

# Highly Connected Framework Materials from Flexible Tetra- Isophthalate Ligands

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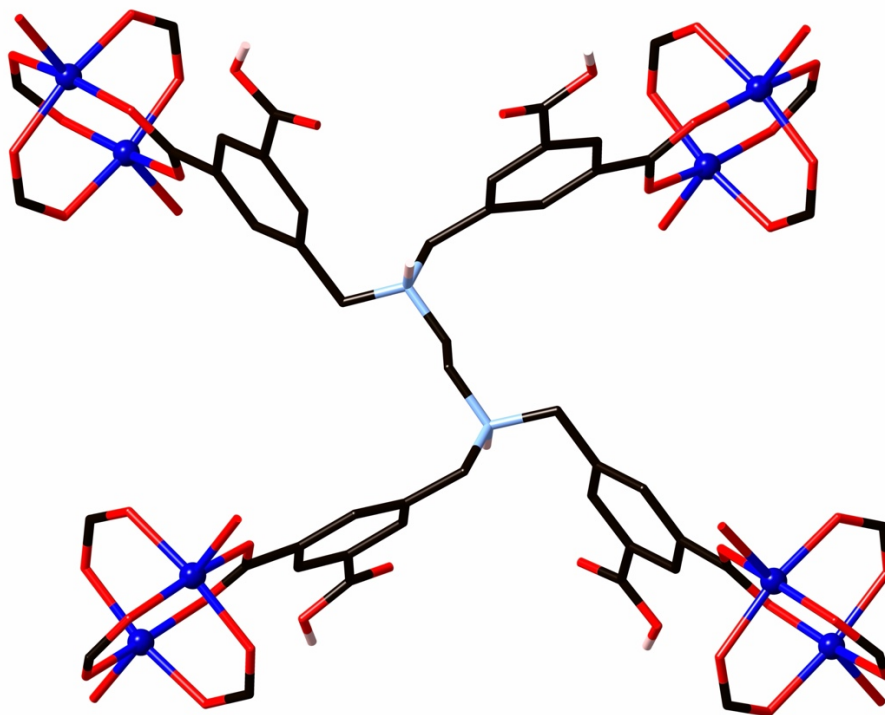
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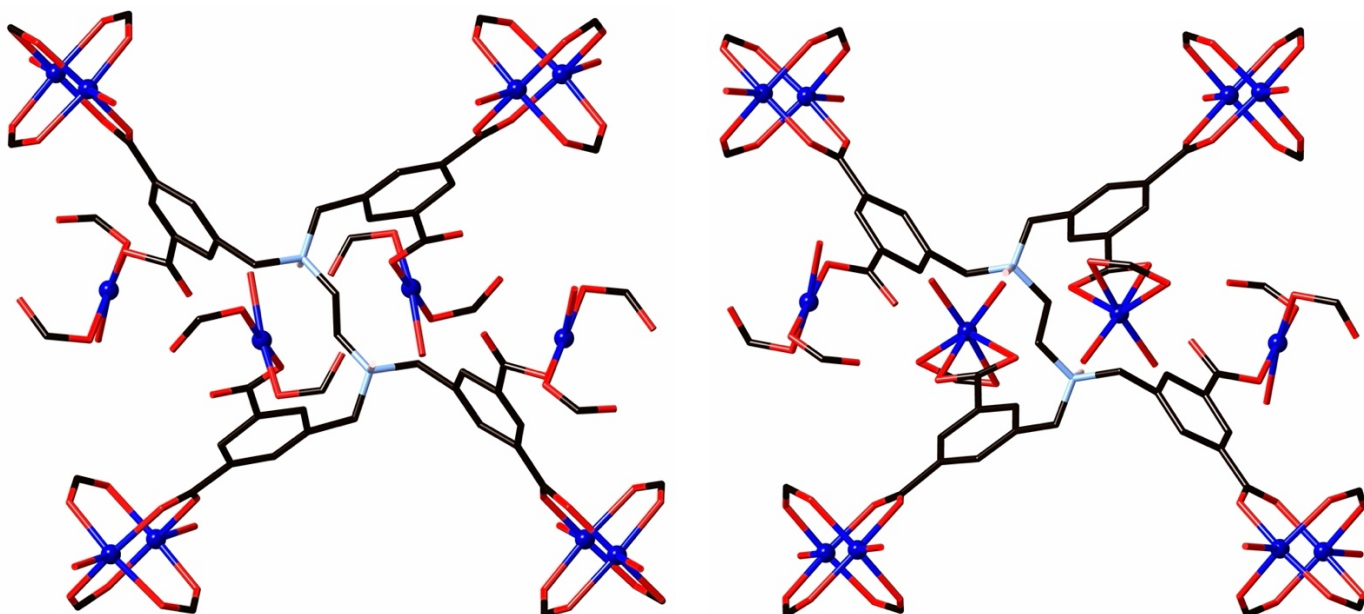
## 1. Conformations and Coordination Modes of the Ligands $H_xL1^{(8-x)-}$ - $H_xL4^{(8-x)-}$

The tetra-isophthalate ligands in the coordination polymers **1** – **11** adopt a variety of protonation states, conformations, and coordination modes. Each of the individual coordination environment of the ligand(s) in each structure are depicted below.

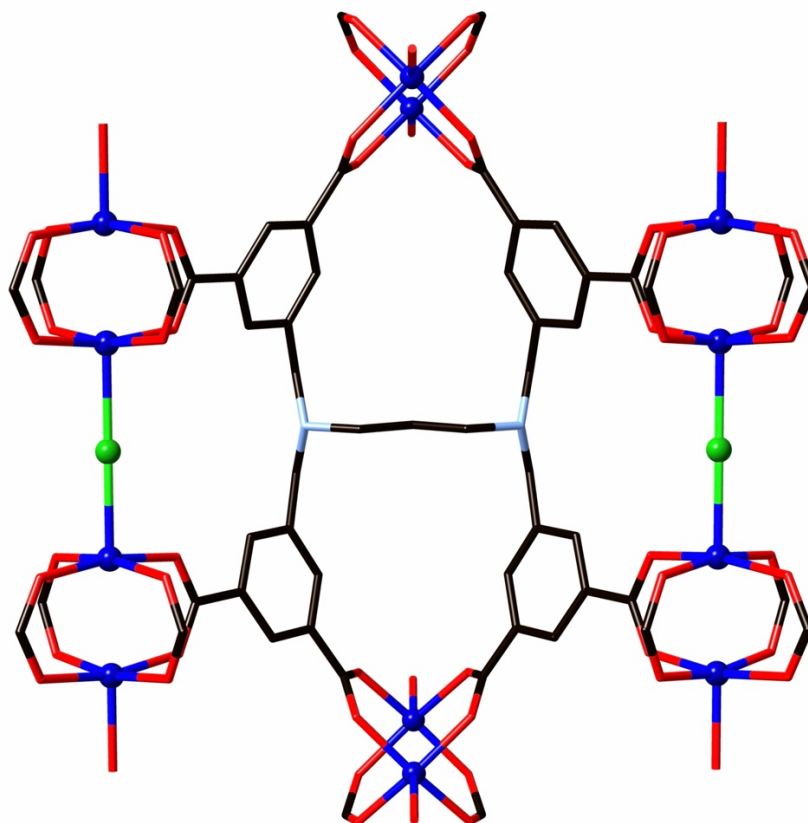
### *poly*-[Cu<sub>2</sub>(H<sub>4</sub>L1)(OH<sub>2</sub>)<sub>2</sub>] (**1**)



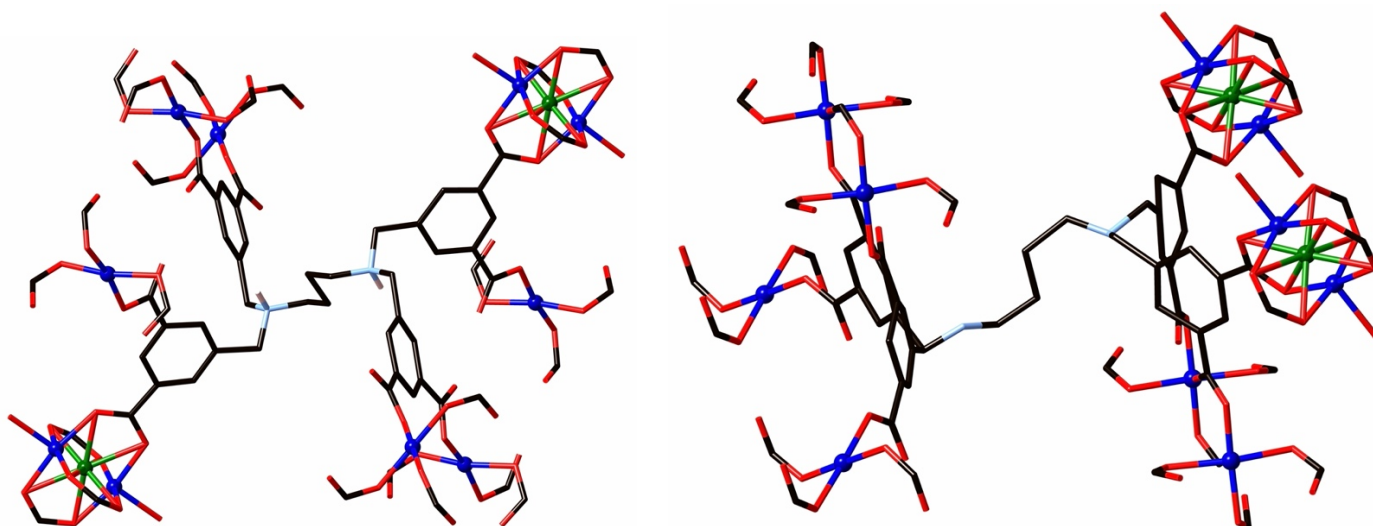
### *poly*-[Cu<sub>3.5</sub>(HL1)(OH<sub>2</sub>)<sub>3</sub>] (**2**)



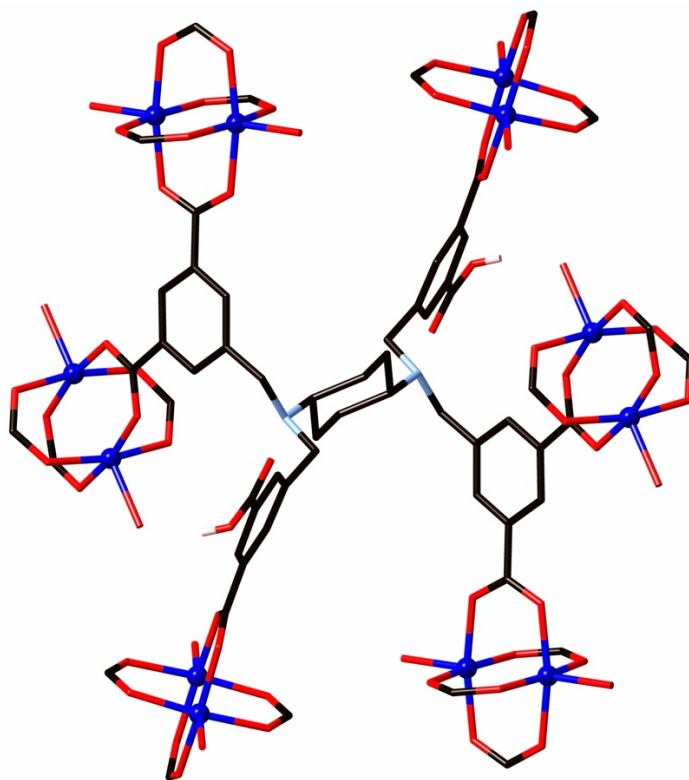
*poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)[Cu<sub>8</sub>(L2)<sub>2</sub>(Cl)(OH<sub>2</sub>)<sub>6</sub>·43H<sub>2</sub>O·4DMF} (3)



