Supplementary Information (SI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2024

Self-Assembly and Dynamic Exchange of Cuboctahedral Metal Organic Cages

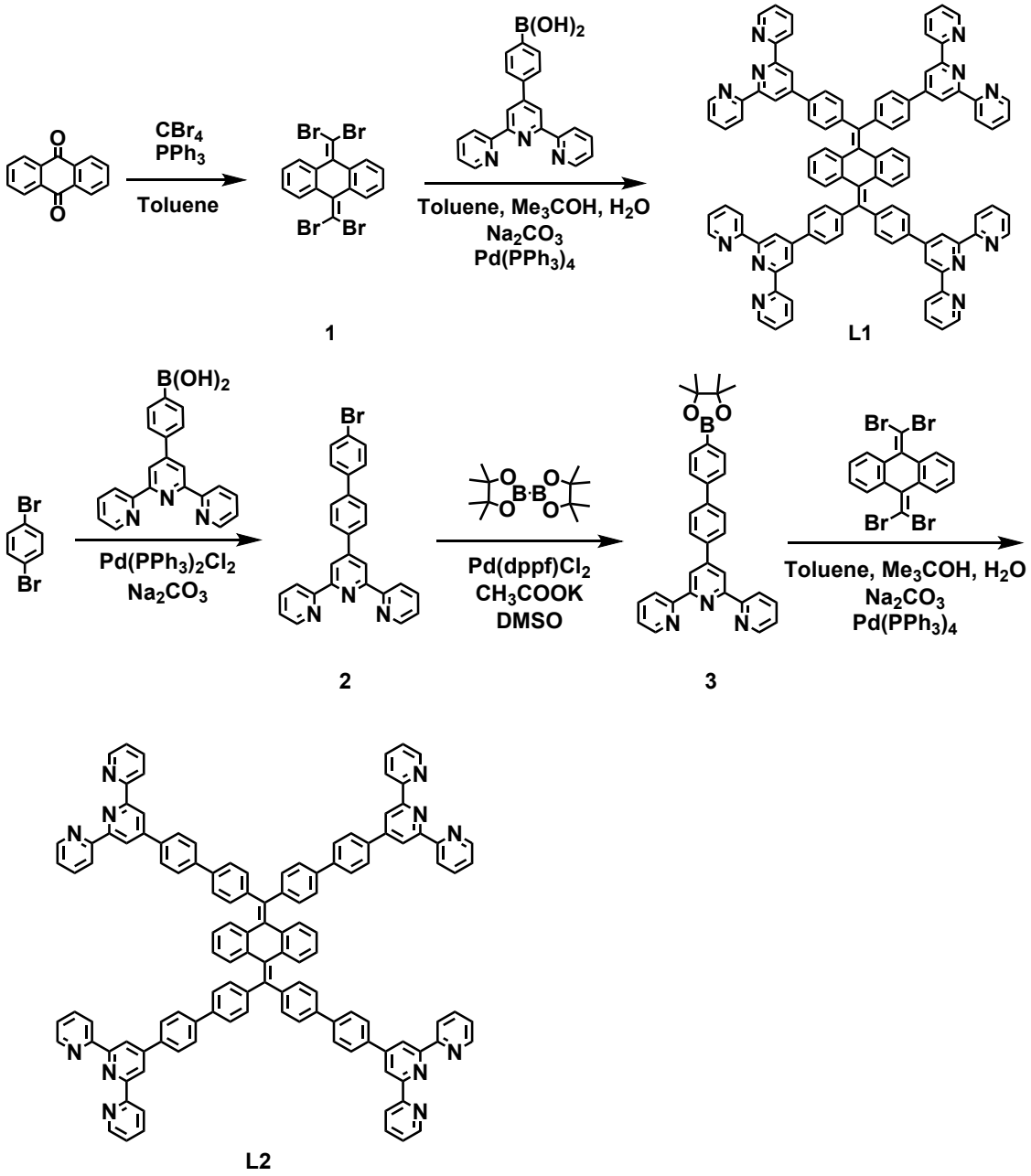
Jialin Liu[a,b], Yan Huang[a], Qixia Bai[a]*, Qiaoan Yang[a], Xinyi Wu[a], Limin Zhang[a], Tun Wu[a], Pingshan Wang[a], Jianqiao Wang[b]*, Zhe Zhang[a]*

[a] *Institute of Environmental Research at Greater Bay Area, Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China. E-mail: 1112116040@e.gzhu.edu.cn; zhezhang2018@gzhu.edu.cn.*

[b] *School of Environmental Science and Engineering, Key Laboratory for Water Quality and Conservation of the Pearl River Delta, Ministry of Education, Guangzhou University, Guangzhou 510006, China. E-mail: wangjq@gzhu.edu.cn*

Table of content

1. Schemes of preparation of ligands L1 and L2



Scheme S1. Synthesis of ligands **L1** and **L2**.

2. Experimental section

General procedures. Chemicals were purchased from Sigma/Aldrich, Fisher Scientific, Energy Chemical, and Alfa Aesar for immediate use. Thin layer chromatography (TLC) was performed on flexible sheets (Baker-flex) pre-coated with Al_2O_3 (IB-F) or SiO_2 (IB2-F) and visualised by UV light. For chromatography, neutral Al_2O_3 (200-300 mesh) and SiO_2 (200-300 mesh) were used as packed columns.1H,13C were recorded on Bruker NMR 400 and 500 MHz. Different NMR solvents were purchased from J&K scientific and Sigma/Aldrich. 0.01 mg of ligand was dissolved in 1 ml of $CHCl_3/CH_3OH$ (1:3, v/v) and 0.5 mg of supramolecule was dissolved in 1 ml of DMF solution, and a Waters Synapt G2-Si tandem mass spectrometer was used to record ESI-MS and TWIM-MS.

TWIM-MS. The TWIM-MS experiments were performed under the following conditions: ESI capillary voltage, 2 kV; sample cone voltage, 35 V; source offset, 42 V; source temperature 150 °C; desolvation temperature, 250 °C; cone gas flow, 10 L/h; desolvation gas flow, 700 L/h (N_2); source gas flow, 0 mL/min; trap gas flow, 3 mL/min; helium cell gas flow, 120 mL/min; ion mobility (IM) cell gas flow, 30 mL/min; sample flow rate, 8 μL/min; IM traveling wave height, 25 V; and IM traveling wave velocity, 1200 m/s. Q was set in rf-only mode to transmit all ions produced by ESI into the triwave region for the acquisition of TWIM-MS data. Data were collected and analyzed by using MassLynx 4.2 and DriftScope 2.9.

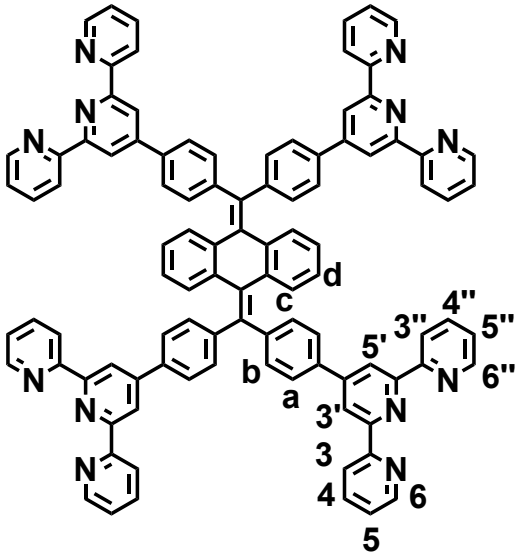
gMS². Gradient tandem mass spectrometry (GTSMS) analysis was carried out under the following conditions: the 15+ charged ions of the free organic supramolecule **S1**, a porphyrin adduct **S1-POR**, in solution after the binding of the host and guest were separated by a quadrupole, followed by collision-induced dissociation (CID), where the collision energy was progressively increased by varying the trap-cell voltage according to the different complexes.

UV-vis absorption, fluorescence properties. UV-vis absorption spectra were

recorded on Thermo Fisher Scientific Evolution 201 spectrophotometer at room temperature (10^{-6} M in DMF) and were corrected with the background spectrum of the solvent. Fluorescence properties were performed on Edinburgh-FS5 Fluorescence spectrometer at 73K (10^{-6} M in DMF).

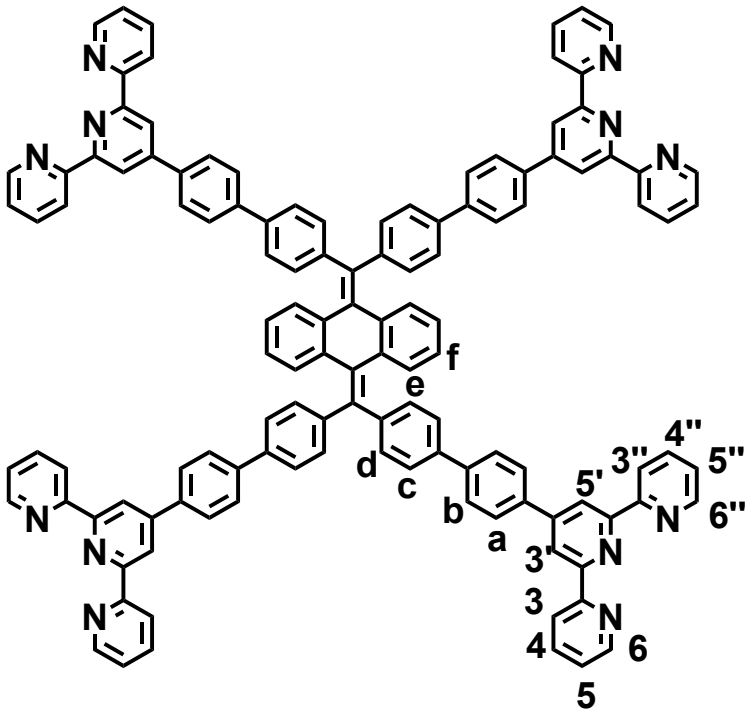
3. Synthesis of ligands and supramolecules

The synthesis of compound **1**, compound **2** and compound **3** can be referred to the reported literature.[1]



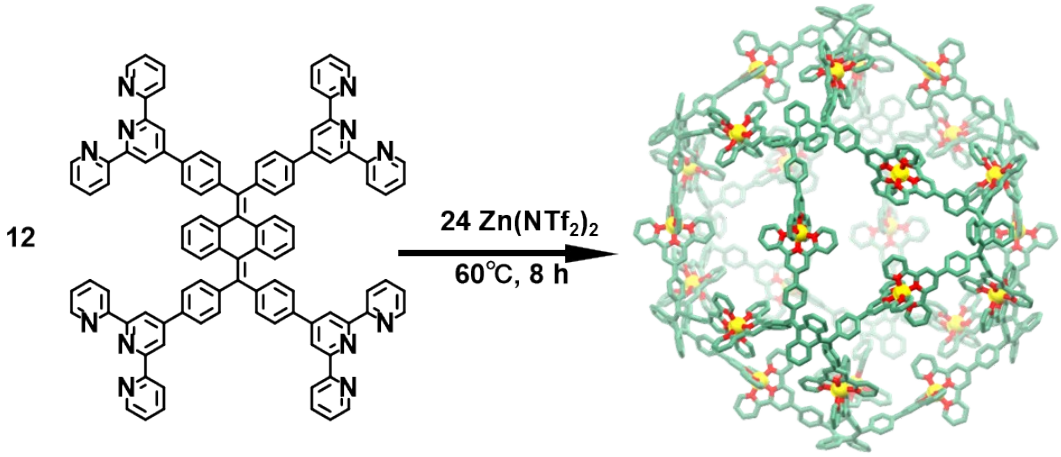
Ligand **L1:** Compound **1** (467.5 mg, 0.9 mmol), tetrakis (triphenylphosphine) palladium (208 mg, 0.18 mmol), 4-tripyridyl-phenylboronic acid (1.905 g, 5.4 mmol) and sodium carbonate (1.145 g, 10.8 mmol) were added to a 500 ml three-necked flask followed by evacuating the entire reaction system and flushing in nitrogen three times to ensure that the experiments were performed in the conducted in a nitrogen atmosphere. After the above operation, the flask was filled with 12 ml of tert-butanol, 24 ml of water and 60 ml of toluene using a needle and shaken with ultrasonic waves and stirred at 80 ºC for 4 days. After stopping the reaction, it was cooled to room temperature and extracted with dichloromethane and saturated saline to collect the lower organic phase. The organic phase was dried with anhydrous Na_2SO_4 and the solvent was removed by vacuum distillation. Due to the poor solubility of the crude product, purification was carried out by dry column chromatography (Al_2O_3) with CH_2Cl_2: CH_3OH (100:0.5, *v/v*) as eluent to give a white solid (1 g) in 77% yield. ^1H NMR (500 MHz, $CDCl_3$, 300 K) δ 7.37 (s, 8H), 7.29-7.22 (m, 16H), 6.56 (d, J = 8.0 Hz, 8H), 6.47 (s, 9H), 6.26 (d, J = 7.0 Hz, 8H), 5.92 (s, 8H), 5.75 (s, 4H), 5.43 (s,

4H).^{13}C NMR (101 MHz, $CDCl_3$, 300 K) δ 156.27 (s), 155.86 (s), 149.92 (s), 149.11 (s), 143.03 (s), 138.67 (s), 137.44 (s), 136.88 (d,), 136.13 (s), 130.42 (s), 128.15 (s), 127.55 (s), 125.81 (s), 123.73 (s), 121.32 (s), 118.95 (s), 77.35 (s), 77.03 (s), 76.71 (s). ESI-TOF (m/z): Calcd. for $[C_{100}H_{64}N_{12}+H]^+$: 1434.54, Found: 1434.54.



