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## ARTICLE

# Small organic molecules based on oxazole/thiazole with excellent performances for green and red phosphorescent organic light-emitting diodes

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Four pure organic molecules based on oxazole/thiazole were designed and characterized, and their relevant thermal, photophysical and electrochemical properties had been fully investigated. All the compounds (2a-2d) exhibited good thermal stabilities with the endothermic glass transitions were over 120 °C, the biggest one was 2d with the endothermic glass transition of 145 °C. Four green devices with 2a-2d served as host materials were fabricated, compound 2d based device exhibited the best performance that a maximum current efficiency of 50.7 cd/A and a maximum power efficiency of 50.1 lm/W. A red device based on 2d was also fabricated with the performance that a maximum current efficiency of 18.7 cd/A and a maximum power efficiency of 17.3 lm/W. These excellent performances of 2a-2d make them as promising alternatives for efficient green and red devices.

## Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have been developed rapidly nowadays due to the dedication of scientists and researchers.<sup>1-5</sup> It is important that the role of the quantum efficiency and lifetime in the electrophosphorescent device, one of the key factors is the host materials.<sup>6,7</sup> The crucial properties of the host materials are the good thermal stability, the suitable HOMO-LUMO level, the high triplet energy ( $E_T$ ) and so on. Various host materials have been investigated recently.<sup>8-12</sup>

Among the researched host materials, the investigated areas are mainly focused on arylamine derivatives,<sup>13-16</sup> anthracene derivatives,<sup>17,18</sup> pure hydrocarbon derivatives<sup>19-22</sup> and so on. However, there is rarely literature that reported pure organic oxazole or thiazole derivatives, especially to make the pure organic oxazole or thiazole derivatives to be the host materials. The most reported oxazole or thiazole derivatives are coordinated with metal ligand such as Ir, Pt, Al and Zn, which are proved to be excellent host materials.<sup>23-26</sup> In view of the price of metal ligand and purity of the coordination molecules, pure organic molecules are good alternatives due to their various structure modifications and easy syntheses. It is well known that the widely usage of carbazole derivatives in electrophosphorescent devices. The advantages of carbazole derivatives are good carrier mobility, rigid structure, high triplet energy and high fluorescent quantum yield.<sup>27-29</sup>

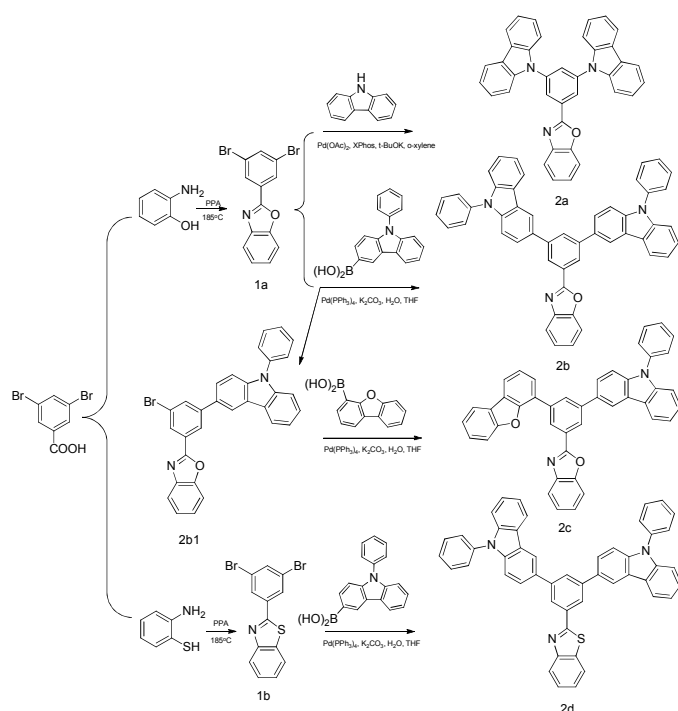
In this work, combining the excellent properties of these two units, the oxazole and thiazole derivatives and the carbazole derivatives, we designed and synthesized four pure organic

molecules (2a-2d). What is more, these four compounds with high yield could be obtained by just two steps. As for the favorable electron-withdrawing ability of oxazole and thiazole derivatives, by introducing these two units into the carbazole backbones, we anticipated that these four molecules could exhibit bipolar charge transport properties and excellent device performances could be obtained.

## Results and discussion

### Synthesis

The synthetic routes of four compounds were showed in Scheme 1. The routes were simple and just two steps could obtain the final compound. Two key intermediates 2-(3,5-dibromophenyl)benzo[d]oxazole and 2-(3,5-dibromophenyl)benzo[d]thiazole were synthesized according to the literature methods.<sup>30</sup> Compound 2a was synthesized by the Buchwald-Hartwig cross coupling reaction with 2-(3,5-dibromophenyl)benzo[d]oxazole and 9H-carbazole, while compounds 2b, 2c and 2d were obtained by the Suzuki coupling reaction of the above two key intermediates and (9-phenyl-9H-carbazol-3-yl)boronic acid and dibenzo[b,d]furan-4-ylboronic acid. The flash column chromatography and subsequent HPLC was performed to purify the intermediates. All the obtained compounds of the synthetic routes were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR and HRMS.



