Control of metallo-supramolecular assemblies via steric, hydrogen bonding and argentophilic interactions; formation of a 3-dimensional polymer of circular helicates.

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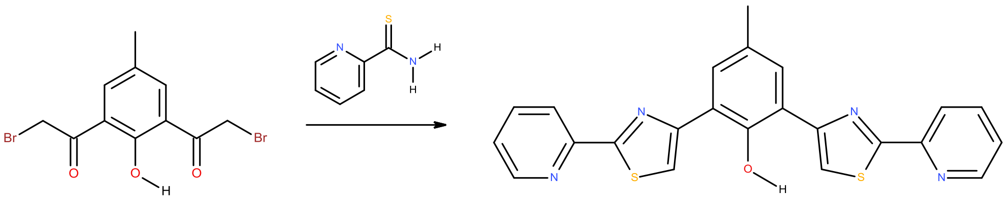
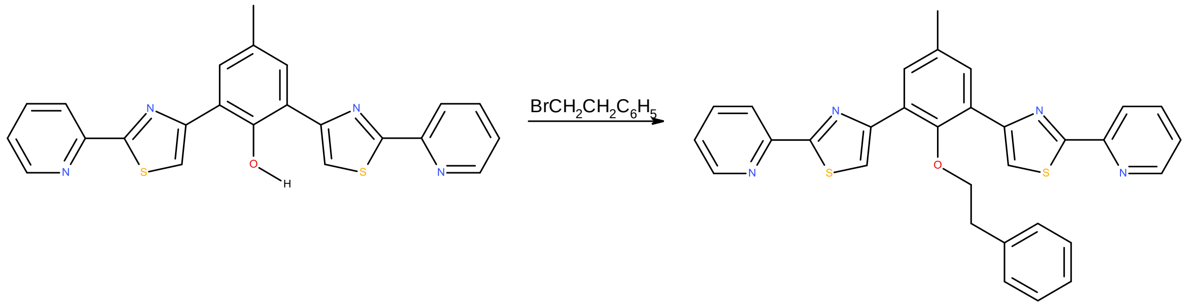
Electronic Supplementary Information.

Synthetic Procedures for ligands $L^1 - L^3$.

Chemicals were purchased and used without further purification apart from 1,3-di(α-bromoacetyl)cresol which was prepared by a previously reported method.[1a] ^{1}H NMR spectra were recorded either on a 400 MHz Bruker Advance DP X400 or on a 500 MHz Bruker Advance 500. Mass spectra were obtained on a Bruker MicroTOF-q LC mass spectrometer.

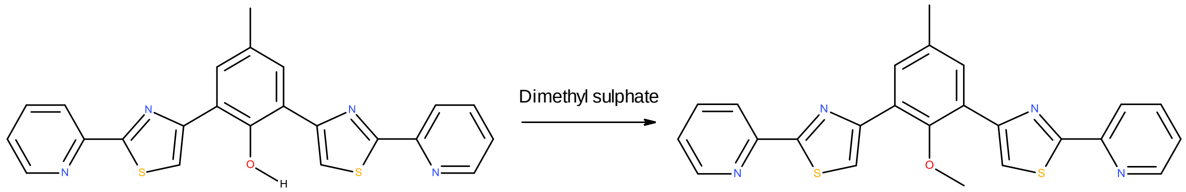


Synthesis of **L^1**. To a round bottomed flask charged with pyridine-2-thioamide (87 mg, 0.63 mmol) and 1,3-di(α-bromoacetyl)cresol (100 mg, 0.29 mmol) and equipped with a magnetic follower was added ethanol (30 ml) and the reaction heated to 60°C under nitrogen for 12 hrs. After this time a yellow precipitate formed, which was isolated by filtration and washed with EtOH (3 x 5 ml) and Et_2O (3 x 5 ml). This solid was then suspended in concentrated aqueous ammonia (sp.G. 0.88, 10 ml) for 12 hrs after which time the yellow solid was isolated by filtration and washing with water (2 x 2 ml), EtOH (2 x 2 ml) and Et_2O (2 x 2 ml) giving pure ligand **L^1** (47 mg, 75 %). ^{1}H NMR (400 MHz, $(CD_3)_2SO$) δ: 12.4 (s, 1H, -OH); 8.7 (d, *J*= 4.52, 2H, py); 8.48 (s, 2H, tz); 8.28 (d, *J*= 7.84, 2H, py); 8.05 (td, *J*= 7.68, 1.48, 2H, py); 7.98 (s, 2H, Ph); 7.57 (dd, *J*= 6.94 Hz, 5.12, 2H, py); 2.42 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.6, 153.3, 151.5, 150.3, 150.2, 138.5, 129.3, 128.5, 126.0, 120.3, 119.9, 119.4, 20.9 ($-CH_3$). ESI-MS *m/z* 428 ($M + H^+$). HR ESI-MS found 429.0832 $C_{23}H_{17}N_4OS_2$ requires 429.0838 (error 1.32 ppm).



