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A Simple Phosphine–Oxide Host with a Multi-insulating Structure: High Triplet Energy Level for Efficient Blue Electrophosphorescence

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It is believed that phosphorescent organic light-emitting diodes (PHOLEDs) can be applied as the highly energy-efficient flat-panel displays, and are promising candidates for the next generation of solid-state lighting.^[1] To restrain the triplet–triplet (T–T) annihilation and concentration quenching effects, the emission layers of most PHOLEDs consist of a charge-transporting host material doped with phosphorescent dyes.^[2] Nevertheless, stable and efficient blue-emitting PHOLEDs remain a significant challenge,^[3,4] because the efficient exothermic energy transfer to blue-emitting phosphors (such as bis[(4,6-difluorophenyl)pyridinato-*N,C2*]picolinatoiridium (FIrpic), for which the first-triplet energy level (T_1) is 2.75 eV) requires hosts with a very high T_1 level (ca. 3.0 eV).^[5] Incorporation of meso, twisted, or insulating linkages, such as carbazole derivatives *N,N*-dicarbazolyl-3,5-benzene (mCP)^[5] and 4,4'-bis(9-carbazolyl)-2,2'-dimethyl-biphenyl (CDBP)^[6] and tetra(aryl)silane derivatives, is commonly used for the construction of efficient hosts with high T_1 levels and relatively large conjugated areas.^[7–9] However, the efficient hosts with both high T_1 levels and the good carrier-injection/transporting ability are still insufficient. Recently, some phosphine oxide (PO) hosts for blue-electrophosphorescence derivatives have been reported.^[10–22] It has been proven that the P=O moieties not only serve as the insulating linkage, but also efficiently polarize the molecules.^[12] Thus, PO hosts can support both good carrier-injection/transporting ability and high T_1 levels. Nevertheless, direct bonding with P=O moieties, especially along the long axis of chromophores, still reduces the T_1 level; this limits further multifunctionalization of PO hosts.

The efficient host for blue electrophosphorescence should have: 1) a high T_1 level, which induces the exothermic energy transfer to guests; 2) small singlet energy gaps, which can facilitate the carrier injection; 3) separated HOMO and LUMO electron clouds, which facilitates balanced carrier injection and transport. The basic question is how to construct the molecules to preserve the T_1 level of the chromophores while introducing functionalizations. Recently, we reported a novel host with *ortho* linkage on the PO moiety.^[23] The unsymmetrical structure is superior in retaining high T_1 levels and polarizing the chromophore. This indicates that the style of linkage of the functional units has significant effects on the comprehensive properties of the host materials.

Herein, we report another effective strategy for multi-insulating linkages of efficient hosts of blue electrophosphorescence, namely by using bis[2-[di(phenyl)phosphino]phenyl]ether oxide (DPEPO). In DPEPO there are two different insulating linkages—an electron-drawing P=O bond and an electron-donating –O– bond. As a result DPEPO is divided into six independent phenyls. Therefore, a high T_1 level is expected. Significantly, because of the strong electron-donating effect of the O atom, the electron-cloud density of the two phenyls bound to O atoms should be much higher than those of the four phenyls only bound to P=O. This may form a bipolar structure and further induce the separated HOMO and LUMO electron clouds of DPEPO. Compared with a similar PO host, 4,4'-bis[di(phenyl)phosphineoxide]biphenyl (PO1),^[10] with a mono-insulating linkage, the T_1 level of DPEPO is improved by nearly 0.3 eV. The stable and efficient blue electroluminescence of the corresponding PHOLEDs has been demonstrated.

The thermal properties of DPEPO were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figure S11 in the Supporting Information). The melting point (T_m) of DPEPO is 280 °C, and no distinct temperature of glass transition (T_g) was observed. Furthermore, the decomposition temperatures (T_d) of DPEPO is 322 °C at a weight loss of 5%; this makes the device fabrication feasible through vacuum evaporation. The molecular structure of the title complex contains one DPEPO molecule and one methanol molecule, which are interlinked with each other through hydrogen-bonding interactions. A close inspection reveals that two kinds of edge-to-face interactions between two adjacent phenyl rings, with the distances of 3.849 and 3.881 Å, respectively, extend the

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molecules into a two-dimensional, layered structure (Figure 1 and Figure SI2 in the Supporting Information). Therefore, only weak intermolecular interactions exist in DPEPO; this facilitates the formation of the stable, amorphous film and the uniformly dispersed guest–host matrix.

