A triple-pore tessellated square array by a metal-hexagonal ligand with reinforced tetra-connectors

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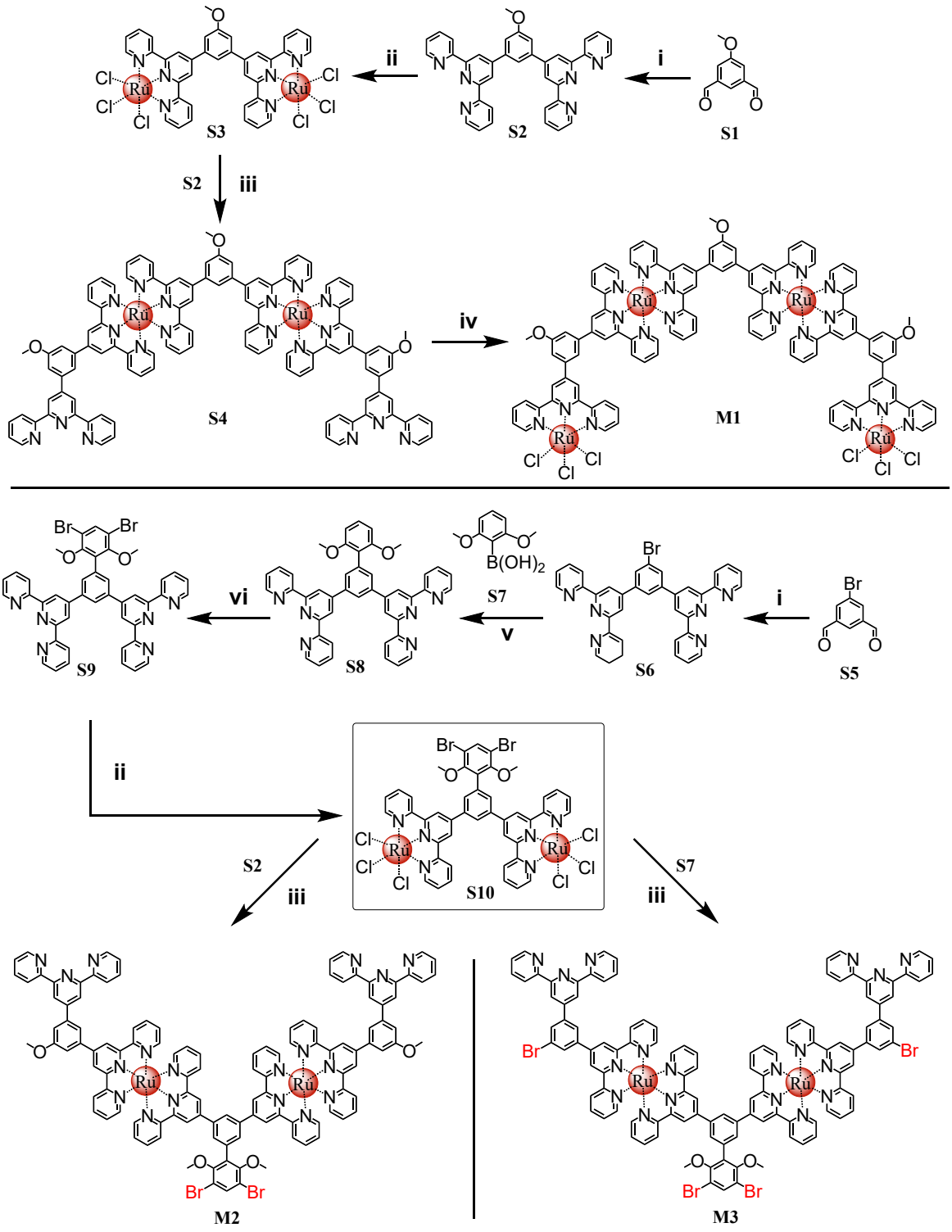
1. General Procedures

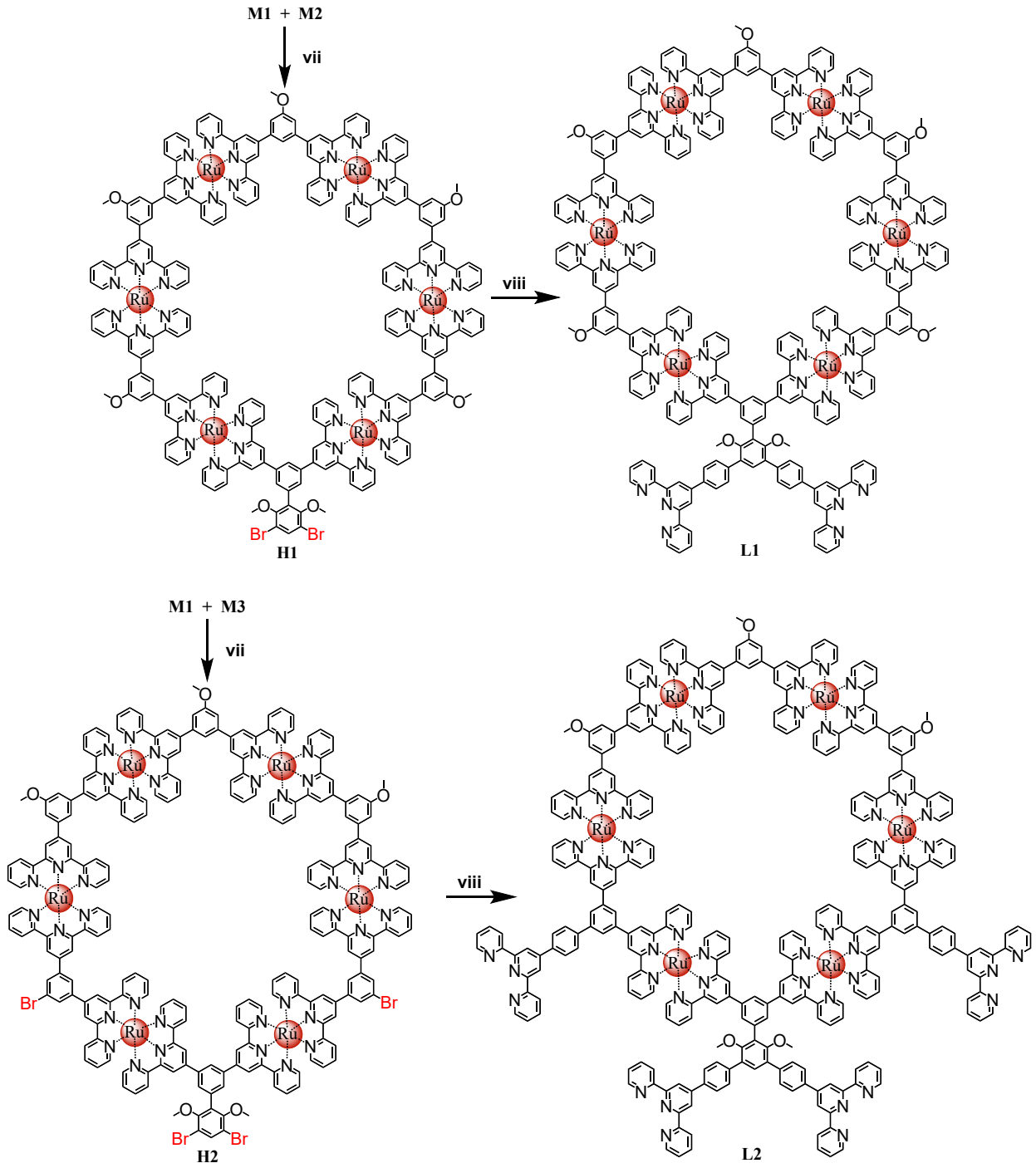
All starting materials were purchased from Aldrich and Alfa Aesar and used without further purification. Compounds 5-Methoxyisophthalaldehyde, 3, 5-diformylbromobenzene and 4′-(4-boronophenyl)-terpyridine were synthesized according to the reported methods.[S1-S3] Column chromatography was conducted using basic Al_2O_3 (Sinopharm Chemical Reagents Co. Ltd, 200-300 mesh) or SiO_2 (Qingdao Haiyang Chemical Co., Ltd, 200-300 mesh) and the separated products were confirmed by ^1H NMR and ^{13}C NMR spectra using a Bruker Avance 400-MHz and 500-MHz NMR spectrometers in $CDCl_3$, CD_3OD, and CD_3CN with a TMS standard. Transmission electron microscopy (TEM) was conducted on JEOL 2010. Electro-spray ionization (ESI) mass spectra were recorded with a Bruker microOTOF-QII or a Waters Synapt HDMS G2-Si instrument, using solutions of 0.01 mg/mL in $CHCl_3$/MeCN (1:3, v/v) for ligands and 0.2 mg/mL in MeCN or MeCN/MeOH (3:1, v/v) for complexes.

TWIM MS. ESI mass spectrometry and traveling wave ion mobility (TWIM) experiments were conducted on a Waters Synapt HDMS G2-Si instrument with a LockSpray ESI source, using the following parameters: ESI capillary voltage, 1.3-3.0 kV; sample cone voltage, 20-25 V; extraction cone voltage, 1.1-3 V; desolvation gas flow, 800 L/h (N_2); trap collision energy (CE), 4 V; transfer CE, 0 V; trap gas flow, 2.0 mL/min (Ar); source temperature, 30 °C; and desolvation temperature, 30 °C. All samples were dissolved in CH_3CN or CH_3CN/CH_3NO_2 (1:1, v/v) and then infused into the -100, KD Scientific). For TWIM experiments, the helium cell gas flow was held at 180.0 mL/min and the ion mobility cell gas flow was held at 90.0 mL/min (N_2). The TWIM DC traveling wave velocity and height were set as 683 m/s and 26.3 V, respectively. Data were collected and analyzed by using MassLynx 4.2 and DriftScope 2.4 (Waters).

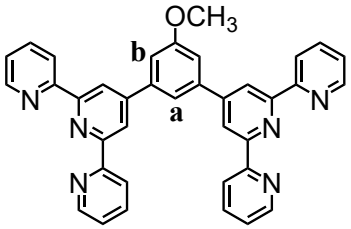
TEM. The samples were dissolved in MeCN at a concentration of ~10^{-7} M. The solutions were dropped cast on to a carbon-coated Cu grid (300-400 mesh) and the extra solution was blotted by filter paper to avoid aggregation. The TEM images of the samples were taken with a JEOL 2010 Transmission Electron Microscope.

2. Synthesis of Hexagon-Containing Metallo-organic Ligands L1 and L2

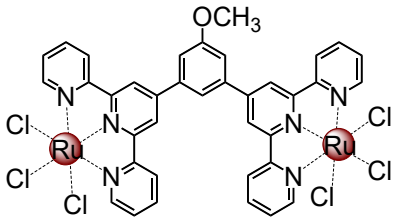




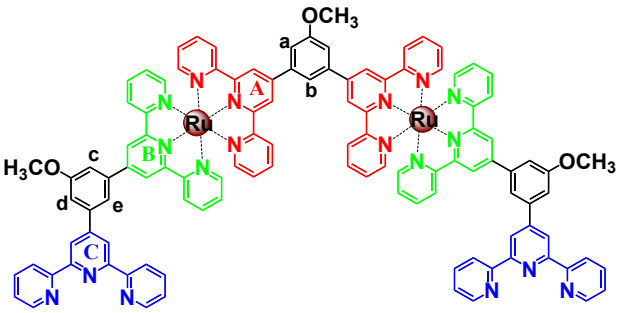
Scheme S1: The synthetic route of metallo-organic ligand **LA** and parallelogram **$Fe_2(LA)_2$**. Reagents and conditions: (i) 2-acetylpyridine, KOH, EtOH, NH_3•H_2O, reflux; (ii) $RuCl_3$·$3H_2O$, EtOH, reflux, 1 d; (iii) N-ethyl morpholine, MeOH:$CHCl_3$ (v/v, 1:1), reflux, 1 d; (iv) $RuCl_3$·$3H_2O$, EtOH, reflux, 1 d; (v) $Pd(PPh_3)_4$, THF, NaOH, reflux, 1 d; (vi) Br_2, CHCl3, reflux; (vii) N-ethyl morpholine, MeOH:$CHCl_3$ (v/v, 1:1), reflux, 2 d; (viii) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, CH_3CN/CH_3OH(V:V, 2:1), K_2CO_3, reflux.



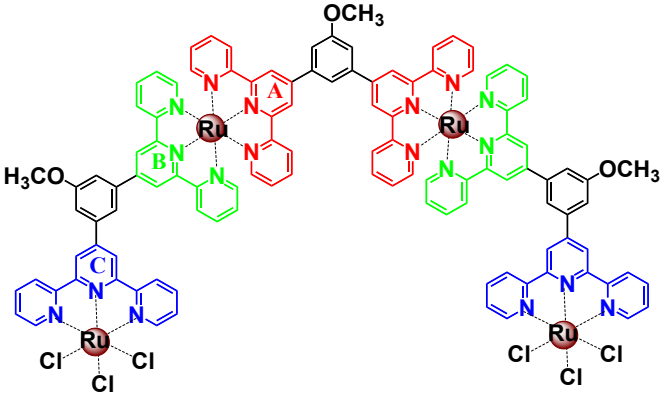
Compound S2: To a solution of 5-Methoxyisophthalaldehyde (3.2 g, 2 mmol) in EtOH (200 mL), 2-acetylpyridine (5.1 g, 4.8 mmol) and NaOH powder (240.0 mg, 6 mmol) was added. After stirring at room temperature for 24 h, aqueous $NH_3•H_2O$ (28%, 150 mL) was added, the resulting mixture was refluxed for 20 h. After cooling to room temperature, the solid was collected by suction filtration and was washed with CH_3OH to give the product as a white solid: 8.1 g, 72.6%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.83 (s, 4H, tpy-$H^{3',5'}$), 8.77-8.76 (d, 4H, J = 2Hz, tpy-$H^{3,3''}$), 8.72-8.70 (d, 4H, J = 4Hz, tpy-$H^{6,6''}$), 7.99 (s, 1H, Ph-H^{a}), 7.93-7.90 (t, 4H, tpy-$H^{4,4''}$), 7.53 (s, 2H, PH-H^{b}), 7.40-7.38 (t, 4H, tpy-$H^{5,5''}$), 4.04 (s, 3H, H^{-OMe}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.67, 156.24, 156.02, 150.21, 149.15, 140.97, 136.89, 123.85, 121.45, 119.33, 119.06, 113.68, 55.87.



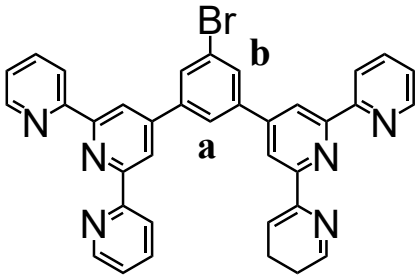
Compound S3: To a solution of **S2** (200.0 mg, 0.4 mmol) and $RuCl_3•3H_2O$ (105.0 mg, 0.4 mmol) in EtOH (50 mL). The mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **S3**: 250.0 mg, 90%.



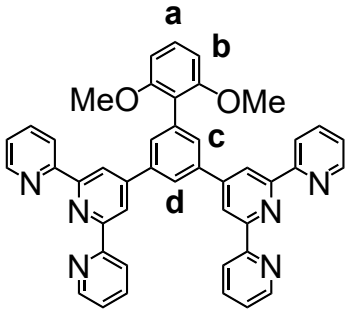
Compound S4: To a flask containing a mixture of **S3** (300 mg, 0.30 mmol)) and **S2** (521 mg, 0.91 mmol), MeOH (150 mL), $CHCl_3$ (150 mL), and 10 drops of N-ethylmorpholine were added. The mixture was stirred at 75 °C for 48 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was obtained, as a red precipitate: 420 mg, 67.1%.^{1}H NMR (400 MHz, CD_3OD) δ 9.67 (s, 4H, A-tpy-$H^{3',5'}$), 9.48 (s, 4H, B-tpy-$H^{3',5'}$), 9.22 (d, *J* = 8.0 Hz, 4H, A-tpy-$H^{3,3''}$), 9.07 (m, 8H, C-tpy-$H^{3',5'}$,B-tpy-$H^{3,3''}$), 8.99 (d, *J =8.0* Hz , 4H, C-tpy-$H^{3,3''}$), 8.94 (s, 1H,H^b), 8.89 (d, *J* = 8.0 Hz, 4H, C-tpy-$H^{6,6''}$),8.53(s, 2H, H^e), 8.34 (t, *J* =8.0 Hz, 4H, C-tpy-$H^{4,4''}$) , 8.13 (s, 2H, H^a), 8.07 (m, 10H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4'}$, H^d), 7.84 (s, 2H, H^c), 7.78 (t, *J* = 8.0Hz , 4H, C-tpy-$H^{5,5''}$), 7.68 (d, *J* = 8.0Hz, 4H, B-tpy-$H^{6,6''}$), 7.64 (d, *J* = 8.0 Hz, 4H, A-tpy-$H^{6,6''}$), 7.34 (m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 4.30 (s, 3H, H^{-OCH3}), 4.19 (s, 6H, H^{-OCH3}). ESI-MS (2055.91 calcd. For $C_{111}H_{78}Cl_4N_{18}O_3Ru_2$): m/z 748.6031 $[M - 4Cl^-]^{4+}$ (calcd m/z: 748.5245), 649.8176 $[M - 3Cl^-]^{3+}$ (calcd m/z: 649.8503), m/z 992.7487 $[M - 2Cl^-]^{2+}$ (calcd m/z: 992.5020).



Compound M1: To a solution of **S4** (200.0 mg, 0.4 mmol) and $RuCl_3•3H_2O$ (105.0 mg, 0.4 mmol) in EtOH (50 mL). The mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **M1**: 250.0 mg, 90%.

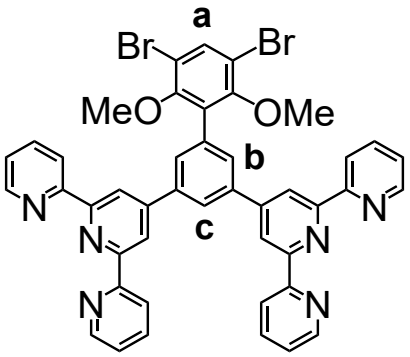


Compound S6: To a solution of NaOH powder (240.0 mg, 6 mmol) in EtOH (200 mL), 3, 5-diformylbromobenzene **S5** (3.54 g, 2 mmol) and 2-acetylpyridine (5.14 g, 4.8 mmol) was added. After stirring at room temperature for 24 h, aqueous $NH_3•H_2O$ (28%, 150 mL) was added, the resulting mixture was refluxed for 20 h. After cooling to room temperature, the solid was collected by suction filtration and was washed with CH_3OH to give the product as a white solid: 9.97 g, 85.0%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (s, 4H, tpy-$H^{3',5'}$), 8.75-8.74 (d, J = 4 Hz, 4H, tpy-$H^{6,6''}$), 8.71- 8.69 (d, J = 8 Hz, 4H, tpy-$H^{3,3''}$), 8.29 (s, 1H, Ph-H^a), 8.12(s, 2H, Ph-H^b), 7.92-7.88 (t, J = 16 Hz, 4H, tpy-$H^{4,4''}$), 7.39-7.36 (t, J = 12 Hz, 4H, tpy-$H^{5,5''}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.21, 155.99, 149.18, 148.75, 141.50, 136.96, 130.78, 125.13, 124.01, 121.47, 119.10, 77.33, 77.22, 77.01, 76.70. ESI-MS (621.54 calcd. For $C_{36}H_{25}BrN_6$): m\z 622.47$[M+H^+]^+$ **(**calcd m/z: 622.55**)**.



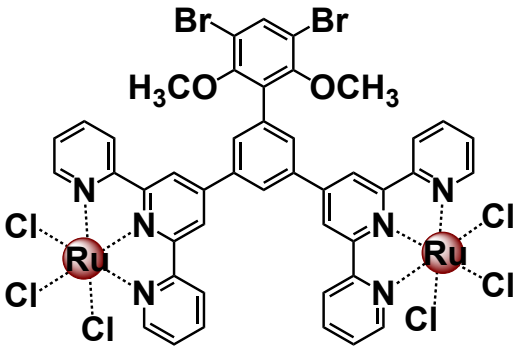
Compound S8: 1, 3-dimethoxybromobenzene **S7** (0.78 g, 3.6 mmol) and **S6** (2.00 g, 3.4 mmol) was added to a 500 mL flask, then THF (250 mL) and NaOH (0.41 g, 10.3 mmol) in 10 mL of water was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol) as the catalyst was added. The mixture was stirred at 85 °C

under nitrogen for 12 h, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al_2O_3), eluting with the mixture of petroleum ether and CH_2Cl_2 to pure the product, as white solid: 1.50 g, 65%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 4H, tpy-$H^{3',5'}$), 8.75-8.74 (d, J = 4 Hz, 4H, tpy-$H^{6,6''}$), 8.72-8.70 (d, J = 8 Hz, 4H, tpy-$H^{3,3''}$), 8.38 (s, 1H, H^{d}), 7.98 (s, 2H, H^{c}), 7.92-7.89 (t, J = 12 Hz, 4H, tpy- $H^{4,4''}$), 7.38-7.35 (m, 5H, tpy-$H^{5,5''}$, Ph-H^{a}) 6.73-6.72 (d, J = 4 Hz, 2H, H^{b}), 3.79 (s, 6H, $H^{\text{-OCH3}}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.86, 158.19, 157.70, 156.34, 155.68, 150.45, 150.29, 149.10, 139.41, 138.90, 136.90, 131.04, 130.85, 124.66, 123.76, 121.45, 119.49, 118.61, 118.47, 105.22, 104.14, 55.93. ESI-MS (676.26 calcd. For $C_{46}H_{32}N_6O_2$): m\z 699.28$[M+Na^+]^+$ **(**calcd m/z: 699.24**)**.

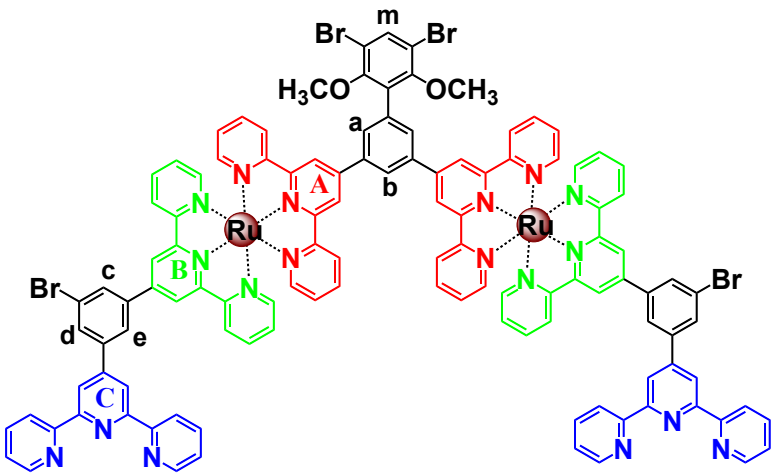


Compound S9: To a solution of **S8** (500.0 mg, 0.74 mmol) in $CHCl_3$ (50 mL), a solution of Br_2 (5 mL, 97.5 mmol) in $CHCl_3$ (5 mL) was added dropwise. After refluxing for 24 h, the mixture was washed by saturated $NaHSO_3$ until colorless. The organic layer was dried (anhydrous Na_2SO_4), and then concentrated in vacuo to give **S9**, as white solid: 494.0 mg, 80%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.87 (s, 4H, tpy-$H^{3',5'}$) , 8.76-8.75 (d, J = 4 Hz, 4H, tpy-$H^{6,6''}$), 8.73-8.71 (d, J = 8 Hz, 4H, tpy-$H^{3,3''}$), 8.49 (s, 1H, H^{c}), 8.12 (s, 2H, H^{b}), 7.94-7.91 (t, J = 12 Hz, 4H, tpy- $H^{4,4''}$), 7.86 (s, 1H, H^{a}), 7.41-7.38 (d, J = 12 Hz, 4H, tpy-$H^{5,5''}$), 3.51 (s, 6H, $H^{\text{-OCH3}}$). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.12,

155.06, 149.75, 149.11, 139.72, 137.01, 135.53, 134.44, 131.48, 129.75, 125.94, 123.95, 121.52, 119.31, 113.31, 60.85.^{13}C NMR (101 MHz, $CDCl_3$) δ 156.29, 156.12, 149.90, 149.21, 136.88, 136.45, 133.73, 133.66, 128.52, 127.38, 125.80, 123.86, 121.39, 119.08, 77.33, 77.01, 76.69. ESI-MS (834.08 calcd. For $C_{46}H_{30}N_6O_2Br_2$): m\z 857.11$[M+Na^+]^+$ **(**calcd m/z: 857.07**)**.

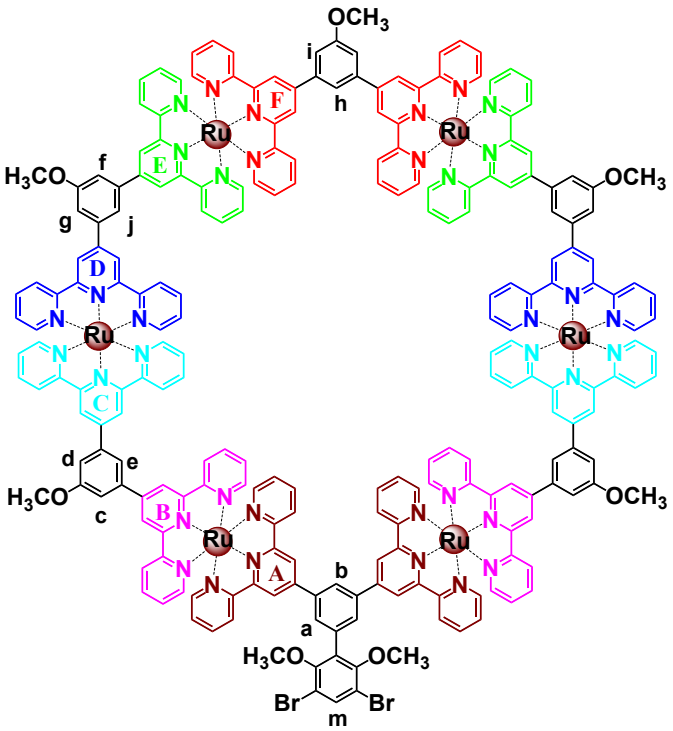


Compound S10: To a solution of **S9** (200.0 mg, 0.4 mmol) and $RuCl_3$•$3H_2O$ (105.0 mg, 0.4 mmol) in EtOH (50 mL). The mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **S10**: 250.0 mg, 90%.



