

# Two Cu(II) Coordination Polymers for Photocatalytic Degradation of Organic Dyes and Efficient Detection of Fe<sup>3+</sup> ions

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## Research Article

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# Abstract

Two new copper-based coordination polymers (CPs),  $\{[\text{Cu}^{\text{I}}(\text{H}_2\text{PO}_4)(\text{dpe})]_5(\text{dpe})_{0.5}(\text{H}_2\text{O})_7\}_n$  (**Cu-dpe(I)**) and  $\{[\text{Cu}^{\text{II}}(\text{HPO}_4)(\text{dpe})(\text{H}_2\text{O})](\text{H}_2\text{O})_3\}_n$  (**Cu-dpe(II)**) (dpe = 1,2-di(4-pyridyl)ethylene), had been successfully constructed by hydrothermal method and ball milling method respectively. The crystal structures of two coordination polymers were determined by single crystal X-ray diffraction. The synthetic temperature caused their structure differences. The differences of structure and properties between these two coordination polymers were discussed. In this work, they both exhibit excellent photocatalytic activity toward the degradation of methylene blue (MB) under visible light. Among them, **Cu-dpe(I)** and **Cu-dpe(II)** could degrade MB more than 88.1% in 120 minutes under visible light. Some active free radicals such as  $\cdot\text{OH}$ ,  $\cdot\text{O}^{2-}$ ,  $e^-$  played an important role in degradation of MB. In addition, luminescent experiment revealed **Cu-dpe(I)** exhibits a relatively high sensitive and selective detection of  $\text{Fe}^{3+}$  ions in water solution. Experimental results show that the fluorescence quenching was caused by competitive absorption of excitation wavelength energy between  $\text{Fe}^{3+}$  and **Cu-dpe(I)**.

## 1 Introduction

Coordination polymers (CPs) are a kind of functional material which are composed of metal ions and organic ligands, and they can be tuned at the molecular level [1]. CPs have attracted much attention in recent years because of a variety of topology structures and broad application prospects such as gas adsorption/separation [2,3], catalysis [4,5], sensor [6,7] and so on. The design and assembly of some new functional materials is also an important research branch, especially the coordination polymers with  $d^{10}$  metal ions and conjugated organic ligands are expected to be used as photosensitive materials and have potential applications for photochemistry [8]. Thus, further construct CPs with new functionality are expected.

Over the years, industrialization and urbanization have led to the release of large amounts of organic pollutants into the environment [9]. Organic dyes are one of the common harmful pollutants in sewage, so they must be removed from the wastewater prior to discharge [9-11]. Among many degradation methods, photocatalysis of organic dyes is an economical and effective method without secondary pollution [11]. At the same time, CP is a semiconductor with an adjustable band gap and is commonly used as a photocatalysis for the degradation of organic dyes [12]. For example, Cui and co-workers reported two Co(II) coordination polymers using rigid and semi-rigid double (imidazole) ligand showed 91.4% degradation efficiency of methylene blue (MB) within 120 minutes under UV-vis irradiation [13]. Yang's group fabricated two 3D supramolecular Cd(II) coordination polymers based on aromatic polycarboxylate and semi-rigidity bis(imidazole) ligands that can degrade 85% of MB within 120 minutes [14].

In addition, the detection of sewage contamination is another challenge for people. Metal ions play important roles in life and environment,  $\text{Fe}^{3+}$  acts as a double-edged sword.  $\text{Fe}^{3+}$  can play an important

role in transmitting oxygen and participating in the human metabolic activities [15-17]. However, deficiency or excess of  $\text{Fe}^{3+}$  ions can lead to a variety of serious dysfunction, including skin diseases, anemia, and decreased immunity [11]. In the recent years, luminescent coordination polymers (LCPs) applied as chemical sensors for the detection of  $\text{Fe}^{3+}$  have been investigated extensively [18, 19]. Synthesis of LCPs with the exposed Lewis basic sites is a common strategy for detection of metal ions [20-22]. This strategy, however, could lower the selectivity toward a special metal ion. This is because of various metal ions as Lewis basic acids could interact with the Lewis basic sites of LCPs and thus lower the selectivity [22]. An overlap mechanism, the degree of overlap between the emission spectrum of the material and the fluorescent probes, could effectively improve the selectivity of LCPs. However, most of the reported LCPs have been prepared from noble or rare earth metals [23, 24]. Therefore, it is necessary to develop inexpensive, highly sensitive and selective detection for  $\text{Fe}^{3+}$  ions.

