

## Electronic Supplementary Information

### **Blue emitters with various electron-donors attached to 9-phenyl-9-phosphafluorene oxide (PhFIOP) moiety and their thermally activated delayed fluorescent (TADF) behavior**

Xi Chen,<sup>a</sup> Siqi Liu,<sup>a</sup> Yuling Sun,<sup>a</sup> Daokun Zhong,<sup>a</sup> Zhao Feng,<sup>a</sup> Xiaolong Yang,<sup>a</sup> Bochao Su,<sup>a</sup> Yuanhui Sun,<sup>a</sup> Guijiang Zhou,<sup>\*,a</sup> Bo Jiao<sup>\*,b</sup> and Zhaoxin Wu<sup>b</sup>

<sup>a</sup> *School of Chemistry, State Key Laboratory for Mechanical Behavior of Materials, Engineering Research Center of Energy Storage Materials and Devices, Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

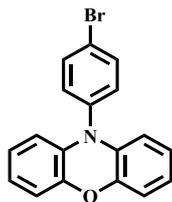
<sup>b</sup> *Key Laboratory of Photonics Technology for Information, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China*

E-mail addresses: zhougj@mail.xjtu.edu.cn (G. Zhou), bojiao@mail.xjtu.edu.cn (B. Jiao).

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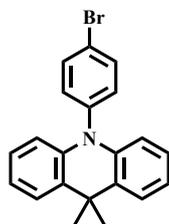
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## 1-1



Under a nitrogen atmosphere, phenoxazine (4 g, 21.8 mmol), 1-bromo-4-iodobenzene (6.1 g, 21.8 mmol), palladium acetate (0.1 g, 0.44 mmol), R-(+)-1,1'-binaphthyl-2,2'-bis(diphenylphosphine) (R-BNIAP) (0.03 g, 0.05 mmol), anhydrous cesium carbonate (14.2 g, 43.7 mmol) and 60 mL of toluene were added into a 250 mL Schlenk reaction tube and stirred at 110 °C overnight. After the reaction, it was cooled to room temperature. Then, the mixture was filtered and the organic phase was collected. The filtrate was concentrated and then purified by column chromatography using petroleum ether: dichloromethane (10: 1, v/v) as the eluent to give a white solid powder (4.8 g, 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.72 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.4 Hz, 2H), 6.71 – 6.57 (m, 6H), 5.91 (dd, *J* = 7.6, 1.6 Hz, 2H).

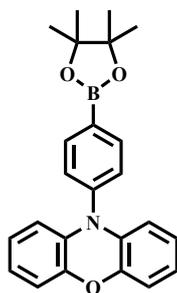
## 1-2



Under a nitrogen atmosphere, acridine (4 g, 19.2 mmol), 1-bromo-4-iodobenzene (6.1 g, 21.8 mmol), palladium acetate (0.1 g, 0.44 mmol), R-(+)-1,1'-binaphthyl-2,2'-bis(diphenylphosphine) (R-BNIAP) (0.03 g, 0.05 mmol), anhydrous cesium carbonate (14.2 g, 43.7 mmol) and 60 mL of toluene were added into a 250 mL Schlenk reaction tube and stirred at 110 °C overnight. After the reaction, it was cooled to room temperature. Then, the mixture was filtered and the organic phase was collected. The filtrate was concentrated and then purified by column chromatography using petroleum ether: dichloromethane (10: 1, v/v) as the eluent to give a white solid powder (5.1 g, 73%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.76 (d, *J* = 8.4 Hz, 2H), 7.45 (dd,

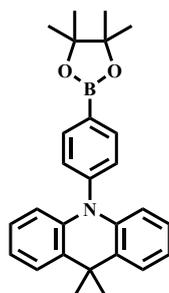
$J = 7.6, 1.6 \text{ Hz, 2H}$ ),  $7.25 - 7.20 \text{ (m, 2H)}$ ,  $7.06 - 6.87 \text{ (4, 1H)}$ ,  $6.25 \text{ (dd, } J = 7.6, 1.6 \text{ Hz, 2H)}$ ,  $1.68 \text{ (s, 6H)}$ .

## 2-1



Under a nitrogen atmosphere, 1-1 (2 g, 5.93 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.2 g, 8.63 mmol), Pd(dppf)Cl<sub>2</sub> (0.21 g, 0.28 mmol), and potassium acetate (2.27 g, 0.02 mmol) were heated to 110 °C for 16 h in the solvent of 1,4-dioxane (60 mL) under vigorous stirring. After the reaction, the mixture was concentrated and then purified by column chromatography, using petroleum ether: dichloromethane (2:1, v/v) as the eluent to obtain a white solid powder (1.8 g, 78%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, δ): 8.02 (d,  $J = 8.0 \text{ Hz, 2H}$ ), 7.35 (d,  $J = 8.0 \text{ Hz, 2H}$ ), 6.68 (dd,  $J = 7.8 \text{ Hz, 1.4 Hz, 2H}$ ), 6.63 (t,  $J = 7.6 \text{ Hz, 2H}$ ), 6.56 (td,  $J = 7.6 \text{ Hz, 1.5 Hz, 2H}$ ), 5.91 (d,  $J = 7.8 \text{ Hz, 2H}$ ), 1.38 (s, 12H)

