Supporting Information

A nanoporous chiral metal-organic framework material that exhibits reversible guest adsorption

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Single crystal structural refinement

Single crystals of 1·X(MeCN/EtOH) were found to be weakly diffracting. Such a problem is relatively common in the field of framework materials and is typical for highly porous materials with extensive structural disorder. Numerous attempts were made at growing the crystals under a variety of conditions to slow the crystallisation process and give less disordered crystals. Various other techniques, such as cold mounting or desolvating the crystals before analysis were also attempted. Data collection at the ChemMatCars beamline at the Advanced Photon Source, Argonne National Laboratory, gave no discernible improvement in data quality. All methods to obtain a better diffraction pattern were unsuccessful, indicating that it is likely that the limitations to the data and resulting refinement model are intrinsic to the inherent structural disorder. The structural model reported was refined against the best diffraction data obtained. When combined with the known chemical composition of the ligand and other structural information from related materials, a sound model of the framework structure was obtained, albeit with no information on anion location.

The structure was solved and refined in both of the enantiomeric, hexagonal chiral space groups P6₁ and P6₅. In each case the chirality of the ligand was held to the known (S,S,S,S) conformation. The space group P6₁ was selected on the basis of a more favourable Flack parameter,¹ 0.13(14) vs. 0.68(15), and after careful analysis of the hydrogen bonding interactions in the two structural models. The space group P6₅ gave a number of highly unlikely short contacts with the methyl groups of the ligand, which in P6₁ become reasonable hydrogen bonding interactions from the alcohol groups. Further, isotropic thermal displacement parameters for the methyl carbon and hydroxyl oxygen atoms were found to refine to more reasonable and similar values in this setting.
With the exception of the Ag(I) ions all atoms were modelled isotropically. A number of atoms in the ligand have unrealistically large thermal parameters and are heavily restrained. However, the composition of the ligand is definitively known from a combination of $^1$H and $^{13}$C NMR, IR and high resolution mass spectrometry. Due to the highly favourable interaction of the π-orbitals throughout the ligand and steric considerations, it is probable that the Schiff base would adopt the $E$ conformation giving a highly planar ligand.$^2$ From this, the conformation of the ligand, while poorly resolved in the model, can be safely assumed to be correct.

Hydrogen atoms were modelled on the aromatic linkers and all chiral centres with the exception of C54 and C64. Accurate hydrogen positions could not be calculated for C54 and C64 due to poor refinement of the chiral centres. As the NO$_3^-$ anions and the Hydrogen atoms not mentioned previously are absent from the model the calculated molecular formula would be incorrect. The crystallographic information has therefore been changed to use the correct formula of [Ag$_4$(L(S))$_3$(NO$_3$)$_4$] (C$_{60}$H$_{78}$N$_{28}$O$_{24}$Ag$_4$). This formula is consistent with the elemental analysis, gives a molecular weight of 2006.93 g mol$^{-1}$ and a calculated crystal density of 1.3057 g cm$^{-3}$. It is these calculated values that were used in all analysis for calculating the number of molecules adsorbed per formula unit. The methyl group C55 and alcohol group O51 are modelled as rotationally disordered over two sites about the C54 chiral centre.
Table S.1 – Summary of crystallographic information from 1·X(MeCN/EtOH)

