Supplementary Material (ESI) for Chemical Communications

Solvothermal versus Bench-top Reactions: Control Over the Formation of Discrete Complexes and Coordination Polymers

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Supplementary Information

X-ray powder diffraction experiments were performed on a Bruker D8 Focus diffractometer using the Diffrac Plus XRD Commander software. Scans were run at a rate of 2 ° min^{-1} using a scan step size of 0.01°. Calculated patterns from single crystal data were made using the Lazy Pulverix interface of X-Seed.

A scan was run of a freshly prepared, finely ground sample of the bulk product from the reaction of $Cu(NO_3)_2$ and Na(dcnm), Figure S1. This shows significant peaks at low 2θ values corresponding to the calculated powder patterns of both **1** and **3** (the methanol and water solvates, respectively) being present. A minor peak at low theta is also observed that corresponds to the desolvated network **4**.

A second scan was run on the fresh sample immediately after the first (i.e. a time lag of approximately one hour since isolated of the product from the reaction mixture). This scan shows no peak corresponding to **1** with the major peaks being assignable to the water solvate **3**, Figure 2. The weaker signals of **4** are also still present.

The sample was then heated in an oven at 75 °C for 16 hours (with a colour change from dark green to pale brown) and the XRPD re-collected. The peaks for **3** are significantly weaker and those for **4** dominate the pattern confirming that heating of **1** and **3** lead to transformation to **4**.

It should be noted that, from observation, single crystals of **1** lose crystallinity on prolonged removal from the mother liquor, effectively ruling out the possibility that the transitions that occur are crystal-to-crystal transformations.

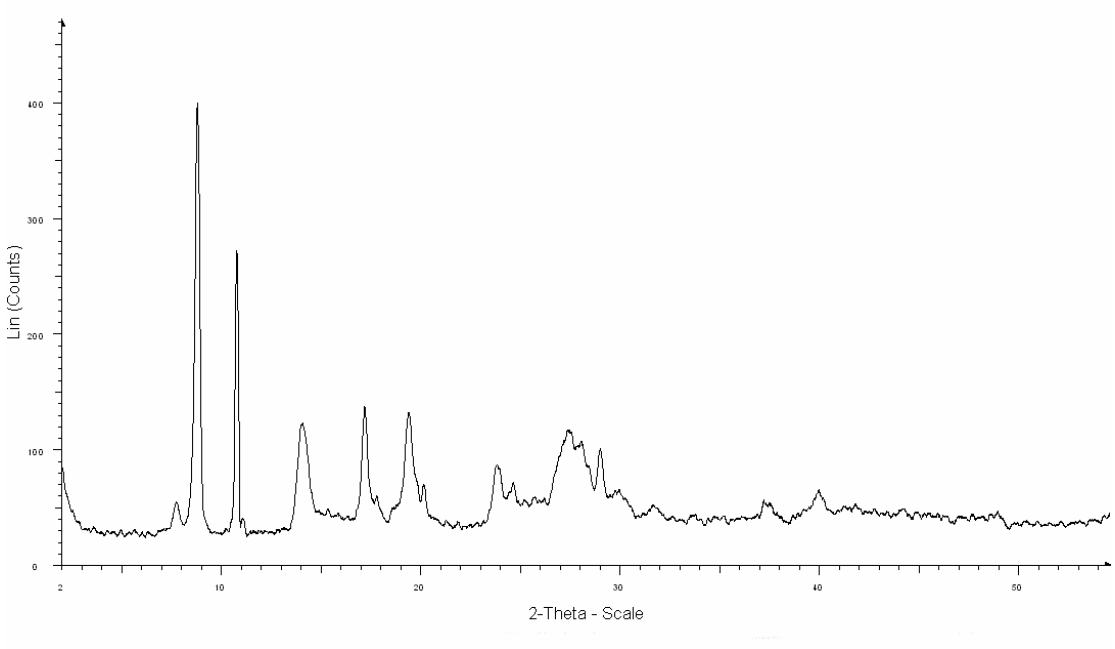

Figure S1: XRPD image of a fresh sample from the reaction of $Cu(NO_3)_2$ with Na(dcnm). Peaks corresponding to both the methanol **1** and water **3** solvates at low 2θ are evident in addition to a small peak corresponding to the desolvated network **4**. Calculated patterns from single crystal data are shown in Figures S3 – S5.

