Design and construction of a microporous metal–organic framework based on the pillared-layer motif†‡

Chaoying Gao, Shuxia Liu,* Linhua Xie, Yuanhang Ren, Jianfang Cao and Chunyan Sun

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A unique porous 3D metal–organic framework has been synthesized based on the insertion of heterogeneous pillars between 2D layers, the permanent porosity of which is confirmed by N_2 adsorption isotherm measurement.

The design and construction of microporous metal–organic frameworks (MOFs) have been receiving considerable attention in recent years due to their intriguing new structural topologies[1] and potential application as functional materials.[2] Although much effort has been made recently in this regard,[3] rational design towards targeted products[4] is still in its infancy. It has been demonstrated that one of the most rational methods in construction of porous frameworks is to connect well-defined two-dimensional (2D) layers with appropriate pillars, which is the so-called "pillaring" strategy.[5] Although this methodology has been successfully used in the syntheses of inorganic compounds, such as pillared montmorillonite and smectite.[6] However, only a handful of porous MOFs have been prepared using this approach.[7–9] Our previous work focused on the zinc-1,3,5-benzenetricarboxylate (BTC)[10a] and iron-BTC[10b] systems under solvothermal conditions. Throughout the investigation of nickel-BTC experiment, we isolated a 2D layered compound [Ni(HBTC)$(DMF)_2$·(guest)] **1** (DMF = *N*,*N*′-dimethylamine). With solvent molecules occupying polar positions on the metal centers, **1** would be an ideal candidate for pillaring. And therefore, we set out to construct a three-dimensional (3D) framework by employing a linear connector with extensive coordination polymer chemistry along with Ni^{2+} and H_3BTC in a one-pot reaction. When 4,4′-bipyridine (4,4′-bipy) was used as the pillaring agent, we successfully obtained a 3D network [Ni(HBTC)(4,4′-bipy)·3DMF] **2** with expected connectivity. In this communication, the syntheses and the crystal structures of the starting 2D layer and the resulting 3D network are reported. And the permanent porosity of compound **2** has been estimated by a N_2 adsorption isotherm measurement.

Compound **1** was prepared by the solvothermal reaction of $Ni(NO_3)_2·6H_2O$ with H_3BTC in DMF and characterized by single-crystal X-ray diffraction§. This compound possesses a 2D layer with honeycomb pores. The coordination environment of the metal centre for **1** is presented in Fig. 1a, where the nickel(II) centre is bounded by three BTC units. One of the BTC units is completely deprotonated and coordinates to three metal centers in a bidentate fashion, whereas each of the other two units coordinates to three metal centers in a monodentate fashion; the remaining free carbonyls, which are partly protonated and could be demonstrated by the absence of the characteristic bands at around 3090 cm^{-1} from the IR spectrum[11] (Fig. S4¶), hydrogen-bond strongly to adjacent free carbonyls.[12] It is worth noting that the hydrogen bonds between the adjacent free carbonyls may play a significant role for the stabilization of this 2D sheet. The polar positions on the nickel(II) centre are occupied by DMF molecules, which disorder at two positions (Fig. S7).† The propagation of alternate nickel centers and BTC linkers leads to infinite extended sheets along the *ab*-plane (Fig. 1c). The sheets stack along the *c*-axis to give the 3D structure, with an approximate distance of 7 Å between adjacent layers. Two similar layered compounds, $CoC_6H_3(COOH)_{1/3}(NC_5H_5)_2·2/3NC_5H_5$ and $Ni_3(H_2O)_6(TMA)_3$–$(TMA)_{23}·2H_2O$ with the same connectivity except for different polar ancillary ligands, have been reported by Yaghi[12] and Chen,[11] respectively. Due to strong π-stacking effect between polar ancillary ligands (pyridine) in $CoC_6H_3(COOH)_{1/3}(NC_5H_5)_2·2/3NC_5H_5$, it even exhibits a robust framework with porosity.

