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Alcohol-Soluble Electron-Transport Small Molecule for Fully Solution-Processed Multilayer White Electrophosphorescent Devices

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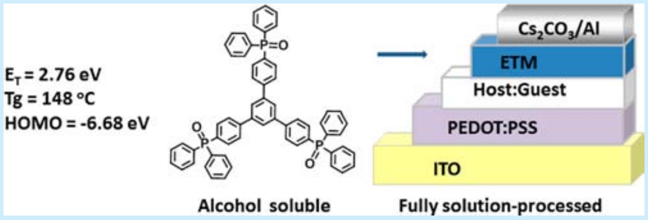
S *Supporting Information*

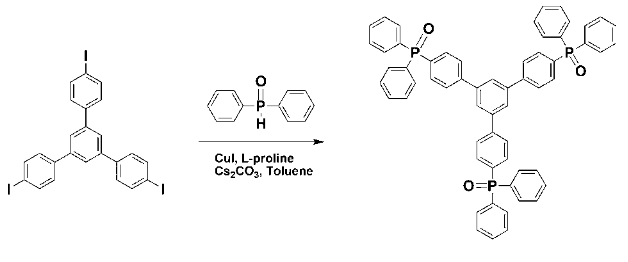
ABSTRACT: A novel alcohol-soluble electron-transport material was designed and synthesized. This material not only possesses a high triplet energy and a low HOMO level but also exhibits excellent electron-transport properties and good film-forming ability. Efficient fully solution-processed multilayer white electrophosphorescent devices have been fabricated by using this alcohol-processable material as an orthogonal electron-transport layer.



During the last two decades, organic lighting-emitting diodes (OLEDs) have attracted intense attention owing to their potential applications in full-color display panels, flexible displays, and solid-state lighting sources.[1] While highly efficient OLEDs have been produced via vacuum evaporation tenchiques, fully solution-processed devices are more desirable for large size flat panel displays and solid-state applications because they are compatible with low cost, large area roll-to-roll manufacturing processes. In order to pursue efficient OLEDs comparable with their inorganic heterjunction counterparts, a multilayer stack of active materials is required, including charge injection/transporting/blocking functionalities. Recently, solution-processable hole-transporting materials, emissive materials and host materials for triplet emitter have been developed.[2] However, a vacuum-deposited 1,3,5-tris(1-phenyl-1*H*-benzo-[*d*]imidazol-2-yl)benzene (TPBi) layer as electron-transporting (ET) and hole-blocking is frequently used in those solution-processed devices to improve device performance, which leads to a costly and complex process. During the fabrication process of fully solution-processed multilayer OLEDs, the most important problem is the lower layer can be affected by the solvent of the subsequent layer. One approach to overcoming such a problem is to utilize orthogonal solvents in the spin-coating process. A sequential solution-processed multilayer was obtained using alcohol-/water-soluble polyelectrolytes as the ET layer (ETL).[3] However, it was reported that the ionic side groups in polyelectrolytes can induce an undesired electrochemical doping effect.[4] In contrast to conjugated polymer counterparts, small molecule ET materials can be conventionally synthezied and purified, which is desirably used in the orthogonal solvent approach to fully solution-processed devices. So far, only a few studies have reported the use of organic acid/water mixture solutions to deposit small molecules as ETLs in multilayer polymer-based blue phosphorescent organic light-emitting diodes (PhOLEDs).[5]

To the best of our knowledge, no report on small molecules as ETLs in fully solution-processed multilayer white PhOLEDs was found in the literature. In this paper, we report the synthesis, thermal and electrochemical properties, and photophysics of a novel star-shaped alcohol-soluble ET material, tris(4-(diphenylphosphoryl)phenyl)benzene (PhPO), for fully small molecule solution-processed multilayer white PhOLEDs. The molecular structure of the PhPO is shown in Scheme 1.

