

# Syntheses, structures, electrochemistry and catalytic oxidation degradation of organic dyes of two new coordination polymers derived from Cu(II) and Mn(II) and 1-(tetrazo-5-yl)-4-(triazolo-1-yl)benzene



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## ARTICLE INFO

### Keywords:

Coordination polymer  
1-(tetrazo-5-yl)-4-(triazolo-1-yl)benzene  
Electrochemical behavior  
Catalytic activity

## ABSTRACT

Two new coordination polymers (CPs), namely,  $[\text{Cu}_2(\text{ttbz})(\text{H}_2\text{btc})_2(\text{OH})]_n$  (**1**) and  $[\text{Mn}(\text{ttbz})_2(\text{H}_2\text{O})_2]_n$  (**2**) (**Httbz** = 1-(tetrazo-5-yl)-4-(triazolo-1-yl)benzene,  $\text{H}_3\text{btc}$  = 1,3,5-benzenetricarboxylic acid), have been hydrothermally synthesized and structurally characterized. Complex **1** exhibits a (3,5,5,5)-connected 2D layer with a Schläfli symbol of  $\{3\cdot 4^2\}\{3\cdot 4^0\cdot 5^2\cdot 6^3\}\{3^2\cdot 0\cdot 4^0\cdot 5^2\cdot 6^2\}\{3^2\cdot 0\cdot 4^0\cdot 5^3\cdot 6\}$ , in which the **ttbz**<sup>-</sup> ligand can be described as  $\mu_5$ -bridge, linking Cu(II) ions into a 2D layer and  $\text{H}_2\text{btc}^-$  ions play a supporting role in complex **1**. The **ttbz**<sup>-</sup> ligand in complex **2** represents the bridging coordination mode, connecting two Mn(II) ions to form the infinite 1D zigzag chains, respectively, which are further connected by two different types of hydrogen bonds to form a 3D supramolecular. Furthermore, catalytic oxidation activities toward organic dyes and electrochemical behaviors of the title complexes have been investigated at room temperature in aqueous solutions, indicating these complexes may be applicable to color removal in a textile wastewater stream and practical applications in areas of electrocatalytic reduction toward nitrite, respectively.

## 1. Introduction

In the recent years, textile industries produce a great deal of dye wastes and discharge of industrial wastewater have presented significant environmental problems as well as brought certain threat to people's health. Therefore, the degradation of pollutants has attracted much attention [1]. Such concerns have required an approach, which be conducted under milder conditions to convert the pollutions chemicals to become cleaner, one way to solve this problem is using suitable catalysis toward the pollutants. Currently, there are a range of materials could serve as catalysts toward organic dyes, and coordination polymers (CPs) are one category of the selectable materials [2]. As we all know, CPs not only possess hierarchical structures and fascinating features, but also have functional properties and potential applications in a wide range of fields, such as catalysis, luminescence, gas storage, ion exchange, magnetism, and so on [3–5]. Of which, catalytic degradation of organic dyes is of considerable importance owing to their potential applications to the environment and it have noticed by some research groups [6]. Xu *et al.* synthesized novel micro-crystals which displayed excellent selectivity in the catalytic degradation of methyl orange and Orange G [6c]. Zhu *et al.* studied the catalytic activities for degradation of dyes aqueous solution of three porous

Cu(II) coordination polymers [2c]. Therefore, the research of using CPs, which constructed by transition metals and organic ligands as catalysts for degrading of organic dyes is meaningful.

The organic ligand 1-(tetrazo-5-yl)-4-(triazolo-1-yl)benzene (**Httbz**), as one of the most important factors to construct coordination polymers, has received considerable attention and the organic ligand containing the tetrazolyl group and triazolyl group may induce new coordination possibility. There are three reasons for selecting the rigid **Httbz** ligand: (i) it includes multiple potential N-coordination sites, which may endow it a specific characteristic to adopt variable coordination modes. (ii) the **Httbz** ligand connecting metal ions could help to create coordination polymers with high stability. (iii) To date, only a limited number of CPs containing **Httbz** ligand have been reported [7].

