

Supporting information

## **Pioneering Research on Blue “Hot Excitons” Polymers and Their Application in Solution-Processed Organic Light-emitting Diodes**

*Jiasen Zhang, Wei Li,\* Lingling Lyu, Qiang Wei,\* Yuanyuan Meng, Deli Li, Zhichuan Wang, Ming Luo, Songyu Du, Xuxu, Xiaoli Zhang, Guohua Xie\*, Ziyi Ge\**

J. S. Zhang, Dr. W. Li, Dr. Q. Wei, Y. Y. Meng, Z. C. Wang, M. Luo, S. Y. Du, Prof. Z. Ge

Zhejiang Provincial Engineering Research Center of Energy Optoelectronic Materials and Devices, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo, 315201, PR China

Center of Materials Science and Optoelectronics Engineering, University of Chinese Academy of Sciences, Beijing, 100049, PR China

E-mail: liwei1987@nimte.ac.cn; weiqiang@nimte.ac.cn; geziyi@nimte.ac.cn

X. Xu, L. Lyu

Ningbo Dayang Technology Co.,Ltd. Ningbo 315000, P. R. China

Dr. D. L. Li,

State Key Laboratory of Luminescent Materials and Devices and Institute of Polymer Optoelectronic Materials and Devices, South China University of Technology, Wushan Road 381, Tianhe District, Guangzhou 510640, Guangdong Province (P. R. China)

Z. C. Wang, Prof. X. L. Zhang,

School of Materials Science and Engineering, Zhengzhou University, Zhengzhou 450001, People's Republic of China

Prof. G.H.Xie

Sauvage Center for Molecular Sciences, Hubei Key Lab on Organic and Polymeric Optoelectronic Materials, Department of Chemistry, Wuhan University, Wuhan 430072, P. R. China.

## Table of Contents:

<b>1. General Information.....</b>	<b>S3</b>
<b>1.1 Computational Methods.....</b>	<b>S3</b>
<b>1.2 Device Fabrication and Characterization .....</b>	<b>S3</b>
<b>2. Synthesis .....</b>	<b>S5</b>
<b>3. Thermal Properties.....</b>	<b>S13</b>
<b>4. Computation.....</b>	<b>S13</b>
<b>5. Photo-Physical Properties .....</b>	<b>S18</b>
<b>6. Energy Level .....</b>	<b>S19</b>
<b>7. Parameters of Photo-Physical Properties .....</b>	<b>S19</b>
<b>8. EL performances .....</b>	<b>S20</b>
<b>9 Reference .....</b>	<b>S21</b>

## 1. General Information

The chemical structure of compounds was identified by  $^1\text{H}$  NMR, (Bruker Avance DPX-300). Molecular weight is measured by time-of-flight mass spectrometry (LC-Q-TOF). The polymer molecular weight is measured by Gel Permeation Chromatography, GPC (HLC8320). The energy levels were measured by Cyclic voltammetry (CV) via Shanghai Chenghua electrochemical workstation. Pt was used as counter electrode, Ag/AgCl as the reference electrode, and electrolyte solution was prepared by a 0.1M tetrabutylammonium hexafluorophosphate (Bu4NPF6) acetonitrile solution. Thermogravimetric Analysis was analyzed by Thermogravimetric/Differential Thermal Comprehensive Thermal Analyzer. The UV-vis absorption spectra were recorded on Perkin-Elmer Lambda 950 spectrophotometer. The fluorescence spectrum and phosphorescence spectrum were measured by Fluorescence spectrometer (FL3-111). The transient PL decays in microsecond ranges at different temperatures were measured by Fluorescence spectrometer (FLS1000).

### 1.1 Computational Methods

All the simulations were performed using the Gaussian 09\_B01 program package<sup>[1]</sup> For all the investigated molecules, the ground state ( $S_0$ ) geometries were optimized using the M06-2X functional with 6-31G\* basis set in vacuum for an initial guess. All the excited state was optimized by TD-DFT/BMK/6-31G\* in toluene with polarizable continuum model (PCM).<sup>[2]</sup>

### 1.2 Device Fabrication and Characterization

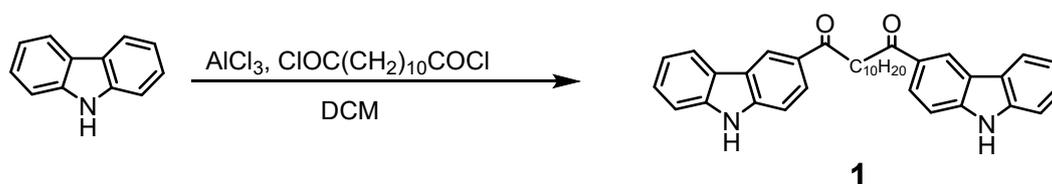
Device fabricate: solution-processed OLED was prepared in a traditional sandwich structure: ITO/ poly(3,4-ethylenedioxythiophene):poly-(styrene-sulfonic acid) (PEDOT:PSS) (30 nm)/ Emitter layer (30 nm)/ (diphenylphosphino)phenyl ether oxide (DPEPO) (10 nm) / 1,3,5-tri(m-pyrid-3-yl-phenyl)benzene (TmPyPB) (50 nm)/ 8-

hydroxyquinolinato lithium (LiF) (1 nm)/ Al (100 nm). First, chlorobenzene solution containing host material and guest material with different weight ratios and concentrations was stirred for several hours in a nitrogen-filled glovebox. Where, the concentration of host and guest materials is all 10 mg/mL in chlorobenzene solution. After being cleaned with deionized water, acetone, and isopropanol, the ITO glass was treated with the UV–ozone for 30 min. The PEDOT:PSS solution was spin-coated at 3000 rpm onto the ITO substrates for 1 min. While the PEDOT:PSS film was heated at 130 °C in air. Then, the emitter was spin-coated on the PEDOT:PSS layer. The devices were transferred to the evaporation tank to deposit DPEPO, TmPyPB, Liq and Al. Deposition rates are 1 – 2 Å s<sup>-1</sup> for organic materials and 2-5 Å s<sup>-1</sup> for aluminum, respectively. Electroluminescence (EL) spectra were recorded by Photo Research PR745. The current density and luminance versus driving voltage characteristics EL spectra were measured by Keithley 2400 and Konica Minolta CS-2000 chromameter. EQEs were automatically calculated from the current density, luminance, and EL spectra, assuming a Lambertian distribution.

## 2. Synthesis

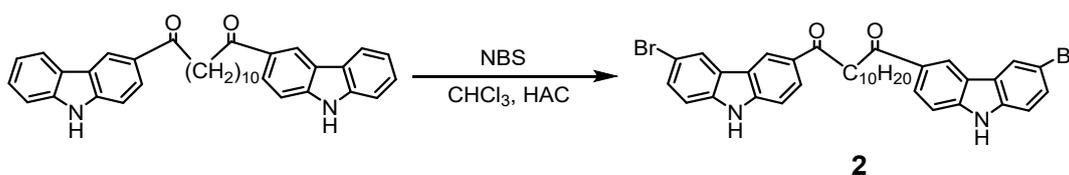
All chemical raw materials were purchased without further purification. Carbazole (CAS No. : 86-74-8), 11-chlorosyldodec-11-enoyl chloride (CAS No.: 112-16-3), 4,4'-Difluorobenzophenone (CAS No. : 345-92-6), 4-Bromophenol (CAS No.: 106-41-2), 1,6-Dibromohexane (CAS No. : 629-03-8), bis(pinacolato)diboron (CAS No. : 73183-34-3), 3-Bromo-9H-carbazole (CAS No. : 1592-95-6), Phenylboronic acid pinacol ester (CAS No. : 24388-23-6), NBS, bis(1,5-cyclooctadiene)nickel (0) (Ni(COD)<sub>2</sub>), 1,5-Cyclooctadiene (COD), 2,2'-bipyridyl (BPY), AlCl<sub>3</sub>, CsCO<sub>3</sub> and dry reagent were all supplied by Alpha –Chemicals.

### The detailed synthetic procedures:



**Scheme S1.** The synthetic route of compound 1.

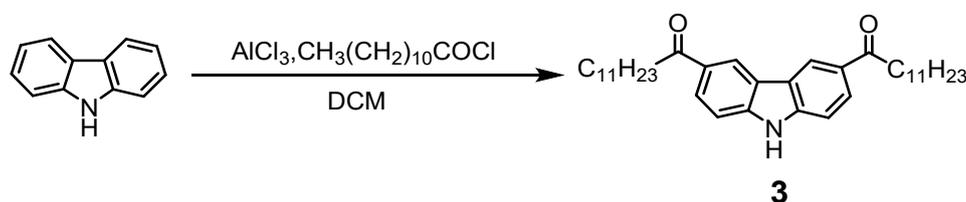
**Synthesis of 1,12-di(9H-carbazol-3-yl)dodecane-1,12-dione (1):** Carbazole (12.54 g, 9.75 mmol), 11-chlorosyldodec-11-enoyl chloride (5.12 g, 18.75 mmol), AlCl<sub>3</sub> (7.50 g, 56.25 mmol) and 250 mL dichloromethane (DCM) were added into a 500 mL flask. The mixture was stirred for 24 hours at 0°C, and then poured into 300mL water, extracted by 100 mL dichloromethane (DCM) for three times. The crude product was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 3:1, v/v) to give **1** as a white solid (11.05g, yield 65%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>-d) δ 8.74 (s, 2H), 8.38 – 7.88 (m, 8H), 7.42 (dt, *J* = 19.8, 8.7 Hz, 6H), 1.57 (s, 20H). TOF-MS (formula<sup>+</sup>): 529.2866, Calculated: 528.6960.