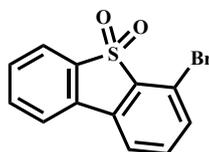
## 2-2



Under a nitrogen atmosphere, 1-2 (2 g, 5.51 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.2 g, 8.63 mmol), Pd(dppf)Cl<sub>2</sub> (0.21 g, 0.28 mmol), and potassium acetate (2.27 g, 0.02 mmol) were heated to 110 °C for 16 h in the solvent of 1,4-dioxane (60 mL) under vigorous stirring. After the reaction, the mixture was concentrated and then purified by column chromatography, using petroleum ether: dichloromethane (2:1, v/v) as the eluent to obtain a white solid powder (1.6 g, 71%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.07 (d,  $J =$

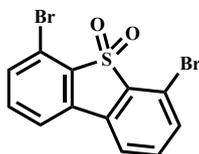
8.0 Hz, 2H), 7.53 – 7.40 (m, 2H), 7.39 – 7.30 (m, 2H), 6.97 – 6.89 (m, 4H), 6.25 (m, 2H), 1.69 (s, 6H), 1.40 (s, 12H).

#### 4-bromodibenzo[b,d]thiophene-5,5-dioxide



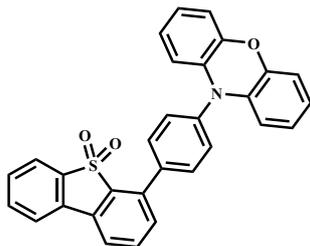
4-bromodibenzo[b,d]thiophene (2 g, 7.63 mmol), 50 mL acetic acid and 2 mL of H<sub>2</sub>O<sub>2</sub> were added dropwise and stirred at 60 °C for 6 h. After the reaction was completed, the mixture was cooled to room temperature and then evaporated to dryness. The final product was obtained as a white solid powder (1.85 g, 83%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.84 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 7.67 – 7.52 (m, 3H), 7.46 (t, *J* = 7.8 Hz, 1H).

#### 4,6-dibromodibenzo[b,d]thiophene-5,5-dioxide



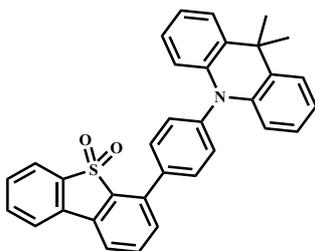
4,6-dibromodibenzo[b,d]thiophene (2 g, 5.88 mmol), 50 mL acetic acid and 2 mL of H<sub>2</sub>O<sub>2</sub> were added dropwise and stirred at 60 °C for 6 h. After the reaction was completed, the mixture was cooled to room temperature and then evaporated to dryness. The final product was obtained as a white solid powder (1.87 g, 86%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.72 (dd, *J* = 7.6, 0.8 Hz, 2H), 7.65 (dd, *J* = 8.0, 0.8 Hz, 2H), 7.49 (t, *J* = 7.6 Hz, 2H).

### PhSO-*o*-Oz



4-bromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.34 mmol), 2-1 (0.16 g, 0.42 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.02 mmol) were heated to 110 °C and stirred overnight under a nitrogen atmosphere in the mixture of 15 mL toluene and 15 mL aqueous potassium carbonate. After the reaction, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The organic phase was dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then purified by column chromatography, using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> (2:1, v/v) as the eluent. The final product was white solid (0.12 g, 74%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 7.98 (d, J = 8.4 Hz, 2H), 7.88 – 7.79 (m, 3H), 7.72 (t, J = 7.6 Hz, 1H), 7.67 (td, J = 7.6 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.48 (d, J = 8.4 Hz, 2H), 6.72 – 6.59 (m, 6H), 6.07 – 6.00 (m, 2H).

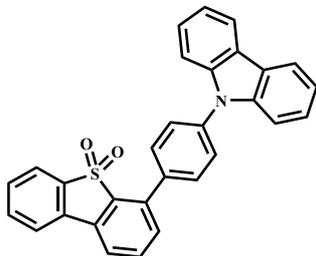
### PhSO-*o*-Ad



4-bromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.34 mmol), 2-2 (0.15 g, 0.37 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.02 mmol) were heated to 110 °C and stirred overnight under a nitrogen atmosphere in the mixture of 15 mL toluene and 15 mL aqueous potassium carbonate. After the reaction, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The organic phase was dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then purified by column chromatography, using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> (2:1, v/v) as the eluent. The final product was white solid (0.13 g, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.02 (d, J = 8.4 Hz, 2H), 7.88 – 7.82 (m, 3H), 7.81 – 7.77 (m,

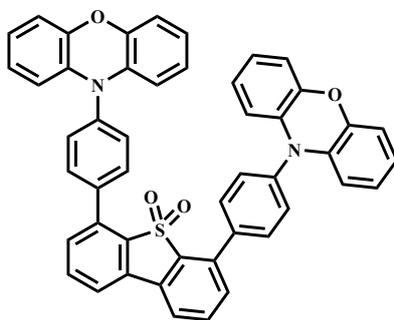
1H), 7.73 (ddd,  $J = 7.6, 4.0, 3.6$  Hz, 1H), 7.70 – 7.63 (m, 2H), 7.50 – 7.44 (m, 4H), 7.04 – 6.98 (m, 2H), 6.93 (td,  $J = 7.6, 1.2$  Hz, 2H), 6.39 (dd,  $J = 8.0, 1.2$  Hz, 2H), 1.79 (s, 6H).

