Assembly of a New Keggin-Templated Supramolecular Compound by Silver Salt and 4, 4'-dipyridine-N, N'-dioxide Ligand

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Abstract

A new polyoxometalate (POM)-templated compound, $\text{Ag}_3(\text{dpdo})_7(\text{H}_2\text{O})_2\text{H}_3 \subset [\text{PW}_{12}\text{O}_{40}]_2$ (dpdo = 4, 4'-dipyridine-N, N'-dioxide) was hydrothermally synthesized, and characterized by elemental analyses, IR spectroscopy, and single X-ray diffraction. Compound **1** crystallizes in the triclinic space group *P*-1, and the basic structure unit of **1** is constructed by $[\text{PW}_{12}\text{O}_{40}]^{3-}$ PW_{12} clusters, Ag^+ cations, and dpdo molecules. In **1**, the dpdo ligand acts as a bi-dentate linkage coordinating with two Ag^+ ions through terminal oxygen atoms to form a two-dimensional (2D) bi-layer, and the neighboring 2D layers are stagger-peaked with each other to form a 3D open framework with the rhombus-like apertures. The PW_{12} anions as templates are encapsulated into the channels and arranged in an A-B-A-B staggered manner. Additionally, the electrochemical studies show that **1** has a good electrocatalytic activity towards reduction of hydrogen peroxide (H_2O_2) and iodated (IO_3^-) and the catalytic efficiency (CAT) of compound **1** toward the reduction of H_2O_2 and IO_3^- is *ca.* 116.7 % and 40.9 %, respectively. The results exhibit that **1** could be used as electrocatalyst in the electrical reduction of H_2O_2 .

Keywords: Keggin; polyoxometalate template; electrocatalytic properties

In recent years, assembly of the supramolecular structures has captivated the attention of many investigators due to their intriguing molecular structure as well as their potential applications [1-7]. An effective synthesis strategy for constructing novel supramolecular compounds is the utilization of templates, which can direct the supramolecular array of building blocks with contrary charges. Polyoxometalates (POMs) are one of perfect anionic templates and charge-compensating guests to stabilize the construction of supramolecular host frameworks owing to their diversity structures, controllable shapes, sizes, high negative charges [8]. Furthermore, the POMs are endowed with particular multifunctionalities, such as, catalytic activity and reversible redox behavior [9, 10]. Thus, incorporating POM into host frameworks may create new opportunities to utilize the redox properties of the POMs and carry out redox reactions within the intercrystalline voids of the supramolecular framework [11-14]. Hereto, remarkable progress about POM-templated supramolecular hybrid

materials have been made based on such a self-assembly reaction [15]. During the assembly process, the matching between open host metal-organic framework and guest POMs molecules is critical for synthetic POM-templated supramolecular hybrid materials. The linear ligand is an appropriate synthon for constructing open host framework. The N-donor ligand especially 4, 4'-bipyridine has been extensively used as linker to construct metal-organic frameworks. In 1999, Zubieta and co-worker published a excellent review that summarized a series of metal-organic frameworks by using 4, 4'-bipyridine as bridging ligand [16], and these frameworks can be as host molecules to encapsulate some small anions (such as Cl^- , Br^- , NO_3^- , BF_4^- , PF_6^- , $[\text{Mo}_8\text{O}_{26}]^{4-}$) to form inorganic-organic entities [17-21]. However, the size of the Keggin type POMs is the nano-metric, which is obviously large in contrast to the above-mentioned small anions. Consequently, the host frameworks that constructed by 4, 4'-bipyridine ligand is difficult to encapsulate Keggin type POMs anions [22]. In order to satisfy the afore-mentioned requirements for POM-templated assembly, the selection of appropriate rigid linear ligand is very important. The 4, 4'-bipyridine-N, N'-dioxide (dpdo) ligand as a derivative of the 4, 4'-bipyridine possesses longer spacer ligand for construction the metal-organic host framework with higher capacity [23-26], and potential coordination sites for hydrogen bonding toward oxygen atoms of POMs and water molecules forming O-H...O interactions [27, 28]. A series of prominent preliminary work about dpdo ligand as bridging ligand for the construction of Keggin-templated supramolecular compounds have been reported by Duan et al. [29-33]. Subsequently, in 2013, our group reported $\text{Ce}^{3+}/\text{Nd}^{3+}$ -dpdo-Keggin complexes and a 3d-4f heterometallic 3D POM-based hybrid constructed by the dpdo ligands [34, 35]. However, the metal ions in these metal-dpdo host frameworks were generally restricted to lanthanide cations [29, 30, 32, 34-36], except for the several examples [31, 32] (please see Table S1, the summarization of POM-based hybrid compounds constructed by dpdo ligand). As is well known, Ag^+ is widely applied in luminescent, antibacterial and catalytic materials [37-39]. Further, Ag^+ possesses flexible coordination modes and high affinity to O donors, which may easily form covalent links between Ag^+ and POMs/ligands [40]. Nevertheless, the use of Ag^+ as metal ion to coordination with dpdo ligand for construction of novel Keggin-templated supramolecular compounds has not been fully realized so far.