In this work, 1,2-di(4-pyridyl)ethylene (dpe) was used as a bridge ligand to construct two different Cu coordination polymers. We successfully synthesized  $\{[\text{Cu}^{\text{I}}(\text{H}_2\text{PO}_4)(\text{dpe})]_5(\text{dpe})_{0.5}(\text{H}_2\text{O})_7\}_n$  (**Cu-dpe(I)**) by hydrothermal method and  $\{[\text{Cu}^{\text{II}}(\text{HPO}_4)(\text{dpe})(\text{H}_2\text{O})](\text{H}_2\text{O})_3\}_n$  (**Cu-dpe(II)**) by mechanical milling of CuO,  $\text{H}_3\text{PO}_4$  and dpe in the ratio of 1 : 1 : 1. The crystal structures were determined by single-crystal X-ray diffraction analysis. Organonitrogen species typically behave not only as ligands but also as a reducing agent in the presence of Cu(II) under the hydrothermal conditions. Therefore, the starting reagent of Cu(II) (CuO) was reduced to Cu(I) by dpe under 140 °C. This is similar to that of previously reported Cu(I) complexes [25], While the reduction cannot occur if the reaction is at room temperature. More importantly, Cu-dpe(I) and Cu-dpe(II) can be act as photocatalysts that can effectively degrade MB at room temperature, the possible degradation mechanism is further discussed. In addition, Cu-dpe(I) can be used for sensing  $\text{Fe}^{3+}$  ions in aqueous solution by fluorescence quenching, with high selectivity and sensitivity.

## 2 Experimental

### 2.1 Materials

CuO, 1,2-di(4-pyridyl)ethylene (dpe), and phosphoric acid ( $\text{H}_3\text{PO}_4$ , 85%) were purchased from Sinopharm Chemical Reagent Co., Ltd., (Shanghai, China). All of the chemicals and solvents used in the synthesis were analytical grade and used without further purification.

### 2.2 Synthesis of the Cu-dpe(I)

CuO (0.796 g, 10 mmol), dpe (1.820 g, 10 mmol) and  $\text{H}_3\text{PO}_4$  (85%, 670  $\mu\text{L}$ , 10 mmol) were dissolved in the deionized water (30 mL) and put into a 50 mL screw glass vial for 72 hours at 140 °C, then cooling to room temperature at 5 °C/min. We obtained the orange needle-like single crystals by filtration and wash with water for 3 times.

### 2.3 Synthesis of the Cu-dpe(II)

CuO (0.796 g, 10 mmol), dpe (1.820 g, 10 mmol) and H<sub>3</sub>PO<sub>4</sub> (85%, 670 μL, 10 mmol) were put into a 10 mL Teflon jar with two steel-cored 10 mm Teflon balls. The mixture was ground for 30 minutes in a GT200 grinder mill operating at 1800 rpm. The powder obtained was soaked in 20 mL water, kept at room temperature and grown for a month to give blue, block-like crystals and blue clarified solution.

