A lanthanide metal–organic framework with high thermal stability and available Lewis-acid metal sites†

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A lanthanide metal–organic framework, $Dy(BTC)(H_2O)\cdot$DMF, with excellent thermal stability shows a high surface area, 655 m² g⁻¹, high hydrogen and carbon dioxide storage capability, and available Lewis-acid metal sites which could be anticipated to use in catalysis and metal-site specific chemical sensor.

Lanthanide metal–organic frameworks have received special attention due to their unusual coordination characteristics and exceptional optical and magnetic properties arising from 4f electrons.[1] Because of the high-coordination number and flexible coordination geometry of lanthanide ions most such frameworks are not as void as those of traditional transition metals and are unavoidable to coordinate with solvent molecules at terminal positions.[2] The dissociation or removal of the terminal coordinated molecules from lanthanide ions could yield more empty frameworks and leave Lewis-metal acid sites, which have potential applications as sensors or catalysts for organic transformations.[2a,b] However, the removal of the terminal coordination molecules always causes the collapse of the framework, even if some of them exhibit solvent reversible exchange.[3] To the best of our knowledge, it is still rare that a structure maintains its crystallinity upon removal of the terminal molecules and maintain a permanent porosity.[4] We present here a lanthanide metal–organic framework, $Dy(BTC)(H_2O)\cdot$DMF (**1**) (H_3BTC = 1,3,5-benzenetricarbocylic acid; DMF = N,N′-dimethylformamide), synthesized under mild conditions, whose terminal water molecules could be removed after calcination at 300 °C. The calcined sample (denoted as **1A**) exhibits permanent porosity, high gas adsorption ability and available Lewis-acid sites.

As a typical preparation procedure, a mixture of $Dy(NO_3)\cdot n$H₂O (40 mg, 0.05 mmol) and H_3BTC (10 mg, 0.05 mmol) was dissolved in DMF (10 mL) and ethanol (2 mL) at room temperature. Two drops of dibutylamine was added to the mixture, and then a small amount of 6 M HNO_3 was added until the mixture became clear. The mixture in a 50-mL beaker was left undisturbed at 60 °C for 7 days to give colorless crystals in 76% yield (based on H_3BTC). The compound was stable in air, insoluble in water and common organic solvents.

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† Electronic supplementary information (ESI) available: TG curve, PXRD patterns, IR spectra and micropore size distribution of compound **1**. See DOI: 10.1039/b605428e

The formula of compound **1**, $Dy(BTC)(H_2O)\cdot$DMF, was determined by single-crystal X-ray diffraction,‡ thermogravimetric analysis (TGA) and elemental analysis studies.[5] The X-ray diffraction study reveals that compound **1** is a three-dimensional framework crystallized in a chiral space group $P4_322$. Each building unit contains one seven-coordinated lanthanide ion (Dy^{3+}), one BTC ligand and one water molecule. The guest DMF molecules are totally disordered in the crystal lattice and are determined by TGA and elemental analysis results. The dysprosium ion is coordinated with six oxygen atoms from six carboxylate groups of BTC ligands and one oxygen atom from a terminal water molecule. The carboxylic O–Dy bond distances are in the range 2.282(10)–2.306(10) Å and Dy–Owt bond distance is 2.415(16) Å, all comparable to reported dysprosium coordination polymers.[6] Two crystallographically equivalent Dy ions are connected by three dimonodentate carboxylate groups from three different BTC ligands and two adjacent carboxylate groups of one BTC ligand (Fig. S1, ESI†). The special connection fashion of Dy ions leads to a one-dimensional helical inorganic chain along the [001] direction, ···Dy–O–C–O–Dy···, which contains a left-hand fourfold screw axis, as shown in Fig. 1(a). The BTC molecule lies on a twofold axis and the dysprosium atom also lies on another twofold axis. The 1D inorganic chains link to each other through phenyl groups of BTC ligands along [100] and [010] directions to lead to impenetrable organic walls and a 3D framework (Fig. 1(b)). The framework contains approximately 6 × 6 Å² circular channels along the [001] direction to which the coordination water
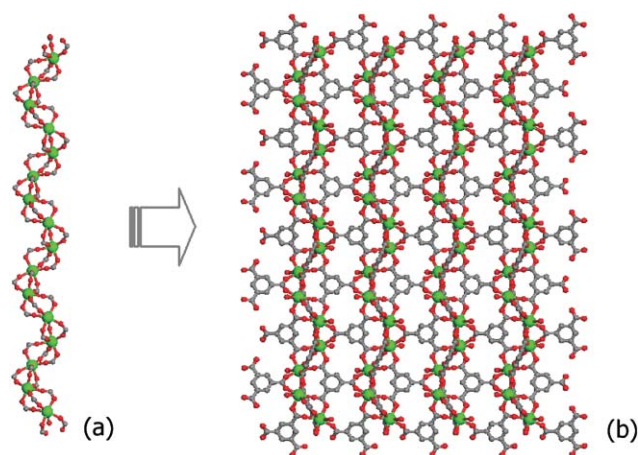

Fig. 1 (a) Each one-dimensional chiral inorganic chain along the [001] direction with a fourfold screw axis (b) connected to each other lead to impenetrable organic walls along [100] and [010] directions (Dy, green; O, red; C, grey). H atoms are omitted for clarity.

molecules point (taking into account the van der Waals radii of the atoms), as seen in Fig. 2(a).