Taking this into account, by choosing $\text{H}_3[\text{PW}_{12}\text{O}_{40}]\cdot 12\text{H}_2\text{O}$, dpdo ligand, and

AgNO₃·H₂O salt, fortunately a new supromolecular compound, Ag₃(dpdo)₇(H₂O)₂H₃ ⊂ [PW₁₂O₄₀]₂ (**1**) has been isolated via using hydrothermal method. Compound **1** show 3D open framework with the rhombus-like apertures, in which the [PW₁₂O₄₀]³⁻ (PW₁₂) templates are encapsulated into the channel and arranged in an A-B-A-B staggered manner. The electrochemical studies show that **1** has a good electrocatalytic activity towards reduction of both hydrogen peroxide (H₂O₂) and iodated (IO₃⁻). Additional, **1**-CPE possesses better electrocatalytic effect in the reduction of H₂O₂.

Compound **1** was prepared under hydrothermal conditions with a mixture of H₃[PW₁₂O₄₀]·12H₂O (300 mg, 0.1 mmol), AgNO₃·H₂O (80mg, 0.4mmol), dpdo (90 mg, 0.5 mmol), and H₂O (10 mL) (pH = 1.5) at 170 °C for 3 days [41]. And **1** crystallizes in triclinic space group *P*-1 [42].

The bond valence sum (BVS) calculations [43] show that all W and Ag atoms of compound **1** are in the +VI and +I oxidation state, respectively. Since **1** was isolated from acidic aqueous solution, the oxygen atoms of POM anions could be protonated in acidic aqueous solution [44, 45]. Three protons were attached to POMs to compensate for charge balance, then **1** is formulated as Ag₃(dpdo)₇(H₂O)₂H₃ ⊂ [PW₁₂O₄₀]₂. In compound **1**, there are two crystallographically unique Ag^I ions (Ag1 and Ag2), which exhibit distinct coordinated modes. Ag1 ion adopts a five-coordinated mode in a distorted trigonal bipyramidal geometry achieved by four O atoms from four dpdo ligands and one O atom from a water molecule. The Ag2 cation is hexa-coordinated mode in a near-octahedral geometry formed by four O atoms from four dpdo ligands, and two O atoms from two water molecules. The dpdo ligand acts as a bi-dentate linkage coordinating with two Ag⁺ ions through terminal oxygen atoms. Consequently, a two-dimensional (2D) bi-layer sheet was formed by the dpdo ligands and silver ions (Fig. 1). From the topological view, when Ag1, Ag2 ions are viewed as three, six connecting nodes, respectively, a (3, 6)-connected topology is generated (Fig. S1). These neighboring identical 2D networks are stagger-peaked with each other to form an open 3D framework with large rhombus-like apertures in a given direction (Fig. S2), The PW₁₂ anion as a "guest"

cluster anion was encapsulated into the open channel structure and well surrounded by these “host” rhombus-like units (Fig. 2). And this kind of packing arrangement may decrease the molecular repulsion with contrary charges and stabilizing the whole crystal structure [8].