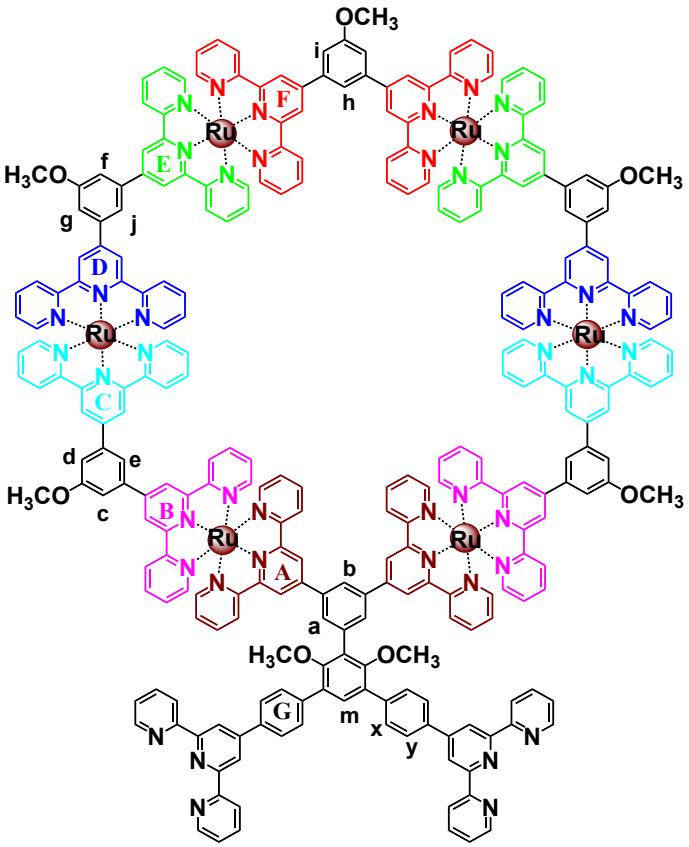
Compound M2: To a flask containing a mixture of **S10** (330 mg, 0.26 mmol) and **S2** (393 mg, 0.63 mmol), MeOH

(150 mL), $CHCl_3$ (150 mL), and 10 drops of N-ethylmorpholine were added. The mixture was stirred at 75 °C for 48 h. After cooling to ambient temperature, the solvent was evaporated in vacuo and the residue was purified by column chromatography (Al_2O_3), eluting with a mixture of MeOH and CH_2Cl_2. The complex was obtained, as a red precipitate: 150 mg, 24%.^{1}H NMR (500 MHz, MeOD) δ 9.74 (s, 4H, A-tpy-$H^{3',5'}$), 9.56 (s, 1H, H^b), 9.47 (s, 4H, B-tpy-$H^{3',5'}$) ,9.23 (d, J =10.0 Hz, 4H, A-tpy-$H^{3,3''}$), 9.03 (d, J = 10.0 Hz, 4H, B-tpy-$H^{3,3''}$), 8.96 (s, 4H, C-tpy-$H^{3',5'}$), 8.86 (s, 2H, H^c), 8.78 (m, 8H, C-tpy-$H^{3,3''}$, C-tpy-$H^{6,6''}$), 8.69 (m, 4H, H^e, H^a) , 8.46 (m, 12H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$), 7.70 (d, J = 5.0 Hz, 4H, A-tpy-$H^{6,6''}$), 7.63 (d, J = 5.0 Hz, 4H, B-tpy-$H^{6,6''}$), 7.57(t, J = 5.0 Hz, 4H, C-tpy-$H^{5,5''}$), 7.34(m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 3.75 (s, 6H, H^{-OCH3}). ESI-MS (2417.56 calcd. For $C_{116}H_{76}Br_4Cl_4N_{18}O_2Ru_2$): m/z 568.9478 $[M - 4Cl^-]^{4+}$ (calcd m/z: 568.9370), 770.6383 $[M - 3Cl^-]^{3+}$ (calcd m/z: 770.4003), m/z 1173.5205 $[M - 2Cl^-]^{2+}$ (calcd m/z: 1173.3270).



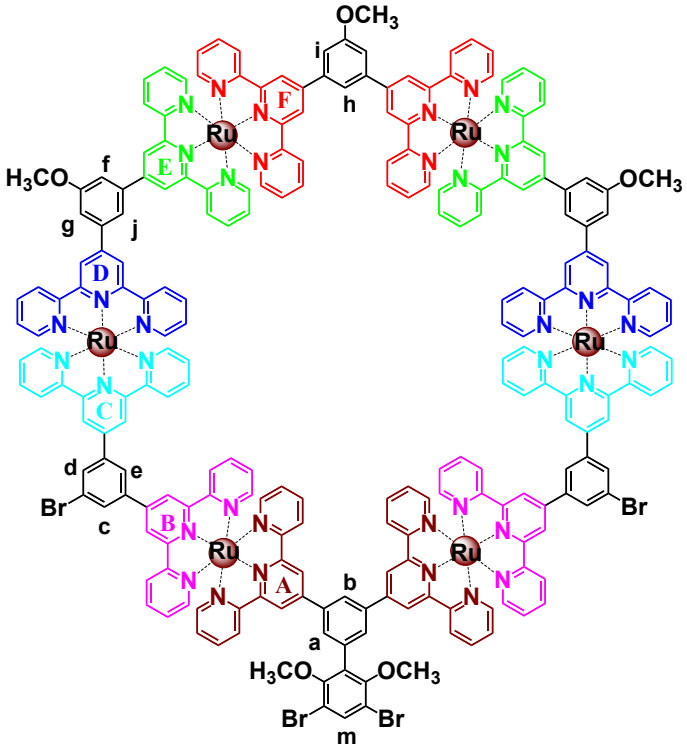
Compound H1: The **M1** (62 mg, 0.025 mmol) and **M2** (58 mg, 0.025 mmol) was added to a 250 mL flask, then

100 mL CH_3OH and 100 mL $CHCl_3$ was added as solvent. After adding 10 drops N-ethyl morpholine, the suspension was refluxed for 48 h. The solvent was evaporated in vacuo to give a residue that was purified with column chromatography (SiO_2) using a H_2O/MeCN/sat.$KNO_{3(aq)}$ (1:12:1; v/v/v) mixture as eluent; the complex was obtained, as a red precipitate: 40 mg, 42%. ^{1}H NMR (500 MHz, CD_3OD) δ 9.31 (m, 24H, A-tpy-$H^{3',5'}$, B-tpy-$H^{3',5'}$, C-tpy-$H^{3',5'}$, D-tpy-$H^{3',5'}$, E-tpy-$H^{3',5'}$, F-tpy-$H^{3',5'}$), 9.20 (s, 1H, H^h), 9.18 (s, 2H, H^j), 9.12 (s, 2H, H^e), 9.01 (s, 1H, H^b), 8.84 (m, 24H, A-tpy-$H^{3,3''}$, B-tpy-$H^{3,3''}$, C-tpy-$H^{3,3''}$, D-tpy-$H^{3,3''}$, E-tpy-$H^{3,3''}$, F-tpy-$H^{3,3''}$), 8.64 (s, 2H, H^i), 8.60 (m, 2H, H^g), 8.56 (m, 2H, H^f), 8.05 (m, 31H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$, D-tpy-$H^{4,4''}$, E-tpy-$H^{4,4''}$, F-tpy-$H^{4,4''}$, H^m, H^a, H^d, H^c), 7.57 (m, 24H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$, E-tpy-$H^{6,6''}$, F-tpy-$H^{6,6''}$), 7.29 (m, 24H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$, E-tpy-$H^{5,5''}$, F-tpy-$H^{5,5''}$), 4.30 (s, 15H, H^{-OCH3}), 3.78 (s, 6H, H^{-OCH3}). ESI-MS (6033.84 calcd. For $C_{229}H_{160}Br_2F_{72}N_{36}O_7P_{12}Ru_6$): m/z 525.3549 $[M - 9PF_6^-]^{9+}$ (calcd m/z: 525.4667), 609.4097 $[M - 8PF_6^-]^{8+}$ (calcd m/z: 609.2700), 717.1891$[M - 7PF_6^-]^{7+}$ (calcd m/z: 717.0171), 860.7324 $[M - 6PF_6^-]^{6+}$ (calcd m/z: 860.6800), 1061.9016 $[M - 5PF_6^-]^{5+}$ (calcd m/z: 1061.808), m/z 1363.6615 $[M - 4PF_6^-]^{4+}$ (calcd m/z: 1363.5).



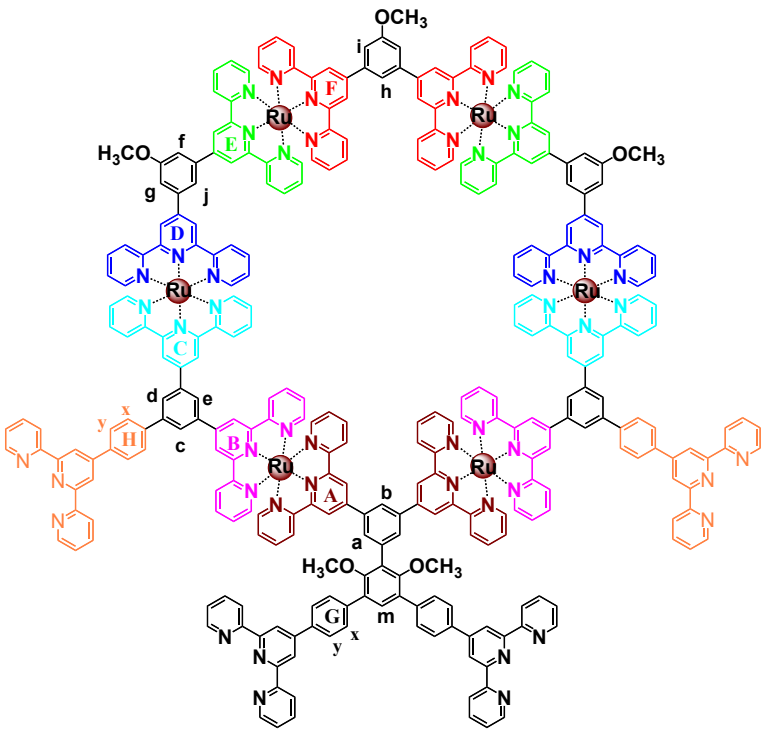
Hexagon-Containing Metallo-organic Ligand L1： To a mixture of **H1** (60.0 mg, 0.01 mmol) and 4′-(4-boronophenyl)-terpyridine (42.0 mg, 0.12 mmol) in CH_3CN (30 mL), aqueous K_2CO_3 (0.24 mL, 1 M) was added. The system was pumped and backfilled with nitrogen; then $Pd(PPh_3)_4$ (7.1 mg, 6 umol) was added. After refluxing for 48 h under argon, the mixture was cooled to 25 °C and added access NH_4PF_6 solution to form the precipitate. The resultant precipitate was washed with 100 mL CH_3OH and purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/CH_3OH to give **L1**, as a red solid, 32.8 mg: 53% yield. ^1H NMR (400 MHz, CD_3CN) δ 9.42 – 9.20 (m, 24H, A-tpy-$H^{3',5'}$, B-tpy-$H^{3',5'}$, C-tpy-$H^{3',5'}$, D-tpy-$H^{3',5'}$, E-tpy-$H^{3',5'}$, F-tpy-$H^{3',5'}$), 9.12 (s, 2H, H^j), 8.97 (s, 1H, H^h), 8.81 (m, 39H, A-tpy-$H^{3,3"}$, B-tpy-$H^{3,3"}$, C-tpy-$H^{3,3"}$, D-tpy-$H^{3,3"}$, E-tpy-$H^{3,3"}$, F-tpy-$H^{3,3"}$, G-tpy-$H^{3,3"}$, G-tpy-$H^{6,6"}$, G-tpy-$H^{3',5'}$, H^e, H^b), 8.61 (s, 2H, H^i), 8.53 (s, 4H, H^g, H^f), 8.12-8.02 (m, 38H, A-tpy-$H^{4,4"}$, B-tpy-$H^{4,4"}$, C-tpy-$H^{4,4"}$, D-tpy-$H^{4,4"}$, E-tpy-$H^{4,4"}$, F-tpy-$H^{4,4"}$, G-tpy-$H^{4,4"}$, H^a, H^c, H^d, H^y, H^x), 7.85 (s, 1H, H^m), 7.51 (m, 28H, A-tpy-$H^{6,6"}$, B-tpy-

$H^{6,6''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$, E-tpy-$H^{6,6''}$, F-tpy-$H^{6,6''}$, G-tpy-$H^{5,5''}$), 7.26 (m, 24H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$, E-tpy-$H^{5,5''}$, F-tpy-$H^{5,5''}$), 4.28 (s, 15H, H^{-OCH3}), 3.54 (s, 6H, H^{-OCH3}). ESI-MS (6490.76 calcd. For $C_{271}H_{188}F_{72}N_{42}O_7P_{12}Ru_6$): m/z 576.3352 $[M - 9PF_6^-]^{9+}$ (calcd m/z: 576.2355), 666.4828 $[M - 8PF_6^-]^{8+}$ (calcd m/z: 666.3850), 782.4011$[M - 7PF_6^-]^{7+}$ (calcd m/z: 782.2914), 936.9478 $[M - 6PF_6^-]^{6+}$ (calcd m/z: 936.8333),1153.1204 $[M - 5PF_6^-]^{5+}$ (calcd m/z: 1153.1920), m/z 1477.8734 $[M - 4PF_6^-]^{4+}$ (calcd m/z: 1477.7300).



Compound H2: The **M1** (100 mg, 0.04 mmol) and **M3** (98 mg, 0.04 mmol) was added to a 250 mL flask, then 100 mL CH_3OH and 100 mL $CHCl_3$ was added as solvent. After adding 10 drops N-ethyl morpholine, the suspension was refluxed for 48 h. The solvent was evaporated in vacuo to give a residue that was purified with column chromatography (SiO_2) using a H_2O/MeCN/sat.$KNO_{3(aq)}$ (1:12:1; v/v/v) mixture as eluent; the complex was obtained, as a red precipitate: 75 mg, 49%. 1H NMR (400 MHz, MeOD) δ 9.56 (s, 8H, A-tpy-$H^{3',5'}$, B-tpy-$H^{3',5'}$), 9.52 (m, 8H, C-tpy-$H^{3',5'}$, D-tpy-$H^{3',5'}$), 9.50 (s, 8H, E-tpy-$H^{3',5'}$, F-tpy-$H^{3',5'}$), 9.46 (s, 1H, H^h), 9.32 (s, 2H, H^j), 9.16

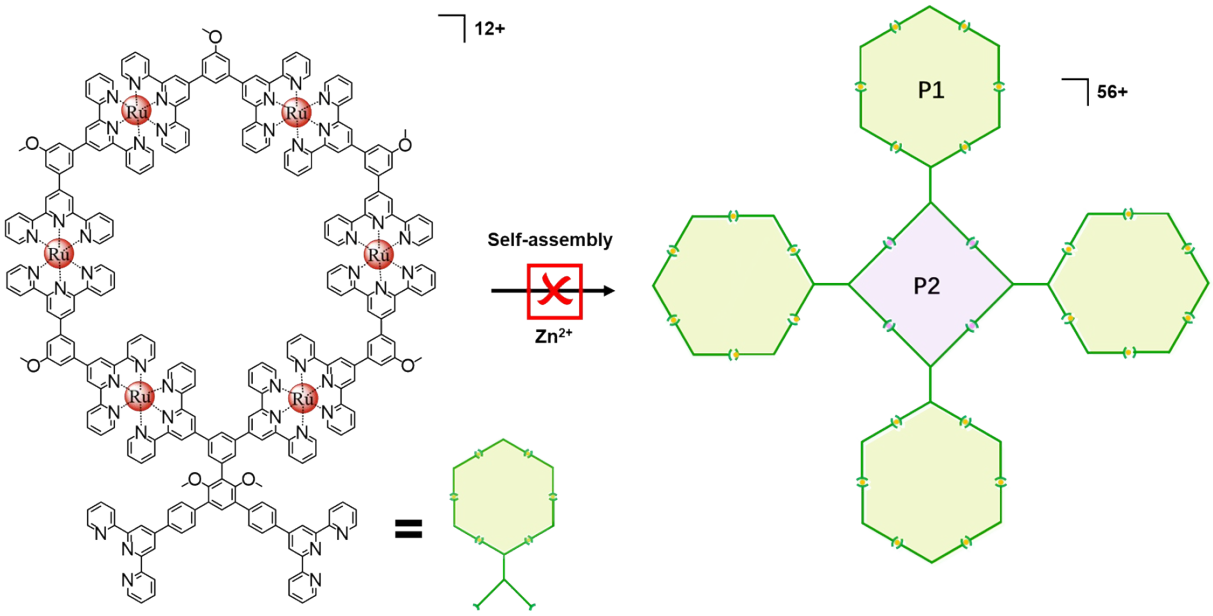
(s, 2H, H^{e}), 9.01 (m, 24H, A-tpy-$H^{3,3"}$, B-tpy-$H^{3,3"}$, C-tpy-$H^{3,3"}$, D-tpy-$H^{3,3"}$, E-tpy-$H^{3,3"}$, F-tpy-$H^{3,3"}$), 8.76 (m, 4H, H^{i}, H^{g}), 8.74 (s, 2H, H^{f}), 8.65 (s, 1H, H^{b}), 8.11 (m, 6H, H^{m}, H^{a}, H^{d}), 8.08 (s, 2H, H^{c}), 8.04 (m, 24H, A-tpy-$H^{4,4"}$, B-tpy-$H^{4,4"}$, C-tpy-$H^{4,4"}$, D-tpy-$H^{4,4"}$, E-tpy-$H^{4,4"}$, F-tpy-$H^{4,4"}$), 7.68 (m, 24H, A-tpy-$H^{6,6"}$, B-tpy-$H^{6,6"}$, C-tpy-$H^{6,6"}$, D-tpy-$H^{6,6"}$, E-tpy-$H^{6,6"}$, F-tpy-$H^{6,6"}$), 7.32 (m, 24H, A-tpy-$H^{5,5"}$, B-tpy-$H^{5,5"}$, C-tpy-$H^{5,5"}$, D-tpy-$H^{5,5"}$, E-tpy-$H^{5,5"}$, F-tpy-$H^{5,5"}$), 4.29 (s, 9H, H^{-OCH3}), 3.75 (s, 6H, H^{-OCH3}). ESI-MS (5136.06 calcd. For $C_{227}H_{154}Br_4N_{48}O_{41}Ru_6$): m/z 508.8199 [M – $9NO_3^-$]$^{9+}$ (calcd m/z: 508.6683), 580.0477 [M – $8NO_3^-$]$^{8+}$ (calcd m/z: 580.0025), 671.7687 [M – $7NO_3^-$]$^{7+}$ (calcd m/z: 671.7178), 794.0674 [M – $6NO_3^-$]$^{6+}$ (calcd m/z: 794.005),965.2892 [M – $5NO_3^-$]$^{5+}$ (calcd m/z: 965.207), m/z 1222.1252 [M – $4NO_3^-$]$^{4+}$ (calcd m/z: 1222.01).



Hexagon-Containing Metallo-organic Ligand L2： To a mixture of **H2** (51 mg, 0.01 mmol) and 4′-(4-boronophenyl)-terpyridine (42 mg, 0.12 mmol) in CH_3CN (30 mL), aqueous K_2CO_3 (0.24 mL, 1 M) was added. The system was pumped and backfilled with nitrogen; then $Pd(PPh_3)_4$ (7.1 mg, 6 umol) was added. After refluxing

for 48 h under argon, the mixture was cooled to 25 °C and added access NH_4PF_6 solution to form the precipitate. The resultant precipitate was washed with 100 mL CH_3OH and purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/CH_3OH to give **L2**, as a red solid, 30.5 mg: 47% yield. ^{1}H NMR (400 MHz, CD_3CN) δ 9.64-9.60 (m, 12H, D-tpy-$H^{3',5'}$, E-tpy-$H^{3',5'}$, F-tpy-$H^{3',5'}$), 9.46 (m, 12H, A-tpy-$H^{3',5'}$, B-tpy-$H^{3',5'}$, C-tpy-$H^{3',5'}$), 9.31 (s, 1H, H^h), 9.09-8.74 (m, 53H, G-tpy-$H^{3',5'}$, H-tpy-$H^{3',5'}$,A-tpy-$H^{3,3"}$, B-tpy-$H^{3,3"}$, C-tpy-$H^{3,3"}$, D-tpy-$H^{3,3"}$, E-tpy-$H^{3,3"}$, F-tpy-$H^{3,3"}$, G-tpy-$H^{3,3"}$, H-tpy-$H^{3,3"}$, G-tpy-$H^{6,6"}$, H-tpy-$H^{6,6"}$, H^j, H^e, H^b), 8.65 (s, 2H, H^a), 8.44 (m, 8H, G-Ph-H^x, H-Ph-H^x), 8.32 (m, 8H, G-Ph-H^y, H-Ph-H^y), 8.16–7.93 (m, 37H, A-tpy-$H^{4,4"}$, B-tpy-$H^{4,4"}$, C-tpy-$H^{4,4"}$, D-tpy-$H^{4,4"}$, E-tpy-$H^{4,4"}$, F-tpy-$H^{4,4"}$, G-tpy-$H^{4,4"}$, H-tpy-$H^{4,4"}$, H^g, H^f, H^d, H^i, H^c), 7.87 (s, 2H, H^m), 7.63 – 7.51 (m, 38H, A-tpy-$H^{6,6"}$, B-tpy-$H^{6,6"}$, C-tpy-$H^{6,6"}$, D-tpy-$H^{6,6"}$, E-tpy-$H^{6,6"}$, F-tpy-$H^{6,6"}$, G-tpy-$H^{5,5"}$,H-tpy-$H^{5,5"}$), 7.29 (m, 24H, A-tpy-$H^{5,5"}$, B-tpy-$H^{5,5"}$, C-tpy-$H^{5,5"}$, D-tpy-$H^{5,5"}$, E-tpy-$H^{5,5"}$, F-tpy-$H^{5,5"}$), 4.29 (s, 9H, H^{-OCH3}), 3.53 (s, 6H, H^{-OCH3}). ESI-MS (7045.42 calcd. For $C_{311}H_{210}F_{72}N_{48}O_5P_{12}Ru_6$): m/z 638.0178 $[M - 9PF_6^-]^{9+}$ (calcd m/z: 637.8644), 735.7637$[M - 8PF_6^-]^{8+}$ (calcd m/z: 735.7175), 861.8739 $[M - 7PF_6^-]^{7+}$ (calcd m/z: 861.5285), 1029.1887 $[M - 6PF_6^-]^{6+}$ (calcd m/z: 1029.2766), 1264.2231 $[M - 5PF_6^-]^{5+}$ (calcd m/z: 1264.124), m/z 1616.5441 $[M - 4PF_6^-]^{4+}$ (calcd m/z: 1616.395).

3. Experimental test of first designed dual-pore tessellated square array



Scheme S2: Experimental test of first designed dual-pore tessellated square array: MOL ligand **L1** (4.0 mg, 0.61 μmol), and $Zn(NO_3)_2 \cdot 6H_2O$ (0.19 mg, 0.61 μmol) or (0.38 mg, 1.22 μmol) was added in a 50 mL flask, then a solvent mixture of CH_3CN/MeOH (20 ml, V:V, 2/1) was added. The mixture was refluxed for 24 h, after cooled to ambient temperature, excess NH_4PF_6 in MeOH was added to get a red precipitate, which was filtered and washed with H_2O and MeOH, to generate a red solid.

