

## pH-Dependent Assembly of Keggin-Based Supramolecular Architecture

Pei-Qing Zheng, Yan-Ping Ren, La-Sheng Long,\* Rong-Bin Huang, and Lan-Sun Zheng

State Key Laboratory of Physical Chemistry of Solid Surface and Department of Chemistry, Xiamen University, Xiamen 361005, China

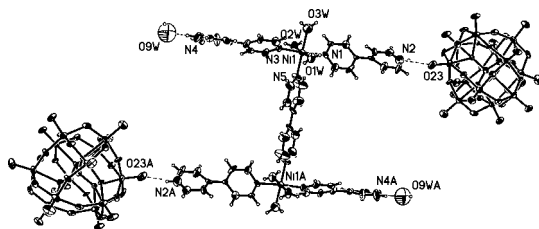
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Three Keggin-based supramolecular architectures were synthesized on the basis of same molecular building units, showing that the pH value of the reaction plays a crucial role in controlling the topological structures of the supramolecular architectures.

Design and assembly of metal-involved supramolecular architectures are currently of great interest in the field of supramolecular chemistry and crystal engineering because they can provide novel topology and functional materials.<sup>1,2</sup> During the past decades, extensive efforts have been focused on the design and assembly of such kinds of supramolecular architectures. By precisely selecting the modular building unit, chemists now have successfully synthesized a great many of 1D, 2D, and 3D supramolecular architectures.<sup>3–5</sup>

\* To whom correspondence should be addressed. E-mail: lslong@jngxian.xmu.edu.cn.

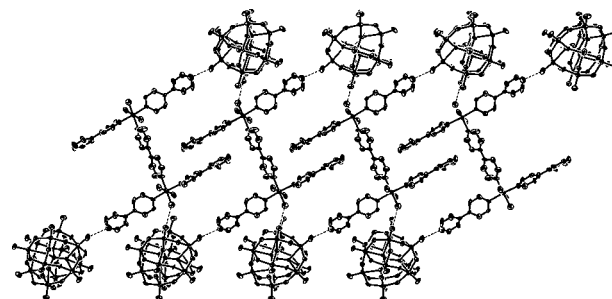
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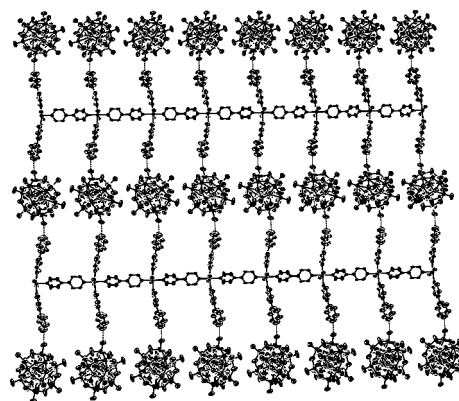
**Figure 1.** ORTEP plot showing H-shaped unit in **1**.

structure<sup>9</sup> reveals that **1** consists of 2 [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> anions, 1 [Ni<sub>2</sub>(Hbpy)<sub>4</sub>(bpy)(H<sub>2</sub>O)<sub>6</sub>] unit, and 16 lattice water molecules. The [Ni<sub>2</sub>(Hbpy)<sub>4</sub>(bpy)(H<sub>2</sub>O)<sub>6</sub>] unit contains two different but symmetrically equivalent Ni(II) centers. Each of the Ni(II) centers lies in a distorted octahedral geometry and is coordinated by three water molecules and three nitrogen atoms with two from the monoprotonated bpy ligands and one from the bpy ligand that is coordinated to symmetry-related Ni(II) center, leading to the [Ni<sub>2</sub>(Hbpy)<sub>4</sub>(bpy)(H<sub>2</sub>O)<sub>6</sub>] unit exhibiting an H-shape.

The two monoprotonated bpy ligands in each side of the [Ni<sub>2</sub>(Hbpy)<sub>4</sub>(bpy)(H<sub>2</sub>O)<sub>6</sub>] unit acting as proton donor are hydrogen-bonded to a Keggin anion and water molecule, respectively (N<sub>2</sub>⋯O<sub>23</sub> = 2.83(2) Å, N<sub>4</sub>⋯O<sub>9W</sub> = 2.604(4) Å), forming a [Ni<sub>2</sub>(Hbpy)<sub>4</sub>(bpy)(H<sub>2</sub>O)<sub>6</sub>][SiW<sub>12</sub>O<sub>40</sub>]<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> subunit as shown in Figure 1. Two adjacent subunits are further joined together by the hydrogen bonding between the Keggin anion in one subunit and the coordinated water molecule in



