

**Supplementary Information**

**Construction of Metallo-Triangles with Cis-TPE Motif and  
Fluorescence Properties**

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## 1. Experimental Section

All reagents were purchased from Bidepharm, Macklin Reagent, and Energy Chemical. And they were used as received unless noted otherwise. Column chromatography was conducted using SiO<sub>2</sub> (VWR, 40-60 μm, 60 Å) and the separated products were visualized by UV light.

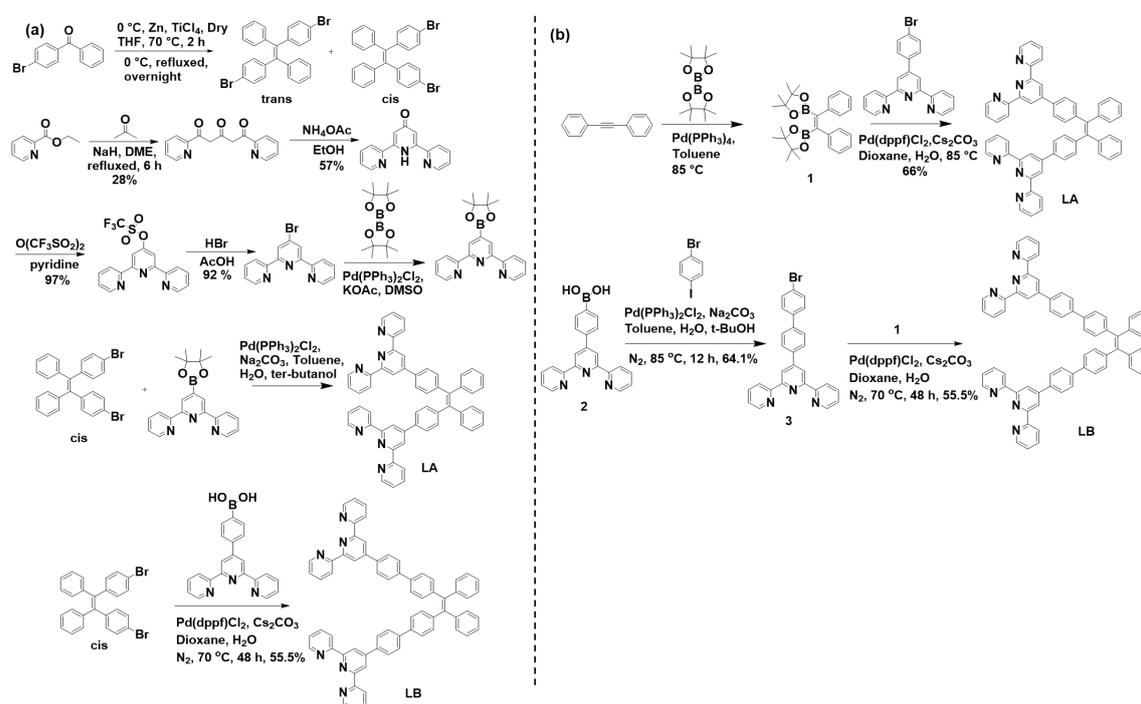
**Nuclear magnetic resonance (NMR).** NMR spectra data were recorded at 25 °C on Bruker 600 MHz, 500 MHz and Qone AS 400-MHz nuclear magnetic resonance instruments using CDCl<sub>3</sub> and CD<sub>3</sub>CN as the solvents.

**Electrospray ionization-mass spectrometry (ESI-MS) and travelling wave ion mobility-mass spectrometry (TWIM-MS).** Both spectra were collected on a Waters Synapt G2 mass spectrometer, using solutions of 0.01 mg sample in 1 mL acetonitrile for the complexes. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 1-3 kV; sample cone voltage, 20-30 V; extraction cone voltage, 3 V; source temperature 100 °C; desolvation temperature, 200 °C; cone gas flow, 10 L/h; desolvation gas flow, 600 L/h (N<sub>2</sub>); source gas control, 0 mL/min; trap gas control, 2 mL/min; helium cell gas control, 100 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 5 μL/min; IM traveling wave height, 25 V; and IM traveling wave velocity, 1000 m/s.

**Ultraviolet visible (UV-Vis) spectrophotometer.** All UV-Vis spectra of solution samples were recorded on a PerkinElmer Lambda 365 spectrophotometer at room temperature. All UV-Vis spectra of solid samples were recorded on a PerkinElmer Lambda 1050+ spectrophotometer at room temperature.

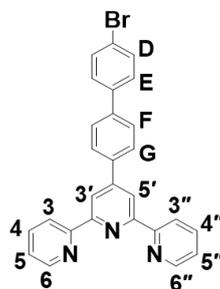
**Fluorescence spectrophotometer.** All emission spectra of solution samples were recorded on a Shimadzu RF-5301pc spectrophotometer. All emission spectra of solid samples and emission quantum yields were determined by FLS980 Spectrometer (Edinburgh Instruments Ltd., Livingston, United Kingdom). Emission quantum yield was measured via an integrating light sphere. Solutions were placed in 1 cm path length quartz cells.

