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Novel electron transporting materials for highly efficient fully solution-processed green PhOLEDs with low rolls-off and drive voltage

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ABSTRACT

Two novel alcohol-soluble electron transporting materials, diphenyl(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl) phosphine oxide (**PhOXDPO**) and ((1,3-phenylenebis(1,3,4-oxadiazole-5,2-diyl))bis(4,1-phenylene))bis(diphenylphosphine oxide) (**Ph2OXDPO**), were synthesized and utilized in fully solution-processed green phosphorescent organic light emitting diodes (PhOLEDs). The photo-physical, electrochemical and thermal properties, and electron mobility of **PhOXDPO** and **Ph2OXDPO** had been investigated in detail. The photo-physical and electrochemical result showed that the **PhOXDPO** and **Ph2OXDPO** had lower highest occupied molecular orbitals (HOMO) level (-6.24 eV and -6.09 eV) and high triplet level (2.79 eV and 2.66 eV). Both **PhOXDPO** and **Ph2OXDPO** achieved high electron mobility of $6.6 \times 10^{-4}\,\mathrm{cm^2\,v^{-1}\,s^{-1}}$ and $6.0 \times 10^{-4}\,\mathrm{cm^2\,v^{-1}\,s^{-1}}$. The current efficiency of the device based on **PhOXDPO** reached $49.5\,\mathrm{cd\,A^{-1}}$, and showed only 1.5% roll-off at $1000\,\mathrm{cd\,m^{-2}}$. Due to the more matchable energy gap and low HOMO level of **PhOXDPO**, the **PhOXDPO** based device presented better efficiency than the device with **Ph2OXDPO** as ETL. Compared with the ETL-free device, the efficiencies of the devices based on **PhOXDPO** and **Ph2OXDPO** increased up to one order of magnitude, and remained a high level ($38.666\,\mathrm{cd\,A^{-1}}$ and $37.834\,\mathrm{cd\,A^{-1}}$, at $10000\,\mathrm{cd\,m^{-2}}$). The device used TPBI as ETL made by vacuum evaporation and the device ultilized Bphen as ETL made by spin-coating showed much lower efficiency and luminance, on every voltage, than the devices based on PhOXDPO and Ph2OXDPO.

1. Introduction

Conventional organic light emitting diodes (OLEDs) are fabricated by vacuum evaporation techniques, with which achieved many high efficient OLEDs with stable and smooth films, including blue [1,2], green [3,4], red [5,6] and white [7,8] OLEDs. Solution-processed technology, compared with vacuum evaporation, were more suitable for flexible devices and large scale low-cost manufactory. However, fully solution-processed OLEDs have their instinct weakness that the solution deposition of an upper layer could inevitably redissolve or destroy the underlying layer, leading to poor film quality and devices performance.

Many methods have been used to solve this problem, such as photo- [9,10] or thermo- [11,12] crosslinking, ink-jet printing [13,14], orthogonal solvents [11,15–21] etc. The orthogonal solvent method has been taken to fabricate fully soluble multi-layer phosphorescent organic light emitting diodes (PhOLEDs). For the requirement of orthogonal solvents, water/alcohol-soluble electron transporting materials (ETMs) are needed. As is known most studies about alcohol-soluble ETMs in PhOLEDs are focused on polymers [15,17,21]. However, Sax, S. demonstrates that the uncontrollable electrochemical doping effects could be caused by the attachment of ionic groups to the polymers' side chains [22]. In Contrast with polyelectrolytes, the synthesis routes of small molecule ETMs are usually more simplified, which makes small molecular ETMs more convenient to purify. Furthermore, the structure of small molecular ETMs tend to be instinct, which is beneficial for the repeatability of PhOLEDs. For the above reasons, small molecular ETMs are more suitable for fully solution-processed devices. A few studies