**Scheme S2.** The synthetic route of compound 2.

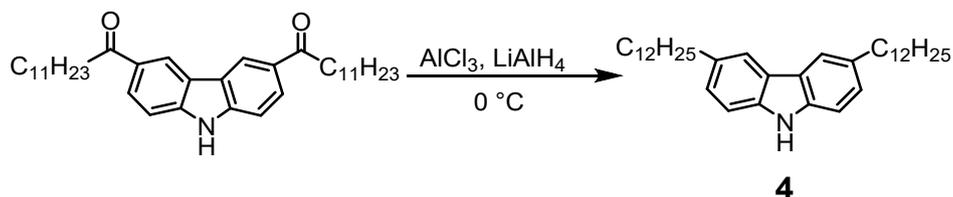
**Synthesis of 1,12-bis(6-bromo-9H-carbazol-3-yl)dodecane-1,12-dione (2):**

Compound **1** (3.00 g, 6.00 mmol), 250 mL mixed solvent of glacial acetic acid and  $\text{CHCl}_3$  (glacial acetic acid:  $\text{CHCl}_3 = 1:1$ , v/v) were added into 500 mL three-necked round bottom flask. The mixture was stirred at 0 °C for 20 min, later NBS (N-bromosuccinimide) (2.60 g, 14.30 mmol) was added into the flask by portions to reaction for 12 h under dark. After that, the mixture was poured into 300 mL water and extracted by 100 mL DCM for three times. The crude product was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 2:1, v/v) to get 2.55g of white powder in yield of 85%.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.14 (d,  $J = 1.7$  Hz, 4H), 8.11 (s, 2H), 7.52 (dd,  $J = 8.6, 1.9$  Hz, 4H), 7.32 (d,  $J = 8.6$  Hz, 4H), 1.53 (s, 10H), 1.25 (s, 10H). TOF-MS (Formula<sup>+</sup>): 687.1055, Calculated: 686.4880.



**Scheme S3.** The synthetic routes of compound **3**.

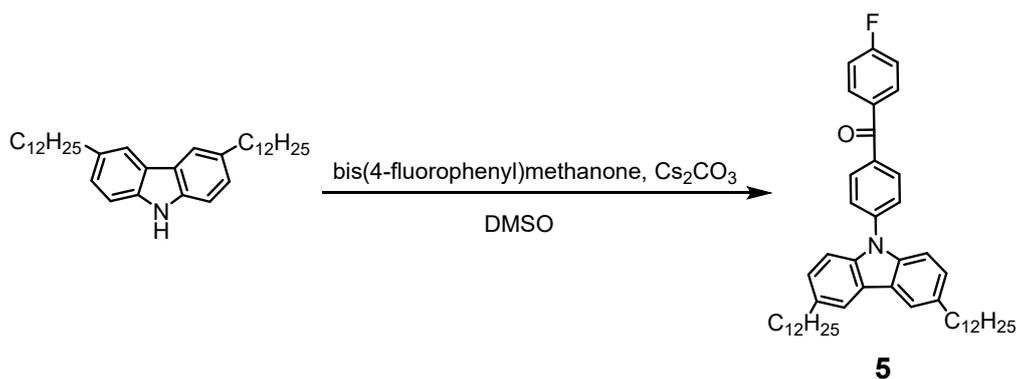
**Synthesis of 1,1'-(9H-carbazole-3,6-diyl)bis(dodecan-1-one) (3):** The synthesis of compound **3** was similar to that of compound **1** generated the pure **3** as a white powder in yield of 65 %.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.87 (s, 1H), 8.79 (s, 2H), 8.14 (dd,  $J = 8.5, 1.1$  Hz, 2H), 7.49 (d,  $J = 8.5$  Hz, 2H), 3.11 (t,  $J = 7.4$  Hz, 4H), 1.91 – 1.73 (m, 4H), 1.53 – 1.10 (m, 32H), 0.91 – 0.80 (m, 6H).  $^{13}\text{C NMR}$  (151 MHz,  $\text{CDCl}_3$ )  $\delta$  199.97, 142.93, 130.22, 127.10, 123.37, 121.67, 110.76, 38.67, 31.93, 29.67, 29.65, 29.57, 29.54, 29.36, 24.84, 22.70, 14.13. TOF-MS (Formula<sup>+</sup>): 532.4158, Calculated: 531.8250



**Scheme S4.** The synthetic route of compound **4**.

**Synthesis of 3,6-didodecyl-9H-carbazole (4):** Compound **3** (5.00 g, 9.40 mmol) and 100 mL tetrahydrofuran (THF) was added into 250 mL constant pressure dropping

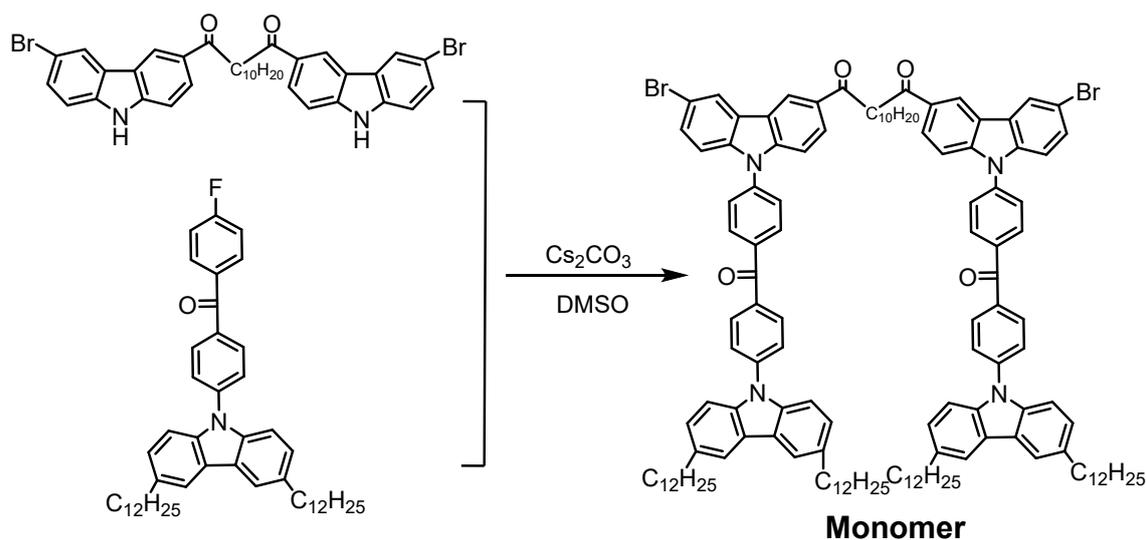
funnel, then AlCl<sub>3</sub> (2.51 g, 18.81 mmol) and 100 mL THF were added into 500 mL three-necked round bottom flask. The mixture was stirred at 0 °C. After that, LiAlH<sub>4</sub> (2.51 g, 18.81 mmol) was dropped into the mixture slowly. Finally, the compound 3 was also dropped into the mixture to reaction for 12 h. After that, the mixture was poured into 200 mL water and extracted by 150 mL DCM for three time. The crude product was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 8:1, v/v) to give a pure-white powder (3.60 g, 76%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 – 7.74 (m, 3H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.22 (dd, *J* = 8.2, 1.4 Hz, 2H), 2.88 – 2.54 (m, 4H), 1.80 – 1.58 (m, 4H), 1.49 – 1.14 (m, 36H), 0.88 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>) δ 138.23, 133.84, 126.40, 123.42, 119.53, 110.18, 36.08, 32.37, 31.94, 29.71, 29.66, 29.62, 29.40, 29.37, 22.70, 14.13. TOF-MS (Formula<sup>+</sup>):504.4575, Calculated: 503.8590.



**Scheme S5.** The synthetic route of compound 5.

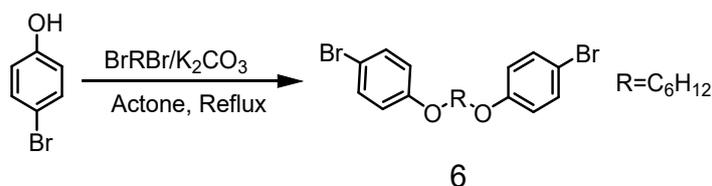
**Synthesis of (4-(3,6-didodecyl-9H-carbazol-9-yl)phenyl)(4-fluorophenyl)methanone (5):** Compound 1 (9.00 g, 17.80 mmol), bis(4-fluorophenyl)methanone (4.68 g, 21.40 mmol), cesium carbonate (7.7 g, 23.4 mmol) and 250 mL dry dimethylsulfoxide (DMSO) were added into a 500 mL three-necked round bottom flask under nitrogen. The mixture was stirred at 100°C for 24 hours and then poured into 300 mL water, extracted by 100 mL DCM for three times. The crude product was purified by column chromatography on silica gel (petroleum ether : dichloromethane = 3:1, v/v) to give a pure-yellow powder (7.00 g, 77%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.4 Hz, 2H), 7.94 (dd, *J* = 9.4, 6.3 Hz, 4H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.47 – 7.41 (m, 2H), 7.23 (dd, *J* = 10.1, 7.0 Hz, 4H), 2.80 (t, *J* = 7.7 Hz, 4H), 1.80 – 1.65 (m, 4H), 1.31 (d, *J* =

39.7 Hz, 36H), 0.88 (t,  $J = 6.7$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  194.14, 166.31, 164.62, 142.31, 138.78, 135.29, 133.78, 133.76, 132.66, 132.59, 132.52, 132.46, 131.68, 126.77, 125.94, 125.88, 124.01, 119.83, 119.73, 115.69, 115.63, 115.54, 115.48, 109.54, 109.44, 36.00, 32.30, 31.93, 29.70, 29.66, 29.61, 29.52, 29.38, 29.37, 29.32, 22.70, 22.67, 14.13. TOF-MS (Formula<sup>+</sup>): 702.5077, Calculated: 702.0554.



