A New Phosphine Oxide Host based on *ortho*-Disubstituted Dibenzofuran for Efficient Electrophosphorescence: Towards High Triplet State Excited Levels and Excellent Thermal, Morphological and Efficiency Stability

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Abstract: An efficient host for blue and green electrophosphorescence, 4,6bis(diphenylphosphoryl)dibenzofuran (o-DBFDPO), with the structure of a short-axis-substituted dibenzofuran was designed and synthesised. It appears that the greater density of the diphenylphosphine oxide (DPPO) moieties in the short-axis substitution configuration effectively restrains the intermolecular interactions, because only very weak π - π stacking interactions could be observed, with a centroid-to-centroid distance of 3.960 Å. The improved thermal stability of o-DBFDPO was corroborated by its very high glass transition temperature (T_{g}) of 191°C, which is the result of the symmetric

Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) are believed to be the most promising candidates for highly energy-efficient flat-panel displays and the next generation of solid-state lighting because of the ideal characteristics of electrophosphorescence, such as the internal quantum efficiency, approaching 100%,^[1,2] resulting from the efficient utilisation of triplet excitons. Because of the longer lifetimes

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disubstitution structure. Photophysical investigation showed **o-DBFDPO** to be superior to the monosubstituted derivative, with a longer lifetime (1.95 ns) and a higher photoluminescent quantum efficiency (61%). The lower first singlet state excited level (3.63 eV) of **o-DBFDPO** demonstrates the stronger polarisation effect attributable to the greater number of DPPO moieties. Simultaneously, an extremely high first triplet state excited level (T_1) of

Keywords: electrophosphorescence • molecular devices • molecular electronics • phosphine oxide • short-axis substitution 3.16 eV is observed, demonstrating the tiny influence of short-axis substitution on T₁. The improved carrier injection ability, which contributed to low driving voltages of blue- and green-emitting phosphorescent organic light-emitting diodes (PHOLEDs), was further confirmed by Gaussian calculation. Furthermore, the better thermal and morphological properties of 0-DBFDPO and the matched frontier molecular orbital (FMO) levels in the devices significantly reduced efficiency roll-offs. Efficient blue and green electrophosphorescence based on the o-**DBFDPO** host was demonstrated.

of triplet excitons and the stronger intermolecular interaction between phosphors, however, triplet-triplet annihilation (TTA) and concentration quenching become worse in neat films of the electrophosphorescent materials and consequently result in significant efficiency roll-offs in PHO-LEDs.^[3] A basic strategy widely used to restrain these effects is to separate the phosphorescent units and to reduce their intermolecular interaction by dispersing them in matrixes.^[4] With this as a goal, integrated host-guest systems (such as electrophosphorescent polymers^[5-9] and dendrimers^[10-15]) and doping/blending systems^[16,17] have been developed to achieve high-efficiency PHOLEDs. Although it is expected that integrated systems should be advantageous in terms of phase stability, most efficient PHOLEDs are still based on doping/blending systems, in which the emission layers consist of the charge-transporting host material doped/blended with phosphorescent guests.^[16] Through this technology the electroluminescent (EL) performance of green- and red-emitting PHOLEDs have approached the requirements for commercial applications. Nevertheless, stable and efficient blue-emitting PHOLEDs remain a significant challenge.^[4]

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The most famous host is 4,4'-bis(9*H*-carbazol-9-yl)biphenyl (CBP), which has bipolar characteristics and a relatively high first triplet state energy level (T₁) of 2.56 eV. However, CBP is not suitable for blue-emitting PHOLEDs, because efficient exothermic energy transfer to blue-emitting phosphors (such as FIrpic, the T₁ of which is 2.75 eV) typically requires hosts to have very high T₁ values ($\approx 3.0 \text{ eV}$).^[18] Brunner et al. have reported that 3,6- or 2,7-linkages of two carbazole moieties can reduce the T₁ values of such compounds to less than 2.6 eV.^[19] This restrains the complicated structure design of carbazole derivatives with high energy gaps. Nevertheless, high T₁ values can be achieved through combinations of 9-linkages and *meso*/twisted linkages, such as in *N*,*N*-dicarbazolyl-3,5-benzene (mCP, T₁=2.9 eV)^[20] and 9,9'-(2,2'-dimethylbiphenyl-4,4'-diyl)bis(9*H*-carbazole)

(CDBP, $T_1 = 3.0 \text{ eV}$).^[18] However, the limited conjugated areas and small natures of the molecules often result in the poor thermal stability and carrier injection/transport. Furthermore, carbazole derivatives often suffer from poor electron injection, which results in high operating voltages of their devices, such as turn-on voltages of more than 5 V. Hosts with high T₁ values can also be achieved through insulating linkages, such as the tetraaryl silane derivatives UGH1-UGH4,^[21-23] the T₁ values of which are as high as 3.5 eV. However, the electronic inertia of the Si atom is also inferior in carrier injection and transport. Although the groups of Yeh^[24] and Tsai^[25] have designed carbazole-based hosts with high T₁ values and incorporating insulating linkage of Si atoms to combine the advantages of hole injection/ transport, high T₁ values and relatively complicated structures, the driving voltages of the corresponding devices are still higher than 5 V.