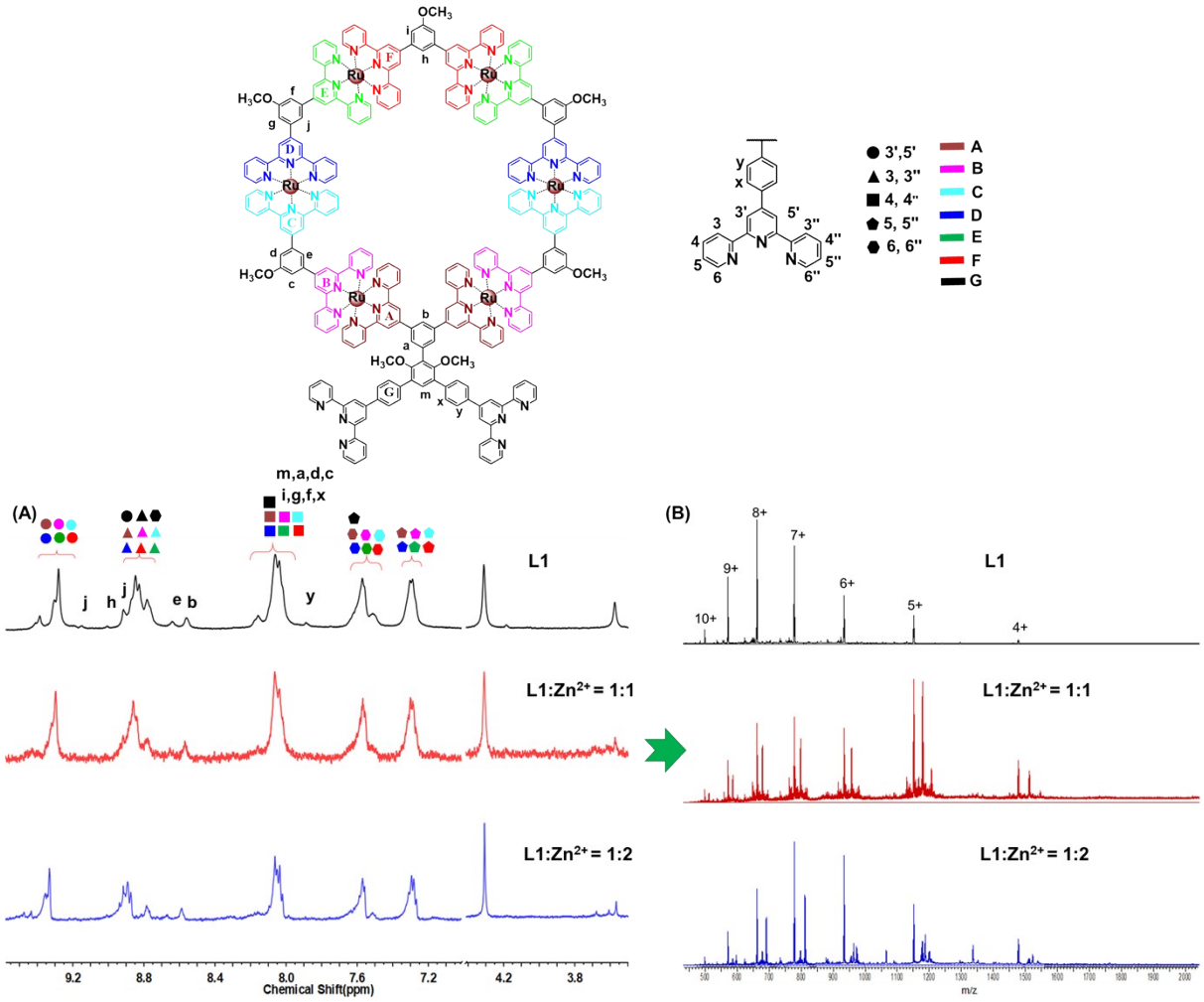


Figure S1: (A) Comparison of the ^{1}H NMR spectra (500 MHz) of hexagon-containing metallo-organic ligand **L1** and the resultant assembly at different stoichiometric ratio (1:1 and 1:2) in CD_3CN; (B) ESI-MS of hexagon-containing metallo-organic ligand **L1** and the resultant assembly at different stoichiometric ratio (1:1 and 1:2). The tpy$H^{6',6''}$ protons of free terpyridine has no expected change in chemical shift, and ESI-MS showed that the resultant assembly is mainly the peak of ligand, suggesting that such a construction has been unsuccessful, we suspected this could be put down to the molecular hexagon framework has relatively large molecular volume and mass, which breaking the coordination connection of singly bridged tpy-Zn(II)-tpy.

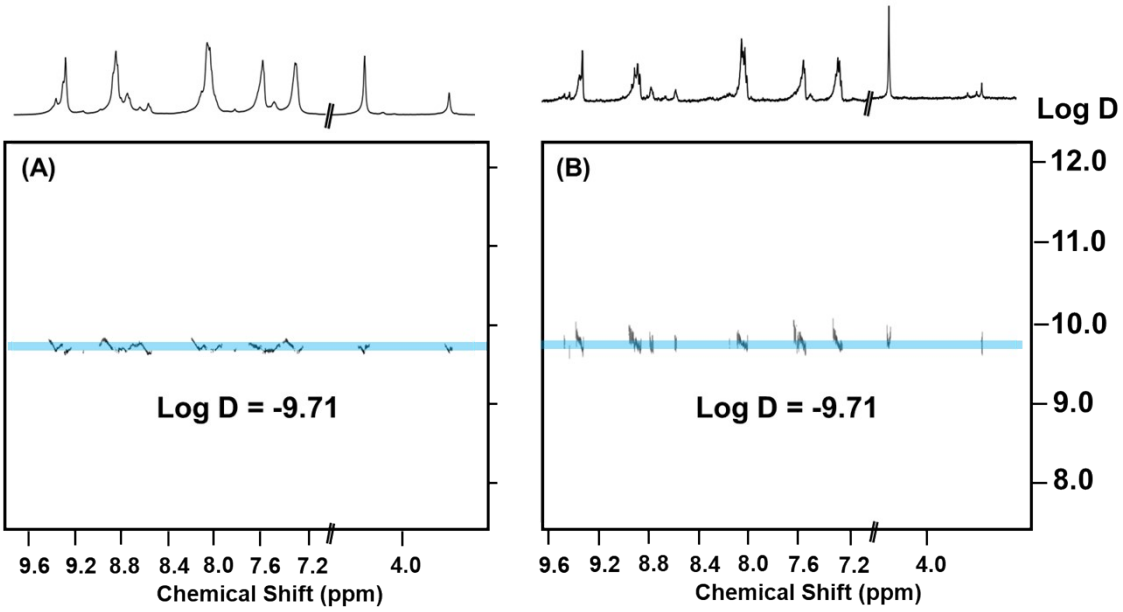
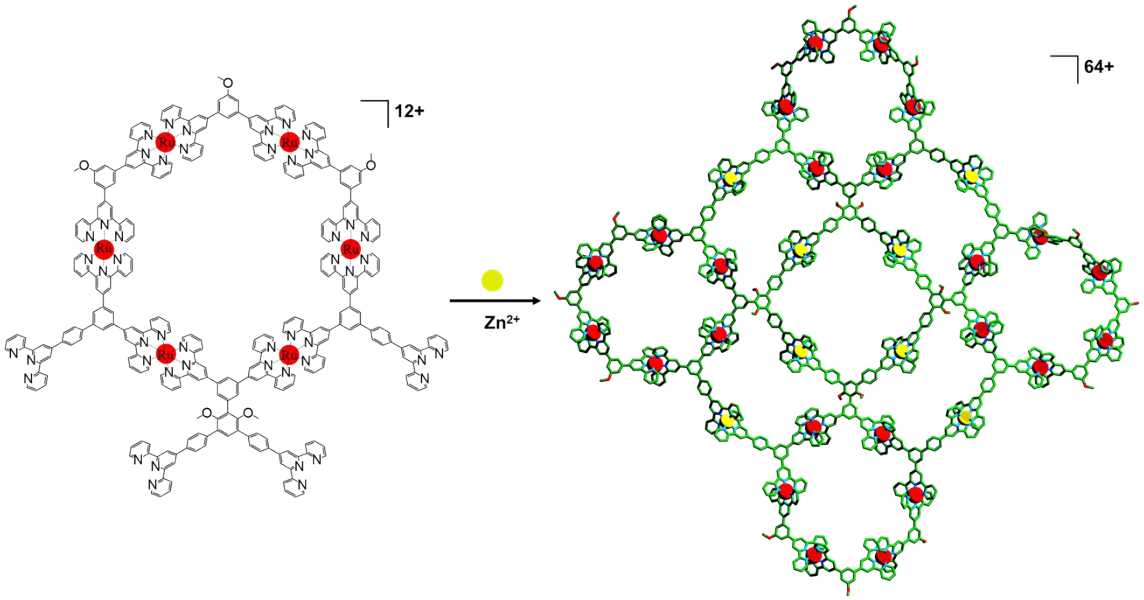
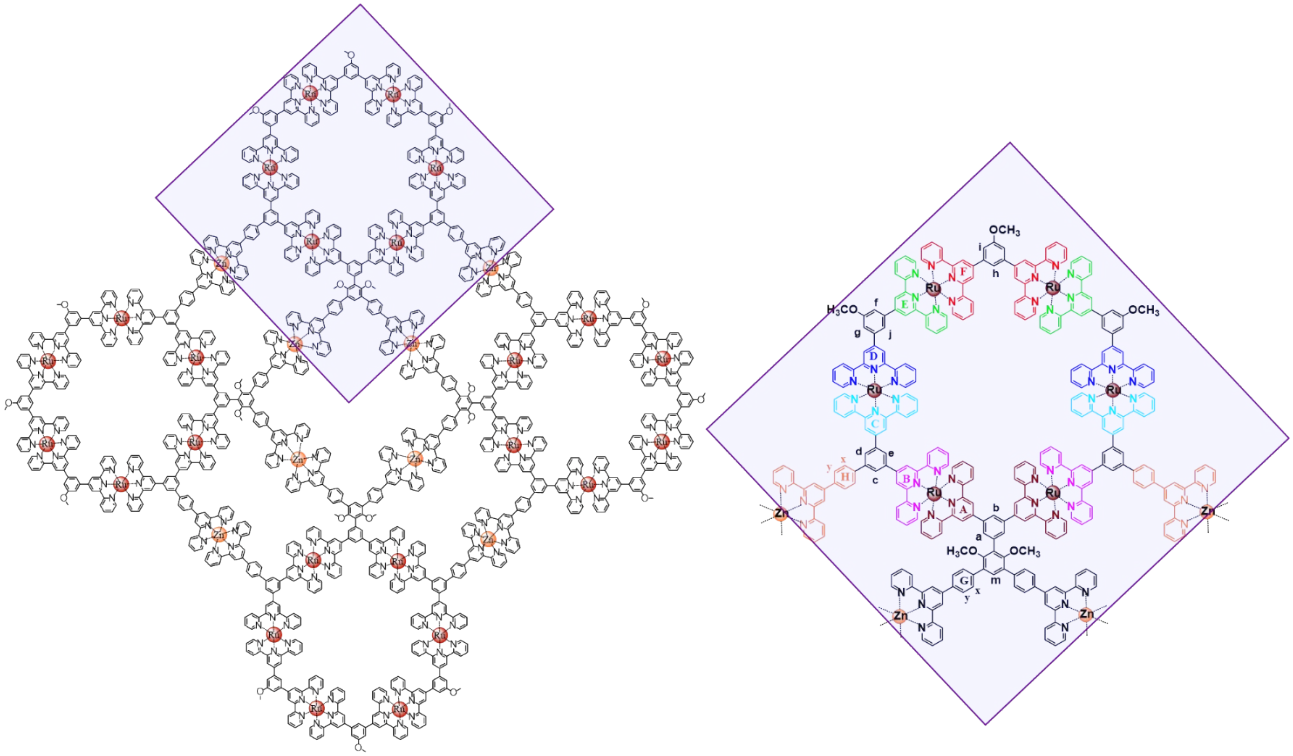


Figure S2: (A) Comparison of the DOSY spectra (500 MHz) of hexagon-containing metallo-organic ligand **L1** and the resultant assembly at a stoichiometric ratio of 1:2 in CD_3CN, both showed narrow bands at log D = −9.71 m^2s^{-1}, also confirmed that the metallo-organic ligand **L1** is the major component.

4. Self-Assembly of supramolecules of tri-pore tessellated square array



Scheme S3: Self-Assembly of supramolecules of tri-pore tessellated square array.



Triple-pore tessellated square array Zn_8L2_4: MOL ligand **L2** (4.0 mg, 0.56 μmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (0.4 mg, 1.2 μmol) was added in a 50 ml flask, then a solvent mixture of CH_3CN/MeOH (20 ml, V:V, 2/1) was added. The mixture was refluxed for 12 h, after cooled to ambient temperature, excess NH_4PF_6 or bistrifluoromethanesulfonimide lithium salt ($LiNTf_2$) in MeOH was added to get a red precipitate, which was filtered and washed with H_2O and MeOH, to generate a red solid (~93%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.48-9.43(m, 12H, D-tpy-$H^{3',5'}$, E-tpy-$H^{3',5'}$, F-tpy-$H^{3',5'}$), 9.33-9.30(m, 12H, A-tpy-$H^{3',5'}$, B-tpy-$H^{3',5'}$, C-tpy-$H^{3',5'}$), 9.20(m, 8H, G-tpy-$H^{3',5'}$, H-tpy-$H^{3',5'}$), 9.09-8.94(4H, H^h, H^j, H^e, H^b), 8.92-8.82(m, 32H, A-tpy-$H^{3,3''}$, B-tpy-$H^{3,3''}$, C-tpy-$H^{3,3''}$, D-tpy-$H^{3,3''}$, E-tpy-$H^{3,3''}$, F-tpy-$H^{3,3''}$, G-tpy-$H^{3,3''}$, H-tpy-$H^{3,3''}$), 8.65-8.62 (m, 6H, H^a, H^d, H^c), 8.43-8.41(m, 4H, G-Ph-H^y, H-Ph-H^y), 8.29-8.22(m, 10H, H^i, H^g, H^f, G-ph-$H^{x'}$, H-ph-$H^{x'}$), 8.16-8.07 (m, 32H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$, D-tpy-$H^{4,4''}$, E-tpy-$H^{4,4''}$, F-tpy-$H^{4,4''}$, G-tpy-$H^{4,4''}$, H-tpy-$H^{4,4''}$), 7.96-7.63(m, 9H, G-tpy-$H^{6,6''}$, H-tpy-$H^{6,6''}$, H^m), 7.70-7.52(m, 32H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$, E-tpy-$H^{6,6''}$, F-tpy-$H^{6,6''}$, G-tpy-$H^{5,5''}$,H-tpy-$H^{5,5''}$), 7.48-7.29 (m, 24H, A-

tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$, E-tpy-$H^{5,5''}$, F-tpy-$H^{5,5''}$), 4.33-4.31 (s, 9H, H^{-OCH3}), 3.68 (s, 6H, H^{-OCH3}). ESI-MS (31024.16 with 64 $PF6^{-}$ calcd. For $C_{1244}H_{840}F_{384}N_{192}O_{20}P_{64}Ru_{24}Zn_8$): m/z 1048.3783 [M – $26PF_6^{-}$]$^{26+}$ (calcd m/z: 1048.2769), 1096.0315 [M – $25PF_6^{-}$]$^{25+}$ (calcd m/z: 1096.0064), 1147.6342 [M – $24PF_6^{-}$]$^{24+}$ (calcd m/z: 1147.7133), 1203.9335 [M – $23PF_6^{-}$]$^{23+}$ (calcd m/z: 1203.9165), 1265.2479 [M – $22PF_6^{-}$]$^{22+}$ (calcd m/z: 1265.2290), m/z 1332.4351 [M – $21PF_6^{-}$]$^{21+}$ (calcd m/z: 1332.3809), 1406.3335 [M – $20PF_6^{-}$]$^{20+}$ (calcd m/z: 1406.248), 1488.1493 [M – $19PF_6^{-}$]$^{19+}$ (calcd m/z: 1487.8905), 1578.9857 [M – $18PF_6^{-}$]$^{18+}$ (calcd m/z: 1578.6044), 1679.99732 [M – $17PF_6^{-}$]$^{17+}$ (calcd m/z: 1679.9905); ESI-MS (39675.11 with 64 NTf_2^{-} calcd. For $C_{1372}H_{840}F_{384}N_{256}O_{276}Ru_{24}S_{128}Zn_8$): m/z 3026.7109 [M – $12NTf_2^{-}$]$^{12+}$ (calcd m/z: 3026.1131), 2771.2622 [M – $13NTf_2^{-}$]$^{13+}$ (calcd m/z: 2771.7855), 2554.0914 [M – $14NTf_2^{-}$]$^{14+}$ (calcd m/z: 2553.7904), 2365.1586 [M – $15NTf_2^{-}$]$^{15+}$ (calcd m/z: 2364.8613), 2200.0632 [M – $16NTf_2^{-}$]$^{16+}$ (calcd m/z: 2199.5483), 2054.3015 [M – $17NTf_2^{-}$]$^{17+}$ (calcd m/z: 2053.684), 1924.6033 [M – $18NTf_2^{-}$]$^{18+}$ (calcd m/z: 1924.0267), 1808.4157 [M – $19NTf_2^{-}$]$^{19+}$ (calcd m/z: 1808.0176), 1703.9834 [M – $20NTf_2^{-}$]$^{20+}$ (calcd m/z: 1703.6095), 1609.6814 [M – $21NTf_2^{-}$]$^{21+}$ (calcd m/z: 1609.1449), 1523.3942 [M – $22NTf_2^{-}$]$^{22+}$ (calcd m/z: 1523.2680), 1445.1146 [M – $23NTf_2^{-}$]$^{23+}$ (calcd m/z: 1444.8587), 1373.2389 [M – $24NTf_2^{-}$]$^{24+}$ (calcd m/z: 1372.9835), 1307.0752 [M – $25NTf_2^{-}$]$^{25+}$ (calcd m/z: 1306.8584).

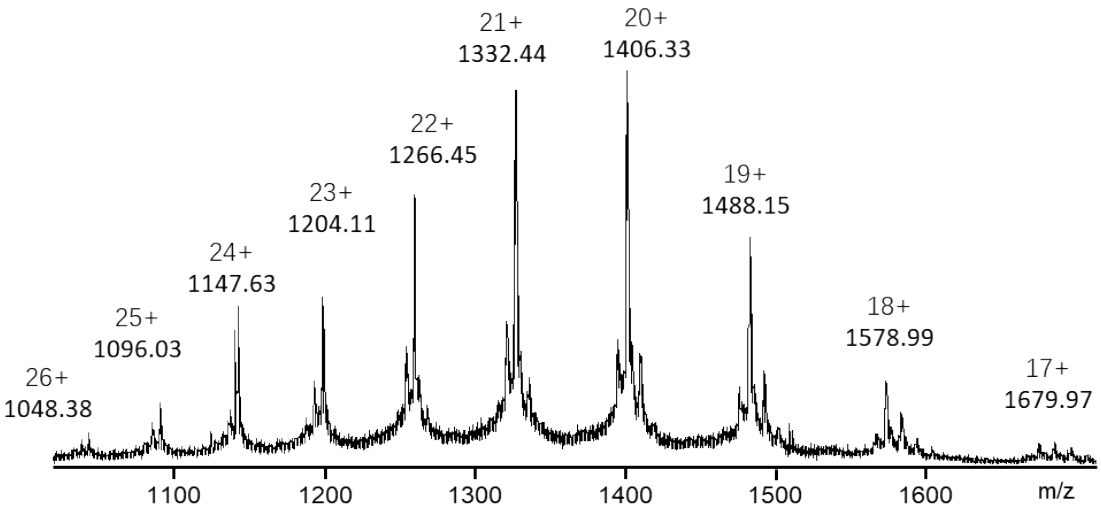


Figure S3: ESI−MS of **Zn_8L2_4**with **$64PF_6^-$**. By further ion exchange, a series of exclusive peaks with successive charge states at m/z 1048.38, 1096.03, 1147.63, 1204.11, 1266.45, 1332.44, 1406.33, 1488.15, 1578.99 and 1679.97 were also observed due to the loss of sequential numbers of PF_6^- anions based on the molecular formula of $(Zn_8L_{24})^{64+}(PF_6^-)^{64-}$ with a molecular weight of 31 024 Da.

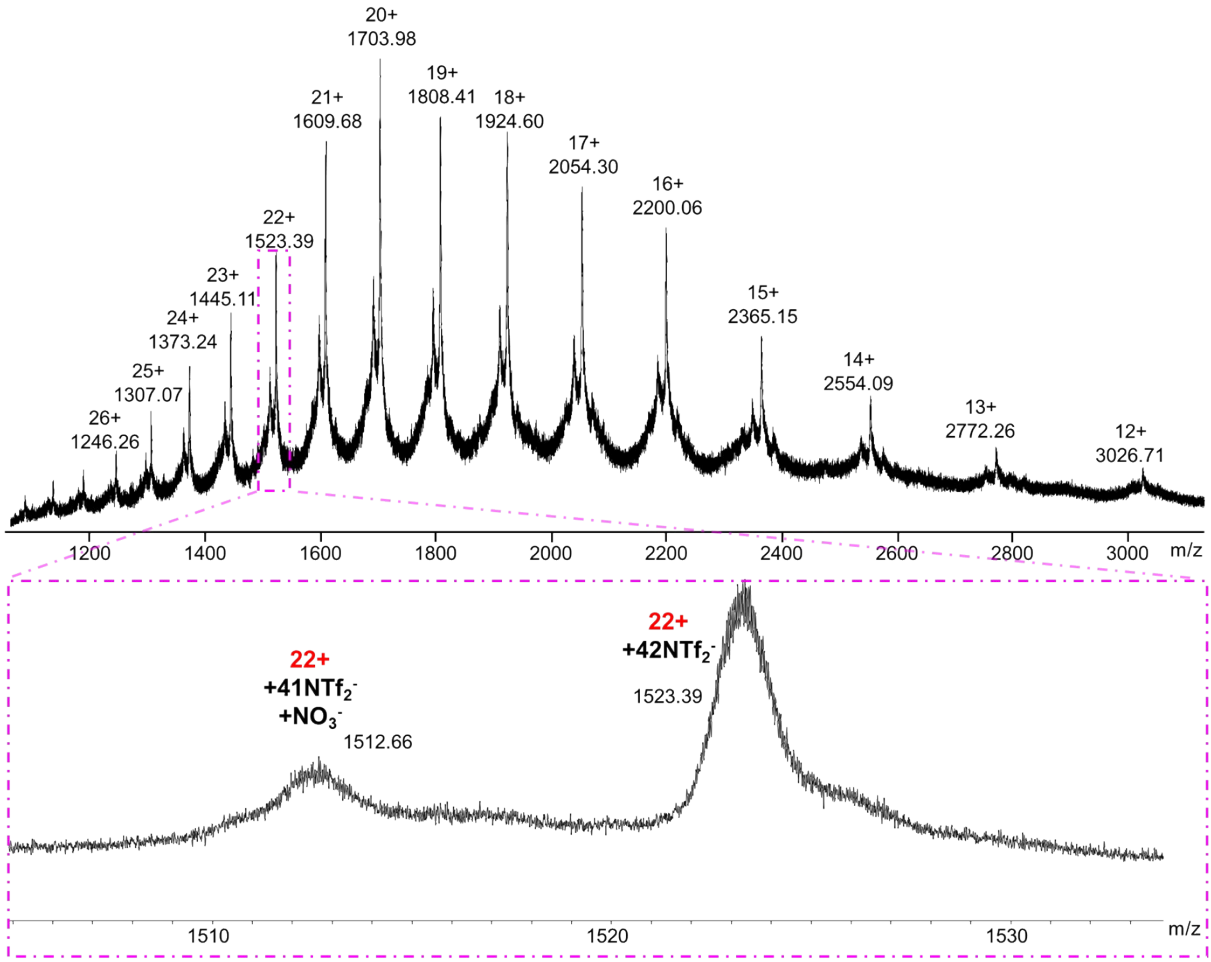


Figure S4: ESI−MS of $\mathbf{Zn_8L2_4}$with **64**$\mathbf{(NTf_2^-)}$.

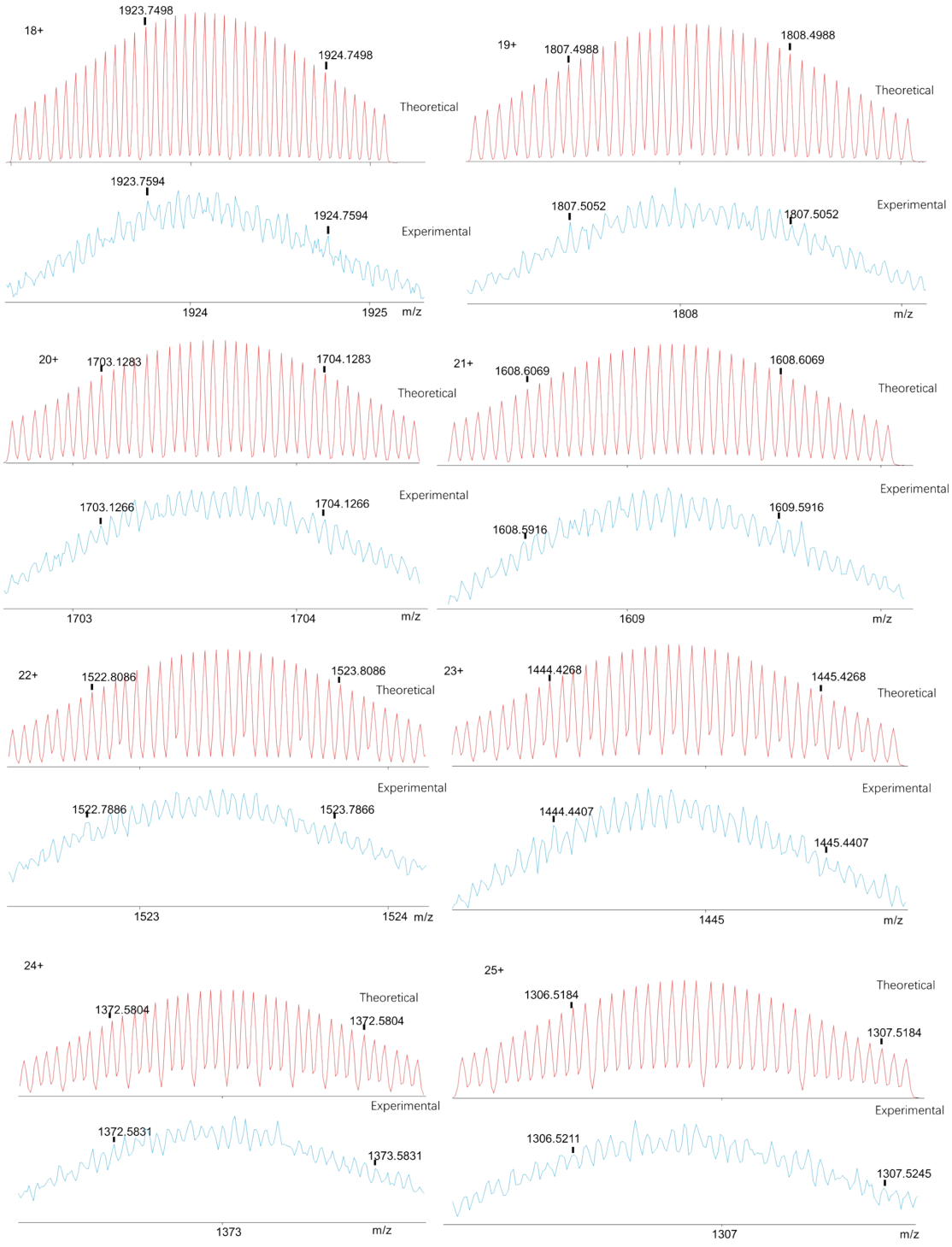


Figure S5: Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from $\mathbf{Zn_8L2_4{\cdot}64(NTf_2^-)}$.

