Clover Leaf-Shaped Supramolecules Assembled by a Predesigned Metallo-Organic ligand

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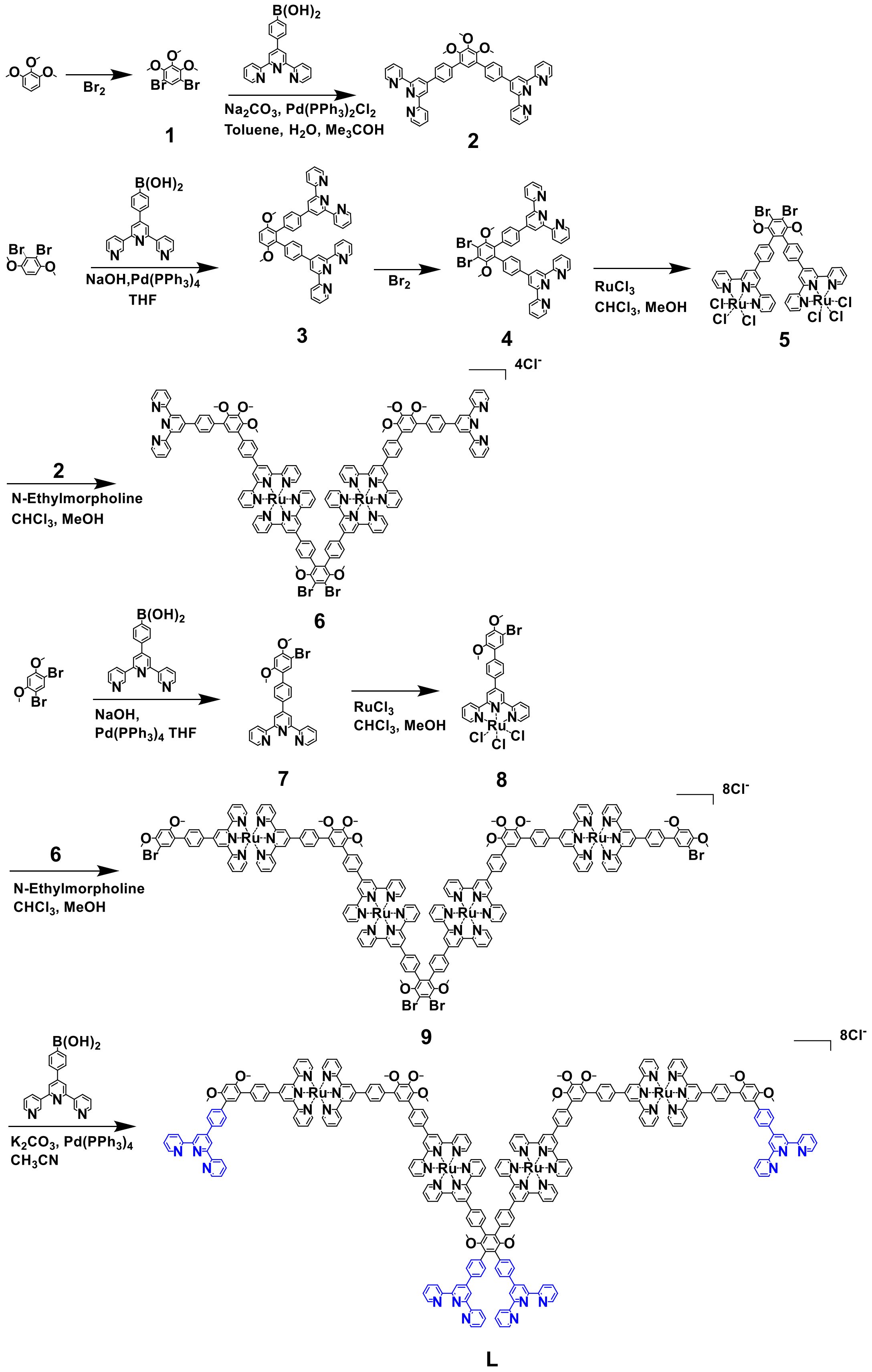
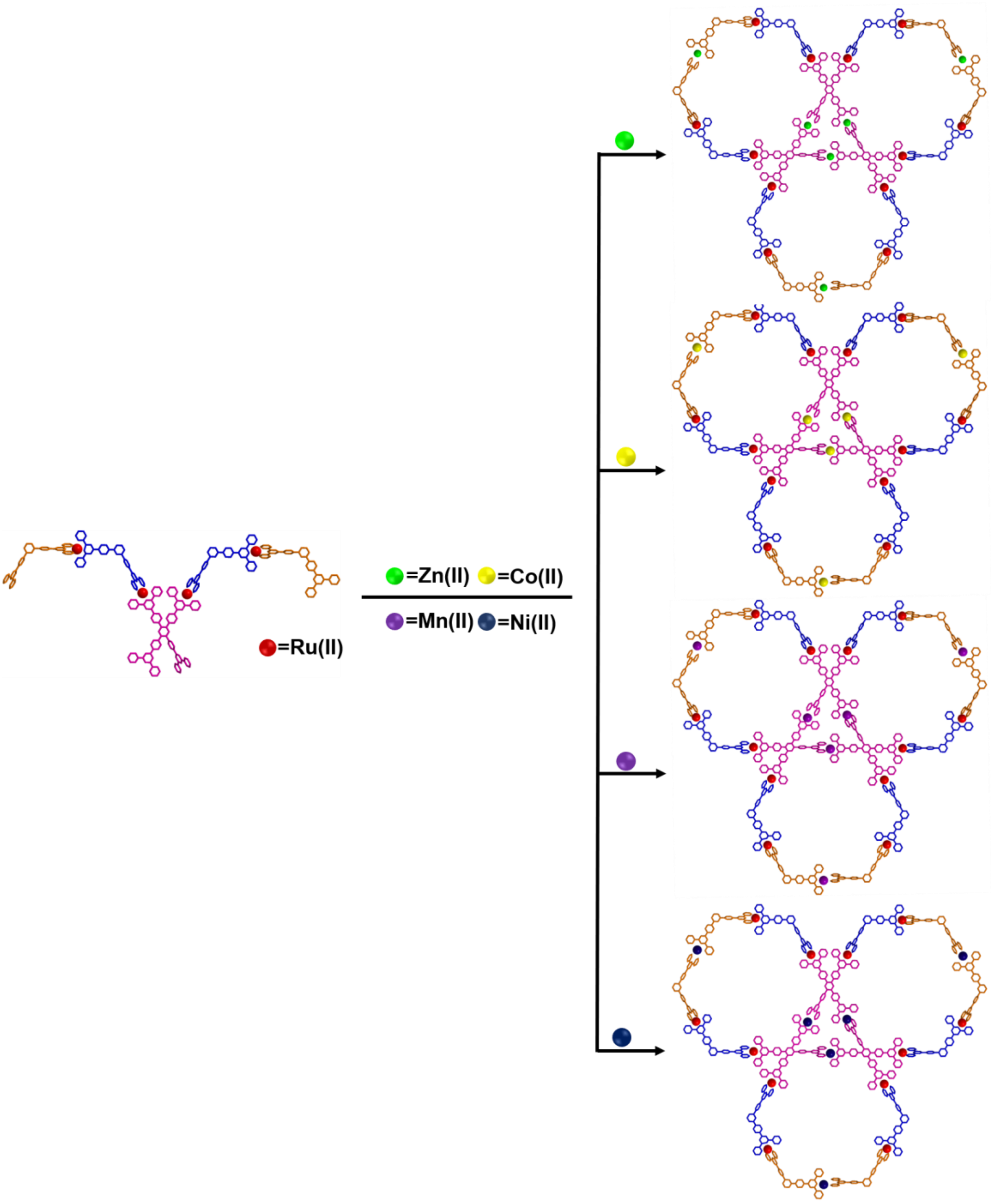
1. Schemes of preparation of ligands L and supramolecules



Scheme S1. Synthesis of ligand **L**



Scheme S2. Self-assembly of **Zn$_6$L$_3$**, **Co$_6$L$_3$**, **Mn$_6$L$_3$** and **Ni$_6$L$_3$**

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 Al_2O_3 (IB-F) or SiO_2 (IB2-F). Column chromatography was conducted using basic Al_2O_3 Brockman Activity I (60-325 mesh) or SiO_2 (60-200 mesh) from Fisher Scientific. NMR spectra were recorded on a Bruker NMR 400 or 500 MHz spectrometer, using $CDCl_3$ for ligands and CD_3CN 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 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 $CHCl_3/CH_3OH$ (1:3, v/v) for ligands or 0.5 mg sample in 1 mL of MeCN/MeOH (3:1, v/v) for complexes. All samples were infused into the ESI source at a flow rate of 6 μL/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 °C; desolvation temperature, 250 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (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 μL/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.

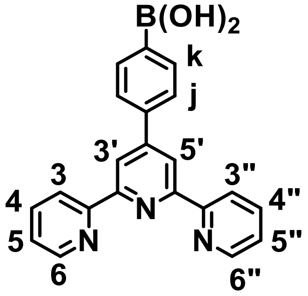
gMS^2. Gradient tandem mass spectrometry was performed under the following conditions: 17+ charged ions of complexes were isolated by quadrupole for the following collision induced dissociation (CID), in which collision energy was gradually increased by changing the voltage of trap cell depended on different complexes.

TEM. Transmission electron microscopy tests were performed on the JEOL JEM-2100F equipment. The sample solutions were drop-casted on to 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.

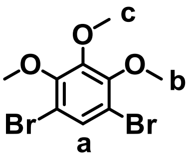
Cyclic Voltammetry. Cyclic voltammetry measurements were performed on a Princeton VersaSTAT 3F potentiost with a standard three-electrode configuration using a glass-carbon working electrode, a platinum-rod auxiliary electrode, and a reference Ag/AgCl electrode. The electrochemical properties of these two complexes in CN_3CN (2×10^{-6} M) were studied in a three-electrode electrochemical cell with Bu_4NPF_6 (0.1 M) as electrolyte.

UV-vis absorption and fluorescence properties. UV-vis absorption spectra were recorded on a Persee TU-1900 UV-visible spectrophotometer at room temperature (3×10^{-6} M in CH_3CN) and were corrected with the background spectrum of the solvent. Fluorescence properties were performed on LSM-365A Exciter at 73K (3×10^{-6} M in CH_3CN).

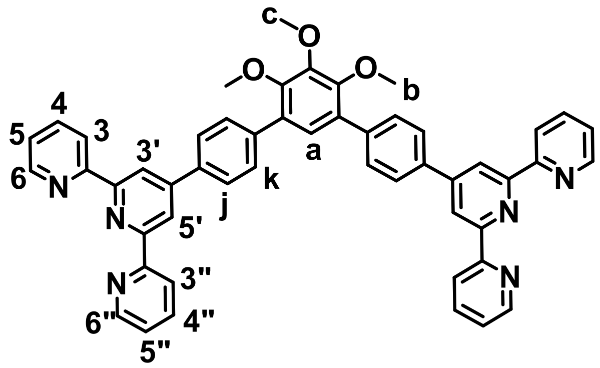
3. Synthesis of the compounds and supramolecules



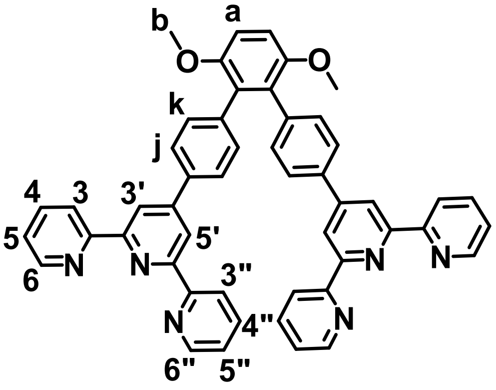
To a solution of NaOH powder (9.6 g, 240 mmol) in EtOH (200 mL), 4-Formylphenylboronic acid (6.0 g, 40 mmol) and 2-acetylpyridine (10.6 g, 88 mmol) was added. After stirring at room temperature for 24 h, aqueous NH_3•H_2O (28%, 150 mL) was added, the resulting mixture was refluxed for 20 h. After cooling to room temperature, the solid was collected by filtration and was washed with $CHCl_3$ to give the product as 11.96 g pale purple solid (yield 84.7%) .[1] ^{1}H NMR (500 MHz, CD_3OD, 300 K, ppm): δ 8.71-8.68 (m, 2H, Tpy-$H^{3',5'}$), 8.68-8.62 (m, 4H, Tpy-$H^{6,6''}$ and Tpy-$H^{3,3''}$), 8.01 (td, J = 7.7, 1.8 Hz, 2H, Tpy-$H^{4,4''}$), 7.78 (d, J = 7.8 Hz, 2H, Ph-H^j), 7.73 (d, J = 8.0 Hz, 2H, Ph-H^k), 7.48 (ddd, J = 7.5, 4.8, 1.1 Hz, 2H, *Tpy*-$H^{5,5''}$); ^{13}C NMR (125 MHz, CD_3OD, 300 K, ppm): δ 157.46, 156.84, 153.10, 149.87, 138.57, 135.29, 134.99, 125.75, 125.11, 122.82, 119.40. ESI-TOF (*m/z*): Calcd. for $[C_{21}H_{16}BN_3O_2+H]^+$: 353.13. Found: 353.14.



Compound 1, To a stirred solution of 1,2,3-trimethoxybenzene (2.30 g, 13.7 mmol) in CH_2Cl_2 (30 mL) at 0 °C, a solution of Br_2 (4.59 g, 28.7 mmol) in CH_2Cl_2 (10 mL) was added drop-wise. After stirring at 25 °C for 12 h, the reaction mixture was washed with saturated Na_2SO_3 solution until colorless, dried over anhydrous $MgSO_4$, and then concentrated in vacuo to give the product as 3.62 g colorless liquid (yield 81%). ^{1}H NMR (500 MHz, CD_3OD, 300 K, ppm): δ 7.47 (s, 1H, *Ph*-H^a), 3.92 (s, 3H, -OCH_3-H^c), 3.86 (s,6H, -OCH_3-H^b); ^{13}C NMR (125 MHz, $CDCl_3$, 300 K, ppm): δ 151.12, 148.55, 129.97, 112.44, 61.50, 61.21.

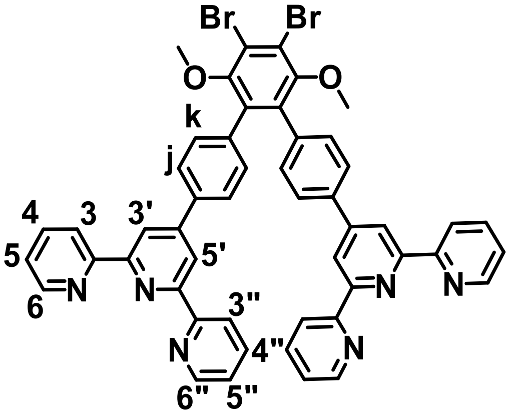


Compound 2, Compound **1** (326 mg,1.00 mmol), 4'-(4-boronatophenyl)-[2,2':6',2'']terpyridine (1.05 g, 3.00 mmol), $Pd(PPh_3)_2Cl_2$ (70.20 mg, 0.10 mmol) and sodium carbonate (1.06 g, 10.00 mmol) were added into a 200 mL three-necked flask. 30 mL H_2O, 80 mL toluene and 10 mL tert-butyl alcohol were added under N_2. The mixture was stirred at 75 ºC for 3 days. After cooling to room temperature, the mixture was extracted with $CHCl_3$. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4, and then concentrated in vacuo, the residue was purified by flash column chromatography (Al_2O_3), eluting with $CHCl_3$ to give the product as 510 mg white solid (yield 65%).[2,3] ^1H NMR (500 MHz, $CDCl_3$, 300 K, ppm): δ 8.82 (s, 4H, *Tpy-*$H^{3',5'}$), 8.75-8.76 (d, J =4.0 Hz, 4H, *Tpy-*$H^{6,6''}$), 8.69-8.71 (d, J = 8.0 Hz, 4H, *Tpy-*$H^{3,3''}$), 7.99-8.01 (d, 4H, J = 8.5Hz, *Ph-*H^{j}), 7.25 (s, 1H, *Ph-*H^{a}), 4.10 (s, 3H, -OCH_3-H^{c}), 3.79 (s, 6H,-OCH_3-H^{b}); ^{13}C NMR (125 MHz, ppm): δ 156.6, 156.2, 151.4, 150.2, 149.4, 147.4, 138.9, 137.4, 137.0, 131.1, 129.9,127.4, 126.3, 124.0, 121.6, 119.0, 61.5, 61.3; ESI-TOF (*m/z*): Calcd. For $[C_{51}H_{38}N_6O_3+H]^+$, 783.35, Found: 783.34. $[C_{51}H_{38}N_6O_3+2H]^{2+}$, 392.17, Found: 392.19.



