Supporting Information

Customized Self-assembled Molecules: Rim Adjustable Coronal Polygons with Multiple-Folds Symmetry

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1. General Procedures

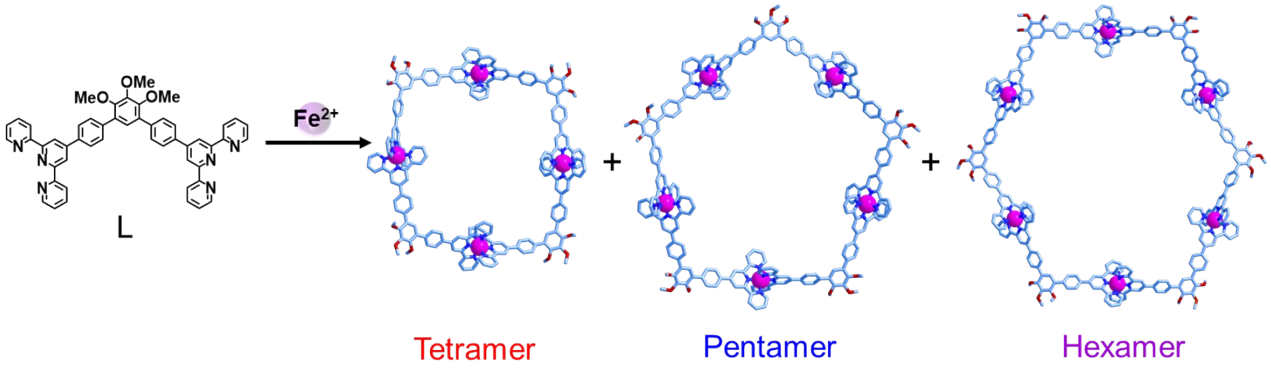
All starting materials were purchased from Aldrich and Alfa Aesar, and used without further purification. Organic ligand **L** and 4'-Boronatopenyl[2,2':6',2"]terpyridine were synthesized according to the reported methods[S1-2]. Column chromatography was conducted using basic Al_2O_3 (Sinopharm Chemical Reagents Co. Ltd, 200-300 mesh) or SiO_2 (Qingdao Haiyang Chemical Co., Ltd, 200-300 mesh) and the separated products were confirmed by NMR spectra using a Bruker Avance 400-MHz or 500-MHz NMR spectrometers in $CDCl_3$, MeOD, 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 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.

ESI and TWIM MS. ESI mass spectrometry and traveling wave ion mobility (TWIM) experiments were conducted on a Waters Synapt HDMS G2 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 4.1 and DriftScope 2.4 (Waters).

Molecular Modeling. Calculations were proceeded with Geometry Optimization and followed by Anneal in Forcite module of Materials Studio version 7.0 program (Accelrys Software, Inc.)., the counterions were omitted.

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. Schematic illustration of a mixture formed from 120° bis-terpyridine ligand L



Scheme 1: Schematic illustration of a mixture formed from 120° bis-terpyridine ligand **L**[S1]

Organic ligand L (3.2 mg, 4.1 μmol), and $FeCl_2 \cdot 4H_2O$ (0.8 mg, 4.1 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 bistrifluoromethanesulfonimide lithium salt ($LiNTf_2$) in MeOH was added to get a violet precipitate, which was filtered and washed with H_2O and MeOH to generate a purplish solid: 5.4 mg (94.7%).

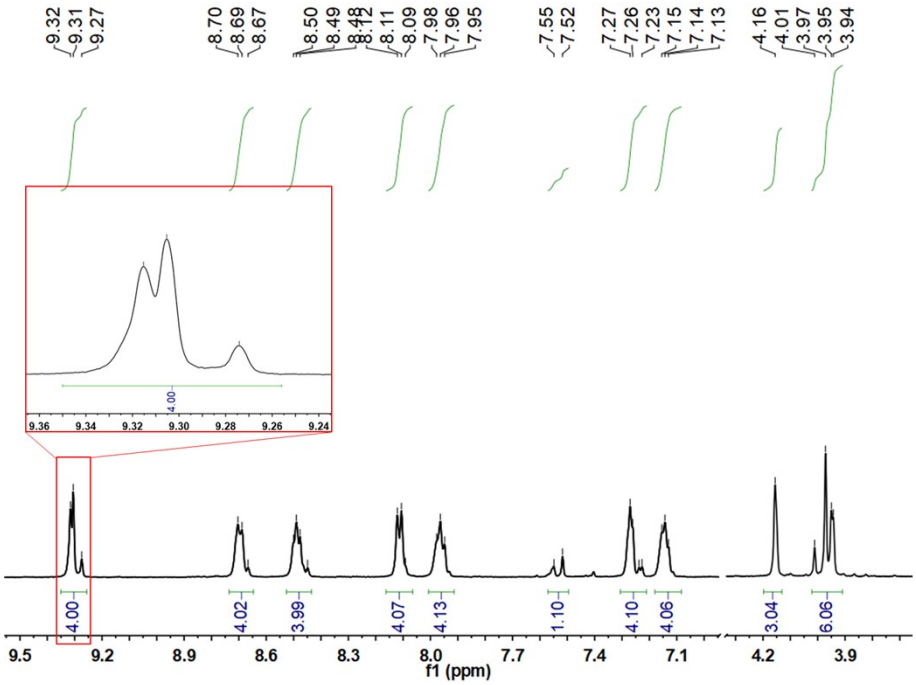


Figure S1: ^1H NMR spectrum (500 MHz) of resultant mixture from ligand **L** in CD_3CN.

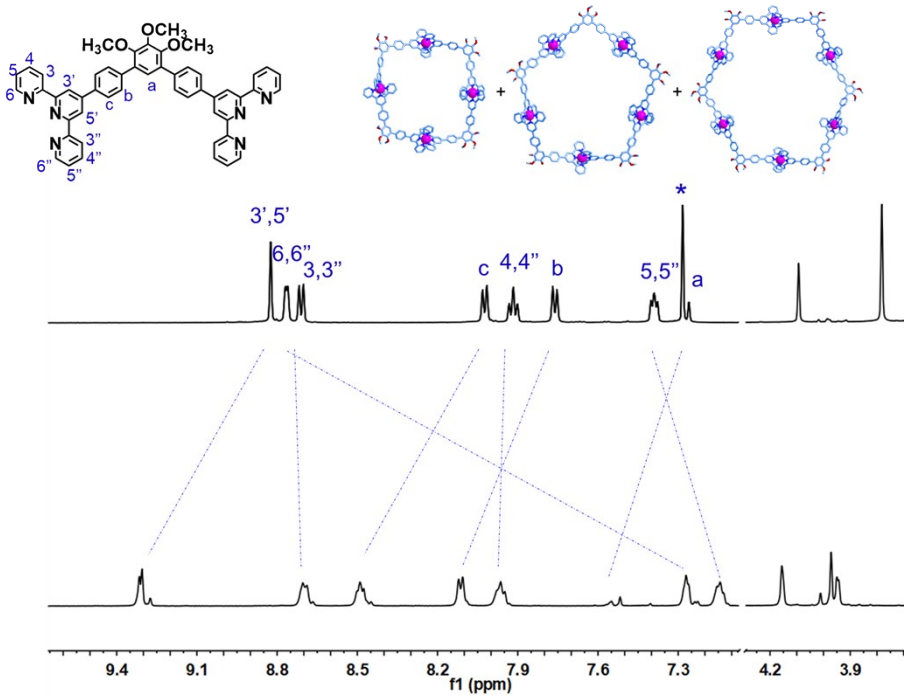


Figure S2: Comparison of the ^{1}H NMR spectra (500 MHz) of ligand **L** in $CDCl_3$ and the resultant mixture in CD_3CN.

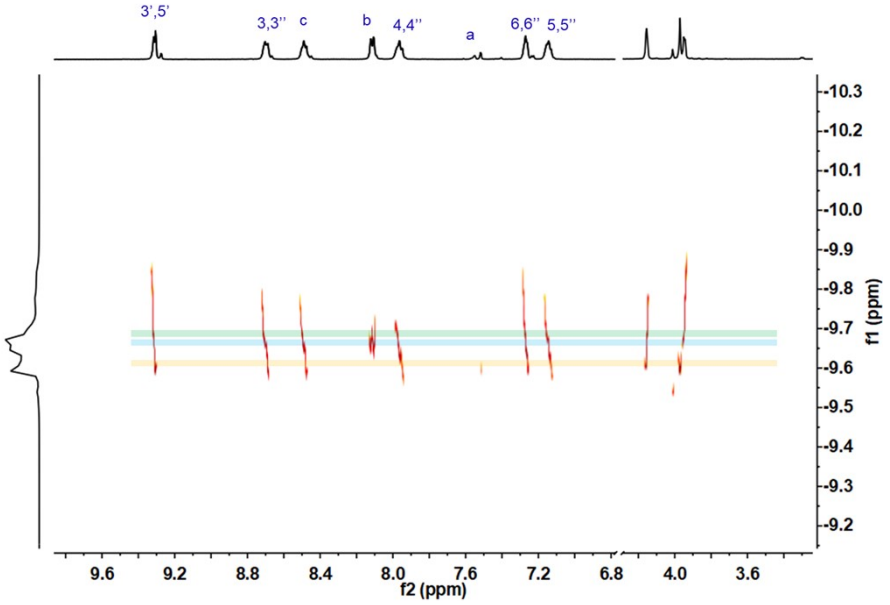


Figure S3: DOSY spectrum (500 MHz) of the resultant mixture in CD_3CN.

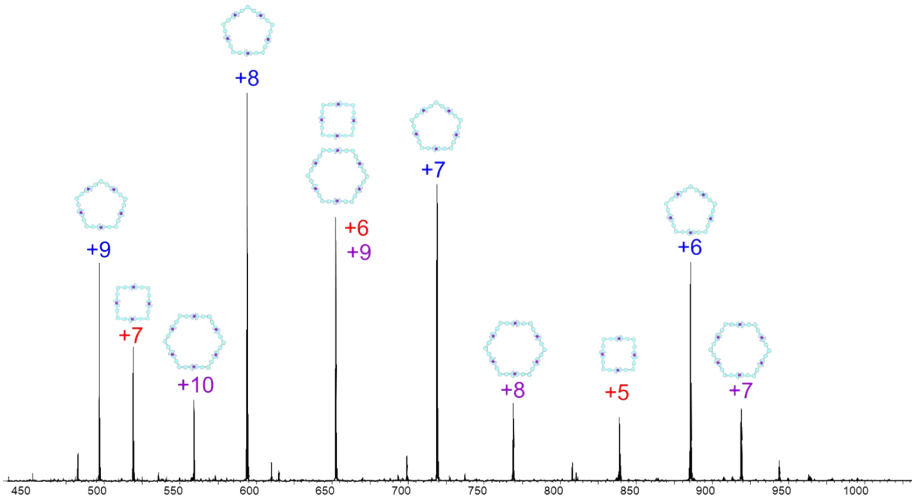
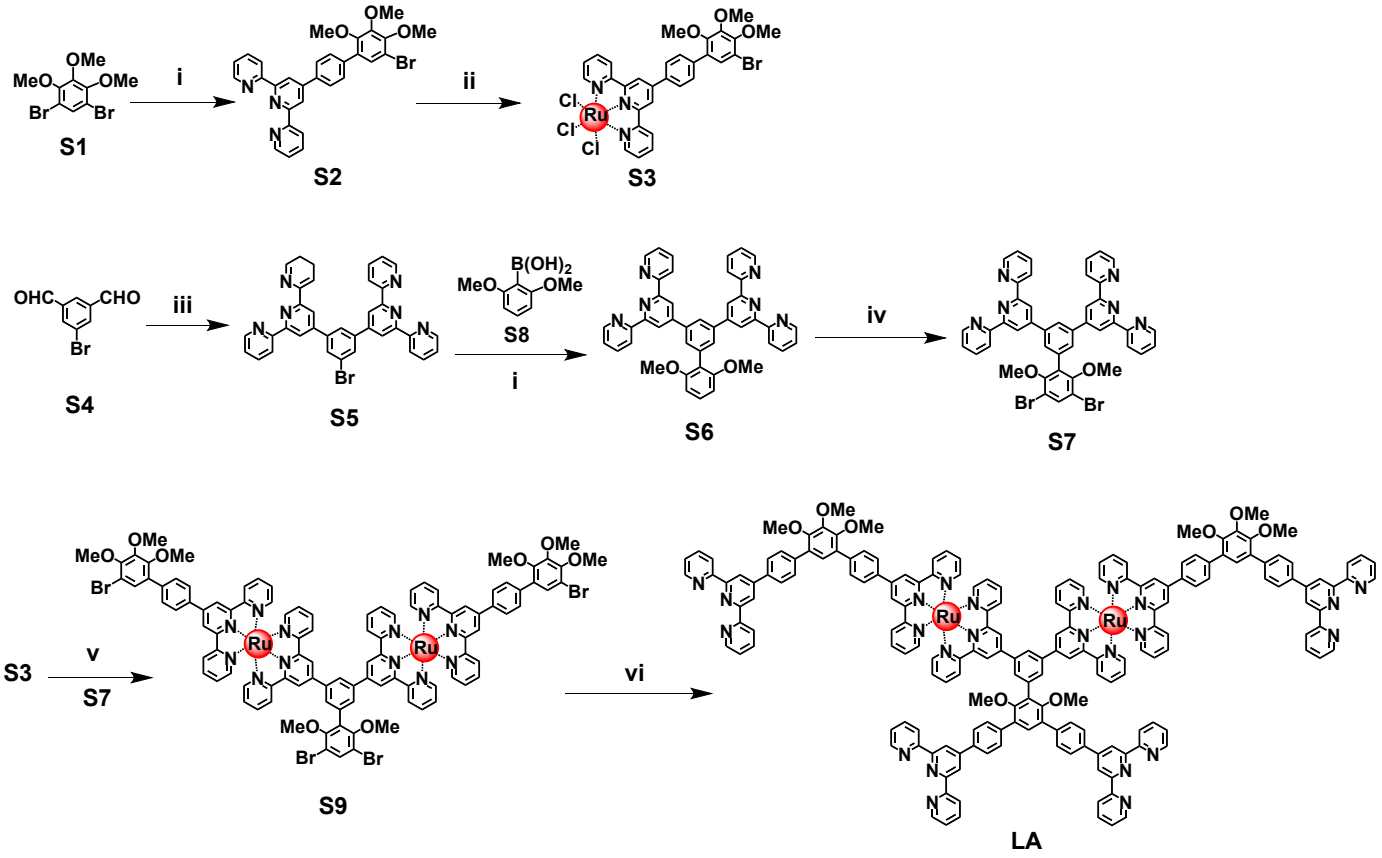
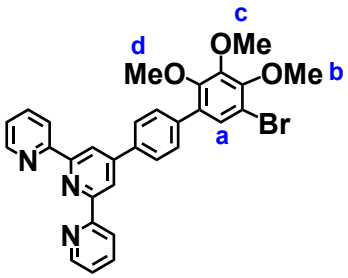


Figure S4: ESI−MS of resultant mixture from ligand **L**.

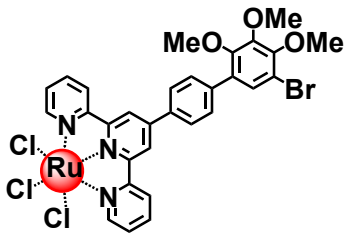
3. Synthesis of the MOL ligand LA and tetragonum wreath Fe_8LA_4



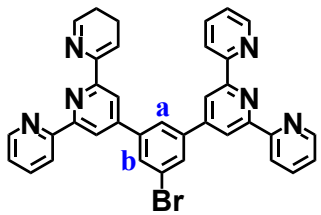
Scheme 2: Synthesis of MOL ligand **A**. Reagent and conditions: (i) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, THF, NaOH, reflux ; (ii) $RuCl_3$•$3H_2O$, EtOH, reflux; (iii) 2-acetylpyridine, KOH, EtOH, NH_3•H_2O, reflux; (iv) Br_2, $CHCl_3$, reflux; (v) N-ethylmorpholine, $CH_3OH/CHCl_3$ (V:V, 1:3), reflux; (vi) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, CH_3CN/CH_3OH(V:V, 2:1), K_2CO_3, reflux.



Compound S2: 1,2,3-trimethoxyl-4,6-dibromobenzene **S1** (3.3 g, 10 mmol) and 4'-Boronatopenyl[2,2':6',2"]terpyridine (3.5 g, 10 mmol) was added to a 500 mL flask, then THF (250 mL) and NaOH (1.2 g, 30 mmol, in 30 mL 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: 3.32 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79(s, 2H, tpy-$H^{3',5'}$), 8.75-8.74 (d, J = 4 Hz, 2H, tpy-$H^{6,6''}$), 8.71-8.69 (d, J = 8 Hz, 4H, tpy-$H^{3,3''}$), 7.98-7.96(d, J = 8 Hz, 2H, tpy-H^{g}), 7.92-7.88 (t, J = 16 Hz, 2H, tpy- $H^{4,4''}$), 7.65-7.63 (d, J = 8 Hz, 2H, tpy-H^{h}), 7.39-7.36 (m, 3H, tpy-$H^{5,5''}$, Ph-H^{a}), 4.00 (s, 3H, H^{c}), 3.97 (s, 3H, H^{b}), 3.68 (s, 3H, H^{d}).

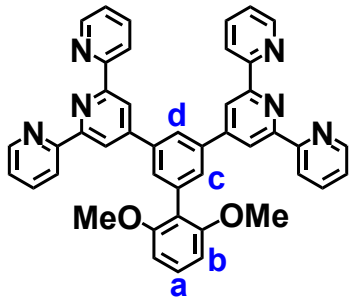


Compound S3: To a solution of **S2** (200.0 mg, 0.4 mmol) and $RuCl_3$•$3H_2O$ (105.0 mg, 0.4 mmol) in EtOH (50 mL). The mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **S3**: 250.0 mg, 90.0%.

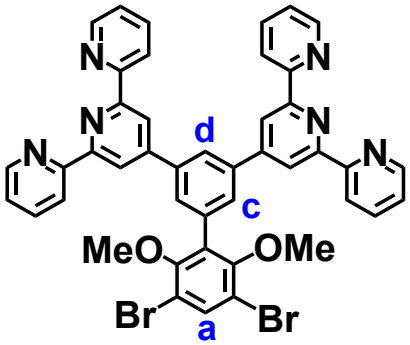


Compound S5: To a solution of NaOH powder (240.0 mg, 6 mmol) in EtOH (200 mL), 3, 5-diformylbromobenzene **S4** (3.54 g, 2 mmol) and 2-acetylpyridine (5.14 g, 4.8 mmol) was added. After stirring at room temperature for 24 h, aqueous NH_3•H_2O (28%, 150 mL) was added, the resulting mixture was refluxed 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.

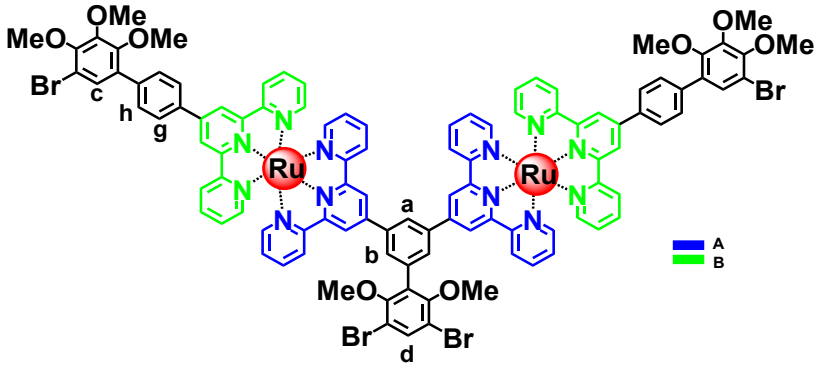


Compound S6: 1, 3-dimethoxybromobenzene **S8** (0.78 g, 3.6 mmol) and **S5** (2.00 g, 3.4 mmol) was added to a 500 mL flask, then THF (250 mL) and NaOH (410.0 mg, 10.3 mmol) in 10 mL of water was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (0.46 g, 0.4 mmol) as the catalyst was added. 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^{-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).

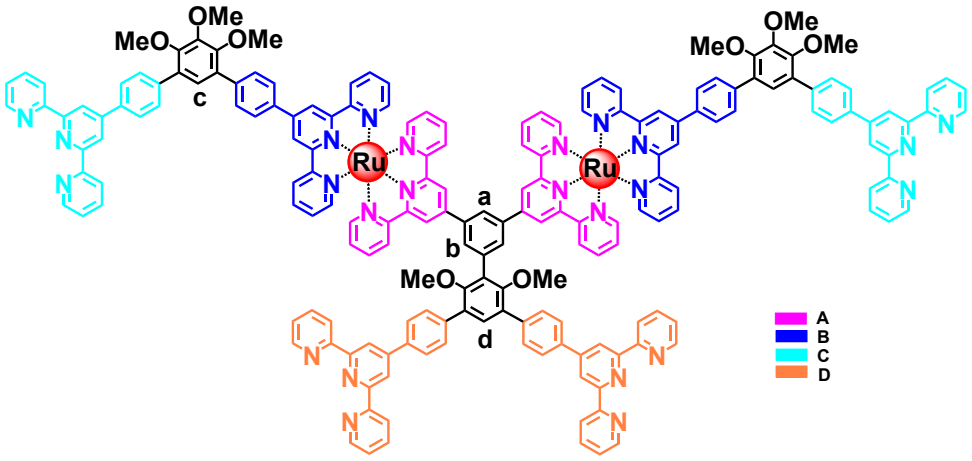


Compound S7: To a solution of **S6** (500.0 mg, 0.74 mmol) in $CHCl_3$ (50 mL), a solution of Br_2 (5 mL, 97.5 mmol) in $CHCl_3$ (5 mL) was added dropwise. After refluxing for 24 h, the mixture was washed by saturated $NaHSO_3$ until colorless. The organic layer was dried (anhydrous Na_2SO_4), and then concentrated in vacuo to give **S7**, 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^{d}), 8.12 (s, 2H, H^{c}), 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^{-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).

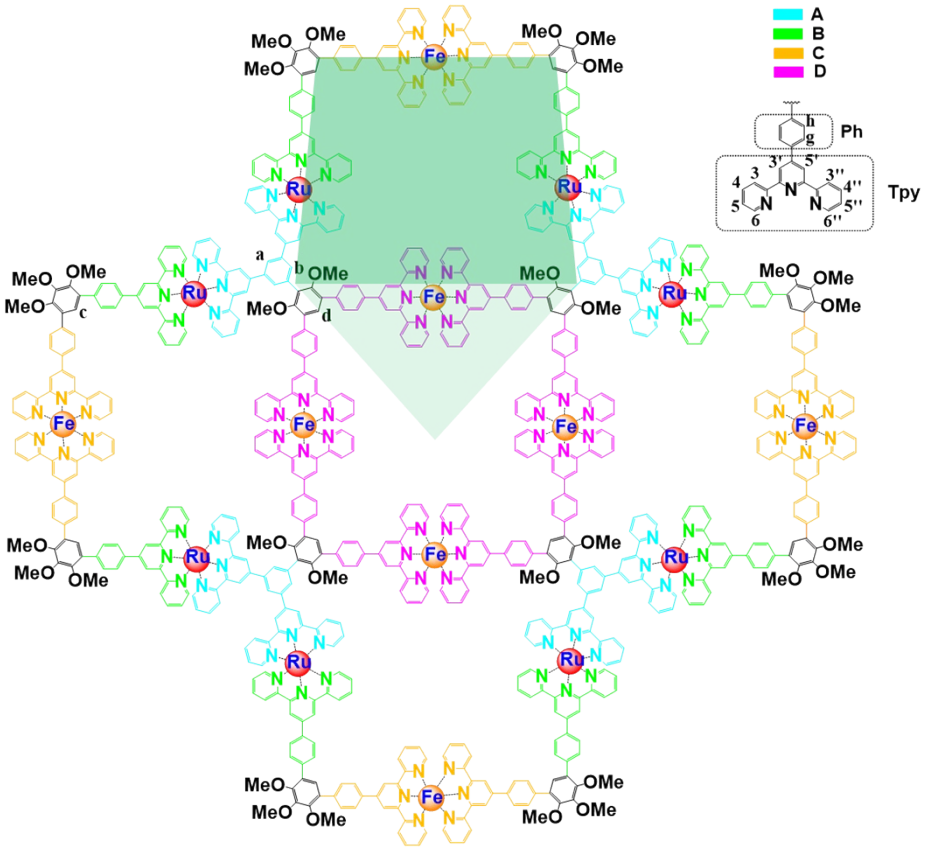


Compound S9: To a flask containing a mixture of **S3** (450.0 mg, 0.6 mmol)) and **S7** (259.0 mg, 0.3 mmol), MeOH (150 mL), $CHCl_3$ (150 mL), and 6 drops of N-ethylmorpholine were added. The mixture was stirred at 75 °C for 24 h. After cooling to ambient temperature, the solvent was evaporated in vacuo 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: 485.0 mg, 70.4%. ^{1}H NMR (400 MHz, CD_3CN) δ 9.36(s, 4H, A-tpy-$H^{3',5'}$), 9.16(s, 1H, H^a), 9.14(s, 4H, B-tpy-$H^{3',5'}$), 8.85-8.83(d, J =8 Hz, 4H, A-tpy-$H^{3,3''}$), 8.75-8.73(d, J =8 Hz, 4H, B-tpy-$H^{3,3''}$), 8.58(s, 2H, H^b), 8.34-8.31(d, J =12 Hz, 4H, H^g), 8.14(s, 1H, H^d), 8.02-7.99(m, 8H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$), 7.91-7.89(d, J =12 Hz, 4H, H^h), 7.53-7.52(m, 9H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6'}$, H^c '), 7.25(m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 4.02(s, 6H, H^{-OCH3}), 3.97(s, 6H, H^{-OCH3}), 3.79(s, 6H, H^{-OCH3}), 3.75(s, 6H, H^{-OCH3}). ESI-MS (2725.46 calcd. For $C_{104}H_{78}Br_4F_{24}N_{12}O_8P_4Ru_2$): m/z 763.60 [M – 3$PF_6^-$]$^{3+}$ (calcd m/z: 763.53), 1217.85[M – 2PF_6^-]$^{2+}$ (calcd m/z: 1217.77).



MOL ligand LA: **S9** (100.0 mg, 0.04 mmol) and 4'-Boronatopenyl[2,2':6',2"]terpyridine (365.0 mg, 1.0 mmol) was added to a 100 mL flask, then acetonitrile (40 mL), methanol (20 mL) and K_2CO_3 (95.0 mg, 0.7 mmol) in 0.7 mL

of water was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (60.0 mg, 50 μmol) as the catalyst was added. The mixture was stirred at 85 °C under nitrogen for 4 d, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al_2O_3), eluting with the mixture of CH_3OH and CH_2Cl_2 to pure the product, as red solid: 72.2 mg, 50.7%. ^{1}H NMR (400 MHz, CD_3CN) δ 9.44(s, 4H, A-tpy-$H^{3',5'}$), 9.19(s, 1H, H^a), 9.16(s, 4H, B-tpy-$H^{3',5'}$), 8.90-8.88(d, J =8 Hz, 4H, A-tpy-$H^{3,3''}$), 8.87(s, 4H, C-tpy-$H^{3',5'}$), 8.84(s, 4H, D-tpy-$H^{3',5'}$), 8.78-8.73(m, 22H, B-tpy-$H^{3,3''}$, C-tpy-$H^{3,3''}$, D-tpy-$H^{3,3''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$, H^b), 8.36-8.34(d, J =8 Hz, 4H, B-H^g), 8.18-8.16(d, J =8 Hz, 4H, C-H^g), 8.09-8.00 (m, 28H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$, D-tpy-$H^{4,4''}$, D-H^g, B-H^h, C-H^h), 7.87-7.85 (m, 5H, D-H^h, H^d), 7.56-7.50 (m, 16H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6''}$, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$), 7.40(s, 2H, H^c), 7.28-7.25(m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 4.08(s, 6H, H^{-OCH3}), 3.88(s, 6H, H^{-OCH3}), 3.85(s, 6H, H^{-OCH3}), 3.54(s, 6H, H^{-OCH3}). ^{13}C NMR (101 MHz, CD_3CN) δ 158.90, 158.79, 158.41, 157.46, 156.88, 156.39, 156.23, 156.03, 153.16, 151.82, 149.94, 138.73, 137.99, 136.43, 136.33, 132.16, 130.81, 130.71, 128.98, 128.61, 128.30, 127.94, 125.45, 125.24, 125.00, 122.02, 121.81, 118.94, 117.99, 2.12, 1.52, 1.31, 1.11, 0.90, 0.69, 0.49, 0.28. ESI-MS (3639.3 calcd. For $C_{188}H_{134}F_{24}N_{24}O_8P_4Ru_2$): m/z 764.87 [M – $4PF_6^-$]$^{4+}$ (calcd m/z: 764.86), 1068.12 [M – $3PF_6^-$]$^{3+}$ (calcd m/z: 1068.14), 1674.61[M – $2PF_6^-$]$^{2+}$ (calcd m/z: 1674.69).



Metallosupramolecular tetragonum wreaths Fe_8LA_4: MOL LA (3.0 mg, 0.8 μmol), and $FeCl_2{\cdot}4H_2O$ (0.3 mg, 1.6 μmol) was added in a 50 mL flask, then a solvent mixture of CH_3CN/glycol (10 mL, V:V, 1:2) was added and heated at 180 °C for 12 h, after cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt ($LiNTf_2$) in MeOH was added to get a purplish precipitate, which was filtered and washed with H_2O and MeOH, to generate a purplish solid: 3.5 mg (96%).^{1}H NMR (500 MHz, CD_3CN) δ 9.45(s, 16H, A-tpy-$H^{3',5'}$), 9.30(m, 36H, C-tpy-$H^{3',5'}$, D-tpy-$H^{3',5'}$, H^a), 9.16(s, 16H, B-tpy-$H^{3',5'}$), 8.90(s, 20H, A-tpy-$H^{3,3''}$, H^b), 8.77-8.69(m, 48H, B-tpy-$H^{3,3''}$,

C-tpy-$H^{3,3"}$, D-tpy-$H^{3,3"}$), 8.55-8.48(m, 16H, C-H^{g}, D-H^{g}), 8.39-8.31(m, 16H, B-H^{g}, C-H^{h}), 8.08-7.95(m, 80H, A-tpy-$H^{4,4"}$, B-tpy-$H^{4,4"}$, C-tpy-$H^{4,4"}$, D-tpy-$H^{4,4"}$, B-H^{h}, D-H^{h}), 7.63-7.59 (m, 32H, A-tpy-$H^{6\ 6"}$, B-tpy-$H^{6\ 6"}$), 7.45(s, 4H, H^{d}), 7.30-7.26(m, 56H, C-tpy-$H^{6\ 6"}$, D-tpy-$H^{6\ 6"}$, A-tpy-$H^{5\ 5"}$, B-tpy-$H^{5\ 5"}$), 7.14(m, 32H, C-tpy-$H^{5\ 5"}$, D-tpy-$H^{5\ 5"}$), 4.15 (m, 24H, $H^{\text{-OCH3}}$), 4.00 (m, 48H, $H^{\text{-OCH3}}$), 3.73 (m, 24H, $H^{\text{-OCH3}}$). ESI-MS (21648.85 calcd. For $C_{816}H_{536}F_{192}Fe_8N_{128}O_{160}Ru_8S_{64}$): m/z 1884.75 [M – 10N$(SO_2CF_3)_2^-$]$^{10+}$ (calcd m/z: 1884.74), m/z 1687.50 [M – 10N$(SO_2CF_3)_2^-$]$^{11+}$ (calcd m/z: 1687.93), m/z 1523.25 [M – 10N$(SO_2CF_3)_2^-$]$^{12+}$ (calcd m/z: 1523.92), m/z 1385.00 [M – 10N$(SO_2CF_3)_2^-$]$^{13+}$ (calcd m/z: 1385.15), m/z 1265.91 [M – 10N$(SO_2CF_3)_2^-$]$^{14+}$ (calcd m/z: 1266.20), m/z 1163.23 [M – 10N$(SO_2CF_3)_2^-$]$^{15+}$ (calcd m/z: 1163.11), m/z 1072.53 [M – 10N$(SO_2CF_3)_2^-$]$^{16+}$ (calcd m/z: 1072.91), m/z 993.05 [M – 10N$(SO_2CF_3)_2^-$]$^{16+}$ (calcd m/z: 993.32).