Scheme 1. The synthesis of compounds 2a-2d.

### Thermal property

The thermal properties of four compounds were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. The obtained data were listed in Table 1 and the corresponding spectra were shown in Fig.1. The thermal decomposition temperatures ( $T_d$ , corresponding to 5% weight loss) were 371 °C, 440 °C, 388 °C and 442 °C for 2a-2d, respectively. What is more, the endothermic glass transition ( $T_g$ ) of 2a-2d were determined to be 120 °C, 124 °C, 123 °C and 145 °C in the heating scan by the DSC scan. Based on the above-mentioned thermal values, they were higher than that of small molecules such as mCP and CBP,<sup>31,32</sup> so the performances of OLED devices based on 2a-2d would be excellent for their good thermal stability.

Table 1. The physical properties of the compounds 2a-2d.

Compound	$\lambda_{\text{abs}}^{\text{max}}$ (nm) <sup>a</sup>	$\lambda_{\text{em}}^{\text{max}}$ (nm) <sup>a</sup>	$E_g$ (eV) <sup>b</sup>	HOMO (eV) <sup>c</sup>	LUMO (eV) <sup>d</sup>	$E_T$ <sup>e</sup>	$T_g$ <sup>f</sup>	$T_d$ <sup>f</sup>	$\Phi_P$ <sup>g</sup>
2a	304	419	3.30	-5.46	-2.16	2.66	120	370	0.48
2b	300	401	3.40	-5.64	-2.06	2.65	124	440	0.78
2c	302	408	3.35	-5.51	-2.16	2.63	123	388	0.48
2d	301	416	3.26	-5.48	-2.22	2.54	145	442	0.38

<sup>a</sup>Measured in tetrahydrofuran. <sup>b</sup>Estimated from onset of the absorption spectra ( $E_g = 1240/\lambda_{\text{onset}}$ ). <sup>c</sup>Calculated from cyclic voltammetry. <sup>d</sup>Calculated by the equation  $E_{\text{HOMO}} = E_{\text{LUMO}} - E_g$ . <sup>e</sup>Calculated by the first peak of phosphorescence spectra measured at 77k. <sup>f</sup>Measured by TGA and DSC. <sup>g</sup>Measured by Quanta-φ F-3029 Integrating Sphere.

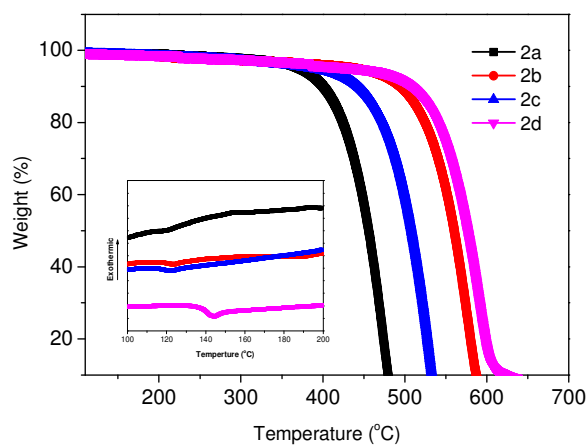


Fig.1. The thermal properties of compounds 2a-2d.

