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# Construct Polyoxometalate Frameworks through Covalent Bonds

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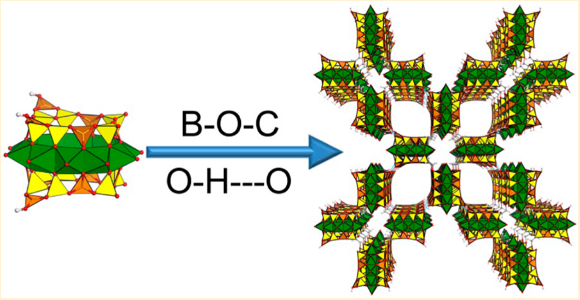
Ⓢ *Supporting Information*



**ABSTRACT:** An emerging strategy for exploring the application of polyoxometalates (POMs) is to assemble POM clusters into open-framework materials, especially inorganic–organic hybrid three-dimensional (3D) open-framework materials, via the introduction of different organic linkers between the POM clusters. This strategy has yielded a few 3D crystalline POMs of which a typical class is the group of polyoxometalate metal–organic frameworks (POMMOFs). However, for reported POMMOFs, only coordination bonds are involved between the linkers and POM clusters, and it has not yet produced any covalently bonded polyoxometalate frameworks. Here, the concept of "covalently bonded POMs (CPOMs)" is developed. By using vanadoborates as an example, we showed that the 3D CPOMs can be obtained by a condensation reaction through the oxolation mechanism of polymer chemistry. In particular, suitable single crystals were harvested and characterized by single-crystal X-ray diffraction. This work forges a link among polymer science, POM chemistry, and open-framework materials by demonstrating that it is possible to use covalent bonds according to polymer chemistry principles to construct crystalline 3D open-framework POM materials.

## ■ INTRODUCTION

Hybrid polyoxometalate (POM) material is an old topic that has been vigorously developed for more than 20 years. To utilize the excellent catalytic properties of POM clusters, different approaches have been employed in constructing hybrid POMs. One strategy was to immobilize the isolated clusters into different types of porous materials, so that the active metal sites of the POMs could be oriented toward the cavity and act as efficient catalytic centers.[1] On the basis of this strategy, many studies have been conducted, such as loading the POM clusters in the channels of metal–organic frameworks (MOFs),[2−6] using POM clusters to modify the wall of mesoporous materials,[7] and linking POM clusters with the amine groups on the surface of polymers.[8,9] Within all the aforementioned methodologies, the POM clusters were treated as guest compositions and mainly loaded in a disordered state with the amount and positions being difficult to control. One exception was the POM clusters loaded in the channels of the MOF HKUST-1, where the position and amount of POMs clusters can be located and refined on the basis of single-crystal X-ray diffraction data.[2] A second strategy was to modify the POMs with different organic functional groups. Through this strategy, the physical and chemical properties of the POMs can be enhanced, and crystalline or noncrystalline hybrid organic POMs could be harvested. Numerous examples were achieved[10−13] with organic amines,[14] bisphosphonates,[15] TRIS-based ligands,[16] or organic silica cross-linkers[17] modified on polyoxometalates with different morphologies or architectures. However, the application of these materials was hindered by the dense packing of the low-dimensional hybrid clusters. To achieve the high crystallinity, hybridization of POMs with an organic linkage into three-dimensional (3D) crystalline framework materials was developed as a new interesting strategy, and it enhances the application of POMs in catalysis.[18,19] After the 3D construction process, not only can the structural diversity of the POMs be enhanced, but also the POM clusters can be isolated and located toward the pores in a designable fashion. Based on this idea, together with the modular construction concept used in MOF synthesis, the polyoxometalate metal–organic frameworks (POMMOFs)[20−24] have been successfully developed in recent years. However, in POMMOFs, the interaction between the POM clusters and organic or metal–organic linkers was limited

