

Synthesis, crystal structure and electrochemical behavior of supramolecular complex $[4, 4'\text{-bipyH}_2][4, 4'\text{-bipyH}]_{2.5}(\text{P}_2\text{W}_{18}\text{O}_{62})[4, 4'\text{-bipyH}_{1.5}] \cdot 2\text{H}_2\text{O}$

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Abstract A Dawson-type supramolecular complex $[4, 4'\text{-bipyH}_2][4, 4'\text{-bipyH}]_{2.5}(\text{P}_2\text{W}_{18}\text{O}_{62})[4, 4'\text{-bipyH}_{1.5}] \cdot 2\text{H}_2\text{O}$ (**1**) has been synthesized hydrothermally and determined by means of IR, UV, cyclic voltammetry (CV) and X-ray single-crystal diffraction methods. Single crystal X-ray structural analysis reveals that the compound **1** exhibits 1D chains constructed from polyanions and 4, 4'-bipy molecules connected together by hydrogen bonds and weak contact. The 1D chains are assembled into 2D networks by weak contacts, and the intermolecular interaction of “water chains” is robust enough to really act as a “supramolecular glue” to assemble the 2D networks into 3D arrays. CV study reveals that compound **1** exhibits four chemically reversible processes.

Keywords Dawson-type structure · Supramolecular · 4, 4'-Bipyridine · Intermolecular interaction · Hydrothermal synthesis · Water chain

Introduction

Polyoxometalates (POMs) are a unique class of ligands characterized by their discrete size, high symmetry, large anionic charge, aqueous stability, and various redox activities [1–6]. Due to these features, POMs have been found to be extremely versatile inorganic building blocks for the construction of supramolecular architectures [7–10] with potential applications in catalysis, medicine, materials [11–15], molecular conductivity [16], geochemistry and nuclear waste processing [17–20]. Hydrogen bonding interactions and other weak intermolecular interactions between small molecules are the well-developed methods to increase structural dimensionality of supramolecular systems in the crystal engineering “toolbox” [21]. While some supramolecular frameworks are open-frameworked and there are guest species occluded by the open-framework host in the structure. Water molecules are the commonly encountered guest species, they usually play an important role in the stabilization of the host. Recently, considerable attention has been paid to the crystal structures incorporating lattice water chains or clusters for their importance in understanding cloud and ice formation, crystallization of protein [22], stabilization and functioning of biomolecules [23], solution chemistry, and so on. So far, discrete water clusters $(\text{H}_2\text{O})_n$ ($n = 2\text{--}16$) [24, 25], metal-water chains [26], as well as polymeric water clusters of 1D chain, 2D layer and 3D water structure have been found in supramolecular networks [27–30]. They play important roles in constructing the supramolecular systems.

However, water chains or clusters trap in the supramolecular framework base on POMs was rare reported [31]. Here we report hydrothermal synthesis and crystal structure of a Dawson-based supramolecular architecture, namely, $[4, 4'\text{-bipyH}_2][4, 4'\text{-bipyH}]_{2.5}(\text{P}_2\text{W}_{18}\text{O}_{62})[4, 4'\text{-bipyH}_{1.5}] \cdot 2\text{H}_2\text{O}$

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(4, 4'-bipy = 4, 4'-bipyridine), in which salient water chains were observed.

Experimental section

Materials and physical measurement

All materials were of analytical grade and were used without further purification. Deionized water was used throughout. Elemental analysis (C, H, and N) was performed on a Perkin-Elmer 2400 elemental analyzer. The infrared spectrum was recorded as a KBr pellet on a Spectrum One fourier transform infra-red spectrometer in the range 4,000–400 cm^{-1} . The electronic absorption spectra were taken on a Shimadzu UV-240 spectrophotometer. Cyclic voltammograms were obtained on a model CHI660C electrochemical analyzer (CH Instruments, Austin, TX, USA) controlled by a personal computer at room temperature. A three-electrode system was used for the measurements, with a bare GCE (3 mm diameter) or C–Ni/GCE used as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum wire as the auxiliary electrode. All experiments were performed at the laboratory temperature.

