

## Metal Ions Determined Self-Assembly Using Terpyridine Building Blocks

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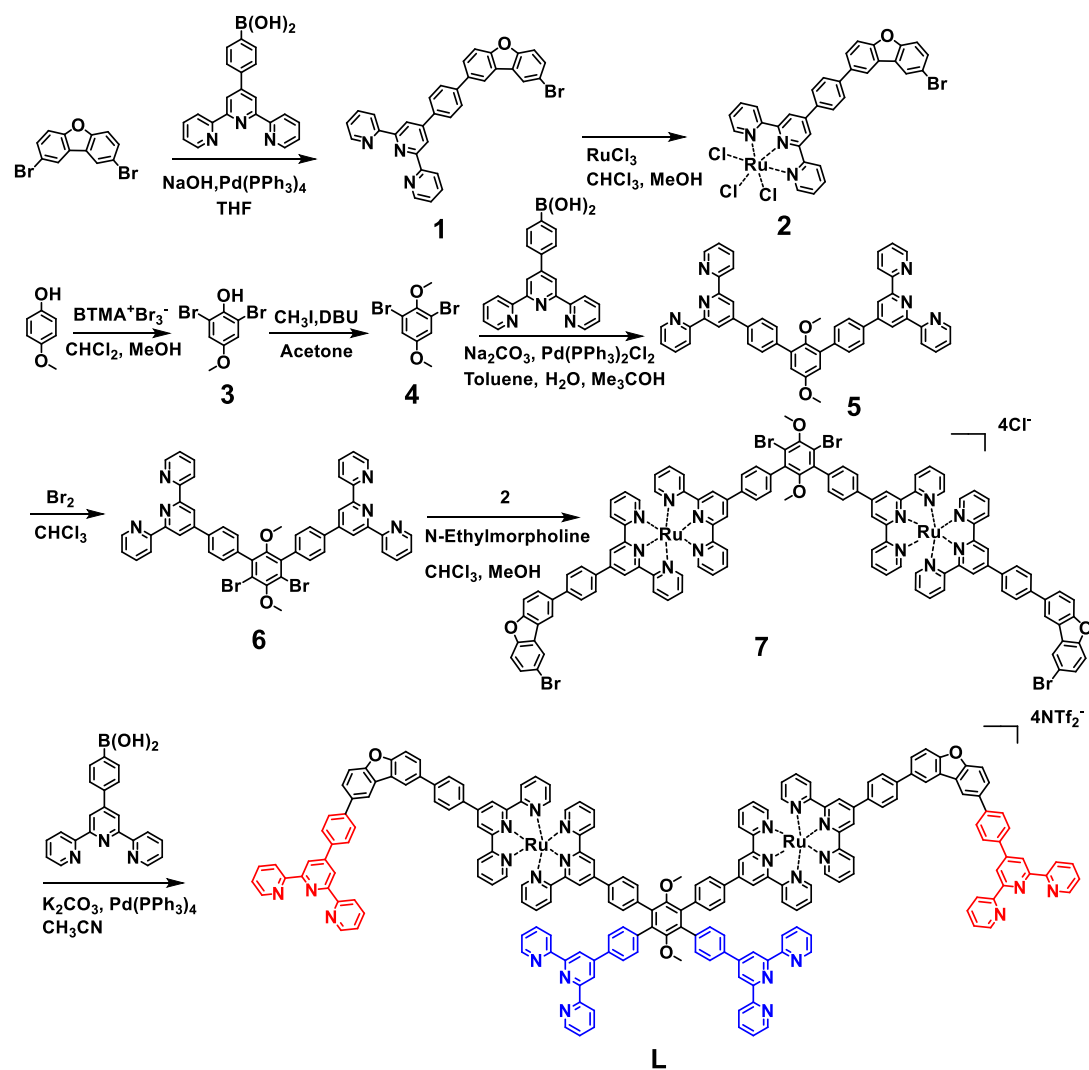
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# 1. Schemes of preparation of ligand L



Scheme S1. Synthesis of ligand L.

## 2. Experimental section

**General procedures.** Chemicals were purchased from Sigma/Aldrich, Fisher Scientific, Energy Chemical, Alfa Aesar and used without further purification. Thin-layer chromatography (TLC) was conducted on flexible sheets (Baker-flex) precoated with  $\text{Al}_2\text{O}_3$  (IB-F) or  $\text{SiO}_2$  (IB2-F). Column chromatography was conducted using basic  $\text{Al}_2\text{O}_3$  Brockman Activity I (60-325 mesh) or  $\text{SiO}_2$  (60-200 mesh) from Fisher Scientific. NMR spectra were recorded on Bruker NMR 400 or 500 MHz spectrometers, using  $\text{CDCl}_3$  and  $\text{CD}_3\text{OD}$  for ligands,  $\text{CD}_3\text{CN}$  for metal products. ESI mass spectrometry (MS) experiments were performed on a Waters Synapt HDMS G2-Si quadrupole/time-of-flight (Q/TOF) tandem mass spectrometer. This instrument contains a triwave device between the Q and TOF analyzers, consisting of three collision cells in the order trap cell, ion mobility cell, and transfer cell. Trap and transfer cells are pressurized with Ar, and the ion mobility cell is pressurized with  $\text{N}_2$  flowing in a direction opposite to that of the entering ions.

**Mass Spectrometry and Ion Mobility.** ESI-MS and TWIM-MS were recorded with a Waters Synapt G2-Si tandem mass spectrometer, using solutions of 0.01 mg sample in 1 mL of  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (1:3, v/v) for ligands or 0.5 mg sample in 1 mL of  $\text{CH}_3\text{CN}/\text{CH}_3\text{OH}$  (3:1, v/v) for complexes. All samples were infused into the ESI source at a flow rate of 6  $\mu\text{L}/\text{min}$  by a syringe pump (KDS-100, KD Scientific). The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 2 kV; sample cone voltage, 35 V; source offset, 42 V; source temperature 150  $^\circ\text{C}$ ; desolvation temperature, 250  $^\circ\text{C}$ ; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h ( $\text{N}_2$ ); source gas control, 0 mL/min; trap gas control, 3 mL/min; helium cell gas control, 120 mL/min; ion mobility (IM) cell gas control, 30 mL/min; sample flow rate, 8  $\mu\text{L}/\text{min}$ ; IM traveling wave height, 25 V; and IM traveling wave velocity, 1200 m/s. Data were collected and analyzed by using Mass Lynx 4.2 and Drift Scope 2.9.

**gMS<sup>2</sup>.** Gradient tandem mass spectrometry was performed under the following conditions: 13+ charged ions of complexes were isolated by quadrupole for the following collision-induced dissociation (CID), in which collision energy was

gradually increased by changing the voltage of trap cell depended on different complexes.

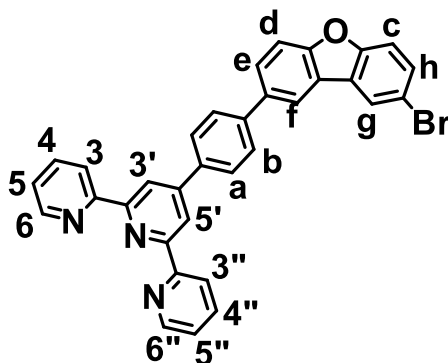
**TEM.** Transmission electron microscopy tests were performed on the JEOL JEM-2100F equipment. The sample solutions were diluted to a concentration of  $10^{-6}$  M using  $\text{CH}_3\text{CN}$ , drop-casted onto a lacey carbon-covered Cu grid (300 mesh, purchased from Ted Pella Inc.) and the extra solution was absorbed by filter paper to avoid aggregation. And the size statistics were obtained by using the software image J.

**AFM.** AFM imaging was performed on a Bruker Dimension Icon AFM system with ScanAsyst and the data was processed by NanoScope Analysis version 2.0 (Bruker Software, Inc.). The sample was diluted to a concentration of  $5 \times 10^{-6}$  M using  $\text{CH}_3\text{CN}$ , dropped on freshly cleaved mica surface, and then dried in the air. Silicon cantilevers tip with a spring constant of around 0.1 N/m was used for the experiments.

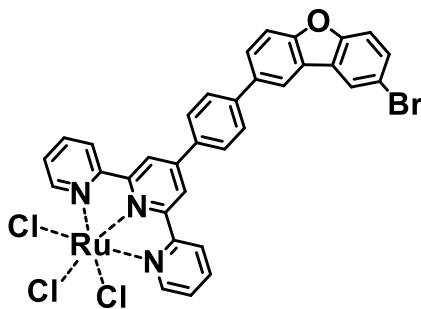
**UV-vis absorption and fluorescence properties.** UV-vis absorption spectra were recorded on a Persee TU-1900 UV-visible spectrophotometer at room temperature ( $10^{-6}$  M in  $\text{CH}_3\text{CN}$ ) and were corrected with the background spectrum of the solvent. Fluorescence properties were performed on Edinburgh-FS5 Fluorescence spectrometer at 73K ( $10^{-6}$  M in  $\text{CH}_3\text{CN}$ ).

**Cyclic Voltammetry.** Cyclic voltammetry measurements were performed on a Princeton VersaSTAT 3F potentiostat with a standard three-electrode configuration using a glass-carbon working electrode, a platinum-rod auxiliary electrode, and a reference Ag/AgCl electrode. The electrochemical properties of these two complexes in  $\text{CN}_3\text{CN}$  ( $10^{-6}$  M) were studied in a three-electrode electrochemical cell with  $\text{Bu}_4\text{NPF}_6$  (0.1 M) as an electrolyte.

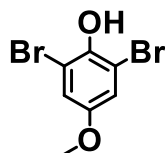
### 3. Synthesis of the compounds and supramolecules



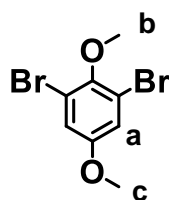
**Compound 1**, 2,8-Dibromodibenzofuran (1.00 g, 3.07 mmol), 4'-(4-boronatophenyl)-[2,2':6',2'']terpyridine (1.19 g, 3.37 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (108 mg, 0.154 mmol) and sodium carbonate (976 mg, 9.21 mmol) were added into a 200 mL three-necked flask. 50 mL toluene, 30 mL H<sub>2</sub>O and 15 mL tert-butyl alcohol were added under N<sub>2</sub>. The mixture was stirred at 85 °C for 8 h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then concentrated in vacuo, the residue was purified by flash column chromatography (silica gel), eluting with CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH (100:0.75, v/v) to give the product as 1.27 g white solid (yield 75%). <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 300 K) δ 8.82 (s, 2H, *Tpy*-H<sup>3',5'</sup>), 8.76 (d, *J* = 5.5 Hz, 2H, *Tpy*-H<sup>6,6''</sup>), 8.70 (d, *J* = 7.9 Hz, 2H, *Tpy*-H<sup>3,3''</sup>), 8.17 (d, *J* = 6.6 Hz, 2H, *Ph*-H<sup>b</sup>), 8.05 (d, *J* = 8.3 Hz, 2H, *Ph*-H<sup>f,g</sup>), 7.90 (t, *J* = 7.7 Hz, 2H, *Tpy*-H<sup>4,4''</sup>), 7.80 (d, *J* = 8.4 Hz, 2H, *Ph*-H<sup>a</sup>), 7.79 – 7.77 (m, 1H, *Ph*-H<sup>d</sup>), 7.65 (d, *J* = 8.5 Hz, 1H, *Ph*-H<sup>e</sup>), 7.58 (d, *J* = 8.7 Hz, 1H, *Ph*-H<sup>h</sup>), 7.48 (d, *J* = 8.7 Hz, 1H, *Ph*-H<sup>c</sup>), 7.40 – 7.35 (m, 2H, *Tpy*-H<sup>5,5''</sup>); <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, 300 K) δ 156.32, 156.03, 149.81, 149.21, 137.13, 129.07, 128.14 – 127.66, 127.4, 127.27, 123.92, 123.69 – 123.63, 121.58, 119.12, 118.85; ESI-TOF (*m/z*): Calcd. for [C<sub>33</sub>H<sub>20</sub>BrN<sub>3</sub>O+H]<sup>+</sup>: 554.45. Found: 554.45.



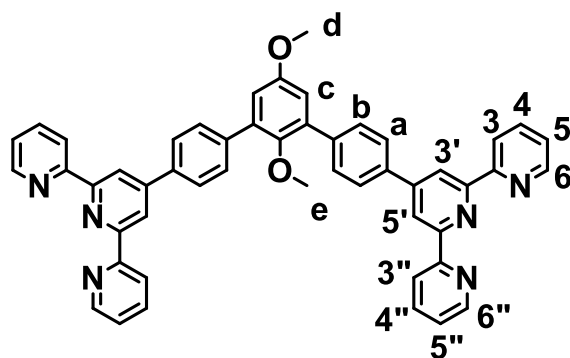
**Compound 2**, Compound 1 (415.5 mg, 0.75 mmol) and  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  (504.5 mg, 2.25 mmol) were mixed in 150 mL  $\text{CHCl}_3/\text{CH}_3\text{OH}$  (v/v, 1:1). The mixture was stirred at 65 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with  $\text{CH}_3\text{OH}$  and  $\text{H}_2\text{O}$  to afford 485 mg compound 2 (yield 85%).



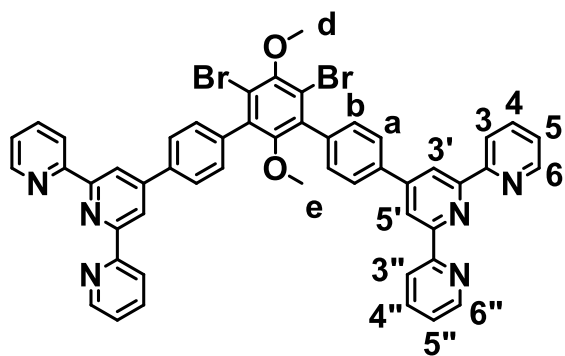
**Compound 3**, Compound 3 was synthesized according to the reported literature.<sup>1</sup>



**Compound 4**, Compound 3 (5.20 g, 18.4 mmol) was added to a 100 mL single bottomed flask, 50 mL of acetone was poured, and then 1,8-diazabicycloundec-7-ene (13.8 mL, 92.2 mmol) was added dropwise to the flask and stirred at room temperature for 30 min. After the reaction was completed, 2 mol/L of HCl solution was added to neutralize the reaction, and when the solution became clarified, the organic phase was extracted with ether. The combined organic layer was washed with brine, dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and then concentrated in vacuo, the residue was purified by flash column chromatography (silica gel), eluting with petroleum ether to give the product as 1.27 g white crystals (yield 75%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  7.05 (s, 2H, *Ph-H*<sup>c</sup>), 3.83 (s, 3H, *-OCH}\_3\text{-H*<sup>a</sup>), 3.76 (s, 3H, *-OCH}\_3\text{-H*<sup>b</sup>);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ , 300 K)  $\delta$  156.42, 148.11, 118.26, 117.92, 60.82, 56.03.



