Supporting information

On/off porosity switching and post-assembly modifications of Cu₄L₄ metal-organic polyhedra

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1. Experimental section

1.2. Materials and measurements

Unless otherwise stated, all chemicals were obtained from commercial sources and used as received. Triethyl amine (NEt$_3$) was distilled from KOH and stored under argon. Tetrahydrofuran (THF) was freshly distilled using a sodium/benzophenone solvent still. Electrospray ionization (ESI) mass spectra were recorded on an Agilent 6230 TOF LCMS. Elemental analyses were performed by the microanalysis laboratory at Macquarie University. Infrared spectra were collected on a Perkin-Elmer Spectrum 100 using a UATR sampling accessory. Thermal gravimetric analysis (TGA) was performed on a Perkin-Elmer STA-6000 instrument or on a TA Instruments Discovery TGA under a constant flow of N$_2$ at a temperature increase rate of 10 °C/min.

Powder X-ray diffraction data were collected on a Bruker Advance D8 diffractometer (capillary stage) using Cu Kα radiation (λ = 1.5418 Å, 50 kW/40mA). 1.0 mm capillaries were filled with the respective solvent before loading crystals of 1-3. This was done to avoid any possible desolvation of the crystalline sample. Simulated powder X-ray diffraction patterns were generated from the single crystal data using Mercury 3.10. Data in figure S14b was collected on a Co-target Bruker D4 Eendavour powder diffractometer (plate stage). The data was converted to Cu wavelength using PowDLL. Gas sorption isotherm measurements were performed on a Micromeritics 3Flex Surface Characterisation Analysyer. UHP grade (99.999 %) N$_2$ was used for all measurements. Temperatures were maintained at 77 K using a cryo-cooler. The isotherms were then analysed to determine the Brunauer Emmett-Teller (BET) surface area and pore-size distribution using the MicroActive software (Version 3.00, Micromeritics Instrument Corp. 2013).

1.3. Synthesis of LH$_2$

**Scheme 1**

1.3.1. Synthesis of methyl 3-ethynylbenzoate (4)

Methyl 3-bromobenzoate (2.98 g, 13.9 mmol) was dissolved in triethylamine (30 mL) under argon atmosphere. Once the solvent was degassed, Pd(PPh$_3$)$_2$Cl$_2$ (207 mg, 0.29 mmol) and CuI (60.1 mg, 0.31 mmol) were added in one portion, followed by ethynyltrimethylsilane (5.0 mL, 36.1 mmol). The reaction mixture was sealed and heated at 65 ºC for 18 h. Once allowed to cool, the reaction mixture was diluted with ethyl acetate (30 mL), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (3:1 hexane/CH$_2$Cl$_2$) to yield a pale-yellow oil.

**1H NMR (500 MHz, CDCl$_3$):** δ 8.14 (d, J = 1.7 Hz, 1H), 7.97 (dt, J = 7.7, 1.4 Hz, 1H), 7.63 (dt, J = 7.7, 1.4 Hz, 1H), 7.38 (t, J = 7.7 Hz, 1H), 3.92 (s, 3H), 0.26 (s, 9H).

$K$_2$CO$_3$ (1.80 g) was added to the oil in methanol (45 mL) and the suspension was stirred at 25 ºC for 2 h. Diethyl ether (50 mL) was added and the suspension was filtered. Water (75 mL) was added and the organic layer was separated and the aqueous layer was further extracted with diethyl ether (3 x 30 mL). The combined extracts were dried over MgSO$_4$ and the solvent was evaporated under reduced pressure, yielding an off-white solid (1.8 g, 81%).

**1H NMR (500 MHz, CDCl$_3$):** δ 8.22 – 8.13 (d, J = 1.8 Hz, 1H), 8.02 (dd, J = 7.7, 1.8 Hz, 1H), 7.67 (dd, J = 7.7, 1.8 Hz, 1H), 7.41 (t, J = 7.7, 1H), 3.93 (s, 3H), 3.12 (s, 1H).

