High-Triplet-Energy Bipolar Host Materials Based on Phosphine Oxide Derivatives for Efficient Sky-Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes with Reduced Roll-off

Journal: Chemistry Letters

Manuscript ID: CL-190412

Manuscript Type: Letter

Date Submitted by the Author: 22-May-2019

Complete List of Authors:
Kim, Jong Uk; Kyushu University, Center for Organic Photonics and Electronics Research
Yin Wong, Michael; University of St Andrews
Kumar, Shiv; University of St Andrews
Hayes, Oliver; University of St Andrews
Duncan, Finlay; University of St Andrews
Chin-Yiu, Chan; Kyushu University, Center for Organic Photonics and Electronics Research
Yiu Wing, Wong; Kyushu University, Center for Organic Photonics and Electronics Research
Ye, Hao; Kyushu University, Center for Organic Photonics and Electronics Research
Cui, Lin-Song; Kyushu University, Center for Organic Photonics and Electronics Research
Nakanotani, Hajime; Kyushu University, Center for Organic Photonics and Electronics Research
Zysman-Colman, Eli; University of St Andrews
Adachi, Chihaya; Kyushu University, Center for Organic Photonics and Electronics Research

Categories: Organic Chemistry, Materials Chemistry
High-Triplet-Energy Bipolar Host Materials Based on Phosphine Oxide Derivatives for Efficient Sky-Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes with Reduced Roll-off

Jong Uk Kim,1,2 Michael Y. Wong,3 Shiv Kumar,3 Oliver G. Hayes,3 Finlay Duncan,2 Chin-Yiu Chan,1 Ben Yiu-Wing Wong,1 Hao Ye,1 Lin-Song Cui,1 Hajime Nakonati,1,2,4 Eli Zysman-Colman1 and Chihaya Adachi1,1,2

1Center for Organic Photonics and Electronics Research (OPERA) and Department of Applied Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
2JST, ERATO, Adachi Molecular Exciton Engineering Project, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
3Organic Semiconductor Centre, EaStCHEM School of Chemistry, University of St Andrews, St Andrews, Fife, UK, KY16 9ST, Fax: +44-1334 463808; Tel: +44-1334 463826
4International Institute for Carbon Neutral Energy Research (WPI-FCNER), Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan

E-mail: adachi@cosf.kyushu-u.ac.jp, eli.zysman-colman@st-andrews.ac.uk

We designed and synthesized two new ambipolar host materials, namely CzPO and Cz3PO, which contain electron-donating carbazole and electron-accepting triphenylphosphine oxide moieties. Thermally activated delayed fluorescence (TADF)-based OLEDs employing CzPO and Cz3PO as host materials and the 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-1,3,6,8-tetramethyl-9H-carbazole (CzTRZ2) as the emitter resulted in improved maximum external quantum efficiencies, EQE_max, of 13.1% and 13.2%, respectively, together with small efficiency roll-offs, while the device based on bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) showed a much more pronounced efficiency roll-off. The reduced efficiency roll-off in the devices based on CzPO and Cz3PO can be ascribed to their improved ambipolar charge transport capacity compared to that of DPEPO, which results in a broader recombination zone in the emitting layer using these ambipolar hosts.

Keywords: Thermally activated delayed fluorescence (TADF) | Organic light-emitting diode (OLED) | Ambipolar host

After the invention of fluorescence-based organic light-emitting diodes (OLEDs) in 19871, the flat panel display market based on OLEDs is emerging to become the dominant technology. Both organic-based fluorescence and organometallic-based phosphorescence emitters are currently used in OLEDs2,3. In 2012, a series of highly efficient OLEDs based on thermally activated delayed fluorescence (TADF) were demonstrated, in which an efficient process of reverse intersystem crossing (RISC) from a triplet excited-state to a singlet excited-state was realized in purely organic molecules4. OLEDs based on TADF emitters achieved comparable an internal quantum efficiency (IQE) of 100%. Since then, a large number of TADF emitters have been reported5. In particular, TADF emitters have shown tremendous potential to replace the state-of-the-art fluorophores in high performance deep-blue OLEDs. During the survey of blue-emitting devices, significant efficiency roll-off at high current density was identified in these devices, and the triplet energies (E_T) of the host materials must be sufficiently high compared to the emitters in order to confine the excitons on the emitters and thereby realize efficient blue OLEDs6. Further, the balance of charge transport carriers must also be considered to mitigate the efficiency roll-off.

