

## Electronic supplementary information

for

# Novel phosphorescent polymers containing both ambipolar segments and functionalized Ir<sup>III</sup> phosphorescent moieties: Synthesis, photophysical, redox, and electrophosphorescent investigation

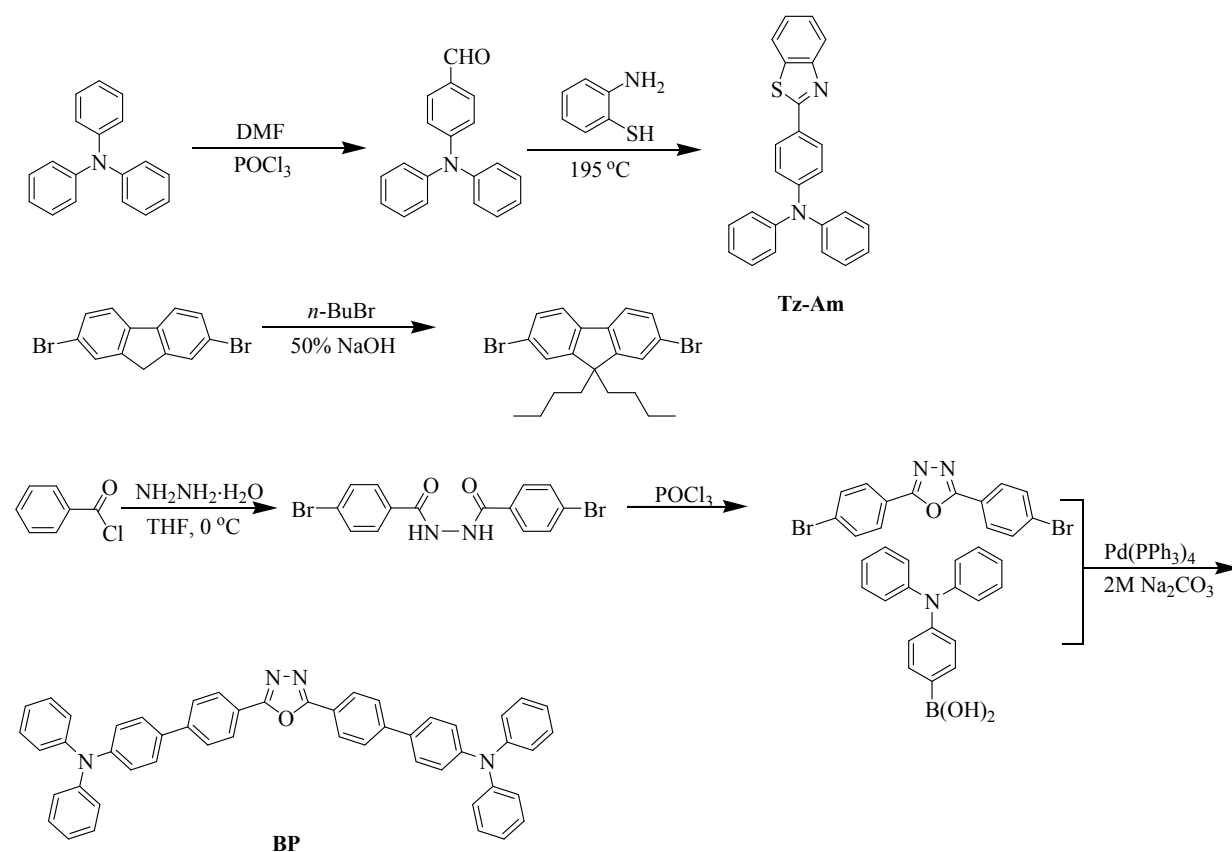
Meng Lian,<sup>a</sup> Yue Yu,<sup>b</sup> Jiang Zhao,<sup>a</sup> Zuan Huang,<sup>a</sup> Xiaolong Yang,<sup>a</sup> Guijiang Zhou,<sup>a</sup>

Zhaoxin Wu<sup>b</sup> and Dongdong Wang<sup>a</sup>

*<sup>a</sup>MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, State Key Laboratory for Mechanical Behavior of Materials, Department of Chemistry, Faculty of Science, Xi'an Jiaotong University, Xi'an 710049, P.R. China. E-mail: zhougj@mail.xjtu.edu.cn. (G. Zhou), Fax: +86-29-8266-3914*

