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# PAPER

# Phosphonate substituted 4,4'-bis(*N*-carbazolyl)biphenyl with dominant electron injection/transport ability for tuning the single-layer device performance of self-host phosphorescent dendrimer<sup>†</sup>

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A novel phosphonate substituted 4,4'-bis(*N*-carbazolyl)biphenyl (CBP), namely PCBP, has been designed and successfully synthesized by an indirect palladium catalyzed Suzuki–Miyaura reaction. X-Ray crystallography analysis from a PCBP single crystal demonstrates that there is a hydrogen bond interaction between the two adjacent molecules due to the presence of phosphonate, which promotes their one-dimensional line arrangement along the *c*-axis. Compared with the prototype CBP (-5.55 eV), in addition, the highest occupied molecular orbital (HOMO) level of PCBP is reduced to -6.00 eV, leading to a large hole injection barrier. On the other hand, the introduction of phosphonate substitutes can endow PCBP with excellent electron injection/transport ability. As a result, PCBP shows an electron-dominated behaviour observed in single carrier devices, which is different from the hole-dominated one for CBP. Such a transition is then used to tune the single-layer device performance of a self-host phosphorescent dendrimer, and the peak luminous efficiency significantly increases from 1.7 cd A<sup>-1</sup> of CBP to 31.4 cd A<sup>-1</sup> of PCBP.

# Introduction

Dendrimers are of great importance for their potential applications in wet-processed organic light-emitting diodes (OLEDs) because they have the well-defined structure of a small molecule and the good solution processability of a polymer.<sup>1,2</sup> In comparison to fluorescent ones, much more attention has been paid to phosphorescent dendrimers owing to their ability to harvest both singlet and triplet excitons to realize theoretical 100% internal quantum efficiency. Among these developed dendrimers, interestingly, there is a class of self-host phosphorescent dendrimers (SHPhDs), which are composed of carbazole-based dendron and iridium (Ir) complex core. Here the Ir complex core acts as the emissive dopant, and the dendron plays the same role as the host. Because of the insensitive doping concentration dependence of device performance, non-doped electrophosphorescent OLEDs (PhOLEDs) are prepared with record high luminous efficiencies of 23.2 and 34.7 cd  $A^{-1}$  for the firstand second-generation green Ir dendrimers with carbazole-based dendrons (G1 and G2), respectively.3

It should be noted that, the introduction of carbazole dendrons endows these SHPhDs with preferential p-type charge transport characteristic. In order to achieve high efficiency, an additional electron transport layer must be deposited on the emitting layer (EML) by vacuum evaporation. This would inevitably increase the cost and time-consumption of PhOLEDs, presenting a significant hurdle to commercialization. In view of this point, a more simplified single-layer structure<sup>4</sup> is highly desirable for such SHPhDs.

As for a single-layer device, in principle, hole and electron fluxes should be balanced to enhance their recombination possibility. Therefore, appropriate electron transport materials (ETMs) should be chosen to be blended with SHPhDs to compose the EML. Through the investigation on literature reported to date, we find that most of the efficient single-layer devices are based on the adoption of two oxadiazole derivatives, 2-tert-butylphenyl-5-biphenyl-1,3,4-oxadiazol (PBD) for green<sup>5,6</sup> and red PhOLEDs,<sup>7,8</sup> and 1,3-bis[2-(4-tert-butylphenyl)-1,3,4-oxadiazol-5-yllbenzene (OXD-7) for blue9,10 and white PhOLEDs.11,12 This phenomenon is very strange but understandable when taking into account that these oxadiazole derivatives show excellent miscibility with triplet emitters to form high quality films via wet technologies, whereas other solution-processable ETMs are scarce. Unfortunately, the relatively low thermal and morphological stability ( $T_g$ : 60 °C for PBD; 77 °C for OXD-7) may hinder their further usage as ETMs in long-lifetime PhOLEDs.13,14 Therefore, de nova design of novel efficient ETMs suitable for solution processes should

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be one of the major subjects of considerable research in the future.

