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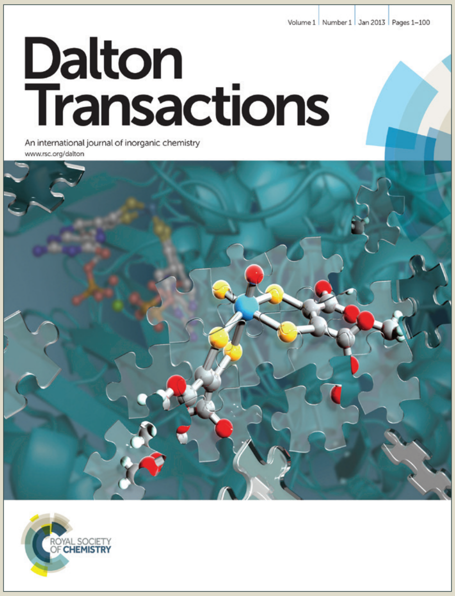

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ARTICLE TYPE

Synthesis of poly-pendant 1-D chain based on 'trans-vanadium' bicapped Keggin-type vanadtungstate and its photocatalytic properties

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A vanadtungstate cluster-based organic–inorganic hybrid material $[NiL_4V^{IV}W^{VI}{}_{10}W^{V}{}_2O_{40}(V^{IV}O)_2]$ (**1**, L = 1,4-bis(imidazol-1-ylmethyl)benzene) was synthesized and characterized by elemental analysis, IR spectra, thermal gravimetric analysis, and single crystal X-ray direction analysis. Structural analysis reveals that compound **1** contains a transition-metal-centered bicapped Keggin-type $\{VW_{12}O_{40}(VO)_2\}$ core, connected by nickel linkers into a 1-D chain. These 1D chains interdigitated with each other achieving an interdigitated 3D supermolecular architecture. Photocatalytic studies indicate that compound **1** is not only active photocatalyst for degradation of dye molecules, but also exhibits selective photocatalytic activity for degradation of cationic dyes in aqueous solution. Further, this photocatalyst is stable and easily separated from the photocatalytic system for reuse as well.

Introduction

Recently, much attention has been paid on the construction of novel organic-inorganic hybrid polymers as their intriguing topological structures and potential applications in various fields.[1-3] Polyoxometalates (POMs), as one kind of unique metal oxide cluster, have been considered as the promising secondary building units for construction of metal-organic frameworks because of their nanosized structures, adjustable compositions, variable topologies as well as their oxygen-rich surface.[4-6] Modifying the surface of POM clusters to build extended structural materials was regarded as one hot topic in the inorganic and material chemistry.[7,8] In this filed, Keggin-type POMs with highly symmetry are well-known as one of the most typical structural feature in POM chemistry. Since the first polyoxoanion $[PMo_{12}O_{40}]^{3-}$ was reported by Berzelius in 1826 and then structurally determined by Keggin,[9] various Keggin-type compounds and their derivatives were explored. They remain the most intriguing family in POM chemistry due to their robust structure and their potential applications in different fields, such as catalysis,[10] elcectrochemitry,[11] magnetism,[12] and medicine.[13] Among these species, the most studies are focused on main-group atom-centered polyoxoanions. Comparably, transition-metal-centered Keggin-type compounds are rarely explored.[14-16]