*<sup>b</sup>Key Laboratory of Photonics Technology for Information School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, P.R. China. E-mail: zhaoxinwu@mail.xjtu.edu.cn. (Z. Wu), Fax: +86-029-82664867*

## Experimental



**Scheme S1** The synthetic protocols for some organic intermediate compounds

### 2,7-Dibromo-9,9-dibutylfluorene

A mixture of 2,7-dibromofluorene (6.0 g, 18.5 mmol), 50% NaOH solution (12.0 mL) and  $\text{Bu}_4\text{NCl}$  (0.16 g, 0.56 mmol) and *n*-butyl bromide (15.2 g, 110.9 mmol) was stirred at 95 °C for 24 h. After cooling to room temperature, the reaction mixture was then poured into water (250 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 100$  mL). The combined organic solution was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and evaporated to dryness. The crude product was further purified by silica gel column chromatography using petroleum ether as the eluent to afford the title product as a white solid (7.5 g, 93%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 7.51–7.49 (m, 2H), 7.45–7.42 (m, 4H), 1.93–1.90 (m), 1.12–1.02 (m, 4H), 0.67 (t,  $J = 7.2$  Hz, 6H), 0.58–0.51 (m,

4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 125.4, 139.0, 130.1, 126.1, 121.3, 121.1 (Ar), 55.5 (quat. C), 40.0, 25.7, 22.9, 13.8 (Bu); FAB-MS:  $m/z$  436  $[\text{M}]^+$ .

#### **4-(Diphenylamino)benzaldehyde**

To DMF (1.3 mL, 19.5 mmol), phosphorus oxychloride ( $\text{POCl}_3$ ) (1.6 mL, 16.8 mmol) was added dropwise at 0 °C. The mixture was allowed to be stirred for 1 h at this temperature. Triphenylamine (3.3 g, 13.3 mmol) was added and the reaction mixture was stirred at 100 °C for 6 h. Then, the mixture was cooled to room temperature, poured into ice water and carefully neutralized to pH 7 with 5% NaOH aqueous solution. The solution was extracted with  $\text{CH}_2\text{Cl}_2$  ( $3 \times 150$  mL). Then, the organic phase was washed with water ( $2 \times 100$  mL) and dried over anhydrous  $\text{MgSO}_4$ . After filtration, the solvent was removed. The crude product was purified by silica gel column chromatography with hexane/ $\text{CH}_2\text{Cl}_2$  (3/1, v/v) to produce pale yellow solid (2.9 g, 80%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 9.81 (s, 1H), 7.67 (d,  $J = 8.8$  Hz, 2H), 7.34 (t,  $J = 8.0$  Hz, 4H), 7.19–7.15 (m, 6H), 7.01 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 190.47, 153.32, 146.10, 131.29, 129.70, 129.02, 126.29, 125.09, 119.29; FAB-MS:  $m/z$  273  $[\text{M}]^+$ .

#### **Tz-Am**

The mixture of 4-(diphenylamino)benzaldehyde (0.27 g, 1.0 mmol) and 2-aminothiophenol (0.16 g, 1.25 mmol) in DMSO (30 mL) was heated to 195 °C under nitrogen flow and held at this temperature for 2 h, and then poured into water. The separated solids were collected, stirred in acetic acid/water (50 mL, 1:4, v/v), filtered, and washed with water and dilute sodium bicarbonate solution. These solids obtained were purified by silica gel column chromatography with petroleum ether/ $\text{CH}_2\text{Cl}_2$  (3/1, v/v) to produce pale yellow solid (0.32 g, 85%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.02 (d,  $J = 8.0$  Hz, 1H), 7.92 (d,  $J = 8.4$  Hz, 2H), 7.87 (d,  $J = 8.0$

Hz, 1H), 7.46 (t,  $J = 7.6$  Hz, 1H), 7.37–7.29 (m, 5H), 7.16 (d,  $J = 8.0$  Hz, 4H), 7.13–7.09 (m, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 167.86, 154.19, 150.44, 146.87, 134.74, 129.50, 128.53, 126.45, 126.19, 125.40, 124.72, 124.04, 122.72, 121.69, 121.48; FAB-MS ( $m/z$ ): 378  $[\text{M}]^+$ .