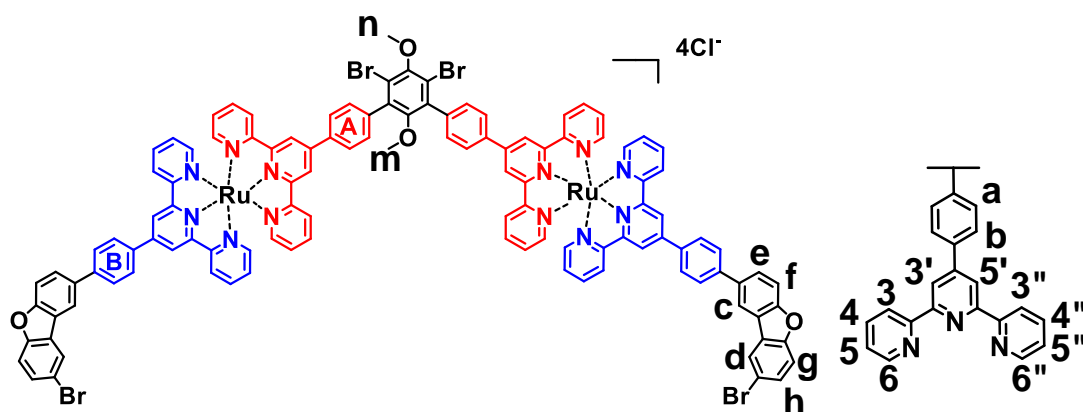
**Compound 5**, Compound 4 (440.8 mg, 1.5 mmol), 4'-(4-boronatophenyl)-[2,2':6',2'']terpyridine (1.59 g, 4.5 mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (105 mg, 0.15 mmol) and sodium carbonate (954 mg, 9 mmol) were added into a 250 mL three-necked flask. 60 mL toluene, 10 mL H<sub>2</sub>O and 25 mL tert-butyl alcohol were added under N<sub>2</sub>. The mixture was stirred at 85 °C for 48 h. After cooling to room temperature, the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub>. The combined organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and then concentrated in vacuo, the residue was purified by flash column chromatography (silica gel), eluting with CH<sub>2</sub>Cl<sub>2</sub>: CH<sub>3</sub>OH (100:1, v/v) to give the product as 880 mg white solid (yield 78%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 300 K) δ 8.82 (s, 4H, *Tpy-H*<sup>3',5'</sup>), 8.75 (d, *J* = 5.6 Hz, 4H, *Tpy-H*<sup>6,6''</sup>), 8.70 (d, *J* = 7.9 Hz, 4H, *Tpy-H*<sup>3,3''</sup>), 8.01 (d, *J* = 8.4 Hz, 4H, *Ph-H*<sup>*j*</sup>), 7.89 (t, *J* = 7.7 Hz, 4H, *Tpy-H*<sup>4,4''</sup>), 7.81 (d, *J* = 8.4 Hz, 4H, *Ph-H*<sup>*k*</sup>), 7.39 – 7.33 (t, 4H, *Tpy-H*<sup>5,5''</sup>), 6.99 (s, 2H, *Ph-H*<sup>*c*</sup>), 3.91 (s, 3H, -OCH<sub>3</sub>-H<sup>*a*</sup>), 3.19 (s, 3H, -OCH<sub>3</sub>-H<sup>*b*</sup>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, 300 K) δ 156.42, 155.86, 150.08, 149.06, 139.41, 137.41, 137.05, 136.02, 129.92, 127.28, 123.93, 121.48, 118.97, 115.50, 60.83, 55.87; ESI-TOF (*m/z*): Calcd. for [C<sub>50</sub>H<sub>36</sub>N<sub>6</sub>O<sub>2</sub>+H]<sup>+</sup>: 753.88. Found: 753.88.



**Compound 6**, To a stirred solution of compound 5 (400 mg, 0.53 mmol) in CHCl<sub>3</sub> (30

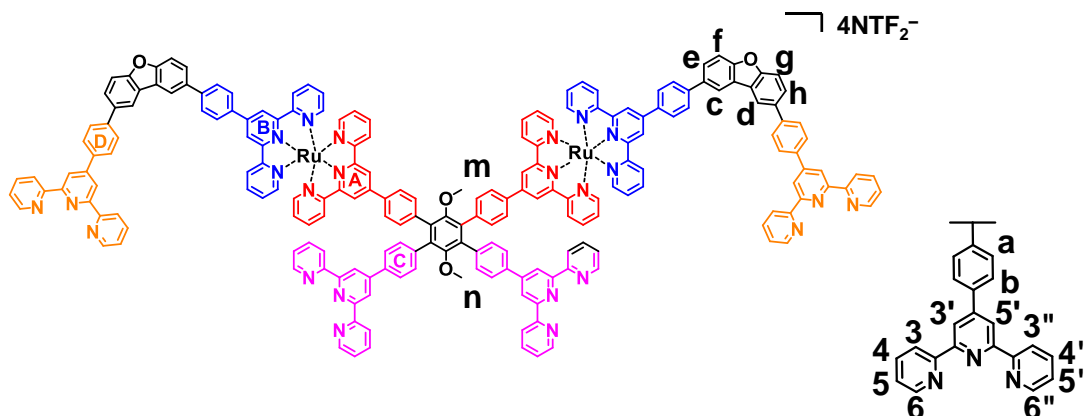


mL) at room temperature, a solution of Br<sub>2</sub> (0.64 g, 4 mmol) in CHCl<sub>3</sub> (15 mL) was added drop-wise. After stirring at 90 °C for 48 h, the reaction mixture was washed with saturated Na<sub>2</sub>SO<sub>3</sub> solution until colorless, dried over anhydrous MgSO<sub>4</sub>, and then concentrated in vacuo to give the product as 310 mg light purple solid (yield 64%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.81 (s, 4H, *Tpy-H*<sup>3',5'</sup>), 8.74 (d, *J* = 5.6 Hz, 4H, *Tpy-H*<sup>6,6''</sup>), 8.69 (d, *J* = 7.9 Hz, 4H, *Tpy-H*<sup>3,3''</sup>), 8.00 (d, *J* = 8.3 Hz, 4H, *Ph-H*<sup>b</sup>), 7.89 (t, *J* = 7.7 Hz, 4H, *Tpy-H*<sup>4,4''</sup>), 7.53 (d, *J* = 8.3 Hz, 4H, *Ph-H*<sup>a</sup>), 7.39 – 7.34 (t, 4H, *Tpy-H*<sup>5,5''</sup>), 3.99 (s, 3H, -OCH<sub>3</sub>-H<sup>d</sup>), 3.06 (s, 3H, -OCH<sub>3</sub>-H<sup>e</sup>); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.22, 155.99, 150.08, 149.18, 138.19, 137.61, 137.07, 130.59, 127.19, 123.94, 121.43, 119.50, 119.12, 77.33, 77.07, 76.75, 61.00, 60.60; ESI-TOF (*m/z*): Calcd. for [C<sub>50</sub>H<sub>36</sub>Br<sub>2</sub>N<sub>6</sub>O<sub>2</sub>]: 910.67. Found: 910.67.

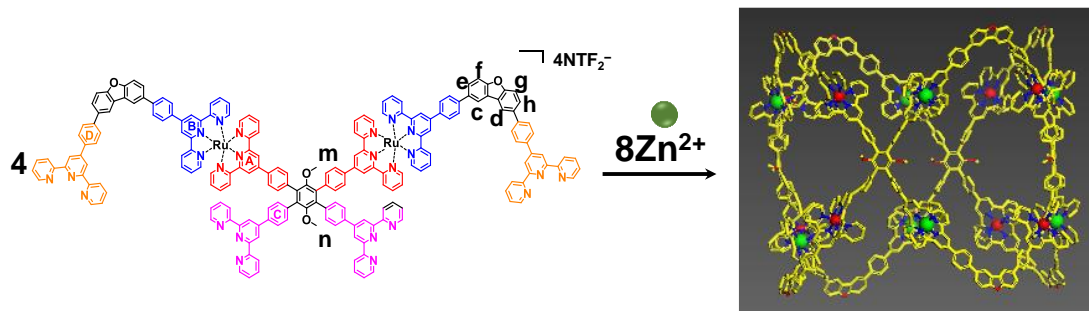


**Compound 7:** To a mixture of compound 6 (200 mg, 0.22 mmol) and compound 2 (502 mg, 0.66 mmol) in CHCl<sub>3</sub>/MeOH (120 mL, *v/v*, 1:1), 500 µl of N-ethylmorpholine were added as reductant. After refluxing for 48 h, the solution was concentrated in vacuo to give a red solid that was chromatographed (Al<sub>2</sub>O<sub>3</sub>) using a mixed solvent of CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>3</sub>OH (100:1.75, *v/v*) to produce the product as 320 mg red powder (yield 62%). ESI-TOF (*m/z*): 555.37 [M-4Cl<sup>-</sup>]<sup>4+</sup> (calcd *m/z*: 555.37), 752.33 [M-3Cl<sup>-</sup>]<sup>3+</sup> (calcd *m/z*: 752.33), 1146.25 [M-2Cl<sup>-</sup>]<sup>2+</sup> (calcd *m/z*: 1146.25); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>OD, 300 K) δ 9.40 (d, *J* = 6.5 Hz, 8H, *Tpy-H*<sup>A,B3,3'</sup>), 8.95 (dd, *J* = 7.8, 4.1 Hz, 8H, *Tpy-H*<sup>A,B3,3''</sup>), 8.54 (s, 2H, *Ph-H*<sup>c</sup>), 8.47 (d, *J* = 8.1 Hz, 8H, *Ph-H*<sup>A,Ba</sup>), 8.40 (d, *J* = 1.9 Hz, 2H, *Ph-H*<sup>d</sup>), 8.16 (d, *J* = 8.3 Hz, 4H, *Ph-H*<sup>Ab</sup>), 8.05 (dd, *J* = 13.8, 5.9 Hz, 10H, *Tpy-H*<sup>A,B4,4''</sup>, *Ph-H*<sup>e</sup>), 7.84 – 7.78 (m, 6H, *Ph-H*<sup>Bb</sup>, *Ph-H*<sup>f</sup>), 7.69 (dd, *J* = 8.7, 2.0 Hz, 2H, *Ph-*

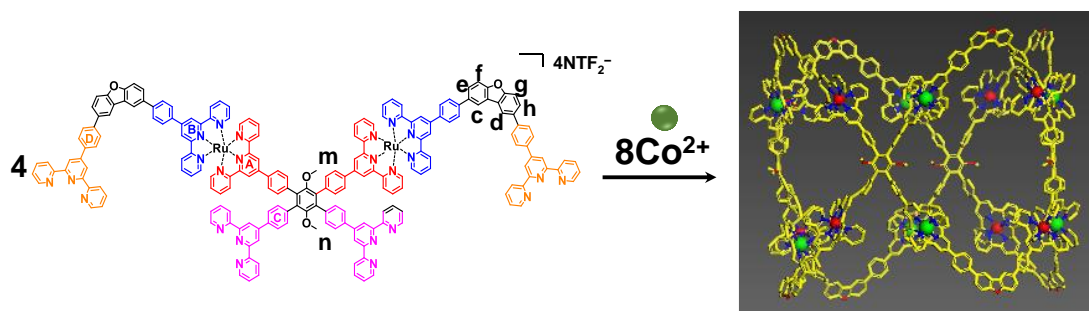
$H^h$ ), 7.64 – 7.59 (m, 10H,  $Tpy-H^{A,B6,6''}$ ,  $Ph-H^g$ ), 7.33 – 7.29 (m, 8H,  $Tpy-H^{A,B5,5''}$ ), 4.06 (d,  $J = 19.9$  Hz, 6H,  $-OCH_3-H^{m,n}$ ).



**Ligand L:** To a solution of 4'-(4-boronatophenyl)-[2,2':6',2'']terpyridine (179 mg, 0.508 mmol) and compound **7** (100 mg, 0.042 mmol) in  $CH_3CN/CH_3OH$  (40 mL,  $v/v$ , 1:1), aqueous  $K_2CO_3$  (70.2 mg, 0.508 mmol, 0.5 mL) was added. The system was degassed for 10 minutes, and then  $Pd(PPh_3)_4$  (38 mg, 0.034 mmol) was added. After refluxing for 4 days under  $N_2$ , the solvent was removed in vacuo to give a residue that was purified by flash column chromatography ( $Al_2O_3$ ) with  $CH_2Cl_2/MeOH$  (100:4.5,  $v/v$ ) to give **L**. Then  $LiNTf_2$  was added to generate red precipitates, which were filtered and washed with  $H_2O$  and  $CH_3OH$  to obtain 75 mg reddish product (yield 43%). ESI-TOF ( $m/z$ ): 783.88  $[M-4 NTf_2^-]^{4+}$  (calcd  $m/z$ : 783.88), 1138.56  $[M-3 NTf_2^-]^{3+}$  (calcd  $m/z$ : 1138.56);  $^1H$  NMR (400 MHz,  $CD_3CN$ , 300 K)  $\delta$  9.11 (s, 4H,  $Tpy-H^{A3'5'}$ ), 9.03 (s, 4H,  $Tpy-H^{B3'5'}$ ), 8.87 (s, 4H,  $Tpy-H^{C3'5'}$ ), 8.80 (s, 4H,  $Tpy-H^{D3'5'}$ ), 8.79 – 8.75 (m, 8H,  $Tpy-H^{A,B3,3''}$ ), 8.69 (d,  $J = 8.4$  Hz, 12H,  $Tpy-H^{C,D3,3''}$ ,  $Ph-H^{c,d}$ ), 8.63 (d,  $J = 7.7$  Hz, 8H,  $Tpy-H^{C,D6,6''}$ ), 8.39 (d,  $J = 8.4$  Hz, 4H,  $Tpy-H^{Aa}$ ), 8.21 (d,  $J = 3.6$  Hz, 8H,  $Tpy-H^{Ba,Ab}$ ), 8.11 (d,  $J = 8.4$  Hz, 2H,  $Ph-H^e$ ), 8.02 (d,  $J = 8.1$  Hz, 8H,  $Tpy-H^{Ca,Da}$ ), 7.98 (d,  $J = 8.0$  Hz, 8H,  $Tpy-H^{A,B3,3''}$ ), 7.93 (dd,  $J = 8.5, 5.4$  Hz, 16H,  $Tpy-H^{C,D4,4''}, C,D6,6''$ ), 7.87 – 7.82 (m, 4H,  $Ph-H^{f,h}$ ), 7.77 (d,  $J = 8.4$  Hz, 4H,  $Tpy-H^{Ba}$ ), 7.65 (s, 2H,  $H^g$ ), 7.51 – 7.47 (m, 8H,  $Tpy-H^{Cb,Db}$ ), 7.44 – 7.41 (m, 8H,  $Tpy-H^{C,D5,5''}$ ), 7.19 – 7.13 (m, 9H,  $Tpy-H^{A,B5,5''}$ ), 3.22 (s, 3H,  $-OCH_3-H^m$ ), 3.16 (s, 3H,  $-OCH_3-H^n$ ).

