# Metallosupramolecular 3D Assembly of Dimetallic $Zn_4[RuL_2]_2$ and Trimetallic $Fe_2Zn_2[RuL_2]_2$

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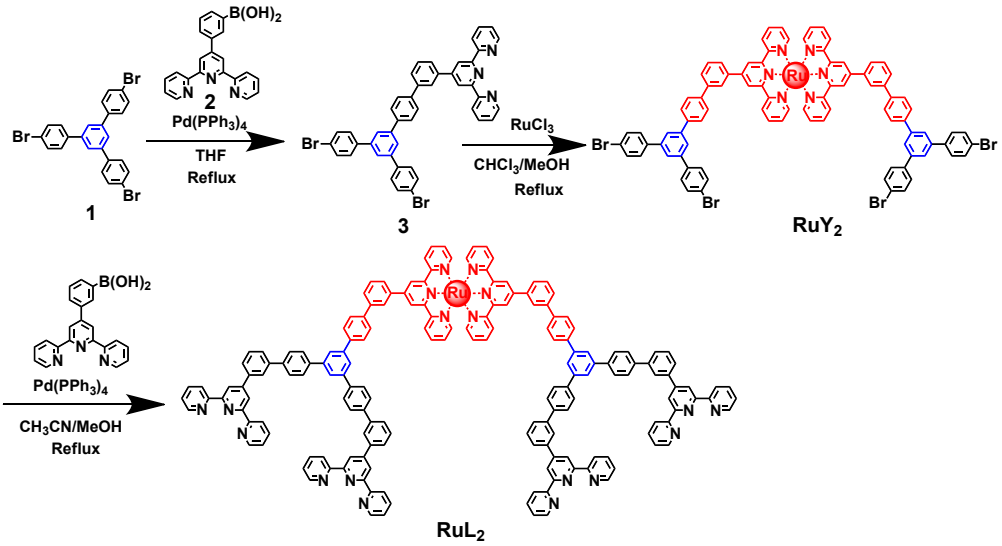
## Table of Contents

# General Procedure

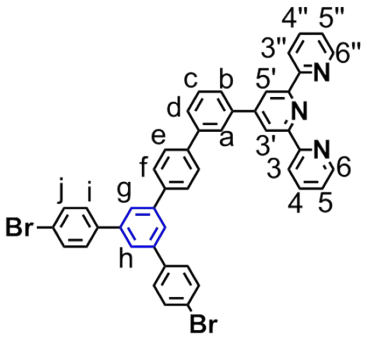
Solvents used in the experimental processes were purified prior to use. 1,3,5-tris(4-bromo-phenyl)benzene, $NH_4PF_6$, and $RuCl_3 \cdot 3H_2O$ and other materials were directly purchased from J & K Chemical Technology and used without further purification. Analytical thin layer chromatography (TLC) was performed on aluminum-backed sheets precoated with $Al_2O_3$ (150 F254 adsorbent, 0.25 mm thick; Merck, Germany). Column chromatography was conducted using neutral $Al_2O_3$ (200-300 mesh) or $SiO_2$ from Sinopharm Chemical Reagent Co. The $^1H$ NMR spectra were recorded at 25 °C on a Bruker spectrometer operating at either 500 or 400 MHz for $^1H$ or $^{13}C$, respectively. Chemical shifts were reported in parts per million (ppm) referenced to the residual solvent peak for $^1H$ and $^{13}C$ NMR, respectively. Transmission electron microscopy measurements were performed on a JEM-2100F TEM operating at 200 kV, the sample was dissolved in MeCN at a concentration of ~$10^{-6}$ M. The solutions were drop cast onto a carbon-coated Cu grid (300-400 mesh) and extra solution was absorbed by filter paper to avoid aggregation, images were taken with a JEOL 2010 Transmission Electron Microscope. Electro-spray ionization (ESI) mass spectra were recorded with a Bruker Q-TOF Qualification Standard Kit., using solutions of 0.1mg sample in 10 mL of $CHCl_3$/ MeCN (1:3, v/v) for ligands or 1 mg in 10 mL of MeCN or MeCN/MeOH (3:1, v/v) for complexes. UV-visible spectrophotometer was corrected for the background spectrum of the solvent. The molecular models were obtained following the same settings in the literature[S1]. Calculations were proceeded with Anneal and Geometry Optimization functions in Forcite module of Materials Studio version 6.1 program (Accelrys Software, Inc.).

**Synthesis of the key metallo-organic ligand, $Ru^{II}$-dimer [$Ru^{2+}L_2$]**

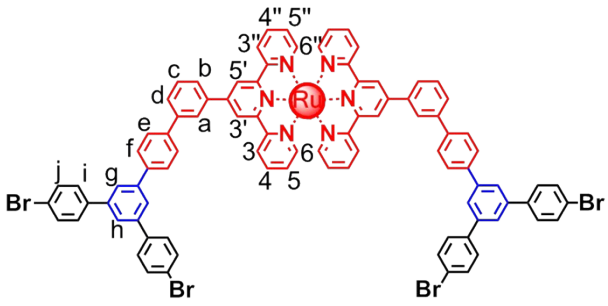



**Scheme S1:** Synthetic route of metallo-organic ligand **$RuL_2$**.

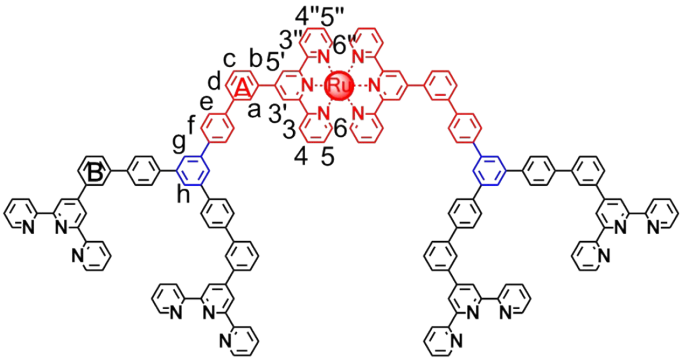
**3'-Boronatophenyl[2,2':6',2'']terpyridine 2** was prepared according to the literature[S2] from 3-formylphenylboronic acid and 2-acetylpyridine.




**3.** 1,3,5-Tris(4-bromophenyl)benzene (543.0 mg, 1.00 mmol) and 3'-boronatophenyl[2,2':6',2'']-terpyridine (211.9 mg, 0.60 mmol) was added to a 250 mL flask, then THF (120 mL) and NaOH (40 mg, 1.00 mmol) in 1 mL of water was added, The system was degassed for 10 min, and $Pd(PPh_3)_4$ (104.0 mg, 0.09 mmol), as the catalyst, was added. The mixture was stirred at 90 °C under nitrogen for 24 h, after cooled to 25 °C, then concentrated *in vacuo* followed by column chromatography ($Al_2O_3$), eluting with the mixture of petroleum ether and $CH_2Cl_2$ to obtain the pure product, as white solid (300 mg, 65%); m.p. 267 °C, $^1$H NMR (500 MHz, $CDCl_3$, ppm) δ8.83 (s, 2H, tpy$H^{3',5'}$), 8.77-8.76 (d, 2H, $J$ = 5 Hz, tpy$H^{6,6''}$), 8.73-8.71 (t, 4H, $J$ = 10 Hz, tpy$H^{3,3''}$), 8.17 (s, 1H, Ph$H^{a}$), 7.95-7.91 (m, 3H, tpy$H^{4,4''}$, Ph$H^{h}$), 7.86-7.81 (m, 4H, Ph$H^{e,f,g}$), 7.78-7.76 (d, 1H, $J$ = 10 Hz, Ph$H^{d}$), 7.73 (s, 1H, Ph$H^{c}$), 7.66-7.59 (m, 9H, Ph$H^{h,i,j}$), 7.41-7.38 (t, 2H, $J$ = 15 Hz, Ph$H^{5,5''}$); $^{13}$C NMR (101 MHz, $CDCl_3$, ppm) δ 156.20, 156.08, 150.37, 149.18, 142.25, 141.43, 141.41, 140.36, 139.91, 139.84, 139.34, 136.95,132.05, 129.51, 128.97, 127.93, 127.76, 126.64, 126.46, 126.09, 125.19, 124.76, 123.92,122.03, 121.44, 119.08; ESI-MS (772.07 calcd. for $C_{45}H_{29}Br_2N_3$): m/z 772.12 $(M + H)^+$.

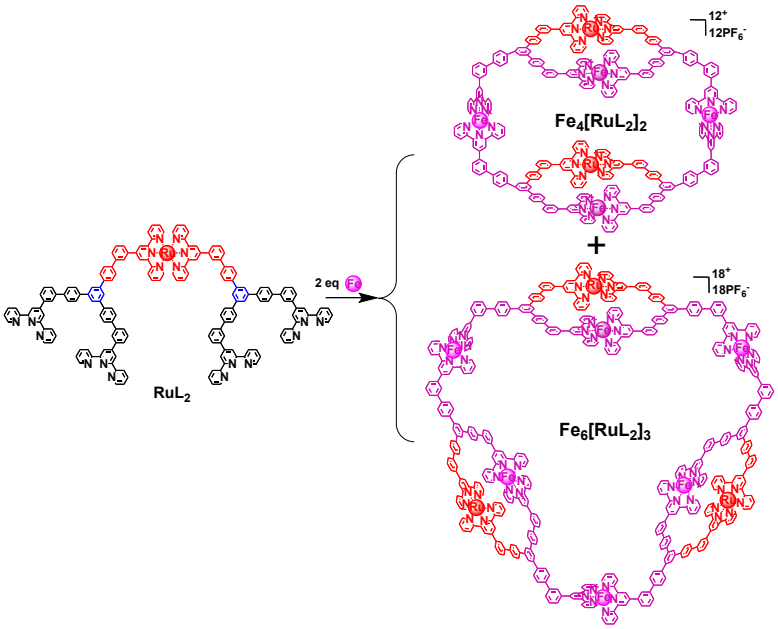



**$RuY_2$.** Ligand **1** (300.0 mg, 38.88 μmol) was dissolved in a 1:1 solution of $CHCl_3$:MeOH (100 mL), then $RuCl_3 \cdot 3H_2O$ (50.0 mg 18.52 μmol) and 3 drop of 4-ethylmorpholine was added. The mixture was stirred at 75 °C for 24 h, After cooled to 25 °C, then concentrated *in vacuo* followed by column chromatography ($Al_2O_3$) eluting with the (1:1) mixture of MeOH and $CH_2Cl_2$ to generate a pure product, as red solid: (198 mg, 60%), m.p. >300 °C; $^1$H NMR (400 MHz, $CD_3CN$, ppm) δ 9.16 (s, 4H, tpy$H^{3',5'}$), 8.75-8.73 (d, $J$ = 8 Hz, 4H, tpy$H^{3,3"}$), 8.57 (s, 2H, Ph$H^{a}$), 8.27-8.25 (d, 2H, $J$ = 8 Hz, Ph$H^{b}$), 8.11-8.04 (m, 12H, Ph$H^{e,f,g,h}$), 8.02-7.98 (t, 4H, $J$ = 16 Hz, tpy$H^{4,4"}$), 7.94-7.90 (m, 4H, Ph$H^{c,d}$), 7.83-7.72 (m, 16H, Ph$H^{i,j}$), 7.49-7.48 (d, 4H, $J$ = 8 Hz, tpy$H^{6,6"}$), 7.25-7.22 (t, 4H, $J$ = 12 Hz, tpy$H^{5,5"}$). $^{13}$C NMR (101 MHz, $CD_3CN$, ppm) δ 158.26, 155.52, 152.35, 148.16, 141.63, 141.12, 140.03, 139.59, 139.53, 138.10, 137.60, 131.89, 130.31, 129.32, 128.80, 128.07, 128.04, 127.77, 127.44, 126.91, 126.31, 124.98, 124.84, 124.53, 121.78, 121.56; ESI-MS (1934.98 calcd. for $C_{90}H_{58}Br_4F_{12}N_6P_2Ru$ with $PF_6^-$ counter ions): m/z 1789.06 $(M - PF_6^-)^+$ and 822.06 $(M - 2PF_6^-)^{2+}$.