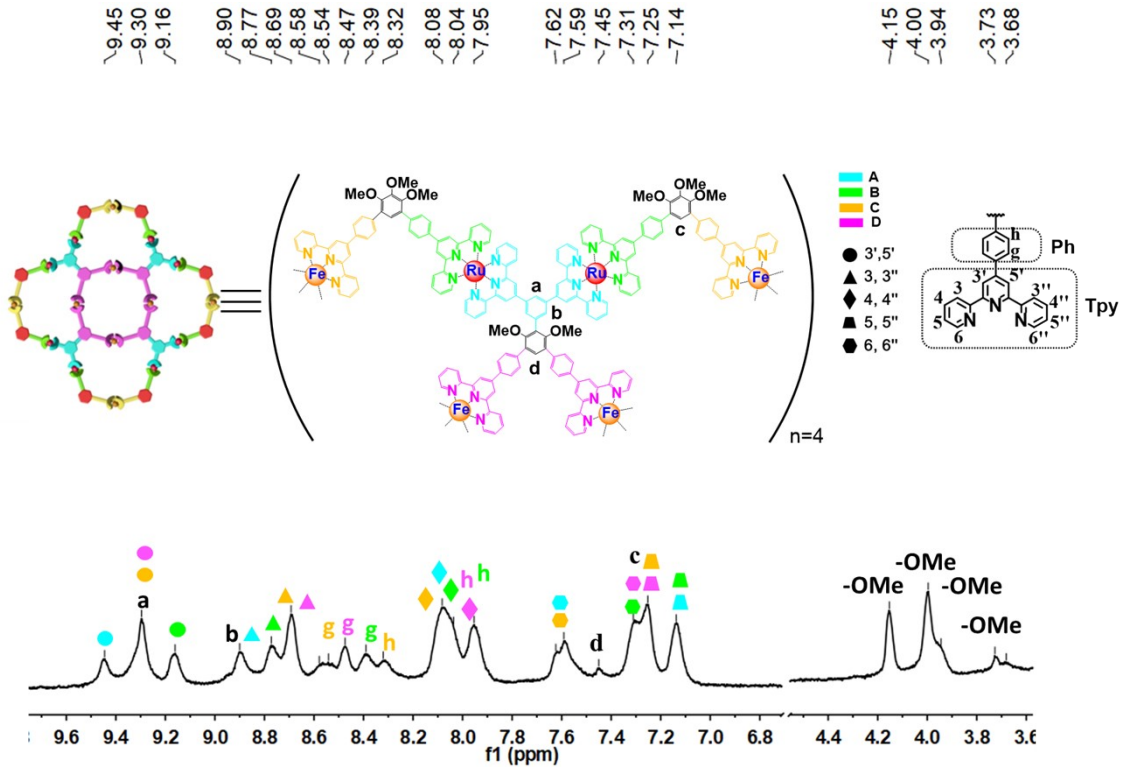


Figure S5: ^{1}H NMR spectrum (500 MHz) of **Fe_8LA_4** in CD_3CN.

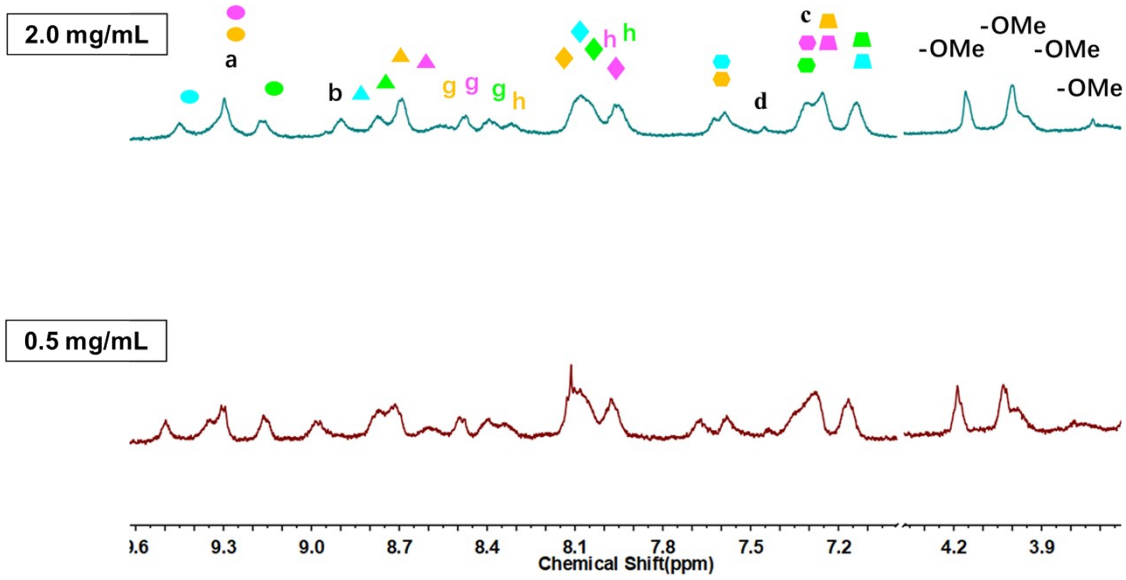


Figure S6: ^{1}H NMR spectrum (500 MHz) of $\mathbf{Fe_8LA_4}$ in CD_3CN under different concentration (2.0 mg/mL and 0.50 mg/mL).

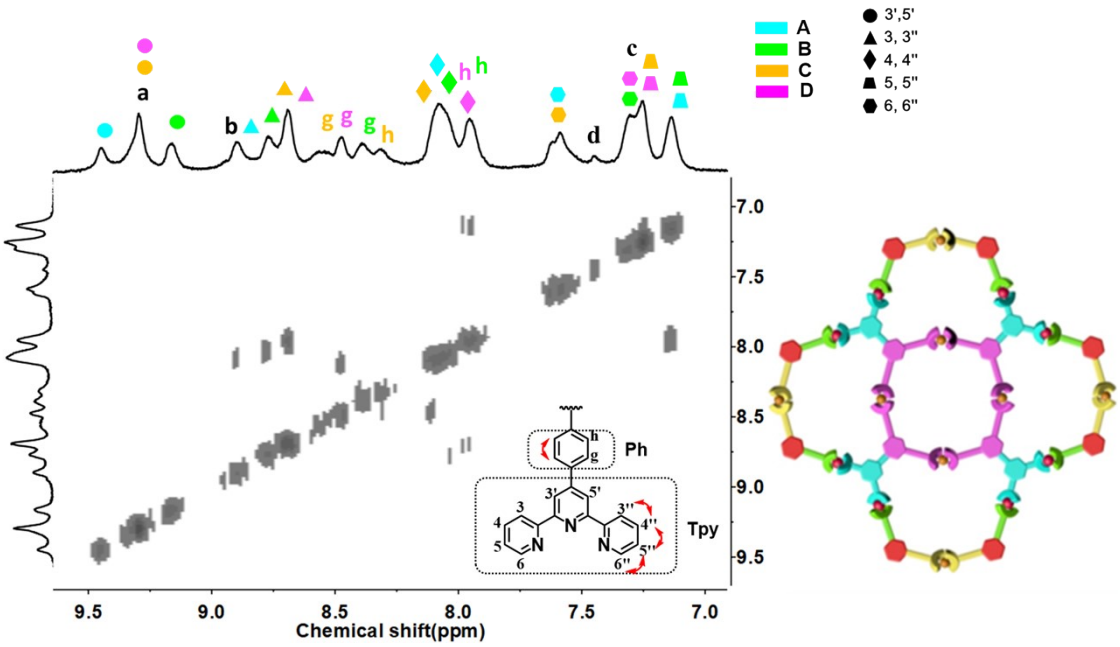


Figure S7: 2D COSY spectrum (500 MHz) of $\mathbf{Fe_8LA_4}$ in CD_3CN.

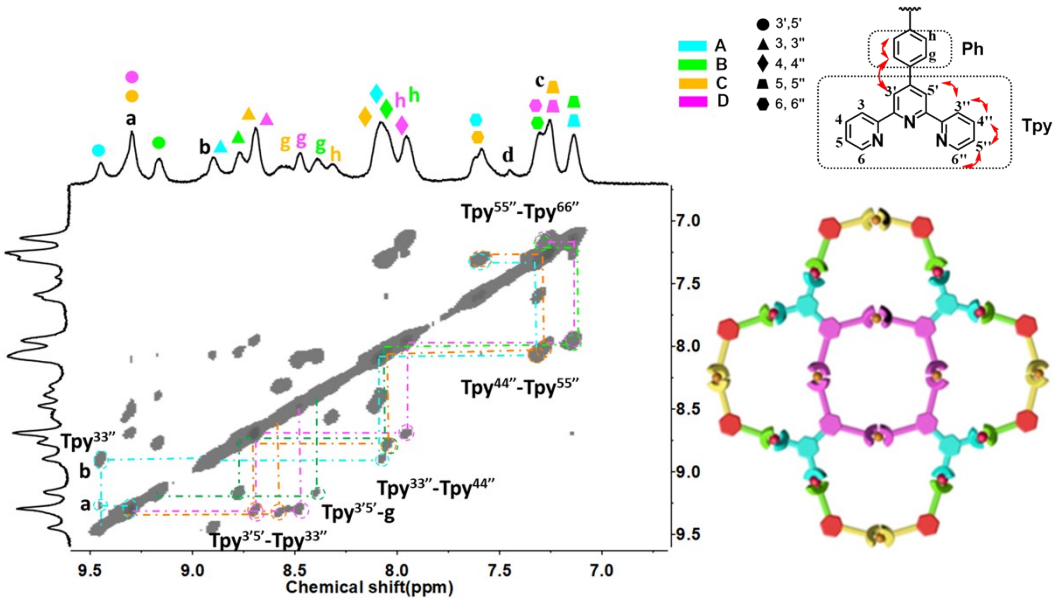


Figure S8: 2D NOESY spectrum (500 MHz) of **Fe_8LA_4** in CD_3CN

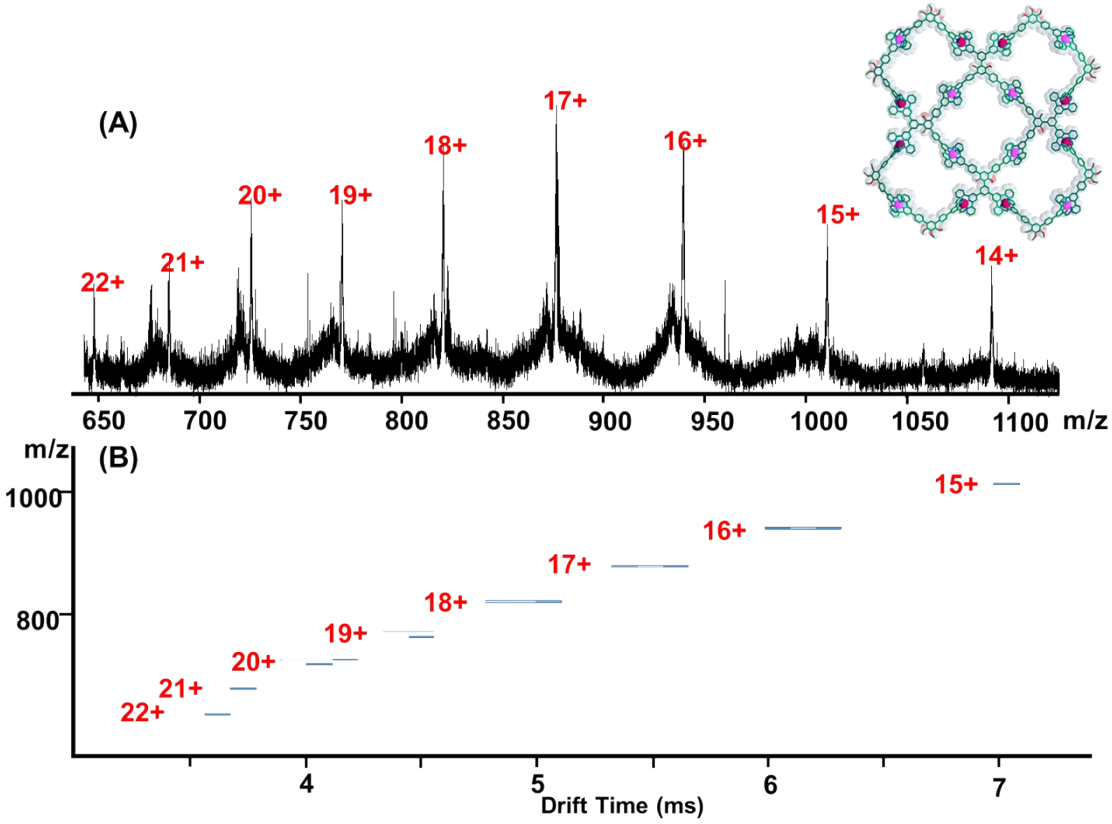


Figure S9: (A) ESI−MS and (B) TWIM−MS plot (m/z vs drift time) of **Fe_8LA_4** with 32 PF_6^-.

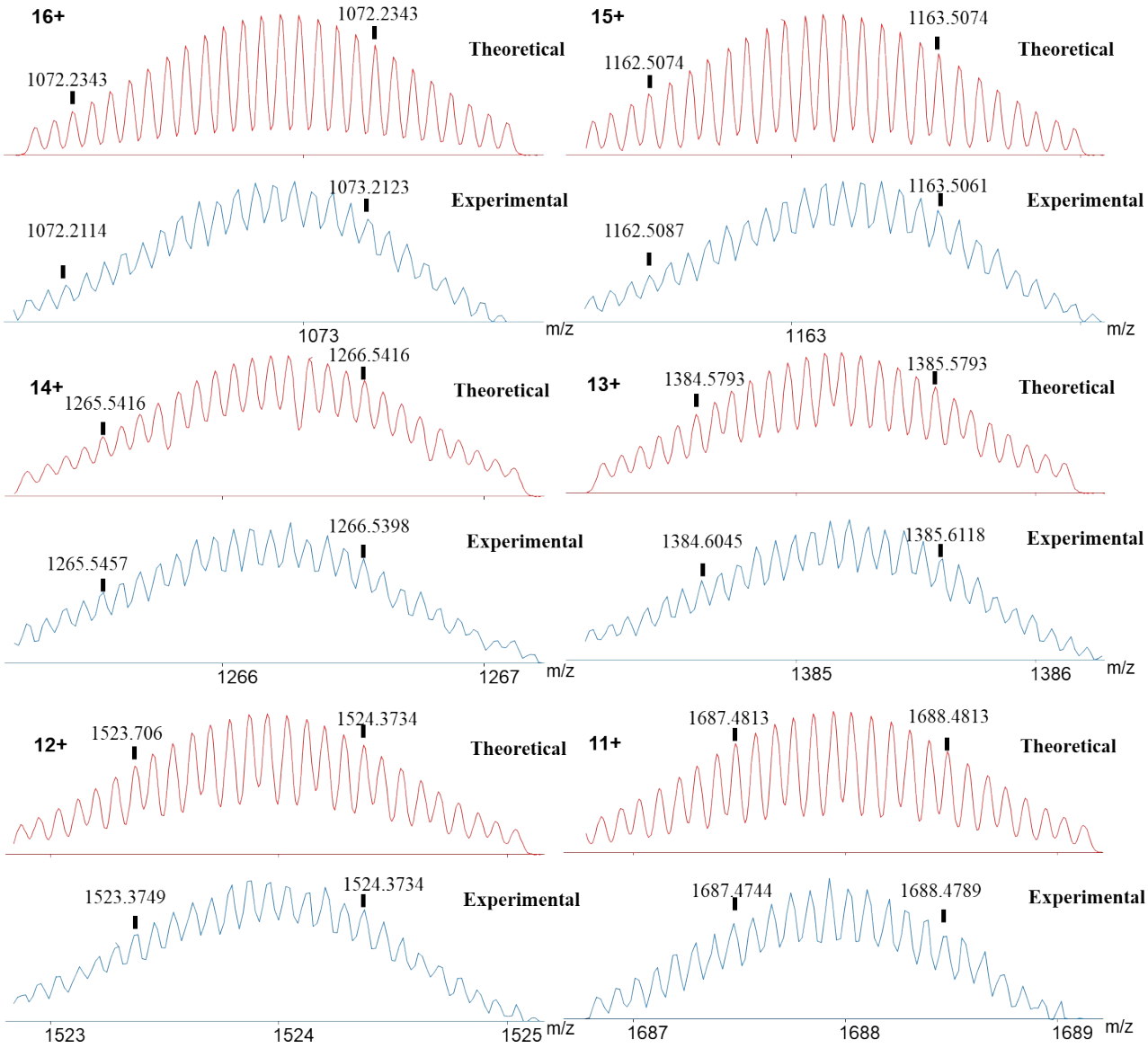
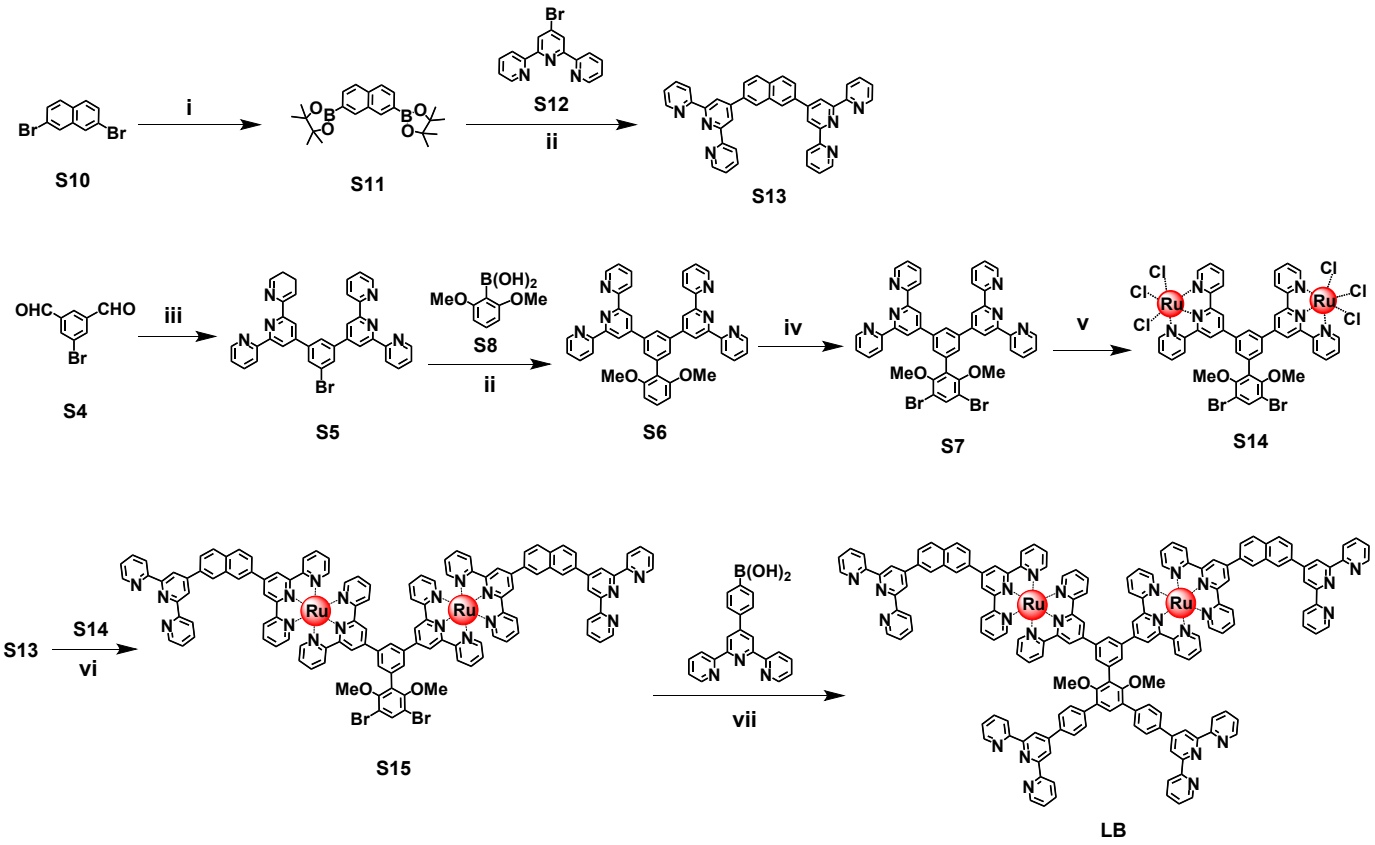
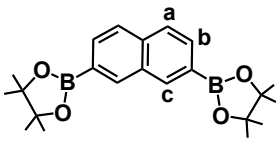


Figure S10: Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from **[Fe_8LA_4]·32(NTf_2^-)**.

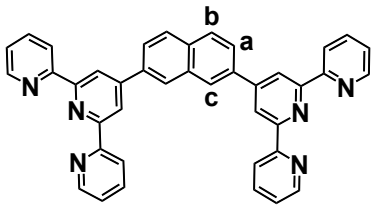
4. Synthesis of the MOL ligand LB and and pentagon wreath $Fe_{10}LB_5$



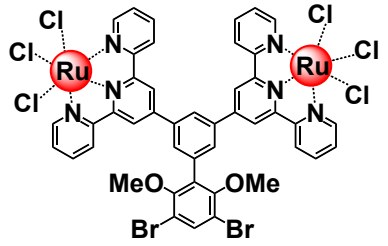
Scheme S3: Synthesis of MOL ligand **B**. Reagent and conditions: (i) bisdiboron, $Pd(PPh_3)_4$, THF, NaOH, reflux; (ii) $Pd(PPh_3)_4$, THF, NaOH, reflux; (iii) 2-acetylpyridine, KOH, EtOH, $NH_3•H_2O$, reflux; (iv) Br_2, $CHCl_3$, reflux; (v) $RuCl_3•3H_2O$, EtOH, reflux; (vi) N-ethylmorpholine, $CH_3OH/CHCl_3$ (V:V, 1:3); (vii) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, CH_3CN/CH_3OH(V:V, 2:1), K_2CO_3, reflux.



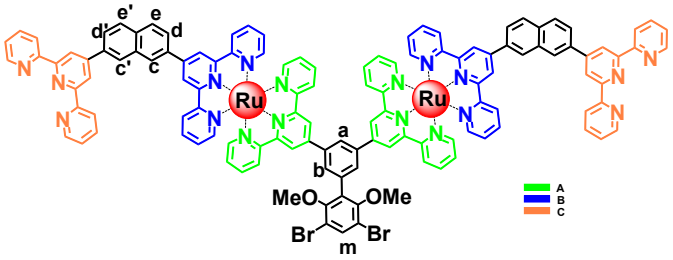
Compound S11: 2, 7 - dibromonaphthalene (500.0 mg, 1.6 mmol), bisdiboron (1.10 g, 4.2 mmol), potassium acetate (1.40 g, 14.3 mmol) was added to a 50 mL round bottom flask, added 15 mL DMSO as solvent. The system was degassed for 10 min, and [1,1'-Bis(diphenylphosphino)ferrocene]dichloropalladium(II) (154.0 mg, 0.2 mmol) as the catalyst was added. The mixture was stirred at 85 °C under nitrogen for 24 h , after cooled to ambient temperature, the system was extracted with water and dichloromethane, then recrystallized with methanol and petroleum etherthen, collected the liquid and recrystallized with methanol and H_2O to pure the product, as white solid: 565.0 mg, 85%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34(s, 2H, H^c), 7.80-7.78 (d, 2H, J=4Hz, H^a), 7.74-7.72(d, 2H, J=4Hz, H^b), 1.31(s, 24H, H^{-CH3}). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.16, 132.44, 131.54, 126.77, 84.63, 83.87, 77.34, 77.01, 76.71, 24.93.



Compound S13: **S11** (500 mg 1.32 mmol) and **S12** 4'-bromo-2,2':6',2"-terpyridine(705.0 mg, 2.2 mmol) was added to a 250 mL flask, then 30 mL H_2O, 30 mL methylbenzene, 10 mL tert-butyl alcohol and K_2CO_3(1.10 g, 7.9 mmol) was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (216.0 mg, 0.2 mmol) as the catalyst was added. The mixture was stirred at 90 °C under nitrogen for 2 d , after cooled to ambient temperature, then the system was 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: 312 mg, 40%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 4H, tpy-$H^{3'\ 5'}$), 8.79-8.78(d, 8H, *J*=2Hz, tpy-$H^{3\ 3''}$), 8.73-8.71(d, 8H, *J*=4Hz, tpy-$H^{6\ 6''}$), 8.56(s, 2H, Ph-H^a), 8.12-8.10(d, 2H, *J*=8Hz, PH-H^b), 8.06-8.04(d, 2H, *J*=8Hz, Ph-H^c), 7.92-7.89(t, 4H, tpy-$H^{4\ 4''}$), 7.39-7.36((t, 4H, tpy-$H^{5\ 5''}$). ESI-MS (590.29 calcd. For $C_{20}H_{26}N_6$): m\z 591.29 $[M+H^+]^+$ (calcd m/z: 591.23).

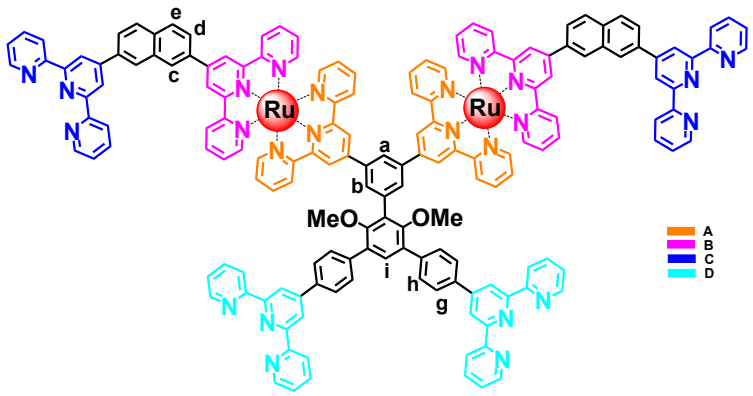


Compound S14: To a solution of **S7** (200 mg, 0.24 mmol) and $RuCl_3$•$3H_2O$ (134.75 mg, 0.53 mmol) in EtOH (50 mL). The mixture was stirred at 75 °C for 2 d. After cooling to ambient temperature, the precipitates were filtered and washed with MeOH to afford **S14**: 275 mg, 92%.

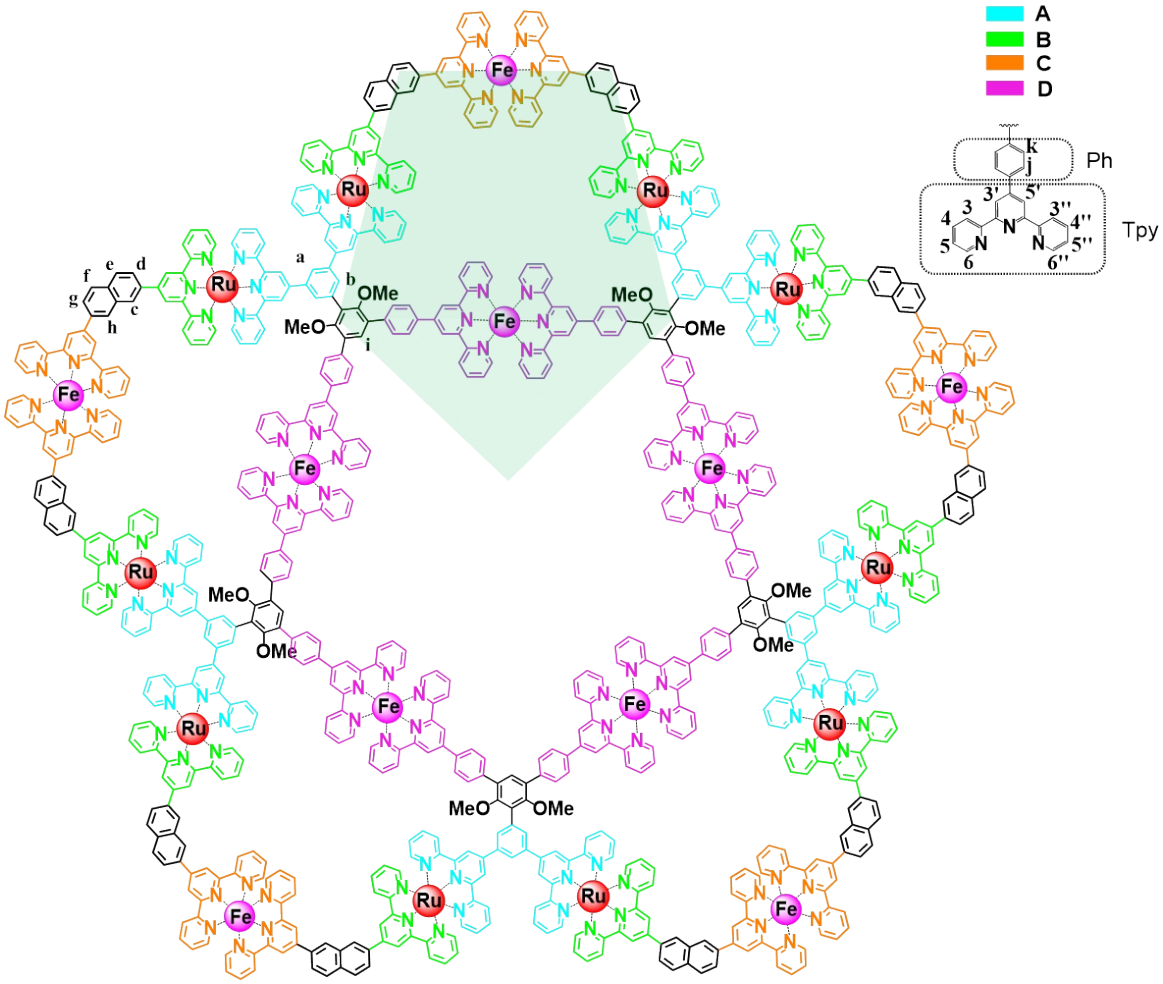


Compound S15: To a flask containing a mixture of **S14** (80.0 mg, 60 μmol) and **S13** (81.6 mg, 0.14 mmol), MeOH (40 mL), $CHCl_3$ (120 mL), and 6 drops of N-ethylmorpholine were added. The mixture was stirred at 75 °C for 2 d. After cooling to ambient temperature, the solvent was evaporated in vacuo 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: 128 mg, 64%. ^{1}H NMR (400 MHz, MeOD) δ 9.75(s, 4H, A-tpy-$H^{3'\ 5'}$), 9.24(s, 4H, B-tpy-$H^{3'\ 5'}$), 9.17(s,

1H, Ph-H^{a}), 9.02-9.01(m, 6H, C-tpy-$H^{3'\ 5'}$, Ph-$H^{e'}$), 8.84-8.73(m, 18H, A-tpy-$H^{3\ 3''}$, B-tpy-$H^{3\ 3''}$, C-tpy-$H^{3\ 3''}$, C-tpy-$H^{6\ 6''}$ Ph-H^{c}), 8.61(s, 2H, Ph-H^{b}), 8.46 (d, 2H, *J*=8Hz, Ph-H^{e}), 8.40 (d, 2H, *J*=8Hz, Ph-$H^{e'}$), 8.29 (d, 2H, *J*=8Hz, Ph-H^{d}), 8.22 (d, 2H, *J*=8Hz, Ph-$H^{d'}$), 8.15 (s, 1H, Ph-H^{m}), 8.05-7.99(m, 12H, A-tpy-$H^{4\ 4''}$, B-tpy-$H^{4\ 4''}$, C-tpy-$H^{4\ 4''}$), 7.59-7.57 (m, 8H, A-tpy-$H^{6\ 6''}$, B-tpy-$H^{6\ 6''}$), 7.51-7.49 (m, 4H, C-tpy-$H^{5\ 5''}$), 7.32-7.27 (m, 8H, A-tpy-$H^{5\ 5''}$, B-tpy-$H^{5\ 5''}$), 3.78(s, 6H, $H^{\text{-OMe}}$). ESI-MS (3338.63 cacld. For $C_{132}H_{82}Br_2F_{24}N_{22}O_{18}Ru_2S_8$): m/z 832.64 $[M–3N(SO_2CF_3)_2^-]^{3+}$ (calcd. m/z: 832.73), 1388.87 $[M–2N(SO_2CF_3)_2^-]^{2+}$ (calcd. m/z: 1389.17).



