Macrospirocyclic Oligomer Based on Triphenylamine and Diphenylphosphine Oxide as a Bipolar Host for Efficient Blue Electrophosphorescent Organic Light-Emitting Diodes (OLEDs)

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S *Supporting Information*

ABSTRACT: A novel bipolar oligomer $(TPA-PO)_3$ was prepared as a host material for efficient blue phosphorescent organic light-emitting diodes (OLEDs). Through the C-9s of the fluorene units, three triphenylamine units attached to diphenylphosphine oxide are connected in series to form a macrocyclic structure. The solution-processed phosphorescent device based on FIrpic and $(TPA-PO)_3$ achieved a maximum current efficiency of 19.4 cd A^{-1} and a maximum luminance of 11 500 cd m^{-2} with a relatively low efficiency roll-off.
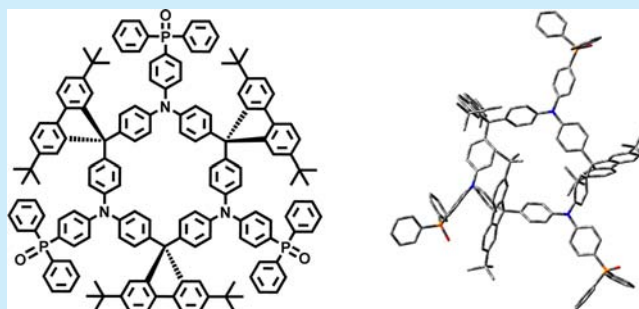
Blue phosphorescent host materials have been intensively studied due to their significance in the development of high efficiency phosphorescent organic light-emitting diodes (PhOLEDs).[1] In order to prevent reverse energy transfer from the guest molecules back to the host molecules within the emitting layer (EML) of a PhOLED, it is favored that the triplet energies (E_T) of host molecules be higher than those of the guest molecules (dopants).[2] This becomes rather challenging for blue phosphorescent host materials, compared with the red and green ones. To achieve such a high E_T, it is crucial to limit the extent of the conjugated system in the host molecules,[1b,3] which often means a relatively small molecular size. On the other hand, bulky and steric molecules tend to form a morphologically stable and uniform amorphous thin film, thus extending the device operation lifetime.[4] Recently, thanks to many special characteristics such as high triplet energy, excellent solution processability as polymers, well-defined molecular structures, ease of purification, and characterization as small molecules, the potential of monodisperse oligomers has been realized as a new class of host materials for solution-processed PhOLEDs with high efficiencies.[5]

In addition, host materials with good carrier transporting properties are required to increase the efficiency of PhOLEDs.[6] Consequently, considerable efforts have been devoted to bipolar host materials which can transport holes and electrons simultaneously to achieve better charge balance in the EML, thereby improving the efficiency of PhOLEDs.[7] To date,

triphenylamine (TPA) as well as carbazole has been widely utilized as a hole transporting (HT) unit for constructing bipolar hosts owing to their good hole transporting ability and high E_T, while the electron transporting (ET) units have many choices.[1c,8] Among them, diphenylphosphine oxide (PO) has been proven to be an effective functional group for electron injection and transportation.[1c,8a,9] The good electron mobility of PO-based materials endows them with a good charge balance in the EML, and the phosphorus center can act to interrupt the $\pi-\pi$ conjugation between adjacent aryl groups, affording a high E_T greater than 2.7 eV.[9b]

Previously, we successfully constructed some monodisperse macrocyclic oligomers by the Friedel–Crafts reaction procedure for blue electroluminescence diodes.[5e,10] In these products, the linkage by the quaternary carbon atoms of the fluorene moiety (C-9) effectively blocks the conjugation extension of the triphenylamine (or carbazole) units, which helps to maintain the triplet energy of TPA. In this letter, we report another novel three-dimensional (3D) oligomer as a bipolar host which employs TPA as an HT unit and PO as an ET unit. In the synthesized molecule, three PO-attached TPA units are connected in series through the sp^3-hybridized C-9s of the fluorene units to form a macrocyclic core, with three fluorene units as pedants. Due to such a bulky and steric

nonconjugated 3D structure with a hollow space, this bipolar macrospirocyclic oligomer may have the advantages of (1) high solubility, (2) reduced intermolecular interaction, (3) high triplet energy, and (4) easy doping capability.

