 cd/A)</td>
<td>(0.322, 0.621)</td>
</tr>
</tbody>
</table>

Table 6.3: Summary of device characteristics of bilayer devices for Dendrimer 13

As Figure 6.12 details, the resultant devices were successful in that they were able to work as a diode and produce light, and to do so efficiently. The Dendrimer 13 neat film device achieved a maximum effi-
Figure 6.12: Bilayer device characteristics for neat and CBP blend films of Dendrimer 13

ciency of 1.8 %, and the CBP blend film a maximum EQE of 1.0 %. Comparing the device performance of the neat and blend film at a standard brightness of 100 cd/m² also emphasised the higher efficiency of the neat film device over that of the blend; in the blend the EQE was only 0.94 %, whereas a neat film device gave an EQE of 1.6 % for no discernable colour change. The CIE coordinates were calculated as (0.341, 0.613) in the neat film device, and (0.322, 0.621) in the CBP blend device.

Intriguingly, replotting the currents through the neat film single and bilayer device on the same graph, as in Figure 6.13 revealed the currents were almost identical up to 15 V (the maximum applied bias in the bilayer device). This implied the TPBI hole blocking/electron transport layer had no role in the bilayer device structure in terms of its effect on the charge injection into the organic emissive layer of Dendrimer 13. The resultant differences in efficiency between the single and bilayer structure arose from the different luminance of the two device structures: the bilayer device at any of the applied voltages considered for this structure was capable of giving out much more light, consequently this device was more efficient.

The results also showed that in both single and bilayer devices, neat films of Dendrimer 13 performed
better than Dendrimer 13-CBP host blend devices. In both cases there was a clear reduction in current and light output, and thus the device efficiency in the CBP host blend film device. It was concluded the use of CBP blend modified the charge balance sufficiently to be detrimental to the device efficiency. Previously it has been found that phosphorescent iridium(III) dendrimers could be successfully blended with a CBP host and an electron transport/hole blocking material (TPBI) in a single layer device structure [123]. If, in this case, Dendrimer 13 was capable of electron transport, the same improvement in the device efficiency might be predicted. The fact that this did not occur indicated Dendrimer 13 was not particularly successful for electron transport despite the presence of the large electron affinity triazine ring within the dendrimer structure. Instead the device behaviour suggests Dendrimer 13 was more likely to be hole transporting in nature as a result of the carbazole dendrons, which Chapter 5 revealed to be hole transporting. In any case it was evident that the use of a triazine ring in combination with carbazole dendrons was unable to obtain a good charge balance within the device structure; the obtainment of highly efficient devices with this dendrimer were not possible.

6.2.5 Triazine dendrimers with diphenylamine dendrons

The previous section considered dendrimers containing triazine groups in an attempt to impart the characteristics of electron transport to the dendrimer in order to improve the charge balance and thereby improve the device efficiency. However the results showed that the use of a triazine ring and carbazole containing dendrons were not able to achieve this. In this section an alternative method was considered where the carbazole groups were replaced with diphenylamine groups as the dendrons. The resulting structure was that of Dendrimer 14 (FI05-63C) shown in Figure 6.19.

Figure 6.13: Comparison of the current through single and bilayer neat film devices of Dendrimer 13
Diphenylamine is known to have a smaller ionisation and oxidation potential than carbazole and possess more delocalised energy levels. It therefore has improved hole charge transport through decreased hopping distances in comparison to the carbazole dendrons. As a result the hole mobility in diphenylamine has been measured to be greater than that of carbazole \[173\]. Consequently diphenylamine is a stronger donor than carbazole, which meant Dendrimer \textbf{14} should have a lower LUMO level and larger singlet energy gap than Dendrimer \textbf{11} \[173\]. In order to establish whether this was true the energy levels of the dendrimers considered were measured through electrochemistry studies by cyclic voltammetry measurements in Oxford by Fumiaki Ito, the full details of which are outside the scope of this thesis.

The oxidation potentials were measured allowing values for the HOMO levels of most of the dendrimers considered in this chapter to be determined, these values were given in Table \[6.1\]. For Dendrimer \textbf{11} a value of 5.75 eV was obtained, for Dendrimer \textbf{12} where the only change from Dendrimer \textbf{11} was the increased alkyl chain length, the HOMO was estimated to be lower at 5.72 eV. For Dendrimer \textbf{13} the HOMO energy was 5.69 eV, this decreased further in Dendrimer \textbf{14} to give a value of 5.52 eV.

Unfortunately only the oxidation potentials of the dendrimers were measured and thus the reversibility or not of the reaction remains questionable. As a result, the technique of using the first absorption peak of the UV-visible absorption spectra with the addition/subtraction of the oxidation potential to establish the unknown reduction potential, and hence from this estimate the LUMO energy could not be reliably assumed to yield the correct number. Albeit, as the HOMO levels obtained for these dendrimers were all close to the HOMO level of an iridium(III) dendrimer with phenylene dendrons at 5.6 eV and emit in the green, a similar value for the LUMO of around the 2.6 eV reported for this dendrimer \[26\].
On making this assumption the ability of the dendrimers with triazine rings included in the structure to impart electron transport ability to the dendrimer becomes questionable. In light of the LUMO levels the dendrimers do not seem to have any particular electron transport (i.e. injection) ability, a fact that has clearly been indicated in the device results so far obtained. Of course, the presence of the triazine ring may have enhanced the electron mobility of the dendrimer, but the device results in no way confirm this. It was also not possible to obtain alternative evidence to support such a claim by for example a measurement of the electron mobility. This was due primarily to the small amounts of dendrimer available, but also due to the difficulty in obtaining a suitable charge generation layer to use in combination with a spin-coated layer of this dendrimer.

Due to the difficulty in synthesis of a dendrimer with diphenylamine dendrons, Dendrimer 14 was made with no surface groups were included within the dendrimer structure. Consequently this dendrimer was not particularly soluble. Nonetheless films were still able to made at a sufficient concentration to allow photoluminescence measurements to be made. The resulting absorption and emission spectra of both solutions and films of Dendrimer 14 are shown in Figure 6.15.

As Figure 6.15 shows, for Dendrimer 14 the solution absorption spectra were very similar, both showed peaks around 208 nm and 278 nm. The second of these peaks was due to the presence of the triazine ring. The dendrimer showed minimal absorption at higher wavelengths.

Considering the emission spectra of a solution and neat film of Dendrimer 14 it was found that on
moving from solution to film there was a large 36 nm red-shift in the spectra, shifting the peak to occur at 566 nm in the film. The CIE coordinates changed from (0.382, 0.590) in solution, to (0.452, 0.533) in film. The size of this large red-shift may be related to the poor quality of the films that were able to be made with this dendrimer. This was also reflected in the measurement of the photoluminescence quantum yield: in solution a value of 69 % was found closely replicating, as shown in Table [6.1] the values obtained for most other dendrimers considered in this chapter. In contrast, for a neat film of Dendrimer 14, a PLQY value of 20 % was measured. This value was three times less than that of the triazine Dendrimer 13 that included solubilising surface groups which enabled good films to be made with the dendrimer. Evidently the choice as whether to use surface groups or not has great consequence on the resultant film quality and hence the quantum efficiency of the dendrimer.

The comparison between Dendrimer 11 (or 12) and Dendrimer 14 was also relevant as the only difference between these dendrimer structures was that of the dendrons: carbazole dendrons were used in Dendrimer 11 (or 12) and diphenylamine dendrons in Dendrimer 14. Figure [6.16] repeats the spectra shown in Figure [6.15] but with the addition of the solution spectra obtained for Dendrimer 11. As the figure details once again it was found that by simply changing the dendron the resultant absorption and emission of the dendrimer could be modified as desired.
### Table 6.4: Summary of device characteristics of single layer devices for Dendrimer 14

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m² or Max Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 14</td>
<td>2.1 % (14.4 V, 1.6 lm/W, 7.5 cd/A)</td>
<td>2.0 % (15.8 V, 1.4 lm/W, 7.2 cd/A)</td>
<td>(0.353, 0.604)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 14:CBP</td>
<td>1.2 % (20.0 V, 0.6 lm/W, 4.0 cd/A)</td>
<td>1.2 % (35 cd/m², 20.0 V, 0.6 lm/W, 4.0 cd/A)</td>
<td>(0.420, 0.559)</td>
</tr>
</tbody>
</table>

#### 6.2.6 Single layer devices from triazine dendrimers with diphenylamine dendrons

The previous section showed how a simple change of the dendron used within a dendrimer structure could lead to large changes in the photophysical properties of the dendrimer. It was also interesting to consider how this change would effect the device properties. Therefore single layer devices were made using the same structure as previously used for Dendrimer 13, that is an ITO anode and a LiF-Al cathode, with both neat films and a 20:80 weight percentage dendrimer-CBP host blend films considered. The device characteristics of the resulting devices are shown in Figure 6.17 and summarised in Table 6.4.

The device results show operational devices were possible using just a film of Dendrimer 14 without the need for other transport or injection layers within the device structure. Despite the low film PLQY of Dendrimer 14, Figure 6.17 actually shows that the neat film device of Dendrimer 14 was considerably more efficient than the comparable device made with Dendrimer 13. In this case the device attained a maximum efficiency of 2.1 %, and at a brightness of 100 cd/m² the EQE was 2.0 %. These efficiencies occurred for an emission spectra that corresponded to a CIE coordinate of (0.353, 0.604), slightly deeper red than the solution photoluminescence spectra but considerably bluer than the neat film PL spectrum of this dendrimer.

In contrast, in a CBP host blended film the device was only slightly more than half as efficient, it achieved a maximum EQE of 1.2 % at the maximum tested applied bias of 20.0 V, which was only capable of giving a brightness of 35 cd/m². For this blend film as the figure shows there was also a considerable red-shift in the emission spectrum leading to a CIE coordinate of (0.420, 0.559), a greater red-shift than that of the neat film PL spectra. Therefore as found for Dendrimer 13, a blend film device of Dendrimer 14 produced less current and light and hence was less efficient than a neat film device of the same dendrimer. Once again this result casted doubt on the ability of the diphenylamine dendrons to provide any electron transport ability to the dendrimer, with instead once again the dendrimer appearing to be hole transporting.
6.2.7 Bilayer devices from triazine dendrimers with diphenylamine dendrons

The previous section showed that in a single layer device structure Dendrimer 14 could be successfully used to give light emission. The effect of using a bilayer device structure with a layer of TPBI in addition to the dendrimer layer was thus considered. The device structure chosen was that of ITO/dendrimer/TPBI/LiF-Al. For the dendrimer layer both neat and CBP host blended films of Dendrimer 14 were attempted. The resulting device characteristics are shown in Figure 6.18 and summarised in Table 6.5.

In the neat film device the maximum efficiency was 0.14 %, and at a brightness of 100 cd/m$^2$ the EQE was 0.12 %, with the emission spectrum giving a CIE coordinate of (0.422, 0.558). For the CBP host blend device the maximum efficiency was 0.78 %, still someway short of that found for a single layer device, albeit this device unlike the blend film single layer case, was able to reach a brightness of 100 cd/m$^2$ giving at this brightness an EQE of 0.75 %. The corresponding CIE coordinate for this device was (0.423, 0.555).

On considering the results for Dendrimer 14 it was noted that in the neat film device case the current in the bilayer device was much greater than that in the single layer device, whereas in the blend film
cases the currents were much more similar. The bilayer device from both a neat and blend film also produced much more light than the equivalent single layer device. It was evident that in the bilayer device structure there was a much greater charge imbalance than in a single layer device that caused the reduction in efficiency.

The results show that the best performing device with Dendrimer 14 occurred for a neat film single layer device where there was no charge confinement, with any attempt to create this, either through blending with a host or through the use of additional layers within the device structure, having a detrimental effect on the device performance. It was not obvious how this result correlated to an improved electron transport (or injection) ability of the dendrimer, in fact these devices performed worse than any of the known hole transporting dendrimers considered in Chapter 4 and Chapter 5. It seemed instead that the use of triazine dendrimers with diphenylamine dendrons did not in any way improve charge balance through the improvement of electron transport, but instead merely acted to the detriment of the hole transport properties of the dendrimer thereby stopping the creation of efficient devices from this dendrimer.
Chapter 6: Dendrimers for Electron Transport

Dendrimer 14

6.2.8 Triazine dendrimers with benzimidazole dendrons for electron transport

The previous triazine dendrimers have attempted to improve the charge transport within the dendrimer structure by combining a high electron affinity triazine ring with hole transporting carbazole or diphenylamine dendrons, an approach that has been clearly shown to be ineffectual. Instead in this section, the hole transporting dendrons were replaced with benzimidazole dendrons. The benzimidazole unit has been seen before in this thesis; it was part of the structure of 1,3,5-tris(2-N-phenylbenzimidazolyl)benzene (TPBI) that has been used throughout this thesis as the electron transport/hole blocking layer for bilayer devices, this structure was shown previously in Figure 2.16. It was hoped that dendrimers with benzimidazole dendrons would be much less hole transporting than those with the carbazole or diphenylamine dendrons.

Unfortunately the synthesis of such a triazine-benzimidazole dendrimer proved to be very difficult. In particular the attachment of the dendrons and surface groups to these dendrons proved tricky. The best resulting structure was Dendrimer 15 (FI05-66C) shown in Figure 6.19. As can be seen from the figure, this structure was very similar to that of Dendrimer 12 with the only difference being the replacement of the carbazole dendrons of Dendrimer 12 with benzimidazole dendrons in Dendrimer 15. Solubility was again attempted to be provided by the long alkyl chain off the nitrogen that was required as before to connect the triazine ring to the phenyl-pyridine linkage.

The lack of adequate surface groups meant the solubility of Dendrimer 15 was very limited. As a result it was found impossible to spin-coat thin films suitable for devices or photoluminescence measurements from this dendrimer. At low concentrations dilute solutions were just possible although even with heat and agitation the solutions often remained slightly cloudy. Nonetheless solution PL measurements were still possible giving the resulting absorption and emission spectra shown in Figure 6.20. As the figure details the absorption spectra gave peaks at 252 nm and 290 nm with minimal absorption at wavelengths beyond 400 nm. The emission spectrum showed green emission with a peak at 512 nm with a
CHAPTER 6: DENDRIMERS FOR ELECTRON TRANSPORT

Figure 6.19: Structure of a triazine dendrimer with benzimidazole dendrons, Dendrimer 15

Figure 6.20: Solution absorption and emission spectra of Dendrimer 15

resultant CIE coordinate of (0.313, 0.605).

The effect of changing the dendrimer surface groups from carbazole (Dendrimers 11 and 12), to diphenylamine (Dendrimer 14), to benzimidazole (Dendrimer 15) is shown in Figure 6.21 where a comparison of all the solution absorption and emission spectra obtained for each dendrimer is shown. The plot shows Dendrimers 11, 12 and 15 all had very similar emission spectra with only the diphenylamine dendrons of Dendrimer 14 leading to any shift in the emission spectra. The change in dendron did of course change the chemical structure of the dendrimer, with each dendron having its own characteristic absorption features that accounted for the shift of the first peak of the absorption spectra observed in the figure.

The solution photoluminescence quantum yield of Dendrimer 15 was measured to be 46 %. The
value obtained was much lower than any of the other dendrimers reported in this chapter, other than Dendrimer 12 which also suffered from solubility problems. It was not clear whether this low quantum yield arose in part due to the poor solubility of the dendrimer, or was due purely to the change of dendron.

The effect of attaching benzimidazole groups onto the triazine ring was not overly clear but it could be concluded it was not overly beneficial. It would be assumed in Dendrimer 15, in comparison to when the much greater hole transporting dendrons were used, the electron mobility would be the greatest, but on the other hand the electron affinity may be too strong causing the trapping of electrons. To determine fully whether such dendrimers were indeed capable of electron transport further measurements of the device and more particularly the mobility would be needed. However the poor solubility of Dendrimer 15 meant films suitable for such measurements were impossible to make, and therefore it remains hard to conclude that Dendrimer 15 in common with the other triazine dendrimers did possess any electron transport properties.

6.2.9 Triazine dendrimers summary

This section has detailed the study of a small family of dendrimers that were all related by the fact each contained a triazine ring within its structure. Triazine is known to have a high electron affinity and thus it was hoped it would be able to improve the electron transport properties of an iridium(III) dendrimer that has been found in all previous cases to be strongly dominated by hole transport. The results showed
that despite numerous synthesis problems, for the first time a number of such dendrimers could be made and then used as the light-emitting layer in devices. Despite this, there was little evidence to suggest that such molecules were capable of, or at least could improve, the electron transport. In fact the results suggested that it was the hole transport that was modified to the detriment of the device efficiency. It is thus surmised that the use of triazine dendrimers was not effective in giving the dendrimers electron transporting ability and an alternative approach was required.

6.3 Benzimidazole dendrimers

The second attempt to impart improved electron transport into a dendrimer structure was by the inclusion within the dendrimer structure of a benzimidazole unit. In the last triazine dendrimer considered (Dendrimer 15) this unit was used in combination with a triazine ring but this was not found to be successful and therefore triazine was not subsequently used in the dendrimer structure. As discussed previously benzimidazole forms part of the structure of 1,3,5,-tris(2-N-phenylbenzimidazolyl)benzene (TPBI) that has been used throughout the thesis as the electron transport/hole blocking layer in bilayer devices. In fact the small dendritic molecule of TPBI, with structure shown in Figure 2.16 has been widely used used as both an electron transport layer and host material for both fluorescent [175] and phosphorescent OLEDs [26, 123]. This use extends from its low electron affinity, high ionisation potential and wide energy gap with a LUMO of 2.7 eV and HOMO of 6.7 eV. This makes it strongly hole blocking in character within a standard device structure and with a low barrier for electron injection. The high electron transport character of TPBI also means the electron mobility through the TPBI layer would be high. The success of this molecule has meant there have been numerous attempts at using polymeric structures containing benzimidazole units for electron transport, for example see Reference [176] for a summary, but there have been very few reports of phosphorescent molecules containing such a unit [177, 178]. This section details the results of incorporating a benzimidazole unit into light-emitting dendrimers.

For the study two dendrimers were synthesised. Each contained a single benzimidazole unit as a dendron branched of the phenyl pyridine ligand. To allow the effect of generation to be studied a zeroth and first generation dendrimer were chosen, the respective resulting structures of Dendrimer 16 (FI03-99B) and Dendrimer 17 (FI04-87C) are shown in Figure 6.22 and Figure 6.23 respectively.
6.3.1 Photophysical properties of benzimidazole dendrimers

The absorption and emission spectra of the two benzimidazole dendrimers are shown in Figure 6.24. For Dendrimer 16 the solution spectra was measured in degassed dichloromethane while Dendrimer 17 was in degassed THF. Despite the lack of surface groups Dendrimer 16 was still soluble albeit only in a minimal range of solvents, hence the change to dichloromethane. Consequently emission spectra were measured by Dr Ruth Harding for both dendrimers from films made at 20 mg/ml concentration in dichloromethane, the same film being used to obtain the absorption spectra of Dendrimer 16, the film absorption spectra of Dendrimer 17 was not measured. All photoluminescence measurements on the benzimidazole dendrimers were performed under old solution-processing protocol conditions and were not able to be repeated following the new protocol technique for solution preparation.

The absorption spectra of Dendrimer 16 shows that on moving from film to solution there was no change in spectral shape although there was a change in the intensity of the relative absorbance peaks. The addition of the biphenyl dendrons in Dendrimer 17 was found to modify the absorption spectra from that of Dendrimer 16; a peak around 272 nm characteristic of this dendron was observed.

The figure also confirmed the emission originated from the core; the addition of the dendron had no effect on the resultant spectra. The solution emission spectra of both dendrimers were similar as were the two film spectra, both of which were red-shifted from the solution spectra. In solution the CIE coordinates were calculated as (0.263, 0.607) for Dendrimer 16 and (0.266, 0.610) for Dendrimer 17. In film the CIE coordinates shifted to (0.350, 0.564) for Dendrimer 16 and (0.346, 0.582) for Dendrimer 17.
The solution and film photoluminescence quantum yields for both Dendrimers 16 and 17 were measured by Dr Ruth Harding (Dendrimer 16 film measurement by Paul Shaw) and are tabulated alongside all the other dendrimers considered in this chapter in Table 6.1. The neat film PLQY of Dendrimer 16 was less than 7 % and increased to only around 8 % on the addition of the biphenyl dendron in Dendrimer 17. The low film PLQY was disappointing as in both cases the solution PLQY of the films was high: 83 % for Dendrimer 16, and 73 % for Dendrimer 17.

In an attempt to understand the large fall in the PLQY on moving from solution to a neat film a measurement of the solid solution PLQY was made for both dendrimers. For this films were made as a 20:80 weight percentage blend of the dendrimer to a CBP host. For Dendrimer 16 a PLQY value of 48 % was found, with 53 % measured for Dendrimer 17. Typically such solid solution PLQY measurements would yield values close to that of the solution measurement [119]. In this case there was evidently significant quenching effects occurring within the films even when they were widely spaced in a CBP matrix. Therefore the prospect for efficient electroluminescence from such dendrimers was not high.

### 6.3.2 Single layer devices with benzimidazole dendrimers

Despite the poor photoluminescence efficiency of neat films of Dendrimers 16 and 17 it was still felt worthwhile to fabricate devices using these dendrimers as the emissive layer, as the results obtained and knowledge gained may better determine if in fact the benzimidazole dendrimers were capable of electron transport.
transport. To begin with, single layer devices were fabricated using a structure of ITO/dendrimer/Ca-Al, where both neat and CBP host blended films of Dendrimers 16 and 17 were used as the emission layer. The resulting device characteristics are shown in Figure 6.25 and Figure 6.26, with the results summarised in Table 6.6.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 16</td>
<td>0.05 % (12.8 V, 0.04 lm/W, 0.15 cd/A)</td>
<td>0.02 % (10.0 V, 0.02 lm/W, 0.07 cd/A)</td>
<td>(0.390, 0.564)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 16:CBP</td>
<td>0.65 % (16.4 V, 0.4 lm/W, 2.2 cd/A)</td>
<td>0.52 % (14.0 V, 0.4 lm/W, 1.7 cd/A)</td>
<td>(0.351, 0.588)</td>
</tr>
<tr>
<td>100 wt % Dendrimer 17</td>
<td>0.28 % (20.0 V, 0.1 lm/W, 0.9 cd/A)</td>
<td>0.22 % (15.4 V, 0.15 lm/W, 0.7 cd/A)</td>
<td>(0.310, 0.607)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 17:CBP</td>
<td>0.21 % (13.8 V, 0.1 lm/W, 0.6 cd/A)</td>
<td>0.17 % (17.4 V, 0.1 lm/W, 0.5 cd/A)</td>
<td>(0.376, 0.558)</td>
</tr>
</tbody>
</table>

Table 6.6: Summary of device characteristics of single layer device for Dendrimers 16 and 17

As Figure 6.25 and Figure 6.26 show, successful light-emitting devices were able to be made from both the benzimidazole dendrimers. For the zeroth generation Dendrimer 16 although devices were
possible they were not efficient, attaining a maximum efficiency of only 0.05 % for a bias 12.8 V. On moving to the first generation Dendrimer 17 the effect of including the dendron was found to have significantly increased the maximum device efficiency. A five times increase was found yielding a maximum EQE for this device of 0.28 % at an applied bias of 20.0 V. Unlike for the hole transporting carbazole dendrimers considered in Chapter 5 but similar to the iridium(III) phenylene dendron dendrimers in Chapter 4, there was in the benzimidazole dendrimers, found to be an improvement in efficiency with dendrimer generation.

A comparison of the neat film devices at the same standard brightness of 100 cd/m$^2$ further emphasised the advantage of increasing dendrimer generation: for the zeroth generation Dendrimer 16 the EQE was 0.02 % at 10.0 V, which increased to 0.22 % at 15.4 V for the first generation Dendrimer 17. The improvement in efficiency with an increased dendrimer generation also corresponded to a narrowing of the emission spectrum. In Dendrimer 16, the device gave a very broad and featureless spectrum corresponding to yellowish-green emission colour that yielded a CIE coordinate of (0.390, 0.564). On increasing the dendrimer generation when moving to Dendrimer 17, the spectrum became more defined.
showing a clear peak and shoulder corresponding to a much deeper green colour, this gave a CIE coordinate of (0.310, 0.607).

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>EQE at 100 cd/m²</th>
<th>100 Film PLQY (%)</th>
<th>( \Phi_{\text{CAPTURE}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 16</td>
<td>0.02 %</td>
<td>7</td>
<td>0.014</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 16:CBP</td>
<td>0.52 %</td>
<td>48</td>
<td>0.054</td>
</tr>
<tr>
<td>100 wt % Dendrimer 17</td>
<td>0.22 %</td>
<td>8</td>
<td>0.138</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 17:CBP</td>
<td>0.17 %</td>
<td>53</td>
<td>0.016</td>
</tr>
</tbody>
</table>

Table 6.7: Summary of single layer device efficiency, film PLQY, and the corresponding calculated value of \( \Phi_{\text{CAPTURE}} \) for Dendrimers 16 and 17

Intriguingly on moving to a Dendrimer 16-CBP blend film device, the yellowish-green emission of the neat film became replaced with a much deeper green emission colour, replicating that of Dendrimer 17, the blend device spectrum corresponded to a CIE coordinate of (0.351, 0.588). There was also over an order of magnitude improvement in the device efficiency. The maximum EQE of the device was 0.65 % at a brightness of 438 cd/m², falling to 0.52 % at the standard brightness of 100 cd/m². The improvement in device performance in the blend film of Dendrimer 16 was accounted for by the large reduction in the current that passed through the device, but this was found to increase the turn-on voltage of the device. However, as the light output in the blend film device was also less than in the neat film device at any given bias, there was a better balance of current and light and hence an improved charge balance. In contrast in the first generation benzimidazole dendrimer, Dendrimer 17, both the current and light output of the CBP host blend film device were approximately equal to that of the neat film device of this dendrimer at all applied voltages up to 15 V.

Consequently the resulting efficiency of the neat and blend film devices were very similar, although due to a broadening of the emission spectra they were not exactly the same. The resultant CIE coordinate of the Dendrimer 17 CBP host blend film device was (0.376, 0.558). As a result of this slight spectral difference the maximum efficiency of the blend film device was lower at 0.21 % for an applied bias of 13.8 V. Also noted was that unlike in the neat film device case for the blend film both the current and light output were found to fall away beyond 15 V, not as in the neat film exponentially increase causing the efficiency to tail-off. As a result the maximum brightness found for the CBP blend film device was only 91 cd/m² and this required a high applied bias of 17.4 V bias to produce it, and gave an EQE of
only 0.17 %. Considering these numbers further and recalling Equation 2.13 where the quantum efficiency of the device was said to be described as the product of four terms; \( \Phi_{\text{CAPTURE}} \), \( \Phi_{\text{RADIATIVE}} \), \( \Phi_{\text{SPIN}} \) and \( \Phi_{\text{ESCAPE}} \), each of which must be optimised for maximum efficiency. In this case for phosphorescent dendrimers it was assumed \( \Phi_{\text{SPIN}} \) was equal to unity, and that if only 20 % of the light could escape from the device then \( \Phi_{\text{ESCAPE}} = 0.2 \). The film PLQY of the dendrimer was assumed to be equal to that of \( \Phi_{\text{RADIATIVE}} \), and so if the quantum efficiency was known an estimate could be made for the \( \Phi_{\text{CAPTURE}} \) term of the equation. \( \Phi_{\text{CAPTURE}} \) is the fraction of injected charges that meet to form an exciton, for this fraction to be a maximum balanced injection and transport of both holes and electrons are required. An estimation of this value remains particularly useful as it gives a measure of the degree of charge balance within the device structure. Using the value of the device efficiency at the standard brightness of 100 cd/m\(^2\) as given previously in Table 6.6 and the value of the film PLQY from Table 6.1, \( \Phi_{\text{CAPTURE}} \) was calculated for each of the neat and blend films of Dendrimers 16 and 17. The resulting numbers are shown in Table 6.7. As shown in the data of the table, in all cases the value obtained for \( \Phi_{\text{CAPTURE}} \) for the neat film Dendrimer 16 device was very much less than one, which indicated that there was a very poor balance of electron and hole injection/transport within this device. The increase in dendrimer generation on moving to the 100 wt % Dendrimer 17 device was found to give nearly a ten times improvement in the \( \Phi_{\text{CAPTURE}} \) term: a value of 0.138 was calculated. This value although still very much less than did show how that the increased dendrimer generation gave dramatic improvements in the device performance.

In both the 20:80 wt % dendrimer-CBP host blended film devices the value of \( \Phi_{\text{CAPTURE}} \) was again very low, and only in Dendrimer 16 was there an improvement over that of the neat film value. The fact that the film PLQY of these CBP host blended films was measured in both cases to be around 50 % showed that the resultant low device efficiency of these devices was not due to poor PLQY but poor charge balance. It was evident that in the simple single layer device structure the lack of charge confinement and poor balance of charge injection/transport severely limited the device performance.

6.3.3 Bilayer devices with benzimidazole dendrimers

The previous section studied single layer devices that used benzimidazole dendrimers as the light-emitting layer. This approach although successful in that it demonstrated the dendrimers were able
to function as such a layer did find some strange results that could not be easily explained. Therefore in an attempt to understand better the complex physics of these benzimidazole dendrimers in this section bilayer devices that used the additional hole transport/electron blocking layer of TPBI within the device structure were attempted. The resulting bilayer device structure was thus ITO/dendrimer or dendrimer-host blend/TPBI/LiF-Al, with a blend ratio of 20:80 wt% of dendrimer to CBP host used. The resultant device characteristics of Dendrimers 16 and 17 are shown in Figure 6.27 and Figure 6.28 respectively, and are summarised in Table 6.8.

For a neat film of Dendrimer 16, the maximum efficiency found through the device was 1.3% for an applied bias of 18.0 V, at a lower bias of 16.6 V the brightness was the standard 100 cd/m² and gave an efficiency of 1.2%. On moving to the CBP host blended film there was, as shown Figure 6.27, a large increase in both the current and light output of the device and the resultant device efficiency was much greater with a peak EQE of 5.4% at a bias of 7.6 V. At the standard 100 cd/m² brightness the device also gave an EQE of 5.4% at a bias of 10.8 V. This device efficiency was the highest obtained for any of the devices so far reported within this chapter. For these benzimidazole dendrimer bilayer

![Figure 6.27: Bilayer device characteristics for neat and CBP blend films of Dendrimer 16](image-url)
devices the value of $\Phi_{\text{CAPTURE}}$ was again calculated and is recorded in Table 6.9. From this calculation it was evident that the improvement in device efficiency on moving from a neat to a host blended film of Dendrimer 16 did not arise due to an improvement in the charge transport, as this change was found to reduce the value calculated for $\Phi_{\text{CAPTURE}}$. Instead the greater than four times improvement in device efficiency on moving from the neat to the blend film arose from the near seven times improvement in the film luminescence efficiency as revealed by the PLQY measurements. It was also noted the blended film emission spectrum was 7 nm blue-shifted from that of the neat film spectrum which gave an emission peak at 508 nm and a much deeper green emission colour. The resulting CIE coordinates calculated for these spectra reflect this change, in the neat film the coordinate was (0.344, 0.592), which shifted to (0.283, 0.608) in the blended film device.

On moving to the first generation benzimidazole dendrimer, Dendrimer 17, the resultant maximum efficiency of the neat film device was almost double that of the maximum efficiency of the equivalent neat film zeroth generation dendrimer device. In particular the maximum efficiency found was 2.6 %. This efficiency occurred at a brightness of 200 cd/m², before falling to an EQE of 2.5 % at the standard
Chapter 6: Dendrimers for Electron Transport

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m$^2$</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 16</td>
<td>1.3 % (18.0 V, 0.7 lm/W, 3.9 cd/A)</td>
<td>1.2 % (16.6 V, 0.7 lm/W, 3.9 cd/A)</td>
<td>(0.344, 0.592)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 16:CBP</td>
<td>5.4 % (7.6 V, 6.9 lm/W, 16.8 cd/A)</td>
<td>5.4 % (10.8 V, 5.1 lm/W, 17.6 cd/A)</td>
<td>(0.283, 0.608)</td>
</tr>
<tr>
<td>100 wt % Dendrimer 17</td>
<td>2.6 % (14.0 V, 1.8 lm/W, 8.1 cd/A)</td>
<td>2.5 % (13.0 V, 1.9 lm/W, 7.9 cd/A)</td>
<td>(0.326, 0.595)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 17:CBP</td>
<td>2.4 % (14.6 V, 1.6 lm/W, 7.2 cd/A)</td>
<td>2.4 % (14.6 V, 1.6 lm/W, 7.2 cd/A)</td>
<td>(0.324, 0.593)</td>
</tr>
</tbody>
</table>

Table 6.8: Summary of device characteristics of bilayer device for Dendrimers 16 and 17

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>EQE at 100 cd/m$^2$</th>
<th>100 PLQY (%)</th>
<th>Φ$^{\text{CAPTURE}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 16</td>
<td>1.2 %</td>
<td>7</td>
<td>0.886</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 16:CBP</td>
<td>5.4 %</td>
<td>48</td>
<td>0.563</td>
</tr>
<tr>
<td>100 wt % Dendrimer 17</td>
<td>2.5 %</td>
<td>8</td>
<td>1.556</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 17:CBP</td>
<td>2.4 %</td>
<td>53</td>
<td>0.222</td>
</tr>
</tbody>
</table>

Table 6.9: Summary of bilayer device efficiency, film PLQY and Φ$^{\text{CAPTURE}}$ for Dendrimers 16 and 17

100 cd/m$^2$ brightness. The emission spectra of the neat film device was calculated to have a CIE coordinate of (0.326, 0.595). In this case the change to a CBP host blended film was found to give little spectra change, the CIE coordinate was very similar at (0.324, 0.593). The dendrimer-CBP blend device also showed a reduction in both the current through the device and the light output of the device, consequently the maximum efficiency of the device was lower giving an EQE of 2.4 % at a brightness of 100 cd/m$^2$.

The fall in efficiency combined with the higher film PLQY of the blend film was reflected, as shown in the numbers given in Table 6.9, in the large drop in the value of Φ$^{\text{CAPTURE}}$ on moving from the neat to the blend film.

### 6.3.4 Benzimidazole dendrimers summary

The results of the previous section have shown that the benzimidazole dendrimers could be used to produce efficient devices, and thus in that respect were superior to the triazine dendrimers of Section 6.2.

Yet in common with the triazine dendrimers no evidence of electron transport was observed in the benzimidazole dendrimers, nor was there in most cases, as the calculations of Φ$^{\text{CAPTURE}}$ revealed, any improvement in charge balance on using the benzimidazole dendrimers.
It was found in order to obtain efficient devices with the benzimidazole dendrimers host blending with CBP was required to give some improvement in the charge balance as observed in the single layer device case, but mainly to give an improvement in the luminescence efficiency of the film. It was evident that in the zeroth generation dendrimer there were very strong intermolecular interactions that acted to quench the luminescence which could only be started to be overcome on blending the dendrimer into a CBP host. In the first generation dendrimer, Dendrimer 17, where the increased molecule size due to the presence of the dendron meant there was a larger degree of bulkiness, the core-core interactions were not as significant. A blend of this dendrimer in a CBP host was found to give a lower current and light output and hence lower efficiency and a large decrease in the value of $\Phi_{CAPTURE}$ from the neat film. It was proposed that on blending the dendrimer became too diluted and thus charge transport became severely hampered so accounting for these observed effects. A further consequence of these results was that it would be interesting to find how if by varying the blending ratio of the zeroth dendrimer generation, Dendrimer 16, to a host material, whether the balance of charge could in fact be tuned to optimise the device efficiency.

### 6.4 Electron-hole transporting dendrimer blends

In an attempt to improve the charge balance found in Dendrimer 16, in this section the effect of blending this dendrimer at different blend ratios with a known hole transporting dendrimer and/or a CBP host was investigated. The approach of blending an iridium(III) cored dendrimer with the electron transport small molecule of TPBI and a CBP host has already been detailed to lead to highly efficient single layer devices with external quantum efficiencies of 10.4 % \cite{123}. It was intuitive to investigate whether such efficiencies could be replicated if the TPBI was replaced in the blend with Dendrimer 16. Devices were made using blends of the zeroth generation benzimidazole dendrimer (Dendrimer 16) with either a CBP host, or the first generation carbazole hole transporting dendrimer (Dendrimer 5) previously studied in Chapter 5.

The efficiency at a standard brightness of 100 cd/m$^2$ for a neat film single layer device with Dendrimer 16 was 0.02 % at 10.0 V, whereas for Dendrimer 5 at this same brightness the EQE was 0.28 % at 6.9 V. These numbers indicated that, as already discussed, there was a large degree of charge imbalance in the device with Dendrimer 16 that lead to the poor efficiencies found in this single layer device. In contrast Dendrimer 5, despite the high hole mobility observed, showed an improved charge balance with
\( \Phi_{\text{CAPTURE}} = 0.038 \), nearly three times that of Dendrimer 16, so explaining why these devices were more efficient.

Nonetheless, the balance of electrons and holes did not reveal the full story of the low device efficiencies of Dendrimer 16, as it was also less luminescent than that of Dendrimer 5. In a measurement of the solution PLQY both dendrimers were found to have similar values, 83 % for Dendrimer 16 and 75 % for Dendrimer 5. In contrast in the neat film, Dendrimer 16 was found to have a film PLQY of 7 % as opposed to 37 % for Dendrimer 5. The degree of molecular interactions was significantly greater in Dendrimer 16 than in Dendrimer 5. The luminescence was quenched much more extensively in Dendrimer 16 and therefore the devices that used this dendrimer were very inefficient. This was further confirmed through a comparison of the solid solution PLQY values that used a 20:80 wt % blend of each dendrimer with a CBP host; 48 % for Dendrimer 16, but 82 % for Dendrimer 5.

### 6.4.1 Single layer devices from electron-hole transporting dendrimer blends

In an attempt to overcome the quenching effect in the single layer device, a number of devices were fabricated using electroluminescent layers formed through blends of Dendrimer 16 and Dendrimer 5 and/or a CBP host. The external quantum efficiencies of the resultant single layer device for each blend ratio considered are plotted in Figure 6.29 with all results summarised in Table 6.10. The results indicated the effect of including within the electroluminescent layer the additional hole carrying properties of either Dendrimer 5 or the CBP host was quite dramatic as it gave greatly increased efficiencies, with the value of the increase depending on the quantity added.

To understand this further the molar ratio [mass(g) / molecular weight(g)] of each blend was calculated. This is plotted in Figure 6.30 as the ratio of the total hole transporting material, HTM, (Dendrimer 5 + CBP) to that of the total material content that could be capable of electron transport, ETM, (Dendrimer 16) against the device external quantum efficiency measured at a standard display brightness of 100 cd/m². The assumption was made that Dendrimer 16 only had electron transport ability and Dendrimer 5 was only hole transporting. In the second two plots of Figure 6.30 the first plot has been subdivided to allow an easier identification of the main contributor to the increase in the device efficiency. The figures show that CBP had a much more influential effect on the device efficiency than blending with the hole transporting Dendrimer 5. In fact due to the similarity of the blend of (Dendrimer 16 + CBP) to that of the blend of (Dendrimer 16 + Dendrimer 5 + CBP) the plots indicated that the inclusion of the
hole transporting dendrimer had little effect on the device efficiency. The device efficiency in these simple single layer devices seemed only to depend on the CBP content present, with in the three component blend an increase in the Dendrimer 5 content found to be detrimental to the device efficiency.

