

Rapid communication

# Synthesis, structure and photochromic properties of a novel 1,6-hexanediamine trimolybdate supramolecular compound

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## Abstract

A novel supramolecular compound 1,6-hexanediamine trimolybdate ((C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>)[Mo<sub>3</sub>O<sub>10</sub>], denoted as HDAMo) has been synthesized by a hydrothermal method and its structure has been characterized by elemental analyses, Fourier transform infrared (FT-IR) spectra, single-crystal X-ray diffraction (XRD) technique. This single crystal compound consists of protonated 1,6-hexanediamine (HDA) cations and polyoxometalate [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> anions. Its crystal structure belongs to monoclinic system (space group *P*2<sub>1</sub>/*n*) with *a* = 7.7508(14), *b* = 11.467(2), *c* = 16.167(3) Å, β = 92.689(3)°, *V* = 1435.3(5) Å<sup>3</sup>, *Z* = 4 and *D*<sub>calc</sub> = 2.619 g cm<sup>-3</sup>. The final statistics based on *F*<sup>2</sup> are GOF = 0.980, *R*<sub>1</sub> = 0.0261 and *wR*<sub>2</sub> = 0.0506 for *I* > 2σ(*I*). XRD analysis revealed that in the crystal structure of HDAMo, novel infinite [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> chains parallel to a axis are made up of distorted MoO<sub>6</sub> octahedra connected by corners and edges. The protonated HDA cations occupy channels formed by [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> chains and exhibit strong hydrogen bond interactions to terminal and bridging oxo groups of the chains. The [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup> chains linked through protonated HAD cations formed a one-dimensional network. The HDAMo compound shows novel photochromic properties, i.e., its color changes from white to reddish brown gradually under UV irradiation. XRD, FT-IR, ESR spectra and XPS are used to investigate the photochromic behavior of the compound.

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**Keywords:** Supramolecular compound; Polyoxometalates; 1,6-Hexanediamine; Trimolybdate; Hydrothermal Synthesis; Photochromic

## 1. Introduction

Polyoxometalate (POM) chemistry has attracted intense interest because of its fascinating structures and potential applications, such as high-density optical storage media, sensors, and the so-called smart windows [1–3]. In recent years, for POM study, much effort has been focused on the synthesis of the novel compounds [4–6]. The novel compounds are mainly such supramolecular compounds in which hydrogen bonding of conventional O–H⋯O and N–H⋯O motifs has been the most commonly connection style between organic and/or inorganic molecular fragments. These supramolecular compounds include POMs and cations derived from electron-rich molecules, such as tetrathiafulvalene, porphyrines, substituted amides, aromatic amines, as well as alkylammonium [7–11]. They may

self-assemble into one-, two-, and three-dimensional structures [12–14]. However, it is still a challenging task in POM chemistry to assemble discrete polyanion units into one-dimensional extended solid frameworks in appropriate ways. To the best of our knowledge, one-dimensional structures composed of alkylammonium cations (ethylenediamine and 1,6-hexanediamine) and polyanions (such as Mo<sub>3</sub>O<sub>10</sub>, and Mo<sub>4</sub>O<sub>13</sub>) are still scarce [15,16]. It is well known that the hydrothermal synthesis has been widely used for obtaining supramolecular compounds and that diamines, such as ethylenediamine, and 1,6-hexanediamine, are usually used as structure-directing unit. Therefore, our interest has been focused on the preparation of one-dimensional alkylammonium polymolybdates using hydrothermal method with diamine as the structure-directing unit.

Here we demonstrate that a novel supramolecular compound (C<sub>6</sub>H<sub>18</sub>N<sub>2</sub>)[Mo<sub>3</sub>O<sub>10</sub>] can be synthesized using MoO<sub>3</sub>·H<sub>2</sub>O and 1,6-hexanediamine by hydrothermal

