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Ultrasound-driven preparation and pair distribution function-assisted structure solution of a copper-based layered coordination polymer

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Nanoparticles of a copper-based layered coordination polymer, STAM-2, have been prepared via an ultrasound mediated transformation from a layered metal-organic
10 **framework, STAM-1. The structure of the material was then solved using pair distribution function analysis to identify the structural units present and the final structural model refined against the pair distribution function data.**

Coordination polymers and metal-organic frameworks (MOFs)
15 have attracted extensive attention in recent years owing to their intriguing structural motifs and potential applications in variety of fields, from gas adsorption, gas storage, and catalysis to biology.[1-5] Many interesting hybrid materials of this type are also layered materials,[6] although they are generally not porous solids.
20 Generally, MOFs are generated from a wide range of organic ligands and metal ions by employing hydrothermal and solvothermal synthetic methods[7]. It is also possible to modify the preformed lattice of the MOF using chemical post-synthetic modifications[8] An alternative method of providing the required
25 energy to form metal-organic coordination polymers is ultrasonication (US), a rapid, facile and environmentally friendly method, already used widely in organic synthesis, has recently been used to synthesize MOFs[9]. Here we show that application of the ultrasonic method to a preformed copper based MOF (STAM-
30 1)[9] leads to the formation of a totally different structural architecture, which we name STAM-2. STAM-2 forms nano particles, making structure solution by conventional Bragg diffraction methods alone difficult. Pair Distribution Function (PDF) analysis is used to identify the Cu-based secondary
35 building unit in the material in order to constrain the model for *ab initio* structure solution, and show that the final structural can be successfully refined against the PDF data.

The recently reported STAM-1 (St-Andrews MOF-1)[10] is an
40 unusual layered MOF with two types of 1-dimensional channel,

one of which is lined by metal ions and the other by organic ester groups. This leads to unique features such as discrimination between the different channels and even switchable adsorption, the control of which channel gases and vapours are adsorbed into.
45 STAM-1 is formed from a solvothermal reaction as hexagonal plate crystals up to several tens of microns in diameter, and contains the well-known 'paddle wheel' copper carboxylate dimeric secondary building unit (SBU) linked by the monomethyl ester of benzene- 1,3,5 -tricarboxylic acid (mmBTC). Dispersion
50 of the STAM-1 crystals in water followed by exposure to pulsed ultrasonic radiation over a few hours leads to significant turbidity in the suspension, accompanied by a slight change in the blue colour. The resulting, very fine powder solid was recovered from the suspension using a centrifuge and powder X-ray diffraction
55 experiments (Figure 1) indicated that the structure of the material was no longer that of STAM-1, but had changed significantly. We called this new material STAM-2. The quality of the powder X-ray diffraction pattern was significantly reduced, with much broader Bragg reflections in the STAM-2 diffraction pattern
60 compared to the STAM-1 starting material, indicative of a loss of crystallinity, a reduction of crystallite size or both (Figure 1). However, it was clear that no STAM-1 remains in the powder as there were no reflections from STAM-1 visible in the STAM-2 powder pattern (it is easiest to see this for the region 10 -12
65 degrees 2θ in Figure 1, where two of the most intense peaks in the STAM-1 pattern align with a region without any reflections in the STAM-2 pattern).
Scanning electron microscopy (Figure 2) of the new material shows that STAM-2 is present as small nanorods, with a
70 maximum width of ~100 nm and maximum length of around 500-1000 nm. Thus the ultrasound treatment produces not only a change in structure of the material but also a significant change in morphology.
Clearly, the small size of the crystallites precludes the use of
75 single crystal X-ray diffraction methods, even those using high intensity synchrotron sources, to solve the crystal structure of the

material. Given that these MOF samples are also very beam sensitive in high resolution electron microscope experiments the only option left open for full structural characterisation of the crystalline structure is *ab initio* structure solution from powder

5 diffraction data. Over the last 20 years or so this has developed from being difficult[11] and quite rarely accomplished into what is now a fairly routine, albeit still time consuming, technique.[12] However, in general it is still limited to good quality data sets from highly crystalline materials. Samples such as STAM-2 that

10 are relatively poorly crystalline with significant overlap of broad peaks pose great challenges for *ab initio* structure determination. Attempts to index the observed powder X-ray diffraction pattern using Treor, ITO and other algorithms had relatively poor figures of merit (M(20) < 10) although there was one triclinic candidate

15 cell which could be refined using the Le Bail full pattern fitting approach using the GSAS suite of diffraction programs, to give a final cell of a = 11.252 Å b = 10.614 Å c = 5.744 Å α = 86.5°, β = 97.7°, γ = 106.8°. Once a suitable unit cell was found, structure factor extraction and structure solution were attempted using a

20 variety of different software packages (SIRPOW Extra, superflip etc as well as structure extraction using GSAS and input into direct methods programs such as SIR and Shelxs). None of these approaches produced any obviously correct models for the STAM-2 structure.