The requirements for an efficient host for blue electrophosphorescence are a high T_1 value for the exothermic energy transfer to blue-emitting phosphors and suitable frontier energy levels facilitating carrier injection and stability. However, it is very difficult to achieve hosts both with high T_1 values and with balanced carrier injection and trans-

porting properties. Furthermore, for practical applications the electrical performance, such as the driving voltage, which directly determines the power efficiency, is also an important indicator.

The design and synthesis of high-efficiency blue-emitting PHOLEDs with excellent electrical performance are therefore still significant challenges. To improve carrier injection capabilities, Kido, Su et al. utilised electron-transporting pyridine moieties instead of phenyls to construct highly efficient hosts.^[26–29] Recently, a special insulating linkage based on P= O has been utilised to form some phosphine oxide (PO) hosts for blue electrophosphorescence.[30-45] It has been established that the P=O moieties not only serve as insulating linkages but also modify the electrical properties of the molecules as a kind of electron-withdrawing group.^[33] PO hosts are thus believed to represent both good carrier injection/ transporting capabilities and high T₁ values. Nevertheless, it is notable that nearly all of the PO hosts reported so far have been produced through substitution with P=O moieties along the long axes of the chromophores, which also influences the T₁ values and limits the complicated modification of PO hosts. Our group recently reported a series of high-performance PO hosts with high T₁ values and relatively balanced carrier injection/transporting capabilities.^[42,43] These showed that the single ortho-linkage structure is superior for retention of high T₁ values and for polarising the chromophore.^[43] The devices exhibited low driving voltages (turnon voltages of about 3 V) and high efficiencies (external quantum efficiencies (EQEs) more than 10%). Although the *ortho*-linkage structure exhibited some advantages, there are still some important points that remain unclear, such as the relationship between the number of P=O moieties and the carrier injection/transporting capability, the effects of unsymmetrical or symmetrical structures on the morphological and optical properties and so on.

In continuation of this work, here we report another efficient host for blue and green electrophosphorescence, based on the structure of a dibenzofuran (DBF) doubly substituted with diphenylphosphine oxide (DPPO) groups and named 4,6-bis(diphenylphosphoryl)dibenzofuran (*o*-DBFDPO, Scheme 1). The structural difference between *o*-DBFDPO and *o*-DBFPPO (from our previous work) is only that of double or single substitution. However, it was shown that the symmetrical structure and the larger size of the *o*-DBFDPO molecule produced very different thermal and morphological properties, whereas the T_1 values of the two compounds were nearly the same, demonstrating both the enhancing effects of double substitution on the thermal and



Scheme 1. Short-axis substitution structure design strategy.

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phase stabilities and the tiny influence of short-axis substitution on the triplet state excited levels. The influence of the greater number of DPPO moieties in **o-DBFDPO** and the effect of different substitution positions on the frontier molecular orbitals (FMOs) were also investigated by Gaussian simulation. The relationship between the number of P=O groups and the electron-injection ability and the effect of short-axis substitution were established. As a result of the high T_1 value of 3.16 eV and the excellent thermal and morphological stabilities of **o-DBFDPO**, efficient blue and green electroluminescence of PHOLEDs based on the compound were achieved.

