



# A one-dimensional Ag(I) coordination polymer as luminescent sensor for detecting $\text{Cr}_2\text{O}_7^{2-}$ and exhibiting highly photodegradation capacities for methylene blue solution

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## ABSTRACT

A silver(I) coordination polymer (CP),  $\{[\text{Ag}(\text{DCTP})_{0.5}(\text{bpy})(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}\}_n$  (**1**) based on 2,5-dichloroterephthalic acid ( $\text{H}_2\text{DCTP}$ ) and 4,4'-bipyridine (bpy) were synthesized under hydrothermal condition. CP **1** features a 1D infinite undulating ladder-like chain, which is further extended into a 3D supramolecular network through classic  $\text{O}-\text{H}\cdots\text{O}$  hydrogen bond interactions. CP **1** exhibits highly selective and sensitive luminescent detection for  $\text{Cr}_2\text{O}_7^{2-}$  in aqueous solution with quenching efficiency up to  $2.00 \times 10^4 \text{ M}^{-1}$  and a low detection limit of  $2.06 \mu\text{M}$ . Further, Hirshfeld surface analyses and the photocatalytic properties of CP **1** have also been investigated in detail. Remarkably, CP **1** presented a rare example of Ag(I)-based CP as luminescent probe and photocatalytic materials simultaneously.

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## 1. Introduction

Along with the industrialization rapid development, heavy metal ion pollutants have become a global issue [1–4]. The dichromate anions,  $\text{Cr}_2\text{O}_7^{2-}$  has been of current interest owing to its hazardous effects on both environment and human health [5–10]. Remarkably,  $\text{Cr}_2\text{O}_7^{2-}$  is listed as a priority pollutant by the U.S. Environmental Protection Agency [11–13]. Therefore, it is significant to develop a simple and sensitive method for  $\text{Cr}_2\text{O}_7^{2-}$  detection.

Coordination polymers (CPs) or metal–organic frameworks (MOFs), constructed from metal centers and organic bridging ligands, have emerged as potential luminescent materials in the past ten years [14–18]. This type of materials can be applied in the selective and sensitive detection of environmental pollutants. The controlled channel size, large surface area, supramolecular interactions between the selective guest analytes and the CP host, and robust stability of luminescent CPs make these materials present a competitive advantage over other conventional inorganic and organic luminescent materials, more analytes can effectively adsorbed in its frameworks of CPs, which ultimately can improve the rate of luminescent response and the detection sensitivity [19–21]. The luminescent sensing activities of CPs mainly depend on the structure and other factors such as choice of the metal cen-

ters/ligands, supramolecular interactions, and coordination bonds between the guest species and the CP [22,23]. To efficiently improve the luminescent ability, we can introduce of electron-rich aromatic ligands, because luminescence quenching mechanism is generally caused by electron transfer of the photoexcited electrons from CPs to the electron-deficient analytes [24,25].

In this work, 4,4'-bipyridine (bpy) and 2,5-dichloroterephthalic acid were selected to construct new ternary mixed ligand CP [26–30]. As we know, Ag(I) has a tendency to display a highly versatile and irregular coordination number and geometry because of its intrinsic electronic configuration, leading to form various types of sophisticated coordination architectures, including grids, helicates, cyclic helicates, and clusters [31,32]. Herein, a luminescent Ag-based coordination polymer  $\{[\text{Ag}(\text{DCTP})_{0.5}(\text{bpy})(\text{H}_2\text{O})]\cdot 0.5\text{H}_2\text{O}\}_n$  (**1**) was prepared under hydrothermal condition. The CP **1** displays 1D ladder-like chain and possesses luminescent sensing activity for highly selective detection of  $\text{Cr}_2\text{O}_7^{2-}$ . Meanwhile, the luminescent sensing mechanism and photocatalytic properties of CP **1** were also investigated.

## 2. Experimental

### 2.1. Materials and measurements

All chemicals were of analytical grade and used without further purification. Elemental analyses (C, H, N) were performed on a

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Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on an Avatar 360 (Nicolet) spectrophotometer with KBr pellets. Thermogravimetric analyses were carried out on a Netzsch TG 209 thermal analyzer under N<sub>2</sub> atmosphere at a heating rate of 10 °C/min. Powder X-ray diffractions (PXRD) were recorded on a Rigaku D/Max-2500 diffractometer. The luminescence spectra were obtained by using FS5 fluorescence spectrophotometer at room temperature. UV/Vis absorption spectra were measured using a UV–Vis Puxi T9 UV–Vis spectrophotometer.

