Terpyridine-based Metallo-Organic Cage and Supramolecular Gelation by Coordination-driven Self-Assembly and Host–Guest Interaction

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Content

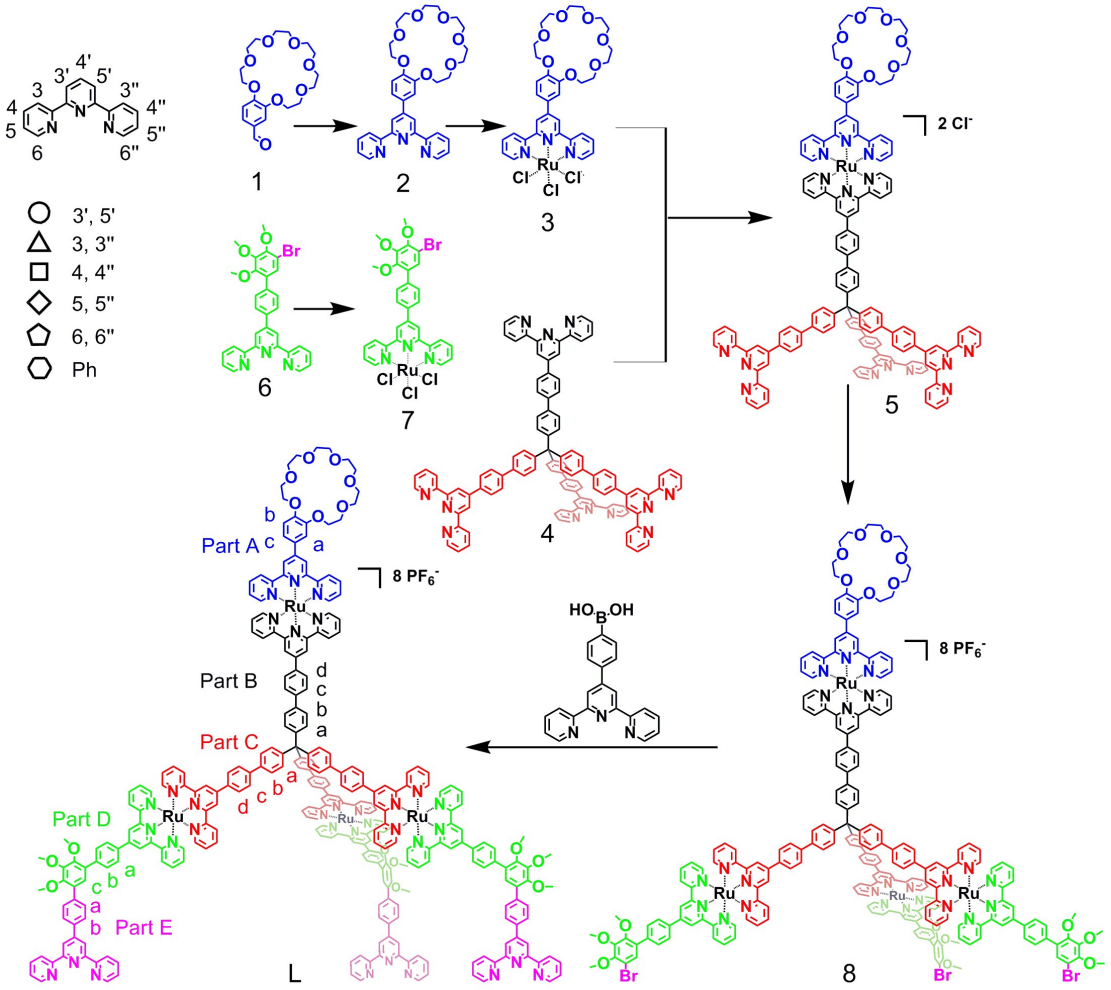
1. Experimental section

NMR spectra were recorded on a Bruker ADVANCE 400 or 500 NMR Spectrometer. ^{1}H NMR chemical shifts are reported in ppm downfield from tetramethylsilane (TMS) reference using the residual protonated solvent as an internal standard.
Mass spectra of complexes and ligands were determined on Waters Synapt G2 Mass Spectrometer under the following conditions: ESI capillary voltage, 3.5 kV; cone voltage, 35 V; desolvation gas flow, 800 L/h. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise specified.

Transmission Electron Microscopy (TEM) The sample was dissolved in CH_3CN at a concentration of ~10^{-7} M. The solutions were dropped cast on to a carbon-coated Cu or Ni grid (300-400 mesh) and extra solution was absorbed by filter paper to avoid aggregation. The TEM images of the drop cast samples were taken with a JEOL 2010 Transmission Electron Microscope.

Molecular Modeling. Energy-minimized structures were obtained following the settings in the literature.[S3] Calculations were proceeded with Geometry Optimization and followed by Anneal in Forcite module of Materials Studio version 7.0 program (Accelrys Software, Inc.).

2. Synthesis and discussion of the related ligands and complexes



Scheme S1 Synthetic route to the ligand **L**

Synthesis of compound **2**: A mixture of **1** (1.5 g, 4 mmol), 2-acetylpyridine (1.9 g, 16 mmol), absolute EtOH (30 mL), and powdered NaOH (640 mg, 16 mmol) were added to a round bottom flask. The resulting solution was stirring at 30 °C for 8 h. After which 20 mL $NH_3 \cdot H_2O$ (25-28%) was added and the mixture was heated at 75 °C for 24 h to give brown solution. The mixture was brought to room temperature and evaporated under reduced pressure, then extracted with CH_2Cl_2. The combined organic fractions were washed with brine, were dried over Na_2SO4, filtered, and concentrated under reduced pressure. After removal of the solvent, the residue was purified by flash column chromatography (Al_2O_3) to give compound **2** (1.4 g, 61%) as white solid. ^{1}H NMR (400 MHz, MeOD) δ 8.67 (d, $tpy^{3,3''}$, 2H), 8.61 (d, $tpy^{6,6''}$, 2H), 8.55 (s, $tpy^{3',5'}$, 2H), 7.98(t, $tpy^{5,5''}$, 2H), 7.41-7.51 (m, $tpy^{4,4''}$, Ph^a, Ph^c , 4H), 7.08 (s, Ph^b, 1H), 4.29 (t, 2H), 4.21 (t, 2H), 3.89-3.94 (m, 4H), 3.76-3.80 (m, 4H), 3.70-3.74 (m, 4H), 3.63-3.66 (m, 8H).^{13}C NMR (400 MHz, MeOD) δ 155.89, 155.57, 150.12, 149.75, 149.25, 148.61, 137.46, 130.83, 124.08, 121.63, 119.91, 117.75, 113.84, 112.29. ESI/MS (m/z): Calcd. for $[C_{33}H_{37}N_3O_7+H]^+$: 588.27, Found: 588.30; $[C_{33}H_{37}N_3O_7+Na]^+$: 610.25, Found: 610.29.

Synthesis of compound **3**: A 100 mL oven-dried round bottom flask was charged with **2** (48 mg, 0.08 mmol) and 15 ml EtOH. Solid $RuCl_3 \cdot 4H_2O$ (44.21 mg, 0.16 mmol) was added very slowly at 80 °C, and kept refluxing for 12 h. The final reaction mixture was dirty red precipitate which was collected by filtration followed by washing with EtOH and dried in vacuum. Isolated yield: 67.85 mg (74%). Elemental analyses (**3** · $2H_2O$): C% = 47.5001411 (Cal: 47.69), N% = 5.0913591 (Cal: 5.06), H% = 4.6175828 (Cal: 4.97). **3** was directly used for next reaction without further purification.

Synthesis of compound **5**: The **3** (67.85 mg, 0.08 mmol) and **4**[1] (262 mg, 0.16 mmol) was added to a 50 mL flask, then 5 mL CH_3OH and 15 mL $CHCl_3$ was added as solvent. After adding 6 drops N-ethylmorpholine, the suspension was stirred at 80 °C for 24 hours. After cooled to ambient temperature, the mixture was filtered under reduced pressure. The solution was precipitated with NH_4PF_6 to afford a dark red solid. After purification with flash column chromatography (Al_2O_3, $CHCl_3$/MeOH) and further washed with MeOH, complex **5** (180 mg, 85%) was collected. The product was used in the next step without further purification. ^{1}H NMR (400 MHz, DMSO) δ 9.58 (s, tpy $B^{3',5'}$, 2H), 9.41 (s, tpy $A^{3',5'}$, 2H), 9.12-9.18 (m, tpy $A^{3,3''}$,tpy B $^{3,3''}$, 4H), 8.80 (s, tpy $C^{3',5'}$, 6H), 8.79 (d, tpy$A^{6,6''}$,tpy $B^{6,6''}$,tpy $C^{6,6''}$, 6H), 8.71 (d, tpy $C^{3,3''}$, 6H), 8.61 (d, Ph B^d , 2H), 8.16 (d, Ph B^c, 2H), 8.04-8,09 (m, tpy $A^{4,4''}$, tpy $C^{4,4''}$, Ph A^c, Ph C^d, 15H), 7.95-8.01 (m, Ph B^b , Ph C^a, Ph C^c, 9H), 7.89 (d, Ph C^b, 2H), 7.54-7.58 (m, tpy $B^{4,4''}$, Ph A^b, Ph B^a, tpy $C^{5,5''}$, 6H), 7.27-7.35 (m, tpy $B^{5,5''}$, 4H), 4.44 (t, 2H), 4.29 (t, 2H), 3.85-3.91 (t, 4H), 3.67-3.71 (t, 4H), 3.61-3.63 (t, 4H), 3.56 (m, 8H). ESI/MS (*m/z*): Calcd. for $[C_{142}H_{109}N_{15}O_7Ru]^{2+}$: 1119.39, Found:1119.46.

Synthesis of compound **6**: To a mixture of 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine (858 mg, 2.63 mmol) and 1,5-dibromo-2,3,4-trimethoxybenzene (557.86 mg, 1.58 mmol) and in 30 mL CH_3CN, NaOH (316 mg, 7.9 mmol) was added. then $Pd(PPh_3)_4$ (182 mg, 0.158 mmol) was added, the system was pumped and backfilled with nitrogen; After refluxed for 1 day under N_2, the mixture was cooled to 25 °C and evaporated under reduced pressure. The residue was washed with 50 mL CH_3OH. The precipitate was dried at 60 °C in vacuo and purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/CH_3OH to give **6**, as a solid 1.09 g (72%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, tpy $^{3',5'}$, 2H), 8.77 (t, tpy $^{5,5''}$, 2H), 8.72 (d, tpy $^{3,3''}$, 2H), 7.99 (t, tpy $^{6,6''}$, 2H), 7.93 (t, tpy $^{4,4''}$, 2H), 7.67 (d, Ph D^b , 2H), 7.40 (Ph D^a, 2H), 7.39 (Ph D^c, 1H), 4.02 (s, 3H), 3.99 (s, 3H), 3.69 (s, 3H). ESI/MS (*m/z*): Calcd. for $[C_{30}H_{24}N_3O_3Br]^{2+}$: 556.10, Found: 556.14.

Synthesis of compound **7**: A 100 mL oven-dried round bottom flask was charged with **6** (200 mg, 0.36 mmol) and 30 ml EtOH. Solid $RuCl_3 \cdot 4H_2O$ (108 mg, 0.4 mmol) was added very slowly at 80 °C, and kept refluxing for 12 h. The final reaction mixture was filtered and washed with EtOH and dried under vacuum. Isolated yield: 183 mg (74%). Elemental analyses (**7** · H_2O): C%= 52.353672 (Cal: 46.20), N%=5.2737012 (Cal: 5.39), H%= 3.3225484 (Cal: 3.36). **7** was directly used for next reaction without further purification.

Synthesis of compound **8**: **5** (60.7 mg, 24 μmol) was dissolved in $CHCl_3$ (10 mL), followed by the addition of MeOH (15 mL), then the mixture was refluxed for 2 h. Solid **7** (78 mg, 102 μmol) was added; the mixture was refluxed for an additional hour. After adding 7 drops N-ethyl morpholine, the stirred solution was refluxed for 24 hours. After cooling to ambient temperature, the resultant

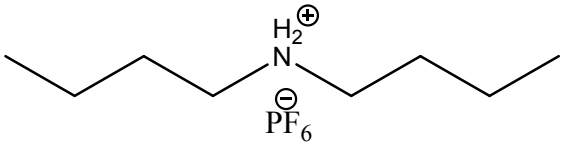
red solution was concentrated in vacuo to give red powder, which was dissolved in $CHCl_3$ and chromatographed through a short column of Al_2O_3 to remove excess of **7**. The solution was precipitated with NH_4PF_6 to afford desired **8**. Isolated yield: 88.57 mg (78%); ^{1}H NMR (400 MHz, CD_3CN) δ 9.06 (m, tpy $A^{3',5'}$, tpy $C^{3',5'}$, tpy $D^{3',5'}$, 14H), 8.97 (s, tpy $B^{3',5'}$, 2H), 8.64-8.68 (m, tpy $A^{3,3''}$, tpy $B^{3,3''}$, tpy $C^{3,3''}$, tpy $D^{3,3''}$, 16H), 8.33 (m, Ph B^a , Ph C^d, 8H), 8.25 (d, Ph D^a, 6H), 8.10 (m, Ph B^b, Ph C^c, 8H), 7.91-7.94 (m, tpy $C^{4,4''}$, tpy $D^{4,4''}$, Ph C^b, 24H), 7.82(d, Ph D^b, 6H), 7.77-7.79 (d, Ph A^a, 1H) 7.68-7.70 (m, Ph B^d, Ph C^a, 8H), 7.46 (s, Ph D^c, 3H), 7.41-7.43 (m, tpy $A^{6,6''}$, tpy $B^{6,6''}$, tpy $C^{6,6''}$, tpy $D^{6,6''}$, 14H), 7.39 (s, Ph A^c, 1H), 7.24-7.26 (d, Ph A^b, 1H), 7.12-7.18 (m, tpy $A^{4,4''}$, tpy $A^{5,5''}$, tpy $B^{4,4''}$, tpy $B^{5,5''}$, tpy $C^{5,5''}$, tpy $D^{5,5''}$, 20H), 4.40 (t, 2H), 4.28 (t, 2H), 4.95 (s, 9H), 3.92 (t, 2H), 3.90 (t, 2H), 3.87 (s, 9H), 3.72 (s, 9H), 3.67 (m, 4H), 3.60 (m, 4H), 3.55 (m, 8H). ESI-MS (*m/z*): 1196.47 $[M\text{-}4PF_6^-]^{4+}$ (calcd. *m/z* = 1196.41), 928.18 $[M\text{-}5PF_6^-]^{5+}$ (calcd. *m/z* = 828.04), 749.34 $[M\text{-}6PF_6^-]^{6+}$ (calcd. *m/z* = 749.20), 621.58 $[M\text{-}7PF_6^-]^{7+}$ (calcd. *m/z* = 621.53).

