Copper(II) coordination polymers of imdc$^-$ (H_2imdc$^+$ = the 1,3-bis(carboxymethyl)imidazolium cation): Unusual sheet interpenetration and an unexpected single crystal-to-single crystal transformation†

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S1. Supplementary information and figures for $[Cu_2(imdc)_2(MeOH)_2]\cdot 2BF_4$ ·solvate and $[Cu_2(imdc)_2(BF_4)_2]$

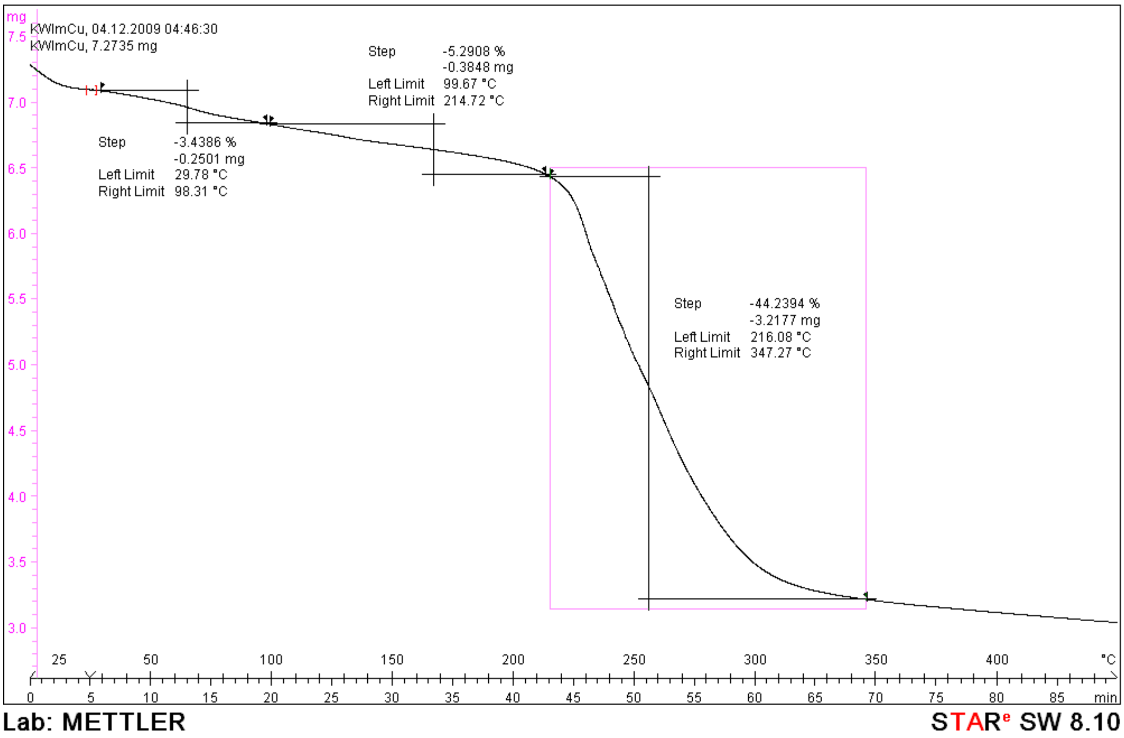

Figure S1a. Thermogravimetric trace for $[Cu_2(imdc)_2(MeOH)_2](BF_4)_2$.solvate. Heating rate: 5°C/minute

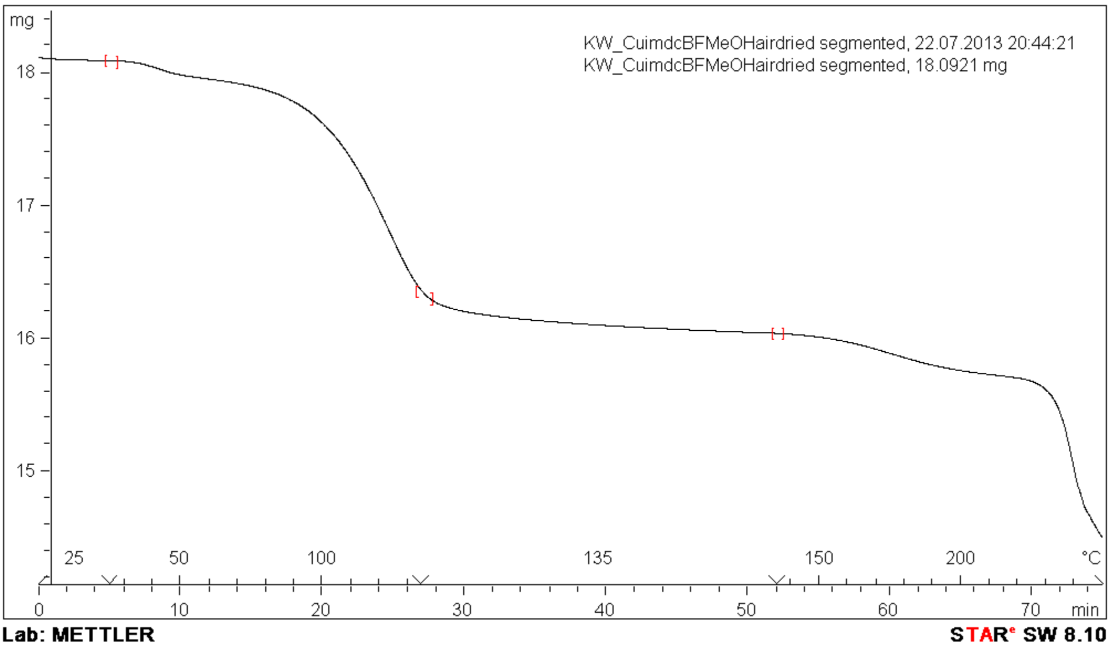

Figure S1b Thermogravimetric trace for $[Cu_2(imdc)_2(MeOH)_2](BF_4)_2$.solvate with the sample held at 130 K for 20 minutes before heating was continued past the decomposition temperature. Heating rate: 5°C/minute