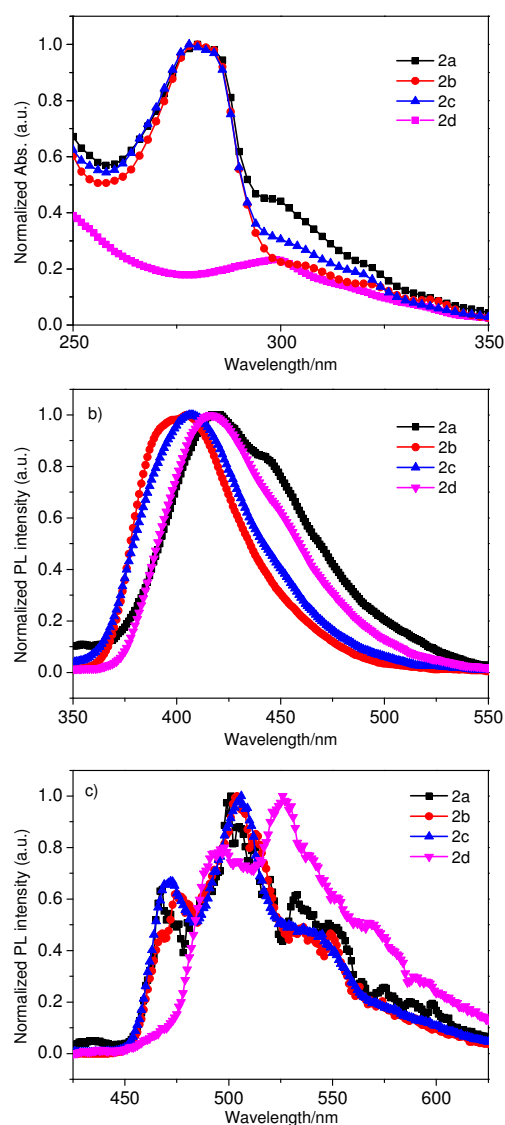
### Photophysical properties

The absorption spectra, photoluminescence spectra (PL) (at room temperature in THF) and phosphorescence spectra (at 77 K in 2-methyl THF) for the four compounds were shown in Fig.2. The pertinent data of these compounds were summarized in Table 1. As shown in Fig.2a, the absorption spectra of 2a-2c were similar, while the absorption spectra of 2d was different with that of 2a-2c. The stronger absorption peaks of 2a-2c were located at 282 nm, which were ascribed to carbazole  $\pi \rightarrow \pi^*$  transitions. The weaker absorption peaks for 2a-2c were located at around 302 nm, which should be derived from the  $n \rightarrow \pi^*$  transitions for extended conjugation of carbazole and benzo[d]oxazole. For the compound 2d, the absorption peaks at 301 nm could be attributed to the  $n \rightarrow \pi^*$  transitions for the conjugation of carbazole and benzo[d]thiazole.<sup>33</sup> From the threshold of the absorption spectra of 2a-2d in THF, their optical energy bandgaps ( $E_g$ ) could be obtained to be 3.30 eV, 3.40 eV, 3.35 eV and 3.26 eV, respectively.

The photoluminescence spectra (PL) (at room temperature) were recorded in Fig.2b, the maximum of PL spectra were located at 419 nm, 401 nm, 408 nm and 416 nm for 2a-2d, respectively. In view of the nature of molecule structure, the maximum of PL spectra of 2a was red-shifted compared with other three compounds due to its large conjugation of the molecule. The maximum of PL spectra of 2c was red-shifted 7 nm compared to that of 2b as a result of the weak electron-withdrawing ability of dibenzofuran and enhanced the integral conjugation of the molecule.

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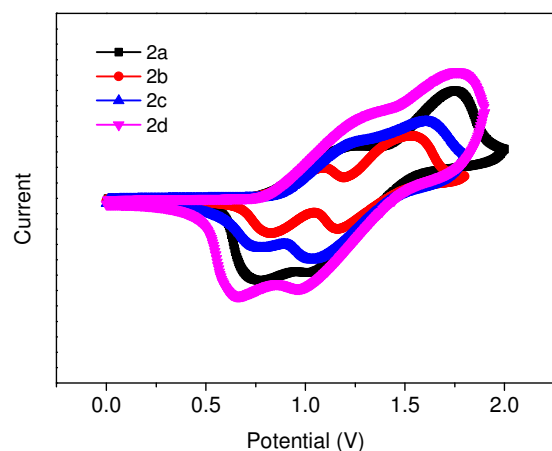
The red-shifted photoluminescence spectra of 2d compared to that of 2b could be ascribed to the stronger electron-withdrawing ability of benzo[d]thiazole than that of benzo[d]oxazole.<sup>34</sup> As also shown in Fig.2c, the phosphorescence spectra of these four compounds were obtained at 77 K in 2-methyl THF, determining their triplet energy ( $E_T$ ) to be 2.66 eV, 2.65 eV, 2.63 eV and 2.54 eV, respectively, which were sufficient for fabricating green and red PhOLED devices.<sup>35,36</sup>



**Fig.2.** Absorption (a), photoluminescence spectra (at room temperature in THF) (b) and phosphorescence spectrum (at 77 K in 2-methyl THF) (c) of 2a-2d.

### Electrochemical properties

To gain further insight into the electrochemical properties of these four compounds, the cyclic voltammetry (CV) were introduced to determine the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). The cyclic voltammograms of these four compounds were shown in Fig.3 with measured in  $\text{CH}_2\text{Cl}_2$  (0.1 M TBAPF<sub>6</sub> as supporting electrolyte at a scan rate of  $100 \text{ mV s}^{-1}$ ), an SCE reference electrode (the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple as external standard), a glassy-carbon working electrodes, and a platinum-wire counter electrode. With obtaining the onset oxidation potentials of these four compounds from Fig.3, the corresponding HOMO values for 2a-2d could be determined to be -5.46 eV, -5.46 eV, -5.51 eV and -5.48 eV. The LUMO values were obtained by the summation of the optical  $E_g$  and the HOMO value, calculated to be -2.16 eV, -2.06 eV, -2.16 eV and -2.22 eV, respectively. These pertinent data were listed in Table 1. It was obvious that the charge carrier injection of these four compounds were guaranteed to be efficient.<sup>37</sup>



**Fig.3.** Cyclic voltammogram of 2a-2d in dichloromethane with tetra(n-butyl)ammonium hexafluorophosphate(0.1 M) as a supporting electrolyte for the oxidation scan.

### Electrophosphorescent PhOLEDs

To investigate the charge transport properties of 2a-2d, the hole only and electron only devices were fabricated. The corresponding device structures were as follow: hole-only, ITO/MoO<sub>3</sub>(5 nm)/Host(100 nm)/MoO<sub>3</sub>(5 nm)/Al(80 nm); electron-only, ITO/LiF(10 nm)/Host(100 nm)/LiF(1 nm)/Al(80 nm). 2a-2d were served as the host in the structures. Fig. 4 showed the relevant current density-voltage curves of these devices. Comparing the current densities of hole only and electron only devices for 2a-2d, the hole current density of 2d

was the most similar to its electron current density, the sequence of proximity between the hole current density and the electron current density was:  $2d > 2a > 2c > 2b$ , which indicated the bipolar charge transport properties of 2a-2d. What is more, from the view of molecule engineering for designing bipolar host, incorporating an electron-withdrawing unit into the molecule with electron-donating property, which could enhance the bipolar charge transport property of the molecule.<sup>38</sup> Therefore, due to the introduction of 2-phenylbenzo[d]oxazole/2-phenylbenzo[d]thiazole unit, all these four hosts exhibited bipolar charge transport properties, excellent performances for these four hosts could be anticipated.