Synthesis of **L**^{2}.

A two necked round bottom flask containing **L**$^{\mathbf{1}}$ (140 mg, 0.26 mmol) and sodium hydride (60% dispersion in mineral oil, 100 mg, 2.5 mmol) was placed under a dinitrogen atmosphere and left to purge for 30 minutes. To this anhydrous DMF (25 mL) was added and left to stir at 80 ^{0}C for 1 h. After this time (2-Bromoethyl) benzene (0.5 ml, 3.7 mmol) was added and left for 12 h. The reaction was cooled to room temperature and methanol was added whilst under N_2. The solvent was removed by rotary evaporation. Purification *via* column chromatography (Al_2O_3, DCM) (66 mg, 48 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.68 (d, *J*= 4.8, 2H, py); 8.37 (d, *J*= 7.92, 2H, py); 8.00 (s, 2H, tz); 7.85 (td, *J*= 7.68, 1.6, 2H, py); 7.71 (s, 2H, Ph); 7.39-7.32 (m, overlapping, 5H, Ph) 7.24 (d, *J*= 6.48, 2H, py); 3.85 (t, *J*= 6.28, 2H, -O$CH_2$$CH_2$); 2.96 (t, *J*= 6.2 Hz, 2H, -O$CH_2$$CH_2$); 2.49 (s, 3H, -$CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.3, 152.5, 152.2, 151.5, 149.5, 138.5, 137.0, 134.3, 130.7, 129.5, 128.7, 128.5, 126.8, 124.5, 119.9, 119.7, 73.6 (-O$CH_2$$CH_2$), 37.3 (-O$CH_2$$CH_2$), 21.1 (-$CH_3$). ESI-MS *m/z* 532 (M + H^+). HR ESI-MS found 532.1385 $C_{31}H_{24}N_4OS_2$ requires 532.1392 (error 1.22 ppm).



Synthesis of L$^{\mathbf{3}}$**.** To a two-necked round bottom flask charged with **L**$^{\mathbf{1}}$ (120 mg 0.28 mmol) and NaH (60% dispersion in mineral oil, 100 mg, 2.5 mmol) and equipped with a magnetic follower was purged with dinitrogen. After 10 mins anhydrous DMF (20 ml) and the reaction heated to 60°C for 1 hr. After this time dimethyl sulphate (0.5 ml, 5 mmol) was added and the reaction stirred at this temperature for at least 24 hrs. After this time EtOH (5 ml) was added (to quench any unreacted sodium hydride) and the solvents removed by rotary evaporation. The resultant brown oil was then suspended in water (20 ml) and extracted in DCM (2 x 50 ml) and after removal of the solvent the product was purified by column chromatography (Al_2O_3, DCM) giving ligand $\mathbf{L^2}$ as an off-white solid (55 mg, 45 %). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.58 (d, *J* = 4.36, 2H, py), 8.30 (d, *J* = 7.92, 2H, py), 8.05 (s, 2H), 7.97 (s, 2H), 7.77 (dt, *J* = 7.7, 1.7, 2H, py), 7.28 (ddd, *J* = 7.4, 4.8, 1.0 Hz, 2H, py), 3.56 (s, 3H, $-OCH_3$), 2.43 (s, 3H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 153.7, 152.6, 151.5, 149.5, 137.1, 134.3, 130.8, 128.2, 124.5, 119.9, 119.8, 60.1 ($-OCH_3$), 21.1 ($-CH_3$). ESI-MS *m/z* 442 (M + H^+). HR ESI-MS found 443.0986 $C_{24}H_{19}N_4OS_2$ requires 443.0995 (error 1.71 ppm).

