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A multifunctional phosphine oxide-diphenylamine hybrid compound as a high performance deep-blue fluorescent emitter and green phosphorescent host;

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A novel phosphine oxide-diphenylamine hybrid compound POA was designed and synthesized with the aim of developing new multifunctional blue fluorophores. POA is the first kind of compound that can be used as a high-efficiency deep-blue emitter (5.4% EQE) and a host to fabricate high-performance green phosphorescent OLEDs (18.1% EQE).

Organic light-emitting diodes (OLEDs) have attracted great interest for their applications in the next-generation flat-panel displays and solid-state lighting sources.¹⁻³ For full-color displays and highquality white light emission, efficient emitters of three primary colors (red, green, and blue) with high color purity and stability are important. Compared with the phosphorescent complexes, blue emitters based on fluorescent molecules show good potential for stable deep-blue emission.^{4–8} Moreover, due to their wide energy gaps, blue fluorophores can serve as host materials for fluorescent and phosphorescent dopants of green and red emission via Förster or Dexter energy transfer.^{9,10} The use of such multifunctional blue fluorophores can simplify the manufacturing process and production cost of monochromatic and white OLEDs.¹⁰⁻¹³ However, common efficient blue fluorophores based on large π -conjugated aromatic structures, such as anthracene,^{14–16} oligomerfluorene,¹⁷ di(styryl)arylene,¹⁸ and pyrene¹⁹ derivatives, are often not suitable

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^c Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, P. R. China. E-mail: apcslee@cityu.edu.hk host materials for phosphorescent dopants due to their unbalanced charge-transporting properties and low triplet energy level (T1). Therefore, much recent efforts have been made on exploration of new types of blue fluorophores with good performance as blueemitters as well as hosts for phosphors.^{11,20-22} Nevertheless, there is still much room for improvement in terms of the efficiency of blue fluorescence and the capability of sensitizing green phosphors. For example, we recently reported a blue OLED with a high external quantum efficiency (EQE) of 4.9% by using a new fluorophore (DPMC). However, when DPMC is used as a host for sensitizing green phosphors, the EQE is limited to 12.3% only.²⁰ On the other hand, Ma and his coworkers achieved efficient green phosphorescent OLEDs with improved maximum EQEs of 15.3 and 15.9%, respectively, by using two blue-emitting metal complexes Be(PPI)₂ and Zn(PPI)₂.²¹ However, Be(PPI)₂ and Zn(PPI)₂ show low efficiencies as blue emitters with maximum EQEs of 2.82 and 2.08%, respectively. Therefore, it is still challenging to develop multifunctional blue fluorophores that can exhibit high-efficiency blue emission and be employed as high performance hosts.

In this work, we designed and synthesized a new compound 4'-(diphenylphosphoryl)-*N*,*N*-diphenylbiphenyl-4-amine (POA) with the aim of developing efficient blue fluorescent emitters that can be employed as high performance hosts for green phosphors. As shown in Scheme 1, POA consists of a diphenylphosphine oxide moiety and a diphenylamine moiety linked by a biphenyl- π -conjugated bridge. The electron-accepting phosphine oxide moiety was selected considering its good electron-transporting ability and relatively high T₁.^{23–27} While phosphine oxide–carbazole hybrid compounds have been used as hosts for sensitizing blue and green phosphors, they usually emit in the near-ultraviolet region and are not suitable for use



Scheme 1 Synthetic route and molecular structure of POA.

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as blue emitters.^{25,28,29} To shift the emission maximum to the visible region, the electron-donating diphenylamine moiety was adopted in POA. The diphenylamine group shows a relatively strong electron-donating ability when compared to that of the carbazole group, which is beneficial for generating long-wavelength emission. Moreover, the electron donor and acceptor are linked *via* a biphenyl- π -conjugation bridge for providing high fluorescent quantum yield (Φ_f) by an effective radiative decay from intramolecular charge-transfer (CT) excitons.^{6,30} Indeed, the carefully designed POA shows excellent optical and electrical properties as both an emitter for deep-blue emission and a host material for green phosphor.