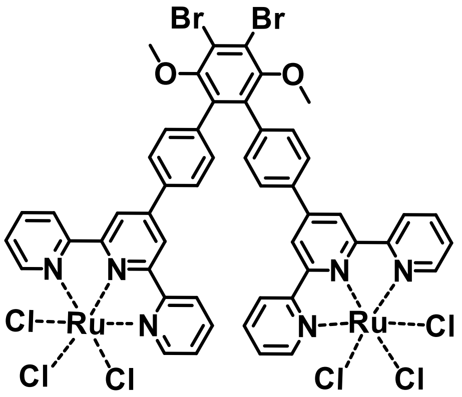
Compound 3, 2,3-dibromo-1,4-dimethoxybenzene (293 mg,1.00 mmol), 4'-(4-

boronatophenyl)-[2,2':6',2'']terpyridine (1.05 g, 3.00 mmol), Pd(PPh$_3$)$_2$Cl$_2$ (70.20 mg, 0.10 mmol) and sodium carbonate (1.06 g, 10.00 mmol) were added into a 200 mL three-necked flask. 30 mL H$_2$O, 80 mL toluene and 10 mL tert-butyl alcohol were added under N$_2$. The mixture was stirred at 75 °C for 3 days. After cooling to room temperature, the mixture was extracted with CHCl$_3$. The combined organic layer was washed with brine, dried over anhydrous Na$_2$SO$_4$, and then concentrated in vacuo, the residue was purified by flash column chromatography (Al$_2$O$_3$), eluting with CHCl$_3$ to give the product as 489 mg white solid (yield 65%). ^{1}H NMR (500 MHz, CDCl$_3$, 300 K, ppm): δ 8.69 (s, 4H, *Tpy-H*$^{3',5'}$), 8.65-8.66 (d, J =4.0 Hz, 4H, *Tpy-H*$^{6,6''}$), 8.60-8.62 (d, J = 8.0 Hz, 4H, *Tpy-H*$^{3,3''}$), 7,80-7.85 (td, J = 7.7Hz, 4H, *Tpy-*$^{4,4''}$), 7.75-7.77 (d, J = 7.7 Hz, 4H, *Ph-H*^{j}), 7.27-7.29 (ddd, J = 7.2 Hz, 4H, *Tpy-H*$^{5,5''}$), 7.23-7.25 (d, J = 7.2, Hz, 4H, *Ph-H*^{k}) 7.05 (s, J = 7.0 Hz, 2H, *Ph-H*^{a}), 3.77 (s, 6H,-*OCH*$_3$*-H*^{b}); ^{13}C NMR (125MHz, ppm): δ 156.4, 155.8, 151.5, 150.0, 149.1, 147.4, 137.7, 136.7, 131.6, 131.5, 126.4,123.6, 121.3, 118.9, 111.4; ESI-TOF (*m/z*): Calcd. For [C$_{50}$H$_{36}$N$_6$O$_2$+H]$^+$, 753.29, Found: 753.30; [C$_{50}$H$_{36}$N$_6$O$_2$+2H]$^{2+}$, 377.15, Found: 377.15.

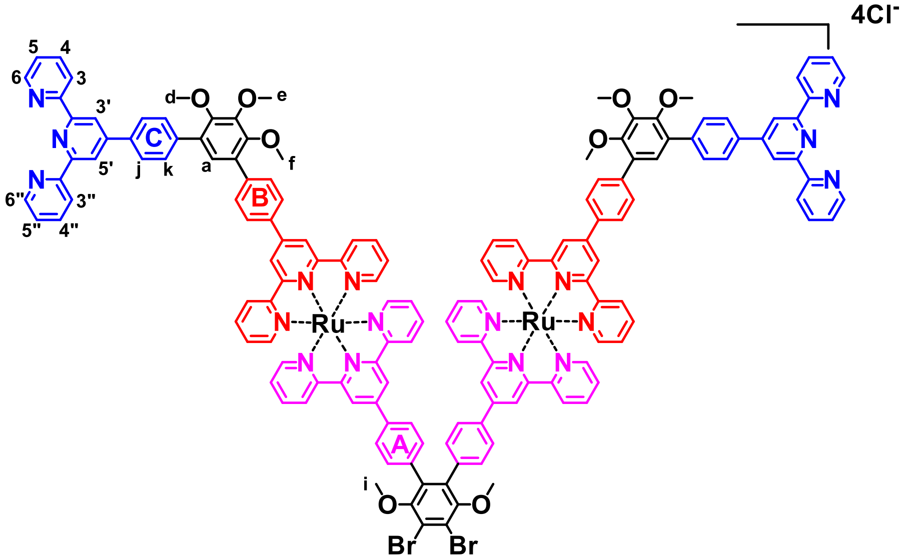


Compound 4, To a stirred solution of compound **3** (1.50 g, 2 mmol) in CH$_2$Cl$_2$ (30 mL) at 0 °C, a solution of Br$_2$ (0.64 g, 4 mmol) in CH$_2$Cl$_2$ (10 mL) was added drop-wise. After stirring at 25 °C for 12 h, the reaction mixture was washed with saturated Na$_2$SO$_3$ solution until colorless, dried over anhydrous MgSO$_4$, and then concentrated in vacuo to give the product as 1.49 g colorless liquid (yield 82%). ^{1}H NMR (500 MHz, CDCl$_3$, 300 K, ppm): δ 8.70 (s, 4H, *Tpy-H*$^{3',5'}$), 8.66-8.67 (d, J =4.0 Hz, 4H, *Tpy-H*$^{6,6''}$), 8.62-8.64 (d, J = 8.0 Hz, 4H, *Tpy-H*$^{3,3''}$), 7.83-7.87 (ddd, J = 7.8Hz, 4H, *Tpy-*$^{4,4''}$), 7.77-7.79

(td, J = 7.7 Hz, 4H, *Ph-H*^{j}), 7.31-7.33 (ddd, J = 7.3 Hz, 4H, *Tpy-H*$^{5,5''}$), 7.29-7.30 (d, J = 7.2, Hz, 4H, *Ph-H*^{k}), 3.41 (s, 6H,-*OCH*$_3$*-H*^{b}); ^{13}C NMR (125MHz, ppm): δ 156.2, 155.9, 152.5, 149.7, 149.1, 137.2, 136.8, 136.2, 135.7,131.2, 126.8,123.8, 121.3, 118.9, 60.5; ESI-TOF (*m/z*): Calcd. for$[C_{50}H_{34}Br_2N_6O_2+H]^+$, 911.67, Found: 911.67.

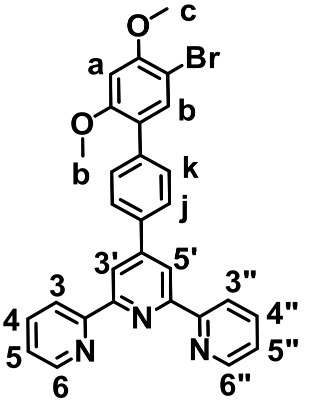


Compound 5, Compound **4** (300.0 mg, 0.33 mmol) and $RuCl_3 \cdot 3H_2O$ (180.0 mg, 0.7 mmol) were mixed in 50 mL $CHCl_3$/MeOH (v/v, 1:1). The mixture was stirred at 72 °C for 48 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford 350 mg compound **5** (yield 80%).



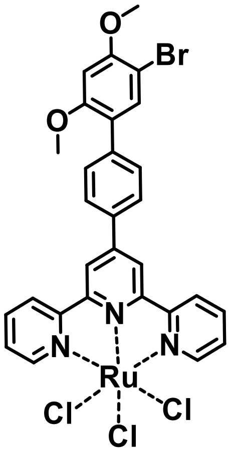
Compound 6: To a mixture of compound **2** (198 mg, 0.25 mmol) and compound **5** (132.0 mg, 0.1 mmol) in $CHCl_3$/MeOH (250 mL, v/v, 1:1), a few drops of N-ethylmorpholine were added as reductant. After refluxing for 48 h, the solution was concentrated in vacuo to give a red solid that was chromatographed (Al_2O_3) using a mixed solvent of CH_2Cl_2/MeOH (100:1.75, v/v) to produce the product as 215 mg red

powder (yield 65%). ESI-TOF (*m/z*): 1374.82 $[M-2Cl^{-}]^{2+}$ (calcd *m/z*: 1374.82), 904.91 $[M-3Cl^{-}]^{3+}$ (calcd *m/z*: 904.91), 669.69 $[M-4Cl^{-}]^{4+}$ (calcd *m/z*: 669.69); ^{1}H NMR (500 MHz, $CDCl_3$,300 K, ppm) δ 9.35-9.31 (d, J = 20 Hz, 4H, $Tpy^{A,B}$-$H^{3',5'}$), 8.91 (s, 4H, $Tpy^{A,B}$-$H^{3,3''}$), 8.83-8.71 (m, 6H, Tpy^{C}-$H^{3',5'}$, Tpy^{C}-$H^{C6,6''}$, Tpy^{C}-$H^{C3,3''}$), 8.41-8.39 (d, J = 10 Hz, 2H, Ph^{B}-H^{j}), 8.33-8.32 (d, J = 5Hz, 2H, Ph^{A}-H^{j}), 8.16-8.05 (m, 4H, Tpy^{C}-$H^{4,4''}$, Ph^{C}-H^{j}), 8.01-7.98 (t, J = 15 Hz, 6H, Tpy^{B}-$H^{4,4''}$, Ph^{B}-H^{j}, Tpy^{A}-$H^{4,4''}$), 7.86-7.84 (d, J = 10 Hz, 2H, Ph^{C}-H^{k}), 7.71-7.69 (d, J =10 Hz, 2H, Ph^{A}-H^{k}), 7.58-7.57 (d, J = 10 Hz, 4H, Tpy^{C}-$H^{5,5''}$, Tpy^{B}-$H^{B6,6''}$), 7.55-7.54 (d, J = 10Hz, 2H, Tpy^{A}-$H^{6,6''}$), 7.35 (s, 1H, Ph-H^{a}), 7.29-7.25 (d, J = 20Hz, 4H, $Tpy^{A,B}$-$H^{5,5''}$), 4.11 (s, 3H, *-OCH3*-H^{e}), 3.86-3.84 (d, J =10 Hz, 6H, *-OCH3*-$H^{d,f}$), 3.59 (s, 3H, *-OCH3*-H^{I}); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.21, 157.92, 157.76, 157.60, 155.73, 155.59, 155.28, 152.67, 151.68, 149.85, 148.68, 148.33, 147.52, 140.28, 139.37, 138.01, 137.86, 137.54, 136.14, 135.86, 135.46, 134.03, 131.97, 131.78, 130.18, 130.12, 127.54, 127.12, 126.89, 126.55, 124.78, 124.54, 124.27, 122.01, 121.83, 121.61, 121.33, 120.88, 118.24, 96.39, 62.64, 61.03, 60.00, 55.28, 55.17, 48.23, 48.11, 48.06, 47.94, 47.89, 47.77, 47.60, 47.43, 47.26, 47.09.

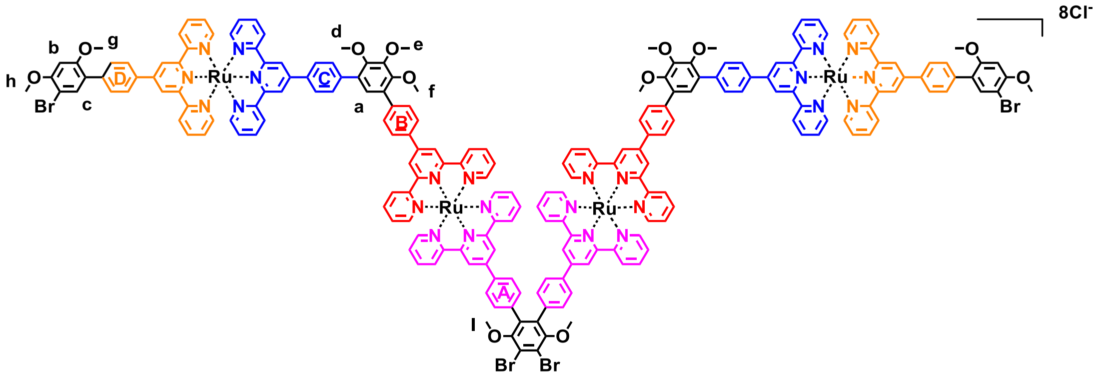


Compound 7, To a solution of 4'-(4-boronatophenyl)-[2,2':6',2"]terpyridine (1.4 g, 4 mmol) and 1,3-dibromo-2,5-dimethoxybenzene (592 mg, 2 mmol) in THF (150 mL), aqueous NaOH (480 mg, 12 mmol) (1 M) was added. The system was degassed for 10 minutes, then $Pd(PPh_3)_4$ (231 mg) was added. After refluxing for 2 days under N_2, the solvent was removed in vacuo to give a residue that was dissolved in $CHCl_3$ and washed with water. The organic layer was dried (anhydrous $MgSO_4$), concentrated in vacuo to give a residue that was purified by flash column chromatography (Al_2O_3) with $CHCl_3$

to give the product as 295 mg white solid (yield 28%).[4] ^{1}H NMR (500 MHz, $CDCl_3$, 300K, ppm) δ 8.84 (s, 2H, *Tpy-H*$^{3',5'}$), 8.79-8.78 (d, J= 5Hz, 2H, *Tpy-H*$^{6,6''}$), 8.73-8.72 (d, J= 5Hz, 2H, *Tpy-H*$^{3,3''}$), 8.01-7.99 (d, J= 10Hz, 2H, *Ph-H*^{j}), 7.95-7.92 (m, 2H, *Tpy-H*$^{4,4''}$),7.67-7.65 (d, J= 10Hz, 2H, *Ph-H*^{k}), 7.59 (s, 1H, *Ph-H*^{b}), 7.42-7.39 (m, 2H, *Tpy-H*$^{5,5''}$), 6.63 (s, 1H, *Ph-H*^{a}), 4.00 (s, 3H, *-OCH$_3$-H*^{c}), 3.89 (s, 3H, *-OCH$_3$-H*^{b}); ^{13}C NMR (126 MHz, $CDCl_3$) δ 156.99, 156.26, 156.12, 150.03, 148.94,137.97, 137.14, 136.80, 134.34, 129.89, 127.07, 124.01, 123.87, 121.52, 118.94, 102.47, 97.27, 56.60, 56.09; ESI-TOF (*m/z*): Calcd. For: $[C_{29}H_{22}BrN_3O_2+H]^+$ 526.09, Found: 526.10.

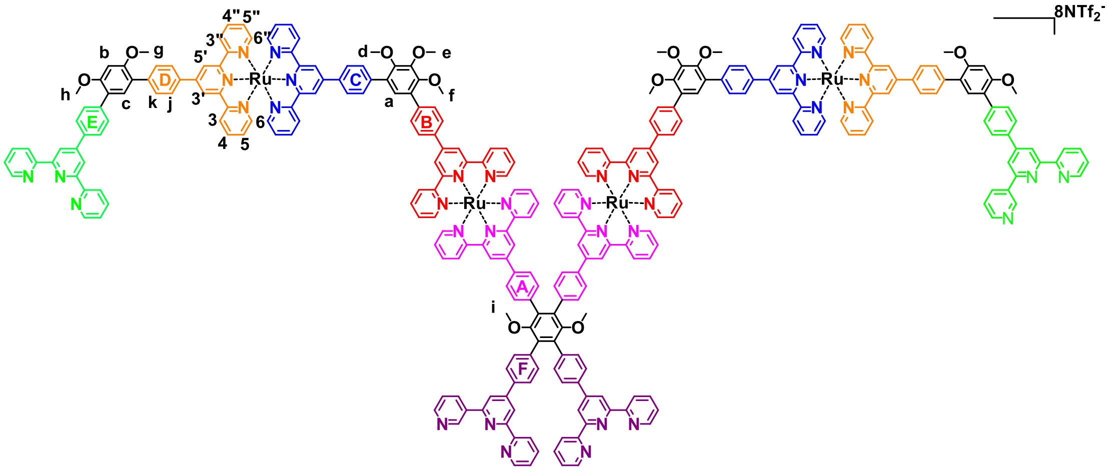


Compound 8, Compound **7** (210 mg, 400 μmol) and $RuCl_3\cdot 3H_2O$ (115 mg, 440 μmol) were added into EtOH (60 mL), and refluxed for 18 h. Then it was filtered to give a solid which was washed by MeOH to afford the product as 244.7 mg brown solid (yield 83.6%). It was used directly without further purification.



