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Template Effect of Chain-Type Polyamines on Pore Augmentation: Five Open-Framework Zinc Phosphates with 16-Ring Channels

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Five new zinc phosphates with differently unique 3D framework topologies, $(H_3dien)[Zn_3(HPO_4)_3(PO_4)]$ (**1**), $(H_2dien)_{1.5}[Zn_3(HPO_4)_3(PO_4)]$ (**2**), $(H_3dien)[Zn_3(H_2PO_4)(HPO_4)(PO_4)_2]$ (**3**), $(H_3dien)[Zn_3(HPO_4)_3(PO_4)]\cdot 1.5H_2O$ (**4**), and $(H_4tepa)_{0.5}[Zn_{2.5}(HPO_4)_2(PO_4)]\cdot 1.5H_2O$ (**5**), where dien $= H_2NC_2H_4NHC_2H_4NH_2$ and tepa $= H_2N(C_2H_4NH)_3C_2H_4NH_2$, have been synthesized under mild hydrothermal or solvothermal conditions and characterized by single-crystal X-ray diffraction, thermal analysis, solid-state NMR, UV–vis, or photoluminescence spectroscopy. Both the 7-atom-skeleton-long dien and the 13-atom-skeleton-long tepa have created 16-membered ring (16R) channels as a common feature in structures **1**–**5**. Their inorganic frameworks are built up with tetrahedra of ZnO_4, PO_4, and HPO_4 (plus H_2PO_4 in **3**) and may all be described as constructed from two-dimensional nets and one- or zero-dimensional units as linkers. Compounds **1**–**4** have the same Zn/P ratio but possess varied amount of nonframework volume. They are the first examples with dien as template in extra-large-channel structures of zincophosphates. In comparison, the framework of **5** contains a higher value in Zn/P and larger nonframework volume than that in the 24R-channel structure of ND-1. The 16R channels in **1** and **2** are one-dimensional while those in **3**, **4**, and **5** are unprecedentedly two-dimensional. In this paper, the synthesis, thermal property, NMR, reflectance UV–vis absorption, and photoluminescence study of **1**–**5** are described; framework topologies, structure relationship, the charge and location of templates, and channel characteristic vs nonframework volume are discussed.

Introduction

Tetrahedral open-framework materials are of great importance in many fields of contemporary research,[1–5] owing to their wide applications as ion exchanger, shape-selective and redox catalysts, medical MRI reagents, low-*k* materials, and zeolite–dye microlasers.[6–10] Recent discovery on extra-large-channel structures has also extended their use to hydrogen gas storage[11] and photoluminescent materials.[12,13] This variability in the property and functionality has advanced with the augmentation of micropores. Among the increasingly synthesized tetrahedral frameworks, the system of metal phosphates and phosphites has shown a greater disposition to form extra-large-pore structures.[14–16] Compared with the 18R channels in zeolite silicates[17] discovered so far, the largest channel in phosphates and phosphites has respectively reached up to 24R and 26R. Their formation involved a proper matching between framework metal ions and organic templates.

In transition metals, divalent zinc ion is extraordinarily capable of building tetrahedral open frameworks. In previously reported two 24R-channel and one 26R-channel structures, ND-1,[14] ZnHPO-CJ1,[15] and NTHU-5,[16] the templates are small organic amine cations with surfactant-like behavior; i.e., their hydrophilic groups point toward the anionic framework and hydrophobic groups cluster together to encircle "voids" within the structure. On the other hand, the use of sizable templates of nonsurfactant type, such as the bulky 4,4′-trimethylenedipyridine or the long-chain diaminohexane, as well, generated 14R- or 20R-channel structures[12,18,19] with either channel size or nonframework