Synthesis of compound **L**: To a mixture of 4'-(4-boronatophenyl)[2,2':6',2"]terpyridine (105 mg, 0.3mmol) and **8** (50 mg, 0.01 mmol) in 30 mL CH_3CN, K_2CO_3 (120 mg, 1.1 mol) was added. Then $Pd(PPh_3)_4$ (3.3 mg) was added, and the system was pumped and backfilled with nitrogen; After refluxing for 3 days under N_2, the mixture was cooled to 25 °C and evaporated under reduced pressure. The residue was washed with 100 mL CH_3OH and the precipitate was dried at 60 °C in vacuo and purified by flash column chromatography (Al_2O_3), eluting with CH_2Cl_2/CH_3OH to give **L**, as a red solid 42 mg (64%); ^{1}H NMR (400 MHz, CD_3CN) δ 9.06-9.07 (m, tpy $B^{3',5'}$, tpy $C^{3',5'}$, tpy $D^{3',5'}$, 14H), 8.97 (s, tpy $A^{3',5'}$, 2H), 8.77 (s, tpy $E^{3',5'}$, 6H), 8.66-8.69 (m, tpy $A^{3,3''}$, tpy $B^{3,3''}$, tpy $C^{3,3''}$, tpy $D^{3,3''}$, tpy $E^{3,3''}$, tpy $E^{6,6''}$, 28H), 8.32-8.34 (m, Ph B^d, Ph C^d, 8H), 8.27 (d, Ph D^a, 6H), 8.09-8.10 (m, Ph B^c ,Ph C^c, 8H), 8.03 (d, Ph E^b, 6H), 7.91-7.98 (m, tpy $A^{4,4''}$, tpy $B^{4,4''}$, tpy $C^{4,4''}$, tpy $D^{4,4''}$, tpy $E^{4,4''}$, Ph B^b, Ph C^b, Ph D^b, 36H), 7.77-7.79 (d, Ph A^a, 1H), 7.79 (d, Ph E^a, 6H), 7.68-7.71 (m, Ph A^c, Ph B^a, Ph C^a , 9H), 7.39-7.46 (m, tpy $A^{6,6''}$, tpy $B^{6,6''}$, tpy $C^{6,6''}$, tpy $D^{6,6''}$, 16H), 7.33 (s, Ph D^c, 3H), 7.25 (d, Ph A^b, 1H), 7.13-7.18 (m, tpy $A^{5,5''}$, tpy $B^{5,5''}$, tpy $C^{5,5''}$, tpy $D^{5,5''}$, tpy $E^{5,5''}$, 22H), 4.40 (t, 2H), 4.28(t, 2H), 4.00 (s, 9H), 3.92 (t, 2H), 3.86 (t, 2H), 3.81 (s, 9H), 3.77 (s, 9H), 3.68 (m, 4H), 3.61 (m, 4H), 3.55 (m, 8H). ESI-MS (*m/z*): 1065.09 $[M\text{-}5PF_6^-]^{5+}$ (calcd. *m/z* = 1065.06), 863.42 $[M\text{-}6PF_6^-]^{6+}$ (calcd. *m/z* = 863.39), 719.38 $[M\text{-}7PF_6^-]^{7+}$ (calcd. *m/z* = 719.34), 611.34 $[M\text{-}8PF_6^-]^{8+}$ (calcd. *m/z* = 611.30).

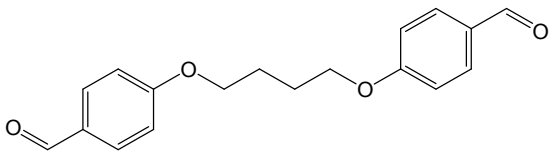
Synthesis of compound [$\mathbf{Zn_3L_2}$]: A stoichiometric ratio (2 : 3) of **L** and $Zn(NO_3)_2$ were mixed in MeCN at 85 °C for 12 h, followed by the incorporation of saturated NH_4PF_6 to attain dark red precipitate, which were entirely washed with pure water and dried at 50 °C in vacuo. ^{1}H NMR (400 MHz, CD_3CN) δ 9.07-9.10 (m, tpy $C^{3',5'}$, tpy $D^{3',5'}$, tpy $E^{3',5'}$, 36H), 9.00 (s, tpy $A^{3',5'}$,tpy $B^{3',5'}$, 8H), 8.67-8.78 (m, tpy $A^{3,3''}$, tpy $B^{3,3''}$, tpy $C^{3,3''}$, tpy $D^{3,3''}$,tpy $E^{3,3''}$, 44H), 8.33-8.39 (m, Ph B^d, Ph C^d ,Ph D^a ,Ph E^b, 40H), 8.16-8.20(m, Ph B^c ,Ph C^c ,tpy $D^{4,4''}$, 28H), 8.01-8.05 (m, tpy $A^{4,4''}$, tpy $B^{4,4''}$, tpy $C^{4,4''}$, tpy $E^{4,4''}$,Ph B^b, Ph C^b, Ph D^b, Ph E^a, 72H), 7.88 (t, tpy $D^{6,6''}$, 12H), 7.83 (d, Ph A^c, 2H),7.75 (m, Ph A^a, Ph B^a ,Ph C^a, 18H), 7.45-7.48 (m, tpy $A^{6,6''}$, tpy $B^{6,6''}$, tpy $C^{6,6''}$, tpy $D^{5,5''}$, tpy $E^{6,6''}$, Ph D^c, 54H), 7.30 (d, Ph A^b, 2H), 7.21 (m, tpy $A^{5,5''}$, tpy $B^{5,5''}$, tpy $C^{5,5''}$, tpy $E^{5,5''}$, 32H), 4.47 (t, 4H), 4.34 (t, 4H), 4.10 (s, 18H), 4.07 (t, 4H), 3.97 (t, 4H), 3.90 (m, 36H), 3.72 (m, 8H), 3.65 (m, 8H), 3.60 (m, 16H). ESI-MS (*m/z*): 1736.04 $[M\text{-}7PF_6^-]^{7+}$ (calcd. *m/z* = 1736.00), 1500.85 $[M\text{-}8PF_6^-]^{8+}$ (calcd. *m/z* = 1500.82), 1318.05 $[M\text{-}9PF_6^-]^{9+}$ (calcd. *m/z* = 1318.01), 1171.67 $[M\text{-}10PF_6^-]^{10+}$ (calcd. *m/z* = 1171.63), 1051.97 $[M\text{-}11PF_6^-]^{11+}$ (calcd. *m/z* = 1051.93), 952.26 $[M\text{-}12PF_6^-]^{12+}$ (calcd. *m/z* =952.22), 867.83 $[M\text{-}13PF_6^-]^{13+}$ (calcd. *m/z* = 867.80), 795.52 $[M\text{-}14PF_6^-]^{14+}$

(calcd. *m/z* = 795.48), 732.79 $[M\text{-}15PF_6^-]^{15+}$ (calcd. *m/z* = 732.75), 677.93 $[M\text{-}13PF_6^-]^{13+}$ (calcd. *m/z* = 677.90).

Synthesis of compound **$[Fe_3L_2]$**:A stoichiometric ratio (2 : 3) of **L** and $FeCl_2$ were mixed in MeCN at 85°C for 24 h, followed by the incorporation of saturated NH_4PF_6 to attain a dark red precipitate, which were entirely washed with pure water and dried at 50 °C in vacuo. ^{1}H NMR (400 MHz, CD_3CN) δ 9.27 (s, tpy $E^{3',5'}$, 12H), 9.09-9.11 (m, tpy $B^{3',5'}$, tpy $C^{3',5'}$, tpy $D^{3',5'}$, 28H), 9.00 (s, tpy $A^{3',5'}$, 4H), 8.66-8.72 (m, tpy $A^{3,3''}$, tpy $B^{3,3''}$, tpy $C^{3,3''}$, tpy $D^{3,3''}$, tpy $E^{3,3''}$, 44H), 8.45 (d, Ph E^b, 12H), 8.37 (m, Ph B^d, Ph C^d,Ph D^a, 28H), 8.15 (m, Ph B^c ,Ph C^c, 16H), 8.03-8.09 (m, Ph D^b, Ph E^a, 24H), 7.97 (m, tpy $A^{4,4''}$, tpy $B^{4,4''}$, tpy $C^{4,4''}$, tpy $D^{4,4''}$, tpy $E^{4,4''}$, Ph B^b, Ph C^b, 60H), 7.82 (d, Ph A^c, 2H),7.74 (m, Ph A^a, Ph B^a ,Ph C^a, 18H), 7.45-7.48 (m, tpy $A^{6,6''}$, tpy $B^{6,6''}$, tpy $C^{6,6''}$, tpy $D^{6,6''}$, Ph D^c, 44H), 7.29 (d, Ph A^b, 2H), 7.21 (m, tpy $A^{5,5''}$, tpy $B^{5,5''}$, tpy $C^{5,5''}$, tpy $D^{5,5''}$, tpy $E^{6,6''}$, 44H),7.11 (t, tpy $E^{5,5''}$, 12H), 4.46 (t, 4H), 4.33 (t, 4H), 4.11 (s, 18H), 4.06 (t, 4H), 3.95 (t, 4H), 3.90 (m, 36H), 3.71 (m, 8H), 3.64 (m, 8H), 3.58 (m, 16H). ESI-MS (*m/z*): 1497.32 $[M\text{-}8PF_6^-]^{8+}$ (calcd. *m/z* = 1497.28), 1314.79 $[M\text{-}9PF_6^-]^{9+}$ (calcd. *m/z* = 1314.75), 1168.86 $[M\text{-}10PF_6^-]^{10+}$ (calcd. *m/z* = 1168.82), 1049.42 $[M\text{-}11PF_6^-]^{11+}$ (calcd. *m/z* = 1049.38), 949.86 $[M\text{-}12PF_6^-]^{12+}$ (calcd. *m/z* = 949.83), 865.67 $[M\text{-}13PF_6^-]^{13+}$ (calcd. *m/z* = 865.64), 793.45 $[M\text{-}14PF_6^-]^{14+}$ (calcd. *m/z* = 793.41), 730.92 $[M\text{-}15PF_6^-]^{15+}$ (calcd. *m/z* = 730.88), 676.17 $[M\text{-}16PF_6^-]^{16+}$ (calcd. *m/z* = 676.13), 627.85 $[M\text{-}16PF_6^-]^{16+}$ (calcd. *m/z* =627.81), 584.93 $[M\text{-}17PF_6^-]^{17+}$ (calcd. *m/z* = 584.90), 546.50 $[M\text{-}16PF_6^-]^{16+}$ (calcd. *m/z* =546.46).

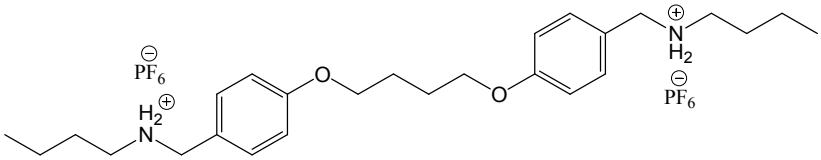


Synthesis of compound **N^1** (ref: S2)**:** Dibutylamine (1.00 g, 1.71 mmol) was dissolved in MeOH (20 mL) at room temperature and then an aqueous solution of HCl was added dropwise. The mixture was kept under stirring for 15 min, then excess NH_4PF_6 solution was added and a white precipitate was formed. The solid was collected by filtration and dried under vacuum, to give derivative as white solid. ^{1}H NMR (400MHz, MeOD): δ 2.98 (m, 4H), 1.97 (m, 2H), 1.63 (m, 4H), 1.40 (t, 4H), 0.95 (t, 6H).



Synthesis of compound **9^{S2}**: A mixture of 4-hydroxybenzaldehyde (915 mg, 7.5 mmol) and 1,4-dibromobutane (1.08 g, 5 mmol) and in 35 mL CH_3CN, K_2CO_3 (691 mg, 5 mmol) was added. The system was pumped and backfilled with nitrogen and refluxing for 1 day under N_2 at 85 °C; The mixture was brought to room temperature and evaporated under reduced pressure, then extracted with CH_2Cl_2 and purified by flash column chromatography (SiO_2), eluting with CH_2Cl_2/PE. ^{1}H NMR (400MHz, $CDCl_3$) δ 9.89 (s, 2H), 7.84 (m, 4H), 7.00 (m, 4H), 4.14 (t, 4H), 2.04 (t, 4H), 1.6

(t, 4H).



Synthesis of compound **N²** (Ref: S2): To a solution of butan-1-amine (113.82 mg) in $CHCl_3$ (2 mL) was added derivate **9** (0.2 g,). The reaction mixture was stirred at room temperature for 30 minutes. The solvent was evaporated to give the imine intermediate as a solid. The solid was used for the next step without further purification. The imine was dissolved in dry MeOH (5 mL) under N_2 and $NaBH_4$ was added at 0 °C and then allowed to warm at room temperature. The solution was kept under stirring for 2 h. The solvent was removed under reduced pressure and the residue partitioned between AcOEt (50 mL) and an aqueous saturated solution of $NaHCO_3$ (50 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure, to give derivative 10 as white solid (0.23 g, 0.45 mmol, 90%). ^{1}H NMR (500 MHz, MeOD) δ 7.40 (d, H^3, 2H), 6.99 (d, H^4, 2H), 4.12 (s, H^{10}, 2H), 4.08 (t, H^2, 2H), 3.31 (t, H^6, 2H), 3.00 (m, H^1, 2H), 1.97 (s, H^5, 2H), 1.68 (m, H^7, 2H), 1.41 (m, H^8, 2H), 0.98 (t, H^9, 2H).^{13}C NMR (500 MHz, MeOD) δ 160.13, 131.13, 122.95, 114.68, 67.29, 50.47, 27.58, 25.52, 19.39, 12.32. ESI-MS (*m/z*): 559.29 $[M\text{-}PF_6^-]^{1+}$ (calcd. *m/z* = 559.33).

3. ESI-MS spectrum

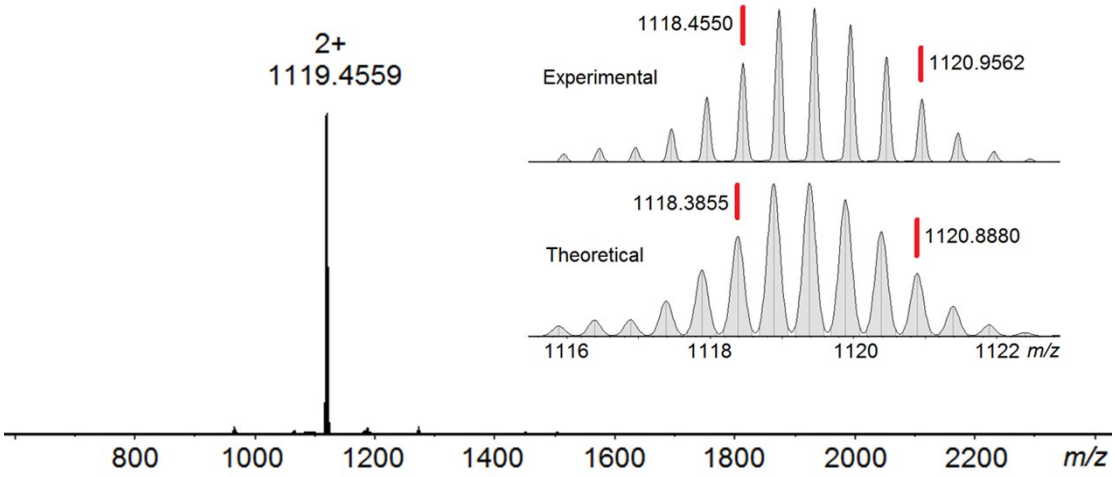


Figure S1. ESI mass spectrum for complex **5** and calculated and measured isotope patterns for the different charge states (PF_6^- as counterion).

