



新型一维钼氧链超分子化合物 $[(\text{H}_2\text{bpe})\text{Mo}_4\text{O}_{13}]$ 的合成与光学性质研究

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Hydrothermal Synthesis, Characterization and Luminescence Property of a New 1D Molybdenum Oxide Chain: $[(\text{H}_2\text{bpe})\text{Mo}_4\text{O}_{13}]$

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Abstract: A new 1D compound $[(\text{H}_2\text{bpe})\text{Mo}_4\text{O}_{13}]$ (**1**) (bpe = *trans*-1,2-Di-(4-pyridyl)-ethylen) was hydrothermally synthesized and characterized. Compound **1** comprises 3D supramolecular network constructed from 1D $[\text{Mo}_4\text{O}_{13}]^{2-}$ anion chains and protonated bpe layers via hydrogen bonds and π - π stacking interactions. The crystal data are the following: $\text{C}_{12}\text{H}_{12}\text{Mo}_4\text{N}_2\text{O}_{13}$, Monoclinic, space group $P2_1/n$, $a=0.968\ 64\ (13)\ \text{nm}$, $b=1.349\ 68\ (18)\ \text{nm}$, $c=1.514\ 9(2)\ \text{nm}$, $\beta=99.766(2)^\circ$, $Z=4$. The inorganic chain built up from only molybdenum oxide building blocks is interesting. The luminescent property of **1** was studied. CCDC: 739954.

Key words: molybdenum oxide chain; crystal structure; luminescent property

Polyoxometalates (POMs) have been widely studied for their structural versatility and potential application in many kinds of fields, such as medicine, catalysis, analytical chemistry, and materials science^[1-3]. POMs have been employed as important inorganic building blocks for constructing novel hybrid materials with various organic molecules^[4-8]. In comparison to the classical Keggin- and Dawson-type heteropolyanions that have attracted more attention in hybrid materials, the research regarding the small sized isopolyanions is expected^[9-11]. Up to now, a large number of polymers based on *di*-, *tri*-, *tetra*-, *penta*-, heptamolybdates with 1D chain, 2D layer and 3D open-framework structures have been studied^[11-16]. However, the solid materials of

one-dimensional structure with only molybdenum oxide frameworks have been reported rarely by comparison with them^[17].

Molybdenum oxide frameworks can be easily modified because of its high reactivity and structural flexibility^[18-20]. So, here we aim to synthesize new structures of molybdenum oxides under hydrothermal conditions using simple molybdate as the starting materials and bpe as the template, and compound **1** was obtained.

1 Experimental

1.1 General

All chemicals were commercially purchased and used without further purification. Elemental analyses

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(C, H, and N) were performed on a Elemental Vario EL elemental analyzer. IR spectra were recorded in KBr pellets with a FTIR-8900 IR spectrometer in the range of 400~4 000 cm^{-1} region. UV spectra were obtained on a Unicam UV-2501PC spectrometer. Thermogravimetric analysis (TG-DTA) was carried out using a Perkin-Elmer TGA-7 instrument in flowing N_2 with a heating rate of 10 $^{\circ}\text{C} \cdot \text{min}^{-1}$. Fluorescent spectra were measured with a Hitachi F-4500 luminescence spectrometer.

1.2 Preparation of $[(\text{H}_2\text{bpe})\text{Mo}_4\text{O}_{13}]$ (1)

A mixture of $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (480 mg, 2 mmol), bpe (45 mg, 0.25 mmol) and H_2O (10 mL) was stirred for 30 min and the pH was adjusted to 4 by 4 mol $\cdot \text{L}^{-1}$ HCl. Then the mixture was transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 $^{\circ}\text{C}$ for 5 days. After the autoclave was cooled to room temperature at a rate of 10 $^{\circ}\text{C} \cdot \text{h}^{-1}$, yellow block-like crystals were obtained in a yield of 52% (based on Mo). The crystals were picked out, washed with distilled water, and dried at air atmosphere. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{Mo}_4\text{N}_2\text{O}_{13}$: C, 18.56; H, 1.55; N, 3.61%. Found: C,

18.41; H, 1.60; N, 3.72%.