**13C NMR (125 MHz, CDCl$_3$) δ 166.40, 136.38, 133.41, 130.64, 129.94, 128.62, 122.74, 82.71, 78.26, 52.44.**
1.3.2. Synthesis of compound 5

3,5-Dibromobenzaldehyde (177 mg, 0.747 mmol) was combined with compound 4 (263 mg, 1.64 mmol) in triethylamine (6 mL) and THF (2 mL) under an argon atmosphere. After the solvent was degassed, Pd(PPh₃)₂Cl₂ (12.0 mg, 0.017 mmol) and CuI (3.4 mg, 0.018 mmol) were added in one portion and the reaction mixture was heated at 75 °C for 18 h. Once allowed to cool, the reaction mixture was diluted with ethyl acetate (10 mL), filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (CH₂Cl₂), yielding dimethyl 3,3’-((5-formyl-1,3-phenylene)bis(ethyne-2,1-diyl))dibenzoate (5) as a pale brown solid (283 mg, 78%). Mp: 139.0 – 140.5 °C ⁠¹H NMR (500 MHz, CDCl₃): δ 10.02 (s, 1H), 8.23 (t, J = 1.7 Hz, 2H), 8.04 (dt, J = 7.7, 1.7 Hz, 2H), 8.00 (d, J = 1.6 Hz, 2H), 7.94 (d, J = 7.7, 1.7 Hz, 2H), 7.47 (t, J = 7.7 Hz, 2H), 3.95 (s, 6H).

¹³C NMR (125 MHz, CDCl₃) δ 190.76, 166.38, 139.71, 136.89, 135.91, 133.07, 132.32, 130.77, 130.00, 128.81, 124.74, 123.01, 90.64, 88.06, 52.51; vₘₐₓ (neat, cm⁻¹): 3568 (m), 1717 (s), 1701 (s), 1590 (m), 1483 (m), 1443 (m). ESI-HRMS (C₂₇H₁₈O₅): calc: 445.1046 [M+Na]⁺; found 445.1046.

Figure S1. ¹H NMR spectrum (500 MHz/CDCl₃) of compound 5.

Figure S2. ¹³C NMR spectrum (125 MHz/CDCl₃) of compound 5.

1.3.3. Synthesis of LH₂

Tetrabutylammonium hydroxide (1M in methanol, 1.8 mL, 1.8 mmol, 4 equiv.) was combined with compound 5 (190 mg, 0.450 mmol) in dry THF (8 mL) and the mixture was stirred at 25 °C for 2 h. The volatiles were removed under an N₂ stream and the residue was acidified to pH = 3 with 1M HCl. The formed precipitate was collected under reduced pressure washing thoroughly with H₂O. The wet solid was then washed with MeOH (2 x 10 mL) and dried under vacuum (18 h) to give 3,3’-((5-formyl-1,3-phenylene)bis(ethyne-2,1-diyl))dibenzoic acid (LH₂) as a white solid (145 mg, 82%). Mp: >260 °C. ¹H NMR (600 MHz, DMSO-d₆) δ 13.30 (s, 2H), 10.05 (s, 1H), 8.16 – 8.13 (m, 4H), 8.01 (dd, J = 7.7, 1.4 Hz, 2H), 7.86 (dt, J = 7.7, 1.4 Hz, 2H), 7.61 (t, J = 7.7 Hz, 2H). ¹³C NMR (151 MHz, DMSO-d₆) δ 191.97, 166.47, 139.12, 136.98, 135.57, 132.30, 132.19, 131.50, 129.99, 129.42, 123.69, 122.04, 90.30, 87.94. vₘₐₓ (neat, cm⁻¹): 2810 (w), 1686 (br, s), 1602 (m), 1589 (m), 1484 (w), 1453 (m). ESI-HRMS (C₂₅H₁₄O₅): calc: 394.0847 [M+H]⁺; found 394.0829.
1.4. Synthesis of 1a-e, 2 and 3.

1.4.1. Synthesis of 1a

In a screw-cap vial L (60 mg, 0.15 mmol) was combined with Cu(OAc)$_2$·H$_2$O (40 mg, 0.20 mmol) in 4.5 mL of DMF. The vial was placed in an oven pre-set to 85 °C and left to stand for 2 h. After allowing to cool to room temperature, the resulting blue solution of 1 was subject to crystallisation conditions outlined in table 1. Slow vapour diffusion of MeOH (2 mL) into the DMF solution of 1 (0.5 mL) gave blue crystals after 4 days. The crystals were soaked in MeOH (x 7) over 24 hrs and isolated under reduced pressure (Yield 65 mg, 87%, based on analysis). ν$_{\text{max}}$ (neat, cm$^{-1}$): 1697.4 (m, HC=O), 1629.3 (m), 1594.9 (m), 1572.8 (m), 1431.3 (m), 1394.9 (s). Found: C 61.58 H 3.45 C$_{102}$H$_{68}$Cu$_{4}$O$_{28}$ ([Cu$_4$L$_4$(MeOH)$_2$(H$_2$O)$_2$]·4H$_2$O) requires: C 61.38 H 3.43.