MOL ligand B: Compound **S15** (40 mg, 0.017 mmol) and 4'-Boronatopenyl[2,2':6',2"]terpyridine (190.4 mg, 0.5 mmol) was added to a 100 mL flask, then acetonitrile (40 mL), methanol (20 mL) and K_2CO_3 (56.3 mg, 0.4 mmol) in 0.5 mL of water was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (47.2 mg, 41 μmol) as the catalyst was added. The mixture was stirred at 85 °C under nitrogen for 4 d, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al_2O_3), eluting with the mixture of MeOH and CH_2Cl_2 to pure the product, as red solid: 29.8 mg, 65%. ^{1}H NMR (400 MHz, CD_3CN) δ 9.41(s, 4H, A-tpy-$H^{3',5'}$), 9.30(s, 4H, B-tpy-$H^{3',5'}$), 9.21(s, 1H, H^{a}), 9.07(s, 2H, H^{b}), 9.05(s, 4H, C-tpy-$H^{3',5'}$), 8.87(s, 4H, D-tpy-$H^{3',5'}$), 8.85-8.82(d, *J* =12 Hz, 4H, A-tpy-$H^{3,3''}$), 8.81-8.76(m, 20H, B-tpy-$H^{3,3''}$, C-tpy-$H^{3,3''}$, D-tpy-$H^{3,3''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$), 8.43(m, 4H, H^{e}), 8.30(m, 4H, H^{d}), 8.17-8.15(d, *J* =8 Hz, 4H, D-H^{g}), 8.09-8.03(m, 21H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$, D-tpy-$H^{4,4''}$, D-H^{h}, H^{i}), 7.88(s, 2H, H^{c}), 7.59-7.58(d, *J* =4 Hz, 8H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6''}$), 7.55-7.51(m, 8H, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$), 7.31-7.28(m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 3.56(s, 6H, $H^{\text{-OCH3}}$).^{13}C NMR (101 MHz, CD_3CN) δ 158.88, 158.78, 158.20, 157.66, 157.62, 157.01, 156.97, 156.37, 156.29, 156.18, 153.23, 153.15, 153.11, 152.44, 152.37, 152.30, 151.21, 149.95, 149.56, 149.42, 149.32, 141.02, 139.25, 139.05, 138.82, 138.75, 138.50, 138.48, 137.96, 137.91, 137.02, 129.11, 129.01, 128.78, 128.26, 127.92, 125.53, 125.04, 125.01, 124.92, 122.81, 122.76, 122.48, 122.44, 121.77, 121.72, 119.27, 119.06, 117.91, 61.51, 1.59, 1.52, 1.39, 1.36, 1.31, 1.18, 1.11, 0.90, 0.69, 0.49, 0.28, -0.47.ESI-MS (3254.87 cacld. For $C_{166}H_{110}F_{24}N_{24}O_2P_4Ru_2$): m/z 668.71 $[M – 4PF_6^-]^{4+}$ (calcd. m/z: 668.76), 939.93 $[M – 3PF_6^-]^{3+}$ (calcd. m/z: 939.99), 1482.34 $[M – 2PF_6^-]^{2+}$ (calcd. m/z: 1482.47).



Metallosupramolecular pentagon wreaths $Fe_{10}LB_5$: **MOL ligand B** (3.0 mg, 0.8 μmol), and $FeCl_2{\cdot}4H_2O$ (0.3 mg, 1.6 μmol) was added in a 50 mL flask, then a solvent mixture of CH_3CN/glycol (10 mL, V:V, 1:2) was added and heated at 180 °C for 12 h, after cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt ($LiNTf_2$) in MeOH was added to get a purplish precipitate, which was filtered and washed with H_2O and MeOH to generate a purplish solid: 5.8 mg (93.5%). ^{1}H NMR (500 MHz, CD_3CN) δ 9.49(s, 20H, A-tpy-$H^{3'\,5'}$), 9.46(s, 20H, B-tpy-$H^{3'\,5'}$), 9.40(s, 20H, C-tpy-$H^{3'\,5'}$), 9.31(m, 25H, D-tpy-$H^{3'\,5'}$, Ph-H^{a}), 9.22(s, 5H, Ph-$H^{c'}$), 9.18(s, 10H, Ph-H^{b}), 9.08(s, 5H, Ph-H^{c}), 8.94-8.85(m, 40H, A-tpy-$H^{3\,3''}$, B-tpy-$H^{3\,3''}$), 8.79-8.75(m, 20H, C-tpy-$H^{3\,3''}$), 8.73-8.68(m, 20H, D-tpy-$H^{3\,3''}$), 8.67-8.51(m, 60H, Ph-$H^{e,d,e',d',h}$), 8.34-8.30(m, 20H, Ph-H^{g}), 8.13 -7.94(m, 85H, A-tpy-$H^{4\,4''}$, B-tpy-$H^{4\,4''}$, C-tpy-$H^{4\,4''}$, D-tpy-$H^{4\,4''}$, Ph-H^{i}), 7.68-7.62(m, 40H, A-tpy-$H^{6\,6''}$, B-tpy-$H^{6\,6''}$), 7.38-7.27(m, 80H, C-tpy-$H^{6\,6''}$, D-tpy-$H^{6\,6''}$, A-tpy-$H^{5\,5''}$, B-tpy-$H^{5\,5''}$), 7.26-7.12(m, 40H, C-tpy-$H^{5\,5''}$, D-tpy-$H^{5\,5''}$), 3.66(s, 30H, $H^{\text{-OMe}}$). ESI-MS (25138.93 calcd . For $C_{910}H_{550}F_{240}Fe_{10}N_{160}O_{170}Ru_{10}S_{80}$): m/z 2233.50 [M – 13N$(SO_2CF_3)_2^-$]$^{10+}$ (calcd m/z: 2233.75), 2005.05 [M – 14N$(SO_2CF_3)_2^-$]$^{11+}$ (calcd m/z: 2005.21), 1814.41 [M – 15N$(SO_2CF_3)_2^-$]$^{12+}$ (calcd m/z: 1814.76), 1653.37 [M – 13N$(SO_2CF_3)_2^-$]$^{13+}$ (calcd m/z: 1653.61), 1515.22 [M – 14N$(SO_2CF_3)_2^-$]$^{14+}$ (calcd m/z: 1515.49), 1395.57 [M – 15N$(SO_2CF_3)_2^-$]$^{15+}$ (calcd m/z: 1395.78), 1291.05 [M – 16N$(SO_2CF_3)_2^-$]$^{16+}$ (calcd m/z: 1291.03), 1198.67 [M – 17N$(SO_2CF_3)_2^-$]$^{17+}$ (calcd m/z: 1198.61), 1116.55 [M – 18N$(SO_2CF_3)_2^-$]$^{18+}$ (calcd m/z: 1116.46), 1042.99 [M – 19N$(SO_2CF_3)_2^-$]$^{19+}$ (calcd m/z: 1042.95), 976.94 [M – 20N$(SO_2CF_3)_2^-$]$^{20+}$ (calcd m/z: 976.80), 916.88 [M – 21N$(SO_2CF_3)_2^-$]$^{21+}$ (calcd m/z: 916.94).

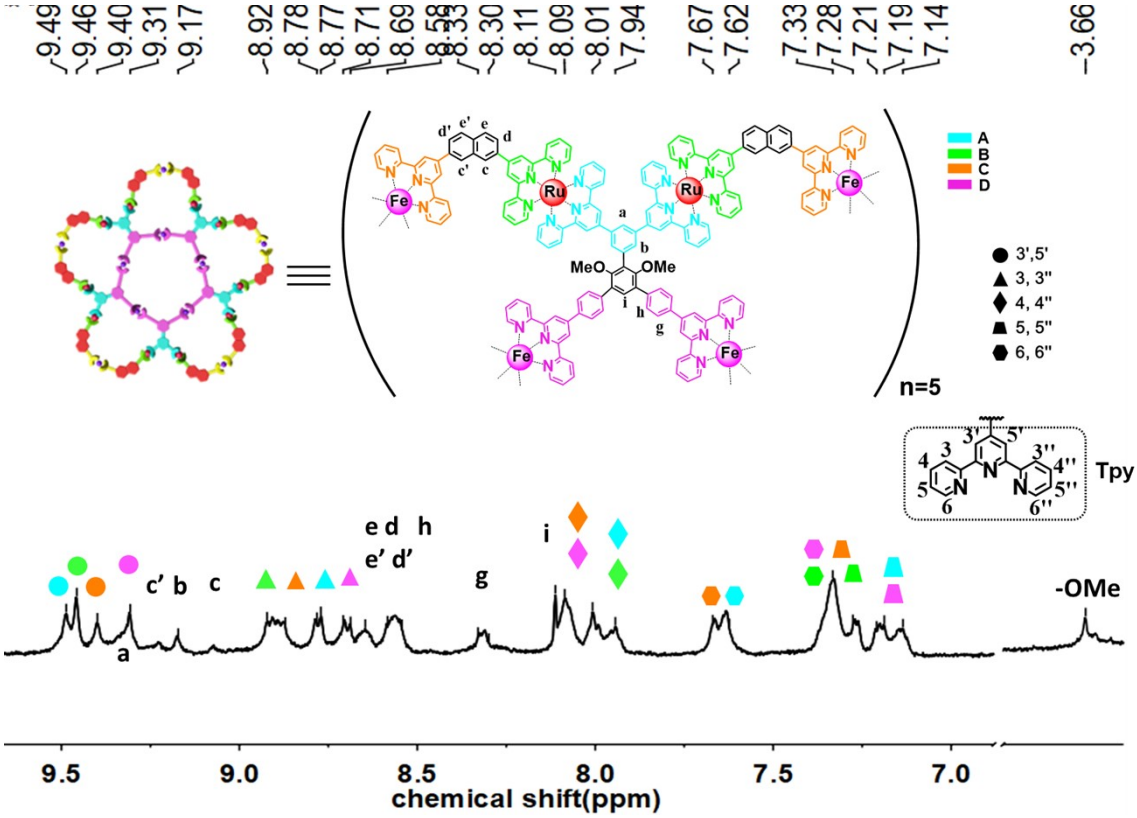


Figure S11: ^{1}H NMR spectrum (400 MHz) of $\mathbf{Fe_{10}LB_5}$ in CD_3CN.

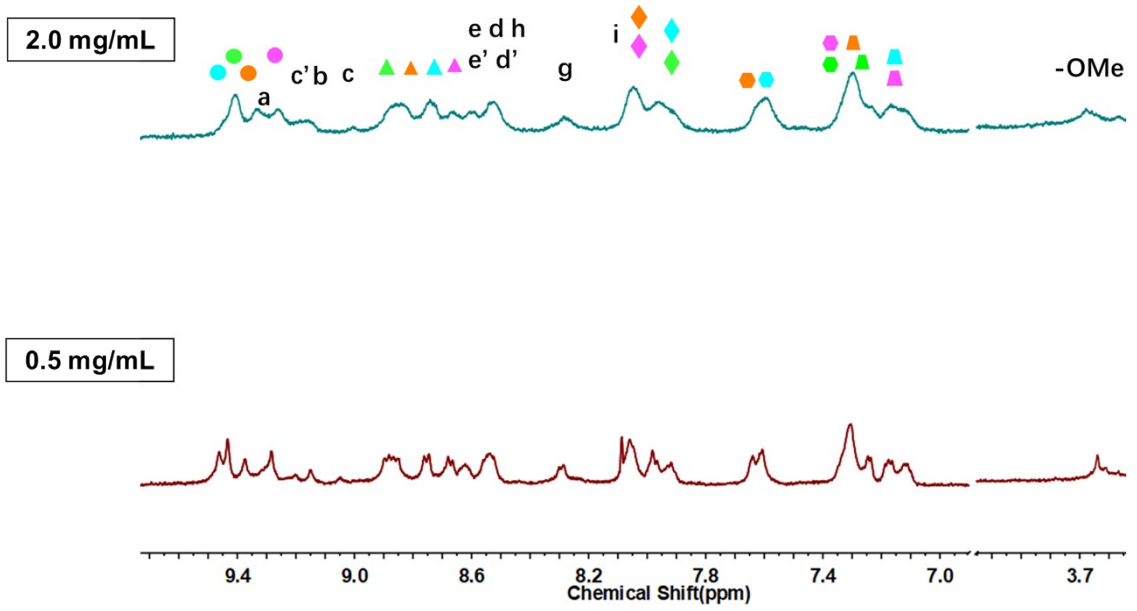


Figure S12: ^{1}H NMR spectrum (500 MHz) of $\mathbf{Fe_{10}LB_5}$ in CD_3CN under different concentration (2.0 mg/mL and 0.50 mg/mL).

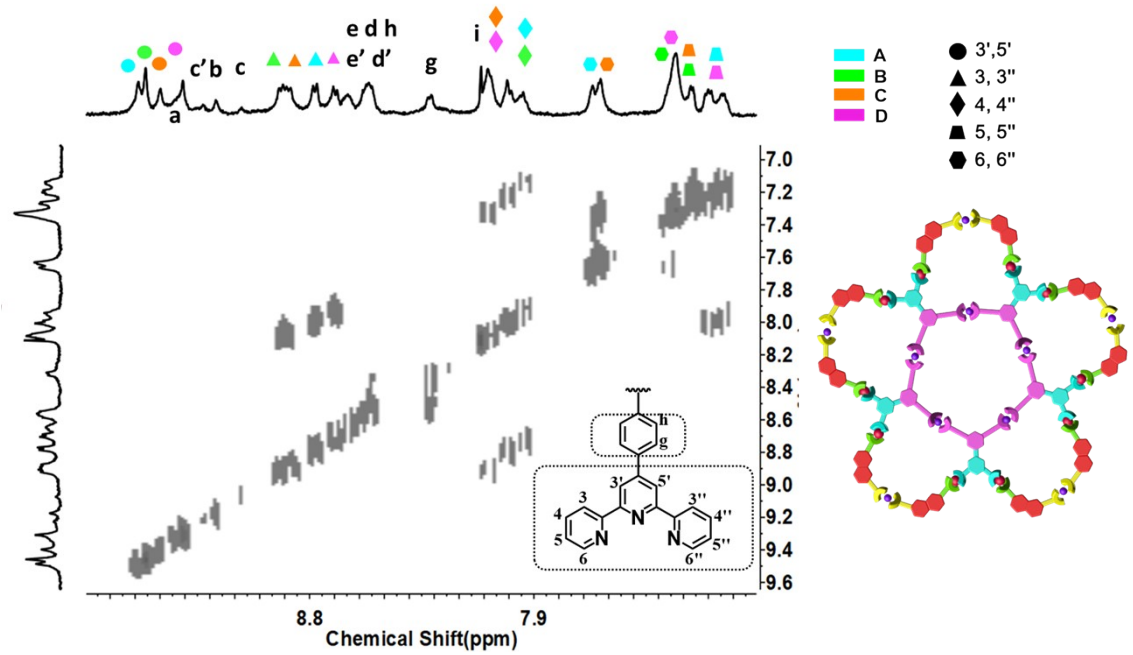


Figure S13: 2D COSY spectrum (400 MHz) of **$Fe_{10}LB_5$** in CD_3CN.

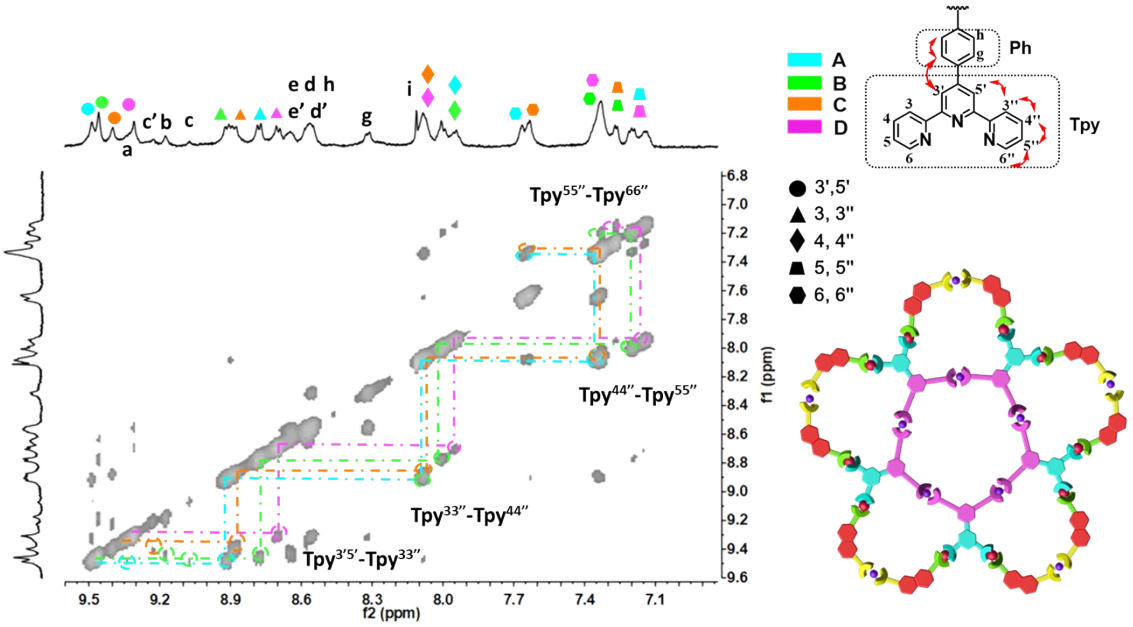


Figure S14: 2D NOESY spectrum (400 MHz) of **$Fe_{10}LB_5$** in CD_3CN.

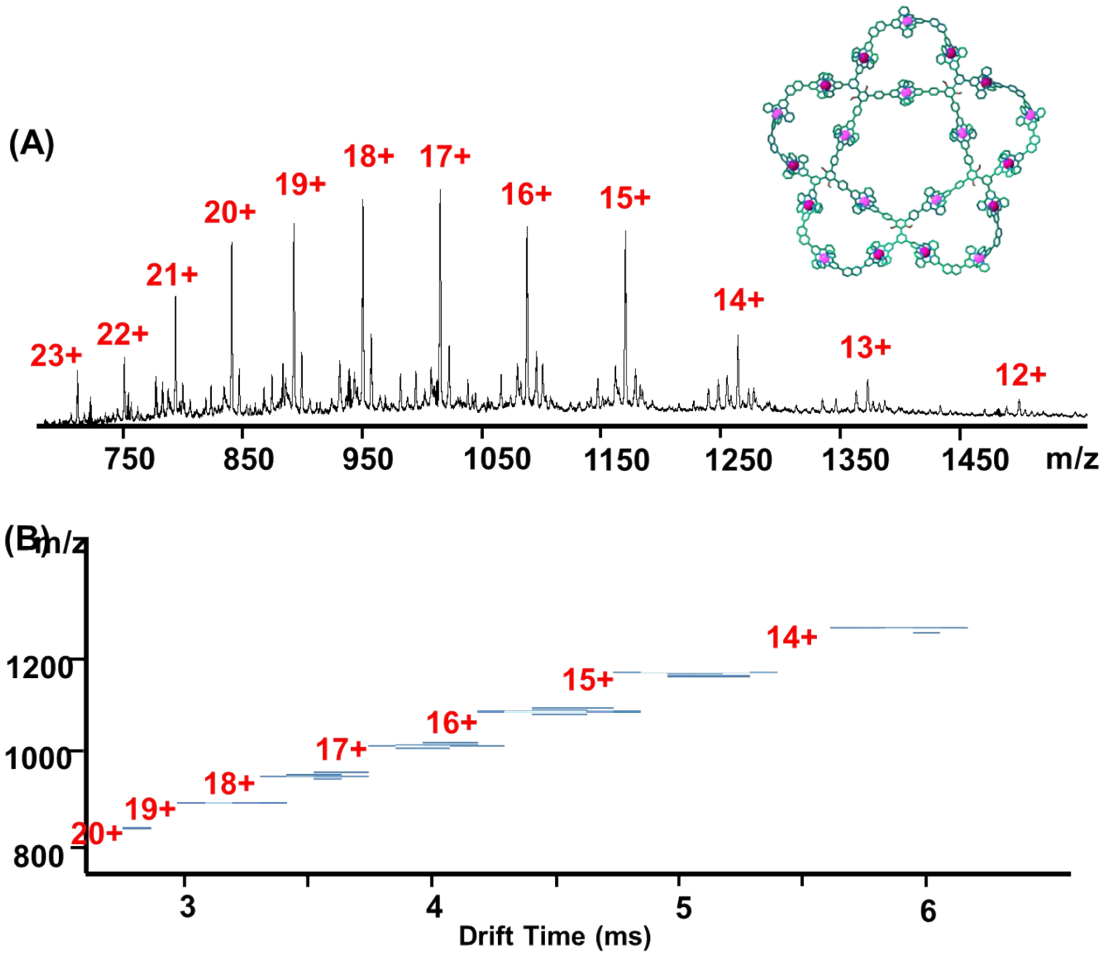


Figure S15: (A) ESI−MS and (B) TWIM−MS plot (m/z vs drift time) of $\mathbf{Fe_{10}LB_5}$ with 40 PF_6^-.

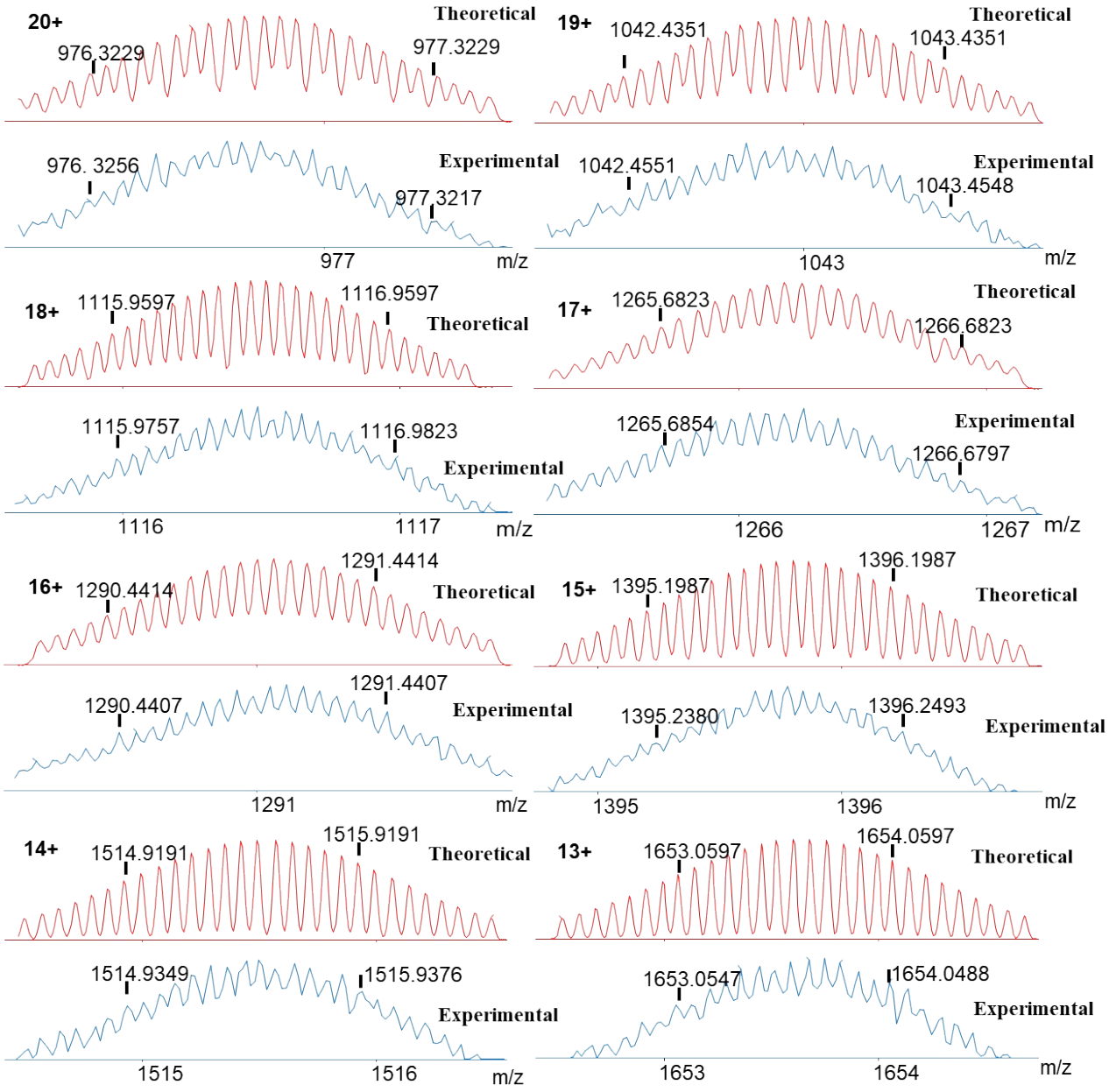
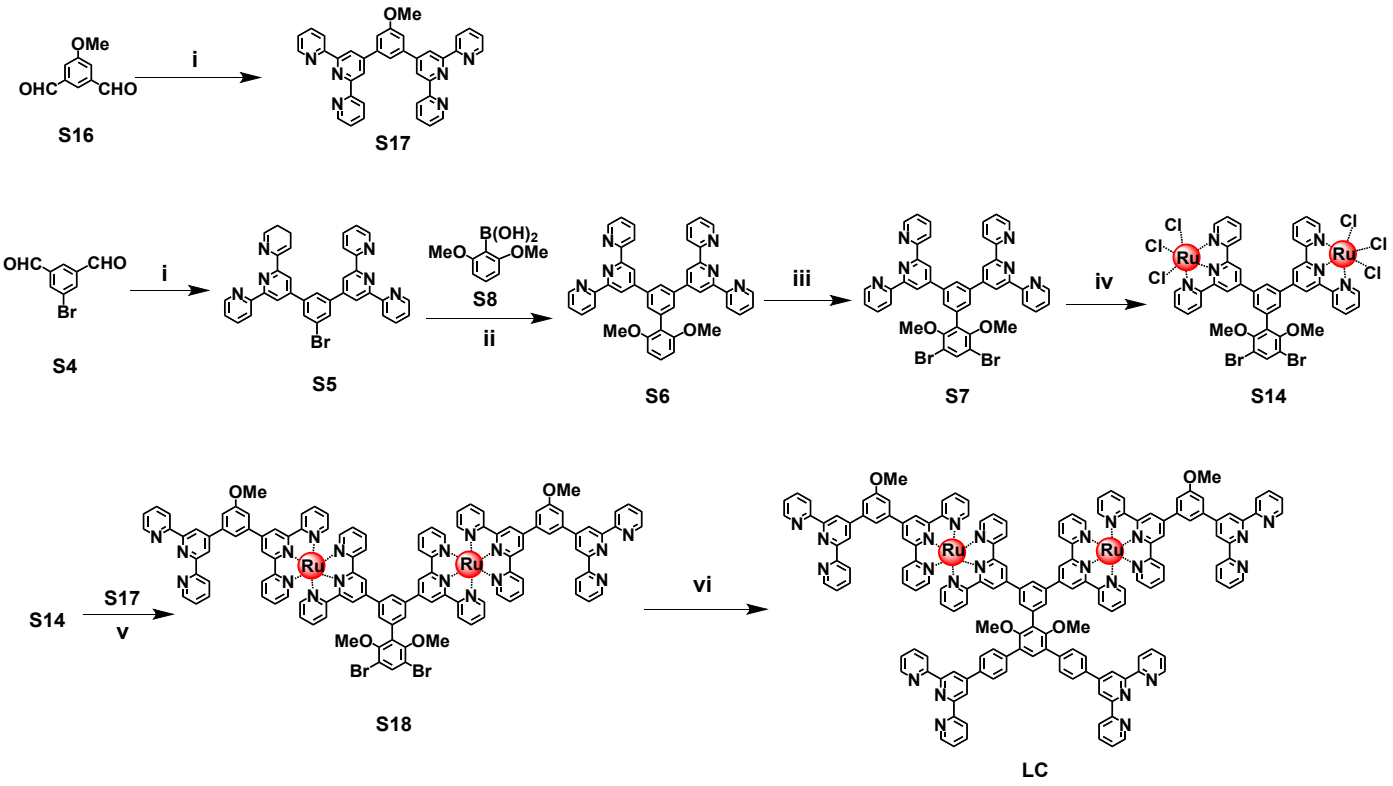
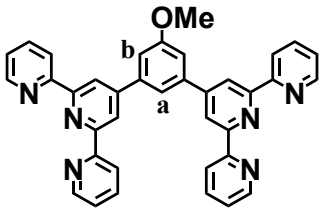


Figure S16: Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from **[$Fe_{10}LB_5$]·40(NTf_2^-)**.