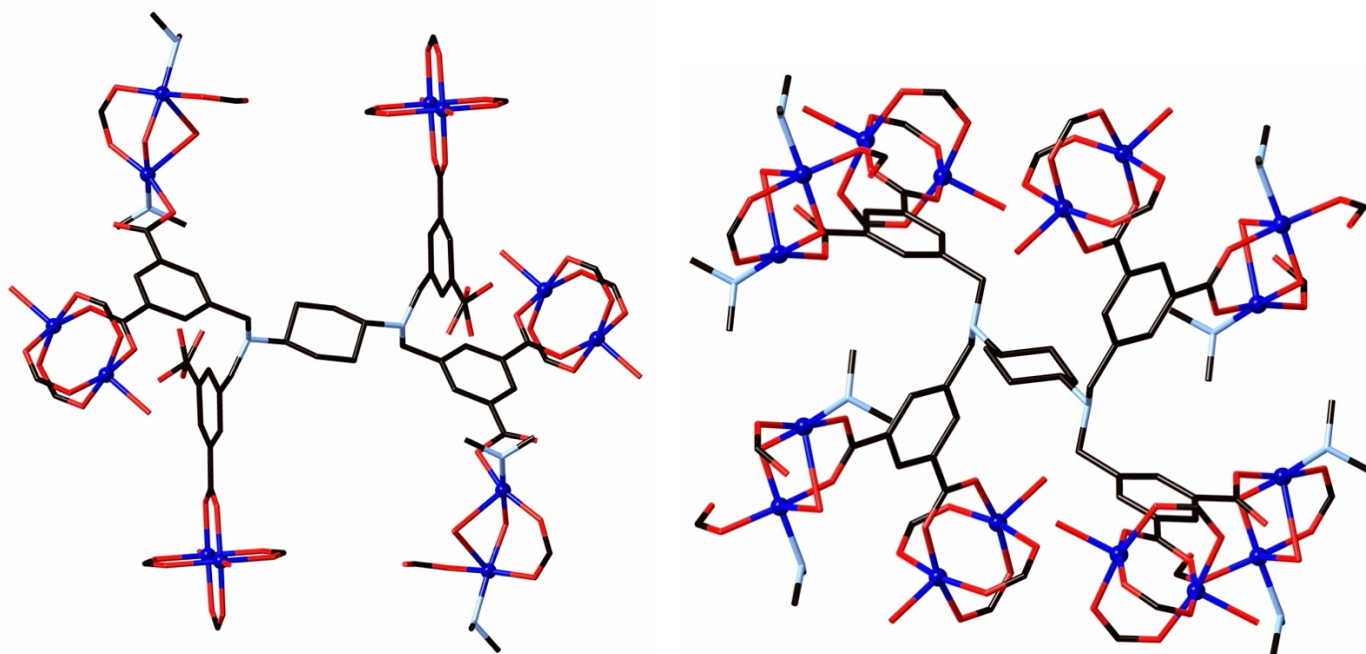
*poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>[Cu<sub>4.8</sub>(H<sub>1.2</sub>L3)<sub>2</sub>(OH<sub>2</sub>)<sub>1.6</sub>]} (4). Note that the disordered eight-coordinate copper within the paddlewheels is shown in green for clarity, and the right image shows only one orientation of the disordered ligand.



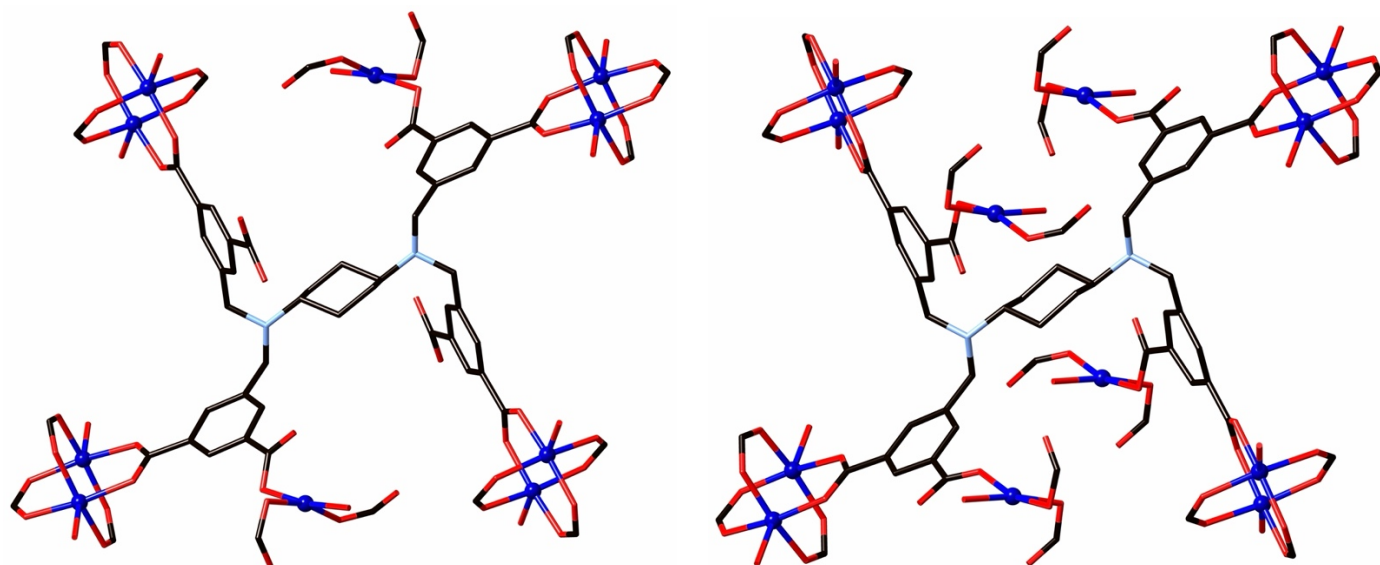
*poly*-[Cu<sub>3</sub>(H<sub>2</sub>L4)(OH<sub>2</sub>)<sub>3</sub>·2.25H<sub>2</sub>O·DMF (5). Note that the disordered non-coordinating carboxylate group is shown in only a single orientation for clarity.



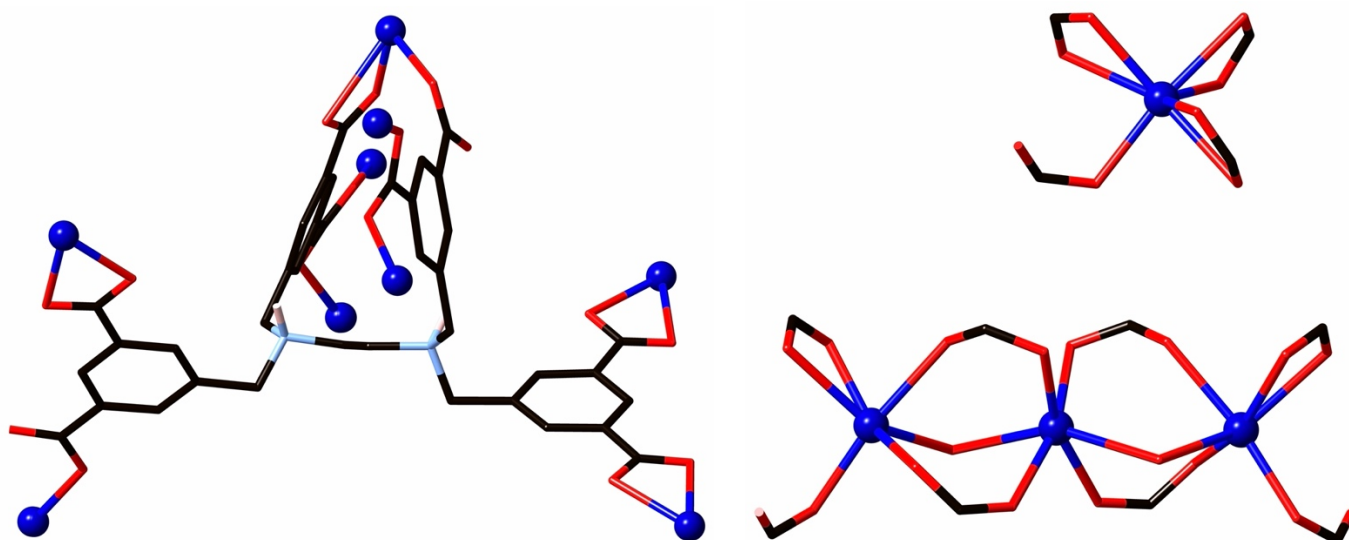
*poly*-[Cu<sub>4</sub>(HL4)(NHMe<sub>2</sub>)<sub>1.5</sub>(μ-OH)(μ-OH<sub>2</sub>)<sub>0.5</sub>(OH<sub>2</sub>)<sub>2.5</sub>·H<sub>2</sub>O (6)



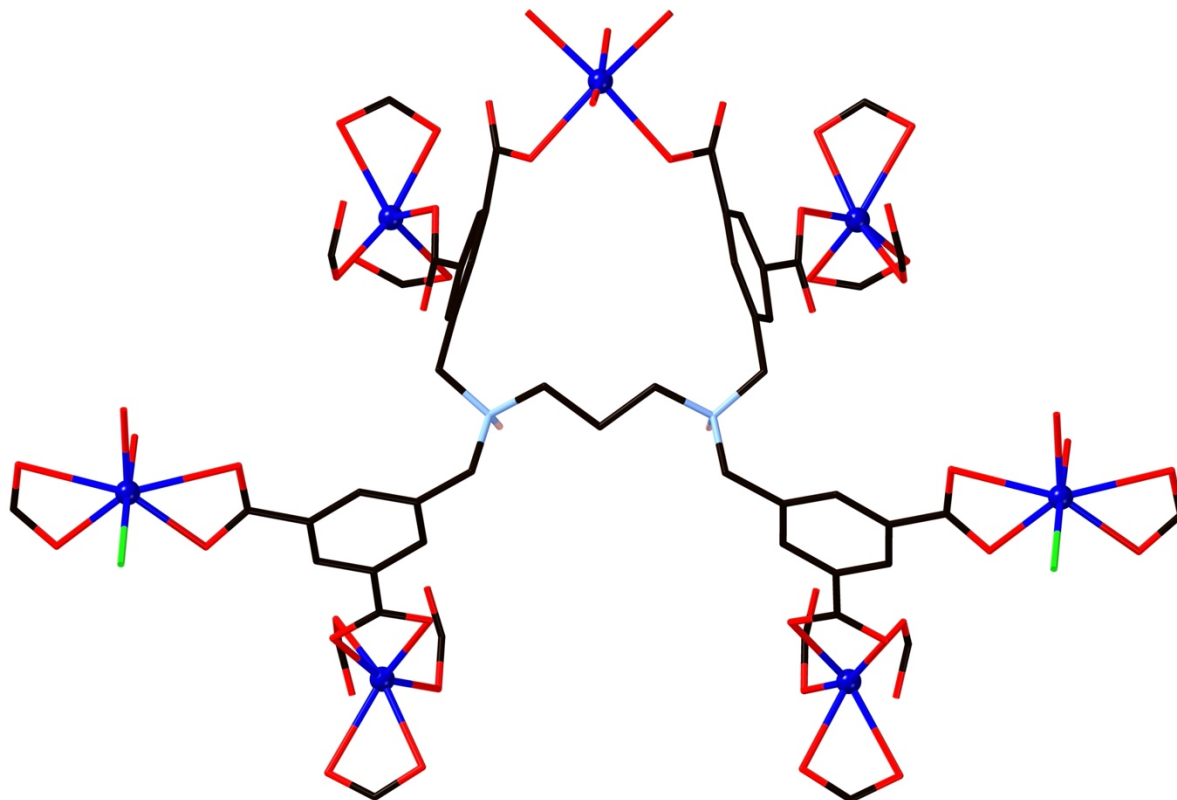
*poly*-[Cu<sub>3</sub>(H<sub>2</sub>L4)(OH<sub>2</sub>)<sub>3</sub>] (7)



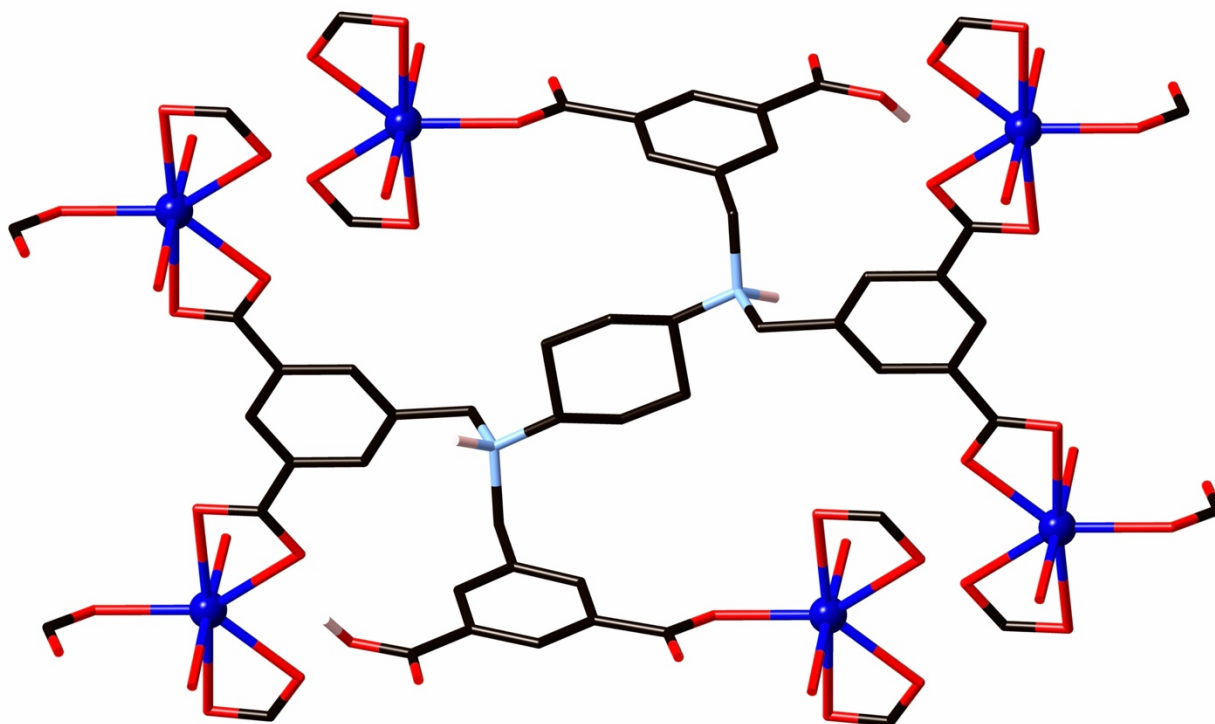
*poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>[Cd<sub>5</sub>(H<sub>2</sub>L1)<sub>2</sub>(μ-OH<sub>2</sub>)<sub>2</sub>]·H<sub>2</sub>O} (8)



*poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)[Cd<sub>3</sub>(H<sub>2</sub>L2)(Cl)(OH<sub>2</sub>)<sub>5.5</sub>]·6H<sub>2</sub>O·0.5DMF} (9). Note that only one position of the disordered parts of the ligand is shown for clarity.

