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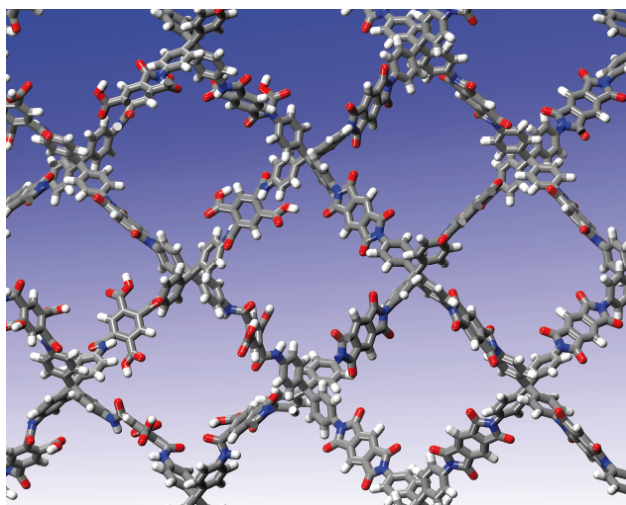


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A metal–organic framework with coordinatively unsaturated metal centers and microporous structure†

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A novel two dimensional porous framework $[\text{Cd}_3(\text{BTB})_2(\text{DEF})_4]_n \cdot 2n\text{DEF}$ (**1**) based on $\{\text{Cd}_3\}$ building blocks with bilayer honeycomb structure constructed from cadmium ion bridged honeycomb layers exhibits promising adsorption for N_2 after activation to obtain coordinatively unsaturated Cd centers, and SEM characterization demonstrates interesting microporous structure inside of the compound.

Porous metal–organic frameworks (MOFs) have emerged as a class of very promising hybrid materials for their potential application in gas storage, separations, sensing and catalysis.^{1–5} The advantage of MOFs over conventional inorganic porous materials is that their pore size, shape, and functionality can be systematically and predictably adjusted *via* synthetic modification of the organic ligand.^{6,7} MOFs with solvent molecules attached as ligands to the metal centers are of special interest because removal of the solvent ligands by thermal activation can generate unsaturated metal centers (UMC) or open metal sites which render them good candidates for selective gas adsorption materials or catalysts.^{8–11}

A variety of porous MOFs featuring 2D or 3D nets have been reported recently. Usually these nets are constructed from clusters^{12a} or inorganic chains.^{12b} The reported clusters are considerably diverse, containing paddle wheel dinuclear, triangle cluster, tetrahedron, *etc.*^{13–15} Herein, we report a unique 2D porous framework $[\text{Cd}_3(\text{BTB})_2(\text{DEF})_4]_n \cdot 3n\text{DEF}$ (**1**) based on linear $\{\text{Cd}_3\}$ building blocks with bilayer honeycomb structure. After solvent exchange and activation under vacuum and heating, this material contains coordinatively unsaturated Cd centers which can be observed by IR spectra, thermogravimetric analysis (TGA), and powder X-ray diffraction. The activated material possesses high porosity demonstrated from N_2 adsorption isotherm.

Solvothermal reaction of $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and H_3BTB (1,3,5-tris(4-carboxyphenyl) benzene) in a molar ratio of 3 : 2 with DEF (*N,N*-diethylformamide) as solvent at 110 °C for 35 h yielded colorless plate-like crystals (ESI, Fig. S1)† of $[\text{Cd}_3(\text{BTB})_2(\text{DEF})_4]_n \cdot 3n\text{DEF}$ (**1**).†

Scanning electron microscope (SEM) characterization of as-synthesized compound **1** revealed an interesting microporous structure. In Fig. 1, the left image exhibits crystal particles with average

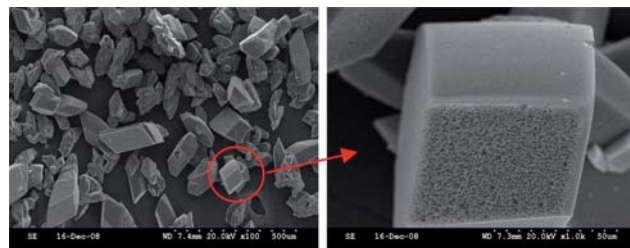


Fig. 1 Surface characterization of **1** using SEM. Left image: crystals of 50 μm average diameter; right: porous surface of a section of the crystal.

