Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

Coordination polymers from a flexible alkyldiamine-derived ligand

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1. Special Refinement Information

ESI 1.1: $(H_6L1)Cl_2 \cdot 3H_2O$

No restraints were required for the model. All carboxylic acids and amine hydrogen atoms were placed in calculated positions. The hydrogen atoms on the three lattice water molecules were allowed to freely refine.

ESI 1.2: Poly-$[Cu_2(L1)(OH_2)_2] \cdot 6DMF \cdot 3H_2O$ (1)

Numerous attempts to collect adequate diffraction data were performed as a result of how weakly the crystals diffracted. The crystals would not diffract past 0.9 Å, and as such a SHEL command was used out to 0.9 Å. The largest residual electron density on the Fourier difference map is located next to the copper metal centres.

Six DFIX commands were used to adjust some long carbon-carbon bonds within the model. The hydrogen atoms on the aqua ligands were placed in calculated positions and allowed to freely refine.

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. None of the lattice solvent molecules could be reasonably modelled, and the remaining electron density had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1]

Analysis of the voids from SQUEEZE results in a total electron count of 2465 e^- within the voids per unit cell, with a void volume of 11036 $Å^3$. The asymmetric unit of **1** is twice the polymeric unit formula, so the calculated solvent number is doubled to 12 DMF and 6 H_2O molecules per asymmetric unit. Since there are 8 formula units within the unit cell, the total solvent electron contribution is calculated to be 4320 e^-. While this value appears to be significantly larger than the value calculated using SQUEEZE, the volume occupied by the calculated solvents is 9504 $Å^3$ (18 $Å^3$ per non-hydrogen atom), which appears to be a reasonable volume of solvent per void per unit cell. This amount of solvent also reasonably matches the 47 % mass loss observed in TGA (ESI 3.1), with a calculated mass of 43 %.

ESI 1.3: Poly-$[Zn(H_2L1)(OH_2)] \cdot DMF \cdot 4H_2O$ (2Zn)

One hydrogen atom has been omitted from the model as it could not be located, however it must be present due to charge-balance considerations. It is believed that it is likely located on the O7/O8 carboxylate, but attempts to model it were unsuccessful as the model would not converge. The hydrogen has been left in the formula within the cif file, which resulted in some cif check alerts.

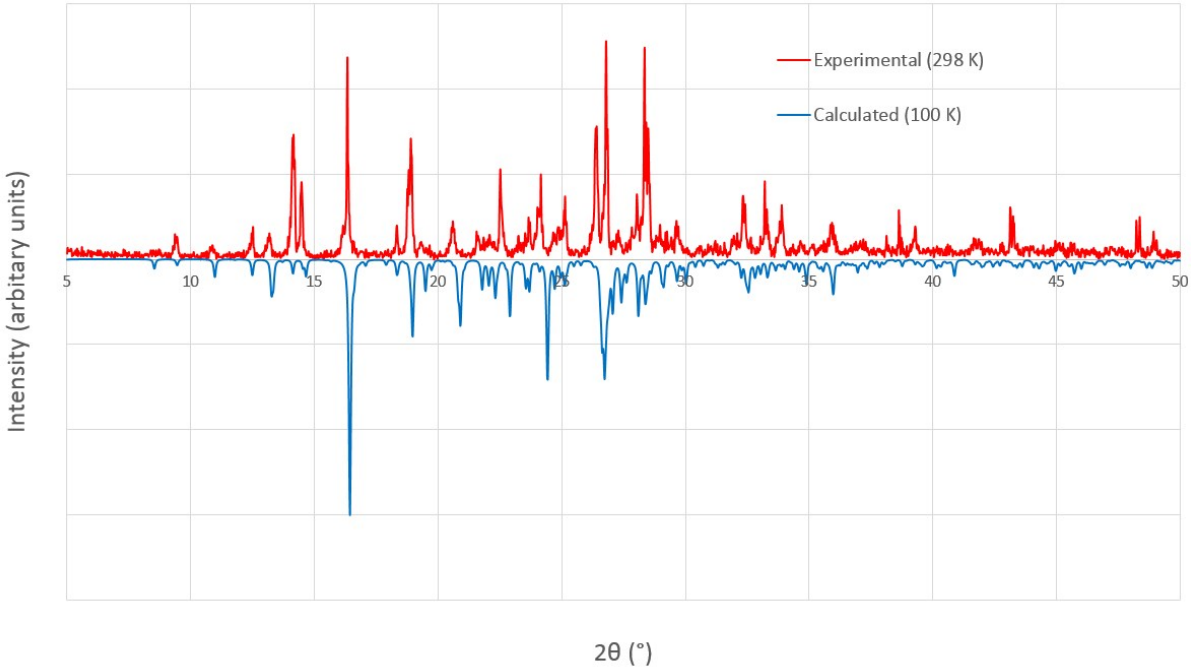
One DANG command was used to prevent a pair of hydrogen atoms (H2 and H10a) from clashing, and allowed them to be modelled in a chemically appropriate orientation.