The synthetic route of oligomer (TPA-PO)$_3$ is shown in Scheme 1. First, 4-bromo-*N*-(4-bromophenyl)-*N*-phenyl-aniline

Scheme 1. Synthetic Route of (TPA-PO)$_3$
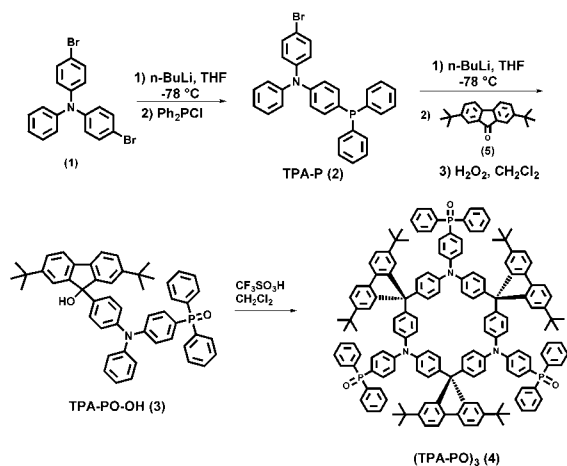
(**1**) was treated with *n*-BuLi at −78 °C in tetra-hydrofuran (THF), followed by adding diphenylphosphine chloride to yield 4-bromo-*N*-(4-(diphenylphosphanyl)phenyl)-*N*-phenyl-aniline (**2**). Then, after lithium−halogen exchange of *n*-BuLi with compound **2** at −78 °C in THF, a solution of 2,7-di-*tert*-butyl-9*H*-fluoren-9-one in THF was added, followed by hydrogen peroxide oxidation of the resulting product to yield the monomer TPA-PO-OH (**3**). Finally, the macrocyclic oligomer was then synthesized by self-condensation of TPA-PO-OH through a Friedel−Crafts reaction. The final Friedel−Crafts reaction afforded a relatively high yield of 41.8% for (TPA-PO)$_3$ (**4**) after column chromatography purification.

The purity and structure of the oligomer were confirmed by MS and NMR spectroscopy. After the Friedel−Crafts reaction, the characteristic peak of the C-9 of the fluorene units moves from 83.7 to 64.7 ppm in ^{13}C NMR spectra, which is due to the disappearance of the electron-withdrawing hydroxyl group and formation of a quaternary carbon center (see the Supporting Information). In addition, the typical triplet peaks of the para-proton on TPA in TPA-PO-OH disappear after the reaction, as can be seen in the ^{1}H NMR spectra. Furthermore, the symmetrical double−double peaks of ortho- and meta-protons on the TPA unit in the ^{1}H NMR spectrum of the oligomer also indicate the symmetric nature of the molecule (see Supporting Information). These results suggest the bond formation between the para-carbon atom of the TPA unit and the C-9 of the fluorene unit after the reaction, which is consistent with what we predicted. Finally, the product was analyzed by MALDI-TOF MS. A single peak at *m/z* 2159.25 in the mass spectrum corresponds to the macrocyclic trimer (calculated *m/z* 2158.00). All of these results show that the desired compound was obtained with high purity.

The thermal properties of (TPA-PO)$_3$ were investigated by differential scanning calorimetry (DSC) and thermal gravi-metric analysis (TGA), with results shown in Figure 1. The TGA curve demonstrates the excellent thermal stability of (TPA-PO)$_3$, with 5% weight loss at a temperature over 450 °C.