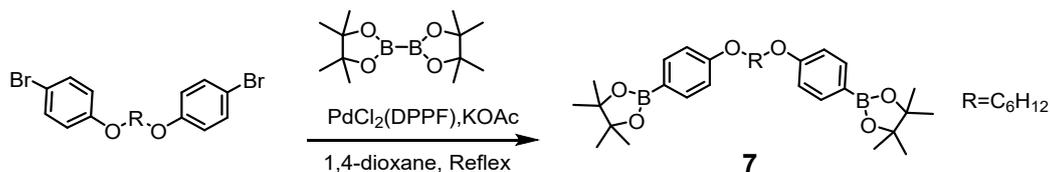
**Scheme S6.** The synthetic route of **Monomer**.

**Synthesis of 1,12-bis(6-bromo-9-(4-(4-(3,6-didodecyl-9H-carbazol-9-yl)benzoyl)phenyl)-9H-carbazol-3-yl)dodecane-1,12-dione (Monomer):** Following the same procedure for synthesis of **5** generated the pure **Monomer** as a yellow powder. Yield (67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.78 (s, 1H), 8.42 – 8.37 (m, 2H), 8.16 (dd,  $J = 15.3, 5.4$  Hz, 9H), 7.95 (s, 4H), 7.85 – 7.75 (m, 8H), 7.63 – 7.55 (m, 4H), 7.54 – 7.44 (m, 7H), 7.29 (d,  $J = 8.4$  Hz, 5H), 3.12 (t,  $J = 7.4$  Hz, 4H), 2.85 – 2.77 (m, 8H), 1.84 – 1.69 (m, 12H), 1.38 (s, 24H), 1.26 (d,  $J = 14.8$  Hz, 60H), 0.88 (t,  $J = 6.8$  Hz, 12H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ )  $\delta$  199.64, 143.09, 142.70, 140.39, 139.78, 138.72, 137.04, 135.41, 134.82, 131.93, 130.58, 129.68, 127.32, 126.81, 126.54, 125.97, 125.63, 124.07, 123.55, 122.52, 121.72, 119.78, 114.33, 111.69, 109.80, 109.45, 38.65, 36.00, 32.30, 31.93, 29.79, 29.27, 24.76, 22.69, 14.13. TOF-MS (Formula<sup>+</sup>): 2051.0502, Calculated: 2050.5860.



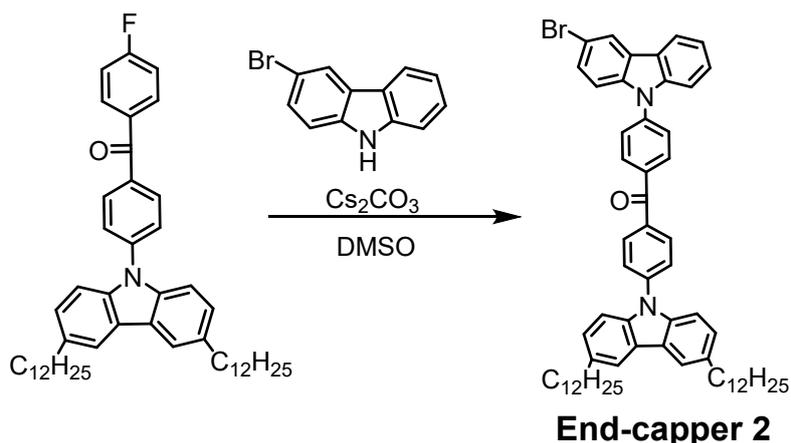
**Scheme S7.** The synthetic route of compound **6**.

**Synthesis of 1,6-bis(4-bromophenoxy)hexane (6):** 4-bromophenol (10.00 g, 57.80 mmol) BrC<sub>6</sub>H<sub>12</sub>Br (6.35g, 26.01mmol), K<sub>2</sub>CO<sub>3</sub> (30.00g, 47.93 mmol) and Acetone (300 mL) were added into a 500 mL flask. After refluxing overnight, the mixture was filtrated, and the filtrate was evaporated to get a white solid. The solid was washed with water and finally recrystallized in ethanol to give pure **6** as white crystals. Yield (9.20 g, 92 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.45 – 7.30 (m, 4H), 6.84 – 6.63 (m, 4H), 3.93 (t, *J* = 6.4 Hz, 4H), 1.99 – 1.68 (m, 4H), 1.61 – 1.36 (m, 4H). <sup>13</sup>C NMR (151 MHz, D<sub>2</sub>O) δ 155.67, 129.70, 113.78, 110.12, 65.64, 26.59, 23.30. TOF-MS (formula<sup>+</sup>):427.9757, Calculated: 425.9830.



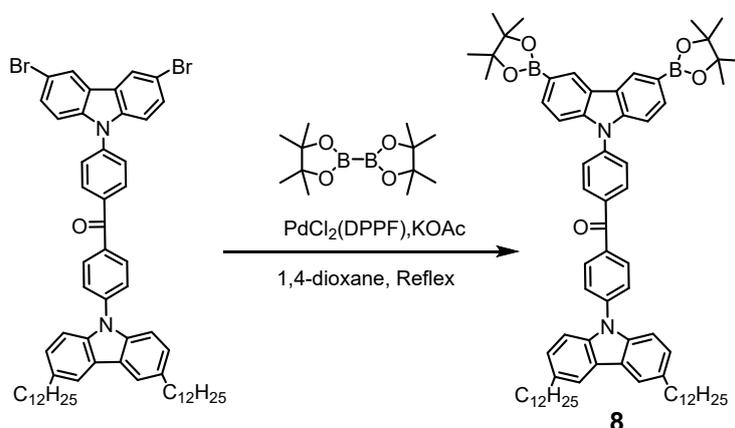
**Scheme S8.** The synthetic routes of compound **7**.

**Synthesis of 1,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenoxy)hexane (7):** Compound **6** (1.00 g, 2.34 mmol), bis(pinacolato)diboron, (3.55 g, 14.01 mmol), KOAc (1.48 g, 7.01 mmol), Pd(DPPF)Cl<sub>2</sub> (0.17 g, 0.23 mmol) and 100 mL 1,4-dioxane were added into 250 mL flask. The mixture was stirred at 100°C for 24h and then poured into 300mL water, extracted by 100 mL DCM for three time. The crude product was purified by column chromatography on silica gel (petroleum ether: dichloromethane = 5:1, v/v) to give pure **7** as white crystals. Yield (7.15 g, 58.6 %). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.5 Hz, 4H), 6.88 (d, *J* = 8.5 Hz, 4H), 3.99 (t, *J* = 6.5 Hz, 4H), 1.95 – 1.69 (m, 4H), 1.43 (d, *J* = 81.5 Hz, 28H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>-*d*) δ 161.68, 136.49, 113.85, 83.51, 67.59, 29.15, 25.85, 24.86. TOF-MS (formula<sup>+</sup>): 523.3350, Calculated: 522.3324.



**Scheme S9.** The synthetic routes of **End-capper 2**.

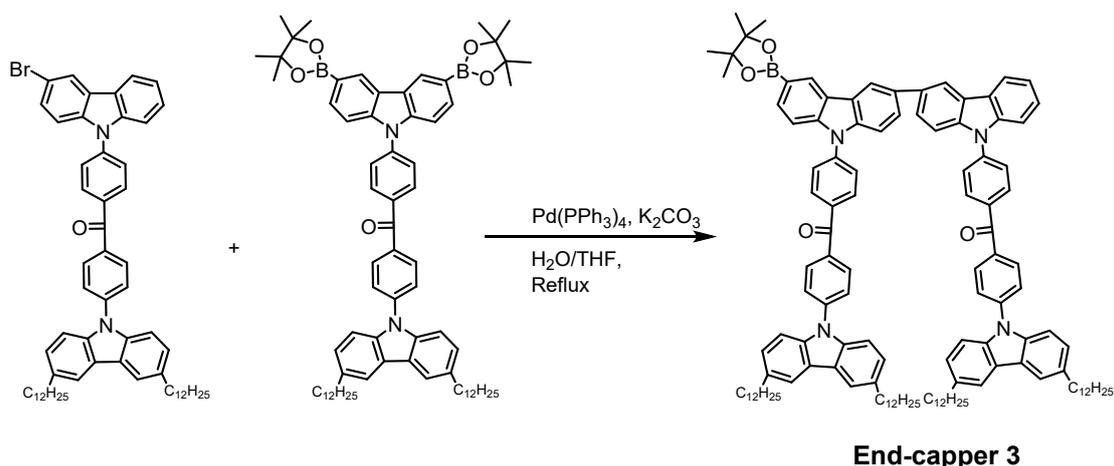
**Synthesis of (4-(3-bromo-9H-carbazol-9-yl)phenyl)(4-(3,6-didodecyl-9H-carbazol-9-yl)phenyl)methanone (End-capper 2):** Following the same procedure for synthesis of **Monomer** generated the pure **End-capper 2** as a yellow powder. Yield (67%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.28 (d,  $J = 1.8$  Hz, 1H), 8.15 (ddd,  $J = 15.8, 10.5, 4.8$  Hz, 5H), 7.93 (d,  $J = 1.0$  Hz, 2H), 7.83 – 7.72 (m, 4H), 7.58 – 7.45 (m, 5H), 7.42 (d,  $J = 8.7$  Hz, 1H), 7.38 – 7.32 (m, 1H), 7.27 (d,  $J = 1.6$  Hz, 1H), 7.25 (d,  $J = 1.6$  Hz, 1H), 2.86 – 2.75 (m, 4H), 1.80 – 1.64 (m, 4H), 1.45 – 1.19 (m, 36H), 0.88 (t,  $J = 6.8$  Hz, 6H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ - $d$ )  $\delta$  194.37, 142.56, 141.23, 140.62, 138.97, 138.76, 136.34, 135.36, 135.05, 131.87, 128.91, 126.99, 126.79, 126.40, 125.96, 125.62, 124.04, 123.26, 122.75, 121.02, 120.68, 119.76, 113.40, 111.27, 110.01, 109.46, 36.00, 32.30, 31.93, 29.80, 29.51, 29.37, 22.70, 14.13. TOF-MS (Formula<sup>+</sup>): 929.4947, Calculated: 928.1560.