To this end, one conceivable strategy is to develop soluble ETMs on the basis of some electron-deficient systems, such as N-containing heterocyclic aromatic compounds.<sup>14-17</sup> However, the variety of n-type organic semiconductors is not as many as p-type ones, limiting their prospects. As an alternative, it seems to be more attractive to modify known p-type "cores" with strong electron-withdrawing substituents for the construction of n-type materials. Although this concept has already been used in n-channel organic thin film transistors (OTFTs), there are few related reports in the field of OLEDs.<sup>18-20</sup>

In this article, we demonstrate our efforts on the achievement of such an interesting transition from dominant hole to electron injection/transport in OLEDs by functionalizing 4,4'-bis(N-carbazolyl)biphenyl (CBP) with phosphonate substituents. The design rationale for this new structure (PCBP, Scheme 1) is the following. CBP is selected as the p-type centre since it is widely adopted as the host for PhOLEDs where holes are the majority carriers. Furthermore, as an electron-withdrawing group, phosphonate can facilitate effective electron injection/transport from LiF/Al cathode.<sup>21,22</sup> Most importantly, the marriage of phosphonate groups with CBP core may not only enable the n-type character of PCBP, but also improve its solubility in common organic solvents. Employing SHPhD G1 as the phosphor, highly efficient single-layer PhOLEDs are fabricated via spin-coating, and the peak luminous efficiency significantly increases from 1.7 cd  $A^{-1}$  of CBP to 31.4 cd  $A^{-1}$  of PCBP. To the best of our knowledge, this is the first report of hole- to electron-dominated conversion in OLEDs, which is successfully applied to modulate the single-layer device performance of SHPhDs.

# **Results and discussion**

# Synthesis and structure characterization

Unlike CBP, the synthesis of PCBP is not an easy and direct task, as shown in Scheme 2. Due to the reduced reactivity toward C–N coupling reaction, initial attempt to use phosphontate functionalized carbazole precursor as the substrate to react with 4,4'-dibromobiphenyl was unsuccessful. To shun this negative effect, two key intermediates, PCz-Br and PCz-B, were prepared at first, which were then linked together to afford PCBP with a yield of 60% by palladium catalyzed Suzuki–Miyaura reaction. The structure of PCBP was fully confirmed by <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectroscopy, elemental analysis, and mass spectrometry. The



decoration of phosphonate ensures PCBP is soluble in both nonpolar and polar organic solvents, such as dichloromethane, toluene, tetrahydrofuran and ethanol. In addition, a high decomposition temperature (5% weight loss) of 316 °C is determined from thermalgravimetric analysis (TGA, Fig. S1<sup>†</sup>), indicative of its thermal stability.

A single crystal of PCBP, suitable for X-ray crystallography analysis, was attained from  $CH_2Cl_2$ -hexane mixed solvents. As shown in Fig. 1, the two central phenyl rings in PCBP are virtually coplanar, identical to that in CBP. However, the torsion between carbazole and biphenyl fragments in crystal state is found to be strengthened from CBP to PCBP, and the dihedral angle consequently increases from 46° to 57°.<sup>23</sup> As can be clearly seen in Fig. 1, PCBP forms a herringbone packing. Meanwhile, because the phosphonate group is a good hydrogen bond acceptor, head-to-tail P–O···H–C interactions (O···H distance 2.403 Å, O···H–C angle: 167.49°) are observed between the adjacent molecules,<sup>24,25</sup> which further promotes one-dimensional line arrangement along the *c*-axis.

# Photophysical properties

The room temperature UV/Vis and photoluminescent (PL) spectra of CBP and PCBP in solutions are shown in Fig. 2, and the photophysical properties are summarized in Table 1. Compared with CBP, the absorption of PCBP blue shifts, and the optical band gap estimated from the absorption onset rises from 3.52 to 3.57 eV. Correspondingly, an about 4 nm hypsochromic shift of the emission maxima is found from CBP to PCBP in toluene solutions. According to the literature, when 3 and 6 positions of carbazole are occupied by electron-rich methyl groups, an opposite bathochromic effect has been reported in a CBP derivative.<sup>26</sup> So it is reasonable to propose that the hypsochromic effect in this case can be ascribed to the electrondeficient nature of phosphonate moieties, which will be discussed below in detail. In addition, the PL spectrum of PCBP undergoes a red shift of 13 nm from solution to film state, indicative of the existence of aggregation to some degree.

The phosphorescent spectra of CBP and PCBP were also measured at 77 K, and the triplet energy was calculated from their maxima of the first vibronic mode  $(S_0^{\nu=0} \leftarrow T_1^{\nu=0})$ . As presented in Fig. S2,† PCBP (2.68 eV) displays a slightly higher triplet energy than CBP (2.66 eV), which is well consistent with the fluorescent spectra at room temperature. Moreover, the triplet energy of PCBP is higher enough than those of green and red-emitting phosphors to prevent triplet energy back transfer. That is to say, PCBP can act as an ideal host for green and red PhOLEDs.