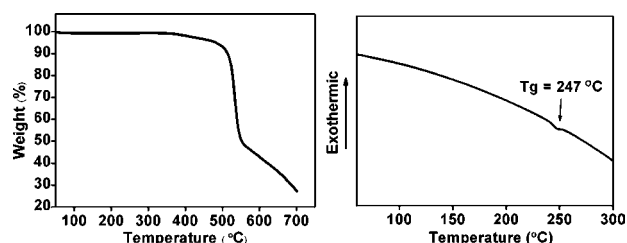**Figure 1.** TGA and DSC curves of oligomer (TPA-PO)$_3$.

Additionally, only an endothermic peak at 247 °C correspond-ing to glass transition is observed on its DSC curve from 50 to 300 °C, indicating that a stable amorphous structure at temperatures below 247 °C can be expected in spin-coated (TPA-PO)$_3$ films. These results reveal the excellent thermal properties of (TPA-PO)$_3$. Atomic force microscopy (AFM) was employed to investigate the morphology of the solution-processed (TPA-PO)$_3$ doped with 15 wt % FIrpic film and (TPA-PO)$_3$ film at an annealing temperature of 120 °C for 2 h under a nitrogen atmosphere on the ITO substrate. The AFM images reveal that the morphologies are quite smooth and homogeneous with a small root-square roughness of 0.39 and 0.38 nm, respectively. This demonstrates that (TPA-PO)$_3$ with a hollow space structure has a good film-forming property and easy doping capability.

Figure 2a shows the UV−vis absorption, photoluminescence (PL) spectra in toluene, and PL spectrum in the thin film of
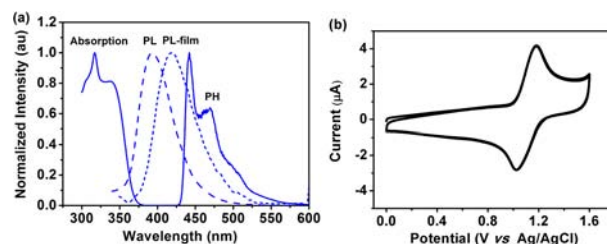

Figure 2. (a) UV−vis absorption and PL spectra in toluene; PL spectrum in thin film; and phosphorescence spectrum of oligomer (TPA-PO)$_3$ in 2-MeTHF glass matrix at 77 K. (b) Cyclic voltammogram (five successive scans) of oligomer (TPA-PO)$_3$ vs Ag/AgCl.

(TPA-PO)$_3$ at room temperature. The maximum absorption and PL peaks are located at 317, 393, and 419 nm, respectively. The phosphorescence (PH) spectrum measured in a 2-methyltetrahydrofuran (2-MeTHF) matrix at 77 K is also depicted in Figure 2. The E_T of (TPA-PO)$_3$ is determined to be 2.81 eV from the highest-energy vibronic sub-band of the phosphorescence spectrum, and it is sufficiently high enough to confine the triplet excitons of FIrpic efficiently. The quantum yield of (TPA-PO)$_3$ was measured to be 0.56 in dilute dichloromethane solution using 9,10-diphenylanthrecene as the fluorescence standard ($\varphi_f = 0.90$ in cyclohexane).

Cyclic voltammetry was performed to investigate the electrochemical properties of (TPA-PO)$_3$, and the cyclic voltammogram (five successive scans for the p-doping process) is shown in Figure 2b. The HOMO energy level determined from the onset of oxidation potential is −5.30 eV for (TPA-PO)$_3$ (relative to vacuum energy level), and the LUMO energy level deduced from HOMO and the photophysical data (absorption onset) is estimated to be −1.92 eV. Noticeably, upon repeated scanning, (TPA-PO)$_3$ exhibits reversible

oxidation behavior, which proves that $(TPA-PO)_3$ is a macrocylic trimer rather than a linear trimer, and the electrochemically active sites of TPA can be effectively blocked with a macrocyclic structure, thereby endowing $(TPA-PO)_3$ with excellent electrochemical stability.[5e]