**Scheme S10.** The synthetic route of compound **8**.

**Synthesis of (4-(3,6-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-carbazol-9-yl)phenyl)methanone (End-capper 2):**

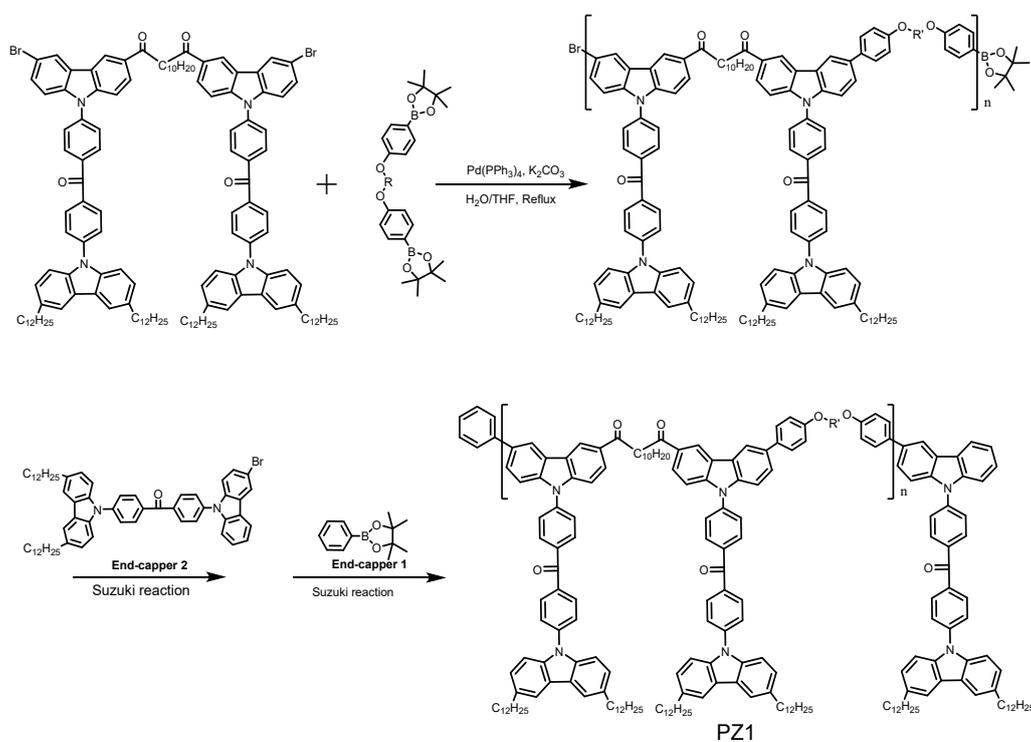
*yl)phenyl)(4-(3,6-didodecyl-9H-carbazol-9-yl)phenyl)methanone (8)*: Following the same procedure for synthesis of **7** generated the pure **8** as a yellow powder. Yield (53%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 27.2 Hz, 2H), 8.17 (dd, *J* = 8.3, 6.6 Hz, 4H), 7.99 – 7.85 (m, 4H), 7.78 (dd, *J* = 8.3, 6.1 Hz, 4H), 7.60 – 7.28 (m, 6H), 2.89 – 2.69 (m, 4H), 1.81 – 1.58 (m, 8H), 1.45 – 1.37 (m, 24H), 1.26 (s, 32H), 0.87 (t, *J* = 6.8 Hz, 6H). <sup>13</sup>C NMR (151 MHz, CDCl<sub>3</sub>-*d*) δ 194.50, 142.83, 142.51, 141.85, 141.59, 140.74, 139.54, 138.81, 136.16, 135.96, 135.33, 135.18, 134.67, 132.88, 132.12, 131.76, 131.61, 127.98, 126.77, 126.69, 126.11, 126.08, 125.75, 124.74, 124.60, 124.20, 123.83, 123.76, 120.73, 119.72, 119.24, 119.00, 116.76, 110.17, 109.97, 109.59, 109.15, 83.94, 83.68, 36.01, 32.30, 31.93, 29.65, 29.38, 24.95, 22.70, 14.13. TOF-MS (Formula<sup>+</sup>): 1101.7351, Calculated: 1100.7349.



**Scheme S11.** The synthetic route of **End-capper 3**.

**Synthesis of ((6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H,9'H-[3,3'-bicarbazole]-9,9'-diyl)bis(4,1-phenylene))bis((4-(3,6-didodecyl-9H-carbazol-9-yl)phenyl)methanone) (End-capper 3):** End-capper 2 (2.45 g, 2.65 mmol), compound **8** (3.20 g, 2.91 mmol), K<sub>2</sub>CO<sub>3</sub> (3.66 g, 26.50 mmol), Tetrakis(triphenylphosphine)palladium (0.18 mg, 0.16 mmol), THF : H<sub>2</sub>O (240 mL, 3:1, v/v) were added into a 500 mL 3 neck round bottom flask under nitrogen. The mixture was stirred at 150°C for 16 hours and then poured into 300mL water, extraction with DCM, The crude product was purified by column chromatography on silica gel (petroleum ether : dichloromethane = 2:1, v/v) to generated the pure **End-capper 3** as a yellow powder. Yield (1.20g, 40%). <sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>-*d*) δ 8.76 (s, 1H),

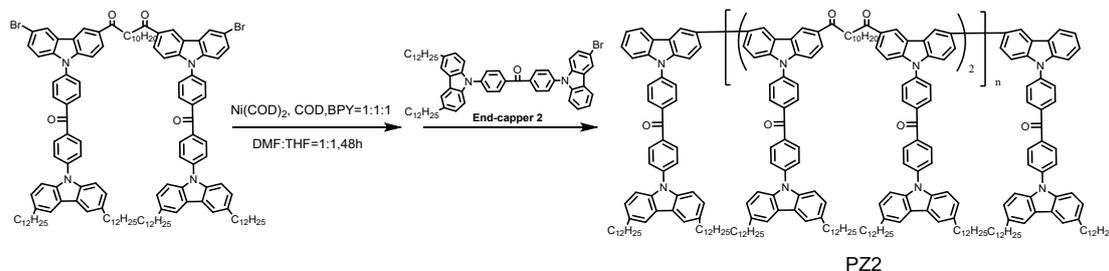
8.63 (s, 1H), 8.60 – 8.53 (m, 1H), 8.31 (d,  $J = 7.7$  Hz, 1H), 8.19 (dt,  $J = 14.7, 7.3$  Hz, 7H), 8.08 – 8.01 (m, 1H), 7.96 – 7.86 (m, 10H), 7.83 (t,  $J = 6.9$  Hz, 4H), 7.76 – 7.69 (m, 2H), 7.68 – 7.60 (m, 2H), 7.52 (dd,  $J = 8.3, 4.0$  Hz, 4H), 7.47 (dd,  $J = 8.4, 4.3$  Hz, 1H), 7.41 (t,  $J = 7.4$  Hz, 1H), 7.29 (dt,  $J = 13.0, 6.5$  Hz, 4H), 7.22 – 7.13 (m, 1H), 2.82 (t,  $J = 7.7$  Hz, 8H), 1.73 (dd,  $J = 14.6, 7.2$  Hz, 8H), 1.47 – 1.21 (m, 84H), 0.89 (t,  $J = 6.7$  Hz, 12H).  $^{13}\text{C}$  NMR (151 MHz,  $\text{CDCl}_3$ - $d$ )  $\delta$  194.48, 142.42, 141.39, 138.79, 136.28, 135.32, 135.15, 132.73, 132.59, 131.89, 128.10, 127.86, 126.80, 126.54, 126.25, 125.98, 124.03, 123.67, 121.00, 120.73, 119.74, 109.87, 109.50, 109.15, 83.75, 83.53, 83.20, 36.01, 32.30, 31.93, 31.62, 29.76, 29.16, 29.08, 24.89, 24.57, 22.70, 14.13. TOF-MS (Formula<sup>+</sup>): 1823.2236, Calculated: 1822.4660.