1.3 Crystal structure determination

The data of compound **1** was collected with the approximate dimensions 0.25 mm \times 0.21 mm \times 0.12 mm on a SMART APEX II CCD Area Detector diffractometer at 298(2) K using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$) and oscillation scans technique in the range $2.03^{\circ}\sim 25.02^{\circ}$. Empirical absorption correction was applied. A total of 9 690 (3 438 unique, $R_{\text{int}}=0.026\ 2$) reflections were measured. The structure was solved by direct method using the program SHELXS-97^[21-22] and refined by full-matrix least-squares methods on F^2 using the SHELXL-97 program package. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Protonated hydrogen atoms attached to nitrogen atoms were located from the difference Fourier map. Hydrogen atoms attached to carbon atoms were fixed at their ideal positions. All the crystal data and structure refinement details for the compound **1** are given in Table 1.

CCDC: 739954.

Table 1 Crystal data and structure refinements for compound 1

Empirical formula	$\text{C}_{12}\text{H}_{12}\text{Mo}_4\text{N}_2\text{O}_{13}$	$F(000)$	1 480
Formula weight	776.00	Crystal size / mm	0.25 \times 0.21 \times 0.12
Temperature / K	298(2)	θ range for data collection / ($^{\circ}$)	$2.03\sim 25.02$
Wavelength / nm	0.071 073	Index ranges	$-11\leq h\leq 10$, $-16\leq k\leq 12$, $-16\leq l\leq 18$
Crystal system	Monoclinic	Reflections collected	9 690
Space group	$P2_1/n$	Independent reflections (R_{int})	3 438 (0.026 2)
a / nm	0.968 64(13)	Completeness to $\theta=25.02^{\circ}$ / %	99.7
b / nm	1.349 68(18)	Absorption correction	Empirical
c / nm	1.514 9(2)	Max. and min. transmission	0.733 and 0.529
β / ($^{\circ}$)	99.766(2)	Refinement method	Full-matrix least-squares on F^2
Volume / nm^3	1.951 9(5)	Data / restraints / parameters	3 438 / 0 / 280
Z	4	Goodness-of-fit on F^2	1.024
Density (calculated) / ($\text{Mg} \cdot \text{m}^{-3}$)	2.641	Final R indices [$I>2\sigma(I)$]	$R_1=0.022\ 4$, $wR_2=0.052\ 9$
Absorption coefficient / mm^{-1}	2.584	R indices (all data)	$R_1=0.031\ 6$, $wR_2=0.060\ 1$

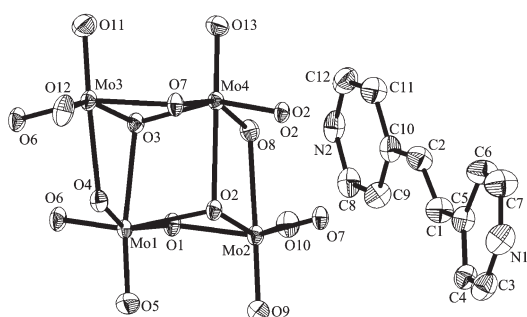
2 Results and discussion

2.1 Crystal structure of compound 1

A single-crystal X-ray diffraction analysis revealed that this compound is constructed from 1D $[\text{Mo}_4\text{O}_{13}]^{2-}$ anion chains integrated by protonated bpe ligands into a 3D framework. This tetramolybdate subunit (Fig.1)

consists of four $\{\text{MoO}_6\}$ octahedral which are further connected through edge- or corner-sharing to form a 1D tetramolybdate chain running along the a -axis (Fig.2).

Also, the tetramolybdate chain may be described as constructed from octamolybdate units fused at two common vertices. The structural feature of this $[\text{Mo}_8\text{O}_{26}]^{4-}$ subunit is similar to that of $\gamma\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ which contains



All the hydrogen atoms are omitted for clarity

Fig.1 ORTEP drawing of **1** with 50% probability level, showing the coordination environments around Mo atoms

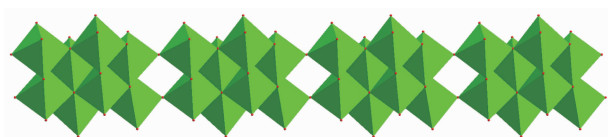
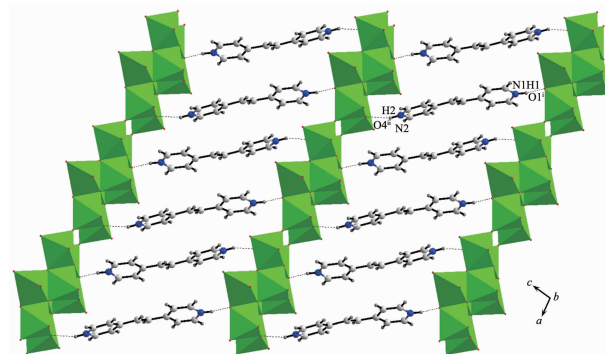