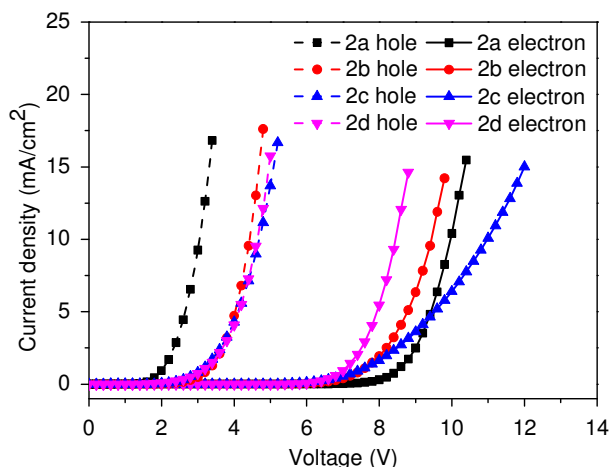


Fig.4. Current density versus voltage characteristics of the hole-only and electron-only devices based on 2a-2d.

Taking the above favorable properties of 2a-2d into consideration, green phosphorescent devices based on 2a-2d were fabricated. Their device structures were: ITO/MoO<sub>3</sub>(5 nm)/NPB(25 nm)/TCTA(8 nm)/Host: Ir(ppy)<sub>2</sub>(acac)(20 nm, 9 wt%)/TPBi(40 nm)/LiF(1 nm)/Al(80 nm). The emitting layer (EML) were composed with 9 wt% Ir(ppy)<sub>2</sub>(acac) doped into the host materials (2a-2d). MoO<sub>3</sub>, NPB and TCTA were acted as the hole injection layers (HIL), the hole transport layers (HTL), and electron block layer (EBL), respectively. LiF was employed as the electron injection layers (EIL) and TPBi was served as the electron transport layers (ETL). The related HOMO and LUMO energy levels of these materials were shown in Fig.5. According to the previous procedure of green phosphorescent device, four green devices based on these materials were fabricated successfully.

Fig.6a shown the current density-voltage-luminance curves of green devices based on 2a-2d, the related data were summarized in Table 2. It was apparent that the turn-on voltages of these four devices were small, determined to be 2.7 V~2.9 V. What is more, the maximum current efficiency for 2a-2d based devices were 50.8, 47.7, 49.2 and 50.7 cd/A, respectively, the corresponding maximum power efficiency were 46.3, 42.8, 43.3 and 50.1 lm/W. These values were considerable big for small pure organic molecules.<sup>6,14,39</sup> The efficiency roll-off for these four host materials based devices

could also be shown from Table 2, for example, even at the practical brightness of 10000 cd/m<sup>2</sup>, the current efficiency and power efficiency of 2d-based device remain 47 cd/A and 30 lm/W, respectively. These excellent performances could be ascribed to the good electron-transport characteristics and balanced charge-combination properties of these four molecules, which could significantly broaden the recombination zero to minimize the number of possible quenching pathways and avoiding charge-carrier loss. Especially for these four organic molecules based on oxazole and thiazole unit, most reported molecules were composed with oxazole/thiazole unit and metal ligand, they were inferior to these four molecules due to these organic molecules were cheap and easily synthesized. It was promising that the usage of phosphorescent devices based on these four host materials.

Fig.6c exhibited the normalized EL spectra of these four devices, the EL spectra of each device were similar, their emission peaks were located at 524 nm and consisted with the triplet emission of Ir(ppy)<sub>2</sub>(acac) (520 nm), therefore, the green emission peak was indicated to be solely originated from the triplet metal ligand charge transfer (<sup>3</sup>MLCT) transition of Ir(ppy)<sub>2</sub>(acac).<sup>40</sup> The color coordinate of these four green phosphorescent devices were determined to be (0.34, 0.62), (0.33, 0.62), (0.34, 0.62) and (0.34, 0.62), respectively.