## 2.4 Photocatalytic Degradation of MB

Photocatalytic experiments were carried out in a multichannel photochemical reaction system (PCX50C, Beijing Perfectlight, China) with one 5W LED lamp as white-light source. Photocatalyst (25 mg) was added to a quartz glass bottle containing 50 mL of MB solution (10 ppm). First, the dark reaction was carried out for 30 min to reach the adsorption equilibrium to avoid the influence of material adsorption on the experiment. After the dark reaction, H<sub>2</sub>O<sub>2</sub> (200 μL) was added to aqueous solution and the light source was turned on for the photolysis reaction for 120 min. Samples were taken every 20 min, and the residual concentration of MB solution was measured by UV-vis spectrophotometer at 664 nm excitation.

## 2.5 Luminescence Sensing Experiments

First, sample (3 mg) was dispersed in 8 mL of deionized water, and the sample was uniformly dispersed by ultrasound for 2 hours. After standing for 2 days, the liquid fluorescence of the sample was measured as a blank experiment. Then, 200 μl M(NO<sub>3</sub>)<sub>x</sub> (x is the charge number for each metal ion) solution (1×10<sup>-3</sup> mol L<sup>-1</sup>, M = K<sup>+</sup>, Na<sup>+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Cu<sup>2+</sup>, Sr<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Cd<sup>2+</sup> and Fe<sup>3+</sup>) was added dropwise to the stationary sample solution to measure the fluorescence intensity. All the liquid fluorescence was tested at the excitation wavelength of 381 nm.

## 2.6 Physical Measurements

The powder X-ray diffraction (PXRD) measurements were recorded on a Rigaku RINT 2200 Ultima diffractometer at 40 kV, 30 mA with a Cu-target tube (Cu Kα radiation, λ = 1.5418 Å) at room temperature. The thermogravimetry analysis (TGA) experiments were performed on a Rigaku TG8120 instrument from room temperature to 500 °C under flowing N<sub>2</sub> with a heating rate of 10 K min<sup>-1</sup>. Sample preparations of the TGA were carried out under air. The Infra-red (IR) Spectroscopy was obtained using a Nicolet ID5 ATR operating in wavelengths of 4000-400 cm<sup>-1</sup> at room temperature. Raman spectra of the samples were obtained by using a Renishaw inVia Micro-Raman spectrometer. Scanning electronic microscopy (SEM) images was carried out using Hitachi FESEM-4800, and complex was dispersed in ethanol by ultrasonication for 30 minutes, then dripped onto the conducting substrates and dried under ambient conditions for SEM measurements. Ultraviolet-visible (UV-vis) absorption spectra was recorded by using a UV-2600 UV-vis spectrometer with BaSO<sub>4</sub> as reflectance scaffold. The fluorescence spectra were performed on a Hitachi F-7000 fluorescence spectrophotometer at room temperature. Single crystal X-ray diffraction measurements were performed with a Rigaku AFC10 diffractometer with Rigaku Saturn Kappa CCD system equipped with a MicroMax-007 HF / VariMax rotating-anode X-ray generator with confocal monochromated MoKα radiation. Data were processed by a direct method (SIR97) [26] and refined by full-

matrix least-squares refinement using the SHELXL-97 computer program [27]. The hydrogen atoms were positioned geometry and refined using a riding model. The deposited number of Cambridge Crystallographic Data Centre (CCDC) is 912031 (293 K) for **Cu-dpe(I)** and 2117855 (173 K) for **Cu-dpe(II)**. A summary of the related crystallographic data, the main bond length and angle of **Cu-dpe(I)** and **Cu-dpe(II)** was summarized in Table S1.

