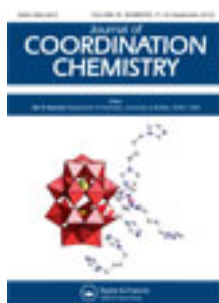


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One polyoxometalate-based hybrid 3-D network: synthesis, structure, photo- and electro-catalytic properties

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One polyoxometalate-based hybrid 3-D network: synthesis, structure, photo- and electro-catalytic properties

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A new polyoxometalate-based inorganic–organic hybrid material, $H_5Ag(Bbi)_{1.5}(Bbi)_2[P_2W_{18}O_{62}]$ (**1**) (Bbi = 1,1-(1,4-butanediyl)-bis(imidazole)), has been hydrothermally synthesized and characterized by single-crystal X-ray diffraction, elemental analyses, IR spectroscopy, and thermogravimetric analysis. In **1**, adjacent $[P_2W_{18}O_{62}]^{6-}$ (short for P_2W_{18}) anions are connected through Ag by equatorially positioned terminal oxygen atoms to generate a 1-D chain. Adjacent chains were further connected through Ag and two-coordinated Bbi ligands into a (6, 3)-layer, which are extended to 3-D supermolecule nets through H bonds. The photo- and electro-catalytic properties of **1** have been studied.

Keywords: Polyoxometalate; Hydrothermal synthesis; Supermolecule framework; Photocatalytic property; Electro-catalytic property

1. Introduction

Polyoxometalates (POMs) have attracted interest in material chemistry due to structural diversity and their attractive properties, such as catalytic activity [1] and photo-chemical activity [2]. Catalytic properties of POMs have obtained extensive attention, with a number of reports. Some industrial projects based on POMs catalysis have also been developed, such as oxidation of methacrolein, hydration of olefins (propene and butenes), and polymerization of tetrahydrofuran [3, 4]. As a rapidly growing field, POMs catalysts exhibit three advantages: (1) POMs possess strong acid properties and oxidation for fast reversible multi-electron redox transformations under mild conditions [5]. (2) POMs exhibit very high solubility in various solvents and fairly high thermal stability in the solid state [6]. (3) Their catalytic properties can be tuned in a wide range by changing their chemical compositions [7]. The above-mentioned properties make POMs potential multi-functional catalysts in homogeneous as well as heterogeneous systems.

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Hydrothermal synthesis has become an important and successful technique for preparation of POM-based inorganic–organic hybrid compounds [8]. However, from the crystal engineering point of view for targeted syntheses, hydrothermal reactions are commonly termed as “black box,” which can be affected by factors such as the nature and stoichiometry of reactants, pH, crystallization temperature, and reaction time [9]. However, to rationalize the reactivity pattern in formation of targeted compounds under hydrothermal conditions, chemists have systematically analyzed the chemistry involved in controlling reactions and, hence, the structures [10, 11]. For example, Long and co-workers have studied the effects of pH, POM anions, and steric hindrance of organic ligands on POM-based inorganic–organic hybrid compounds [12–14]. Zubieta’s group has discussed the influences of ligands and metal ions on the structures of molybdenum oxide networks [15, 16].

A large number of inorganic–organic polymeric compounds based on typical POMs, such as Keggin- [17], Anderson- [18], and Lindqvist-type [19] polyanions, have been reported. However, study on Wells–Dawson polyanions is relatively less [20]; Wells–Dawson-type polyanions have unique properties. First, given 18 terminal and $36\mu_2$ oxygen atoms, the Wells–Dawson-type polyanion offers many potential coordination sites to link metal–organic units, making their modification easier by metal–organic coordination fragments to form more complex high-dimensional structures. Second, there are two categories of M ($M = W/Mo$) in a Wells–Dawson anion, i.e., six polar M and 12 equatorial M atoms, which can provide a chance to bring about unsymmetrical structures. These merits promote POM chemists to extend the Wells–Dawson POM coordination polymer family. Hybrid compounds combining M-organic ($M = Ln, Cu, Zn, \text{ and } Cd$) coordination fragments and Wells–Dawson polyanions have been studied [21, 22]. Recently, Dawson-based hybrid 3-D compounds have attracted interest, and some fascinating hybrid architectures based on it have been reported [23]. An’s group reported a series of new hybrid compounds constructed from Dawson-type phosphomolybdates and metal–organic coordination complexes. Niu’s group reported two new hybrid Dawson-based polyoxotungstates.

