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Hydrothermal syntheses and structures of four new polyoxometalate based supramolecular architectures

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ABSTRACT

Four new supramolecular architectures based on Keggin polyoxometalates (POMs): $[(HSiMo_{12}O_{40})(H4,4'-bpy)_2][(H4,4'-bpy)_2][(H4,4'-bpy)_2](H4,4'-bpy)_2][(H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)_2](H4,4'-bpy)$

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1. Introduction

Supramolecular chemistry has developed at a tremendous rate, driven by the growing knowledge regarding synthetic techniques and characterization methods for complex structures in the past 30 years [1]. The directed assembly of supramolecular arrays from discrete molecular building blocks is a topic of significant interest with potential applications in catalysis, molecular electronics, sensor design and optics [2,3]. In the construction of supramolecular materials, one strategy is using low-dimensional building blocks to extend to high-dimensional networks through weak intermolecular interactions, including hydrogen-bonding, $\pi \cdots \pi$ stacking and van der Waals interactions, etc. Doubtless, the different kinds of hydrogen bonds are the most familiar organizing force in supramolecular assemblies by virtue of their unique strength and directionality that may control short-range packing [4].

Chemistry of polyoxometalates (POMs) has been investigated intensively for a long time because of their current and potential applications in many areas [5–11,12–23]. However, supramolecular compounds based on POMs have been unexplored in past decades, though the spherical surface of POMs gives a better opportunity in forming different kinds of hydrogen bonds with the organic/inorganic moieties. In recent years, extensive efforts have been focused on the design and assembly of such kind of supramolecular architectures and a few high-dimensional supramolecular architectures have been synthesized [24–29].

4,4'-bpy and 2,2'-bpy ligands are widely used in coordination chemistry and hybrid compounds based on POMs and metal coordination complexes, however, only few supramolecular hybrids based on POMs directly combined with the 4,4'-bpy or 2,2'-bpy ligands were reported. To the best of our knowledge, only three such compounds were reported recently [27–29]. In this paper, we reported the syntheses and characterizations of four new compounds directly combined with 4,4'-bpy or 2,2'-bpy ligands and POMs: $[(HSiMo_{12}O_{40})(H4,4'-bpy)_2][(H4,4'-bpy)(H_2O)_2]\cdot 2H_2O(1), [(HSiW_{12})_2]\cdot 2H_2O(1), [(HSiW_$ O_{40})(H4,4'-bpy)₂][(H4,4'-bpy)(H₂O)₂]·2H₂O (**2**), [(SiW₁₂O₄₀)(H4,4' $bpy_{4}] \cdot (4,4'-bpy) \cdot 2H_{2}O$ (**3**) and $[H_{4}SiW_{12}O_{40}](2,2'-bpy)_{4}$ (**4**). Compounds 1-3 are based on POMs and 4,4'-bpy ligands, while compound **4** is based on POMs and 2,2'-bpy ligands. Compounds 1 and 2 are isomorphous, both of which contain the same 2D layer structures. Compound **3** exhibits a novel supramolecular double chain structure. Compound 4 contains a 1D chain structure with two 2,2'-bpy ligands as double bridges. It should be noted that compound **4** is the first example of hybrid compounds based on 2,2'-bpy ligands and POMs.

2. Experimental

2.1. General procedures

All chemicals used were of reagent grade purchased from China National Medicines Corporation Ltd. and used as supplied, without



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further purification. C, H, N elemental analyses were carried out on a Perkin-Elmer 2400 CHN elemental analyzer. The elemental analyses of Si, Mo and W were determined by inductively coupled plasma (ICP) analyses on a Perkin-Elmer Optima 3300DV ICP spectrometer. Infrared spectra were recorded as KBr pellets on a Perkin-Elmer SPECTRUM ONE FTIR spectrometer. Emission/excitation spectra were recorded on a RF-540 fluorescence spectrophotometer. XPS analyses were performed on Thermo ESCALAB 250 spectrometer with an Mg–K (1253.6 eV) achromatic X-ray source. The UV–Vis spectra were recorded on a Shimadzu UV-3100 spectrophotometer as saturated solution of *N*,*N*-dimethylformamide.