## 2. Synthetic route, NMR and ESI-MS analysis

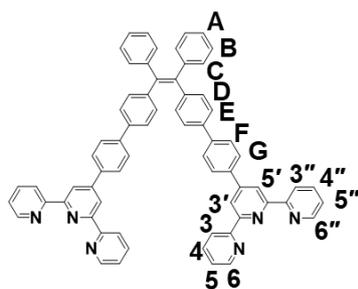


**Scheme S1.** (a) the tedious synthetic route and (b) our synthetic route.

**Ligand LA:** The synthetic procedure was reported in reference.<sup>[1]</sup>

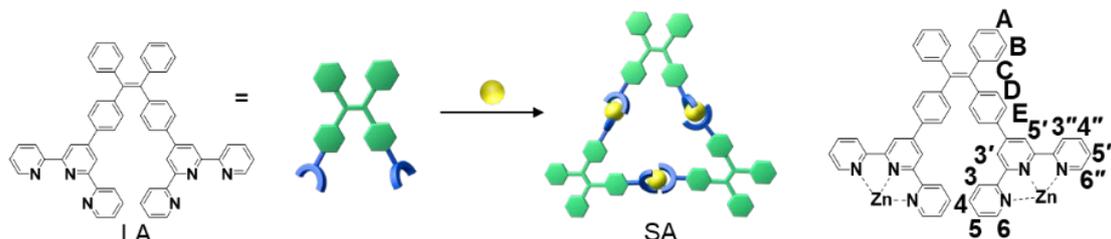


**Compound 3:** The mixture of 4-Bromoiodobenzene (17.0 mmol, 4.8 g), compound **2** (9 mmol, 3.0 g) and Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (0.11 mmol, 80.0 mg) in 200 mL Schlenk flask was degassed three times. Then 50 mL toluene, 25 mL 1 M Na<sub>2</sub>CO<sub>3</sub> aqueous solution and 11 mL t-BuOH was added in N<sub>2</sub>. The resultant mixture kept at 85 °C for 8 h. After cooling to the room temperature, the solution was extracted by CHCl<sub>3</sub> three times and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel (CHCl<sub>3</sub>/EtOH=200/1) to give compound **3** as white solid (3.5 g, 64.1%).<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.77 (s, 2H, tpy-*H*<sup>3',5'</sup>), 8.74 (d, *J* = 3.7 Hz, 2H, tpy-*H*<sup>6,6''</sup>), 8.67 (d, *J* = 7.8 Hz, 2H, tpy-*H*<sup>3,3''</sup>), 7.97 (d, *J* = 8.0 Hz, 2H, Ph-*H*<sup>D</sup>), 7.87 (t, *J* = 7.3 Hz, 2H, tpy-*H*<sup>4,4''</sup>), 7.67 (d, *J* = 8.0 Hz, 2H, Ph-*H*<sup>E</sup>), 7.57 (d, *J* = 8.2 Hz, 2H, Ph-*H*<sup>F</sup>), 7.50 (d, *J* = 8.2 Hz, 2H, Ph-*H*<sup>G</sup>), 7.38 – 7.32 (m, 2H tpy-*H*<sup>5,5''</sup>). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 156.31, 156.10, 149.62, 149.25, 140.63, 139.40, 137.77, 136.99, 132.08, 128.78, 127.94, 127.47, 123.97, 122.03, 121.49, 118.76.



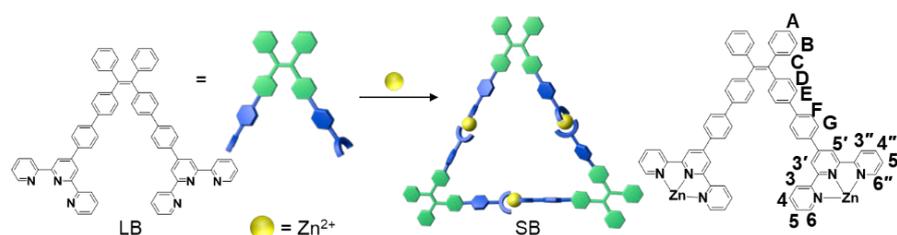
**Ligand LB:** A mixture of compound **1** (0.36 mmol, 156.5 mg), compound **3** (1.09 mmol, 502.9 mg),  $\text{Cs}_2\text{CO}_3$  (1.09 mmol, 353.9 mg) and  $\text{Pd}(\text{PPh}_3)_4$  (0.02 mmol, 14.6 mg) in 100 mL Schlenk flask was degassed three times. Then 15 mL dioxane and 3 mL  $\text{H}_2\text{O}$  were added under  $\text{N}_2$ . The resultant mixture was kept at 70 °C for 48 h. After cooling to the room temperature, the solution was extracted by  $\text{CHCl}_3$  three times and the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel ( $\text{CHCl}_3/\text{EtOH}=50/1$ ) to give ligand LB as white solid (255 mg, 75%).  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (s, 4H, tpy- $H^{3',5'}$ ), 8.74 (d,  $J = 4.5$  Hz, 4H, tpy- $H^{6,6''}$ ), 8.68 (d,  $J = 8.0$  Hz, 4H, tpy- $H^{3,3''}$ ), 7.98 (d,  $J = 8.3$  Hz, 4H, Ph- $H^G$ ), 7.89 (t,  $J = 7.7$  Hz, 4H, tpy- $H^{4,4''}$ ), 7.74 (d,  $J = 8.3$  Hz, 4H, Ph- $H^F$ ), 7.49 (d,  $J = 8.3$  Hz, 4H, Ph- $H^E$ ), 7.38 – 7.35 (m, 4H, tpy- $H^{5,5''}$ ), 7.21 (d,  $J = 8.3$  Hz, 4H, Ph- $H^D$ ), 7.14 (m, 6H, Ph- $H^A$  and Ph- $H^B$ ), 7.11 (dd,  $J = 7.4, 2.0$  Hz, 4H, Ph- $H^C$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.41, 156.07, 149.92, 149.25, 143.90, 143.42, 143.33, 141.41, 140.91, 138.35, 137.26, 137.05, 132.09, 131.62, 127.88, 127.82, 127.48, 126.71, 126.52, 123.96, 121.55, 118.84.