**Figure 2.** ORTEP plot showing band-like chain in **1**. The hydrogen atoms were omitted for clarity.



**Figure 3.** ORTEP plot showing 2D structure in **2**. Hydrogen atoms were omitted for clarity.

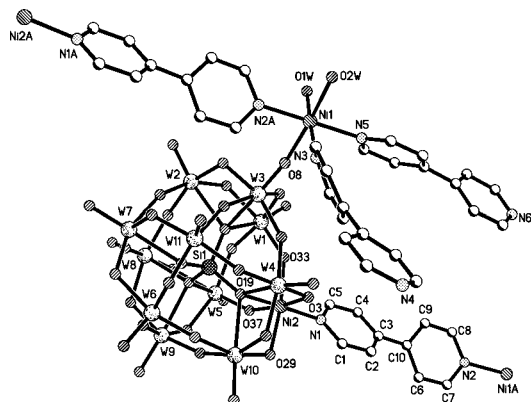
(8) Complex **1** was synthesized as follows: A mixture of H<sub>4</sub>[SiO<sub>4</sub>(W<sub>3</sub>O<sub>9</sub>)<sub>4</sub>]-H<sub>4</sub>O<sub>40</sub>SiW<sub>12</sub> (1.15 g, 0.4 mmol), 4,4'-bpy (0.06 g, 0.4 mmol), Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.23 g, 0.8 mmol), H<sub>2</sub>O (10 mL) in a molar ratio of ca. 1:1:2:1389 was adjusted to approximately pH = 4–5 with 1 mol·L<sup>-1</sup> NaOH, then transferred and sealed in a 25 mL Teflon-lined stainless steel container. The container was heated to 200 °C and held at that temperature for 2 days, then cooled to 100 °C at a rate of 5 °C h<sup>-1</sup>, and held for 10 h, followed by further cooling to 30 °C at the same rate. Pale green sheets of **1** were collected in 10% yield. IR spectra (KBr, cm<sup>-1</sup>): 3451s, 3235w, 3082m, 1612s, 1491w, 1416m, 1221m, 1015m, 972s, 923s, 796s, 535s. Complexes **2** and **3** were prepared in the similar way as illustrated for **1**; the only difference among **1**, **2**, and **3** is the pH value of the solution. In **2** and **3**, the pH value of the solution was adjusted to ca. 6 and 7, respectively. IR spectra (KBr, cm<sup>-1</sup>) for **2**: 3447s, 3230w, 3070m, 2924m, 1611s, 1490w, 1415m, 1221w, 1015m, 972s, 923s, 797s, 534s. IR spectra (KBr, cm<sup>-1</sup>) for **3**: 3436s, 2924m, 2854m, 1612s, 1478s, 1415m, 1384s, 1016m, 972s, 923s, 797s.

(9) Diffraction data were collected at 298(2) K for **1** (crystal size 0.17 × 0.15 × 0.05 mm<sup>3</sup>), **2** (crystal size 0.28 × 0.20 × 0.07 mm<sup>3</sup>), and **3** (crystal size 0.30 × 0.26 × 0.10 mm<sup>3</sup>) on a Smart Apex 2000 diffractometer with Mo Kα radiation. The measured intensities were reduced to *F*<sup>2</sup> and corrected for absorption with SADABS.<sup>13</sup> Structure solution, refinement, and data output were carried out with the SHELXTL-NT program.<sup>14</sup> All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of organic ligands were generated geometrically [C–H) 0.96 Å], and those of the aqua ligands were calculated with PLATON.<sup>15</sup> All the hydrogen atoms were assigned the same isotropic temperature factors and included in the structure-factor calculations. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Crystal data for **1**: monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 14.043(2) Å, *b* = 25.291(4) Å, *c* = 18.492(3) Å, β = 100.935(3)°, *V* = 6448.3(16) Å<sup>3</sup>, *Z* = 2, ρ<sub>calcd</sub> = 3.630 g cm<sup>-3</sup>, *M* = 7047.30, μ(Mo Kα) = 21.72 mm<sup>-1</sup>, *R*<sub>1</sub> = 0.0700, *wR*<sub>2</sub> = 0.1457. Crystal data for **2**: monoclinic, space group *C*2/*c*, *a* = 24.642(5) Å, *b* = 11.399(2) Å, *c* = 22.597(5) Å, β = 101.346(4)°, *V* = 6223(2) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 3.787 g cm<sup>-3</sup>, *M* = 3547.70, μ(Mo Kα) = 22.505 mm<sup>-1</sup>, *R*<sub>1</sub> = 0.0766, *wR*<sub>2</sub> = 0.1786. Crystal data for **3**: monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 15.530(3) Å, *b* = 15.127(3) Å, *c* = 29.923(6) Å, β = 103.773(3)°, *V* = 6827(2) Å<sup>3</sup>, *Z* = 4, ρ<sub>calcd</sub> = 3.452 g cm<sup>-3</sup>, *M* = 3547.62, μ(Mo Kα) = 19.113 mm<sup>-1</sup>, *R*<sub>1</sub> = 0.0527, *wR*<sub>2</sub> = 0.1292.

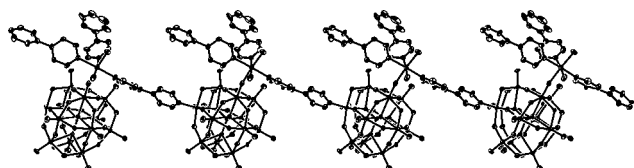
the other unit (O3W⋯O21 or their symmetry equivalents, 2.888(19) Å) to form the band-like chain with the Keggin anions at each side as shown in Figure 2.