<table>
<thead>
<tr>
<th>Title</th>
<th>1·X(MeCN/EtOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{60}H_{78}N_{28}O_{24}Ag_{4}</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Hexagonal</td>
</tr>
<tr>
<td>Space Group</td>
<td>$P6_1$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>22.683(2)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>22.683(2)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>34.369(6)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>120</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>15314(3)</td>
</tr>
<tr>
<td>Z</td>
<td>6</td>
</tr>
<tr>
<td>Formula Weight (g mol⁻¹)</td>
<td>2006.93</td>
</tr>
<tr>
<td>Crystal Size (mm)</td>
<td>0.55×0.09×0.09</td>
</tr>
<tr>
<td>Theta Range (°)</td>
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<tr>
<td>Reflections Collected</td>
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<tr>
<td>Independent Reflections [$R_{int}$]</td>
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<tr>
<td>Data/Restraints/parameters</td>
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<tr>
<td>Goodness of Fit on $F^2$</td>
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<tr>
<td>$R_1$ indices [$I&gt;2\sigma(I)$]</td>
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</tr>
<tr>
<td>wR2 indices [$I&gt;2\sigma(I)$]</td>
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</tr>
<tr>
<td>R1 all data</td>
<td>0.1539</td>
</tr>
<tr>
<td>wR2 all data</td>
<td>0.3905</td>
</tr>
<tr>
<td>Flack Parameter</td>
<td>0.13(14)</td>
</tr>
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Table S2 - Ag-N and Ag-Ag distances in the Ag₄(triazole)₆ metallocycle cluster.

<table>
<thead>
<tr>
<th>Equatorial</th>
<th>Axial</th>
<th>Ag-Ag</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atoms</td>
<td>Distance (Å)</td>
<td>Atoms</td>
</tr>
<tr>
<td>Ag1-N31</td>
<td>2.22(2)</td>
<td>Ag1-N11</td>
</tr>
<tr>
<td>Ag1-N21</td>
<td>2.18(2)</td>
<td>Ag1-N41</td>
</tr>
<tr>
<td>Ag2-N51</td>
<td>2.13(2)</td>
<td>Ag2-N10</td>
</tr>
<tr>
<td>Ag2-N60</td>
<td>2.16(2)</td>
<td>Ag2-N40</td>
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<tr>
<td>Ag3-N20</td>
<td>2.11(2)</td>
<td>Ag3-N11</td>
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<td>Ag3-N50</td>
<td>2.07(2)</td>
<td>Ag3-N40</td>
</tr>
<tr>
<td>Ag4-N30</td>
<td>2.11(2)</td>
<td>Ag4-N10</td>
</tr>
<tr>
<td>Ag4-N61</td>
<td>2.14(2)</td>
<td>Ag4-N41</td>
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</table>
Figure S1 – SEM images of bulk synthesised, microcrystalline 1. Scale bars show 200 μm (left) and 20 μm (right).

Figure S2 – PXRD patterns of ground single crystals of 1·X(MeOH) (—), bulk synthesised microcrystalline powder of 1·X(MeOH) (—), and simulated from the single crystal structure of 1·X(MeCN/EtOH) (—)
Figure S3 – Topological analysis of 1·X(MeCN/EtOH) illustrating the overall topology (A), larger hexagonal right handed ($P$) helix (B), and smaller left handed ($M$) triangular helix.

Figure S4 – Illustration of the triply interpenetrating networks (A), and the 1D channels that form on the intersection of the networks (B) in 1·X(MeCN/EtOH).
Figure S5 – IR spectra of 1·X(MeOH) (—), and L(S) (—).

Figure S6 – TG analysis of 1·X(MeOH)
Figure S7 – VT-PXRD analysis of 1·X(MeOH)
Figure S8 – 77 K N\textsubscript{2} sorption isotherm for 1

(--- adsorption, — desorption).
BET Surface Area Report

BET Surface Area: 505.8817 ± 0.3809 m²/g  
Slope: 0.192804 ± 0.000145 g/mmol  
Y-Intercept: 0.000073 ± 0.000004 g/mmol  
C: 2648.251354  
Qm: 5.18465 mmol/g  
Correlation Coefficient: 0.9999867  
Molecular Cross-Sectional Area: 0.1620 nm²

Figure S9 – BET analysis of N₂ adsorption at 77 K in 1.³

Langmuir Surface Area Report

Langmuir Surface Area: 530.1272 ± 1.3233 m²/g  
Slope: 0.184056 ± 0.000459 g/mmol  
Y-Intercept: 0.120513 ± 0.011837 mbar g/mmol  
b: 1.527267 1/mbar  
Qm: 5.43313 mmol/g  
Correlation Coefficient: 0.999854  
Molecular Cross-Sectional Area: 0.1620 nm²

