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# Photo-electrochemical and physical characterizations of a new single crystal POM- based material. Application to Rhodamine B photodegradation

D. Meziani<sup>a</sup>, K. Abdmeziem<sup>a,\*</sup>, S. Bouacida<sup>b,c</sup>, M. Trari<sup>d</sup>, H. Merazig<sup>c</sup>

<sup>a</sup> USTHB, Faculté de chimie, Laboratoire d'électrochimie-corrosion, métallurgie et chimie minérale, Equipe de chimie inorganique,

BP 32 El Alia, 16111 Alger, Algérie

<sup>b</sup> Département Sciences de la Matière, Faculté des Sciences Exactes et Sciences de la Nature et de la Vie, Université, Oum El Bouaghi 04000, Algérie

<sup>c</sup> Unité de Recherche de Chimie de l'Environnement et Moléculaire Structurale (UR CHEMS) Université Mentouri Constantine, 25000 Algérie

<sup>d</sup> Laboratory of Storage and Valorization of Renewable Energies, USTHB, BP 32, 16111 Algiers, Algeria

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## ABSTRACT

The physical and photoelectrochemical characterizations of a new inorganic–organic hybrid single crystal material, synthesized by hydrothermal route, based on  $\alpha$ -Keggin-type polyoxotungstate and Cu(I)–(trz) coordination complex, namely  $[\text{Cu}_6(\text{trz})_6][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot \text{H}_2\text{O}$ , [trz = 1H-1,2,4-triazole] are investigated for the first time. The crystal structure, determined by single-crystal X-ray diffraction, reveals a 3-D supramolecular host-guest structure with Keggin anion as template. The diffuse reflectance indicates an optical transition at 2.91 eV, directly allowed, attributed to the Keggin polyoxoanions. The physical characterization shows a semiconductor behavior and the conductivity follows an exponential type law associated to a small polaron hopping between neighboring ions. The thermo-power measurement indicates *n*-type conduction with an electron mobility ( $0.54 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ), thermally activated. The photoelectrochemical study, performed in  $\text{Na}_2\text{SO}_4$  medium, confirms *n*-type conduction with a flat band potential of  $-0.65 \text{ V}_{\text{SCE}}$  and electrons density of  $6.59 \times 10^{18} \text{ cm}^{-3}$ . The electrochemical impedance spectroscopy reveals the predominance of the bulk contribution with a constant phase element and Warburg diffusion. As application, the photo-degradation of Rhodamine B upon sunlight and UV irradiation is achieved by the radicals  $\text{O}_2^{\bullet}$  and  $\text{OH}^{\bullet}$ . The improved activity is attributed to the wide depletion width (460 nm) and the potentials of the valence and conduction bands close to the radicals levels.

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## 1. Introduction

Today's world is confronted to the major crisis of the energy supply and environmental protection. In this respect, the solar energy is attractive owing to its cleanliness and availability [1,2]. The photocatalytic reactions on semiconductors have proved their effectiveness in the removal of dyes since they work under soft conditions [3]. Over the last years, there has been an active research in the synthesis of novel inorganic–organic composite materials for the solar energy conversion [4–6]. However, the conversion mechanism is based on the knowledge of the crystal structure. So, the design of different architectures and topologies led to the generation of new band diagrams and consequently to various properties.

\* Corresponding author. Tel./fax: +21321247311.

E-mail address: [kaissabdmeziem@gmail.com](mailto:kaissabdmeziem@gmail.com) (K. Abdmeziem).

In this regard, the polyoxometalates (POMs)-based inorganic–organic hybrid compounds have attracted a great deal of attention not only for their various architectures, but also for their properties and applications in many areas such as catalysis, magnetism, electrochemistry, photochemistry and biochemistry [7–9]. Recently, many POM-based hybrid compounds have been obtained from POMs as inorganic templates with organo-nitrogen ligands, including pyridyl, pyrazine, triazole ligands, etc. They are commonly used for their conformational freedom to link to the coordination ions [10].