## 3 Results And Discussion

### 3.1 Characterization of Coordination Polymers

Single-crystal X-ray diffraction analysis indicates **Cu-dpe(I)** belongs to the monoclinic crystal system with space group  $C2/c$  (Table S1). The crystal structure of **Cu-dpe(I)** contains Cu(I) metal centers, dpe ligands, and monovalent  $H_2PO_4^-$  anions. In a triangular coordination geometry, each Cu(I) center is coordinated with two nitrogens from the dpe ligand and one oxygen from the phosphate group, as shown in Fig. 1a. Each dpe ligand bridges two  $Cu^+$  ions equatorially to build the extended one-dimensional (1D) chain.  $H_2PO_4^-$  anions are located in the interspaces of the anionic 1D chain running along the  $b$  axis. The P–OH distance ranges from 1.53 to 1.58 Å, and the P=O distances are in the range of 1.49–1.51 Å. There are two hydrogen bonds (H-bonds) between every two orthophosphates. The O–H $\cdots$ O hydrogen bond distance is in the range of 2.4–2.6 Å (Fig. S1). As shown in Fig. 1b, the protonated oxygen atoms are constructed in a three-dimensional (3D) network through the weak hydrogen bonding interactions.

The crystal structure of **Cu-dpe(II)** contains Cu(II) metal centers, one dpe ligand, one  $HPO_4^{2-}$  anion and one water molecule. Cu(II) ion adopts five-coordination geometry, each Cu(II) center is coordinated with two nitrogens from two dpe ligands and three oxygens from two phosphate groups and a water molecule, as shown in Fig. 1c. The whole structure is extended into a two-dimensional layered structure. The layers are filled with guest water molecules. These water molecules stabilize the layered structure of the whole molecule by piling up with each other.

The powder X-ray diffraction (PXRD) pattern of **Cu-dpe(I)** and **Cu-dpe(II)** at room temperature is identical to the simulated pattern from the single crystal structure (Fig. 2a). **Cu-dpe(I)** is an orange, rod-shaped crystal and **Cu-dpe(II)** is a green block-like crystal, as shown in the inset of figure 2b and 2c, respectively. Thermogravimetric analysis (TGA) profile of **Cu-dpe(I)** shows no clear weight loss below 200 °C but a gradual decrease in weight above 200 °C, as shown in Fig. S2. The first ca. 6 % weight loss is due to the release of guest water molecules (calcd. 6.53%) from 80 °C to 200°C. The second weight loss from 250 to 310 °C is around 26 %, which attributed to the absence of free dpe ligands in the structure. The thermal stability of **Cu-dpe(II)** is worse than that of **Cu-dpe(I)**. From 64 °C to 95 °C, a weight loss of about 17%, which is mainly attributed to the remove of the guest water molecules (calcd. 13.06%) and coordinate water molecules (calcd. 4.35%). When the temperature rises to 150 °C, the main framework of the compound gradually collapses. Infra-red (IR) spectroscopy and Raman of **Cu-dpe(I)** and **Cu-dpe(II)** was performed in the figure S3. In IR, the characteristic band shown at  $1073\text{ cm}^{-1}$  is confirmed by the

antisymmetric and symmetric Cu–O(P) stretching, while the stretching vibrations of P-OR group is in the range of 1000 to 400  $\text{cm}^{-1}$  [28, 29]. The stretching vibrations of C-N on the aromatic ring of dpe is at 1583 and 1420  $\text{cm}^{-1}$  [30]. A strong Raman band located at 1635  $\text{cm}^{-1}$  is observed, which is the stretching vibrations of  $\nu(\text{C}=\text{N})$  [31].

Complexes with a  $d^{10}$  metal center have attracted extensive interest due to their excellent photoluminescence properties. In addition, N-pyridyl ligands form a charge transfer interaction with the metal center relatively easily due to the presence of both  $n$ - and  $\pi$ -electrons [32,33]. UV-vis absorption spectra of **Cu-dpe(I)** and **Cu-dpe(II)** (Fig. S4) in the wavelength of 200 to 1000 nm were observed. The dpe has a wide absorption band from 200 to 420 nm, which attributed to the  $\pi$ - $\pi^*$  transition of large conjugated  $\pi$ -electron systems [34]. There is a broad metal-to-ligand charge transfer (MLCT) ( $d \rightarrow \pi^*$ ) in the visible region around 430 nm [35]. As a result, **Cu-dpe(I)** exhibits a broader absorption band and a significant red-shift compared to the free dpe ligands. The absorption intensity of **Cu-dpe(II)** extends to the near infrared (NIR) range compared with the dpe ligand, and the complex has better light absorption performance in the range of 200-1000 nm. The adsorption band of **Cu-dpe(II)** shows a significant blue shift compared with the ligand, which is different from that of **Cu-dpe(I)**. This can be attributed to metal-to-ligand charge transfer (MLCT) [13,36]. In addition, **Cu-dpe(I)** with a band gap of approximately 2.05 eV and **Cu-dpe(II)** with a band gap of approximately 3.03 eV are obtained from the Tauc plot, as shown in Fig. S4b. CPs with a band gap from 1.91 eV to 3.15 eV are appropriate candidates as photocatalysts [37,38]. Therefore, **Cu-dpe(I)** and **Cu-dpe(II)** can be considered as ideal photocatalytic materials.