The synthesis of compound **2** was based on introducing the 4,4′-bipy ligand under similar conditions to **1**. Compared with **1**,

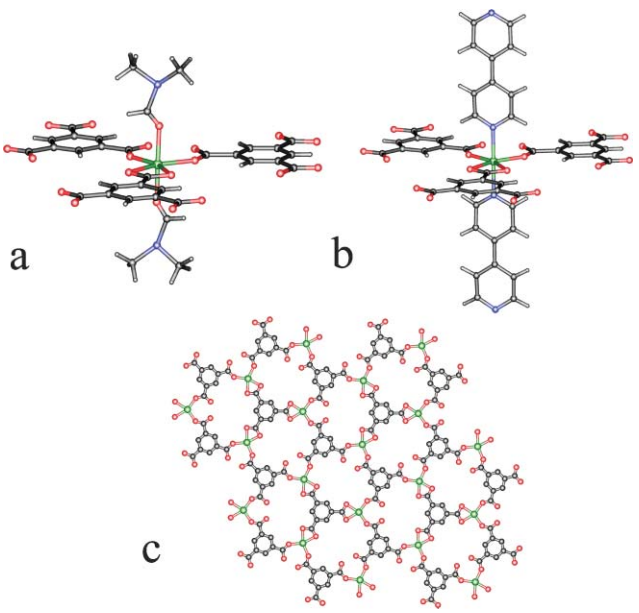

Fig. 1 Coordination environments of Ni(II) ions in the asymmetric units of (a) compound **1** and (b) compound **2**, and a fragment of the 2D layer (c) included both in **1** and **2**. For clarity the hydrogen atoms in (c) have been omitted. Ni: green; N: blue; O: red; C: black.

Key Laboratory of Polyoxometallates Science of Ministry of Education, College of Chemistry, Northeast Normal University, Changchun City, JiLin, P. R. China 130024. E-mail: liusx@nenu.edu.cn

† Electronic supplementary information (ESI) available: TGA curves, XPRD patterns, IR spectra and additional figures related to the framework. See DOI: 10.1039/b704433j

‡ CCDC reference numbers 636900 and 636901. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b704433j

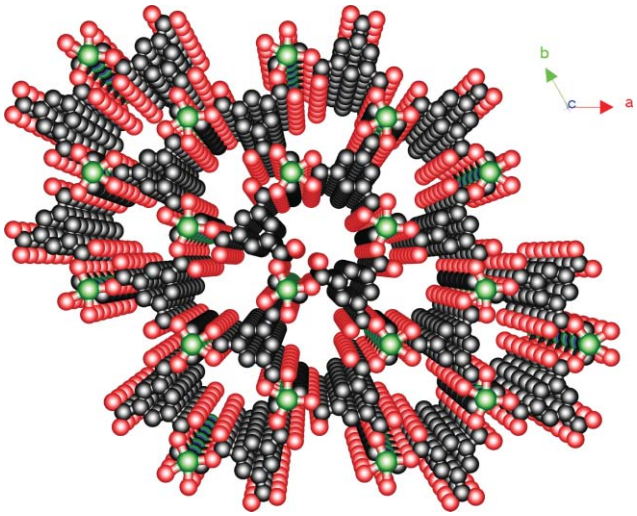

Fig. 2 Perspective view of the framework along the *c*-axis in **2**. For clarity the hydrogen atoms have been omitted. Ni: green; N: blue; O: red; C black.

the color of the crystals changed from yellow–green to green, without any change in the crystal morphology. X-Ray analysis§ performed on a single crystal of **2** revealed that the honeycomb grid layers constructed by Ni^{2+} ions and BTC groups as in **1**, are linked by 4,4′-bipy pillars to form a 3D highly porous framework (Fig. 1b). The 4,4′-bipy pillars are disordered at three positions along the crystallographic threefold axis (Fig. S8).†[13] The most striking feature of **2** is that two distinct types of channels exist: the opening of the Ni(HBTC) layers are aligned to generate honeycomb channels (their dimensions are approximately 8 Å at the widest and 5 Å at the narrowest spacing considering the van der Waals radii of O atoms in the framework) running along the *c*-axis (Fig. 2); normal to [100] and [010], the 4,4′-bipy pillars give further rectangle channels (the cross section is around 7 Å in height and 6 Å in width taken into account the van der Waals radii of the C atoms in the framework) parallel to the layers extending throughout the *ab*-plane (Fig. 3), The effective free volume of **2** was calculated by PLATON analysis as 54.8% of the crystal volume (1476.4 $Å^3$ out of the 2691.9 $Å^3$ unit cell volume). This value compares favorably with the void fractions (0.47 to 0.50) of the most open zeolites, such as the faujasite, paulingite, and zeolite A families.[14] Rosseinsky and co-workers[15] have reported an analogue $[Ni_3(BTC)_2(4,4'\text{-bipy})_3(C_2H_6O_2)_3(H_2O)_3\cdot(\text{guest})]$ synthesized by a diffusing method, rendering the material noncrystalline upon removal of the guest molecules. With a dissimilar synthetical route and the connectivity, the compound **2** shows its predominance for avoiding collapsing in the absence of guest molecules (*vide infra*), the ability of which lies at the core of determining its suitability for applications.