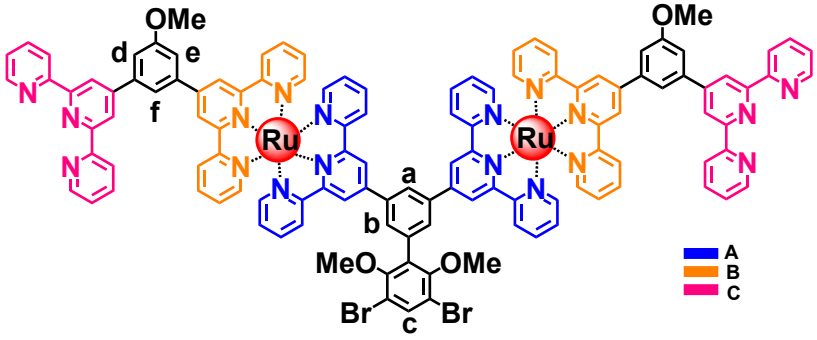
5. Synthesis of the MOL ligand LC and hexagon wreath $Fe_{12}LC_6$



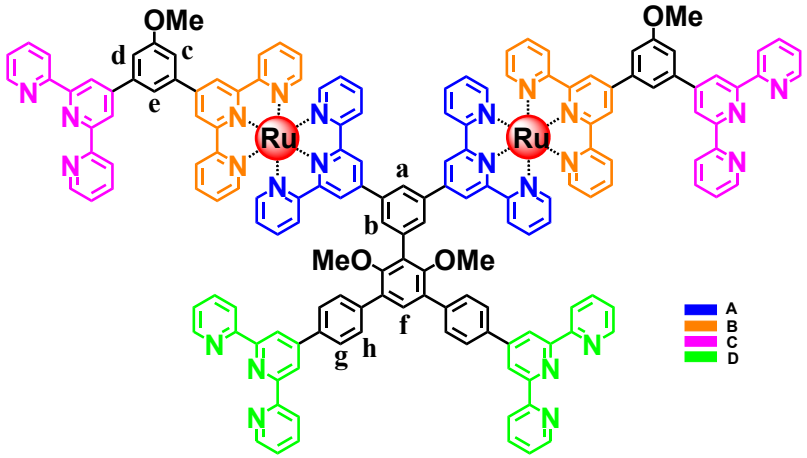
Scheme S4: Synthesis of **MOL ligand C**. Reagent and conditions: (i) 2-acetylpyridine, KOH, EtOH, NH_3•H_2O, reflux; (ii) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, THF, NaOH, reflux; (iii) Br_2, $CHCl_3$, reflux; (iv) $RuCl_3$•$3H_2O$, EtOH, reflux; (v) N-ethylmorpholine, $CH_3OH/CHCl_3$ (V:V, 1:3) , reflux; (vi) Tpy-$B(OH)_2$, $Pd(PPh_3)_4$, CH_3CN/CH_3OH(V:V, 2:1), K_2CO_3, reflux.



Compound S17: To a solution of **S16** (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, $H^{\text{-OMe}}$). ^{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.

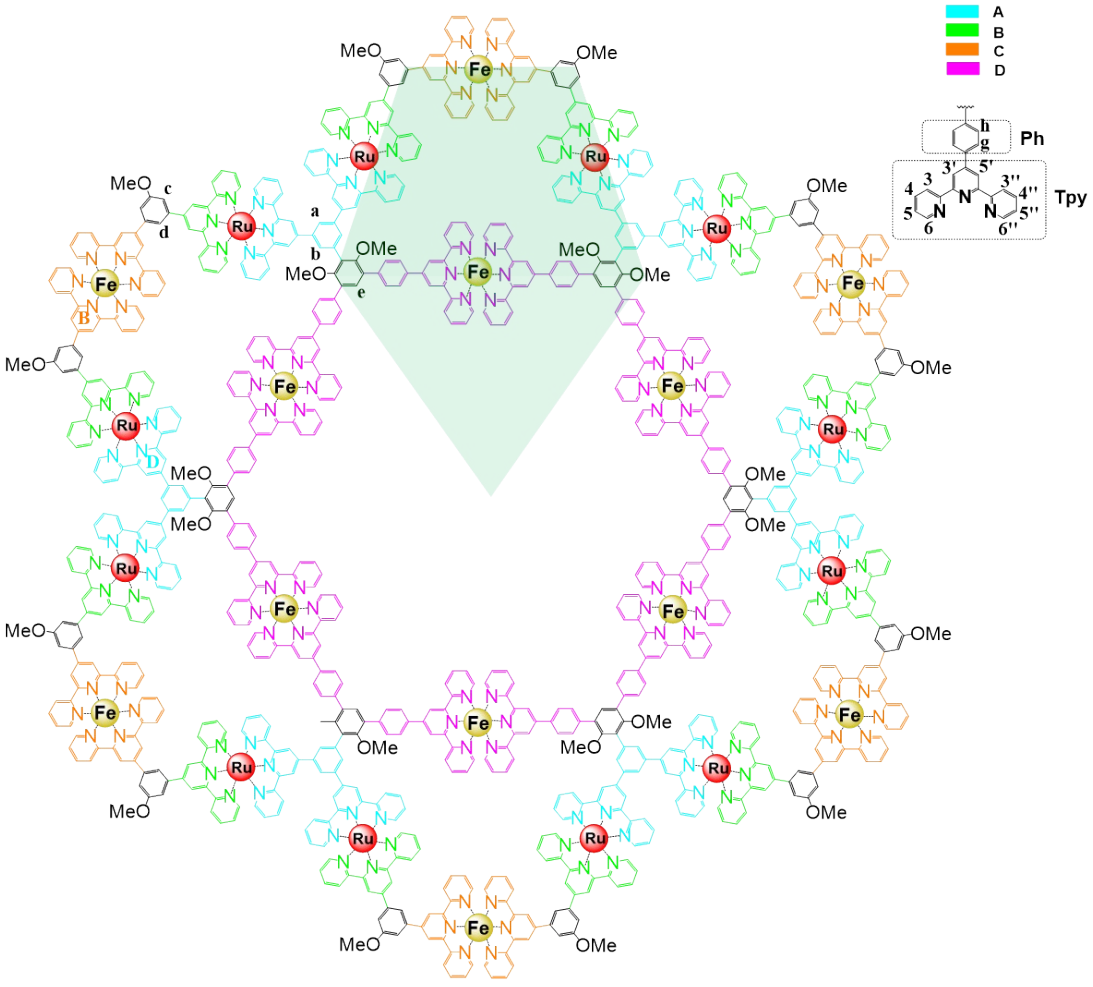


Compound S18: To a flask containing a mixture of **S14** (80.0 mg, 0.06 mmol) and **S17** (86.0 mg, 0.15 mmol), MeOH (40 mL), $CHCl_3$ (120 mL), and 6 drops of N-ethylmorpholine were added. The mixture was stirred at 75 °C for 2 d. After cooling to ambient temperature, the solvent was evaporated in vacuo 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: 101.8 mg, 72.3%.^{1}H NMR (500 MHz, MeOD) δ 9.76(s, 4H, A-tpy-H$^{3',5'}$), 9.57(s, 1H, H^a), 9.47 (s, 4H, B-tpy-H$^{3',5'}$), 9.26-9.24 (d, 4H, *J* = 4 Hz, A-tpy-H$^{3,3''}$), 9.06-9.05 (d, 4H, *J* = 4 Hz, B-tpy-H$^{3,3''}$), 8.97 (s, 4H, C-tpy-H$^{3',5'}$), 8.81-8.80 (m, 8H, C-tpy-H$^{3\ 3}$", C-tpy-H$^{6\ 6}$"), 8.70(s, 2H, H^b), 8.48(s, 2H, H^d), 8.11-8.05 (m, 15H, A,B,C-tpy-H$^{4,4''}$, H^e, H^c), 7.86 (s, 2H, H^f), 7.71-7.70 (d, 4H, *J* = 2 Hz,B-tpy-H$^{6\ 6}$"), 7.66-7.65 (d, 4H, J = 2 Hz, A-tpy-H$^{6\ 6}$"), 7.60-7.59 (d, 4H, *J* = 2 Hz, C-tpy-H$^{5,5''}$), 7.37-7.35 (m, 8H, A,B-tpy-H$^{5,5''}$), 4.21 (s, 6H, H^{-OMe}), 3.77 (s, 6H, H^{-OMe}). ^{13}C NMR (101 MHz, CD_3CN) δ 159.66, 158.89, 158.78, 157.10, 157.08, 157.03, 157.02, 156.98, 156.39, 156.29, 156.27, 156.17, 156.03, 154.36, 153.21, 153.19, 153.13, 153.09, 153.06, 150.24, 149.96, 148.69, 148.53, 148.03, 147.75, 147.31, 147.01, 138.89, 138.83, 138.76, 138.61, 138.53, 138.13, 131.27, 131.17, 129.72, 128.26, 128.18, 127.33, 127.19, 125.38, 125.15, 122.68, 122.48, 122.39, 121.97, 119.45, 119.37, 117.99, 113.32, 61.62, 61.27. ESI-MS (2319.82 calcd. For $C_{118}H_{82}Br_2Cl_2N_{18}O_4Ru_2$): m/z 737.82 $[M - 3Cl^-]^{3+}$ (calcd m/z: 737.82), 1124.46 $[M - 2Cl^-]^{2+}$ (calcd m/z: 1124.46).



MOL ligand C: Compound **S18** (60 mg, 0.02 mmol) and 4'-Boronatopenyl[2,2':6',2"]terpyridine (109.0 mg, 0.31 mmol) was added to a 100 mL flask, then acetonitrile (40 mL), methanol (20 mL) and K_2CO_3 (69 mg, 0.5 mmol) in 0.5 mL of water was added. The system was degassed for 10 min, and $Pd(PPh_3)_4$ (29.0 mg, 0.03 mmol) as the

catalyst was added. The mixture was stirred at 85 °C under nitrogen for 2 d, after cooled to ambient temperature, then concentrated in vacuo followed by column chromatography (Al_2O_3), eluting with the mixture of MeOH and CH_2Cl_2 to pure the product, as red solid: 45.0 mg, 63%. ^{1}H NMR (400 MHz, CD_3CN) δ 9.39(s, 4H, A-tpy-$H^{3',5'}$), 9.18(s, 5H, B-tpy-$H^{3',5'}$, H^{a}), 9.00(s, 4H, C-tpy-$H^{3',5'}$), 8.90(s, 4H, D-tpy-$H^{3',5'}$), 8.86-8.84(d, J =8 Hz, 4H, A-tpy-$H^{3,3''}$), 8.81-8.76(m, 22H, B-tpy-$H^{3,3''}$, C-tpy-$H^{3,3''}$, D-tpy-$H^{3,3''}$, C-tpy-$H^{6,6''}$, D-tpy-$H^{6,6''}$, H^{b}), 8.29(s, 2H, H^{e}), 8.16-8.14 (d, J =8 Hz, 4H, D-H^{g}), 8.08-8.00 (m, 18H, A-tpy-$H^{4,4''}$, B-tpy-$H^{4,4''}$, C-tpy-$H^{4,4''}$, D-tpy-$H^{4,4''}$, D-H^{h}), 7.92(s, 2H, H^{c}), 7.87(s, 1H, H^{f}), 7.75(s, 2H, H^{d}), 7.58-7.55 (m, 16H, A-tpy-$H^{6,6''}$, B-tpy-$H^{6,6''}$, C-tpy-$H^{5,5''}$, D-tpy-$H^{5,5''}$), 7.29-7.27 (m, 8H, A-tpy-$H^{5,5''}$, B-tpy-$H^{5,5''}$), 4.18(s, 6H, $H^{\text{-OCH3}}$), 3.55(s, 6H, $H^{\text{-OCH3}}$).^{13}C NMR (126 MHz, CD_3CN) δ 161.39, 158.27, 158.19, 156.47, 156.30, 155.99, 155.72, 155.52, 152.61, 152.44, 149.78, 149.56, 149.38, 149.34, 147.99, 147.07, 141.71, 139.27, 138.88, 138.19, 138.17, 137.48, 137.35, 137.28, 130.99, 130.12, 130.07, 127.67, 127.56, 127.30, 124.76, 124.46, 124.35, 122.17, 121.83, 121.27, 121.20, 121.08, 119.11, 119.02, 118.65, 118.28, 114.66, 60.82, 55.86, 48.87. ESI-MS (3755.49 calcd. For $C_{168}H_{110}F_{24}N_{28}O_{20}Ru_2S_8$): m/z 971.42 [M – 3 $N(SO_2CF_3)_2^-$]$^{3+}$ (calcd m/z: 971.68), 1597.52 [M – 2 $N(SO_2CF_3)_2^-$]$^{2+}$ (calcd m/z: 1597.60).



Metallosupramolecular hexagon wreaths $Fe_{12}LC_6$: MOL ligand C (3.0 mg, 0.09 μmol), and $FeCl_2{\cdot}4H_2O$ (0.4 mg, 0.19 μmol) was added in a 50 mL flask, then a solvent mixture of CH_3CN/glycol (10 mL, V:V, 1:2) was added and heated at 180 °C for 12 h, after cooled to ambient temperature, excess bistrifluoromethanesulfonimide lithium salt ($LiNTf_2$) in MeOH was added to get a purplish precipitate, which was filtered and washed with H_2O and MeOH,

to generate a purplish solid: 3.1 mg (96.4%). ^{1}H NMR (500 MHz, CD3CN) δ 9.45-9.20(m, 102H, A-tpy-$H^{3'\ 5'}$, B-tpy-$H^{3'\ 5'}$, C-tpy-$H^{3'\ 5'}$, D-tpy-$H^{3'\ 5'}$, Ph-H^{a}), 9.00-8.51(m, 144H, A-tpy-$H^{3\ 3''}$, B-tpy-$H^{3\ 3''}$, C-tpy-$H^{3\ 3''}$, D-tpy-$H^{3\ 3''}$, Ph-H^{b}, Ph-H^{h}), 8.35-7.82(m, 144H, A-tpy-$H^{4\ 4''}$, B-tpy-$H^{4\ 4''}$, C-tpy-$H^{4\ 4''}$, D-tpy-$H^{4\ 4''}$, Ph-H^{g}, Ph-H^{c}, Ph-H^{d}), 7.69-7.48(m, 78H, A-tpy-$H^{6\ 6''}$, B-tpy-$H^{6\ 6''}$, C-tpy-$H^{6\ 6''}$, Ph-H^{e}), 7.32-7.06(m, 120H, D-tpy-$H^{6\ 6''}$, A-tpy-$H^{5\ 5''}$, B-tpy-$H^{5\ 5''}$, C-tpy-$H^{5\ 5''}$, D-tpy-$H^{5\ 5''}$), 4.33(s, 36H, $H^{\text{-OMe}}$), 3.59(s, 36H, $H^{\text{-OMe}}$). ESI-MS (29926.30 cacld. For $C_{1056}H_{660}F_{288}Fe_{12}N_{192}O_{216}Ru_{12}S_{96}$): m/z 1590.19 [M – 16N$(SO_2CF_3)_2^-$]$^{16+}$ (calcd m/z: 1590.24), 1480.07 [M – 17N$(SO_2CF_3)_2^-$]$^{17+}$ (calcd m/z: 1480.22), 1382.12 [M – 18N$(SO_2CF_3)_2^-$]$^{18+}$ (calcd m/z: 1382.43), 1294.76 [M – 19N$(SO_2CF_3)_2^-$]$^{19+}$ (calcd m/z: 1294.92), 1215.88 [M – 20N$(SO_2CF_3)_2^-$]$^{20+}$ (calcd m/z: 1216.17), 1144.84 [M – 21N$(SO_2CF_3)_2^-$]$^{21+}$ (calcd m/z: 1144.92), 1080.04 [M – 22N$(SO_2CF_3)_2^-$]$^{22+}$ (calcd m/z: 1080.14), 1020.93 [M – 23N$(SO_2CF_3)_2^-$]$^{23+}$ (calcd m/z: 1021.00), 966.63 [M – 24N$(SO_2CF_3)_2^-$]$^{24+}$ (calcd m/z: 966.78).

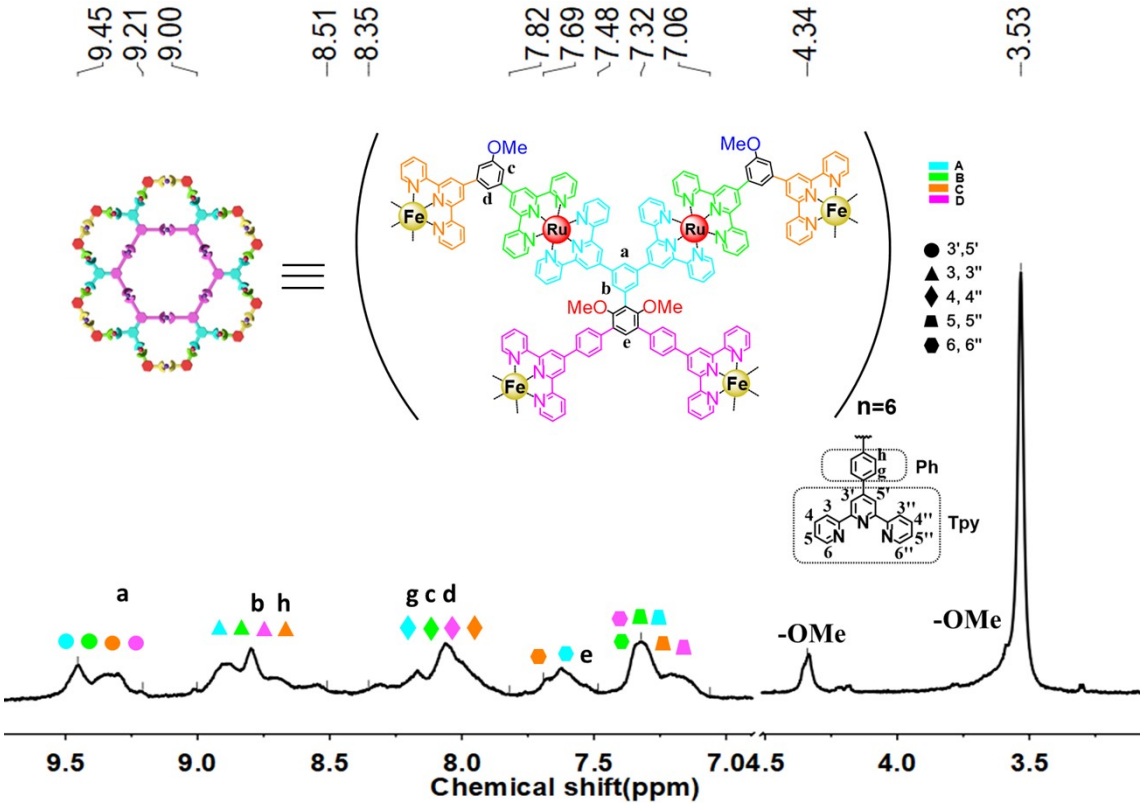


Figure S17: ^{1}H NMR spectrum (500 MHz) of **$Fe_{12}LC_6$** in CD_3CN.

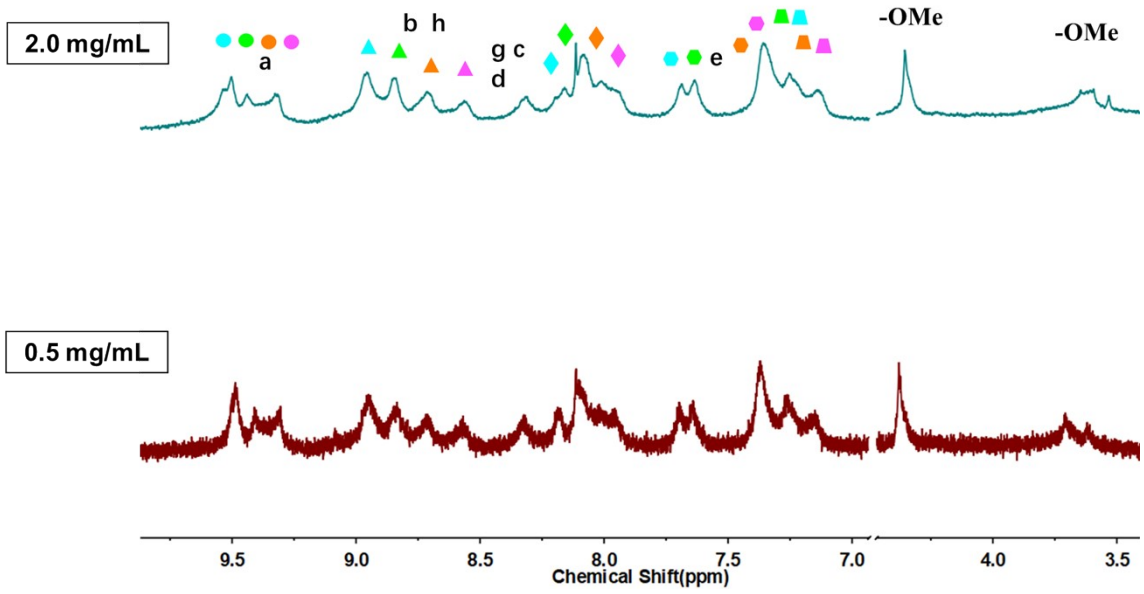


Figure S18: ^{1}H NMR spectrum (500 MHz) of $\mathbf{Fe_{12}LC_6}$ in CD_3CN under different concentration (2.0 mg/mL and 0.50 mg/mL).

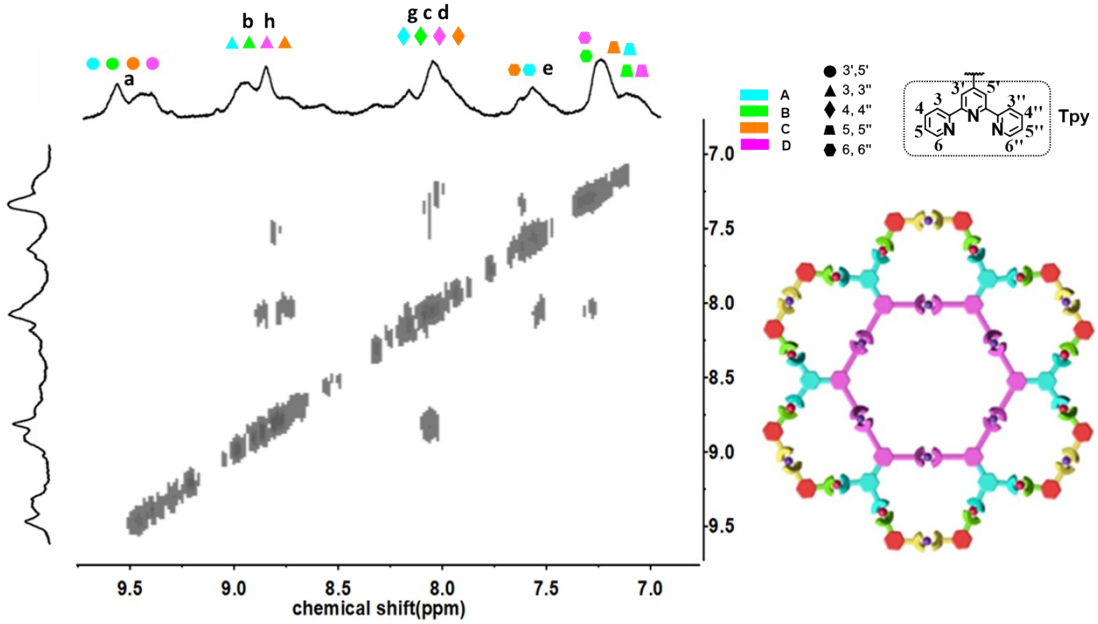


Figure S19: 2D COSY spectrum (400 MHz) of $\mathbf{Fe_{12}LC_6}$ in CD_3CN.

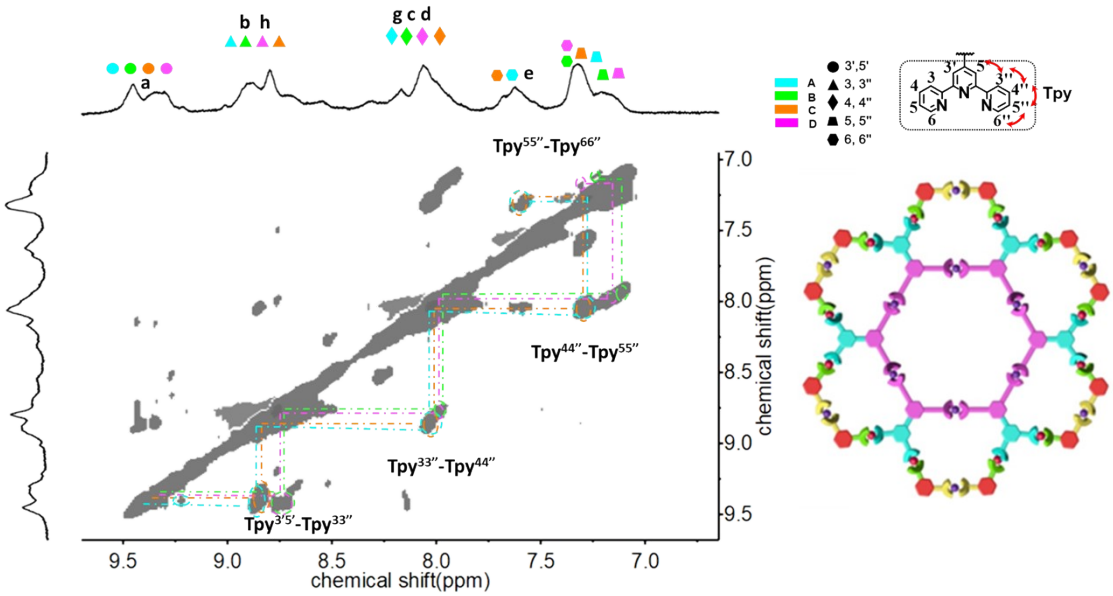


Figure S20: 2D NOESY spectrum (400 MHz) of $\mathbf{Fe_{12}LC_6}$ in CD_3CN.

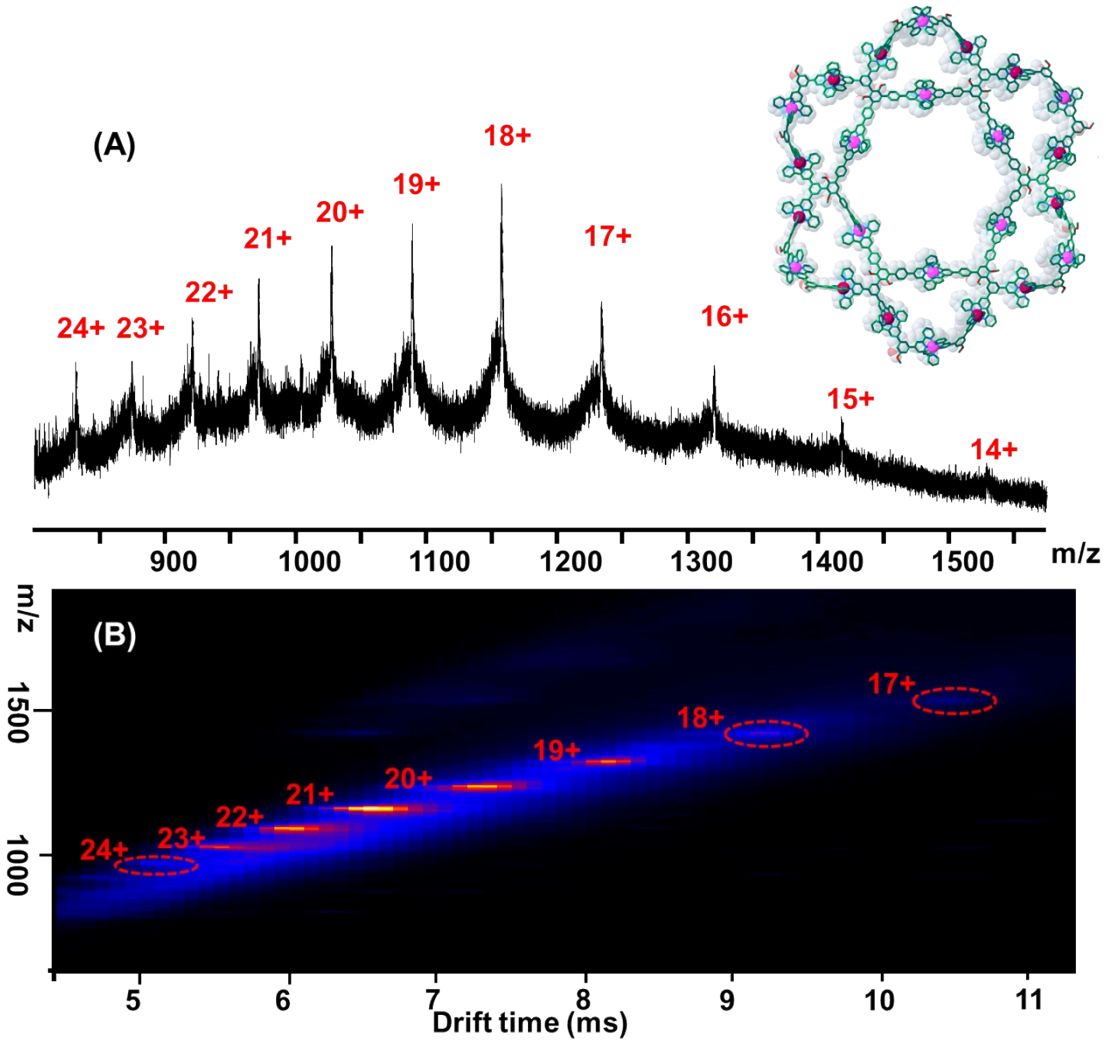


Figure S21: (A) ESI−MS and (B) TWIM−MS plot (m/z vs drift time) of $\mathbf{Fe_{12}LC_6}$ with 48 PF_6^-.

