

## Study on visible photocatalytic activity of an oxalate-extended Co(II) coordination polymer

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### ABSTRACT

A two-dimensional (2D) coordination polymer [Co(ox)(bpy)] **1** (ox = oxalate, bpy = 4,4'-bipyridine) was prepared by hydrothermal synthesis using CoCl<sub>2</sub>·5H<sub>2</sub>O, oxalic acid, bpy as raw material. Compound **1** is a 2D structure extended by ox and bpy, and it has excellent visible photocatalytic performance. The photocatalytic efficiency of compound **1** could reach up to 98.13% with pH = 10 when two drops of H<sub>2</sub>O<sub>2</sub> were added to methylene blue. The photocatalytic degradation results could be described by the first-order kinetic. Besides, after five cycles, the degradation efficiency decreased only 4.11% (without H<sub>2</sub>O<sub>2</sub>) and 5.22% (with H<sub>2</sub>O<sub>2</sub>). Meanwhile, the solid fluorescence and UV-Visible diffuse reflection of compound **1** were also studied. What's more, the visible light photocatalytic mechanism of compound **1** was analyzed more clearly by free radical trapping experiment and Mott-Schottky curve.

**Keywords:** Water pollution; Coordination polymer; Oxalate; Photocatalysis; Visible light

### 1. Introduction

In recent years, printing and dyeing water pollution has become more and more serious with the rapid development of industry, which not only destroys the ecological environment, but also has a serious impact on human health. In order to solve this problem, people have taken many methods to purify sewage, for example membrane separation [1], adsorption method [2], activated sludge treatment, biological treatment [3], etc. Although these methods have yielded some results, they all have a number of drawbacks as well. For instance, the membranes of membrane separation technology are easy to form an attachment layer, which

affects the purification results [4]. And the main disadvantage of adsorption method is easy to reach adsorption saturation, and exists secondary pollution [5]. The operation of activated sludge process is complicated and it is easy to produce a large amount of sludge [6]. Biological treatment is costly and inefficient [7]. The emergence of photocatalysis has effectively solved the above problems. In the past several years, photocatalysis have made many achievements in dyeing wastewater treatment. George et al. [8] prepared Co-doped ZnO nanomaterials to perform photocatalytic degradation of dyes and found that the degradation rate was 70% after 60 min. Aravinthkumar et al. [9] synthesized Cr:STO-7 material and used it for visible light photocatalytic

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degradation of methylene blue (MB). The degradation efficiency was up to 88% at 120 min. Therefore, the key of photocatalysis is the choice of photocatalyst. Titanium dioxide and zinc oxide are commonly used photocatalysts, but these photocatalysts have shortcomings such as low quantum conversion efficiency and narrow response spectrum range [10]. Consequently, researching and developing new photocatalysts has become a focal point of domestic and international research.

It is found that the structure of coordination polymer is diverse and its physical and chemical properties are superior, so it is widely used in catalysis, medicine, magnetism and so on [11]. Especially in photocatalysis, coordination polymers take full their advantages of high specific surface area, high coordination pattern and orderly structure [12]. Hu et al. [13] synthesized two novel coordination polymers ( $[\text{Zn}(\text{L})(2,2'\text{-bipy})]$ ,  $[\text{Zn}(\text{L})(\text{bbi})_{0.5}]$ ) for photocatalytic degradation of organic dyes. For the first compound, the efficiency of degradation of the dye template was found to be 65.44% after 100 min. The degradation efficiency was 78.54% for the second compound. Lu et al. [14] synthesized coordination polymers with three different ligands  $\{[\text{Ni}(\text{L}^1)_{1.5}(\text{HBTC})(\text{H}_2\text{O})]$ ,  $[\text{Ni}(\text{L}^2)_2(\text{HBTC})\times 2\text{H}_2\text{O}]$ ,  $[\text{Cu}_2(\text{L}^3)_{0.5}(\text{BTC})(\mu_3\text{-OH})\times 2\text{H}_2\text{O}]$  and their degradation rates of CR (Congo red) were 93.10%, 44.25%, 90.85%, respectively [14]. However, there are few reports on photocatalytic degradation of organic dyes under visible light. In order to obtain visible light responsive photocatalytic coordination polymers, it is a very good idea to select inorganic metal ions with good catalytic activity as well as conjugated organic ligands with good photophysical properties. Oxalic acid ( $\text{H}_2\text{ox}$ ) is a conjugated system with large  $\pi$  bonds. This structural advantage plays an important role in the synthesis of coordination polymers and enhances the photocatalytic degradation efficiency under visible light. Dridi et al. [15] synthesized a Cd(II) coordination polymer with ox ( $\text{ox}$  = oxalate) ligand and investigated its photocatalytic performance. 4,4'-bipyridine (bpy) plays an important role in the construction of coordination polymers due to the symmetric N atoms on the two benzene rings in its structure. More importantly, its structural advantage of having a large  $\pi$ -bonded conjugated system also facilitates the photocatalytic performance under the visible light. Hou et al. [16] chose bpy to synthesize the polymer and found that the polymer had superior photocatalytic degradation properties for methyl orange and methylene blue.  $\text{Co}^{2+}$  also have strong catalytic activity. Muslim et al. [17] synthesized coordination polymer of  $\text{Co}^{2+}$  for degradation of organic dyes. Therefore, we selected  $\text{Co}^{2+}$  as the central metal,  $\text{H}_2\text{ox}$  and 4,4'-bpy as ligands to synthesize a coordination polymer  $[\text{Co}(\text{ox})(\text{bpy})] \mathbf{1}$  and investigated its photocatalytic degradation effect. It was found that compound **1** had superior photocatalytic performance under the visible light. Finally, when added  $\text{H}_2\text{O}_2$  in methylene blue (MB), the visible photocatalytic performance of compound **1** could reach 98.13% with pH = 10 at 70 min. This degradation effect is higher than that of some photocatalysts previously reported [18,19]. After 5 cycles, the photocatalytic efficiency of compound **1** decreased by 5.22% and 4.11%, respectively with and without  $\text{H}_2\text{O}_2$ , and X-ray diffraction (XRD) showed that the structure of compound **1** was stable. In conclusion, compound **1** is a potential visible light photocatalyst.