Results and Discussion

Design and synthesis: For most reported aryl PO hosts, the substitution of P=O moieties is along the long axis of the chromophore group, which can include dibenzofuran, dibenzothiophene, carbazole or fluorene, because bromination is feasible at their 2,8-, 3,6- or 2,7-positions, determining the final substitution positions of the P=O moieties, such as in p-DBFDPO in Scheme 1. Although it is believed that the DPPO moiety, as a kind of insulating group, does not influence the excited energy levels of the molecules, these longaxis-substitution configurations still have an effect on reducing T_1 values and weakening the polarising effect of the electron-withdrawing DPPO, as already shown in our previous work^[43] and discussed in depth in this paper. An effective strategy to solve this problem is to substitute the chromophore groups along their short axes (Scheme 1). Configurations of this kind not only completely retain high T₁ values of the chromophore groups, but also amplify the polarisation effect of the P=O moieties because the electronwithdrawing effects of the P=O moieties in the long-axissubstitution configuration are cumulative but partly cancel each other out. Short-axis substitution is therefore outstanding in offering two advantages for the P=O moieties: 1) preservation of high T₁ values and 2) polarisation of molecules to enhance the carrier-transporting capabilities. In our previous work we reported the asymmetric PO host o-DBFPPO (Scheme 1) with the structure of a monosubstituted DBF. Both because of its unsymmetrical structure and because of its small molecular volume, its thermal stability is insufficient ($T_{\rm g} < 100$ °C). To form a symmetrical structure, o-DBFDPO, based on double substitution of DPPO moieties at the 4- and 6-positions of DBF, was designed. Improved thermal and morphological stability can be expected. On the other hand, the influence of the presence of more DPPOs on the excited energy levels and the carrier-transporting properties of the whole molecule, as well as the relationship between them, were also focused on.

o-DBFDPO was conveniently prepared through a threestep procedure involving regioselective lithiation, phosphorisation and oxidation, in a good total yield of over 60% (Scheme 2). Structure characterisation was achieved by mass spectrometry, NMR spectroscopy and elemental analysis.



Scheme 2. Synthetic procedure for *o*-DBFDPO.

The molecular structure was further confirmed by singlecrystal X-ray diffraction analysis (Figure 1 a). Weak aromatic π - π stacking interactions between adjacent **o-DBFDPO** molecules, giving rise to a dimer with a centroid-to-centroid distance of 3.960 Å, can be observed as shown in Figure 1 b. Weak π - π interaction of this kind contributes to the stability of the solid films. Nevertheless, no further π - π stacking or hydrogen-bonding interactions exist between the dimers. This is far different from the case of the corresponding *para*-linked DBF phosphine oxide derivative (*p***-DBFDPO**), in which much closer π - π interactions (3.385 Å) between the DBF bridges are observed in the solid state accompanied by two close P-O-H-C interactions (all C-O distances \approx 3.4 Å) with the DBF ring on adjacent molecules. The



Figure 1. a) Crystal structure of **o-DBFDPO**, and b) intermolecular interaction.

density of DPPO moieties in the short-axis-substitution configuration thus effectively restrains the intermolecular interactions, which is beneficial for reduction of concentration quenching and TTA.

Thermal properties: The thermal properties of o-DBFDPO were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Its temperature of decomposition (T_d) is as high as 364 °C (Figure S1 in the Supporting Information), which is an improvement of 70 °C relative to o-DBFPPO and makes device fabrication through vacuum evaporation more feasible. DSC analysis shows that the melting point (T_m) of *o***-DBFDPO** is 356 °C (Figure S1, inset in the Supporting Information), which is nearly 170°C higher than that of o-DBFDPO and attributable to the enhanced π - π intermolecular interaction. Significantly, the glass transition temperature (T_{s}) of *o***-DBFDPO** is as high as 191°C, about 100 and 90°C higher than those of o-DBFPPO^[43] and p-DBFDPO,^[33] respectively, and is outstanding among the small molecular hosts. Obviously, the symmetrical structure of o-DBFDPO greatly improves the thermal performance. The compact structure resulting from the short-axis substitution amplifies the strong steric effect of neighbouring DPPO moieties, which restrains the structure adjustment of the whole molecule and results in the high T_{g} value. It has been shown that the symmetrical structure is superior to the asymmetrical structure in thermal and morphological stability, so potential phase separation through thermal effects in the film of o-DBFDPO during device operation can be effectively suppressed. This is very important for improving device lifetime.

Optical properties: UV/Vis and photoluminescence (PL) spectra of *o***-DBFDPO** in dilute CH₂Cl₂ solutions (1× $10^{-6} \text{ mol L}^{-1}$) and in films were measured to investigate its photophysical properties (Figure 2). The weakest duplicate absorption peaks at 322 and 336 nm are attributed to the $n \rightarrow \pi^*$ transition of DBF, whereas the three stronger peaks at 274, 289 and 306 nm originate from the $\pi \rightarrow \pi^*$ transition



Figure 2. UV/Vis and PL spectra of *o*-DBFDPO. UV of DBFDPO in CH_2Cl_2 (—); UV of DBFDPO in film (---), FL of DBFDPO in CH_2Cl_2 (**•**), PH of DBFDPO at 77 K (**•**), FL of DBFDPO in film (**•**).

of DBF. Another absorption peak at 252 nm is ascribed to the $\pi \rightarrow \pi^*$ transitions of the phenyl groups in the DPPO moieties. It indicates that DBF serves as the chromophore group and determines the excited state energy levels of the whole molecule. In films, all of the bands show bathochromic shifts. Nevertheless, the main peaks can be recognised, such as 254 nm for $\pi \rightarrow \pi^*$ transitions of phenyl groups and 274, 300 and 311 nm for $\pi \rightarrow \pi^*$ transition of DBF, which also implies weak intermolecular interaction in *o*-DBFDPO in the solid state.