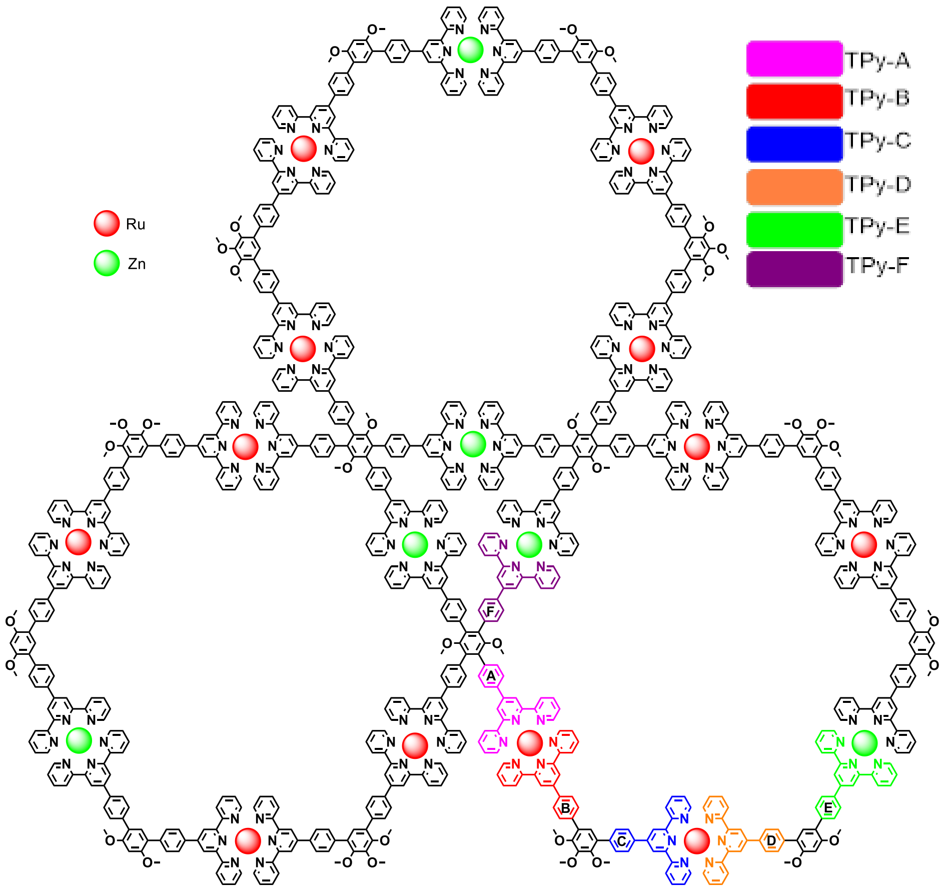
Compound 9: To a mixture of compound **8** (215 mg, 0.076 mmol) and compound **6** (118.0 mg, 0.16 mmol) in $CHCl_3$/MeOH (250 mL, v/v, 1:1), a few drops of N-ethyl morpholine were added as reductant. After refluxing for 48 h, the solution was

concentrated in vacuo to give a red solid that was chromatographed (Al_2O_3) using a mixed solvent of CH_2Cl_2/MeOH (100:4.5, v/v) to give 180 mg red powder as the product (yield 54%). ESI-TOF (*m/z*): 1018.17 $[M-4Cl^{-}]^{4+}$ (calcd *m/z*: 1017.9), 807.35 $[M-5Cl^{-}]^{5+}$ (calcd *m/z*: 807.21), 666.79 $[M-6Cl^{-}]^{6+}$ (calcd *m/z*: 669.76); ^{1}H NMR (500 MHz, $CDCl_3$, 300k, ppm) δ 9.40-9.39 (d, J = 5 Hz, 4H, *Tpy-*$H^{C,D3'5'}$), 9.35 (s, 4H, *Tpy-*$H^{A,B3',5'}$), 8.98-8.93 (m, 8H, *Tpy-*$H^{A,B,C,D3,3''}$), 8.47-8.46 (d, J = 5 Hz, 4H, *Ph-*$H^{C,Dj}$), 8.36-8.33 (t, J = 15 Hz, 4H, *Ph-*$H^{A,Bj}$), 8.10-7.98 (m, 12H, *Tpy-*$H^{A,B,C,D4,4''}$, *Ph-*$H^{C,Dk}$), 7.89-7.87 (d, J = 10 Hz, 2H, *Ph-*H^{Bk}), 7.71-7.70 (d, J = 5 Hz, 2H, *Ph-*H^{Ak}), 7.63-7.56(m, 9H, *Ph-*H^{a}, *Tpy-*$H^{A,B,C,D66''}$), 7.44 (s, 1H, *Ph-*H^{c}), 7.36–7.26 (m, 8H, *Tpy-*$H^{A,B,C,D55''}$), 6.90 (s, 1H, *Ph-*H^{b}), 4.14 (s, 3H,-OCH_3-H^{e}), 4.03 (s, 3H,-OCH_3-H^{h}), 3.98 (s, 3H,-OCH_3-H^{g}), 3.89 (s, 6H,-OCH_3-$H^{d,f}$), 3.58 (s, 3H, -*OCH3-*H^{i}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.47, 157.93, 155.55, 151.98, 140.72, 138.02, 133.60, 130.36, 130.22, 127.55, 127.18, 124.64, 121.16, 55.59, 55.20, 55.15, 48.24, 48.09, 48.02, 47.88, 47.81, 47.60, 47.38, 47.17, 46.96.



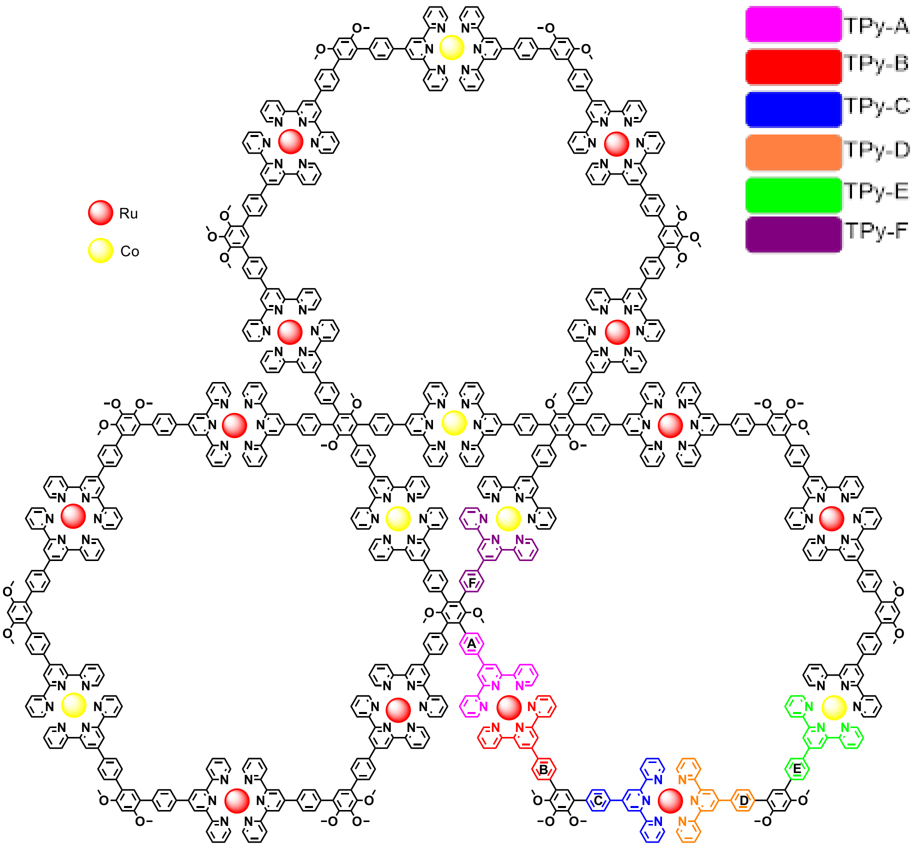
Ligand: To a solution of 4'-(4-boronatophenyl)-[2,2':6',2"]terpyridine (120 mg, 338 μmol) and compound **9** (60 mg, 14.1 μmol) in CH_3CN (40 mL), aqueous K_2CO_3 (25 mg, 181 μmol, 0.5 mL) was added. The system was degassed for 10 minutes, and then $Pd(PPh_3)_4$ (19 mg, 16 μmol) was added. After refluxing 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

MeOH to obtain 75 mg reddish product (yield 68%). ESI-TOF (*m/z*): 1136.83 $[\mathrm{M}{-}5\mathrm{NTf_2}^{-}]^{5+}$ (calcd *m/z*: 1136.83), 900.72 $[\mathrm{M}{-}6\mathrm{NTf_2}^{-}]^{6+}$ (calcd *m/z*: 900.72), 732.07 $[\mathrm{M}{-}7\mathrm{NTf_2}^{-}]^{7+}$ (calcd *m/z*: 732.07); ^{1}H NMR (400 MHz, CD_3CN) δ 9.10–9.03 (m, 8H, *Tpy-H*$^{A,B,C,D3',5'}$), 8.82 (s, 2H,*Tpy-H*$^{E3',5'}$), 8.75–8.64 (m, 18H,*Tpy-H*$^{A,B,C,D,E,F3,3''}$, *Tpy-H*$^{F3',5'}$, *Tpy-H*$^{E,F6,6''}$), 8.35-8.31 (m, 4H,*Ph-H*^{A,Dj}), 8.28-8.26 (d, J = 8 Hz, 4H, *Ph-H*^{B,Cj}), 8.02–7.82 (m, 27H, *Ph-H*^{c}, *Tpy-H*$^{A,B,C,D,E,F4,4''}$, *Ph-H*^{c,A,B,C,D,Ek}, *Ph-H*^{E,Fj}), 7.55 (s, 2H, *Ph-H*^{Fk}), 7.48–7.39 (m, 13H, *Ph-H*^{a}, *Tpy-H*$^{A,B,C,D6,6''}$, *Tpy-H*$^{E,F5,5''}$), 7.2–7.11 (m, 8H, *Tpy-H*$^{A,B,C,D5,5''}$), 6.94 (s, 1H, *Ph-H*^{b}), 4.10 (s, 3H, *-OCH$_3$-H*^{e}), 4.02-4.00 (d, J = 8 Hz, 6H, *-OCH$_3$-H*^{g,h}), 3.88 (s, 6H, *-OCH$_3$-H*^{d,f}), 3.15 (s, 3H, *-OCH$_3$-H*^{i}); ^{13}C NMR (126 MHz, CD_3CN) δ 158.26, 157.98, 157.86, 157.75, 155.69, 155.46, 155.34, 155.07, 152.43, 148.95, 148.04, 138.05, 134.74, 132.24, 130.65, 130.38, 127.48, 127.41, 126.82, 124.63, 121.78, 121.45, 121.39, 121.19, 118.64, 118.58, 118.31, 117.34, 96.84, 55.85, 55.80, 55.76, 48.90.

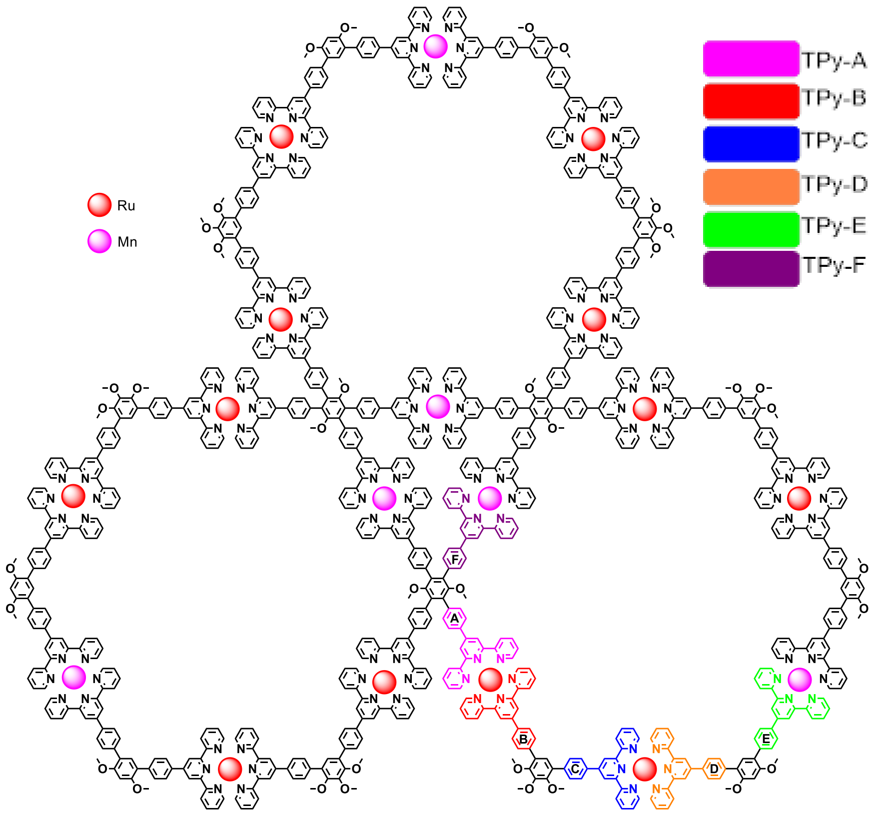


Zn_6L_3: To a solution of **L** (15 mg, 2.1 μmol) in MeCN (12 mL), $Zn(NTf_2)_2$ (1.25 mg, 4.2 μmol) in MeOH was added; then the mixture was stirred at 80 °C for 8 hours.