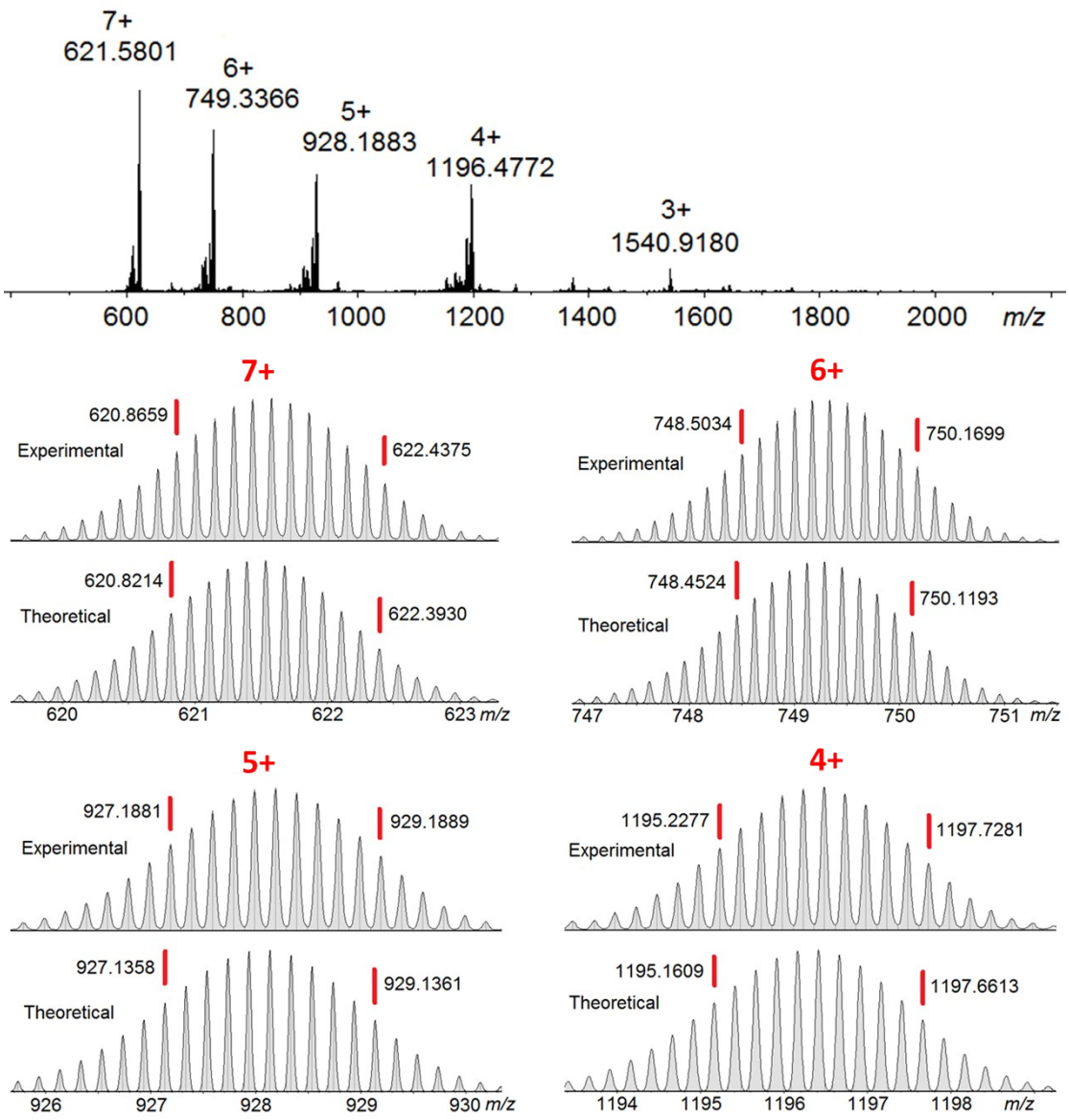


Figure S2. ESI mass spectrum for complex **8** and calculated and measured isotope patterns for the different charge states (PF_6^- as counterion).

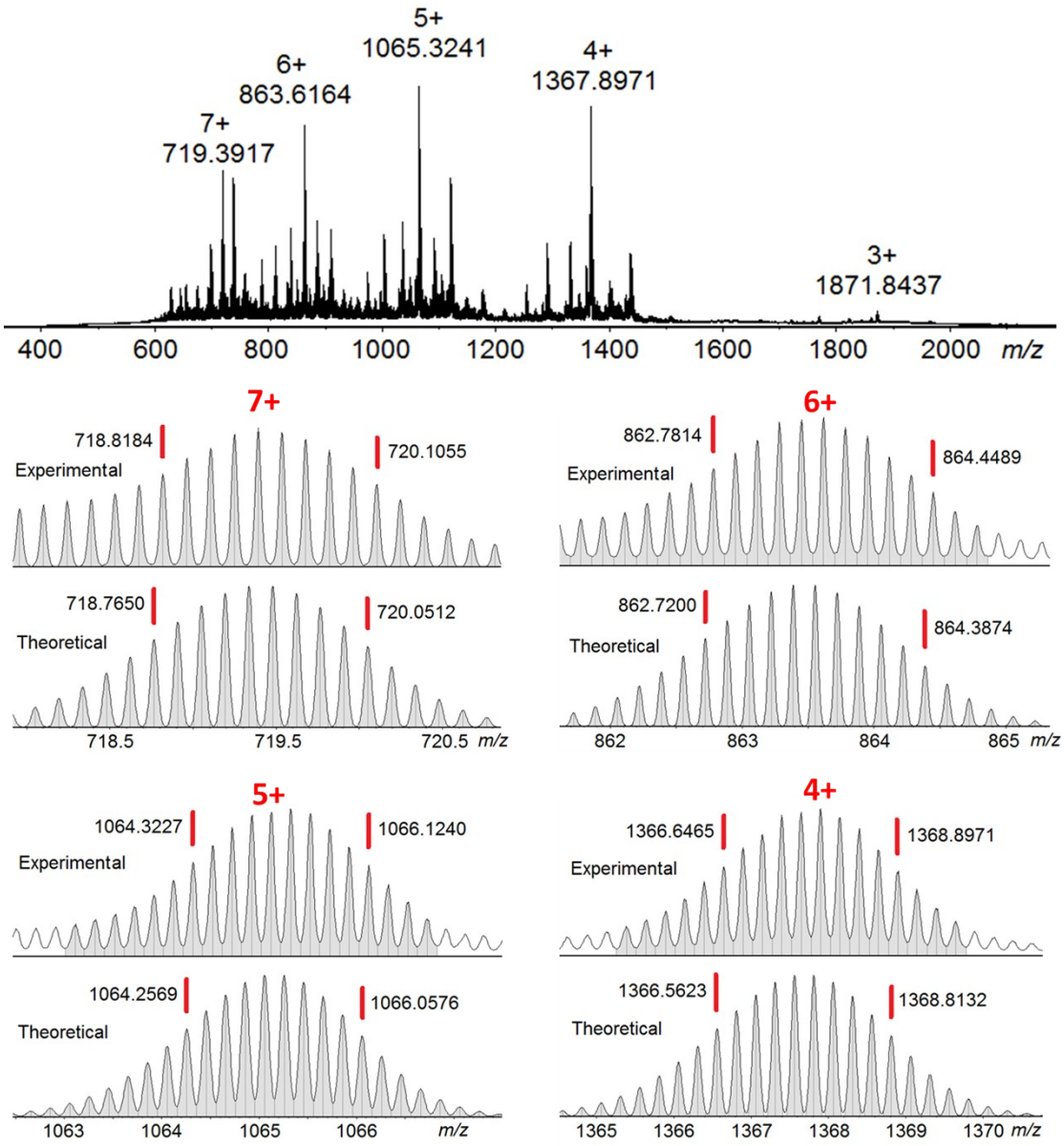


Figure S3. ESI mass spectrum for complex **L** and calculated and measured isotope patterns for the different charge states (PF_6^- as counterion).

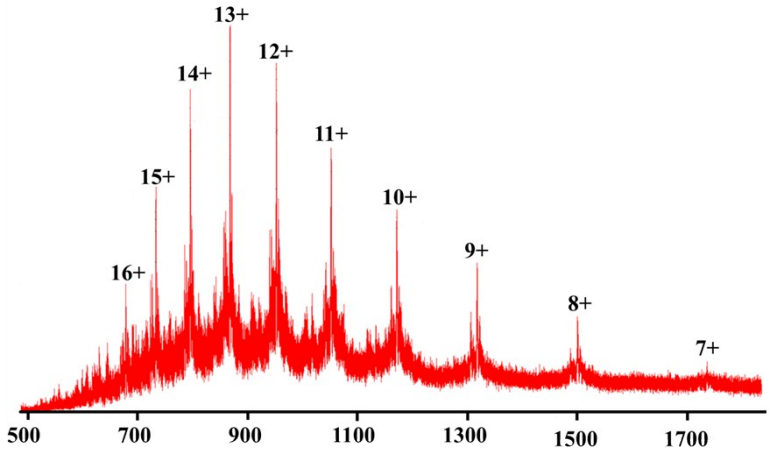
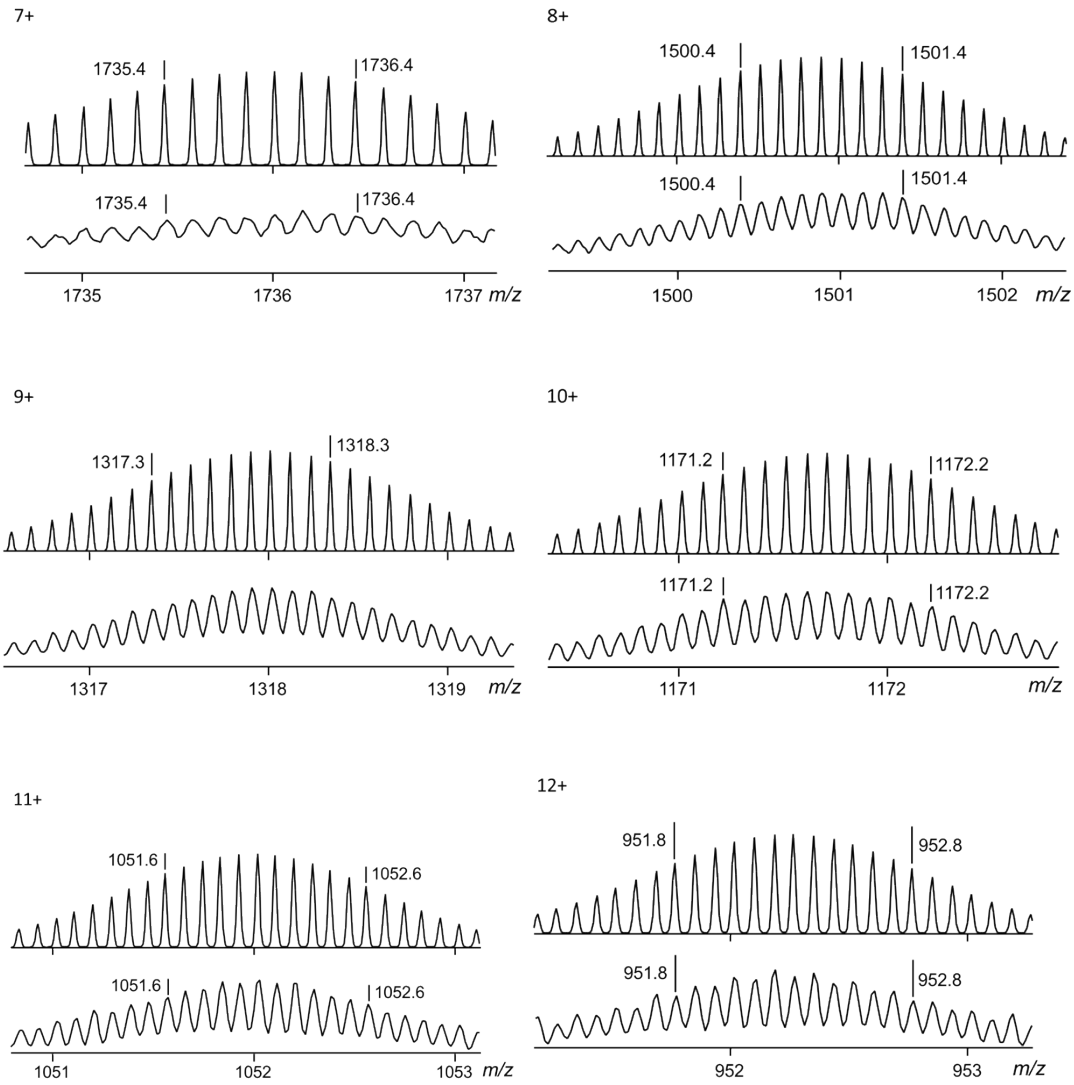


Figure S4. ESI mass spectrum for [$\mathbf{Zn_3L_2}$]



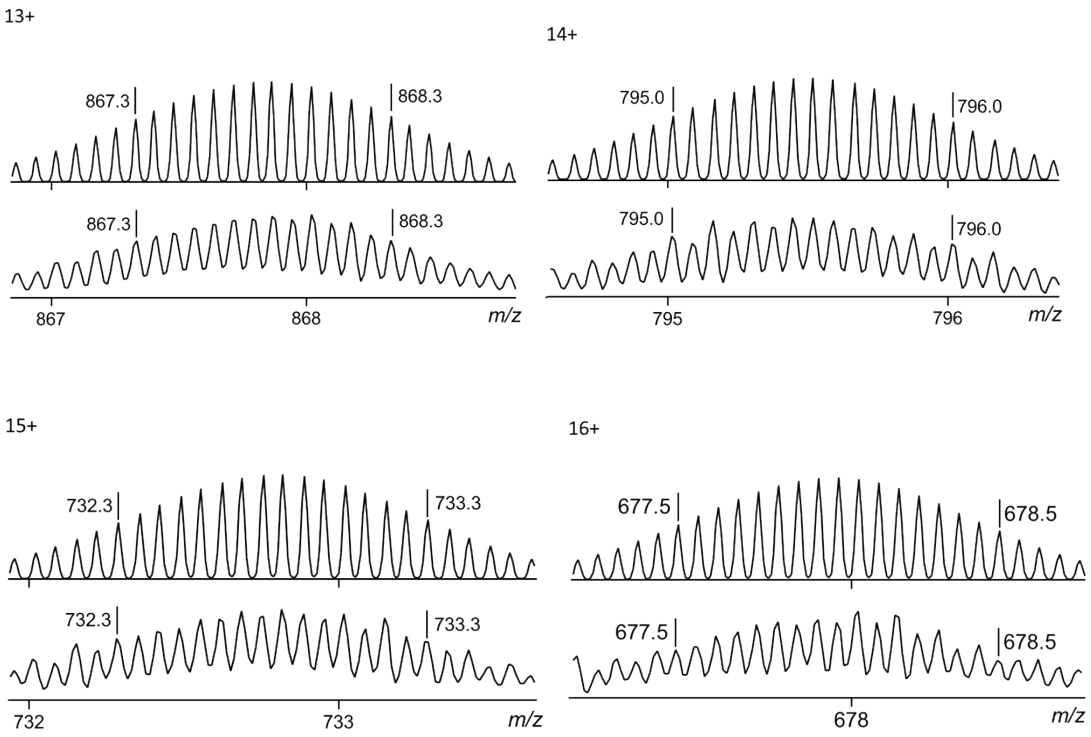


Figure S5. Calculated (top) and measured (bottom) isotope patterns for the different charge states (7+ to 16+) observed from [$\mathbf{Zn_3L_2}$] (PF_6^- as counterion).