## 2.2. Synthesis of {[Ag(DCTP)<sub>0.5</sub>(bpy)(H<sub>2</sub>O)]·0.5H<sub>2</sub>O}<sub>n</sub> (1)

A mixture of AgOAc (0.2 mmol, 33.4 mg), bpy (0.1 mmol, 19.2 mg), H<sub>2</sub>DCTP (0.2 mmol, 47.0 mg), and distilled water (10 mL) was transferred to a 25 mL Teflon-lined stainless steel vessel and heated to 140 °C for 72 h. After cooled to room temperature at a rate of 5 °C h<sup>-1</sup>, colorless block crystals were obtained by filtration and washed with distilled water. Yield 32.9% based on bpy. Elemental analysis (%) calcd for C<sub>28</sub>H<sub>24</sub>N<sub>4</sub>Ag<sub>2</sub>Cl<sub>2</sub>O<sub>7</sub> (815.16): C, 41.26; H, 2.97; N, 6.87. Found (%): C, 41.09; H, 2.84; N, 6.72. IR (cm<sup>-1</sup>): 3429(s), 2926(w), 2852(w), 1615(s), 1544(s), 1480(w), 1432(w), 1377(s), 1088(s), 965(w), 780(w), 712(m).

## 2.3. X-ray crystallography

X-ray crystallographic data for CP **1** was collected on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda$  = 0.71073 Å) at 296(2) K with  $\omega$ -scan mode. A semi-empirical absorption correction was applied using the SADABS program [33]. The structure was solved by direct methods, and all the non-hydrogen atoms were refined anisotropically on F<sup>2</sup> by the full-matrix least-squares technique using the SHELXL-2016 crystallographic software package [34]. All hydrogen atoms of organic ligands were placed in calculated positions and included as riding atoms with isotropic displacement parameters. The residual hydrogen atoms of water molecules were located on a difference Fourier map. Crystallographic data and structure parameters for CP **1** are summarized in Table 1. Selected bond lengths and bond angles are listed in Table S1.

## 2.4. Luminescence sensing properties

In order to investigate the potential application of CP **1** for sensing anions, 4 mg powders of sample were immersed into 4 mL of

aqueous solutions containing 0.001 M K<sub>y</sub>N (N<sup>y-</sup> = CrO<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, or IO<sub>3</sub><sup>-</sup>), respectively, which was treated by ultrasonication for 1.0 h. Aging for 10 h, shaking, filtering, and drying in air, luminescence sample was obtained, the corresponding fluorescence emission spectra were recorded at room temperature. The blank experiment is carried out with the aqueous solutions without any anions under the similar condition. Further, the details of interference experiments are as follows: 0.4 mL of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> (0.01 M) and 0.4 mL of other anions (CrO<sub>4</sub><sup>2-</sup>, MnO<sub>4</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, ClO<sub>3</sub><sup>-</sup>, BrO<sub>3</sub><sup>-</sup>, or IO<sub>3</sub><sup>-</sup>) (0.01 M) were injected into 3.2 mL of water solutions containing the suspension of CP **1**, respectively.

## 3. Results and discussion

### 3.1. Structure analysis of {[Ag(DCTP)<sub>0.5</sub>(bpy)(H<sub>2</sub>O)]·0.5H<sub>2</sub>O}<sub>n</sub> (1)

CP **1** crystallizes in the monoclinic C2/c space group. Its asymmetric unit is built by one Ag(I) center, one bpy ligand, half of the DCTP<sup>2-</sup> ligand, one coordinated water molecule, and a half lattice water ligand. As shown in Fig. 1a, each Ag(I) center is in distorted tetrahedral coordination geometry and is four-coordinated by two nitrogen atoms (N1, N2#1; symmetry codes: #1:  $x + 1, -y + 1, z + 1/2$ ) from two different bpy ligands, one oxygen atom (O1W) from water molecule, and one oxygen atom (O1) from the DCTP<sup>2-</sup> ligand. The values of Ag–N bond distances are 2.179(3) and 2.191(3) Å, and the Ag–O bond separations are 2.748(3) and 2.588(2) Å, which are similar to those of other related Ag(I)-based CPs [35].