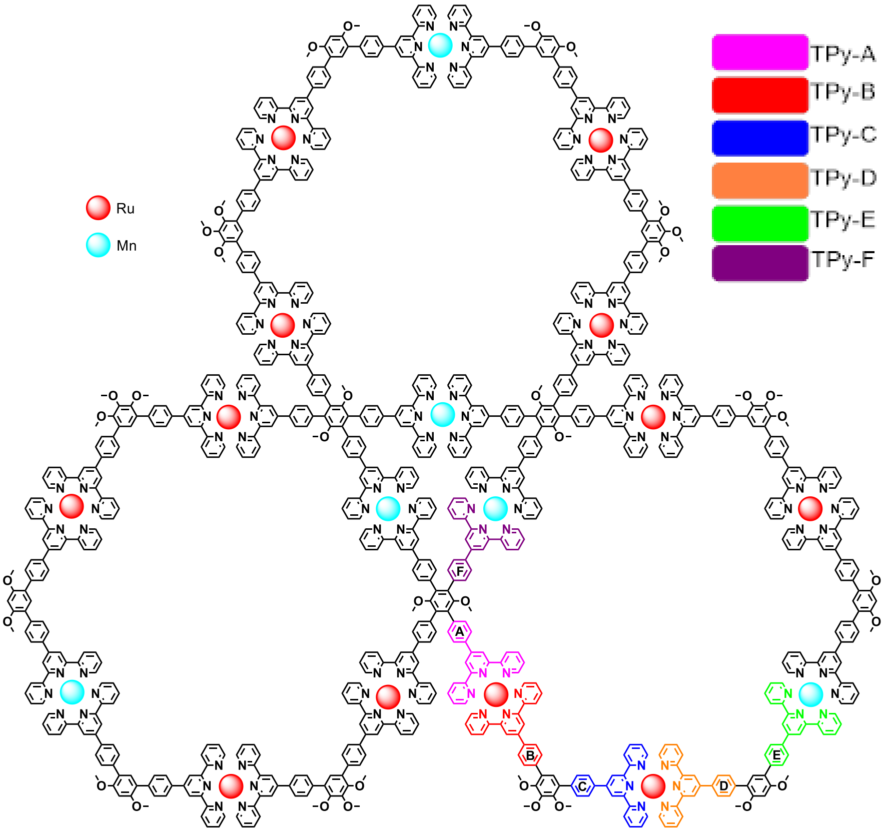
Subsequently, $LiNTf_2$ was added to generate red precipitates, which were filtered and washed with H_2O and MeOH to obtain 50 mg reddish product (yield 98%). ESI-TOF (*m/z*): 1993.27 $[M{-}11\ NTf_2^{-}]^{11+}$ (calcd *m/z*: 1993.27), 1803.82 $[M{-}12NTf_2^{-}]^{12+}$ (calcd *m/z*: 1803.82), 1643.51 $[M{-}13NTf_2^{-}]^{13+}$ (calcd *m/z*: 1643.51), 1506.11 $[M{-}14NTf_2^{-}]^{14+}$ (calcd *m/z*: 1506.11), 1387.02 $[M{-}15NTf_2^{-}]^{15+}$ (calcd *m/z*: 1387.02), 1282.83 $[M{-}16NTf_2^{-}]^{16+}$ (calcd *m/z*: 1282.83), 1190.45 $[M{-}17NTf_2^{-}]^{17+}$ (calcd *m/z*: 1190.45), 1109.16 $[M{-}18NTf_2^{-}]^{18+}$ (calcd *m/z*: 1109.16), 1036.04 $[M{-}19NTf_2^{-}]^{19+}$ (calcd *m/z*: 1036.04), 970.23 $[M{-}20NTf_2^{-}]^{20+}$ (calcd *m/z*: 970.23), 910.69 $[M{-}21NTf_2^{-}]^{21+}$ (calcd *m/z*: 910.69); ^{1}H NMR (400 MHz,CD_3CN) δ 9.12 (s,12H, *Tpy-H*$^{A,B,C,D3'5'}$, *Tpy-H*$^{E,F3',5')}$ 8.72 (s,12H, *Tpy-H*$^{A,B,C,D,E,F3,3''}$), 8.48–8.14 (m, 16H, *Ph-H*^{A,B,C,D,E,Fj}, *Tpy-H*$^{E,F4,4''}$), 8.10–7.82 (m, 24H, *Tpy-H*$^{A,B,C,D4,4''}$, *Tpy-H*$^{E,F6,6''}$, *Ph-H*^{A,B,C,D,E,Fk}), 7.69 (s, 1H,*Ph-H*^{c}), 7.62 (s, 1H, *Ph-H*^{a}), 7.48 (s,12H, *Tpy-H*$^{A,B,C,D6,6''}$, *Tpy-H*$^{E,F6,6''}$), 7.23 (s, 8H, *Tpy-H*$^{A,B,C,D5,5''}$), 7.02 (s, 1H, *Ph-H*^{b}), 4.12 (s, 3H, -OCH_3-H^{e}), 4.07-4.05 (d, $J = 8$ Hz, 6H, -OCH_3-$H^{g,h}$), 3.92 (s, 6H, -OCH_3-$H^{d,f}$), 3.28 (s, 3H, -OCH_3-H^{i}).



Co_6L_3: To a solution of **L** (5 mg, 0.7 μmol) in MeCN (2 mL), $CoCl_2 \cdot 6H_2O$ (0.325 mg, 1.4 μmol) in MeOH was added; then the mixture was stirred at 80 °C for 8 hours. Subsequently, $LiNTf_2$ was added to generate red precipitates, which were filtered and washed with H_2O and MeOH to obtain 17 mg reddish product (98% yield). ESI-TOF (*m/z*): 1989.75 $[M-11\ NTf_2^{-}]^{11+}$ (calcd *m/z*: 1989.75),1800.59 $[M-12NTf_2^{-}]^{12+}$ (calcd *m/z*: 1800.59), 1640.54 $[M-13NTf_2^{-}]^{13+}$ (calcd *m/z*: 1640.54), 1503.34 $[M-14NTf_2^{-}]^{14+}$ (calcd *m/z*: 1503.34), 1384.45 $[M-15NTf_2^{-}]^{15+}$ (calcd *m/z*: 1384.45), 1280.41 $[M-16NTf_2^{-}]^{16+}$ (calcd *m/z*: 1280.41), 1188.47 $[M-17NTf_2^{-}]^{17+}$ (calcd *m/z*: 1188.47), 1107.01 $[M-18NTf_2^{-}]^{18+}$ (calcd *m/z*: 1107.01), 1034.01 $[M-19NTf_2^{-}]^{19+}$ (calcd *m/z*: 1034.01), 968.30 $[M-20NTf_2^{-}]^{20+}$ (calcd *m/z*: 968.30), 908.85 $[M-21NTf_2^{-}]^{21+}$ (calcd *m/z*: 908.85), ^1H NMR (500 MHz, CD_3CN) δ 99.22 (s, *Tpy-*$H^{E,F6,6''}$), 57.80 (dd, *Tpy-*$H^{E,F3,3''}$), 53.33 (m, *Tpy-*$H^{E3',5'}$), 52.99 (m, *Tpy-*$H^{F3',5'}$),33.69(s, *Tpy-*$H^{E,F5,5''}$), 14.97(s, *Tpy-*$H^{E4,4''}$), 10.11(s, *Tpy-*$H^{F4,4''}$)9.37 (s, *Tpy-*$H^{A,B,C,D3',5'}$), 9.15 (s, *Tpy-*$H^{A,B,C,D3,3''}$), 8.86 (s, *Ph-*$H^{A,B,C,D,E,Fj,k}$), 8.74 (s, *Tpy-*$H^{A,B,C,D4,4''}$), 8.08–7.52 (m, *Tpy-*$H^{A,B,C,D6,6''}$, *Ph-*H^{a}), 7.54 (s, *Ph-*H^{c}), 7.54 (s, *Ph-*H^{b}), 7.29 (s, *Tpy-*$H^{A,B,C,D,5,5''}$), 4.14 (s, $-OCH_3-H^{e}$,$-OCH_3-H^{g,h}$), 3.93 (s, $-OCH_3-H^{d,f}$,$-OCH_3-H$).



Mn_6L_3: To a solution of **L** (6 mg, 0.84 μmol) in MeCN (2 mL), $MnClO_4$•$6H_2O$ (0.64 mg, 1.68 μmol) in MeOH was added, then the mixture was stirred at 80 °C for 8 hours. Subsequently, $LiNTf_2$ was added to generate red precipitates, which were washed filtered and with H_2O and MeOH to obtain 20 mg reddish product (yield 98%). ESI-TOF (*m/z*): 1987.57 $[M-11\ NTf_2^-]^{11+}$ (calcd *m/z*: 1987.57), 1798.59 $[M-12NTf_2^-]^{12+}$ (calcd *m/z*: 1798.59), 1638.69 $[M-13NTf_2^-]^{13+}$ (calcd *m/z*: 1638.69), 1501.63 $[M-14NTf_2^-]^{14+}$ (calcd *m/z*: 1501.63), 1382.84 $[M-15NTf_2^-]^{15+}$ (calcd *m/z*: 1382.84), 1278.91 $[M-16NTf_2^-]^{16+}$ (calcd *m/z*: 1278.91), 1187.62 $[M-17NTf_2^-]^{17+}$ (calcd *m/z*: 1187.62), 1105.68 $[M-18NTf_2^-]^{18+}$ (calcd *m/z*: 1105.68), 1032.74 $[M-19NTf_2^-]^{19+}$ (calcd *m/z*: 1032.74), 967.10 $[M-20NTf_2^-]^{20+}$ (calcd *m/z*: 967.10), 907.71 $[M-21NTf_2^-]^{21+}$ (calcd *m/z*: 907.71).



Ni_6L_3: To a solution of **L** (7.2 mg, 1 μmol) in MeCN (2 mL), $NiSO_4 \cdot 7H_2O$ (0.6 mg, 2 μmol) in MeOH was added; then the mixture was stirred at 80 °C for 8 hours. Subsequently, $LiNTf_2$ was added to generate red precipitates, which were washed filtered and with H_2O and MeOH to obtain 19 mg reddish product (yield 80%). ESI-TOF (*m/z*): 2216.92 $[M-11NTf_2^{-}]^{10+}$ (calcd *m/z*: 2216.92), 1989.86 $[M-11\ NTf_2^{-}]^{11+}$ (calcd *m/z*: 1989.86), 1800.90 $[M-12NTf_2^{-}]^{12+}$ (calcd *m/z*: 1800.90), 1640.86 $[M-13NTf_2^{-}]^{13+}$ (calcd *m/z*: 1640.86), 1503.71 $[M-14NTf_2^{-}]^{14+}$ (calcd *m/z*: 1503.71), 1384.81 $[M-15NTf_2^{-}]^{15+}$ (calcd *m/z*: 1384.81), 1280.77 $[M-16NTf_2^{-}]^{16+}$ (calcd *m/z*: 1280.77), 1188.52 $[M-17NTf_2^{-}]^{17+}$ (calcd *m/z*: 1188.52), 1107.27 $[M-18NTf_2^{-}]^{18+}$ (calcd *m/z*: 1107.27).

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

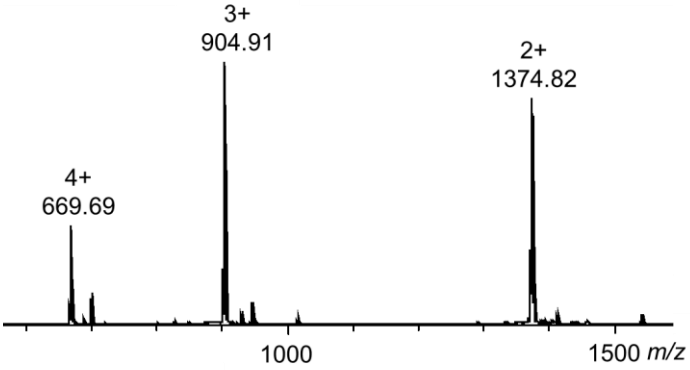


Figure S1. ESI-MS of compound **6** (Cl^{-} as counterion).

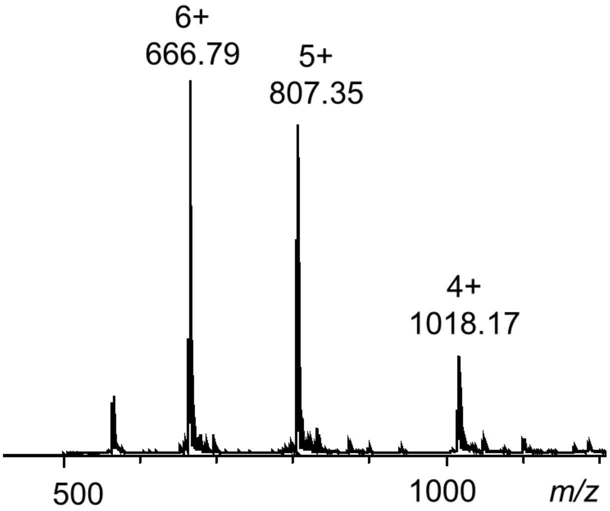


Figure S2. ESI-MS of compound **9** (Cl^{-} as counterion)

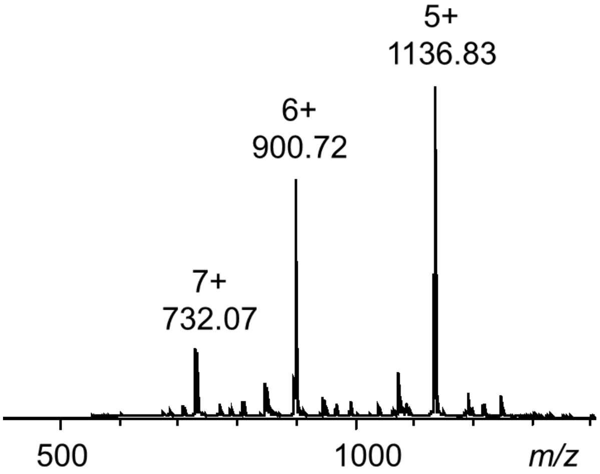


Figure S3. ESI-MS of **L** (NTf$_2^{-}$ as counterion).

5. ESI-MS spectra data of supramolecules (NTf_2^- as counterion)

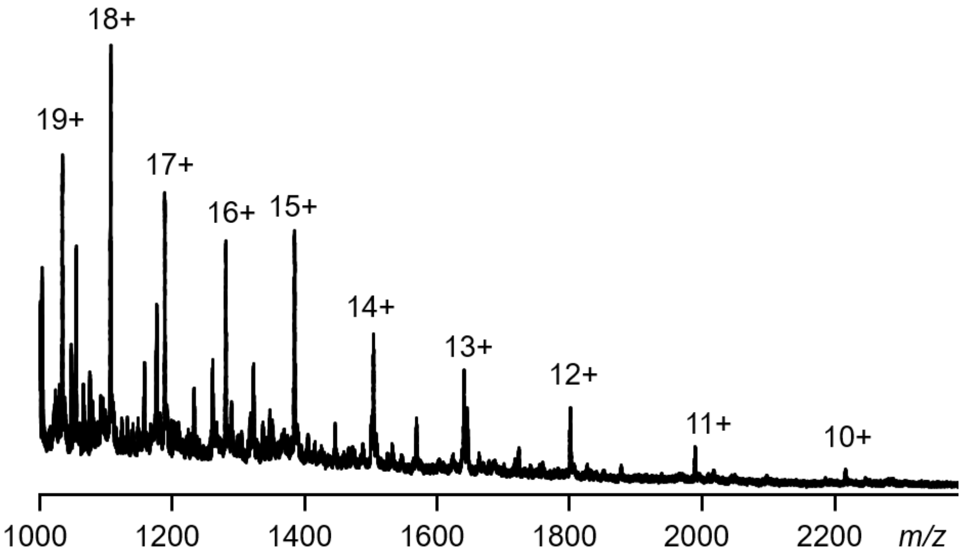


Figure S4. ESI-MS of **Ni_6L_3** (NTf_2^- as counterion).

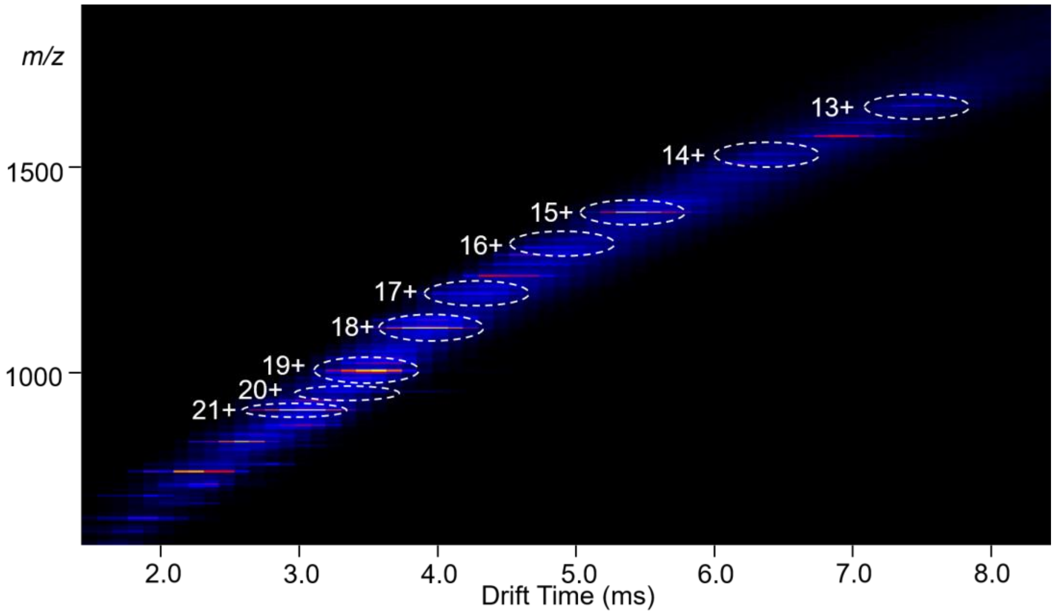


Figure S5. TWIM-MS plots (*m/z* vs drift time) of **Ni_6L_3** (NTf_2^- as counterion).