One of the main purposes of blending with a host material is to obtain the benefits of increased core-to-core separation of the dendrimers in order to reduce concentration quenching effects and thus maximise the luminescence efficiency of the organic material. It has previously been shown that on blending a dendrimer with phenylene dendrons with CBP, the hole charge transport in the dendrimer system was via hopping between dendrimer cores, with the CBP and the dendrons playing no role in the transport of the charge; the CBP acted merely to space the dendrimers apart [167]. It was concluded in this single layer device on blending Dendrimer 5 with Dendrimer 16 it caused Dendrimer 5 to no longer work effectively as a hole transporting dendrimer. A possible reason for this could have been phase separation between the blends of the two dendrimers, but this has been shown not to occur in other iridium(III) dendrimer-CBP blends [135] and so can be ruled out as being unlikely to have occurred.
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Figure 6.30: Plots of ratio the efficiency of single layer devices against the ratio of hole to electron molar weight for blends of Dendrimer 16, and Dendrimer 5 and a CBP host

<table>
<thead>
<tr>
<th>Electroluminescent layer</th>
<th>Blend Ratio (%)</th>
<th>EL Efficiency at cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 16</td>
<td>100</td>
<td>0.02 % (10.0 V, 0.02 lm/W, 0.07 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 16:CBP</td>
<td>30:70</td>
<td>0.14 % (13.8 V, 0.1 lm/W, 0.4 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 16:CBP</td>
<td>20:80</td>
<td>0.52 % (14.0 V, 0.4 lm/W, 1.8 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>20:80</td>
<td>0.05 % (13.4 V, 0.04 lm/W, 0.1 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>50:50</td>
<td>0.08 % (12.0 V, 0.07 lm/W, 0.3 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>80:20</td>
<td>0.11 % (11.6 V, 0.1 lm/W, 0.3 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>95:5</td>
<td>0.12 % (11.6 V, 0.1 lm/W, 0.4 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5</td>
<td>100</td>
<td>0.24 % (7.2 V, 0.4 lm/W, 0.9 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:CBP</td>
<td>20:80</td>
<td>0.98 % (9.8 V, 1.1 lm/W, 3.5 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16:CBP</td>
<td>40:30:30</td>
<td>0.07 % (13.2 V, 0.06 lm/W, 0.2 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16:CBP</td>
<td>20:28:52</td>
<td>0.12 % (16.8 V, 0.1 lm/W, 0.40 cd/A)</td>
</tr>
</tbody>
</table>

Table 6.10: Summary of single layer device efficiencies for electron-hole transporting dendrimer blends

in this case also. An alternative and more probable explanation is that the charge transport behaviour of Dendrimer 16 was by core-to-core hopping as found in the phenylene dendronised iridium(III) cored dendrimers [93], and was then competing against and countering the different process of charge transport through the carbazole dendrons that occurred in Dendrimer 5 as discussed in Chapter 5. Furthermore, it was recalled from Chapter 5 or repeated again in Figure 6.29 that a neat film of the Dendrimer 5 was not as efficient as the CBP host blended film due to the decreased number of intermolecular interactions that were present. By blending Dendrimer 16 with Dendrimer 5 although the balance of charge transport may be have been slightly improved, there appeared to be no reduction in the number of core-to-core interactions, and thus the efficiency did not undergo the same increase as seen when blended with a CBP host.
6.4.2 Bilayer devices from electron-hole transporting dendrimer blends

The most effective way of improving charge balance in OLEDs to give highly efficient devices has been found to be the inclusion within the device structure of extra layers that can reduce or limit the number of charges entering and/or leaving the recombination zone within the electroluminescence layer [7]. Unfortunately, due to the high solubility of dendrimers further layer deposition onto a dendrimer layer was restricted to a choice of materials that could be evaporated and thus the structure of any device was severely limited. Consequently, to investigate blended dendrimer films using a second organic layer to optimise the charge transport the bilayer structure chosen again consisted of an evaporated layer of the electron transport/hole blocking layer TPBI on top of the spin-coated dendrimer. The use of such an additional layer also gave the advantage of shifting the recombination further from the cathode thereby reducing any quenching this may cause in the single layer device so leading to a further increased device efficiency.

Figure 6.31: EQE plots for bilayer devices with emission layers of blends of Dendrimer 16, and Dendrimer 5 and a CBP host

The results of neat film bilayer devices using emissive layers of Dendrimer 16 and Dendrimer 5 were
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Figure 6.32: Plots of ratio the efficiency of bilayer devices against the ratio of hole to electron molar weight for blends of Dendrimer 16 and Dendrimer 5, and a CBP host

<table>
<thead>
<tr>
<th>Electroluminescent layer</th>
<th>Blend Ratio (%)</th>
<th>EL Efficiency at cd/m²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 16</td>
<td>100</td>
<td>1.2 % (16.6 V , 0.7 lm/W, 3.9 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 16:CBP</td>
<td>30:70</td>
<td>0.6 % (11.6 V , 0.5 lm/W, 1.9 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 16:CBP</td>
<td>20:80</td>
<td>5.4 % (10.8 V, 5.1 m/W, 17.6 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>20:80</td>
<td>2.1 % (8.4 V , 2.6 lm/W, 6.8 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>50:50</td>
<td>3.4 % (8.2 V, 4.5 lm/W, 11.8 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16</td>
<td>95:5</td>
<td>5.6 % (6.8 V, 9.3 lm/W, 19.9 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5</td>
<td>100</td>
<td>4.8 % (3.8 V, 14.4 lm/W, 17.4 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:CBP</td>
<td>20:80</td>
<td>9.5 % (4.8 V, 25.5 lm/W, 38.1 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16:CBP</td>
<td>40:30:30</td>
<td>4.6 % (6.8 V, 7.6 lm/W, 16.3 cd/A)</td>
</tr>
<tr>
<td>Dendrimer 5:Dendrimer 16:CBP</td>
<td>20:28:52</td>
<td>6.3 % (8.6 V, 9.0 lm/W, 23.0 cd/A)</td>
</tr>
</tbody>
</table>

Table 6.11: Summary of bilayer device efficiencies for electron-hole transporting dendrimer blends

shown previously and are repeated in Figure 6.31. The figure also shows a number of device results obtained on blending these two dendrimers together and with a CBP host in various different ratios. The device results detailing the efficiencies measured at a brightness of 100 cd/m² are summarised in Table 6.11. As the table shows, a neat film bilayer device of Dendrimer 16 at the standard brightness of 100 cd/m² was found to have an efficiency of 1.2 % at 16.6 V. The table also shows that if this dendrimer was then blended to form the electroluminescence layer in a bilayer device, the resultant pattern of device efficiencies was similar to that seen for single layer devices; the device efficiency increased as the content of hole transporting material (HTM) increased.

On blending with Dendrimer 16 the CBP host material was found to enhance the device efficiency more effectively when compared to a blend with Dendrimer 5. Despite this the maximum efficiency of all the blending systems was found for a 20:28:52 wt % blend of Dendrimer 5:Dendrimer 16:CBP with an EQE value of 6.6 % (255 cd/m², 7.2 V). In this system, the efficiency was proportional to the CBP content. Similarly as found for the single layer devices, the bilayer device efficiency decreased as the
content of Dendrimer 5 in blend increased. This is shown in Figure 6.32 which, similar to Figure 6.30 plots the ratio of hole (HTM) to electron transport material (ETM) for the bilayer devices.

It is noted that for simplification, in the calculation of the HTM/ETM ratio the contribution to the charge transport and recombination and thus the device efficiency from the hole blocking and electron transporting TPBI layer that was used to produce the bilayer device structure was ignored. Despite this it was still clear that as the hole content of the blend increased so did the device efficiency. Intuitively this was what might what could be expected when it was considered that all dendrimers so far considered in this thesis have, in addition to being very efficient, also been hole transporters, while further it was not clear that Dendrimer 16 itself was indeed capable of electron transport.

6.4.3 Electron-hole transporting dendrimer blends summary

This section has considered the effect on the resultant device efficiency by blending dendrimers to form the electroluminescent layer in devices. It was found that the blend ratio chosen does have a major influence on the resultant device efficiency but with careful tuning the efficiency could be optimised. In particular it was shown a large hole carrier concentration was more beneficial to device performance, but the most efficient devices were on host blending with a CBP host. However the resultant device efficiency of this blend was still somewhat short of the EQE of 10.4 % found previously for a biphenyl dendronised dendrimer-electron transporter (TPBI)-CBP host blend [123]. It was evident no evidence of electron transport was observed in the benzimidazole dendrimers.

6.5 Summary

The chapter has consisted of a study into two types of dendrimer each of which was hoped would be capable of improving the charge balance within dendrimers by improving the electron transport, the first time such an approach in dendrimers has been considered. The first type of dendrimer contained triazine groups while the second used benzimidazole groups in an attempt to provide this electron transport functionality.

For the triazine dendrimers the results showed that despite numerous synthesis problems, for the first time a number of such dendrimers could be synthesised and then made into successful light-emitting devices. Despite this there was little evidence to suggest that the triazine dendrimers were capable of, or
at least could improve, electron transport and thus improve the charge balance. In fact the results indicated that if anything it was the hole transport that was modified to the detriment of the device efficiency. The study of triazine dendrimers was thus discontinued and the alternative approach of benzimidazole dendrimers instead considered.

Once again although the benzimidazole dendrimers were capable of being used to make successful light-emitting devices, as for the triazine dendrimers no evidence of electron transport was observed. Instead the use of benzimidazole groups in the dendrimer structure gave no improvement in charge balance and was only found to give reasonable efficiencies on blending with a carbazole containing host or dendrimer.

To ascertain whether the triazine or benzimidazole units did indeed improve electron transport or mobility it would have been desirable to measure the electron mobility of the dendrimer by a method such as the time-of-flight technique. Unfortunately due primarily to the small amounts of dendrimer available, but also due to the difficulty in obtaining a suitable charge generation layer to use in combination with a spin-coated dendrimer layer such measurements were not possible.

It was therefore concluded that the dendrimers incorporating moieties intended for electron transport considered in this chapter were not successful in giving the dendrimer improved electron transport characteristics. It was not clear if this new approach of incorporating electron transport functionality into the dendrimer structure was appropriate with instead the common standard techniques of using separate electron transporting layers, as in References [176-178], being a better direction for future development. In any case the work reported within this chapter has made important first steps towards the goal of obtaining such dendrimers that can ultimately be combined with hole transporting dendrons thus giving multi-functional dendrimers capable of bipolar charge transport.
Chapter 7

Charge transport in dendrimer devices

7.1 Introduction

Current display research is focussed on the three classes of organic molecules: small molecules, polymers and dendrimers. For all these organic semiconductors for the development and understanding of such devices made from them it remains desirable to develop models that can describe the charge injection and transport behaviour within the device. Consequently many models have already been applied to small molecules and polymers to study and describe the operation of OLEDs that contain layers of such organics [57, 78, 94, 97, 179–181]. That is, the processes of charge injection, electron-hole capture and radiative recombination followed by luminous emission that occur within these devices.

This chapter considers current-voltage (I-V) characteristics of unipolar and bipolar diodes that used phosphorescent dendrimers as the organic semiconducting layer. A model was chosen that allowed the obtainment of key parameters from the I-V characteristics such as the electric field-dependent mobility and the heights of the injection barriers at each of the interfaces. With this model the measured I-V characteristics were simulated to determine the parameters for each device. To do so, a number of devices were fabricated using a range of various metal contacts.

The most efficient dendrimers developed so far were those discussed in Chapter 4, namely a fac-
tris(2-phenylpyridyl) iridium(III) [(Irppy)₃] cored dendrimer with covalently attached phenylene den-
drons and 2-ethylhexyloxy surface groups. The simplest example of this was Dendrimer 1 (Ir-G1) with chemical structure shown in Figure 7.1 Chapter 4 showed that this dendrimer could be used to make
highly efficient OLEDs both when blended with suitable hosts and as neat films. The zero-field hole mobility has been reported for this dendrimer to be $9.3 \times 10^{-7}$ cm$^2$/Vs [23], where in this reference this dendrimer was compared with other dendrimers with the same core and surface groups. Furthermore, it has been shown in this thesis that a step change in efficiency can result on blending a phosphorescent dendrimer with a carbazole containing host for the light-emitting layer in a dendrimer OLED.

A way to modify the charge transport was found in Chapter 5 by the use of dendrimers that contained dendrons which actively participated in the charge transport. The dendrimers considered consisted of an iridium(III) complex core, charge transporting carbazole dendrons, and 9,9-di-$n$-propylfluorenyl surface groups. The effect of incorporating carbazole moieties into the structure of phosphorescent dendrimers was also investigated in Reference [157], where a dendrimer with a similar structure to Dendrimer 5, (Dendrimer 7 of Scheme 1 of that paper), was shown to have a much higher hole mobility than a first-generation dendrimer with 2-ethylhexyloxy surface groups and phenylene dendrons. Molecular orbital calculations suggested that this result was due to the HOMO energy being located not only on the core but also on the dendrons. This allowed holes to hop between dendrons, whereas in the phenylene dendron case hole transport was between the cores of the dendrimers.

This chapter considered and compared the characteristics of devices that used emissive layers of dendrimers containing either non-charge transporting phenylene dendrons or charge transporting carbazole dendrons. To simplify the comparison first generation dendrimers with one level of branching in the dendrons were considered. The resulting dendrimers were therefore Dendrimer 1 and Dendrimer 5. The structures of these dendrimers are repeated in Figure 7.1 and Figure 7.2 respectively.
Another important factor determining device efficiency is the ease of carrier injection, an aspect that has not been addressed in the earlier work on dendrimers. This work is motivated by photoemission measurements of charge injection barriers in devices made with small organic molecules [182]. This has shown that a contact made under the commonly used conditions for organic devices is not ‘ultraclean’ but can contain a layer of absorbed molecules. The layer acts to reduce the surface dipole at the contact by such a large amount that the charge injection barriers can become insensitive to the underlying metal [183]. It is therefore important to use a model of the I-V characteristics that allowed the injection barrier height to be fitted independently of the charge mobility, and to look at devices where the dendrimer layers were sandwiched between a range of electrode materials.

For this work a drift-diffusion model was chosen that has been previously used previously to describe the charge injection and transport behaviour within a device structure [181]. For the work presented in this chapter the model was updated to include a more recent formulation for charge injection that was valid for organic materials [184]. The model used required a large number of simulation parameters such; as the band edge density of states, the carrier mobility, and the field dependence of mobility, the barrier height for the thermionic emission. Therefore to simplify the modelling process the number of fitting parameters required for the model was reduced. That is, parameters were kept constant by using values obtained from experiment wherever possible. One method of doing so was to consider devices where only kind of charge carrier was present. More precisely, through careful electrode choice, one carrier was preferentially injected while the other carrier was prevented from doing so. This was due to the large size of the energy level barrier that must be surmounted for it to enter the organic layer. In this way either hole-only, or electron-only, devices could be fabricated. With the knowledge gained from the more simpler single carrier case the bipolar structure of a standard device could be more easily modeled. Albeit even then, the disperse nature of the electron transport in these systems meant the electrons did not have a well defined mobility. Hence the use of the bipolar drift diffusion model still could not quite fully describe the behaviour within the OLED. Nonetheless, the process did allow the determination of electron barrier heights through fitting to an expression for the tunneling current at high bias [185].

It is acknowledged that all the modelling work presented in this Chapter was undertaken by Jonathan Williams at the University of Bath, thanks are extended to him, and his supervisor Dr Alison Walker, for their contribution and considerable help and fruitful discussion that have enabled this chapter to occur.
CHAPTER 7: CHARGE TRANSPORT IN DENDRIMER DEVICES

7.1.1 Device fabrication

As discussed in Section 2.5.3 the choice of OLED electrode configuration will have a considerable effect on the resultant performance of the device. In this chapter the choice of anode and cathode material was deliberately varied so as to change the injection (and extraction) barrier of charges into the OLED. In each case a basic sandwich structure of an injecting bottom contact, spin-coated electroluminescent layer, and a top metal contact was used. In this chapter to avoid confusion the term anode is used solely to refer to the bottom contact, and cathode for the top contact, whatever the polarity of the applied bias. For the electroluminescent layer, films of either Dendrimer 1 or Dendrimer 5 were spin-coated from a chloroform solution at a concentration of 20 mg/ml to yield films approximately 100 nm thick onto the desired substrate. The substrates were then used to construct devices of various geometries.

For the anode contact initially transparent indium tin oxide (ITO) was used, before varying this to gold (Au) or platinum (Pt). The cathode materials were aluminium (Al), Au and Pt. To investigate the effect of enhanced electron injection into the organic layer, devices with a calcium (Ca) anode, and a Ca cathode capped with Al to avoid oxidation of this layer, were also made. When used, prior to the spin-coating of the dendrimer, the gold anode was cleaned by the method of Scott et al. [186], that is by washing in the spinning solution, or by a short oxygen plasma ash. No difference was observed in the device characteristics on the use of either of these methods. A table of the literature values of work functions of these materials, and the energy levels of the dendrimers considered in this chapter, is given in Table 7.1.

All metal electrodes were deposited by evaporation techniques. Consequently this meant that after the evaporation of a metal anode layer the device was removed from the evaporator in order to spin-coat the dendrimer layer. On returning the device to the evaporator the cathode layer was then deposited. The device characterisation was performed at room temperature in air, and in the dark. The fact that it was not possible to keep the device in vacuum throughout the entire fabrication and testing process meant that impurities would have been likely to have been taken up by the device, which may have adverse effect on the device properties performance. This point is discussed further in the subsequent sections of this chapter.
Table 7.1: Energy levels for the dendrimers, and literature values of the work functions, that were used within this chapter

7.1.2 Model

In earlier modelling studies undertaken within the group [93], the model of Davids et al. [94] was used to describe the behaviour of Dendrimer 1, however the inorganic formalism of this model was not best suited when applied to organic semiconductors due to their inherent disordered structure. Consequently, the model utilised here was one where the molecular nature of the chromophores within the macromolecular structure of the organic semiconductor was explicitly included for charge injection [184]. It was assumed that the surface recombination of charge carriers with their image charges was analogous to Langevin bimolecular recombination [95]. The model was then that first proposed by Scott et al. [95], and also more recently used by Barker et al. [96]. The simulation of injection, transport and recombination of charges with an electric field-dependent carrier mobility are given by the Poole-Frenkel equation,

\[ \mu = \mu_0 \exp \left( \gamma \sqrt{E} \right) \]  

(7.1)

where \( \mu_0 \) is the zero-field mobility, E is the electric field strength, and \( \gamma \) is a constant determining the field dependence of the mobility.

For the simulation of the I-V characteristics of the device structures considered, the process involved changing the magnitude of the current to match the experimental results. This was achieved by varying the barrier to hole injection from the dendrimer HOMO into the anode electrode. It was found that the variation of the value of the injection barrier height and the zero-field mobility did not affect the gradient of the current, only its magnitude. An increase in the injection barrier height by 0.1 eV was
found to have a similar effect on the current magnitude as decreasing the hole mobility by a factor of 10 \[^{[185]}\]. In this case, as the zero-field mobility was known for both dendrimers this parameter could be fixed. The simulation process was reduced to fitting the experimental data using the methodology used in Reference \[^{[97]}\] for the magnitude of the current by varying the barrier height to hole injection into the devices, \(\phi_{Bp}\). The method allowed the test of whether the injection barrier height could be deduced from the values of the dendrimer HOMO and LUMO levels and the vacuum measured metal work functions from the literature, as given in Table \[^{7.1}\].

The experimental values of \(\mu_0\) and \(\gamma\) have been published previously for Dendrimer \(^1\) as \(9.3 \times 10^{-11} \text{m}^2/\text{Vs}\) and \(3.4 \times 10^{-4} \text{m}^{1/2}/\text{V}^{1/2}\) \[^{[97]}\]. For Dendrimer \(^5\), as found in Chapter \[^5\] mobility measurements gave values of \(1.2 \times 10^{-9} \text{m}^2/\text{Vs}\) and \(3.0 \times 10^{-4} \text{m}^{1/2}/\text{V}^{1/2}\) respectively for these parameters.

To enable fitting of I-V characteristics with different gradients the method of including a series resistance, \(R_I\), in the circuits \[^{[98]}\] was used. In essence this meant that, starting from the literature values given in Table \[^{7.1}\], the values of the injection barrier were varied to give the correct order of magnitude for the current through the device, if a suitable fit was obtained then \(R_I = 0\). If however a suitable fit was not possible; a finite resistance in series with the organic layer was assumed to be present. From Ohm’s law, the potential difference across the resistance can be obtained for the given current, and with the bias across the dendrimer layer known, from the original data the current can be evaluated. In this way, \(R_I\) and the injection barrier height at the anode became the only fitting parameters. This is expressed mathematically as,

\[
V_{Dendrimer} = V_{System} - IR_I,
\]

where \(V_{Dendrimer}\) and \(V_{System}\) were the potential differences across the dendrimer and the entire system respectively, and \(I\) was the current through the device. Fits of the I-V characteristics were thus actually plotted as \(V_{System} = (V_{Dendrimer} + IR_I)\) against the current \((I)\). Albeit in the actual numerical simulation, there was no resistance present, and so the results obtained from the numerical model are \(V_{Dendrimer}\) and the current \[^{[185]}\].

For the other parameters used in the model experimental data was used where available. In particular, the thickness of the dendrimer layers were measured as 100 nm, and with all measurements performed at room temperature it was assumed for the modelling a temperature of 300 K. In the absence of mea-
surements of the dielectric permittivity, a value of 3.0, typical for organic semiconductors, was assumed. The conduction and valence band densities of states each were assumed to be $10^{27}$ m$^{-3}$, as used in Reference [96].

### 7.2 Dendrimer 1 hole carrier modelling results

The device structures and key parameters for all the hole-only devices considered in this section that used Dendrimer 1 as the organic layer are summarised in Table 7.2. A comparison between experimental and simulated results of the current-voltage (I-V) characteristics for a number of the device structures (those with an * in Table 7.2) is shown in Figure 7.3. While all the devices in the table were simulated, only a sample of the data was chosen to be displayed in the figure such that only one I-V characteristic for each injecting electrode material was shown [185].

To produce a barrier height for hole injection at the anode, given by $\phi_{Bp}$ in the table, this parameter was varied until the I-V characteristics showed the optimum agreement, judged by eye. In the table $R_I$ is the series resistance. For the electrode of ITO-Au, the ITO coating was maintained on the substrate prior to the deposition of the Au anode. In the Schottky-Mott model estimates for the hole injection barrier $\phi_{Bp}^{(SM)}$ for the anode assume the workfunction of Au. The LUMO and HOMO energy levels of Dendrimer 1 were as given in Table 7.1 [26].

### 7.2.1 Dendrimer 1 devices with an ITO anode

In the first instance, the simple device structure of an ITO anode and an aluminium cathode was considered for an organic layer of Dendrimer 1. The resulting structure of this device was ITO/Dendrimer 1/Al and is denoted as Device A in Table 7.2. The Schottky-Mott theory would predict that, for an Al cathode, with workfunction of 4.1 eV, there would be a large barrier to electron injection, as the dendrimer has a LUMO energy of 2.5 eV. In contrast the ITO anode, with work function 4.9 eV, would have a much easier charge injection (of holes) into the dendrimer HOMO located at 5.6 eV. While the work function of ITO starts around 4.9 eV, after standard surface treatments [53] values as high as 5.1 eV have been reported [54]. The hole injection from the ITO anode can be improved with such treatments. Consequently this device was assumed to be a hole-only device.

To begin the fitting of this device, as detailed in Table 7.2, a value for the hole injection barrier at the
Table 7.2: For the measured device structures shown, the hole injection barrier heights obtained from simulation $\phi_{Bp}$ are compared with values deduced from the Schottky-Mott model, $\phi_{Bp}^{(SM)} = E_{HOMO} - \phi_m$ where $\phi_m$ is the metal workfunction and $E_{HOMO}$ the HOMO level. To find $\phi_{Bp}^{(SM)}$, $E_{HOMO}$ was assumed to be 5.6 eV below the vacuum, the workfunctions of treated ITO, clean Au, clean Pt, and Al are assumed to be as given in Table 7.1. The fitted value of the series resistance $R_I$ is also shown. The injecting contact is underlined. I-V curves for the asterisked devices are plotted in Figure 7.3 \[185\].

<table>
<thead>
<tr>
<th>Device</th>
<th>Structure</th>
<th>Bias</th>
<th>$\phi_{Bp}$ (eV)</th>
<th>$\phi_{Bp}^{(SM)}$ (eV)</th>
<th>$R_I$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ITO/Dendrimer 1/Al*</td>
<td>Forward</td>
<td>0.40</td>
<td>0.5-0.7</td>
<td>$1.2 \times 10^4$</td>
</tr>
<tr>
<td>B</td>
<td>ITO/Dendrimer 1/Au</td>
<td>Forward</td>
<td>0.48</td>
<td>0.5-0.7</td>
<td>$7 \times 10^4$</td>
</tr>
<tr>
<td>C</td>
<td>ITO/Dendrimer 1/Pt</td>
<td>Forward</td>
<td>0.74</td>
<td>0.5-0.7</td>
<td>$7 \times 10^4$</td>
</tr>
<tr>
<td>D</td>
<td>Au/Dendrimer 1/Al*</td>
<td>Forward</td>
<td>0.69</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>E</td>
<td>Au/Dendrimer 1/Au</td>
<td>Forward</td>
<td>0.64</td>
<td>0.5</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td>F</td>
<td>Au/Dendrimer 1/Au</td>
<td>Forward</td>
<td>0.50</td>
<td>0.5</td>
<td>$4 \times 10^8$</td>
</tr>
<tr>
<td>G</td>
<td>Au/Dendrimer 1/Pt</td>
<td>Forward</td>
<td>0.70</td>
<td>0.5</td>
<td>$5 \times 10^8$</td>
</tr>
<tr>
<td>H</td>
<td>Au/Dendrimer 1/Au</td>
<td>Reverse</td>
<td>0.57</td>
<td>0.5</td>
<td>$1.1 \times 10^8$</td>
</tr>
<tr>
<td>I</td>
<td>Au/Dendrimer 1/AI*</td>
<td>Reverse</td>
<td>0.64</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>J</td>
<td>ITO-Au/Dendrimer 1/Au*</td>
<td>Forward</td>
<td>0.76</td>
<td>0.5 (Au)</td>
<td>0</td>
</tr>
<tr>
<td>K</td>
<td>ITO-Au/Dendrimer 1/Al</td>
<td>Reverse</td>
<td>0.55</td>
<td>1.5</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td>L</td>
<td>Pt/Dendrimer 1/Au*</td>
<td>Forward</td>
<td>0.61</td>
<td>-0.75</td>
<td>0</td>
</tr>
<tr>
<td>M</td>
<td>Pt/Dendrimer 1/Au</td>
<td>Reverse</td>
<td>0.65</td>
<td>0.5</td>
<td>$2 \times 10^8$</td>
</tr>
<tr>
<td>N</td>
<td>Au/Dendrimer 1/Pt</td>
<td>Reverse</td>
<td>0.67</td>
<td>-0.75</td>
<td>$7 \times 10^8$</td>
</tr>
</tbody>
</table>

anode ($\phi_{Bp}^{(SM)}$) was set initially at 0.5-0.7 eV as would be assumed purely from the Schottky-Mott model. In actual fact to fit this curve successfully, as revealed in the table, a barrier ($\phi_{Bp}$) of 0.4 eV was required, indicating an ITO work function of 5.2 eV. A value that lies just outside the range predicted by theory, but given that the ITO anode of Device A did undergo surface treatment prior to the deposition of the dendrimer layer, it is not unlikely that such a value of work function could have been obtained. As plotted in Figure 7.3, a large current was observed in Device A, despite this no light emission was observed confirming the hole-only nature of its structure. This indicated there was insufficient electron injection from the Al cathode to allow charge recombination to occur that would lead to light emission \[185\].

To confirm this, Device B of configuration ITO/Dendrimer 1/Au was studied. The change from a cathode of Al in Device A to a cathode of Au in Device B would, from Schottky-Mott theory, lead to increase in the cathode work function by around 1 eV. The current-density against applied electric field (J-E) plot for this device structure is shown in Figure 7.4 in comparison to that of the equivalent plots of the other devices that used an ITO anode (Devices A and C). The J-E plot has been used to account for
Figure 7.3: I-V characteristics for Dendrimer 1 with different electrode materials, Device A (+), Device D (○), Device I (□), Device J (○), and Device L (△). Symbols are experimental data, solid lines are modelling data [185]

As Figure 7.4 shows, the change from an Al to an Au cathode gave a reduction in the current density by a factor of around 10. To fit this device behaviour the fit of the hole barrier height was required to be increased by 0.08 eV from 0.40 eV to 0.48 eV. The result implied that the cathode electrode, which would be non-injecting, had a significant effect on the device performance.

Absorption of atmospheric contaminants by the Au cathode during or after deposition would be expected to have modified the Dendrimer 1/Au interface. Such effects would reduce the Au work function from its literature value of 5.1 eV [183, 189], and create a thin barrier layer for hole extraction. Further support of this hypothesis was provided by an increase in the series resistance. The large reduction in current found on changing the cathode indicated clearly that both Devices A and B were hole-only. The device characteristics could not be completely explained by a lower electron current from the increased barrier to electrons at the cathode, as to give such a large decrease would mean that almost 90% of the current through Device A would have to been an electron current, an unrealistic and unphysical possibility. Consequently, the model used, only considered that a hole current was present in the device [185].

Further evidence of this was provided in Device C. In this device, the same ITO/Dendrimer 1 configuration was used, but now with a Pt cathode. In this way the work function of the cathode was increased over that of Au, and consequently the current through the device, as shown in Figure 7.4, was much less
than in either Device A or B. To fit this device a higher hole injection barrier height of 0.74 eV was required.

By fitting to the characteristics of the devices with a series resistance \( R_I \), the gradient of the I-V curve could be adjusted, as the barrier height scales the current by approximately the same amount at all biases. Since the device areas were all similar at \( \sim 10^{-2} \) cm\(^2\), the values found for \( R_I \) for the ITO anodes were comparable to the previous result of \( \sim 10^4 \) \( \Omega \) cm\(^{-2}\) obtained for conjugated polymers in Reference [98]. Since the barrier heights for hole injection were considerably less with an Al anode than with an Au anode, which in turn was less than that with a Pt anode, the current in the devices became progressively lower. There was a larger voltage dropped across \( R_I \), and therefore the value for \( R_I \), shown in Table 7.2 became increasing larger [185].

### 7.2.2 Dendrimer 1 devices with an Au anode

Having detailed the case of the devices with an ITO anode, this section considered those devices with an Au anode. In this case a number of devices were fabricated using an evaporated layer of Au on a glass substrate as the anode, onto this the Dendrimer 1 layer was then spin-coated. The samples were returned to the evaporator where the cathode layer was deposited, with as detailed in Table 7.2 a number of various configurations considered. Both forward and reverse bias cases were investigated for a number of the devices. The J-E characteristics for the forward biased Devices D, E, F and G are plotted in Figure 7.5.

The change from an ITO anode to an Au anode, would be expected from Schottky-Mott theory
to reduce the barrier height for hole injection at the anode, and thus increase the current through the device. In fact, the current through the devices with an Au anode was less than that of the device with the same cathode but with an ITO anode. For example, consider Figure 7.3, the plot shows the current in Device A with structure ITO/Dendrimer I/Al was much greater than that of Device D with structure Au/Dendrimer I/Al.

This result, unexpected from the Schottky-Mott theory, indicated that the interface between Au and Dendrimer I was of poorer quality than that of an oxygen plasma ashed ITO anode. Furthermore, this result implied that to explain the characteristics of devices, it was not sufficient just to take the injection barrier at the interface as being equal to the difference between the literature value of the work function of the anode and the dendrimer HOMO energy. An assumption that is often made, for example in the modelling studies of Crone et al. [190].

For an Au anode, taking the barrier height as the difference between the Au work function and Dendrimer I HOMO, would give a value of 0.5 eV. However in Device D, with structure ITO/Dendrimer I/Al, a hole injection barrier of 0.69 eV was found to be needed to fit the characteristics successfully. On changing to an Au cathode, in Device E, the barrier height needed for fitting was 0.64 eV. In Device F, in a double Au sandwich structure, the barrier height was equal to the literature value of 0.50 eV, but with a cathode of Pt the barrier to hole injection at the anode was 0.70 eV in Device G. In all cases the hole injection barrier values were different, and in all cases greater than that of the devices with an ITO anode, despite the higher literature work function of ITO [185]. In previous reports the anomalous behaviour of polymer-gold interfaces has been explained by the presence of interface dipoles [182, 189, 191]. These dipoles were caused by the repulsion between the electrons of the organic and the metal layer. This gave a suppression of the metal electron density tail which acted to lower the metal work function and hence increase $\phi_B$, as has been found for the devices reported here.

Of the four devices with an Au anode tested in forward bias, as detailed in Table 7.2, only Device D gave a series resistance of 0 $\Omega$. Notably the reverse bias case of this device (Device I) also gave no series resistance. In all other cases a large series resistance was required to give suitable fits to the experimental data. The fact that no series resistance was required with an Al cathode, but such a large series resistance was needed for the Au or Pt anode devices suggested, that the use of this second evaporated layer further acted to deteriorate the device performance.


**7.2.3 Dendrimer 1 devices with an ITO-Au anode**

For Devices J and K the anode was formed from an ITO layer that was subsequently coated with Au. Device J had a cathode of Au and was tested in forward bias. The resulting J-E characteristic for Device J is plotted in Figure 7.6. Device K had a cathode of Al and was tested in reverse bias.

To fit the characteristics of Device J a $\phi_{Bp}$ of 0.76 eV was required, the largest barrier height found for any device with Dendrimer 1 as the organic layer. For this device no series resistance was required for the fit. In contrast the reverse biased Device K required a very large series resistance in order to give a good fit [185]. It was proposed that in these devices the Au layer hindered the device performance, while the ITO underlayer gave no help in increasing the current, with in fact the current in Device J being, as shown in Figure 7.3 the least through any of the device structures.

**7.2.4 Dendrimer 1 devices with a Pt anode**

In the final set of Dendrimer 1 hole-only devices the use of a Pt anode was considered. In Devices L and M this was combined with a cathode of Au, with Device L tested in forward bias and Device M in reverse bias. In Device M the structure was reversed, the anode was Au and the cathode was Pt, but as this device was tested in reverse bias, theoretically it should behave the same as Device L.

In this case the current through Device L was greater than that of Device J with an ITO-Au anode, but was less than that of Device B that used the same Au cathode but had an anode of ITO. The result of Device J was particularly intriguing because the work function of the Pt anode is greater than the dendrimer HOMO energy level. Theoretically this should mean there was no barrier to hole injection.
To account for this in the model, extraction at the Au contact was instead considered. The fact that the barrier values obtained for the three devices with a Pt anode were all similar suggested this fitting approach was appropriate. Furthermore, when Pt was used as the cathode contact in Devices C, G and N again similar barrier heights were found, but in these cases a large series resistance was required to fit the characteristics. Incorporating a series resistance into the circuit was found only to improve the fit at high values of the applied bias where the current was greatest, and therefore a larger fraction of the applied potential was dropped across the resistive layer. The fact that no series resistance was needed to fit Device L implied the possibility of an extraction barrier at the Pt contact. This was in addition to an injection barrier; a Schottky barrier was needed for injection, and a significant series resistance needed for when Pt formed the non-injecting cathode [185].

7.3 Dendrimer 5 hole carrier modelling results

The previous section established the effectiveness of the model in describing a series of devices that used an organic layer of Dendrimer 1. To further explore the applicability of the method to other dendrimers, in this section the model was applied to Dendrimer 5. This dendrimer, as described in Chapter 5, is known from the nature of its carbazole dendrons to possess greater hole-mobility than that of Dendrimer 1. To study the effect that this may have on the resulting device characteristics a number of devices using Dendrimer 5 as the organic layer sandwiched between two electrodes were considered. The resulting devices are summarised in Table 7.3. As for Dendrimer 1, while all the device results were simulated successfully, only those with an * in Table 7.3 have been plotted in the comparison I-V plot of the experimental and modeled characteristics [185]. This plot is shown in Figure 7.8, where the parameters are as defined previously.

7.3.1 Dendrimer 5 devices with an ITO anode

Dendrimer 5 was first considered in a device structure with an ITO anode. In Device O, the cathode was Al, and for Devices P and Q the cathode was Au. Devices O and P were tested in forward bias, and Device Q in reverse bias.

For these ITO anode devices, again as for the Dendrimer 1 devices, it was found that the change in cathode contact, despite having no role in the hole injection from the anode, gave large variations in


<table>
<thead>
<tr>
<th>Device</th>
<th>Structure</th>
<th>Bias</th>
<th>$\phi_B \ (eV)$</th>
<th>$\phi_B^{(SM)} \ (eV)$</th>
<th>$R_I \ (\Omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>ITO/Dendrimer 5/Al</td>
<td>Forward</td>
<td>0.68</td>
<td>0.5-0.7</td>
<td>$1 \times 10^9$</td>
</tr>
<tr>
<td>P</td>
<td>ITO/Dendrimer 5/Au*</td>
<td>Forward</td>
<td>0.54</td>
<td>0.5-0.7</td>
<td>$7 \times 10^9$</td>
</tr>
<tr>
<td>Q</td>
<td>ITO/Dendrimer 5/Au</td>
<td>Reverse</td>
<td>0.55</td>
<td>0.5</td>
<td>$4 \times 10^6$</td>
</tr>
<tr>
<td>R</td>
<td>Au/Dendrimer 5/Al*</td>
<td>Forward</td>
<td>0.71</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>S</td>
<td>Au/Dendrimer 5/Al</td>
<td>Forward</td>
<td>0.60</td>
<td>0.5</td>
<td>$3 \times 10^6$</td>
</tr>
<tr>
<td>T</td>
<td>Au/Dendrimer 5/Au</td>
<td>Forward</td>
<td>0.80</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>U</td>
<td>Au/Dendrimer 5/Au</td>
<td>Forward</td>
<td>0.82</td>
<td>0.5</td>
<td>$1 \times 10^8$</td>
</tr>
<tr>
<td>V</td>
<td>Au/Dendrimer 5/Au</td>
<td>Reverse</td>
<td>0.80</td>
<td>0.5</td>
<td>0</td>
</tr>
<tr>
<td>W</td>
<td>Au/Dendrimer 5/Al</td>
<td>Reverse</td>
<td>0.72</td>
<td>1.5</td>
<td>0</td>
</tr>
<tr>
<td>X</td>
<td>ITO-Au/Dendrimer 5/Al*</td>
<td>Forward</td>
<td>0.48</td>
<td>0.5 (Au)</td>
<td>$4 \times 10^4$</td>
</tr>
<tr>
<td>Y</td>
<td>ITO-Au/Dendrimer 5/Al*</td>
<td>Reverse</td>
<td>0.56</td>
<td>1.5</td>
<td>$6 \times 10^4$</td>
</tr>
</tbody>
</table>

Table 7.3: Parameter values are as in Table 7.3 but now here shown for Dendrimer 5 devices. The HOMO level of Dendrimer 5 was assumed to be 5.7 eV below the vacuum. The injecting contact is underlined. I-V curves for the asterisked devices are plotted in Figure 7.8 [185].

