Communication

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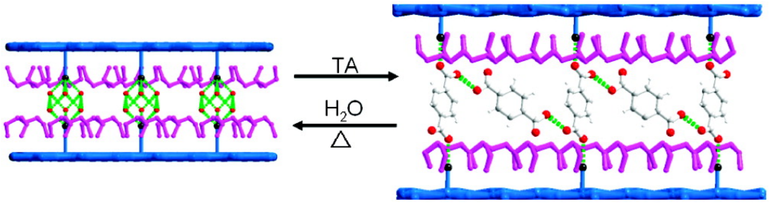

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Discrete Water Hexamers and Template-Assisted Molecular Recognition in an Elastic Zincophosphate Lattice

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Zeolite and zeolite-like materials are tetrahedral frameworks of aluminosilicates and microporous metallophosphates, which have widespread applications,[1] from traditional catalysts and molecular sieves to modern low-K materials,[2] zeolite dye microlasers,[3] and photoluminant phosphor.[4,5] In the last two decades, new zeotype microporous materials have continued to emerge at an increasingly rapid pace.[6−8] The syntheses of these materials are tactically performed by employing an organic template. The molecular size and shape of this template often have strong influence on the dimensions of channels or micropores in the inorganic framework. On the other hand, the template is usually loosely tied to the framework and bound to be removed for higher surface area and larger pore volume. At the practical level, the efficacy in the molecular sieve or molecular recognition applications appears irrelevant to the prior template.

However, there exist certain types of microporous materials in which the organic template cannot be removed without collapsing the structures.[9,10] Strong hydrogen bonding (HB) or electrostatic force often exists between such irremovable template and framework. It is thus questionable if the presence of this irremovable template would exert any pronounced effect on the functionality of the material. Recently, we have prepared an interesting photoluminescent zincophosphate, $(H_3tren)_2[Zn_3(PO_4)_4]\cdot 6H_2O$ (tren = trisaminoethylamine), designated as NTHU-3.[11] Its irremovable template, H_3tren^{3+} ion, forms intriguing dynamic HB pattern on the hexa-charged $_\infty[Zn_3(PO_4)_4]^{6-}$ (designated as ZnPO) sheets, with the capability of assisting molecular recognition. In NTHU-3, we also observed the remarkable water hexamers, $(H_2O)_6$, to be individually isolated by the template ions. It is noted that the $(H_2O)_6$ clusters without intercluster HB for holding self-stabilization have never been perceived due to the predisposition toward polymerization.[12] Herein, we report the explicit structure of $(H_2O)_6$ in the confinement of tetrahedral ZnPO lattice, as well as the role of irremovable template in NTHU-3 in the molecular recognition of organic supramolecules.

The water hexamers in NTHU-3 exhibit a chair conformation (Figure 1A), and each has 3-bar symmetry and six equivalent intracluster hydrogen bonds (2.034 Å for $O_w\cdots H_w$ and 2.843 Å for $O_w\cdots O_w$). It is for the first time that the hydrogen atoms in $(H_2O)_6$ are conclusively determined from single crystal, and specific hydrogen bonds are clearly elucidated. The hexamers form a monolayer (Figure 1B) in a pattern similar to ice, I_h, but are differently separated apart from each other between the ZnPO strata. Each $(H_2O)_6$ cluster is located in a seemingly hydrophobic octahedral cage (Figure 1C) surrounded by six H_3tren^{3+} ions without HB between $(H_2O)_6$ and H_3tren^{3+} ions. However, these two counter species, respectively, form HB to the inorganic. The $(H_2O)_6$ clusters are bound to phosphate oxygens (O_p) of the sheets in the form of cubane-like $[6H_2O-2O_p]$ units (Figure 1D). The HB distances are 1.907 Å for $O_p\cdots H_w$ and 2.771 Å for $O_p\cdots O_w$, comparatively shorter than those of the above-mentioned intracluster hydrogen bonds.

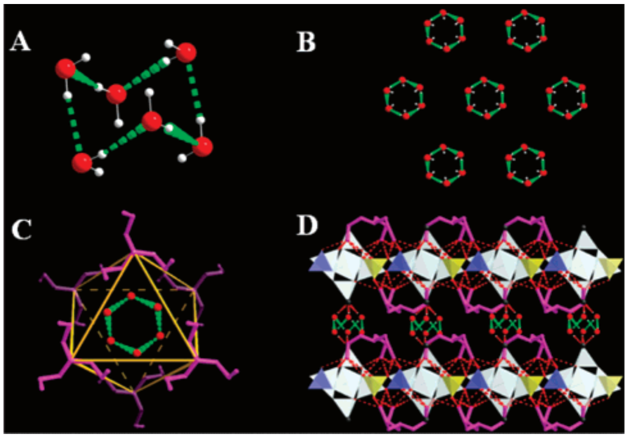

Figure 1. Water hexamers in NTHU-3: (A) cyclic $(H_2O)_6$ with a chair conformation and intracluster hydrogen bonds (green dotted lines); (B) monolayer of $(H_2O)_6$ with ice I_h-like pattern; (C) $(H_2O)_6$ isolated in the hydrophobic cage (yellow lines) of six H_3tren^{3+} ions (purple wires); and (D) the hexamers are bound to O_p (dark balls) of the ZnPO tetrahedral sheets in the form of cubane-like $[6H_2O-2O_p]$ units. Red dotted lines are the hydrogen bonds between counter species and the ZnPO lattice.

