Supporting Information

Multi-Responsive Metal-Organic Lantern Cages in Solution

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Contents

1. General Information

Solution NMR spectra were recorded in deuterated solvent at room temperature. Proton (^{1}H), carbon (^{13}C), COSY, HSQC and HMBC NMR experiments were performed on a Bruker AVANCEIII 500 MHz NMR. Chemical Shifts are given in parts per million (ppm). All spectra were processed with Topspin 2.1 (Bruker Biospin) and further plotted with MestreNova, version 8.1 (Mestrelab Research, Santiago de Compostela, Spain). Variable Temperature (VT) NMR experiments were recorded on a Varian Oxford 400 MHz NMR.

All reactions were monitored using silica gel 60 F_{254} analytical TLC plates with UV detection (λ = 254 nm and 365 nm). Silica gel (60 Å, 40-63 μm) was used as stationary phase for column chromatography. The spectrophotometric measurements of compounds were carried out in DMF of spectrophotometric quality. UV-Vis absorption spectra were recorded using a Shimadzu UV-2401-PC spectrophotometer. Fluorescence measurements were performed on a single-photon-counting Horiba Fluorolog spectrofluorimeter. Melting points were recorded with Mel-Temp device and are uncorrected. Thermo-gravimetric analyses (TGA) were carried out on a TA Q50 analyzer under N_2 atmosphere with 10°C min^{-1} scan rate. Powder Xray diffraction patterns (PXRD) were recorded on a Bruker D8 ADVANCE diffractometer with graphite monochromatised Cu-Kα radiation (λ = 1.54056 Å). Dynamic Light Scattering Measurements were performed on a Wyatt DynaPro NanoStar using a 1 µmL quartz cuvette. Elemental analysis for C, H and N content was carried out in the Atlantic Microlab, 6180 Atlantic Blvd., Suite M, Norcross, GA 30071. High-resolution mass spectral (HRMS) analyses of ligands were performed by the University of Michigan mass spectrometry facility in ESI+ mode. LTQ Linear Ion-Trap and Fourier Transform Ion Cyclotron Resonance Mass Spectrometry (LTQ-FTMS) of cage **1** was performed by the University of Cincinnati R. Marshall Wilson Mass Spectrometry Facility on a ThermoFinnigan LTQ Linear Ion-Trap FTMS.

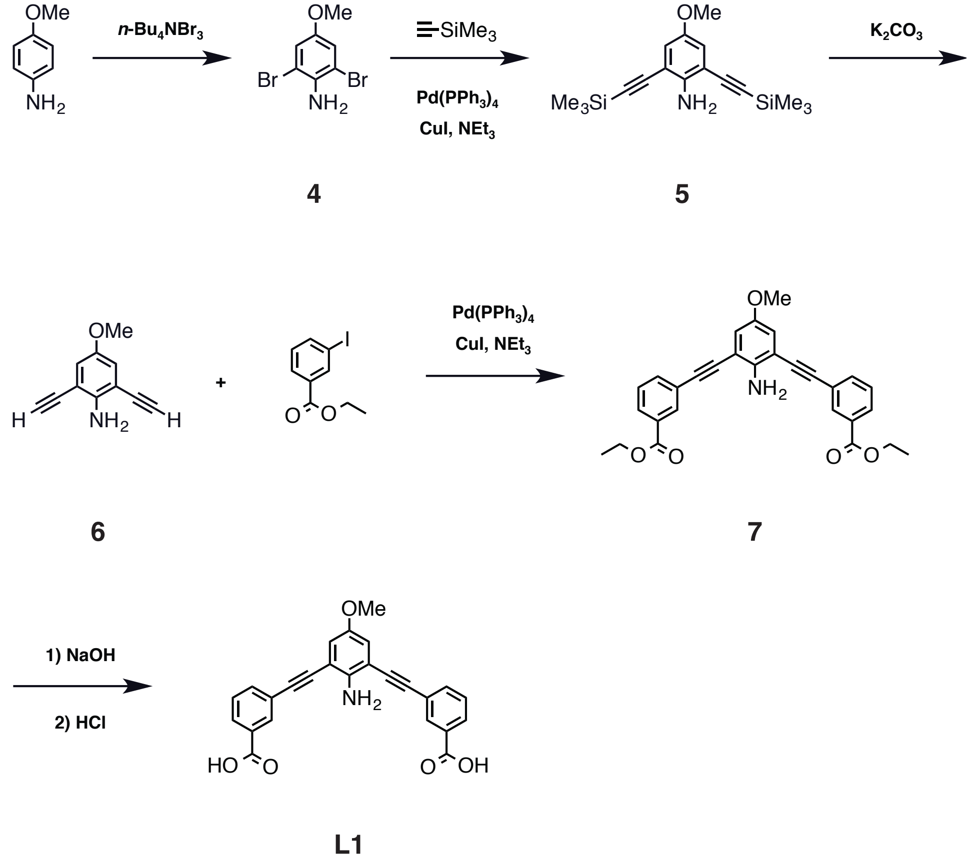
Single crystal diffraction data were collected at 100 K on either a Bruker APEX II CCD diffractometer or on a Bruker Prospector CCD diffractometer using monochromatic Mo Kα or Cu Kα radiation, respectively. Data for the compounds were collected, their unit cells determined, and the data integrated and corrected for absorption and other systematic errors using the Apex2 suite of programs.[1] The space groups were assigned and the structures were solved by direct methods using the SHELXTL suite of programs[2] and refined by full matrix least squares against F^2 with all reflections using Shelxl2013[3] using the graphical interface Shelxle.[4] H atoms attached to carbon and nitrogen atoms were positioned geometrically and constrained to ride on their parent atoms, with carbon hydrogen bond distances of 0.95 Å for alkene and aromatic C-H, 1.00, 0.99 and 0.98 Å for aliphatic C-H, CH_2 and CH_3 and 0.88 Å for N-H moieties, respectively. Methyl H atoms were allowed to rotate but not to tip to best fit the experimental electron density. U_{iso}(H) values were set to a multiple of U_{eq}(C/N) with 1.5 for CH_3 and 1.2 for C-H, CH_2 and N-H units, respectively. For disorder models, see individual structures in section 7. All images were generated with PyMOL.[5]

Complete crystallographic data, in CIF format, have been deposited with the Cambridge Crystallographic Data Centre. CCDC 1038504 – 1038507 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

2. Chemicals

All starting materials and solvents were purchased from VWR or Fisher Scientific and, unless otherwise specified, were used without further purification. Tetra-*n*-butylammonium tribromide (*n*-Bu_4NBr_3),[6] 1-decyloxy-4-nitrobenzene (**8**) and 4-decyloxyaniline (**9**) were synthetized according to a literature procedure.[7] Deuterated solvents were purchased from Cambridge Isotope Laboratories.

3. Syntheses



Scheme 1. Synthesis of Ligand **L1**

3.1 Synthetic procedures for Ligand L1

2,6-Dibromo-4-methoxyaniline (**4**)
Into a 200 ml round-bottom flask were placed *p*-anisidine (3.5 g, 28.4 mmol), CH_2Cl_2 (120 ml) and methanol (60 ml). *n*-Bu_4NBr_3 (27.4 g, 56.8 mmol) was added in one portion. The resulting purple mixture was stirred for 40 min at room temperature. Diethyl ether (140 ml) and a saturated aqueous solution of Na_2SO_3 (140 ml) were added. The organic layer was collected, washed with water (2x140ml) and brine (140 ml), dried over $MgSO_4$ and filtered through a Silica plug. The solvent was removed and the brown-red oil obtained was purified by column chromatography (SiO_2, hexanes:ethyl acetate = 9:1) to give 3.5 g of a white solid (Yield = 44%). All the spectral properties match literature values.[8]
mp = 79-80°C
^{1}H-NMR (300 MHz, $CDCl_3$): δ 7.01 (s, 2H), 4.19 (*b*s, 2H), 3.72 (s, 3H).
^{13}C-NMR (75 MHz, $CDCl_3$): δ 152.16, 136.32, 118.15, 109.24, 56.22.

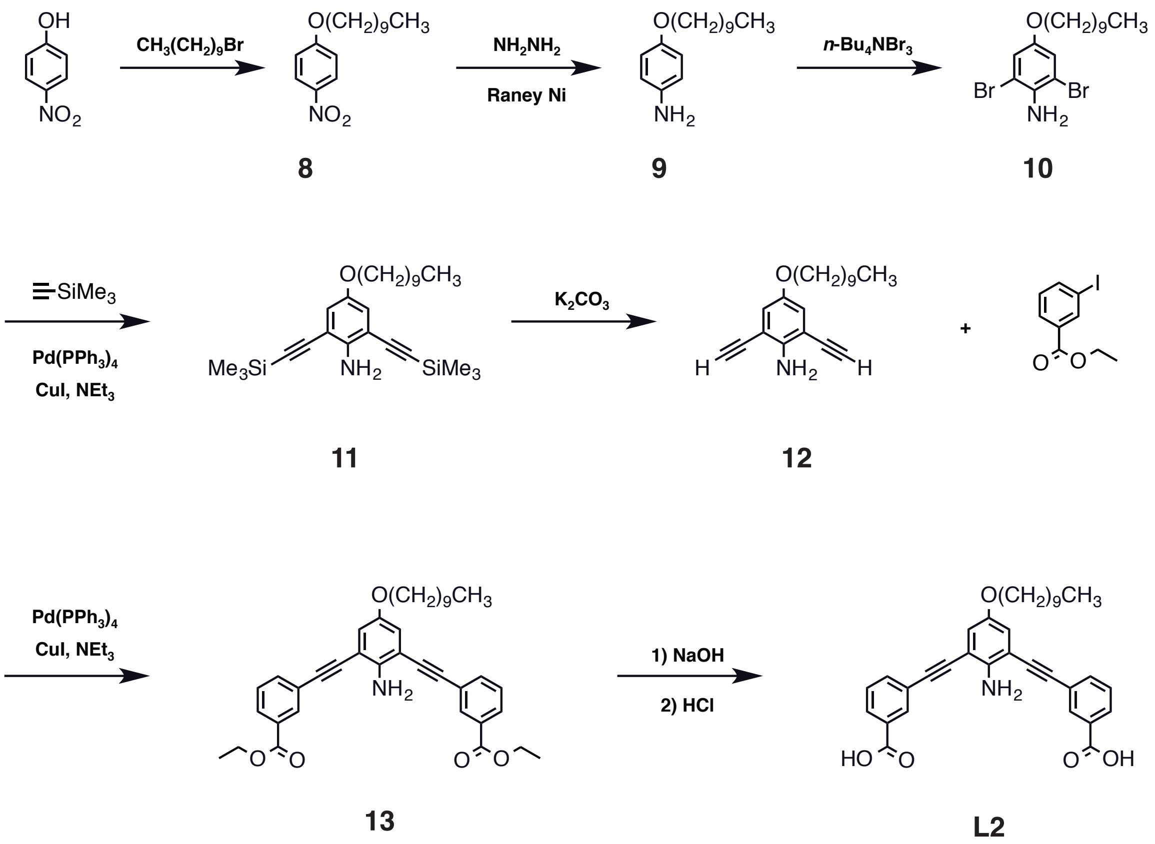
4-Methoxy-2,6-bis((trimethylsilyl)ethynyl)aniline **(5)**
A 50 ml round-bottom flask was flushed with vacuum and nitrogen three times. 2,6-dibromo-4-methoxyaniline (2.0 g, 7.1 mmol), CuI (0.068 g, 0.356 mmol) and $Pd(PPh_3)_4$ (0.411 g, 0.357 mmol) were added and flushed with vacuum and nitrogen three times. Trimethylsilyl-acetylene (5.07 ml, 35.59 mmol) and triethylamine (17 ml) were added through a septum. The reaction was sealed, stirred at room temperature for one hour, then heated at 80°C for 14 hours. A saturated aqueous solution of EDTA (20 ml) was added and the solution was extracted with CH_2Cl_2. The organic layer was collected, washed with water (5x20ml), dried over $MgSO_4$ and filtered. The solvent was removed and the crude product was

purified by column chromatography (SiO_2, hexanes then hexanes:ethyl acetate = 9:1) to give a bright yellow solid (2.1 g, Yield = 93%).
mp = 94-95°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 2H), 4.52 (*b*s, 2H), 3.71 (s, 3H), 0.26 (s, 18H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.67, 144.79, 118.73, 108.26, 101.27, 100.45, 56.10, 0.20.
HRMS (ESI+): *m/z* calc for $C_{17}H_{25}NOSi_2$ $[M+H]^+$ 316.1553, found 316.1555.

2,6-Diethynyl-4-methoxyaniline **(6)**
Into a 50 ml round-bottom flask, 4-methoxy-2,6-bis((trimethylsilyl)ethynyl)aniline (1.7 g, 5.4 mmol) was dissolved in CH_2Cl_2 (10 ml) and methanol (10 ml). K_2CO_3 (1.6 g, 11.6 mmol) was added and the resulting mixture was stirred for 3 hours at room temperature, then the solvent was removed. The solid obtained was dissolved in water (10 ml) and extracted with CH_2Cl_2 (3x20 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed to give a yellow solid (0.9 g, Yield = 97%).
^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 2H), 4.54 (*b*s, 2H), 3.72 (s, 3H), 3.40 (s, 2H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.69, 145.14, 119.45, 107.29, 83.04, 80.11, 56.09.

Diethyl 3,3'-((2-amino-5-methoxy-1,3-phenylene)bis(ethyne-2,1-diyl)dibenzoate **(7)**
A 50 ml round-bottom flask was flushed with vacuum and nitrogen three times, CuI (0.047 g, 0.247 mmol) and $Pd(PPh_3)_4$ (0.286 mg, 0.247 mmol) were added and flushed with vacuum and nitrogen three times. 2,6-diethynyl-4-methoxyaniline (0.847 g, 4.947 mmol) was dissolved in triethylamine (15 ml) and the solution was added through a septum. Ethyl-3-iodobenzoate (2.1 ml, 12.4 mmol) was added and the flask was equipped with a condenser and heated at 88°C under N_2 for 12 hours. A saturated aqueous solution of EDTA (20 ml) was added and the solution was extracted with CH_2Cl_2 (3x20 ml). The organic layer was collected, washed with water (5x20 ml), dried over $MgSO_4$ and filtered. The solvent was removed and the crude product was purified by column chromatography (SiO_2, hexanes: ethyl acetate = 95:5 then hexanes: ethyl acetate = 4:1) to give 1.3 g of a yellow solid (Yield = 56%).
mp = 86-87°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.21 (t, *J* = 1.5 Hz, 2H), 8.03 (dt, *J* = 7.9, 1.3 Hz, 2H), 7.71 (dt, *J* = 7.7, 1.4 Hz, 2H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.00 (s, 2H), 4.64 (*b*s, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 3.78 (s, 3H), 1.42 (t, *J* = 7.1 Hz, 6H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ 166.01, 151.12, 143.93, 135.65, 132.71, 131.03, 129.57, 128.72, 123.45, 118.83, 108.27, 94.21, 86.40, 61.45, 56.15, 14.48.
HRMS (ESI+): *m/z* calc for $C_{29}H_{25}NO_5$ $[M+H]^+$ 468.1811, found 468.1811.

3,3'-((2-Amino-5-methoxy-1,3-phenylene)bis(ethyne-2,1-diyl)dibenzoic acid **(L1)**
Into a 10 ml round-bottom flask, 3,3'-((2-amino-5-methoxy-1,3-phenylene)bis (ethyne-2,1-diyl)dibenzoate (0.370 g, 0.791 mmol) was dissolved in THF (2 ml) and methanol (2 ml). NaOH 3 M solution (2.2 ml) was added, the flask was equipped with a condenser and heated at 50°C for 12 hours. The solvent was removed, the solid obtained was dissolved in water (5 ml) and HCl 4 M was added. The yellow precipitate was filtered under vacuum (0.321 g, Yield = 99%).
mp = 204-205°C
^{1}H-NMR (500 MHz, DMSO-*d*$_6$): δ 8.19 (t, *J* = 1.5 Hz, 2H), 7.95 (dt, *J* = 7.8, 1.4 Hz, 2H), 7.88 (dt, *J* = 7.7, 1.3 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.04 (s, 2H), 3.72 (s, 3H).
^{13}C-NMR (126 MHz, DMSO-*d*$_6$): δ 166.66, 149.68, 144.73, 135.48, 132.14, 131.26, 129.26, 129.08, 122.97, 118.93, 106.86, 93.62, 86.93, 55.71.
HRMS (ESI-): *m/z* calc for $C_{25}H_{17}NO_5$ $[M-H]^-$ 410.1028, found 410.1029.



Scheme 2. Synthesis of Ligand **L2**

3.2 Synthetic procedures for ligand L2

2,6-Dibromo-4-decyloxyaniline **(10)**
Into a 100 ml round-bottom flask were placed 4-decyloxyaniline (2.3 g, 9.2 mmol), CH_2Cl_2 (45 ml) and methanol (22.5 ml). n-Bu_4NBr_3 (8.9 g, 18.5 mmol) was added in one portion. The resulting purple mixture was stirred for 40 min at room temperature. A saturated aqueous solution of Na_2SO_3 (40 ml) was added and the solution was extracted with diethyl ether (3x40 ml). The organic layer was collected, washed with water (2x40 ml) and brine (40 ml), dried over $MgSO_4$ and filtered through a short silica plug. The solvent was removed and the brown-red oil obtained was purified through a silica plug (hexanes:ethyl acetate = 98:2) to give 1.5 g of a white solid (Yield = 40%).
mp = 42-43°C
^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.01 (s, 2H), 4.18 (*b*s, 2H), 3.84 (t, *J* = 6.5 Hz, 2H), 1.76 – 1.67 (m, 2H), 1.46 – 1.21 (m, 14H), 0.88 (t, 3H).
^{13}C-NMR (126 MHz, $CDCl_3$): δ 151.74, 136.19, 118.86, 109.24, 69.28, 32.05, 29.71, 29.69, 29.49, 29.47, 29.33, 26.09, 22.84, 14.28.
HRMS (ESI+): *m/z* calc for $C_{16}H_{25}Br_2NO$ $[M+H]^+$ 406.0381, found 406.0378.

4-Decyloxy-2,6-bis((trimethylsilyl)ethynyl)aniline **(11)**
A 10 ml round-bottom flask was flushed with vacuum and nitrogen three times. 2,6-dibromo-4-decyloxyaniline (0.5 g, 1.2 mmol), CuI (0.023 g, 0.123 mmol) and $Pd(PPh_3)_4$ (0.142 g, 0.123 mmol) were added and flushed with vacuum and nitrogen three times. Trimethylsilyl-acetylene (0.88 ml, 6.14 mmol) and triethylamine (3 ml) were added through a septum. The reaction was sealed, stirred at room temperature for one hour, then heated at 80°C for 24 hours. A saturated aqueous solution of EDTA (5 ml) was added and the solution was extracted with CH_2Cl_2 (3x10 ml). The organic layer was collected, washed with water (5x10ml), dried over $MgSO_4$ and filtered. The solvent was removed and the crude

product was purified through a silica plug (hexanes then hexanes:ethyl acetate = 9:1) to give a yellow solid (0.4 g, Yield = 75%).

mp = 59-60°C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.86 (s, 2H), 4.51 (*b*s, 2H), 3.83 (t, *J* = 6.6 Hz, 2H), 1.75 – 1.65 (m, 2H), 1.40 (p, *J* = 7.0 Hz, 2H), 1.35 – 1.23 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.25 (s, 18H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.04, 144.56, 119.57, 108.07, 101.20, 100.14, 69.00, 31.90, 29.58, 29.55, 29.36, 29.32, 29.28, 25.97, 22.69, 14.13, 0.06.

HRMS (ESI+): *m/z* calc for $C_{26}H_{43}NOSi_2$ $[M+H]^+$ 442.2961, found 442.2965.

