Volume 1 | Number 1 | Jan 2013 | Pages 1–100

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Enhanced water stability of a microporous acylamide-functionalized Metal-Organic Framework via interpenetration and methyl decoration†

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A microporous acylamide-functionalized MOF with 2-fold interpenetrated and methyl decorated framework (HNUST-4) has been designed and synthesized from $[Cu_2(COO)_4]$ motifs
10 **and a C_2-symmetric acylamide-linking tetracarboxylate, which exhibits good water stability, permanent porosity, high and selective CO_2 uptake at ambient temperature.**

Metal−organic frameworks (MOFs) have become a leading class of porous crystalline materials for potential applications
15 in gas storage[1], gas separation[2] and catalysis[3]. These applications mainly hinge on two important properties of MOFs: porosity and stability. Currently, remarkable breakthroughs in the construction of MOFs with ultrahigh porosity have been reported and several landmark MOFs
20 display large experimental BET surface area with values exceeding 5000 m^2/g.[4] However, most of such highly porous MOFs are not robust enough and prone to collapse at humid environments, which greatly hinders their practical gas storage/separation applications. Thus, how to design and
25 address porous materials with high hydrostability is one of the key challenges we now face in MOF chemistry, and several strategies are envisaged to achieve this goal: (i) strengthening the metal-ligand coordination bonds by judicious choice of metal ions/clusters and organic ligands (e.g. high oxidation
30 state metals such as Fe^{3+}, Cr^{3+}, Al^{3+} and Zr^{4+}, etc for carboxylate-based MOFs[5] and nitrogen-containing linkers such as pyrazole, imidazole and pyridyl-carboxylate, etc for transition-metal based MOFs or ZIFs[6]); (ii) utilizing interpenetration or catenation[7] to narrow the pore size; (iii)
35 doping hybrid composites (e.g. carbon nanotubes, hetero-metal) to the frameworks[8] and (iv) decorating the pores by

hydrophobic groups (e.g. methyl, ethyl ester, etc).[9]

In pursuing new high-performance gas storage/separation materials, we are specially interested in the design and
40 construction of porous MOFs from large multidentate carboxylate ligands with linking polar functional groups (e.g. acylamide, oxalamide, etc.) and dicopper(II) paddlewheel cluster, because such an approach may facilitate the generation of expanded MOFs with high surface area, open
45 copper sites and pre-designed polar functionalities that are all beneficial to improve the gas (especially for CO_2) adsorption and separation property of materials.[10] To extend our research in this area, herein we report a novel 2-interpenetrated microporous acylamide-functionalized MOF decorated by
50 methyl groups, termed HNUST-4 (HNUST denotes Hunan Univeristy of Science and Technology), designed from a nanosized flexible tetracarboxylate 5,5'-[(5-methyl-1,3-phenylene)bis(carbonylimino)]diisophthalic acid (MPBD). Interestingly, HNUST-4 represents a rare example of water-
55 stable MOFs constructed from paddlewheel SBUs and pure carboxylate ligands, its crystallinity can be sustained even after immersion in boiling water for a day. In addition, HNUST-4 exhibits a moderate BET surface area of 1136 $m^2 \cdot g^{-1}$, high and selective CO_2 uptake at ambient temperature.

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† Electronic supplementary information (ESI) available: Experimental details, TGA plots, heat adsorption of H_2, CO_2 and CH_4, sorption selectivity calculations. CCDC 1006012. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b000000x/
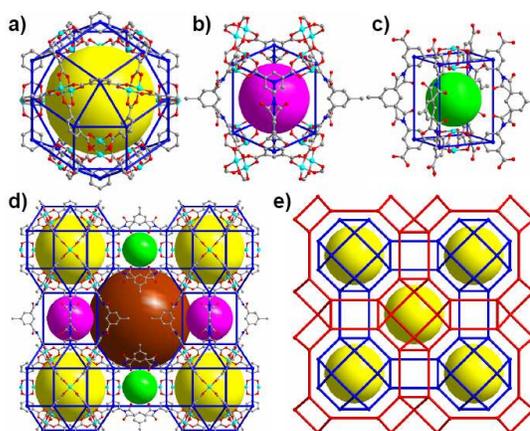

60 **Fig. 1** The crystal structure of HNUST-4. a-c) different cages in the crystal structure; d-e) single and 2-interpenetrated network viewed from *b* and *c* axis, respectively. Cu, blue-green; C, black; O, red; N, blue. Water molecules and H atoms have been omitted for clarity.