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Table 1. Crystallographic Information for SUT-10 and SUT-11 from Single-Crystal X-ray Diffraction

| | SUT-10 | SUT-11 |
|---|---|---|
| formula weight | 2554.9 | 2815.4 |
| temperature (K) | 100 | 100 |
| wavelength (Å) | 0.71073 | 0.71073 |
| crystal system | hexagonal | orthorhombic |
| space group | $P6_122$ | $Cmmm$ |
| unit cell dimensions (Å) | $a$ = 17.0389(2) | $a$ = 37.4162(13) |
| | $b$ = 17.0389(2) | $b$ = 39.2677(11) |
| | $c$ = 58.1335(9) | $c$ = 16.5126(6) |
| volume (Å$^3$) | 14616.4(3) | 24261.1(14) |
| $Z$ | 6 | 16 |
| density (calculated) | 1.380 | 1.032 |
| absorption coefficient | 1.005 | 0.803 |
| $F(000)$ | 5994 | 7312 |
| crystal size | 0.52 mm × 0.25 mm × 0.20 mm | 0.45 mm × 0.19 mm × 0.13 mm |
| $\theta$ range for data collection (deg) | 3.10−25.02 | 3.22−25.03 |
| index ranges | $-20 \le h \le 14$; $-18 \le k \le 20$; $-69 \le l \le 69$ | $-44 \le h \le 43$; $-46 \le k \le 46$; $-19 \le l \le 18$ |
| no. of reflections collected | 53066 | 66313 |
| no. of independent reflections | 8605 | 11463 |
| completeness to $\theta_{max}$ (%) | 99.7 | 99.7 |
| absorption correction | Multiscan | Gaussian |
| maximum and minimum transmission | 0.744 and 0.816 | 0.714 and 0.903 |
| data/restraints/parameters | 8605/6/502 | 11463/9/518 |
| $R_{int}$ | 0.0431 | 0.0777 |
| goodness of fit on $F^2$ | 1.072 | 1.075 |
| final $R$ indices [$I > 2\sigma(I)$] | 0.0533 | 0.0893 |
| $R$ indices (all data) | 0.0564 | 0.1135 |
| largest difference peak and hole | 0.610 and −0.401 | 1.631 and −1.022 |

by coordination bonds, and the number of 3D frameworks also remains relatively limited.[15,25−27]

Parallel to the development of POM immobilization, two other recent major advances in the construction of crystalline organic contained framework materials have been the development of covalent organic frameworks (COFs)[28−30] through a covalent bond by a polymerization process and the hydrogen-bonded organic frameworks (HOFs)[31−35] through the assembly of hydrogen bonds. In COF materials, the different organic motifs connected together mainly through covalent bonds, such as B—O—B, C—O—B,[28,29] N—O—X, and N═N[30] bonds, and the dehydrate polymerization mechanism can be successfully employed in COF synthesis. In HOF materials, the hydrogen bonds are mainly generalized between the organic motifs through intermolecular hydrogen bonds denoted as X—H···X (X = C, N, O, B, Si, P, or S).

Although many POMMOFs, COFs, or HOFs have been reported, 3D framework materials with the POM clusters linked through covalent bonds or hydrogen bonds have not been studied. To explore the structural diversity of 3D crystalline POM materials through covalent bond connection, we designed a strategy to utilize the -OH groups in POMs to react with the -OH groups in ethylene glycol through the dehydrate oxolation mechanism to construct 3D covalently bonded POMs (CPOMs).

## ■ EXPERIMENTAL SECTION

**Materials.** Ammonium metavanadate (99%, Sigma-Aldrich), boric acid (99.5%, Sigma-Aldrich), ammonium pentaborate octahydrate (99%, Sigma-Aldrich), diethylenetriamine (99%, Sigma-Aldrich), and ethylene glycol (99.8%, Sigma-Aldrich) were used without further purification.

**Synthesis of SUT-10.** Single crystals of SUT-10 suitable for single-crystal X-ray diffraction were prepared under solvothermal conditions from a mixture of $NH_4VO_3$ (1 mmol, 0.117 g), $NH_4B_5O_8\cdot4H_2O$ (5 mmol, 1.365 g), diethylenetriamine (8 mmol, 0.88 mL), and $HOCH_2CH_2OH$ (6 mL). The final $NH_4VO_3$:$NH_4B_5O_8\cdot4H_2O$:$NH(CH_2CH_2NH_2)_2$:$HOCH_2CH_2OH$ molar ratio is 1:5:8:106. The mixture was stirred for 1 h in a 23 mL glass vial until a homogeneous solution was formed; the glass vial was sealed tightly and heated in a 100 °C oven for 7 days. Light green crystals of SUT-10 with block-like morphology were filtered and washed with ethanol and dried at room temperature overnight; the yield is around 90% (based on $NH_4VO_3$). Single crystals of SUT-10 can also be harvested using $NH_4B_5O_8\cdot4H_2O$ together with $H_3BO_3$ as boron sources, but if only $H_3BO_3$ is used in the synthesis, no single-crystal SUT-10 is obtained under similar experimental conditions. Slightly changing the synthesis conditions can produce the zero-dimensional structures or other vanadium amine phases.