### PhSO-*o*-Cz



4-bromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.34 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (0.11 g, 0.37 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.02 mmol) were heated to 110 °C and stirred overnight under a nitrogen atmosphere in the mixture of 15 mL toluene and 15 mL aqueous potassium carbonate. After the reaction, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The organic phase was dried over by anhydrous Na<sub>2</sub>SO<sub>4</sub> and then purified by column chromatography, using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> (2:1, v/v) as the eluent. The final product was white solid (0.11 g, 70%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>,  $\delta$ ): 8.17 (dt,  $J = 7.6, 1.2$  Hz, 2H), 8.06 – 8.00 (m, 2H), 7.86 (dt,  $J = 7.6, 6.8$  Hz, 3H), 7.78 – 7.72 (m, 3H), 7.68 (td,  $J = 7.6, 1.2$  Hz, 1H), 7.61 – 7.54 (m, 4H), 7.45 (ddd,  $J = 8.0, 7.6, 1.2$  Hz, 2H), 7.35 – 7.29 (m, 2H).

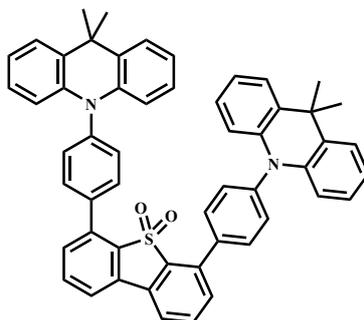
### PhSO-*o*-2Oz



4,6-dibromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.27 mmol), 2-1 (0.23 g, 0.60 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.02 mmol), and 15 mL of toluene and 15 mL of aqueous potassium carbonate were added into a 100 mL Schlenk reaction tube under a nitrogen atmosphere with stirring at 110 °C overnight. After the reaction, the

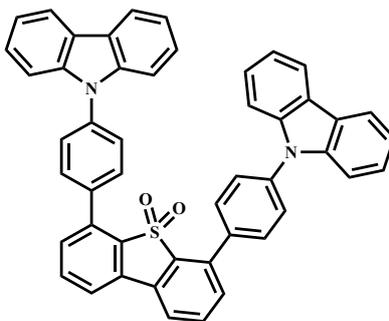
mixture was extracted with  $\text{CH}_2\text{Cl}_2$  three times and the organic phase was dried over by anhydrous  $\text{Na}_2\text{SO}_4$  and then purified by column chromatography, using petroleum ether:  $\text{CH}_2\text{Cl}_2$  (1:1, v/v) as the eluent to obtain a white solid powder (0.12 g, 62%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 7.94 (t,  $J = 7.6$  Hz, 6H), 7.76 (t,  $J = 7.6$  Hz, 2H), 7.55 (dd,  $J = 7.6, 0.4$  Hz, 2H), 7.52 – 7.44 (m, 4H), 6.73 – 6.57 (m, 12H), 6.04 (dd,  $J = 7.6, 1.6$  Hz, 4H).

### PhSO-*o*-2Ad



4,6-dibromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.27 mmol), 2-2 (0.25 g, 0.60 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (0.02 g, 0.02 mmol), and 15 mL of toluene and 15 mL of aqueous potassium carbonate were added into a 100 mL Schlenk reaction tube under a nitrogen atmosphere with stirring at 110 °C overnight. After the reaction, the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  three times and the organic phase was dried over by anhydrous  $\text{Na}_2\text{SO}_4$  and then purified by column chromatography, using petroleum ether:  $\text{CH}_2\text{Cl}_2$  (1:1, v/v) as the eluent to obtain a white solid powder (0.12 g, 59%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ,  $\delta$ ): 8.00 (d,  $J = 8.4$  Hz, 4H), 7.94 (d,  $J = 7.6$  Hz, 2H), 7.77 (t,  $J = 7.6$  Hz, 2H), 7.61 (d,  $J = 7.6$  Hz, 2H), 7.46 (t,  $J = 7.6$  Hz, 8H), 7.00 (td,  $J = 7.6, 1.2$  Hz, 4H), 6.93 (td,  $J = 7.6, 1.2$  Hz, 4H), 6.39 (dd,  $J = 8.0$  Hz, 4H), 1.68 (s, 12H)

## PhSO-*o*-2Cz



4,6-dibromodibenzo[b,d]thiophene-5,5-dioxide (0.1 g, 0.27 mmol), (4-(9H-carbazol-9-yl)phenyl)boronic acid (0.17 g, 0.60 mmol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.02 g, 0.02 mmol) were heated to 110 °C and stirred overnight under a nitrogen atmosphere in the mixture of 15 mL toluene and 15 mL aqueous potassium carbonate. After the reaction, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The organic phase was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and then purified by column chromatography, using petroleum ether: CH<sub>2</sub>Cl<sub>2</sub> (1:1, v/v) as the eluent. The final product was white solid (0.11 g, 63%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ): 8.14 (d, J = 7.6 Hz, 4H), 7.98 (d, J = 7.6 Hz, 4H), 7.93 (d, J = 7.6 Hz, 2H), 7.80 – 7.74 (m, 2H), 7.71 (d, J = 7.6 Hz, 4H), 7.56 (dd, J = 13.6 Hz, 6H), 7.41 (t, J = 7.6 Hz, 4H), 7.30 (d, J = 7.6 Hz, 2H), 7.30 (d, J = 6.8 Hz, 2H).