4-Decyloxy-2,6-diethynylaniline **(12)**

Into a 10 ml round-bottom flask, 4-decyloxy-2,6-bis((trimethylsilyl)ethynyl)aniline (0.563 g, 1.274 mmol) was dissolved in CH_2Cl_2 (2.5 ml) and methanol (2.5 ml). K_2CO_3 (0.388 g, 2.807 mmol) was added and the resulting mixture was stirred for 3 hours at room temperature, then the solvent was removed. The solid obtained was dissolved in water (5 ml) and extracted with CH_2Cl_2 (3x10 ml). The organic layer was dried over $MgSO_4$ and the solvent was removed to give a yellow solid (0.339 g, Yield = 89%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 6.93 (s, 2H), 4.53 (*b*s, 2H), 3.85 (t, *J* = 6.6 Hz, 2H), 3.39 (s, 2H), 1.76 – 1.67 (m, 2H), 1.40 (q, *J* = 7.1 Hz, 2H), 1.35 – 1.23 (m, 12H), 0.88 (t, *J* = 6.8 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ 150.08, 144.92, 120.23, 107.12, 82.78, 80.04, 69.01, 31.91, 29.58, 29.56, 29.38, 29.33, 29.27, 25.99, 22.70, 14.14.

Diethyl 3,3'-((2-amino-5-decyloxy-1,3-phenylene)bis(ethyne-2,1-diyl) dibenzoate **(13)**

A 10 ml round-bottom flask was flushed with vacuum and nitrogen three times, CuI (0.011 mg, 0.056 mmol) and $Pd(PPh_3)_4$ (0.065 g, 0.056 mmol) were added and flushed with vacuum and nitrogen three times. 2,6-diethynyl-4-decyloxyaniline (0.336 mg, 1.131 mmol) was dissolved in triethylamine (3.5 ml) and the solution was added through a septum. Ethyl-3-iodobenzoate (0.48 ml, 2.82 mmol) was added and the flask was equipped with a condenser and heated at 88°C under N_2 for 16 hours. A saturated aqueous solution of EDTA (5 ml) was added and the solution was extracted with CH_2Cl_2 (3x10 ml). The organic layer was collected, washed with water (5x10 ml), dried over $MgSO_4$ and filtered. The solvent was removed and the crude product was purified by column chromatography (SiO_2, hexanes: ethyl acetate = 9:1) to give 0.253 g of a yellow oil (Yield = 38%).

^{1}H-NMR (500 MHz, $CDCl_3$): δ 8.21, (t, *J* = 1.5 Hz, 2H), 8.02 (dt, *J* = 7.9, 1.3 Hz, 2H), 7.71 (dt, *J* = 7.7, 1.3 Hz, 2H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.00 (s, 2H), 4.63 (*b*s, 2H), 4.41 (q, *J* = 7.1 Hz, 4H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.45-1.43 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 6H), 1.39-1.20 (m, 14H), 0.88 (t, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ 166.03, 150.65, 143.85, 135.64, 132.70, 131.02, 129.53, 128.71, 123.50, 119.77, 108.23, 94.11, 86.48, 69.20, 61.44, 32.05, 29.86, 29.71, 29.54, 29.48, 29.46, 26.16, 22.84, 14.48, 14.28.

HRMS (ESI+): *m/z* calc for $C_{38}H_{43}NO_5$ $[M+H]^+$ 594.3219, found 594.3219.

3,3'-((2-Amino-5-decyloxy-1,3-phenylene)bis(ethyne-2,1-diyl)dibenzoic acid **(L2)**

Into a 10 ml round-bottom flask, 3,3'-((2-amino-5-decyloxy-1,3-phenylene)bis (ethyne-2,1-diyl)dibenzoate (0.150 mg, 0.252 mmol) was dissolved in THF (0.6 ml) and methanol (0.6 ml). NaOH 3 M solution (0.7 ml) was added, the flask was equipped with a condenser and heated at 50°C for 12 hours. The solvent was removed, the solid obtained was dissolved in water (5 ml) and HCl 4 M was added. The yellow precipitate was filtered under vacuum (0.115 g, Yield = 85%).

mp = 173-174°C

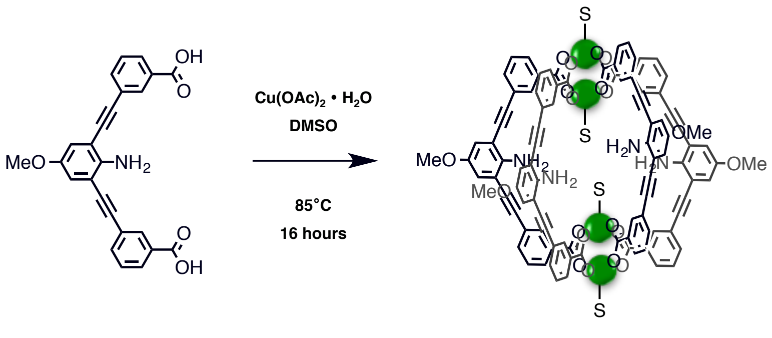
^{1}H-NMR (500 MHz, DMSO-d_6): δ 13.21 (*b*s, 2H), 8.19 (t, *J* = 1.8 Hz, 2H), 7.95 (dt, *J* = 7.8, 1.5 Hz, 2H), 7.88 (dt, *J* = 7.6, 1.4 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.03 (s, 2H), 5.48 (*b*s, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 1.68 – 1.64 (m, 2H), 1.41 – 1.26 (m, 14H), 0.85 (t, 3H).

^{13}C-NMR (126 MHz, DMSO-d_6): δ 166.72, 149.00, 144.85, 135.51, 132.16, 131.29, 129.28, 129.12, 123.05, 119.82, 106.80, 93.60, 87.00, 68.32, 31.37, 29.07, 29.01, 28.77, 25.50, 22.17, 14.03.

HRMS (ESI-): *m/z* calc for $C_{34}H_{35}NO_5$ $[M-H]^-$ 536.2437, found 536.2419.

4. Syntheses of metal-organic materials

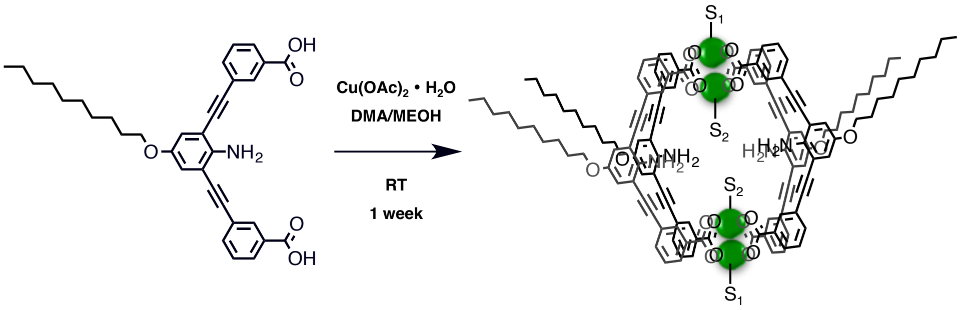
4.1 Syntheses of metal-organic cage 1



S = DMSO

Ligand **L1** (30 mg, 73 μmol) was dissolved in DMSO (7.5 ml) and $Cu(OAc)_2$•H_2O (14.6 mg, 73 μmol) was added. The resulting green solution was divided in 2 ml vials and placed in the oven at 85°C. Green crystals (24 mg) formed after 16 hours together with a brown colloidal suspension, which was discarded by decantation. Green single crystals were characterized by SXRD. Elemental analysis of dried material (Found): C, 58.96; H, 3.70; N, 2.80; (Calc.) for [$(C_{100}H_{60}Cu_4N_4O_{20})$ •4(DMSO)]: C, 58.85; H, 3.84; N, 2.54.

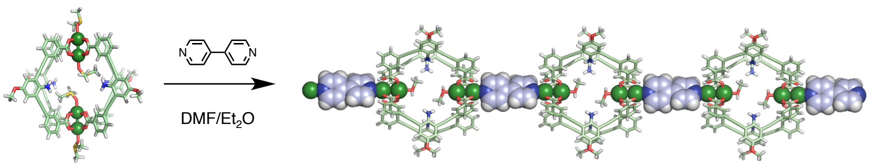
4.2 Syntheses of metal-organic cage 2



S_1 = MeOH S_2 = H_2O

In a small test tube, Ligand **L2** (5.0 mg, 8.3 μmol) was dissolved in DMA (1 ml) and $Cu(OAc)_2$•H_2O (1.7 mg, 8.3 μmol) was added. The test tube was capped and a steel needle placed in the cap, then put in a 20 ml scintillation vial containing MeOH. Green crystals grew on the needle and test tube surfaces after one week and crystals from the needle surface were characterized by SXRD.

4.3 Syntheses of 1D metal-organic polymer 3



Crystals of cage **1** (4 mg) were dissolved in DMF (2 ml). A DMF solution (2 ml) of 4,4’-bipyridine (5.6 mg) was added. The resulting green solution was divided in small test tubes and slow diffusion of Et_2O resulted in the formation of green needle-shaped crystals after 3 days.

5. NMR spectra

5.1 Ligand L1

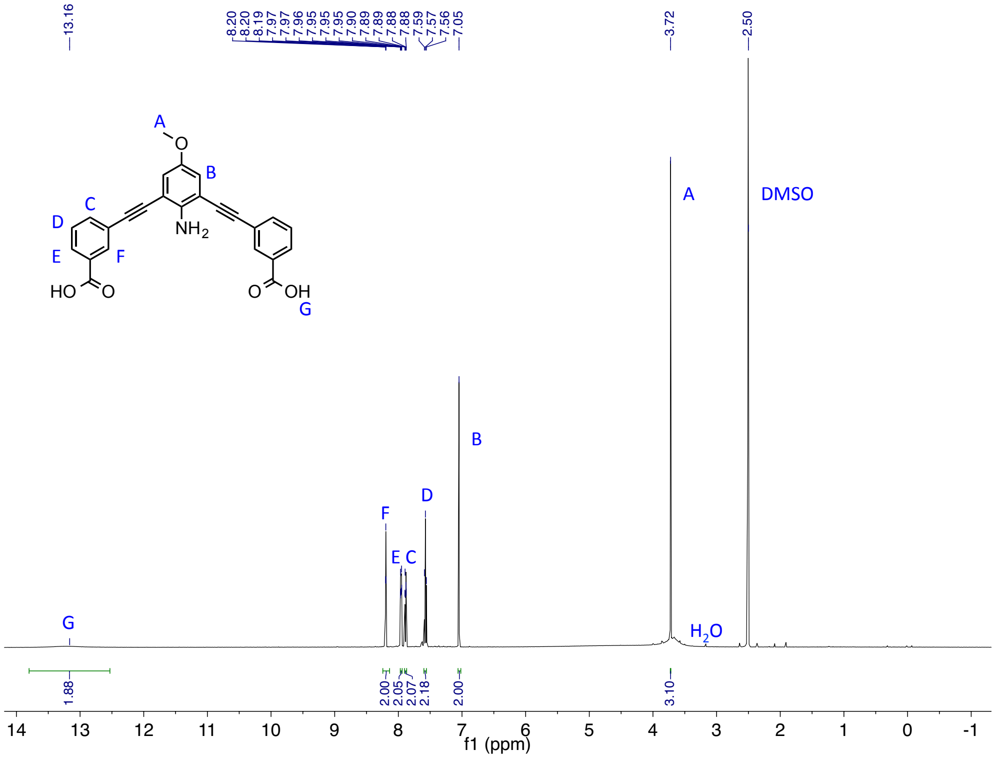


Figure S1: 500 MHz ^{1}H-NMR (DMSO-d_6) of ligand **L1**.

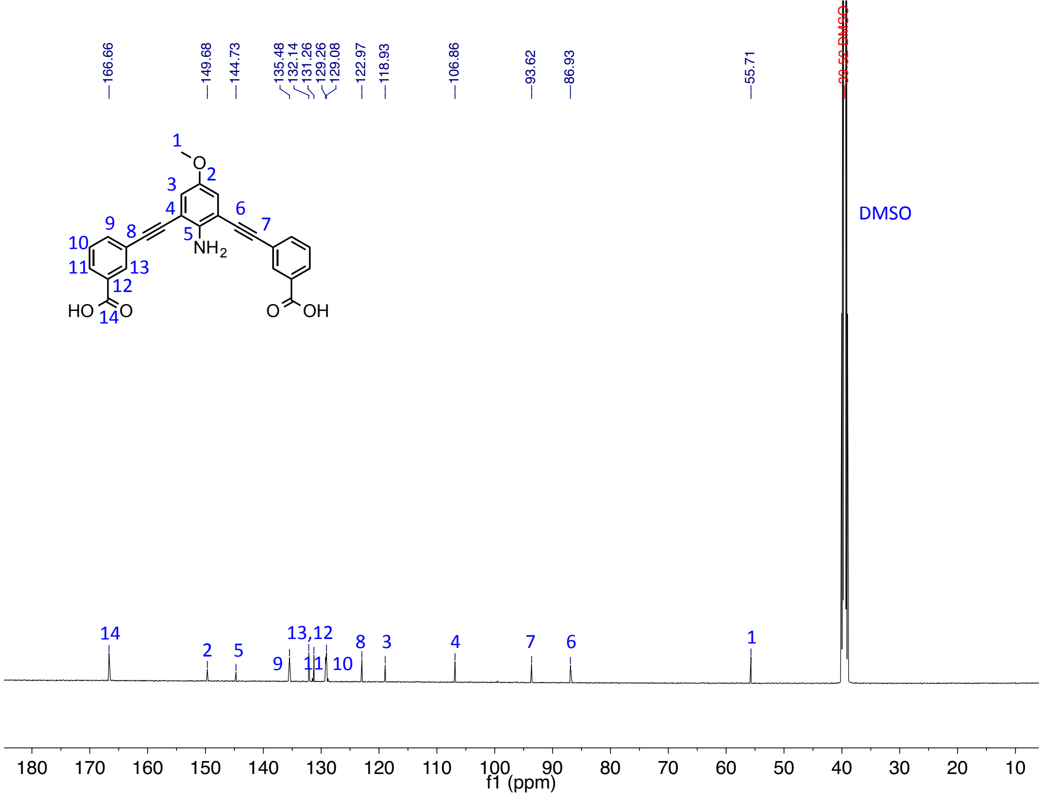


Figure S2: 126 MHz ^{13}C-NMR (DMSO-d_6) of ligand **L1**.

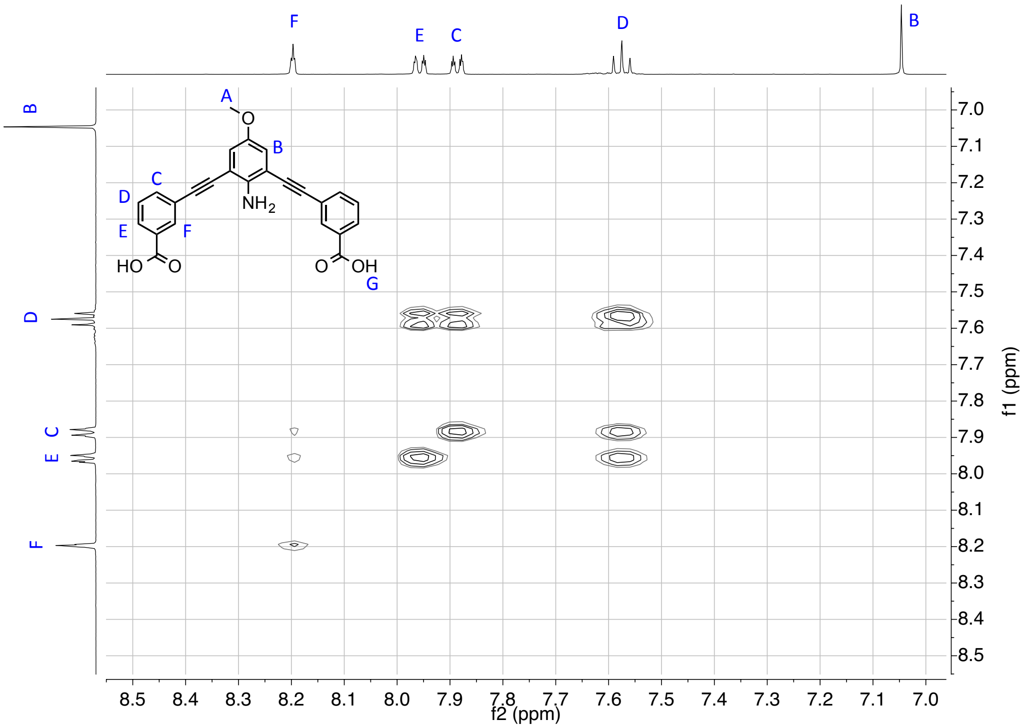


Figure S3: COSY NMR (DMSO-d_6) of ligand **L1** (aromatic region).

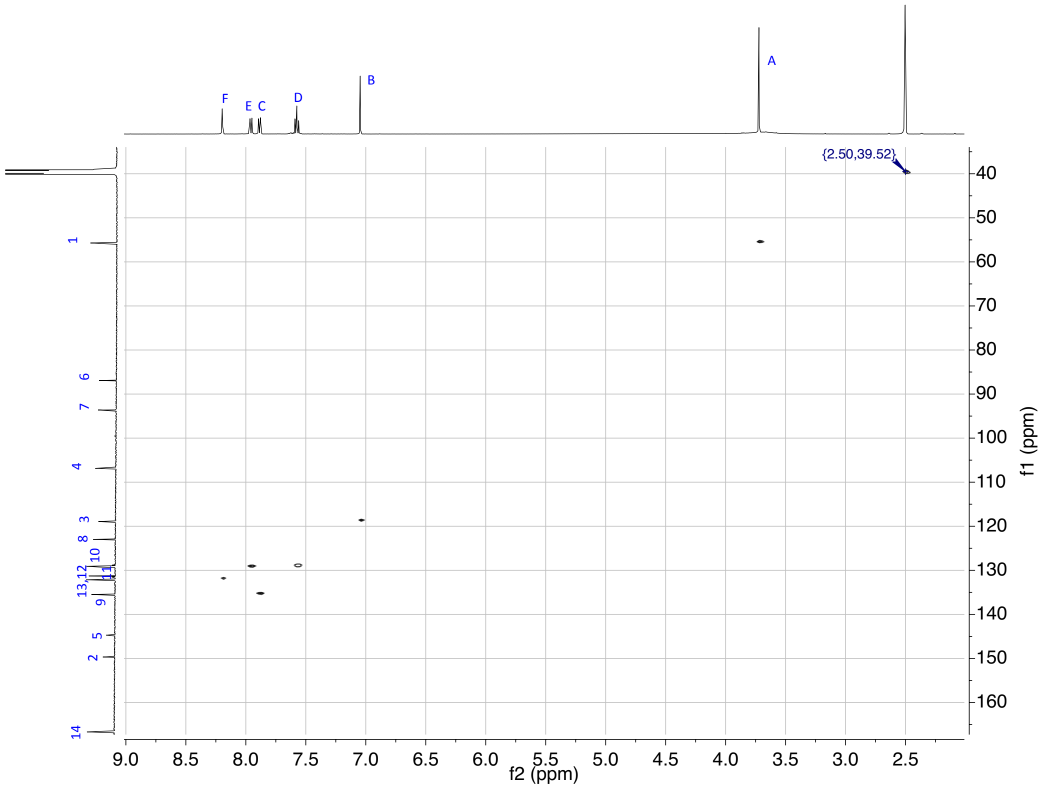


Figure S4: HSQC NMR (DMSO-d_6) of ligand **L1**.

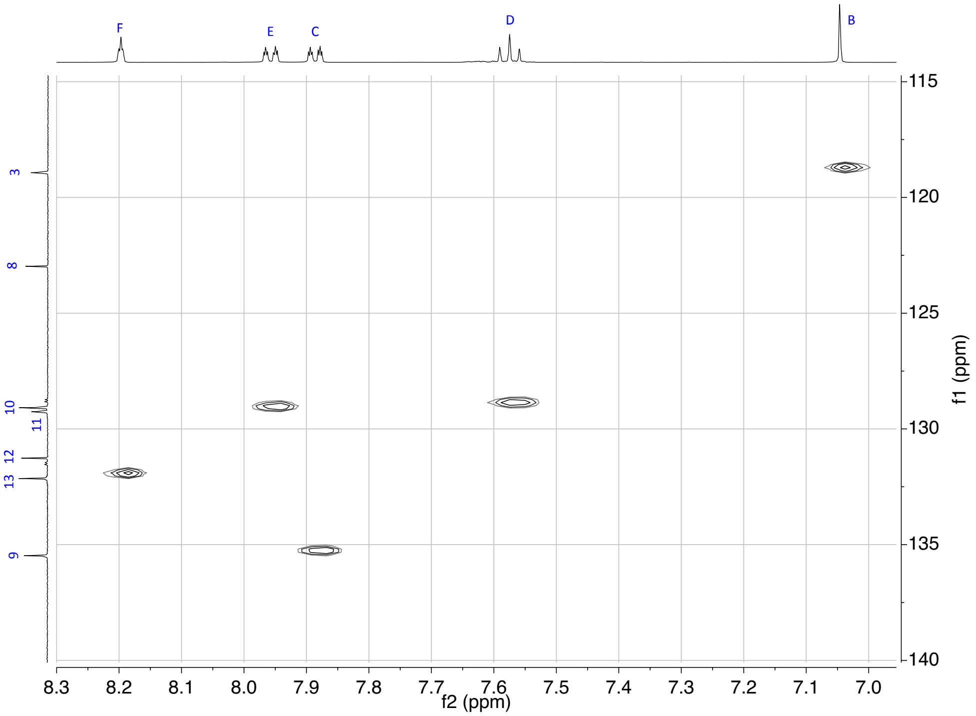


Figure S5: HSQC NMR (DMSO-d_6) of ligand **L1** (aromatic region).