**Synthesis of SUT-11.** Single crystals of SUT-11 suitable for single-crystal X-ray diffraction were prepared under similar solvothermal conditions from a mixture of $NH_4VO_3$ (1 mmol, 0.117 g), $H_3BO_3$ (3 mmol, 0.185 g), $NH_4B_5O_8$·4H2O (6 mmol, 1.653 g), tetraethylenepentamine (12 mmol, 2.3 mL), and $HOCH_2CH_2OH$ (6 mL). The final $NH_4VO_3$:$H_3BO_3$:$NH_4B_5O_8\cdot4H_2O$:$(NH_2CH_2CH_2NHCH_2CH_2)_2NH$:$HOCH_2CH_2OH$ molar ratio is 1:3:6:12:106. The mixture was stirred for 1 h in a 23 mL Teflon tube until a homogeneous solution was formed; the Teflon tube was sealed tightly in steel and heated in a 100 °C oven for 7 days. Dark green crystals of SUT-11 with block morphology were filtered and washed with 2-propanol and dried at room temperature overnight. The yield is ∼40% based on $NH_4VO_3$; 0.5 mmol of $Cu(NO_3)_2\cdot3H_2O$ can facilitate the productivity of SUT-11 up to 80% without introducing any impurity phases.

**Single-Crystal X-ray Diffraction.** Single-crystal X-ray diffraction data for structure determination were collected at 100 K on a supernova Atlas diffractometer, with Mo K$\alpha$ radiation ($\lambda$ = 0.71073 Å). Data integration and absorption correction were conducted by the CrysAlis software package from Oxford Diffraction.[36] The structure was determined by direct methods in SHELXS, and non-hydrogen atoms were located directly from difference Fourier maps. Final structure refinements were performed with the SHELXL program[37] by minimizing the sum of the squared deviation of $F^2$ using a full matrix technique. The high symmetry and porous structure of the compounds as well as disorders of the guest composition (templates, $NH_4^+$, and ethylene glycol) in the pores precluded the location of these guest molecules. The PLATON/SQUEEZE program was used to remove the scattering contribution from disordered guest molecules and to produce solvent-free diffraction intensities, which were used in the final structure refinement.[38] Crystallographic data for SUT-10 and SUT-11 are listed in Table 1.

**Ion-Exchange Experiments.** Ion-exchange experiments were performed by using 100 mg of SUT-10 with 1 mol/L $Ni(NO_3)_2$, $Co(NO_3)_2$, and methyl viologen dichloride of their ethylene glycol solution; 100 mg of SUT-10 crystal was added to the corresponding solution in a sealed glass bottle and stirred for 2 h. Afterward, the crystals were filtered and collected for PXRD measurement.

**Other Characterization.** The CHN elemental analysis of the as-made materials was performed on an ElementarVario MICRO CUBE elemental analyzer. Results observed for SUT-10 (%): C, 15.01; N, 6.81; H, 4.70. Calcd (%): C, 15.02; N, 7.11; H, 4.45. The sum of the chemical formula is $V_{10}B_{20}O_{49}(OH)_3(OCH_2CH_2O)_4(OCH_2CH_2OH)_3 \cdot 3HOCH_2CH_2OH \cdot 3NH(CH_2CH_2NH_3)_2 \cdot 4NH_4$. Results observed for SUT-11 (%): C, 15.82; N, 9.32; H, 5.02. Calcd (%): C, 15.35; N, 10.40; H, 4.83. The sum of the chemical formula is $V_{10}B_{24}O_{58}(OH)_4(OCH_2CH_2O)_2 \cdot 3NH(CH_2CH_2NHCH_2CH_2NH_3)_2 \cdot 4HOCH_2CH_2OH \cdot 6NH_4$. Thermogravimetric (TG) analysis was conducted using a PerkinElmer TGA7 instrument under a nitrogen atmosphere in a platinum crucible between 20 and 800 °C at a heating rate of 10 °C $min^{-1}$. The powder X-ray diffraction experiment was performed on an X'Pert PANalytical Pro MRD instrument using Cu K$\alpha$ radiation ($\lambda$ = 1.5418 Å) and variable divergent slits. X-ray photoelectron spectroscopy (XPS) (AXIS Ultra, Kratos Analytical Ltd.) was performed on the crystals using a monochromatic Al K$\alpha$ X-ray source ($h\nu$ = 1486.7 eV). IR spectroscopy was performed on a Varian 670 spectrometer. The topology of SUT-10 and SUT-11 was determined with the TOPOS software package.[39]