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volume comparable to that of the 24R channels in ND-1. In contrast to diamine, the size effect of polyamine templates on pore augmentation was inconspicuous or even opposite. We noted that the 10-atom-skeleton tetramine $H_2NC_2H_4NHC_2H_4NHC_2H_4NH_2$ has directed the formation of the 16R-channel structure of $(C_6H_{22}N_4)_{0.5}[Zn_3(HPO_4)(PO_4)_2]$[20] with 26.7% nonframework space whereas the triamine $H_2NC_2H_4NHC_3H_6NH_2$ with only 8-atom skeleton also resulted in 16R channels but with a larger nonframework volume (36.5%) in $(C_5H_{18}N_3)_{0.5}[Zn_3(HPO_4)_3(PO_4)]$.[21] Both are inferior to the diamine $H_2N(C_2H_4)_6NH_2$, which is also 8-atom skeleton in length but could generate a 20R-channel structure with 45.7% nonframework space.[22] These existing examples seemingly indicated that the size effect of a polyamine template is reduced with increasing number of amino groups and that nonframework volume in the structures increases in proportion to the channel size. In an attempt to further explore the effect of nonsurfactant type polyamine templates on generating extra-large pores, we have aimed at the synthesis of zinc phosphates with linear triamine and pentamine molecules. Here we report five unique open-framework zinc phosphates with 16R-channel containing structures, $(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]$ (**1**), $(C_4H_{15}N_3)_{1.5}[Zn_3(HPO_4)_3(PO_4)]$ (**2**), $(C_4H_{16}N_3)[Zn_3(H_2PO_4)(HPO_4)(PO_4)_2]$ (**3**), $(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]\cdot 1.5H_2O$ (**4**), and $(C_8H_{27}N_5)_{0.5}[Zn_{2.5}(HPO_4)_2(PO_4)]\cdot 1.5H_2O$ (**5**). Being the first two-dimensional 16R-channel structure templated by pentamine $(H_2NC_2H_4NHC_2H_4)_2NH$ (tepa), the unique framework of **5** showed gigantic nonframework space and extremely low framework density (FD) ever observed in zincophosphates with channel size over 16 rings. Templating with the same triamine $H_2NC_2H_4NHC_2H_4NH_2$ (dien), the frameworks of **1–4** all have 16R channels but different nonframework content and channel characteristic, i.e., **1** and **2** being one-dimensional and **3** and **4** two-dimensional 16R-channel structures. No zincophosphate structures having two-dimensional 16R channels were previously documented. In this paper, the synthesis, thermal property, NMR, reflective UV–vis absorption, and photoluminescence study are described; framework topologies, structure relationship, the charge and location of templates, and channel characteristic vs nonframework space are discussed.

Experimental Section

Synthesis and Initial Characterization. All five compounds were synthesized via typical hydrothermal or solvothermal reactions which were carried out at 160 °C for compounds **1**, **2**, and **5** and 180 °C for **3** and **4** for 3 days in a Teflon-lined acid digestion bomb (internal volume of 23 mL) followed by slow cooling at 6 °C h^{-1} to room temperature. Two linear organic amines, diethylenetriamine (dien) and tetraethylenepentamine (tepa), were used as structure directing reagents. Other chemicals included $ZnCl_2$, $Zn(NO_3)_2\cdot 6H_2O$, 85% H_3PO_4, $H_2C_2O_4\cdot 2H_2O$, In_2O_3, and ethylene glycol (EG). Single-phased transparent equant crystals of $(H_3dien)[Zn_3(HPO_4)_3(PO_4)]$ (**1**) with yield of 90.8% (based on Zn) were obtained from a reaction mixture of dien, $Zn(NO_3)_2\cdot 6H_2O$, H_3PO_4,H_2O in a molar ratio of 4:2:9:555. By replacing the reactant $Zn(NO_3)_2\cdot 6H_2O$ with $ZnCl_2$ and the solvent H_2O with EG in the above reaction, transparent needle-shaped crystals of $(H_2dien)_{1.5}[Zn_3(HPO_4)_3(PO_4)]$ (**2**) emerged in the product. A major phase of **2** could be prepared from a mixture of dien, $ZnCl_2$, H_3PO_4, and EG in a molar ratio of 6.4:1:15:180. However, the slender crystals cold not be completely separated from minor impurties. By decreasing the amount of dien from 6.4 to 4.6 mmol and increasing temperature to 180 °C, transparent needle-like crystal of $(H_3dien)[Zn_3(H_2PO_4)(HPO_4)(PO_4)_2]$ (**3**) as a minor phase in the product was obtained. The reaction condition was further modified to molar ratios of dien:$ZnCl_2$:H_3PO_4:EG = 4:1:10:36; it yielded another single-phase product of transparent chunky crystals of $(H_3dien)[Zn_3(HPO_4)_3(PO_4)]\cdot 1.5H_2O$ (**4**) (yield 92.7% as based on Zn). When the longer chain pentamine, tepa, was substituted for dien in the synthesis, no crystalline product could be produced until In_2O_3 and $H_2C_2O_4\cdot 2H_2O$ (ox) were included.[23] Finally from a reaction mixture of tepa, $ZnCl_2$, In_2O_3, H_3PO_4, $H_2C_2O_4\cdot 2H_2O$, and H_2O in the molar ratios 2:0.4:0.5:3:2:555, we observed the formation of transparent prismatic crystals of $(H_4tepa)_{0.5}[Zn_{2.5}(HPO_4)_2(PO_4)]\cdot 1.5H_2O$ on the wall of Teflon cup with unreacted yellow powders of In_2O_3 as precipitate in the product. All five chemical formulas were determined from single-crystal structure analysis (vide infra) and confirmed either through solid-state NMR, TGA, or EA data. These measurements as well as UV–vis and PL spectra were performed on samples with individual purity preliminarily checked by powder XRD patterns. The EA data confirmed the stoichiometry of organic amines for three compounds. Found/calcd: C, 7.25/7.01; H, 2.30/2.79; N, 6.22/6.13% for **1**; C, 6.90/6.74; H, 1.44/3.11; N, 5.96/5.90% for **4**; C, 8.42/8.37; H, 3.35/3.25; N, 6.08/6.11% for **5**.

