



Organic–inorganic heteropoly blue based on Dawson-type molybdosulfate and organic dye and its characterization and application in electrocatalysis



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ABSTRACT

A new organic–inorganic heteropoly blue based on Dawson-type molybdosulfate and organic dye, $(\text{MB})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\cdot\text{CH}_3\text{CN}$ ($\text{MB} = \text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$), was synthesized under ambient conditions and characterized by IR, fluorescence spectrum, single crystal X-ray diffraction, magnetism measurement and X-ray photoelectron spectroscopy analysis. X-ray diffraction analysis shows that the polyoxoanions fill in the interspace formed by the MB cations and acetonitrile and interacted by Coulombic forces, complex hydrogen bonds, such as $\text{C}-\text{H}\cdots\text{O}$, $\text{C}-\text{H}\cdots\text{S}$ and $\text{C}-\text{H}\cdots\text{N}$, and $\text{C}-\text{H}\cdots\pi$, $\pi\cdots\pi$ stacking interactions. The XPS data and magnetic measurements show that the polyanion was mixed valence as a result of one electron reduction. The monotonous decrease of $\chi_{\text{M}}T$ from $0.28\text{ cm}^3\text{ mol}^{-1}$ at ambient temperature down to $0.13\text{ cm}^3\text{ mol}^{-1}\text{ K}$ at 2 K indicates the presence of antiferromagnetic interactions among the mono-electron reduction polyanions, $\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}^{5-}$. Studies of the photoluminescent properties in acetonitrile solution suggest the presence of the formation of ion pairs of $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ anion and MB cation or charge-transfer transitions between the cationic MB donor and the POM acceptor. Furthermore, the organic–inorganic heteropoly blue was used to fabricate a modified carbon paste electrode (1-CPE), which exhibits five pair redox peaks in the potential range -300 mV to 700 mV and more positive first redox potentials than $\text{P}_2\text{Mo}_{18}\text{O}_{62}^{6-}$, higher stability and good electrocatalytic activity toward the reduction of nitrite, chlorate, bromate and hydrogen peroxide in acidic ($1\text{ M H}_2\text{SO}_4$) aqueous solution.

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1. Introduction

Growing attention has been concentrated on the polyoxometalates (POMs), a class of transition-metal oxygen cluster, due to their diverse molecular and electronic structures, which lead to potential applications in catalysis, photochemistry and materials science [1–3]. One of special properties of POMs is that they have the ability to undergo a series of reversible one- and two-electron reductions and give rise to active mixed valency clusters (heteropoly blue) without affecting their structure [4–6], these properties make heteropolyanions attractive as redox catalysts for indirect electrochemical processes [7,8]. The most reported polyoxometalates used as electrocatalysts are Keggin-type and Dawson-type ($\text{XM}_{12}\text{O}_{40}^{n-}$ and $\text{X}_2\text{M}_{18}\text{O}_{62}^{n-}$, X = heteroatom, such as P^{5+} , As^{5+} , Si^{4+} or Ge^{4+} , M = W, Mo) [9–12]. The average potential of the first redox pairs increases linearly with an increase in the

valence of the central heteroatom, i.e., a decrease in the negative charge of the heteropolyanions [7]. The Keggin- and Dawson-type polyanions containing S^{6+} as the central heteroatom are specially interesting because they are not only most excellent electron acceptors, such as $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ can accept up to 26 electrons [13], but also impose a relatively low anionic charge and consequent positive reduction potentials [14,15]. However, the Keggin- and Dawson-type polyanions containing S^{6+} as the central heteroatom are unstable in aqueous solution, which limited their application in functional materials. One of effective ways to stabilize the sulfur-polyoxometalates is by the formation of organic–inorganic hybrids which are very advantageous to expand POM-based materials application in chemically bulk-modified electrodes owing to poor solubility in water and in common organic solvent, some of them combining the advantages of organic molecules and expected synergistic effects among organic groups and metal-oxo clusters, for example, charge-transfer salts formed by POM acceptor and organic donor [16–18], in which delocalized electrons coexist in both the organic network and the inorganic clusters [7]. In 2004, Wang et al. reported a chemically bulk-modified graphite organosilicate