Table S1: Crystallisation condition employed to obtain phases 1a-e

| Solvents x/y; slow-vapour diffusion of y into x | Crystallised phase |
|-----------------------------------------------|-------------------|
| DMF/MeOH                                      | 1a                |
| DMF/CH$_3$CN                                   | 1a                |
| DMSO$^b$                                       | 1b                |
| DMA/MeOH                                       | 1b                |
| DMF/ether                                      | 1c                |
| DMF/acetone                                    | 1c                |
| DMF/H$_2$O$^a$                                 | 1c                |
| DMA/ether                                      | 1d                |
| DMA/H$_2$O$^a$                                 | 1d                |
| Acetone$^c$                                    | 1e                |

$^a$Vial was left open to the air; $^b$crystals formed upon heating LH$_2$ and Cu(OAc)$_2$ at 85 °C for 16 h; $^c$Crystals of 1c were washed with acetone (x4) and left to soak for 3 weeks at 25 °C.
Figure S5. A photo of dried samples of 1 dissolved in DMF (left) and DMA (right). Typical concentrations = 3.8 mM. Due to their solubility, phases 1a-1e can be recycled through recrystallisation (Table S1).

Figure S6. UV-Vis spectra of 1, LH₂ and Cu(OAc)₂ measured in DMF at 25 °C. a) Overlay of LH₂ (dash-dot line, black), Cu(OAc)₂ (dashed line, green) and 1 (solid line, teal). Both LH₂ and 1 show similar features in the spectrum, however the high energy band observed in LH₂ (288 nm) is red-shifted in 1 (294 nm); b) the same spectrum shown between 550 – 800 nm, highlighting the d-d band characteristic of the copper paddlewheel node.
Figure S7. Images of the crystalline phases 1a-1e; a) 1a; b) 1b; c) 1c; d) 1e (crystals shown in c) which have been soaked in acetone for 3 weeks); e) 1d; f) the same sample shown in e) when exposed to in MeOH for 2 minutes. Photos were taken using a smartphone camera and crystals were visualised on a Meiji EMZ-13 microscope.

Figure S8. $^1$H NMR spectra (500 MHz) of crystals of 1c soaked in a) methanol-d$_4$ (1 wash). Note: the DMF signals originate from the coordinated solvent in 1c. As can be observed, 1 is not soluble in MeOH even in the presence of DMF; b) acetone-d$_6$ (2 washes); c) acetone-d$_6$ 4 washes. As can be observed, 1c is soluble in acetone only in the presence of trace amounts of DMF. Similar results were observed for 1d. After further washing with acetone, signals corresponding to 1 (indicated in green) disappear.
1.4.2. Post-synthetic modification of 1

General procedure: in an 5mm NMR tube, a dried powder of 1 (5 mg, ~2.7 μmol) was dissolved in 0.65 mL of DMF-d$_7$ with the aid of sonication and heating. Afterwards, 16 equivalents of the aniline derivative (o-toluidine or 3-Amino-9-ethylcarbazole) was added, followed by Sc(OTf)$_3$ (~0.1 mg). The mixture was shaken and heated overnight at 45 °C. Slow vapour diffusion of diethyl ether (2 mL) into the reaction mixture produced crystals suitable for X-ray analysis.

2: $\nu_{\text{max}}$ (neat, cm$^{-1}$): 1619.4 (m), 1594.3 (m), 1572.9 (m), 1484.9 (w)

3: $\nu_{\text{max}}$ (neat, cm$^{-1}$): 1630.0 (m), 1594.4 (m), 1571.3 (m), 1478.0 (m).