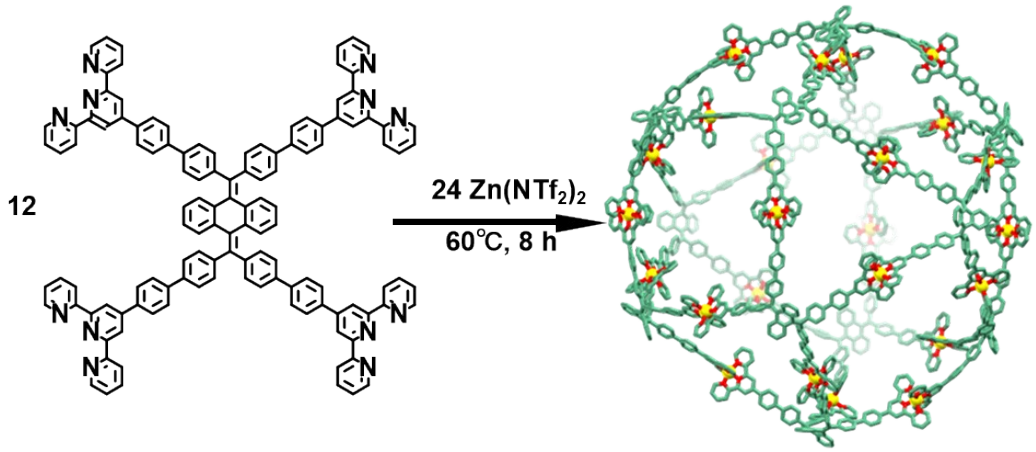
Ligand **L2:** Compound **1** (100 mg, 0.192 mmol), Compound **3** (590 mg, 1.154 mmol), Pd $(PPh_3)_4$ (44 mg, 0.2 mmol) and sodium carbonate (244 mg, 2.304 mmol) were added to a 250 ml three necked flask. The mixture was evacuated with nitrogen 3 times each and 50 ml of toluene, 30 ml of H_2O and 20 ml of tert-butanol were added. The mixture was stirred at 85ºC for 4 days. After cooling to room temperature, the mixture was extracted with CH_2Cl_2. The combined organic layers were washed with brine, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by dry column chromatography (Al_2O_3) eluting with CH_2Cl_2: CH_3OH (100:1, v/v) to give 150 mg of white solid (44.9% yield). ^{1}H NMR (500 MHz, $CDCl_3$, 300 K,) δ 7.26 (d, J = 2.0 Hz, 8H), 7.20 (d, J = 5.0 Hz, 9H), 7.14 (d, J = 8.0 Hz, 8H), 6.48 (d, J = 8.0 Hz, 8H), 6.35 (t, J = 8.0 Hz, 9H), 6.26 (d, J = 7.5 Hz, 9H), 6.17 (d, J = 8.0 Hz, 8H), 6.09 (d, J = 8.0 Hz, 8H), 5.82 (t, J = 6.0 Hz, 9H), 5.67 (s, 4H), 5.33 (s, 4H).^{13}C NMR (101 MHz,

$CDCl_3$, 298 K) δ 156.27 (s), 155.95 (s), 149.77 (s), 149.15 (s), 141.81 (s), 141.25 (s), 138.66 (s), 137.72 (s), 137.24 (s), 136.87 (s), 130.36 (s), 128.18 (s), 127.72 (s), 127.47 (s), 127.07 (s), 125.58 (s), 123.81 (s), 121.38 (s), 118.71 (s), 77.28 (d), 77.02 (s), 76.70 (s). ESI-TOF (m/z): Calcd. for $[C_{124}H_{80}N_{12}+H]^+$: 1739.09, Found: 1739.09.



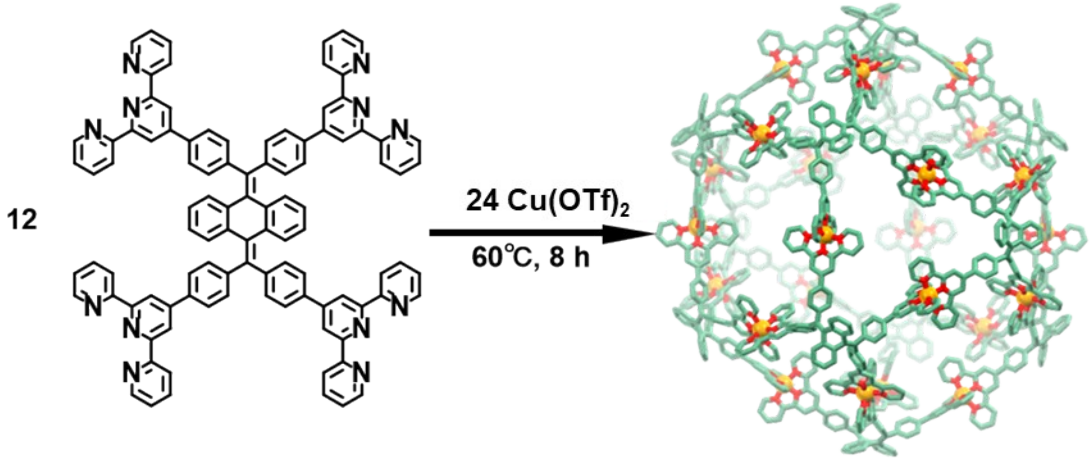
Complex **S1-Zn [$Zn_{24}L1_{12}$]:** The ligand **L1** (5.0 mg, 3.48 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $Zn(NTf_2)_2$ (4.36 mg, 6.96 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times.The product was obtained as light yellow solid (9.0 mg, 96.3%). ESI-TOF (*m/z*): 3299.83 $[M-9\ NTf_2^-]^{9+}$ (calcd *m/z*: 3299.83), 2941.86 $[M-10\ NTf_2^-]^{10+}$ (calcd *m/z*: 2941.86), 2649.05 $[M-11\ NTf_2^-]^{11+}$ (calcd *m/z*: 2649.05), 2404.90 $[M-12\ NTf_2^-]^{12+}$ (calcd *m/z*: 2404.90), 2198.61 $[M-13\ NTf_2^-]^{13+}$ (calcd *m/z*: 2198.61), 2021.54 $[M-14\ NTf_2^-]^{14+}$ (calcd *m/z*: 2021.54), 1868.16 $[M-15\ NTf_2^-]^{15+}$ (calcd *m/z*: 1868.16), 1733.83 $[M-16\ NTf_2^-]^{16+}$ (calcd *m/z*:

1733.83), 1615.40 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1615.40), 1510.09 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1510.09), 1415.83 [M−19 NTf_2^-]$^{19+}$ (calcd *m/z*: 1415.83), 1331.09 [M−20 NTf_2^-]$^{20+}$ (calcd *m/z*: 1331.09), 1254.29 [M−21 NTf_2^-]$^{21+}$ (calcd *m/z*: 1254.29).

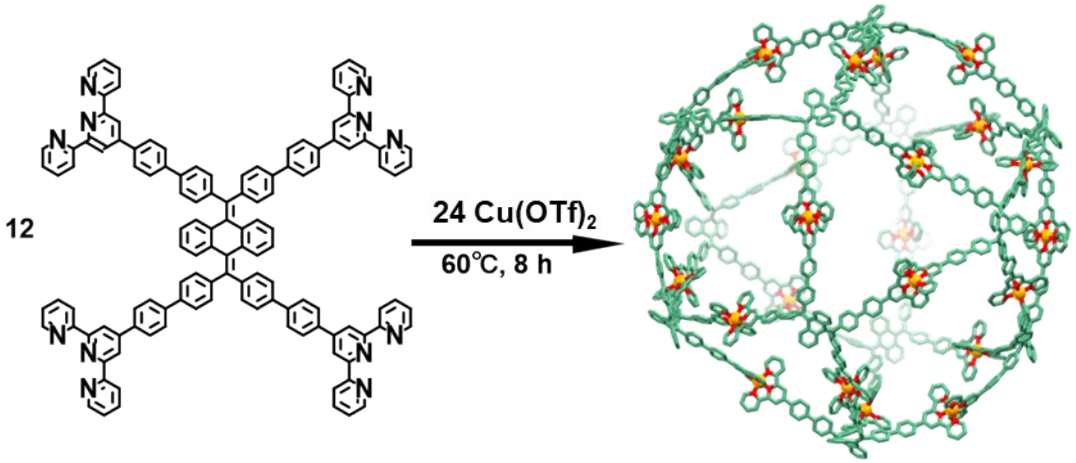


Complex **S2-Zn [$Zn_{24}L2_{12}$]:** The ligand **L2** (5.0 mg, 2.87 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $Zn(NTf_2)_2$ (3.599 mg, 5.75 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times. The product was obtained as light yellow solid (8.17 mg, 95.0%). ESI-TOF (*m/z*): 2981.81 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2981.81), 2709.77 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z*: 2709.77), 2479.87 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2479.87), 2282.85 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2282.85), 2111.98 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 2111.98), 1962.41 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1962.41), 1830.51 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1830.51), 1713.25 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1713.25), 1608.28 [M−19 NTf_2^-]$^{19+}$ (calcd *m/z*: 1608.28), 1512.96 [M−20 NTf_2^-]$^{20+}$ (calcd *m/z*: 1512.96), 1428.44 [M−21 NTf_2^-]$^{21+}$ (calcd *m/z*:

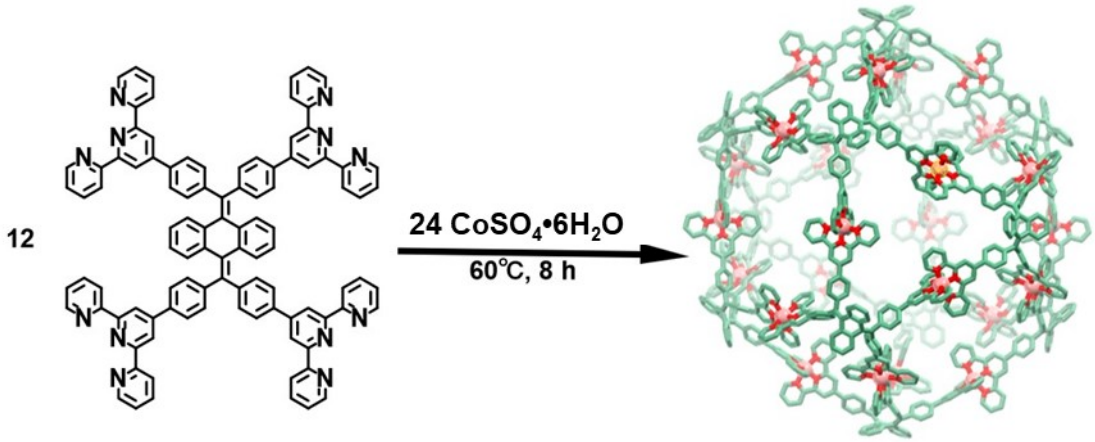
1428.44) , 1350.73 [M−22 NTf_2^-]$^{22+}$ (calcd *m/z*: 1350.73), 1250.89 [M−23 NTf_2^-]$^{23+}$ (calcd *m/z*: 1250.89) , 1214.99 [M−24 NTf_2^-]$^{24+}$ (calcd *m/z*: 1214.99).



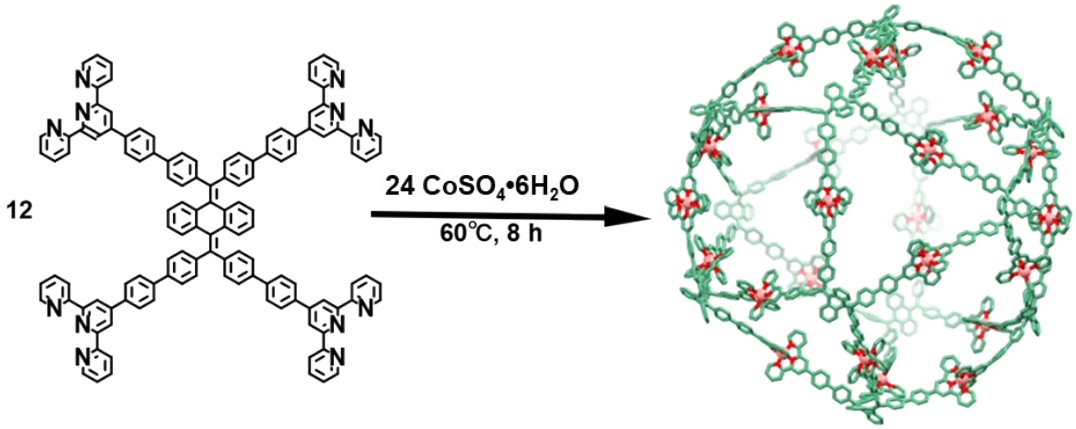
Complex **S1-Cu [$Cu_{24}L1_{12}$]:** The ligand **L1** (5.0 mg, 3.48 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $Cu(OTf)_2$ (2.52 mg, 6.96 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times. The product was obtained as light green solid (6.3 mg, 83.8%). ESI-TOF (*m/z*): 3294.97 [M−9 NTf_2^-]$^{9+}$ (calcd *m/z*: 3294.97), 2937.456 [M−10 NTf_2^-]$^{10+}$ (calcd *m/z*: 2937.46), 2644.95 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2644.95), 2401.19 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z*: 2401.19), 2194,93 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2194.93), 2018.14 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2018.14), 1864.92 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 1864.92), 1730.86 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1730.86), 1612.56 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1612.56), 1507.41 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1507.41), 1413.33 [M−19 NTf_2^-]$^{19+}$ (calcd *m/z*: 1413.33), 1328.658 [M−20 NTf_2^-]$^{20+}$ (calcd *m/z*: 1328.658), 1252.05 [M−21 NTf_2^-]$^{21+}$ (calcd *m/z*: 1252.05).