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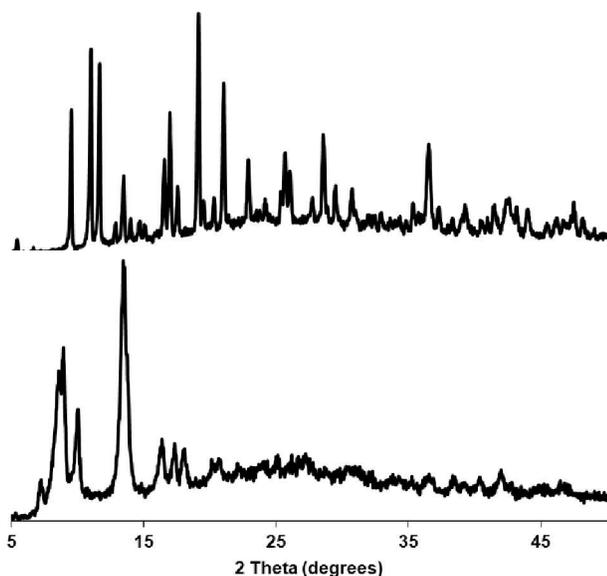
Figure 1. The X-ray powder diffraction patterns of the STAM-1 starting material (top) and the product STAM-2 (bottom).

30 Given that the structure of the STAM-1 starting material is known from previous work the strategy we then employed was to look for techniques that would allow us to directly compare features from the structures. One possible change that might have occurred during the transformation from STAM-1 to STAM-2 is

35 that the ester group on the mmBTC group may have been hydrolysed. However, solid-state NMR of STAM-2 indicates that the methyl ester is still present.

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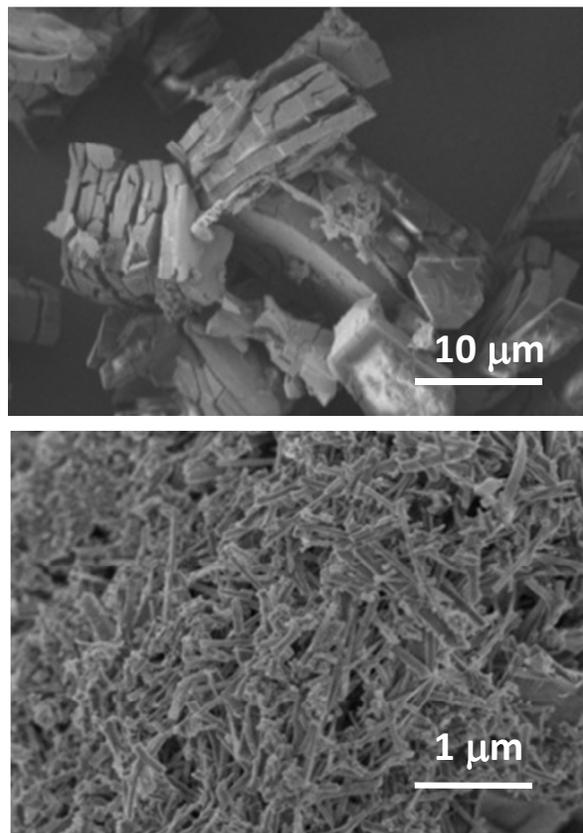
Figure 2. Scanning electron microscope images of the starting material STAM-1(top) and the product, STAM-2 (bottom) showing the significant reduction in crystallite size after the ultrasound treatment.