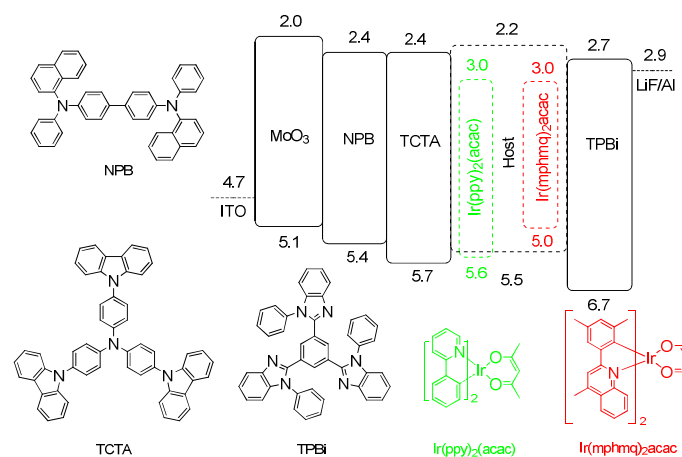
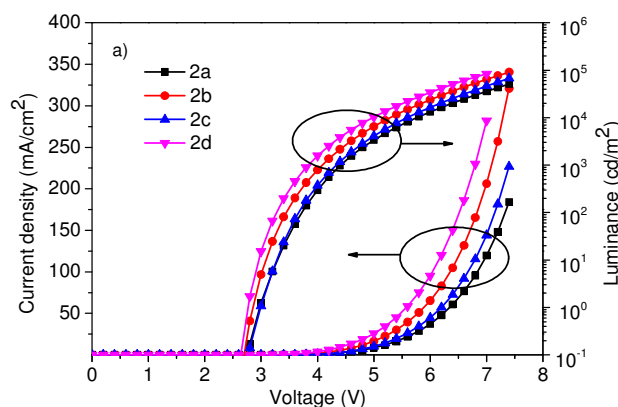
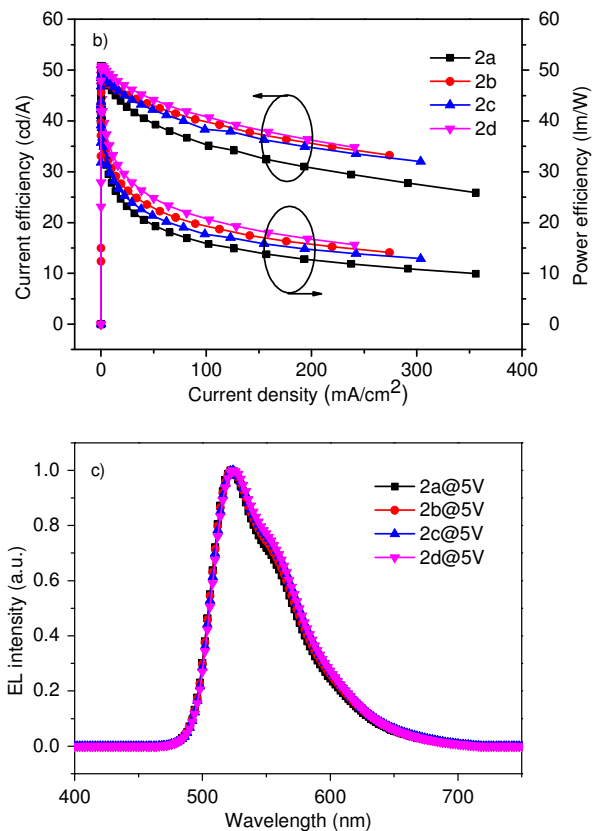


Fig.5. Energy-level diagram of green and red PHOLEDs.





**Fig. 6.** a) Current density-voltage-luminance data of green PHOLEDs; b) Current efficiency-current density curves and power efficiency-luminance curves of green PHOLEDs; c) Electroluminescence spectra of green PHOLEDs.

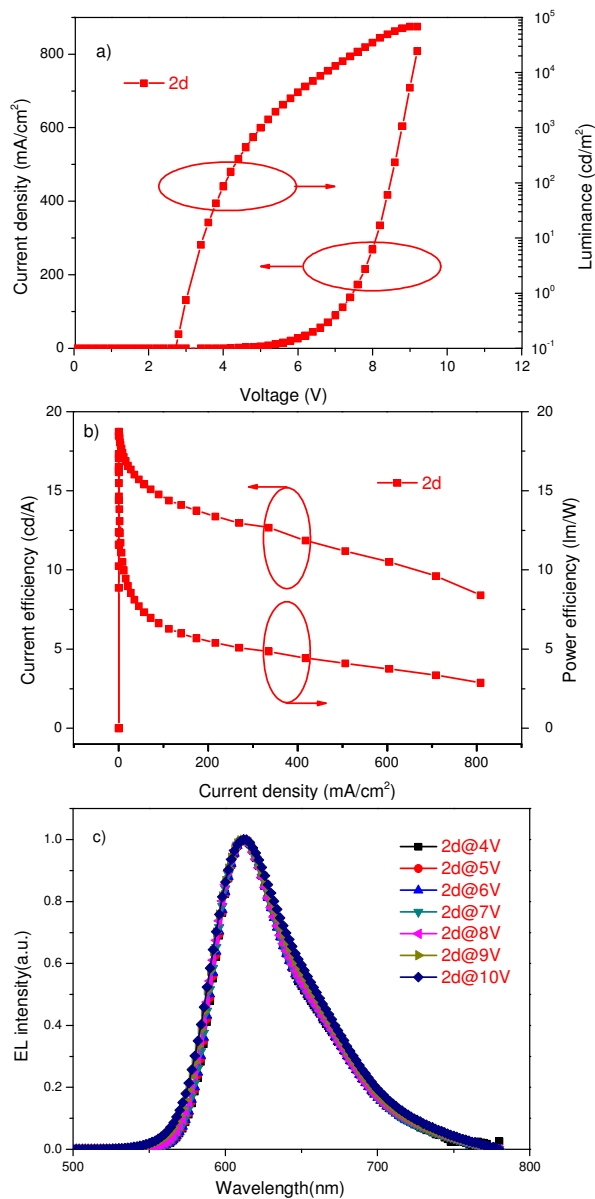
**Table 2.** EL properties of green and red devices using 2a-2d as the host materials.