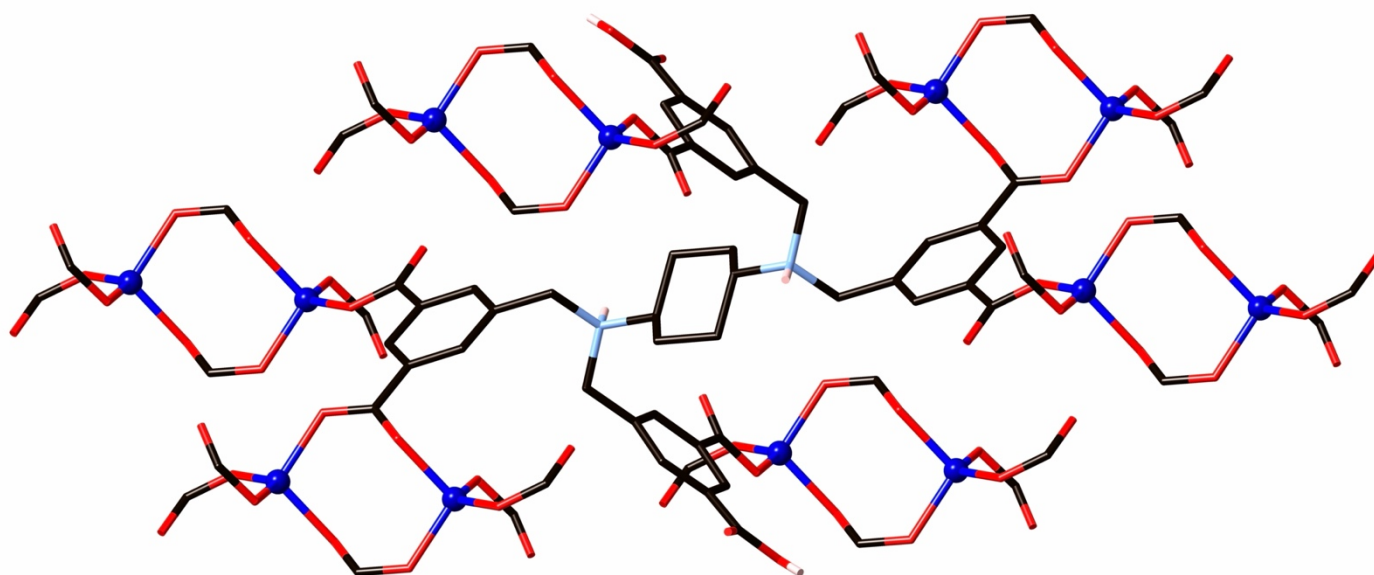


*poly*-[Cd<sub>2</sub>(H<sub>4</sub>L4)(OH<sub>2</sub>)<sub>4</sub>]·10H<sub>2</sub>O·1.25DMF (10)

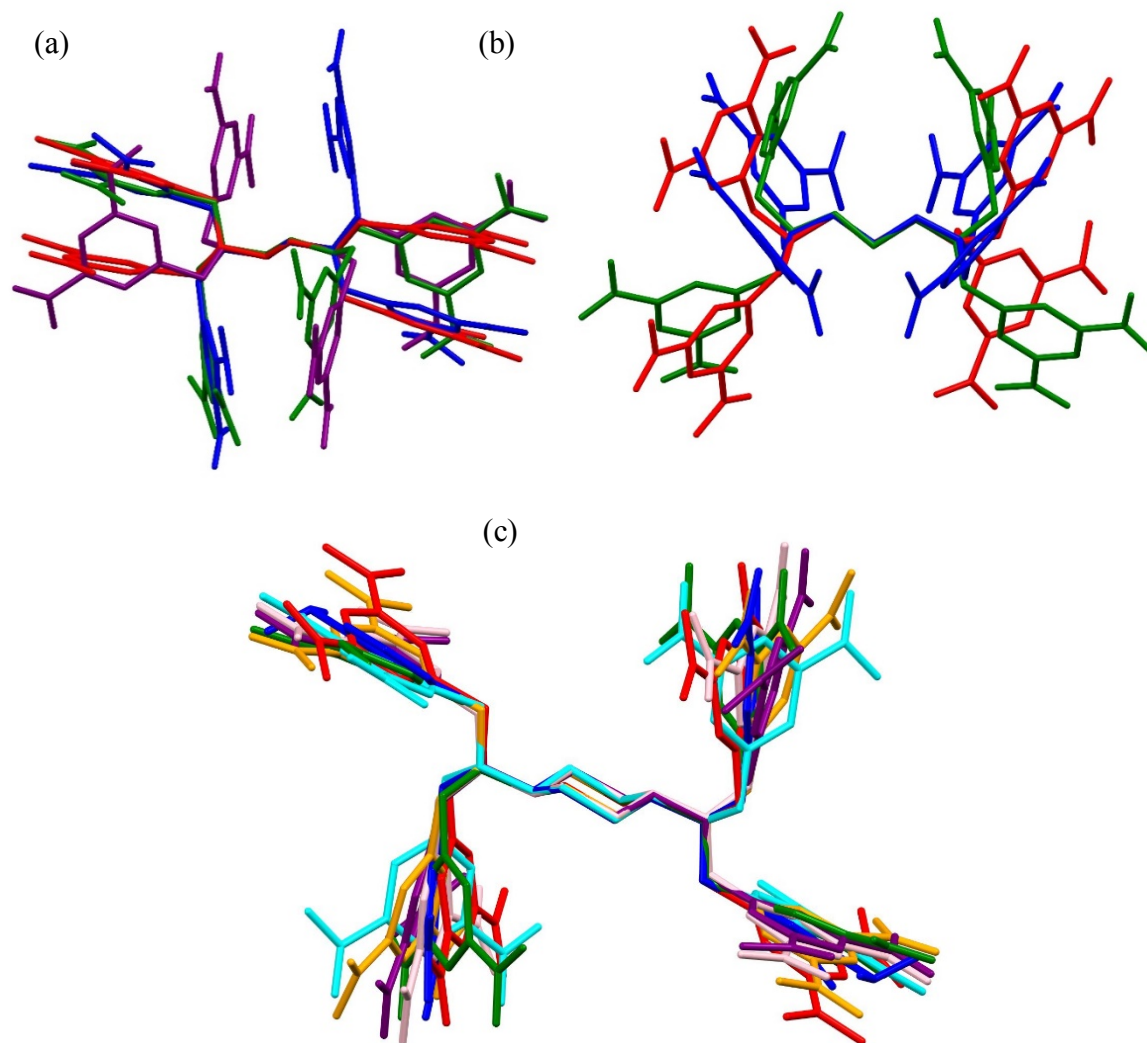




*poly*-[Zn<sub>2</sub>(H<sub>4</sub>L4)]·3H<sub>2</sub>O·2DMF (11)



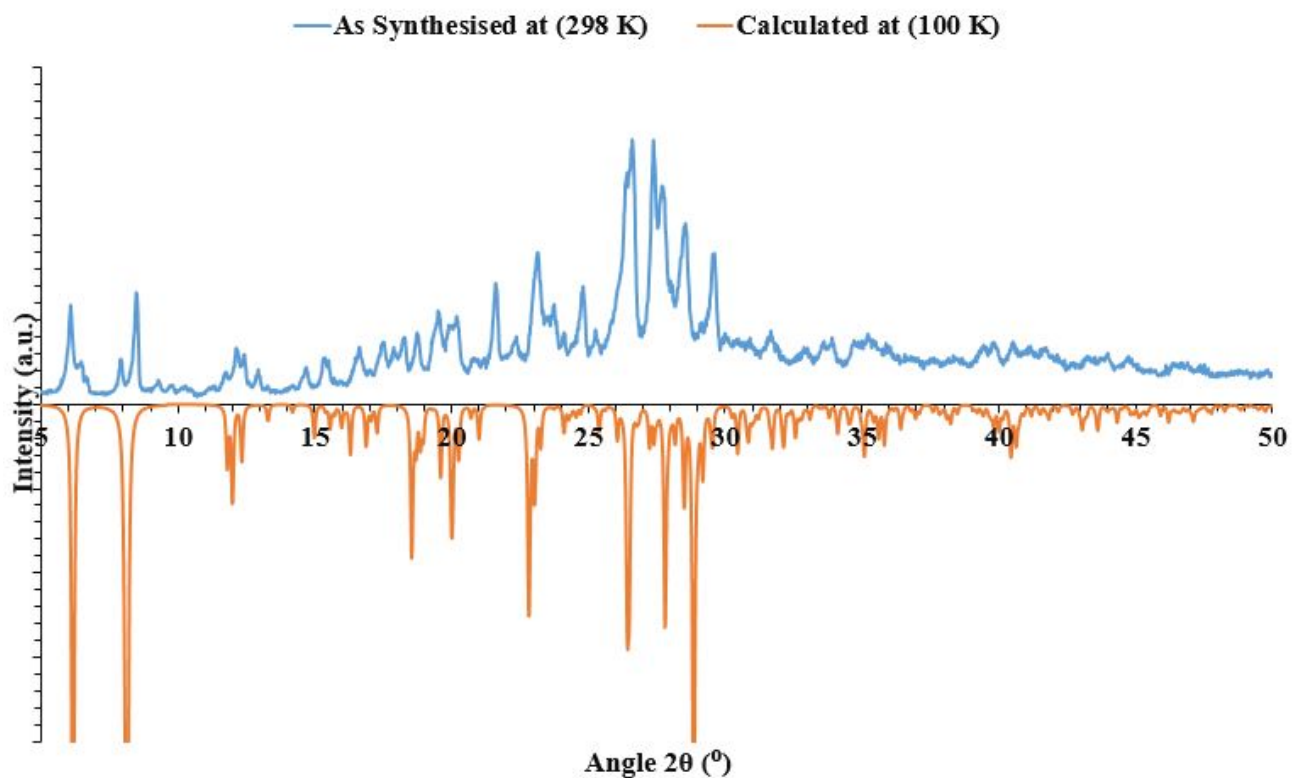
## 2. Overlays of Ligand Conformations (L1, L2 and L4)



