

Research Article

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A new 3D supramolecular Cu(II) framework: Crystal structure and photocatalytic characteristics

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Abstract: Reported here is a new Cu(II) compound with the formula of $\{\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})(4\text{-NH}_2\text{-py})_4\}_n$ (**1**, 4-NH₂-py = 4-amino-pyridine). The analysis of X-ray diffraction shows that the complex **1** indicates a 0D separated skeleton with $\{\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})\}$ tetranuclear cluster. The interactions of H-bond between the amino groups and $\mu_2\text{-Cl}$ anions from adjacent 0D cluster further extended this 0D cluster into a 3D supramolecular framework. In addition, this compound has excellent photocatalytic activities for the degradation of methyl blue under UV radiation. The cyclic testing results indicate that complex **1** exhibits good recyclability, as it can be repeated for as many as five cycles with no noticeable loss of performance, revealing its potential application in pollutant degradation within the environmental field.

Keywords: Cu(II) compound, tetranuclear cluster, supramolecular framework, photocatalysis

1 Introduction

Being a kind of ordered crystalline material, the metal-organic frameworks (MOFs) have been widespread explored mainly on account of their promising application properties in gas storage and separation, magnetism, luminescence, ion exchange, photocatalysis, and various areas [1–5]. Despite

the MOFs being simply obtainable via the solvothermal or hydrothermal self-assembly of polytopic organic ligands and metal ions, how to acquire MOFs with ideal performances and structures is still a huge challenge [6–8]. In order to synthesize MOFs with predictable structures, it is pivotal to not only carefully select organic ligands with suitable flexibility, symmetry, and coordination groups but also carefully select central metal ions with appropriate coordination geometries [9–11].

With the development of economy, more and more organic dye wastes were directly discharged to environment that caused significant pollution problem to human beings. To remove these organic wastes, photocatalytic technology is considered to be one of the most effective methods that can employ inexhaustible sunlight to decompose these organic dyes into harmless small molecules. According to the reported literature, it can be found that numerous MOFs can be served as photocatalysts and reveal outstanding photocatalytic activities in the organic dye degradation, such as methyl blue (MB), methyl orange, methyl violet, etc. [12–14]. Among these MOFs, most of them are on the basis of Cd(II), Co(II), and Cu(II) metal centers [15–17]. For example, after investigating the relevant literature, copper ions are selected to construct MOFs, mainly because copper ions are considered to have high solubility and stability, and can form a stable chemical structure, making copper complexes in solution exist for a long time. At the same time, copper ions in aqueous solution have a better uniformity, can be fully mixed with other ligands, and form a homogeneous complex structure. Moreover, it can react with a variety of ligands of different properties to form a diversity of metal complexes. These complexes can have different structures, properties, and functions, and are widely used in catalysts, dyes, drugs, and other fields. In addition, copper ions can be used as active centers of catalysts and participate in a variety of organic reactions. They can promote the chemical reaction and improve the reaction rate and selectivity. Overall, the advantages of copper ions as building metal complexes lie in their stability, homogeneity, diversity, and catalytic activity [18]. These properties make

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copper complexes important functional materials in many fields. For example, Astakhov *et al.* synthesized piperazine-linked MOFs from cage Cu(II), Na-phenylsilyl, Cu₆ complexes liganded by silyl dioxyhexacycles, and ethylenediamine ligands. The study found that the prepared material can catalyze the oxidation reaction of cyclohexane with H₂O₂, producing cyclohexanone and cyclohexanol [19]. A great deal of work has been done by other chemists in the preparation and catalytic study of the characteristics of MOFs as basis of copper ions [20]. Among them, relevant article on UV irradiation to achieve methyl bromide degradation have been reported [21]. However, the conventional UV irradiation method for MB catalysis has several major drawbacks: conventional UV irradiation for MB catalysis requires a high-energy UV light source, which has a low-energy utilization efficiency. The cost of equipment for obtaining a high-energy UV light source is high, and the selectivity of the reaction in conventional UV-IR MB catalysis may be low, resulting in the generation of uncontrollable by-products. This may have a negative impact on the environment or adversely affect the purity of the desired product. In addition, conventional UV irradiation-catalyzed reactions are usually limited by conditions such as reaction temperature and pressure. This may lead to difficult operation of the reaction, less controllable reaction conditions, and longer reaction times. In order to overcome these drawbacks, we would like to develop an organic framework based on copper ions for efficient and convenient UV-induced degradation of methyl bromide [22]. To design new MOF-based photocatalyst, in this study, we used 4-amino-pyridine as a terminal ligand in that the uncoordinated amino group could be considered as hydrogen bond donor to construct new supramolecular framework. The use of 4-aminopyridine as a ligand for Cu(II) compounds is mainly based on the following considerations: (1) The nitrogen atom in 4-aminopyridine contains a lone pair of electrons that can form relatively strong coordination bonds with Cu(II). This high affinity makes 4-aminopyridine an effective Cu(II) ligand. (2) The coordination compounds formed by 4-aminopyridine with Cu(II) have relatively high stability. This stability is important for the continuation of the catalyzed reaction and improves the efficiency and lifetime of the catalyst. (3) 4-Aminopyridine can act synergistically with other ligands or substrates by forming coordination bonds with Cu(II). This synergistic effect may improve the rate, selectivity, and yield of the reaction. (4) 4-Aminopyridine has strong coordination ability and certain acidic properties as a ligand. This allows it to have diverse functions in different types of catalytic reactions and is suitable for different reaction systems. (5) By changing the structure of 4-aminopyridine or introducing other functional groups, its coordination