## 2. Experimental section

### 2.1. Materials and characterization

Raw materials used in this experiment were purchased commercially without further processing. The elemental analysis was carried out on a PerkinElmer 2400 LS II Elemental Analyzer (PerkinElmer Enterprise Management (Shanghai) Co., Ltd., 1670 Zhangheng Road, Zhangjiang Hi-Tech Park, Shanghai, China). A Perkin Elmer Spectrum One FTIR Spectrometer was used to record the infrared spectra in the  $4,000\text{--}400\text{ cm}^{-1}$  range of the powder samples on a KBr plate. The thermogravimetric (TG) property was determined on a PerkinElmer TGA 7 Instrument (PerkinElmer Instruments (Shanghai) Co., Ltd., Building 4, Lane 67, Libing Road, Zhangjiang Hi-Tech Park, Shanghai, China) that was heated in air at a rate of  $10^\circ\text{C}/\text{min}$ . An LS 55 fluorescence/phosphorescence spectrophotometer was used to measure the solid-state fluorescence spectra at room temperature. UV-Vis diffuse reflectance spectra (DRS) was recorded using a SolidSpec-3700 UV-Vis spectrophotometer in the  $240\text{--}800\text{ nm}$  range with  $\text{BaSO}_4$  baseline correction. The absorbance of the MB solution was measured using a 722E type visible spectrophotometer with an absorption wavelength of 664 nm, and the photocatalytic degradation efficiency (DE) of compound **1** was calculated according to Eq. (1).

$$\frac{(A_t - A_0)}{A_0} = \text{DE} \quad (1)$$

### 2.2. Synthesis of compound **1**

#### 2.2.1. $[\text{Co}(\text{ox})(\text{bpy})] \mathbf{1}$

A mixture of  $\text{CoCl}_2\cdot 5\text{H}_2\text{O}$  (0.50 mmol, 118 mg), 4,4'-bpy (0.50 mmol, 78 mg),  $\text{H}_2\text{ox}$  (0.50 mmol, 63 mg) were dissolved into  $\text{H}_2\text{O}$  (15 mL). The mixture was stirred for 4 h at ambient temperature. Its pH was then adjusted to 5 with saturated oxalic acid solution. The obtained mixture was sealed in a 25 mL Teflon autoclave reactor and heated at  $170^\circ\text{C}$  for 4 d under autogenous pressure. The red crystals were finally got in 45% yield (based on  $\text{Co}(\text{II})$ ). Anal. Calcd. for  $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4\text{Co}$  (%): C, 44.85; H, 2.25; N, 5.78. Found: C, 43.24; H, 2.68; N, 6.18. IR ( $\text{cm}^{-1}$ ): 3,440 s, 2,358 s, 1,600 s, 1,530 s, 1,409 w, 1,326 s, 1,220 s, 768 m, 684 w, and 517 m.

### 2.3. X-ray crystallography

A Siemens SMART CCD diffractometer (Siemens (China) Co., Ltd., 7 Wangjing Zhonghuan South Road, Chaoyang District, Beijing, China) with Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) was used to collect crystallographic data for compound **1**. The structure has been solved by direct methods using the program SHELXTL and it has been specified on  $F^2$  using the package SHELXL-2014 by means of full-matrix least-squares methods. The non-hydrogen atoms of compound **1** are anisotropic and the hydrogen atoms of the ligand are in the calculated positions. CCDC number is 2285086. The crystallographic data of compound **1** is shown in Table 1.