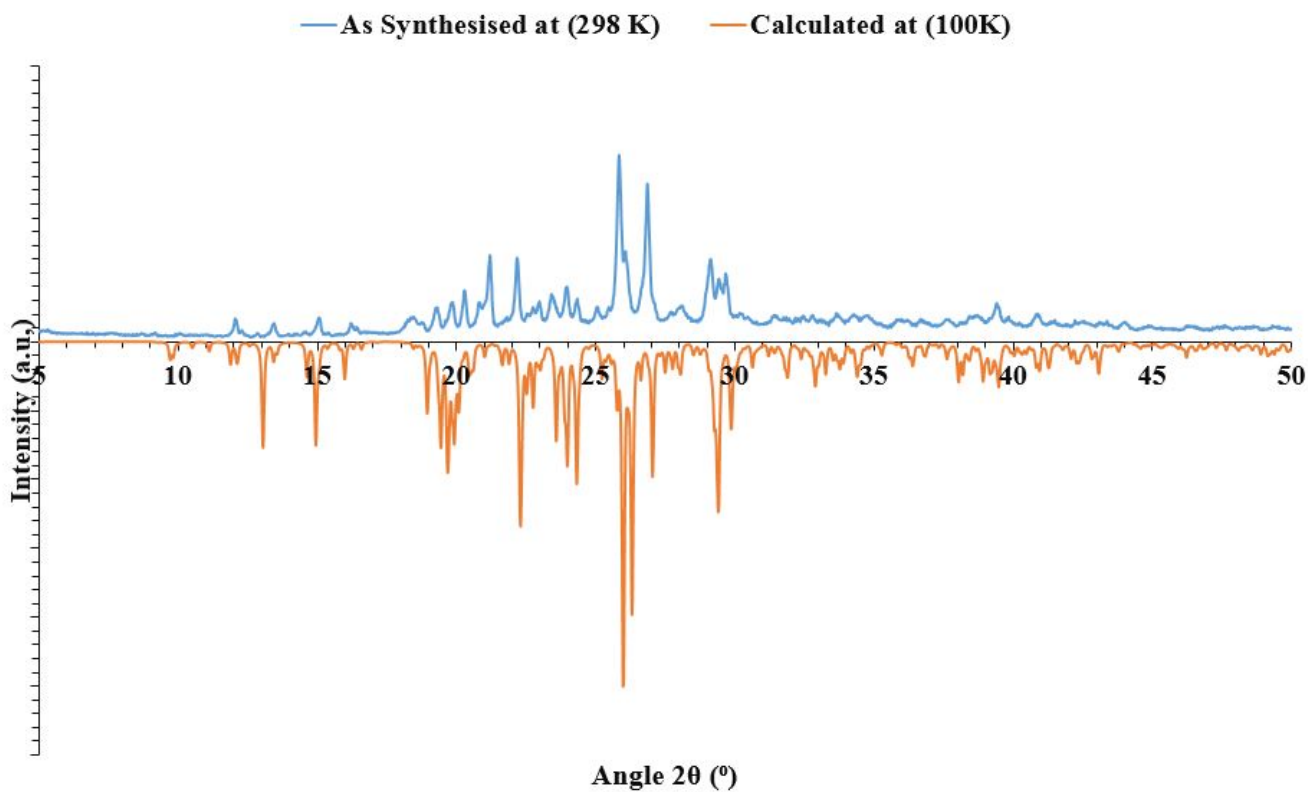
**Figure S2.1.** (a) Overlaid ligand conformations of  $H_xL1^{(8-x)-}$  from the structures of  $(H_{10}L1)Cl_2 \cdot 4H_2O$  in red, **1** in purple, **2** in blue and **8** in green. (b) Overlaid ligand conformations obtained in  $(H_9L2)Cl \cdot 3H_2O$  shown in red, **3** shown in blue and **9** shown in green. Hydrogen and disordered atoms were hidden for clarity. (c) Overlay of all crystal structures obtained with ligand L4:  $(H_{10}L4)Cl_2$  shown in red,  $(H_{10}L4)Cl_2 \cdot 3H_2O$  shown in orange, **5** shown in blue, **6** shown in purple, **7** shown in pink, **10** shown in cyan and **11** shown in green. Hydrogen atoms were omitted for clarity.



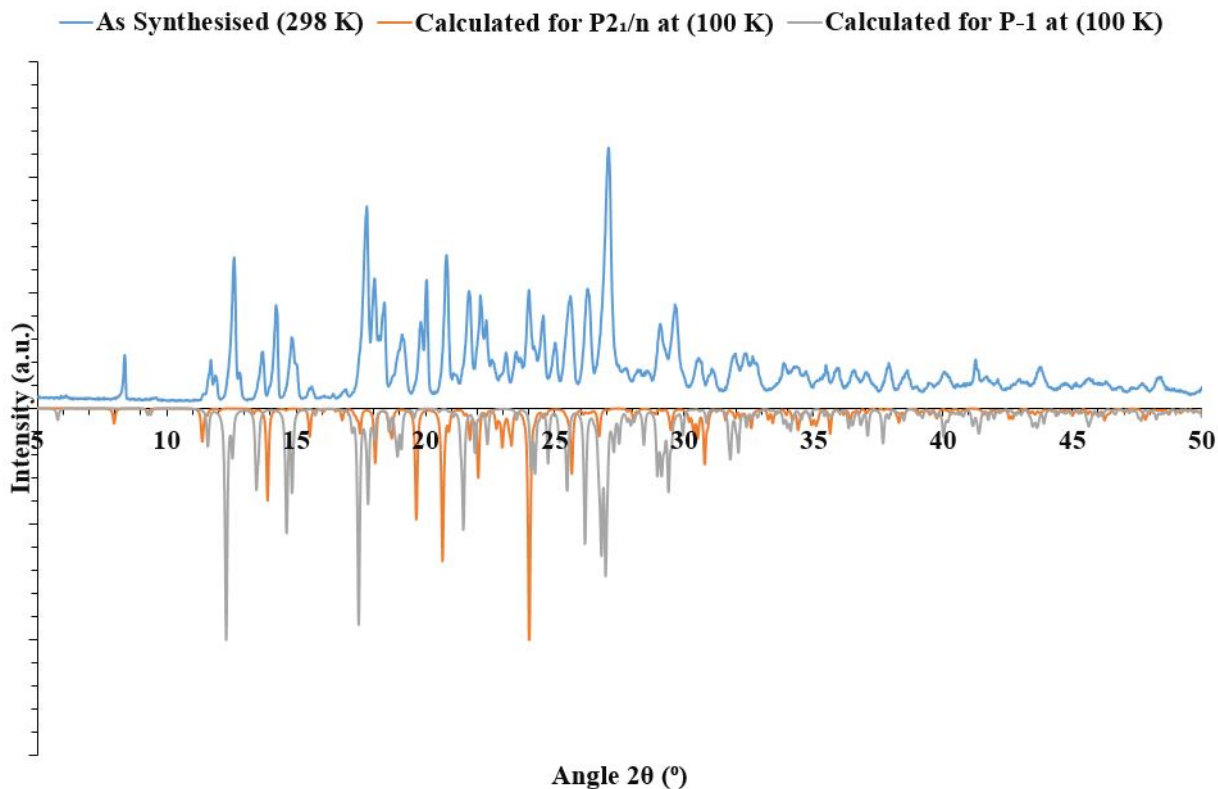
### 3. Powder X-Ray Diffraction (PXRD) Data



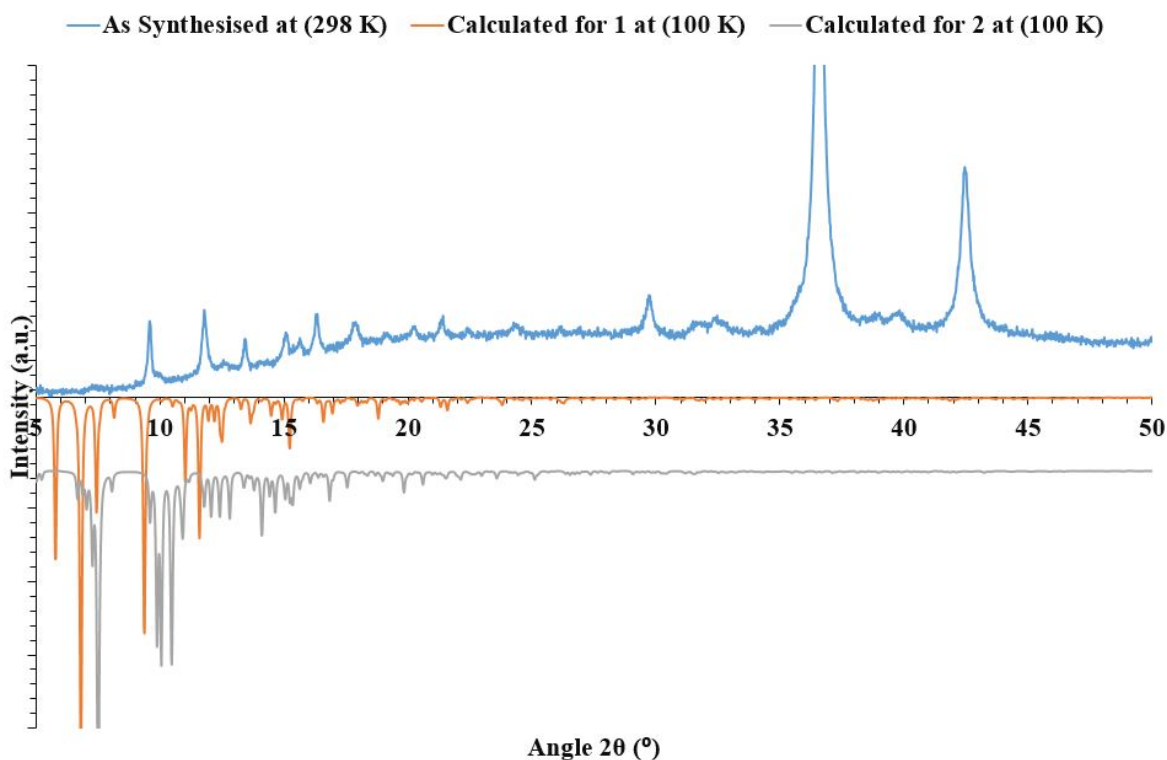
**Figure S2.1.** PXRD data for  $(\text{H}_{10}\text{L1})\text{Cl}_2 \cdot 4\text{H}_2\text{O}$  (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



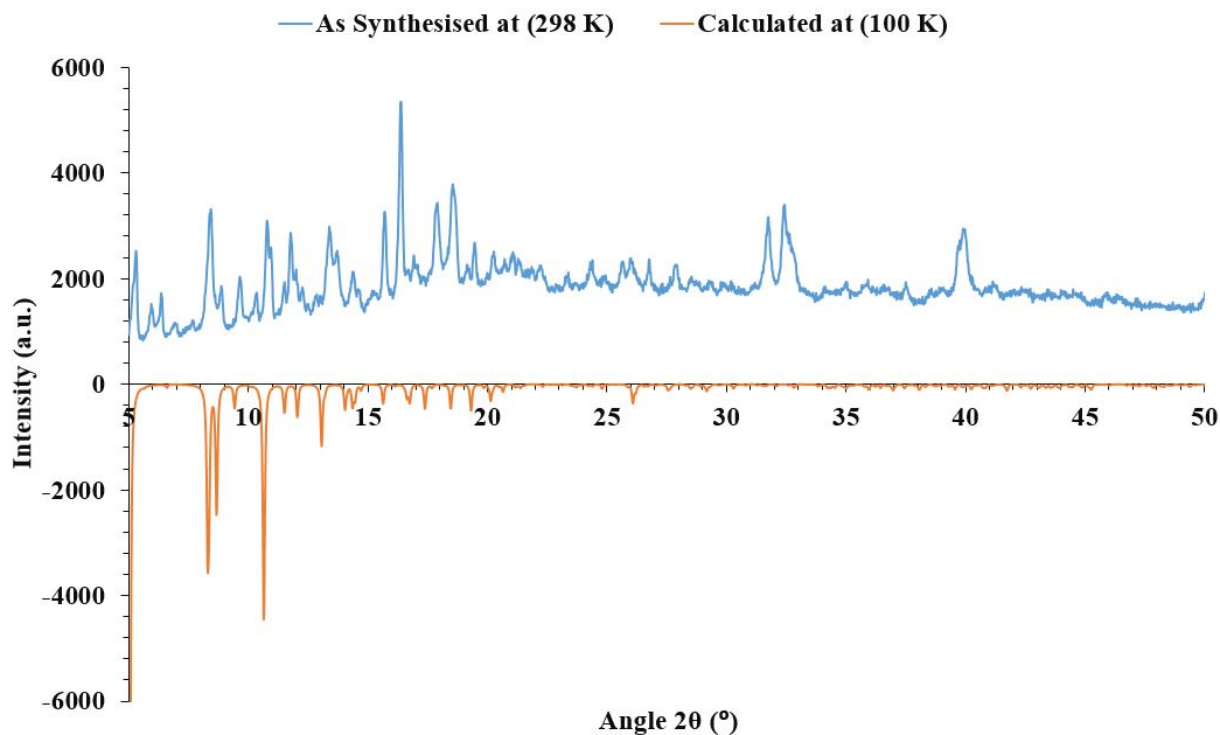
**Figure S2.2.** PXRD data for  $(\text{H}_{10}\text{L2})\text{Cl}_2 \cdot 3\text{H}_2\text{O}$  (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