The TGA study is performed under an air atmosphere and shows that compound **1** is stable up to 350 °C (Fig. S2, ESI†). The gradual weight loss of 19.03% from 100 to 300 °C indicates that there is one guest DMF molecule in the channel of the compound, which is consistent with the elemental analysis result, and is attributed to the loss of one guest DMF molecule and one terminal coordinated water molecule (calc. 19.78%). The sharp weight loss above 400 °C corresponds to the decomposition of the compound and the remaining weight of 40.32% is the Dy and O components, Dy_2O_3 (calc. 40.48%). Considering the thermal stability of compound **1**, X-ray powder diffraction (PXRD) studies were performed for the as-synthesized sample and the samples heated at 100, 300, 350 and 400 °C, respectively. The PXRD patterns for samples heated at 300 °C (sample **1A**) and 350 °C are similar to that of the as-synthesized sample, which indicates that the departure of the guest molecule and coordinated water molecule does not lead to an obvious phase transformation (Fig. S3, ESI†). Only a slight position shift of the first peak of sample **1A** compared with that of as-synthesised sample is observed which indicates a pore contraction. When the sample is heated at 400 °C, the long-range order of the structure is lost and forms an amorphous phase. To confirm the removal of the coordinated molecule, we recorded the IR spectra of the as-synthesized sample, sample **1A** and the *in situ* IR spectrum of the sample **1A** heated at 120 °C under vacuum (Fig. S4, ESI†). Comparing the IR spectra with the *in situ* IR spectrum, we find that nearly total disappearance of the broad band centered at 3500 cm^{-1} in the *in situ* IR spectrum, which is ascribed to H-bonded ν(OH) groups of the coordinated water molecule.[7]

Encouraged by the stability of compound **1** sufficient to remove the coordinated molecule, nitrogen, hydrogen and carbon dioxide adsorption properties are investigated for the sample (Fig. 3). The nitrogen isotherm measured at 77 K exhibits a typical type I isotherm with a BET surface area of 655 $m^2 g^{-1}$ for sample **1A** and 202 $m^2 g^{-1}$ for the sample heated at 350 °C, which is comparable to MOF-5 heated at such a temperature.[1a,8] The HK pore distribution plot of sample **1A** shows that the pore size is approximate 5.5 Å (Fig. S5, ESI†). Adsorption of hydrogen at 77 or 87 K has been used as an effective method to evaluate hydrogen storage materials. The hydrogen uptake of the sample **1A** is 1.32 wt% at 77 K, 1 atm. The CO_2 adsorption isotherms of the sample **1A** and zeolite 13X powder sample were examined
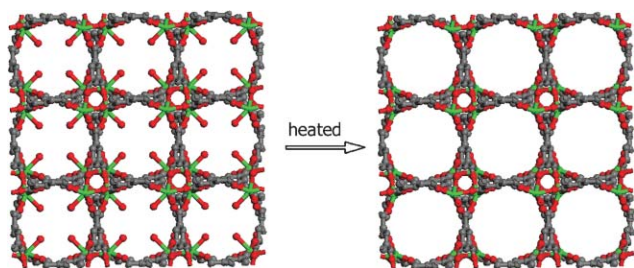

Fig. 2 (a) A three-dimensional network with approximately 7 × 7 Å² circular channels along [001] direction to which the coordinated water molecules point, (b) which could be removed through heating the sample at 300 °C to yield micropores.
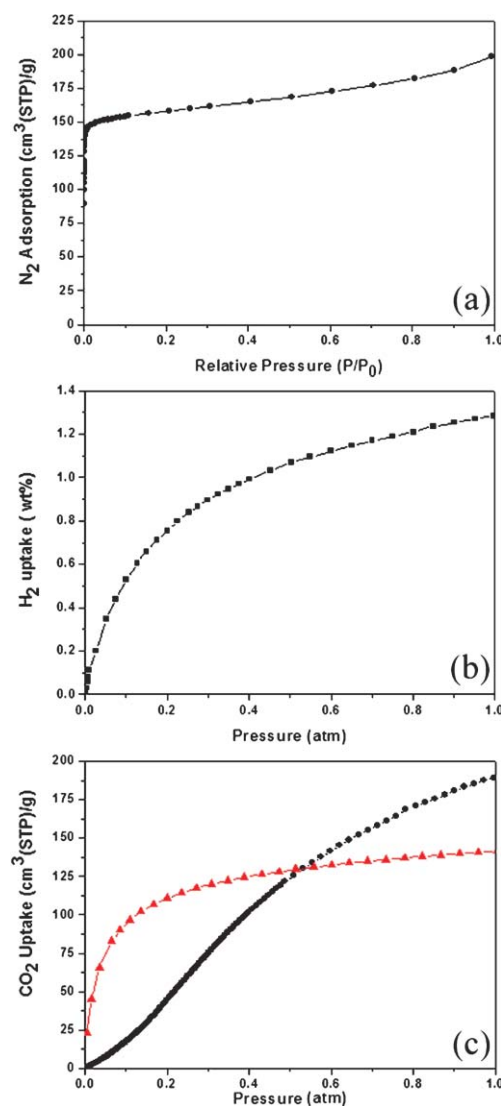