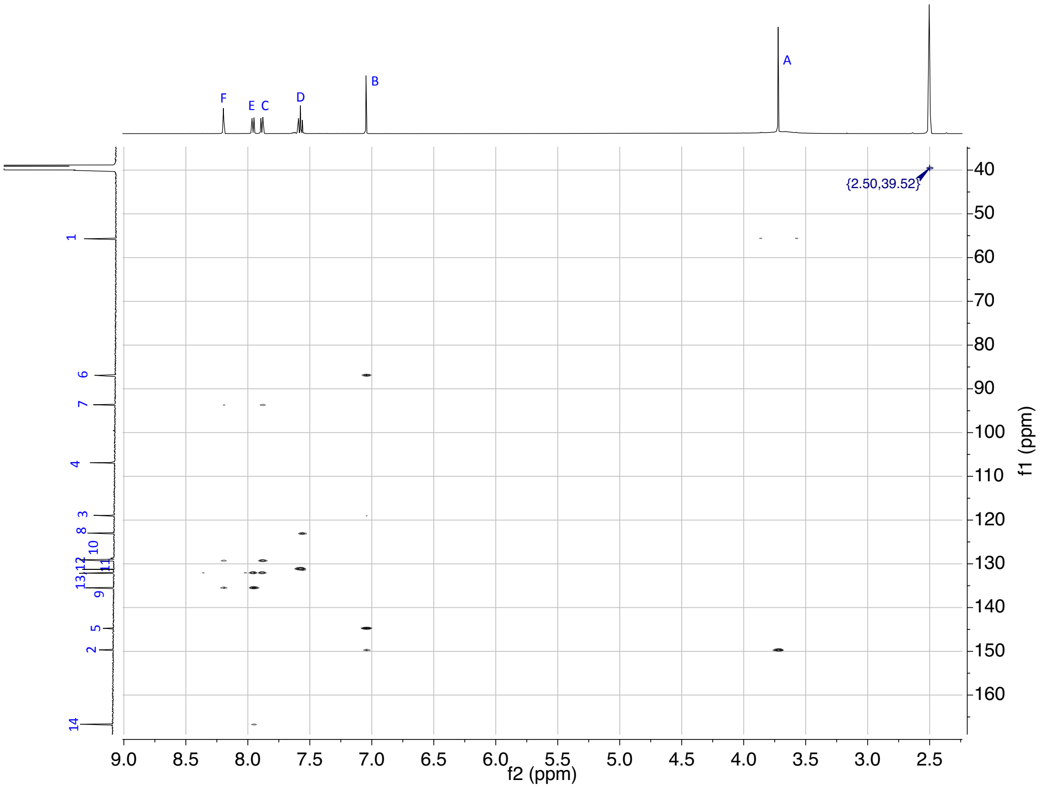


Figure S6: HMBC NMR (DMSO-d_6) of ligand **L1**.

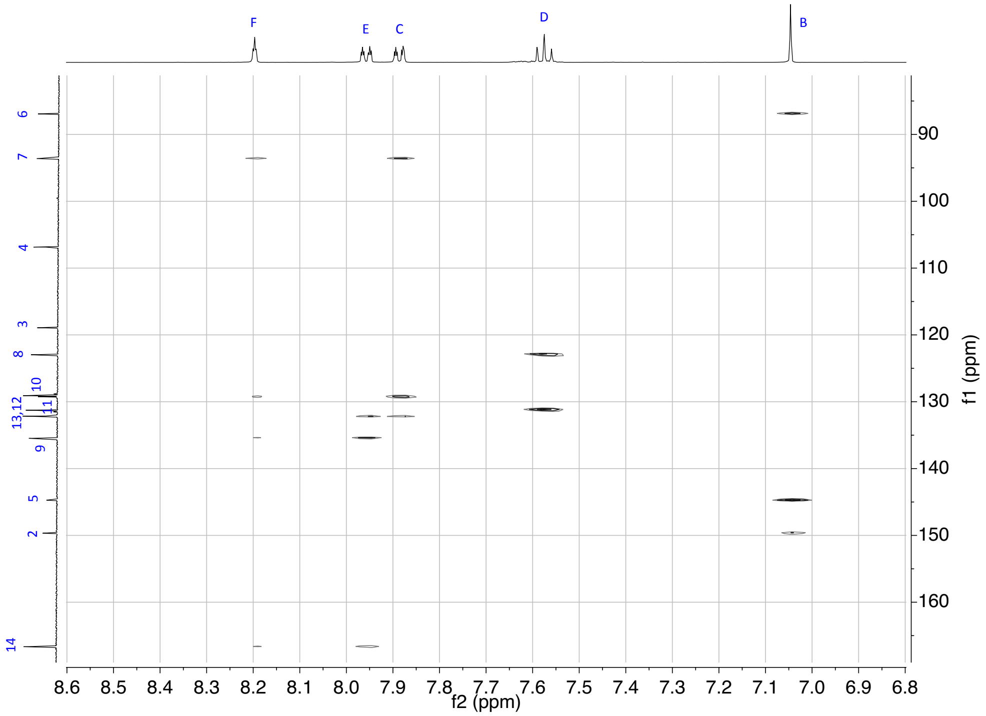


Figure S7: HMBC NMR (DMSO-d_6) of ligand **L1** (aromatic region).

5.2 Ligand L2

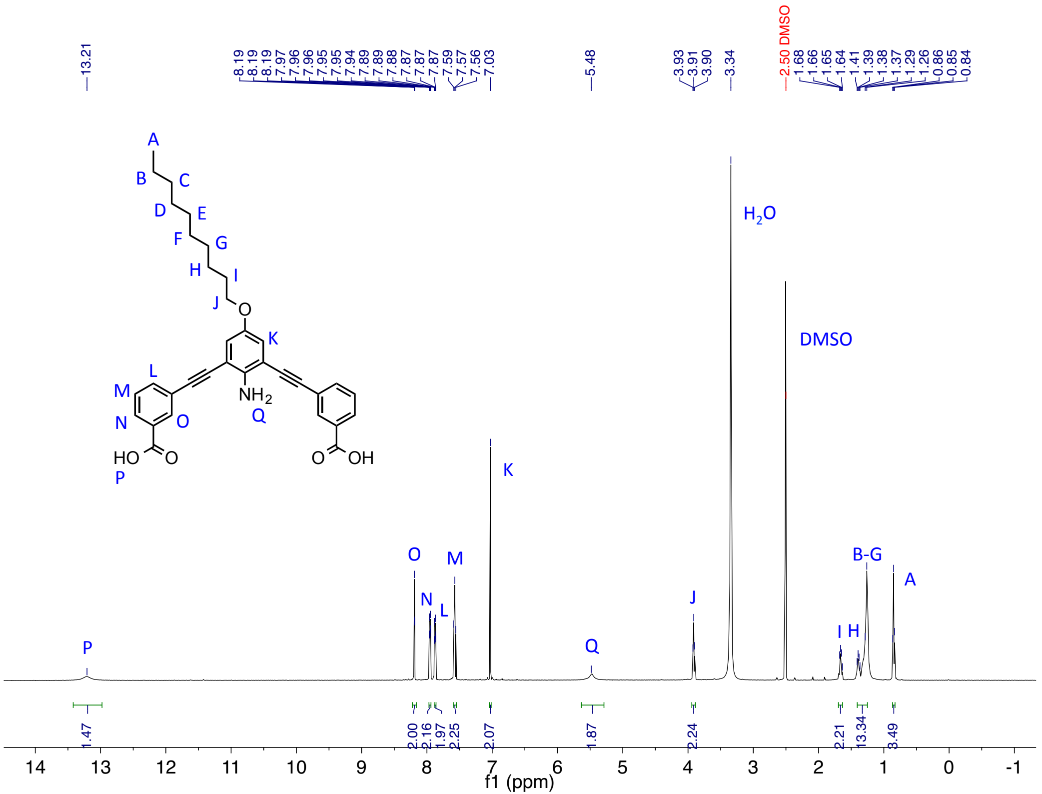


Figure S8: 500 MHz ^{1}H-NMR (DMSO-d_6) of ligand **L2**.

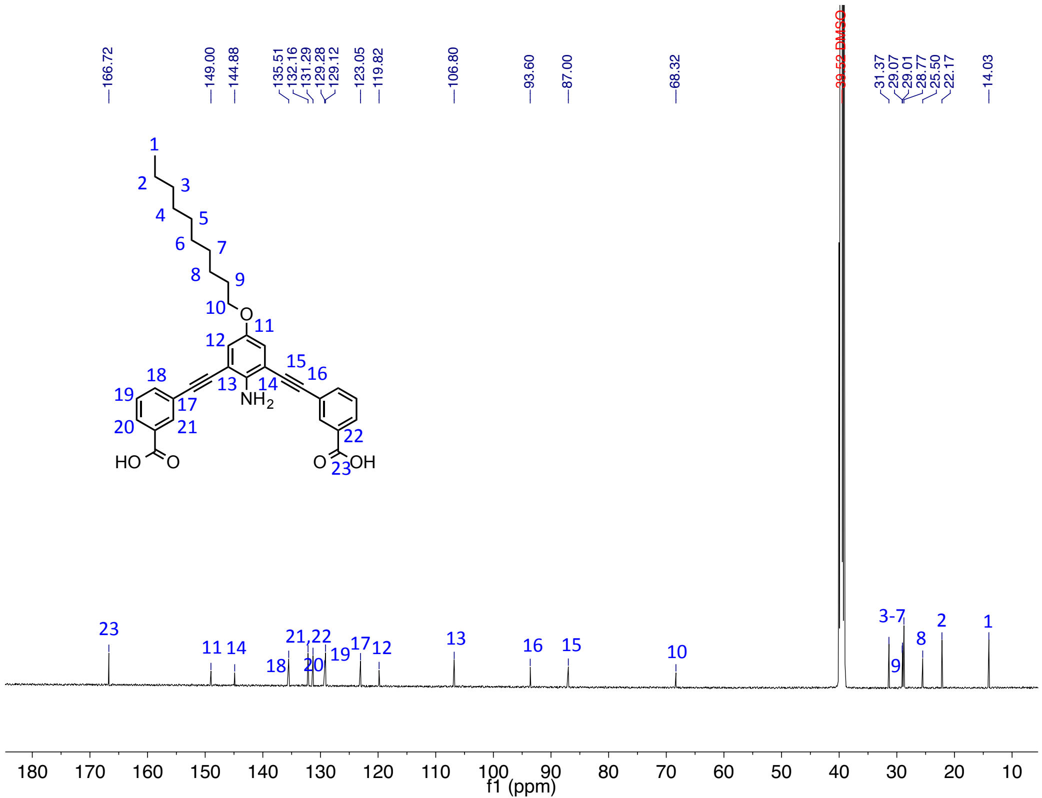


Figure S9: 126 MHz ^{13}C-NMR (DMSO-d_6) of ligand **L2**.

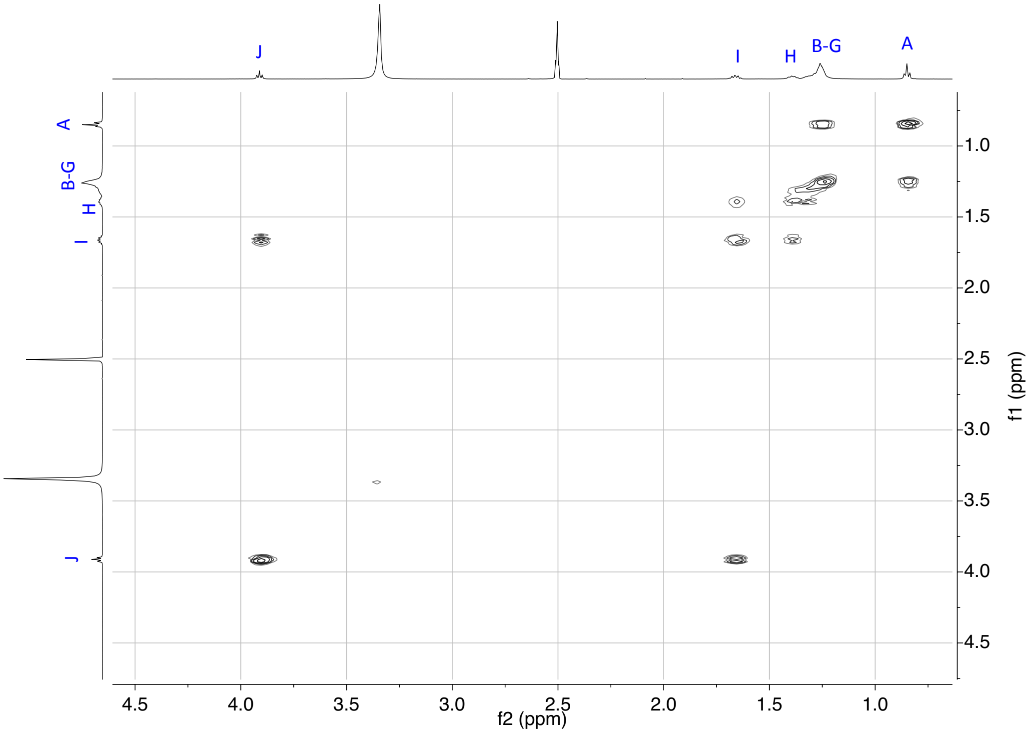


Figure S10: COSY NMR (DMSO-d_6) of ligand **L2** (aliphatic region).

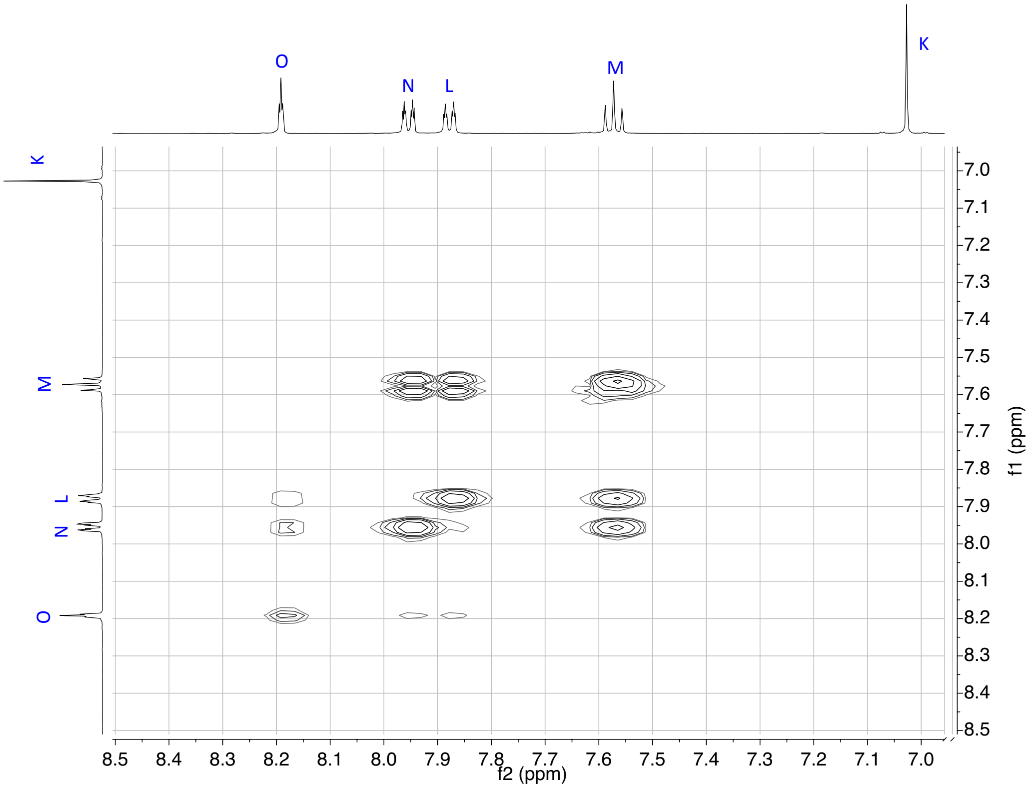


Figure S11: COSY NMR (DMSO-d_6) of ligand **L2** (aromatic region).

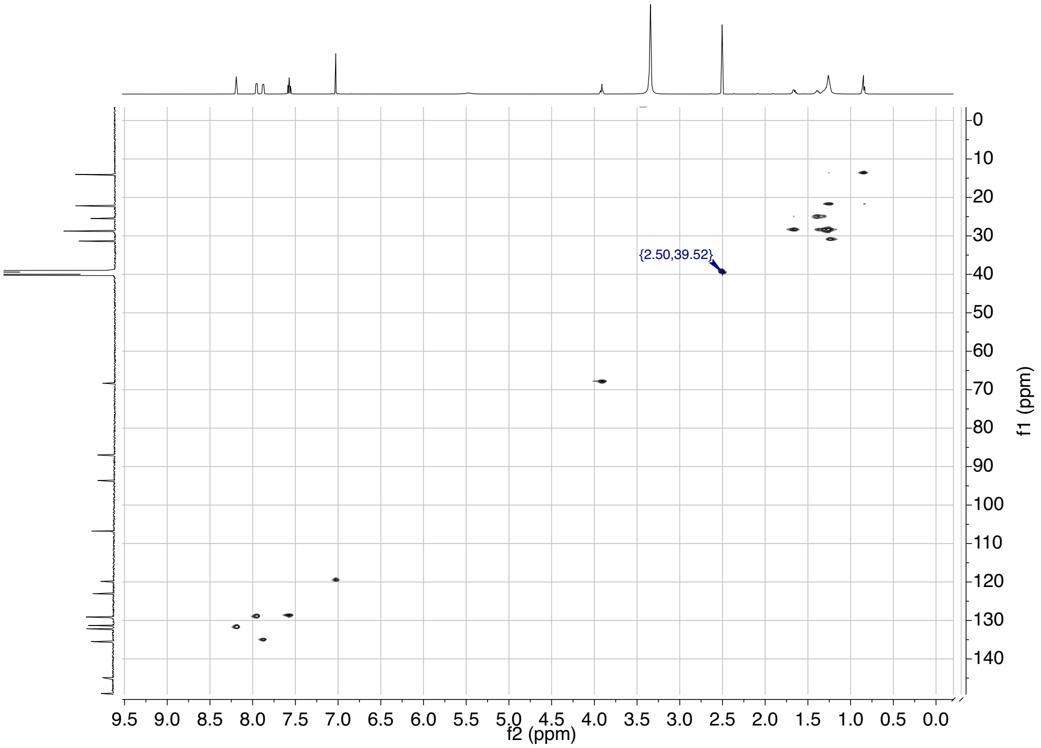


Figure S12: HSQC NMR (DMSO-d_6) of ligand **L2**.