Figure S9. a) $^1$H NMR (500 MHz/DMF-d$_7$) spectra of covalent PAM reactions (i) the mixture of 1 and o-toluidine before heating; (ii) the reaction mixture after addition of Sc(OTf)$_3$ and heating at 45 °C/16 hrs; (iii) the mixture of 1 and 9-ethyl-9H-carbazol-3-amine before heating; (iv) the reaction mixture after addition of Sc(OTf)$_3$ and heating at 45 °C/16 hrs. Both reaction mixtures show the absence of the aldehyde proton at ~10 ppm (red) and appearance a new imine proton (green) which appears between 8 and 9 ppm. (b) IR spectra of crystals of (i) 3; (ii) 2; (iii) 1; (iv) ligand LH$_2$. The success of the PAM reaction can be seen by the absence of the C=O aldehyde stretch at 1699 cm$^{-1}$ and appearance of new C=N stretches.

Figure S10. UV-Vis spectra of 1, 2 and 3, measured in DMF at 25 °C a) Full spectrum of 1 (blue line), 2 (khaki line) and 3 (green line); b) the same spectrum shown between 225 – 460 nm.
2. Powder X-ray diffraction

Figure S11. Powder X-ray diffraction patterns of 1a showing solvent washing and activation: a) 1a simulated; b) 1a as-synthesised; c) 1a acetone exchanged (soaked over 3 months); d) 1a MeOH exchanged (over 6 hrs); e) 1a activated sample. Note: minor discrepancies ($2\theta>$7°) are observed between a) – d) due to the overall flexibility of the MOP solid in accommodating different coordinating solvent molecules in the crystal lattice.
Figure S12. Powder X-ray diffraction patterns of 1a-MeOH showing its metastability (up to 9 hrs) and subsequent slow conversion to give 1b-MeOH. Note: 1a-MeOH was prepared by exchanging an as-synthesised sample of 1a with MeOH (5 x) over a period of 3 hrs. The sample was then loaded in a capillary filled with MeOH and measurements were performed every 2 hrs.
Figure S13. Powder X-ray diffraction patterns of 1b showing solvent washing and activation: a) 1b-DMSO simulated; b) 1b-DMSO as-synthesised; c) 1b-DMA as-synthesised, obtained from DMA/MeOH; d) 1b acetone exchanged (soaked over 3 months); e) 1b MeOH exchanged, f) 1b activated sample.

Figure S14. Powder X-ray diffraction patterns of 1c showing solvent washing and transformations; a) 1c simulated; b) 1c as-synthesised; c) 1c soaked in acetone for 3 weeks; d) 1c soaked in MeOH for 5 minutes; e) 1e simulated pattern; f) the same pattern as shown in c); g) 1b simulated; h) the same pattern as shown in d). As can be seen in e) – h), 1c transforms to 1e or 1b upon exposure of the crystals to acetone or MeOH respectively.
Figure S15. Powder X-ray diffraction patterns of 1d showing solvent washing and transformations; a) 1d simulated; b) 1d as-synthesised; c) 1d soaked in acetone for 3 weeks; d) 1d soaked in MeOH for 5 minutes; e) 1d as-synthesised; f) the same pattern as shown in c); g) 1e as-synthesised, obtained by exposing 1c to acetone (shown for comparison); h) 1b simulated; i) the same pattern as shown in d). As can be seen in e) – h), 1d transforms to 1e or 1b upon exposure of the crystals to acetone or MeOH respectively. We note that the conversion to 1e does not proceed as cleanly as the same transformation from 1c. The diffraction peaks at 2θ = 4.9 and 9.8 suggest the presence of the parent phase 1d in the transformed sample.

Figure S16. Powder X-ray diffraction patterns of 1e showing solvent washing and activation: 1e simulated; b) 1e as-synthesised (1c recrystallised from acetone); c) 1e MeOH exchanged, f) 1e activated sample.
Figure S17. Powder X-ray diffraction patterns of a) 1e as-synthesised (obtained from the slow recrystallisation of 1c in acetone); b) the solid obtained by heating and stirring equimolar amounts of L + Cu(OAc)₂ in acetone at 60 °C for 2h. The pattern in b) does not coincide with 1a-e.

Figure S18. Powder X-ray diffraction patterns of PAM structures 2 and 3; a) 2 simulated; b) 2 as-synthesized; c) 2 desolvated; d) 3 simulated; e) 3 as-synthesized; f) 3 desolvated.