The main emission peak of o-DBFDPO in CH2Cl2 solution is at 328 nm. A weaker shoulder peak at 376 nm attributed to the dimer is also observed. In film, because of the enhanced intermolecular interaction, the emission peak of the dimers at 374 nm has become stronger than that of the monomer. It is shown that the PL emissions of o-DBFDPO both in solution and in film at room temperature range from 300 to 500 nm, completely overlapping with the metal-toligand charge transfer (MLCT) absorption peaks of the blue-emitting phosphor iridium(III) bis[4,6-(difluorophenyl) pyridinato-N,C2]picolinate (FIrpic) and the green-emitting phosphor iridium(III) bis(2-phenylpyridinato-C2,N)acetylacetonate, Ir(ppy)₂acac. At the same time, the PL lifetime of o-DBFDPO is 1.95 ns (Figure S2 in the Supporting Information), which is longer than that of o-DBFPPO (1.57 ns, Figure S3 in the Supporting Information). A more stable excited state is superior in facilitating energy transfer to the guests. Furthermore, the PL quantum yield (PL QY) of o-DBFDPO is 61%, which is 14% higher than that of o-DBFPPO. A higher PL QY usually corresponds to less nonradiative loss of excited energy, so efficient energy transfer between o-DBFDPO and phosphorescent guests can be expected. An essential condition for a suitable host for a blueemitting PHOLED is a high T_1 value of more than 3.0 eV. The phosphorescence spectrum of o-DBFDPO at 77 K was measured to determine an extremely high T₁ value of 3.16 eV, estimated from the $v_{0,0}$ transition identified as the highest-energy band (393 nm). As hypothesised, the T_1 of *o*-**DBFDPO** is as the same as that of *o*-**DBFPPO**.^[43] This strongly indicates that the short-axis substitution hardly influences the triplet state excited levels of the whole molecules. Simultaneously, it is notable that the first singlet energy level (S₁) of **o-DBFDPO** estimated from its absorption edge is only 3.63 eV, so the energy gap between S₁ and $T_1 (\Delta E_{ST})$ of *o***-DBFDPO** is only 0.47 eV. A small ΔE_{ST} value has a positive effect on facilitating the carrier injection and transport in a PHOLED.^[26] The unique characteristics of o-DBFDPO imply that the short-axis substitution can effectively preserve the T_1 value of the chromophore and simultaneously reduce S_1 , which can be attributed to the enhanced insulating structure and polarisation effects of the P=O moieties.

Theoretical calculation: To understand the nature of the optical properties of *o*-DBFDPO and the influence of shortaxis substitution on FMOs, DFT calculations were conducted with the aid of the Gaussian 03 package at the B3LYP6–

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31G* level. The corresponding calculation on *p*-DBFDPO was also performed for comparison. The calculated highest occupied molecular orbitals (HOMOs) of *o*-DBFDPO and *p*-DBFDPO are -6.258 and -6.340 eV, respectively, whereas the calculated lowest unoccupied molecular orbital (LUMOs) of *o*-DBFDPO and *p*-DBFDPO are -1.333 and -1.279 eV, respectively (Figure 3). The HOMO-LUMO



Figure 3. Calculation results (Gaussian) for *o*-DBFDPO and *p*-DBFDPO.

energy gap (E_g) in **o-DBFDPO** is 4.925 eV, which is 0.14 eV smaller than that in **p-DBFDPO**. With the lower LUMO and higher HOMO, **o-DBFDPO** can be expected to be more effective in double-carrier injection than **p-DBFDPO**. It is also noticed that in relation to the FMOs of **o-DBFPPO**, both the HOMO and the LUMO of **o-DBFDPO** are significantly reduced by about 0.1 eV, which should be attributed to the more strongly electron-withdrawing P=O moieties in *o*-DBFDPO. Nevertheless, the E_g of *o*-DBFDPO is 0.025 eV smaller than that of o-DBFPPO, whereas the E_g values of *p***-DBFDPO** and *p***-DBFPPO** are nearly the same. This also shows the stronger polarisation effect of short-axis substitution. Furthermore, the differences between LUMO-1/LUMO and HOMO/HOMO+1 in o-DBFDPO are 0.265 and 0.082 eV, respectively, much smaller than those in o-DBFDPO (0.462 and 0.109 eV, respectively). It is believed that the small intramolecular energy gaps are advantageous for carrier hopping between different molecules, and consequently improve carrier transport.^[46] The contour plots of the FMOs are presented in Figure 3. It is shown that because of their symmetric structures the electron cloud density distributions of FMOs of o-DBFDPO are, on average, on DBF or phenyls, unlike in o-DBFPPO. Nevertheless, it is notable that all of FMOs of o-**DBFDPO** include a contribution from DBF, whereas the electron clouds of the LUMO-1 and the LUMO of o-DBFDPO are localised at DPPO moieties and DBF, respectively and its HOMO and HOMO+1 are thoroughly localised on DBF. Because of the small difference between LUMO and LUMO-1 of o-DBFDPO, hole- and electroninjection into DPPOs and DBF, respectively, can be expected, which should facilitate the balanced carrier injection in the host matrix.

