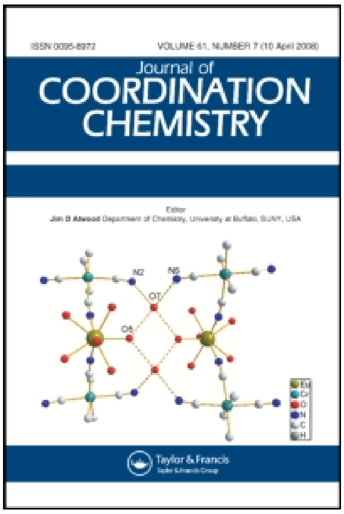

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Polyoxotungstate clusters: syntheses, characterization, and crystal structures of $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ and $[Cu^{I}(phen)_2]_3[\alpha\text{-}PW_{12}O_{40}]$

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Two new copper–phosphotungstate complexes $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ (**1**) and $[Cu^{I}(phen)_2]_3[\alpha\text{-}PW_{12}O_{40}]$ (**2**) (1,3-dap = 1,3-diaminopropane, phen = 1,10-phenanthroline) have been synthesized and characterized by elemental analyses, IR spectroscopy, UV spectroscopy, thermogravimetric analyses, fluorescence spectroscopy, X-ray photoelectron spectroscopy, and single-crystal X-ray diffraction. Single-crystal diffraction analyses indicate that both **1** and **2** consist of a saturated α-Keggin phosphotungstate fundamental building unit as polyoxoanions and several metal–organic moieties as counter-cations. In **1**, two $[Cu(1,3\text{-dap})]^{2+}$ complex cations are capped on the polyoxoanion $[PW_{10.5}Cu^{II}_{1.5}O_{40}]^{9-}$ through four bridging oxygens and the other two $[Cu(1,3\text{-dap})_2]^{2+}$ coordination cations are grafted on the terminal oxygens of the polyoxoanion, whereas in **2**, three $[Cu(phen)_2]^{2+}$ complex cations are discrete. Fluorescence reveals that **2** exhibits a broad emission band at 437 nm upon excitation at 380 nm.

Keywords: Polyoxometalate; Hydrothermal conditions; Crystal structure; Fluorescence

1. Introduction

Polyoxometalates (POMs), as important molecular building units, exhibit fascinating properties in medicine, material science, photochemistry, electrochemistry, and magnetism [1–4]. Among the different types of POMs, the most useful are the Keggin-type polyoxoanions, especially phosphotungstate anions. Various structurally characterized Keggin-based phosphotungstate metal–organic complexes or organic–inorganic hybrid materials have been reported [5–24]. In 2000, You *et al.* [21] first reported a discrete α-Keggin heteropolyanion-supported transition metal complex $[Ni(2,2'\text{-bipy})_3]_{1.5}[PW_{12}O_{40}Ni(2,2'\text{-bipy})_2(H_2O)]\cdot 0.5H_2O$. In 2006, Wang *et al.* [22] prepared two interesting 1-D potassium ion-bridged chain-like heteropolytungstates assembled

