Nanoporous Materials

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Network Topology of a Hybrid Organic Zinc Phosphate with Bimodal Porosity and Hydrogen Adsorption**

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In the last decade, the synthesis of nanoporous materials with extended network topologies has advanced extensively owing to the increasing demand for functional materials in applications involving molecular recognition, shape-selective catalysis, fluid separation, and hydrogen gas storage.[1] Until now, two major categories of nanoporous structures have been under intense investigation: one with whole inorganic framework, such as silica-based zeolites, germanates, and phosphorous-based metal oxides; and another with organic–inorganic hybrid frameworks; that is, porous coordination polymers[2] and metal–organic frameworks (MOFs).[3] The largest pore and/or channel opening that has been observed in inorganic frameworks are 18-membered rings (18MR) in silicates,[4] 24MR in metal phosphates,[5] 26MR in metal phosphites,[6] and 30MR in germanates.[7] In the hybrid frameworks, however, the cavities were determined from pore structure analysis based upon gas sorption studies. By using bulky organic units to co-construct the framework, even higher porosity or larger pores can be produced. For example, the pore size found in the framework MIL-101[8] was up to 4.6 nm, and the void space in MOF-177[9] was reported to increase the size of a unit-cell volume by up to 81 %, thus substantially surpassing the volume of inorganic structures.

Exploration of enhanced porosity and even new properties in the inorganic framework have thus been pursued by mediating with organic building units. To date, transforming inorganic frameworks into hybrid frameworks has only been possible in phosphate/phosphite (MPO) systems; few organic molecules are found to be suitable, for example, the smallest oxalate linker and certain polyamine molecules. Encouragingly however, quite a few unique three-dimensional metal oxalatophosphates[10] and pillar-layered organo–metallophosphates (OMPO)[11] have been formed that have extra-large channels with interesting properties. The oxalate-mediated nanoporous gallium phosphates of NTHU-6[10a] or NTHU-7,[10b] with their unprecedented photoluminescence properties, has established a new class of LED color-conversion phosphors. Aryl carboxylates, such as benzene dicarboxylate (bdc) or benzene-1,2,4,5-tetracarboxylate (btec), which are effective organic building units of MOFs or coordination polymers, had not been found to adapt to MPOs until the discovery of $(H_2tmdp)[(ZnHPO_4)_2(bdc)]$ (tmdp = 4,4′-trimethylenedipyridine; NTHU-2),[11a] the first bdc-mediated OMPO compound, in 2004. This compound has gismondine-like inorganic sheets pillared by bdc to give nanometer-sized channels and a remarkable gas sorption behavior; of vital importance, this sorption revealed bimodal pore-size distributions. To gain a deeper insight into the intriguing and useful porous properties, we have focused on the study of carboxylate-incorporated MPO frameworks. Herein we report the first btec-mediated metal phosphate compound, $(Hbpy)[Zn_2PO_4(btec)(Hbpy)_2]$ (bpy = 4,4′-bipyridine), designated NTHU-8. This compound exhibits an unusual network topology (Figure 1), and has porosity and hydrogen gas adsorption that is superior to previously reported OMPOs.

Transparent colorless columnar crystals of NTHU-8 were prepared under mild solvothermal conditions (see Experimental Section). The three-dimensional structure of NTHU-8[12] is built up of two types of tetrahedra (ZnO_3N and PO_4),

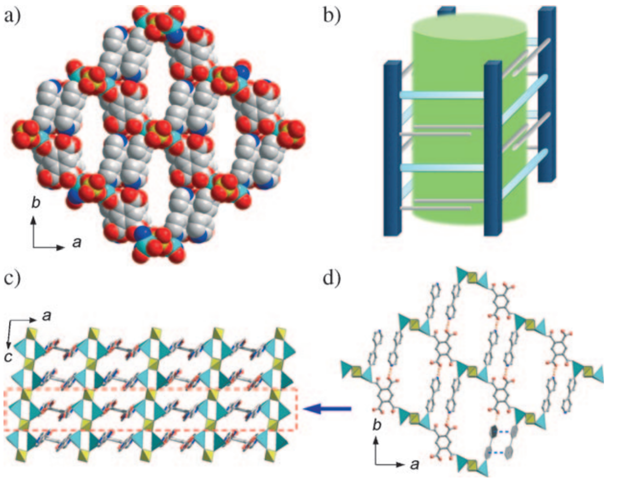

Figure 1. The structure of NTHU-8 Hydrogen atoms are omitted for clarity. a) Space-filling model showing oval-shaped channel windows (Zn cyan, P yellow, O red, N blue, C gray); b) representative drawing showing the one-dimensional inorganic columns ($_\infty[Zn_2PO_4]$ in navy blue) with two organic ligands (btec in cyan and Hbpy in gray); c) view perpendicular to the channel direction; d) section of a two-dimensional hydrogen-bonded sheet (region marked in red in (c)), showing face-to-face π–π pairs formed by Hbpy ligands (blue dashes).

