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Open metal sites dangled on cobalt trigonal prismatic clusters within porous MOF for CO_2 capture†

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Open metal sites are devised to dangle on cobalt trigonal prismatic secondary building units (SBUs) of a porous MOF, when a rigid octacarboxylate ligand, 1,3,6,8-tetra(3,5-dicarboxylphenyl)pyrene, assembled with $Co(NO_3)_2$ under solvothermal conditions. The functional role of dangled open metal sites is exploited for CO_2 capture studies.

Over the last two decades, metal–organic frameworks (MOFs)[1] have been established as a promising type of porous material that have revolutionized the fields of materials science and adsorbent development since their discovery. Built from metal ions or *in situ* generated clusters (also known as secondary building units (SBUs)) and organic ligands, MOFs have been bestowed with the distinctive features of designability and modularity, which means that a desired framework can thus be targeted by judicious selection of the SBU and organic ligand.[2] Furthermore, the modularity of MOFs implies that their properties (for example, pore size, pore walls and surface area) can also be fine-tuned by custom design of organic ligands on the basis of certain SBUs.[3] Their features such as designability of structures, and tunability of properties by virtue of crystal engineering strategies[4] endow MOFs with great potential for practical applications in a variety of areas, such as gas adsorption,[5] gas separation,[6] heterocatalysis,[7] sensors[8] and others.[9]

Amongst more than 20 000 structures studied, a large number of them remains, however sustained by only a handful of highly symmetrical SBUs, predominated by octahedral $[Zn_4O(COO)_6]$, square paddlewheel $[Cu_2(COO)_4]$ and trigonal prismatic $[M_3(\mu_3\text{-}O)(COO)_6]$ (M = Cr, Fe, Mn, Ni, In and others) clusters.[2,10] Given that the $[M_3(\mu_3\text{-}O)(COO)_6]$ SBU (Fig. 1(b)) demonstrates remarkable robustness and stability, the trigonal prismatic cluster facilitates a plethora of prototype polyhedral nets and highly porous materials, as exemplified by MIL-100 and MIL-101.[11] However, according to CSD search, there are very limited porous MOF structures by virtue of the $[Co_3(\mu_3\text{-}O)(COO)_6]$ cluster as the SBU to build MOF networks.[12] In this contribution, we report a unique example of a porous MOF (labelled as **1**) assembled from $[Co_3(\mu_3\text{-}O)(COO)_6]$. The extra open metal sites are observed for the first time to be dangled on the cobalt trigonal prismatic clusters, which provide active interaction towards guest molecules and other species. CO_2 adsorption studies are thus exploited on these interesting porous MOFs, featuring dangled open metal sites.

Purple block-shaped crystals of **1** were obtained by reacting $Co(NO_3)_2{\cdot}6H_2O$ with the 1,3,6,8-tetra(3,5-dicarboxyphenyl)pyrene (H_8tdcppy) ligand (Fig. 1(a))[13] in a solvent mixture of *N*,*N*-dimethylformamide (DMF)–methanol–H_2O under solvothermal conditions for 36 hours (see ESI†). Single-crystal X-ray diffraction analysis conducted at the Advanced Photo Source, Argonne National Laboratory revealed that **1** crystallizes in the space group of *Pnma*.‡ Close inspection of the structure of **1** indicates that an exceptional type of trigonal prismatic cluster is employed as the mono-SBU to merge into a three-dimensional (3D) framework. A conventional trigonal prismatic SBU is composed of three octahedrally coordinated metal ions linked to a central oxygen ion in a planar environment, serving as 3-, 6-, 9-connected nodes. It is worth mentioning here that three open metal sites of the trigonal prism of **1** are occupied by disordered solvent molecules, providing oxygen atoms as binding sites. Exceptionally, in **1**, two partially occupied cobalt

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‡ X-ray crystal data for **1**: $C_{56.15}H_{18}Co_4N_{2.65}O_{24.68}$, f_w = 1360.22, orthorhombic, *Pnma*, a = 33.152(2) Å, b = 14.4302(10) Å, c = 14.0799(10) Å, Z = 4, T = 100(2) K, ρ_{calcd} = 1.341 g cm^{-3}, $R_1(I > 2\sigma(I))$ = 0.0705, wR_2 (all data) = 0.2175, CCDC 1031895.