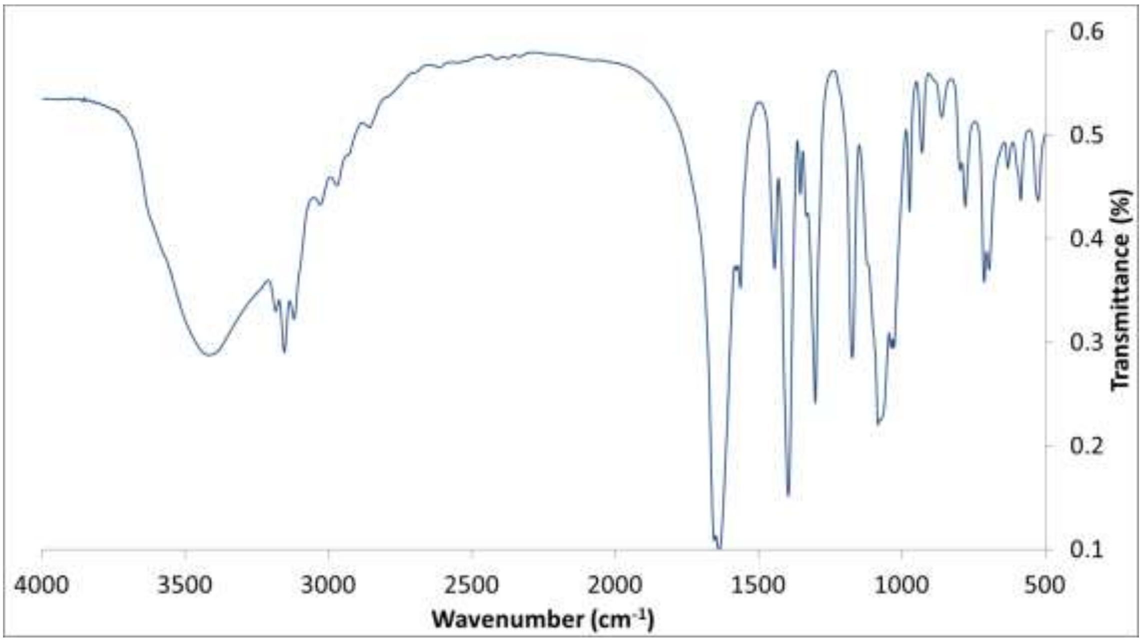

Figure S1c. FT-IR spectra for $[Cu_2(imdc)_2(MeOH)_2](BF_4)_2$.solvate.

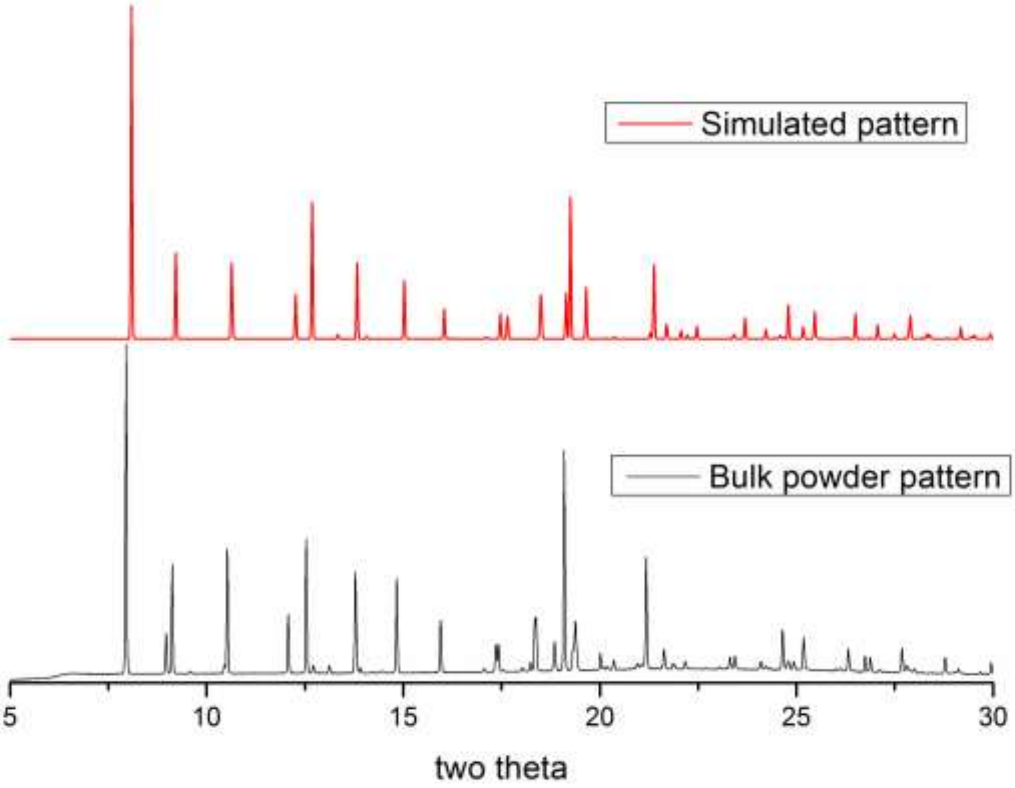

Figure S1d. Bulk powder pattern obtained from the Australian Synchrotron powder diffraction beam line and the simulated powder pattern for $[Cu_2(imdc)_2(MeOH)_2](BF_4)_2$.solvate. The diffraction pattern was measured on a slurry in which the solid was suspended in solvent inside a glass capillary tube. The 2θ values have been rescaled to match Cu radiation.