...current through the device. Consequently the fitted barrier heights and series resistances widely varied, with the barrier heights again different from those expected from the literature values [185]. The result again implied, as found for Dendrimer 1, that it was not enough just to assume the literature values of the work functions when describing the behaviour of organic devices.

### 7.3.2 Dendrimer 5 devices with an Au anode

Table 7.3 also details devices fabricated for Dendrimer 5 with an Au anode. In this instance six devices were made using either Al or Au as the cathode layer. The devices were tested in both forward and reverse bias. The J-E characteristics of the forward biased devices (Devices R, S, T and U) are plotted in Figure 7.10.

Considering the results it was noted that, as found for Dendrimer 1, the hole currents in these hole-only devices with Au anodes were much less than when an ITO anode was used, despite the increase in work function this change in anode might be expected to give. Consequently the barrier heights were larger for Au anode devices. Additionally, in Devices V, T and U with an anode and a cathode of Au, the fitted barrier height was increased relative to the barrier height when there was only one injecting Au electrode in Device S. The results of this section gave further evidence for a possible barrier for charge extraction at the dendrimer/Au interface, and were consistent with the results noted previously...
CHAPTER 7: CHARGE TRANSPORT IN DENDRIMER DEVICES

Figure 7.8: I-V characteristics for Dendrimer 5 with different electrode materials, Device P (○), Device R (□), Device X (○), and Device Y (△). The symbols are the experimental data, the solid lines are the modelling data [185] for Dendrimer 1 with a non-injecting cathode of the high work function metal Pt.

The current through the Au/Dendrimer 5/Al device (Device R) was greater than that through the Au/Dendrimer 1/Al device (Device G) where $R_I = 0$. The increase in current occurred despite the larger barrier height to hole injection in Dendrimer 5: 0.69 eV in Device G, and 0.71 eV in Device R [185]. The increased current despite the larger barrier to hole injection gave evidence for the increased hole mobility of Dendrimer 5 over that of Dendrimer 1. The change in hole mobility arising due to the different charge transport behaviour in the two dendrimers, namely core-to-core hopping in Dendrimer 1 [93], and charge transport via the carbazole dendrons in Dendrimer 5 as found in Chapter 5.

7.3.3 Dendrimer 5 devices with an ITO-Au anode

In Devices X and Y the use of ITO-Au as the anode was investigated. For both these devices the cathode used was Al, with Device X tested in forward bias and Device Y in reverse bias. The J-E curve of Device X is shown in Figure 7.11 and the current through this device is also shown in the comparison plot of Figure 7.8. As both plots reveal, the current through this device was larger than has been observed in any of the other Dendrimer 5 devices.

For Device X, the injection barrier was found to be 0.48 eV and $R_I = 4 \times 10^4 \, \Omega$. The value of this barrier height was thus unexpectedly low in comparison to the barrier height of 0.76 eV found in
Figure 7.9: J-E plot for Dendrimer 5 hole-only devices with an ITO anode (Devices O and P)

Figure 7.10: J-E plot for Dendrimer 5 hole-only devices with an Au anode (Devices R, S, T and U)

Figure 7.11: J-E plot for a Dendrimer 1 hole-only device with an ITO-Au anode (Device X)

Device J for Dendrimer 1 that used the same anode. The HOMO of Dendrimer 5 was located at 5.7 eV and thus was 0.1 eV lower than the HOMO of Dendrimer 1. For the Dendrimer 1 device with an ITO-Au anode, the cathode was Au, whereas for the Dendrimer 5 device with the same anode, the cathode was Al. It was shown that for the Dendrimer 1 device that the use of Au for the cathode could diminish the current obtained; this result for Dendrimer 5 gave further evidence of this effect. A barrier to electron extraction has been observed before, where in fact it was found to be beneficial to device performance. This was explained as arising due to a build up of electrons at the barrier which acted to increase the electric field strength. In this way the barrier to hole injection was increased [192, 193].

7.4 Bipolar carrier modelling results

The previous two sections have shown the model could be successfully applied to dendrimers within a single carrier device structure. While this was an important advancement in device knowledge and
understanding, real devices to be capable of light emission must have two charge carriers. In this section, the applicability of the model to bipolar device characteristics was considered. However, to allow this to occur with suitably accuracy, the characteristics of electron-only devices must first be obtained in order to provide information on the electron charge carrier transport and injection in the device structure.

### 7.4.1 Electron-only devices

Electron-only devices were fabricated using a sandwich structure of the dendrimer layer between two Ca electrodes. Devices with dendrimer layers of both Dendrimer 1 and Dendrimer 5 were considered. Ca has a vacuum work function of 2.9 eV, which is close to the LUMO energy of 2.5 eV for both dendrimers, and was therefore could be expected to provide efficient electron injection into either dendrimer layer. To prevent oxidation of the device, the cathode side was capped with Al, with all fabrication and testing performed in a N2 glovebox. On testing, due to significant noise in the experimental currents, the applied biases used in these devices were run up to 50 V, compared with 15 V for the hole-only devices considered previously. The large values of the applied bias in the electron-only device structures meant that it was likely that tunneling was the dominant component of the current [194]. A characteristic electron-only device I-V curve for both dendrimers is shown in Figure 7.12. As the figure reveals, for both devices, there was a change in the gradient of the I-V characteristic at high bias. Such a change denotes the onset of tunneling controlling the device behaviour.

In the modelling of the hole-only devices considered previously, no tunneling component in the injected current was included. In the electron-only devices, as tunneling was present the same model could not be used, instead the Fowler-Nordheim formalisation, introduced in Section 2.5.2.1 was considered.
Figure 7.13: Fowler-Nordheim graphs for electron-only devices with Ca-Al injecting anodes for Dendrimer 1 (○) and Dendrimer 5 (□). The solid lines indicate the region at high electric field where Equation 7.3 is assumed to be valid [185].

From the Fowler-Nordheim plot the height of the injection barrier can be determined [195]. The gradient of this plot, $\kappa$, then gives the injection barrier height from

$$\kappa = \frac{8\pi (2m^*)^{1/2} \phi_{Bp}^{3/2}}{3he},$$  \hspace{1cm} (7.3)

where $m^*$ is the electron effective mass (the free electron mass was used for this), $\phi_{Bp}$ is the height of the barrier and $h$ is Planck’s constant.

The Fowler-Nordheim plots for the electron-only devices considered here are shown in Figure 7.13. From the figure, barrier heights to electron injection can be determined as 0.6 eV and 0.3 eV for Dendrimers 1 and 5 respectively. The difference in barrier heights cannot be explained by Schottky-Mott theory since the two dendrimers have a common LUMO level, and so should have a common electron injection barrier height. Once again the applicability of simply assuming the validity of the literature work functions to describe the behaviour of real devices is questioned. Also noted was that the Dendrimer 1 device showed a less linear relationship than for the Dendrimer 5 device. This result suggested that for Dendrimer 1, tunneling injection was not the dominant component, and there was a finite thermionic emission component to the injection current.
CHAPTER 7: CHARGE TRANSPORT IN DENDRIMER DEVICES

7.4.2 Bipolar device results

Having obtained parameters for the electron barrier height these could be combined with the hole barrier heights obtained previously in a model to describe the behaviour of bipolar OLEDs. In the bipolar model the same value of $\gamma$ was assumed for electrons and holes. In the absence of experimental data, the assumption was made that the zero-field electron mobility $\mu_0 = 10^{-2} \mu_0$, as in References [179, 196, 197].

A bipolar I-V characteristic for a device of ITO/Dendrimer 5/Ca-Al is shown in Figure 7.14. The figure plots both the experimentally obtained characteristic and the modeled fit to this data [185]. While the fitted current was of the correct order of magnitude, the gradient of the curve was too low. In this device the current was dominated by electrons, which indicated a better fit could be obtained by increasing the mobility field dependence parameter, $\gamma_n$ from its current value of being equal to the experimentally obtained value for $\gamma_p$, as used in the hole-only device simulations. It was not found possible to fit the data for the Dendrimer 1 bipolar device with the model, as the current was roughly a factor of about 100 too low. As a result the electron injection barrier height obtained from the Fowler-Nordheim plot was too large.

Figure 7.15 plots for the bipolar device structure of ITO/dendrimer/Ca-Al, the experimental current and external quantum efficiency (EQE) obtained for both Dendrimer 1 and 5. The device for Dendrimer 5
was the same as discussed above and plotted in Figure 7.14. As the figure shows the current in both bipolar devices was greater than that measured in any of the single carrier devices. The implication of this result was, in the bipolar device, there were a significant number of injected electrons present. Both bipolar devices used the same structure only differing in the choice of the organic emissive layer. From Table 7.1 the two dendrimers are shown to have the same LUMO energy, and only differ in HOMO energy by 0.1 eV. It is also known, from Chapter 5, that the hole mobility of Dendrimer 5 was greater than that of Dendrimer 1, and that in Dendrimer 1 charge transport was via core-to-core hopping, whereas in Dendrimer 5 it was via the charge transporting carbazole dendrons. Nonetheless, as Figure 7.14 shows, the current in the bipolar Dendrimer 1 device was approximately one order of magnitude greater than that of the Dendrimer 5 bipolar device, despite the lower hole mobility of this dendrimer. In OLEDs, high efficiency requires balanced injection and transport [194]. Consequently at a standard brightness of 100 cd/m², the Dendrimer 1 device gave an external quantum efficiency of 0.21 % (at 6.0 V), whereas at the same brightness, Dendrimer 5 was less efficient, with an efficiency of 0.14 % (at 8.8 V). Assuming there were similar barriers to electron injection in each device, the difference in the current through the devices was attributed to an increased hole barrier at the ITO anode-Dendrimer 5 interface. Whilst the charge transporting carbazole dendrons produce a higher hole mobility for Dendrimer 5, it might also be expected that the electron mobility will be lower in this dendrimer due to the larger dendrons, and the fact that hole transport was via these dendrons. If so, then the low current of the bipolar Dendrimer 5 device could be more easily understood. The importance of good charge balance and transport for high OLEDs has been demonstrated before. More specifically, device efficiencies of 16 % have been achieved with Dendrimer 1, when a host blended solution, and an additional electron transport/hole blocking layer were used within the device structure [26].

7.4.3 Space charge effects

In this section it was considered whether space charge effects have any influence on the device behaviour. A plot of the simulated electron and hole density against the distance from anode in the ITO/Dendrimer 5/Ca-Al device is shown in Figure 7.16 [185]. The device used was that considered previously at an applied bias of 12 V.

The plot showed that in this device the electron density was greater than the hole density. This arose because the low electron injection barrier height in this device meant the current was dominated by the
Figure 7.15: Bipolar device characteristics for Dendrimers 1 and 5 in a device structure of ITO/dendrimer/Ca-Al, (a) I-V characteristics, and (b) EQE against voltage characteristics

electrons. A peak in the electron density curve was observed at the the left hand side figure, that is at the anode. This occurred despite there being no barrier for extraction as considered in Reference [192] at this anode electrode. This arose because the extraction rate for charge carriers in the simulation was proportional to the carrier mobility [184]. Since the assumption was made in the simulation that the electron mobility was only 1% of that of the hole mobility, the electrons had a tendency to accumulate at the anode contact. Figure [7.16] also showed that carrier density of the hole carriers was around four orders of magnitude less than that of the electron density [185]. The hole carriers therefore had a minimal contribution to the resultant electric field profile of the device. The simulation predicted a decrease in the hole density at the cathode side of the device. This was accounted for by the larger value of the hole mobility within the dendrimer.

The resultant electric field profile of the device is shown in Figure [7.17] [185]. From the figure it was observed the electric field had a negative gradient across the device. Evidently the electron density had a major influence on the electric field within the device. In the absence of any space charge effects, the electric field would be equal to 100 MVm\(^{-1}\) uniformly across the device. However, as shown in Figure [7.17] the increased electron density at the anode had minimal effect on the field and thus the electron current.
CHAPTER 7: CHARGE TRANSPORT IN DENDRIMER DEVICES

7.4.4 Modelling without a series resistance

Given the insensitivity of the hole barrier height to the change in the electrode material found for both dendrimers, the barrier heights for all the measured I-V characteristics were recalculated without a series resistance to cut down on the number of adjustable parameters in the model. Although some of the fits became worse, it enabled a more broad overview of the variation with electrode material to be obtained. The values of injecting electrode work functions were found to lie in the range \((5 \pm 0.1)\) eV, with only three values, namely 4.8, 5.25, 5.3 eV, outside this range [185].

In Reference [183], Grobosch et al. considered a similar experimental result for the hole injection barrier at the interface between the oligomer \(\alpha\)-sexithiophene (6T) and the metals Ag, Pd, Au and Pt. For these materials the vacuum work functions varied by more than 1 eV, but their work showed that the resultant injection barrier varied by no more than \(\sim 0.2\) eV. Similarly to the devices reported here, the devices considered in Reference [183] were exposed to air, and thus potentially contaminated with impurities.

However, the effects reported in this chapter were more pronounced than was observed in Reference [183]. More specifically, uniform injection barrier heights, differing by as little as 0.1 eV, were found. This occurred despite the change in the metal contacts leading to changes in the literature values of the work functions by more than 2 eV.
7.5 Summary

This chapter has considered a detailed analysis of the I-V characteristics of single and two carrier devices that used phosphorescent dendrimers as the organic layer. Two dendrimers were considered and compared. The first dendrimer, Dendrimer 1, had phenylene dendrimers that were not capable of charge transport, while the second dendrimer, Dendrimer 5, had charge transporting carbazole dendrons. Using these two dendrimers a number of device structures were fabricated using various anode and cathode configurations.

The resulting device characteristics were then modeled by Jonathan Williams at the University of Bath. The model used contained realistic boundary conditions, with drift-diffusion transport used to simulate the device currents to deduce key parameters such as the height of the injection barrier at the injecting contact. The results showed that the fitted barrier heights did not agree with the Mott-Schottky model and were susceptible to contamination. In particular, the use of an Au contact, both as an anode and as a non-injecting cathode electrode, was found to be disadvantageous to the device performance. On using Pt electrodes, the high work function of this metal meant that, in addition to an injection barrier, a blocking (Schottky) barrier was needed to describe the charge injection. In both cases the importance of also considering the non-injecting cathode electrode in describing the behaviour of the device was demonstrated, something which has often been overlooked in the modelling of organic devices [190]. Furthermore, the results gave additional confirmation of recent photoemission measurements indicating that the resultant injection barrier varies by no more than ∼ 0.2 eV [183], regardless of the underlying metal.

The conclusion was reached that it was important not to just assume the common practice of the validity of the Mott-Schottky model, where injection barriers are equal to the difference between bare electrode work functions and molecular orbital levels. Instead the results of this chapter have shown that, particularly for Au contacts, a careful model charge injection of charge injection must be used when device parameters such as charge mobilities are desired to be deduced from I-V characteristics.

A comparison of the characteristics obtained for the two dendrimers considered again showed them to be quite different. In similar bipolar device structures, Dendrimer 1, despite having a lower hole mobility was able gave a larger current than Dendrimer 5. This change in behaviour was accounted for by the differing dendrons of the dendrimers, and how these control the charge transport within the dendrimers; via core-to-core hopping in Dendrimer 1, and via the carbazole dendrons in Dendrimer 5.
The studies therefore reconfirmed that different heteroaromatic units in the dendrons could give significant differences in the charge transporting properties of the dendrimers, and so once again reiterated the significant advantages of the dendrimer concept.
Chapter 8

Cross-linkable dendrimers

8.1 Introduction

Until recently the only successful organic light-emitting diodes (OLEDs) made from solution-processing techniques were from one solution cast layer and perhaps one evaporated layer between the anode and cathode. Consequently such devices were usually only capable of monochrome emission, and the optimisation of their efficiency was restricted as the charge injection and transport into the organic layer was not always easy to control. In addition to the requirement of higher efficiencies, the creation of multi-colour devices, such as RGB (red-green-blue) matrix displays, would greatly enhance the commercial viability of such displays. In particular white light can be generated from spatially separated emissive components of the three different primary colors. In this way each colour can be individually optimised; the colour balance can be tuned; and of particular advantage, the differential aging of the three colours can be compensated for so improving display lifetime. The pixelation of the emissive layer thus remains one of the key challenges for the production of full-color displays based on electroluminescent organic semiconductors.

The vacuum deposition techniques used for small molecule organics have already allowed this potential to be reached, but this method suffers from long and expensive fabrication techniques. The benefits of all-solution-processable devices are evident: cheap and simple manufacture, larger area devices, flexible devices, etc. Thus far although considerable progress has been made, there remains considerable issues in combining the solution-processing approach with the high-resolution patterning techniques required to produce a pixelated display.
CHAPTER 8: CROSS-LINKABLE DENDRIMERS

One technique for the creation of multi-layer solution-processable devices was the use of organics that can behave similar to standard photoresist, that is they were photo-patternable. This was possible through the attachment of sidegroups to the organic material that were capable of photochemically cross-linking, thus turning a previously highly soluble organic layer that could be easily washed away into an insoluble network which although fixed still possessed all the functionalities and properties of the soluble organic.

The photo-patterning of organic polymers was not a new technique, but to begin with suffered from the fact the irradiation of the polymer with ultra-violet (UV) light that was required to cause the photo-patterning acted to quench the luminescence of the polymer [198]. Consequently the performance of devices that contained a cross-linked layer were less than that of a reference device that used a noncross-linked polymer as the organic layer [199]. The techniques used either reactive side or main chain polymers with pendent polymerisable moieties [199], or monomers with several reactive groups to produce the polymer network [200, 201]. Reference [202] suggests a reason for the decrease in performance on cross-linking may have related to the occurrence of undesirable side reactions that acted to effect the electrical properties of the film. Alternatively the shrinkage of the polymer network upon polymerisation may have led to crack formation and hence current leakage paths which ultimately gave rise to short circuits. The technique although suitable for creating patterns of emissive and non-emissive regions in a single organic layer, to give, for example, light-emitting logos, was no good for giving red, green, and blue-light emitting pixels for three colour displays, or for displays with multiple emissive layers.

In 2003 however, Müller in a report in Nature [203], showed that a three-colour (RGB) OLED was possible to be fabricated from emissive polymer layers with photo-patternable properties. The approach used followed that of their successful photo-patternable hole-transport materials where oxetane surface groups were attached to the organic as reactive polymerisable groups to provide the cross-linkable function [200, 202]. The alkyl ether unit between the aromatic system and the oxetane unit was present to act as both a linker and as a spacer; it provided flexibility to the oxetane units while also improved the solubility of the monomer. Finally it also helped to improve the formation of homogenous films by assisting in crystallisation prevention [204]. The approach was found to be highly successful with the demonstration that both electrical and optical properties could be simultaneously maintained even with the deposition of multiple organic layers.

Oxetane is the name given to the organic compound possessing a four-membered ring with three
Chapter 8: Cross-linkable Dendrimers

Figure 8.1: Structure of the photo-initiator (PI) used in this chapter to provide cross-linking carbon atoms and one oxygen atom, that is the structure with the molecular formula $C_3H_6O$. The term is often assigned to any organic compound containing an oxetane ring. With high basicity and ring strain, oxetane compounds have the highest ring-opening polymerisability among the various cyclic ethers including epoxy compounds. This cationic ring opening polymerization (CROP) of the oxetane units under UV exposure is what makes the oxetane unit so interesting. As a cationic process it possess all the advantages of such a technique: low shrinkage and thus good adhesion to substrates; no oxygen inhibition makes fast cures possible, and good quality and tough films; low photo-initiator contents are required to provoke the cross-linking; it causes little modification of the electrical and optical properties; and it is also chemically safe to use.

The polymerisation of oxetane occurs cationically with initiation by the presence of photo-acid or photo-initiator (PI). Typically the electron-rich, highly fluorescent compound (4-[2-(hydroxytetradecyl)oxyl]-phenyl)- phenyliodoniumhexafluoro-antimonate, with structure shown in Figure 8.1, as used by Müller [203] and others [205], acts as the PI material. Upon UV illumination, the photo-initiator decomposes via a multiple-step mechanism and eventually generates protons $H^+$. The process is summarised in Figure 8.2. The generated protons open up the oxetane ring and start the polymerisation before being themselves consumed in the polymerisation. As the polymer films remain soluble after UV irradiation, a heat cure step is used to further promote the cross-linking. Furthermore, in an unwanted but unavoidable side reaction between the polymer and the photo-initiator, electron transfer radical cations are formed in the EL layer. These cations can act to quench the electroluminescence of the polymer, albeit this can be recovered by heating at a sufficient temperature ($180^\circ$ C). To ensure the complete removal of any such remaining cations, often the films are subjected to an additional wash in solvent. As an alternative to the use of PI to act as the proton donor to start the cross-linking, an equivalent reaction can be produced from the use of a PEDOT/PSS layer located immediately below the organic layer. In this case no PI is required to cross-link the film only the heating cure step.

Initially oxetane units to provide cross-linkable functionality to polymers were used to make cross-linkable hole-transport layers to improve the charge injection into the organic layer [200, 202]. The success of this approach meant it was soon extended to allow photo-patternable emissive polymers to
be successfully made into three-colour multi-layer solution-processable OLEDs \cite{203,207}. Since these early publications a number of efficient solution-processable multi-layer devices have been reported, see for example References \cite{204,208,217}. However thus far no demonstration of a phosphorescent cross-linked material has been reported. Instead in most cases fluorescent polymers were the cross-linkable organic material. In a few other instances, a new and alternative method of using a small molecule phosphorescent dopant compound, typically one based on an Ir(III) core such as Ir(ppy)$_3$, co-polymerised with a cross-linkable matrix has been employed \cite{214-216}. This later technique was the first demonstration of solution-processed, highly efficient OLEDs that used an electrophosphorescent iridium-containing triplet emitter where both the cross-linkable triplet emitting dopant as well as all other organic layers were spin-coated from solution. However in this case the cross-linkable functionality was not a property of the emissive polymer but of the host matrix into which the polymer was doped. At the time of writing, and to the best of our knowledge, no demonstration has yet been reported of the direct and successful incorporation of functional cross-linkable groups such as oxetane into a phosphorescent organic material.

The previous chapters have introduced the dendrimer concept, whereby it was demonstrated that through careful choice and modification of the dendrimer structure the resultant emissive properties of the dendrimer could be changed as desired. It has been clearly evident dendrimers provide a highly attractive methodology of achieving the hitherto so far unattainable cross-linkable phosphorescent organic semiconductor. This chapter presents a study into such dendrimers and their use in multi-layer solution-
processed devices. The materials considered in this chapter were all synthesised by Chih-Lei Chen at the University of Oxford. The initial sections introduce the various cross-linkable dendrimers and transport materials before detailing some photophysical results obtained for the cross-linkable dendrimers. The chapter continues with a section describing the performance and success of OLEDs made with cross-linkable dendrimers, before concluding with a study into the optimisation of the photo-initiator concentration for maximum performance.

As in previous chapters I would again thank and acknowledge the contributions of Dr Ruth Harding in measuring the solution PLQY values reported within this chapter.

8.1.1 Cross-linkable hole-transport layer dendrimers

The structures of the cross-linkable hole-transport layers (HTL) used in this chapter are shown in Figure 8.3 and Figure 8.4. The right hand structure, Dendrimer 19 (Oxford batch code CLC01-84), was a cross-linkable version of the common hole transport material TPD (N,N’-diphenyl-N,N’-bis(3-methylphenyl)-(1,1’biphenyl)-4,4’-diamine), that has been successively used as such a layer elsewhere [203, 207]. As described in the previous section the cross-linking function was provided via the attachment of oxetane groups to the ends of the molecule [203]. The left hand structure, Dendrimer 18 (CLC01-68A), was a first generation version of this dendrimer.

Cross-linking was performed by the method of UV exposure followed by heating. In particular this involved the exposure of the spin-coated dendrimer film to the 365 nm line of a UV lamp for 10 seconds followed by a heating cure step for five minutes at approximately 200 °C in a N₂ glovebox. If subsequently employed, solvent washing was performed in a solvent mixture of 1:9 triethylamine:toluene followed by a further rinse in toluene. Spinning solvents were either toluene or THF.

8.1.2 Cross-linkable electron-transport layer dendrimers

In previous chapters it was shown that the most efficient devices were achieved when the charge injection and transport of both holes and electrons was balanced in order to maximise the \( \Phi_{CAPTURE} \) term in the calculation of the external quantum efficiency in Equation 2.13. This was obtained through the use of a bilayer structure where the small molecule material TPBI was used as an electron transport/hole blocking layer within the device structure. The TPBI was in all cases deposited by evaporation onto the spin-coated dendrimer emissive layer.
An all solution-processable device would require that for maximum device performance that the electron transport/hole blocking layer (if needed) was able to be deposited from solution. However as this layer was the uppermost organic layer it was decided that it did not need to be cross-linkable. Consequently Dendrimer 20 (CLC01-83A) was synthesised with structure as shown in Figure 8.5. This dendrimer contained benzimidazole units to confer to it electron transporting properties. Such units were used for the same purpose in a number of the dendrimers considered in Chapter 6 and also appear in the standard TPBI material (see structure shown in Figure 2.16). Solubility was provided to Dendrimer 20 through tert-butyl groups attached to its periphery and thus this dendrimer could easily be spin-coated from any polar aprotic organic solvent. Typically CH$_2$Cl$_2$ was chosen as the solvent with a concentration of 20 mg/ml used to yield films approximately 60 nm thick, a thickness comparable to that used for the evaporated layer of TPBI whenever this layer was used in the devices reported in the previous chapters.
8.1.3 Cross-linkable electroluminescent layer

The structure of the first cross-linkable dendrimer, a single dendron first generation dendrimer, Dendrimer 21 (CLC01-61), for use as an electroluminescence layer is shown in Figure 8.6. As for the hole-transport layer the ability for the dendrimer to cross-link was provided by the attachment of oxetane surface groups to the periphery. As can be noted from the figure the dendrimer structure was simply that of Dendrimer 1 (Ir-G1) but with the 2-ethylhexyloxy surface groups replaced by oxetane groups that were capable of cross-linking. A second cross-linkable dendrimer was also considered in this chapter, this dendrimer, Dendrimer 22, was a double dendron dendrimer with structure as shown in Figure 8.7.

8.2 Photophysical properties of the first generation cross-linkable electroluminescent dendrimer

The similarity in structure of Dendrimer 21 to that of Dendrimer 1 meant it might be predicted the resulting photophysical properties would be similar. However this was in fact not the case in photoluminescence. In solution Dendrimer 1 gave a PLQY of 70 - 80 %, whereas Dendrimer 21 (with no PI present) was measured by Dr Ruth Harding to give a much lower value of around 48 %. The reason for the much lower PLQY was not clear but it seemed that the presence of the photo-activated oxetane.
groups had an adverse effect on the PLQY. It is commented that while Dendrimer 1 has been measured multiple times to give a range of values, the measurement of Dendrimer 21 was only made twice with on each occasion the same value being obtained.

Since the adoption of the new solution-processing protocol as described in Chapter 4, the neat film PLQY of Dendrimer 1 has always been measured to be in the range of values of approximately 60-65%. Under this new solution-processing protocol a similar range of values were also found for Dendrimer 21 in its uncross-linked form (and without PI present in the solution). Evidently in film at least, the change in surface groups had little effect on the photoluminescence efficiency.

Of more interest was the film PLQY of Dendrimer 21 after cross-linking. In the same measurement process cycle, an uncured (or uncross-linked) film (i.e. a film with no PI) of Dendrimer 21 was measured to have a film PLQY of 60%, whereas a fresh sample of this dendrimer with PI present in the film (at a concentration of 1 wt %) after UV curing and heating to cause cross-linking of the film was found to have a lower film PLQY of 49%. Having such a small drop in film PLQY after curing was highly promising as it offered, for the first time, the possibility of being able to use such films to create efficient phosphorescent dendrimer devices as an alternative to the polymers and cross-linkable host matrices [203, 204, 207, 210, 214, 215] that have been reported so far.

A comparison between the absorption and emission spectra of an uncured film (no PI present) and cured film (PI present) of Dendrimer 21 are shown in Figure 8.8. As revealed in the figure there was no change found in the corresponding absorption spectra on curing, but there was a 6 nm red-shift in the peak of emission spectrum on the addition of PI and subsequent curing. The resultant spectral shift gave a change in the CIE coordinates of (0.351, 0.607) in the uncured film to (0.364, 0.602) in the cured film. This spectral change and the corresponding decrease in film PLQY was attributed to be due to either oxidation effects, or the presence of radical cations in the film that were not completely removed by the heating cure step and thus were left to quench the PL.

## 8.3 Multi-layer devices

In this section the use of the cross-linkable dendrimers when used within device structures was investigated. To begin the studies in the first experiment the standards were found for the basic bilayer neat film dendrimer device with and without an additional PEDOT/PSS layer included within the device struc-
As was the case previously, a bilayer device was defined as an electroluminescent layer plus an additional electron transport/hole blocking layer; in this case an evaporated layer of TPBI. For the electroluminescent layer the basic first generation iridium(III) cored dendrimer of Dendrimer 1 (Ir-G1) was used, the structure of this dendrimer was shown previously in Figure 2.14 and was repeated in Figure 4.1. The resulting devices, device structure A (that of the basic bilayer OLED as in Figure 2.17) without a PEDOT/PSS layer and device structure B with a layer of PEDOT/PSS included, were simply those studied in Section 4.5. The characteristics of these devices were plotted in Figure 4.16 and are repeated in Figure 8.11 with the relevant device data summarised again in Table 8.1.

Device structure A  ITO/Dendrimer 1/TPBI/LiF/Al

Device structure B  ITO/PEDOT/Dendrimer 1/TPBI/LiF/Al

As shown in Table 8.1 or plotted in Figure 8.11 for device structure A the maximum efficiency was 8.5 % at a brightness of 1700 cd/m² (5.6 V), while at the standard display brightness of 100 cd/m² the EQE was 4.9 % (4.0 V), while the emission spectrum gave a CIE coordinate of (0.331, 0.626). With a PEDOT/PSS layer included within the device structure for device structure B the resulting maximum device efficiency was 9.4 % at a brightness of 1100 cd/m² (5.2 V), and at a brightness of 100 cd/m² the EQE was 8.6 % (3.8 V), and the emission spectrum gave a CIE coordinate of (0.335, 0.623). The results lead to the conclusion that PEDOT/PSS gave marginal improvements in efficiency and would also, as found in Chapter 4, help improve the device lifetime.
In Chapter 4, it was found that the greatest efficiency recorded in any neat film bilayer device with an electroluminescent layer of Dendrimer 1 was a very high 12%, with an average of all the devices made with this dendrimer being around 10%. Even a 10% efficient device remains somewhat less than the maximum theoretically possible given the neat film photoluminescence quantum yield of Ir-G1 was around 65%. One method of improving the device efficiency is through improvement of the charge balance and injection into the organic layer. In this section this was attempted with the use of an additional hole-transport layer (HTL) below the neat film dendrimer electroluminescent (EL) layer in the device structure. This was of course only possible if the hole-transport layer would not be removed by the spin-coating of the emission layer on top. To ensure this the cross-linked hole-transport layer Dendrimer 18 was used.

To cross-link a 30 nm film of this dendrimer one percent by weight of the photo-initiator (PI), with structure shown in Figure 8.1, was used. Devices were subsequently fabricated using this additional layer with and without a PEDOT/PSS layer included below the HTL. The devices also contained an evaporated layer of TPBI as the electron transport/hole blocking layer (ETL/HBL). The structures of the devices were therefore those of device structure C and D (note these were different structures to those termed structures C and D in Section 4.5). Schematic drawings of these structures are shown in Figure 8.9 and Figure 8.10.

Device structure C  
ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al

Device structure D  
ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al

A summary of the device characteristics of device structures C and D is given in Table 8.2. Figure 8.11 shows the device characteristics obtained for these devices, and includes for comparison the standard bilayer device cases without an HTL that were device structures A and B considered previously. From the results it was evident that the inclusion of the additional cross-linked HTL did not

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>ITO/Dendrimer 1/TPBI/LiF/Al</td>
<td>8.5 % (5.6 V, 17.5 lm/W, 31.2 cd/A)</td>
<td>4.9 % (4.0 V, 14.4 lm/W, 18.3 cd/A)</td>
<td>(0.331, 0.626)</td>
</tr>
<tr>
<td>B</td>
<td>ITO/PEDOT/Dendrimer 1/TPBI/LiF/Al</td>
<td>9.4 % (5.2 V, 20.8 lm/W, 34.4 cd/A)</td>
<td>8.6 % (3.8 V, 25.9 lm/W, 31.3 cd/A)</td>
<td>(0.335, 0.623)</td>
</tr>
</tbody>
</table>

Table 8.1: Summary of device characteristics for device structures A and B

8.3.1 Multi-layer devices with a cross-linkable hole-transport layer

In Chapter 4, it was found that the greatest efficiency recorded in any neat film bilayer device with an electroluminescent layer of Dendrimer 1 was a very high 12%, with an average of all the devices made with this dendrimer being around 10%. Even a 10% efficient device remains somewhat less than the maximum theoretically possible given the neat film photoluminescence quantum yield of Ir-G1 was around 65%. One method of improving the device efficiency is through improvement of the charge balance and injection into the organic layer. In this section this was attempted with the use of an additional hole-transport layer (HTL) below the neat film dendrimer electroluminescent (EL) layer in the device structure. This was of course only possible if the hole-transport layer would not be removed by the spin-coating of the emission layer on top. To ensure this the cross-linked hole-transport layer Dendrimer 18 was used.

To cross-link a 30 nm film of this dendrimer one percent by weight of the photo-initiator (PI), with structure shown in Figure 8.1, was used. Devices were subsequently fabricated using this additional layer with and without a PEDOT/PSS layer included below the HTL. The devices also contained an evaporated layer of TPBI as the electron transport/hole blocking layer (ETL/HBL). The structures of the devices were therefore those of device structure C and D (note these were different structures to those termed structures C and D in Section 4.5). Schematic drawings of these structures are shown in Figure 8.9 and Figure 8.10.

Device structure C  
ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al

Device structure D  
ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al

A summary of the device characteristics of device structures C and D is given in Table 8.2. Figure 8.11 shows the device characteristics obtained for these devices, and includes for comparison the standard bilayer device cases without an HTL that were device structures A and B considered previously. From the results it was evident that the inclusion of the additional cross-linked HTL did not
increase the device efficiency considerably over that of basic device structure A where no HTL was used. With a HTL but with no PEDOT/PSS layer included for device structure C a maximum efficiency of 8.1 % at 13.6 V was found, which fell to give an EQE of 4.1 % at 11.0 V at the standard brightness of 100 cd/m$^2$. A marginal increase in the device performance was found in device structure D when a layer of PEDOT/PSS was included within the device. Here the maximum EQE increased to 9.9 %, and at a brightness of 100 cd/m$^2$ the EQE was 7.7 %.

From the figure it was noted that despite the presence of the additional HTL there was no benefit in terms of efficiency, but nor was there any significant drop in efficiency, or a colour shift of the emission spectrum. Albeit the device efficiencies recorded were very good and were much higher in efficiency than those obtained elsewhere (using polymers) when a cross-linkable hole-transport layer was included within the device structure [203, 210].

The comparison plots showed the current through device structures A and B was greater than that through device structures C and D at any applied voltage greater than the turn-on voltage. The turn-on
voltage for device structures C and D was over double that of device structures A and B. Consequently the low currents in device structures C and D lead to low luminance compared to those found in device structures A and B. Despite this the resultant efficiency performance, in terms of the maximum efficiency obtained, was very similar between the four device structures.

Finally it was noted from the final plot of Figure 8.11 that showed the device emission spectra, neither the use of an additional HTL or a layer of PEDOT/PSS within the device structure gave any contribution to the resulting device emission spectra. Consequently across the four device structures there was found to be little change in the CIE coordinates.

8.3.2 Multi-layer devices with a cross-linkable emission layer

The previous sections showed that although efficient devices were possible using the Ir-G1 dendrimer as the electroluminescent layer, to give any further increase of the efficiency of the devices made with this dendrimer did not prove to be straightforward. Also, as Ir-G1 was not cross-linkable, further layers could not be deposited on top of it from solution, thereby preventing it from being used in an all-solution-processable device. The use of cross-linkable light-emitting layers is also important for photo-patterning
of the emission layer which is useful to define pixels of different light emitting colours for OLED displays, and also possibly for solid state lighting applications. A possible solution to such problems the Ir-G1 dendrimer was replaced as the electroluminescent layer by the cross-linkable Dendrimer 21 which has the structure shown previously in Figure 8.6.

In device structure E, the emissive layer of Dendrimer 21 was used as a neat uncured film, it contained no PI and so remained uncross-linked. In device structure F, Dendrimer 21 was again used as the emissive layer but now with 1 wt % of PI added in order to give a cross-linked (cured) film of this dendrimer. In this way it was possible to see if the decrease in the film PLQY observed on curing the cross-linkable dendrimer was also reflected in the device performance. In device structure G, an uncured film of Dendrimer 21 was used as the EL layer spin-coated onto a PEDOT/PSS layer. As in device structure E no PI was used in this dendrimer layer and it thus remained uncross-linked. Finally in device structure H, the positive charge giving properties of the PSS in the PEDOT/PSS layer were realised to provide the cross-linking function to the Dendrimer 21 layer spin-coated on top [213]. The resulting device structures were:

Device structure E: ITO/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(Dendrimer 21 uncured with no PI)

Device structure F: ITO/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(Dendrimer 21 PI cured with UV and heat)

Device structure G: ITO/PEDOT/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(Dendrimer 21 uncured with no PI)

Device structure H: ITO/PEDOT/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(Dendrimer 21 PI cured by PEDOT/PSS)

The device characteristics obtained for these device structures are shown in Figure 8.12 with all the pertinent device data summarised in Table 8.3. In the first case for device structure E, where an uncured layer of Dendrimer 21 was used in a bilayer device structure with an ETL/HBL of TPBI, the resulting device efficiency appeared similar to that of device structure A with a non cross-linked EL layer of Ir-G1. However as shown in Figure 8.13, this was despite both the current through device structure E and the resulting brightness being much less than that through device structure A. This implied there was either a reduction in charge transport or mobility on moving from Dendrimer 1 to Dendrimer 21. Nevertheless,
it seemed that in each case the current was still balanced to the brightness output and thereby gave very efficient devices.

In particular for device structure E the maximum EQE was 9.7 % at 9.2 V, and at a brightness of 100 cd/m² the EQE was 9.5 % at 7.8 V. Figure 8.13 also shows that there was a slight change in the emission spectra between device structures A and E. This could be caused by the change in surface groups resulting in a slightly different film morphology and thickness which would mean there would be a differing amount of light transmitted/reflected between the two devices. In consequence the CIE coordinates shifted from (0.331, 0.626) in device structure A, to (0.343, 0.613) in device structure E.