**Ligand $Ru^{2+}L_2$.** $RuY_2$ (150.00 mg, 87.40 μmol) and 3'-boronatophenyl[2,2':6',2"]terpyridine (741.00 mg, 2.10 mmol) was added to a 250 mL flask, then added in a 5:1 solution of MeCN : MeOH (100 mL), and $K_2CO_3$ (241.20 mg, 1.75 mmol) dissolved in 1.7 mL of water was added. The mixture was degassed for 10 min, and $Pd(PPh_3)_4$ (121.0 mg, 105.0 μmol), as the catalyst, was added. The mixture was stirred at 90 °C under nitrogen for 4 d, then concentrated *in vacuo* followed by column chromatography ($Al_2O_3$) eluting with a mixed solvent of MeOH and $CH_2Cl_2$ to give the pure the product, as red solid (157 mg, 60%); m.p. >300 °C, $^1$H NMR (400 MHz, DMSO, ppm) δ 9.08 (s, 4H, $^{A}$tpy$H^{3',5'}$), 8.66-8.64 (d, 4H, $J$ = 8 Hz, $^{A}$tpy$H^{3',3"}$), 8.29 (s, 8H, $^{B}$tpy$H^{3',5'}$), 8.26-8.25 (d, 8H, J = 4 Hz, $^{B}$tpy$H^{6,6"}$), 8.21 (s, 2H, $^{A}$Ph$H^{a}$), 8.19-8.17 (d, 8H, $J$ = 8 Hz, $^{B}$tpy$H^{3,3"}$), 7.93-7.91 (d, 2H, $J$ = 8 Hz, $^{A}$Ph$H^{b}$), 7.70 (s, 4H, $^{B}$Ph$H^{a}$), 7.67-7.48 (m, 36H, $^{A}$tpy$H^{4,4"}$, B-tpy-$H^{4,4"}$, $^{A}$Ph$H^{c,d,e,f}$, $^{B}$Ph$H^{e}$, Ph$H^{g}$), 7.45-7.37 (m, 16H, $^{B}$Ph$H^{b,d,f}$), 7.24-7.20 (t, 4H, $J$ = 16 Hz, $^{B}$Ph$H^{c}$), 7.08-7.07 (d, 4H, $J$ = 4 Hz, $^{A}$tpy$H^{6,6"}$), 7.04-7.01 (m, 10H, $^{B}$tpyH$^{5,5"}$, Ph$H^{h}$), 6.80-6.77 (t, 4H, $J$ = 12 Hz, $^{A}$tpy$H^{5,5"}$); ESI-MS (2848.79 calcd. for $C_{174}H_{114}F_{12}N_{18}P_2Ru$ with $PF_6^-$): m/z 1278.79 $(M - 2PF_6^-)^{2+}$.

**Self-assembly of dimetallic $Fe_4[RuL_2]_2$, $Fe_6[RuL_2]_3$, $Zn_4[RuL_2]_2$ and trimetallic $Fe_2Zn_2[RuL_2]_2$ supramolecules**




**Scheme S2:** Synthetic route of bimetallic supramolecules dimer $Fe_4[RuL_2]_2$ and trimer $Fe_6[RuL_2]_3$ *via* terpyridinyl metallo-organic ligand $\mathbf{Ru^{2+}L_2}$.

**Mixture of the dimetallic dimer $Fe_4[RuL_2]_2$ and trimer $Fe_6[RuL_2]_3$.** Ligand $\mathbf{RuL_2}$ (15.2 mg, 17.0 μmol) and $FeCl_2{\cdot}4H_2O$ (7.4 mg, 37.4 μmol) were dissolved in MeCN (40 mL). The solution was heated at 90 °C for 12 h. After cooled to 25 °C, excess $NH_4PF_6$ in MeOH was added to get a purple precipitate, which was filtered and washed with MeOH to generate a red solid. The precipitate was filtered and residue was flash column chromatographed ($SiO_2$) eluting with MeCN/sat. $KNO_3$ (aq)/$H_2O$ (100:30:1 to 100:15:1) to generate the $Fe_4[RuL_2]_2$ and trimer $Fe_6[RuL_2]_3$, as the purple precipitates after then the counterion exchanged to $PF_6^-$; m.p. >300 °C.

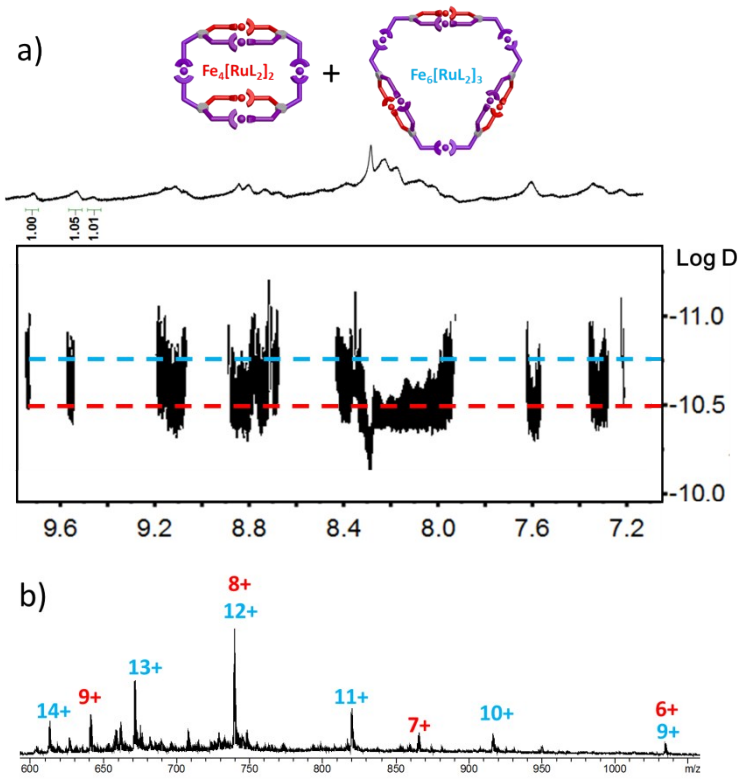
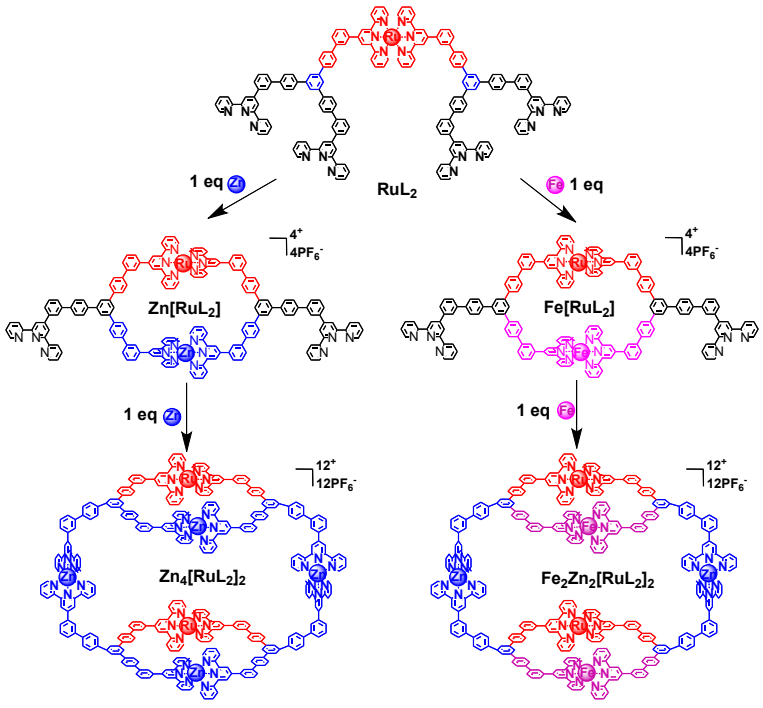
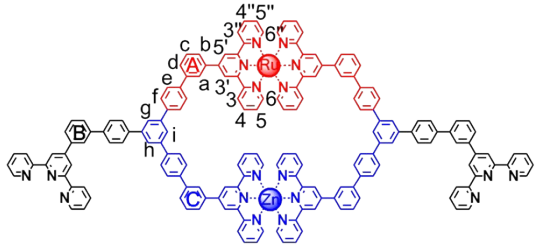


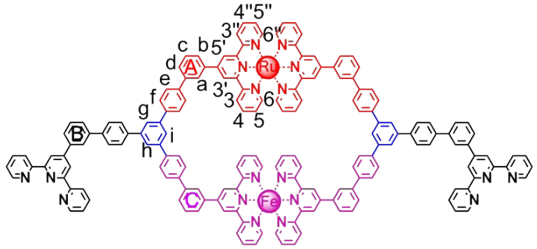

**Figure S1. a)** $^{1}$H NMR and 2D NMR DOSY spectrum (500 MHz) of a mixtures of dimer $\mathbf{Fe_4[RuL_2]_2}$ and trimer $\mathbf{Fe_6[RuL_2]_3}$ in DMSO shows two singles band at log D = -10.50 and -10.75. **b)** The ESI-MS spectrum of mixture of $Fe_4[RuL_2]_2$ and $Fe_6[RuL_2]_3$.



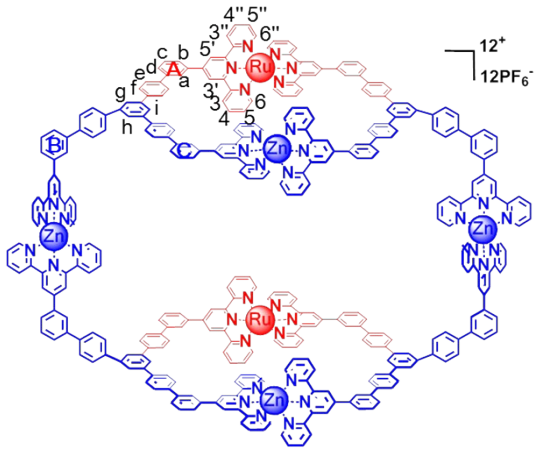

**Scheme S3:** Synthetic route of supramolecular dimetallic $\mathbf{Zn_4[RuL_2]_2}$ and trimetallic $\mathbf{Fe_2Zn_2[RuL_2]_2}$ *via* intermediate $Zn[RuL_2]$ and $Fe[RuL_2]$, respectively.



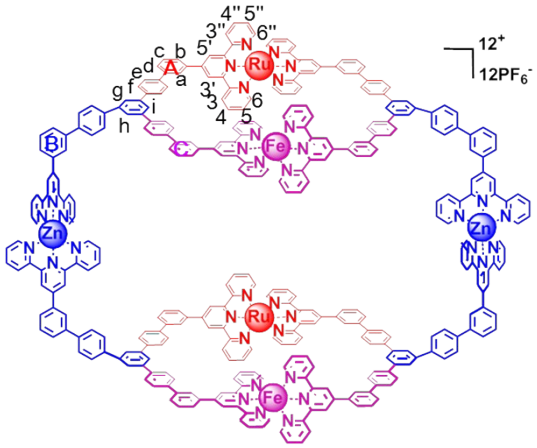
**Ligand Zn[RuL$_2$]**. Ligand RuL$_2$ (3.80 mg, 1.33 μmol) was dissolved in 3:1 solution $CHCl_3$: MeOH (120 mL), then ultrasonically dispersed for 5 min, $Zn(NO_3)_2 \cdot 6H_2O$ (dissolved in MeOH) (1.33 mg, 6.81μmol) was added, then heated at 90 °C for 12 h, After cooled to 25 °C, excess $NH_4PF_6$ in MeOH was added to give a purple precipitate, which was filtered and washed with MeOH to generate a red solid: m.p. >300 °C; $^1$H NMR (500 MHz, $CD_3CN$, ppm): δ 9.40 (s, 4H, $^{A}$tpy$H^{3',5'}$), 9.34 (s, 4H, $^{C}$tpy$H^{3',5'}$), 9.02-9.00 (d, 4H, $J$ = 10 Hz, $^{C}$tpy$H^{3,3''}$), 8.97-8.95 (d, 4H, $J$ = 10 Hz, $^{A}$tpy$H^{3,3''}$), 8.89 (s, 4H, $^{B}$tpy$H^{3',5'}$), 8.80-8.79 (d, 4H, $J$ = 5 Hz, $^{B}$tpy$H^{6,6''}$), 8.76-8.74 (d, 4H, $^{B}$tpy$H^{3,3''}$), δ8.62 (s, 2H, $^{A}$Ph$H^{a}$), 8.60 (s, 2H, $^{C}$Ph$H^{a}$), 8.32-8.28 (m, 6H, $^{A}$Ph$H^{b}$, $^{B}$Ph$H^{a}$, $^{C}$Ph$H^{b}$), 8.20-8.11 (m, 32H, $^{C}$tpy$H^{4,4''}$, $^{A}$Ph$H^{d,e,f}$, $^{B}$Ph$H^{b}$, $^{C}$Ph$H^{d,e,f}$, Ph$H^{g,h,i}$), 8.04-8.02 (t, 4H, $J$ = 10 Hz, $^{B}$tpy$H^{4,4''}$), 8.00-7.90 (m, 22H, $^{A}$tpy$H^{4,4''}$, $^{C}$tpy$H^{6,6''}$, $^{A}$Ph$H^{c}$, $^{B}$Ph$H^{d,e,f}$, $^{C}$Ph$H^{c}$), 7.78-7.75 (t, 2H, $J$ = 15 Hz, $^{B}$Ph$H^{c}$), 7.55-7.50 (m, 8H, $^{A}$tpy$H^{6,6''}$, $^{B}$tpy$H^{5,5''}$), 7.45-7.43 (t, 4H, $J$ = 10 Hz, $^{C}$tpy$H^{5,5''}$), 7.25-7.22 (t, 4H, $J$ = 15 Hz, $^{A}$tpy$H^{5,5''}$); ESI-MS (3203.65 calcd. for $C_{174}H_{114}F_{24}N_{18}P_4RuZn$ with $PF_6^-$): m/z 1456.33 $(M - 2PF_6^-)^{2+}$ , m/z 922.57 $(M - 3PF_6^-)^{3+}$ and m/z 655.69 $(M - 4PF_6^-)^{4+}$.