#### **4-Bromo-N'-(4-bromobenzoyl)benzohydrazide**

4-Bromobenzoyl chloride (2.63 g, 12 mmol) and hydrazine monohydrate (0.3 g, 5 mmol) were mixed in THF at 0 °C for 1 h, and then the mixture was stirred for another 2 h at room temperature. The resulting precipitate was filtered, washed with saturated aqueous  $\text{NaHCO}_3$  solution ( $3 \times 15$  mL) and dried to get white solid (1.65 g, 83%).  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm): 10.67 (s, 2H), 7.86 (d,  $J = 8.4$  Hz, 4H), 7.75(d,  $J = 8.4$  Hz, 4H);  $^{13}\text{C}$  NMR (100MHz,  $\text{DMSO}-d_6$ ,  $\delta$ , ppm):  $\delta$  (ppm) 165.43, 132.10, 132.01, 130.03, 126.21; FAB-MS ( $m/z$ ): 380  $[\text{M}]^+$ .

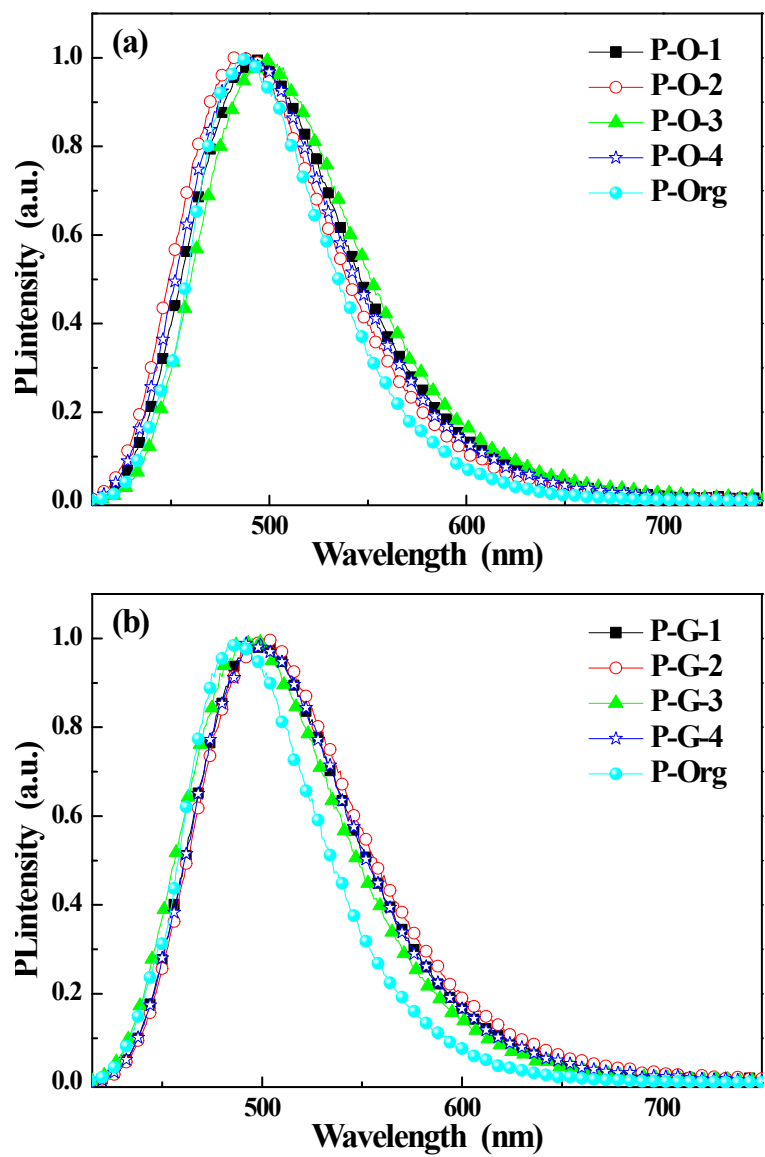
#### **2,5-Bis(4-bromophenyl)-1,3,4-oxadiazole**

