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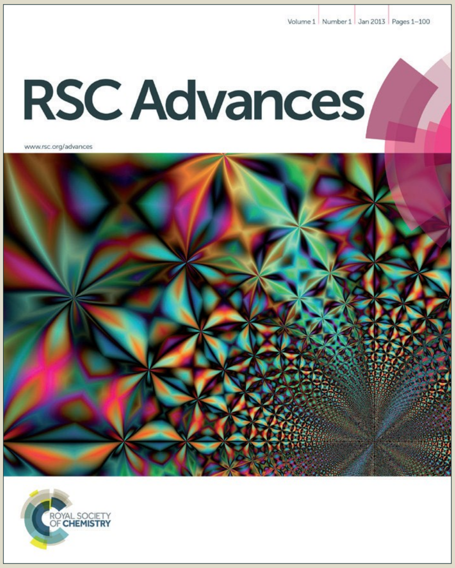

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COMMUNICATION

Cu(I)Cu(II)BTC, a microporous mixed-valence MOF via reduction of HKUST-1

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Metal-organic frameworks (MOFs) are typically crystalline microporous materials with metal ions of usually one oxidation state (although mixed-valence MOFs have been reported) and one type of co-ordination structure. Here, a microporous mixed-valence Cu(I,II)-MOF featuring a unique network of distinct Cu(I) and Cu(II) coordination sites is prepared by solvothermal reduction of HKUST-1. Like HKUST-1, this compound is assembled solely from Cu ions and benzene 1,3,5-tricarboxylate (BTC) ligands. The new MOF exhibits dual micropore size distribution and shows superior water stability than HKUST-1.

Metal-organic frameworks (MOFs) are crystalline materials, usually with permanent porosity, formed by linkage of inorganic moieties (metal ions or clusters) with multitopic organic ligands. By careful design and use of the organic ligands and metal ions, the pore metrics and topologies can be finely tuned to suit various applications including gas storage, separation, catalysis and drug delivery.[1] One of the earliest and most widely studied MOFs is the iconic $Cu_3(BTC)_2$ (BTC = benzene 1,3,5-tricarboxylate), also known as HKUST-1.[2] It comprises a network that consists of two kinds of nodes: Square planar dicopper paddlewheel units and trigonal planar BTC ligands are linked to form a cubic structure (Fm-3m) of permanent porosity. HKUST-1 is commercially available by the trade name Basolite^{TM} C300 manufactured by BASF.[3] On the removal of guest molecules, the coordinatively unsaturated Cu^{2+} sites exhibit Lewis acid property and offer potential for various applications.[2-3] HKUST-1 has been extensively used in gas adsorption and separation,[4] chromatography,[5,6] catalysis,[7] and proton conductivity.[8]

Here we report that reduction of HKUST-1 yields a mixed valence MOF which, like HKUST-1, is assembled solely from Cu ions and BTC ligands. Hydrothermal treatment of the characteristic blue octahedral HKUST-1 crystals at 160 °C for 16 hours in the presence of hydroquinone as reducing agent gave dark green crystals (Fig. 1). The powder X-ray diffraction (PXRD) pattern showed that a different crystalline material was produced (Fig. 1). The new crystalline materials was further characterised with single crystal X-ray diffraction (SC-XRD) as a novel crystalline material of composition $Cu(I)Cu(II)BTC(H_2O).2H_2O$ (**1**) containing both Cu(I) and Cu(II) ions. The compound crystallises in space group P4/nmm exhibiting one-dimensional channels running parallel to [001]. Cu(I) and Cu(II) ions reside in distinct coordination environments: The Cu(II) ions are part of the familiar Cu_2-paddlewheel motif characteristic of the original HKUST-1 structure,[2] while the Cu(I) ions are part of tetrameric macrocycles containing four Cu(I) ions and four carboxylate groups (Fig. 2). In return, every trianionic BTC ligand contributes one carboxylate group to the tetrameric Cu(I) macrocycle and two to the dimeric Cu(II) junctions.