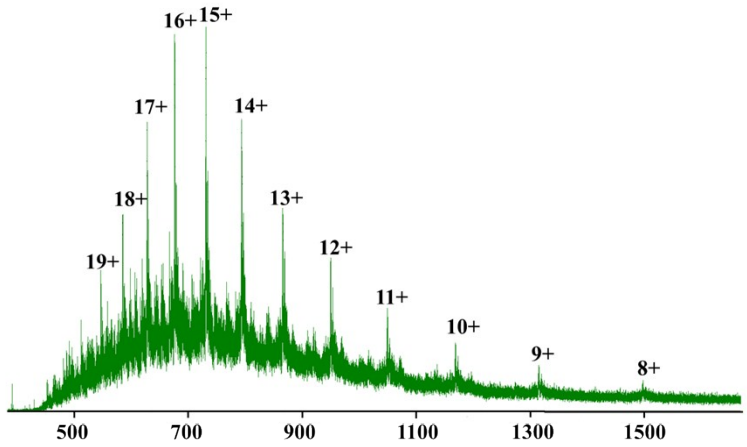
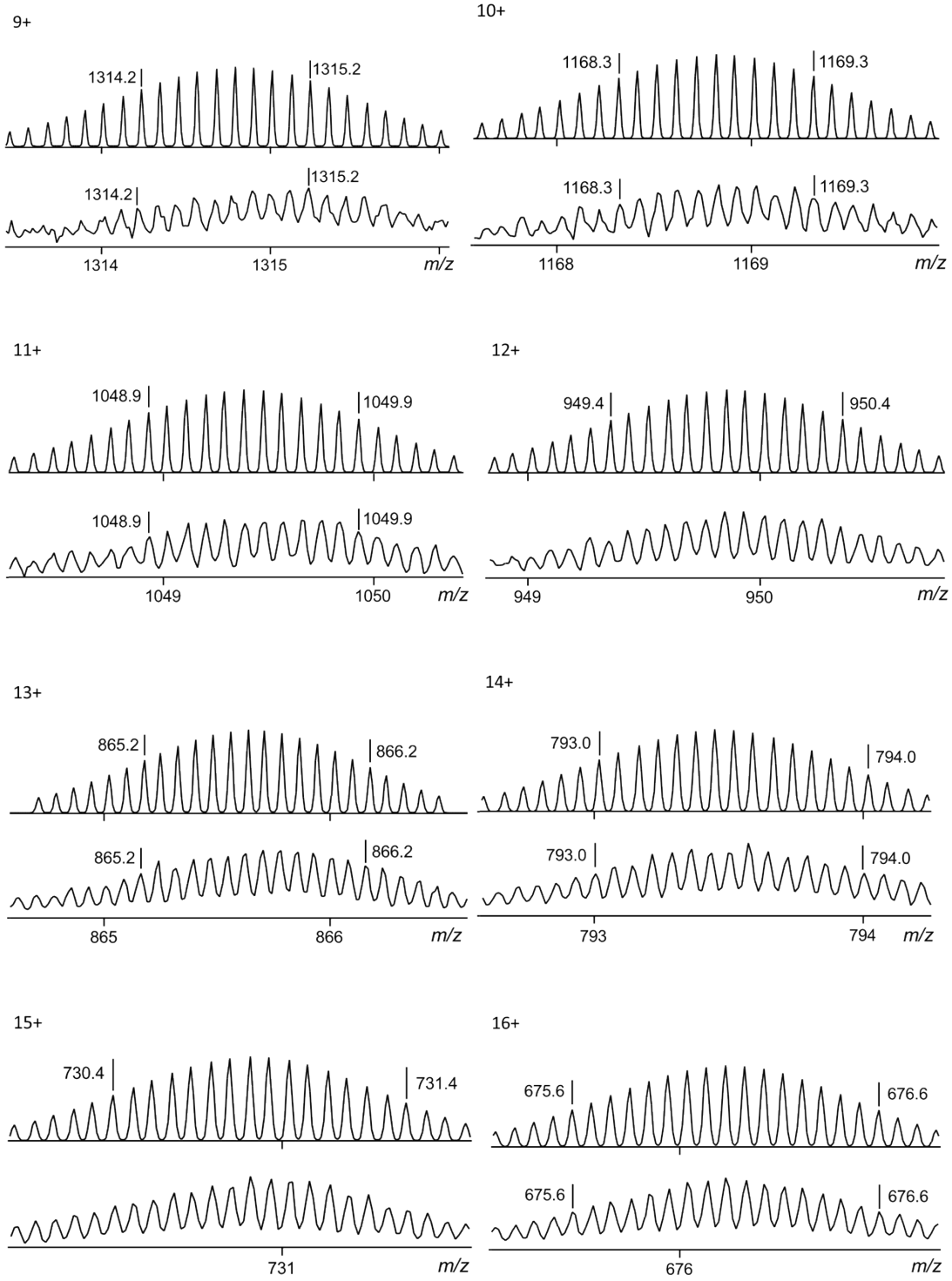


Figure S6. ESI mass spectrum for [$\mathbf{Fe_3L_2}$]


9+
1314.2
1315.2
1314.2
1315.2
1314
1315
m/z
10+
1168.3
1169.3
1168.3
1169.3
1168
1169
m/z
11+
1048.9
1049.9
1048.9
1049.9
1049
1050
m/z
12+
949.4
950.4
949
950
m/z
13+
865.2
866.2
865.2
866.2
865
866
m/z
14+
793.0
794.0
793.0
794.0
793
794
m/z
15+
730.4
731.4
731
m/z
16+
675.6
676.6
675.6
676.6
676
m/z

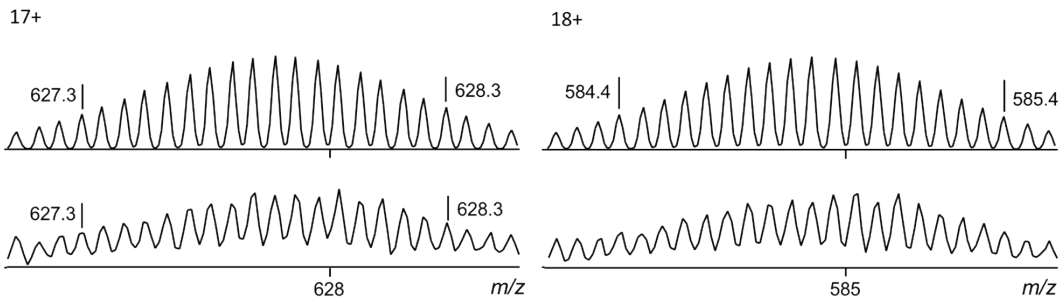


Figure S7. Calculated (top) and measured (bottom) isotope patterns for the different charge states (7+ to 18+) observed from [$\mathbf{Fe_3L_2}$] (PF_6^- as counterion).

4. Molecular modeling results

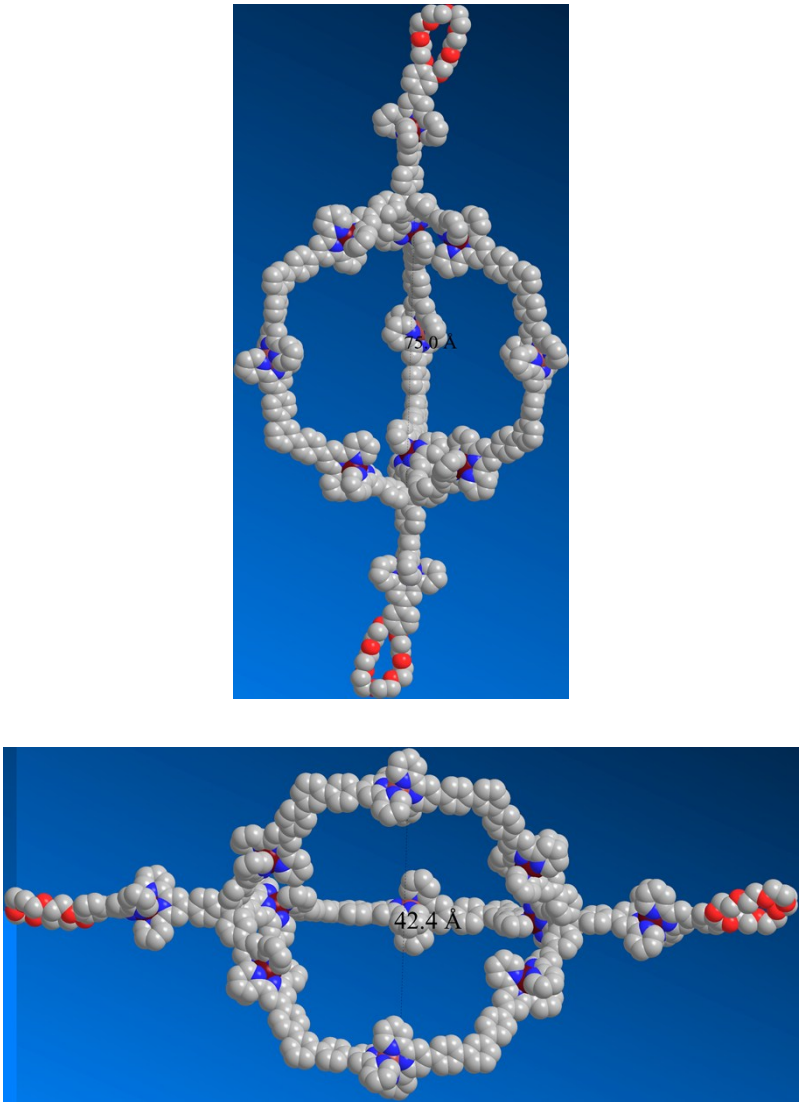


Figure S8. Representative energy-minimized structures of [$\mathbf{M_3L_2}$].

5. ^{1}H NMR, ^{13}C NMR, COSY, NOESY and DOSY spectra, TEM data, DLS data, SEM data, AFM data.

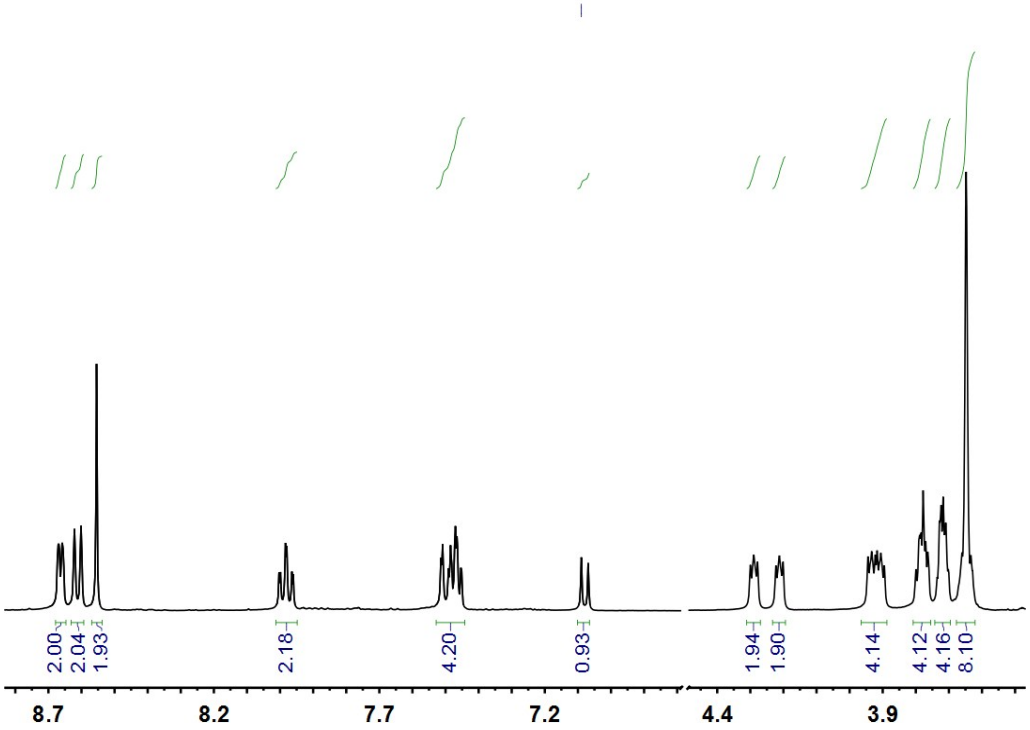


Figure S9.[1] H NMR spectrum (400 MHz, MeOD, room temperature) of compound **2**.

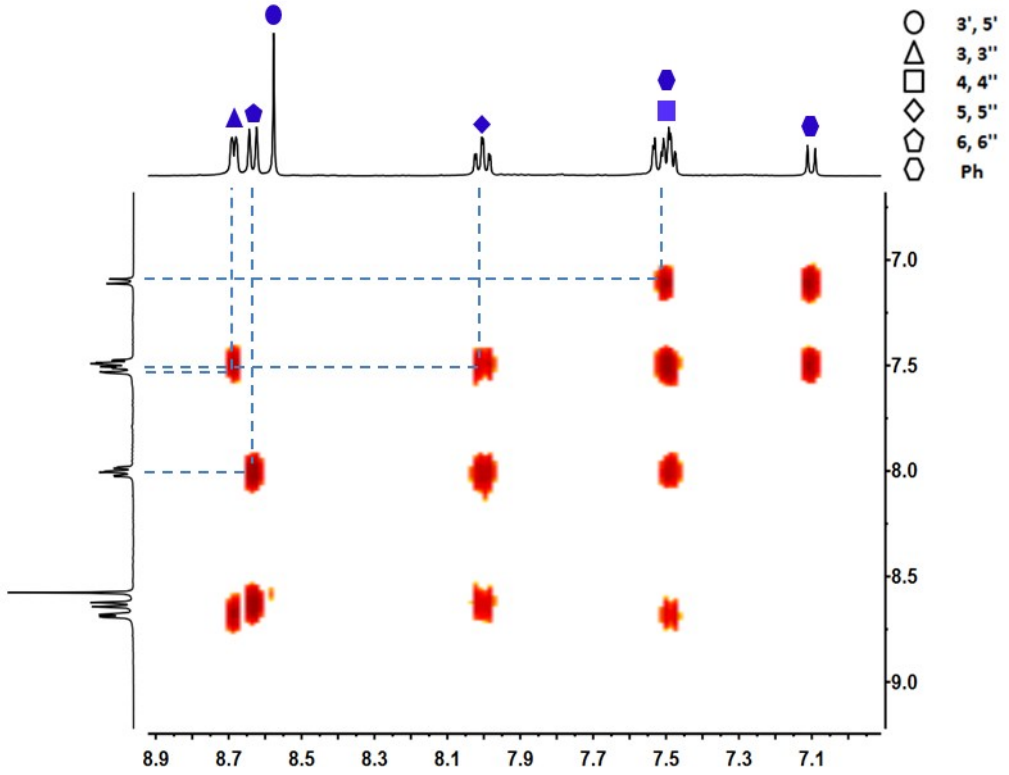


Figure S10.COSY NMR spectrum (400 MHz, MeOD, room temperature) of compound **2**.

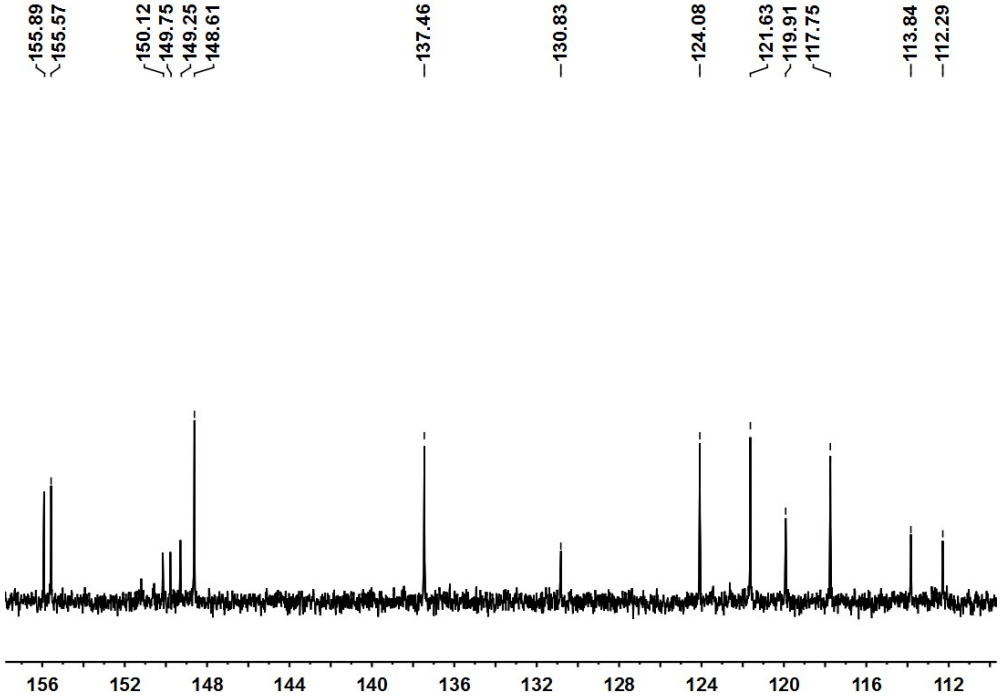


Figure S11.[13]C NMR spectrum (400 MHz, MeOD, room temperature) of compound 2.

