

## Zeolite Ionic Crystals Assembled through Direct Incorporation of Polyoxometalate Clusters within 3D Metal–Organic Frameworks

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Received February 11, 2007

Polyoxometalate-based metal–organic frameworks  $\{[\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{PMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\text{CH}_3\text{CN}\}_n$  (**2**),  $\{[\text{Dy}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{PMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\text{CH}_3\text{CN}\}_n$  (**3**),  $\{[\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{dpdo})_{0.5}(\text{CH}_3\text{CN})_{0.5}(\text{H}_2\text{O})_3\}_n$  (**4**),  $\{[\text{Ho}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{dpdo})_{0.5}(\text{CH}_3\text{CN})_{0.5}(\text{H}_2\text{O})_3\}_n$  (**5**),  $\{[\text{Ni}(\text{dpdo})_2(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2]_2(\text{SiMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\}_n$  (**6**), and  $\{[\text{Ni}(\text{dpdo})_3]_4(\text{PW}_{12}\text{O}_{40})_3[\text{H}(\text{H}_2\text{O})_{27}(\text{CH}_3\text{CN})_{12}]\}_n$  (**7**) (where dpdo is 4,4'-bipyridine-*N,N'*-dioxide) were constructed via self-assembly by embedding Keggin-type polyanions within the intercrystalline voids as guests or pillars. Compounds **2** and **3** are isomorphous and exhibit three-dimensional (3D) noninterwoven  $6^4$  frameworks with distorted-honeycomb cavities occupied by the polyanions. Compounds **4** and **5** are comprised of 3D noninterwoven frameworks formed by linking the adjacent folded sheets through hydrogen bonds and  $\pi$ - $\pi$  stacking interactions relative to the free isolated dpdo ligand. Compound **6** is a pillar-layered framework with the  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions located on the square voids of the two-dimensional bilayer sheets formed by the dpdo ligands and nickel(II) ions. Compound **7** is a 3D metal–organic framework formed by nickel(II) and 4,4'-bipyridine-*N,N'*-dioxide with the globular Keggin-structure  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anion as the template. A large protonated water cluster  $\text{H}^+(\text{H}_2\text{O})_{27}$  is trapped and stabilized within the well-modulated cavity.

## Introduction

Porous metal–organic frameworks (MOFs) have emerged as a promising new class of materials that often have crystalline, well-defined cavities (or channels) and can be used for the inclusion of various guest species.<sup>1–4</sup> Whereas the initial focus was on synthesis and structural aspects, more

recently, the attention has shifted to possible applications of these materials, preponderantly in gas storage, catalysis, and chemical separations.<sup>3,4</sup> Bearing unique properties and exhibiting a diverse compositional range, polyoxometalates (POMs) represent an outstanding class of molecular building blocks for the construction of such kinds of materials.<sup>5,6</sup> Despite the remarkable progress in the construction of three-dimensional (3D) POM-based coordination polymers<sup>7</sup> and ionic crystals composed by POMs and large discrete cations,<sup>8</sup> the rational design and assembly of POM-based coordination polymers, especially POM-based open MOFs, remains an

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arduous task for coordination chemists due to the large number of potential coordination sites and the relatively weak coordination ability of POMs. To overcome the obstacles at presented here, a new adopted synthetic approach to embed POMs into the frameworks of the coordination polymers by constructing 3D POM-based coordination polymers was developed.<sup>9</sup> Very recently, this new synthetic strategy was improved by carefully adjusting the stoichiometric proportion of the highly charged POMs and the metal–organic units.<sup>10</sup> The presence of nanosized highly charged anions, like the well-known Keggin heteropolyanions, as building blocks, not only prevented the occurrence of lattices interpenetration but also made the cavities partially occupied by the anions, from which the porous MOF **1** was achieved.<sup>10</sup> Since the elaboration of the new synthetic pathways to access novel topologies and, more importantly, a better understanding of their assemblage, the correlation of building block geometrical information to the resultant structure is of significant scientific interest. Herein, lanthanide ions that generally adopt coordination numbers higher than six were chosen to prepare novel MOFs.

On the other hand, solvated protons are key elements in the dissociation and transport phenomena of aqueous chemistry and biological systems.<sup>11</sup> Despite recent remarkable experimental progress, structural characterization is still far more difficult to achieve.<sup>12,13</sup> Therefore, both the accurate calculations based on gas-phase models and the crystallographic characterizations in condensed phase will be emerging to help understand the existing experimental data.

Since the charges of the Keggin heteropolyanions can be easily adjusted without changing the basic structures, different charged polyanions  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  and  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  are selected to construct POM-based 3D MOFs with different charges. It can be expected that to maintain the neutrality of the whole crystal different solvated protons might be formed and stabilized within these frameworks. 4,4'-Bipyridine-*N,N'*-dioxide (dpdo) was used as the suitable longer spacer ligand, not only because of the excellent hard acid/hard base complementarity of the lanthanide cations/first-row transition-metal ions and the N-oxide donor but also because of the small steric size of this ligand that avoids crowding at the metal centers and encourages high connectivity and a large volume of voids.<sup>14</sup>

## Experimental Section

**General Procedure.** All organic solvents and materials used for synthesis were of reagent grade and used without further purification. The metal chlorides  $\text{LnCl}_3 \cdot 6\text{H}_2\text{O}$  (Ln = Gd, Dy, Ho) were prepared by dissolving  $\text{Ln}_2\text{O}_3$  (99.9%) in hydrochloric acid, followed by drying and crystallization.  $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ ,  $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ , and  $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$  were prepared according to a literature method<sup>15</sup> and characterized by IR spectra and thermogravimetric analyses (TGA). Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240C analyzer. IR spectra were recorded on a Vector 22 Bruker spectrophotometer with KBr pellets in the 400–4000  $\text{cm}^{-1}$  regions at room temperature. Laser Raman spectra of the single crystals of the title compounds were measured with a JY HR-800 spectrometer using the 488 Å line as the exciting source in the 100–2000  $\text{cm}^{-1}$  region at 123 K. TGA studies of compounds **2**–**7** were carried out on a Perkin-Elmer thermal analyzer in an atmosphere of  $\text{N}_2$ .

**Synthesis of  $[\{\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3\}(\text{PMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\text{CH}_3\text{CN}]_n$  (**2**).** The formation of heteropolyacid gadolinium salts was accomplished by neutralization of the acids.  $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$  (41 mg, 0.02 mmol) and  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$  (8 mg, 0.02 mmol) were dissolved in water (2 mL), and the solution was heated to saturation at 80 °C in a water bath. Yellow crystals were formed after cooling the saturated solution and slow evaporation at room temperature and were characterized by their IR spectrum. A buffer layer of a solution (10 mL) of acetonitrile/water (3:2, v/v) was carefully layered over an 4 mL aqueous solution of 4,4'-bipyridine-*N,N'*-dioxide hydrate (0.1 mmol, 22 mg). Then, an acetonitrile/water (3:1, v/v) solution (4 mL) of resultant heteropolyacid gadolinium salts was carefully layered over the buffer layer. Orange crystals appeared after 4–5 weeks and were collected and dried in air after quickly being washed with water. Yield: 79%, based on  $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{45}\text{N}_8\text{O}_{53}\text{PMo}_{12}\text{Gd}$ : C, 17.62; H, 1.58; N, 4.40. Found: C, 17.48; H, 1.92; N, 4.55. IR (KBr): four

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characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{Mo}-\text{Oc})$  (794  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Ob})$  (880  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}=\text{Ot})$  (960  $\text{cm}^{-1}$ ), and  $\nu(\text{P}-\text{Oa})$  (1062  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules, namely,  $\nu(\text{N}-\text{O})$  (1233  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1472  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1181  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (838  $\text{cm}^{-1}$ ).