However, study on hybrid compounds containing Ag coordination fragments and Wells–Dawson polyanions is scarce. In this article, a new POMs-based inorganic–organic hybrid, $H_5Ag(Bbi)_{1.5}(Bbi)_2[P_2W_{18}O_{62}]$ (**1**), has been obtained under hydrothermal conditions, and its electro- and photo-catalytic properties have been studied.

2. Experimental

2.1. General methods and materials

All reagents were purchased commercially and used without purification. Elemental analysis of W, P, and Ag were performed by a Leaman inductively coupled plasma spectrometer, and C, H, and N were performed on a Perkin-Elmer 2400 CHN elemental analyzer. IR spectra were recorded from 400 to 4000 cm^{-1} on an Alpha Centaur FT/IR spectrophotometer with pressed KBr pellets. Thermogravimetric (TG) analysis was carried out on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of $10^\circ\text{C min}^{-1}$. Cyclic voltammograms (CVs) were obtained by a CHI 660 electro-chemical workstation at room temperature. Platinum gauze was used as counter electrode and an

Ag/AgCl electrode as the reference electrode. Chemically bulk-modified carbon paste electrodes (CPES) were used as working electrodes.

2.2. Synthesis of compound

2.2.1. Synthesis. A mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.5 g, 1.5 mmol), Ag_2SO_4 (0.31 g, 1 mmol), 85% H_3PO_4 (0.1 mL), Bbi (0.06 g, 0.3 mmol), and H_2O (6 mL) was stirred for half an hour at room temperature, transferred to a Teflon-lined autoclave (23 mL) and kept at 180°C for 3 days. After the autoclave was slowly cooled to room temperature at 10°C h^{-1} , it stood for one day. Green crystals were obtained and washed with acetone, and dried in a desiccator (yield 60% based on W). The initial and final pH values of the solution are 5.00 and 6.50, respectively. Elemental analysis for $\text{H}_5\text{Ag}(\text{Bbi})_{1.5}(\text{Bbi})_2[\text{P}_2\text{W}_{18}\text{O}_{62}]$ (**1**) Calcd (%): C, 8.18; H, 1.06; N, 3.81; Ag, 2.10; P, 1.20; W, 64.36; Found (%): C, 8.17; H, 1.09; N, 3.79; Ag, 2.21; P, 1.28; W, 64.07.

2.3. X-ray crystallography

Crystal data for **1** were collected on a Rigaku R-AXISRAPID IP diffractometer equipped with a normal focus 18 kW sealed tube X-ray source (Mo-K α radiation, $\lambda = 0.71073 \text{ \AA}$) operating at 50 kV and 200 mA. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL 97 software package [24]. The positions of the hydrogen atoms on carbons were calculated theoretically. Crystallographic data are given in table 1.

Table 1. Crystal data and structure refinement for **1**.

Compound	1
Empirical formula	$\text{Ag}_2\text{P}_4\text{W}_{36}\text{C}_{70}\text{H}_{103}\text{N}_{28}\text{O}_{124}$
Formula weight	10175.20
Temperature (K)	293(2)
Wavelength (\AA)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (\AA , $^\circ$)	
a	14.657(3)
b	25.820(5)
c	25.425(7)
α	90.00
β	122.35(2)
γ	90.00
Volume \AA^3 , Z	8129(3), 2
Calculated density (Mg m^{-3})	4.157
Absorption coefficient (mm^{-1})	25.740
$F(000)$	8852
Data/restraints/parameters	13,864/0/754
Goodness-of-fit on F^2	1.037
$R_1(I > 2\sigma(I))^a$	$R_1 = 0.0681$
wR_2^b	$wR_2 = 0.1254$

^a $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; ^b $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