A mixture of 4-bromo-N'-(4-bromobenzoyl)benzohydrazide (1.0 g, 2.50 mmol) and  $\text{POCl}_3$  (20 mL) was refluxed for 3 h. After cooling to room temperature, the reaction mixture was poured slowly on ice. The resulting precipitate was filtered, washed with water, dried and recrystallized from ethanol to obtain needle crystals (0.79 g, 82%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 8.01 (d,  $J = 8.8$  Hz, 4H), 7.69 (d,  $J = 8.4$  Hz, 4H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ,  $\delta$ , ppm): 164.08, 132.52, 128.36, 126.66, 122.64; FAB-MS ( $m/z$ ): 378  $[\text{M}]^+$ .

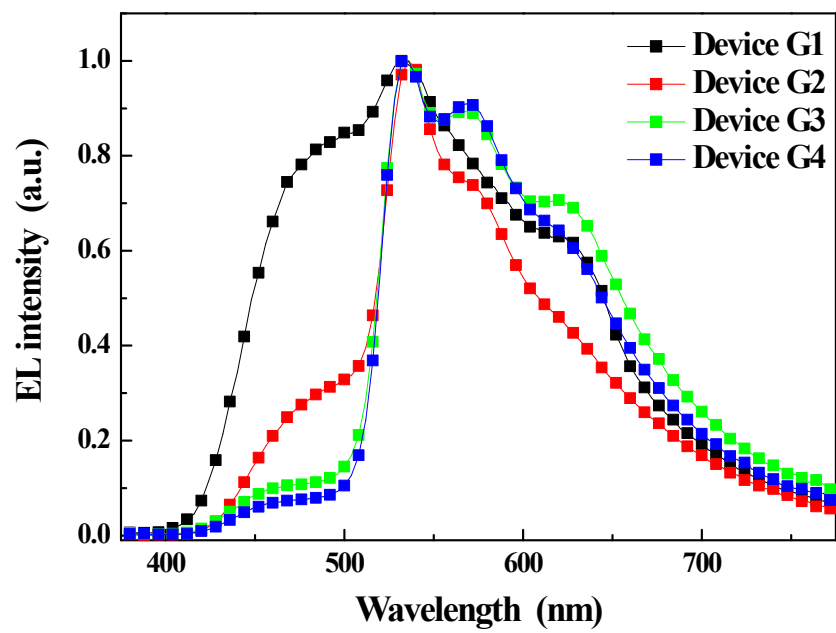
#### **BP**

Under a  $\text{N}_2$  atmosphere, 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (1.0 g, 2.65 mmol), 4-tripenylaminoboronic acid (1.68 g, 5.83 mmol) and  $\text{Pd}(\text{PPh}_3)_4$  (0.15 g) as a catalyst were added to a THF/2M  $\text{Na}_2\text{CO}_3$  mixture (30 mL, 1:1, v/v). The reaction was allowed to proceed at 110 °C for 16 h. After cooling to room temperature, the reaction mixture was poured into a separating