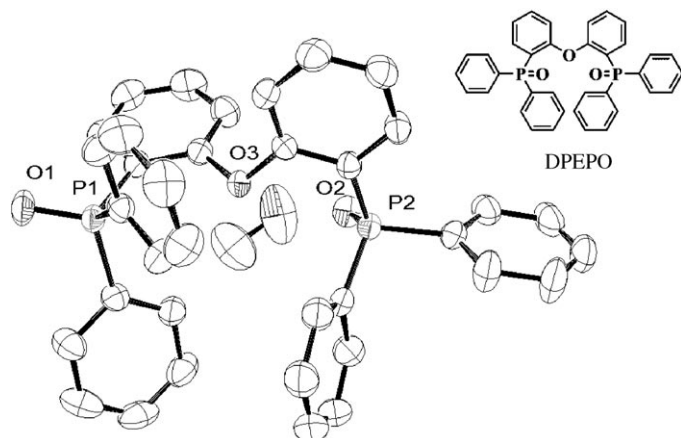


Figure 1. ORTEP diagrams of DPEPO with thermal ellipsoids at 30% possibility.

The optical properties of DPEPO was investigated with UV-vis absorption spectroscopy and photoluminescent (PL) spectroscopy (in CH_2Cl_2 , $1 \times 10^{-6} \text{ mol L}^{-1}$, Figure 2). The absorption and fluorescence (FL) spectra were measured at room temperature, whereas the phosphorescent (PH) spectra were measured at 77 K in a CH_2Cl_2 glass with a delay of 2 ms after the excitation pulse. For comparison, the spectra of diphenyl ether (DPE) were also measured under the same conditions. DPEPO and DPE have the same absorption band at 231 nm, which is attributed to the π – π^* transition of phenyls bound to O atoms. DPE has another weaker bond at 261 nm attributed to n – π^* transition. In the absorption spectrum of DPEPO, this bond shifts red and becomes weaker; this is induced by the electron-withdrawing effect

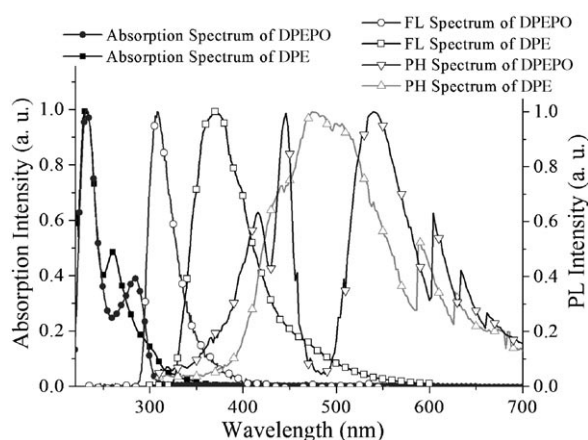


Figure 2. Absorption and emission spectra of DPEPO and DPE in CH_2Cl_2 ($1 \times 10^{-6} \text{ mol L}^{-1}$).

of P=O and the much bigger dihedral angle (115°) between the two phenyls bound to O atoms. However, compared with DPE the emission of DPEPO remarkably shifts blue by 526 cm^{-1} . Therefore, the Stokes shift of DPEPO is only 273 cm^{-1} , which is 848 cm^{-1} less than that of DPE. This should be attributed to the more similar configurations of excited and ground states of DPEPO, which is induced by the strong steric effect of the di(phenyl)phosphine oxide (DPPO) moieties. The PH spectra showed that the T_1 level of DPEPO is 2.995 eV, which is calculated according to the 0–0 transition band at 414 nm. The 0–0 transition band of DPE is at 440 nm, which corresponds to the much lower T_1 level of 2.818 eV. The increase of the triplet level of DPEPO should be attributed to the more twisted configuration of the DPE moieties in DPEPO. Significantly, the T_1 level of DPEPO is 0.275 eV higher than that of PO1. Because the main structural difference between PO1 and DPEPO is the different bridging groups (diphenyl in PO1 and insulating DPE in DPEPO), the much higher T_1 level of DPEPO actually originates from the multi-insulating structure; this confirms our strategy.

