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Three host materials (hCP, sCP and pCP) by changing the introduction of different connection groups were designed and synthesized. The sCP exhibited bipolar. The green PhOLEDs using Ir(ppy)<sub>3</sub> as phosphorescent dopants were fabricated.



# Three Carbazole-based Host Materials: Facile Synthesis, Photophysical

# Properties and Performances in PhOLED

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Abstract: Three host materials based on the carbazole were designed and facilely 9-(6-(9-carbazolyl)hexyl)carbazole i. synthesized, (hCP), e. 9-(4-(2-thiophene-based)phenyl) carbazole (sCP) and 9-(4-(9-carbazolyl)phenyl)carbazole(pCP). The relationships between the structures and photophysical, electrochemical and electrophosphorescent performances were investigated. Their emission peaks are located in UV region and the optical band gap are 3.51, 3.57 and 3.89 eV, respectively. Hence, they can be used as hosts in phosphorescent organic light-emitting devices (PhOLEDs). The PHOLEDs were fabricated by doping tris(2-phenylpyridine)iridium  $(Ir(ppy)_3)$  in host as light-emitting materials. The maximum current efficiency of the PhOLEDs employed sCP as host was 44.88 cd/A.

Key words: Carbazole, PhOLED, Bipolar host material, Thiophene

# 1. Introduction

The PHOLEDs have been paid much attention as the candidate for full-color flat-panel displays and light sources due to the unique characteristics of harvesting both singlet and triplet excitons and the theoretical internal quantum efficiency can reach 100%.<sup>1-8</sup> However, the serious concentration quenching and triplet-triplet (T-T)

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annihilation limit their applications.<sup>8-12</sup> The phosphorescent light-emitting materials must be doped in host as light-emitting layer in PhOLEDs. The characteristics of host materials directly determine the performances of PhOLEDs and generally require wide band gap, high carrier mobility and triplet state  $(T_1)$  level.<sup>13, 14</sup>

Molecules based carbazole have been widely used as host materials for PhOLEDs due to their high  $T_1$  and excellent hole-transporting properties.<sup>15</sup> For example, 4,4'-bis(9*H*-carbazol-9-yl)biphenyl (CBP) is a prominent host for green and red triplet emitters.<sup>16</sup> However, CBP is prone to crystallization due to its rather-low glass-transition temperature (62 °C),<sup>15b</sup> especially under low dopant concentrations.<sup>16b</sup> Thus, it is highly urgent to develop the host material that has a  $T_1$  higher than that of the phosphorescent guest emitter, a relatively wider  $E_g$  with an appropriate the highest occupied molecular orbital (HOMO) level, and good carrier-transporting properties. Consequently, highly efficient, low-driving-voltage PhOLEDs could be realized.

In this work, to overcome these issues, we designed and synthesized a series of phosphorescent host materials with higher triplet energy level and higher  $T_g$  than CBP by the simple method. The phosphorescent devices based on them (xCP) have been prepared. To increase the solubility of host, the compound of hCP was synthesized by using alkyl chain to connect two carbazole. To obtain higher  $T_1$ , the compound of pCP was synthesized by breaking the conjugation of hCP. To improve the charger-transport ability, the bipolar host materials sCP was synthesized by introducing the thiophene moiety as electron-withdrawing and carbazole as electron-donating groups. The synthetic scheme of the xCP is represented in Scheme 1.

## 2. Experimental section

#### 2.1 General information

All of the chemicals and reagents are used in their original form without further purification. Solvents for chemical synthesis are purified according to the standard procedures. All chemical reactions are performed in a nitrogen atmosphere.

<sup>1</sup>H NMR and <sup>13</sup>C NMR data are recorded using a Switzerland Bruker DR×600 NMR spectrometer relative to tetramethylsilane (TMS) as internal standard.

