# **Inorganic Chemistry**

# Evans–Showell-Type Polyoxometalates Constructing High-Dimensional Inorganic–Organic Hybrid Compounds with Copper– Organic Coordination Complexes: Synthesis and Oxidation Catalysis

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**S** Supporting Information

**ABSTRACT:** Four new hybrid architectures containing a  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ polyoxoanion, (en) $[Cu_3(ptz)_4(H_2O)_4][Co_2Mo_{10}H_4O_{38}]\cdot 24H_2O$  (1), (Hbim)<sub>2</sub>[{Cu-(b i m) <sub>2</sub> (H<sub>2</sub>O) <sub>2</sub>} <sub>2</sub> { C o <sub>2</sub> M o <sub>1</sub> <sub>0</sub> H <sub>4</sub> O <sub>3</sub> <sub>8</sub> } ] · 5 H <sub>2</sub> O (2), H<sub>2</sub> $[Cu(dpdo)_3(H_2O)_4][{Cu_2(dpdo)_3(H_2O)_4(CH_3CN)}_2{Co_2Mo_{10}H_4O_{38}}_2]\cdot 9H_2O$ (3), and (H<sub>2</sub>bpp)<sub>4</sub>[{Cu(H<sub>2</sub>O)<sub>2</sub>}{NaCo\_2Mo\_{10}H\_4O\_{38}}\_2]\cdot 10H\_2O (4), where ptz = 5-(4-pyridyl)-1H-tetrazole, en = ethylenediamine, bim = benzimidazole, dpdo = 4,4'bipyridine-*N*,*N'*-dioxide, and bpp = 1,3-bis(4-pyridyl)propane, have been prepared and characterized through elemental analysis, thermogravimetric analysis, IR spectroscopy, and powder and single-crystal X-ray diffraction. Compound 1 shows a 3D host–guest framework composed of 3D Cu-ptz as the host and Evans– Showell-type polyoxoanion  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  as the guest. Compound 2 is constructed from  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanions and Cu-bim coordination complexes to form a 2D covalent layer. Compound 3 also exhibits a 2D hybrid



network based on  $[Co_2Mo_{10}H_4O_{38}]^{6^-}$  polyoxoanions linked by Cu-dpdo coordination groups. Compound 4 is a 1D doublechain structure composed of  $[Co_2Mo_{10}H_4O_{38}]^{6^-}$  polyoxoanions joined together by Na<sup>+</sup> and Cu<sup>2+</sup> cations. As far as we know, compound 1 is the first host-guest compound with an Evans-Showell-type polyoxometalate as the guest, and compounds 2 and 3 are the first 2D inorganic-organic hybrid architectures constructed from Evans-Showell-type polyoxometalates. Compounds 1-4 are redox catalysts that heterogeneously prompt sulfide and alcohol oxidation with excellent efficiency.

## ■ INTRODUCTION

Polyoxometalates (POMs) are well-known inorganic metal oxide clusters possessing unmatched physical and chemical properties that allow them to have significant applications in catalysis, electronics, magnetism, optics, medicine, etc.<sup>1-5</sup> In this area, constructing POM-based inorganic-organic hybrid materials is always of great interest to researchers<sup>6-10</sup> because of not only their charming structures but also their attractive properties along with their chemical stability. Some classic POMs such as Anderson, Keggin, Lindqvist, Dawson, Waugh, and octamolybdate have been extensively studied as building units to fabricate versatile inorganic-organic hybrid architectures.<sup>11-16</sup> In contrast, Evans-Showell-type polyoxoanions as inorganic building blocks have rarely been explored since this kind of polyoxoanion was first synthesized by Keller and Friedheim<sup>17</sup> and structurally characterized by Evans and Showell at 1969.<sup>18</sup> So far, only a few 0D and 1D hybrid structures using an Evans-Showell-type polyoxoanion as the building unit have recently been reported by our group. Those are  $(4-H_2pya)_4[(H_2O)_6M][Co_2Mo_{10}H_4O_{38}]\cdot SH_2O$  (M = Zn, Cd, Co, Ni, Cu),<sup>19</sup> [Zn<sub>2</sub>(H<sub>2</sub>O)<sub>5</sub>(4,4'-bipy)<sub>3</sub>]H<sub>2</sub>[Co<sub>2</sub>Mo<sub>10</sub>-H<sub>4</sub>O<sub>38</sub>]·SH<sub>2</sub>O, [Zn<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>(bpe)<sub>3</sub>]H<sub>2</sub>[Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>]·6H<sub>2</sub>O, and  $[Zn(H_2O)_4(H_2bpp)_2][Co_2Mo_{10}H_4O_{38}] \cdot 2H_2O$ .<sup>20</sup> Thus, the design and synthesis of high-dimensional hybrid materials based on Evans-Showell-type polyoxoanions with unique functionality are highly desirable but remain challenging.

Among the POMs' applications, oxidation catalysis is one of the most attractive properties that has been considered in the last few decades because of both resistance to oxidation and compatibility with various oxygen sources.<sup>21-23</sup> One of the most valuable oxidation reactions is the oxidation of sulfides to sulfoxides and sulfones, which can be used in the chemical industry, biology, and medical chemistry.<sup>24-26</sup> The other important oxidation reaction is the oxidation of alcohols to aldehydes or acids in the laboratory and in the chemical industry because the products are important precursors in synthetic organic chemistry.<sup>27,28</sup> Various POMs have been utilized extensively as efficient homogeneous catalysts in the oxidation of sulfides and alcohols.<sup>29–31</sup> The catalytic selectivity and activity of homogeneous POMs are excellent; however, such catalysts are difficult to recycle because of their solubility in the catalytic reaction system. To solve the problem of catalyst reusability, it is imperative to design and synthesize recoverable POM-based heterogeneous catalysts. Various porous supports such as silica, carbons, zeolites, or polymers have been utilized for the dispersion and heterogeneity of POMs,<sup>32-34</sup> whereas such systems often suffer from ill-defined structures, low loading efficiency, inactivation of active sites, and leaching. A valuable alternative strategy to develop a

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Received: June 19, 2017
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heterogeneous catalyst system is the combination of POM catalysts with metal–organic coordination complexes to construct crystalline POM-based host–guest frameworks or high-dimensional hybrid networks.<sup>35</sup>

Thanks to the pioneering work of Liu, Su, Hill, Duan, Niu, Wu, and other groups, some crystalline 3D host-guest structures or high-dimensional hybrid architectures based on POMs have been successfully synthesized that can act as heterogeneous catalysts, efficiently catalyzing the hydrolysis of esters, the removal of nerve gas, the detoxification of various sulfur compounds, the asymmetric dihydroxylation of aryl olefins, the oxidation of alkylbenzenes, and the scavenging of dyes, etc.  $^{36-43}$  In contrast, there have been very few examples of the oxidation reaction of sulfides and alcohols catalyzed by crystalline POM-based host-guest or high-dimensional hybrid species up to now. Recently, Li and co-workers successfully combined Keggin-type POMs with triazole-based metalorganic frameworks to produce POM@MOF hybrid compounds that can act as heterogeneous catalysts for the oxidative desulfurization reaction.<sup>44</sup> Hu's group recently synthesized three novel inorganic-organic hybrid copper vanadates,  $\alpha$ - $[Cu(mIM)_4]V_2O_6$ ,  $\beta$ - $[Cu(mIM)_4]V_2O_6$ , and  $[Cu(mIM)_2)]$ - $(VO_3)_2$ , which can catalyze the oxidation of sulfides and alcohols with high activity and selectivity.45 Lysenko et al. prepared two 2D copper molybdate hybrid species,  $[Cu_4(\mu_4$ - $O)(tr_2ad)_2(MoO_4)_3].7.5H_2O$  and  $[Cu_2(tr_2ad)_4](Mo_8O_{26})$  $[tr_2ad = 1,3-bis(1,2,4-triazol-4-yl)adamantane]$ , which are heterogeneous catalysts in the oxidation of benzyl alcohol (BzOH) in the presence of *tert*-butyl hydroperoxide oxidant.<sup>4</sup> In the research area of the oxidation of sulfides and alcohols. choosing suitable POM precursors and metal-organic subunits to fabricate crystalline novel high-dimensional hybrid materials becomes a crucial factor in the design of efficient heterogeneous POM catalysts.

