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Incorporation of active metal sites in MOFs *via in situ* generated ligand deficient metal–linker complexes†

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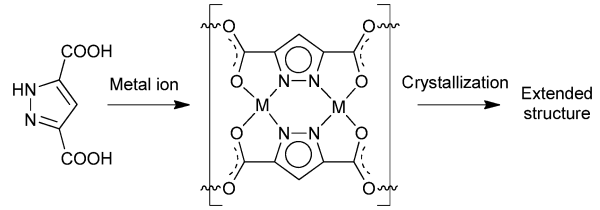
Two novel 3D MOFs, namely MOF-647A and MOF-648 (previously unknown trinodal 4-connected net), comprised of Cu ions and pyrazole-3,5-dicarboxylate were synthesized and characterized. A strategy for incorporating open metal sites in MOFs was investigated by utilizing an *in situ* generated metal–linker complex as a precursor to construct MOF-648.

Metal–organic frameworks (MOFs) were discovered to be among the most intriguing candidates for diversification of their inherent properties. Due to their fascinating topologies and pore size tunability,[1] the resultant nature of the MOFs such as high surface area and large pore volume is expected to be utilized in gas storage, separation and catalysis.[2] Since the properties of the pores could be varied by functionalization of the organic struts, it is believed that the incorporation of active sites in the framework could additionally open up promising avenues to enhance the storage and catalytic performance.[2] To this end, several procedures have been proposed: (i) creation of open metal sites by removing coordinated solvents[3] and (ii) postsynthetic metalation of MOFs having metal binding sites.[4] Although these are powerful techniques, there is still a limitation to such kinds of available species as well as difficulty in the preparation of organic linkers with metal binding sites. If one can prepare small metal–linker complexes as precursors and can connect them to build an extended structure (Scheme 1), the proposed frameworks would be replete with potential accessible metal sites (after removal of leaving groups). Keeping this in mind, we chose 1*H*-pyrazole-3,5-dicarboxylic acid as an organic linker with the ability to generate two types of binding moieties (*i.e.* carboxylate and pyrazole functionalities).



Scheme 1 The square unit (middle) can be utilized to form a MOF structure.

Indeed, there are many examples of pyrazole-bridged cyclic dinuclear complexes where two identical metals (like Cu^{2+}, Ni^{2+}, Pd^{2+}, Pt^{2+}, and V^{4+} ions) are bridged by this bifunctional unit.[5] These dinuclear complexes could act as squared bridging units enabling further extension of structural motifs. In general, utilization of square bridging ligands is expected to lead to the formation of a framework with numerous topologies such as **sql**, **cag**, **nbo**, and **cds** nets,[6] although the connectivity with the MOFs should be influenced by the coordinating capabilities of the central metal ions and the metal oxide cluster units.[7]

It is interesting to note that despite the multifunctional coordination ability of pyrazole-3,5-dicarboxylate, reports about transition metal based, non-hydrogen bonded, 3D structures are rare; furthermore, in some cases the framework was achieved by the use of pillar ligands.[5c–e,8] In this study we used Cu^{2+} as the metal source for the following reasons: (i) it can easily form dinuclear metallacycles and (ii) it has versatile coordination ability which might facilitate the formation of 3D structures. Here we describe the synthesis and structural characterization of MOF-647A ($[Cu_3(\mathbf{L})_2\cdot(DMF)_2(H_2O)_3]$), MOF-647B ($[Cu_3(\mathbf{L})_2\cdot(THF)_2\ (H_2O)_2]$) and MOF-648 ($[Cu_{12}(\mathbf{L})_8\cdot(DMF)_9]\cdot(DMF)_2(H_2O)_2$) (where **L** = pyrazole-3,5-dicarboxylate)‡ §[9] and the attempted activation of MOF-648, which has been constructed from the pyrazole-bridged cyclic dinuclear unit.