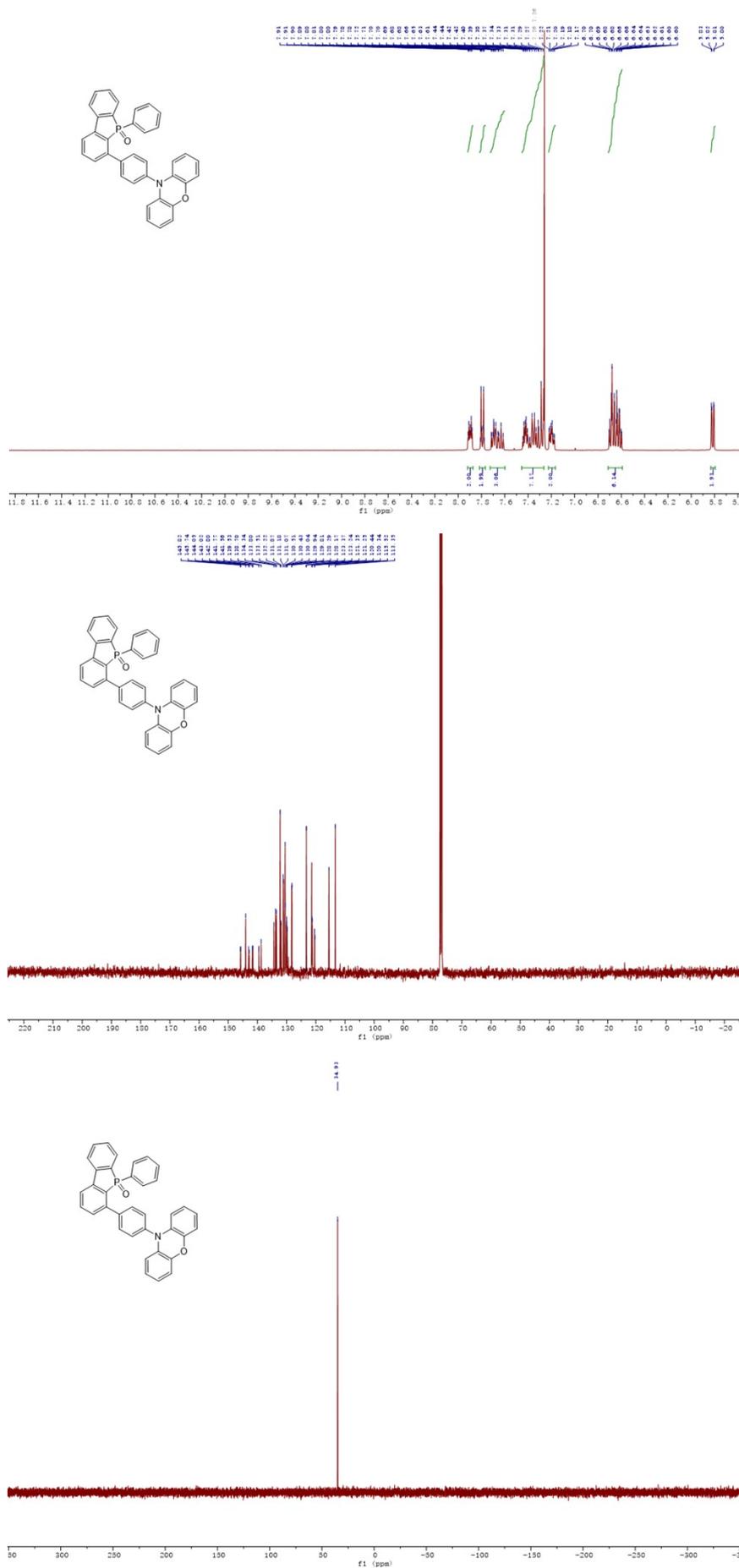
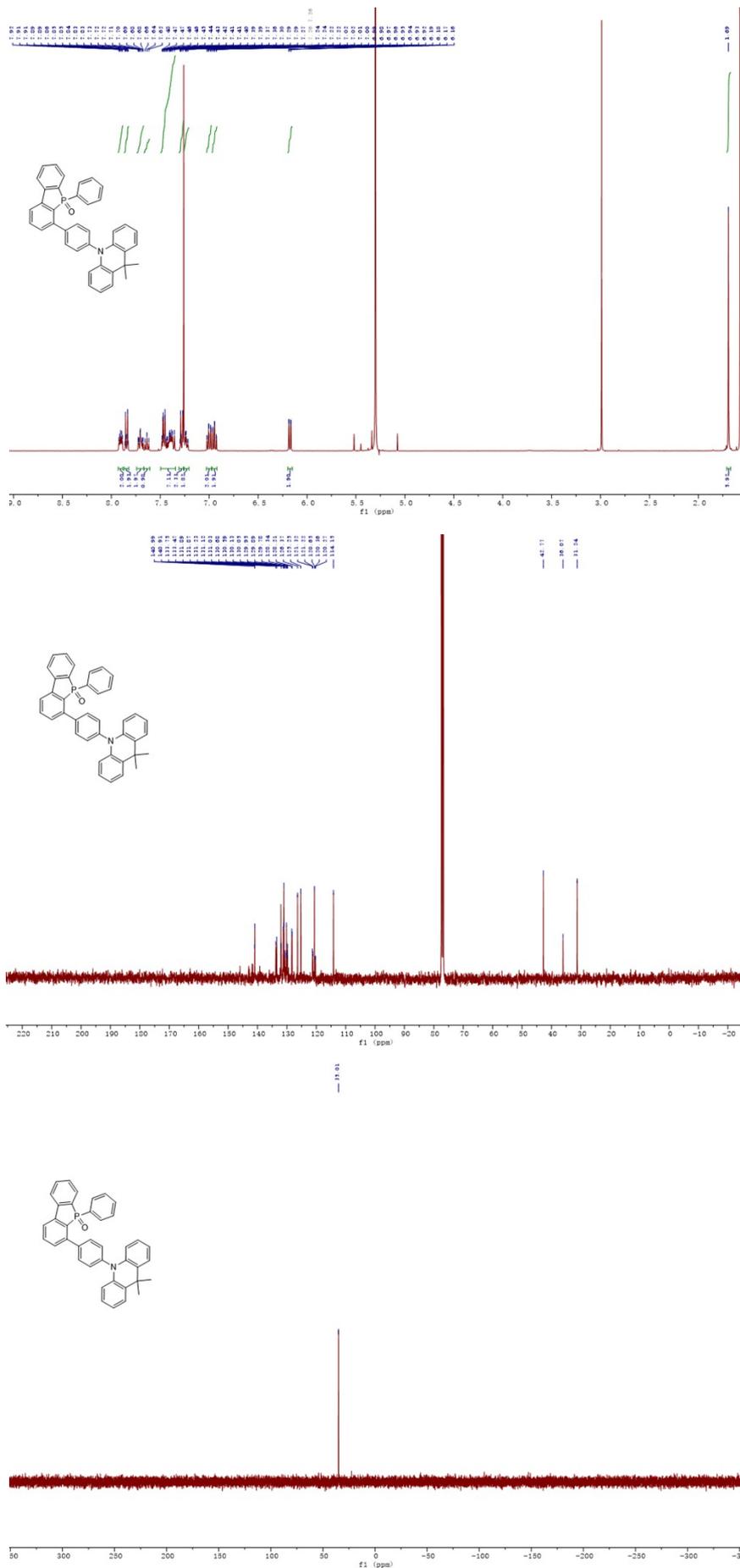