Elemental analyses were performed using a Vario EL elemental analyzer. The single crystals grow from the mixed solutions of CH<sub>2</sub>Cl<sub>2</sub> and hexane. The final structure was confirmed by X-ray diffraction analysis (Bruker-Nonius SMART APEX II CCD), with graphite-monochromatic M<sub>o</sub> K<sub>a</sub> ( $\lambda = 0.71073$  Å). Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Center (CCDC). CCDC reference numbers for hCP, pCP and sCP are 1500354, 1500355 and 1500356, respectively. UV-vis absorption spectra were recorded on a Hitachi U-3900 spectrophotometer and the photoluminescence (PL) spectra were recorded using a Fluoromax-4 spectrophotometer in diluted CH<sub>2</sub>Cl<sub>2</sub> solution at room temperature. Thermogravimetric analyses (TGA) was performed using a Netzsch TG 209 at a heating rate of 10 °C/min in nitrogen atmosphere. The melting point (T<sub>m</sub>) was measured by the SGW<sub>®</sub>X-4 micro melting point measuring instrument. Differential scanning calorimetry (DSC) measurements were performed at both heating rate of 10 °C/min and cooling rate of 20 °C/min under nitrogen atmosphere under nitrogen atmosphere, using DSC Q100 V9.4 Build287 apparatus. Cyclic voltammetry was performed using Autolab/PG STAT302 in a one-compartment electrolysis cell consisting of a platinum wire as working electrode, a platinum electrode as counter, and a calomel electrode as reference. Tetrabutylammonium perchlorate was used as a supporting electrolyte (0.1 M), and cyclic voltammetric runs were monitored at a scan rate of 50 mV/s.

All calculations were performed using the Gaussian 03 package by employing experimental parameters determined by X-ray singlecrystal diffraction as an input file. The geometry optimization by density functional theory (DFT) was carried out using the B3LYP functional with 6-31G(d) basis sets.<sup>17-19</sup>

## 2.2 Device Fabrication and Characterization

To investigate the electroluminescent properties of the xCP, doped electroluminescent devices with the configuration of ITO/ MoO<sub>3</sub> (30 nm)/ TCTA (30 nm)/ Ir(ppy)<sub>3</sub> (7 wt%): xCP (20 nm)/ TPBi (45 nm)/ LiF (1 nm)/ Al (300 nm) were fabricated by high-vacuum ( $3 \times 10^{-4}$  Pa) thermal evaporation onto a glass substrate pre-coated with ITO. MoO<sub>3</sub> and Tris(carbazol-9-yl)-triphenylamine (TCTA) were

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used as hole injecting/transporting materials, and  $Ir(ppy)_3$  acts as emitting layer. 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) was employed as electron-transporting and hole-blocking material. LiF was the electron injection layer, and Al was evaporated as cathode. Luminance-voltage-current density (L-V-J) characteristics of devices were recorded on Keithley 2400 Source Meter and L-2188 spot Brightness Meter. The active area of ITO was (3×3) mm<sup>2</sup>. The electroluminescent spectra were recorded on PR-655 spectrophotometer. The voltage-current density (V-J) characteristics of PhOLEDs were recorded using Keithley 2400 Source Meter and ST-900M Spot Brightness Meter.

## 2.3 Synthesis of complexes

## 2.3.1 Synthesis of hCP

Carbazole (5.02 g, 30 mmol) and 1,6-dibromohexane (3.66 g, 15 mmol) were dissolved in 80 mL toluene. Tertbutyl ammonium bromide (TBAB) (0.5 g, 1.5 mmol) dissolved in 5 mL deionized water and the 2 M K<sub>2</sub>CO<sub>3</sub> solution were added subsequently. The mixture was heated to reflux for 24 h and then washed with deionized water and dried over Na<sub>2</sub>CO<sub>3</sub>. The precipitate was purified by column chromatography (silica gel, dichloromethane: petroleum ether = 1:20) to obtain the white crystal product (4.99 g, yield: 80%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.09 (d, *J* = 7.8 Hz, 4H), 7.43 (ddd, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 6.0 Hz, *J*<sub>3</sub> = 1.2 Hz, 4H), 7.33 (d, *J* = 8.4 Hz, 4H), 7.22 (ddd, *J*<sub>1</sub> = 7.2 Hz, *J*<sub>2</sub> = 6.0 Hz, *J*<sub>3</sub> = 1.2 Hz, 4H), 4.24 (t, *J* = 7.2 Hz, 4H), 1.85-1.81 (m, 4H), 1.41-1.37 (m, 4H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  143.28, 128.50, 125.74, 123.26, 121.67, 111.48, 45.71, 31.70, 29.96. Anal. Calcd for C<sub>30</sub>H<sub>28</sub>N<sub>2</sub>(%): C, 86.54; H, 6.73; N, 6.73; found: C, 87.23; H, 6.78; N, 6.67.

