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New Approach to the Synthesis of an Organopolymolybdate Polymer in Aqueous Media by Linkage of Multicarboxylic Ligands

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The reaction of molybdates with multicarboxylic ligands resulted in the crystalline materials of $[Na_8(Mo^{VI}_{10}O_{32}EDTA)(H_2O)_{35}]_n$ (**1**) and $(NH_4)_{8n}[Mo^{VI}_{10}O_{32}PDTA]_n(H_2O)_{30n}$ (**2**) (EDTA = 1,2-diaminoethanetetraacetate; PDTA = 1,3-diaminopropanetetraacetate). In the two compounds, decamolybdate clusters are covalently linked by multicarboxylic ligands to form unusual meso-helical chains. For the first time, the synthesis of an organopolyoxometalate polymer is realized in aqueous media, which opens a green chemical approach to the fabrication of polyoxometalate-based polymers. The photochromic properties of **1** in the poly(vinyl alcohol) film displayed reddish-brown coloration upon UV irradiation, providing a new coloration material for photochromic films.

Introduction

Polyoxometalates (POMs) are a well-known class of metal–oxygen clusters with a large variety of compositions and structures.[1–3] Thus, the rational design and synthesis of multifunctional hybrid materials by using covalently linked POM building blocks and organic molecules have drawn considerable attention in the past decade.[4–9] So far, the most effective approach to the functionalization of POMs is the modification of Lindqvist-type POMs by organoimido ligands.[10–23] However, the reactions strongly depend on an unhydrous organic solvent and usually result in a mixture of multiple-functionalized products.[18] Also, the products are only dissolved in an organic solvent, which limits the application of such materials in an aqueous phase. It is well-known that POM anions are water-soluble inorganic building blocks, so the functionalization of POMs should also be feasible in aqueous media. In fact, driven by the development of green chemistry, there have been increasing efforts toward exploring organic reactions in water to minimize the use of

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toxic or carcinogenic organic solvents.[24–27] The functionalization of POMs in water is a environmentally benign approach to the synthesis of hybrid materials. This motivation lies not only in the synthesis of hydrophilic organopolyoxometalate in an ecofriendly way but also in the exploration of possible electronic and optical properties.[28–30] Particularly, organopolyoxometalates are potential electro- or photochromic materials.[31–35]

To realize the functionalization of POMs in aqueous media, the organic linkers should be water-soluble and possess strong coordinating ability. By a survey of organomolybdate compounds, we find in some 0D complexes that multicarboxylic groups can coordinate to Mo atoms,[36–40] suggesting a possibility for the functionalization of polymolybdates by multicarboxylic ligands. In addition, multicarboxylic groups acting as water-soluble multidentate ligands are effective linkers to induce various coordination polymers.[41–44] By these considerations, we try to synthesize organopolymolybdate polymers with covalently linked multicarboxylic ligands in aqueous media. Using 1,2-diaminoethanetetraacetate (EDTA) or 1,3-diaminopropanetetraacetate (PDTA) as the organic group in a reaction with molybdate, two decamolybdate polymers, $[Na_8(Mo^{VI}_{10}O_{32}EDTA)(H_2O)_{35}]_n$ (**1**) and $[(NH_4)_8(Mo^{VI}_{10}O_{32}PDTA)(H_2O)_{30}]_n$(**2**), were successfully isolated. To our knowledge, it is the first time that an organopolymolybdate polymer with covalently linked multicarboxylic ligands is realized in aqueous media; this opens a new route to fabricating functionalized POM polymers by a green chemical process. Interestingly, the functionalized polyanions in the two compounds display unusual meso-helical structures. In this paper, we describe the syntheses and crystal structures of compounds **1** and **2**, and the photochromic properties of **1** in the poly(vinyl alcohol) (PVA) film were also discussed.

Experimental Section

Materials and Methods. All reagents were purchased commercially and used without further purification. Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer; Mo analyses were determined by a Leaman inductively coupled plasma spectrometer. The IR spectra were obtained on an Alpha Centaurt FTIR spectrometer in the 400–4000 cm^{-1} region with a KBr pellet. UV–vis spectra were recorded with a Hitachi UV-3010 spectrophotometer. Photochromic experiments were carried out by using a portable 28-W BD-TN100 lamp (254 nm/365 nm; Suzhou Bozhao Science Instrument Co., Suzhou, China) as light sources.