Among the organic linkers, 1, 2, 4-triazole has been little used in the design of inorganic–organic systems, due to its short bridging length [11]. It possesses a strong and typical coordination capacity for bridging metal ions resulting in polynuclear clusters with unusual structural diversity. In particular, Cu (II) ion can be easily converted into Cu (I) in presence of reducing agents [12]. The mixed valences and versatile coordination environments make copper attractive as controllable linker. However, there are only few papers on the photocatalytic activity of POMs-hybrid

materials and the photo-electrochemical (PEC) study is little investigated [13–15].

In this work, we report on the synthesis, structural characterization and (PEC) properties of a new inorganic–organic single crystal compound, constructed from Keggin-type polyoxometalate and copper-organic units, namely  $[\text{Cu}_6(\text{trz})_6][\alpha\text{-PW}_{12}\text{O}_{40}]_2 \cdot \text{H}_2\text{O}$ ; the hybrid compound exhibits a 3-D supramolecular host-guest structure. As application, the photocatalytic experiments have been successfully demonstrated and the photodegradation of Rhodamine B (RhB) under both UV irradiation and sunlight is used as reaction test.

## 2. Experimental

### 2.1. Synthesis

All reagents were purchased commercially and used without any further purification.  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (0.72 g, 0.25 mmol), Cu  $(\text{CH}_3\text{-COO})_2 \cdot 6\text{H}_2\text{O}$  (0.149 mg, 0.75 mmol), trz (0.035 g, 0.5 mmol) were dissolved in 10 mL of distilled water and stirred for 3 h to obtain a homogeneous mixture; the pH of the solution averaged 2. The mixture was then transferred in a Teflon-lined stainless steel autoclave (23 mL capacity), kept under autogenous pressure at 180 °C for 3 days and slowly cooled to room temperature. The dark red crystals were recovered by filtration, washed with distilled water and dried at room temperature (60% yield based on Cu). The chemical analysis of the compound (6560.89): (wt%) Calc.: P, 0.94; Cu, 5.81; W, 67.25 is very close to the experimental one: P, 0.93; Cu, 5.77; W, 67.70.

### 2.2. Materials and methods

Powder X-ray diffraction (PXRD) was taken on a Panalytical X'Pert Pro instrument with Cu  $K_\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ) at 293 K. SEM images were obtained with a JSM-6700F field emission scanning electron microscope operating at 5.0 kV. The FT-IR spectra were recorded with a Perkin Elmer Spectrum Two FT-IR spectrometer, in the region ( $400\text{--}4000 \text{ cm}^{-1}$ ) using the routine KBr technique. UV-vis spectra were obtained, in the solid state, using a Jasco V-650 spectrophotometer equipped with an integrating sphere attachment, within the wavelength range (200–750 nm),  $\text{BaSO}_4$  was used as a reflectance standard. The thermal analysis (TG) was carried out with a Perkin Elmer STA 6000 instrument under  $\text{N}_2$  flow at a heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$ .

**Table 1**

Crystal data and structure refinement parameters.

Formula	$[\text{Cu}_6(\text{trz})_6][\text{PW}_{12}\text{O}_{40}]_2 \cdot \text{H}_2\text{O}$
Fw	6560.89
Temp/K	150
Crystal system	Triclinic
Space group	$P\bar{1}$
a / $\text{Å}$	12.6893
b / $\text{Å}$	12.6893
c / $\text{Å}$	12.7039
$\alpha / ^\circ$	87.672
$\beta / ^\circ$	87.672
$\gamma / ^\circ$	87.758
V / $\text{Å}^3$	2040.75
Z / Z'	2/1
$R_{\text{int}}$	0.0301
$R_1^a [I > 2 \text{ sigma}(I)]$	0.0281
$wR_2^b$ (all data)	0.0579
GOF	1.206

$$^a R_1 = \frac{\sum ||F_o| - |F_c||/|F_o|}{\sum w(|F_o|^2 - |F_c|^2)^2 / (w|F_o|^2)^2}^{1/2}$$

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

The electrical conductivity was measured by the probe technique over the range (300–550 K) using an Agilent LCR meter 4363B. The thermo-power (S) was determined from the voltage gradient ( $\Delta V$ ) to the temperature gradient ( $\Delta T$ ) with home-made equipment; ( $\Delta T$ ) was determined by two pairs of chromel alumel thermocouples whereas the ( $\Delta V$ ) was measured with a digital Multimeter (GDM-8200A Series). The electrochemical study was performed with a Voltalab PGZ 301 at room temperature in a Pyrex cell. Platinum gauze was used as a counter electrode and Hg/HgCl<sub>2</sub> (saturated calomel electrode, SCE) as reference electrode.