Figure S19. Powder X-ray diffraction patterns of all as-synthesised solvatomorphs (1a-e); a) 1a; b) 1b-DMSO; c) 1c; d) 1d; e) 1e.
Figure S20. Powder X-ray diffraction patterns of samples of 1a, 1b and 1e after activation and re-solvating in MeOH (a-d) and mother liquor (e-f); a) 1b-MeOH; b) 1a activated, then re-solvated in MeOH; c) 1b activated, then resolvated in MeOH; d) 1e activated, then resolvated in MeOH; e) 1a as synthesised; f) 1a activated, then resolvated in a 1:6 mixture of DMF:MeOH; g) 1b as synthesised; h) 1b activated, then resolvated in a 1:6 mixture of DMA:MeOH; i) 1e as synthesised; j) 1e activated, then resolvated in acetone.

Figure S21. Powder X-ray diffraction patterns comparing the activated and post-adsorption samples of 1a, 1b and 1e; a) 1a as-synthesised; b) 1a after activating a 100 °C; c) the activated sample of 1a post N2 adsorption; d) 1b as-synthesised; e) 1b after activating a 100 °C; f) the activated sample of 1b post N2 adsorption; g) 1e as-synthesised; h) 1e after activating a 100 °C; i) the activated sample of 1b post N2 adsorption.
3. Thermal gravimetric analysis (TGA)

Figure S22. TGA trace overlay of 1a-as synthesised (green) and 1a-MeOH (teal). Thermal decomposition of the solids occurs at ca. 310 °C.

Figure S23. TGA trace overlay of 1b-as synthesised (1b-DMA, green) and 1a-MeOH (teal). Thermal decomposition of the solids occurs at 300 – 310 °C.
Figure S24. TGA trace overlay of 1e-as synthesised (1e-acetone, green) and 1e-MeOH (teal). Thermal decomposition of the solids occurs at 290 – 310 °C.

Figure S25. TGA trace of an activated sample (e.g. 1b) after adsorption analysis. Upon exposure to air, the samples quickly change from deep blue to a light blue colour. Accordingly, a gradual loss of H₂O (4%) is observed which corresponds to the loss of four water molecules per cage. Thermal decomposition of the solid occurs at ca. 300 °C.
4. Gas adsorption

Prior to activation, 1a, 1b and 1e were soaked in MeOH (x 7) over a period of 24 h. To verify whether complete exchange of the parent solvent with MeOH had taken place after, samples were digested in DMSO/DCI and analysed by $^1$H NMR spectroscopy (figure below).

![Figure S26. $^1$H NMR (500 MHz/DMSO) spectra of digested samples of 1; a) 1a as-synthesised (DMF/MeOH); b) 1a methanol exchanged; c) 1b as-synthesized (DMA/MeOH); d) 1b MeOH exchanged; e) 1e as-synthesised (acetone); e) 1e MeOH exchanged.](image)

All samples were activated from MeOH at 100 °C under vacuum for 6 hrs. $^1$H NMR digestions in DMSO/DCI confirmed complete removal of the solvent (e.g. figure below).

![Figure S27. $^1$H NMR (500 MHz/DMSO) of a digested sample of 1 after activation from MeOH. * indicates residual MeOH of <0.2%. Further heating under vacuum did not improve the BET surface area of samples of 1.](image)
5. X-ray crystallography

4.1. General methods

Single crystals were mounted in paratone-N oil on a plastic loop. X-ray diffraction data for 1a, 1b, 1e, 2 and 3 were collected at 100(2) K on the MX-1 beamline of the Australian Synchrotron. X-ray diffraction data for 1c and 1d were collected at 150(2) K on an Oxford X-Calibur single crystal diffractometer ($\lambda = 0.7107$ Å). Data sets were corrected for absorption using a multi-scan method, and structures were solved by direct methods using SHELXT and refined with SHELXL and ShelXle as a graphical user interface. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were included as invariants at geometrically estimated positions. X-ray experimental data is given in Table S2 and S3.