**Synthesis of  $\{[\text{Dy}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{PMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\text{CH}_3\text{CN}\}_n$  (3).** Compound **3** was prepared in the same way as **2**, using  $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$  (0.02 mmol) to replace  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ . Orange crystals appeared after 4–5 weeks and were collected and dried in air after quickly being washed with water. Yield: 71%, based on  $\alpha\text{-H}_3\text{-PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{42}\text{H}_{45}\text{N}_9\text{O}_{53}\text{PMo}_{12}\text{Dy}$ : C, 17.58; H, 1.58; N, 4.40. Found: C, 17.61; H, 1.65; N, 4.52. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{Mo}=\text{Ot})$  (960  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Ob})$  (880  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Oc})$  (795  $\text{cm}^{-1}$ ), and  $\nu(\text{P}-\text{Oa})$  (1062  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules, namely,  $\nu(\text{N}-\text{O})$  (1233  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1473  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1180  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (838  $\text{cm}^{-1}$ ), respectively.

**Synthesis of  $\{[\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{dpdo})_{0.5}(\text{CH}_3\text{CN})_{0.5}(\text{H}_2\text{O})_3\}_n$  (4).** Compound **4** was prepared in the same way as **2**, using  $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$  (40 mg, 0.02 mmol) instead of  $\alpha\text{-H}_3\text{PMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Orange single crystals appeared after 5 weeks and were collected and dried in air after quickly being washed with water. Yield: 82%, based on  $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{46}\text{H}_{52.5}\text{N}_{9.5}\text{O}_{56}\text{GdMo}_{12}\text{Si}$ : C, 18.59; H, 1.78; N, 4.48. Found: C, 18.36; H, 1.63; N, 4.26. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{Mo}=\text{Ot})$  (951  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Ob})$  (865  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Oc})$  (793  $\text{cm}^{-1}$ ), and  $\nu(\text{Si}-\text{Oa})$  (905  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules, namely,  $\nu(\text{N}-\text{O})$  (1228  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1470  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1181  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (838  $\text{cm}^{-1}$ ).

**Synthesis of  $\{[\text{Ho}(\text{dpdo})_4(\text{H}_2\text{O})_3](\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{dpdo})_{0.5}(\text{CH}_3\text{CN})_{0.5}(\text{H}_2\text{O})_3\}_n$  (5).** Compound **5** was prepared in the same way as **4**, using  $\text{HoCl}_3 \cdot 6\text{H}_2\text{O}$  (0.02 mmol) to replace  $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ . Orange-yellow single crystals appeared after 4–5 weeks and were collected and dried in air after quickly being washed with water. Yield: 80%, based on  $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{46}\text{H}_{52.5}\text{N}_{9.5}\text{O}_{56}\text{HoMo}_{12}\text{Si}$ : C, 18.55; H, 1.78; N, 4.47. Found: C, 17.95; H, 2.16; N, 4.16. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{Mo}=\text{Ot})$  (950  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Ob})$  (865  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Oc})$  (792  $\text{cm}^{-1}$ ), and  $\nu(\text{Si}-\text{Oa})$  (905  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules, namely,  $\nu(\text{N}-\text{O})$  (1228  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1471  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1180  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (838  $\text{cm}^{-1}$ ).

**$\{[\text{Ni}(\text{dpdo})_2(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2](\text{SiMo}_{12}\text{O}_{40})(\text{H}_2\text{O})_2\}_n$  (6).** The formation of heteropolyacid nickel salts (yellowish-green crystals) was accomplished by the neutralization of the acids in the same way as gadolinium phosphomolybdate ( $\alpha\text{-H}_4\text{SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$  (41 mg, 0.02 mmol) and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (10 mg, 0.04 mmol)). Compound **6** was prepared in the same way as **2**, using more 4,4'-bipyridine-*N,N'*-dioxide hydrate (0.15 mmol, 33 mg). Yellow block crystals appeared after 3 weeks and were collected and dried in air after quickly being washed with water. Yield: 80%, based on  $\alpha\text{-H}_4\text{-SiMo}_{12}\text{O}_{40} \cdot 14\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{44}\text{H}_{50}\text{N}_{10}\text{O}_{54}\text{Ni}_2\text{Mo}_{12}\text{Si}$ : C, 18.35; H, 1.75; N, 4.87. Found: C, 18.51; H, 1.76; N, 4.69. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{Mo}=\text{Ot})$  (951  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Ob})$  (861  $\text{cm}^{-1}$ ),  $\nu(\text{Mo}-\text{Oc})$  (792  $\text{cm}^{-1}$ ), and  $\nu(\text{Si}-\text{Oa})$  (905  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules,

namely,  $\nu(\text{N}-\text{O})$  (1214  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1470  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1178  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (839  $\text{cm}^{-1}$ ).

**Synthesis of  $\{[\text{Ni}(\text{dpdo})_3]_4(\text{PW}_{12}\text{O}_{40})_3[\text{H}(\text{H}_2\text{O})_{27}(\text{CH}_3\text{CN})_{12}]\}_n$  (7).** The formation of heteropolyacid nickel salts (greenish crystals) was accomplished by the neutralization of the acids in the same way as gadolinium phosphomolybdate ( $\alpha\text{-H}_3\text{PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$  (90 mg, 0.03 mmol) and  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  (7.5 mg, 0.03 mmol)). Compound **7** was prepared in the same way as **2**, using heteropolyacid nickel salts to replace gadolinium phosphomolybdate. Red block crystals appeared after 2 weeks and were collected and dried in air after quickly being washed with water. Yield: 83%, based on  $\alpha\text{-H}_3\text{-PW}_{12}\text{O}_{40} \cdot 6\text{H}_2\text{O}$ . Anal. Calcd for  $\text{C}_{144}\text{H}_{187}\text{N}_{36}\text{O}_{171}\text{Ni}_4\text{P}_3\text{W}_{36}$ : C, 14.29; H, 1.56; N, 4.17. Found: C, 13.91; H, 1.63; N, 4.02. IR (KBr): four characteristic asymmetric vibrations resulting from heteropolyanions with the Keggin structure:  $\nu(\text{W}=\text{O}_i)$  (978  $\text{cm}^{-1}$ ),  $\nu(\text{W}-\text{O}_b)$  (895  $\text{cm}^{-1}$ ),  $\nu(\text{W}-\text{O}_c)$  (810  $\text{cm}^{-1}$ ), and  $\nu(\text{P}-\text{O}_a)$  (1080  $\text{cm}^{-1}$ ); four characteristic vibrations resulting from dpdo molecules, namely,  $\nu(\text{N}-\text{O})$  (1225  $\text{cm}^{-1}$ ),  $\nu(\text{ring})$  (1475  $\text{cm}^{-1}$ ),  $\delta(\text{C}-\text{H}, \text{in plane})$  (1180  $\text{cm}^{-1}$ ), and  $\delta(\text{N}-\text{O})$  (840  $\text{cm}^{-1}$ ).

**Crystallography.** Intensity data for the complexes **2–7** was collected on a Siemens SMART-CCD diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ), using the SMART and SAINT<sup>16</sup> programs. The structures were solved by direct methods and refined on  $F^2$  by using full-matrix least-squares methods with the SHELXTL program, version 5.1.<sup>17</sup> All non-hydrogen atoms except some disordered solvent molecules were refined anisotropically. For compounds **2** and **3**, four lattice water molecules were refined disordered with the site occupancy factors (sof) fixed at 0.5. For compounds **4** and **5**, four lattice water molecules were refined disordered with the sof refined using free variables, and one acetonitrile molecule was refined disordered with the sof for the atoms in it fixed at 0.5. These disordered atoms were refined isotropically. For compound **6**, several oxygen atoms in the polyanion were refined disordered with the sof fixed at 0.5 for all these disordered atoms; however, these atoms were refined anisotropically. For compound **7**, one water molecule was refined disordered with the sof fixed at 0.25 for O(3W); this oxygen atom and the O(4W) were refined isotropically. The hydrogen atoms of the organic molecules were localized in their calculated positions and refined using a riding model. Hydrogen atoms of the ligands were localized in their calculated positions and refined using a riding model. The hydrogen atoms of the coordinated water molecules were found by difference Fourier maps and refined by fixing the O–H bond of 0.85  $\text{\AA}$  and the isotropic temperature factors at 1.2 times that of the mother oxygen atoms attached. For compounds **2–5**, hydrogen atoms of the disordered lattice solvent molecules were not treated. For compound **6**, hydrogen atoms of the solvent molecules were found by difference Fourier maps and refined by fixing the O–H bond of 0.85  $\text{\AA}$ , the C–H bond of 0.93  $\text{\AA}$ , and the isotropic temperature factors at 1.2 times that of the mother atoms attached. For compound **7**, only the hydrogen atoms of acetonitrile molecules were found by difference Fourier maps and refined by fixing the C–H bond of 0.93  $\text{\AA}$  and the isotropic temperature factors at 1.2 times that of the mother atoms attached. The crystal parameters, data collection, and refinement results for compounds **2–7** are summarized in Table 1.

