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1,4-Naphthalenedicarboxylic acid functionalized phosphomolybdate: Synthesis, crystal structure and optical properties



You-Jing Huang-Fu^a, Xue-Yan Chen^a, Wei Yang^a, Yan Bai^{a,b,*}, Dong-Bin Dang^{a,*}

^a Key Laboratory of Polyoxometalate Chemistry of Henan Province, Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, PR China

^b State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, PR China

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ABSTRACT

One inorganic–organic hybrid phosphomolybdate $H_{12}[(PMo_6O_{21})_2(1,4-NDC)_3] \cdot 37.5H_2O$ (**1**) (1,4- $H_2NDC=1,4$ -naphthalenedicarboxylic acid) has been synthesized and well-characterized. Compound **1** exhibits a lantern-type dimer constructed by Mo–O–C bonds between a couple of $[PMo_6O_{21}]^{3-}$ polyoxoanions and three 1,4- NDC^{2-} ligands, and displays obvious fluorescent emission at room temperature as a result of the use of functional organic component. The spectroscopic experiments show that compound **1** displays a sensitive and reversible fluorescence response to the pH values in the aqueous solution.

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1. Introduction

Polyoxometalate (POM) is a polyatomic ion, that consists of three or more group 5 or group 6 transition metal oxyanions linked together by shared oxygen atoms to form a large, closed 3-dimensional framework [1,2]. Currently, POMs are an attractive and vast class of inorganic materials with a virtually unmatched range of physical and chemical properties applicable to diverse areas of research such as catalysis, photochemistry, sorption, biology and medicine [3–5]. A great deal of interest has arisen in the modification and functionalization of POMs as a result of their unique structures and fascinating optical, electronic, and magnetic properties [6–8]. In this sense, the introduction of functional organic components to POMs via covalent bonds is an efficient and attractive synthetic approach, since the desired physical properties can be imparted to target products [9–11]. Examples suggest that carboxylic acids are a better selection for constructing the functionalization of POMs, due to their oxygen donors are more likely to substitute for the terminal oxygen atoms of POMs forming metal–oxygen–carbon connectivity combination [12–14]. In this kind of composite, some benzene–carboxylic acids and aliphatic carboxylic acids were selected, and their coordination to metal atoms of POMs leads to a variety of

carboxylate-functionalized polyanions [13,14]. However, introducing functional carboxylic acid to the design of luminescent POMs-based hybrid species is rare. The luminescence, with huge technical potential, brings about high speed development and widespread applications in display, lighting, sensing and optical devices [15]. POM-based hybrids have attracted considerable attention in the fields of luminescent materials, since the properties of products can be adjusted by the judicious choice of conjugated organic groups and POM units. In the present study, we opted to use 1,4-naphthalenedicarboxylic acid as functional component to synthesize a POM-based inorganic–organic hybrid compound $H_{12}[(PMo_6O_{21})_2(1,4-NDC)_3] \cdot 37.5H_2O$ (**1**). The title compound exhibits luminescent emission at room temperature in H_2O solution and in the solid state, respectively. The luminescence recognition behaviors suggest that the emission intensity of compound **1** is dramatically affected by the pH values of the solution.

2. Experimental

Synthesis: $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (0.86 mmol), 1,4-naphthalenedicarboxylic acid (1,4- H_2NDC) (1.5 mmol) and H_3PO_3 (1 mmol) were dissolved in water (15 mL), and then the mixture was stirred approximately 2 h at 72 °C. After cooling to room temperature, the resulting solution was filtered and left for slowly evaporation at room temperature to obtain colorless block crystals **1** suitable for single crystal X-ray structure determination after about four weeks. Yield: ca. 54% for **1** (based on H_3PO_3). The general chemical formula sum is $C_{36}H_{69}Mo_{12}P_2O_{91.50}$. Anal. Calcd(%): C, 13.60; H,

* Corresponding authors at: Key Laboratory of Polyoxometalate Chemistry of Henan Province, Institute of Molecular and Crystal Engineering, School of Chemistry and Chemical Engineering, Henan University, Kaifeng 475004, PR China. #Tel./fax: +86 371 23881589.