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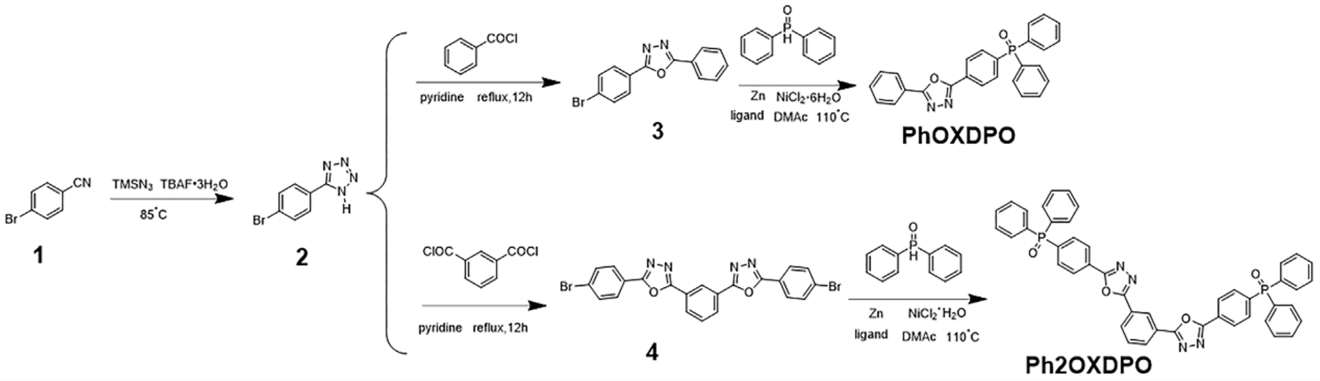

Scheme 1. Synthetic pathway of the electron transporting materials **PhOXDPO** and **Ph2OXDPO**.

focused on the small molecular ETMs [23–28]. The characteristics of some ETMs were not sufficiently demonstrated, which makes it hard to choose suitable ETMs for solution-processed PhOLEDs. So more studies about novel alcohol-soluble ETMs should be performed.

In this work, we designed and synthesized two novel alcohol-soluble ETMs, diphenyl(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)phosphine oxide (**PhOXDPO**) and ((1,3-phenylenebis(1,3,4-oxadiazole-5,2-diyl)) bis(4,1-phenylene))bis(diphenylphosphine oxide) (**Ph2OXDPO**). The molecular structures are shown in Scheme 1. These compounds consist of diphenyl-phosphine oxide and oxadiazole. Oxadiazole, an excellent electron accepting component, is considered an ideal part for ETMs with high electron mobility. Diphenyl-phosphine oxide (DPPO) is considered a desirable part for alcohol-soluble property [20,29], and many ETMs containing P = O moiety have been investigated [30–32]. What's more, the molecular design has taken the following aspects into consideration: 1) p-conjugation of oxadiazole derivatives can be restricted within the ring to form wide bandgap, which is effective to forbid triplet energy transfer from emitters to ETMs so as to strengthen exciton blocking [33,34]; 2) the P = O bond in DPPO will form insulating linkages, which makes it possible to construct so-called ‘charge – exciton separation (CES)’ strategy, endowing ETMs low highest occupied molecular orbitals (HOMO) and high triplet level to reduce the interfacial quenching of electron transporting layers (ETLs) and emitters [35,36], then achieve high efficient and low roll-off PhOLEDs [37,38]. Photophysical, electrochemical and thermal properties, and electron mobility of **PhOXDPO** and **Ph2OXDPO** were investigated. Utilizing **PhOXDPO** and **Ph2OXDPO** as ETMs, fully solution-processed PhOLEDs were fabricated. Also investigated were a series of device measurements, such as electroluminescence (EL) spectrum, luminance and efficiency.

2. Experimental section

2.1. Materials

All materials were used as received from commercial supplier (Tianjin Heowns Biochemical Technology Co., Ltd.) without further purification. All solvents were purchased from Tianjin Guangfu Fine Chemical Research Institute.