## ■ RESULTS AND DISCUSSION

Our strategy aims to use the -OH groups in the POM clusters to react with -OH groups in ethylene glycol through the condensation polymerization reaction of the oxolation mechanism by the dehydration process. The -OH groups are commonly found in various types of POMs such as $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, etc. All these POMs are potentially suitable for such a condensation reaction. Herein, we take the vanadoborate as an example to demonstrate our idea because of the well-known structural diversity of vanadoborate clusters under different experimental conditions based on our previous studies,[40−42] and also the weak acid feature of these kinds of compounds that are difficult to deprotonate under highly basic conditions. Moreover, as reported, the inorganic borates are very reactive with different types of alcohols to form B−O−C bonds through the dehydrate reaction.[43−46] In addition, the vanadoborate clusters that had a B−O−H feature similar to that of inorganic borate should react with the -OH groups on ethanol through the condensation process by eliminating the $H_2O$ molecules. To test this idea, we employed a reactant system similar to that used for the synthesis of SUT-6 and SUT-7[40,41] but replaced the solvents with ethylene glycol. Two 3D open-framework vanadoborates were successfully harvested. The first one, SUT-10, is constructed from the $V_{10}B_{20}$ cluster linked by B−O−C bonds; the other one, SUT-11, is formed of the $V_{10}B_{24}$ cluster linked through B−O−C bonds and O−H···O hydrogen bonds.

SUT-10 is composed of a novel type of vanadoborate cluster denoted $V_{10}B_{20}$ (Figure S1b) covalently linked by ethylene glycol (Figure 1a) to form a 3D framework (Figure 2).[40] The vanadoborate cluster is composed of one 10-vanadium ring (Figure S3a) sandwiched by two boron 10-membered rings (Figure S3b), which is slightly different from other reported vanadoborates. Among the 10 ethylene glycol molecules covalently bonded to one $V_{10}B_{20}$ cluster, four of them are connected to other $V_{10}B_{20}$ clusters to form a 3D framework while the other six have the other ends dangling in the pores. The four connected $V_{10}B_{20}$ clusters run along the *c*-axis following the $6_1$ symmetry with a chiral channel. Different views of the 3D framework of SUT-10 are shown in Figure 2. Topologically, if we consider the clusters together with the six dangling ethylene glycol molecules as nodes and the four bridging ethylene glycol molecules as edges, SUT-10 forms the $\alpha$-quartz network.

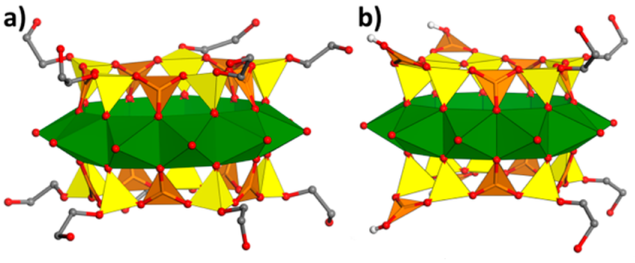

**Figure 1.** Building units in SUT-10 and SUT-11. (a) Ethylene glycol-linked $V_{10}B_{20}$ cluster in SUT-10. (b) Ethylene glycol-linked $V_{10}B_{24}$ cluster in SUT-11. Color code: C, gray; O, red; $VO_5$, green; $BO_3$, brown; $BO_4$, yellow.