Figure S10 – Langmuir analysis of N₂ adsorption at 77 K in 1.⁴
Figure S11 - Experimentally determined 77 K N2 adsorption isotherm 1 (●) and fitted NLDFT model (—).5

Figure S12 – Surface area and pore volume distributions determined from the NLDFT model for 1. Surface area (→), and pore volume (←).
Figure S13 – Kinetic data at $P/P_0=0.09$ (20 mbar) for adsorption of methanol, illustrating the anomalous adsorption behaviour: $P/P_0$ (•) and number of molecules per ASU (◦) vs. time.

Figure S14 – 303 K sorption isotherms for (S)-2-butanol (--- adsorption, --- desorption) and (R)-2-butanol (--- adsorption, --- desorption).

Figure S15 - Kinetic data for (S)-2-butanol at $P/P_0=0.258$, illustrating the two stage kinetics (● $P/P_0$), and (◆ Number of molecules per ASU).
Ligand Synthesis

(S,S)-4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole

The following procedure is adapted from the initial synthesis reported by Mendoza and co-workers.6

(S)-lactic acid (10.5 g, 0.12 mol) and hydrazine hydrate (10.5 g, 0.21 mol) were combined and heated to 100 °C for 5 hr. The excess hydrazine and water (7.5 mL) were distilled off by slowly increasing the temperature to 160 °C for 4 hr (reaction temperature 120 °C). The reaction was then heated at reflux for a further 14 hr. The reaction was allowed to cool to room temperature and reduced to a thick yellow oil in vacuo. To this was added acetonitrile (500 mL) and the suspension heated to reflux. The solution was cooled slowly to give a white crystalline solid. The solid was filtered off, washed with cold MeCN (5 × 10 mL) and dried in vacuo to yield the desired product, 6.64 g (66%). \[\alpha\]_D^25 =+22.3° (c=1.5, water). All other spectroscopic data was in agreement with that reported by Mendoza and co-workers.6

1,4-benzylidene-bis-(S,S)-4-yl-3,5-bis(1-hydroxyethyl)-1,2,4-triazole) (L(S))

(S,S)-4-amino-3,5-bis(1-hydroxyethyl)-1,2,4-triazole (4.00 g, 23.2 mmol) and terephthalaldehyde (1.40 g, 10.5 mmol) were ground to a fine powder and transferred to the reaction vessel. The yellow reaction mixture was then heated to 100 °C under a constant stream of N₂ for 12 hr. The resulting bright yellow mass was allowed to cool before being suspended in EtOH (400 mL). The suspension was filtered through a G4 sinter and the filtrate reduced to oil in vacuo. 1,4-Dioxane (200 mL) was added and heated to reflux, during which time a white precipitate formed. The precipitate was then filtered whilst hot, washed with 1,4-dioxane (4 × 10 mL) and acetone (3 × 10 mL) before being dried in vacuo (4.42 g, 95%). \[\alpha\]_D^25 =+87.5° (c=1.50, MeOH). \(^1\)H-NMR (25 °C, d₆-DMSO): 9.11 (s, 2H, C=N-H), 8.10 (s, 4H, Ar), 5.63 (d, 6.1Hz, 4H, OH), 4.98 (m, 4H, CH), 1.55 (d, 6.6Hz, 12H, CH₃); δ (ppm); \(^1^3\)C-NMR (25 °C, d₆-DMSO): δ (ppm); 166.17 (HC=N), 154.34 (N=C-N), 135.67 (ipso-Ar), 129.59 (Ar-CH), 59.93 (HC-OH), 21.02 (CH₃); HREI MS (Positive, MeOH/CHCl₃), 465.197095 m/z (error 3.6×10⁻⁷). IR (inter alia, cm⁻¹, KBr) 3280 (br), 2978, 1617, 1508, 1413, 1374, 1306, 1118, 1076, 1049, 895, 872.
Framework Synthesis

All syntheses of \([\text{Ag}_4(\text{L}(S))_3](\text{NO}_3)_4\cdot\text{Guest}\) were carried out in the absence of light as AgNO₃ is known to be photosensitive. However, the resulting framework showed no photosensitivity and no special handling conditions were required.