Synthesis of 1. A total of 1.0 g of $Na_2MoO_4 \cdot 2H_2O$ and 0.12 g of 1,2-diaminoethanetetraacetic acid were dissolved in 25 mL of water upon stirring. The pH of the solution was adjusted to about 3.9–4.0 by the addition of 4 M HCl. Then the solution was refluxed at 70 °C for about 2 h. After cooling to room temperature, the solution was filtered into a 50-mL beaker. Slow evaporation of the solvent at room temperature led to prism crystals of **1** suitable for X-ray diffraction about 40 days later (yield 41% based on Mo). Elem anal. Calcd (found): Na, 6.2 (6.4); Mo, 32.1 (31.8); C, 4.0 (4.2); H, 4.2 (4.5); N, 0.9 (0.8). IR (KBr): 1646, 1616, 1558, 1540, 1472, 1394, 944, 887, 836, 682, 592, 483 cm^{-1}.

Synthesis of 2. A total of 1.0 g of $(NH_4)_6Mo_7O_{24} \cdot 7H_2O$ and 0.075 g of 1,3-diaminopropanetetraacetic acid were dissolved in 25 mL of water upon stirring. The pH of the solution was adjusted to 3.7–3.8 by the addition of 4 M HCl. Then the solution was refluxed at 70 °C for about 1.5 h. After cooling to room temperature, the solution was filtered into a 50-mL beaker. Slow evaporation of the solvent at room temperature led to prism crystals of **2** about 1 month later (yield 19% based on Mo). Elem anal. Calcd (found): Mo, 43.1 (42.9); C, 5.9 (5.7); H, 2.0 (2.5); N, 6.3 (5.8). IR (KBr): 1652, 1616, 1551, 1538, 1482, 1398, 938, 884, 844, 669, 582, 480 cm^{-1}.

Fabrication of the Photochromic Solid Film. Poly(vinyl alcohol) (PVA; M_w 25 000) was dissolved in 10 mL of deionized water with a concentration of 5×10^{-3} M under vigorous stirring at 50 °C. Then a 5 mL (2.5×10^{-3} M) solution of **1** was added to the above solution. After stirring for 1 h, the composite solution was cooled to room temperature. The final transparent viscous solution was used to prepare a composite film on a glass substrate by a spin-coating process (rotation speed as 3500 rps for 50 s). The obtained film on a glass substrate was solidified under vacuum at room temperature for about 1 week.

X-ray Crystallography. Crystal data for compounds **1** and **2** were collected on aBruker Smart CCD Apex II diffractometer with Mo Kα monochromatic radiation ($\lambda = 0.710\,73$ Å) at 293 K. The structures were solved by direct methods and refined by full-matrix least squares on F^2 by using the *SHELXTL* crystallographic software package.[45,46] All non-H atoms were refined anisotropically. The positions of the H atoms on C or N atoms were calculated theoretically. The other H atoms were not identified. The ammonium

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Table 1. Crystal Structure and Refinement Data for **1** and **2**

	1	**2**
empirical formula	$Mo_{10}Na_8O_{55}N_2C_{10}H_{42}$	$Mo_{10}O_{55}N_{10}C_{11}H_{76}$
fw (g/mol)	2213.73	2188.16
temperature (K)	293(2)	293(2)
wavelength (Å)	0.710 73	0.710 73
space group	*C*2/*c*	$P\bar{1}$
a (Å)	30.317(6)	10.481(3)
b (Å)	21.295(4)	13.605(4)
c (Å)	13.384(3)	23.413(7)
α (deg)	90	73.694(4)
β (deg)	114.19(3)	79.384(4)
γ (deg)	90	74.610(4)
V (Å^3)	7882(3)	3067.7(15)
Z	2	1
D_{calcd} (g/mL)	1.890	2.223
F(000)	4260.0	1948.0
crystal size (mm^3)	0.42 × 0.34 × 0.23	0.38 × 0.35 × 0.24
θ range (deg)	3.25−27.48	1.60−27.48
data/restraints/param	8880/0/358	13691/0/737
GOF on F^2	1.052	0.984
R indices [$I > 2\sigma(I)$]		
R1	0.0556	0.0474
wR2	0.1598	0.1093
R indices (all data)		
R1	0.0705	0.1015
wR2	0.1725	0.1224
largest diff peak/hole (e/Å^3)	1.895/−1.148	1.074/−0.852

