BODIPY star-shaped molecules as solid state colour converters for visible light communications

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In this paper we study a family of solid-state, organic semiconductors for visible light communications. The star-shaped molecules have a boron-dipyrromethene (BODIPY) core with a range of side arm lengths which control the photophysical properties. The molecules emit red light with photoluminescence quantum yields ranging from 22-56 %. Thin films of the most promising BODIPY molecules were used as a red colour converter for visible light communications. The film enabled colour conversion with a modulation bandwidth of 73 MHz, which is 16 times higher than of a typical phosphor used in LED lighting systems. A data rate of 370 Mbit/s was demonstrated using On-Off keying modulation in a free space link with a distance of ~15 cm.

Organic semiconductors have been widely studied in the last few decades for optoelectronic devices such as transistors[1], lasers[2,3,4] amplifiers[5], solar cells[6,7] explosive sensors[8] and organic light emitting devices (OLEDs)[9]. They are broadband visible emitters whose emission can be tuned by changing the chemical structure, and can have high photoluminescent quantum yields (PLQY) of up to 90% in undiluted films[5,9,10]. This combined with simple and low cost solution processing techniques make them attractive materials for optoelectronic devices.

An emerging application area for organic semiconductors is in the field of visible light communications (VLC). Increasing demand for wireless communications has driven research into improving data transmission concepts[11-21]. The concept of VLC is to use solid state room lighting to transfer data. This idea can exploit lighting installations to their full potential by providing illumination and data communication simultaneously, in an efficient, safe and low cost method. White LED lighting commonly uses blue LEDs coated with a yellow-emitting phosphor which acts as a colour converter for some of the blue light. An important consideration is the excited state lifetime of the phosphor/colour converter. High data transmission rates require short excited state lifetimes. Phosphors typically have a microsecond lifetime which severely limits the data transmission rate, so there is a need for colour converters with much shorter lifetimes.

Organic semiconductors are attractive alternatives to using phosphors as colour converters for VLC because they have faster radiative lifetime and high PLQY. They can also be modified to emit at any visible wavelength, allowing tuneable colour converters. The potential of using conjugated polymers for VLC has recently been demonstrated, using the commercial polymer Super yellow (Merck) in solution. The experiment combined the yellow emission of the polymer with a blue LED to produce white light and a data rate of 1.68 Gbit/s over a distance of 3 cm[22]. Improved colour rendering or wavelength division multiplexing requires fast red colour converters. We have recently shown that boron-dipyrromethene (BODIPY) molecules in solution can give a saturated red emission. a modulation bandwidth of 39 MHz and data rates of ~ 98 Mbit/s[23,24]. However, for practical applications, a compact and solid state structure is required. In this paper we study a family of star-shaped BODIPY molecules in the solid state, and demonstrate that they have an increased bandwidth allowing a data transfer rate of 370 Mb/s at a distance of 15 cm with simple on-off keying.

The molecules (shown in figure 1, top) have a star shape with boron-dipyrromethene as the core (BODIPY) and oligofluorene arms in a 'Y' shaped arrangement. The size of the molecule is modified by increasing the number of fluorene units in each arm from 1 to 4, and the corresponding molecules are labelled as Y1, Y2, Y3 and Y4[25].

The oligofluorene arms have a substituent effect on the BODIPY core and therefore the increase in the number of arms influences the photophysics of the material.

Solid state colour converters were spin-coated from solution to make thin films on quartz substrates for the photophysical studies. Films of thickness ca. 100 nm were deposited from solutions at concentrations of 10 and 20 mg/ml for photophysical and communications measurements respectively. These were spin-coated at 1500 rpm for 60 seconds. Figure 1 (bottom) shows the absorption and PL spectra of the films for each molecule. The absorption spectra show peaks at 450 and 620 nm for Y1; 350, 473 and 626 nm for Y2; 350, 477 and 625nm for Y3; and 366, 480 and 625nm for Y4. The absorption band below 400 nm is attributed to the fluorene arms and increases in intensity with arm length. Y1 has a peak in absorption at 450 nm matching well the emission of the blue LEDs used for lighting, and this feature shifts slightly to longer wavelengths for longer arms as seen in Figure 1. The peak emission wavelengths were in the red region of the spectrum, 663, 679, 682, 682 nm for Y1, Y2, Y3 and Y4 respectively. The red PL emission comes from an extended conjugation across the BODIPY core and adjacent fluorene units as has been described previously[24]. The bathochromic shift from Y1 to Y2 is also evident in solution[23,24] and indicates that there is a further delocalisation of the excited state across the BODIPY and neighbouring fluorene units.