E-mail addresses: baiyan@henu.edu.cn (Y. Bai), dangdb@henu.edu.cn (D.-B. Dang).

2.19; Mo, 35.81; P, 1.93. Found: C, 13.44; H, 2.37; Mo, 33.66; P, 2.02. IR (cm^{-1} , KBr pellet): 3450(s), 3172(s), 2417(w), 1627(m), 1562(s), 1461(s), 1421(s), 1372(s), 1264(w), 1212(w), 1167(w), 1074(s), 1000(w), 933(s), 897(s), 835(m), 798(m), 684(s), 567(m).

3. Results and discussion

Description of the crystal structure of compound 1: Compound 1 exhibits a lantern-type dimer by coordinative connectivity combination between a couple of $[\text{PMo}_6\text{O}_{21}]^{3-}$ polyoxoanions and three 1,4-NDC²⁻ ligands (Fig. 1). Analogous to the reported structure, all of the carboxyl groups are both in $\mu_2\text{-}\eta^1\text{:}\eta^1$ fashion to connect molybdenum centers via Mo–O–C bonds, obtaining a carboxylate-functionalized heteropolyanion [13]. It is worth pointing out that, the other side of the naphthalene rings is spread outside the dimer for forming a lantern-type structure. On the other hand, three types of C–H \cdots O hydrogen bonds and one type of C–H \cdots π interaction are found in compound 1, which plays an important role in stabilizing the structure [16–18]. The C \cdots M separation and C–H \cdots M angle is 4.00 Å and 127.9°.

$[\text{PMo}_6\text{O}_{21}]^{3-}$ polyoxoanion of 1 is a well-known α -Anderson structure composed of six corner- or edge-sharing MoO_6 octahedra (Fig. S1). The central P atom is surrounded by three μ_3 -O atoms with the average P–O distance of 1.527 Å and the O–P–O angles of 111.3

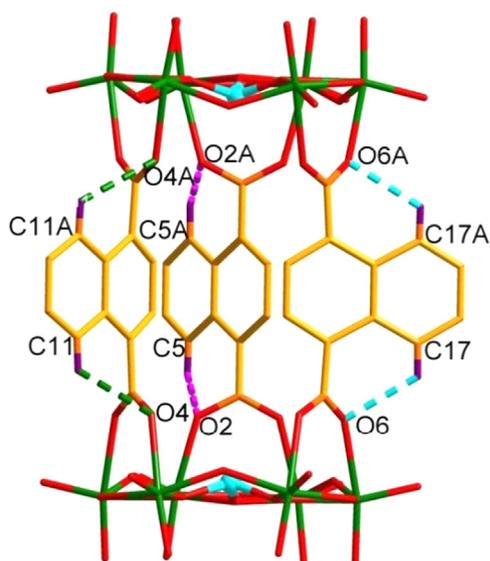


Fig. 1. The illustration of the lantern-type dimer for compound 1 showing C(5)–H(5A)···O(2) (pink), C(11)–H(11A)···O(4) (green) and C(17)–H(17A)···O(6) (turquoise) hydrogen bonds in dashed lines. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

(3)–111.9(3)°. The MoO_6 octahedra are distorted, with Mo–O distances that can be grouped into four ranges depending on the kind of oxygen atoms bound to the molybdenum atoms. The longest distance is that towards the triply bridging oxygen atoms in the range of 2.330(4)–2.362(5) Å. The distances between the molybdenum atoms and the oxygen atoms from six O–C bonds are in the range of 2.270(5)–2.322(4) Å. The doubly bridging and the terminal oxygen atoms are at distances from the molybdenum atoms of 1.703(5)–1.717(5) Å and 1.898(5)–1.947(5) Å, respectively.

