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# Carboxylate-Functionalized Phosphomolybdates: Ligand-Directed Conformations

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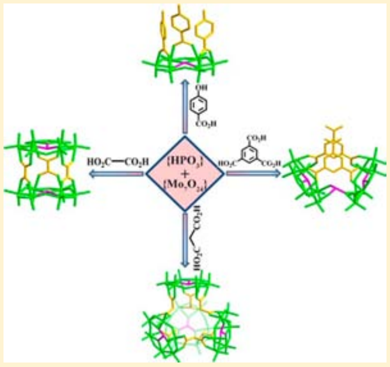
Ⓢ *Supporting Information*

**ABSTRACT:** The $[HPMo_6O_{21}]^{2-}$ units and carboxylate linkers can be combined to build novel polyanions by a carefully designed complementary system in self-assembly processes depending only on the number of carboxyl groups and the nature of carboxylic acids. Complexes $(NH_4)_5[HPMo_6O_{21}(O_2CC_6H_4OH)_3]\cdot 4H_2O$ (**1**), $(NH_4)_8H_2[(HPMo_6O_{21})_2(C_2O_4)_3]\cdot 13H_2O$ (**2**), $(NH_4)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]\cdot 17H_2O$ (**3**), and $Cs_2(NH_4)_{10}[(HPMo_6O_{21})_2(HPO_3)\{C_6H_3(CO_2)_3\}_2]\cdot 5H_2O$ (**4**) have been synthesized by a simple one-pot reaction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $H_3PO_3$, and carboxylic acid ligands in aqueous solution. Formation of these compounds is critically dependent on the identifying carboxylic acids, which play the important templated role in assembly processes. The stability of these clusters was explored using electrospray ionization mass spectrometry (ESI-MS) and $^{31}P$ NMR spectroscopy, and electron paramagnetic resonance (EPR) experiments further demonstrated the result of the interesting photochromic property.



## INTRODUCTION

Polyoxometalates (POMs), especially incorporated with organic groups, are of great interest because of their remarkable structural varieties and attractive properties, which can be used in catalysis, medicine, and materials science.[1] Preparation of POM-based inorganic−organic hybrids, therefore, has gained increasing attention; in particular, covalent binding of organic groups onto POM clusters has afforded a huge class of materials.[2] Over the past two decades, a number of carboxyl-functionalized polyoxomolybdates have been synthesized and characterized. Most derivatives are based on isopolymolybdate anions, such as $\{Mo_8O_{28}\}^{4-}$,[3] $\{Mo_2O_4\}^{2+}$,[4] $\{Mo_{2n}O_{2n}S_{2n}(OH)\}_{2n}$,[5] and other isopolymolybdate anions bridged by carboxylate ligands.[6] Despite Kortz and co-workers having reported a series of amino acids functionalized heteropolymolybdates, $[XMo_6O_{21}(O_2CRNH_3)_3]^{n-}$ ($n$ = 2, X = $Se^{IV}$, $Te^{IV}$, POH, $PCH_3$, $PC_2H_5$, PH; $n$ = 3, X = $As^{III}$, $Sb^{III}$, $Bi^{III}$; R = $CH_2$, $C_2H_4$, $C_3H_6$, $CHCH_3$, $CH(CH_2)_4NH_2$),[7] multicarboxylic acids functionalized heteropolymolybdates are still largely unexplored.

Encouraged by the diversity of coordination modes and the high structural direction of carboxylic acids, we continued the research and decided to explore the interaction of carboxylic acids with heteropolymolybdates. (i) As we know, carboxylic acid is a good oxygen-containing organic ligand, which can directly link to the metallic center by substituting the oxo group of the POM. (ii) The nature of carboxylic acids has a profound effect on constructing POM-based architectures,[8] and compared with amino acid, multicarboxylic acid can connect two or more polyanions to generate diverse structures. (iii) Phosphate is generally used to create heteropolyanions; however, heteropolyanions templated by phosphite are rarely explored. Rational design (target-oriented synthesis) of structures and functionalities of these hybrids requires fine tuning of both organic molecules and inorganic clusters. In this context, we chose the system of POMs with monocarboxylic, bicarboxylic, or tricarboxylic acids in constructing novel polyanions with different shapes and sizes since the number of carboxyl groups may be stereochemically oriented and conformationally ordered in the assemblies.