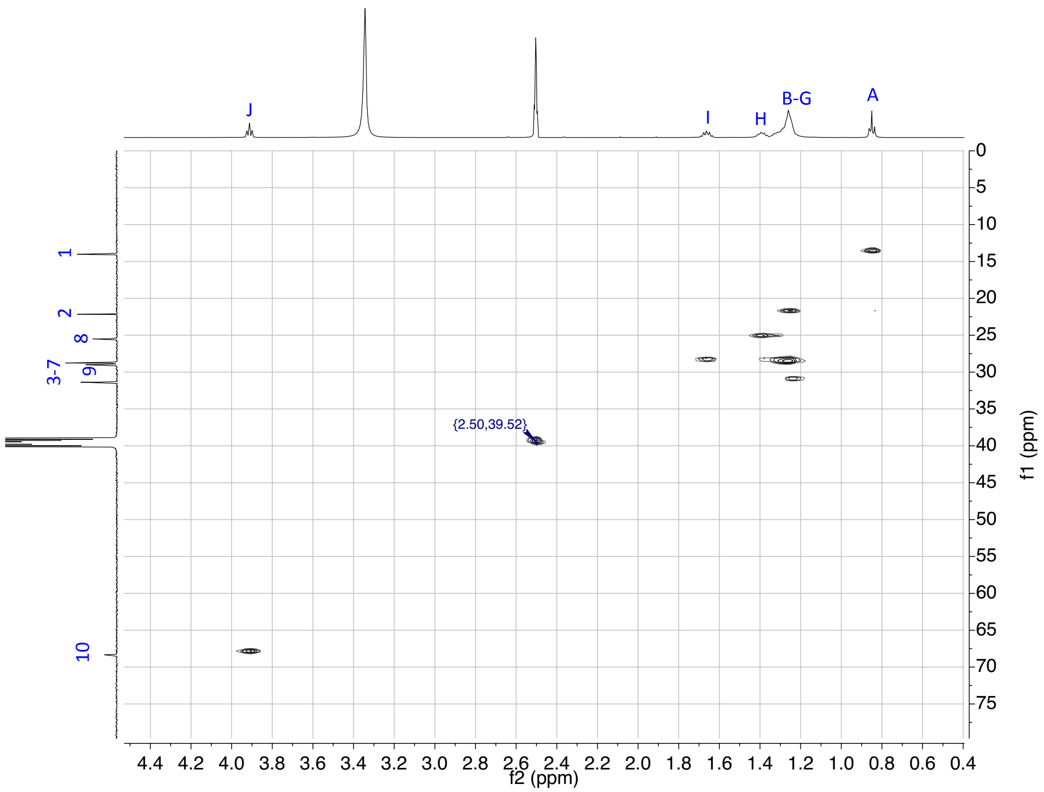


Figure S13: HSQC NMR (DMSO-d_6) of ligand **L2** (aliphatic region).

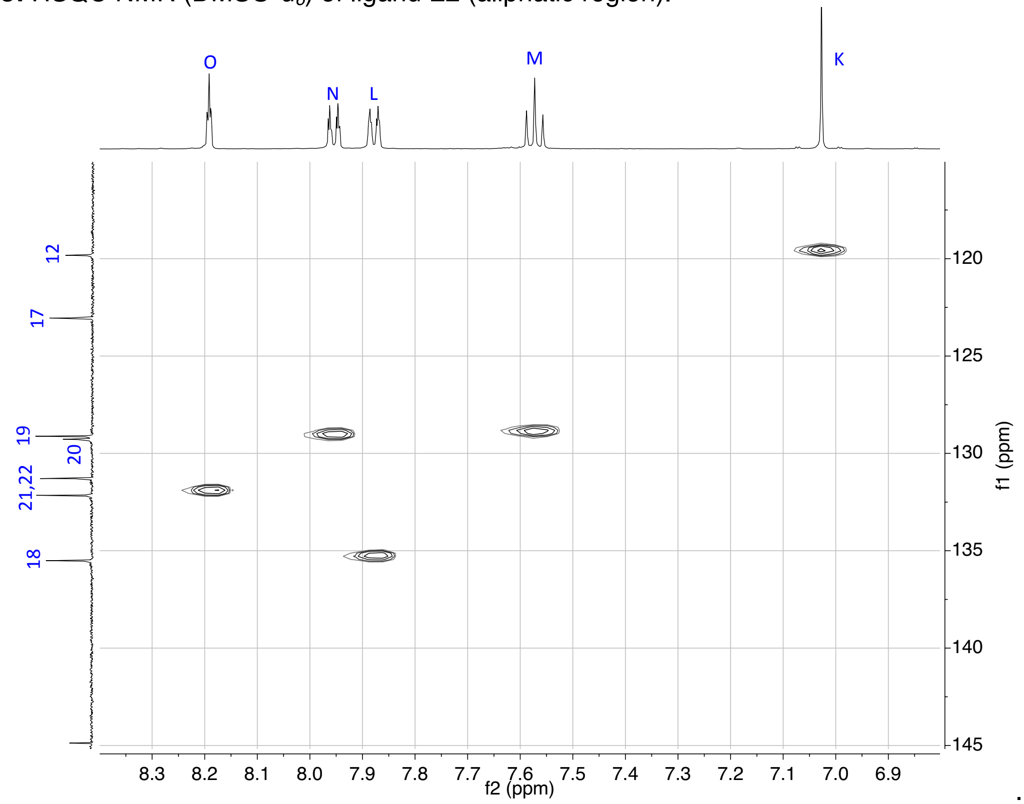


Figure S14: HSQC NMR (DMSO-d_6) of ligand **L2** (aromatic region).

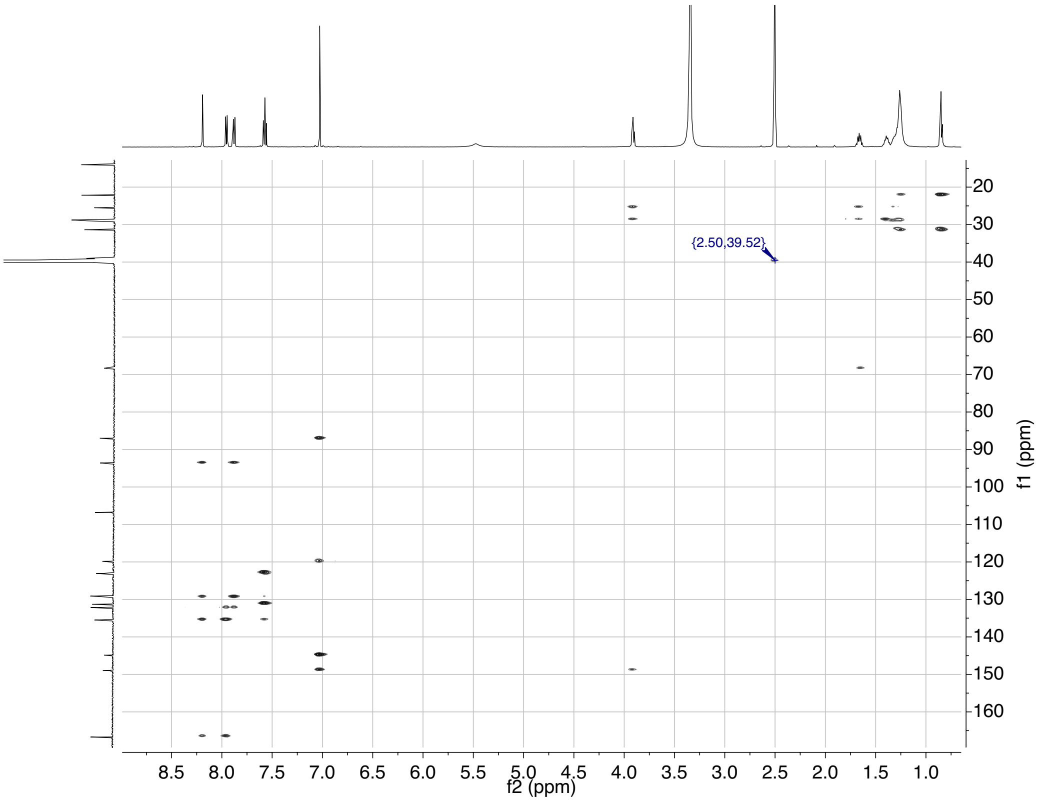


Figure S15: HMBC NMR (DMSO-d_6) of ligand **L2** .

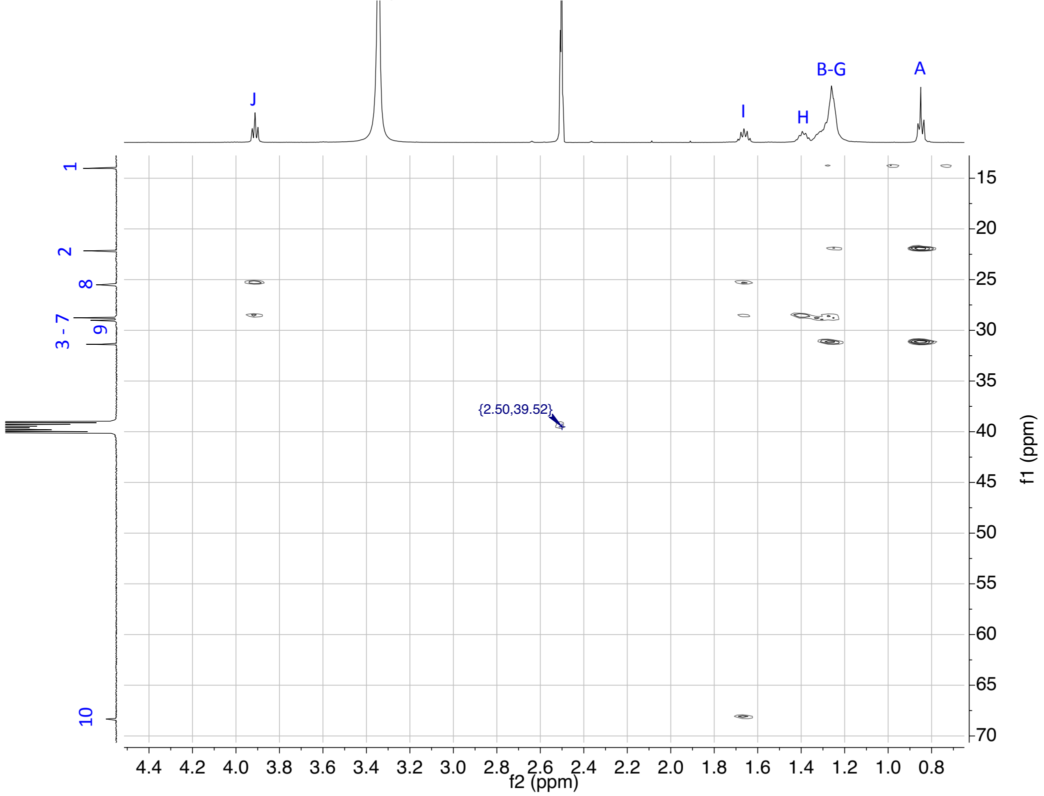


Figure S16: HMBC NMR (DMSO-d_6) of ligand **L2** (aliphatic region).

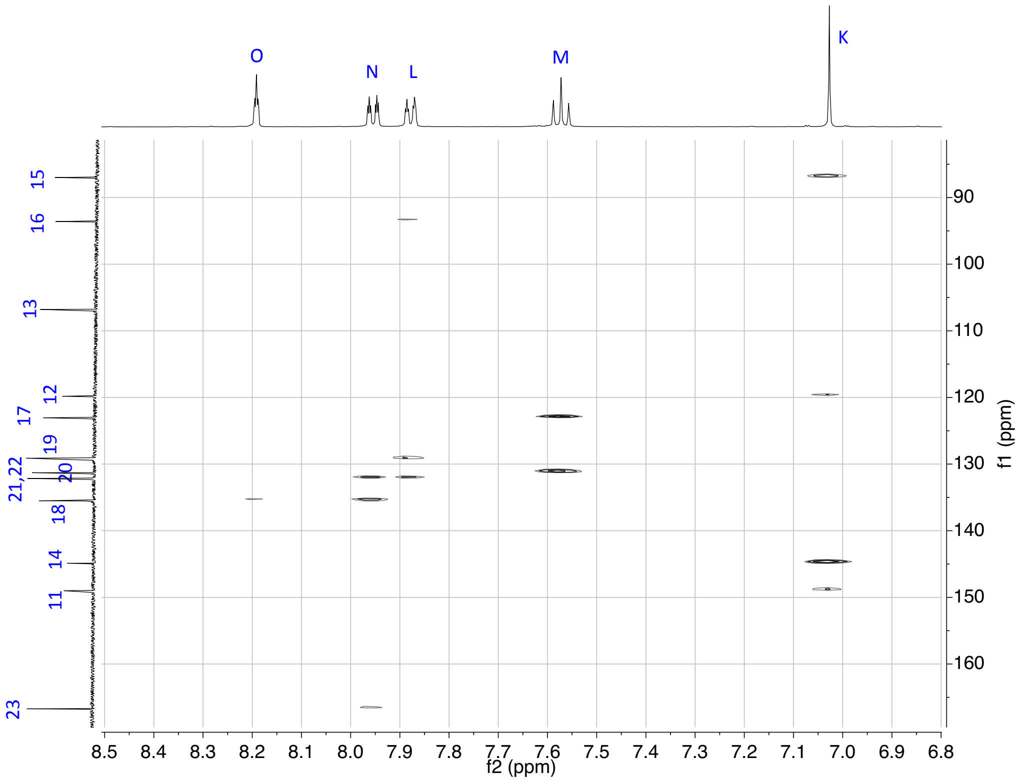


Figure S17: HMBC NMR (DMSO-d_6) of ligand **L2** (aromatic region).

5.3 NMR titration of Ligand L1 with $Cu(OAc)_2 \bullet H_2O$

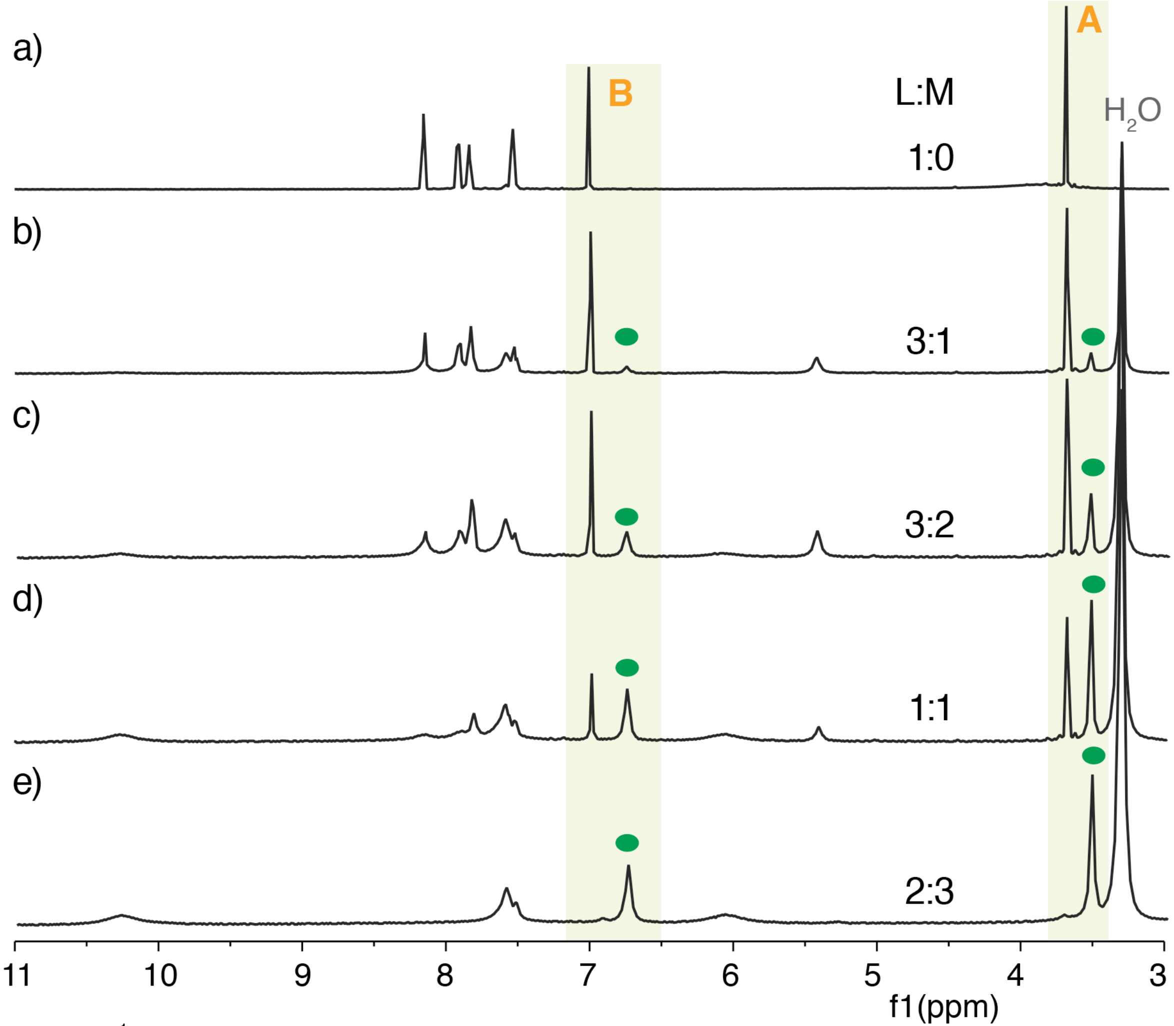


Figure S18: ^{1}H-NMR Titration experiment: a) ligand **L1**, b) **L1** + 0.33 eqv. of $Cu(OAc)_2 \bullet H_2O$, c) **L1** + 0.66 eqv. of $Cu(OAc)_2 \bullet H_2O$, d) **L1** + 0.99 eqv. of $Cu(OAc)_2 \bullet H_2O$, e) **L1** + 1.33 eqv. of $Cu(OAc)_2 \bullet H_2O$ in DMSO-d_6 at RT. Mixing time ~ 5 m.

5.4 VT NMR of cage 1

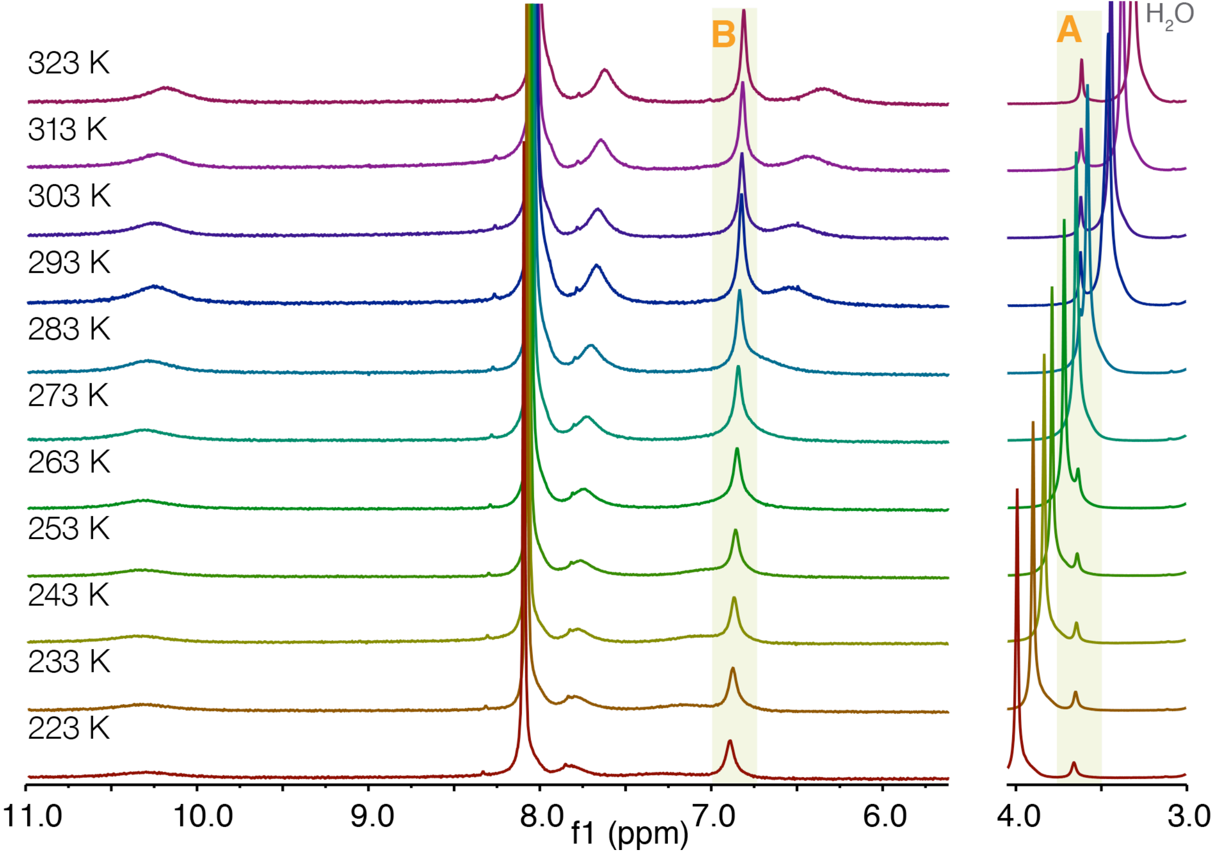


Figure S19: VT NMR (DMF-d_7) of cage **1**.