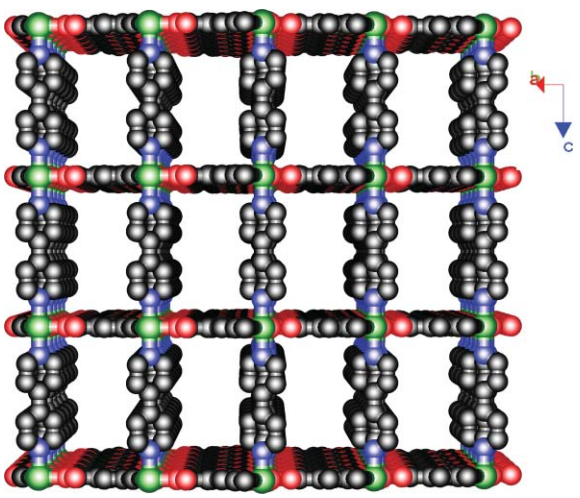

Fig. 3 Perspective view of the framework normal to the [100] plane in **2**. For clarity the hydrogen atoms have been omitted. Ni: green; N: blue; O: red; C: black.

In order to examine the stability of the framework, thermal gravimetric analysis (TGA) and desolvation experiment were carried out. The TGA curve shows release of guest DMF molecules between 25 and 235 °C leading to a weight loss of 34.11%, which suggests a pore filling of 3 DMF molecules per Ni centre. Above 235 °C, the sample shows no further weight loss up to 272 °C at which temperature the compound decomposed. For the desolvation experiment, the as-synthesized crystalline solid was placed in a high vacuum oven at 150 °C for 6 h with a 34.16% (calculated 34.30%) weight loss to get the evacuated solid. The structure of this phase was studied by measuring the XRD patterns. Fig. 4 shows the observed XRD patterns compared with that of as-synthesized compound **2** as well as the simulated powder patterns obtained from the single-crystal model of **2**. The good agreement of the peaks in all diagrams demonstrates that the long-ring order of the framework structures of **2** was retained upon a complete removal of the guest molecules.

The permanent porosity of **2** has been confirmed by N_2 adsorption isotherm measurement. A sample of **2** was evaluated at 150 °C for 6 h under vacuum to remove the included solvent molecules before N_2-adsorption measurement was attempted. As shown in Fig. 5, the isotherm reveals a reversible type I behavior and shows no significant hysteresis between the sorption and desorption traces. The accessible void space is fully saturated with N_2 molecules at relatively low pressures ($P/P_0 \approx 0.1$) with a total weight uptake of 290 $cm^3\ g^{-1}$. By applying the Langmuir equations, the Langmuir surface area is estimated to be $S_{Langmuir}$ = 1282.3 $m^2\ g^{-1}$. Also obtained from the adsorption/desorption

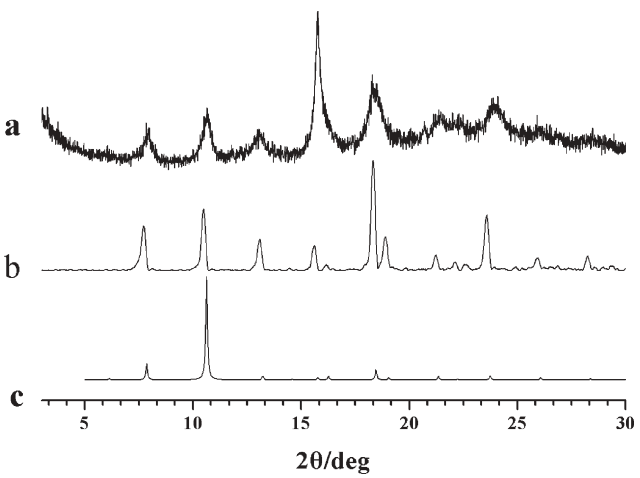

Fig. 4 XRPD patterns of the (a) evacuated, (b) as-synthesized and (c) simulation for compound **2**.