For blue TADF-based OLEDs, there are some general requirements for the host material: (1) the E_T of host materials must be higher than that of the emitter to prevent back energy transfer7; (2) to facilitate effective charge injection, both the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the host materials should be well matched with both those of the emitter and the other layers of the device8; (3) a good host material should possess ambipolar character to best manage charge transport through the emissive layer9. In general, the recombination region tends to occur closer to the emissive layer/electron-transporting layer (EML/ETL) interface when using hole-transporting (HT) hosts. Likewise, the recombination region is likely to be located in the EML/HTL interface when using an electron-transporting (ET) host such as the frequently used DPEPO. It has been found that poor and unbalanced carrier mobility within the EML is responsible for inferior efficiencies, low stability and efficiency roll-off10. OLEDs with narrow charge recombination zones lead to devices presenting severe efficiency roll-off due to the local accumulation of high-density triplet excitons, especially at high current densities11. As a result, an ambipolar host is more suitable for improving the device performance in blue OLEDs. The simple incorporation of both HT and ET moieties within host materials should give rise to ambipolar host materials12. DPEPO is the most popular host material for blue-emitting OLEDs13. However, the use of such ET-type host materials is usually coupled with reduced device stability and efficiency roll-off14-16. Thus, in this study, we designed two host materials, CzPO and...
**Cz3PO**, by linking carbazole donor units with an electron-accepting triphenylphosphine oxide group (Fig. 1). Both hosts show high $E_T$ and ambipolar charge transport properties. Sky-blue OLEDs based on these two bipolar host materials not only showed smaller efficiency roll-off characteristics but also operated under relatively low driving voltages.

![Figure 1](image1.png)

**Figure 1.** Molecular structures, HOMO, LUMO, $S_1$, and $T_1$ energy levels of CzPO and Cz3PO characterized by DFT calculations at the PBE0/6-31G(d) level of theory, and the electron density distributions of the frontier molecular orbitals and spin density distributions of $T_1$ energy levels.

The energy levels of CzPO and Cz3PO were first investigated computationally using the Gaussian 16 program package. Ground-state geometries in the gas phase were optimized at the PBE0/6-31G(d) level, and the lowest singlet and triplet excited states were calculated using time-dependent density functional theory (TD-DFT) based on the optimized ground-state geometries. The electron density distribution of the HOMOs and LUMOs of CzPO and Cz3PO are depicted in Fig. 1 along with their energies and the energies of the singlet and triplet excited states and the spin density distribution of the $T_1$ states. The HOMOs of both host materials are delocalized over the electron-donating carbazole units and bridging phenylene while the LUMOs are mainly localized over the electron-accepting phosphine oxide moiety.

![Figure 2](image2.png)

**Figure 2.** UV-Vis absorption spectra of CzPO, Cz3PO and DPEPO in toluene (10$^{-5}$ M) and (b) PL emission spectra of CzPO, Cz3PO and DPEPO in toluene (10$^{-5}$ M) and neat films.

The UV-Vis absorption and photoluminescence (PL) spectra of CzPO, Cz3PO and DPEPO are shown in Fig. 2 respectively. The photophysical data are summarized in Table S1. In toluene, all host materials show strong absorption bands below 300 nm, which are assigned as $\pi-\pi^*$ transitions of the phosphine oxide moiety. The absorption band beyond 300 nm is absent in DPEPO, and the lowest-energy absorption bands ranging from 310 to 350 nm are attributed to the $\pi-\pi^*$ transition of the 9-phenylcarbazole unit in CzPO and Cz3PO. In toluene, CzPO shows emission maxima ($\lambda_{em}$) at 344 and 359 nm, while Cz3PO shows $\lambda_{em}$ at 361 nm. DPEPO shows the most hypochromically shifted emission at 290 nm. The bathochromically shifted emission in Cz3PO is due to the presence of three donor groups within the molecule. In neat films, only CzPO and Cz3PO display red-shifted emission at 377 and 406 nm, respectively, whereas DPEPO show an additional emission band at 437 nm that may be ascribed to excimer emission. In the present study, CzTRZ2 was used as the TADF emitter in the emitting layer as the absorption spectrum of CzTRZ2 overlaps strongly with the neat film emission spectra of CzPO and Cz3PO, thereby assuring efficient Förster resonance energy transfer (FRET) from the excited hosts to CzTRZ2.

![Figure 3](image3.png)

**Figure 3.** (a) Phosphorescence spectra of CzPO, Cz3PO and DPEPO in toluene matrices at 77 K. (b) Phosphorescence spectra of donor and acceptor moieties in toluene matrices at 77 K.