### 2.4. Photocatalytic degradation

MB was used to test the photocatalytic degradation rate of the compound **1** under visible light. Prepare MB solution

Table 1  
Crystallographic data for compound 1

Compound	1
Formula	C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> O <sub>4</sub> Co
<i>M</i>	303.13
Crystal system	Orthorhombic
Space group	<i>I</i> <sub>mmm</sub>
<i>a</i> (Å)	5.4021(5)
<i>b</i> (Å)	10.9756(11)
<i>c</i> (Å)	11.3896(10)
<i>a</i> (°)	90
<i>b</i> (°)	90
<i>g</i> (°)	90
<i>V</i> (Å <sup>3</sup> )	675.30(11)
<i>Z</i>	2
<i>D<sub>c</sub></i> (g/cm <sup>3</sup> )	1.491
<i>m</i> (Mo-Kα) (mm <sup>-1</sup> )	1.280
<i>F</i> (000)	306
Total data	1,531
Unique data	366
<i>R</i> <sub>int</sub>	0.0205
GO <sub>F</sub>	1.452
<i>R</i> <sub>1</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.0355
<i>wR</i> <sub>2</sub> (all data)	0.1241

with the absorbance of **1** and adjust its pH to 4, 7, 10 with NaOH and H<sub>2</sub>SO<sub>4</sub>. 40 mg of compound **1** was dissolved in 80 mL MB solution and treated in the dark for 30 min to achieve the equilibrium of adsorption and desorption. Finally, the solution was irradiated with a xenon lamp and visible light for 70 min. The samples were removed every 10 min and centrifuged to measure the absorbance.

### 3. Results and discussion

#### 3.1. Hydrothermal synthesis of coordination polymer

Hydrothermal synthesis is one of the most commonly method for compound synthesis. In the process of hydrothermal synthesis, the factors affecting crystal growth are reaction time, temperature and pH. So, we explored the optimal reaction conditions for compound synthesis. Compound **1** was heated at 170°C for 4 d. The crystals shape are regular and have high purity at pH = 5.

#### 3.2. Structural description

The crystal structure analysis reveals that compound **1** is a two-dimensional (2D) layer Co<sup>2+</sup> coordination polymer with H<sub>2</sub>ox and bpy ligands. Its space group is *I*<sub>mmm</sub>. As shown in Fig. S1, the asymmetric unit of compound **1** includes one Co<sup>2+</sup>, two H<sub>2</sub>ox molecules and two bpy molecules. Co<sup>2+</sup> is located in a six-fold coordination field as a center metal consisting of two N atoms on bpy (N1, N1b) and four O atoms on H<sub>2</sub>ox (O1, O1b, O1d, O1i). The bond of Co–O<sub>ox</sub> is 2.085 (3) and Co–N<sub>bpy</sub> is 2.154 (5). These are comparable to the reported bond lengths of the compounds [20,21]. As shown

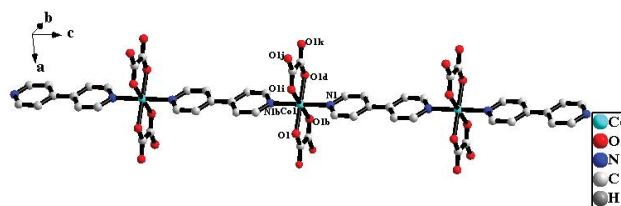


Fig. 1. One-dimensional chain structure for compound **1** (symmetric code b:  $x, -y + 1, -z$ ; d:  $-x + 1, -y + 1, z$ ; i:  $-x + 1, y, -z$ ; j:  $x - 1, y, z$ ; k:  $x - 1, -y + 1, -z$ ; l:  $x, y, z - 1$ ).

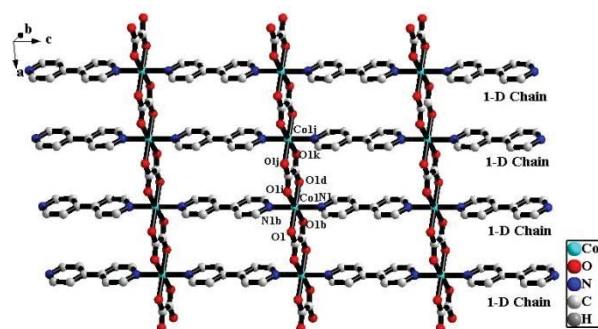


Fig. 2. Two-dimensional layer structure for compound **1** (symmetric code b:  $x, -y + 1, -z$ ; d:  $-x + 1, -y + 1, z$ ; i:  $-x + 1, y, -z$ ; j:  $x - 1, y, z$ ; k:  $x - 1, -y + 1, -z$ ; l:  $x, y, z - 1$ ).

in Fig. 1, the N atoms on bpy bind the central metal Co<sup>2+</sup> to form a one-dimensional (1D) chain structure in the *c*-direction. H<sub>2</sub>ox adopt  $\mu_2$  coordination mode and extend the 1D chain into a 2D layer structure in the *ac* direction by four oxygen atoms (O1d, O1i, O1j, O1k) (Fig. 2).

#### 3.3. IR analysis

As shown in Fig. S2, the infrared absorption peak of compound **1** is 3,440 s, 2,358 s, 1,600 s, 1,530 s, 1,409 w, 1,326 s, 1,220 s, 768 m, 684 w, and 517 m. Compound **1** has an infrared absorption peak at 1,600 cm<sup>-1</sup>, which is the stretching vibration peak of carboxyl group, indicating that during the formation of compound **1**, carboxyl acid has a coordination with metal [22]. There are distinct peaks at 1,530 and 1,220 cm<sup>-1</sup> attributed to C=N and C–N stretching vibrations, respectively, which indicate 4,4'-bpy was successfully coordinated with the metal during the synthesis of compound **1** [23].