1a. S. Bullock, L. P. Harding, M. Moore, S. A. F. Piela, C. R. Rice, L. Towns-Andrews and M. Whitehead, *Dalton Trans.*, 2013, **42**, 5805–5811.

Crystallography.

Single crystal X-ray diffraction data was collected at 150(2) K on either a Bruker Apex Duo diffractometer equipped with a graphite monochromated Mo(Kα) radiation source or a Bruker Venture diffractometer equipped with a Cu-IμS source and a cold stream of N_2 gas. Solutions were generated by conventional heavy atom Patterson or direct methods and refined by full-matrix least squares on all F^2 data, using SHELXS-97 and SHELXL software respectively. Absorption corrections were applied based on multiple and symmetry-equivalent measurements using SADABS.

For $[Ag_n(\mathbf{L}^2)_n]^{n+}$ the tetrafluoroborate counter anions were disordered and these were modelled in two positions using the *PART* instruction. In all cases of disordered atoms/molecules *DELU, SIMU*, *SADI*, and in some cases *ISOR*, constraints were used in the least-squares refinement. Furthermore, the structure contained disorder that could not be satisfactorily modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids in the crystal structure.[1b] The solvent mask removed a total of 208.9 electrons in the unit cell which corresponds to five molecules of nitromethane and a molecule of diisopropylether in the unit cell.[1b]

For $[Ag_6(\mathbf{L}^3)_6]^{6+}$ one of the tetrafluoroborate counter anions was disordered and refined poorly. It was constrained using *DELU, SIMU, SADI,* and in some cases *ISOR* and its occupancy was fixed to 10.50 and using this the molecule refined reasonably well. Due to this the occupancy of the counter anions is low (e.g. six silver ions and five tetrafluoroborate anions) however, the valance of the cation is not in any doubt and the structure refined well using this value. Furthermore, the structure contained disorder that could not be satisfactorily modelled and as a result the diffuse electron density was removed using the solvent mask facility in Olex2, resulting in voids in the crystal structure.[1b] The solvent mask removed a total of 644.3 electrons in the unit cell (107.4 per asymmetric unit) which corresponds to five molecules of acetonitrile in the asymmetric unit (30 in the unit cell).

Synthesis of $[Ag_2(\mathbf{L^1})_2]^{2+}$. To a suspension of $\mathbf{L}^1$ (0.01 g 0.023 mmol) in MeCN (2 ml) was added $Ag(ClO_4)$ (0.005 g, 0.024 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a yellow solution. To this chloroform was allowed to slow diffuse into the solution giving yellow crystals after a few days (0.009g 66%). ^1H NMR (400 MHz, CD_3CN) δ (ppm) 12.45 (s, 1H, OH), 8.62 (d, *J* = 4.8, 2H, py), 8.09 (d, *J* = 8.5, 2H, py), 8.08 (s, 2H, tz), 7.95 (dt, *J* = 7.8, 1.5, 2H, py), 7.77 (s, 2H, Ph), 7.51 (ddd, *J* = 7.5, 4.8, 0.8 Hz, 2H, py), 2.31 (s, 3H, -CH_3). ESI-MS *m/z* = 1171 corresponding to $\{[Ag_2(\mathbf{L}^1)_2](ClO_4)\}^+$. Small amounts of a black impurity were present (presumably reduction of Ag(I)) which made a satisfactory elemental analysis unobtainable.

Synthesis of $[Ag_n(\mathbf{L^2})_n]^{n+}$. To a suspension of $\mathbf{L}^2$ (0.01 g 0.019 mmol) in $MeNO_2$ (2 ml) was added $Ag(BF_4)$ (0.004 g, 0.024 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a colourless solution. To this diisopropyl ether was allowed to slow diffuse into the solution giving colourless crystals after a few days (0.01 g 73%). ^1H NMR (400 MHz, CD_3NO_2) δ (ppm) 8.63 (brs, 2H), 8.25 (brs, 5H overlapping), 7.85 (brs, 2H), 7.75 (brs, 2H), 7.09 (brs, 3H, overlapping), 6.86 (brs, 2H), 3.81 (brs, 2H), 2.81 (brs, 2H) and 1.81 (brs, 3H). ESI-MS *m/z* = 897 corresponding to $\{[Ag_2(\mathbf{L}^2)](trif)\}^+$, 1173 corresponding to $\{[Ag(\mathbf{L}^2)_2]\}^+$, 1429 corresponding to $\{[Ag_2(\mathbf{L}^2)_2](trif)\}^+$ and 1687 corresponding to $\{[Ag_3(\mathbf{L}^2)_2(trif)_2\}^+$. In the same manner as $[Ag_2(\mathbf{L^1})_2]^{2+}$ small amounts of silver metal was present negating the use of elemental analysis.