**Scheme S12.** The synthetic routes of **PZ1**.

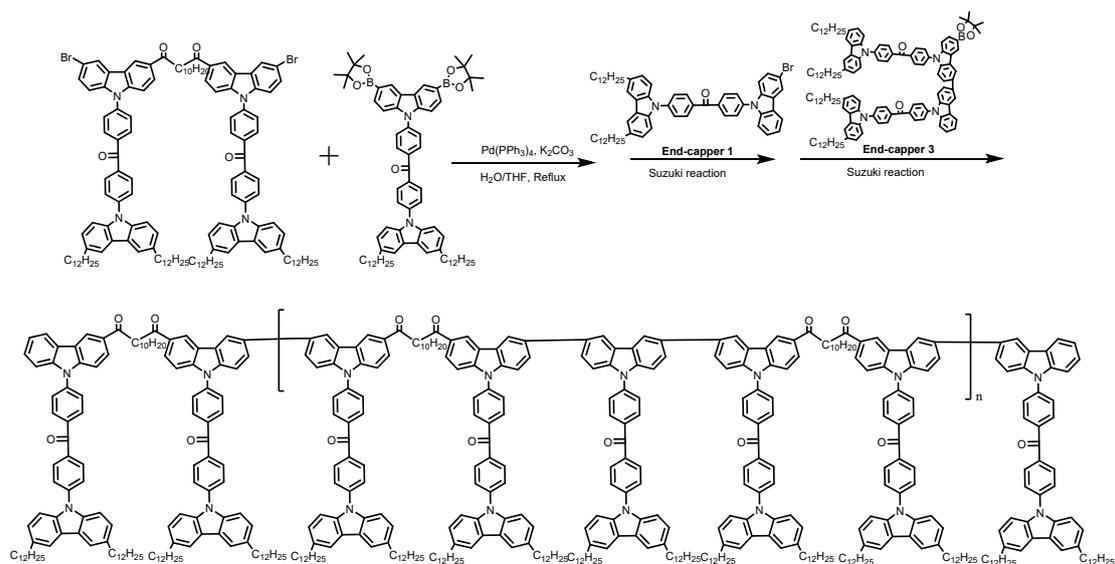
**Synthesis of Target Polymer PZ1:** Monomer (100.00 mg, 0.05 mmol), compound 7 (24.00 mg, 0.05 mmol),  $\text{Pd}(\text{pPh}_3)_4$  (3.38 mg, 0.01 mmol),  $\text{K}_2\text{CO}_3$  (33.72 mg, 0.25 mmol) and THF: $\text{H}_2\text{O}$  (2.00 mL, 4:1, v/v) were added into a 10 mL Schlenk tube. The reaction mixture was stirred at 80 °C for 48 h. Then **End-capper 2** (22.68 mg, 0.05 mmol) and **End-capper1** (9.95 mg, 0.10 mmol) were added sequentially for end-capping for 12 h. Then, the reaction mixture was quenched by 5 mL of chloroform and later precipitated in 150 mL of a mixture of aqueous HCl, acetone and methanol (1: 1 : 1 by volume).

The precipitate and solution were stirred for 2 h and then the polymer was collected by filtration and dried in an oven at 40 °C overnight. Finally, the polymer was successively extracted by methanol, acetone, and chloroform, each for 24 h in a Soxhlet apparatus. After evaporation of the solvent, 80.00 mg of yellowish green **PZ1** was obtained. Yield (80%). Mw: 12645, PDI:1.58.



**Scheme S13.** The synthetic routes of **PZ2**.

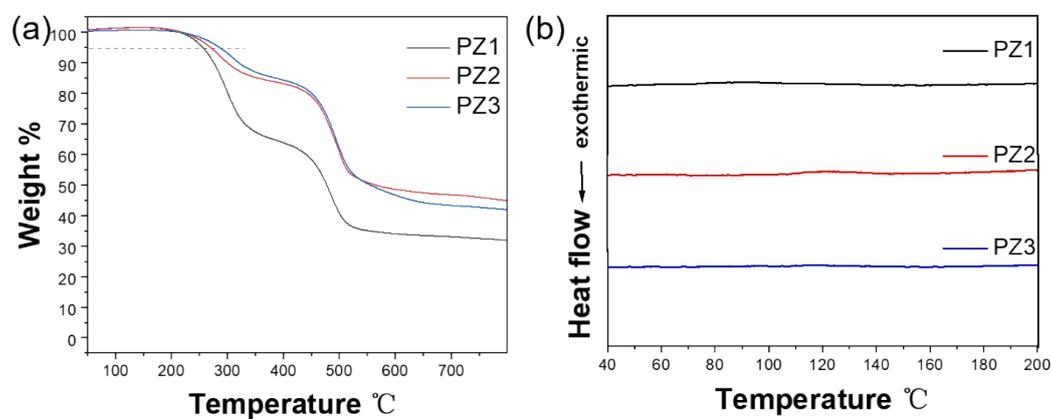
**Synthesis of Target Polymer PZ2:** Yamamoto catalytic system of Bis(1,5-cyclooctadiene) nickel (0) ( $\text{Ni}(\text{COD})_2$ ) (34.00 mg, 0.12 mmol), 1,5-Cyclooctadiene (COD) (16.80  $\mu\text{L}$ , 0.12 mmol) and 2,2'-bipyridyl (BPY) (20.00 mg, 0.12 mmol) was added into a 10 mL Schlenk tube and dissolved in 0.4 mL of anhydrous DMF. Another Schlenk tube was charged with monomer (100.00 mg, 0.05 mmol) and 0.4 mL anhydrous THF. The catalyst solution was heated at 50 °C for 30 minutes before it was transferred into the monomer solution. The reaction mixture was stirred at 80 °C for 48 h. Then **End-capper 2** (90.00 mg, 0.01 mmol) was added for end-capping for 12 h. Then, the reaction mixture was diluted with 5 mL of chloroform and later precipitated in 150 mL of a mixture of aqueous HCl, acetone and methanol (1: 1: 1 by volume). The mixtures were stirred for 2 h and then the polymer was collected by filtration and dried in an oven at 40 °C overnight. Finally, the polymer was successively extracted by methanol, acetone, and chloroform, each for 24h in a Soxhlet apparatus. After evaporation of the solvent, 85.00 mg of yellowish green polymer was obtained, Yield (85%). Mw: 11323, PDI:1.44.



**Scheme S14.** The synthetic routes of **PZ3**.

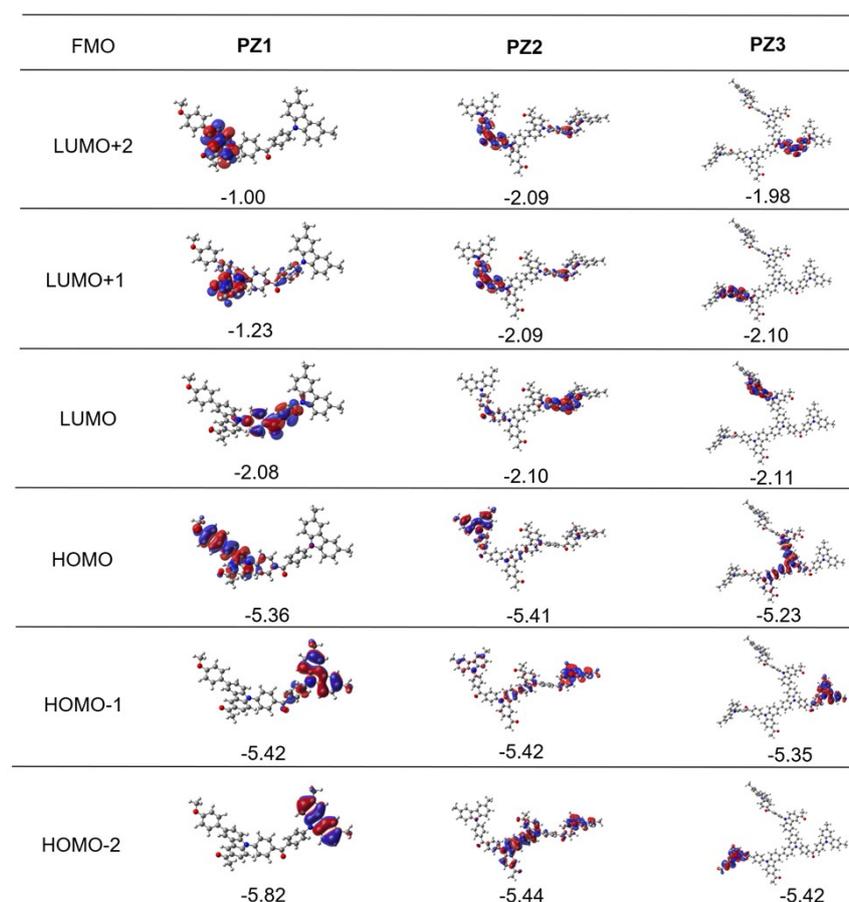
**PZ3:** The synthesis of PZ3 was like that of PZ1. It was obtained as a yellow powder in yield of 75%. Mw: 37544, PDI:2.49.

