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## Fluorene-Based Phosphine Oxide Host Materials for Blue Electrophosphorescence: An Effective Strategy for a High Triplet Energy Level

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Electrophosphorescence has attracted much interest, with the potential of 100% internal quantum efficiency, generated from both singlet and triplet excitons. Phosphorescent organic light-emitting diodes (PHOLEDs) based on electrophosphorescent materials can be applied to highly energyefficient, flat-panel displays and are also promising candidates for the next generation of solid-state lighting.<sup>[1]</sup> However, the longer lifetime of triplet excitons increases the possibility of triplet-triplet annihilation and concentration quenching. To improve the device performance, an effective approach is doping the phosphors in host materials.<sup>[2]</sup> Nevertheless, the creation of stable and efficient blue-emitting PHOLEDs remains a significant challenge.<sup>[3]</sup> For blue-emitting electrophosphorescent doping systems, the efficient, positive-energy transfer to the guest (such as bis(4,6-difluorophenylpyridinato-N,C2)picolinatoiridium (FIrpic)) requires a very high first triplet energy level  $(T_1)$  of the host  $(T_1)$  $\approx 3.0 \text{ eV}$ ).<sup>[4]</sup> Besides the high T<sub>1</sub>, a low operating voltage is another significant factor that requires an excellent carrier injection/transporting ability of the host.<sup>[3a-e]</sup> Usually, a high T<sub>1</sub> requires a small conjugated area, which is detrimental to the carrier injection and transporting ability. Therefore, the key issue for high-performance blue-emitting PHOLEDs is how to develop efficient host materials with a high  $T_1$  and excellent carrier injection/transporting ability.

To expand the conjugated area, most of the hosts are designed to incorporate meso, twisted, or insulating linkages, such as N,N-dicarbazoyl-3,5-benzene (mCP<sup>[4]</sup>), 9,9'-(2,2'-dimethylbiphenyl-4,4'-diyl)bis(9*H*-carbazole) (CDBP<sup>[5]</sup>), and

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tetraaryl silane derivatives.<sup>[6]</sup> However, the poor electron-injection ability of carbazole derivatives, or the electrical inertia of silicon.<sup>[7a]</sup> induces an unbalanced carrier injection/ transporting ability, which increases the operating voltage. Recently, a number of aryl phosphine oxides (APO) derivatives have shown excellent host characteristics for blue-emitting PHOLEDs and attracted intense interest.<sup>[7]</sup> Results indicate that the  $T_1$  of the APO hosts is determined by the chromophores in the molecules. Furthermore, in contrast to other insulating systems, the P=O moieties can efficiently polarize the molecules to enable contributions to the lowest unoccupied molecular orbital (LUMO).[7b] Therefore, APOs can support both an efficient carrier injection/transporting ability and a high T<sub>1</sub>. Nevertheless, for nearly all of the APO hosts reported so far, the P=O moieties are directly bonded to the chromophores along the long axis of the molecules; for example, the 2,7-substitution of fluorene,[7b,f-h] the 3,6-substitution of carbazole,<sup>[7a]</sup> and the 2,8-substitution of dibenzofuran.<sup>[7c]</sup> Such structures are ineffective in maintaining a high T<sub>1</sub> because the P=O bond can still slightly reduce the energy gap and the excited levels.<sup>[7a,d,e]</sup> Therefore, one of the key problems for high-performance APO hosts is the development of a suitable linkage mode of PO moieties and chromophores to preserve a high  $T_1$  and facilitate further multifunctionalization of the hosts. Recently, we reported a novel APO host with an ortho-linked phosphine oxide moiety.<sup>[8]</sup> This proved that the unsymmetrical structure is superior in maintaining a high  $T_1$  and polarizing the chromophore. To further improve the  $T_1$  of the APO hosts, we believed that an indirect linkage of the chromophore and phosphine oxide moieties may be another effective strategy.

