Electronic Supplementary Material (ESI) for Chemical Communications

"M_3L_2 metallo-cryptophanes: [2]catenane and simple cages"

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Supplementary Material

Synthesis

Chemicals were obtained from commercial sources and used without further purification. Cyclotriguaiacylene was synthesised by literature methods.[1] NMR spectra were recorded by automated procedures on either a Bruker DPX300 or a Bruker ARX 250 NMR spectrometer. Electrospray (ES) mass spectra were measured on a Bruker MicroTOF-Q in positive ion mode. Infra-red spectra were recorded as solid phase samples on a Perkin-Elmer Spectrometer. Microanalyses were performed by the University of Leeds microanalytical service, and samples were dried under vacuum prior to analysis. NMR and MS spectra of metal complexes were run on appropriate solutions of metal salt and ligand and not on redissolved crystals of the complex, hence represent solution phase self-assembly behaviour.

3-Bromomethyl pyridine

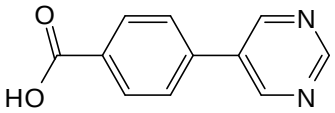
Saturated aqueous sodium carbonate (~10 mL) was added dropwise to a stirred solution of 3-bromomethyl pyridine hydrobromide (620 mg, 2.45 mmol) in distilled water (20 mL) at 0 °C to reach pH 7. The 3-bromomethyl pyridine was extracted with dichloromethane (30 mL), dried over magnesium sulfate and filtered. The filtrate was used immediately, without further purification, as 3-bromomethyl pyridine polymerizes in the solid state.

(±)-2,7,12-trimethoxy-3,8,13-tris(3-pyridylmethyloxy)-10,15-dihydro-5H-tribenzo[a,d,g]cyclononane (tris(3-pyridylmethyl)cyclotriguaiacylene) 1

Sodium hydride (60% NaH dispersed in mineral oil, 145 mg, 3.57 mmol) was added in small portions to a stirred solution of cyclotriguaiacylene (145 mg, 0.355 mmol) in dry DMF (6 mL). The

reaction mixture was stirred for 30 minutes under N_2 atmosphere. A solution of 3-bromomethyl pyridine (2.45 mmol) in dichloromethane (30 mL) was added via syringe and the reaction mixture stirred for a further 48 hours. Water (100 mL) and dichloromethane (100 mL) were added and the aqueous layer washed with dichloromethane (2 × 100 mL). The combined organic layers were washed with water (5 × 100 mL), brine (2 × 100 mL), dried over magnesium sulfate and solvent removed *in vacuo*. The residue was purified by column chromatography (silica, 5% methanol in dichloromethane), and triturated in ether to afford (tris(3-pyridylmethyl)cyclotriguaiacylene) **1** as an off-white solid. Yield 146 mg: 44.1%. Melting point 149.0 – 151.1 °C; HR MS (ES^+): *m/z* 682.2938 (MH^+); calculated for $C_{42}H_{40}O_6N_3$ 682.30. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 3.50 (d, 3H, endo-C<u>H</u>$_2$, J = 13.7 Hz), 3.76 (s, 9H, OC<u>H</u>$_3$), 4.71 (d, 3H, exo-C<u>H</u>$_2$, J = 13.7 Hz), 5.11 (m, 6H, O-C<u>H</u>$_2$), 6.72 (s, 3H, aryl-<u>H</u>), 6.85 (s, 3H, aryl-<u>H</u>), 7.29 (dd, 3H, Py-<u>H</u>^{5}, J = 5.1, 7.7 Hz), 7.76 (d, 3H, Py-<u>H</u>^{4}, J = 7.7 Hz), 8.58 (d, 3H, Py-<u>H</u>^{6}, J = 4.3 Hz), 8.69 (s, 3H, Py-<u>H</u>^{2}); ^{1}H NMR (500 MHz, DMSO-D_6) δ (ppm) = 3.54 (d, 3H, endo-C<u>H</u>$_2$, J = 13.2 Hz), 3.81 (s, 9H, OC<u>H</u>$_3$), 4.73 (d, 3H, exo-C<u>H</u>$_2$, J = 13.2 Hz), 5.14 (m, 6H, O-C<u>H</u>$_2$), 6.76 (s, 3H, aryl-<u>H</u>), 6.88 (s, 3H, aryl-<u>H</u>), 7.33 (dd, 3H, Py-<u>H</u>^{5}, J = 5.1, 7.8 Hz), 7.79 (d, 3H, Py-<u>H</u>^{4}, J = 7.8 Hz), 8.65 (d, 3H, Py-<u>H</u>^{6}, J = 4.3 Hz), 8.76 (s, 3H, Py-<u>H</u>^{2}); ^{1}H NMR (300 MHz, D_7-DMF) δ (ppm) = 3.67 (d, 3H, endo-C<u>H</u>$_2$, J = 13.83 Hz), 3.81 (s, 9H, OC<u>H</u>$_3$), 4.88 (d, 3H, exo-C<u>H</u>$_2$, J = 13.83 Hz), 5.20 (s, 6H, O-C<u>H</u>$_2$), 7.26 (s, 3H, aryl-<u>H</u>), 7.41 (s, 3H, aryl-<u>H</u>), 7.42 (m, 3H, Py-<u>H</u>^{5}), 7.92 (d, 3H, Py-<u>H</u>^{4}, J = 7.63 Hz), 8.57 (d, 3H, Py-<u>H</u>^{6}, J = 4.77 Hz), 8.75 (s, 3H, Py-<u>H</u>^{2}); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) = 149.4, 148.76, 148.71, 146.6, 135.2, 133.2, 132.9, 131.7, 123.6, 116.8, 113.8, 69.4, 56.2, 36.5. Infrared analysis (FT-IR, cm^{-1}) 3006 (m, aliphatic <u>C-H</u>), 2932 (m, C=<u>C-H</u>), 1668 (m, aromatic C=N), 1517 (s, aromatic C=C), 1129 (m, C-O). Analysis for $C_{42}H_{40}O_6N_3$ (calculated, found) C (73.88, 74.09), H (5.90, 6.10), N (6.15, 5.85).

