Ligand-to-metal ratio controlled assembly of nanoporous metal–organic frameworks†

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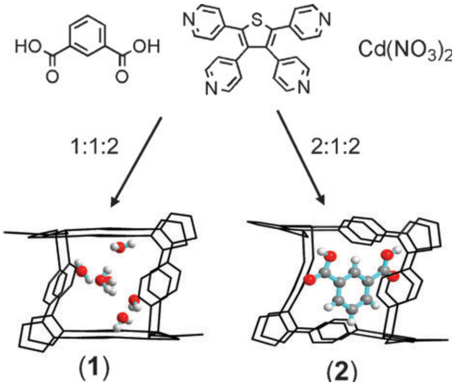
Two bilayered metal–organic frameworks with nanoporous channels were synthesized at different ligand-to-metal ratios, which demonstrated an interesting crystal-to-crystal transformation property and a special fluorescent response to the different guest molecules included.

Controlling the self-assembly of porous metal–organic frameworks (MOFs) is currently considered as one of the most active areas in coordination and supramolecular chemistry.[1] A strong motivation in this field is that nanosized porous MOFs may provide a new approach to various potential applications in many fields.[2] However, stable host frameworks are still posing a great challenge in porous materials research. Therein, structural transformation of MOFs (also called single crystal-to-single crystal transformation) triggered by guest exchange or a physical stimulus is more interesting since such materials may serve as the next generation of porous materials.[3] Up to now, reported guest molecules have been limited to small molecules or liquid-state organic molecules.[4,5] However, transformation of MOFs by controlling the ligand-to-metal ratio or by removing a large solid-state guest molecule is hitherto unknown for porous MOFs.

Recent studies focus mainly on the effective technique of stoichiometry control of metal complexes constructed from flexible mixed-donor ligands.[6,7] Here, we report an interesting example of cadmium(II) porous MOFs based on two organic rigid ligands tetra(4-pyridyl)thiophene (TPT) and 1,3-benzenedicarboxylic acid (H_2BDC), which are effective in promoting non-interpenetrated frameworks and can be widely utilized to construct rigid porous MOFs.[8] Notably, the H_2BDC-to-Cd(II) ratio plays a vital role in the formation of the porous bulk and structural diversification of the MOFs. In addition, structural transformation by removing large solid guest molecules using a subtle chemical reaction was achieved.

Porous MOFs $[Cd(TPT)(BDC)]\cdot 6H_2O$ (**1**) and $[Cd(TPT)(BDC)]\cdot H_2BDC$ (**2**) were obtained under hydrothermal reaction conditions (see Scheme 1 and ESI†), which enables the porous architectures to be maintained after removing the guest molecules. The X-ray crystal structure analyses reveal that **1** and **2** crystallize in an orthorhombic space group *Fdd*$_2$ and monoclinic space group $P2_1/c$, respectively.‡ Both of them have similar two-dimensional (2-D) non-interpenetrated bilayered frameworks that encapsulate free water and H_2BDC molecules, respectively (Fig. 1). As depicted in Fig. S1†, the asymmetric unit in **1** (or **2**) consists of one cadmium(II) ion, one TPT, one BDC^{2-} anion, and six lattice water molecules (or one free H_2BDC molecule).

These two 2-D bilayers are built from the co-ligands of TPT and BDC^{2-}. In **1** and **2**, TPT adopts the same μ_3-coordination mode through three N-donors (N2 is uncoordinated) to link three cadmium(II) ions, while 1,3-BDC^{2-} serves as a linear bridge. Within the bilayered structure, there are 1-D parallelogram channels with the effective cavity size being *ca.* 10.06 Å × 7.45 Å along the [101] or [10−1] direction in **1** (Fig. 1a). The 1-D nanosized channels are full of free water molecules, which are further stabilized by hydrogen bonds to form a fascinating 1-D aqua chain inside each channel (see Fig. S2†). A calculation using PLATON[9] led to a potential solvent area of 4353.3 Å^3 per unit cell volume of 14464.2 Å^3 in **1**, namely 30.1% of the total crystal volume. The calculated solvent area is consistent with six water molecules per unit cell, and is also in agreement with the results of elemental analyses. The adjacent 2-D bilayers of **1** are stacked in an intersectant fashion (rotary angle is 38.6°) with a repeat sequence of *ABAB* (Scheme 2a). Merely changing the ligand-to-metal ratio resulted in the formation of **2**. As to **2**, there exist large channels along the *b* axis with an effective cavity size of 12.1 Å × 11.9 Å in the bilayered structure (Fig. 1b). A calculation using



Scheme 1 The ligand-to-metal ratio controlled assembly of **1** and **2**.