In this paper, we report full details of the synthesis of these four complexes and their molecular structures. The four phosphorus-containing derivatives, $(NH_4)_5[HPMo_6O_{21}(O_2CC_6H_4OH)_3]\cdot 4H_2O$ (**1**), $(NH_4)_8H_2[(HPMo_6O_{21})_2(C_2O_4)_3]\cdot 13H_2O$ (**2**), $(NH_4)_{20}[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]\cdot 17H_2O$ (**3**), and $Cs_2(NH_4)_{10}[(HPMo_6O_{21})_2(HPO_3)\{C_6H_3(CO_2)_3\}_2]\cdot 5H_2O$ (**4**), confirm our hypothesis that different carboxylate ligands with different number of carboxyl groups can generate $\{Mo_6O_{21}\}$-based monomer, dimer, and tetramer frameworks (Figure S1, Supporting Information). Their formation conditions differ widely by the number of carboxyl groups and the nature of carboxylic acids (Figure S2, Supporting Information):

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Table 1. Crystallographic Data for **1**−**4**

| | **1** | **2** | **3** | **4** |
|---|---|---|---|---|
| formula | $C_{21}H_{44}Mo_6N_5O_{34}P$ | $C_6H_{62}Mo_{12}N_8O_{67}P_2$ | $C_{18}H_{130}Mo_{24}N_{20}O_{125}P_4$ | $C_{18}H_{59}Cs_2Mo_{12}N_{10}O_{62}P_3$ |
| $M_r$ (g mol$^{-1}$) | 1517.22 | 2531.84 | 5053.84 | 2917.76 |
| space group | $P-1$ | $P-1$ | $P2(1)/n$ | $P-1$ |
| cryst syst | triclinic | triclinic | monoclinic | triclinic |
| $a$ (Å) | 12.473(2) | 11.8644(8) | 16.5531(19) | 14.360(2) |
| $b$ (Å) | 14.023(2) | 13.9090(9) | 30.271(3) | 15.222(3) |
| $c$ (Å) | 16.024(2) | 22.4975(15) | 30.990(4) | 24.149(5) |
| $\alpha$ (deg) | 93.372(3) | 96.1060(10) | 90 | 71.831(6) |
| $\beta$ (deg) | 105.949(3) | 98.6960(10) | 94.132(3) | 77.438(7) |
| $\gamma$ (deg) | 91.991(3) | 100.2300(10) | 90 | 69.986(9) |
| $V$ (Å$^3$) | 2686.5(7) | 3577.5(4) | 15488(3) | 4676.0(15) |
| $Z$ | 2 | 2 | 4 | 2 |
| cryst size (mm$^3$) | 0.42 × 0.24 × 0.12 | 0.49 × 0.21 × 0.19 | 0.44 × 0.36 × 0.22 | 0.41 × 0.28 × 0.16 |
| $D_{calcd}$ (g cm$^{-3}$) | 1.876 | 2.348 | 2.167 | 2.072 |
| $\mu$ (mm$^{-1}$) | 1.480 | 2.195 | 2.024 | 2.466 |
| $R_{int}$ | 0.0285 | 0.0135 | 0.0935 | 0.0189 |
| limiting indices | $-14 \le h \le 14$ | $-14 \le h \le 14$ | $-19 \le h \le 18$ | $-16\le h \le 17$ |
| | $-16\le k \le 16$ | $-16 \le k \le 16$ | $-36 \le k \le 34$ | $-11 \le k \le 18$ |
| | $-14 \le l \le 19$ | $-22 \le l \le 26$ | $-34 \le l \le 36$ | $-28 \le l \le 28$ |
| no. of reflns collected | 13552 | 18260 | 77492 | 23827 |
| no. of independent reflns | 9360 | 12456 | 27181 | 16240 |
| no. of params | 653 | 907 | 1837 | 1093 |
| GOF on $F^2$ | 1.018 | 1.045 | 1.070 | 1.074 |
| $R_{1,}$ $wR_2$ [$I > 2\sigma(I)$] | 0.0626 0.1799 | 0.0369 0.1075 | 0.1116 0.2662 | 0.0542 0.1676 |
| $R_{1,}$ $wR_2$ [all data] | 0.0878 0.1958 | 0.0499 0.1141 | 0.1635 0.2832 | 0.0706 0.1802 |

*p*-hydroxybenzoic acid ($HO_2CC_6H_4OH$), oxalic acid ($H_2C_2O_4$), malonic acid ($HO_2CCH_2CO_2H$), and 1,3,5-benzenetricarboxylic acid ($C_6H_3(CO_2H)_3$).