5.5 DOSY NMR

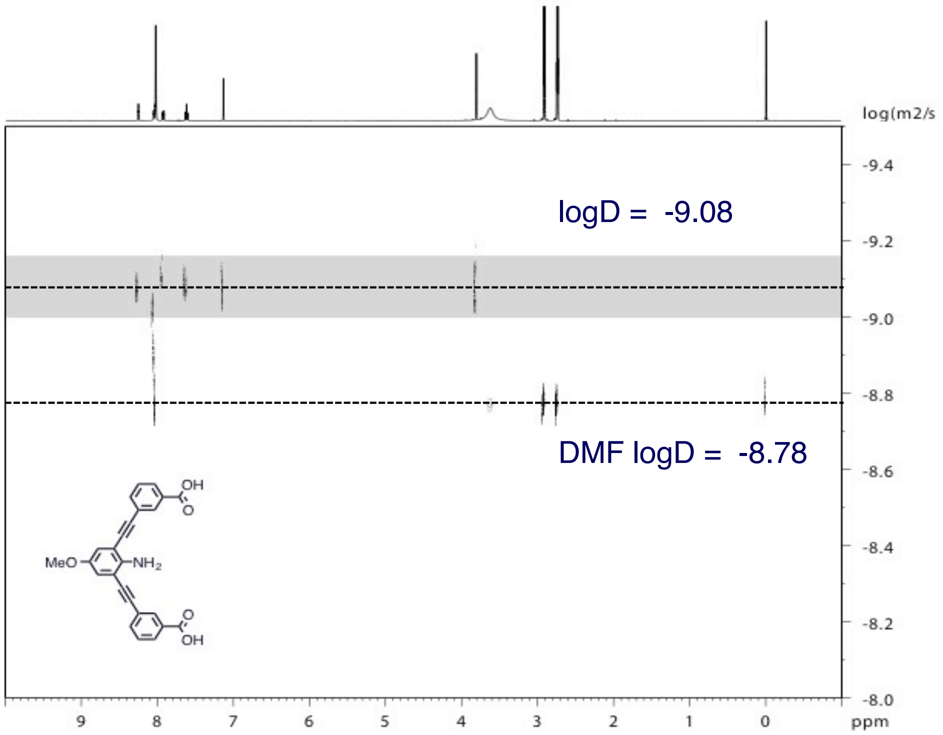


Figure S20: DOSY NMR in DMF-d_7 of ligand **L1** (D20 = 40 ms ; P30 = 2 ms).

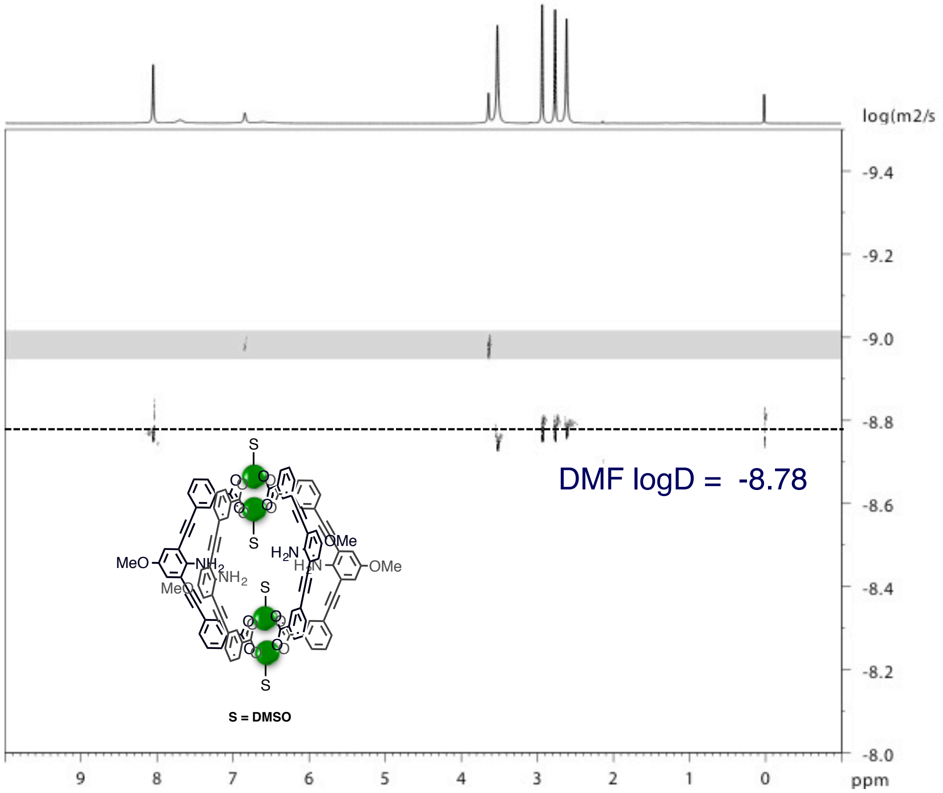


Figure S21: DOSY NMR of crystals of cage **1** redissolved in DMF-d_7 (D20 = 40 ms ; P30 = 2 ms).

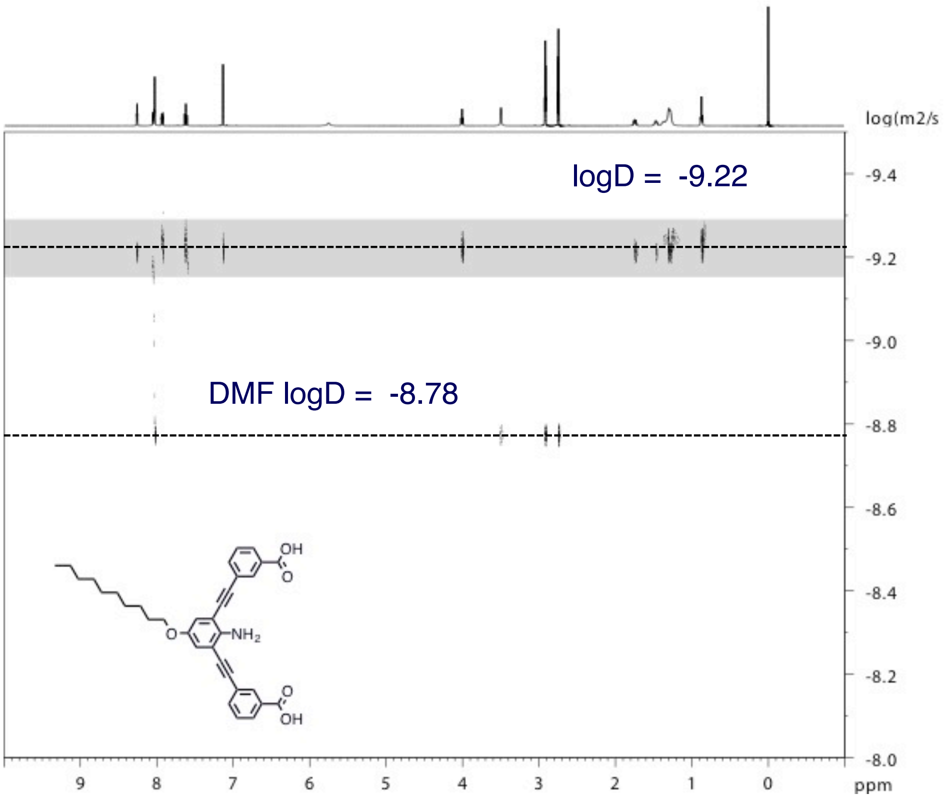


Figure S22: DOSY NMR in DMF-d_7 of ligand **L2** (D20 = 40 ms; P30 = 1.8 ms).

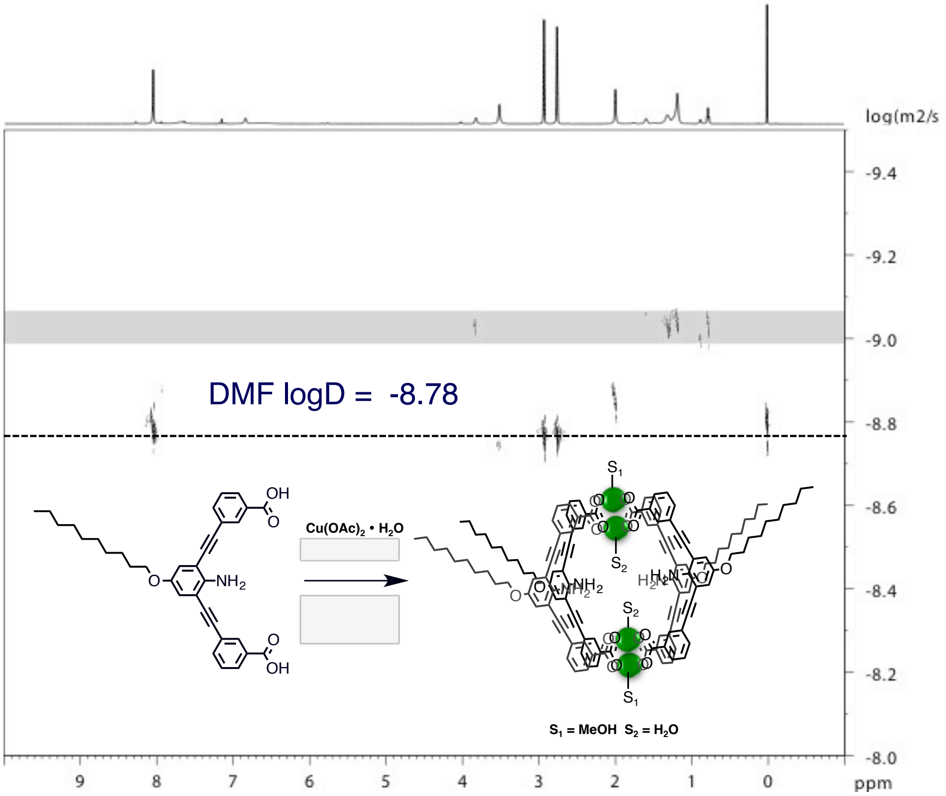


Figure S23: DOSY NMR in DMF-d_7 of ligand **L2** + 1 eqv of Cu(OAc)$_2$•H$_2$O (D20 = 50 ms ; P30 = 3 ms).

6. UV-Vis and fluorescence measurements

Ligand **L1** in DMF has a high-energy band maximum of 280 nm and an intramolecular donor-acceptor charge transfer band centered at 400 nm. The absorption spectrum of cage **1** dissolved in DMF show the same features of the spectrum of the ligand, with a d-d band centered at 700 nm characteristic of the copper paddle-wheel SBU. The emission spectra (λ_{exc} = 400 nm) of ligand **L1** and of cage **1** in DMF present maxima at 475 nm. The emissive properties of cage **1** are ascribed to ligand-centered transitions involving p-types molecular orbitals.

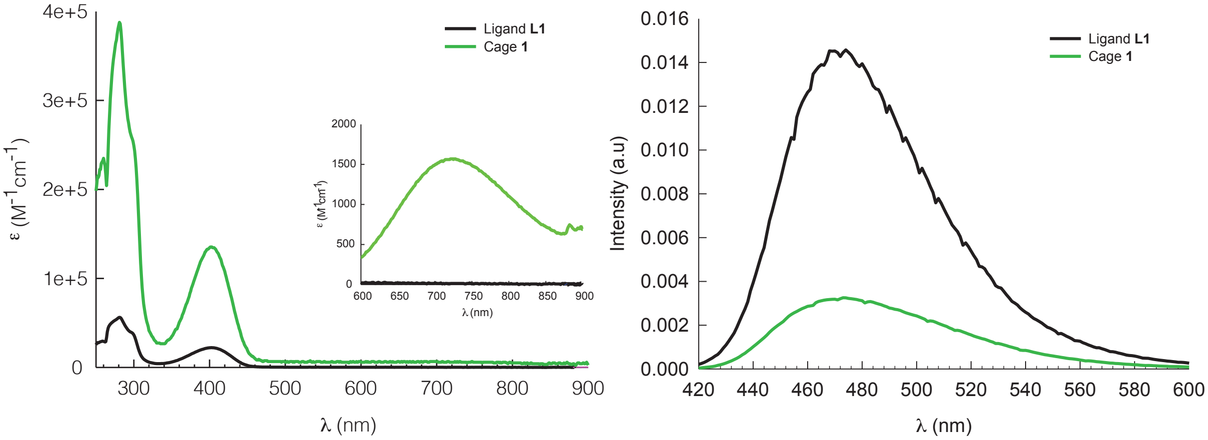


Figure S24: a) UV-Vis absorption spectra of Ligand **L1** and cage **1** in DMF and b) Fluorescence spectra (λ_{exc} = 400 nm) of Ligand **L1** and cage **1** in DMF (Relative Intensity).

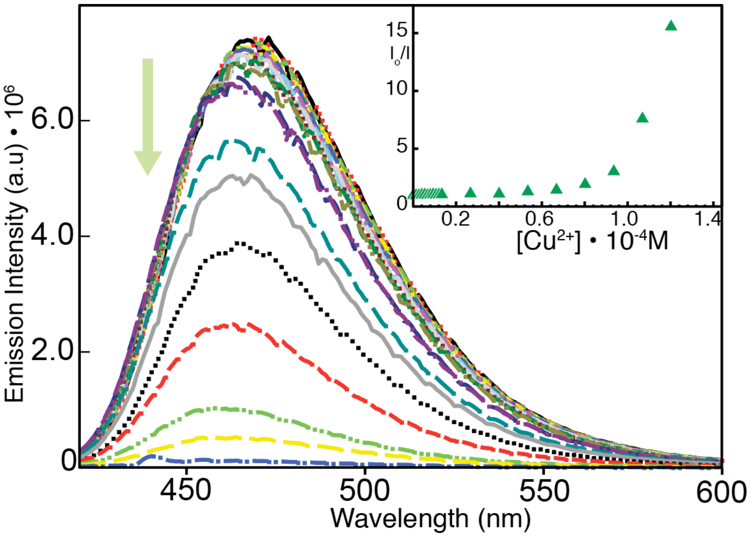


Figure S25: Fluorescence titration (λ_{exc} = 400 nm) of a solution $1.458 \cdot 10^{-6}$ M of Ligand **L1** with a solution $1.336 \cdot 10^{-4}$ M of $Cu(OAc)_2 \cdot H_2O$ in DMF. The Stern-Volmer plot is shown in the inset.

7. Single crystal X-Ray diffraction analyses

7.1 Cage 1

Table S1: Crystallographic data for cage **1**

Chemical formula	$C_{108}H_{84}Cu_4N_4O_{24}S_4{\cdot}0.56(O)$
M_r	2213.95
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	14.935 (5), 16.106 (6), 16.995 (6)
α, β, γ (°)	105.989 (4), 109.453 (4), 104.285 (5)
V (Å^3)	3438 (2)
Z	1
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.73
Crystal size (mm)	0.32 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker AXS APEXII CCD diffractometer
Absorption correction	Multi-scan Apex2 v2013.4-1 (Bruker, 2013)
T_{min}, T_{max}	0.471, 0.746
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	40624, 19952, 11327
R_{int}	0.048
(sin θ/λ)$_{max}$ (Å^{-1})	0.733
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, Σ	0.074, 0.222, 1.05
No. of reflections	19952
No. of parameters	812
No. of restraints	490
H-atom treatment	H-atom parameters constrained
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	1.43, -1.20

Computer programs: Apex2 v2013.4-1 (Bruker, 2013), *SAINT* V8.30C (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev645 (Hübschle *et al.*, 2011), *SHELXTL* (Bruker, 2003).

Large sections of the structure are occupied by disordered solvate molecules. In some sections partially occupied DMSO could be identified. The overall disorder did however not allow for definition of a satisfactory solvate molecule model, and the electron density for the solvate molecules was instead corrected for by reverse Fourier transform methods using the Squeeze procedure as implemented in the program Platon. 379 electrons from 1123 Å^3 of volume (ca 33% of the unit cell volume) were corrected for. This equals approximately nine DMSO molecules per unit cell or formula unit. See Squeeze report appended to the cif file.

In addition to the excessive disorder of solvate molecules, disorder in the cage structure is observed. The two copper coordinated DMSO molecules are disordered. One was refined to be disordered over two positions, the other over three positions. All refined DMSO molecules were restrained to have similar geometries. The ADPs of disordered sulfur atoms and of some methyl C atoms (C51A and C51B, C54A and C54B) were constrained to be identical. C54A was restrained to be approximately isotropic. The three fold disordered DMSO molecules were subjected to a rigid bond restraint. Subject to these conditions the occupancy rates refined to: 0.690(2) and 0.310(2); and 0.723(2), 0.151(2) and 0.126(2).

Electron density overlapping with one of the minor occupied DMSO moieties of the triply disordered molecule was not properly accounted for by the Squeeze procedure. In was incorporated into the model as a partially occupied oxygen atom, acknowledging that it is most likely part of a disordered solvate molecule partially removed by the squeeze procedure. The occupancy of the O atom, left isotropic, refined to 0.282(11).

A disordered methoxy group induces disorder of the adjacent aminobenzene unit. The groups were refined as disordered over four different positions, which were restrained to have similar geometries. Equivalent atoms, with the exception of the methyl C atoms, were constrained to have identical ADPs. The ADPs of disordered atoms were subjected to a similarity restraint, the minor moiety methoxy groups to a rigid bond restraint and C50B, C50C and C50D were restrained to be approximately isotropic. The methoxy O and amino N atoms were restrained to lie within the plane of the benzene ring. Subject to these conditions, the occupancies refined to 0.292(3), 0.453(3), 0.145(3) and 0.110(3).

Several low angle reflections were affected by the beam stop and were omitted from the refinement. The omitted reflections are 1 -1 1, 0 0 1, -1 -1 1, 0 -1 1, 1 0 0, 0 1 0, -1 1 0, -1 0 1, 0 1 1.

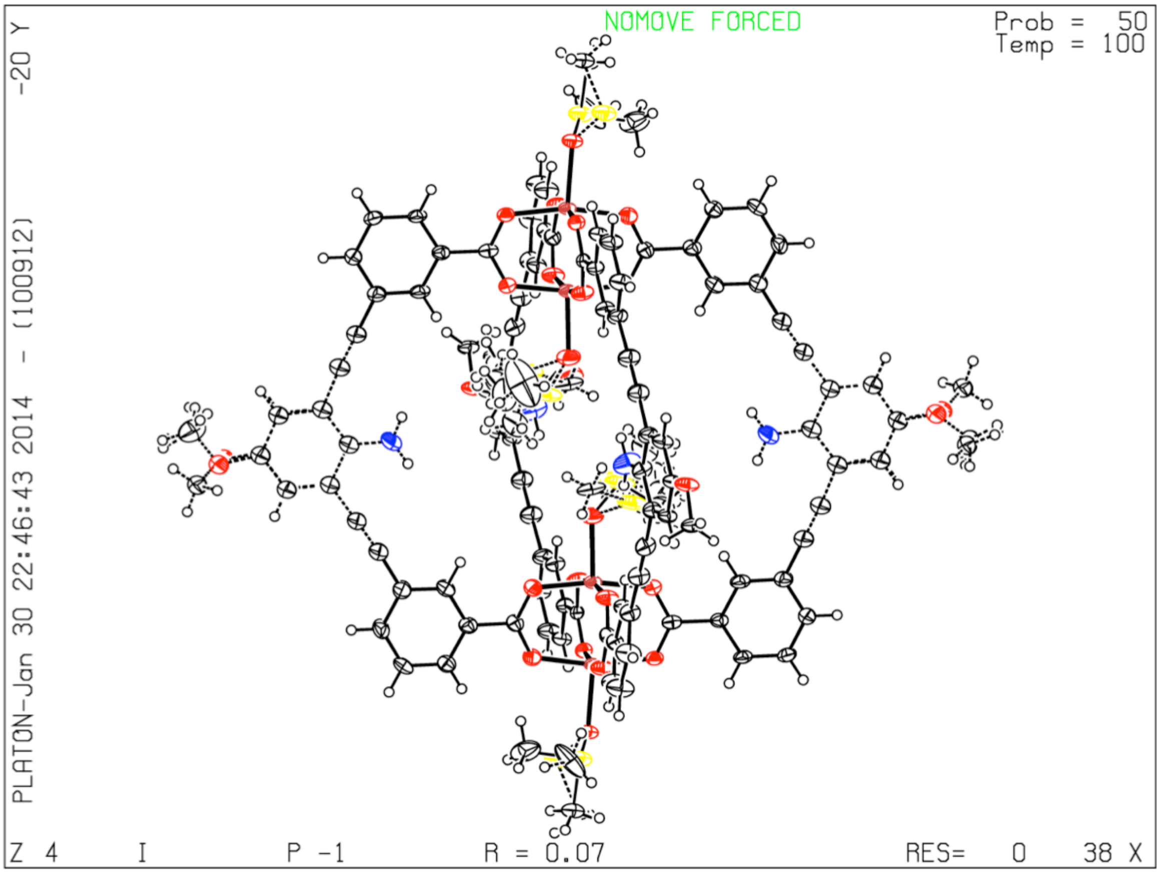


Figure S26: ORTEP drawing of cage **1**. Thermal ellipsoids set to 50% probability level.