Inspired by the significant properties of the Evans–Showelltype POM  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  in catalyzing the water oxidation reaction and its unique structure featuring two terminal O atoms linked to each Mo atom,<sup>47,48</sup> we are interested in investigating whether high-dimensional hybrid frames based on such POM can effectively catalyze the oxidation of sulfides and alcohols as heterogeneous catalysts. Moreover, interest in the  $Cu^{2+}$  cation with flexible coordination ability has significantly grown over the past years because copper-based compounds can act as excellent candidates for many catalytic oxidation reactions.<sup>49</sup> Taking these into account, it is very intriguing to combine copper–organic subunits with Evans–Showell-type POMs to make new high-dimensional hybrid materials featuring the function of catalyzing the oxidation of sulfides and alcohols.

Fortunately, we obtained four high-dimensional hybrid frameworks built up from Evans–Showell-type POMs and copper–organic coordination fragments from this reaction system: (en)[Cu<sub>3</sub>(ptz)<sub>4</sub>(H<sub>2</sub>O)<sub>4</sub>][Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>]·24H<sub>2</sub>O (1), (Hbim)<sub>2</sub>[{Cu(bim)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>}{Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>}]·5H<sub>2</sub>O (2), H<sub>2</sub>[Cu(dpdo)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>][{Cu<sub>2</sub>(dpdo)<sub>3</sub>(H<sub>2</sub>O)<sub>4</sub>(CH<sub>3</sub>CN)}<sub>2</sub>-{Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>}<sub>2</sub>]·9H<sub>2</sub>O (3), (H<sub>2</sub>bpp)<sub>4</sub>[{Cu(H<sub>2</sub>O)<sub>2</sub>}{NaCo<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>}<sub>2</sub>]·10H<sub>2</sub>O (4), where ptz = 5-(4-pyridyl)-1H-tetrazole, en = ethylenediamine, bim = benzimidazole, dpdo = 4,4'-bipyridine-N,N'-dioxide, and bpp = 1,3-bis(4-pyridyl)-propane, among which compound 1 represents the first 3D host–guest structure and compounds 2 and 3 are the first 2D hybrid architectures constructed from Evans–Showell-type POMs. The magnetic properties of four compounds from 2

to 300 K have been investigated. More interestingly, four hybrid compounds as heterogeneous catalysts show high activity and interesting selectivity in the oxidation reactions toward the corresponding sulfoxides and acids, accompanied by the advantages of steady reuse and easy recovery. As far as we know, they are the first examples that inorganic—organic hybrid species built up from Evans—Showell-type POMs catalyze the oxidation reactions of sulfides and alcohols.

#### EXPERIMENTAL SECTION

Chemicals and Measurements. All of the purchased chemicals were not purified prior to use.  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]\cdot 7H_2O$  was prepared by the method in the literature<sup>50,51</sup> and further characterized by IR spectroscopy. A PerkinElmer 2400 CHN elemental analyzer was used to measure elemental analyses of H and N atoms; a PLASMA-SPEC (I) ICP atomic emission spectrometer was used to measure Mo, Co, Cu, and Na atoms. An Alpha Centaur Fourier transform infrared (FTIR) spectrometer was utilized to measure IR spectra from 400 to 4000 cm<sup>-1</sup> with KBr pellets. A PerkinElmer TGA7 instrument was utilized to measure thermogravimetric analysis (TGA) curves with a heating rate of 10 °C min<sup>-1</sup> in flowing N<sub>2</sub>. A Rigaku Dmax 2000 X-ray diffractometer was used to record powder X-ray diffraction (PXRD) patterns of the samples by graphite-monochromatized Cu K $\alpha$ radiation. A Cary 500 spectrophotometer containing a 110-mmdiameter integrating sphere was used to measure the diffusereflectance spectra of finely ground samples, in the range of 200-800 nm. A SPECORD S600 spectrometer was used to measure the UV-vis spectra. A SQUID magnetometer (MPMS-7) with an 1 kOe applied field was used to measure the variable-temperature magnetic susceptibility data from 2 to 300 K. Pascal's constants were used to correct for diamagnetism. After the catalytic reaction was finished, gas chromatography (GC; with naphthalene as the internal standard substrate) and GC-mass spectrometry (MS) were used to analyze the resulting mixture. GC analysis was performed with an Agilent HP6890 spectrometer with a flame ionization detector, which was used to monitor the conversion and selectivity. GC-MS at the final time point was used to confirm the identity of the products. The GC-MS spectra were measured on an Agilent HP6890/5973MSD spectrometer.

Synthesis of  $(en)[Cu_3(ptz)_4(H_2O)_4][Co_2Mo_{10}H_4O_{38}]\cdot24H_2O$  (1). In the synthesis of 1,  $CuCl_2\cdot 2H_2O$  (0.068 g, 0.4 mmol) and ptz (0.014 g, 0.1 mmol) were in order dissolved in 15 mL of water.  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]\cdot7H_2O$  (0.192 g, 0.1 mmol) dissolved in 10 mL of water was introduced. Subsequently, 0.5 mL of en was added to the solution. The initial pH value of the mixture was 8.5, which was adjusted to 3.0 by 2 M HNO<sub>3</sub>. After the solution was stirred at 85 °C for 2 h, the filtrate was placed at room temperature. Dark-green crystals of 1 with rectangular shape were prepared with 30% yield in about 2 weeks (based on Mo). FTIR data (cm<sup>-1</sup>): 3427(m), 3018(m), 1598(m), 1506(m), 1454(w), 1318(w), 1172(w), 1038(w), 942(vs), 850(s), 675(vs), 608(vs), 559(s), 523(s), 482(s). Elem anal. Calcd for 1: Co, 3.89; Mo, 31.64; Cu, 6.28; C, 10.29; H, 2.90; N, 10.15%. Found: Co, 3.54; Mo, 31.30; Cu, 6.47; C, 10.01; H, 3.15; N, 9.96%.

Synthesis of  $(Hbim)_{2}[{Cu(bim)_{2}(H_{2}O)_{2}}_{2}Co_{2}Mo_{10}H_{4}O_{38}].5H_{2}O$  (2). In the synthesis of 2,  $CuCl_2$  (0.068 g, 0.4 mmol) and bim (0.012 g, 0.1 mmol) were in order dissolved in 15 mL of water. Then,  $(NH_4)_6 [Co_2Mo_{10}H_4O_{38}] \cdot 7H_2O$  (0.192 g, 0.1 mmol) dissolved in 10 mL of water was added. The initial pH value of the mixture was 4.2, which was adjusted to 3.0 by 2 M HNO3. After the solution was stirred at 85 °C for 2 h, the filtrate was placed at room temperature. Darkgreen crystals of 2 with rectangular shape were prepared with 50% yield in about 1 week. FTIR data (cm<sup>-1</sup>): 3407(vs), 2845(w), 1620(m), 1502(w), 1448(w), 1419(w), 1303(w), 1249(w), 939(vs), 902(vs), 744(s), 657(vs), 626(vs), 523(m), 430(m). Elem anal. Calcd for 2: Co, 5.09; Mo, 41.48; Cu, 5.49; C, 21.79; H, 2.59; N, 7.26%. Found: Co, 5.31; Mo, 41.65; Cu, 5.22; C, 21.58; H, 2.90; N, 7.04%. Synthesis of  $H_2$  [Cu(dpdo)<sub>3</sub>( $H_2$ O)<sub>4</sub>] - [{Cu<sub>2</sub>(dpdo)<sub>3</sub>( $H_2$ O)<sub>4</sub>( $CH_3$ CN)}<sub>2</sub>{Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>}<sub>2</sub>]·9H<sub>2</sub>O (**3**). The synthesis method of 3 was similar to that of 2. The difference is that dpdo (0.019 g, 0.1 mmol) and  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  (0.068 g, 0.4 mmol) were in