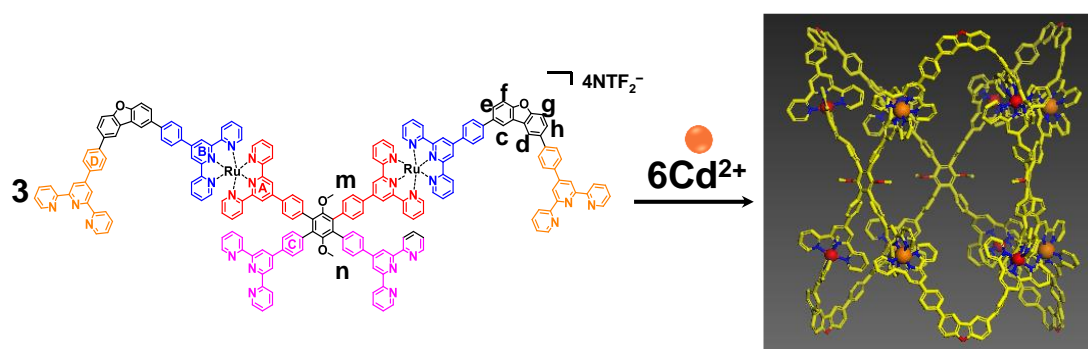


**Zn<sub>8</sub>L<sub>4</sub>:** To a solution of **L** (10 mg, 2.34  $\mu\text{mol}$ ) in  $\text{CH}_3\text{CN}$  (12 mL),  $\text{Zn}(\text{NTf}_2)_2$  (2.94 mg, 4.68  $\mu\text{mol}$ ) in  $\text{CH}_3\text{OH}$  was added; then the mixture was stirred at 60  $^\circ\text{C}$  for 8 hours. Subsequently,  $\text{LiNTf}_2$  was added to generate red precipitates, which were filtered and washed with  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  to obtain 11.3 mg reddish product (yield 98%). ESI-TOF ( $m/z$ ): 1555.65  $[\text{M}-12\text{NTf}_2^-]^{12+}$  (calcd  $m/z$ : 1555.65), 1414.44  $[\text{M}-13\text{NTf}_2^-]^{13+}$  (calcd  $m/z$ : 1414.44), 1293.40  $[\text{M}-14\text{NTf}_2^-]^{14+}$  (calcd  $m/z$ : 1293.40), 1188.49  $[\text{M}-15\text{NTf}_2^-]^{15+}$  (calcd  $m/z$ : 1188.49), 1096.71  $[\text{M}-16\text{NTf}_2^-]^{16+}$  (calcd  $m/z$ : 1096.71), 1015.72  $[\text{M}-17\text{NTf}_2^-]^{17+}$  (calcd  $m/z$ : 1015.72), 943.73  $[\text{M}-18\text{NTf}_2^-]^{18+}$  (calcd  $m/z$ : 943.73), 879.31  $[\text{M}-19\text{NTf}_2^-]^{19+}$  (calcd  $m/z$ : 879.31);  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{CN}$ , 300 K)  $\delta$  9.17 – 9.06 (br, 8H,  $\text{Tpy-H}^{A,B,C,D3'5'}$ ), 8.80 – 8.74 (br,  $J = 22.4$  Hz, 10H,  $\text{Tpy-H}^{A,B,C,D3,3''}$ ,  $\text{Ph-H}^{c,d}$ ), 8.47 – 8.39 (br, 4H,  $\text{Tpy-H}^{A,B4,4''}$ ), 8.35 – 8.30 (br, 4H,  $\text{Tpy-H}^{\text{Ca,Da}}$ ), 8.26 – 8.18 (br, 8H,  $\text{Tpy-H}^{A,B6,6''}$ ,  $\text{Tpy-H}^{\text{Cb,Db,Aa,Ba}}$ ), 8.12 – 8.09 (br, 2H,  $\text{Ph-H}^e$ ), 8.01 – 7.85 (br,  $J = 33.7$  Hz, 14H,  $\text{Tpy-H}^{A,B6,6''}, \text{C,D4,4''}$ ,  $\text{Ph-H}^h$ ), 7.52 – 7.38 (br,  $J = 4.2$  Hz, 10H,  $\text{Tpy-H}^{A,B5,5''}, \text{C,D6,6''}$ ,  $\text{Ph-H}^g$ ), 7.25 – 7.16 (br, 4H,  $\text{Tpy-H}^{\text{C,D5,5''}}$ ), 3.45 (d,  $J = 7.0$  Hz, 3H,  $-\text{OCH}_3\text{-H}^{m,n}$ ).



**Co<sub>8</sub>L<sub>4</sub>:** To a solution of **L** (8 mg, 1.87  $\mu\text{mol}$ ) in  $\text{CH}_3\text{CN}$  (2 mL),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  (0.89 mg, 3.76  $\mu\text{mol}$ ) in  $\text{CH}_3\text{OH}$  was added; then the mixture was stirred at 60  $^\circ\text{C}$  for 8 hours. Subsequently,  $\text{LiNTf}_2$  was added to generate red precipitates, which were filtered and washed with  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{OH}$  to obtain 7.8 mg reddish product (98% yield). ESI-TOF

(*m/z*): 1989.75 [M-11 NTf<sub>2</sub><sup>-</sup>]<sup>11+</sup> (calcd *m/z*: 1989.75) 1551.36 [M-12NTf<sub>2</sub><sup>-</sup>]<sup>12+</sup> (calcd *m/z*: 1551.36), 1410.47 [M-13NTf<sub>2</sub><sup>-</sup>]<sup>13+</sup> (calcd *m/z*: 1410.47), 1289.71 [M-14NTf<sub>2</sub><sup>-</sup>]<sup>14+</sup> (calcd *m/z*: 1289.71), 1185.06 [M-15NTf<sub>2</sub><sup>-</sup>]<sup>15+</sup> (calcd *m/z*: 1185.06), 1093.48 [M-16NTf<sub>2</sub><sup>-</sup>]<sup>16+</sup> (calcd *m/z*: 1093.48), 1012.68 [M-17NTf<sub>2</sub><sup>-</sup>]<sup>17+</sup> (calcd *m/z*: 1012.68), 940.86 [M-18NTf<sub>2</sub><sup>-</sup>]<sup>18+</sup> (calcd *m/z*: 940.86), 876.60 [M-19NTf<sub>2</sub><sup>-</sup>]<sup>19+</sup> (calcd *m/z*: 876.60).



**Cd<sub>6</sub>L<sub>3</sub>:** To a solution of **L** (9 mg, 2.11 μmol) in CH<sub>3</sub>CN (12 mL), Cd(NO<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O (1.3 mg, 4.22 μmol) in CH<sub>3</sub>OH was added; then the mixture was stirred at 60 °C for 8 hours. Subsequently, LiNTf<sub>2</sub> was added to generate red precipitates, which were filtered and washed with H<sub>2</sub>O and CH<sub>3</sub>OH to obtain 9.5 mg reddish product (yield 98%). ESI-TOF (*m/z*): 1400.29 [M-10NTf<sub>2</sub><sup>-</sup>]<sup>10+</sup> (calcd *m/z*: 1400.29), 1247.53 [M-11NTf<sub>2</sub><sup>-</sup>]<sup>11+</sup> (calcd *m/z*: 1247.53), 1120.22 [M-12NTf<sub>2</sub><sup>-</sup>]<sup>12+</sup> (calcd *m/z*: 1120.22), 1012.50 [M-13NTf<sub>2</sub><sup>-</sup>]<sup>13+</sup> (calcd *m/z*: 1012.50), 920.17 [M-14NTf<sub>2</sub><sup>-</sup>]<sup>14+</sup> (calcd *m/z*: 920.17), 840.15 [M-15NTf<sub>2</sub><sup>-</sup>]<sup>15+</sup> (calcd *m/z*: 840.15), 770.13 [M-16NTf<sub>2</sub><sup>-</sup>]<sup>16+</sup> (calcd *m/z*: 770.13), 708.35 [M-17NTf<sub>2</sub><sup>-</sup>]<sup>17+</sup> (calcd *m/z*: 708.35); <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 300 K) δ 9.17 – 9.02 (br, *J* = 29.5 Hz, 8H, *Tpy-H<sup>A,B,C,D3,3'</sup>*), 8.82 – 8.66 (br, 10H, *Tpy-H<sup>A,B,C,D3,3'</sup>*, *Ph-H<sup>c,d</sup>*), 8.41 – 8.16 (br, *J* = 80.4 Hz, 17H, *Tpy-H<sup>A,B4,4'',A,B5,5''</sup>*, *Tpy-H<sup>Aa,Ba,Cb,Db</sup>*, *Ph-H<sup>e</sup>*), 8.02 – 7.83 (br, 13H, *Tpy-H<sup>C,D4,4''</sup>*, *Ph-H<sup>Ab,Bb,Ca,Da</sup>*, *Ph-H<sup>h</sup>*), 7.51 – 7.41 (br, 9H, *Tpy-H<sup>A,B5,5''</sup>*, *Tpy-H<sup>C,D6,6''</sup>*, *Ph-H<sup>g</sup>*), 7.24 – 7.17 (br, 4H, *Tpy-H<sup>C,D5,5''</sup>*), 3.27 (s, 3H, -OCH<sub>3</sub>-*H<sup>m,n</sup>*).

4. ESI-MS spectra data of compounds ( $\text{Cl}^-$  or  $\text{NTf}_2^-$  as counterion)

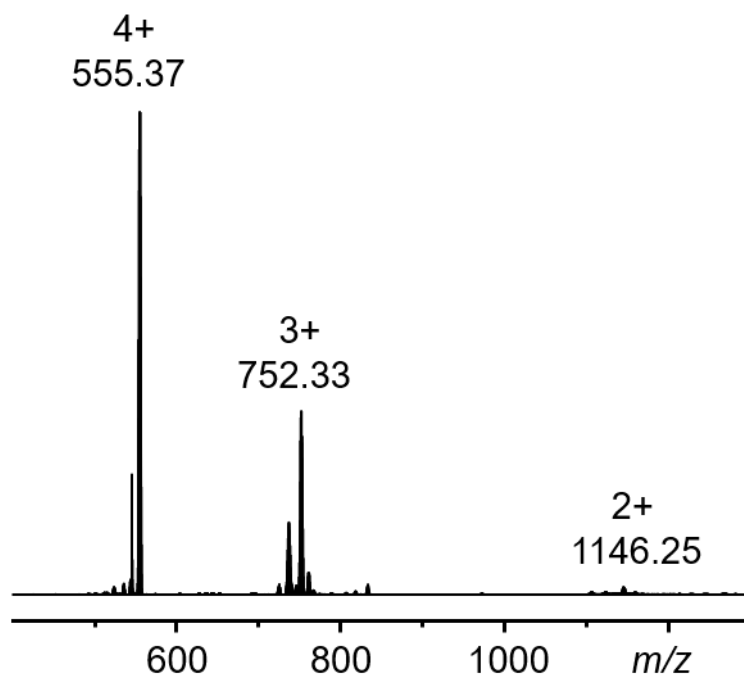


Figure S1. ESI-MS of compound 7 ( $\text{Cl}^-$  as counterion).

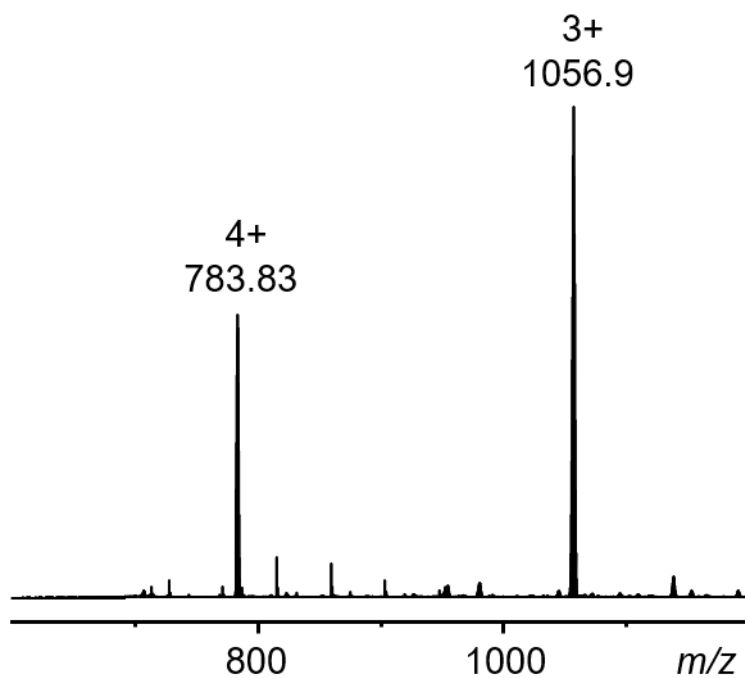
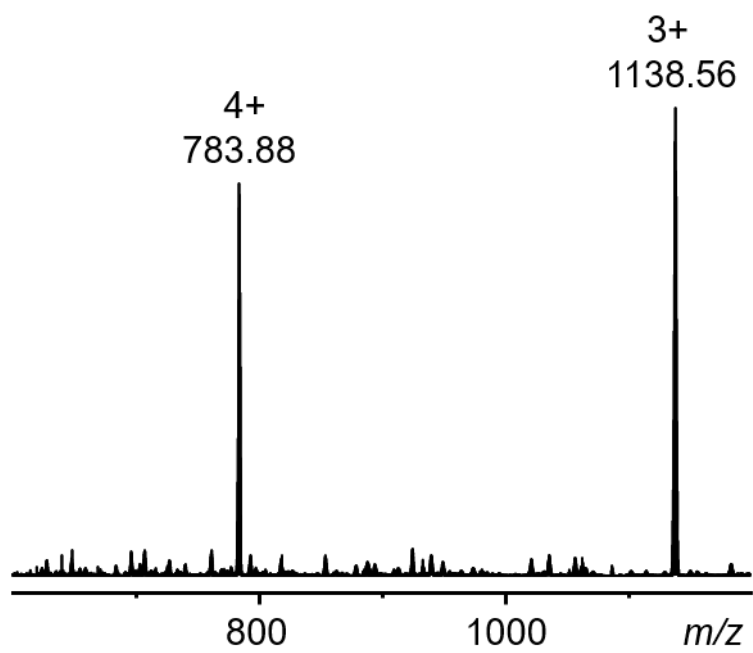


Figure S2. ESI-MS of ligand L ( $\text{Cl}^-$  as counterion).



**Figure S3.** ESI-MS of **ligand L** ( $\text{NTf}_2^-$  as counterion).

5. ESI-MS spectra data of supramolecules ( $\text{NTf}_2^-$  as counterion)

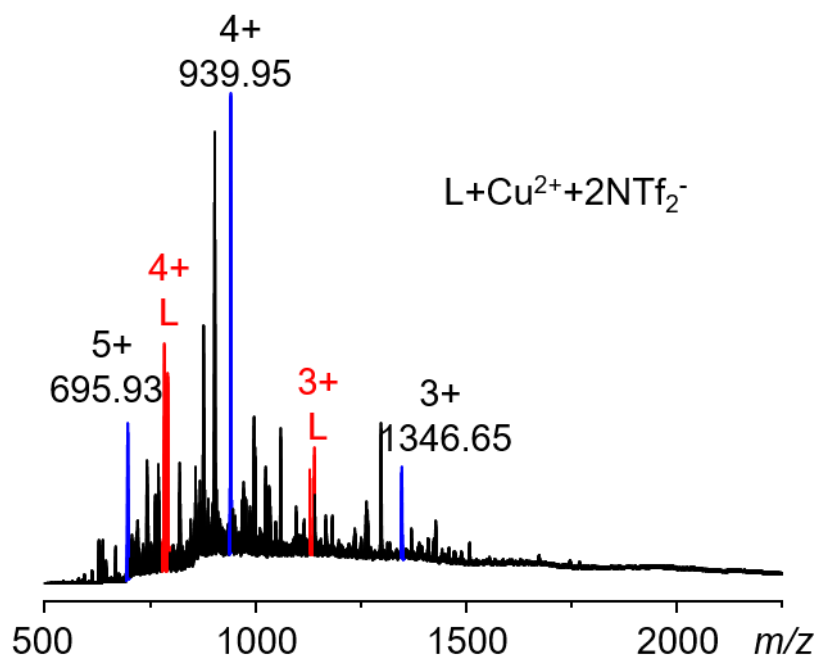


Figure S4. ESI-MS of L with  $\text{Cu}(\text{OTf})_2$  ( $\text{NTf}_2^-$  as counterion).