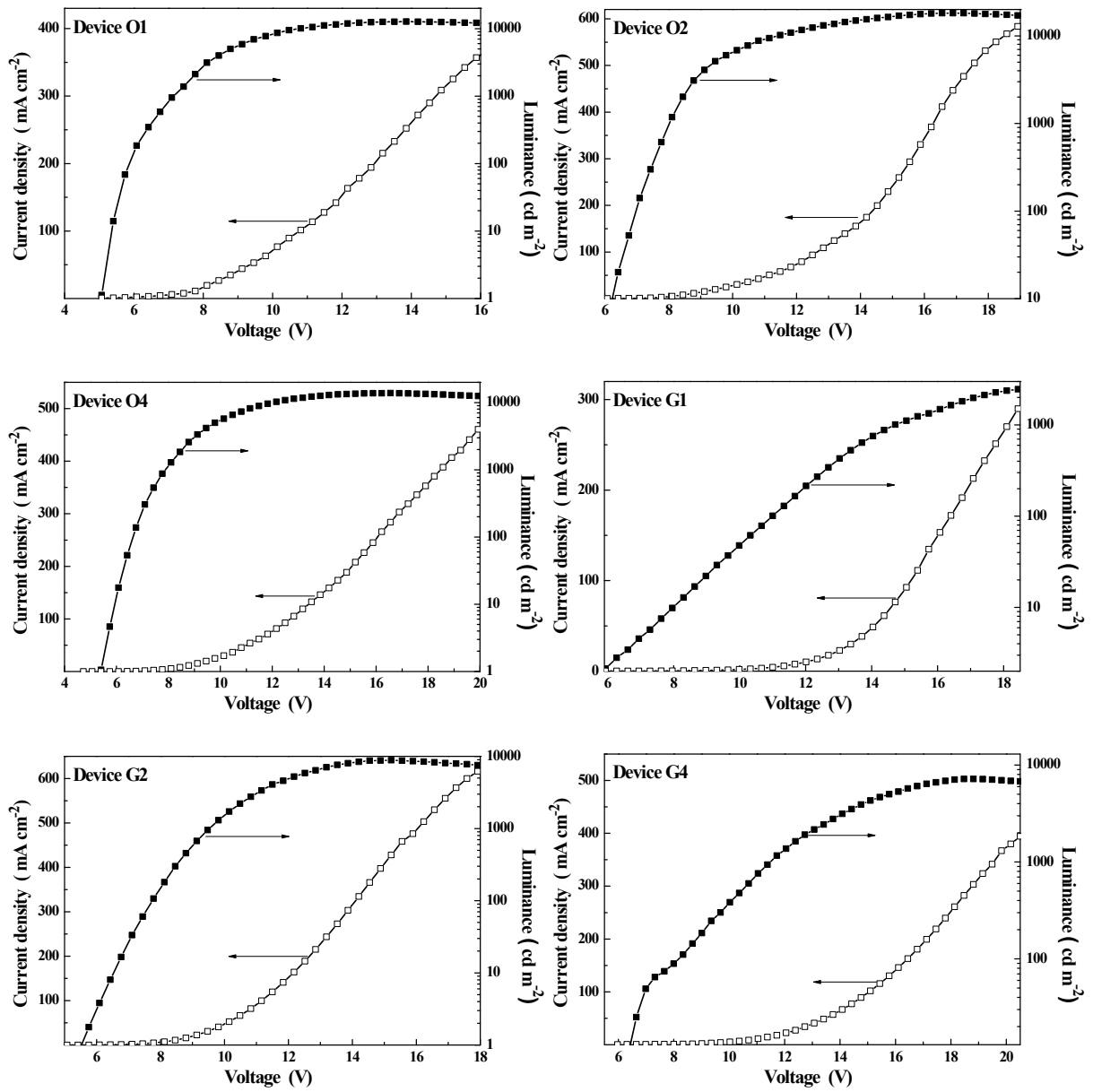
funnel and CH<sub>2</sub>Cl<sub>2</sub> (150 mL) was added. The mixture was washed with water (3 × 100 mL). The organic phase was dried over anhydrous MgSO<sub>4</sub>. The solvent removed and the residue was purified by column chromatography eluting with CH<sub>2</sub>Cl<sub>2</sub>/petroleum ether (2:1, v/v). The title product was obtained as yellow solid (1.6 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ, ppm): 8.20 (d, *J* = 8.0 Hz, 4H), 7.74 (d, *J* = 8.0 Hz, 4H), 7.54 (d, *J* = 8.4 Hz, 4H), 7.29 (t, *J* = 8.0 Hz, 8H), 7.15 (t, *J* = 5.2 Hz, 12H), 7.07 (t, *J* = 7.2 Hz, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ, ppm): 164.52, 148.12, 147.44, 143.87, 133.17, 129.39, 127.81, 127.41, 127.03, 124.76, 123.40, 123.34, 122.10; FAB-MS (*m/z*): 708 [M]<sup>+</sup>.