EL properties: Inspired by the improved thermal and optical properties of *o*-DBFDPO, we fabricated blue- and green-emitting PHOLEDs based on *o*-DBFDPO to investigate its role as a host material. Devices **A** and **B** (Scheme 3), which are blue-emitting, with the compositions ITO/MoO_x (2 nm)/4,4',4"-tris(*N*-3-methylphenyl-*N*-phenylamino)triphenylamine (*m*-MTDATA):MoO_x (15 wt.%, 30 nm)/*m*-MTDATA (10 nm)/tris(phenylpyrazole)iridium (Ir(ppz)₃, 10 nm)/FIrpic:*o*-DBFDPO (10%, *y* nm)/4,7-diphenyl-1,10-phenanthroline (BPhen) (50–*y* nm)/LiF (1 nm)/Al (*y*=10 nm for **A** and 20 nm for **B**) were fabricated. MoO_x and LiF served here as hole- and electron-injecting



Scheme 3. Structures of the materials in the devices and the energy level diagram.

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layers, *m*-MTDATA and BPhen as hole- and electron-transporting layers (HTL and ETL), and $Ir(ppz)_3$ was used as hole-transporting and electron-blocking material. The green-emitting devices **C** and **D** were designed with the same configuration except for the different guest, Ir-(ppy)₂acac, and the different doping concentration of 6%. The thicknesses of the emitting layers (EMLs) of devices **C** and **D** were 10 and 20 nm, respectively.

Devices **A** and **B** had lower turn-on voltages of 3.2 V (Figure 4). A practical luminance of 1000 cdm^{-2} was achieved at low driving voltages of less than 4.8 V (1465 cdm⁻²



Figure 4. Brightness/current density/voltage curves of devices $A \ (\bullet)$ and $B \ (\bullet).$

for **A** and 1357 cdm^{-2} for **B** at 4.8 V). The operating voltages of A and B were much lower than those of FIrpic-based PHOLEDs with *p*-DBFDPO as the host, for which 800 cd cm⁻² can be achieved at 5.4 V.^[33] This also demonstrates the stronger carrier injection ability of o-DBFDPO relative to *p*-DBFDPO, which can be attributed to the stronger polarisation effect of short-axis substitution and further confirms the conclusions of optical and theoretical calculation analysis. It was shown that devices A and B have almost identical brightness/voltage (B/V) characteristics. The thicker EML did not induce an increase in the driving voltage. This implies excellent carrier injection in the EMLs, which can be attributed to the small barrier of 0.1 eV for electron injection and the comparable electron transport capabilities of o-DBFDPO and Bphen (Scheme 3). Nevertheless, device **A** exhibited better current density/voltage (J/V)characteristics. Because the barrier between Ir(ppz)₃ and *o*-**DBFDPO** is as high as 1.1 eV, the hole injection in EMLs is through filled-assistant carrier capture by FIrpic. Because few candidates show superior electron mobility to Bphen, the inferior J/V characteristics of device **B** suggest intrinsic electron-dominating characteristic of our devices with heavily p-doping structure and somewhat inferior electron mobility of *o*-DBFDPO to Bphen, the electron mobility of which is among the highest values reported.^[51]

Because of the lower J value and similar brightness of **B**, its current efficiency (CE) was higher than that of **A** at the

same luminance (Figure 5). This is consistent with the conclusion that a wider emission zone should increase the rate of recombination and reduce the concentration quenching.



Figure 5. Efficiency curves of devices $A(\bullet)$ and $B(\bullet)$.