Fig. 3 (a) Nitrogen adsorption isotherm (77 K) and (b) hydrogen adsorption isotherm (77 K) for sample **1A** of Dy(BTC)(H₂O)·DMF, and (c) carbon dioxide sorption isotherm (273 K) for sample **1A** of Dy(BTC)(H₂O)·DMF (black) and 13X (red).

using an ice-water bath. The sample **1A** exhibits an increasing uptake accompanied with the increasing of pressure and it is clear that the capacity does not saturate at 1 bar, so anticipating the uptake of more CO_2 at higher pressure. The isotherm of zeolite 13X has a typical type I isotherm in which the more intense gas adsorption at low pressure forms a "knee". Compound **1** takes up more CO_2 than zeolite 13X when the pressure is higher than 0.6 bar.

The dissociation of the terminal water molecule from the dysprosium ions means that the ions become coordinatively unsaturated in the resulting porous solid.[2a,b] To explore the Lewis-acid sites, we investigated the interaction of pyridine with sample **1A** through temperature-programmed desorption (TPD).[9,10] As shown in Fig. 4, the desorption spectrum with an obvious band at 500 K indicates that Lewis-acid metal sites are available. Given the definite evidence of available Lewis-acid sites and the thermal stability, it is not unreasonable to anticipate the
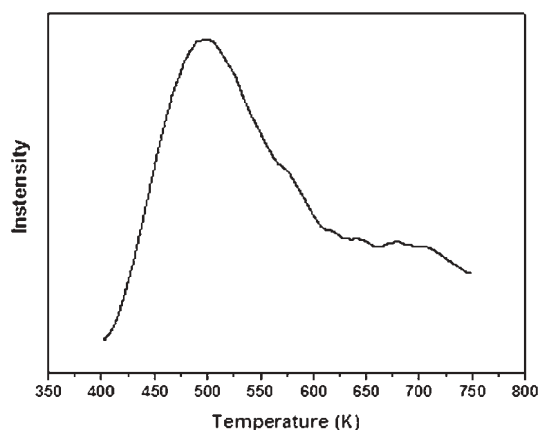
Fig. 4 TPD spectrum of the sample **1A**.

use of the compound in catalysis and as a metal-site specific chemical sensor.

This study demonstrates a multifunctional lanthanide metal–organic framework, Dy(BTC)(H$_2$O)·DMF, with sufficient thermal stability to remove the guest molecule and terminal coordinated water molecule to lead to available Lewis-acid metal sites. The sample after removal the guest molecule and terminal coordinated molecule shows high surface area, 655 m^2 g^{-1}, and high capacity for storage of hydrogen and carbon dioxide. Extension of this work will focus on how to use the chiral channels and Lewis-acid metal sites for enantioselective separation and catalysis.

Notes and references

‡ *Crystal data* for Dy(BTC)(H$_2$O)·DMF: C$_{12}$H$_{12}$NO$_8$Dy, M = 460.7, tetragonal, space group P4$_3$22 (no. 95), a = 10.3131(4), b = 10.3131(4), c = 14.4950(13) Å, V = 1541.69(16) Å^3, T = 293(2) K, Z = 4, μ(Mo-Kα) = 4.860 mm^{-1}, Flack parameter = 0.01(5), R = 0.0468; 8873 reflections measured, 1696 unique (R_{int} = 0.0886) which were used in all calculations. The final $wR(F^2)$ was 0.0937 (all data). CCDC 604441. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605428e

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5 Elemental analysis for compound **1**. Calc: C, 31.28; H, 2.63; N, 3.04. Found: C, 31.99; H, 2.61; N, 3.03%.

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9 The temperature-programmed desorption (TPD) was carried out in a flow apparatus with nitrogen as carrier gas (3 L h^{-1}). A thermal conductivity detector (TCD) were used for evolved gas detection. The sample was equilibrated with pyridine vapor with nitrogen as carrier gas at 120 °C. For each experiment 200 mg the sample was compressed into pellets as measuring the IR spectrum and subsequently powdered (0.2–0.4 mm). At first all samples were flushed with nitrogen at room temperature for a period of 1 h and then a linear temperature program (10 K min^{-1}) was started.

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