Time-resolved fluorescence measurements were conducted using the time correlated single photon counting (TCSPC) technique, exciting the materials at 375 nm and detecting at the corresponding peak PL wavelengths. The 375 nm excitation is absorbed by the oligofluorene arms, and results in a fast energy transfer to the emitting state that is delocalised across the BODIPY core. The energy transfer is very fast and cannot be resolved by the TCSPC apparatus. The resulting PL dynamics are shown in figure 2 and have bi-exponential decays. The lifetime values are given in table 1in the nanosecond range and show Y3 having the shortest average decay. The PLQY of the films also differ, showing lower values compared to solutions. In films the PLQY values range from 22-56%, whereas in solution form they were previously measured to be 55-62%[23].

Films of Y3 were selected for bandwidth and data transmission measurements as they have the shortest lifetime and high PLQY. Samples were encapsulated under glass using the UV cured epoxy NORLAND 68 on top of the BODIPY Y3 film. UV curing was performed with an 8 W lamp at 365 nm for 1.5 minutes. The encapsulation process was conducted in a nitrogen-filled glove box which had a controlled and inert atmosphere to avoid exposure to water and oxygen molecules, thus reducing photo-oxidation effects during measurements. The photophysical properties of Y3 were not changed by the encapsulation process.

The capacity of the data link scales with its modulation bandwidth. To assess the bandwidth of Y3, the experimental setup presented in figure 3b was used. The fast (broad bandwidth) excitation source and detector used were a diode laser emitting at 450 nm and an avalanche photodiode. To eliminate any residual excitation light at the detector, a reflectance geometry was adopted in combination with a suitable long-pass dichroic filter. The excitation source was driven by an amplified sinusoidal voltage generated by the network analyser, this was combined with a DC voltage from a power source using a bias-T. The signal received from the APD was recorded by the network analyser. To measure the bandwidth of the system the AC amplitude of the received signal was recorded as a function of the modulation frequency. To factor out the bandwidth contribution of the different components of the experimental setup, first the bandwidth of the measuring system was evaluated by directing the excitation light into the detector. This bandwidth was subsequently subtracted by the network analyser from the recorded bandwidth spectrum for the material. Figure 3a shows the results of the bandwidth measurement of the Y3 BODIPY as well as, for comparison, the bandwidth of a commercial phosphor plate CL-840 (Intematix ChromaLit). It is evident in figure 3 that the BODIPY material has a much higher -3 dB bandwidth (75.5 MHz) than that of the phosphor (5 MHz). The Y3 film bandwidth is also twice that measured with the same material in solution.

The data transfer capabilities were also studied using the same setup as for bandwidth measurements. The excitation laser was modulated in intensity using a binary On-Off Keying (OOK)[2626] modulation scheme i.e. a binary ‘one’ was represented by a light pulse of duration 1/Rb, where Rb is the data rate and a ‘zero’ was represented by the absence of the pulse. At the receiver, a simple threshold decoding was used in which the received signal was compared against a fixed threshold level based on the expected signal level for ‘zero’ and ‘one’. If the received signal was above the threshold level, it was assumed to be ‘one’, otherwise ‘zero’. Figure 4 shows the measured bit error rate (BER) as a function of transmitted data rate for OOK modulation. The measurements were taken using a pseudorandom binary sequence (PRBS) of 2^{14}-1, of which ~ 82000 bits were analysed at the receiver for errors. Hence, the minimum BER level is limited to 10^{-4} to have statistically high confidence level. By considering the forward error correction (FEC) floor of 3.8×10^{-3} (as recommended by the International Telecommunication Union (ITU) standard), a data rate of 370 Mb/s was achieved which is 4 times higher than previously reported for BODIPY colour convertors in solution.

To summarise, BODIPY cored-polyfluorene semiconducting polymers have been studied in the solid state to establish their feasibility as a red colour converter for VLC applications. The solid-state films exhibit PL lifetimes

shorter than their solution based counterparts and therefore result in a higher bandwidth, for Y3, of 73 MHz and a data transmission rate of 370 Mb/s, which are respectively two and four times higher than measured for Y3 in solution. This bandwidth is 16 times higher than common commercially available phosphors and shows that these organic materials are promising as colour converters for VLC.

