

Cite this: *CrystEngComm*, 2012, 14, 4153–4156

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Highly rigid and stable porous Cu(I) metal–organic framework with reversible single-crystal-to-single-crystal structural transformation†

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Received 19th December 2011, Accepted 21st March 2012

DOI: 10.1039/c2ce06701c

A simple room temperature reaction of $\text{Cu}(\text{NO}_3)_2$ and 2,3-pyrazinedicarboxylic acid (H_2pyzdc) in the presence of dihydroxyfumaric acid (DHFA) resulted in the formation of a highly stable 3D Cu(I) coordination polymer, $\{[\text{Cu}_2(\text{pyzdc})] \cdot 0.83\text{H}_2\text{O}\}_n$ where DHFA acts as a reducing agent. It possesses a 1D water filled channel along the crystallographic c direction and the framework shows reversible single-crystal-to-single-crystal structural transformation upon dehydration and rehydration.

In recent years there is an upsurge in the design and synthesis of metal–organic frameworks (MOFs) or porous coordination polymers (PCPs) due to their promising application in the gas-storage, separation, sensing, catalysis, magnetism, and drug delivery.¹ Among a plethora of MOFs explored with the different metal ions, the porous properties of MOFs based on Cu(I) are yet to be explored properly.² However, coordination chemistry of Cu(I) has been of paramount importance due to its role in biological processes,³ catalytic activity,⁴ solar energy sensors,⁵ and photophysical properties.⁶ On the other hand synthesis and stabilization of Cu(I) complexes in open atmosphere is a great challenge due to intrinsic instability of the cuprous state and facile oxidation to Cu(II).⁷ 2,3-dihydroxyfumaric acid (DHFA) is a redox active reagent and using this reducing agent recently we have synthesized versatile Cu(I) and mixed-valent porous Cu(I)/Cu(II) frameworks stabilized by pyrazine or pyridine based linkers as well as Ag/Au nanostructures in aqueous medium under aerobic conditions.⁸ Expanding this strategy for synthesizing new porous Cu(I)-MOFs we used pyrazinedicarboxylate as a linker and were able to isolate an extraordinarily stable 3D Cu(I) framework. In this communication, we report the synthesis, reversible single-crystal-to-single-crystal structural transformation and selective

adsorption properties of a unique Cu(I)-MOF, $\{[\text{Cu}_2(\text{pyzdc})] \cdot 0.83\text{H}_2\text{O}\}_n$ (**1**).

DHFA acts as a two electron donor in the reaction to reduce two moles of Cu(II) to Cu(I) and pyzdc acts as a linker to form the 3D structure (Scheme 1). The judicious choice of pyzdc, as a stabilizer and linker for fabricating a 3D Cu(I) MOF is based on two facts. Firstly, it contains a pyrazine ring which is a well-known heterocyclic ring for stabilizing Cu(I) *via* coordination to softer nitrogen atoms.^{8a} Secondly, two carboxylates are orthogonal to each other and consequently a higher dimensional structure based on oxygen coordination is expected compared to the linker where two carboxylates are present in the same plane.

The single-crystals of compound **1** have been synthesized by a slow diffusion reaction of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 2,3-pyrazinedicarboxylic acid (pyzdc) in the presence of alkaline 2,3-dihydroxyfumaric acid (DHFA) in an aqueous methanol medium.‡ Compound **1** crystallizes in the monoclinic crystal system with the space group $C2/c$. In the asymmetric unit there are three crystallographically independent Cu(I) centres (Cu1, Cu2 and Cu3), one pyzdc linker and 0.83 water molecule, where Cu2 and Cu3 atoms lie on the same two fold axis and Cu1 is at the general position (Fig. 1). The highly distorted tetrahedral geometry around each Cu1 centre is formed by one chelated pyzdc (N1, O1), one carboxylate oxygen (O3) and one pyrazine nitrogen atom (N2) from another pyzdc linker. Two Cu1–O bond lengths are 2.096(6) and 2.194(6) Å whereas the Cu1–N1/N2 bond lengths are 1.956(5) Å. The distortion around Cu1 is reflected in surrounding bond angles which are in the range of 80.7(2)–140.7(3)°. Each Cu2 centre is connected to four bridging (μ_2 -O) carboxylate oxygen atoms