Herein, two fluorene-based APO hosts, 9-(4'-butylphenyl)-9-(diphenylphosphorylphenyl)fluorene (FSPO) and 9,9bis(diphenylphosphorylphenyl)fluorene (FDPO) were designed and synthesized (Scheme 1). In both FSPO and FDPO, the diphenylphosphine oxide (DPPO) moieties were bonded to fluorene through phenyl at the 9-position. This structure has three advantages: 1) the twisted linkage between fluorene and APO moieties at the 9-position is effective in maintaining the excited level; 2) DPPO moieties bond with fluorene on the short axis of the molecules, which is more effective for polarization; 3) their unsymmetric structures and the strong steric effect of DPPOs on both

2592

## COMMUNICATION



Scheme 1. Procedure used for the synthesis of FSPO and FDPO.

sides of fluorene can strongly reduce the  $\pi$ - $\pi$  interactions between two different fluorene rings. Compared to values reported in the literature,<sup>[7c]</sup> the T<sub>1</sub> of these two fluorenebased APO hosts are improved by more than 0.2 eV. The stable and efficient blue electroluminescence (EL) of the corresponding PHOLEDs was then demonstrated. FSPO and FDPO were conveniently prepared from fluorenone by using a three-step procedure, which included a Friedel-Crafts reaction, a Sandmeyer reaction, and a phosphorylization reaction, to give total yields of 38 and 65 %, respectively (Scheme 1). The structure characterization was established by using mass spectrometry, NMR spectroscopy, and elemental analysis.

The molecular structures were further confirmed by X-ray crystallography (Figure 1). The X-ray data reveal that the unit cell of FSPO contains one molecule each of FSPO, ethanol, and *n*-hexane. It is interesting to note that no hydrogen-bonding aromatic and packing interactions exist between adjacent FSPO molecules (Figure SI1 in the Supporting Information). The formation of the crystals can be attributed to a van der Waals force. The unit cell of FDPO consists of one FDPO molecule and one water molecule. Two FDPO molecules are interlinked by two water molecules to form a dimer motif (Figure SI2 in the Supporting Information). Furthermore, adjacent dimers are interconnected by P=O···H-C hydrogen bonds between the phenyl ring of fluorene and the P=O fragment, to give a two-dimensional layer structure as shown in Figure SI3 in the Supporting Information. The three-dimensional supramolecular networks are formed by intermolecular C-H…O(water) hydrogen-bonding interactions (Figure SI4 in the Supporting Information). For the 2,7-substituted fluorene derivatives (2,7bis(diphenylphosphine)-9,9-dimethylfluorene, PO6),<sup>[7b]</sup> both the hydrogen-bonding interaction and the edge-to-face C-H $\cdots\pi$  contacts provide strong intermolecular interactions that are detrimental to the morphology stability of its thin film and the stability of its doping systems. Evidently, the stronger steric effect of DPPO at the 9-position of FSPO and FDPO effectively eliminates the intermolecular  $\pi$  contact. In addition, the long *n*-butyl of FSPO further reduces the intermolecular interaction because only van der Waals forces exist. It is known that a weak intermolecular interac-



Figure 1. ORTEP diagrams of FSPO (top) and FDPO (bottom) with thermal ellipsoids at 30% possibility.

tion is advantageous in forming the stable amorphous state during film formation and in facilitating the uniform dispersion of the guest molecule in the host matrix.

The thermal properties of FSPO and FDPO were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure SI5 in the Supporting Information). It is known that the alkyl modification may improve the compatibility of host with the guest; however, at the same time the flexible alkyl groups may remarkably decrease the thermal performance. Even though there is a butyl group in FSPO, the melting point ( $T_m$ ) and the temperature of glass transition ( $T_g$ ) of FSPO are still as high as

Chem. Eur. J. 2011, 17, 2592-2596

www.chemeurj.org

165 °C and 97 °C, respectively. The  $T_g$  is much higher than that of mCP (60 °C). Furthermore, the decomposition temperature ( $T_d$ ) of FSPO is 315 °C, which makes the device fabrication feasible through vacuum evaporation. These data are comparable those found for PO6,<sup>[7b]</sup> which has a  $T_g$ and  $T_m$  of 105 and 193 °C. FDPO exhibits much improved thermal properties, with a  $T_m$  of 273 °C and a  $T_g$  of up to 142 °C. In addition, the  $T_d$  of FDPO is near to 400 °C. FDPO has the best thermal properties, particularly film morphology stability, compared to other small molecular host materials.