To gain insight into the electronic structure of the oligomer, density functional theory (DFT) calculations with the B3LYP and 6-31G(d,p) basis set were performed using the Gaussian 09 package (see the Supporting Information for details). The optimized geometry of $(TPA-PO)_3$ shown in Figure 3 suggests
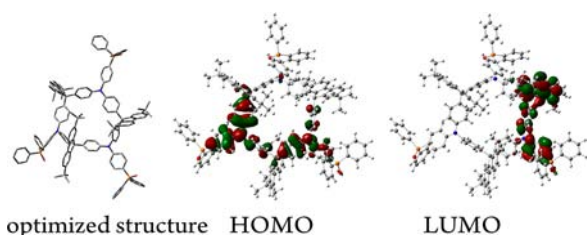

optimized structure   HOMO   LUMO

Figure 3. Optimized geometry and HOMO−LUMO spatial distributions of oligomer $(TPA-PO)_3$.

that the 3D architecture of the molecule consists of three PO-attached triphenylamine units connected in series through three sp^3-hybridized carbon atoms as the ring and three fluorene units as pedants, affording a highly steric molecular structure. This steric 3D structure is expected to effectively suppress intermolecular interactions, aggregation, and excimer formation in the EML, which, consequently, can enhance PhOLED efficiency.[11] The HOMO and LUMO energy levels of $(TPA-PO)_3$ were calculated to be −5.09 and −0.95 eV, respectively. As shown in Figure 3, the HOMO and LUMO of $(TPA-PO)_3$ are quite separated, with the HOMO mainly localized on the core triphenylamine units and LUMO predominately on fluorene units. The separation of the HOMO and LUMO is preferable for efficient carrier transport and the prevention of reverse energy transfer in the EML of PhOLEDs.[12]

The hole-only and electron-only devices with configurations of ITO/PEDOT:PSS (15 nm)/$(TPA-PO)_3$ (30 nm)/mCP (15 nm)/Ag and ITO/TPBI (15 nm)/$(TPA-PO)_3$ (30 nm)/TPBI (15 nm)/Ca (10 nm)/Ag were fabricated (see the Supporting Information). The results reveal that the oligomer has a bipolar property. The relatively lower hole-transporting capacity of $(TPA-PO)_3$ probably results from its highly steric configurations, which decreases the solid stacking density of the film, and therefore weakens the hole-transporting property. To evaluate the suitability of using the oligomer as a host material for solution-processed blue PhOLEDs, we prepared the phosphorescent device with the following device structure: ITO/PEDOT:PSS (25 nm)/$(TPA-PO)_3$:15 wt % FIrpic (35 nm)/TPBI (35 nm)/Ca (10 nm)/Ag. The electroluminescence (EL) spectra of the $(TPA-PO)_3$-based device over the entire range of operating voltages are shown in Figure 4. The EL spectra exhibit typical emissions from FIrpic with no emission originating from the adjacent organic layers, which suggests that triplet energy was efficiently transferred from $(TPA-PO)_3$ (host) to FIrpic (guest) resulting from the higher triplet energy of $(TPA-PO)_3$ and that PEDOT:PSS and TPBI effectively confined the excitons within the EML. Figure 4 also displays the current density−voltage−luminance characteristics and the current efficiency−luminance−power efficiency curve of this PhOLED. A relatively high turn-on voltage of 6 V
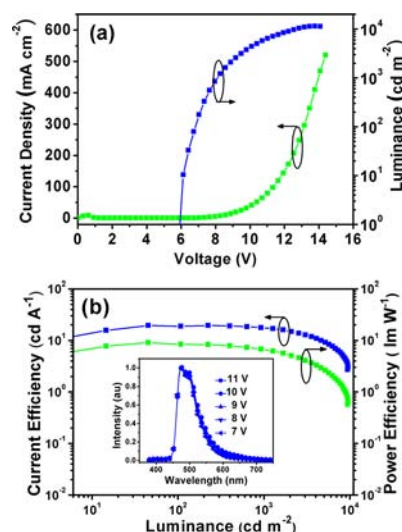