(16) SMART and SAINT, Area Detector Control and Integration Software; Siemens Analytical X-ray Systems, Inc.: Madison, WI, 1996.

(17) G. M. Sheldrick. SHELXTL V5.1 Software Reference Manual; Bruker AXS, Inc.: Madison, WI, 1997.

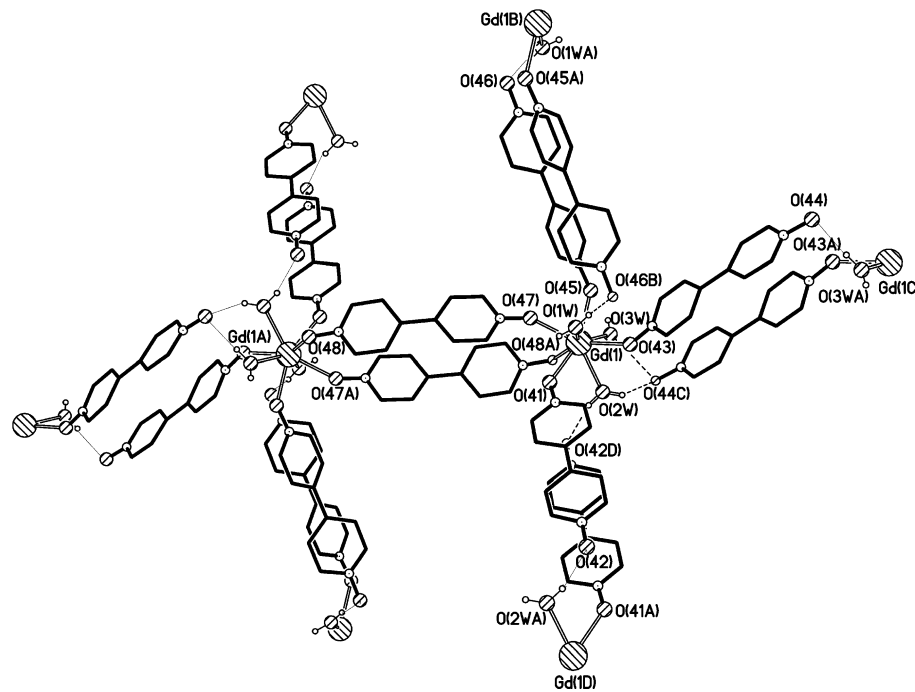
**Table 1.** Crystal Data and Structure Refinement for Complexes 2–7

	2	3	4	5	6	7
formula	C <sub>42</sub> H <sub>45</sub> N <sub>9</sub> O <sub>53</sub> <sup>-</sup> GdMo <sub>12</sub> P	C <sub>42</sub> H <sub>45</sub> N <sub>9</sub> O <sub>53</sub> <sup>-</sup> DyMo <sub>12</sub> P	C <sub>46</sub> H <sub>52.5</sub> N <sub>9.5</sub> O <sub>56</sub> <sup>-</sup> GdMo <sub>12</sub> Si	C <sub>42</sub> H <sub>52.5</sub> N <sub>9.5</sub> O <sub>54</sub> <sup>-</sup> HoMo <sub>12</sub> Si	C <sub>44</sub> H <sub>50</sub> N <sub>10</sub> O <sub>54</sub> <sup>-</sup> Ni <sub>2</sub> Mo <sub>12</sub> Si	C <sub>144</sub> H <sub>187</sub> N <sub>36</sub> O <sub>171</sub> <sup>-</sup> Ni <sub>4</sub> P <sub>3</sub> W <sub>36</sub>
fw	2863.37	2868.62	2971.10	2978.78	2879.73	12104.65
cryst syst	triclinic	triclinic	triclinic	triclinic	triclinic	cubic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>Im</i> 3
<i>a</i> /Å	11.736(4)	11.699(1)	13.222(3)	13.210(3)	11.430(3)	23.133(1)
<i>b</i> /Å	17.472(7)	17.476(2)	16.498(4)	16.532(3)	12.242(3)	23.133(1)
<i>c</i> /Å	18.857(7)	18.847(2)	18.489(5)	18.518(4)	14.279(3)	23.133(1)
$\alpha$ /deg	92.186(6)	92.071(2)	88.827(4)	88.736(4)	106.196(4)	
$\beta$ /deg	97.799(6)	97.642(2)	82.058(5)	81.983(4)	94.316(4)	
$\gamma$ /deg	98.882(7)	98.840(2)	83.139(5)	83.310(4)	98.294(3)	
<i>V</i> /Å <sup>3</sup>	3778 (2)	3767.2(6)	3965.6(18)	3977.3(14)	1884.5(7)	12379.3(10)
<i>Z</i>	2	2	2	2	1	2
<i>D<sub>c</sub></i> /g cm <sup>3</sup>	2.517	2.529	2.488	2.487	2.537	3.247
$\mu$ /mm <sup>-1</sup>	2.918	3.038	2.783	2.936	2.544	17.08
data unique	16 416	16 141	17 232	15 447	8019	2553
<i>R</i> (int)	0.0787	0.0507	0.0747	0.0540	0.0360	0.1031
GOF	1.029	1.057	1.008	1.032	0.998	1.020
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0613	0.0555	0.0639	0.0574	0.0745	0.0743
w <i>R</i> 2 (all data)	0.1543	0.1561	0.1646	0.1301	0.1711	0.2498