Synthesis of the title compound

A mixture of $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (0.9863 g, 3.0 mmol), H_3PO_4 (0.3 mL, 85%), $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (0.0474 g, 0.22 mmol), 1, 10-phen (0.0988 g, 0.49 mmol), $\text{C}_{10}\text{H}_8\text{N}_2 \cdot 10\text{H}_2\text{O}$ (0.0465 g, 0.24 mmol) and H_2O (15 mL) was stirred for half an hour in air, and pH value of the solution was adjusted to 3.8 by the addition of KOH (0.5 M) solution. The mixture was then transferred to a Teflon-lined stainless steel autoclave (25 mL) and kept at 170 °C for 4 days. After the autoclave had cooled to room temperature, dark yellow plate crystals were filtered off, washed with distilled water, and air-dried to give a yield of 13% based on W. Anal. Calcd. for $\text{C}_{45}\text{H}_{46}\text{N}_9\text{W}_{18}\text{O}_{64}\text{P}_2$: C, 10.58%; H, 0.91%; N, 2.47%. Found: C, 10.26%; H, 0.89%; N, 2.83%.

Single crystal structure determination

Suitable single crystals of **1** was selected and mounted in air onto thin glass fibers. X-ray intensity data were measured at 291 K on a Bruker SMART APEX CCD-based diffractometer with graphite-monochromatic Mo $\text{K}\alpha$ radiation ($\lambda = 0.71073$ Å). Data reductions and absorption corrections were performed with the SAINT and SADABS software packages, respectively [32]. All structures were solved by a combination of direct methods and difference Fourier syntheses and refined against F^2 by the full-matrix

least-squares technique. Anisotropic displacement parameters were refined for all non-hydrogen atoms except for the disordered atoms. Hydrogen atoms were added theoretically and were riding on their parent atoms. The crystal parameters, data collection, and refinement results are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. More details on the crystallographic studies as well as atom displacement parameters are presented in the Supporting Information.

Results and discussion

Synthesis

Hydrothermal reaction has been proved to be an effective technique for preparation of numerous of solid-state oxides and organic–inorganic hybrid materials due to special reaction conditions in which different solubility problems are minimized. In a specific hydrothermal process, many factors can affect the formation and crystal growth of products, such

Table 1 Crystallographic data for **1**

Empirical formula	$\text{C}_{45}\text{H}_{46}\text{N}_9\text{W}_{18}\text{O}_{64}\text{P}_2$
Formula weight	5,107.97
Temperature	291 K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P-1$
Unit cell dimensions	$a = 13.2636(13)$ Å, $\alpha = 78.308(2)^\circ$ $b = 14.1766(14)$ Å, $\beta = 83.862(2)^\circ$ $c = 26.951(3)$ Å, $\gamma = 68.097(2)^\circ$
Volume	$4601.6(8)$ Å ³
Z	2
Density (calculated)	3.687 g cm^{-3}
Absorption coefficient	22.532 mm^{-1}
$F(000)$	4,506
Crystal size	$0.10 \times 0.12 \times 0.20$ mm ³
Theta range for data collection	$1.5\text{--}26.0^\circ$
Index ranges	$-16 \leq h \leq 16$; $-17 \leq k \leq 17$; $-31 \leq l \leq 33$
Reflections collected	47,004
Unique reflections	17,761 ($R_{\text{int}} = 0.028$)
Obs. Reflections [$I > 2\sigma(I)$]	14,201
Goodness-of-fit on F^2	1.05
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0435$, $wR_2 = 0.1011$
Largest diffraction peak and hole	1.04 and $-2.54e$ Å ⁻³

$$(a) R_1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$$

$$(b) wR_2 = \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]}^{1/2}$$

$$(c) w^{-1} = [\sigma^2(F_o^2) + (0.06P)^2 + 1.99P], P = (F_o^2 + 2F_c^2)/3$$

Table 2 Selected bond lengths (Å) and angles (°)