2.2. Preparation

2.2.1. Preparation of [(HSiMo₁₂O₄₀)(H4,4'-bpy)₂]](H4,4'bpy)(H₂O)₂]-2H₂O (**1**)

Compound **1** was hydrothermally synthesized by reacting of Na₂MoO₄·2H₂O (0.5 g, 2.07 mmol), Na₂SiO₃·9H₂O (0.5 g, 1.759 mmol), NiCl₂·6H₂O (0.333 g, 1.4 mmol), 4,4'-bpy (0.267 g, 1.387 mmol) and distilled water (18 ml) in a 20 ml Teflon-lined autoclave. The pH of the mixture was necessarily adjusted to 4 with HCl solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Yellow block crystals could be isolated in about 50% yield (based on Mo). *Anal.* Calc. for C₃₀H₃₆Mo₁₂N₆O₄₄Si: Mo, 48.70; Si, 1.19; C, 15.24; H, 1.53; N, 3.56. Found: Mo, 48.46; Si, 1.03; C, 15.15; H, 1.24; N, 3.39%. FT-IR (KBr, cm⁻¹): 1594, 1488, 1411, 1205, 954, 902, 783, 530, 378, 338.

2.2.2. Preparation of [(HSiW₁₂O₄₀)(H4,4'-bpy)₂][(H4,4'bpy)(H₂O)₂]·2H₂O (**2**)

Compound **2** was hydrothermally synthesized by reacting of $H_4SiW_{12}O_{40}$, nH_2O (0.5 g, 0.17 mmol), $CdCl_2 \cdot 2.5H_2O$ (0.333 g, 1.458 mmol), 4,4'-bpy (0.267 g, 1.387 mmol) and distilled water (18 ml) in a 20 ml Teflon-lined autoclave. The pH of the mixture was necessarily adjusted to 5 with NH₃·H₂O solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Pale yellow block crystals could be isolated in 45% yield (based on W). *Anal.* Calc. for $C_{30}H_{36}W_{12}N_6O_{44}Si$: W, 64.53; Si, 0.82; C, 10.54; H, 1.06; N, 2.46. Found: W, 64.25; Si, 0.54; C, 10.55; H, 1.18; N, 2.83%. FT-IR (KBr, cm⁻¹): 1594, 1515, 1489, 1412, 1358, 1234, 1207, 1015, 973, 921, 787, 532, 419, 383, 352.

2.2.3. Preparation of $[(SiW_{12}O_{40})(H4,4'-bpy)_4] \cdot (4,4'-bpy) \cdot 2H_2O(3)$

Compound **3** was hydrothermally synthesized by reacting of $H_4SiW_{12}O_{40'}nH_2O$ (0.722 g, 0.251 mmol), $CdCl_2 \cdot 2.5H_2O$ (0.28 g, 1.225 mmol), $H_2C_2O_4 \cdot 2H_2O$ (0.253 g, 2.0 mmol), 4,4'-bpy (0.193 g, 1.0 mmol) and distilled water (20 ml) in a 25 ml Teflon-lined autoclave. The pH of the mixture was necessarily adjusted to 5 with NH₃·H₂O solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature. Pale pink crystals could be isolated in 45% yield (based on W). *Anal.* Calc. for $C_{50}H_{48}N_{10}O_{42}SiW_{12}$: W, 59.70; Si, 0.76; C, 16.25; H, 1.31; N, 3.79. Found: W, 59.85; Si, 0.54; C, 16.55; H, 1.18; N, 3.73%. FT-IR (KBr, cm⁻¹): 1591, 1491, 1403, 1211, 1067, 1014, 973, 920, 885, 790, 530, 383, 335.