**Fig. S1** The PL spectra for the phosphorescent polymers in  $\text{CH}_2\text{Cl}_2$  at 298K.

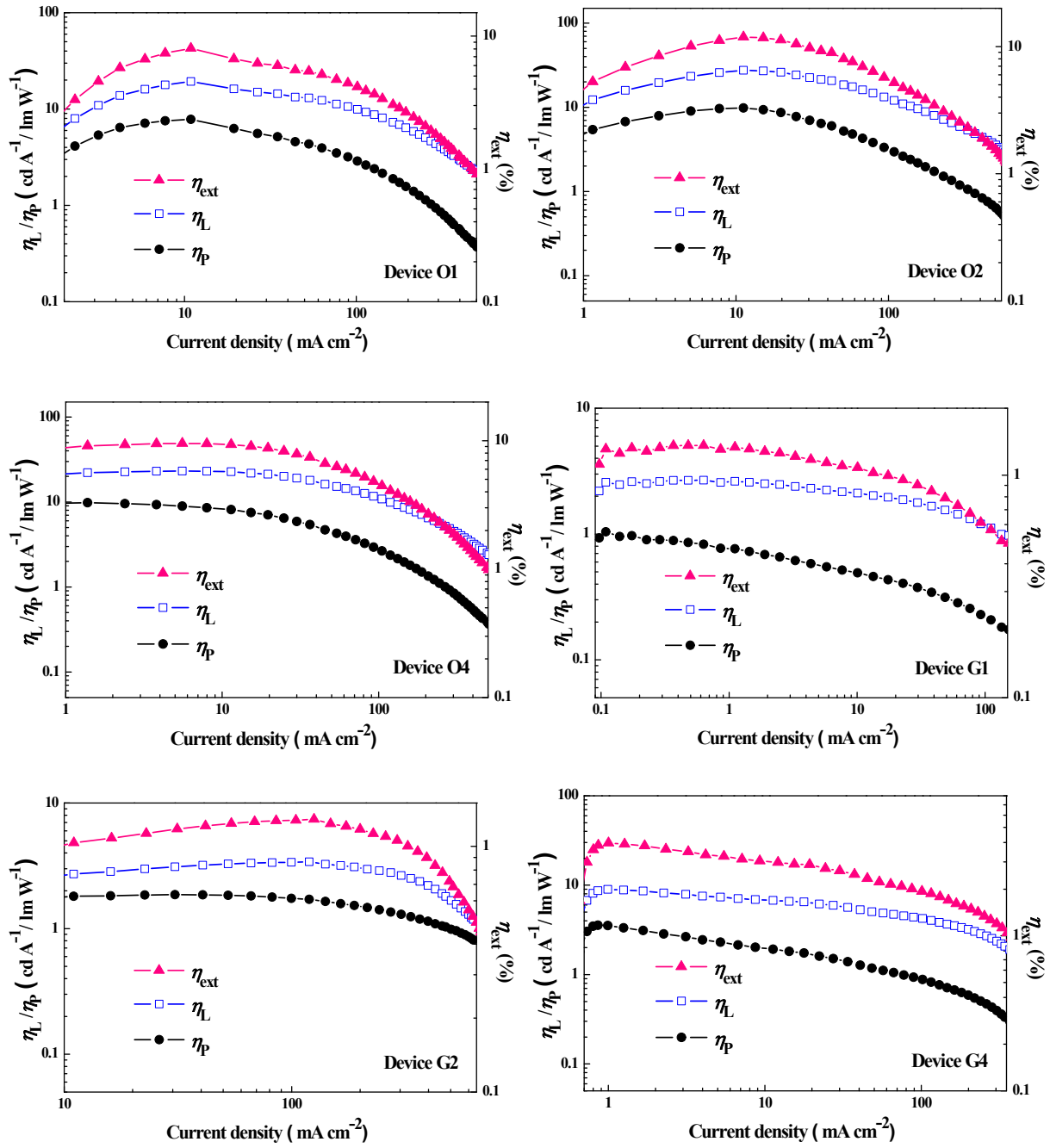


**Fig. S2** The EL spectra for the devices **G1–G4** at *ca.* 12 V.



**Fig. S3** The  $J$ - $V$ - $L$  curves for the devices **O1**, **O2**, **O4**, **G1**, **G2**, and **G4**.





**Fig. S4** The dependence of EL efficiencies on the current density for the devices O1, O2, O4, G1, G2, and G4.