## 2.3.2 Synthesis of pCP

A mixture of CuI (0.57 g, 3 mmol), 18-Crown-6 (0.264 g, 1 mmol), K<sub>2</sub>CO<sub>3</sub> (16.6 g, 120 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (2 mL), dibromobenzene (7.1 g, 30 mmol) and carbazole (10 g, 60 mmol) were heated at 170 °C for 11 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was filtered and was washed with NH<sub>3</sub>·H<sub>2</sub>O and water. The grey solid was recrystallized twice from chloroformto afford as colorless crystals (19.3 g, yield: 79%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.19 (d, J = 7.8 Hz, 4 H), 7.82 (s, 4 H), 7.57 (d, J = 8.4 Hz, 4 H), 7.48(ddd,  $J_1 = 7.2$  Hz,  $J_2 =$ 

6.0 Hz,  $J_3 = 1.2$  Hz, 4 H), 7.34 (ddd,  $J_1 = 7.2$  Hz,  $J_2 = 6.0$  Hz,  $J_3 = 1.2$  Hz, 4 H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>): δ 146.36, 143.72, 139.76, 136.50, 131.16, 130.38, 130.19, 128.92, 128.26, 126.53, 123.26, 122.93, 112.72. Anal. Calcd for C<sub>30</sub>H<sub>20</sub>N<sub>2</sub> (%): C, 88.24; H, 4.90; N, 6.86; found: C, 88.28; H, 4.98; N, 6.74.

#### 2.3.3 Synthesis of sCP

9-(4-bromophenyl)carbazole: A mixture of CuI (0.190 g, 1 mmol), 18-Crown-6 (0.159)g, 0.6 mmol),  $K_2CO_3$ (8.291 g, 60 mmol), 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) (20)mL), dibromobenzene (4.718 g, 20 mmol) and carbazole (1.672 g, 10 mmol) were heated at 180 °C for 16 h under nitrogen. After cooling to room temperature, the mixture was quenched with 1 N HCl, the precipitate was filtered and washed with NH<sub>3</sub>·H<sub>2</sub>O and water. The grey solid was purified with column chromatography using hexane as eluant (1.5 g, yield: 46.6%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.25 (d, J = 7.8 Hz, 2 H), 7.86 (dt,  $J_1 = 3$  Hz,  $J_2 = 1.8$  Hz,  $J_3 = 8.4$  Hz, 2 H), 7.61 (d,  $J_1 = 3$  Hz,  $J_2 = 1.8$  Hz,  $J_3 = 8.4$  Hz, 2 H), 7.43-7.45 (m, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.29-7.31 (m, 2 H).