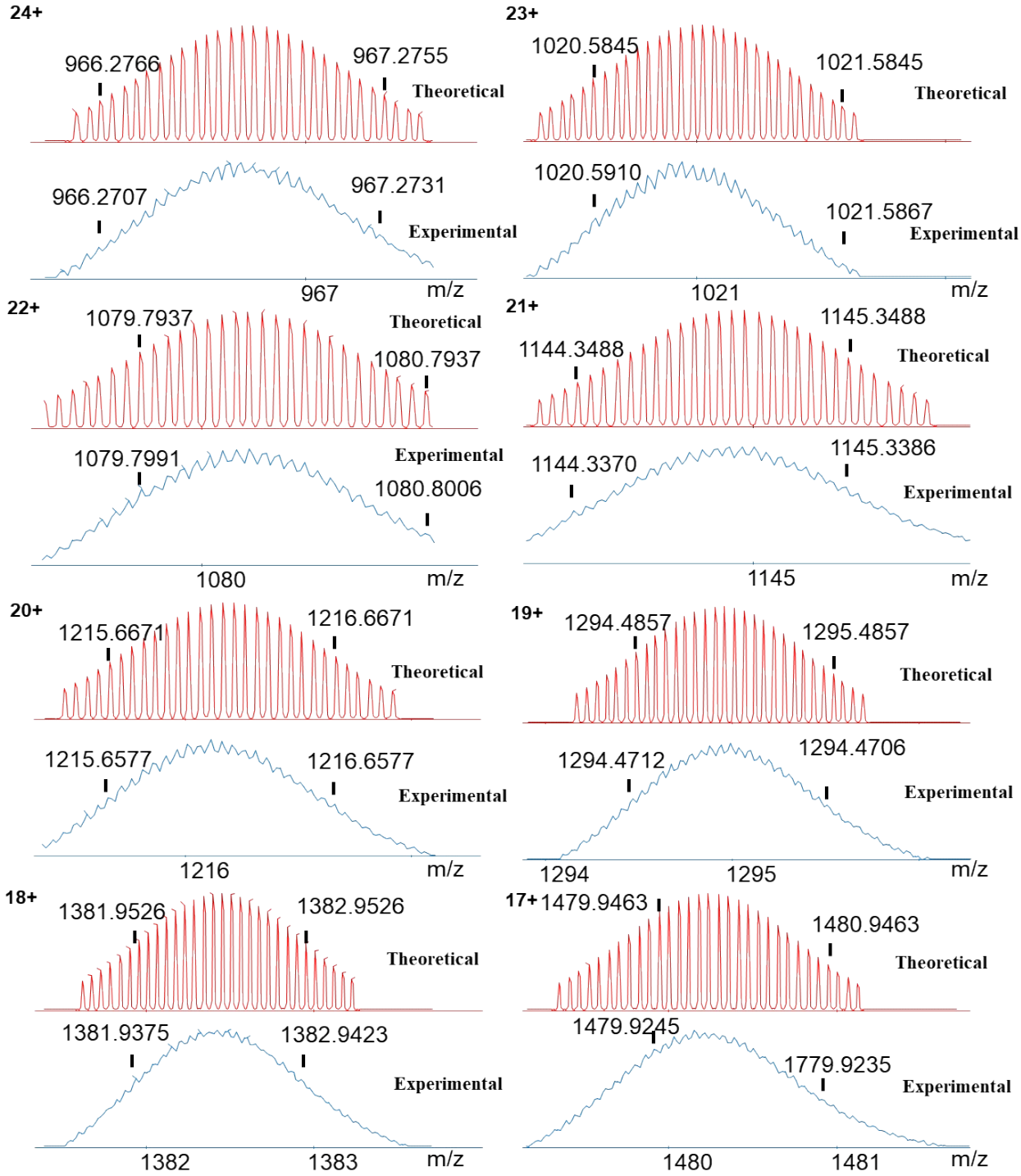


Figure S22: Theoretical (top) and experimental (bottom) isotope patterns for the different charge states observed from **[$Fe_{12}LC_6$]·48(NTf_2^-)**.

6. ^{1}H NMR, ^{13}C NMR, COSY and NOESY spectra of other compounds

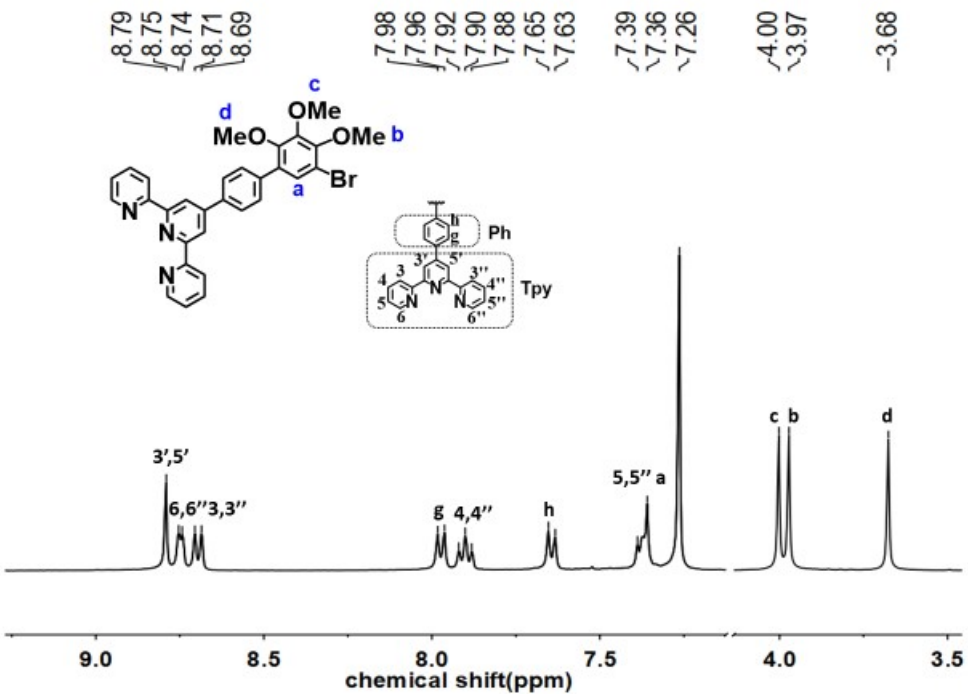


Figure S23: ^{1}H NMR spectrum (500 MHz) of **S2** in $CDCl_3$

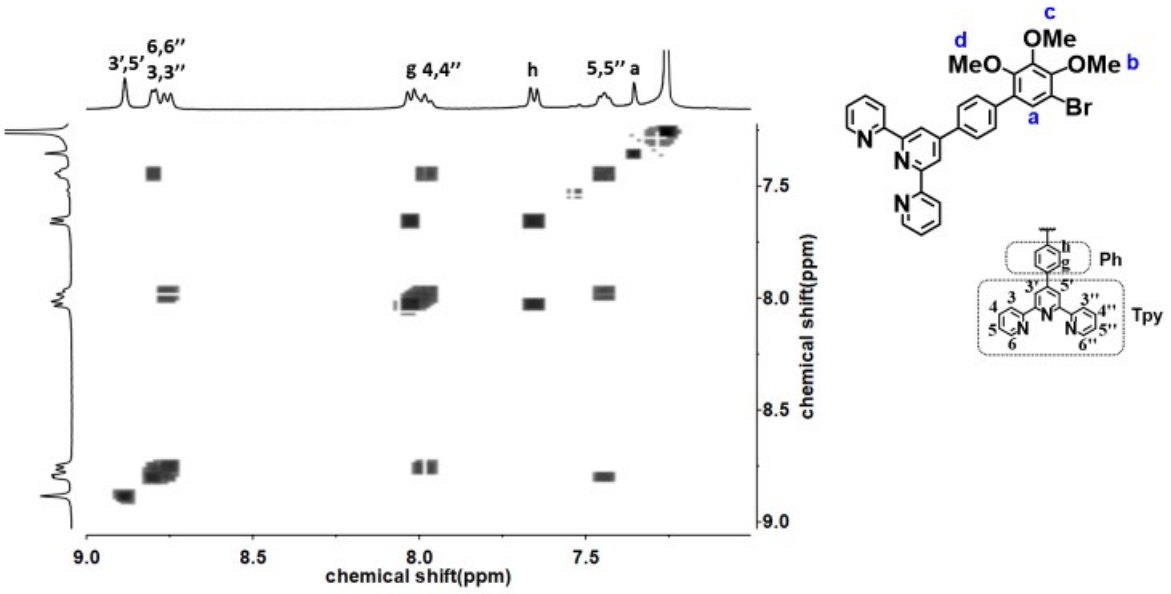


Figure S24: 2D COSY spectrum (500 MHz) of **S2** in $CDCl_3$.

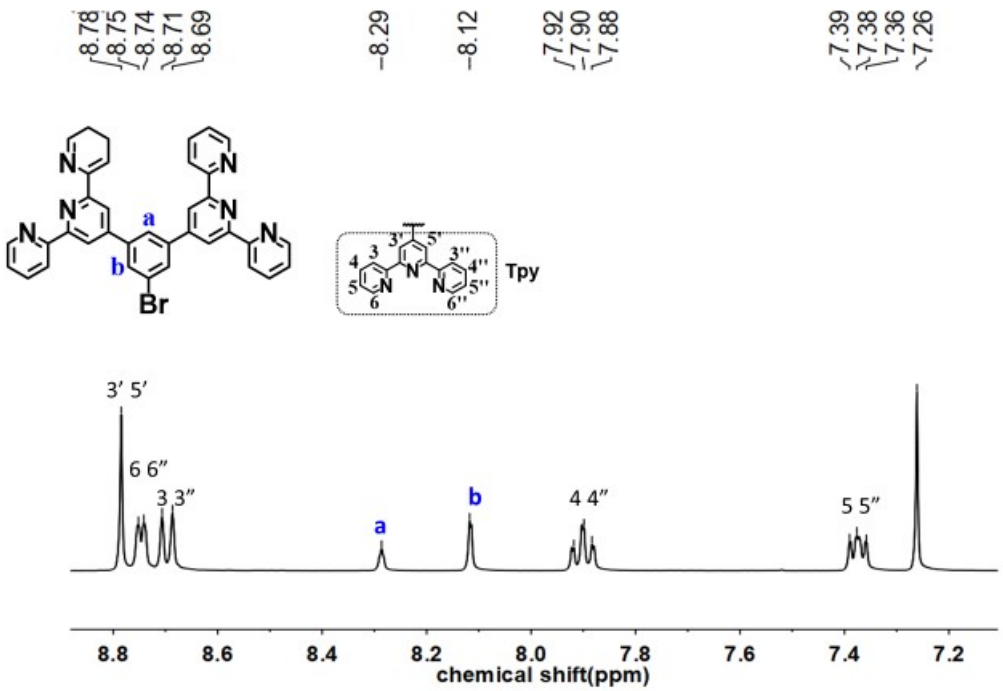


Figure S25: ^{1}H NMR spectrum (500 MHz) of **S5** in $CDCl_3$

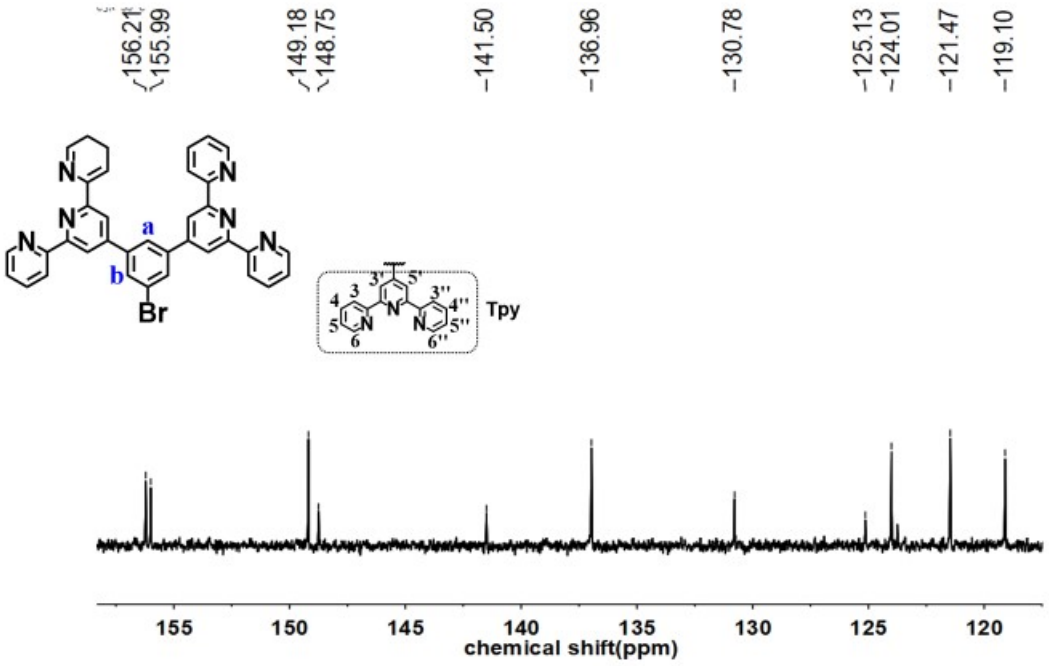


Figure S26: ^{13}C NMR spectrum (100 MHz) of **S5** in $CDCl_3$.

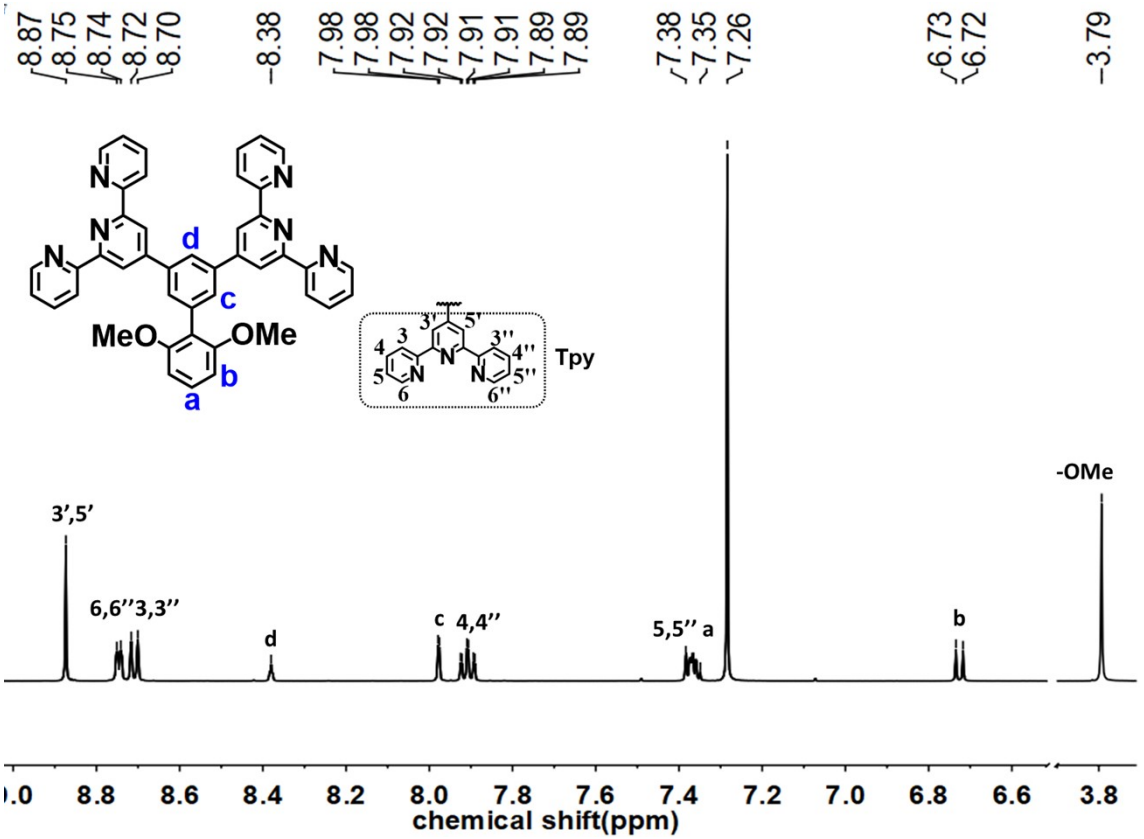


Figure S27: ^{1}H NMR spectrum (400 MHz) of **S6** in $CDCl_3$

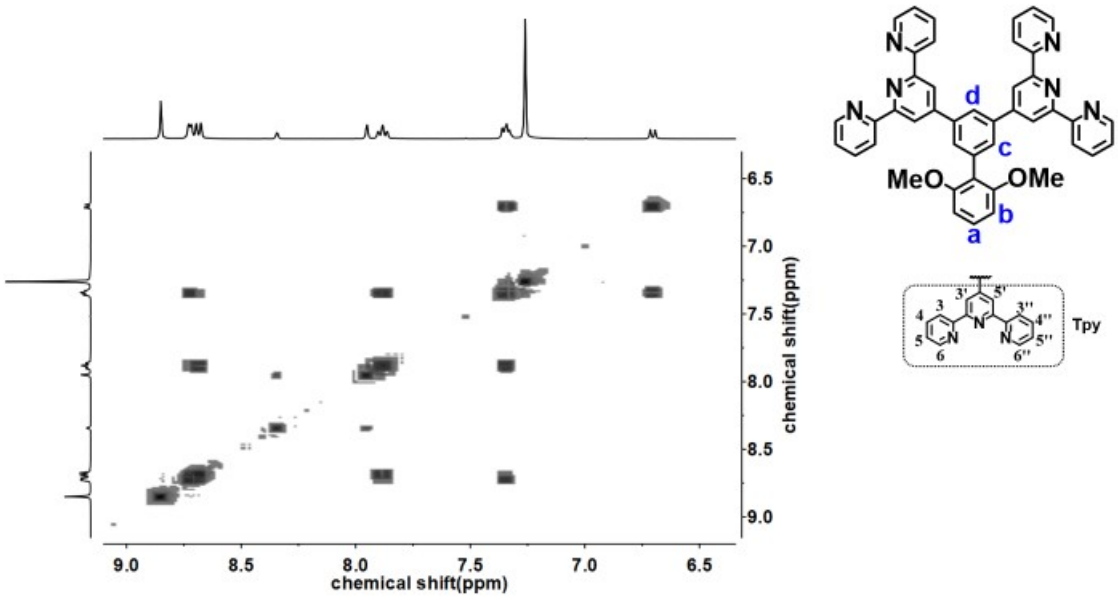


Figure S28: 2D COSY spectrum (400 MHz) of **S6** in $CDCl_3$.

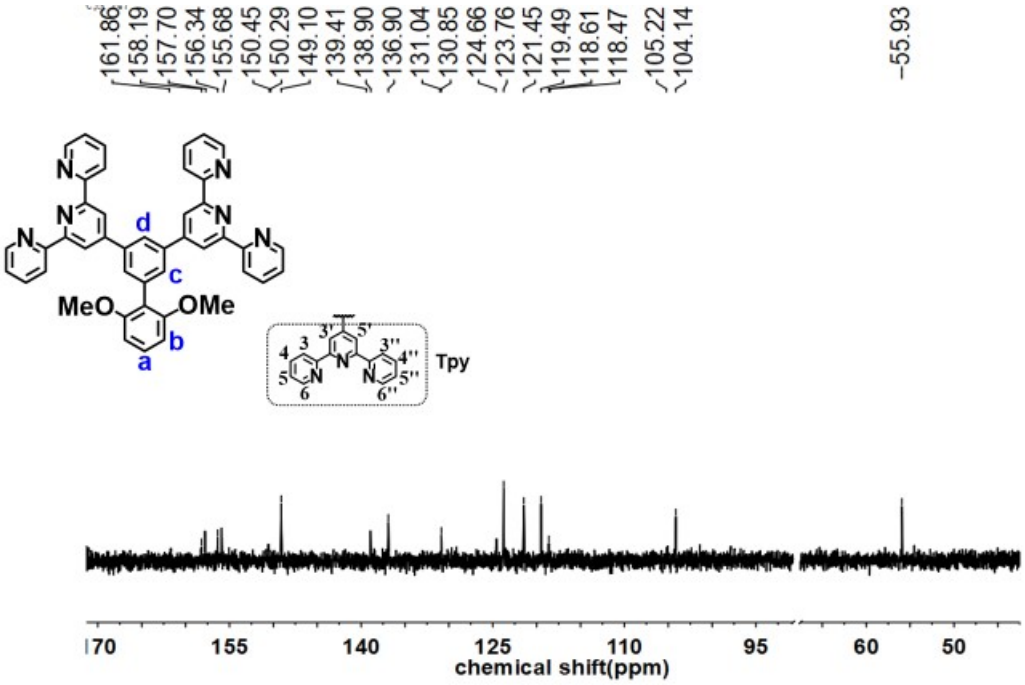


Figure S29: ^{13}C NMR spectrum (100 MHz) of **S6** in $CDCl_3$.

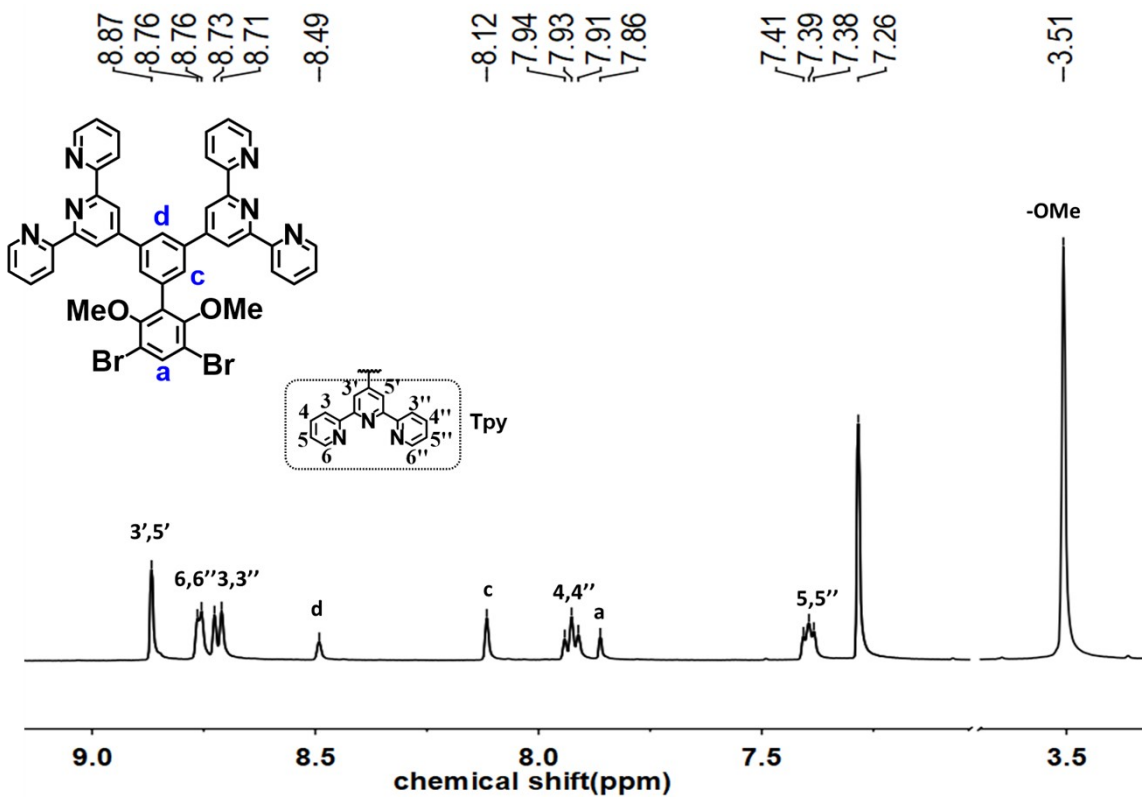


Figure S30: ^{1}H NMR spectrum (400 MHz) of **S7** in $CDCl_3$.

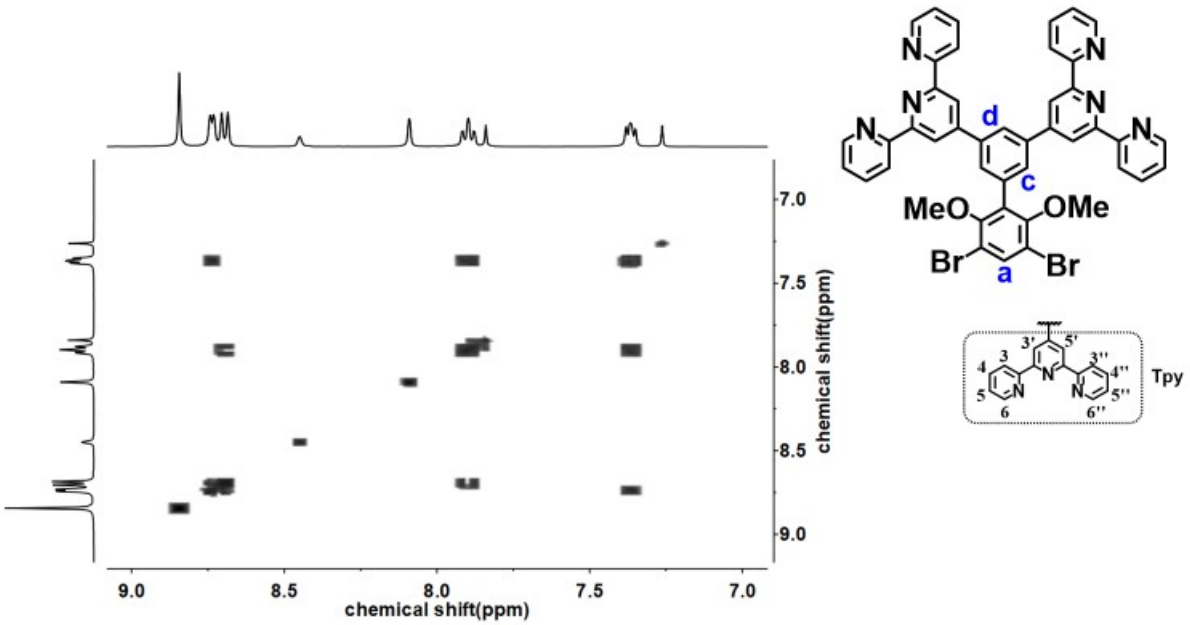


Figure S31: 2D COSY spectrum (400 MHz) of **S7** in $CDCl_3$.

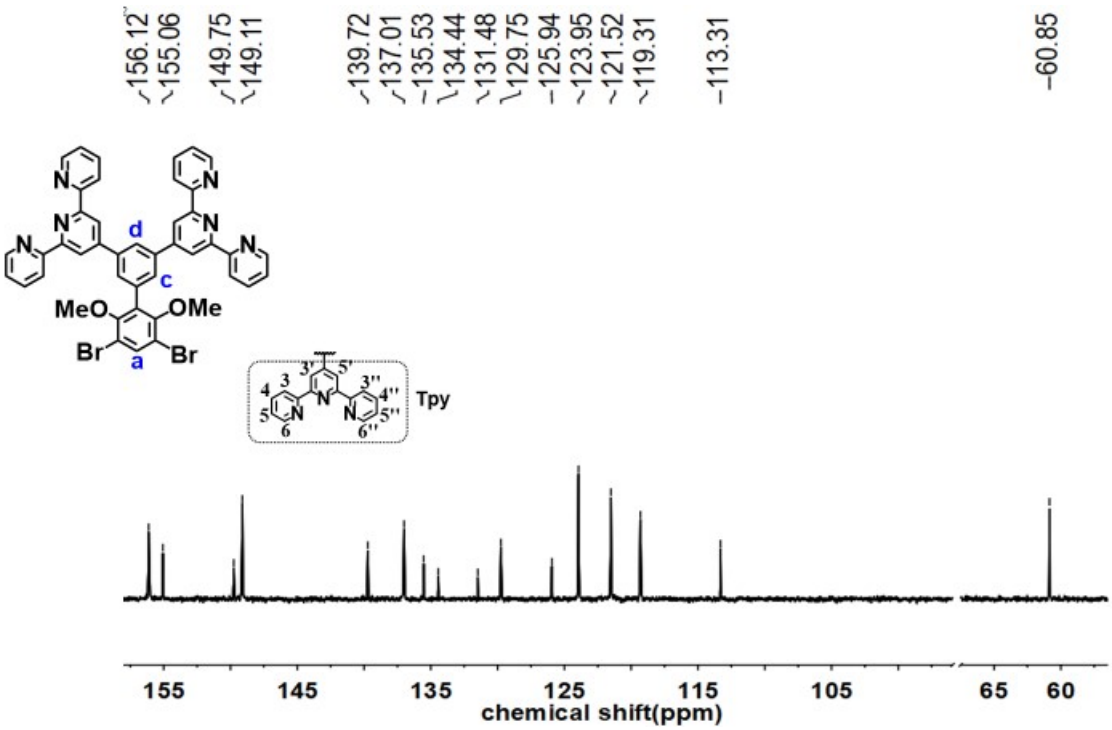


Figure S32: ^{13}C NMR spectrum (100 MHz) of **S7** in $CDCl_3$.

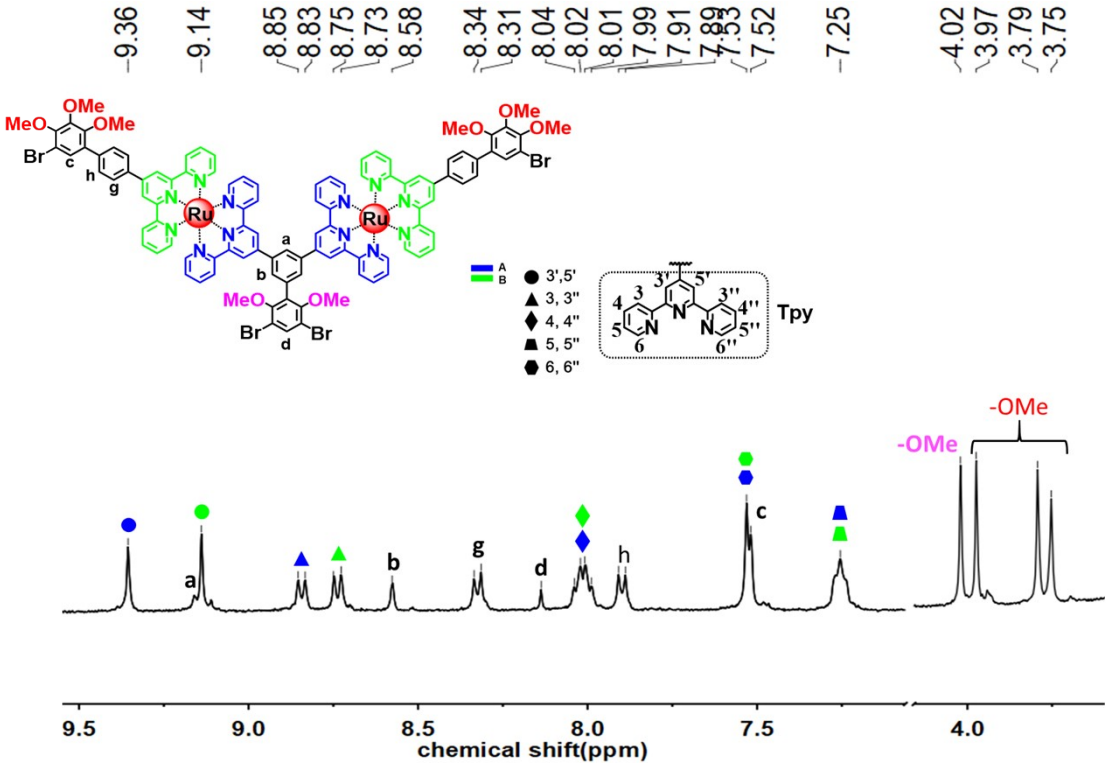


Figure S33: ^{1}H NMR spectrum (500 MHz) of **S9** in CD_3CN.