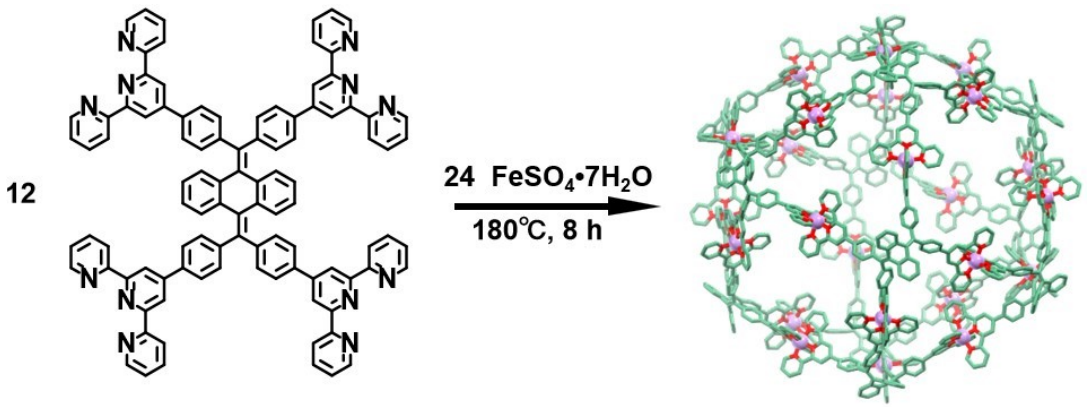
Complex **S2-Cu [$Cu_{24}L2_{12}$]:** The ligand **L2** (5.0 mg, 2.87 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $Cu(OTf_2)_2$ (2.08 mg, 5.75 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times. The product was obtained as light green solid (6.8 mg, 96.0%). ESI-TOF (*m/z*): 2977.01 $[M-11NTf_2^-]^{11+}$ (calcd *m/z*: 2977.01), 2705.58 $[M-12\ NTf_2^-]^{12+}$ (calcd *m/z*: 2705.58), 2475.91 $[M-13\ NTf_2^-]^{13+}$ (calcd *m/z*: 2475.91), 2279.05 $[M-14\ NTf_2^-]^{14+}$ (calcd *m/z*: 2279.05), 2108.44 $[M-15\ NTf_2^-]^{15+}$ (calcd *m/z*: 2108.44), 1959.15 $[M-16\ NTf_2^-]^{16+}$ (calcd *m/z*: 1959.15), 1827.43 $[M-17\ NTf_2^-]^{17+}$ (calcd *m/z*: 1827.43), 1710.34 $[M-18\ NTf_2^-]^{18+}$ (calcd *m/z*: 1710.34), 1605.58 $[M-19\ NTf_2^-]^{19+}$ (calcd *m/z*: 1605.58), 1511.29 $[M-20\ NTf_2^-]^{20+}$ (calcd *m/z*: 1511.29), 1425.99 $[M-21\ NTf_2^-]^{21+}$ (calcd *m/z*: 1425.99) , 1348.44 $[M-22\ NTf_2^-]^{22+}$ (calcd *m/z*: 1348.44), 1277.63 $[M-23\ NTf_2^-]^{23+}$ (calcd *m/z*: 1277.63) , 1212.72 $[M-24\ NTf_2^-]^{24+}$ (calcd *m/z*: 1212.72).



Complex **S1-Co [$Co_{24}L1_{12}$]:** The ligand **L1** (5.0 mg, 3.48 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $CoSO_4$•$6H_2O$ (2.02 mg, 6.96 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times. The product was obtained as light red solid (6.5 mg, 92.6%). ESI-TOF (*m/z*): 3276.12 [M−9 NTf_2^-]$^{9+}$ (calcd *m/z*: 3276.12), 2920.49 [M−10 NTf_2^-]$^{10+}$ (calcd *m/z*: 2920.49), 2629.53 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2629.53), 2387.05 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z*: 2387.05), 2181.88 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2181.88), 2006.03 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2006.03), 1853.61 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 1853.61), 1720.26 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1720.26), 1602.58 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1602.58), 1497.99 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1497.99), 1404.40 [M−19 NTf_2^-]$^{19+}$ (calcd *m/z*: 1404.40), 1320.18 [M−20 NTf_2^-]$^{20+}$ (calcd *m/z*: 1320.18), 1243.97 [M−21 NTf_2^-]$^{21+}$ (calcd *m/z*: 1243,97).



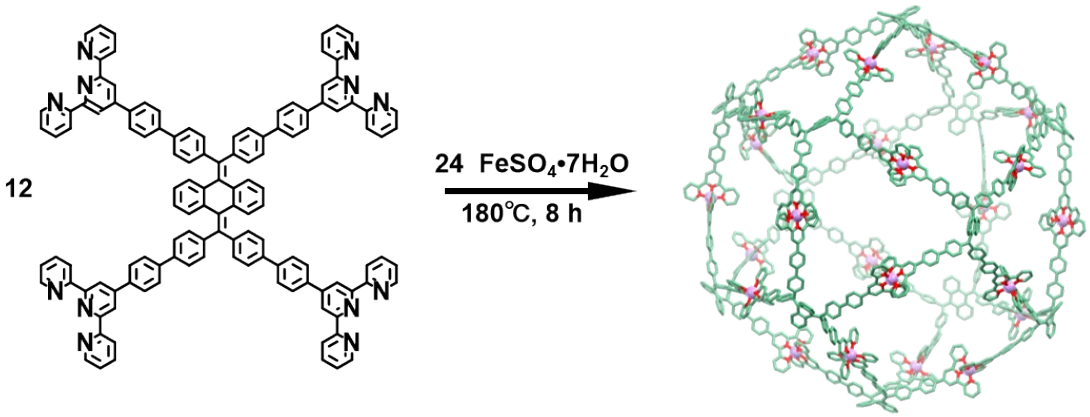
Complex **S2-Co [$Co_{24}L2_{12}$]:** The ligand **L2** (5.0 mg, 2.87 μmol) was accurately weighed using an electronic balance and transferred to a 20 mL vial. 5 mL of $CHCl_3$ and 5 mL of CH_3OH were added and sonicated to ensure ligand solubilisation, followed by addition of a solution of $CoSO_4$•$6H_2O$ (1.67 mg, 5.75 μmol) in CH_3OH (2 mg/mL). the solution was stirred at 60 °C for 8 h. After the reaction was completed, the solution was cooled to room temperature, and 10 times the amount of $LiNTf_2$ was added for anion exchange to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, and distilled water and a small amount of CH_3OH were added, and the mixture was well shaken and centrifuged again, and the solid was dried in a vacuum after repeating the above operation for three times. The product was obtained as light red solid (6.2 mg, 93.0%). ESI-TOF (*m/z*): 2966.95 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2966.95), 2696.36 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z*: 2696.36), 2467.39 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2467.39), 2271.14 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2271.14), 2101.06 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 2101.06), 1952.23 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1952.23), 1820.92 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1820.92), 1704.19 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1704.19), 1599.75 [M−19 NTf_2^-]$^{19+}$ (calcd *m/z*: 1599.75), 1505.76 [M−20 NTf_2^-]$^{20+}$ (calcd *m/z*: 1505.76), 1420.71 [M−21 NTf_2^-]$^{21+}$ (calcd *m/z*: 1420.71) , 1343.40 [M−22 NTf_2^-]$^{22+}$ (calcd *m/z*: 1343.40), 1272,81 [M−23 NTf_2^-]$^{23+}$ (calcd *m/z*: 1272.81) .



Complex **S1-Fe [$Fe_{24}L1_{12}$]:** Ligand **L1** (6.4 mg, 4.46 μmol) was weighed and transferred to a 20 mL vial, dissolved in 6 mL of $CHCl_3$ and 6 mL of ethylene glycol, sonicated to ensure that the ligand was dissolved, and a solution of $FeSO_4$•$7H_2O$ (2.48 mg, 8.92 μmol) in CH_3OH (1 mg/mL) was prepared and slowly added dropwise to the $CHCl_3$ and ethylene glycol mix of the ligand. The solution was slowly added dropwise to the mixed $CHCl_3$ and ethylene glycol solution of the ligand, followed by the addition of 3 mL of ethylene glycol to ensure that no precipitate would precipitate. The system was heated at 65 °C with open-top heating and stirred for 30 min, and then the system was heated to 180 °C under airtight condition with stirring by tightening the cap of the mouth of the tube, and the system was heated to 180 °C under airtight condition with stirring overnight, and then the system was cooled down to room temperature after the completion of the reaction, and anion-exchange was carried out by adding 10-fold excess of $LiNTf_2$ to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, distilled water was added to wash, the mixture was shaken well and centrifuged again, and the solid was dried under vacuum after repeating the above operation for three times, and the product was obtained as a dark purple solid (8.1 mg, 93%). ^{1}H NMR (400 MHz, DMF-d_7) δ 9.68 (br, 96H), 9.05 (br, 97H), 8.80 (br, 94H), 8.26 (br, 192H), 8.02-7.87 (m, 97H), 7.64-7.37 (m, 145H), 7.25-7.10 (m, 96H).

ESI-TOF (*m/z*): 3274.41 [M−9 NTf_2^-]$^{9+}$ (calcd *m/z*: 3274.41), 2918.87 [M−10 NTf_2^-]$^{10+}$ (calcd *m/z*: 2918.87), 2628.08 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2628.08),

2385.74 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z:* 2385.74), 2180.69 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2180.69), 2004.86 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2004.86), 1852.54 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 1852.54), 1719.39 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1719.39), 1601.67 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1601.63), 1497.13 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1497.13).



Complex **S2-Fe [$Fe_{24}L2_{12}$]:** Ligand **L2** (7.0 mg, 4.02 μmol) was weighed and transferred to a 20 mL vial, dissolved in 6 mL of $CHCl_3$ and 6 mL of ethylene glycol, sonicated to ensure that the ligand was dissolved, and a solution of $FeSO_4$•$7H_2O$ (2.24 mg, 8.04 μmol) in CH_3OH (1 mg/mL) was prepared and slowly added dropwise to the $CHCl_3$ and ethylene glycol mix of the ligand. The solution was slowly added dropwise to the mixed $CHCl_3$ and ethylene glycol solution of the ligand, followed by the addition of 3 mL of ethylene glycol to ensure that no precipitate would precipitate.The system was heated at 65 °C with open-top heating and stirred for 30 min, and then the system was heated to 180 °C under airtight condition with stirring by tightening the cap of the mouth of the tube, and the system was heated to 180 °C under airtight condition with stirring overnight, and then the system was cooled down to room temperature after the completion of the reaction, and anion-exchange was carried out by adding 10-fold excess of $LiNTf_2$ to form a precipitate. After complete conversion, the solution was transferred to a 15 mL centrifuge tube and centrifuged, the solid was retained and the supernatant was poured off, distilled water was added to wash, the mixture was shaken well and centrifuged again, and the solid was dried under vacuum after repeating the above operation for three times, and the product was obtained as a dark purple solid

(8.3 mg, 90%). ^{1}H NMR (400 MHz, DMF-d_7) δ 10.09 (br, 96H), 9.42 (br, 96H), 8.99 (br, 95H), 8.44 (br, 96H), 8.33-8.27 (br, 192H), 8.14 (br, 96H), 7.85 (br, 96H), 7.55-7.44 (br, 144H), 7.16 (br, 42H). ESI-TOF (*m/z*): 3680.29 [M−9 NTf_2^-]$^{9+}$ (calcd *m/z*: 3680.29), 3284.24 [M−10 NTf_2^-]$^{10+}$ (calcd *m/z*: 3284.24), 2960.21 [M−11 NTf_2^-]$^{11+}$ (calcd *m/z*: 2960.21), 2690.18 [M−12 NTf_2^-]$^{12+}$ (calcd *m/z:* 2690.18), 2461.69 [M−13 NTf_2^-]$^{13+}$ (calcd *m/z*: 2461.69), 2265.85 [M−14 NTf_2^-]$^{14+}$ (calcd *m/z*: 2265.85), 2096.12 [M−15 NTf_2^-]$^{15+}$ (calcd *m/z*: 2096.12), 1947.60 [M−16 NTf_2^-]$^{16+}$ (calcd *m/z*: 1947.60), 1816.56 [M−17 NTf_2^-]$^{17+}$ (calcd *m/z*: 1816.56), 1700.07 [M−18 NTf_2^-]$^{18+}$ (calcd *m/z*: 1700.07).

4. ^{1}H NMR and ^{13}C NMR of ligands and supramolecules.

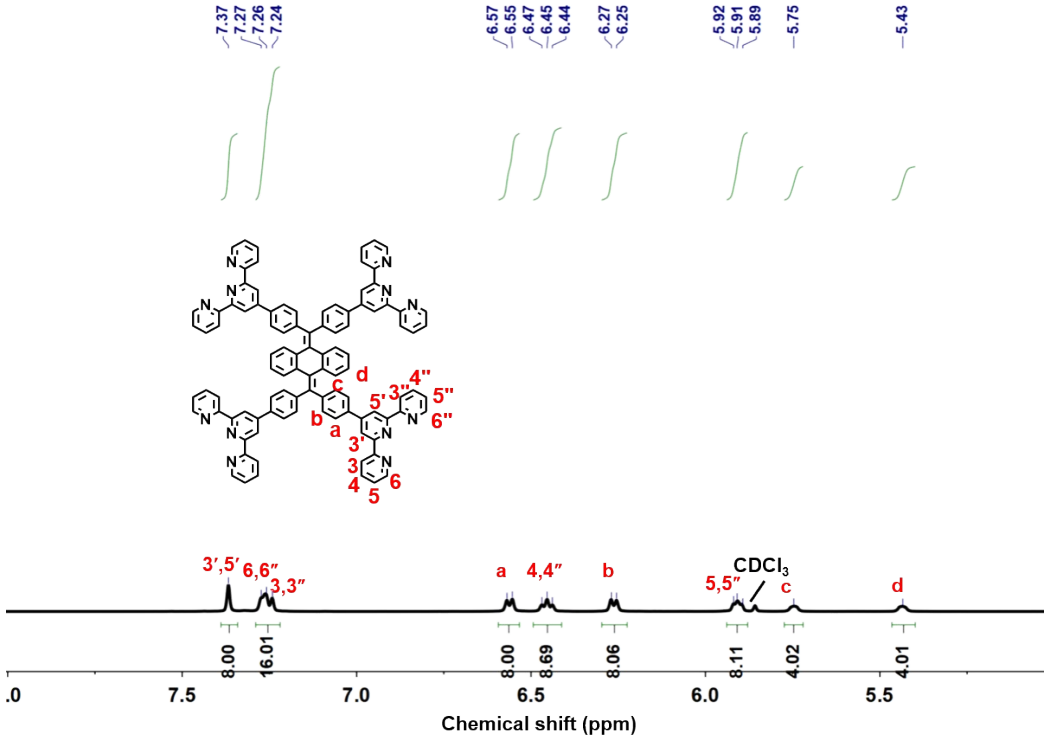


Figure S1. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1**.

