Large H_2 storage capacity of a new polyhedron-based metal–organic framework with high thermal and hygroscopic stability†

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Two metal–organic frameworks (MOFs) based on metal–organic cuboctahedra were prepared using a rigid C_3 symmetric ligand, where Zn polyhedron-based MOF (PMOF-2(Zn)) did not show any significant gas sorption behavior, whereas the isostructural Cu polyhedron-based MOF (PMOF-2(Cu)) showed a large surface area of ~4180 $m^2\ g^{-1}$, high hydrothermal stability, and very promising H_2 sorption properties.

Development of an on-board hydrogen storage system is one of the key technologies needed for transportation application based on fuel cells. Porous metal–organic frameworks (MOFs) with large surface area have received the attentions of researchers for their potential as hydrogen storage materials.[1] Currently the highest material-based gravimetric and volumetric excess H_2 uptake values reported for MOF-177[2] at 77 K are 7.5 wt% and 43.9 g L^{-1}, respectively. However, these storage capacities are material-based but not system-level, and the MOFs are not stable enough at hygroscopic conditions. The storage capacities and the stabilities of the MOFs still need to be improved. For high H_2 uptakes, the high surface area of the frameworks is the single factor of utmost importance. The pore size/geometry and the presence of strongly interacting functional groups, such as exposed metal sites in high site density, also play important roles in high H_2 uptake.[3]

MOFs based on metal–organic polyhedra (MOP) have been demonstrated to be very effective for the construction of the MOFs of high surface areas and large H_2 storage capacities.[4–6] In this study we synthesized two isostructural MOP-based MOFs (PMOFs) using a C_3 symmetric hexacarboxylic ligand, 1,3,5-tris(3,5-dicarboxylphenylethynyl)benzene (H_6L), containing three 3,5-benzenedicarboxylate (bdc) units well known as a primary building unit for the construction of a paddle-wheel-based edge-directed corner-linked metal–organic cuboctahedron (MOC) with potential exposed metal sites.[3b–f,7] The introduction of a sterically less demanding but rigid 1,3,5-triethynylbenzene group in the ligand could lead to the formation of a highly porous and rigid PMOF, where the MOCs could be covalently linked in triangular arrangement for a close packed structure (Scheme S1, ESI†).

The solvothermal reaction of $Zn(NO_3)\cdot 6H_2O$ with the ligand in *N*,*N*′-dimethylformamide (DMF) led to cube-shaped colorless crystals that could be analyzed by single crystal X-ray diffraction analysis.‡ The crystal structure of $[Zn_{24}L_8(H_2O)_{12}]$, **1** (PMOF-2(Zn), Fig. 1 and Fig. S1, ESI†), was isoreticular with the reported structure prepared using a C_3-symmetric hexacarboxylic ligand, 5,5′,5″-[1,3,5-benzenetriyltris(carbonylimino)]tris-1,3-benzenedicarboxylic acid.[7]

The bdc moieties in **1** were involved in the formation of MOCs with a cavity of ~1.2 nm in diameter (Fig. 1 and Fig. S1a, ESI†), which in turn were interconnected *via* quadruple covalent linkages to a cubic close-packing arrangement (Fig. S2, ESI†). This in turn led to the formation of two different kinds of supercages, one face-directed edge-linked superoctahedron (Fig. 1 and Fig. S1b, ESI†) having a cavity of ~2.0 nm in diameter, and another supertetrahedron (Fig. 1 and Fig. S1c, ESI†) having a cavity of ~1.4 nm in diameter. The cavities of these three cages were interconnected through three different windows of triangular (~3.7 Å in