As well known, transition metal vanadium is flexible in coordination geometries (such as octahedra, square pyramids and tetrahedra), and has a strong tendency to offer mixed-valence states.[17,18] Further, it is important that V-containing Keggin systems have provided direct data for optimization of catalysis.[19,20] For example, the mono-, Di- and Tri-V-substituted Keggin-type polyoxotungstates $SiW_{11}VO_{40}$, $PV_2W_{10}O_{40}$, $XW_9V_3O_{40}$ (X = Si and P), $PW_8V_4O_{40}$, and these POMs-based composites, exhibit high catalytic efficiency toward the alkylarenes, alcohols, dibenzothiophene and formaldehyde reaction. During the last decade, an important advancement in this field is the appearance of V-centered POMs. For example, $VMo_{12}O_{40}$, $VMo_{12}O_{40}(VO)_6$, $VNb_{12}O_{40}(VO)_2$, $VNb_8V_8O_{44}$ most of these studies are focused on V-Mo/Nb systems.[17a,21,22] In polyoxotungstate chemistry, several V-centered POMs were also explored.[23,24] We have focused on this field for a long time, and isolated several V-centered Keggin POMs: $[Ni(bix)_2][VW_{12}O_{40}]\cdot(H_2bix)\cdot H_2O$, $[Co(bix)_2][VW_{12}O_{40}]\cdot(H_2bix)\cdot 2H_2O$, they are all based on the Keggin $VW_{12}O_{40}$ anion.[25] In this paper, we obtained a transition-metal-centered bivanadium capped-Keggin-type POM $\{VW_{12}O_{40}(VO)_2\}$, which was further connected by the NiL_4 groups into an organic-inorganic hybrid 1-D chain, $[NiL_4V^{IV}W^{VI}{}_{10}W^{V}{}_2O_{40}(V^{IV}O)_2]$ (**1**). The introduction of the V capping units into the POM can greatly improve its photocatalytic activity. Photocatalytic studies indicate that compound **1** is not only active photocatalysts for degradation of dye molecules, but also exhibits selective photocatalytic actavity for degradation of cationic dyes in aqueous solution. Also, it is very stable and easily separated from the reaction system for reuse as well.

Results and Discussion

Crystal structure

Crystal structure analysis reveals that compound **1** consists of two crystallographically distinct motifs (Fig. 1a), the bicapped Keggin-type $\{V^{IV}W^{VI}{}_{10}W^{V}{}_2O_{40}(V^{IV}O)_2\}$ (abbreviated as $\{VW_{12}V_2\}$), and a propeller-shaped complex $[NiL_4]^{2+}$ (Fig. S1). As is shown in Fig. 1, the $\{VW_{12}V_2\}$ cluster can be described as a α-Keggin core anion $\{VW_{12}O_{40}\}$ with central vanadium atom as the heteroatom, decorated by two other vanadium

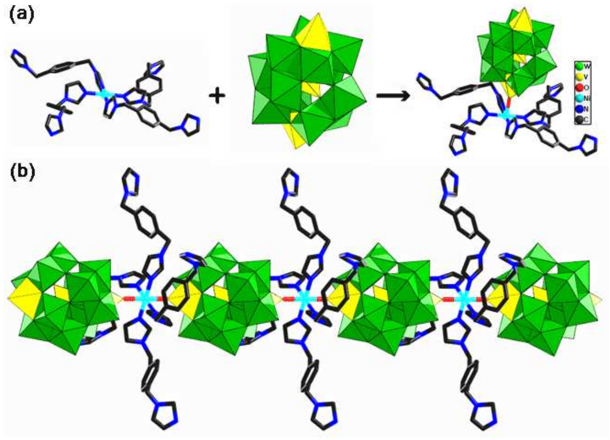

Fig. 1 (a) The fundamental unit of **1**; (b) 1D poly-pendant infinite chain in compound **1**.

atoms capping two opposite pits. The central V (V2) atom is surrounded by four oxygen atoms, the V-O distance is 1.604 Å, O-V-O bond angles vary from 109.3(4)° to 109.7(7)°. The V-O bond distance 1.597(11) Å is longer than the corresponding bond distance (1.538 Å) in the fully oxidized Keggin-like isopolyvanadate $[V_{15}O_{42}]^{9-}$.[23b,26] The V center in **1** is in IV oxidation state. The Keggin-type polyoxoanion $\{V^{IV}W^{VI}{}_{10}W^{V}{}_{2}O_{40}\}^{6-}$ represents a two-electron-reduced heteropoly blue. The assignments of oxidation states are confirmed by X-ray photoelectron spectroscopy (XPS) measurements (Fig. S2 and S3). The presence of the reduced $\{V^{IV}O_4\}$ and $\{W^{V}O_4\}$ group may be ascribed to the existance of the organitrogen species, generally acting not only as ligands but also as reducing agents under hydrothermal conditions. The similar trends have been observed in other compound.[27] The capping vanadium atoms are both coordinated by four oxygen atoms on the $\{W_4O_4\}$ faces and a terminal oxygen atoms. Thus, a square pyramidal coordination geometry of capping vanadium atoms is generated. This structural feature could be comparable to that of the polyoxoniobate $\{VNb_{12}O_{40}(VO)_2\}$.[22] In the polyoxotungstate family, the bi-vanadium-capping polyoxoanion was firstly observed here. In the $[NiL_4]^{2+}$ unit, the Ni^{2+} ion shows a distorted octahedral coordination environment completed by four imidazolyl N atoms from four different bix ligands (the averalge bond length: Ni_1-N_3 = 2.060(15) Å), and two terminal O atoms from $\{VO_5\}$ square pyramidal of two different $\{VW_{12}V_2\}$ clusters. The Ni_1-O_{11} distance is 2.115(13) Å. As shown in Fig. S1, each L ligand adopts a ‘‘Z-type’’ conformation to coordiante the nickel ion with one terminal N atom, leading to the windmill-shape structure of the $[NiL_4]^{2+}$ fragment. These fragments are further connected by the terminal oxygen of $\{VW_{12}V_2\}$ clusters via Ni–O–V bonds to construct a 1D poly-pendantstraight chain (Fig. 1b).