**1·X(MeCN, EtOH) [Ag₄(L(S))₃](NO₃)₄·X(MeCN, EtOH)**

Crystals were synthesised by the “vial-in-a-vial” method whereby a small vial (2 mL) containing AgNO₃ (11.0 mg, 0.065 mmol) in MeCN was placed inside a larger vial (20 mL) containing \(\text{L}(S)\) (29.0 mg, 0.065 mmol) in EtOH. Neat solvent was then slowly layered upon these two solutions until the level reached ~3 mm above that of the small vial. The vial was sealed and left in complete darkness for 2 weeks, during which time colourless hexagonal rod shaped single crystals formed.

**1·X(MeOH) [Ag₄(L(S))₃](NO₃)₄·X(MeOH)**

The reaction was carried out as per the synthesis of the MeCN/EtOH solvate but using different quantities of reagents: \(\text{L}(S)\) (29.0 mg, 0.065 mmol) and AgNO₃ (15.0 mg, 0.087 mmol). Neither reagents were dissolved during the layering process and neat MeOH was used as the solvent as before.

**Bulk Microcrystalline Powder**

**1·X(MeOH) [Ag₄(L(S))₃](NO₃)₄·X(MeOH)**

In complete darkness a solution of \(\text{L}(S)\) (100 mg, 0.26 mmol) in MeOH (40 mL) was heated to reflux. To this was added dropwise a solution of AgNO₃ (51 mg, 0.30 mmol) in MeOH (40 mL). The solution was heated at reflux with gentle stirring for 4 hr after which the solution was left cool and then stand without stirring for 3 days. The resulting white suspension was filtered, washed with MeOH (5 × 10 mL) and resuspended in fresh MeOH (10 mL). Calc. for **1·1.6(H₂O)**: C, 35.40; H, 4.02; N, 19.27. Found: C, 35.39; H, 4.10; N, 19.31.
Nuclear Magnetic Resonance (NMR)

$^1$H NMR spectra were collected using Bruker Avance 300 (300.13 MHz) and 200 (200.13 MHz) spectrometers. $^{13}$C NMR spectra were collected using a Bruker Avance 300 (75.47 MHz). All spectra were recorded at 300 K and chemical shifts were referenced to internal solvents. Commercially available deuterated solvents were used for the measurements.

Infra-red (IR) Spectroscopy

Diffuse reflectance infrared Fourier transform spectra (DRIFTS) were collected in a potassium bromide (KBr) matrix over the range 400 – 4000 cm$^{-1}$ using a Varian FTS-800 Scimitar series infrared spectrometer. The samples were dried under vacuum for 12 hr prior to analysis with 3.0 mg of material per 200 mg of KBr used for each analysis.

Scanning Electron Microscopy (SEM)

All scanning electron microscopy images were collected on a Phillips XL30 at the University of Sydney Electron Microscope Unit with the assistance of Dr Ian Kaplin. All samples were prepared by sputter coating with platinum to a thickness of ~10 nm. A working distance of ~10 mm and an accelerator voltage of 15 kV were used.

