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Rational Synthesis of Microporous Aluminophosphates with an Inorganic Open Framework Analogous to $Al_4P_5O_{20}H{\cdot}C_6H_{18}N_2$

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The suitable organic templates for the formation of 3-D interrupted open-framework aluminophosphate can be predicted in terms of nonbonding interaction energies of host−guest through molecular dynamics simulations by Cerius^2. The prediction is well proven by the successful syntheses of $Al_4P_5O_{19}(OH){\cdot}C_5N_2H_{16}$ (**1**) and $Al_4P_5O_{19}(OH){\cdot}C_4N_3H_{15}$ (**2**) through rational selection of 1,5-pentanediamine and diethylenetriamine template molecules based on energy calculations. The structures of **1** and **2** are anionic $Al_4P_5O_{19}(OH)^{2-}$ open-frameworks, which are analogous to $Al_4P_5O_{20}H{\cdot}C_6H_{18}N_2$ (AlPO-HDA) with 12- and 8-membered ring intersecting channels. Single-crystal X-ray diffraction analysis shows that **1** crystallizes in the triclinic space group *P*1 with lattice parameters $a = 9.2450(9)$ Å, $b = 12.688(2)$ Å, $c = 5.0657(5)$ Å, $\alpha = 96.02(1)°$, $\beta = 105.89(1)°$, and $\gamma = 102.88(1)°$. The as-synthesized compound **2** is characterized by powder X-ray diffraction, ICP, MAS NMR, and TG analyses. It has an empirical formula of $Al_4P_5O_{19}(OH){\cdot}C_4N_3H_{15}$ and possesses the same open-framework structure as AlPO-HDA.

Introduction

The synthesis of new microporous materials is of continuous interest because of their widespread applications in catalysis and separations, as well as in the field of advanced microporous materials and host−guest assembly chemistry.[1−7] However, their formation, which is normally facilitated by organic templates,[8] is not yet well understood due to the complexity of hydrothermal or solvothermal reactions. This renders rational synthesis very difficult. Recently, computational modeling and simulation approaches have greatly enhanced the researcher's ability to target materials with specific structures and properties.[9] For example, Lewis et al. described a method for *de novo* design of template molecules that can be computationally "grown" in the desired inorganic framework.[10] Catlow et al. investigated the relative templating efficacy of organic species within a large range of known zeolite frameworks in terms of the interactions between the templates and frameworks,[11] and investigated the nucleation, growth, and templating in hydrothermal synthesis by computer modeling.[12] Fogg et al. predicted guest orientations in layered double hydroxide intercalates using computer simulations.[13] Zones et al. investigated the guest−host relationships in the synthesis of novel cage-based zeolites SSZ-35, SSZ-36, and SSZ-39. This work shows that understanding the effects of the nonbonding energy of the organic structure-directing agent (SDA)−zeolite interaction on zeolite phase selectivity will play a fundamental role in the future discovery of new zeolite phases through rational SDA design.[14] Recently, we have developed a methodology for investigating the templating ability of organic amines in the formation of 2-D layered compounds in terms of the energies of nonbonding interactions dominated by H-bonding between the host inorganic network and guest template molecules.[15] In this work, we further extend this method

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to a 3-D interrupted microporous aluminophosphate system (i.e. containing terminal oxygens in the framework that interacts with the template through H-bonds). This is proven by the successful synthesis of aluminophosphates $Al_4P_5O_{19}(OH)\cdot C_5N_2H_{16}$ (**1**) and $Al_4P_5O_{19}(OH)\cdot C_4N_3H_{15}$ (**2**) with anionic open-frameworks, which are analogous to the structure of $Al_4P_5O_{20}H\cdot C_6H_{18}N_2$ (AlPO-HDA) reported before.[16]

Experimental Section

Modeling Method. *A. Building Models.* (i) Choosing the experimental framework of AlPO-HDA as a host, its structural model was built up according to single-crystal structural data using the Cerius^2 package.[17] (ii) The unit cell and the postions of framework atoms were first fixed. (iii) The crystal symmetry was decreased to *P*1 in order to fit various kinds of organic molecules. (iv) The number of the template molecules in one unit cell was determined on the basis of the charge balance. (v) The template molecules were placed into the channels of the host.