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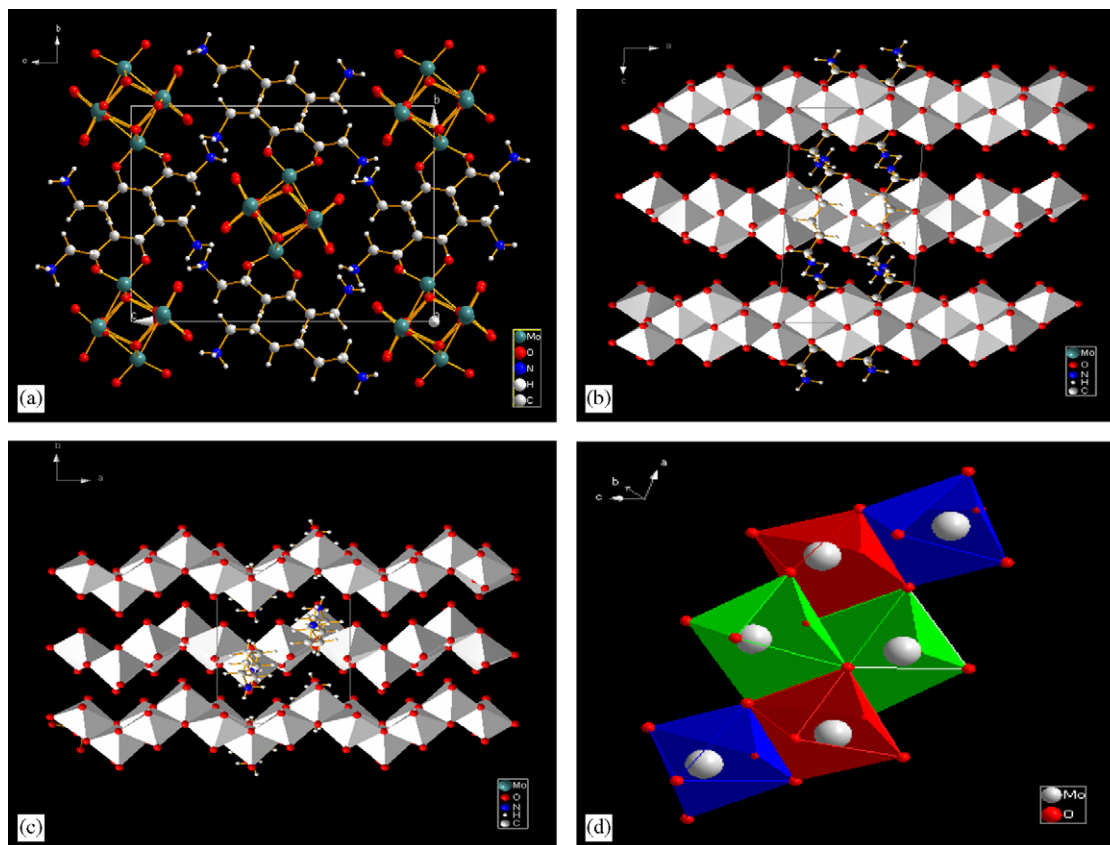


Fig. 1. Crystal structure of HDAMo: (a) view of alternating  $[\text{Mo}_3\text{O}_{10}]^{2-}$  anionic chains and  $(1,6\text{-HDAH}_2)^{2+}$  cations along  $a$ -axis; (b) and (c) polyhedral view of the one-dimensional chains and the locations of  $(1,6\text{-HDAH}_2)^{2+}$  cations along  $b$ - and  $c$ -axis; (d) structural moiety of the  $[\text{Mo}_3\text{O}_{10}]^{2-}$  chains.

method at  $180^\circ\text{C}$ . The compound exhibits novel one-dimensional polymeric molybdenum oxides. Meantime, X-ray diffraction (XRD), Fourier transform infrared (FT-IR), electron spin resonance (ESR), X-ray photoelectron spectra (XPS), and UV–Vis diffuse reflectance spectra (DRS), have been employed to characterize samples of HDAMo (hydrothermally obtained and UV-light irradiated).

## 2. Results and discussion

### 2.1. Structure description

The perspective view of the molecular unit of HDAMo is shown in Fig. 1a. The details of crystal data collection and refinement parameters of the compound are summarized in Table 1, and selected bond lengths and angles of the compound are listed in Table 2. In the crystal structure of HDAMo, infinite chains  $[\text{Mo}_3\text{O}_{10}]^{2-}$  are linked through protonated HDA cations into a one-dimensional network by hydrogen bonds. A novel infinite chain  $[\text{Mo}_3\text{O}_{10}]^{2-}$  is exhibited in the Fig. 1b and c. It is made up of distorted  $\text{MoO}_6$  octahedron connected by edges and corners (Fig. 1d). Each octahedron has two short, two medium, and two long molybdenum–oxygen bonds (Table 2). The two short distances in each  $\text{MoO}_6$  octahedron correspond to two terminal oxygen atoms. Each trimer unit consists of