Single-Crystal Structure Analysis. Crystals of dimensions 0.30 × 0.40 × 0.40 mm for **1**, 0.20 × 0.05 × 0.05 mm for **2**, 0.30 × 0.05 × 0.05 mm for **3**, 0.30 × 0.10 × 0.15 mm for **4**, and 0.25 × 0.16 × 0.2 mm for **5** were selected for indexing and intensity data collection at 295 K. The diffraction measurements were performed on Bruker Smart Apex CCD diffractometer systems equipped with a normal focus, 3 kW sealed-tube X-ray source ($\lambda = 0.710\ 73$ Å). Intensity data were collected in 1315 (**2** and **5**) and 2028 (**1**, **3**, and **4**) frames with increasing ω (0.3° per frame). Unit cell dimensions were determined by a least-squares fit of 6935 reflections for **1**, 5470 reflections for **2**, 7536 reflections for **3**, 6224 reflections for **4**, and 8276 reflections for **5**. Empirical absorption corrections based on symmetry equivalents were applied ($T_{min}/T_{max} = 0.50/0.95$ for **1**, 0.73/0.93 for **2**, 0.33/0.94 for **3**, 0.62/0.95 for **4**, and 0.70/0.95 for **5**). On the basis of systematic absences and statistics of intensity distributions, the space groups were determined to be $P\bar{1}$ for **1**, **3**, and **4**, $P2_1/c$ for **2**, and $I\bar{4}2d$ for **5**. The structures were solved by direct methods with all non-hydrogen atoms located on electron-density maps. On the basis of results from bond-valence-sum calculations,[24] the atoms O(4), O(14), O(20), O(24), O(25), and O(32) in **1**, O(5), O(10), O(16), O(21), O(28), and O(30) in **2**, O(4), O(5), and O(6) in **3**, O(3), O(9), and O(15) in **4**, and O(7) and O(10) in **5** were assigned hydroxyl oxygen atoms. The final cycles of refinements, including the atomic coordinates and anisotropic thermal parameters for all non-H atoms and fixed atomic coordinates

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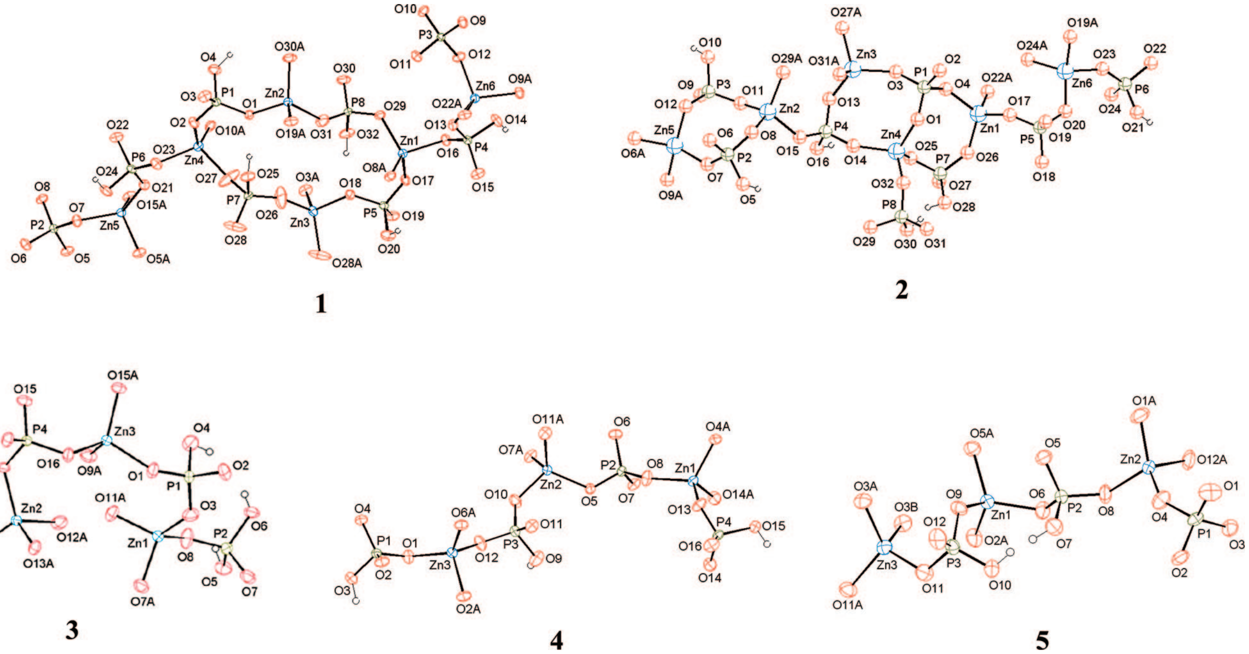
Table 1. Crystal Data for $(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]$ (1), $(C_4H_{16}N_3)[Zn_3(H_2PO_4)(HPO_4)(PO_4)_2]$ (3), $(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]\cdot 1.5H_2O$ (4), and $(C_8H_{27}N_5)_{0.5}[Zn_{2.5}(HPO_4)_2(PO_4)]\cdot 1.5H_2O$ (5)