NTHU-3 emits blue luminescence at 460 nm as excited by 250 nm wavelength. Combined TGA and PXRD studies showed that all $(H_2O)_6$ clusters could be removed at 180 °C, with the structure sustained, but the interlayer spacing shrunk from 12.7 to 11.3 Å, without luminescence property. Further heating of the anhydrous over 190 °C would change the crystalline structure into amorphous. Even so, this amorphous−anhydrous NTHU-3 can resume original crystallinity by exposure to humidity or soaking in water.[13] In the rehydration process, either gaseous or liquid water molecules could be readily adsorbed, and on the basis of relative HB distances, they are presumably bound to the ZnPO strata first and then self-assembled into $(H_2O)_6$. However, the chronological sequence of the two bonding mechanisms could not be detected in this study. Nonetheless, the dehydration−rehydration and crystalline-to-amorphous cycles were able to be reversibly conducted and monitored by PXRD or PL measurements.

The H_3tren^{3+} ions are hydrogen bonded into an intriguing 2D HB pattern on both sides of each ZnPO sheet (Figure S13). Solid-state ^{13}C NMR spectra showed that their chemical shifts were essentially the same as those of the bulk tren molecules. These ions were thermally stable up to 280 °C and would not undergo ion exchange reactions. However, when solids of terephthalic acid (TA) and NTHU-3 were stirred in water, the $(H_2O)_6$ clusters could be completely replaced by TA to form TA−NTHU-3,[14] which had a layer interval propped up to ~17.8 Å and emitted purple luminescence at 433 nm instead. In TA−NTHU-3, the originally achiral TA molecules adopt noncyclic-dimer and a single HB linkage to form infinite supramolecular $(TA)_\infty$ chains (Figure 2), which are arranged into a uniform single tier between the ZnPO sheets and differ drastically in molecular conformation, HB mode,

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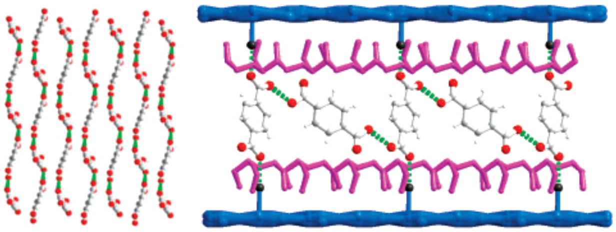

Figure 2. Supramolecular $(TA)_\infty$ chains in TA−NTHU-3: (left) a projection of the single-tiered chiral $(TA)_\infty$ chains; and (right) adjacent TA molecules tilt in different angles (79.4 and 93.5°) along the chain direction. In the plot, ZnPO sheets are represented by blue wires.

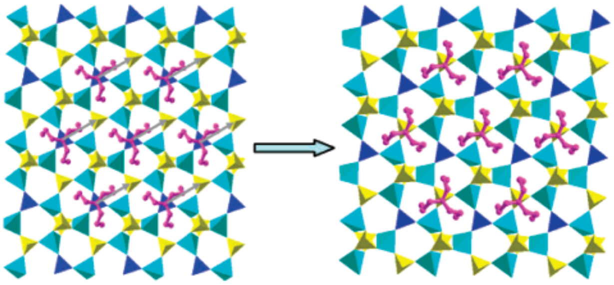

Figure 3. Dynamic templates with different conformations on the Δ-ZnPO sheets: (left) δ-H_3tren^{3+} ions lodging on the face-down PO_4 (blue tetrahedral) in NTHU-3, and (right) λ-H_3tren^{3+} ions lodging on the face-up PO_4 (yellow tetrahedral) in TA−NTHU-3.

and $\pi-\pi$ interaction from those in the bulk or on the surface.[15] Only every other monomer along the chain direction connects to the hydrophilic O_p site of the ZnPO sheets (2.451 Å for $O_p\cdots O_{TA}$). Thus, the adjacent two TA molecules tilt in different angles (79.4 and 93.5°), leading the $(TA)_\infty$ chains, deviated from linear to a wavy shape with chiral conformation. The $\pi-\pi$ interaction between adjacent $(TA)_\infty$ chains is seemingly stronger in TA−NTHU-3 than in solid TA for the interchain distance is relatively shorter, 4.33 versus 5.03 Å.