The influence of the multi-insulating linkage on the frontier molecular orbitals (FMO) was further investigated by DFT calculations (Figure 3). The configurations and FMOs of DPE (Figure SI3 in the Supporting Information), PO1, and 2,2'-bis[di(phenyl)phosphineoxide]biphenyl (*o*-PO1) were also simulated for comparison. Compared with DPE, the energy levels of the LUMO and HOMO of DPEPO remarkably decrease by 0.517 and 0.381 eV, respectively. Therefore, the introduction of DPPO moieties efficiently improves the electron-injection ability of DPEPO. Furthermore, because the difference between the HOMOs of DPEPO and DPE is smaller than that between the respec-

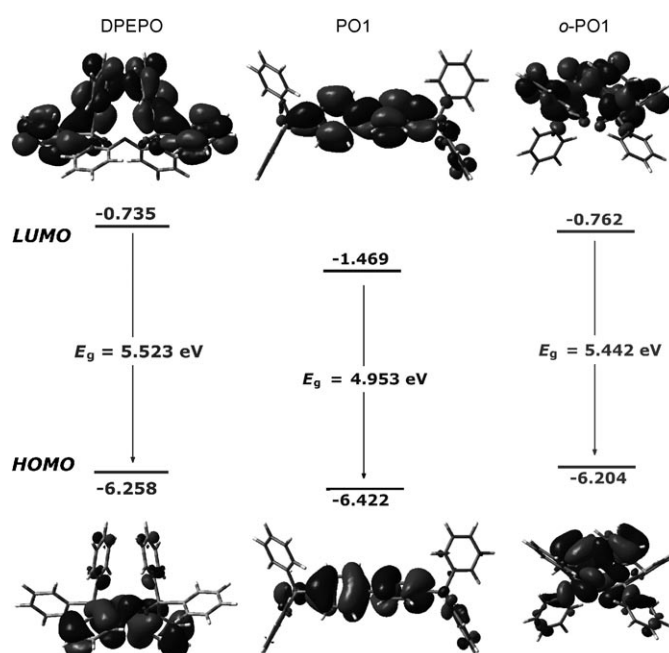


Figure 3. DFT-calculation results of DPEPO, PO1, and *o*-PO1.

tive LUMOs, a balanced hole and electron injection/transport can be expected in DPEPO. The LUMO of PO1 is 0.734 eV lower than that of DPEPO, whereas the HOMO of PO1 is only 0.164 eV lower than that of DPEPO. Thus, the energy gap of DPEPO is 0.57 eV bigger than that of PO1. This indicates that DPEPO has much higher excited levels than PO1, which should be attributed to the multi-insulating structure. This is proven by another diphenyl-based arylphosphine-oxide compound, *o*-PO1. Because the *ortho* positions of diphenyl are substituted by the steric DPPO moieties, diphenyl is twisted and the conjugated area is reduced in *o*-PO1. As a result, the FMO levels and the energy gap of *o*-PO1 are similar to those of DPEPO. However, it is noticeable that both the HOMO and the LUMO electron clouds of *o*-PO1 are located at the biphenyl moieties; this is the same as for PO1. Therefore, although the twisted linkage can realize the high excited energy levels, it can hardly influence the electron-cloud distributions of the whole molecule. In contrast, the HOMO electron cloud of DPEPO is located at the DPE moiety, whereas the LUMO electron cloud is located at the DPPO moieties. It is believed that the separated HOMO and LUMO distributions facilitate the balanced carrier injection/transport. It has been proven that through choosing different insulating linkage moieties to form the multi-insulating structure, the frontier energy levels of the compounds can be tuned and balanced carrier injection/transport can be expected.