Figure 4. (a) Current density−voltage−luminance characteristics and (b) current efficiency−luminance−power efficiency characteristics of the blue PhOLED with configuration of ITO/PEDOT:PSS (25 nm)/$(TPA-PO)_3$:15 wt % FIrpic (35 nm)/TPBI (35 nm)/Ca (10 nm)/Ag. Inset: EL spectra of the device at 7, 8, 9, 10, and 11 V, respectively.

may result from the electron injection barrier at the TPBI/emitting layer interface due to the higher-lying LUMO energy level of −1.92 eV for $(TPA-PO)_3$. The device achieved a maximum current efficiency of 19.4 cd A^{-1} at 45 cd m^{-2} with a maximum power efficiency of 9.0 lm W^{1-} and a maximum external quantum efficiency (EQE) of 8.2%. The luminance reached 11 500 cd m^{-2} at 13.8 V. Notably, at the luminance levels of 100 and 1000 cd m^{-2}, the current efficiencies remain as high as 18.7 cd A^{-1} (8.4 lm W^{1-} and EQE of 8.0%) and 17.7 cd A^{-1} (6.7 lm W^{1-} and EQE of 7.5%), respectively, manifesting a relatively low efficiency roll-off at high driving voltages. This efficiency compares very well to the performance of dendritic oligomer based blue electrophosphorescent devices fabricated by a solution procedure.[5a,b]

In conclusion, we have synthesized a novel macrospirocyclic oligomer $(TPA-PO)_3$ using a simple Friedel−Crafts reaction. The extended molecular size with nonconjugated structure improves the solution process ability and thermal stability, without lowering its triplet energy and affecting its optical properties. The solution-processed blue PhOLED based on FIrpic and $(TPA-PO)_3$ has achieved a maximum current efficiency of 19.4 cd A^{-1} and a maximum luminance of 11 500 cd m^{-2} with a relatively low efficiency roll-off, demonstrating its promise as a blue host material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures, ^{1}H NMR, ^{13}CNMR, ^{31}P NMR, MALDI-TOF-MS spectra, AFM images, and current density−voltage characteristics of the single-charge devices. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) (a) Baldo, M.; O'Brien, D.; You, Y.; Shoustikov, A.; Sibley, S.; Thompson, M.; Forrest, S. *Nature* **1998**, *395*, 151. (b) Tao, Y.; Yang, C.; Qin, J. *Chem. Soc. Rev.* **2011**, *40*, 2943. (c) Yook, K.; Lee, J. *Adv. Mater.* **2012**, *24*, 3169. (c) Xiao, L.; Chen, Z.; Qu, B.; Luo, J.; Kong, S.; Gong, Q.; Kido, J. *Adv. Mater.* **2011**, *23*, 926. (d) Yook, K. S.; Lee, J. Y. *Adv. Mater.* **2012**, *24*, 3169.

(2) (a) Holmes, R.; Forrest, S.; Tung, Y.; Kwong, R.; Brown, J.; Garon, S.; Thompson, M. *Appl. Phys. Lett.* **2003**, *82*, 2422. (b) Kavitha, J.; Chang, S.; Chi, Y.; Yu, J. K.; Hu, Y.; Chou, P.; Peng, S.; Lee, G.; Tao, Y.; Chien, C.; Carty, A. *Adv. Funct. Mater.* **2005**, *15*, 223.

(3) Li, Y.; Liu, T.; Liu, H.; Tian, M. Z.; Li, Y. *Acc. Chem. Res.* **2014**, *47*, 1186.

(4) (a) Wong, K.; Chen, Y.; Lin, Y.; Su, H.; Wu, C. *Org. Lett.* **2005**, *7*, 5361. (b) Jiang, Z.; Chen, Y.; Yang, C.; Cao, Y.; Tao, Y.; Qin, J.; Ma, D. *Org. Lett.* **2009**, *11*, 1503.