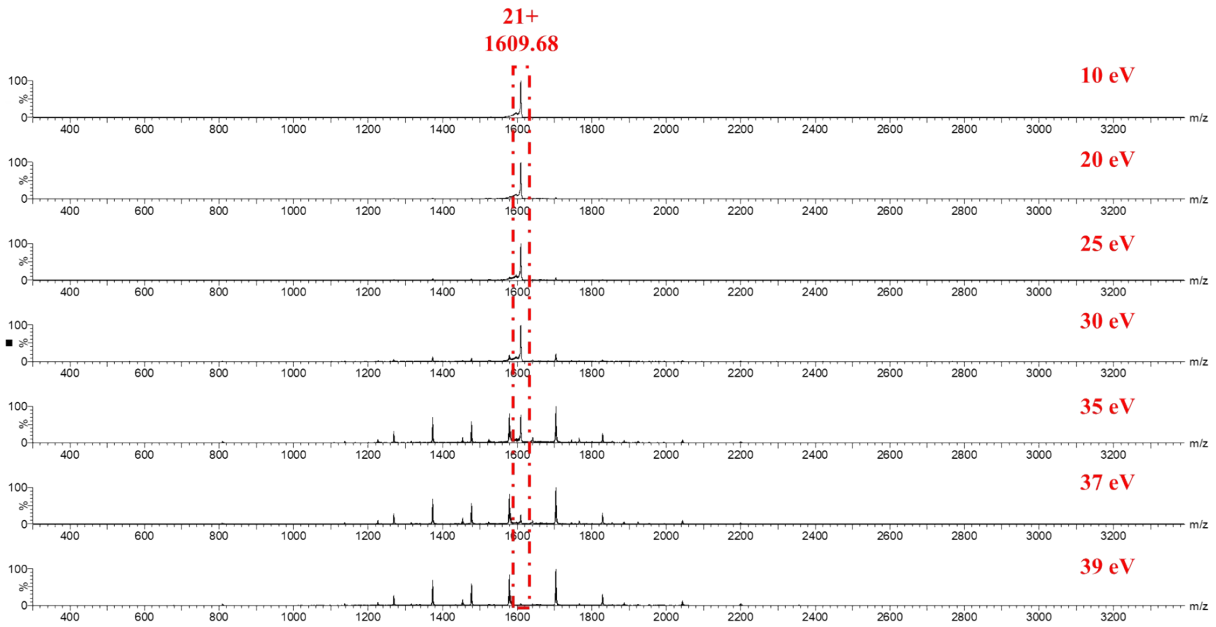


Figure S6: gMS^2 of **Zn_8L2_4·64(NTf_2^-)** at m/z 1609.68 with different collision energies.

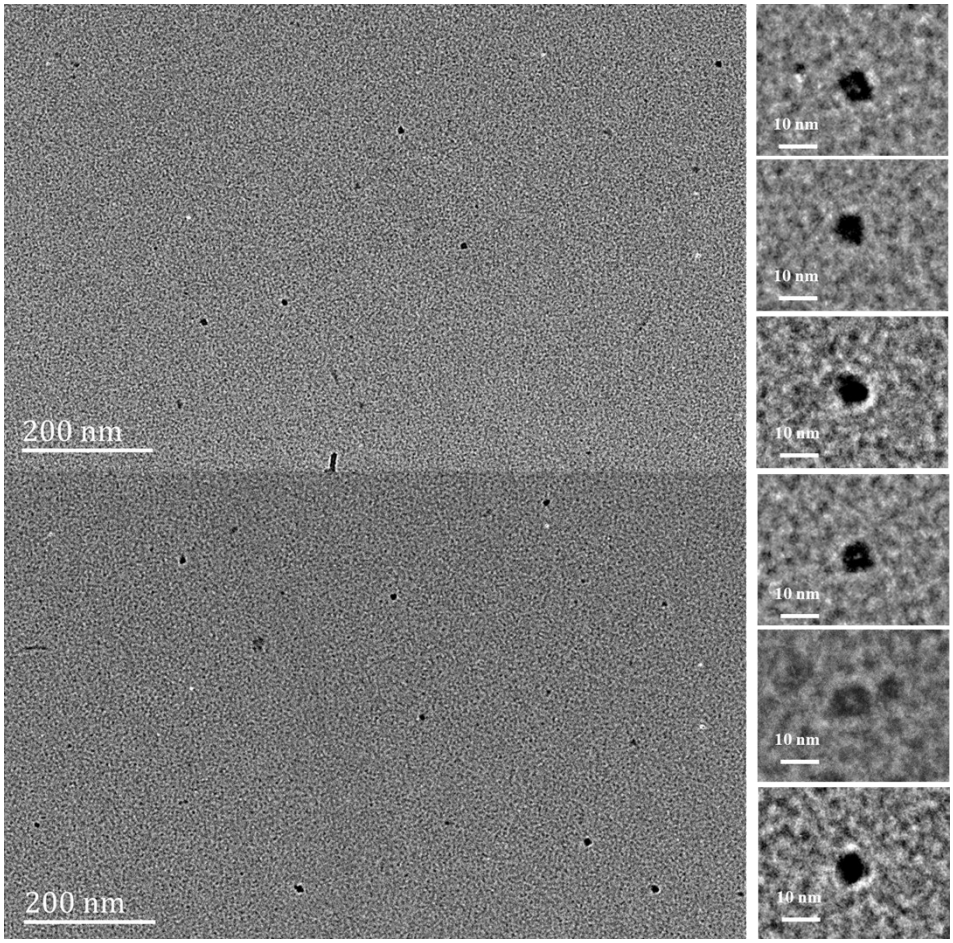


Figure S7: TEM imaging of discrete tessellated square array **Zn_8L2_4**.

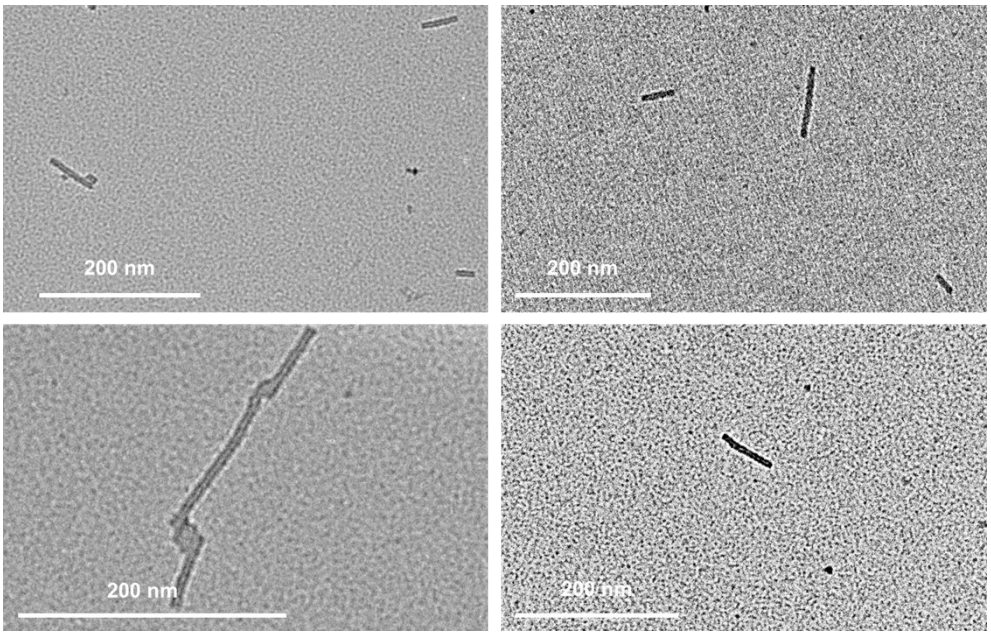


Figure S8: TEM imaging of tubular-like nanostructures assembled by $\mathbf{Zn_8L2_4}$.[S4]

5. NMR spectra data of ligands and complexes

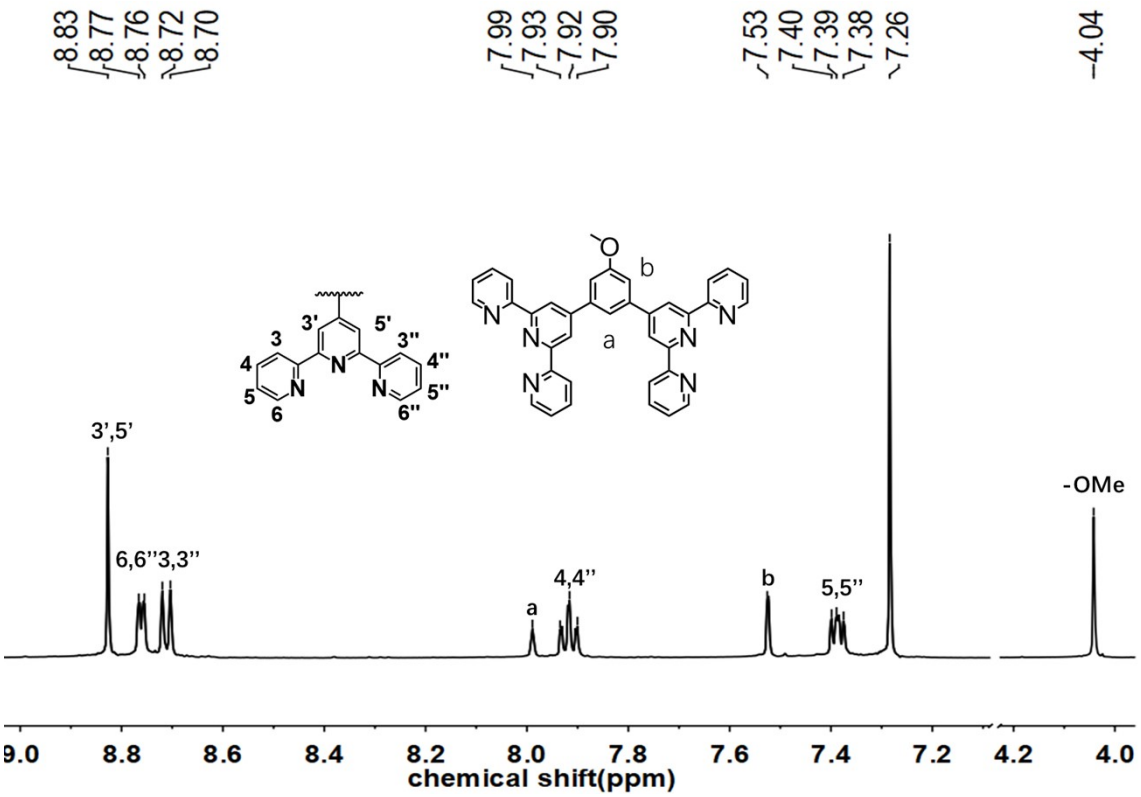


Figure S9: ^{1}H NMR spectrum (400 MHz) of **S2** in $CDCl_3$

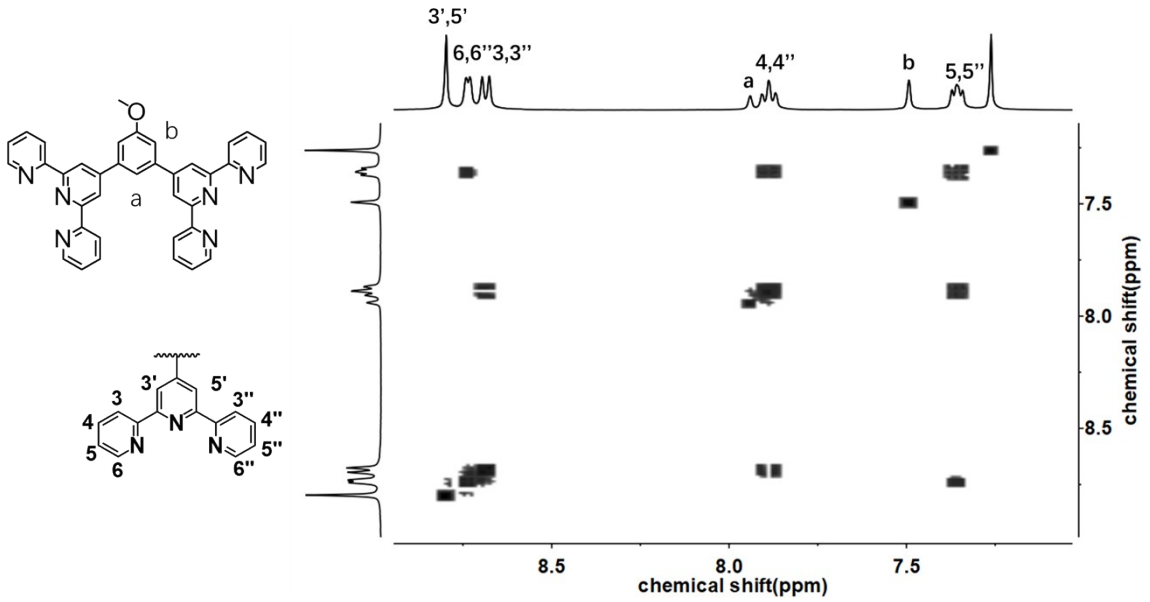


Figure S10: 2D COSY spectrum (400 MHz) of **S2** in $CDCl_3$.

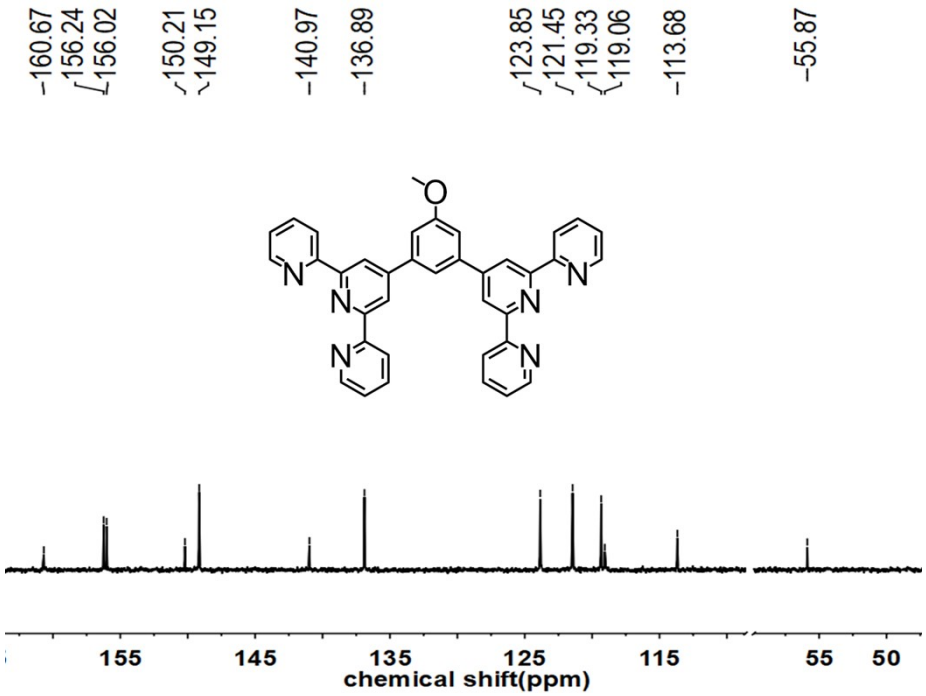


Figure S11: ^{13}C NMR spectrum (400 MHz) of **S2** in $CDCl_3$.

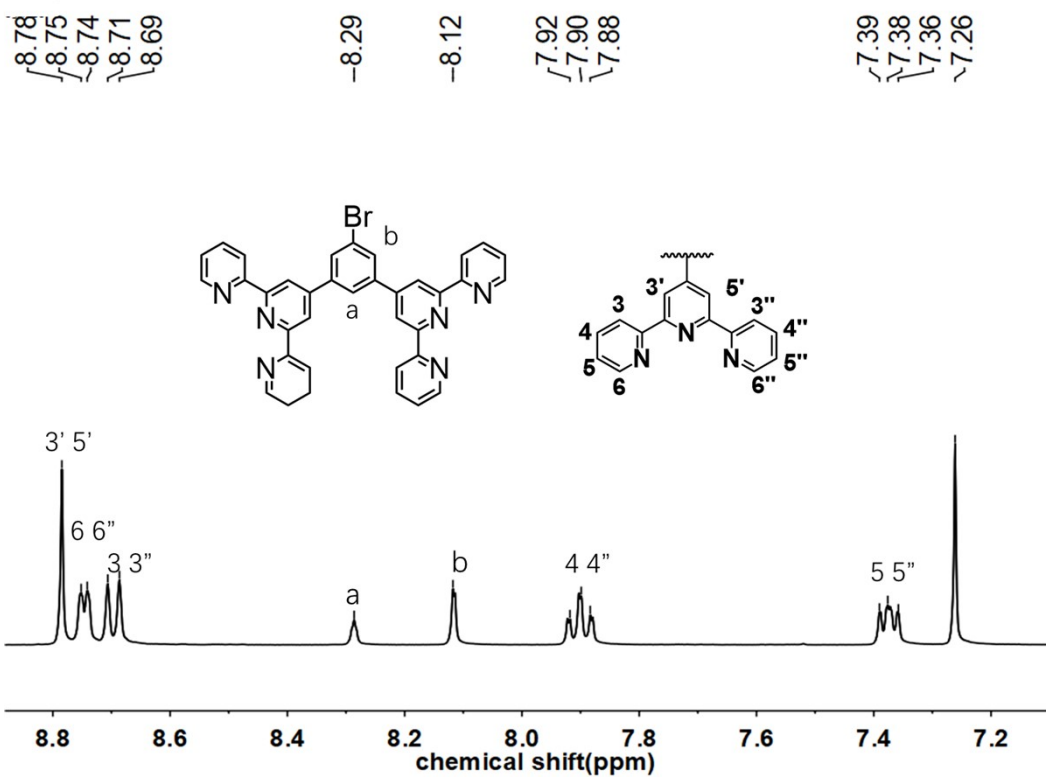


Figure S12: ^{1}H NMR spectrum (500 MHz) of **S6** in $CDCl_3$

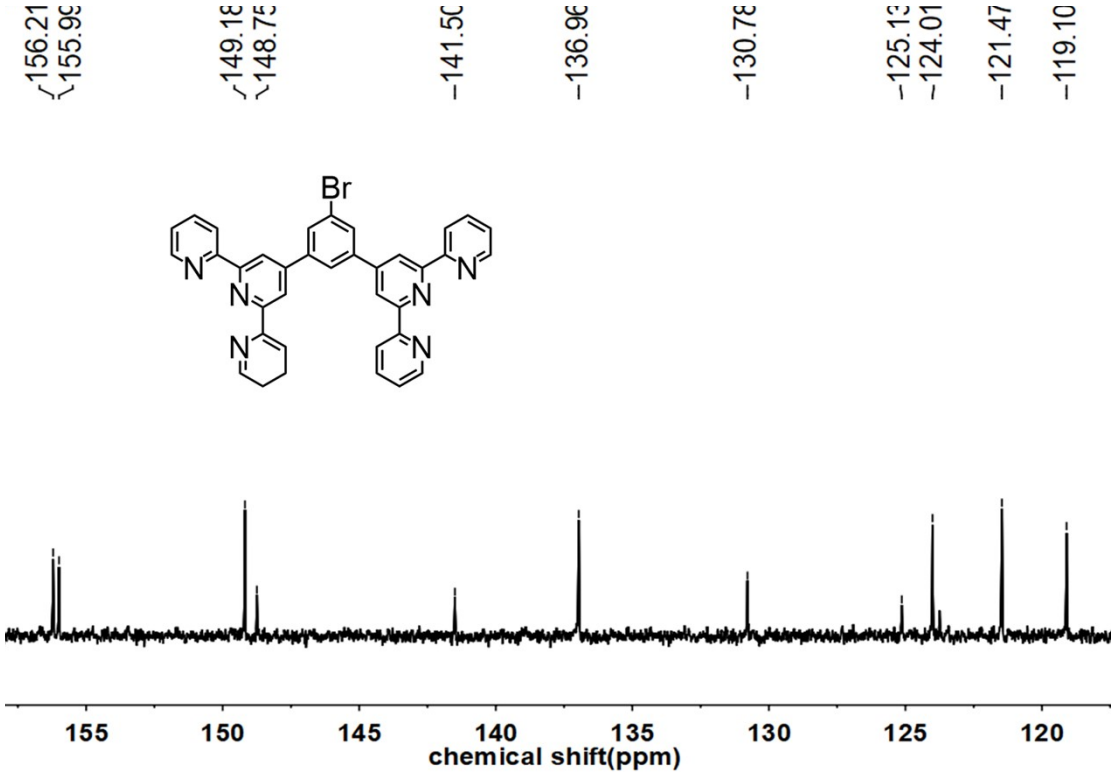


Figure S13: ^{13}C NMR spectrum (100 MHz) of **S6** in $CDCl_3$.

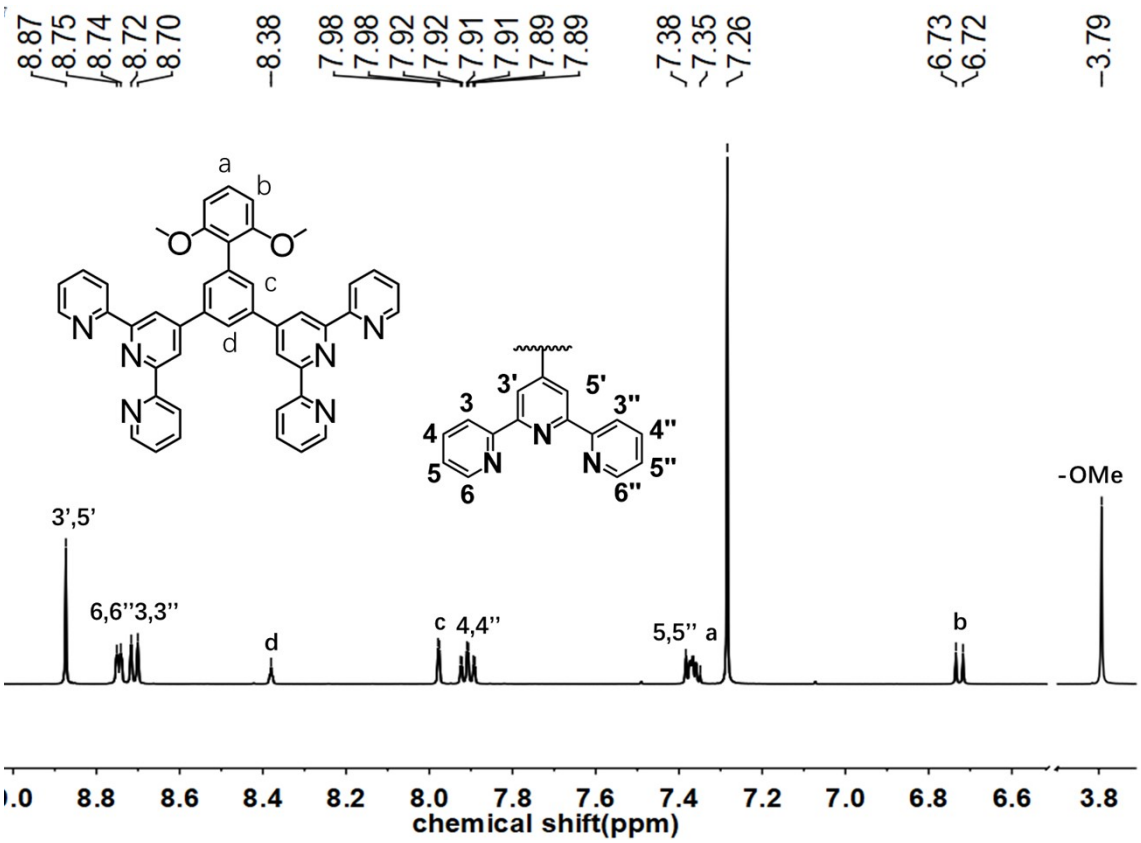


Figure S14: ^{1}H NMR spectrum (400 MHz) of **S8** in $CDCl_3$

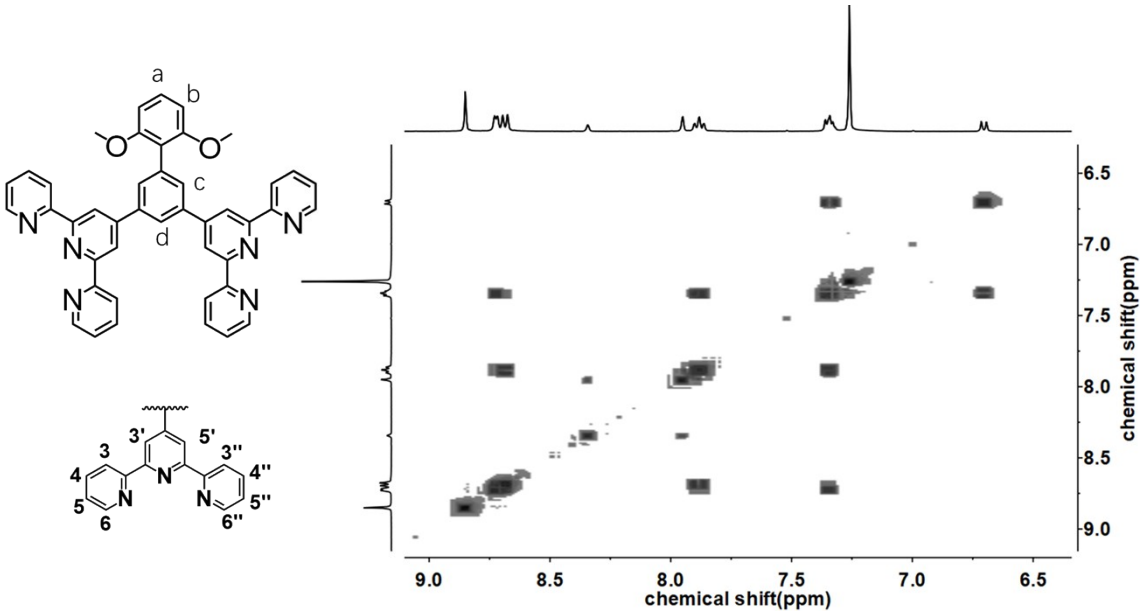


Figure S15: 2D COSY spectrum (400 MHz) of **S8** in $CDCl_3$.