The preparation of the MOFs was conducted using $Cu(NO_3)_2\cdot 2.5H_2O$ and 1*H*-pyrazole-3,5-dicarboxylic acid in *N*,*N*-dimethylformamide (DMF). The solvent mixture of the two reagents was heated to 100 °C for 20 h, whereupon a mixture of MOF-647A and MOF-648 was obtained (ESI†, Section S2).[10] Single-crystal X-ray diffraction (SXRD) analysis revealed that MOF-647A is comprised of the basic trinuclear repeat unit $[Cu_3(\mathbf{L})_2\cdot(DMF)_2(H_2O)_3]^9$ (Fig. 1a) to form a doubly interpenetrated **dia** framework (Fig. 1b; Fig. S2 (ESI†)). All the

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† Electronic supplementary information (ESI) available: Full synthetic procedures and characterization data including TGA, IR, PXRD, N_2, H_2 and CO_2 isotherms and single crystal X-ray diffraction data. CCDC 829034–829036. For ESI and crystallographic data in CIF or other electronic format, see DOI: 10.1039/c1cc14387e

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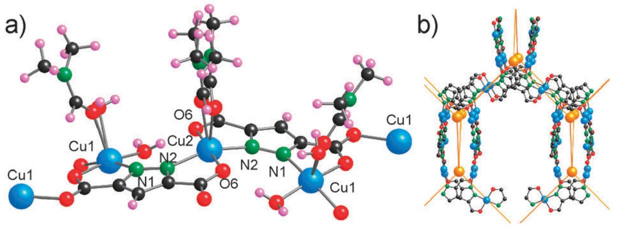

Fig. 1 (a) Part of the single crystal X-ray structure of MOF-647A, exhibiting the trinuclear repeating unit with selected atoms numbered. To simplify the 3D network (**dia** net) in MOF-647A, orange balls can be displaced (b) (Fig. S2, ESI†). Atom colors: Cu, aqua; O, red; C, black; N, green; H, pink.

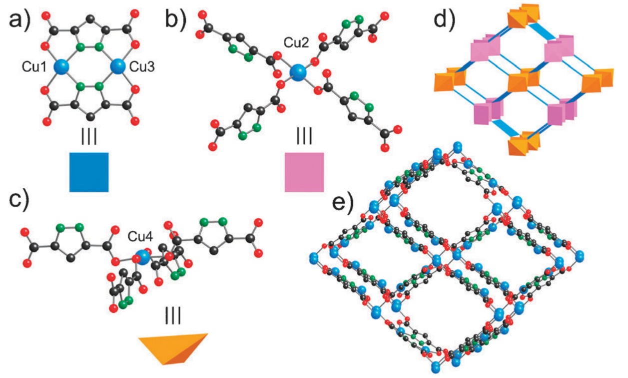

Fig. 2 The square planar nodes generated from a six membered bimetallacycle (a) are connected *via* Cu(2), which also act as square planar nodes (b), and Cu(4) (the tetrahedral nodes (c)) to compose a non-interpenetrated trinodal 4-connected net (d) in MOF-648. (e) Part of the X-ray single crystal structure of MOF-648 viewed down the crystallographic *b* axis. Atom colors: Cu, aqua; O, red; C, black; N, green. Coordinated and free guests and hydrogen atoms are omitted for clarity.

five-coordinated distorted square pyramidal Cu^{2+} ions of a trinuclear subunit are chelated by trianionic pyrazolate ligands. The central five-coordinated copper ion, Cu(2), lies on a crystallographic two-fold axis. Axial–equatorial carboxylate bridges between Cu(1) atoms of adjacent trimer units lead to formation of the extended 3D structure (Fig. S3, ESI†). The DMF guest of the as-prepared MOF-647A was exchanged with anhydrous THF to give $[Cu_3(\mathbf{L})_2\cdot(THF)_2(H_2O)_2]$ (MOF-647B). The formula was established based on SXRD, TGA and powder X-ray diffraction (PXRD) experiments (ESI†, Sections S2, S4 and S5).§ The analysis of the SXRD structure of MOF-647B provided evidence that the overall structural integrity was retained as MOF-647A with the exception of minor changes in the crystallographic parameters (Fig. S4 and Table S1, ESI†).