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composite electrode (GOSE) based on $\text{Ru}(\text{bpy})_3]_2[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ by a sol–gel process, which presents good electrocatalytic activity not only toward the reduction of bromate, but also toward the oxidation of arsenite [19]. Recently, our group reported two carbon paste electrodes (CPEs) based on inorganic–organic hybrids composed of Keggin polyoxometalate and methylene blue ($\text{MB} = \text{C}_{16}\text{H}_{18}\text{N}_3\text{S}$), $[\text{MB}]_4[\text{PMo}_{12}\text{O}_{40}] \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$ and $[\text{MB}]_4[\text{GeMo}_{12}\text{O}_{40}] \cdot 2\text{DMF} \cdot \text{H}_2\text{O}$, which present stability and have good electrocatalytic activities toward the reduction of chlorate, bromate and nitrite [20]. In the present investigation, we report the synthesis and characterization of a new mix-valence inorganic–organic hybrid based on Dawson-type molybdosulfate and organic dye, $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\text{CH}_3\text{CN}$. Furthermore, the organic–inorganic heteropoly blue was used to fabricate a modified carbon paste electrode (1-CPE). In contrast to our previous work [20], 1-CPE exhibits more complex redox processes, especially more positive first redox potential. Its stability in aqueous solution and electrocatalytic activity toward the reduction of nitrite, chlorate, bromate and oxydol are also investigated.

2. Experimental

2.1. General materials and measurement

The experiment was carried out in the open air, $[\text{NBu}_4]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ was synthesized according to the literature procedure [21]. Other experiment materials were AR grade. The elemental analyses (C, H and N) were performed on a Vario EL III CHN elemental analyzer. FTIR spectra were obtained on a EQUINOX55 IR spectrometer with KBr pellets. Cyclic voltammetry studies were carried out in 1 M sulfuric acid solution at ambient temperature. A CHI 660 Electrochemical Workstation connected to a Digital-586 personal computer was used for control of the electrochemical measurements and for data collection. A conventional three-electrode system was used. Calomel electrode was used as the reference electrode, 1-CPE as the working electrode and a platinum wire as the counter electrode. Fluorescence spectra were measured at room temperature on a Hitachi F4500 fluorescence spectrophotometer equipped with a 450 W xenon lamp as the excitation source. Magnetism measurements were performed on a Quantum Design MPMS SQUID magnetometer. The X-ray powder diffraction (XRPD) data were collected on a BRUKER SMART APEX II CCD diffractometer with $\text{Cu K}\alpha$ radiation. X-ray photoelectron spectroscopy (XPS) measurement was performed on an ESCALab220i-XL electron spectrometer from VG scientific with 300 W Mg $\text{K}\alpha$ radiation. The base pressure was about 3×10^{-9} mbar.

2.2. Syntheses of $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\text{CH}_3\text{CN}$ (**1**)

$[\text{NBu}_4]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ (0.935 g, 0.25 mmol) was dissolved in 15 mL acetonitrile. After methylene blue (0.4 g, 1.25 mmol) dissolved in 15 mL acetonitrile solution was added, the yellow solution turned dark green. The solution was stirred for 15 min and filtered. The filtrate was slowly evaporated at ambient condition. In about half a month, bluish violet massive crystals were isolated (yield: 34% based on $[\text{NBu}_4]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$). Anal. Calcd for $\text{C}_{82}\text{H}_{93}\text{N}_{16}\text{Mo}_{18}\text{O}_{62}\text{S}_7$ ($M_r = 4246.06$): C, 23.2; H, 2.2; N, 5.3; Found: C, 23.5; H, 2.3; N, 5.3%. IR (KBr pellet, cm^{-1}) 797(m), 878(w), 959(m), 1064(w), 1128(m), 1174(m), 1148(m), 1320(s), 1394(s), 1482(w), 1595(s) (Fig. S1). The XPRD pattern of the compound is presented in Fig. S2. The diffraction peaks of the simulated and experimental patterns match well in the key position, which indicates the purity of the compound.