Compound **1** possesses of an interdigitated architecture structure, which was constructed from the molecular zippers. The construction of the interdigitated architecture can be described in two steps. Firstly, each of $\{VW_{12}V_2\}$ clusters acts as a bidentate linker to connect two propeller-shaped $[NiL_4]^{2+}$ complexes by sharing its two opposite terminal oxygen atoms, while each of the $[NiL_4]^{2+}$ complexes coordinated with two $\{VW_{12}V_2\}$ clusters, resulting in a poly-pendant 1D infinite chain along the *c* axis. In this 1D infinite chain, the mono-coordinated L ligands, acting as pendants, are approximately perpendicular to the chain (Fig. 1b). The distance between two adjacent L pendants is ca. 15.430 Å, resulting in a large gap (Fig. S4). As well known, the large gaps in the crystal structure are usually occupied by solvent molecules or guest molecules to achieve the structural stabilization. Or else, the interdigitation phenomena may occur, then the gaps are filled by one or more independent structural motifs. In the structure of **1**, these gaps of one chain are interdigitated by the protruding mono-coordinated L pendants from the adjacent chains (Fig. 2b). Secondly, the gaps of the zipper-like motifs are further interdigitated by L pendants from adjacent four identical molecular zippers (Fig. 2a). As a result, a 1D + 1D → 3D interdigitated architecture is achieved (Fig. 2).

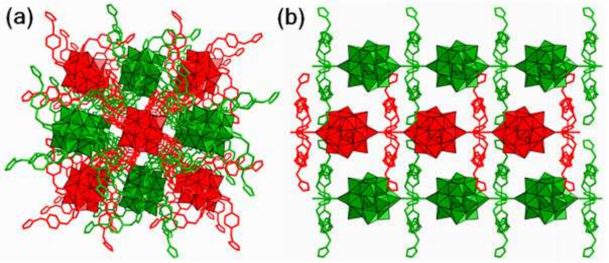

Fig. 2 The crystal packing diagram showing each zipper-like motifs interdigitated by four identical motifs (a) view along c axis; (b) view along b axis.

IR spectra and thermal analyses

The IR spectrum of compound **1** is shown in Fig. S5. In the IR spectrum, there are four characteristic bands which can be attributed to ν(W-Ot), ν(V-Ot), ν(W-Ob) and ν(V-Oc), appearing at 1080, 960, 904, and 796 cm^{-1}.[23b] The characteristic bands in the 1164–1643 cm^{-1} region in the IR spectrum are attributed to characteristic peaks of the L ligands. To study the thermal stability of compound **1**, TG analyses was carried out. As shown in Fig. S6, the 1D infinite chain could keep stable up to the temaperature of 375 °C. Then, a weight loss of 34.69% from 375 to 880 °C was obseved, which corresponds to the loss of L ligands (Cal 34.03%).

Photocatalytic properties

Methylene blue (MB) and rhodamine B (RhB) are typical dye molecules that can be used for evaluating the activity of photocatalysts for the purification of waste water. In the photocatalytic process, the MB and RhB degraded from 100% to 4% and 12% during 3 h in the presence of compound **1**. The degradation rate curve is nearly linear, corresponding to about 32% and 29.3% per hour (Fig. 3). A control photolysis experiment was also completed under the same conditions without **1**. Almost no degradation of MB or RhB was observed in this control experiment. Additionally, after four cycles of the photocatalytic degradation of MB and RhB, no significant loss in the photocatalytic activity was observed for compound **1** (Fig. S7). These results reveal that compound **1** is the active photocatalyst for the degradation of MB and RhB in aqueous solution.