As discussed previously in photoluminescence measurements on neat films of Dendrimer 21, a decrease in the quantum yield was found after cross-linking the film. Considering the device results of device structure F, in comparison to those of the uncured device structure E, it was notable that large decrease in the device efficiency occurred. Specifically, for device structure F the maximum EQE was 2.1 %, and at a brightness of 100 cd/m² the efficiency was 1.8 %. The decreased device efficiency could largely be attributed to the reduction in luminescence efficiency as a result of the cross-linking process, which seemed therefore to have a greater effect in devices than in PL measurements. It was also noted
that the current through the cross-linked device was less than that through the uncross-linked device structure which indicated that cross-linking may also have had an effect on the charge transport through the electroluminescence layer, it was proposed there was a morphology change in the film layer after cross-linking.

In device structure G, where a PEDOT/PSS layer was used beneath a neat film layer of Dendrimer 21 (without PI), the performance of the resultant device was similar to that of device structure E where similarly no PEDOT/PSS layer was used. This result repeated what was found on using the Ir-G1 dendrimer (Dendrimer 1) as the emissive layer. For device structure G, the maximum efficiency was again high at 9.8 %, and at the standard 100 cd/m² brightness the EQE was 9.3 %.

In device structure F while a PEDOT/PSS layer was used it had no cross-linking function for the Dendrimer 21 film layer spin-coated onto it. Device structure H differed from this device in that the PEDOT/PSS layer was used to cross-link the Dendrimer 21 film, this was despite the presence of 1 wt % PI in the film. In this way, following the method of [213], no UV exposure step was required. In device structure H the efficiency gave a maximum EQE of 3.6 %, and at a brightness of 100 cd/m² the EQE was 3.5 %. The efficiency was significantly lower than that of the devices with uncross-linked dendrimer films, but was almost double that of the efficiency of device structure F where cross-linking

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>ITO/Dendrimer 21/TPBI/LiF/Al (Dendrimer 21 uncured with no PI)</td>
<td>9.7 % (9.2 V, 11.1 lm/W, 32.8 cd/A)</td>
<td>9.5 % (7.8 V, 15.1 lm/W, 37.2 cd/A)</td>
<td>(0.343, 0.613)</td>
</tr>
<tr>
<td>F</td>
<td>ITO/Dendrimer 21/TPBI/LiF/Al (Dendrimer 21 PI cured with UV and heat)</td>
<td>2.1 % (13.4 V, 1.7 lm/W, 7.1 cd/A)</td>
<td>1.8 % (12.2 V, 1.6 lm/W, 6.3 cd/A)</td>
<td>(0.358, 0.606)</td>
</tr>
<tr>
<td>G</td>
<td>ITO/PEDOT/Dendrimer 21/TPBI/LiF/Al (Dendrimer 21 uncured with no PI)</td>
<td>9.8 % (11.0 V, 9.8 lm/W, 34.2 cd/A)</td>
<td>9.3 % (9.4 V, 10.9 lm/W, 32.5 cd/A)</td>
<td>(0.340, 0.613)</td>
</tr>
<tr>
<td>H</td>
<td>ITO/PEDOT/Dendrimer 21/TPBI/LiF/Al (Dendrimer 21 PI cured by PEDOT)</td>
<td>3.6 % (4.6 V, 9.0 lm/W, 13.2 cd/A)</td>
<td>3.5 % (5.6 V, 7.2 lm/W, 12.8 cd/A)</td>
<td>(0.342, 0.617)</td>
</tr>
</tbody>
</table>

Table 8.3: Summary of device characteristics for device structures E, F, G and H
was achieved by a UV exposure step. The result indicated that for cross-linking the use of PEDOT/PSS could be preferable.

It was also observed that for both with and without a PEDOT/PSS layer included in the device structure, as found through photoluminescence measurements, there was a slight red-shift of the emission spectrum after cross-linking. On cross-linking the CIE coordinates were found to shift from (0.343, 0.613) to (0.358, 0.606) without PEDOT/PSS (device structure E and F), and from (0.340, 0.613) to (0.342, 0.617) when a layer of PEDOT/PSS was used within the device structure (device structures G and H).

### 8.3.3 Multi-layer devices with a cross-linkable emission and hole-transport layer

The previous section showed that the cross-linkable Dendrimer 21 could be used as an electroluminescent layer in a bilayer OLED. Unfortunately, the performance of the resulting device was not optimum. In this section to improve the device performance the properties of the cross-linkable hole-transport dendrimer (Dendrimer 18) that was first considered in Section 8.3.1 were utilised to create a device with multiple cross-linkable layers. As previously a 30 nm film of the HTL dendrimer was cross-linked using 1 wt %
of photo-initiator (PI). A 100 nm thick film of the cross-linkable dendrimer was then spin-coated on top, again using 1 wt % PI to cross-link. The resulting devices were fabricated using both these layers, and with and without a PEDOT/PSS layer below the HTL in an otherwise identical fabrication process. As before a layer of evaporated TPBI was used as the electron transport/hole blocking layer (ETL/HBL). Hence in this experiment the device structures were similar to those of device structures C and D with the only change being in the choice of the emission layer. The resultant structures considered were:

Device structure **I**  ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al

Device structure **J**  ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al

The resulting device characteristics are shown in Figure 8.14 and the data is summarised in Table 8.4. A consideration of these results again revealed that the device efficiency using cross-linkable layers was less than that of the uncross-linked dendrimers. Figure 8.15 shows a comparison of the results of device structure **F** with a single cross-linked electroluminescent layer to that of device structure **I** where an additional cross-linked HTL was also used. The figure reveals that the use of the second layer did give a marginal improvement in the device performance. In particular for device structure **I** the maximum
EQE was 4.4 % at 7.8 V, and at a brightness of 100 cd/m$^2$ the EQE was 3.1 % at a bias of 13.8 V. This was almost double the efficiency of device structure F where only the cross-linkable EL layer was used. Intriguingly the EQE of device structure I with the additional HTL was similar to that of device structure H where a layer of PEDOT/PSS was used in addition to the cross-linkable EL layer, this was despite the large difference in current and luminance through each of these devices. This result again reflected the importance of balanced charge injection and transport for efficiency optimisation.

If however a layer of PEDOT/PSS was used in combination with both a cross-linkable HTL and emission layer, as in device structure J, the resulting device performance dramatically suffered. The device achieved a maximum EQE of 1.1 % at 18.0 V, and at a brightness of 100 cd/m$^2$ the EQE was 0.7 % at 13.0 V. In this structure, despite the presence of the PEDOT/PSS layer in the device structure, for both cross-linkable layers the cross-linking was achieved using the standard method of UV exposure and heating of the PI present in each film. This result indicated that in such a structure with PEDOT/PSS this approach was not ideal.

Figure 8.14 also plots the emission spectra of both device structures I and J from which the CIE coordinates were calculated for device structure I without a PEDOT/PSS layer as (0.346, 0.613), and with a PEDOT/PSS layer in device structure J to have shifted slightly to (0.387, 0.582).

It was also noted that the turn-on voltages of device structures I and J that used the cross-linkable dendrimer were greater than those with standard neat film Ir-G1 devices (device structures A and B). The current and the luminance levels recorded at any voltage were also lower. This may have related to the increased total device thickness with the use of these additional layers in the device. Although the poor performance of these devices in comparison to the others attempted previously also indicated the

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m$^2$</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al</td>
<td>4.4 % (7.8 V, 6.3 lm/W, 15.7 cd/A)</td>
<td>3.1 % (13.8 V, 2.5 lm/W, 10.9 cd/A)</td>
<td>(0.346, 0.613)</td>
</tr>
<tr>
<td>J</td>
<td>ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al</td>
<td>1.1 % at (18.0 V, 0.6 lm/W, 3.6 cd/A)</td>
<td>0.7 % (13.0 V, 0.5 lm/W, 2.2 cd/A)</td>
<td>(0.387, 0.582)</td>
</tr>
</tbody>
</table>

Table 8.4: Summary of device characteristics for device structures I and J
Figure 8.15: Comparison of device characteristics for one and two layer cross-linked layer devices

possibility of intermixing of the layers through incomplete cross linking.

8.3.4 Multi-layer devices with an alternative cross-linkable hole-transport layer

In Sections 8.3.1 and 8.3.3 devices were attempted that used the cross-linkable hole-transport layer of Dendrimer 18. The results showed that although successful OLEDs could be fabricated with this HTL the resultant efficiency of the devices were not greater than when this layer was not used within the device structure. To understand why this was the case the energy levels of each of the layers used in this device are plotted in Figure 8.16. The HOMO and LUMO energy levels of Dendrimer 1 are known to be 5.62 eV and 2.47 eV respectively [26]. A similar HOMO energy has been determined for Dendrimer 21 and so due to the similarity of these dendrimers, which only differ in their surface groups, it can be assumed that the LUMO of Dendrimer 21 is also around 2.47 eV. The HOMO and LUMO energy levels of Dendrimer 18 have been measured to be 5.68 eV and 2.73 eV respectively.

With knowledge of these numbers an energy level diagram can be drawn such as shown in Figure 8.16. From the figure it was evident that despite the intended function of Dendrimer 18 as a HTL there was large barrier to hole injection from the ITO to the emissive dendrimer layer which the inclusion
of Dendrimer 18 did nothing to assist, in fact its presence increased this barrier to hole injection. It appeared at least from an energy level viewpoint that Dendrimer 18 was not overly suitable to act as a HTL in this device structure. Of course it may have been beneficial in terms of charge transport improvements through a suitably matched hole mobility but no test was made of this. Unfortunately, the knowledge of the energy levels of Dendrimer 18 were not available until late in the project and therefore this dendrimer was often used as the HTL.

To overcome the energy level mismatch the second HTL layer dendrimer, Dendrimer 19 with structure shown in Figure 8.4, was considered. As discussed previously this dendrimer was a cross-linkable version of the common hole transport material TPD that has been successively used as such a layer elsewhere [203, 207]. The HOMO and LUMO energy levels of this material have been published to be 5.32 eV and 1.9 eV respectively [215]. Figure 8.17 redraws the energy level diagram of the device structure containing Dendrimer 19 as the HTL. As the figure shows, the HOMO energy of the HTL now lies, as desired, between that of the ITO anode and the emissive dendrimer layer. The deep lying LUMO energy of Dendrimer 19 also ensured this layer acted as an effective electron blocking layer, which would increase the efficiency of charge recombination within the emissive layer.

To investigate whether Dendrimer 19 was effective as the HTL a set of devices were fabricated that used this layer. In the first case Dendrimer 1 (Ir-G1) was the emissive layer, whilst in the second case a cross-linked layer of Dendrimer 21 formed this layer. The resulting device structures were:

Device structure \( K \) \( \text{ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 1)/TPBI/LiF/Al} \)

Device structure \( L \) \( \text{ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF/Al} \)
A summary of the resulting device characteristics are shown in Table 8.5. For the emissive layer of Dendrimer 1 (Ir-G1) in device structure K, the maximum EQE recorded was 8.7 %, and at a brightness of 100 cd/m² the EQE was 6.9 %. Comparison plots of the device results with the two different HTLs of Dendrimer 18 and 19 with an emissive layer of Dendrimer 1 are shown in Figure 8.18. In the figure the device results for when Dendrimer 18 was used the HTL were those of device structure C previously discussed in Section 8.3.1. The plot shows that with Dendrimer 19 as the HTL the resultant current and light output of the device was slightly greater and thus consequently the resultant device efficiency was greater than that of the device when Dendrimer 18 was the HTL. The increased current through the device with a HTL of Dendrimer 19 corresponded to the reduction in the hole injection barrier with this dendrimer which would result in an improvement in the hole injection into the emissive dendrimer layer.

Finally as also shown in Figure 8.18 there was little spectral shift in the emission spectra on changing the HTL. The CIE coordinate of the emission spectrum of device structure C was (0.332, 0.622), whereas for device structure K the CIE coordinate of the emission layer was calculated to be (0.319, 0.633).

The corresponding plots comparing the performance of the two different HTL layers with a cross-linked layer of Dendrimer 21 are shown in Figure 8.19. For the device with Dendrimer 18 as the HTL the device results are those of device structure I replotted, device structure L used Dendrimer 19 as the HTL. With this dendrimer as the HTL the maximum EQE of the device was 3.6 %, and at a brightness of 100 cd/m² the EQE was 2.9 %. In this case despite the apparent improvement in the energy levels on changing the HTL there was, unlike for Dendrimer 1, found to be no improvement in device performance. In fact, in a complete reversal of what was found for Dendrimer 1, as Figure 8.19 shows, the current and light output and hence efficiency was less when Dendrimer 19 was used as the HTL instead of Dendrimer 18. It was not evident why there should be an improvement in device performance with

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 1)/TPBI/LiF/Al</td>
<td>8.7 % (11.6 V, 8.6 lm/W, 31.7 cd/A)</td>
<td>6.9 % (9.6 V, 8.3 lm/W, 25.4 cd/A)</td>
<td>(0.319, 0.633)</td>
</tr>
<tr>
<td>L</td>
<td>ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF/Al</td>
<td>3.6 % (24.5 V, 1.6 lm/W, 12.7 cd/A)</td>
<td>2.9 % (20.5 V, 1.6 lm/W, 10.4 cd/A)</td>
<td>(0.354, 0.612)</td>
</tr>
</tbody>
</table>

Table 8.5: Summary of device characteristics for device structures K and L.
Dendrimer 1 but not Dendrimer 21; the results may have indicated that assumption that both these dendrimers share the same energy levels was not valid. Instead the energy levels of Dendrimer 21 could be closely aligned to the HTL energy levels of Dendrimer 18, and those of Dendrimer 19 to those of Dendrimer 1.

Figure 8.19 also shows a comparison of the EL emission spectra from the devices using either of the HTLs. As the figure shows there was a slight narrowing of the emission spectra attributed to a micro-cavity effect on moving from a Dendrimer 18 to Dendrimer 19 HTL within the device structure. For device structure I with a HTL of Dendrimer 18 the CIE coordinate was (0.346, 0.613), whereas for the HTL of Dendrimer 19 in device structure L the CIE coordinate shifted slightly to (0.354, 0.612).

8.3.5 Multi-layer devices with solvent washed layers

In Sections 8.3.3 and 8.3.4 it was established that the inclusion of an additional cross-linkable hole transport layer (HTL) within the device structure could lead to improvements in the efficiency of devices containing this layer. However, the presence of photo-initiator (PI) to cause the cross-linking of the hole-
transport layer such that another layer could be deposited on top of it was found in Sections 8.3.1 and 8.3.2 to lead to a drop in the device efficiency. This caused by the decrease in luminescence efficiency that occurred after cross-linking.

In this section the effect of washing the film layer in solvent immediately after cross-linking was investigated. The procedure of solvent washing, as described in Section 8.1, was found to be required in the early reports of cross-linkable polymers by Müller [203]. This was to ensure that any radical cations produced during the polymerisation processes that cause the cross-linking process were removed and thus could not subsequently act to reduce the luminescence efficiency of the film. The process also removed any unreacted solvent (uncross-linked areas). In general the mixture used for solvent washing was a 1 to 9 blend of triethylamine to toluene followed by a further rinse in toluene, but washes in either pure toluene or pure THF were also found to be equally successful. For a 1 wt % concentration of PI in the solution it was found for Dendrimer 21 there was approximately a 10 % reduction in film thickness after solvent washing. In particular, the thickness of an uncured dendrimer film was measured to be 90 nm, which fell to around 80 nm after the solvent wash step. To ensure the film was fully cross-linked

![Figure 8.19: Comparison of device characteristics on varying the HTL dendrimer with cross-linkable Dendrimer 21 as the EL layer](image-url)
a sufficient ratio of PI must be used, which required a careful trade-off as it has been clearly shown that
the presence of PI in the cross-linked film reduced the luminescence efficiency of the film.

The technique of solvent washing was initially applied to the cross-linkable hole transport layer of
Dendrimer 18 onto which the emissive layer of a Dendrimer 1 film was afterwards spin-coated, this gave
device structure M. In the second device structure, that of device structure N, Dendrimer 1 was then
replaced with the cross-linkable Dendrimer 21 as the emissive layer where both this layer and the cross-
linkable HTL layer below underwent the solvent washing step. In device structure O, the same device
structure was used but only the HTL was solvent washed. Finally, in device structure P, two cross-
linkable layers were used with both layers solvent washed, where in this case Dendrimer 19 formed the
HTL. The resulting device structures considered were:

Device structure M  ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al
(with solvent washing on Dendrimer 18 layer)
Device structure N  ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(with solvent washing on both cross-linkable layers)
Device structure O  ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(with solvent washing on Dendrimer 18 layer only)
Device structure P  ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF/Al
(with solvent washing on both cross-linkable layers)

The resulting device characteristics are plotted in Figure 8.20 and summarised in Table 8.6. The
results showed that in device structure M, with Dendrimer 1 (Ir-G1) as the emission layer and a HTL of a
solvent washed layer of Dendrimer 18, the device was able to attain a maximum EQE of 6.1 % (16.5 V),
and at a brightness of 100 cd/m² the EQE was 5.9 % (14.5 V).

Figure 8.21 compares the device results of device structure M with that of the equivalent device struc-
ture C that did not use the solvent washing step on the 30 nm thick hole transport layer of Dendrimer 18.
The figure showed that despite the expected 10 % reduction in the film thickness of the HTL after the
solvent washing step, there was no corresponding decrease in the turn-on voltage of the device. In fact
the turn-on voltage was greater in device structure M with the solvent washed layers, and therefore both
the current and light output were less than that in device structure C at any given voltage. Consequently,
the resultant device efficiency was found to have decreased on inclusion of the solvent washing step on
the HTL in the device fabrication process. It was noted that the emission spectrum of the device remained unaffected by the curing and solvent washing step of the HTL, and so the reduced device efficiency was attributed to an unfavourable modification of the charge transfer balance within the dendrimer emissive layer.

In device structure N, where Dendrimers 18 and 21 were used respectively as the HTL and EL layers, with both cross-linked and solvent washed, the resultant maximum efficiency of the device was 0.9 %, and at the standard brightness of 100 cd/m² the EQE was 0.7 %. Comparing these numbers to those obtained in the equivalent non-solvent washed case of device structure I, which obtained a maximum efficiency of 4.4 %, it was again found that the solvent washing process lead to a decrease in the quantum efficiency of the device.

Table 8.6: Summary of device characteristics for device structures M, N, O and P

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al (with solvent washing on Dendrimer 18 layer)</td>
<td>6.1 % (16.5 V, 4.1 lm/W, 21.6 cd/A)</td>
<td>5.9 % (14.5 V, 4.6 lm/W, 21.4 cd/A)</td>
<td>(0.335, 0.621)</td>
</tr>
<tr>
<td>N</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al (with solvent washing on both cross-linkable layers)</td>
<td>0.9 % (30.0 V, 0.3 lm/W, 3.2 cd/A)</td>
<td>0.7 % (26.5 V, 0.3 lm/W, 2.4 cd/A)</td>
<td>(0.359, 0.605)</td>
</tr>
<tr>
<td>O</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF/Al (with solvent washing on Dendrimer 18 layer only)</td>
<td>1.8 % (24.0 V, 0.8 lm/W, 6.3 cd/A)</td>
<td>1.8 % (23.5 V, 0.8 lm/W, 6.2 cd/A)</td>
<td>(0.356, 0.607)</td>
</tr>
<tr>
<td>P</td>
<td>ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF/Al (with solvent washing on both cross-linkable layers)</td>
<td>2.2 % (21.0 V, 1.2 lm/W, 7.7 cd/A)</td>
<td>1.2 % (14.5 V, 1.2 lm/W, 5.4 cd/A)</td>
<td>(0.353, 0.610)</td>
</tr>
</tbody>
</table>
As Figure 8.20 shows, a considerable improvement in device performance was found if only one of these layers was cross-linked. In particular in device structure O, where only the HTL of Dendrimer 18 was solvent washed, the maximum device efficiency was twice that of the double solvent washed case of device structure N. In device structure O the maximum EQE was 1.8 % (24.0 V), and at a brightness of 100 cd/m² the EQE was 1.8 % (23.5 V). In this case the improved efficiency over that of double solvent washed device structure N indicated that the more solvent washes used the worse the device got. A deterioration in film quality on repeated solvent washes could be a possible reason for this.

Finally in device structure P, the alternate HTL of Dendrimer 19 was used with both this layer and the cross-linkable Dendrimer 21 emission layer solvent washed. Here the device was able to attain a maximum EQE of 2.6 % (at 21.5 V), and an EQE of 1.3 % (at 14.5 V) at a brightness of 100 cd/m². Despite this improved performance this device, as in all the structures considered in this section, still showed a performance worse than that of the equivalent non-solvent washed device. In particular the non-solvent washed equivalent of device structure P was device structure L, where in that device a maximum EQE of 3.6 % was found, a significant improvement over device structure P where solvent
Figure 8.21: Device characteristics on using a solvent washing step (device structure M) or not (device structure C) on the Dendrimer 18 HTL for an Dendrimer 1 emission layer

As noted previously the inclusion of a solvent washing step into the device fabrication procedure was found to have little effect on the resultant emission spectral properties of the devices. With Dendrimer 1 as the EL layer for device structure C the CIE coordinate was (0.332, 0.622), with a negligible shift to (0.335, 0.621) for the equivalent solvent washed device structure M. For Dendrimer 21 as the emission layer in the double solvent washed case of device structure N the CIE coordinate was (0.359, 0.605), and (0.356, 0.607) for the single solvent washed case of device structure O. Finally with the change in HTL in device structure P the CIE coordinate shifted marginally to (0.353, 0.610), and was very similar to the value of (0.354, 0.612) found in the non-solvent washed equivalent case of device structure L.

It has therefore been found in this section that although the inclusion of a solvent wash step did not modify the emissive spectral properties of the device it did affect the electrical properties of the device. Despite the slight reduction in film thickness solvent washing was found to give, the operating voltages of the devices which contained films that had undergone such a step were in fact greater than those of the equivalent devices with layers that were not solvent washed. A possible reason for the reduction in
device performance after solvent washing was a slight but undesirable modification of the charge transfer balance within the dendrimer emissive layer that the small change in film thickness brought about. It was also found that the film quality could be decreased by solvent washing, with the extent of this effect being particularly demonstrated if a number of such steps were used in the fabrication process.

8.3.6 Multi-layer devices with cross-linkable electron-transport layers

In the previous sections an evaporated layer of the small molecule TPBI was always used as the electron transport/hole blocking layer within the device in order to improve the balance of charge balance and injection thereby leading to an increase in the resultant device efficiency. The deposition of such a layer is tedious and time consuming and thus if this layer could be replaced by one that could provide this function but be solution-processable considerable processing advantages would immediately occur. In this section the cross-linkable properties of Dendrimer 21 were utilised to allow the solution deposition of such an electron transport layer provided by Dendrimer 20, which has the structure shown previously in Figure 8.5. For simplicity in all cases the solution washing process, as described in the last section, was not used in this experiment.

The resulting device structures considered were:

- Device structure Q: ITO/EL Layer (Dendrimer 1)/ETL (Dendrimer 20)/LiF/Al
- Device structure R: ITO/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure S: ITO/PEDOT/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure T: ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure U: ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al

In device structure Q the emission layer used was Dendrimer 1 (Ir-G1), onto this layer the electron transporting Dendrimer 20 was then attempted to be spin-coated. CH₂Cl₂ was used as the solvent for both Dendrimer 1 and Dendrimer 21. Consequently it would not be a surprise to learn that on spin-coating the Dendrimer 21 layer, the Dendrimer 1 layer below was easily washed away, and no device was able to formed using device structure Q, and thus no results have been reported. For device structure R, with an emission layer of the cross-linkable Dendrimer 21, although in this case a device could be successfully fabricated with two solution processed layers, no current-voltage characteristics were able to be measured for the resultant device. It was not apparent why on this occasion that the cross-linking procedure failed,
CHAPTER 8: CROSS-LINKABLE DENDRIMERS

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m² or Max Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>ITO/PEDOT/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>2.6 % (18.2 V, 1.6 lm/W, 9.4 cd/A)</td>
<td>2.6 % (20.0 V, 4 cd/m², 1.5 lm/W, 9.3 cd/A)</td>
<td>(0.351, 0.611)</td>
</tr>
<tr>
<td>T</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>0.04 % (20.0 V, 0.01 lm/W, 0.05 cd/A)</td>
<td>0.04 % (20.0 V, 0.3 cd/m², 0.01 lm/W, 0.05 cd/A)</td>
<td>(0.364, 0.599)</td>
</tr>
<tr>
<td>U</td>
<td>ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>0.02 % (17.0 V, 0.01 lm/W, 0.05 cd/A)</td>
<td>0.01 % (17.0 V, 0.1 cd/m², 0.01 lm/W, 0.05 cd/A)</td>
<td>(0.367, 0.598)</td>
</tr>
</tbody>
</table>

Table 8.7: Summary of device characteristics for device structures S, T, and U

as the same cross-linking procedure with 1 wt % of PI, heat and UV exposure that was successfully able to cross-link all other films was followed here.

In contrast device structures S, T, and U all did give device characteristics and these are shown in Figure 8.22 and the relevant data summarised in Table 8.7. In each case, both the current and light output of all the devices was very low. Consequently the three devices were inefficient; all were unable to attain a brightness in excess of the standard value of 100 cd/m² at any voltage tested.

In device structure S, the cross-linkable dendrimer was spin-coated on a PEDOT/PSS layer with PI and heating used to provide the cross-linking function. Onto this layer a layer of the solution-processable electron transporting Dendrimer 20 was spin-coated. This device resulted in a maximum brightness of only 4 cd/m² that occurred at a bias voltage of 20 V and gave a corresponding external quantum efficiency of 2.6 %, the device therefore was not good. The conditions used for the deposition of the PEDOT/PSS layer and the Dendrimer 21 emissive layer for the fabrication of this device were the same as used for device structure H, the only change was that of the method of deposition of the ETL layer: an evaporated ETL of TPBI in device structure H, and a spin-coated layer of Dendrimer 20 in device structure S. A comparison of these two device structures showed just how poor the performance of the device with the solution-processable ETL actually was. In particular, although the solution-processable ETL gave a high maximum EQE, the device with an evaporated layer of TPBI was, unlike device structure S, easily able to achieve the standard brightness of 100 cd/m², where at this brightness the EQE was 1.8 %.

Careful choice was made to ensure that layer thicknesses in all equivalent devices were comparable.
the thickness of the spin-coated ETL was equivalent to that of an evaporated layer of TPBI. Consequently
the currents in both device structures H and S could be readily compared as the electric field across the
total device thickness for both device structures can be assumed to be the same. Figure 8.23 shows
plots comparing the current density (device areas were also the same) and the EQE against the total field
across the device for both the device structures. As the figures show, the change from an evaporated to
a solution-processable ETL resulted in over a three order of magnitude reduction in the current density
through the device at high fields. The plots also emphasised that the turn-on field for device structure S
was much greater than that of device structure H. While it was not evident why this should be the case,
the similarity of the emission spectra of both devices showed that the change in ETL gave no change in
the emissive properties of the device. The emission spectrum of device structure H gave a CIE coordinate
of (0.342, 0.617), while that of device structure S gave a CIE coordinate of (0.351, 0.611). The difference
therefore in the device characteristics was likely to be related to the poorer charge transport properties of
the solution-processable ETL layer of Dendrimer 21 in comparison to the evaporated layer of TPBI.

To investigate whether the poor performance of device structure S could be improved with the ad-
tion of a HTL in the device, device structure T was fabricated. This device contained a layer of the cross-linkable Dendrimer 18 as the HTL. However, as the device characteristics reveal, this change actually brought about a decrease in device performance, with the maximum luminance unable even to reach a value of 1 cd/m².

In the final case for device structure U a four-layer solution-processable device was considered whereby the configuration of device structure T was augmented by a PEDOT/PSS layer beneath the HTL of Dendrimer 18. The change was found to bring no improvement in device performance; the maximum efficiency of the device was 0.02 %, this also occurred at the maximum brightness of 0.1 cd/m² at an applied bias of 17.0 V. The addition of a PEDOT/PSS layer on moving from device structure T to device structure U gave no discernable change in the resulting device emission spectrum with the CIE coordinates essentially the same, that is (0.364, 0.599) and (0.367, 0.598) for device structures T and U respectively.

The results of this section have enabled an important step to be made on the road to an all-solution-processable device with use of a soluble ETL layer within a device structure. Unfortunately, the resultant device performance on using this layer was not an improvement over that of a traditional evaporated material such as TPBI. Possible reasons for this are suggested as poor charge balance, transport and energy level mismatches with this new solution-processable ETL. Hence, in order to obtain the maximum efficiency for a device utilising a soluble dendrimer as the ETL further material modification was evidently required. Consequently, for the remaining devices of this chapter an evaporated layer of TPBI was used.
as the ETL in order achieve the best possible performance in each device structure.

8.3.7 Multi-layer devices with cross-linkable electron-transport layers and solvent washed layers

Section 8.3.6 established that although an all-solution-processable device was possible the resultant device was very inefficient. In order to simplify slightly the fabrication process of these devices in Section 8.3.6 the solvent washing technique as described in Section 8.3.5 was not used. Although the solvent washing technique was previously not found to be overly beneficial to the device performance, it was still believed to be worthwhile to investigate whether the inclusion of this procedure could help improve the characteristics of devices that used a solution-processable Dendrimer 21 as the ETL. In this section the successful device structures S - U of Section 8.3.6 were repeated, but with the fabrication procedure including an additional step of the solvent wash process after each cross-linking stage. The cross-linking procedure was therefore: spin, UV cure, heat, and solvent wash. The devices investigated in this section were:

- Device structure V: ITO/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure W: ITO/PEDOT/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure X: ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al
- Device structure Y: ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al

The resulting device characteristics are shown in Figure 8.24 and summarised in Table 8.8. The data revealed that the devices were, as in the non-solvent washed devices of Section 8.3.6 not very good. Nonetheless, despite the decreased device performance, as seen previously in Section 8.3.5 with the inclusion of a solvent washing step, it did seem that, if in this particular case only, there was a slight improvement in the device performance on the inclusion of the solvent washing process within the device fabrication procedure.

In device structure V, that used the basic structure of the cross-linked Dendrimer 21 and as the ETL a layer of the solution-processable Dendrimer 20 as the ETL, the standard brightness of 100 cd/m² was unable to be reached. Instead the device gave a maximum brightness of 2.4 cd/m² (0.14 %).

The inclusion of a PEDOT/PSS layer in device structure W lead to a dramatic improvement of the device performance: the device was able to attain the standard 100 cd/m² brightness, which occurred at
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Table 8.8: Summary of device characteristics for device structures V, W, X and Y

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m² or Max Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>ITO/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>0.1 % (29.2 V, 0.05 lm/W, 0.4 cd/A)</td>
<td>0.1 % (30.0 V, 2 cd/m², 0.05 lm/W, 0.4 cd/A)</td>
<td>(0.406, 0.560)</td>
</tr>
<tr>
<td>W</td>
<td>ITO/PEDOT/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>1.5 % (15.4 V, 1.1 lm/W, 5.4 cd/A)</td>
<td>1.5 % (15.4 V, 1.1 lm/W, 5.4 cd/A)</td>
<td>(0.362, 0.602)</td>
</tr>
<tr>
<td>X</td>
<td>ITO/HTL Layer (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>0.1 % (30.0 V, 0.05 lm/W, 0.4 cd/A)</td>
<td>0.1 % (20.0 V, 5 cd/m², 0.05 lm/W, 0.4 cd/A)</td>
<td>(0.367, 0.598)</td>
</tr>
<tr>
<td>Y</td>
<td>ITO/PEDOT/HTL Layer (Dendrimer 18)/EL Layer (Dendrimer 21)/ETL (Dendrimer 20)/LiF/Al</td>
<td>0.2 % (18.2 V, 0.1 lm/W, 0.7 cd/A)</td>
<td>0.2 % (20.0 V, 61 cd/m², 0.1 lm/W, 0.6 cd/A)</td>
<td>(0.375, 0.593)</td>
</tr>
</tbody>
</table>

an applied bias voltage of 15.4 V. Here the EQE was 1.5 % which also corresponded to the maximum efficiency measured for this device. The improvement in device performance did come with a shift and narrowing of the emission spectra with the CIE coordinates changing from (0.406, 0.560) to (0.362, 0.602) with the inclusion of a PEDOT/PSS layer on moving from device structure V to W. Yet it was noted that the CIE coordinates of device structure V were very far from those found previously for any device structure that used a layer of Dendrimer 21 as the emissive layer, whereas those for device structure W were closer to the results of the other device structures. The large shift in the CIE coordinate of device structure V appeared to have arisen from the presence of a large shoulder around 560 nm in the emission spectra.

For device structure X, that used all three solution-processable dendrimer layers, of which two were cross-linked and solvent washed, the resulting device performance was again not good. Here the device obtained a maximum luminance of 5 cd/m² at the maximum 20 V bias applied to the bias, the voltage at which also corresponded to the maximum efficiency of 0.13 % found for this device. Nevertheless, this as still an improvement on the equivalent non-solvent washed case of device structure T, which was found in Section 8.3.6 to have a maximum EQE of 0.04 cd/m².

Device structure Y formed the most complicated device studied in that it utilised the maximum of four all-solution-processable layers. These were a layer of PEDOT/PSS requiring a cure step, and three
dendrimer layers, with two of the dendrimer layers cross-linked and subsequently solvent washed. It was found that with the inclusion of a PEDOT/PSS layer, but still with the use of a UV cure and heat step to initiate cross-linking, the device performance did show a marginal improvement over that of device structure X where no PEDOT/PSS layer was used. The inclusion of a PEDOT/PSS layer increased the maximum brightness to 62 cd/m$^2$ at 20 V bias which gave an EQE of 0.17 %. The inclusion of the PEDOT/PSS layer within the device structure also resulted in a slight shift in the emission spectrum with the CIE coordinates changing from (0.367, 0.598) for structure X, to (0.375, 0.593) for structure Y where a PEDOT/PSS layer was included within the device structure.

Therefore, despite in some cases the slight improvement in device performance on the inclusion of the solvent washing procedure within the device fabrication process for devices that also contained a solution-processable ETL, in all cases the devices were still less efficient than when an evaporated layer of TPBI was used as the ETL. The conclusion was again reached that in order to obtain the maximum efficiency in a device structure an evaporated layer of TPBI should be used as the ETL in subsequent device structures.
8.3.8 Multi-layer devices cross-linked without photo-initiator

The previous sections established that although in some cases efficient device structures could be fabricated in general the device performance decreased as the device complexity increased through the inclusion of additional layers within the device structure. In this section a more simpler case was considered - a device structure that contained in addition to the anode and cathode layers, a hole-transport layer and a non-cross-linkable emission layer (Dendrimer 1, Ir-G1). To improve charge balance an electron-transport layer of evaporated TPBI was also included within the device structure. The resultant device structure was effectively that of device structure D, the only difference was that in this device no UV cure step was used to initiate the cross-linking of the HTL, instead this function is performed by the use of a PEDOT/PSS layer beneath the emissive layer. The process was the same as that used in device structure H to cross-link the cross-linkable emission layer. The resulting device structures considered were:

Device structure Z  ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al
(Dendrimer 18 cured only by heating PEDOT, no PI)

Device structure AA  ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al
(Dendrimer 18 with PI cured by heating PEDOT)

The difference between the two device structures was that device structure Z did not contain any PI within the HTL solution, whereas in device structure AA for the HTL PI was still used. In both cases cross-linking occurred solely from the heating of HTL layer after spinning over the PEDOT/PSS layer, that is no UV cure step was used for these devices. The resulting device characteristics of both devices are shown in Figure 8.25 and summarised in Table 8.9.

For device structure Z, the maximum EQE of the device was 10.4 %, and at a standard brightness of 100 cd/m² the EQE was slightly less at 10.2 %. The performance of this device is compared in Figure 8.26 to the equivalent device structure D that used a UV cure step in the curing procedure of the HTL. The comparison showed that although the current through device structure Z was less than that through device structure D, and it required a greater voltage to produce the same brightness, the resultant device efficiency was still greater in device structure Z. The result was significant as it showed that a level of cross-linking could be attained even without the presence of PI in the film. This was particularly beneficial as it meant the effect of the reduction PL and more particularly EL efficiency found after
Chapter 8: Cross-linkable Dendrimers

Figure 8.25: Device characteristics on cross-linking with and without PI

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z</td>
<td>ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al (Dendrimer 18 cured only by heating PEDOT, no PI)</td>
<td>10.4 % (12.0 V, 10.1 lm/W, 38.8 cd/A)</td>
<td>10.1 % (11.0 V, 12.4 lm/W, 43.5 cd/A)</td>
<td>(0.330, 0.629)</td>
</tr>
<tr>
<td>AA</td>
<td>ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 1)/TPBI/LiF/Al (Dendrimer 18 with PI cured by heating PEDOT)</td>
<td>8.4 % (15.0 V, 6.6 lm/W, 31.4 cd/A)</td>
<td>7.6 % (11.5 V, 7.7 lm/W, 28.3 cd/A)</td>
<td>(0.327, 0.628)</td>
</tr>
</tbody>
</table>

Table 8.9: Summary of device characteristics for device structures Z and AA
using PI to result in cross-linking, which has been found to be a particular problem, could be avoided. Albeit, both device structures D and Z were still less efficient than device structures A or B where no cross-linkable layer was used in addition to the standard Ir-G1 emission layer.

With the presence of PI within the HTL in device structure AA, the resultant maximum efficiency of the device was 8.4 %, and at the standard brightness the 100 cd/m$^2$ was 7.6 %. The device was thus less efficient than device structure Z, again reflecting that the presence of PI acted to reduce luminescence efficiency of the dendrimer layer. As also observed previously, the presence of PI within the device was found to give no discernable change in the emission spectra of the device; the shift in colour from device structure Z to AA was almost negligible with the CIE coordinates changing only slightly from (0.330, 0.629) to (0.327, 0.628).

From this experiment it was apparent that the layer immediately above the PEDOT/PSS could still be effectively cross-linked without the use of PI to perform this function. As discussed, this discovery was particularly useful as the presence of PI has clearly been found to reduce the luminescence efficiency of the dendrimer which has been found to be particularly bad problem in devices, and thus by eliminating
the need for PI to cross-link films means efficiency optimisation in devices containing cross-linkable films becomes possible.

8.3.9 Multi-layer devices with photo-initiator but no cross-linking

In previous sections the presence of PI was shown to cause a reduction in the luminescence efficiency of the dendrimer layer which has been found to be of particular problem in devices leading to a reduction in device efficiency. To consider whether in part the reduction was a consequence of cross-linking the film, in this section devices were fabricated that contained PI in the film but were not subsequently cross-linked. To investigate this, the presence of PI in both the cross-linkable Dendrimer 21 and the standard Ir-G1 (Dendrimer 1) was considered. The resulting device structures were:

Device structure **AB**  
ITO/EL Layer (Dendrimer 1)/TPBI/LiF/Al (with PI)

Device structure **AC**  
ITO/EL Layer (Dendrimer 21)/TPBI/LiF/Al (with PI but uncross-linked)

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AB</strong></td>
<td>ITO/EL Layer (Dendrimer 1)/TPBI/LiF/Al (with PI)</td>
<td>2.6 % (4.5 V, 6.5 lm/W, 9.3 cd/A)</td>
<td>2.6 % (4.5 V, 6.5 lm/W, 9.3 cd/A)</td>
<td>(0.326, 0.625)</td>
</tr>
<tr>
<td><strong>AC</strong></td>
<td>ITO/EL Layer (Dendrimer 21)/TPBI/LiF/Al (with PI but uncross-linked)</td>
<td>4.8 % (4.5 V, 11.5 lm/W, 16.4 cd/A)</td>
<td>3.8 % (4.0 V, 10.2 lm/W, 13.0 cd/A)</td>
<td>(0.351, 0.607)</td>
</tr>
</tbody>
</table>

Table 8.10: Summary of device characteristics for device structures **AB** and **AC**

The resulting device characteristics of the two devices are shown in Figure 8.27 and the data summarised in Table 8.10. The device results of device structure **AB** were also compared with those of the equivalent device that did not contain any PI in the film, that of device structure **A**. This comparison plot is shown in Figure 8.28.