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Figures

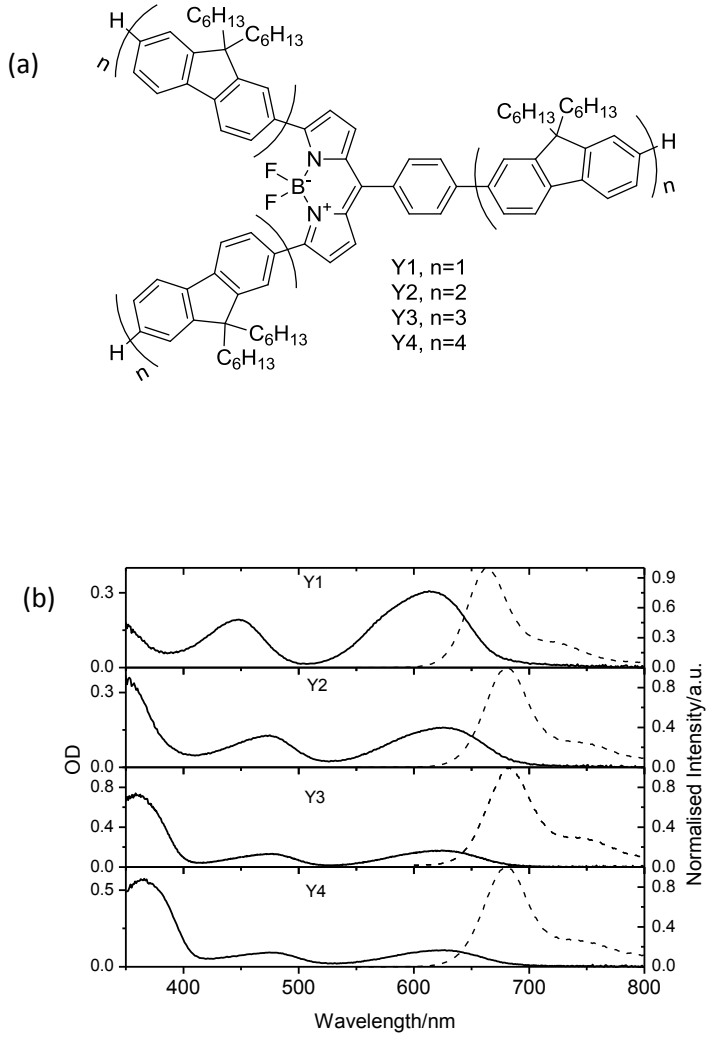


Figure 1: a) Molecular structure. b) Absorption and emission spectra of Y-BODIPY films

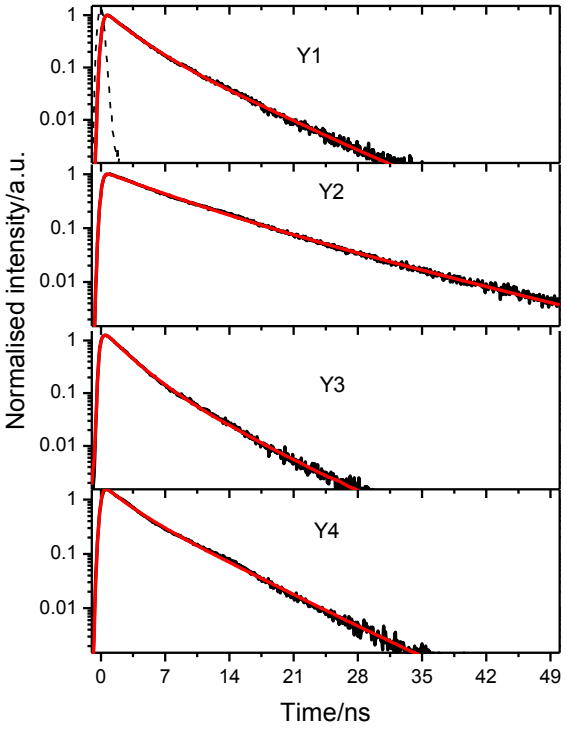
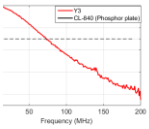


Figure 2: Time-resolved fluorescence measurements of Y-BODIPY films (black) and their fit (red) with the instrument response function (dashed line).