N and water O atoms in compound **2** could not be determined easily. Thus, the number of ammonium ions was set in agreement with the charge balance. Crystallographic data of **1**: monoclinic, $a = 30.317(6)$ Å, $b = 21.295(4)$ Å, $c = 13.384(3)$ Å, $\beta = 114.19(3)°$, $V = 7882(3)$ Å^3, $T = 293(2)$ K, space group *C*2/*c*, $Z = 2$, 35 937 reflections measured, 8880 unique ($R_{int} = 0.0409$), which were used in all calculations; R1 = 0.0556, wR2 = 0.1598 for $I > 2\sigma(I)$. Crystallographic data of **2**: triclinic, $a = 10.481(3)$ Å, $b = 13.605(4)$ Å, $c = 23.413(7)$ Å, $\alpha = 73.694(4)°$, $\beta = 79.384(4)°$, $\gamma = 74.610(4)°$, $V = 3067.7(15)$ Å^3, $T = 293$ K, space group $P\bar{1}$, $Z = 1$, 18 276 reflections measured, 13 691 unique ($R_{int} = 0.0535$), which were used in all calculations; R1 = 0.0474, wR2 = 0.1093 for $I > 2\sigma(I)$. CCDC-615681 (for **1**) and -615682 (for **2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. The crystal data and structure refinement for **1** and **2** are listed in Table 1.

Results and Discussion

Compound **1** was prepared by conventional methods starting from EDTA and $Na_2MoO_4 \cdot 2H_2O$, while single crystals of **2** were only obtained by using PDTA and $(NH_4)_6Mo_7O_{24} \cdot 7H_2O$. Single-crystal X-ray diffraction reveals that **1** consists of decamolybdate subunits, EDTA ligands, Na ions, and free water molecules. The structure of the decamolybdate subunit in **1** is different from the reported $[Mo^{VI}_{10}O_{34}]^{8-}$ polyanion that consists of a *γ*-octamolybdate subunit capped by two additional $\{MoO_4\}$ tetrahedra.[47,48] In contrast, the decamolybdate subunit in **1** is capped by two six-coordinated $\{MoO_5N\}$ octahedra (Figure 1). Thus, the decamolybdate subunit in **1** is a new type of decamolybdate polyanion. **1** can be also considered as an *γ*-octamolybdate linked by $[Mo^{VI}_2O_6EDTA]^{4-}$ anions. The capped Mo atom (Mo4) is coordinated by two O atoms of a carboxyl group and one N atom of an amino group. The other three coordination sites are two terminal O atoms and one bridging O atom by corner sharing with the other Mo atom (Mo3), which thus displays a severely distorted octahedron. The bond distances and angles around Mo4 are 2.122(4) Å [Mo4−O14(OOC)], 2.173(5) Å [Mo4−O9(OOC)], 1.690(5) Å [Mo4−O8(O_t)], 1.711(5) Å [Mo4−O10(O_t)], 1.812(4) Å [Mo4−O1(O_b)], and 2.373(4) Å (Mo4−N), with a little difference from those in the $Na_4[Mo^{VI}_2O_6EDTA] \cdot 8H_2O$[36] complex of 2.176 Å and 2.213 Å for Mo−O(OOC), 1.731−1.750 Å for Mo−O_t, and 2.399 Å for Mo−N. The bond lengths of 1.812(4) Å (Mo4−O1) and 1.984(4) Å (Mo4−O1) are similar to those in the $[Mo^{VI}_{10}O_{34}]^{8-}$ anion of 1.819(4) and 2.011(4) Å.[48] As for the *γ*-octamolybdate subunit in **1**, the Mo atoms are all in the distorted octahedral environments with Mo−O distances ranging from 1.697(4) to 2.430(3) Å within the reported values. Bond valence sum calculations[49] showed that the oxidation state of all of the Mo atoms is located in the range of 6.002–6.021, in agreement with the expected value of 6.00. The capped Mo atoms belonging to the same decamolybdate are strictly trans-trapped, and EDTA ligands are almost perpendicular to the chain direction to adopt stable coordination environments. The decamolybdates and EDTA connect alternately to form a 1D chain along the [1, 0, −1] direction, thus forming the first example of organopolymolybdate hybrid polymers being synthesized in aqueous media (Figure 2a). It should be noteworthy that such a polyanionic chain is not the common zigzag chain or chiral helix but shows a meso-helical feature with a figure-8-like linking style (Figure 2b). The octamolybdate subunits are located along a hypothetical 2_1 screw axis and arrange each other by a rotation of 90°, while the EDTA ligands and capped Mo atoms are periodically surrounding the 2_1 screw axis. To our knowledge, such a meso-helical structure was first shown in the POM system. Up to now, knowledge about the meso-helical system has remained limited and only a few examples have been reported.[50–54] As a result, **1** is valuable for the further investigation and synthesis of a new meso-helix or helical system based on polymolybdate building blocks. In the solid-state structure of **1**, the polyanionic chains are linked by four kinds of Na cations to form a 3D open framework containing a 1D channel with a dimension of ca. 11.236 × 8.084 Å^2 along the *c* axis (Figure 3). The Na ions are located between the neighboring chains and connected by coordinated water molecules to form dendritic clusters (Figure S1 in the

