

A Zeolitic Organo–Metallophosphate Hybrid Material with Bimodal Porosity

Yueh-Chun Liao, Fen-Ling Liao, Wei-Kuo Chang, and Sue-Lein Wang*

Department of Chemistry, National Tsing Hua University, Hsinchu 30043, Taiwan

Received October 13, 2003; E-mail: slwang@mx.nthu.edu.tw

Zeolites are open-framework aluminosilicates built up by a silica network around certain template molecules that are later removed to leave behind molecular-sized pores.^{1,2} In natural zeolite structures, the largest pore observed is 0.8 nm, found in faujasite, which has 12-membered ring (12R) channels. In the synthetic structure of UTD-1 there are 14R channels, the largest ring prepared in silicates thus far.³ Phosphate-based metal oxides (MPOs) with variable pore sizes up to 24R were reported.^{4–7} Recently, multidentate organic ligands have been incorporated into MPO frameworks for the enhancement of structural adaptability and the efficacy of rational design of crystalline solids through their coordinating propensities and geometries. Oxalate- and bipyridine-type ligands are the common organic variants in the formation of organo–metallophosphate (OMPO) frameworks. They have shown new structural features and interesting properties, yet no porosity has been discovered in OMPO materials.^{8,9}

To prepare porous OMPO materials, large organic amines combined with dicarboxylate-type ligands, which were efficaciously used in the preparation of MOF materials,¹⁰ were adopted in our solvothermal reactions. This has led to the discovery of (H₂tmdp)-[(ZnHPO₄)₂(BDC)] (BDC = 1,4-benzene dicarboxylate or terephthalic anion; tmdp = 4,4'-trimethylene dipyridine), designated as NTHU-2, the first metal carboxylatophosphate compound with a highly porous framework built up with tetrahedral inorganic sheets pillared by BDC groups. According to a literature search, no prior carboxylato-MPO materials have been reported. The magnitude of channel openings in NTHU-2 nearly transcends those in VPI-5 (AlPO, 18R),¹¹ JDF-20 (AlPO, 20R),¹² ASFe-1 (FePO, 20R),¹³ ND-1 (ZnPO, 24R),⁴ NTHU-1 (GaPO, 24R),⁵ and VSB-5 (NiPO, 24R).⁶ Herein, we report the synthesis, structure, sorption, photoluminescence, and dissolution properties and an inverting mixed molecular crystal of NTHU-2.

Transparent brown crystals of NTHU-2 were prepared from the reaction mixture of ZnCl₂, C₁₃N₂H₁₄ (tmdp), *p*-C₆H₄(COOH)₂ (terephthalic acid or BDC), H₃PO₄, ethylene glycol, and H₂O in the molar ratio 1:6.4:1.2:6:107:333 under mild solvothermal conditions.¹⁴ They grew in clumps (Figure 1a) wherein the sword-shaped lamellar crystals were entirely twinned. The conclusive structure¹⁵ was solved and refined using the intensity data collected from a lamellar twin. The 3D anionic framework (Figure 1b) is built up with neutral ZnHPO₄ layers and BDC anions acting as pillars. In the inorganic layers, each ZnO₄ tetrahedron shares three oxygen atoms with HPO₄ tetrahedra, resulting in three-connected two-dimensional nets [4.8²]. A similar 2D topology can be observed in zeolite gismondine, where the porous nets are flat with the SiO₄ tetrahedra around the 8R apertures all pointing to the same direction. Here, the inorganic nets are curved with the sequence of alternating ZnO₄ and HPO₄ tetrahedra being UUUUDDDD (U up, D down). The arching of the layer can be attributed to the fourth Zn–O (O atom from BDC) bond toward the interlayer space. The resulting network has multidimensional intersecting channels running along

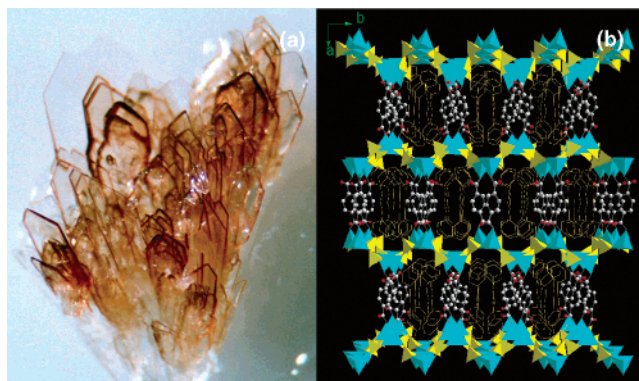


Figure 1. Crystal morphology and 3D plot of the structure of NTHU-2: (a) Brown and white sword-shaped crystals form in clumps. The colors are darker on the edges and brighter near the root; (b) a perspective view along the *c*-axis. The ZnO₄ tetrahedra are indicated in cyan and PO₄ in yellow. BDC units are represented in ball-and-stick model (O, red; C, white). Within channels are the diprotonated tmdp molecules. The H atoms are omitted for clarity.