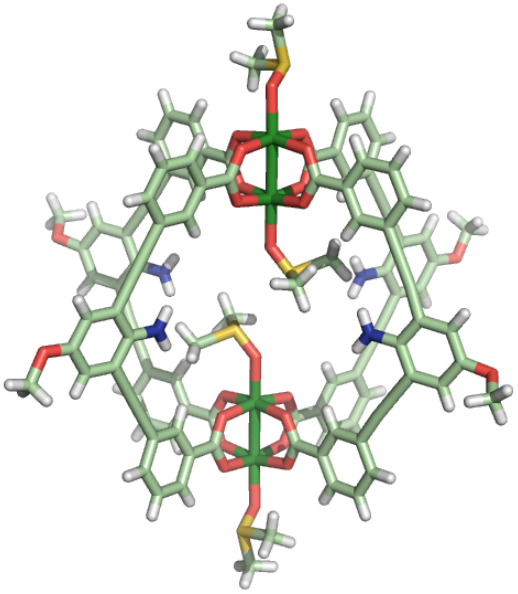


Figure S27: X-ray crystal structure of cage **1**. Included solvent molecules and ligand disorder removed for the sake of clarity. See figure S26.

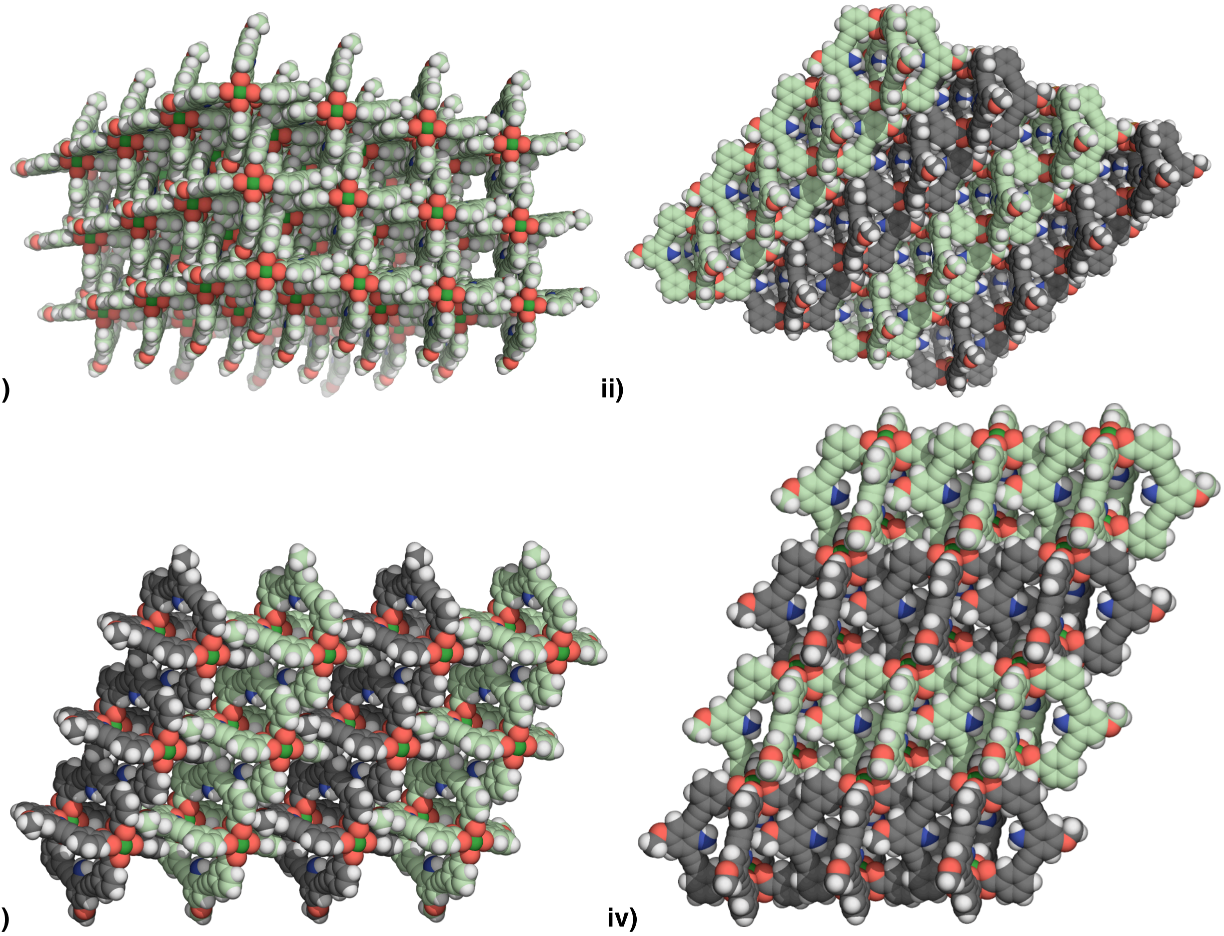


Figure S28: Views along the i) top, ii) a, iii) b, and iv) c axes showing packing for cage **1**. Apical and included solvent molecules and ligand disorder removed for the sake of clarity. See Figure S26.

7.2 Cage 2

Table S2: Crystallographic data for cage **2**

Chemical formula	$C_{137.18}H_{142.36}Cu_4N_4O_{24}\cdot 1.82(C_4H_9NO)\cdot 6.07(CH_4O)\cdot 2.14(H_2O)$
M_r	2877.26
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100
a, b, c (Å)	18.2648 (11), 27.0741 (17), 16.6959 (9)
β (°)	110.078 (2)
V (Å^3)	7754.4 (8)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.21
Crystal size (mm)	0.21 × 0.19 × 0.15
Data collection	
Diffractometer	Bruker AXS Prospector CCD diffractometer
Absorption correction	Multi-scan Apex2 v2014.1-0 (Bruker, 2014)
$T_{\min}$, $T_{\max}$	0.638, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	34555, 13282, 11546
R_{int}	0.022
$(\sin\theta/\lambda)_{\max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, Σ	0.051, 0.146, 1.05
No. of reflections	13282
No. of parameters	1267
No. of restraints	971
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.70, -0.46

Computer programs: Apex2 v2014.1-0 (Bruker, 2014), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev645 (Hübschle *et al.*, 2011).

The alkyl chains of the main complex, some of the adjacent phenoxy groups, and large sections of the solvent regions of the structure are disordered. The alkyl chains were both refined to be disordered over two moieties. For both chains, the oxygen atom is included in the disorder. For the chain of O8, the adjacent three phenylene C atoms were also included. The disordered sections were each restrained to have similar geometries (SAME command of SHELXL), were subjected to a rigid bond restraint (RIGU command of SHELXL), and ADPs of nearby atoms (regardless if bonded or not) were restrained to be similar (SIMU command of SHELXL). Atoms O8 and O8B were constrained to have identical ADPS. Subject to these restraints, the major moiety alkyl chain occupancies refined to 0.634(5) and 0.637(2).

A DMF molecule is disordered with one water and one methanol molecule on the outside of the complex. No restraints were applied for the disordered molecules. The major moiety occupancy refined to 0.683(6).

Extensive disorder is observed within the cavity of the main complex. Disorder was modeled using DMF, methanol and water molecules. The geometry of the DMF molecule was restrained to be similar to that of the DMF molecule on the outside of the cavity (see above) (SAME command of SHELXL), and the DMF atoms were subjected to a rigid bond restraint (RIGU command of SHELXL). The copper coordinated entity was refined as disordered between two differently oriented methanol molecules and a water molecule. No geometry restraints were applied for disordered methanol and water molecule C and O atoms. Atoms O22 and C80 were constrained to have identical ADPs. Atom C83 was restrained to be close to isotropic. Subject to these conditions, occupancies of methanol and water molecules refined to values between 0.227(3) and 0.518(7).

Water H atoms were initially refined and restrained positionally based on hydrogen bonding considerations, and then set to ride on their carrying O atoms.

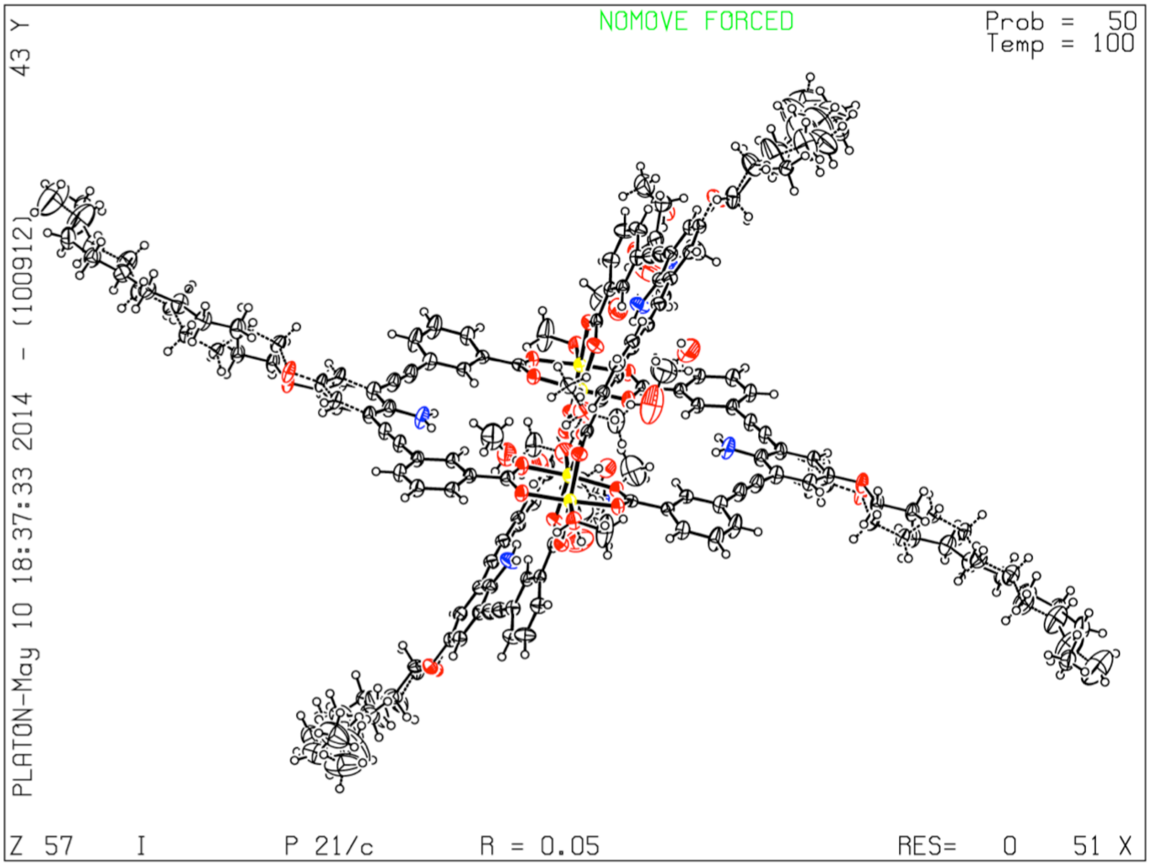


Figure S29: ORTEP drawing of cage **2**. Thermal ellipsoids set to 50% probability level.

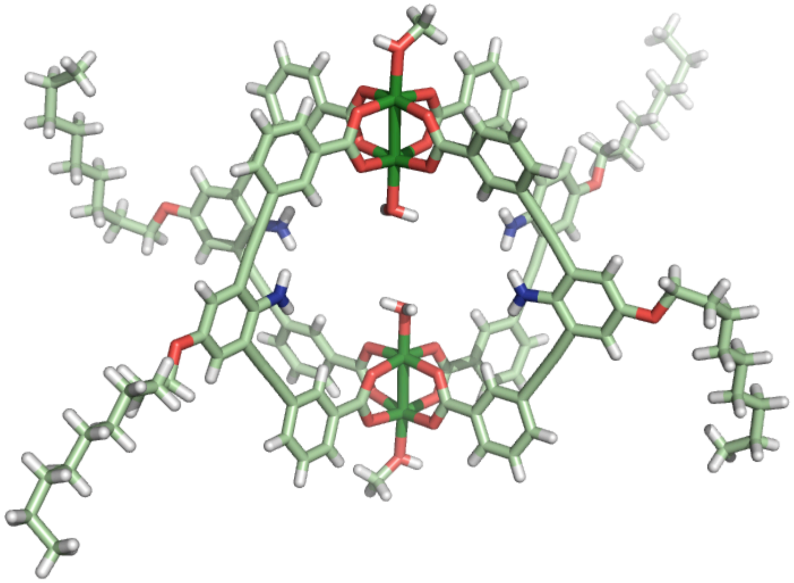


Figure S30: X-ray crystal structure of cage **2**. Included solvent molecules and ligand disorder removed for the sake of clarity. See figure S29.

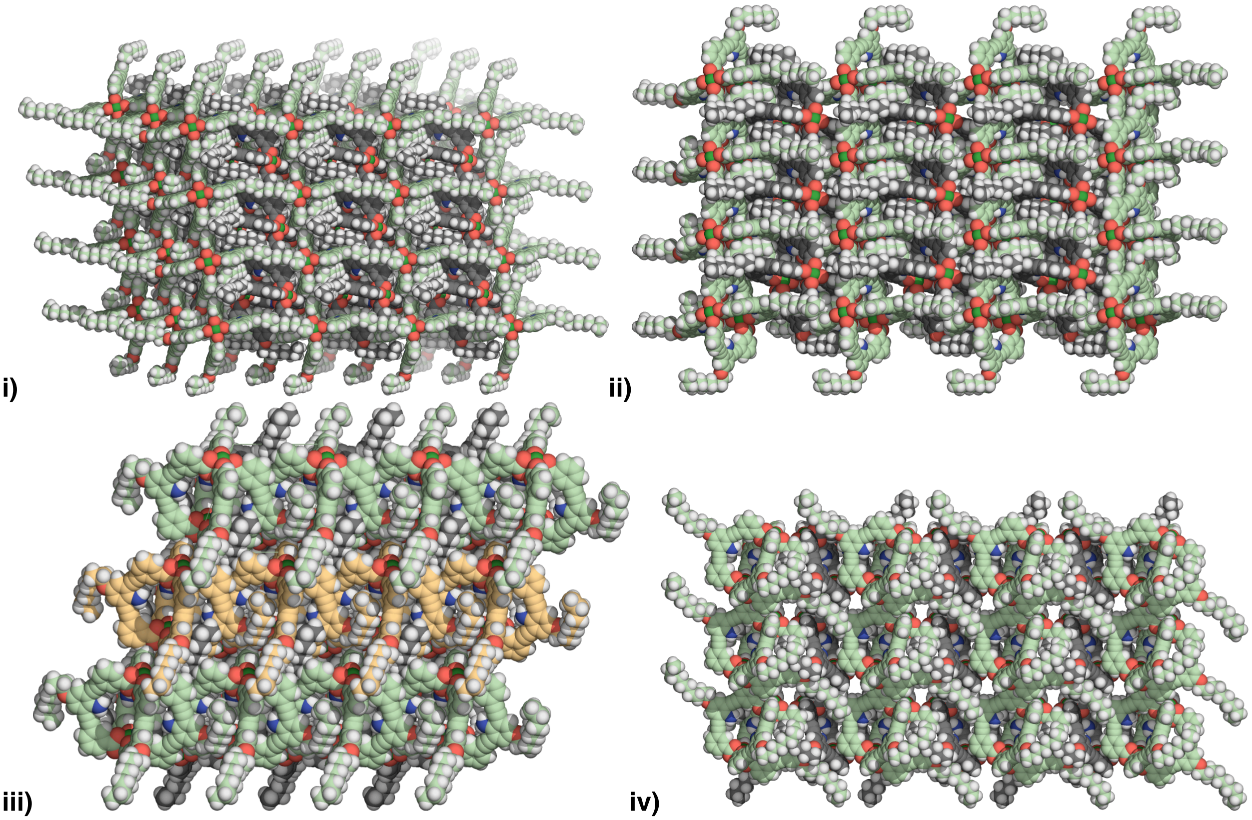


Figure S31: Crystal packing for cage **2** with views along the i) top, ii) a, iii) b, and iv) c axes. Apical and included solvent molecules and ligand disorder removed for the sake of clarity. See Figure S29.

7.3 Cage 1'

Table S3: Crystallographic data for cage **1'**

Chemical formula	$C_{136.45}H_{149.05}Cu_4N_{16.15}O_{34.15}$
M_r	2815.82
Crystal system, space group	Monoclinic, *C*2/*c*
Temperature (K)	100
a, *b*, *c* (Å)	22.7256 (6), 27.9980 (6), 23.4326 (5)
β (°)	91.880 (1)
V (Å^3)	14901.5 (6)
Z	4
Radiation type	Cu $K\alpha$
μ (mm^{-1})	1.27
Crystal size (mm)	0.18 × 0.14 × 0.12
Data collection	
Diffractometer	Bruker AXS Prospector CCD diffractometer
Absorption correction	Multi-scan Apex2 v2014.1-0 (Bruker, 2014)
T_{min}, T_{max}	0.673, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	53517, 13021, 12202
R_{int}	0.023
(sin θ/λ)$_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, Σ	0.058, 0.157, 1.07
No. of reflections	13021
No. of parameters	1323
No. of restraints	2459
H-atom treatment	H-atom parameters constrained
	$w = 1/[s^2(F_o^2) + (0.0722P)^2 + 59.1573P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.95, -0.44

Computer programs: Apex2 v2014.1-0 (Bruker, 2014), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev645 (Hübschle *et al.*, 2011).

The structure consists of well-defined complex molecules, including a coordinated water and DMF molecule, and heavily disordered solvent molecules located both within the cavity of the complex molecules, and in between complexes in the crystal lattice. Within the cavity are located mostly heavily disordered DMF molecules. For these, a tentative model could be developed. All DMF molecules were restrained to have a geometry similar to that of the non-disordered coordinated DMF molecule. ADPs of disordered DMF molecules were restrained using various commands of SHELXL (SIMU, RIGU, and ISOR for most molecules. FLAT for one molecule). Subject to these conditions, occupancy rates for the molecules refined to values between 0.549(5) and 0.139(8). One of the DMF molecules was 1:1

disordered across a two-fold axis. H atoms of the coordinated water molecule were split over two equally occupied sites to avoid close contacts of H atoms with nearby disordered DMF molecules.

Channels between complex molecules are occupied by unidentified solvate molecules other than DMF (based on the channel shape and crystallization solvents, most likely diethyl ether). No model could be devised for these regions, and the content of the voids was instead corrected for using reverse Fourier transform methods as implemented in the Squeeze algorithm of Platon. Two voids of each 539 Å^3 (ca 2 x 3.6% of the unit cell volume) were corrected for 139 electrons each (corresponding to 26.5 ether molecules per unit cell).

Reflections -1 1 1, 2 2 1, 0 2 1, 1 1 0 and 0 0 2 were affected by the beam stop and were omitted from the refinement.