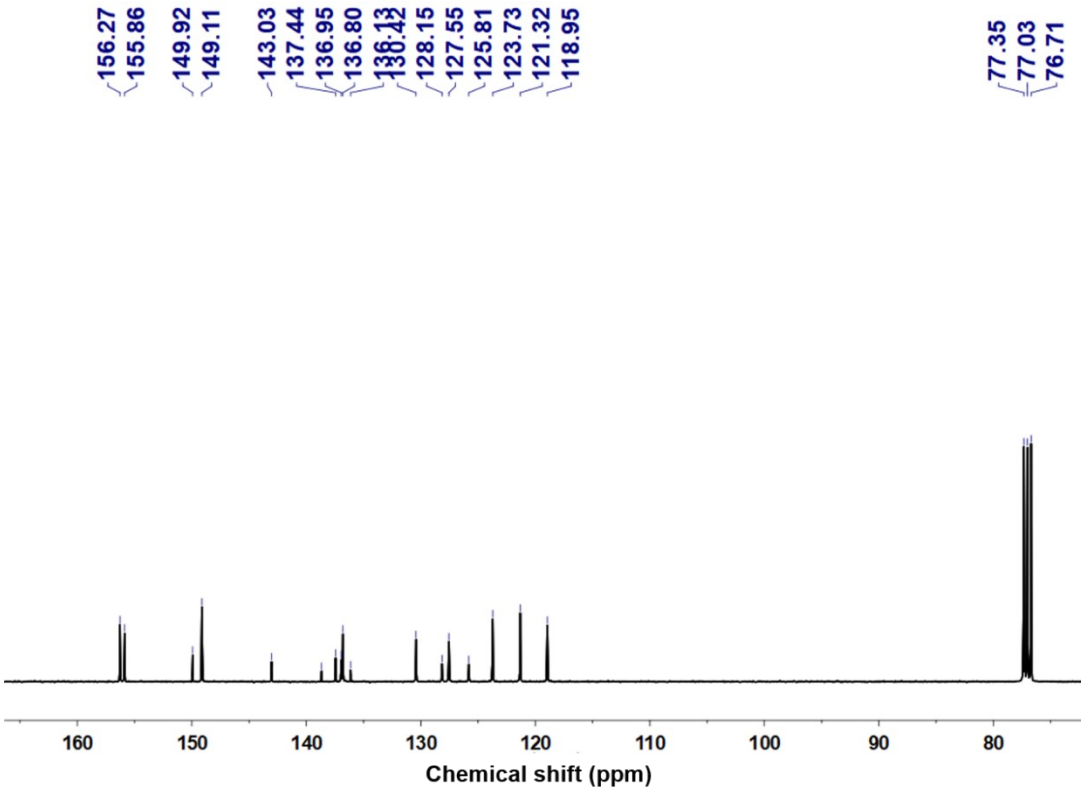


Figure S2. ^{13}C NMR (101 MHz, $CDCl_3$, 300 K) spectrum of ligand **L1.**

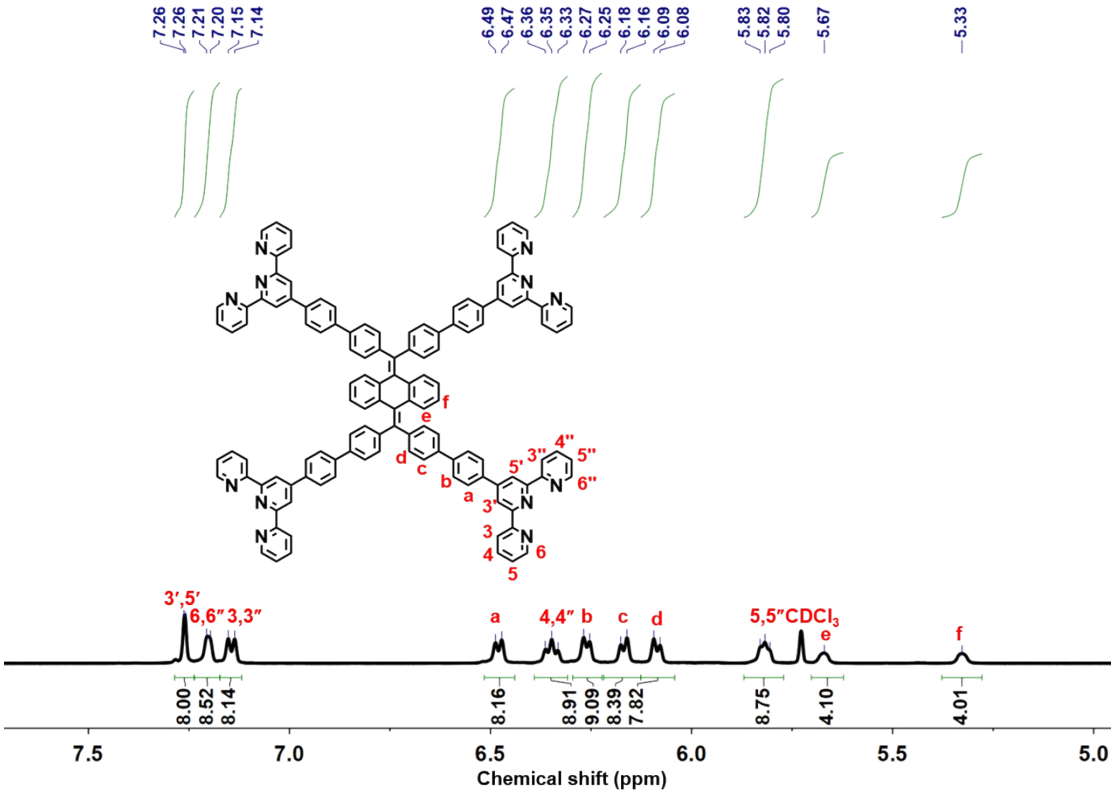


Figure S3. ^{1}H NMR (500 MHz, $CDCl_3$, 300 K) spectrum of ligand **L2**.

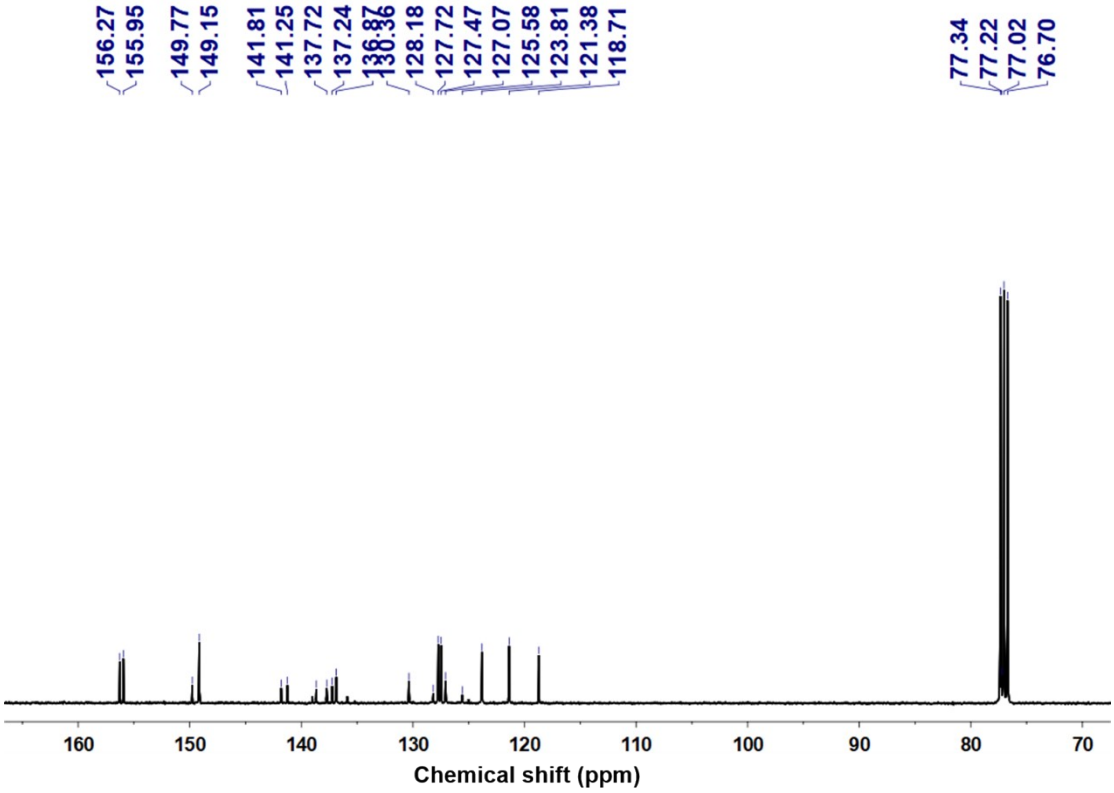


Figure S4. ^{13}C NMR (101 MHz, $CDCl_3$, 300 K) spectrum of ligand **L2**.

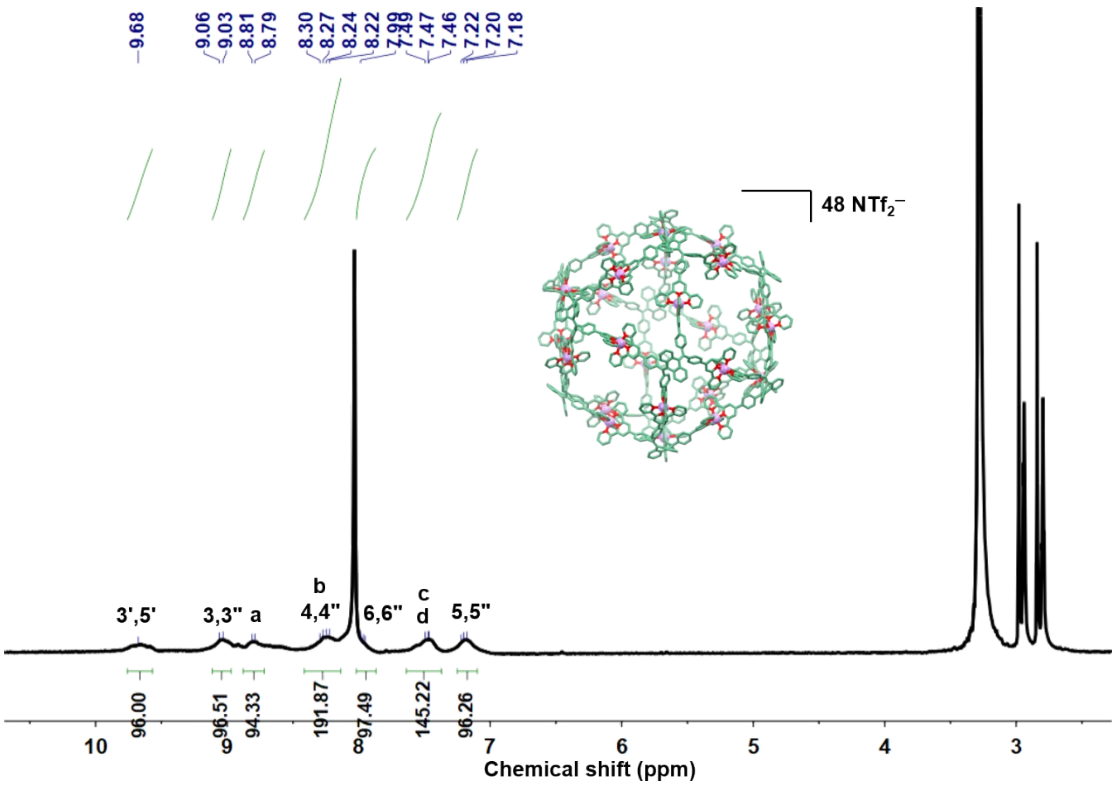


Figure S5. ^{1}H NMR (400 MHz, DMF-d_7, 300 K) spectrum of **S1-Fe**.

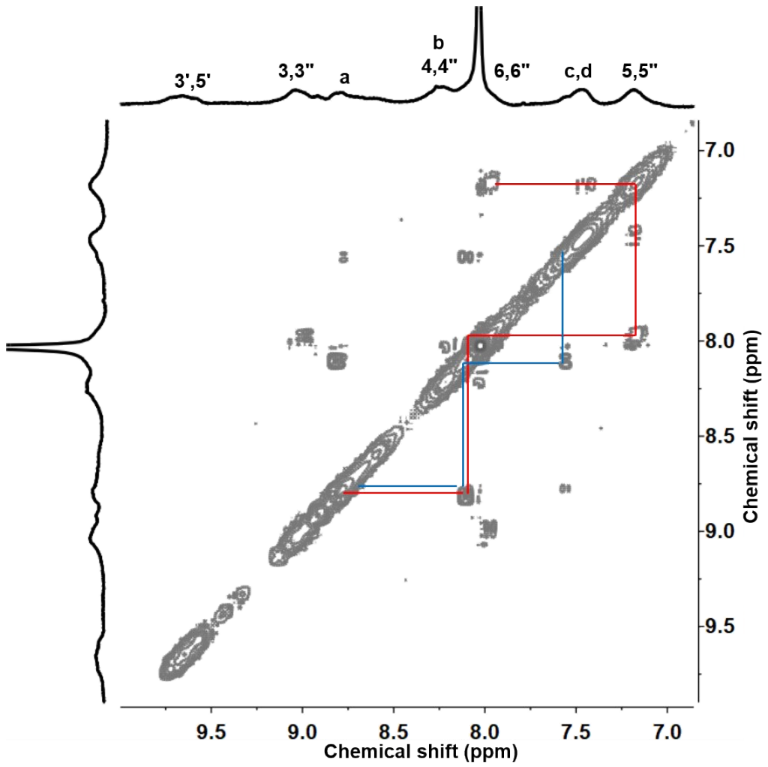


Figure S6. 2D COSY NMR (400 MHz, DMF-d_7, 300 K) spectrum of complex **S1-Fe** (aromatic region).

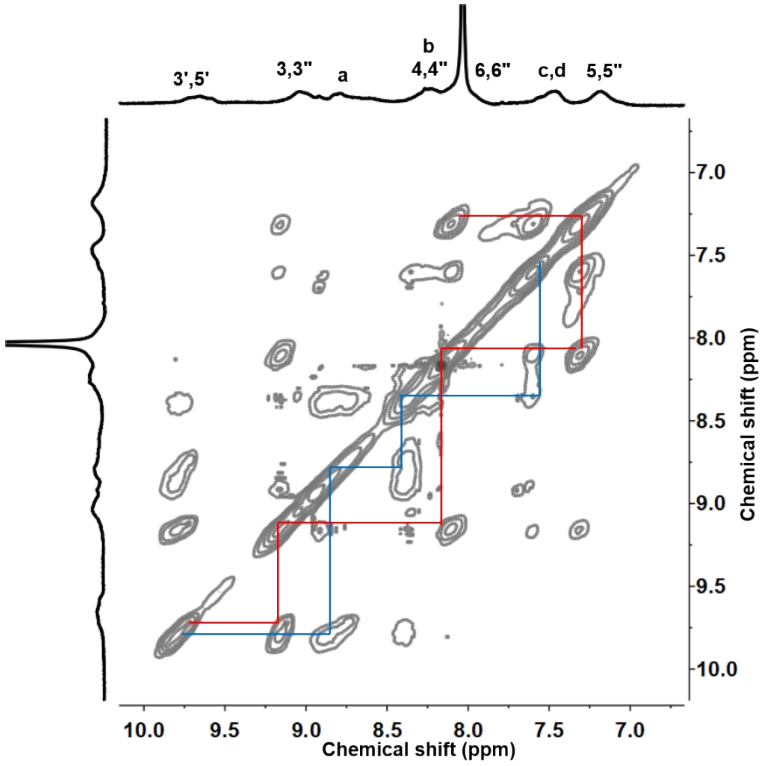


Figure S7. 2D NOESY NMR (400 MHz, DMF-d_7, 300 K) spectrum of complex **S1-Fe** (aromatic region).