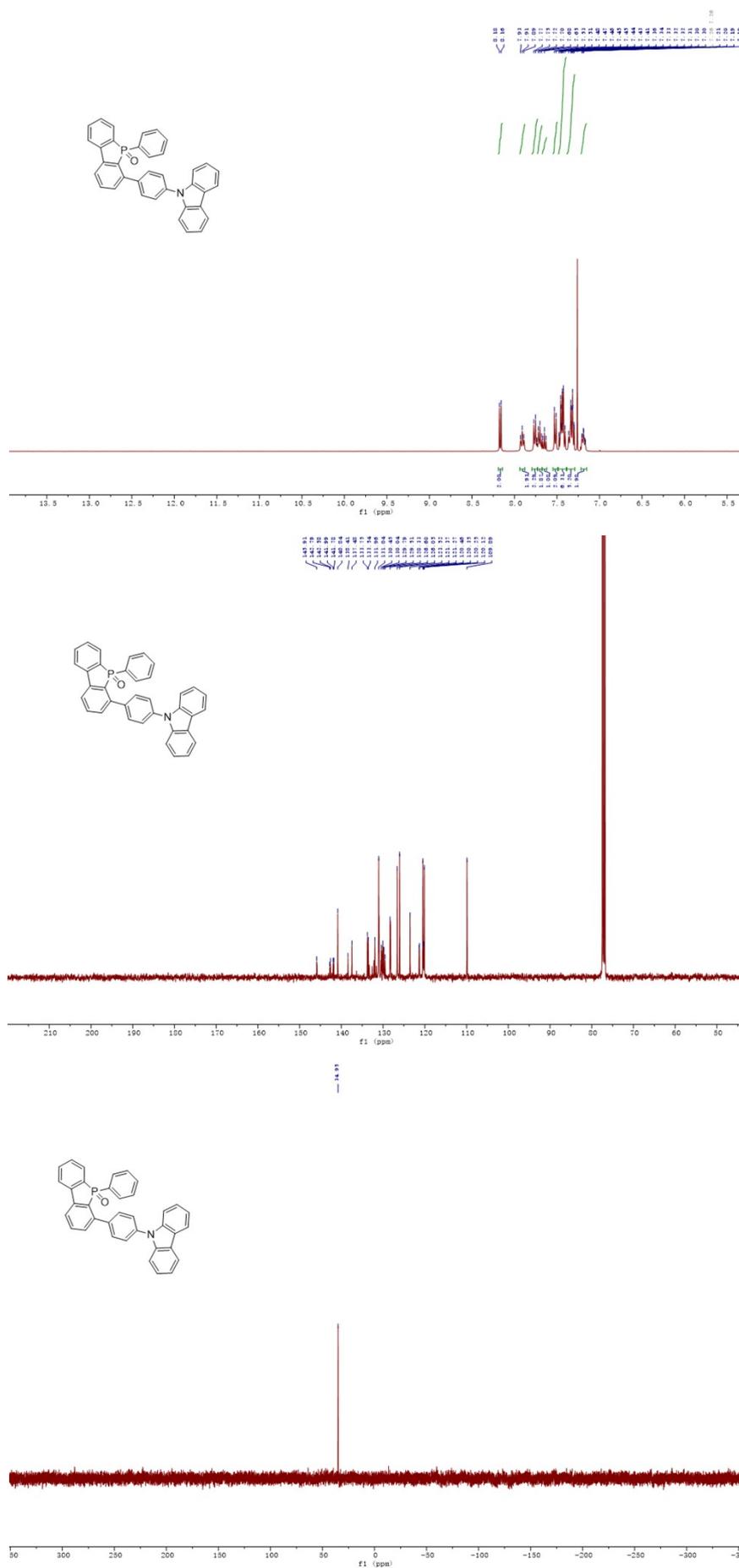