The figures show that the presence of PI was found to considerably reduce the device performance in comparison to the case when no PI was present. With PI used in the Dendrimer 1 emissive layer in device structure **AB**, the maximum EQE was 2.6 % (4.5 V), which also occurred at the closest brightness to the standard of 100 cd/m². In contrast where no PI was included in the emissive Dendrimer 1 layer in device structure **A** the maximum EQE was 10.3 % (5.8 V). As the comparison plots of Figure 8.28 show, although a similar current was passed through each device there was a considerable drop in luminance.
in device structure AB when PI was used, which accounted for the lower efficiency found in this device. This result showed that the presence of PI within the film was enough to reduce the luminescence efficiency of the emissive dendrimer film layer within a device even without cross-linking, that is the reduction in device efficiency was a consequence of the photo-initiator and not the cross-linking procedure itself. Furthermore, as also shown in the figures the presence of PI in the film resulted in no change (within error) in the emission spectrum. This was reflected in the CIE coordinates, device structure AB gave a CIE coordinate of (0.326, 0.625), while for device structure A the CIE coordinate was (0.331, 0.626).

There was also found, as shown in Figure 8.27, to be a reduction of the device efficiency when PI was included in the emissive dendrimer layer in device structure AC where the EL layer used was the cross-linkable Dendrimer 21. This data was replotted alongside those of the characteristics of device structures E and F in Figure 8.29. While all these devices used exactly the same layer configuration, in device structure E no PI was used and the dendrimer layer remained uncross-linked, whereas in device structure F the dendrimer was cross-linked using PI. The figure shows that, as discussed in Section 8.3.2, the presence of PI in the dendrimer layer caused the device efficiency to decrease, even when the film was
not cross-linked. With PI but the dendrimer layer uncross-linked in device structure AC the maximum EQE was 4.7 % (4.5 V), and at a brightness of 100 cd/m² the EQE was 3.8 % (4.0 V). This device efficiency was greater, as Figure 8.29 shows, to that of the efficiency of device structure F where the PI was used to cross-link the dendrimer, but was much less efficient than that of device structure E where no PI was used within the device.

The presence of PI within the emissive dendrimer layer was again found to give no significant emission spectral changes. In device structures E and F the CIE coordinates were (0.343, 0.613) and (0.358, 0.606), and for device structure AC where PI was used but the film not cross-linked the CIE coordinate was (0.351, 0.607).

On consideration of the results of this experiment it was apparent that, as found previously, the presence of PI, whether used to cross-link or not, appeared to significantly reduce the luminescence efficiency of the emissive dendrimer layer when used in a device structure. Subsequent cross-linking of this layer caused an even further reduction in efficiency. The decrease in efficiency on cross-linking was also found to be much more significant in devices than in PL. The fact that this also occurred in a standard device with an Ir-G1 emissive layer that contained PI, suggested that although the technique was able
to cross-link films satisfactorily, in order to obtain maximum efficiencies in the devices an alternate PI that did not lead to such a loss in EL efficiency was required. Unfortunately, an alternative PI was not available during the project and thus the current photo-initiator was used throughout.

### 8.3.10 Multi-layer devices with cross-linked HTL and uncross-linked emission layer

The previous sections considered the case of multi-layer devices that contained two layers which were both subsequently cross-linked. To conclude the study, multi-layer devices were fabricated where only the first of these layers, the HTL, was cross-linked. Onto this cross-linked HTL a layer of the cross-linkable Dendrimer 21 was spin-coated, this layer although it contained PI was not subsequently cross-linked. Devices with an additional layer of PEDOT/PSS beneath the HTL were also considered. Here the PEDOT/PSS layer was not used to provide any cross-linking function, instead this was performed by the standard UV cure and heating method that was used for all the cross-linking performed in the devices reported in this section. The resulting device structures considered were:

Device structure **AD**  ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF-Al

---

Figure 8.29: Device characteristics with and without PI included in an EL layer of the cross-linkable Dendrimer 21
Table 8.11: Summary of device characteristics for device structures AD, AE, AF and AG

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD</td>
<td>ITO/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF-Al (with Dendrimer 21 containing PI but not cross-linked)</td>
<td>0.02 % (20.0 V, 0.01 lm/W, 0.05 cd/A)</td>
<td>0.01 % (19.0 V, 0.01 lm/W, 0.03 cd/A)</td>
<td>(0.370, 0.591)</td>
</tr>
<tr>
<td>AE</td>
<td>ITO/PEDOT/HTL (Dendrimer 18)/EL Layer (Dendrimer 21)/TPBI/LiF-Al with Dendrimer 21 containing PI but not cross-linked</td>
<td>0.6 % (18.5 V, 0.3 lm/W, 1.8 cd/A)</td>
<td>0.5 % (12.5 V, 0.3 lm/W, 1.3 cd/A)</td>
<td>(0.430, 0.546)</td>
</tr>
<tr>
<td>AF</td>
<td>ITO/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF-Al (with Dendrimer 21 containing PI but not cross-linked)</td>
<td>0.6 % (13.5 V, 0.4 lm/W, 1.7 cd/A)</td>
<td>0.6 % (12.5 V, 0.4 lm/W, 1.6 cd/A)</td>
<td>(0.443, 0.538)</td>
</tr>
<tr>
<td>AG</td>
<td>ITO/PEDOT/HTL (Dendrimer 19)/EL Layer (Dendrimer 21)/TPBI/LiF-Al (with Dendrimer 21 containing PI but not cross-linked)</td>
<td>0.7 % (11.0 V, 0.6 lm/W, 1.9 cd/A)</td>
<td>0.5 % (8.0 V, 0.6 lm/W, 1.5 cd/A)</td>
<td>(0.426, 0.549)</td>
</tr>
</tbody>
</table>

The resulting device characteristics of the device structures are shown in Figure 8.30 and the relevant data is summarised in Table 8.11. A consideration of these results revealed that for device structure AD,
with a single cross-linked layer and no PEDOT/PSS layer within the device structure, the device gave a very inefficient maximum external quantum efficiency of 0.02 % at 20.0 V, and 0.01 % (19.0 V) at the standard brightness of 100 cd/m² with minimal power efficiencies in each case. The resulting emission spectrum of the device gave a CIE coordinate of (0.370, 0.591).

When a layer of PEDOT/PSS was included within the device for device structure AE the performance was found to have improved considerably with a maximum EQE of 0.6 % (18.5 V) reached, and at a brightness of 100 cd/m² the EQE was 0.5 % (12.5 V). This improvement in performance was accompanied by a large spectral shift as shown in Figure 8.30. This resulted in the CIE coordinate of device structure AE as (0.430, 0.546). It was not apparent what may have caused this large shift in the emission which had not been observed previously in other devices. For example in device structure AF with the alternative HTL of a cross-linked layer of Dendrimer 19 and with no PEDOT/PSS layer, the CIE coordinate was (0.443, 0.538), and shifted to (0.426, 0.549) when a layer of PEDOT/PSS was used in device structure AG.

The performance of both device structures AE and AF was thus found to be considerably worse than that of the equivalent devices that used two cross-linkable layers both with no PEDOT/PSS layer (device structure I), and with a PEDOT/PSS layer (device structure J) also included within the device structure. This result indicated that the improvement in device performance on cross-linking the emission layer arose due to the consumption of PI in the film during the cross-linking procedure; once the film was cross-linked the PI was used up and thus could not subsequently act to reduce the luminescence efficiency of the dendrimer layer. In device structures AD and AE where no cross-linking of the emission layer was performed, this PI was still present and so acted to continually reduce the luminescence efficiency of the dendrimer in the same way as was demonstrated to occur in a number of the devices considered in the previous sections of this chapter.

Moreover, the poor device performance of the devices with a HTL of Dendrimer 18, indicated again that this dendrimer was not ideal for use as a HTL. Consequently in the remaining devices of this set the alternative cross-linkable HTL layer of Dendrimer 19 was used. For device structures AF and AG, on top of a cross-linked layer of Dendrimer 19 a layer of the cross-linkable Dendrimer 21 was spin-coated, and while this dendrimer layer contained PI it was not cross-linked. As before devices with and without PEDOT/PSS layers in the structure were made, but when used the PEDOT/PSS layer had no cross-linking function. For device structure AF with no PEDOT/PSS layer included within the device
structure, the maximum EQE of the device was 0.6 %, which was also the efficiency at the standard brightness of 100 cd/m². Including a layer of PEDOT/PSS within the device structure in device structure AG, gave a slight increase the maximum efficiency, 0.7 % was found at 13.5 V, with at a lower applied bias of 8.0 V a lower EQE of 0.5 % at the standard brightness of 100 cd/m².

As in the case for a HTL of Dendrimer 18, the use of Dendrimer 19 as the HTL in combination with a non cross-linked layer of Dendrimer 21 was found to give no improvement in device performance in device structures AF and AG in comparison to the equivalent device that used the same layers but in a cross-linked form (device structure L). This device gave at a brightness of 100 cd/m² an EQE of 2.9 %. Again the improvement in device performance on using cross-linked versions of both layers could be attributed to the consumption of PI in the film during the cross-linking. In this way once the PI was used it could not act afterwards to quench the luminescence and thus reduce the efficiency of dendrimer layer. The results of this section have therefore showed that the use of an emissive layer containing PI but which is then not cross-linked was not beneficial to obtaining maximum device performance.
8.3.11 Multi-layer devices summary

The previous sections have considered a number of multi-layer devices that used various combinations of cross-linkable dendrimers. The approach was found to be successful in that for the first time it demonstrated multi-layer devices could be fabricated from solution-processable phosphorescent dendrimers, thereby opening up the possibility of obtaining in the future an all-solution-processable dendrimer device. Devices were considered that used cross-linkable hole transport layers in combination with the standard Ir-G1 dendrimer in an attempt to optimise the efficiency of this device structure. The replacement of this dendrimer as the emissive layer with one possible of being cross-linked also allowed a further solution-processable electron transported layer to be added to the device structure to give a device containing three solution-processable layers. The addition of a further layer of PEDOT/PSS to the device structure further increased the complexity of the device and gave four solution-processable layers, with this device still found to give successful light emission.

While in many cases this section has detailed that a number of efficient devices could be created using a combination of such layers, these studies have generally showed that the early materials used for the devices were, perhaps on reflection back, not best suited in some cases to the function they were desired to fulfil. For example the hole transport layers dendrimers were chosen from the fact they have been shown to be successful when used with emissive polymer layers [200, 202, 203]. When used with electrophosphorescent dendrimers it was found their HOMO energy levels were not best matched to the dendrimer HOMO energy level and thus made charge injection more difficult. In addition the PI chosen for use was one that has been employed previously by others [200, 202, 203], but here it was found its presence within a dendrimer film resulted in a fall in PL efficiency, which became even more pronounced within devices. It was suggested this PI was not best suited for the cross-linking of dendrimers considered in this thesis.

Therefore, for further improvement and efficiency optimisation of an OLED structure that employs cross-linkable dendrimers, further material design and optimisation would be required. This however is a time consuming and expensive process that was not possible to be completed within the duration of the project. Consequently, in the next section simple changes in the cross-linking process were investigated to see if in fact the process could be improved such that when applied in device fabrication procedures improvements in device efficiency would arise.
8.4 Photo-initiator photophysical studies

The results of both the device and photoluminescence measurements detailed in the previous sections of this chapter have showed that the photo-initiator (PI) used, with structure shown in Figure 8.1, which was used to provide the cross-linking function, also had the detrimental effect of reducing the PL and EL efficiency of the dendrimer film layer. Although the PI chosen has been standard in the literature for the cross-linking of fluorescent polymers (e.g. see References [203, 207]) this reduction in efficiency has so far not been described. What has been noted from the literature is that the concentration of PI required in the film to provoke the cross-linking was often different. In Reference [203] a ratio of 0.5 wt % was used, whereas in later work by the same group this ratio was as low as 0.2 wt % [206], or as high as 2 wt % [210]; the weight percentage of PI chosen was thus dependent on the organic material required to be cross-linked. For the devices so far considered in this chapter following discussion with the chemists who synthesised the materials the concentration of PI recommended for use was one percent by weight. In this section it was investigated whether this was in fact a suitable ratio, or instead the performance could be improved by using a lower PI concentration whilst still obtaining the same degree of cross-linking function. Therefore in this section the effect of varying the photo-initiator concentration on both the photoluminescence quantum yield and the degree of cross-linking was investigated.

8.4.1 Effect of photo-initiator concentration on curing

In the first instance a number of films of both Dendrimer 1 (Ir-G1) and the cross-linkable Dendrimer 21 were made containing various concentrations of PI, where the Ir-G1 dendrimer was used as a control measurement. After spin-coating the film the absorption and emission spectra and the photoluminescence quantum yield were immediately measured. In this case the film did not undergo the standard cure procedure despite the presence of PI in the film. Instead only after the PL measurements of the film were the standard UV and heat cure steps used to cross-link the dendrimer, or in the case of the Ir-G1 control films to ensure any reduction found in the PLQY was due to the presence of the PI. Following this cure process a remeasurement of the PL properties of the film was then made. The details of all the samples used are summarised in Tables 8.12 and 8.13, the tables also recording the resultant values of the PLQY after each step of the outlined procedure.

As can be noted from the data contained in both of the tables the presence of PI in a film was found
to decrease the PLQY from the value of the case where no PI was used in the film, with the greater the weight percentage of PI used the lower the PLQY measured, intriguingly however the relationship was not completely linear. This decrease in film PLQY with an increase in PI concentration was found in both Dendrimer 1 and 21, which indicated that regardless of the dendrimer chosen the PI used quenched the PLQY. The non-linearity of the relationship suggested that in the cross-link process it was not the entire PI that was converted to the form of cations. The quenching effect might have arose from the active PI or from the remaining cations. Nevertheless, the fact that the luminescence quenching did in general increase with PI content while low PI concentrations gave only a small quenching effect is an important discovery. More specifically it implied that the lowest concentration of PI required to cross-link the film would give the most efficient luminescence after cross-linking and used subsequently within a device structure.

After performing the cure step, at all but the lowest PI concentrations the film PLQY of Dendrimer 21 was found to be slightly greater than that of Dendrimer 1. Moreover, for all PI concentrations considered, for either dendrimer, the film PLQY was found to increase after the curing step. For Dendrimer 21 this was accounted for by the fact that PI, as a low energy level compound, would easily quench the PLQY with as more PI added the quenching effect increasing. After curing, the PI was decomposed either by the UV light or the heat used in performing the cure step. Only a small residue would then remain which would have a less significant quenching effect on the PLQY, with only the active PI which

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Before/After Cure</th>
<th>PI wt %</th>
<th>PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>0</td>
<td>65</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>0</td>
<td>62</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>0.01</td>
<td>47</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>0.01</td>
<td>55</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>0.05</td>
<td>41</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>0.05</td>
<td>60</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>0.1</td>
<td>25</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>0.1</td>
<td>49</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>0.5</td>
<td>30</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>0.5</td>
<td>35</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>1</td>
<td>12</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>1</td>
<td>23</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>Before</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Dendrimer 1</td>
<td>After</td>
<td>2</td>
<td>24</td>
</tr>
</tbody>
</table>

Table 8.12: PL summary of effect on varying PI concentration on films of Dendrimer 1
was not decomposed remaining to reduce the luminescence. A similar explanation could be proposed for the Dendrimer 1 results. Despite this dendrimer not being cross-linkable the PI acted to quench the luminescence, but as the UV exposure and heat curing could remove some of the PI, the PLQY measurements after curing were greater than those beforehand.

As implied by the high film PLQY results of the film with 0 wt % PI for either dendrimer in comparison to the other values in the tables, a UV exposure and heat step alone was not sufficient to change or improve the PLQY. At low PI concentrations the exposure to heat and UV acted to remove the majority of the PI from the film. This gave an increased PLQY after the cure step and a value that was still close to that of the value with 0 wt % PI present. However, as the weight percentage of PI in the film was increased the amount of PI that could be removed by the heat and UV exposure step became proportionally reduced. Consequently on the measurement of the PLQY after the cure step the film PLQY, although higher than before the cure, still had a sufficient amount of PI remaining to quench the luminescence such that its ability to recover to the 0 wt % value became proportionally decreased.

The corresponding absorption and emission spectra of each of the films are shown in Figure 8.31 for Dendrimer 1 and Figure 8.32 for Dendrimer 21. For both dendrimers as the left hand figures show for the before the cure measurements, the addition of PI to the film was found to change the absorption spectra for both dendrimers but particularly that of the cross-linkable Dendrimer 21. For this dendrimer there was a slight decrease in the absorption spectra over the entire wavelength range with a pronounced

<table>
<thead>
<tr>
<th></th>
<th>Before/After Cure</th>
<th>PI wt %</th>
<th>PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0</td>
<td>43</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0</td>
<td>46</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.01</td>
<td>37</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.01</td>
<td>42</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.05</td>
<td>41</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.05</td>
<td>50</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.1</td>
<td>35</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.1</td>
<td>54</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.5</td>
<td>36</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.5</td>
<td>39</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>1</td>
<td>18</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>1</td>
<td>29</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>2</td>
<td>15</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>2</td>
<td>28</td>
</tr>
</tbody>
</table>

Table 8.13: PL summary of effect on varying PI concentration on films of Dendrimer 21
decrease in the absorption found around 230 nm. Specifically for this dendrimer, it was found that once the PI was added no matter the quantity used there was little subsequent change in the absorption spectra. Moreover, it was found that even a very low PI concentration of 0.01 wt % was sufficient to change the absorption spectra.

Prior to curing the presence of the PI was also found to give no contribution to the emission properties of either dendrimer with little change (within error) observed in the spectra. Even after the cure step there was found to be little spectral change showing that, as found in the devices, the addition of PI to a dendrimer film had no effect on the colour of the resultant emission. In contrast after curing there was found to be large changes in the absorption spectra of both dendrimers. In the case of the cross-linkable
Dendrimer 21 this was evidently because the curing procedure in some cases was able to produce a larger degree of cross-linking than others. That is, for some PI concentrations, the dendrimer molecule had cross-linked and changed structure with the opening of the oxetane groups, while in other cases there was an insufficient amount of PI to fully promote cross-linking and hence the resultant film was a mixture of cross and uncross-linked parts. The changed film composition resulted in differing absorption spectra for each PI concentration. For the absorption spectra of Dendrimer 1 there was in all cases a peak around 290 nm, and although the spectra shape was similar the magnitude was different in all cases with no particular pattern apparent. This further suggested that the role and quantity of PI in these uncross-linkable films after the cure step has not been fully explained.

8.4.2 Effect of photo-initiator concentration after solvent-washing

The previous section established that the degree of luminescence quenching found on adding PI to a dendrimer was directly proportional to the amount of PI added. In this section an investigation was given into what was the lowest concentration of PI required to fully cross-link a dendrimer film. To give a measurement of how cross-linked the film was the technique of solvent washing as described previously was used - if the film was cross-linked solvent washing would remove little of the film; in contrast if insufficient photo-initiator was used the film should be completely or partially removed during the solvent washing. For this the same films used in Section 8.4.1 for the measurement of the film PLQY before and after curing were, after the second PLQY measurement, subjected to the solvent washing technique. The photoluminescence quantum yield and absorption and emission spectra were then measured again.

Figure 8.33 shows a photo of the resultant films under illumination with UV light (from the right hand side). The photo was taken after the completion of PLQY measurement after the solvent washing step had been performed on all the films. In the figure the top row of films are those of Dendrimer 1, with films of Dendrimer 21 shown in the bottom row. For both dendrimers as move from left to right the quantity of PI in the film changes as 0, 0.01, 0.05, 0.1, 0.5, 2, and 1 wt %. After the solvent washing step, as all the films in top row of the figure show, there was for Dendrimer 1 no film left remaining, in each case the dendrimer was completely removed by the solvent washing step. With no film present for any of these Dendrimer 1 films no further PL or PLQY measurements were possible.

In contrast for the cross-linkable Dendrimer 21 films it was noticeable even to the naked eye that some of the films were still present after the solvent washing step. Under UV light, as shown in the lower
Figure 8.33: Picture of Dendrimer 1 (upper row) and Dendrimer 21 (lower row) films with varying concentrations under UV light after solvent washing. In both cases as move from left to right the quantity of PI in the film is 0, 0.01, 0.05, 0.1, 0.5, 2, and 1 wt %

row of Figure 8.33 this was even more apparent. In particular, as move further right along the bottom row of the figure where the greater PI concentrations were used, an increasing vibrant luminous emission can be observed under the UV light.

For Dendrimer 21 evidence of the presence of the film remaining after a solvent washing step was found down to PI concentrations in the film as low as 0.1 wt %. It was therefore concluded that 0.1 wt % of PI was the minimum concentration of PI needed to cross-link a film of Dendrimer 21. The value measured for the PLQY of this film, as detailed in Table 8.14, was only 1 % after the solvent wash. In contrast a much greater value of 54 % was found after the cure step used on this film, as detailed previously in Section 8.4.1. The result suggested that while 0.1 wt % of PI was sufficient to cross-link some of the film the majority remained uncross-linked and was removed on solvent washing.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>PI wt %</th>
<th>PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 21</td>
<td>0.1</td>
<td>1</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>0.5</td>
<td>39</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>1</td>
<td>40</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>2</td>
<td>29</td>
</tr>
</tbody>
</table>

Table 8.14: PL summary of effect on varying PI concentration on films of Dendrimer 21 after solvent washing

Evidence of that this was true is clearly shown in Figure 8.34. In the left hand side of the figure the plot is of the non-normalised absorption spectra for the Dendrimer 21 films after the solvent washing step for each of the considered weight percentages of PI. For 0.1 wt % PI there was a minimal absorption signal recorded across all the wavelength range measured. Another method to show this is given in the right hand side of Figure 8.34. The figure shows the maximum the maximum absorbance (excluding peak at 200 nm) intensity measured in the non-normalised absorption spectra plotted against the PI
CHAPTER 8: CROSS-LINKABLE DENDRIMERS

Figure 8.34: Left hand figure plots the non-normalised absorption spectra of Dendrimer 21 films after solvent washing with varying concentrations of PI, with right hand figure plotting the peak absorption (excluding peak at 200 nm) against the PI concentration.

Increasing the weight percentage of PI in the film to 0.5, 1 and 2 wt % did, as the figure shows, lead to a large increase in the absorption of the film. The result indicated that at these higher PI concentrations much more of the film had been cross-linked and remained after solvent washing. The greatest absorption for any of the films measured was found for the 1 wt % PI film, that is the 1 wt % film was more cross-linked than with the greater PI concentration of 2 wt %. This can also be seen in the picture of Figure 8.33, where the film furthest to the right with 1 wt % PI is brighter than that of the film with with 2 wt % PI immediately to its left.

The values for the PLQY for the solvent washed films at each of the four PI concentrations are tabulated in Table 8.14. As shown by the data in the table, for the 0.5 wt % and 1 wt % PI concentrations the film PLQY after solvent washing remained much higher and comparable to, if not greater than, the value measured before the solvent washing step, that is the measurement after the cure step. A further increased PI concentration of 2 wt % was, as indicated by the reduced absorption in this film, found to be detrimental to the PLQY as it gave a value of only 29 % after the solvent washing step. Therefore, to give a fully cross-linked film with the maximum possible luminescence efficiency the recommended concentration for PI used to cross-link films of Dendrimer 21 would be 0.5 wt %.

8.4.3 Effect of photo-initiator concentration on PLQY after curing and solvent-washing

To further investigate the effect of PI concentration on the film PLQY a second set of films were made, with in this case, unlike in the previous sections, the films spin-coated and then cured before mea-
measurements of the PLQY and PL were made. Afterwards the films were then solvent washed and the measurements repeated, the results obtained are detailed in Table 8.15.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Before/After solvent washing</th>
<th>PI wt %</th>
<th>PLQY (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.1</td>
<td>57</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.1</td>
<td>4</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>0.5</td>
<td>38</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>0.5</td>
<td>33</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>1</td>
<td>39</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>1</td>
<td>27</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>Before</td>
<td>2</td>
<td>23</td>
</tr>
<tr>
<td>Dendrimer 21</td>
<td>After</td>
<td>2</td>
<td>22</td>
</tr>
</tbody>
</table>

Table 8.15: PL summary of effect on varying PI concentration on films of Dendrimer 21 before and after solvent washing

As the data in the table shows, in all cases the value of the PLQY before solvent washing was greater than the measurement after solvent washing. For a 0.1 wt % PI film, the decrease was very pronounced and indicated, as found in the previous section, that this low concentration of PI was not sufficiently high enough to produce a fully cross-linked film. Again, as found in Section 8.4.2, a PI concentration in the film of 0.5 - 1 wt % was needed to fully cross-link the film, while values greater (2 wt %) acted to increase the quenching of the luminescence efficiency and thus lead to a decrease in the PLQY value.

The maximum PLQY value found after both curing and solving washing a Dendrimer 21 film was obtained for the film containing 0.5 wt % PI. This suggested once again that it could be beneficial to decrease the wt % of PI used in devices from the 1 wt % used thus far to a lower 0.5 wt % in order to potentially maximise the device efficiency.

### 8.4.4 Low photo-initiator concentration devices

The previous section indicated that a reduction in the PI concentration from the 1 wt % used previously in devices to a concentration of 0.5 wt % could lead to possible efficiency improvements without being detrimental to the ability to give a cross-linked film. To establish whether this was true devices were made using the same structure of ITO/Dendrimer 21/TPBI/LiF-Al as used in Section 8.3.2 for device structures E and F. Previously for device structure E no PI was used in the film (and thus the emissive layer remained uncross-linked), while device structure F used 1 wt % of PI to give a cross-linked layer of Dendrimer 21 as the emission layer. The new device of this section, with device structure AH, used
Chapter 8: Cross-linkable Dendrimers

Figure 8.35: Device characteristics for Dendrimer 21 with varying concentrations of PI. Device structure E with 0 wt % PI, device structure F with 1 wt % PI and device structure AH with 0.5 wt % PI

0.5 wt % of PI to cross-link the dendrimer layer. The characteristics of this new device is compared to these two previous devices in Figure 8.35 with the data for the three devices summarised in Table 8.16

<table>
<thead>
<tr>
<th>Device Number</th>
<th>wt % of PI</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>0</td>
<td>9.7 %</td>
<td>9.5 %</td>
<td>(0.343, 0.613)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(9.2 V, 11.1 lm/W, 32.8 cd/A)</td>
<td>(7.8 V, 15.1 lm/W, 37.2 cd/A)</td>
<td></td>
</tr>
<tr>
<td>F</td>
<td>1</td>
<td>2.1 %</td>
<td>1.8 %</td>
<td>(0.358, 0.606)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(13.4 V, 1.7 lm/W, 7.1 cd/A)</td>
<td>(12.2 V, 1.6 lm/W, 6.3 cd/A)</td>
<td></td>
</tr>
<tr>
<td>AH</td>
<td>0.5</td>
<td>4.9 %</td>
<td>4.1 %</td>
<td>(0.363, 0.600)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(5.4 V, 9.9 lm/W, 16.9 cd/A)</td>
<td>(9.2 V, 4.8 lm/W, 13.9 cd/A)</td>
<td></td>
</tr>
</tbody>
</table>

Table 8.16: Summary of device characteristics for device structures E, F and AH

For device structure AH, the EQE at 100 cd/m² was 4.1 %, which meant, as the data in the figure and data show, the device was less efficient than device structure E when no PI was used within the film, but was over twice as efficient as device structure F that contained 1 wt % PI. It was therefore concluded that the reduction in PI concentration to 0.5 wt % was beneficial to device performance and this ratio should be used in future to cross-link layers of Dendrimer 21 for both device and PL measurements.
8.4.5 Photo-initiator photophysical studies summary

This section has considered the validity of the assumption that 1 wt % of PI was the correct concentration to use in order to cross-link films of Dendrimer 21 for device and PL studies. To test this assumption numerous films of Dendrimer 21 were made of varying PI concentrations before subjecting the films to various processes before measuring the PLQY.

The investigations revealed that in general the PLQY of a film increased after the curing step, and as the content of PI in the film increased so did the quenching of the luminescence. For maximum PLQY as little PI as possible was found to be best. However, without enough PI present the film was not found to be fully cross-linkable. The best balance between giving a fully cross-linked film whilst still maintaining a high photoluminescence efficiency was found at PI concentration of 0.5 wt %. Using this concentration in a simple device structure was then shown to give an increase in the device efficiency over that of an equivalently cross-linked device structure that used the previous standard of 1 wt % PI. It was suggested that future device investigations should commence with the use of this weight percentage of PI in order to cross-link the film without sacrificing the device efficiency.

8.5 Dendrimer 22 characterisation

Having considered devices that used the single dendron cross-linkable emissive dendrimer (Dendrimer 21) in the previous sections of this chapter, to conclude this chapter a brief study was given to the second phosphorescent emissive dendrimer, that of Dendrimer 22. The structure of this dendrimer was shown previously in Figure 8.7 whereby it was seen to be similar to that of Dendrimer 21 but with the addition of a second dendron to make it a double dendron dendrimer. The effect of the inclusion of a second dendron into the dendrimer structure was first considered in Chapter 4 for Dendrimers 2 and 4. The studies of these dendrimers revealed that if such a second dendron was connected to the core without breaking the conjugation (as in Dendrimer 2), a red-shift in the emission peak resulted.

The solution absorption and emission spectra of Dendrimers 21 and 22 were measured by Dr Ruth Harding and are compared in Figure 8.36. As shown in figure, on moving from the single to the double dendron dendrimer there was, as has been previously found, a red-shift in the colour of the emission spectrum. Consequently the vibrant green coloured emission of Dendrimer 21 was replaced by a yellow-green coloured emission in Dendrimer 22.
As reported previously Dendrimer 21 was measured by Dr Ruth Harding to have a solution PLQY of 48 %, a value somewhat less than that of Dendrimer 1 which only differed in the choice of its surface groups. The measurement of the solution PLQY for Dendrimer 22, also performed by Dr Ruth Harding, was found to give the same value of 48 %. It was evident that for these cross-linkable dendrimers, unlike considered previously in Chapter 4 for Dendrimers 2 and 4, the inclusion of the second dendron did not act to improve the luminescence efficiency of the dendrimer when measured in solution.

Fortunately, the quenching observed in a solution of Dendrimer 22 was not observed in a film PLQY measurement, this yielded for a neat uncross-linked film with no PI present, as detailed in Table 8.17, a value of 62 %. This value was approximately within error equal to that of Dendrimer 21 and also to that of the non-cross-linkable Dendrimer 1. As commented previously, and unlike in solution, it appeared the choice of surface groups used had little effect on resulting photoluminescence efficiency of the film.

The effect of the addition of PI to the film is also reported in Table 8.17. For the two films that
CHAPTER 8: CROSS-LINKABLE DENDRIMERS

Figure 8.37: absorption and emission spectra of Dendrimer 22 with and without PI added.

contained PI, the films were cross-linked using UV exposure and heat before the PLQY measurement (no solvent washing was used in this case). The results revealed that presence of PI in the Dendrimer 22 film resulted in a decrease in the PLQY. However, for both Dendrimer 22 films with PI, the PLQY values measured were slightly greater than those for an equivalent amount of PI in the single dendron case of Dendrimer 21. A result that again reflected the increased protection the second dendron could give to the core.

Figure 8.37 plots the absorption and emission of the Dendrimer 22 films shown in Table 8.17 with and without PI included in the Dendrimer 22 film. As the plot shows, while the addition of PI to the film caused little change in the emission spectra there was a slight decrease in the 280 nm peak of the absorption spectra. This decrease was suggested to have arisen from the modified molecular structure of the film after cross-linking.

8.5.1 Dendrimer 22 devices

The studies of Dendrimer 22 were concluded with fabrication of bilayer devices that used films of this dendrimer as the electroluminescent layer. The devices also used an electron transport/hole blocking layer of an evaporated layer of TPBI. The resulting device structure was ITO/dendrimer/TPBI/LiF/Al. For the dendrimer films both uncross-linked and cross-linked films were considered, where for cross-
Table 8.18: Summary of device characteristics for device structures \textbf{AI}, \textbf{AJ}, \textbf{AK} and \textbf{AL}

<table>
<thead>
<tr>
<th>Device</th>
<th>Device Structure</th>
<th>wt % of PI</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m$^2$</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textbf{AI}</td>
<td>ITO/EL Layer (Dendrimer 22)/TPBI/LiF/Al</td>
<td>0</td>
<td>2.8 % (7.4 V, 3.0 lm/W, 7.1 cd/A)</td>
<td>2.6 % (9.6 V, 2.2 lm/W, 6.6 cd/A)</td>
<td>(0.497, 0.498)</td>
</tr>
<tr>
<td>\textbf{AJ}</td>
<td>ITO/EL Layer (Dendrimer 22)/TPBI/LiF/Al</td>
<td>0.5</td>
<td>3.4 % (11.8 V, 2.4 lm/W, 9.0 cd/A)</td>
<td>3.3 % (13.4 V, 2.0 lm/W, 8.8 cd/A)</td>
<td>(0.498, 0.498)</td>
</tr>
<tr>
<td>\textbf{AK}</td>
<td>ITO/EL Layer (Dendrimer 22)/TPBI/LiF/Al</td>
<td>1</td>
<td>3.8 % (11.2 V, 3.2 lm/W, 11.2 cd/A)</td>
<td>3.6 % (13.6 V, 2.5 lm/W, 10.7 cd/A)</td>
<td>(0.481, 0.513)</td>
</tr>
<tr>
<td>\textbf{AL}</td>
<td>ITO/PEDOT/EL Layer (Dendrimer 22)/TPBI/LiF/Al</td>
<td>0.5</td>
<td>5.0 % (5.6 V, 7.6 lm/W, 13.6 cd/A)</td>
<td>4.7 % (8.4 V, 4.79 lm/W, 12.6 cd/A)</td>
<td>(0.491, 0.505)</td>
</tr>
</tbody>
</table>

linking PI concentrations of 0.5 wt \% and 1 wt \% were investigated. The effect of the inclusion of a PEDOT/PSS layer within the device structure was also considered. The resulting device characteristics are shown in Figure 8.38 and are summarised for ease of comparison alongside in Table 8.18.

For device structure \textbf{AI}, that used an uncrossed film of Dendrimer 22 the resulting maximum efficiency of the device was 2.8 \% at 36 cd/m$^2$, and at a brightness of 100 cd/m$^2$ the efficiency was 2.6 \%. This device gave a yellow emission colour similar to that found in the PL measurements with a CIE coordinate of (0.497, 0.498).

In device structure \textbf{AJ}, the film of Dendrimer 22 was cross-linked using 0.5 wt \% PI. For this device the maximum efficiency was greater than that of the uncross-linked film at 3.4 \% (at 42 cd/m$^2$), and at 100 cd/m$^2$ the efficiency was 3.3 \%. The cross-linked film showed no change in emission colour from that of the uncross-linked film of device structure \textbf{AI}, in that it gave a CIE coordinate of (0.498, 0.498). A similar device performance was found for device structure \textbf{AK}, where the PI content in the film was increased to 1.0 wt \%, this device gave a maximum EQE of 3.8 \% (at 29 cd/m$^2$), and at a brightness of 100 cd/m$^2$ the EQE was 3.6 \%. However, the resulting emission spectra of this device was slightly less broad than either of the two previous cases and consequently the CIE coordinate was different at (0.481, 0.513). Such a slight change was likely to have arisen from a micro-cavity effect.

Finally in device structure \textbf{AL}, the device structure was augmented with a layer of PEDOT/PSS immediately beneath the dendrimer layer, and although such a layer has been shown to be capable of cross-linking the dendrimer without the need for PI, in this case 0.5 wt \% PI was used within the film.
Cross-linking of the film was by the UV exposure and subsequent heating of the dendrimer film layer. The resulting device was found to be the most efficient of the set giving a maximum efficiency of 5.0% but at a low brightness of only 7 cd/m². At the standard display brightness of 100 cd/m², the efficiency of the device was 4.7%. A picture of device structure AL emitting yellow coloured light which corresponded to a CIE coordinate of (0.491, 0.505), is shown in Figure 8.39. The colour showed little shift from that of the equivalent device structure AJ where no PEDOT/PSS layer was used.

The improvement in device performance on cross-linking was in contrast to the behaviour found in the single dendron cross-linkable dendrimer of Dendrimer 21 reported previously in this chapter. For example, in Section 8.3.2 with device structure E, where the dendrimer layer was not cross-linked and no PI was used, the device gave a maximum EQE of 9.7%. On adding 1 wt % PI to cross-link the dendrimer layer, in device structure F, the EQE fell to a maximum of 2.1%. In Section 8.4.4 an improvement in efficiency was found on reducing the PI content to 0.5 wt % (device structure AH), but even then there was still found to be a greater than 50% reduction in the maximum EQE from that of device structure E.
where no PI was used. In contrast, for the double dendron Dendrimer 22, while the device efficiency in the no PI case was low, there was found to be an improvement in device efficiency after cross-linking the dendrimer layer. While not as apparent in PL results as for the device measurements, it seemed that the inclusion of the second dendron into the dendrimer structure was able to improve the protection of the core, and thus the quenching effect of the presence of PI in the film was not as pronounced as in the single dendron case.

### 8.5.2 Dendrimer 22 characterisation summary

This section has considered both PL and device measurements for the double dendron cross-linkable Dendrimer 22. The studies have shown that this dendrimer had a similar PL efficiency in both film and solution to that of the equivalent cross-linkable single dendron dendrimer, but in common with the double dendron dendrimers considered in Chapter 4 showed a red-shifted spectrum to give a yellow coloured emission. Dendrimer 22 gave efficient devices both in an uncross-linked and cross-linked form, where in contrast to the single dendron cross-linkable dendrimer, the device that used a cross-linked film was more efficient than an uncross-linked film device. In the best case an maximum efficiency of 5.0 % was reported in a device using a cross-linked film of Dendrimer 22.

### 8.6 Summary

This chapter has addressed one of the practical application of dendrimers, where by demonstrating the benefits of the versatility of the dendrimer approach photo-patternable phosphorescent dendrimers were developed. This was an important step for phosphorescent organics as previously solution-processed devices have suffered from one particular disadvantage in comparison to evaporated organic devices.
namely that it has been very hard to deposit subsequent layers onto a solution deposited layer. It was thus extremely difficult to achieve pixelation of the emissive layer and the fabrication of multi-layer devices (for efficiency optimisation).