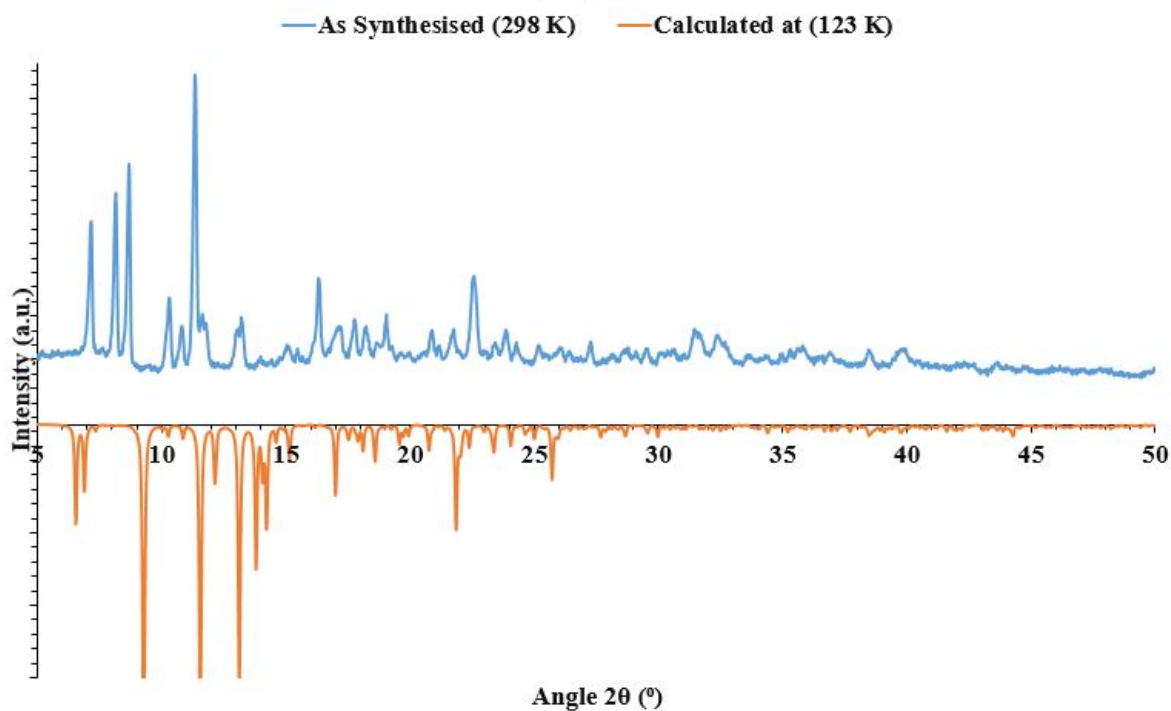
**Figure S2.3.** PXRD of the mixed product containing  $(\text{H}_{10}\text{L4})\text{Cl}_2 \cdot 2\text{H}_2\text{O}$  and  $(\text{H}_{10}\text{L4})\text{Cl}_2$  collected at room temperature compared to those calculated from single crystal data at 100 K (grey = dihydrate, orange = anhydrous).



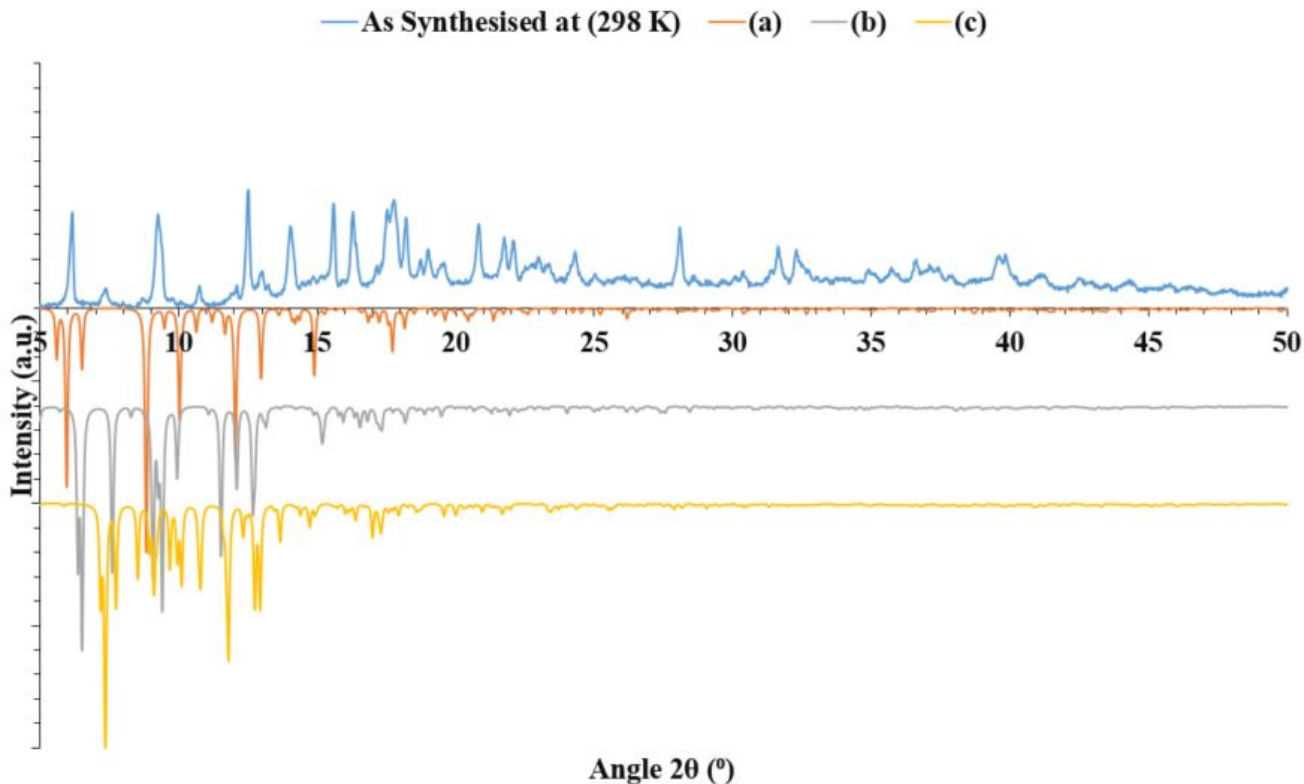
**Figure S2.4.** PXRD of the product containing **1** and **2** compared to calculated patterns. Compound **1** appears to be the main coordination polymer formed, although characterisation is hampered by the presence of CuO.



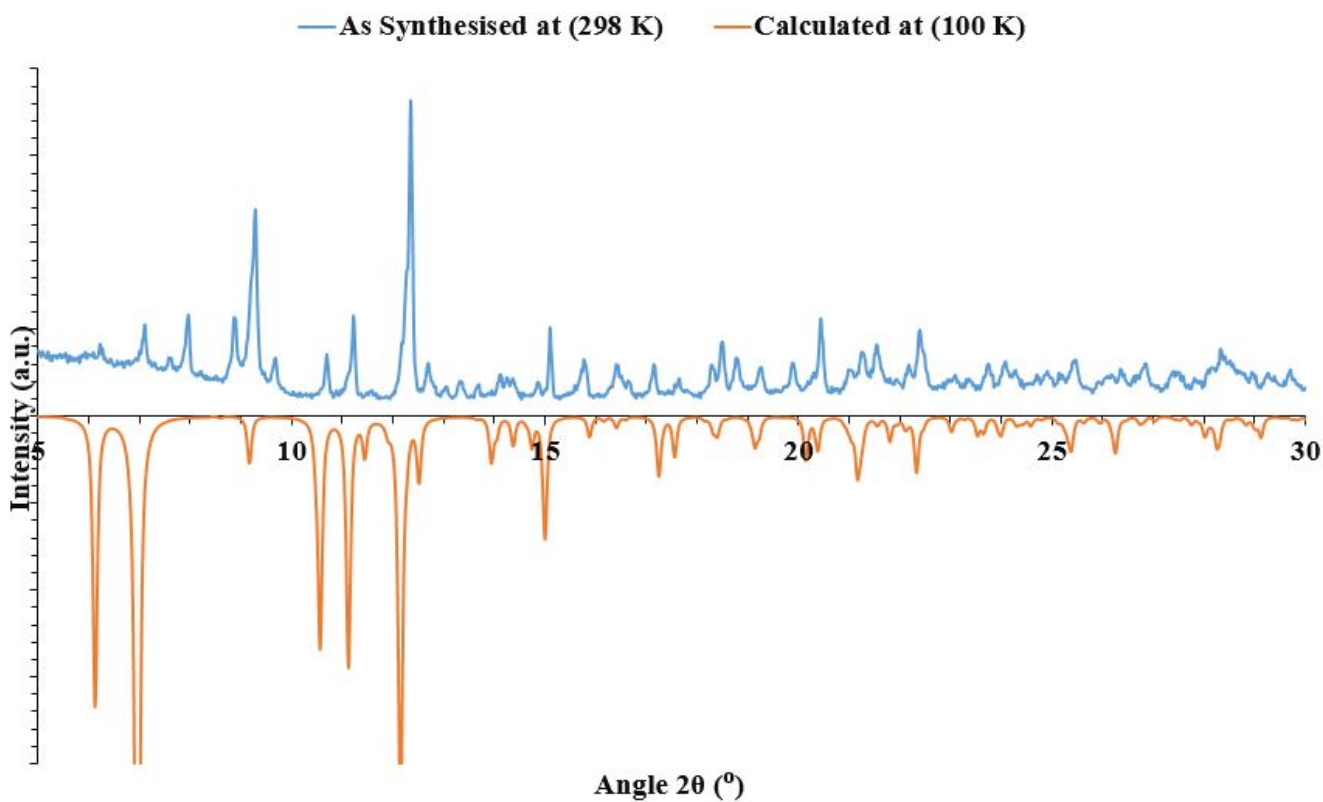
**Figure S2.5.** PXRD data for **3** (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



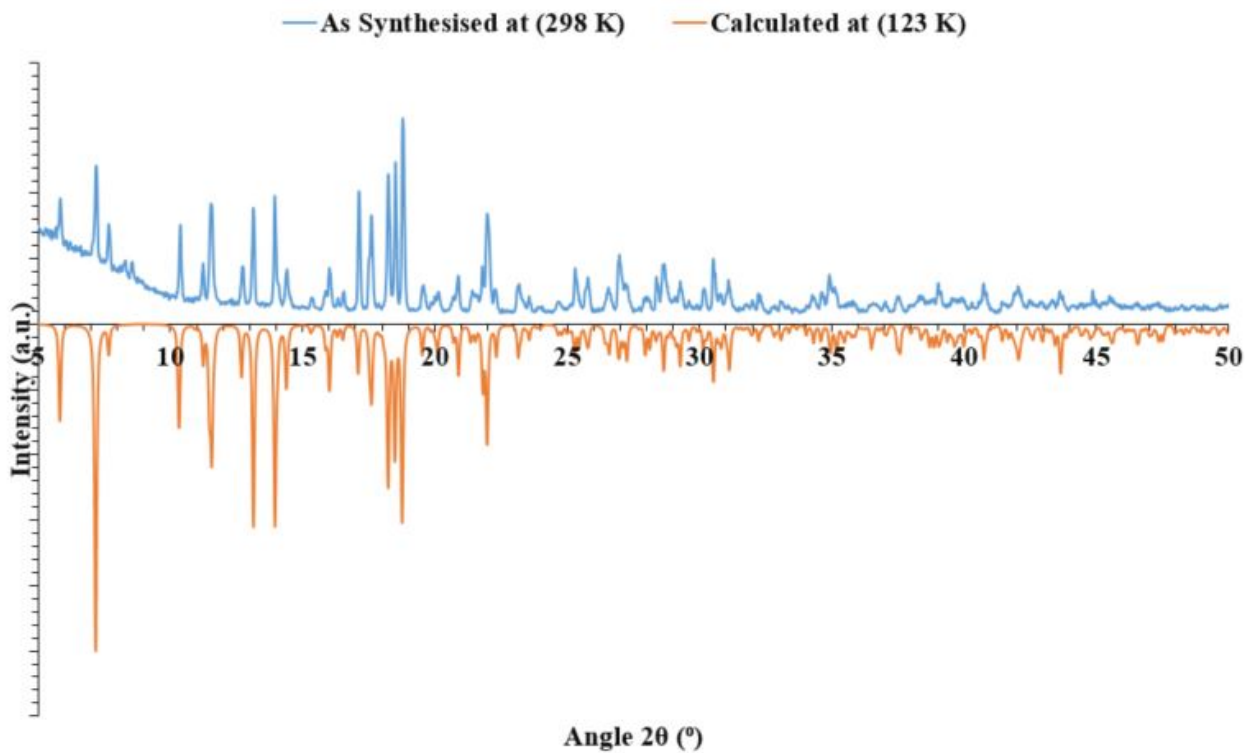
**Figure S2.6.** PXRD data for **4** (blue) and the calculated pattern from single crystal data inverted for comparison (orange). The experimental pattern shows a crystalline impurity that could not be identified.