#### 3.4. TG analysis

The thermogravimetric analysis of compound **1** was tested at 60°C–800°C (Fig. 3). It was found that compound **1** underwent one-step weight loss in the range of 320°C–400°C. The weight loss in this step was attributed to the loss of all ligands (Found: 73.10%, Calcd: 75.29%). The final remaining product is CoO (Found: 26.90%, Calcd: 24.71%).

#### 3.5. Solid fluorescence analysis

As shown in Fig. 4, the emission peak of **1** is 423 nm, with a certain redshift compared to H<sub>2</sub>ox ( $\lambda_{em} = 335$  and

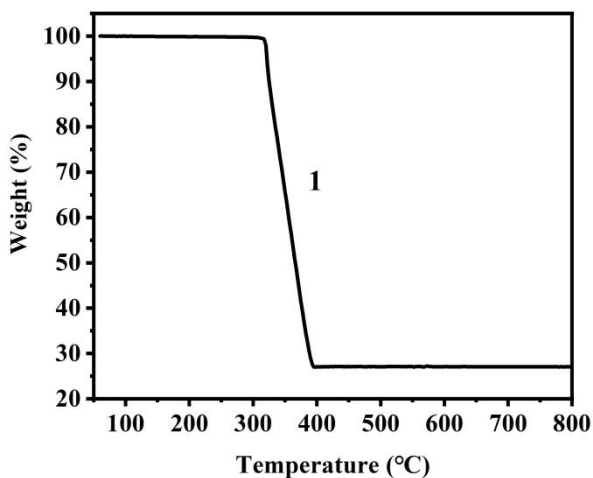


Fig. 3. Thermogravimetric curve of compound 1.

350 nm) and bpy ( $\lambda_{em} = 359$  nm), which may be related to the charge transfer from the ligand to the metal (LMCT) [24–26].

### 3.6. UV-Vis absorption spectra and band gap

The UV-Visible diffuse reflection of compound 1 was tested between 240–800 nm at room temperature. It can be seen from Fig. 5 that compound 1 has a certain absorption intensity between 400–800 nm, indicating that compound 1 has a light response at visible light Eq. (2):

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \quad (2)$$

where  $\alpha$  is absorption index,  $h$  is Planck constant,  $\nu$  is frequency,  $A$  is constant [27]. The band gap energy  $E_g = 2.6$  eV is calculated. Since compound 1 with a narrow gap band can produce electron–hole pairs from low-energy photons, it can exhibit better photocatalytic properties.

### 3.7. Photocatalytic property

#### 3.7.1. Effect of solution pH and addition of $H_2O_2$ on photocatalysis

MB was selected as the template of organic dye and the photocatalytic activity of the compound 1 was tested by calculating MB's absorbance. Researches had shown that there are a number of factors could affect photocatalysis. pH is a critical condition, so we studied the photocatalytic effect of compound 1 at three different pH (pH = 4, 7, and 10). As shown in Fig. 6, with the increase of pH, the photocatalytic degradation efficiency of compound 1 increases continuously (pH = 4: 50.90%; pH = 7: 67.87%; pH = 10: 75.40%). The self-degradation rate of MB was pH = 4: 11%; pH = 7: 28.2%; pH = 10: 31.5% (Fig. S3). This is likely because electrons are generated on the surface of the catalyst when exposed to visible light. With the increases of pH, there will be more  $OH^-$  in the solution.  $OH^-$  will be reduced to hydroxyl radicals by electrons, which can hinder the recombination of electrons and holes. Thus, the photocatalytic performance is improved [28].  $H_2O_2$  is also

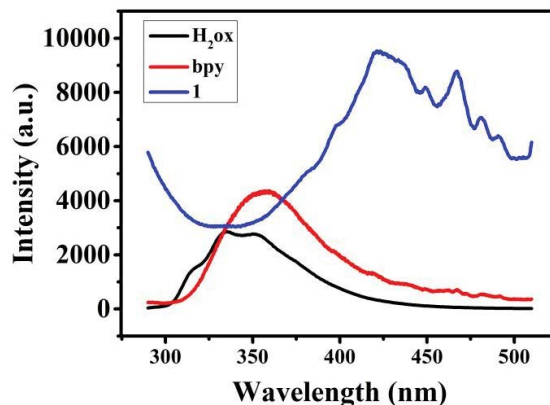


Fig. 4. Solid-state photoluminescence emission spectra of compound 1,  $H_2Ox$  and bpy.

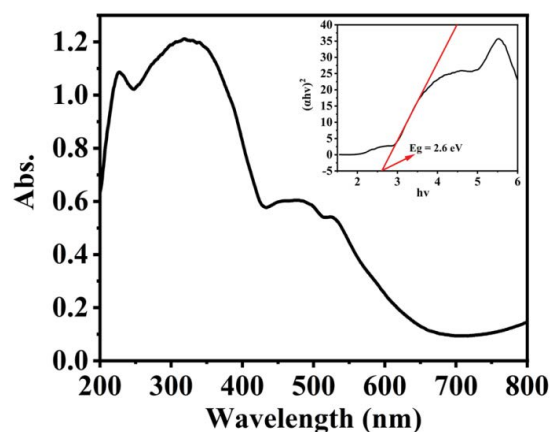


Fig. 5. UV-Vis absorption spectra and Tauc plots of compound 1.

an important factor affecting the photocatalytic performance, so the photocatalytic degradation efficiency with and without  $H_2O_2$  was compared. As shown in Fig. 6, it is found that the degradation efficiency of adding  $H_2O_2$  (pH = 4: 70.19%; pH = 7: 91.10%; pH = 10: 98.13%) is higher than that without adding  $H_2O_2$  (pH = 4: 50.90%; pH = 7: 67.87%; pH = 10: 75.40%) at the same pH. This is because  $H_2O_2$  can generate  $\cdot OH$  under the visible light, which can increase the efficiency of photocatalytic degradation [29].