The maximum CEs of **A** and **B** were $18.1 \text{ cd } \text{A}^{-1}$ at 209 cd m^{-2} and 19.5 cd A^{-1} at 194 cd m^{-2} , respectively. The CEs of **A** and **B** were $16.2 \text{ cd } \text{A}^{-1}$ (1037 cd m⁻²) and 17.9 cd A^{-1} (961 cd m^{-2}), respectively. The corresponding efficiency roll-offs were 10.5 and 9.2%. The maximum power efficiencies (PEs) of A and B were achieved as 14.2 and 15.3 Lm W⁻¹ at the same luminance, corresponding to the maximum external quantum efficiencies (EQEs) of 9.3 and 10.0%. The EQE roll-offs of A (at 1037 cdm^{-2}) and B (at 961 cd m^{-2}) were 9.7 and 8.7%, respectively. Although except for their EQEs the maximum efficiencies of PHO-LEDs based on *p*-DBFDPO are higher than those based on o-DBFDPO, those data are obtained at very low J values (about tens of microamps per square cm). At high luminance and J, the PEs and EQEs of A and B were even higher than those of PHOLEDs based on *p*-DBFDPO. Significantly the efficiency roll-offs (at 800 cd m⁻²) of PHO-LEDs based on *p*-DBFDPO are notably higher than those of A and B (22% for CE, 52% for PE and 18% for EQE, double those of A and B). This significant difference should have its origin in the different natures of the hosts. From the single-crystal and thermal analysis, o-DBFDPO has stronger morphological stability and displays much weaker intermolecular interaction than *p*-DBFDPO. This facilitates the uniform dispersion of the dopants in o-DBFDPO and keeps the compositions of the films stable at high voltage and Jvalues. The weaker intermolecular interaction between hosts and host/guest results in restraint of multiparticle annihilaprocesses, such as triplet-triplet annihilation tion (TTA),^[47,48] triplet-polaron quenching (TPQ)^[49] and collision-induced exciton dissociation.^[50] Furthermore, the small barrier to electron injection reduced the driving voltages of A and B, and to some degree restrained the field-assisted exciton dissociation. The better thermal and morphological properties of o-DBFDPO and the well-matched FMO levels of EMLs with those of the carrier-transporting layers are

therefore some of the main reasons for the remarkably reduced efficiency roll-offs of **A** and **B**. Their excellent efficiency stabilities at high luminance also reflects the good loading capabilities of the whole devices for higher voltages and higher currents, which are directly related to the operating lifetime. Although it is believed that a narrow EML might reduce efficiency because of the relatively high exciton concentration, it was found that the differences in efficiencies between **A** and **B** were small. Here, a wide EML seems not to play a major role in improving the efficiency.^[48] Some other mechanisms are believed to contribute to the evolution of the efficiencies.

The EL spectra of **A** and **B** both consisted only of the emission bands from FIrpic: a main peak at 472 nm and a shoulder peak at 500 nm (Figure 6). The intensity ratio of



Figure 6. EL spectra of devices $A(\bullet)$ and $B(\bullet)$.

the main peak and shoulder peak was 1:0.7 for both **A** and **B**, whereas for the *p*-DBFDPO-based devices it was almost 1:1.^[33] Because the hole-injection barrier between $Ir(ppz)_3$ and *o*-DBFDPO is as high as 1.1 eV, holes were directly injected into EML and were trapped at the dopant sites. The stable EL spectra therefore also imply the balanced distribution of the carrier in the EMLs of **A** and **B**.

The green-emitting devices C and D were also fabricated to demonstrate the potential of o-DBFDPO as a universal host material. Devices C and D had the same low turn-on voltage of 3.2 V (Figure 7). Practical luminance around 1000 cd m⁻² was achieved at 4.8 V for **C** and at 5.0 V for **D**. The low operating voltages were also attributable to barrierfree injection of electrons in o-DBFDPO and efficient holetrapping in Ir(ppy)₂acac. The maximum CEs and PEs of C and **D** were 24.8 and 24.6 cd A^{-1} and 18.1 and 18.0 Lm W^{-1} , accompanied by maximum EQEs of 6.91 and 6.87%, respectively (Figure 8). Significantly, C and D also showed excellent efficiency stability. The efficiency roll-offs of C and D were only 2.5 and 4.9% for CE, 12.7 and 18.3% for PE and 2.9 and 8.3% for EQE. The moderate efficiencies of C and **D** are ascribed mainly to the extremely high T_1 value, close to 3.2 eV, of *o*-DBFDPO, because the huge triplet energy gap of 0.77 eV between o-DBFDPO and Ir(ppy)2acac involves some nonradiative transitions in the energy-transfer



Figure 7. Brightness/current density/voltage curves of devices $C(\bullet)$ and $D(\bullet)$.