**Ligand Fe[RuL$_2$]**. Ligand RuL$_2$ (19.40 mg, 6.81 μmol) was dissolved in DMSO (50 mL), $FeCl_2 \cdot 4H_2O$ (dissolved in MeOH) (1.33 mg, 6.81μmol) was added, then heated at 90 °C for 12 h, After cooled to 25 °C, excess $NH_4PF_6$ in MeOH was added to get a purple precipitate, which was filtered and washed with MeOH to generate a dark purple solid: m.p. >300 °C; $^1$H NMR (500 MHz, $CD_3CN$, ppm) δ 9.32 (s, 4H, $^{C}$tpy$H^{3',5'}$), 9.15 (s, 4H, $^{A}$tpy$H^{3',5'}$), 8.93 (s, 4H, $^{B}$tpy$H^{3',5'}$), 8.82-8.78 (m, 8H, $^{B}$tpy$H^{3,3''}$, $^{B}$tpy$H^{6,6''}$), 8.73-8.71 (d, 4H, $J$ = 10 Hz, $^{A}$tpy$H^{3,3''}$), 8.69-8.67 (d, 4H, $J$ = 10 Hz, $^{C}$tpy$H^{3,3''}$), 8.55 (s, 2H, Ph$H^{a}$), 8.36-8,34 (d, 2H, $J$ = 10 Hz, $^{C}$Ph$H^{b}$), 8.30 (s, 2H, $^{B}$Ph$H^{a}$), 8.25-8.13 (m, 32H, $^{A}$Ph$H^{b,d,e,f}$, $^{B}$Ph$H^{b}$, $^{C}$Ph$H^{a,d,e,f}$, Ph$H^{g,h,i}$), 8.06-8.05 (t, 4H, $J$ = 5 Hz, $^{B}$tpy$H^{4,4''}$), 8.02-7.92 (m, 22H, $^{A}$tpy$H^{4,4''}$, $^{C}$tpy$H^{4,4''}$, $^{A}$Ph$H^{c}$, $^{B}$Ph$H^{d,e,f}$, $^{C}$Ph$H^{c}$), 7.81-7.77 (m, 2H, $J$ = 20 Hz, $^{B}$Ph$H^{c}$), 7.54-7.49 (m, 8H, $^{A}$tpy$H^{6,6''}$, $^{B}$tpy$H^{5,5''}$), 7.27-7.26 (d, 4H, $J$ =5 Hz, $^{C}$tpy$H^{6,6''}$), 7.24-7.20 (t, 4H, $J$ = 20 Hz, $^{A}$tpy$H^{5,5''}$), 7.15-7.12 (t, 4H, $J$ = 15 Hz, $^{C}$tpy$H^{5,5''}$); ESI-MS (3194.66 calcd. for $C_{174}H_{114}F_{24}FeN_{18}P_4Ru$ with $PF_6^-$): m/z 919.60 $(M - 3PF_6^-)^{3+}$ and m/z 653.46 $(M - 4PF_6^-)^{4+}$.




**Dimetallic $Zn_4[RuL_2]_2$**. Ligand **Zn[RuL$_2$]** (3.40 mg, 1.19 μmol) was dissolved in 3:1 solution $CHCl_3$: MeOH (120 mL), then ultrasonically dispersed for 5 min, $Zn(NO_3)_2{\cdot}6H_2O$ (dissolved in MeOH) (0.71 mg, 2.39 μmol) was added, then heated at 90 °C for 12 h, After cooling to 25 °C, excess $NH_4PF_6$ in MeOH was added to give a red precipitate, which was filtered and washed with MeOH to generate a red solid: m.p. >300 °C; $^1$H NMR (500 MHz, $CD_3CN$, ppm) δ9.18 (s, 8H, $^{A}$tpy$H^{3',5'}$), 9.15 (s, 8H, $^{C}$tpy$H^{3',5'}$), 9.12 (s, 8H, $^{B}$tpy$H^{3',5'}$), 8.87-8.85 (d, 8H, $J$ = 10 Hz, $^{A}$tpy$H^{3,3"}$), 8.81-8.79 (d, 8H, $J$ = 10 Hz, $^{B}$tpy$H^{3,3"}$), 8.74-8.73 (d, 8H, $J$ = 5 Hz, $^{C}$tpy$H^{3,3"}$), 8.63 (s, 4H, $^{A}$Ph$H^{a}$), 8.58 (s, 4H, $^{C}$Ph$H^{a}$), 8.55 (s, 4H, $^{B}$Ph$H^{a}$), 8.30-8.13 (m, 100 H, $^{A}$tpy$H^{4,4"}$, $^{B}$tpy$H^{4,4"}$, $^{A}$Ph$H^{b,d,e,f}$, $^{B}$Ph$H^{b,d,e,f}$, $^{C}$Ph$H^{b,d,e,f}$, Ph$H^{g,h,i}$), 8.01-7.91 (m, 36H, $^{A}$tpy$H^{6,6"}$, $^{B}$tpy$H^{6,6"}$, $^{C}$tpy$H^{4,4"}$, $^{A}$Ph$H^{c}$, $^{B}$Ph$H^{c}$, $^{C}$Ph$H^{c}$), 7.53-7.49 (m, 16H, $^{A}$tpy$H^{5,5"}$, $^{C}$tpy$H^{6,6"}$), 7.46-7.44 (t, 8H, $J$ = 10 Hz, $^{B}$tpy$H^{5,5"}$), 7.25-7.22 (t, 8H, $J$ = 15 Hz, $^{C}$tpy$H^{5,5"}$).




**Trimetallic $Fe_2Zn_2[RuL_2]_2$**. Ligand **Fe[RuL$_2$]** (2.70 mg, 0.85 μmol) was dissolved in 3:1 solution $CHCl_3$:MeOH (100 mL), then ultrasonically dispersed for 5 min, $Zn(NO_3)_2{\cdot}6H_2O$ (dissolved in MeOH) (0.25 mg, 0.85 μmol) was added, then heated at 90 °C for 12 h, After cooled to 25 °C, excess $NH_4PF_6$ in MeOH was added to get a purple precipitate, which was filtered and washed with MeOH to generate a dark purple solid: m.p. >300 °C; $^1$H NMR (500 MHz, DMSO, ppm) δ 9.78 (s, 8H, $^{C}$tpy$H^{3',5'}$), 9.59 (s, 8H, $^{A}$tpy$H^{3',5'}$), 9.28 (s, 8H, $^{B}$tpy$H^{3',5'}$), 9.16-9.15 (m, 8H, $^{A}$tpy$H^{3,3"}$), 9.12-9.11 (m, 16H, $^{B}$tpy$H^{3,3"}$, $^{C}$tpy$H^{3,3"}$), 8.98-8.96 (m, 4H, $^{C}$Ph$H^{d}$), 8.87 (s, 4H, $^{B}$Ph$H^{a}$), 8.82 (s, 4H, $^{C}$Ph$H^{a}$), 8.76-8.74 (m, 4H, $^{B}$Ph$H^{b}$), 8.70 (s, 4H, $^{A}$Ph$H^{a}$), 8.61-8.60 (m, 4H, $^{B}$Ph$H^{d}$), 8.53-8.51 (m, 4H, $^{C}$tpy$H^{b}$), 8.48-8.46 (m, 4H, $^{A}$Ph$H^{d}$), 8.42-8.40 (m, 4H, $^{A}$Ph$H^{b}$), 8.33-7.95 (m, 104H, $^{A}$tpy$H^{4,4"}$, $^{B}$tpy$H^{4,4"}$, $^{B}$tpy$H^{6,6"}$, $^{C}$tpy$H^{4,4"}$, $^{A}$Ph$H^{c,e,f}$, $^{B}$Ph$H^{c,e,f}$, $^{C}$Ph$H^{c,e,f}$, Ph$H^{g,h,i}$), 7.61-7.59 (m, 16H, $^{C}$tpy$H^{6,6"}$, $^{B}$tpy$H^{5,5"}$), 7.35-7.29 (m, 16H, $^{A}$tpy$H^{6,6"}$, $^{C}$tpy$H^{5,5"}$), 7.23-7.20 (m, 8H, $^{A}$tpy$H^{5,5"}$).

**Molecular cartoons for $Zn_4[RuL_2]_2$:**

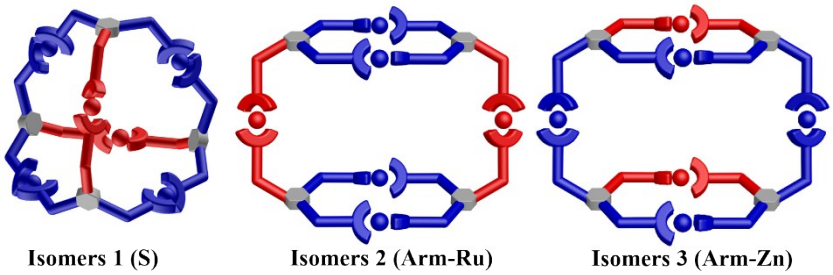



**Figure S2.** Illustration three possible $Zn_4[RuL_2]_2$ isomers ($^1$H NMR spectrum for **1** and **2** should have two singlets for tpy$H^{3'5'}$ and for **3** should be three singlets for tpy$H^{3'5'}$).[S3]