2.3. Preparation of 1-CPE

The carbon paste electrode based on the compound $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\text{CH}_3\text{CN}$ was fabricated according to the procedure as follows: 50 mg graphite powder and 15 mg compound **1** were mixed and ground together by agate mortar and pestle to achieve an even and dry mixture, then 5 mL acetone was added to the mixture and the mixture was ultrasonically mixed during which the acetone was evaporated. To the mixture, 3 drops of paraffin oil were added and stirred with a glass rod. The homogenized mixture was used to pack 3 mm inner diameter glass tubes to a length of 0.8 cm from one of their ends, and the surface was wiped with pan paper; electrical contact was established with copper rod through the back of the electrode.

2.4. X-ray crystallography

A selected crystal of compound **1** was mounted on a glass fiber capillary which was put on a BRUKER SMART APEX II CCD diffractometer with Mo $\text{K}\alpha$ monochromatic radiation at 296(2) K. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix-block least-squares method on F^2 . Heavy atoms (Mo and S) and the framework oxygen atoms of the polyanion were refined with anisotropic displacement parameters, the other atoms were refined isotropically. Hydrogen atoms were not included. A summary of the crystal data and structure refinements for **1** is given in Table S1.

3. Results and discussion

3.1. Structure for compound **1**

The X-ray structural analysis demonstrates that compound **1** crystallizes in the triclinic space group $P\bar{1}$. The asymmetric unit of **1** is composed of one Dawson type $[\alpha\text{-S}_2\text{Mo}_{18}\text{O}_{62}]^{5-}$, five MB cations and one acetonitrile molecule. The bond distances of four types of Mo–O (Mo–O_t, Mo–O(μ 2), Mo–O(μ 3), Mo–O(μ 4)) are in the range of 0.1630(9)–0.1714(9), 0.1837(10)–0.2015(9), 0.2495(10)–0.2528 and 0.2469(9)–0.2503(9) nm, respectively, and S–O distances are from 0.1417(11) to 0.1505(9) nm. Fig. 1 shows the packing of the compound in solid state, the polyoxoanions fill in the interspace formed by the MB cations and acetonitrile molecules and there exist complex interreactions in the supramolecular compound, including Coulombic forces, complex hydrogen bonds among the framework oxygen atoms of the polyanion and MB cations as well as CH_3CN molecules, and $\pi \cdots \pi$ stacking interactions between the approximately parallel MB cations.

3.2. Fluorescence property for $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\text{CH}_3\text{CN}$

The fluorescence spectra of 3×10^{-5} M solution of $(\text{C}_{16}\text{H}_{18}\text{N}_3\text{S})_5[\text{S}_2\text{Mo}_1^{\text{V}}\text{Mo}_{17}^{\text{VI}}\text{O}_{62}]\text{CH}_3\text{CN}$, and corresponding starting materials, $[\text{NBu}_4]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$ and MB, in dry acetonitrile at room temperature upon excitation at 380 nm are compared in Fig. 2. There are two emission bands centered at 691 and 434 nm for MB molecule, attributed to the emissions between HOMO and LUMO energy levels; a strong broad emission band centered at 430 nm for POM assigned to O–W charge-transfer transition. Compared with the starting materials, compound **1** exhibits very intensive emission band at ca. 431 nm, which is due to the superposition O–W charge-transfer transition and the emissions between HOMO and LUMO energy levels of and MB molecule, as well as a new weak emission bands centered at 673 nm. Compared with the emission band centered at 691 nm for MB molecule, its

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