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and two types of organic units, namely anionic btec and monoprotonated bpy (Hbpy).[13] The inorganic part in the one-dimensional $_\infty[Zn_2PO_4]$ column[14] (Figure 1c) is formed of 4MRs of alternate zinc- and phosphorus-containing tetrahedra linked by common corner-shared PO_4 units. In addition to two phosphate oxygen ligands, the outward zinc-containing tetrahedra are each completed by a third oxygen atom from anionic btec and one nitrogen atom from Hbpy. The btec units bridge the two $[Zn_2PO_4]$ columns along *ab* diagonals, whereas Hbpy ligands are terminal, with their protonated ends directed toward proximal btec units on *ab* planes. The hydrogen-bonding to ligand Hbpy (Figure 1d) allows each bis-monodentate btec units to gain two more mimicking linking sites, which connect another two $_\infty[Zn_2PO_4]$ columns along the *b* axis direction. This linking results in two-dimensional hydrogen-bonded sheets running parallel to *ab* planes and the porous sheets stacking along the *c* axis, with two adjacent sheets being symmetry-related by two-fold rotation and interlocking on a common PO_4 unit (Supporting Information, Figure S4).

The structure of NTHU-8 also has an embedded one-dimensional supramolecular chain composed entirely of organic ligands. As depicted in Figure 1d, each Hbpy has a neighboring Hbpy ligand at a distance of 3.52 Å to form an face-to-face π–π pair. Accordingly, organic ligands aligned in the *b* axis direction are either in hydrogen-bonding or in π–π pairs, such that they make up the first supramolecular $[btec(Hbpy)_2]$ chains observed in nanoporous structures. The structure may also be viewed as inorganic $_\infty[Zn_2PO_4]$ columns perpendicular the organic supramolecular chains (Figure 2). The two one-dimensional lattices are interlocked by coordinative $Zn-O_{BDC}$ bonds to give nanometer-sized channels along the *c* axis, with window dimensions of 7.5 Å × 16.5 Å (Figure 1a). Templating Hbpy ions fill in the channels and balance the charge. Usually, bpy molecules tend to remain neutral as bridging linkers.[11b,c] Protonated forms of bpy, especially the monoprotonated, are relatively seldom in phosphate-containing structures. To our knowledge, this dual role of Hbpy has not been observed in porous solids before. Normally, a similar amount of torsion is observed between the two pyridyl rings for neutral bpy molecules, as either template or ligand, with dihedral angles around 25° (Supporting Information, Figure S5).[11c] However, in NTHU-8, the degree of torsion is found to be much different in the ligand Hbpy and template Hbpy, with the dihedral angles being 10.0° and 19.2°, respectively. The decrease in the dihedral angle for the ligand Hbpy may be explained by constraints imposed by both $Zn-N_{bpy}$ bonds and Hbpy–Hbpy π–π pairs in the $\{btec(Hbpy)_2\}$ supramolecular chain.