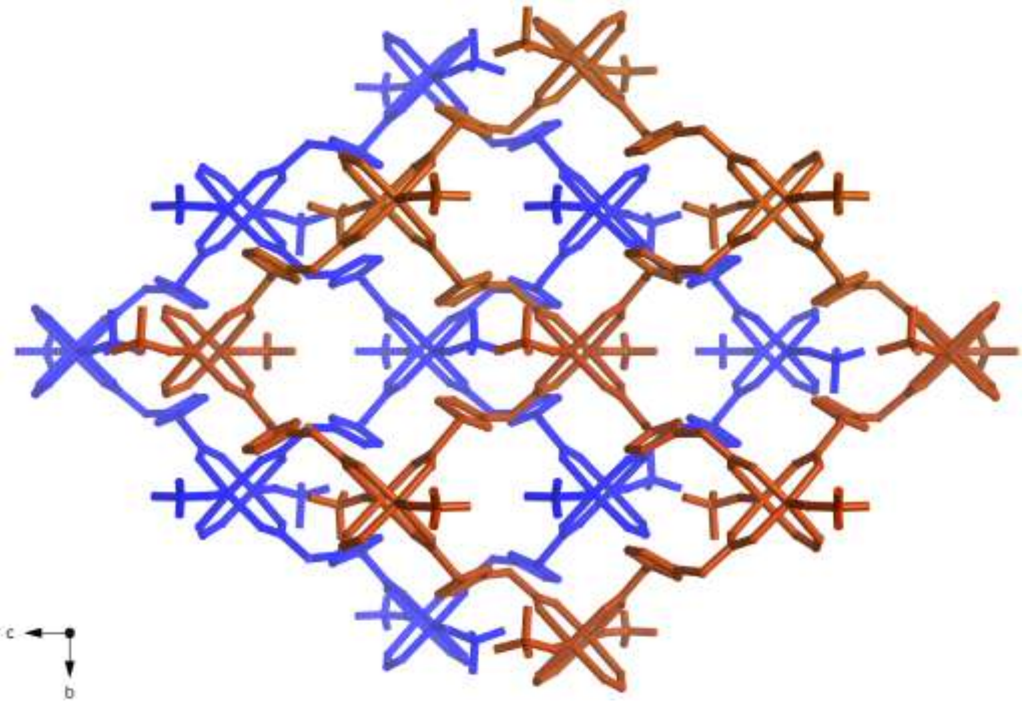

Figure S1e. A view of the structure of [$Cu_2(imdc)_2(BF_4)_2$], showing the relative arrangement of the 2D networks viewed along the stacking direction (along the *a* axis).

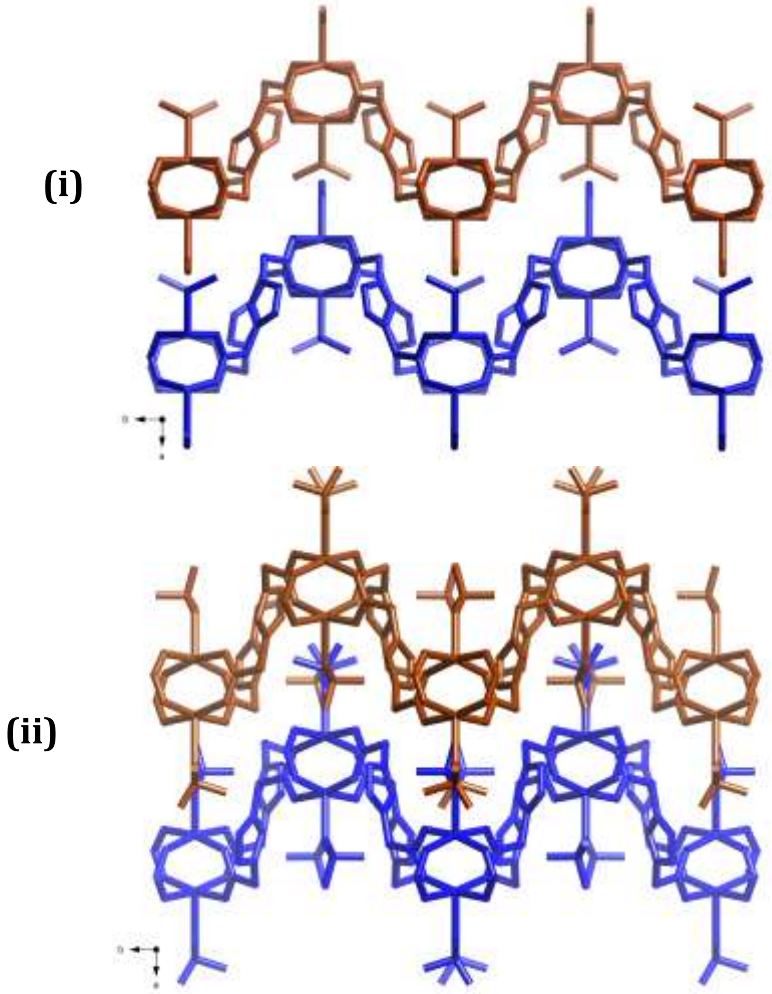

Figure S1f. A comparison of the ‘in phase’ layering (along the *c* axis) of the structures of (i) $[Cu_2(imdc)_2(MeOH)_2](BF_4)_2$.solvate and (ii) $[Cu_2(imdc)_2(BF_4)_2]$. For clarity non-coordinated solvent molecules and BF_4^- ions have been omitted from (i).

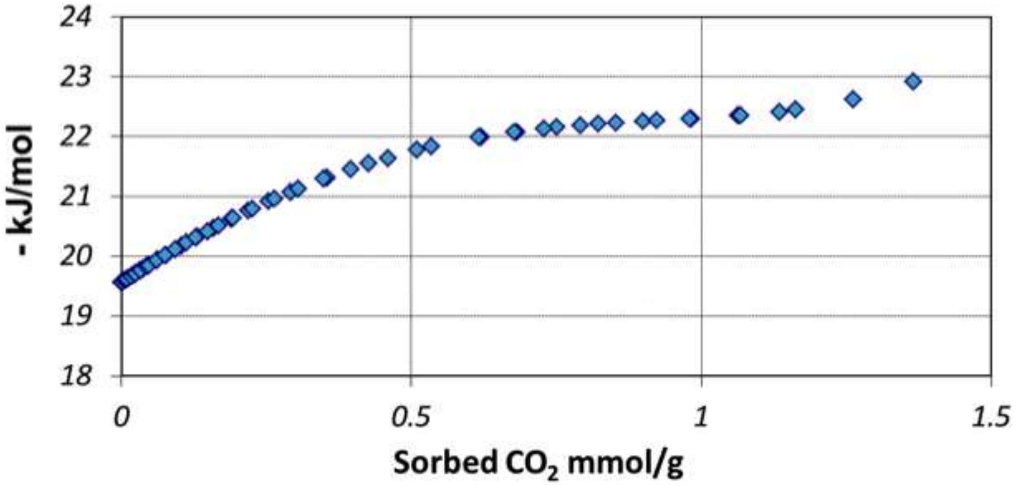

Figure S1g. CO_2 sorption enthalpy versus CO_2 sorbed.