Scheme 1. Synthetic Route for PhPO



PhPO

PhPO comprises a 1,3,5-tri(phenyl)benzene core and three diphenylphosphine oxide (PO) peripheries. As a result, the newly synthesized molecule possess seveal important characteristics: (i) PO is a well-known electron-accepting component for building ET materials with high electron mobility.[6] Accordingly, PhPO containing three PO units can be a promising ET material for OLEDs. (ii) The introduction of polar phosphine

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oxide units can improve their solubility in the polar solvents, such as methanol, ethanol, and 2-propanol, which enabled an efficient multilayer device to be fabricated by full solution-processing. (iii) Owing to the star-shaped configuration, PhPO exhibits relatively high morphological and thermal stability. Furthermore, the nonconjugation linkage mode keeps the molecule at a high triplet energy level to efficiently confine the excitons in the emission layer (EML). (iv) With its deep highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) values, it is well suited as a hole-blocking layer (HBL) and facilitates electron injection in the device. A two-color multilayer white PhOLEDs was fabricated by orthogonal sequential solution-processing of triplet emitters codoped with Cz-TCB-based[7] EML and our new alcohol-soluble ET material PhPO. The device exhibited a maximum luminous efficiency (LE) of 32.6 cd A^{-1} with an external quantum efficiency (EQE) of 11.5%, which are close to the reported values of solution-processed multilayer white PhOLEDs with a vacuum-deposited TPBi layer.[2e,8]

The arylphosphine oxide derivatives are usually synthesized by coupling reactions between lithiated intermediates and diphenylchlorophosphine and then oxidized with an excess of hydrogen peroxide. As shown in Scheme 1, PhPO was easily synthesized by the Ullmann coupling reaction.[9] The intermediate compound 1,3,5-tri(4-iodophenyl)benzene was prepared in 80% yield by a modification of the reported procedure,[10] followed by coupling with excess diphenylphosphine oxide in the presence of catalytic amounts of CuI and L-proline to give the desired PhPO in 60% yield. PhPO was purified with the silica column method and recrystallized, producing very pure powders. $^1H/^{13}C$ NMR, mass spectrometry, and elemental analysis were employed to confirm the chemical structure as described in the experimental details (Supporting Information).

The thermal properties of the new compound were investigated by thermal gravimetric analyses (TGA) and differential scanning calorimetry (DSC). As shown in Figure 1, the TGA curve confirmed the high thermal stability of PhPO, and no loss of weight was noted below 462 °C. The DSC curve revealed a well-defined glass transition temperatures (T_g = 148 °C), which is much higher than those of commonly used ET materials such as 4,7-diphenyl-1,10-phenanthroline (BPhen) (62 °C) and 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (83 °C).[11]The nonplanar molecular configuration is strongly beneficial to the thermal stability, which suggests that PhPO could form morphologically stable and uniform amorphous films. As a result, the solution-deposited PhPO ET layer has a smooth surface with a root-mean-square (RMS) roughness value of 0.48 nm (Supporting Information).

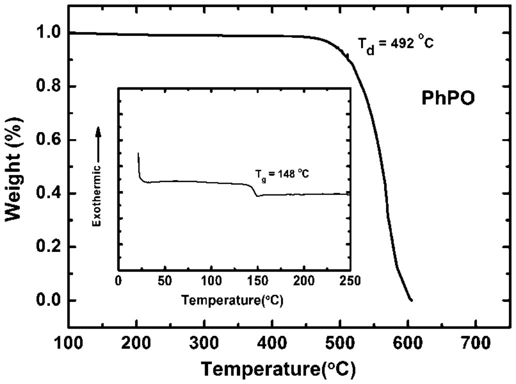

Figure 1. TGA traces of PhPO recorded at a heating rate of 10 °C min^{-1}. Inset: DSC measurement recorded at a heating rate of 10 °C min^{-1}.