There were significant regions of disordered electron density detected in the residual Fourier difference map after the refinement of all framework atoms. Only one lattice water molecule could be reasonably modelled, and the remaining electron density that could not be sensibly modelled had its contribution to the diffraction data accounted for with the SQUEEZE routine within PLATON.[1]

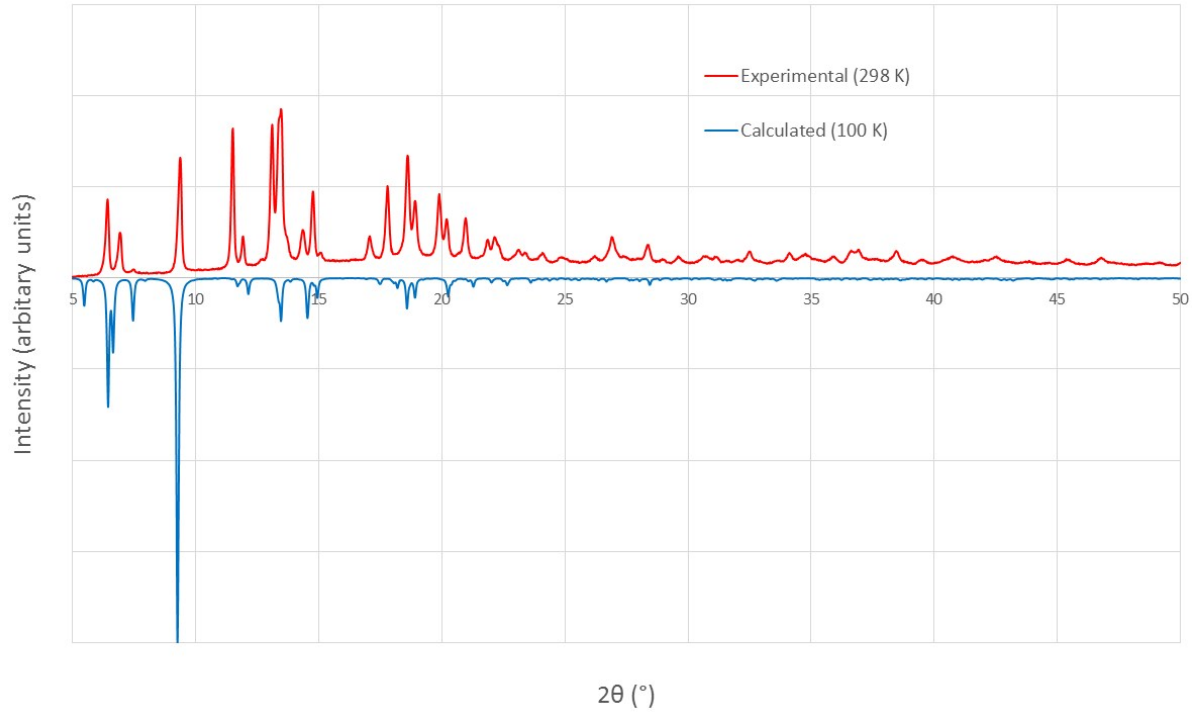
Analysis of the voids from SQUEEZE results in a total electron count of 493 e^- within the voids per unit cell. Since there are 8 formula units within the unit cell, the total solvent electron contribution is calculated to be 560 e^-, which reasonably agrees with the calculated total. This amount of solvent also reasonably matches the 21 % mass loss observed in TGA (ESI 3.2), with a calculated mass of 20 %.