In the present work, we selected **Httbz** and the carboxylate ligand ( $\text{H}_3\text{btc}$ ) to obtain CPs. Complexes **1–2**, which were formulated as  $[\text{Cu}_2(\text{ttbz})(\text{H}_2\text{btc})_2(\text{OH})]_n$  (**1**) and  $[\text{Mn}(\text{ttbz})_2(\text{H}_2\text{O})_2]_n$  (**2**) ( $\text{H}_3\text{btc}$  = 1,3,5-benzenetricarboxylic acid), have been prepared under hydrothermal conditions. The complexes have been confirmed by single-crystal X-ray diffraction analyses and they have been further characterized by elemental analyses, infrared (IR) spectroscopy, powder X-ray diffraction (PXRD) and thermogravimetric (TG) analyses. Furthermore, fluorescence properties of **1–2** have been investigated.

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And catalytic oxidation activities toward rhodamine B (RhB) and methylene blue (MB) as well as electrocatalytic activities toward the reduction of nitrite of complexes **1–2** have been investigated, respectively.

## 2. Experimental

### 2.1. Materials and characterization

All chemicals were obtained from commercial sources and were used without further purification. Elemental analyses (C, H, N) were carried out with a Perkin-Elmer 2400 CHN elemental analyzer at room temperature. FTIR spectra (KBr pellets) were recorded in the 4000–400  $\text{cm}^{-1}$  range on a Nicolet 170SX spectrophotometer at room temperature. Powder X-ray diffraction (PXRD) data was collected using a Siemens D5005 diffractometer (Cu K $\alpha$  radiation,  $\lambda$  1.5410 Å). Thermogravimetric (TG) analyses of complexes **1–2** were carried out on a Exstar SII TG/DTA 7200 thermal analyzer with a heating rate of 10 °C/min at temperatures between 30 °C and 800 °C under the protection of N<sub>2</sub> atmosphere. Luminescent spectra for the solid samples were performed with a Hitachi F-7000 FL spectrophotometer at room temperature. UV–Vis absorption spectra were taken on a TU-1901 UV–vis spectrophotometer. Electrochemical measurements were measured on a CHI 660E Electrochemical Quartz Crystal Microbalance. The complex bulk-modified carbon paste electrode (CPE), Ag/AgCl and the platinum wire were used as the working electrode, reference electrode and auxiliary electrode, respectively.

### 2.2. Synthesis of $[\text{Cu}_2(\text{ttbz})(\text{H}_2\text{btc})_2(\text{OH})]_n$ (**1**)

A mixture of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (36.24 mg, 0.15 mmol),  $\text{H}_3\text{btc}$  (25.22 mg, 0.12 mmol), **Httbz** (25.57 mg, 0.12 mmol), NaOH (12.00 mg, 0.30 mmol) and water (12 mL) was placed in a sealed 25 mL Teflon-lined reactor and heated at 160 °C for three days. After the reactor was cooled to room temperature, green block crystals of complex **1** were obtained in a yield of about 34% (based on Cu). Anal. Calc. for  $\text{C}_{27}\text{H}_{17}\text{Cu}_2\text{N}_7\text{O}_{13}$ : C, 41.87; H, 2.21; N, 12.66%; found: C, 41.90; H, 2.19; N, 12.67%. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3129(s), 2152(w), 1722(s), 1625(s), 1556(s), 1515(m), 1459(m), 1404(s), 1293(m), 1223(s), 1189(w), 1134(w), 1023(m), 961(s), 919(w), 898(w), 856(s), 829(w), 780(m), 739(s), 683(m), 670(s), 552(s), 497(w), 434(s).

### 2.3. Synthesis of $[\text{Mn}(\text{ttbz})_2(\text{H}_2\text{O})_2]_n$ (**2**)

The synthetic method of complex **2** was similar to that of complex **1**, except that  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  was replaced by  $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$  (36.76 mg, 0.15 mmol). The light red crystals were obtained. Yield: ~33% (based on Mn). Anal. Calc. for  $\text{C}_{18}\text{H}_{16}\text{MnN}_4\text{O}_2$ : C, 41.95; H, 3.13; N, 38.05%; found: C, 41.98; H, 3.09; N, 38.04%. IR data (KBr pellet,  $\text{cm}^{-1}$ ): 3122(s), 2291(w), 1771(w), 1674(s), 1612(s), 1584(m), 1543(s), 1515(m), 1452(s), 1383(s), 1362(m), 1272(s), 1203(s), 1099(m), 1050(s), 1009(m), 968(s), 891(m), 850(s), 815(m), 752(s), 663(s), 635(m), 537(s), 490(s), 441(m).