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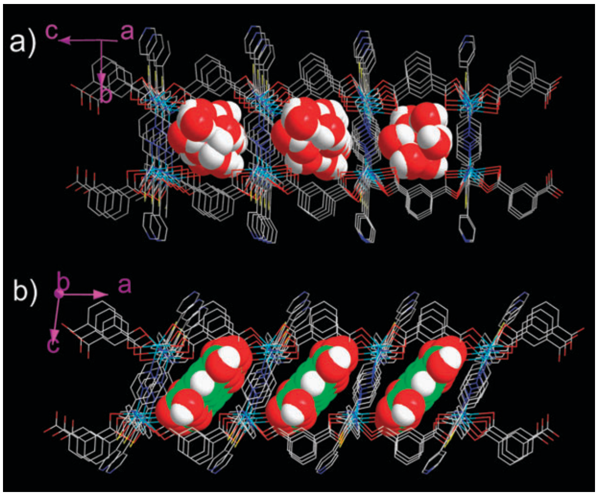
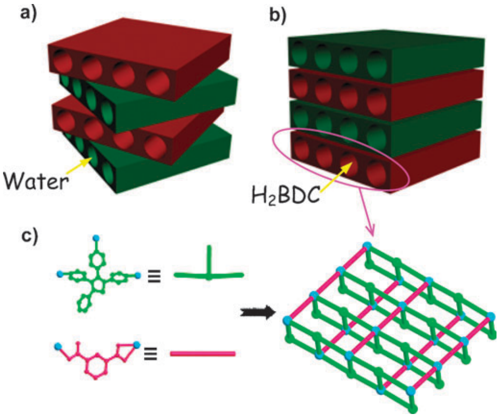


Fig. 1 Perspective view of the bilayered frameworks with nanosized channels encapsulating free water molecules in **1** (a) and guest H_2BDC molecules in **2** (b).

PLATON led to a potential solvent area of 1162.4 Å^3 per unit cell volume of 3650.7 Å^3 in **2**, namely 31.8% of the total crystal volume. The free H_2BDC molecules filled in the nanosized channels of **2**. Unlike **1**, the adjacent 2-D bilayers of **2** are stacked in a slightly off-set parallel fashion with a repeat sequence of *AAAA* (Scheme 2b). Such a space-templating method has been employed for the syntheses of porous materials with a wide range of chemical compositions such as aluminosilicate zeolites, microporous aluminophosphates as well as coordinated complexes, resulting in the discovery of novel materials with stimulus-responsive properties.[10,11] Moreover, if each metal center was considered as a node and the TPT ligand as a three-connecting node in **1** and **2**, the whole structure should be an unprecedented 3,5-connected network with a Schäfli symbol of $(4^2{\cdot}6)(4^2{\cdot}6^7{\cdot}8)$[12] (Scheme 2c). Besides, the 2-D structures are further linked *via* $\pi\cdots\pi$ interactions between adjacent bilayers, thus resulting in the non-interpenetrated 3-D supramolecular frameworks (see Fig. S3†).

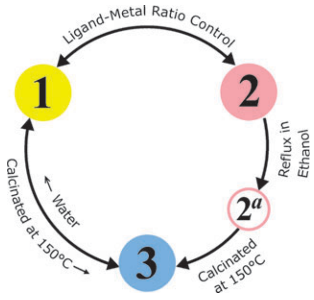
To verify whether the MOFs can be sustained after the removal of the guest molecules, the products were analysed using powder X-ray diffraction (PXRD) and thermal gravimetric analysis (TGA). PXRD analyses of the as-synthesized products of **1** and **2** were in excellent agreement with the calculated PXRD patterns produced using single crystal data (see Fig. S4†). The TGA diagram of **1** reveals that the release of the guest water molecules occurs below 100 °C, and the decomposition of the whole network begins above 310 °C (see Fig. S5†). Therefore, the as-synthesized samples of **1** were calcinated at 150 °C and 1022 Torr for 24 h to fully dispose of water molecules. The dehydrated samples were designated as complex **3**. PXRD analysis (Fig. S6†) of **3** was in excellent agreement with **1**, indicating the porous network was retained in the absence of guest water molecules. Immersing **3** (50 mg) in 10 ml water solvent for two hours produced the same new crystalline solid as **1**, and the same recovery could be obtained when **3** was exposed to air for two days. The contrastive PXRD and elemental analyses indicate that the robust nanotabular porous material did maintain its structural integrity upon removal and sorption of guest water molecules within the host channels. And the dehydration–hydration cycles could be repeated many times in the porous materials.



Scheme 2 Schematic representation of the stacking modes of the bilayers for **1** (a) and **2** (b). Topology analysis for one bilayer (c).