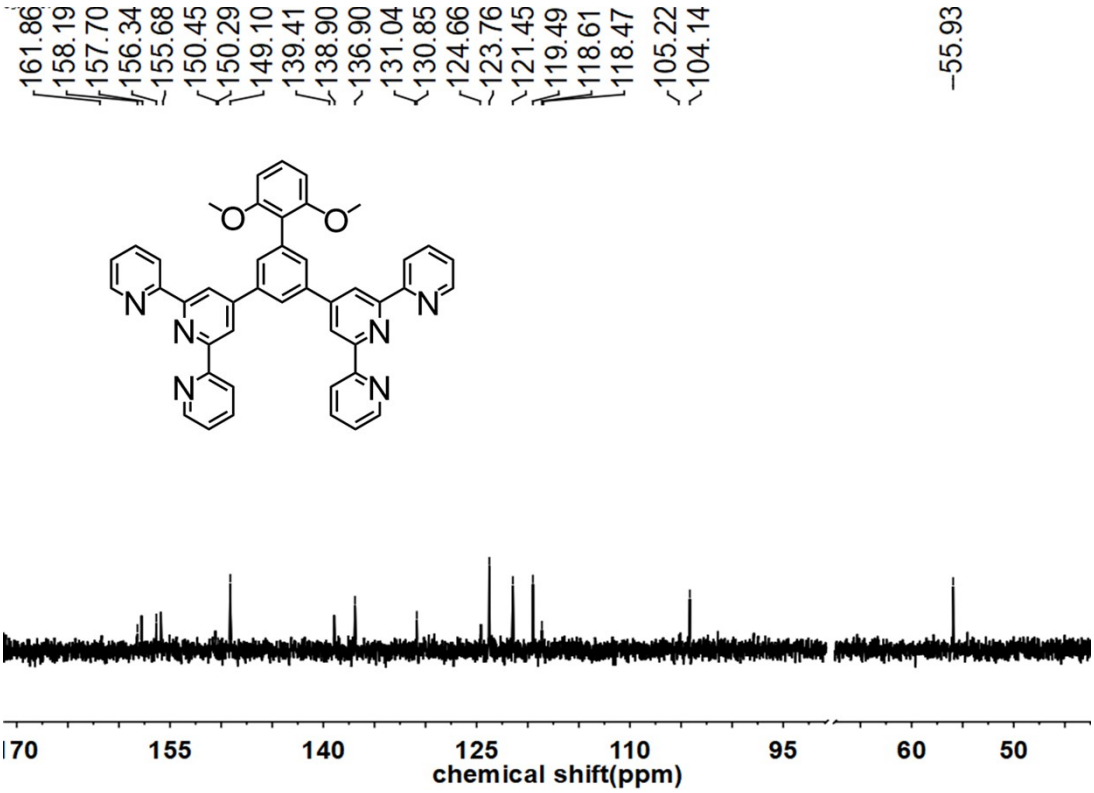


Figure S16: ^{13}C NMR spectrum (100 MHz) of **S8** in $CDCl_3$.

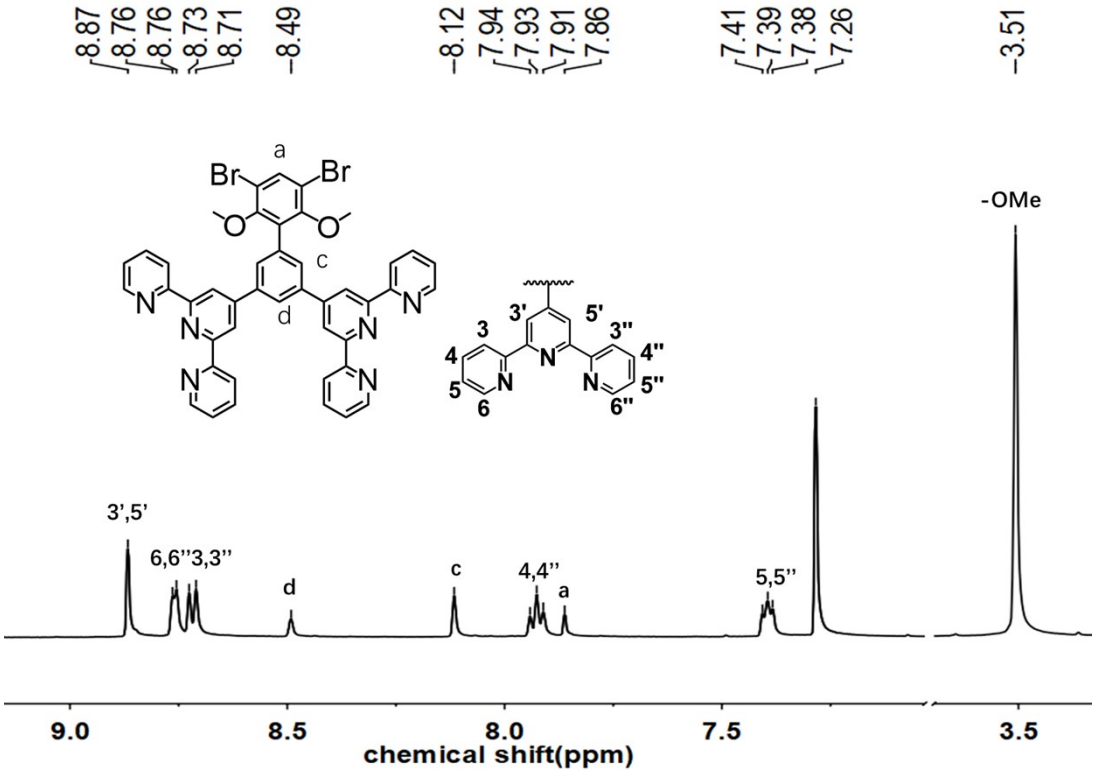


Figure S17: ^{1}H NMR spectrum (400 MHz) of **S9** in $CDCl_3$.

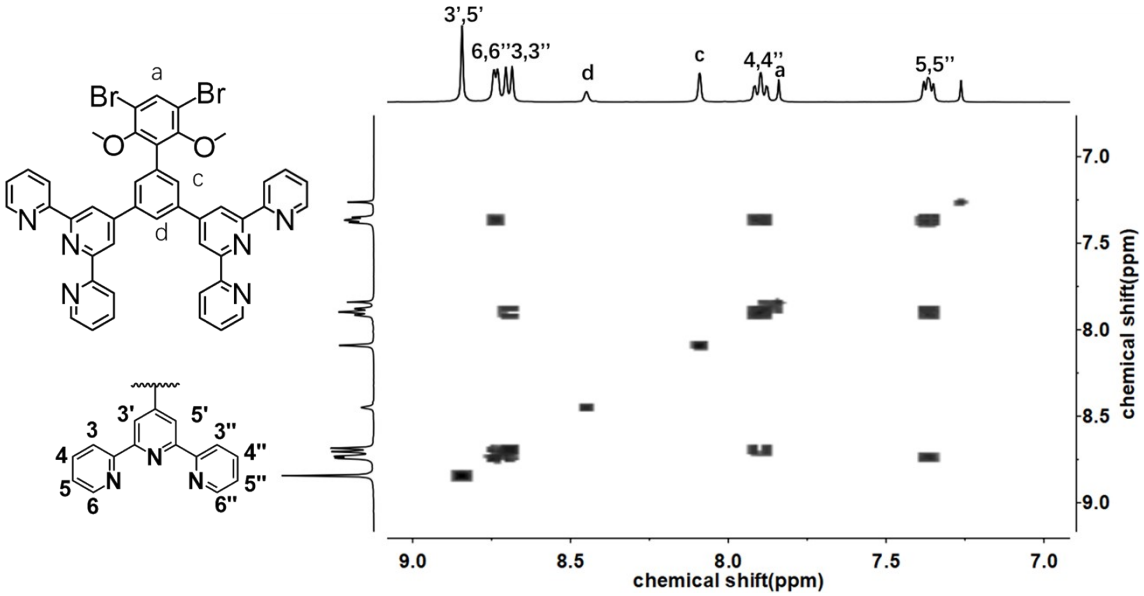


Figure S18: 2D COSY spectrum (400 MHz) of **S9** in $CDCl_3$.

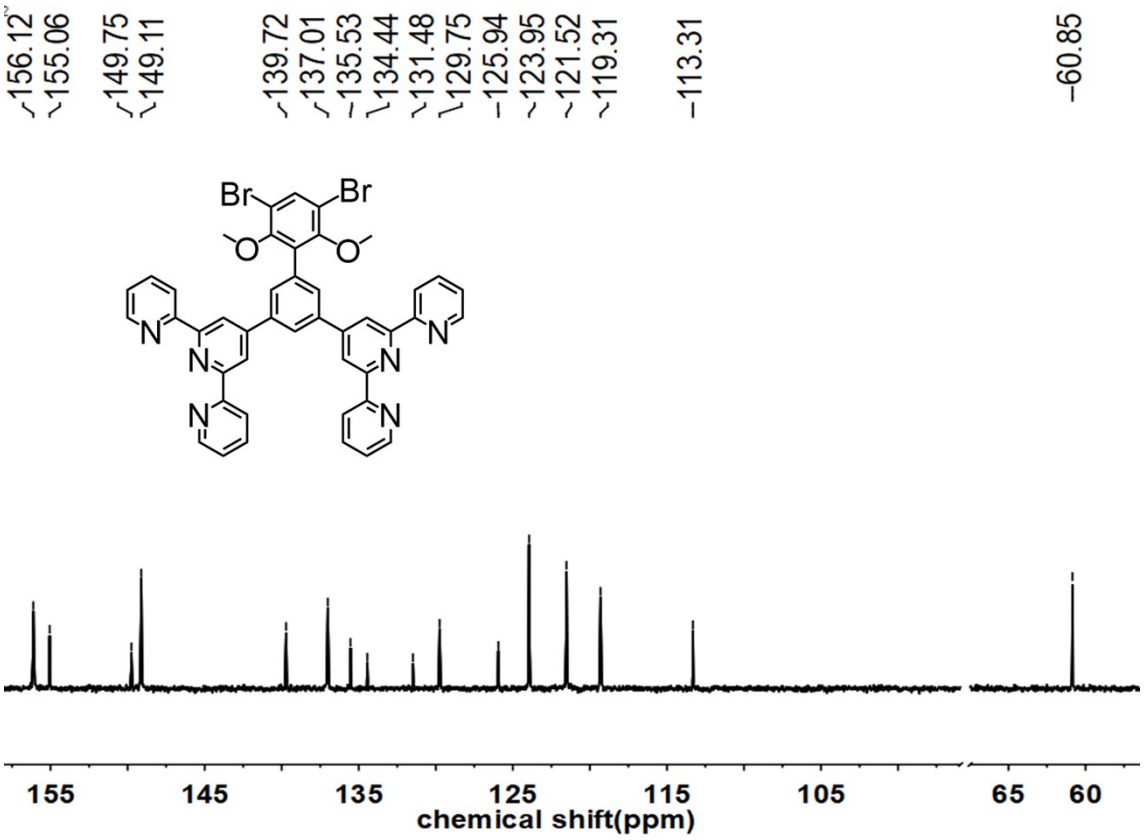


Figure S19: ^{13}C NMR spectrum (100 MHz) of **S9** in $CDCl_3$.

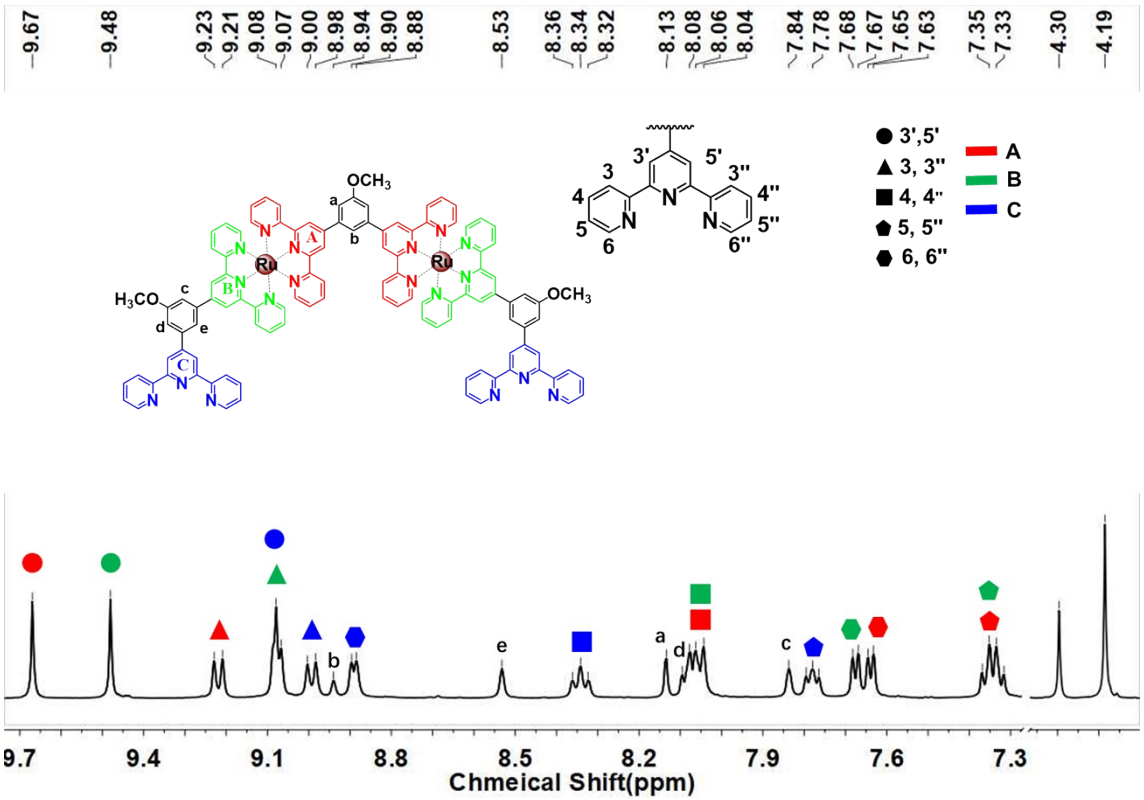


Figure S20: ^{1}H NMR spectrum (400 MHz) of **S4** in CD_3OD.

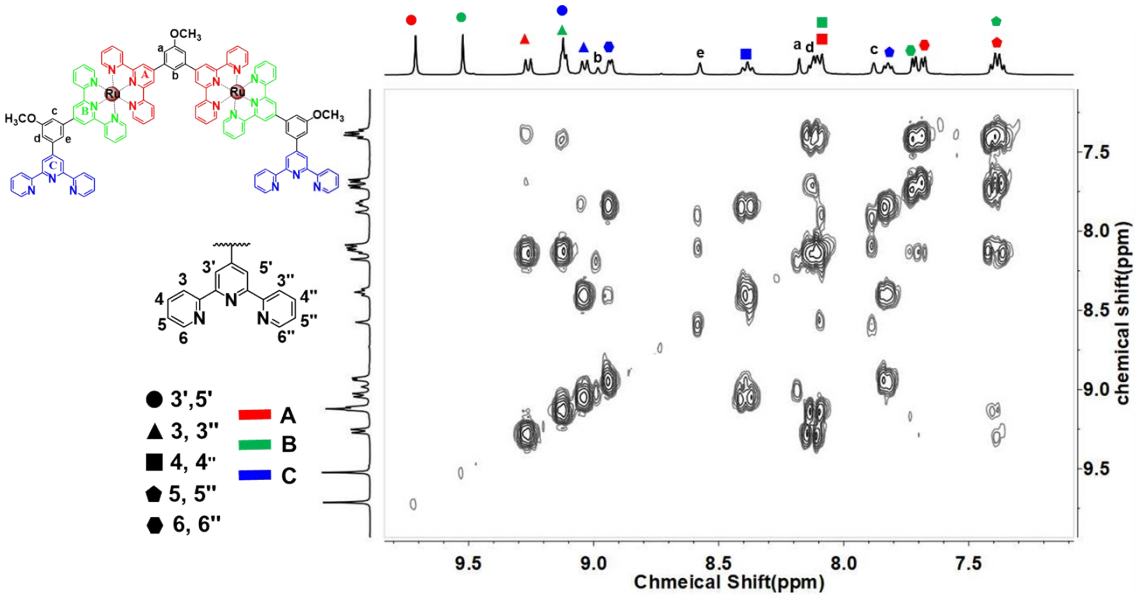


Figure S21: 2D COSY spectrum (400 MHz) of **S4** in CD_3OD.

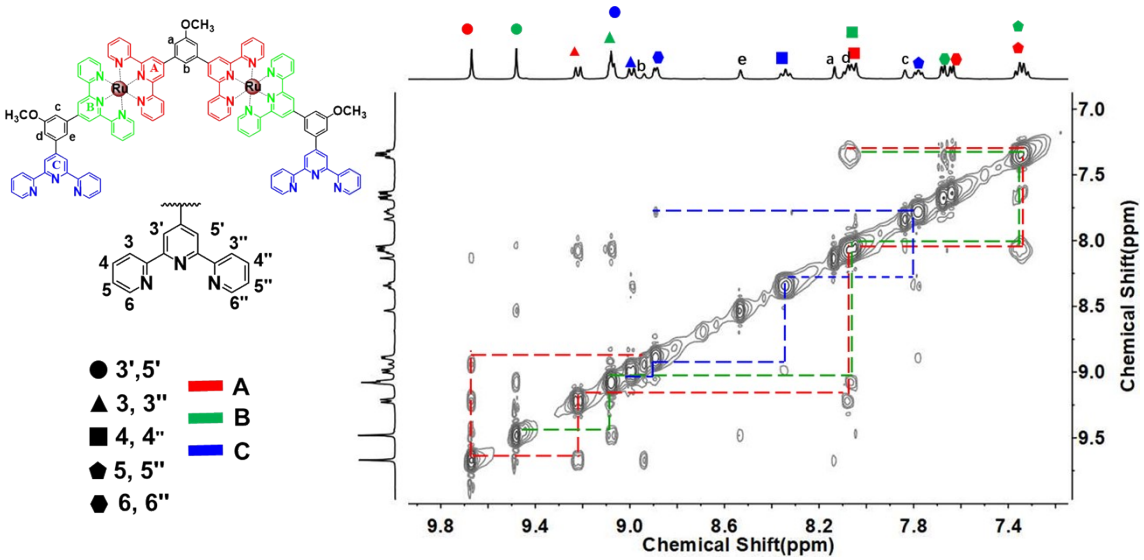


Figure S22: 2D NOESY spectrum (400 MHz) of **S4** in CD_3OD.

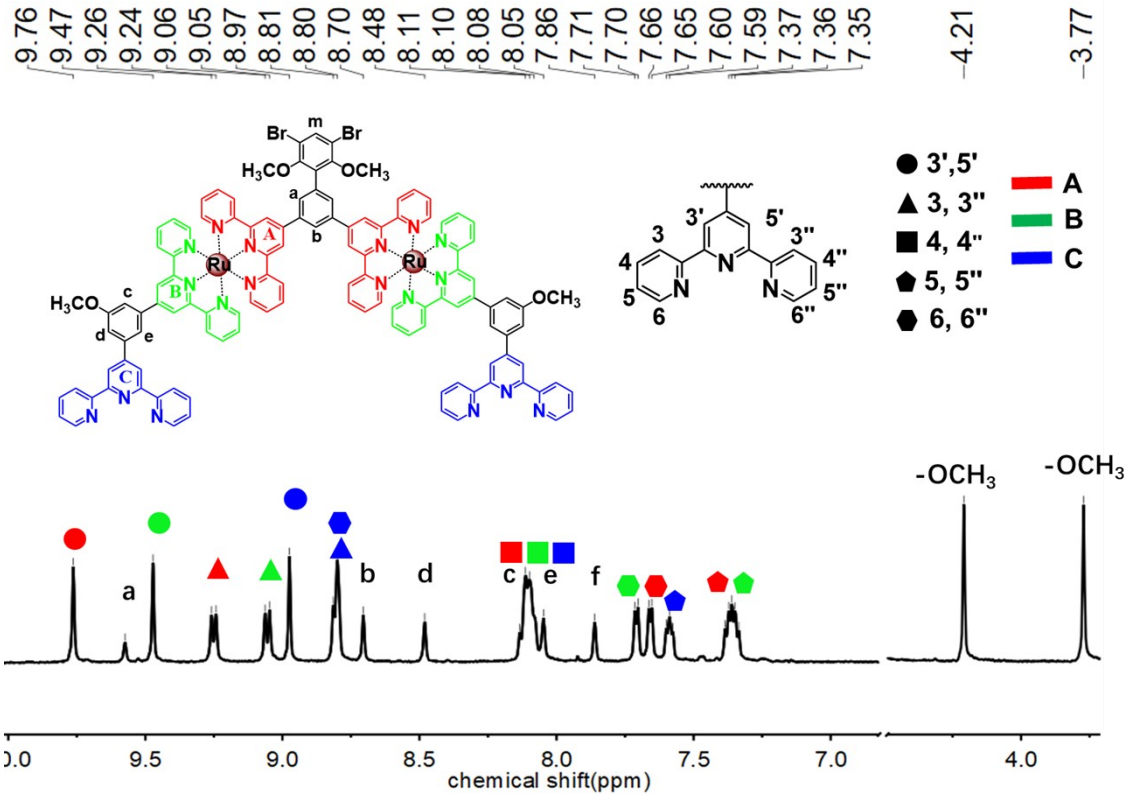


Figure S23: ^1H NMR spectrum (400 MHz) of **M2** in CD_3OD.

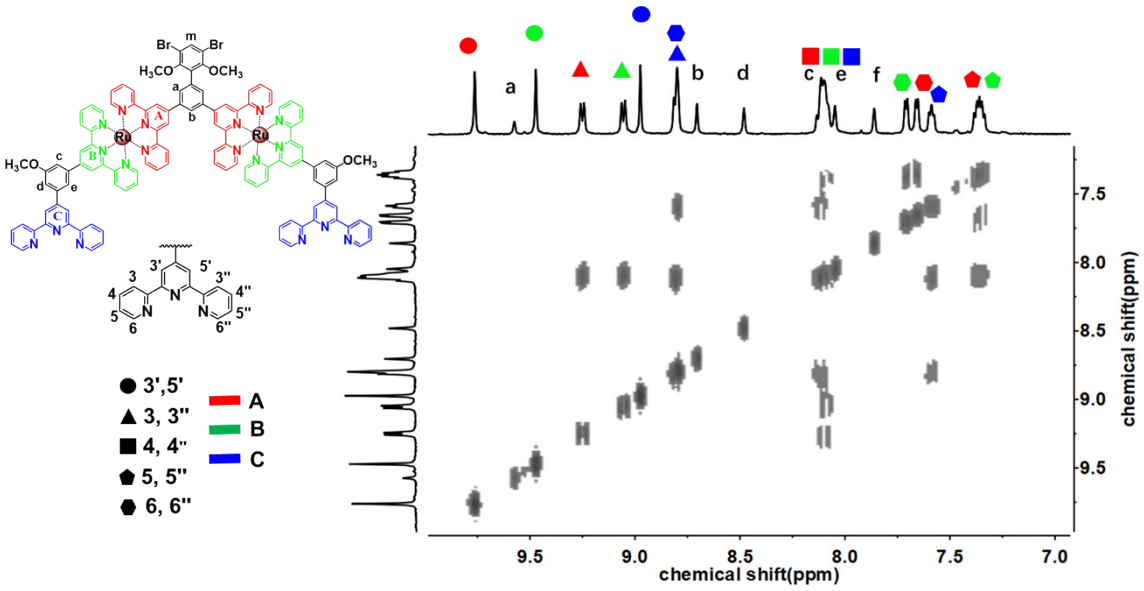


Figure S24: 2D COSY spectrum (400 MHz) of **M2** in CD_3OD.

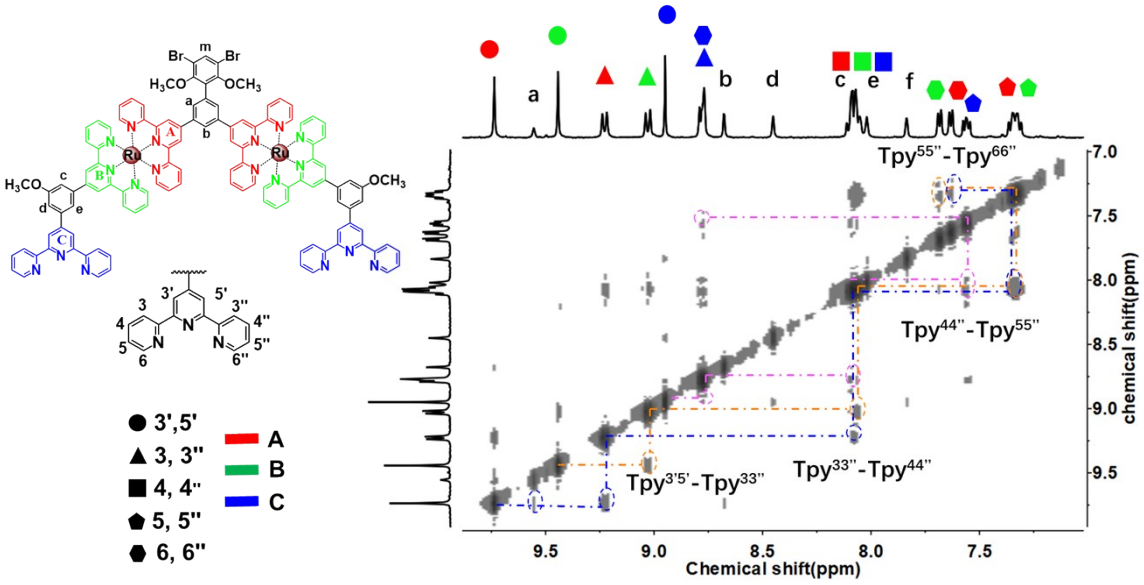


Figure S25: 2D NOESY spectrum (400 MHz) of **M2** in CD_3OD.