The conversion process from NTHU-3 into TA−NTHU-3 may encompass the self-assembly of supramolecular $(TA)_\infty$ chains followed by evacuating and disassembling of water hexamers and TA−molecule insertion. Besides the changes in layer intervals, we scrutinized other adjustments adapted by the irremovable template ions and the inorganic lattice as well. The ZnPO sheets, which are constructed from tricyclic structural motifs with two distinct twists, actually exhibit two conformations (denoted as Δ and Λ).[13] The clutch-like H_3tren^{3+} ions, as well, display two conformations (i.e., δ and λ). We observed that, in NTHU-3, overlaid on both sides of the Δ-sheets are δ-H_3tren^{3+} ions, and that of Λ-sheets are λ-H_3tren^{3+} ions, that is, two types of template-and-sheet combinations, $\delta\Delta\delta$ and $\lambda\Lambda\lambda$, exist with all H_3tren^{3+} ions lodging on the face-down PO_4 tetrahedra (Figure 3). In TA−NTHU-3, however, the two types of template-and-sheet combinations become $\lambda\Delta\lambda$ and $\delta\Lambda\delta$, with the H_3tren^{3+} ions lodging on the face-up PO_4 tetrahedra instead, causing the HB pattern to turn into one-dimension (refer to Figure S13). It implies that the irremovable H_3tren^{3+} ions can relocate with synchronous self-changes in HB and conformation to adapt to varied supramolecular insertions, that is, from $(H_2O)_6$ clusters to $(TA)_\infty$ chains. Furthermore, TA−NTHU-3 could be converted back to NTHU-3 in hot water,[14] indicating that the template ions could translate back and forth on the elastic inorganic layers (interval changed between 12.7 and 17.8 Å), along with HB patterns reversibly tuned from 2D to 1D.

In this study, we have demonstrated that the irremovable template H_3tren^{3+} ions have exerted pronounced effect on stabilizing the ice-like $(H_2O)_6$ clusters in an isolated state, keeping the recoverable amorphous-to-crystalline property for NTHU-3 and, moreover, the self-assembly of supramolecular $(TA)_\infty$ chains between the ZnPO strata. The explicit hydrogen bonding structure retrieved from $(H_2O)_6$ in NTHU-3 is unprecedented and may provide important insights into the properties of bulk ice.[16] It is also for the first time important to prepare organic supramolecular infinite chains in a layered metal phosphate, providing prospect syntheses of hybrid organic−inorganic bionanocomposites in phosphates, as in LDHs. The irremovable template is so dynamic that even by mixing up solids of TA and NTHU-3 at ambient temperature would TA−NTHU-3 be produced. The reaction is selective since the other isomers of benzene dicarboxylic acid (i.e., IPA and PA) could not react with NTHU-3 under solid state in air. This molecular recognition process can be readily monitored by PL or PXRD measurements. IPA molecules may self-assemble into helical $(IPA)_\infty$ chains in the lamellar space between ZnPO sheets in solution.[13] Preparing more chiral organic supramolecules from achiral monomers via the dynamic-template-containing NTHU-3 lattice is in progress.

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Supporting Information Available: PL, TGA, rehydration curves, and crystallographic CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Transparent crystals of NTHU-3 were prepared from the reaction mixture of $Zn(NO_3)_2{\cdot}6H_2O$, $C_6N_4H_{18}$ (tren), H_3PO_4, and H_2O (molar ratio 1:4:6:555) at 160 °C for 3 days. The yield was 90% based on zinc. Crystal data: $Zn_3P_4O_{22}N_8C_{12}H_{54}$, trigonal, $P\bar{3}c1$, $Z = 2$, Mr = 982.62, and $a = 8.7914(4)$ Å, $c = 25.748$ (1) Å, $V = 1723.4$ (1) Å^3, $R1 = 0.0438$.
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(14) Crystal data for TA-NTHU-3: $Zn_3P_4O_{24}N_8C_{28}H_{54}$, monoclinic, $C2/c$, $Z = 4$, Mr = 1206.78, and $a = 15.0239(9)$ Å, $b = 8.5826(5)$ Å, $c = 36.299(2)$ Å, $\beta = 100.684(1)°$, $V = 4599.5(5)$ Å^3, $R1 = 0.0490$. A single phase of crystalline powder of TA−NTHU-3 was obtained by stirring 1 mmol of NTHU-3 with 5 mmol of $C_8O_4H_6$ (TA) in 20 mL of water at room temperature for 12 h. Larger crystals of TA−NTHU-3 could be prepared from the reaction mixture of $Zn(NO_3)_2{\cdot}6H_2O$, $C_6N_4H_{18}$ (tren), H_3PO_4, TA, and H_2O (molar ratio 1:4:6:2:555) at 160 °C for 3 days under hydrothermal conditions. Conversion of TA−NTHU-3 into NTHU-3 could be achieved by heating 2 mmol of TA−NTHU-3 in 100 mL of water at 80 °C for 12 h.
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