## EXPERIMENTAL SECTION

**Materials and Physical Measurements.** All chemical reagents were purchased from commercial sources and used without further purification. IR spectra were recorded on a Bruker VERTEX 70 IR spectrometer using KBr pellets in the range of 4000−400 cm$^{-1}$. C, H, and N elemental analyses were performed on a Perkin-Elmer 2400-II CHNS/O analyzer. Mass spectra measurements were made in the negative-ion mode on an Agilent 6520 Q-TOF LC/MS mass spectrometer coupled to an Agilent 1200 LC system. EPR experiment of compound **2** was performed on a Bruker ER-2000-DSRC10 spectrometer at the X-band at 300 K. $^{31}$P NMR spectra were recorded in 5 mm tubes with $^1$H decoupling using a Bruker AC-300 spectrometer operating at 121.5 MHz. $^{31}$P chemical shifts were referenced to the external standard of 85% $H_3PO_4$. For all compounds, ~20 mg of sample was dissolved in $D_2O$ (700 μL).

*Synthesis of* ***1***. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.06 g, 0.86 mmol) and $H_3PO_3$ (0.08 g, 0.98 mmol) were dissolved in water (15 mL), and *p*-hydroxybenzoic acid (0.41g, 3.00 mmol) was added. The solution was stirred approximately 2 h at 70 °C to result in a pale yellow solution. After cooling to room temperature, the pH of the resultant solution was 4.4. The solution was filtered, and the filtrate was left in an open beaker at room temperature. Pale yellow block crystals of **1** were obtained by slow evaporation at room temperature after about 1 month. Yield: 0.36 g (24%) for **1** based on $H_3PO_3$. Anal. Calcd for $C_{21}H_{44}Mo_6N_5O_{34}P$ (**1**): C, 16.62; H, 2.92; N, 4.62. Found: C, 16.38; H, 3.62; N, 4.24. IR (KBr pellet): 3435(s), 3177(s), 2426(w),1602(s), 1538(s), 1410(s), 1271(m), 1241(m), 1174(m), 1070(s), 1009(w), 928(s), 894(s), 786(m), 677(s), 629(s), 598 (m) cm$^{-1}$.

*Synthesis of* ***2***. Same procedure as for **1** using 0.19 g (1.51 mmol) of oxalic acid instead of *p*-hydroxybenzoic acid. The pH of the resultant colorless solution was 3.6. Yield: 0.35 g (28%) for **2** based on $H_3PO_3$. Anal. Calcd for $C_6H_{62}Mo_{12}N_8O_{67}P_2$ (**2**): C, 2.85; H, 2.47; N, 4.43. Found: C, 2.65; H, 2.73; N, 4.61. IR (KBr pellet): 3479(s), 3139(s), 2402(w), 1635(s), 1401(s), 1332(s), 1084(s), 1006(w), 932(s), 902(s), 780(s), 677(s), 569(m), 540(m), 442 cm$^{-1}$ (w).

*Synthesis of* ***3***. Same procedure as for **1** using 0.16 g (1.54 mmol) of malonic acid instead of *p*-hydroxybenzoic acid. The pH of the resultant colorless solution was 3.5. Yield: 0.76g (61%) for **3** based on $H_3PO_3$. Anal. Calcd for $C_{18}H_{130}Mo_{24}N_{20}O_{125}P_4$ (**3**): C, 4.28; H, 2.59;, N, 5.54. Found: C, 4.35; H, 3.14; N, 5.17. IR (KBr pellet): 3450(s), 3164(s), 1591(s), 1403(s), 1356(s), 1073(s), 996(w), 932(s), 897(s), 787(m), 677(s), 569(m), 538 cm$^{-1}$ (m).