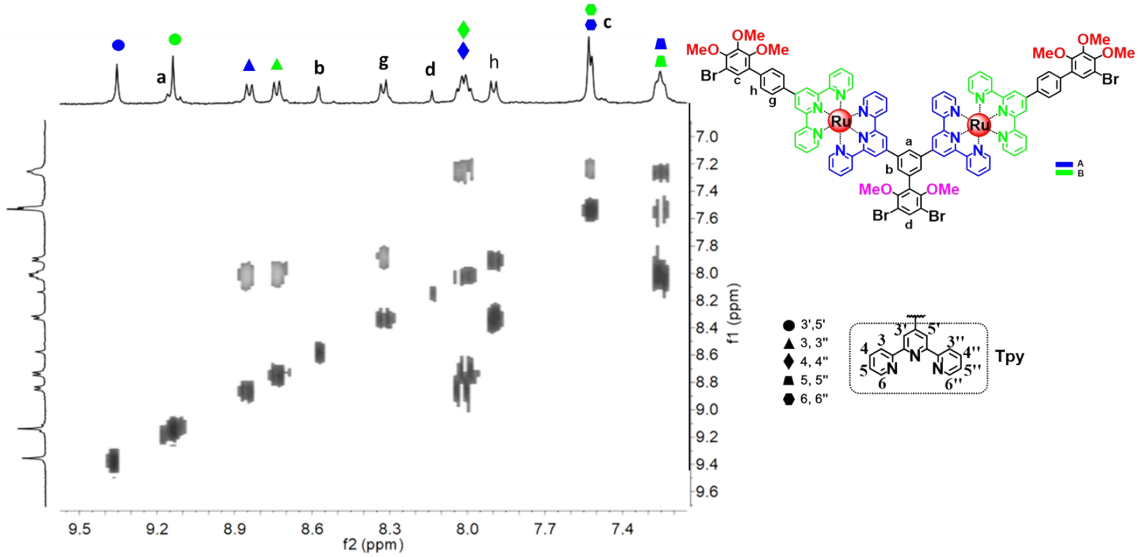


Figure S34: 2D COSY spectrum (500 MHz) of **S9** in CD_3CN.

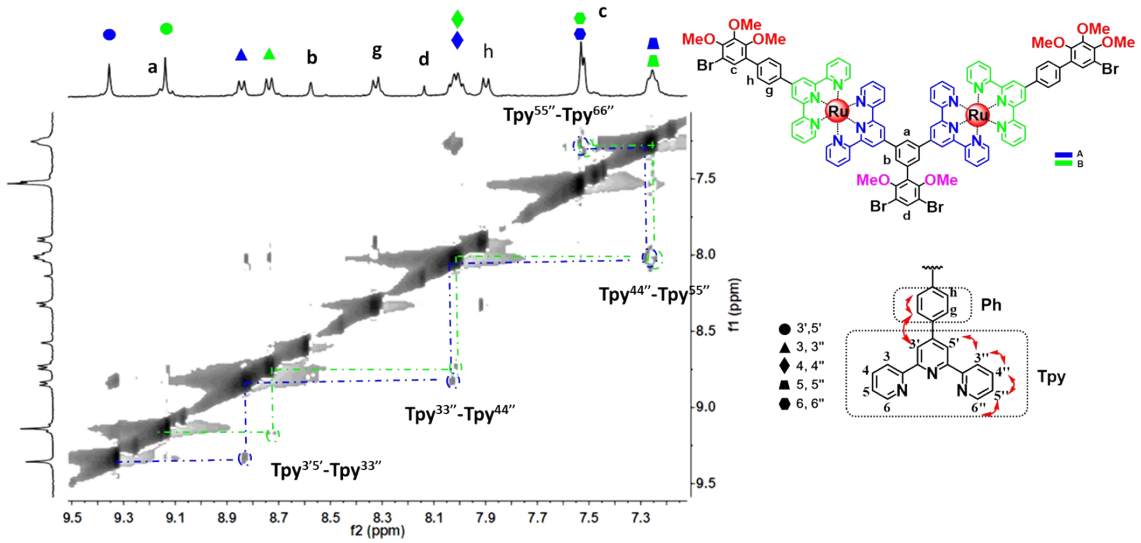


Figure S35: 2D NOESY spectrum (400 MHz) of **S9** in CD_3CN .

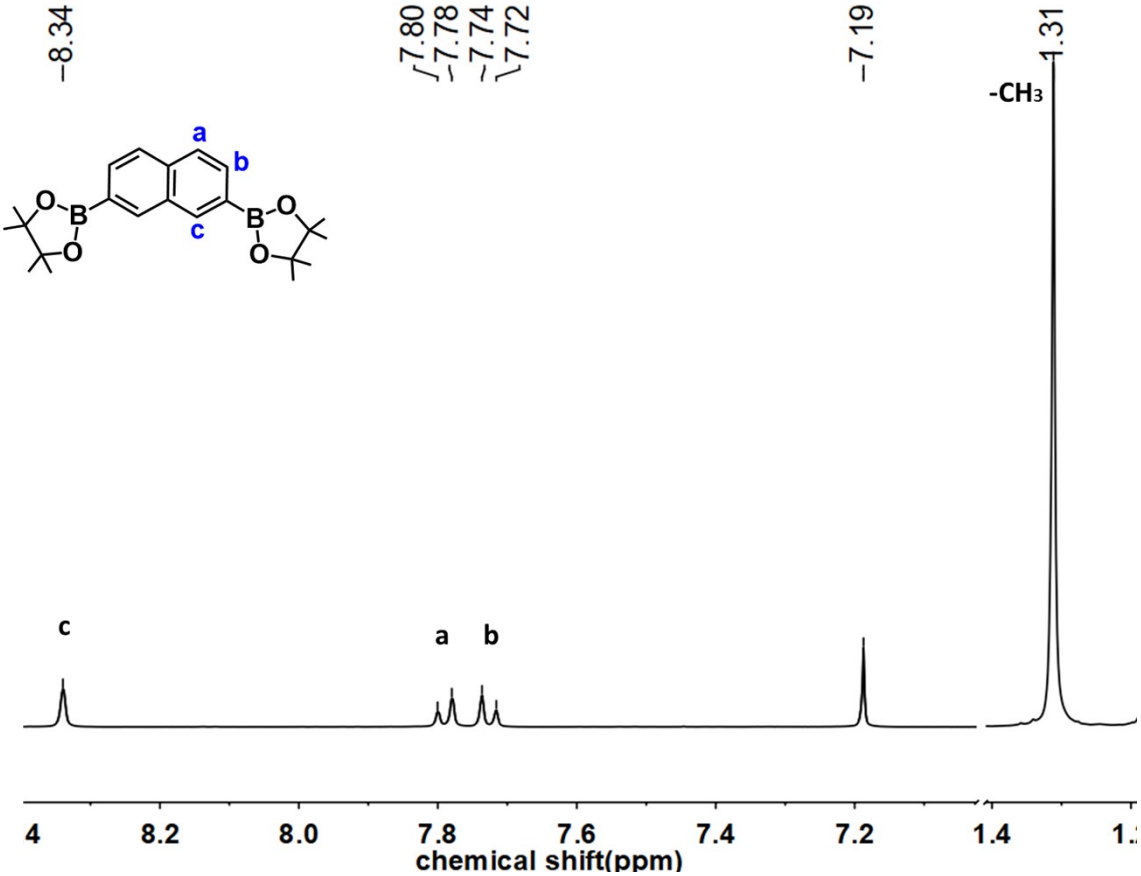


Figure S36: ^1H NMR spectrum (500 MHz) of **S11** in $CDCl_3$.

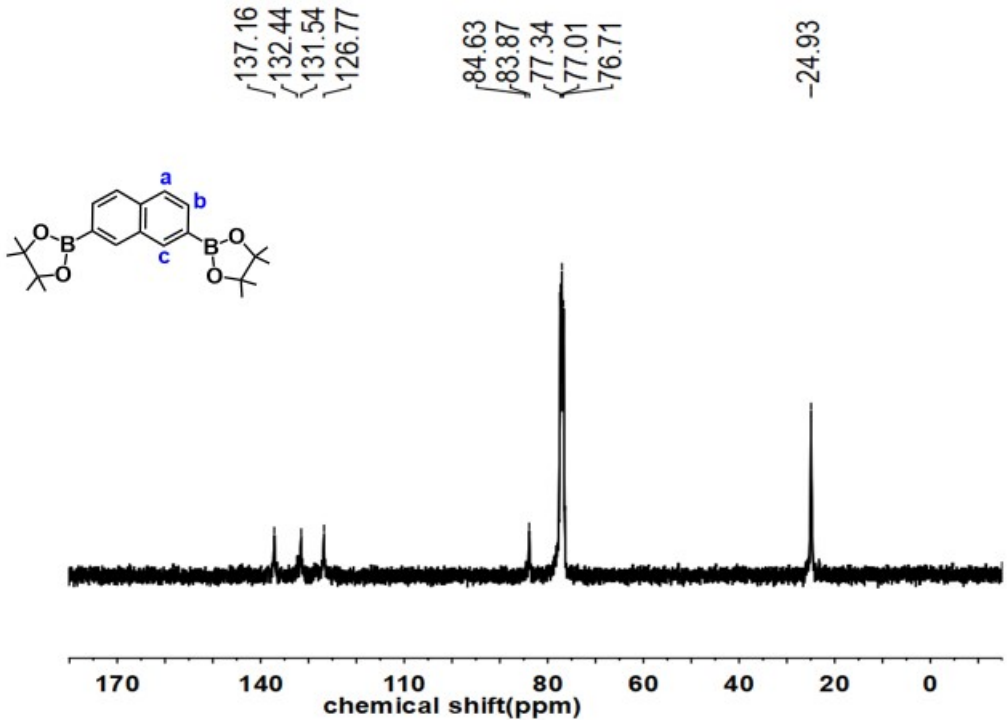


Figure S37: ^{13}C NMR spectrum (125 MHz) of **S11** in $CDCl_3$.

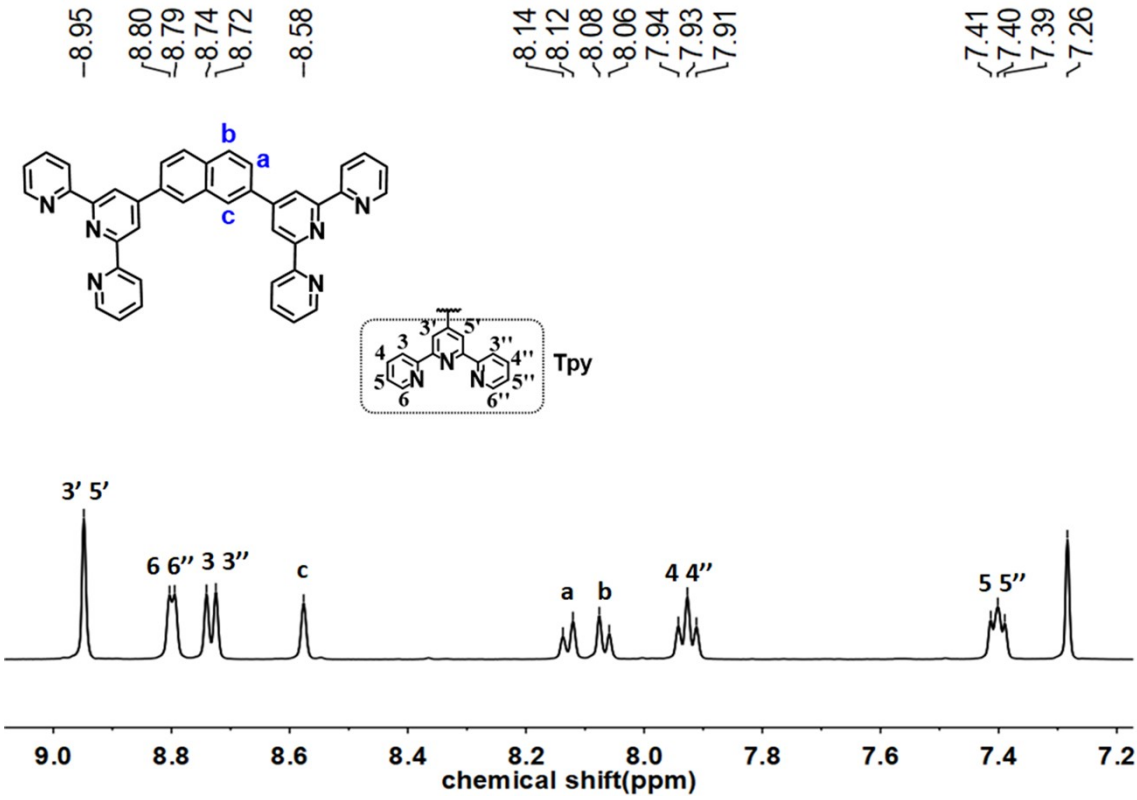


Figure S38: ^{1}H NMR spectrum (500 MHz) of **S13** in $CDCl_3$.

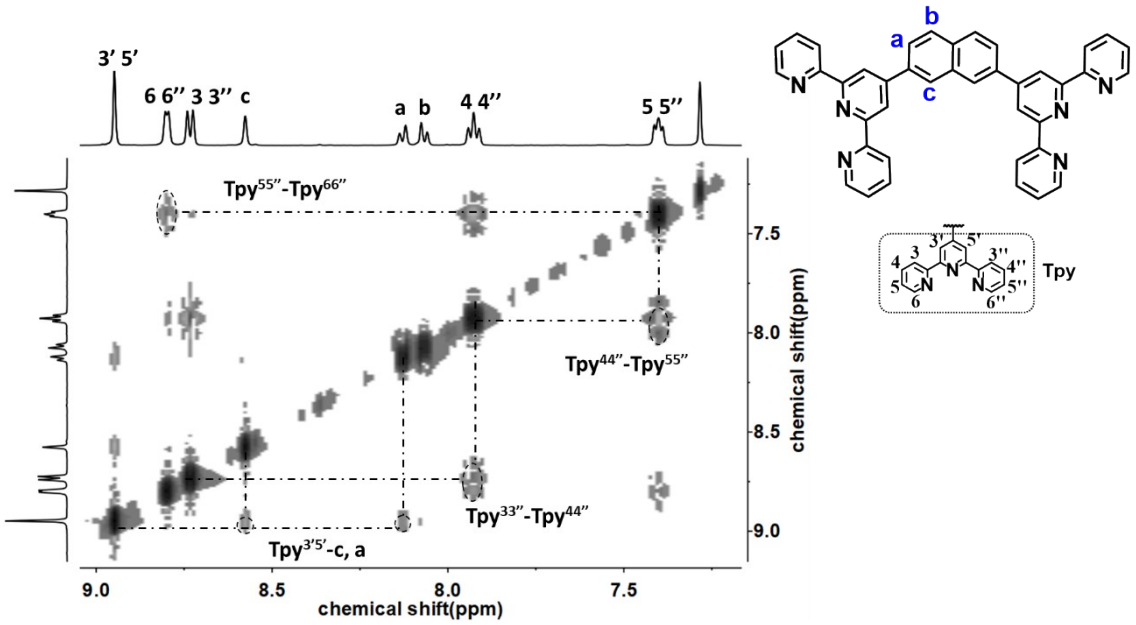


Figure S39: 2D NOESY spectrum (500 MHz) of **S13** in $CDCl_3$.

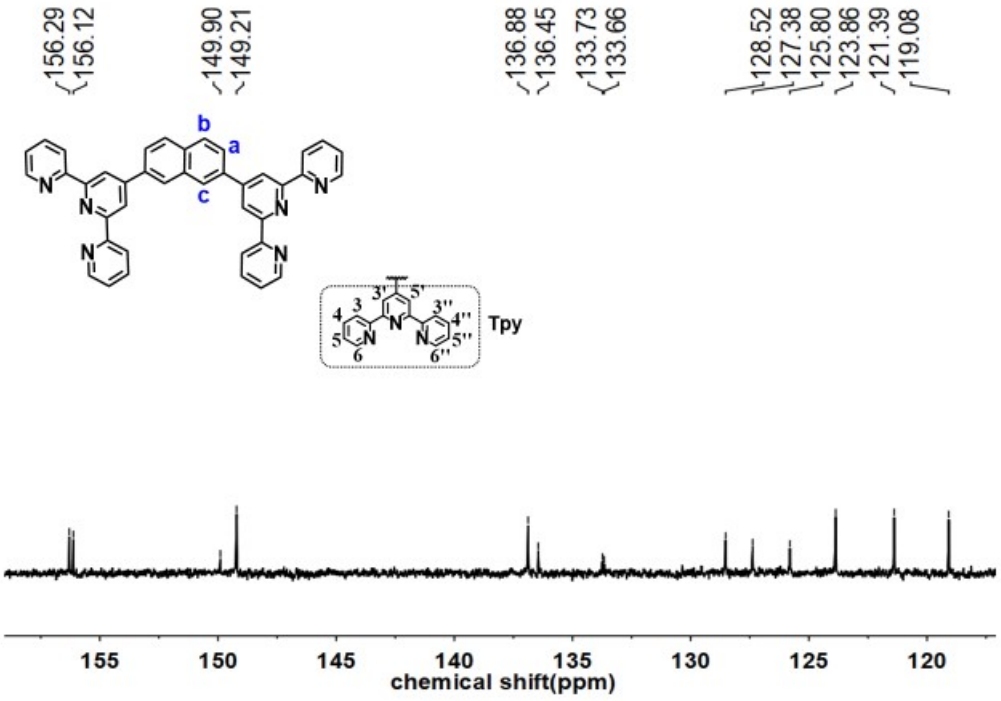


Figure S40: ^{13}C NMR spectrum (125 MHz) of **S13** in $CDCl_3$.

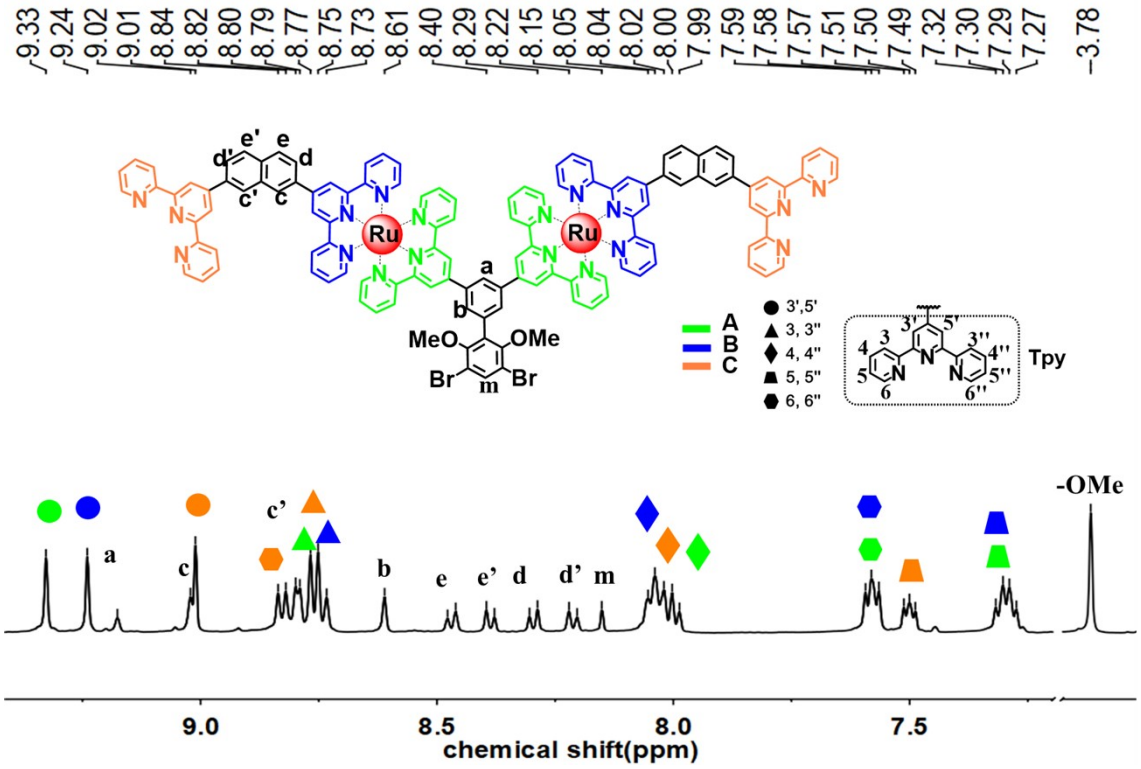


Figure S41: ^{1}H NMR spectrum (400 MHz) of **S15** in CD_3CN.

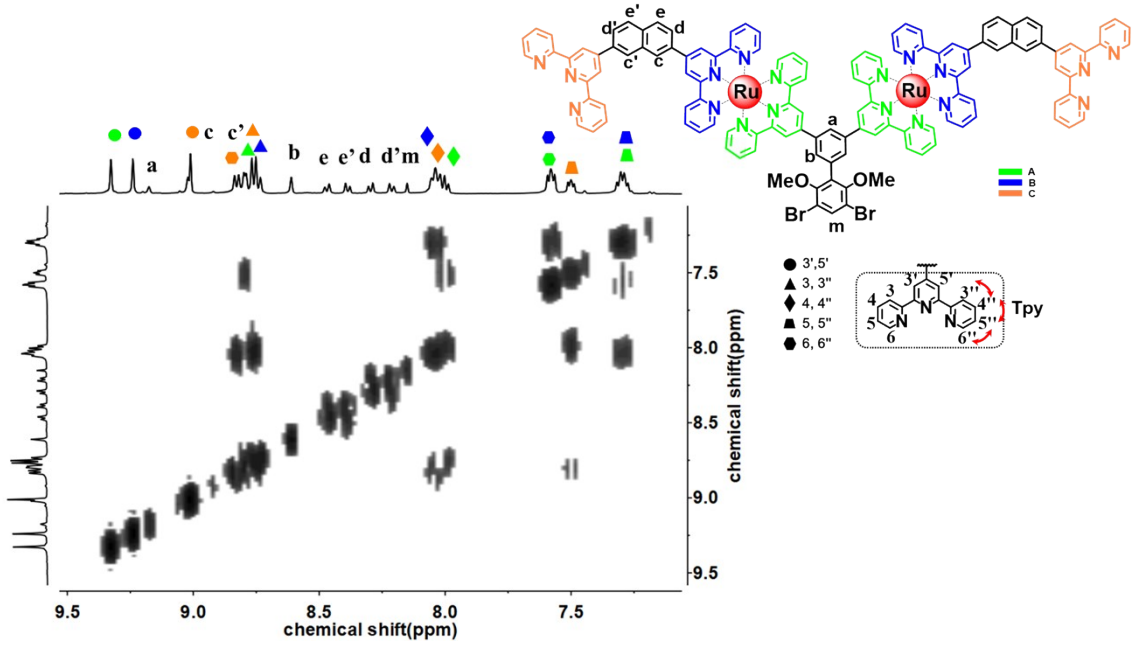


Figure S42: 2D COSY spectrum (500 MHz) of **S15** in CD_3CN .

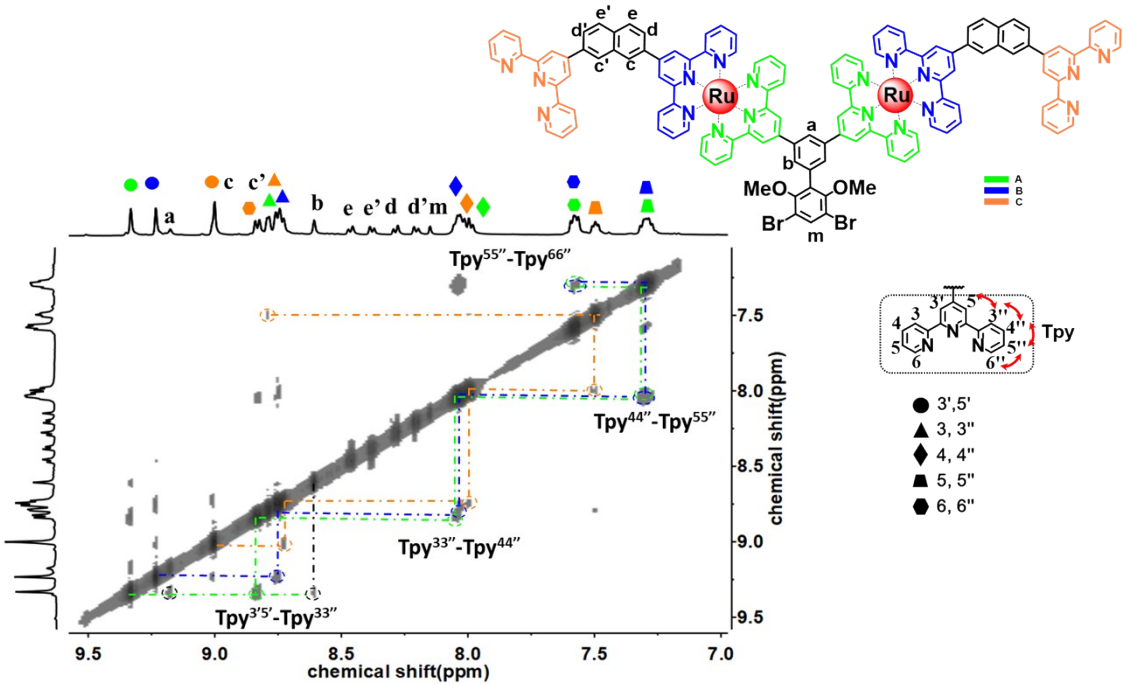


Figure S43: 2D NOESY spectrum (400 MHz) of **S15** in CD_3CN .

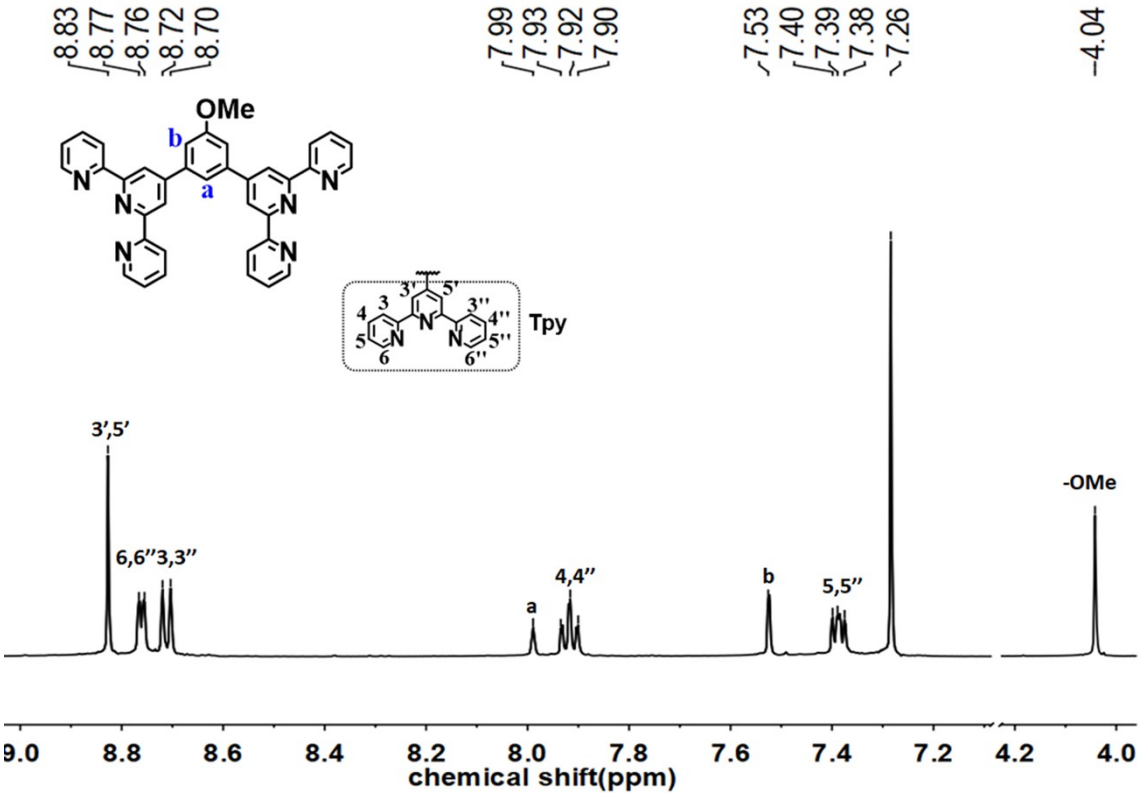


Figure S44: ^1H NMR spectrum (400 MHz) of **S17** in $CDCl_3$

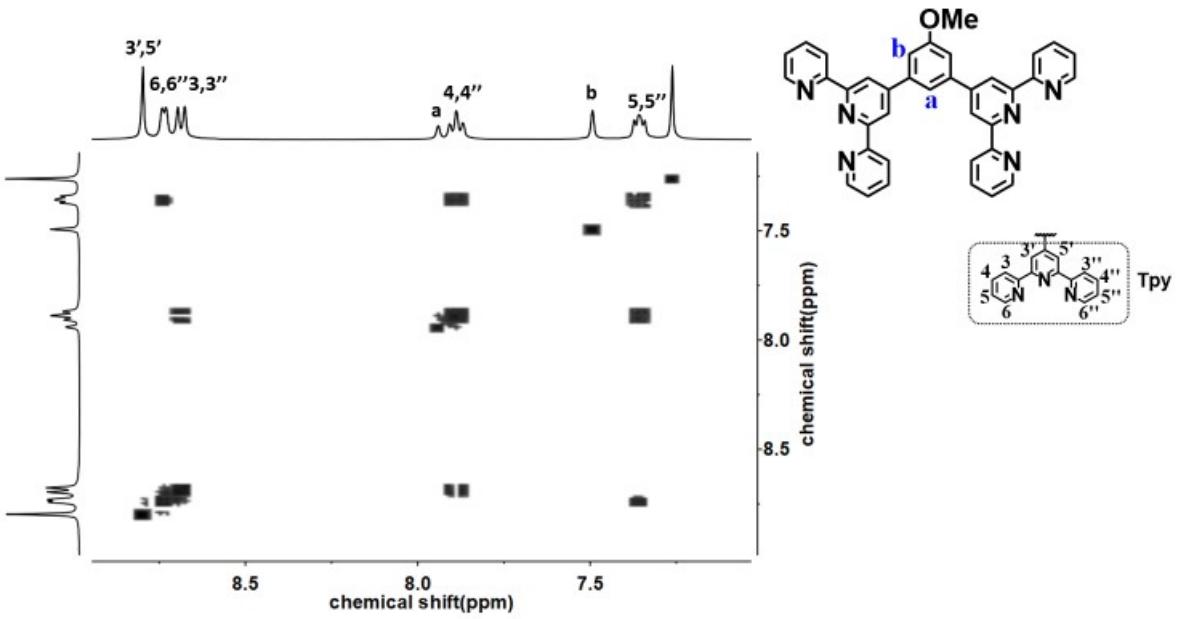


Figure S45: 2D COSY spectrum (400 MHz) of **S17** in $CDCl_3$.