2. Powder X-ray Diffraction Results

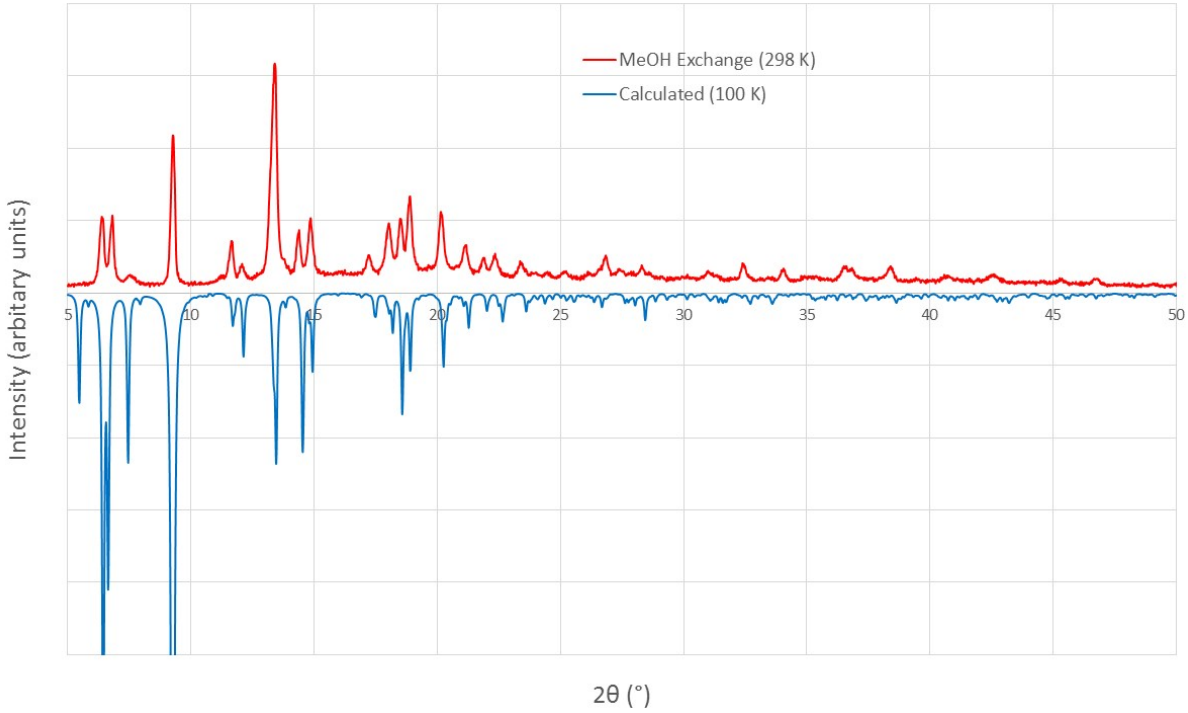
ESI 2.1: $(H_6L1)Cl_2 \cdot 3H_2O$



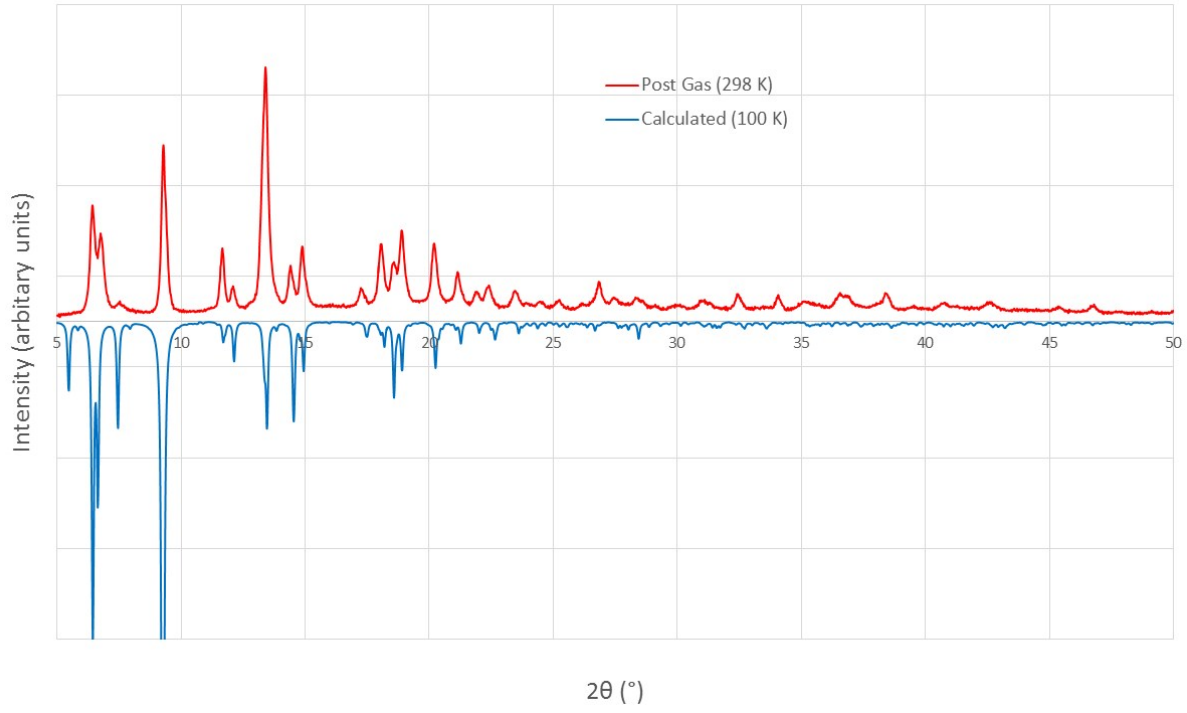
ESI 2.2: Poly-$[Cu_2(L1)(OH_2)_2] \cdot 6DMF \cdot 3H_2O$ (1)