Synthesis of $[Ag_6(\mathbf{L^3})_6]^{6+}$. To a suspension of $\mathbf{L}^3$ (0.01 g 0.23 mmol) in $MeNO_2$ (2 ml) was added $Ag(BF_4)$ (0.0045 g, 0.24 mmol) and the reaction briefly heated and sonicated until all the ligand dissolved and gave a colourless solution. To this diisopropyl ether was allowed to slow diffuse into the solution giving pale yellow crystals after a few days which were isolated by filtration and dried under vacuum (0.009 g, 62 %). Found: C, 44.7; H, 2.8; N, 8.7%; $C_{24}H_{18}N_4OS_2AgBF_4$ requires C, 45.2; H, 2.8; N, 8.8%. ^1H NMR (400 MHz, CD_3CN) δ (ppm) 8.62 (d, *J* = 4.8, 2H, py), 8.22 (d, *J* = 7.9, 2H, py), 8.04 (s, 2H, tz), 7.99 (dt, *J* = 7.7, 1.6, 2H, py), 7.89 (s, 2H, Ph), 7.51 (ddd, *J* = 7.5, 5.0, 0.7 Hz, 2H), 3.48 (s, 3H, -OCH_3), 2.24 (s, 3H, -CH_3). ESI-MS *m/z* = 3735 corresponding to $\{[Ag_6(\mathbf{L}^3)_6](BF_4)_5\}^+$ along with lower molecular weight species e.g. $\{[Ag_n(\mathbf{L}^3)_n](BF_4)_{n-1}\}^+$ where n = 1 to 5.

1b. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339-341.

Compound Reference	$[\mathrm{Ag}_2(\mathbf{L}^1)_2]^{2+}$	$[\mathrm{Ag}_n(\mathbf{L}^2)_n]^{n+}$	$[\mathrm{Ag}_6(\mathbf{L}^3)_6]^{6+}$
CCDC	1507028	1507029	1507030
Chemical Formula	$C_{48}H_{34}Ag_2Cl_8N_8O_{10}S_4$	$C_{127}H_{105}Ag_4B_4F_{16}N_{19}O_{10}S_8$	$C_{144}H_{108}Ag_6B_5F_{20}N_{24}O_6S_{12}$
Formula Mass	1510.47	3092.64	3736.71
Crystal System	Triclinic	Triclinic	Trigonal
a/Å	7.5797(2)	7.820(4)	26.047(11)
b/Å	10.6965(3)	18.768(9)	26.047(11)
c/Å	17.3538(5)	25.836(12)	41.751(2)
α/°	103.551(1)	80.419(16)	90
β/°	101.676(1)	82.135(19)	90
γ/°	90.482(1)	83.58(3)	120
Unit cell volume/Å^3	1337.20(7)	3688(3)	24530.9(19)
Temperature/K	150(2)	150(2)	150(2)
Space group	P -1	P -1	R -3 c
No. of formula units per unit cell, Z	1	1	6
Radiation type	Mo K\α	Mo K\α	Mo K\α
Absorption coefficient, μ/mm^{-1}	1.356	0.715	0.939
No. of reflections measured	31032	101583	41376
No. of independent reflections	8125	18381	8300
R_{int}	0.0438	0.0990	0.0510
Final R_1 values ($I>2\sigma(I)$)	0.0492	0.0588	0.0547
Final $wR(F^2)$ values ($I>2\sigma(I)$)	0.1297	0.1467	0.1432
Final R_1 values (all data)	0.0705	0.0961	0.0983
Final $wR(F^2)$ values (all data)	0.1424	0.1640	0.1697
Goodness of fit on F^2	1.068	1.0362	1.0586
largest peak and hole (eÅ^{-3})	1.735 / -2.228	1.792 / -1.444	2.301 / -0.760