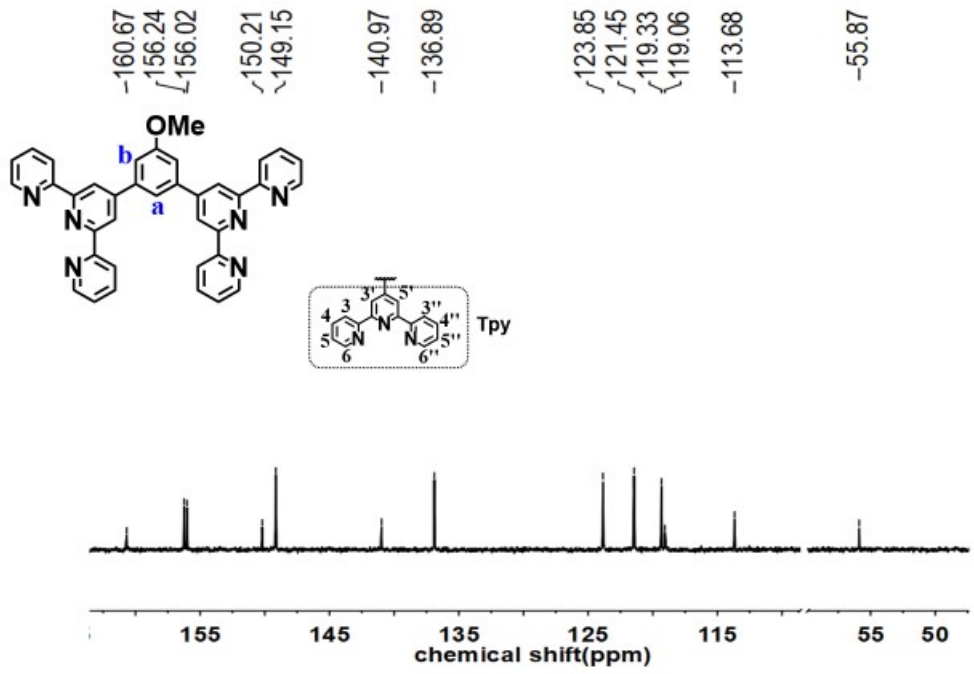


Figure S46: ^{13}C NMR spectrum (400 MHz) of **S17** in $CDCl_3$.

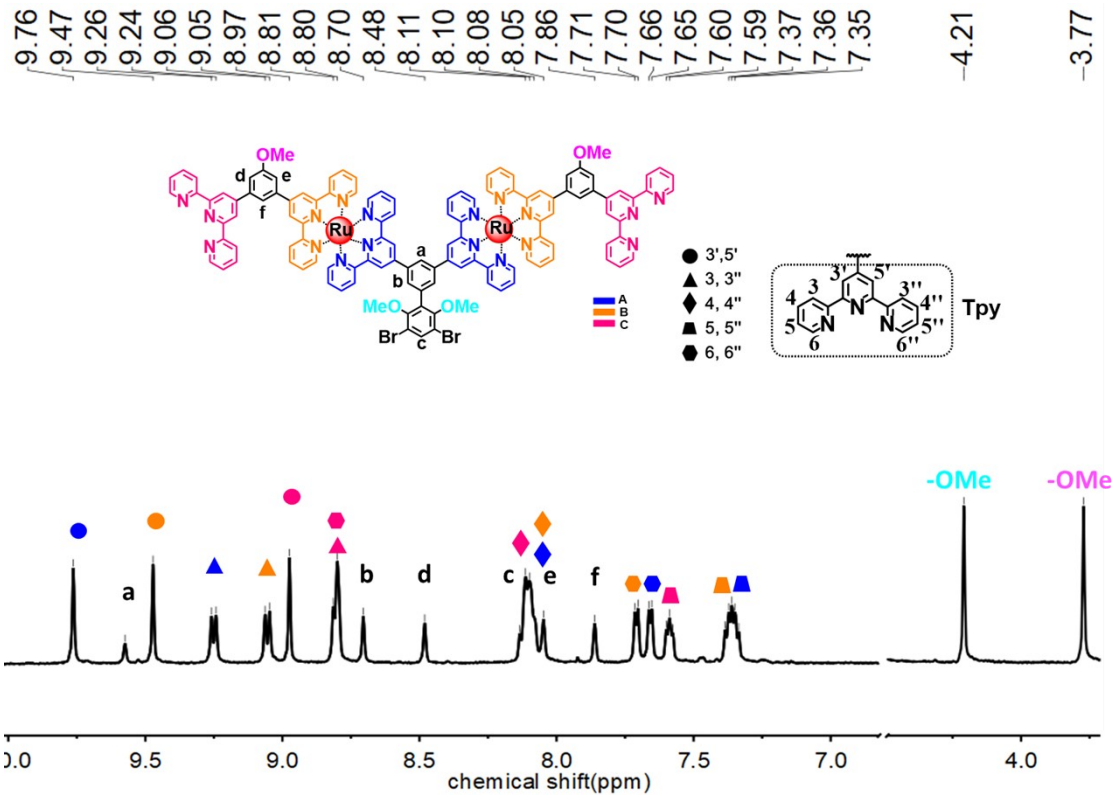


Figure S47: ^{1}H NMR spectrum (400 MHz) of **S18** in CD_3CN.

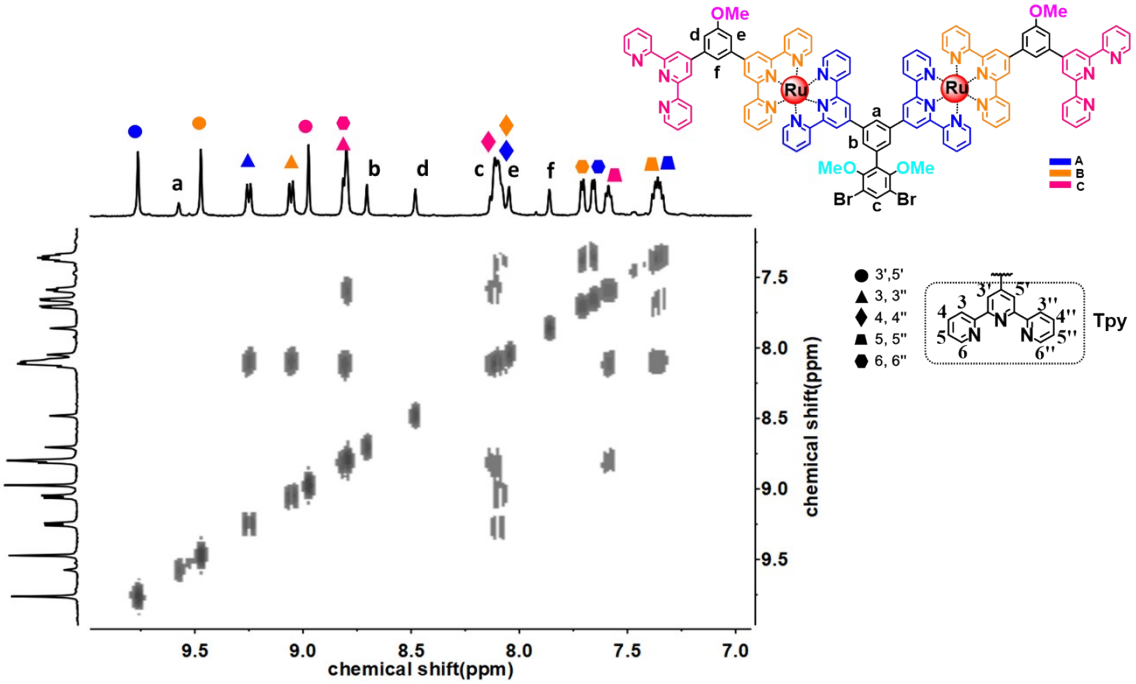


Figure S48: 2D COSY spectrum (400 MHz) of **S18** in CD_3CN.

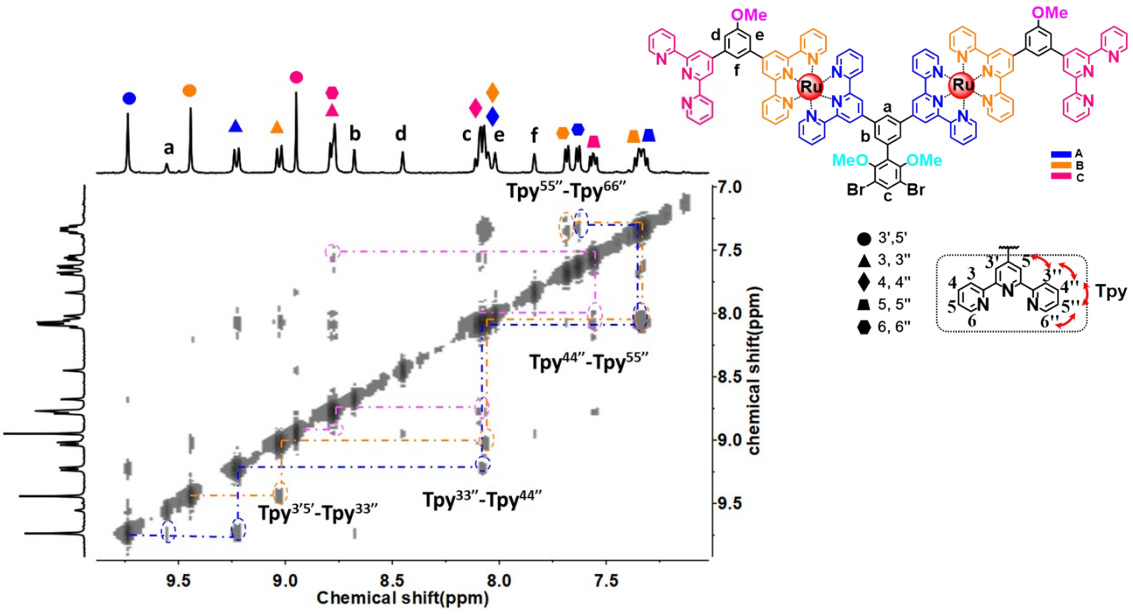


Figure S49: 2D NOESY spectrum (400 MHz) of **S18** in CD_3CN .

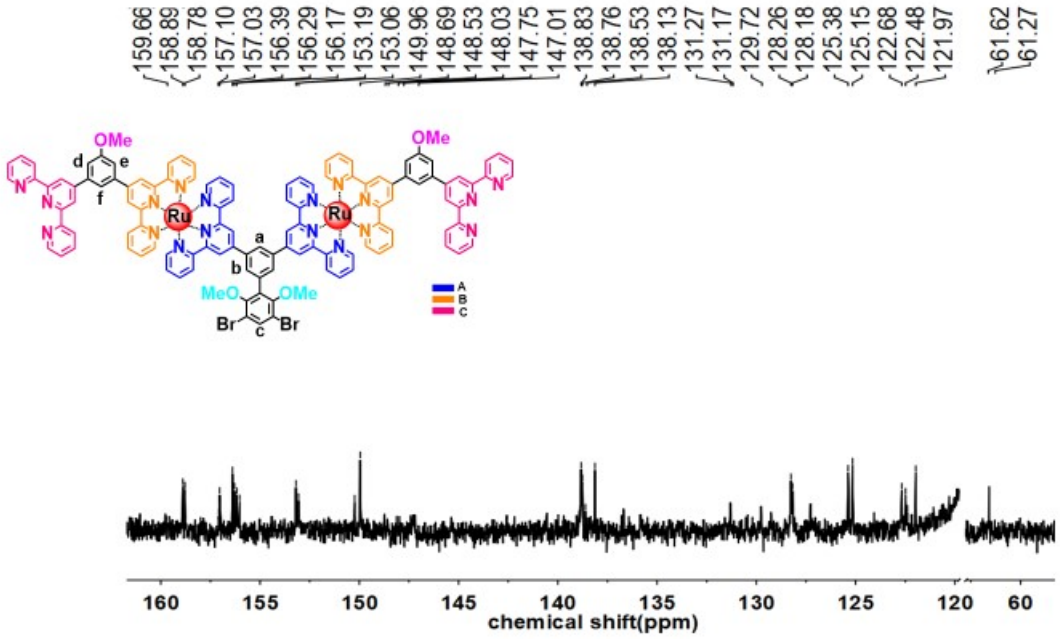


Figure S50: ^{13}C NMR spectrum (125 MHz) of **S18** in CD_3CN.

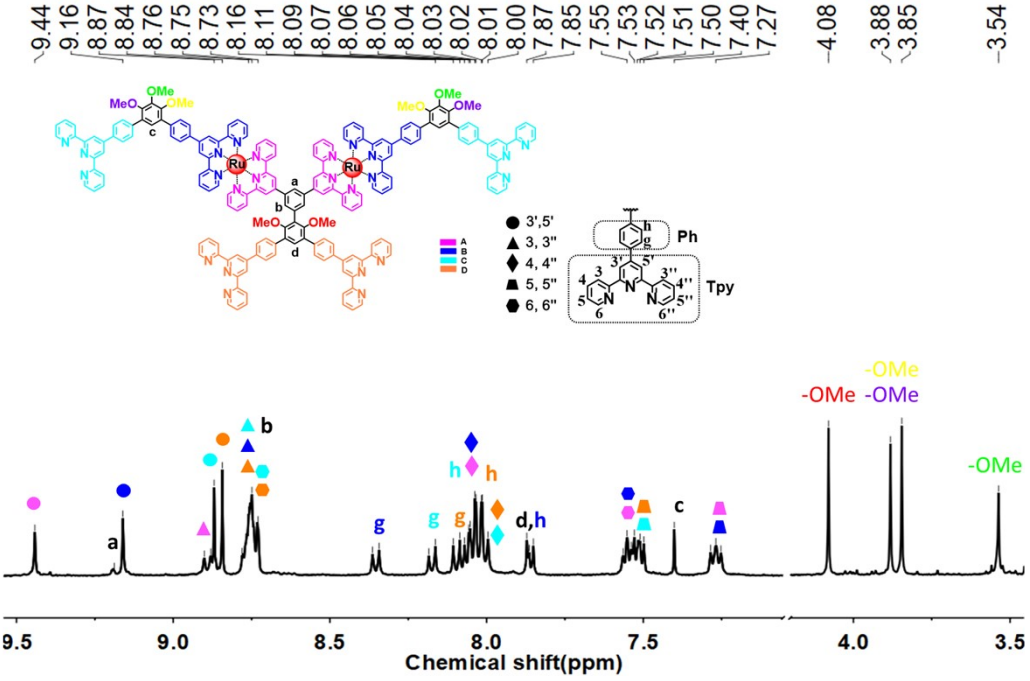


Figure S51: ^{1}H NMR spectrum (500 MHz) of **LA** in CD_3CN.

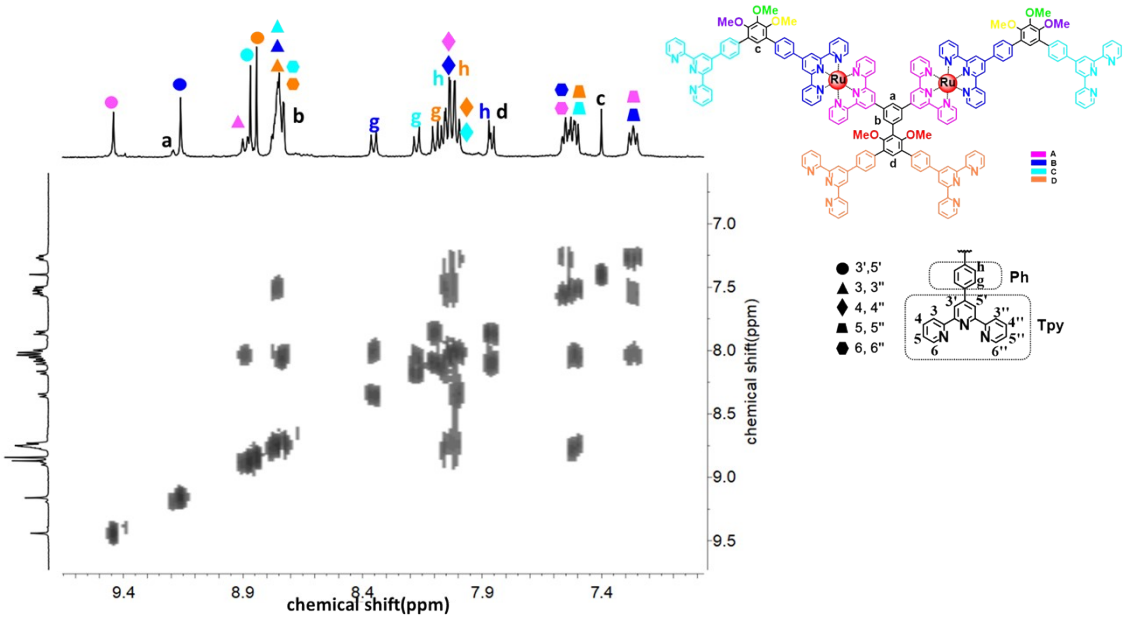


Figure S52: 2D COSY spectrum (400 MHz) of **LA** in CD_3CN.

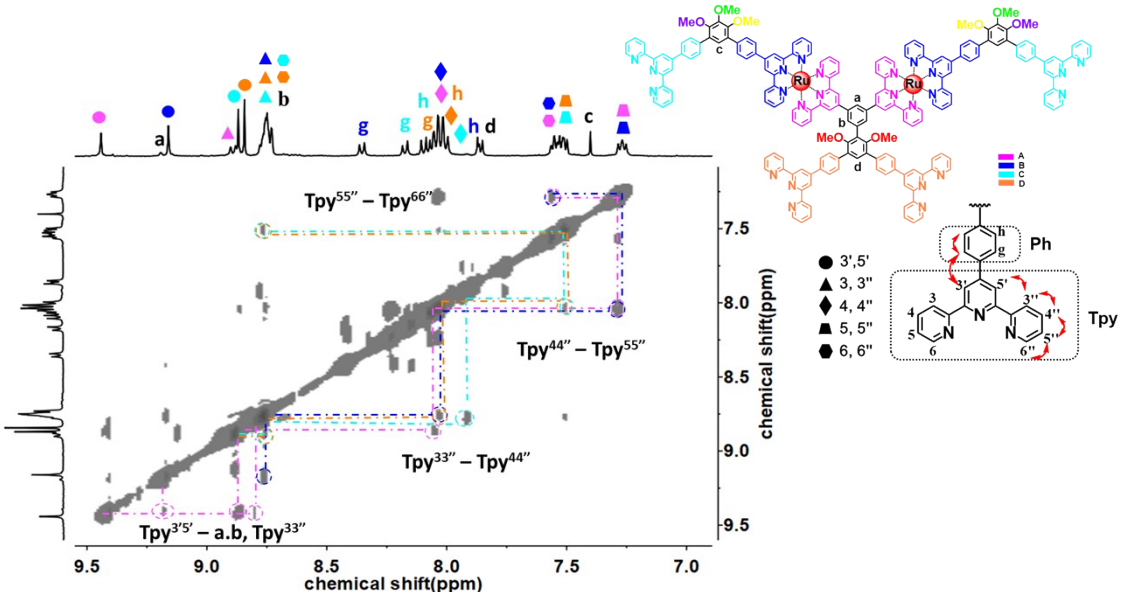


Figure S53: 2D NOESY spectrum (500 MHz) of **LA** in CD_3CN.

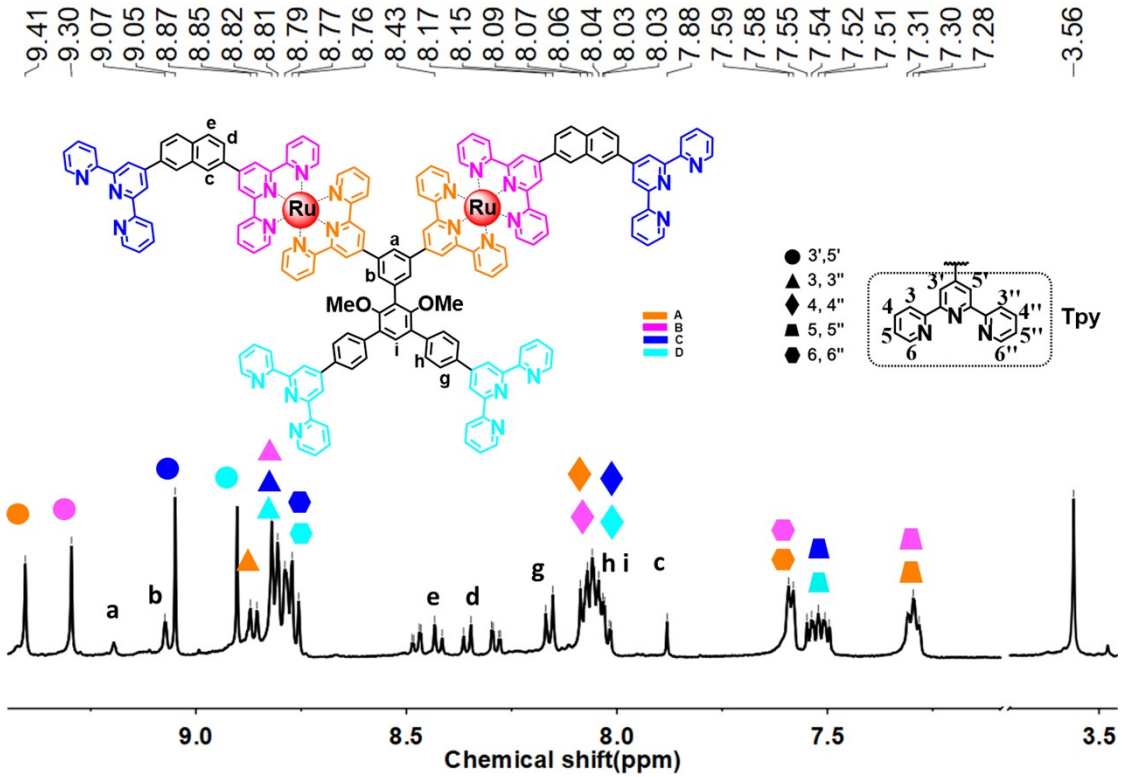


Figure S54: ^1H NMR spectrum (500 MHz) of **LB** in CD_3CN.

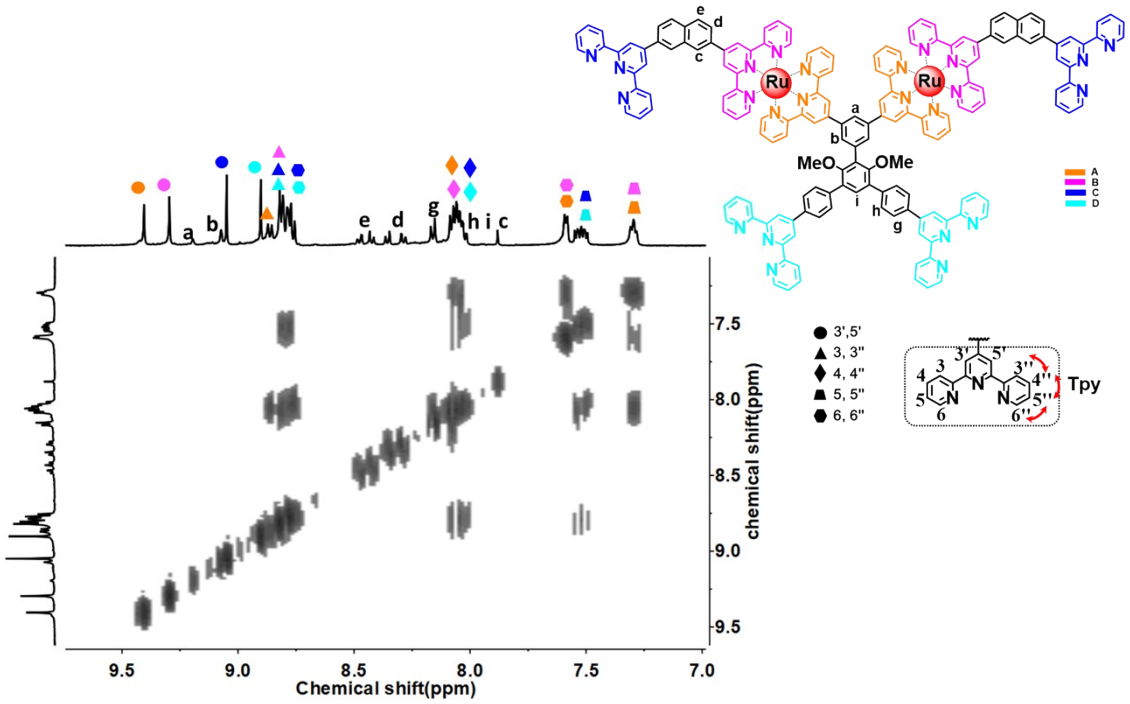


Figure S55: 2D COSY spectrum (400 MHz) of **LB** in CD_3CN.

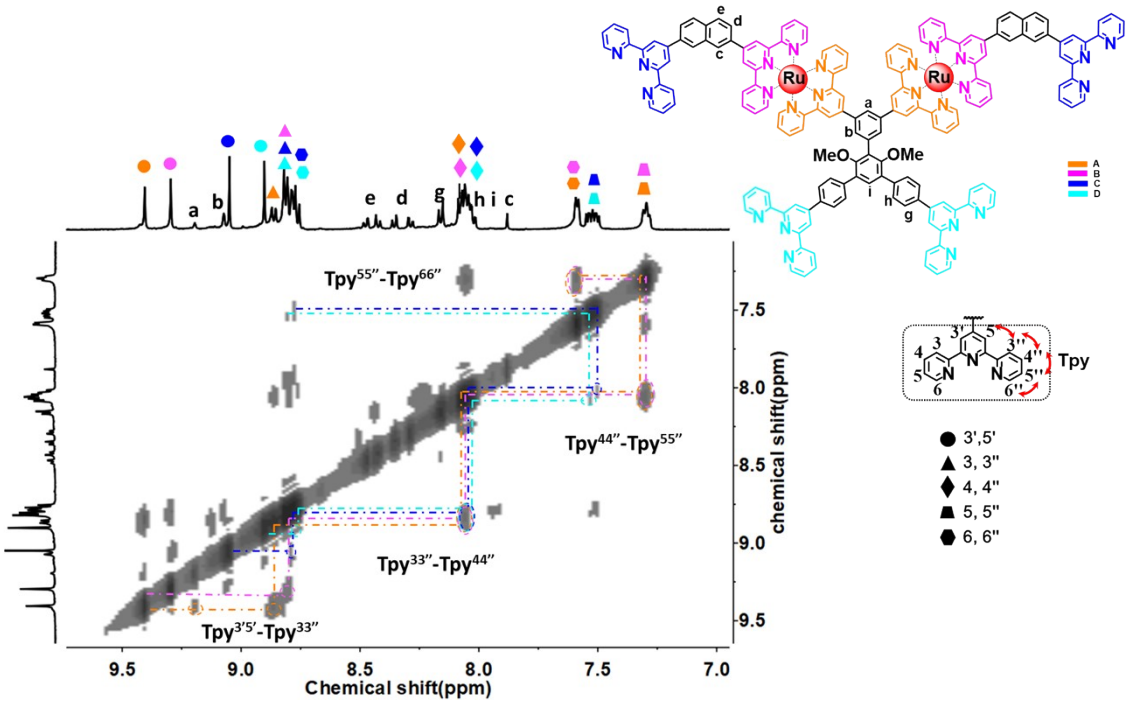


Figure S56: 2D NOESY spectrum (400 MHz) of **LB** in CD_3CN .

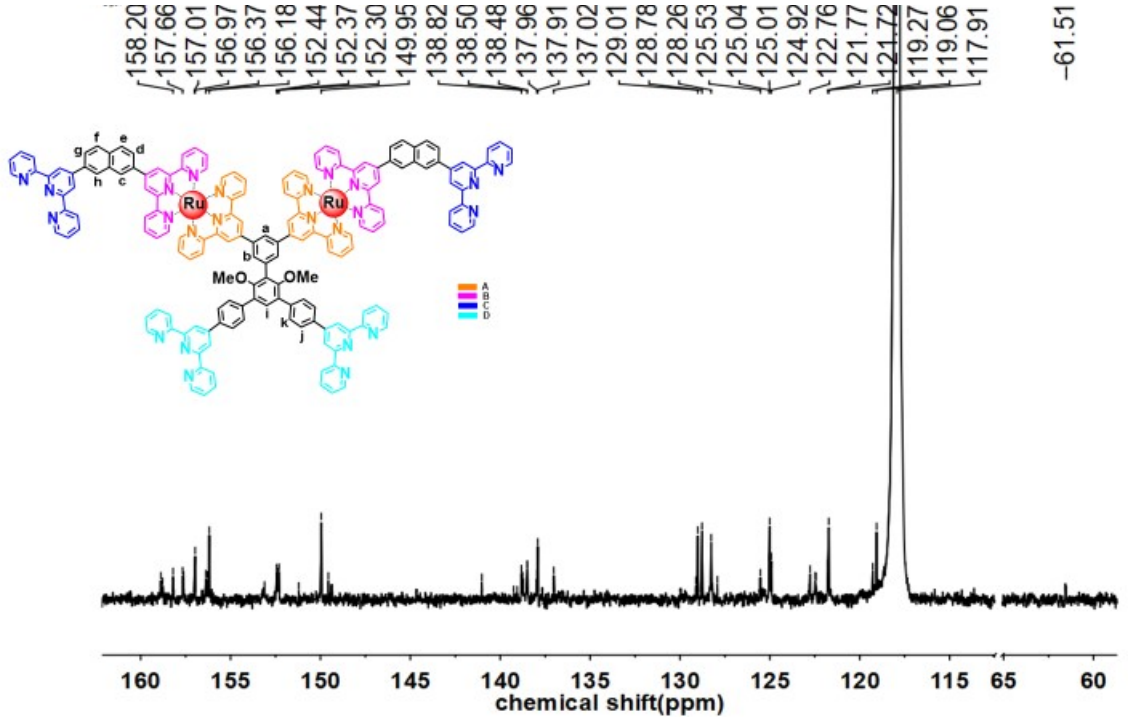


Figure S57: ^{13}C NMR spectrum (125 MHz) of **LB** in CD_3CN.