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from bisupporting Keggin units $K[M(phen)_2(H_2O)]_2[PW_{12}O_{40}] \cdot 2H_2O$ ($M = Fe^{II}$, Cu^{II}, phen = 1,10-phenanthroline). In the same year, Long *et al.* [23] synthesized five Keggin-based 3-D coordination polymers and investigated the influence of steric hindrance of organic ligand on the structures of Keggin-based coordination polymers. Interestingly, Duan *et al.* [24] discovered a large protonated-water-cluster $[H(H_2O)_{27}]^+$ trapped 3-D metal–organic framework with cubic cavities formed by cobalt(II) and 4,4′-bipyridine-N,N′-dioxide. In 2007, Xu *et al.* [25] obtained a 1-D linear chain $Na_4(OH)[(Cu_2EDTA)PW_{12}O_{40}] \cdot 17H_2O$ built by Keggin-type $[PW_{12}O_{40}]^{3-}$ polyanions and dimeric $[Cu_2(EDTA)]$ complexes by the reaction of Keggin polyoxotungstate with copper(II)–EDTA complex under mild conditions. In 2008, Lu *et al.* [26] isolated a new optical supramolecular phosphotungstate $[(H_3O)(C_{12}H_{10}N_3)_2(PW_{12}O_{40})]$. In the past several years, our group has also made some efforts toward the construction of Keggin-based phosphotungstate metal–organic derivatives [27–33]. For example, in 2004, we reported a 1-D double-chain heteropoly complex $\{[Ba(DMSO)_3(H_2O)_3][C_5H_6N]PW_{12}O_{40} \cdot DMSO \cdot 2H_2O\}_n$, in which two parallel chains are connected through $W–O_t–Ba$ links [27]. As a part of our work, here we report the hydrothermal syntheses and crystal structures of two new discrete organic–inorganic phosphotungstates $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ (**1**) and $[Cu^{I}(phen)_2]_3[\alpha\text{-}PW_{12}O_{40}]$ (**2**). In **1**, two $[Cu(1,3\text{-dap})]^{2+}$ complex cations are capped on the polyoxoanion $[PW_{10.5}Cu^{II}{}_{1.5}O_{40}]^{9-}$ through four bridging oxygens and the other two $[Cu(1,3\text{-dap})_2]^{2+}$ coordination cations are grafted on the terminal oxygens of the polyoxoanion, while in **2**, three $[Cu(phen)_2]^+$ complex cations are discrete. Fluorescence reveals that **2** exhibits a broad emission band at 437 nm upon excitation at 380 nm.

2. Experimental

2.1. *Instruments and materials*

$Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$ was synthesized according to the procedures described in the literature [34]. $Cu(CH_3COO)_2 \cdot H_2O$, phen, and 1,3-dap were commercially available and used without purification. FT-IR spectra were recorded from KBr pellets at 4000–400 cm^{-1} with a Nicolet 170 FT-IR spectrometer. UV spectra were obtained on a U-4100 spectrometer (distilled water as solvent) from 400 to 190 nm. Photoluminescence measurements were performed on a F-7000 fluorescence spectrometer. Thermogravimetric (TG) analyses were performed under N_2 on a Perkin Elmer 7 instrument with a heating rate of $10^{\circ}C\ min^{-1}$ from 25°C to 600°C. X-ray photoelectron spectroscopy (XPS) analysis was performed on an Axis Ultra spectrometer with an Al-Kα achromatic X-ray source. Elemental analyses (C, H, and N) were performed on a Perkin Elmer 2400 CHN elemental analyzer.

2.2. *Preparations of complexes*

2.2.1. $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ (1). $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$ (1.4 g, 0.55 mmol), $Cu(CH_3COO)_2 \cdot H_2O$ (0.2 g, 1 mmol), and 1,3-dap (0.2 mL, 2.4 mmol) were successively dissolved in 15 mL of distilled water and the pH of the mixture solution was adjusted to 6.7 with 1.0 M NaOH. After stirring for 2.5 h, the solution was sealed in a 30 mL Teflon-lined autoclave and kept at 180°C for 5 days. After slowly cooling to room temperature, black crystals were obtained by filtering. The crystals were washed with distilled water and dried in air. Yield: 31% (based on $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$). Anal. Calcd (%): C, 6.36; H, 1.81; N, 4.95. Found (%): C, 6.52; H, 1.96; N, 4.87.

2.2.2. $Cu^I(phen)_2]_3[\alpha\text{-}PW_{12}O_{40}]$ (2). $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$ (0.517 g, 0.20 mmol), $CuCl_2 \cdot 2H_2O$ (0.13 g, 0.76 mmol), and $CeCl_3 \cdot 7H_2O$ (0.13 g, 0.35 mmol) were successively dissolved in 15 mL of distilled water, and then a solution of 4 mL methanol : water (1 : 1, volume ratio) containing 1,10-phenanthroline (0.05 g, 0.28 mmol) was added dropwise. After stirring for 2.5 h, the resulting solution was sealed in a 30 mL Teflon-lined autoclave, and kept at 170°C for 7 days. After slowly cooling to room temperature, black crystals were obtained by filtering. The crystals were washed with distilled water and dried in air. Yield: 56% (based on $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$). Anal. Calcd (%): C, 20.84; H, 1.17; N, 4.05. Found (%): C, 20.72; H, 1.36; N, 3.91.

