



# Synthesis, structure, luminescence and photocatalytic properties of an uranyl-2,5-pyridinedicarboxylate coordination polymer



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## ABSTRACT

An uranium coordination polymer, namely  $[(\text{UO}_2(\text{pydc})(\text{H}_2\text{O})) \cdot \text{H}_2\text{O}]$  (**1**) ( $\text{H}_2\text{pydc}$  = 2,5-pyridinedicarboxylic acid), has been obtained by hydrothermal method and characterized by X-ray single crystal structure determination. Structural analysis reveals that complex **1** exhibits 1D chain coordination polymer, in which  $\text{UO}_2^{2+}$  ions are bridged by 2,5-pyridinedicarboxylate ligands and the chains are connected into a 3D supramolecular network by O–H  $\cdots$  O hydrogen bond interactions and  $\pi$ – $\pi$  stacking interactions. The photocatalytic properties of **1** for degradation of methylene blue (MB), Rhodamine B (RhB) and methyl orange (MO) under Hg-lamp irradiation have been performed, and the amount of the catalyst as well as Hg-lamp irradiation with different power on the photodegradation efficiency of MB have been investigated. Elemental analyses, infrared spectroscopy, TG-DTA analyses and luminescence properties were also discussed.

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## 1. Introduction

In recent decades, considerable research efforts have been focused on the rational design, synthesis, and understanding of coordination polymers with different compositions and structures, due to their intriguing architectures which have been studied for their potential applications in the functional materials field regarding gas adsorption, luminescence as well as photoelectric conversion and photocatalysis [1]. Therefore, some methods used in synthesizing coordination polymers have been developed, such as hydrothermal [2], solid state reaction [3], ionic liquids [4] and surfactant [5], and so on. On account of the unique excitation and electrochemistry properties of the  $\text{UO}_2^{2+}$  unit, uranyl coordination polymers have been recognized as a new kind of attracting coordination polymers. The uranyl cation ( $\text{UO}_2^{2+}$ ) presents a specific linear configuration with two terminal oxygen atoms seated in the axis and favors 4–6 additional coordination sites in the equatorial plane, yielding tetragonal, pentagonal, and hexagonal bipyramidal geometries [6]. In addition to the structural diversity, uranyl coordination polymers show many interesting physical or chemical properties, including photoluminescence, photocatalysis, and photoelectric conversion, among which the photocatalysis behavior as an effective and economical technique to reduce the

concentration of organic pollutants has been attracting a great deal of attention and becoming a hot research topic [7]. Traditional water treatment methods such as adsorption, separation by ion exchange and coagulation usually suffer from high operating costs, even generate other secondary pollutants in the process. In turn, photocatalytic degradation has demonstrated green ecological elimination and high efficiency [8]. Research finds that, the aqueous solution of uranyl ion ( $\text{UO}_2^{2+}$ ) can be excited to form a catalytically active center under lights, if a suitable substrate with the excited uranyl form active transition state, energy transfer between the molecules would occur, leading to the oxidation of organic reagents [9]. Therefore, Uranyl coordination polymers have a promising future in photocatalytic degradation of organic pollutant. Chen et al. first reported the applications of uranyl coordination polymers in photocatalytic degradation of organic pollutants, studying metal 3D porous U-Ni MOF photocatalytic performance with methylene blue to simulate pollutant under UV irradiation [10]. More recently, Xing and Sun groups also reported some uranyl coordination polymers for photocatalytic degradation of organic pollutants [11].

Herein, we reported an uranyl-2,5-pyridinedicarboxylate coordination polymer and its photocatalytic properties were investigated. The catalysts amount, different dyes and Hg lamp irradiation with different power on the catalytic efficiency were explored. Furthermore, the fluorescence properties and the diffuse reflectance spectroscopy (DRS) spectra of the title complex have been examined.

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## 2. Experimental section

### 2.1. Materials

All chemicals of reagent grade were commercially available and used without further purification.

### 2.2. Physical methods

PXRD measurements were carried out with a Bruker D8 Focus X-ray diffractometer using Cu K $\alpha$ 1 radiation of wavelength 1.54012 Å at a scan speed of 10° min<sup>-1</sup> to check the phase purity. Single crystal X-ray diffraction data were collected by Rigaku R-Axis Rapid X-ray diffractometer. The C, H and N microanalyses were performed with a Perkin Elmer 2400II elemental analyzer. The infrared spectra were recorded from KBr pellets in the range 4000–400 cm<sup>-1</sup> on a Shimadzu FTIR-8900 spectrometer. Thermogravimetric measurements were carried out from room temperature to 950 °C on preweighed samples in a nitrogen stream using a Seiko Exstar 6000 TG/DTA apparatus with a heating rate of 10 °C min<sup>-1</sup>. The photoluminescence properties were measured at room temperature using a Hitachi F-4600 Molecular fluorescence spectrometer. The diffuse reflectance spectroscopy (DRS) spectra were recorded by using a DR-UV-vis spectrometer Lambda 950, and the wavelength range from 200 to 800 nm. The photocatalytic performance was performed with a Bilon BL-GHX-V photochemical reaction instrument. The concentration of dye (RhB, MB and MO) was analyzed through a UV-vis spectrophotometer (Shimadzu, UV-2501) by checking the absorbance at 554 nm, 664 nm and 465 nm.