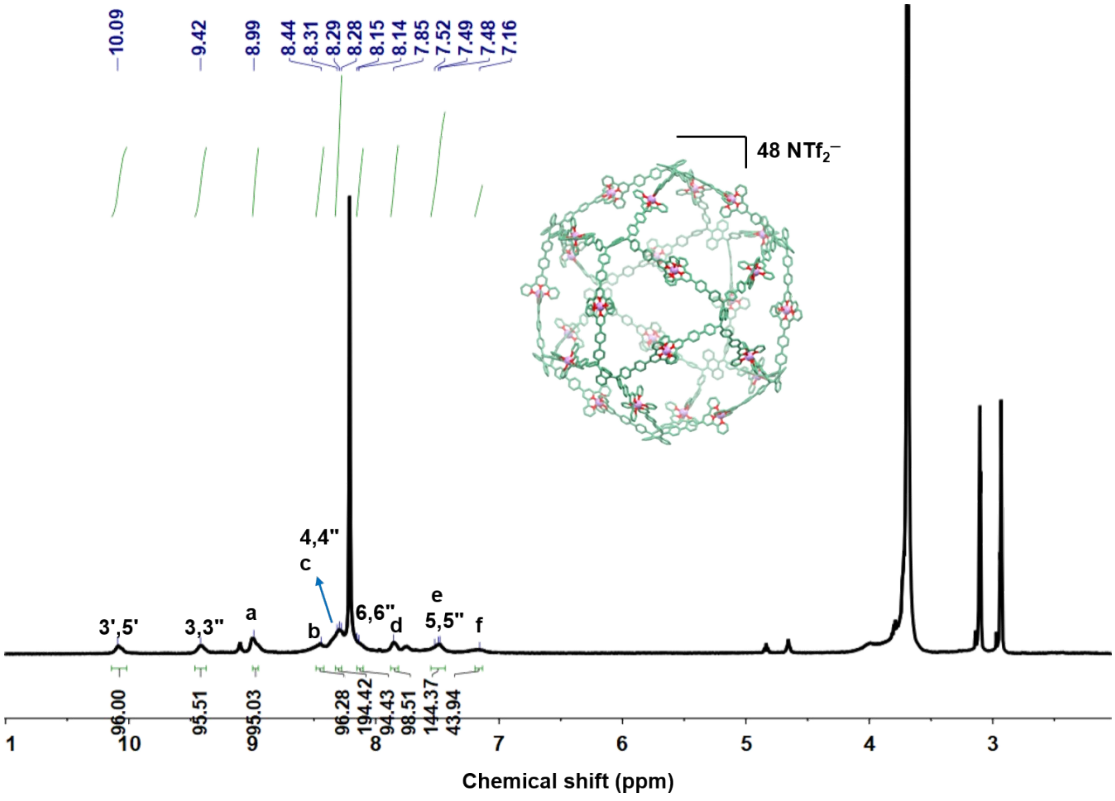


Figure S8. ^{1}H NMR (400 MHz, DMF-d_7, 300 K) spectrum of **S2-Fe**.

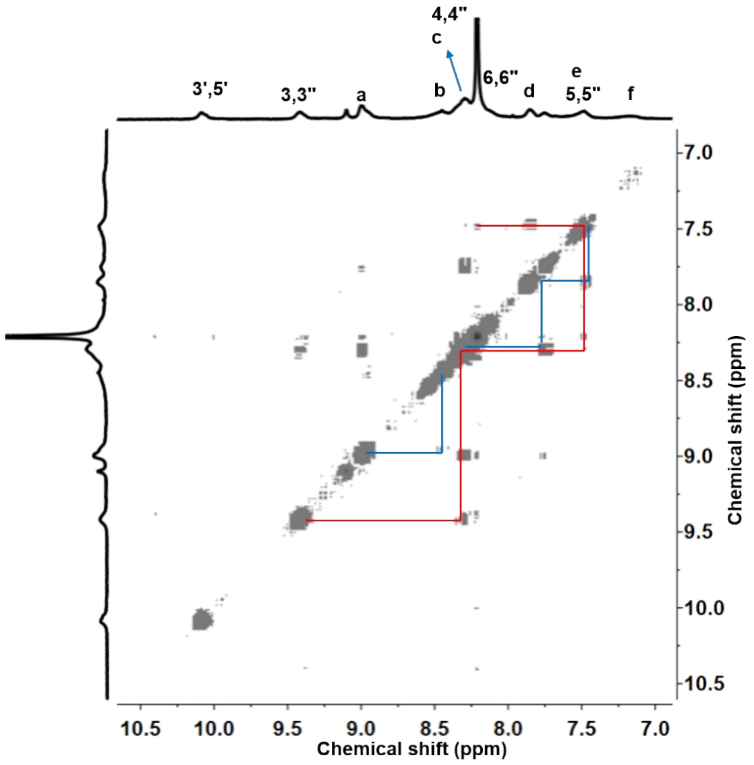


Figure S9. 2D COSY NMR (400 MHz, DMF-d_7, 300 K) spectrum of complex **S2-Fe** (aromatic region).

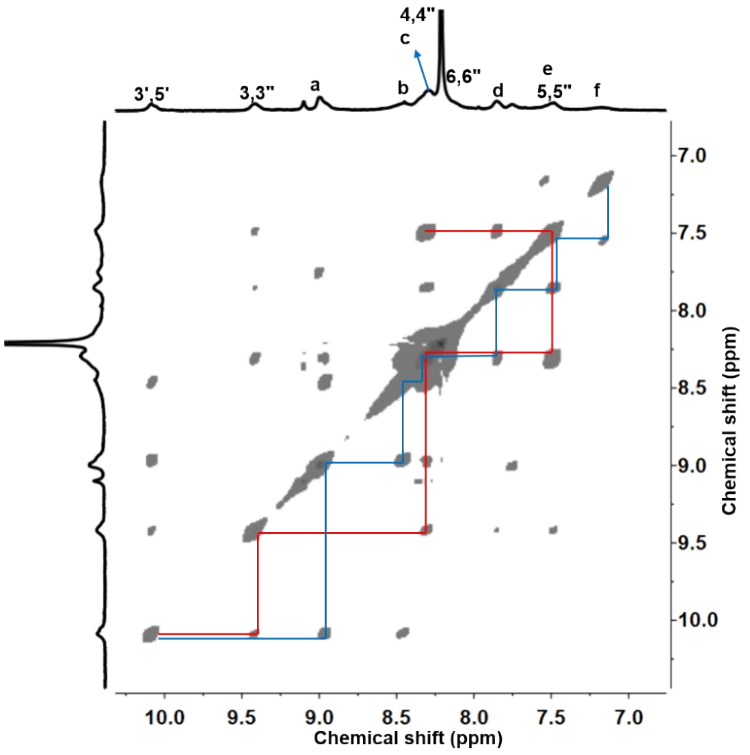


Figure S10. 2D NOESY NMR (400 MHz, DMF-d_7, 300 K) spectrum of complex **S2-Fe** (aromatic region).

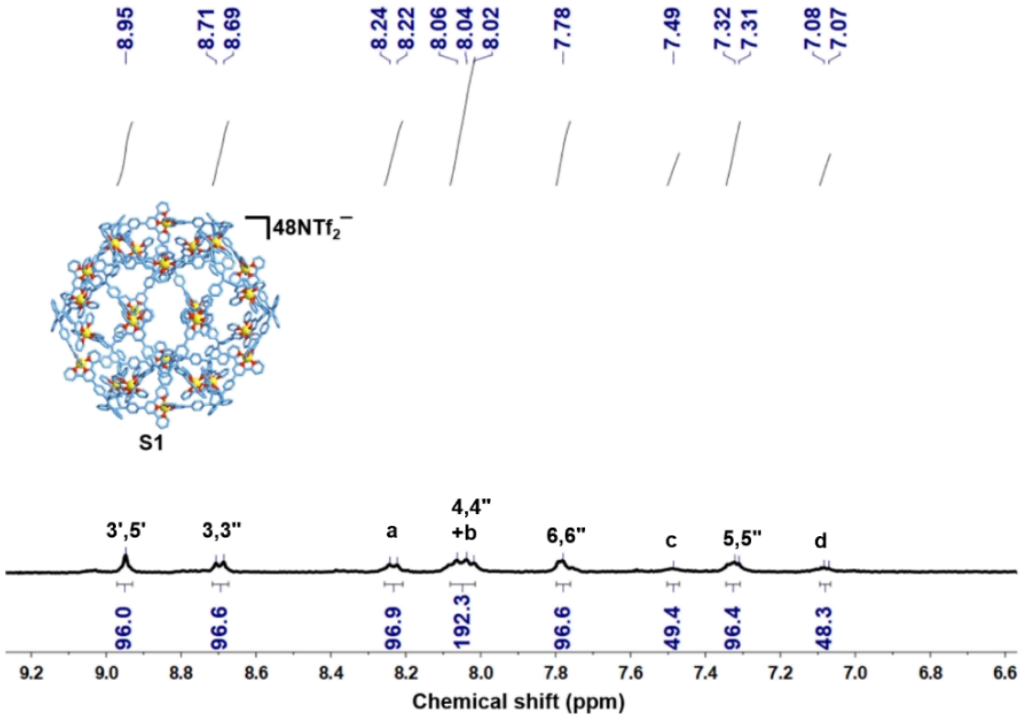


Figure S11. ^{1}H NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S1-Zn** (aromatic region).[1]

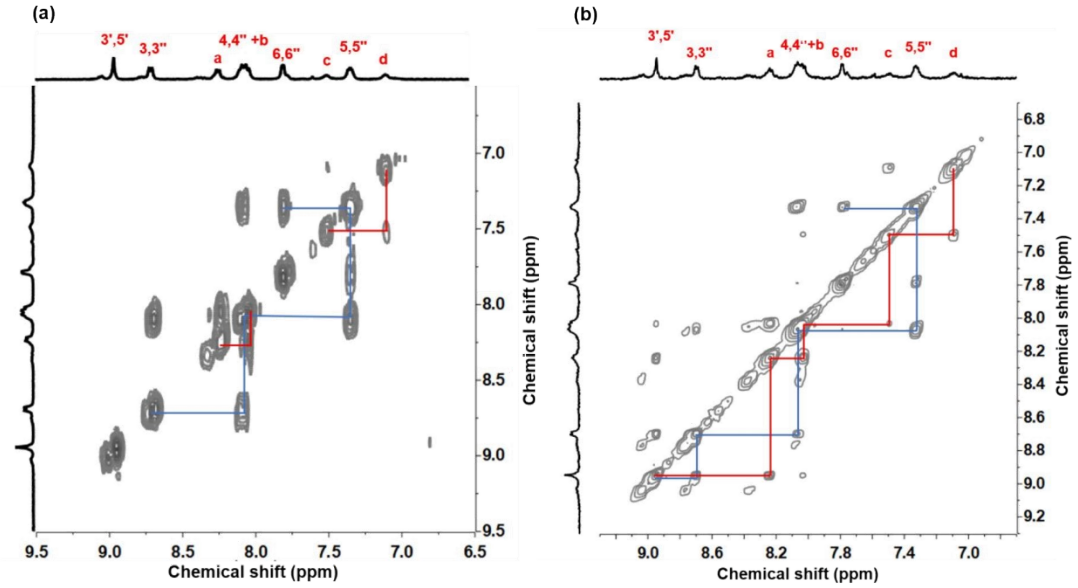


Figure S12. (a) 2D COSY NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S1-Zn** (aromatic region); (b) 2D NOESY NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S1-Zn** (aromatic region).

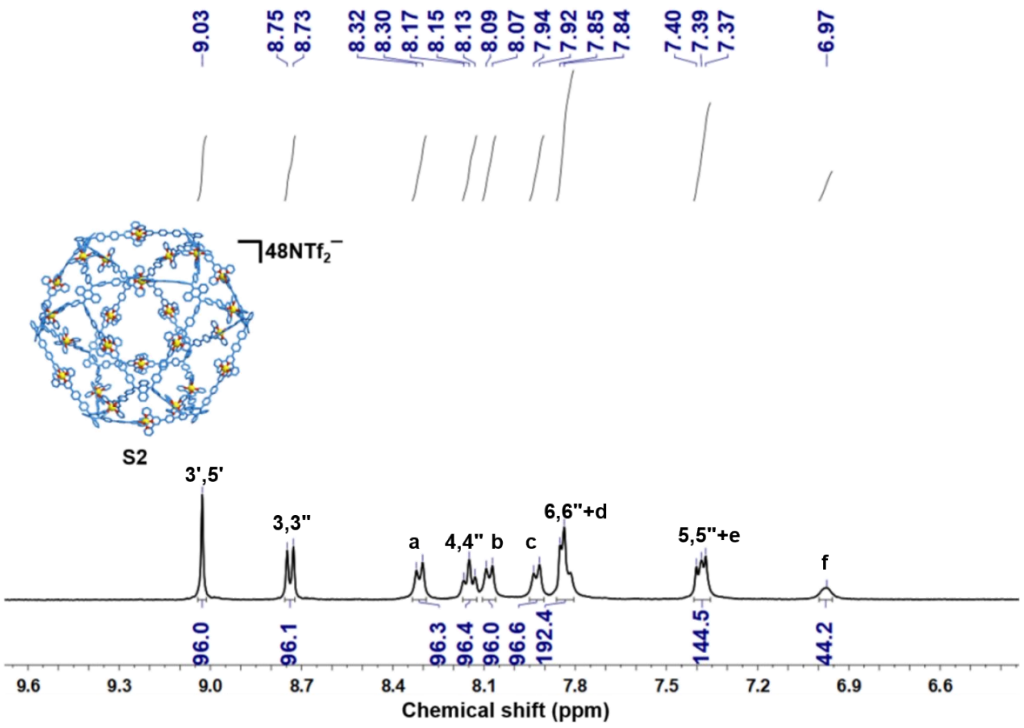


Figure S13. ^{1}H NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S2-Zn** (aromatic region).