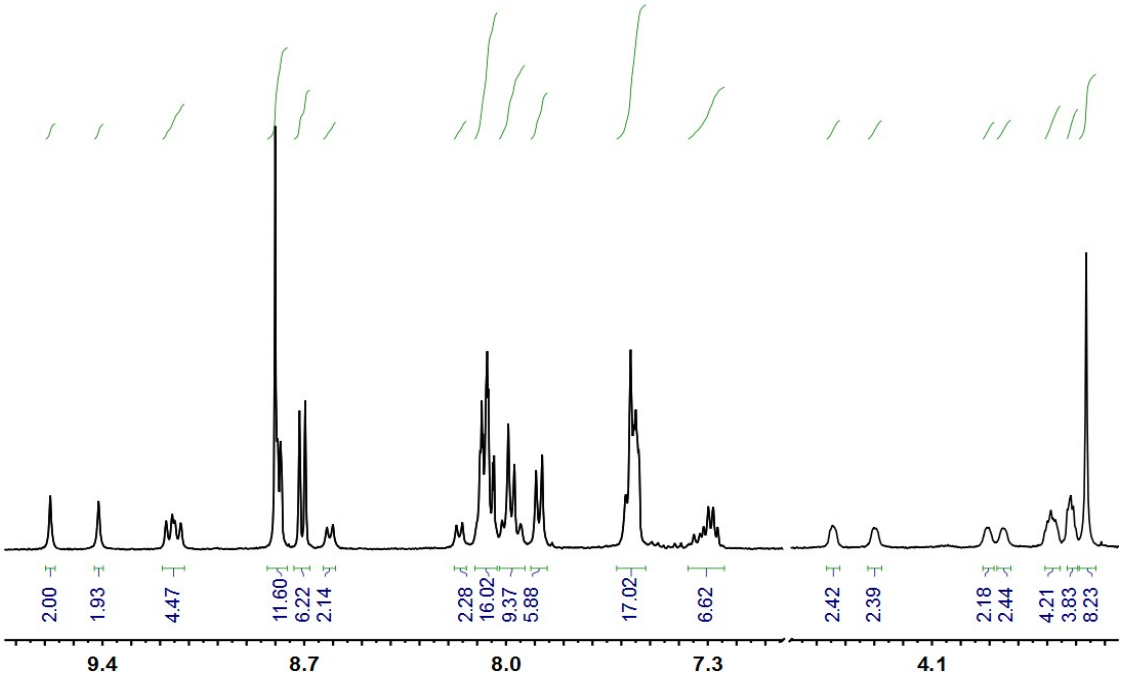


Figure S12.[1] H NMR spectrum (400 MHz, DMSO, room temperature) of compound **5**.

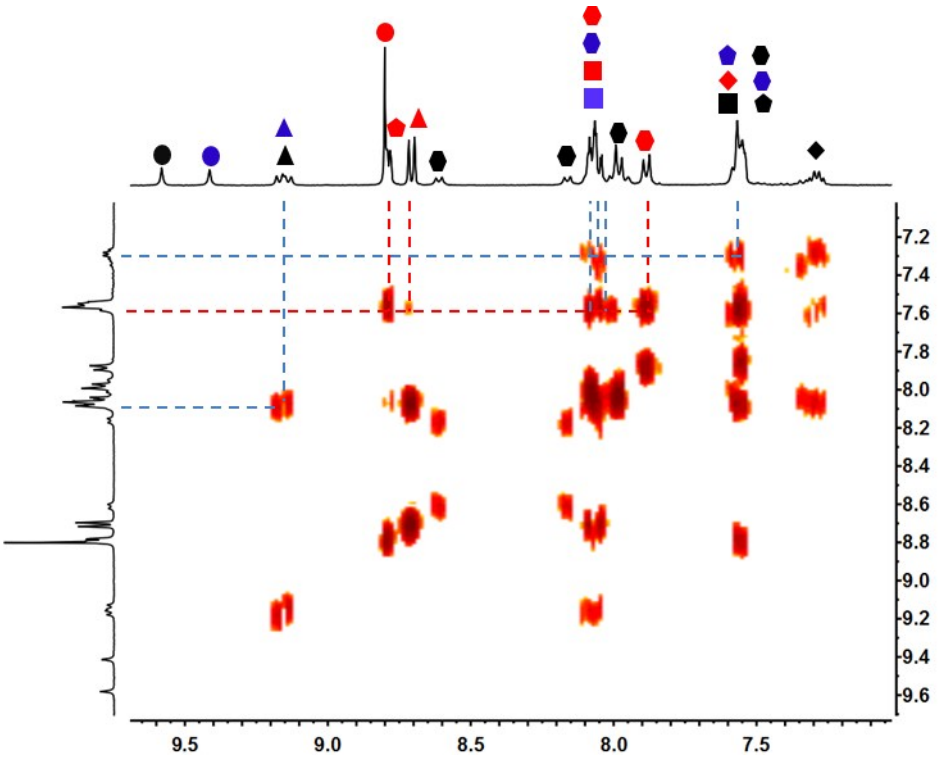


Figure S13.COSY NMR spectrum (400 MHz, DMSO, room temperature) of compound **5**.

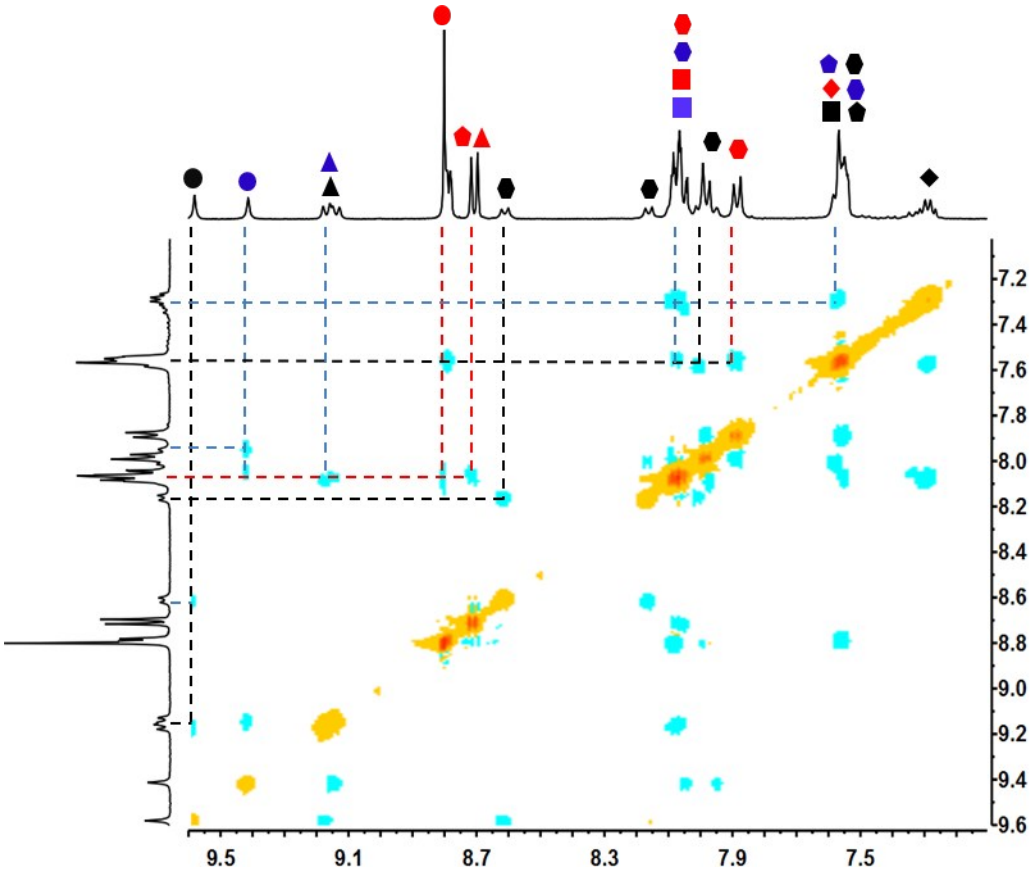


Figure S14.ROESY NMR spectrum (400 MHz, DMSO, room temperature) of compound **5**.

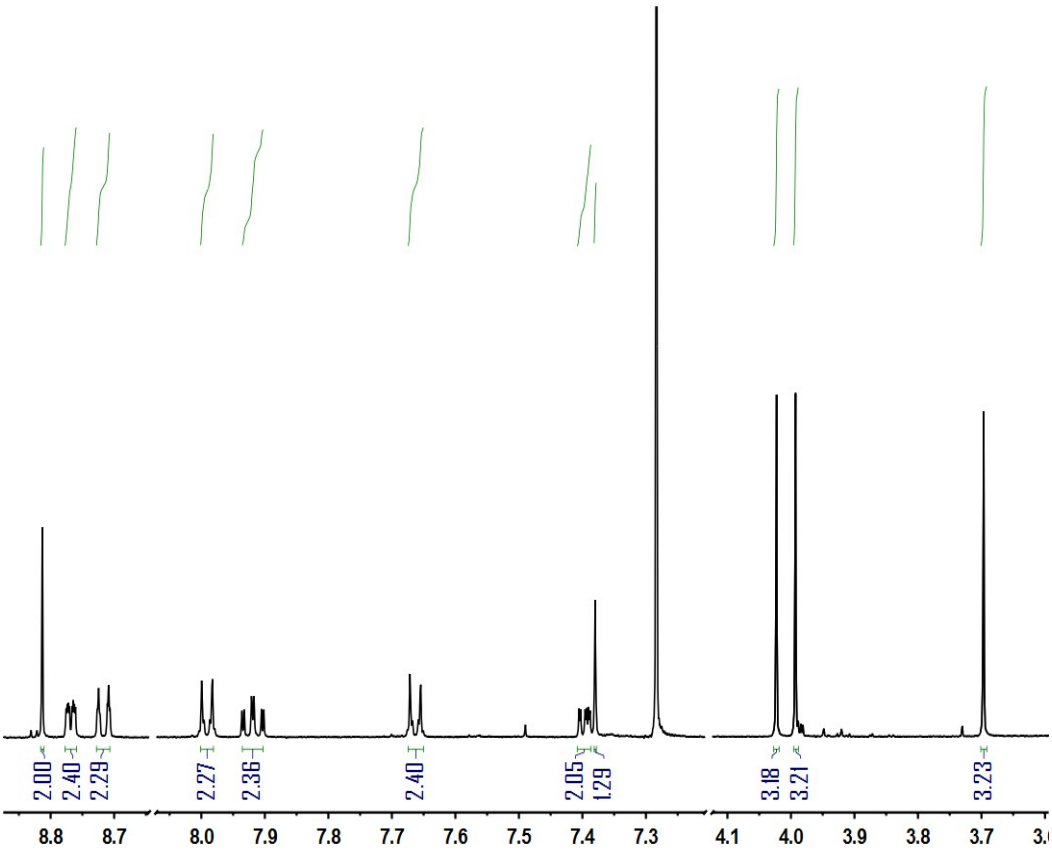


Figure S15.[1] H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of compound **6**.

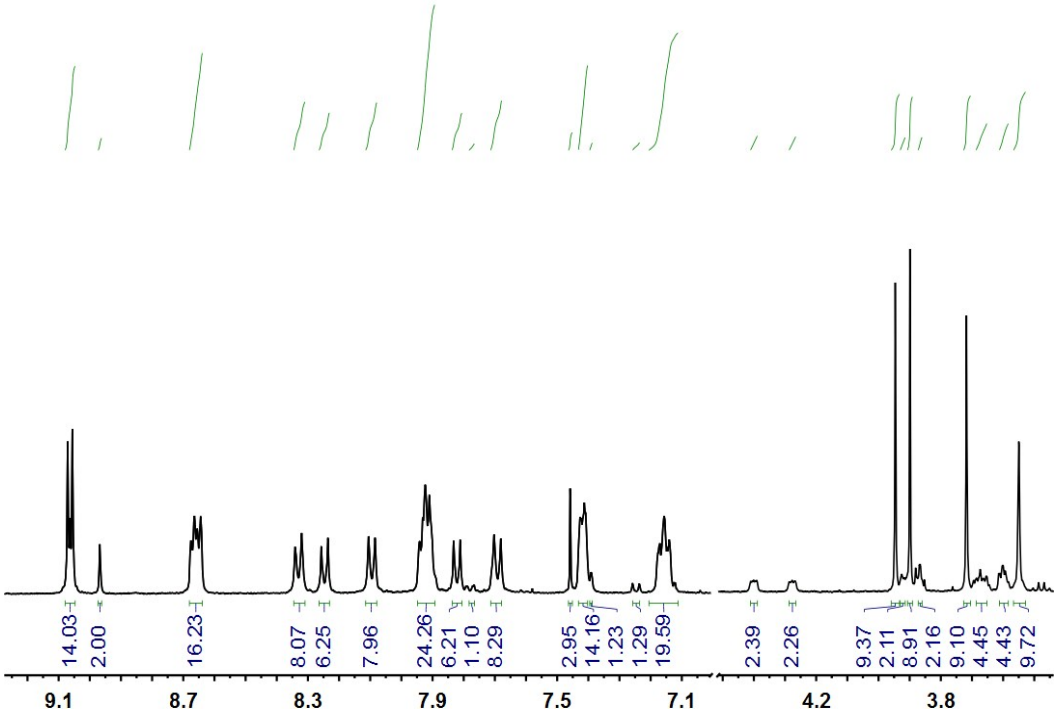


Figure S16.[1] H NMR spectrum (400 MHz, MeOD, room temperature) of compound **8**.

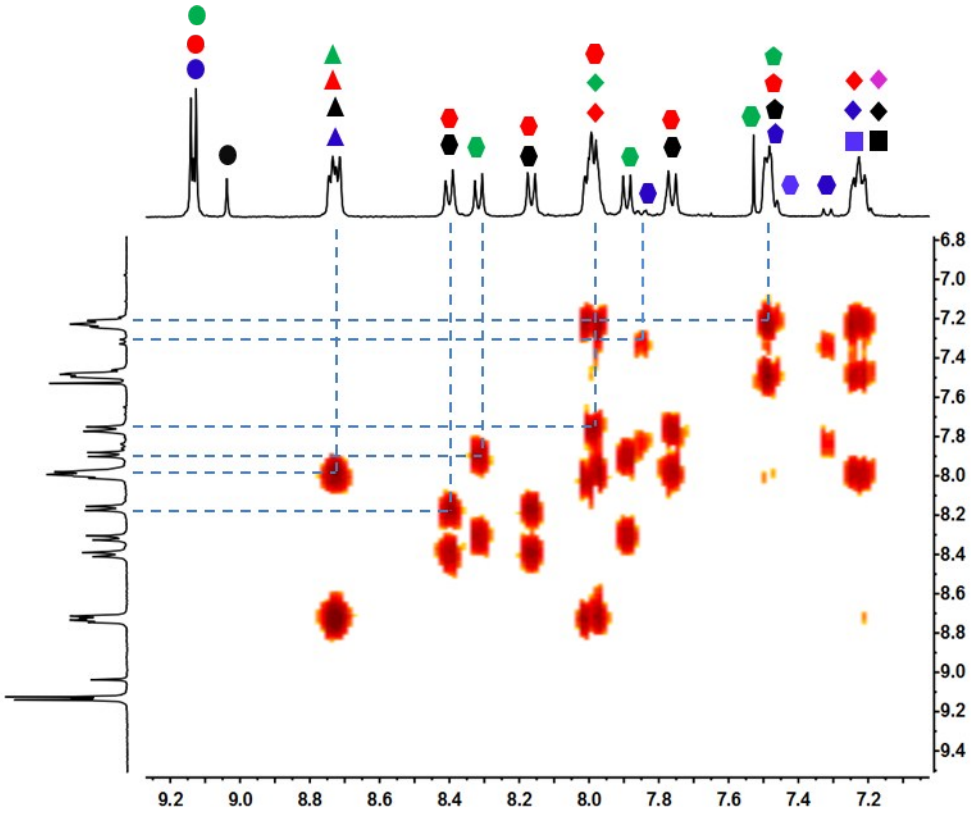


Figure S17.COSY NMR spectrum (400 MHz, CD_3CN, room temperature) of compound **8**.