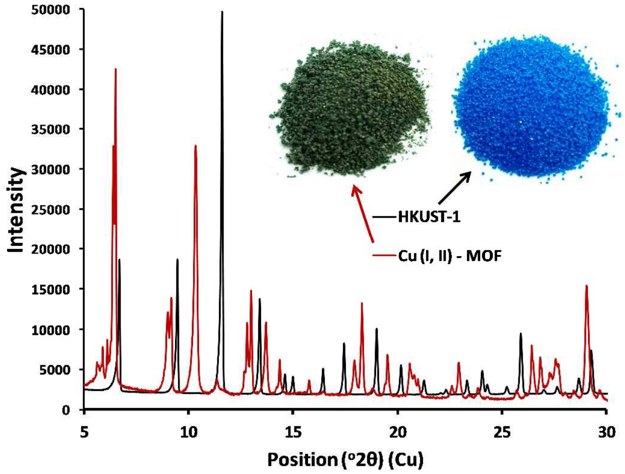

Fig. 1 Comparison of the PXRD patterns of the synthesized HKUST-1 (black line) and the Cu(I,II)-MOF (**1,** red line).

The framework consists of two interpenetrating three-dimensional nets which are assembled from three distinct vertices: Square planar Cu(II) dimers and trigonal planar BTC ligands form corrugated 2D-grids (analogous to the layered structure of Cu(II)BDC (BDC = 1,3-benzene dicarboxylate);[9] while tetrameric Cu(I) macrocycles act as tetrahedral nodes

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Electronic Supplementary Information (ESI) available: Experimental details, SEM, and TGA data. See DOI: 10.1039/x0xx00000x connecting every second grid whilst penetrating through the grid of the other net (Fig. 3). This is topologically equivalent to a **mmm-c** net.[10] The grid structure described above is also permeated by the 1-D channels which are about 8 Å in diameter as measured between the hydrogen atoms of Cu-coordinated water molecules. The solvent accessible volume makes up 25% of the unit cell. The X-ray structure of freshly made crystals also contains two water molecules (per formula unit) which occupy the channels and are located in hydrogen bonding distance to the water ligands that are coordinated to Cu(II) ions.

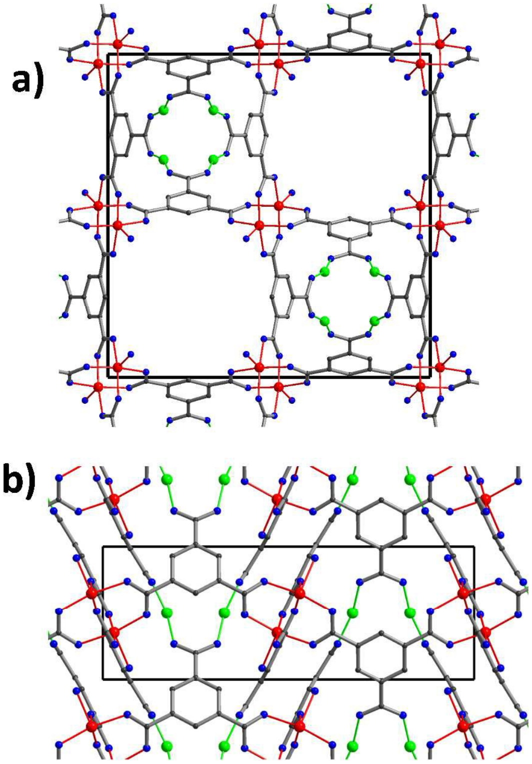

Fig. 2 Crystal structure of **1**. a): view along [001]; b): view along [100]; Cu(II), red; Cu(I), green; O, blue; C, grey. Black lines indicate the unit cell; H-atoms are omitted for clarity.