Fig.2 1D [Mo₈O₂₆]⁴ⁿ⁻ inorganic chain in **1**

six {MoO₆} octahedra and two {MoO₅} square pyramids^[23]. The {MoO₆} octahedra are all distorted and the Mo-O bond lengths are in the range of 0.168 6 (3)~0.248 3(3) nm. The octamolybdate unit in **1** can also be found in K₂Mo₄O₁₃^[24], (NH₄)₂Mo₄O₁₃^[25] and (NH₄)₆[Mo₈O₂₇]·4H₂O^[26], [H₂enMe]₂[Mo₈O₂₆]^[27]. In these reported compounds, octamolybdate units are only isolated cluster and don't extend into one-dimensional structure. To the best of our knowledge, the similar octamolybdate chain once appeared in (Me-NC₅H₅)_{4n}[Mo₈O₂₆]_n^[28] and (H₂bbi)₂[Mo₈O₂₆]^[29].

Non-covalent interactions are essentially necessary for the basis of the order of inorganic and organic components in supramolecular frameworks^[30]. In compound **1**, π - π interactions and hydrogen bonds both play important roles in the formation of crystal framework. As shown in Fig.3, the two adjacent molybdenum oxide chains are linked up together to form a 2D layer through

(N-H \cdots O=Mo) hydrogen bonds of which distances are shown in Table 2, and π - π stacking interactions of bpe molecules with the distance of 0.350 7~0.384 8 nm (Fig. 4). Then, the 2D layers are stacked to a 3D framework in parallel staggering fashion.



Symmetry codes: ⁱ 1/2+x, 1/2-y, -1/2+z; ⁱⁱ -1/2+x, 1/2-y, -3/2+z

Fig.3 2D supramolecular structure of **1**

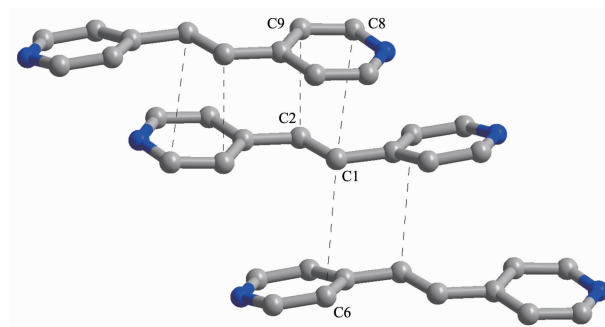


Fig.4 A view showing π - π stacking interactions among bpe molecules in **1**

Aromatic nitrogen heterocycles (pyridine, bipyridines, etc.) are usually used to construct π - π interactions because of their low π -electron density. In our previous work, bpy, bpp and pbpy (bpy = 2,4'-bipyridine; bpp = 1,3-bis (4-pyridyl)propane; pbpy = 5-phenyl-2-(4-pyridinyl)pyridine) have all been selected to assemble POMs. A Keggin-based hybrid (Hbpy)₄[SiMo₁₂O₄₀]^[31] was once reported by using bpy molecule,

Table 2 Hydrogen bond distances in compound **1**

D-H \cdots A	D-H / nm	H \cdots A / nm	D \cdots A / nm	\angle D-H \cdots A / (°)
N(1)-H(1) \cdots O(1 ⁱ)	0.086	0.210	0.281 9(4)	140
N(2)-H(2) \cdots O(4 ⁱⁱ)	0.086	0.193	0.276 3(4)	162
C(1)-H(1A) \cdots O(11 ⁱⁱⁱ)	0.093	0.239	0.329 6(5)	164
C(6)-H(6) \cdots O(9 ^{iv})	0.093	0.232	0.319 1(6)	155
C(9)-H(9) \cdots O(11 ⁱⁱⁱ)	0.093	0.235	0.327 9(5)	175
C(11)-H(11) \cdots O(1 ^{iv})	0.093	0.258	0.349 7(6)	169

Symmetry codes: ⁱ 1/2+x, 1/2-y, -1/2+z; ⁱⁱ -1/2+x, 1/2-y, -3/2+z; ⁱⁱⁱ x, -1+y, -1+z; ^{iv} x, y, -1+z.