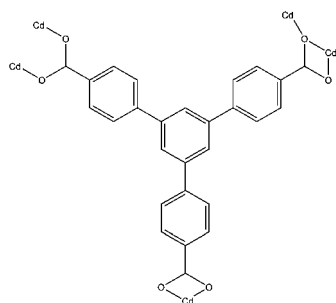
diameter of 50 μm, and the right image shows the macroporous structure observed from a section of a broken crystal particle. Figures in supplementary information present further detail of pores with an average diameter of 500 nm, which indicates the potential of this MOF material as a catalyst support. Such interesting microporous structure is not often visible in MOFs.

The X-ray crystallographic analysis of compound **1** reveals a porous 2D bilayer structure constructed from two identical Cd^{2+} ions bridged honeycomb sheets. There are one and a half Cd^{2+} ions, a BTB ligand and two coordinated DEF molecules in the asymmetric unit. Both the crystallographically unique Cd^{2+} ions are six coordinated by oxygen atoms. Cd1 atom lies on an inversion center, which is coordinated by two BTB ligands and their inversion-related species as well as by one DEF molecule and its inversion-related molecule. Thus, Cd1 is coordinated by four oxygen atoms from four BTB ligands and two oxygen atoms from two DEF molecules with an octahedral geometry. Cd2 is coordinated by five oxygen atoms from three BTB ligands and an oxygen atom of a DEF molecule with distorted octahedral geometry (ESI, Fig. S2).† The Cd–O bond lengths range from 2.173(3) Å to 2.374(3) Å. The BTB ligand acts as a μ_5 -bridge to link five Cd^{2+} ions together, in which three carboxylate groups adopt a chelating, μ_2 - η^1 : η^1 -bridging mode and μ_2 - η^2 : η^1 -bridging mode, respectively (Scheme 1).

In the framework of compound **1**, the Cd2 centers are linked by BTB ligands to give rise to a 2D honeycomb layer with large hexagonal cavities (Fig. 2a). In the view of topology, this layer can be simplified as a (6, 3) net (Fig. 2b), treating the Cd2 centers and BTB ligands as nodes. Two parallel honeycomb layers are further bridged to generate a bilayer structure by Cd1–O2 bonds (Fig. 2c). Each honeycomb layer is offset from the next layer by approximately half of the hexagonal width. Notably, the bilayer structure is based on symmetric carboxylate bridged $\{\text{Cd}_3\}$ clusters with Cd...Cd distance of 3.878 Å. Each $\{\text{Cd}_3\}$ cluster connects to six BTB ligands while each BTB ligand connects to three $\{\text{Cd}_3\}$ clusters. Therefore, treating the $\{\text{Cd}_3\}$ clusters and BTB ligands as nodes, the bilayer sheet can be specified as a 2D (3, 6) connected CdCl_2 -type net with $(4^3 \cdot 4^6)$ symbol

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† Electronic supplementary information (ESI) available: Materials synthesis and activation details, crystallographic information, powder-XRD pattern, SEM characterization, TGA curves, elemental analysis, FTIR pattern, and nitrogen adsorption isotherm of crystal **1**. CCDC reference number 763063. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001485k