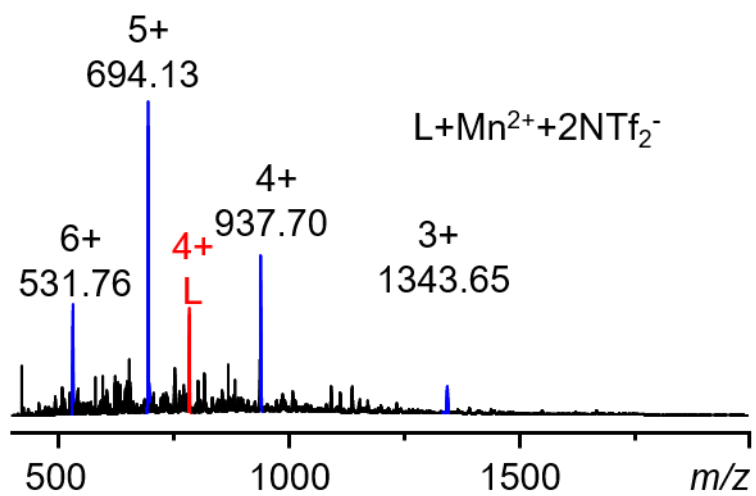
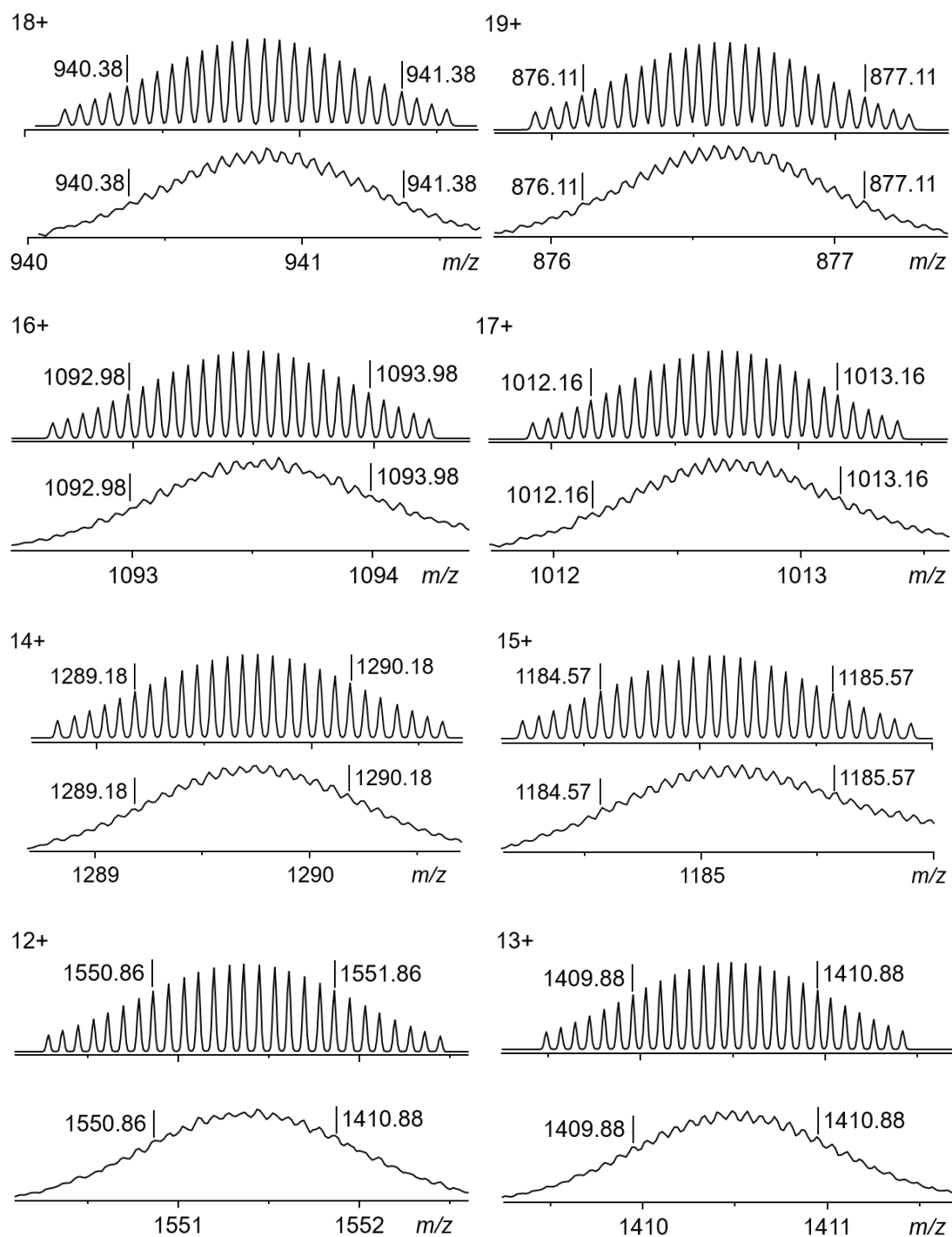
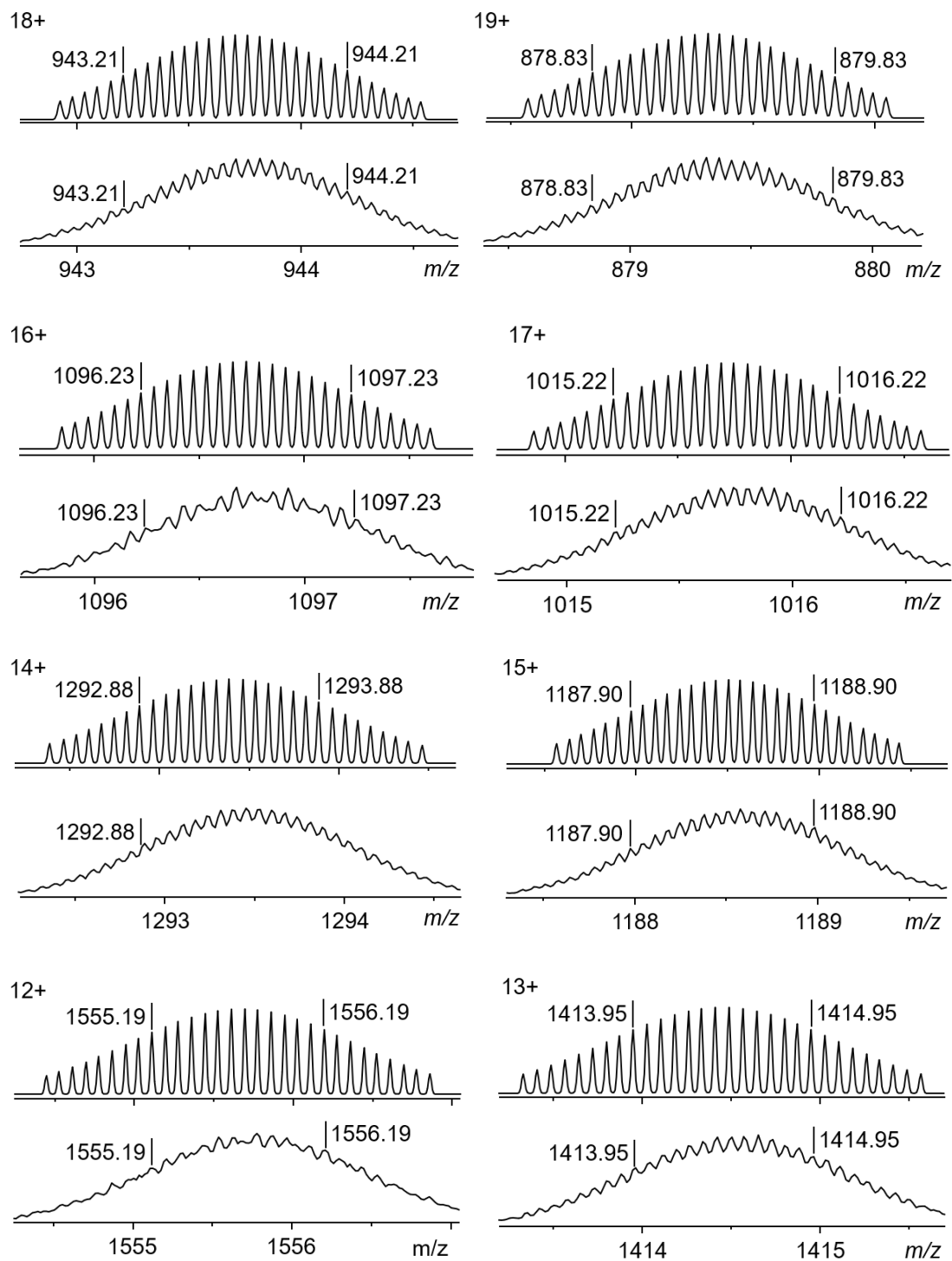


Figure S5. ESI-MS of L with  $\text{MnClO}_4 \cdot 6\text{H}_2\text{O}$  ( $\text{NTf}_2^-$  as counterion).

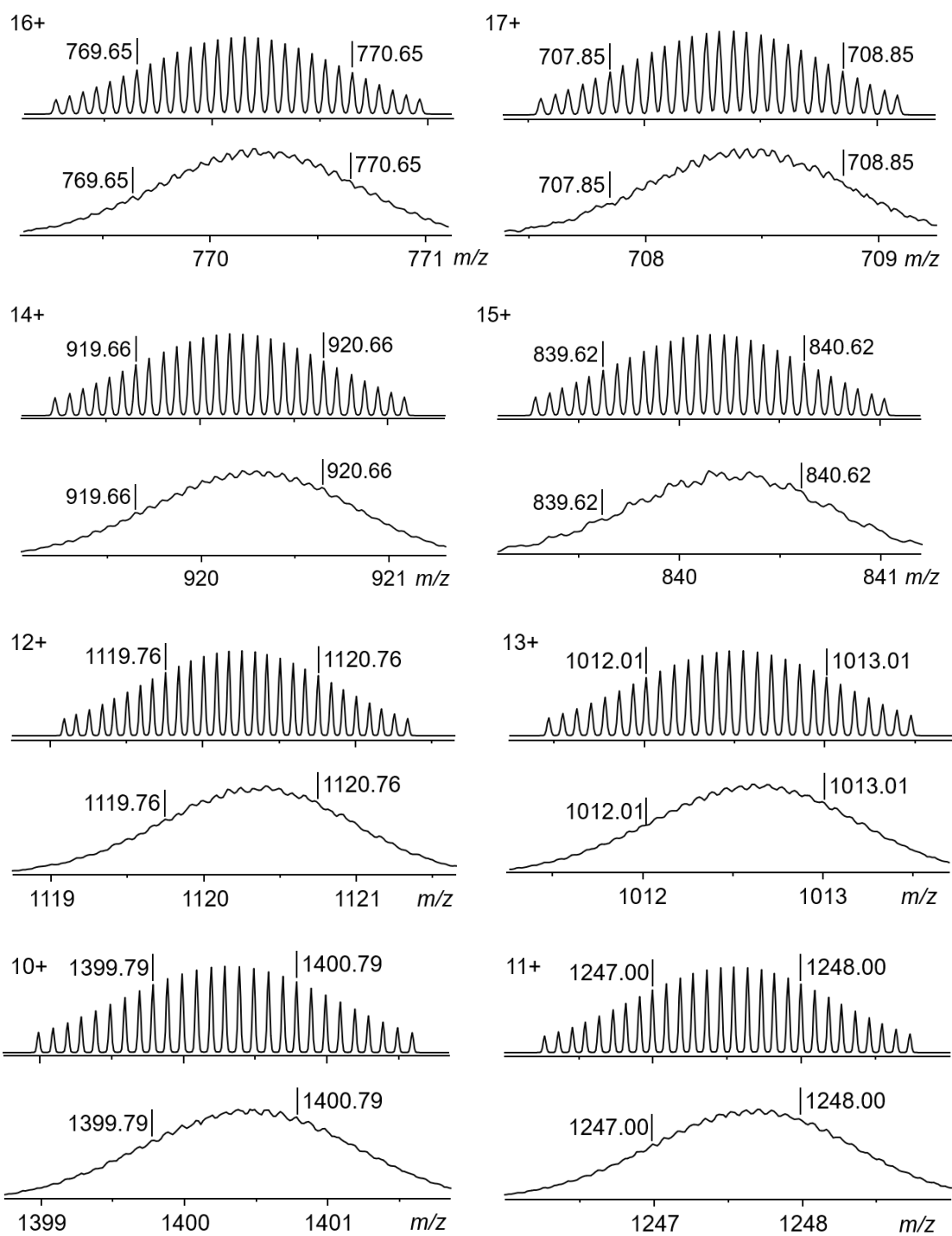


**Figure S6.** Measured (bottom) and calculated (top) isotope patterns for different charge states observed from  $[\text{CosL4}]$  ( $\text{NTf}_2^-$  as counterion).

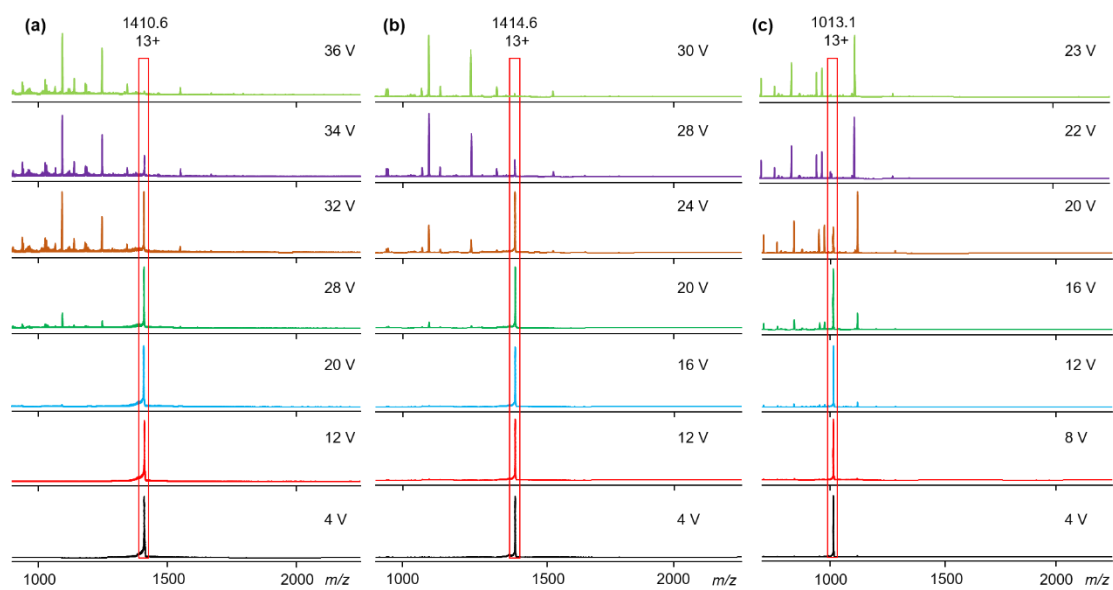




**Figure S7.** Measured (bottom) and calculated (top) isotope patterns for different charge states observed from  $[\text{Zn}_8\text{L}_4]$  ( $\text{NTf}_2^-$  as counterion).



**Figure S8.** Measured (bottom) and calculated (top) isotope patterns for different charge states observed from  $[\text{Cd}_6\text{L}_3]$  ( $\text{NTf}_2^-$  as counterion).



**Figure S9.** gMS<sup>2</sup> of (a) **Co<sub>8</sub>L<sub>4</sub>** at  $m/z$  1410.6 with different collision energies, (b) **Zn<sub>8</sub>L<sub>4</sub>** at  $m/z$  1414.6 with different collision energies, (c) **Cd<sub>6</sub>L<sub>3</sub>** at  $m/z$  1013.1 with different collision energies.