We investigated the solid-state fluorescence of **Cu-dpe(I)**, **Cu-dpe(II)** and dpe ligand at room temperature to further understand its photoluminescent property. The maximum emission peaks are observed at 366 nm for dpe ligand ( $\lambda_{\text{ex}} = 332$  nm) while 388 nm for **Cu-dpe(I)** ( $\lambda_{\text{ex}} = 247$  nm) and 399 nm for **Cu-dpe(II)** ( $\lambda_{\text{ex}} = 247$  nm) (Fig. S5). In contrast to the dpe ligand, **Cu-dpe(I)** shows a red-shift (22 nm) and **Cu-dpe(II)** shows a red-shift (33 nm) while they also shows an intense emission intensity. The red shift of the emission peak may be due to the metal-to-ligand charge transfer [16, 39]. An intense emission intensity is originate from the coordinated N-donor ligands to Cu(I/II) centers, which could enhance the conformational rigidity of the ligands in compound and thereby reducing the energy loss [19, 40]. This effect thus results in a higher fluorescence intensity in Cu(I/II) complex.

### 3.2 Photocatalytic Degradation of MB

Based on the above characterizations, **Cu-dpe(I)** and **Cu-dpe(II)** are a potential semiconductor catalytic material. **Cu-dpe(I)** have  $d^{10}$  metal center and conjugated organic bonding group, it is expected to be used as photosensitive materials. The surface areas of **Cu-dpe(I)** and **Cu-dpe(II)** are 1.290  $\text{m}^2/\text{g}$  and 1.317  $\text{m}^2/\text{g}$  respectively, which are quite limited. Therefore, the degradation of dye should be attribute to photocatalytic degradation rather than adsorption. Several studies have shown that photocatalytic degradation can be performed using non-porous CPs. Accordingly, we evaluated the photocatalytic degradation of MB for these two compounds. The change of MB photocatalytic degradation rate with

reaction time under different conditions was studied (Fig. 3a). The blank experiments show that MB degrades slowly under visible light, but the degradation efficiency is very low and can be ignored. Under the visible light, with the only addition of **Cu-dpe(I)** or **Cu-dpe(II)** is not conducive to the photocatalytic degradation of MB, and the degradation rate is approximately 20%.  $\text{H}_2\text{O}_2$  has photocatalytic activity to degrade dyes under visible light, but the degradation effect is not good and only 40% of MB is degraded. Therefore,  $\text{H}_2\text{O}_2$  has photocatalytic activity for MB under visible light. Further, when the catalyst and  $\text{H}_2\text{O}_2$  are both added to the aqueous solution, the degradation efficiency of MB is significantly improved under visible light. The photocatalytic degradation efficiency of **Cu-dpe(I)** is 88.1%, and that of **Cu-dpe(II)** is 97.2% within 120 minutes. The combination of **Cu-dpe(I/II)** and  $\text{H}_2\text{O}_2$  shows good degradation effect on MB. This indicates that the catalyst has good photocatalytic activity, and the degradation effect of **Cu-dpe(II)** is slightly higher than that of **Cu-dpe(I)**.