### 3. Thermal Properties

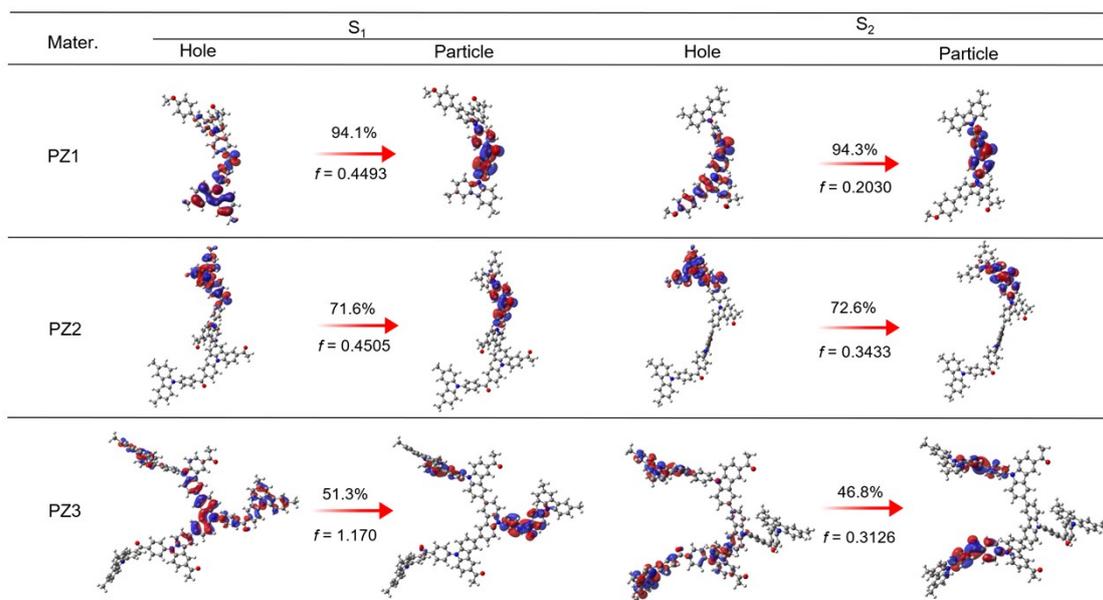


**Figure S1.** a) Thermogravimetric analysis (TGA) and b) Differential scanning calorimetry (DSC) of **PZ1**, **PZ2** and **PZ3**, respectively.

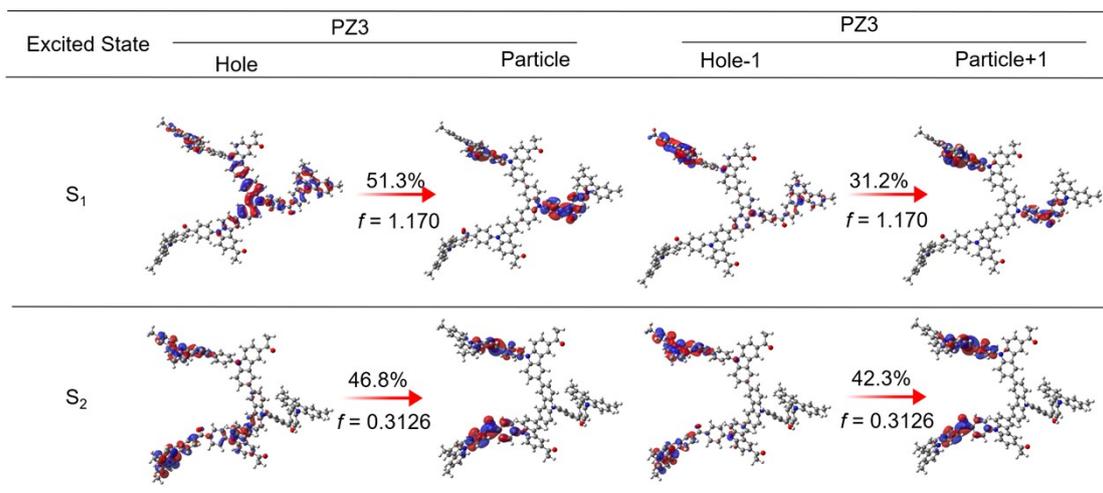
### 4. Computation



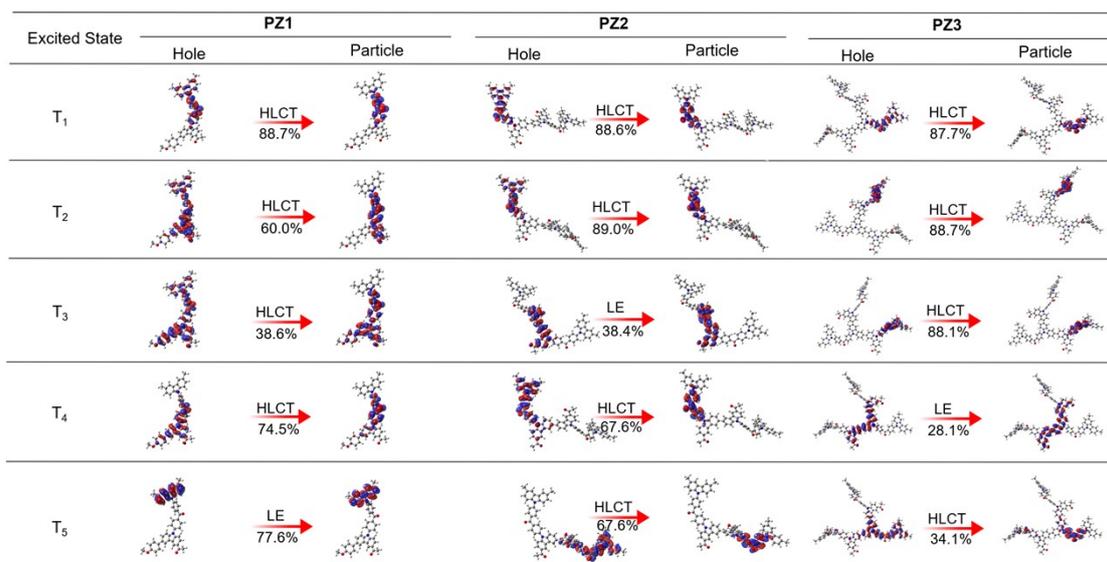
**Figure S2.** The FMOs distributions of **PZ1**, **PZ2** and **PZ3**, respectively.



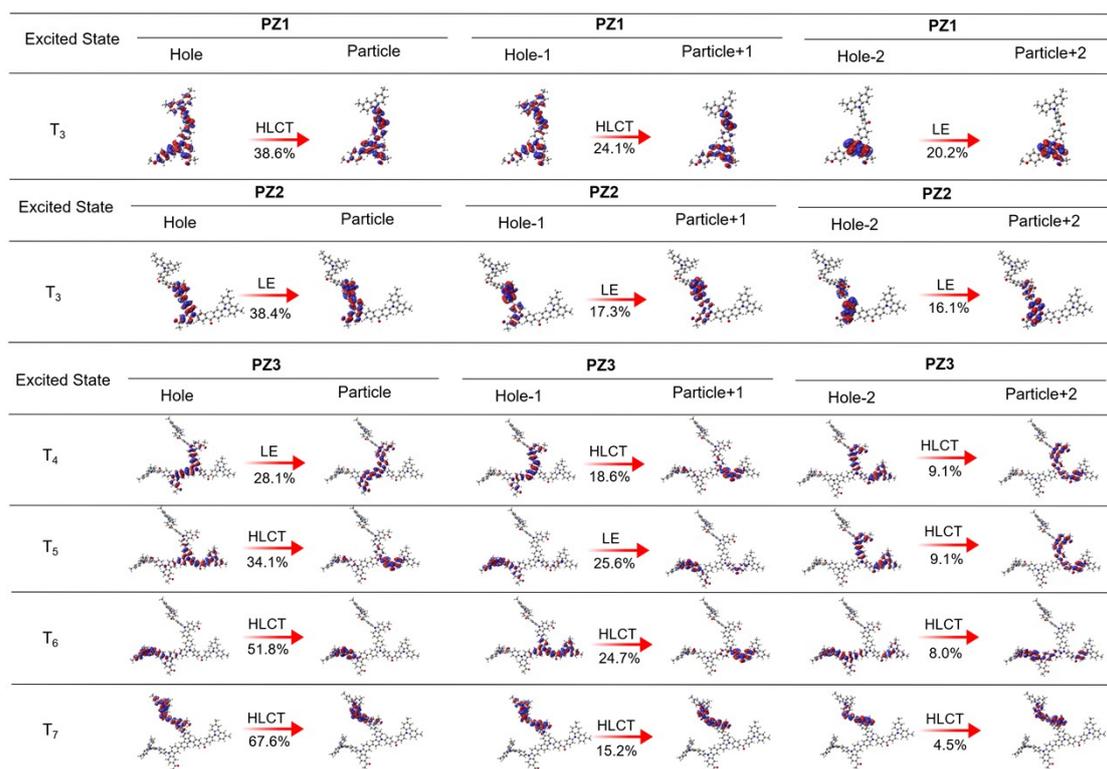
**Figure S3.** The hole and particle distributions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  vertical transitions, the corresponding transition energies, and oscillator strength ( $f$ ) values of **PZ1**, **PZ2** and **PZ3**, respectively.



**Figure S4.** The hole and particle distributions of  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow S_2$  vertical transitions, the corresponding transition energies, and oscillator strength ( $f$ ) values of **PZ3**.



**Figure S5.** The hole and electron NTOs based on the results of TD-DFT for the T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>, T<sub>4</sub> and T<sub>5</sub> states of **PZ1**, **PZ2** and **PZ3**, respectively.



**Figure S6.** The hole and electron NTOs based on the results of TD-DFT for the T<sub>3</sub> state of **PZ1**, **PZ2** and T<sub>4</sub>, T<sub>5</sub>, T<sub>6</sub> and T<sub>7</sub> of **PZ3**.