45 Another feature of MOFs and coordination polymers is the presence of different SBUs in different structures. The dimeric 'paddle wheel' found in STAM-1 is found in several other structures, for example the extremely well-known HKUST-1 material, and our first thoughts were that it was likely that this

50 unit is also present in STAM-2. To probe this we collected pair distribution function (PDF) data.[13] A pair distribution function is a weighted histogram of atom-atom distances in a structure. The PDF is experimentally accessible through the Fourier transform of the total scattering intensity; both the Bragg scattering and the

55 diffuse scattering, which are treated with equal weighting in analysis. Because of this, there is no necessity of long range order in a sample, and PDF analysis can therefore be used to gain information about structures where issues of disorder or particle size limits the use of conventional Bragg crystallographic

60 techniques which rely on long range order.

Total Scattering data for STAM-2 were collected at 11-ID-B at Argonne National Laboratory, IL, USA. Full details of data collection and reduction can be found in the supplementary information. PDFs for STAM-1 and STAM-2 (Figure 3) were

65 extracted from the total scattering data using PDFGetX2[14].
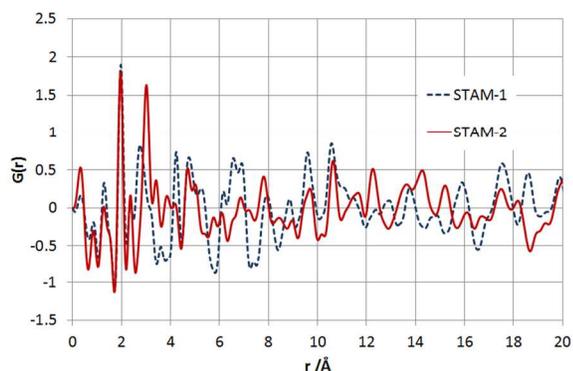
Figure 3. PDF for STAM-1 (dotted line) and STAM-2 (red line)

PDF is a particularly useful technique when looking for the presence (or absence) of small subunits in the structures that are characterised by particular interatomic distances. The paddle wheel dimer in STAM-1 is characterized by a short Cu-Cu of ~2.6 Å. It is clear from Figures 3 and 4 that the characteristic Cu-Cu peak from the paddle wheel unit is absent in the STAM-2 data, proving beyond doubt that STAM-2 does not contain a paddle wheel SBU. However, the intense peaks at 3.0 Å and 3.4 Å are likely to be due to Cu-Cu distances in the material, and indicate a different SBU. A search of known MOF structures with different SBUs indicated that a copper tetramer found in the recently reported Cu-SIP-3 material had two independent Cu-Cu distances of ~ 3.0 and 3.4 Å, matching nicely the positions of the peaks in the STAM-2 experimental PDF. The calculated Cu-Cu partial PDFs (i.e. a calculated PDF including only copper-copper distances and no others) are shown in Figure 4, compared with the experimental data for STAM-2. This clearly shows that Cu-tetramer from Cu-SIP-3 matches well for peak position, but not for relative peak intensity, indicating that the SBU is similar, but not identical, to the one present in Cu-SIP-3.
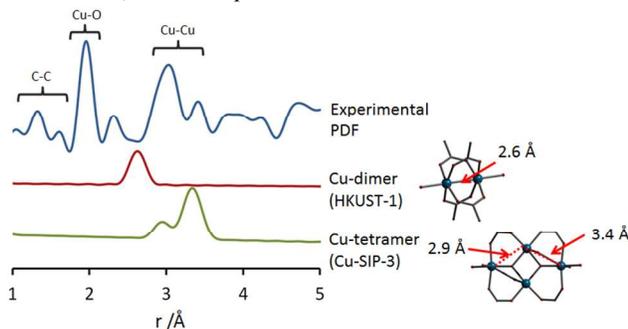
Figure 4. Experimental PDF of STAM-2 (top) compared to simulated partial Cu-Cu PDFs for two known Cu-SBUs, the paddle wheel found in STAM-1 and HKUST-1 (middle) and the copper tetramer found in Cu-SIP-3 (bottom).