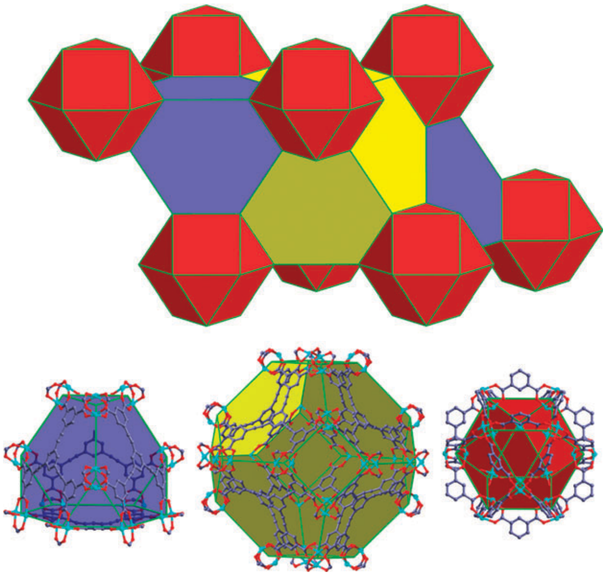

Fig. 1 A schematic packing diagram of PMOF-2(Zn), where cuboctahedra (red polyhedra) are interconnected to a cubic close packing arrangement, which leads to the generation of two different types of supercages, superoctahedra (yellow polyhedra) and supertetrahedra (blue polyhedra).

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diameter), square (~6.6 Å in diameter) and rectangular shape (5.5 × 7.4 Å^2), respectively (Fig. S3, ESI†). These interconnections of the three different types of pores lead to a PMOF with 3D porosity. Although the MOCs were in the cubic close packing arrangement in the framework, the total solvent cavity volume of the framework **1** was extremely large, 59 607 Å^3 per unit cell (*i.e.* 75.7% of the total unit cell volume, where all the solvent, including the ligated solvent molecules were excluded from the framework for the solvent cavity volume calculation). The presence of the sterically non-demanding but rigid 1,3,5-triethynylphenyl group in the ligand probably renders such a large solvent cavity in the framework.

The copper analogue of **1**, [$Cu_{24}L_8(H_2O)_{24}$] **2** (PMOF-2(Cu)), could also be obtained in a crystalline form under very similar reaction conditions. A solvothermal reaction of $Cu(NO_3)_2{\cdot}3H_2O$ and H_6L in DMF in the presence of a small amount of HCl forms crystalline material **2** (see ESI†). X-Ray diffraction analysis of a single crystal revealed that the copper analogue is isostructural with PMOF-2(Zn), the only difference being the replacement of zinc metal ions in **1** with copper metal ions in **2**.‡

The similarity of the powder X-ray diffraction (PXRD) pattern of the freshly harvested bulk sample of **1** with that simulated from the single-crystal structure of **1** indicated that the single crystal is representative of the bulk sample (Fig. 2). **1a**, which was prepared by soaking **1** in DMF, methylene chloride, and then vacuum-drying overnight at ambient temperature, showed significant reduction in peak intensity. The PXRD pattern of the freshly harvested **2** was also very similar with that simulated from the single crystal structure of **2**. The sharp PXRD pattern of sample **2a**, which was prepared by soaking **2** in DMF for 2 days, in methanol for 2 days, and then vacuum-drying overnight at 150 °C, indicated the high thermal stability of the framework in contrast to that of **1**. The variable-temperature PXRD (VT PXRD) of PMOF-2(Cu) (Fig. S4, ESI†) also indicated the high thermal stability of the framework up to 250 °C, and the framework decomposed around 300 °C. The PXRD pattern of sample **2b**, which was further soaked in water overnight and dried at ambient temperature, indicated the complete loss of crystallinity. However, sample **2c**, which was further soaked in DMF overnight, completely recovered its crystallinity when the sample was reactivated by vacuum-drying at 150 °C overnight. PMOF-2(Cu) is even stable at hygroscopic conditions and could be recovered to its original state by the activation.