2.3. *Crystal structure determination*

A suitable single crystal with dimensions of $0.12 \times 0.10 \times 0.09\,mm^3$ for **1** and $0.19 \times 0.16 \times 0.13\,mm^3$ for **2** was attached to the end of a glass fiber with enamel adhesive. Intensity data were obtained on a Bruker APEX-II CCD using Mo-Kα monochromated radiation ($\lambda = 0.71073$ Å) at 296(2) K. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXTL-97 software [35]. Lorentz polarization and empirical absorption corrections were applied. Hydrogens associated with water were not located from the difference Fourier map. The hydrogens attached to carbon and nitrogen were geometrically placed. All hydrogens were refined isotropically as a riding mode using the default SHELXTL parameters. A summary of the crystallographic data and structural determination for **1** and **2** are listed in table 1.

3. Results and discussion

3.1. *Synthesis*

The hydrothermal method has been proved as a routine method in the preparation of novel inorganic–organic composite materials. Both **1** and **2** were hydrothermally synthesized by the reaction of trivacant Keggin POM precursors in the presence of ligands. Complex **1** was isolated with a yield of 31% by the reaction of $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-}$, $Cu(CH_3COO)_2 \cdot H_2O$, and 1,3-dap, while **2** was synthesized by the reaction of $Na_9[A\text{-}\alpha\text{-}PW_9O_{34}] \cdot 7H_2O$, $CuCl_2 \cdot 2H_2O$, and $CeCl_3 \cdot 7H_2O$ with the addition of a solution of methanol : water (1 : 1, volume ratio) containing 1,10-phenanthroline. The experimental results indicated that ethanol and Ce^{3+} ions are necessary for the formation of **2**, although both were not observed in the product. In the presence of the Ce^{3+} ion and ethanol, **2** can be isolated with a good yield (56%). If no Ce^{3+} ion or ethanol exists

Table 1. Summary of crystallographic data and structure refinements for **1** and **2**.

	1	**2**
Empirical formula	$C_{18}H_{61}N_{12}O_{40}Cu_{5.5}PW_{10.5}$	$C_{72}H_{48}N_{12}O_{40}Cu_3PW_{12}$
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	26.205(5)	14.0187(13)
b	20.583(4)	15.5564(14)
c	13.249(3)	20.3800(19)
α	90	83.450(2)
β	119.166(3)	89.661(2)
γ	90	78.262(2)
Volume (Å^3), Z	6240(2), 4	4322.5(7), 2
θ range for data collection (°)	1.33–25.00	1.99–25.00
Limiting indices	$-30 \le h \le 31$; $-20 \le k \le 24$; $-15 \le l \le 15$	$-16 \le h \le 15$; $-18 \le k \le 16$; $-24 \le l \le 23$
Independent reflections	5429 [R(int) = 0.0352]	15,128 [R(int) = 0.0328]
Completeness to $\theta = 25.00$ (%)	98.9	99.2
Data/restraints/parameters	5429/18/407	15128/12/1261
Goodness-of-fit on F^2	1.171	1.005
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0577$, $wR_2 = 0.1315$	$R_1 = 0.0423$, $wR_2 = 0.0965$

in the reaction system, only powder samples are obtained. However, the detailed roles of Ce^{3+} and ethanol in this reaction system remain unclear. Similar phenomenon has been observed previously [36].

The transformation of $[A\text{-}\alpha\text{-}PW_9O_{34}]^{9-} \rightarrow [\alpha\text{-}PW_{12}O_{40}]^{3-}$ must have occurred in the formation of **1** and **2**. Such transformation of trivacant Keggin polyoxoanions to saturated Keggin polyoxoanions under hydrothermal conditions has been previously reported [37]. Cu(I) ion was not used in the starting materials in **2**; the Cu(I) in **2** must have come from the reduction of Cu(II) in the presence of phen as a reducing agent. High oxidation state metals are commonly reduced by nitrogen ligands under hydrothermal conditions [38, 39].