The phosphorescence spectra of CzPO, Cz3PO and DPEPO are depicted in Fig. 3a and these are cross-compared with the phosphorescence spectra of N-phenylcarbazole and triphenylphosphine oxide (Fig. 3b), which act as reference electron-donor and electron-acceptor moieties. From the phosphorescence spectra, the ET values were determined to be 3.06 and 3.05 eV for CzPO and Cz3PO, respectively. The $E_T$ of CzPO and Cz3PO are higher than that of CzTRZ2 (2.85 eV)$^{54}$ ensuring a suppression of back energy transfer. Both CzPO and Cz3PO show similar vibronic-structured emission profiles and $E_T$ to that of N-phenylcarbazole. Therefore, the lowest $T_1$ excited state of each of CzPO and Cz3PO is localized on the donor moieties, consistent with the computed spin density simulation.

![Figure 4](image4.png)

**Figure 4.** (a) Steady-state PL spectra and (b) time-resolved PL decay profiles of 6 wt.%-CzTRZ2:host doped thin films (host = CzPO, Cz3PO, and DPEPO) measured at 300 K under N$_2$. (excitation wavelength: 280 nm).
The PL spectra of 6 wt%-CzTRZ2 doped films in CzPO, Cz3PO and DPEPO are nearly identical, indicating efficient FRET (Fig. 4a). The CzPO-, Cz3PO- and DPEPO-doped films of CzTRZ2 show broad and structureless sky-blue emission with high \( \Phi_{\text{PL}} \) of 81%, 75%, and 92%, respectively. The transient decay profiles of the doped films clearly show biexponential decay respectively, at 300 K (Figs. S1 and 4b). Such behavior is characteristic of the TADF emission previously reported for this compound. Furthermore, both hosts materials possess a high decomposition temperature, \( T_d \) of 365 and 454 °C, for CzPO and Cz3PO, respectively, which is indicative of high thermal and morphological stabilities (Fig. S2). The \( T_d \) values are substantially higher than that of DPEPO (\( T_d = 322 \) °C)26.

![Figure 5. (a) The EL spectra measured at 8 V, and (b) external quantum efficiency (\( \eta_{\text{el}} \))–current density curves of the TADF-based OLEDs.](image)

We next evaluated the EL performance in OLEDs using CzTRZ2 as the TADF emitter and CzPO- and Cz3PO and DPEPO as host matrices in the EML. The devices were fabricated with the following architecture: ITO (100 nm)/HATCN (10 nm)/TAPC (40 nm)/mCP (10 nm)/6 wt%-CzTRZ2: host (20 nm)/PPT (50 nm)/LiF (0.8 nm)/HATCN (10 nm)/TAPC (40 nm)/mCP (10 nm)/Al (100 nm), in which 2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexazatriphenylene (HATCN) is the hole-injection layer, 1,1-bis(4-diethylaminophenyl) cyclohexane (TAPC) and 1,3-bis(N-carbazolyl)benzene (mCP) are the hole-transporting layer and electron-blocking layer, respectively. The EML layer consists of 6 wt.% of CzTRZ2 doped in CzPO, Cz3PO or DPEPO, 2,8-Bis(diphenylphosphoryl) dibenzothiophene (PPT) is the hole-blocking layer and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi), LiF and Al serve as the electron-transporting layer, the electron-injection layer and cathode, respectively. The ET of electron-blocking and hole-blocking layers, i.e., mCP (2.9 eV) and PPT (2.9 eV), respectively, are higher than that of CzTRZ2, which ensures confinement of the triplet excitons within the EML27. The EL spectra and EQE characteristics of the corresponding OLEDs are shown in Fig. 5. Devices based on CzPO and Cz3PO as host materials resulted in high EQE_max of 13.1 and 13.2% respectively. By contrast, the device based on DPEPO showed a higher EQE_max of 16.7%. Despite the higher EQE_max, the DPEPO-based devices showed a significantly serious efficiency roll-off with an EQE of only 1% at 100 mA cm\(^{-2}\). Meanwhile, the CzPO- and Cz3PO-based devices exhibited reduced efficiency roll-off with EQE_100 of 4.2% and 4.2%, respectively, at a display-relevant current density of 100 mA cm\(^{-2}\). All the device data are shown in Table S2.

