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Two organic–inorganic hybrids constructed from metal/ttb segments and different polyoxometalates: Syntheses, structures and multifunctional catalytic properties

Xiang Wang *, Lin Lin, Xiaowen Yu, Jiahuan Liu, Hongyan Lin, Guocheng Liu

Department of Chemistry, Bohai University, Jinzhou 121000, PR China

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ABSTRACT

Two organic–inorganic hybrids self-assembled from metal/ttb segments and polyoxometalates, $[Co_2(ttb)_2(H_2O)_4(H_2P_2W_{18}O_{62})]\cdot 10H_2O$ (**1**) and $[Cu_2(ttb)_2(H_2O)_4](SiW_{12}O_{40})$ (**2**) [ttb = 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethyl benzene], have been synthesized hydrothermally. Both **1** and **2** have 3D supramolecular structures, where the combination of the ttb ligands and metal centers gives two kinds of metal–organic segments, namely, a 1D metal–organic belt $[Cu_2(ttb)_2(H_2O)_4]_n^{4n+}$ in **1**, a 2D cationic layer $[Cu_2(ttb)_2(H_2O)_4]_n^{4n+}$ in **2**. Interestingly, compound **1** displays multifunctional catalytic properties, including not only the electrocatalytic reduction for hydrogen peroxide, but also the electrocatalytic oxidation for ascorbic acid, as well as the photocatalytic degradation of MB under UV irradiation.

1. Introduction

Owing to their intriguing architectures [1,2] and potential applications in the field of catalysis [2–5], electrochemistry [6,7], biology [8], lithium-ion battery [9,10], magnetism [11] and so on, the design and synthesis of organic–inorganic hybrid materials containing polyoxometalates (POMs) have attracted extensive contemporary attention. A common strategy for the preparation of these hybrid materials is to employ organic ligands with especial configurations in the self-assembly process. For example, it has been shown that the using of flexible N-donor ligands can lead to pseudo-rotaxane POM-based networks [12]; the employment of tripodal carboxylate ligands can result in the cage-containing POM-based frameworks [13–15]; the combination of rigid and chiral ligands can generate a good functional POM-based framework [16].

The exploitation of tripodal N-donor ligand, 1,3,5-tris(triazol-1-ylmethyl)-2,4,6-trimethyl benzene (abbreviated as ttb), has presented the possibility of generating intriguing architectures for the construction of metal–organic complexes [17–19], where three triazolyl groups of the ttb ligand exhibits six potential N-donor group termini, giving rise to diverse linking modes with metal centers, such as mono-, bi-, tri- and tetra-dentate modes, and so on. Additionally, the torsion of the methylene group between the triazolyl and phenyl groups results in the *cis*- and *trans*- configurations of the ttb ligand, which may play important roles in constructing various architectures (Scheme S1).

Until now, the hybrids constructed from metal/ttb segments and POMs have been only reported by Ma and coworkers [20,21], where three kinds of POMs, including α-, β-octamolybdate anions and sandwich-type polyoxomolybdate cluster $\{Mo_{20}Cd_2\}$, were mentioned. Meanwhile, the pH, metal centers and POMs display important influences on the formation of the final structures.

To further synthesize the such hybrids assembled from metal/ttb segments and POMs, herein, the $[P_2W_{18}O_{62}]^{6-}$ and $[SiW_{12}O_{40}]^{4-}$ anions are introduced into the reaction systems based on the ttb ligand and different metal ions, respectively. Two hybrids, $[Co_2(ttb)_2(H_2O)_4(H_2P_2W_{18}O_{62})]\cdot 10H_2O$ (**1**) and $[Cu_2(ttb)_2(H_2O)_4](SiW_{12}O_{40})$ (**2**) have been synthesized hydrothermally. In the 3D supramolecular structures of **1** and **2**, the ttb ligands in *trans*-configuration and tri-dentate linking mode, are connected by metal centers into two kinds of metal–organic motifs, namely, a 1D metal–organic belt $[Cu_2(ttb)_2(H_2O)_4]_n^{4n+}$, further extended into a 2D layer by $[P_2W_{18}O_{62}]^{4-}$ anions for **1**, a 2D cationic layer $[Cu_2(ttb)_2(H_2O)_4]_n^{4n+}$ in **2**. The electrochemical and catalytic properties of compounds **1** and **2** have also been studied.

