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A Three-Dimensional Porous Metal−Organic Framework Constructed from Two-Dimensional Sheets via Interdigitation Exhibiting Dynamic Features

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A three-dimensional porous metal−organic framework (PCN-18) was constructed through interdigitating two-dimensional grid sheets composed of 4,4′-(anthracene-9,10-diyl)dibenzoate and copper paddlewheel secondary building units, and its dynamic features were evidenced by gas sorption isotherms.

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The past decade has witnessed the rapid development of metal−organic frameworks (MOFs)[1] as a new type of material that exhibits great potential for applications in gas storage,[2] gas separation,[3] and catalysis.[4] Meanwhile, the advancement of crystal engineering has made it possible to synthesize predetermined MOF topologies with one- (1D), two- (2D), or three-dimensional (3D) networks through judicious selection of the organic linkers and metal ions or metal clusters [also known as secondary building units (SBUs)].[5]
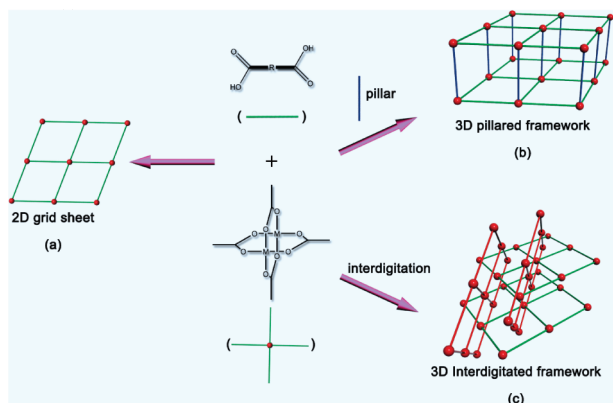
The preparation of many 3D pillared MOFs based on the paddlewheel metal cluster $M_2(COO)_4$ (M = Cu, Co, Zn, Mn, etc.) joined by bicarboxylate ligands in two dimensions and bidentate linkers in the third dimension presents a well-documented example of topological prediction (Scheme 1b).[6] The assembly of linear ditopic carboxylate ligands with paddlewheel SBUs usually generates default 2D grid sheet structures (Scheme 1a), as well illustrated by Yaghi et al.[7]

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Scheme 1. Illustration of Approaches to Constructing a 3D Framework from a 2D Grid Sheet

Figure 1. (a) adba ligand; (b) copper paddlehweel SBU.

Linking the 2D grid sheets with bidentate pillars (usually N-containing linkers) can lead to 3D frameworks with primitive cubic α-Po topology (Scheme 1b).[6] The dynamic features may usually be imparted by framework interpenetration, which can be achieved via increasing the length of the dicarboxylates or pillars.[8] An alternative approach to building 3D frameworks from the 2D grid sheets, as reported in this contribution, can utilize interdigitation (also known as inclined interpenetration) of multiple 2D nets inclined with respect to each other, generating an entangled network that is 3D overall (Scheme 1c).[9] Herein, we designed a new linear ditopic carboxylate ligand, 4,4′-(anthracene-9,10-diyl)dibenzoic acid (adba; Figure 1a). The assembly of the adba ligand with a copper paddlewheel SBU (Figure 1b) in dimethylacetamide (DMA) afforded a 3D framework, designated as PCN-18 (PCN stands for a "porous coordination network"). PCN-18 is interdigitated by two sets of parallel 2D grid sheets, and the freedom of rotation of the central anthracene ring of the ligand is expected to exert some dynamic features on the framework.