3.2. *Description of crystal structure*

Although **1** and **2** were prepared under hydrothermal conditions, both crystal systems and space groups are distinct. Complex **1** crystallizes in the monoclinic space group $C2/c$ whereas **2** belongs to the triclinic space group $P\bar{1}$. Single-crystal diffraction analyses indicate that **1** and **2** consist of a saturated α-Keggin phosphotungstate fundamental building unit as polyoxoanion and several metal–organic moieties as countercations. The asymmetric unit of **1** consists of $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ polyoxoanion. Intriguingly, in $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ polyoxoanion, two $[Cu(1,3\text{-dap})]^{2+}$ cations coordinate to $[PW_{10.5}Cu_{1.5}O_{40}]^{9-}$ through four bridging oxygens from the polyoxoanion and the other two $[Cu(1,3\text{-dap})_2]^{2+}$ coordination cations are linked to the terminal oxygens of the polyoxoanion skeleton (figure 1a). Such connection motif between metal–organic complex cations and bridging oxygens on POM units in **1** has been previously observed [40–43]. In these reported organic–inorganic hybrid Keggin-based POMs, each metal–organic complex cation is connected to the Keggin-type polyoxoanion *via* one bridging

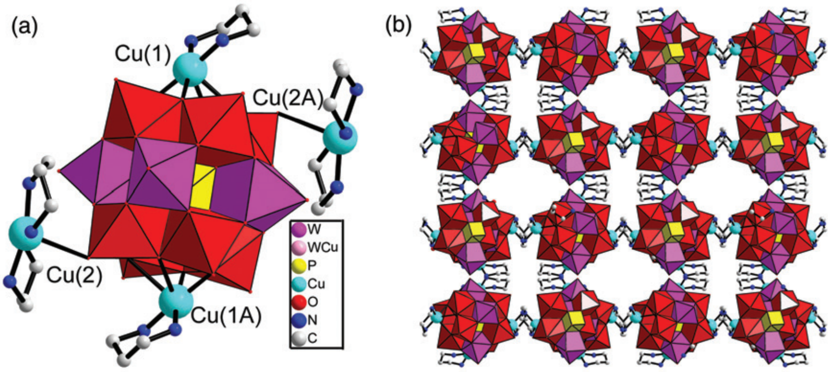

Figure 1. (a) Perspective view of the molecular structural unit for **1**. (b) View of the crystal packing along the *c*-axis for **1**.

and one terminal oxygen or only a bridging oxygen, while in **1**, each $[Cu(1,3\text{-dap})_2]^{2+}$ cation is bonded to $[PW_{10.5}Cu_{1.5}O_{40}]^{9-}$ through four bridging oxygens rather than a terminal and a bridging oxygen or only one bridging oxygen. Bond valence sum (BVS) calculations illustrate that the oxidation states of all coppers in $[Cu(1,3\text{-dap})_2]^{2+}$ and $[Cu(1,3\text{-dap})]^{2+}$ are +2 [44, 45]. Considering the charge balance requirement of **1** along with two $[Cu(1,3\text{-dap})_2]^{2+}$ and two $[Cu(1,3\text{-dap})]^{2+}$ cations, one proton is required in the chemical formula of **1**, which is in good accordance with the acidic environment of the reaction system ($pH = 6.7$).

The $[PW_{10.5}Cu_{1.5}O_{40}]^{9-}$ polyoxoanion is the classical Keggin-type polyoxoanion, further confirmed by the IR spectrum of **1**. In $[PW_{10.5}Cu_{1.5}O_{40}]^{9-}$, W(2) and W(2A, $0.5-x$, $0.5-y$, $1-z$) sites are simultaneously statistically occupied by 75% W^{VI} and 25% Cu^{II}, and the W(4) and W(4A, $0.5-x$, $0.5-y$, $1-z$) sites are simultaneously statistically occupied by 50% W^{VI} and 50% Cu^{II}, resulting in 1.5 expected $copper^{II}$ ions per Keggin cage. This phenomenon that one site is simultaneously statistically occupied by two elements has been encountered in reported polyoxotungstates [29, 37, 46].