A mixture of 9-(4-bromophenyl)carbazole (3.22 g, 10 mmol) and 2-thiopheneboronic acid (1.28 g, 10 mmol) was added to anhydrous toluene (50 mL). After 2 M aqueous K<sub>2</sub>CO<sub>3</sub> was added to the stirred mixture, the reaction mixture was degassed with nitrogen for 1 h. Then Pd(PPh<sub>3</sub>)<sub>4</sub> (0.03 g, 0.05 mmol) was added to the mixture. The solution was further refluxed under a nitrogen atmosphere for 24 h. After the reaction solution was cooled to room temperature, the whole mixture was poured into water, and the organic layer was separated and washed with water. The organic extracts were dried over MgSO<sub>4</sub>. The crude product was further purified by column chromatography on silica gel using hexane as the eluent to yield compound as a white solid (2.27 g, yield: 70%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, TMS):  $\delta$  8.15 (ddd,  $J_1$  = 7.8 Hz,  $J_2$  = 7.2 Hz,  $J_3$  = 0.6 Hz, 2 H), 7.85-7.83 (m, 2 H), 7.60-7.58 (m, 2 H), 7.46 (ddd,  $J_1$  = 8.40 Hz,  $J_2$  = 1.2 Hz,  $J_3$  = 0.6 Hz, 2 H), 7.84-7.41 (m, 3 H), 7.35 (dd,  $J_1$  = 5.40 Hz,  $J_2$  = 1.2 Hz, 1 H), 7.30 (ddd,  $J_1$  = 7.8 Hz,  $J_2$  = 6.6 Hz,  $J_3$  = 1.2 Hz, 2 H), 7.15 (dd,  $J_1$  = 5.40 Hz,  $J_2$  = 3.6 Hz, 1 H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>):  $\delta$  143.47, 140.84, 136.88, 133.61, 128.29, 127.49, 127.30, 126.05, 125.38, 123.65, 123.52, 120.39,

120.10, 109.85. Anal. Calcd for C<sub>22</sub>H<sub>15</sub>NS (%): C, 81.23; H, 4.61; N, 4.31; S, 9.85; found: C, 81.75; H, 4.69; N, 4.17; S, 9.32.



Scheme. 1 Synthetic scheme of hCP, pCP and sCP

# 3. Results and discussion

#### 3.1 Single-crystal structures

The X-ray single-crystal structure diffraction studies were carried out to reveal their exact structures. The structure data are shown in Table 1. Their single crystals were grown from  $CH_2Cl_2$ /hexane solution. Their crystal structures are all the orthogonal crystal system (Fig. 1). The space group of hCP is P2(1)2(1)2(1) in which the bond length of C(13)-N(1) and C(18)-N(2) are 1.453(3) and 1.457(3) Å are slightly smaller than the standard C-N key bond length (1.47-1.50 Å).<sup>19</sup> Thus bond energy is bigger and the material is more stable. In addition, at both ends of carbazole groups for the planar configuration, the torsion angle between alkyl chain and carbazole groups are -178.7(2) and 176.0(2)°, respectively.

The pCP is Pbca space group in which the bond length of C(13)-N(1) and C(16)-N(2) are 1.430(3) and 1.430(3) Å and smaller than that of hCP.<sup>20</sup> The torsion angle between carbazole and benzene are -124.4(2) and  $124.6(2)^{\circ}$  respectively. The

torsion angle of C(19)-N(2)-C(16) is 124.6(2)°. The sCP is Pbca space group. The torsion angle of C(11)-N(1)-C(8) is 126.40(19)°. The torsion angle of C-N-C of sCP and pCP are both smaller than that of hCP. Aomg them the torsion angle of C(x)-N(1)-C(y) of hCP is the smallest, the flexibility is the best. The rigid strong stereo space configuration is beneficial to increase the molecular steric hindrance, weaken the conjugate effect between adjacent carbazole groups and widen exciton diffusion area which can help to improve the T<sub>1</sub> level.

	hCP	sCP	рСР	
Empirical formula	$C_{30}H_{28}N_2$	C <sub>22</sub> H <sub>15</sub> NS	$C_{30}H_{20}N_2$	
Crystal size/mm <sup>3</sup>	0.36×0.21×0.20	$0.23 \times 0.19 \times 0.13$	$0.2\times0.15\times0.12$	
Formula weight	416.54	325.41	408.48	
Temperature (K)	296(2)	299.84	299.59	
Wavelength (Å)	0.71073	0.71073	0.71073	
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	
Space group	P2(1)2(1)2(1)	Pbca	Pbca	
C(x)-N-C(y) (deg)	-178.7(2)	124.93(19)	108.4(2)	
a (Å)	5.844(2)	16.9032(6)	8.210(2)	
b (Å)	12.001(5)	7.7378(3)	16.562(4)	
c (Å)	32.444(13)	25.4653(9)	32.036(8)	
a (deg)	90	90	90	
b (deg)	90	90	90	
g (deg)	90	90	90	
Volume/ Å <sup>3</sup>	2275.5(16)	3330.7(2)	4355.7(18)	
Z	4	8	8	
Reflections collected	16228	31414	40995	
Goodness-of-fit on $F^2$	1.009	1.048	0.989	
R indexes (all data)	$R_1 = 0.0963,$	$R_1 = 0.0934,$	$R_1 = 0.1905,$	