In order to further compare the photocatalytic degradation efficiency, the kinetic behavior of the photocatalyst was investigated, and the photodegradation reactions were all in accordance with the pseudo-first-order reaction kinetic model (Fig. 3b). The relationship between  $\ln(C_0/C)$  and time is shown in the Fig. 3b. Among them, the rate constants  $K$  of degradation reactions of **Cu-dpe(I)** and **Cu-dpe(II)** containing  $\text{H}_2\text{O}_2$  to degrade MB were  $0.0147 \text{ min}^{-1}$  and  $0.0286 \text{ min}^{-1}$ , respectively, which were higher than those of the other three groups (MB, MB +  $\text{H}_2\text{O}_2$ , MB + catalyst). This indicates that the reaction rate of catalyst with  $\text{H}_2\text{O}_2$  is higher than that of any other three components.

It seemed that the degradation mechanism should be associated with photo-Fenton-like process. We did free radical trapping experiments to investigate the main actives in the photocatalytic reaction. (Fig. 3c). The main actives were removed by introducing  $\text{CCl}_4$  ( $e^-$  trapping agent), isopropyl alcohol (IPA,  $\cdot\text{OH}$  trapping agent),  $\text{N}_2$  ( $\cdot\text{O}^{2-}$  trapping agent) and EDTA ( $\text{h}^+$  trapping agent). The results show that  $\cdot\text{OH}$  is the key active group for the degradation of MB for **Cu-dpe(I)**. For **Cu-dpe(II)**,  $\cdot\text{OH}$  plays a major role in the degradation process,  $\cdot\text{O}^{2-}$  plays the secondary role in the reaction rate, followed by  $e^-$  has a slight promotion effect on the degradation reaction.  $\text{H}_2\text{O}_2$  is the precursor of  $\cdot\text{OH}$ , which is an effective and highly active oxidizing substance. In the photocatalytic process of coordination polymers, ultraviolet and visible light can induce the coordination polymers to produce oxygen or nitrogen-metal charge transfer by driving electrons from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO), which strongly requires an electron to return to its stable state. Thus,  $\text{H}_2\text{O}_2$  or  $\text{H}_2\text{O}$  captures an electron, and then reduces to form  $\cdot\text{OH}$  which can effectively decompose MB [1]. While  $e^-$  can be transferred to the surface of catalyst to form  $\cdot\text{O}^{2-}$  with  $\text{O}_2$ , and further capture  $\text{H}_2\text{O}$  to form  $\cdot\text{OH}$ . Therefore, inhibition of  $e^-$  and  $\cdot\text{O}^{2-}$  in **Cu-dpe(II)** will lead to poor degradation effect [1]. As shown in Fig. 3e, **Cu-dpe(I)** and **Cu-dpe(II)** retained effective MB degradation after three cycles. The complexes possess good structural stability after three cycles of MB photodegradation.

### 3.3 Luminescence Sensing Properties

Copper-based LCPs, including Cu(II) and Cu(I), is an interesting alternative fluorescence complex. Cu(II) absorbs light of the longer wavelengths in the visible to near-infrared spectral region [41], indicates a low possibility of overlap mechanism for detection of metal ions [22]. Cu(I), on the other hand, have a  $d^{10}$  electronic configuration and thus no d-d transitions. This could be effective to improve the selectivity of LCPs toward  $Fe^{3+}$  through a possible overlap mechanism. However, there are rare examples of the Cu(I) complexes for the detection of  $Fe^{3+}$  ions [42] and no reported with an overlap mechanism.