$[Cu(1)(1,3\text{-dap})]^{2+}$ shows a severely distorted octahedral geometry formed by two nitrogens from 1,3-dap [$d_{Cu–N}$: 1.97(2)–1.981(19) Å] and four bridging oxygens [$d_{Cu–O}$: 1.993(13)–2.7214(178) Å] from Keggin polyoxoanion. The connection modes between the coordination cation and four bridging oxygens of POM units in **1** have been reported in several complexes [47, 48]. The $[Cu(2)(1,3\text{-dap})_2]^{2+}$ coordination cation also utilizes a distorted square-pyramidal coordination configuration, in which four nitrogens from two 1,3-dap ligands [$d_{Cu–N}$: 1.983(15)–2.043(14) Å] are situated on the plane (table S1) and one terminal oxygen [$d_{Cu–O}$: 2.6748(116) Å] from Keggin polyoxoanion occupies the axial site. The Cu–N and Cu–O distances in **1** are comparable with the corresponding analogs in the literature [46, 49].

Figure 1(b) shows the crystal packing viewed down the *c*-axis. Neighboring $[Cu^{II}(1,3\text{-dap})_2]_2[Cu^{II}(1,3\text{-dap})]_2H[\alpha\text{-}PW_{10.5}Cu^{II}_{1.5}O_{40}]$ molecular units are orderly aligned in the –ABAB– mode to form a 3-D supramolecular structure *via* hydrogen-bonding interactions between the surface oxygen on $[PW_{10.5}Cu_{1.5}O_{40}]^{9-}$ and nitrogen on $[Cu(1,3\text{-dap})_2]^{2+}$ and $[Cu(1,3\text{-dap})]^{2+}$ coordination cations with $O\cdots H–N$ distances of 3.03(3)–3.54(2) Å. In addition, the stacking of polyoxoanions forms circular channels with dimensions of *ca* 10.9 × 9.89 Å.

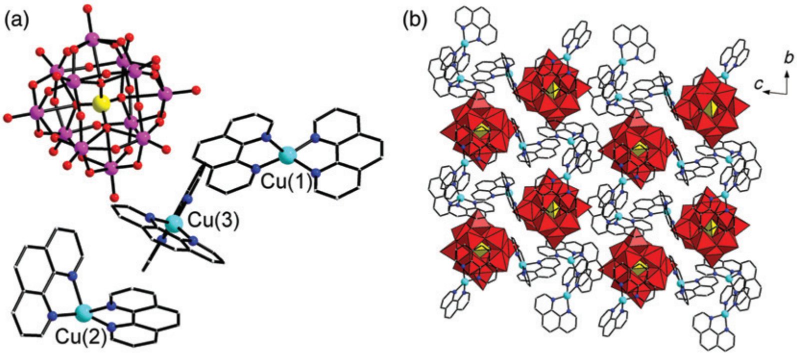

Figure 2. (a) Perspective view of the molecular structural unit for **2**. (b) View of the crystal packing along the *a*-axis for **2**.