With regard to **2**, to verify whether the host framework can be sustained after the removal of the guest H_2BDC molecules, the as-synthesized sample of **2** was refluxed in ethanol solvent; the resulting product was designated as $\mathbf{2^a}$. Elemental analysis of $\mathbf{2^a}$ {C, 50.25; H, 2.27; N, 11.64% corresponding to $[Cd(TPT)(BDC)]{\cdot}2.5C_2H_5OH$} shows that the free H_2BDC molecules have been removed in the course of reflux, which is also confirmed by IR spectroscopy, with the disappearance of the absorption peak around 1700 cm^{-1} for a protonated carboxylic group (see Fig. S7†). In addition, the guest H_2BDC molecule in **2** can also be removed by other solvents such as methanol and DMF *via* an identical procedure. The as-synthesized samples of $\mathbf{2^a}$ were calcinated at 150 °C and 1022 Torr for 24 h, then the resulting product was proved to be the same as **3**. The permanent porosity of **3** is confirmed by its N_2 adsorption–desorption isotherm with typical Type-II gas sorption behavior and a dinitrogen uptake of approximately 154 cm^3(STP) g^{-1}, which reveals a Langmuir surface area of 572.4 m^2 g^{-1} and a pore volume of 0.14 cm^3 g^{-1} (see Fig. S8†). The whole PXRD analyses (Fig. S6†) show that after removal of H_2BDC molecules from **2**, the bilayered network has been subtly rearranged, which converts to the same cell parameters as discovered in **1**. As illustrated in Scheme 3, **1** and **2** can be easily obtained by controlling the ligand-to-metal ratio in the syntheses, and **2** can be further converted into **1** by convenient approaches.

The solid-state luminescence of complexes **1**, **2**, $\mathbf{2^a}$ and **3**, as well as the free ligand TPT (L) were investigated at room temperature and are shown in Fig. 2. The emission spectra for **1**, $\mathbf{2^a}$, **3**, and **2** exhibit main peaks at 397, 404, 412 and 427 nm, respectively. Since a weakly similar emission (λ_{max} = 396 nm) is also observed for L, the luminescence of these complexes is tentatively assigned to ligand-to-ligand charge-transfer (LLCT)



Scheme 3 The overall transformations for these compounds.

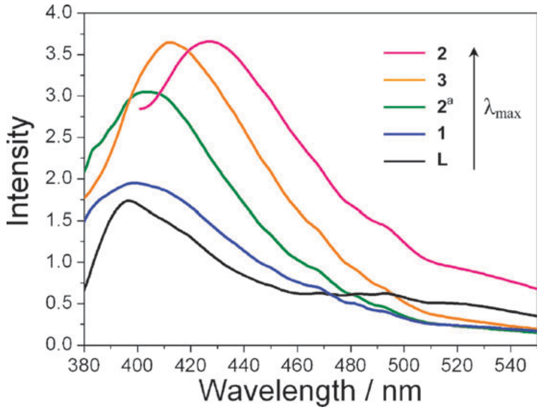


Fig. 2 Luminescence spectra of TPT ligand (L) and complexes **1**, **2**, **2^a**, and **3** in the solid state at room temperature.

bands.[13] Time-dependent density functional theory calculations were carried out to validate the nature of the fluorescence emissions (see Fig. S9†). The calculations using the hybrid B3LYP functional were performed on the framework with the ground-state geometry adopted from the truncated X-ray data. Compared with L, the enhancement of fluorescence intensity in the complexes is probably due to the unique coordination of L to the Cd(II) centre increasing the conformational rigidity of the ligand, thereby reducing the non-radiative decay of the intraligand (π–π*) excited state.[14] Remarkably, compared with the corresponding vacant framework of **3**, obvious shifts of the emissions take place (blue shift in **1** and **2^a** when the channels included water and ethanol molecules, respectively; red shift in **2** when the channels included the aromatic molecules of H_2BDC). This is presumably due to the fact that different guest molecules or solvent molecules have a distinctive effect on their host framework. These results indicate that nanotubular porous MOFs have a potential application in detecting guest molecules in the framework.[15]

In summary, this study demonstrates that changes in the ratios of ligand-to-metal have a significant effect on the structural characteristics of nanoporous MOFs. We also carried out a single crystal-to-single crystal transformation by removing large solid guest molecules with a subtle chemical reaction. It is noteworthy that porous bilayered frameworks embodying different guest molecules and exhibiting fluorescence-responsive behaviour have been successfully prepared. This approach is expected to be valuable for the construction of many novel and interesting porous MOFs.

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Notes and references

‡ X-Ray structure determination of **1** and **2**. Data were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. All the structures were solved by direct methods and refined with the full-matrix least-squares technique using the SHELXS-97 and SHELXL-97 programs. Crystal data for **1**: $C_{32}H_{32}CdN_4O_{10}S$, orthorhombic, space group Fdd_2, a = 28.6911(19), b = 50.103(3), c = 10.0620(7) Å, V = 14464.3(17) Å^3, Z = 16, T = 293(2) K, R = 0.0845, wR_2 = 0.1853, GOF = 1.026. Crystal data for **2**: $C_{40}H_{26}CdN_4O_8S$, monoclinic, space group $P2_1/c$, a = 10.0936(18), b = 15.105(3), c = 24.167(4) Å, β = 97.780(3)°, V = 3650.8(12) Å^3, Z = 4, T = 293(2) K, R = 0.0391, wR_2 = 0.0597, GOF = 1.000. CCDC 675548 (**1**) and 675549 (**2**).

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