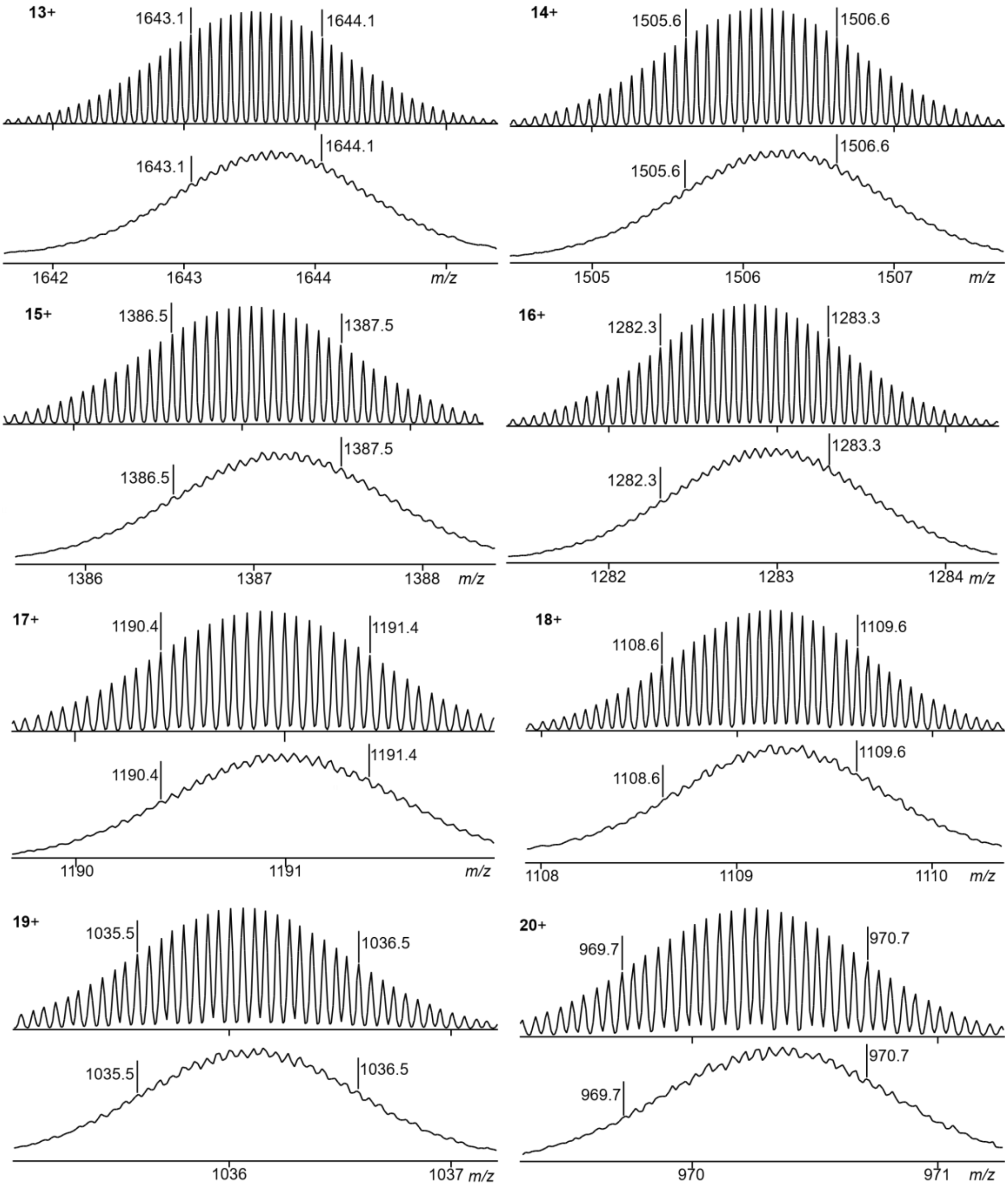


Figure S6. Measured (bottom) and calculated (top) isotope patterns for different charge states observed from **[Zn$_6$L$_3$]** (NTf$_2^-$ as counterion).

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

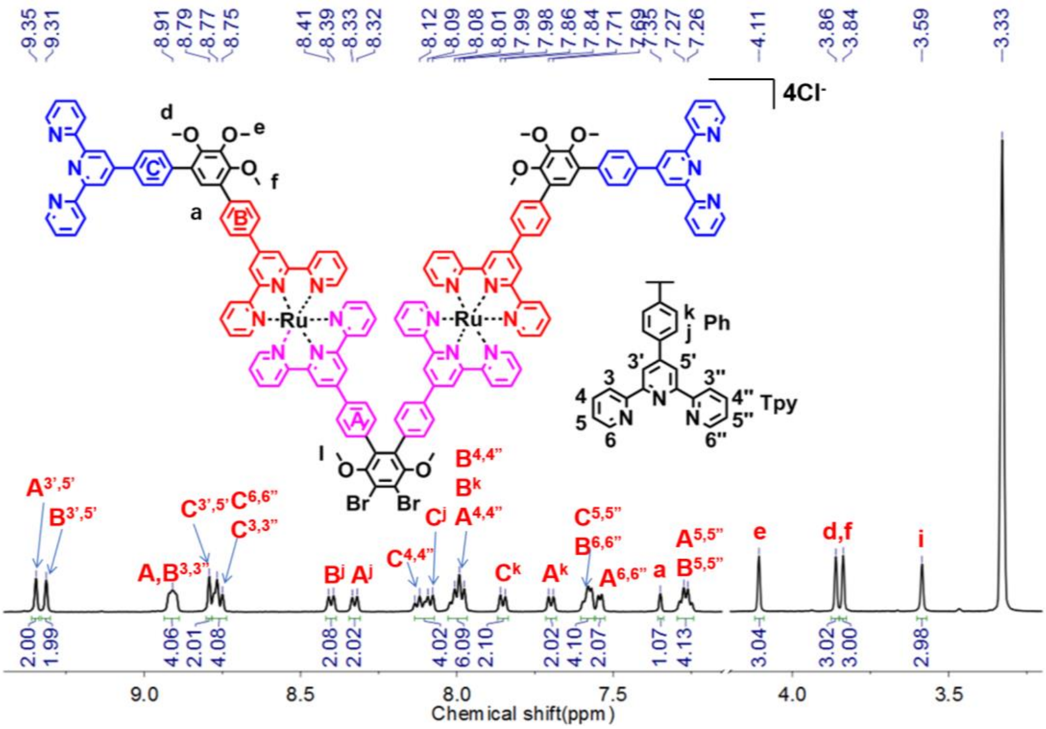


Figure S7. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **6**.

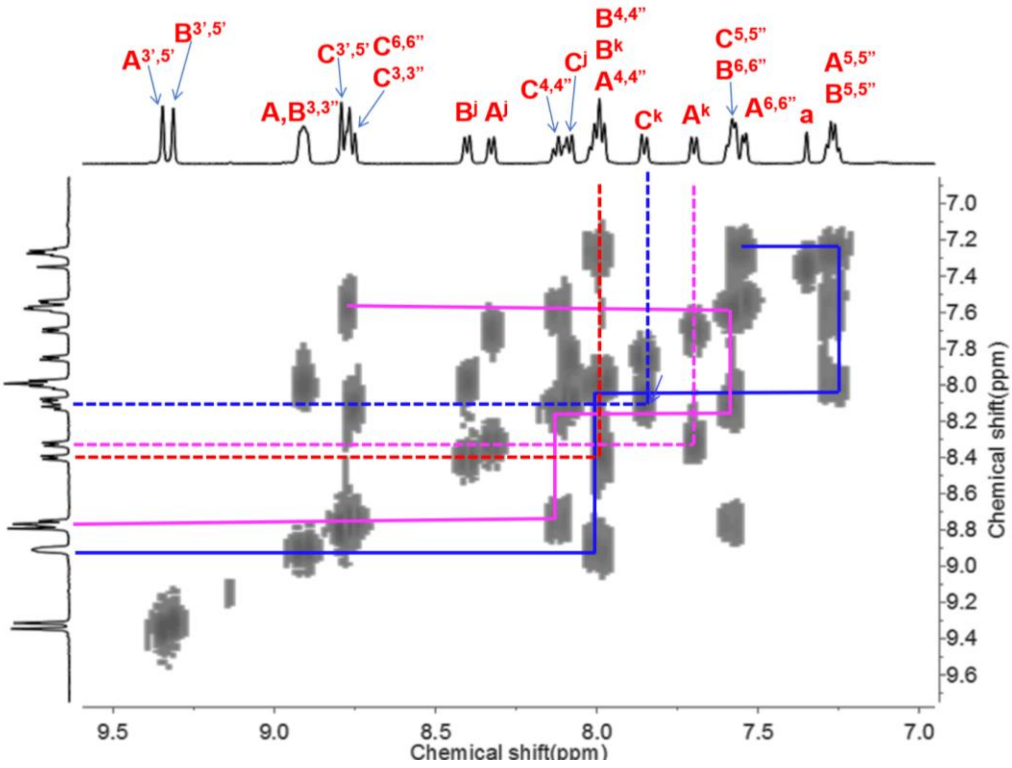


Figure **S8.** 2D COSY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **6** (aromatic region).

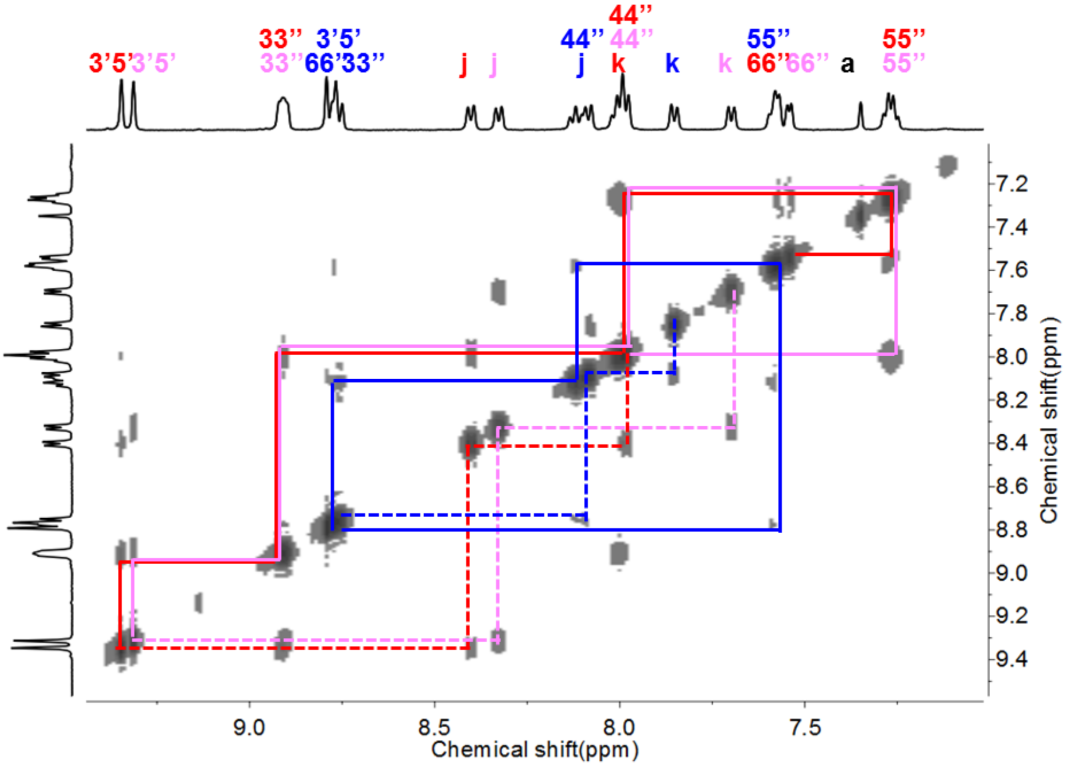


Figure S9. 2D NOESY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **6**.

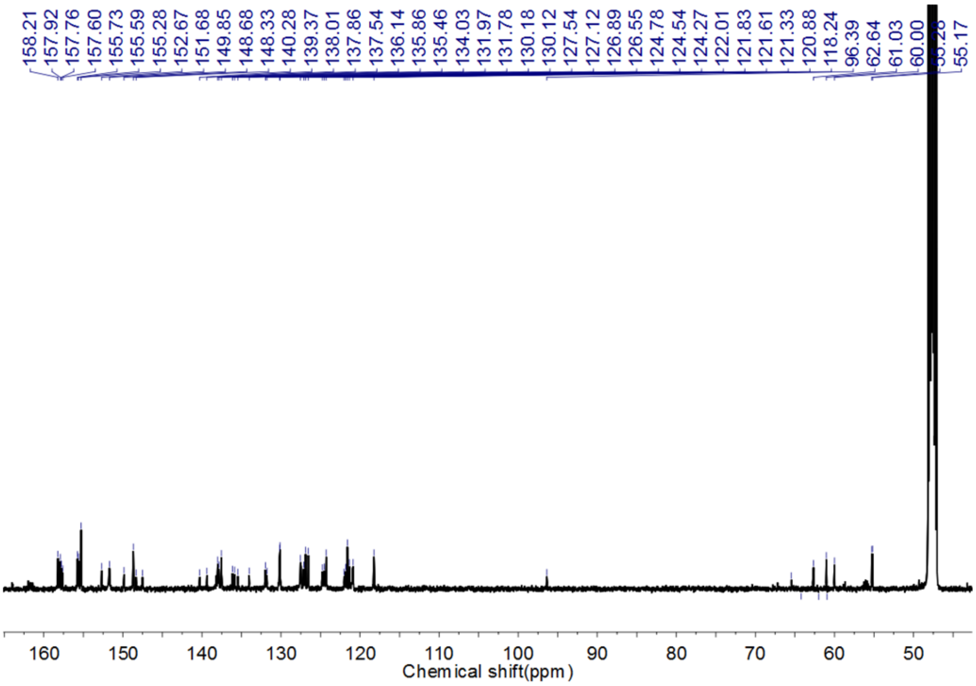


Figure S10. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) spectrum of compound **6**.

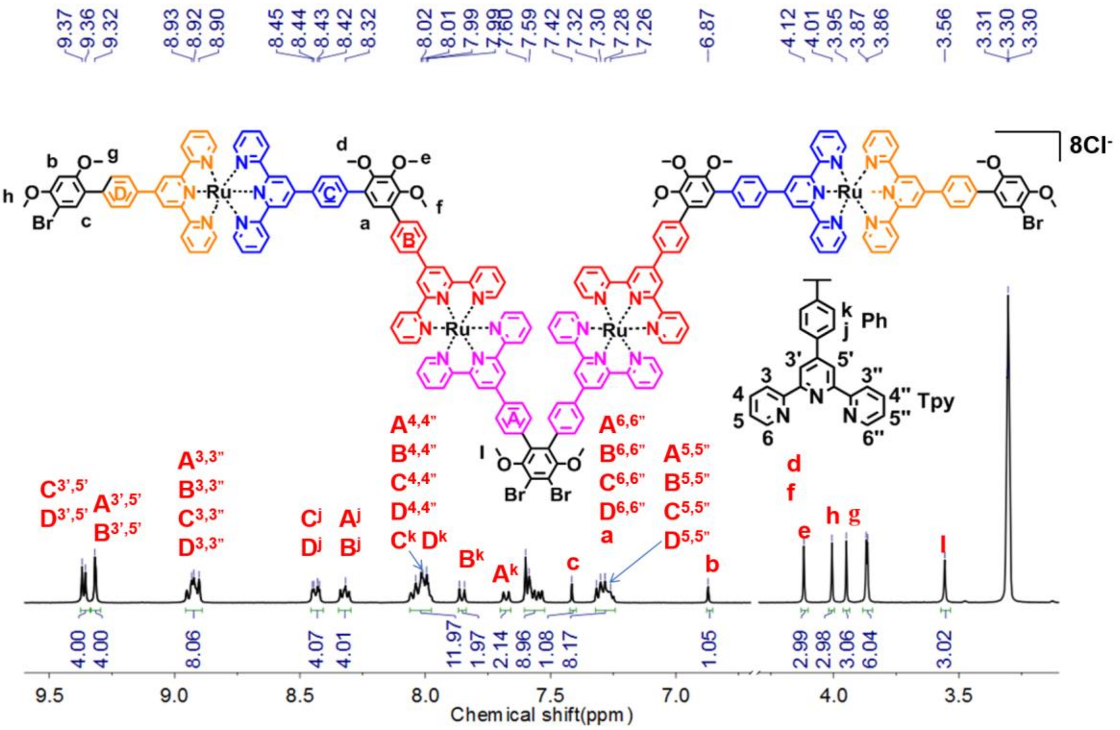


Figure S11. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **9**.