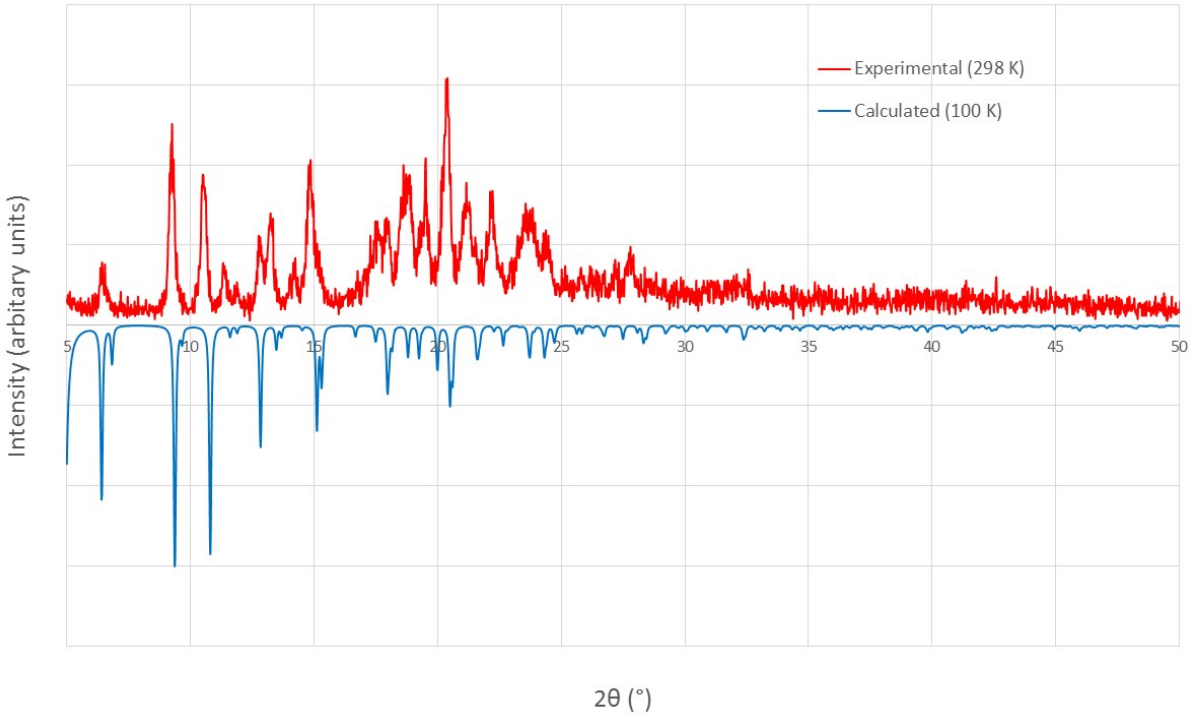
ESI 2.3: Poly-$[Cu_2(L1)(OH_2)_2]\cdot 6DMF\cdot 3H_2O$ (1) after methanol exchange