(5) (a) Ding, J.; Zhang, B.; Lu, J.; Xie, Z.; Wang, L.; Jing, X.; Wang, F. *Adv. Mater.* **2009**, *21*, 4983. (b) Lee, C. C.; Leung, M. K.; Lee, P. Y.; Chiu, T. L.; Lee, J. H.; Liu, C.; Chou, P. T. *Macromolecules* **2011**, *45*, 751. (c) Gong, S.; Fu, Q.; Wang, Q.; Yang, C. L.; Zhong, C.; Qin, J. G.; Ma, D. G. *Adv. Mater.* **2011**, *23*, 4956. (d) Zhang, B.; Tan, G.; Lam, C. S.; Yao, B.; Ho, C. L.; Liu, L.; Xie, Z.; Wong, W. Y.; Ding, J.; Wang, L. *Adv. Mater.* **2012**, *24*, 1873. (e) Fan, Z. K.; Li, N. Q.; Quan, Y. W.; Chen, Q. M.; Ye, S. H.; Fan, Q. L.; Huang, W.; Xu, H. *J. Mater. Chem. C* **2014**, *2*, 9754.

(6) Chaskar, A.; Chen, H.; Wong, K. *Adv. Mater.* **2011**, *23*, 3876.

(7) Zacharias, P.; Gather, M.; Rojahn, M.; Nuyken, O.; Meerholz, K. *Angew. Chem., Int. Ed.* **2007**, *46*, 4388.

(8) (a) Hsu, F.; Chien, C.; Shih, P.; Shu, C. *Chem. Mater.* **2009**, *21*, 1017. (b) Lee, C.; Lee, J. *Adv. Mater.* **2013**, *25*, 5450. (c) Gong, S.; Zhong, C.; Fu, Q.; Ma, D.; Qin, J.; Yang, C. *J. Phys. Chem. C* **2013**, *117*, 549.

(9) (a) Jeon, S.; Yook, K.; Joo, C.; Lee, J. *Adv. Funct. Mater.* **2009**, *19*, 3644. (b) Koech, P.; Polikarpov, E.; Rainbolt, J.; Cosimbescu, L.; Swensen, J.; Von Ruden, A.; Padmaperuma, A. *Org. Lett.* **2010**, *12*, 5534. (c) Yu, D.; Zhao, F.; Han, C.; Xu, H.; Li, J.; Zhang, Z.; Deng, Z.; Ma, D.; Yan, P. *Adv. Mater.* **2012**, *24*, 509.

(10) (a) Lu, Y.; Zhou, Y.; Quan, Y.; Chen, Q.; Chen, R.; Zhang, Z.; Fan, Q.; Huang, W.; Ding, J. *Org. Lett.* **2010**, *13*, 200. (b) Kong, Q.; Zhu, D.; Quan, Y.; Chen, Q.; Ding, J.; Lu, J.; Tao, Y. *Chem. Mater.* **2007**, *19*, 3309.

(11) (a) Markovitsi, D.; Germain, A.; Milli, P.; Lcuyert, P.; Gallos, L.; Argyrakis, P.; Bengs, H.; Ringsdorf, H. *J. Phys. Chem.* **1995**, *99*, 1005. (b) Luo, J.; Zhou, Y.; Niu, Z.; Zhou, Q.; Ma, Y.; Pei, J. *J. Am. Chem. Soc.* **2007**, *129*, 11314. (c) Lee, C.; Lee, J. *Adv. Mater.* **2013**, *25*, 596.

(12) (a) Tao, Y.; Wang, Q.; Yang, C.; Zhong, C.; Zhang, K.; Qin, J.; Ma, D. *Adv. Funct. Mater.* **2010**, *20*, 304. (b) Jin, J.; Zhang, W.; Wang, B.; Mu, G.; Xu, P.; Wang, L.; Huang, H.; Chen, J.; Ma, D. *Chem. Mater.* **2014**, *26*, 2388.