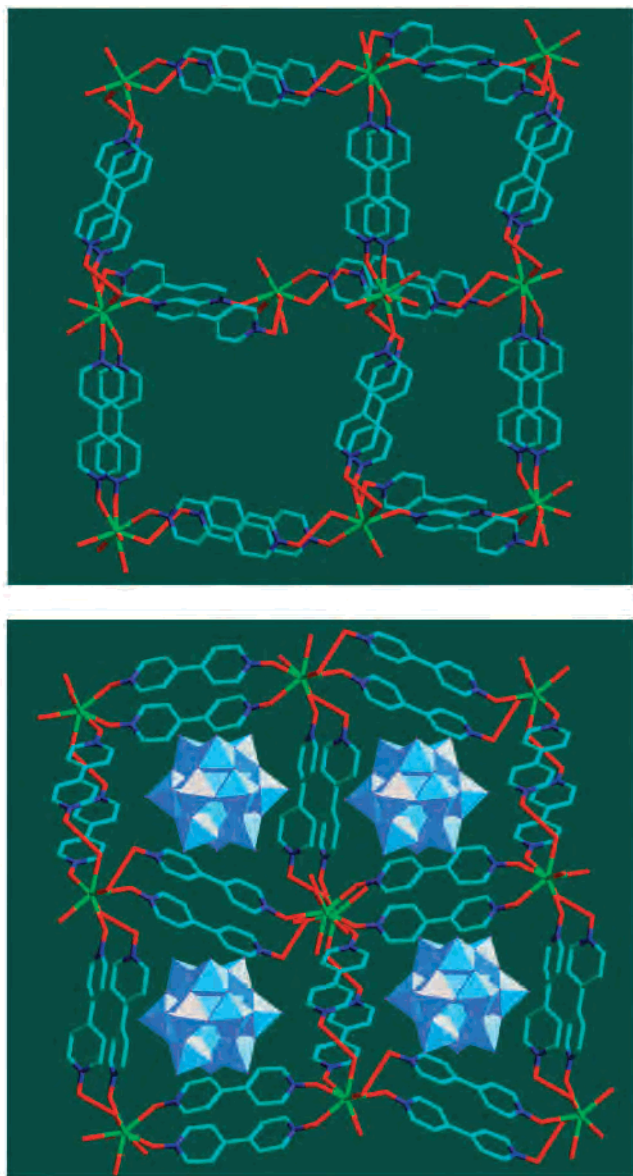
## Results and Discussion

**Lanthanide-Based Zeolite Ionic Crystals.** The reaction of gadolinium phosphomolybdate or dysprosium phosphomolybdate with 4,4'-bipyridine-*N,N'*-dioxide (dpdo) in acetonitrile/water solution gave compounds {Gd(dpdo)<sub>4</sub>(H<sub>2</sub>O)<sub>5</sub>(PMO<sub>12</sub>O<sub>40</sub>)(CH<sub>3</sub>CN)}<sub>n</sub> (**2**) or {Dy(dpdo)<sub>4</sub>(H<sub>2</sub>O)<sub>5</sub>(PMO<sub>12</sub>O<sub>40</sub>)(CH<sub>3</sub>CN)}<sub>n</sub> (**3**), respectively, which were isomorphic and exhibited 3D noninterwoven frameworks with distorted-honeycomb cavities occupied by the anions. In compound **2**, each Gd<sup>3+</sup> cation is coordinated in a distorted-square-antiprismatic geometry by three aqua ligands, four oxygen atoms

from four independent dpdo ligands, and one oxygen atom from a symmetrically relative dpdo ligand. Of the four independent dpdo ligands, the one containing the two oxygen atoms O(47) and O(48) acts as a bridging ligand to link two identical metal centers in a centrosymmetrically dimeric fashion, while the other three ligands act as the terminal monodentate ligands to each connect with one coordinated water molecule from different neighbors through hydrogen bonds. And each of the three coordinated water molecules of O(1W), O(2W), and O(3W) connects to the symmetric dpdo ligand resulting in three centrosymmetrically 2-fold hydrogen-



**Figure 1.** Perspective of the coordinated geometry of the Gd<sup>3+</sup> ion in compound **2** showing the four-connected node through the centrosymmetric double-bridging linkers. Hydrogen atoms of the ligands are omitted for clarity. Selected bond distances (Å) for compound **2**: Gd(1)–O(45) 2.335(6), Gd(1)–O(47) 2.346(6), Gd(1)–O(48A) 2.353(6), Gd(1)–O(43) 2.346(6), Gd(1)–O(41) 2.389(6), Gd(1)–O(3W) 2.413(6), Gd(1)–O(1W) 2.430(6), Gd(1)–O(2W) 2.432(7); O(1W)···O(46B) 2.63(2), O(1W)···N(9A) 2.78(2), O(2W)···O(44C) 2.80(2), O(2W)···O(42D) 2.78(2), O(3W)···O(44C) 2.85(2), O(3W)···O(48A) 2.79(2). For Dy<sup>3+</sup>, the ion in compound **3** has the same coordinated geometry. Selected bond distances (Å) for compound **3**: Dy(1)–O(45) 2.287(6), Dy(1)–O(47) 2.324(6), Dy(1)–O(48A) 2.336(6), Dy(1)–O(43) 2.345(6), Dy(1)–O(41) 2.354(6), Dy(1)–O(3W) 2.399(7), Dy(1)–O(1W) 2.405(7), Dy(1)–O(2W) 2.410(6); O(1W)···O(46B) 2.65(2), O(1W)···N(9A) 2.79(2), O(2W)···O(44C) 2.83, O(2W)···O(42D) 2.79, O(3W)···O(44C) 2.84, O(3W)···O(48A) 2.76(2). Symmetry code: A, 1 – *x*, 1 – *y*, 1 – *z*; B, 1 – *x*, 1 – *y*, 1 – *z*; C, 1 – *x*, –*y*, 2 – *z*; D, –*x*, –*y*, 1 – *z*.



**Figure 2.** 3D  $6^4$  net formed by the  $[\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3]^{3+}$  units in compound **2** (top) and the 3D noninterwoven framework with distorted-honeycomb cavities occupied by the polyanions (bottom). Hydrogen atoms and the lattice solvent molecules are omitted for clarity.

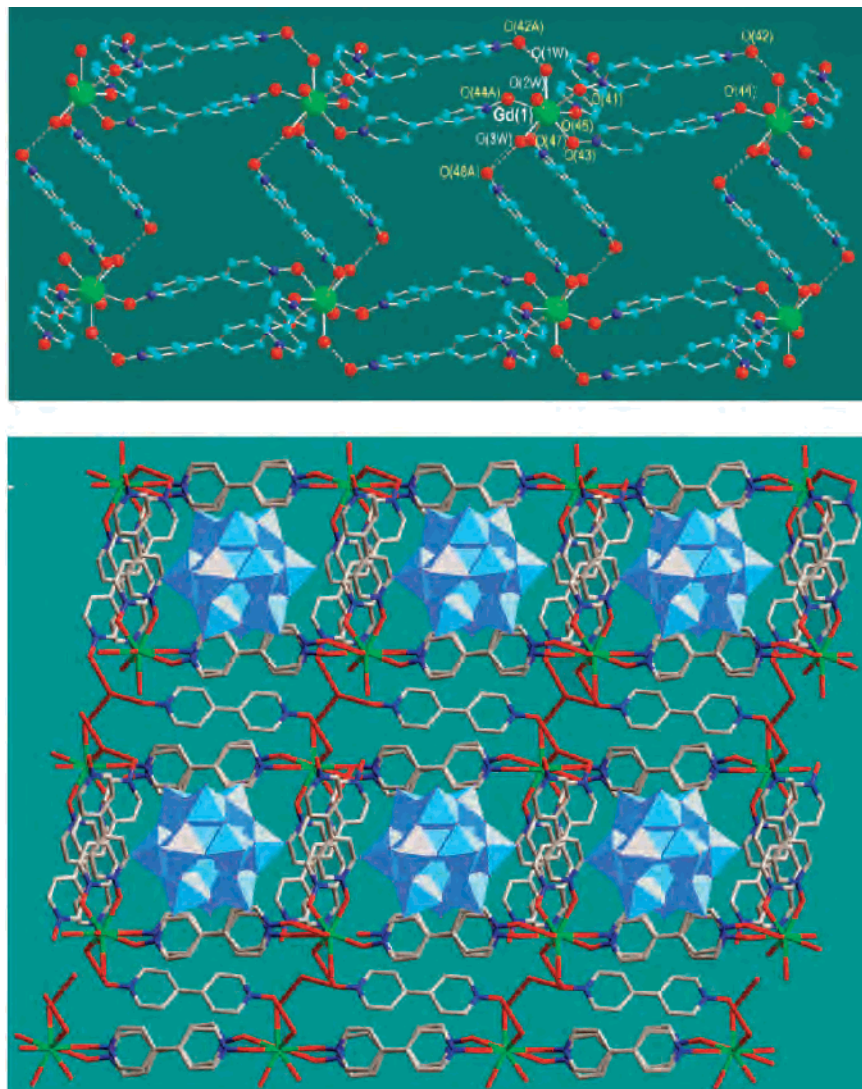
bonding linkers. Thus a  $\text{Gd}^{3+}$  center acts as a four-connected node (Figure 1) to form a 3D noninterwoven  $6^4$  net with distorted-honeycomb cavities occupied by the polyanions (Figure 2). The intermolecular  $\pi$ - $\pi$  stacking interactions between the pyridyl rings within each pair of the centrosymmetrically double-bridging linker are likely to stabilize the formed framework. To embed the Keggin-type  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anions for charge compensation, each honeycomb cavity is heavily distorted with one direction heavily condensed. The acetonitrile solvent molecule and disordered lattice water molecules (O(4W), O(5W), and O(6W)) are presented in the channels. In compound **2**, the bond lengths of P-O and Mo-O are 1.524(5)–1.535(5) and 1.662(6)–2.446(5) Å, respectively, and in compound **3**, the bond lengths of P-O and Mo-O are 1.524(5)–1.535(5) and 1.662(6)–2.446(5) Å, respectively. The bond lengths of P-O and Mo-O in compounds **2** and **3** are comparable to those of 1.494(7)–

