Polyamine-Cladded 18-Ring-Channel Gallium Phosphites with High-Capacity Hydrogen Adsorption and Carbon Dioxide Capture

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S *Supporting Information*

ABSTRACT: In this study, we synthesized a unique inorganic framework bearing the largest 18-membered-ring channels in gallium phosphites, denoted as NTHU-15, which displayed genuine porosity even though large organic templates were present. The idea of using the "template-cladded" strategy succeeded in releasing channel space of up to ~24% of the unit-cell volume as highly positive-charged organic templates were manipulated to cling to the anionic inorganic walls. NTHU-15 showed both high H_2 uptake of 3.8 mmol/g at 77 K and effective CO_2 adsorption of ~2.4 mmol/g at 298 K, which surpassed those of all other known extra-large-channel inorganic framework structures. NTHU-15 has been successful at overcoming the long-standing problem of organic-templated extra-large-channel structures as opposed to a "true open" framework. Moreover, it realized practical gas sorption functionality in innovated metal phosphites. In view of its high stability in hot water and high selectivity for CO_2 adsorption, NTHU-15 may be the first novel inorganic framework material to be applied to the field of flue gas cleaning.

In the last three decades, synthetic research on crystalline porous solids has grown rapidly, and various chemical systems with extraordinary novel structures[1] and versatile functions[2] have been created. These chemical systems have influenced the development of advanced technologies for dealing with increasingly urgent problems, such as hydrogen storage and carbon dioxide capture.[3] Advancements in this field began with the study of purely inorganic frameworks of aluminophosphates,[4] followed by other group 13 elements and transition-metal phosphate/phosphite systems (MPOs),[5] germanium oxides,[6] and, more recently, metal−organic frameworks (MOFs).[7] All of these systems are manipulated using organics as the common measure to induce porosity, despite the dissimilarity in connectivity. The formation of desired pores is far more difficult to control in the inorganic framework systems than in MOFs because the organics are not a building unit in the former. Innovations in the field of novel porous topology and new applications are therefore slower for purely inorganic systems. Recent breakthroughs were made with a zincogallium phosphite system, NTHU-13,[1b] which has shown success in rational-design synthesis as well as drastic improvement in pore diameters from the microregime to the mesoregime. However, NTHU-13 has not shown a significant improvement in sorption properties. Even previously known MPO structures with extra-large channels have not shown the expected "real porosity".

The problem with novel MPOs lacking porosity is that, unlike aluminosilicates and aluminophosphate zeolites, they are not stable enough to withstand postsynthetic treatments, such as ion exchange or calcination. Filling of the pores/channels with large templates often results in little free space within the structure. A prior study[8] showed that using a small surfactant-type template could produce a hydrophobic space for receiving solvent molecules, e.g., ND-1. However, the likelihood is very low that a small template that can minimize channel obstruction on the one hand as well as can create the desired large pores on the other hand. The use of increasingly large templates is a necessity, especially when it comes to the rational synthesis of extra-large-channel structures. Therefore, choosing smaller templates may not conquer the main problem of lacking porosity.

Remarkably, while non-covalently linked organic templates can obstruct channels, they can also interact with inorganic frameworks to yield interesting properties and unexpected functionality. For instance, MPOs containing certain protonated template cations exhibit tunable yellow-to-white photoluminescence, such as the first lanthanide-free nanoporous MPO solids, which are used as light-emitting diode (LED) color-conversion phosphors.[9] The organic templates were also observed to enhance the affinity of the structures for polar gas molecules, as some mesoporous materials with amine loading showed an improvement in CO_2 capture.[10] This suggests that the presence of amine-type templates may be an advantage, especially if the CO_2 adsorption property is to be pursued in MPOs. Therefore, it is important to explore other ways to increase the porosity without actually removing the templates.