3. Results and discussion

3.1. Structure description

Single-crystal X-ray diffraction analysis reveals that **1** contains one P_2W_{18} anion, one crystallographically independent Ag^I , and three and a half Bbi ligands in the asymmetric unit. Bbi ligands in **1** can be divided into three groups (figure S1): two non-coordinated protonated Bbi, a half bi-coordinated Bbi ligand, and one monocoordinated Bbi. In **1**, each Ag^I has a four-coordinate distorted tetrahedral geometry which is defined by two nitrogen atoms from two different kinds of Bbi and two equatorial terminal oxygen atoms from P_2W_{18} anion (figure 1). Adjacent P_2W_{18} anions are connected through Ag by equatorial terminal oxygen atoms to generate a 1-D chain (figure 2). Adjacent chains are further connected through Ag and bi-coordinated Bbi ligands into a (6, 3)-layer (figure 3a and b). These layers are further linked to form a 3-D supramolecular framework *via* hydrogen-bonding interactions (figure S2).

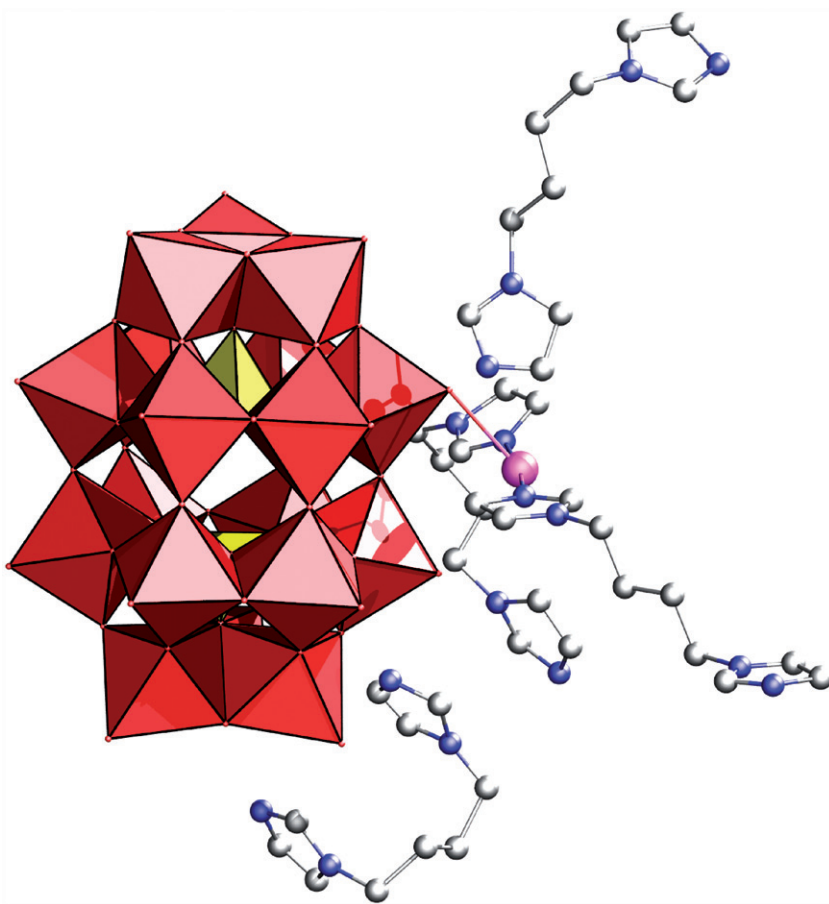


Figure 1. Polyhedral and ball-and-stick representation of the unit cell of **1**.

3.2. FT-IR spectrum

In the IR spectrum of **1**, characteristic bands at 1087, 958, 914, and 788 cm^{-1} are attributed to $\nu(\text{P}-\text{O}_a)$, $\nu(\text{W}-\text{O}_d)$, $\nu(\text{W}-\text{O}_b-\text{W})$, and $\nu(\text{W}-\text{O}_c-\text{W})$ of P_2W_{18} polyanions. Bands at 1707–1238 cm^{-1} are characteristics of Bbi (figure S3) [25].