To investigate the performance of DPEPO as a host, devices with the following configuration were fabricated: ITO|MoO₃ (10 nm)|NPB (80 nm)|TCTA (5 nm)|DPEPO:10% Flrpic (20 nm)|TPBi (45 nm)|LiF (1 nm)|Al; where MoO₃ and LiF served as hole- and electron-injecting layers, NPB is 4,4'-bis(*N*-phenyl-1-naphthylamino)biphenyl and served as a hole-transporting layer (HTL), TCTA is 4,4',4''-tris(carbazol-9-yl)triphenylamine and served as an exciton-blocking layer, and TPBi is 1,3,5-tris(1-phenyl-1H-benzo[d]imidazol-2-yl)benzene and was used as electron-transporting and hole-blocking materials. The turn-on voltage of the device was only 3.5 V, which is much lower than for devices based on simple carbazole derivatives, such as mCP.^[5] The maximum brightness was 10393 cd m⁻² (14.9 V, 382.95 mA cm⁻²). The maximum power and current efficiencies (P.E. and C.E.) of the device were 15.8 lm W⁻¹ and 17.6 cd A⁻¹, respectively (Figure 4, inset). At the brightness of 100 cd m⁻², the efficiencies remained 6.9 lm W⁻¹ and 12.6 cd A⁻¹. For comparison, a device with TCTA as the host was fabricated under the same conditions (Figure SI4 in the Supporting Information). The device based on TCTA had lower operating voltages, higher current densities, and bigger luminance than those based on DPEPO. However, with DPEPO as the host, the device realized higher efficiencies at low-current densities. This indicates that the carrier-injection/transporting ability of TCTA is stronger than that of DPEPO, because of the bigger conjugated area of TCTA, but the carrier injection/transport in DPEPO is more balanced to realize higher efficiencies. It is showed that DPEPO realized an electroluminescence (EL) performance comparable to that of

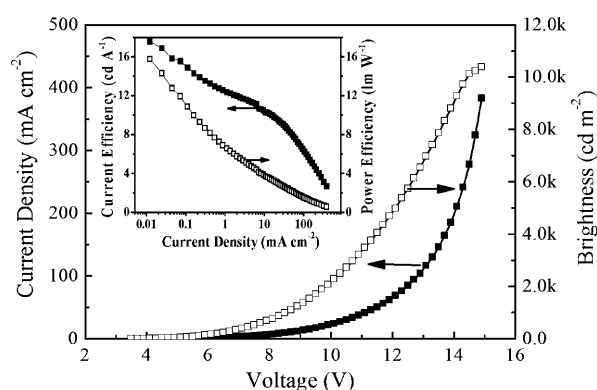


Figure 4. Brightness-current density-voltage curve and efficiencies curves (inset) of the doping device based on DPEPO and Flrpic.

TCTA through a much simpler structure. The efficient energy transfer from DPEPO to Flrpic was demonstrated by the EL spectra of the device (Figure SI5 in the Supporting Information), in which only the stable emissions from Flrpic were observed at different driving voltages. The improved EL performance of DPEPO-based devices was further proven by comparison with several representative hosts of Flrpic. These results are even comparable with functionalized hosts (Table 1).

Table 1. EL performance of representative Flrpic-based devices.

Host	Driving voltage [V] ^[a]	Max. efficiency ^[b]
mCP ^[5]	> 5, –, –	7.7, –, 6.1
CDBP ^[6]	> 5, ≈ 8.0, ≈ 11.0	10.5, 20.4, 10.4
PO1 ^[10]	< 3.9, –, –	–, 20.8, 7.8
DPEPO	3.5, 5.7, 8.7	15.8, 17.6, 6.9
SPPO1 ^[18]	3.0, –, 6.1	28, –, 11.5

[a] In the order of: onset voltage, at 100 cd m⁻², and at 1000 cd m⁻². [b] In the order of: P.E. [lm W⁻¹], C.E. [cd A⁻¹], and external quantum efficiency (E.Q.E.) [%].

In conclusion, a simple phosphine-oxide compound, DPEPO, with two different insulating linkages was used as the host for blue electrophosphorescence. Substitution with DPPO moieties improves the thermal and morphological stability. Furthermore, with the electron-donating insulating linkage of C–O–C and the electron-drawing insulating linkage of P=O, the T₁ level of DPEPO is almost 3.0 eV, which is 0.275 eV higher than that of PO1. The different linkages induce the separation of the HOMO and LUMO electron clouds of DPEPO. The efficient energy transfer from DPEPO to Flrpic was further demonstrated through the doped OLEDs. These results suggest that the multi-insulating linkage is an effective strategy for achieving high excited energy levels and balanced carrier-injection/transporting ability. It can be also expected that this kind of structures is superior in constructing multifunctionalized hosts for blue electrophosphorescence. Further modification of DPEPO for high-performance host materials is ongoing in our laboratory.

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Keywords: electrophosphorescence • high triplet level • density functional calculations • multi-insulating linkage • phosphines

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