B. Force Field and Parameter. The Burchart1.01−Dreiding2.21 force field was chosen for energy optimization and calculation. Because the P═O bond type is not addressed in the force field, parameters concerning the bond energy for P═O, Ro = 1.480 and Do = 87.3428, were added according to the literature.[17,18] Other parameters are the same as those used in the Burchart1.01−Dreiding2.21 force field given in the Cerius^2 package.

C. Energy Calculation. The interaction energies (E_{inter}) between the inorganic framework and organic templates are studied, since the low-energy nonbonding host−guest interactions, that is, van der Waals (VDW) and H-bonding interactions, can affect the choice of template. Therefore, the Coulombic interactions between the framework and the template are ignored in the calculation. We assume $E_{inter} = E - E_f - E_R$, where E is the total energy of the whole structure, E_f is the energy of the framework, and E_R is the energy of the encapsulated organic template itself. Energy optimization was carried out by using energy-minimization to roughly optimize the structure first, and then the Anneal Dynamics-NVT ensembles of Molecular Dynamics were used to make global optimization. The parameters of Anneal Dynamics used were the default data in the Cerius^2 package.

Synthesis. In the synthesis of compounds **1** and **2**, 2.0 g of aluminum triisopropoxide for both **1** and **2** was first dispersed into 17 mL of H_2O and 20 mL of EG, respectively, under stirring. Then 1.6 mL and 1.2 mL of H_3PO_4 (85 wt % in water), respectively, were added dropwise to the individual slurries, respectively. Finally, 1.5 mL of 1,5-pentanediamine and 0.53 mL of diethylenetriamine were added slowly to the above reaction mixtures, respectively. The reaction mixtures for **1** and **2** were sealed in Teflon-lined stainless autoclaves and heated under static conditions for 7 days at 180 and 200 °C, respectively. The products containing single crystals of **1** and the powder phase of **2**, respectively, were filtered and washed thoroughly using deionized water, and dried in air at room temperature.

Characterization. Powder X-ray patterns for **1** and **2** were recorded on a Philips PW3050 X-ray diffractometer with Cu Kα radiation ($\lambda = 1.542$ Å) and a curved graphite monochromator. The step size used was 0.02, and the step time was 10 s.

Solid-state NMR experiments were performed with magic-angle spinning (MAS) on a JEOL JNM-A-400WB spectrometer operating at frequencies of 104.17 and 161.83 MHz for ^{27}Al and ^{31}P, respectively. Chemical shifts were referenced to an external standard of $Al(H_2O)_6^{3+}$ for ^{27}Al and 85% H_3PO_4 for ^{31}P. The sample was spun at 10 and 5.2 kHz for ^{27}Al and ^{31}P, respectively.

Single-Crystal Anaylsis. A colorless thin platelike single crystal ($0.20 \times 0.05 \times 0.02$ mm^3) of **1** was selected for the structural analysis. The intensity data were measured by using Mo Kα radiation ($\lambda = 0.710\,69$ Å) on a Rigaku R-AXIS CS equipped with an imaging-plate detector together with a rotating anode X-ray tube and an incident beam monochromator. On the other hand, the lattice constants were determined by applying the least-squares method to 25 2θ values of well-centered reflections measured on a Rigaku AFC7R diffractometer. The possible lattice transformation of $a' = 2a + c$, $b' = c$, $c' = b$ produces a pseudo-monoclinic C-centered cell ($a' = 17.784(1)$ Å, $b' = 5.066(2)$ Å, $c' = 12.688(1)$ Å, $\alpha = 83.98(1)°$, $\beta = 105.17(1)°$, $\gamma = 90.01(1)°$), and the intensity distribution suggests that the fundamental structure of the present structure of **1** is similar to that of AlPO-HDA (Cc, $a = 17.682(1)$, $b = 5.108(1)$, $c = 25.488(1)$, $b = 103.07(1)$). The program package SIR92 was used for obtaining an initial structural model, and the parameters were refined by the least-squares program SHELXL97. During the refinement for framework positions and non-hydrogen atoms of the template, a high degree of disorder was detected at the middle chain of 1,5-pentanediamine. The accuracy of the present data could not allow us to obtain reasonable positions of C4, C4s, C5, and C5s, in particular, and the values of corresponding bond distances reflect this inconvenience. P(5) shares only two oxygens with adjacent Al atoms, leaving two terminal oxygens: O(17) and O(20). The shorter bond distance of P(5)−O(17) implies some double-bonding character, while the longer distance of P(5)−O(20) suggests the location of a hydroxylic O(20). According to these discussions, diprotonated 1,5-pentanediamine molecules were assumed in the structure of **1** to preserve charge balance. All atoms were refined isotropically, and hydrogen atoms were located geometrically. It should be noted that the possible hydrogen location near O(20) could not be confirmed by the present analysis.