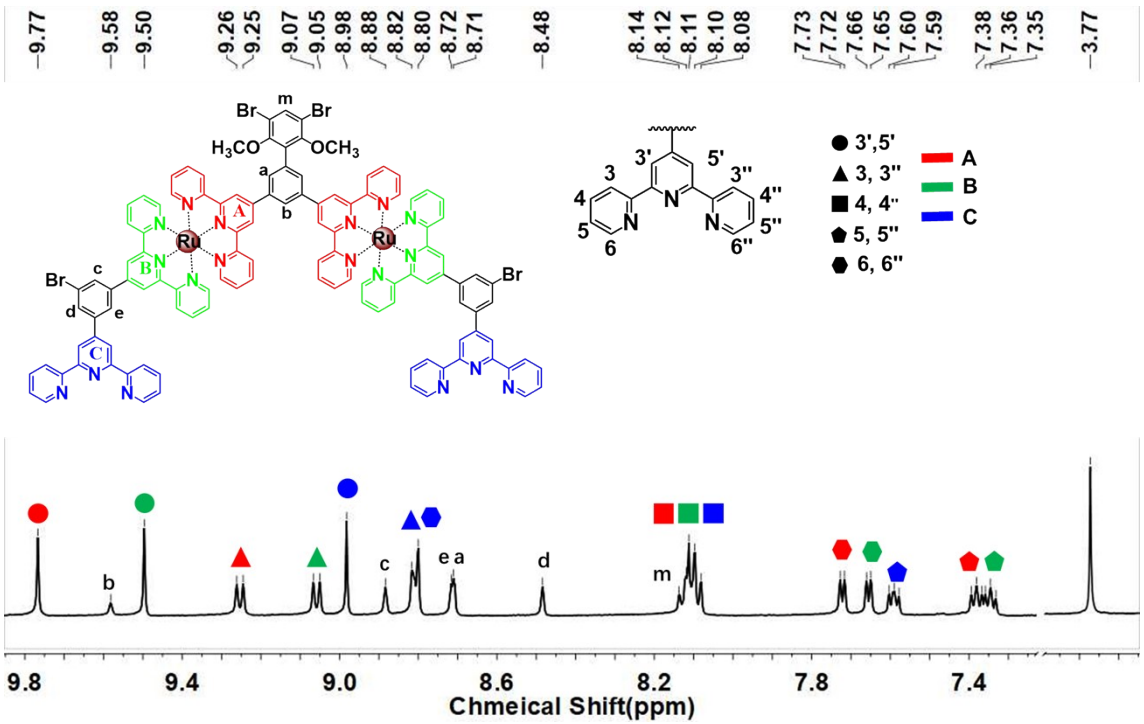


Figure S26: ^{1}H NMR spectrum (400 MHz) of **M3** in CD_3OD.

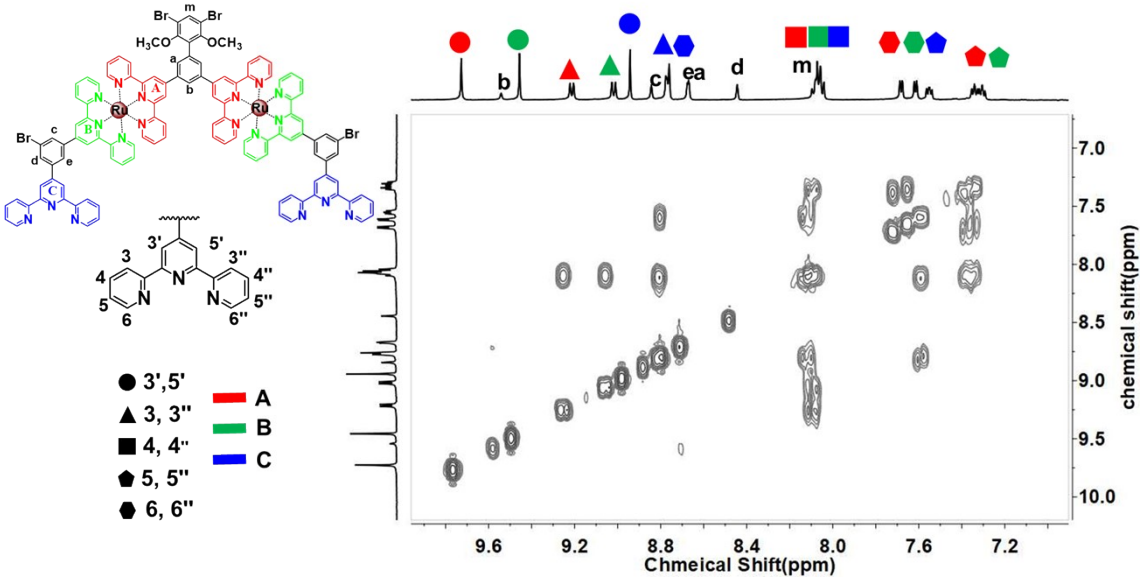


Figure S27: 2D COSY spectrum (400 MHz) of **M3** in CD_3OD.

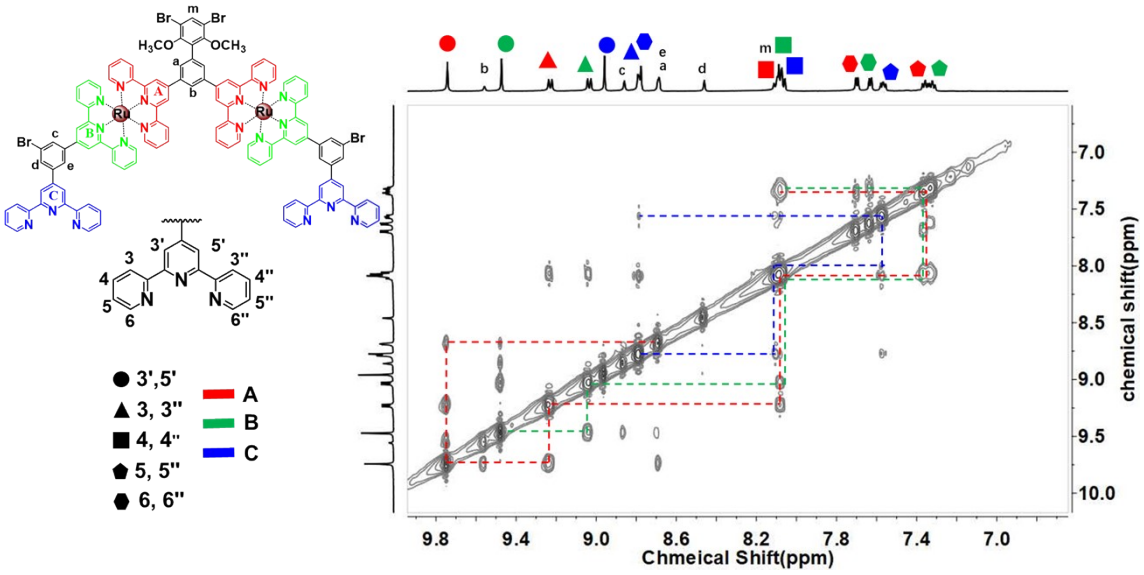


Figure S28: 2D NOESY spectrum (400 MHz) of **M3** in CD_3OD.

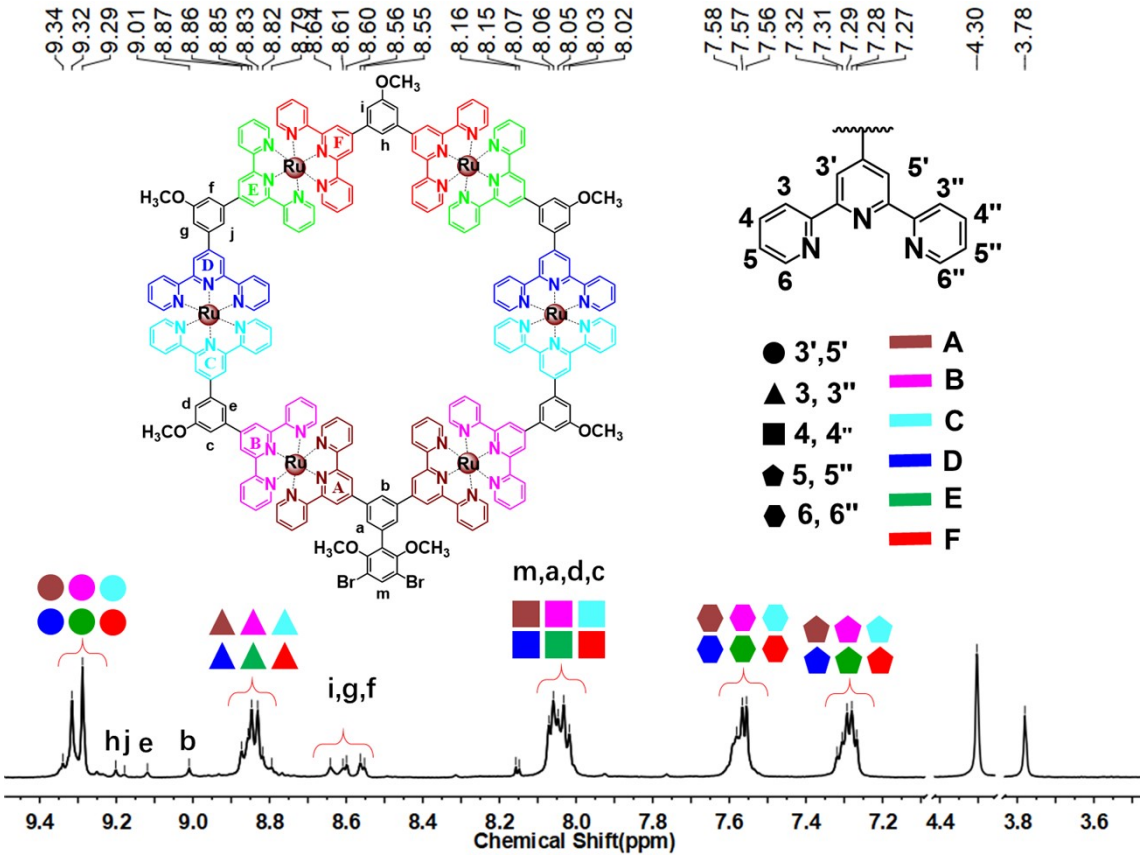


Figure S29: ^{1}H NMR spectrum (400 MHz) of **H1** in CD_3CN.

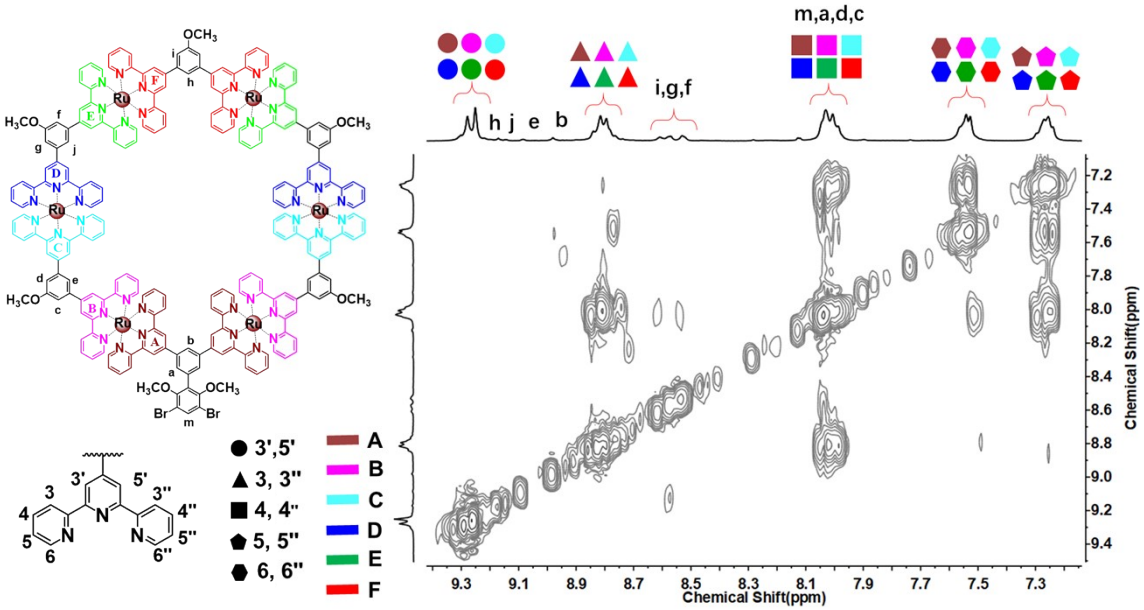


Figure S30: 2D COSY spectrum (400 MHz) of **H1** in CD_3CN.

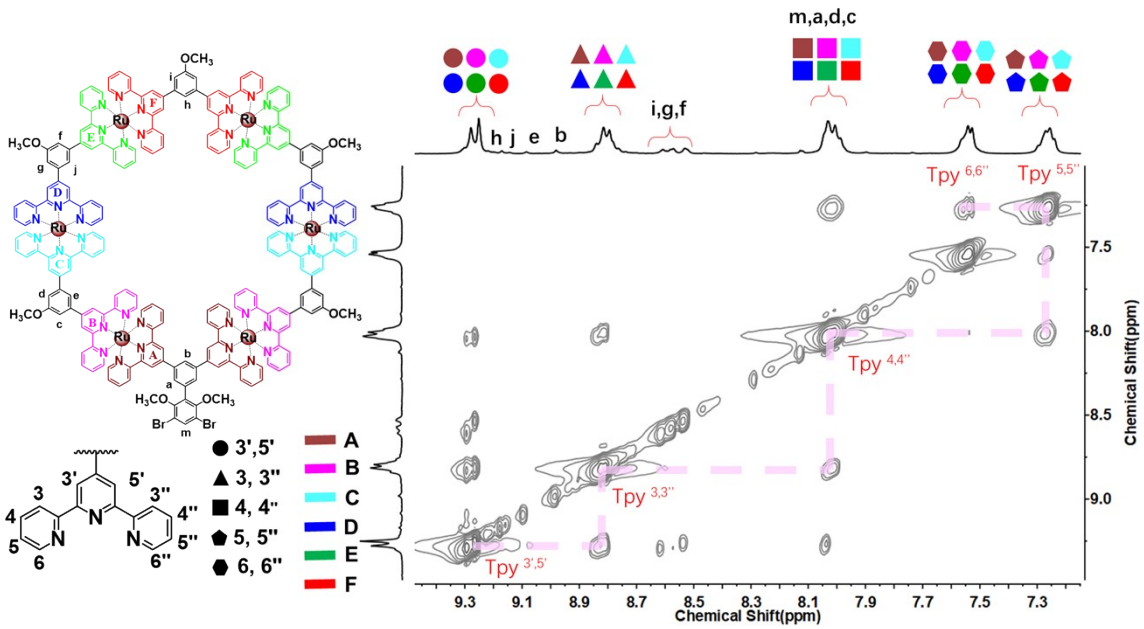


Figure S31: 2D NOESY spectrum (400 MHz) of **H1** in CD_3CN.

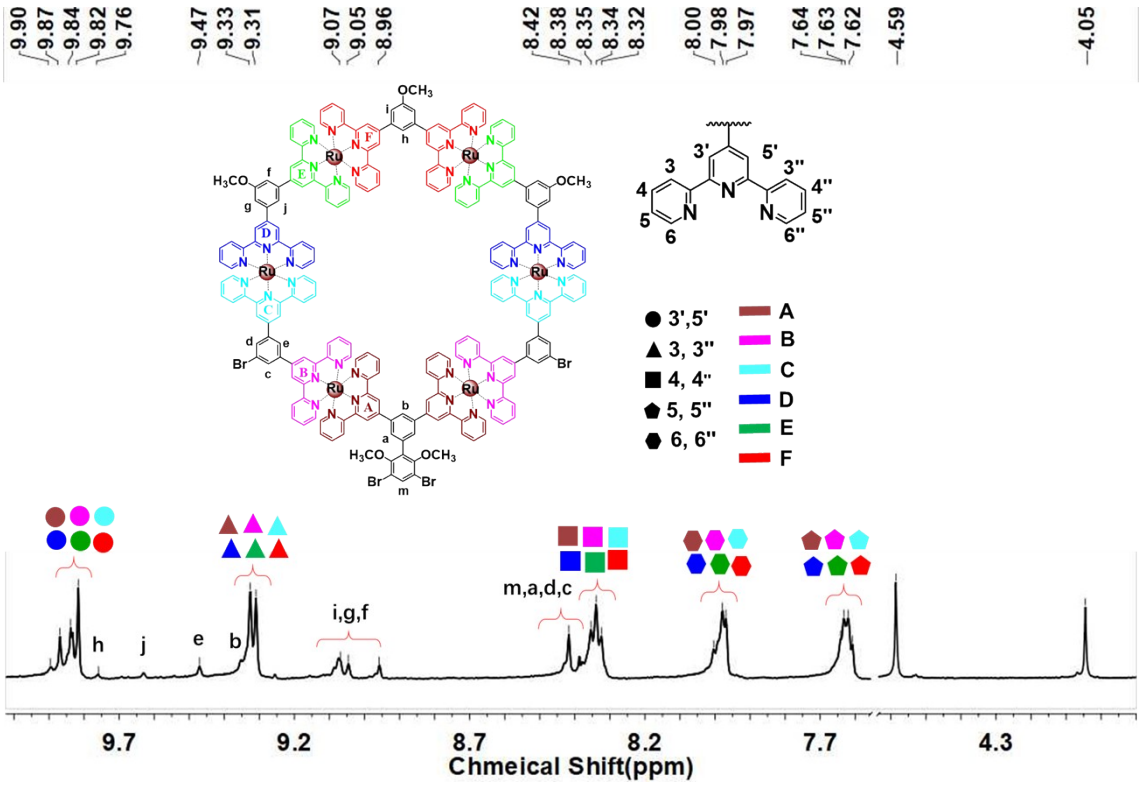


Figure S32: ^{1}H NMR spectrum (400 MHz) of **H2** in CD_3CN.

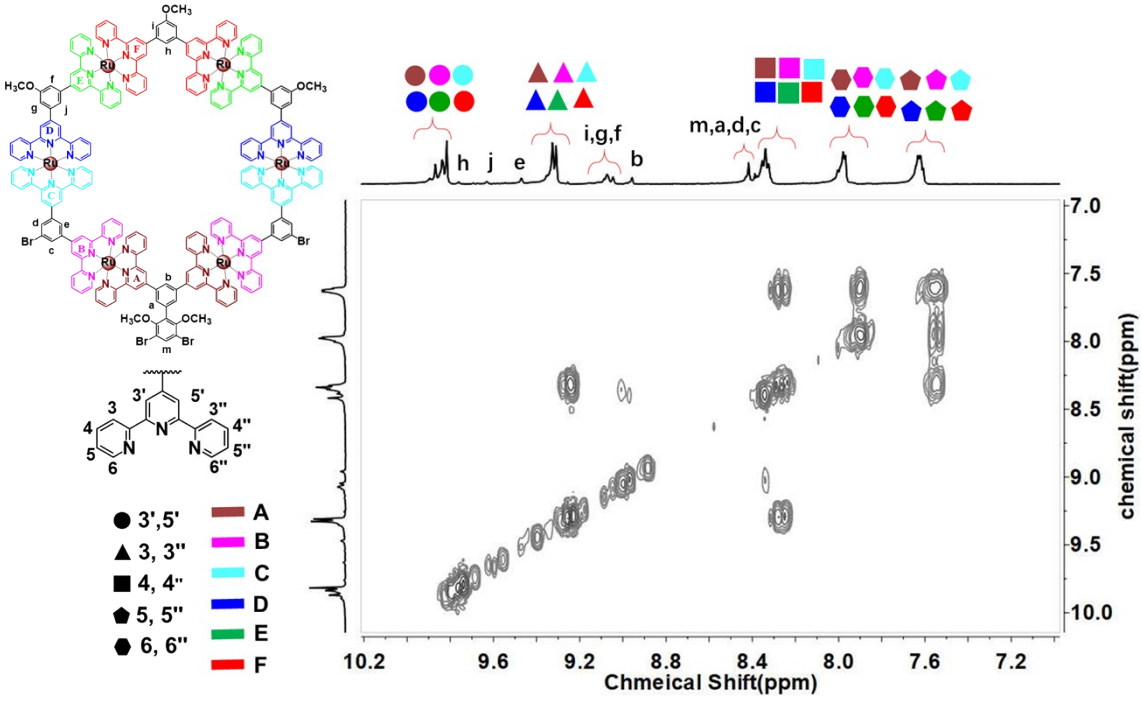


Figure S33: 2D COSY spectrum (400 MHz) of **H2** in CD_3CN.

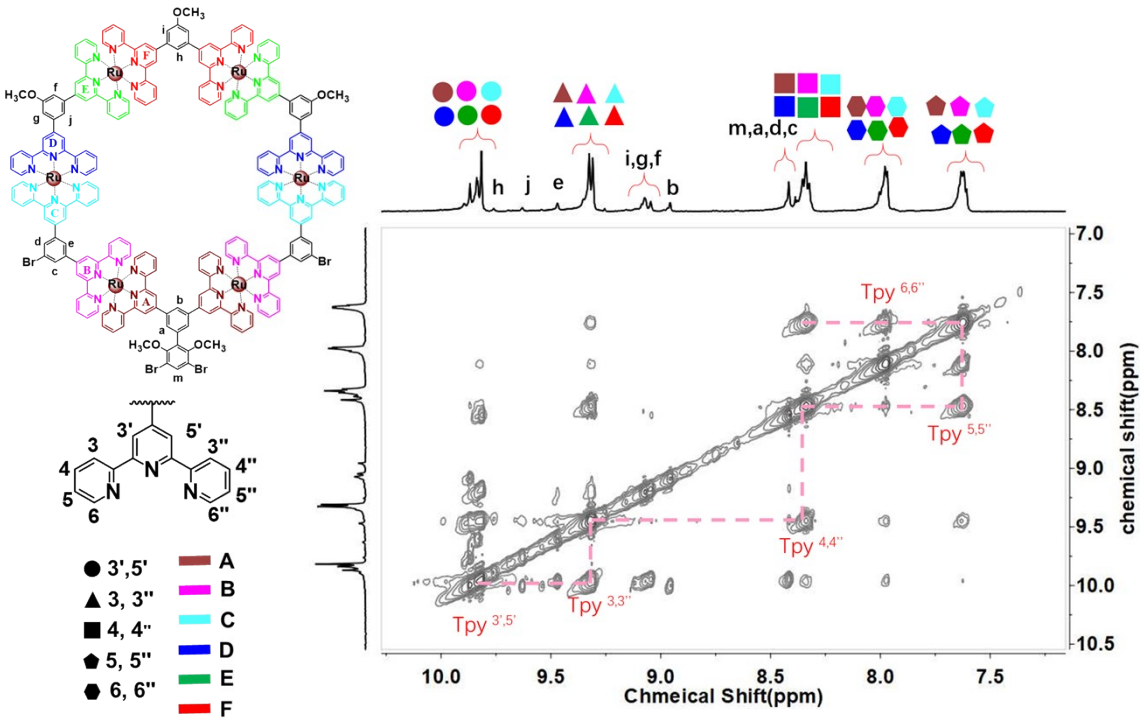


Figure S34: 2D NOESY spectrum (400 MHz) of **H3** in CD_3CN.

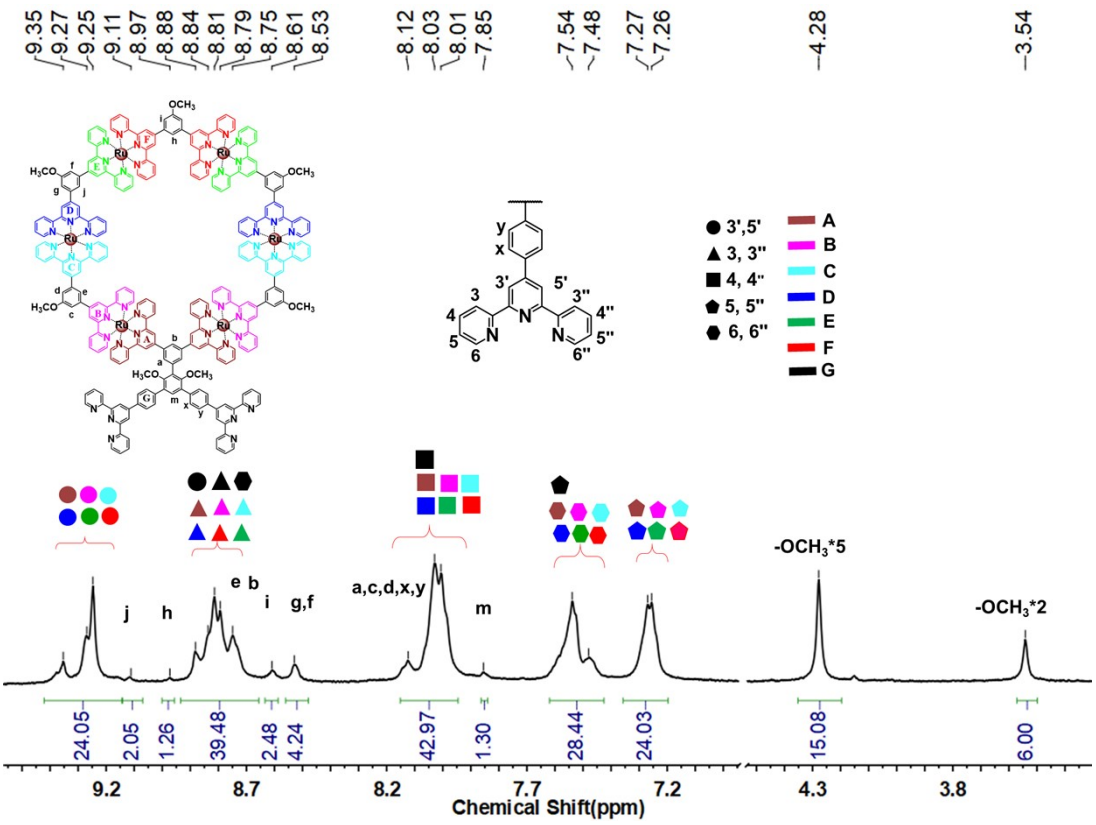


Figure S35: ^1H NMR spectrum (400 MHz) of **L1** in CD_3CN.