P1–O19	1.389(8)	P2–O23	1.548(9)
P1–O20	1.553(9)	P2–O24	1.639(9)
P1–O21	1.512(8)	P2–O25	1.563(8)
P1–O22	1.823(8)	P2–O26	1.529(8)
W1–O1	1.717(8)	W2–O2	1.680(8)
W1–O19	2.463(8)	W2–O19	2.398(8)
W1–O27	1.938(9)	W2–O27	1.902(8)
W1–O29	1.892(7)	W2–O28	1.972(9)
W1–O30	1.827(9)	W2–O32	1.976(8)
W1–O31	1.859(8)	W2–O33	1.956(8)
W3–O3	1.679(7)	W4–O4	1.620(8)
W3–O19	2.428(8)	W4–O20	2.078(8)
W3–O28	1.909(9)	W4–O30	1.913(8)
W3–O29	1.925(6)	W4–O36	1.854(9)
W3–O34	1.977(8)	W4–O41	1.874(8)
W3–O35	1.890(7)	W4–O42	1.856(8)
N1–C5	1.413(16)	N4–C16	1.394(16)
N1–C1	1.373(15)	N4–C20	1.340(16)
N2–C10	1.399(15)	N5–C21	1.367(17)
N2–C6	1.399(17)	N5–C25	1.399(15)
N3–C15	1.396(17)	N6–C30	1.403(18)
N3–C11	1.330(16)	N6–C26	1.356(16)
N7–C31	1.391(18)	N7–C35	1.380(18)
N8–C40	1.346(16)	N8–C36	1.398(15)
N9–C41	1.374(17)	N9–C45	1.375(19)
O19–P1–O20	106.8(5)	O23–P2–O24	108.0(5)
O19–P1–O21	109.7(5)	O23–P1–O25	108.4(5)
O19–P1–O22	101.4(4)	O23–P1–O26	106.3(5)
O20–P1–O21	117.0(4)	O24–P1–O25	106.9(4)
O20–P1–O22	117.3(4)	O24–P1–O26	114.3(4)
O21–P1–O22	103.6(4)	O25–P1–O26	112.7(4)

as the type of initial reactants, the filling volume, starting concentrations, pH values, the stoichiometry of starting materials, reaction time and temperature. The compound **1** was readily prepared under the hydrothermal reaction conditions described in the experimental section.

The pH value of the reaction system was about 3.8–4.1. No product was obtained when the pH value was changed to 4.4–4.6. In our experiment, we used **1**, 10-phen and 4, 4'-bipy as mixed-ligand and Zn(II) as center atom, but no **1**, 10-phen molecular and Zn(II) atom can be found in the product, maybe they act as template in the synthesis. The 4, 4'-bipy molecules have been protonated and act as counteraction to balance the negative charge on polyanion $[P_2W_{18}O_{62}]^{6-}$.

Description of the crystal structure

Single crystal X-ray diffraction analysis reveals that the asymmetric unit of **1** contains four and half protonated 4, 4'-bipy molecules, one polyanion of $[P_2W_{18}O_{62}]^{6-}$ and two

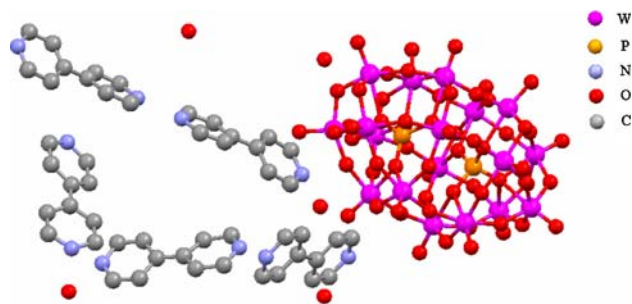
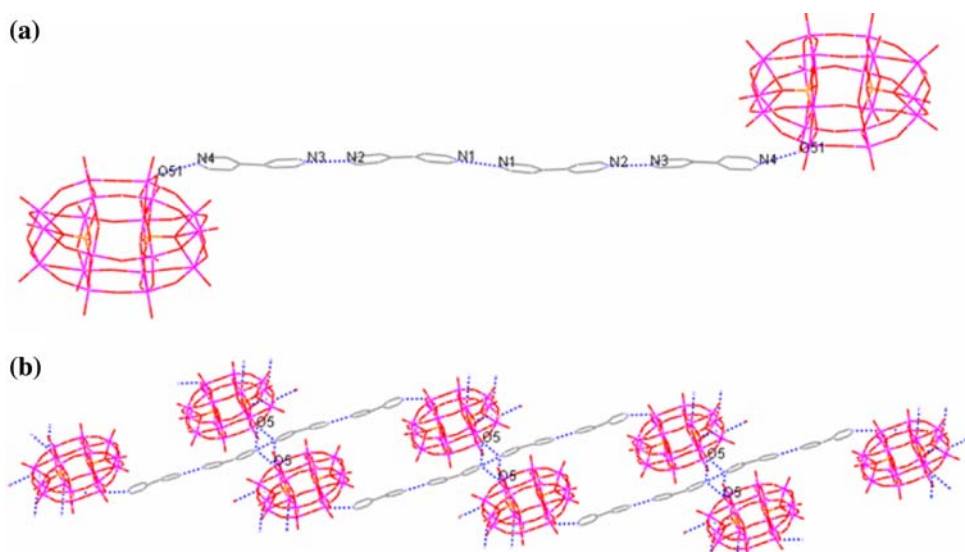