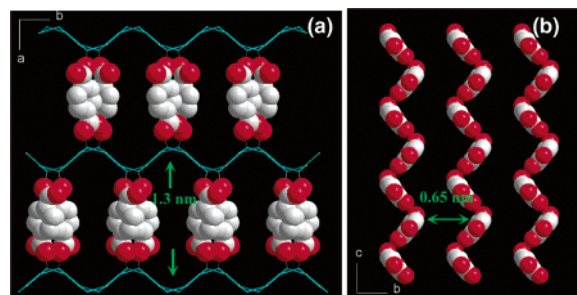


Figure 2. Two views of the channels along *c* in NTHU-2 showing (left) the oval-shaped opening between ZnHPO₄ layers (cyan wires) and adjacent BDC pillars; (right) the zigzag channels flanked by BDC units. All balls are sketched using van der Waals radii.

[011], [111], and all three axial directions with the template H₂tmdp cations locating at channel intersections.

The channels running along *c* are zigzag with spacious interior and oval-shaped opening of 1.3 nm × 0.65 nm (free diameter) on the *ab* plane (Figure 2). The nonframework space in NTHU-2 was calculated to take up to 48% of the unit cell volume.¹⁶ Preliminary TG/DT analyses indicated that a major weight loss occurred at ~300 °C. A single-crystal X-ray structure analysis was performed on a burned crystal (heated at 250 °C in air for 4 h), and the result indicated nearly unaltered cell constants and an unchanged framework but partial occupancies for the template molecules. To further evacuate tmdp molecules from the structure for BET pore surface area and pore structure analysis, another sample was heated at 250 °C under vacuum (~10⁻³ Torr) for 22 h. Nearly 50% of amine template along with BDC pillar was evacuated under this condition.¹⁷ In contrast to the type 1 isotherm for microporous materials, the sorption of N₂ gas revealed a reversible type 4 isotherm with a

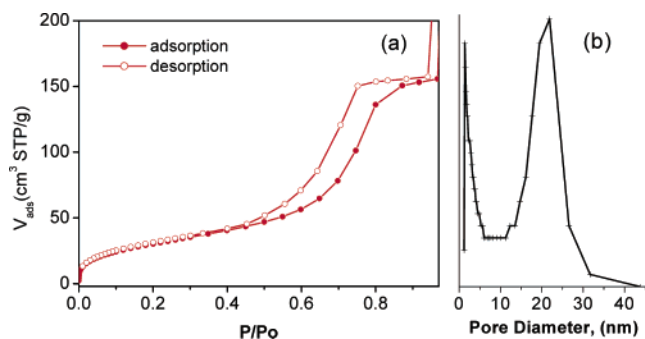


Figure 3. Gas sorption analysis on a sample treated at 250 °C. (a) Nitrogen gas sorption isotherms at 77 K, showing type H2 hysteresis loop (b) PSD derived from the adsorption isotherm, showing a micropore contribution at 1.36 nm and a mesopore contribution at 21.8 nm.

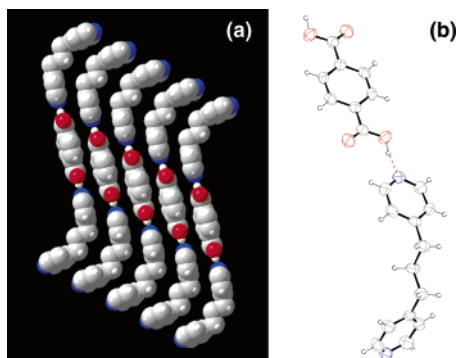


Figure 4. The mixed-crystal generated from NTHU-2. (a) The molecules of 4,4'-trimethylenedipyridine and terephthalic acid are packing in a face-to-face/center-to-edge geometry. (b) An ORTEP drawing showing H bonds (dashed lines) connecting the acid and amine molecules.