**NMR spectra of ligand and complex**

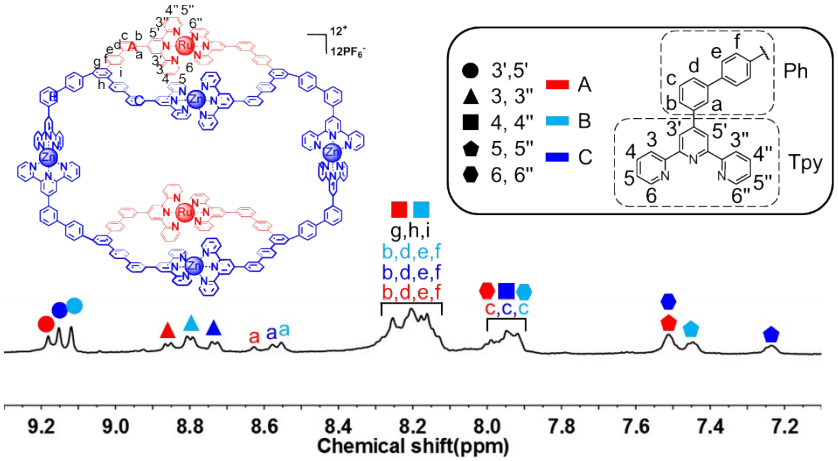



**Figure S3.** $^1$H NMR spectrum (400 MHz) of **$Zn_4(RuL_2)_2$** in $CD_3CN$.

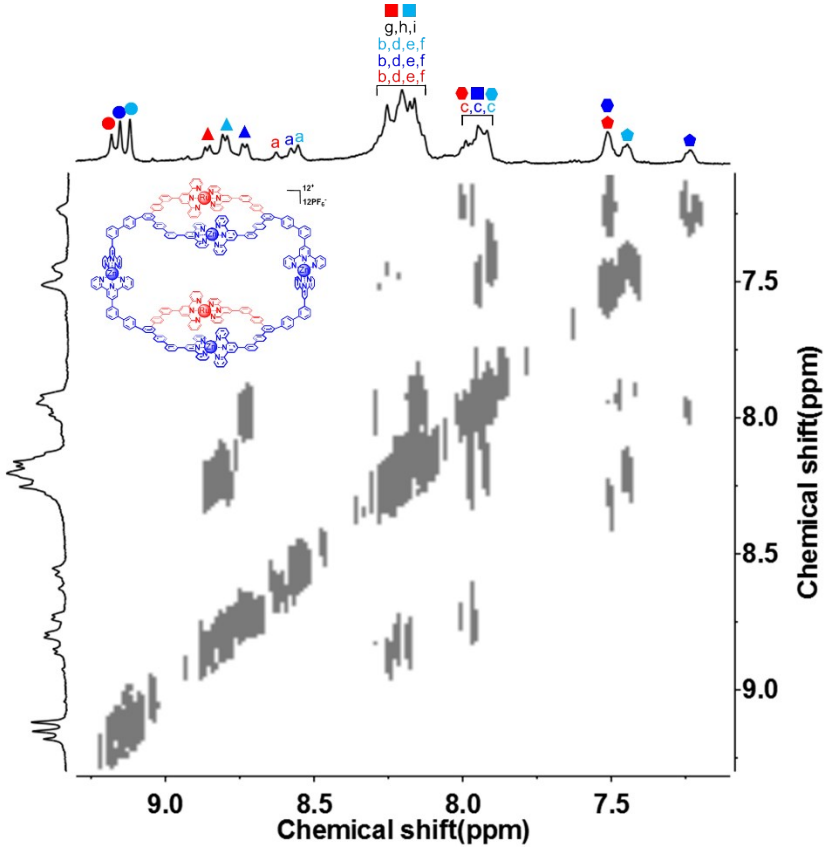



**Figure S4.** 2D COSY spectrum (400 MHz) of $\mathbf{Zn_4(RuL_2)_2}$ in $CD_3CN$.

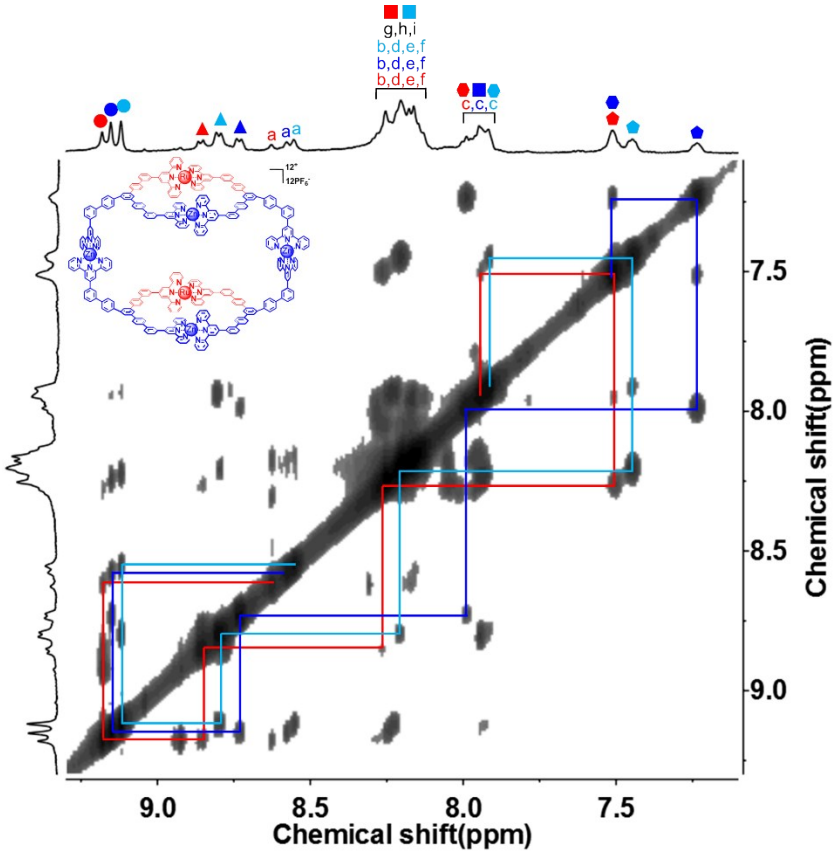



**Figure S5.** 2D NOESY spectrum (400 MHz) of $\mathbf{Zn_4(RuL_2)_2}$ in $CD_3CN$.

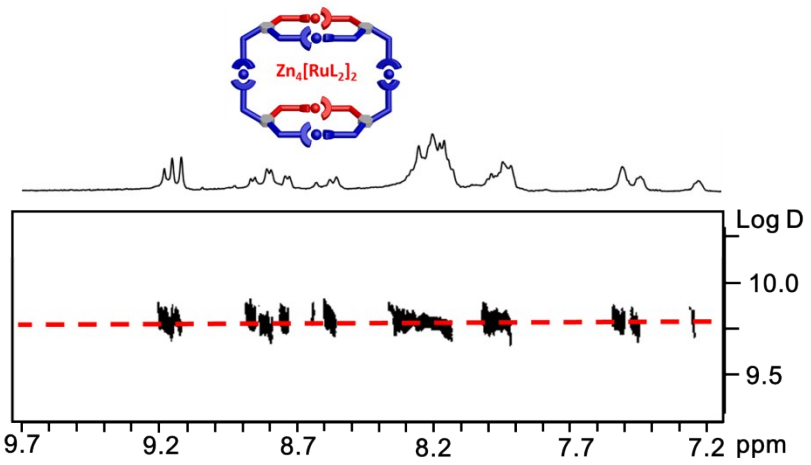



**Figure S6.** 2D DOSY spectrum (500 MHz) of $\mathbf{Zn_4(RuL_2)_2}$ in $CD_3CN$.

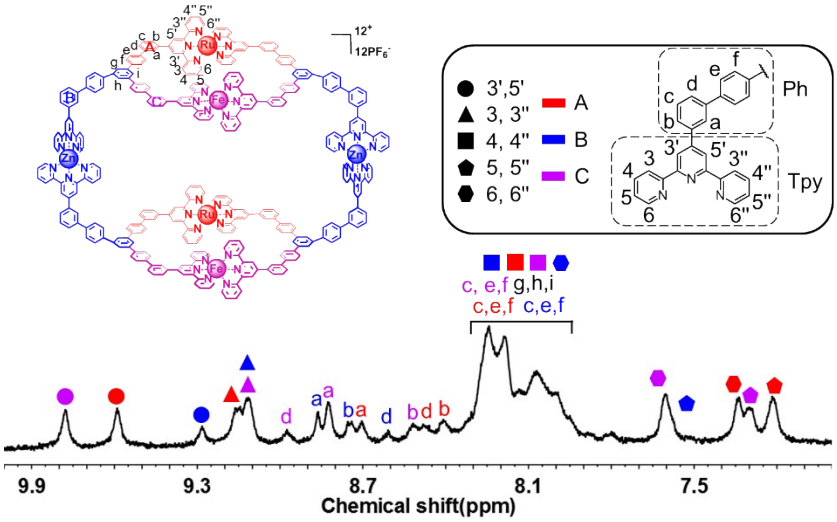



**Figure S7.** $^1H$ NMR spectrum (500 MHz) of $\mathbf{Fe_2Zn_2(RuL_2)_2}$ in DMSO-$d_6$.

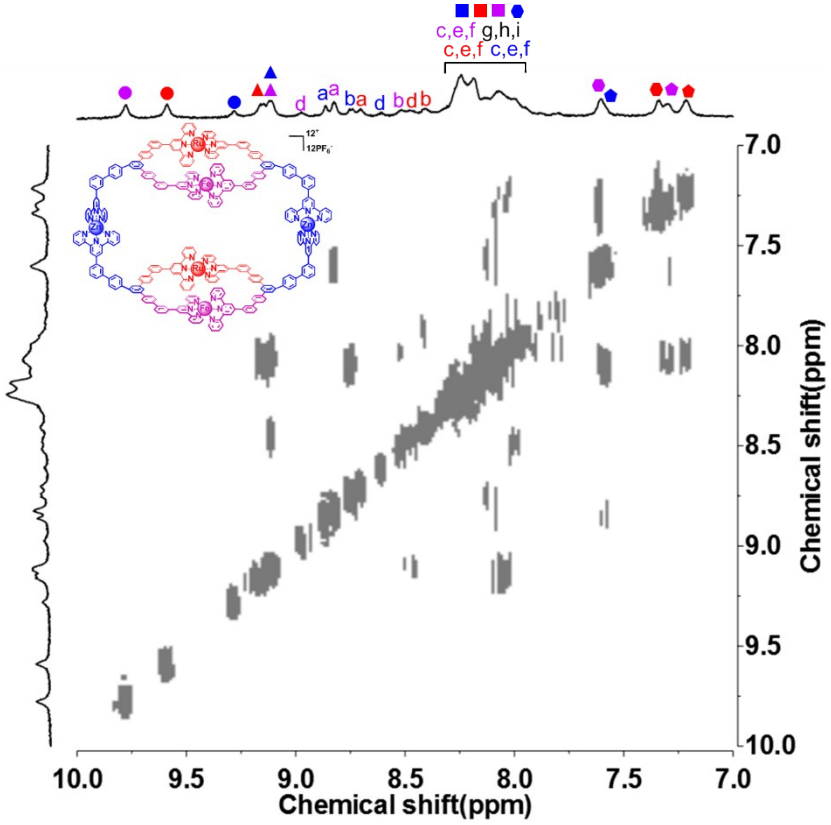



**Figure S8.** 2D COSY spectrum (500 MHz) of $\mathbf{Fe_2Zn_2(RuL_2)_2}$ in DMSO-$d_6$.

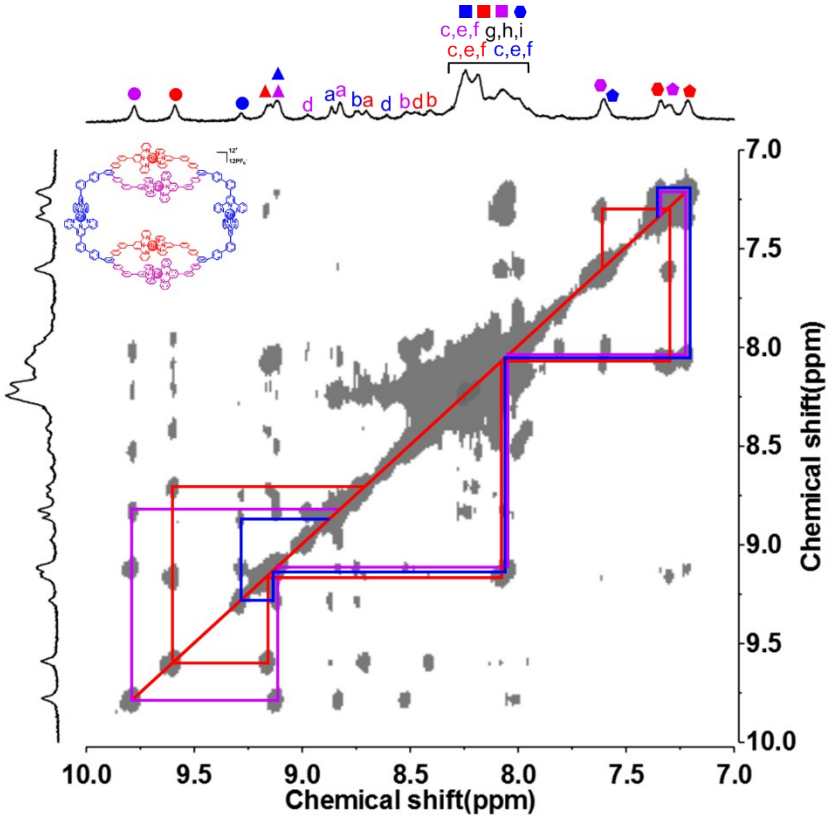



**Figure S9.** 2D NOESY spectrum (500 MHz) of $\mathbf{Fe_2Zn_2(RuL_2)_2}$ in DMSO-$d_6$.

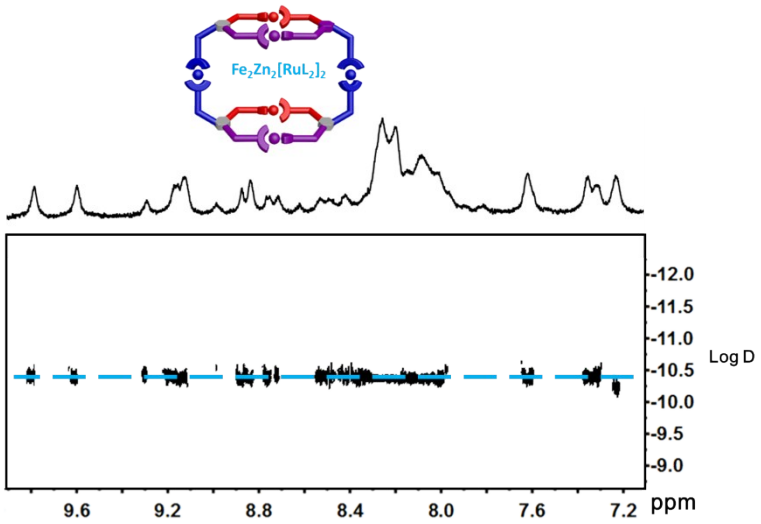