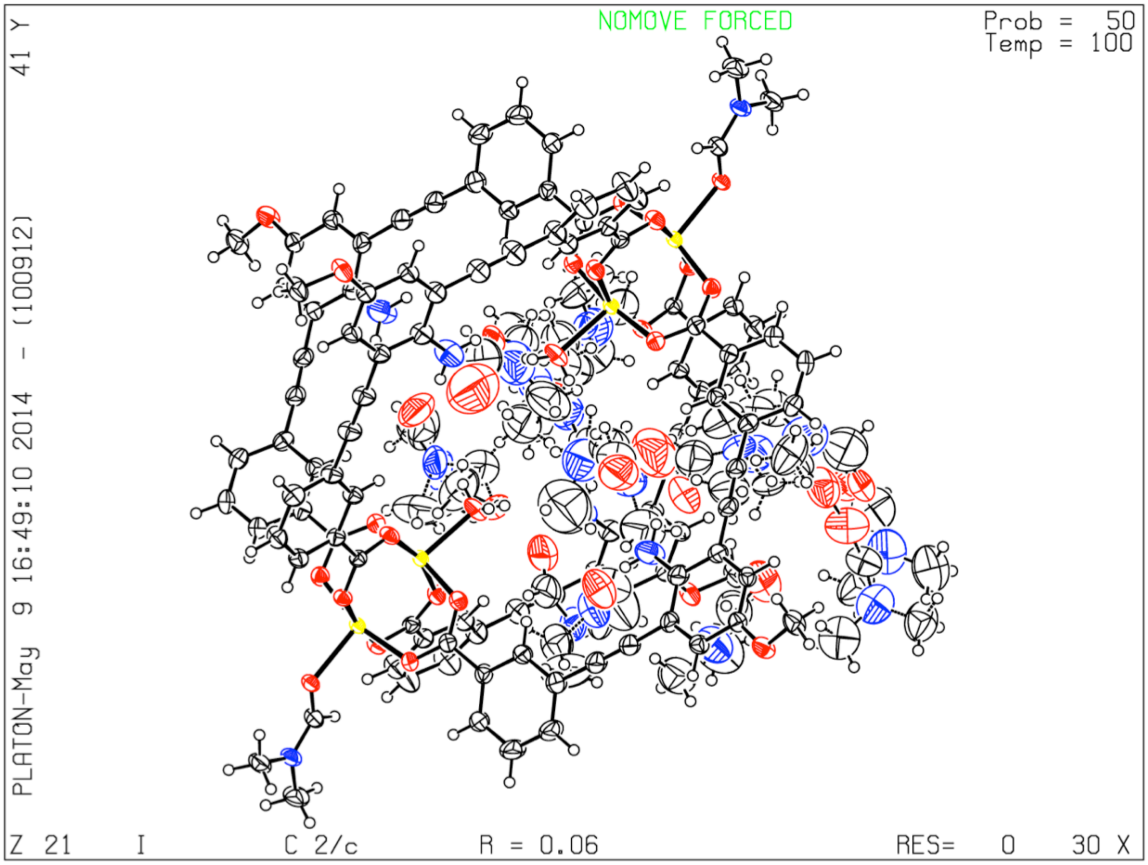


Figure S32: ORTEP drawing of cage **1’**. Thermal ellipsoids set to 50% probability level.

7.4 Supramolecular 1D chain 3

Table S4: Crystallographic data for supramolecular chain **3**

Chemical formula	$C_{56}H_{38}Cu_2N_3O_{11}$
M_r	1055.97
Crystal system, space group	Triclinic, $P\bar{1}$
Temperature (K)	100
a, b, c (Å)	16.1748 (7), 17.1245 (8), 17.3765 (8)
α, β, γ (°)	61.699 (2), 79.187 (2), 79.168 (2)
V (Å^3)	4135.1 (3)
Z	2
Radiation type	Cu $K\alpha$
μ (mm^{-1})	0.96
Crystal size (mm)	0.21 × 0.12 × 0.10
Data collection	
Diffractometer	Bruker AXS Prospector CCD diffractometer
Absorption correction	Multi-scan Apex2 v2014.1-0 (Bruker, 2014)
T_{min}, T_{max}	0.487, 0.753
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	59479, 14174, 9805
R_{int}	0.081
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, Σ	0.108, 0.323, 1.05
No. of reflections	14174
No. of parameters	682
No. of restraints	350
H-atom treatment	H-atom parameters constrained
	$w = 1/[s^2(F_o^2) + (0.179P)^2 + 21.2156P]$ where $P = (F_o^2 + 2F_c^2)/3$
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.43, -1.49

Computer programs: Apex2 v2014.1-0 (Bruker, 2014), *SAINT* V8.34A (Bruker, 2014), *SHELXS97* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2013), SHELXLE Rev645 (Hübschle *et al.*, 2011).

Large sections of this structure are composed of ill-defined solvent molecules. Attempts were made to at least partially refine the content of these regions, but the results were not completely satisfactory. Instead, all solvent molecules were corrected for using the Squeeze algorithm of Platon. Squeeze corrected for 636 electrons in 2043 Å^3, or 15.9 molecules of DMF in 49.4% of the unit cell volume (the attempt to refine the DMF molecules yielded 11.38 DMF molecules). See the Squeeze report appended to the cif file for details. Disorder was also observed within the supramolecular chain. The bipyridine molecule is disordered across a crystallographic inversion center in a 1:1 ratio. The disorder also extends to the neighboring atoms, and Cu was included in the disorder model. Atoms pseudo-related by the inversion center were constrained to have identical ADPs. All bipyridine atoms and the disordered copper atoms were also subjected to a rigid bond restraint and to be approximately isotropic. Bipyridine rings were restrained to be coplanar with the copper ion they are bonded to. The atoms of a methanol molecule coordinated to Cu2 showed extremely elongated ADPs and the C and O atoms were restrained to be approximately isotropic. One phenylene ring and adjacent atoms showed extreme thermal libration and were modeled as disordered over two moieties. The two sections were restrained to have similar geometries, equivalent atoms were constrained to have identical ADPs. The disordered phenylene rings and disordered adjacent atoms were restrained to be flat, were also subjected to a rigid bond restraint and to be approximately isotropic.

Reflections -1 1 1 and 1 0 0 were affected by the beam stop and were omitted from the refinement.

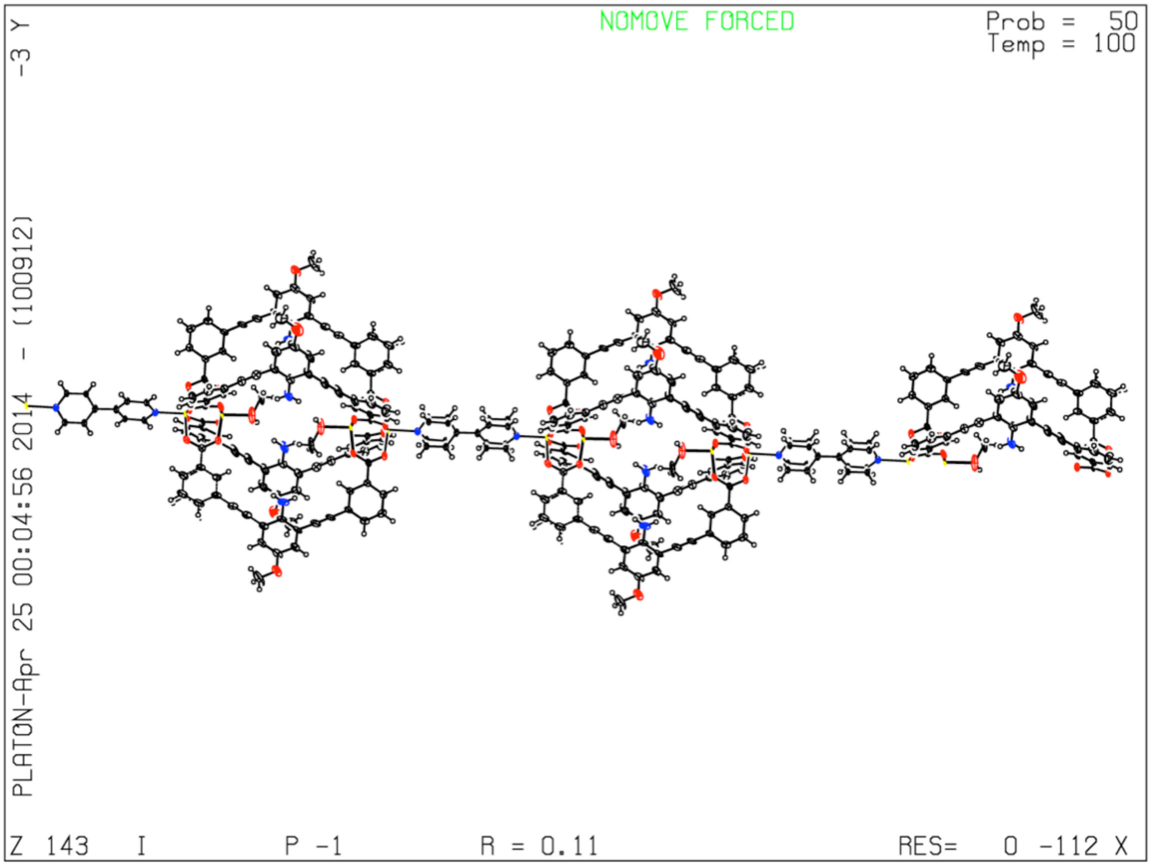


Figure S33: ORTEP drawing of polymer **3**. Thermal ellipsoids set to 50% probability level.

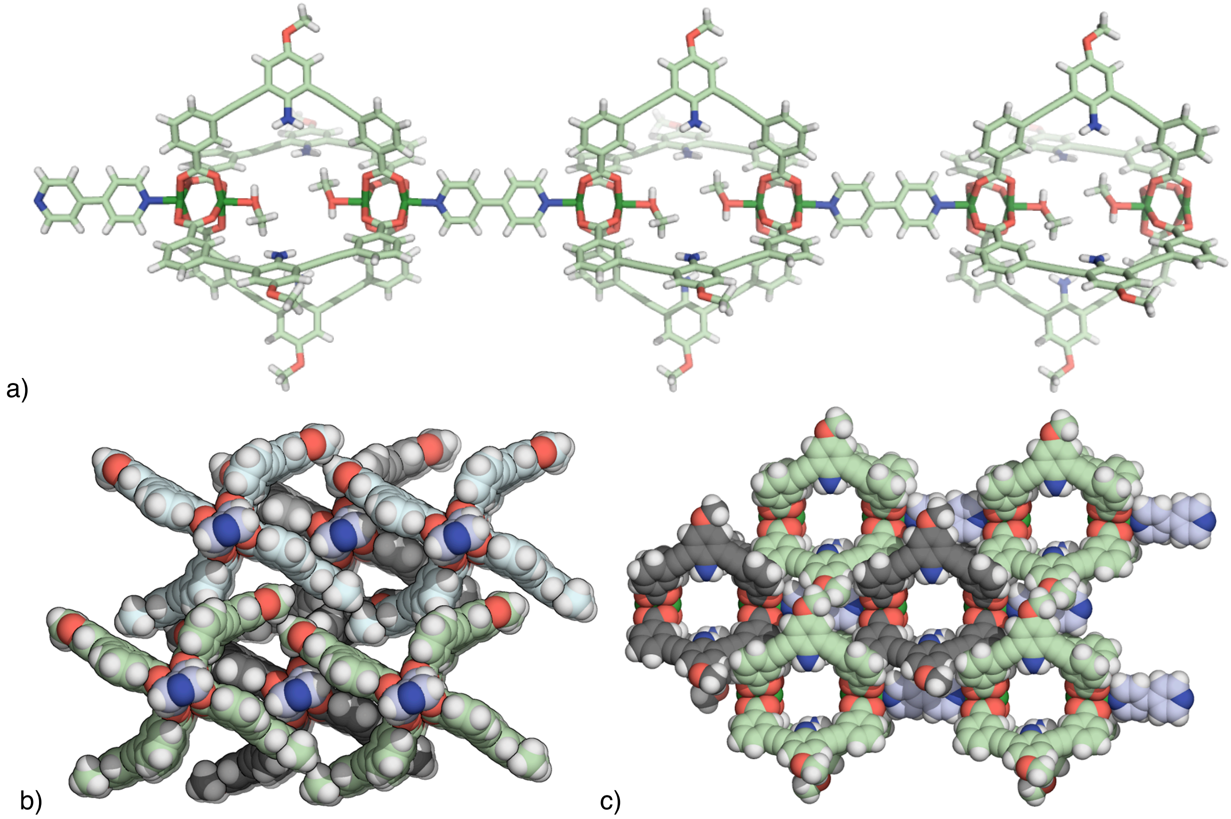


Figure S34: a) Supramolecular 1D chain from crystals of **3**. b) Top and c) side views showing off-set, close packing of 1D chains in the crystal structure of **3**. Included solvent molecules and ligand disorder removed for the sake of clarity. See Figure S33.

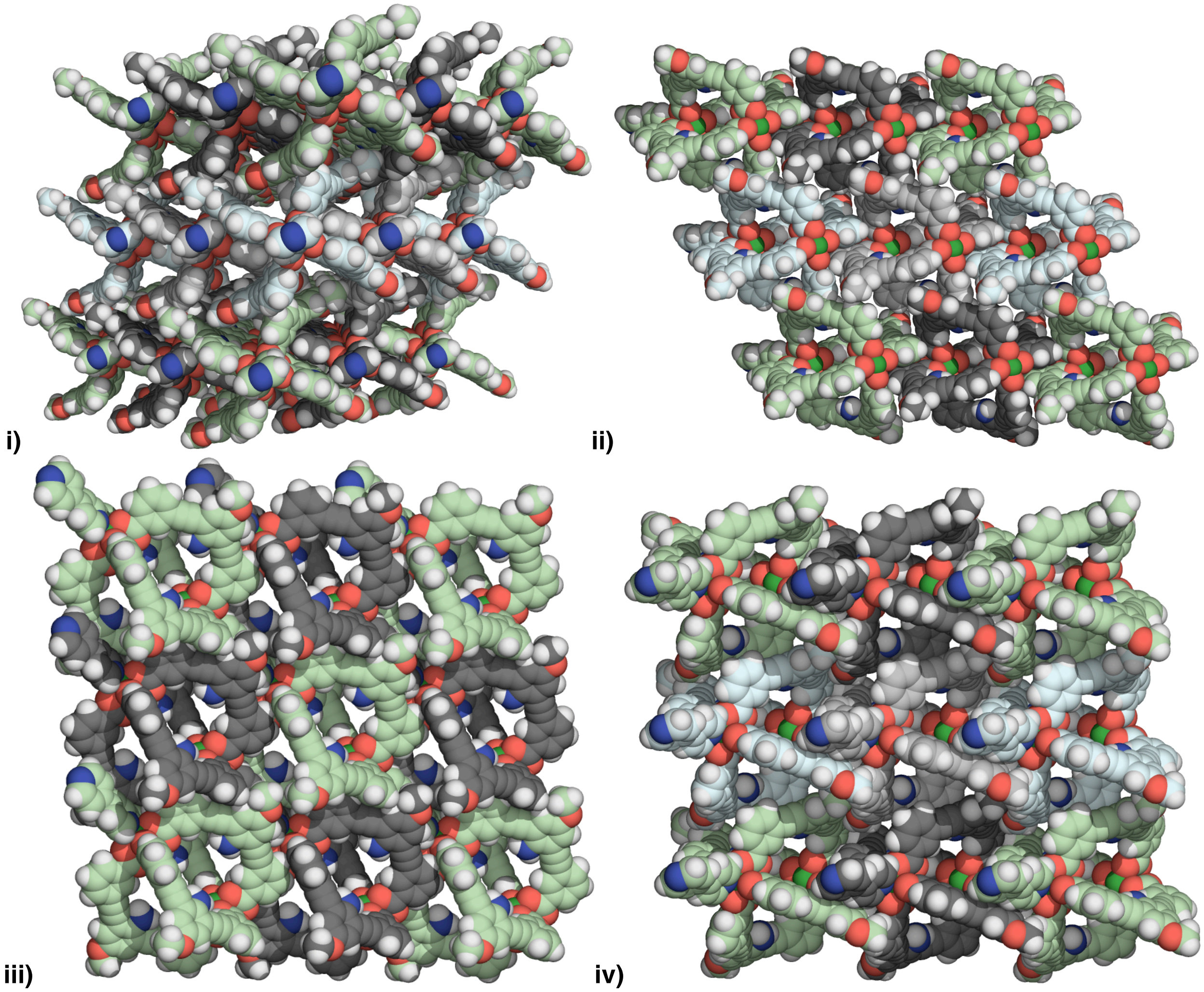


Figure S35: Crystal packing for polymer **3** with views the i) top, ii) a, iii) b, and iv) c axes. Included solvent molecules and ligand disorder removed for the sake of clarity. See Figure S33.

8. Powder X-ray diffraction patterns*

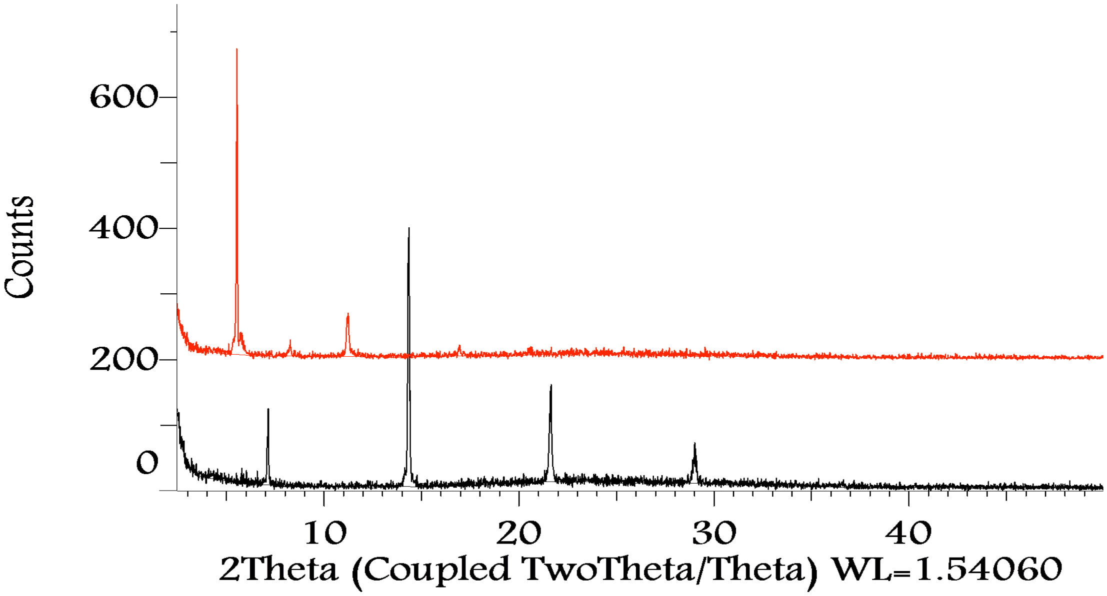


Figure S36: PXRD patterns of as-synthesized supramolecular chain **3** (red) and cage **1** (black).

9. TGA Analysis*

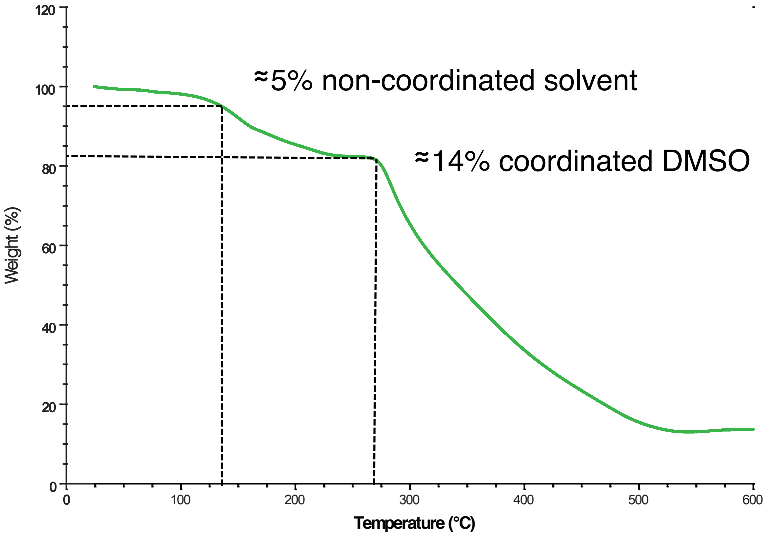


Figure S37: TGA plot of as-synthesized cage **1** under N_2 flow with 10°C min^{-1} scan rate.