Results and Discussion

The framework of $Al_4P_5O_{20}H\cdot C_6H_{18}N_2$ (AlPO-HDA) possesses intersecting 12- and 8-membered ring (MR) channels along the [010] and [100] directions, respectively, with terminal P−OH and P═O groups protruding into the channel. The template agent, diprotonated 1,6-hexanediamine (HDA) molecule is located in the main 12-MR and interacts with the framework through H-bonds (see Figure 1a). As a comparison, Figure 1b shows an isolated HDA molecule at its lowest energy state. It can be seen that the conformations of the isolated HDA molecule and the encapsulated HDA molecule in the channel are quite different. The energy of the encapsulated HDA (14.03 kcal/mol) is much higher than that of the isolated HDA (−1.09 kcal/mol). However, the configuration of the encapsulated HDA ensures the lowest host−guest interaction energy. This implies that host−guest interaction is important for the stabilization of the framework of AlPO-HDA. Our calculation is based on the Burchart1.01−Dreiding 2.21 force field that combines the Burchart force field,[19] which is used to treat the frameworks of zeolites, and the Dreiding II force field,[20] which is used to treat the intra- and intermolecular interactions.

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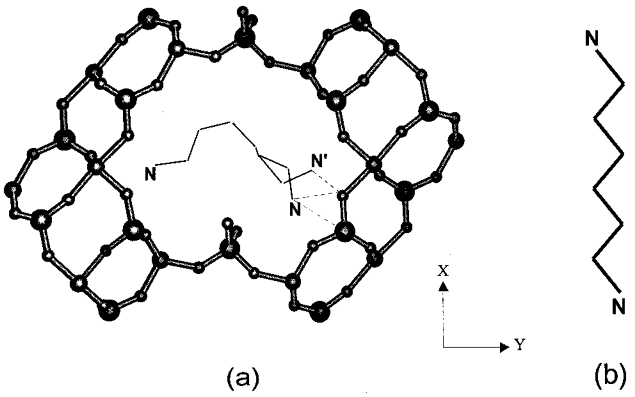

Figure 1. (a) Open-framework structure of $Al_4P_5O_{20}H \cdot C_6H_{18}N_2$ (AlPO-HDA) with 1,6-hexanediammonium cation located in the 12-membered ring (H-bonds are indicated by dashed lines) and (b) isolated 1,6-hexanediamine molecule at its lowest energy state.

Table 1. Interaction Energies (E_{inter}) of Templates−Host per Unit of $[Al_4P_5O_{20}H]^-$ (kcal/mol)[a]

1	$H_2N(CH_2)_6NH_2$	−18.34	0.00	−8.34
2	$HNC_6H_{10}NH$	−16.21	−2.12	−18.33
3	$H_2NCHC_6H_{10}CHNH_2$	−12.94	0.00	−12.94
4	$H_2N(CH_2)_5NH_2$	−19.03	−2.37	−21.40
5	$H_2N(CH_2)_4NH_2$	−15.67	−3.48	−19.15
6	$H_2N(CH_2)_7NH_2$	−15.21	−0.17	−15.39
7	$H_2N(CH_2)_3NH_2$	−11.94	−2.31	−14.26
8	$H_2N(CH_2)_2NH_2$	−8.72	−3.33	−12.05
9	TETA	−15.99	−−2.61	−18.60
10	DETA	−19.61	−1.69	−21.30
11	$H_2N(CH_2)_8NH_2$	1.16	−0.28	0.88
12	$H_2NCH(CH_3)CH_2NH_2$	−10.78	−3.74	−14.52
13	$H_2NCH_2CH(CH_3)CH_2NH_2$	−11.82	−1.83	−13.36

[a] TETA: $H_2N(CH_2)_2NH(CH_2)_2NH(CH_2)_2NH_2$. DETA: $H_2N(CH_2)_2NH(CH_2)_2NH_2$.