Figure 8. Efficiency curves of devices $C(\bullet)$ and $D(\bullet)$.

process, such as vibration relaxation. Nevertheless, the efficiency stabilities of **C** and **D** were outstanding among devices based on hosts with high T_1 values. Similarly to those of **A** and **B**, the EL spectra of **C** and **D** were also very stable, with the main peak at 520 nm much stronger than the shoulder peak at 548 nm (Figure 9).

The EL performances of the devices are listed in Table 1. It is shown that no matter which dopant is used, *o*-



Figure 9. EL spectra of devices \mathbf{C} (\Box) and \mathbf{D} (\bigcirc).

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Device	Voltage [V] ^[a]	$CE \ [cd A^{-1}]^{[b]}$	$PE \ [Lm W^{-1}]^{[b]}$	EQE. [%] ^[b]	Efficiency roll-off [%] ^[c]	CIE $[x, y]^{[d]}$
A	3.2, 4.0, 4.6	18.11, 16.23, 7.37	14.42, 11.08, 3.74	9.33, 8.37, 3.80	10.38, 23.16, 10.29	0.157, 0.307
В	3.2, 4.0, 4.6	19.49, 17.89, 8.44	15.31, 12.22, 4.02	10.00, 9.14, 4.31	8.21, 20.18, 8.60	0.158, 0.310
С	3.2, 4.0, 4.8	24.84, 24.21, 17.94	18.08, 15.85, 9.39	6.91, 6.73, 4.99	2.54, 11.99, 2.60	0.313, 0.624
D	3.2, 4.2, 5.0	24.61, 23.38, 17.22	18.00, 14.69, 8.73	6.87, 6.30, 4.50	5.00, 18.39, 8.30	0.314, 0.622

[a] In the order of at about 1, 100 and 1000 cd m⁻². [b] In the order of maximum, at 1000 and 5000 cd m⁻². [c] At 1000 cd m⁻² in the order of CE, PE and EQE [d] At 1000 cd m⁻².

DBFDPO is superior in reducing annihilation effects and improving carrier injection/transport. These advantages are the result of the fine structure design of short-axis substitution and the resulting physical properties.

Conclusion

An efficient host material, o-DBFDPO, for blue and green PHOLEDs was designed and synthesised to validate an effective strategy named short-axis substitution. It appears that, relative to *p*-DBFDPO, with its long-axis substitution structure, the amplified steric effect induced by the ortho linkage significantly improves the thermal and morphological performance of o-DBFDPO. A high T_g value and weaker intermolecular interaction are observed. At the same time, o-DBFDPO is also superior to the unsymmetrical *o***-DBFPPO** in thermal stability, with only weak π - π interaction introduced, demonstrating the advantage of symmetric structures in film stability. The optical investigations showed that short-axis-substituted DPPO groups do not influence the triplet state excited level of the chromophore, because the T₁ values of *o*-DBFDPO and of *o*-DBFPPO are equivalent. Furthermore, the $\Delta E_{\rm ST}$ value of *o***-DBFDPO** is 0.27 eV lower than that of o-DBFPPO, which strongly corroborates the enhanced polarisation effect ascribed to short-axis substitution structure. The stronger polarisation of DBF in o-DBFDPO was further verified by Gaussian calculations, which indicated a lower LUMO and a higher HOMO in o-DBFDPO than in p-DBFDPO and the partially separated electron clouds of the FMOs of o-DBFDPO. The improved EL performance from o-DBFDPO-based blue- and green-emitting PHOLEDs, such as low driving voltages and stable efficiencies, reflects the advantages of short-axis substitution: 1) an effectively polarising chromophore to improve carrier injection/transport and consequently to reduce the driving voltages, 2) a high T_1 value to facilitate exothermic energy transfer to the dopants and 3) reduction of intermolecular interaction to form a uniform film and to restrain annihilation effects. These results indicate that short-axis substitution is an effective strategy for achieving high-performance hosts for electrophosphorescence. However, the hole injection and transporting capabilities of the PO hosts are also only sufficient, depending on the polarisation effects of the P=O moieties. To solve this problem, further multi-functionalisation modification based on short-axis substitution is imperative, and is already in progress in our laboratory.

Experimental Section

Materials and instruments: All reagents and solvents used for the synthesis of the title compound were purchased from the Aldrich and Acros companies and used without further purification.