#### 3.7.2. Kinetic model of photocatalytic reaction

The experimental results showed that the photocatalytic degradation efficiency became better and better with the increase of time within 70 min. Therefore, a first-order kinetic study was conducted on the degradation results, and it was found that the photocatalytic degradation effect and time could be described by Eq. (3):

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (3)$$

where  $C_0$  is the initial absorbance of MB,  $C_t$  is the absorbance of compound 1 to MB at time  $t$ , and  $k$  is the rate constant

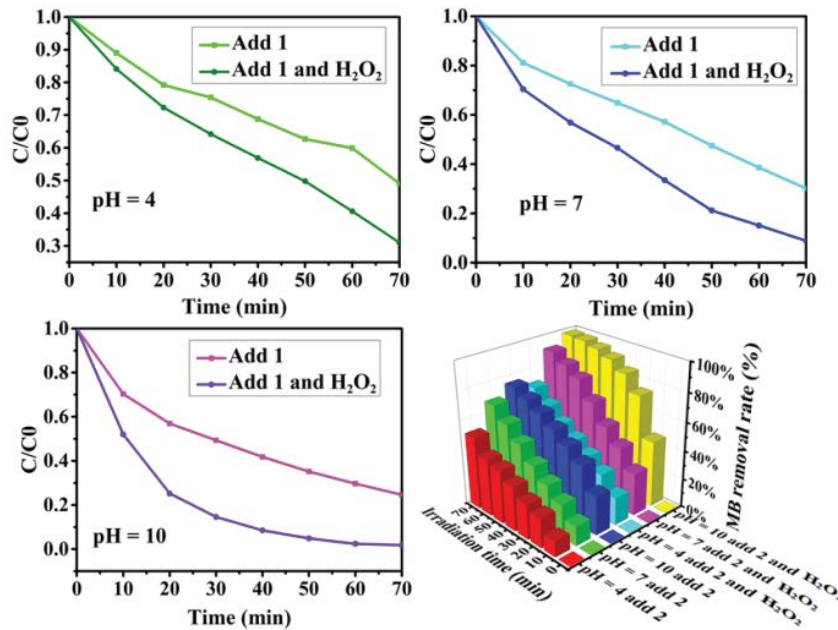


Fig. 6. Methylene blue degradation profile of different conditions under visible light irradiation.

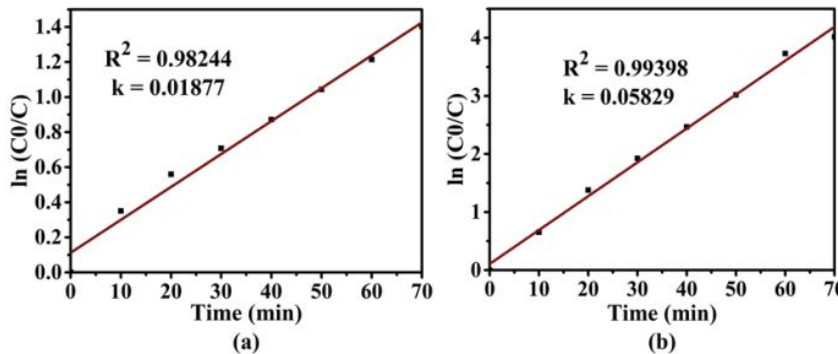


Fig. 7. Determination of kinetic parameters. Conditions: pH = 10, add compound 1 for (a) and pH = 10, add compound 1 and H<sub>2</sub>O<sub>2</sub> for (b).

[30]. As shown in Fig. 7, under different conditions with and without H<sub>2</sub>O<sub>2</sub>, the *k* is 0.01877 and 0.05829, respectively.

### 3.7.3. Recyclability of catalyst

In order to study the stability of the compound 1, five cyclic degradation experiments were carried out. The results showed that the degradation efficiency decreased by 4.11% when H<sub>2</sub>O<sub>2</sub> was not added and by 5.22% when H<sub>2</sub>O<sub>2</sub> was added (Fig. 8). After these five cycles degradation experiments, degradation efficiency decreased to a certain extent, which may be because there was a certain loss of samples in each recycling experiment.

### 3.7.4. XRD analyses

The purity of the synthesized sample and the crystal state after five times of recycling were analyzed by XRD (Fig. 9). The XRD spectra obtained by single crystal data simulation

are consistent with those obtained experimentally, indicating that the synthesized compound 1 is a pure phase. The spectra of the samples obtained after 5 cycles of recovery was also relatively consistent, which declared that the framework of compound 1 was well maintained.