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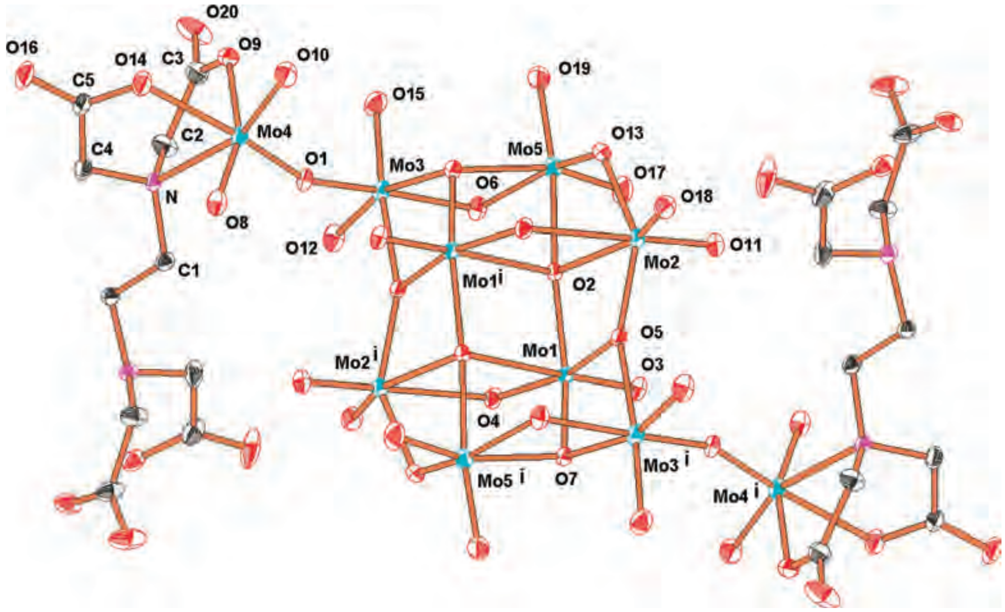


Figure 1. Displacement ellipsoid (25% probability) representation of **1**. All H atoms, Na ions, and water molecules are omitted for clarity. Symmetry code: (i) $^{1}/_{2} - x$, $^{1}/_{2} - y$, $1 - z$.

