Rational assembly of a 3D metal–organic framework for gas adsorption with predesigned cubic building blocks and 1D open channels†

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A novel 3D metal-organic framework with predesigned cubic building blocks and 1D open channels exhibiting significant N_2 adsorption has been synthesized and characterized by single crystal X-ray diffraction analysis.

Open metal–organic frameworks (MOFs) are widely regarded as promising materials for many applications, such as catalysis, separation, gas storage, sensing, magnetism and ion exchange.[1–6] Compared to conventionally used microporous inorganic materials such as zeolites, these organic structures have the potential for more flexible rational design, through control of the architecture and functionalization of the pores. In particular, those ordered porous materials are capable of selective sorption of a certain gas which would be useful in sensing and separating the gas.[7,8] However, especially as a new gas storage material, MOFs are still confronted with the difficulty of a general lack of control over the character of the solids produced from traditional synthetic methods, which is directly related to the fact that the starting entities do not maintain their structures during the reaction, leading to poor correlation between reactants and products. In addition, the target with a large channel is fraught with difficulties during synthesis, including the presence of counter-anions in the channels, the need to readily form an interpenetrating network, and the disruption of the channel network upon removal of the guest molecules.

Therefore, the development of rational synthetic routes for the construction of structurally well-defined solids is the most significant point for the creation of porous MOF compounds. An emerging approach in the rational assembly of networks is through the use of secondary building blocks, which are most commonly metal-containing aggregates that dictate the direction of polymer extension.[1,4,9] The use of secondary building blocks is attractive in part because of their steric requirements and rigidity, which dramatically reduce the number of possible network topologies arising for a given node–linker combination.[10] In this paper, we report a novel 3D coordination polymer, $\{[Na_{16}(Ni_8L_{12})(H_2O)_{20}(H_3O)_4](CH_3CN)(H_2O)_{18.5}\}_\infty$ (**1**), where H_3L = 4,5-imidazoledicarboxylic acid. For this compound, we deliberately selected the Ni_8L_{12} cube as the predesigned secondary building block for the construction of a coordination framework with high dimensionality; to the best of our knowledge, a related discrete cubic structure has been reported just recently.[11] A difference from the reported compound is that the ligand of the title compound has been totally deprotonated, which is mainly ascribed to the stronger basicity of sodium hydroxide and the intriguing coordination ability of Na^I ions. The Na^I ions are liable to act as counterions and result in bridging bond sites among the adjacent $[M_8L_{12}]^{20-}$ cubic units, as well as probably binding sites for guest molecules. It is worth noting that the synthesis of complex **1** was carried out in a sub-stoichiometric NaOH solution, resulting in four H_3O^+ ions incorporated in the structure as opposed to additional Na^I ions to obtain charge balance.‡

Complex **1** crystallizes in the orthorhombic space group *Pnnm* and consists of $[M_8L_{12}]^{20-}$ cubes bridged by Na^I ions. Fig. 1 illustrates two different kinds of cavities: (1) the $[M_8L_{12}]^{20-}$ cube building block, Fig. 1a, and (2) the cavity, Fig 1b, constructed by the sodium-bridged adjacent $[M_8L_{12}]^{20-}$ cubic building blocks. Each $[M_8L_{12}]^{20-}$ unit consists of eight Ni^{II} ions occupying the vertices of the cube, and are linked in a bi-chelating fashion by twelve L ligands. Each Ni^{II} ion is coordinated to three N and three O atoms from three separate L ligands, producing the slightly distorted octahedral coordination geometry. Ni–N and Ni–O

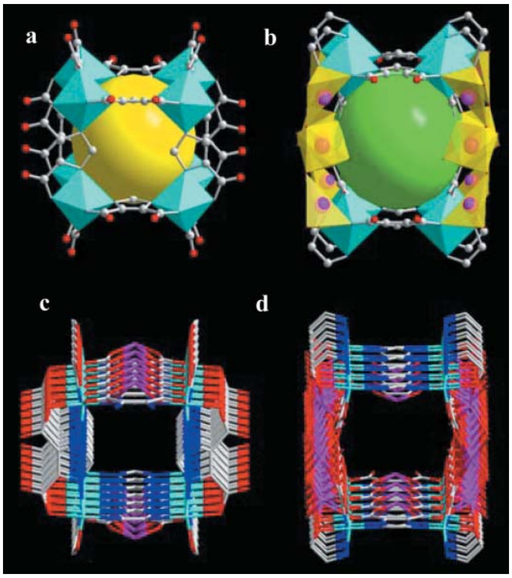

Fig. 1 (a) Structure of the hydrophobic $[M_8L_{12}]^{20-}$ cubic building block, (b) the hydrophilic cavity constructed by sodium-bridged adjacent $[M_8L_{12}]^{20-}$ cubic building blocks, (c) the 1D hydrophobic channel, and (d) the 1D hydrophilic channel of **1**. Carbon (grey), nitrogen (blue), oxygen (red), nickel (cyan), and sodium (purple).