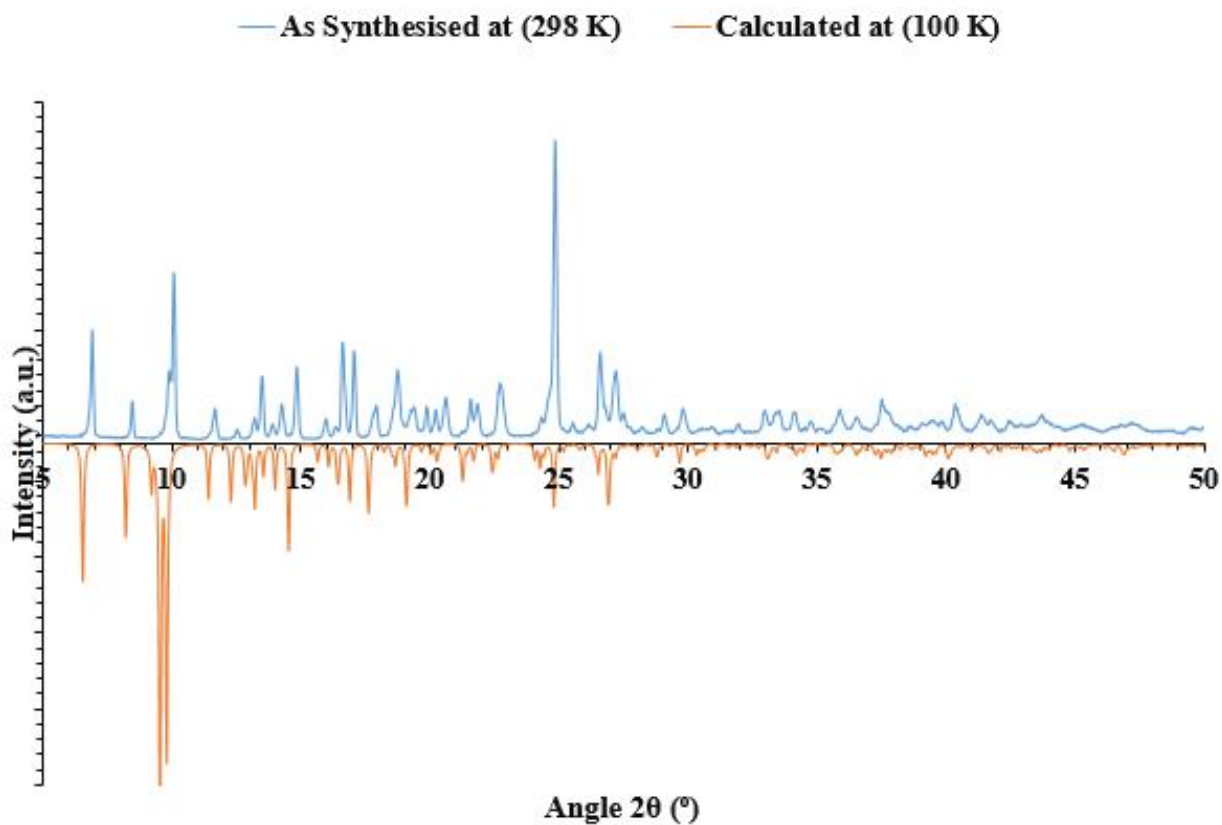
**Figure S2.7.** PXRD of the product containing three concomitant products (**5**, **6**, and **7**) collected at room temperature compared to those calculated from single crystal data at 100 K for **5** (a), **6** (b), and **7** (c).



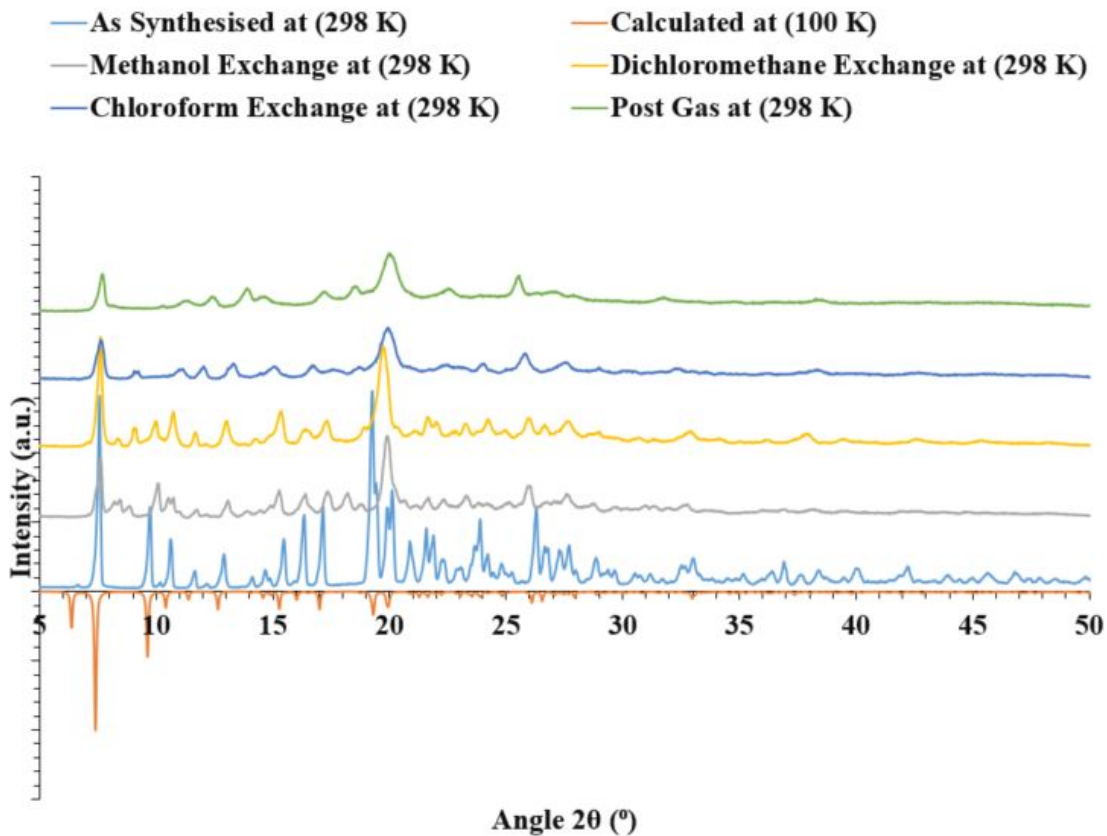
**Figure S2.8.** PXRD data for **8** (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



**Figure S2.9.** PXRD data for **9** (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



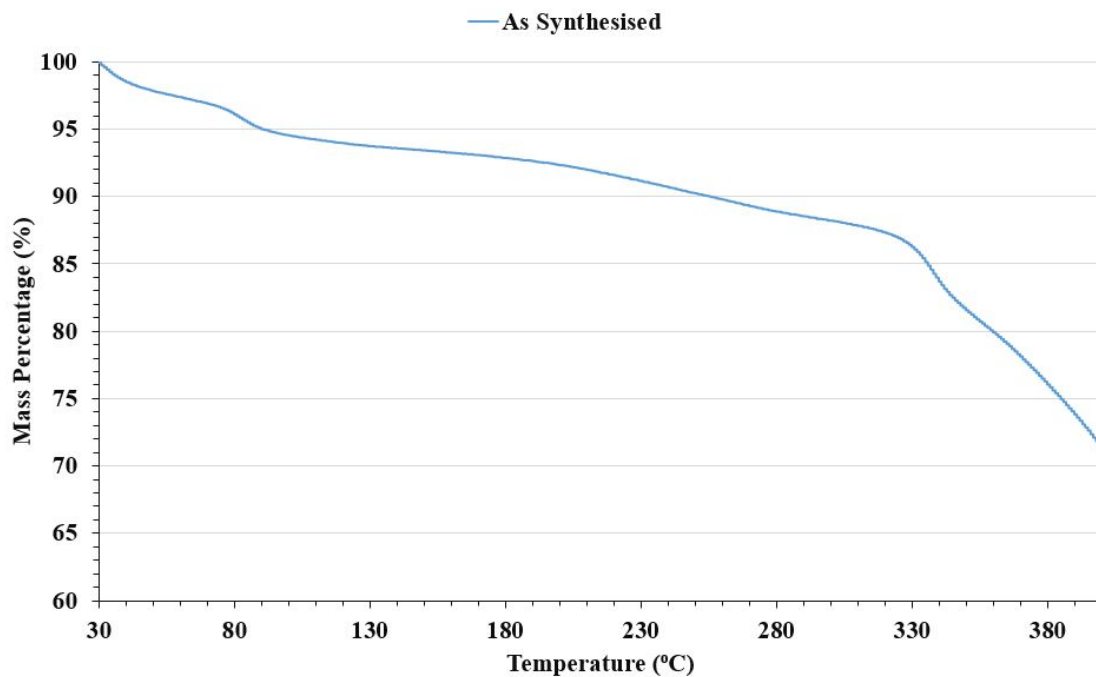
**Figure S2.10.** PXRD data for **10** (blue) and the calculated pattern from single crystal data inverted for comparison (orange).



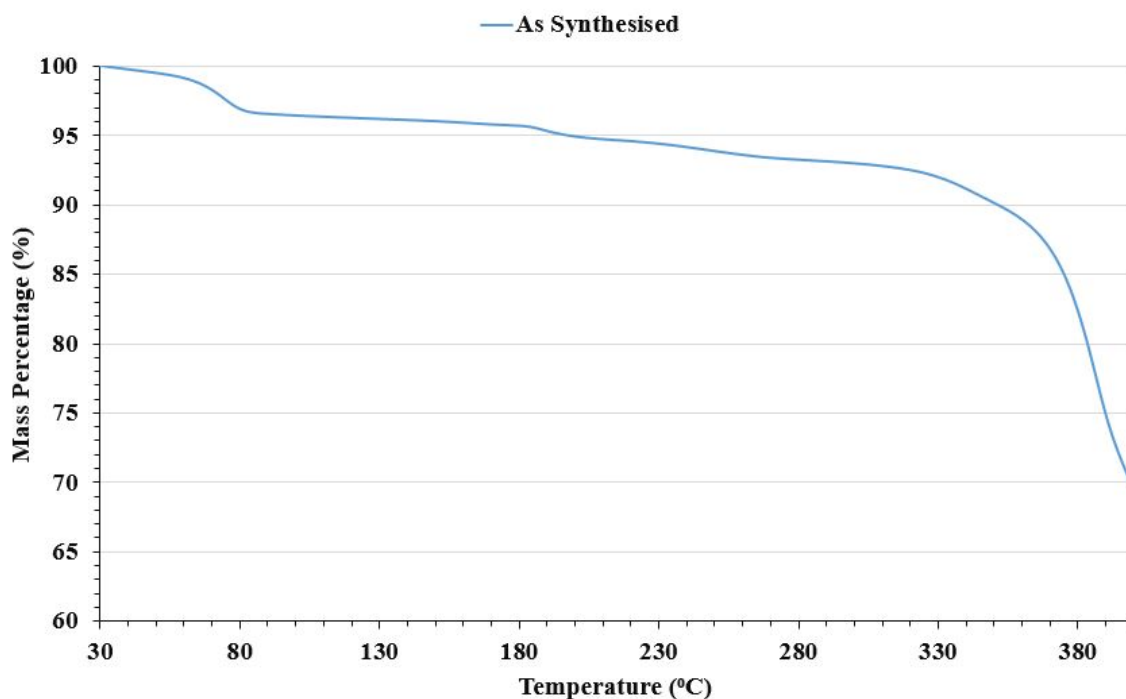
**Figure S2.11.** PXRD data for as synthesised **11** (blue), after methanol exchange (grey), after dichloromethane exchange (yellow), after chloroform exchange (dark blue), after gas adsorption (green), and the calculated pattern from single crystal data inverted for comparison (orange).