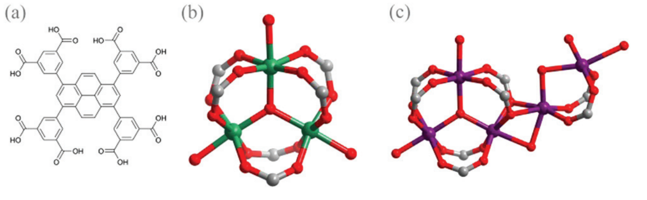

Fig. 1 (a) 1,3,6,8-Tetra(3,5-dicarboxyphenyl)pyrene (H_8tdcppy) ligand used to construct **1**; (b) $[M_3(\mu_3\text{-O})(COO)_6]$ SBU (M = Cr, Fe, Mn, Ni, In and others); (c) open metal sites dangled on the cobalt trigonal prismatic SBU of **1**.

sites are dangled around the trigonal prismatic cluster (Fig. 1(c)), which consists of trimeric cobalt cations interconnected by six carboxylate groups from six different tdcppy ligands and bridged by a μ_3-O in the centre. The neighbouring Co4 with 0.61 occupancy coordinates to six oxygen atoms, two of which are ligated by two μ_2-O from the carboxylate group of the trigonal prism, two from another two independent carboxylate groups of two different tdcppy ligands, and two from the μ_2-O of the disordered bridging solvents. The other adjacent Co site (split into Co5 (occupancy = 0.20) and Co6 (occupancy = 0.20)) is not only bridged by the two independent carboxylate groups with Co4, but also linked by a μ_2-O of the disordered bridging water with Co4. In addition, the corresponding fourth and fifth coordinated oxygen atoms to this Co site come from the solvent molecules. While eight carboxylate groups coordinatively bind to each of the cobalt multinuclear cluster (distorted cobalt trigonal prism), they are provided by only six individual tdcppy ligands. In terms of the octacarboxylate ligand of tdcppy, six carboxylate groups participate in composing the regular parts of six trigonal prismatic clusters and two carboxylate groups functionalize in bridging the dangled cobalt sites.

Topologically, **1** can be described as a binodal nia network derived from TOPOS analysis,[14] in which each distorted cobalt trigonal prismatic SBU, serving as a 6-connected trigonal prismatic node, is bridged by six tdcppy ligands serving as the 6-connected octahedral nodes. As demonstrated, combining the rather robust trigonal prismatic cluster with the rigid tdcppy ligand, the framework of **1** is generated to be a porous 3D structure (shown in Fig. 2(a) and (b)) with certain expected robustness. Meanwhile, the combination of the default robust SBU and the rigid ligand compromises with each other, ending up with the "flexible" adapted or distorted metal clusters, as further exemplified by the previously reported MMPF-2.[15]

The phase purity of **1** was verified by powder X-ray diffraction (PXRD) studies, which indicate that the diffraction patterns of the fresh sample are consistent with the calculated ones (Fig. S1, ESI†). Thermogravimetric analysis (TGA) was performed on the fresh sample of **1** (Fig. S2, ESI†). A continuous weight loss of ~34% from 25 °C to ~90 °C is observed, corresponding to the loss of guest solvent molecules trapped in the cavities of **1**. The plot is followed by a relatively steady plateau from 90 °C to 190 °C. Before its decomposition at ~420 °C, the TGA plot shows a two-step slow weight loss from ~61% to ~43%, which corresponds with the monodentate and bidentate guest solvent molecules, respectively. TGA studies were also conducted on the activated sample of **1**. It reveals that a continuous weight loss of ~15% from 25 °C to 120 °C, which originates from the absorbed moisture, while the activated sample is exposed to the air prior to the TGA test. Then the plot is followed by a constant plateau until 420 °C before complete collapse of the framework. This result underlines the high affinity of the dangled open metal sites to the moisture, and highlights the robustness of the structure of **1**. Furthermore, this also confirms that the activation has removed guest species or coordinated solvent molecules from the sample of **1**.

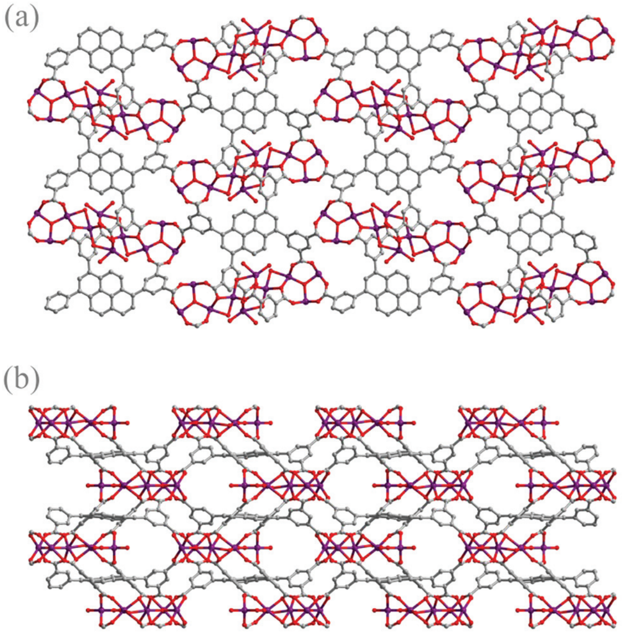

Fig. 2 (a) The structure of **1** viewed along the *b* direction and (b) the structure of **1** viewed along the *c* direction.