**Figure S10.** 2D DOSY spectrum (500 MHz) of **$Fe_2Zn_2(RuL_2)_2$** in DMSO-$d_6$.

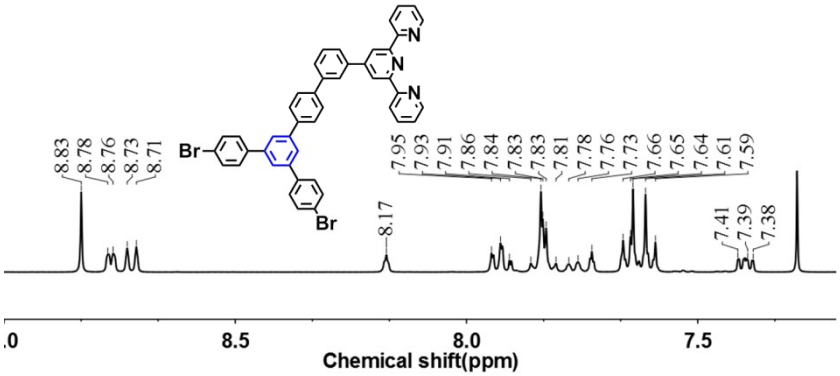



**Figure S11.** $^1$H NMR spectrum (500 MHz) of ligand **3** in $CDCl_3$.

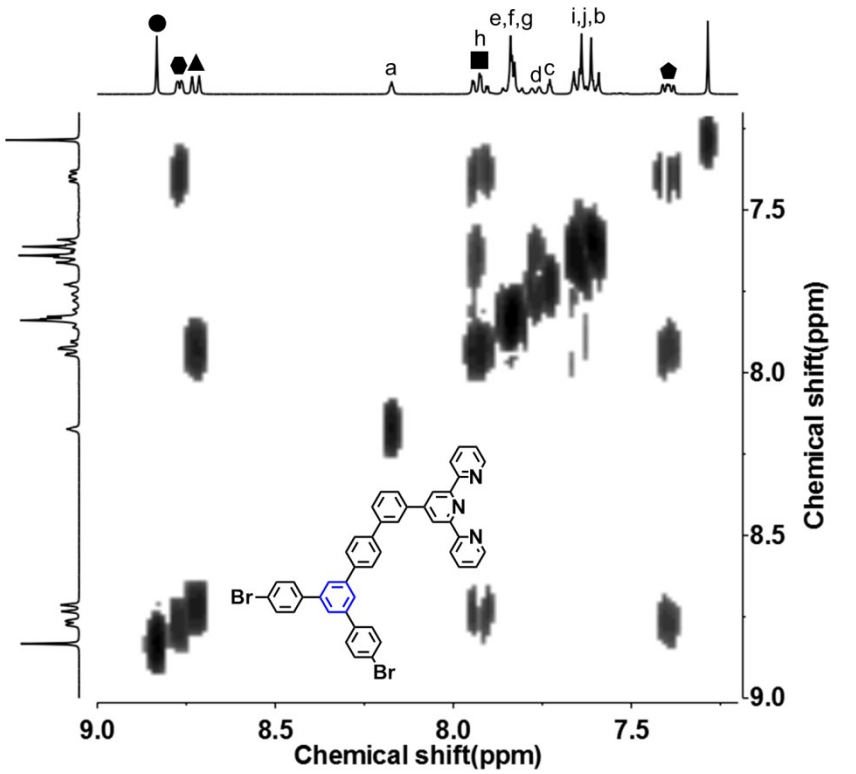



**Figure S12.** 2D COSY spectrum (500 MHz) of ligand **3** in $CDCl_3$.

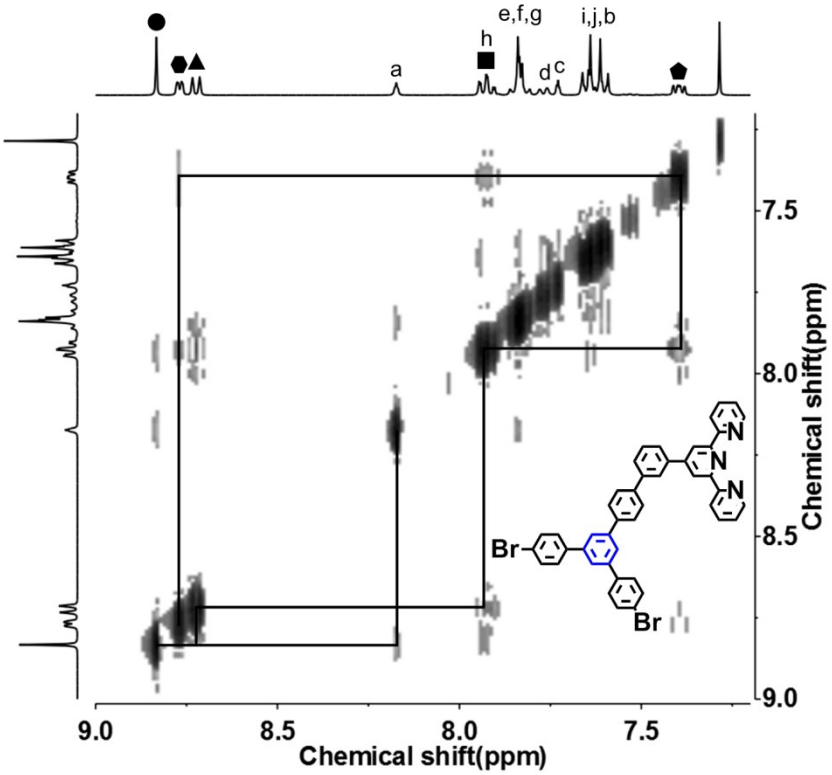



**Figure S13.** 2D NOESY spectrum (500 MHz) of ligand **3** in $CDCl_3$.

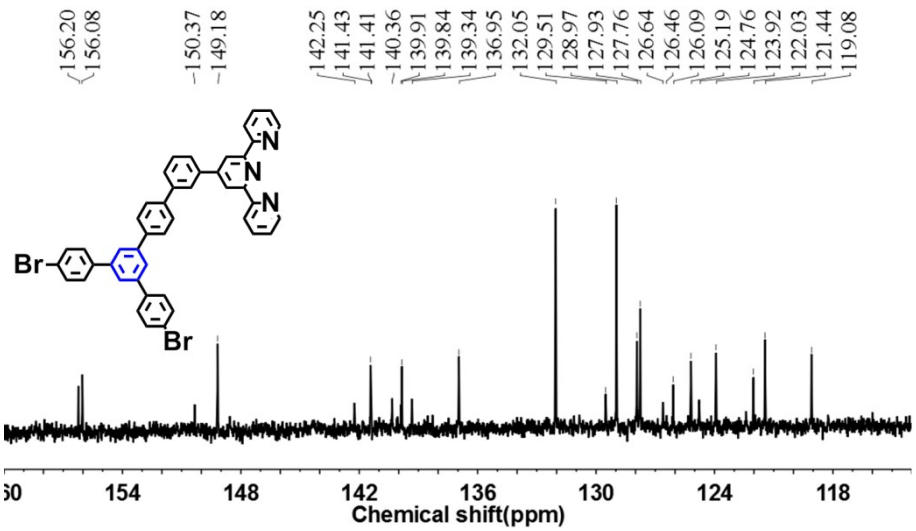



**Figure S14.** $^{13}C$ spectrum (400 MHz) of ligand **3** in $CDCl_3$.

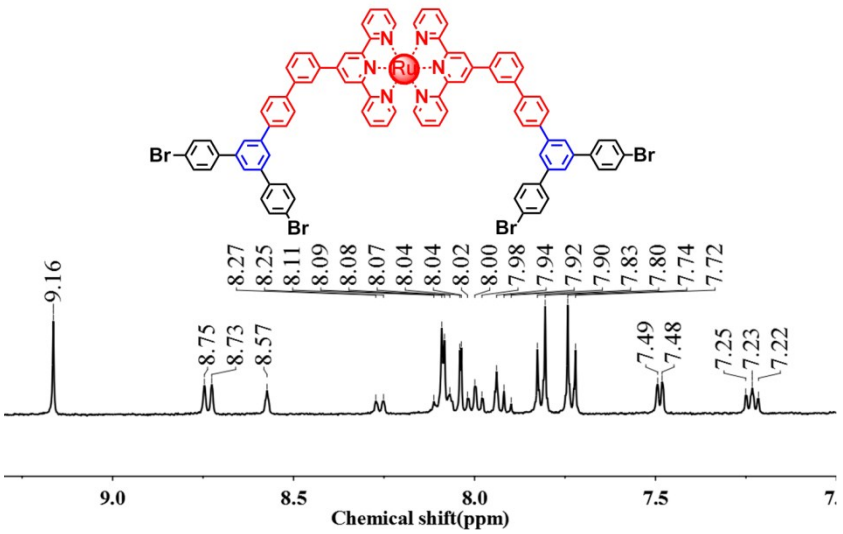



**Figure S15.** $^{1}H$ NMR spectrum (400 MHz) of $\mathbf{RuY_2}$ in $CD_3CN$.

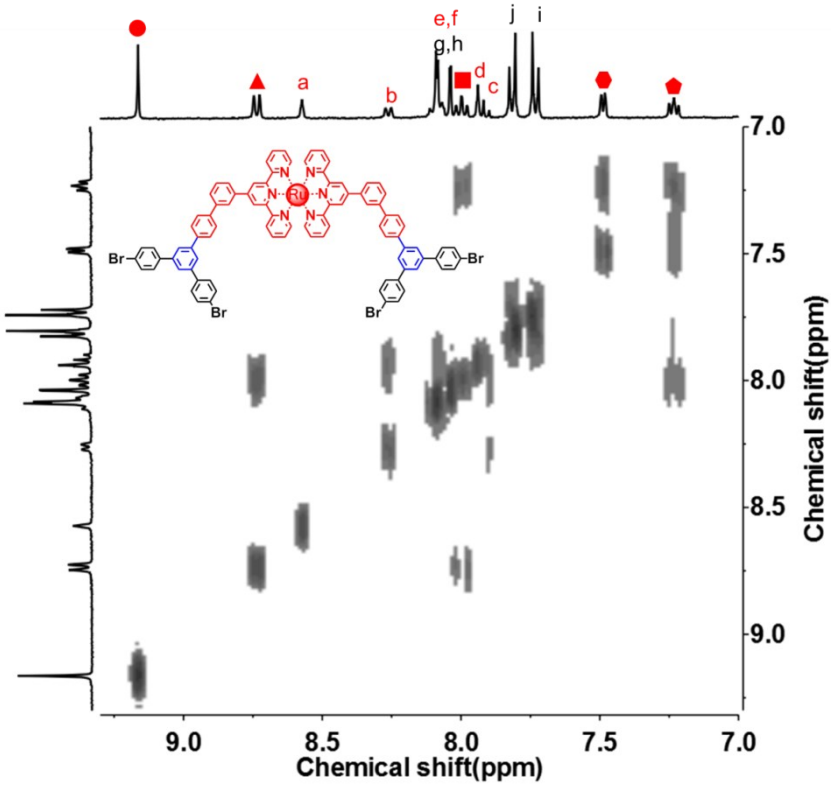



**Figure S16.** 2D COSY spectrum (400 MHz) of $\mathbf{RuY_2}$ in $CD_3CN$.

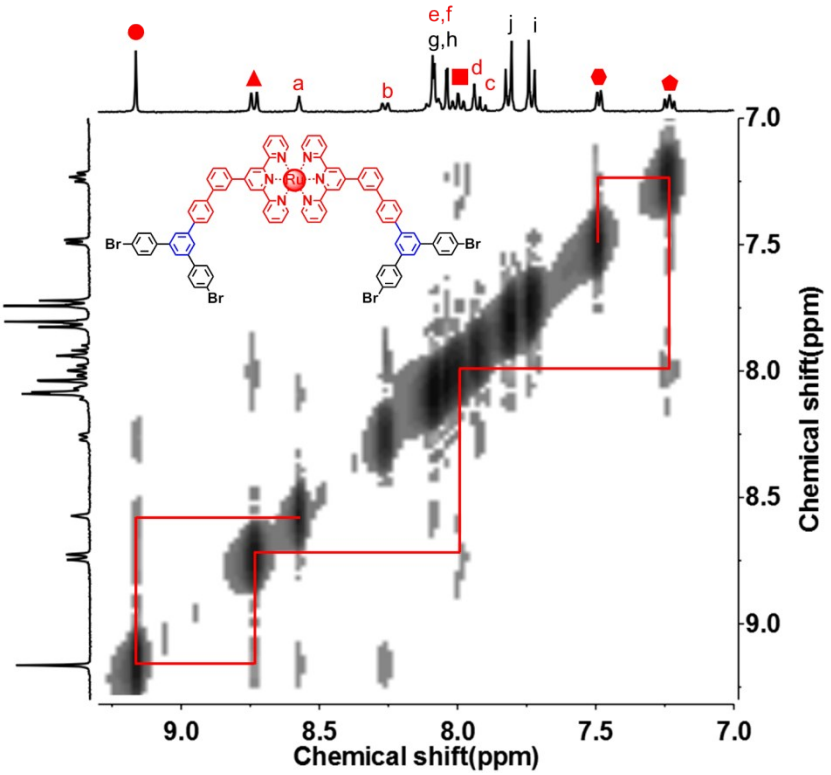



**Figure S17.** 2D NOESY spectrum (400 MHz) of $\mathbf{RuY_2}$ in $CD_3CN$.

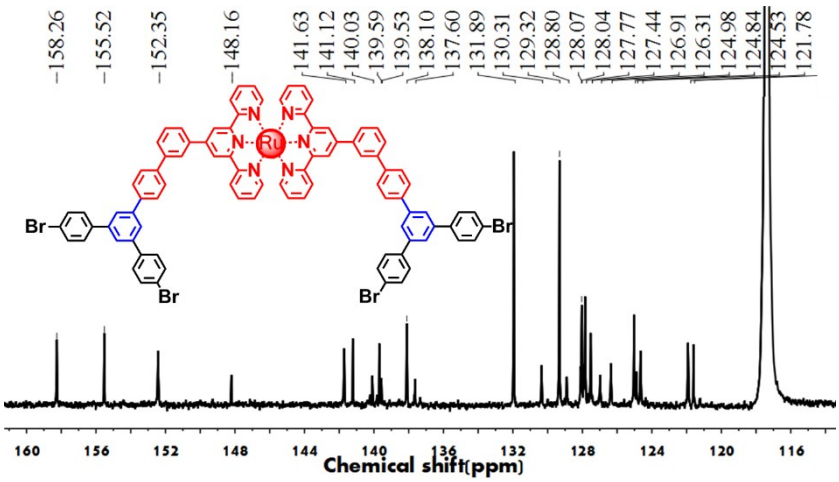