1.532(7) and 1.637(8)–2.472(10) Å, respectively, in the  $[\text{Cu}_3(2,3\text{-Me}_2\text{pz})_3(\text{PMo}_{12}\text{O}_{40})]$  complex,<sup>8c</sup> and also comparable to those lengths of 1.529(6)–1.532(3) and 1.683(3)–2.435(2) Å, respectively, in the  $\{[\text{Cu}(2\text{-Mepz})_{1.5}]_3(\text{PMo}_{12}\text{O}_{40})\cdot(\text{H}_2\text{O})_{3.5}\}_n$  complex.<sup>9c</sup>

Replacing the  $[\text{PMo}_{12}\text{O}_{40}]^{3-}$  anion by  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  to follow the assembly with the corresponding lanthanide ions ( $\text{Gd}^{3+}$  and  $\text{Ho}^{3+}$ ) gave isomorphous compounds  $\{\text{Gd}(\text{dpdo})_{4.5}\cdot(\text{H}_2\text{O})_6(\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{CH}_3\text{CN})_{0.5}\}_n$  (**4**) and  $\{\text{Ho}(\text{dpdo})_{4.5}\cdot(\text{H}_2\text{O})_6(\text{H}_3\text{O})(\text{SiMo}_{12}\text{O}_{40})(\text{CH}_3\text{CN})_{0.5}\}_n$  (**5**), respectively. An asymmetric unit of these two compounds consists of one Keggin-structure anion, one lanthanide ion, four coordinated dpdo ligands, and half a free dpdo ligand. As in compound **2**, the  $\text{Gd}^{3+}$  ion in compound **4** is also coordinated by three water molecules, four oxygen atoms from four independent dpdo ligands, and one oxygen atom from a symmetry-related dpdo ligand. Compound **4** consists of 1D chain polymers along the  $a$  axis with a  $\text{Gd}\cdots\text{Gd}$  separation of 13.21 Å. Hydrogen bonds between the coordination water molecule O(1W) and the oxygen atom O(42A) from a neighboring parallel terminal ligand are found to stabilize the chains through cooperative interactions. One of the other two terminal dpdo ligands containing oxygen atoms O(47) and O(48A) contacts a coordinated water molecule O(3W) from the centrosymmetrically related lanthanide ion to form two-fold hydrogen bonds. These interactions complete the formation of an one-dimensional (1D) ribbon (Figure 3). Face-to-face  $\pi$ - $\pi$  stacking interactions within these bridging pairs are also found to stabilize the ribbons.

Adjacent ribbons are linked together through hydrogen bonds between the oxygen atom O(49) of the free dpdo ligand and the coordinated water molecule O(3W) to form a two-dimensional (2D) sheet (Figure 3). Intermolecular  $\pi$ - $\pi$  stacking interactions between the free and the coordinated dpdo ligands are also found to stabilize the 2D sheet. One lattice water molecule O(4W) also precipitates the interactions, linking one coordination water molecule O(2W) and the oxygen atom O(49) from a free ligand through hydrogen bonds to stabilize the sheet. Being heavy “building blocks”, the  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions position at the two sides of the sheets above and below the voids of the tetragons and connect adjacent sheets together, featuring a 3D framework. Intermolecular  $\pi$ - $\pi$  stacking interactions between the pyridine rings within the adjacent dpdo ligands contribute to the stabilization of the 3D framework. These stacked aromatic rings divide the framework into rooms, with a centrosymmetrically related shoulder-to-shoulder dimeric anion embedded in each room (Figure 4).

Though the basic structure of the POM-based polymer could easily be determined based on the X-ray structure analysis, it is not clear whether the proton sits near the oxygen atoms of the free dpdo ligand or around the water molecules. It was reported that, based on high-resolution solid-state  $^1\text{H}$  and  $^{31}\text{P}$  NMR, there were at least three different states for protons of  $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot n\text{H}_2\text{O}$ : (i) protons present in highly hydrated samples, (ii) protonated water which is hydrogen bonded to terminal oxygen,  $\text{W} = \text{O}\cdots\text{H}^+(\text{H}_2\text{O})_2$  ( $n = 6$ ), and (iii) protons which are directly bonded to



**Figure 3.** View of the 1D ribbon based on  $[\text{Gd}(\text{dpdo})_4(\text{H}_2\text{O})_3]^{3+}$  units (top) and the 2D sheets with the uncoordinated dpdo molecules as hydrogen-bonding bridges (bottom) in compound **4**. Hydrogen atoms are omitted for clarity. Selected bond distances ( $\text{\AA}$ ) for compound **4**: Gd(1)–O(45) 2.365(6), Gd(1)–O(47) 2.394(5), Gd(1)–O(44A) 2.342(6), Gd(1)–O(43) 2.349(6), Gd(1)–O(41) 2.426(5), Gd(1)–O(3W) 2.405(6), Gd(1)–O(1W) 2.398(7), Gd(1)–O(2W) 2.393(6); O(1W)···O(42A) 2.57(2), O(1W)···O(44A) 2.60(2), O(2W)···O(4WC) 2.73(2), O(3W)···O(48B) 2.67(2), O(3W)···O(49) 2.85(2), O(4W)···O(49B) 2.76(2). For compound **5**: Ho(1)–O(45) 2.329(6), Ho(1)–O(47) 2.365(6), Ho(1)–O(44A) 2.296(6), Ho(1)–O(41) 2.431(7), Ho(1)–O(3W) 2.365(6), Ho(1)–O(1W) 2.350(6), Ho(1)–O(2W) 2.352(6); O(1W)···O(42A) 2.62(2), O(1W)···O(44A) 2.58(2), O(2W)···O(4WC) 2.73(2), O(3W)···O(48B) 2.66(2), O(3W)···O(49) 2.85(2), O(4W)···O(49B) 2.73(2). Symmetry code: A,  $1 + x, y, z$ ; B,  $2 - x, 1 - y, 1 - z$ ; C,  $x, 1 + y, z$ .

bridging oxygen,  $\text{W}-\text{OH}-\text{W}$  ( $n = 0$ ).<sup>18</sup> More recently, it was reported that, based on REDOR experiments, acidic protons are localized on both bridging ( $\text{O}_c$ ) and terminal ( $\text{O}_d$ ) oxygen atoms of the Keggin unit in the anhydrous state of  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ .<sup>19</sup>