X-ray photoelectron spectroscopy (XPS) was used to investigate the oxidation states of Cu. Fig. 4 shows four peaks in the Cu2p$_{3/2}$ region. The peak at 932.6 eV is attributed to Cu(I) and the peak at 934.6 eV is attributed to Cu(II). The two peaks located at 946 – 938 eV are shake-up features associated with the Cu(II) oxidation state. These occur when the Cu electronic configuration is unsaturated (d^9), thus allowing p → d hybridization. Such features are not present in the Cu(I) oxidation state as the electronic configuration is d^{10} and only the one peak is seen in the 2p$_{3/2}$ region.[11] Therefore, the Cu 2p$_{3/2}$ spectrum in Fig. 4 demonstrates the co-existence of Cu(I) and Cu(II) in the framework. The relative abundance of Cu(I) and Cu(II) can be obtained by a peak fitting procedure performed on the Cu 2p$_{3/2}$ signal and its shake-up features.[12] The background was subtracted via Shirley construction and two pure Gaussian curves were fitted, one for Cu(I), one for Cu(II), separated by 2.0 eV, as per the procedure. The calculation of the areas of the Cu(I) peak and the Cu(II) structure (including main peak and two shake-up feature peaks), gave a ratio of 43% Cu(I) to 57% Cu(II).

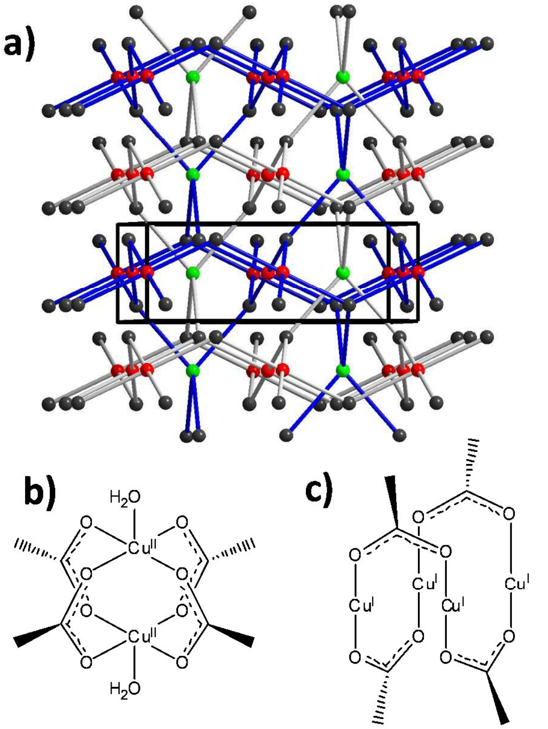

Fig. 3 a) Illustration of the network topology of the two interpenetrating nets of Cu(I,II)-MOF (**1**). Nets are coloured in grey and blue; nodes are depicted as follows: BTC ligands, dark grey; Cu(II) dimers (b), red; Cu(I) macrocylces (c), green. Black lines indicate the unit cell.

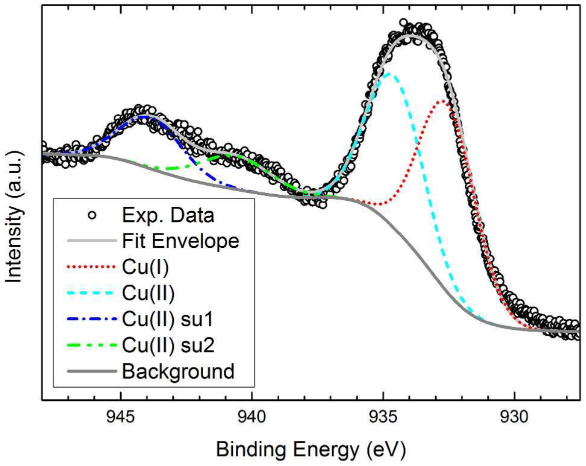

Fig. 4 The Cu 2p3/2 XPS spectrum of Cu(I,II)-MOF (**1**).

The presence of Cu(I) sites in the structure of **1** is somewhat surprising since Cu(I) ions are known to be prone to disproportionation reactions in aqueous media. Nevertheless, here they were forming under hydrothermal conditions and in the absence of soft Cu(I) stabilising ligands. Molecular complexes with corresponding tetrameric copper(I) carboxylate macrocycles have been reported.[13] However, these are very sensitive to disproportionation and must be kept in inert, anhydrous environments. We assume that the stability of Cu(I) sites in **1** is a result of the rigid coordination and the effective shielding from the open channel structure.