A single-crystal X-ray crystallographic study, conducted using synchrotron microcrystal diffraction at the Advanced Photon Source, Argonne National Laboratory (ANL), revealed that PCN-18 crystallizes in orthorhombic space group *Ibam*.[10] As expected, PCN-18 adopts the well-known copper paddlewheel as the SBU, which serves as the node to connect with adba ligands and extend into 2D grid sheets (Figure 2a), with the terminal aqua ligands pointing out of the 2D sheet plane. The grids of the sheet are not square but rhombic, with an included acute angle[8b] of ~70° and a side length of 19.428 Å. The anthracene rings of each rhombic grid are almost on the same plane with the four dicopper units. The diagonal distances of the rhombic grid are 31.841 and 22.270 Å (atom-to-atom distance), and the distances of the
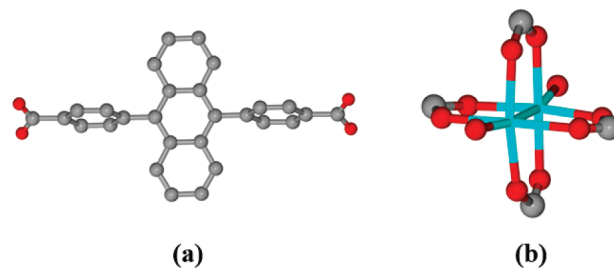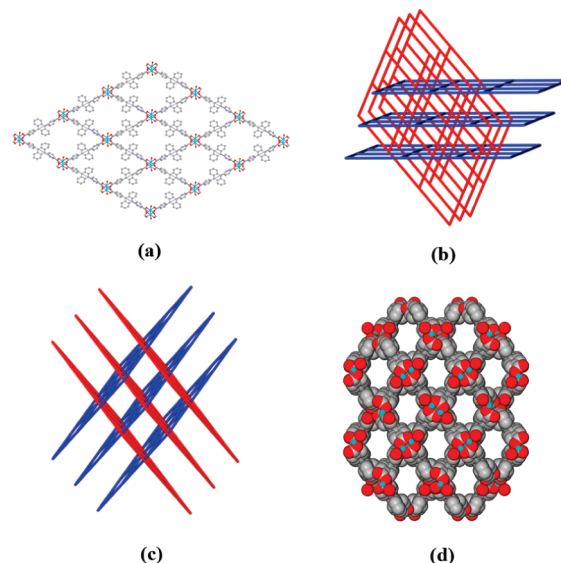

Figure 2. (a) 2D grid sheet formed by adba ligands and copper paddlewheel SBUs; (b) interdigitation of two sets of parallel 2D grid sheets; (c) 1D rhombic channels resulting from entanglement viewing along the (0 0 1) direction; (d) space-filling model of 1D channels along the (0 0 1) direction.

opposite anthracene rings in the grid are 12.092 Å (atom-to-atom distance). The wide opening of the grid not only provides free space for anthracene rings to rotate but also allows the insertion of another sheet. The parallel 2D sheets of one set are displaced with each other half the length of the grid side (as shown for the set of blue 2D sheets in Figure 2b) and are interdigitated with another set of parallel 2D sheets (as depicted for the set of red 2D sheets in Figure 2b) along the long diagonal of every rhombic grid whose center is occupied by the copper paddlewheel node. This interdigitation leads to a layer-by-layer separation of 10.769 Å between every two parallel 2D sheets (Figure S1 in the Supporting Information) and a dihedral angle of 78.659° for every two interdigitated sheets (Figure S2 in the Supporting Information). The two sets of parallel 2D sheets are entangled with each other to form 1D rhombic channels along the (0 0 1) direction (Figure 2c) with a channel size of 10.983 Å × 10.983 Å (atom-to-atom distance). PCN-18 has a total solvent-accessible volume of 50.0%, as calculated using the *SQUEEZE* module of the *PLATON* routine.[11]

To test the permanent porosity of PCN-18, a freshly prepared sample was soaked in methanol to exchange the less volatile DMA solvent, followed by evacuation under a dynamic vacuum at room temperature overnight. As shown in Figure 3a, the desolvated (activated at 50 °C) PCN-18

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(10) X-ray crystal data for PCN-18: $C_{28}H_{18}O_5Cu$, M_r = 497.96, orthorhombic, *Ibam*, a = 13.923(3) Å, b = 17.382(4) Å, c = 31.841(6) Å, V = 7706 (3) Å^3, Z = 8, T = 100 K, ρ_{calcd} = 0.858 g/cm^3, R1 [$I > 2\sigma(I)$] = 0.0756, wR2 = 0.1877, GOF = 0.916. CCDC reference number for PCN-18: 708306.