Table 1  
Crystal data and structure refinement for HDAMo

Empirical formula	$\text{C}_6\text{H}_{18}\text{Mo}_3\text{N}_2\text{O}_{10}$
Formula weight	566.04
Temperature (K)	293(2)
Wavelength ( $\text{\AA}$ )	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
$a$ ( $\text{\AA}$ )	7.7508(14)
$b$ ( $\text{\AA}$ )	11.467(2)
$c$ ( $\text{\AA}$ )	16.167(3)
$A$ (deg.)	90
$\beta$ (deg.)	92.689(3)
$\gamma$ (deg.)	90
Volume ( $\text{\AA}^3$ )	1435.3(5)
$Z$	4
Density (calculated) ( $\text{g cm}^{-3}$ )	2.619
Absorption coefficient ( $\text{mm}^{-1}$ )	2.632
$F(000)$	1096
Crystal size (mm)	$0.58 \times 0.03 \times 0.03$
$\theta$ range for data collection (deg.)	$2.18$ to $26.39$
Limiting indices	$-9 \leq h \leq 9, -14 \leq k \leq 7, -20 \leq l \leq 20$
Reflections collected	8082
Independent reflections	2935 [ $R(\text{int}) = 0.0383$ ]
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	2935/0/192
Goodness-of-fit on $F^2$	0.980
Final $R$ indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0261, wR_2 = 0.0506$
$R$ indices (all data)	$R_1 = 0.0333, wR_2 = 0.0534$
Largest diff. peak and hole	0.749 and $-0.545 \text{ e \AA}^{-3}$