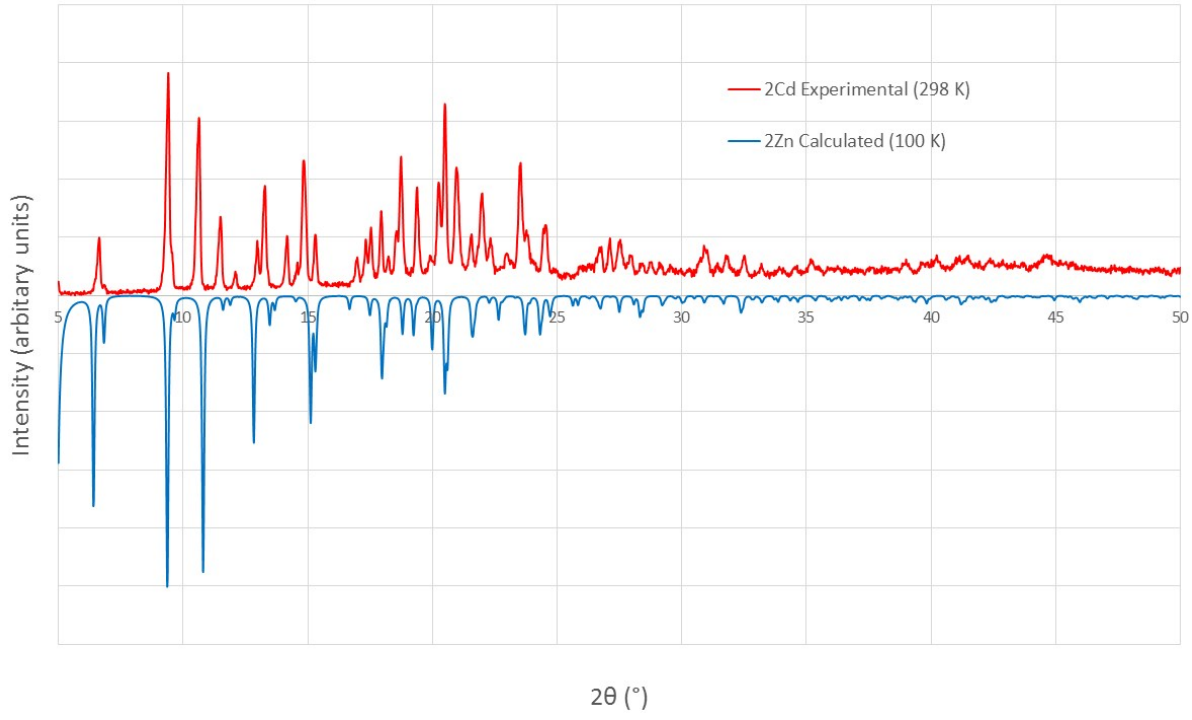
ESI 2.4: Poly-$[Cu_2(L1)(OH_2)_2]\cdot 6DMF\cdot 3H_2O$ (1) after gas adsorption



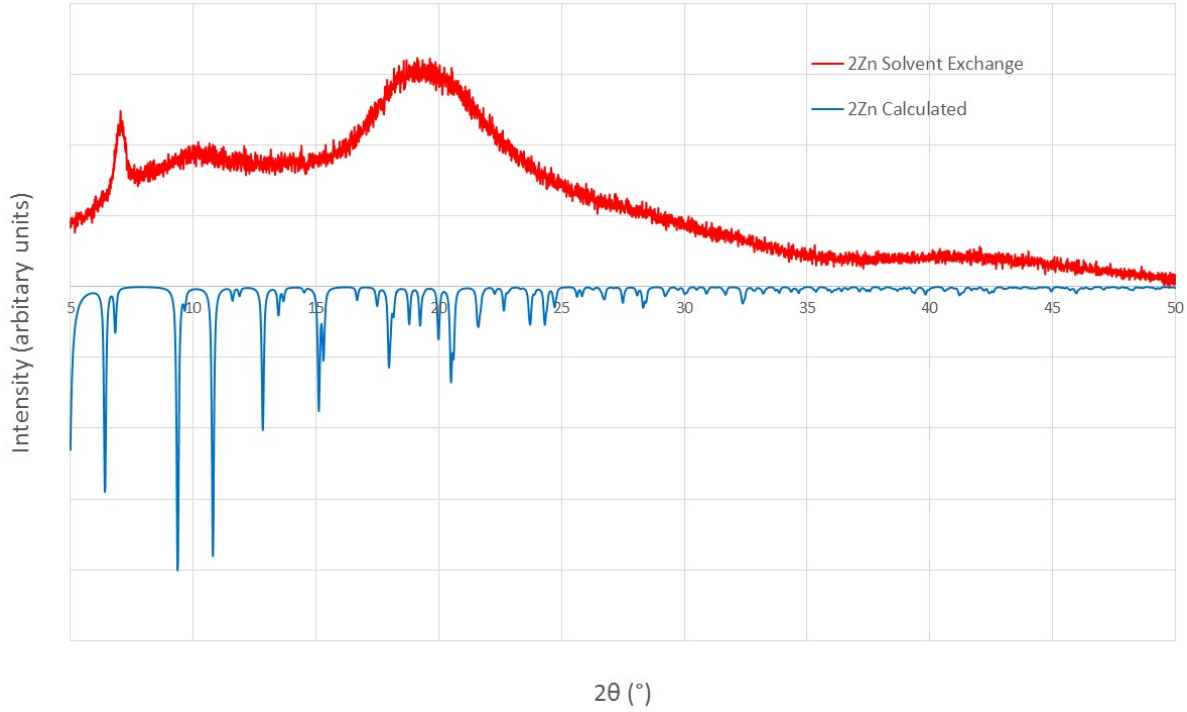
ESI 2.5: Poly-[Zn(H_2L1)(OH_2)]·DMF·4H_2O (2Zn)