We speculated that free space inside the channels would be created if the organic template were pushed toward the inorganic channel walls. This process would require strong interactions between the templates and the walls. In 2005, we reported a two-dimensional structure of a zinc phosphate, NTHU-3,[11] in which triprotonated amine templates were anchored on both sides of negatively charged inorganic sheets of $[Zn_3(PO_4)_4]^{6-}$. This formed compact composite layers with a neutral interlayer space. This space caused water hexamers to exist in an isolated discrete state. It is conjectured that besides lamellar systems, such compressed template−host composites

could be replicated in a channel system. Templates of highly charged and resilient skeletons may be required to produce strong interactions with the wall. Therefore, we chose long-alkyl-chain polyamines, i.e., tetraethylenepentamine with five amino groups (TEPA, 5N) and pentaethylenehexamine with six amino groups (PEHA, 6N), as templating reagents. Using these potential templates in a suitable solvent system, we successfully synthesized a unique 18-membered-ring (18R) channelled system composed of gallium phosphites, designated as NTHU-15 (Figure 1). The 18R channels are filled with large
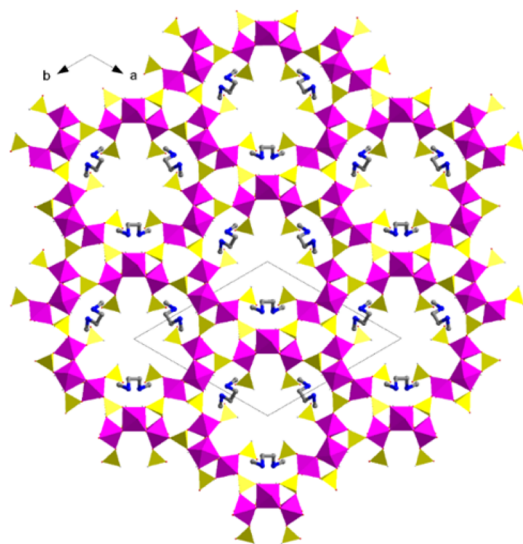

Figure 1. Structure of NTHU-15 viewed along the c axis, showing the 18R channels surrounded by 12 GaO_6 octahedra (in magenta) and 12 HPO_3 tetrahedra (in yellow). The polyamine template moieties are depicted as ball-and-stick models, with C atoms in gray and N atoms in blue. The structure displays free space of up to ~24% of the unit-cell volume.

polycharged polyamine templates that cannot be removed without collapsing the structure. Remarkably, the structure displayed free space of up to ~24% of the unit-cell volume in addition to high adsorption capacities for both H_2 and CO_2. For the first time, an organic-templated extra-large-channel structure that cannot withstand the removal of countercharged templates is proven to be a true open framework and to possess significantly high porosity.

Needle-shaped, transparent, colorless crystals of NTHU-15 (Figure S1) were obtained as a single-phase product by heating of a reaction mixture containing 0.25 mmol of $Ga(NO_3)$, 4 mmol of H_3PO_3, 1 mmol of polyamine (TEPA or PEHA), and 10 mL of H_2O in a 23 mL Teflon-lined autoclave at 120 °C for 2 days. The product yields were estimated to be ~50% (based on gallium). The composition of the inorganic framework was determined by single-crystal structure analysis (Table S1) to be $[(GaOH)_9(HPO_3)_{12}]^{6-}$, with the negative charge balanced by the fully protonated templates (H_5TEPA^{5+} or H_6PEHA^{6+}). On the basis of thermogravimetric analysis (TGA) and elemental analysis (EA) data (Figure S2 and Table S2), the full chemical formulas for the two crystals prepared from the different amine templates (TEPA and PEHA) were determined to be $(H_5TEPA)_{1.2}[(GaOH)_9(HPO_3)_{12}]\cdot xH_2O$ (NTHU-15-TEPA) and $(H_6PEHA)[(GaOH)_9(HPO_3)_{12}]\cdot xH_2O$ (NTHU-15-PEHA), where x = 12−14. They are abbreviated as 15-TEPA and 15-PEHA, respectively.