2. Experimental

2.1. Materials and methods

All reagents were purchased commercially and used without further purification. The ttb ligand was synthesized according to

* Corresponding author.
E-mail address: xwang@bhu.edu.cn (X. Wang).

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the Ref. [20]. The IR spectra were recorded on Alpha Centaurt FT-IR spectrometer with KBr pellet in the range 400–4000 cm^{-1} region. The powder X-ray diffraction (PXRD) data was carried on a Rigaku RINT2000 diffractometer at room temperature. Elemental analyses (C, H and N) were given on a Thermo Flash 2000 CHNS/O elemental analyzer. The thermal gravimetric analyses (TGA) were performed on a Perkin-Elmer DTA 1700 differential thermal analyzer. The electrochemical experiments were performed on a CHI 660 electrochemical workstation in a 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution.

2.2. Synthesis of $[Co_2(ttb)_2(H_2O)_4(H_2P_2W_{18}O_{62})]\cdot 10H_2O$ (**1**)

A mixture of $CoCl_2\cdot 6H_2O$ (0.2 g, 0.84 mmol), ttb (0.05 g, 0.15 mmol), α-$K_6P_2W_{18}O_{62}\cdot 14H_2O$ (0.4 g, 0.1 mmol) and 10 mL water was stirred for 1 h at room temperature. After the pH value was adjusted to 2.53 with 1.0 $mol\cdot L^{-1}$ HCl aqueous solution, the solution was transferred to a Teflon-lined autoclave and kept at 170 °C for 3 days. Orange crystals were hand-picked under microscope and washed with deionized water (Yield, 54%, based on Co). *Anal.* Calc. for $C_{36}H_{70}Co_2N_{18}O_{76}P_2W_{18}$ (5459.95): C 7.92, H 1.29, N 4.62. Found: C 7.81, H 1.23, N 4.58. IR (solid KBr pellet, cm^{-1}): 3130 (w), 2356 (s), 2336 (s), 1625 (w), 1531 (w), 1093 (s), 960 (s), 910 (s), 795(s).

2.3. Synthesis of $[Cu_2(ttb)_2(H_2O)_4](SiW_{12}O_{40})$ (**2**)

A mixture of $Cu(CH_3COO)_2\cdot H_2O$ (0.2 g, 1 mmol), ttb (0.05 g, 0.15 mmol), $H_4SiW_{12}O_{40}\cdot 14H_2O$ (0.3 g, 0.1 mmol) and 10 mL water was stirred for 1 h at room temperature. After the pH value was adjusted to 4.25 with 1.0 $mol\cdot L^{-1}$ HCl aqueous solution. The resulting solution was transferred to a Teflon-lined autoclave and kept at 170 °C for 3 days. Blue crystals were hand-picked under microscope and washed with deionized water (Yield, 42%, based on Cu). *Anal.* Calc. for $C_{36}H_{50}Cu_2N_{18}O_{44}SiW_{12}$ (3800.13): C 11.38, H 1.33, N 6.63. Found: C 10.91, H 1.45, N 6.30. IR (solid KBr pellet, cm^{-1}): 3131 (w), 2361 (s), 2335 (s), 1624 (w), 1534 (w), 971 (s), 921 (s), 881(w), 797(s).

2.4. The electrochemical and electrocatalytic experiments

The bulk-modified carbon paste electrodes (CPEs) modified by **1** (**1**−CPE) and **2** (**2**−CPE) were prepared according to literature [22]. Platinum gauze, CPEs and Ag/AgCl electrode were used as a counter, working and referenced electrode, respectively. The chemical behaviors were carried out in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous solution at different scan rates. The electrocatalytic activities were carried out in 0.1 M H_2SO_4 + 0.5 M Na_2SO_4 aqueous containing hydrogen peroxide (H_2O_2) or ascorbic acid (AA).

2.5. The photocatalytic experiments

The 20 mg catalyst sample was added into the 100 mL 10.0 $mg\cdot L^{-1}$ methylene blue (MB) solution in a 500 mL water-cooled cylindrical quartz container. After stirred magnetically in the dark for ca. 30 min, the above mixture was stirred continuously under a high-pressure 125 W mercury lamp. 5 mL solution was taken out every 30 min during irritation and analyzed by using a SP-1900 UV/Vis spectrophotometer.