4-(5-pyrimidyl)benzoic acid



Prepared according to literature methods with minor modifications.[2]

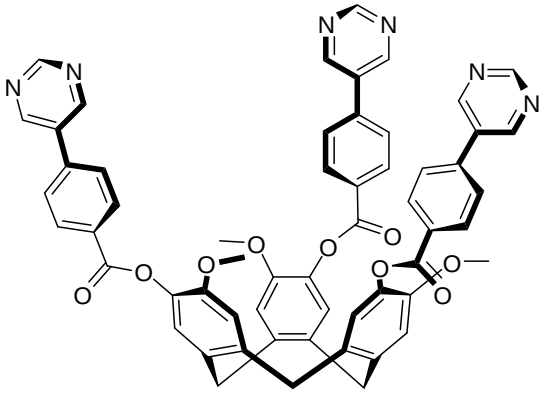
$Pd(PPh_3)_4$ (0.94 g, 0.81 mmol) was added to a degassed solution 4-carboxybenzene boronic acid (2.553 g, 15.39 mmol) and 5-bromopyrimidine (2.446 g, 15.38 mmol) in 0.4 M Na_2CO_3 solution (75 mL) and acetonitrile (75 mL). The mixture was heated at 90°C under N_2 for 16 hours. The hot

suspension was filtered. The filtrate was acidified with 1 M HCl and the volume reduced by half *in vacuo*. The white solid was collected by filtration to give 4-(5-pyrimidyl)benzoic acid partially as the hydrochloride salt. Yield 2.84 g, 85 %. ^{1}H NMR (500 MHz, d_6-DMSO): δ (ppm) 9.23 (1H, s, pyrimidine H^{2}), 9.20 (2H, s, pyrimidine H^{4}), 8.06 (2H, d, phenyl H^{2}, J = 8.6 Hz), 7.95 (2H, d, phenyl H^{3}, J = 8.6 Hz). ^{13}C NMR (75 MHz, d_6-DMSO): δ (ppm) 167.2, 158.2, 155.4, 138.3, 132.7, 131.4, 130.4, 127.5. Elemental analysis: Found C 60.35, H 3.75, N 12.25; $C_{11}H_8N_2O_2(HCl)_{0.5}$ requires C 60.49, H 3.92, N 12.83 %.

4-(5-pyrimidyl) benzoyl chloride hydrochloride

4-(5-Pyrimidyl)benzoic acid hydrochloride (1.09 g, 4.62 mmol) was heated at reflux under N_2 in thionyl chloride (10 mL) containing a few drops of DMF for 24 hours. The thionyl chloride was removed *in vacuo* and the off-white solid washed with diethyl ether to give 4-(5-pyrimidyl) benzoyl chloride hydrochloride as an off-white powder in approximately quantitative yield. The crude product was used without further purification.