The unique three-dimensional framework of NTHU-15 consists of two independent Ga sites in the octahedral center of $Ga(OH)_2O_4$ and three P sites in the center of pseudotetrahedral HPO_3. One of the striking structural features of NTHU-15 is that, with a Ga/P ratio of 3:4, there are edge-sharing bioctahedral units formed by two Ga(1) octahedra. The Ga(1) dimers each share two cis corners with two Ga(2) octahedra, where each of the Ga(2) octahedra interlinks two Ga(1) dimers by a skew edge. As a result, infinite Ga−OH−Ga chains running along the c axis are created (Figure S4). The GaPO chain appears as a concavelike GaPO block on the ab plane, making the topology of NTHU-15 look similar to that hexagonal tungsten bronze-type structure (Figure S5). As depicted in Figure 1, the 18R channels are surrounded by six concavelike blocks that are related by 6-bar symmetry. In addition, there are 6R channels surrounded by three concave-like blocks. Lateral 10R channels are also located along [100], [010], and [110], respectively (Figure S5). These channels are filled with counterspecies that account for one-fifth of the mass of NTHU-15, e.g., water molecules (in 6R, 10R, and 18R) and template H_5TEPA^{5+} or H_6PEHA^{6+} cations (in 18R). The unique multichannel topology and large quantity of guest species all imply the porous attribute of NTHU-15.

The crystalline solids of NTHU-15 were very stable in boiling water for days (Figure S6). The TGA curves showed that lattice water molecules could readily escape from the structure upon heating; the weight loss before 150 °C, ~10−11%, should correspond to the removal of lattice water (Figure S2). Rehydration was slow under ambient conditions and not complete unless the sample was immersed in water. Variable-temperature powder X-ray diffraction (PXRD) patterns showed that the as-synthesized sample remained intact at 150 °C during in situ measurements. (Figure S7). The nonframework volume, estimated in terms of solvent-accessible volume (SAV), was ~45%, which is not the highest compared with other 18R-channel structures (Table S3). However, NTHU-15 is the only MPO structure that possesses ~24% of the unit-cell volume[12] as SAV even when large template species such as H_5TEPA^{5+} or H_6PEHA^{6+} are present (Figure S8 and Table S3). Apparently, the presence of the templates does not obstruct the channels.

As shown in Figure 2, the linear-shaped H_5TEPA^{5+} and H_6PEHA^{6+} ions are located on the back of each concavelike block, with all of the ammonium heads on each individual template oriented toward the same side of the negatively charged inorganic wall to form strong hydrogen bonds. The free space is primarily located in the center of the 18R channels since the organic templates cling to the channel walls with the HPO_3 groups enfolded into them. The aperture of the 18R channels is defined by the terminal HPO_3 groups pointing toward the channel centers with the P−H bonds sticking out. The free diameter in NTHU-15, which was estimated as the shortest distance between the hydride (H) atoms of the two HPO_3 groups crossing the channel, is ~5 Å, which is comparable to that of 24R-channel structure ND-1 (Figure S9). This was confirmed by N_2 gas adsorption/desorption experiments (vide infra).