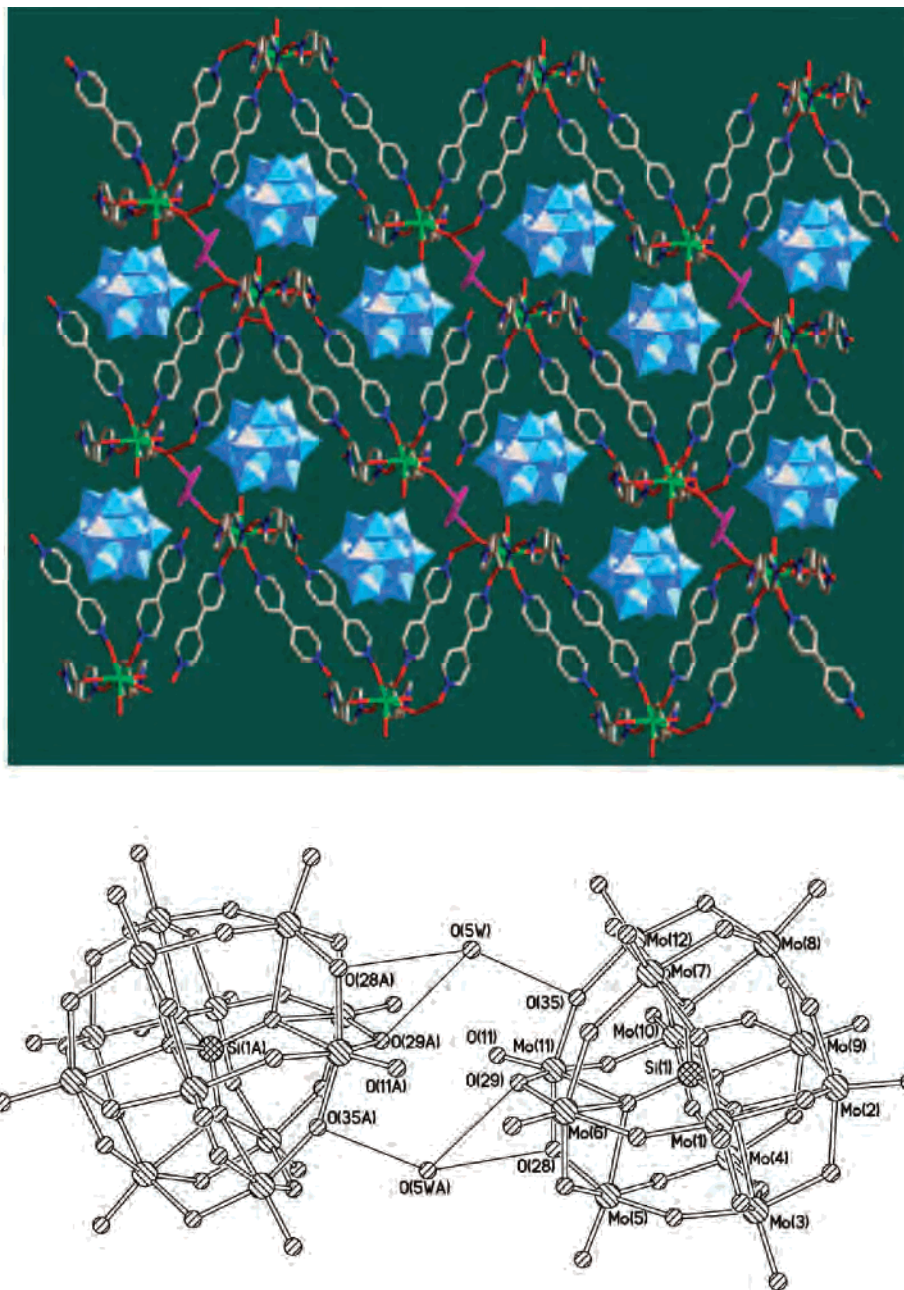
In compounds **4** and **5**, there are four lattice water molecules and the separations between them are too long to form oligomers such as  $\text{H}_5\text{O}_2^+$  or  $\text{H}_3\text{O}_7^+$  for stabilizing the excess proton. Whereas for dpdo ligands, since N-oxide groups have formal partial negative and positive charges on the oxygen and nitrogen atoms, respectively, it is difficult to protonate the oxygen atoms. To our knowledge, no

examples of the protonation of the oxygen atoms of dpdo ligands have been reported. Furthermore, in such a crystallization condition, the protonation of the surfaces of a Keggin-structure  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anion is impossible, and the O(5W) centers are sited closely to the anions with the two shoulder-to-shoulder polyanions being too close (the shortest atom···atom separation of O(29)···O(11A) is 3.4  $\text{\AA}$ ); the most possible distribution of the excess proton is to attach to the oxygen atom O(5W), so the presence of positive charged species could bring the anions together.

**Nickel-Based Ionic Crystals.** Compound **6** was synthesized by using the POM  $\text{Ni}_2(\text{SiMo}_{12}\text{O}_{40})\cdot\text{H}_2\text{O}$  and the dpdo ligands. A symmetric unit consists of one coordinated cation  $[\text{Ni}(\text{dpdo})_2(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})]^{2+}$ , half a polyanion  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$ , and one lattice water molecule. As shown in Figure 5, each  $\text{Ni}^{2+}$  ion is six-coordinated by two water molecules at the

(18) Kanda, Y.; Lee, K. Y.; Nakata, S.; Asaoka, S.; Misono, M. *Chem. Lett.* **1988**, 139–142.

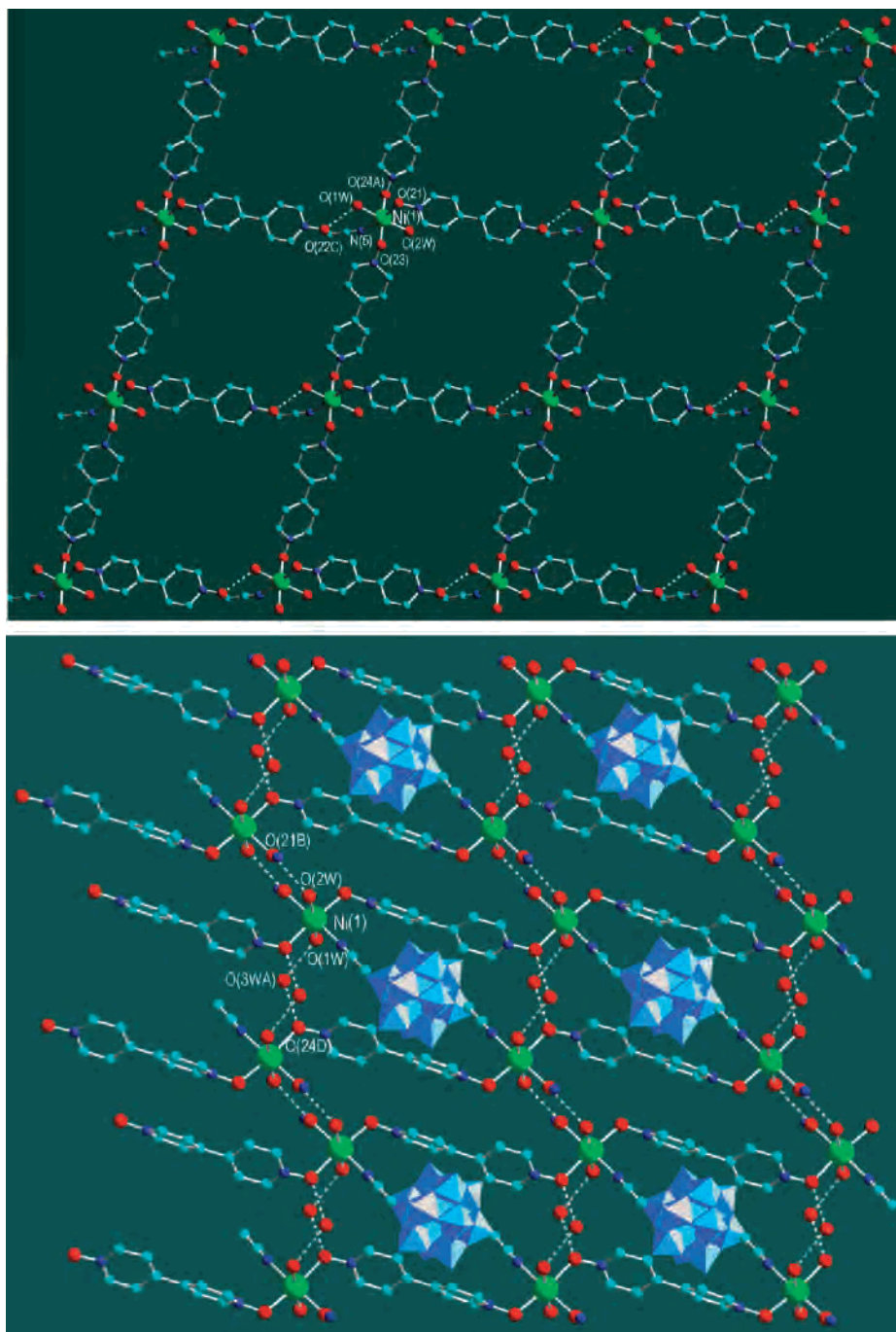
(19) Yang, J.; Janik, M. J.; Ma, D.; Zheng, A.; Zhang, M.; Neurock, M.; Davis, R. J.; Ye, C.; Deng, F. *J. Am. Chem. Soc.* **2005**, *127*, 18274–18280.