Table 2  
Bond lengths (Å) and angles (deg.) for HDAMo

Mo(1)–O(6)	1.705(3)	C(6)–N(2)	1.476(5)
Mo(1)–O(7)	1.713(2)	C(1)–N(1)	1.481(5)
Mo(1)–O(2)	1.934(2)	C(6)–H(6A)	0.9700
Mo(1)–O(3)	1.942(2)	C(6)–H(6B)	0.9700
Mo(1)–O(1)	2.260(2)	C(5)–H(5A)	0.9700
Mo(1)–O(10)#1	2.277(3)	C(5)–H(5B)	0.9700
Mo(2)–O(9)	1.712(3)	C(4)–H(4A)	0.9700
Mo(2)–O(8)	1.727(3)	C(4)–H(4B)	0.9700
Mo(2)–O(10)	1.866(2)	C(3)–H(3A)	0.9700
Mo(2)–O(3)	2.097(2)	C(3)–H(3B)	0.9700
Mo(2)–O(1)	2.102(2)	C(2)–H(2D)	0.9700
Mo(2)–O(3)#1	2.279(2)	C(2)–H(2E)	0.9700
Mo(3)–O(5)	1.712(3)	C(1)–H(1A)	0.9700
Mo(3)–O(4)	1.727(3)	C(1)–H(1B)	0.9700
Mo(3)–O(1)	1.875(2)	N(2)–H(2A)	0.8900
Mo(3)–O(10)#2	2.089(2)	N(2)–H(2B)	0.8900
Mo(3)–O(2)#3	2.107(2)	N(2)–H(2C)	0.8900
Mo(3)–O(2)	2.268(2)	N(1)–H(1C)	0.8900
C(6)–C(5)	1.501(5)	N(1)–H(1D)	0.8900
C(5)–C(4)	1.503(6)	N(1)–H(1E)	0.8900
C(4)–C(3)	1.496(6)		
C(3)–C(2)	1.509(6)		
C(2)–C(1)	1.478(6)		
O(6)–Mo(1)–O(7)	104.97(13)	Mo(3)#4–O(10)–Mo(1)	99.76(10)
O(6)–Mo(1)–O(2)	102.82(11)	Mo(1)–O(3)–Mo(2)	110.50(10)
O(7)–Mo(1)–O(2)	103.86(11)	Mo(1)–O(3)–Mo(2)#1	102.15(10)
O(6)–Mo(1)–O(3)	104.04(11)	Mo(2)–O(3)–Mo(2)#1	106.81(11)
O(7)–Mo(1)–O(3)	101.65(11)	C(6)–N(2)–H(2A)	109.5
O(2)–Mo(1)–O(3)	136.31(11)	C(6)–N(2)–H(2B)	109.5
O(6)–Mo(1)–O(1)	87.86(11)	H(2A)–N(2)–H(2B)	109.5
O(7)–Mo(1)–O(1)	166.96(11)	C(6)–N(2)–H(2C)	109.5
O(2)–Mo(1)–O(1)	74.87(9)	H(2A)–N(2)–H(2C)	109.5
O(3)–Mo(1)–O(1)	72.41(9)	H(2B)–N(2)–H(2C)	109.5
O(6)–Mo(1)–O(10)#1	166.55(11)	N(2)–C(6)–C(5)	112.2(4)
O(7)–Mo(1)–O(10)#1	88.37(11)	N(2)–C(6)–H(6A)	109.2
O(2)–Mo(1)–O(10)#1	71.69(9)	C(5)–C(6)–H(6A)	109.2
O(3)–Mo(1)–O(10)#1	74.24(10)	N(2)–C(6)–H(6B)	109.2
O(1)–Mo(1)–O(10)#1	78.88(9)	C(5)–C(6)–H(6B)	109.2
O(9)–Mo(2)–O(8)	103.59(12)	H(6A)–C(6)–H(6B)	107.9
O(9)–Mo(2)–O(10)	98.74(12)	C(6)–C(5)–C(4)	111.8(4)
O(8)–Mo(2)–O(10)	100.72(12)	C(6)–C(5)–H(5A)	109.2
O(9)–Mo(2)–O(3)	94.73(11)	C(4)–C(5)–H(5A)	109.2
O(8)–Mo(2)–O(3)	152.90(11)	C(6)–C(5)–H(5B)	109.2
O(10)–Mo(2)–O(3)	95.96(10)	C(4)–C(5)–H(5B)	109.2
O(9)–Mo(2)–O(1)	97.70(11)	H(5A)–C(5)–H(5B)	107.9
O(8)–Mo(2)–O(1)	84.85(11)	C(3)–C(4)–C(5)	114.8(4)
O(10)–Mo(2)–O(1)	160.84(10)	C(3)–C(4)–H(4A)	108.6
O(3)–Mo(2)–O(1)	72.89(9)	C(5)–C(4)–H(4A)	108.6
O(9)–Mo(2)–O(3)#1	165.71(10)	C(3)–C(4)–H(4B)	108.6
O(8)–Mo(2)–O(3)#1	90.42(11)	C(5)–C(4)–H(4B)	108.6
O(10)–Mo(2)–O(3)#1	75.54(10)	H(4A)–C(4)–H(4B)	107.6
O(3)–Mo(2)–O(3)#1	73.19(11)	C(4)–C(3)–C(2)	112.2(4)
O(1)–Mo(2)–O(3)#1	86.17(9)	C(4)–C(3)–H(3A)	109.2
O(5)–Mo(3)–O(4)	103.76(12)	C(2)–C(3)–H(3A)	109.2
O(5)–Mo(3)–O(1)	98.77(11)	C(4)–C(3)–H(3B)	109.2
O(4)–Mo(3)–O(1)	100.30(11)	C(2)–C(3)–H(3B)	109.2
O(5)–Mo(3)–O(10)#2	96.86(11)	H(3A)–C(3)–H(3B)	107.9
O(4)–Mo(3)–O(10)#2	85.80(11)	C(1)–C(2)–C(3)	116.0(4)
O(1)–Mo(3)–O(10)#2	161.30(10)	C(1)–C(2)–H(2D)	108.3
O(5)–Mo(3)–O(2)#3	94.99(11)	C(3)–C(2)–H(2D)	108.3
O(4)–Mo(3)–O(2)#3	152.89(11)	C(1)–C(2)–H(2E)	108.3
O(1)–Mo(3)–O(2)#3	95.90(10)	C(3)–C(2)–H(2E)	108.3
O(10)#2–Mo(3)–O(2)#	72.51(9)	H(2D)–C(2)–H(2E)	107.4
O(5)–Mo(3)–O(2)	166.25(11)	C(2)–C(1)–N(1)	112.4(4)
O(4)–Mo(3)–O(2)	89.71(10)	C(2)–C(1)–H(1A)	109.1

Table 2 (continued)

Mo(1)–O(6)	1.705(3)	C(6)–N(2)	1.476(5)
O(1)–Mo(3)–O(2)	75.75(10)	N(1)–C(1)–H(1A)	109.1
O(10)#2–Mo(3)–O(2)	86.70(9)	C(2)–C(1)–H(1B)	109.1
O(2)#3–Mo(3)–O(2)	73.36(11)	N(1)–C(1)–H(1B)	109.1
Mo(3)–O(1)–Mo(2)	156.69(14)	H(1A)–C(1)–H(1B)	107.9
Mo(3)–O(1)–Mo(1)	103.91(11)	C(1)–N(1)–H(1C)	109.5
Mo(2)–O(1)–Mo(1)	99.08(9)	C(1)–N(1)–H(1D)	109.5
Mo(1)–O(2)–Mo(3)#3	111.46(11)	H(1C)–N(1)–H(1D)	109.5
Mo(1)–O(2)–Mo(3)	101.68(10)	C(1)–N(1)–H(1E)	109.5
Mo(3)#3–O(2)–Mo(3)	106.64(11)	H(1C)–N(1)–H(1E)	109.5
Mo(2)–O(10)–Mo(3)#4	155.21(14)	H(1D)–N(1)–H(1E)	109.5
Mo(2)–O(10)–Mo(1)#1	104.76(11)		