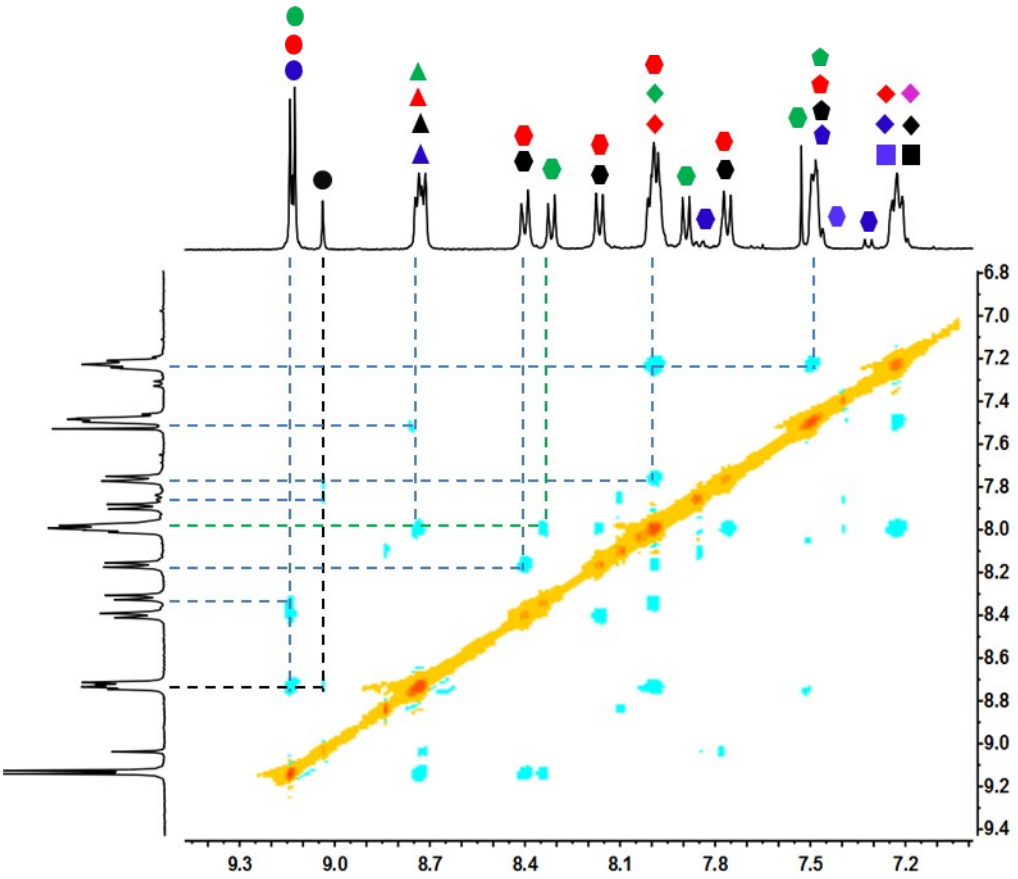


Figure S18.ROESY NMR spectrum (400 MHz, CD_3CN, room temperature) of **8**.

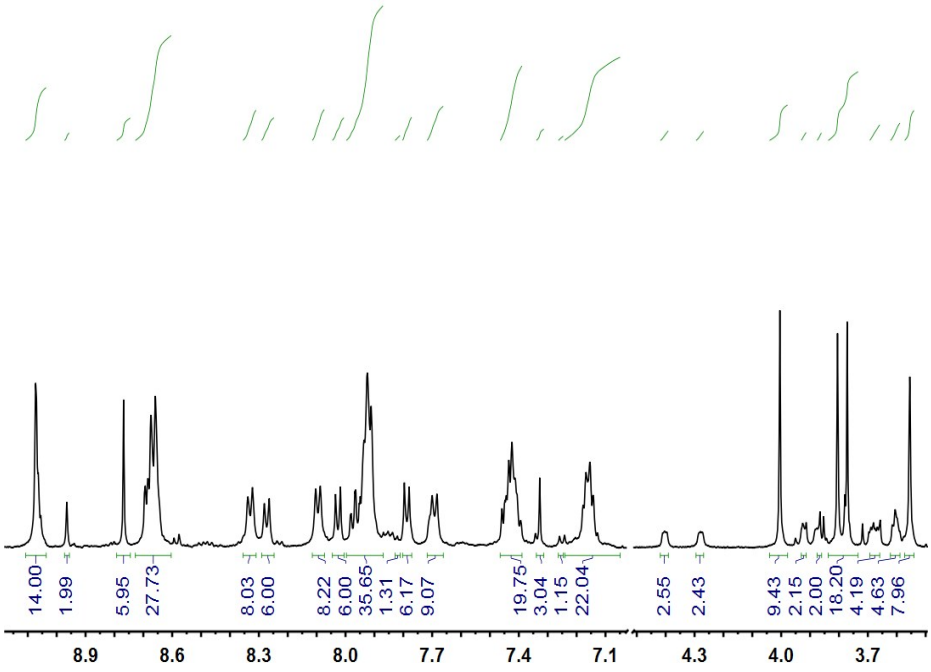


Figure S19.[1] H NMR spectrum (400 MHz, CD_3CN, room temperature) of **L**.

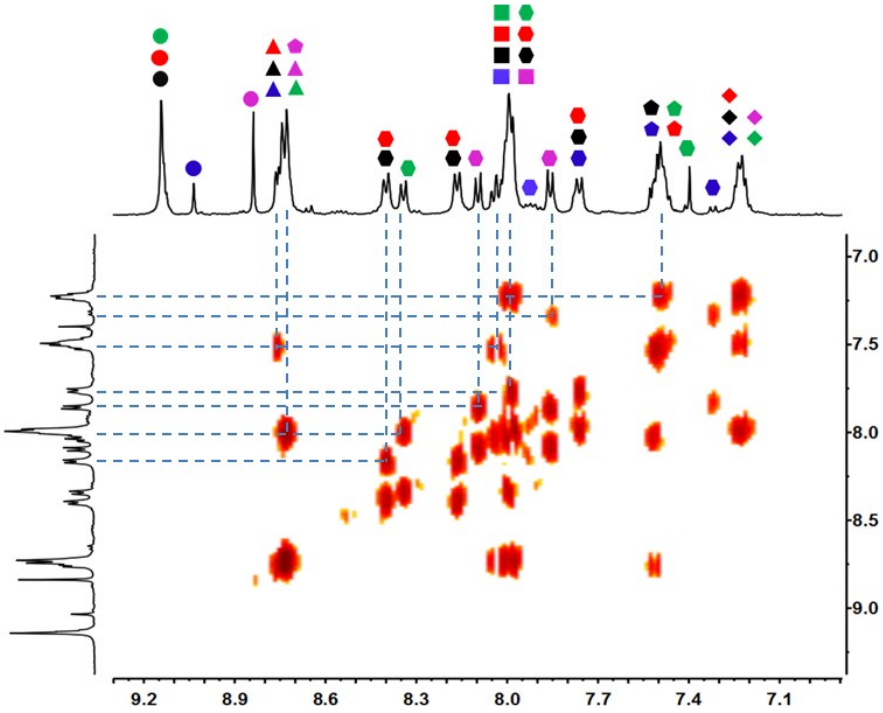


Figure S20.COSY NMR spectrum (400 MHz, CD_3CN, room temperature) of **L** .

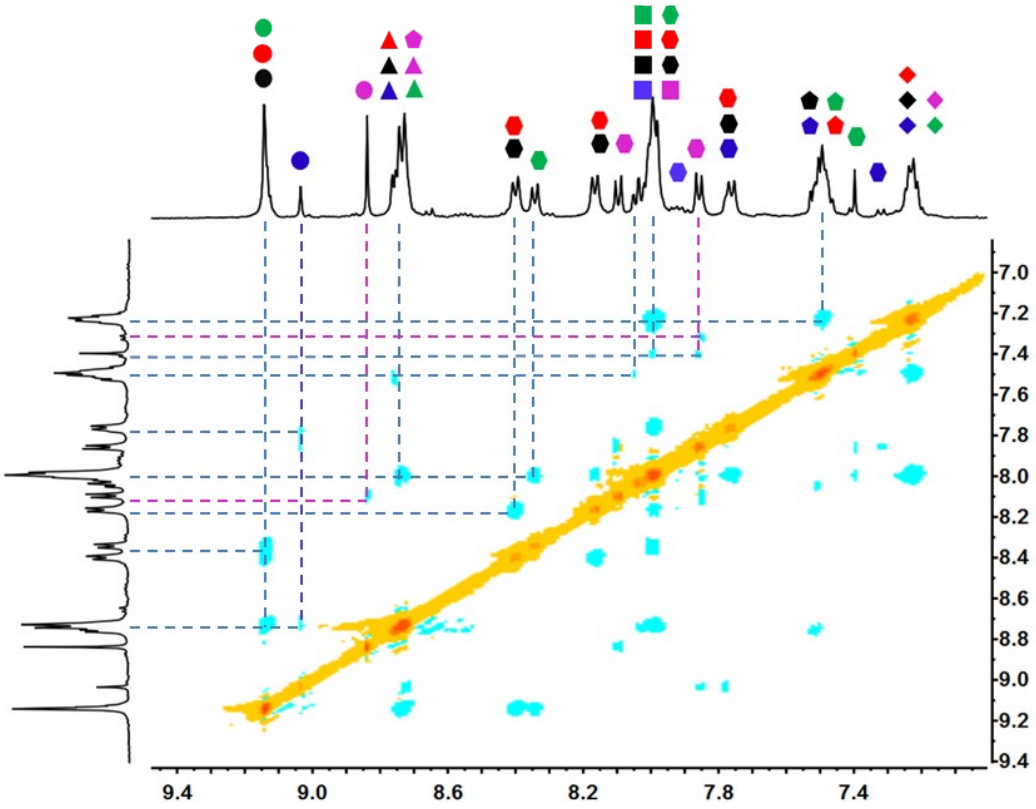


Figure S21.ROESY NMR spectrum (400 MHz, CD_3CN, room temperature) of **L**.

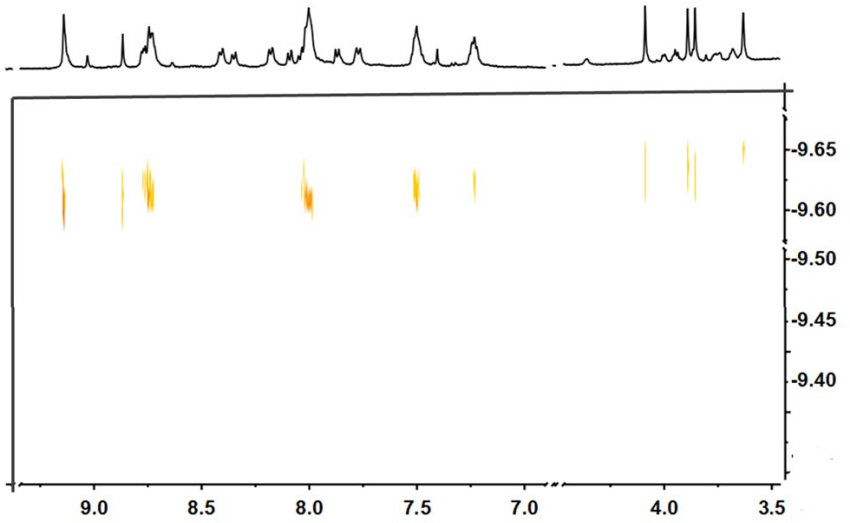


Figure S22. DOSY NMR spectrum (500 MHz, CD_3CN, room temperature) of **L**

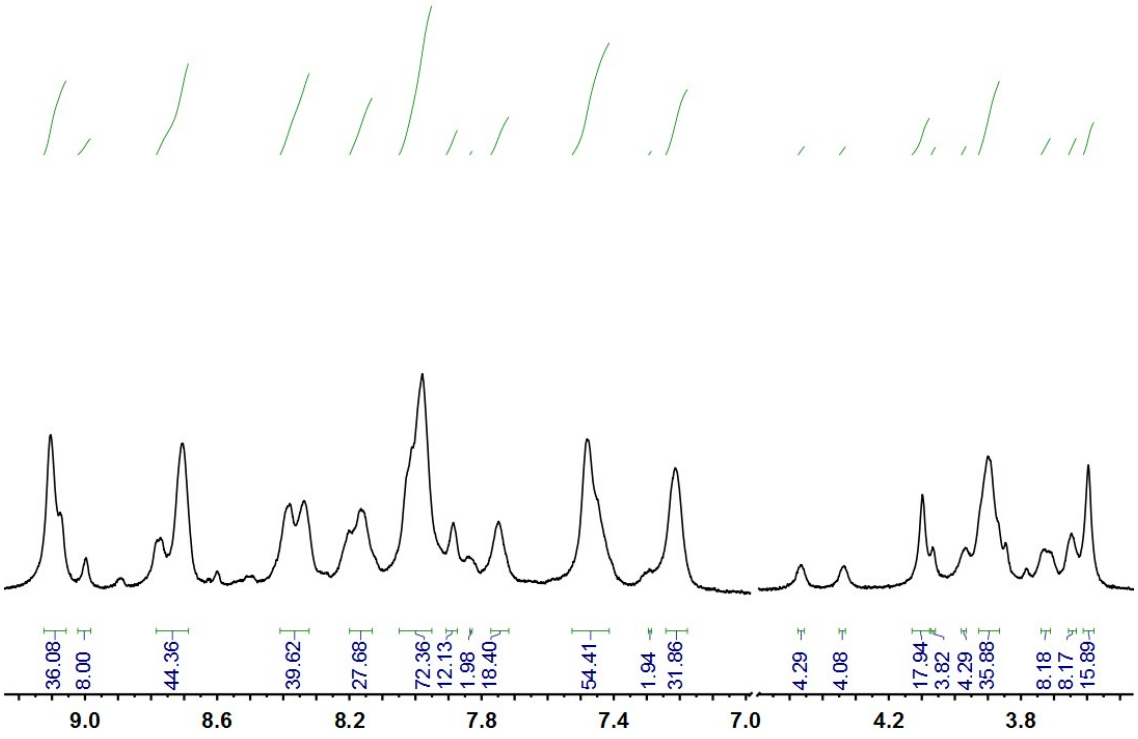


Figure S23.[1] H NMR spectrum (400 MHz, CD_3CN, room temperature) of [$\mathbf{Zn_3L_2}$].

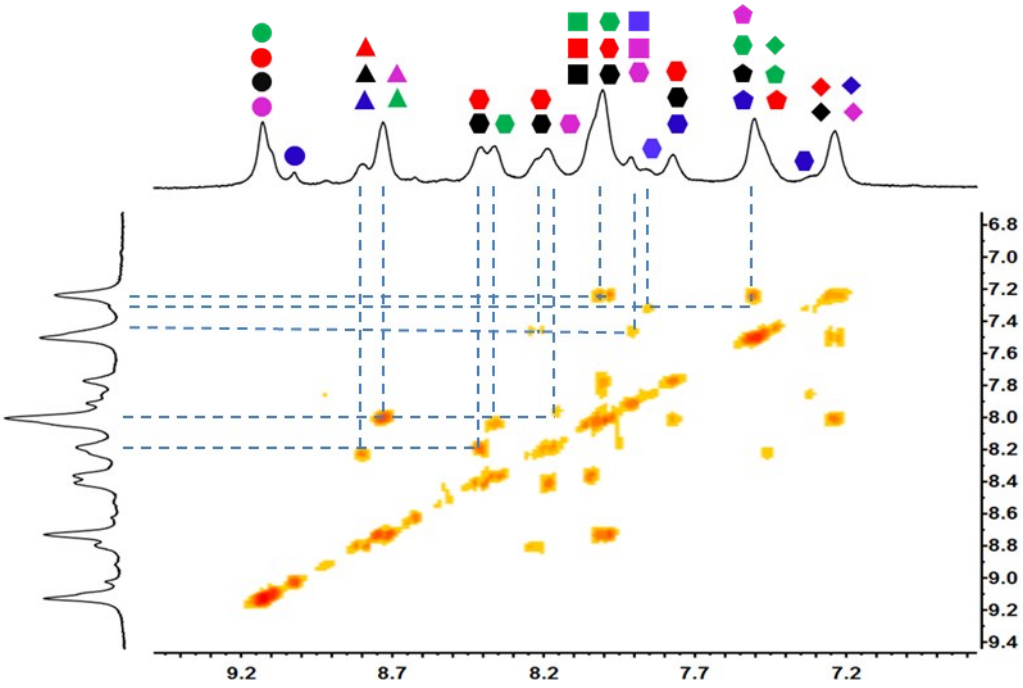


Figure S24.COSY NMR spectrum (400 MHz, CD_3CN, room temperature) of [$\mathbf{Zn_3L_2}$].