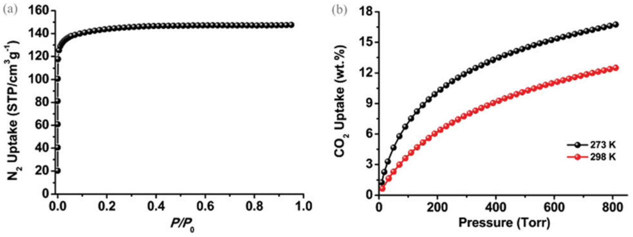

Fig. 3 (a) N_2 adsorption isotherm of **1** at 77 K and (b) CO_2 adsorption isotherms of **1** at 273 K (black) and 298 K (red).

To examine the permanent porosity of **1**, gas adsorption studies were performed on the above-mentioned activated sample. As shown in Fig. 3(a), the N_2 adsorption isotherm collected at 77 K indicates that **1** exhibits an uptake capacity of ~147 $cm^3\ g^{-1}$ at 1 atmospheric pressure with typical type-I adsorption behaviour of microporous materials. On the basis of the N_2 adsorption data at 77 K, **1** possesses a Brunauer–

Emmett–Teller (BET) surface area of ~554 $m^2\ g^{-1}$ (P/P_0 = 0.0001–0.1), corresponding to a Langmuir surface area of ~625 $m^2\ g^{-1}$ (P/P_0 = 0.0001–0.1). Density functional theory (DFT) pore size distribution analysis (Fig. S3, ESI†) based on the N_2 adsorption data at 77 K reveals that the pore size of **1** is narrowly distributed at around 8.0 Å and 11.0 Å, which is in good agreement with the width of the channels observed in the crystal structure from *b* and *c* axes, respectively.

It has been well-documented that open metal sites (unsaturated metal centers) in porous MOFs play a crucial role in increasing gas binding affinity, facilitating gas selectivity and creating catalytically active centers.[16] However, the dangled metal sites in this case, as a peculiar type of open metal site, are rarely discussed and explored. Thus these dangled open metal sites on the trigonal prism prompted us to exploit their functional role in CO_2 uptake performances, which provided the high affinity of the activated sample to the moisture. As shown in Fig. 2(b), **1** can adsorb substantial amounts of CO_2 with the uptake capacities of 16.4 wt% (83.5 $cm^3\ g^{-1}$) at 273 K and 12.1 wt% (61.6 $cm^3\ g^{-1}$) at 298 K under 1 atmospheric pressure. Considering the practical conditions of atmospheric pressure and room temperature, **1** exhibits a comparable uptake value to the prototype NH_2-MIL-53(Al) that features highly active amine groups (12.0 wt%, 298 K, 1 atm)[17] but is moderate compared to some highly porous MOFs[6a,18] due to the low surface area of **1**. However, the shape of CO_2 adsorption isotherms manifests the relatively strong interactions between the framework of **1** and CO_2 gas molecules.[19] The heats of adsorption (Q_{st}) of CO_2 for **1** were calculated based on CO_2 adsorption isotherms at 273 K and 298 K using the virial method. As shown in Fig. S4, ESI,† the Q_{st} of **1** is steadily yet slowly dropped from the initial value of ~30 kJ mol^{-1} to ~27 kJ mol^{-1} at high loadings, which distinguishes itself from other MOFs decorated with primary amine groups or open metal sites, whose Q_{st} usually decreases abruptly to 20–22 kJ mol^{-1} with the increase of CO_2 loading.[20] This can be tentatively attributed to the high density of open metal sites allocated on the limited accessible surface of **1**.

In summary, a porous MOF, **1**, has been assembled from the cobalt-based trigonal prismatic SBU and the rigid pyrene-derived octacarboxylate ligand, which features open metal sites dangled on the trigonal prism. **1** represents the first porous MOF constructed by cobalt-trigonal prismatic clusters. **1** exhibits permanent porosity with a Langmuir surface area of ~625 $m^2\ g^{-1}$, and demonstrates high affinity to CO_2 gas molecules. The strategy of employing a rigid organic ligand with a default robust SBU opens up a tentative way to build some "flexible" adapted or distorted SBU.

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