#### Triangle SA

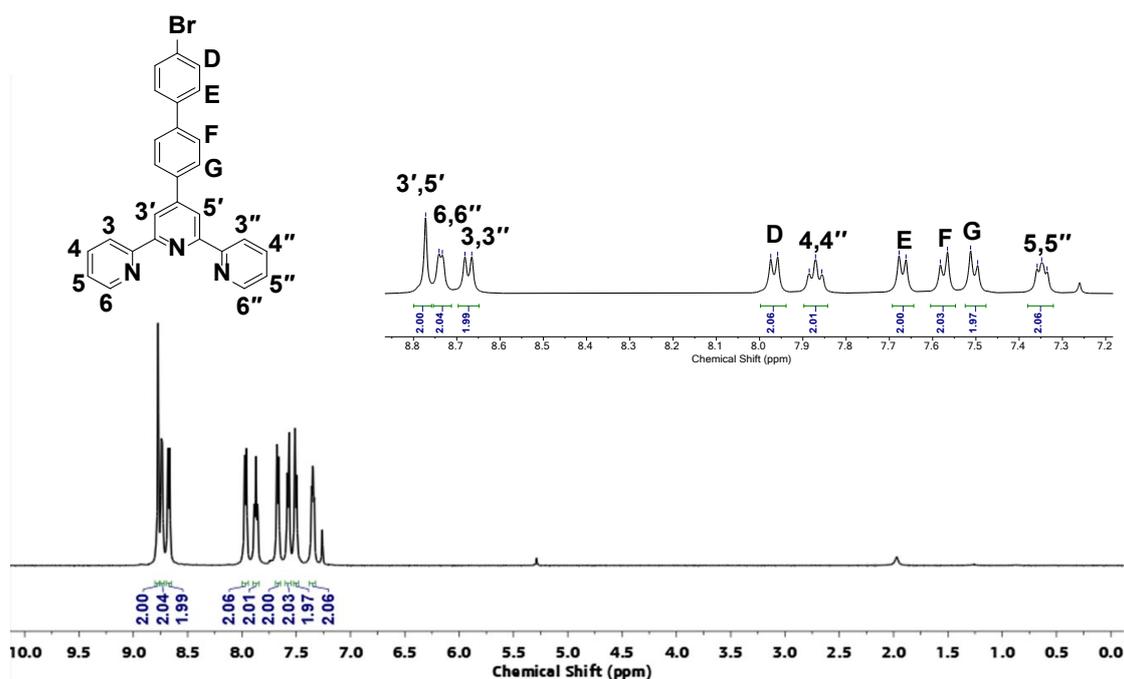


**SA:** To a solution of ligand **LA** (34.7  $\mu\text{mol}$ , 27.6 mg)  $\text{CHCl}_3$  (8.0 mL), a solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (34.7  $\mu\text{mol}$ , 10.3 mg) in MeOH (8.0 mL) was added, then the mixture was kept in 50 °C for 12 h. After cooling to room temperature, excess  $\text{NH}_4\text{PF}_6$  (around 300 mg) was added to generate a yellow precipitate (34.1 mg, 90%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  8.90 (s, 4H, tpy- $H^{3',5'}$ ), 8.65 (d,  $J = 8.1$  Hz, 4H, tpy- $H^{3,3''}$ ), 8.05 (m, 8H, tpy- $H^{4,4''}$ , Ph- $H^E$ ), 7.78 (d,  $J = 4.7$  Hz, 4H, tpy- $H^{6,6''}$ ), 7.51 (d,  $J = 8.4$  Hz, 4H, Ph- $H^D$ ), 7.32 (dd,  $J = 7.0, 5.2$  Hz, 4H, tpy- $H^{5,5''}$ ), 7.29 – 7.22 (m, 10H, Ph- $H^A$ , Ph- $H^B$ , and Ph- $H^C$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  156.56, 150.70, 148.89, 148.77, 147.42, 143.94, 142.39, 142.09, 135.43, 133.17, 131.94, 129.05, 128.58, 128.42, 128.13, 124.12, 122.23. ESI-MS ( $m/z$ ): calcd. for  $[\text{M}-3\text{PF}_6^-]^{3+}$  1004.5, found 1004.5; calcd. for  $[\text{M}-4\text{PF}_6^-]^{4+}$  717.1, found 717.1; calcd. for  $[\text{M}-5\text{PF}_6^-]^{5+}$  544.5, found 544.5; calcd. for  $[\text{M}-6\text{PF}_6^-]^{6+}$  429.6, found 429.6.