Temp /K	258, 273
a0	-2351.77
a1	-758.637
a2	428.27
a3	122.2064
a4	-85.1659
a5	-38.3618
b	1794719
R^2	0.98709339

Table S1. Optimised virial coefficients for modelling excess CO_2 sorption on $[Cu_2(imdc)_2(BF_4)_2]$.

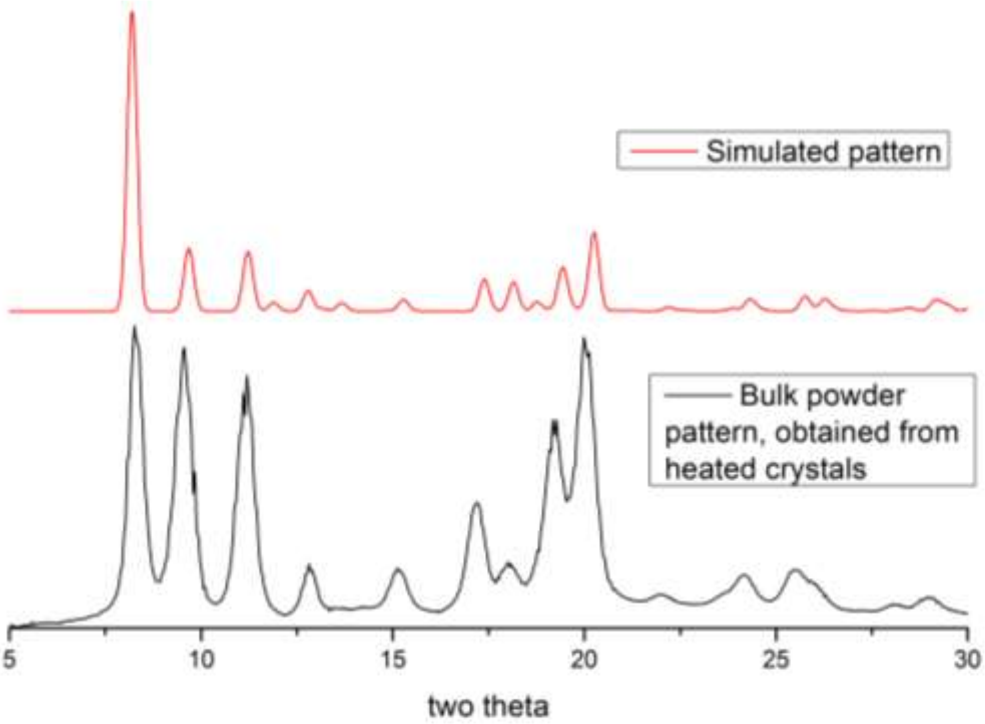

Figure S1h. Powder pattern obtained on desolvated crystals of $[Cu_2(imdc)_2(MeOH)_2]\cdot(BF_4)_2$.solvate i.e. compound **2** and the simulated powder pattern for $[Cu_2(imdc)_2(BF_4)_2]$ (**2**). Data collected on an Oxford Diffraction SuperNova diffractometer.

S2. Supplementary experimental data for $[Cu_3(OH)_2(imdc)_2]\cdot SiF_6\cdot 2H_2O\cdot 2MeOH$

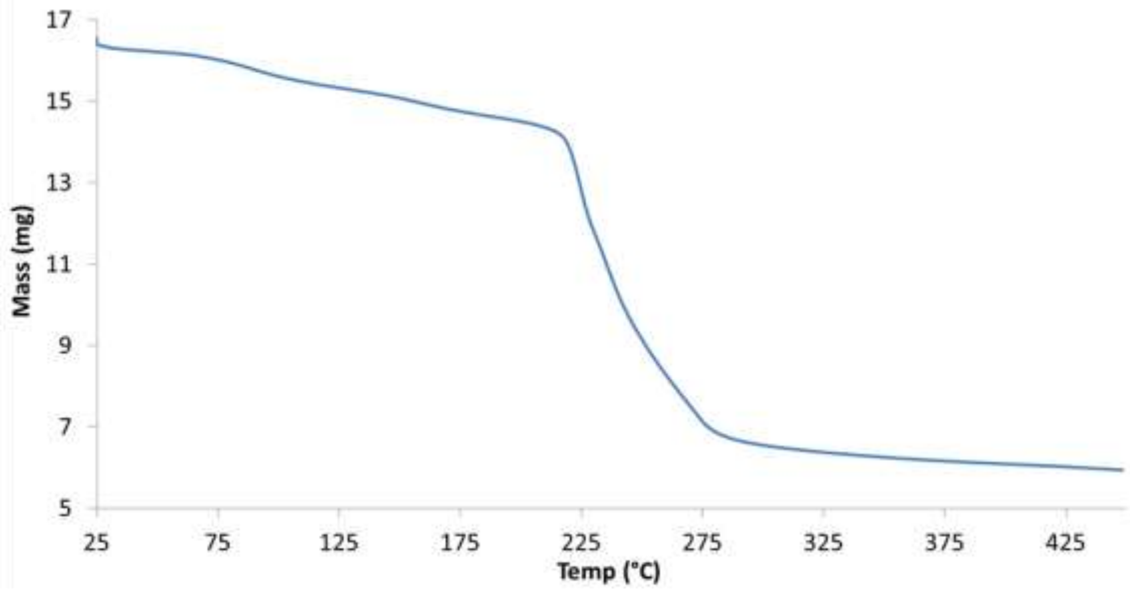

Figure S2a. Thermogravimetric trace for $[Cu_3(OH)_2(imdc)_2]SiF_6\cdot 2H_2O\cdot 2MeOH$.