Optical Rotation

Optical rotations were determined on a polAAr 2001 Automatic polarimeter, with the sodium D line at 589 nm used for all measurements. Sucrose was used as a standard giving a specific rotation of $[\alpha]^D_{25} = +66.5^\circ$ (c=26.0, H$_2$O), which agrees well with the literature value $[\alpha]^D_{25} = +66.57^\circ$.7

Mass Spectrometry (MS)

Electrospray mass spectra (ESI) were recorded on a Finnigan LCQ mass spectrometer with a Trace GC having a ZB-5 column, 5% phenyl 95% dimethylpolysiloxane (GCMS) at the University of Sydney by Dr Keith Fisher. High resolution mass spectra (HRMS) were recorded on a Finnigan MAT 900 XL mass spectrometer at the University of Queensland.
Elemental Analysis

Elemental analyses were conducted at the Campbell Microanalytical Laboratory, University of Otago, New Zealand. For safety, all samples were sent dry and were redried under vacuum (5 mbar) at 40 °C for 4 hr prior to analysis.

Single Crystal X-ray Diffraction (SC-XRD)

Diffraction data were collected on a Bruker Smart 1000 CCD equipped with Mo-Kα (λ = 0.71073 Å) radiation and Oxford Instruments nitrogen gas (100 – 375 K) cryostream. Crystals were mounted on a mohair fibre in a thin film of perfluoropolyether oil and quench cooled to 150 K. Matrix collections were performed to determine unit cells (3 × 15 frames of 10 sec exposure intensity data). Full spheres of data, 2000 frames, were collected over a range of incident angles, with varied exposure times of 30 sec. Unless otherwise stated, empirical absorption corrections were applied to all data using SADABS.¹ The structures were solved with SHELXS-97² and refined with SHELXL-97¹⁰ from data reduced with SAINT+ V.6.02.¹¹ All solvent accessible (VOID) volumes were calculated within PLATON.¹² Channel/pore dimensions were calculated following subtraction of the relevant atomic van der Waals radii. Illustrations were produced using the programs WebLab ViewerPro,¹³ Mercury,¹⁴ ORTEP-3¹⁵ and OLEX.

Variable Temperature Single Crystal X-ray Diffraction

Crystals were mounted with a thin smear of grease in an open-ended glass capillary to allow the guest molecules to be liberated as the temperature was ramped to 360 K (100 K hr⁻¹). Multiple matrix collections of 3 × 15 sets of intensity data were performed automatically using slam-style command files within the SMART interface.¹¹ Temperature calibration was based on the time of collection of the mid-point frame of the second series of frames in each matrix collection. After the data collection the unit cells were re-analysed automatically using a second slam-style command file, enabling the extraction of three data points per matrix.

Powder X-ray Diffraction (PXRD)

Powder X-ray Diffraction patterns were obtained using Cu-Kα radiation (λ = 1.54056 Å). Data were collected at various temperatures using a Shimadzu S-6000 Diffractometer (40 kV, 30 mA, divergence and anti-scatter slits 1°, receiver slit 0.3 mm). Data were collected within the angle interval of 2θ = 3 to 30° with a step size of 0.02° in 2θ.
Variable Temperature PXRD (VT-PXRD)

To study samples at high temperature and controlled atmospheres, an Anton-Paar HTK 1200 attachment was used. The atmosphere was a flow of dry N₂ (0.1 L min⁻¹). The patterns were collected within the angle interval of 2θ = 3 to 30° with a step size of 0.02°. For variable temperature measurements multiple diffraction patterns were collected at 25 K intervals with heating and cooling.

Thermogravimetric (TG) Analysis

Measurements were carried out on a TA Instruments Hi-Res TGA 2950 Thermogravimetric Analyser under a flow of dry N₂ (0.1 L min⁻¹). To identify the approximate temperatures of guest loss and thermal decomposition the sample temperature was ramped at 2 °C min⁻¹ from 20 to 500 °C under a dry N₂ atmosphere.