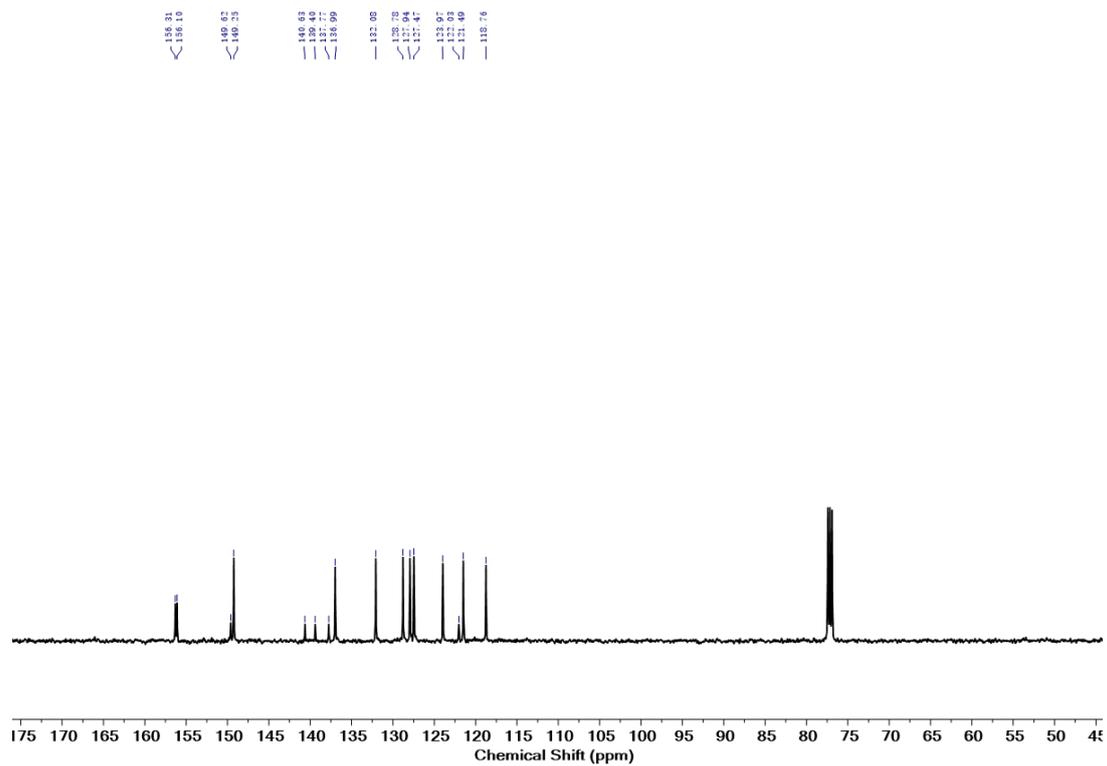
## Triangle SB



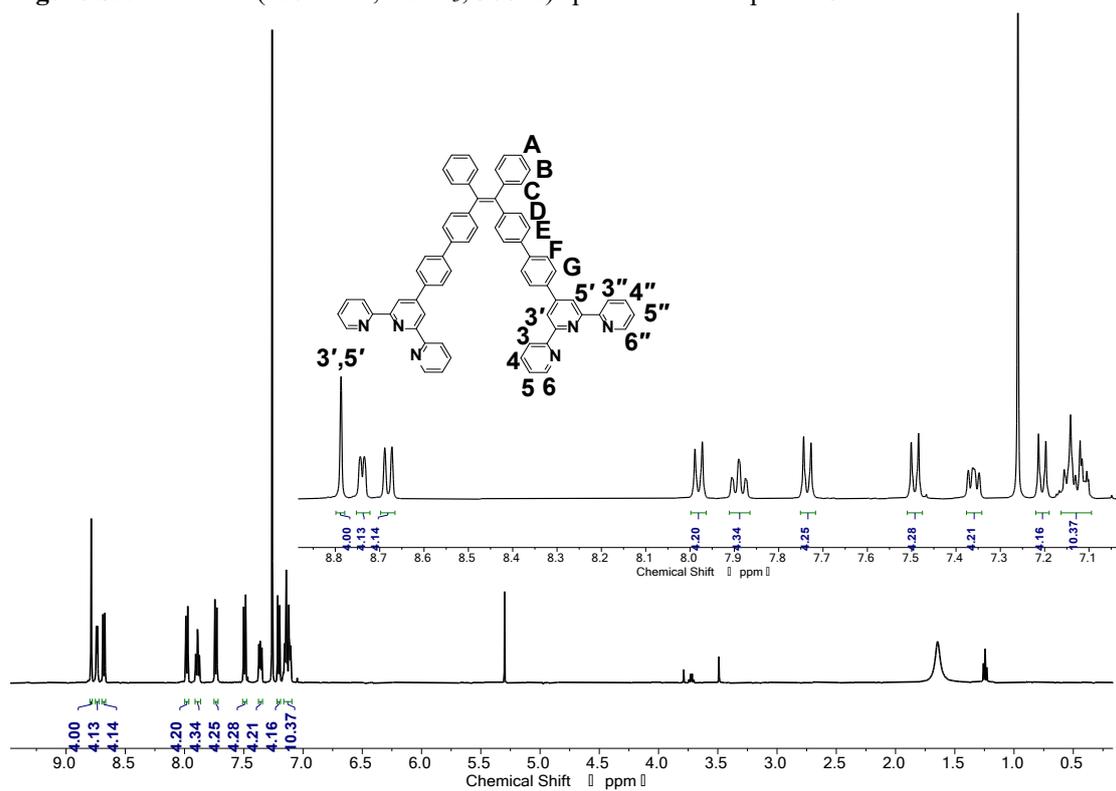
**SB:** To a solution of ligand **LB** (18.0  $\mu\text{mol}$ , 17.0 mg)  $\text{CHCl}_3$  (5.0 mL), a solution of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (18.0  $\mu\text{mol}$ , 5.34 mg) in MeOH (5.0 mL) was added, then the mixture was kept in 50  $^\circ\text{C}$  for 12 h. After cooling to room temperature, excess  $\text{NH}_4\text{PF}_6$  (around 150 mg) was added to generate a yellow precipitate (20.1 mg, 91%).  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  9.00 (s, 4H, tpy- $H^{3',5'}$ ), 8.72 (d,  $J = 8.1$  Hz, 4H, tpy- $H^{3,3''}$ ), 8.27 (d,  $J = 8.4$  Hz, 4H, Ph- $H^G$ ), 8.15 (td,  $J = 7.9, 1.4$  Hz, 4H, tpy- $H^{4,4''}$ ), 8.01 (d,  $J = 8.4$  Hz, 4H, Ph- $H^F$ ), 7.83 (d,  $J = 4.9$  Hz, 4H, tpy- $H^{6,6''}$ ), 7.69 (d,  $J = 8.3$  Hz, 4H, Ph- $H^E$ ), 7.38 (dd,  $J = 7.3, 5.3$  Hz, 4H, tpy- $H^{5,5''}$ ), 7.31 (d,  $J = 8.2$  Hz, 4H, Ph- $H^D$ ), 7.25 – 7.16 (m, 10H, Ph- $H^A$ , Ph- $H^B$ , and Ph- $H^C$ ).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$  156.62, 150.79, 148.95, 148.85, 144.87, 144.46, 143.83, 142.17, 142.04, 138.45, 135.87, 132.75, 131.94, 129.58, 128.88, 128.74, 128.44, 127.79, 127.43, 124.17, 122.21. ESI-MS ( $m/z$ ): calcd. for  $[\text{M}-3\text{PF}_6]^{3+}$  1156.6, found 1156.9; calcd. for  $[\text{M}-4\text{PF}_6]^{4+}$  831.2, found 831.2; calcd. for  $[\text{M}-5\text{PF}_6]^{5+}$  635.9, found 635.9; calcd. for  $[\text{M}-6\text{PF}_6]^{6+}$  505.8, found 505.8.



**Figure S1.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound **3**.



**Figure S2.**  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound **3**.



**Figure S3.**  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of **LB**.

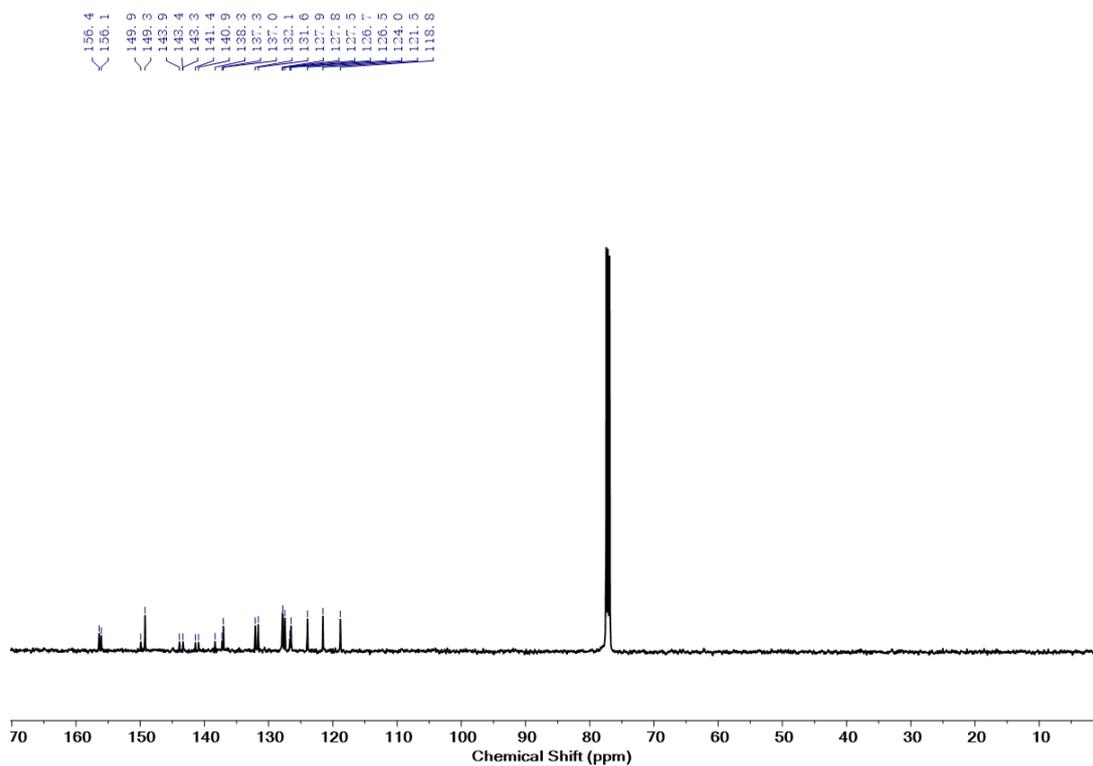


Figure S4.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of LB.