	1	3	4	5
chemical formula	$C_4H_{19}N_3Zn_3P_4O_{16}$	$C_4H_{19}N_3Zn_3P_4O_{16}$	$C_4H_{22}N_3Zn_3P_4O_{17.5}$	$C_4H_{18.5}N_{2.5}Zn_{2.5}P_3O_{13.5}$
fw	685.21	685.21	712.24	574.05
a/Å	8.5463(3)	8.2558(4)	8.4552(7)	16.0829(8)
b/Å	13.4903(5)	8.5393(4)	10.0614(8)	
c/Å	16.9043(6)	13.5627(6)	12.822(1)	29.805(2)
α/deg	69.533(1)	87.244(1)	109.012(1)	
β/deg	89.581(1)	81.731(1)	90.922(2)	
γ/ deg	86.715(1)	80.492(1)	91.298(2)	
V/Å^3	1822.7(1)	932.92(8)	1030.6(1)	7709.3(8)
Z	4	2	2	16
space group	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)	$P\bar{1}$(No. 2)	$I\bar{4}2d$ (No. 122)
T/°C	23	20	23	23
λ(Mo K)/Å	0.71073	0.71073	0.71073	0.71073
ρ_{calcd}/g cm^{-3}	2.497	2.439	2.295	1.978
μ(Mo K)/cm^{-1}	43.6	42.6	38.6	34.1
reflections collected	21461	9882	11962	27355
unique reflections	8103	4109	4303	4349
goodness-of-fit on F^2	1.063	1.053	1.078	1.118
R_1[a]	0.0268	0.0351	0.0296	0.0488
wR_2[b]	0.0721	0.0955	0.0894	0.1459

[a] $R_1 = F_o| - |F_c|/|F_o|$ for $F_o > 4\sigma(F_o)$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, $P = [\mathrm{Max}(F_o) + 2(F_c)^2]/3$, where a/b = 0.0380/1.03 for **1**, 0.053/1.23 for **3**, 0.0461/0.66 for **4**, and 0.0976/0.00 for **5**.



1 2 3 4 5

Figure 1. ORTEP drawing of the building units in the structures of **1**–**5**. Thermal ellipsoids are given at 50% probability, and small open circles are H atoms.

and isotropic thermal parameters for H atoms,[25] converged at $R1/wR2 = 0.0268/0.0721$ for **1**, 0.1332/0.3320 for **2**,[26] 0.0351/0.0963 for **3**, 0.0291/0.0886 for **4**, and 0.0561/0.1656 for **5**. Neutral-atom scattering factors were used for all the atoms. Anomalous dispersion and secondary extinction corrections were applied. All calculations were performed by using the PC version of the SHELXTL program package.[27] Crystallographic data are listed in Table 1, and ORTEP drawings are shown in Figure 1.