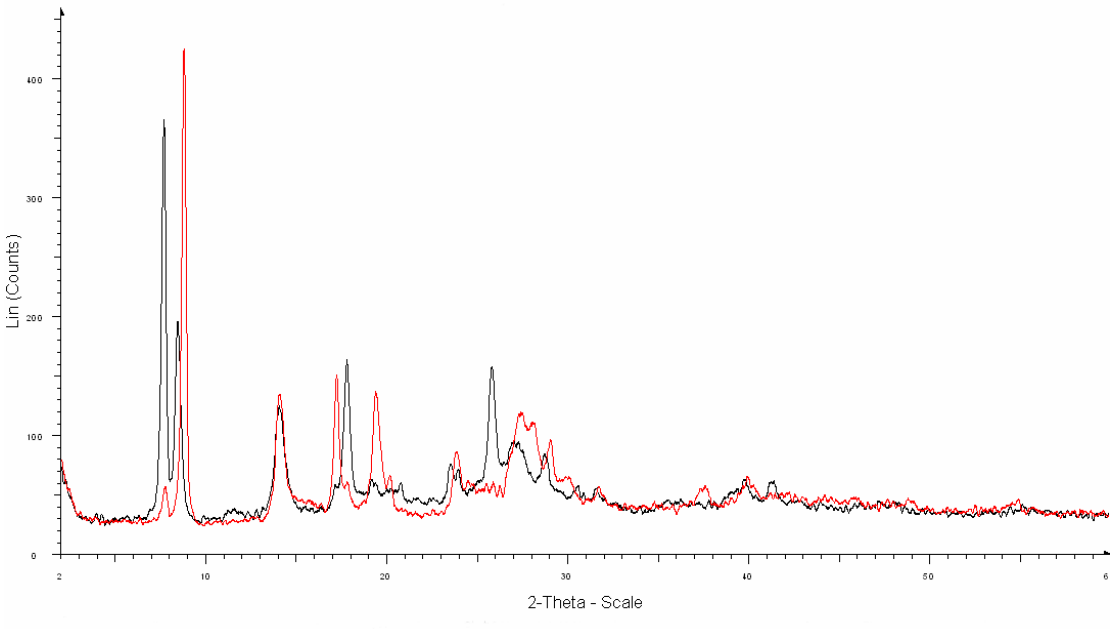

Figure S2: Overlayed powder patterns of the reaction mixture after standing for one hour (red) and after heating at 75 °C overnight (black). The peaks corresponding to **3** are strongest in the pre-heated sample (with those due to **1** being absent) whilst after heating the pattern of **4** is predominant, despite a significant residual amount of **3**. Calculated patterns from single crystal data are shown in Figures S3 – S5.

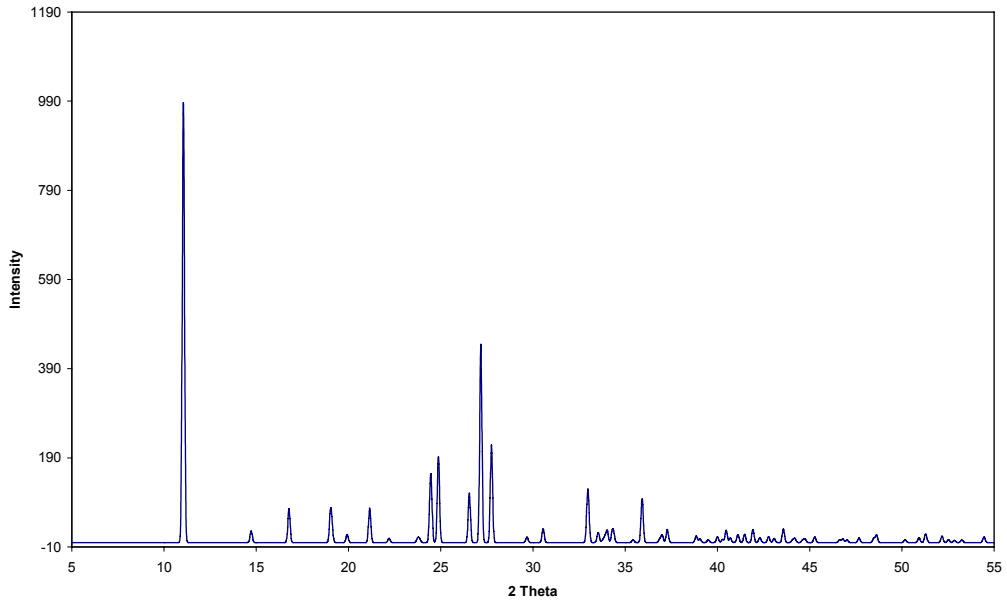

Figure S3: Generated XRPD plot of **1** from single crystal data.