POA was synthesized through a coupling reaction of chlorodiphenylphosphine with 4'-bromo-N,N-diphenylbiphenyl-4-amine³¹ followed by oxidation (Scheme 1). Room-temperature UV-Vis absorption and photoluminescence (PL) spectra of POA in ethyl acetate and thin films are shown in Fig. 1. In ethyl acetate, the first absorption band at around 305 nm can be assigned to the triphenylaminecentered $n-\pi^*$ transition, while the strong absorption band peaking at 345 nm can be attributed to the delocalized transition from the electron-rich diphenylamine moiety to the electron-deficient diphenylphosphine oxide group. From the onset of the solid-state absorption spectrum, the energy gap (E_g) of POA is estimated to be 3.07 eV. POA shows deep-blue emissions peaked at around 433 nm in both ethyl acetate and the thin film. Moreover, the full width at half maximum (FWHM) of the solid-state emission spectrum of POA is 58 nm. The $\Phi_{\rm f}$ of POA was determined to be 0.80 in ethyl acetate by using 9,10-diphenylanthracence ($\Phi_f = 0.90$ in cyclohexane)³² as a standard and the value in the deposited film was calculated to be 0.48. Fig. 1 also shows a phosphorescence spectrum of POA in 2-methyltetrahydrofuran at 77 K. The characteristic vibrational structure for triphenylamine around 495 and 528 nm indicates that the T₁ state is a ${}^{3}\pi\pi^{*}$ state located mostly on the electron donating moiety.³³ The T₁ energy of POA is estimated to be 2.50 eV from the highest-energy peak of its phosphorescence spectrum, which is sufficiently high to excite green phosphorescent dopants.

Thermal properties of POA were determined by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Fig. S1, ESI†). The decomposition temperature (corresponding to 5% weight loss) of POA is high at 310 °C and the glass transition temperature is determined to be 75 °C. Cyclic voltammetry was used to investigate the electrochemical properties of POA. From the onset of its oxidation potential with respect



Fig. 1 Room-temperature UV-Vis absorption spectra, PL spectra of POA in ethyl acetate and thin films, as well as its phosphorescence spectrum in 2-methyltetrahydrofuran at 77 K.

to that of ferrocene (Fig. S2, ESI[†]),³⁴ the HOMO energy level was determined to be -5.22 eV. As no clear reduction curve was observed, the LUMO energy level was calculated to be -2.15 eV from the HOMO energy level and E_{g} . To gain insight into the structure-property relationship of POA at the molecular level, density functional theory (DFT) calculations were performed at the B3LYP/6-31G (d) level. Molecular orbital distributions in POA are shown in Fig. S3 (ESI[†]). The LUMO is mainly localized at the biphenyl π bridge, P, O and N atoms, while the HOMO resides primarily at the diphenylamine moiety and the N-phenyl ring. The separation between these two orbitals maintains the individual electronic properties of the functional groups and benefits the molecule's efficient hole- and electron-transporting properties.^{21,35} On the other hand, there is still enough LUMO-HOMO overlap to give a highly emissive intramolecular CT excited state as demonstrated by its high PL quantum yield.30

We first characterized the electroluminance performance of POA as a blue emitter by fabricating a non-doped OLED with a configuration of ITO/NPB (30 nm)/TCTA (10 nm)/POA (30 nm)/ TPBI (30 nm)/LiF (1.5 nm)/Al. In this device, ITO (indium tin oxide) and LiF/Al are the anode and the cathode, respectively; NPB (4,4'-bis[N-(1-naphthyl)-N-phenyl amino] biphenyl) is the holetransporting layer (HTL); TCTA (4,4',4"-tris(N-carbazolyl)triphenylamine) is the exciton-blocking layer; and TPBI serves as the electron-transporting layer (ETL), the hole-blocking layer and the exciton-blocking layer. The non-doped device exhibits deep-blue emission with CIE coordinates of (0.15, 0.06), and remains almost unchanged over a wide range of luminance (Fig. S4, ESI[†]). The device has a low turn-on voltage (at a brightness of 1 cd m⁻²) of 3.0 V and maximum current and external quantum efficiencies of 2.0 cd A^{-1} and 5.4%, respectively. Such high efficiencies may result from the high $\Phi_{\rm f}$ and bipolar carriertransporting property^{27,35} of POA. To the best of our knowledge, these performance parameters are comparable with the highest values reported for non-doped blue OLEDs with CIE_v below 0.06.6 Moreover, the current efficiency (CE) and EQE of the device is maintained at 1.2 cd A⁻¹ and 3.0%, respectively, at a high brightness of 1000 cd m⁻², indicating relatively mild efficiency roll-offs.