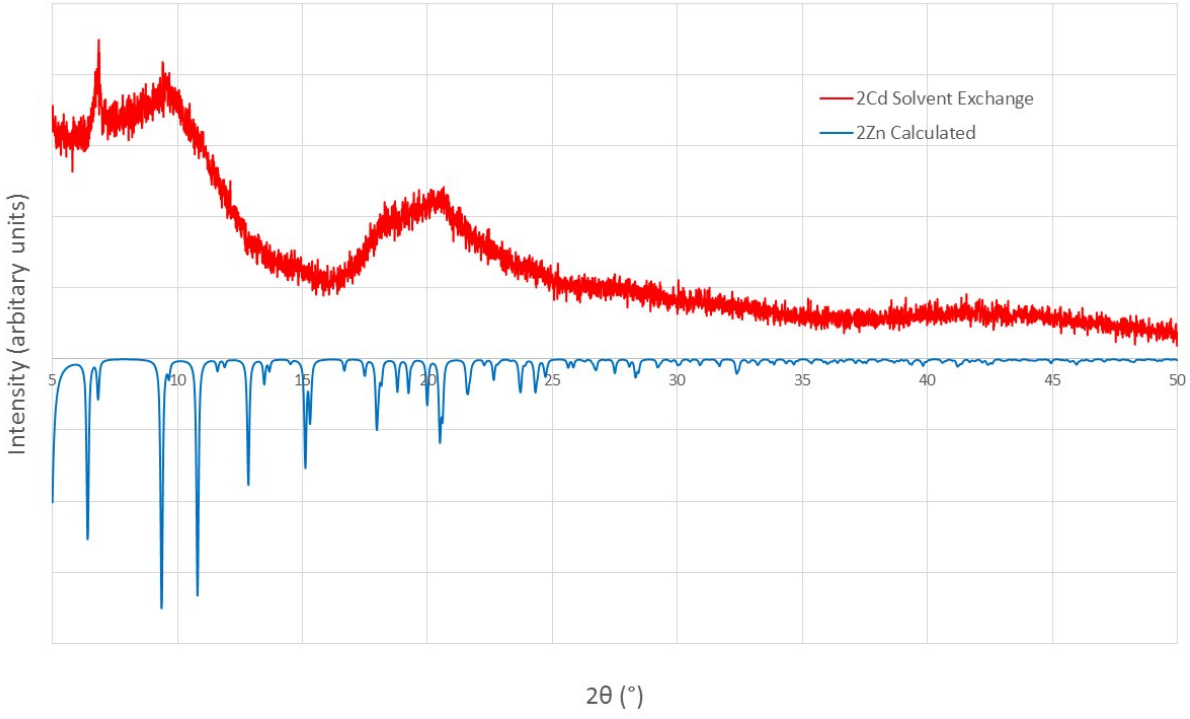
ESI 2.6: Poly-[Cd(H_2L1)(OH_2)]·DMF·3H_2O (2Cd)