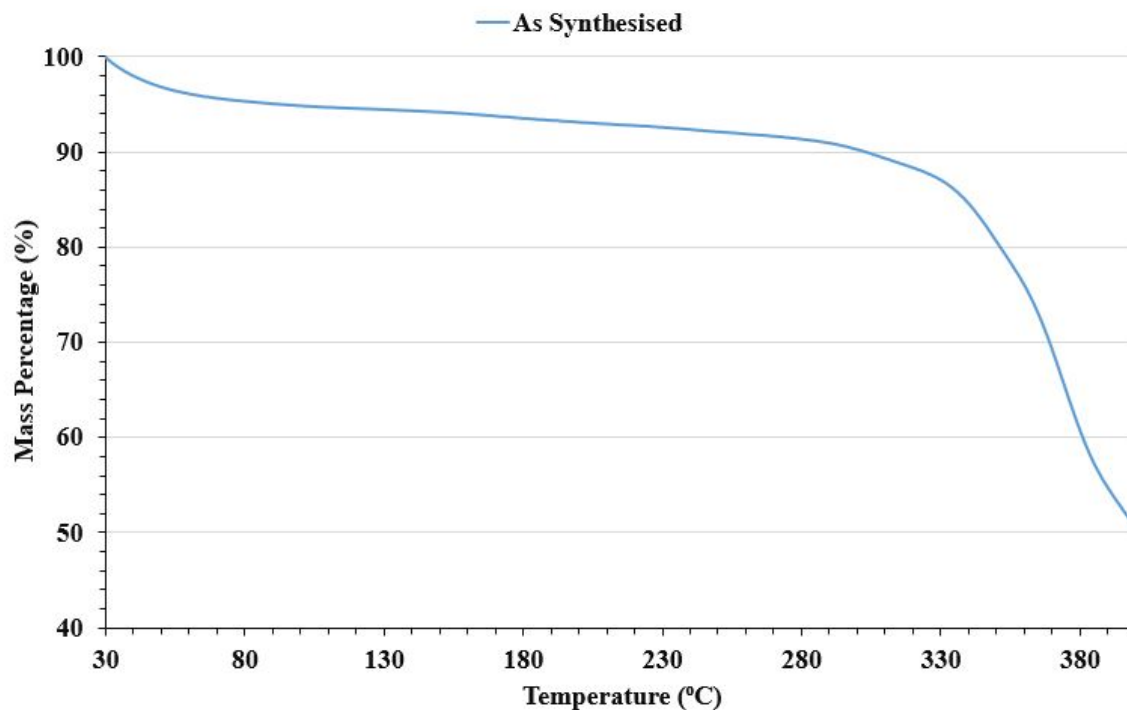
#### 4. Thermal Gravimetric Analysis (TGA) Plots



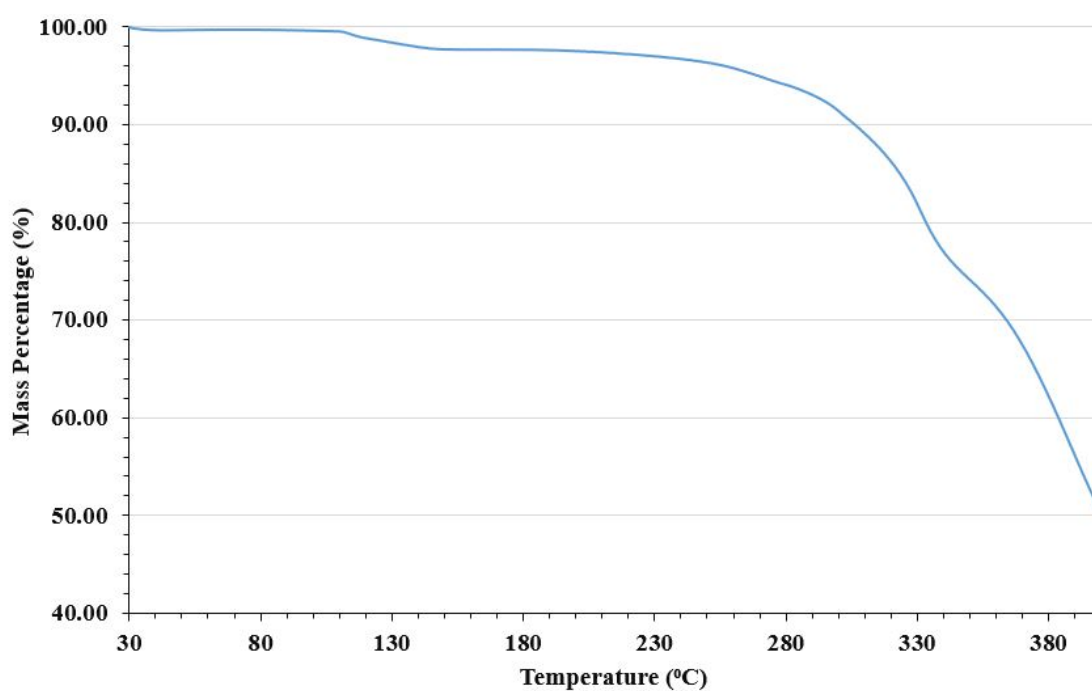
**Figure S3.1.** TGA trace for (H<sub>10</sub>L1)Cl<sub>2</sub>·4H<sub>2</sub>O showing a mass loss of 7% in the range 30-125 °C, corresponding to 3.5 H<sub>2</sub>O (calc. 7% for 3.5 H<sub>2</sub>O). The sample started to decompose at 203 °C.



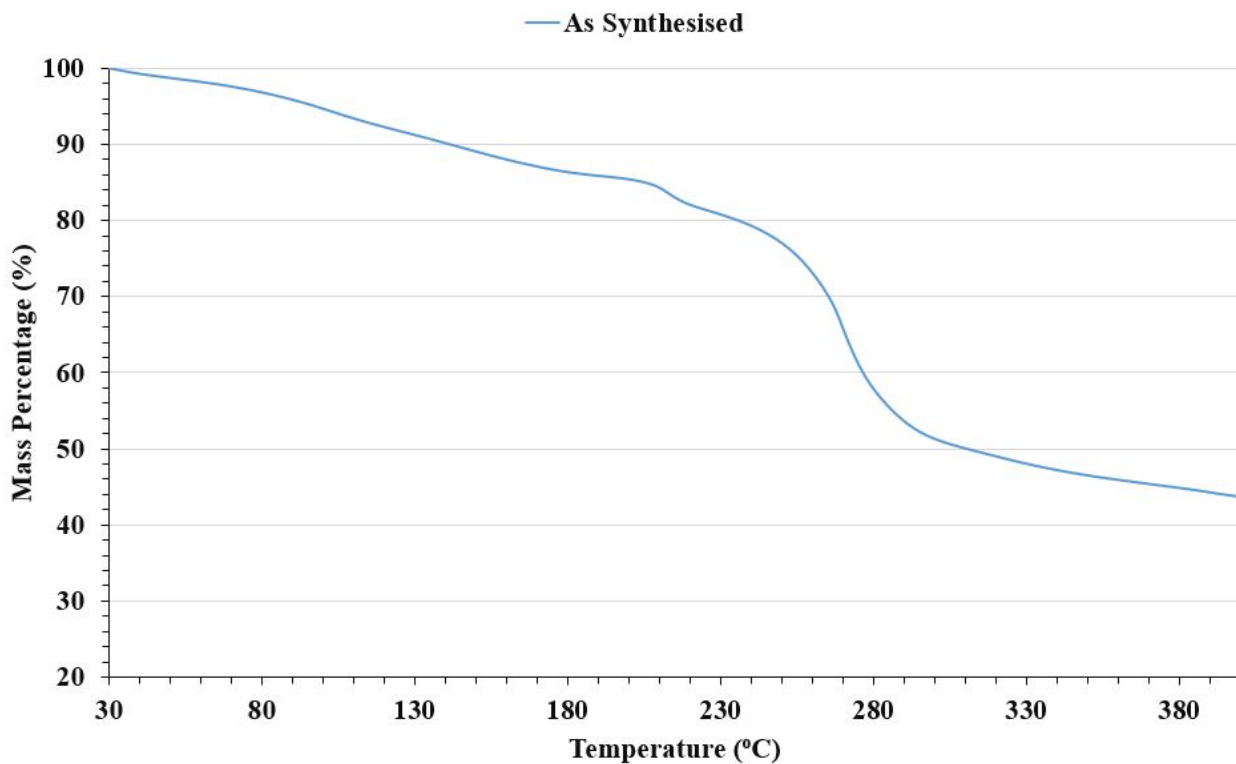
**Figure S3.2.** TGA trace for (H<sub>9</sub>L2)Cl·3H<sub>2</sub>O showing a mass loss of 4% in the range 30-101 °C, corresponding to 1.9 H<sub>2</sub>O (calc. 4% for 1.9 H<sub>2</sub>O). The sample started to decompose at 180 °C.



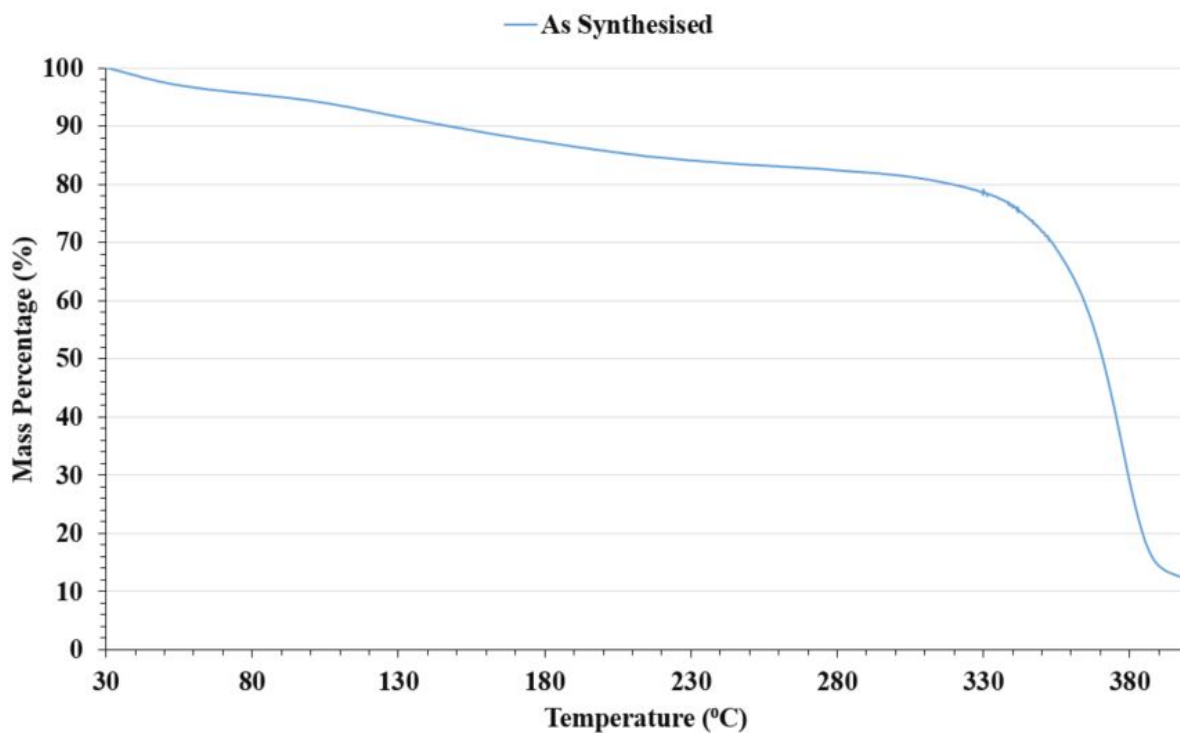
**Figure S3.3.** TGA trace for (H<sub>10</sub>L3)Cl<sub>2</sub>·3H<sub>2</sub>O showing mass loss of 6% in the range 30-133 °C, corresponding to 3 H<sub>2</sub>O (calc. 6% for 3 H<sub>2</sub>O). The sample started to decompose at 280 °C.



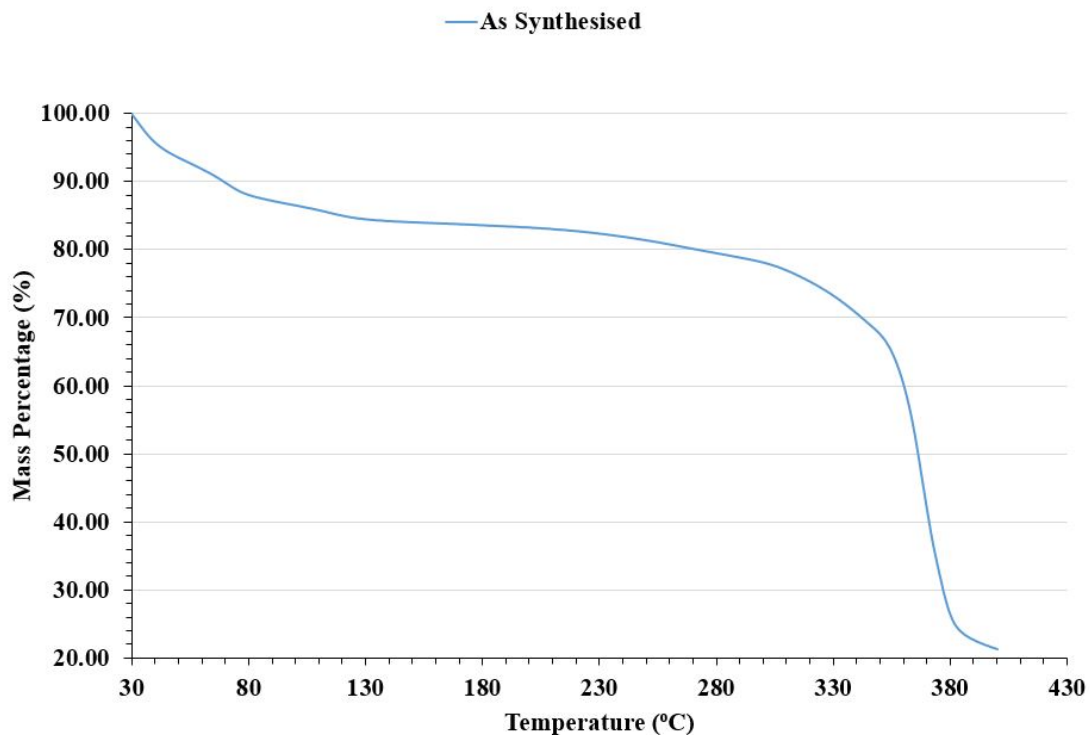
**Figure S3.4.** TGA trace for (H<sub>10</sub>L4)Cl<sub>2</sub>·2.75H<sub>2</sub>O showing mass loss of 2% in the range 30-130 °C, corresponding to 1 H<sub>2</sub>O (calc. 2% for 1 H<sub>2</sub>O). The sample started to decompose at 260 °C.