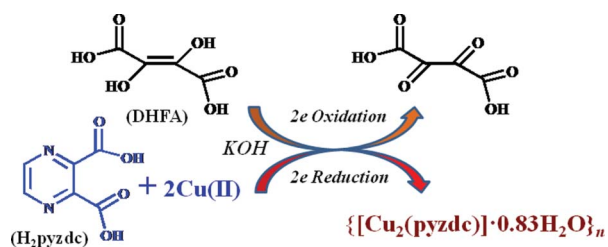
‡ An aqueous solution (10 mL) of DHFA (1 mmol; 0.184 g) was mixed with an aqueous solution (10 mL) containing 2,3-pyrazinedicarboxylic acid (pyzdc) (1 mmol; 0.168 g) with constant stirring. Then aqueous KOH (0.4 M) solution was drop wise added to the above solution and the pH was adjusted to ≈ 6.0 and 25 mL of the aqueous ligand solution was prepared. $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ (2 mmol; 0.465 g) was dissolved in 25 mL of MeOH and 2 mL of this solution was slowly and carefully layered on top of 2 mL of the above ligand solution using 1 mL buffer (H_2O and MeOH; 1 : 1 (= v/v)). Dark red block shaped crystals were obtained after one week which were washed with MeOH and water and dried. Bulk amounts of the compound was obtained by direct mixing of the respective reagents using the same molar ratio as indicated above in aqueous medium. Yield: 0.558 g (70% based on Cu). Anal Calcd for $\text{C}_6\text{H}_2\text{Cu}_2\text{N}_2\text{O}_5$ (**1**): C 23.15, H 1.28, N 8.99%. Found: C 23.05, H 1.37, N 9.06%. IR (KBr pellet, cm^{-1}): 3420 s $\nu(\text{O-H})$; 1653 s $\nu_a(\text{COO}_{\text{unidentate}})$, 1598 s $\nu_a(\text{COO}_{\text{bridging}})$, 1358 m $\nu_s(\text{COO})$. (Fig. S4, ESI†).

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† Electronic supplementary information (ESI) available: CIF files, supporting figures and measurement details. CCDC reference numbers 859368–859370. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2ce06701c



Scheme 1 Mechanism of the formation of $\{[\text{Cu}_2(\text{pyzdc})]\cdot 0.83\text{H}_2\text{O}\}_n$ in presence of DHFA.

(O1, O1a, O4b and O4c) from the four different pyzdc linkers (Fig. 1). The Cu2–O bond lengths are 2.728(6) and 2.789(5) Å for Cu2–O4 and Cu2–O1, respectively. The coordination geometry of Cu2 is neither tetrahedral nor trigonal pyramidal as the bond angles around the Cu2 centre are in the range of 80.44(17)–172.20(17)°. Such unusual coordination geometry of Cu2 is stabilized by the weak interaction with the bridging carboxylate oxygen atoms (O2, O2a) at a distance of 2.880(5) Å. The most remarkable point is that Cu3 is connected to two carboxylate oxygen atoms (O2 and O2a) at a distance of 2.663(5) Å and the corresponding angle is about 88.20(17)°. However, Cu3 undergoes weak interaction with the crystalline water molecule O1w and its symmetry related counterpart at a distance of 2.95(2) Å (Fig. 1). A 2D sheet is formed by the coordination of Cu(I) to nitrogen atoms (N1, N2) and carboxylate oxygen atoms (O1, O2) which are present in the same plane of the pyrazine ring (Fig. S1, ESI†). Orthogonal carboxylate oxygens O3 and O4 (perpendicular to the plane containing the pyrazine ring) and pyrazine nitrogen (N2) act as connectors between the 2D sheets to form a 3D framework (Fig. S1, ESI† and Fig. 2). This is clearly indicating the orthogonal carboxylate group has a significant role in extending the structure into 3D. The 3D framework contains a 1D water filled channel along the crystallographic *c*-axis (left side of Fig. 2). Moreover, the water molecule present in the pore has an unusual coordination to Cu3 as its distance is 2.95 Å and can be considered as semi-coordination. The dimension of the channels is about 2.54 ×

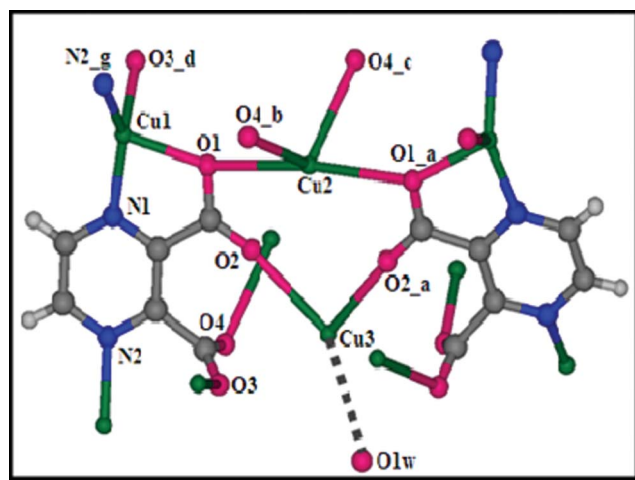


Fig. 1 View of the coordination environment around different Cu(I) centres connected by pyzdc in **1**. a = $-x, y, -1/2 - z$, b = $-x, 1 - y, -z$, c = $x, 1 - y, -1/2 + z$, d = $x, 1 - y, 1/2 + z$, g = $1/2 - x, 1/2 + y, 1/2 - z$.