2.2.4. Preparation of [H₄SiW₁₂O₄₀](2,2'-bpy)₄ (**4**)

Compound **4** was hydrothermally synthesized by reacting of $H_4SiW_{12}O_{40}$ · nH_2O (0.722 g, 0.251 mmol), $H_2C_2O_4$ · $2H_2O$ (0.253 g, 2.0 mmol), $MnCl_2$ · $4H_2O$ (0.197 g, 0.997 mmol), 2,2'-bpy (0.156 g, 1.0 mmol) and distilled water (20 ml) in a 25 ml Teflon-lined autoclave. The pH of the mixture was necessarily adjusted to 5 with NH_3 · H_2O solution. The mixture was heated under autogenous pressure at 160 °C for 5 days and then left to cool to room temperature.

Pale pink crystals could be isolated in 55% yield (based on W). *Anal.* Calc. for $C_{40}H_{36}N_8O_{40}SiW_{12}$: W, 62.98; Si, 0.80; C, 13.72; H, 1.04; N, 3.20. Found: W, 62.85; Si, 0.54; C, 13.55; H, 0.68; N, 3.23%. FT-IR (KBr, cm⁻¹): 1601, 1585, 1528, 1434, 1319, 1245, 1277, 1218, 1162, 1084, 1012, 970, 921, 881, 793, 757, 530, 384, 334.

2.3. X-ray crystallographic analysis

All the reflection intensity data of **1–4** were collected on a Bruker Apex II diffractometer equipped with graphite monochromated Mo K α (λ = 0.71073 Å) radiation at room temperature. The structures of **1–4** were solved by direct methods, and the four structures were further refined using the full-matrix least-squares on F^2 using SHELXTL-97 crystallographic software package. Anisotropic thermal parameters were refined for all the non-hydrogen atoms in **1–4**. All the hydrogen atoms of the ligands were placed in geometrically calculated positions and refined with fixed isotropic displacement parameters using a riding model except the lattice water molecules in compounds **1–3**. A summary of the crystallographic data and structure refinements for **1–4** is given in Table 1.

3. Results and discussion

3.1. Discussions

We initially want to synthesize compounds based on POMs and transition metal coordination complexes (TMCs), unfortunately, which is not successful. The metal atoms in these starting materials were not coordinated by the organic ligands to form TMCs, and then the metal ions were not introduced into the final products.

Compound 1 was synthesized with NiCl₂·6H₂O as one of the starting materials while Ni element was not included in the final product. Both compounds 2 and 3 were synthesized with CdCl₂·2.5H₂O as one of the starting materials, compound 4 was synthesized with MnCl₂·4H₂O as one of the starting materials, however, Cd and Mn elements were not included in the final products, respectively. Such phenomenon is very common for the hydrothermal syntheses. If these reagents (NiCl₂·6H₂O for 1, CdCl₂·2.5H₂O for 2 and 3, MnCl₂·4H₂O for 4) were removed from the starting materials, there will be no resulting compounds synthesized under current hydrothermal conditions. We speculate that these reagents perhaps will influence ion strength of the mixture solutions for compounds 1-4, which will finally influence the syntheses and crystal growth for compounds 1-4. The ion strength for the mixture of compound 1 is 0.87 mmol/ml, of compound 2 is 0.51 mmol/ml, of compound **3** is 0.55 mmol/ml, and of compound **4** is 0.57 mmol/ml. But if we did not added these metal sources, the ion strength for the mixture of compound 1 will become 0.64 mmol/ml, of compound 2 will be 0.21 mmol/ml, of compound 3 will be 0.35 mmol/ml, and of compound 4 will be 0.35 mmol/ml. From the comparison, we could see that the ion strength changed very much after we added the metal sources.

3.2. Crystal structures

3.2.1. Crystal structures of 1 and 2

Compounds **1** and **2** are isomorphous, belonging to the monoclinic space group C2/c. Here compound **1** was detailedly described as below as an example.

The X-ray crystallographic study reveals that the asymmetric unit for compound **1** consists of half of an α -Keggin [HSiMo₁₂O₄₀]^{3–} anion, one and a half mono-protonated independent H4,4'-bpy ligand (N3 and N1 H4,4'-bpy ligand), and two water molecules. The [HSiMo₁₂O₄₀]^{3–} may be viewed as a shell of {Mo₁₂O₃₆} encapsulating a SiO₄ moiety present at its centre with Si–O distances of

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