ESI 2.7: Poly-[$Zn(H_2L1)(OH_2)$]·DMF·$4H_2O$ (2Zn) after solvent exchange

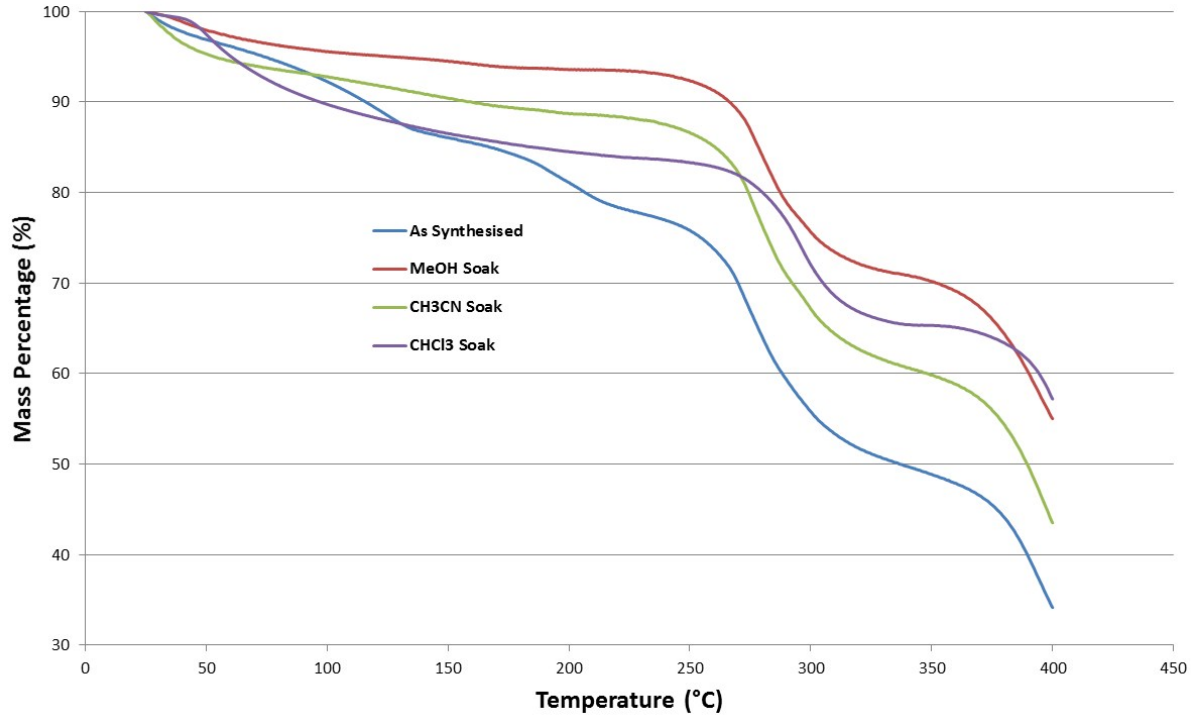


ESI 2.8: Poly-[$Cd(H_2L1)(OH_2)$]·DMF·$3H_2O$ (2Cd) after solvent exchange

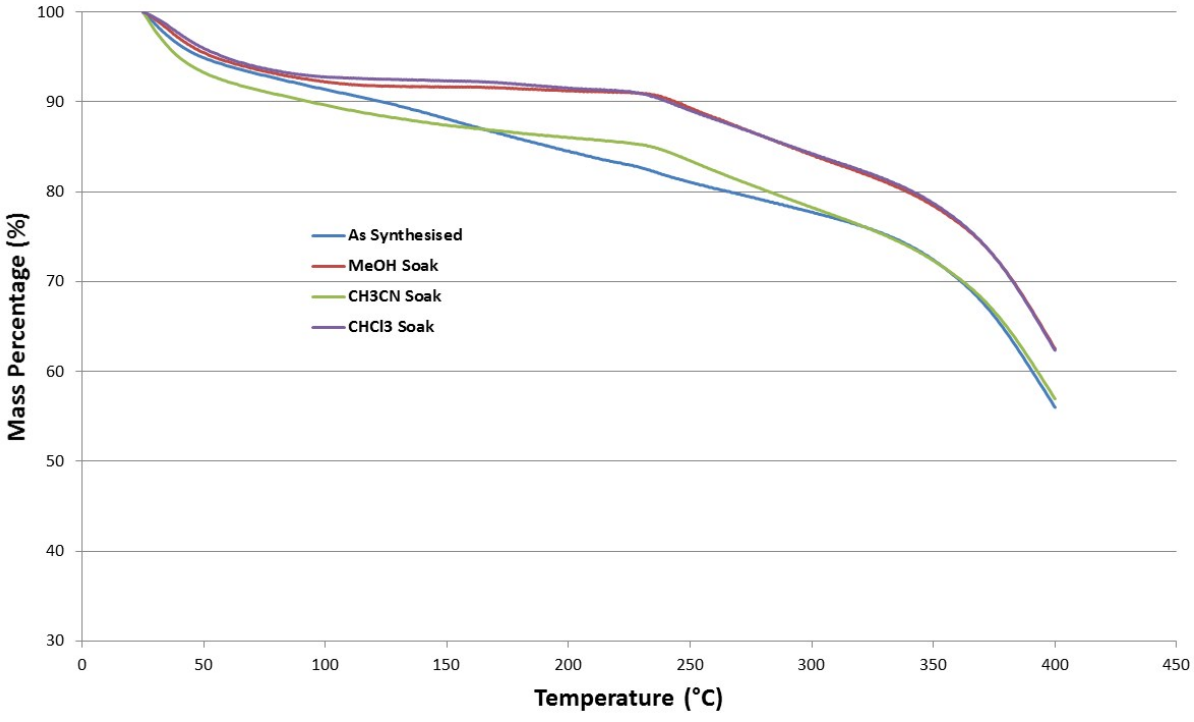


3. Thermogravimetric Analysis Results