in which protonated bpy cations exhibited interesting organic double helical chains by N-H \cdots N interaction. Recently, we reported a new compound $(\text{H}_2\text{bpp})_2[\beta\text{-Mo}_8\text{O}_{26}]^{[32]}$ constructed from one $\beta\text{-}[\text{Mo}_8\text{O}_{26}]^{4-}$ anionic cluster and two protonated bpp cations through the intermolecular hydrogen bonds (N-H \cdots O-Mo and C-H \cdots O-Mo) and π - π interaction. In another compound $(\text{pbpy})_8\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 2\text{H}_2\text{O}^{[33]}$, the pbpy molecules are approximately parallel to each other so as to create π - π stacking interactions. While in compound **1**, there is a rather extensive π - π network. The py groups of bpe are almost parallel and this aromatic distances of the planes of the aromatic moieties fall into a range of 0.350 7 ~ 0.384 8 nm, indicating that these interactions are of the face-to-face π -stacking type. In comparison with bpy, pbpy and bpp, these results indicate that bpe is easier to form the intermolecular face-to-face π -stacking interaction induced by POMs. A reasonable explain may be ascribed to the structure of bpe with a double bond contacting two pyridine rings, which makes the molecule a large conjugated system and creates a more balanced distribution of electron density to further increase the tendency of the face-to-face π -stacking.

2.2 FTIR spectroscopy and TG analysis

The IR spectrum of **1** reveals the characteristic strong bands in the range 956~619 cm^{-1} attributed to $\nu(\text{Mo}=\text{O})$ and $\nu(\text{Mo}-\text{O}-\text{Mo})$. The absorption bands in the range of 1 628~1 193 cm^{-1} can be assigned to characteristic peaks of bpe. The broad peak at 3 461 cm^{-1} can be assigned to the stretching vibration of N-H bond. The thermal stability is investigated on crystalline sample under an air atmosphere from 25 to 850 $^{\circ}\text{C}$. It exhibits two steps of continuous weight losses of 23.35% between 265 to 520 $^{\circ}\text{C}$ which attributes to the loss of protonated bpe and agrees with the calculated value (23.71%).

2.3 UV-Vis spectroscopy and luminescent property

The UV-Vis spectrum of **1** in methanol (Fig.5a) displays two main peaks at 302 and 310 nm, which are attributable to the O-Mo ligand-to-metal charge-transfer (LMCT) bands^[34-35].

The photoluminescence properties of **1** and the free bpe at room temperature are shown (Fig.5b). It can

be observed that the maximum emission wavelength of **1** occurs at 540 nm ($\lambda_{\text{ex}}=490$ nm) which is red-shifted as compared to that of the pure bpe ligands ($\lambda_{\text{em}}=510$ nm and $\lambda_{\text{ex}}=460$ nm). The origin of the emission for **1** might be attributable to the intraligand π - π^* transitions of bpes^[36-38]. The result shows that **1** may be a candidate for potential photoluminescence materials.

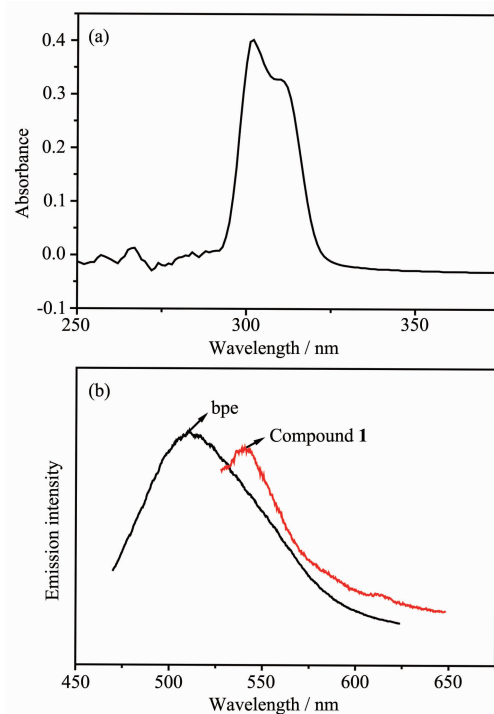


Fig.5 UV-Vis spectroscopy (a) and luminescent property (b)

3 Conclusion

In summary, we have hydrothermally prepared and structurally characterized a new compound $[(\text{H}_2\text{bpe})\text{Mo}_4\text{O}_{13}]$ constructed from 1D $[\text{Mo}_4\text{O}_{13}]^{2-}$ anion chains integrated by protonated bpe ligands. The π - π interactions and hydrogen bonds both play important roles in the formation of its framework. It exhibits luminescent property caused by π - π^* intraligand transitions. Future research will focus on the study of the reaction between molybdates and other different organic ligands in an effort to obtain novel compounds with diverse dimensionalities and structural features combined with interesting luminescent properties.

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