[Insert Fig. 1]

[Insert Fig. 2]

The size of the rhombus-like units of the open framework is *ca.* 12.29×12.23 Å, which is enough large to accommodate nanoscale Keggin POM anion. In each tunnel, the PW₁₂ templates are arranged in staggered manner in an A-B-A-B model (see Fig. 3), furthermore, top view of the part channel shows that the PW₁₂ anions adopt stagger-peaked with approximate intersection angle of 30° (illustrated in Fig. 3b). As is known, most of the already known structures feature of the fashion that the POM anions act as templates existing in the channels along one direction. However, this work represents the first 3D supramolecular structure with noncoordinating POM anions act as templates in different angles.

[Insert Fig. 3]

The IR spectra of compounds **1** is shown in Figure S3. Characteristic peaks at 1013.8, 966.2, 934 and 772.2 cm⁻¹ for **1**, are attributed to ν (P–O), ν (W= O), and ν (W–O–W) [46-49], respectively. The bands at 1622.6, 1503, 1387, 1345 cm⁻¹ in IR spectra could be regarded as the characteristic peaks of the dpdo ligand [50].

The XRD pattern for compounds **1** was presented in Figure S4. The diffraction peaks of both simulated and experimental patterns match in the key positions. The difference in reflection intensities between the simulated and the experimental patterns may be due to the different orientation of the crystals in the sample [45, 51]. In addition, the diffraction peaks of both simulated and experimental patterns do not match well in some positions, which may be just ascribed to that the sample has been deposited for long time and might be partly pulverized. Thus, the phase purity of the **1** is basically good.

The Keggin-type POMs are known to exhibit well defined redox waves and are usually considered to be electron reservoirs [52]. One of their domains of application

thus concerns electro catalysis [53]. In order to study the electrochemical behavior of **1**, the compound was used as solid modifier to fabricate three-dimensional bulk-modified carbon paste electrode (CPE) by direct mixing method due to its insolubility. The CPE was prepared according to the previous method [54]. The cyclic voltammetric behavior for **1**-CPE in 0.2 M Na₂SO₄/H₂SO₄ buffer solution (pH = 4.5) was recorded in the potential range of -1.0 to 0.8 V, as shown in Fig. S5. There exist two pairs of reversible redox peaks with half-wave potentials $E_{1/2}$ at -0.31 (III-III') and -0.19 V (II-II'), which can be ascribed to redox process of tungstate in **1** [55]. In addition, there is one irreversible anodic peak (I) at +0.22 V, which is assigned to the oxidation of Ag⁺ [56-59]. When the scan rates varied from 40 to 240 mV·s⁻¹, the peak potentials change gradually: the cathodic peak potentials shift toward the negative direction and the corresponding anodic peak potentials to the positive direction with increasing scan rates. Furthermore, up to 240 mV s⁻¹ the peak currents are proportional to the scan rate, which indicates that the redox processes are surface-controlled, and the exchanging rate of electrons is fast [60] (Fig. S6).