## Electrochemical properties and theoretical calculations

To elucidate the effect of the phosphonate groups on the frontier molecular orbitals, the electrochemical properties of CBP and PCBP were studied in acetonitrile solutions. Different from the irreversible oxidation of CBP, a reversible oxidation wave was detected for PCBP during anodic sweeping (Fig. 3). This is because the 3- and 6-substitution can prohibit the dimerization of carbazole units at these positions, and intensify the electrochemical stability.<sup>27,28</sup> During cathodic sweeping, both CBP and



Scheme 2 Synthetic route of PCBP.



**Fig. 1** (a) Single crystal structure of PCBP with thermal ellipsoid plotted at 30% probability level. For clarity,  $CH_2Cl_2$  molecule is omitted; (b) the packing of PCBP molecules in the crystals; (c) the hydrogen bonds between two head-to-tail PCBP molecules (viewed along the *c* axis).

PCBP revealed quasi-reversible reduction processes. By comparison to CBP, an additional novel reduction wave appears at a more positive potential for PCBP. With the ferrocene/ferrocenium couple as the reference, the highest occupied and lowest unoccupied molecular orbital (HOMO and LUMO) levels of PCBP are estimated to be -6.00 and -2.30 eV, respectively. It is worthy noting that, the HOMO level of PCBP behaves more sensitively to the incorporated phosphonate groups than the LUMO does. For instance, compared with CBP (HOMO: -5.55 eV; LUMO: -2.19 eV), PCBP exhibits a decrease of 0.45 and 0.11 eV for its HOMO and LUMO levels, respectively.

This discord between HOMO and LUMO level variance can be further verified by theoretical calculation results. Based on the molecular geometry from crystal data, density functional theory (DFT) calculations were performed using B3LYP hybrid functional theory with 6-31G\* basis sets. On going from CBP to



Fig. 2 The room temperature UV/Vis absorption spectra in dichloromethane solutions ( $10^{-5}$  M), PL spectra in toluene solutions ( $10^{-6}$  M) of CBP and PCBP, and PL spectrum in film state of PCBP.

PCBP, the calculated decline in HOMO is 0.54 eV (Table 1), which is 0.18 eV larger than that in the LUMO. The trend correlates well with the electrochemical data, and can be explained by the electron cloud distribution of the frontier molecular orbitals. As illuminated in Fig. 4, the HOMO is distributed over the whole molecular  $\pi$  backbone, while the LUMO is mainly restricted to the central biphenyl unit in CBP. When phosphonate groups are directly tethered to carbazole moieties to form PCBP, imaginably, the LUMO will be less affected by the inductive effect of phosphonate than the HOMO. This would result in the enhancement of the band gap of PCBP relative to CBP, in accordance with the aforementioned blue shift in the absorption and PL spectra.

#### Single carrier devices and electroluminescent properties

Single carrier devices were then fabricated to investigate the charge injection/transport capability of PCBP compared with CBP. The structures of electron-only and hole-only devices are ITO/Al/CBP or PCBP/LiF/Al and ITO/PEDOT/CBP or PCBP/Au, respectively. Fig. 5 depicts their current density–voltage characteristics of CBP and PCBP. As for CBP, electron injection is forbidden by a large mismatch of about 1.9 eV between the work function of the cathode (-4.1 eV) and its LUMO level (-2.19 eV). Hence the electron current is negligible relative to the hole one as seen in Fig. 5a, suggesting the dominant hole injection/transport of CBP. In contrast, PCBP displays an

	$\lambda_{\rm abs} \ (\log \xi)^a \ [{\rm nm}]$	$E_{\rm opt}^{\ \ b}$ [eV]	$\lambda_{\rm sol}^{c}$ [nm]	$E_{\mathrm{T}}^{d} [\mathrm{eV}]$	HOMO <sup>e</sup> [eV]	LUMO <sup>e</sup> [eV]
PCBP	240(5.0), 249(5.0), 270(4.9), 288(4.6), 308(4.5), 336(4.0)	3.57	363	2.68	-6.00 (-5.74)	-2.30 (-1.61)
CBP	239(4.9), 293(4.6), 318(4.4), 327(4.4), 341(4.3)	3.52	367	2.66	-5.55 (-5.20)	-2.19 (-1.25)