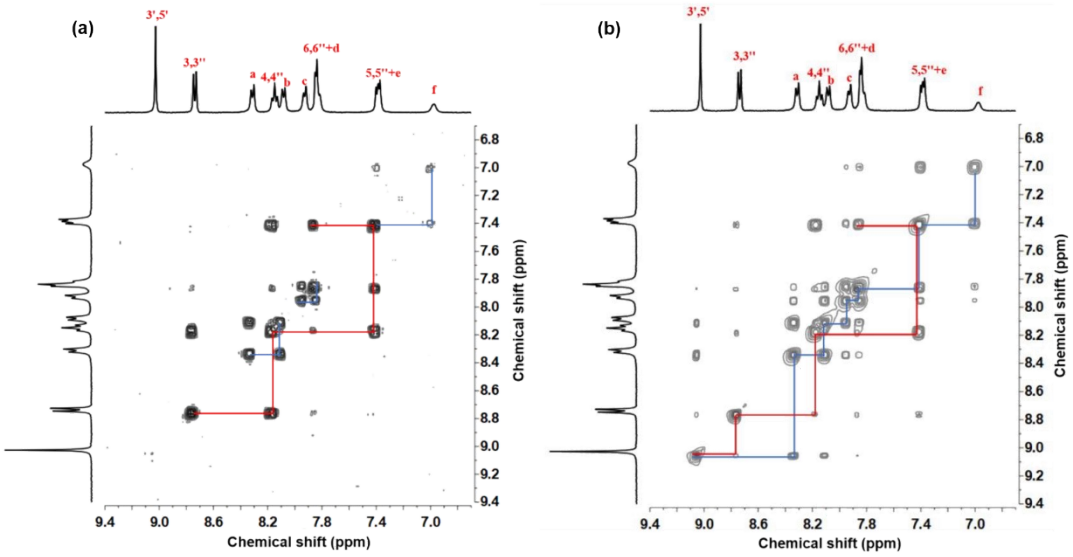
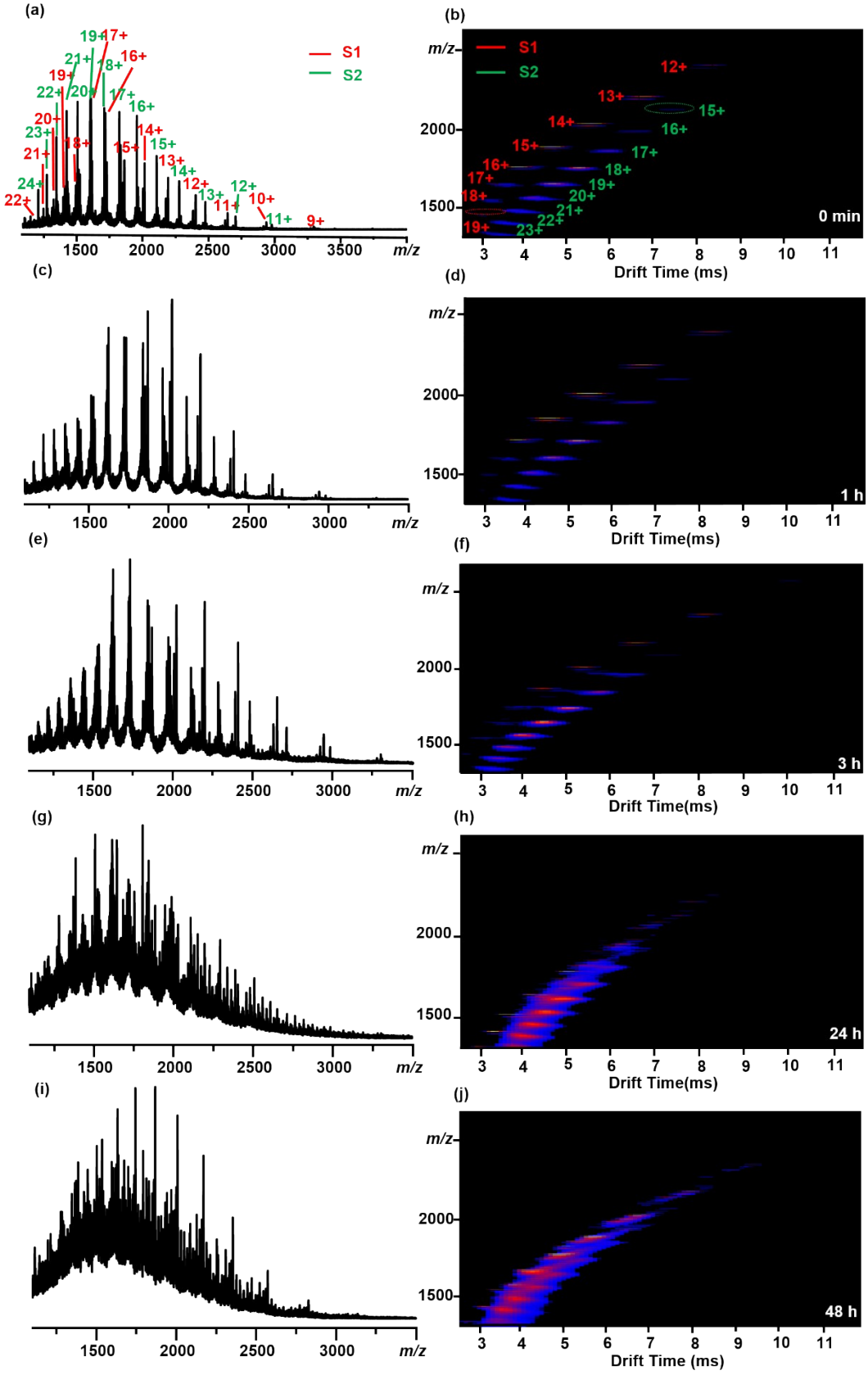


Figure S14. (a) 2D COSY NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S2-Zn** (aromatic region); (b) 2D NOESY NMR (400 MHz, CD_3CN, 300 K) spectrum of complex **S2-Zn** (aromatic region).

5. Dynamic exchange of preassembled S1 and S2



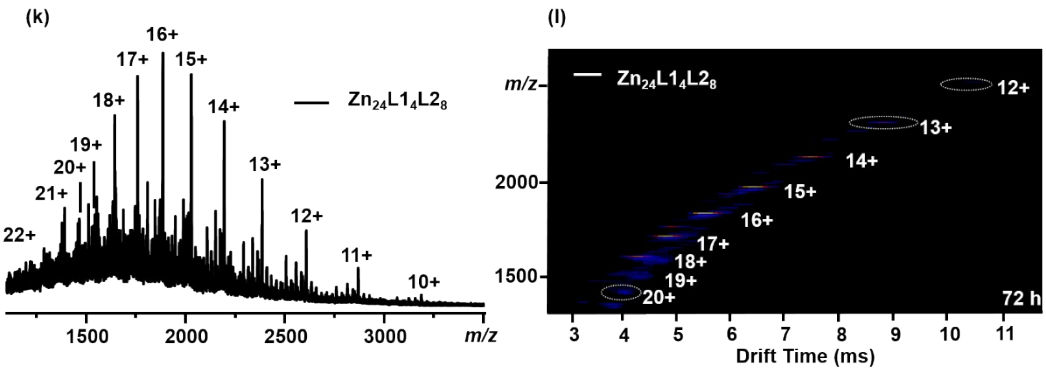
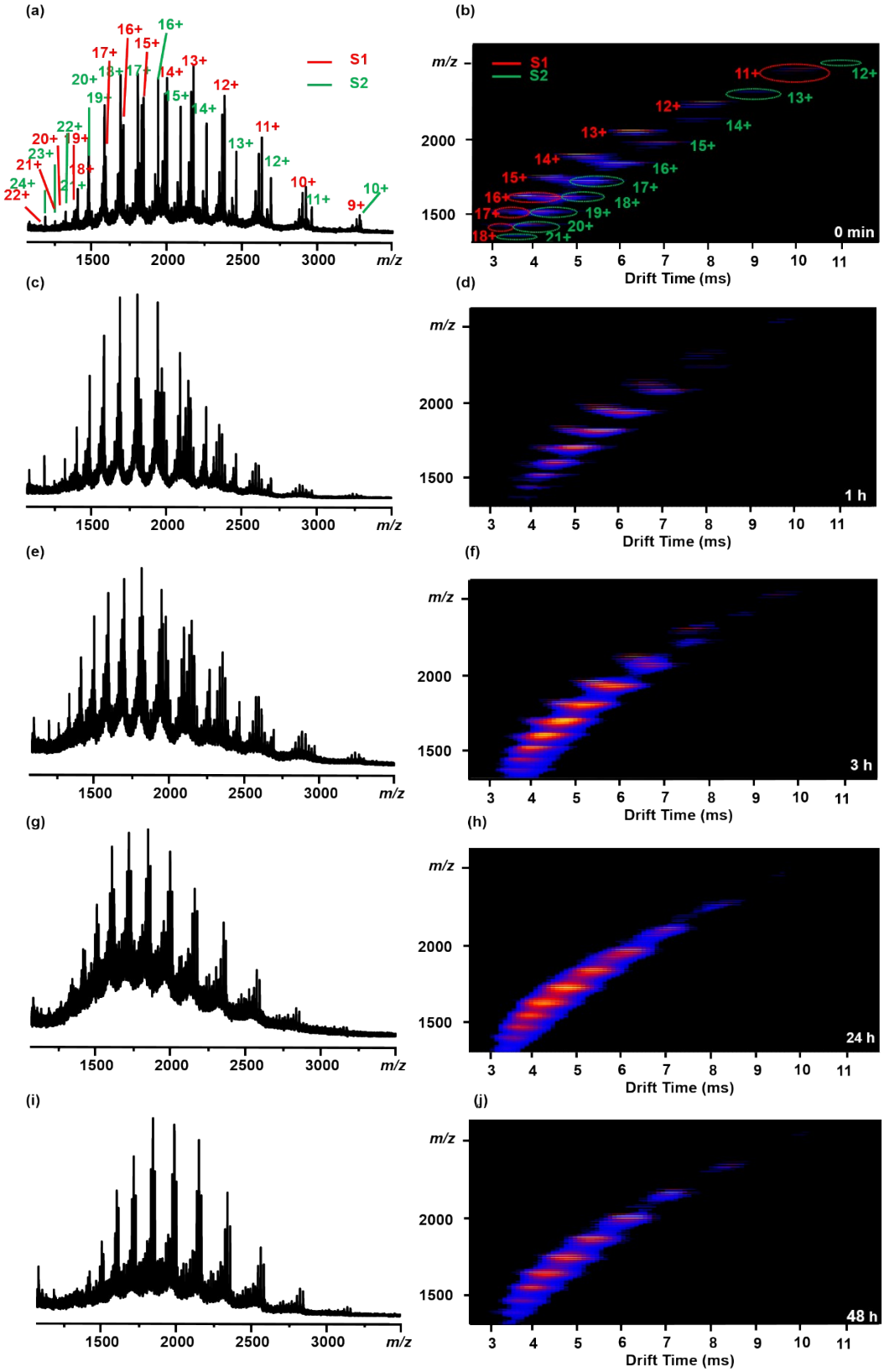


Figure S15. Diagram of the dynamic exchange process of **S1-Zn** and **S2-Zn**. (a, c, e, g, i, k) ESI-MS and (b, d, f, h, j, l) 2D ESI-TWIM-MS plots of equimolar amounts of **S1-Zn** and **S2-Zn** mixed for 0 min, 1 h, 3 h, 24 h, 48 h and 72 h at room temperature.


(a)
S1
S2
m/z
(b)
0 min
Drift Time (ms)
(c)
(d)
1 h
(e)
(f)
3 h
(g)
(h)
24 h
(i)
(j)
48 h

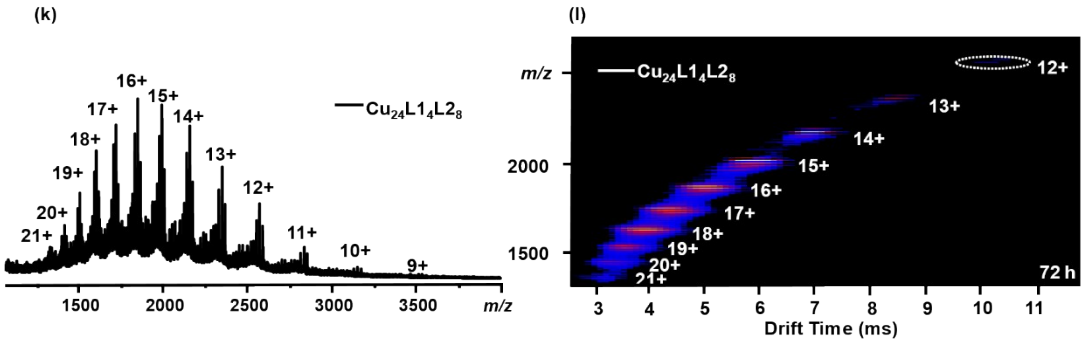


Figure S16. Diagram of the dynamic exchange process of **S1-Cu** and **S2-Cu**. (a, c, e, g, i, k) ESI-MS and (b, d, f, h, j, l) 2D ESI-TWIM-MS plots of equimolar amounts of **S1-Cu** and **S2-Cu** mixed for 0 min, 1 h, 3 h, 24 h, 48 h and 72 h at room temperature.