#### Table 1. Crystal Data and Structure Refinement for 1-4

	1	2	3	4	
formula	$C_{26}H_{88}Co_2Cu_3Mo_{10} N_{22}O_{66}$	$C_{42}H_{60}Co_2Cu_2Mo_{10} N_{12}O_{47}$	$C_{94}H_{130}Co_4Cu_5Mo_{20}N_{20}O_{115}$	$C_{52}H_{96}Co_4CuMo_{20}N_8Na_2O_{88}$	
fw	3033.06	2313.40	5852.45	4505.42	
T (K)	293(2)	293(2)	293(2)	293(2)	
cryst syst	monoclinic	triclinic	monoclinic	triclinic	
space group	C2/c	$P\overline{1}$	P21/c	$P\overline{1}$	
a (Å)	28.550(3)	11.9813(5)	16.0897(8)	11.2217(2)	
b (Å)	14.3054(16)	12.3330(6)	28.5090(15)	13.8819(3)	
c (Å)	21.376(2)	25.7926(12)	24.8105(13)	19.6178(4)	
$\alpha$ (deg)	90	79.810(3)	90	78.2020(10)	
$\beta$ (deg)	108.087(2)	79.066(3)	129.402(3)	78.9640(10)	
γ (deg)	90	88.911(3)	90	78.1120(10)	
U (Å <sup>3</sup> )	8299.3(16)	3682.6(3)	8793.9(8)	2891.53(10)	
Ζ	4	4	2	1	
$\mu \ (\mathrm{mm}^{-1})$	2.723	2.751	2.439	2.944	
reflns collected	20355	12892	36319	17018	
indep reflns	7280	24868	15436	10000	
R(int)	0.0295	0.0434	0.0900	0.0179	
GOF on F <sup>2</sup>	1.250	1.022	1.021	1.055	
$R_1^a [I > 2\sigma(I)]$	0.0851	0.0564	0.0775	0.0221	
$wR_2^{b} [I > 2\sigma(I)]$	0.1869	0.1333	0.1905	0.0538	
$R_1$ (all data)	0.0906	0.0771	0.1369	0.0255	
$wR_2$ (all data)	0.1895	0.1458	0.2261	0.0559	
${}^{a}R_{1} = \sum   F_{o}  -  F_{c}   / \sum  F_{o} . {}^{b}wR_{2} = \sum [w(F_{o}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{o}^{2})^{2}]^{1/2}.$					

order dissolved in 15 mL of acetonitrile/water (3:2, v/v) in the synthesis of **3**. The initial pH value (3.8) was then adjusted to 3.0 by 2 M HNO<sub>3</sub>. Bar crystals of **3** colored dark green were prepared with 40% yield in about 1 week. FTIR data (cm<sup>-1</sup>): 3405(s), 3107(s), 1625(m), 1546(w), 1470(s), 1424(m), 1317(w), 1215(vs), 1179(s), 1029(m), 939(vs), 913(vs), 835(vs), 682(vs), 604(vs), 559(vs), 519(s), 482(s). Elem anal. Calcd for **3**: Co, 4.03; Mo, 32.79; Cu, 5.43; C, 19.27; H, 2.22; N, 4.78%. Found: Co, 3.87; Mo, 32.49; Cu, 5.53; C, 19.57; H, 2.48; N, 4.52%.

Synthesis of  $(H_2bpp)_4[{Cu(H_2O)_2}{NaCo_2Mo_{10}H_4O_{38}}_2]\cdot 10H_2O$  (4). The synthesis method of 4 was similar to that of 2. The difference is that bpp (0.0198 g, 0.1 mmol) was added to replace bim, and NaCl (0.011g, 0.2 mmol) was introduced in the synthesis of 4. The initial pH value (3.7) was adjusted to 3.0 by 2 M HNO<sub>3</sub>. Block crystals of compound 4 were prepared with 25% yield after 2 weeks. FTIR data (cm<sup>-1</sup>): 3428(s), 3090(m), 1634(m), 1507(m), 1346(w), 1209(w), 952(s), 919(vs), 870(s), 733(m), 682(s), 625(vs), 564(m). Elem anal. Calcd for 4: Co, 5.23; Mo, 42.60; Cu, 1.41; Na, 1.02; C, 13.85; H, 2.13; N, 2.49%. Found: Co, 5.01; Mo, 42.84; Cu, 1.69; Na, 1.38; C, 13.55; H, 2.46; N, 2.31%.

General Methods for Catalyzing the Oxidation of Sulfides and Alcohols. Sulfide oxidation: Compound 1 (11.3 mg, 3.75  $\mu$ mol), *tert*-butyl hydroperoxide (TBHP; 0.5 mmol), sulfide (0.25 mmol), and acetonitrile (0.5 mL) were put in a glass bottle. The catalytic reaction was carried out at 40 °C for 4 h. Alcohol oxidation: Compound 1 (11.3 mg, 13.75  $\mu$ mol), alcohol (0.25 mmol), TBHP (0.75 mmol), and acetonitrile (1.0 mL) were put in a glass bottle. The catalytic reaction was carried out at 75 °C for 8 h/24 h. After the catalytic reaction was finished, GC and GC–MS were used to analyze the resulting mixture.

**X-ray Crystallography.** A Bruker Smart CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) was used to collect the crystallographic data of four compounds at 293 K by  $\theta$  and  $\omega$  scan modes. The method of empirical absorption correction was adopted. SHELXTL-97 software was used to solve the structures of 1–4 and refine the data.<sup>52</sup> In 1–4, most non-H atoms are refined anisotropically, and only some of water molecules were excepted. From Fourier difference maps, some H atoms of the water molecules were located, whereas the H atoms linked to the C and N atoms were not located and were fixed in their ideal positions. Because of the disorder of the partial crystal water molecules, their site occupancies were intended to

be <1 by refining their thermal parameters. To get reasonable thermal parameters and atom sites, some commands such as "isor" and "dfix" were utilized. Table 1 summarizes the structural determination and crystallographic data for 1-4.

The CCDC reference numbers for 1–4 are 1555698–1555701, respectively.

#### RESULTS AND DISCUSSION

Synthesis. With different types of N-donor ligands (ptz, bim, and bpp) or a O-donor ligand (dpdo) (Figure S1), the interaction of  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]$ ·7H<sub>2</sub>O and Cu<sup>2+</sup> has been investigated. Four hybrid species with 3D host-guest pairs, 2D layers, and 1D chains were obtained. Compounds 1-4 were prepared by changing the organic ligands under similar synthesis conditions. When the ptz ligand was used, compound 1 with a 3D host-guest structure, made up of a Cu-ptz coordination complex as the 3D host and an Evans-Showelltype polyoxoanion as the guest, was isolated. In 1, each rigid ptz ligand acts as a multidentate bridging ligand directly linked to Cu<sup>2+</sup> cations to yield a 2D layer. Because of 2D layers being packed together, a 3D supramolecular channel frame is constructed, which has large enough cavities to accommodate Evans-Showell-type polyoxoanions. When the bim molecule was used in place of ptz, compound 2 with a 2D covalent layer was obtained, in which each bim molecule is a monodentate ligand coordinating to a Cu<sup>2+</sup> cation to form [Cu- $(bim)_2(H_2O)_2$  subunits that are linked with the terminal O atoms of the  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanions. The differences of the ptz and bim ligands in coordination mode result in different hybrid structures. When a flexible dpdo ligand was used, compound 3 showing a different 2D layer was prepared, in which the dpdo ligand utilizes its O donors coordinating to Cu<sup>2+</sup> cations to produce Cu-dpdo coordination fragments that then are linked with the  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanions. Compounds 2 and 3 are the first 2D inorganic–organic hybrids built up from Evans-Showell-type POMs. Considering the



Figure 1. (a) Ball-stick view of the 1D coordination complex chain in 1, showing the alternately arranged trinuclear clusters. (b) View of the 2D layer in 1 along the a axis. Color code: Cu, light blue; C, gray; N, dark blue; O, red.

different coordination behaviors and ligand lengths of rigid bim and flexible dpdo molecules, both 2D structures have different topological structures, respectively showing a 4-connected 4<sup>4</sup> chiral net and a 3-connected 6<sup>3</sup> net. Also, the window of the 2D structure in compound 3 is larger than that in compound 2 because of the longer dpdo ligand. When the bpp ligand was used, the flexible bpp molecule does not coordinate to the Cu<sup>2+</sup> cation, just situating in the cavities and linking to the polyoxoanions through extensive hydrogen bonds. The above results revealed that the lengths and geometries of organic ligands play very important roles in the formation of hybrid structures. Compounds 1–4 show different structures as a result of the introduction of different ligands, which can be compared with our reported 0D chiral hybrid compound (4-H<sub>2</sub>pya)<sub>4</sub>[Cu(H<sub>2</sub>O)<sub>6</sub>][Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>]·SH<sub>2</sub>O.<sup>19</sup>