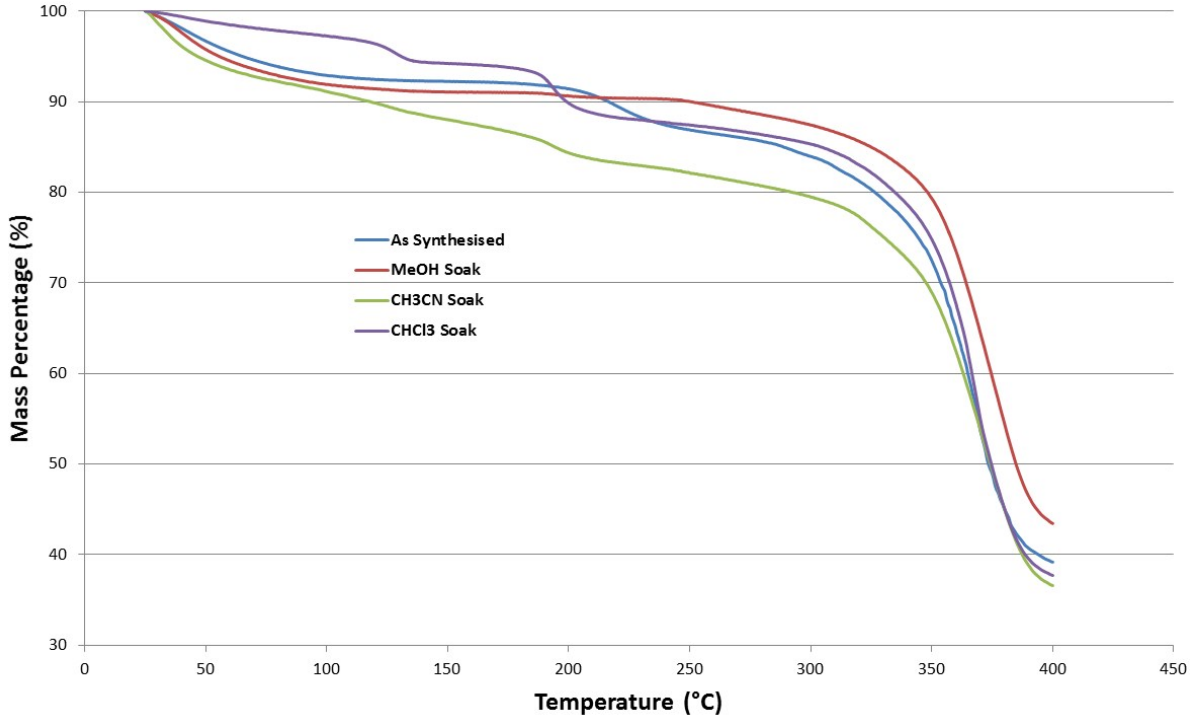
ESI 3.1: Poly-[$Cu_2(L1)(OH_2)_2$]·6DMF·3H_2O (1)



ESI 3.2: Poly-[$Zn(H_2L1)(OH_2)$]·DMF·4H_2O (2Zn)



ESI 3.3: Poly-[Cd(H_2L1)(OH_2)]·DMF·3H_2O (2Cd)



References

[1] A. L. Spek, *Acta Crsytallogr., Sect. C: Cryst. Struct. Commun.* **2015**, *71*, 9-18.