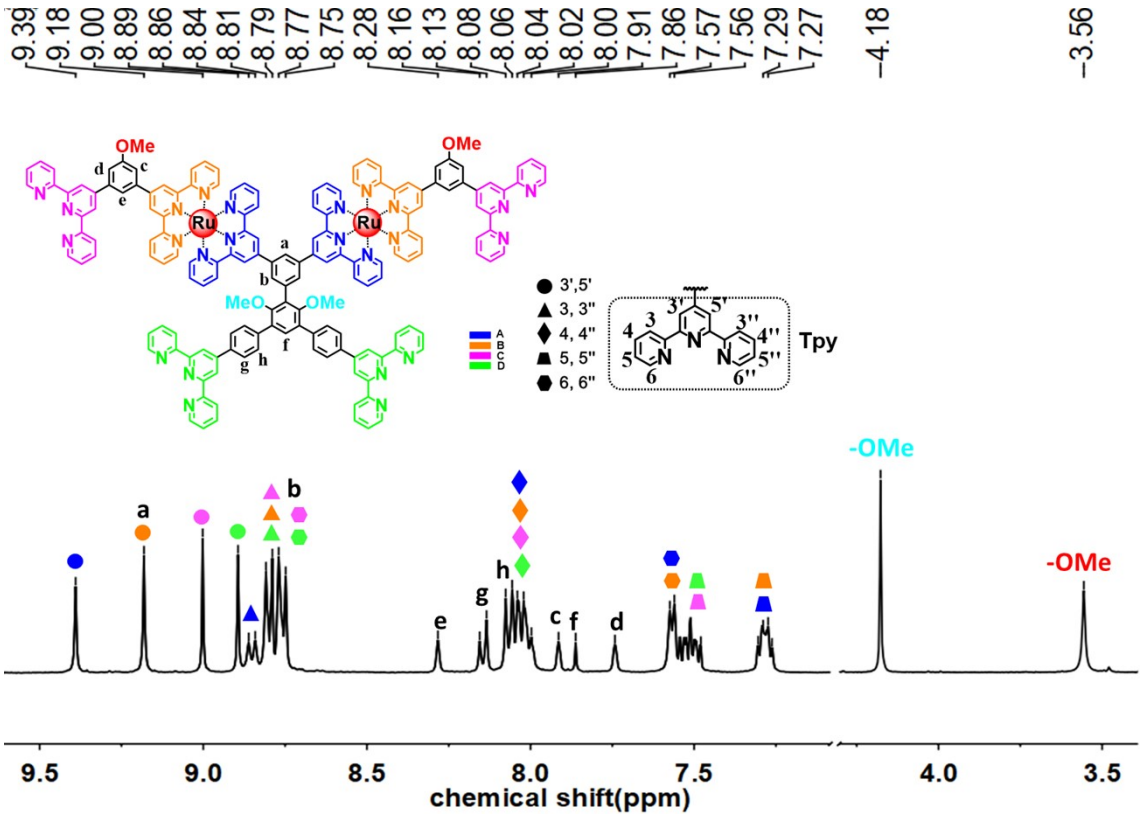


Figure S58: ^{1}H NMR spectrum (400 MHz) of **LC** in CD_3CN.

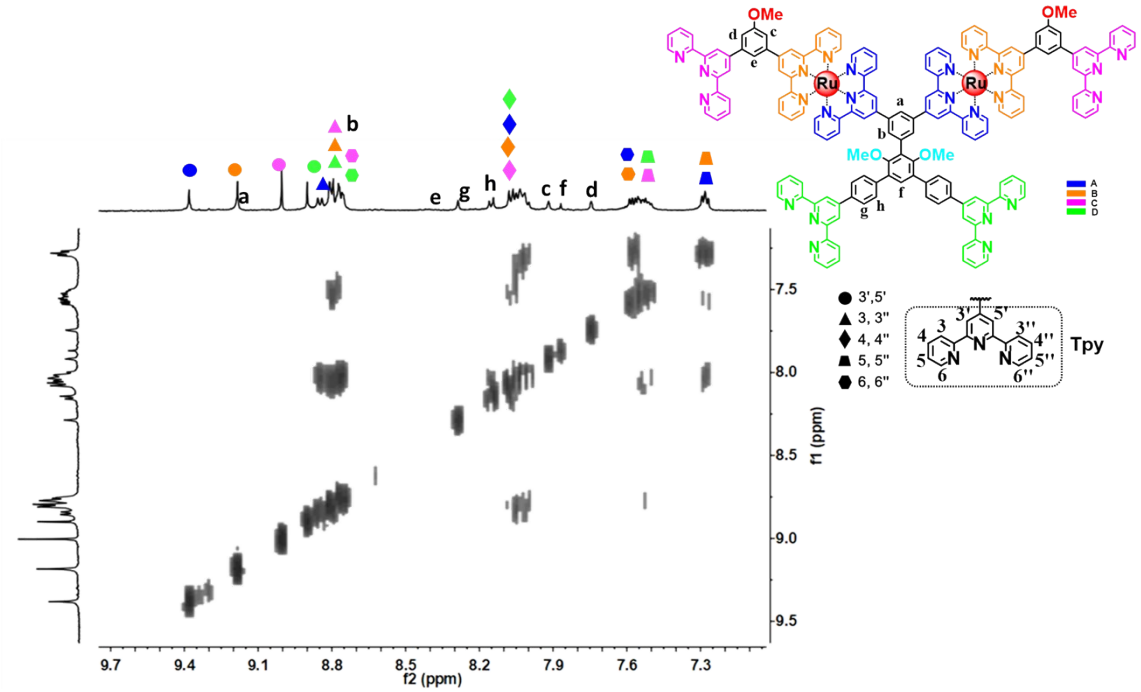


Figure S59: 2D COSY spectrum (400 MHz) of **LC** in CD_3CN.

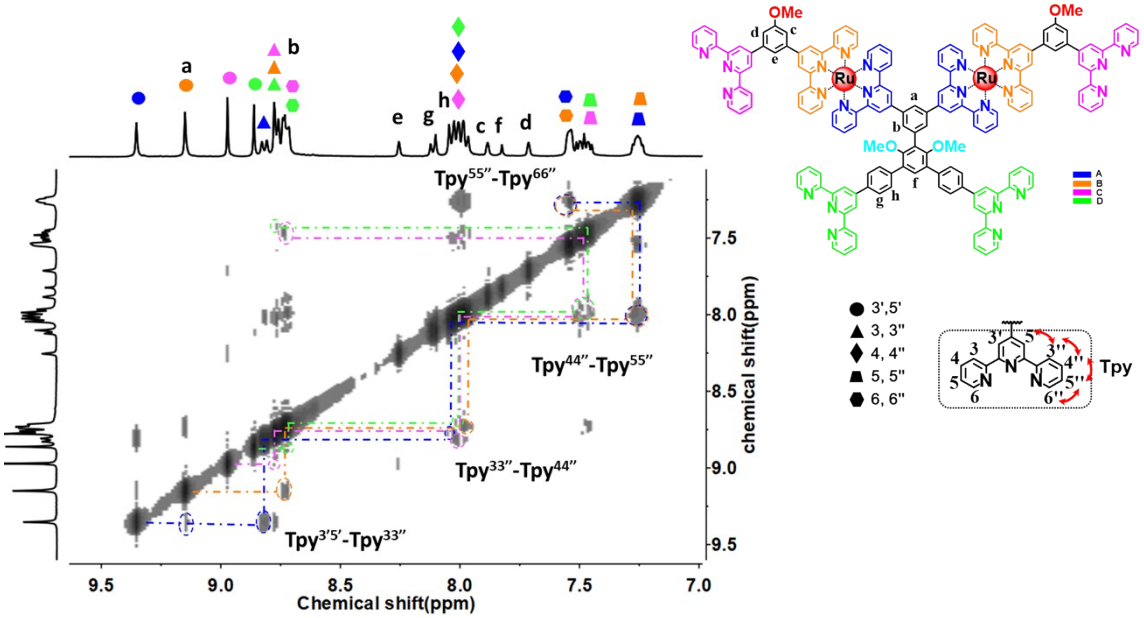


Figure S60: 2D NOESY spectrum (400 MHz) of **LC** in CD_3CN .

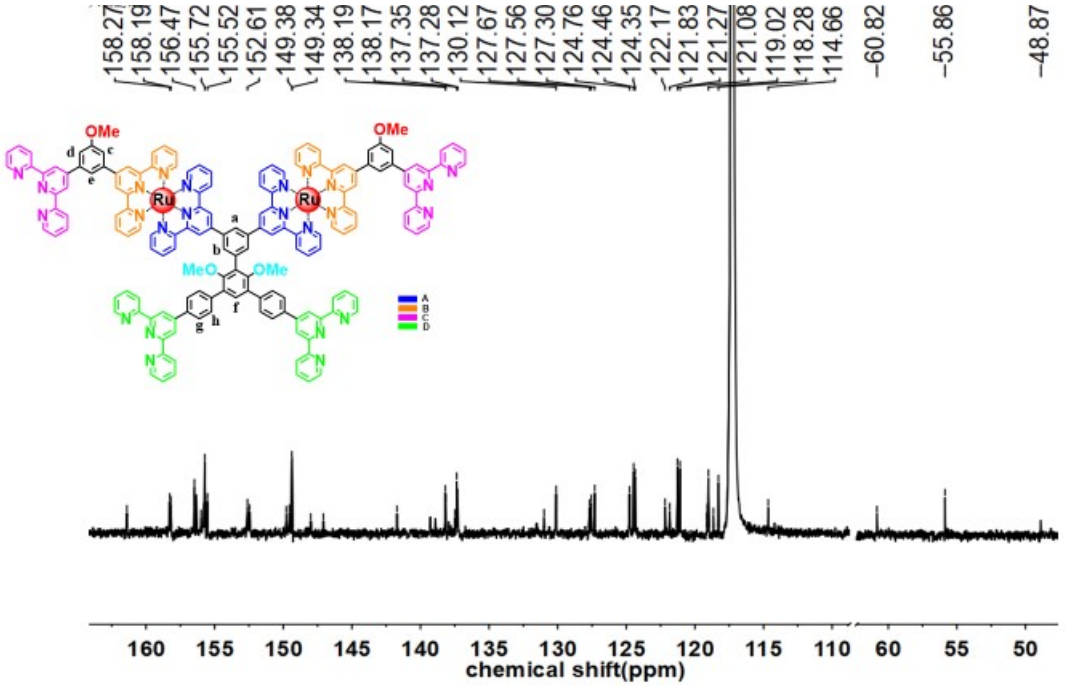


Figure S61: ^{13}C NMR spectrum (400 MHz) of **LC** in CD_3CN.

7. ESI-MS spectra data of ligands and complexes

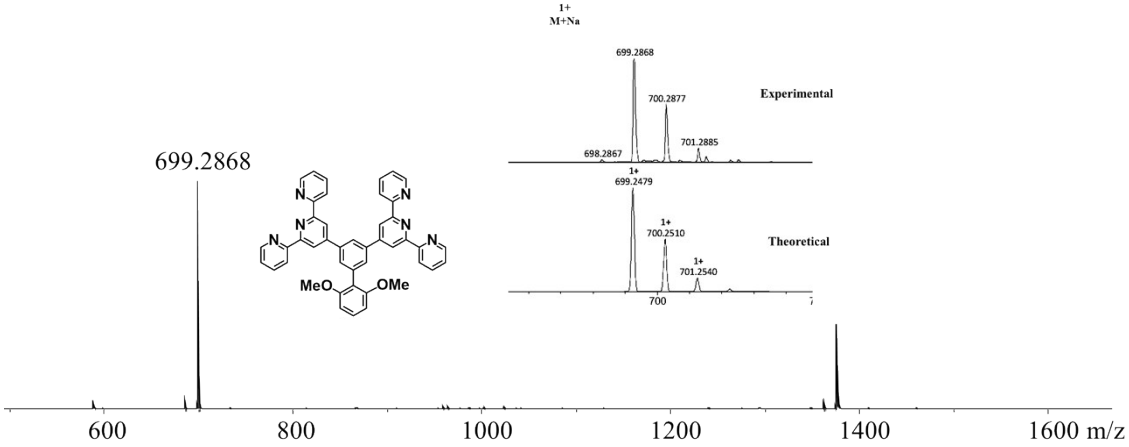


Figure S62: Isotope patterns and ESI-MS spectrum of **S6**.

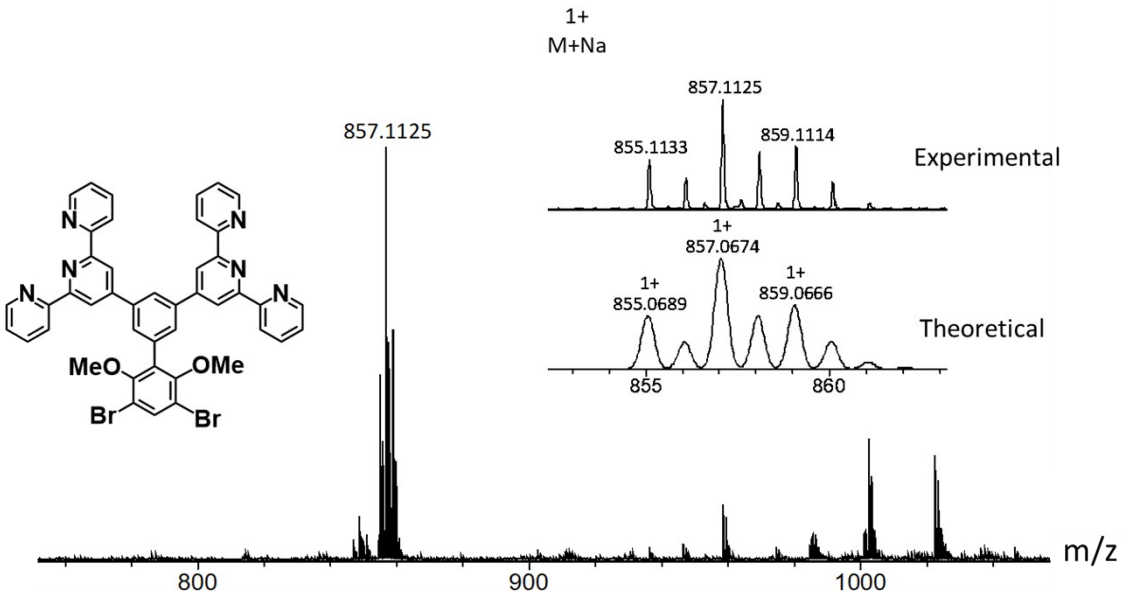


Figure S63: Isotope patterns and ESI-MS spectrum of **S7.**

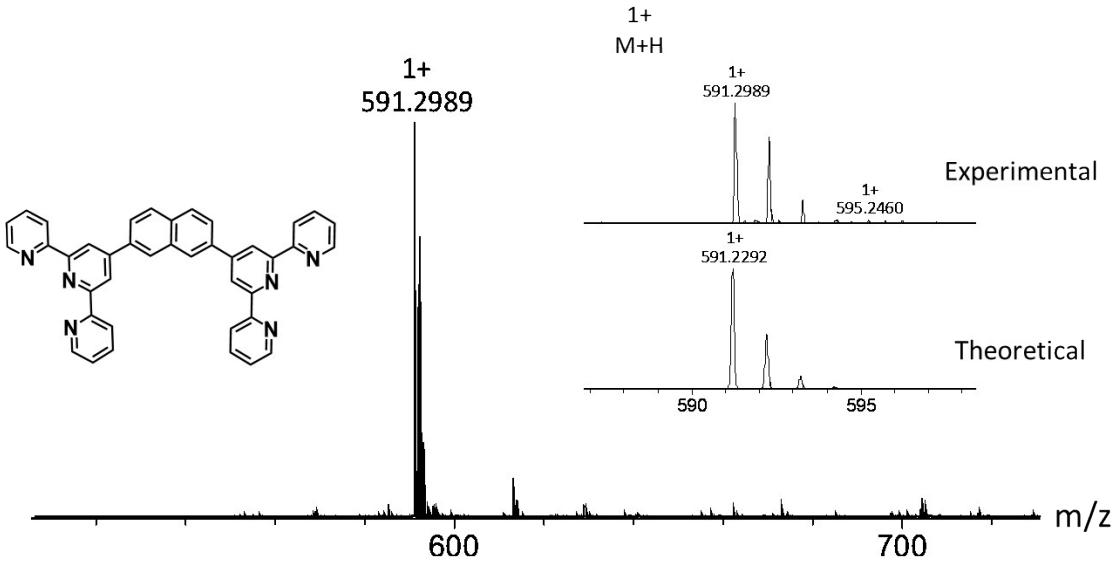


Figure S64: Isotope patterns and ESI-MS spectrum of **S13**

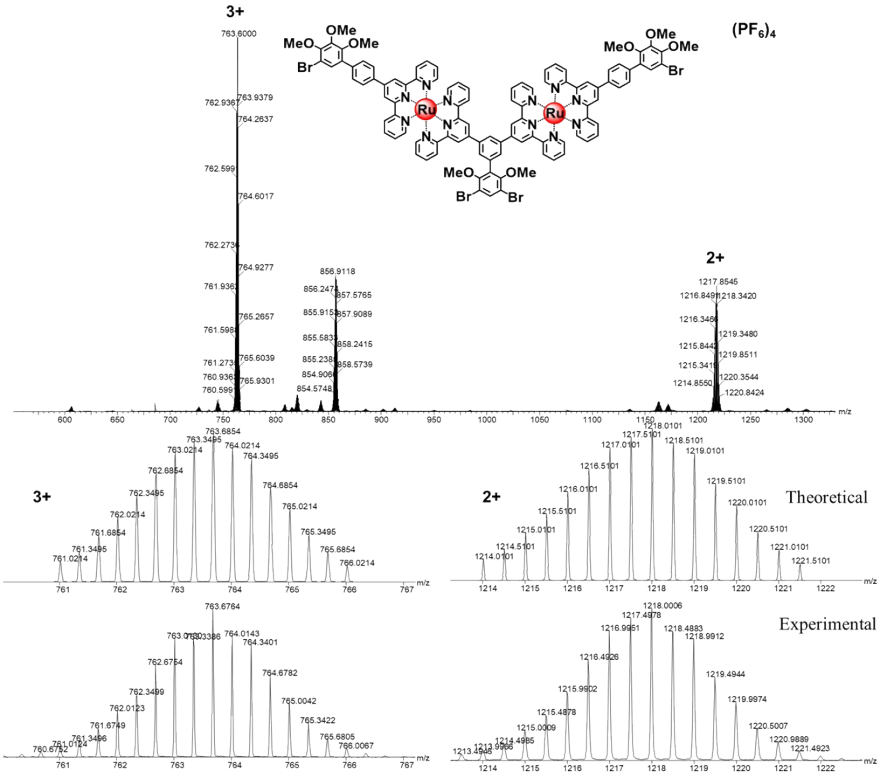


Figure S65: Isotope patterns and ESI-MS spectrum of **S9.**

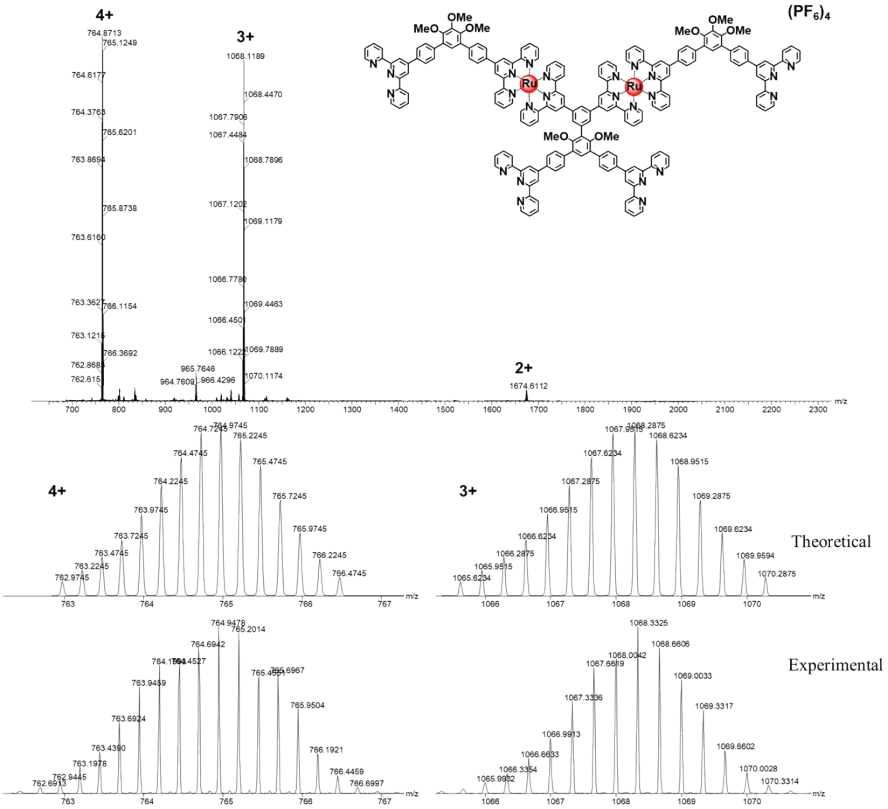


Figure S66: Isotope patterns and ESI-MS spectrum of **LA.**

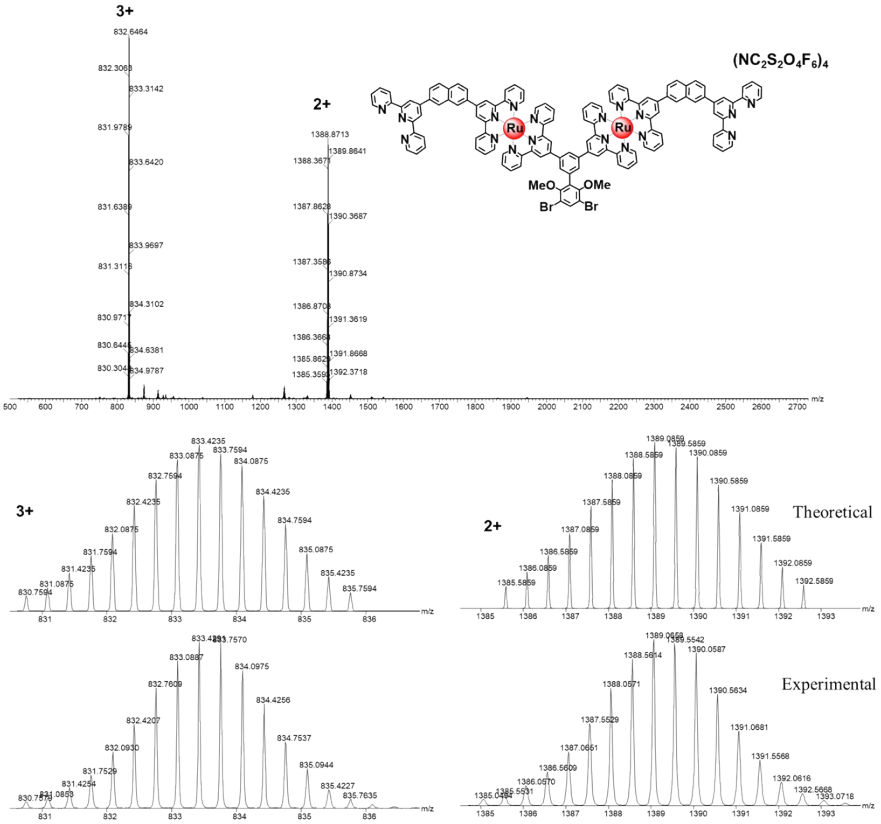


Figure S67: Isotope patterns and ESI-MS spectrum of **S15.**

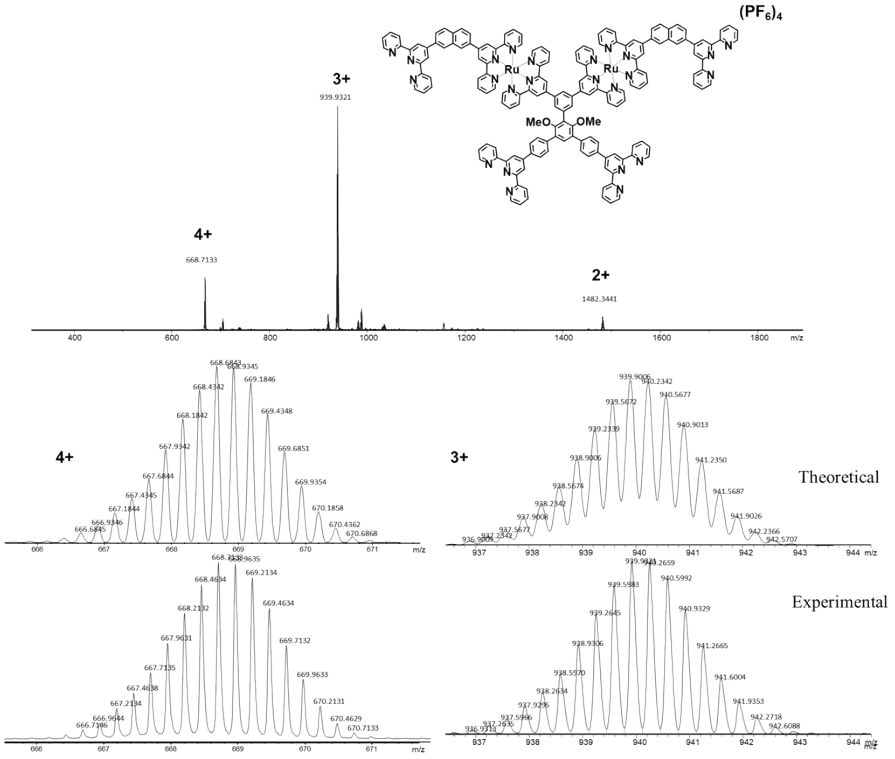


Figure S68: Isotope patterns and ESI-MS spectrum of **LB.**

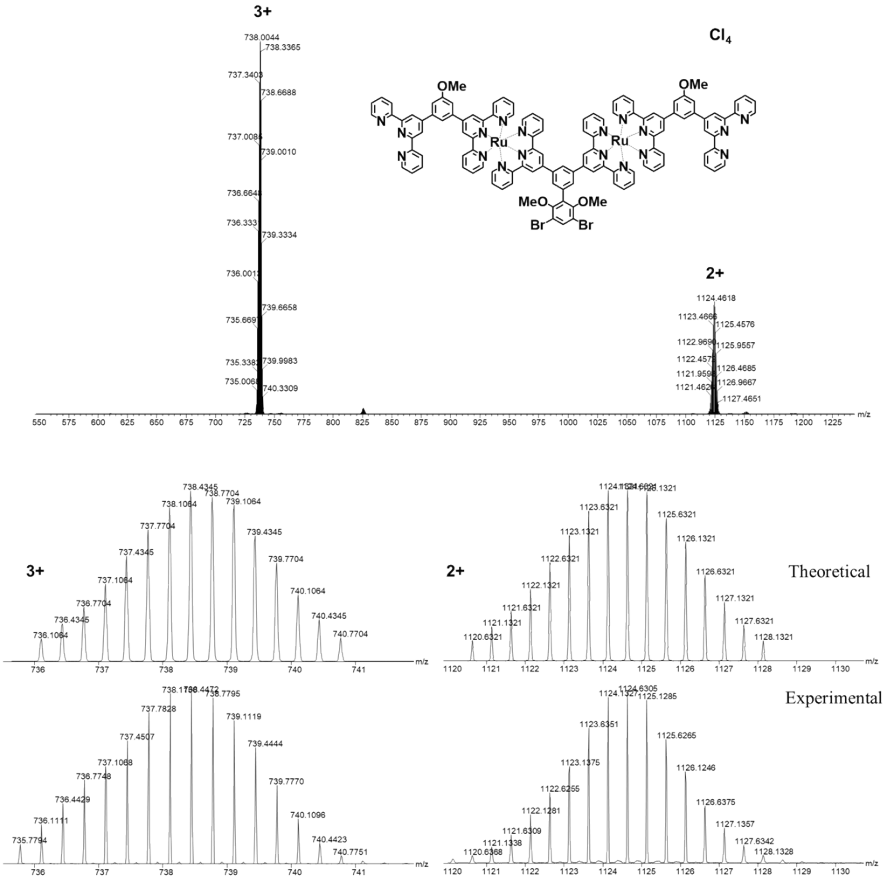


Figure S69: Isotope patterns and ESI-MS spectrum of **S18.**

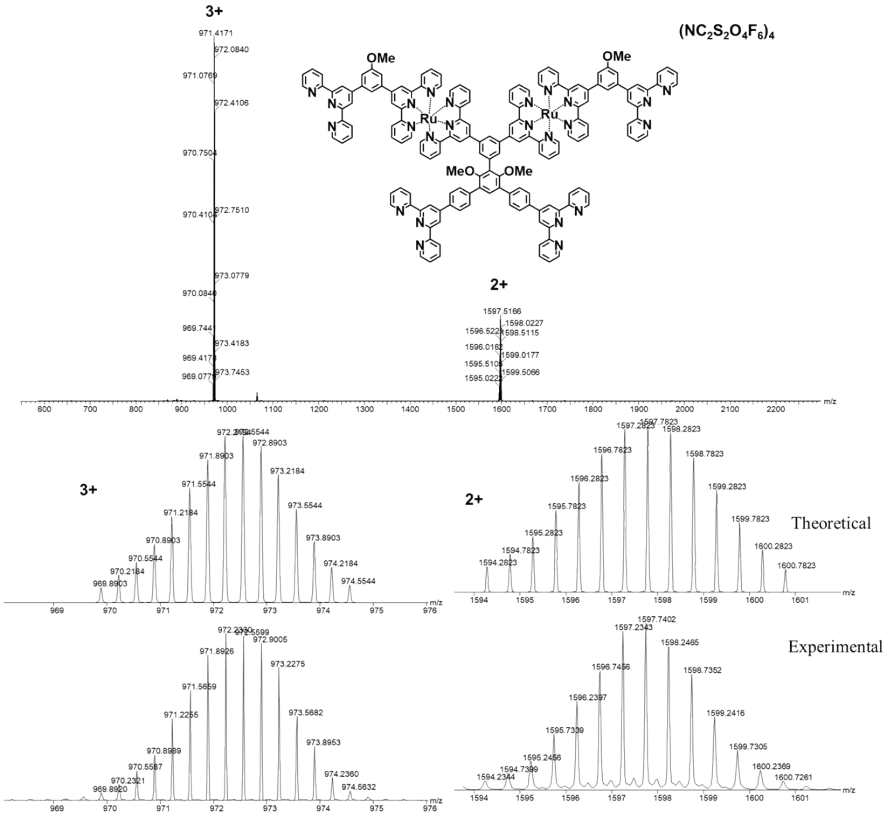


Figure S70: Isotope patterns and ESI-MS spectrum of **LC.**

8. References

S1. J. L. Wang, X. Li, X. Lu, I. F. Hsieh, Y. Cao, C. N. Moorefield, C. Wesdemiotis, S. Z. Cheng and G. R. Newkome, *J. Am. Chem. Soc.*, 2011, **133**, 11450-11453

S2. M. Chen, J. Wang, S.-C. Wang, Z. Jiang, D. Liu, Q. Liu, H. Zhao, J. Yan, Y.-T. Chan and P. Wang, *J. Am. Chem. Soc.*, 2018, **140**, 12168-12174.