6.  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, 2D COSY NMR, 2D NOESY NMR, 2D DOSY NMR

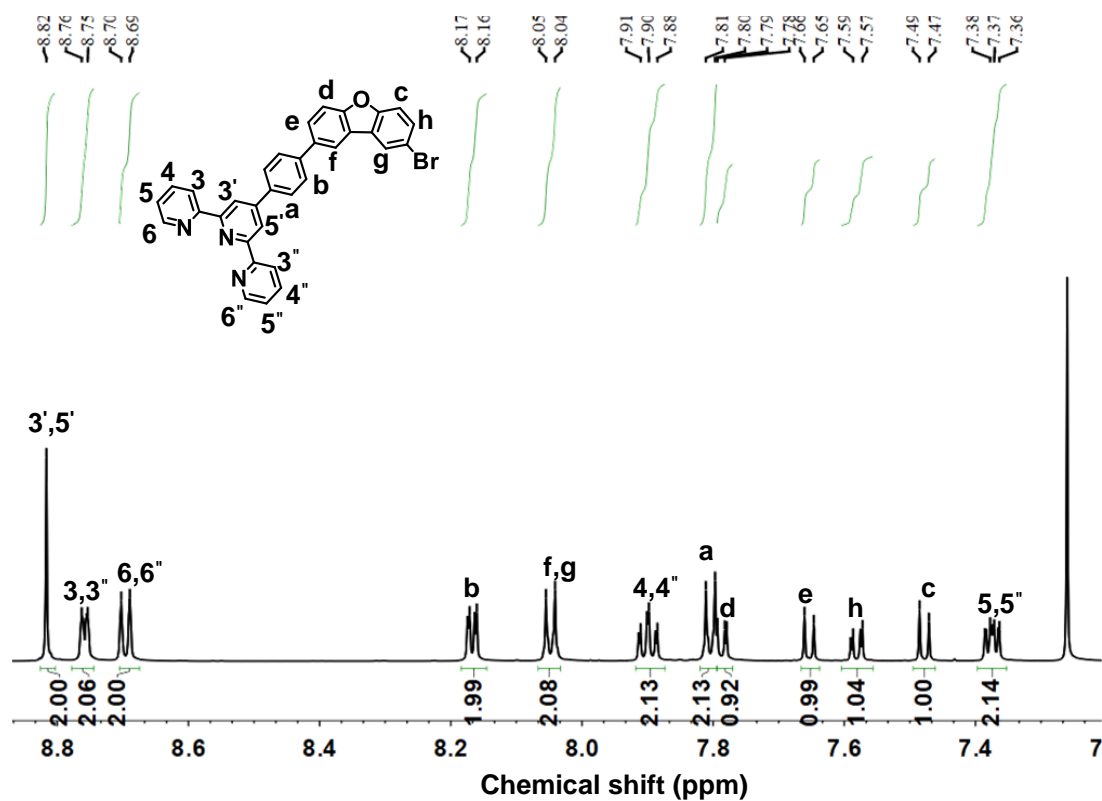


Figure S10.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 1.

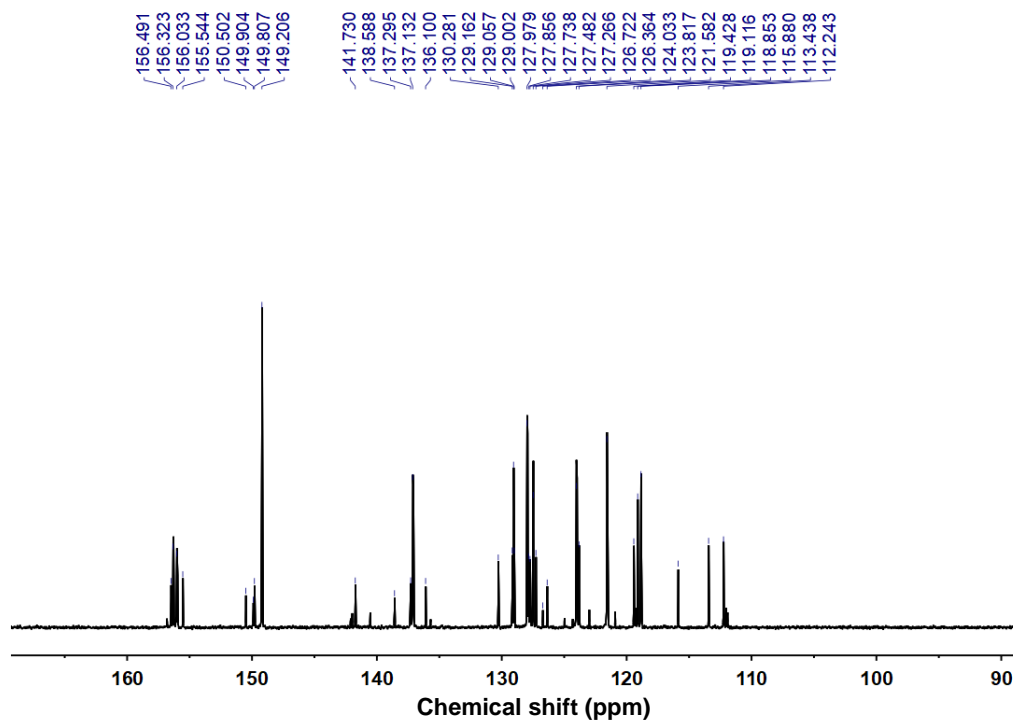


Figure S11.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 1.

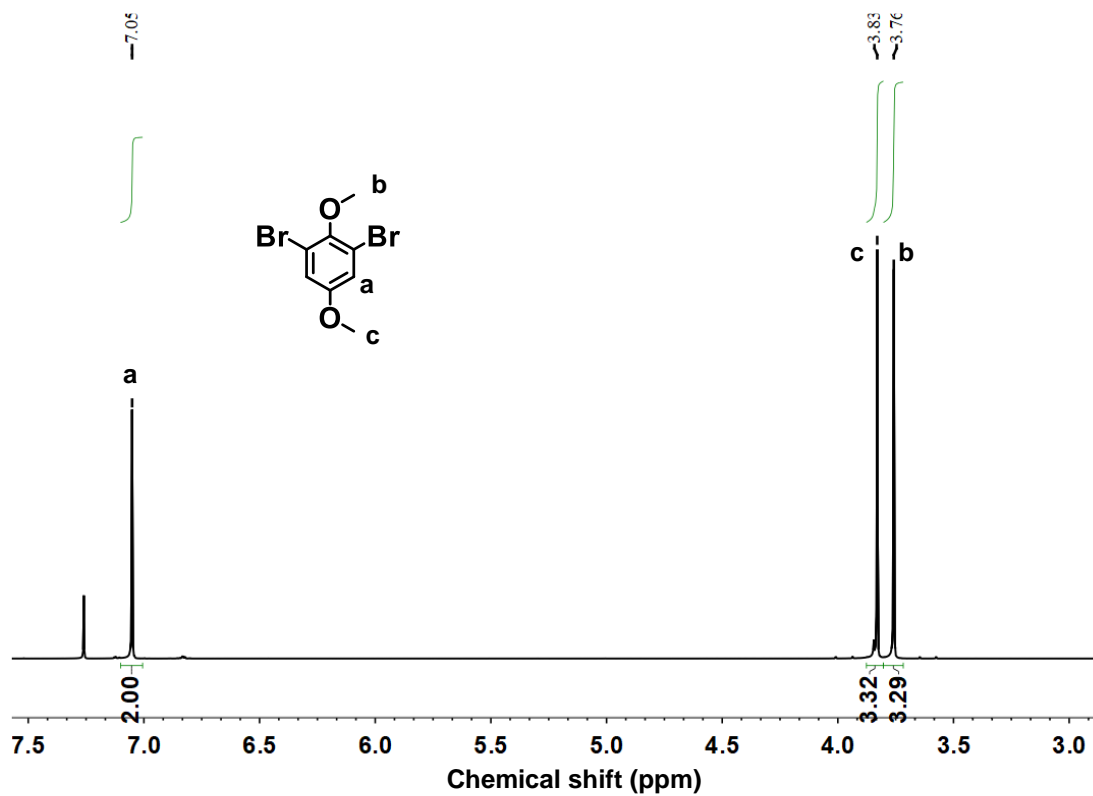


Figure S12.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 4.

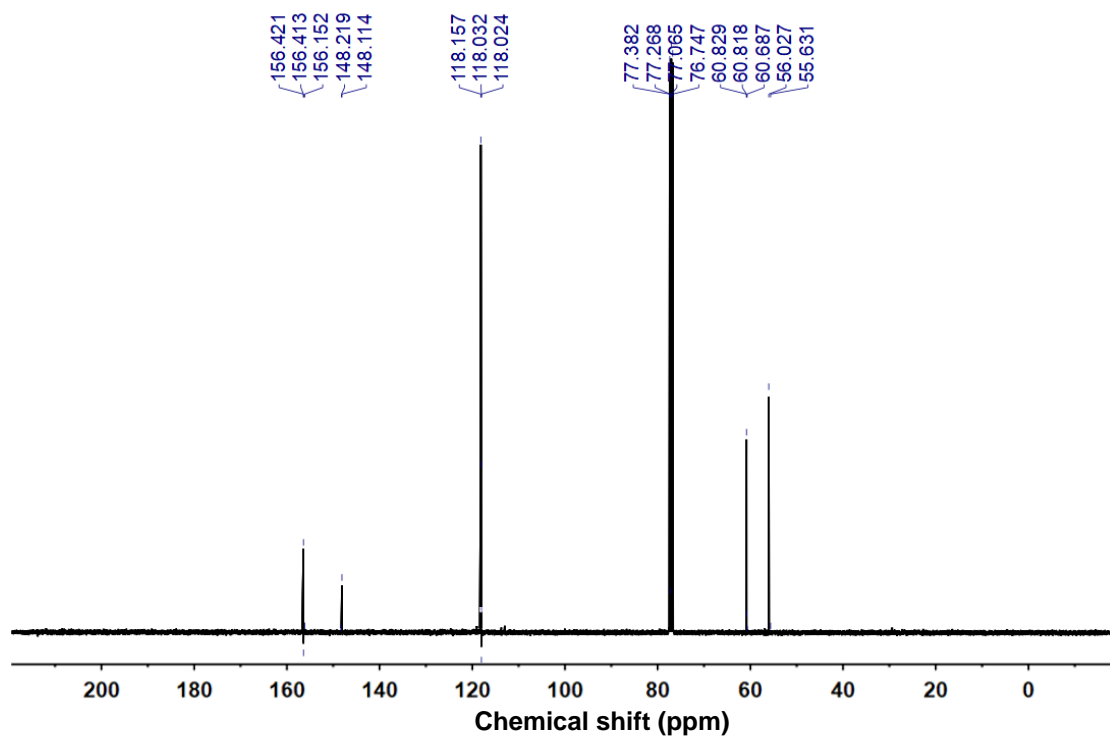


Figure S13.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 4.

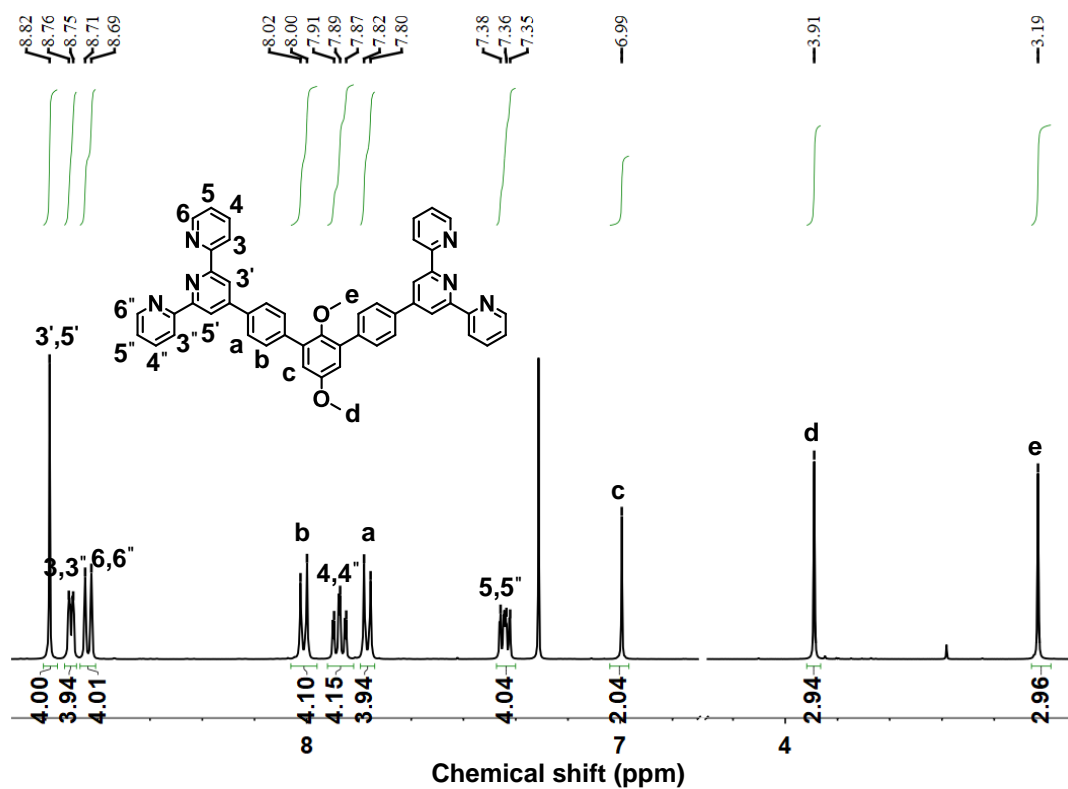


Figure S14.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 5.

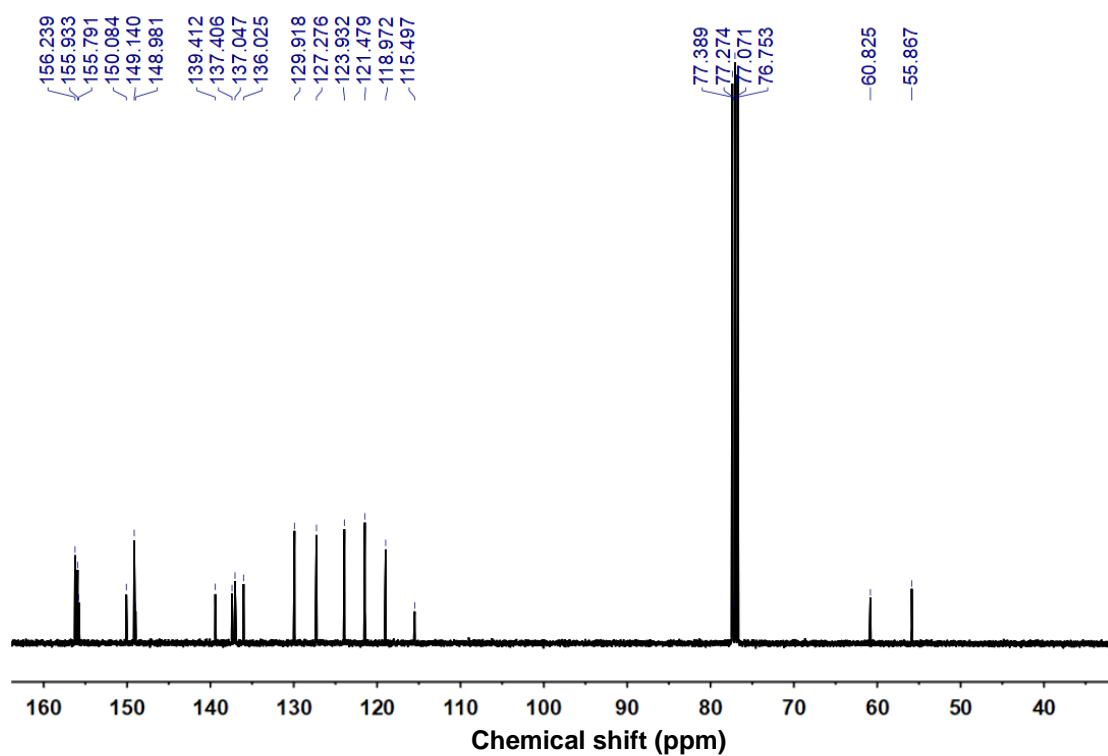


Figure S15.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound 5.