In the synthesis of compound 1, the en molecule needs to be added to the reaction system because the en molecule participates in the crystallization of 1. If the en molecule was not added, no crystals could be obtained. In the synthesis of compounds 2-4, when en was added, no crystals could be isolated. During the preparation of compound 4, the NaCl salt was necessary to obtain a single crystal due to the Na<sup>+</sup> cation coordinating to the terminal O atoms of the polyoxoanions. If NaCl was not introduced into the reaction solution, only a mass of precipitate was obtained. When NaCl was added to the solution of the other three compounds, no affects on the final structures were observed. In addition, the quality of the crystals can be influenced by the stoichiometry of  $Cu^{2+}/$  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ , the reactive pH value, and the synthetic temperature of the reaction systems, which can be manifested by many parallel experiments. The stoichiometry of Cu<sup>2+</sup>/  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  can obviously affect the final products. Compounds 1–4 can be well-isolated by the 4:1  $Cu^{2+}/$  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  ratio. When the  $Cu^{2+}/[Co_2Mo_{10}H_4O_{38}]^{6-}$ 

ratio was decreased from 4:1 to 3:1 or 2:1, the yield was reduced or no crystal could be separated. All four compounds can be well-prepared in the pH range of 2.5–3.5. When the pH value is higher (pH> 3.5), a mass of precipitates will be obtained; when the pH value is lower (pH < 2.0), no products could be obtained. Also, the temperature is an important factor. At lower temperature (25 °C), precipitates could be obtained; at higher temperature (100 °C), poor-quality crystals could be obtained. The optimal synthetic temperature is 85 °C.

Crystal Structure of 1. Compound 1 shows a unique 3D host-guest frame, derived from Evans-Showell-type anions  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  and trinuclear  $[(H_2O)_4(ptz)_4Cu_3]^{6+}$  fragments by solving the single-crystal diffraction data. The asymmetric unit in 1 contains half of a unique  $[\dot{Co}_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanion, two ptz ligands, and one and half  $Cu^{II}$  cations (Figure S2a). The structure of  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  can be considered as a dimer of two monolacunary Anderson ions  $[CoMo_5H_2O_{19}]^{3-}$ , which are joined together by two edge-sharing CoO<sub>6</sub> octahedra and produce a ~45° intersection angle (Figure S2b). Evans and Showell have suggested that the polyoxoanion  $[{\rm Co_2Mo_{10}H_4O_{38}}]^{6-}$  possesses two enantiomers, with a point group symmetry  $D_2$  (Figure S3). Because compound 1 crystallizes in the C2/c space group, it can be concluded that two enantiomers should coexist in the structure. In the polyoxoanion  $[Co_2Mo_{10}H_4O_{38}]^{6\text{-}}\text{, two O}$  atoms attached to each Co<sup>3+</sup> ion are linked with two H atoms, according to bondvalence-sum (BVS) calculations and the electron density map. In terms of the coordination modes of O atoms in the cluster, there are five classes of O atoms. The central oxygen Oc is linked to two Mo atoms and a Co atom as the  $\mu_3$ -OH atom; the central oxygen Od is linked to three Mo atoms and a Co atom as the  $\mu_4$ -O atom; the central oxygen Oq is linked to two Mo atoms and two Co atoms as the  $\mu_4$ -O atom; the terminal



**Figure 2.** (a) View of one channel with dimensions of ca. 13 Å × 8 Å in the host frame. (b) View of one guest anion,  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ , with dimensions of ca. 12 Å × 7 Å. (c) Polyhedral and ball–stick representation of the 3D host–guest framework in 1 along the *b* axis, with two enantiomers of the  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anion as guests situating in two kinds of channels. Free water molecules are omitted for clarity. Color code: Co, yellow; Mo, purple/green; Cu, light blue; C, gray; N, dark blue; O, red.

oxygen Ot is linked to one Mo atom; the double-bridging oxygen Ob is linked to two Mo atoms. Then, the Mo–O bond lengths are classified as five different groups: Mo–Oc bond lengths are from 2.252(9) to 2.293(9) Å, Mo–Od are from 1.998(1) to 2.361(9) Å, Mo–Oq are from 2.275(9) to 2.290(9) Å, Mo–Ot are from 1.692(1) to 1.730(9) Å, and Mo–Ob are from 1.876(1) to 1.926(1) Å in **1**. The Co–O distances vary from1.869(9) to 1.941(9) Å, and the O–Co–O angles vary from 84.3(4) to 176.0(4)°. Corresponding to the results of the previous study, the above bond lengths and angles are within the normal ranges.<sup>19,20,48</sup>

One and half crystallization-independent Cu<sup>II</sup> cations exist in the complex. The unique Cu(1) cation is coordinated by three N atoms from three ptz ligands [Cu-N 1.997(1)-2.036(1) Å] and three water molecules [Cu-OW 1.963(1)-2.670(1) Å] to finish a distorted octahedral geometry. The Cu(2) cation with half-occupancy is bound to two bridging O atoms [Cu-O 2.483(1) Å] by its axial sites and four N atoms of four ptz molecules [Cu-N 1.988(1)-2.028(1) Å] by its equatorial sites to also have an octahedral environment. One Cu(2) and two Cu(1) cations build a trinuclear cationic subunit,  $[(H_2O)_4(ptz)_4Cu_3]^{6+}$ , bridged by ptz and water molecules (Figure S2c). Two crystallographically independent ptz molecules utilize two N atoms of each tetrazole part, linking neighboring Cu cations to produce such a subunit. One of the unique ptz ligands is a tridentate ligand, further linking trinuclear subunits together by using the N atom of the pyridyl part.

Interestingly, in 1, trinuclear coordination complex clusters  $[(H_2O)_4(ptz)_4Cu_3]^{6+}$  are first joined together to generate a 1D linear structure by pyridyl groups of the ptz ligands (Figure 1a). The planes of the adjacent tricopper units are almost perpendicular. Then, a 2D coordination complex sheet is formed by the covalent connection of 1D chains to one another along the a axis (Figure 1b). Furthermore, the parallel packing of the adjacent 2D sheets produces a 3D supramolecular host structure by  $\pi$ - $\pi$ -stacking interactions of ptz ligands between which the face-to-face distance is 3.9 Å. From Figure 2, it can be seen that many strip-type channels with dimensions of ca. 12.9  $Å \times 8.3$  Å are generated by stacking the adjacent layers. Each channel just holds one Evans–Showell-type anion (ca. 11.8 Å  $\times$ 6.7 Å). In the structure, Evans-Showell-type anions are supposed as templates in the process of formation and trinuclear subunits are assembled around them by electrostatic and hydrogen-bonding interactions, so that the 3D host-guest structure is produced (Figures S4 and S5). One kind of chiral  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anion forms one kind of chiral channel, and the opposite-handed anion produces another kind of chiral channel, which results in an achiral host-guest architecture of 1. So far, such a host-guest structure with an Evans-Showelltype anion as the template has never been reported. Thus, compound 1 represents the first example of host-guest architecture built up from such kinds of POMs. Moreover, weak hydrogen-bonding interactions (O13 - H - C11 = 3.125)Å) between C atoms of ligands and O atoms of the

 $[{\rm Co_2Mo_{10}H_4O_{38}}]^{6-}$  clusters are important to stabilize the 3D host–guest structure.

Crystal Structure of 2. When bim was used as the organic ligand, compound 2 was obtained. Compound 2 is a 2D structure sheet comprised of Evans-Showell-type [Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>]<sup>6-</sup> polyoxoanions, Cu-bim coordination units, and isolated protonated bim molecules by single-crystal structural analyses. In terms of the coordination modes of O atoms in the cluster, there are six classes of O atoms. The central oxygen Oc is linked to two Mo atoms and a Co atom as the  $\mu_3$ -OH atom; the central oxygen Od is linked to three Mo atoms and a Co atom as the  $\mu_4$ -O atom, the central oxygen Oq is linked to two Mo atoms and two Co atoms as the  $\mu_4$ -O atom; the terminal oxygen Ot is linked to one Mo atom; the terminal oxygen Ot' is linked to Cu<sup>2+</sup>; the double-bridging oxygen Ob is linked to two Mo atoms. Then, Mo-O bond lengths are classified as six groups: Mo-Oc bond lengths are from 2.244(6) to 2.302(6) Å, Mo-Od are from 1.985(6) to 2.339(6) Å, Mo-Oq are from 2.246(6) to 2.322(6) Å, Mo-Ot are from 1.674(8) to 1.728(6) Å, Mo-Ot' are from 1.710(6) to 1.725(6) Å, and Mo-Ob are from 1.862(7) to 1.975(6) Å in 2. Similar to those of compound 1, the central Co-O distances vary from 1.862(5) to 1.957(6) Å and the O-Co-O angles vary from 83.4(2) to 176.6(3)°.