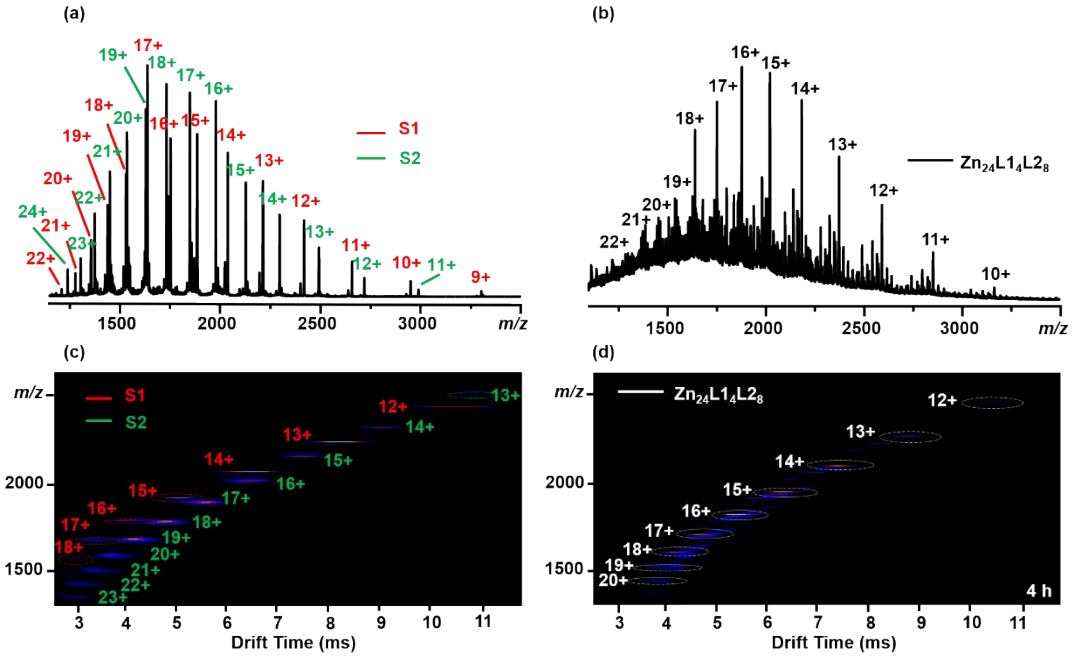


Figure S17. Dynamic exchange diagrams of **S1-Zn** and **S2-Zn** under heating conditions. (a) and (b) are ESI-MS and ESI-TWIM-MS for 0 min of mixing, respectively. (c) and (d) are the ESI-MS and ESI-TWIM-MS for 4 h of heating, respectively.

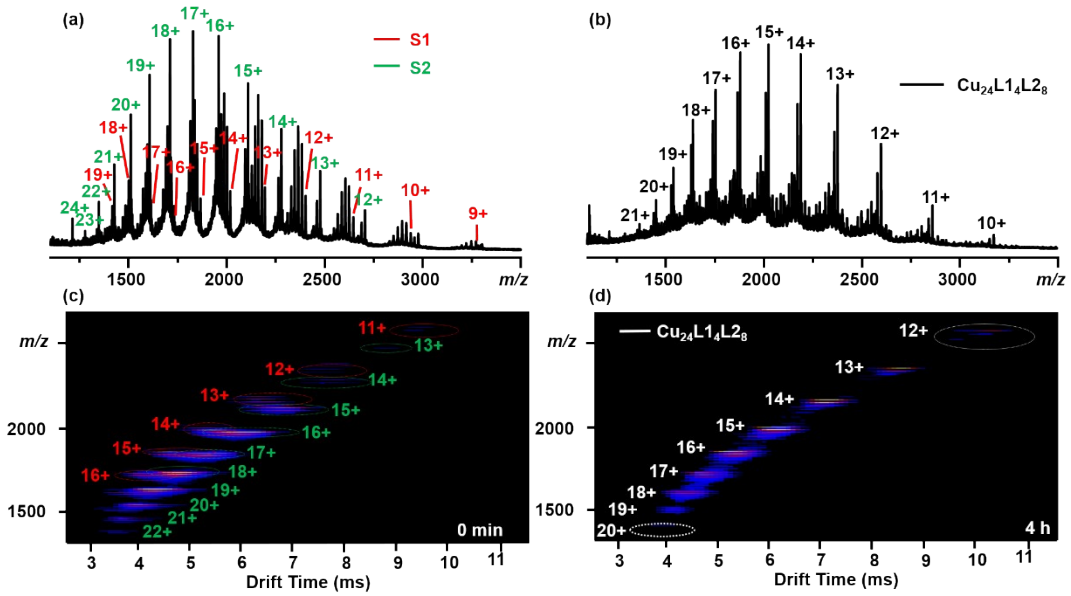


Figure S18. Dynamic exchange diagrams of **S1-Cu** and **S2-Cu** under heating conditions. (a) and (b) are ESI-MS and ESI-TWIM-MS for 0 min of mixing, respectively. (c) and (d) are the ESI-MS and ESI-TWIM-MS for 4 h of heating, respectively.

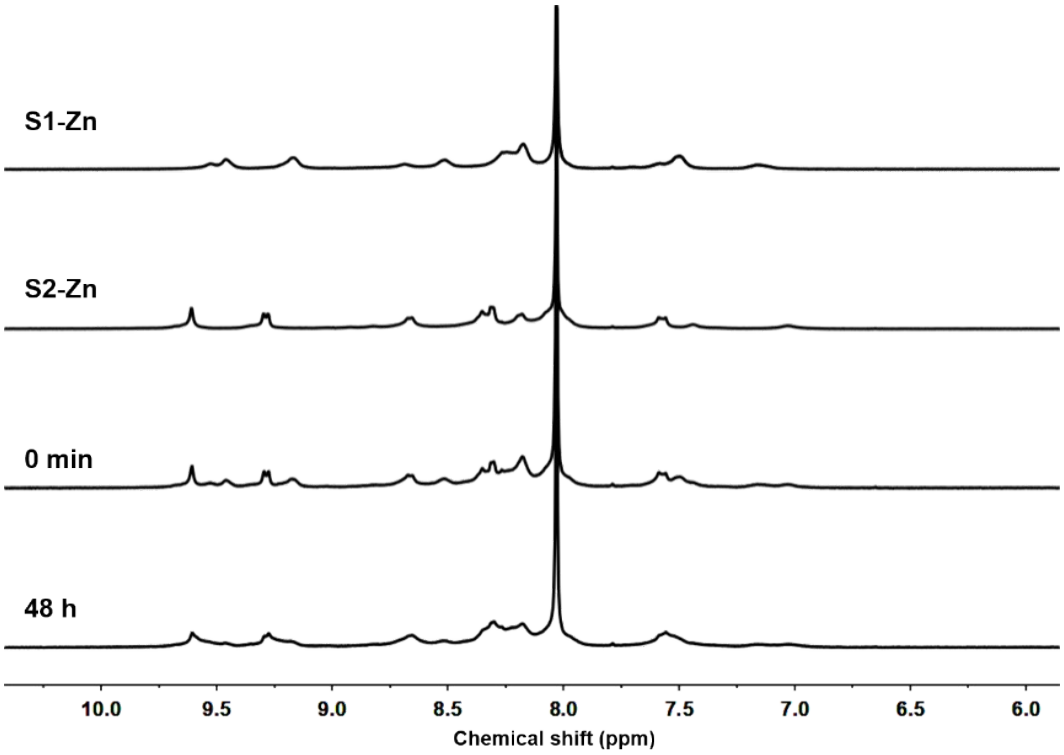


Figure **S19**. The ^{1}H NMR (400 MHz, DMF-d_7, 300 K) of metal-organic cages **S1-Zn** and **S2-Zn**, **S1-Zn**, **S2-Zn** after 0 min to 48 h of mixing.

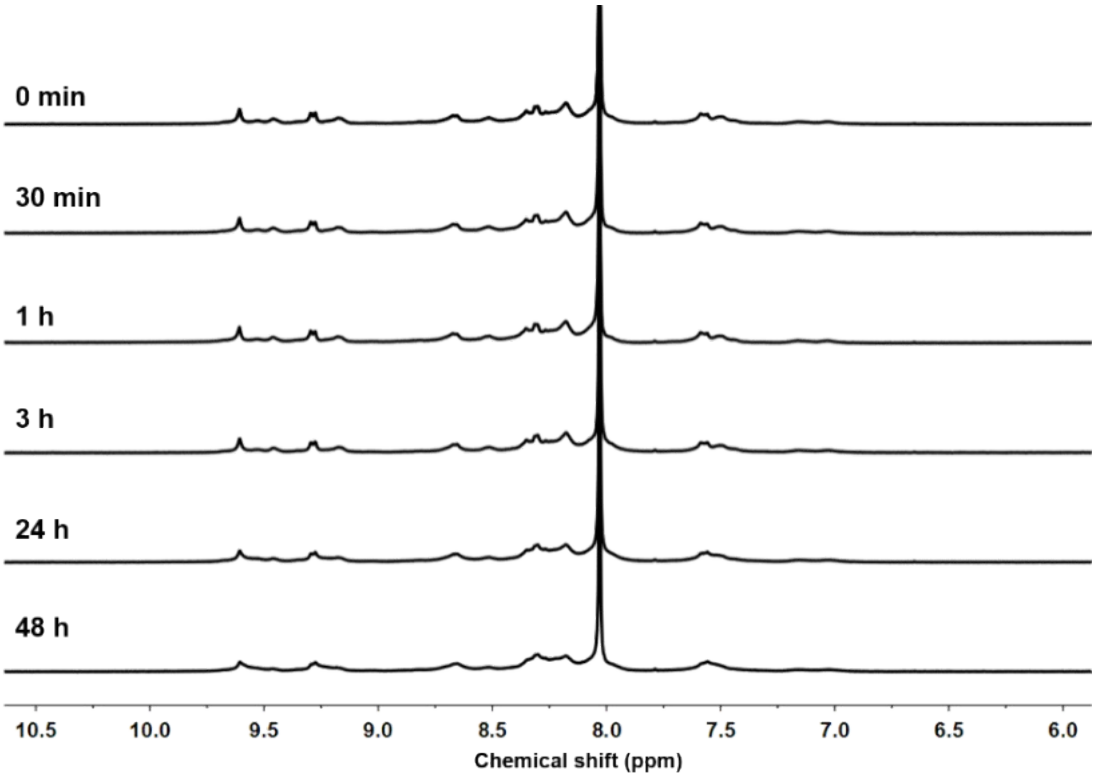


Figure **S20**. The ^{1}H NMR (400 MHz, DMF-d_7, 300 K) of metal-organic cages **S1-Zn** and **S2-Zn** from 0 min to 48 h of mixing.

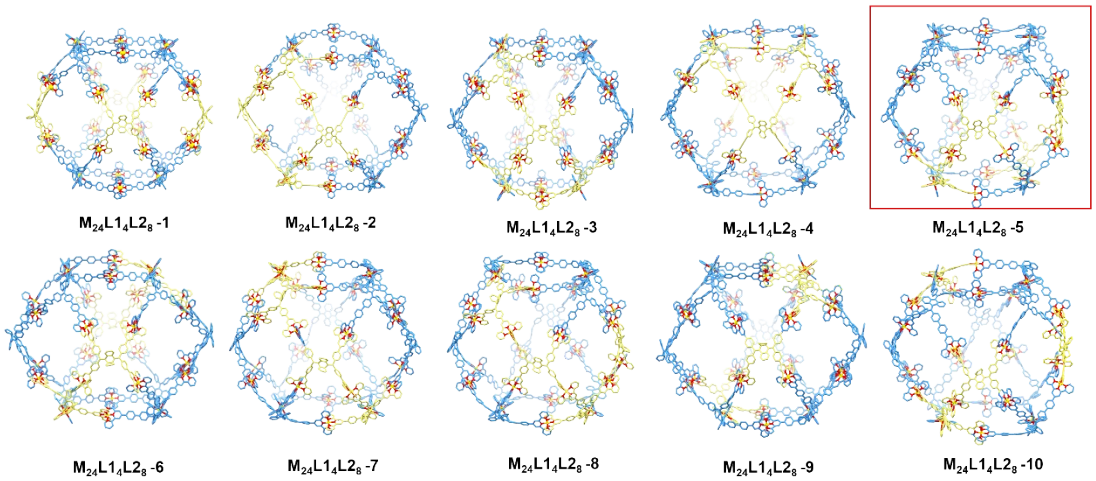


Figure S21. Simulated structures of isomers generated by $\mathbf{M_{24}L1_4L2_8}$ due to different ligand positions.

Table S1. Energies of isomers generated by $\mathbf{M_{24}L1_4L2_8}$ due to different ligand positions calculated with Universal Force Field.

Structure	Valence energy (diag. terms)	Valence energy (cross terms)	Non-bond energy	van der Waals	Electrostatic	Total energy
$\mathbf{M_{24}L1_4L2_8}$**-1**	9681.265	0.00	2134.646	2134.646	0.00	11815.91
$\mathbf{M_{24}L1_4L2_8}$**-2**	9722.402	0.00	2144.467	2144.467	0.00	11866.87
$\mathbf{M_{24}L1_4L2_8}$**-3**	9662.993	0.00	2151.665	2151.665	0.00	11814.66
$\mathbf{M_{24}L1_4L2_8}$**-4**	9726.258	0.00	2158.079	2158.079	0.00	11884.34
$\mathbf{M_{24}L1_4L2_8}$**-5**	9627.635	0.00	2151.857	2151.857	0.00	11779.49
$\mathbf{M_{24}L1_4L2_8}$**-6**	9710.253	0.00	2153.361	2153.361	0.00	11863.61
$\mathbf{M_{24}L1_4L2_8}$**-7**	9730.626	0.00	2163.560	2163.560	0.00	11894.19
$\mathbf{M_{24}L1_4L2_8}$**-8**	9712.433	0.00	2156.313	2156.313	0.00	11898.75
$\mathbf{M_{24}L1_4L2_8}$**-9**	9708.615	0.00	2153.254	2153.254	0.00	11861.87
$\mathbf{M_{24}L1_4L2_8}$**-10**	9692.424	0.00	2145.823	2145.823	0.00	11838.25