 Table 1
 Photophysical and electrochemical properties of PCBP and CBP

<sup>*a*</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub> solution of 10<sup>-5</sup> M at 298 K. <sup>*b*</sup> Calculated from the onset of the absorption in CH<sub>2</sub>Cl<sub>2</sub>. <sup>*c*</sup> Measured in toluene solution of 10<sup>-6</sup> M at 298 K. <sup>*d*</sup> Estimated from the highest energy vibronic band of the phosphorescent spectra at 77 K. <sup>*e*</sup> The HOMO and LUMO levels are calculated according to the equations  $E_{\text{HOMO}} = -e [E_{\text{ox onset}} + 4.8 \text{ V}]$  and  $E_{\text{LUMO}} = -e [E_{\text{red onset}} + 4.8 \text{ V}]$ , respectively. The theoretical calculation data are also listed in the parentheses.



Fig. 3 The cyclic voltammograms of CBP and PCBP in acetonitrile solution, at a scanning rate of 100 mV s<sup>-1</sup>.



**Fig. 4** The distribution of HOMO and LUMO density in the molecular framework, calculated using density functional theory (B3LYP/6-31G\*).

electron-dominated behaviour (Fig. 5b), which could be attributed to two combination factors. On one hand, the presence of phosphonate can effectively improve the electron injection/ transport arising from a favorable dipole and coordinate effect between phosphonate and LiF/Al cathode together with a possible n-doping effect by release of free Li atom under the thermal vacuum deposition conditions.<sup>22,29</sup> On the other hand, holes can hardly inject from the PEDOT : PSS coated anode because of the deep HOMO level (-6.00 eV) of PCBP. Therefore, from CBP to PCBP, an attractive hole- to electron-dominated transition is achieved.

Considering the dominant n-type feature of PCBP, we next dispersed the SHPhD G1 into PCBP to form the EML to



**Fig. 5** The current density–voltage (J-V) characteristics of electron-only (filled squares) and hole-only devices (empty squares) for (a) CBP and (b) PCBP.

evaluate the performance of single-layer PhOLEDs. The device A with a configuration of ITO/PEDOT : PSS/PCBP : G1 (30 wt%)/LiF/Al was fabricated by spin-coating, where the doping concentration of G1 was optimized to be 30 wt% (Fig. 6). For comparison, the control device B was prepared at the same time with CBP as the host instead of PCBP. Their device data are tabulated in Table 2. As depicted in Fig. S5,† device A gives green electroluminescence (EL) entirely from G1 with a peak wavelength of 531 nm and Commission Internationale de L'Eclairage (CIE) coordinates of (0.38, 0.59).

Fig. 7a and b show the current density–voltage–brightness characteristics of CBP and PCBP, and their luminous efficiency as a function of current density, respectively. The turn-on voltage (defined as the bias at the brightness of 1 cd m<sup>-2</sup>) decreases from 12.0 V for CBP to 5.8 V for PCBP. Concomitantly, the maximum



Fig. 6 The energy diagram of light-emitting devices and molecular structure of G1.

	$V_{\mathrm{on}}{}^a$ [V]	$L_{\rm max}  [{\rm cd}  {\rm m}^{-2}]$	$\eta_{\rm c\ max}  [{\rm cd} \; {\rm A}^{-1}]$	$\eta_{\rm p\ max}\ [{ m lm\ W^{-1}}]$	EQE [%]	$\lambda_{max} [nm]$	CIE ( <i>x</i> , <i>y</i> ) (at 15 V)
PCBP	5.8	$1.6 \times 10^4$	31.4	10.3	9.2	531	(0.38, 0.59)
CBP	12.0	$8.2 \times 10^{2}$	1.7	0.28	0.5	526	(0.39, 0.58)
<sup><i>i</i></sup> The apr	lied voltage at 1	$l \text{ cd } m^{-2}$ .					