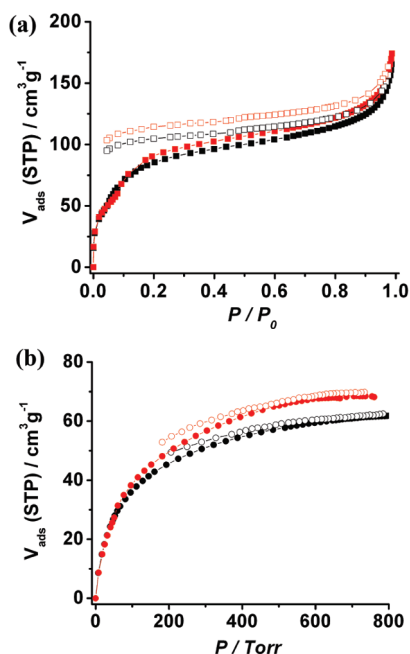(11) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.

Figure 3. Gas sorption isotherms of PCN-18 at 77 K: (a) dinitrogen; (b) dihydrogen. Symbols: solid, adsorption; open, desorption; black, desolvated (activated at 50 °C); red, dehydrated (activated at 150 °C).

sample (black symbols) does not exhibit the classical type I isotherm expected for microporous materials but instead shows significant hysteresis for dinitrogen uptake. These kinds of hysteretic dinitrogen sorption isotherms have also been observed in some other porous MOFs[8,12] and can be attributed to the dynamic features of the frameworks.[13] The dynamic feature of PCN-18 might arise from the interactions between dinitrogen gas molecules and terminal aqua ligands of copper paddlewheel SBUs by initial intuition.[13] However, similar hysteresis can also be observed for dinitrogen sorption isotherms of the dehydrated (activated at 150 °C) PCN-18 sample (red symbols) with the terminal aqua ligands removed. Thus, its dynamic feature should originate from a different source, and we reason that it mainly arises from the rotation of the anthracene rings of the adba ligand allowed by some free space of the structure (Figure S3 in the Supporting Information),[6,14] although the rotation of the two phenyl rings may also contribute partially, as indicated by Férey et al. in the studies of MIL-88.[15] Derived from the dinitrogen adsorption data, dehydrated PCN-18 has a Brunauer−Emmett−Teller surface area of

$381 \ m^2/g$ and a pore volume of $0.26 \ cm^3/g$. The much lower experimental pore volume compared to the theoretically calculated one (0.26 vs $0.64 \ cm^3/g$) can be presumably attributed to the fact that the pores of PCN-18 are not fully open under low pressure.

To investigate the dihydrogen sorption behavior of PCN-18, low-pressure dihydrogen sorption measurements were also performed at 77 K. As demonstrated in Figure 3b, appreciable hysteresis resulting from the framework flexibility can also be observed for dihydrogen sorption isotherms. The less profound dihydrogen sorption hysteresis can be ascribed to the relatively weak dihydrogen−framework interactions.[16] At 77 K and 760 Torr, dehydrated PCN-18 can uptake 70 cm^3/g hydrogen, which is ~15% higher than the desolvated one (61 cm^3/g). This dihydrogen uptake enhancement can be attributed to the exposure of open copper sites resulting from the removal of terminal aqua ligands of SBUs.[17]

In summary, a 3D porous MOF, PCN-18, has been constructed via interdigitating 2D grid sheets based on the adba ligand and copper paddlewheel SBU. The strategy of interdigitation (or inclined interpenetration) reported here paves a new way to achieve a 3D network from 2D sheets in MOFs that are based on linear ditopic carboxylate ligands and paddlewheel SBUs, although this type of inclined interpenetration is well-established outside of ditopic carboxylate chemistry.[9] Gas sorption studies revealed dynamic features of PCN-18 that can be mainly attributed to the free rotation of the anthracene ring of the adba ligand. The investigation of a detailed mechanism for the dynamic features is ongoing in our laboratory.

Supporting Information Available: Experimental procedures for the synthesis of the adba ligand and PCN-18 and structure picture drawings of PCN-18. This material is available free of charge via the Internet at http://pubs.acs.org.

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