As a  $\mu_2$ -bridge mode, bpy ligands link Ag(I) centers to form 1D [Ag(bpy)]<sub>n</sub> zigzag chain, in which the distance between two adjacent Ag(I) centers is 11.425(3) Å, the angle of Ag···Ag···Ag is 157.03(8)°, and the dihedral angle of the two pyridine rings of entire bpy ligands is 15.70(1)° (Fig. 1b). Meanwhile, the DCTP<sup>2-</sup> ligand shows a [2.11] (as described using Harris notation) coordination mode [36], connecting neighboring Ag(I) centers with the non-bonding Ag···Ag length of about 11.096(4) Å. Then, these DCTP<sup>2-</sup> ligands as connectors link the 1D infinite [Ag(bpy)]<sub>n</sub> chains to generate 1D undulating ladder-like chain containing parallelogram units, in which the dimensions are 11.425(3) Å × 11.096(4) Å defined by Ag···Ag separations. The adjacent 1D chains are further packed into a 3D supramolecular framework based on classic O–H···O (O1W–H1WA···O2#3, H1WA···O2 = 2.022(2) Å, O1W–H1WA···O2 = 166.46(2)°; O2W–H2WA···O1W, H2WA···O1W = 1.986(2) Å, O2W–H2WA···O1W = 173.54(2)°; O1W–H1WB···O2, H1WB···O2 = 1.949(3) Å, O1W–H1WB···O2 = 167.78(2)°; symmetry codes: #3:  $-x + 1/2, -y + 1/2, -z$ ) hydrogen bonding interactions between the DCTP<sup>2-</sup> ligands and water molecules (Fig. 1c). The 3D supramolecular network is also stabilized by other hydrogen-bonding interactions (O2W–H2WB···O1W#4, H1WA···O2 = 2.024(2) Å, O1W–H1WA···O2 = 159.24(2)°; symmetry codes: #4:  $-x + 1, y, -z + 1/2$ ), as well as intermolecular  $\pi$ – $\pi$  stacking interactions between pyridinyl groups of bpy ligands (Tables 2 and 3).

Interestingly, a tetramer forms between two DCTP<sup>2-</sup> ligands and two water molecules that builds 1D chains which are further connected via water molecules to give the 2D supramolecular layer (Fig. 1d). The tetramer can be represented using graph set notation as R2 4(8). In the tetramer, the O···O separations vary from 2.7812 to 2.8537 Å, the average O···O separation of ca. 2.8175 Å in the tetrameric core is shorter than that of ca. 2.8268 Å (O2W–H2WA···O1W) connecting dangling water molecules. The tetramers are further linked by oxygen (O2W) atoms of uncoordinated water molecules to form infinite parallel chains intercalated in CP **1**. Simultaneously, four coordinated water molecules and two distinct water ligands, and two DCTP<sup>2-</sup> ligands through hydrogen

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

	CP <b>1</b>
Chemical formula	C <sub>28</sub> H <sub>24</sub> N <sub>4</sub> Ag <sub>2</sub> Cl <sub>2</sub> O <sub>7</sub>
Formula weight	815.16
Crystal system	Monoclinic
Space group	C2/c
<i>a</i> (Å)	10.007(4)
<i>b</i> (Å)	17.623(6)
<i>c</i> (Å)	16.482(6)
$\alpha$ (°)	90
$\beta$ (°)	105.006(4)
$\gamma$ (°)	90
<i>V</i> (Å <sup>3</sup> )	2807.6(17)
<i>Z</i>	4
<i>D</i> <sub>calc</sub> (g/cm <sup>3</sup> )	1.928
$\mu$ (mm <sup>-1</sup> )	1.641
<i>F</i> (000)	1616
<i>R</i> <sub>int</sub>	0.0228
GOF	1.102
<i>R</i> <sub>1</sub> ( <i>I</i> > 2 $\sigma$ ( <i>I</i> ))	0.0353
<i>wR</i> <sub>2</sub> (all data)	0.1057

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