6. Metal-organic cages structure and 5,10,15,20-tetrakis(3,4,5-trimethoxyphenyl) porphyrin-Zn host-guest chemistry

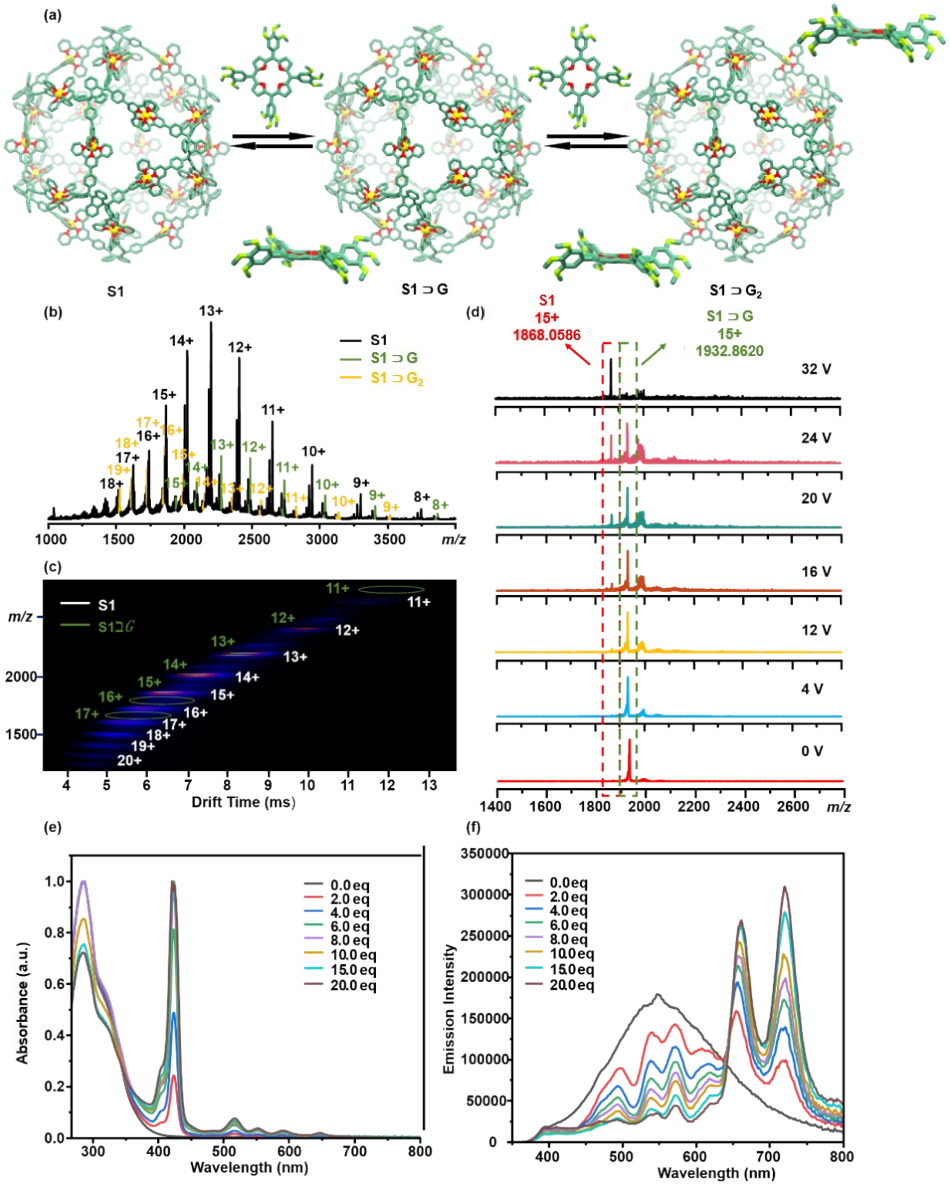


Figure S22. (a) Simulation of the external binding of **G** to **S1-Zn**. (b) and (c) ESI-MS and TWIM-MS of the supramolecular metal-organic cage **S1-Zn** alone (black), one **G** adduct (green), and two **G** adducts (yellow). (d) The mass spectrum of gMS^2 of one **G** adduct at *m/z* 1932.862 was obtained using various collision energies. (e) UV-Vis spectrum of **S1-Zn** with varying amounts of **G**. (f) fluorescence spectrum of **S1-Zn** with varying amounts of **G**.

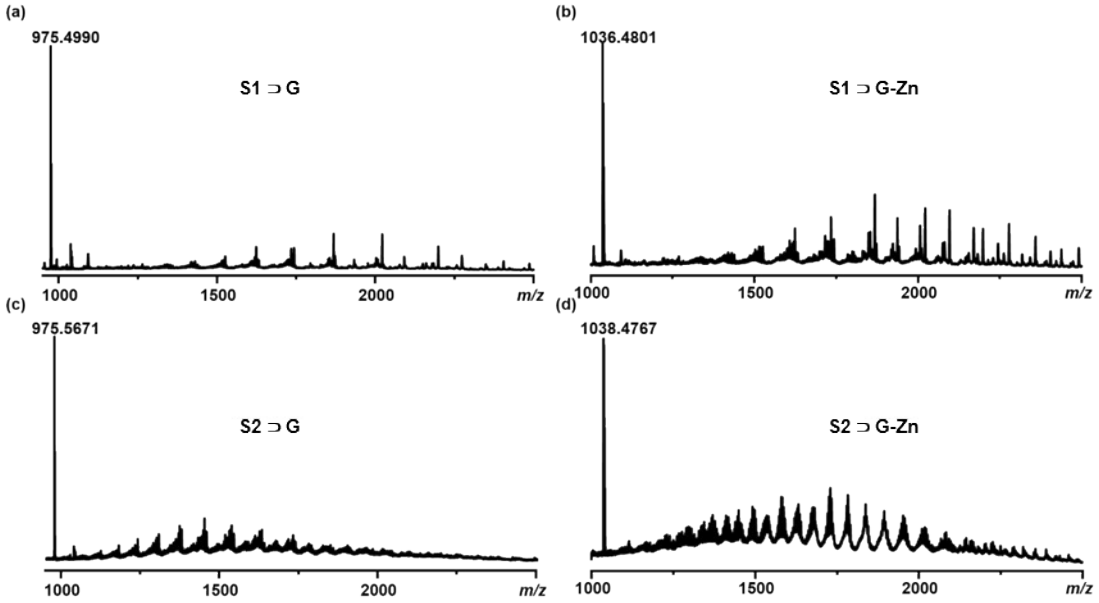


Figure S23. ESI-MS of supramolecular host-guest assembly with porphyrin and zinc porphyrin. (a) **S1⊃G**; (b) **S1⊃G-Zn**; (c) **S2⊃G**; (d) **S2⊃G-Zn.**

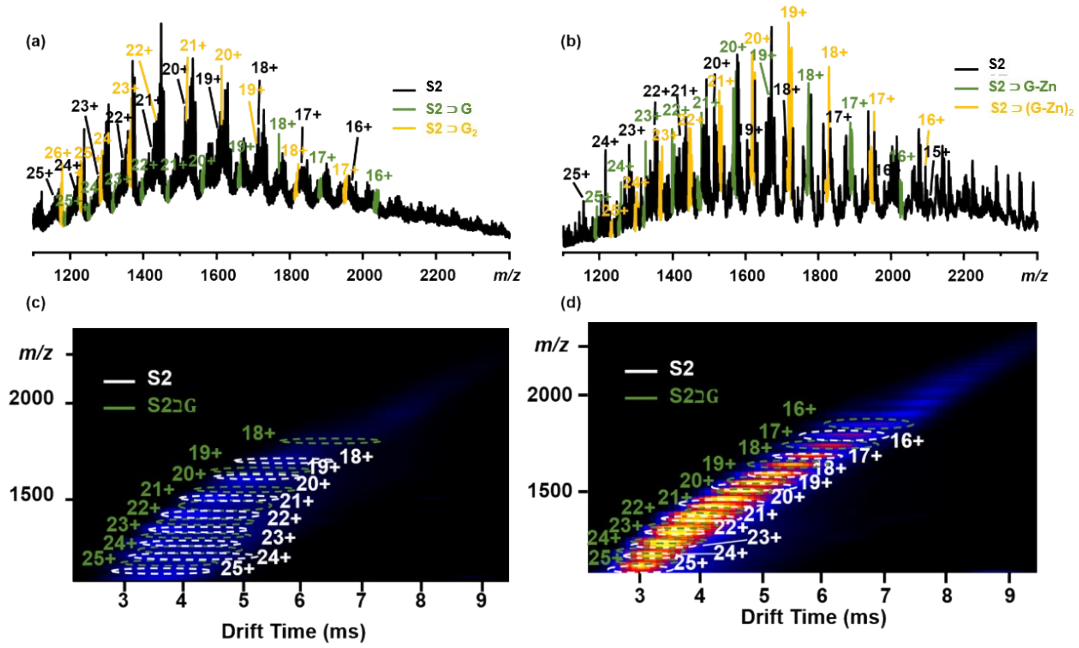


Figure S24. Host-guest exchange diagrams of supramolecular **S2** at room temperature. (a) and (c) are ESI-MS and TWIM-MS of **S2⊃G**. (b) and (d) are ESI-MS and TWIM-MS of **S2⊃G-Zn**.

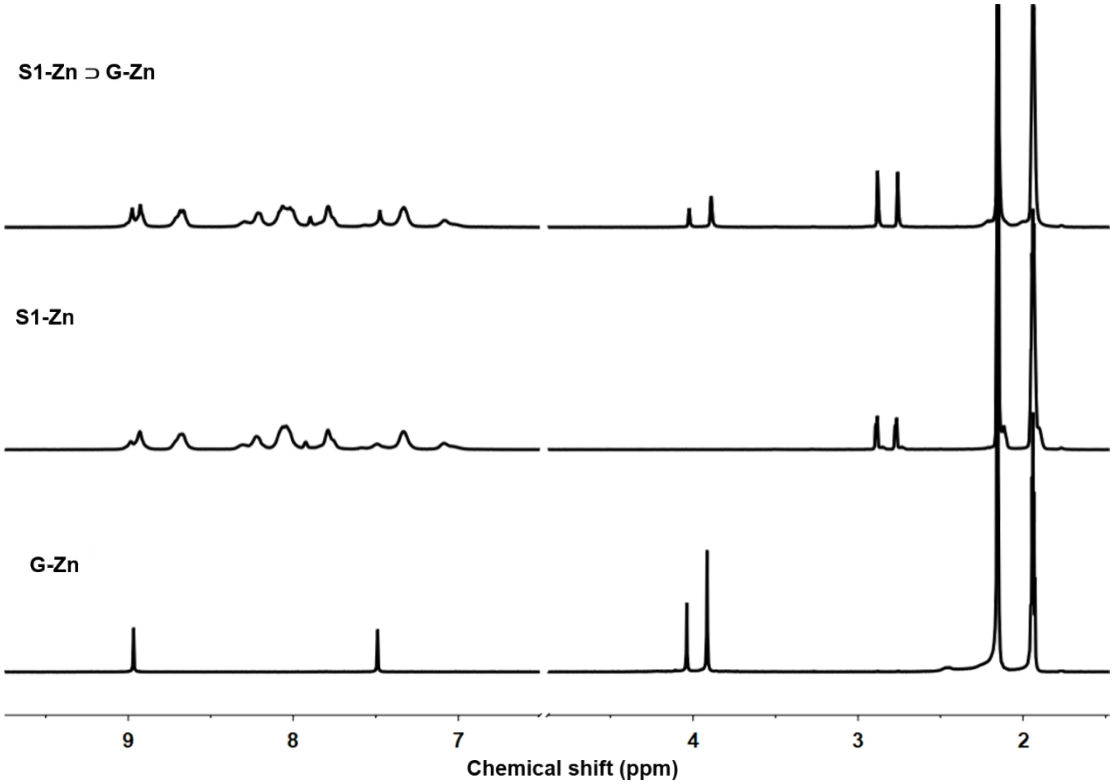


Figure **S25**. ^{1}H NMR NMR spectrum of **S1-Zn** and **S1-Zn** combing **G-Zn** in CD_3CN.

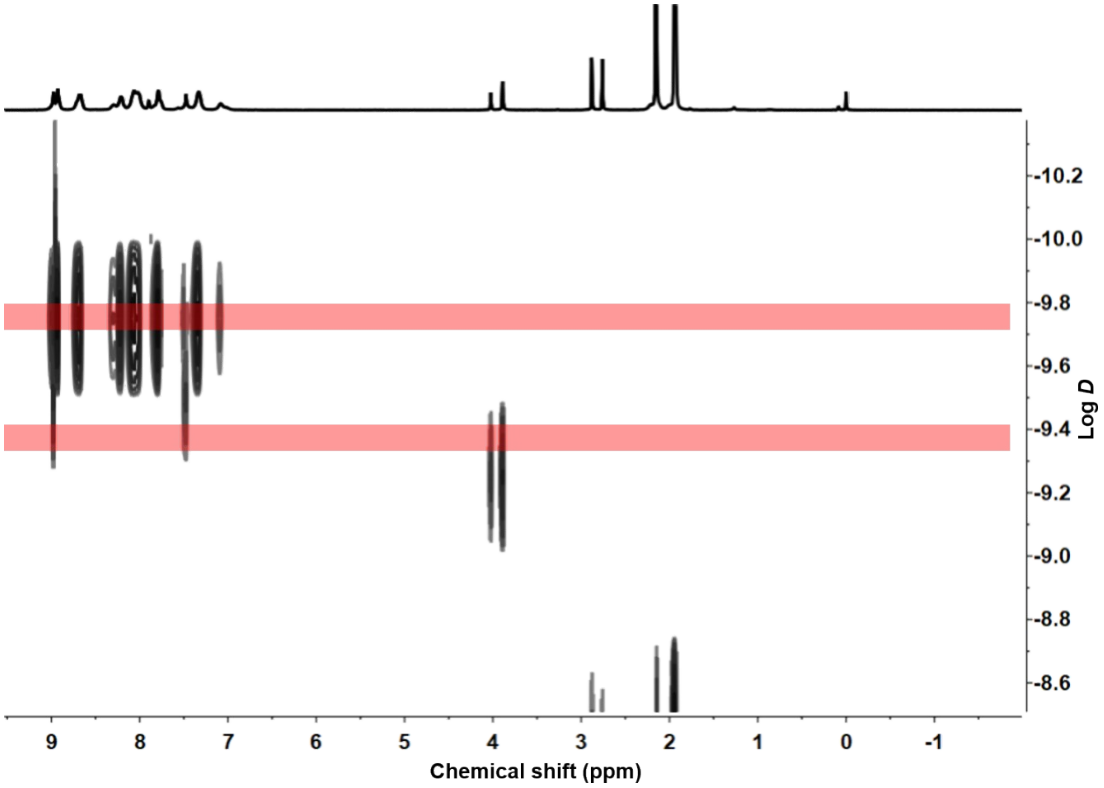


Figure **S26**. 2D DOSY NMR spectrum of **S1-Zn** combing **G-Zn** in CD_3CN.

.

7. References

[1] Z. Zhang, Y. Huang, Q. Bai, T. Wu, Z. Jiang, H. Su, Y. Zong, M. Wang, P.-Y. Su, T.-Z. Xie and P. Wang, *JACS Au*, 2022, **2**, 2809-2820.