3.1.1. Specific refinement details for 1a and 1c

Stereochemical restraints for DMF solvent molecules (residue defined as DMF) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. A GRADE dictionary for SHELXL contains target values and standard deviations for 1,2-distances (DFIX) and 1,3-distances (DANG), as well as restraints for planar groups (FLAT). This help to resolve the disorder of the coordinate DMF solvent molecules in both 1a and 1c. All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP’s for carbon, nitrogen and oxygen atoms was enabled by a combination of similarity restraints (SIMU) and rigid bond restraints (RIGU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

3.1.2. Specific refinement details for 1b

Stereochemical restraints for DMSO solvent molecules (residue defined as SUL) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. This helped to refine and resolve the disorder about the coordinated DMSO ligands. All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP’s for
carbon, nitrogen and oxygen atoms was supported by a combination of similarity restraints (SIMU) and rigid bond restraints (RIGU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

3.1.5. Specific refinement details for 1d

Stereochemical restraints for DMA solvent molecules (residue defined as DMA) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. This helped to resolve the disorder of the coordinated DMA molecules. All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was supported by similarity restraints (SIMU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

3.1.4. Specific refinement details for 1e

All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was supported by similarity restraints (SIMU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

3.1.6. Specific refinement details for 2

All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was supported by similarity restraints (SIMU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

3.1.7. Specific refinement details for 3

Stereochemical restraints for DMF solvent molecules (residue defined as DMF) were generated by the GRADE program using the GRADE Web Server (http://grade.globalphasing.org) and applied in the refinement. All displacements for non-hydrogen atoms were refined anisotropically. The refinement of ADP's for carbon, nitrogen and oxygen atoms was supported by similarity restraints (SIMU). The contribution of the electron density from disordered, pore-bound solvent molecules, which could not be modelled with discrete atomic positions were handled using the SQUEEZE routine in PLATON, which strongly improved all figures of merit (FOM).

Table S2: X-ray experimental data for 1a, 1b, 1c and 1d

| Compound | 1a | 1b | 1c | 1d |
|----------|----|----|----|----|
| CCDC number | 1969623 | 1969620 | 1969621 | 1969625 |
| Empirical formula | C_{218}H_{138}Cu_{8}N_{6}O_{48} | C_{108}H_{72}Cu_{4}O_{24}S_{4} | C_{38}H_{31}Cu_{2}NO_{12} | C_{116}H_{84}Cu_{4}N_{2}O_{24} |
| Formula weight | 4117.66 | 2136.05 | 1000.87 | 2172.03 |
| Crystal system | Triclinic | Monoclinic | Monoclinic | Monoclinic |
| Space group | P-1 | C2/c | C2/m | P2_1/c |
| a (Å) | 13.914(3) | 14.151(3) | 25.8186(7) | 14.0177(5) |
| b (Å) | 20.891(4) | 32.563(7) | 22.6806(6) | 28.7314(8) |
| c (Å) | 21.446(4) | 26.766(5) | 27.2079(6) | 17.0738(6) |
| α (°) | 71.94(3) | 90 | 90 | 90 |
| β (°) | 87.87(3) | 102.26 | 109.690(3) | 110.611(4) |
| γ (°) | 81.20(3) | 90 | 90 | 90 |
| Volume (Å³) | 5857(2) | 12052(4) | 15000.9(7) | 6436.3(4) |
| Z | 1 | 4 | 8 | 2 |
| Density (calc.) (Mg/m³) | 1.167 | 1.177 | 0.886 | 1.121 |
| Absorption coefficient (mm⁻¹) | 0.780 | 0.827 | 0.608 | 0.714 |
| Compound | 1e   | 2     | 3     |
|----------|------|-------|-------|
| CCDC number | 1969624 | 1969619 | 1969622 |
| Empirical formula | C\textsubscript{106}H\textsubscript{60}Cu\textsubscript{4}O\textsubscript{24} | C\textsubscript{140}H\textsubscript{104}Cu\textsubscript{4}N\textsubscript{12}O\textsubscript{20} | C\textsubscript{168}H\textsubscript{124}Cu\textsubscript{4}N\textsubscript{8}O\textsubscript{20} |
| Formula weight | 1971.70 | 2472.47 | 2884.94 |
| Crystal system | Monoclinic | Triclinic | Monoclinic |
| Space group | C2/m | P-1 | P2\textsubscript{1}/n |
| a (Å) | 19.687 (4) | 14.987(3) | 20.979(4) |
| b (Å) | 28.163 (6) | 16.858(3) | 21.168(4) |
| c (Å) | 10.475 (2) | 17.478(4) | 23.760(5) |
| α (°) | 90 | 116.53(3) | 90 |
| β (°) | 97.91 (3) | 107.31(3) | 108.37(3) |
| γ (°) | 90 | 93.21(3) | 90 |
| Volume (Å\textsuperscript{3}) | 5753 (2) | 3678.4(16) | 10014(4) |
| Z | 2 | 1 | 2 |
| Density (calc.) (Mg/m\textsuperscript{3}) | 1.138 | 1.116 | 0.957 |
| Absorption coefficient (mm\textsuperscript{-1}) | 0.791 | 0.631 | 0.472 |
| F(000) | 2008 | 1276 | 2984 |
| Crystal size (mm\textsuperscript{3}) | 0.11x0.08x0.07 | 0.15x0.13x0.09 | 0.05x0.04x0.02 |
| θ range for data collection (°) | 1.963 to 24.111 | 1.384 to 25.681 | 1.131 to 24.413 |
| Reflections collected | 31901 | 46313 | 115160 |
| Observed reflections [R(int)] | 4464 [0.0286] | 12313 [0.0260] | 15671 [0.1473] |
| Goodness-of-fit on F\textsuperscript{2} | 1.054 | 1.027 | 1.024 |
| R\textsubscript{l} [I>2σ(I)] | 0.0429 | 0.0431 | 0.1220 |
| wR\textsubscript{2} (all data) | 0.1216 | 0.1324 | 0.3929 |
| Largest diff. peak and hole (e.Å\textsuperscript{-3}) | 0.566, -0.508 | 0.447 and -1.005 | 1.998 and -0.869 |
| Data / restraints / parameters | 4464/222/315 | 12313/0/781 | 15671/723/926 |