Device	At 100 cd/m <sup>2</sup> [cd/A]/[lm/W]	At 10000 cd/m <sup>2</sup> [cd/A]/[lm/W]	$\eta_{c,max}$ (cd/A)	$\eta_{p,max}$ (lm/W)	CIE <sub>(x,y)</sub> <sup>a</sup>
Green-2a	50/43	43/23	50.8	46.3	(0.34, 0.62)
Green-2b	46/41	45/26	47.7	42.8	(0.33, 0.62)
Green-2c	49/41	45/25	49.2	43.3	(0.34, 0.62)
Green-2d	50/48	47/30	50.7	50.1	(0.34, 0.62)
Red-2d	16.5/9.7	11.9/3.8	18.7	17.3	(0.65, 0.35)

<sup>a</sup>Measured from the EL spectra at 5V by inverting into chromaticity coordinates on the CIE 1931 diagram.

Considering the best performance of 2d among these four compounds, a red phosphorescent device based on 2d was also fabricated to investigate the electrophosphorescent property. The device structure was: ITO/MoO<sub>3</sub>(5 nm)/NPB(30 nm)/TCTA(10 nm)/Host3: Ir(mphmq)<sub>2</sub>acac(20 nm, 7.24%)/TPBi(40 nm)/LiF(1 nm)/Al(80 nm). The relevant layers were same with the above-mentioned green devices except the dopants. The current density-voltage-luminance curves, the current and power efficiencies curves and the normalized EL spectra were shown in Fig.7. The performance of device was that the maximum current efficiency was 18.7

cd/A and the maximum power efficiency were 17.3 lm/W. These data were also bigger than that of small organic molecules.<sup>15</sup> What is more, the normalized EL spectra were recorded by different voltages of 4 V~10 V, there was rarely change for these normalized EL spectra, the color coordinate of the red phosphorescent device was similar and determined to be (0.65, 0.35). Therefore, from the aforementioned performances of devices based on these hosts, they were proved to be excellent for green and red phosphorescent devices.



**Fig. 7.** a) Current density-voltage-luminance data of red PHOLEDs; b) Current efficiency-current density curves and power efficiency-luminance curves of red PHOLEDs; c) Electroluminescence spectra of red PHOLEDs.

## Experimental

**General Information** All the solvents and chemicals that we have used in the route were purchased from Shanghai Taoe

chemical technology Co., Ltd. and received without further purification. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were obtained using a Bruker AM 400 spectrometer, the mass spectra were recorded on a Waters LCT Premier XE spectrometer. The UV/Vis spectra and PL spectra were recorded on a Nicolet CARY 100 spectrophotometer and a Varian Cary fluorescence spectrophotometer, respectively. The cyclic voltammograms were obtained using a Versastat II electrochemical workstation with conventional three electrodes containing an SCE reference electrode (the ferrocene/ferrocenium ( $\text{Fc}/\text{Fc}^+$ ) redox couple as external standard), a glassy-carbon working electrodes and a platinum-wire counter electrode. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere on a NETZSCH STA 409 PC/PG instrument and a TGA instrument, respectively.

**2-(3,5-dibromophenyl)benzo[d]oxazole(1a).** In a one-neck flask, 3,5-dibromobenzoic acid (5.0 g, 18.0 mmol) and 2-aminophenol (2.0 g, 18.0 mmol) were dissolved in 20 mL polyphosphoric acid, then heat the mixture to 185 °C for 6 h. After the reaction was finished, poured 20 mL water into the mixture and the crude product was obtained by filtration. Then recrystallize from methanol to afford an off-white solid (3.8 g, 61%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.30 (d,  $J = 2.0$  Hz, 2H), 7.79 (d,  $J = 2.4$  Hz, 1H), 7.77-7.75 (m, 1H), 7.59-7.57 (m, 1H), 7.40-7.35 (m, 2H).

**2-(3,5-dibromophenyl)benzo[d]thiazole(1b).** Compound 1b was synthesized by the same procedure as described above for compound 1a using 3,5-dibromobenzoic acid and 2-aminobenzenethiol. Yield: 58%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.17 (d,  $J = 1.6$  Hz, 2H), 8.09 (d,  $J = 8.4$  Hz, 1H), 7.93 (d,  $J = 7.6$  Hz, 1H), 7.78 (t,  $J = 1.6$  Hz, 1H), 7.57-7.51 (m, 1H), 7.47-7.41 (m, 1H).