Figure S1. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectrum of FIOP-*o*-Oz.

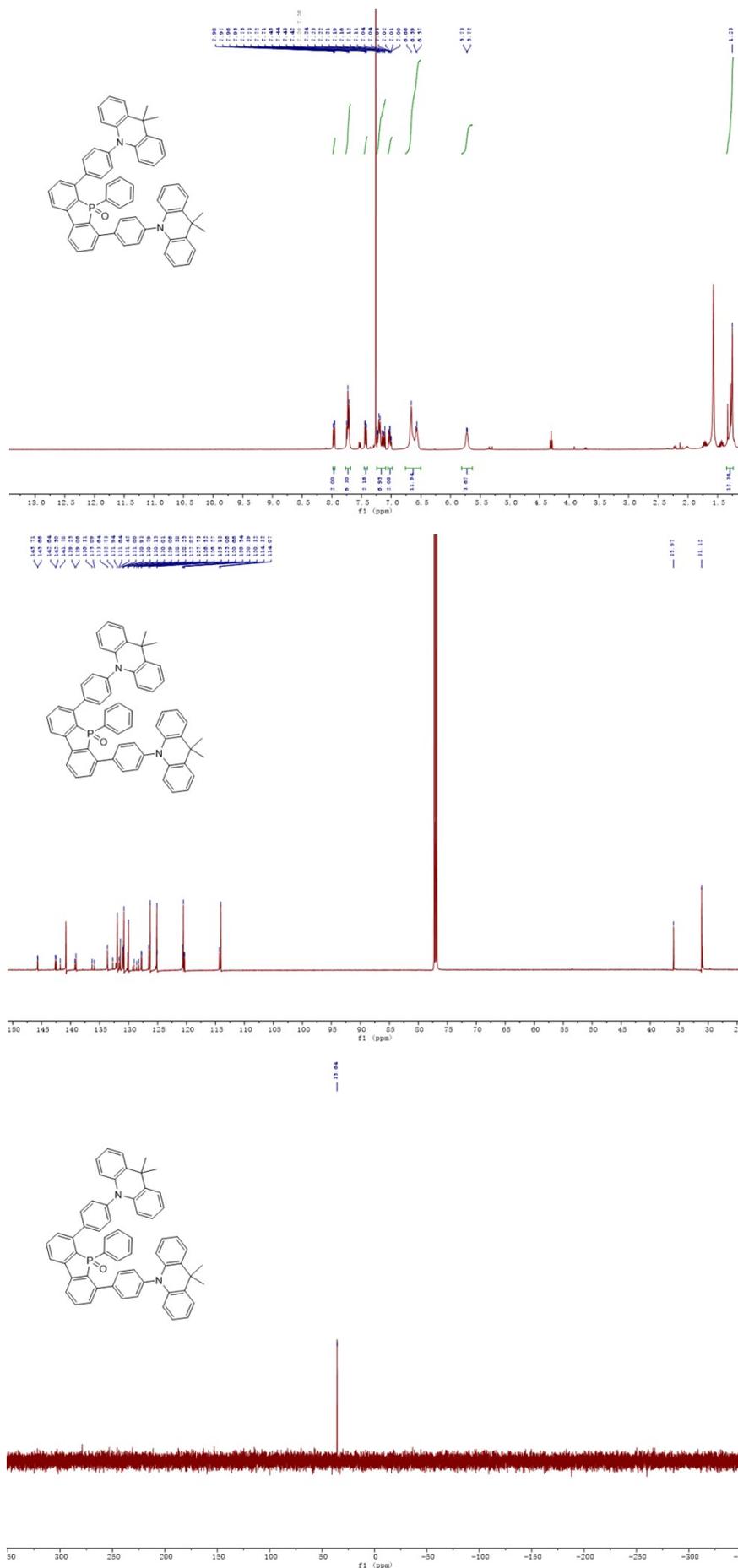


**Figure S2.** <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectrum of FIOP-*o*-Ad.

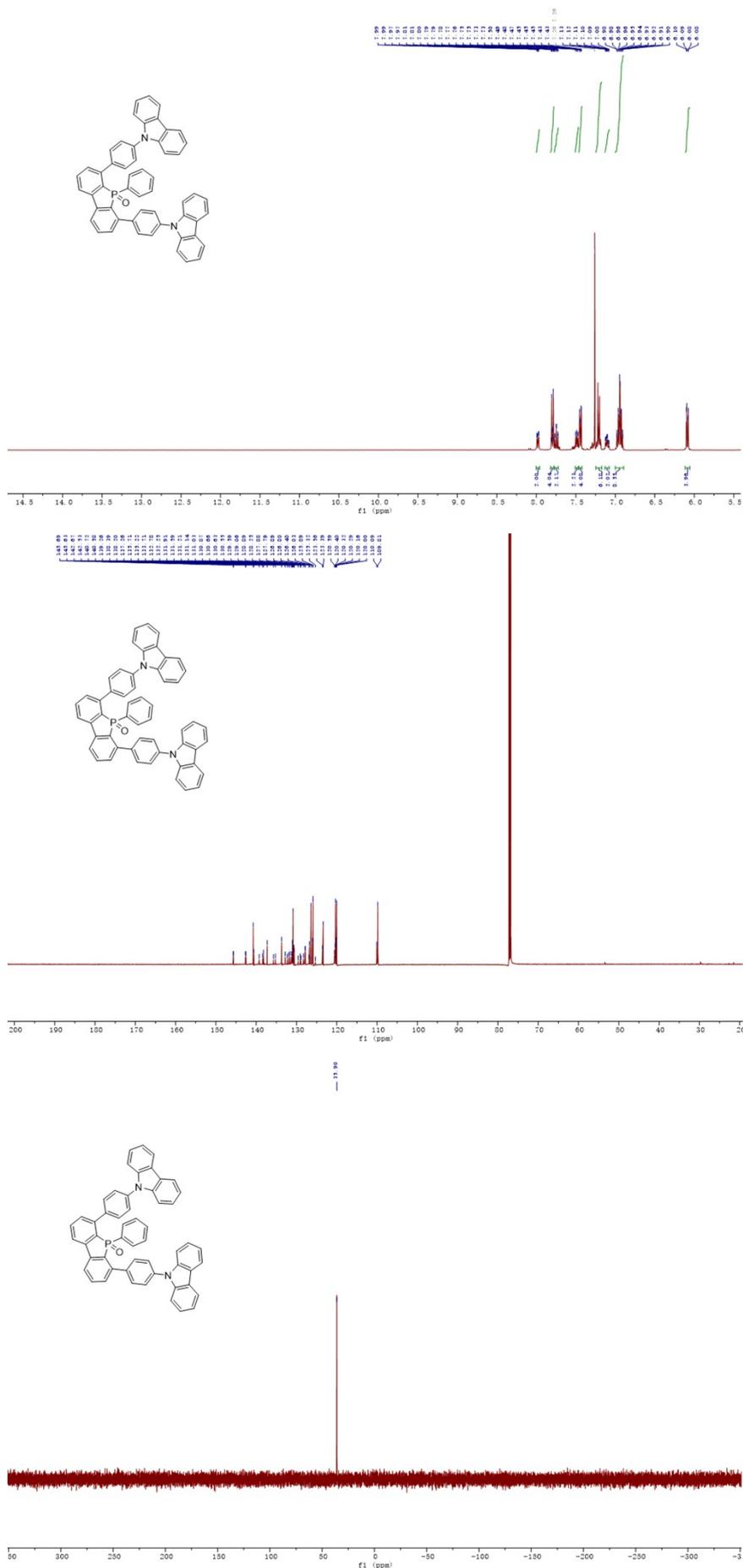


**Figure S3.** <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectrum of FIOP-*o*-Cz.