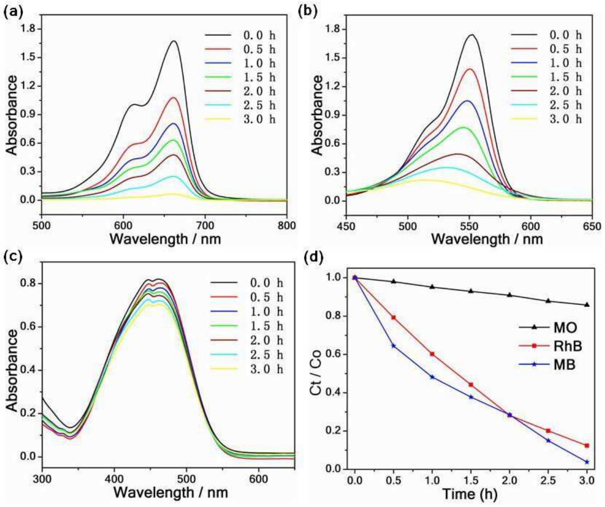

Fig. 3. Photocatalytic degradation of RhB (a) / MB (b) / MO (c) by compound **1**; Plot of Ct / C_0 of MO / RhB / MB versus irradiation time under UV light in the presence of compound **1** (d).

Methyl orange (MO), a negatively charged dye, was further selected to evaluate the phocotacalytic activity of the hybrid materials. In the photocatalytic process, a little degradation of MO was observed during 3 h in the presence of compound **1** (Fig. 3). These results show that compound **1** possess of selective photocatalytic actavity for degradation of cationic dyes in aqueous solution. The same catalyst with different effects on degradation of dyes related to the charge of the dye molecules and the structure of the solid material. As well known, POMs are a kind of hydrophilic metal-oxo cluster compounds with high negative charge. There will be an interaction between the polyoxoanions and the cationic dye molecules, which will make them closer than that between the polyoxoanions and the anionic dye molecules.

By contrast, the simple photolysis comparative experiment was also completed under the same conditions with the use of $[Ni(bix)_3(H_2O)][VW_{12}O_{40}]$ (abbreviated as VW_{12}). In the photocatalytic process, the RhB degraded from 100% to 12% and 53% during 3 h in the presence of compounds **1** and VW_{12}, respectively. The degradation rate curves are nearly linear, corresponding to about 29.3% and 15.7% per hour (Fig. S8). It can be seen that the photocatalytic performance of compound **1** was much better than that of VW_{12}. The two compounds were composed of the same transition metal ion, ligand. An obvious difference between them is that two V atoms capped on the Keggin anion $VW_{12}O_{40}$ in the title compound. We supposed that the existence of the VO^{2+} groups could enhance the potocatalytical activity of these organic-inorganic hybrid materials.

As shown in Fig. S9, the PXRD pattern of compound **1** (as-synthesized) is in good agreement with that of the simulated one from the single crystal data, which proves the phase purity of the as-synthesized product. Further, PXRD pattern of the photocatalyst after the photocatalytic reaction also shows similar peaks with that of the as synthesized sample, revealing that the photocatalyst is stable in the photocatalytic reaction.

Experimental Section

Materials and methods

All chemicals were commercially purchased and used without further purification. Elemental analyses for W, V and Ni were performed with a Leaman inductively coupled plasma (ICP) spectrometer. IR spectrum was recorded in the range 400-4000 cm^{-1} on an Alpha Centaurt FT/IR Spectrophotometer using KBr pellets. UV-Vis absorption spectra were recorded on a 756 CRT UV-Vis spectrophotometer. TG analyses were performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}.