**2-(3,5-di(9H-carbazol-9-yl)phenyl)benzo[d]oxazole(2a).** In a 50 mL one-neck flask, 1a (0.5 g, 1.4 mmol), 9H-carbazole (0.5 g, 3.0 mmol), t-BuOK (0.3 g, 2.8 mmol), Pd(OAc) $_2$  (30 mg) and XPhos(90 mg) were put into 30 mL o-xylene, heat the mixture to reflux under nitrogen for 8 h, when the reaction was finished, cool the mixture to the room temperature and poured 30 mL  $\text{H}_2\text{O}$  into the mixture, using the  $\text{CH}_2\text{Cl}_2$  (20 mL  $\times$  3) to extract the mixture, after drying these by anhydrous  $\text{MgSO}_4$  and concentrated using a rotary evaporator. The pure materials were obtained by silica gel column chromatography (petroleum ether/ $\text{CH}_2\text{Cl}_2 = 5 : 1$  v/v) to give a white solid (0.4 g, 66%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.54 (d,  $J = 2.0$  Hz, 4H), 8.11 (d,  $J = 7.6$  Hz, 1H), 7.93 (t,  $J = 2.0$  Hz, 1H), 7.76 – 7.72 (m, 1H), 7.57 – 7.52 (m, 5H), 7.45 – 7.38 (m, 4H), 7.36 – 7.31 (m, 2H), 7.31 – 7.25 (m, 4H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.88, 141.99, 140.44, 140.27, 130.83, 127.72, 126.39, 125.90, 125.02, 124.52, 123.83, 120.70, 120.58, 120.49, 110.87, 109.68. HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{37}\text{H}_{24}\text{N}_3\text{O}$ , 526.1919; found, 526.1918. Anal. calcd for  $\text{C}_{37}\text{H}_{23}\text{N}_3\text{O}$ : C, 84.55; H, 4.41; N, 7.99. Found: C, 84.47; H, 4.51; N, 7.83%.

**2-(3,5-bis(9-phenyl-9H-carbazol-3-yl)phenyl)benzo[d]oxazole(2b).** In a one-neck flask, 1a (0.5 g, 1.4 mmol), (9-phenyl-9H-carbazol-3-yl)boronic acid (0.9 g, 3.1

mmol),  $\text{K}_2\text{CO}_3$  (0.4 g, 2.8 mmol),  $\text{H}_2\text{O}$  (2 mL) and  $\text{Pd}(\text{PPh}_3)_4$  (20 mg) were dissolved in 25 mL THF. Then heat the mixture to reflux under nitrogen for 6 h, after the reaction was completed, poured 20 mL  $\text{H}_2\text{O}$  into the mixture and extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  3), dried the combined organic layer over anhydrous  $\text{MgSO}_4$  and concentrated using a rotary evaporator. The crude materials were purified by silica gel column chromatography (petroleum ether/ $\text{CH}_2\text{Cl}_2 = 5 : 1$  v/v) to obtain a white solid (0.7 g, 71%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.61 (d,  $J = 1.6$  Hz, 2H), 8.57 (d,  $J = 1.6$  Hz, 2H), 8.27 (d,  $J = 8.0$  Hz, 2H), 8.23 (s, 1H), 7.89 – 7.84 (m, 3H), 7.70 – 7.61 (m, 9H), 7.57 – 7.49 (m, 4H), 7.46 (d,  $J = 4.0$  Hz, 4H), 7.42 – 7.39 (m, 2H), 7.38 – 7.32 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 150.88, 143.43, 141.60, 140.73, 137.60, 136.79, 134.52, 132.49, 131.69, 129.99, 129.15, 127.64, 127.13, 126.29, 125.62, 124.77, 124.60, 124.02, 123.61, 123.45, 121.70, 120.58, 120.27, 119.20, 110.20, 110.01. HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{49}\text{H}_{32}\text{N}_3\text{O}$ , 678.2545; found, 678.2556. Anal. calcd for  $\text{C}_{49}\text{H}_{31}\text{N}_3\text{O}$ : C, 86.83; H, 4.61; N, 6.20. Found: C, 86.64; H, 4.65; N, 5.97%.

**2-(3-bromo-5-(9-phenyl-9H-carbazol-3-yl)phenyl)benzo[d]oxazole(2b1).** Compound 2b1 was synthesized by the same procedure as described above for compound 2a using 1a and (9-phenyl-9H-carbazol-3-yl)boronic acid. Yield: 81%.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.56 (t,  $J = 1.6$  Hz, 1H), 8.44 (d,  $J = 1.6$  Hz, 1H), 8.38 (t,  $J = 1.6$  Hz, 1H), 8.25 (d,  $J = 7.6$  Hz, 1H), 8.02 (t,  $J = 1.6$  Hz, 1H), 7.86 – 7.80 (m, 1H), 7.72 (m, 1H), 7.68 – 7.59 (m, 5H), 7.54 – 7.47 (m, 2H), 7.47 – 7.44 (m, 2H), 7.42 – 7.39 (m, 2H), 7.35 (m, 1H).