2.2. General procedures

Ultraviolet–visible absorption (UV–Vis) and photo-luminance (PL) spectra were obtained on a Thermo Evolution 300 UV–Visible spectrometer and a HitachiF-4500 fluorescence spectrometer, respectively. The phosphorescence spectrum was operated on a Spectrofluorometer F7000. Differential scanning calorimetry (DSC) was recorded on a TA Q20 instrument operated with heating rate of 10 °C min^{-1} from 25 °C to 350 °C in nitrogen atmosphere (N_2). The glass transition temperature (*T*g) was determined from the second heating scan loop. Temperature at a 5% weight loss was used as the decomposition temperature (*T*d). Thermal gravity analysis (TGA) was recorded on a METTLER TOLEDO TGA/DSC1 Thermogravimetric Analyzer heating rate of 10 °C min^{-1} from 30 °C to 600 °C in N_2. X-ray diffraction curves were recorded on a Rigaku Miniflex 600 with 2θ range of 0°–90°, scanning at a rate of 1° min^{-1}. ^{1}H NMR and ^{13}C NMR were recorded with a AVANCE III HD (400 MHz) spectrometer in chloroform-d ($CDCl_3$), Dichloromethane-d2 (CD_2Cl_2) or dimethyl sulfoxide-d6 (DMSO-d_6) with tetramethysilane as reference. The element analysis was performed with a VarioMICRO CHNOS elemental analyzer. Fourier transfer infrared spectra (FT-IR) were measured as a KBr disk on a Thermo NICOLET380 spectrometer. High resolution mass spectrum (HRMS) was performed with a Bruker MicrOTOF-QII.

2.3. OLED fabrication and measurements

Two fully solution-processed multilayer green PhOLEDs A and B using **PhOXDPO** and **Ph2OXDPO** as alcohol-soluble ETLs were fabricated with the following structure: ITO/PEDOT:PSS (40 nm)/PVK (20 nm)/Host2:IrG = 95:5 (50 nm)/**PhOXDPO** or **Ph2OXDPO** (15 nm)/CsF/Al. An ETL-free device C was designed as control device with the structure as follow: ITO/PEDOT:PSS (40 nm)/PVK (20 nm)/Host2:IrG = 95:5 (50 nm)/CsF/Al. The emitting layer consisted of host material Host2 and doped with the green phosphorescent dye IrG. PEDOT:PSS served as hole injection layer, and CsF was used as electron injection layer. PVK served as hole transporting layer.

Indium tin oxide (ITO) glass substrates with sheet resistance of 10 Ω per square were cleaned by ultrasonic wave with isopropanol, acetone, detergent, diluted water and isopropanol, then dried in an oven. After O_2 plasma treatment for 2 min, an anode modified layer was achieved by spin-coating the PEDOT: PSS (CLEVIOSTM P VP AI 4083) colloidal solution on the ITO side at 3000 rpm, followed with baking at 150 °C for 30 min. The 10 mg mL^{-1} concentrated PVK was spin-coated on the PEDOT:PSS film. A 20 nm thick emitter layer was achieved after baking at 150 °C for 20 min. The 10 mg mL^{-1} concentrated host2: IrG = 95:5 was spin-coated on the PVK film. A 50 nm thick emitter layer was achieved after baking at 150 °C for 20 min. The 10 mg mL^{-1} concentrated **PhOXDPO** or **Ph2OXDPO** isopropanol solution was spin-coated on the emitter film. Then above substrate was immediately transferred into the deposition chamber with a vacuum degree of 2×10^{-6} pa. Then 1.5 nm cesium fluoride (CsF) and 100 nm aluminium (Al) were deposited successively at a rate of ∼0.1 Å s^{-1} and ∼4 Å s^{-1}, respectively. The thicknesses of the spin-coated films were measured by a Dektak 150 surface profiler terrace detector. The active area of the device is 4×4 mm^2, determined by the cross breadth between the cathode (Al) and the anode (ITO). The electroluminescent spectra were measured by a Ocean Optics USB2000 + photometer. Steady current-voltage-luminance characteristics were measured by a Keithley 2400 source meter and Konica Minolta Chroma Meter CS-200