three octahedra. Mo(1)O<sub>6</sub> octahedron is connected to Mo(2)O<sub>6</sub> and Mo(3)O<sub>6</sub> by a shared edge. Mo(2)O<sub>6</sub> and Mo(3)O<sub>6</sub> octahedra are connected by a corner. Each trimer unit is then joined up with another symmetry related moiety by sharing two edges of an octahedron to form a unit of six octahedra (see Fig. 1d). The hexamer units are connected together by sharing edges (Mo(1)O<sub>6</sub> octahedra) and corners (Mo(2)O<sub>6</sub> and Mo(3)O<sub>6</sub> octahedra) to form infinite chains. In the crystal structure of HDAMo, HDA cations are located between these chains and are connected to the oxygens of the molybdate units by hydrogen bonds. It can be observed from Table 2 that in (1,6-HDAH<sub>2</sub>)<sup>2+</sup>, the C–C bond lengths (between 1.478 and 1.509 Å) are shorter than the paraffinic C–C single bond length (1.54 Å), while the C–N bonds lengths (1.476–1.481 Å) are longer than the C–N single bond length (1.47 Å). This may be attributed to the hydrogen bonds formed between [MoO<sup>-</sup>⋯(–NH<sub>3</sub>)<sup>+</sup>] and their steric constraint due to their location.

## 2.2. The thermal gravimetric analysis (TGA) and the differential thermal analysis (DTA)

Fig. 2 displays the TGA and DTA curves for HDAMo. There are two major weight loss of 20.73% and 65.40% that appear over the range of 240–500 and 700–900 °C, respectively. The first one is due to the removal of 1,6-HAD, which weighs 20.89% of the total weight. The second one is due to fracture of the framework of POM.

## 2.3. XRD and FT-IR absorption spectra

In order to examine whether the structure of the HDAMo is changed after UV irradiation, we investigated the XRD and FT-IR spectra of the as-synthesized and the colored samples. The XRD patterns (Fig. 3a) show that the crystal structure of the HDAMo remains almost unchanged except slight structure distortion during irradiation process. Fig. 3b gives FT-IR spectra of the samples before and after UV irradiation. They have almost the same characteristic spectra. The similar phenomenon for the alkylammonium polyoxomolybdate compounds irradiated by UV light has also been observed and reported by Yamase et al. [17] and Yamase and Ikawa [18]. This means

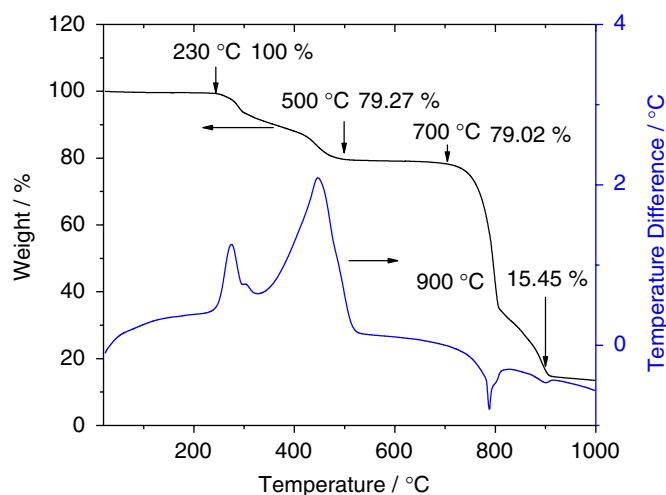


Fig. 2. TGA and DTA curves of the as-synthesized sample.

that influence of UV irradiation on the molecule frameworks of the HDAMo under experimental conditions could be very small or even negligible. The absorption bands in the range of 1000–400 cm<sup>-1</sup> are mainly characteristic absorption bands of the [Mo<sub>3</sub>O<sub>10</sub>]<sup>2-</sup>, whereas in the range of 3300–1000 cm<sup>-1</sup> are mainly characteristic absorption bands of the protonated hexanediamine. All these imply that the inorganic skeleton does not almost change upon irradiation.