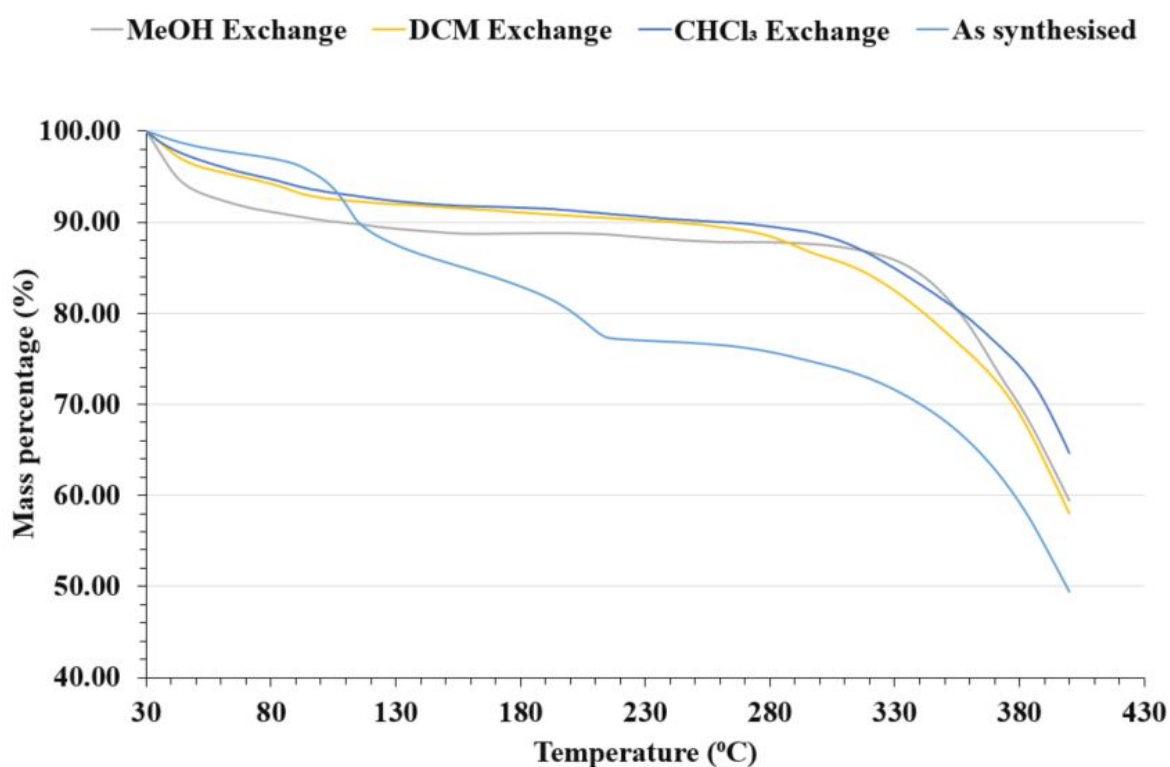
**Figure S3.5.** TGA trace for **3** showing mass loss of 15% in the range 50-185 °C, corresponding to 12 H<sub>2</sub>O and 2 DMF (calc. 15% for 12 H<sub>2</sub>O and 2 DMF). The sample started to decompose at 220 °C.



**Figure S3.6.** TGA trace for **9** showing mass loss of 18% in the range 30-280 °C corresponding to 10 H<sub>2</sub>O and 1 DMF molecules (calc. 18 % for 10 H<sub>2</sub>O and 1 DMF molecules). The sample started to decompose at 330 °C.



**Figure S3.7.** TGA trace for **10** showing mass loss of 20.5 % in the range 30-280 °C, corresponding to 10.6 H<sub>2</sub>O and 0.8 DMF molecules (calc. 20.5 % for 10.6 H<sub>2</sub>O and 0.8 DMF molecules). The sample started to decompose at 300 °C.



**Figure S3.8.** The TGA for the compound **11** freshly synthesised (blue), after methanol exchange (grey), after dichloromethane exchange (yellow) and after chloroform exchange (dark blue), indicating that the solvent was successfully exchanged.

## 5. Special Crystallographic Refinement Details

### **(H<sub>10</sub>L<sub>4</sub>)Cl<sub>2</sub>·3H<sub>2</sub>O**

One disordered water molecule was modelled over two close positions (O10A and O10B) with fixed chemical occupancies of ½, as was a disordered carboxylate oxygen (O7A and O7B). A further included water molecule was also assigned ½ occupancy.

### ***poly*-[Cu<sub>2</sub>(H<sub>4</sub>L1)(OH<sub>2</sub>)<sub>2</sub>] (1)**

The structure was refined as an inversion twin. Four crystallographically unique carboxylate/carboxylic acid groups were non-coordinating and were assigned as mixed positions with hydrogen atoms at ½ occupancy as part of a hydrogen bonding dimer with a disordered hydrogen atom. The amine groups were protonated, determined by location of electron density in the Fourier difference map. The final model was treated with the SQUEEZE routine in PLATON (3382 e<sup>-</sup> in 12427 Å<sup>3</sup> per unit cell).<sup>1</sup>

### ***poly*-[Cu<sub>3.5</sub>(H<sub>1</sub>L1)(OH<sub>2</sub>)<sub>3</sub>] (2)**

The sample was very poorly diffracting, with a resolution limit of 1.26 Å using synchrotron radiation. The structure was refined with isotropic restraints applied for all atoms. The final model was treated with the SQUEEZE routine in PLATON (1967 e<sup>-</sup> in 10083 Å<sup>3</sup> per unit cell).<sup>1</sup>

### ***poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)[Cu<sub>8</sub>(L<sub>2</sub>)<sub>2</sub>(Cl)(OH<sub>2</sub>)<sub>6</sub>]·43H<sub>2</sub>O·4DMF} (3)**

The dimethyl ammonium cation was disordered over a mirror plane, with the carbon atoms coincidental to the plane; these methyl hydrogen atoms were not modelled but are included in the formula. A slightly large unresolved peak of residual electron density (1.9) was located 1.6 Å from a water molecule but could not be sensibly modelled (it lies close to the channels and is likely part of the disordered solvent content that does not fall within the SQUEEZE probe mask). The final model was treated with the SQUEEZE routine in PLATON (1139 e<sup>-</sup> in 5177 Å<sup>3</sup> per unit cell).<sup>1</sup>

### ***poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>[Cu<sub>4.8</sub>(H<sub>1.2</sub>L<sub>3</sub>)<sub>2</sub>(OH<sub>2</sub>)<sub>1.6</sub>]} (4)**

There are two sites within the structure where a copper paddlewheel motif was disordered with a single eight-coordinate copper(II). In both instances, initial refinement as only paddlewheels left a large residual peak at the Cu···Cu midpoint. These two sites were modelled with fixed 75:25 and 90:10 occupancies (in favour of the paddlewheel in both instances). Partial occupancy axial aqua ligands terminate these paddlewheels. The average protonation state at each ammonium site must be 0.6 to bring charge balance to the overall structure. One ligand displayed disorder of the diaminobutane carbon atoms, the methylene spacers, and one of the isophthalate rings. These disordered positions were refined with fixed occupancies (50:50). Diffuse electron

density within the channels was removed and quantified using the SQUEEZE routine within PLATON (748 e<sup>-</sup> in 4414 Å<sup>3</sup> per unit cell).<sup>1</sup>

***poly*-[Cu<sub>3</sub>(H<sub>2</sub>L4)(OH<sub>2</sub>)<sub>3</sub>]·2.25H<sub>2</sub>O·DMF (5)**

One carboxylate group was disordered over two positions (75:25), and consequently no electron density corresponding to a hydrogen atom could be located (and was therefore omitted from the model due to nearby disorder adding to a complicated arrangement). Disordered water molecules were located close to these carboxylic acid groups, and their hydrogen atoms could also not be assigned. A significant region of electron density existed within the channels that could not be satisfactorily modelled, and thus it was removed and quantified using the SQUEEZE routine within PLATON (1216 e<sup>-</sup> in 5703 Å<sup>3</sup> per unit cell).<sup>1</sup> These values suggested *ca.* 122 H<sub>2</sub>O or 30 DMF molecules per unit cell (15 H<sub>2</sub>O or 4 DMF per formula unit). This was not assigned to the formula unit since further characterisation was hindered by lack of a pure product.

***poly*-[Cu<sub>4</sub>(HL4)(NHMe<sub>2</sub>)<sub>1.5</sub>(μ-OH)(μ-OH<sub>2</sub>)<sub>0.5</sub>(OH<sub>2</sub>)<sub>2.5</sub>]·H<sub>2</sub>O (6)**

A non-coordinated carboxylic acid group was disordered over two positions (60:40) and modelled with ISOR restraints; hydrogen atoms were placed in idealised positions. Two partial occupancy water molecules, acting as hydrogen bond acceptors to disordered positions of the μ-OH ligand, were modelled without hydrogen atoms as no acceptors could be crystallographically located within the channels (these H atoms are included in the formula). Diffuse electron density within the channels was removed and quantified using the SQUEEZE routine within PLATON (620 e<sup>-</sup> in 3235 Å<sup>3</sup> per unit cell).<sup>1</sup> These values suggested *ca.* 62 H<sub>2</sub>O or 16 DMF molecules per unit cell (31 H<sub>2</sub>O or 8 DMF per formula unit). This was not assigned to the formula unit since further characterisation was hindered by lack of a pure product.

***poly*-[Cu<sub>3</sub>(H<sub>2</sub>L4)(OH<sub>2</sub>)<sub>3</sub>] (7)**

The sample had a diffraction limit of *ca.* 1 Å using synchrotron radiation. In the ASU a non-coordinated carboxylic acid group was refined isotropically as the apparent disorder could not be modelled. There was a large unresolved residual peak (2.08) at a chemically non-reasonable position (1.58 Å from a Cu<sup>II</sup> ion). Diffuse electron density within the channels was removed and quantified using the SQUEEZE routine within PLATON (985 e<sup>-</sup> in 2931 Å<sup>3</sup> per unit cell).<sup>1</sup> These values suggested *ca.* 99 H<sub>2</sub>O or 25 DMF molecules per unit cell (49 H<sub>2</sub>O or 12 DMF per formula unit). This was not assigned to the formula unit since further characterisation was hindered by lack of a pure product.

***poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>2</sub>[Cd<sub>5</sub>(H<sub>2</sub>L1)<sub>2</sub>(OH<sub>2</sub>)<sub>2</sub>]·H<sub>2</sub>O} (8)**

The model was refined as an inversion twin. A disordered cadmium(II) ion was modelled as disordered between two positions (refined to 89:11). Diffuse electron density within the channels was removed and



quantified using the SQUEEZE routine within PLATON (1323 e<sup>-</sup> in 5280 Å<sup>3</sup> per unit cell).<sup>1</sup> These values suggested *ca.* 13 H<sub>2</sub>O or 33 DMF molecules per unit cell (2 H<sub>2</sub>O or 4 DMF per formula unit). This was not assigned to the formula unit since further characterisation was hindered by lack of a pure product.

***poly*-{(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)[Cd<sub>3</sub>(H<sub>2</sub>L2)(Cl)(OH<sub>2</sub>)<sub>5.5</sub>]·6H<sub>2</sub>O·0.5DMF} (9)**

Two carboxylate groups of one isophthalate moiety were modelled as disordered (fixed 1:1 and 2:1 occupancies). Hydrogen atoms could not be sensibly assigned to some solvent molecules nor to the methyl groups of the disordered cation (although they are included in the molecular formula). A number of restraints were used on the interstitial solvent molecules and cations (see CIF).

***poly*-[Cd<sub>2</sub>(H<sub>4</sub>L4)(OH<sub>2</sub>)<sub>4</sub>]·10H<sub>2</sub>O·1.25DMF (10)**

The largest remaining residual peak (3.3) was located in a chemically non-sensical position 0.89 Å from the cadmium(II) ion. Two lattice water molecules per formula unit were assigned crystallographically. Further diffuse electron density within the channels was removed and quantified using the SQUEEZE routine within PLATON (129 e<sup>-</sup> in 491 Å<sup>3</sup> per unit cell).<sup>1</sup> These values are consistent with an additional 8 H<sub>2</sub>O molecules and 1.25 DMF molecule per unit cell/formula unit.

***poly*-[Zn<sub>2</sub>(H<sub>4</sub>L4)]·3H<sub>2</sub>O·2DMF (11)**

One DMF molecule was modelled with ½ chemical occupancy. There was also an apparent disordered DMF/H<sub>2</sub>O site, with both species assigned ½ occupancy. The hydrogen atoms on this partial water molecule were not modelled but were included in the formula.

1. A. Spek, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2015, **71**, 9-18.