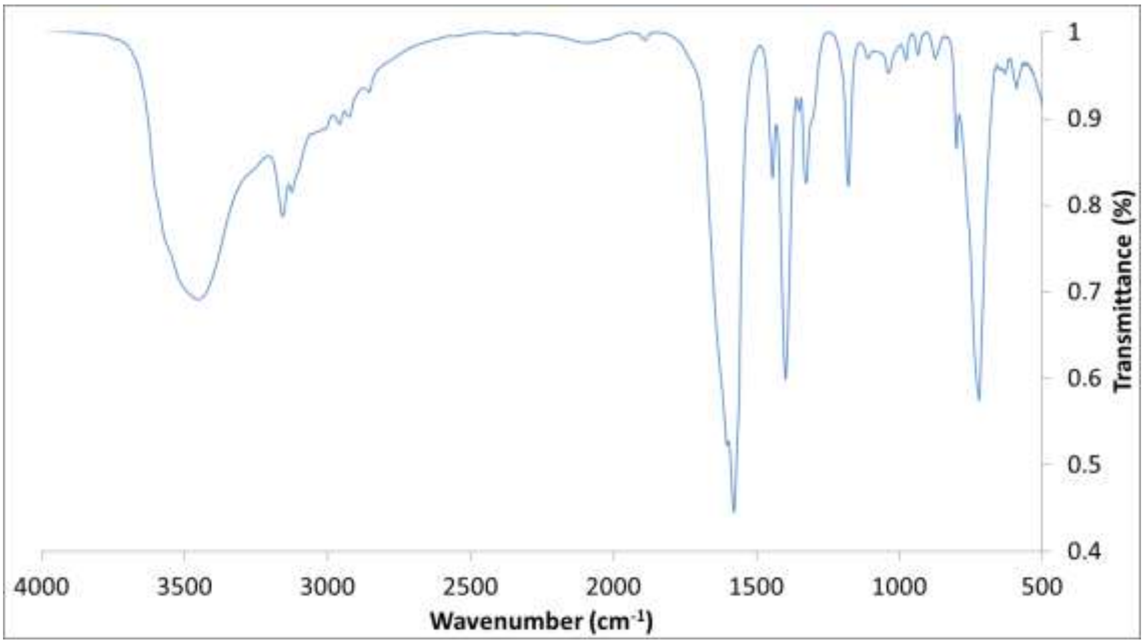

Figure S2b. FT-IR spectra for $[Cu_3(OH)_2(imdc)_2]\cdot SiF_6\cdot 2H_2O\cdot 2MeOH$.

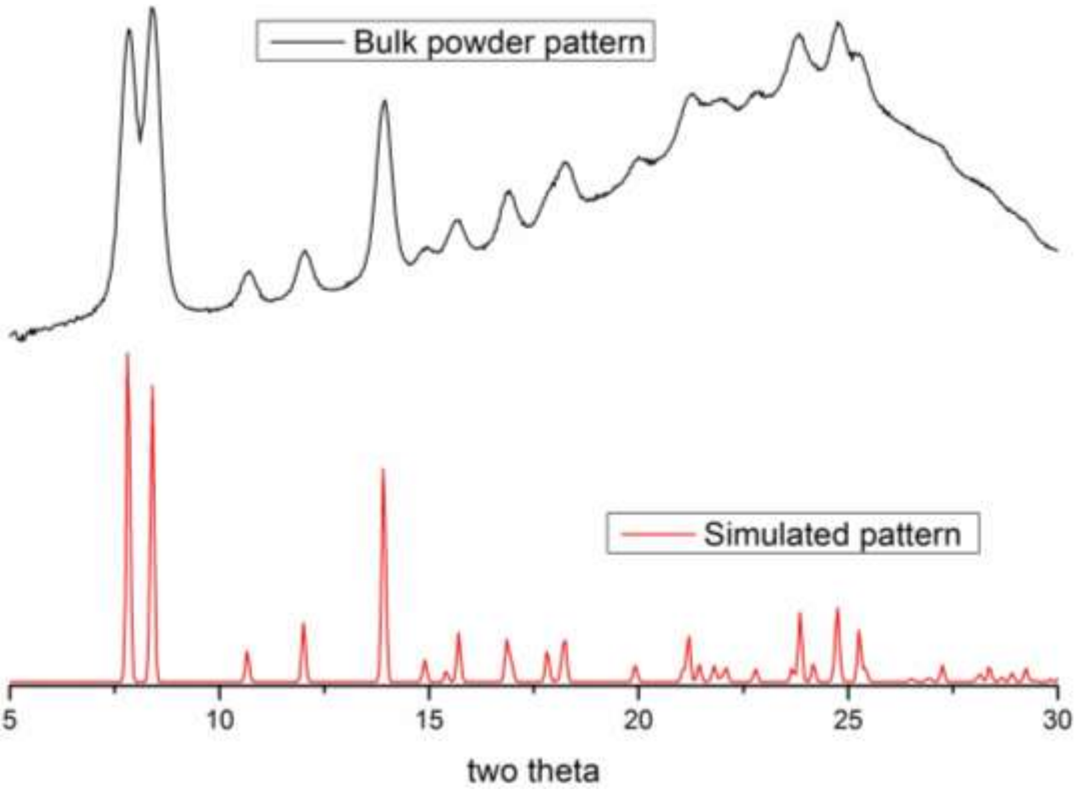

Figure S2c. Bulk powder pattern and the simulated powder pattern for $[Cu_3(OH)_2(imdc)_2]\cdot SiF_6 \cdot 2H_2O\cdot 2MeOH$. Data collected on an Oxford Diffraction SueperNova diffractometer. 2θ values have been rescaled to match Cu radiation.