3.3. TG analysis

The TG curve of **1** exhibits two weight loss steps (figure S4). The first of 7.38% from 290°C to 367°C corresponds to loss of two free Bbi molecules, in accord with the calculated value of 7.40%. The other weight loss is 5.53% from 367°C to 462°C, assigned to removal of 1.5 coordinated Bbi ligands (Calcd: 5.54%).

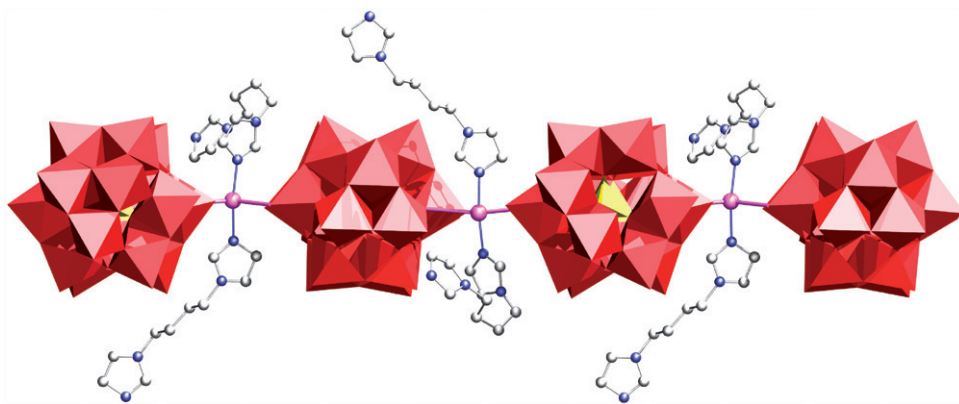


Figure 2. Polyhedral and ball-stick representation of the 1-D structure of **1**.

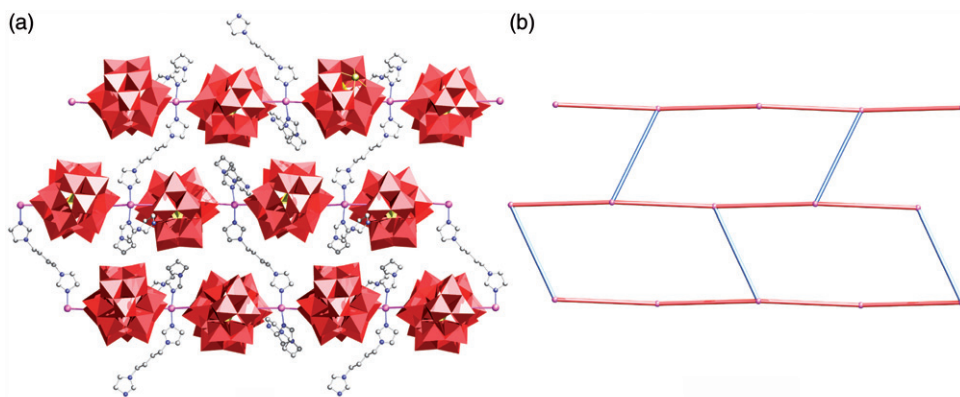


Figure 3. Polyhedral and ball-and-stick representation of the 2-D layer in **1** (a) and the topological representation of the 2-D layer in **1** (b) (the nodes symbolize the Ag center, the sticks symbolize Bbi ligands and P_2W_{18} clusters).