The gas sorption properties of NTHU-15 were studied using N_2, H_2, CO_2, and CH_4 (Figure 3 and Table S5). N_2 gas sorption measurements for Brunauer−Emmett−Teller pore surface area and pore structure analysis were conducted at 1 bar and 77 K. The adsorption isotherms (Figure S10) revealed NTHU-15 to be a microporous system with an average pore diameter of 5.6 Å (Figure S11), and the surface areas for 15-
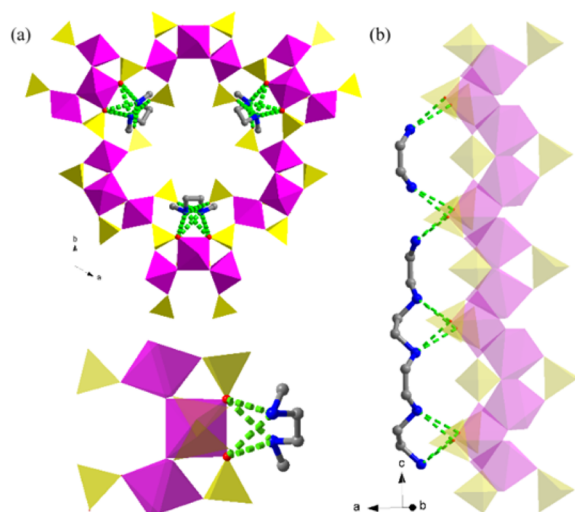
Figure 2. Polyamine-cladded channels in NTHU-15: (a) the 18R channel is enclosed by six concavelike GaPO blocks, and the template cations are hydrogen-bonded to the back side of these concavelike blocks; (b) all of the ammonium heads on each individual template are oriented toward the same side of the negatively charged inorganic wall.
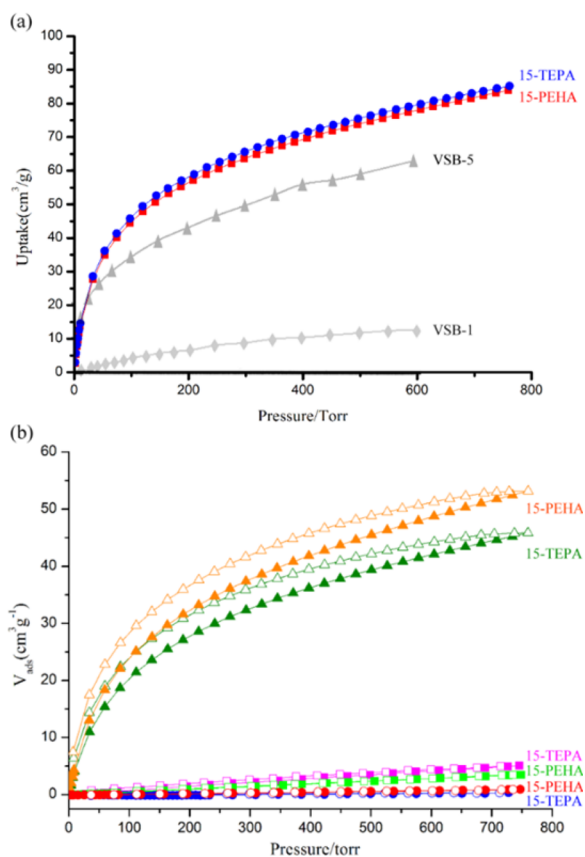

Figure 3. Gas sorption isotherms of NTHU-15: (a) effective H_2 adsorption curves measured at 77 K, which are compared with those of VSB-5 and VSB-1; (b) sorption isotherms of CO_2 (triangles), CH_4 (squares), and N_2 (circles) for 15-TEPA and 15-PEHA at 298 K, with solid symbols for adsorption and open symbols for desorption.

TEPA (324 m²/g) and 15-PEHA (276 m²/g) were derived. Under the same conditions, the hydrogen uptakes were found to be 85.2 cm³/g (3.80 mmol/g) and 83.9 cm³/g (3.75 mmol/g) for 15-TEPA and 15-PEHA, respectively (Figure 3a). It

should be noted that except for the 24R-channel structures of VSB-1 and VSB-5,[13] no other extra-large-channel structures have been reported to show the same ability in hydrogen adsorption. The high uptake of H_2 for NTHU-15 is unprecedented among organic-templated MPOs.