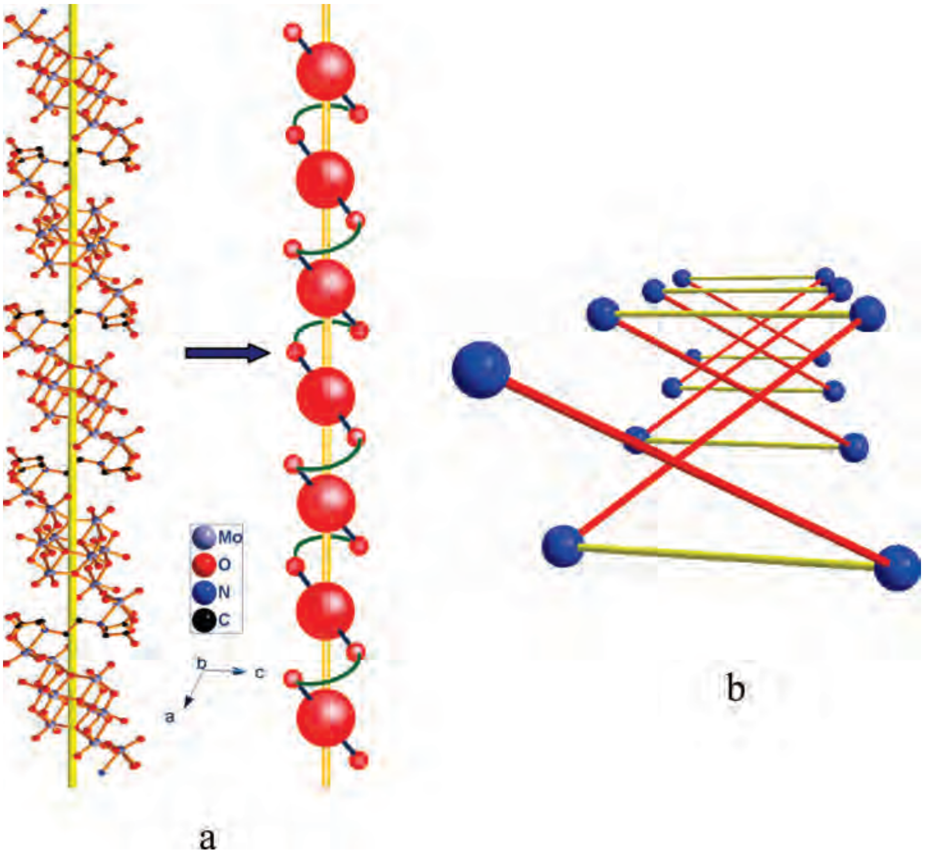


Figure 2. (a) Left: Detail of the meso-helical chain structure of **1** (all H atoms are omitted). Right: Schematic illustration of the meso-helical chain. (b) Perspective view of the meso-helical structure of **1** along the chain direction. (Only the capped Mo atoms are drawn as blue balls, while the octamolybdate subunits and organic ligands are omitted for clarity.)

Supporting Information). These Na ions also directly link the MoO_6 groups of the chains by a corner- or edge-sharing mode. The Na−O distances are in the range of 2.196−2.671 Å. The neighboring polyanionic chains associate with each other by dimeric or trimeric sodium clusters. Thus, in compound **2**, the Na ions not only act as countercations but also connect the polyanionic chains to construct a 3D framework. This result also indicates that such polyanionic chains can be further used to synthesize 3D porous structures by reaction with metal cations or cationic metal complexes.

To confirm the practicability of the above strategy for similar structures, compound **2** was also obtained. As

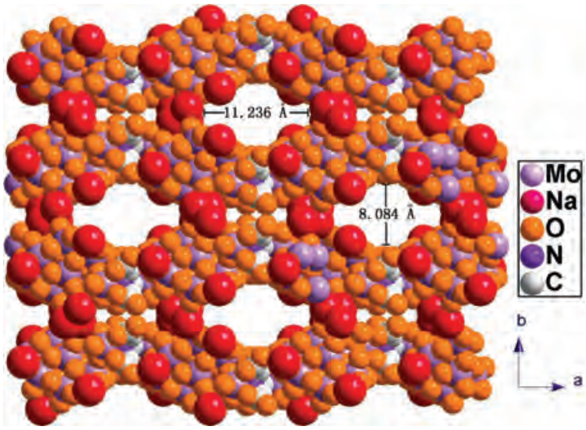


Figure 3. Space-filling diagram of the 3D framework of **1**. Isolated water molecules in the channels are omitted for clarity.