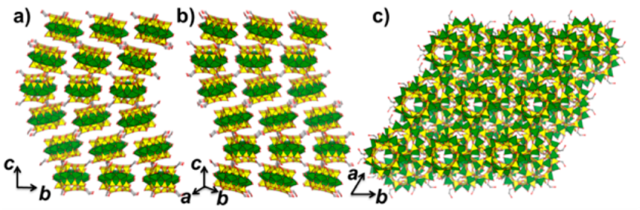

**Figure 2.** 3D framework of SUT-10. Viewed along (a) [100], (b) [110], and (c) [001].

The larger the organic structure-directing agents (OSDAs), the larger the voids in the resulting materials. This strategy has been demonstrated to be very successful in the synthesis of other types of open-framework materials,[47,48] such as large pore size open-framework germanates, phosphates, and zeolites.[47,49−51] Herein, via replacement of the OSDA of diethylenetriamine with the larger tetraethylenepentamine in the synthesis, another 3D vanadoborate, SUT-11, was obtained.

SUT-11 is constructed from another novel $V_{10}B_{24}$ cluster with a different arrangement of $BO_3$ and $BO_4$ compared to the clusters in SUT-7 and SUT-10 (Figure 1b and Figure S3). The $V_{10}$ ring in SUT-11 is similar to that in SUT-10. The V−O and V═O distances are in the ranges of 1.916(4)−2.006(4) and 1.619(5)−1.643(6) Å, respectively, slightly larger than those in SUT-10. The $V_{10}B_{24}$ clusters are first linked by ethylene glycol to form a columnar structure along the *c*-axis as shown in Figure 3a, and these columns are then connected through hydrogen bonds in the *a*−*b* plane to form a 3D framework structure. There are two different types of channels in the SUT-

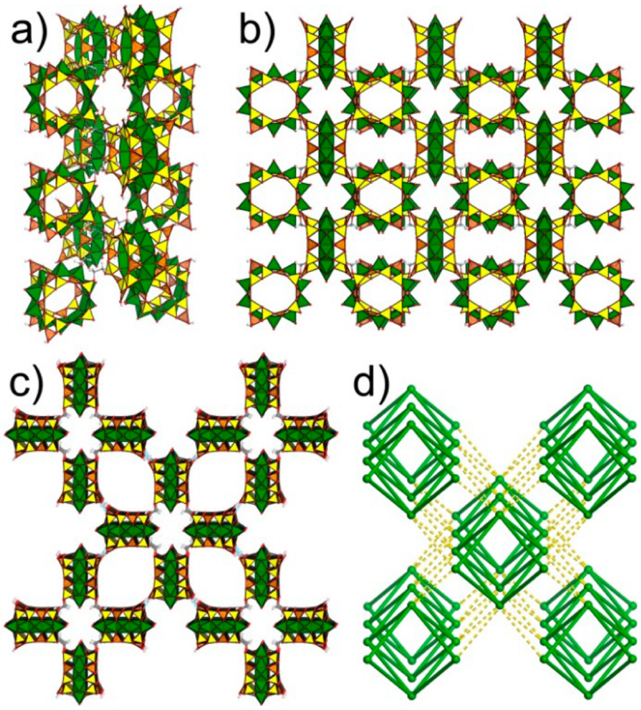

**Figure 3.** Framework structure of SUT-11: (a) covalently bonded column, (b) along the *a*-axis, (c) along the *c*-axis, and (d) topology of SUT-11 where solid and dashed lines present the connections through covalent bonds and hydrogen bonds, respectively.

11 framework along the *a*-axis as shown in Figure 3b: one is contributed by the opening feature of the $V_{10}$ ring cluster with a pore size of 5.9 Å × 5.7 Å, and the other is constructed by the clusters linked by ethylene glycol. Two different types of channels are also observed along the *c*-axis as shown in Figure 3c: one is inside the covalently bonded column with a size of 4.7 Å × 4.7 Å, and the other is between these columns with a pore size of 10.6 Å × 9.7 Å. Considering $V_{10}B_{24}$ clusters as nodes, they are connected by covalent bonds inside the column along the *c*-axis and then further connected by the O39−H39⋯O9 hydrogen bond [O9⋯O39, 2.809(2) Å] in the *a*−*b* plane as shown in Figure 3d.