X-ray powder diffraction: To confirm whether the crystal structure is truly representative of the bulk material, the X-ray powder diffraction patterns of 1 were recorded. The peak positions of experimental patterns are in good agreement with the corresponding simulated ones, demonstrating the phase purity of the products (Fig. S2). The dissimilarities in intensity may be due to the preferred orientation of the crystalline powder samples.

Optical band gap: The UV–vis absorption spectrum of 1 in solid state shows two strong absorption peaks at 236 nm and 310 nm (Fig. S3). The higher energy spectral band can be assigned to $p\pi$ (Oterminal)– $d\pi^*$ (Mo) electronic transitions in the Mo=O bonds, whereas the lower energy spectral band can be attributed to $d\pi$ – $p\pi$ – $d\pi$ electronic transitions between the energetic levels of the Mo–O–Mo bonds [19].

In order to explore the conductivity potential of 1, the measurement of diffuse reflectance spectrum for powder sample was conducted to obtain the band gap (E_g). The band gap is determined as the intersection point between the energy axis and the line extrapolated from the linear portion of the absorption edge in a plot of Kubelka–Munk function F , $F=(1-R)^2/2R$ (R is the reflectance of an infinitely thick layer at a given wavelength), against energy E . The optical absorption related to the E_g value can be accessed at 3.38 eV, exhibiting the energy value of an electron from the highest valence band to the lowest conduction band, which shows the nature of semiconductivity for 1 (Fig. 2) [20]. Compared with the reported POM-based inorganic–organic hybrid solids $[(\text{H}_2\text{toym})_4(\text{Mo}_8\text{O}_{26})_2] \cdot 15\text{H}_2\text{O}$ ($E_g=2.99$ eV) (toym=2,4,6-tris[1-(4-oxidoxyridinium)-ylmethyl]-mesitylene), and $(n\text{-Bu}_4\text{N})_2[\text{Mo}_6\text{O}_{17}(\text{NAr})_2]$ ($E_g=2.25$ eV) ($\text{Ar}=o\text{-CH}_3\text{OC}_6\text{H}_4$), compound 1 shows a wider band gap [21,22].

Luminescence properties: A strategy of the incorporation of 1,4-naphthalenedicarboxylic acid into POM-based system is anticipated to obtain functional hybrid materials with excellent optical properties, in which naphthalene ring could act as the chromophoric group of a photochemically active compound. As we expected, compound 1 shows luminescent emission maximum at 403 nm ($\lambda_{\text{ex}}=300$ nm) in the solid state (Fig. 2) and 428 nm ($\lambda_{\text{ex}}=330$ nm) in aqueous solution (Fig. S4), respectively, which may be assigned to the intraligand $\pi^*\text{--}\pi$ charge transfer. Compared to the free ligand 1,4- H_2NDC with the emission peak of 472 nm, obvious blueshift may result from the formation of Mo–O–

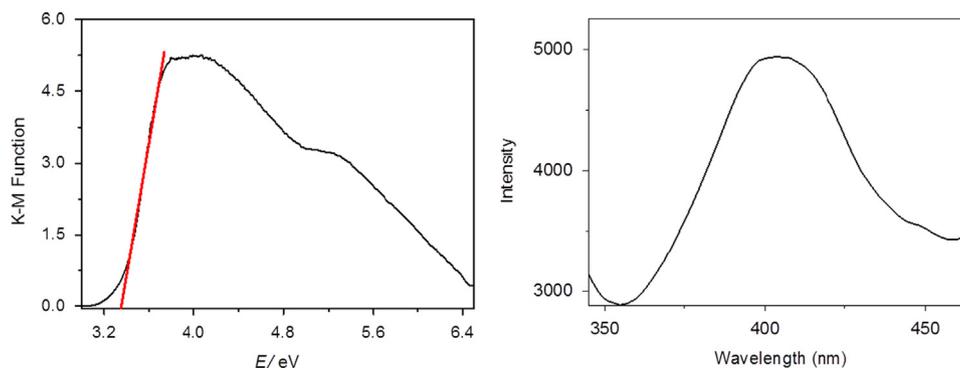


Fig. 2. Diffuse reflectance UV–vis spectrum of K–M function versus E (left) and luminescent spectrum (right) of compound 1 in solid state.