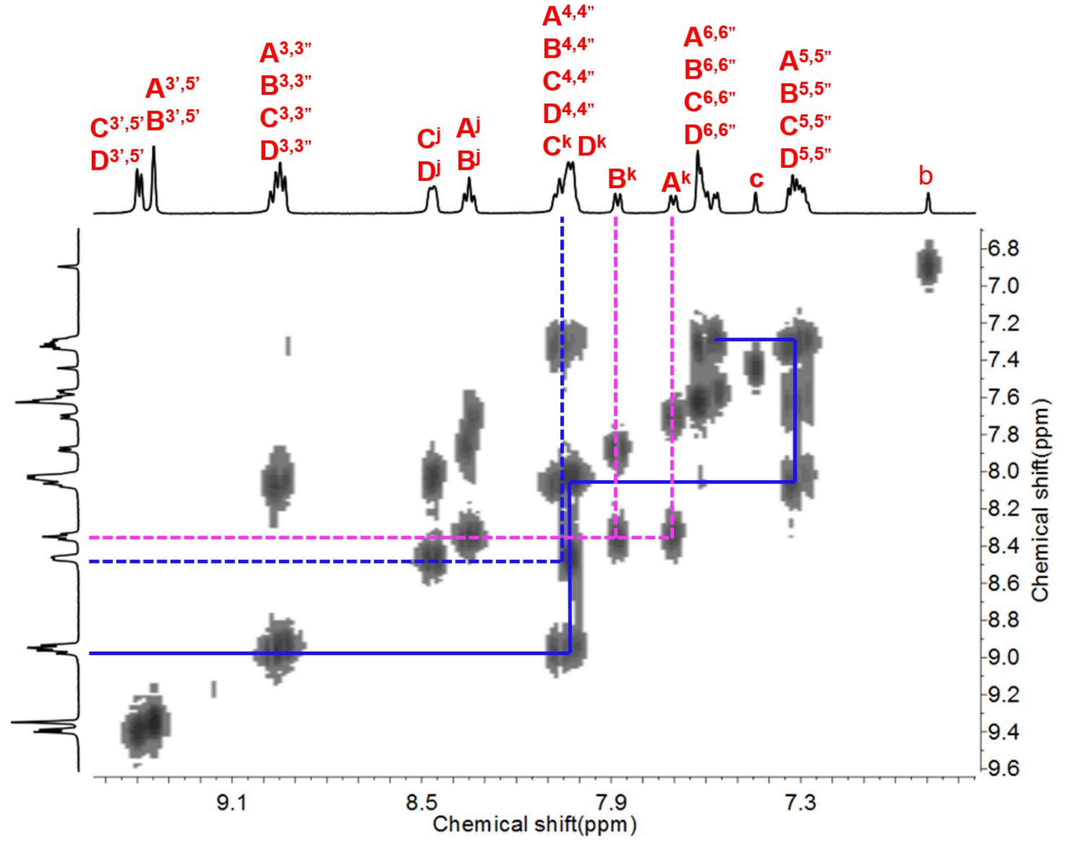


Figure S12. 2D COSY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **9**.

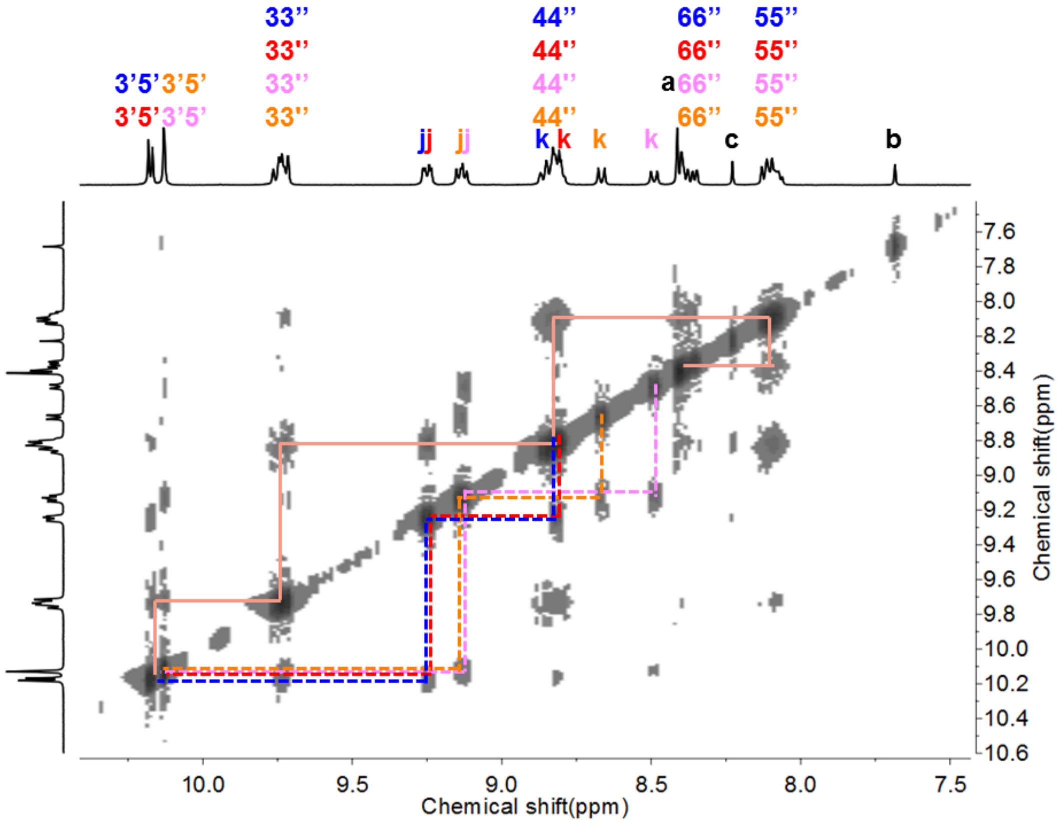


Figure S13. 2D NOESY NMR (500 MHz, $CDCl_3$, 300 K) spectrum of compound **9** (all cross peaks of Tpy-Ru-Tpy are illustrated by Rose-Bengal line).

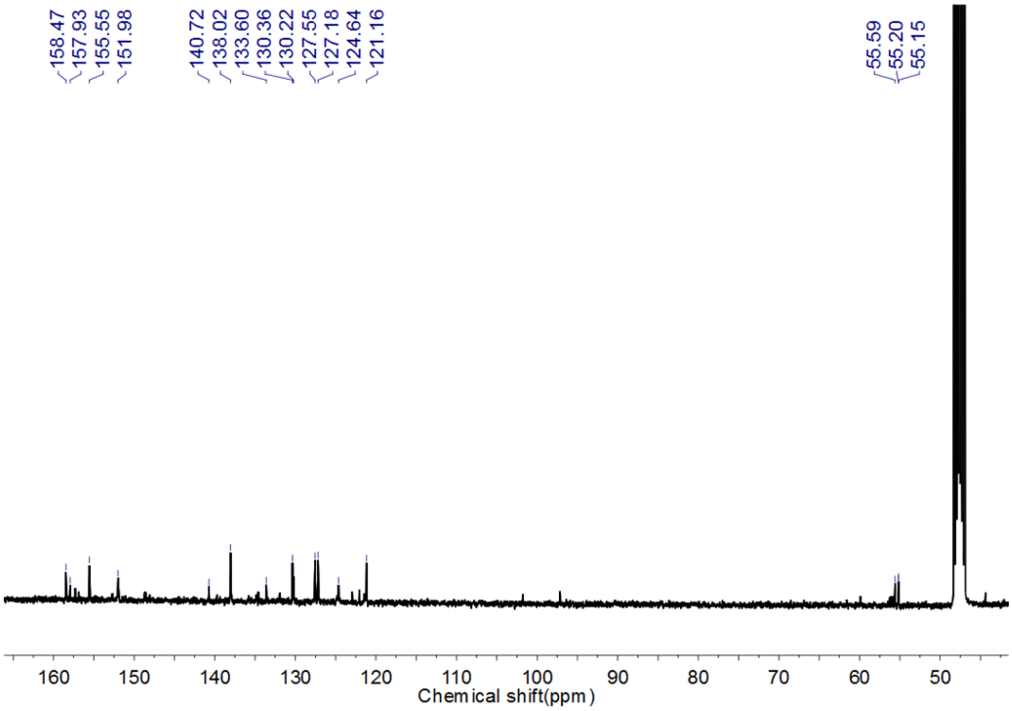


Figure S14. ^{13}C NMR (125 MHz, $CDCl_3$, 300 K) spectrum of compound **9**.

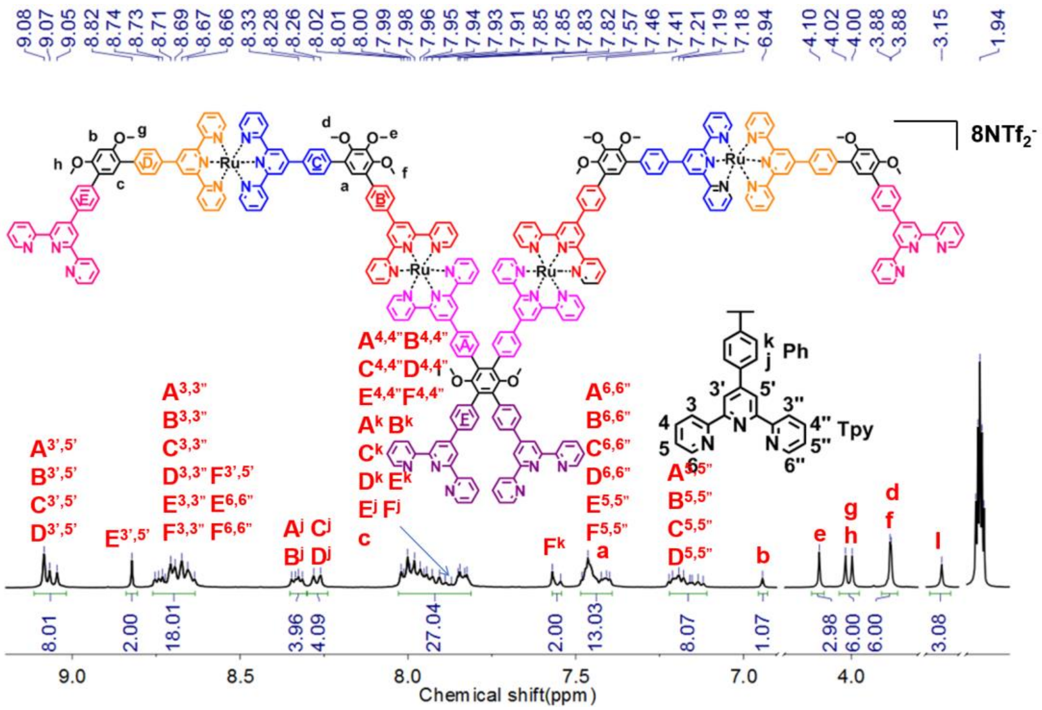


Figure S15 ^{1}H NMR (500 MHz, CD_3CN, 400 K) spectrum of **L**.

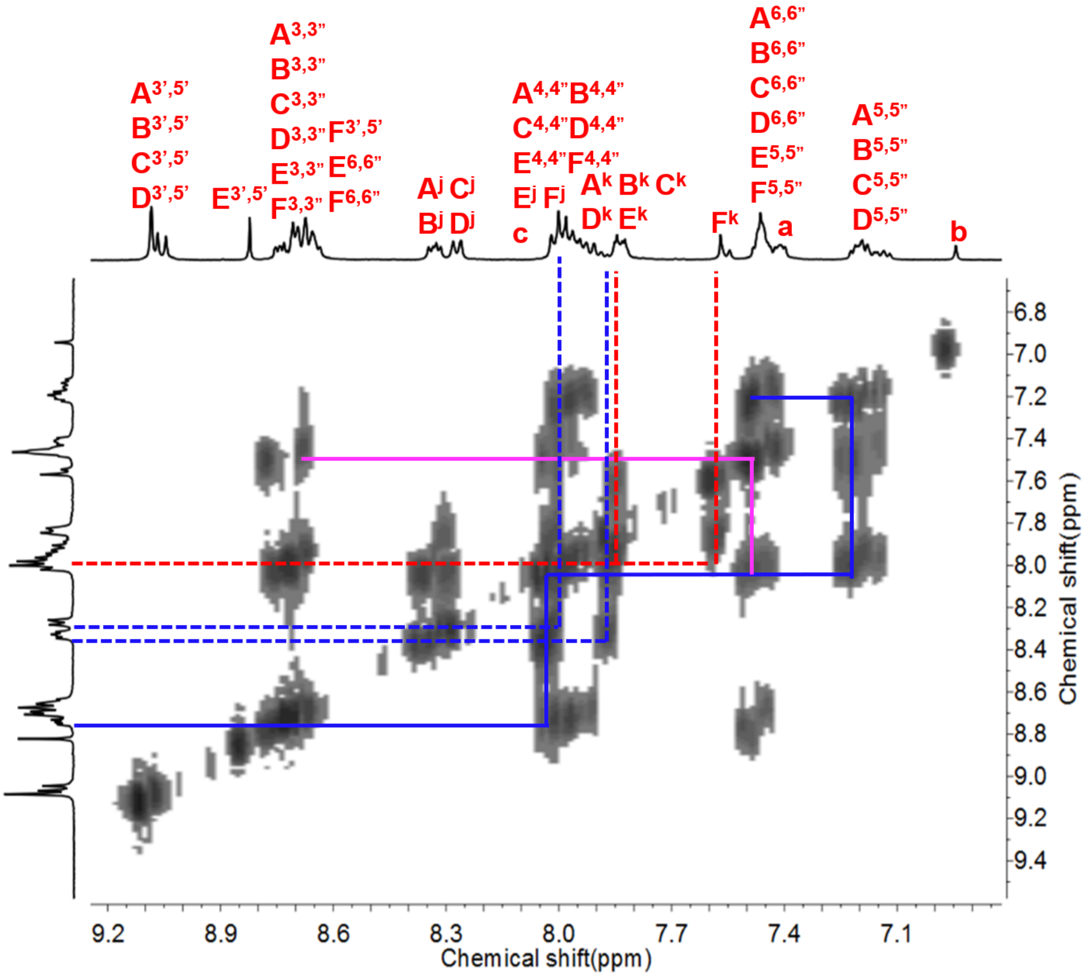


Figure S16. 2D COSY NMR (500 MHz, CD_3CN, 300 K) spectrum of **L**.