In our efforts to obtain single phase crystalline material of MOF-648 we inferred that the solvent to substrate ratio, as well as the metal to ligand stoichiometry, play an important role in the control of the self-assembly. Indeed, performing the solvothermal reaction using the metal to ligand ratio of 2 : 1 under dilute conditions yielded phase pure crystals of MOF-648 (ESI†, Section S2).[10] The SXRD analysis revealed formation of the bimetallacyclic Cu_2N_4 ring (Fig. 2a) where the center-to-center distance between the two Cu^{2+} ions (*i.e.* Cu(1) and Cu(3)) is 3.99 Å. Both Cu ions are doubly chelated by two pyrazole ligands to form distorted squares (Scheme 1), and in addition one or two DMF molecules are coordinated to Cu(1) and Cu(3), respectively (Fig. S5, ESI†). In the overall 3D structural connectivity, the bimetallic square unit ($Cu_2\mathbf{L}_2$) (essentially acting as 4-connected square planar nodes) is connected to the adjacent squares *via* coordination to Cu(2) (which also acted as 4-connected square planar nodes (Fig. 2b)) and Cu(4) (acts as a tetrahedral node (Fig. 2c)) to establish the trinodal 4-connected network structure. To comprehend the network connectivity of MOF-648 requires more than routine attention and can be described as a novel trinodal 4-connected net (**sbr**) having the minimum number of kinds of edge (2) for the trinodal net (Fig. 2d; Fig. S6, ESI†).

MOF-648 possesses two nearly rhombic channels along the crystallographic *b* axis, whose diameters without contacting the interior van der Waals surface are approximately 6.4 Å (Fig. 2e). The free channels are occluded by guest coordinated and non-coordinated DMF and H_2O molecules. If the occluded and coordinated guests are removed, the accessible void space is estimated to be 66%. To access the porous structure with evenly distributed open metal sites, as-prepared crystals of MOF-648 were soaked in anhydrous acetone for 3 days, during which the activation solvent was decanted and freshly replenished three times. Unfortunately, the PXRD data indicate that our attempts to evacuate the pore, followed by a heat treatment (up to 80 °C) of the acetone exchanged sample, lead to structural decomposition (Fig. S10, ESI†). Indeed, N_2 and H_2 isotherms did not show meaningful uptake in the low-pressure range, probably due to the loss of microporosity. To mitigate the structural collapse, supercritical CO_2 activation (SCD) was performed using the acetone-exchanged material.[2d] The activation of the acetone exchanged MOF-648 at 45 °C for 24 h following SCD allowed us to remove the free guests.

The N_2 uptake in the low-pressure region at 77 K was still low, and the BET surface area was determined to be 26 m^2 g^{-1}. Surprisingly, the uptake started to increase at around P/P_0 = 0.05 and a large hysteresis loop was observed (Fig. S17, ESI†). If we use a desorption branch for the estimation, the Langmuir surface area can be calculated to be 690 m^2 g^{-1}. The reason for the hysteresis is not well understood; however, it can probably be attributable to structural transformation as confirmed by the PXRD measurements (Fig. S11, ESI†). Although we were unable to determine the cell parameters of the activated MOF-648 owing to the low resolution of the PXRD pattern, it is likely that the framework was compressed along the crystallographic *c*-axis (Fig. S12, ESI†). In such a scenario, the expected pore diameter should be smaller than 5 Å, even if all guests are removed from the pore, which can be responsible for the significant hysteresis in the N_2 isotherm. However, it is unlikely that the pore shape was fully re-expanded by the adsorption of N_2, because the N_2 uptake is only half the expected value if the pore is fully evacuated. In addition, the PXRD pattern of the resolvated sample deviates significantly from either the original or the activated MOF-648 structures (Fig. S13, ESI†), which may indicate that the framework is not flexible enough to allow a reversible structural transformation as demonstrated with MIL-53.[11]

We also recorded the H_2 and CO_2 isotherms because the kinetic diameter of these gases is smaller than that of N_2;[2h] however, the H_2 uptake (12 cm^3 g^{-1}, Fig. S18, ESI†) by the

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activated MOF-648 at 77 K and 800 torr was close to that of N_2 at $P/P_0 = 0.05$, which is even smaller than that of another MOF with a similar pore volume.[12] This indicates that only a limited number of H_2 molecules can diffuse into the pores. Interestingly, the activated MOF-648 can take up an appreciable amount of CO_2 at 298 K (Fig. S19, ESI†) and the value is comparable to another MOF having a similar pore volume.[12] Considering that CO_2 generally has a larger adsorption enthalpy than H_2 and N_2, the released heat can be compensated to obtain the energy to diffuse into the pores.