150 10<sup>8</sup> a) --- PCBP 10 120 ---- CBP 90 10<sup>3</sup> 10<sup>2</sup> <sup>7</sup> m pg / 7 J/ mA cm<sup>-2</sup> 60 30 10<sup>1</sup> 288ap 10 0 -25 30 0 10 15 20 V/V36 b) - PCBF 30 - CBP 24 n, / cd A<sup>-1</sup> 18 12 20 40 60 100 // mA cm

Fig. 7 (a) The current density-voltage-brightness (J-V-L) and (b) luminous efficiency-current density  $(\eta_c - J)$  characteristics of CBP and PCBP.

brightness dramatically increases from 820 cd m<sup>-2</sup> for CBP to 16 000 cd m<sup>-2</sup> for PCBP, regardless of their comparable current density (Fig. 7a). As indicated in Fig. 7b, the device efficiency has been greatly improved by the replacement of CBP with PCBP. The peak luminous efficiency of device A is  $31.4 \text{ cd } \text{A}^{-1}$ , about 18 times higher than that of device B (1.7 cd  $A^{-1}$ ). The salient improvement in device performance can be interpreted from the following reason. Due to its shallow HOMO level (-4.91 eV) and high doping concentration (30 wt%), G1 can contribute to the efficient hole injection/transporting for both device A and B (Fig. 6). However, the electron injection/transport route of device A is different from that of device B. In device B, it is very difficult to inject electrons from LiF/Al cathode into CBP molecules. Therefore, there would be only a small amount of excitons directly generated on G1 cations (formed through hole injection into G1 molecules) by Coulomb attracting electrons from the cathode. Consequently, high current density but low brightness and poor efficiency are observed for device B. On the contrary, in device A, besides Coulomb attraction, sufficient electrons can be easily injected into PCBP molecules, then transferred to G1, and finally recombine holes to form substantive excitons. As a consequence, more balanced carrier flux is obtained for device A, leading to superior device efficiency.

The state-of-art performance is among the best by solution processed single-layer PhOLEDs.4,5,30,31 Compared with the previously reported systems, noticeably, there are two other advantages here. Firstly, an environmental-friendly and stable

LiF/Al cathode is used in place of water and oxygen sensitive materials, such as Ca and Ba. Additionally, the EML only consists of two components, different from the commonly used three-component system. This is a very favorable feature for solution processed PhOLEDs, because the decrease of the number of blend components involved in the EML may reduce the possibility of phase segregation, simplify the device fabrication process and lower the product cost.

# **Experimental**

# General information

All chemicals and reagents were used as received from commercial sources without further purification. Solvents for chemical synthesis were purified according to the standard procedures. 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole<sup>32</sup> and PCz-B<sup>33</sup> were prepared according to the literature procedure. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded at room temperature on a Bruker Avance 300 NMR spectrometer. Among them, <sup>31</sup>P NMR spectrum was referenced to external 85% H<sub>3</sub>PO<sub>4</sub> (0 ppm). Elementary analysis was carried out on a Bio-Rad elemental analysis system. MALDI-TOF mass spectrum was performed on an AXIMA CFR MS apparatus (COMPACT). UV-Visible absorption and photoluminescence spectra were recorded on Perkin-Elmer Lambda 35 UV-vis spectrometer and Perkin-Elmer LS 50B spectrofluorometer, respectively. Thermal properties were tested on a Perkin-Elmer-TGA 7 instrument. Cyclic voltammetry was performed on an EG&G 283 (Princeton Applied Research) potentiostat-galvanostat system. The samples were tested in 1 mM solution using the ferrocene/ferrocenium couple as the reference. The supporting electrolyte was 0.1 M tetrabutylammonium perchlorate (n-Bu<sub>4</sub>NClO<sub>4</sub>). Crystal data collection was performed on a Bruker Smart APEX diffractometer. Theoretical calculations were carried out by density functional theory (DFT) using Gaussian 03.

# Synthesis of PCz-Br

Under inert atmosphere, a mixture of Pd(OAc)<sub>2</sub> (0.14 g, 0.61 mmol), 1,1'-bis(diphenylphosphino)ferrocene (dppf, 0.68 g, 1.22 mmol), anhydrous KOAc (0.24 g, 2.44 mmol) and THF (25 mL) were stirred under reflux for 15 min. A red black solution was obtained. Then, a THF solution (50 mL) of 9-(4-bromophenyl)-3,6-diiodo-9H-carbazole (7.00 g, 12.2 mmol) and diethyl phosphite (3.15 mL, 24.4 mmol) was added to the catalytic solution, and stirred under reflux for 8 hours. After THF was removed by distillation, dichloromethane was added to dissolve the residue. The dichloromethane solution was washed with saturated aqueous sodium chloride. The organic layer was separated and dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was