(±)-2,7,12-trimethoxy-3,8,13-tris[4-(5-pyrimidyl)benzoyl]-10,15-dihydro-5H-tribenzo[a,d,g]cyclononane (tris[4-(5-pyrimidyl)benzoyl]cyclotriguaiacylene) 2



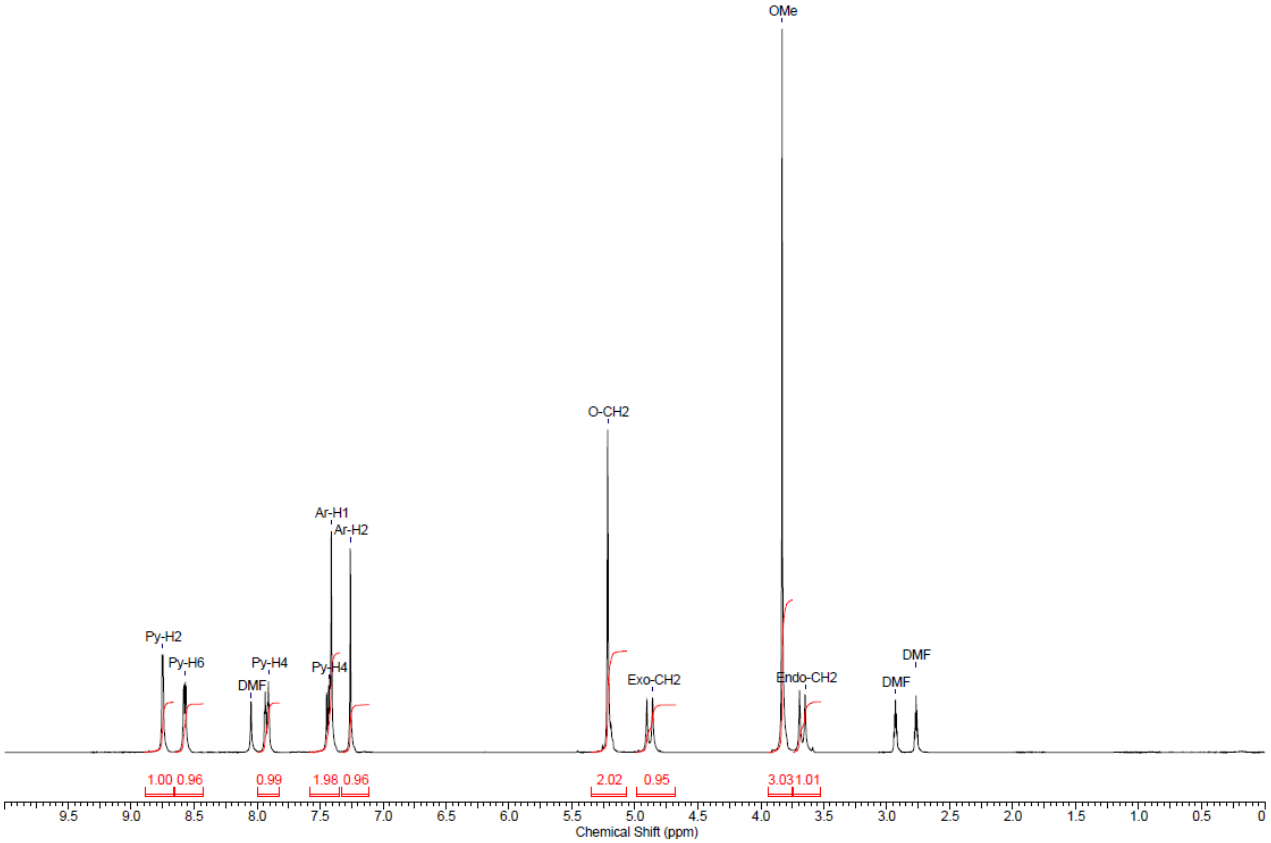
Cyclotriguaiacylene (1.02 g, 2.50 mmol) was dissolved in dry THF (160 mL) under a N_2 atmosphere and cooled to -78°C in an ice bath. Triethylamine (10 mL) was added to the reaction, which was stirred for 30 minutes. 4-(5-Pyrimidyl) benzoyl chloride hydrochloride (3.20 g, 12.5 mmol) was added to the solution which was stirred at -78°C for one hour, and then at room temperature for 2 days. The solution was taken to dryness *in vacuo* and the residue triturated with ethanol to give crude tris[4-(5-pyrimidyl)benzoyl]cyclotriguaiacylene (L^{10}) as a white solid. The crude product was purified by column chromatography (alumina, 0-1.5 % MeOH in CH_2Cl_2). Yield 1.93 mg (81%). M.p. > 270 °C. HR MS (ES^{+}): *m/z* 955.3108 (*MH*$^{+}$); calcd. for $C_{57}H_{43}N_6O_9$ 955.3086. ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 9.27 (3H, s, pyrimidine H^{2}), 9.02 (6H, s,