In conclusion, the given conceptually new approach for incorporation of active metal sites in MOFs could be investigated *via* the formation of $[Cu_{12}(\mathbf{L})_8{\cdot}(DMF)_9]{\cdot}(DMF)_2(H_2O)_2$ (MOF-648). The highly open framework of MOF-648 might become a prototype, from which numerous new MOFs having potentially accessible metal sites can be derived.

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Notes and references

‡ MOF-647A: $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.276 g, 1.15 mmol) and 1*H*-pyrazole-3,5-dicarboxylic acid (0.072 g, 0.415 mmol) were dissolved in 8 mL of DMF in a 20 mL glass vial. After capping tightly, the vials were heated to 75 °C at a rate of 2 °C min^{-1} for 48 h in an isothermal oven. The vials, containing thin plate blue crystals, were removed from the mother liquor and washed with DMF (3 × 5 mL).

MOF-648: $Cu(NO_3)_2{\cdot}2.5H_2O$ (0.11 g, 0.57 mmol) and 1*H*-pyrazole-3,5-dicarboxylic acid (0.050 g, 0.28 mmol) were dissolved in 20 mL of DMF in a 50 mL glass vial. After capping tightly, the vials were heated to 100 °C at a rate of 1 °C min^{-1} for 12 h in an isothermal oven. The vials, containing dark blue-green block crystals, were removed from the mother liquor and washed with DMF (3 × 5 mL).

§ Crystal data for MOF-647A: $C_{15.71}H_{21.51}Cu_3N_{5.9}O_{13}$, tetragonal, space group $I4_1/acd$, a = 17.6342(6), b = 17.6342(6), c = 33.4999(11) Å, $\alpha = \beta = \gamma = 90°$, V = 10417.3(6) $Å^3$, Z = 16, d_{calcd} = 1.762 Mg m^{-3}, crystal size 0.13 × 0.09 × 0.05 mm^3, T = 153(2) K, λ = 0.71073 Å, R_1 = 0.0399 [$I > 2\sigma(I)$], wR_2 = 0.0930 (all data, 24 570 reflections), R_{int} = 0.1413, GOF = 0.738. Crystal data for MOF-647B: $C_{73}H_{85}Cu_{12}N_{27}O_{45}$, orthorhombic, space group $Pbcm$, a = 15.3345(1), b = 14.5465(1), c = 26.2229(3) Å, $\alpha = \beta = \gamma = 90°$, V = 5849.37(9) $Å^3$, Z = 2, d_{calcd} = 1.603 Mg m^{-3}, crystal size 0.34 × 0.23 × 0.17 mm^3, T = 153(2) K, λ = 0.71073 Å, R_1 = 0.0535 [$I > 2\sigma(I)$], wR_2 = 0.1820 (all data, 87 527 reflections), R_{int} = 0.0721, GOF = 1.037. MOF-648: $C_{18}H_{22}Cu_3N_4O_{12}$, tetragonal, space group $I4_1/acd$, a = 17.1637(5), b = 17.1637(5), c = 34.0665(6) Å, $\alpha = \beta = \gamma = 90°$, V = 10 035.7(5) $Å^3$, Z = 16, d_{calcd} = 1.792 Mg m^{-3}, crystal size 0.19 × 0.10 × 0.04 mm^3, T = 183(2) K, λ = 0.71073 Å, R_1 = 0.0731 [$I > 2\sigma(I)$], wR_2 = 0.2363 (all data, 11 076 reflections), R_{int} = 0.0433, GOF = 0.921.

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9 For simplicity the crystallographic formula of MOF-647A, $[Cu_3(\mathbf{L})_2{\cdot}(DMF)_{1.9}(H_2O)_{3.1}]$, is represented as $[Cu_3(\mathbf{L})_2{\cdot}(DMF)_2(H_2O)_3]$.

10 Microanalysis for MOF-647A, $[Cu_3(\mathbf{L})_2{\cdot}(DMF)_{1.9}(H_2O)_{3.1}]$, calcd: C, 27.28; H, 3.13; N, 11.95%. Found: C, 26.8; H, 3.28; N, 11.5%. For MOF-648,$[Cu_{12}(\mathbf{L})_8{\cdot}(DMF)_9]{\cdot}(DMF)_2(H_2O)_2$, calcd: C, 31.04; H, 3.03; N, 13.40%. Found: C, 30.1; H, 3.9; N, 13.36%.

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