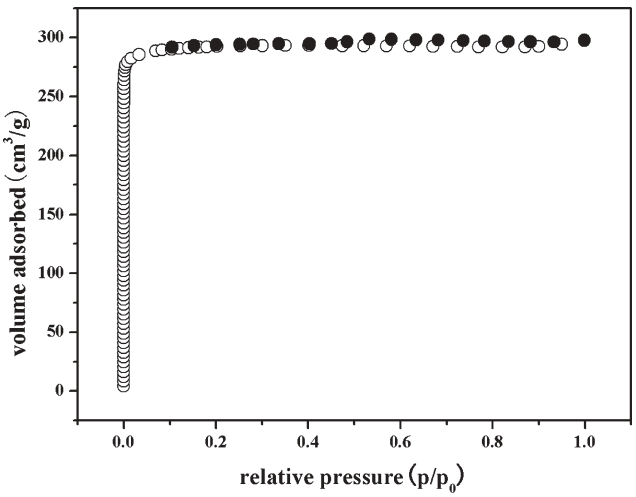

Fig. 5 N_2 gas sorption isotherms (77 K) of **2** measured at 150 °C. Open symbols, sorption; filled symbols, desorption; P_o = 1 atm.

isotherm study are the Brunauer-Emmett-Teller (BTC) surface area (969.1 $m^2\ g^{-1}$) and the single-point total pore volume (0.432 $cm^3\ g^{-1}$).

In summary, we present a novel, highly porous metal–organic framework using the "pillaring" approach. The unusual combination leads to a stable network with permanent porosity. We are attempting to modify the pillars to realize controlling the channel size as well as the chemical functionality.

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Notes and references

§ *Crystal data for* **1**: $NiC_{15}H_{18}N_2O_8$, M = 412.02, hexagonal, *P*6(3)/*mcm*, a = 16.609(2) Å, b = 16.609(2) Å, c = 14.325(3) Å, V = 3422.2(10) Å^3, T = 293 K, Z = 6, μ = 0.886 mm^{-1}, d_{calc} = 1.200 g cm^{-3}, 25128 reflections measured, 1115 unique (R_{int} = 0.0765), Siemens SMART CCD diffractometer (0.71073 Å). $R1$ = 0.0511, $wR2$ = 0.1416 for $I > 2\sigma(I)$, $R1$ = 0.0586, $wR2$ = 0.1469 for all data, GOF = 1.193, 82 parameters and 0 restraints. Solvents within the voids were not crystallographically well defined and these data were processed with the SQUEEZE routine within PLATON. CCDC 636901.

Crystal data for **2**: $NiC_{28}H_{33}N_5O_9$, M = 642.2833, hexagonal, *P*-62*m*, a = 16.634(2) Å, b = 16.634(2) Å, c = 11.234(2) Å, V = 2691.9(7) Å^3, T = 293 K, Z = 1, μ = 0.560 mm^{-1}, d_{calc} = 0.760 g cm^{-3}, 21183 reflections measured, 1774 unique (R_{int} = 0.0959), Siemens SMART CCD diffractometer (0.71073 Å). R_1 = 0.0472, wR_2 = 0.1188 for $I > 2\sigma(I)$, R_1 = 0.0505, wR_2 = 0.1206 for all data, GOF = 1.086, 114 parameters and 14 restraints. Solvents within the channels were not crystallographically well defined and this data was treated with the SQUEEZE routine within PLATON. The guest solvents were confirmed by TGA, IR and elemental analysis. CCDC 636900.

¶ *Synthesis of* **1**: A mixture of H_3BTC (0.105 g, 0.5 × 10^{-3} mol) and $Ni(NO_3)_2{\cdot}6H_2O$ (0.145 g, 0.5 × 10^{-3} mol) in 10 ml DMF was sealed in a 23 ml Teflon-lined autoclave and heated at 130 °C for 3 d. The resultant yellow–green hexagon crystals were washed with DMF to give the pure sample (yield: 65%).

Synthesis of **2**: A mixture of H_3BTC (0.105 g, 0.5 × 10^{-3} mol), $Ni(NO_3)_2{\cdot}6H_2O$ (0.145 g, 0.5 × 10^{-3} mol) and 4,4′-bipy (0.079 g, 0.5 × 10^{-3} mol) in 10 ml DMF was sealed in a 23 ml Teflon-lined autoclave and heated at 130 °C for 3 d. The resultant green hexagon crystals were washed with DMF to give the pure sample (yield: 83%). Anal. calcd. for **2** (%): C, 52.36; H, 5.18; N, 10.90; found: C, 52.64; H, 5.43; N, 11.17.

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13 We solved the metal–organic framework structure of **2** in the space groups *P*3 and *P*1, respectively. The both results showed the same disorder of the 4,4′-bipy pillars proving that the high site symmetry is not the origin of the disorder.

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