pyrimidine H^4), 8.35 (6H, d, phenyl H^2, J = 8.6 Hz), 7.73 (6H, d, phenyl H^3, J = 8.6 Hz), 7.21 (3H, s, aryl CH), 6.98 (3H, s, aryl CH), 4.86 (3H, d, CTG CH_2, J = 13.7 Hz), 3.82 (9H, s, CH_3), 3.71 (3H, d, CTG CH_2, J = 13.7 Hz). ^{1}H NMR (500 MHz, d_6-DMSO): δ (ppm) 9.27 (3H, s, pyrimidine H^2), 9.25 (6H, s, pyrimidine H^4), 8.23 (6H, d, phenyl H^2, J = 8.1 Hz), 8.06 (6H, d, phenyl H^3, J = 8.1 Hz), 7.57 (3H, s, aryl CH), 7.35 (3H, s, aryl CH), 4.91 (3H, d, CTG CH_2, J = 13.2 Hz), 3.70-3.75 (12H, d, CTG CH_2 and CH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.5, 158.6, 155.4, 150.3, 139.5, 139.0, 138.5, 133.8, 132.0, 131.8, 130.5, 127.5, 124.5, 114.8, 56.7, 37.0. IR (solid state): ν (cm^{-1}) 3039 (w), 2962 (w), 2936 (w), 2852 (w), 1730 (s), 1610 (m), 1575 (w), 1551 (m), 1506 (s), 1477 (w), 1446 (w), 1414 (m), 1398 (m), 1327 (m), 1263 (s), 1206 (m), 1180 (s), 1141 (m), 1094 (s), 1065 (s), 1019 (w), 1001 (m), 924 (w), 907 (m), 853 (m), 764 (m), 747 (m), 724 (m), 696 (m), 640 (m), 624 (m), 587 (w), 545 (w), 529 (w). Found C 70.90, H 4.45, N 8.55; $C_{57}H_{42}N_6O_9(H_2O)_{0.5}$ requires C 71.02, H 4.50, N 8.72 %

$[Ag_6(1)_4(DMF)].6(ClO_4).n(solvent)$ $AgClO_4.H_2O$ (5.04 mg, 0.02235 mmol) and **1** (10.01 mg, 0.01495 mmol) were dissolved in dimethylformamide (DMF) (~2 mL). Diethylether vapours were diffused into the solution. Small colourless crystals formed after ~4 days, and were analyzed via single crystal X-ray analysis. ***CAUTION: Although we experienced no problems, perchlorate salts are known to be shock sensitive and should be handled with due care.*** Yield 0.0532 mg. MS (ES^+): *m/z* 790.2 $[Ag(\mathbf{1})]^+$ (calcd. 789.2), 1887.2 $\{[Ag_3(\mathbf{1})_2(ClO_4)_2\}^+$ (calcd. 1885.0), 2567.5 $\{[Ag_3(\mathbf{1})_3(ClO_4)_2\}^+$ (calcd. 2566.3), 2774.3 $\{[Ag_4(\mathbf{1})_3(ClO_4)_3\}^+$ (calcd. 2773.6), 3457.6 $\{[Ag_4(\mathbf{1})_4(ClO_4)_3\}^+$(calcd. 3454.9), 3663.4 $\{[Ag_5(\mathbf{1})_4(ClO_4)_4\}^+$ (calcd. 3662.3).

^{1}H NMR (300 MHz, DMF-D_6) δ (ppm) = 3.70 (d, 3H, endo-C<u>H</u>$_2$), 3.78 (s, 9H, OC<u>H</u>$_3$), 4.88 (d, 3H, exo-C<u>H</u>$_2$), 5.27 (s, 6H, O-C<u>H</u>$_2$), 7.26 (s, 3H, aryl-<u>H</u>), 7.41 (s, 3H, aryl-<u>H</u>), 7.73 (m, 3H, Py-<u>H</u>^{4}), 8.18 (m, 3H, Py-<u>H</u>^{5}), 8.75 (s, 3H, Py-<u>H</u>^{6}), 8.86 (d, 3H, Py-<u>H</u>^{2}). Broadening of the peaks makes elucidation of integration and splitting patterns difficult, see figure S1.