*Synthesis of* ***4***. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (1.06 g, 0.86 mmol), $H_3PO_3$ (0.08 g, 0.98 mmol), 1,3,5-benzenetricarboxylic acid (0.21 g, 1.00 mmol), and CsCl (0.17 g, 1.01 mmol) were added in water (30 mL); then the white suspension was refluxed for 1 h. After cooling to room temperature, the resulting mixture was filtered and the filtrate left in an open beaker at room temperature. The pH of the resultant colorless solution was 3.9. Colorless block crystals of **4** were obtained by slow evaporation at room temperature after about 1 month. Yield: 0.32 g (34%) for **4** based on $H_3PO_3$. Anal. Calcd for $C_{18}H_{59}Cs_2Mo_{12}N_{10}O_{62}P_3$ (**4**): C, 7.41; H, 2.04; N, 4.80. Found: C, 7.07; H, 2.65; N, 4.19. IR (KBr pellet): 3460(s), 3156(s), 2368(w), 1716(w), 1615(s), 1561(s), 1440(s), 1400(s), 1275(w), 1120(m), 1075(s), 1000(w), 928(s), 896(s), 757(m), 723(s), 674(s), 598 cm$^{-1}$ (m).

*X-ray Crystallography.* Crystallographic and experimental details of crystal structure determinations are given in Table 1. Intensity data were collected at 293 or 296 K on a Bruker APEX-II CCD diffractometer for **1**−**4** using graphite-monochromated Mo Kα radiation ($\lambda$ = 0.71073 Å). Routine Lorentz and polarization corrections were applied, and an absorption correction was performed using the SADABS program. Direct methods were used to solve the structure and refined by full-matrix least-squares on $F^2$ using the SHELXTL-97 program package. Non-hydrogen atoms were refined anisotropically. Moreover, $NH_4^+$ and lattice $H_2O$ could not be distinguished based on electron densities, and we thus determine the lattice water molecules and $NH_4^+$ ions by elemental analysis. CCDC reference numbers 922413−922416 are for **1**−**4**, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_ request/cif.

## ■ RESULTS AND DISCUSSION

**Syntheses.** Compared with the noncovalent POM-based hybrids, the hybrids in which the POMs and the organic groups are linked through covalent interactions have been far less explored. Covalent combination of POMs with organic groups is an attractive technology to improve the directionality and synergetic effect between the inorganic and the organic components. Though a large variety of carboxyl-functionalized polyoxomolybdates have been reported, linking of heteropolymolybdates with multicarboxylic acids has remained largely undeveloped. Additionally, it is difficult to design or predict relevant geometric relationships between the POM clusters and the carboxylic acid ligands. Herein, we report a strategy of constructing four carboxylate-functionalized phosphomolybdates using ligand control. Actually, these simple chemical systems allow planning the rational and deliberate design and synthesis of covalent POM-based hybrids, because formation of these POM species can be drastically altered by different carboxylic acids. The four precursors exhibit the same {P}/{Mo}/{COO} stoichiometry and differ in their composition only by the carboxylic acids. Parallel experiments show that several factors affect formation of **1**−**4**. (1) The reaction stoichiometry reflects the composition of the final products in the synthetic procedure. The molar ratio of Mo/P plays an important role in the syntheses of **1**−**4**, and the best yield is achieved at a 6:1 ratio, while the product is $[(HP)_2Mo_5O_{21}]^{4-}$ when the molar ratio is 5:2 or more higher. Moreover, the molar ratio of Mo/{COO} can influence the composition and yield of the product. It would be possible for higher solubility ligands to harvest good productivity. The solubility of 1,3,5-benzenetricarboxylic acid is quite low, which reduces the opportunity of the reaction among different reactants; probably because of this, compound **4** has not formed a larger structure. (2) The reaction temperature affects formation of **1**−**4**, as **1**−**3** could be obtained in the range of 70−100 °C. 1,3,5-Benzenetricarboxylic acid is dissolved incompletely at 70 °C, but it is dissolved completely after refluxing. However, also a lot of 1,3,5-benzenetricarboxylic acid is precipitated when the reaction temperature cools to room temperature. (3) The reaction time varies from 2 to 1 h with the rise of the reaction temperature for **1**−**3**. In addition, the resultant solution **1** shows that adopting stirring and cooling it is easy to create a white precipitate, while it creates the pellucid solution without stirring.