Energy calculations show that the experimental and optimized interaction energies E_{inter} between the framework and template molecules in AlPO-HDA are −17.83 and −18.34 kcal/mol (per unit of $[Al_4P_5O_{20}H]$), respectively. To find suitable templates that can potentially direct the formation of the framework of AlPO-HDA, some typical organic diamines and polyamines, such as 1,5-pentanediamine, 1,4-butanediamine, 1,3-propanediamine, diethylenetriamine, triethylenetetramine, and so forth, are placed in the main 12-membered ring opening followed by energy optimization. The optimized interaction energies of the host framework and the theoretical templates are presented in Table 1. Some suitable templates can be predicted by choosing those with lower interaction energies, as indicated by the italic type in Table 1, of which 1,5-pentanediamine and diethylenetriamine exhibit the lowest host−guest interaction energies of −21.40 and −21.30 kcal/mol, respectively. On the basis of energy calculation results, we selected these two organic amines as the templates to carry out the syntheses of aluminophosphates with open-framework structures analogous to AlPO-HDA.

First, 1,5-pentanediamine was selected as a template agent. Large single crystals of **1** were crystallized in the gel mixture 1.0 $Al(^iPrO)_3$/2.4 H_3PO_4/1.3 1,5-pentanediamine/96 H_2O at 180 °C for 7 days. The experimental powder X-ray diffraction (XRD) pattern of **1** is shown in Figure 2a, which basically accords with the simulated XRD pattern in Figure 2b derived from structure analysis data. The difference in reflection intensity between the simulated and experimental patterns may be due to a certain degree of preferred orientation of the sample.

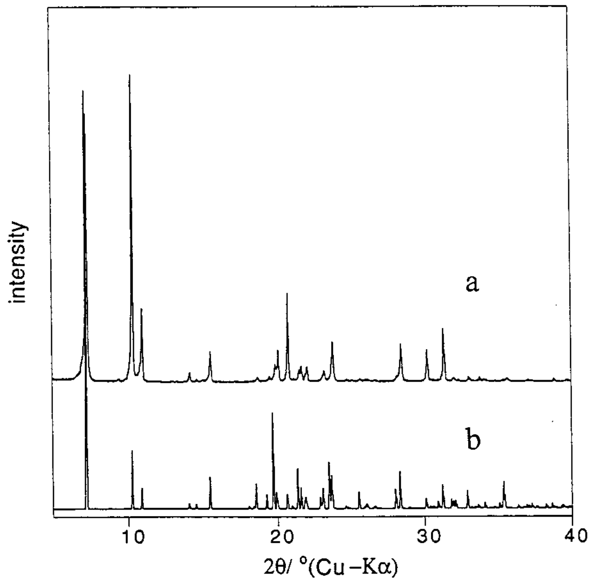

Figure 2. (a) Experimental and (b) simulated XRD patterns for **1**.

Single-crystal analysis shows that **1** crystallizes in triclinic space group *P*1 with lattice parameters a = 9.2450(9) Å, b = 12.688(2) Å, c = 5.0657(5) Å, α = 96.02(1)°, β = 105.89(1)°, and γ = 102.88(1)°. As with AlPO-HDA, the structure of **1** consists of an open-framework macroanion $[Al_4P_5O_{20}H]^{2-}$ (Figure 3a). Each asymmetric unit contains four crystallographically distinct Al atoms. Al(1) and Al(2) are tetrahedrally coordinated and share four oxygens with adjacent P atoms. The Al−O bond lengths are in the range 1.724−1.750(12) Å. Al(3) and Al(4) are pentacoordinated and share five oxygens with adjacent P atoms. Their Al−O bond lengths vary within the range 1.771(10)−1.913(11) Å. Of the five crystallographically distinct PO_4 tetrahedra, P(1), P(2), P(3), and P(4) each has four oxygens bridging to adjacent Al atoms. Their P−O bond lengths are in the range 1.502(11)−1.550(12) Å. P(5) shares two oxygens with adjacent Al atoms, with the remaining two vertexes being P═O (1.497(12) Å) and P−OH (1.581(10) Å) groups.

The template molecule, diprotonated 1,5-pentanediamine cations occupy the main 12-membered ring, as seen in Figure 3a. It is noted that the template molecules are strongly disordered in the position of C4 and C5. N1 forms two weak H-bonds to O(2) and O(16) with the N···O separations of 3.084 and 3.011 Å, respectively. N2 forms two H-bonds to framework oxygen O(6) and terminal O(17) with the N···O separation of 3.002 and 3.073 Å, respectively. The manner of H-bonding between the template and framework is in good agreement with the theoretical prediction, as shown in Figure 3b.