As anticipated, microanalysis indicates a higher level of solvation than refined in the crystal structure, SQUEEZE indicates that there is sufficient void space in the lattice for added solvent. Additional solvent added to formula accounts for 1280 e.). Analysis for $[Ag_6(C_{42}H_{39}N_3O_6)_4].6(ClO_4).6DMF.8(H_2O)$ (% calcd., found) C (49.04, 48.65), H (4.74, 4.63), N (5.54, 5.85). Infrared analysis (FT-IR, cm^{-1}) 3425 (broad), 2937, 1654, 1609, 1511, 1443, 1387, 1265, 1090 (Cl-O), 945 (Cl-O), 802, 678, 623 (Cl-O).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Ar-H2
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Py-H6
Py-H4
DMF
Py-H4
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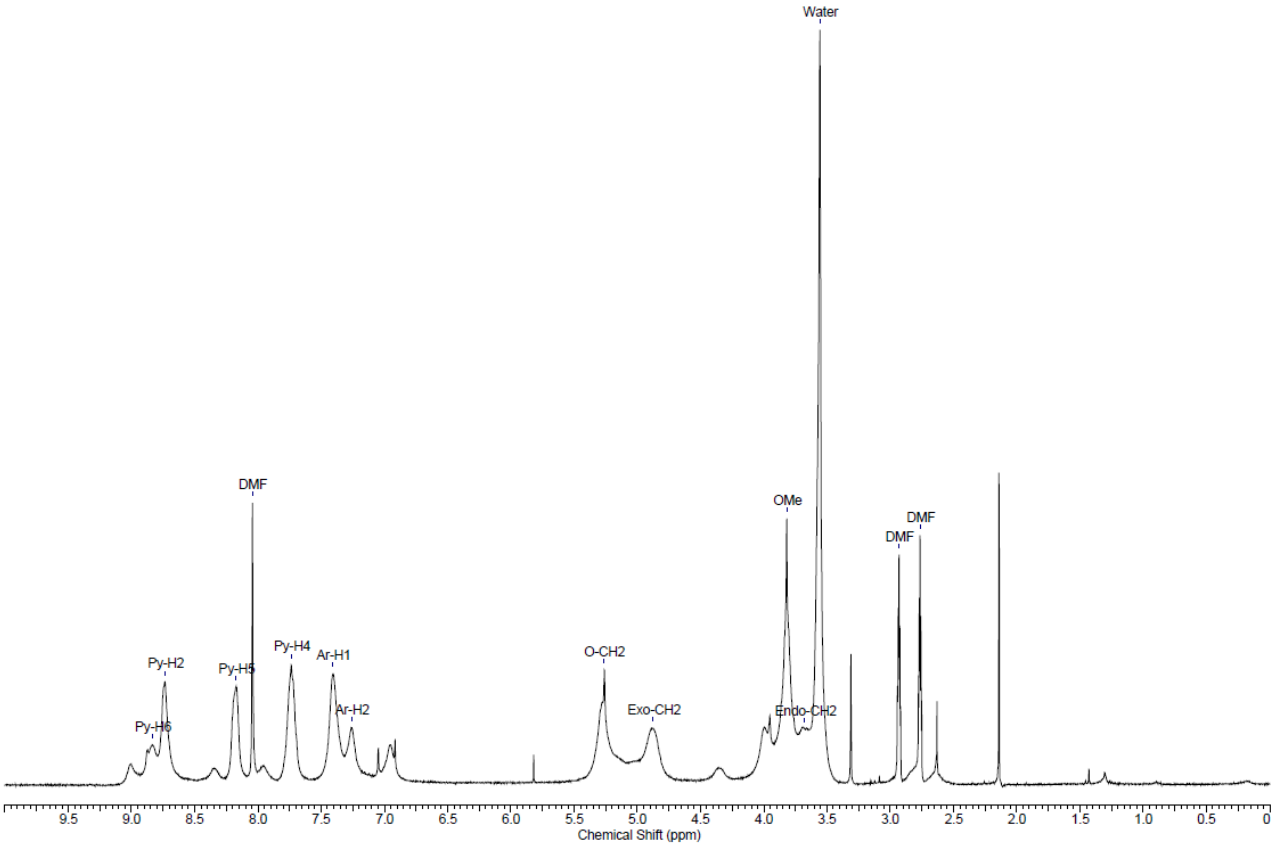
Chemical Shift (ppm)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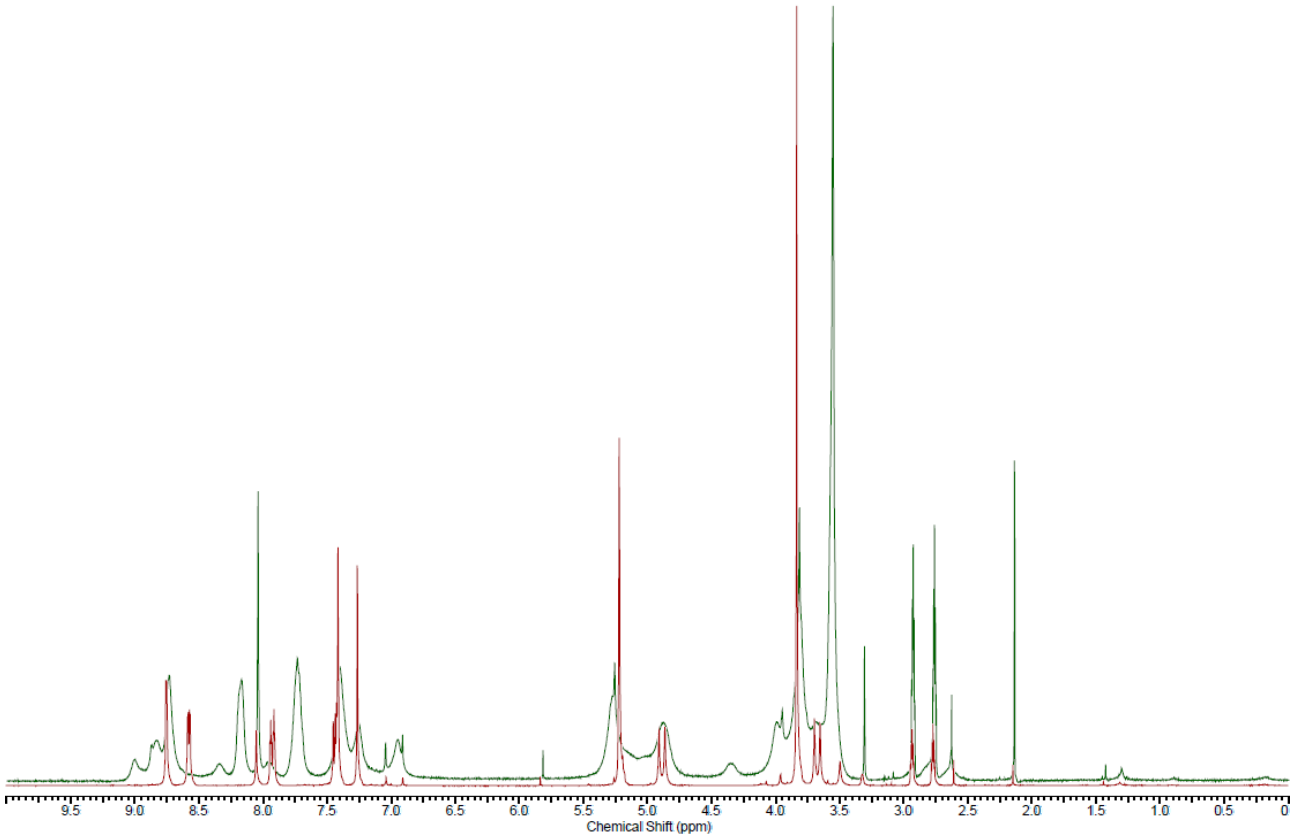