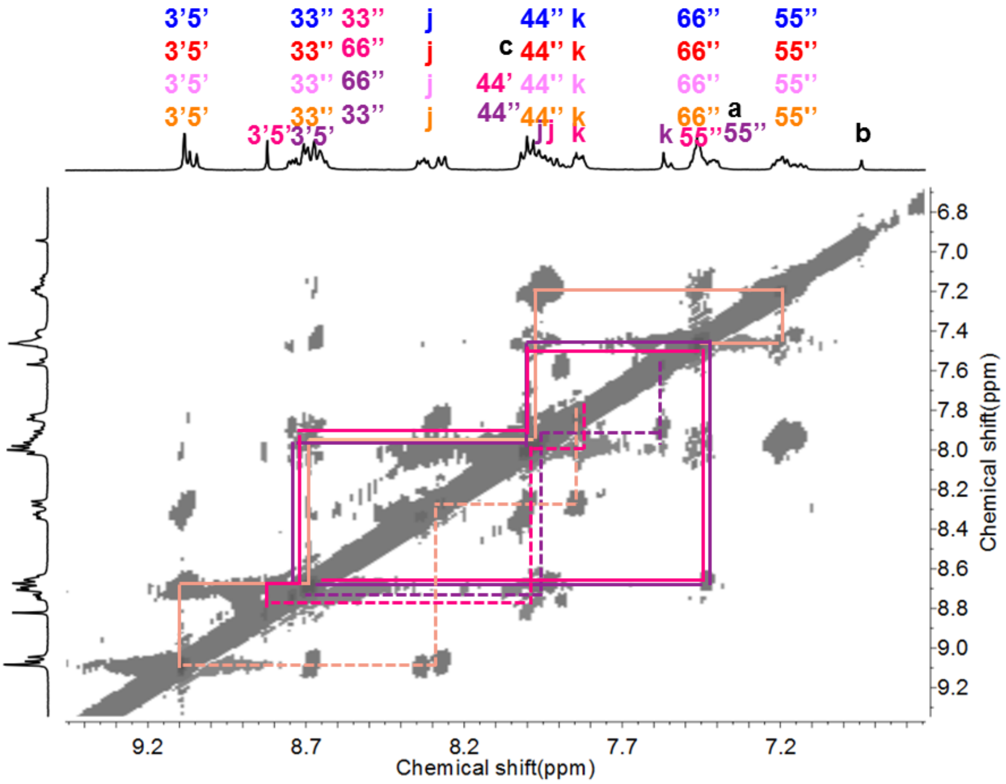


Figure S17. 2D NOESY NMR (500 MHz, CD_3CN, 300 K) spectrum of **L** (all cross peaks of Tpy-Ru-Tpy are illustrated by Rose-Bengal line).

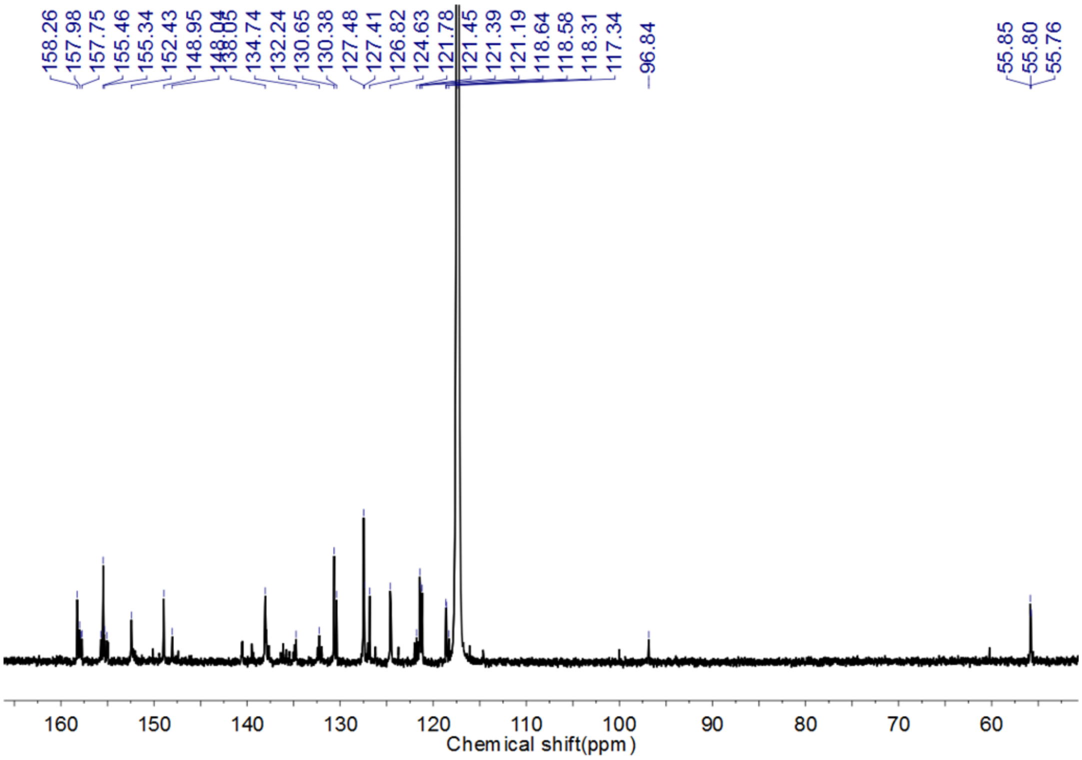


Figure S18. ^{13}C NMR (125 MHz, CD_3CN, 300 K) spectrum of **L**.

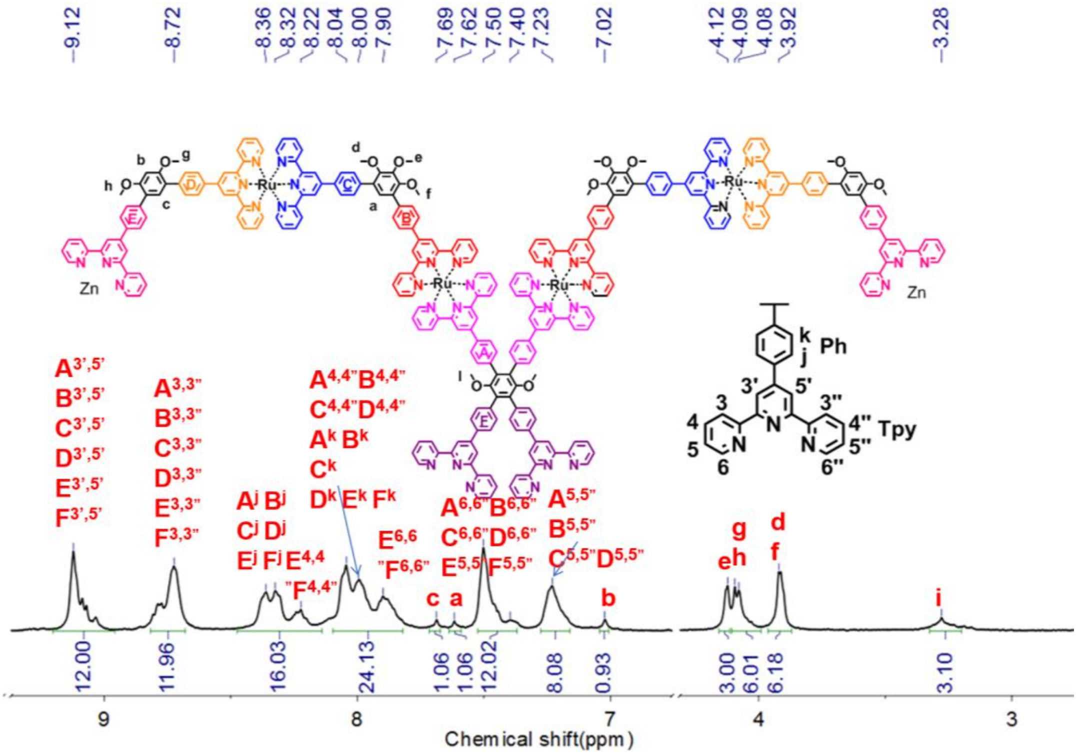


Figure S19. ^{1}H NMR (500 MHz, CD_3CN, 300 K) spectrum of $\mathbf{Zn_6L_3}$.

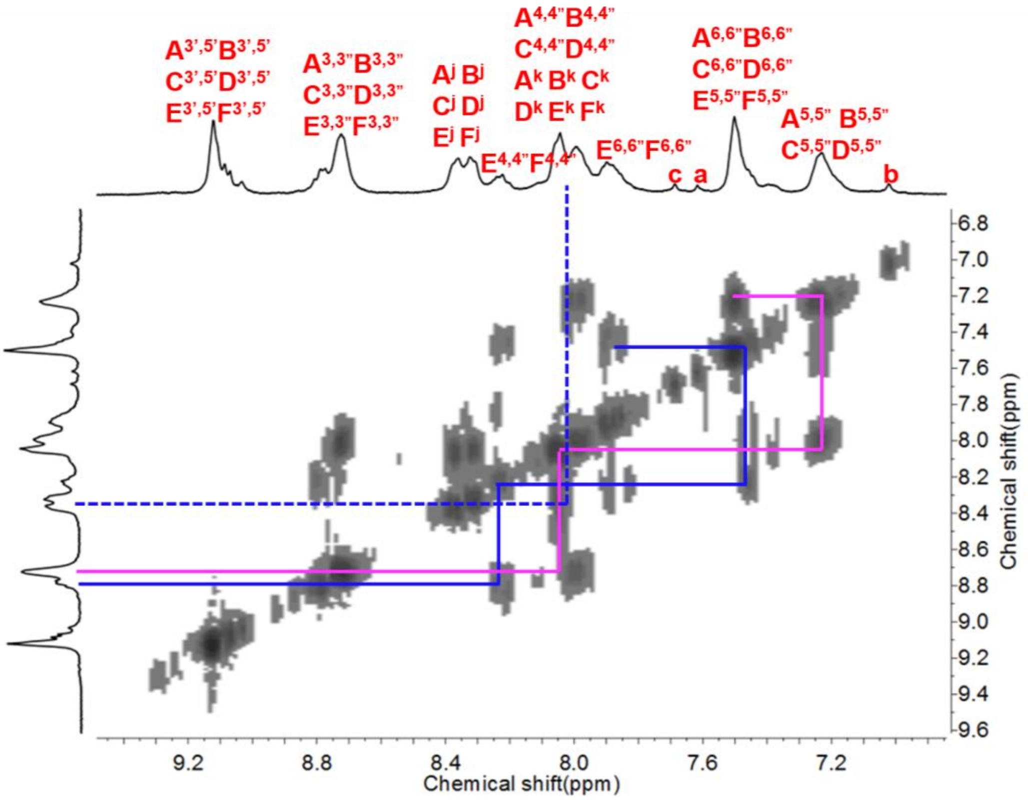


Figure S20. 2D COSY NMR (500 MHz, CD_3CN, 300 K) spectrum of $\mathbf{Zn_6L_3}$.

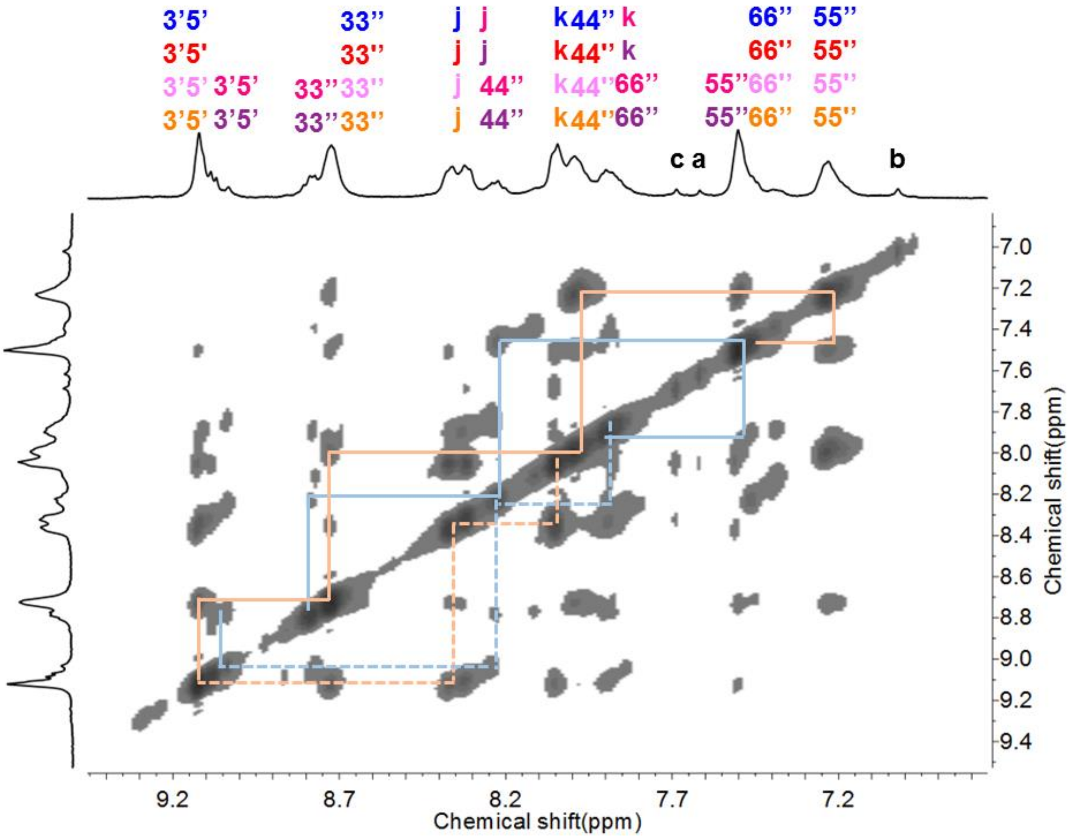


Figure S21. 2D NOESY NMR (500 MHz, CD_3CN, 300 K) spectrum of **Zn_6L_3** (all cross peaks of Tpy-Ru-Tpy are illustrated by orange line, all cross peaks of Tpy-Zn-Tpy are illustrated by blue line).

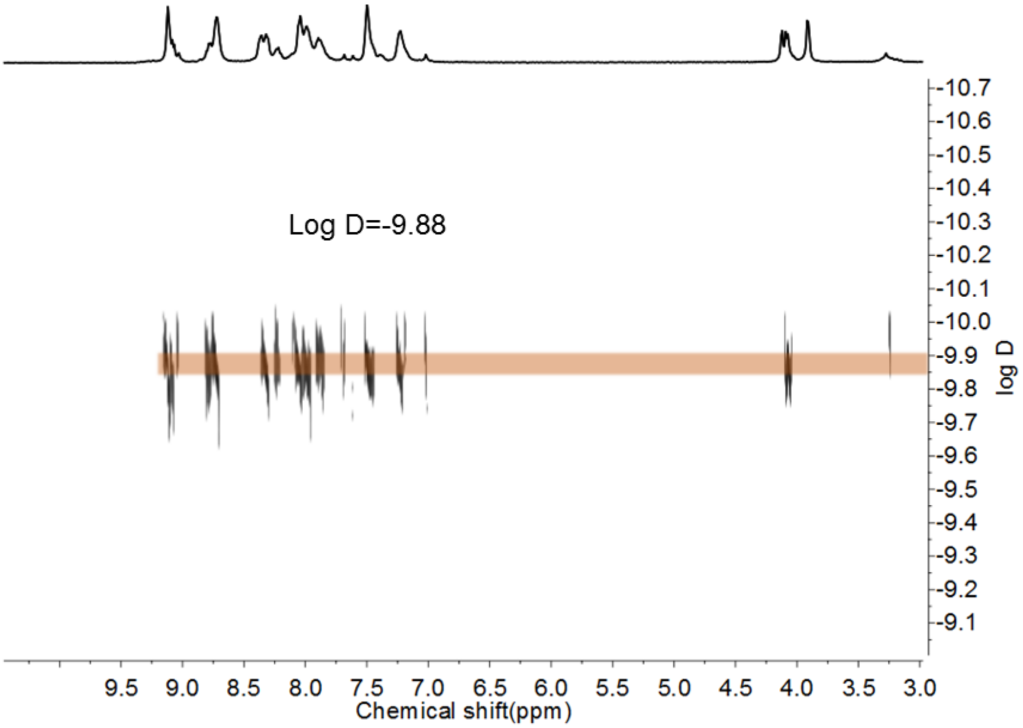


Figure S22. DOSY (500 MHz, CD_3CN, 300 K) spectra of **Zn_6L_3.**

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:

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

$D = 10^{-9.88}$ m^2 s^{-1}

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

$T = 298$ K

$\mu = 3.43\times 10^{-4}$ N m^{-2} s (CD_3CN)

$R = \frac{kT}{6\pi\mu D} = 4.83\times10^{-9}$ m ≈ 2.42 nm

The radius of **Zn_6L_3** was determined to be 4.84 nm, which is consistent with the results of computer modeling.

