Electronic Supplementary Material (ESI) for Chemical Science

Pair distribution-derived mechanism of a single-crystal to disordered to single-crystal transformation in a hemilabile metal-organic framework

Phoebe K. Allan[a], Karena W. Chapman[b], Peter J. Chupas[b], Joseph A. Hriljac[c], Catherine L. Renouf[a], Timothy C. A. Lucas[c], Russell E. Morris[a]*

Single Crystal X-ray diffraction frames

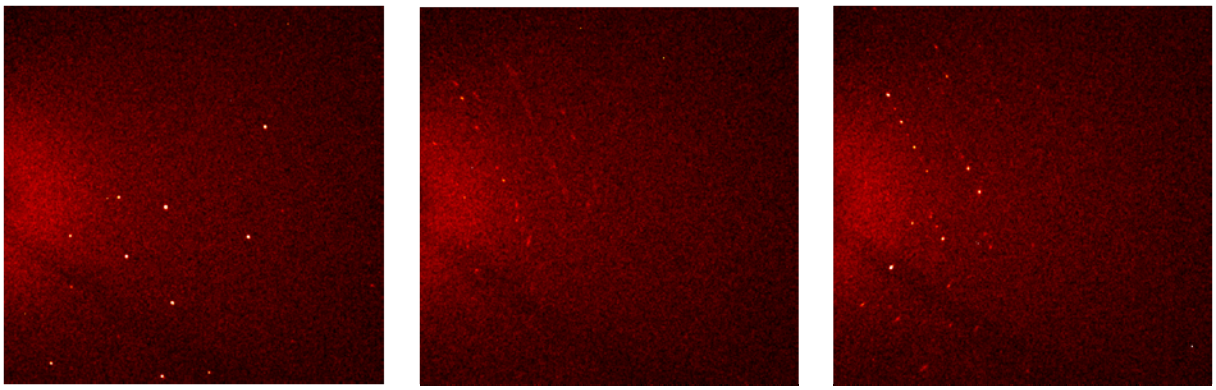

Figure S1 Diffraction frames from variable-temperature single-crystal experiments, with the same ω value shown for each temperature. Left: *T* = 300 K, good Bragg diffraction, discrete peaks, low-temperature structure obtained; middle: *T* = 390 K, little Bragg diffraction, diffracted intensity smeared out into diffuse scattering, no structure obtained; right: *T* = 465 K, good Bragg diffraction returns high-temperature structure obtained

Powder diffraction patterns (sample-only diffraction scattering intensity, I(Q))

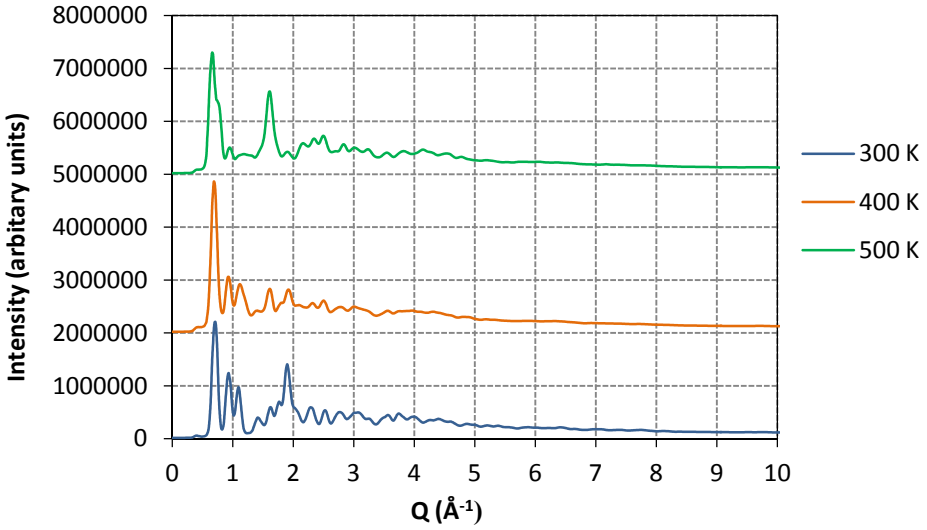

Figure S2: I(Q) in the range of 0 – 10 $Å^{-1}$ for the hydrated material (300 K), partially dehydrated material (400 K) and dehydrated material (500 K). 400 K and 500 K are offset by $2x10^6$ and $5x10^6$ intensity units respectively. The diffuse 'background' scattering for the material increases for the higher temperature data sets.

Refinement of the PDFs at 300 K and 500 K

Refinements of the structure models at 300 K and 500 K against PDF data sets were done in the range of 1 to 30 Å using the program PDFGui. Q_{damp} was set to an initial value 0.08 and refined for the 300 K data set before being fixed for the 500 K data set. Short range correlated motion of atoms was accounted for by S_{ratio} which was set to an initial value of 0.5 with a cut off distance, r_{cut} of 3.6 Å. Atomic displacement parameters were set isotropic with $U_{11} = U_{22} = U_{33} = 0.05$ $Å^2$ with $U_{12} = U_{23} = U_{31} = 0$ with an initial value of 0.005 $Å^2$. ADPs were constrained according to atom type and chemical environment; for example ADPs for Cu-atoms were constrained to refine as one parameter, those for sulfur to be another, those for carbon to be another. Hydrogen ADPs were not considered in the refinement. Oxygen atoms were divided up into carboxylate oxygens, sulfonate oxygens, hydroxyl oxygens and water oxygens and each defined as one ADP parameter. Model scale factor, Q_{damp}, S_{ratio}, ADPs for all atoms and Cu-positions were refined until stable. Final refinement gave R_w = 0.272391 for the 300 K data set and R_w = 0.299982 for the 500 K data set.