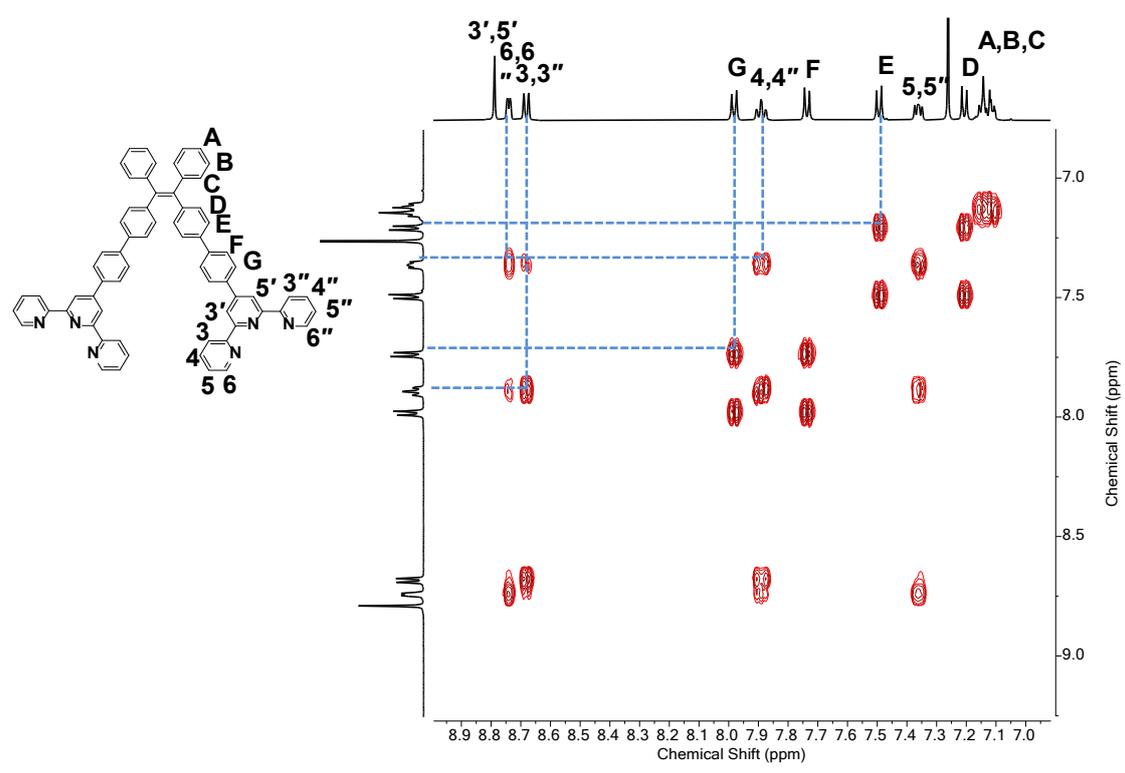


Figure S5. 2D COSY NMR (500 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of LB.

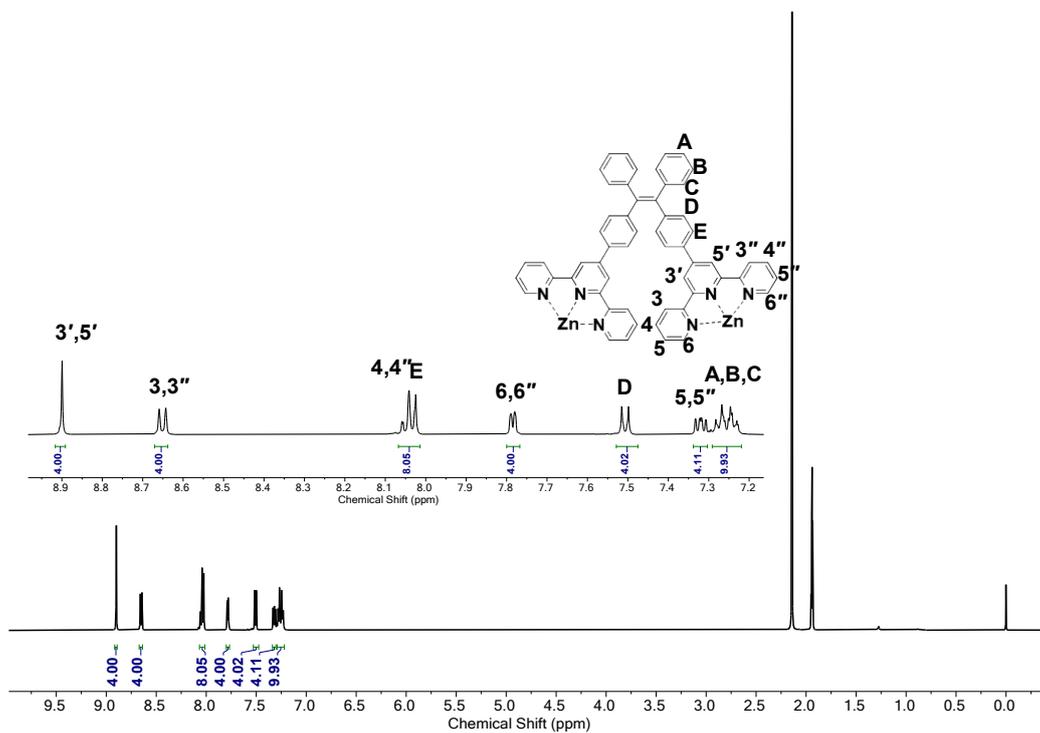


Figure S6. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K) spectrum of SA.