Building on the work of Meerholz on photo-patternable fluorescent polymers [200, 202–204, 206, 214–216] dendrimers with oxetane units on the dendrons were developed. The first time such an approach has ever been considered. The resulting dendrimer became cross-linked under UV exposure and by remaining fixed in position subsequent layers could be spin-coated on top. Initially it was shown that such groups could be attached to hole transporting molecules, and for the first time, solution-processable electrophosphorescent dendrimers. In the first case this was demonstrated with a single dendron iridium(III) cored dendrimer before later showing the same technique could be equally successfully applied to a double dendron iridium(III) cored dendrimer, and thus by extension the technique could readily be applied to any dendrimer. In this way it could be become possible that cross-linkable dendrimers in each of the three emissive colours could be created so bringing the prospect of the pixelation of the emissive layer somewhat closer.

The chapter also detailed that by using the cross-linkable green-emitting iridium(III) cored dendrimer multi-layer devices could be fabricated. The success of these devices opens up the possibility of obtaining an all-solution-processable dendrimer device where the optimisation of each individual layer becomes achievable. Progress towards such a goal was further demonstrated through the inclusion of a solution-processable electron transport layer within a device structure to give a device containing three solution-processable layers. Adding a PEDOT/PSS layer further increased the device complexity to four solution-processable layers, and yet still the resultant device was capable of successful light emission.

While the efficiencies of the cross-linked multi-layer devices reported were lower than has been published elsewhere, where for a green emitting cross-linked films values of around 7 cd/A have been reported [203, 206] these were with photo-patternable fluorescent polymers. For photo-patterned phosphorescent complexes high efficiencies of 59 cd/A have been reported [214, 215], but the organics used while phosphorescent were themselves not cross-linked but were required to be co-polymerised in a blend with a cross-linkable matrix. In this work simple and effective phosphorescent dendrimers were demonstrated that did not need to be host blended or used within complicated device structures in order to be cross-linked. The results reported thus show considerable promise that by using this technique very efficient cross-linked dendrimers will be possible.
This chapter has therefore detailed significant early steps towards the goal of multi-layer devices and the pixelation of the emissive layer, and in so doing identified a number of important improvements that must be met in order to attain this goal. While the results have indicated that changes in material choice may be required, they have also revealed that simple changes such as a reduction in the PI content used to cross-link the film were enough to lead to improvements in device performance. Therefore suggesting the goal of pixelated and multi-layer solution-processed dendrimer devices does not remain too far away.
Chapter 9

Highly efficient dendrimers - double dendron dendrimers

9.1 Introduction

Most current display systems are based on a three colour red-green-blue pixel configuration and thus require each of these colours to be efficiently produced throughout the entire display lifetime.

Chapters 5, 6 and 8 of this thesis all focused on methods to improve the device efficiency through respectively improving hole and electron transport, or by the use of multi-layer device structures, but in each case green-emitting devices were considered. Similarly, in Chapter 4 efficient green-emitting OLEDs were obtained through improvements in the device fabrication technique and the use of advanced dendrimer structures, namely double dendron dendrimers. In this chapter the effectiveness of the dendrimer concept was demonstrated by extending the double dendron approach to obtain the thus far ignored red and blue emission required for a three colour display.

The first part of this chapter consists of a brief study of the photophysical and device properties of a new double dendron red light-emitting dendrimer synthesised by Dr Chris Shipley at the University of Oxford. In the second and majority part of this chapter, attention was focussed on the progressional study of the attainment of efficient deep-blue light-emitting dendrimers. This work details a number of dendrimers that were all synthesised by Dr Shih-Chun Lo at the University of Oxford.

For the majority of the photophysical results presented in this chapter, and for a number of very
helpful discussions and advice, I would once again thank and acknowledge the contributions of Dr Ruth Harding. The early efforts of Dr Raghu Nath Bera in the measurements of a number of blue dendrimers some of which have been reported again here is acknowledged, as are his numerous discussions that were of great assistance in many of the early device studies. The support of CDT in financing the research of this chapter is also acknowledged.

## 9.2 Double Dendron Red

As already established, current full-colour display applications require red, green and blue electroluminescent organic semiconducting materials. The poor response of the eye in the deep-red spectral region means that to give an equivalent brightness to all the pixels in a three colour red-green-blue display, the red-emitting pixels require considerably more power and thus higher driving voltages than the other pixels [14]. Therefore the obtainment of an extremely efficient red-emitting organic semiconductor is greatly desired.

The search for efficient red OLED materials has been successfully ongoing for some time and is now well advanced due to the comparative ease of obtaining materials that have a suitable bandgap. In particular, the presence of red phosphorescence was quickly identified in platinum porphyrin complexes such as in Reference [21], and then later in iridium complexes that achieved efficiencies of 5.5 % [218]. Since these and many other attempts, red emission has also been successfully demonstrated within the group using dendrimer structures [116, 219, 220]. In particular in Reference [116], deep-red emission in a device with CIE coordinates of (0.64, 0.36), at a maximum external quantum efficiency of 5.7 % for a blend of a red-emitting dendrimer with a CBP host was reported. The dendrimer had the structure shown in Figure 9.1. This was a heteroleptic iridium(III) cored dendrimer with two dendronised 2-phenylpyridyl ligands and one benzothienylpyridyl (btp) ligand. For this dendrimer the film PLQY was measured to be 49 % in a CBP blend and 7 % in a neat film. This work demonstrated that dendrimers could successfully be used to create high efficiency deep red-emitting OLEDs.

Furthermore, because of the modular nature of the dendrimer approach, the same phenylene dendrons that were used to achieve efficient green emission were through modification of the core shown to be capable of being used to give a dendrimer with efficient red emission. By combining such red and green light-emitting dendrimers in different blending ratios it was reported that the device colour and
efficiency could easily be tuned as desired \[220\]. Unfortunately, the low quantum yields of these early red-emitting dendrimers prevented further efficiency improvements, but given the correct materials this has been shown to be possible with efficiencies in excess of 10 % now demonstrated \[216, 221\]. This section attempts to apply the double dendron approach as used successfully for green(-yellow) emitting dendrimers \[121\] to improve the efficiency of devices that contain red-emitting dendrimers.

### 9.2.1 Double dendron red-emitting dendrimers

In the previous studies of red-emitting dendrimers two dendrimers were considered \[116, 219\]. The first with structure shown in Figure 9.1 had an asymmetric structure with a single btp ligand and was found to be slightly more efficient than the second symmetric dendrimer, with structure shown in Figure 9.2 which had three btp ligands each with a dendron attached to it. In this second dendrimer, as shown in the figure, the attachment of the first phenyl ring of each dendron was in conjugation with the btp ligand. Consequently this dendrimer gave longer wavelength (deeper red) emission than that of the first dendrimer. For both these dendrimers it was found the photoluminescence quantum yield (PLQY) had a strong dependence on the dendrimer structure. The PLQYs of the asymmetric and symmetric dendrimers were in solution 47 % and 29 %, and 10 % and 7 % in a neat film respectively. The comparatively larger decrease in PLQY for the asymmetric dendrimer in the solid state was ascribed to the increased core-core interactions. The intermolecular interactions were greater in the asymmetric dendrimer because there was no dendron on the btp ligand. These studies suggested that the symmetric dendrimer was more...
suited for further development as a double dendron dendrimer for higher efficiency devices.

The resultant structure of the double dendron dendrimer was that of Dendrimer 23 (Oxford batch code CS01-057e) which is shown in Figure 9.3. In this new dendrimer, the structure was that of the published symmetric dendrimer, but with the addition of a second dendron attached in conjugation to the bottom of the btp ligand.

Unfortunately the synthesis of this dendrimer proved to be not straightforward. The asymmetric chelate ligands used in the metal d6 tris-complexes of dendrimers and small molecules means that either a facial (fac) or a meridional (mer) configuration is possible. The two configurations are shown in Figure 9.4. For the fac isomer shown in part (a) of this figure there are three approximately linear C–Ir⋯N bonds calculated to lie at an angle of 173° to each other [222]. In contrast, for the mer isomer shown in part (b) of the figure, while one C–Ir⋯N bond is the same the remaining bonds are different. The first is formed from a C–Ir–C bond where the bond length is longer than in the fac isomer, while the other bond is N⋯Ir⋯N where the bond length is shorter than in the fac isomer.

This difference in configuration results in greatly different properties, and although mer isomers
have been shown to make successful OLEDs [223], it has commonly been found that the mer isomer was less thermodynamically stable than the fac isomer. The photoluminescent and consequently electroluminescent efficiencies of the mer isomers have also been reported to be much smaller than those of the corresponding fac isomers [222, 224]. Generally the synthesis procedures followed were performed at high enough temperatures to only obtain the fac isomer, or at least convert any mer isomer into the fac form [224].

In all the tris(2-phenylpyridyl) iridum(III) dendrimer structures considered and published so far, the fac isomer, as shown in Figure 9.5(a), was used due to its greater efficiency. The synthesis of this isomer had never previously proved to be a problem with in the final reaction product no remaining mer isomer, with structure as shown in Figure 9.5(b), ever detected. However, for Dendrimer 23 the synthesis proved to be more challenging, with the complete purification or separation to the fac isomer proving impossible to achieve, instead the final product obtained was always a nine to one ratio of the mer to fac isomer. Consequently the dendrimer studied for characterisation was in this impure and less efficient form and therefore at an immediate disadvantage to the other dendrimers considered.

### 9.2.2 Photophysics of double dendron red-emitting dendrimers

The absorption and emission spectra of Dendrimer 23 are shown in Figure 9.6, whereby it can be seen that the resultant film and solution spectra were very similar. Both absorption spectra show strong absorption
Chapter 9: Highly Efficient Dendrimers - Double Dendron Dendrimers

Figure 9.6: Absorption and emission spectra of the double dendron red dendrimer, Dendrimer 23 in the region of 250-375 nm due to the ligand and dendron absorption, with a peak at 272 nm. The presence of the iridium atom core gave a small absorption at wavelengths in the range 375-525 nm. The absorption spectra were similar to that obtained previously for the single dendron fac isomer reported in References [116, 219].

Also similar were the solution and film emission spectra, each had a peak around 623 nm and a large emission shoulder around 680 nm. Consequently the resulting CIE coordinates were approximately the same: (0.681, 0.314) in solution and (0.680, 0.315) in film. In Figure 9.7 these coordinates are plotted on the CIE Chromaticity Diagram (1931 version) introduced in Figure 2.23 of Section 2.6.4. As revealed by the figure the red emission colour was very deep-red, deeper than that of the standard CIE red coordinate according the red standard of the PAL convention which has CIE coordinates of (0.64, 0.33) (indicated by the point of the black triangle shown on the figure). This deep-red colour combined with the eye’s poor response in this region means that the resultant luminous efficiencies will be further reduced in this mer isomer.

The solution PLQY of the red (fac isomer) single dendron dendrimer was reported to be 29% [219]. A value that was over double that of value of 14% that Dr Ruth Harding measured for the double dendron dendrimer - a result that showed clearly the mer isomer was much less efficient than the equivalent fac isomer. Despite the lower solution PLQY, due to the presence of the double dendron the neat film PLQY of 16% was actually greater than the 10% reported in References [116, 219] for an equivalent
measurement of the single dendron dendrimer. The low PLQY of the published dendrimers was found to be improved significantly through a reduction in the concentration quenching on blending with a CBP host. Furthermore, the similarity in PLQY between the solution and film PLQY of Dendrimer 23 suggested that concentration quenching was not a major factor in this dendrimer with the low PLQY being resultant from the nature of the less efficient mer isomer \[163\]. A similar increase in film PLQY in attaching a second dendron to the dendrimer structure was also observed for green-emitting double dendron dendrimers in Chapters 4.

### 9.2.3 Double dendron red-emitting dendrimer devices

Despite the low film PLQY of the red double dendron dendrimer, it was still believed to be worthwhile to attempt to make devices with this dendrimer. For this bilayer devices with an ETL/HBL of an evaporated layer of TPBI were made. The device structure as used previously for red devices \[116\] was again employed, that is the cathode consisted of an additional layer of Ca prior to the deposition of the LiF and Al layers in a device structure of ITO/dendrimer/TPCI/Ca/LiF/Al. For the emissive dendrimer layer the use of both neat and CBP blend films of Dendrimer 23 were investigated. The resulting characteristics are shown in Figure 9.8 and summarised in Table 9.1.

From the devices it was found that the 20:80 wt % blend of dendrimer to a CBP host was able to
attain a maximum efficiency of 4.4 % (at 14.0 V), with the neat film device giving a maximum quantum efficiency of 5.7 % at 5.8 V applied bias. These high efficiencies despite the low film (and solution) PLQY of this dendrimer were equal to the maximum obtained for a single dendron red dendrimer blend, albeit the luminous power efficiencies of 0.6 lm/W and 3.0 cd/A are considerably lower than those obtained previously [116].

Similarly at a luminance of 100 cd/m², although both neat and blend films gave high quantum efficiencies which were comparable to those of the single dendron more efficient fac isomer, the corresponding luminous power efficiencies were considerably lower. In particular, for the neat film at a brightness of 100 cd/m² the EQE was 4.7 % (9.0 V), decreasing in the blend to an EQE of 3.2 % (15.2 V). The lower efficiency of the host-blend film device in comparison to the neat film device again confirmed that, as found in PL, there were minimal concentration quenching effects in this double dendron dendrimer, and also implied that there was good charge transport in the double dendron neat film device that lead to the high efficiencies found.

The deep-red colour found in PL was also found in the devices as Figure 9.8 shows. Consequently,
CHAPTER 9: HIGHLY EFFICIENT DENDRIMERS - DOUBLE DENDRON DENDRIMERS

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 23</td>
<td>5.7 % (5.8 V, 1.6 lm/W, 3.0 cd/A)</td>
<td>4.7 %, (9.0 V, 0.9 lm/W, 2.5 cd/A)</td>
<td>(0.691, 0.308)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 23:CBP</td>
<td>4.4 % (14.0 V, 0.6 lm/W, 2.8 cd/A)</td>
<td>3.2 % (15.2 V, 0.4 lm/W, 2.0 cd/A)</td>
<td>(0.681, 0.313)</td>
</tr>
</tbody>
</table>

Table 9.1: Summary of device characteristics of bilayer devices for Dendrimer 23

Figure 9.9: Device characteristics of neat film optimised bilayer devices for Dendrimer 23

as in PL, the emission colour CIE coordinates again were beyond the standard PAL triangle; for the neat film the CIE coordinate was (0.691, 0.308), which shifted slightly to (0.681, 0.313) in the blend film.

9.2.4 Optimised double dendron red-emitting dendrimer devices

With the establishment of the new protocol for solution-processing it was attempted to optimise the device performance of a Dendrimer 23 double dendron red-emitting device. This was achieved through repeated device fabrication runs which revealed that, contrary to what was published previously in Reference [116], the use of LiF/Al in place of Ca/LiF/Al as the cathode gave improved performance. This gave the best device structure as ITO/Dendrimer 23/TPBI/LiF-Al. Similarly, by changing the spin-coating solvent from chloroform to dichloromethane a further improvement in device performance was obtained. The resultant optimised device curves are shown in Figure 9.9 with the relevant data summarised in Table 9.2 In this optimised device the maximum EQE was improved to 6.1 % (7.6 V), and at a brightness of 100 cd/m² the EQE was 5.9 % (8.4 V). The emission spectra yielded CIE coordinates of (0.691, 0.308) which when plotted on the CIE Chromaticity Diagram, as in Figure 9.10, again showed how deep-red this emission was. Figure 9.11 shows an image of this device emitting deep-red coloured light.
### Table 9.2: Summary of optimised device characteristics of bilayer devices for Dendrimer 23

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 23</td>
<td>6.1 % (7.6 V, 1.5 lm/W, 3.6 cd/A)</td>
<td>5.9 % (8.4 V, 1.3 lm/W, 3.5 cd/A)</td>
<td>(0.691, 0.308)</td>
</tr>
</tbody>
</table>

Figure 9.10: CIE diagram showing EL CIE coordinates for Dendrimer 23

#### 9.2.5 Double Dendron Red summary

The results of this section have showed that efficient red-emitting OLEDs with an EQE in excess of 6 % could be obtained. This result improved on the efficiency of the published single dendron red-emitting dendrimer, despite the lower solution PLQY of the new double dendron dendrimer. The inclusion of the second dendron was thus found to be very effective in increasing device efficiency.

The performance of the device was still somewhat less than obtained elsewhere for evaporated phos-

Figure 9.11: Image of bilayer device emission from a neat film of Dendrimer 23
phorescent small molecules where maximum EQEs of 12 - 13 % have been reported \[216, 225\]. Perhaps
more relevant is a comparison to spin-coated devices, but again this is not favourable, with the best
values of about 12 % reported by Cao et al. for phosphorescent polymer LEDs with saturated red emis-
sion \[226\], a value again reported recently by Wang et al. \[221\]. Nonetheless, such efficiencies were
obtained either in complicated multi-layer structures, or by host blending of the emissive layer. It was
recalled that Dendrimer 23 is an inefficient mer isomer with a low film PLQY. Hence, if the equivalent
and more efficient fac isomer of this double dendron dendrimer could be synthesised successfully that
could maintain the solution PLQY of 29 % found in the mer isomer, and translate this efficiency to film,
then it could be expected that an optimised device using this double dendron fac isomer dendrimer could
double the device efficiency to give EQEs of around 12 %. In this way the performance would equal
and could even possibly improve on the phosphorescent emitters that have so far been reported in the
literature.

### 9.3 Double Dendron Blue

Currently one of the main limiting factors that are preventing OLEDs from becoming the dominant
display type is the short lifetime of the blue-emitting organic semiconducting layer. This arises, because
to produce a blue emission colour, semiconductors with a large energy bandgap are required. This
often results in semiconductors with low electron affinities, and makes the efficient injection of charges
(holes and electrons) into the organic layer much more difficult than for red and green emission \[227\].
A common method of achieving efficient blue electrophosphorescence in OLEDs has been by energy
transfer from a fluorescent host to a phosphorescent guest molecule \[228, 229\]. Yet there are obstacles
to using energy transfer to excite deep-blue guest phosphors. In particular, as the energy gap of the
guest becomes wider, for efficient exothermic energy transfer from host to guest, the energy gap of the
host must also become wider. While there are some wide bandgap hosts \[230, 232\], to electrically inject
carriers and form excitons on them remains difficult due to the large energy barriers that can still exist
between the host and guest \[230\].

The technique of host blending is often followed to aid charge transport and prevent concentration
quenching of the guest material. However several considerations have to be taken into account when
choosing a suitable host for a phosphorescent material. Firstly, in order for exothermic energy transfer
to occur, the triplet energy level of the host must be greater than that of the guest, and the energy transfer
rate from the host to the guest must be much faster than the decay rate of the host. Secondly, the host must have a higher energy bandgap than that of the guest blue-emitting material to facilitate efficient energy transfer from the host to the guest. Thirdly, the energy levels of the host must allow charges to be preferentially trapped on the guest, and the host must be capable of charge transport. Lastly, the film forming properties of the host must be sufficient to ensure phase separation or pinhole formation does not occur.

For these reasons with blue-emitting semiconducting materials the common CBP host used in green-emitting OLEDs, which has a bandgap 3.1 eV, would be normally replaced with a larger bandgap host such as mCP (bandgap of 3.5 eV). Nevertheless, although great progress has been made in the obtainment of efficient sky-blue emission [117, 143, 230–235], there remains still such scope for the development of a very-efficient and very deep-blue emitting organic semiconductor.

As has been described previously, the function of the host is to increase the phosphorescent chromophore spacing which acts to reduce the effects of the concentration quenching of the phosphorescence and thus increases the luminescence efficiency [34, 118, 119]. An alternative method to achieve this same effect has been demonstrated in dendrimers, where through the choice of dendrons used the intermolecular interactions could be controlled. More specifically, the addition of a second or double dendron to the dendrimer structure has been shown, in both red and green light-emitting dendrimers, to increase both the photoluminescent and electroluminescent efficiency. In this way the need for blending in a host material to reduce intermolecular interactions was negated. This result was particularly promising for efficient deep-blue emission, because if no host was needed, the problem of the lack of suitable deep-blue hosts becomes eliminated.

The discovery of a highly efficient blue phosphorescent material that was capable of being solution-processed would have immediate implications for displays. Hence deep-blue phosphorescence formed the main focus of one of the areas of the collaborative research programme with Dr Paul Burn and group at the University of Oxford, and CDT Ltd. Previous work had established a provisional direction of research in order to obtain this aim through the synthesis and photophysical studies of a number of single dendron dendrimers and small molecular cores [117, 163, 235, 236]. Through such studies, knowledge had been gained on, for example, the role of the intermolecular interactions in the dendrimer as revealed through variations in the PLQY values and through charge transport measurements. This had enabled the standard iridium(III) cored dendrimers, that have been successfully used for green-emitting OLEDs,
to be adapted through, for example, changing the ligands and dendrons to gradually tune the emission to give a bluer emission. Unfortunately, until recently, such changes have also caused a reduction in both the PL and EL efficiency. This work therefore started from the studies of a highly efficient dendrimer that emitted light with a sky-blue colour before using the knowledge gained from this dendrimer to gradually improve the colour of the emitted light whilst still retaining high efficiency, so leading ultimately to a highly efficient deep-blue emitting phosphorescent solution-processable dendrimer.

9.3.1 Highly efficient light-blue emitting non-fluorinated dendrimers

The early reports of phosphorescent blue devices were from heteroleptic complexes of bis[2-(2,4-difluorophenyl)pyridyl]-iridium(III) with either a co-ligand of acetylacetonate [FIr(acac)], or picolinate (FIrpic) [228]. This blue emission arose from the attachment of two fluorine (F) atoms to the ligand phenyl ring ortho and para to the pyridyl moiety of the what would be a normally green-emitting parent core of the standard fac-tris(2-phenylpyridyl) iridium [Ir(ppy)]$_3$. Fluorine is known as the most chemically reactive and electronegative of all the elements, and can readily form compounds with most other elements. The attachment of fluorine atoms while decreasing the stability of the molecule was able to shift the emission to give a sky-blue colour with corresponding CIE coordinates of (0.16, 0.29). Even then this depth of blue colour was only possible through the inclusion of a copper phthalocyanine hole transport layer within the device structure that could act to absorb some of the longer wavelength emission. While the approach gave some subsequent interesting and good results, there was a limit to the depth of the blue colour possible by using homoleptic and heteroleptic iridium(III) complexes such as FIr6 as in References [230, 231] that were based on this 2-(2,4-difluorophenyl)pyridyl ligand.

Prior to the commencement of the work detailed in this thesis, it was decided that, to obtain high efficiency deep-blue phosphorescence from iridium(III) complexes, a new type of ligand was required. Approaches such as the use of arylpyrazolyl ligands [224], or fluorine free carbene-containing ligands [232], have since been investigated elsewhere with some success. The method adopted here to obtain blue emission was to replace the pyridyl moiety of the 2-phenylpyridyl ligand with a triazole ring to give a homoleptic fac-tris(5-aryltriazolyl)iridium(III) complex [235]. Through calculations it was known triazole has a higher LUMO energy than that of pyridine [224], and thus the energy band gap was increased and a bluer emission arises. A further blue shift in the emission spectra was induced by the attachment of electron-withdrawing groups, or atoms such as fluorine to the phenyl ring of the fac-tris(phenyltriazolyl)-
iridium(III) complexes.

The structure of the non-fluorinated core material subsequently synthesised (Core A), fac-tris(1-methyl-5-phenyl-3-n-propyl-1H-[1,2,4]triazolyl)iridium(III) is shown in Figure 9.12(a). The structure of a first generation single dendron version of this dendrimer with biphenyl dendrons is shown in Figure 9.12(b). The neat film emission spectrum of non-fluorinated Core A was taken by Dr Raghu Nath Bera (data not shown) and was found to give CIE co-ordinates of (0.207, 0.303), while for the dendrimer a slight red-shift in the spectrum gave the CIE co-ordinate as (0.184, 0.319). It was also observed that the PL spectrum of the dendrimer was narrower than that of the core which indicated intermolecular interactions were reduced due to the incorporation of the chromophore inside the dendrimer architecture.

For the non-fluorinated core material a film PLQY value of 9% was found, which increased to 32% with the addition of the dendron. A similar improvement in PLQY was found in a measurement of the solution PLQY of the materials; 66% for the non-fluorinated core, and 73% for the non-fluorinated single dendron dendrimer. All these measurements were performed by Dr Raghu Nath Bera. Solid-state PL lifetimes of the two materials were also measured by Dr Raghu Nath Bera, with the decay observed to be non-exponential in nature with a longer average lifetime found in the single dendron dendrimer. While the results indicated that the attachment of the dendron reduced the intermolecular interactions significantly, the non-exponential nature of the decay suggested that intermolecular interactions were not completely controlled by the attachment of a single dendron, and thus the PL and consequently EL efficiency was limited [236].

To further enhance the efficiency, the approach could have been to attach higher generation of dendrons [135], and/or by attaching more dendrons to the core [121]. After the success of the double dendron approach for both efficient green and red emission it was decided that this later approach was again to be followed for blue-emitting dendrimers. The resulting structure of the double dendron dendrimer was as shown in Figure 9.12(c), this Dendrimer 24 (Oxford batch code SCL28-19AB), was non-fluorinated with biphenyl-based dendrons, and contained a non-conjugated linkage to attach the second dendron which, as described in Chapter 4, was used to reduce the red-shift of the ligand to potentially give a deeper blue emission [117].
Figure 9.12: Non-fluorinated molecular structures of (a) the phenyltriazolyl core, Core A, (b) a first generation single dendron phenyltriazolyl dendrimer, and (c) the double dendron Dendrimer 24

9.3.1.1 Photophysics of the non-fluorinated double dendron light-blue emitting dendrimer

The absorption and emission spectra of Dendrimer 24 were measured by Dr Ruth Harding and are plotted in Figure 9.13. For this dendrimer the absorption spectra in solution and film were very similar and showed only one clear peak located around 270 nm. The absorption in this region was due to $\pi - \pi^*$ transitions of the ligands. In Dendrimer 24 there was found to be a slight broadening of the emission spectra on moving from solution to film, which can be attributed to concentration quenching effects in the film. The result was that in the film the shoulder around 500 nm became less pronounced, and the resulting colour was then a much lighter blue. In solution the PL spectra was measured by Dr Ruth Harding to give a CIE coordinate of (0.157, 0.297), and in film a CIE coordinate of (0.166, 0.399). It thus seemed that the addition to the corresponding core of one and then two biphenyl dendrons (Dendrimer 24) caused a stepwise decrease of the depth of the blue emission colour [163].

Yet it is important before proceeding with further material development to establish how the change in the blue colour related to changes in the photoluminescence efficiency. Thus the photophysical properties in solution and film of Dendrimer 24 were measured by Dr Ruth Harding. The values recorded are detailed in Table 9.3 alongside those of the previously measured relevant non-fluorinated core and single
Figure 9.13: Absorption and emission spectra of the non-fluorinated Dendrimer 24

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Solution PLQY (%)</th>
<th>Solution CIE coordinate</th>
<th>Film PLQY (%)</th>
<th>Film CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core A</td>
<td>66</td>
<td>(0.159, 0.203)</td>
<td>9</td>
<td>(0.159, 0.203)</td>
</tr>
<tr>
<td>Single dendron</td>
<td>73</td>
<td>(0.160, 0.290)</td>
<td>32</td>
<td>(0.184, 0.319)</td>
</tr>
<tr>
<td>Double dendron (Dendrimer 24)</td>
<td>69</td>
<td>(0.157, 0.297)</td>
<td>48</td>
<td>(0.166, 0.339)</td>
</tr>
</tbody>
</table>

Table 9.3: Summary of the photoluminescence properties of Dendrimer 24 in comparison to its non-fluorinated core molecule (Core A), and the single dendron version, the structures of these three molecules were shown in Figure 9.12.

dendron dendrimer (measurements made by Dr Raghu Nath Bera).

As Table 9.3 shows for Dendrimer 24, that while the PLQY values in solution showed little change all being around 70%, there was on the addition of one and then two biphenyl dendrons, found to be a stepwise improvement in PL efficiency with a value of 48% measured for the double dendron dendrimer. The increase in efficiency with corresponding decrease of blue colour depth is shown effectively in a pictorial representation in the CIE chromaticity diagram of Figure 9.14. It appeared for Dendrimer 24 the addition of biphenyl dendrons was able to reduce the concentration quenching effects commonly observed on moving from a solution to film, with the more dendrons that were added the more such effects were reduced in the film. Albeit the addition of the dendrons did cause a loss in the depth of the blue colour.
9.3.2 Highly efficient light-blue emitting fluorinated dendrimers

The previous section demonstrated the double dendron approach was suitable for obtaining high solution and film photoluminescence efficiencies in blue-emitting dendrimers. Unfortunately, it was also found the increasing addition of more dendrons also decreased the depth of the blue colour. In order to improve the depth of this blue colour the method of attaching a fluorine (F) atom to the ligand phenyl ring of the iridium core was investigated. The attachment of the fluorine unit to the phenyl rings of the core complex has two main effects; first, the emission is blue shifted and second the materials become less luminescent. For the simple iridium(III) complex the blue shift in the emission has been reported to be due a stabilisation of the highest occupied molecular orbital that is greater than lowest unoccupied molecular orbital [228].

The resultant fluorinated core (Core B), had a structure as shown in Figure 9.15. The PL spectra of the fluorinated core gave a much deeper blue colour than the non-fluorinated equivalent of Core A, giving a CIE coordinate of (0.156, 0.163) in solution [237]. This core was also measured by Dr Ruth Harding to give a solution PLQY of 40 %, and thus showed improved luminescence efficiency over that of the non-fluorinated core [163, 237].

With the knowledge of the success of this core complex a fluorinated double dendron dendrimer was
thus synthesised using this core. The resultant structure of this dendrimer, Dendrimer 25 (SCL28-40BB), is shown in Figure 9.16. The difference between this dendrimer and the non-fluorinated biphenyl double dendron dendrimer was the attachment of the fluorine (F) atom to the phenyl ring in conjugation with the iridium atom, and the replacement of the biphenyl dendrons and 2-ethylhexyloxy surface groups with tert-butyl side groups.

9.3.2.1 Photophysics of the fluorinated double dendron light-blue emitting dendrimer

The absorption and emission spectra of the fluorinated double dendron Dendrimer 25 were measured by Dr Ruth Harding and are plotted in Figure 9.13. As for the non-fluorinated version of this dendrimer, the absorption spectra in solution and film were very similar. A peak in both spectra was observed at approximately 255 nm. As previously, the $\pi - \pi^*$ transitions of the ligands cause the absorption in this region [163].

For Dendrimer 25, the solution and film emission spectra both were slightly different and thus had different CIE coordinates. In solution the spectrum was quite narrow with two distinct peaks located at 442 nm and 469 nm, and this gave a CIE coordinate of (0.153, 0.152), a coordinate close to that obtained for the core complex. The depth of this blue colour showed that the inclusion of the fluorine atom to achieve such an affect was successful. On moving to the neat film spectra it was evident a large degree of concentration quenching was present despite the use of the double dendron. The emission
Figure 9.17: Absorption and emission spectra of the fluorinated double dendron Dendrimer 25

spectra broadened and the peak around 440 nm disappeared. The resulting CIE coordinates were (0.197, 0.242), indicating the depth of blue colour found in the core complex had decreased on adding the double dendron.

The solution and film PLQY were measured by Dr Ruth Harding and are detailed in Table 9.4 alongside the values previously measured for the relevant fluorinated core (Core B) [163, 237]. As the data in Table 9.4 shows, for Dendrimer 24 the addition of the two dendrons was found to increase significantly the value of the solution PLQY; from a value of 40 % in the fluorinated core, to 63 % in the double dendron Dendrimer 25. In this fluorinated dendrimer the neat film PLQY was approximately equal, at a value of 21 %, to the 20 % found for the core. Therefore in this case, unlike for the non-fluorinated dendrimer, the dendrons were not effective in reducing concentration quenching effects on moving to the solid state. The increased quenching in the fluorinated dendrimer structure has been attributed to an increase in non-radiative decay and vibrational coupling with the attachment of the fluorine atom [163, 237].

9.3.3 Double dendron light-blue emitting dendrimer devices

The high film PLQY of the non-fluorinated double dendron Dendrimer 24 suggested high efficiency devices could be possible with this dendrimer. While the fluorinated double dendron Dendrimer 25 suggested a good blue emission colour could be achieved with this dendrimer. Consequently to maximise the
CHAPTER 9: HIGHLY EFFICIENT DENDRIMERS - DOUBLE DENDRON DENDRIMERS

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Solution PLQY (%)</th>
<th>Solution CIE coordinate</th>
<th>Film PLQY (%)</th>
<th>Film CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Core B</td>
<td>40</td>
<td>(0.156, 0.163)</td>
<td>20</td>
<td>(0.183, 0.215)</td>
</tr>
<tr>
<td>Double dendron</td>
<td>63</td>
<td>(0.153, 0.152)</td>
<td>21</td>
<td>(0.197, 0.242)</td>
</tr>
</tbody>
</table>

Table 9.4: Summary of the photoluminescence properties of the fluorinated double dendron Dendrimer 25 in comparison to its fluorinated core molecule (Core B)

Figure 9.18: Device characteristics of bilayer devices for Dendrimer 24

Device performance of both dendrimers bilayer devices were immediately attempted with Dendrimer 24 and 25. For these devices the standard bilayer structure was used containing a layer of the electron transport/hole blocking material TPBI evaporated onto the spin-coated dendrimer layer prior to the evaporation of a LiF-Al cathode. The resulting device characteristics are summarised in Table 9.5 and plotted for Dendrimer 24 in Figure 9.18 and for Dendrimer 25 in Figure 9.19.

From Figure 9.19 it can be determined that for Dendrimer 25 the maximum external quantum efficiency (EQE) of the device was 1.1 % at an applied bias of 6.1 V, this efficiency was maintained to a bias of 6.7 V where the standard brightness of 100 cd/m² was achieved. The resultant emission spectrum is also shown in Figure 9.18 from which it can be noted that the spectrum was much broader than the corresponding photoluminescence spectrum, and hence the emission colour was a much lighter blue,

Figure 9.19: Device characteristics of bilayer devices for Dendrimer 25
**Table 9.5: Summary of bilayer device characteristics for Dendrimers 24 and 25**

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 24</td>
<td>9.5 % (5.8 V, 9.2 lm/W, 16.9 cd/A)</td>
<td>8.9 % (7.3 V, 6.9 lm/W, 15.6 cd/A)</td>
<td>(0.167, 0.321)</td>
</tr>
<tr>
<td>100 wt % Dendrimer 25</td>
<td>1.1 % (6.1 V, 1.5 lm/W, 3.0 cd/A)</td>
<td>1.1 % (6.7 V, 1.3 lm/W, 2.8 cd/A)</td>
<td>(0.197, 0.334)</td>
</tr>
</tbody>
</table>

**Figure 9.20:** CIE diagram showing location of CIE coordinates of the EL spectra of neat film bilayer devices from Dendrimers 24 and 25 corresponding to a CIE coordinate of (0.197, 0.334). The depth of this blue colour can be seen from the location of this coordinate when plotted on the CIE chromaticity diagram of Figure 9.20.

In contrast as Figure 9.18 shows, in the alternate double dendron non-fluorinated structure of Dendrimer 24, the blue colour found in the photoluminescence film spectra was maintained, albeit the original colour was a lighter blue than in the fluorinated structure. Nonetheless, the colour that resulted with CIE coordinates of (0.167, 0.321), was still, as the CIE chromaticity diagram of Figure 9.20 shows, slightly deeper than in the device with the fluorinated dendrimer.

The improvement in the blue colour with Dendrimer 24 also came with an improvement in the device efficiency. The higher neat film PLQY of this Dendrimer resulted in the device having a very high maximum efficiency of 9.5 % at a bias of 5.8 V for which the luminance was 34 cd/m². At the standard 100 cd/m² brightness, the high EQE was maintained giving 8.9 % at 7.3 V. These device results were
very good, considering the maximum efficiency possible given the neat film PLQY of the dendrimer, and the fact that no attempt was made to improve the $\Phi_{ESCAPE}$ factor of the EQE equation (Equation 2.13). The results showed that the double dendron approach was effective, and an improvement on the low efficiency and greenish-blue emission colour of the previously considered single dendron blue-emitting dendrimers [117]. In that case, a deeper blue colour with high device efficiency was only able to be realised on blending the single dendron dendrimer into a host material. The benefits of eliminating the need for a host material have already been outlined. The fact that such a high efficiency could be obtained without the use of a host by using a dendrimer with a double dendron structure, was an important step in obtaining very efficient and deep-blue emission.

**9.3.4 High triplet energy dendrimers for deep-blue emission**

For efficient phosphorescent OLEDs it was often found that host blending was required [21, 25, 27, 116, 117, 123, 135, 142, 145]. To be effective, the host should have higher triplet ($T_1$) energy than the guest, and an energy gap ($E_g$) greater than that of the host [228, 230]. Consequently a wide bandgap dendron with high triplet energy was required. Similarly, to avoid energy transfer to the dendrons, the triplet energy of dendron must be greater than that of the core, with no exciton delocalisation from the core to dendron to avoid energy transfer to the dendrons. The radiative lifetime of the triplet state will increase with respect to core as the dendron triplet state has a very long radiative lifetime. Additionally, the dendrons no longer separate emissive cores effectively in the neat film, which results in the quenching of the photoluminescence and broadening of the emission spectrum due to increased intermolecular interactions. Strong vibrational coupling effects have also been shown to have lead to an increased non-radiative decay of the luminescence, and thus a reduced PLQY. The activation energy for non-radiative decay has been found to depend on the environment, with the non-radiative decay rate decreasing when the emissive materials were placed in a solid host, and/or higher generations or multiple dendrons were used [163, 237].

Previous dendrimer work has found, that despite improvement in the solution PLQY, there was no improvement in the neat film PLQY for a fluorinated version of the biphenyl double dendron Dendrimer 24 with respect to a measurement purely of the fluorinated phenyl-triazine iridium core. There was instead found to be a 15 nm red-shift in the solution emission spectra and an increase in the red tail, while there was a broadening of the emission spectrum on moving from solution to film. It was concluded the use
of biphenyl dendrons was not effective for deep-blue emission in inhibiting intermolecular interactions that caused quenching. While such dendrons, have been successfully used with red [116], green [26] and sky-blue [117] emissive iridium(III) complexes to give highly efficient solution processed OLEDs, they have low triplet energies and were concluded not to be suitable for deep-blue phosphorescent complexes. A new type of high triplet energy dendron was required [163].

In designing the new dendrimer structure it was important to ensure that the dendrons used did not have a lower triplet energy than the core so as to avoid the effects of phosphorescence quenching [230]. For the deep-blue emissive core considered previously of fac-tris(1-methyl-5-phenyl-3-n-propyl-1H-[1,2,4]triazolyl)iridium(III) with structure shown in Figure 9.12(a), the triplet energy was calculated to be 2.79 eV. To give a new dendrimer with high triplet energy dendrons, the dendrimer considered comprised diphenylethylene groups with saturated ethylene moieties breaking the conjugation. The basic core was again that of the fluorinated core (Core B), with structure fac-tris[1-methyl-5-(4-fluorophenyl)-3-propyl-[1,2,4]triazolyl]iridium(III) shown in Figure 9.15. For this core a triplet energy of 2.89 eV was calculated, and Dr Ruth Harding has measured a solution PLQY of 40 % and a film PLQY of 20 %. The attachment of the diphenylethylene dendrons to the core gave the double dendron dendrimers of Dendrimer 26 (SCL32-95) and Dendrimer 27 (SCL34-46), with structures shown in Figure 9.21 and Figure 9.22 respectively. The saturated or non-conjugated ethylene moieties used in the dendrons for these dendrimers gave the effect of making the dendrons ‘floppy’, and the final product of the synthesis was a sticky oil rather than the usual powder. Dendrimer 27 differed from that of Dendrimer 26 in that it did not use any 2-ethylhexyloxy surface groups on the ends of the dendrons. By not attaching solubilising surface groups it was hoped the glass transition temperature (T_g) of the dendrimer would be increased and thus help make the final synthesis reaction product less oily. While this was found to increase the T_g, the dendrimer was still equally oily.