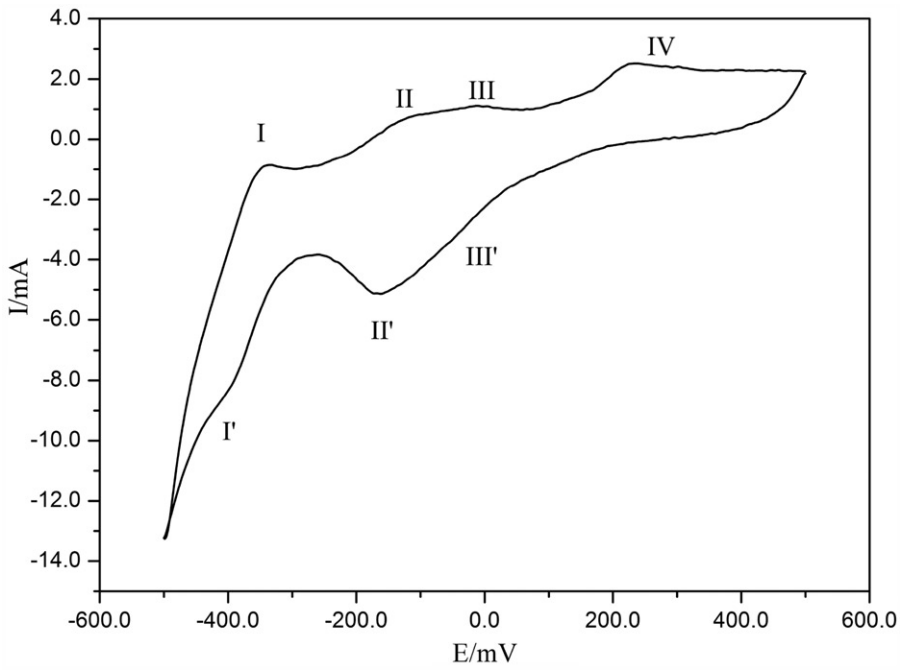


Figure 4. CV curve of **1** in $1 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ aqueous solution at 50 mV s^{-1} .

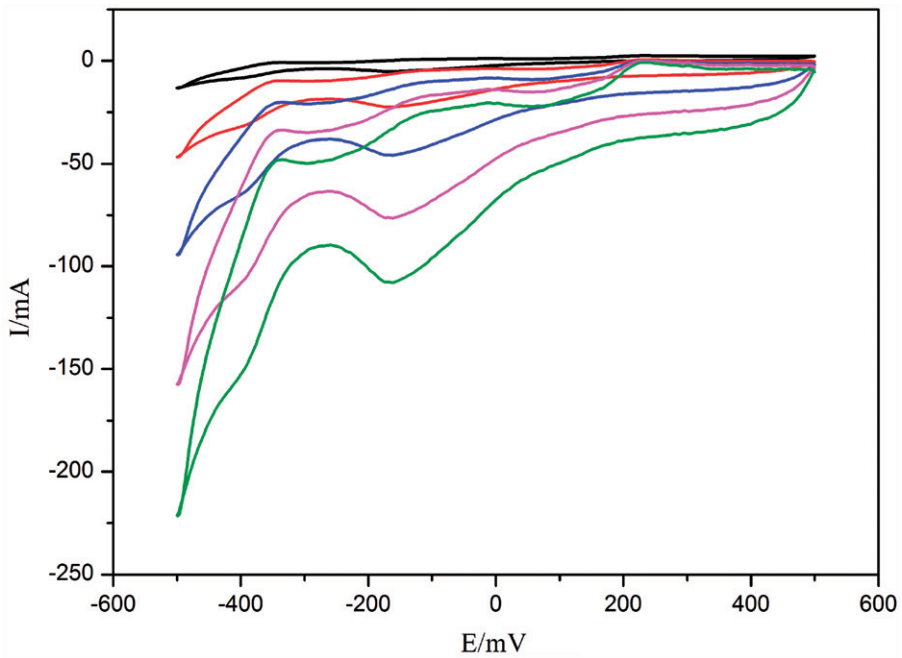


Figure 5. Electro-catalytic activity to reduce nitrite for **1**.