Figure 2 presents the electrochemical properties of PhPO. Upon cathodic sweeping in acetonitrile, PhPO exhibits one irreversible reduction peak at a voltage of −2.25 V, which occurs on the electron-accepting PO moiety. No oxidation wave during the anodic scan was observed. On the basis of the onset potentials for reduction, we estimated the LUMO energy levels of PhPO to be −2.55 eV, with regard to ferrocene (−4.8 eV below vacuum).[12] It is believed that the LUMO level of PhPO was low enough to easily accept electrons from the Cs_2CO_3/Al (work function = −2.2 eV). The energy band gap (E_g) of 4.13 eV for PhPO was determined by the absorption edge of the UV−vis absorption spetrum (Figure 3). The estimated HOMO (HOMO = LUMO − E_g) value of −6.68 eV shows a rather deep energy level for the this class of alcohol/water-soluble ET materials, which leads to the excellent HBL in PhOLEDs.[5]

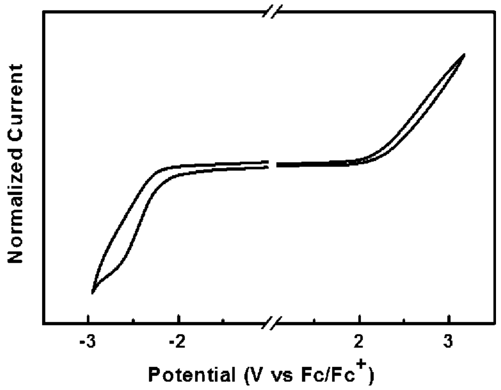

Figure 2. Electrochemical properties of PhPO.

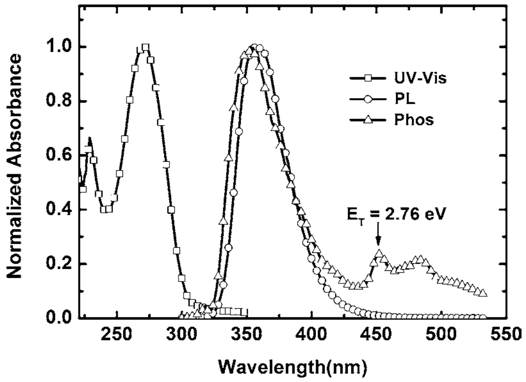

Figure 3. Absorption and emission spectra of PhPO in CH_2Cl_2 and phosphorescent spectra of PhPO in 2-methyltetrahydrofuran at 77 K.

The UV−vis absorption and photoluminescence (PL) spectra of PhPO have been investigated. As shown in Figure 3, the absorption peak at around 270 nm could be attributed to the lowest $\pi-\pi^*$ transitions of the 1,3,5-tri(phenyl)benzene core. Upon UV excitation, the PL spectrum has the emission peak at 352 nm with respected to the 1,3,5-tri(phenyl)benzene core emission. The respective spectra are similar to those of the

1,3,5-tri(phenyl)benzene chromophore because the P=O group prevents electron communication between the central 1,3,5-tri(phenyl)benzene core and the outer phenyl group in PhPO resulting in high energy UV emission.[6b] The low-temperature photoluminescence spectrum of PhPO exhibits a maximum at 449 nm, corresponding to a triplet energy level of 2.76 eV, which is higher than that of typical triplet-emitters, such as iridium(III) bis(4,6-difluorophenylpyridinato)picolinate (FIrpic) and bis[2-(9,9-diethyl-9*H*-fluoren-2-yl)-1-phenyl-1*H*-benzoimidazol-N,C^3]iridium(acetylacetonate) [$(fbi)_2Ir(acac)$]. We measured the PL quantum yield of 10% FIrpic-doped PhPO film by using an integrating sphere as 72%, which is closed to the value previously reported.[13] The high triplet energy level of PhPO can effectively confine the triplet excitons in the EML and improve charge recombination in the devices. The exciton confinement property was further confirmed by transient photoluminescence measurements. As shown in Figure S6 (Supporting Information), the decay curve of 4 wt % FIrpic-doped TPBi film shows a long decay component, which indicated the exothermic back-energy transfer from FIrpic to TPBi, while 4 wt % of FIrpic-doped PhPO film exhibits a monoexponential decay curve, indicating that the FIrpic exciton quenching can be suppressed at the EML/ETL interface. As a result, the triplet energy level of PhPO (2.76 eV) is sufficiently high for confining the excitons on the blue phosphor.