The UV/Vis absorption spectra and photoluminescent (PL) spectra of FSPO and FDPO in  $CH_2Cl_2$  ( $10^{-6}$  mol $L^{-1}$ ) are shown in Figure 2. The absorption and fluorescence



Figure 2. Absorption and emission spectra of FSPO, FDPO, and fluorene in  $CH_2Cl_2$  ( $1 \times 10^{-6}$  M). Absorption spectra: —\_\_\_\_: FSPO, ----\_\_: FDPO; ....: fluorene. FL spectra: • FSPO; • FDPO; • fluorene. PH spectra: • FSPO; • FDPO; • fluorene.

(FL) spectra were measured at room temperature, and the phosphorescent (PH) spectra were measured in CH<sub>2</sub>Cl<sub>2</sub> glass at 77 K. For comparison, the absorption and PL spectra of fluorene was also measured under the same conditions. The absorption spectra of the phosphine oxide substituted fluorene and unsubstituted fluorene (from 250 to 350 nm) were nearly the same (Figure 2). The redshifts of all the bands from fluorene in FSPO and FDPO were very small (750-1100 cm<sup>-1</sup>) and approximately half of that reported for the 2,7-DPPO-modified fluorene derivative (1500–2000 cm<sup>-1</sup>). The main absorption peaks of FSPO and FDPO are at 233 nm, originating from the DPPO moieties (Figure 2). The FL spectra of the phosphine oxides consist of two peaks at 312 and 324 nm and the shape of the FL curves of FSPO and FDPO are very similar to that of fluorine (Figure 2). Furthermore, the redshift between them is only 730 cm<sup>-1</sup>. Notably, the absorption coefficient increased remarkably from fluorene FSPO to FDPO, which means that with more phenyl groups, the DPPO moieties at the 9position on fluorene can efficiently sensitize the molecules, but only slightly affect the singlet excited state properties of the chromophore core fluorene. The relative quantum efficiencies of FSPO and FDPO are 0.63 and 0.56, which were measured by using 9,10-diphenylanthracene as the standard. The PH spectrum of fluorene, FSPO, and FDPO showed that the 0–0 transition band of fluorene is at 412 nm, corresponding to a first triplet energy level ( $T_1$ ) of 3.01 eV. Significantly, this band was maintained in the PH spectra of FSPO and FDPO, although it became much weaker with a smaller redshift of 3 nm. It is evident that the substitution of DPPO moieties at the 9-position of fluorene can preserve the triplet excited state level of the chromophore at 2.99 eV, which is 0.27 eV higher than that of the 2,7-DPPO-substituted fluorine,<sup>[7b]</sup> therefore proving our molecular design strategy to be effective.

The influence of DPPO substitution on the frontier molecular orbitals of FSPO and FDPO was investigated by DFT calculations (Figure 3). Compared with 9,9-diphenyl-



Figure 3. DFT calculation results of FSPO and FDPO.

fluorene, the lowest unoccupied molecular orbitals (LUMO) of FSPO and FDPO remarkably decrease to 0.082 and 0.218 eV, respectively. Simultaneously, their highest occupied molecular orbitals (HOMO) also decrease to 0.082 and 0.191 eV, respectively. Furthermore, the LUMO-1 of FSPO and FDPO are 0.33 and 0.47 eV lower than that of 9,9-diphenylfluorene (Figure 3). This proves that the substitution of DPPO moieties at the 9-position of fluorene can effectively improve the electron-injection ability of the chromophore. The electron-cloud densities of the LUMO and HOMO of FSPO and FDPO are almost located on the fluorene cores, as is similar with that of 9,9-diphenylfluorene. Compared with 9,9-diphenylfluorene, with the exception of 9,9-diphenyl, DPPO moieties give remarkable contributions to the electron-cloud density of the LUMO-1 of FSPO and FDPO. Thus, the pendent DPPO moieties may play an important role in electron transport. It is also noticeable that

# COMMUNICATION

the energy gap  $(E_g)$  of FSPO is nearly the same as that of 9,9-diphenylfluorene; however, the  $E_g$  of FDPO is slightly smaller than those of FSPO and 9,9-diphenylfluorene (Figure 3). It is known that a smaller host  $E_g$  is beneficial to the balanced carrier injection/transport in the emitting layers. Therefore, although the effect of DPPO moieties on  $E_g$  is not very strong, a more balanced carrier injection/transporting of FSPO and FDPO can be expected.