### Synthesis of PCBP

PCz-Br (0.52 g, 0.88 mmol), PCz-B (0.55 g, 0.86 mmol) and K<sub>2</sub>CO<sub>3</sub> (0.24 g, 1.8 mmol) were dissolved in 8 mL mixed solvent of ethylene glycol mono methyl and water ( $V_{\text{ethylene glycol mono methyl}}$ :  $V_{\text{water}} = 3:1$ ). The solution was added Pd(OAc)<sub>2</sub> (1.9 mg, 8.7 µmol) and stirred at room temperature for 7 hours. And the color of the solution finally turned to dark brown. After the solvent was removed by vacuum distillation, the residue was purified by column chromatography on silica gel (200-300 mesh) with ethyl acetate/methanol (15:1) as eluent. Final product was obtained as white solid (0.53 g, 60.0%). <sup>1</sup>H NMR (DMSO, 300 MHz,  $\delta$ ): 8.89 (d, J = 13.7 Hz, 4H), 8.17 (d, J = 8.5 Hz, 4H), 7.91-7,82 (m, 3.10 Hz), 7.91-7,82 (m, 38H), 7.62 (dd, J = 2.9, 8.5 Hz, 4H), 4.15–4.00 (m, 16H), 1.29 (t, J = 7.0 Hz, 24H). <sup>13</sup>C NMR (DMSO, 75 MHz,  $\delta$ ): 143.67 ( $J_{C-P}$  = 2.2 Hz), 140.07, 136.20, 130.78 ( $J_{C-P} = 11.7$  Hz), 129.10 ( $J_{C-P} =$ 85.3 Hz), 126.39 ( $J_{C-P} = 11.5$  Hz), 123.18 ( $J_{C-P} = 17.5$  Hz), 122.07, 119.55, 111.34 ( $J_{C-P} = 15.8$  Hz), 62.44 ( $J_{C-P} = 5.2$  Hz), 17.11 ( $J_{C-P} = 5.9$  Hz). <sup>31</sup>P NMR (DMSO, 121 MHz,  $\delta$ ): 22.64. Anal. Calcd for C<sub>52</sub>H<sub>60</sub>N<sub>2</sub>O<sub>12</sub>P<sub>4</sub>: C, 60.70; H, 5.88; N, 2.72; found: C, 60.57; H, 6.01; N, 2.30%. Calcd mass: 1208.3; MALDI-TOF found (m/z): 1029.3 [M + H<sup>+</sup>].

#### Device fabrication and characterization

Single-layer PhOLEDs were fabricated with structures of ITO/ PEDOT : PSS (40 nm)/30 wt% G1 doped into PCBP or CBP (90 nm)/LiF (1 nm)/Al (100 nm). Indium-tin oxide (ITO) with a sheet resistance of 20  $\Omega$  per square was used as the substrate and it was cleaned with surfactant and then deionized water. Oxygen plasma treatment was made for 25 min to improve the contact angle before film coating. Poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS) film was spin-coated with thickness of 40 nm onto the ITO glass to improve the hole injection and avoid the possibility of current leakage. PEDOT : PSS film was baked at 120 °C in air for 40 minutes. Next, the sample solutions in chlorobenzene were spincoated on top of PEDOT : PSS film and then baked at 120 °C for 30 min in a glove box. The thickness of the emitting layer was about 90 nm. In succession, a 1 nm thick film of LiF and a 100 nm-thick film of aluminium were vacuum deposited onto the active layer under the pressure of  $10^{-4}$  Pa. The typical active area of the devices was 0.14 cm<sup>2</sup>. By using a PR650 spectra colorimeter, the EL spectra were measured. By using a Keithley 2400/ 2000 source meter and a calibrated silicon photodiode, the current-voltage and brightness-voltage curves of devices were measured. The device performance was tested at room temperature under ambient conditions.

At the same time, according to a similar procedure, hole-only and electron-only devices were also prepared with configurations of ITO/PEDOT : PSS (40 nm)/CBP or PCBP (50 nm)/Au (100 nm) and ITO/Al (100 nm)/CBP or PCBP (50 nm)/LiF(1 nm)/Al (100 nm), respectively.

# Conclusion

In summary, we have illuminated a hole- to electron-dominated transition in OLEDs by modifying CBP with phosphonate groups. Such a conversion is then applied to engineer the single-layer device performance of SHPhDs. Compared with the prototype CBP, an about 18-folds improvement of the luminous efficiency is achieved for PCBP. We believe that, phosphonate will be an appealing substituent to tune the electronic properties of p-type semiconductors, and this simple design strategy is extendable to other p-type ones rather than CBP.

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