**Figure 4.** Packing diagram of a 3D structure in compound **4** stabilized by the interlayer stacking interactions between these dpdo ligands (top). View of the structure of the shoulder-to-shoulder polyanions and the intermediate hydronium ions (bottom). Hydrogen atoms and solvent molecules of crystallization are omitted for clarity. Selected atom···atom separations (Å): O(5W)···O(28A) 3.18(2), O(5W)···O(29A) 3.15(2), O(5W)···O(35) 3.05(2). Symmetry code: A, 1 - x, 1 - y, 1 - z.

axial positions, three oxygen atoms from three dpdo ligand and one nitrogen atom from the acetonitrile molecule at the equatorial plane, respectively. Compound **6** consists of a 1D chainlike structure along the *b* axis, with the Ni···Ni separation distance of 12.24 Å bridged by a single dpdo molecule. The chains are further linked together into a four-connected 2D structure through hydrogen bonds between the terminal oxygen atoms O(21B) in the terminal dpdo ligands and the coordinated water molecules O(1W) of adjacent chains. The two adjacent layers are connected through the hydrogen bonds between the oxygen atoms O(22C) of the terminal dpdo ligands in one layer and the coordinated water molecules O(2W) in another layer, leading to a bilayer

fashion. Intermolecular  $\pi$ ··· $\pi$  stacking interactions between the bridging dpdo ligands are also found to stabilize the bilayer packing fashion. These layers are further linked together through hydrogen bonds arising from a lattice water molecule O(3WA) featuring a 3D cation network of **6** (Figure 5). Each water molecule O(3WA) acts as a diaqua bridge that connects with one coordinated water molecule O(1W) and one oxygen atom O(24D) of the bridging dpdo ligand, directly incorporating the  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions within the pores. In other words, these positive charged 2D sheets are pillared by the  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions to form a pillar-layered framework. The methyl groups of the coordinated acetonitrile



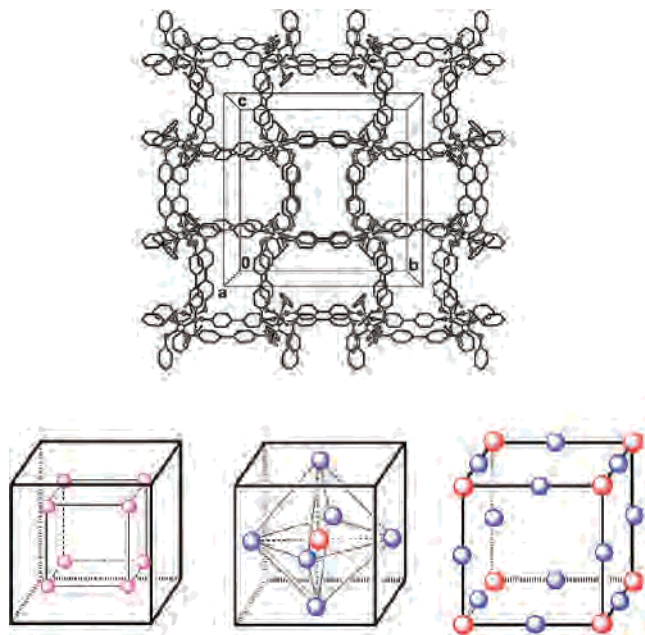
**Figure 5.** Four-connected 2D structure of **6** (top) and the 3D structure based on the connection of these bilayers through hydrogen bonds (bottom). The  $[\text{SiMo}_{12}\text{O}_{40}]^{4-}$  anions acting as pillars directly incorporate within the pores to form a pillar-layered framework. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) for compound **6**: Ni(1)–O(23) 2.058(6), Ni(1)–O(24A) 2.089(6), Ni(1)–O(21) 2.096(6), Ni(1)–N(5) 2.124(10), Ni(1)–O(1W) 2.098(8), Ni(1)–O(2W) 2.068(7), O(1W)···O(24A) 2.85(2), O(1W)···O(3W) 2.65(2), O(2W)···O(21B) 2.76(2), O(2W)···O(22C) 2.65(2), O(3W)···O(24D) 2.82(2). Symmetry code: A,  $x, 1 + y, z$ ; B,  $-x, -y, -y$ ; C,  $x, y, 1 + z$ ; D,  $1 - x, -1 - y, -z$ .

molecules all point to the channels of the 3D framework, resulting in hydrophobic channels without any other solvent molecules.

The reaction of  $\text{NiHPW}_{12}\text{O}_{40}$  with 4,4'-bipyridine-*N,N'*-dioxide (dpdo) in acetonitrile/water solution gave the compound  $\{[\text{Ni}(\text{dpdo})_3]_4[\text{PW}_{12}\text{O}_{40}]_3[\text{H}(\text{H}_2\text{O})_{27}(\text{CH}_3\text{CN})_{12}]\}_n$  (**7**). The crystal data of compound **7** were collected at 123 K. X-ray crystallographic study reveals that both compounds **7** and **1** (at 123 K)<sup>10</sup> have the same noninterwoven 3D framework with cubic cavities and guest molecules, except

that nickel(II) ions have replaced cobalt(II) ions. It is well-known that Ni(II) and  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  give greenish and transparent-to-yellowish colors, respectively, while the crystal color of compound **7** is red; this may be due to the coordination bonds between nickel ion and dpdo ligands and there being no coordination bonds between the nickel ion and water molecules. In addition, the bond valence sum of the Ni ion in compound **7** gave a value of 2.16, indicating that the valence of the Ni ion is two.<sup>20</sup> Each nickel(II) ion is bound by six identical dpdo ligands in an ideal octahedral

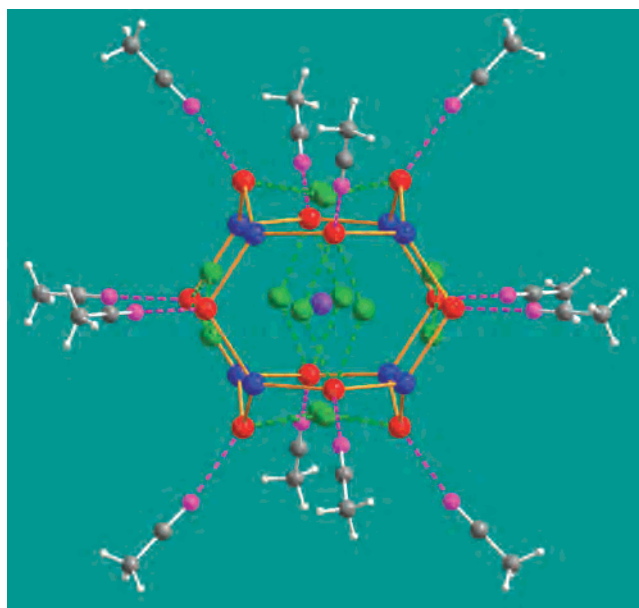




**Figure 6.** Perspective of the 3D framework  $\{[\text{Ni}(\text{dpdo})_3]_n\}^{2n+}$  in compound **7** showing crystallographic  $O_h$  symmetry (top) and models (bottom) of a unit cell showing the positions of the nickel(II) centers (pink), the protonated water clusters (red), and the anions having Keggin structure (blue).

geometry, with each dpdo ligand bridging two identical nickel(II) centers alternatively to form a 3D framework with cubic cavities (the Ni $\cdots$ Ni separation is about 11.6 Å). The trivalent Keggin  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anions (the diameter is about 10.4 Å) occupy three-quarter of these cavities as templates preventing the interpenetration. The remaining one-fourth of the cavities is inhabited by the protonated water clusters,  $\text{H}^+(\text{H}_2\text{O})_{27}$ , which are the same as those in compound **1**. As shown in Figure 6, in a unit cell, the eight nickel (II) ions occupy the special positions  $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$  and their symmetric related positions, the two protonated water clusters occupy the vertexes and  $I$  centers, and the six  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anions are positioned at the centers of the six faces and the middle regions of the twelve edges. Around each water cluster, eight  $\text{Ni}^{2+}$  ions occupied the vertexes of the cubic cavity and six identical trivalent  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anions occupied the centers of six neighboring cavities to form the positive- and negative-charged fields, respectively (Figure 6). Such a specific pseudospherical static field in the solid state not only provides an ideal environment for stabilizing protonated water clusters with their characteristic structures but also makes the excess proton prefer to be positioned in the center of the water cluster rather than on the surface of the water cluster. Twelve acetonitrile solvent molecules act as pillars linking the anions (through C–H $\cdots$ O hydrogen bonds) and the water cluster (through O–H $\cdots$ N hydrogen bonds) to create a special hydrophilic environment around the water cluster in the cavity.