type H2 hysteresis loop¹⁸ for NTHU-2 (Figure 3a). The surface area from BET analysis is 112 m² g⁻¹, which is the highest surface area reported to date for anionic MPO frameworks. The data from the adsorption isotherm was fitted to a Horvath–Kawazoe differential pore/volume plot (Figure 3b), which showed not only one sharp peak at a pore radius of 1.36 nm but also a broad peak at 21.8 nm, suggesting bimodal porosity. These results indicate that NTHU-2 contain both micro- and mesopores. The extra-porosity may be attributed to the presence of defect sites (absence of templates and pillaring BDC units) in the framework upon heating. This may correspond to the mesoporosity created in postsynthesis treatments of parent zeolites such that the gas transport characteristics are improved.¹⁹

NTHU-2 exhibits intense blue photoluminescence upon photoexcitation at 280 nm.²⁰ The emission spectra measured at room temperature showed a maximum at ca. 478 nm. The solid is stable in air for months, insoluble in common nonpolar solvents, but slightly dissoluble in water. The brown colors on the crystals of NTHU-2 would begin to diminish due to the dissolution of the clumps (Figure 1a) in the water. Some transparent crystals started to develop around the clumps, grew larger and ampler, and began to suspend in water within days. Crystallographic analysis on one of the crystals revealed a monoclinic structure of mixed 4,4'-tmdp and terephthalic acid in the ratio 1:1 (Figure 4), indicating both template amines and pillaring BDC units discharged from NTHU-2. The intimate 1:1 acid–base type of mixed crystals has not been reported previously.²¹ As to the inorganic residues, a powder X-ray diffraction analysis revealed it to be a crystalline mixture of unknown phases.

In conclusion, the synthesis and characteristics of the first zeolitic phosphate-based organic–inorganic hybrid material are described. NTHU-2 contains the largest genuine pores ever observed in metal silicates and anionic phosphate frameworks. Partial evacuation of amine templates and pillars would result in micropores as well as mesopores, as indicated by the type 4 isotherm character associated with H2 loop. Two pore diameters peaked separately at 1.36 and 21.8 nm, clearly reveal the bimodal porosity. Crystals of NTHU-2 are also photoluminescent and can disassemble in the water to give a unique acid–base type of mixed crystals, providing a novel mode for the engineering of molecular crystals²² and recovering organic reagents.

Acknowledgment. The work was supported by the National Science Council of Taiwan (92-2113-M-007-029).

Supporting Information Available: X-ray crystallographic file, in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (14) The reaction mixture was placed in a Teflon-lined Parr bomb (60% filling) and heated at 160 °C for 5 days. The resulting product contained brown crystals of NTHU-2 with an optimum yield up to ~70% (based on Zn) and a small quantity of unknown phase. EPMA data confirmed the Zn:P ratio to be 1:1 for the brown crystals and the results of EA confirm the organic content. Found/calcd. (%): C, 36.86/36.71; N, 4.20/4.08; H, 3.40/3.23.
- (15) Crystal data for NTHU-2: Zn₂P₂O₁₂N₂C₂₁H₂₂, monoclinic, space group P2₁/c; *a* = 27.581(4) Å, *b* = 9.111 (1) Å, *c* = 9.979(2) Å, β = 92.213-(3)°, *V* = 2505.9(7) Å³, *Z* = 4, *M_r* = 687.0, *R*₁ = 0.0767. The structure was solved and refined on intensity data of a twinned crystal. It exhibits nonmerohedral twinning with contributions of the twin components being 0.33:0.67.
- (16) The calculation was performed by a PLATON analysis. Ref: Spek, L. *Acta Crystallogr., Sect A* **1990**, *46*, C34.
- (17) EA results for NTHU-2 degassed at 250 °C: Found (%): C, 25.27; N, 2.69; H, 2.72. Powder XRD pattern revealed that the framework of NTHU-2 was sustained.
- (18) Type 4 isotherm is a typical behavior of mesoporous materials with the hysteresis indicative of reasonably large pores (*d* ≥ 4 nm). Also see Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*; Academic Press: New York, 1981; Chapters 3, 4–4.
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- (20) It was found that tmdp itself was neither photoexciting nor emitting, whereas BDC was luminant at 402 nm.
- (21) This 1:1 tmdp/BDC is a neutral molecular crystal instead of salt. Different acid–base type cocrystals were prepared by self-assembly. They have different ratios and components. (cf. Kapildev K. et al. *J. Org. Chem.* **2003**, *68*, 9177–9185.)
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JA0390146