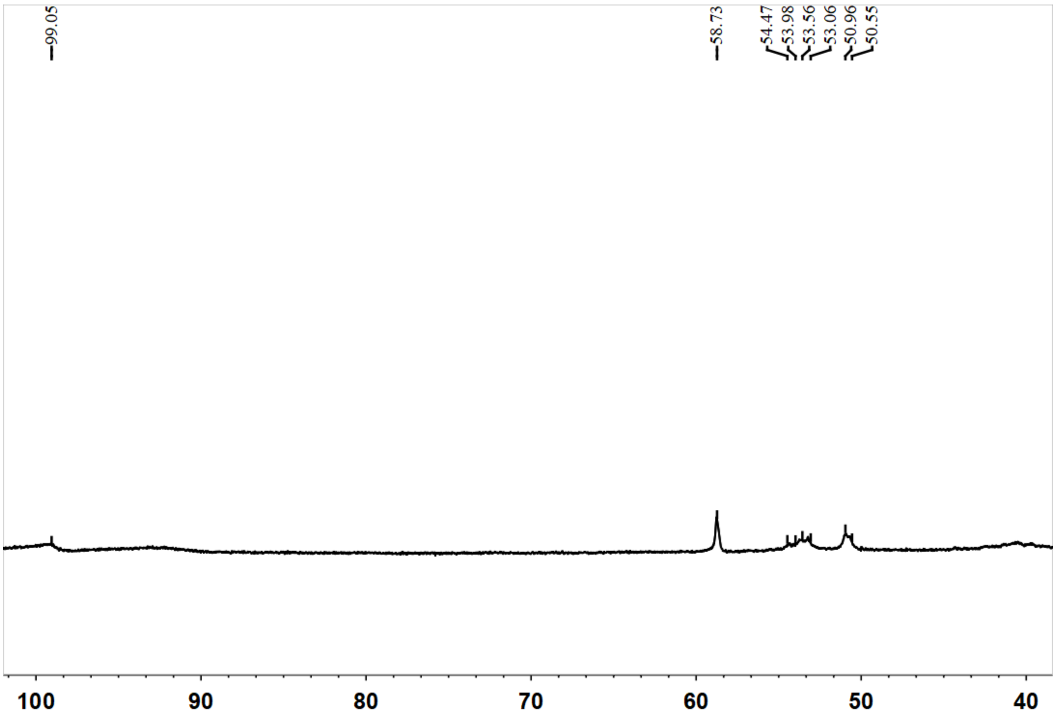


Figure S23. ^{1}H NMR (500 MHz, CD_3CN, 300 K) spectrum of **Co_6L_3** (40-100 ppm).

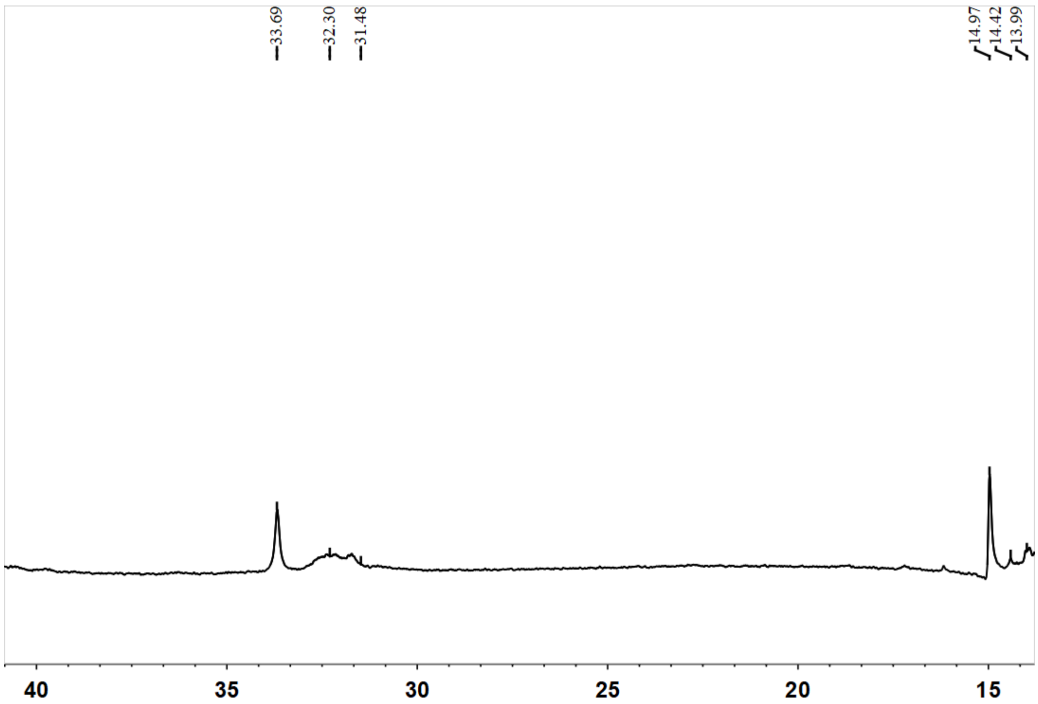


Figure S24. ^{1}H NMR (500 MHz, CD_3CN, 300 K) spectrum of **Co_6L_3** (15-40 ppm).

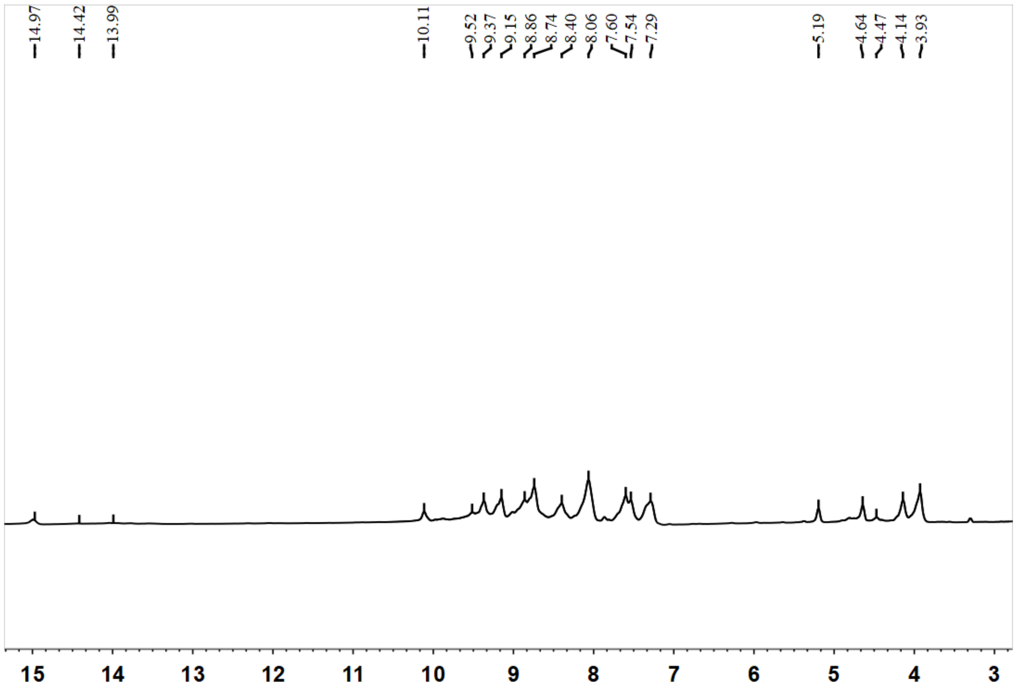


Figure S25. ^{1}H NMR (500 MHz, CD_3CN, 300 K) spectrum of **Co_6L_3** (3-15 ppm).

7. TEM images of supramolecules (NTf_2^- as counterion)

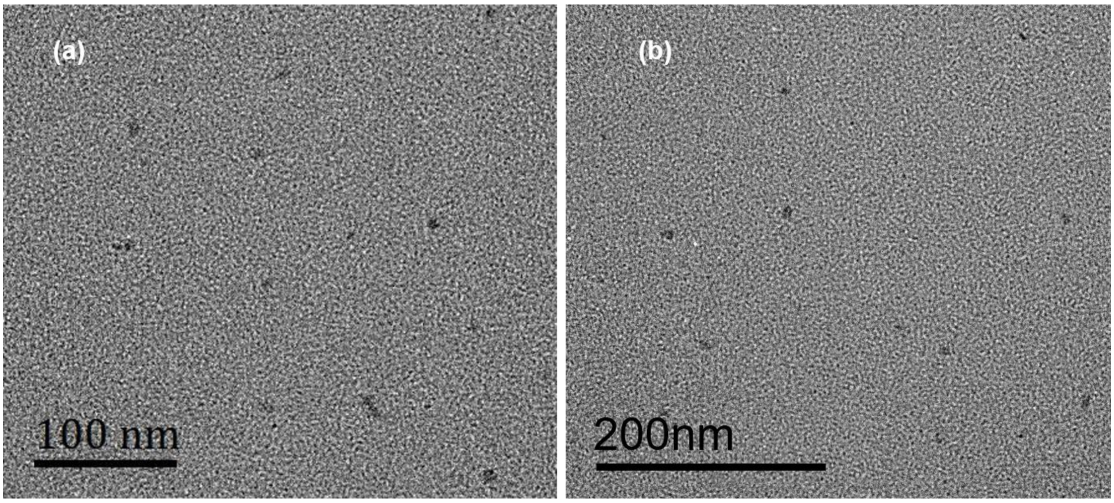


Figure S26. TEM images of **Mn_6L_3** on the lacey carbon coated Cu grid.

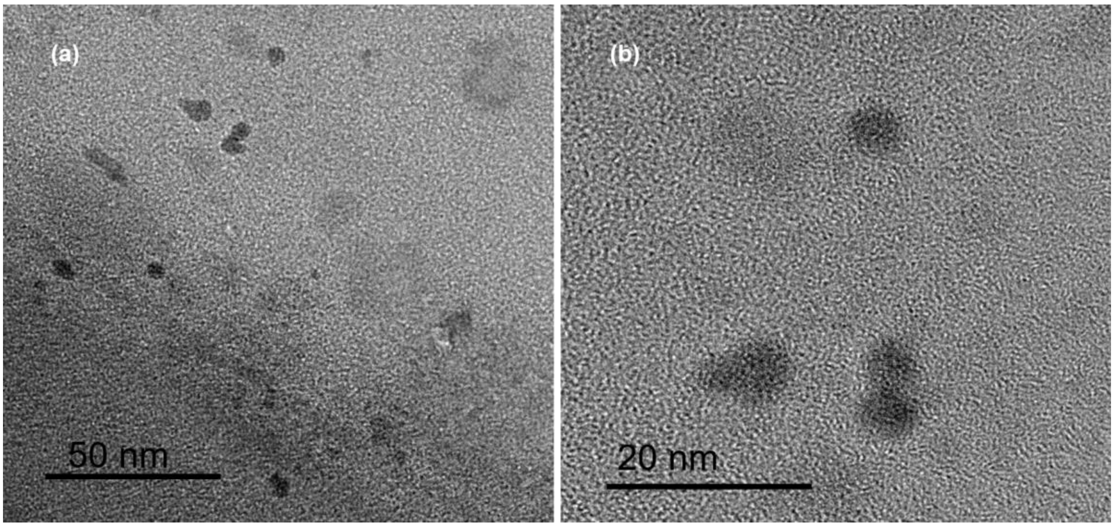


Figure S27. TEM images of **Zn_6L_3** on the lacey carbon coated Cu grid.

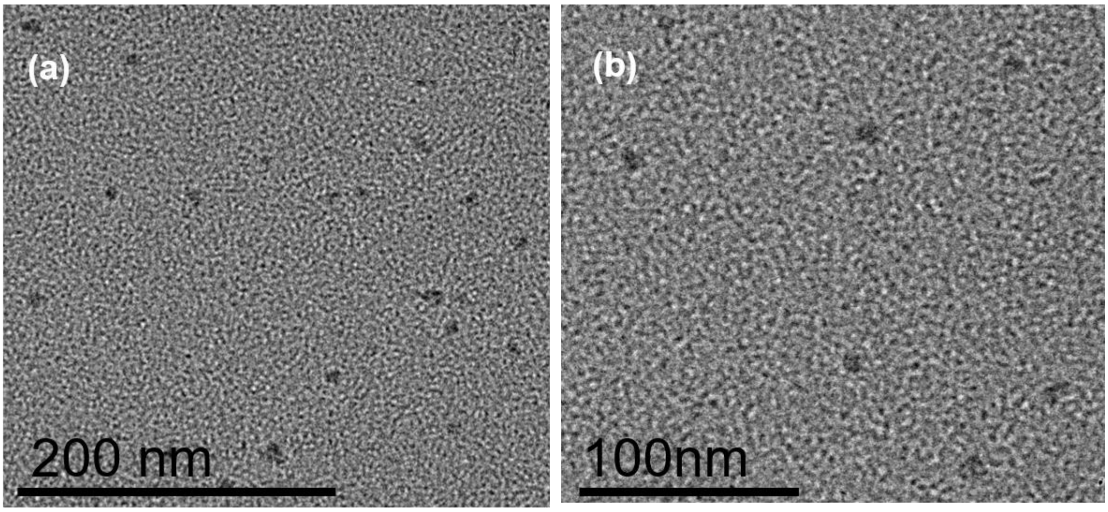


Figure S28. TEM images of **Co_6L_3** on the lacey carbon coated Cu grid.

8. UV-vis and emission of L and supramolecules (NTf$_2^-$ as counterion)

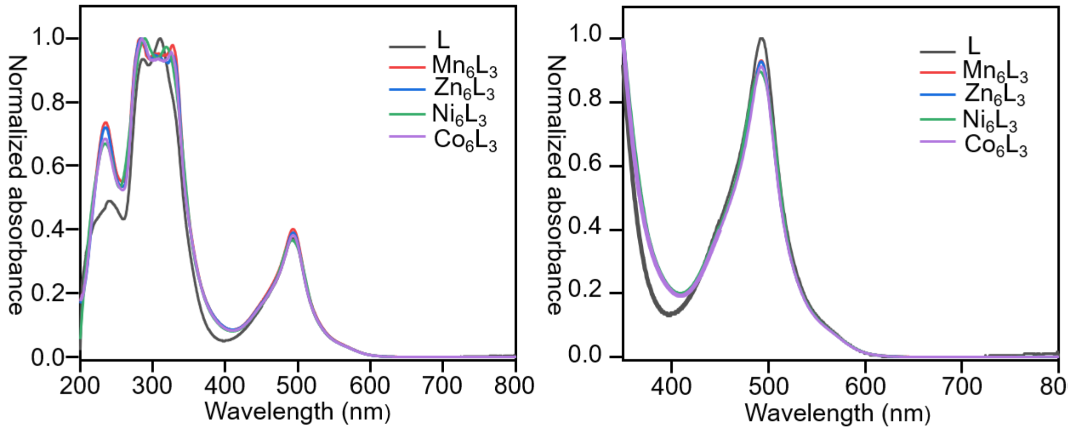


Figure S29. UV-vis (3×10^{-6} M in CH_3CN, room temperature) of **L and supramolecules.**

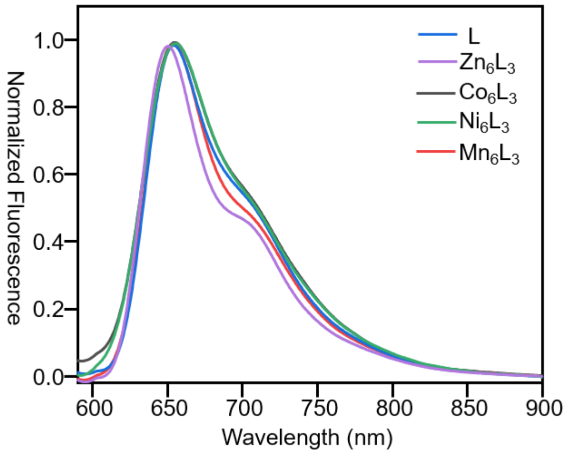


Figure S30. Emission (3×10^{-6} M in CH_3CN, 73K, λ_{ex}=365 nm) of **L and supramolecules.**

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