Thermal Analysis. Thermogravimetric analyses (TGA), using a Perkin-Elmer TGA-7 analyzer, were performed on powder samples of **1** (5.85 mg), **4** (2.01 mg), and **5** (2.36 mg) under flowing nitrogen at a heating rate of 10 °C min^{-1}. TG curves (Figure S11) clearly revealed that **1** could be thermally stable until ~220 °C before losing weight while **4** and **5** immediately losing lattice water upon heating. The following mass loss was due to the dehydration of hydrogen phosphate groups and decomposition of the organic templates. The total observed weight loss, 23.1% for **1**, 25.11% for **4**, and 27.06% for **5**, can be compared with the calculated, 22.9% ($6H_2O$ + 2dien) for **1**, 25.83% ($4.5H_2O$ + dien) for **4**, and 27.43% ($3.5H_2O$ + 0.5tepa) for **5**. From a combined thermal treatment and powder XRD study, we confirmed that the structure could sustain up to 200 °C (see Supporting Information Figure S10).

Photoluminescence and Reflectance UV–vis Study. Solid-state PL spectra were measured on powder samples of **1**, **4**, and **5** at room temperature on a Hitachi F-4500 FL spectrophotometer equipped with a Xe lamp (150 W) as the excitation light source. Both the excitation and emission slit widths were set at 5 mm. The

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(26) The quality of the crystals of **2** was always too poor to give better refinement results.
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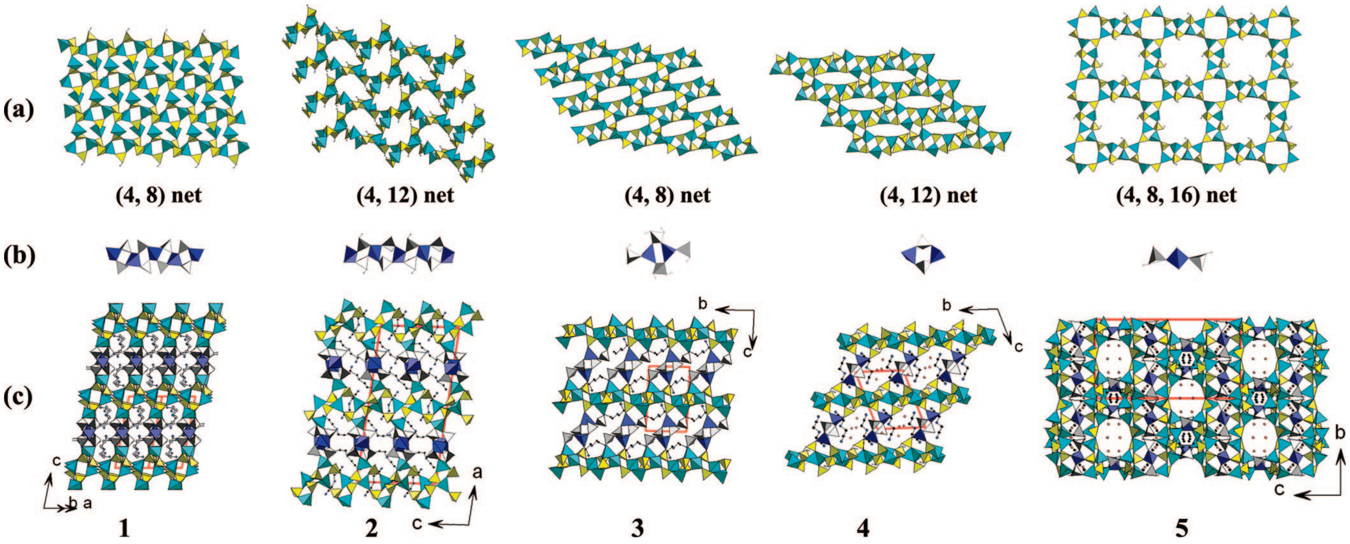

Figure 2. Structures of **1–5**. (a) Five kinds of 2D nets: (4, 8) nets in **1** and **3**, (4, 12) nets in **2** and **4**, and (4, 8, 16) net in **5**. (b) Three types of linkers. (c) Perspective view of 3D frameworks. The H_4tepa^{4+} cations in **5** are residing in 10R channels embedded within the "thick wall" composed of linker sandwiched by two (4, 8, 16) nets. Various polyhedra: Zn–O tetrahedra in cyan (for 2D nets) and blue (for linkers) and P–O tetrahedra in yellow (for 2D nets) and gray (for linker). Amine cations and water molecules are in a ball-and-stick model (C, black; N, blue; O, red). Small open circles are H atoms. The H atoms bonded to N and C atoms are not shown.

excitation and emission spectra were respectively recorded at 320 and 395 nm for **1**, 340 and 400 nm for **4**, and 330 and 385 nm for **5**. All three samples showed photoluminescence peaks in the blue to purple region.