NTHU-8 is the first OMPO material with both a pyridine derivative and an aryl carboxylate participating in the framework. Based on a combined study of thermal gravimetric anylysis, heat-treatment, and powder X-ray diffraction measurements, the thermal stability of the organic-rich NTHU-8 was found to be similar to the bdc-incorporated NTHU-2: both could sustain heating up to 270°C without structural collapse. Even though these structures are geometrically opposed to each other, the N_2 gas sorption behavior measured for NTHU-8 revealed similar type IV isotherms (Figure 3a) and type H2 hysteresis loop, thus indicating the presence of bimodal pore-size distributions in NTHU-8. BET analysis on the adsorption isotherm for NTHU-8 revealed a surface area of 250 m^2g^{-1} (Langmuir model: 356 m^2g^{-1}), which is more than twice for NTHU-2 (112 m^2g^{-1}). The pore-size distribution with a DFT model resulted in two peaks: a sharp peak at 1.36 nm, and a broad peak centered at about 5 nm (Figure 3b). The dual pores might be attributed to the removal of Hbpy from the structure during template extraction. The conjecture was based on ^1H NMR measurements, which revealed the extracted substances were primarily bpy (Supporting Information, Figure S8). It is worth noting that a preliminary study of hydrogen gas sorption under 1 bar and 77 K revealed about 0.56% H_2 storage capacity for NTHU-8, which is the highest value ever observed in OMPO materials (Supporting Information, Figure S10). Compared to the inorganic ZSM-5, which showed the highest H_2 uptake for zeolite,[15] NTHU-8 exhibits a capacity for H_2 sorption threefold that of ZSM-5 (Figure 3c). Moreover, the steeper slope than for other inorganic metal phosphates (VSB-1 and VSB-5)[16] might indicate a different sorption mechanism in the hybrid material of NTHU-8.

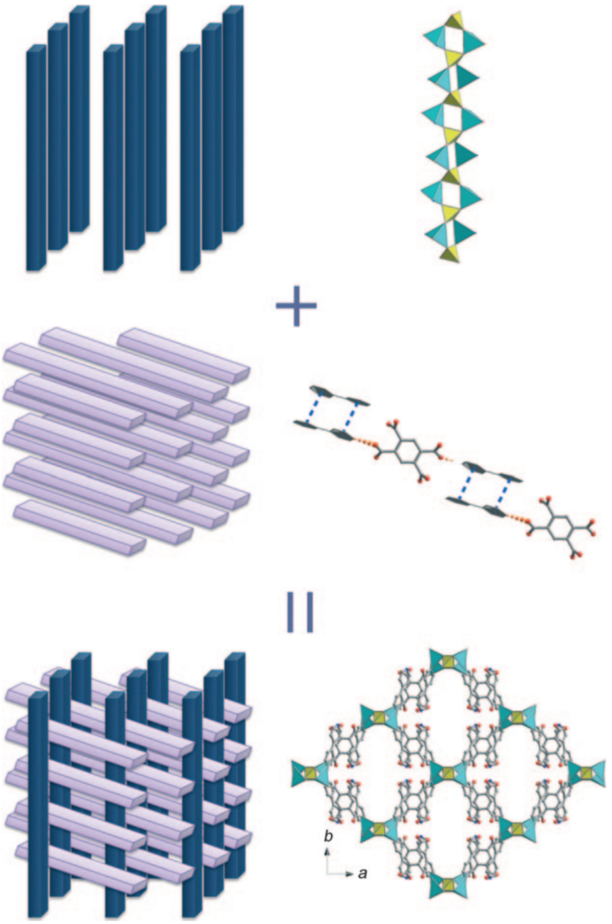

Figure 2. Simplified representation of NTHU-8 showing how the network topology may be built from a one-dimensional inorganic lattice interlinked by one-dimensional supramolecular chains. See Figure 1 for color scheme.

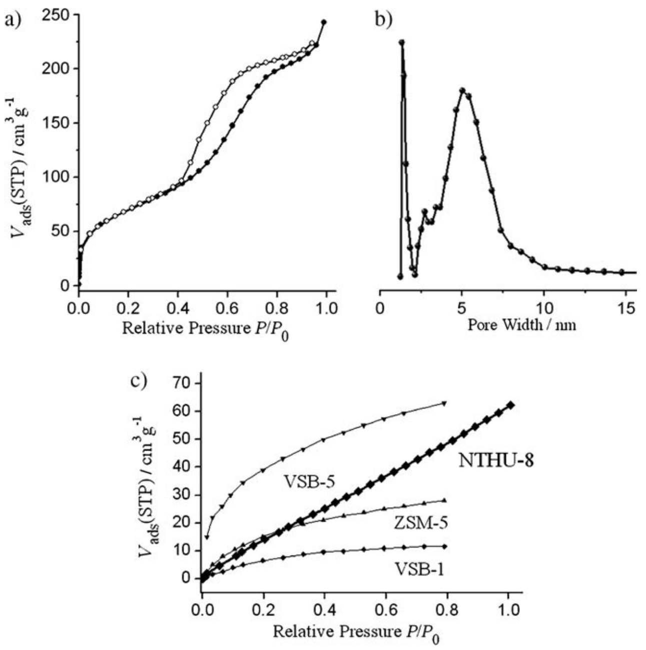

Figure 3. Porous properties of NTHU-8. a) N_2 adsorption (●)/desorption (○) isotherms; b) pore-size distribution derived from the N_2 adsorption isotherms showing bimodal pore distributions; (c) hydrogen uptake for NTHU-8 compared with other microporous materials. STP = standard temperature and pressure.