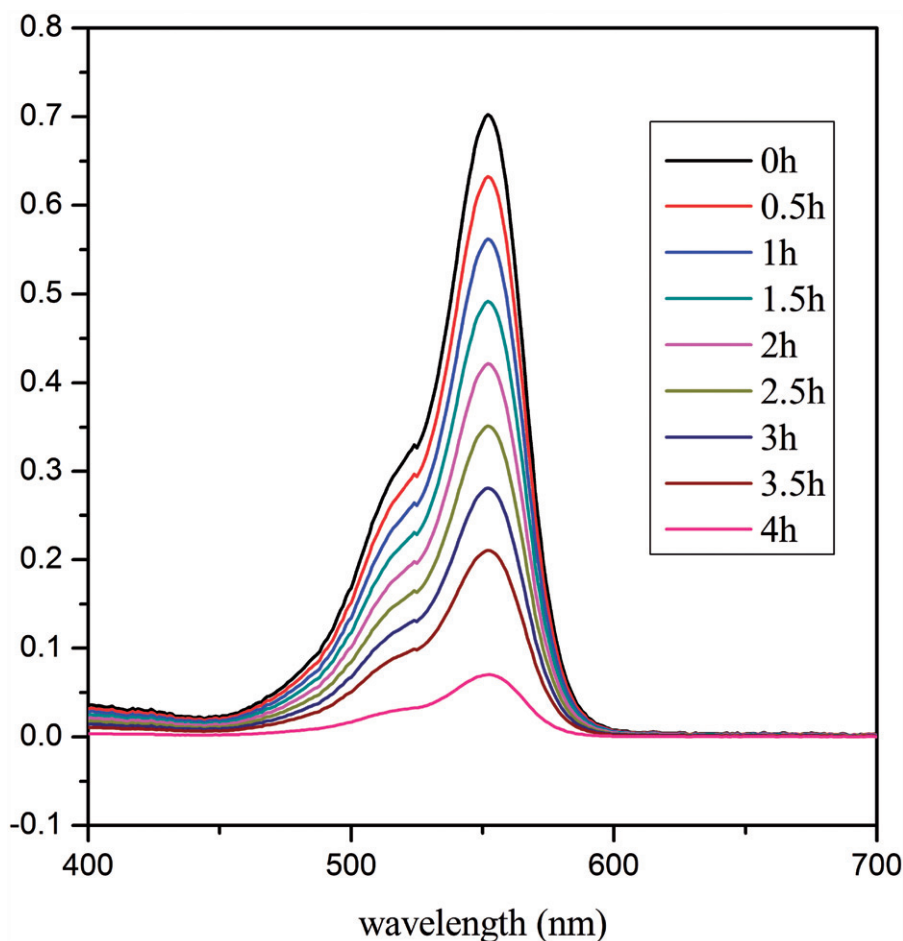


Figure 6. The photo-catalysis behaviors to reduce RhB in solution of **1**.

3.4. The electro-chemical and electro-catalytic properties

In order to investigate the electro-chemical behavior of **1**, the compound has been used as a modifier to fabricate chemically modified carbon paste electrodes (**1**-CEP) due to its high thermal stability and low solubility in water and common organic solvents.

The CV for **1**-CEP in 1 mol L⁻¹ H₂SO₄ aqueous solution at a scan rate of 50 mV s⁻¹ is presented in figure 4. In the potential range of +400 to -800 mV, there are three pairs of redox peaks (I-I', II-II', III-III') with peak potentials $E_{1/2} = (E_{pa} + E_{pc})/2$ of -374.5, -139.5, and -6.0 mV, respectively. The redox peaks can be ascribed to redox of W^{VI/V} in the polyanions [26]. The irreversible anodic peak IV from 200 to 400 mV is assigned to oxidation of Ag centers [27].

1-CPE possesses high stability. When the potential range is maintained between +400 and -800 mV, the peak currents remain unchanged over 200 cycles at a scan rate of 50 mV s⁻¹. After **1**-CPE was stored at room temperature for 1 month, the peak current decreased only 5% and could be renewed by squeezing a little carbon paste out of the