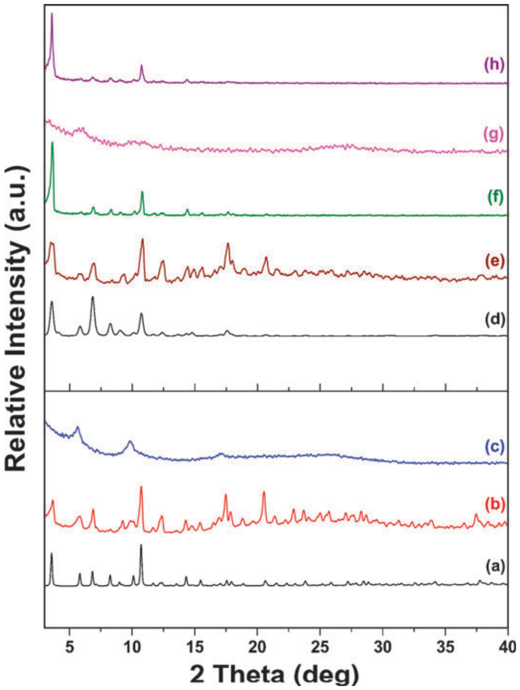

Fig. 2 PXRD patterns of MOFs. (a) A simulated PXRD pattern from the single-crystal structure of **1**, (b) **1**, as-synthesized, (c) **1a**, wet-ground in DMF, then vacuum-dried at ambient temperature overnight. (d) A simulated PXRD pattern from the single-crystal structure of **2**, (e) **2**, as-synthesized, (f) **2a**, wet-ground in DMA, then vacuum-dried at 150 °C overnight, (g) **2b**, soaked in water overnight, then dried at ambient temperature, (h) **2c**, prepared by soaking **2a** in water overnight, in DMA overnight, then vacuum-drying at 150 °C overnight.

Because the PXRD of the activated sample **1a** indicated some degree of crystallinity, **1a** was subjected to gas adsorption using N_2 and H_2 at 77 K. The estimated Brunauer–Emmett–Teller (BET) surface area from the N_2 sorption isotherm, 72 m^2 g^{-1}, and the H_2 uptake, 0.2 wt% at 77 K and 1 atm, were much smaller than the plausible values expected from the solvent cavity size of the single crystal structure of PMOF-2(Zn) (Fig. S5†). These poor sorption behaviors might come from inappropriate treatment of the framework. Despite extensive efforts, we have not yet succeeded finding the appropriate activation conditions for gas sorption on **1**.

PMOF-2(Cu) was also subjected to gas adsorption using N_2 and H_2. The N_2 sorption isotherm on **2a** at 77 K is presented in Fig. 3. The adsorbed N_2 amount was approximately 960 mL g^{-1} (at STP) and the estimated Langmuir surface area was ~4180 m^2 g^{-1} (estimated BET surface area ~3730 m^2 g^{-1}), which was smaller than the highest reported value for MIL-101 (~5900 m^2 g^{-1})^{1i} or MOF-177 (~5250 m^2 g^{-1} by gravimetric measurement and ~5640 m^2 g^{-1} by volumetric

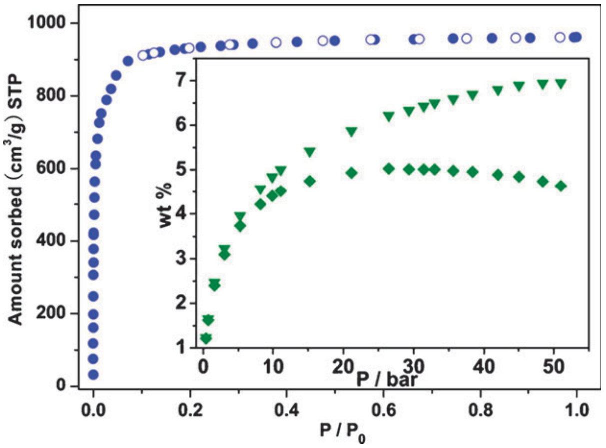

Fig. 3 N_2 sorption isotherm on **2a** at 77 K. (inset) High-pressure H_2 sorption isotherms on **2a** at 77 K, where blue filled and open circles represent N_2 adsorption and desorption isotherms, respectively, and green filled triangles and rhomboids represent the total and excess H_2 sorption capacities, respectively.

measurement),[2] but was comparable to that of MOF5 (~4400 $m^2 g^{-1}$).[8]