Scheme 1 Coordination mode of BTB 3^- ligand in the structure of **1**

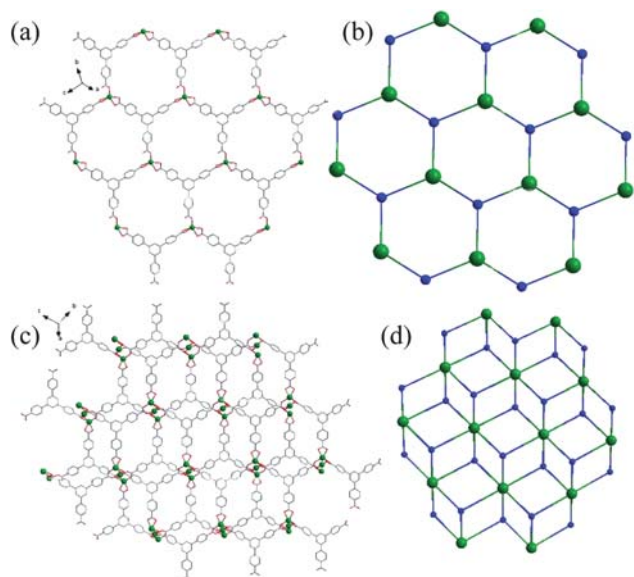


Fig. 2 (a) The honeycomb layer with hexagonal cavities in **1**; (b) topology view of the honeycomb layer with (6,3) net; (c) the bilayer structure based on $\{Cd_3\}$ clusters; (d) topology view of the bilayer treating the $\{Cd_3\}$ cluster and BTB ligands as nodes.

(Fig. 2d). Comparing against this 2D $CdCl_2$ topology type, MOF-177 displays 3D (6,3) net regarding Zn_4O clusters and BTB ligands as nodes, which was termed as **qom** type, related to the **pyr** type;¹⁶ while MOF-39 produces a 3D (3,4) network or a decorated-expanded (3,6) network considering Zn_3O clusters and BTB ligands as nodes.¹⁷

These 2D bilayer sheets are further stacked together in a repeating fashion to form a 3D supramolecular structure with two kinds of rhombus channels along the *a*-axis: the large one (A) has approximate dimensions of $8.45 \times 8.45 \text{ \AA}$ and the small one (B) has approximate dimensions of $8.16 \times 8.16 \text{ \AA}$ after removing coordinated DEF molecules (Fig. 3).

To remove the coordinated DEF molecules, **1** was immersed in a mixture of acetone and dichloromethane for a few days, then filtered and activated in a vacuum oven. TGA data indicate that all coordinated DEF molecules can be removed from **1** at 210°C , and thermal stability of the crystal is up to 410°C as shown in Fig. 4. The comparison of FT-IR patterns (ESI, Fig. S5)[†] for as-synthesized compound **1** and activated sample confirms the successful removal of DEF molecules as well. The C=O bond in a DEF molecule has a reduced bond order compared to the carboxylic group due to the nitrogen atom. The stretching frequency of C=O in DEF is lower than that of an unsubstituted C=O bond, which is usually around

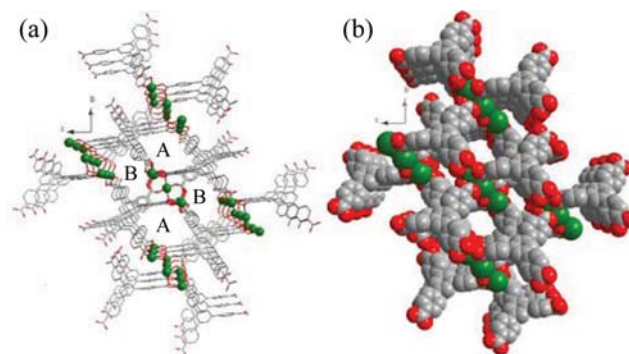


Fig. 3 The 3D supramolecular structure of compound **1** showing two kinds of channels (A and B).

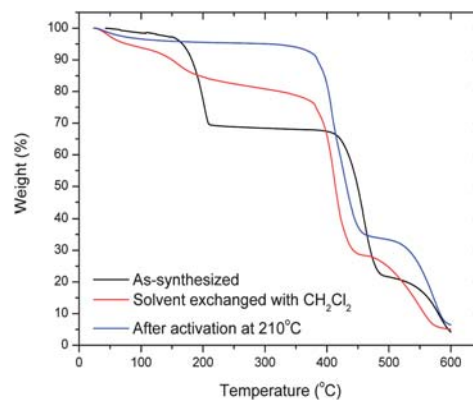


Fig. 4 TGA trace of compound **1**.