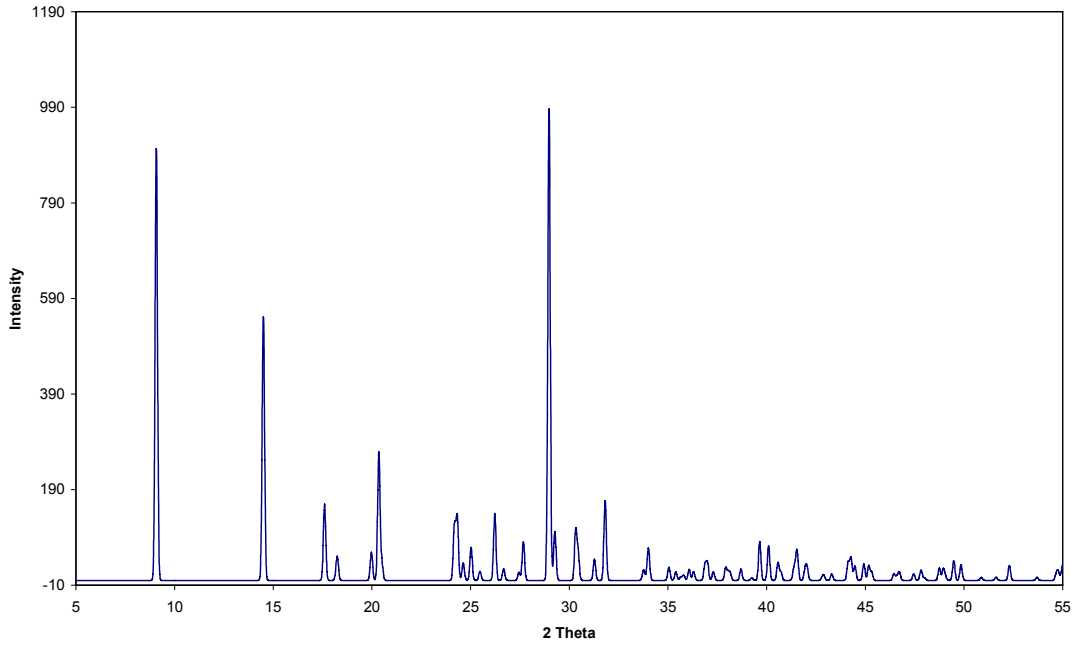

Figure S4: Generated XRPD plot of **3** from single crystal data.

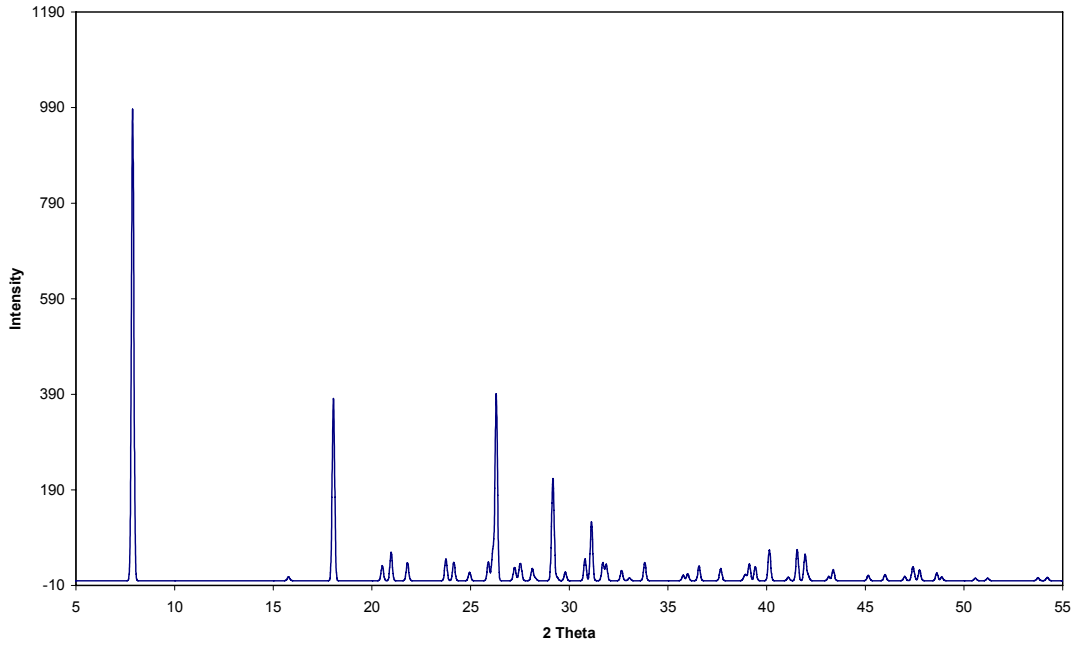

Figure S5: Generated XRPD plot of **4** from single crystal data.