**Structure of the Anions.** X-ray crystal structure analyses reveal that **1**−**4** contain the $\{PMo_6\}$ unit (Figure 1), which is composed of a central heteroatom P surrounded by a ring of six $MoO_6$ octahedra sharing edges and corners alternately. Each carboxyl group of carboxylate ligands is bound to two edge-sharing Mo centers on the same side of the ring, being similar with previous reports.[7] In all polyanions, the central P atom is located slightly above the plane of six Mo atoms and coordinates to three $\mu_3$-oxo groups. Additionally, X-ray photoelectron spectroscopy (XPS) analyses demonstrate that the P is trivalent (Figure S3, Supporting Information). Some closely related hexamolybdates with phosphorus $[(O_3PCH_2PO_3)Mo_6O_{18}(H_2O)_4]^{4-}$, $[(O_3POPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$, and $\{Na[Mo^{V}_6O_{12}(OH)_3(O_3PC_6H_5)_4]_2\}^{9-}$ have been stabilized by water molecules and phosphonates.[9] Indirectly, it may be inferred that the six terminal oxygen atoms on one side of the $\{Mo_6\}$ unit are potential reactive sites; therefore, the $\{Mo_6\}$ ring could be easily coordinated to oxygen-containing ligands. In this case, it seems reasonable to suppose that these carboxylic acids direct the self-assembly process toward formation of POM clusters construction and participate directly to their stabilization.

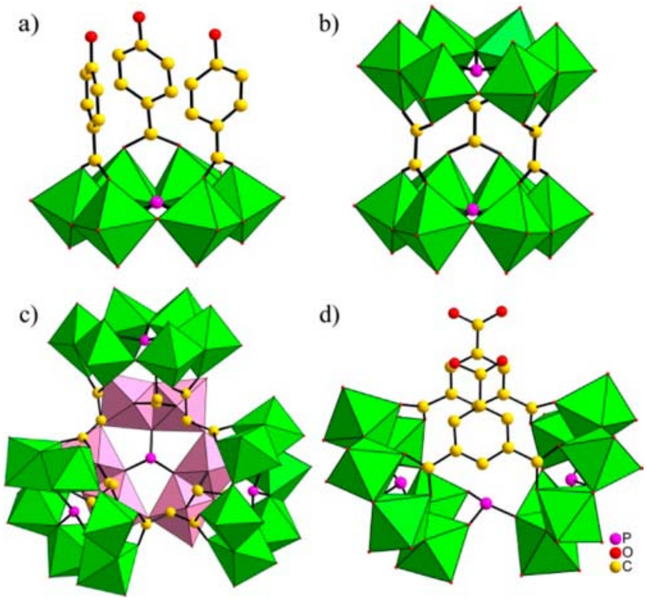

**Figure 1.** Ball-and-stick/polyhedral representation of compounds **1** (a), **2** (b), **3** (c), and **4** (d) ($MoO_6$ octahedra, green and pink) $NH_4^+$, $H_2O$, and hydrogen atoms are omitted for clarity.

In polyanion $[HPMo_6O_{21}(O_2CC_6H_4OH)_3]^{5-}$ (**1a**), three *p*-hydroxybenzoate ligands are each coordinated to two edge-sharing Mo centers belonging to the $\{HPMo_6O_{21}\}$ subunit (Figure 1a), analogous to the derivatives of amino acids.[7,10] In an attempt to find more interesting carboxylate-functionalized heteropolyanions, we envisioned whether a dimer could be isolated if dicarboxylate ligand was used in the system. As expected, when oxalate is exploited in the preparation, a dimer polyanion $[(HPMo_6O_{21})_2(C_2O_4)_3]^{10-}$ (**2a**) is obtained. X-ray crystal structure analysis of **2** reveals that two $[HPMo_6O_{21}]^{2-}$ units connect each other through three oxalate linkers (Figure 1b), which act as parallel pillars within the scaffold structure. Both $[HPMo_6O_{21}]^{2-}$ clusters appear nearly superimposed, properly described with the idealized $D_{3h}$ symmetry.