In conclusion, we have reported the first synthesis of an OMPO three-dimensional framework containing nanometer-sized channels with intriguing bimodal porosity and hydrogen gas storage property that ever observed in zinc phosphates and other OMPOs. The most interesting aspect of the structure is that it is constructed from one-dimensional metal phosphate 4MR columns with a high zinc to phosphorus ratio, and one-dimensional supramolecular chains formed of btec and Hbpy units. The structural topology differs from the pillared-layer type commonly adopted by amine-incorporated OMPOs. Unlike MOFs which can be prepared with a wide choice of organic carboxylates, few OMPOs have been synthesized with aryl carboxylates. One of the key factors for the formation of this functional OMPO appears to be the synergistic effect of the organic ligands btec and Hbpy in that they are strongly hydrogen bonded to each other. This hydrogen bonding also explains why btec is two-connected to zinc centers instead of the typical four-connected pattern.[17] Another factor is a solvent effect, in that DMF was indispensable to create a structure with pyridine and carboxylate coexisting as ligands. Without DMF, a different structure would otherwise result in which bpy acts as template only.[18] Added to the novelty of the NTHU-8 structure is the gas sorption properties, which are superior to conventional inorganic metal phosphate materials. Besides the previously reported NTHU-2, NTHU-8 is the second example of a phosphate structure that has both micropores and mesopores, indicating that bimodal pore-size distributions may be a characteristic of the carboxylate-incorporated MPO system. Moreover, the hydrogen adsorption property of NTHU-8 may be conferred by the availability of intraframework carboxylate moieties. Further studies are necessary to establish the generality of the unique gas sorption property for carboxylate-incorporated OMPO structures.

Experimental Section

Transparent colorless columnar crystals of NTHU-8 were prepared from a reaction mixture containing $Zn(NO_3)_2 \cdot 6H_2O$ (0.2975 g, 1 mmol), H_3PO_4 (0.27 mL, 4 mmol), benzene-1,2,4,5-tetracarboxylic acid (H_4btec; 0.289 g, 1.13 mmol), 4,4′-bipyridine (bpy, 0.312 g, 2 mmol), dimethylformamide (DMF, 5 mL, 65 mmol), and H_2O (5 mL, 278 mmol). The mixture was heated in a 23 mL Teflon-lined autoclave at 180 °C for 1 day. The product was a single phase, with a yield of 80 % based on zinc.

CCDC 723828 (NTHU-8) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

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[12] Crystal data for NTHU-8: Monoclinic, space group $C2/c$, $M_r = 943.36$, $a = 22.8823(6)$, $b = 18.4474(5)$, $c = 9.6823(3)$ Å, $\beta = 95.477(1)°$, $V = 4068.4(2)$ Å^3, $Z = 4$. Intensity data were measured at 293 K, giving 5044 independent reflections with $2\theta_{max} = 56.63°$. Final refinement converged at $R1 = 0.0382$ and $wR2 = 0.0845$ for 3516 reflections with $I > 2\sigma(I)$ and 297 parameters.

[13] The protonated form of bpy was confirmed by ^{1}H NMR data (Supporting Information, Figure S11) and X-ray structure analysis. Only one hydrogen atom per bpy molecule was located on the difference map. Two-thirds of Hbpy played a role as ligand, with the neutral nitrogen atom coordinating to zinc and the protonated nitrogen atom bonding to btec ($d_{N-H\cdots O} = 2.6$ Å; $\sphericalangle N{-}H\cdots O = 176°$). The other one-third of Hbpy acted as a template and counterion, and thus the overall charge of the compound was balanced.

[14] The $_\infty[Zn_2PO_4]$ column in NTHU-8 has the highest zinc to phosphorus ratio (Zn/P = 2:1) of all known one-dimensional zinc phosphate chains.

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[18] A layer structure without bpy coordinating to zinc resulted when DMF was eliminated from the reaction mixture.