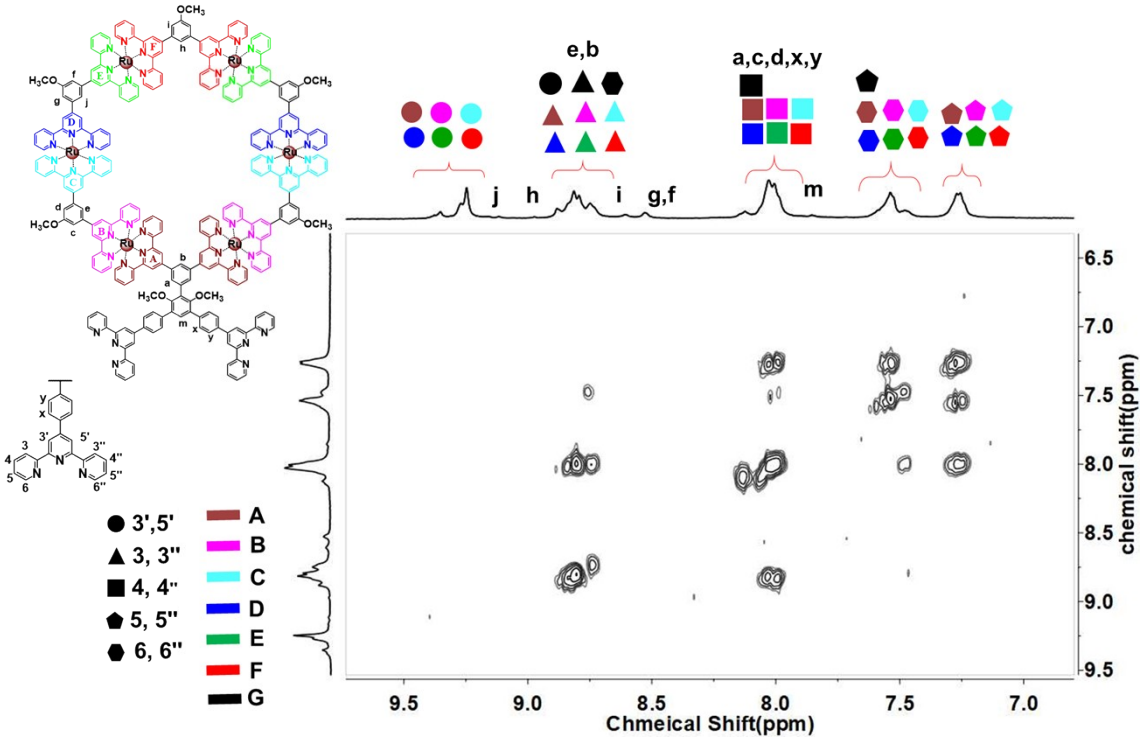


Figure S36: 2D COSY spectrum (400 MHz) of **L1** in CD_3CN.

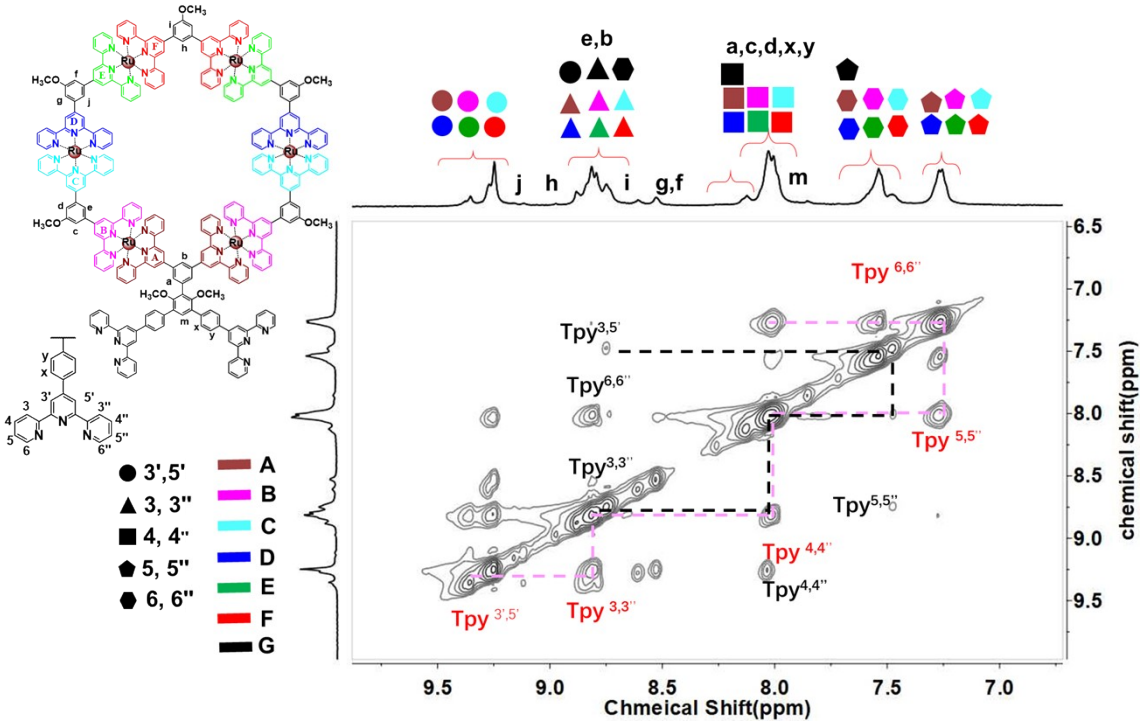


Figure S37: 2D NOESY spectrum (400 MHz) of **L1** in CD_3CN.

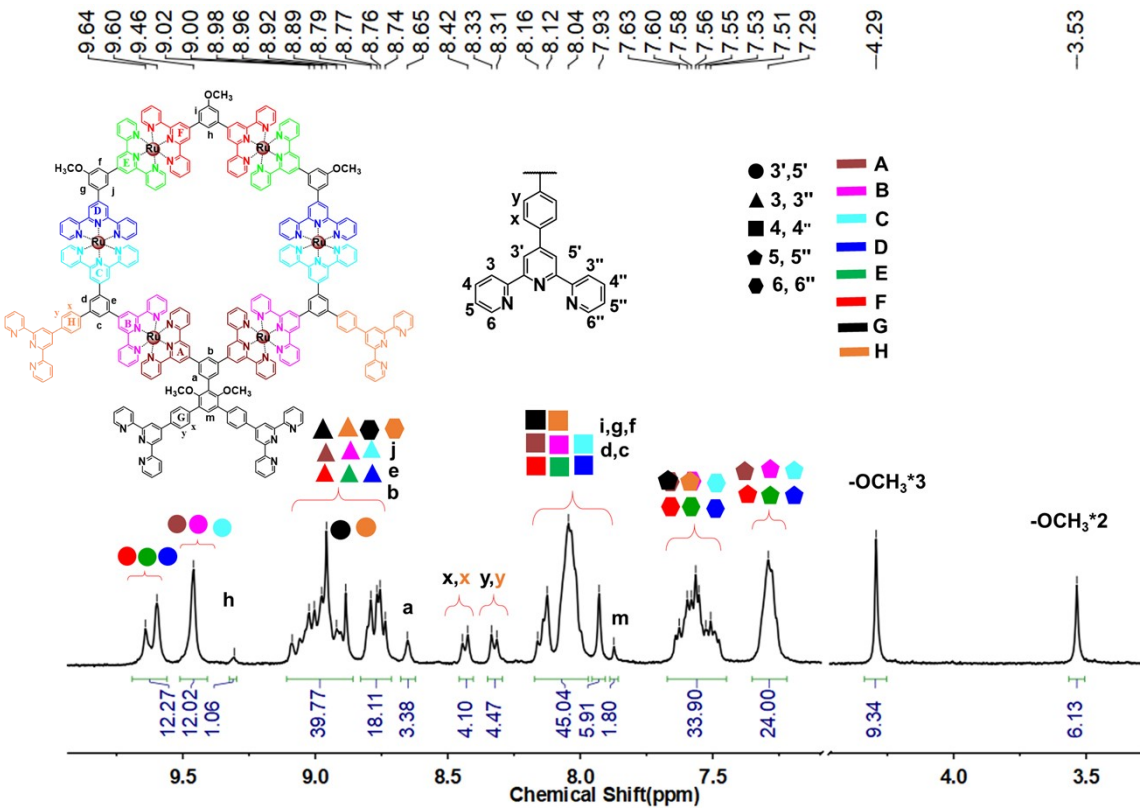


Figure S38: ^{1}H NMR spectrum (400 MHz) of **L2** in CD_3CN.

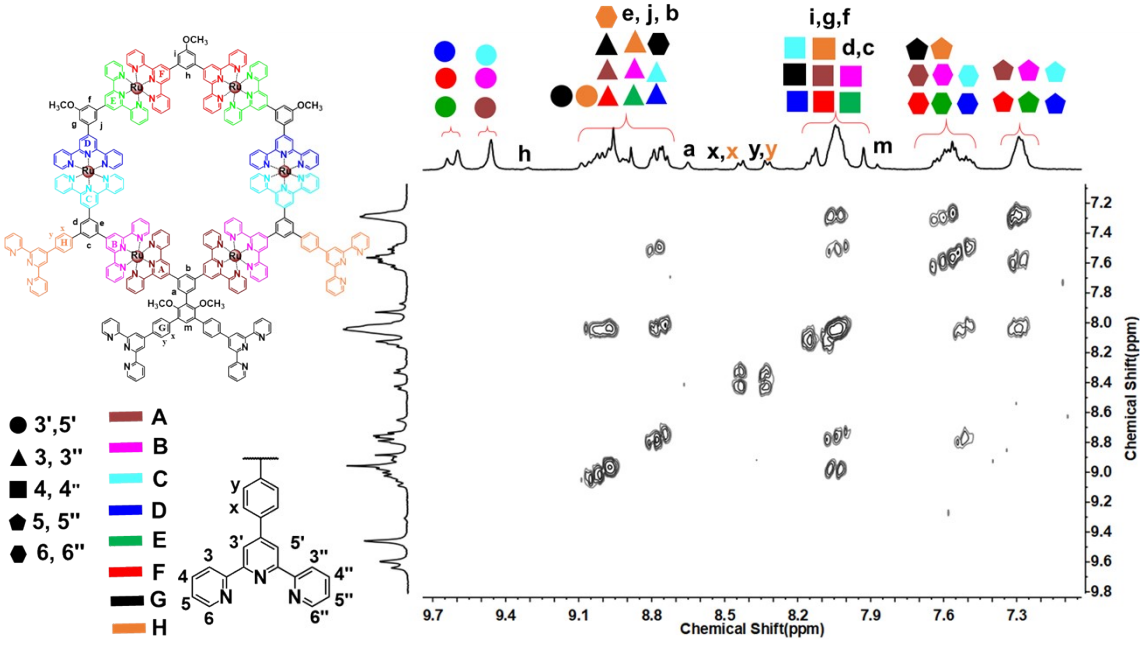


Figure S39: 2D COSY spectrum (400 MHz) of **L2** in CD_3CN.

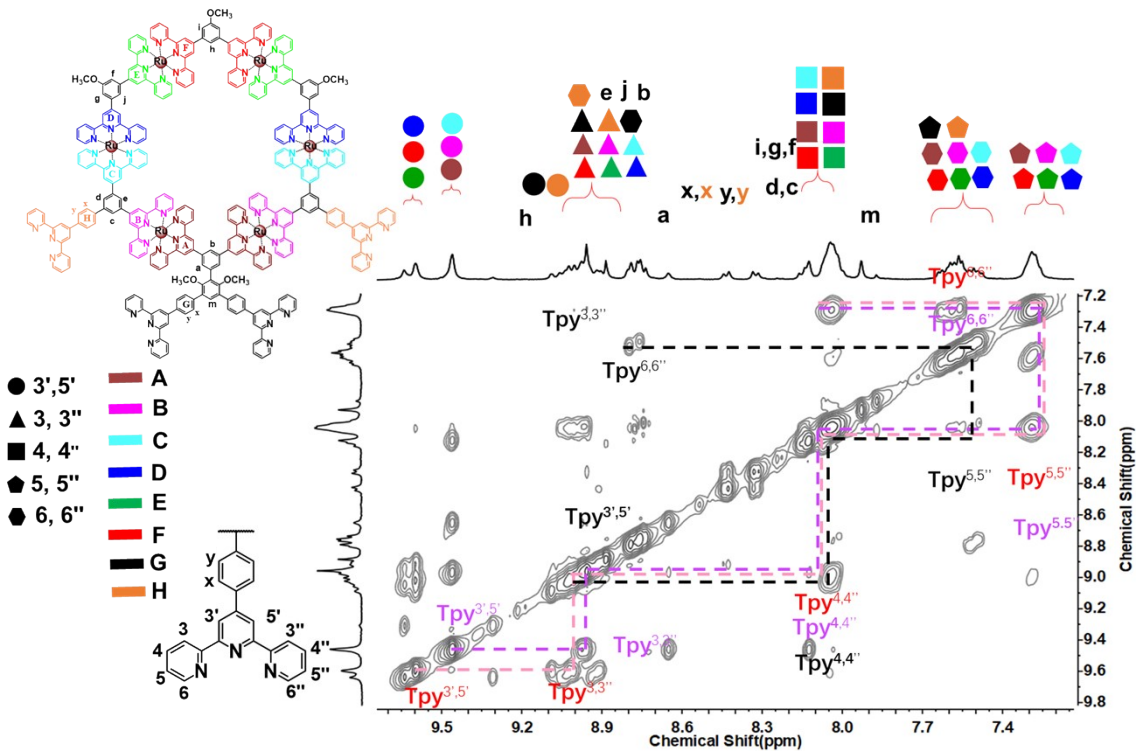


Figure S40: 2D NOESY spectrum (400 MHz) of **L2** in CD_3CN.

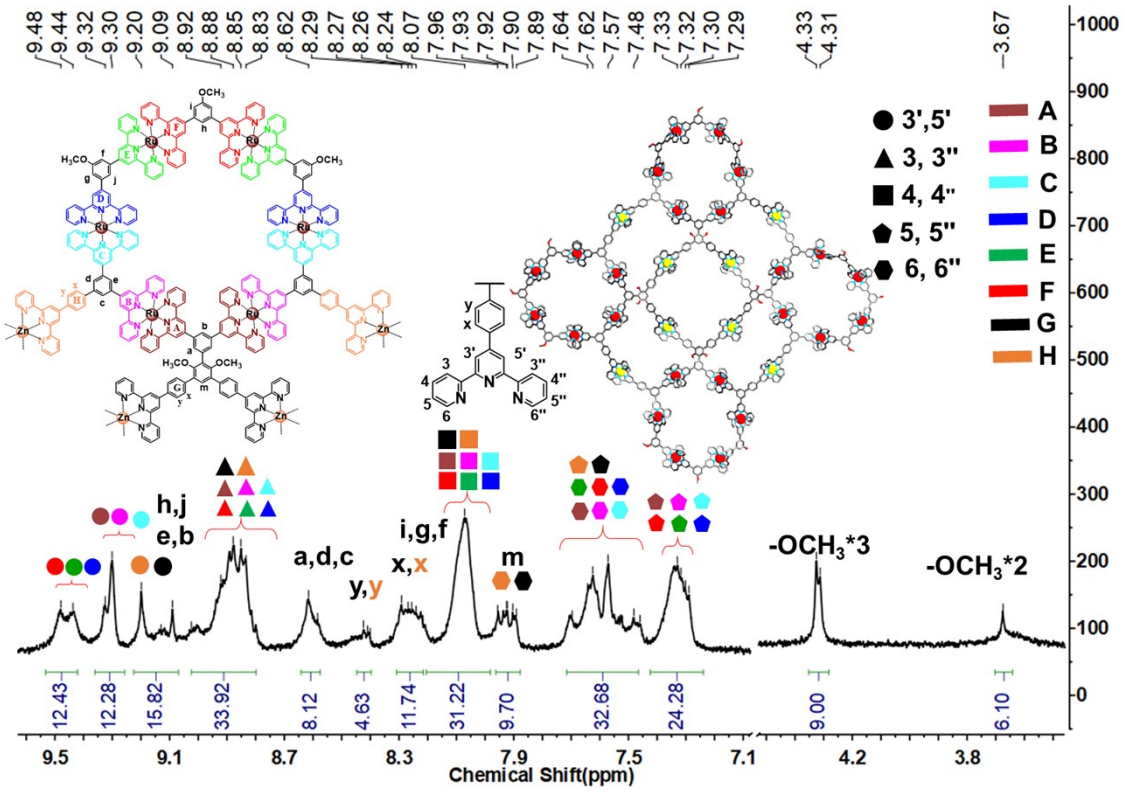


Figure S41: ^1H NMR spectrum (400 MHz) of $\mathbf{Zn_8L2_4}$ in CD_3CN.

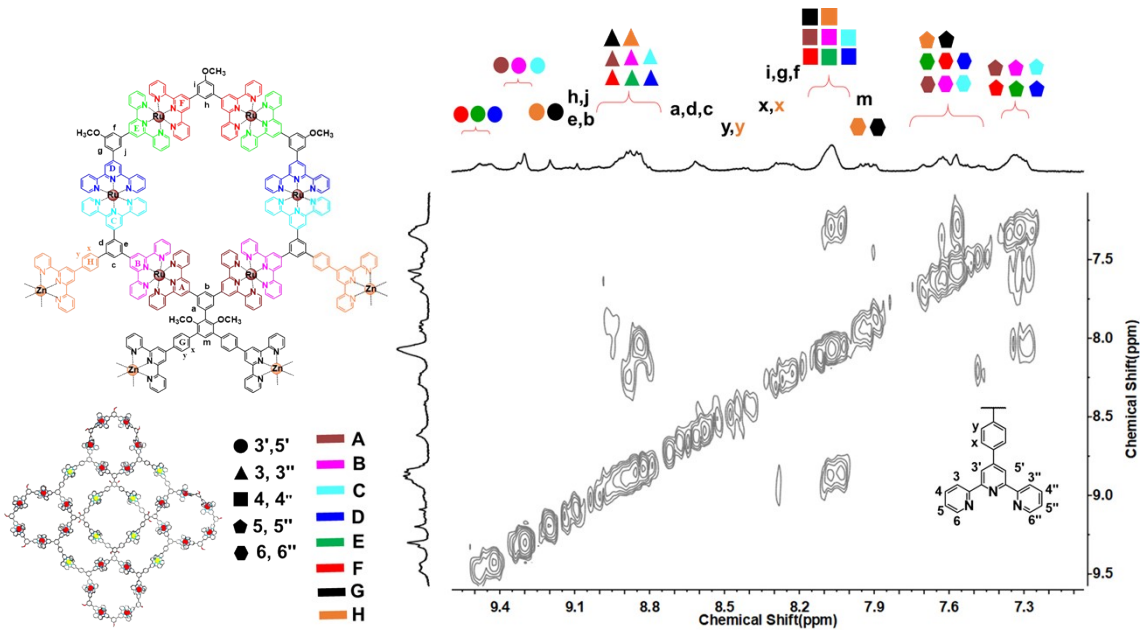


Figure S42: 2D COSY spectrum (400 MHz) of $\mathbf{Zn_8L2_4}$ in CD_3CN.

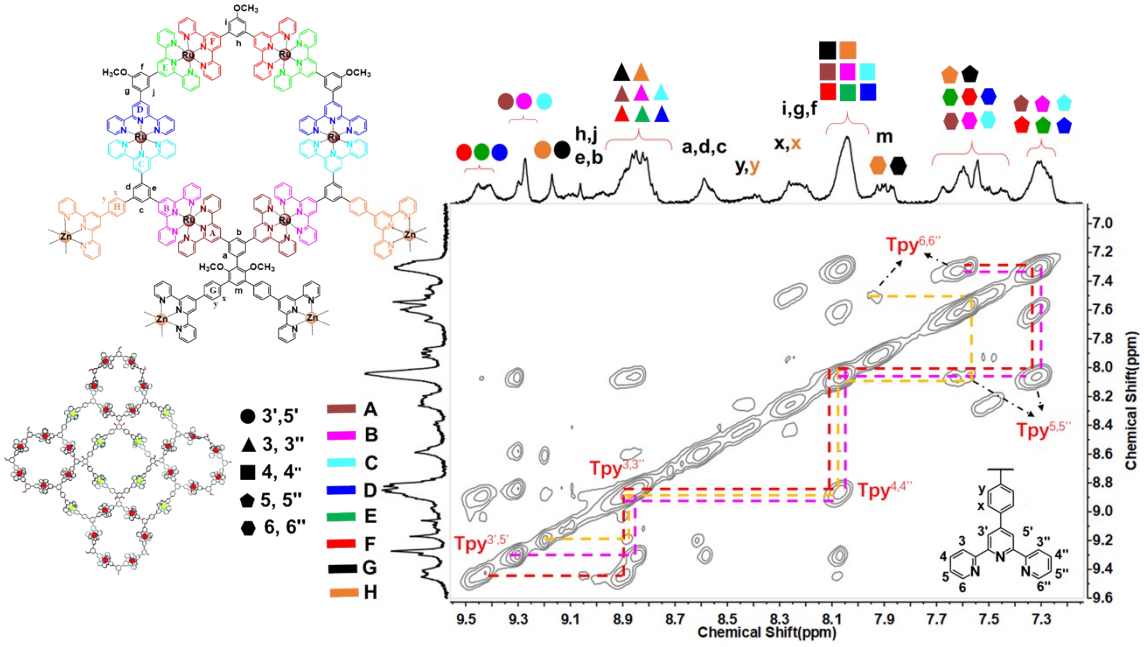


Figure S43: 2D NOESY spectrum (400 MHz) of $\mathbf{Zn_8L2_4}$ in CD_3CN.

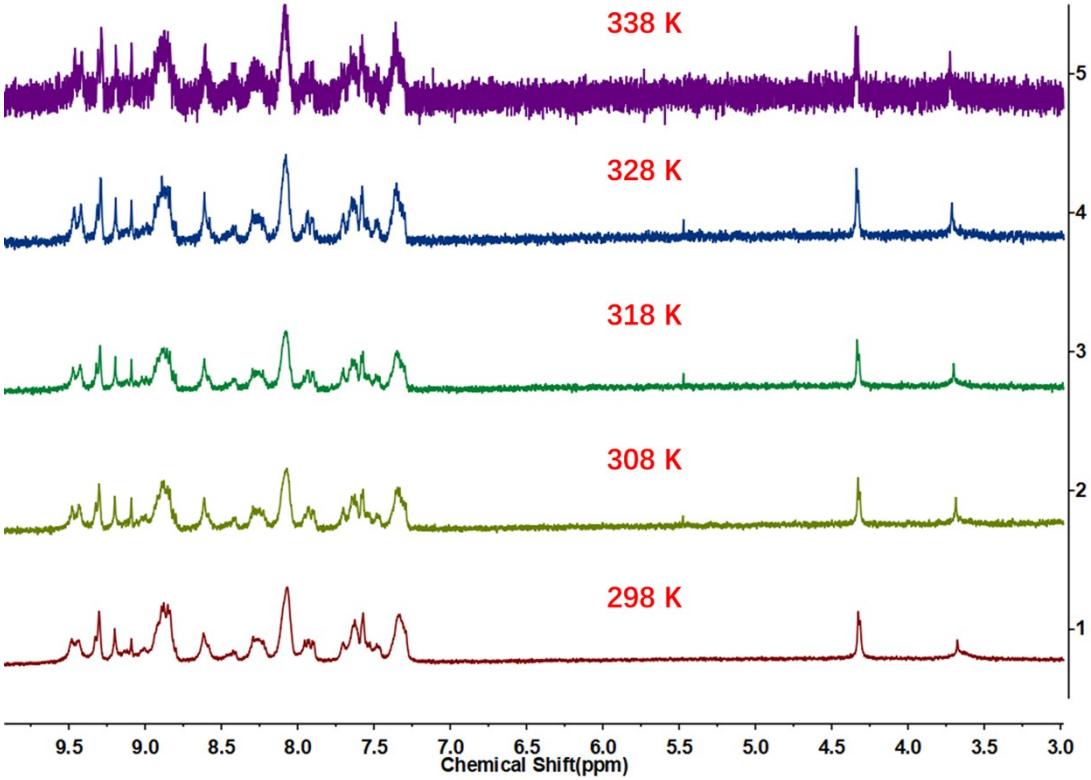


Figure S44: Variable temperature ^{1}H NMR spectra (500 MHz) of $\mathbf{Zn_8L2_4}$ in CD_3CN (from 298 K to 338 K).