S3. Supplementary experimental data for Cu(imdc)$_2$

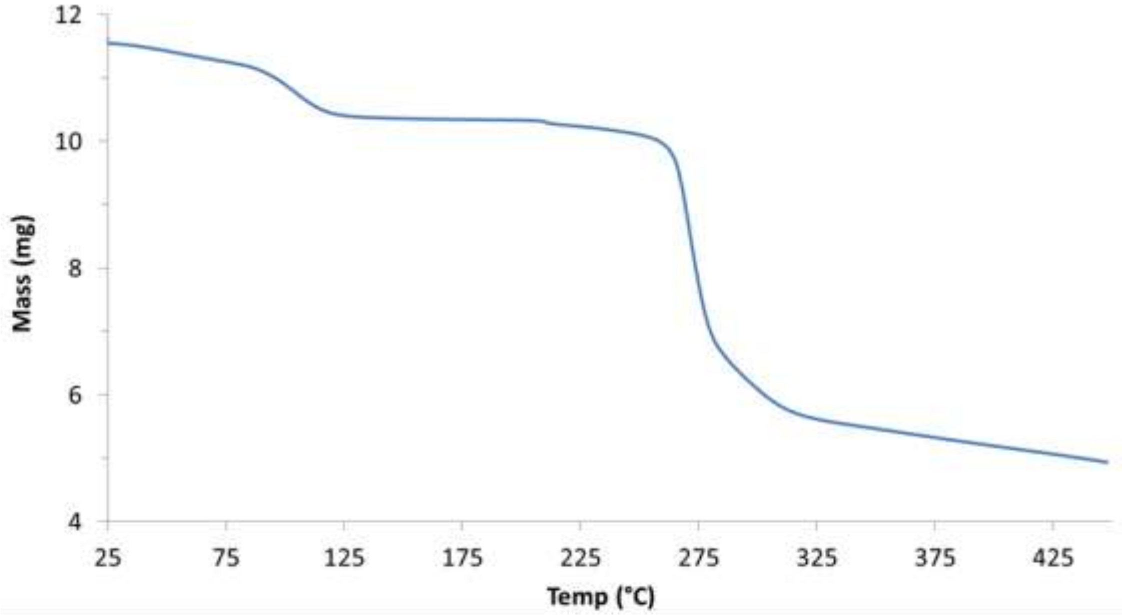

Figure S3a. Thermogravimetric trace for [Cu(imdc)$_2$].

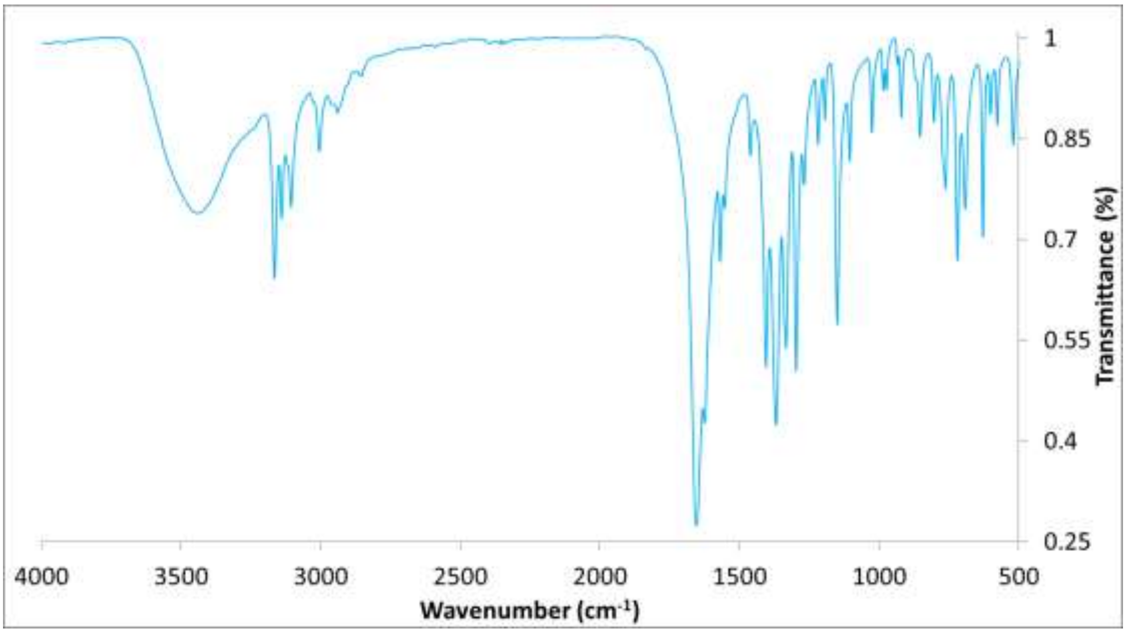

Figure S3b. FT-IR spectra for [Cu(imdc)$_2$].