## 3.8. Analysis of photocatalytic mechanism

### 3.8.1. Free radical capture experiments

In order to investigate which active substance plays a role in the whole tube catalysis process, we conducted a free radical capture experiment. p-benzoquinone (PBQ) was used as superoxide radical trapping agent, isopropyl alcohol (IPA) as hydroxyl radical trapping agent, EDTA as hole trapping agent [31]. As shown in Fig. 10, the comparison of experimental results shows that the degradation efficiency decreases by 0.1% when PBQ is added and by 6.8% when IPA is added. The degradation rate of MB was reduced less

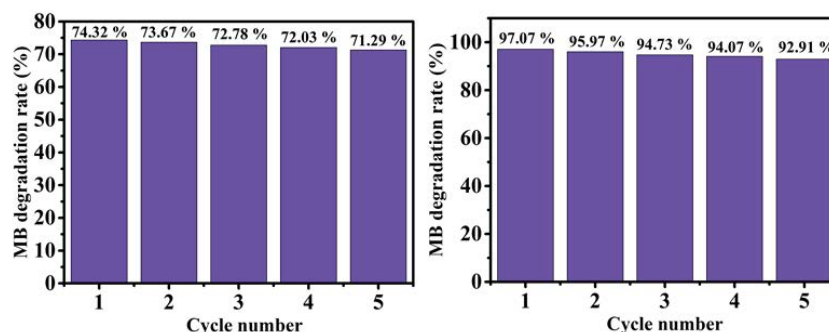


Fig. 8. Recycling experiments in methylene blue photodegradation for compound 1. Conditions: pH = 10, add compound 1 for (a) and pH = 10, add compound 1 and H<sub>2</sub>O<sub>2</sub> for (b).

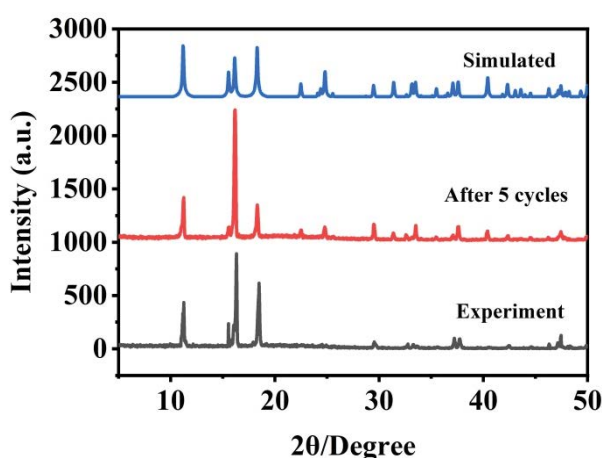


Fig. 9. X-ray diffraction patterns of compound 1.

when the two trapping agents were used. However, when EDTA was added, the reduction efficiency decreased by 25.96%, which was a large decrease. Therefore, holes played a leading role in the photocatalytic process.

### 3.8.2. Mott–Schottky curve

The Mott–Schottky curve of compound 1 was tested in order to understand the band energy level of compound 1 and to provide a clearer explanation of the photocatalytic mechanism of compound 1. Fit Mott–Schottky's curve, if the slope is negative, compound 1 is a *p*-type semiconductor, and if the slope is positive, it is an *n*-type semiconductor. Fig. 11 shows that compound 1 is an *n*-type semiconductor and has a flat-band potential of  $-0.49$  eV. For *n*-type semiconductors, the conduction band (CB) potential is  $0.1$  eV smaller than the flat band potential [32]. So, the CB potential is  $-0.59$  eV vs. Ag/AgCl. Its CB potential with respect to the hydrogen electrode ( $-0.393$  V) is calculated from the equation  $E_{\text{NHE}} = E_{\text{Ag/AgCl}} + 0.197$  V [33]. This is lower than the potential which O<sub>2</sub> is reduced to  $\cdot\text{O}_2^-$  ( $-0.33$  eV). So, step (II) can occur. Compound 1 has  $E_g = 2.6$  eV, so its valence band (VB) is  $2.207$  eV (vs. NHE). This value is greater than the value for the oxidation of OH<sup>-</sup> to  $\cdot\text{OH}$  ( $1.99$  eV) and less than the value for the reduction of H<sub>2</sub>O to  $\cdot\text{OH}$  ( $2.38$  eV) [34], so step

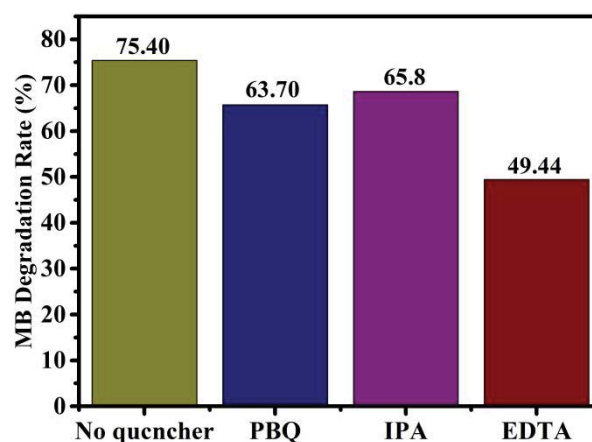


Fig. 10. Photocatalytic degradation efficiency of methylene blue by compound 1 in different scavengers.