POA was then employed as the host material for a green phosphorescent OLED. The device structure is ITO/NPB (30 nm)/TCTA (10 nm)/POA:Ir(ppy)₃ (30 nm)/TPBI (30 nm)/LiF (1.5 nm)/Al. In this device, the optimized doping concentration of Ir(ppy)₃ (*fac*-tris(2-phenylpyridine)iridium(m)) is 4 wt%. The CE-luminance–EQE plots of the non-doped and the green phosphor doped devices are shown in Fig. 2, while their luminance–voltage–current density characteristics are shown in Fig. S5 (ESI[†]). The doped device



Fig. 2 CE-luminance-EQE plots of (a) the non-doped blue fluorescent device and (b) the green phosphorescent device doped with $Ir(ppy)_3$.

 Table 1
 Electroluminescence properties of compounds used as blue emitters as well as hosts for green phosphor

Compd.	Dopant	$V_{\mathrm{on}}{}^{a}\left[\mathrm{V} ight]$	Max efficiencies ^b [cd A ⁻¹ /%]	$\operatorname{CIE}(x, y)^c$
POA	_	3.0	2.0/5.4	(0.15, 0.06)
	$Ir(ppy)_3$	2.7	61.2/18.1	(0.29, 0.62)
DPMC ²⁰	_	4.9	2.4/4.9	(0.15, 0.09)
	$Ir(ppy)_3$	4.5	41.6/12.3	(0.27, 0.63)
$Zn(PPI)_2^{21}$		3.2	2.06/2.08	(0.15, 0.09)
	$Ir(ppy)_3$	2.7	58.0/15.9	(0.30, 0.63)

 a Turn-on voltage. b Maximum current efficiency and external quantum efficiency. c At 100 cd m $^{-2}.$

shows a low turn-on voltage of 2.7 V and high maximum efficiencies of 61.2 cd A⁻¹ for CE and 18.1% for EQE. These CE and EQE values are the best results for green phosphorescent OLEDs hosted by blue emitters reported so far (Table 1). Moreover, these efficiencies show little roll-off at high brightness. At a brightness of 1000 cd m^{-2} , the CE and EQE decrease by only 8.8 and 8.3%, respectively, from their maxima. The electroluminescence spectra of the doped device did not exhibit any other residual emission (Fig. S4, ESI⁺). This observation with the high efficiencies reflects a complete energy transfer from the host to the dopant. Clearly, high performance blue fluorescent and green phosphorescent devices can be achieved by using a simple material system. To the best of our knowledge, POA is the first kind of compound that can be used as a high-efficiency deep-blue emitter and the host to fabricate high-performance green phosphorescent OLEDs, which has great potential to reduce the production cost and simplify the manufacturing process for the devices.

In summary, a novel phosphine oxide–diphenylamine hybrid compound POA has been carefully designed and synthesized for the purpose of being used as a high performance blue emitter as well as a host material for green phosphors. The rational molecular design strategy ensures that the singlet energy of POA can offer a high-quantum-yield blue fluorescence and the triplet energy is sufficiently high to excite green phosphorescent dopants. In fact, POA has been used not only as an emitter for non-doped blue OLEDs with high efficiencies, but also a host material for highly efficient green OLEDs. We here successfully present a new strategy for the molecular design of multifunctional blue fluorophores that can exhibit high-efficiency blue emission and be employed as high performance hosts.

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