## 2.4. UV-Vis DRS

Fig. 4 shows that pictures of the samples under different irradiation time. It may be observed from these pictures that color of the samples changes from white to reddish brown gradually with irradiation time increasing. Their corresponding UV-visible DRS are exhibited in the Fig. 5. There are strong broad absorption bands in the range of 200–400 nm, which are mainly composed of two overlap absorption bands centered at ca. 235 and 300 nm, respectively. The strong absorption bands are assigned to intrinsic absorption bands of the compound, that is, a transition from its valence band to its conduction. In visible range, the absorption gradually increases with increasing irradiation time. A broad optical absorption in

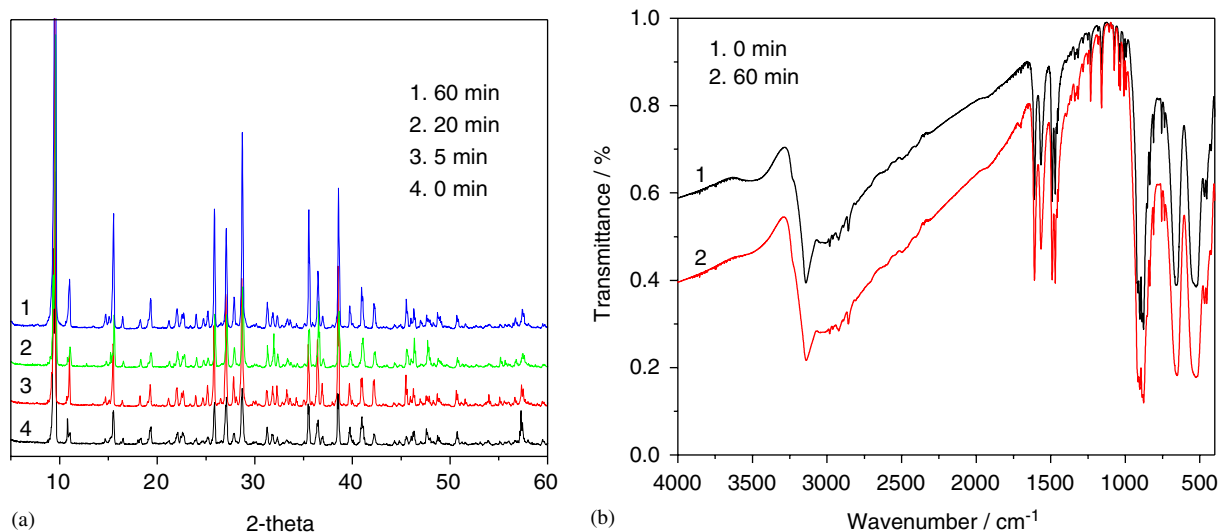


Fig. 3. XRD patterns (a) and FT-IR spectra (b) of irradiated sample and as-synthesized sample.

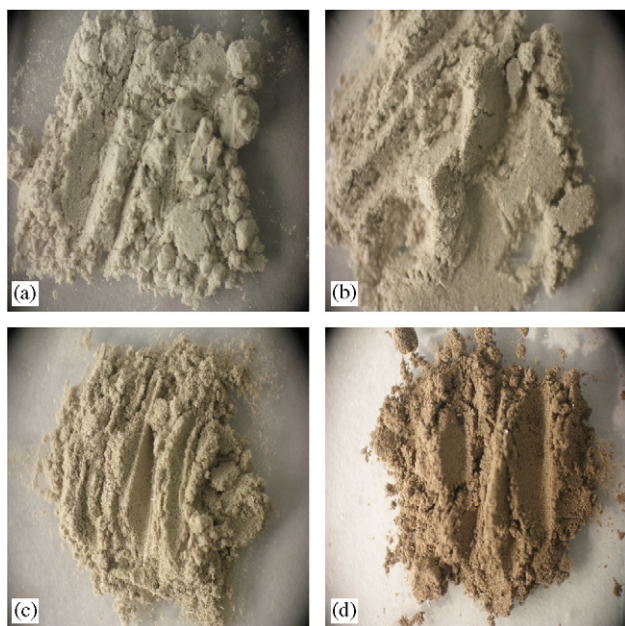


Fig. 4. Pictures of the samples under different irradiation time ((a) 0 min, (b) 5 min, (c) 20 min and (d) 60 min).

visible region for the colored HDAMo compound is observed. It can be summarily attributed to Mo (V)–O–Mo (VI) → Mo (VI)–O–Mo (V) intervalence charge transfer (IVCT) and/or *d-d* transition of Mo (V) ( $4d^1$ ) although there still remain elusive from literature [19]. The Mo (V) atoms with one *4d* electron produced through UV photo-reduction of Mo (VI) atoms have also been confirmed by means of ESR analyses and XPS results.