¹H NMR spectra were recorded with a Varian Mercury plus 400NB spectrometer relative to tetramethylsilane (TMS) as internal standard. Molecular masses were determined with a Finnigan LCQ Electro-Spraying Ionisation-Mass Spectrometer (ESI-MS) or a MALDI-TOF MS. Elemental analyses were performed with a Vario EL III elemental analyzer. Absorption and PL emission spectra of the target compound were measured with a SHIMADZU UV-3150 spectrophotometer and a SHIMADZU RF-5301PC spectrophotometer, respectively. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with Shimadzu DSC-60A and DTG-60A thermal analysers under nitrogen at a heating rate of 10 °C min⁻¹. Cyclic voltammetric (CV) studies were conducted with an Eco Chemie B. V. AUTOLAB potentiostation with a typical three-electrode cell with a platinum sheet working electrode, a platinum wire counter electrode and a silver/silver nitrate (Ag/Ag⁺) reference electrode. All electrochemical experiments were carried out under nitrogen at room temperature in acetonitrile. Phosphorescence spectra were measured in dichloromethane with an Edinburgh FPLS 920 fluorescence spectrophotometer at 77 K with liquid nitrogen cooling. The crystal suitable for single-crystal X-ray diffraction analysis was obtained through the slow evaporation of an ethanol solution of the compound at room temperature. All diffraction data were collected at 295 K with a Rigaku Raxis-Rapid diffractometer and graphite monochromatised Mo-K α (λ = 0.71073 Å) radiation in ω scan mode. All structures were solved by direct methods and difference Fourier syntheses. Non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. The hydrogen atoms attached to carbons were placed in calculated positions with C-H=0.93 Å and $U(H)=1.2 U_{eq}(C)$ in the riding model approximation. All calculations were carried out by use of the SHELXL97 program.

Synthesis

4,6-Bis(diphenylphosphoryl)dibenzofuran (DBFDPO): A solution of nbutyllithium (2.4 m in n-hexane, 12.5 mL, 30 mmol) was added dropwise at -78°C to a stirred solution of dibenzofuran (1.6819 g, 10 mmol) and N.N.N'.N'-tetramethylethylenediamine (TMEDA, 4.57 mL, 30 mmol) in diethyl ether (50 mL). After all the n-butyllithium had been added, the cooling bath was removed, and the reaction mixture was allowed to warm to room temperature. After 16 h, the mixture was cooled to -78°C, and a solution of chlorodiphenylphosphine (5.92 mL, 33 mmol) in diethyl ether was added dropwise. The cooling bath was removed, and the reaction mixture was stirred for another 16 h. The reaction was quenched with water (10 mL), and the mixture was extracted with dichloromethane $(3 \times 30 \text{ mL})$. The organic layer was dried with anhydrous Na₂SO₄. The solvent was removed in vacuo. The residue was dissolved in dichloromethane (50 mL). Hydrogen peroxide (30%, 3 mL) was added, and the reaction mixture was stirred for 4 h. The reaction was extracted with saturated sodium hydrogensulfite solution. The organic layer was dried with anhydrous Na₂SO₄. The solvent was removed in vacuo. Yield: 3.4 g of white powder (60%). ¹H NMR (400 MHz, CDCl₃, TMS): $\delta =$ 8.185 (d, J=7.6 Hz, 2H), 7.782 (dd, J=7.4, 13 Hz, 2H), 7.691-7.590 (m, 8H), 7.520-7.432 (m, 6H), 7.401-7.307 ppm (m, 8H); LDI-TOF: m/z (%): 568 (100) $[M]^+$; elemental analysis calcd (%) for $C_{36}H_{26}O_3P_2$: C 76.05, H 4.61, O 8.44; found C 76.09, H 4.62, O 8.56.

Theoretical calculations: Computations on the electronic ground states of the compounds were performed by use of Becke's three-parameter density functional in combination with the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP).^[52,53] The 6–31G(d) basis sets were employed. The ground-state geometries were fully optimised at the B3LYP level. All computations were performed with the Gaussian 03 package.^[54]

Device fabrication: Prior to the device fabrication, the patterned ITOcoated glass substrates were scrubbed and sonicated consecutively with acetone, ethanol, and deionised water. All the organic layers were thermally deposited in vacuum ($\approx 4.0 \times 10^{-4}$ Pa) at a rate of 1-2 Ås⁻¹ monitored in situ with the quartz oscillator. To reduce the ohmic loss, a layer heavily *p*-doped with MoO_x (because of the low doping efficiencies of transition-metal-oxide-based acceptors in amorphous organic matrixes) was directly deposited onto the ITO substrate for each sample. After the deposition of LiF, the samples were transferred to a metal chamber, , experiencing a vacuum break due to the change of the shadow masks to determine the active area. The current/voltage/luminance characteristics were measured with a PR650 spectrascan spectrometer and a Keithley 2400 programmable voltage-current source. All the samples were measured directly after fabrication without encapsulation under ambient atmosphere at room temperature.

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