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† Electronic supplementary information (ESI) available: complementary drawings for crystal structure figures, TG figure of **1**. See http://www.rsc.org/suppdata/cc/b5/b503667d/

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bonds fall in the normal ranges of 2.007(4)–2.039(5) and 2.104(4)–2.128(4) Å, respectively. Each L chelates two individual nickel ions to form two five-membered rings coplanar with the imidazole ring. The regularity of the cube is indicated by the fact that Ni···Ni···Ni angles lie between 89.9° and 90.5°, and Ni···Ni distances along the edges are all in the narrow range 6.219–6.278 Å. The distance from the cube center to the closest non-hydrogen atom of the imidazole ring is 3.236 Å, thus the inner cavity has an estimated volume of *ca.* 52 Å^3. The adjacent $[M_8L_{12}]^{20-}$ cubic building blocks are linked to form a 1D hydrophobic open channel along the *a* axis through sodium coordinating to the O atoms of L from the separate $[M_8L_{12}]^{20-}$ cubic building blocks (Fig. 1c). The size of the cavity **b** is larger than the one of **a** with the distance of 3.717 Å from the cavity center to the closest Na(5) atom. Thus the inter cavity shown in Fig. 1b has an estimated volume of *ca.* 80 Å^3. These adjacent cavities are further linked to form a 1D hydrophilic open channel through the sodium-bridged adjacent $[M_8L_{12}]^{20-}$ cubic building blocks (Fig. 1d).

It is worth noting that sodium ions play an important role to self-assemble complex **1** into a 3D porous MOF. All the sodium ions have intricate coordination symmetries and can be simply classified into two different kinds: (1) Na(5) atom which bridges the adjacent $[M_8L_{12}]^{20-}$ cubic building blocks to form 1D hydrophobic channels with unique four-coordinate tetragonal pyramid configuration, and (2) Na(1)–Na(4) atoms which assemble into 2D networks with novel 16-membered macrometallocycles (SI-1,2, see ESI†). The Na–O and Na–Na distances fall into the normal ranges, respectively.[12] The hydrophilic channels of **1** are filled by water and acetonitrile molecules (Fig. 2).

To examine the thermal stability of these porous networks, thermal gravimetric (TG) analyses (SI-3†) and powder X-ray diffraction (PXRD) measurements were carried out. The TG curve of **1** indicates the release of guest molecules up to 100 °C to give its desolvated form. At 265 °C, the ligand molecules start to be released. No chemical decomposition was observed between the desolvating and ligand-releasing temperatures. Fig. 3 shows the observed PXRD patterns of **1**. The PXRD patterns of **1** indicate that the solids after removal of the solvent molecules by heating at 100 °C under vacuum for 10 h (Fig. 3b) and after re-adsorption of the solvent molecules (Fig. 3c) retain the initial framework of **1**. The slight shift and splitting of the peaks may be attributed to the removal or re-inclusion of solvent molecules so that the subtle changes in the relative positions of some atoms take place in the crystal lattice.

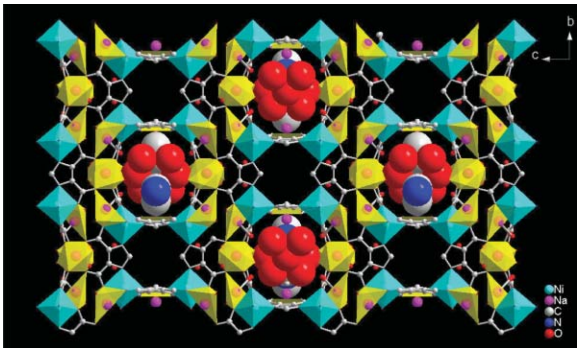

Fig. 2 View of the 3D metal–organic framework of **1** with water and acetonitrile molecules included in the hydrophilic channels.

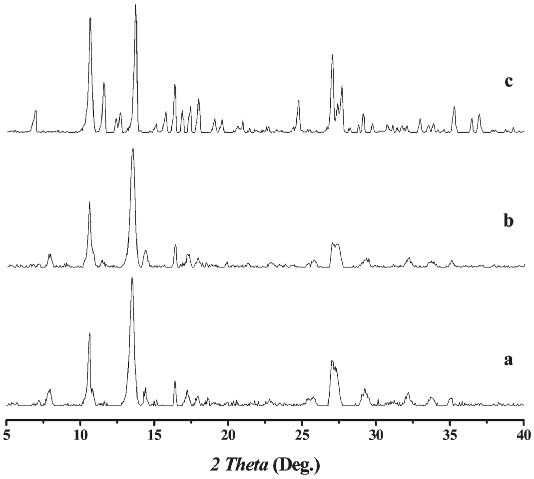

Fig. 3 PXRD patterns for **1**: (a) before removal of guest solvent molecules, (b) after removal of guest solvent molecules, and (c) after re-adsorption of solvent molecules.