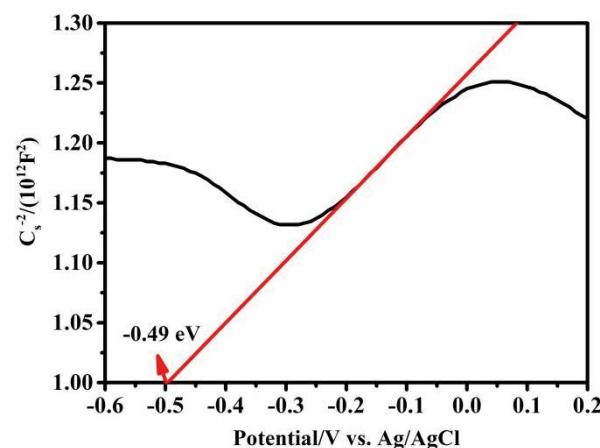


Fig. 11. Mott–Schottky plots of compound 1.

(II) can proceed. In summary, the visible light photocatalytic mechanism of compound 1 was deduced as follows (Fig. 12).



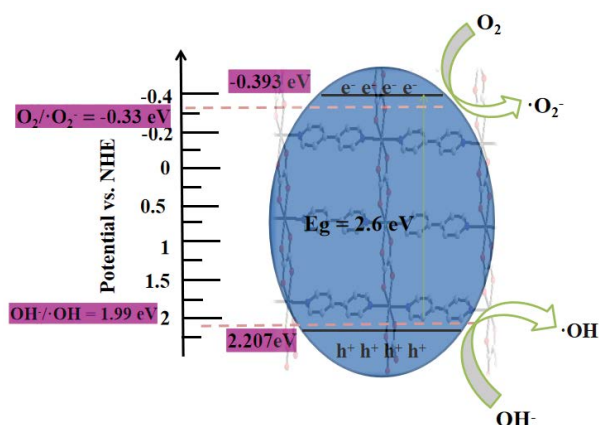
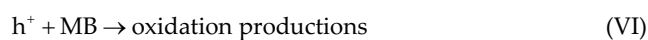
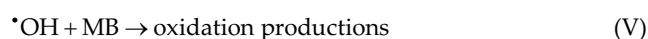
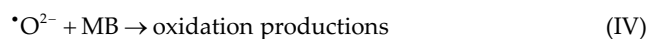


Fig. 12. Possible photocatalytic mechanism of compound 1 in visible light.



#### 4. Conclusions

In short, [Co(ox)(bpy)] **1** was prepared via facile hydrothermal synthesis. Through the analysis of its structure and properties, we can come to some conclusions as follows: (i) H<sub>2</sub>ox and bpy ligands extend compound **1** into a 2D structure. (ii) TG analysis showed that compound **1** lost weight in one step at 320–400°C and had good thermal stability. (iii) The solid fluorescence of compound **1** has a certain red shift compared to the ligand, which is caused by the charge transfer from the ligand to the metal. (iv) The UV-visible diffuse reflectance of compound **1** was analyzed and its  $E_g = 2.6$  eV, which indicates that **1** had a light response in the visible region. (v) Importantly, compound **1** has superior photocatalytic property under the visible light. MB degradation efficiency could reach 98.13% and degradation results were consistent with the first-order kinetic model. (vi) Compound **1** was used for cycle degradation of MB. After 5 cycles, it was found that the degradation effect decreased by 4.10% (without H<sub>2</sub>O<sub>2</sub>) and by 5.22% (with H<sub>2</sub>O<sub>2</sub>), which indicated its repeatability was fine. More importantly, XRD showed that the structure of compound **1** did not change after five cycles. (vii) Through free radical capture experiments, we found that hydroxyl radicals, superoxide radicals and holes all played roles in the whole photocatalytic degradation process, but holes were dominant in the whole process. (viii) The visible light photocatalytic mechanism of compound **1** was analyzed more clearly by Mott-Schottky

curve. Therefore, the photocatalytic experiments showed that compound **1** is a potential photocatalyst for visible light.

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## Supporting information

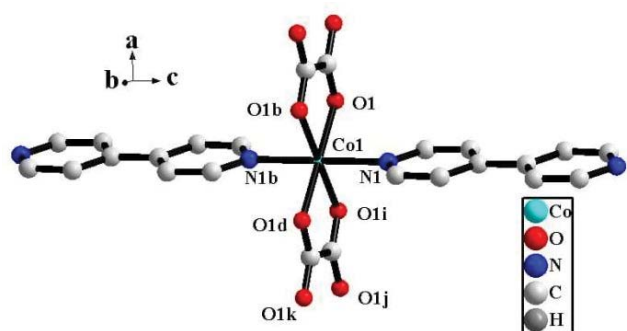


Fig. S1. Coordination environment of  $\text{Co}^{2+}$  center for compound 1 (symmetric code b:  $x, -y + 1, -z$ ; d:  $-x + 1, -y + 1, z$ ; i:  $-x + 1, y, -z$ ; j:  $x - 1, y, z$ ; k:  $x - 1, -y + 1, -z$ ; l:  $x, y, z - 1$ ).