To further study the effect of the nature of carboxylic acids, we explored using flexible ligands assembly of compound **3**. Simple extension of carboxylic acid affects formation of the structural framework. It is very interesting to note that the use of malonic acid affords a novel hybrid cage **3** (Figure 2). As shown in Figure 1c, four $[HPMo_6O_{21}]^{2-}$ units are joined together by six V-type dicarboxylate ligands to form the asymmetric unit of polyanion $[(HPMo_6O_{21})_4(O_2CCH_2CO_2)_6]^{20-}$ (**3a**) with an inner cavity diameter of approximately 5.8 Å. Likewise, six malonate ligands all coordinate to one side of four $[HPMo_6O_{21}]^{2-}$ clusters. Finally, use of tricarboxylic acid also affords dimer **4**, greatly differing from **2a**; one $[HPO_3]^{2-}$ unit and two 1,3,5-benzenetricarboxylate linkers connect two $[HPMo_6O_{21}]^{2-}$ units forming the polyanion $[(HPMo_6O_{21})_2(HPO_3)\{C_6H_3(CO_2)_3\}_2]^{12-}$ (**4a**) (Figure 1d). In **4a**, the right $\{Mo_6\}$ cluster is different from what is known as here a group of $Mo_2O_9$ is formed by two face-sharing $MoO_6$ octahedra (Figure S4, Supporting Information). To the best of our knowledge, the face-sharing octahedron of $MoO_6$ is rare; only a few examples have been reported, such as tetranuclear

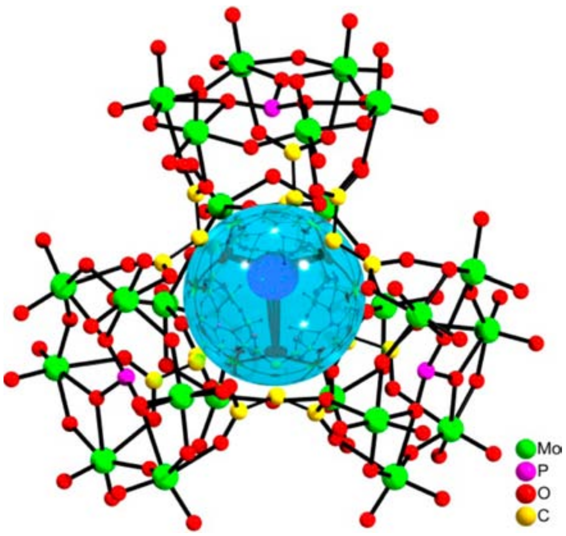

**Figure 2.** Structure of the molecular cage in **3**. Hydrogen atoms are omitted for clarity.

polyoxoanion $[(H_2CO_2)Mo_4O_{12}(OH)]^{3-}$, hexanuclear polyoxoanion $[(PhAs)_2Mo_6O_{24}(H_2O)]^{4-}$, and cage-like structure $[AgAs_2Mo_{15}O_{54}]^{11-}$.[11−13]

**Vibrational Spectra.** IR spectra of **1**−**4** (Figure S5, Supporting Information) show similar features for the skeletal vibrations in the region between 450 and 1650 cm$^{-1}$, indicating that polyanions **1**−**4** almost have the same basic framework, which are in good agreement with the results of single-crystal X-ray structural analyses. The terminal Mo−O$_t$ vibrations are seen as strong bands at 928 and 894 cm$^{-1}$ for **1**, 932 and 902 cm$^{-1}$ for **2**, 932 and 897 cm$^{-1}$ for **3**, and 928 and 896 cm$^{-1}$ for **4**. The Mo−O bridges vibrations are seen at 786, 677, and 629 cm$^{-1}$ for **1**, 780 and 677 cm$^{-1}$ for **2**, 787 and 677 cm$^{-1}$ for **3** and 757, 723, and 674 cm$^{-1}$ for **4**. The P−O vibration bands in **1**−**3** appear at 1070, 1084, and 1073 cm$^{-1}$. The spectrum of **4** exhibits bands at 1075 and 1023 cm$^{-1}$ which are assigned to different environment phosphorus. The $\nu_{as}$(COO) vibrations of **1**−**4** all shift to low frequency in comparison with uncoordinated acid (1700−1740 cm$^{-1}$) as a result of the carboxylate interaction with metal ion.[4d] Assignment of the characteristic bands is given in Table S1, Supporting Information.