Second, diethylenetriamine was chosen as the template. **2** was successfully prepared in the gel mixture of

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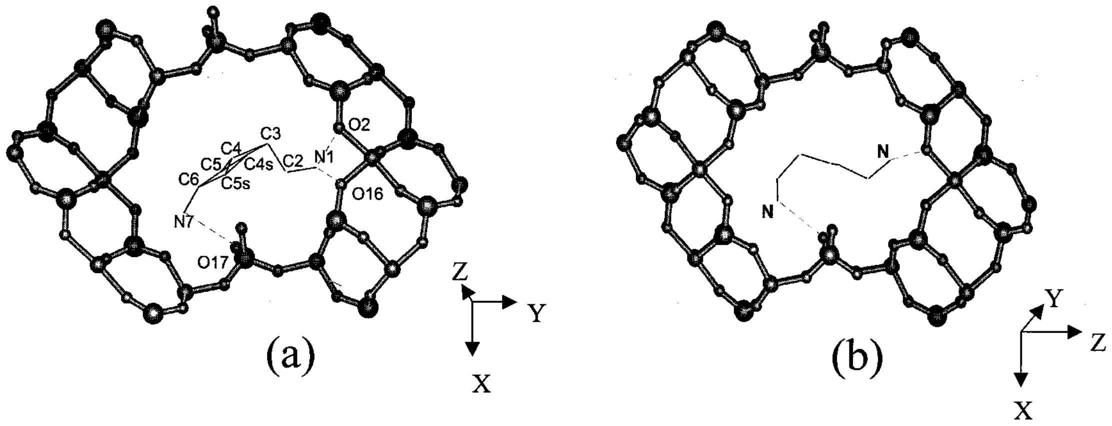

Figure 3. (a) Experimental 1,5-pentanediamine located in the 12-membered ring of **1** and (b) predicted atomic positions of 1,5-pentanediamine inside the 12-membered ring (H-bonds are indicated by dashed lines).

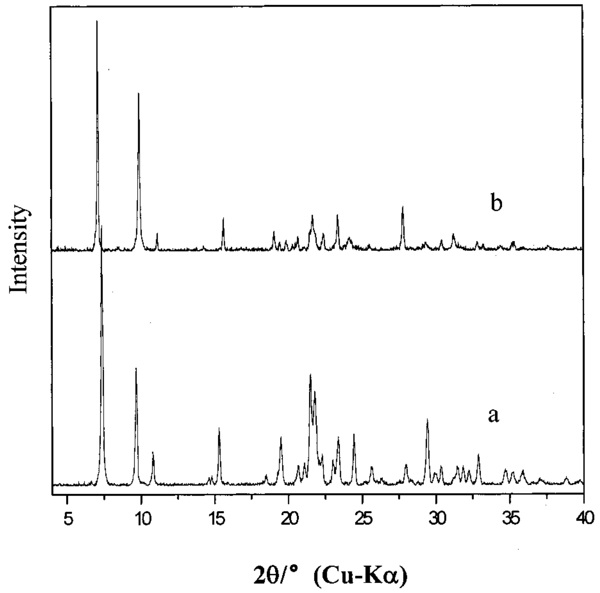

Figure 4. Experimental XRD patterns of (a) **2** and (b) AlPO-HDA.

1.0 Al(^{i}PrO)$_3$/1.8 H_3PO_4/2.1 diethylenetriamine/90 H_2O at 200 °C for 7 days. The powder XRD pattern as shown in Figure 4a is similar to that of AlPO-HDA in Figure 4b, indicating that the framework structure of **2** might have a similar structure to AlPO-HDA. Further chemical analysis of **2** by plasma spectroscopy (ICP) and microanalysis gives the atomic ratio of Al/P/C/N/H to be 1.00:1.23:1.10:0.76:4.07. Thus, the empirical formula of **2** is $Al_4P_5O_{19}(OH)\cdot C_4N_3H_{15}$, which is in agreement with the anionic $Al_4P_5O_{20}H^{2-}$ stoichiometry of AlPO-HDA. The ^{27}Al and ^{31}P MAS NMR spectra of **2** are shown in Figure 5. Two signals at 41.5 and 10.8 ppm in the^{27}Al spectrum indicate that the Al atoms are in two coordination states, that is, AlO_4 and AlO_5, respectively. The ^{31}P spectrum shows four peaks at −10.8, −15.5, −20.2, and −25.6 ppm and suggests that all P atoms are in the four-coordination state.