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Solvothermal reaction of MPBD and $Cu(NO_3)_2 \cdot 3H_2O$ in DMF/ethanol/H_2O (5:3:2 in volume) at 75 °C for 48 hours afforded pale blue block crystals of HNUST-4. HNUST-4 crystallizes in space group *I4/mmm* and the framework consists of $[Cu_2(COO)_4]$ paddlewheels linked by $MPBD^{4-}$ ligands. $MPBD^{4-}$ exhibits two crystallographically independent conformations (*syn*- and *anti*-) and the carbonyl moiety of acylamide group is disordered over two positions with equal probability (Fig. S1). Similar to the isostructural PMOF-3 and analogues[11], the overall structure of HNUST-4 exhibits 2-fold interpenetration and each single framework can be viewed as the packing of three types of cages in 3D space (Fig. 1a-c): Cage A is a cuboctahedron composed of twenty-four isophthalate units and twelve paddlewheels with a diameter of 1.2 nm. Cage B, a tetragonal prismatic junction-like cage about 1.3 nm in diameter, is formed from four paddlewheels and four *anti*-$MPBD^{4-}$ linkers. Cage C is also a tetragonal prismatic junction-like cage of about 0.8 nm diameter, surrounded by four *syn*-$MPBD^{4-}$ and two paddlewheels. Each cage A is connected to six neighboring cages A via two cages B and four cages C to form a 3D framework with a simple cubic network topology, in which there exists large 1D rounded-like channel along the *c* axis with a diameter of about 3.0 nm (Fig. S1). Notably, this channel is further filled by cage A from the other interpenetrating framework due to the large void sapce, despite that the channel has been occupied by methyl groups, resulting in a 2-fold interpenetrated structure (Fig. 1e) of HNUST-4 with a total potential solvent accessible volume of about 53.6 % upon removal of guest molecules calculated by PLATON[12].
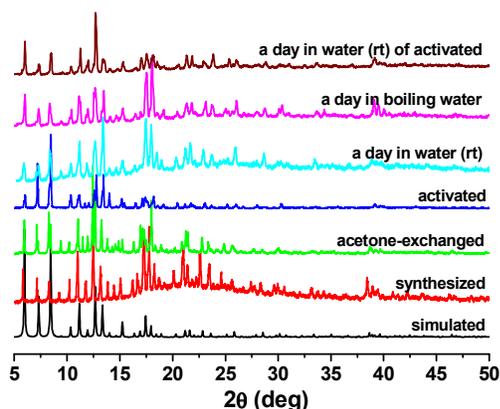

Fig. 2   Powder X-ray diffraction patterns of HNUST-4, showing the framework stability upon treatment at different conditions.

To assess the framework stability of HNUST-4, both the thermogravimetric analysis (TGA) and powder X-ray diffraction (PXRD) measurements have been performed. The TGA curve indicates that HNUST-4 can be thermally stable up to 300 °C (Fig. S3). In addition, as shown in Fig. 2, the PXRD patterns of HNUST-4 demonstrate that the single crystal is representative of the pure bulk sample, and the framework can be retained after removal of guest molecules. Most interestingly, HNUST-4 exhibits good water stablity and