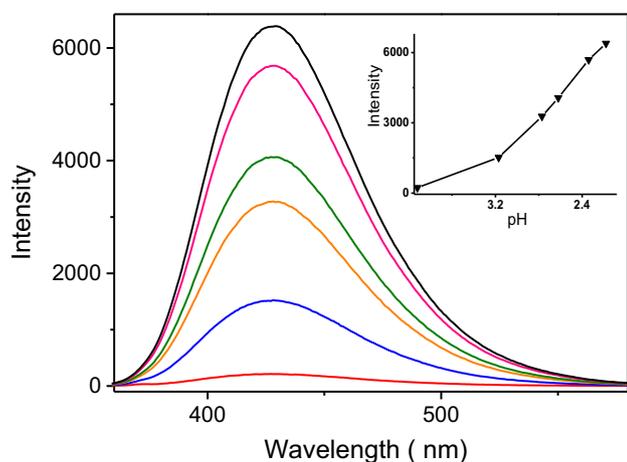


Fig. 3. pH-dependent fluorescence responses of **1** in aqueous solution. pH=2.18, Black; 2.34, Pink; 2.62, Olive; 2.77, Orange; 3.17, Blue; 4.02, Red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

C bonds between $[\text{PMo}_6\text{O}_{21}]^{3-}$ polyoxoanions and ligands. These results have been commonly observed in other 1,4- H_2NDC -containing systems [23–25].

The influence of the pH value on the luminescence properties of compound **1** was studied in the aqueous solution, as shown in Fig. 3. The solution was adjusted using HCl solution. The reactions were conducted at room temperature for 2 min, and then the luminescence spectra were monitored, respectively. Upon the addition of H^+ , the emission intensity of compound **1** significantly increases at 428 nm. As the pH value is reduced to 2.18, the emission intensity of the system increases by about 28 times ($I/I_0=27.52$, where I_0 and I are the fluorescence emission intensities of before and after H^+ was added, respectively). When the pH value less than 2.18, nearly no change is observed for the emission intensity. And then NaOH solution was added to the above solution (pH=2.18). The emission intensity of compound **1** significantly decreases at 428 nm with increasing added NaOH solution. When the pH value is 4.02 the fluorescence of the system is almost completely quenched (Fig. S5). These experiments reveal that the process of consecutive addition of HCl or NaOH is reversible, which is important for probe material.

The ^{31}P NMR spectra of **1** in aqueous solution indicate the structure remains stable over a period of 3 days (Fig. S6). Otherwise, the solution of compound **1** in various pH values has also been measured via UV–vis spectra, indicating the structure is still stable in the pH range of 2.18–4.96 in 3 days (Fig. S7). As a result, it may be concluded that compound **1** displays a sensitive and reversible fluorescence response to the pH values in the aqueous solution and would be used as pH probe.

4. Conclusion

In summary, we presented a carboxylate-functionalized lantern-type phosphomolybdate exhibiting interesting fluorescence as a result of the introduction of 1,4-naphthalenedicarboxylic acid

ligand. Notably, compound **1** exhibits a sensitive and reversible fluorescence response to the pH values in the aqueous solution, and it may be an excellent candidate for pH probe. Herein, we have demonstrated an effective strategy to yield fluorescent POM-based compounds in which functional organic acids are introduced into hybrid systems, which subsequently give access to design such compounds into optical functional materials.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2015.04.102>.

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