To investigate the performance of FSPO and FDPO as hosts, the devices with the configuration of ITO | MoO<sub>3</sub> (10 nm) NPB (80 nm) TCTA (5 nm) HOST: x% FIrpic (20 nm)|TPBi (45 nm)|LiF (1 nm)|Al were fabricated, in which MoO<sub>3</sub> and LiF served as hole- and electron-injecting layers, respectively, NPB served as hole-transporting layer (HTL), TCTA served as exciton-blocking layer, and TPBi was used as electron-transporting and hole-blocking material. Devices A and B were based on FSPO doping with 5 and 7% FIrpic, respectively, whereas devices C and D were based on FDPO doping with 6 and 8% FIrpic, respectively. The turn-on voltage of A was 3.5 V, whereas those of B-D were about 3.3 V (Figure 4 top left). The maximum brightness of A-D were 3132 (11.1 V, 250.6 mA cm<sup>-2</sup>), 6977  $(11.3 \text{ V}, 304.7 \text{ mA cm}^{-2}), 6962 (11.7 \text{ V}, 386.8 \text{ mA cm}^{-2}), and$  $7682 \text{ cd m}^{-2}$  (11.7 V, 435.1 mA cm<sup>-2</sup>), respectively. It should be noted that, in addition to the increasing of the dye concentration, the current-density-voltage (J-V) curves of the devices based on FSPO shifted to low voltages and the increasing of the concentration of FIrpic can improve the car-

rier injection and transport in the emitting layer, as evidenced by the lower operating voltages and higher current densities of B. Furthermore, the brightness of B was much higher than that of A at the same voltages. This implies that the charge-trapping in FIrpic was the main mechanism for the emission process of the devices based on FSPO, and had an important effect on improving the EL performance. However, for FDPO, increasing the doping concentration did not remarkably affect the EL performance, therefore the energy transfer is the main mechanism for C and D, which have the same turn-on voltages. The higher doping concentration of D facilitated the formation of an exciton, which induces its slightly higher current density and brightness compared to C. The maximum power and current efficiency of B were  $12.5 \text{ Im } \text{W}^{-1}$  and  $14.5 \text{ cd } \text{A}^{-1}$ , respectively (Figure 4 top right). The highest maximum efficiencies were achieved from D, which were  $13.8 \text{ lm W}^{-1}$  and  $14.6 \text{ cd A}^{-1}$ . When increasing the doping concentrations, it was found that the efficiencies of the devices did not decrease; in fact, the efficiencies of B were nearly twice of those of A at same current densities. This demonstrates that FSPO and FDPO can effectively disperse the dyes uniformly so as to reduce the concentration quenching and triplet-triplet anihilation. The efficient energy transfer from FSPO and FDPO to FIrpic was proved by the EL spectra of the devices (Figure 4 bottom), in which only the emission from FIrpic was observed. The spectra were very stable during the increase in voltage.



Figure 4. Top left: Voltage/luminance (filled symbols)/current-density (open symbols) characteristics of the devices based on FSPO and FDPO with different doping concentrations. Top right: Current- and power-efficiency curves of the devices. Bottom left: EL spectra of the devices based on FSPO (7%) at 4, 6, 8 and 10 V. Bottom right: EL spectra of the devices based on FDPO (8%) at 4, 6, 8 and 10 V.

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In conclusion, two novel APO hosts for blue electrophosphorescence were designed and synthesized according to an effective strategy of the indirect linkage of the chromophore and the phosphine oxide moieties. With the 9-substituted structure, the T<sub>1</sub> triplet state of the chromoophore fluorene is almost preserved. The energies of the T<sub>1</sub> states of FSPO and FDPO are 2.99 eV, which are 0.27 eV higher than PO6 and ensure the positive energy transfer from the hosts to FIrpic. The high thermal and morphology stability and the effect of APO moieties on the carrier injection/transporting ability of the hosts were proved by thermal analysis and Gaussian simulation. The efficient energy transfer from FSPO and FDPO to FIrpic was further demonstrated through the doping of OLEDs. These results suggest that the indirect linkage of the chromophore and P=O moieties is advantageous in preserving  $T_1$  of the chromophore and superior in constructing high-performance hosts for blue electrophosphorescence.

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2596 -