As described previously in compound **1**, based on the results of the X-ray diffraction study and the calculation, in compound **7**, the protonated water cluster,  $\text{H}^+(\text{H}_2\text{O})_{27}$  also comprises a 26 water shell  $(\text{H}_2\text{O})_{26}$  as the “host” and a



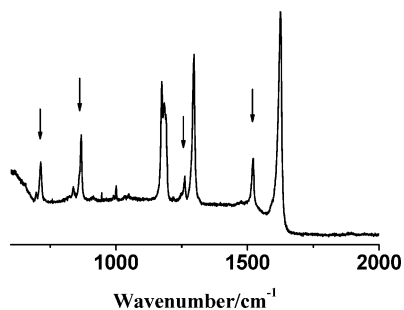
**Figure 7.** Perspective of the  $[\text{H}^+(\text{H}_2\text{O})_{27}(\text{CH}_3\text{CN})_{12}]$  cluster, showing the  $(\text{H}_2\text{O})_{26}$  shell formed by the O(1W) (red), O(2W) (blue), and O(3W) (green) positions that each statistically occupies at two positions and the monowater center O(4W) (purple) as well as the acetonitrile dangling outside with the nitrogen atoms (pink) H bonding to the O(1W) centers. Selected atom $\cdots$ atom separations (Å): O(1W) $\cdots$ O(2W) 2.78(4), O(1W) $\cdots$ O(3W) 2.62(7), O(1W) $\cdots$ N(2) 2.78(4).

hydronium ion ( $\text{H}_3\text{O}^+$ ) as the “guest” (Figure 7). Eight O(2W) molecules and 12 O(1W) molecules are linked together, creating a  $(\text{H}_2\text{O})_{20}$  hexahedron with each face an octagonal water ring  $(\text{H}_2\text{O})_8$ . The residual ample space of the cavity was filled by six additional disordered water molecules that embedded in the six faces of the  $(\text{H}_2\text{O})_{20}$  hexahedral shell; that is, six O(3W) centers, which are disordered in twelve positions, occupy the six faces of the  $(\text{H}_2\text{O})_{20}$  hexahedron. The O $\cdots$ O separations of hydrogen-bonding pairs O(1W) $\cdots$ O(2W) and O(1W) $\cdots$ O(3W) are 2.74 and 2.64 Å, respectively. Just like in compound **1**, considering the most rational distribution of charges in the solid-state structure of **7** with the cubic symmetry, it is suggested that the excess proton should be positioned in the center and occur in the context of the  $\text{H}_3\text{O}^+$  (Eigen) form of a hydronium ion.<sup>10</sup>

After considering the easy growth of single crystals and the high cubic symmetry of its space group, we selected Raman spectroscopy as the suitable spectroscopic method. The single-crystal laser Raman spectrum was measured at 123 K. As shown in Figure 8, the spectrum of compound **7** at 123 K obviously exhibits a peak at 1188  $\text{cm}^{-1}$  resulting from the polyanions<sup>21</sup> and features at 1296 and 1620  $\text{cm}^{-1}$ , which are assigned to the dpdo ligands. The bands at 1520 and 1260  $\text{cm}^{-1}$  are probably attributed to the vibration of the protonated water cluster. Considering the presence of an isolated Eigen-type hydronium  $\text{H}_3\text{O}^+$  in the center core, degenerate bending fundamentals  $\nu_4$  and  $\nu_2$  of a  $\text{H}_3\text{O}^+$  ion are suggested for the bands at 1520 and 1260  $\text{cm}^{-1}$ ,

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**Figure 8.** Single-crystal laser Raman spectrum in the range of 600–2000  $\text{cm}^{-1}$  of compound **7** at 123 K. Those bands assigned to the  $\text{H}_3\text{O}^+$  ion are indicated by arrows.

respectively.<sup>22</sup> The bands at low frequencies are generally assigned to the librational and translational modes of  $\text{H}_2\text{O}$ .<sup>23</sup>

**Thermogravimetric Analyses.** Thermogravimetric analyses of the powder of the crystalline samples of compounds **2** and **3** in an  $\text{N}_2$  atmosphere show a weight loss (3.24 and 3.22% for **2** and **3**, respectively) in the temperature range of 25–155  $^\circ\text{C}$ , corresponding to two solvent water molecules and one acetonitrile molecule (calcd. 2.69 and 2.68% for **2** and **3**, respectively). The frameworks began to slowly decompose at 230  $^\circ\text{C}$  due to the loss of three coordinated water molecules. TGA studies of the powder of the crystalline samples of compounds **4** and **5** in an atmosphere of  $\text{N}_2$  show a weight loss (4.66 and 4.64% for **4** and **5**, respectively) in the temperature range of 25–200  $^\circ\text{C}$ , corresponding to four solvent water molecules, three coordinated water molecules, and half an acetonitrile molecule (calcd. 4.93 and 4.92% for **4** and **5**, respectively). The anhydrous compounds began to rapidly decompose at 340  $^\circ\text{C}$ . The TGA of the powder of the crystalline sample of compound **6** in the atmosphere of  $\text{N}_2$  shows a weight loss (4.11%) in the temperature range of 150–215  $^\circ\text{C}$ , corresponding to two solvent water molecules, two coordinated water molecules, and an coordinated acetonitrile molecule (calcd. 3.93%). The anhydrous compounds began to slowly decompose at 220  $^\circ\text{C}$ . TGA of the powder of the crystalline sample of

compound **7** in the atmosphere of  $\text{N}_2$  shows a weight loss (7.44%) in the temperature range of 25–300  $^\circ\text{C}$ , corresponding to 27 water molecules and 12 acetonitrile molecules (calcd. 8.07%). The framework began to decompose at 300  $^\circ\text{C}$ , corresponding to the disrupting of the structural skeletons of the cation metal–organic framework  $[\text{Ni}(\text{dpdo})_3]^{2+}$  and the template anion  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ . The TGA diagrams of compounds **2–7** are in the Supporting Information. The results of TGA studies of these compounds suggest that compounds **2** and **3** have the same MOFs, which can be retained below 230  $^\circ\text{C}$  by the loss of solvent molecules, compounds **4** and **5** have the same MOFs, which have lower thermal stability than those of compounds **2** and **3** by the loss of solvent molecules and coordinated water molecules, and that the MOFs of compounds **6** and **7** could be retained below 200  $^\circ\text{C}$  and 300  $^\circ\text{C}$ , respectively. We could see that compound **7** has the highest thermal stability among these compounds, indicating that such a noninterwoven 3D framework with cubic cavities is a suitable host for researching protonated water clusters.

In summary, POM-based metal–organic frameworks represent an outstanding class of functional materials and are regarded as green materials. In this paper, several POM-based MOFs were prepared via self-assembly from transition-metal ions or lanthanide ions that generally adopt coordination numbers higher than six to elaborate new synthetic approaches to access novel topologies and to develop a better understanding of correlating building block geometrical information to the resultant structure. By carefully adjusting the charges of the Keggin anions, a 3D porous metal–organic cationic framework was assembled, in which a protonated clathrate hydrate  $\text{H}^+(\text{H}_2\text{O})_{27}$  was captured and stabilized. The successful syntheses of these POM-based materials not only provide novel examples of MOFs that can recognize special guests but also may open the door to the formation and stabilization of nanosized protonated water clusters. The further investigation of the chemical/physical properties related to the protonated water cluster inhabited in such a MOF is underway.

**Acknowledgment.** This work is supported by the National Natural Science Foundation of China.

**Supporting Information Available:** X-ray crystallographic files for **2–7** in CIF format and a PDF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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