The electrocatalytic properties of **1**-CPE have also been investigated towards the reduction of hydrogen peroxide (H₂O₂) and iodated (IO₃⁻) in 0.2 M Na₂SO₄/H₂SO₄ solution (scan rate: 80 mV·s⁻¹). With addition of H₂O₂ and IO₃⁻, the reduction peak currents for II and III increase gradually while the corresponding oxidation peak currents decrease. The nearly equal current steps for each addition of H₂O₂ and IO₃⁻ demonstrate stable and efficient electrocatalytic activity of **1**-CPE (see the insert figures of Fig. 4a, b). Furthermore, to compare the electrocatalytic activity of **1**-CPE for reduction of H₂O₂ and IO₃⁻, the catalytic efficiency (CAT) of **1**-CPE can be roughly calculated by using CAT formula [61]. From the chart of the CAT, the CAT values toward the reduction of H₂O₂ and IO₃⁻ are *ca.* 116.7% and 40.9%, respectively, when the concentrations of H₂O₂ and IO₃⁻ are 4 mM (Fig. 5). The results show **1**-CPE has obvious electrocatalytic effect in the reduction of H₂O₂, which suggest that compound **1** could be used as potential electrocatalyst in the electrical reduction of H₂O₂.

[Insert Fig. 4]

[Insert Fig. 5]

In summary, by choosing dpdo ligand that is a derivative of the 4, 4'-bipyridine, Ag^+ cation and PW_{12} Keggin polyanion, a new compound has been synthesized from the hydrothermal reaction. The compound shows an intriguing 3D open supramolecular framework encapsulated by PW_{12} templates, which represents the first example of POM-based hybrid constructed by dpdo ligand and Ag^+ cation. Also, the compound possesses good electrocatalytic activities towards reduction of both H_2O_2 and IO_3^- . To some extent, this work further confirmed that the dpdo molecule with longer spacer ligand than 4, 4'-bipyridine molecule is a suitable synthon, reacting with Ag^+ cation or generally lanthanide cations, for construction the metal-organic host framework with higher capacity.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version.

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pH was adjusted to 1.5 with 1 M HNO₃, then the mixture was transferred to an 18 mL Teflon-lined reactor and kept under autogenous pressure at 170 °C for 3 days. The reactor was slowly cooled to room temperature over a period of 10 °C/h. Brown like block crystals of **1** were filtered, washed with water, and dried at room temperature. Yield: 40% based on Ag. C₇₀H₆₃Ag₃N₁₄O₉₆P₂W₂₄ (7434): Calcd: C, 11.31; H, 0.85; N, 2.64; Ag, 4.35; P, 0.83; W, 59.35 %; Found: C, 11.35; H, 0.92; N, 2.60; Ag, 4.28; P, 0.85; W, 59.18 %.

- [42] Crystal data for Ag₃(dpdo)₇(H₂O)₂H₃⊂[PW₁₂O₄₀]₂: Mr = 7434, triclinic, space group *P*-1, *a* = 12.297(5) Å, *b* = 15.990(5) Å, *c* = 16.616(5) Å, *V* = 3206.3(19) Å³, *Z* = 1, *D*_c = 3.847 Mg/m³, *F*(000) = 3289.0, *T* = 293(2) K, *R*_{int} = 0.0594. Structure solution and refinement based on 16400 independent reflections with [*I* > 2σ(*I*)] and 11301 parameters gave *R*₁ and *wR*₂ were 0.0797 and 0.2178, respectively. CCDC reference number 1490174.
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Figure captions

Fig. 1. The coordination modes of Ag (I) ions and dpdo ligand, and view of the 2D bi-layer sheet.

Fig. 2. Polyhedron (a and c) and space-filling (b and d) diagrams representation of the

3D packing arrangement based on 2D layers in which the PW_{12} anion as a "guest" cluster anion was encapsulated into the open channel along different directions.

Fig. 3. (a) View of the 3-D framework "host" sandwiching the Keggin ions of **1** (b) View of the arrangement of Keggin ions in the tunnels. The polyoxoanions in lay A, Olive green; in lay B, Purple.

Fig. 4. Reduction of hydrogen peroxide (a) and iodate (b) at **1**-CPE in various concentrations (from inner to outer): 0, 1, 2, 3, 4 mM. The inset shows a linear dependence of the cathodic catalytic current of wave III for **1**-CPE with H_2O_2 concentration (a), and IO_3^- concentration (b).

Fig. 5. Chart of the CAT *vs* concentration of the H_2O_2 and IO_3^-

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