*Figure S1: ^{1}H NMR spectra in d_7-DMF of (a) ligand **1**; (b) 3:2 mixture of $Ag(ClO_4)$ and ligand **1**; (c) over-laid plots of ligand **1**(red) and complex (green)..*

$[Cu_3(2)_2(H_2O)_6](NO_3)_6.n(solvent)$ A solution of $Cu(NO_3)_2.2.5H_2O$ (4 mg, 0.017 mmol) in DMF (0.5 mL) was added to a solution of **2** (10 mg, 0.010 mmol) in DMF (1 mL). Diethyl ether vapour diffusion into the solution resulted a small quantity of blue crystals which were suitable for X-ray crystallography. Yield 6 mg. ES MS (DMF solution): 2989.8 $\{Cu(\mathbf{2})_3(NO_3)\}^+$ (calcd. 2988.4), 2035.5 $\{Cu(\mathbf{2})_2(NO_3)\}^+$ (calcd. 2036.5), 1079.2 $\{Cu(\mathbf{2})(NO_3)\}^+$ (calcd. 1080.2), 954.3 $\{\mathbf{2}H\}^+$ (calcd. 955.3). IR (solid state): ν (cm^{-1}) 1731 (s), 1645 (s), 1610 (m), 1504 (m), 1418 (m), 1394 (s), 1359 (s), 1206 (m), 1176 (s), 1137 (m), 1091 (m), 1061 (m), 1010 (m), 941 (w), 926 (w), 908 (w), 858 (m), 766 (m), 748 (w), 711 (m), 699 (m), 665 (w), 655 (w), 643 (w), 623 (w). $[Cu_3(C_{57}H_{42}N_6O_9)_2].3(NO_3).(DMF).4(H_2O)$ (% calcd., found) C (57.77, 57.30), H (4.11, 4.20), N (9.22, 9.40).