Given the information provided by the PDF we then revisited the trial solutions from the *ab initio* powder X-ray diffraction work described earlier, but this time specifically searching in the solutions for interatomic distances of ~3.0 and 3.4 Å consistent with the Cu tetramer SBU. The structure solution from the charge flipping algorithm incorporated into the program superflip[15] was the only one to show such interatomic distances between any of the high electron density peaks (ranked number 1 and number 5 by electron count). Further investigation of the peaks in this

solution found two potential oxygen atoms at interatomic distances of ~2 Å from the proposed copper atoms. This was enough information to then begin building up the coordination around the copper atoms and identify the SBU present in the structure as a chain of vertex-shared copper tetramers shown in Figure 5, similar to that seen in the MOF known as Cu-SIP-3.[16] The Cu-Cu distances in this structure are similar to those in the isolated tetramer SBUs in Cu-SIP-3, but of course the number of individual Cu-Cu interactions is now different because of the shared vertices. This accounts for the similarity in peak positions and the differences in relative intensities shown in Figure 4.
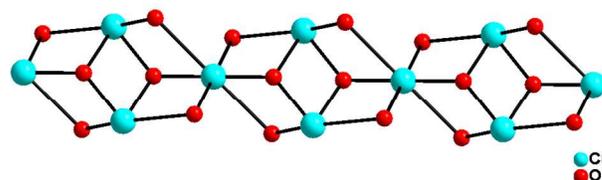
Figure 5. The chain of vertex-shared copper tetramers found in STAM-2. The copper tetramers in Cu-SIP-3 are similar, but isolated from each other and linked through the organic groups.

The remaining carbon and oxygen atoms in the structure could then be placed by calculating the positions of the benzene ring and assuming that the ester group is coplanar with this ring. The carbon of the methylester group could only be sensibly placed in one of the possible two positions to avoid chemically unfeasible distances. This structural model was then used as a starting point for Rietveld analysis against the powder X-ray diffraction data (See supplementary material). The final refinement details are, not surprisingly given the low crystallinity of the sample and the poor quality of the diffraction data, not as good as one would hope for in a nicely crystalline material (The final Rp values were still > 20%). The structural model required strong restraints to retain chemically sensible interatomic distances and geometries, and even then could not really be said to have unambiguously characterised the structure.

The model from the Rietveld analysis was then refined against the PDF data set. Initial fits from the refinement of damping, unit cell, correlation functions and thermal parameters were poor due to the overestimated Cu-O bond lengths in the XRD model. However, when the symmetry constrained copper and oxygen bond lengths were allowed to refine the fit improved substantially (Figure 6). It was then possible to refine the positions of the carbon atoms in the data range 2.0 Å to 15 Å, with only a slight loss of geometrical integrity in the structure, leading to, for example slight non-planarity of the aromatic ring in the structure. It is important to note that the refinement required no restraints on the bond distances, etc. to remain stable, and the resulting structure retains chemical sense. The chemical structure could be improved slightly by treating the benzene ring as a rigid body (see supplementary information). The final R_w value for refinement against the PDF data was 0.28 (note that R_w values from PDF refinement are normally higher than those for Rietveld and single-crystal X-ray diffraction refinements). Given the reasonable refinement against both the XRD and PDF date we are therefore confident that the main features of the structure are correct.
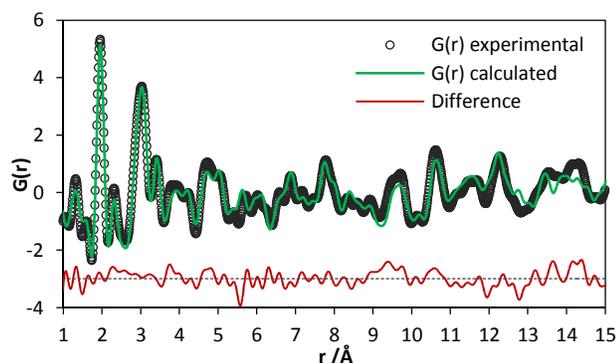
Figure 6. Refinement of the STAM-2 model against the PDF data. The black circles are the experimental data, the green line is the calculated PDF from the model and the red line is the difference between the two, offset by -3 for clarity.
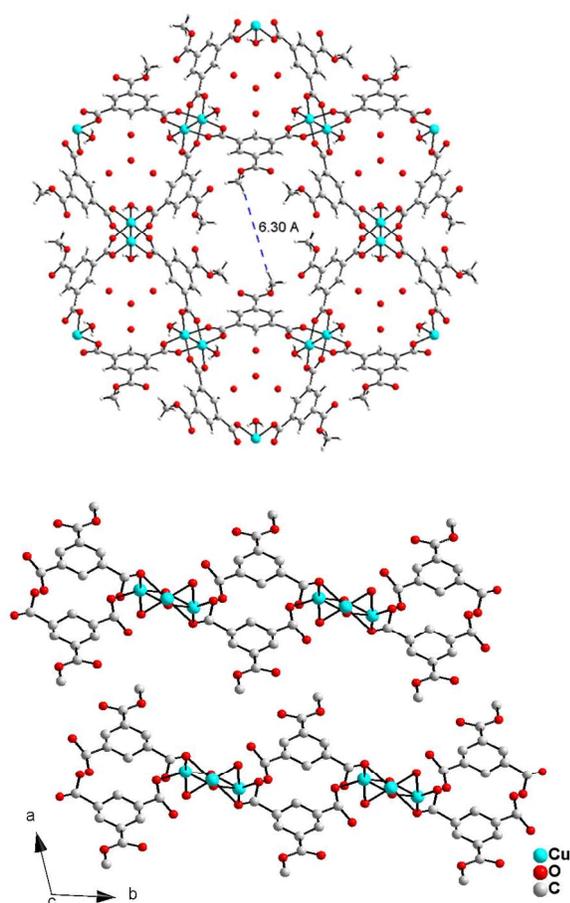
Figure 7. The overall structures of STAM-1 (top) and STAM-2 (bottom), both viewed parallel to the crystallographic c-axes. Note the significant change in local structure around the copper atoms and in the connectivity of the linker.