The above results clearly indicate **Cu-dpe(I)** is a promising photoluminescent CPs and thus maybe useful in the detection of metal ions. We first measured the fluorescence response of **Cu-dpe(I)** ( $I_{ex} = 381$  nm) and **Cu-dpe(II)** ( $I_{ex} = 322$  nm) to various solvents (Acetonitrile, Methanol, Ethanol, DCM, Acetone, DMF, THF, and  $H_2O$ ) (Fig. 4a, 4b). It shows that **Cu-dpe(I)** has an obvious fluorescence response to a pure water. However, **Cu-dpe(II)** has no specific fluorescence response to many kinds of solutions. Therefore, it is not suitable for use as a fluorescent probe. Due to excellent fluorescence properties of **Cu-dpe(I)**, we further explored the reaction of **Cu-dpe(I)** in aqueous solutions for the detection of metal ions. We measured the emission spectra of **Cu-dpe(I)** in aqueous solutions containing trace amounts of various metal ions. As shown in Fig. 4c,  $Fe^{3+}$  exhibited a drastic quenching effect on the luminescence of **Cu-dpe(I)**, while no significant influence was observed for other metal ions.

The concentration-dependent luminescence behavior of  $Fe^{3+}$  ion was performed to further assess the sensitivity of **Cu-dpe(I)** to  $Fe^{3+}$ . As shown in Fig. 4d, the fluorescence intensity of **Cu-dpe(I)** in the aqueous solution gradually decreased as the  $Fe^{3+}$  concentrations increased from 20 mM to 200 mM. The emission intensity was almost completely quenched when the concentration of  $Fe^{3+}$  was up to 200 mM. The Stern–Volmer equation ( $I_0/I = K_{sv}[M] + 1$ ) [43] was used to analyze the corresponding quenching coefficient of  $Fe^{3+}$ . Here,  $I_0$  is the original fluorescence intensity,  $I$  is the fluorescence intensity, and  $[M]$  is the molar concentration of  $Fe^{3+}$  ( $mmol L^{-1}$ ). A linear relationship was observed when  $Fe^{3+}$  ion ( $[M]$ ) at low concentrations (inset of Fig. 4e). As a result, the quenching constant  $K_{sv}$  was estimated to be  $1.25 \times 10^4 M^{-1}$ , which is comparable to those of other reported  $Fe^{3+}$  quenching coefficients (Table S3) [16, 44-48]. In addition, we measured the fluorescence behaviors of **Cu-dpe(I)** in both metal ions solutions of  $M^{n+}$  with and without  $Fe^{3+}$  ( $M = K^+, Na^+, Pb^{2+}, Cr^{3+}, Cu^{2+}, Sr^{2+}, Ni^{2+}, Zn^{2+}, Co^{2+},$  and  $Cd^{2+}$ ) to further understand the selectivity of **Cu-dpe(I)** towards  $Fe^{3+}$ . As shown in Fig. S6, the fluorescence intensity of **Cu-dpe(I)** was sharply decreased when  $Fe^{3+}$  ions were added into the solutions. Furthermore, a control experiment was conducted with  $M^{n+}/Fe^{3+}$  mixed ions. These results indicate **Cu-dpe(I)** has excellent selectivity and sensitivity for  $Fe^{3+}$  ions in aqueous solution.

Currently, the luminescent quenching of  $Fe^{3+}$  ions can be attributed to the collapse of the frameworks, cation exchange, and competitive absorption between the  $Fe^{3+}$  ions and the LCPs (overlap mechanism) [22, 49]. As the PXRD results shown in Fig. S7, there are no changes in the crystal structure of **Cu-dpe(I)** were observed after being immersed in the  $Fe^{3+}$  ions solution for 24 hours, suggesting the quenching is not related to the structural collapse. Moreover, it is hard for a neutral LCPs of **Cu-dpe(I)** to capture  $Fe^{3+}$

ions through a cation exchange mechanism [50]. Therefore, the resonance energy transfer is another mechanism maybe responsible for the quenching effect [51]. If the emission spectrum of the fluorophore (donor) has a certain degree of overlap with the absorption of the analyte (acceptor), resonance energy transfer from the donor to the acceptor can be observed [52]. As shown in Fig. 4f, a large overlap between the absorption spectrum of  $\text{Fe}^{3+}$  ions solution and the excitation wavelength of compound **Cu-dpe(I)** is observed, while not for the other metal ion solutions. We thus confirm that this high selectivity for  $\text{Fe}^{3+}$  ions is contributed by the competitive absorption.