Table 1 Crystallographic data for hCP, sCP and pCP



Fig. 1 Single-crystal structures of hCP, pCP and sCP

# 3.2 Thermal properties

The good thermal stability of compounds is indicated by their high decomposition temperatures  $T_d$  (corresponding to 5% weight loss). The  $T_d$  of hCP, pCP and sCP are 321, 301 and 161 °C, respectively, as can be seen in Fig. 2a. In addition, both hCP and pCP with two carbazole groups have higher  $T_d$  owing to the better rigidity of carbazole. In Fig. 2b, the glass-transition temperatures ( $T_g$ ) of hCP and pCP are 93 °C and 129 °C, respectively, which are much higher than that of analogous carbazole-based host such as CBP (62 °C) and 1,3-di(9H-carbazol-9-yl)benzene (mCP) (60 °C).<sup>14b</sup> And the higher  $T_g$  is expected to improve the stability of the device. The flexibility of hCP molecular is better than sCP and pCP and easy to improve the decomposition temperature. And the  $T_m$  of hCP, pCP and sCP are 127.9-128.4, 335.4-336.1 and 188.1-188.9 °C, respectively.



# 3.3 Photophysical properties

Fig. 3 displayed the UV-vis and photoluminescent (PL) spectra of xCP in dilute  $CH_2Cl_2$  solution (5×10<sup>-6</sup> mol/L) and the PL emission spectra of sCP in different solution. The absorption peaks around 236-264 nm corresponds to the  $\pi$ - $\pi$ \* electron transition of benzene ring. And the absorption peak around 293 nm can be assigned to

the carbazole-centered matrix  $\pi$ - $\pi$ \* transitions, whereas the absorptions in the range of 320-346 nm could be attributed to the n- $\pi$ \* electron transfer of c arbazole.<sup>21-23</sup> The absorption maximum ( $\lambda_{max}$ ) was observed at 237 nm (molar extinction coefficient  $\epsilon$ = 1.14 × 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>) for hCP, 241 nm ( $\epsilon$  = 1.25 × 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>) for pCP and 235 nm ( $\epsilon$  = 1.58 × 10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup>) for sCP.



Fig. 3 (a) The UV-Vis absorption and PL spectra of hCP, sCP and pCP in CH<sub>2</sub>Cl<sub>2</sub> solution and (b) The PL spectra of sCP in different solutions

The optical energy gaps ( $E_g$ ) of the compounds were calculated according to their absorption edges and are listed in Table 2.  $E_g$  of hCP, sCP and pCP are 3.51, 3.57 and 3.89 eV, which are higher than that of CBP.<sup>24</sup> The compounds hCP and sCP show lower  $E_g$  than pCP due to the increased conjugation.

The PL emission spectra of hCP, sCP and pCP were measured in CH<sub>2</sub>Cl<sub>2</sub> solution which show near-ultraviolet emissions (Fig. 3a). The emission spectra of hCP have the maximum peaks at 351 and 368 nm, and the emission wavelength of sCP is located at 382 nm and pCP appears at around 355 and 363 nm respectively. Compared with that of CBP, the maximum emission peaks have the obvious blue shifts.<sup>24, 25</sup> The emission peaks of pCP has samller red shift than that of sCP due to the larger distortion. The conjugate degree of hCP is the minimum so as to the blue shift than that of pCP and sCP.

The PL emission spectra of hCP and pCP have almost no change with the change of solution polarity. The PL emission spectra of sCP in different solution were measured, as can been seen in Fig. 3(b). The emission spectra have obvious red shifted 43 nm and the fine structure disappeared with the increase of solvent polarity. This result indicated that there are intramolecular charge transfer (ICT) state.