Reflectance UV–vis spectra were measured on powder samples of **4** and **5** plus ZnO (as a check in band gap determination) at room temperature on a Hitachi U-3310 spectrometer equipped with an integrating sphere attachment. The results of calculation based on the spectral data of ZnO gave a band gap of 3.2 eV (387 nm), which is in comparable agreement with its empirical value of 3.3 eV (376 nm). The same calculation performed on measured spectral data yielded band gaps 3.0 and 2.7 eV respectively for **4** and **5**.

Results and Discussion

Framework Topology and Structure Relationship. Each of the three-dimensional anionic frameworks of **1–5** is unique with 16R channels built up with ZnO_4, HPO_4, and PO_4 tetrahedra in common. The chemical compositions of the inorganic frameworks of **1–4** are alike with the same Zn/P ratio while that of **5** is different with a higher Zn content. Their frameworks may all be described as constructed from two-dimensional nets and one- or zero-dimensional units as linkers (Figure 2). Between the stacking nets and linkers are located extra-large channels with 16R apertures. Figure 2a depicts five kinds of 2D tetrahedral nets which are conformably formed of 4-ring units of Zn–O and P–O tetrahedra, namely, (4, 8) nets in **1** and **3**, (4, 12) nets in **2** and **4**, and (4, 8, 16) net in **5**. The (4, 8) net in **1** contains infinite chains of corner-shared 4-ring units of $Zn_2PO_4(HPO_4)$, whereas that in **3** contains infinite chains of edge-shared 4-ring units of $Zn_2(PO_4)_2$. The (4, 12) net in **2** is also different from that in **4** since the 4-ring units are mixed corner- and edged-shared in **2** but purely edge-shared in **4**. Figure 2b describes three types of linkers: infinite 4-ring chains which run parallel to the 2D nets in **1** and **2**; single 4R units which orient upright to the 2D nets in **3** and **4**, and linear tri-tetrahedal units lying between the tetrahedral nets in **5**. Because of the tetragonal symmetry, both the (4, 8, 16) nets and tri-tetrahedral linkers orient into two directions and form a higher symmetric framework than those of **1–4** (Figure 2c).

Charge and Location of Templates. Dien molecules served as a template or ligand in four previously reported zinc phosphates,[28–31] none of which possessed channels with aperture size over 10R. The structures of **1–4** are the first examples which unfold the match between template dien and the divalent metal ion Zn^{2+} on generating 16R-channel structures. Dien molecules in **1**, **3**, and **4** were fully protonated as H_3dien^{3+} and residing in 16R channels, whereas they were merely diprotonated in **2**, presumably due to a less acidic reaction condition with inorganic solvent. Moreover, these discharged cations are not only residing in the 16R channels but also in the 12R windows within (4, 12) nets. Therefore, 50% more of the dien template was observed in **2** than in **1**, **3**, and **4**. Interactions between the organic templates and the inorganic frameworks are primarily cation–anion interactions plus weak hydrogen-bonding between $-NH_3$ and HPO_4 groups. The seven-atom-skeleton-long dien cations are stretching along the radial direction in the 16R channels and all deformed to various extents with the length of skeleton (distance between two terminal N atoms) being 5.50 Å in **1**, 6.18 Å in **2**, 6.05 Å in **3**, and 6.25 Å in **4**. Interestingly, the organic cations within the 12R windows in **2** showed a much longer length of 6.88 Å. We found the shape of these H_2dien^{2+} cations were nearly linear (170° for the angle among the three amino N atoms), in contrast to those distorted (139°) in 16R channels.

In the structure of **5**, the template, tepa, was disordered with only fragments being able to locate on electron density maps. Even so, the possibility that tepa might have decom-

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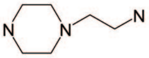
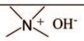
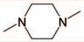
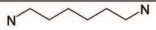
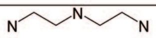
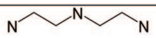
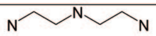
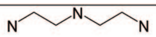
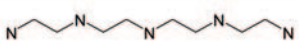
Table 2. Chemical Formula, Template Type and Framework Characteristics of Existing Zinc Phosphates with Channel Apertures of 16R or up