Further measurements showed that NTHU-15 can effectively adsorb CO_2, surpassing all other known extra-large-channel inorganic framework compounds. The CO_2 uptake was found to reach 53.2 cm³/g (2.37 mmol/g) at 1 bar and 298 K (Figure 3b), which is comparable to those of many MOFs and better than most zeolitic imidazolate framework (ZIF) materials[14] that have good selective CO_2 uptake (Figure 4). To understand the
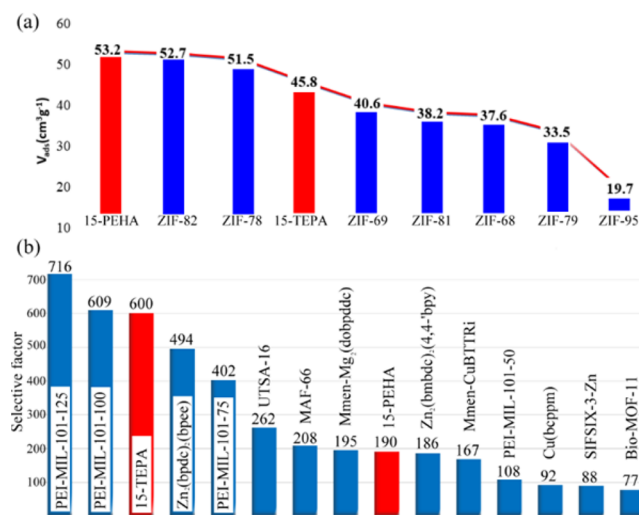

Figure 4. Comparison of NTHU-15 and famous MOFs: (a) CO_2 uptakes of NTHU-15 and ZIF materials at 298 K; (b) CO_2/N_2 selective factors of NTHU-15 and selected MOFs.

CO_2 adsorption of NTHU-15, we calculated the isosteric heat of adsorption (Q_{st}) from the adsorption isotherms measured at 273 K (Figure S12) and 298 K. The Q_{st} values for CO_2 were −33.7 kJ/mol for 15-TEPA and −40.6 kJ/mol for 15-PEHA (Figure S13), which are both much higher than that for BPL carbon (~24 kJ/mol).[15] The data also revealed that NTHU-15 could compare well with the functionality type of porous materials[16] in CO_2 adsorption, which suggests that very strong interactions between NTHU-15 and CO_2 exist. Because of the very low adsorption of N_2 at 298 K (0.015 mmol/g for 15-TPEA and 0.04 mmol/g for 15-PEHA), we estimated the CO_2/N_2 selectivity using ideal adsorbed solution theory (IAST) and the single-component CO_2 and N_2 adsorption isotherms. The CO_2/N_2 selectivity factors were calculated under postcombustion conditions (0.15 bar CO_2 and 0.75 bar N_2) at 298 K. The value for 15-TEPA was 600, which is extremely high and exceeds the values for many MOF materials[17] exhibiting CO_2-selective capture (Figure 4b). The results could be attributed to a strong affinity for CO_2 by NTHU-15 caused by its unique anionic framework with abundant polar HPO_3 groups and positively charged amino groups that are preferentially attracted to molecules with a quadrupole moment.[18] NTHU-15 may also have the potential for CO_2/CH_4 selectivity because of the low adsorption of CH_4 at 298 K (Figure 3b).

In summary, we have prepared the foremost pure inorganic frameworks that can overcome the disadvantages of lacking neutrality and having nonremovable organic template cations. The "template-cladded" strategy developed in this study can

serve as an effective solution to the long-standing problem of low porosity in the field of organic-templated inorganic frameworks, particularly innovative metal phosphates/phosphites. NTHU-15 is the largest channel structure ever prepared in gallium phosphites, and we have shown that it is unnecessary to remove large organic templates from the host structure to attain a "true" open framework. By the use of amine molecules with multiple amino groups and linear-shaped skeletons, it is possible to manipulate the templates to anchor onto the inorganic channel walls in order to release channel space, as substantiated by the high H_2 uptake and effective adsorption of CO_2 in 15-TEPA and 15-PEHA. In contrast to all other existing crystalline inorganic frameworks and even many hybrid frameworks, NTHU-15 has high water stability and high affinity and selectivity for CO_2 adsorption that can be practically applied to the field of flue gas cleaning. Further research on this theme is in progress.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b03305.

> Crystal images, ORTEP drawing, structural plots, crystal data, TGA curves, EA data, PXRD patterns, and gas sorption isotherms (PDF)

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Notes

The authors declare no competing financial interest.

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