Fig. 4 The PL spectra of hCP, sCP and pCP in 2-methyltetrahydrofuran matrix at 77 K

The properties of triplet excited states for the compounds were studied by low-temperature (77 K) PL spectra in 2-methyltetrahydrofuran (2-MeTHF), as shown in Fig. 4. The T<sub>1</sub> of hCP, sCP and pCP were calculated as 3.01, 3.02 and 2.84 eV, respectively. They are suitable for the phosphorescent host materials and the T<sub>1</sub> of  $Ir(ppy)_3$  is 2.4 eV.<sup>13</sup>

In order to further investigate the luminescent properties of these three host materials, their ground state structures were optimized and the frontier molecular orbitals were shown in Fig. 5. As for hCP, the HOMO are largely located at one of carbazole groups and the lowest unoccupied molecular orbital (LUMO) are absolutely located at another carbazole groups. The HOMO and LUMO are well separated, without overlapping, leading to the bule-shift spectra. The HOMO of sCP distributed on the molecular skeleton and the LUMO distributed in thiophene group and benzene ring. The HOMO and LUMO of the sCP are well overlapping and the ambipolar property of it leads easily to transfer electron.



Fig. 5 Optimized molecular structure and molecular orbital amplitude plots for the HOMO and LUMO of hCP, pCP and sCP

Compared with hCP and pCP, the fluorescence emission of sCP has a large red shift, and the HOMO level is decreased which make a wider band gap formed and reduce the hole injection barrier. The HOMO of pCP distributed in the molecular skeleton and the LUMO distributed in the carbazole groups at both ends of the molecule.

# 3.4 Electrochemical properties

Cyclic voltammetry (CV) were performed to investigate the electrochemical properties of the compounds (Fig. 6). And the values of  $E_{HOMO}$  and  $E_{LUMO}$  were obtained according to the equation  $E_{LUMO} = E_g - E_{HOMO}$  and are also listed in Table 2.

The HOMO/LUMO levels of hCP, sCP and pCP are -5.98/-2.47, -6.04/-2.57 and -5.95/-2.06 eV.



Fig. 6 The cyclic voltammetry curves of hCP , sCP and pCP  $% \mathcal{A}$ 

Table 2 Photophysical, electrochemical and thermal properties of xCP

Host	$\lambda_{ab}$	$\lambda_{PL}{}^a$	$T_1$	LUMO <sup>b</sup>	Eg <sup>c</sup>	Tg	T <sub>d</sub>
	( nm )	( nm )	(eV)	(eV)	(eV)	(°C)	(°C)
hCP	264, 294, 346	412	3.01	-2.47	3.51	93	321
sCP	257, 302, 325	410	3.02	-2.57	3.57		299
pCP	257, 302, 325	436	2.84	-2.06	3.89	129	161

<sup>a</sup> PL spectra at 77 K in 2-methyltetrahydrofuran solution. <sup>b</sup> LUMO = HOMO -  $E_g$ . <sup>c</sup>  $E_g$  obtained from the onset of UV-vis absorption spectra.

# 3.5 Electroluminescent properties

To prove the bipolar property of sCP, the hole-only and electron-only devices were fabricated with the structures of ITO/ MoO<sub>3</sub> (3 nm)/ NPB (30 nm)/ sCP (40 nm)/ NPB (10 nm)/ Al (hole-only) and ITO/ Bphen (10 nm)/ sCP (40 nm)/ Bphen (10 nm)/ LiF (1 nm)/ Al (electron-only), respectively. Where MoO<sub>3</sub> and LiF served as holeand electron-injecting layers, N,N'-Bis-[(1-naphthalenyl)-N,N'-bis-phenyl]-(1,1'-biphenyl)-4,4'-diamine (NPB) was used as the hole-transport layer and 4,7-diphenyl-1,10-phenanthroline (BPhen) as electron-transport/hole-block layer (Fig. 7). The current density (J) of electron-only based sCP was much higher than that of hole-only device at the same voltage, which indicated that the electron-transport ability is superior to that of hole-transport.