The solid-state structure of **2**<sup>9</sup> consists of one [SiW<sub>12</sub>O<sub>40</sub>]<sup>4-</sup> Keggin anion, one [Ni(Hbpy)<sub>2</sub>(bpy)(H<sub>2</sub>O)<sub>2</sub>] unit, and six lattice water molecules. In the [Ni(Hbpy)<sub>2</sub>(bpy)(H<sub>2</sub>O)<sub>2</sub>] unit, the Ni(II) ion is also in a distorted octahedral environment, and defined by two water molecules at the apical positions and four nitrogen atoms at the basal plane with two from monoprotonated bpy ligands and two from the bpy ligands. Connection of adjacent Ni(II) ions through the coordination of each terminal nitrogen atom of the bpy ligand forms a 1D chain of [Ni(Hbpy)<sub>2</sub>(bpy)(H<sub>2</sub>O)<sub>2</sub>]<sub>*n*</sub>. Each Keggin anion acting as a proton acceptor is hydrogen-bonded to two monoprotonated bpy ligands from two adjacent 1D chains, respectively (N2⋯O9 = 2.740(16) Å), generating a 2D supramolecular layer as shown in Figure 3.

Complex **3**<sup>9</sup> consists of six lattice water molecules, a diprotonated 4,4'-bpy guest, a Ni(Hbpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> fragment, and a [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] unit. In the fragment of Ni(Hbpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>, the Ni<sup>2+</sup> ion is octahedrally coordinated by three oxygen atoms with two from water molecules and one from the [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] unit, and three nitrogen atoms with two from 4,4'-Hbpy and one from the 4,4'-bpy of the adjacent [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] unit as shown in Figure 4. The solid structure of **3** can be viewed as a 1D Z-shaped chain in which adjacent [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] units are linked by a Ni(Hbpy)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> fragment through the N atom (N5) from one [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] unit and a terminal oxygen atom (O39) from the other [SiW<sub>11</sub>O<sub>39</sub>Ni(4,4'-bpy)] unit, as illustrated in Figure 5.



**Figure 4.** ORTEP plot showing the  $[\text{SiW}_{11}\text{O}_{39}\text{Ni}(4,4'\text{-Hbpy})]$  unit and the coordination environment of Ni(II) ions in **3**. Hydrogen atoms were omitted for clarity.



**Figure 5.** ORTEP plot showing 1D Z-shaped chain in **3**. Hydrogen atoms were omitted for clarity.

Since the only difference in synthetic conditions among **1**, **2**, and **3** is the pH value of the reactions, their structural differences ambiguously indicate that the assembly process is pH-dependent, which is understandable from acid–base chemistry. As we know, the bpy ligand is a stronger base than the water molecule; i.e., the bpy ligand is protonated prior to water molecule. Hence, the pH value of the reaction is, in fact, indicative of protonated extent of bpy in the reaction. At pH ca. 4–5, being highly protonated, the concentration ratio of bpy to Hbpy is low, and the complex with low ratio of bpy to Hbpy would be expected. At pH ca. 6, the concentration ratio of bpy to Hbpy would be increased in comparison with the reaction of **1**. Being a harder base than water molecule, the coordinated water at the basal plane in **1** would be replaced by bpy ligand, and the 1D chain of **2** is formed. In principle, the concentration ratio of bpy to Hbpy would be further increased at pH ca. 7 in comparison with the reaction of **2**, and the complex with the highest ratio of bpy to Hbpy would be expected. However, not only is the ratio of bpy to Hbpy in **3** comparable to that in **2**, but also complex **3** exhibits much different structural character from those of **1** and **2**, which may be attributed to (1) the high pH value favoring the formation of Ni(II)-substituted Keggin unit,<sup>10</sup> (2) while the formation of Ni(II)-substituted Keggin unit would decrease

the pH value of the reaction. It must be mentioned that, although pH-dependent assembly of **1** and **2** is well explained according to the acid–base chemistry, in contrast to successful achievement of the pH-dependent assembly of **2** and **3**, the preparation of **1** accompanies the appearance of **2** in most cases, probably due to the concentration ratio of bpy to Hbpy which in this case is between that of **1** and **2**.

Keggin-based supramolecular architecture is regarded as one of the most promising materials potentially applied in the field of chemistry, biology, and material sciences.<sup>11,12</sup> However, how to design and assemble the materials with desired structures and functions remains a great challenge. One of the important reasons is that, in addition to the modular building blocks, the external chemical stimuli also play a key role in the assembly process. In this work, we, based on the same modular building unit, have successfully prepared three structurally and topologically different Keggin-based supramolecular architectures under the different pH conditions, revealing the role of pH in the assembly of Keggin-based supramolecular architectures. Together with the investigation of the reason for the pH value of the reaction in the control of the assembly of the supramolecular architectures, present work may be helpful to our rational design and assembly of Keggin-based supramolecular architectures.

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

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