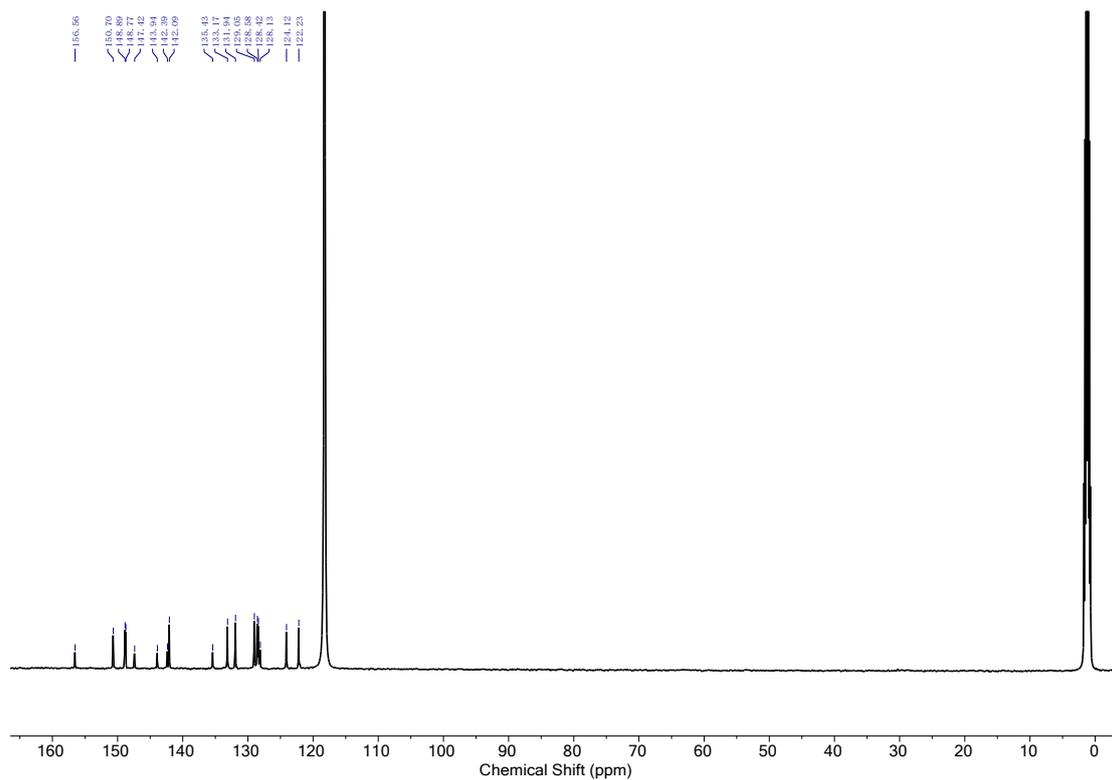
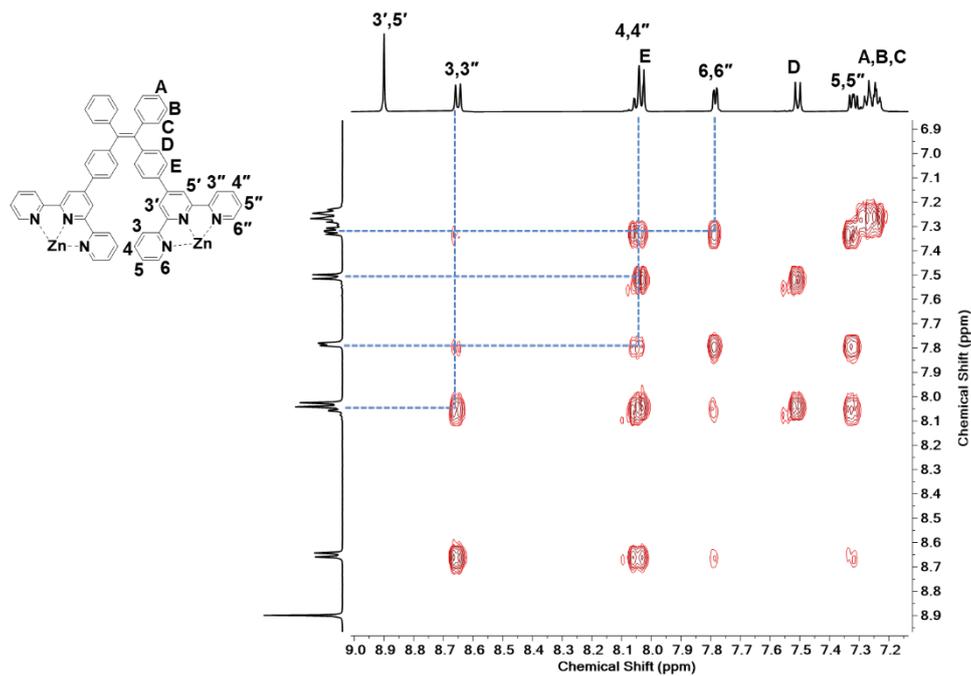
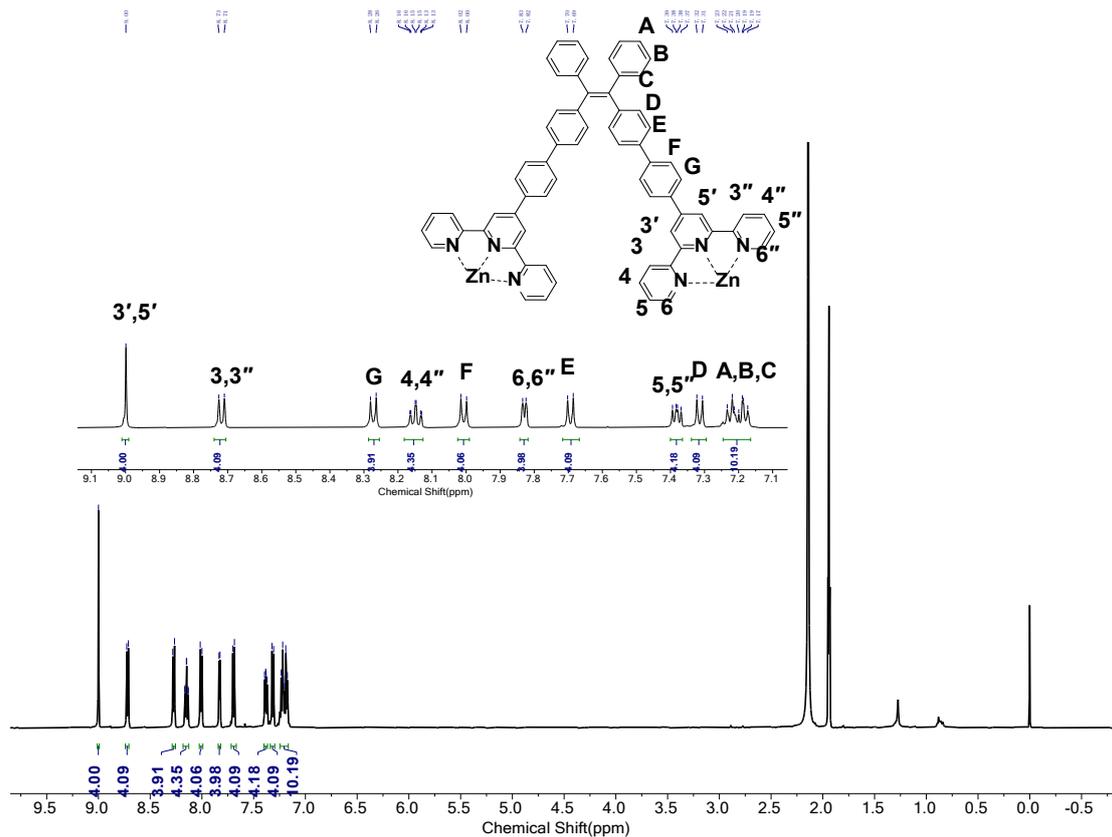


Figure S7. <sup>13</sup>C NMR (125 MHz, CD<sub>3</sub>CN, 300 K) spectrum of SA.