The asymmetric unit of **2** is constructed by a α-Keggin $[\alpha\text{-}PW_{12}O_{40}]^{3-}$ polyoxoanion and three discrete $[Cu(phen)_2]^+$ cations (figure 2a). Like the well-known Keggin structure, the polyoxoanion is formed from 12 WO_6 octahedra and one PO_4 tetrahedron. The P–O distances vary from 1.524(6) to 1.544(6) Å, while the W–O distances can be classified into four groups (O_a, oxygen of the PO_4 group; O_b, bridging oxygen in different W_3O_{13} triads; O_c, bridging oxygen in one W_3O_{13} triad; and O_t, terminal oxygen): W–O_a 2.410(5)–2.453(5); W–$O_{b(c)}$ 1.876(6)–1.937(11); and W–O_t 1.679(6)–1.705(6) Å. All the values are consistent with those obtained from the previous studies [37, 40]. Three $[Cu(phen)_2]^+$ coordination cations have distorted tetrahedral geometry defined by four nitrogens from two phen ligands. For $[Cu(1)(phen)_2]^+$, the Cu–N distances are in the range 1.958(9)–2.095(8) Å, with an average value of 2.024 Å, the standard deviations (SDs) of the planes containing C(1)–C(12) and C(13)–C(24) atoms from their least-squares planes are 0.0171 and 0.0383 Å, respectively, and their dihedral angle is 82.1°. For $[Cu(2)(phen)_2]^+$, the Cu–N distances vary between 1.948(8) and 2.129(9) Å, with an average value of 2.043 Å, and the SDs of the planes involving C(25)–C(36) and C(37)–C(48) are 0.0264 and 0.0301 Å, respectively, and their dihedral angle is 73.0°. For $[Cu(3)(phen)_2]^+$, the Cu–N distances range from 2.006(8) to 2.033(8) Å, with an average value of 2.019(8) Å; and the SDs of the plane containing C(49)–C(60) and C(61)–C(72) from their least-squares plane are 0.0514 Å and 0.0313 Å, respectively, and their dihedral angle is 86.6°. Similar metal–phen coordination phenomena have been reported [22, 49, 50]. The 3-D structures in **2** have been formed through C–H $\cdots$ O hydrogen bonds $(C \cdots O = 2.928(12) - 3.441(11))$ between phen ligands and the oxygen of the POMs (figure 2b).

3.3. *TG analysis*

The TG analyses were examined on pure samples of **1** and **2** under flowing nitrogen. The TG curve of **1** gives a loss of 13.8% in the range of 25–600°C (Supplementary material, figure S1), associated with the decomposition of six 1,3-dap ligands (Calcd 13.1%). The TG curve of **2** also exhibits one weight loss stage in the range of 25–600°C

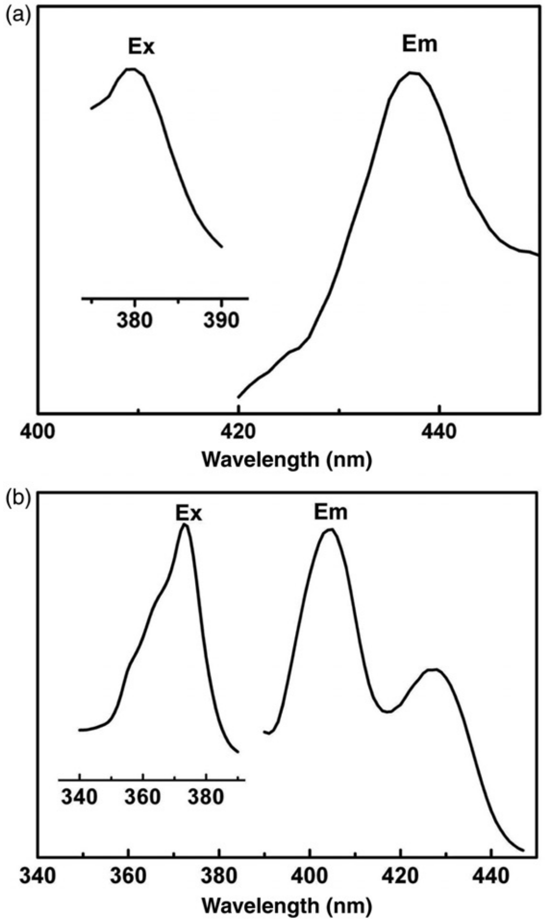

Figure 3. (a) Emission spectrum of phen in the solid state at room temperature. (b) Emission spectrum of **2** in the solid state at room temperature.

(Supplementary material, figure S1). The weight loss of 26.6% between 227°C and 478°C is assigned to the loss of six phen molecules (Calcd 26.1%).