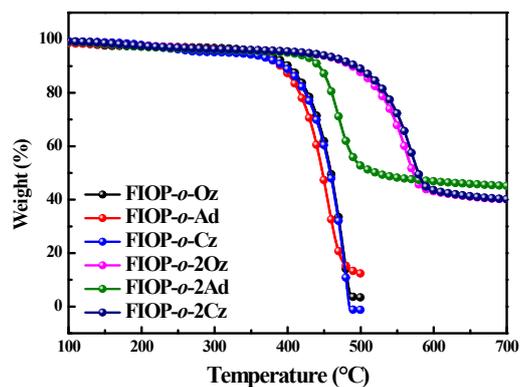




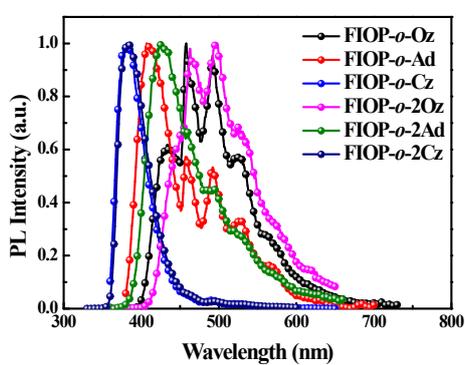
**Figure S5.** <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectrum of FIOP-*o*-2Ad.



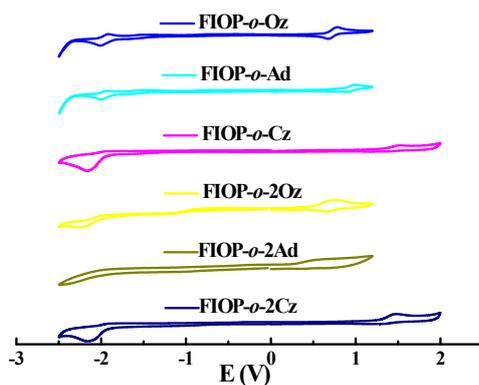
**Figure S6.** <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>31</sup>P NMR spectrum of FIOP-*o*-2Cz.