Fig. 1 Molecular structure of the title compound. All hydrogen atoms are omitted for clarity

water molecules (Fig. 1). The structure of polyoxoanion $[P_2W_{18}O_{62}]^{6-}$, which is based on two central PO_4 tetrahedron surrounded by eighteen $\{WO_6\}$ octahedral arranged in six groups of three edge-shared octahedral W_3O_{13} . The six trimetallic groups W_3O_{13} were linked by sharing corners and linked to the PO_4 tetrahedron [33]. The P–O distances are in the range of 1.389(8)–1.823(8) Å with an average bond distance of 1.570(3) Å; and O–P–O bond angles vary from 101.4(4)–117.3(4)°. Comparing the O–P–O bond angles with that of regular tetrahedron (109.5°), the PO_4 in **1** has been distorted greatly. There are two categories of W atoms: six at ‘polar’ positions and 12 at ‘equator’ positions. Oxygen atoms in $[P_2W_{18}O_{62}]^{6-}$ can be divided into four groups according to their coordination number [34]: O_t (terminal oxygen atoms connecting only one W atom), O_b (oxygen atoms located in the share corners between two W_3O_{13} units), O_c (oxygen atoms connecting edge sharing WO_6 octahedrons in the same W_3O_{13} unit) and O_a (oxygen atoms connecting the P heteroatom and W atoms). Relevant W–O bond distances in the anion can be classified into three groups: $W-O_t$ 1.599(9)–2.382(7) Å, $W-O_{b,c}$ 1.801(8)–2.391(7) Å, $W-O_a$ 2.356(8)–2.463(8) Å. Their mean bond distances are 1.740(3), 1.966(6), and 2.403(6) Å, respectively. While W–O–W bond angles vary from 70.6(3)–174.7(4)°. The data indicate that all W atoms are in a distorted geometry environment.

Interestingly, all the 4, 4'-bipy molecules in **1** are protonated (electron charge of the protonated nitrogen atoms are N1 (+0.5), N2 (+0.5), N3 (+0.5), N4 (+1.0), N5 (+1.0), N6 (+1.0), N8 (+1.0), N9 (+0.5), respectively) with a total six of positive charges balanced the negative charges on polyoxoanion $[P_2W_{18}O_{62}]^{6-}$ to make compound **1** electric neutrality. Two polyoxoanions are linked to four 4, 4'-bipy molecules by hydrogen bonds (N4–H4a...O51i 2.608 Å, N1–H1a...N1ii 2.586 Å, Symmetry codes: (i) $x, 1 + y, -1 + z$ and (ii) $2 - x, -y, 1 - z$, respectively) and weak contact (N2–H2a...N3 2.562 Å) (Fig. 2a) to form a one-dimensional chain. The chains then are stacked into a two-dimensional network via weak interactions of the 4, 4'-bipy and another two polyanions (Fig. 2b). The other two and

Fig. 2 (a) View of the 1D chain and (b) 2D network of compound **1**. Some of the organic molecules, H atoms and water molecules are omitted for clarity



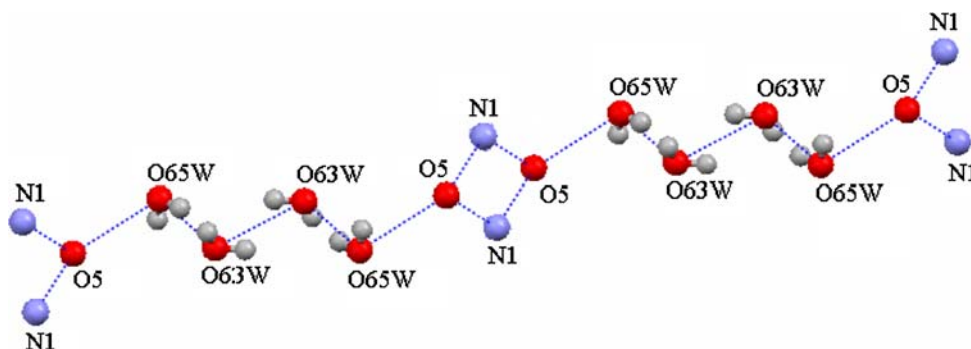
half of 4, 4'-bipy molecules act as counteranions connected to discrete water molecules and polyoxometalates to further stabilizing the 2D structure.