Fig. 7 The J-V characteristic curves of single-carrier based-sCP devices

Based on the triplet energies and other agreeable parameters of these three host materials, PhOLEDs were fabricated with an doping concentration of 7 wt%  $Ir(ppy)_3$  as the emitter. The structures of devices A-C are ITO/ MoO<sub>3</sub> (30 nm)/ TCTA (30 nm)/ Ir(ppy)<sub>3</sub> (7 wt%): host (20 nm)/ TPBi (45 nm)/ LiF (1 nm)/ Al (300 nm), which host are hCP (device A), sCP (device B), pCP (device C), respectively. The EL spectra of devices A-C exhibit the same peak at 512 nm with Commission Internationale de L'Eclairage (CIE) of around (0.30, 0.62), which are identical to the PL spectra of Ir(ppy)<sub>3</sub> in Fig. 8. This result demonstrated that the effective energy transfers were achieved from host to guest. The spectra have no obvious with the change of voltage, indicating that the devices exhibited the good color stability.



Fig. 8 EL spectra of devices A-C at voltage of 8 V

The current density-voltage-luminance (J-V-L) characteristics for the devices A-C are in Fig. 9 and the corresponding data are listed in Table 2. The maximum luminance ( $L_{max}$ ) of the device B is 35 610 cd/m<sup>2</sup> and has a lower turn-on voltage ( $V_{on}$ : the voltage at the luminance of 1 cd/m<sup>2</sup>) of 3.0 V. The based-pCP device (device C) has inferior performances with the  $L_{max}$  of 9 497 cd/m<sup>2</sup> and  $V_{on}$  of 5.5 V.



Fig. 10 shows the current efficiency  $(\eta_L)$  - current density (J) for the devices A-C. The device B exhibited the excellent electroluminescent properties with the maximum  $\eta_L$  of 44.88 cd/A, the maximum power efficiency  $(\eta_p)$  of 37.75 lm/W and the external quantum efficiency (EQE) of 13.08%, as shown in Table 3. On the other hand, the device C displayed the  $\eta_{L,max}$  of 35 cd/A and maximum EQE of 10.07%. The balanced carrier transport improved the performances in device B owing to the bipolar property of sCP. What's more, the higher T<sub>1</sub> of sCP can effectively prevent back energy from guest to host.



Fig. 10 The current efficiency- current density of devices A-C

	Table 3 Devic	es performan	ces of PhOLEDs
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Device	Host	$V_{on}^{\ a}$	V <sub>on</sub> <sup>a</sup> L <sub>max</sub> <sup>b</sup>		$\eta_{pmax}^{\ \ d}$	CIE	EQE	
		(V)	$(cd/m^2)$	(cd/A)	(lm/W)	$(\mathbf{x}, \mathbf{y})^{\mathrm{e}}$	(%)	
А	hCP	4.5	2876	21.3	16.08	(0.30,0.62)	6.0	
В	sCP	3	35610	44.88	37.75	(0.31,0.60)	13.08	
С	pCP	5.5	9497	35	13.42	(0.30,0.62)	10.07	

<sup>a</sup> Voltages at 1 cd·m<sup>-2</sup>. <sup>b</sup> Maximum luminance. <sup>c</sup> Maximum current efficiency. <sup>d</sup> Maximum power efficiency. <sup>e</sup> CIE measured at 8 V.

## 4. Conclusions

In summary, we have synthesized three host materials by changing the introduction of different connection groups. The emission spectra of hCP have the maximum peaks at 351 and 368 nm, and the emission wavelength of sCP is located at 382 nm and pCP appears at around 355 and 363 nm respectively. The T<sub>1</sub> of hCP, sCP and pCP are 3.01, 3.02 and 2.84 eV, respectively. The PhOLEDs used sCP as host exhibited higher maximum  $\eta_L$  of 44.88 cd/A with the  $\eta_p$  37.75 lm/W and the maximum EQE of 13.08%. Thus, these hosts have the potential applications in the

blue PhOLEDs.

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