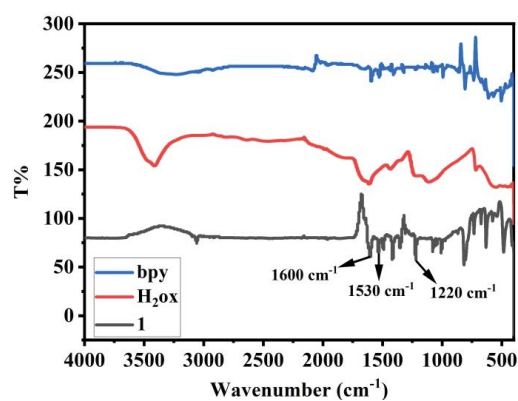


Fig. S2. Infrared spectrum of compound 1, bpy and  $\text{H}_2\text{Ox}$ .

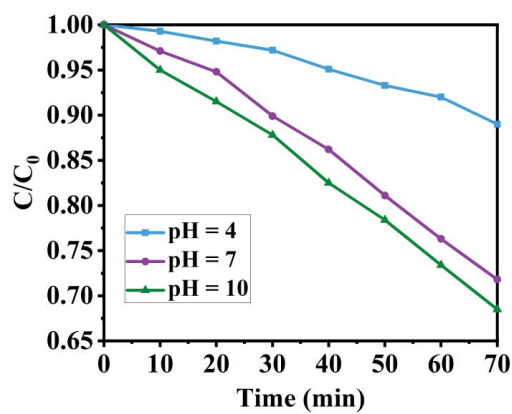


Fig. S3. Self-degradation efficiency of methylene blue (pH = 4: 11%; pH = 7: 28.2%; pH = 10: 31.5%).

**Datablock 1**

Bond precision:	C–C = 0.0070 Å		Wavelength = 0.71073
Cell:	$a = 5.4021(5)$	$b = 10.9756(11)$	$c = 11.3896(10)$
	$\alpha = 90$	$\beta = 90$	$\gamma = 90$
Temperature:	293 K		
	Calculated	Reported	
Volume	675.30(11)	675.30(11)	
Space group	$I_{mmm}$	$I_{mmm}$	
Hall group	$-I_{22}$	$-I_{22}$	
Moiety formula	$C_{12}H_8CoN_2O_4$	$C_{12}H_8CoN_2O_4$	
Sum formula	$C_{12}H_8CoN_2O_4$	$C_{12}H_8CoN_2O_4$	
$M_r$	303.13	303.13	
$D_x$ , g/cm <sup>3</sup>	1.491	1.491	
Z	2	2	
Mu (mm <sup>-1</sup> )	1.280	1.280	
F000	306.0	306.0	
F000'	306.83		
$h, k, l_{max}$	6,13,13	6,13,13	
$N_{ref}$	372	366	
$T_{min}/T_{max}$	0.858,0.880		
$T_{min}'$	0.858		
Correction method = Not given			
Data completeness = 0.984	$\theta(max) = 25.098$		
R(reflections) = 0.0355(353)	$wR2(reflections) = 0.1241(366)$		
S = 1.452	$N_{par} = 41$		

The following ALERTS were generated. Each ALERT has the format

test-name\_ALERT\_alert-type\_alert-level.

Click on the hyperlinks for more details of the test.

**Alert level C**

PLAT052\_ALERT\_1\_C Info on Absorption Correction Method Not Given Please Do!  
 PLAT088\_ALERT\_3\_C Poor Data/Parameter Ratio ..... 9.07 Note  
 PLAT250\_ALERT\_2\_C Large U3/U1 Ratio for Average  $U(i,j)$  Tensor ..... 2.1 Note  
 PLAT341\_ALERT\_3\_C Low Bond Precision on C–C Bonds ..... 0.007 Ang

**Alert level G**

PLAT004\_ALERT\_5\_G Polymeric Structure Found with Maximum Dimension ..... 2 Info  
 PLAT012\_ALERT\_1\_G No \_shelx\_res\_checksum Found in CIF ..... Please Check  
 PLAT199\_ALERT\_1\_G Reported \_cell\_measurement\_temperature ..... (K) 293 Check  
 PLAT200\_ALERT\_1\_G Reported \_diffn\_ambient\_temperature ..... (K) 293 Check  
 PLAT300\_ALERT\_4\_G Atom Site Occupancy of C2 Constrained at 0.5 Check  
**And 3 other PLAT300 Alerts**  
 More ...  
 PLAT301\_ALERT\_3\_G Main Residue Disorder ..... (Resd 1) 34% Note  
 PLAT789\_ALERT\_4\_G Atoms with Negative \_atom\_site\_disorder\_group # 4 Check  
 PLAT822\_ALERT\_4\_G CIF-embedded. res Contains Negative PART Numbers 1 Check  
 PLAT883\_ALERT\_1\_G No Info/Value for \_atom\_sites\_solution\_primary. Please Do!  
 PLAT967\_ALERT\_5\_G Note: 2 $\theta$  Cutoff Value in Embedded. res ..... 50.2°