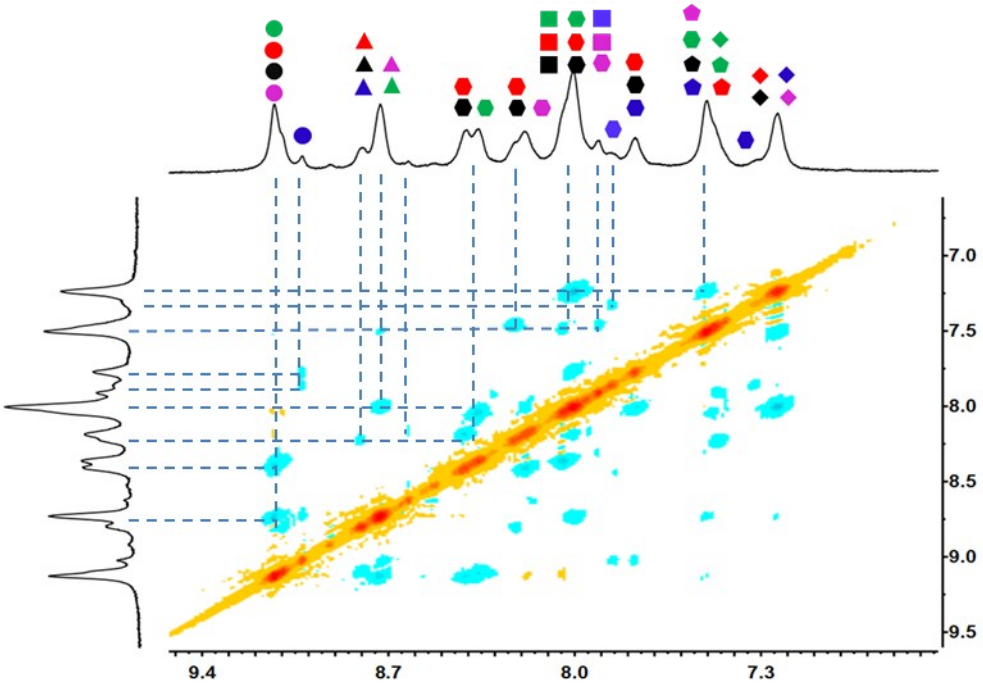


Figure S25.ROESY NMR spectrum (400 MHz,CD_3CN, room temperature) of [$\mathbf{Zn_3L_2}$].

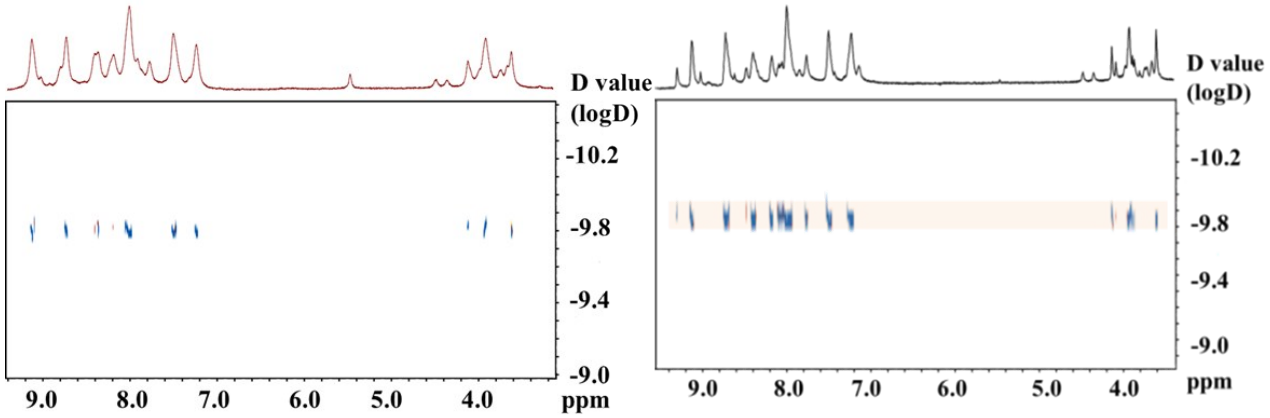


Figure S26. DOSY NMR spectrum (400 MHz, CD_3CN, room temperature) of [$\mathbf{Zn_3L_2}$](left)and [$\mathbf{Fe_3L_2}$](right).

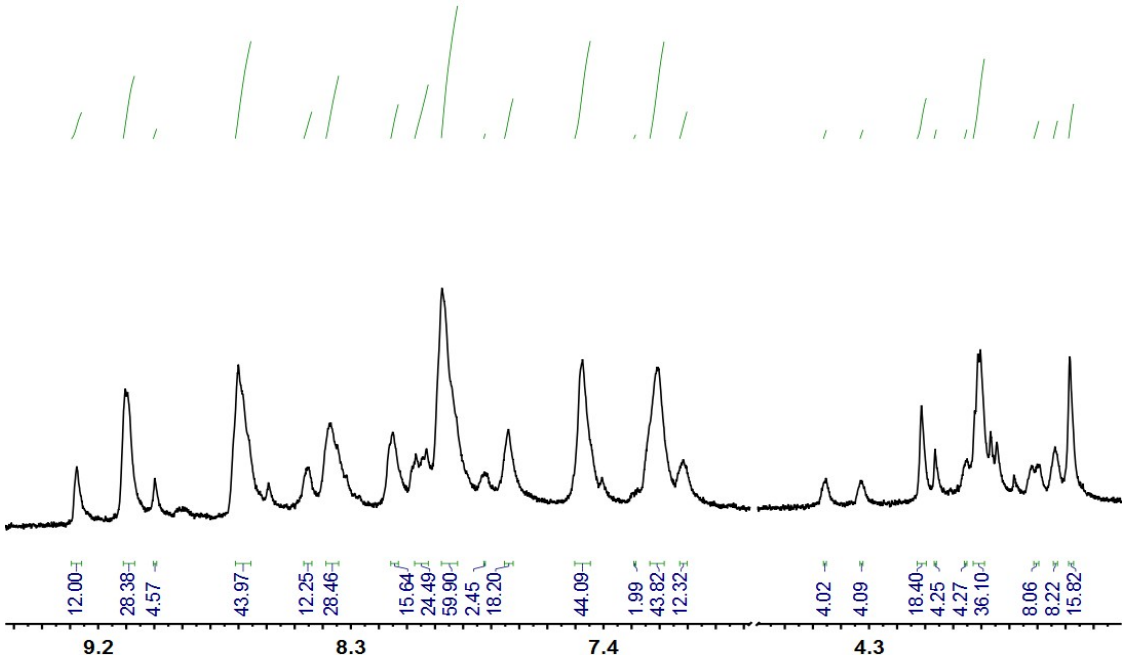


Figure S27.[1] H NMR spectrum (400 MHz, CD_3CN, room temperature) of **[$\mathbf{Fe_3L_2}$]**.

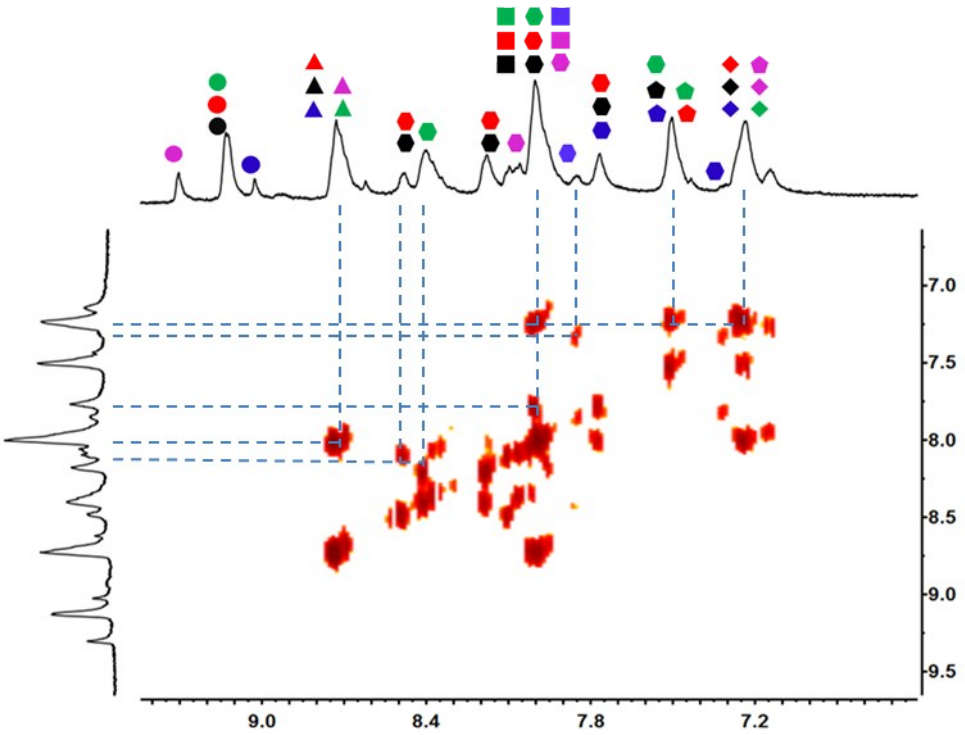


Figure S28.COSY NMR spectrum (400 MHz, CD_3CN, room temperature) of **[Fe_3L_2]** .

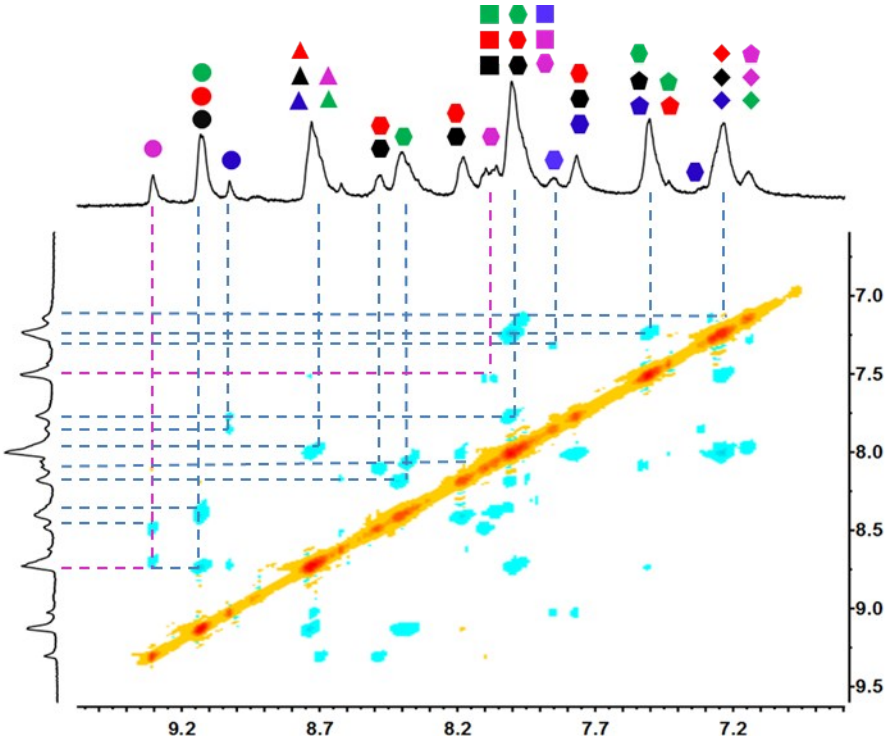


Figure S29.ROESY NMR spectrum (400 MHz,CD_3CN, room temperature) of **[Fe_3L_2]**.

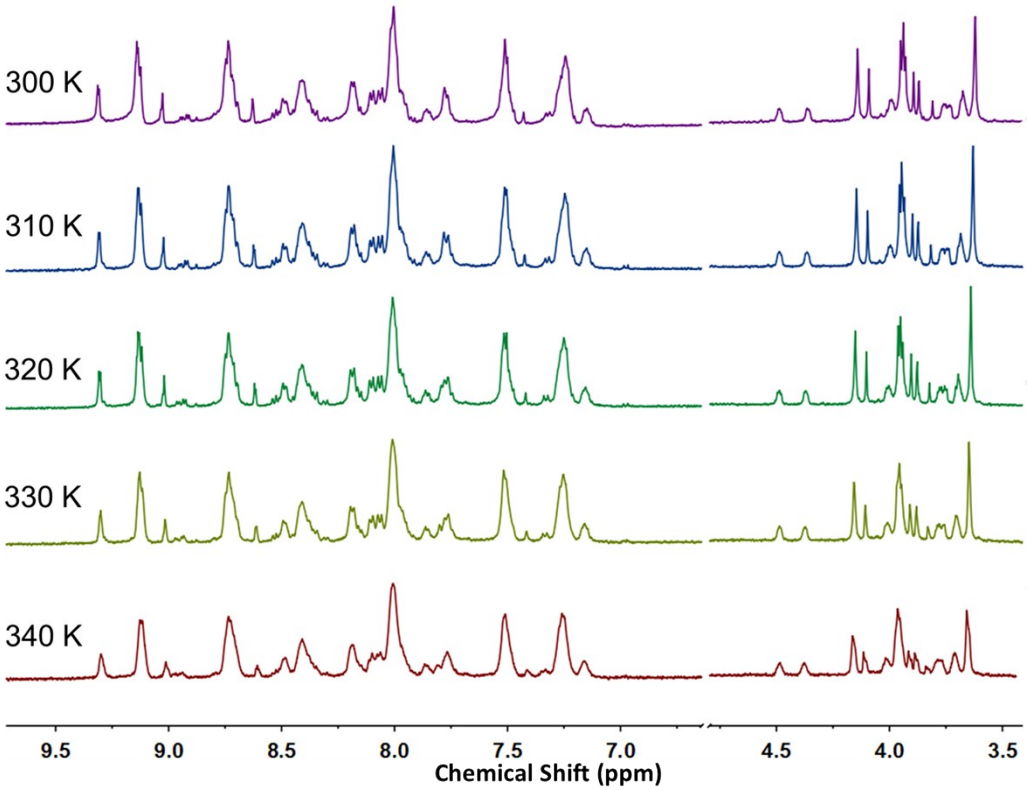


Figure S30. ^{1}H NMR spectrum (500 MHz,CD_3CN, different temperature) of **[Fe_3L_2]**

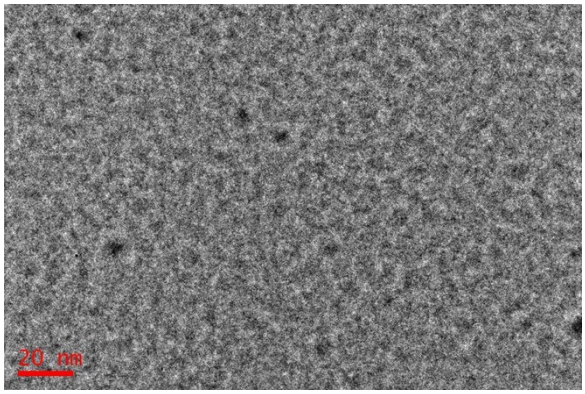


Figure S31. TEM image of metallo-organic cages [**Zn_3L_2**].

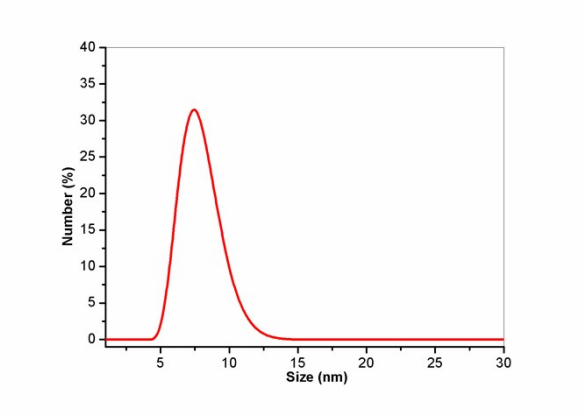
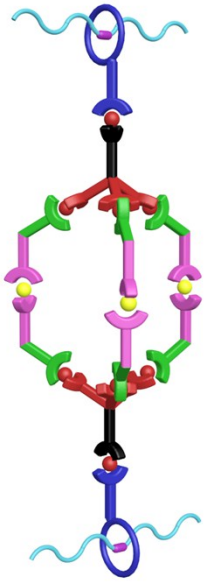


Figure S32. The dynamic light scattering (DLS) graph of cage **[Fe_3L_2]**.