**$^{31}$P NMR and ESI-MS Analyses.** $^{31}$P NMR spectroscopy and ESI-MS are powerful ways to determine whether the structural frameworks are maintained in solution and further infer the nature of compounds present in solution. The nondecoupled $^{31}$P NMR spectra in $D_2O$ of **1**−**4** (Figure 3) present a pair of singlets at 8.98 and 13.20 ppm ($^1J_{PH}$ = 683.2 Hz), 6.12 and 10.20 ppm ($^1J_{PH}$ = 660.6 Hz), 8.32 and 12.54 ppm ($^1J_{PH}$ = 683.2 Hz), and 8.99 and 13.21 ppm ($^1J_{PH}$ = 683.2 Hz) for **1**, **2**, **3**, and **4**, respectively, due to $^1$H coupling. Decoupled $^{31}$P NMR spectra of **1**−**4** (Figure S6, Supporting Information) show the expected signal due to $^1$H coupling. Chemical shifts of **1**, **3**, and **4** are very similar, but in comparison, **2** is obviously different. The $^{31}$P NMR spectrum of **2** indicates the presence of anion $[HPMo_6O_{21}]^{2-}$, whereas it degrades rapidly into intermediate species in **1**, **3**, and **4**; meanwhile, the increase of chemical shifts probably is due to the decreasing electron density around the P atom. Moreover, no free phosphite signal can be observed (Figure S7, Supporting Information). Solutions of **1**−**4** remain unchanged over a period of at least 1 day (Figure S8, Supporting Information). It is worth noting that $^{31}$P NMR spectra of freshly prepared synthetic solutions of **1**−**4** (Figure S9, Supporting Information) are similar to those of crystals in $D_2O$. In this sense, the influence of pH value on the formation and stability of polyanions has also been detected by changing the pH of freshly prepared synthetic solutions. As shown in Figure 4, the pH stable ranges of synthetic solution of the unit $[HPMo_6O_{21}]^{2-}$ are about 1.0−6.5. When the pH value gradually decreases near 1.0, there is a light yellow precipitate generated after about 30 min, and when the pH value increases above 6.5, the polyanion $[HPMo_6O_{21}]^{2-}$ is gradually decomposed and then decomposed into free phosphite at pH = 7.6 (Figure S10, Supporting Information).

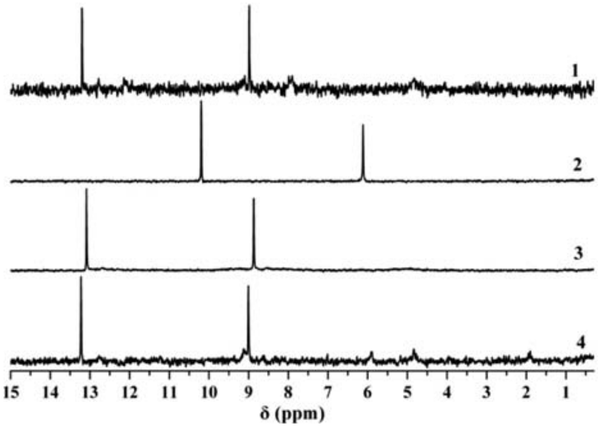

**Figure 3.** $^{31}$P NMR spectra of **1**−**4** dissolved in $D_2O$.

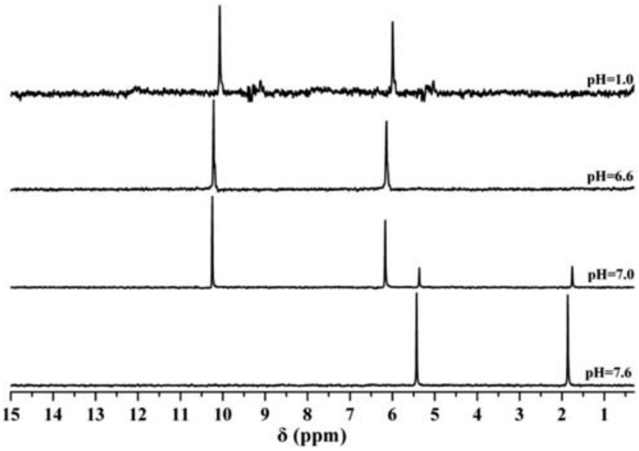

**Figure 4.** $^{31}$P NMR spectra of freshly prepared solution of **2** in different pH values.

The results of ESI-MS also demonstrate the above views. The mass spectrum of **2** in deionized water shows that clusters $[HPMo_6O_{21}]^{2-}$ and $[HMo_4O_{13}]^{-}$ are present in solution (Figure S11, Supporting Information), while the mass spectra of **3** and **4** are very similar: no peak corresponding to the cluster $[HPMo_6O_{21}]^{2-}$ is observed and each peak has the same charge, respectively (Figures S12 and S13, Supporting Information). From the findings we assume that **1**−**4** are decomposed in solution, and several kinds of fragments could be observed in the ESI process, which may infer the possible mechanism of self-assembly of polyoxometalate clusters in solution.