### 2.3. Syntheses of [(UO<sub>2</sub>(pydc)(H<sub>2</sub>O)) · H<sub>2</sub>O] (1)

UO<sub>2</sub>(Ac)<sub>2</sub> · 2H<sub>2</sub>O (220 mg, 0.5 mmol), 2,5-pyridinedicarboxylic acid (H<sub>2</sub>pydc) (83 mg, 0.5 mmol) were successively added to a stirred aqueous solution (2 mL deionized water and 1 mL acetonitrile), and then 30 µL tetramethylammonium hydroxide (25% volume ratio) was added. The mixture was stirred 30 min at room temperature and transferred to a 23 mL Teflon-lined stainless-steel autoclave, which was heated to 140 °C and kept at this temperature for 3 days, the autoclaves were then cooled to room temperature naturally. Yellow block crystals suitable for X-ray diffraction studies were obtained. (yield: 57% based on UO<sub>2</sub>(Ac)<sub>2</sub> · 2H<sub>2</sub>O). The phase purity of the crystalline product was confirmed by comparing experimental PXRD pattern with the corresponding one simulated on the basis of single-crystal data (Fig. S1). Anal. Calc. for C<sub>7</sub>H<sub>7</sub>U<sub>2</sub>NO<sub>8</sub> (1): C, 17.83; H, 1.49; O, 27.17; N, 2.97 (%). Found: C, 17.92; H, 1.56; O, 27.09; N, 3.05 (%). IR (KBr pellet, cm<sup>-1</sup>): 3189(s), 3099(vw), 1614(vs), 1551(w) 1392(vs), 1352(vs), 1149(vw), 1037(w), 926(m), 815(w), 757(w), 523(s).

### 2.4. X-ray crystallography

Suitable single crystal was selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers which were then mounted on a Rigaku R-Axis Rapid diffractometer with graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) for cell determination and subsequent data collection. The reflection intensity in the  $\theta$  range 3.0–27.5° for **1**, was collected at 293(2) K using the  $\omega$  scans technique. The employed single crystal exhibits no detectable decay during the data collection. The data were corrected for  $L_p$  and absorption effects. The direct method employing the SHELXL-97 program gave the initial positions for part of non-hydrogen atoms, and the subsequent difference Fourier syntheses using SHELXL-97 program [12] resulted in initial positions for the rest non-hydrogen atoms. The

**Table 1**  
Crystal structure data for complex 1.

Compounds	[(UO <sub>2</sub> (pydc)(H <sub>2</sub> O)) · H <sub>2</sub> O]
Empirical formula	C <sub>7</sub> H <sub>7</sub> NO <sub>8</sub> U
Formula weight	471.17
Description	Yellow, block
Crystal size (mm)	0.38 × 0.25 × 0.10
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
<i>a</i> (Å)	7.378(2)
<i>b</i> (Å)	7.962(2)
<i>c</i> (Å)	10.404(2)
$\alpha$ (°)	103.90(3)
$\beta$ (°)	95.50(3)
$\gamma$ (°)	113.37(3)
Volume (Å <sup>3</sup> )	532.0(3)
<i>Z</i>	2
<i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )	2.941
<i>F</i> (000)	424.0
$\mu$ (mm <sup>-1</sup> )	15.287
$\theta$ range (deg)	3.0–27.5
Reflections collected	5278
Unique reflections ( <i>R</i> <sub>int</sub> )	2422
Data, restraints, parameters	2240, 18, 166
Goodness of fit on <i>F</i> <sup>2</sup>	1.045
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> ≥ 2 $\sigma$ ( <i>I</i> )] <sup>a</sup>	0.0422, 0.0963
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data) <sup>a</sup>	0.0458, 0.1074
<i>A</i> , <i>B</i> values in <i>w</i> <sup>b</sup>	0.0432, 1.9065
$\delta\rho_{\max}$ , $\delta\rho_{\min}$ (e Å <sup>-3</sup> )	3.015, -2.961

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

<sup>b</sup>  $w = [s^2(F_o^2) + (AP)^2 + BP]^{-1}$  with  $P = (F_o^2 + 2F_c^2)/3$ .

hydrogen atoms on the organic ligands were geometrically generated, while those of water molecules were located from the successive difference Fourier syntheses. The full-matrix least-squares technique was applied for refinement of positions and anisotropic displacement parameters of all the non-hydrogen atoms, as well as the positions of the hydrogen atoms using riding mode with isotropic displacement parameters set to 1.2 times and 1.5 times of the values for C atoms and O atoms, respectively. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

### 2.5. Photocatalytic activity measurements

The photocatalytic degradation process is arranged as follows. Methylene blue (MB), Rhodamine (RhB) and methyl orange (MO) were used as model organic contaminants for photocatalysis experiments. The as-prepared samples were evaluated by the degradation of dye under UV light irradiation using a 165 W Hg lamp. 10 mg samples were suspended in seven replicates of 20 mg L<sup>-1</sup> dye aqueous solution in 10 mL quartz tubes respectively. Before irradiation, magnetically stirred in the dark for about 40 min to ensure the establishment of an adsorption-desorption equilibrium. Afterward, the solution was under the irradiation of a 165 W Hg lamp. A sample was continually taken from the reaction cell and collected by centrifugation at 15 min intervals during the irradiation, suspensions were sampled and centrifuged with a HC-3518 high speed centrifuge at 9000 rpm for 5 min to remove the uranyl sample and then analyzed by using a Shimadzu UV-vis 2501PC recording spectrophotometer. With the aim to have a deep insight and further investigate the degradation efficiency of the dye, we also studied the degradation efficiency under UV light illumination with different irradiation as the way described above. In addition, In order to investigate the amount of the catalyst on the degradation efficiency of MB, different quantity samples (2.5 mg, 5 mg, 7.5 mg, 10 mg, 12.5 mg and 15 mg) are performed by the same way.

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