A fully solution-processed multilayer white PhOLED using the alcohol-soluble ET material PhPO was fabricated with the following structure: ITO/PEDOT:PSS/Cz-TCB:OXD-7(30 wt %):FIrpic(10 wt %):$(fbi)_2Ir(acac)$(0.2 wt %)/PhPO/Cs_2CO_3/Al. The EML consisted of a blend of host material Cz-TCB and ET material OXD-7 and codoped with the blue phosphorescent dye FIrpic and the orange phosphorescent dye $(fbi)_2Ir(acac)$ as described in the experimental details (Supporting Information). The PhPO was deposited from a 2propanol solution onto the EML. The scheme of the energy alignment is depicted in Figure 4 (a). The current density−voltage and luminance−voltage characteristics are shown in Figure S5 (Supporting Information). The device using PhPO as ET material showed a turn-on voltage of 5.8 V (corresponding to 1 cd m^{-2}) and gave a maximum LE of 32.6 cd A^{-1} with a corresponding EQE of 11.5%. As shown in Figure 4 (b), the electroluminescence (EL) spectrum of the PhPO-based device is warm white emission with the Commission Internationale de L'Eclairage (CIE) coordinates of (0.34, 0.45), which is in accord with the reported value of two-color-based phosphorescent WOLEDs.[14] Two intense peaks around 474 and 552 nm were clearly observed, which originate from the triplet emission of FIrpic and dye $(fbi)_2Ir(acac)$. No additional emissions were observed for host materials and ET material, which demonstrated efficient energy transfer from the host to triplet emitter and effective recombination within the EML due to the low HOMO and high triplet energy of PhPO. To the best of our knowledge, this is the first time an alcohol-soluble ET material has been used as hole and exciton blocking layer for the small molecule based fully solution-processed multilayer white PhOLEDs. Moreover, the obtained result is comparable with the value of the corresponding device base on a vacuum-deposited TPBi layer (5.6 V, 34.2 cd A^{-1}, 12.2%; see the Supporting Information, Figure S7).

To summarize, a novel ET material based on diphenylphosphine oxide units was synthesized, and its photophysical, electrochemical, and EL properties were characterized. Owing to the star-shaped configuration, PhPO exhibited high decomposition and glass transition temperatures. The low-lying HOMO energy level (−6.68 eV) and high triplet energy (2.76 eV) of PhPO enabled application as a hole and exciton-blocking layer. Furthermore, alcohol-soluble PhPO has enabled orthogonal sequential solution processing of multilayered white small-molecule-based PhOLEDs with high efficiency.

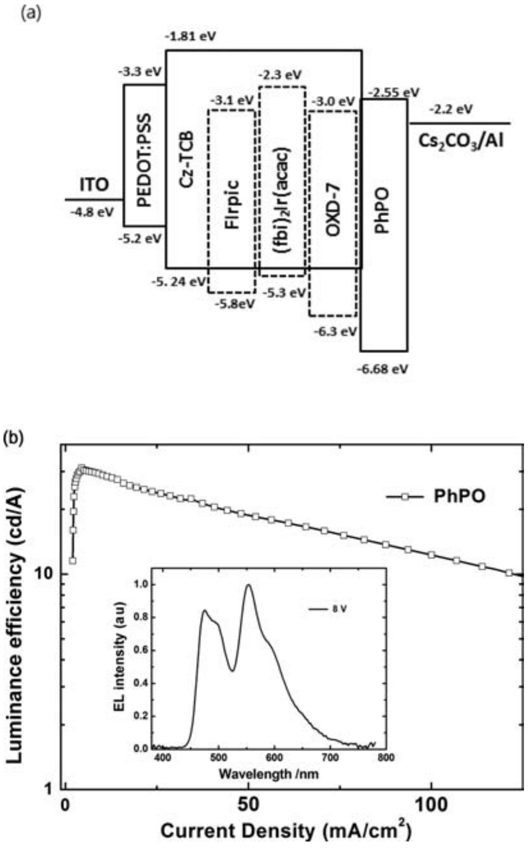

Figure 4. (a) Schematic energy-level diagram of the device. (b) Current efficiency versus current density of device. Inset: normalized EL spectrum.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental and characterization details of the new compound. 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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