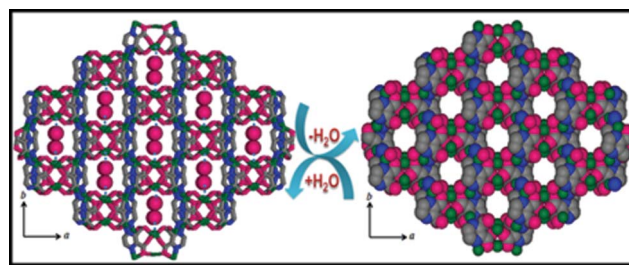


Fig. 2 View of the 3D coordination framework of **1** and **1'**. Left side: 1D coordination channels along the crystallographic *c*-axis occupied by the water molecules; Right side: CPK diagram of the dehydrated compound, $\{[\text{Cu}_2(\text{pyzdc})]\}_n$ (**1'**) showing 1D channels with unsaturated Cu(I) sites.

3.05 Å². The void space of the desolvated framework is about 18.3% to the total volume as suggested by PLATON.⁹ In the 3D framework the nearest neighbour distance between the Cu1···Cu2, Cu1···Cu3 and Cu2···Cu3 is about 4.7999(10), 3.9325(10) and 3.8896(7) Å, respectively.

Thermogravimetric analysis (TGA) of the framework **1** suggests the release of the water molecule in the temperature range of 100–130 °C and the dehydrated framework is stable up to 225 °C (Fig. S2, ESI†). Such high temperature release of the water molecule also correlates the presence of the interaction of water molecules with Cu3. The PXRD pattern of the dehydrated framework $\{[\text{Cu}_2(\text{pyzdc})]\}_n$ (**1'**) shows no changes in terms of peak positions and Bragg's intensities compared to as-synthesized **1** suggesting the framework is highly rigid (Fig. 3). High framework stability and structural integrity as observed from the TGA and PXRD pattern inspired us to determine the structure of the compound after removal of the water molecule. The structure determination from *in situ* X-ray diffraction study of a single-crystal after heating at 180 °C reveals that no water molecule is present inside the pore (see ESI†) and the 3D framework structure remains intact (right side of Fig. 2). Moreover, when the same crystal was exposed to water vapour for 24 h a framework regenerated with a water molecule inside the pore (Fig. 2). The single-crystal data of the as-synthesized, dehydrated and rehydrated crystal shows almost

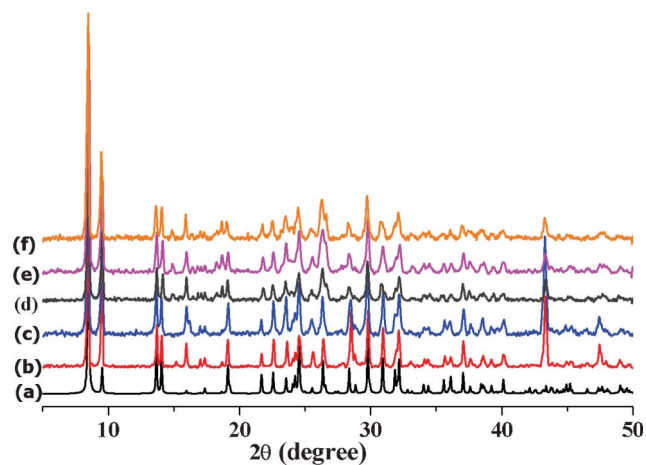


Fig. 3 PXRD pattern of compound **1** in different states. (a) simulated from single-crystal data; (b) as-synthesized $\{[\text{Cu}_2(\text{pyzdc})]\cdot 0.83\text{H}_2\text{O}\}_n$; (c) dehydrated $\{[\text{Cu}_2(\text{pyzdc})]\}_n$ (**1'**); (d) rehydrated form of **1'**; (e) **1'** exposed to the MeOH vapor and (f) **1'** exposed to the MeCN vapor.

identical cell parameters, also suggesting the framework is highly rigid and robust (Table S4, ESI†). We categorized this compound as a second generation of porous coordination polymer as classified by one of the authors.^{1b} The single-crystal-to-single-crystal structural transformation based on dehydration in a porous Cu(I) coordination polymer is rarely explored due to its inherent instability of the cuprous state. The unusual geometry of Cu(I) centres by the mixed oxygen and nitrogen donor atoms renders high thermal and atmospheric stability in the framework which is an unprecedented feature for the Cu(I) system.