**Table S1.** The calculated energy and oscillator strengths ( $f$ ) in excited states.

Compounds	State	$E$ (eV)	$f$
<b>PZ1</b>	S <sub>1</sub>	2.873	0.4493
	S <sub>2</sub>	2.976	0.2030
	T <sub>1</sub>	2.600	-
	T <sub>2</sub>	2.716	-
	T <sub>3</sub>	2.960	-
<b>PZ2</b>	S <sub>1</sub>	2.885	0.4505
	S <sub>2</sub>	2.922	0.3433
	T <sub>1</sub>	2.588	-
	T <sub>2</sub>	2.595	-
	T <sub>3</sub>	2.756	-
	T <sub>4</sub>	2.769	-
	T <sub>5</sub>	2.921	-
<b>PZ3</b>	S <sub>1</sub>	2.823	1.1700
	S <sub>2</sub>	2.824	0.3126
	S <sub>3</sub>	2.867	0.4205
	S <sub>4</sub>	2.927	0.0330
	T <sub>1</sub>	2.595	-
	T <sub>2</sub>	2.598	-
	T <sub>3</sub>	2.611	-
	T <sub>4</sub>	2.686	-
	T <sub>5</sub>	2.707	-
	T <sub>6</sub>	2.715	-
T <sub>7</sub>	2.912	-	

**Table S2.** The calculated energy and oscillator strengths ( $f$ ) in excited states.

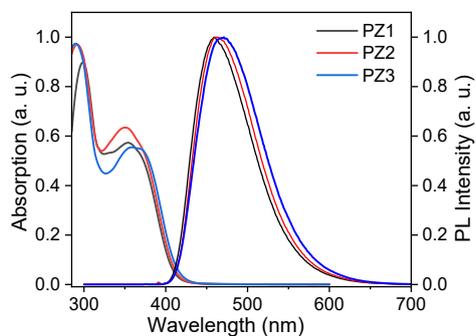
Compounds	State	$\Delta E$ (S <sub>n</sub> -T <sub>n</sub> ) (eV)			
		S <sub>1</sub>	S <sub>2</sub>	S <sub>3</sub>	S <sub>4</sub>
<b>PZ1</b>	T <sub>1</sub>	0.273	0.376	0.710	0.910
	T <sub>2</sub>	0.157	0.260	0.594	0.794
	T <sub>3</sub>	0.087	0.016	0.350	0.550
<b>PZ2</b>	T <sub>1</sub>	0.297	0.334	0.402	0.422
	T <sub>2</sub>	0.290	0.327	0.395	0.415
	T <sub>3</sub>	0.129	0.166	0.234	0.254
	T <sub>4</sub>	0.116	0.153	0.221	0.241
	T <sub>5</sub>	-0.036	0.001	0.069	0.089

<b>PZ3</b>	T <sub>1</sub>	0.228	0.229	0.272	0.332
	T <sub>2</sub>	0.225	0.226	0.269	0.329
	T <sub>3</sub>	0.212	0.213	0.256	0.316
	T <sub>4</sub>	0.137	0.138	0.181	0.241
	T <sub>5</sub>	0.116	0.117	0.160	0.220
	T <sub>6</sub>	0.108	0.109	0.152	0.212
	T <sub>7</sub>	-0.089	-0.088	0.045	0.015

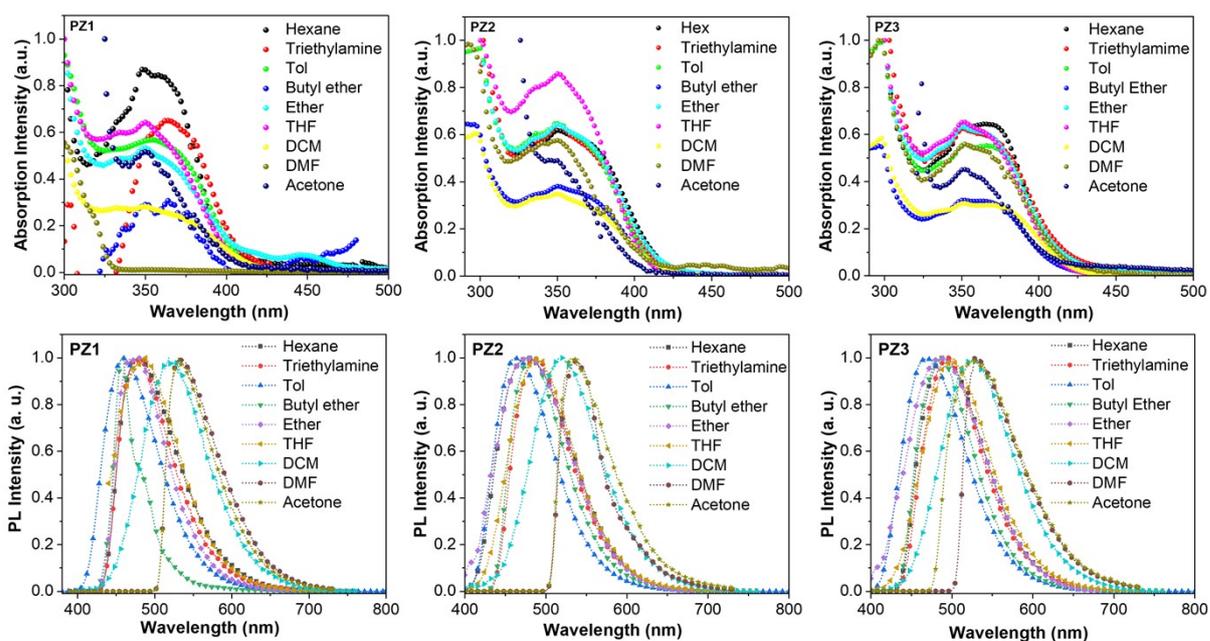
**Table S3.** Summarize of spin-orbit coupling matrix element (SOCME) values between the S<sub>1</sub>, S<sub>2</sub> states and respective triplet states.

<b>SOCME (cm<sup>-1</sup>)</b>							
<b>PZ1</b>							
	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>		
S <sub>1</sub>	23.5	10.9	17.5	4.69	0.85		
S <sub>2</sub>	11.6	4.7	4.5	1.31	1.84		
S <sub>3</sub>	6.17	7.28	0.74	0.44	0.10		
<b>PZ2</b>							
	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>		
S <sub>1</sub>	23.9	11.47	2.1	1.0	18.34		
S <sub>2</sub>	10.8	4.84	1.1	0.6	3.69		
S <sub>3</sub>	0.11	0.10	11.09	2.46	0.07		
<b>PZ3</b>							
	T <sub>1</sub>	T <sub>2</sub>	T <sub>3</sub>	T <sub>4</sub>	T <sub>5</sub>	T <sub>6</sub>	T <sub>7</sub>
S <sub>1</sub>	23.02	24.58	10.66	2.2	2.7	3.0	5.4
S <sub>2</sub>	3.73	2.32	0.88	0.9	1.0	1.6	7.4
S <sub>3</sub>	12.14	3.14	1.28	0.41	0.18	5.09	9.8

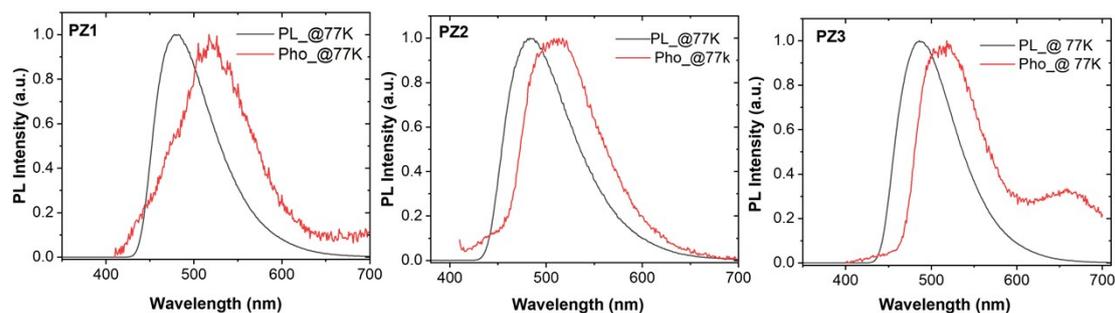
## 5. Photo-Physical Properties



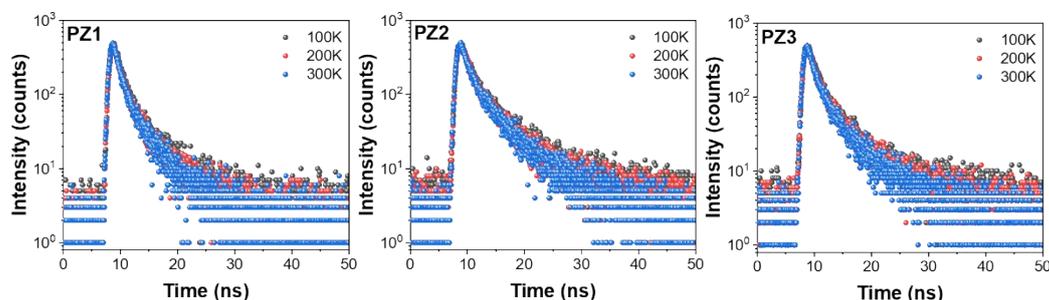
**Figure S7.** The absorption and PL spectra of **PZ1**, **PZ2** and **PZ3** in dilute toluene solution.