Vapour Sorption

The adsorption isotherms for methanol, ethanol, (R) and (S)-2-butanol, toluene and cyclohexane were all conducted using an Intelligent Gravimetric Analyser (IGA) supplied by Hiden Analytical Ltd. All solvents used were obtained from commercial sources and further purified by standard methods.¹⁶

In a general procedure, 20 - 50 mg of sample, still containing a small amount of methanol, was loaded into the sample basket. The sample was then heated to 40 °C, at 1 °C min⁻¹, under vacuum (~10⁻⁸ mbar) for typically 4 hours, to give a rate of mass loss less than 2 μg hr⁻¹. The sample was then cooled to the analysis temperature under vacuum, at which point the dry mass was recorded. The temperature of the sample was typically stable to ±0.1 °C, although larger swings were often observed for the initial pressure point. In such cases, the temperature was allowed to stabilise and no attempt was made to obtain kinetic fits to the data. The sample chamber was then pressurised to a set pressure of the adsorbate with a ramp time of 120 sec. Two pressure transducers with ranges of 0 - 100 mbar and 0 - 10 bar were used depending on the analysis pressure. Once the pressure had reached 95 % of the desired value the mass change as a function of time was recorded. During this time the pressure and temperature were kept constant. The mass as a function of time was recorded until the equilibration requirements were met. The equilibration requirements were defined by a minimum time, typically 5 - 20 min and a maximum time, typically 30 - 120 min. The kinetic data were fitted in real time to the linear driving force model (LDF)¹⁷ (equation 1) and if the amount adsorbed was within 98 % of the modelled equilibrium uptake, defined by the asymptote, and the
minimum time had passed then the analysis would proceed to the next set pressure point. This process was repeated for each adsorption and desorption pressure point until the complete isotherm was obtained. It was found that much of the kinetic data could not be modelled sufficiently by the LDF model; in these situations the Avarami\textsuperscript{18} model (equation 2) was used:

\[
u(t) = u_0 + \Delta u \left( 1 - \exp \left( \frac{-[t-t_0]}{k} \right) \right) \quad \text{Equation 1}
\]

\[
u(t) = u_0 + \Delta u \left( 1 - \exp \left( \frac{-[t-t_0]}{k} \right) \right) \quad \text{Equation 2}
\]

where \(u_0\) is the uptake at the arbitrary time origin \(t_0\), \(k\) is the time constant, \(x\) is a variable power, and \(\Delta u\) is the change in uptake. The asymptotic uptake is then equal to \(u_0 + \Delta u\).

**Gas Sorption**

The adsorption isotherms for \(N_2\) (99.99%) were conducted using an Accelerated Surface Area & Porosimetry System (ASAP) 2020 supplied by Micromeritics Instruments Inc. The instrument utilised isolated dual analysis and outgas vacuum systems to maintain gas purity. Three pressure transducers (1333, 13 and 1.33 mbar) were used with resolutions of \(10^{-3}\), \(10^{-5}\) and \(10^{-6}\) mbar respectively. Liquid \(N_2\) (77.35 K) was used for temperature control and an isothermal jacket was used to maintain constant cryogen level on the sample tube and \(P_0\) tube during analysis as evaporation occurs. The free space was determined by \(He\) (99.999%) at 298 and 77 K. Adsorption standards were routinely run on Zeolite 13X for \(N_2\), adsorption, with an excellent agreement between the observed isotherm and the literature being found.

In a general procedure, the sample (~100 mg) was loaded into the glass analysis tube in a small amount of methanol. The sample was then heated to 40 °C at 1 °C min\(^{-1}\), under vacuum (~\(10^{-8}\) mbar) for typically around 4 - 12 hr until the outgas rate was less than 4 \(\mu\)bar hr\(^{-1}\). The sample was then backfilled with \(N_2\) before being transferred to the analysis port where it was evacuated for at least a further 60 min before the analysis was started.
References

8. G. M. Sheldrick, in *SADABS, Empirical adsorption correction program for area detector data*, University of Göttingen, Germany, 1996.
10. G. M. Sheldrick, in *SHELXL-97, Program for crystal structure refinement*, University of Göttingen, Germany, 1997.