1710 cm^{-1} for saturated carboxylic acids. Thus, for as-synthesized compound **1**, the existence of a strong peak at 1650 cm^{-1} indicates C=O in DEF molecule. Furthermore, the disappearance of the peak at 1650 cm^{-1} in the FT-IR pattern of activated compound **1** confirms the removal of DEF molecules after activation. This FT-IR pattern change can also be seen in $[Zn_9O_3(2,7\text{-ndc})_6(\text{DMF})_3]^{12a}$ and $[\text{Mn}(\text{NDC})(\text{DEF})]_n$.¹⁸ After DEF molecules are successfully removed, the Cd centers have open coordination sites that are accessible to incoming sorbate molecules and can influence gas storage, adsorption separations, and catalysis.

The adsorption isotherm for nitrogen at 77 K in activated compound **1** is presented in Fig. 5. The isotherm is similar to the type-IV isotherm according to BDDT classification. As shown in the figure, the micropore is filled quickly at low pressure. From the second to third adsorption points (relative pressure of 0.05 to 0.075), a steep slope on the isotherm indicates that capillary condensation is occurring in the mesopores. With further increase in pressure, a reproducible, step-style adsorption isotherm develops, which indicates the existence of mesopore and macropore size distribution in the crystals. The N_2 isotherm demonstrated a hysteresis loop upon desorption. Such hysteresis phenomena have also been observed in other porous MOFs.¹⁸ The BET surface area is calculated as $504 \text{ m}^2 \text{ g}^{-1}$, while total pore volume is $0.35 \text{ cm}^3 \text{ g}^{-1}$.

In conclusion, a novel MOF material $[Cd_3(\text{BTB})_2(\text{DEF})_4]_n \cdot 2n\text{-DEF}$ (**1**) with unsaturated metal centers has been synthesized. This material exhibited an interesting microporous structure as shown by SEM characterization. TGA trace confirmed that the thermal

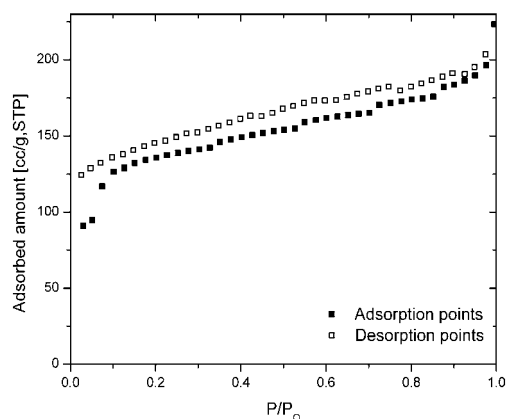


Fig. 5 N₂ isotherm of activated compound **1** at 77 K.

stability is up to 410 °C. In addition, after activation under heating and vacuum conditions, coordinated DEF molecules on Cd metal sites can be removed to obtain unsaturated metal centers (UMCs) which is confirmed from TGA data and FT-IR patterns. Finally, N₂ isotherm at 77 K demonstrated the porosity of this material, which possesses BET surface area of 504 m² g⁻¹ and total pore volume of 0.35 cm³ g⁻¹.

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Notes and references

† Crystal data: C₇₄Cd₃O₁₆N₄H₇₄, $M = 1612.66$, triclinic, space group $P\bar{1}$, $a = 10.4595(9)$, $b = 14.3920(13)$, $c = 14.7634(13)$ Å, $\alpha = 69.6080(10)$, $\beta = 82.4760(10)$, $\gamma = 88.0430(10)$, $U = 2065.0(3)$ Å³, $T = 193(2)$ K, $D_c = 1.297$ g cm⁻³, $Z = 1$, $F(000) = 818$, $R_{\text{int}} = 0.0300$, 22 830 reflections collected, 11 602 unique. GOF = 1.040, $\mu = 0.825$ mm⁻¹, $R_1(wR_2) = 0.0698$ (0.1471) for total 11 602 reflections and $R_1(wR_2) = 0.0562$ (0.1389) for 9303 reflections with $I > 2\sigma(I)$.

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