The TGA curve of **2** shows an obvious weight loss at ~370 °C. The total weight loss of ~15%, which is attributed to the decomposition of diethylenetriamine molecules trapped in the main 12-membered ring channels, is consistent with the calculated value (15.2%) of one diethylenetriamine per formula of $Al_4P_5O_{19}(OH)\cdot C_4N_3H_{15}$.

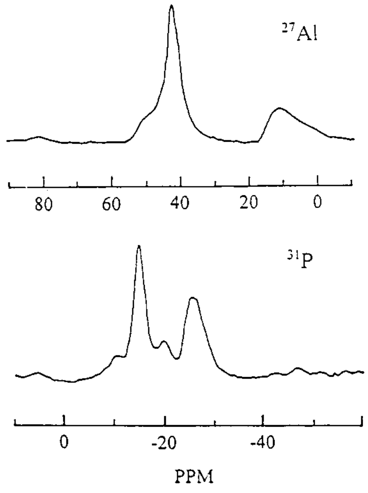

Figure 5. MAS NMR spectra of (a) ^{27}Al and (b) ^{31}P for **2**.

The X-ray powder diffraction, compositional, MAS NMR, and TG analyses all indicate that **2** has an open-framework structure analogous to AlPO-HDA.

On the other hand, in contrast to the conclusion that organic amines that have lower interaction energies with the framework are suitable templates, organic amines that have higher interaction energies are predicted to be unsuitable templates for the synthesis. For example, energy calculations show that the interaction energies of $H_2N(CH_2)_8NH_2$ (no. 11) and $H_2N(CH_2)_2NH_2$ (no. 8) are 0.88 and −12.05 kcal/mol, respectively, indicating that they are not favorable template candidates for the formation of the open-framework structure of AlPO-HDA. To further validate the efficacy of our method, we selected these two organic amines as the template molecules to carry out the synthesis. Using $H_2N(CH_2)_8NH_2$ as a template, only a layer phase $[Al_3P_4O_{16}H_3]\cdot 1.5[H_3N(CH_2)_8NH_3]$ analogous to SCS-22[22] can be obtained in the gel system of Al(^{i}PrO)$_3$−H_3PO_4−$NH_2(CH_2)_8NH_2$−H_2O. Using $H_2N(CH_2)_2NH_2$ as a template, one-dimensional chains, $[AlP_2O_8][H_3N(CH_2)_2NH_3][NH_4]$[23] and $[AlP_2O_8H][H_3N(CH_2)_2NH_3]$,[24] and a two-dimensional layer, $[Al_3P_4O_{16}][H_3N(CH_2)_2NH_3][H_2O$-

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$(CH_2)_2OH]$,[25] could be obtained in the gel system Al($^iPrO)_3/H_3PO_4/H_2N(CH_2)NH_2$/EG. Varying the synthesis conditions, no crystalline phase with structure analogous to AlPO-HDA could be obtained.

Conclusion

In terms of the nonbonding interaction energies of host open-framework and guest organic amine molecules, several organic diamines and polyamines are investigated for their templating ability in the formation of open-framework $Al_4P_5O_{20}H{\cdot}C_6H_{18}N_2$ (AlPO-HDA). We can predict suitable template molecules that have lower interaction energies with the host framework as compared with host−guest interaction energies in the experimental AlPO-HDA structure. By rational selection of 1,5-pentanediamine and diethylenetriamine as the templates, which are predicted to be suitable templates through our energy calculations, aluminophosphates $Al_4P_5O_{19}(OH){\cdot}C_5N_2H_{16}$ (**1**) and $Al_4P_5O_{19}(OH){\cdot}C_4N_3H_{15}$ (**2**) are successfully synthesized. Structural characterizations indicate that they have the same framework structure as AlPO-HDA. This work has further demonstrated that suitable template candidates can be effectively predicted for a given host experimental open-framework in terms of energy calculation. Our method should be applicable to other organically templated microporous metallophosphates and extend to other fields of chemistry involving host−guest recognitions.

Supporting Information Available: Tables of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, and hydrogen coordinates and isotropic displacement parameters for AlPO-PDA. This material is available free of charge via the Internet at http://pubs.acs.org.

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