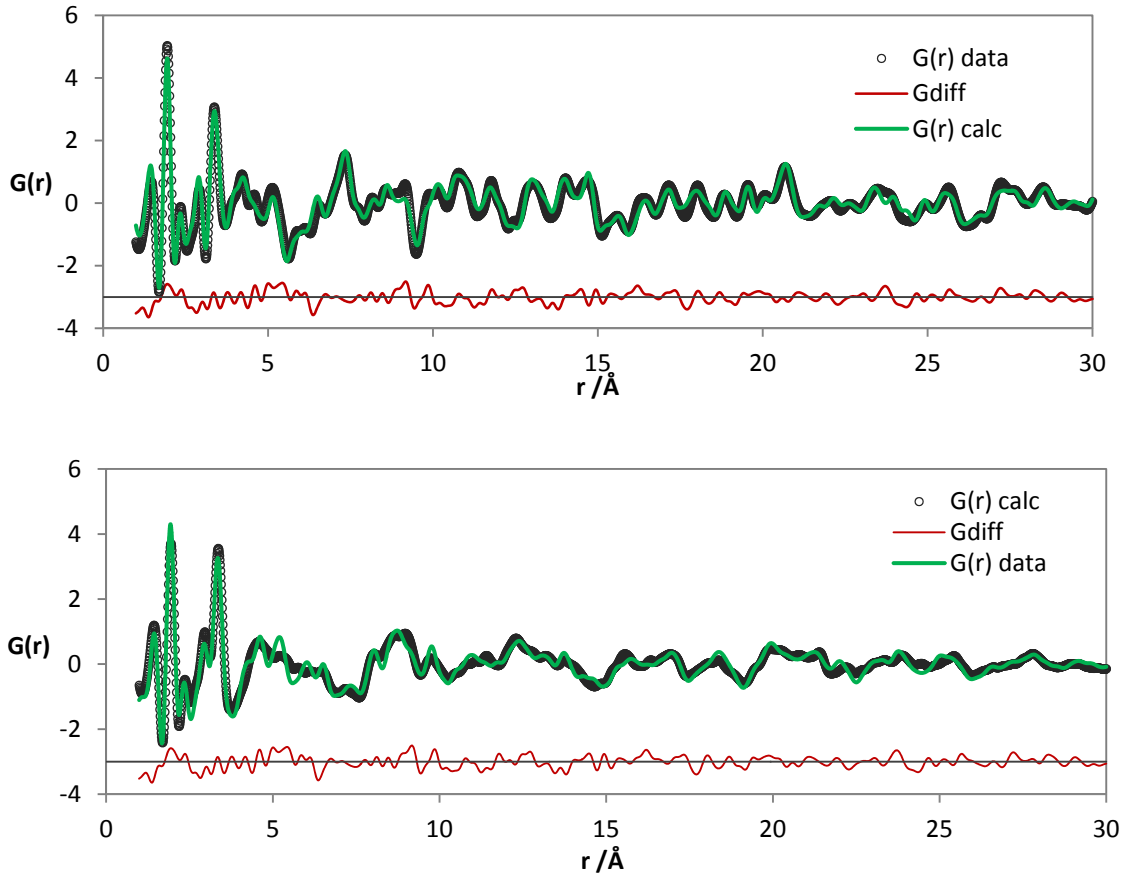

Figure S3. Refinements of the PDF data sets for Cu-SIP-3 at 300 K (top) and 500 K (bottom) Green line shows experimental data. Black circles show PDF calculated from model structure. Red line is the residual curve, $G(r)_{obs} - G(r)_{calc}$

Two phase refinement of intermediate temperature data sets

A two phase refinement was done in PDFGui. The refined models from the 300 K and 500 K data sets were used as the starting point for the refinements. Refinements were done against G(r) data collected at 10 K intervals by refinement of the phase scale factor. The scale factor of the dehydrated structure constrained to be $1 - SF_{hyd}$, where SF_{hyd} is the scale factor of the hydrated structure.

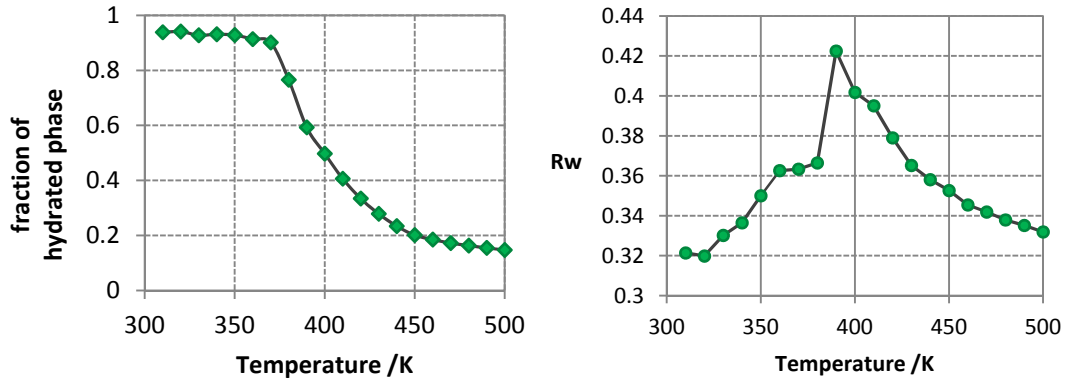

Figure S3. Binary phase refinement of Cu-SIP-3 in intermediate regions. Left: phase fraction as a function of temperature. Right: R_w values for the fits produced using PDFGui