	Empirical Formula	Template	Zn/P	Max. aperture (dimension)	Void space*	F. D.	Ref.
a	$(C_6H_{16}N_2)[Zn_3(HPO_4)(PO_4)_2]\cdot 2H_2O$		1/1	24 (1D)	49.8%	12.1	14
b	$(C_6H_{18}N_3)[Zn_4(PO_4)(HPO_4)_4]_3\cdot 2H_2O$,		4/5	20 (1D)	32.7%	14.7	19
c	$(C_6H_{18}N_3)[Zn_3(HPO_4)_3(PO_4)]$		3/4	16 (1D)	31.8%	14.3	35
d	$(C_4H_{12}N)_2[Zn_3(HPO_4)_4]$		3/4	16 (1D)	45.6%	12.21	36
e	$(C_6H_{16}N_2)_{0.5}(C_5H_{14}N_2)[Zn_6(PO_4)_5(H_2O)]$		6/5	16 (1D)	42.1%	14.88	37
f	$(C_2H_8N)[Zn_3(HPO_4)_2(PO_4)]\cdot H_2O$	$[(NCH_3)_2]_3PO$	1/1	16 (1D)	26.5%	17.35	38
g	$(C_4H_{12}N_2)_{0.5}[Zn(H_2PO_4)(HPO_4)]$		1/2	16 (1D)	28.4%	14.26	39
h	$(C_6H_{18}N_2)[Zn_4(HPO_4)_2(PO_4)_2]\cdot 3H_2O$		1/1	20 (1D)	45.7%	13.3	22
i	$(C_5H_{18}N_3)[Zn_3(HPO_4)_3(PO_4)]$		3/4	16 (1D)	36.5%	13.68	21
j	$(C_6H_{22}N_4)_{0.5}[Zn_3(HPO_4)(PO_4)_2]$		1/1	16 (1D)	26.7%	17.03	20
1	$(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]$		3/4	16 (1D)	27.6%	15.36	this work
2	$(C_4H_{15}N_3)_{1.5}[Zn_3(HPO_4)_3(PO_4)]$		3/4	16 (1D)	36.6%	13.43	this work
3	$(C_4H_{16}N_3)[Zn_3(H_2PO_4)(HPO_4)(PO_4)_2]$		3/4	16 (2D)	27.3%	15.01	this work
4	$(C_4H_{16}N_3)[Zn_3(HPO_4)_3(PO_4)]\cdot 1.5H_2O$		3/4	16 (2D)	33.7%	13.58	this work
5	$(C_8H_{27}N_5)_{0.5}[Zn_{2.5}(HPO_4)_2(PO_4)]\cdot 1.5H_2O$		5/6	16 (2D)	51.7%	11.4	this work

* Void space is defined as nonframework volume which can be accessed by solvent molecules. This value was calculated via PLATON analysis.[40]

posed into triamine or tetraamine was ruled out. The existence of smaller amine cations in **5** could not match with other data. Furthermore, despite that the tepa molecule was pentaprotonated in two reported zincophosphates,[32,33] it is only tetraprotonated in **5** with their presence as H_4tepa^{4+} confirmed by ^{13}C NMR spectroscopy.[34] It is also the first time that this pentamine can behave as an effective template in generating an extra-large-channel ZnPO structure. In contrast to H_3dien^{3+} cations residing in the main 16R channels in **1**, **3**, and **4**, the H_4tepa^{4+} cations in **5** were dissimilarly observed in 10R channels embedded within the "thick wall" composed of linker sandwiched by two (4, 8, 16) nets (see Figure 2c). The 16R channels in **5** are instead filled with lattice water molecules only.

Channel Characteristic vs Nonframework Space. Extra-large-channel zincophosphates with apertures of 16R or up were coherently one-dimensional in all previously reported structures (Table 2). The frameworks of **1** and **2** are having the same characteristic of one-dimensional 16R channels, but those of **3**, **4**, and **5** have unprecedented two-dimensional 16R channels instead. The two-direction 16R channels intersect with each other in the structures of **3** and **4** but run crisscross without interception in **5** (Figure 3). But in common with each other, secondary channels with different directions from the main were observed in all five structures, i.e., 8R in **1** and **3**, 10R in **2**and **5**, or 12R in **4**. The nonframework volume in **1**–**4**, namely the void space in structure, seized by the same kind of template seems to correlate closely with the multichanneled characteristic. As shown in Table 2, the nonframework space calculated for **2** and **4** is larger than those for **1** and **3** due to the possession of larger secondary channels in the former two. Furthermore, because of the possession of nonintersecting two-dimensional 16R and 10R channels, the nonframework space calculated for **5** is even larger than that for ND-1 (51.7% vs 49.8%). The structure of **5** is evidently unique for its highest nonframework volume as well as its lowest FD value (11.4 tetrahedra per 1000 Å^{-3}) among all 3D open-framework zincophosphates with channel size over 16 rings.