**Figure S8.** 2D COSY NMR (500 MHz, CD<sub>3</sub>CN, 300 K) spectrum of SA.



**Figure S9.** <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K) spectrum of SB.

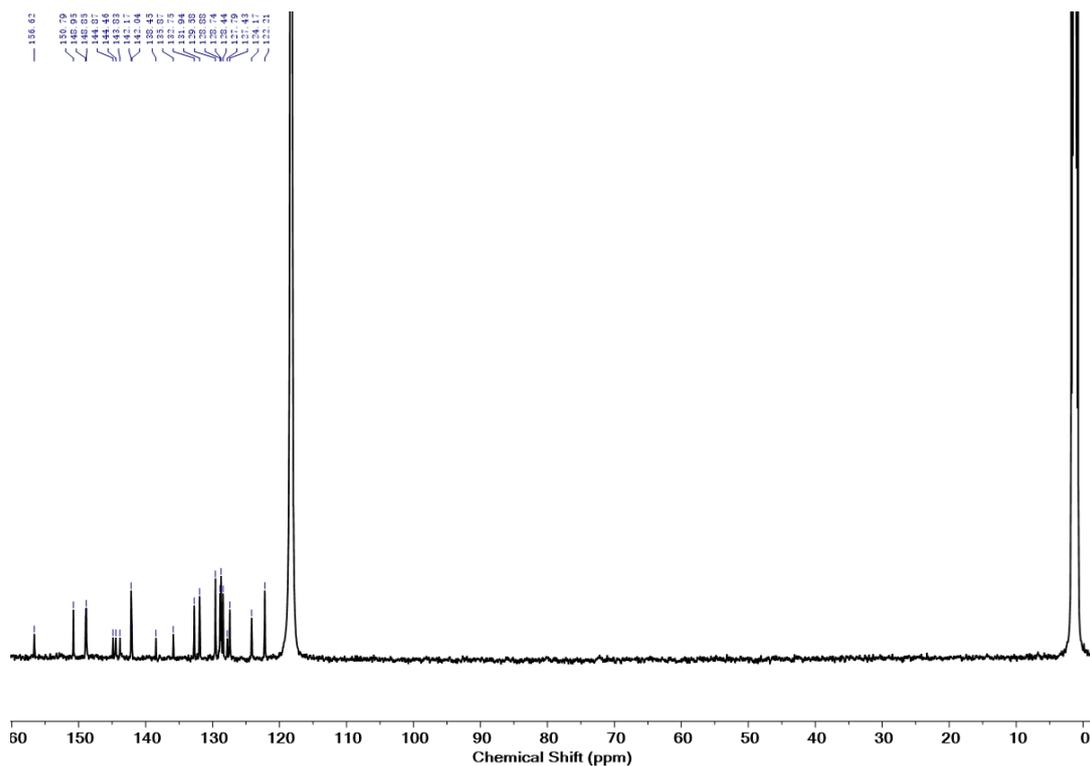


Figure S10.  $^{13}\text{C}$  NMR (125 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectrum of SB.