Synthesis

A mixture of $Na_2WO_4 \cdot 2H_2O$ (0.33 g, 1.0 mmol), V_2O_5 (0.20 g, 1.0 mmol), $NiCl_2 \cdot 6H_2O$ (0.071 g, 0.3 mmol), L (0.12 g, 0.5 mmol), and H_2O (10 mL) was stirred for 30 min in air. Then, the pH of the mixture was adjusted to 6.5 with 1.4 M HNO_3. The mixture was transferred to a Teflon-lined autoclave (23 mL) and kept at 160 °C for 5 days. After the mixture was slowly cooled to room temperature, brown crystals were filtered off, washed with distilled water, and dried at room temperature to give a yield of 52% based on W. Anal. calcd for **1** (%): W, 45.47; V, 3.78; Ni, 1.45; C, 16.62; N, 5.54; Found: W, 45.72; V, 3.45; Ni, 1.67; C, 16.42; N, 5.78.

X-ray Crystallography

The measurement for compound **1** was performed on a Rigaku R-AXIS RAPID IP diffractometer. In all cases, the data was collected at 293 K, and graphite monochromated Mo-*K*α radiation (λ = 0.71073Å) was used. The structure was solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXL-97 software.[26] In the refinement, the restraint command 'isor' was employed to restrain several C and N atoms so as to avoid the ADP and NPD problems in the crystal data **1**. Such refinements led to the restraint value of 81. The hydrogen atoms attached to organic ligands were fixed in calculated positions. The crystal data and structure refinements of compound **1** is summarized in Table 1. Further details of the crystal structure can be obtained from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif with CCDC-1005395.

Photocatalytic experiments

In a typical experiment, 10 mg of compound **1** / VW_{12} was added to 100 mL of 10.0 mg·L^{-1} dye (MB, RhB or MO) solutions, then the obtained suspensions were magnetically stirred in the dark for about 30 min to ensure the equilibrium of the working solution. The solution was then exposed to UV irradiation from a 125 W Hg lamp with a distance of 3-5 cm between the liquid surface and the lamp, kept stirring during irradiations.

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

	Compound **1**
Formula	$C_{56}H_{56}N_{16}NiO_{42}V_3W_{12}$
Mr	4042.90
Temp (K)	293(2)
Fw	4042.90
Crystal system	Tetragonal
Space group	*I41/a*
a (Å)	22.9275
b (Å)	22.9275
c (Å)	15.4303
V (Å3)	8111(3)
Z	4.00
μ (mm^{-1})	17.93
T (K)	293(2)
λ (Å)	0.71073
$R1$, wR_2 [I>2σ(I)]	0.0604, 0.1820
$R1$, wR_2 (all data)	0.0684, 0.1869

^{a} $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = \Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]^{1/2}$

Conclusions

In summary, a transition-metal-centered bicapped-Keggin-type polyoxoanion $\{VW_{12}O_{40}(VO)_2\}$ was obtained, which was further connected by the metal-organic complex into a 1D chain. Photocatalytic studies revealed that compound **1** is not only active photocatalyst for degradation of dye molecules, but also exhibits selective photocatalytic actavity for degradation of cationic dyes in aqueous solution. Further study shows that the introduction of the vanadium capping units into the POM cluster could greatly improve its photocatalytic activity.

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Notes and references

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Graphical abstract

Synthesis of poly-pendant 1-D chain based on ‘trans-vanadium’ bicapped Keggin-type vanadtungstate and its photocatalytic properties

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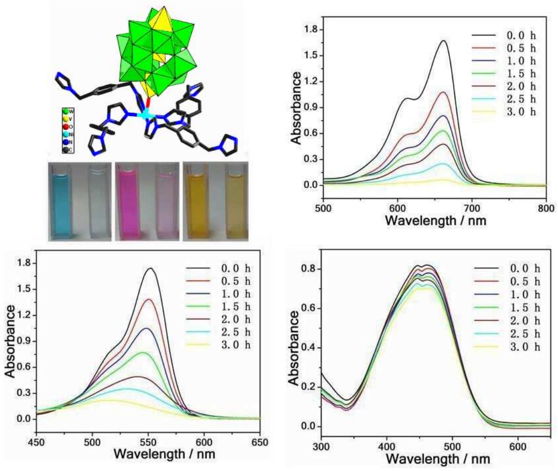

A vanadtungstate cluster-based organic-inorganic hybrid material $[NiL_4V^{IV}W^{VI}_{10}W^{V}_2O_{40}(V^{IV}O)_2]$ was synthesized, which is not only active photocatalyst for degradation of dye molecules, but also exhibits selective photocatalytic actavity for degradation of cationic dyes in aqueous solution.