$[Ag_3(2)_2](BF_4)_3.n(solvent)$ A solution of $[Ag(MeCN)_4]BF_4$ (11 mg, 0.031 mmol) in DMSO (0.5 mL) was added to a solution of **2** (15 mg, 0.016 mmol) in DMSO (1 mL). Ethyl acetate vapour diffusion into the solution resulted in colourless crystals of $[Ag_3(\mathbf{2})_2](BF_4)_3$ which were suitable for

single crystal X-ray crystallography. Analysis for $[Ag_3(C_{57}H_{42}N_6O_9)_2].3(BF_4).(DMSO)$ (% calcd., found) C (54.14, 54.00), H (3.53, 3.45), N (6.54, 6.60). ^{1}H NMR of a d_6-DMSO solution of $[Ag(MeCN)_4]BF_4$ and **2** showed no shifts with respect to the spectrum of **2** alone. ES MS (DMSO solution): 2973.8 $\{Ag(\mathbf{2})_3\}^+$ (cald. 2973.8), 2017.5 $\{Ag(\mathbf{2})_2\}^+$ (cald. 2018.5), 1063.2 $\{Ag(\mathbf{2})\}^+$ (calcd. 1064.2).

Crystal Structure Analysis

Crystals were mounted on a fibre under oil and flash frozen to 150(1) K using a stream of cold N_2. Data were collected on a Bruker-Nonius X8 diffractometer with a Mo-rotating anode (λ = 0.71073 Å). Data were corrected for Lorenztian and polarization effects and absorption corrections were applied using multi-scan methods. The structures were solved by direct methods using SHELXS-97 and refined by full- or block-matrix on F^2 using SHELXL-97. [3] Unless otherwise specified, all non-hydrogen atoms were refined as anisotropic, and hydrogen positions were included at geometrically estimated positions. In all three structures there was significant void space within the lattice containing diffuse residual electron density that could not be meaningfully refined as solvent or counter-anions. Hence the SQUEEZE routine of PLATON[4] was employed and led to significant reductions in *R*-values in all cases. Additional details of the refinements are given below.

$[Ag_6(1)_4(DMF)].6(ClO_4).3(DMF)$ The crystals were weakly diffracting and no high angle data was observed. The structure is disordered and the limited data available also limits the quality of the refinement. Oxygen positions of perchlorates, all positions of solvent DMF, disordered methyl groups and one ring carbon were refined isotropically. Most perchlorate anions showed considerable positional disorder of the O atoms, and one perchlorate anion was refined across two molecular sites. Some Cl-O bond lengths were restrained. All aromatic rings were refined with a rigid body refinement. Some U_{ij} values of C and N atoms in the ligands were restrained to be similar. The crystal was a racemic twin with refined Flack parameter 0.59(4). The structure could not be solved in space group *C*2/*c*, and the refinement in space group *Cc* solution did not show correlations between parameters on different atoms, and the ADDSYM routine of PLATON[4] did not identify additional symmetry.