In 2, the asymmetric unit is comprised of one unique  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanion, two  $Cu^{2+}$  cations, and six bim molecules (Figure S6a). Both unique  $Cu^{2+}$  cations [Cu(1) and Cu(2)] have an octahedral coordination environment, defined by two N atoms from the bim ligands [Cu-N 1.963(8) and 2.047(9) Å], two terminal O atoms from two  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anions [Cu-O 2.199(6) and 2.438(6) Å], and two water O atoms [Cu-OW 1.988(8) and 2.064(8) Å] (Figure S6b,c). Four of the six crystallographically independent bim molecules act as monodentate ligands coordinating to Cu cations, and the others as protonated molecules balance the charges. The compound was synthesized at about pH 3.0, so the imidazole group of the isolated bim molecule is protonated. BVS calculations and the charge balance of the whole molecule can confirm this point.

Strikingly, in 2, one kind of chiral  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anion generates a 1D chiral chain, linked by some  $[(bim)_2Cu(H_2O)_2]$ units (see Figure 3a). Neighboring same-handed chiral chains generate a 2D chiral layer along the c axis, interconnected by other  $[(bim)_2Cu(H_2O)_2]$  fragments (Figure 3b). A 2D chiral hybrid architecture built up from Evans-Showell-type POMs is first observed in compound 2. From the view of topology, each Cu cation is bonded to two  $[Co_2Mo_{10}H_4O_{38}]^{6-1}$  anions, and each  $[Co_2Mo_{10}H_4O_{38}]^{6-1}$  anion is linked with four adjacent Cu cations. As a result, the 2D framework exhibits a 4-connected 4<sup>4</sup> chiral net with Cu cations as linkers and  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ units as nodes (Figure S7). A racemic 3D supramolecular framework (shown in Figure 4) can be formed by stacking opposite-handed chiral 2D sheets together via hydrogen bonds (N2-H.O23 = 3.09 Å; N8-H.O7 = 2.96 Å) and  $\pi-\pi$ stacking interactions of bim molecules (3.8 Å). By these kinds of connection modes, 1D supramolecular channels are produced and occupied by crystal water molecules and protonated bim molecules.

*Crystal Structure of* **3**. When dpdo was used as an organic ligand, compound **3** was obtained. Compound **3** also is a 2D covalent framework assembled by Evans–Showell-type polyoxoanions  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  and Cu-dpdo coordination complex fragments by single-crystal structural analyses. In



**Figure 3.** (a) Polyhedral and ball–stick view of the 1D homochiral chain in 2. (b) View of the 2D homochiral sheet in 2 along the c axis. Color code: Co, yellow; Mo, purple; Cu, light blue; C, gray; N, dark blue; O, red.



**Figure 4.** Polyhedral and ball–stick representation of the 3D supramolecular achiral framework of **2** along the *a* axis, showing the hydrogen-bonding and  $\pi$ – $\pi$ -stacking interactions. Color code: Co, yellow; Mo, purple/green; Cu, light blue; C, gray; N, dark blue; O, red.

terms of the coordination modes of O atoms in the cluster, there are six classes of O atoms. Then, Mo–O bond lengths are classified as six groups: Mo–Oc bond lengths are from 2.246(9) to 2.312(9) Å, Mo–Od are from 1.971(1) to 2.430(1) Å, Mo–Oq are from 2.246(9) to 2.329(9) Å, Mo–Ot are from 1.689(1) to 1.738(9) Å, Mo–Ot' are from 1.701(9) to 1.714(9) Å, and Mo–Ob are from 1.881(1) to 1.996(9) Å in 3. Corresponding to the reported results,<sup>19</sup> O–Co–O angles vary from 83.5(4) to 176.6(4)° and Co–O distances vary from 1.853(9) to 1.942(9) Å.

In 3, the asymmetric unit is comprised of one unique  $[{\rm Co_2Mo_{10}H_4O_{38}}]^{6-}$  anion, two and half Cu cations, and four and half dpdo molecules (Figure S8a). Cu(1) possesses an octahedral coordination, bonded to one dpdo molecule, two  $[{\rm Co_2Mo_{10}H_4O_{38}}]^{6-}$  units, and three water molecules through

six O atoms. The Cu-O distances are from 1.968(1) to 2.340(9) Å (Figure S8b). Cu(2) also adopts an octahedral geometry, being defined by four dpdo molecules and one water molecule through five O atoms and one acetonitrile molecule through one N atom. The Cu–O distances are from 1.927(1) to 2.476(1) Å, and the Cu-N distance is 2.001(1) Å. Four dpdo ligands make two neighboring Cu(2) cations join together to construct a dinuclear coordination cluster  $[(CH_3CN)_2(bpdo)_4Cu_2]^{4+}$  (Figure S8c). A half-occupancy Cu(3) cation exists as an isolated coordination unit, which adopts a square-pyramidal geometry and is defined by three water molecules and two dpdo molecules through five O atoms. The Cu-O distances are from 1.918(2) to 2.33(3) Å. There are four and half crystallographically independent dpdo molecules. Three dpdo ligands among them act as bidentate ligands, linking two adjacent Cu cations together, and others as monodentate ligands, coordinating to Cu cations.

Intriguingly, in 3, two kinds of chiral  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anions generate a 1D achiral linear structure, alternately joined by Cu(1)-dpdo coordination groups (Figure 5a). Adjacent



**Figure 5.** (a) Polyhedral and ball–stick view of the 1D achiral chain in 3. (b) 2D achiral layer in 3 showing the adjacent chains joined up together by dinuclear coordination complex clusters. Color code: Co, yellow; Mo, purple/green; Cu, light blue; C, gray; N, dark blue; O, red.

chains are parallelly interconnected by dinuclear coordination complex clusters  $[(CH_3CN)_2(dpdo)_4Cu_2]^{4+}$  to produce a 2D achiral network (Figure 5b). From the view of topology, each Cu(1) as a 3-connected node links to two  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ anions in the chain and one  $[(CH_3CN)_2(dpdo)_4Cu_2]^{4+}$  cluster to form the 2D structure. Thus, the 2D sheet exhibits a 3connected 6<sup>3</sup> net with Evans–Showell-type POM units, Cu(2) cations as linkers, and Cu(1) cations as nodes (Figure S10). Furthermore, a 3D supramolecular framework can be formed by these 2D sheets joining together through hydrogen bonds (O15…O4W 2.902 Å; Figure 6). Free water molecules take part in extensive hydrogen-bonding interactions, by which the small voids of the structure are filled.



**Figure 6.** Polyhedral and ball–stick representation of the 3D supramolecular achiral framework of **3** along the *c* axis showing hydrogen-bonding interactions. Color code: Co, yellow; Mo, purple/ green; Cu, light blue; C, gray; N, dark blue; O, red.

Crystal Structure of 4. When bpp was used as an organic ligand, compound 4 was obtained. Compound 4 exhibits a 1D extended structure assembled by Evans-Showell-type polyoxoanions  $[Co_2Mo_{10}H_4O_{38}]^{6-}$ ,  $Cu^{2+}$  cations, and Na<sup>+</sup> cations by single-crystal structural analyses. In terms of the coordination modes of O atoms in the cluster, there are seven kinds of O atoms. Then, Mo-O bond lengths are classified as seven groups: Mo-Oc bond lengths are from 2.235(2) to 2.302(2) Å; Mo-Od are from 1.979(2) to 2.344(2) Å; Mo-Oq are from 2.267(2) to 2.309(2) Å; Mo-Ot are from 1.684(2) to 1.719(2) Å; Mo-Ot' are from 1.716(2) to 1.752(2) Å; Mo-Ot'' are from 1.708(2) to 1.716(2) Å; Mo-Ob are from 1.873(2) to 1.957(3) Å in 4. Similar to compounds 1-3, the central Co-O distances vary from 1.867(2) to 1.953(2) Å and the O-Co-O angles vary from 84.14(9) to 175.83(1)°.

In 4, the asymmetric unit is comprised of one unique  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanion, one  $Cu^{2+}$  cation, one Na<sup>+</sup> cation, and two bpp molecules (Figure S11). The crystallographically unique  $Cu^{2+}$  ion has an octahedral coordination geometry, which is linked with two water molecules and four  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  units through six O atoms. The Cu–O distances are from 1.960(2) to 2.428(2) Å. A unique Na<sup>+</sup> cation also adopts an octahedral geometry, being defined by two  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyoxoanions through six O atoms, with the Na–O distances varying from 2.360(3) to 2.505(3) Å. Each crystallographically independent bpp molecule is protonated, which can be confirmed by the synthetic pH value (3.0) and BVS calculations.