To examine the permanent porosity, the dehydrated framework **1'** was subjected to sorption studies with N₂ (kinetic diameter 3.6 Å) at 77 K and CO₂ (3.3 Å) at 195 K. Both the isotherms show type-II profiles according to the IUPAC classification (Fig. S3, ESI†). The adsorption amount at $P/P_0 \sim 1$ is 8 mL g⁻¹ (for N₂) and 12 mL g⁻¹ (for CO₂) suggesting no inclusion of N₂ and CO₂ molecules into the pores and relates to the surface adsorption. This can be correlated to the smaller pore size of **1'** compared to the kinetic diameter of N₂ and CO₂. Inspired by the small pores with highly reactive unsaturated Cu(I) sites, we anticipated that **1'** could selectively adsorb solvent molecules on the basis of size and polarity. H₂O (kinetic diameter 2.65 Å), MeOH (4.0 Å), MeCN (4.3 Å) and EtOH (4.5 Å) vapour sorption isotherms were measured at ambient conditions. As shown in Fig. 4 the sorption profile of H₂O shows a typical type-I curve with steep uptake at low pressure regions indicating the strong interaction of H₂O molecules with the pore surface. The amount of final uptake is about 127 mL g⁻¹ at $P/P_0 \sim 1$ which corresponds to 1.66 H₂O molecules per formula unit of **1'**. The higher uptake of H₂O during adsorption may be rationalized to the strong adsorbate–adsorbate interaction after filling the specific unsaturated Cu(I) adsorption site by one H₂O molecule which undergoes strong interaction. The strong interaction with unsaturated Cu(I) site of H₂O is further supported by the hysteretic incomplete desorption profile of H₂O. It is worth mentioning that the MeOH sorption profile also revealed a type I profile, however the MeCN and EtOH adsorption profiles reveal typical type II

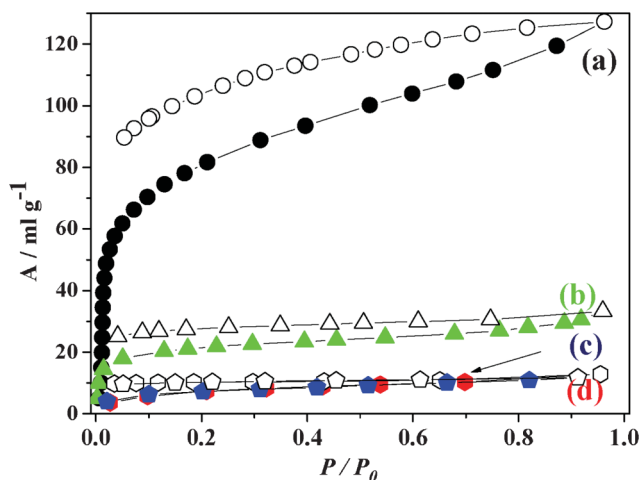


Fig. 4 Solvent vapor sorption isotherms for compound **1'** (a) H₂O; (b) MeOH; (c) MeCN and (d) EtOH.

curves suggesting only surface adsorption. The framework uptakes about 0.5 molecules of MeOH per formula unit and this smaller amount of MeOH uptake can be correlated to the bigger size of MeOH compared to the H₂O molecule. The occlusion of slightly bigger size MeOH molecules is driven by the stronger interaction ability compared to MeCN and EtOH molecules. All the profiles were analyzed by the DR equation,¹⁰ and the values of βE_0 are 7.35 and 3.20 kJ mol⁻¹ for H₂O and MeOH, respectively, indicating the strong hydrophilic character of the pore surface. Structural rigidity of the compound has also been confirmed from unchanged PXRD patterns of the compound after dehydration–rehydration and exposing to different solvent vapors.

To the best of our knowledge this is the first reported porous Cu(I) metal–organic framework with coordinatively unsaturated sites showing single-crystal-to-single-crystal structural transformation and interesting vapour sorption property.

In conclusion, we have synthesized a novel extraordinarily stable Cu(I) MOF utilising DHFA as a reducing agent. The judicious choice of the pyzdc as a ligand produces a 3D framework of Cu(I) which has various interesting structural aspects. The framework is stable in the open atmosphere with a high thermal stability. Selective hysteretic water adsorption property has been correlated to the smaller size of the pore and the presence of coordinatively unsaturated Cu(I) centre. An analogous compound with a bigger pore and higher surface area may find some application as storage materials for ethylene, acetylene like gases.

Acknowledgements

S. M is thankful to CSIR, Government of India for the fellowship.

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