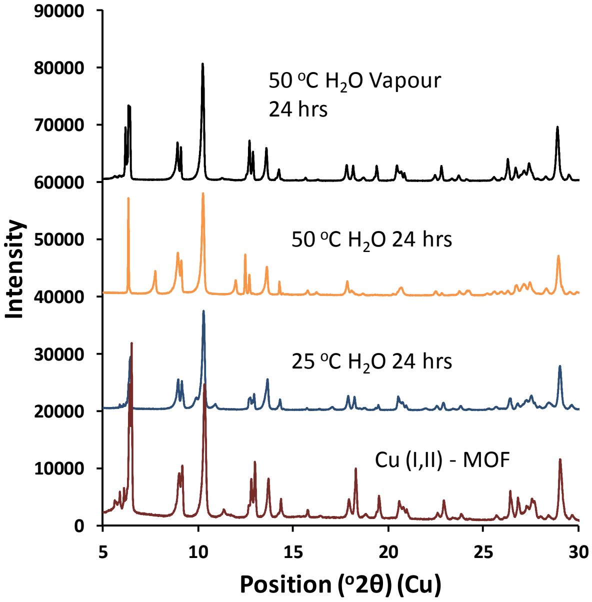

Fig. 5 PXRD patterns of the Cu(I,II)-MOF (**1**) treated in water or water vapour under different conditions.

Many polycarboxylate-based MOFs including HKUST-1 have very low hydrolytic stability, which prevents their use and storage in an ambient atmosphere.[14] However, **1** showed significantly improved water stability in comparison to HKUST-1. All the typical peaks remained (although with slight changes in some peak intensities) after the material was immersed in water at 25 °C for 24 hours, suggesting that the framework structure was maintained (Fig. 5). Only when soaked at 50 °C for 24 hours an additional crystalline phase started to show up in the PXRD pattern indicating slow disintegration of 1 under these conditions. However, **1** was still stable when exposed to water vapour at 50 °C for 24 hours, with all the typical peaks observed on the PXRD pattern (Fig. 5). In contrast, HKUST-1 readily loses its structural integrity when immersed in water or exposed to its vapour.[15] The thermal stability of **1** is similar to that of HKUST-1. Thermogravimetric analysis shows that the channels desolvate when heated to 110 °C, followed by rapid decomposition at around 350 °C (Fig. S1). HKUST-1 was prepared as crystalline microparticles with no macropores.[16] However, SEM imaging of Cu(I,II)-MOF showed macroporous microparticles consisted of needle or plate-like crystals (Fig. S2). N_2 sorption studies showed that **1** was microporous taking up 11.5 mmol/g with a BET surface area of 760 m^2/g (Langmuir surface area 1126 m^2/g) and a pore volume of 0.42 cm^3/g (Fig. 6). The rapid increase of uptake at low partial pressure for both isothermal curves indicated the Cu(I,II)-MOF was microporous (Fig. 6a). The pore size distribution by density functional theory (DFT) calculation using the cylindrical pores model (pores in pillared clay) showed a shark peak at 10.2 Å for the HKUST-1 material.[2,16] However, two peaks (7.7 Å and 11.3 Å) were observed for the Cu(I,II)-MOF (Fig. 6b), in agreement with its crystalline structure.