In 4, one kind of chiral  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  polyanion generates a 1D chiral structure, first joined together by Na<sup>+</sup> cations (Figure 7a). Then, an achiral double chain is produced by interconnecting adjacent opposite-handed chiral chains by Cu<sup>2+</sup> cations. Hydrogen bonds between one kind of bpp molecule and polyoxoanions (N3–H…O4 = 2.729 Å; C14–H…O16 = 2.985 Å; C14–H…O25 = 3.343 Å; C18–H…O20 =



**Figure 7.** (a) Polyhedral and ball–stick view of the 1D chiral chain in 4. (b) View of the 2D achiral layer constructed from achiral double chains linked by dpp ligands via hydrogen bonds. Color code: Co, yellow; Mo, purple/green; Cu, light blue; C, gray; N, dark blue; O, red; Na, orange.

3.375 Å; C23–H···O20 = 3.378 Å) link double chains together to form a 2D supramolecular layer (Figure 7b). Extensive hydrogen bonds between other kinds of bpp molecules and polyoxoanions (N1–H···O36 = 2.739 Å; C1–H···O16 = 3.121 Å; C9–H···O29 = 3.311 Å; C13–H···O28 = 3.073 Å; C19–H···O10 = 3.341 Å) make these 2D layers pack together to produce a 3D supramolecular framework (Figure S12). Free water molecules take part in extensive hydrogen-bonding interactions with the polyoxoanions, by which the small voids of the structure are filled.

As confirmed by BVS calculations, the oxidation states of the Mo, Co, Cu, and Na atoms are respectively 6+, 3+, 2+, and 1+.<sup>53</sup>

**FTIR Spectroscopy.** Parts a–d of Figure S13 display the IR spectra of compounds 1–4. The characteristic peaks of the Evans–Showell-type POM  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  can be clearly observed, similar to those in the literature. <sup>19,20,48</sup> The N–H and O–H stretching vibrations are located in the 3600–2800 cm<sup>-1</sup> range; the N–H and O–H bending vibrations are located in the 1650–1000 cm<sup>-1</sup> range; the Mo–Ot stretching vibrations are observed in the 1000–830 cm<sup>-1</sup> range; the Mo–Ob–Mo/Co stretching vibrations are observed at 750–500 cm<sup>-1</sup>. The Mo–Oc stretching vibrations mixed with the bending vibrations of the Mo–Ob and Mo–Ot bonds are found below 500 cm<sup>-1</sup>.

**TGA.** Figure S14a displays the TGA plot of 1, which provides a total weight loss of 39.4% from 40 to 750 °C by multistep continuous-weight-loss processes, corresponding to the calculated value (39.2%). The 9.1% weight loss at 45-140 °C comes from losing partial crystal water molecules (calcd 14.2%). The 6.1% weight loss at 140-290 °C is caused by losing the residual crystal and coordinated water molecules.



**Figure 8.** (a) Temperature dependence of the product  $\chi_M T$  (hollow square) and reciprocal magnetic susceptibility  $\chi_M^{-1}$  (solid square) for compound **1**. (b) Temperature dependence of the product  $\chi_M T$  (hollow squares) and reciprocal magnetic susceptibility  $\chi_M^{-1}$  (solid squares) for compound **2**. (c) Temperature dependence of the product  $\chi_M T$  (hollow squares) and reciprocal magnetic susceptibility  $\chi_M^{-1}$  (solid squares) for compound **3**. (d) Temperature dependence of the product  $\chi_M T$  (hollow squares) and reciprocal magnetic susceptibility  $\chi_M^{-1}$  (solid squares) for compound **3**. (d) Temperature dependence of the product  $\chi_M T$  (hollow squares) and reciprocal magnetic susceptibility  $\chi_M^{-1}$  (solid squares) for compound **4**.

The 15.2% weight loss at 290–405  $^\circ$ C arises from losing the composition water, en, and some ptz molecules. The 9.0% weight loss at 405–580  $^\circ$ C is due to losing residual ptz molecules.

Figure S14b displays the TGA plot of 2, which provides a total weight loss of 39.5% from 40 to 750 °C by multistep continuous-weight-loss processes, corresponding to the calculated value (39.2%). The 5.2% weight loss at 40-170 °C comes from losing all crystal and some coordinated water molecules. The 7.0% weight loss at 170–350 °C is due to losing the residual coordinated water, composition water, and some bim molecules. The 27.3% weight loss at 350–730 °C arises from losing residual bim molecules.

The TGA plot of **3** is similar to that of **1**, which provides a total weight loss of 39.6% at 40–750 °C, corresponding to the calculated value of 38.9% (Figure S14c). The 6.4% weight loss at 40–190 °C comes from losing crystal and coordinated water molecules (calcd 6.5%). The 7.6% weight loss at 190–330 °C is due to losing the composition water, acetonitrile, and some dpdo molecules. The 25.6% weight loss at 330–720 °C arises from losing residual dpdo molecules.

The TGA plot of 4 provides a total weight loss of 24.9% at 40–750 °C by multistep continuous-weight-loss processes, corresponding to the calculated value of 24.0% (Figure S14d). The 3.8% weight loss at 40–160 °C comes from losing crystal water molecules (calcd 4.0%). The 2.9% weight loss at 210–270 °C is due to losing other water molecules (calcd 2.4%). The two-step continuous weight loss of 18.2% at 270–680 °C comes from losing bpp molecules (calcd 17.6%).

**PXRD Characterization.** To characterize the phase purities, the PXRD patterns of four compounds were measured (Figure S15). The experimental diffraction peaks of these compounds match well with the calculated patterns, indicating that they are pure phase. Compounds 1–4 have different structures by single-crystal X-ray analyses, which are confirmed by the differences of their PXRD patterns.

**UV–Vis Diffuse-Reflectance Spectroscopy.** The diffusereflectance spectra of four solid samples were measured and are displayed as absorption (*A*) versus wavelength ( $\lambda$ ) plots in Figure S16. The function  $A = \log(1/R\%)$  was used to calculate the absorption data, in which *R* represents the reflectivity. There are two intense characteristic peaks situated at 224 and 300 nm for 1, 225 and 300 nm for 2, 229 and 315 nm for 3, and 222 and 300 nm for 4 in the UV region, which are attributed to  $O \rightarrow$  Mo charge-transfer peaks for Evans–Showell-type POMs. In the visible region, there are also two absorption peaks at 443 and 608 nm for 1, 444 and 610 nm for 2, 474 and 611 nm for 3, and 445 and 607 nm for 4, which are respectively assigned to the  ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$  and  ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$  transition of low-spin Co<sup>3+</sup> with a regular octahedral configuration in the [Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>]<sup>6–</sup> anion.<sup>54</sup>

**Magnetic Properties.** Considering the magnetic  $Cu^{2+}$  center ( $Co^{3+}$  is diamagnetic), we investigate the magnetic properties of crystalline samples 1–4 by measuring their magnetic susceptibilities from 2.0 to 300.0 K at a 1 kOe magnetic field. The plots of  $\chi_M T$  and  $1/\chi_M$  versus T are shown in Figure 8a–d. In order to manifest that  $Co^{3+}$  is diamagnetic, the magnetic susceptibility plot of the raw material  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]\cdot7H_2O$  was measured from 2.0 to 300.0 K (Figure S17). The  $\chi_M T$  product at 300.0 K is 0.12 emu K mol<sup>-1</sup>, due to low-spin  $Co^{3+}$  with a diamagnetic S = 0. When the temperature is decreased,  $\chi_M T$  approaches zero and shows a linear behavior, which can be caused by paramagnetic

impurities. According to the literature,<sup>55,56</sup> the content of the impurities is under 3%. Other compounds containing octahedral Co<sup>3+</sup> have shown similar diamagnetic behavior.<sup>55,56</sup>