![Figure 6. Current density–voltage (J–V) characteristics of (a) hole-only devices (HODs) and (b) electron-only devices (EODs) based on the CzPO, Cz3PO and DPEPO hosts.](image)

To investigate the reason for the reduced roll-off characteristics, hole-only devices (HODs) and electron-only devices (EODs) with different host materials were fabricated to evaluate the carrier transporting properties of the corresponding OLEDs. These device configurations were: ITO/HAT-CN (10 nm)/TAPC (20 nm)/host (60 nm)/TAPC (20 nm)/Al (100 nm) for the HODs and ITO/TPBi (20 nm)/host (60 nm)/TPBi (20 nm)/LiF (0.8 nm)/Al (100 nm) for the EODs. Figure 6 showed the J–V curves of the fabricated HODs and EODs. For the HODs (Fig. 6a), the Cz3PO and Cz3PO-based devices showed hole transporting/injection properties due to the presence of more electron-donating carbazole units, while no significant electron current was observed in DPEPO-based device. In contrast, for EODs, the order of the electron transporting/injection properties of devices was DPEPO > CzPO > Cz3PO (Fig. 6b). From both the HODs and EODs characteristics, CzPO and Cz3PO were confirmed to be ambipolar in nature, in which CzPO- and Cz3PO-based devices exhibited balanced hole and electron transporting/injection properties. Thus, the well-balanced charge flux and broad distribution of the charge-recombination zones within the EML resulted in low efficiency roll-off characteristics for CzPO- and Cz3PO-based OLEDs.

In summary, reduced efficiency roll-offs were demonstrated in sky blue TADF-based OLEDs using CzPO and Cz3PO as ambipolar hosts compared to the device with the reference DPEPO host. Sky blue TADF-OLEDs based employing CzPO and Cz3PO host materials showed maximum EQE of 13.1 and 13.2%, respectively, and reduced roll-offs with EQEs of 4.2% and 4.2%, respectively, at current densities of 100 mA cm\(^{-2}\).

This work was supported by a grant fund from the Regional Innovation Eco-System Program sponsored by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan, JST ERATO (Grant Number JPMJER1305), the International Institute for Carbon Neutral Energy Research (WPI-FCNER) sponsored by MEXT, and JSPS KAKENHI (Grant Numbers 00H00000). EZ-C the EPSRC (EP/R035164/1; EP/P010482/1) and the University of St Andrews and for SK the European Commission Marie Sklodowska-Curie Individual Fellowship (MCIF; No. 748430- THF-OLED)
References


We designed and synthesized two new ambipolar host materials, namely CzPO and Cz3PO, which contain electron-donating carbazole and electron-accepting triphenylphosphine oxide moieties. Thermally activated delayed fluorescence (TADF)-based OLEDs employing CzPO and Cz3PO as host materials and the 9-(4-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)-1,3,6,8-tetramethyl-9H-carbazole (CzTRZ2) as the emitter resulted in improved maximum external quantum efficiencies, $\text{EQE}_{\text{max}}$, of 13.1% and 13.2%, respectively, together with small efficiency roll-offs, while the device based on bis[2-(diphenylphosphino)phenyl]ether oxide (DPEPO) showed a much more pronounced efficiency roll-off. The reduced efficiency roll-off in the devices based on CzPO and Cz3PO can be ascribed to their improved ambipolar charge transport capacity compared to that of DPEPO, which results in a broader recombination zone in the emitting layer using these ambipolar hosts.

**High-Triplet-Energy Bipolar Host Materials Based on Phosphine Oxide Derivatives for Efficient Sky-Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes with Reduced Roll-off**

Jong Uk Kim, Michael Y. Wong, Shiv Kumar, Oliver G. Hayes, Finlay Duncan, Chin-Yiu Chan, Ben Yiu-Wing Wong, Hao Ye, Lin-Song Cui, Hajime Nakanotani, Eli Zysman-Colman and Chihaya Adachi.

---

For Peer Review

Graphical Abstract

Textual Information

A brief abstract (required)

Title (required)

High-Triplet-Energy Bipolar Host Materials Based on Phosphine Oxide Derivatives for Efficient Sky-Blue Thermally Activated Delayed Fluorescence Organic Light-Emitting Diodes with Reduced Roll-off

Authors' Names (required)

Jong Uk Kim, Michael Y. Wong, Shiv Kumar, Oliver G. Hayes, Finlay Duncan, Chin-Yiu Chan, Ben Yiu-Wing Wong, Hao Ye, Lin-Song Cui, Hajime Nakanotani, Eli Zysman-Colman and Chihaya Adachi.

Graphical Information

<Please insert your Graphical Abstract: The size is limited within 100 mm width and 30 mm height, or 48 mm square> (required)