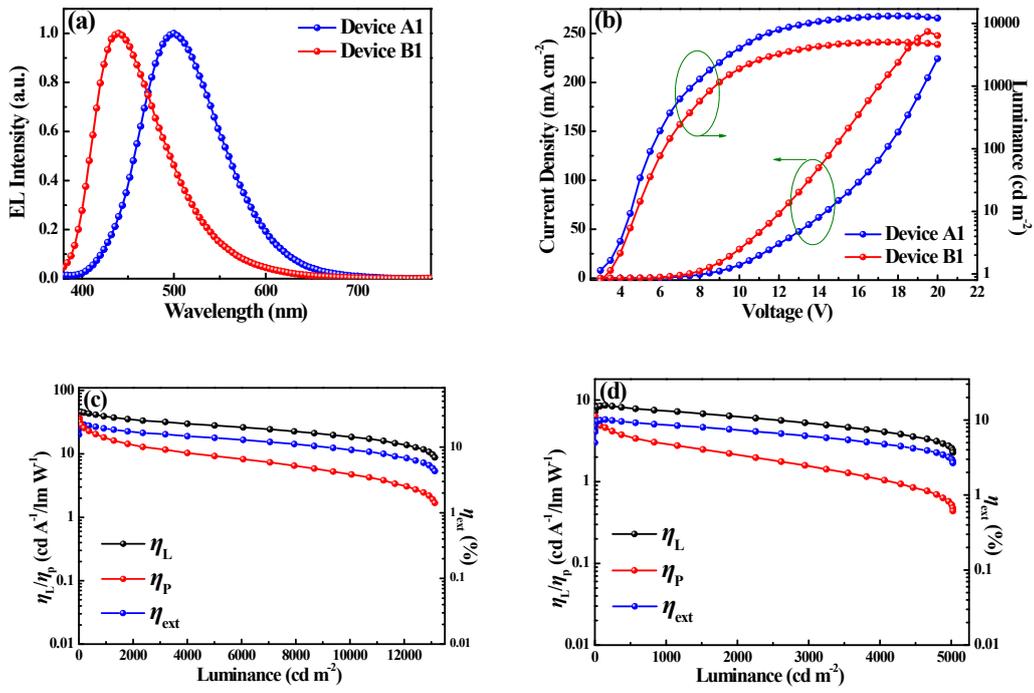
**Figure S7.** TGA curves of PhFIOP-based emitters.



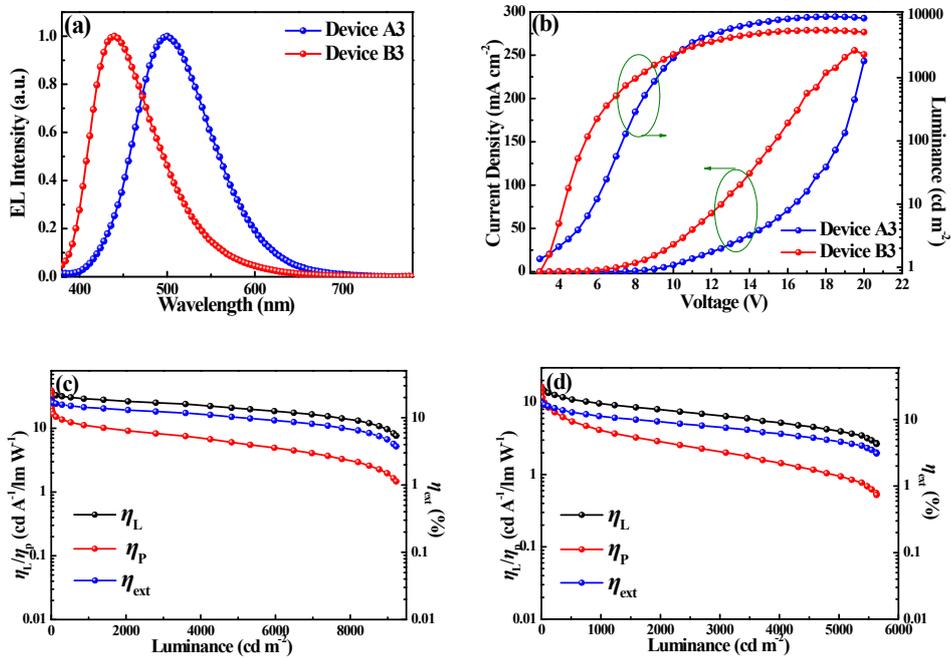
**Figure S8.** PL spectra of PhFIOP-based emitters at 77K.



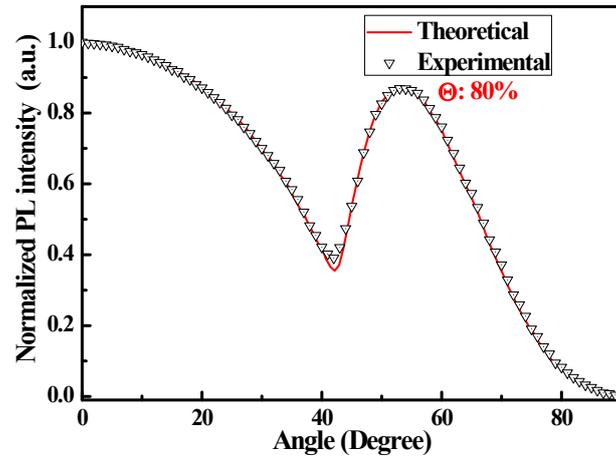
**Figure S9.** CV curves of these PhFIOP-based emitters tested in  $\text{CH}_3\text{CN}$  at room temperature



**Figure S10** (a) EL spectra of Device **A1** and Device **B1** (b) Current density-voltage-luminance ( $J$ - $V$ - $L$ ) characteristics for the optimized devices. Relationship between EL efficiencies and luminance of (c) Device **A1**, and (d) Device **B1**.



**Figure S11.** (a) EL spectra of Device **A3** and Device **B3** (b) Current density-voltage-luminance ( $J$ - $V$ - $L$ ) characteristics for the optimized devices. Relationship between EL efficiencies and luminance of (c) Device **A3**, and (d) Device **B3**.



**Figure S12.** Measured (symbols) *p*-polarized PL intensity versus emission angle curves for **FIOP-*o*-2Oz**.