the as-synthesized sample can sustain its crystallinity even when immersed in boiling water for a day. Furthermore, the desolvated HNUST-4, which can be obtained by heating the acetone-exchanged sample under high vacuum at 100 °C for 12 h, also demonstrates framework stability after treatment in water at room temperature. To the best of our knowledge, HNUST-4 thus represents the second example of water stable acylamide-functionalized MOFs constructed from paddlewheel SBUs and pure carboxylate ligands. Another instance, PCN-124 with a self-interpenetrated (3, 36)-connected 3D structure recently reported by Zhou group[7b], also shows moderate water stability at room temperature. The excellent hydrostability of HNUST-4 may be attributed to the interpenetrated framework and incorporated hydrophobic methyl groups, both factors are believed to can effectively enhance the hydrostability of MOFs.[7,9]
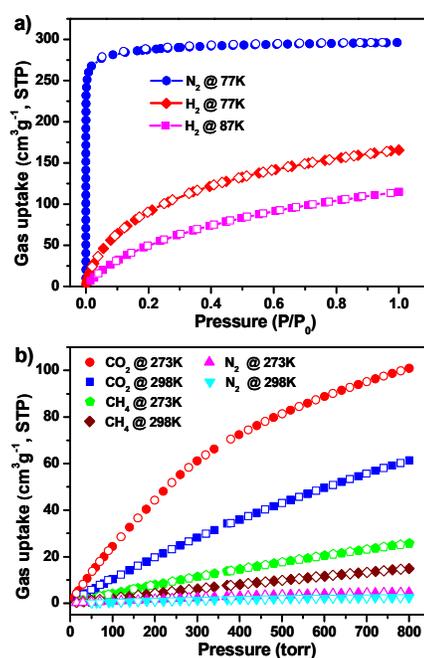

Fig. 3 Gas sorption isotherms of HNUST-4 up to 1 bar at different temperatures.

The permanent porosity of desolvated HNUST-4 was examined via low-pressure N_2 adsorption measurements at 77 K. HNUST-4 shows completely reversible type-I adsorption behavior, characteristic of microporous materials with the high limiting N_2 uptakes of 296 cm^3 g^{-1} (Fig. 3a). The estimated apparent Brunauer–Emmett–Teller (BET) surface area is 1136 m^2 g^{-1} (Langmuir surface area ~ 1284 m^2 g^{-1}) and the total pore volume is 0.458 cm^3 g^{-1}, which is comparable to the theoretically total framework pore volume (0.536 cm^3 g^{-1}) calculated by PLATON. In addition, HNUST-4 possesses a pore-size distribution with the pore sizes centered at 8.6, 9.3 and 11.8 Å, respectively (Fig. S5), consistent with the single crystal data.

The permanent porosity, open copper sites and acylamide functional groups within the hydrostable framework of HNUST-4 prompted us to study its gas adsorption performance, especially that for CO_2 capture and separation (CCS). Thus, low-pressure H_2,