9.3.4.1 Photophysics of high triplet energy dendrimers for deep-blue emission

The absorption and emission spectra of both Dendrimers 26 and 27 were measured by Dr Ruth Harding and are shown in Figure 9.23 and Figure 9.24 respectively. For Dendrimer 26 the absorption spectra in solution and film were very similar in that both showed a peak around 343 nm with minimal absorption elsewhere. The emission spectra in solution and film were also similar, and showed no broadening on moving from solution to film. This suggested there were no intermolecular interactions in the solid
state. Both emission spectra had two peaks, one around 439 nm and one around 473 nm. In solution the emission spectra gave, as detailed in Table 9.6, a CIE coordinate of (0.159, 0.181). There was thus a red-shift in wavelength of the spectra with respect to that of the core, which gave a spectrum yielding CIE coordinates of (0.156, 0.163) in solution (data not shown). Although the attachment of the dendrons did give a blue-shift in the film spectral colour with respect to the core. In the core the CIE coordinates were (0.183, 0.215) in film, and shifted to (0.167, 0.191) in the neat Dendrimer 26 film [163].

The photoluminescence quantum yields in both solution and film were measured by Dr Ruth Harding for Dendrimer 26 and are tabulated in Table 9.6 alongside those of the core molecule with structure shown in Figure 9.15. In solution the PLQY was 45 %, a slightly increased number over that of the measurement of the core. For a neat film, the PLQY was 49 % which was over double that of the core complex, and very close to that of the value measured in solution. The result gave a further indication that there was no increase in the intermolecular interactions in the solid state. Therefore, a high photoluminescence efficiency and a deep-blue colour has been observed using a double dendron dendrimer. Furthermore, the use of non-conjugated double dendrons was found to be very effective in controlling intermolecular interactions for deep-blue emission [163].

A comparison of this dendrimer to the highly efficient but light-blue emitting non-fluorinated double dendron Dendrimer 24 is shown in Figure 9.25. The figure plots the CIE coordinates of the film spectra of the two dendrimers on a CIE chromaticity diagram. As the indicated by the figure, the addition of the
fluoride to Dendrimer 26 successfully improved the depth of the blue colour. The change to high triplet energy dendrons avoided the effect of energy transfer to the dendron and thus quenching effects were reduced, so meaning there was no accompany loss in luminescence efficiency in the film. The results give great promise for future device development.

For Dendrimer 27, where the 2-ethylhexyloxy surface groups were not used, the resulting emission spectra in solution was found to be equivalent to that of Dendrimer 26 where surface groups were used. Therefore, the surface groups made no contribution to the emission spectra. The corresponding CIE coordinates for the solution emission spectrum of Dendrimer 27 were (0.160, 0.178), and thus showed little change from those of core or Dendrimer 26. As for Dendrimer 26, in a neat film of Dendrimer 27 there was a blue-shift in the emission colour from that of the core; the dendrimer gave CIE coordinates of (0.157, 0.182) [163].

The solution PLQY of Dendrimer 27 was measured by Dr Ruth Harding and is recorded in Table 9.6 to be 42 %, a value that was slightly lower than that of Dendrimer 26 but still within error reflecting the
similarity of these two dendrimers in solution. In a neat film however, a value of only 21% was measured by Dr Ruth Harding, similar to that of the core but almost half that of Dendrimer 26. It was proposed that this reduction in film PLQY arose from the ‘floppy’ nature of the dendrons. The non-conjugated ethylene moieties are expected to collapse, and in this case, without the surface groups, to do in such a way as to be detrimental to the luminescence efficiency.

9.3.4.2 High triplet energy dendrimer devices from Dendrimer 26

For Dendrimer 26 bilayer devices were attempted using neat and mCP host blended films of the dendrimer as the emissive layer in a standard bilayer structure. This used an evaporated ETL/HBL of TPBI and a LiF-Al cathode. Unfortunately this attempt was not successful, due to what appeared to be a significant oxidation of the cathode, and/or reaction of the cathode layer with the layers below. In particular, on removal from the evaporator the Dendrimer 26 neat film device had very white, possibly oxidised, aluminium cathodes that were not smooth. A similar problem, although not to the same extent, was observed in the devices that used the mCP blend films. Consequently the neat film devices were unable to be electrically tested due to an inability to make contact to the metal layers. The mCP blend films were slightly better with, in some cases, contact possible but the resultant devices were not efficient. Possible causes for this may have been: firstly, a reaction of the dendrimer layer with either the TPBI layer, and/or the cathode layers; or secondly, due to poor device fabrication caused by problems with the evaporation - due to problems with the evaporator, the evaporation of the cathode layers was performed using a higher
CHAPTER 9: HIGHLY EFFICIENT DENDRIMERS - DOUBLE DENDRON DENDRIMERS

Figure 9.25: CIE diagram showing location of CIE coordinates of the film PL spectra for the double dendron Dendrimers 24 and 26

than normal pressure and consequently a higher rate - this may have lead to unequal layer deposition and consequently non-homogeneous films.

To investigate whether the first of these suggestions was the cause of the problems observed, further devices could have been made without the TPBI layer (i.e. single layer devices), or also with a different cathode layer configuration. Also it would be desirable to know the PLQY of mCP blend films and also the PLQY of a blend of the dendrimer with TPBI. In this way it would be determined whether the blending with such materials acted to change the PLQY, and if so would there be an optimum blending ratio to obtain a maximum in the PLQY. Unfortunately there was an insufficient quantity of Dendrimer 26 to allow such measurements to be made.

Instead it was decided, with the small amount of remaining Dendrimer 26, to investigate the second of the reasons detailed above for the poor device fabrication. For this, a second set of bilayer devices were fabricated but this time taking extra care to ensure no issues were observed in the fabrication process. More precisely, care was taken during the evaporation to ensure that the evaporation pressure was as good as possible throughout, and the evaporation rates were kept low and as steady as possible. For the devices the same basic bilayer structure as before was used, with both neat and host blended (mCP and CBP) films of Dendrimer 26 used as the emissive layer.
As in the first device fabrication attempt, the neat film devices on removing from the evaporator, were significantly whiter than those of the blended films, the top aluminium cathode layer did not appear smooth, and these devices were unable to be electrically tested. For both types of the blend film devices, testing was possible even though the films were not smooth. The resultant emission was not homogeneous across the entire device area but was instead patchy with areas of bright and darker emission.

In any case, the resulting device characteristics of the best 20:80 wt % Dendrimer 26:CBP blend device are shown in Figure 9.26 with the relevant data summarised in Table 9.7. As shown in the data of the table, for this device the maximum efficiency was 0.4 % for a bias of 11.0 V. At the standard brightness of 100 cd/m² the EQE was 0.2 % at a bias voltage of 18.8 V. Although the efficiency of this device was lower the blue colour, as seen in PL, was much deeper than in the Dendrimer 25 devices, with a spectrum corresponding to a CIE coordinate of (0.195, 0.251) found.

The resulting device characteristics of the 20:80 wt % Dendrimer 26:mCP blend device are shown in Figure 9.27 and are summarised in Table 9.7. The results indicated that the change to the higher triplet energy host of mCP gave an improvement in the device performance. The maximum EQE obtained was double that of the CBP blend device at value of 0.8 % for a bias of 18.2 V and at a brightness of 55 cd/m². An increase in the applied bias to 19.4 V raised the light output of the device to a luminance
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Table 9.7: Summary of bilayer device characteristics for Dendrimer 26

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:80 wt % Dendrimer 26:CBP</td>
<td>0.4 % (11.0 V, 0.2 lm/W, 0.7 cd/A)</td>
<td>0.2 % (18.8 V, 0.1 lm/W, 0.4 cd/A)</td>
<td>(0.195, 0.251)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 26:mCP</td>
<td>0.8 % (18.2 V, 0.2 lm/W, 1.3 cd/A)</td>
<td>0.7 % (19.4 V, 0.2 lm/W, 1.2 cd/A)</td>
<td>(0.197, 0.227)</td>
</tr>
</tbody>
</table>

Figure 9.28: Figure showing how EL emission spectra for 20:80 wt % Dendrimer 26:mCP devices changes with applied bias voltage of 100 cd/m², which caused a slight fall in efficiency to an EQE of 0.7 %. The deep-blue colour of the device showed a slight improvement over that of the CBP blend to give a CIE coordinate of (0.197, 0.227), but in both cases the colour of the device emission was less blue than in PL.

It was further noted that although the blueness of the colour did fade after testing (as seen in a number of blue emitters and particularly the early phosphorescent blue dendrimers [236]), the general emission spectral shape did seem notably stable with voltage. On increasing voltage, as shown in Figure 9.28 the spectra did become increasingly whiter, and on reducing the voltage maintained this white colour. Although Dendrimer 24 was far more stable in the standard device structure and consequently far more efficient than Dendrimer 26, the fluorinated high triplet energy dendrimer was capable of giving a much deeper blue emission colour than in Dendrimer 24. Regardless, in both cases the device structure was not optimised, which must occur in order for the high PLQY seen in films indicating the possibility in devices of a high internal quantum efficiency to be realised in a device structure.
9.3.4.3 High triplet energy dendrimer devices from Dendrimer 27

Dendrimer 27 was, as discussed previously, completely analogous to Dendrimer 26 other than that it was made without for any surface groups in an attempt to increase the $T_g$ and thus make the dendrimer less oily. This dendrimer was synthesised after the study of Dendrimer 26 when the problems with the devices outlined in the previous sections had been found. It was hoped that by making this change the less oily dendrimer would be more stable and thus reduce any possible reaction of the dendrimer with the cathode that may have caused the problems described. Despite the lack of surface groups no solubility problems were observed with this dendrimer and hence both neat and host blended film devices were able to be fabricated. To begin with the standard bilayer structure was attempted using an evaporated layer of TPBI as the ETL/HBL with a cathode of LiF and Al.

Unlike in the devices with Dendrimer 26, the problems with the LiF-Al cathode were not found to the same extent with the devices that used films of Dendrimer 27. Although a very slight whitening of the cathode was still observed in the neat film device. Consequently, both the neat film and mCP host blended film devices were able to be tested; the resulting device characteristics are shown in Figure 9.29 and Figure 9.30. The resultant data for these two devices is summarised in Table 9.8.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m² or Max Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 27</td>
<td>0.3 % (12.0 V, 0.1 lm/W, 0.4 cd/A)</td>
<td>0.1 % (9.2 V, 0.1 lm/W, 0.2 cd/A)</td>
<td>(0.164, 0.219)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 27:mCP</td>
<td>2.1 % (15.0 V, 0.6 lm/W, 2.8 cd/A)</td>
<td>2.1 % (9 cd/m², 15.0 V, 0.6 lm/W, 2.8 cd/A)</td>
<td>(0.151, 0.170)</td>
</tr>
</tbody>
</table>

Table 9.8: Summary of neat and blend film bilayer device characteristics for Dendrimer 27 using a LiF-Al cathode

Figure 9.29: Device characteristics of bilayer devices with a LiF-Al cathode for Dendrimer 27 emission layer
For the neat film device the maximum efficiency recorded was 0.3 % at 12.0 V, and at a brightness of 100 cd/m\(^2\) the EQE was 0.1 % at a bias of 9.2 V. The device efficiency was low, reflecting the poor film quality, but there was found to be a further improvement in the blue colour in comparison to the Dendrimer 26 devices, with the emission spectrum corresponding to a CIE coordinate of (0.164, 0.219).

For the 20:80 wt % Dendrimer 27:mCP blend film device the characteristics shown in Figure 9.30 were obtained. The inclusion of the host material was found to lead to a seven times improvement in the maximum device efficiency obtained, with the blend device giving a maximum EQE of 2.1 %. This EQE occurred at the maximum applied voltage of 15.0 V for a maximum luminance of 9 cd/m\(^2\), and thus, despite the efficiency improvement over that of the neat film device, the low luminance of this device meant it was not a good device.

The Dendrimer 27-mCP host blended film device did show a further improvement of the depth of blue emission colour. In this case the emission spectrum gave a CIE coordinate of (0.151, 0.170), the first time one of our phosphorescent dendrimer blue-emitting devices has produced a CIE y-coordinate less than 0.2. Thus far there have been very few other demonstrations of such deep-blue phosphorescence. In 2004, CC Wu \textit{et al.} reported a non-doped device based on a deep-blue terfluorene emitter that gave a maximum EQE of 5.3 % for a very deep-blue CIE coordinate of (0.158, 0.041) [53]. In 2005 Holmes \textit{et al.} in Reference [232] demonstrated, for the first time, efficient, saturated blue electrophosphorescence using fluorine-free \textit{fac} and \textit{mer} isomers of a phosphorescent iridium small molecule to give a CIE coordinate of (0.17, 0.08) for a peak EQE of 5.8 %. This device, used a multi-layer evaporated structure, and still remains one of the very few reports of deep-blue electrophosphorescence. Also that same year Lee \textit{et al.} reported efficient blue electroluminescence in a device that utilised a mono(styryl)amine as a dopant in 2-methyl-9,10-di(2-naphthyl)-anthracene to obtain a maximum EQE of 5.1 % and a CIE coordinate...
of (0.14, 0.13) [238]. In another report in 2005, Duan et al. used devices based on a distyrylbenzene derivative as the host emitter and obtained a CIE coordinate of (0.16, 0.13) for a peak current efficiency of 4.88 cd/A [239].

In 2007 Tonzola et al. used n-type oligoquinolines to obtain devices with a maximum EQE of 6.56 % with CIE coordinates of (0.15, 0.16) [227]. Also later that year, Yang et al. in References [233, 234], reported the second instance of deep-blue electroluminescence from a phosphorescent iridium emitter, this device, again used a highly complex device structure, gave a CIE coordinate of (0.16, 0.18) for a maximum EQE of 5.8 %. Finally, in the early part of 2008, K-C Wu et al. reported a high device efficiency of 5.2 %, with a CIE coordinate of (0.15, 0.11), using pyrene-based diarylbenzenes as the emissive layer [240]. All these reports required complicated device structures with, in most cases, many evaporated layers, and/or host blending to achieve such deep-blue emission at high efficiency. While reports such as the one by Tang et al. exist, detailing deep-blue emission with a CIE coordinate of (0.16, 0.05) obtained from a spin-coated organic layer, the organics used were not phosphorescent and thus the devices were not efficient. The reasonable efficiency and more particularly the depth of the blue colour obtained from the phosphorescent Dendrimer 27 device thus compares favourably with the current literature, but does so using a simple device architecture with a spin-coated emissive layer. The Dendrimer 27 device reported has thus demonstrated a considerable advancement towards obtaining deep-blue emission at high efficiency.

9.3.4.4 Improving the efficiency of high triplet energy dendrimer devices from Dendrimer 27

The previous section detailed significant progress towards obtaining highly efficient deep-blue emission in an OLED structure by obtaining for the first time a phosphorescent dendrimer that was capable of achieving an emission colour corresponding to a CIE y-coordinate of less than 0.2. With this device the depth of blue colour of our phosphorescent dendrimers became comparable to those achieved previously using fluorescent dendrimers [241]. The fact that such deep-blue emission was possible in a device that had visual defects in its cathode layer suggested a further increased efficiency could be possible should such be problems be eliminated.

The problem of the whitening of the cathode layers observed after the evaporation stage has been suggested to be perhaps related to the use of the LiF-Al cathode in these devices. To determine whether this was true a new device set was attempted using a simple single layer device structure of ITO/Dendrimer 27/
Ca-Al, where no TPBI as a HBL/ETL was included within the device structure. For this simple configuration, which had no charge confinement, the efficiencies of the devices were very low, less than 0.03% (data not shown). Nevertheless the change in cathode formation was found to be successful, with no problems observed with the cathode layers in this device structure on removal from the evaporator.

Having established that the problems observed with the LiF-Al cathode were not present when a cathode of Ca-Al was used in a simple device structure, in order to improve the device performance a method of charge confinement was introduced. For this a further device set was attempted using a layer of TPBI included within the device to give a bilayer structure of ITO/Dendrimer 27/TPBI/Ca-Al. For the emissive layer both neat and mCP host blended layers of Dendrimer 27 were investigated. The resulting device characteristics are summarised in Table 9.9 with the current-voltage and EQE-voltage curves and the emission spectra plotted in Figures 9.31 and 9.32. As the data revealed, in this case, for both neat and mCP blend film devices, there was found to be a great improvement in device performance with both devices reaching the standard 100 cd/m² luminance at reasonable efficiencies. For the neat film device at this 100 cd/m² brightness, the EQE was 0.9%, and increased to a maximum of 1.0% at a bias of 6.2 V. The mCP blend device gave at the 100 cd/m² luminance an EQE of 1.9% (19.4 V), which was also equal to the maximum efficiency of the device.

This device performance was thus a considerable improvement on the results obtained for a device with a LiF-Al cathode, both for Dendrimer 26 and Dendrimer 27. The neat film device gave similar CIE coordinates with either cathode configuration; (0.164, 0.219) with LiF-Al, and (0.167, 0.252) with Ca-Al cathodes. For the blend film device with a Ca-Al cathode there was found to be an enhancement in the depth of the blue emission colour, presumably from a large and favourable micro-cavity effect that did not occur in the neat film device and the blend device with a LiF-Al cathode. This latter device gave an emission spectrum that corresponded to a CIE coordinate of (0.147, 0.158). Figure 9.33 shows an image of this Dendrimer 27 device emitting blue light, while the colour of this emission is plotted on a CIE chromaticity diagram in Figure 9.34 in comparison to the best devices achieved from Dendrimers 24 and 25. As the figure shows, the change to the high triplet energy dendrons in Dendrimer 27 was very successful in increasing the depth of the blue emissive colour with respect to Dendrimer 25 which had a similar blue solution PL CIE coordinate of (0.153, 0.152).
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<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 27</td>
<td>1.0 % (6.2 V, 0.8 lm/W, 1.7 cd/A)</td>
<td>0.9 % (9.8 V, 0.5 lm/W, 2.6 cd/A)</td>
<td>(0.167, 0.252)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 27:mCP</td>
<td>1.9 % (20.0 V, 0.4 lm/W, 2.4 cd/A)</td>
<td>1.9 % (19.4 V, 0.4 lm/W, 2.4 cd/A)</td>
<td>(0.147, 0.158)</td>
</tr>
</tbody>
</table>

Table 9.9: Summary of neat and blend film bilayer device characteristics for Dendrimer 27 using a Ca-Al cathode

Figure 9.31: Device characteristics of bilayer devices with a Ca-Al cathode for Dendrimer 27 emission layer

9.3.4.5 High triplet energy dendrimers summary

This section has demonstrated a key achievement in the development of very efficient and deep-blue emitting OLEDs. The results demonstrated that deep-blue emission was possible in electroluminescence as well as photoluminescence. For the first time a phosphorescent dendrimer capable of achieving an emission colour corresponding to a CIE y-coordinate of less than 0.2 was reported, equating the performance in terms of colour depth of phosphorescent dendrimers with our fluorescent dendrimers [241]. In the best case, for a bilayer device with an emissive layer of a Dendrimer 27 and mCP host blend, a CIE coordinate of (0.147, 0.158) was recorded, for a maximum device efficiency of just under 2 %. This result was particularly promising, as although the device efficiency was lower than has been reported in the literature for a similar depth of colour, this device was, unlike those in the literature, made in a simple structure that used a spin-coated emissive layer. These devices therefore bring the prospect of simple-to-fabricate, and hence low-cost, high performance blue-emitting OLEDs ever closer.
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9.3.5 Deep-blue phosphorescence with twisted methyl substituted biphenyl units

The previous section detailed the considerable progress made in obtaining deep-blue phosphorescent OLEDs through the use of high triplet energy dendrons comprised of diphenylethylene groups. While the approach was in many ways successful, a key disadvantage found with the use of such ‘floppy’ dendrons was that the resultant dendrimer was oily and could not be made into a powder, which gave significant processing disadvantages. In this section it was investigated whether the depth of the blue colour and the PL and EL efficiency could be improved by using an alternative dendron type that did not result in this oily formation.

A number of possibilities were proposed and ultimately rejected after consideration of their likely ease of synthesis, and the analysis and calculation of the triplet energies. Consequently, it was decided twisted methyl substituted biphenyl units would be suitable for use. Mesitylene, or the 1,3,5-isomer of trimethylbenzene (C₉H₁₂), is an aromatic hydrocarbon which has three methyl substituents attached to a benzene ring. When such groups were used as the dendrons, the steric crowding caused a large degree of twisting, restricting the conjugation length and therefore widening the energy gap, and so giving a high
For such dendrons the same fluorinated core (Core B shown in Figure 9.15) that was successfully used for deep-blue emission in Dendrimers 25, 26 and 27 was again used. The resulting fluorinated double dendron dendrimer with highly twisted mesitylene dendrons was that of Dendrimer 28 (SCL35-42), with structure shown in Figure 9.35. An alternative version of this dendrimer was also synthesised without the 2-ethylhexyloxy surface groups to give Dendrimer 29 (SCL35-53), with structure shown in Figure 9.36. The change in surface groups changes the molecular weight of the dendrimer and thus its $T_g$ and melting point. The change in surface group also changes the degree of twist slightly, and thus in the less confined dendrimer structure of Dendrimer 29 (without surface groups), the triplet energy will be marginally greater than that of more confined Dendrimer 28 structure.

As Dendrimer 28 shared the same basic core as Dendrimers 26 and 27, it was calculated to have the same triplet energy of 2.89 eV in comparison to the value of 2.79 eV for Core A used in the initial blue double dendron dendrimer of Dendrimer 24. Similarly the HOMO and LUMO energy levels of Dendrimer 28 were calculated as 5.88 eV and 2.3 eV respectively, which show a much deeper HOMO level than the 5.69 eV found for the light-blue emitting Dendrimer 24 for the same LUMO energy. Dendrimer 29 possessed similar values as Dendrimer 28, that is the removal of the surface groups has
minimal effect on the HOMO and LUMO energy levels of the dendrimer \[163\].

### 9.3.5.1 Photophysics of mesitylene dendrons for deep-blue emission

The high triplet energy of Dendrimer 28 (and 29) gave promise that a deep-blue colour could be possible in the photoluminescence spectra. On measuring the spectrum of both dendrimers in film and solution, shown in Figure 9.37 for Dendrimer 28 and Figure 9.38 for Dendrimer 29, this was indeed found to be the case. For the solution spectra of Dendrimer 28, the CIE coordinate was (0.162, 0.167) in degassed THF, and (0.157, 0.156) in degassed toluene. On moving to the neat film of Dendrimer 28, the deep-blue colour was maintained, with the spectra yielding a similar CIE coordinate of (0.159, 0.164). The similarity in these coordinates, as shown in the similarity in the emission spectra, suggested there were minimal core-to-core interactions in the solid state. To establish if this was true, the photoluminescence quantum yield was measured in both solution and film. For a degassed THF solution of Dendrimer 28 a value of 62\% was found, increasing to 77\% in a degassed toluene solution, whereas for a neat film (spun from CH\(_2\)Cl\(_2\)) a PLQY of 60\% was measured. The similarity of these values (within error) confirmed that minimal quenching occurred in the solid state \[163\].

A similar deep-blue colour in solution was also found for Dendrimer 29, as the spectra in Figure 9.38 show, giving a CIE coordinate of (0.159, 0.175) in degassed toluene solution. The neat film spectrum was not as defined missing the peak around 436 nm and showing only a single peak around 469 nm.
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Figure 9.37: Solution emission spectra of Dendrimer 28

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Solution PLQY (%)</th>
<th>Solution CIE coordinate</th>
<th>Film PLQY (%)</th>
<th>Film CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dendrimer 28</td>
<td>77</td>
<td>(0.157, 0.156)</td>
<td>60</td>
<td>(0.159, 0.164)</td>
</tr>
<tr>
<td>Dendrimer 29</td>
<td>71</td>
<td>(0.159, 0.175)</td>
<td>12</td>
<td>(0.171, 0.222)</td>
</tr>
</tbody>
</table>

Table 9.10: Summary of the photoluminescence properties of the double dendron deep-blue emitting dendrimers, Dendrimers 28 and 29. Solution PLQY values measured in toluene.

Figure 9.38: Solution emission spectra of Dendrimer 29
Consequently the CIE coordinate of the neat film spectra was not as deep blue and only gave a CIE coordinate of (0.171, 0.222). The PLQY of the neat film was also low at 12 %. The PLQY for a degassed toluene solution was 71 %, and for a solid solution film with mCP a value of 35 % was found, but for a deep-blue colour with a CIE coordinate of (0.157, 0.193).

It thus appeared that in Dendrimer 29, unlike Dendrimer 28, suffered from some solid state quenching effects. As the purity of both dendrimers has been confirmed to be very high and thus can not account for the differences between them, it was evident that the surface groups had a very important role in these dendrimers. Such an effect on simply changing the surface groups has not been observed for other dendrimers. In this case it was proposed that the effect observed may have been related to differing non-radiative decay rates. This would have resulted from the change in the configuration of dendrimer structure that arose due to change in confinement of the highly twisted mesitylene dendrons on removal of the surface groups.

The CIE coordinate of the film emission spectrum of Dendrimer 28 is plotted in Figure 9.39 on a CIE chromaticity diagram alongside those of the highly efficient but light blue-emitting Dendrimer 25, and the first high triplet energy dendrimer of Dendrimer 26. As the indicated by the figure, the change from Dendrimer 25 to 26 to 28 gave a gradual but significant improvement in the depth of the blue emission.
colour, and furthermore increased the photoluminescence efficiency of the film.

9.3.5.2 Single layer deep-blue emitting devices with Dendrimer 28

The high PL efficiency and deep-blue colour from the double mesitylene dendron Dendrimer 28 was promising for devices. To investigate this, single layer neat film devices were made using a structure of ITO/dendrimer/Ca-Al, where a neat film of Dendrimer 28 was used as the emissive layer. The resulting device was successful in that it showed no whitening of the cathode layer on removal from the evaporator, as has been observed for the previous dendrimers, and was able to give deep-blue light emission. The characteristics of the device are shown in Figure 9.40 and summarised in Table 9.11.

Despite having no charge confinement within the single layer device structure, the device was still capable of attaining a maximum EQE of 0.6 % at a high applied bias of 30.0 V. At the standard brightness of 100 cd/m², the EQE was 0.4 % for 27.0 V applied bias. The colour of the emission, as the figure shows, was very deep-blue and yielded a spectrum close to that of the PL spectrum, and gave a CIE coordinate of (0.173, 0.205). An image of the device emitting deep-blue light is shown in Figure 9.41.

![Figure 9.40: Device characteristics of single layer devices for Dendrimer 28](image)

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 28</td>
<td>0.6 % (30.0 V, 0.1 lm/W, 0.9 cd/A)</td>
<td>0.4 % (27.0 V, 0.1 lm/W, 0.7 cd/A)</td>
<td>(0.173, 0.205)</td>
</tr>
</tbody>
</table>

Table 9.11: Summary of neat film single layer device characteristics for Dendrimer 28

9.3.5.3 Single layer deep-blue emitting devices with Dendrimer 29

Single layer devices of structure ITO/dendrimer/Ca-Al were also fabricated for Dendrimer 29 using both neat and mCP host blended films of the dendrimer as the emissive layer. The resulting device
characteristics are shown in Figure 9.42 and summarised in Table 9.12. In this case the neat and blend film device performance was very poor. For the neat film device, the maximum brightness was 36 cd/m$^2$ at the maximum applied voltage of 30.0 V for an efficiency of 0.1 %. As the figure shows, the device emission spectrum was also very weak and noisy, and gave a lighter blue emission than was found for Dendrimer 28, this corresponded to a CIE coordinate of (0.250, 0.347). It was proposed that the low PL efficiency of this dendrimer in a neat film accounted for its low EL efficiency.

An improvement in the spectral stability and colour was found on moving to a 20:80 wt % Dendrimer 29:mCP blend film device which gave CIE coordinates of (0.169, 0.150). There was however no corresponding increase in device efficiency, with the maximum EQE again occurring at the maximum luminance, but in this case this was 19 cd/m$^2$, and gave an EQE of 0.1 % at a bias of 26.5 V.

As for Dendrimer 28 the low efficiency of the Dendrimer 29 devices arose from the lack of charge carrier confinement in the single layer device structure. In such a simple structure the faster hole carriers were easily capable of reaching the cathode before they had a chance to recombine and thus the luminescence efficiency was low. To improve the recombination and therefore the device efficiency, an additional electron transporting/hole blocking layer would be required within the device structure.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>Maximum Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 29</td>
<td>0.1 % (30.0 V, 0.02 lm/W, 0.2 cd/A)</td>
<td>0.1 % (36 cd/m$^2$, 30.0 V, 0.02 lm/W, 0.2 cd/A)</td>
<td>(0.250, 0.347)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 29:mCP</td>
<td>0.1 % (26.5 V, 0.01 lm/W, 0.1 cd/A)</td>
<td>0.1 % (19 cd/m$^2$, 26.5 V, 0.01 lm/W, 0.1 cd/A)</td>
<td>(0.169, 0.150)</td>
</tr>
</tbody>
</table>

Table 9.12: Summary of device characteristics of single layer devices for Dendrimer 29
9.3.6 Bilayer devices for deep-blue emission

In the previous sections for devices with both Dendrimers 28 and 29, the lack of an electron transporting/hole blocking layer within the single layer device structure was found to severely limit the device efficiency. Unfortunately due to the deep energy and triplet levels of these dendrimers an ideally energy matched material to form such a layer does not exist. In the meantime a range of commercially available materials were identified as possibilities that could be successfully evaporated onto the dendrimer layer to try to provide some of the functions of an electron transporting/hole blocking layer. TPBI has been successively used as an electron transporting layer to improve the luminescence efficiencies in both red [116] and green-emitting OLEDs [26, 124], but could be predicted to quench the phosphorescence in deep-blue devices due to its lower triplet energy. In addition the HOMO and LUMO energy levels of TPBI are poorly aligned to those of the deep-blue dendrimers making charge injection and transport far from optimum.

In contrast a series of (triphenylsilyl)benzene small molecule complexes have been successfully used by Forrest and others as ultrawide energy gap hosts (UGHs) [230-232]. In particular, both p-
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Figure 9.43: The structures of (a) UGH2, (b) UGH3 and (c) PBD

bis(triphenylsilyl) benzene (UGH2) and \( m \)-bis-(triphenylsilyl)benzene (UGH3) with structures shown in Figure 9.43(a) and (b) have been found to lead to successful and very efficient light-blue emission. These materials have a HOMO energy of 7.2 eV and a LUMO energy of 2.8 eV, and so have a very large bandgap. Also both have a very high triplet energy of 3.5 eV. The reports of such materials in the literature have been as host materials deposited by co-evaporation with the emissive guest. Such a technique is not possible with spin-coated dendrimers, and as they were found to be insoluble in all solvents attempted, their use was restricted to discrete injection/transport layers evaporated onto the dendrimer layer and not as alternative host materials.

The final material selected was an oxadiazole small molecule capable of electron transport with a chemical formula of 2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), with structure shown in Figure 9.43(c). This material has been frequently used as a co-host or layer to improve the electron transport within a device structure, for example see References [242–245]. The deep energy levels of PBD, which has a HOMO energy of 6.3 eV and a LUMO energy of 2.4 eV, would suggest it may act as a suitable host and/or transport-injection layer for deep-blue emission. This material also gave the additional advantage of being soluble in standard solvents so also potentially could be used as a possible alternative host material. In this section these materials were attempted in various multi-layer device geometries. For these devices the fluorinated highly twisted mesitylene double dendron Dendrimer 28 was used as the emissive dendrimer layer.

9.3.6.1 Dendrimer 28 bilayer devices with TPBI

As TPBI has been established as the standard hole blocking /electron transport layer (HBL/ETL) in the dendrimer devices so far attempted, it was thought worthwhile to establish the benchmark of performance of a device containing this layer. Devices with a 60 nm thick evaporated layer of TPBI in a structure of
ITO/dendrimer/TPBI/LiF-Al were therefore fabricated. The emissive layer was formed from both neat and dendrimer-host blends of Dendrimer 28. The hosts used were mCP, PBD, and a blend of mCP and PBD. The dendrimer was doped at a 20:80 wt % concentration of dendrimer to host for the single host, and 20:52:28 wt % blend ratio of dendrimer-mCP-PBD for the double host.

No device characteristics were able to be obtained from the devices that used PBD as a host material, or those that used a blend of mCP and PBD as a double host. The devices that used a single host of mCP and those of the neat dendrimer film devices proved more successful. The resulting device characteristics of these devices are shown in Figures 9.44 and 9.45 with the data of both devices summarised in Table 9.13.

For the neat film device the maximum EQE recorded was 3.4 % (24.8 V), and at the standard brightness of 100 cd/m² the EQE was 2.2 % (18.0 V). The emission colour of the device was very deep-blue, with an emission spectrum that corresponded to a CIE coordinate of (0.154, 0.143). For the 20:80 wt % Dendrimer 28:mCP blend device the maximum EQE found was lower than in the neat film giving 1.0 % (23.4 V), and at a brightness of 100 cd/m² the EQE was 0.8 % (23.4 V). The corresponding emission spectrum was also slightly less deep-blue than the neat film and yielded CIE coordinates of (0.148, 0.186). The high efficiency of these device with a TPBI layer, that was, as discussed above, not ideally suited to the function of hole blocking/electron transport for blue-emitting dendrimers, was promising for further improvements in efficient deep-blue emission should materials with more suitable energy and triplet levels be found.

![Graphs](image)

Figure 9.44: Device characteristics of bilayer devices with an ETL/HBL of TPBI for Dendrimer 28

### 9.3.6.2 Dendrimer 28 bilayer devices with PBD

The previous section established that TPBI was not ideally suited to act as an injection or transport layer for deep-blue emission in dendrimer OLEDs. In this section the use of the alternate organic material of

Figure 9.45: Device characteristics of bilayer mCP blend devices with an ETL/HBL of TPBI for Dendrimer 28

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 28</td>
<td>3.4 % (24.8 V, 0.5 lm/W, 4.2 cd/A)</td>
<td>2.2 % (18.0 V, 0.5 lm/W, 2.6 cd/A)</td>
<td>(0.154, 0.143)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 28:mCP</td>
<td>1.0 % (23.4 V, 0.2 lm/W, 1.4 cd/A)</td>
<td>0.8 % (23.4 V, 0.2 lm/W, 1.1 cd/A)</td>
<td>(0.148, 0.186)</td>
</tr>
</tbody>
</table>

Table 9.13: Summary of the characteristics of bilayer devices with an HBL/ETL of TPBI for Dendrimer 28

2-(4-biphenylyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD), with structure shown in Figure 9.43(c), was attempted as this layer. Devices were fabricated with an evaporated 40 nm thick layer of PBD in a device structure of ITO/dendrimer/PBD/LiF-Al to give the device structure shown in Figure 9.46. The emissive dendrimer layer was formed from either a neat film or a mCP host blended film of Dendrimer 28. The resulting device characteristics are shown in Figures 9.47 with the results summarised in Table 9.14.

Figure 9.46: Structure of a device with a PBD layer

For the neat film device of Dendrimer 28 with a PBD layer included within the structure, the resultant maximum efficiency was 3.9 %, and at a brightness of 100 cd/m² the EQE was 2.1 %. The
Figure 9.47: Device characteristics of bilayer devices with PBD for Dendrimer 28

depth-blue emission of the single layer device was also maintained with the spectrum giving a CIE coordinate of (0.159, 0.174). On blending the dendrimer with a mCP host, the depth-blue colour was further improved with the CIE coordinate as (0.161, 0.144) with no loss in efficiency. For this 20:80 wt % Dendrimer 28:mCP blend, the maximum EQE was 3.8 %, which occurred at a brightness of 100 cd/m².

Both the neat and blend film devices of Dendrimer 28 in this new bilayer structure, incorporating the oxadiazole small molecule of PBD as a second layer within the device structure, were very good. The devices showed a slight improvement over the efficiency of the devices with a TPBI layer, and an eight times increase in the efficiency over that of the single layer device structure, whilst still maintaining a very deep-blue emission colour. It seemed that the electron transport nature of the oxadiazole moieties within the PBD molecule were successful in improving the electron transport, and thus the charge balance within the device structure, and so gave an improvement in the device efficiency.

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 28</td>
<td>3.9 % (5.0 V, 3.4 lm/W, 5.4 cd/A)</td>
<td>2.1 % (15.0 V, 0.61 lm/W, 2.9 cd/A)</td>
<td>(0.159, 0.174)</td>
</tr>
<tr>
<td>20:80 wt % Dendrimer 28:mCP</td>
<td>3.8 % (16.6 V, 0.8 lm/W, 4.6 cd/A)</td>
<td>3.8 % (16.2 V, 0.89 lm/W, 4.6 cd/A)</td>
<td>(0.161, 0.144)</td>
</tr>
</tbody>
</table>

Table 9.14: Summary of bilayer (with PBD) device characteristics for Dendrimer 28
Figure 9.48: CIE diagram showing location of CIE coordinates of the EL spectra of bilayer devices from Dendrimers 24, 25, 27 and 28

Figure 9.48 showed that with this device another significant step was made towards highly efficient deep-blue emission. The figure plots on the CIE chromaticity diagram the CIE coordinate of the 20:80 wt % Dendrimer 28:mCP blended film device alongside those of the best performing devices obtained from Dendrimers 24, 25 and 27, as plotted previously in Figure 9.34. The fact such improvements were possible through simple structural changes in the dendron used was a good demonstration of the effectiveness of the dendrimer concept. Furthermore, as the resultant device efficiency was still much less than maximum theoretically possible, given the high 60 % neat film PLQY of Dendrimer 28, it remains highly probable these efficient devices could be further improved. Such improvements could arise from, for example, the further optimisation of the layer thickness, or the use of additional layers in the device structure to control both the recombination zone and the charge balance.

9.3.6.3 Dendrimer 28 bilayer devices with UGH2

The previous sections established that TPBI, despite its success as an electron transport/injection layer to improve the luminescence efficiencies of both red [116] and green-emitting OLEDs [26, 27], was not suitable for deep-blue emission in dendrimer OLEDs. An improvement in efficiency, and thus device performance, was found on changing to the use of the oxadiazole small molecule of PBD as this layer.
To investigate whether the device performance can be further improved, in this section another alternative material was investigated. The ultrahigh energy gap material $p$-bis(triphenylsilyl)benzene (UGH2) with a HOMO energy level of 7.2 eV, and LUMO of 2.8 eV, has been used elsewhere as a successful host for blue emission [230–232]. The structure of UGH2 was shown in Figure 9.43(a).