## 4 Conclusions

In summary, two novel copper-based coordination polymers have been successfully synthesized and structurally characterized. We confirmed that divalent copper can be hydrothermally reduced to monovalent copper under 140 °C, with the coexistence of pyridyl ligand and phosphoric acid. More importantly, both of them shown efficient photocatalytic activity for the degradation of MB, and **Cu-dpe(II)** can degrade MB up to 97.2% in 120 minutes under visible light. Some active free radicals such as  $\cdot\text{OH}$ ,  $\cdot\text{O}^{2-}$ ,  $e^-$  play an important role in degradation of MB. Moreover, **Cu-dpe(I)** also possesses a relatively high selectivity and sensitivity for  $\text{Fe}^{3+}$  ions in aqueous solution. The experiments indicate that the competitive absorption of excitation wavelength energy between  $\text{Fe}^{3+}$  and **Cu-dpe(I)** led to the fluorescence quenching. This metal complex, to the best of our knowledge, is the first example of Cu(I) LCPs for the detection of  $\text{Fe}^{3+}$  ions with an overlapping mechanism. This work provides a promising approach for designing coordination polymers based on the Cu LCPs for MB degradation and  $\text{Fe}^{3+}$  ion sensors.

## Declarations

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The authors declare no competing financial interest.

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## Figures

### Figure 1

**a** The 1D chain structure of Cu-dpe(I) view along z axis. **b** The 3D structure of Cu-dpe(I). **c** The 3D structure of Cu-dpe(II). Cu(I), Cu(II), P, N, O and C atoms are shown in brown, dark blue, yellow, light blue, red, and gray, respectively. H atoms have been omitted for clarity. Guest molecules were also omitted.

### Figure 2

**a** PXRD pattern of Cu-dpe(I) and Cu-dpe(II). **b** The SEM and the photograph (inset) of single crystal Cu-dpe(I). **c** The SEM and photograph (inset) of single crystal Cu-dpe(II).

### Figure 3

**a** Photocatalytic degradation of MB. **b** Kinetic fitting curve of degradation reaction. **c** Free radical trapping experiment of Cu-dpe(I) and Cu-dpe(II). **d** Photocatalytic reaction mechanism of the MB solution on CPs. **e** Cycling catalytic degradation reaction for Cu-dpe(I) and Cu-dpe(II). **f** The PXRD patterns for photocatalyst before and after MB degradation

### Figure 4

**a** Emission spectra of Cu-dpe(I) to different solvents. The inset represents photographs of Cu-dpe(I) in pure methanol (3000 mL methanol, right) and methanol/water mixtures (300 mL water and 3000 mL methanol, left) ( $I_{\text{ex}} = 381 \text{ nm}$ ). **b** Emission spectra of Cu-dpe(II) to different solvents ( $I_{\text{ex}} = 322 \text{ nm}$ ). **c** Fluorescence quenching spectrum of Cu-dpe(I) in the presence of different metal ions in the water solutions ( $I_{\text{ex}} = 381 \text{ nm}$ ). **d** Fluorescence spectra of Cu-dpe(I) in a water solution with different  $\text{Fe}^{3+}$  concentrations ( $I_{\text{ex}} = 381 \text{ nm}$ ,  $[\text{Fe}^{3+}] = 1 \times 10^{-3} \text{ mol L}^{-1}$ ). **e** Stern–Volmer plot for Cu-dpe(I) with different concentrations of  $\text{Fe}^{3+}$  in an aqueous solution. Inset is the linear correlation plot of Cu-dpe(I) at low  $\text{Fe}^{3+}$  concentrations. **f** The UV-vis absorption spectra of various metal ions aqueous solutions and the excitation spectrum of Cu-dpe(I).

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