3.4. *Fluorescence*

Emission and excitation spectra of **2** in the solid state at room temperature are depicted in figure 3. Complex **2** exhibits strong photoluminescence with an emission maximum at 438 nm ($\lambda_{ex} = 380$ nm; figure 3a). In order to understand the nature of the emission band, photoluminescence of free phen has also been studied, the emission maxima of which exhibit two emission bands at 403 and 427 nm ($\lambda_{ex} = 374$ nm; figure 3b). When the free phen ligands were coordinated by Cu^+, the emission band of **2** has a red-shift and shows only one emission band, the major reason of which may be the interaction between phen and copper(I). According to previous reports [51–57], the emission is

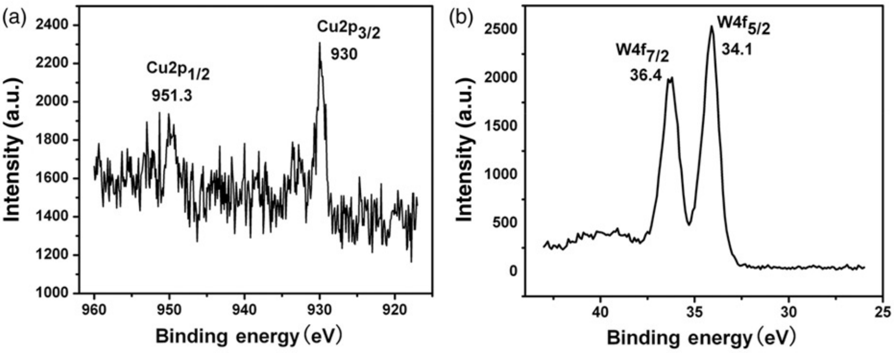

Figure 4. X-ray photoelectron spectra of **2**.

assigned to a mixed excited state of Cu^I and ligand-to-metal charge-transfer (LMCT) transitions. The above analysis shows that the complex is a potential photoactive material.

3.5. *IR and UV spectra*

IR spectra of **1** and **2** (figure S2) are very useful for the identification of characteristic vibration bands of Keggin polyoxoanions and organic components in products. In IR spectra of **1** and **2**, bands at 700–1100 cm^{-1} are indicative of Keggin-type polyoxoanions. The four characteristic bands at 943, 864, 792, and 701 cm^{-1} for **1**, and 975, 892, 815, and 721 cm^{-1} for **2** are attributed to $\nu_{as}(W–O_d)$, $\nu_{as}(P–O_a)$, $\nu(W–O_b)$, and $\nu_{as}(W–O_c)$, respectively, in accordance with the saturated Keggin-type polyoxoanions [58]. In addition, vibrations in the 3446–2878 cm^{-1} region in **1** are indicative of 1,3-dap groups. Vibration bands at 1077–1621 cm^{-1} in **2** are assigned to phen.

Figure S3 shows the UV spectra of **1** and **2** performed in aqueous solution in the range of 400–190 nm. Both **1** and **2** reveal two characteristic peaks, the strong absorptions centered at 192 nm for both and the weak at 252 and 271 nm, respectively. The higher energy absorption can be assigned to $p\pi$–$d\pi$ charge-transfer transitions of the $O_d \rightarrow W$ bonds, whereas the lower energy absorption is attributed to the $p\pi$–$d\pi$ charge-transfer transition of $O_{b,c} \rightarrow W$ bonds [6].

3.6. *X-ray photoelectron spectroscopy*

The oxidation states of W and Cu in **2** are further confirmed by XPS measurements (figure 4). The XPS spectra exhibit two overlapped peaks at 36.4 and 34.1 eV, attributed to W^{6+} ($4f_{7/2}$) and W^{6+} ($4f_{5/2}$), respectively, and two peaks at 930.0 and 951.3 eV can be assigned to Cu^+ ($2p_{3/2}$) and Cu^+ ($2p_{1/2}$) [59, 60], respectively.

4. Conclusion

Two organic–inorganic POMs containing saturated α-Keggin phosphotungstate fundamental building blocks have been synthesized by hydrothermal conditions, structurally characterized, and investigated by thermal behavior. The fluorescence measurement reveals that **2** exhibits a broad emission band at 437 nm upon excitation at 380 nm. From our investigation, we suggest that these two complexes may have applications in medicine, catalysis, and photochemistry.

Supplementary material

Crystallographic data for the structural analyses reported in this article have been deposited with the Cambridge Crystallographic Data Centre with CCDC nos 753139 for **1** and 753140 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

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