*Due to the small quantities of crystals of **2** and **3** obtained, TGA and EA analyses were not performed. PXRD analyses of cage **2** were problematic due to the small quantities and their proclivity to collapse when removed from the needle surface and mother liquor.

10. Mass Spectrum of cage 1

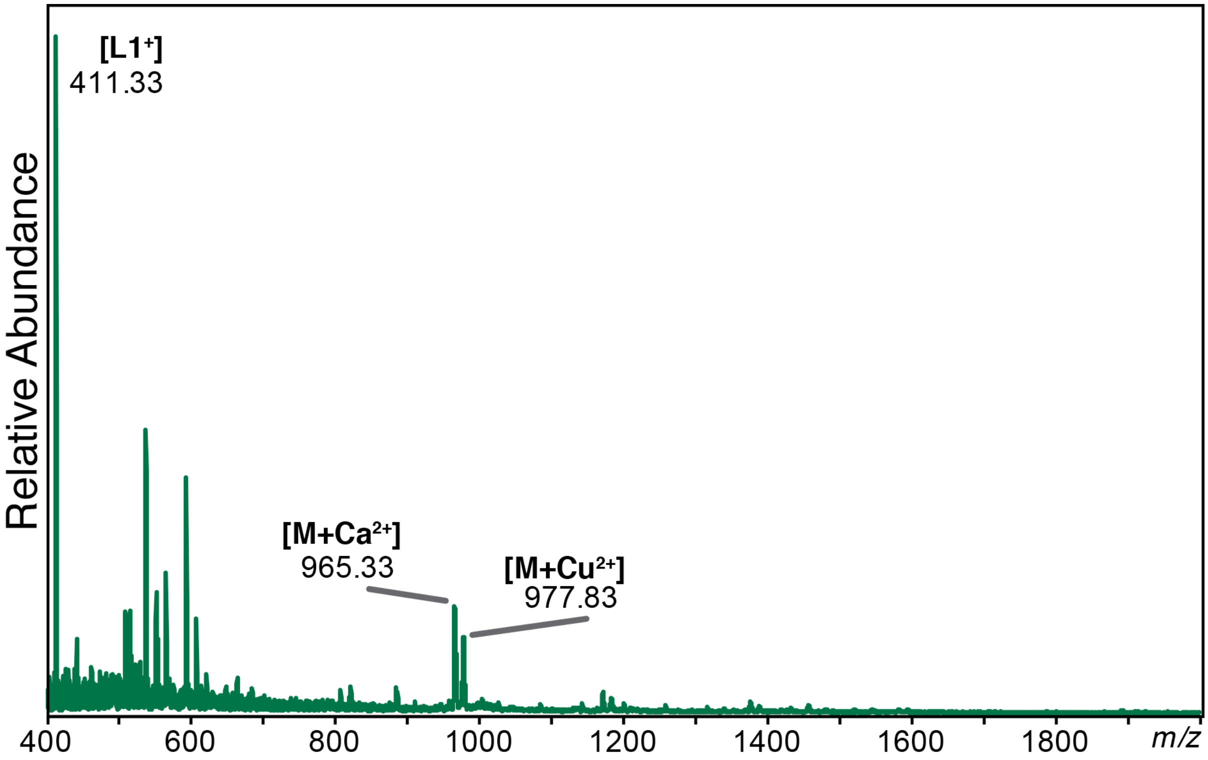


Figure S38: LTQ trace of as-synthesized cage **1**.

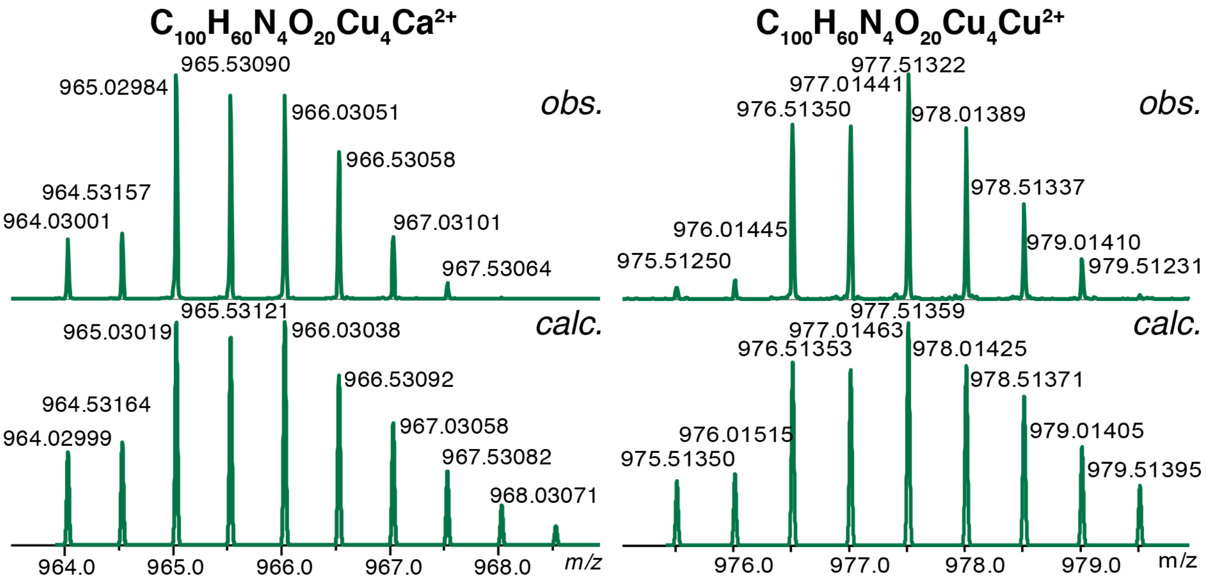


Figure S39: FT-ICR traces of cage 1 showing isotope patterns for the peaks at m/z = 965.33 [M•Ca^{2+}] Error = 16 ppb and b) 977.83 [M+Cu^{2+}] Error = -1024 ppb.

11. AFM and DLS Measurements

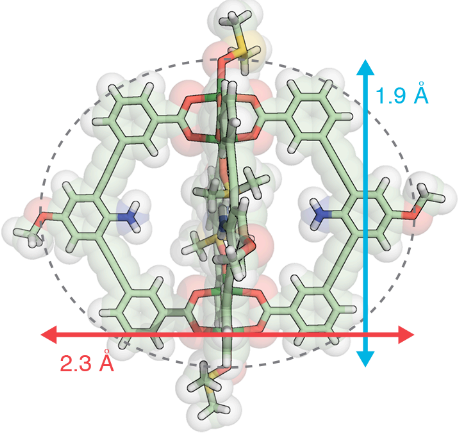


Figure S40. Crystal structure of cage **1** showing length of major and minor axes.

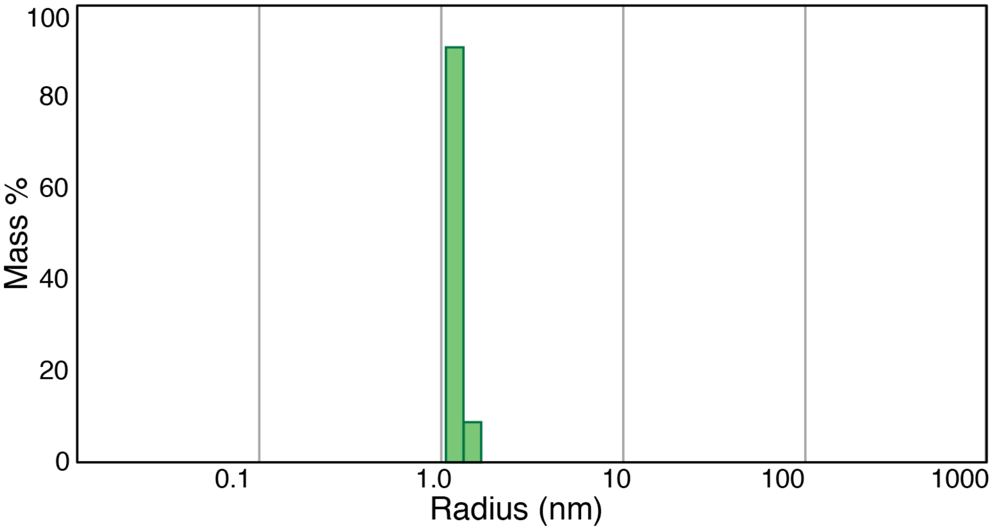


Figure S41. Particle size and distribution from dynamic light scattering measurements of cage **1** in DMF. Observed diameter = 2.4 nm, polydispersity = 7.4%.

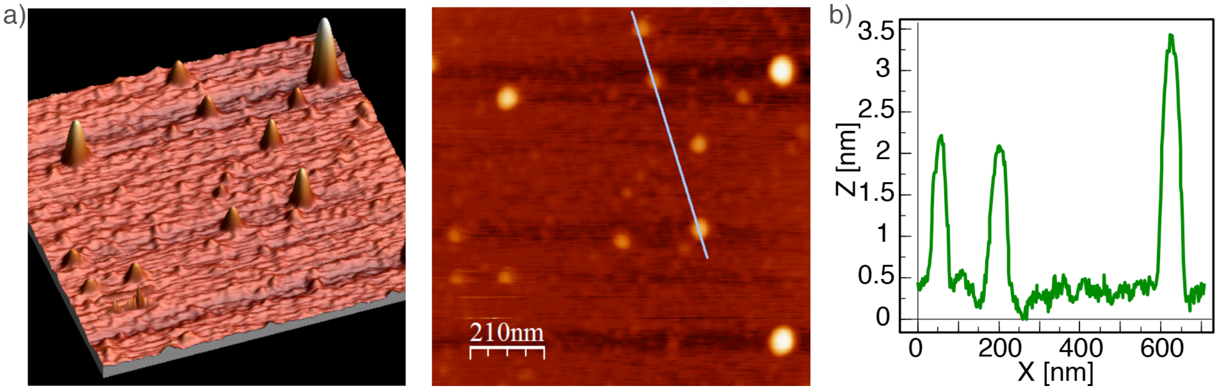
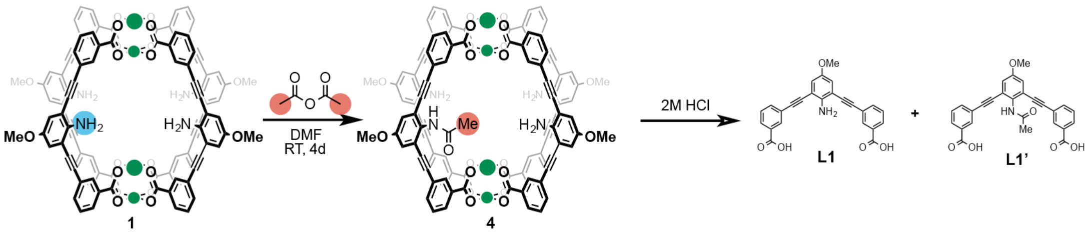


Figure S42. AFM image from a DMF solution of cage **1** on mica slide showing b) single particles ca. 2.2 nm in height.

12. Post-synthetic modification of cage 1



Synthetic procedure: 9 mg of cage **1** were dissolved in dry DMF (1 ml). 10 μl of acetic anhydride were added under N_2. The resulting solution was stirred under N_2 at room temperature for 4 days. DMF was removed under vacuum at RT. The green solid obtained was washed with MeOH (3 x 2 ml) and dried. The solid was sonicated for 10 min in HCl 2M and extracted with Et_2O to give a yellow solid.

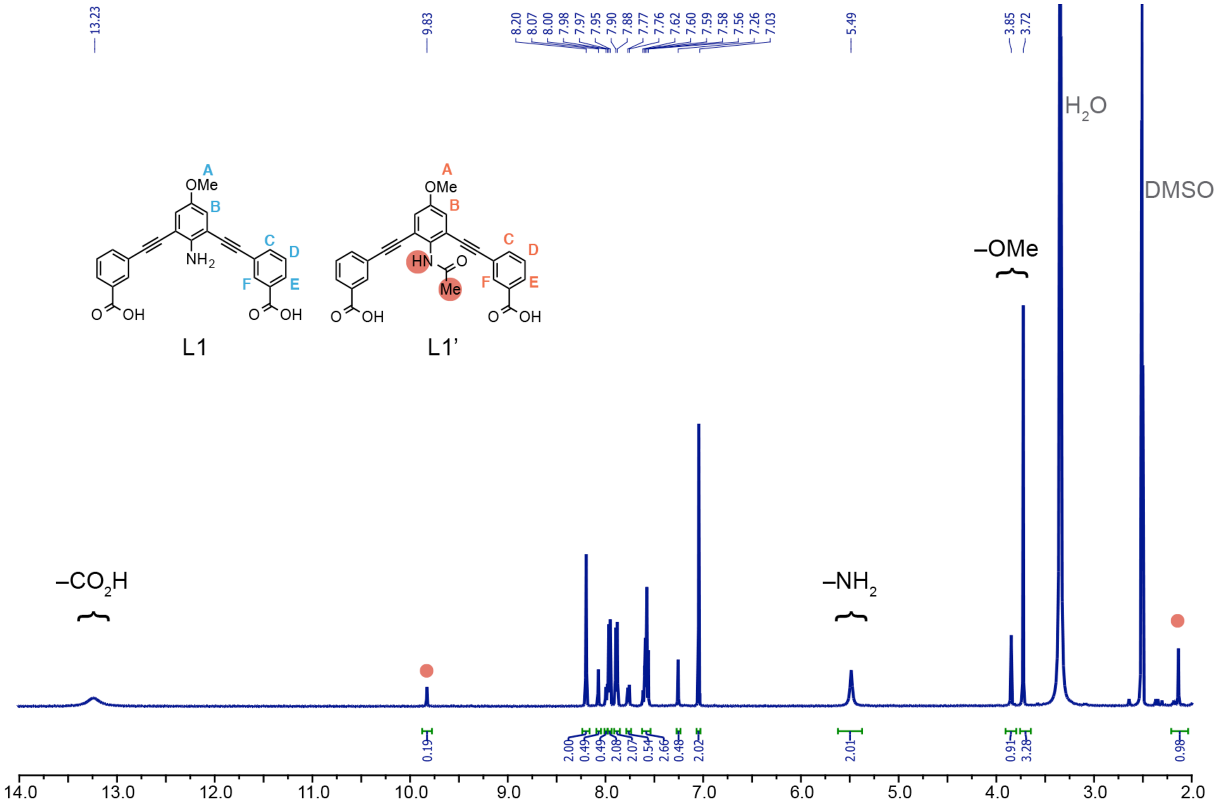


Figure S43: ^{1}H-NMR (DMSO-d_6) of recovered ligand with new signals corresponding to the amide and methyl hydrogens of **L1'** labeled with red circles.

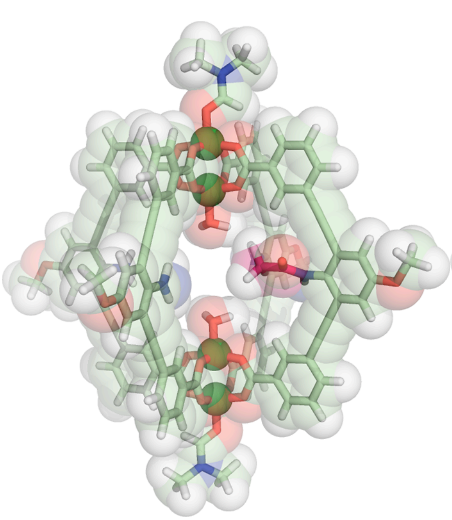
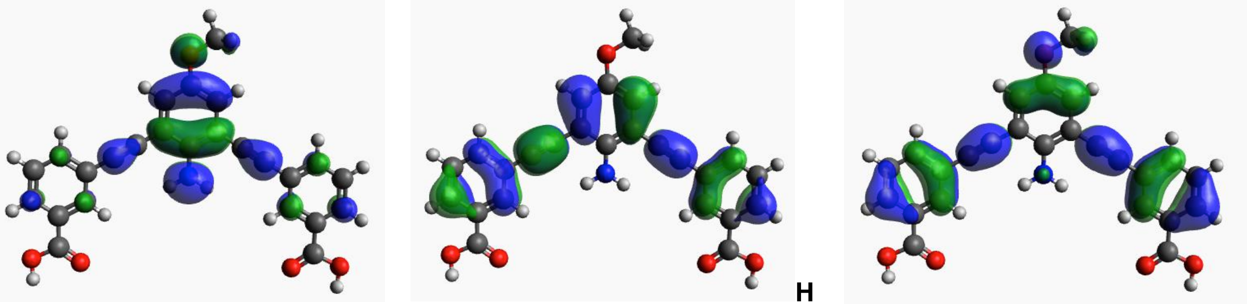
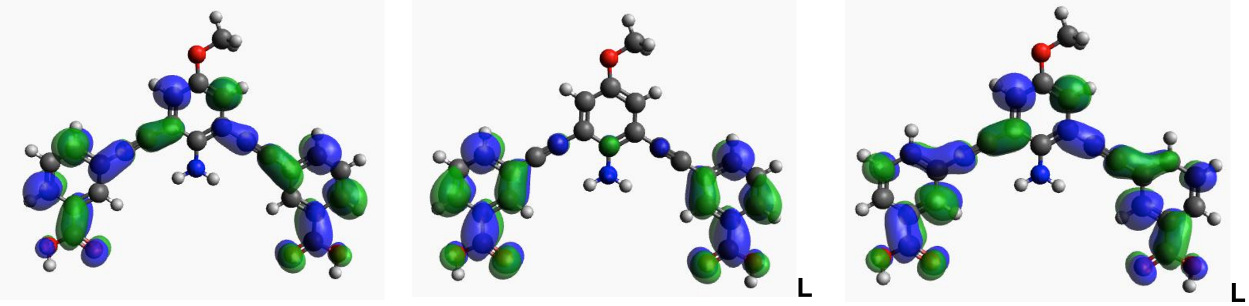


Figure S44: Minimized structures for post-synthetically modified **4** with two internal water molecules, or a single water and DMF solvent molecule coordinated to the internal copper atoms. Calculated using forcite in Materials Studios.[9]

13. Molecular Orbitals for ligand L1



HOMO = -5.034 eV **OMO-1 = -5.905 eV** **HOMO-2 = -6.667 eV**



LUMO = -1.796 eV **UMO+1 = -1.687 eV** **UMO+2 = -1.415 eV**

Figure S45: Molecular Orbitals for Ligand **L1** calculated by the DFT/B3LYP method *in vacuo* with Gaussian 09[10] and visualized with Avogadro.[11]

14. References

[1] *Apex2*, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, **2013**.

[2] *SHELXTL (Version 6.14) (2000-2003)*, Bruker Advanced X-ray Solutions, Bruker AXS Inc., Madison, Wisconsin, USA, **2000**.

[3] G. M. Sheldrick, *SHELXL2013*, University Of Göttingen, Germany, **2013**.

[4] C. B. Hübschle, G. M. Sheldrick, B. Dittrich, *J. Appl. Crystallogr.* **2011**, *44*, 1281–1284.

[5] W. L., *The Pymol Molecular Graphics System*, Schrodinger, LLC, **2010**.

[6] J. H. Tidwell, S. L. Buchwald, *J. Am. Chem. Soc.* **1994**, *116*, 11797–11810.

[7] Z. Li, H. Xing, G. Huang, X. Sun, J. Jiang, L. Wang, *Sci. China Chem.* **2011**, *54*, 1726–1734.

[8] A. V. Aggarwal, S.-S. Jester, S. M. Taheri, S. Förster, S. Höger, *Chem. - Eur. J.* **2013**, *19*, 4480–4495.

[9] *Materials Studio*, Accelrys Software Inc., San Diego, CA, **2014**.

[10] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, et al., *Gaussian 09*, Gaussian, Inc., Wallingford, CT, USA, **2009**.

[11] M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeersch, E. Zurek, G. R. Hutchison, *J. Cheminformatics* **2012**, *4*, 17.

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