The H_2 uptake of PMOF-2(Cu) obtained using a volumetric sorption measurement method was 2.29 wt% at 77 K and 1 atm. The isosteric heat of adsorption of PMOF-2(Cu) was calculated using a modified version of the Clausius–Clapeyron equation by fitting a second H_2 adsorption isotherm at 87 K (Fig. S6a and S6b†).[9] The initial isosteric heat of adsorption at 0.02 wt% H_2 loading on **2a**, 9.2 kJ mol^{-1}, decreased to 5.0 kJ mol^{-1} at a loading of 1.46 wt% H_2. This range of the isosteric heat of adsorption was similar to other MOFs having exposed metal sites in similar Cu(II) paddle-wheel units.[10] A high-pressure H_2 sorption study was performed on **2a** using the volumetric measurement method. The inset of Fig. 3 shows the excess and total H_2 adsorption isotherms at 77 K. The excess gravimetric H_2 adsorption capacity of **2a** reached its maximum value of 5.0 wt% around 30 bar and the total gravimetric H_2 uptake was 7.0 wt% at 50 bar, values that were smaller than those of MOF-5 with a similar surface area. The corresponding total volumetric H_2 uptake of **2a**, 39.2 g L^{-1}, is also smaller than that of MOF-5. This reduced efficiency of PMOF-2(Cu) for H_2 uptake might come from the large average cavity diameter of the MOF[11] and/or the incomplete removal of the non-reacted or partially reacted reactants in the pores.§

In conclusion, we prepared two isostructural MOFs based on covalently interconnected metal–organic cuboctahedra. Although the structural elements resembled one another, the stability and sorption behaviors of the MOFs were completely different. The framework of PMOF-2(Zn) was not stable when the sample was activated. When the solvents in the cavity were removed, its N_2 sorption and the corresponding surface area were very small, probably because of the collapse of the cavity caused by the instability of the Zn(II) paddle-wheel secondary building unit. In contrast, the framework of PMOF-2(Cu) was stable up to 250 °C. The N_2 sorption study of the activated sample of PMOF-2(Cu) revealed extremely large BET and Langmuir surface areas, ~3730 and ~4180 $m^2 g^{-1}$, respectively. The framework with exposed metal sites was thermally and hygroscopically stable and showed high adsorption enthalpy. PMOF-2(Cu) is a new type of MOF having very interesting H_2 sorption properties. Further studies on the sorption behaviors of this MOF are currently in progress.

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Notes and references

‡ *Crystal data* for **1**: $Zn_{24}C_{288}H_{144}O_{120}$: M = 7092.91, cubic, space group $Fm\bar{3}m$, a = 42.854(5), V = 78 699(16) Å^3, T = 100(2) K, Z = 4, μ(synchrotron, λ = 0.77489 Å) = 0.752 mm^{-1}, 147 398 reflections were collected of which 4347 were unique (R_{int} = 0.0576). $R1$ ($wR2$) = 0.0653 (0.2344) for 3890 reflections [$I > 2\sigma(I)$], $R1$ ($wR2$) = 0.0699 (0.2434) for all 4347 reflections. *Crystal data* for **2**: $Cu_{24}C_{288}H_{144}O_{120}$: M = 7048.99, cubic, space group $Fm\bar{3}m$, a = 42.833(3) Å, V = 78 583(10) Å^3, T = 173(2) K, Z = 4, μ(Mo-Kα, λ = 0.71073 Å) = 0.670 mm^{-1}, 95 044 reflections were collected of which 3375 were unique (R_{int} = 0.1675). R_1 (wR_2) = 0.0944 (0.1721) for 2860 reflections [$I > 2\sigma(I)$], R_1(wR_2) = 0.1228 (0.1846) for all 3375 reflections.

§ The IR spectrum of **2a** (Fig. S7†) indicates the presence of some carboxylic acid in the activated sample. We could not succeed in removing this carboxylic acid from the framework even though the sample was extensively washed and/or soaked using various organic solvents.

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