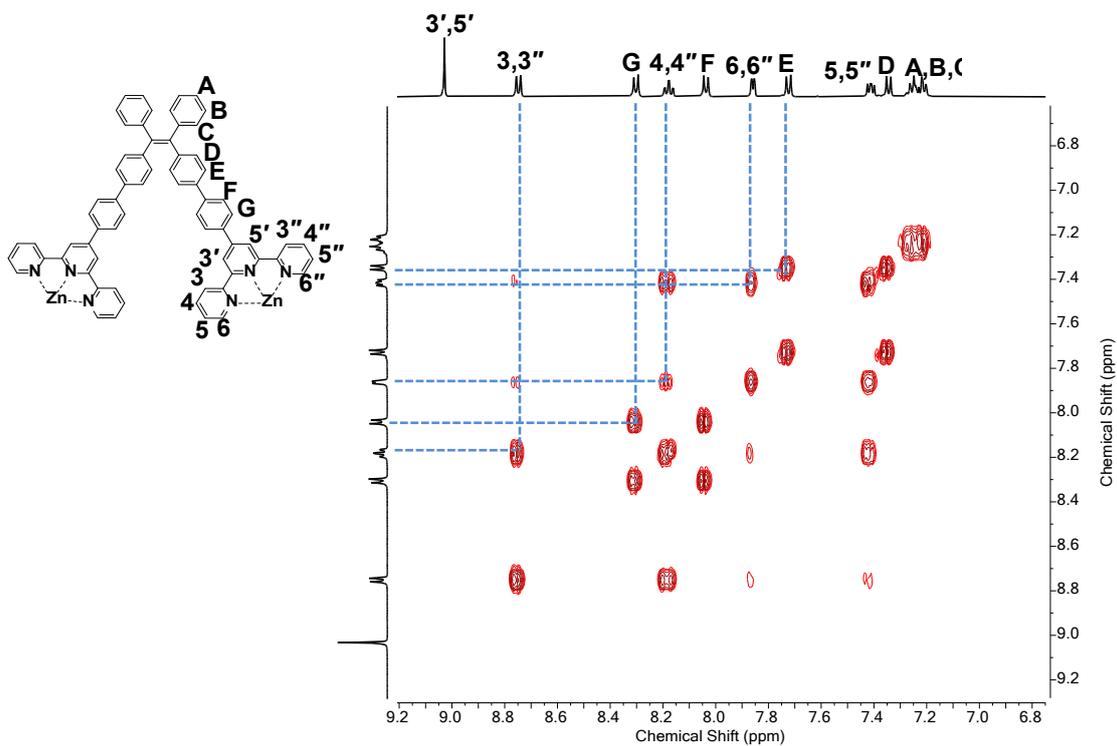
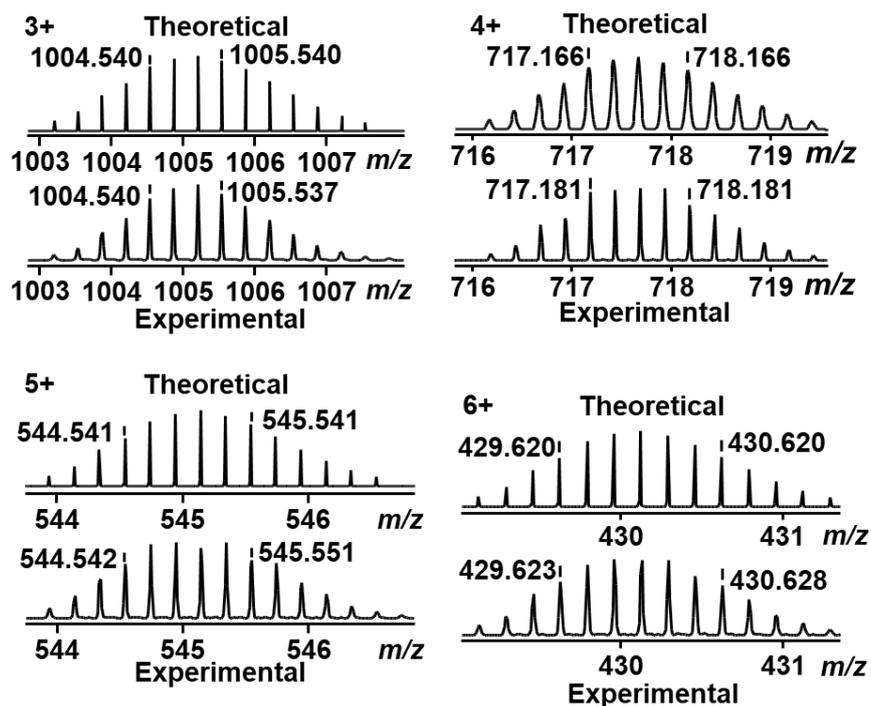
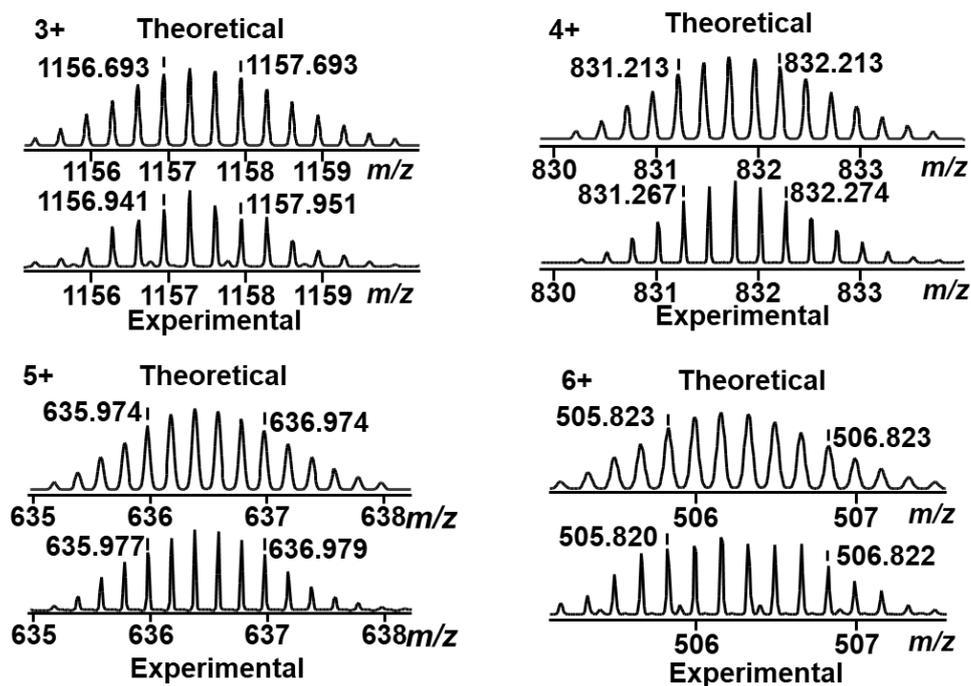


Figure S11. 2D COSY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectrum of SB.



**Figure S12.** Measured (bottom) and calculated (top) isotope patterns for different charge states observed from SA (PF<sub>6</sub><sup>-</sup> as counterion).



**Figure S13.** Measured (bottom) and calculated (top) isotope patterns for different charge states observed from SB (PF<sub>6</sub><sup>-</sup> as counterion).

### 3. UV-vis and Fluorescence Spectra

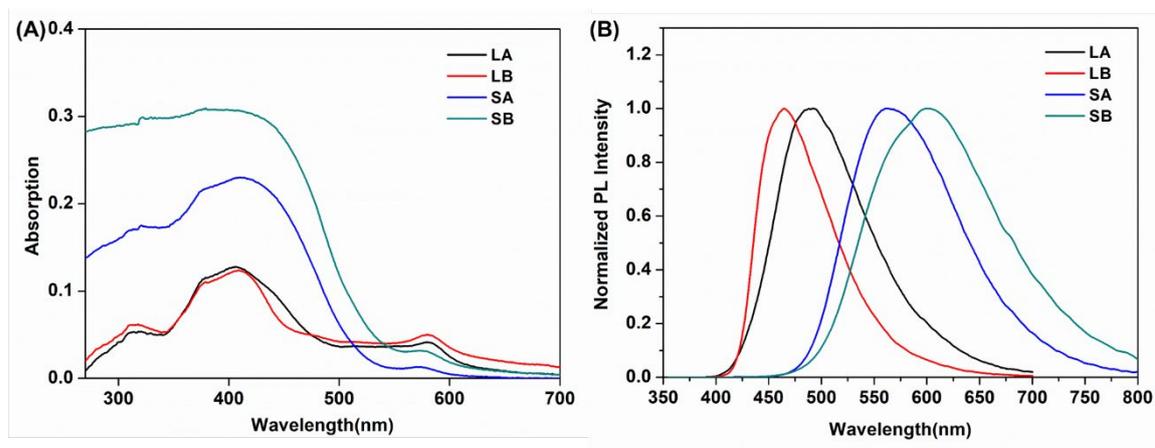


Figure S14. UV-vis (A) and normalized PL intensity (B) of LA, LB, SA, and SB.

Table S1. Absolute quantum yields of SA and SB in aggregation (different diethyl ether fractions,  $c=10^{-6}$  M) and solid states.

	Aggregation states						Solid states
	0%	10%	30%	50%	70%	90%	---
SA	1.27%	1.56%	2.15%	2.28%	3.25%	28.18%	18.35%
SB	1.24%	1.40%	1.71%	1.92%	2.27%	10.88%	7.29%

Table S2. Quantum yields for SA and SB in different solvents.

$\Phi_F$	Acetone	CH <sub>3</sub> NO <sub>2</sub>	CH <sub>3</sub> CN	DMF	DMSO
SA	3.33%	0.61%	2.05%	1.60%	0.99%
SB	1.92%	0.37%	0.68%	0.84%	1.89%

Reference:

1. Ma, J.; Han, N.; Yu, H.; Li, J.; Shi, J.; Wang, S.; Zhang, H.; Wang, M., *Small* **2022**, e2202167.