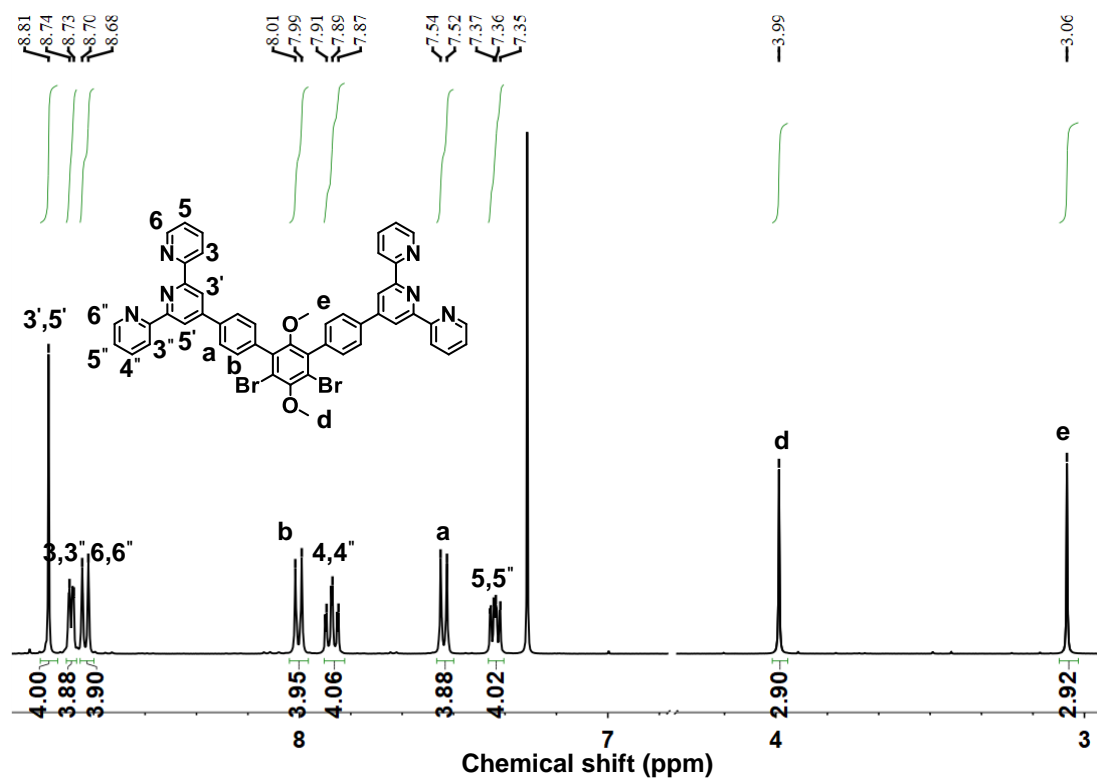


Figure S16.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound **6**.

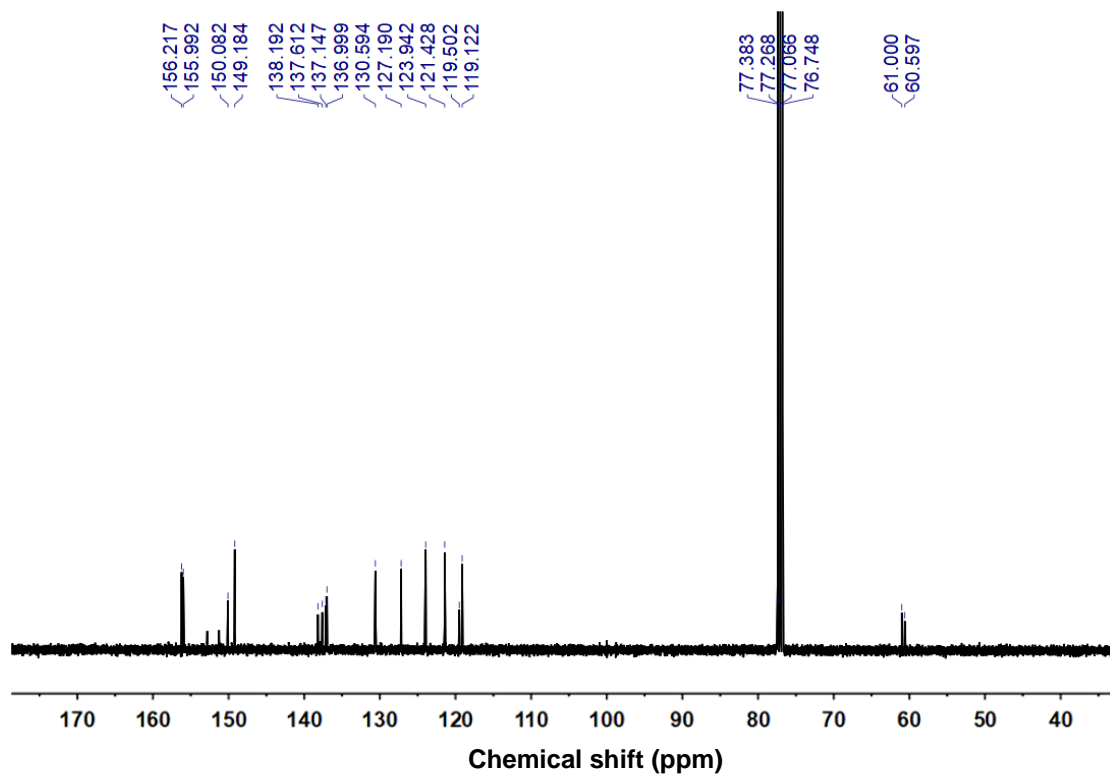


Figure S17.  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ , 300 K) spectrum of compound **6**.

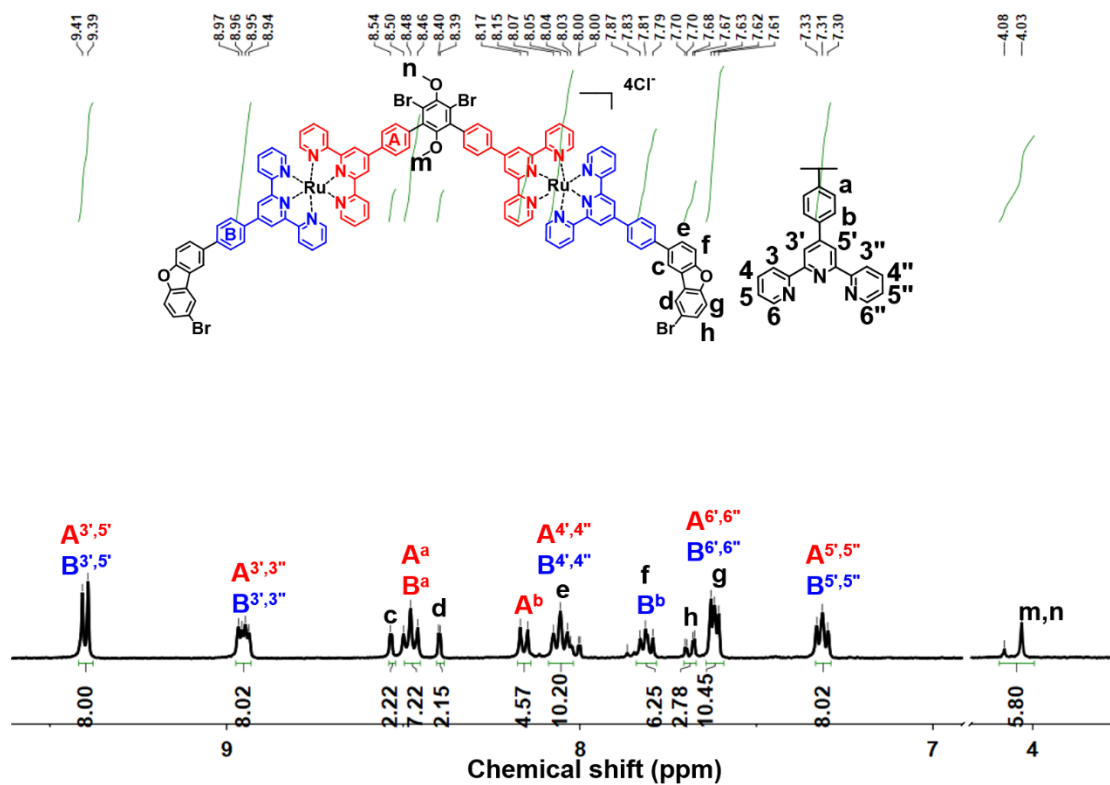


Figure S18.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_3\text{OD}$ , 300 K) spectrum of compound 7.

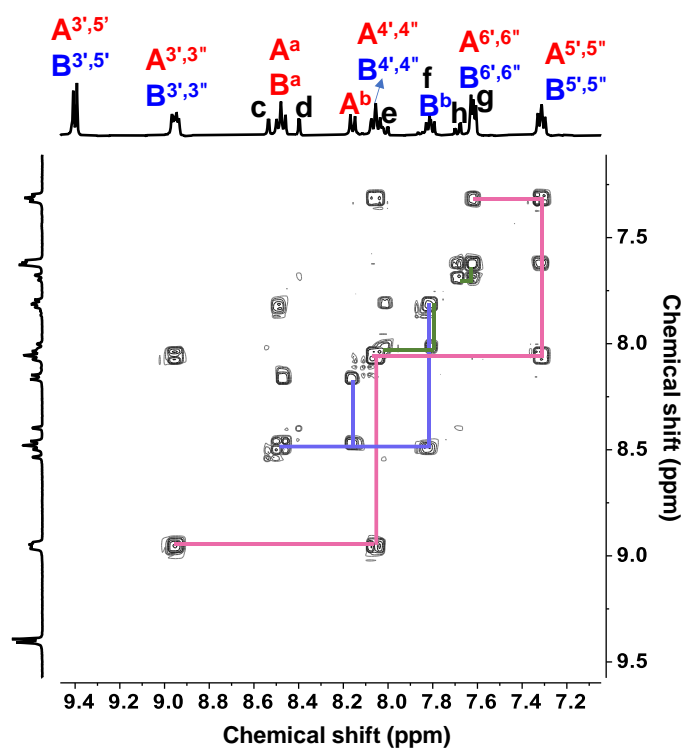
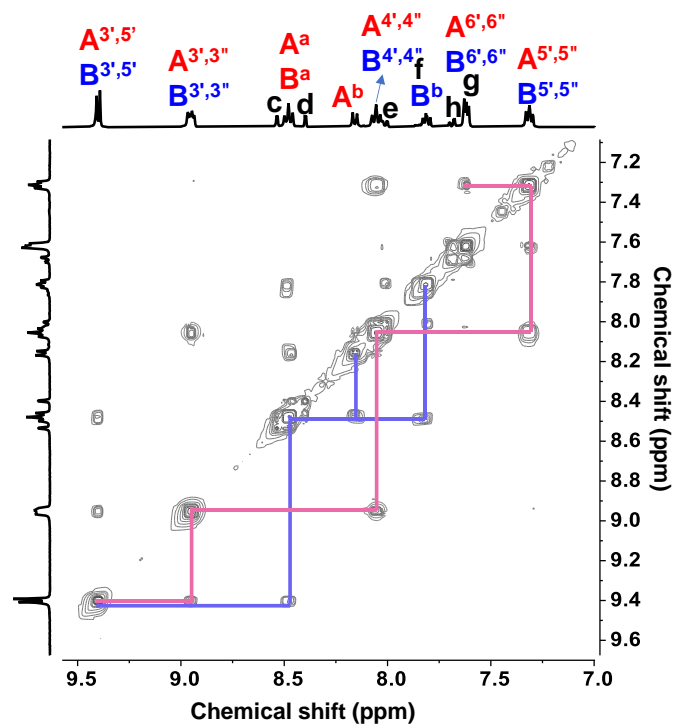
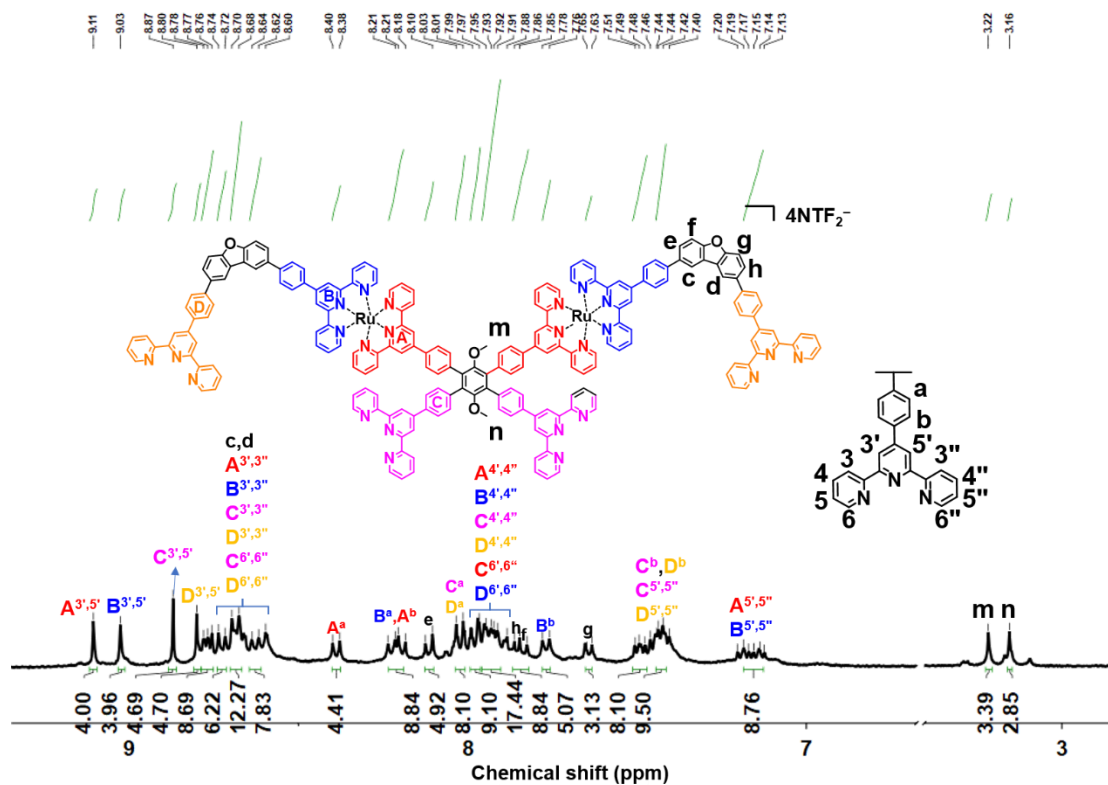


Figure S19. 2D COSY NMR (400 MHz,  $\text{CD}_3\text{OD}$ , 300 K) spectrum of compound 7 (aromatic region).