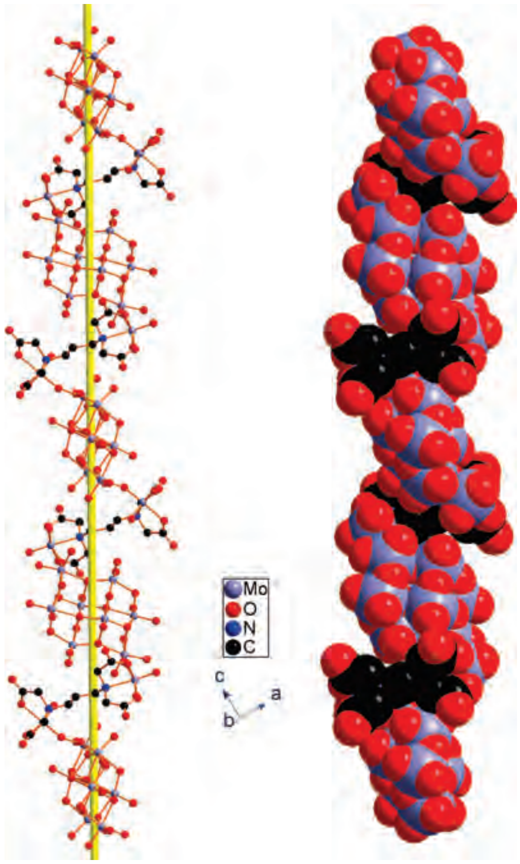
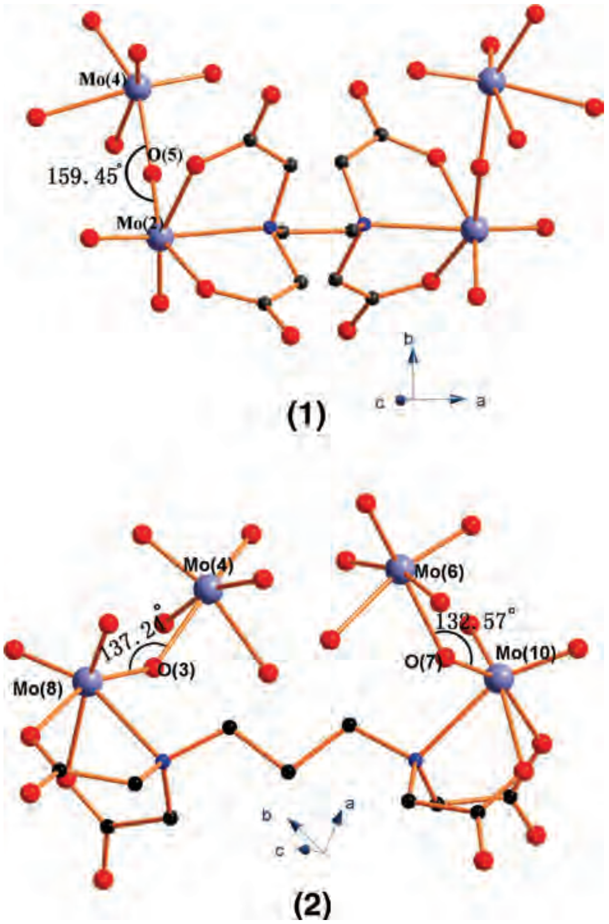


Figure 4. Ball-and-stick (left) and space-filling (right) diagrams of the meso-helical structure of **2**.

compared to **1**, single crystals with good quality were only formed when $(NH_4)_6Mo_7O_{24}\cdot 7H_2O$ served as starting materials, suggesting that the counterions strongly affected the crystal growth in the reaction system. If the counterions and free water molecules are ignored, the basic chains of **1** and **2** are very similar. As expected, compound **2** also displays an unusual meso-helical structure (Figure 4). However, PDTA adopts a cis style to coordinate two capped Mo atoms (Figure 5). Because of the longer PDTA ligand, it is easy to infer that the distance between the two PDTA-coordinated Mo atoms is longer than that of **1** (**1**, 7.795 Å; **2**, 8.480 Å). The angles 137.24° for Mo4−O3−Mo8 and 132.57° for Mo6−O7−Mo10 are smaller than 159.30° (Mo4−O1−Mo3) of **1**, suggesting that the capped $\{MoO_5N\}$ octahedron can swing over the sharing O atom when the coordination environment changes. The longer PDTA ligand does not lead to an increase of the screw pitch; on the contrary, the value 26.057 Å is a little smaller than 27.672 Å of **1**. This can be explained by the fact that EDTA and PDTA are almost perpendicular to the chain direction and the dangling $\{MoO_5N\}$ octahedron counteracts the effect of the longer PDTA ligand. The lattice–water molecules and ammonium ions are located between the neighboring chains, as shown in Figure S2 in the Supporting Information, most of which link the carboxylic or polyanionic O atoms by hydrogen-bonding interactions with N···O and O···O distances in the range of 2.760−3.005 Å. There are also hydrogen bonds among the lattice–water molecules and ammonium ions with N···O, N···N, and O···O distances ranging from 2.703 to 3.054 Å. On the basis of these weak interactions, **2** can also be considered as a 3D supramolecular complex. The successful synthesis of **2** further confirmed that the multicarboxylic ligand is an effective linkage for the synthesis of organopolymolybdate polymers.



(1)

(2)

Figure 5. Local coordination styles of organic ligands in **1** (top) and **2** (bottom). All H atoms are omitted.