### 2.5. The ESR spectra and the XPS

The ESR in Fig. 6 indicate that the as-synthesized sample exhibits no ESR signals, while the irradiated

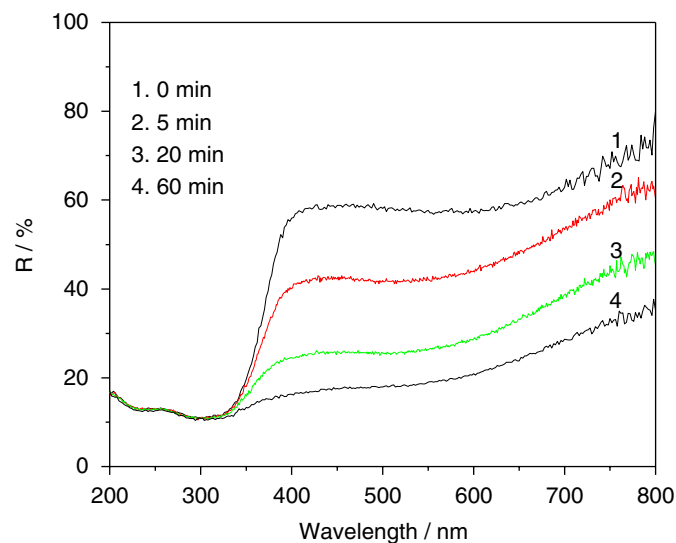


Fig. 5. UV-vis DRS of the samples under different irradiation time.

samples exhibit characteristic ESR signals of Mo (V) atoms [11,20–22]. It can be concluded from this that Mo (VI) atoms are reduced to Mo (V) atoms after the as-synthesized samples were irradiated by UV light. Furthermore, the XPS analyses show that uncolored samples have two bands at binding energy of 232.5 and 235.7 eV, respectively, which correspond to of Mo (VI) atoms only, while colored samples have two more bands at binding energy of 231.4 and 234.6 eV, respectively, corresponding to Mo (V) atoms. This implies that parts of the Mo (VI) atoms for the irradiated sample were reduced to Mo (V) during the photochromic coloration process, which is in agreement with ESR result.

Yamase [11] studied photochromic properties of the single crystal alkylammonium polyoxomolybdates and proposed a photochromic mechanism which is widely accepted in this field [22–25]. According to Yamase's photochromic mechanism, a

possible HDAMo's photochromic mechanism can be illustrated (see Scheme 1). Photoexcitation results in the HDAMo's ligand-to-metal ( $O \rightarrow Mo$ ) charge transfer (LMCT) transition and transfer of a hydrogen atom from the nitrogen of 1,6-HDA towards the bridge oxygen atom at the photoreduced site in the edge-shared  $MoO_6$  octahedral lattices. Simultaneously, a charge-transfer complex is formed and Mo (V) is produced. A study on the detailed photochromic mechanism is underway.

### 3. Conclusion

In summary, a novel supramolecular compound 1,6-hexanediamine trimolydate has been successfully synthesized by a hydrothermal method and its structure characterized. In the crystal structure, infinite chains  $[Mo_3O_{10}]^{2-}$  are made up of distorted  $MoO_6$  octahedron connected by edges and corners. Furthermore, we have found that the compound having one-dimensional framework displays photochromic properties and may be applied to the field of photosensitive materials.

## 4. Experimental section

### 4.1. Materials and synthesis of compound

All reagents were of analytical grade and were used as received from commercial sources without further purification.