The structure of STAM-2 can be considered as a layered coordination polymer network, comprising the chain of vertex-shared copper tetramers shown in Figure 5. The chains run parallel to the crystallographic c-axis and are linked into layers via coordination to the two carboxylate groups of the mmBTC ligand. The methyl ester of the mmBTC ligand then points into the interlayer space in the structure.

Conclusions

Ultrasound irradiation of the metal-organic framework STAM-1 leads to the formation of a new layered coordination polymer, STAM-2, that forms only as nanocrystals. A combination of pair distribution function (PDF) analysis and powder X-ray diffraction was used to solve and refine the model structure of the material. The key aspect of the work is the realisation that the nanostructured nature of the STAM-2 material necessarily leads to X-ray diffraction of lower quality than would normally be the case. The use of PDF analysis to augment the information available allowing identification of the correct structural features in the material, which in turn enabled the solution of the structure. Without the invaluable information provided by PDF the structure solution from the XRD data would have been significantly more difficult. In addition, because of the poor quality of the powder X-ray diffraction patterns, Rietveld refinement of the structural model was less than satisfactory, and in some ways refinement against the PDF data yielded a better overall structure.

Experimental

Synthesis of STAM-1 was carried out as described in reference 9. The STAM-1 solid was then suspended in water in a beaker surrounded by an ice bath. The suspension was then irradiated with ultrasound for 260 minutes using a Branson Digital Sonifier 250, with 20 KHz ultrasound (50% intensity) pulsed at 3 seconds on followed by 1 second off. The resultant blue nanoparticulate powder of STAM-2 was recovered by centrifugation.

Total scattering data were collected at beamline 11-ID-B at the Advanced Photon Source, Argonne National Laboratory, IL, USA. A wavelength of 0.21280 Å was used for all experiments with a frame exposure time of 5 minutes. All data were recorded using a Perkin Elmer amorphous silicon area detector. The sample-to-detector distance was determined as 151.338 mm by the use of a CeO_2 powder standard. The program FIT2D was used to integrate data.[2] An empty Kapton capillary was run for the same counting time in order to measure the air and Kapton contributions to the scattering intensity. These contributions were removed in data processing in PDFgetX2. Other standard corrections were applied to the total scattering data, and G(r) was obtained by the Fourier Transform of the corrected total scattering data using the program PDFGetX2. Gaussian functions are fitted to peaks of interest in the PDF produced using the program Fityk.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental
10 details and final structure of STAM-2.

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Ultrasound-driven preparation and pair distribution function-assisted structure solution of a copper-based coordination polymer

Graphical Abstract
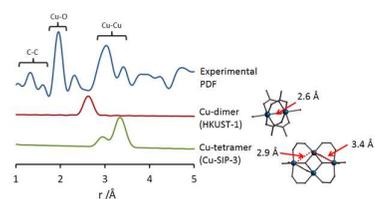
Pair distribution function analysis has been used to solve the structure of a coordination polymer material formed by ultrasound treatment of a metal-organic framework.