Table S3: X-ray experimental data for 1e, 2 and 3
5.2. Thermal ellipsoid plots

**Figure S29.** The asymmetric unit of the X-ray structures of a) 1a and b) 1b with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.

**Figure S30.** The asymmetric unit of the X-ray structures of a) 1c and b) 1e with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.
Figure S31. The asymmetric unit of the X-ray structures of a) 1d and b) 2 with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.

Figure S32. The asymmetric unit of the X-ray structures of 3 with all non-hydrogen atoms shown as ellipsoids at the 50% probability level.
5.3. Additional information on 1a-e

**Figure S33.** The coordination sphere of phases 1a-e. 1a and 1c have either chemically (1a) or crystallographically (1c) unique paddle-wheel centres and are thus shown in two colours.

**Figure S34.** A scheme depicting the cage-to-cage relationship in the packing of 1c and 1d, along with a possible mechanism behind solid-state transformations to 1b that occurs upon washing these samples with MeOH a) 1c transforming to 1b; 1e transforming to 1b. For 1c, we propose that the transformation to 1b occurs through two rotations about one cage molecule with respect to the other. For 1d, we suggest a sliding motion about the ligand backbone of adjacent cage molecules (Fig. S27).
6. Lattice energy calculations

Lattice energy calculations for each of the polymorphs were calculated based on the periodic density functional theory (DFT) as implemented in the software package VASP 5.4.4. The initial model for the DFT simulations were taken from the experimental CIF files where the solvent molecules are removed, and the disorder atoms are refined. A unit cell was employed for all the polymorph structures except for polymorph 1c, a primitive cell is used. It is well-known that standard DFT methods based on generalized gradient approximation do not fully account for the long-range dispersion interactions and hence we included the dispersion corrections using DFT-D3 method. Electron exchange and correlation were described using the generalized gradient approximation Perdew, Burke, and Ernzerhof (PBE) form and the projector-augmented wave potentials were used to treat core and valence electrons. In all cases, we used a plane-wave kinetic energy cutoff of 600 eV and a Gamma-point mesh for sampling the Brillouin zone. The ionic coordinates and cell parameters were fully relaxed until the Hellman-Feynman ionic forces were less than 0.01 eV/Å.