**Figure S18.** $^{13}C$ spectrum (400 MHz) of ligand $\mathbf{RuY_2}$ in $CDCl_3$.

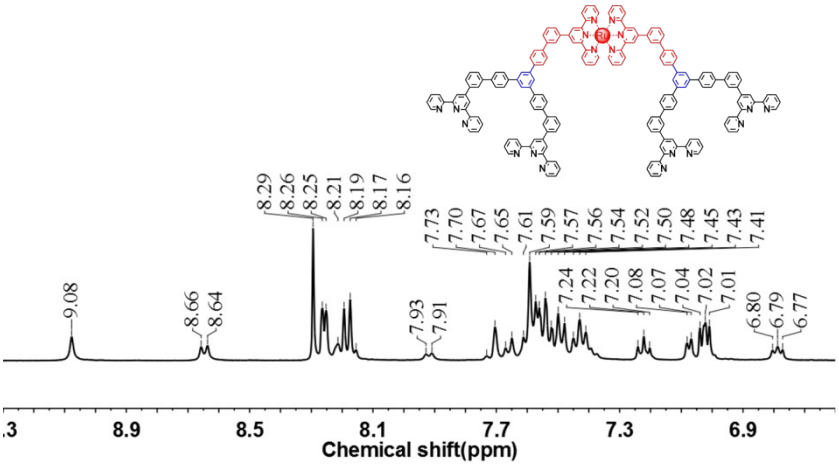



**Figure S19.** $^{1}H$ NMR spectrum (400 MHz) of ligand $\mathbf{RuL_2}$ in DMSO-$d_6$.

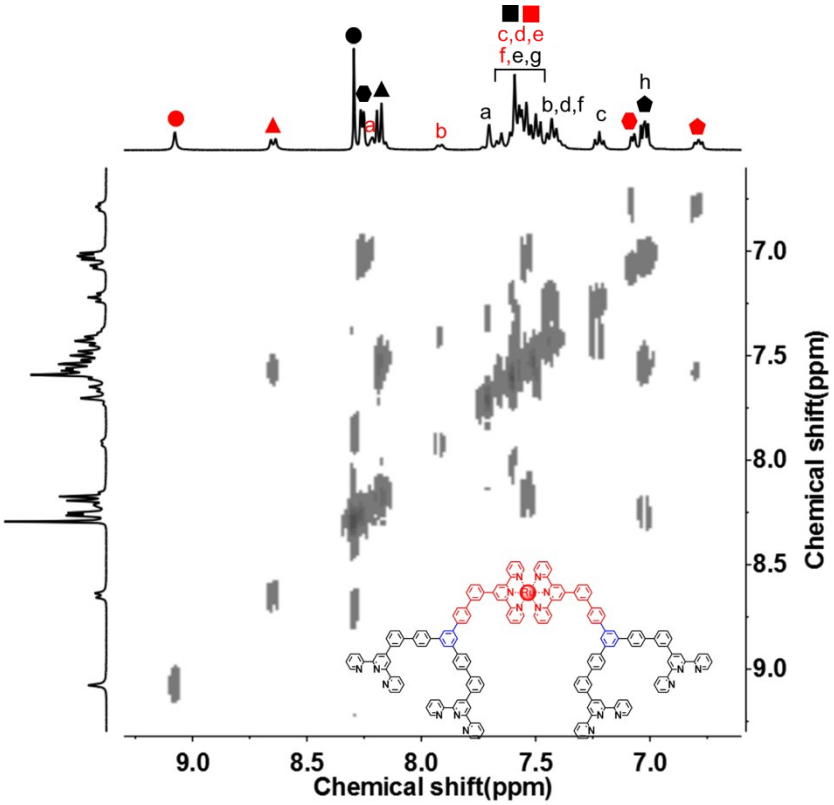



**Figure S20.** 2D COSY spectrum (400 MHz) of ligand $\mathbf{RuL_2}$ in DMSO-$d_6$.

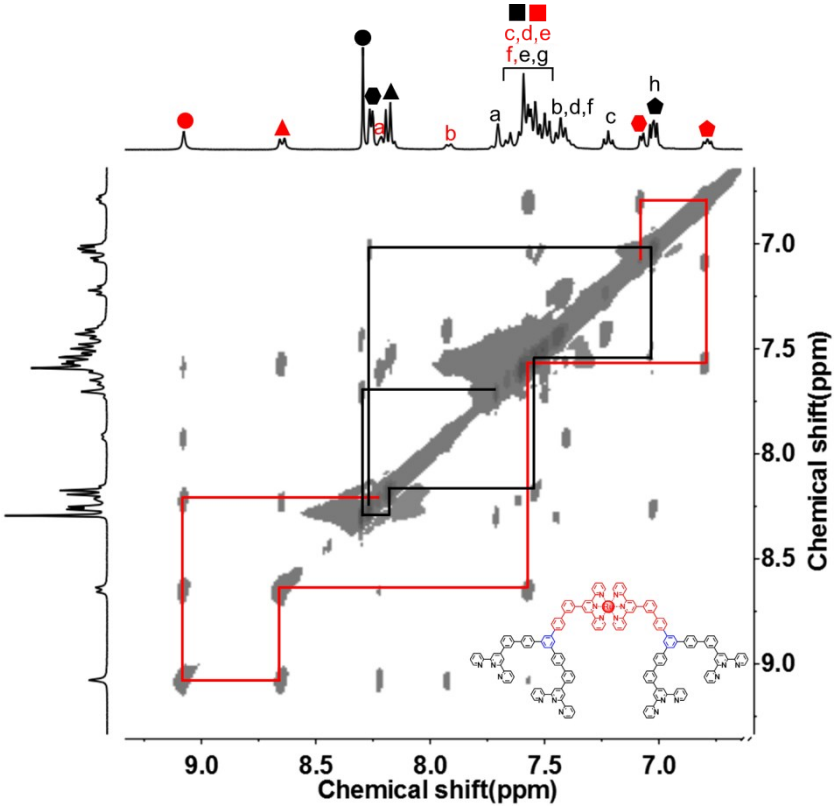



**Figure S21.** 2D NOESY spectrum (400 MHz) of ligand $\mathbf{RuL_2}$ in DMSO-$d_6$.

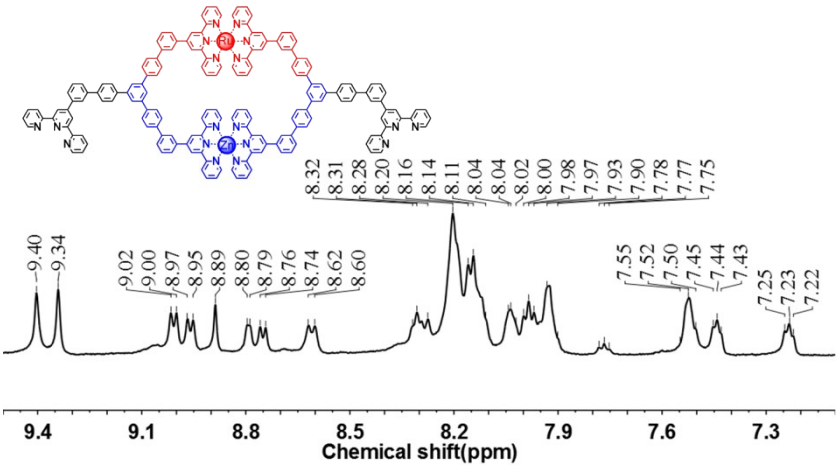



**Figure S22.** $^{1}$H NMR spectrum (500 MHz) of ligand **Zn[RuL$_2$]** in $CD_3CN$.

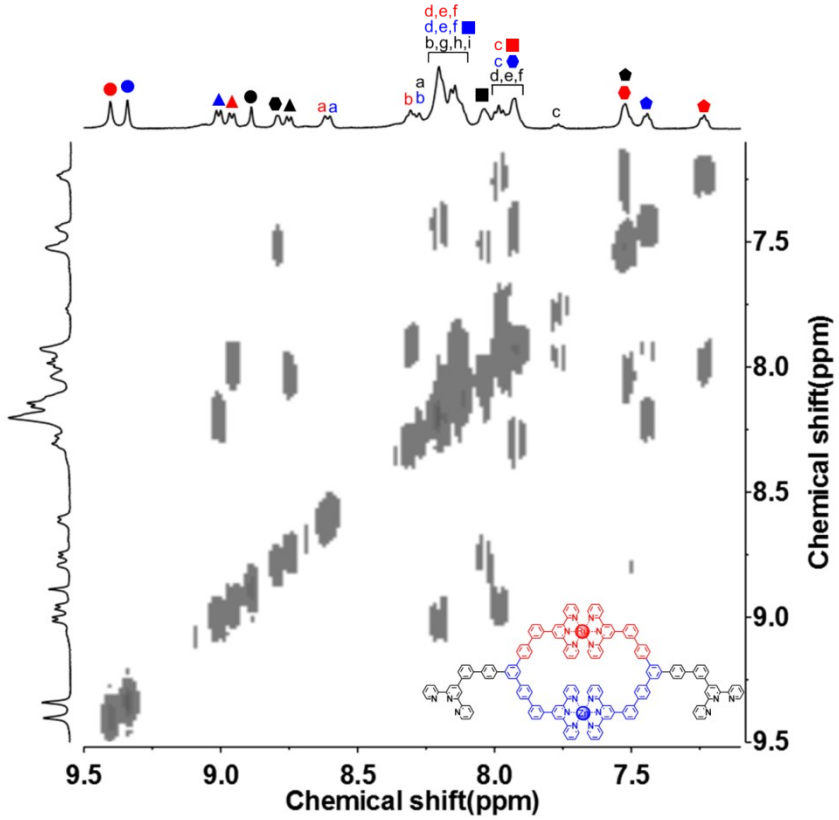



**Figure S23.** 2D COSY spectrum (500 MHz) of ligand **Zn[RuL$_2$]** in $CD_3CN$.

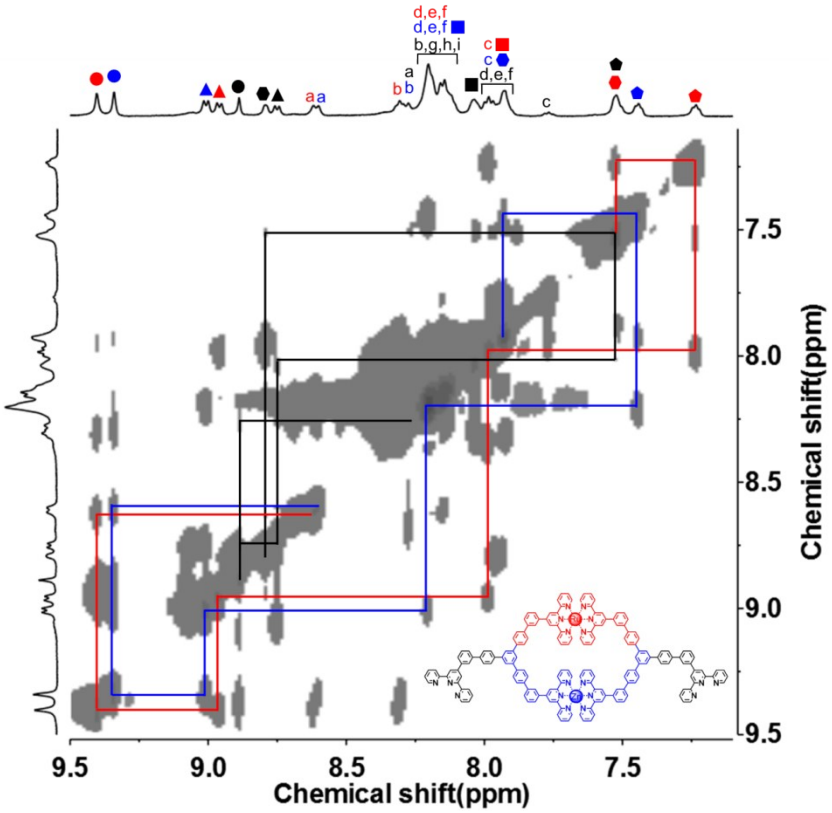



**Figure S24.** 2D NOESY spectrum (500 MHz) of ligand **Zn[RuL$_2$]** in $CD_3CN$.

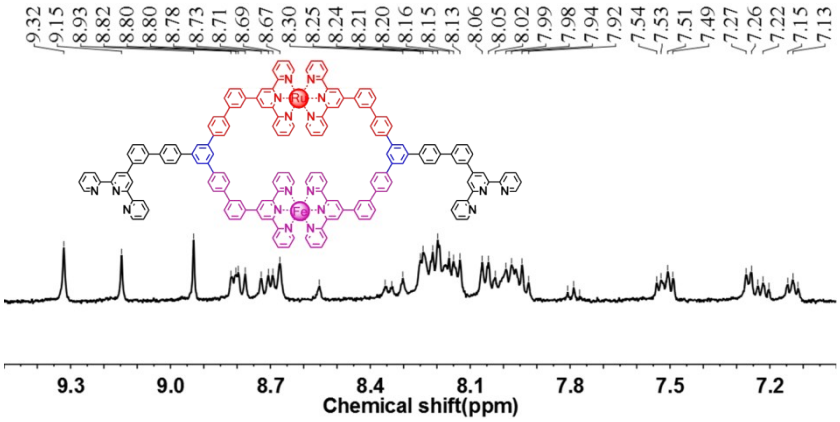



**Figure S25.** $^1$H NMR spectrum (500 MHz) of ligand **Fe[RuL$_2$]** in $CD_3CN$.

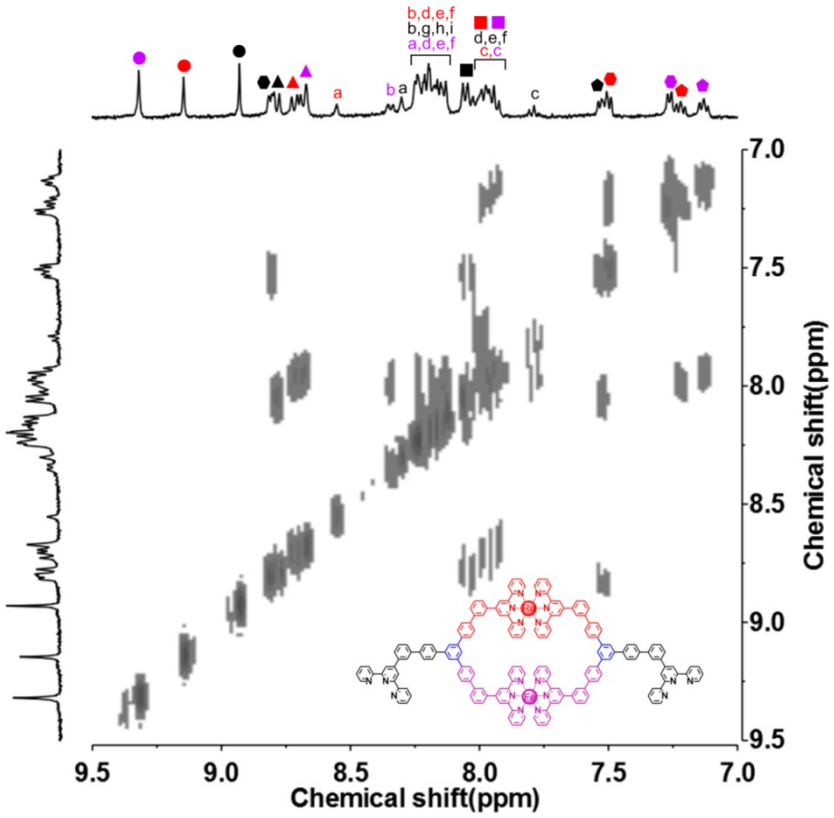