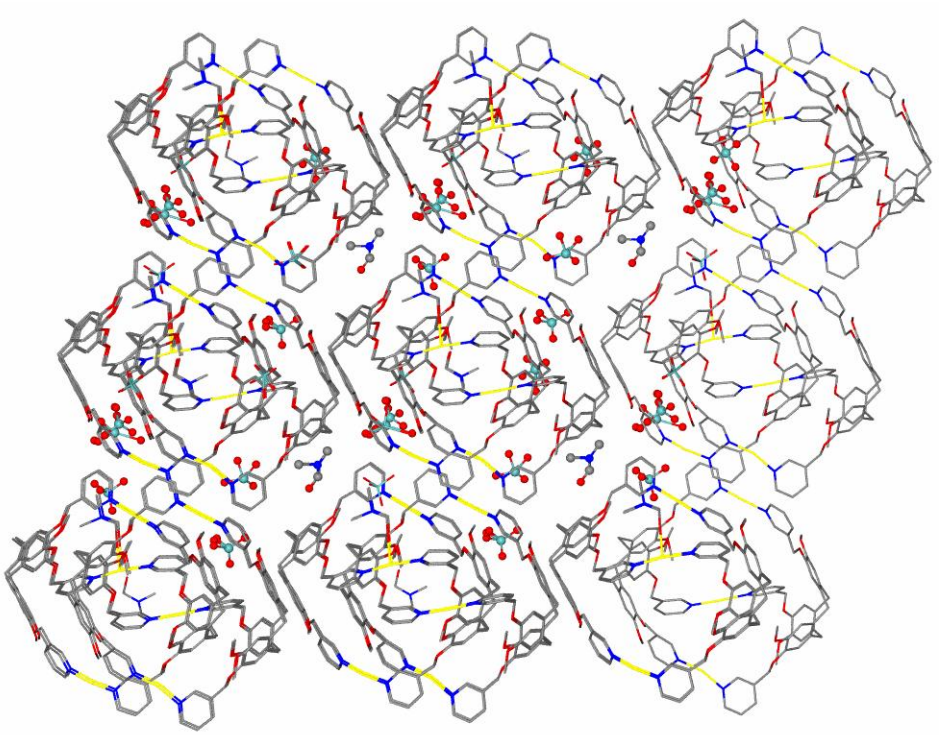

*Figure S2: Packing diagram of complex [Ag_6(**1**)$_4$(DMF)].6(ClO_4).3(DMF)*

[Cu_3(2)$_2$(H_2O)$_6$](NO_3)$_6$ Terminal aquo and nitrate ligands were disordered with each O atom refined across two positions each at 50% occupancy, Figure S3. These disordered ligands were refined isotropically.

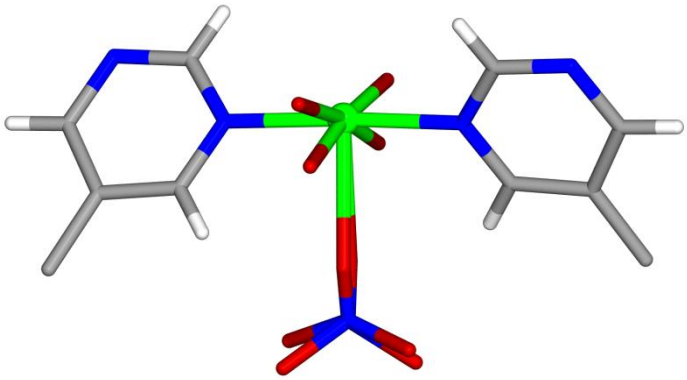

Figure S3: Disorder of aquo and nitrate ligands around Cu centre (green).

[Ag_3(2)$_2$](BF_4)$_3$.solvent $C_{114}H_{84}Ag_3B_3F_{12}N_{12}O_{18}$, *Mr* = 2493.97, trigonal, *a* = 16.5508(8), *c* = 106.295(11) Å, V = 25215(3) Å^3, space group *R*-3*c*, Z = 6, θ_{max} = 25.99°, 223 parameters, R_1 = 0.1113 (for 4700 data $I>2\sigma(I)$), wR_2=0.3260 (all 5516 data). CCDC 812989. Counter-anions and

solvent molecules could not be located in the difference map and were not included in the refinement (counter-anions are included in molecular formula).

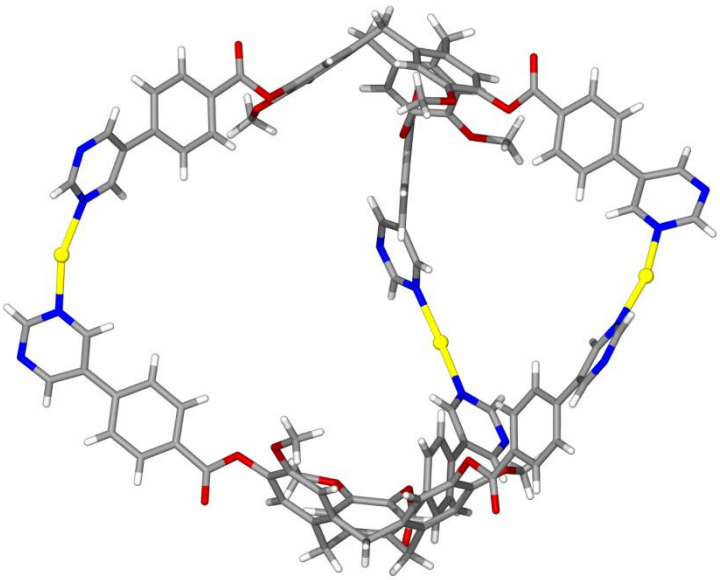

Figure S4: Metallo-cryptophane from the crystal structure of complex $[Ag_3(2)_2](BF_4)_3$.

1. J. Canceill, J. Gabard, and A. Collet, *Chem. Commun*, 1983, 1278.
2. Y. Gong and H. W. Pauls, *Synlett*, 2000, 829.
3. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
4. A. L. Spek, *Acta Cryst.*, 1990, **A46,** C34.

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