Complex **1** possesses a BET surface area of 147 m^2 g^{-1}, and the micropore volume is 0.26 cm^3 g^{-1}. The surface area observed for **1** is consistent with its percent effective free volume of 28.6% (total potential solvent volume of 1988.9 Å^3 out of every unit cell volume of 6955.2 Å^3) calculated with PLATON. The nitrogen adsorption behavior of **1** has been examined at 77 K. Nitrogen adsorption isotherms were taken using automatic volumetric adsorption equipment (ASAP2010, Shimadzu). A known weight (500 mg) of the as-synthesized sample was placed in the quartz tube, which, prior to measurement, was dried under a high vacuum at 100 °C for 10 h to remove the solvent molecules. Approximately 166 ml of N_2 was adsorbed per 1.0 g of desolvated sample at 1 atm (Fig. 4). Moreover, adsorption and desorption experiments with N_2 almost trace the same isotherms, which further indicates that the channel structure is retained through this process.

In conclusion, we have successfully synthesized and characterized a novel 3D metal–organic framework with predesigned cubic

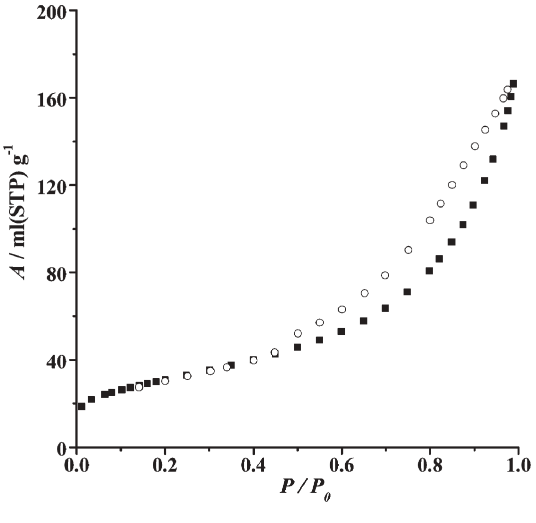

Fig. 4 Isotherms for the adsorption (squares) and desorption (circles) of N_2 at 77 K (A = absolute adsorption; STP = standard temperature and pressure).

building blocks that exhibits significant N_2 uptake at 77 K. The observations should allow the optimization of rational synthetic routes for the construction of structurally well-defined MOFs.

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Notes and references

‡ Synthesis of **1**: H_3L (234 mg, 1.5 mmol) was added to an aqueous NaOH solution. An acetonitrile solution of $Ni(NO_3)_2\cdot 6H_2O$ (291 mg, 1 mmol) was carefully layered on top of the aqueous solution and the mixture allowed to stand for one month. The green rectangular crystals obtained were collected by filtration (60% yield). IR (KBr pellet): v = 3421vs, 1586vs, 1467vs, 1383vs, 1248s, 1099m, 816m, 659m cm^{-1}. Single-crystal X-ray structure determination on **1**: The data were collected at 183(2) K on a Smart CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation. The structure was solved by direct methods using SHELXS-97 and extended using Fourier techniques. Crystal data: $C_{15.50}H_{26}N_{6.25}Na_4Ni_2O_{22.625}$, Mr = 871.31, orthorhombic, space group *Pnnm*, a = 16.365(2) Å, b = 16.441(2) Å, c = 25.852(2) Å, V = 6955.2(11) Å^3, Z = 8, μ = 1.276 cm^{-1}, ρ_{cald} = 1.672 g cm^{-3}, λ(Mo-Kα) = 0.71073 Å, GOF = 1.052, $R1$ (w$R2$) = 0.0888 (0.2314) [8248 observed ($I > 2\sigma(I)$)] for 40830 (Rint = 0.0263) independent reflections out of a total of 8248 reflections with 484 parameters. It is worth noting the hydrogen atoms of all solvent molecules are missing from the refinement, and the free H^+ ion attached to the O(1 W) atom was easily found in a difference map, which clearly illustrates an H_3O^+ site. CCDC 265712. See http://www.rsc.org/suppdata/cc/b5/b503667d/ for crystallographic data in CIF or other electronic format.

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