Table S4 Absolute lattice energies for polymorphic structures of 1a-e

| Structure | Lattice energy (kJ/mol) |
|-----------|-------------------------|
| 1a        | -363.768                |
| 1b        | -386.109                |
| 1c        | -279.820                |
| 1d        | -317.136                |
| 1e        | -370.838                |

Table S5: DFT optimised lattice parameters of phases 1a-e. The values in the bracket refers to the experimental value.

| Structures | DFT optimised Lattice parameter | % change in lattice cell parameters with respect to experimental values |
|------------|---------------------------------|---------------------------------------------------------------------|
|            | a (Å)  | b (Å)  | c (Å)  | α (°)  | β (°)  | γ (°)  | a (Å)  | b (Å)  | c (Å)  |
| 1a         | 12.423 (13.914) | 21.258 (20.891) | 20.762 (21.446) | 66.47 (71.94) | 92.16 (87.87) | 78.80 (81.20) | 10.71 | -1.75 | 3.19   |
| 1b         | 14.068 (14.151) | 30.961 (32.563) | 26.892 (26.766) | 90 (90)  | 100.91 (102.26) | 90 (90)  | 0.58  | 4.9   | -0.47  |
| 1c         | 19.262 (19.025) | 18.478 (19.025) | 24.185 (27.208) | 59.35 (60.89) | 60.67 (60.89) | 77.13 (73.17) | -1.24 | 2.87  | 11.11  |
| 1d         | 14.173 (14.017) | 28.161 (28.731) | 16.146 (17.073) | 90 (90)  | 110.63 (110.61) | 90 (90)  | -1.11 | 1.98  | 5.43   |
| 1e         | 20.823 (19.687) | 25.775 (28.163) | 10.402 (10.475) | 90 (90)  | 104.87 (97.91) | 90 (90)  | -5.77 | 8.45  | 0.70   |
Table S6: Density of the structures after DFT optimisation with solvent removed and the corresponding lattice energy. The values in the bracket refers to the experimental density with the solvent molecule removed.

| Structures | Density (g/cm³) | Lattice Energy (kJ/mol) |
|------------|----------------|------------------------|
| 1a         | 1.238 (1.167)  | -363.768               |
| 1b         | 1.053 (1.005)  | -386.109               |
| 1c         | 0.938 (0.807)  | -279.820               |
| 1d         | 1.004 (0.941)  | -317.136               |
| 1e         | 1.122 (1.053)  | -370.838               |

Figure S35. Overlay of polymorph 1a before (blue) and after DFT optimisation (red) with a RMSD of 4.15 Å.
Figure S36. Overlay of polymorph 1b before (blue) and after DFT optimization (red) with a RMSD of 2.98 Å.

Figure S37. Overlay of polymorph 1c before (blue) and after DFT optimization (red) with a RMSD of 5.46 Å.
Figure S38. Overlay of polymorph 1d before (blue) and after DFT optimisation (red) with a RMSD of 0.725 Å.

Figure S39. Overlay of polymorph 1e before (blue) and after DFT optimisation (red) with a RMSD of 1.523 Å.

7. References
1 V. Brega, M. Zeller, Y. He, H. Peter Lu and J. K. Klosterman, Chem. Commun., 2015, 51, 5077–5080.
2 N. P. Cowieson, D. Aragao, M. Clift, D. J. Ericsson, C. Gee, S. J. Harrop, N. Mudie, S. Panjikar, J. R. Price, A. Riboldi-Tunnicliffe, R. Williamson and T. Caradoc-Davies, *J. Synchrotron Radiat.*, 2015, **22**, 187–190.

3 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2015, **71**, 3–8.

4 G. M. Sheldrick, *Acta Crystallogr. Sect. C*, 2015, **71**, 3–8.

5 C. B. Hubschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Crystallogr.*, 2011, **44**, 1281–1284.

6 A. Thorn, B. Dittrich and G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2012, **68**, 448–451.

7 A. Spek, *Acta Crystallogr. Sect. C*, 2015, **71**, 9–18.

8 A. Spek, *Acta Crystallogr. Sect. D*, 2009, **65**, 148–155.

9 G. Kresse, J. Hafner, *Phys. Rev. B*, 1993, **48**, 13115-13118.

10 S. Grimme, S. Ehrlich, L. Goerigk, *J. Comp. Chem.*, 2011, **32**, 1456-1465

11 J. P. Perdew, K. Burke, M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865-3868.

12 G. Kresse, D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758-1775