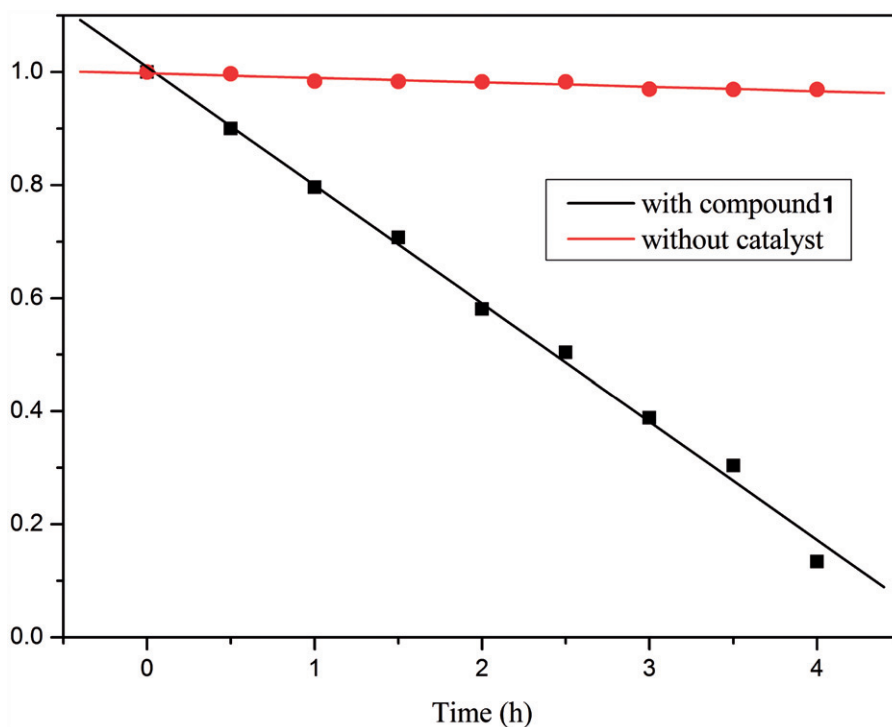


Figure 7. The rate curve of photo-catalysis to reduce RhB.

tube. The high stability of **1**-CPE could be ascribed to the neutral inorganic–organic hybrid material of **1** that stabilizes the polyoxoanions in the compound. Further, **1** is insoluble in the acidic aqueous medium of this experiment, avoiding loss of the modifier during measurements. Thus, **1**-CPE could be an ideal electrode material to investigate electro-catalytic properties.

1-CPE displays good electrocatalytic activity to reduce nitrite (figure 5). At **1**-CPE, with the addition of nitrite, all reduction peak currents of W^{VI} centers on POMs increased while the corresponding oxidation peak currents dramatically decreased, suggesting that nitrite was reduced by reduced polyoxoanion species [28–31]. Furthermore, the catalytic activities were enhanced with increasing extent of the polyoxoanion reduction. In contrast, reduction of nitrite at a bare electrode generally requires a large overpotential and no obvious response was observed at a bare CPE.

3.5. Photo-catalytic property

In a typical process, an aqueous suspension of Rhodamine B (RhB) ($1.8 \times 10^{-5} \text{ mol L}^{-1}$) and 15 mg of **1** was magnetically stirred in the dark for 30 min to ensure the equilibrium of the working solution. The solution was then exposed to UV irradiation from a 125 W Hg lamp at 4–5 cm between the liquid surface and the lamp. The solution was stirred during irradiation. At given time intervals, 3 mL aliquots were

sampled and centrifuged to remove particles. The filtrates were analyzed by UV-Visible spectroscopy [32]. The RhB degradation of **1** is from 100% to 13.4% during 4 h (sampled once each half hour, figure 6). The degradation rate of **1** is nearly linear at about 21.7% an hour. The simple photolysis comparative experiment was also completed under the same conditions without any catalyst (figure 7). Compound **1** had a higher photo-catalytic activity for degradation of RhB.

3.6. Powder X-ray diffraction

Powder X-ray diffraction (PXRD) was measured to confirm the phase purity. The experimental and simulated PXRD patterns of **1** are shown in figure S5. Peak positions are in good agreement with each other, indicating the phase purity of the products. The differences in intensity may be due to preferred orientation of the powder samples.

4. Conclusion

In this article, a new POMs-based inorganic–organic hybrid was synthesized, which exhibits photo- and electro-catalytic properties. The synthesis of **1** enriches the diversity of POMs chemistry. Further research on the inorganic–organic hybrid compounds of POMs is currently underway.

Supplementary material

The crystallographic data for **1** have been deposited in the Cambridge Crystallographic Data Center with CCDC number 847933 for **1**. The data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif, 12 Union Road, Cambridge CB2 1EZ, UK, via Fax (+44 1 223 336 033) or E-mail (deposit@ccdc.cam.ac.uk). X-ray crystallographic files in CIF format; TG curves; the IR spectra; selected bond lengths (Å); and angles (°) for **1**.

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