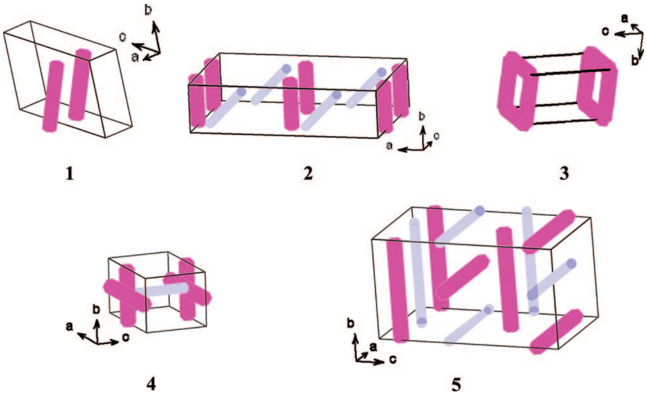


Figure 3. Schematic drawings of the distribution and orientation of channels in **1**–**5**. 16R channels in all five structures are shown in purple columns. Columns in gray are 10R channels (**2** and **5**) and 12R channels (**4**). 8R channels in **1** and **3** are not shown.

Conclusion

We have demonstrated that five unique zinc phosphate structures, **1**–**5**, all featuring in 16R channels, could be

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(32) Liu, Y. L.; Liu, W.; Xing, Y.; Shi, Z.; Fu, Y. L.; Pang, W. Q. *J. Solid State Chem.* **2002**, *166*, 265.

(33) Neeraj, S.; Natarajan, S. *J. Phys. Chem. Solids* **2001**, *62*, 1499.

(34) See Supporting Information Figure S9.

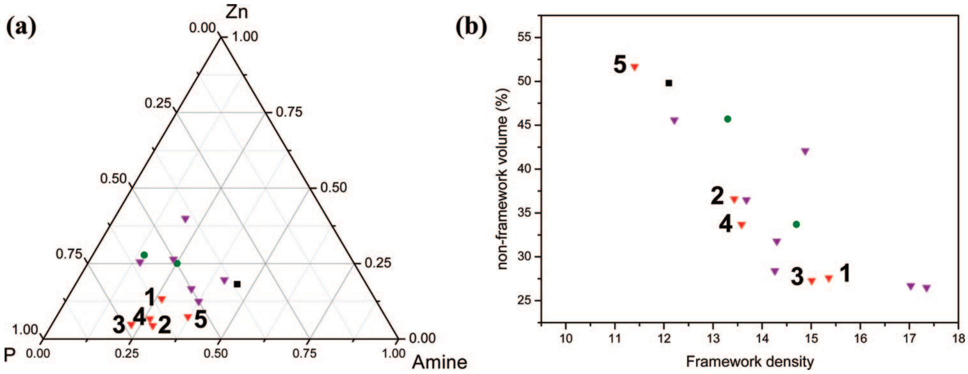

Figure 4. Diagrams of compositional space (a) and correlation between the nonframework volume and FD value (b). Structure with channels of 24R[14] in black square, 20R[19,22] in green circle, 16R in purple (previously reported),[20,21,35,39]and red (this work, **1–5**).

prepared by using chain-type polyamines as template molecules in reaction conditions shown in the composition space (Figure 4). It is for the first time that one kind of triamine template, dien, can be used to generate four different multichannel frameworks with maximum 16R channels but varied void content. The longer chain pentamine template tepa resulted in 16R channels as well. Although the size of template molecules was of no avail against the channel aperture, the nonframework space has been substantially augmented with increasing length and amino groups in tepa. Correlation between the nonframework space and FD values in the system of zincophosphates is shown in Figure 4b, in which **5** is disclosed containing the highest nonframework space and lowest FD value among those with channel sizes over 16Rs. It is inspiring that the nonframework space is significantly augmented with polyamine varied from triamine to pentamine which were predicted to decrease on the basis of previous studies.[20–22] Investigation on the template effect of longer chain polyamines to prepare more porous metal phosphates is in progress.

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Supporting Information Available: X-ray crystallographic information files (CIF) and tables of bond lengths and bond angles for **1**, **3**, **4**, and **5**; powder XRD patterns and PL spectra for **1**, **4**, and **5**; reflectance UV–vis spectra for **4** and **5** and ^{13}C NMR for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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