The photocatalytic experiments were performed by dispersing 50 mg of the compound in 100 mL of RhB aqueous solution at a concentration ( $C_o$ ) of 10 mg/L. Before irradiation, the system was magnetically stirred in the dark for 30 min to ensure the adsorption equilibrium. The suspension was then irradiated; 3 mL were collected every 30 min of irradiation and centrifuged to remove the photocatalyst particles. The remaining RhB concentration (C) was determined by measuring the absorbance ( $\lambda_{\text{max}} = 554 \text{ nm}$ ) with a double beam spectrophotometer (Jasco V-650).

### 2.3. Crystal structure determination

A suitable single crystal (0.27, 0.19, 0.14 mm) was carefully selected under the optical microscope and glued to a thin glass fiber. The single crystal X-ray intensities were collected on a Bruker APEXII diffractometer with a graphite-monochromated Mo  $K_\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 150 K. Multiscan absorption corrections were performed using SADABS [16]. The structure was solved with sir2002 program [17], and refined by the full-matrix least-squares methods on  $F^2$  by using SHELX-97 program package [16]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms (carbon), with C–H = 0.93  $\text{Å}$ , and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ . The crystal data and structure refinements are summarized in Table 1.

## 3. Results and discussion

### 3.1. Structure description

The single-crystal X-ray analysis confirms that the as-synthesized compound crystallizes in the triclinic structure with the space group  $P\bar{1}$  and a pseudo symmetry R3 with two formula weights per unit cell. In the asymmetric unit cell, there are one Keggin type polyoxoanion  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , three Cu(I) cations with three triazole molecules and a half water molecule  $\text{O}_1(\text{w})$  located in the inversion center (Fig. S1). As a result, there are two Keggin anions  $[\text{PW}_{12}\text{O}_{40}]^{3-}$ , one hexanuclear macrocycle cation  $[\text{Cu}_6(\text{trz})_6]^{6+}$  and one water molecule (Fig. 1).

There are four types of oxygen atoms in the  $\alpha$ -Keggin structure with different coordination modes in the cluster: terminal oxygen atoms ( $\text{O}_t$ ), central oxygen atoms ( $\text{O}_c$ ), bridging oxygen atoms to two octahedra edge sharing an ( $\text{O}_b$ ) and bridging oxygen atoms between two octahedra sharing a corner ( $\text{O}_b$ ), the bond distances ( $\text{Å}$ ) are: W– $\text{O}_t$  1.686–1.707(6), W– $\text{O}_c$  2.422–2.455(5), W– $\text{O}_b$  1.905–1.928(5), W– $\text{O}_b$  1.890–1.921(5) (Table S1). The  $\text{PO}_4$  groups and O–P–O angles are in the range  $\{109.3\text{--}109.7(3)^\circ\}$  (Table S2) with P– $\text{O}_c$  distances varying from 1.531 to 1.536(5)  $\text{Å}$  ( $\text{O}_c$  represent the tetrahedral oxygen atoms), indicating that the tetrahedron  $\text{PO}_4$  is distorted. Each Cu(I) is linearly coordinated to two trz ligands through nitrogen bridging mode with Cu–N distances  $\{1.893(7)\text{--}1.908(6) \text{ (Å)}\}$  and N–Cu–N angle of  $168.2(3)^\circ$ , forming calyx[3] arene  $[\text{Cu}_6(\text{trz})_6]$  macrocycle whose center is occupied by the water molecule. The  $[\text{Cu}_6(\text{trz})_6]^{6+}$  cations are arranged into 1-D tubular channels along the [111] direction (Fig. S2), while the  $[\text{PW}_{12}\text{O}_{40}]^{3-}$  anions are inserted in the cavities (Fig. 2). The

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