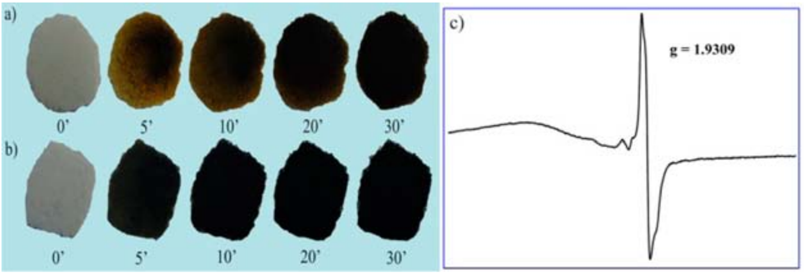

**Figure 5.** Color variations of **1** (a) and **2** (b) after 0, 5, 10, 20, and 30 min irradiation. (c) EPR spectrum of compound **2**.

**Photochemistry of Polymolybdate.** From a structural point of view, organopolymolybdates are also photochromic materials.[6e,14] All of the powder materials of **1**−**4** show a white coloration in their ground state. It is found that irradiation of powders **1** and **2** induced obvious photochromism by a xenon lamp (300 W) at room temperature for 15 min but not for **3** and **4**. Meanwhile, compound **2** has been stained to a gray color by exposure in the sun for more than 4 h, which may indicate the low energy triggering the photochromic reaction. Under irradiation of the xenon lamp, materials **1** and **2** show strong photochromic responses with high coloration contrasts, the color of **1** and **2** gradually shifts from white to dark blue (almost black) with irradiation time, and photoinduced color varies with the nature of POMs. The photoinduced color does not evolve after approximately 30 min for **1** and 10 min for **2**, as illustrated in Figure 5a and 5b. When irradiation was taken off, only a slight color change could be observed in the darkness for about 1 week.

To date, the photochromism mechanism of such hybrid materials is commonly explained in terms of Yamase's model.[15] Here, photoexcitation of **1** transfers an electron from the Ot atom of the POM block to the adjacent $Mo^{6+}$ site and trapped by a metastable $Mo^{5+}$ ion. Formally, a bridged O atom at the photoreduced site gains a labile proton of the hydrogen-bonded hydroxyl group of the *p*-hydroxybenzoic acid molecule; then the photogenerated hole at the O 2p block interacts with the nonbonding hydroxyl O atom with formation of a "charge-transfer complex".[3d] Because only $NH_4^+$ containing molybdate salts are reported to be not UV sensitive[14b,15] ($(NH_4)_6[Mo_7O_{24}]\cdot 4H_2O$ is not photochromic at all under excitation of the xenon lamp), suggesting that electron transfer may occur between the organic ligands and the heteropolyanions.[16] The result can be illustrated by means of EPR analysis. Irradiated compound **2** exhibits a significant paramagnetic signal, attributing to $Mo^{5+}$ with $g = 1.93$[17](Figure 5c), and the coloration is due to photoreduction of $Mo^{6+}$ ($4d^0$) to $Mo^{5+}$ ($4d^1$). A further systematic study of the photochromic mechanism for these materials is in progress.

## ■ CONCLUSION

In summary, we reported the synthesis of inorganic−organic POM-based hybrids in which the carboxylic acids are covalently connected to the inorganic POM framework. Formation of these hybrids has made it possible to plan the rational and deliberate design in the synthesis of covalently functionalized hybrid POM clusters and predict the relevant geometric relationships between the carboxylic acid ligands and the POM architectures. The coordinated carboxylate linkers play an important templated role in formation of the polyanions. Moreover, the structural type of functionalized phosphomolybdates could be controlled by selecting appropriate carboxylic acid ligands. Compounds **1** and **2** exhibit photochromic properties and may be applied in the field of photosensitive materials.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

Details on equipment used for complexes **1**−**4**, and Figures S1−S15. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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