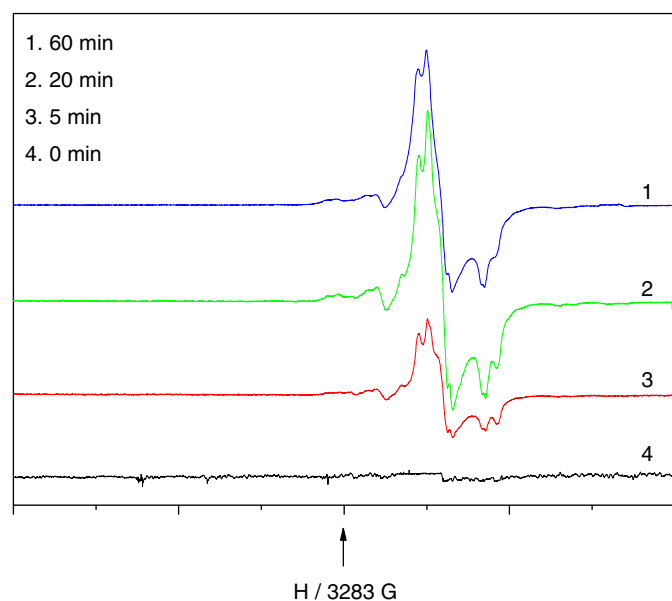
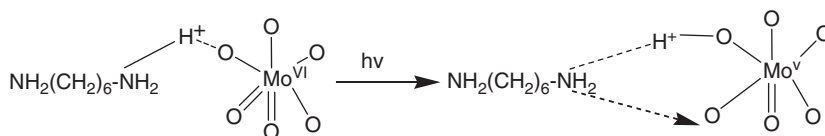


Fig. 6. ESR spectra of the samples under different irradiation time.



Scheme 1. The model of photochromic mechanism.

Crystals of  $(C_6H_{18}N_2)[Mo_3O_{10}]$  were synthesized by hydrothermal method under autogenous pressure. In a typical synthesis, a mixture of  $MoO_3 \cdot H_2O$ , 1,6-hexanediamine, and deionized  $H_2O$  in a molar ratio 1:1:144 was stirred for 30 min, and then acidified using 6 M HCl solution to obtain the pH of 5–7. The white mixture was transferred to a teflon-lined reactor and heated at 180 °C for 24 h, and then cooled to room temperature at a rate of 2 °C/9 min. Fibrillar colorless crystals were recovered by washing, filtering, and drying at 45 °C in air. Anal. Calc. for  $C_6H_{18}N_2O_{10}Mo_3$ : C, 12.73; H, 3.21; N, 4.95; Mo, 50.85. Found: C, 13.59; H, 3.12; N, 5.07; Mo, 51.74. IR ( $cm^{-1}$ ): 3448 (m), 3142 (m), 1609 (s), 1565 (s), 1470 (m), 1232 (w), 1159 (w), 1074 (w), 1033 (w), 1008 (w), 902 (s), 877 (s), 836 (w), 755 (w), 663 (s), 548 (s). Bleached experiments of the colored samples were carried out in  $FeCl_3$  ethanol solution. The experimental results indicate that the colored samples can be bleached and the bleached samples can be also colored again by UV light. This means the process is reversible.

### 4.2. Physical measurements

Elemental analyses for Mo was performed by inductively coupled plasma atomic emission spectroscopy and mass spectroscopy (ICP-AES/MS) measurement with a TJA-POEMS spectrometer, and for C, N, and H by a Vario Element Analyzer. The TGA and the DTA were carried out under  $O_2$  using a 2960 SDT differential thermal analyzer at a rate of 10.0 °C/min in the range of 0–1000 °C. XRD was made on a D/Max 2500 V/PC X-ray diffractometer using high-intensity  $CuK\alpha_1$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). FT-IR absorption spectra were recorded in the range of 4000–400  $cm^{-1}$  on a model FTS135 infrared spectrophotometer (American BIO-RAD Company) operated at a resolution of 1  $cm^{-1}$ . UV–vis DRS measurements were obtained on a HITACHI U-4100 Spectrophotometer. The XPS were performed on a VG ESCALAB MK II (England) photoelectron spectrometer using monochromatic  $MgK\alpha$  (1253.6 eV) radiation. The ESR spectra of the colored samples were recorded on a JESFE-3AX spectrometer at 77 K. The photochromic experiments were carried out using a 500 W high-pressure mercury lamp as a light source with wavelength of 365 nm under cooling condition. The distance between the lamp and the sample was 8 cm. The sample was maintained in contact with air during irradiation.

### 4.3. X-ray crystallographic study

A colorless single crystal with dimensions  $0.58 \times 0.03 \times 0.03 \text{ mm}^3$  was mounted on a glass fiber and XRD data were

collected on a CCD area detector with graphite-monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The structure was solved by the direct method and refined by the full-matrix least-squares method on  $F^2$  using the SHELXL-97 software. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located from difference Fourier maps. Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-609352. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (44) 1223 336-033; e-mail: deposit@ccdc.cam.ac.uk)."

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