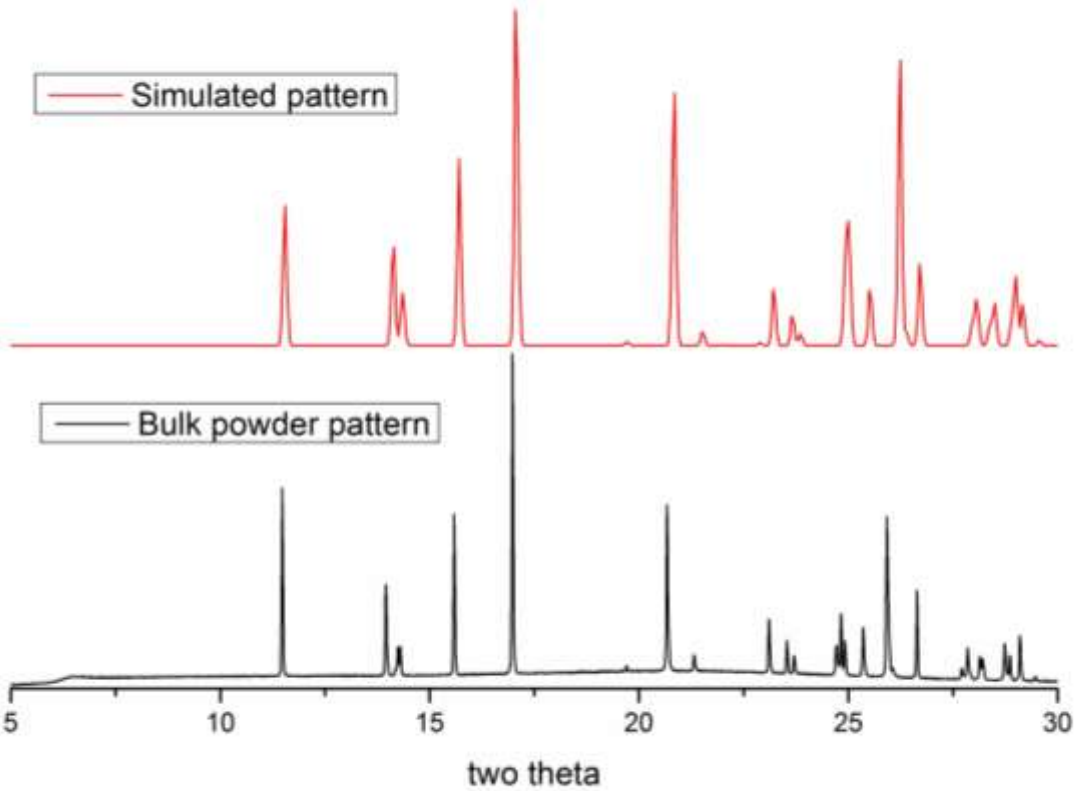

Figure S3c. Bulk powder pattern obtained from the Australian Synchrotron powder diffraction beam line and the simulated powder pattern for [Cu(imdc)$_2$]. 2θ values have been rescaled to match Cu radiation.

S4. Supplementary experimental data for $[Cu_2(imdc)_4]\cdot NaBF_4\cdot 7H_2O$

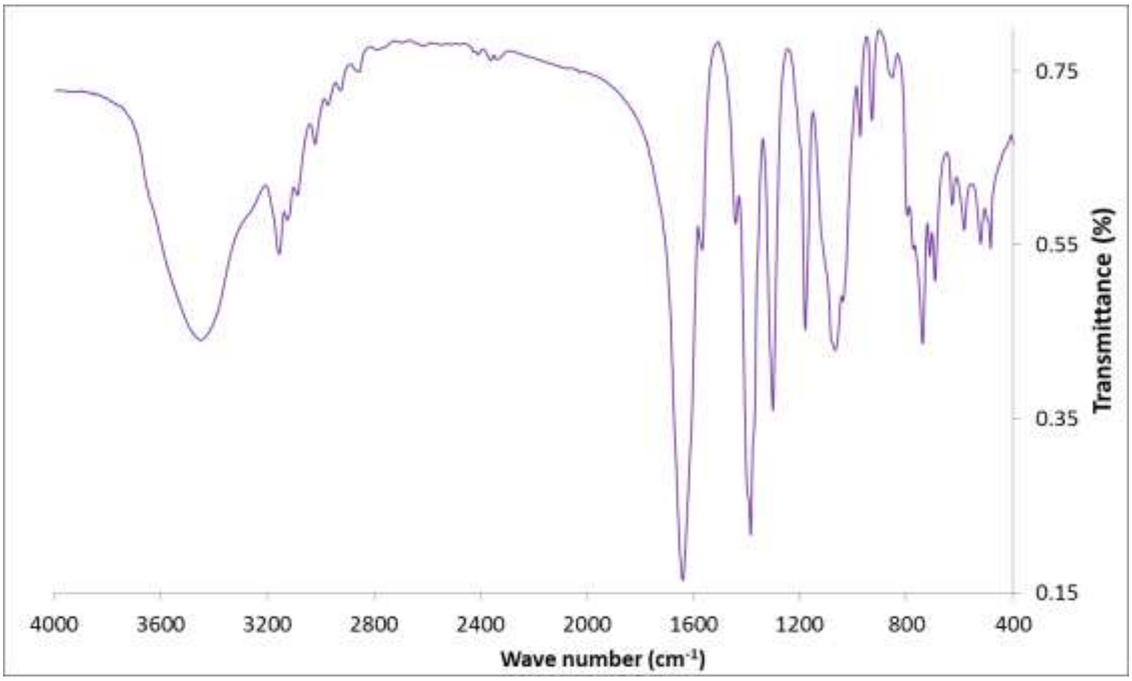

Figure S4a. FT-IR spectra for $[Cu_2(imdc)_4](NaBF_4)\cdot 7H_2O$.