Another interesting structural feature is to note that the water molecules (O65W, O63W, O63Wⁱⁱⁱ, O65Wⁱⁱⁱ, Symmetry codes: (iii) $1-x, -y, 1-z$; (iiii) $1+x, -1+y, z$, respectively) are connected into a chain (H₂O)₄ tetramer in ABAB fashion through strong intermolecular interactions. The O...O distances are in the range of 2.271–2.913 Å (O65W...O63W 2.271 Å, O63W...O63Wⁱⁱⁱ 2.913 Å), and the O65W...O63W...O63Wⁱⁱⁱ angle is 113.99°, both the distances and angle are in the range found in ice and water clusters [35, 36]. While these water tetramers are linked together by a plane that is form by four atoms (O5, N1, O5#, N1#) with an O5...O65W distance of 2.921 Å and an O5...O65W...O63W angle of 108.20° to give a “water chain” (Fig. 3). These “water chains” link the two-dimensional network into a three-dimensional framework and behave as glue to stabilize the 3D network (Fig. 4).

IR spectrum

The IR spectrum of compound **1** exhibits a band at 1,090 cm⁻¹ attributed to ν (P–O) and characteristic bands

Fig. 3 A close view of the water chain present in **1** showing the atom numbering scheme



at 958 cm⁻¹ attributed to ν (W–O_t), 912 and 782 cm⁻¹ attributed to ν (W–O_{b/c}), respectively; Comparing the IR spectra of compound **1** with that of α -H₆P₂W₁₈O₆₂ · nH₂O [37], the vibration peak of W–O_t and W–O_c bonds shifted from 961 to 958 cm⁻¹ and 780 to 782 cm⁻¹, respectively. While the P–O and W–O_b bonds appear nearly identical to that of α -H₆P₂W₁₈O₆₂ · nH₂O. These results indicate that the polyanions of the title compound still retain the basic Wells-Dawson structure. In addition, bands in the 1,615–1,206 cm⁻¹ region are ascribed to characteristic vibration of 4, 4'-bipy groups. The band at 3,501 cm⁻¹ can be assigned to O–H stretching.

UV spectrum

The UV spectrum of the title compound (Fig. 5) in DMSO exhibits two absorption peaks at 206 and 239 nm. The former is very weak, while the latter is strong and sharp, which can be ascribed to the charge-transition absorption of O_t→W. According to model MOL₅ which is C_{4v} symmetry, the charge-transition of O_{b,c}→W is symmetry forbidden transition, this is why the characteristic absorption peaks of the Wells-Dawson type polyanion (310 nm) [38] is not obvious in the UV spectrum of the title compound.

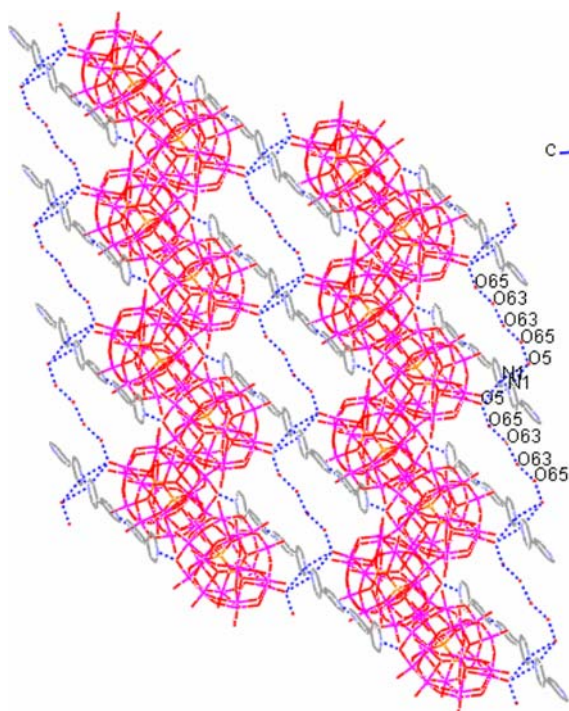


Fig. 4 Packing arrangement view of compound **1**. All hydrogen atoms, water molecules and some of the organic molecules are omitted for clarity