**Figure S20.** 2D NOESY NMR (400 MHz, CD<sub>3</sub>OD, 300 K) spectrum of compound 7 (aromatic region).



**Figure S21.** <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN, 300 K) spectrum of ligand L.

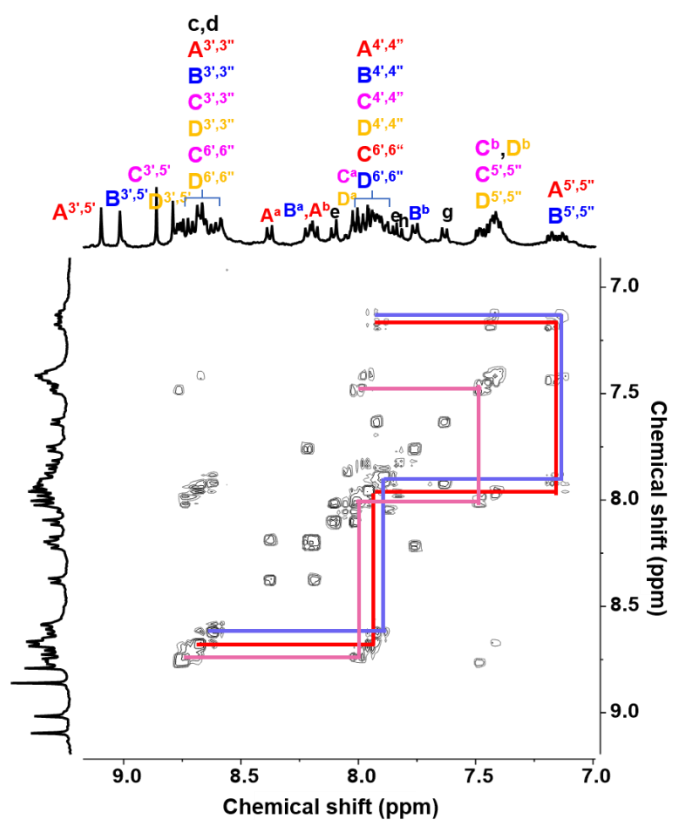


Figure S22. 2D COSY NMR (400 MHz, CD<sub>3</sub>OD, 300 K) spectrum of ligand L (aromatic region).

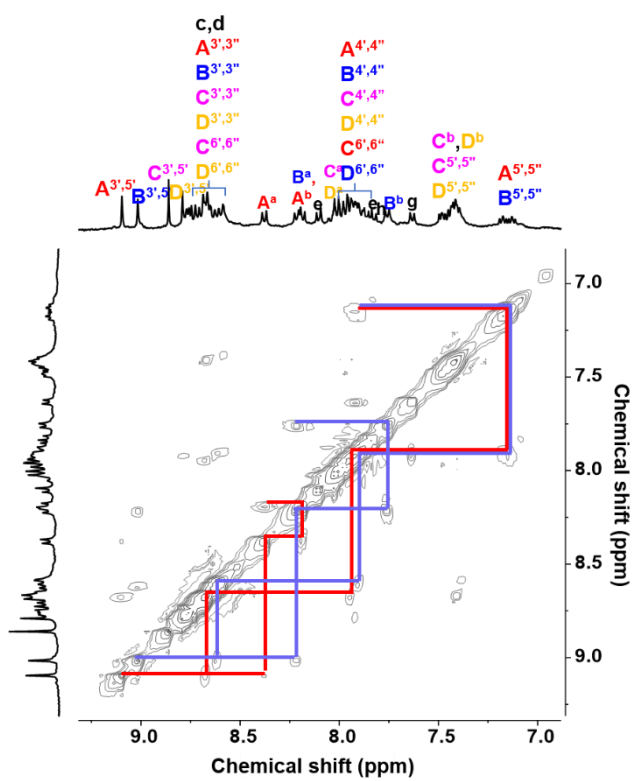


Figure S23. 2D NOESY NMR (400 MHz, CD<sub>3</sub>OD, 300 K) spectrum of ligand L (aromatic region).

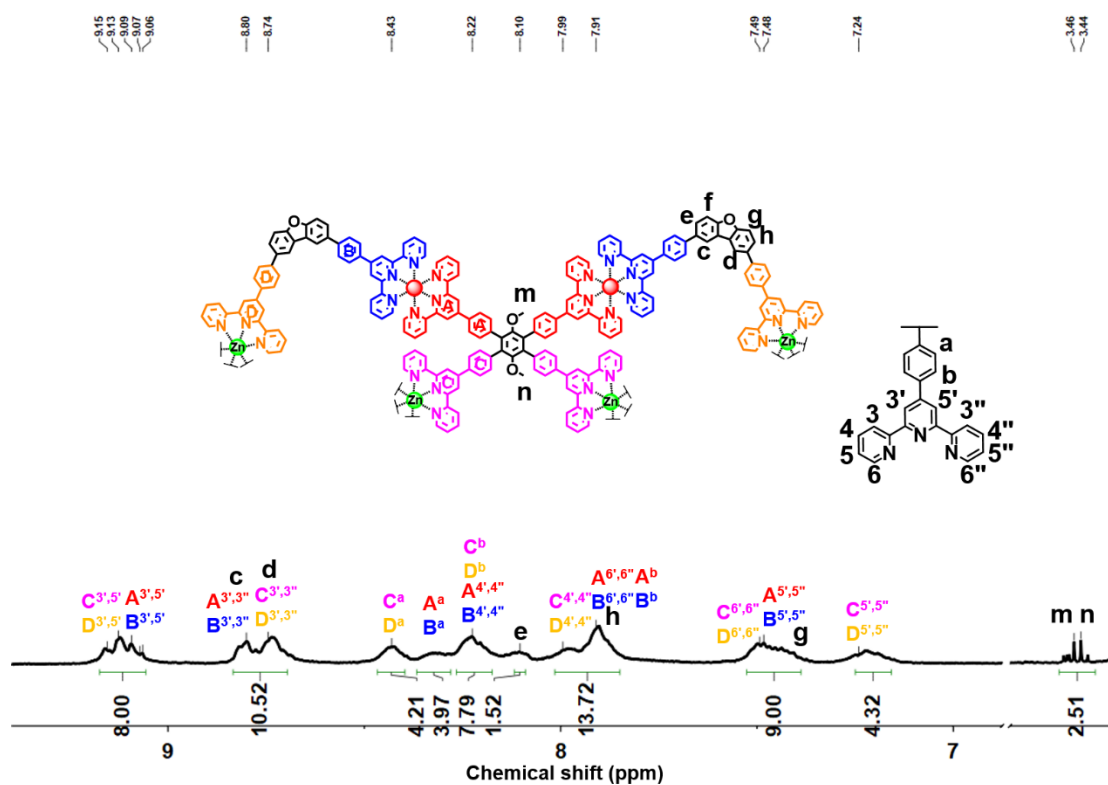


Figure S24. <sup>1</sup>H NMR (500 MHz, CD<sub>3</sub>CN, 300 K) spectrum of Zn<sub>8</sub>L<sub>4</sub>.

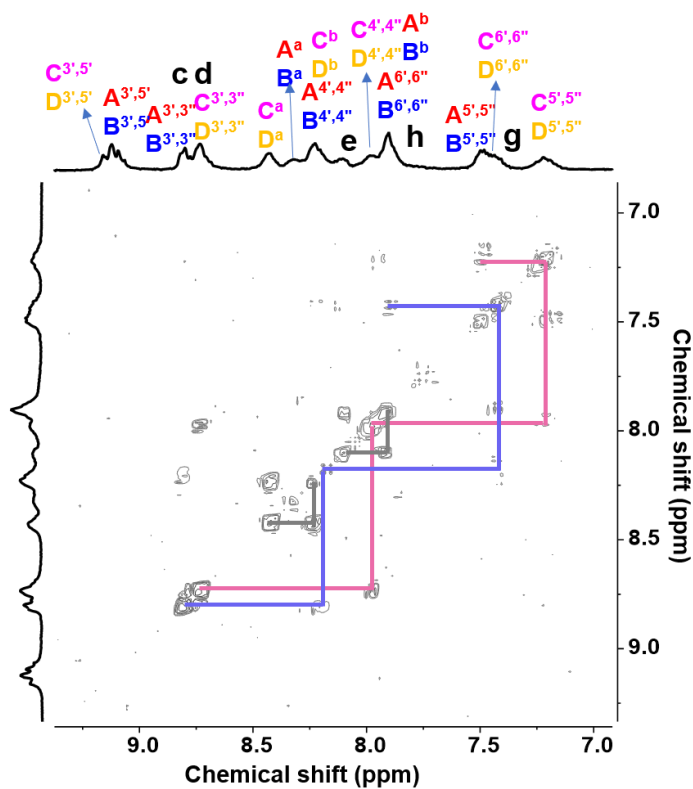
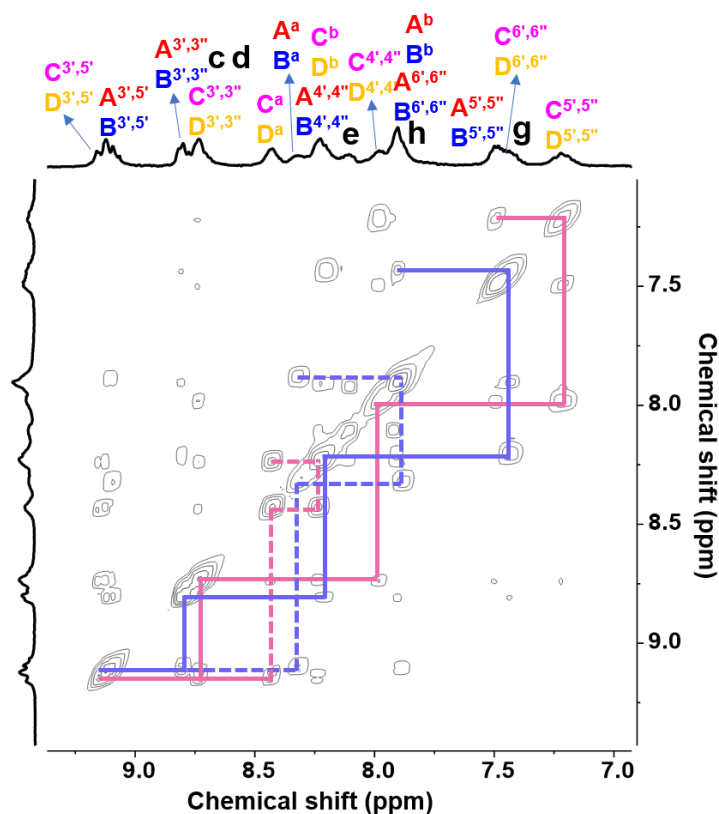
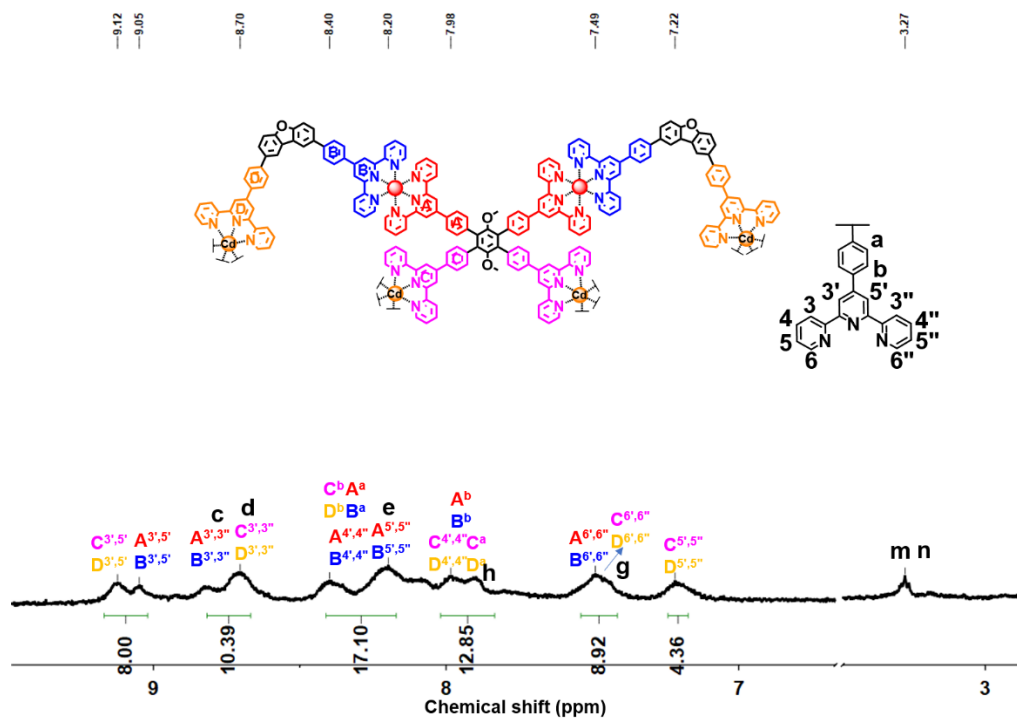


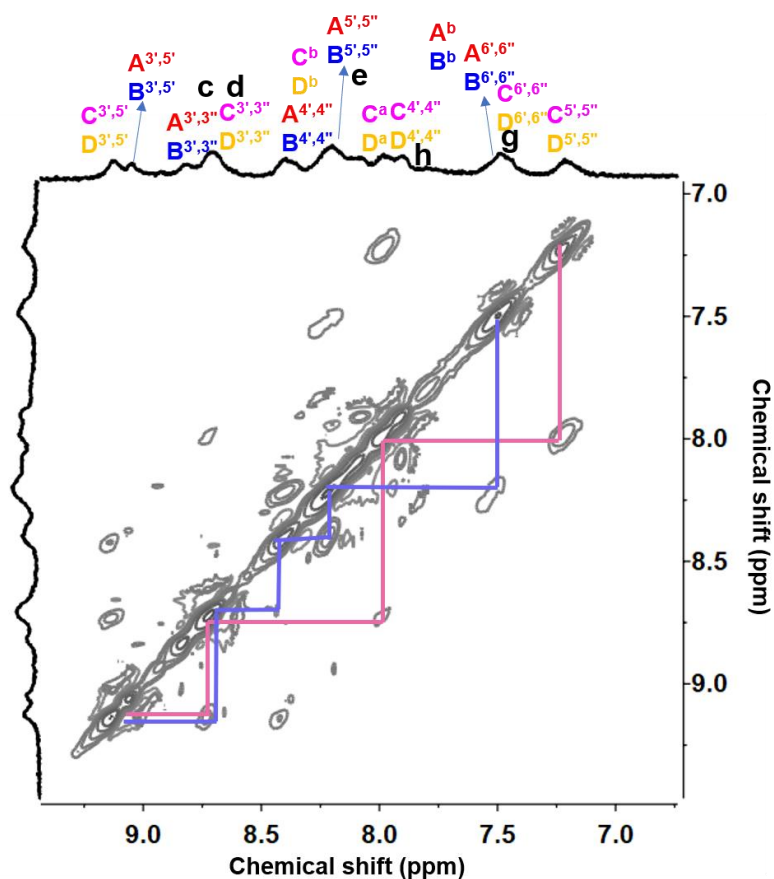
Figure S25. 2D COSY NMR (500 MHz, CD<sub>3</sub>CN, 300 K) spectrum of Zn<sub>8</sub>L<sub>4</sub> (all cross-peaks of Tpy-Ru-Tpy are illustrated by a blue line, all cross-peaks of Tpy-Zn-Tpy are illustrated by pink line).