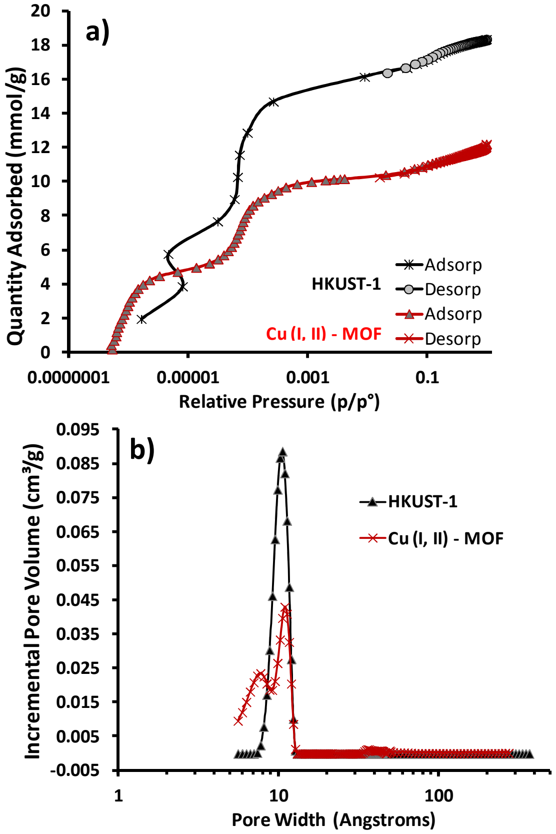

Fig. 6 Characterization of Cu(I,II)-MOF (1) by N_2 sorption in comparison with the synthesized HKUST-1. (a) The isothermal curves. (b) The plot of micropore size distributions calculated by the NLDFT cylindrical pores in pillared clay (regularization value 0.2) model.

Mixed valence compounds are classified into three groups ranging from those with localized valences residing at distinct sites (Class 1) to systems where the valences are fully delocalized between sites (Class 3).[17] The framework **1** with its geometrically distinct and well separated coordination environments evidently belongs to Class 1. The few coordination networks featuring distinct Cu(I) and Cu(II) sites all contain stabilising N- or S-donor ligands.[18,19] In all these compounds the cause for the reduction of the Cu(II) precursor remained somewhat unclear. It was attributed to oxidation of organic solvent of excess ligand under solvothermal conditions. In similar fashion, a mixed-valence Cu(I,II) network of Class 3 has been obtained in which the valences are delocalised within a Cu_2 paddlewheel unit surrounded by three carboxylate groups.[18] It was observed that prolonged solvothermal treatment of

HKUST-1 in ethanol generates copper residues hinting at the reducing role of the solvent. There is also evidence that a significant proportion of Cu_2 paddlewheels in HKUST-1 can be reduced to be in a mixed-valence state of Cu(I,II) while the integrity of the framework is retained.[20]

Preparation of mixed valence MOFs has been reported and such MOFs have shown interesting redox-activities which promise applications in catalysis and electrochemistry.[21-23] In the reported mixed valence MOFs, the location of the ions with different oxidation states may be exchangeable and there is only one type of framework structure, normally the same as their standard MOFs.[21-23] In our study, the Cu(I,II)-MOF shows two crystalline environments and two distinct micropores. The Cu^+ and Cu^{2+} are located in the separately different framework structures. The reaction mechanism is not clear yet. The inductively coupled plasma (ICP) analysis of Cu ion concentrations during the course of the reaction was performed. It showed there was partial dissolution of the HKUST-1 (Table S1). It was possible that the released Cu^{2+} was reduced by the presence of hydroquinone and formed the new hybrid Cu(I,II)-MOF. But this did not exclude the possibility that the reduction might occur on the HKUST-1 because there was still Cu ions present (at ~200 pm) at the end of the reaction. It is reasonable to say that the formation of Cu(I,II)-MOF was not the result of a simple dissolution/recrystalisation process. This is because the structural change of HKUST-1 in water is irreversible.[15] The regeneration of HKUST-1 may be carried out via acid-base treatment but in ethanol-water rather than water only.[24]

In summary, reduction of HKUST-1 in the presence of hydroquinone under hydrothermal conditions produced $Cu(I)Cu(II)BTC(H_2O)$, a novel microporous mixed valence MOF featuring a unique network of distinct Cu(I) and Cu(II) coordination sites. This material is surprisingly stable considering the presence of Cu(I) ions, showing greater resistance towards hydrolysis than HKUST-1. Bearing in mind the significance of HKUST-1 in the field of metal organic frameworks, these findings may pave the way towards new interesting mixed-valence MOFs based on Cu and polycarboxylate building blocks and the use of them for exciting potential applications.

Acknowledgement

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TOC Graphic

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A microporous mixed-valence Cu(I,II)-BTC MOF is produced and exhibits two crystalline environments, bi-modal micropores, and superior water stability.