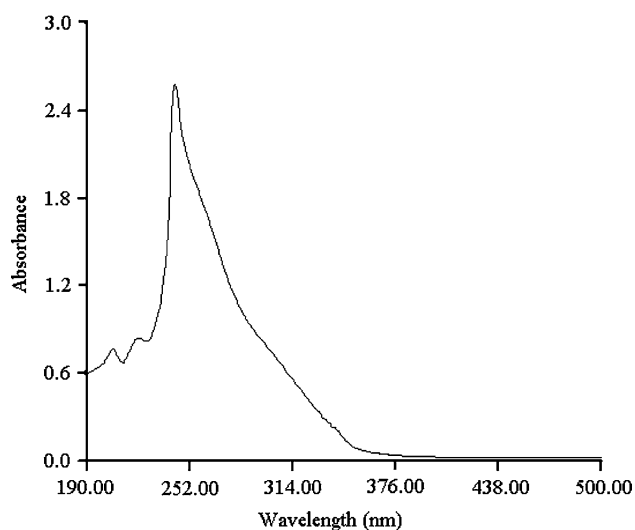


Fig. 5 UV spectra of the title compound in DMSO

Electrochemical behavior of $[P_2W_{18}O_{62}]^{6-}$

Figure 6 shows a cyclic voltammogram of 2×10^{-3} mM compound **1** in DMF containing $HClO_4$ with a scan rate (v) of 300 mV s^{-1} . In the potential range from 0.3 to -0.8 V , four well-defined redox waves appeared with a (ΔE_p (the difference between the anodic peak potential and the cathodic peak potential) value of 18 mV ($E_{pa} = -0.606 \text{ V}$,

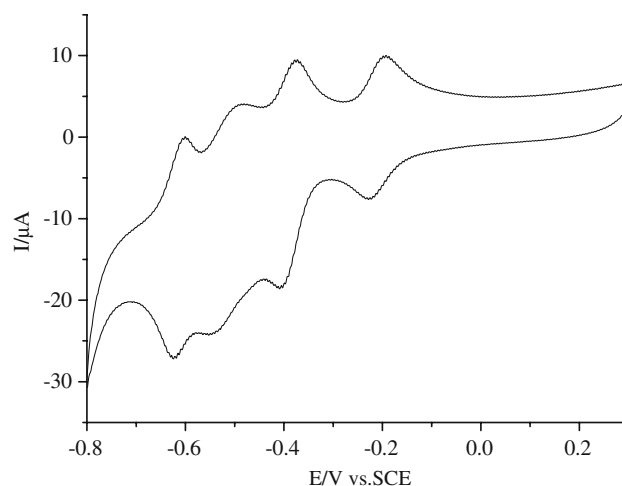
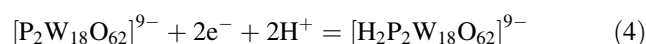
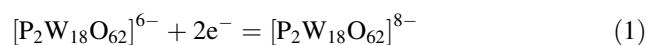


Fig. 6 Cyclic voltammograms of compound **1** (2×10^{-3} mM) in DMF + $HClO_4$; scan rate: 300 mVs^{-1} ; working electrode: glassy carbon disk

$E_{pc} = -0.624 \text{ V}$) for step I, $\Delta E_p = 64 \text{ mV}$ ($E_{pa} = -0.481 \text{ V}$, $E_{pc} = -0.545 \text{ V}$) for step II, $\Delta E_p = 35 \text{ mV}$ ($E_{pa} = -0.372 \text{ V}$, $E_{pc} = -0.407 \text{ V}$) for step III and $\Delta E_p = 34 \text{ mV}$ ($E_{pa} = -0.193 \text{ V}$, $E_{pc} = -0.227 \text{ V}$) for step IV, respectively. Thus, the reversibility of $[P_2W_{18}O_{62}]^{6-}$ was significantly improved. From the CV spectrum, E_{pa} values and $E_{pa/2}$ values of the four steps were obtained, they are -0.606 , -0.481 , -0.372 , -0.193 and -0.632 , -0.531 , -0.403 , -0.226 V , respectively. For a reversible system, $|E_p - E_{p/2}| = 56.5/n$ [39], using this formula, the electron transfer number n of the four redox steps can be calculated to be 2, 1, 2 and 2, respectively. As reported by [40], the first wave is monoelectronic and diffusion-controlled, while the third and fourth reversible two-electron reductions are accompanied by protonations. but in our experiment, the first wave was two-electron wave, the reason may be that the absent of $HClO_4$ may it converted into two-electron wave in a complex manner. While the last two waves still undergo reversible two-electron two-proton reduction as reported by others. The four reversible redox waves are summarized as show in Eq. 1–4.



Supplementary material

Crystallographic data for the structure reported in this paper have been deposited with Cambridge Crystallographic Data Center as supplementary publication No.

654284. Copies of the data can be obtained free from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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