**Figure S26.** 2D COSY spectrum (500 MHz) of ligand **Fe[RuL$_2$]** in $CD_3CN$.

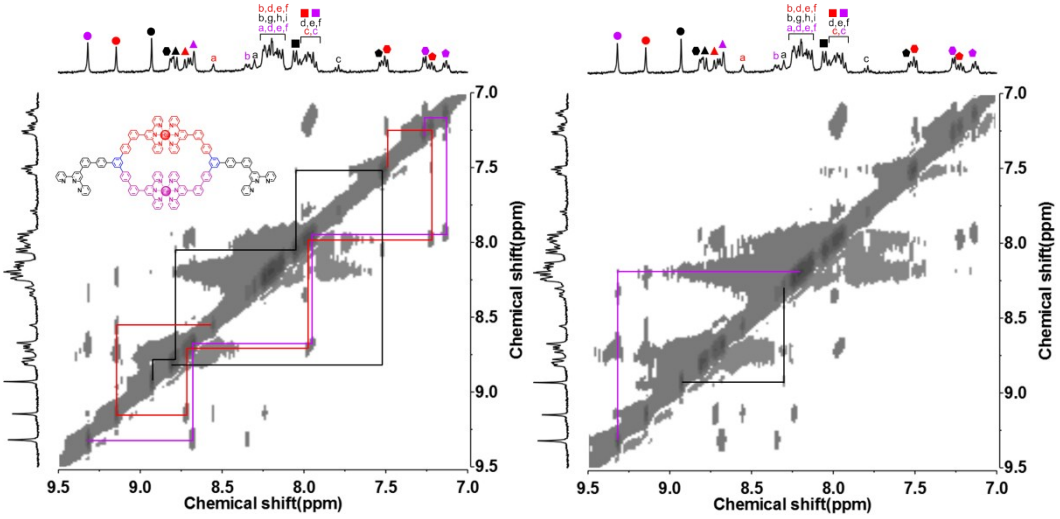



**Figure S27.** 2D NOESY spectrum (500 MHz) of ligand **Fe[RuL$_2$]** in $CD_3CN$.

**ESI-MS spectra data of of ligand and complex**

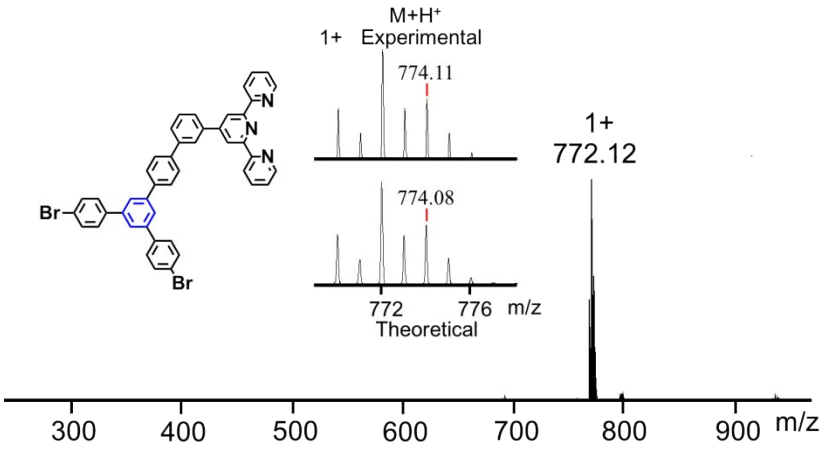



**Figure S28.** The ESI-MS spectrum of ligand **3**.

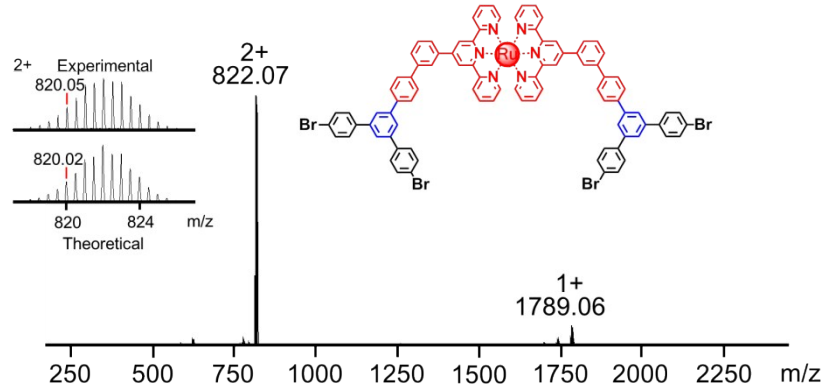



**Figure S29.** The ESI-MS spectrum of $\mathbf{RuY_2}$.

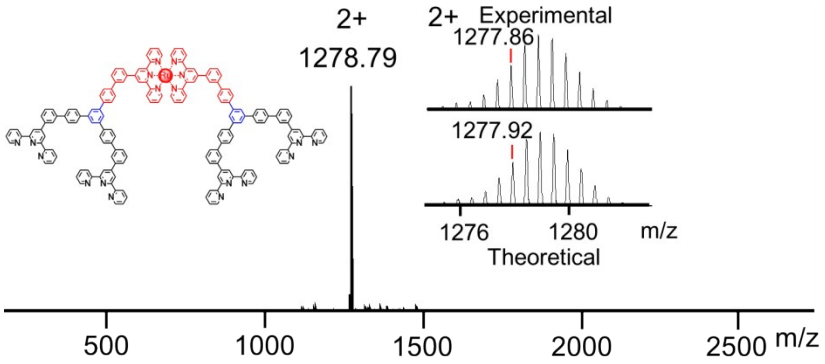



**Figure S30.** The ESI-MS spectrum of $RuL_2$.

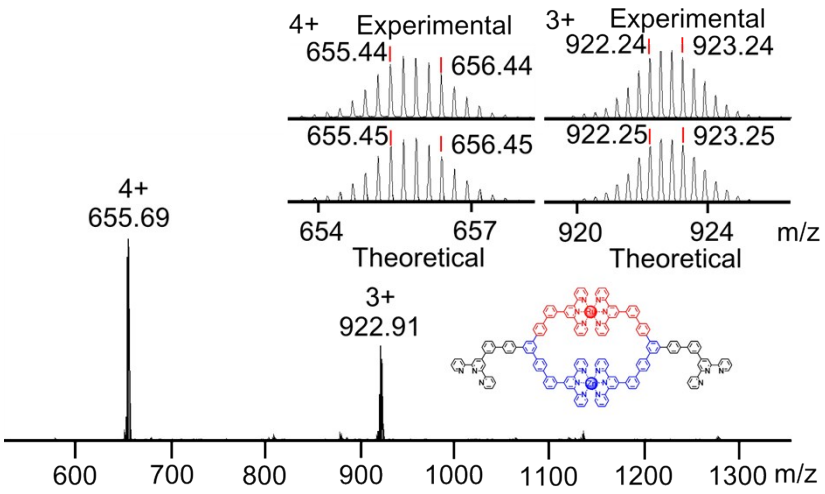



**Figure S31.** The ESI-MS spectrum of ligand **Zn[RuL$_2$]**.

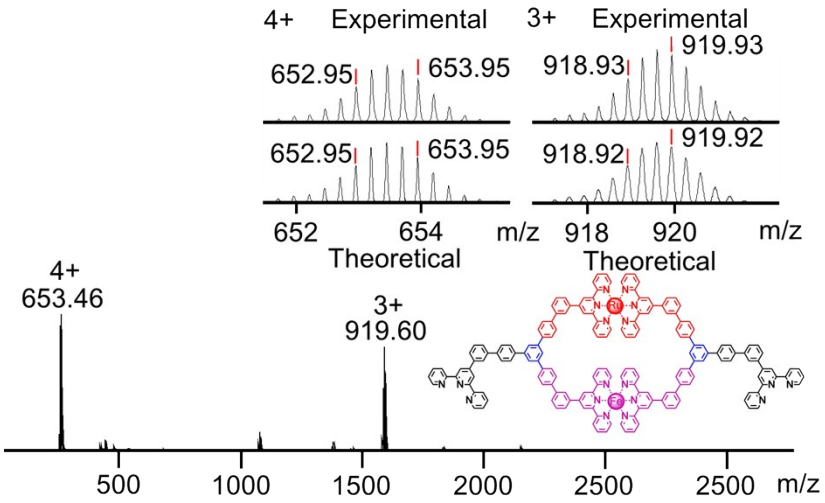



**Figure S32.** The ESI-MS spectrum of ligand **Fe[RuL$_2$]**.

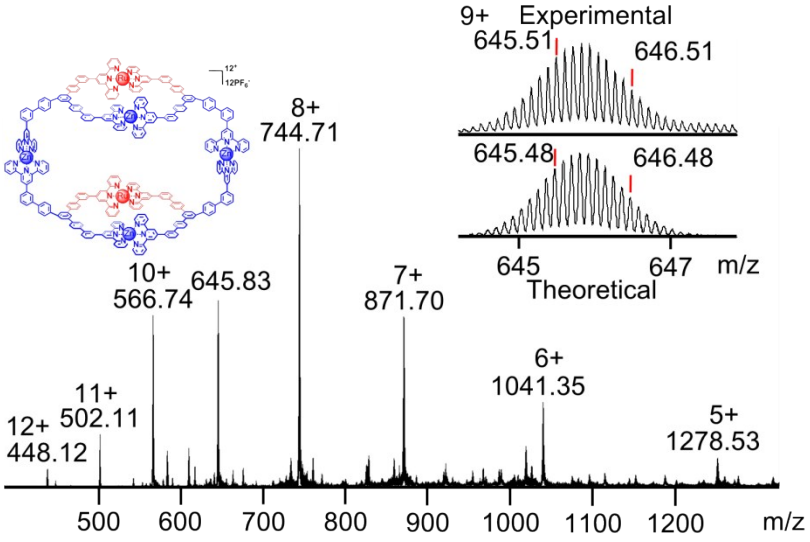



**Figure S33.** The ESI-MS spectrum of **Zn$_2$[RuL$_2$]**.

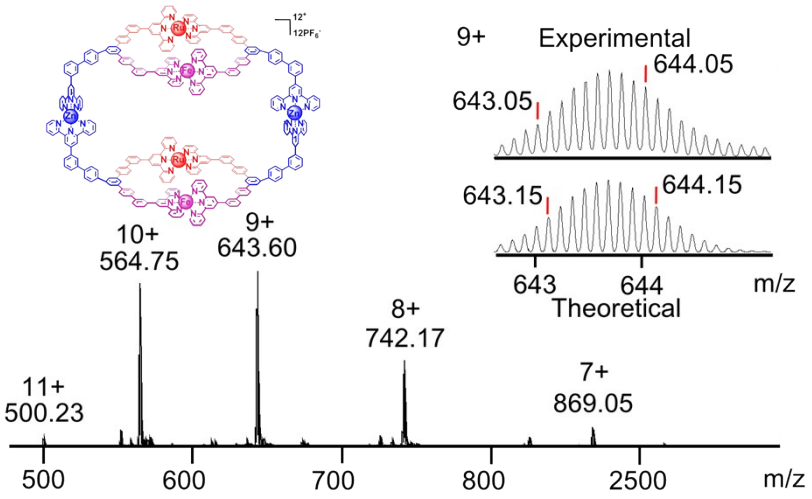



**Figure S34.** The ESI-MS spectrum of $\mathbf{Fe_2Zn_2[RuL_2]_2}$.

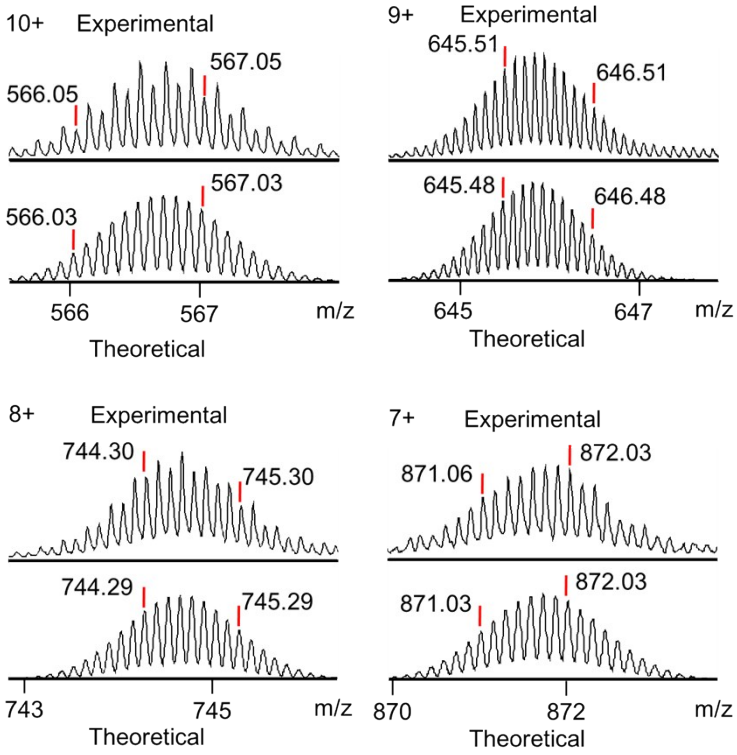