For 1, the  $\chi_M T$  product of 1.70 emu K mol<sup>-1</sup> at 300.0 K is close to the theoretical value of 1.125 emu K mol<sup>-1</sup> for three isolated Cu<sup>2+</sup> cations ( $S = \frac{1}{2}$  and g = 2.0). When cooling, the  $\chi_{\rm M}T$  value remains constant down to 120 K, at which it reduces further until 2.0 K, reaching a minimum of 0.80 emu K mol<sup>-1</sup>. A weak antiferromagnetic Cu-Cu coupling exists according to this plot. Other complexes containing Cu<sup>2+</sup> also exhibit similar trends.<sup>57</sup> The  $1/\chi_{\rm M}$  versus T plot is fitted by the Curie–Weiss law from 2.0 to 300.0 K. The Curie constant (C) is 1.65 emu K mol<sup>-1</sup>, and the Weiss constant ( $\theta$ ) is -2.04 K. The fitting result further proves that antiferromagnetic Cu-Cu interactions occur. For 2, the  $\chi_{\rm M}T$  value of 0.90 emu K mol<sup>-1</sup> at 300 K approximates the theoretical value of 0.75 emu K mol<sup>-1</sup> for two isolated Cu<sup>2+</sup> cations ( $S = \frac{1}{2}$  and g = 2.0). When cooling, the  $\chi_{\rm M}T$  product tardily reduces until 13.0 K and slightly increases to 10.0 K, where it decreases rapidly, reaching 0.64 emu K mol<sup>-1</sup> at 2.0 K. The  $1/\chi_{\rm M}$  versus T plot is fitted by the Curie– Weiss law from 2.0 to 300.0 K. The C value is 0.90 emu K mol<sup>-1</sup>, and the  $\theta$  value is -4.47 K. The fitting result further proves that antiferromagnetic Cu-Cu interactions occur. For 3, at 300 K, the  $\chi_{\rm M}T$  value of 2.83 emu K mol<sup>-1</sup> is higher than the theoretical value of 1.875 emu K mol<sup>-1</sup> for five isolated Cu<sup>2+</sup> cations (S = 1/2 and g = 2.0). When the temperature is decreased, the  $\chi_{\rm M}T$  product lowers gradually, reaching a minimum of 0.72 emu K mol<sup>-1</sup> at 2 K. The  $1/\chi_{\rm M}$  versus T plot is fitted by the Curie-Weiss law from 2.0 to 300.0 K. The C value is 2.91 emu K mol<sup>-1</sup>, and the  $\theta$  value is -6.98 K. The fitting result also reveals that antiferromagnetic Cu-Cu coupling occurs. For 4, at 300 K, the  $\chi_{\rm M}T$  value of 0.93 emu K mol<sup>-1</sup> is higher than the theoretical value of 0.375 emu K mol<sup>-1</sup> for one isolated Cu<sup>2+</sup> cation ( $S = \frac{1}{2}$  and g = 2.0). When the temperature is decreased, the  $\chi_{\rm M}T$  product tardily reduces until 2 K, reaching a minimum of 0.32 emu K mol<sup>-1</sup>. The  $1/\chi_{\rm M}$ versus T plot is fitted by the Curie-Weiss law from 58.0 to 300.0 K. The C value is 1.23 emu K mol<sup>-1</sup>, and the  $\theta$  value is -83.02 K. The fitting result also indicates that weak antiferromagnetic Cu-Cu coupling exists. Other POMs containing copper-organic coordination complexes also have similar trends.<sup>58</sup> It is unfortunate that suitable theoretical models have not been found to fit the experimental magnetic data of these compounds.

**Catalytic Oxidation Study.** Because sulfoxides are very important for the chiral auxiliary intermediates of biologic molecules and oxo-transfer reagents, getting sulfoxides is very desirable through the high selective oxidation of sulfides.<sup>59</sup> Herein, the performances of compounds 1-4 catalyzing the oxidation reactions of sulfides are tested in detail.

First, methyl phenyl sulfide was chosen as a model substrate to assess the catalytic abilities of four compounds (Scheme 1). In the catalytic reaction, 1.5 mol % catalyst was used with TBHP as the oxidant in acetonitrile at 40  $^{\circ}$ C for 4 h. Table 2 displays the catalytic results. These compounds efficiently

Scheme 1. Oxidation of Methyl Phenyl Sulfide to the Corresponding Sulfoxide



Compound	Substrate	Time	Conv.(%)	Sele.(%) <sup>b</sup>	reaction
compound		(h)			system
1		4	99.0	100.0	heterogeneous
2		4	98.4	95.2	heterogeneous
3		4	94.8	95.1	heterogeneous
4	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	4	96.7	96.3	heterogeneous
(NH <sub>4</sub> ) <sub>6</sub> [Co <sub>2</sub> Mo <sub>10</sub> H <sub>4</sub> O <sub>38</sub> ]		4	45.0	68.4	homogeneous
CuCl <sub>2</sub>	~	4	28.0	94.8	homogeneous
$(NH_4)_6[Co_2Mo_{10}H_4O_{38}] + CuCl_2$		4	50.3	83.2	homogeneous
_					

<sup>*a*</sup>Reaction conditions: sulfide (0.25 mmol, 1 equiv), catalyst (3.75  $\mu$ mol, 1.5 mol %), TBHP (2 equiv), acetonitrile (0.5 mL), at 40 °C, for 4 h. <sup>*b*</sup>Selectivity to sulfoxides; the byproduct was sulfone.

catalyzed the oxidation of methyl phenyl sulfide with a conversion of 94.8–99% and a selectivity of 95.1–100%. If  $H_2O_2$  was used as the oxidant instead of TBHP, compound 1 can catalyze oxidation of the methyl phenyl sulfide reaction with a conversion of 96% and a selectivity of 94% as the homogeneous catalyst within 2 h. The catalytic reaction using  $H_2O_2$  needs less time, but the selectivity is lower than that using TBHP, and compound 1 as the homogeneous catalyst is not easily recovered. Therefore, TBHP was chosen as a suitable oxidant.

It is worth noting that compound **1** shows the best catalytic effect for oxidizing methyl phenyl sulfide to only sulfoxide with a conversion of 99% under optimized conditions. Their different catalytic activities may have originated from their different structures. Compound 1 with a 3D host-guest architecture may expose more active sites than 2D covalent frames of compounds 2 and 3 and 1D chain of compound 4. Interestingly, the conversion (96.7%) and selectivity (96.3%) of compound 4 were higher than those of compound 3 (conversion 94.8%; selectivity 95.1%). After careful examination of their structures, it was found that, in compound 4, the Cu center is only coordinated to polyoxoanion and water molecules, whereas in compound 3, all Cu centers are linked by dpdo ligands, which will increase the steric hindrance of the organic substrate coordinating to the active metal center. So, the differences in the structure result in the different conversions and selectivities. The performances of these catalysts were compared with those of POM-based species in the literature such as  $\alpha$ -[Cu(mIM)<sub>4</sub>]V<sub>2</sub>O<sub>6</sub>,  $\beta$ -[Cu(mIM)<sub>4</sub>]- $V_2O_6$ ,  $[Cu(mIM)_2)](VO_3)_2)$ ,<sup>45</sup>  $PW_{11}Ni-Cd-MOM$ ,<sup>60</sup>  $[(n-C_4H_9)_4N]_4(Mo_8O_{26})$ ,<sup>61</sup> and  $\{[Yb(PDCH_2)_2(PDCH)]Na (H_2O)_2[Na(PDCH)(H_2O)_2]]_2[P_2W_{18}O_{62}]^{.62}$  It was found to be comparative to the first one (methyl phenyl sulfide; conversion 98.7%; selectivity 100%), higher than the middle three, which uses more catalyst (3.4 mol %) or longer reaction time (18 h), and lower than the latter two (homogeneous: 10 min, conversion 99%, selectivity 98%; 5 min, conversion 100%, selectivity 100%).