6. host–guest interactions of terpyridine-based 3D cages



Scheme S2 Cartoon representation of host-guest reaction of metallo-organic cages **[M_3L_2]** with ammonium salt **N1**

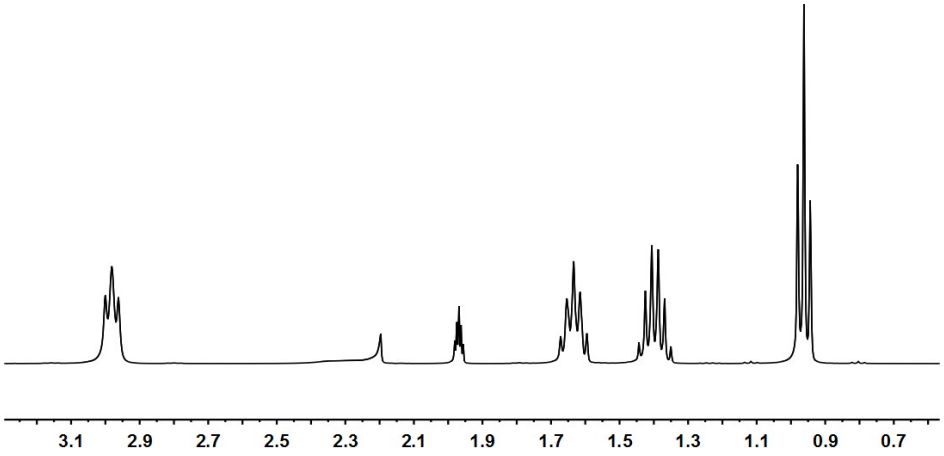


Figure S33 ^{1}H NMR spectrum (500 MHz, CD_3CN, room temperature) of **N1**.

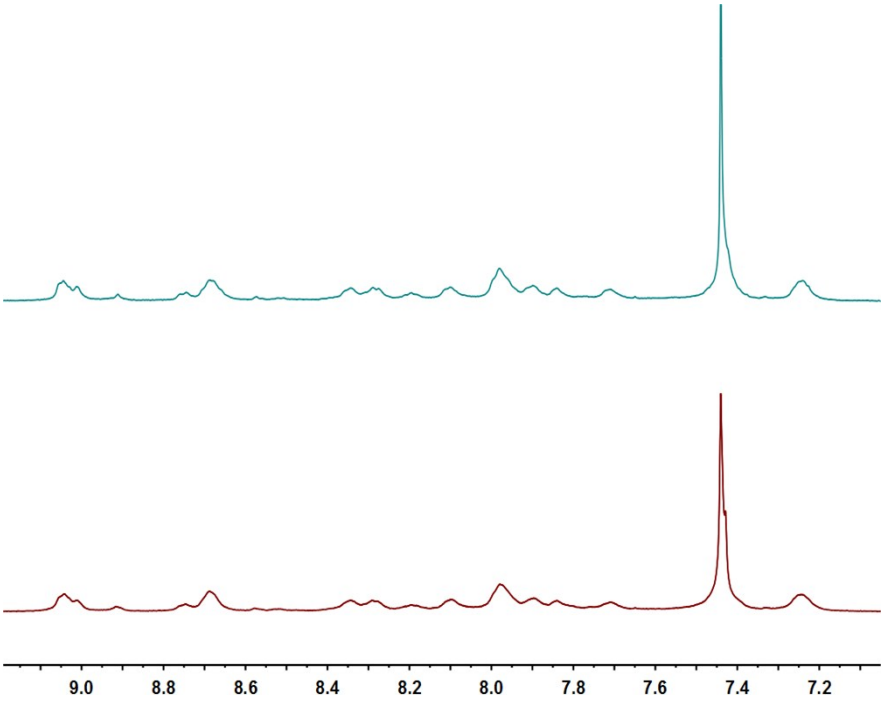


Figure S34. Aromatic region ^{1}H NMR spectrum (500 MHz, $CD_3CN/CDCl_3$=1:2, room temperature) of **[Zn_3L_2]** (top), **[Zn_3L_2]-**ammonium salt (bottom).

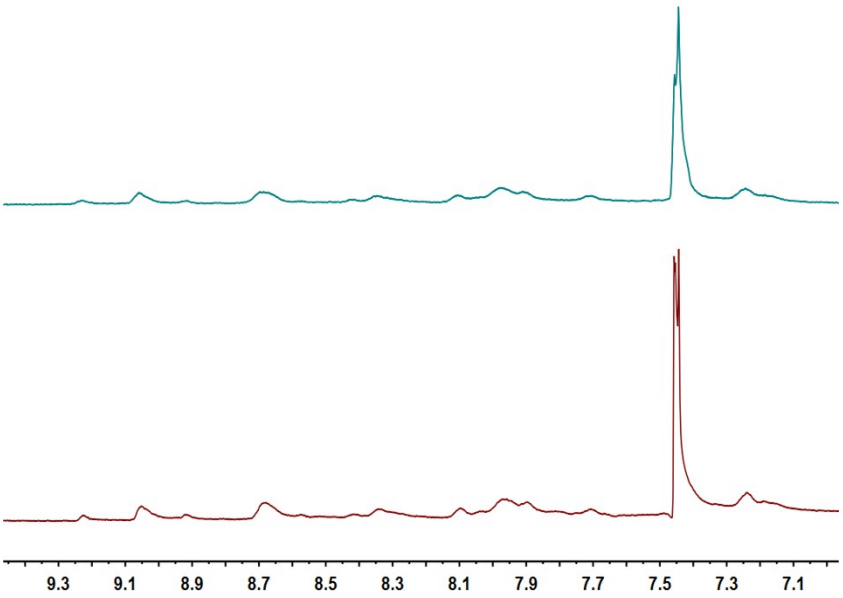


Figure S35. Aromatic region ^{1}H NMR spectrum (500 MHz, $CD_3CN/CDCl_3$=1:2, room temperature) of **[Fe_3L_2]** (top), **[Fe_3L_2]**-ammonium salt (bottom).

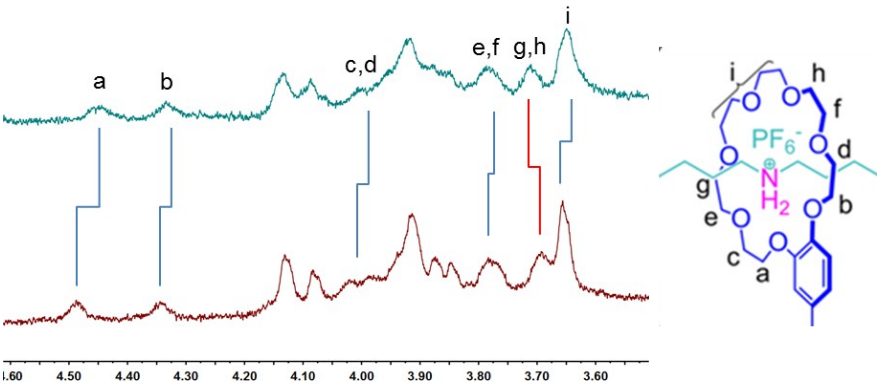


Figure S36. Crown ether region ^{1}H NMR spectrum (500 MHz, $CD_3CN/CDCl_3$=1:2, room temperature) of **[Zn_3L_2]** (top), **[Zn_3L_2]**-ammonium salt **N2** (bottom).

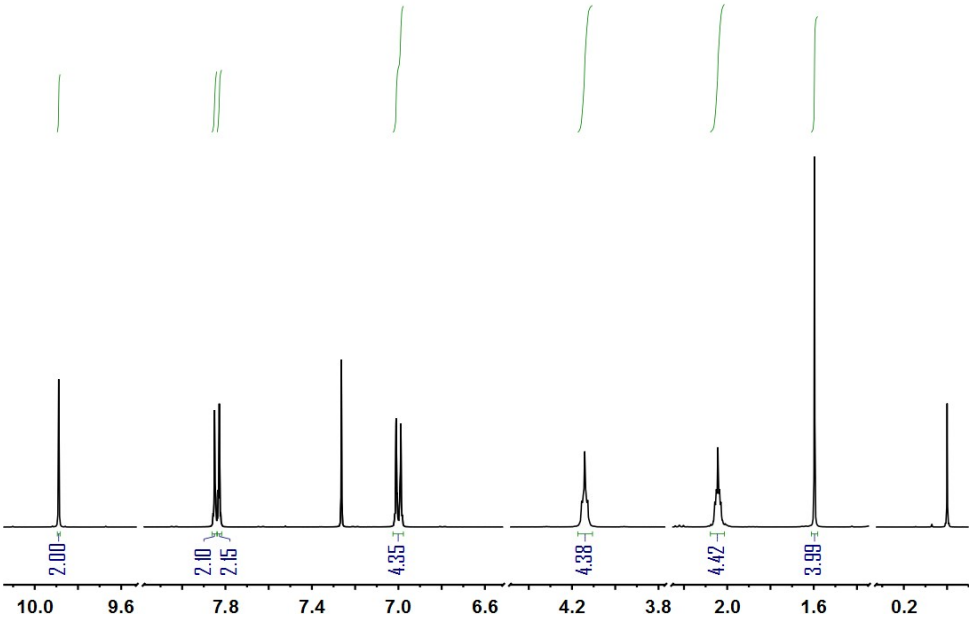


Figure S37.[1] H NMR spectrum (400 MHz, $CDCl_3$, room temperature) of **9**.

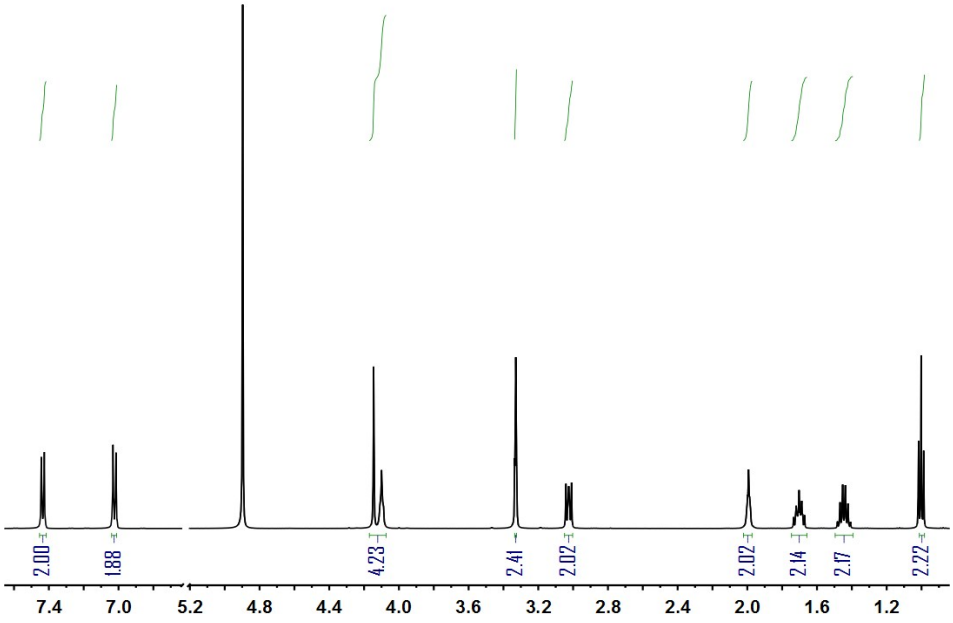


Figure S38.[1] H NMR spectrum (500 MHz, MeOD, room temperature) of **N2**.

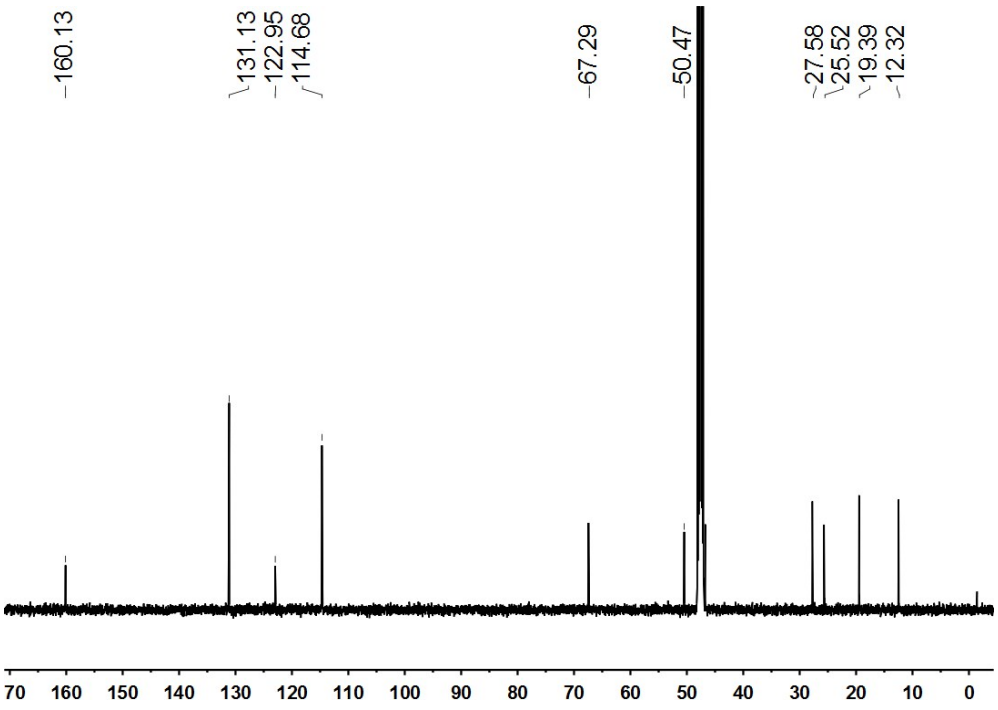


Figure S39. ^{13}C NMR spectrum (500 MHz, MeOD, room temperature) of **N2**.

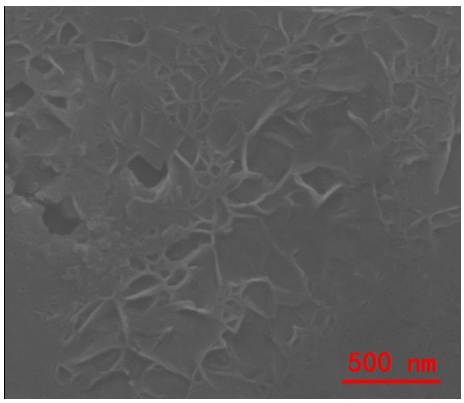


Figure S40.SEM image of gels formed by host-guest reaction of metallo-organic cages [$\mathbf{Zn_3L_2}$] with bis-ammonium salt **N2**

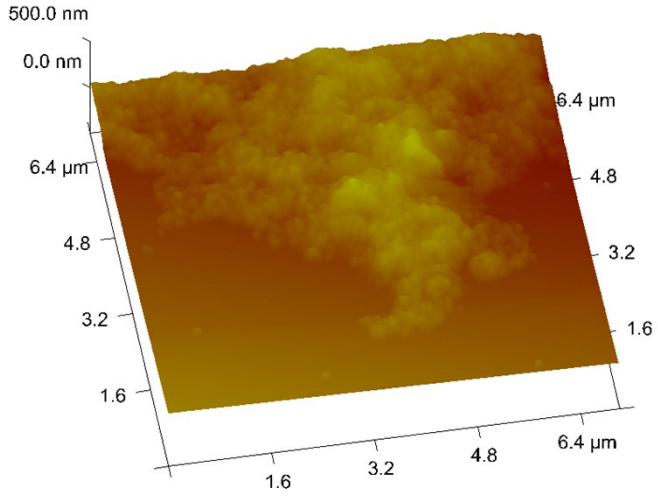


Figure S41. AFM image of gels formed by host-guest reaction of metallo-organic cages [$\mathbf{Zn_3L_2}$] with bis-ammonium salt **N2**

7. References

1. T. Bauer, A. Dieter Schlüter, J. Sakamoto, Towards 2D and 3D Coordination Polymers: Synthesis of Shape-Persistent Star Monomers with 2,2′:6′,2″-Terpyridin-4′-yl Units at the Periphery, *Synlett.*, **2010**, *6*, 877-880.

2. C. Talotta, C. Gaeta and P. Neri, Stereo-Programmed Direct Synthesis of Calixarene-Based [3]Rotaxanes , *Org. Lett.*, **2012**, *14*, 3104-3107.