**Figure S35.** Theoretical and measured isotope patterns for various charge states of $\mathbf{Zn_4[RuL_2]_2}$ ($PF_6^-$, as counterion).

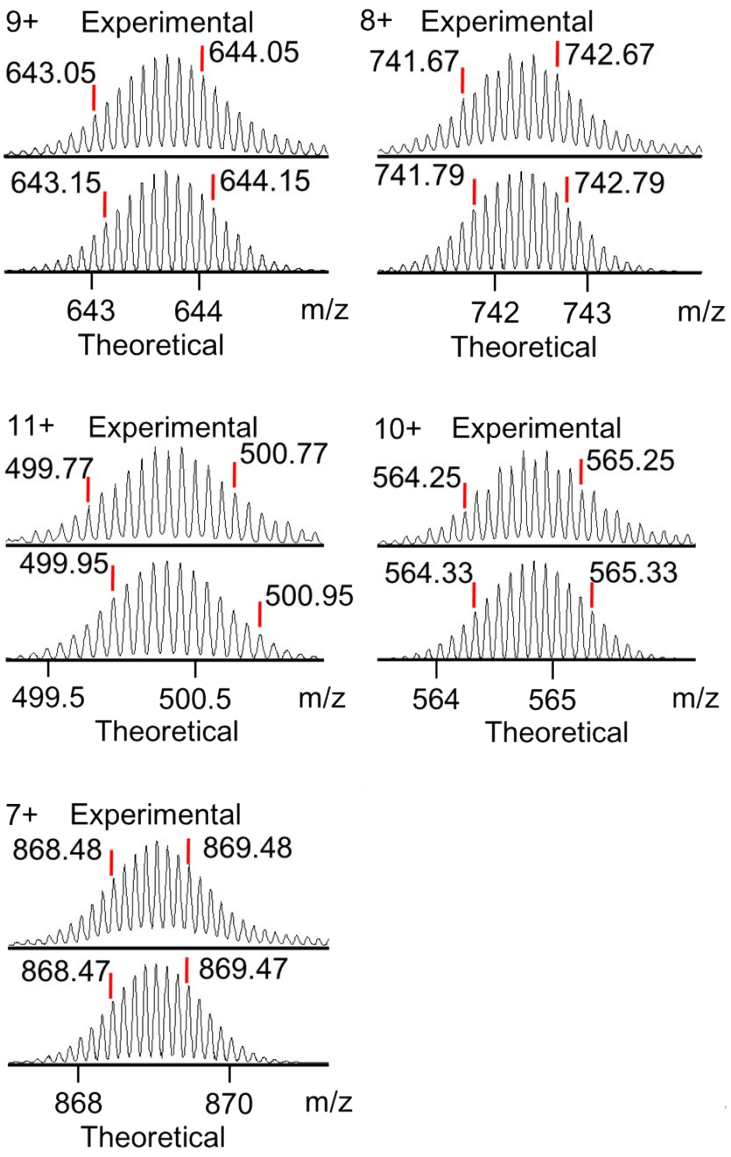



**Figure S36.** Theoretical and measured isotope patterns for various charge states of $\mathbf{Fe_2Zn_2[RuL_2]_2}$ ($PF_6^-$, as counterion).

**Molecular models**

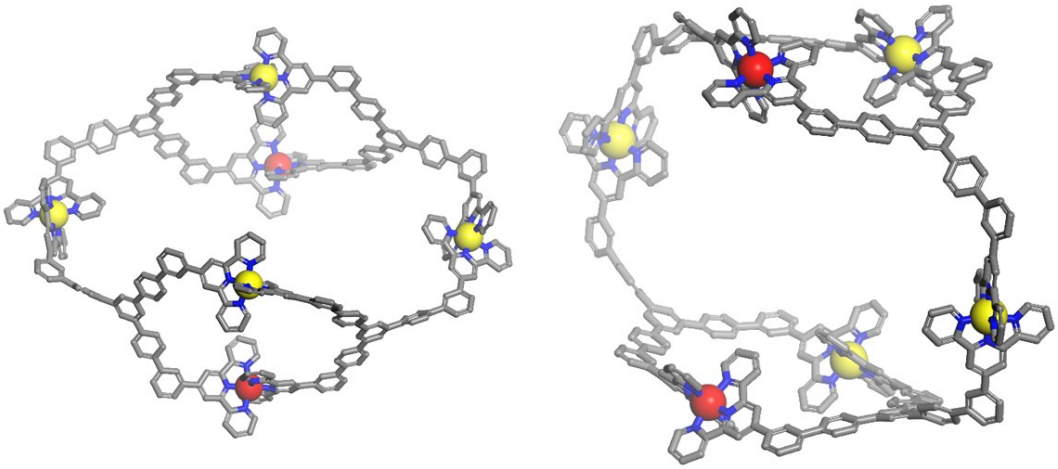


**Figure S37.** Energy-minimized structure of $Zn_4[RuL_2]_2$.

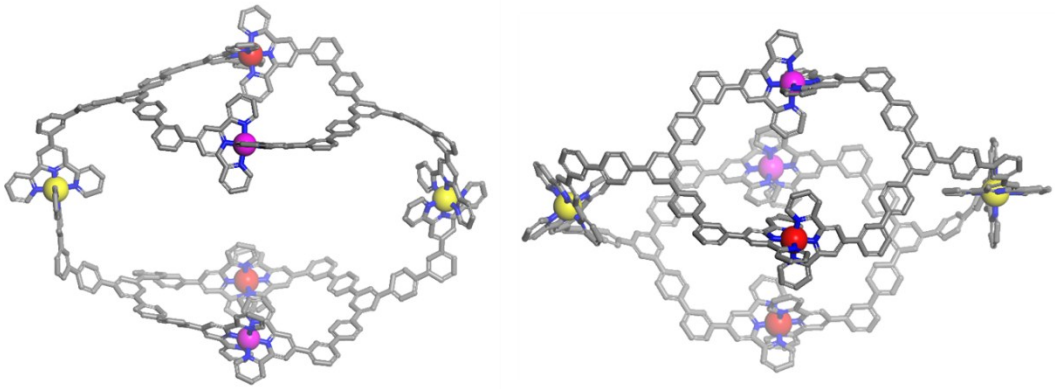


**Figure S38.** Energy-minimized structure of $Fe_2Zn_2[RuL_2]_2$.

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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.

S2: T.-Z. Xie, S.-Y. Liao, K. Guo, X. Lu, X. Dong, M. Huang, C. N. Moorefield, S. Z. D. Cheng, X. Liu, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2014, **136**, 8165.

S3: S. Chakraborty, W. Hong, K. J. Endres, T. Z. Xie, L. Wojtas, C. N. Moorefield, C. Wesdemiotis and G. R. Newkome, *J. Am. Chem. Soc.*, 2017, **139**, 3012.