CO_2, CH_4 and N_2 sorption isotherms of HNUST-4 at different temperatures have been measured (Fig. 3). All isotherms are fully reversible and HNUST-4 can adsorb 1.52 and 1.02 wt% (170.3 and 114.6 cm^3 g^{-1}) at 77 and 87 K (1 bar) without saturation, respectively, which is quite close to the performance of MOFs PCN-6′ (1.37 wt %)[13a] and HKUST-1 (1.44 wt %)[13b] at 77 K and 1 bar. Based on the adsorption isotherms measured at 77 K and 87 K, the zero coverage H_2 adsorption enthalpy (Q_{st}) of HNUST-4 is calculated to be 7.0 kJ mol^{-1} by the virial method (Fig. S6), comparable with those of MOFs with exposed metal sites.[14] Noticeably, HNUST-4 exhibits high CO_2 uptakes of 100.9 and 62.9 cm^3 g^{-1} under 1 bar at 273 and 298 K, respectively. This CO_2 storage capacity is lower than those of other acylamide-functionalized MOFs such as HNUST-1[10c] (156.4 cm^3 g^{-1} at 273 K and 1 bar), HNUST-3[10d] (168.7 cm^3 g^{-1} at 273 K and 1 bar) and PCN-124[7b] (204 cm^3 g^{-1} at 273 K and 1 bar) owing to the relatively low BET surface area, but fairly comparable to that of SUN-50[15a] (106 cm^3 g^{-1} at 273 K and 1 bar) and PCN-124 analogue Cu_2L[15b] [63.5 cm^3 g^{-1} at 298 K and 1 bar, L = 3,5-bis(3,5-dicarboxyphenylethynyl) pyridine], and quite larger than that of the best performing ZIF material ZIF-20[15c-d] (69.8 cm^3 g^{-1} at 273 K and 1 bar). In sharp contrast to CO_2, HNUST-4 can only uptake limited amounts of CH_4 (24.7 and 14.3 cm^3 g^{-1}) and N_2 (4.4 and 2.5 m^3 g^{-1}) under 1 bar at 273 and 298 K, indicating that HNUST-4 has the ability to selectively adsorb CO_2 over CH_4 and N_2. The CO_2/CH_4 and CO_2/N_2 adsorption selectivities calculated from the slopes of the isotherms reach up to 6.3 and 29.9 at 273 K, respectively (the values still reach 4.9 and 20.6 at 298 K, Fig. S7), much higher than the corresponding values of most MOFs with high surface area (mainly in the ranges of 3−10 and 10−50 for CO_2/CH_4 and CO_2/N_2 selectivity at 298 K).[16]

To better understand these observations, the coverage-dependent Q_{st} of HNUST-4 to CO_2 and CH_4 were also calculated by the virial method, from fits of the adsorption isotherms collected at 273 and 298 K. As shown in Fig. S6, the Q_{st} of CO_2 is 27.2 kJ mol^{-1} at the zero coverage, which compares well with the reported data for other acylamide-functionalized MOFs such as $[Cu_{24}(TPBTM^{6-})_8]$ (26.3 kJ mol^{-1})[9a], indicating a strong interaction between CO_2 and HNUST-4. As for CH_4, HNUST-4 exhibits a lower Q_{st} value (18.5 kJ mol^{-1}) at zero coverage. The excellent CO_2 adsorption behaviour of HNUST-4 may be attributed to the large dipole moment of the -CONH- groups, which may facilitate strong dipole-quadrupole interactions between the acylamide groups within HNUST-4 and CO_2.

In summary, by utilizing a nanosized acylamide-bridging tetracarboxylate (MPBD) as the linker and a copper(II) paddlewheel as the SBU, we have successfully designed and constructed a new microporous acylamide-functionalized MOF (HNUST-4). HNUST-4 possesses 2-fold interpenetrated structure with decorated methyl groups, exhibiting good water-stability, a moderate BET surface area of 1136 m^2 g^{-1}, high CO_2 uptake capacity (100.9 and 62.9 cm^3 g^{-1} under 1 bar at 273 and 298 K), as well as excellent CO_2/CH_4 and CO_2/N_2 selectivity at ambient temperature. This work demonstrates that the strategy of interpenetration together with hydrophobic methyl decoration is an effective method to enhance the hydrostability of MOF materials. Ongoing investigations are addressing such water stable acylamide-functionalized MOFs with even higher surface area and pore volume by using larger linkers or highly connected SBUs to further improve the CO_2 uptake and separation property.

Notes and references

‡ Crystal data for HNUST-4: $C_{75}H_{38}N_6O_{36}Cu_6$ (guest molecules removed with PLATON SQUEEZE[12]), M_r = 1980.41, Tetragonal, *I4-mmm*, $a = b$ = 29.627(3) Å, c = 29.627 Å, $\alpha = \beta = \gamma = 90°$, V = 26005(4) Å^3, Z = 8, D_c = 1.012 g cm^{-3}, T = 293(2) K, GOF = 1.199 based on F^2, final R_1 = 0.0958, wR_2 = 0.3059 [for 6539 data $I > 2\sigma(I)$]; CCDC: 1006012.

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