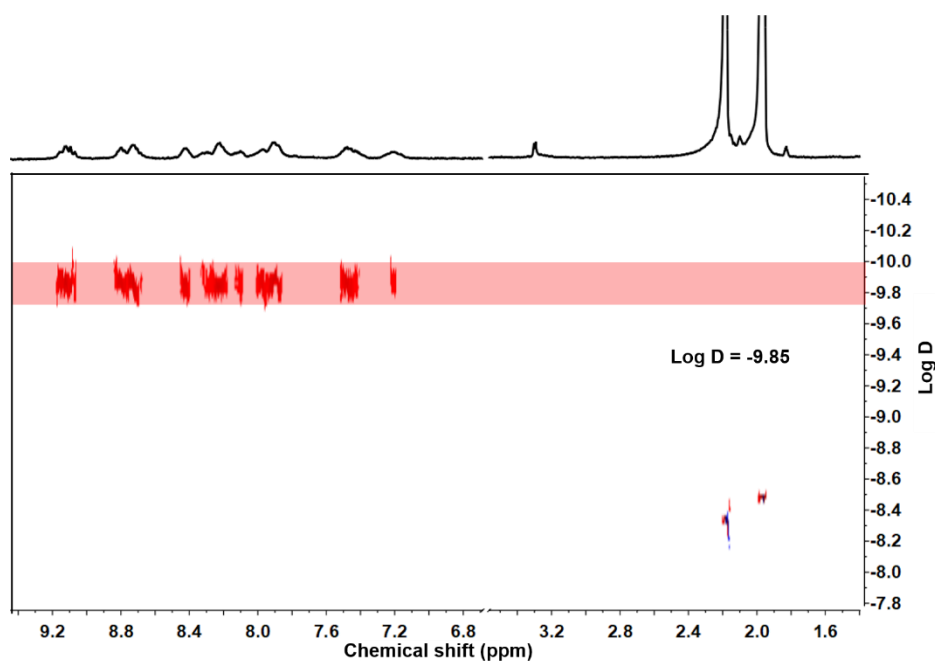
**Figure S26.** 2D NOESY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectrum of  $\text{Zn}_3\text{L}_4$  (all cross-peaks of Tpy-Ru-Tpy are illustrated by a blue line, all cross-peaks of Tpy-Zn-Tpy are illustrated by pink line).



**Figure S27.**  $^1\text{H}$  NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectrum of  $\text{Cd}_6\text{L}_3$ .



**Figure S28.** 2D NOESY NMR (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectrum of  $\text{Cd}_6\text{L}_3$  (all cross-peaks of Tpy-Ru-Tpy are illustrated by a blue line, all cross-peaks of Tpy-Zn-Tpy are illustrated by pink line).



**Figure S29.** DOSY (500 MHz,  $\text{CD}_3\text{CN}$ , 300 K) spectra of  $\text{Zn}_8\text{L}_4$ .

### Specific calculation process

The sphere's hydrodynamic radius was estimated according to the Stokes-Einstein Equation, where **D** is the diffusion constant, **k** is the Boltzmann's constant, **T** is the temperature, **μ** is the viscosity of solvents, and **R** is the radius:

$$D = \frac{kT}{6\pi\mu R}$$

$$D = 10^{-9.85} \text{ m}^2 \text{ s}^{-1}$$

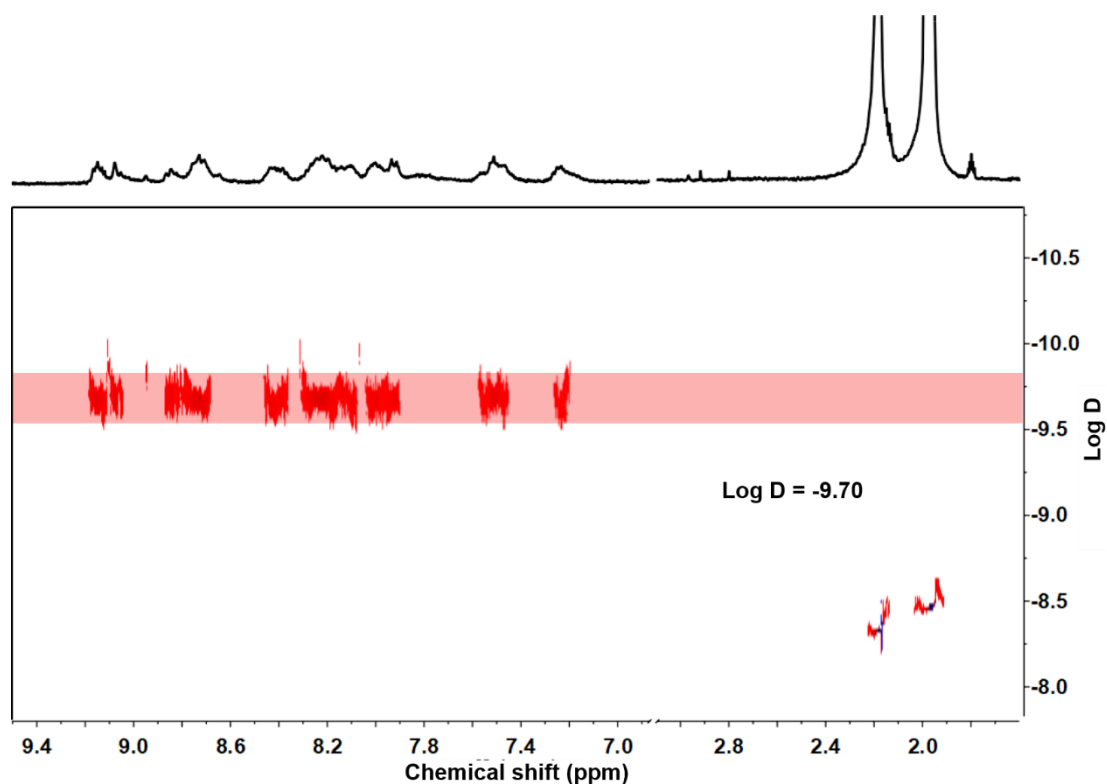
$$k = 1.38 \times 10^{-23} \text{ N m K}^{-1}$$

$$T = 298 \text{ K}$$

$$\mu = 3.43 \times 10^{-4} \text{ N m}^{-2} \text{ s (CD}_3\text{CN)}^{2,3}$$

$$R = \frac{kT}{6\pi\mu D} \approx 2.11 \times 10^{-9} \text{ m} = 2.11 \text{ nm}$$

The radius of **Zn<sub>8</sub>L<sub>4</sub>** was determined to be 4.22 nm, which is consistent with the results of computer modeling.



**Figure S30.** DOSY (500 MHz, CD<sub>3</sub>CN, 300 K) spectra of **Cd<sub>6</sub>L<sub>3</sub>**.

### Specific calculation process

The sphere's hydrodynamic radius was estimated according to the Stokes-Einstein Equation, where **D** is the diffusion constant, **k** is the Boltzmann's constant, **T** is the temperature, **μ** is the viscosity of solvents, and **R** is the radius:

$$D = \frac{kT}{6\pi\mu R}$$

$$D = 10^{-9.70} \text{ m}^2 \text{ s}^{-1}$$

$$k = 1.38 \times 10^{-23} \text{ N m K}^{-1}$$

$$T = 298 \text{ K}$$

$$\mu = 3.43 \times 10^{-4} \text{ N m}^{-2} \text{ s (CD}_3\text{CN)}$$

$$R = \frac{kT}{6\pi\mu D} \approx 1.62 \times 10^{-9} \text{ m} = 1.62 \text{ nm}$$

The radius of **Cd<sub>6</sub>L<sub>3</sub>** was determined to be 3.24 nm, which is consistent with the results of computer modeling.

## 7. TEM and AFM images of supramolecules (NTf<sub>2</sub><sup>-</sup> as counterion)

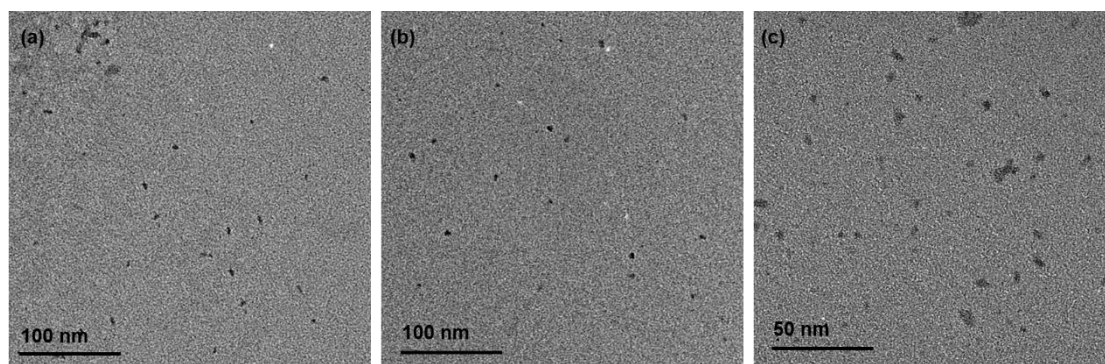


Figure S31. TEM images of (a) **Co<sub>8</sub>L<sub>4</sub>**, (b) **Zn<sub>8</sub>L<sub>4</sub>**, and (c) **Cd<sub>6</sub>L<sub>3</sub>** on the lacey carbon-coated Cu grid ( $c=10^{-6}$  M in CH<sub>3</sub>CN).

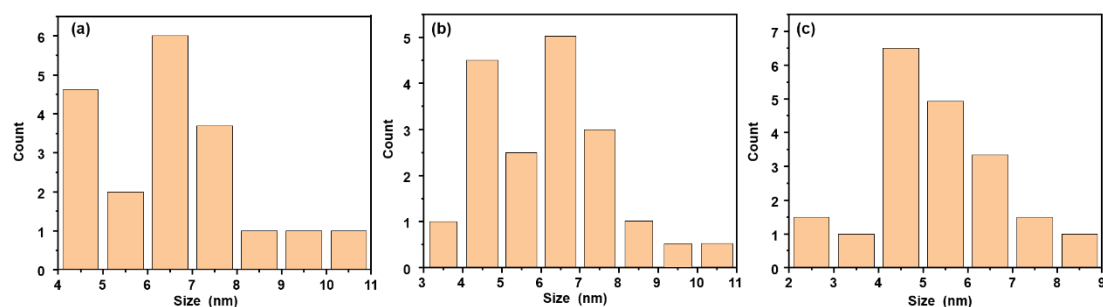


Figure S32. TEM size statistical histogram of (a) **Co<sub>8</sub>L<sub>4</sub>**, (b) **Zn<sub>8</sub>L<sub>4</sub>**, and (c) **Cd<sub>6</sub>L<sub>3</sub>**.

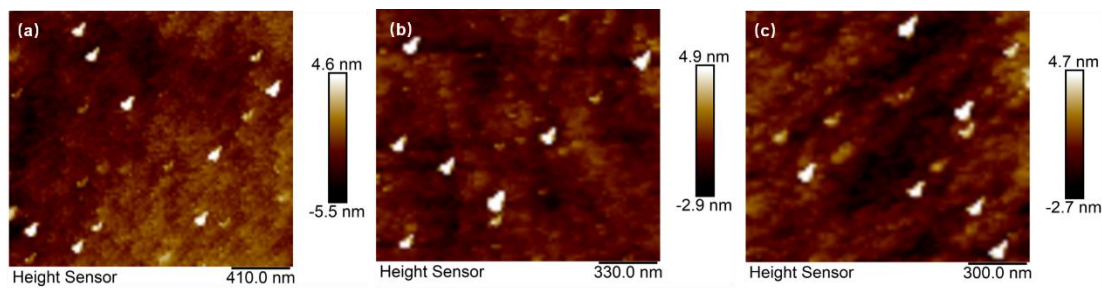


Figure S33. AFM 2D images of (a) **Co<sub>8</sub>L<sub>4</sub>**, (b) **Zn<sub>8</sub>L<sub>4</sub>**, and (c) **Cd<sub>6</sub>L<sub>3</sub>**.<sup>4</sup>

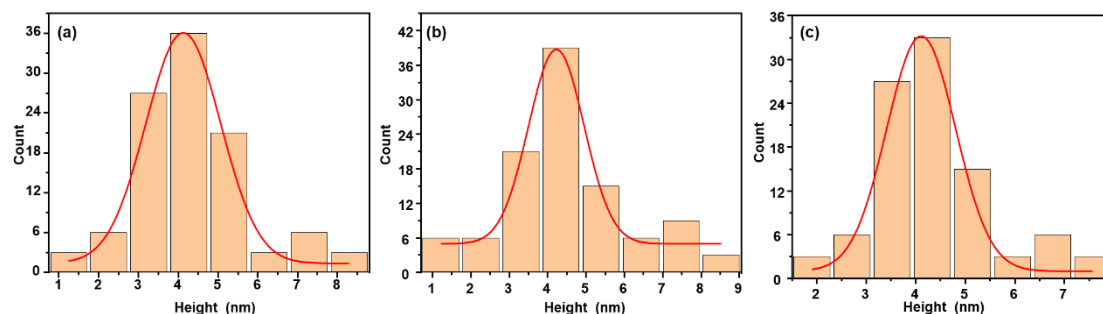
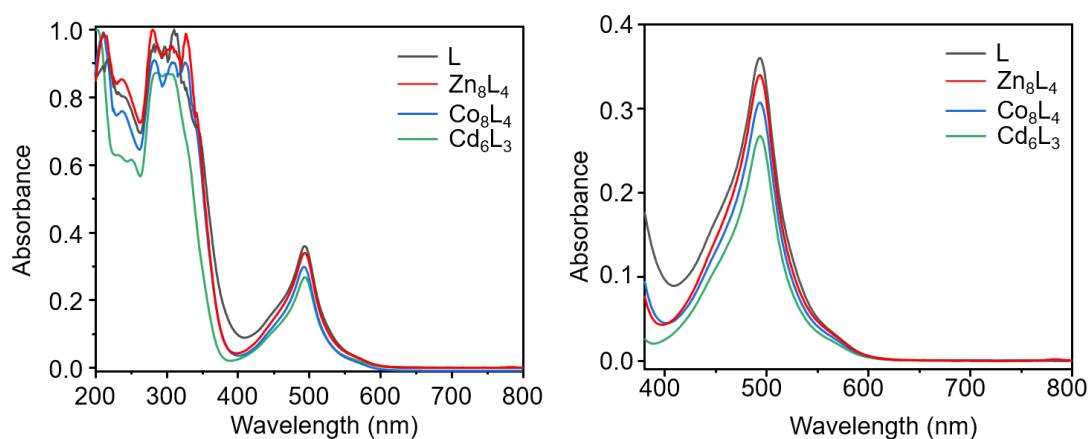


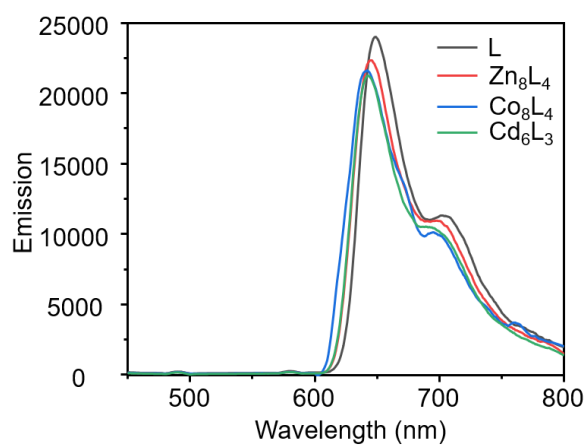
Figure S34. AFM height statistical histogram for 100 particles of (a) **Co<sub>8</sub>L<sub>4</sub>**, (b) **Zn<sub>8</sub>L<sub>4</sub>**, and (c) **Cd<sub>6</sub>L<sub>3</sub>**.



## 8. UV-vis and emission of **L** and supramolecules ( $\text{NTf}_2^-$ as counterion)



**Figure S35.** UV-vis ( $10^{-6}$  M in  $\text{CH}_3\text{CN}$ , room temperature) of **L** and supramolecules.



**Figure S36.** Emission ( $10^{-6}$  M in  $\text{CH}_3\text{CN}$ , 73K) of **L** and supramolecules.

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