**Figure S8.** The absorption and PL spectra of **PZ1**, **PZ2** and **PZ3** in different solutions.

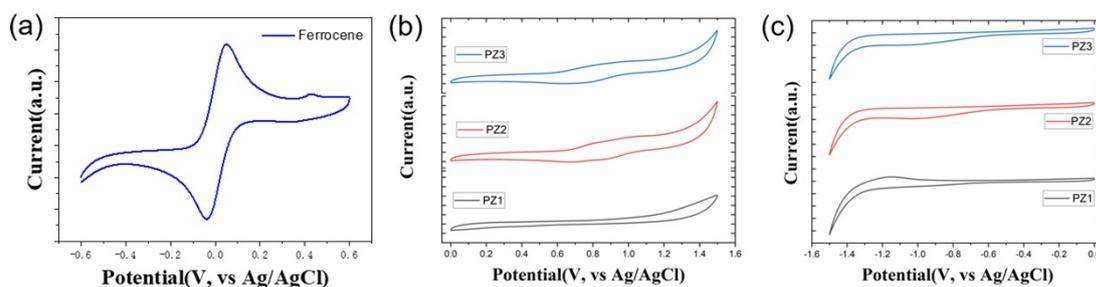


**Figure S9.** The low temperature PL (77K) and Pho (77K) spectra of **PZ1**, **PZ2** and **PZ3** in neat films.



**Figure S10.** The transition PL decay curves of doped films under different temperatures of **PZ1**, **PZ2** and **PZ3**

## 6. Energy Level



**Figure S11.** a) Cyclicvoltammety characteristics of Ferrocene, b) HOMO, c) LUMO of **PZ1**, **PZ2** and **PZ3** (performed in neat films).

## 7. Parameters of Photo-Physical Properties

**Table S4.** Photophysical and electrochemical properties of **PZ1**, **PZ2** and **PZ3**.

Compounds	$\lambda_{ABS}$ <sup>a)</sup> (nm)	$\lambda_{PL}$ <sup>a)</sup> (nm)	$T_d$ <sup>b)</sup> (°C)	$\tau_p$ <sup>c)</sup> (ns)	$\Delta E_{ST}$ <sup>d)</sup> (eV)	$E_{HOMO}$ <sup>e)</sup> (eV)	$E_{LUMO}$ <sup>f)</sup> (eV)	$E_{opt}^g$ (eV)	$PLQY$ <sup>h)</sup> (%)
<b>PZ1</b>	300/420	460	260	2.14	0.46	-5.91	-2.93	2.98	32.9
<b>PZ2</b>	300/420	460	270	2.39	0.41	-5.92	-2.97	2.95	40.4

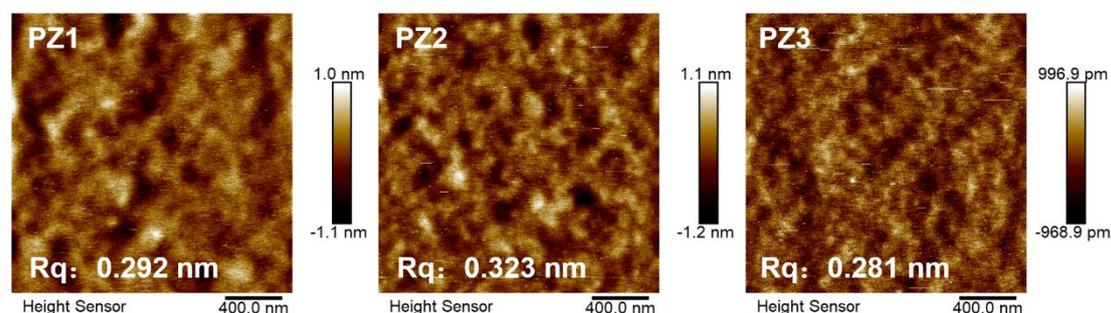
**PZ3**    300/420    470    290    2.95    0.43    -5.81    -2.88    2.93    38.8

a) Measured in dilute toluene solution; b) Thermal decomposition temperature; c) The fluorescence lifetime in mCP matrixes; d) The  $S_1$  and  $T_1$  states energy splitting. e) Measured from the onset of the oxidation potential; f) calculated by the formula of  $E_{LUMO} = E_{HOMO} - E_{opt}^{opt}$ ; g) optical bandgap: obtained from the onset of the UV-vis absorption spectra. h) Photoluminescence quantum yield determined by a calibrated integrating sphere.

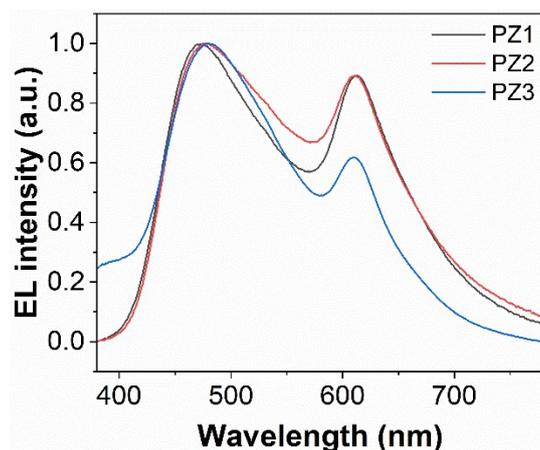
**Table S5.** Detailed absorption and emission peak positions of **PZ1**, **PZ2** and **PZ3** in different solvents

Solvents	$\Delta f$	<b>PZ1</b>	<b>PZ2</b>	<b>PZ3</b>
		$V_a-V_f$ (cm <sup>-1</sup> )	$V_a-V_f$ (cm <sup>-1</sup> )	$V_a-V_f$ (cm <sup>-1</sup> )
Hexane	0.0012	3724	2477	3318
Toluene	0.014	2532	2304	2533
Triethylamine	0.048	2394	3191	2956
Butyl ether	0.096	3261	2696	2746
Ether	0.167	2788	2477	3149
THF	0.210	3814	3478	3809
DCM	0.217	4578	4582	4572
DMF	0.276	7624	5405	4564
Acetone	0.284	5510	5232	4838

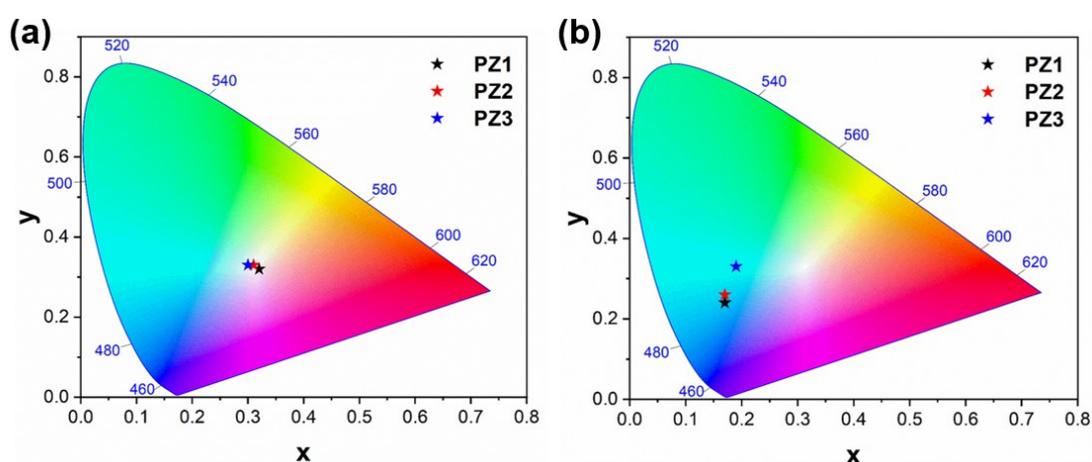
## 8. EL performances



**Figure S12.** Scanning probe microscope spectra of **PZ1**, **PZ2** and **PZ3**



**Figure S13.** EL spectra of non-doped devices based on **PZ1**, **PZ2** and **PZ3**



**Figure S14.** CIE color coordinates of a) non-doped and b) doped OLEDs based on **PZ1**, **PZ2** and **PZ3**

**Table S6** EL performance of the non-doped OLEDs based on **PZ1**, **PZ2** and **PZ3**.

Emitter	$L_{\max}^{\text{a)}}$	CIE	CRI
	[ $\text{cd m}^{-2}$ ]		
<b>PZ1</b>	20.25	0.32, 0.32	83
<b>PZ2</b>	39.38	0.31, 0.33	89
<b>PZ3</b>	84.60	0.30, 0.33	84

**Table S7** EL performance of the OLEDs based on **PZ1**, **PZ2** and **PZ3**.

Emitter	$\lambda_{\text{EL}}^{\text{a)}}$	$\text{EQE}_{\max/1000}^{\text{b)}}$	$V_{\text{on}}^{\text{c)}}$	$\eta_{\text{PE}_{\max}}^{\text{d)}}$	$\eta_{\text{CE}_{\max}}^{\text{e)}}$	CIE
	[nm]	[%]	[V]	[ $\text{lm W}^{-1}$ ]	[ $\text{cd A}^{-1}$ ]	
<b>PZ1</b>	470	1.1/-	5.5	1.1	2.0	0.17, 0.24
<b>PZ2</b>	475	1.7/-	4.8	1.9	3.1	0.17, 0.26
<b>PZ3</b>	484	3.8/0.87	5.0	3.7	8.4	0.19, 0.33

a) The peak emission of EL spectra; b) The maximum external quantum efficiency; c)  $V_{\text{on}}$ =turn-on voltage at  $1 \text{ cd m}^{-2}$ ; d) The maximum power efficiency; e) The maximum

current efficiency.

## 9. Reference

- [1] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09, Revision B.01*; Gaussian, Inc.: Wallingford, CT, **2010**.
- [2] a) E. Runge, E. K. U. Gross, *Phys. Rev. Lett.* **1984**, *52*, 997; b) M. A. L. Marques, E. K. U. Gross, *Annu. Rev. Phys. Chem.* **2004**, *55*, 427 – 455.
- [3] M. Kasha, R. Rawls, M. A. El-Bayoumi, *Pure Appl. Chem.* **1965**, *11*, 371-392.