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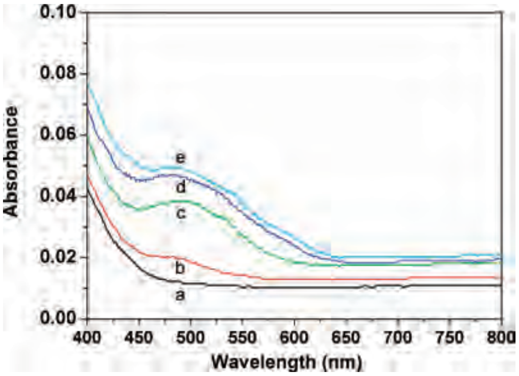
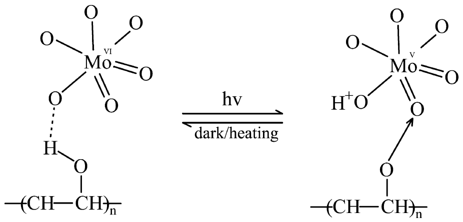


Figure 6. UV–vis spectrum of the **1**/PVA hybrid film without UV (254 nm) irradiation (a) and with UV irradiation for 2 min (b), 5 min (c), 15 min (d), and 35 min (e).

Not only from a structural viewpoint, organopolymolybdates are also photochromic materials.[55–58] Because of the similar anionic structures of **1** and **2**, here only the photochromic properties of **1** were investigated. Photochromism of carboxylate-modified octamolybdate, being induced by intramolecular electron transfer, has been confirmed to display a color change upon UV exposure.[59] However, under irradiation at 254 or 365 nm excitation for more than 2 h, no transparent color change can be observed for a solid sample of **1**, which indicates the high energy to trigger the photochromic reaction. This also relates to the fact that the carboxyl groups do not directly coordinate to the Mo atoms of the octamolybdate cluster but only chelate to the capped Mo atoms. Thus, we further explored the photochromism of **1** in a PVA film on a glass substrate. The hybrid **1**/PVA film is sensitive to irradiation at 254 nm; however, under irradiation at 365 nm, only a slight color change can be observed, suggesting a slow coloration process. The absorption band at 485 nm upon 254 nm irradiation becomes more intense upon irradiation duration (Figure 6). Meanwhile, the photochromism of the **1**/PVA film can also be confirmed by the color change from pale-yellow to reddish-brown after irradiation for more than 5 min. The photoinduced color does not evolve after approximately 35 min. When irradiation was taken off, the colored film began to fade gradually in the darkness for about 1 week. A moderate heating at 50 °C can accelerate a return to the pale-yellow state. Up to now, the reported POM-based photochromic films only show blue coloration due to their combination of classical Keggin- or Dawson-type polyanions.[56,57] Therefore, the solid **1**/PVA film first shows a pale-yellow to reddish-brown photochromism among the POM-based hybrid films. This phenomenon suggests that the multicolor photochromic films are possibly realized by the mixture of different POM components. The reddish-brown coloration has been observed in other polymolybdates as solid samples.[55] The photochromism of these powder materials is commonly explained by Yamase's model.[3] Thus, we speculate that the chromic mechanism of the **1**/PVA film is induced similarly. Under the 254 nm UV irradiation, an electron belonging to a terminal O atom of the octamolybdate cluster is transferred into the Mo^{6+} 4d block and trapped by a metastable Mo^{V} ion. Then, a bridging O atom at the photoreducible site gains a proton from the hydrogen-bonded hydroxyl group belonging to the PVA molecule. Simultaneously, the photogenerated hole left at the O atom interacts with the nonbonding hydroxyl O atom, forming a charge-transfer complex. Scheme 1 shows the above possible mechanism of one MoO_6 site in the hybrid film. A further systematic investigation of the photochromic properties for these two compounds is in progress.

Scheme 1. Possible Model of the Photochromic Mechanism of the **1**/PVA Film



Conclusion

In summary, two multicarboxylic ligand-functionalized decamolybdates were isolated. The organic ligands covalently bond to two capped Mo atoms and connect the decamolybdate clusters to form unusual meso-helical chains. It is the first time to isolate organopolyoxometalate polymers in aqueous media, which opens a new route to synthesizing the POM-based polymers by a green chemical process. Furthermore, as compared to the blue coloration photochromic films, the **1**/PVA film shows a color change from pale-yellow to reddish-brown, which provides new coloration materials.

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Supporting Information Available: Figures and selected bond lengths (Å) and angles (deg) for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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