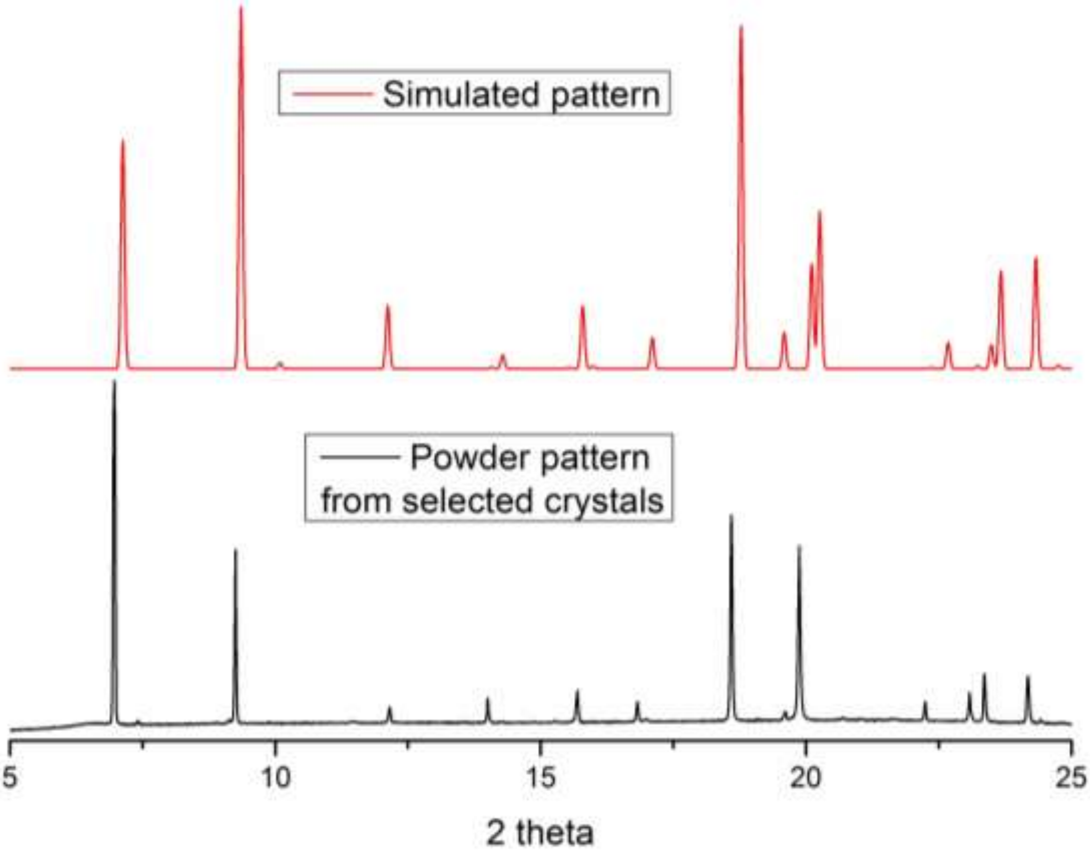

Figure S4b. Powder pattern obtained from the Australian synchrotron powder beam line and the simulated powder pattern for $[Cu_2(imdc)_4](NaBF_4)\cdot 7H_2O$. 2θ values have been rescaled to match Cu radiation.

S5 Further crystallographic details relating to the single crystal structure determinations

Compound 1

The structural refinement of compound 1 indicated that the solvent molecules within the crystal, methanol and water molecules, are disordered. Atom O2S is an oxygen of a methanol molecule coordinated to Cu2; both atoms lie on a mirror plane. The methyl group bound to this oxygen atom is disordered across the mirror plane. A second methanol forms a hydrogen bond with O2S and it too is disordered across the mirror plane with the location of the second methanol molecule dependent upon the orientation of the methyl group bound to atom OS2.

Atom Cu1 also lies on a mirror plane but in this case the hydroxyl group and the carbon atom of the coordinated methanol are also located on the mirror plane. The methyl protons are disordered over two sites related to each other by the mirror plane.

The hydroxyl group of the coordinated methanol located on a mirror plane, acts as a hydrogen bond donor to a non-coordinated water molecule that is disordered over two sites related by mirror symmetry.

There are two unique tetrafluoroborate anions the B atoms of which are located on a mirror plane. Inspection of the Fourier difference map indicated that the BF_4^- anions are orientationally disordered, particularly the F atoms bound to atom B1. The fluorine atoms were modeled over a number sites with appropriate site occupancies assigned.

Compound 2

The crystal structure analysis on compound **2** was performed on a crystal of **1** that had been heated in an oven at 135 °C. This process led to considerable broadening of the reflections however it was still possible to obtain a satisfactory structure determination.

In compound 2 the two crystallographically distinct BF_4^- anions are coordinated to the Cu centres. The BF_4^- anion bound to Cu2 is located on a mirror plane and is disordered over a pair of symmetry related sites with the B atom (B2) located on the mirror plane. The BF_4^- anion bound to Cu1 is also located on a mirror plane but this time the B atom (B1) was disordered across two closely separated, symmetry related sites an arrangement resulting from two distinct orientations for the anion.

Following assignment of the network and anion atoms the maximum and minimum peaks of residual electron density apparent in the difference Fourier map were +0.835 and -0.835 respectively. Following a suggestion from a referee the SQUEEZE routine within PLATON[1] was used to calculate the resdiual electron density within the voids that occurs upon solvent loss. The SQUEEZE results indicated 7.5 electrons in a volume of 68 $Å^3$ per asymmetric unit.

Compound 3

Compound 3 adopts the non-centrosymmetric space group *Cc*. Careful checks were performed to ensure that the space group was not in fact *C*2/*c*. The Flack parameter was found to be 0.01(3) indicating the correct absolute structure.

Compound 4

Inspection of the diffraction pattern of the crystalline sample used in the determination of compound 4 revealed significant twinning. The structure determination was performed on data obtained from one of the crystal fragments. Due to overlapping reflections the data used in the structure solution and refinement is of lower quality than would normally be expected from a non-twinned sample. Despite these problems, which have resulted in a slightly elevated *R*1 value (0.0818) and high residual electron density (2.64 eÅ^{-3}), the structure determination is unambiguous with all atomic positions clearly defined.

Compound 5

As indicated in the manuscript the Na^+ ions are disordered over four closely separated, symmetry-related sites, about a site of 222 symmetry. Whilst the six water molecules bound to the Na^+ ions are also disordered over a number of sites, the water molecules are reasonably well-defined and can be seen to form hydrogen bonds with non-coordinated carboxylate oxygen atoms; the hydrated sodium ions are located in the less congested holes of the 2D network. The oxygen atoms of the water molecules and the sodium ions were refined with isotropic displacement parameters and appropriate site occupation factors.

The BF_4^- ions also exhibit disorder around a 222 sites but in this case the ion is disordered over two overlapping sites with the B atoms located on a 2-fold axis. Hydrogen bonding interactions occur between the fluorine atoms and the water molecules bound to the Na^+ ions. The oxygen atom of a water molecule, not associated with the Na^+ ion, was found to be disordered over two symmetry-related sites that were located on the same 2-fold axis as the B atoms. The BF_4^- atoms and the oxygen atom of the water molecule were refined with appropriate site occupancies and isotropic displacement parameters.

1. A.L.Spek, *Acta Cryst.* 2009, **D65**, 148.