Polymer	PLQY %	A_1	τ_1 (ns)	A_2	τ_2 (ns)	τ_{avg} (ns)
Y1	22.4	0.44	2.35	0.56	5.3	4
Y2	55.9	0.53	5.87	0.47	10.72	8.2
Y3	40.6	0.48	1.9	0.52	4.3	3.2
Y4	49.2	0.26	2.07	0.74	5.08	4.3

Table 1: Photoluminescence quantum yield excited at 375 nm and lifetime of Y-BODIPY films

(a)



(b)

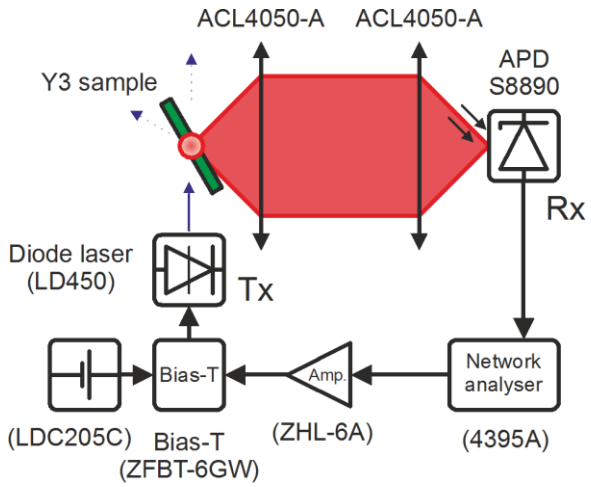


Figure 3: a) Result of small signal modulation bandwidth measurement for the Y3 BODIPY. The dotted line corresponds to -3 dB attenuation which defines the bandwidth of the system. b) Experimental setup used for the bandwidth and data transfer measurements.

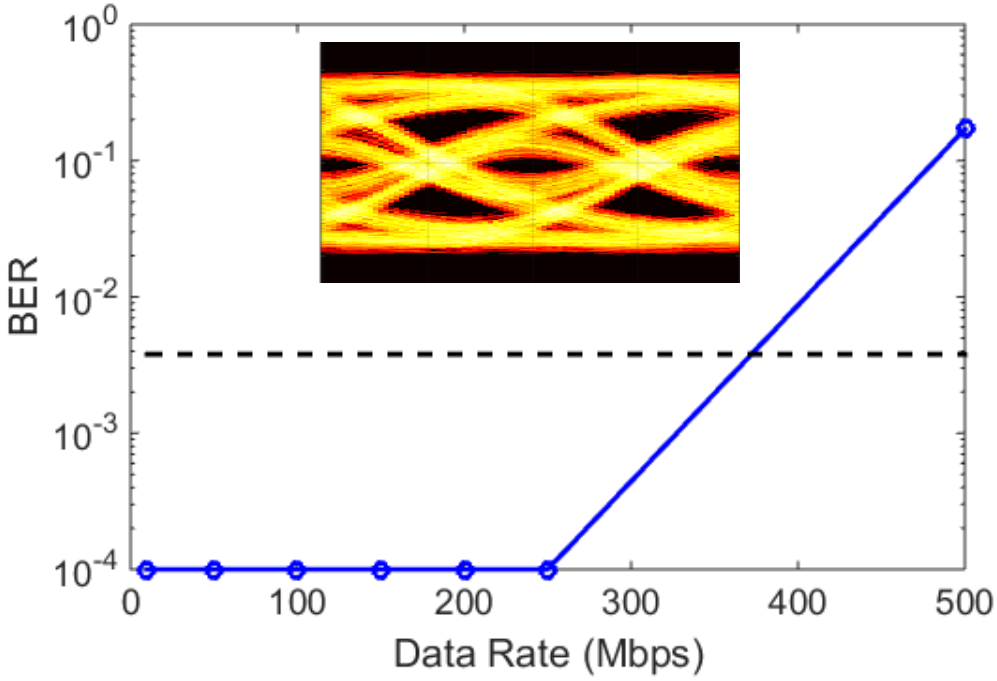


Figure 4: Plot of BER versus data rate for OOK. The dashed line corresponds to BER of 3.8×10^{-3} which is defined as the acceptable error floor for VLC. As inset, the eye diagrams at 250 Mb/s are presented.