2.6. X-ray crystallographic study

X-ray diffraction data of **1** and **2** were collected on an Oxford Diffraction Gemini R Ultra diffractometer with graphite-monochromated Mo Kα (λ = 0.71073 Å) at 293 K. The crystal structures were solved by direct methods and refined on F^2 by full-matrix least squares methods using the *SHELXTL* package [23,24]. The hydrogen atoms attached to water molecules were not located, but were included in the structure factor calculations. A summary of the crystal data and structure refinements of **1** and **2** are given in Table 1. The crystallographic data for the structures **1** and **2** have been deposited in the Cambridge Crystallographic Data Center with CCDC Nos. 1572447 and 1572448.

3. Results and discussion

3.1. Structure of compound **1**

Compound **1** consists of one $[P_2W_{18}O_{62}]^{6-}$ (simplified as P_2W_{18}) anion, two Co(II) atoms, two ttb ligands, four coordinated and ten crystallization water molecules. The Co1 atom is an octahedral coordination geometry, surrounded by three nitrogen atoms (N7, N8, N9) from the triazolyl groups, one oxygen atom (O2) of the P_2W_{18} anion and two water molecules, as shown in Fig. S1. The P_2W_{18} anion offers two oxygen atoms (O2, O2#3) to connect with two Co(II) atoms. Each of two ttb ligands in a *trans*-configuration utilizes three nitrogen atoms of triazolyl groups to link three Co (II) atoms (Fig. 1a). The corresponding bond lengths and angles are listed in Table S1.

The 3D supramolecular structure of **1** is constructed from POM-based 2D layers *via* hydrogen bond interactions, where the ttb ligands are linked each other by Co(II) atoms to form a 1D ladder-shaped metal–organic belt $[Co_2(ttb)_2(H_2O)_4]_n^{4n+}$ (Fig. 1b), and the bond lengths are 2.139 Å, 2.126 Å and 2.090 Å for Co1-N7, Co1-N8 and Co1-N9, respectively. Then the P_2W_{18} anions link these metal–organic belts into a 2D layer (Fig. 2), in which each P_2W_{18} anion offers two terminal oxygen atoms to coordinate with Co(II) atoms from two adjacent belts, and the Co1-O2 bond length is 2.091 Å. Finally, these layers are extended into a 3D supramolecular structure through hydrogen bond interactions (Fig. S2).

3.2. Structure of compound **2**

Compound **2** comprises one discrete $[SiW_{12}O_{40}]^{4-}$ (simplified as SiW_{12}) anion, two Cu(II) atoms, two ttb ligands and two coordinated water molecules. The Cu1 atom is a pyramid-shaped coordination geometry, formed by three nitrogen atoms (N4, N5, N8)

Table 1
Crystal data and structure refinement for **1** and **2**.

Compound	**1**	**2**
Chemical formula	$C_{36}H_{70}Co_2N_{18}O_{76}P_2W_{18}$	$C_{36}H_{50}Cu_2N_{18}O_{44}SiW_{12}$
Fw	5459.95	3800.13
Crystal system	monoclinic	monoclinic
Unit cell dimensions		
a (Å)	14.271(5)	12.632(5)
b (Å)	25.476(5)	12.853(5)
c (Å)	14.724(5)	22.032(5)
α (°)	90.000(5)	90.000(5)
β (°)	100.168(5)	98.894(5)
γ (°)	90.000(5)	90.000(5)
V (Å^3)	5269(3)	3534(2)
T (K)	293(2)	293(2)
Space group	P2(1)/m	P2(1)/n
Z	4	2
μ (mm^{-1})	20.000	20.152
D_c ($g\ cm^{-3}$)	3.424	3.564
F(000)	4816.0	3392.0
Final R_1[a], wR_2[b] [$I > 2\sigma(I)$]	0.0455, 0.1178	0.0567, 0.1498
Final R_1[a], wR_2[b] (all data)	0.0683, 0.1333	0.0895, 0.1690
Goodness-of-fit (GOF) on F^2	0.948	1.021

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