Subsequently, because the activity of compound 1 outperforms that of compounds 2–4, we continuously investigate the properties of compound 1 by catalyzing various organic sulfides with different electronic and steric effects transformed to the corresponding sulfoxide (Table 3). Whether introducing electron donor or acceptor groups with less steric hindrance in the monophenyl sulfides, the catalytic activity did not obviously decrease. Organic sulfides having electron-donating substituents are more easily oxidized than those having electron-withdrawing groups, similar to what the literature Table 3. Results of the Selective Oxidation of Various Sulfides Catalyzed by 1 Using TBHP as the Oxidant<sup>a</sup>

Entry	Substrates	Products	Conv.(%)	Sele. $(\%)^b$
1	SS	O S	99.0	100
2	S S S S S S S S S S S S S S S S S S S	No N	97.4	97.7
3	CI S	CI	90.0	95.4
4	O <sub>2</sub> N S	O O2N	52.5 85.6 <sup>c</sup>	100 90.2 <sup>c</sup>
5			44.3 66.3 <sup>c</sup>	98.2 94.3 <sup>c</sup>
6	∫ <sup>s</sup> ∖ )	S S S S S S S S S S S S S S S S S S S	15.4 60.5 <sup>c</sup>	100 93.4 <sup>c</sup>

<sup>*a*</sup>Reaction conditions: sulfide (0.25 mmol, 1 equiv), catalyst (3.75  $\mu$ mol, 1.5 mol %), TBHP (2 equiv), acetonitrile (0.5 mL), 40 °C, for 4 h. <sup>*b*</sup>Selectivity to sulfoxides; the byproduct was sulfone. <sup>*c*</sup>Reaction time, 8 h.

supports.<sup>63</sup> In contrast, sulfides containing large steric resistance as substrates, such as diphenyl sulfide and dibenzyl sulfide, result in the catalytic activity being acutely reduced. Furthermore, as the reaction time grows, the conversion of diphenyl sulfide and dibenzyl sulfide did not increase efficiently but sacrificed the selectivity to sulfoxide (Table 3, entries 5 and 6).

The recyclability and stability of catalysts were further studied in the catalytic process. Take compound 1 as an example. By simple filtration, the catalyst was easily recovered from the catalytic oxidation system. The filtrate had no catalytic effect on the oxidation of methyl phenyl sulfide, revealing that it is a heterogeneous catalyst. The catalytic performance remains high (conversion 95.6–99%) when the isolated catalyst is reused three times. In addition, the PXRD patterns before and after the catalytic reaction are identical (Figure S18). The IR spectrum of compound 1 after reaction also retains the characteristic peaks of the compound, indicating that the structural components are stable (Figure S19). Therefore, the above evidence shows that compound 1 is an excellent heterogeneous catalyst of the oxidation of methyl phenyl sulfide.

In addition, to probe the active site of compound 1 in the selective oxidation of methyl phenyl sulfide, we studied the activity of transition-metal salt CuCl<sub>2</sub> and the original POM precursor  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]$ . As shown in Table 2, the low conversion of methyl phenyl sulfide (28%) and excellent selectivity toward sulfoxide (94.8%) were catalyzed by CuCl<sub>2</sub>. When the original POM precursor  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]$  was used as the catalyst, the conversion reached to 45%. From the above results, we can surmise that the combination of the Cu site and  $(NH_4)_6[Co_2Mo_{10}H_4O_{38}]$  cluster can promote the heterogeneous catalyst with excellent conversion and wonderful selectivity in the catalytic oxidation of methyl phenyl sulfide. In short, the cooperation of copper and the molybdenum oxide

cluster plays some synergistic role in the oxidation process of sulfides, which can promote the catalytic effect. According to the above-mentioned results and the previous reports,<sup>64–66</sup> a possible mechanism of sulfide oxidation has been summarized in Figure S20. The product distribution of almost exclusively sulfoxide products points to an electrophilic route rather than a radical mechanism. Moreover, when TBHP was added to the methanol solution of compound 1, the interaction between compound 1 and TBHP was noticed according to the changes of the UV absorption spectrum in the peak positions (Figure S21).<sup>67</sup> Thus, the catalyst reacts with TBHP to form an active peroxomolybdenum and copper species, which leads to the electrophilic attack on the S atom of the sulfide, generating the corresponding sulfoxides.

In light of the excellent activity and selectivity of the oxidation of methyl penyl sulfide, it prompted us to explore the oxidation of other organic compounds. As we all know, benzoic acid is industrially produced and wildly applied as food preservation compounds, flavors, drugs, and fragrances.<sup>68</sup> In the meantime, the combination of copper with molybdenum catalysts has been successfully used for the oxidation of benzyl alcohol (BzOH) to benzaldehyde (PhCHO).<sup>46</sup> Therefore, compound 1 was further employed as a catalyst for the oxidation of BzOH. When O<sub>2</sub> was used as the oxidant, the catalytic effects were not so satisfactory. In contrast, the catalytic reaction of BzOH using TBHP as the oxidant led to PhCHO and PhCOOH in the presence of compound 1.

As shown in Table 4, the reaction of BzOH using TBHP as the oxidant and acetonitrile as the cosolvent, at 75 °C, produced PhCHO and PhCO<sub>2</sub>H as the main reaction products. Under optimized conditions, BzOH can be efficiently oxidized to the product PhCO<sub>2</sub>H by compound 1, with a high conversion of 98.7% and a high selectivity of 92% in a 24 h reaction. In order to explore the applicability of the procedure for oxidation of alcohol, various aromatic alcohols were explored according to the protocol. It is worth noting that introducing electron-donating or electron-withdrawing groups onto the aromatic alcohols can cause an obvious decrease of the conversion, with conversions between 40.5% and 93.5% (Table 4, entries 2-7), due to steric hindrance. These results indicated that compound 1 possesses superior catalytic performance in the conversion of BzOH to PhCO<sub>2</sub>H. Also, the catalyst can be easily recycled (Table S3).

#### CONCLUSIONS

In summary, four hybrid compounds are reported, by introducing different organic ligands to the reaction system of Evans-Showell-type POMs and Cu2+ cations, among which compound 1 is by now the only 3D host-guest structure and compounds 2 and 3 are the first 2D species built up from Evans-Showell-type POMs. All four compounds show better catalytic activities than their precursor (NH<sub>4</sub>)<sub>6</sub>[Co<sub>2</sub>Mo<sub>10</sub>H<sub>4</sub>O<sub>38</sub>] in heterogeneously catalyzing the oxidation of sulfides and alcohols. These results indicate that the combination of copper-organic coordination fragments with POM clusters may expose more active centers at the molecular level, making POM-based crystalline catalysts possess high catalytic activity. The success of preparing these compounds is certain to promote the research of developing crystalline POM-based hybrid materials for heterogeneously catalyzing the selective oxidation of sulfides and alchols.

Table 4. Results of the Selective Oxidation of Various Alcohols Catalyzed by  $1.^{a}$ 

	TBHP	RCHO	+ RCOOF	ł	
	catalyst	- Kello	1 10000		
Parton	C-1-starter	Conv.(%) at	Product sele.(%) at 8/24h		
Entry	Substrates	8/24h	PhCHO	PhCO <sub>2</sub> H	
1	CH <sub>2</sub> OH	59.7/98.7	100/0	0/92	
2	CH20H OH	42.4/93.5	100/8.3	0/76.1	
3	CH <sub>2</sub> OH	27.9/73.2	100/13.2	0/66.6	
4	CH <sub>2</sub> OH	25.6/69.7	100/23.7	0/65.3	
5	CH <sub>2</sub> OH	22.3/65.1	100/27.3	0/62.2	
6	CH <sub>2</sub> OH NO <sub>2</sub> CH <sub>2</sub> OH	21.9/61.7	100/26.8	0/56.9	
7	CH(CH <sub>2</sub> )	13.2/40.5	100/20.7	0/78.9	
8	СН_СН3/2	10.1/25.2	100/18.9	0/80.2	

<sup>a</sup>Reaction conditions: alcohol (0.25 mmol, 1 equiv), catalyst (3.75  $\mu$ mol, 1.5 mol %), TBHP (3 equiv), acetonitrile (1 mL), 75 °C, for 8 and 24 h.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01564.

Structures of four organic ligands, two enantiomers of the  $[Co_2Mo_{10}H_4O_{38}]^{6-}$  anion, ORTEP drawings for 1– 4, 3D space-filling diagram of the host framework in 1, 2D topology in 2 and 3, 3D supramolecular framework in 4, IR spectra, TGA plots, PXRD patterns, and UV–vis diffuse-reflectance spectra for 1–4, catalytic mechanism, selected bond lengths and angles for 1–4 (Table S1), and reutilization data for the oxidation of methyl phenyl sulfide (Table S2) and BzOH (Table S3) with 1 as the catalyst (PDF)

#### Accession Codes

CCDC 1555698–1555701 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

### ACKNOWLEDGMENTS

The National Natural Science Foundation of China (Grants 20901013, 21274015, and 21371027), Fundamental Research Funds for the Central Universities (Grants DUT15LN18 and DUT15LK02), and Natural Science Foundation of Liaoning Province (Grant 2015020232) provided financial support for this work.

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