6. ESI-MS spectra data of ligands and complexes

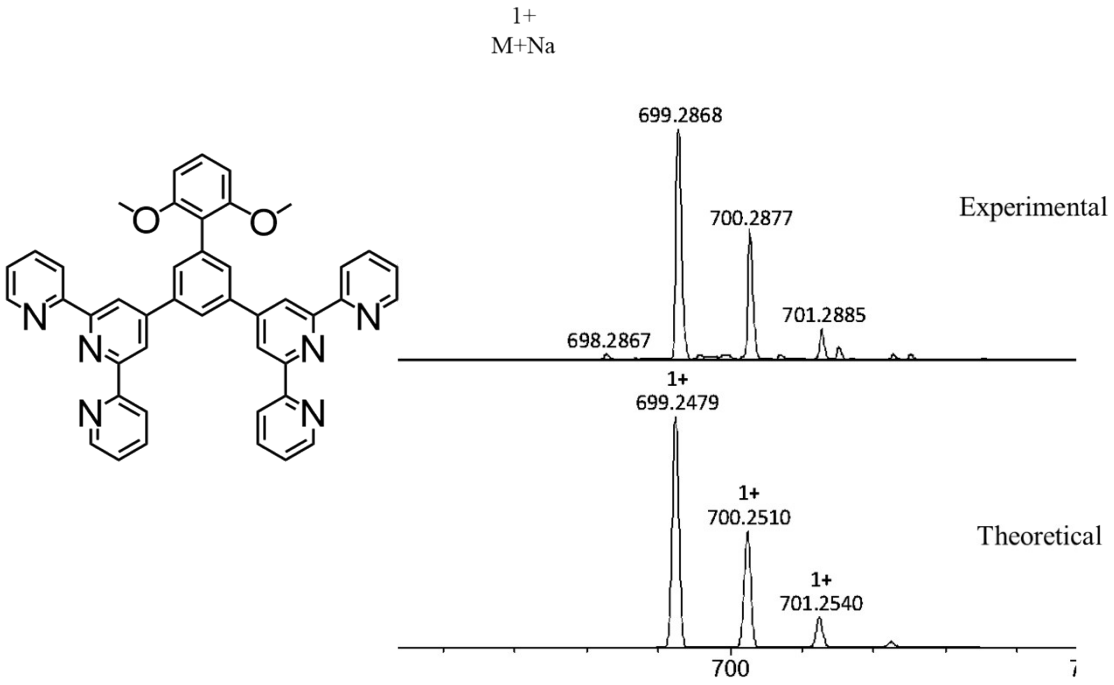


Figure S45: ESI-MS spectrum of **S8**.

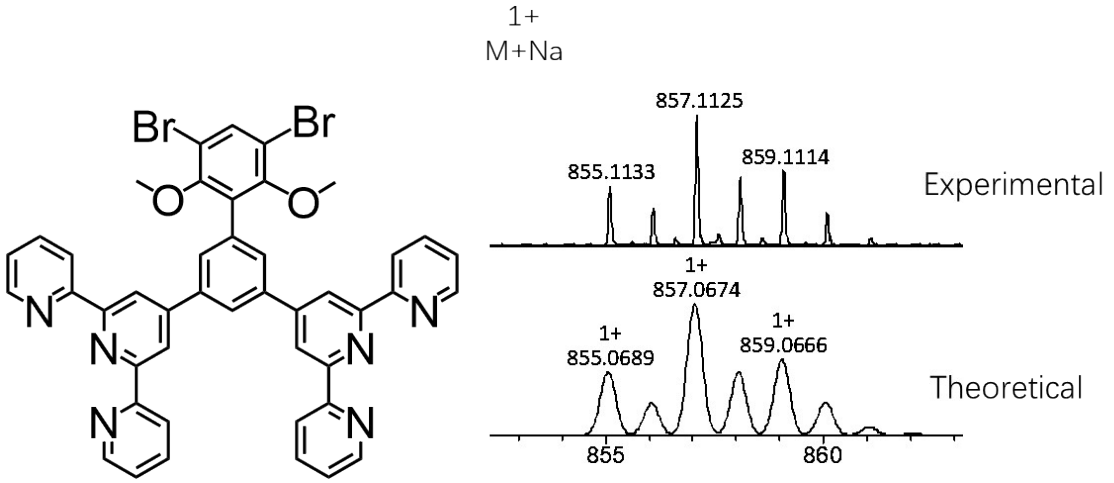


Figure S46: ESI-MS spectrum of **S9**.

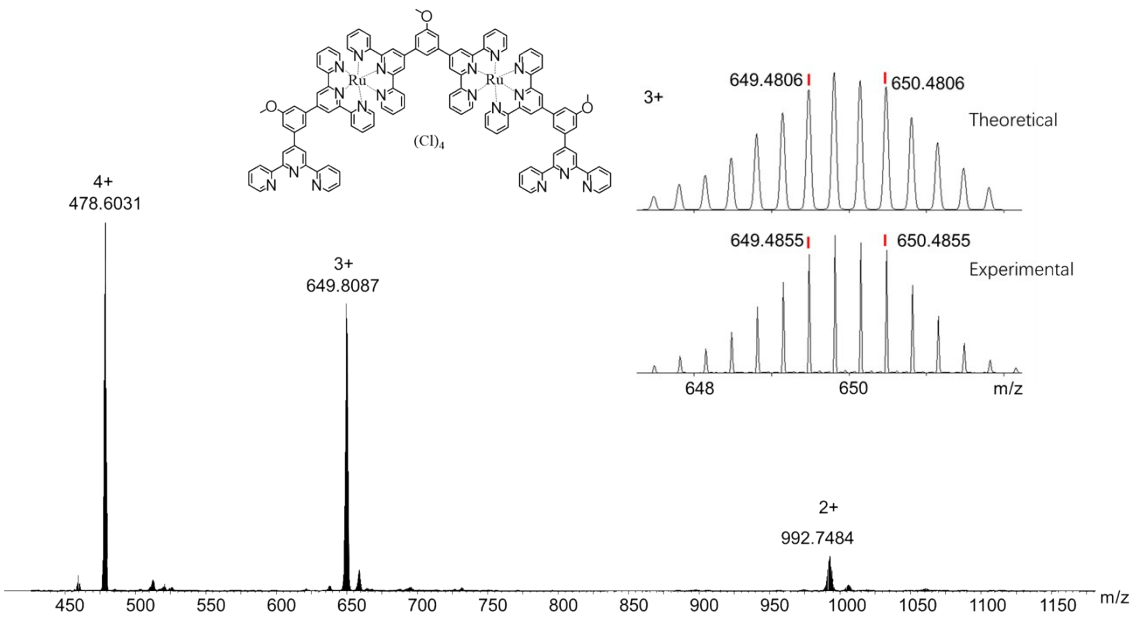


Figure S47: ESI-MS spectrum of **S4**.

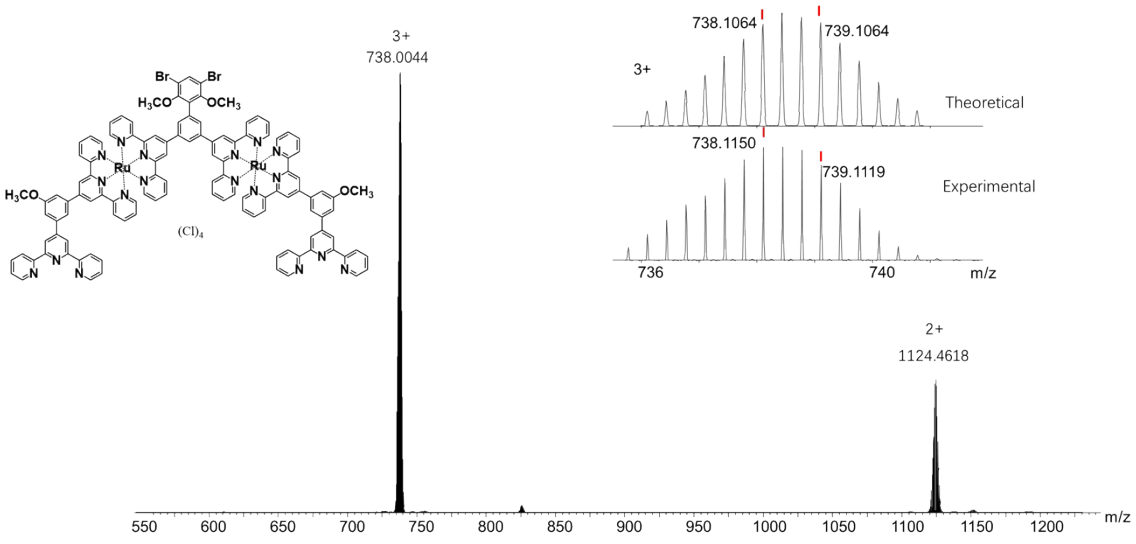


Figure S48: ESI-MS spectrum of **M2**.

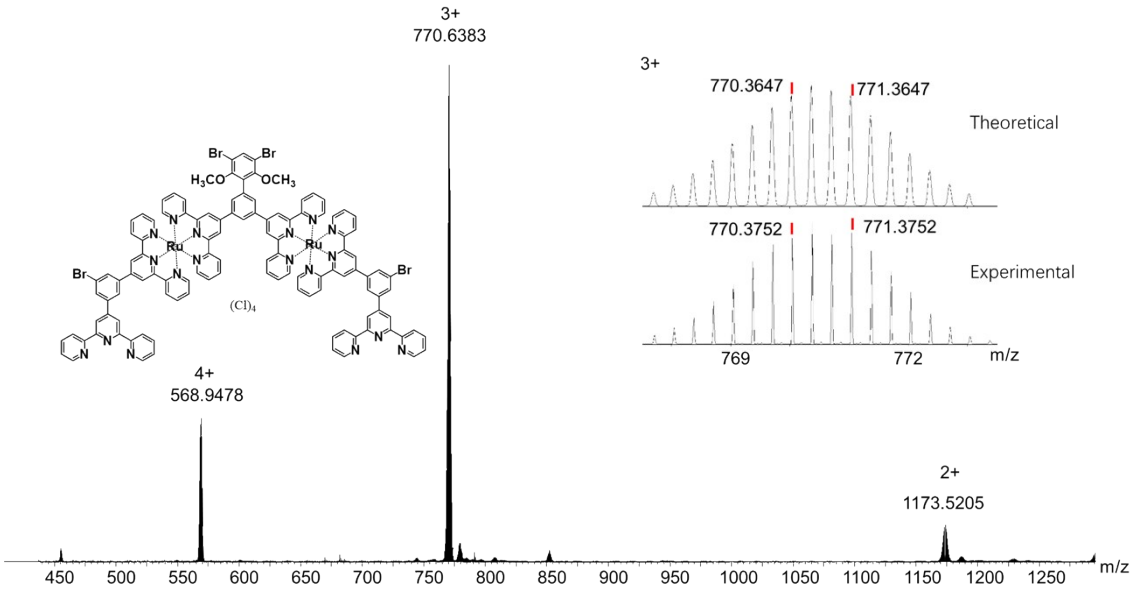


Figure S49: ESI-MS spectrum of **M3**.

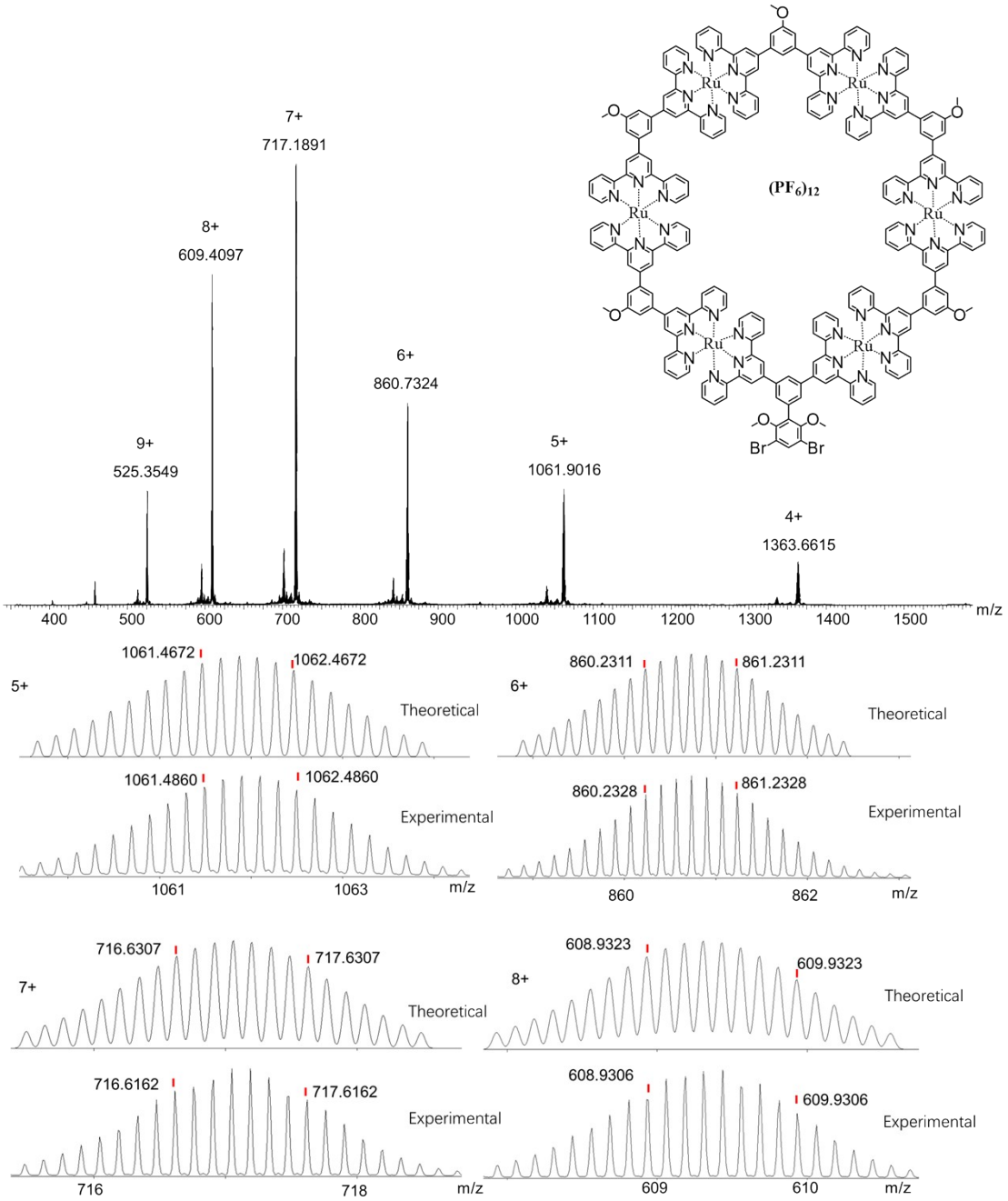


Figure S50: Isotope patterns and ESI-MS spectrum of **H1**.

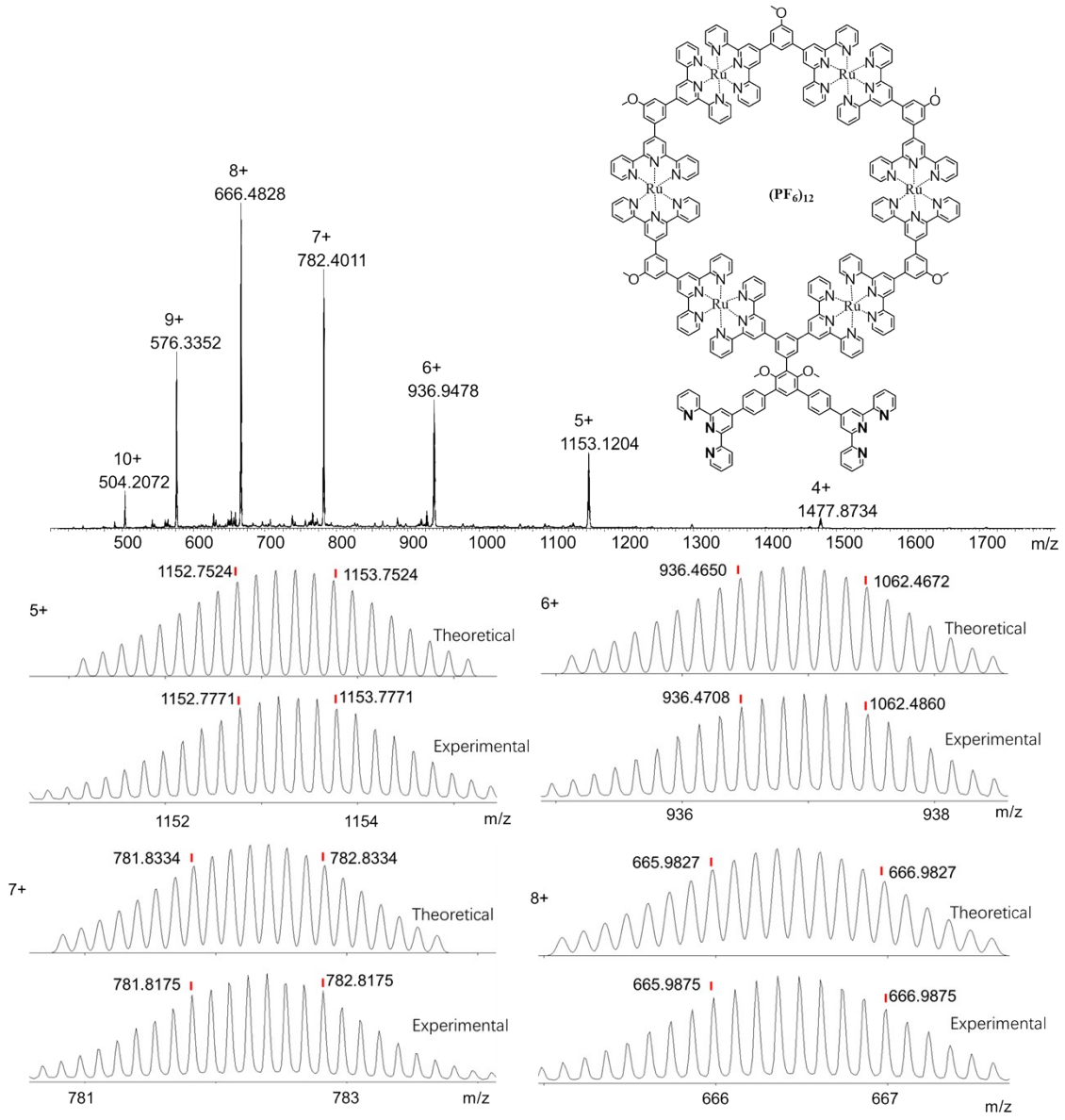


Figure S51: Isotope patterns and ESI-MS spectrum of **L1**.

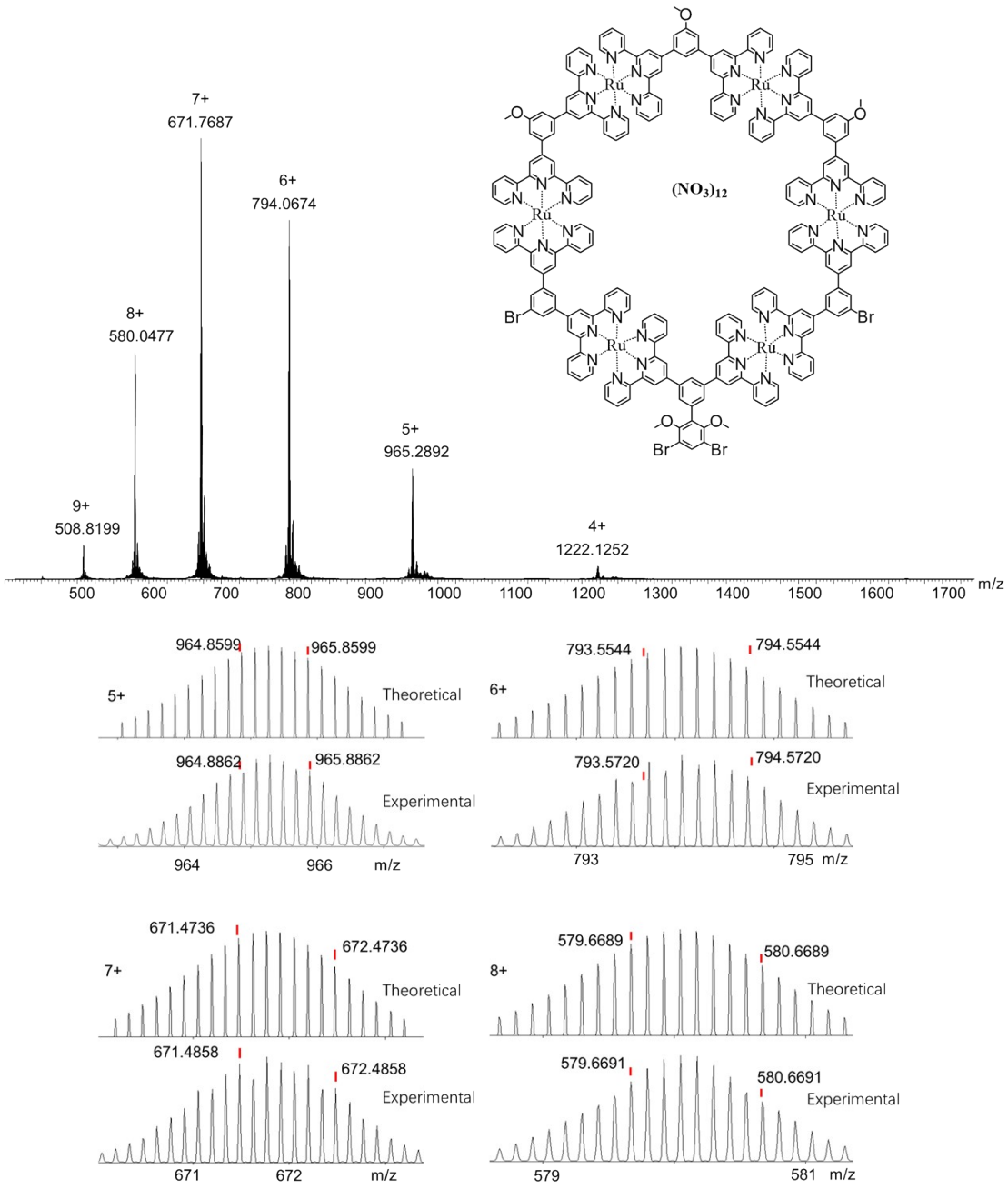


Figure S52: Isotope patterns and ESI-MS spectrum of **H2**.

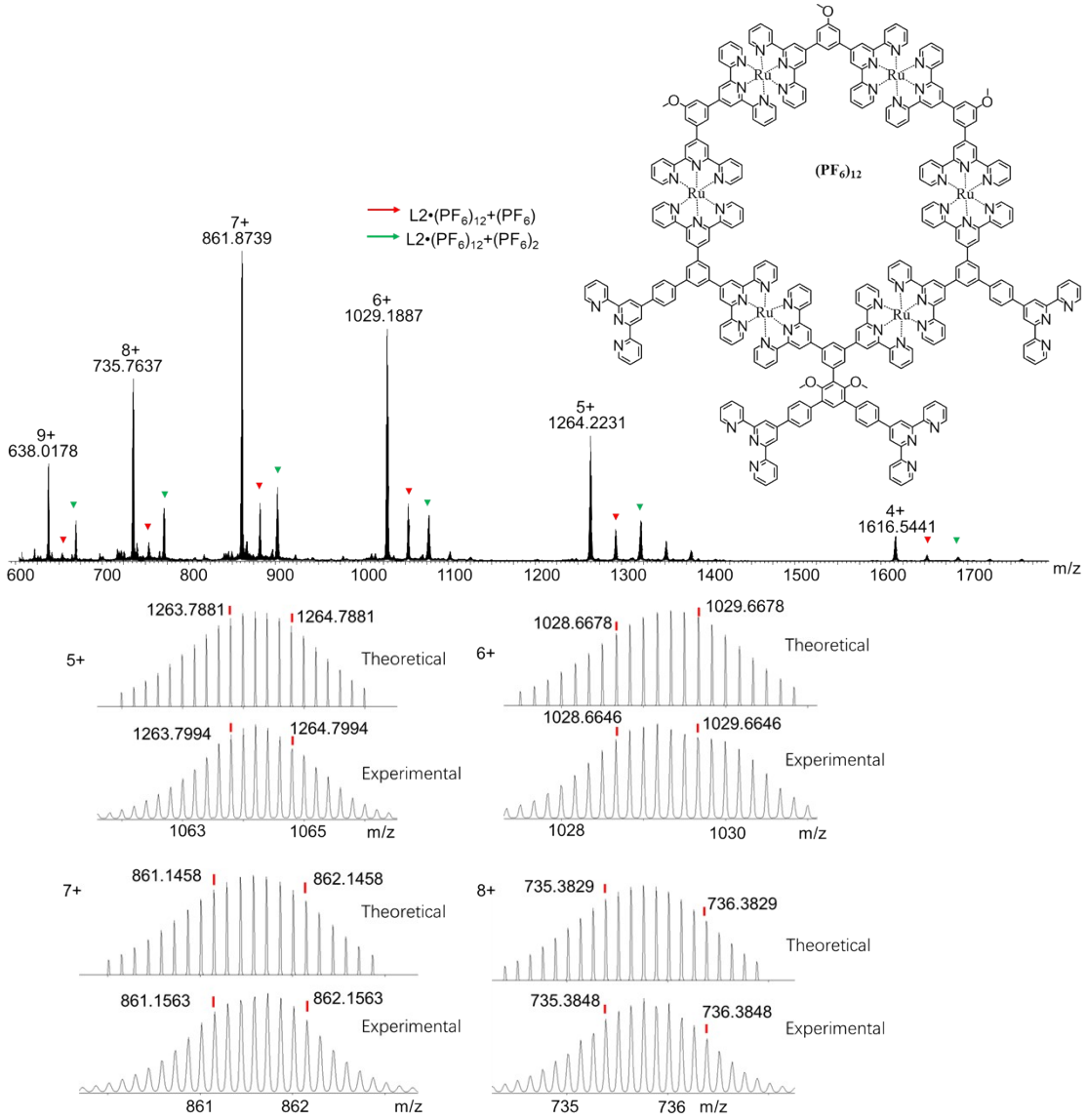


Figure S53: Isotope patterns and ESI-MS spectrum of **L2**.

7. Reference

S1. G. R. Newkome, T. J. Cho, C. N. Moorefield, G. R. Baker, R. Cush, P. S. Russo, *Angew. Chem. Int. Ed*. **1999**, *38*, 3717.

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