**2-(3-(dibenzo[b,d]furan-4-yl)-5-(9-phenyl-9H-carbazol-3-yl)phenyl)benzo[d]oxazole(2c).** Compound 2c was synthesized by the same procedure as described above for compound 2a using 2b1 and dibenzo[b,d]furan-4-ylboronic acid. Yield: 81%.  $^1\text{H}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.64 (m, 2H), 8.51 (d,  $J = 1.6$  Hz, 1H), 8.39 (t,  $J = 1.6$  Hz, 1H), 8.18 (d,  $J = 7.6$  Hz, 1H), 7.98 – 7.93 (m, 2H), 7.82 – 7.76 (m, 2H), 7.74 (m, 1H), 7.61 – 7.53 (m, 6H), 7.49 – 7.41 (m, 4H), 7.38 (d,  $J = 3.6$  Hz, 2H), 7.33 (m, 3H), 7.27 (m, 1H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 156.26, 143.26, 142.20, 137.93, 131.03, 130.00, 128.12, 127.65, 127.38, 127.13, 126.89, 126.30, 125.98, 125.65, 125.27, 125.13, 124.70, 124.17, 123.43, 123.37, 122.93, 120.77, 120.26, 120.13, 119.25, 112.08, 110.75, 110.23, 101.52. HRMS (m/z):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{43}\text{H}_{27}\text{N}_2\text{O}_2$ , 603.2073; found, 603.2061. Anal. calcd for  $\text{C}_{43}\text{H}_{26}\text{N}_2\text{O}_2$ : C, 85.69; H, 4.35; N, 4.65. Found: C, 85.40; H, 4.40; N, 4.58%.

**2-(3,5-bis(9-phenyl-9H-carbazol-3-yl)phenyl)benzo[d]thiazole(2d).** Compound 2d was synthesized by the same procedure as described above for compound 2a using 1b and (9-phenyl-9H-carbazol-3-yl)boronic acid. Yield: 80%.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 8.55 (d,  $J = 1.6$  Hz, 2H), 8.42 (d,  $J = 1.6$  Hz, 2H), 8.27 (d,  $J = 8.0$  Hz, 2H), 8.18 (s, 1H), 7.97 (d,  $J = 8.0$  Hz, 1H), 7.85 (m, 2H), 7.75 – 7.62 (m, 9H), 7.57 – 7.49 (m, 6H), 7.46 (d,  $J = 4.0$  Hz, 4H), 7.37 – 7.32 (m, 2H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$ : 154.26, 143.53, 141.46, 140.71, 137.62, 135.21, 134.64, 132.65, 129.99, 129.13, 127.63, 127.13, 126.39, 126.28, 125.67, 125.27, 124.70, 124.02,

123.46, 123.32, 121.70, 120.58, 120.23, 119.20, 110.19, 110.00. HRMS (m/z): [M+H]<sup>+</sup> calcd for C<sub>49</sub>H<sub>32</sub>N<sub>3</sub>S, 694.2317; found, 694.2311. Anal. calcd for C<sub>49</sub>H<sub>31</sub>N<sub>3</sub>S: C, 84.82; H, 4.50; N, 6.06. Found: C, 84.59; H, 4.38; N, 5.92%.

## Conclusions

Four pure organic molecules based on the oxazole and thiazole derivatives and carbazole derivatives had been successfully synthesized and characterized. The thermal, photophysical and electrochemical properties of these four compounds were fully investigated. They exhibited good thermal stability with all the endothermic glass transitions were over 120 °C. What is more, the performances of compound 2d based on thiazole derivatives were better than that of the compounds (2a, 2b, 2c) based on oxazole derivatives. Both green and red phosphorescent devices were fabricated for 2d, for green phosphorescent device, its maximum current efficiency was 50.7 cd/A and maximum power efficiency was 50.1 lm/W; for red phosphorescent device, its maximum current efficiency was 18.7 cd/A and maximum power efficiency was 17.3 lm/W. These values were considerable big as compared to other small pure organic molecule-based green and red electrophosphorescent devices. Given the obtained excellent performances of the oxazole and thiazole derivatives, other serials of thiazole derivatives with application of PHOLED are in further research.

## Notes and references

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Electronic Supplementary Information (ESI) available: [The normalized emission spectra of 2a-2d in different solvents at the concentration of 1.0×10<sup>-5</sup>; The spectra (<sup>1</sup>H NMR, <sup>13</sup>C NMR, HRMS) for compounds 2a-2d].

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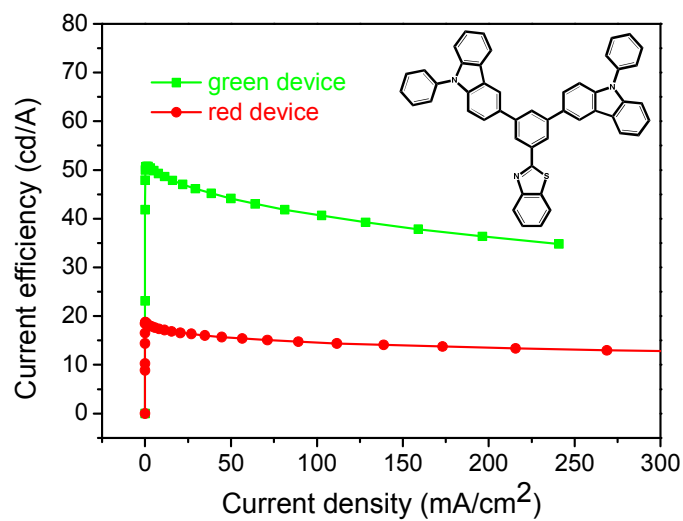
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Four small organic host materials based on oxazole/thiazole have been synthesized and fully characterized, which exhibited excellent performances for green and red phosphorescent organic light-emitting diodes. The best performance of compound 2d was a maximum current efficiency of 50.7 cd/A for green device and a maximum current efficiency of 18.7 cd/A for red device.