The oxidation states of the vanadium in these compounds were always difficult to resolve.[52] Bond valence summation showed that vanadium has an average bond valence sum of approximately +4.2018 without any preferential occupancies for $V^{4+}$ and $V^{5+}$ in SUT-10, consistent with its dark green color.[40] This result was further confirmed by the XPS results with a peak at 516.3 eV with a shoulder beside, corresponding to $V^{4+}$ $2p^{3/2}$ and $V^{5+}$ $2p^{3/2}$ (Figure S4).[41] Different from that of SUT-10, the bond valence summation for vanadium in SUT-11 clusters is +4.05, indicated by the slightly longer bond lengths and light green color (Figure S6).[53] The XPS spectrum also confirms its 4+ oxidation states by a sharp peak centered at 516.1 eV (Figure S5). The reduction of the vanadium is ascribed by the organic amine, which is frequently observed in other vanadoborate synthesis. Because of the sensitivity to water molecules in air, we failed to obtain good PXRD patterns (Figures S7 and S8). Moreover, because of the low stability and the anionic feature of these two frameworks, good gas adsorption data for both SUT-10 and SUT-11 cannot be achieved. A possible reason is that the OSDAs interact with the framework very strongly and make it difficult to release them without destroying the framework. Ion-exchange experiments performed by using SUT-10 in an ethylene glycol solution with $Co^{2+}$, $Ni^{2+}$, and methyl viologen dichloride hydrate show that the SUT-10 underwent an amorphization process during the exchanging process (Figure S9), which could be ascribed to the strong interaction between the space filling species and the framework. When a space filling species such as $NH_4^+$, ethylene glycol molecules, exchanged out from the framework channels, the ethylene group linker between the vanadoborates clusters might be too flexible to maintain the crystallinity of the framework. It should also be interesting to investigate the catalytic properties of these materials if proper reaction conditions that could prevent the collapse of the framework can be found.

The formation of B−O−C bonds in SUT-10 and SUT-11 is further supported by the FT-IR spectra in Figures S10 and S11. Compared with the B−O stretching bands and C−O stretching bands in the raw materials, the B−O and C−O stretching bands were shifted to 1368 $cm^{-1}$ (B−O), 1297 $cm^{-1}$ (B−O), 1103 $cm^{-1}$ (C−O), and 1023 $cm^{-1}$ (C−O) in SUT-10 and 1368 $cm^{-1}$ (B−O), 1275 $cm^{-1}$ (B−O), 1070 $cm^{-1}$ (C−O), and 1002 $cm^{-1}$ (C−O) in SUT-11. The multiplicity of the C−O and B−O stretching bands in both compounds can be explained by the diverse chemical environments of the B−O groups and C−O groups. Thus, on the basis of our strategy, the vanadoborate clusters were successfully linked through covalent B−O−C bonds to form 3D framework structures in a simple one-pot solvothermal process. The unexpected hydrogen bonds also helped in the assembly of SUT-11. The basic reaction mechanism employed in our strategy should be the polymerization reaction through the condensation of the POM clusters and diols. It would be interesting to monitor the reaction progress in each step. However, because of the complexity of solvothermal feature of the reaction, attempts to use the mass spectrum to monitor the reaction products failed. Here we propose a most likely mechanism for their formation. $NH_4VO_3$ and boric acid were first reacted to form the vanadoborate clusters in solution; then the OH groups in the vanadoborate clusters reacted with ethylene glycol through the co-condensation reaction by eliminating a water molecule. The condensation is normally very fast and results in small crystals,[54] but under our synthesis condition, this reaction is reversible, which facilitates the formation of high-quality large single crystals. This strategy can be used not only for vanadoborates but also for other types of POMs, because the typical POM clusters with V, Mo, W, etc., also have diverse V−O−C,[55−61] Mo−O−C,[62−65] and W−O−C[66−69] fragments in the reported zero-dimensional structures.

## ■ CONCLUSIONS

In conclusion, two 3D open-framework vanadoborates with new types of vanadoborate clusters were successfully constructed through covalent B−O−C bonds and hydrogen bonds. The possible mechanism was also proposed. Although no application was explored in this project, the reported strategy of using B−O−C bonds to construct 3D covalently bonded POMs demonstrated a new way to enrich the structural diversity. This strategy can be expanded to other types of POM clusters with different covalent bonds and enrich their applications.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b01326.

IR, TG, and PXRD data (PDF)
Cif file (CIF)
Cif file (CIF)

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### Notes

The authors declare no competing financial interest.

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