### 2.4. Preparation of 1-CPE

The complex **1** bulk-modified carbon paste electrode (**1-CPE**) was fabricated by the following steps. Graphite powder 0.50 g and complex **1** 0.030 g were mixed together with an agate mortar for about half an hour to achieve a mixture. About 0.35 mL paraffin oil was added into the mixture with stirring uniformly, which was used to pack 3 mm inner diameter glass tubes with 0.8 cm length [8]. The electrical contact was built with the copper stick, and the surface of the modified electrode was polished on a piece of weighing paper.

**Table 1**

Crystal data and structure refinements for complexes **1–2**.

Complex	<b>1</b>	<b>2</b>
Empirical formula	$\text{C}_{27}\text{H}_{17}\text{Cu}_2\text{N}_7\text{O}_{13}$	$\text{C}_{18}\text{H}_{16}\text{MnN}_4\text{O}_2$
Formula weight	774.56	515.39
Crystal system	Monoclinic	Triclinic
Space group	$P2_1(1)/c$	P-1
<i>a</i> (Å)	16.3897(16)	7.5072(7)
<i>b</i> (Å)	6.8807(6)	7.6928(8)
<i>c</i> (Å)	24.192(2)	9.6615(9)
$\alpha$ (°)	90.00	99.223(2)
$\beta$ (°)	96.243(1)	97.762(2)
$\gamma$ (°)	90.00	110.582(3)
<i>V</i> (Å <sup>3</sup> )	2712.0(4)	504.42(8)
<i>Z</i>	4	1
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.897	1.697
$\mu/\text{mm}^{-1}$	1.658	0.709
<i>F</i> (000)	1560	263
<i>R</i> <sub>int</sub>	0.0556	0.0447
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0406	0.0567
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	0.0742	0.1340
GOF	1.048	1.051
$\Delta \rho$ max (e Å <sup>-3</sup> )	0.486	0.719
$\Delta \rho$ min (e Å <sup>-3</sup> )	-0.467	-0.488

$$^a R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|.$$

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

### 2.5. X-ray crystallographic study

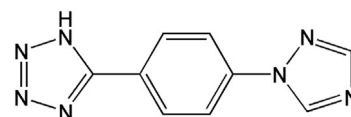
Single-crystal X-ray diffraction data for complexes **1–2** were performed on a Bruker APEX diffractometer equipped with graphite-monochromatic Mo-K $\alpha$  radiation with a radiation wavelength of 0.71073 Å at 298 K for **1**, 293 K for **2**. All structures were solved by direct methods and refined by the full-matrix least-squares methods on *F*<sup>2</sup> with the SHELXTL package [9]. A summary of the crystallographic data and structural determination for complexes **1–2** are provided in Table 1. Selected bond lengths and angles are given in Table S1–S2. Crystallographic data for the structures reported in this paper have been deposited in the Cambridge Crystallographic Data Center with CCDC 1500203–1500204 for **1–2**, respectively (Schemes 1 and 2).

## 3. Results and discussion

### 3.1. Description of the structures

#### 3.1.1. $[\text{Cu}_2(\text{ttbz})(\text{H}_2\text{btc})_2(\text{OH})]_n$ (**1**)

Single crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the monoclinic  $P2_1(1)/c$  space group. The asymmetry unit consists of two separate Cu(II) ions, one **ttbz**<sup>-</sup> ligand, two  $\text{H}_2\text{btc}^-$  and one hydroxyl. As shown in Fig. 2, Cu1 was located in the distorted  $[\text{CuN}_3\text{O}_3]$  octahedral coordination configuration, in which Cu1 is coordinated by three nitrogen atoms of three separate **ttbz**<sup>-</sup> ligands and three oxygen atoms of two  $\text{H}_2\text{btc}^-$  anions and one hydroxyl. The distances of Cu1–N and Cu1–O are 2.053–2.335 Å and 1.954–2.046 Å, respectively. The Cu2 is five-coordinated by two nitrogen atoms from two separate **ttbz**<sup>-</sup> ligands [Cu2–N = 1.966 Å], one oxygen atom from one  $\text{pbda}^{2-}$  ion and two oxygen atoms from two hydroxyls [Cu2–O = 2.014–2.391 Å], taking a distorted  $[\text{CuN}_2\text{O}_3]$  trigonal bipyramidal coordination geometry. In complex **1**, the **ttbz**<sup>-</sup> ligand can be described as  $\mu_5$ -bridge: each triazole ring coordinates to a Cu(II) ion and four nitrogen atoms of tetrazole ring completely coordinated with Cu(II)



**Scheme 1.** The **Httbz** ligand.

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