Devices were fabricated using a thin 20 nm layer of UGH2 as the evaporated injection/blocking layer, in a device structure of ITO/dendrimer/UGH2/LiF-Al as shown in Figure 9.49, where Dendrimer 28 was used as the emissive dendrimer layer. The corresponding energy levels of the device structure are shown in Figure 9.50. With this structure the devices were not good, obtaining a maximum efficiency of less than 0.05 %, and thus the data has not been reported within this thesis.

In an attempt to improve this poor device performance a second set of devices were fabricated using a thicker UGH2 layer. For these devices the UGH2 layer thickness was increased to 34 nm. The film thickness of the dendrimer layer also varied to elucidate whether there was any EL layer thickness dependency on the device efficiency. This was done by using two different concentrations of the neat dendrimer in solution; one at 10 mg/ml, and one at 20 mg/ml. In this case the resulting devices were successful and yielded the characteristic device curves shown in Figure 9.51, with the relevant device data summarised in Table 9.15.

At the lower concentration of 10 mg/ml, the resulting maximum device efficiency of the neat film device was 2.6 %, and at a brightness of 100 cd/m$^2$ the EQE was 1.1 %. For this device the emission spectrum gave a CIE coordinate of (0.174, 0.198). A doubling of the dendrimer in solution concentration to 20 mg/ml, and thus an increase in the emissive layer thickness, was found to result in an improvement
in the device efficiency. In this case the maximum device efficiency was 3.3%. However this efficiency was obtained at the maximum luminance of 42 cd/m² at a bias of 20.0 V, and so this device was actually in many ways worse than that of the device with a thinner emissive layer. The increase in film thickness did however result in a favourable micro-cavity effect that improved the depth of the blue emissive colour slightly to give a spectra corresponding to CIE coordinates of (0.169, 0.168). The results suggested that there was an emission layer thickness dependence on the resultant device efficiency.

Moreover, in any case it was evident that a layer of evaporated UGH2, immediately on top of the dendrimer layer and below the LiF-Al cathode layer, did not lead to any improvement in device performance. It seemed that the UGH2 layer was not suited to the role it was trying to provide in this device structure for deep-blue emission. It was likely that the deep energy levels of this material, were, as shown in Figure 9.50, not favourable to charge injection and transport, and consequently the resultant device was not efficient.

### 9.3.6.4 Dendrimer 28 bilayer devices with UGH3

The previous section established that UGH2 was not ideally suited to provide the function of an electron injection or transport layer directly between the dendrimer emission layer and the metal cathode layer. In this section it was considered whether the second ultrahigh energy gap host of m-bis-
Table 9.15: Summary of bilayer (with UGH2) device characteristics for Dendrimer 28

<table>
<thead>
<tr>
<th>Dendrimer</th>
<th>Conc. (mg/ml)</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m^2 or Max Brightness</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 wt % Dendrimer 28</td>
<td>20</td>
<td>3.3 % (20.0 V, 0.69 lm/W, 4.4 cd/A)</td>
<td>3.3 % (42 cd/m^2, 20.0 V, 0.69 lm/W, 4.4 cd/A)</td>
<td>(0.169, 0.168)</td>
</tr>
<tr>
<td>100 wt % Dendrimer 28</td>
<td>10</td>
<td>2.6 % (20.0 V, 0.62 lm/W, 3.9 cd/A)</td>
<td>1.1 % (18.0 V, 0.31 lm/W, 1.8 cd/A)</td>
<td>(0.174, 0.198)</td>
</tr>
</tbody>
</table>

(triphenylsilyl)benzene (UGH3) \([230, 232]\) was able to improve on the device performance.

Bilayer devices were attempted from spin-coated neat films of Dendrimer 28 in combination with an evaporated layer of UGH3 as the injection/transport layer. The device structure was ITO/Dendrimer 28/UGH3/LiF-Al. In this case the device gave a maximum luminance of only 3 cd/m^2 at a bias of 20.0 V, for which the device was only 0.002 % efficient. The performance was therefore worse than that of the device with a UGH2 layer and hence the device results have not been reported within the thesis.

It is clear that as with the case of a UGH2 layer, with the deep energy levels of UGH3 there was as before very poor charge injection and transport within the device structure. A further reason for the poor device efficiency may also have arisen from the UGH layers causing a quenching of the luminescence, this factor was considered in subsequent sections. In any case, the device results have shown that neither UGH2 nor UGH3 were suitable for providing the function of an electron injection or transport layer within a device structure.

### 9.3.6.5 Multi-layer devices

The poorly matched energy levels of TPBI to the blue-emitting dendrimers would be predicted to give a device with poor charge transport and thus low efficiency. In actual fact, as the results of the previous sections have demonstrated, the devices that used TPBI were found to be capable of producing efficient (at 100 cd/m^2 the EQE was 2.2 %) devices using blue-emitting dendrimers. The attempts to replace TPBI with the ultrahigh energy UGH materials, that have been used elsewhere as host materials, were found to be unsuccessful. The poor device performance was thought to have arisen from either the UGH quenching the luminescence, or more likely from charge imbalance and poor charge transport due to the deep energy levels of the UGH materials.
The poor performance of devices with UGH layers initiated the study of other layers that could be used instead in its place. For this both mCP and PBD were considered. When used as such an evaporated layer in a structure of ITO/dendrimer/mCP/LiF-Al, the inclusion of the mCP layer was found to give very inefficient devices (EQE < 0.1%) (data not shown), and therefore it was concluded to be unsuitable to provide this function. Of more interest proved PBD, through which efficient devices were able to be obtained as detailed in Section 9.3.6.2. For a neat film of the fluorinated high triplet energy deep-blue emitting dendrimer (Dendrimer 28), a maximum device efficiency of 3.9% (2.1% at 100 cd/m²) was found. It is recalled that in Section 9.3.3 a neat film device of the non-fluorinated Dendrimer 24 in a bilayer structure with TPBI as the ETL/HBL, had a maximum efficiency of 9.5%, and an EQE of 8.9% at a brightness of 100 cd/m². A 20:80 wt % blend of this dendrimer with a CBP host gave a maximum EQE of 6.5% (6.4% at 100 cd/m²). In this section an investigation into the use of a PBD layer in place of TPBI in devices with an emissive layer of Dendrimer 24 was conducted to see if the efficiency of light-blue emitting OLEDs was improved also.

A set of devices were fabricated using a structure of ITO/dendrimer/PBD/LiF-Al. The dendrimer layer was formed from either neat or CBP host blended films of the non-fluorinated light-blue emitting Dendrimer 24. For the resulting devices there was found to be no improvement in efficiency in the neat film device case (data not shown), but with the 20:80 wt % Dendrimer 24-CBP host blend film, and with
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Device Structure | Max EQE | EQE at 100 cd/m² | CIE coordinate
--- | --- | --- | ---
ITO/20:80 wt % Dendrimer 24:CBP/PBD/LiF-Al | 12.3 % (8.0 V, 10.5 lm/W, 26.6 cd/A) | 11.4 % (10.6 V, 7.3 lm/W, 24.6 cd/A) | (0.202, 0.338)
ITO/20:80 wt % Dendrimer 24:CBP/TPBI/LiF-Al | 6.5 % (13.6 V, 3.4 lm/W, 14.8 cd/A) | 6.4 % (15.6 V, 2.9 lm/W, 14.5 cd/A) | (0.200, 0.365)
ITO/100 wt % Dendrimer 24/TPBI/LiF-Al | 9.5 % (5.8 V, 9.2 lm/W, 16.9 cd/A) | 8.9 % (7.3 V, 6.9 lm/W, 15.6 cd/A) | (0.167, 0.321)

Table 9.16: Comparison of device characteristics for Dendrimer 24 with various device structures

As the data reveals, the host blended films with either of the two ETLs of TPBI and PBD passed a similar current through the device, with the device with PBD giving a slightly greater light output. Consequently, the device with the PBD layer was much more efficient than that of the blend film device with an ETL of TPBI. Also noticeable was that the current through the neat film device with a TPBI layer as the ETL was much greater than that of both blend film devices. This increase in current, allied with a lower luminance of the device at high voltages, meant the efficiency of the blended film device with a PBD layer was greater than that of the neat film device with a TPBI layer. The resulting emission spectrum of the blend device with a PBD layer was however slightly different from that of both the neat and blend film devices that used a TPBI layer, this reflecting the slight loss in blue colour found with the PBD layer. Consequently the resulting CIE coordinate of the device with PBD reflected this, giving a coordinate of (0.202, 0.338).

These results prompted the question of how the devices could be further optimised. One possible method would be to replicate the multi-layer evaporated structures of the devices reported in the literature that have successfully used UGH as host materials [230-232]. In these reports the maximum quantum efficiency obtained was 11.6 % for a light-blue emission colour corresponding to a CIE coordinate of (0.16, 0.26). Regrettably, the exact replication of these published structures was not possible, due in
part to the lack of all the materials, and moreover the insolubility of the UGH host at concentrations suitable for spin-coated devices. Consequently a number of alternative multi-layer device structures were considered using, in addition to a spin-coated emissive dendrimer layer, further spin-coated layers of PEDOT/PSS and PVK at the anode side to improve hole injection; with evaporated layers of mCP, UGH2, PBD used to improve electron injection/transport.

The studies were made using the fluorinated deep-blue emitting Dendrimer 28 as the emissive layer. For this a number of device structures were attempted with varying degrees of success. The studies revealed the best device performance was obtained from a device with a structure of ITO/PEDOT/PVK/mCP/dendrimer/UGH2/PBD/LiF-Al. For this device the PEDOT/PSS layer was deposited by spin-coating onto the ITO layer. PVK (poly-N-vinylcarbazole) has HOMO and LUMO energies of 5.5 eV and 2.0 eV respectively, and thus has been used successfully to aid the injection of holes and to help prevent electrons from reaching the anode both in polyfluorene (PFO) based OLEDs [246], and in fluorescent blue dendrimer devices [241]. The advantage of PVK is that it is only soluble in a small range of solvents. By using a solvent of chlorobenzene a layer of PVK was then spin-coated onto the annealed PEDOT/PSS layer to provide a clean heterojunction interface. The ITO/PEDOT/PVK sample was then transferred to an evaporator where 12 nm of mCP was deposited by thermal evaporation. After removal of the sample from the evaporator the emissive layer of Dendrimer 28 was spin-coated on top of the mCP layer. The sample was then transferred back to the evaporator where the fabrication was completed with the evaporation of 30 nm of UGH2 and 20 nm of PBD followed by the LiF-Al cathode. The final structure appeared as shown in Figure 9.53. The corresponding energy level diagram of this multi-layer device structure is shown in Figure 9.54.

For this device the maximum efficiency was 4.4 %, this efficiency was obtained at a brightness less than 2 cd/m² for a bias voltage of 8.2 V. At the standard brightness of 100 cd/m², the device EQE was 2.0 % (at 14.4 V); the device data has been summarised in Table 9.17. The table also shows, for ease of comparison, the performance of the ITO/dendrimer/PBD/LiF-Al device considered in Section 9.3.6.2. The characteristic curves of these two devices are also compared in the plots shown in Figure 9.55.

As the revealed by the figure, there was little improvement in the device performance in terms of the current and luminance with the use of the many additional layers. These layers acted to increase the turn-on voltage of the device with little benefit of an efficiency increase in comparison to the work involved in fabricating the additional layers. The use of the additional layers was also found to lead
Figure 9.53: Structure of a multi-layer device for deep-blue emission  

Table 9.17: Comparison of device characteristics for Dendrimer 28 with various device structures

<table>
<thead>
<tr>
<th>Device Structure</th>
<th>Max EQE</th>
<th>EQE at 100 cd/m²</th>
<th>CIE coordinate</th>
</tr>
</thead>
<tbody>
<tr>
<td>ITO/100 wt % Dendrimer 28/PBD/LiF-Al</td>
<td>3.9 % (5.0 V, 3.4 lm/W, 5.4 cd/A)</td>
<td>2.0 % (15.0 V, 0.6 lm/W, 2.9 cd/A)</td>
<td>(0.159, 0.174)</td>
</tr>
<tr>
<td>ITO/PEDOT/PVK/mCP/100 wt % Dendrimer 28/UGH2/PBD/LiF-Al</td>
<td>4.4 % (8.2 V, 2.7 lm/W, 7.0 cd/A)</td>
<td>2.0 % (14.4 V, 0.7 lm/W, 3.1 cd/A)</td>
<td>(0.180, 0.205)</td>
</tr>
</tbody>
</table>

9.3.6.6 Photoluminescence quenching of deep-blue dendrimers

The previous sections established that UGH2 and UGH3 performed poorly as the electron transport layers within a device, in contrast to the successful application of PBD (and TPBI) as this layer. The deep energy transition of the G1 dendrimer 25:CBP/PBD/LiF-Al, that gave a maximum EQE of 12.3 % (11.4 % at 100 cd/m²), was best for efficient light-blue phosphorescent devices.
levels of all these materials, suggested the reduction in electroluminescence efficiency may have arisen from poor charge transport or injection within the device structure. Alternatively, and/or additionally, these materials could have acted to quench the high luminescence efficiency of the dendrimer.

Quenching can occur when the triplet energy level of the dendrimer is greater than that of the host material or adjacent transport layer and thus energy transfer occurs between the dendrimer and host. This would be a problem in a device as excitons could be transferred to the material where non-radiative decay would occur so limiting the device efficiency. If the energy level of guest and host are similar there may still be delayed luminescence or quenching, depending if there is back energy transfer to the luminescent complex. To investigate whether this was the case, quenching studies on the fluorinated high triplet energy Dendrimer 28 were performed by Dr Ruth Harding, the results of which are described below [163].

The PL quenching was measured by comparing the PL lifetime of a blend of Dendrimer 28 and a host, with that of Dendrimer 28 in a blend of the inactive host material PMMA, where quenching has been found not to occur. The technique of blending the dendrimer and host was preferred as in this way the interface between the materials was maximised since PL is a bulk measurement. In some cases, due to the insolubility of the small molecules used, it was not possible to form such a blend structure, and thus in this case a layer of the material was evaporated over a thin layer of Dendrimer 28.
As commented above a dendrimer PMMA blend was found to give a similar phosphorescence lifetime to a neat film, that is a blend with PMMA gave no quenching effects. In contrast mCP, TPBI and PBD all displayed quenching effects, however no quenching was observed for either UGH2 or UGH3, as shown in Figure 9.56. As shown in the figure the decay of Dendrimer 28 was faster in the mCP blend than with PMMA, showing that some quenching occurred due to mCP. This behaviour was explained from the similarity of triplet energy levels (2.89 eV for Dendrimer 28, compared with 2.90 eV for mCP).

For the Dendrimer 28-TPBI blend film the initial decay was much faster than with the PMMA blend (and mCP blend), showing quenching happened due to energy transfer to the TPBI. Again a consideration of the triplet energies shows why this occurred: TPBI has a slightly lower triplet energy of 2.85 eV compared to the 2.89 eV of Dendrimer 28. Therefore, blending Dendrimer 28 with TPBI gave PL quenching and it was this quenching that would limit the efficiency in devices with TPBI in a bilayer structure. This partly explains why, unlike for the green-emitting iridium(III) cored dendrimers which have lower triplet energies, this material was unable to fully realise the high PLQY of the deep-blue emitter.

As Figure 9.56 shows, the greatest degree of quenching was found to occur in the Dendrimer 28-PBD blend film. The large degree of quenching found in this case indicated that PBD had a much lower triplet
energy than Dendrimer 28. This then resulted in energy transfer to PBD, as from the relative HOMO and LUMO energy levels of PBD and Dendrimer 28 it would be unlikely that the alternative means of quenching of the PL by exciton dissociation would have occurred in this case \[163\].

In contrast, the similarity of the neat film PL decay curve to that of the neat film of Dendrimer 28 plus either a film of UGH2 or UGH3 deposited onto the dendrimer layer, has shown that these materials did not give any quenching effects. This behaviour was explained by the analysis of the triplet energy levels; UGH2 and UGH3 are known to have very high triplet energies of 3.5 eV \[230,232\], and thus are much greater than that of the value of 2.89 eV calculated for Dendrimer 28. Therefore the evaporation of a layer of UGH2 or UGH3 onto a thin layer of Dendrimer 28 did not result in any quenching of the PL of the dendrimer. From a purely photophysical point of view these materials should be suitable for use in devices with Dendrimer 28. The fact that when both UGH2 and UGH3 were used within device structures the device performance was not very good, suggested this resulted not from PL quenching effects, but from poor charge injection and transport due to the deep energy levels of these materials.

Finally it is noted that, although blending Dendrimer 28 with PBD gave severe PL quenching which could be predicted to severely reduce device efficiency, this material actually did lead to the most efficient devices. This implied that quenching in devices with PBD was not so severe as in PL which suggested excitons may not have formed at the dendrimer-PBD interface. However, as the resultant device efficiency was still someway less than the maximum efficiency theoretically possible, some PL quenching may still occur within this device structure.

9.3.7 Double dendron blue summary

This section has focused on the gradual development of a light-emitting dendrimer capable of deep-blue emission and high efficiency. To do this the double dendron approach that was successfully used to improve the efficiency of both red and green-emitting dendrimers was again followed.

The work started by the consideration of a non-fluorinated double dendron dendrimer. This dendrimer, Dendrimer 24, with structure shown in Figure 9.12 was found to give both very efficient emission in both PL and EL. In particular the maximum device efficiency for a neat film was 9.5 % (8.9 % at 100 cd/m²). The neat film PLQY of this dendrimer was 48 %, and thus this device strongly realised the maximum efficiency possible given this PLQY. The colour of the both the PL and device emission spectra was light-blue reflecting that this dendrimer was non-fluorinated. Therefore while the efficiency
of the Dendrimer 24 device and the depth of blue colour was less than has been archived elsewhere, notably in Reference [230] that used FLr6 as the emissive layer to obtain a maximum EQE of 11.6 % and CIE coordinate of (0.16, 0.26), it did improve on the efficiencies of when FLrpic was the emissive layer in Reference [228], which gave a maximum EQE of 5.7 %, albeit for a deeper blue colour corresponding to a CIE coordinate of (0.16, 0.29).

To improve the colour depth of the blue emission, a fluorinated double dendron dendrimer, Dendrimer 25, with structure shown in Figure 9.16 was considered. The attachment of the fluorine atom was found to be successful in that it improved the blue colour depth (in solution). However the PL efficiency of this dendrimer was not high and thus the devices with this dendrimer were not efficient.

To improve the luminescence efficiency of the dendrimer with respect of the core, without a loss of blue colour, a new approach was required. A successful method was found by using the same fluorinated core and the use of high triplet energy dendrons. By replacing the standard phenylene dendrons with dendrons comprised of diphenylethylene groups with saturated ethylene moieties breaking the conjugation, the triplet energies of Dendrimers 26 and 27 was found to be greater than that of Dendrimer 24 without any loss in film PLQY. On making devices with Dendrimer 27, after overcoming a number of fabrication problems, it was demonstrated that for the first time deep-blue emission from a spin-coated film was possible in electroluminescence as well as photoluminescence, with the device yielding an emission spectrum corresponding to a CIE y-coordinate of less than 0.2. In the best case, for a bilayer device with an emissive layer of a Dendrimer 27 and mCP host blend, the CIE coordinate was (0.147, 0.158) with a maximum device efficiency of just under 2 % obtained. This device finally equated the performance of our phosphorescent dendrimers to that of our fluorescent dendrimers [241]. Moreover, there still remains very few reports of blue-emitting phosphorescent devices that show a similar depth of blue colour (CIE y < 0.2) for a reasonable device efficiency [232–234], yet such devices required complicated evaporated multi-layer structures, and so the obtainment of a similarly deep-blue emission from a simple spin-coated layer was an important progression.

While the high triplet energy dendrons comprised of diphenylethylene groups proved very successful, a key disadvantage of the technique was that with the use of such ‘floppy’ dendrons the resultant dendrimer was oily and could not be made into a powder, which gave significant processing disadvantages. Consequently an alternative method of obtaining a high triplet energy dendron was obtained from the use of twisted methyl substituted biphenyl units as the dendrons. Using the same fluorinated core,
the resulting Dendrimer 28 had a structure as shown in Figure 9.35. The change in dendron was found, as shown in Figure 9.39, to give an improvement in both the PL efficiency and the depth of the blue emission colour. The PL of this dendrimer suggested good devices could be possible, and so a number of device structures were attempted using Dendrimer 28 as the emissive layer in order to optimise its EL efficiency. From these studies, the best device efficiency and colour was found when the oxadiazole PBD, with structure shown in Figure 9.43(c), was used as the electron transport/hole blocking layer in a device with a structure of ITO/dendrimer/PBD/LiF-Al. For an emissive layer of a 20:80 wt % Dendrimer 28:mCP blended film, the maximum EQE was 3.8 % (also the EQE at 100 cd/m$^2$), while the emission spectrum of this device gave a CIE coordinate of (0.161, 0.144). The improvement in device performance, found with this simple dendron modification, was shown in Figure 9.48 which plotted on a CIE chromaticity diagram the CIE coordinate and efficiency of each of the best performing devices obtained from Dendrimers 24, 25, 27 and 28. This high device efficiency was achieved despite the large degree of PL quenching that was demonstrated to occur in a Dendrimer 28-PBD film. Moreover, this efficiency was still significantly less than maximum theoretically possible given the high 60 % neat film PLQY of Dendrimer 28. Therefore it is still highly probable that through, for example, the use of more suitable additional layers in the device structure, compared to those considered, in order to control both the recombination zone and the charge balance, the efficiency of Dendrimer 28 devices could be further increased.

9.4 Double Dendron Summary

This chapter comprised of a study into the photophysical and device properties of a number of double dendron dendrimers. In the first instance it was shown how by simple modifications of the ligand structure an efficient light-emitting dendrimer capable of green emission could be changed to give efficient red emission. This concept had already been shown within the group with the creation of a red-light-emitting single dendron dendrimer [116, 219]. By adopting the double dendron approach to this dendrimer, the new dendrimer, Dendrimer 23, with structure shown in Figure 9.3, was synthesised, but unfortunately in the less efficient $mer$ isomer form. Nonetheless, the neat film PLQY of this dendrimer was found to be greater than that of the single dendron fac isomer. Dendrimer 23 was found, after optimisation of the device structure, to give an EQE of 6.1 %, and an EQE of 5.9 % at a brightness of 100 cd/m$^2$. This result was an improvement over that of the published single dendron dendrimer. The emission colour of Den-
drimer 23 in both PL and EL was deep-red, such that when plotted on the CIE Chromaticity Diagram the CIE coordinates actually lay outside the PAL standard for red. However while the inclusion of the second dendron was found to be very effective in increasing device efficiency over that of the single dendron dendrimer the device performance was still less than what has been achieved elsewhere with alternative organic emitters. For example maximum EQEs of 12-13 % have been reported \[216, 225\], but this required the evaporation of phosphorescent small molecules and a complicated device structure to produce this efficiency. In devices with spin-coated emissive layers similar efficiencies have been demonstrated, by amongst others Cao et al. [226], and Wang et al. [221], however the device structures they used were again complex. In the first case the doping of the phosphorescent iridium emitter into a polymer was required, while in the second both host blending with CBP and the use of many additional evaporated layers was found necessary to produce this high device efficiency. Thus despite the Dendrimer 23 devices being less efficient, they have significant ease of processing advantages over the alternatives. Moreover, this Dendrimer 23 was an inefficient mer isomer with a relatively low film PLQY, and therefore if the more efficient fac isomer of this dendrimer could be synthesised the results of the mer isomer suggest such a dendrimer could improve on the so far reported efficiencies of red phosphorescent OLEDs.

Having considered the improvement of light-emitting dendrimers for red emission, the remainder of this chapter then focused on finding whether the double dendron concept could be equally successful in improving the efficiency and colour of light-emitting dendrimers for blue emission. While the progress towards efficient (and long lifetime) red and green emission from organic semiconductors is well advanced, the same success has not been matched in efficient and deep-blue emission.

There are a number of reasons for this. The large energy gap of blue makes the efficient injection of charges difficult. For efficient energy transfer a wide band gap host is required. While a small number of wide bandgap hosts do exist \[230,232\], there has been minimal success in achieving deep-blue emission. Blue materials often have a low luminescence efficiency and suffer from quenching in the solid state \[228,229\]. This chapter investigated the method of negating the need for such a host by utilising the double dendron concept, which has been shown repeatedly to be an effective method of increasing both the photoluminescent and electroluminescent efficiency by acting to reduce the effects of concentration quenching \[34,118,119\].

This chapter then detailed the gradual development of a light-emitting dendrimer capable of deep-blue emission and high efficiency. To do so a non-fluorinated dendrimer that emitted light with a sky-blue
To improve the blue colour a strategy of fluorination was followed for the double dendron dendrimers. This was found to improve the blue colour, but significant quenching effects were observed in neat films. This was due to energy transfer to the dendrons and thus for deep blue emission at high efficiency, high triplet energies were required. In the first instance such dendrons comprised of diphenylethylene groups with saturated ethylene moieties to break the conjugation were considered. Twisted methyl substituted biphenyl units as the dendrons were then investigated. In both cases the approach was found to be very successful in that it was able to avoid quenching effects in a neat film. In particular, a large improvement in the reduction in PL quenching was found for the twisted dendrons since they had a reduced non-radiative decay rate due to decreased vibrational quenching \[163\]. These dendrimers again used a fluorinated structure, which meant deep blue and efficient luminescence in a dendrimer could be demonstrated. It was then shown that such deep-blue emission was possible from a spin-coated film in electroluminescence as well as photoluminescence, with a number of devices that yielded an emission spectrum with a CIE \(y\)-coordinate of less than 0.2. Various device structures were considered and the best device in terms of both colour and efficiency was found from a configuration of ITO/dendrimer/PBD/LiF-Al. In this device structure, by using a 20:80 wt % Dendrimer \(28\):mCP blended film as the emissive layer, the maximum EQE was 3.8 % (also the EQE at 100 cd/m\(^2\)). The deep-blue colour of this device gave a CIE coordinate of (0.161, 0.144), and thus showed similar colour to the best reports of electrophosphorescent blue emission available in the literature \[232, 234\]. The fact that this was possible from a simple spin-coated layer was a major step forward for deep-blue phosphorescence.

The chapter has shown that the double dendron technique is a powerful and effective approach towards eliminating the need for host blending of organics. It was found to be beneficial in improving the efficiency of both red and blue-emitting OLEDs, and thus promising dendrimers for each of three primary colours have now been developed. The devices presented in this chapter thus bring the prospect of simple-to-fabricate, and hence low-cost, high performance OLEDs ever closer.
Chapter 10

Conclusions

This thesis has focused on the advancement of light-emitting organic semiconductors for use in flat-panel display applications. While most of the work in the world has been on long established materials such as evaporated small molecules and polymers, this thesis focussed on light-emitting dendrimers. Dendrimers are branched macromolecules, shaped like a snowflake in three dimensions, and are made up of central metal atom core from which branches radiate, the ends of which are attached with solubilising surface groups. As the core controls the electronic properties such as the colour of the emitted light, and the conjugated dendrons control the intermolecular interactions of the core, both the electronic and processing conditions can be independently optimised. This thesis has demonstrated how improvements in each of these areas can, by increasing the knowledge of dendrimer device physics, lead to improvements in practical efficient solution-processed organic light-emitting diodes (OLEDs). The particular interest in dendrimers arises because they have been shown to give solution-processed phosphorescent devices with high efficiency [26, 27]. The solubility of the dendrimers opens the way for simple processing and a new class of flat-panel displays.

The thesis introduced various techniques of electroluminescence and photoluminescence measurements before applying such methods to study a large number of light-emitting dendrimers in order to explore the role of intermolecular interactions, how they are related to molecular structure, and how this determines photophysical and charge transporting properties of the dendrimers. By doing so a number of highly efficient light-emitting dendrimers were identified, while the efficiency of devices made from these dendrimers was improved.

In particular, Chapter 4 focused on methods to optimise the solution-processing technique of thin
films of light-emitting \textit{fac}-tris(2-phenylpyridyl) iridium(III) [Ir(ppy)$_3$] cored dendrimers by minimising the photodegradation processes present in solutions of such dendrimers. Previous dendrimer device publications have reported that for maximum device efficiency the dendrimer used was required to be first blended in a carbazole containing CBP host prior to spin-coating \[26, 27\]. Unfortunately, CBP and dendrimers have widely varying degrees of solubility: the majority of dendrimers dissolve instantly, while CBP can take a couple of hours to fully dissolve and only then with a small number of solvents.

Through studies of a first generation iridium(III) cored dendrimer, it was learnt that by careful control of the preparation conditions this dendrimer could in fact be used to give highly efficient host-free dendrimer OLEDs. The improvement in the neat film performance was established to arise from a corresponding improvement in the photoluminescence efficiency of the dendrimer through the reduction of the photoactivated degradation processes. These degradation effects were particularly extenuated when solutions of the dendrimer were prepared from chloroform and kept under illumination for a significant length of time prior to spin-coating.

Consequently with this knowledge, the film preparation protocol was able to be improved thereby allowing the external quantum efficiency of a simple neat film bilayer device of a first generation iridium(III) dendrimer to be more than doubled to a maximum of 9.8 \% at a brightness of 1700 cd/m$^2$, a result that has since been published in Reference \[124\]. By further improvements and optimisation of the processing conditions it was shown that the previously required technique of blending with host materials was no longer needed to give external quantum efficiencies greater than 10 \% for green-emitting OLEDs. In the best case, by following this technique, the efficiency of a neat film of a green-light-emitting first generation Ir(ppy)$_3$ dendrimer was able to give an EQE of over 12 \% at a brightness of 110 cd/m$^2$. The chapter also showed that the adoption of this new technique could lead to lifetime improvements through the ability to incorporate PEDOT/PSS into the device structure. The results of this chapter were also relevant to other solution-processed phosphorescent materials. In particular, in Chapter 4 it was demonstrated that by applying the new solution protocol to a series of iridium(III) dendrimers both the PL and EL efficiency could be improved. Consequently this new solution protocol technique was then adopted in the remaining chapters of the thesis to give all the results reported.

In Chapter 5 and Chapter 6 the development of dendrimers with charge transporting dendrons was investigated. Previous iridium(III) cored dendrimers studied have used phenylene dendrons, which were found to have no role in hole charge transport. In these dendrimers the hole charge transport within the
dendrimer film was by hopping between the dendrimer cores \[93\].

In Chapter 5, by considering a family of dendrimers with dendrons consisting of the hole carrying carbazole units commonly used in host molecules such as CBP, it was shown that the functions of the host material could be successfully and easily incorporated into the dendrimer structure without the loss of photoluminescence efficiency \[160\]. The inclusion of these carbazole dendrons was demonstrated to have significant effects on the electroluminescence and charge transporting properties of the dendrimers as measured through device and hole-mobility measurements. More specifically, the change in dendron was discovered to lead to a change in the hole charge transport behaviour from the core-to-core hopping present in dendrimers with phenylene dendrons to charge transport via the hole transporting carbazole dendrons. For the carbazole dendrimers higher generations of dendrimer had higher hole mobility, the opposite of the situation for dendrimers with phenylene dendrons. Molecular orbital calculations showed this to have arisen from a change in the residual location of the majority of the HOMO density from the core to the dendron, with as the dendrimer generation increased, the amount remaining on the core becoming increasing smaller. The improved hole-mobility and thus charge transport but lower device efficiency of the carbazole dendrimers, in comparison to dendrimers with phenylene dendrons, indicated how important knowledge of the effect of the carrier mobility was on device performance in order to obtain improvements in the understanding of the device behaviour.

In Chapter 6 the case of electron transport via the dendrons was explored. Two types of dendrimer were studied, each of which was hoped would be capable of improving the charge balance within dendrimers by improving the electron transport, the first time such an approach in dendrimers has been considered. The first type of dendrimer contained triazine groups while the second used benzimidazole groups attached to the phosphorescent iridium(III) core in an attempt to provide this electron transport. For both cases the results showed that despite numerous synthesis problems, for the first time a number of such dendrimers could be synthesised and then made into successful light-emitting devices. Unfortunately, in both cases there was also little evidence to suggest the dendrons used were capable of, or at least could improve, the electron transport in the dendrimer and thus improve the charge balance within a device. Nevertheless, this chapter detailed some important first steps towards the goal of obtaining dendrimers capable of electron transport that could ultimately be combined with hole transporting dendrons to give multi-functional dendrimers capable of bipolar charge transport.

The thesis then switched focus in Chapter 7 to further study the charge transport behaviour in den-
CONCLUSIONS

drimers. This consisted of a detailed analysis of current-voltage characteristics of single and two carrier devices that used phosphorescent dendrimers as the organic layer in various sandwich structures. In particular a dendrimer with phenylene dendrons, Dendrimer 1 first studied in Chapter 4 was considered in comparison to a dendrimer with hole transporting carbazole dendrons, that of Dendrimer 5 first studied in Chapter 5. Using these two dendrimers a number of device structures were fabricated using various electrode configurations. The device results were then in a collaboration with Jonathan Williams and Dr Alison Walker at the University of Bath simulated using a device model that included a recent description of charge injection. In this way fittings were made to the current-voltage characteristics of each structure to deduce key parameters such as the height of the injection barrier at the injecting contact. In doing so it was revealed that the fitted barrier heights did not agree with the Mott-Schottky model and were susceptible to contamination. The importance of modelling charge injection carefully and not just assuming the validity of the Mott-Schottky model when deducing device parameters such as charge mobilities from current-voltage characteristics was thus concluded. The results of this chapter also emphasised once again the significant advantages of the dendrimer concept; a simple change of dendron could be used to give significant changes in the resultant charge transport properties of the dendrimer.

In addition to these considerations, the practical application of dendrimers was also addressed in Chapter 8 where the benefits of the versatility of the dendrimer approach were demonstrated again but in a very different way, in this case through the development of photo-patternable phosphorescent dendrimers. While the benefits of solution-processed devices have been detailed, they do suffer from one particular disadvantage in comparison to evaporated organic devices: after spin-coating one layer it becomes very hard to solution deposit any subsequent layers without washing away this initial layer. Pixelation of the emissive layer and the fabrication of multi-layer devices (for efficiency optimisation) were thus very hard to achieve.

Dendrimers with oxetane units on the dendrons were therefore developed building on the work of Meerholz on photo-patternable fluorescent polymers [200, 202, 204, 206, 214, 216]. These photosensitive units replaced the standard ethylhexyloxy surface groups and meant the dendrimer was able to become cross-linked under UV exposure, and so by remaining fixed in position further layers could be spin-coated on top. It was shown that such groups could be attached to hole transporting molecules, and for the first time, solution-processable electrophosphorescent dendrimers, with both single and double dendron cross-linkable dendrimers were demonstrated.
In this way, the possibility of obtaining an all-solution-processable dendrimer device was opened up, where the optimisation of each individual layer was achievable. Progress towards such a goal was furthered through the use of a solution-processable electron transport layer within the device structure. The addition of a PEDOT/PSS layer further increased the device complexity to four solution-processable layers, and yet still the resultant device was capable of successful light emission. While still much work remains to be completed in order to fully optimise a multi-layer solution-processed device structure, thanks to the work detailed in Chapter 8 a number of significant, if early, steps were made towards this goal.

Finally, in Chapter 9 the experimental results chapters of the thesis concluded with a study into the development of highly efficient deep-red and deep-blue phosphorescent OLEDs. This was possible through an improvement of the control of the core-to-core interactions that would normally quench the luminescence. This was achieved by having two dendrons per ligand attached to the metal core.

Using the double dendron approach significant advancements in the field of OLED displays were made. In particular, to begin with, it was demonstrated how by simple modification of the dendrimer structure an efficient light-emitting dendrimer capable of green-emission could be changed to give efficient red light emission. The double dendron dendrimer considered was found, after optimisation of the device structure, to give an improved EQE over that of a previously published single dendron dendrimer [116, 219]. In particular, for this device the maximum EQE was 6.1%, and at a brightness of 100 cd/m² the EQE of 5.9%. The colour of emission in both PL and EL was such a deep-red that on plotting it on the CIE Chromaticity Diagram the CIE coordinates actually lay outside the PAL standard for red. While the efficiency of the dendrimer was less than has been achieved in the literature, such higher efficiency devices required complicated device structures, and/or used evaporated small molecules. The fact that such highly efficient OLEDs could be made using an inefficient mer isomer of a dendrimer with a relatively low film PLQY, suggests that if the more efficient fac isomer of the dendrimer could be produced then such a dendrimer could show considerable improvement over the so far reported efficiencies of red phosphorescent emitters.

The challenge of obtaining efficient and deep-blue phosphorescence has so far proved very difficult with only a small number of reports of this existing in the literature [232, 234]. The large energy gap of a blue emitter and finding a host material that could improve the charge injection into the organic have so far proved very difficult problems to surmount. The control of intermolecular interactions to reduce the
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effects of the concentration quenching of the phosphorescence provided by the double dendron concept has been shown in both green and now red-emitting dendrimers to provide a powerful method of negating the need for a host material. The effectiveness of the approach was thus investigated for blue-emitting OLEDs. Following this double dendron approach a sky-blue light-emitting dendrimer device with a maximum efficiency of 9.5 % (8.9 % at 100 cd/m²) was obtained. This result demonstrated that the double dendron concept could be effectively applied to dendrimers capable of all emission colours. By modifying the dendrimer structure through the use of dendrons with high triplet energies the depth of blue emission colour was improved significantly whilst still maintaining a high photoluminescence efficiency. Such high triplet energy dendrimers were able to give a number of devices that had an emission spectra with a CIE y-coordinate of less than 0.2. This was the first time such deep-blue emission has been possible from a spin-coated dendrimer film in electroluminescence as well as photoluminescence. For the best device in terms of both colour and efficiency using a structure of ITO/dendrimer/PBD/LiF-Al with an emissive layer of a 20:80 wt % Dendrimer 28:mCP blended film, the maximum EQE was 3.8 % (also the EQE at 100 cd/m²). The deep-blue colour of this device gave a CIE coordinate of (0.161, 0.144). While the few literature reports [232–234] of such similar deep-blue electrophosphorescence are of higher efficiency, they required to obtain this efficiency more complicated evaporated multi-layer structures. The fact that dendrimers could obtain a similar deep-blue emission colour from a simple spin-coated layer was a major step forward for deep-blue phosphorescence.

The double dendron technique was proven to be a powerful and effective approach for controlling intermolecular interactions and thus reduced the luminescence quenching effects that have been found in dendrimers, consequently the need for host blending became reduced. The approach was shown to be beneficial in improving the efficiency of green, red and blue-emitting OLEDs meaning promising materials for each of three primary colours have now been developed. In this way the prospect of simple-to-fabricate, and hence low-cost, high performance OLEDs is brought ever closer.

This thesis has therefore lead to important advances towards the goal of obtaining highly efficient light-emitting diodes in each of the three primary colours of red, green and blue thereby bringing closer the prospect of dendrimer light-emitting diodes being the future display type of choice. This has been achieved through the development of highly efficient neat film dendrimer devices; the increased knowledge of dendrimer device physics; and the first demonstrations of the production of photo-patternable phosphorescent dendrimers for multi-layer devices; and high efficiency deep-red and deep-blue emitting
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OLEDs. The work of this thesis has thus as intended made a significant contribution to the improvement of efficient solution-processed phosphorescent OLEDs.
Bibliography


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