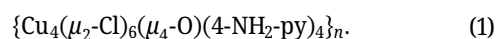
properties and reaction mechanism can be adjusted. This makes 4-aminopyridine an important component of tunable catalytic systems. Via the hydrothermal self-assembly reactions of CuCl₂·2H₂O, 4-amino-pyridine, and NaCl, we acquired a novel Cu(II) compound, called {Cu₄(μ₂-Cl)₆(μ₄-O)(4-NH₂-py)₄}_n (**1**, 4-NH₂-py = 4-amino-pyridine). The structural analysis of X-ray exhibited that the complex **1** reveals a 0D separated skeleton with tetranuclear cluster {Cu₄(μ₂-Cl)₆(μ₄-O)}. These 0D isolated clusters expand into 3D supramolecular skeletons via N-H...Cl hydrogen bonding, these 0D isolated clusters extend into a three-dimensional supramolecular backbone. Furthermore, we examined the thermal stability and photocatalytic activity of the samples, as well as their photocatalytic degradation activity towards the organic dye MB. We also discussed the corresponding catalytic mechanisms in conjunction with the literature.

2 Experimental method

2.1 Materials and instrumentation

All the initial solvents and reagents used in our work were obtained commercially and ready to use. Vario EL III analyzer was employed to analyze the elements H, N, and C. The powder X-ray diffraction (PXRD) studies were carried out with a step size of 0.05° using a PANalytical X'Pert Pro diffractometer at ambient conditions with Cu/Kα irradiation (λ of 1.54056 Å). The Thermo Gravimetric analysis (TGA) was performed with a NETSCH STA-449C TGA under a nitrogen gas flow, and the heating rate was 10°C min⁻¹ to complete the analysis in the range of 30–800°C. The photocatalytic experiments were performed in a Persee TU-1950 ultraviolet-visible spectrophotometer.

2.2 Synthesis of compound



The solution formed by 0.200 mmol CuCl₂·2H₂O, 0.2 mmol 4-NH₂-pyridine, 0.2 mmol NaCl, and 8.0 mL of H₂O was mixed together in the stainless steel container lining with Teflon (23 mL) and this mixture was warmed for 72 h under 170°C. After the product was slowly cooled to the ambient condition, the colorless blue crystals of complex **1** were separated with 36% yielding in the light of Cd(NO₃)₂·4H₂O. Elemental analysis calculated for the C₂₀H₂₄Cl₆Cu₄N₈O

(859.37): N, 13.03, C, 27.93, and H, 2.79%. Found: N, 13.06, C, 27.89, and H, 2.82%.

2.3 X-ray crystallography

Structural details of single crystals have been obtained at ambient conditions by graphite monochromatic Mo-K α radiation (λ of 0.71073 Å) utilizing a computer operated Mercury CCD. By exploiting double straightforward means, the composition of the compounds could be resolved by ShelXS, and then applying SHELXL to refine the structure by least squares [23]. The result of crystallography for this compound is concluded in Table 1. The CCDC number is 2087277.

2.4 Degradation experiment

Aqueous solutions of the dyes were prepared by dissolving MB powder in deionized water. Working solutions of these dyes were obtained by serial dilution of the supply solution with deionized water. The concentration of MB dye was determined at 664 nm by UV-Vis spectroscopy. To examine the effect of original dye concentration, 20 mg of adsorbent was added to 100 mL of MB solution and stirred at 300 rpm for the required time at room temperature, then separated by centrifugation and the equilibrium concentration was determined by UV-vis analysis.

3 Results and discussion

3.1 Crystal structure of compound 1

The architectural analysis of SXRD exhibited that compound **1** crystallizes in a $I4_1/a$ space group of tetragonal system and reflects a 0D isolated framework with a tetranuclear $\{\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})\}$ cluster. The fundamental unit of the complex **1** involves a Cu(II) ions, a terminal 4-NH₂-py ligand, one and a half $\mu_2\text{-Cl}$ anions, as well as a quarter $\mu_4\text{-O}$ anion. As shown in Figure 1a, the Cu1 ions are pentacoordinated and they reveal a coordination structure of trigonal bipyramid, and its basal level is defined via 3 $\mu_2\text{-Cl}$ anions, while the apical positions are taken over via a $\mu_4\text{-O}$ anion and a N donor derived from q ligand of 4-NH₂-py. The separations of Cu–N and Cu–O are 1.955(4) Å and 1.9103(9) Å, and the spacing of Cu–Cl are varied from 2.3607(19) to 2.4722(18) Å, which are in a normal range. As shown in Figure 1b, four neighboring Cu(II) arranged in a tetrahedron are bridged by one $\mu_4\text{-O}$ anion and six $\mu_2\text{-Cl}$ anions into a tetranuclear diamond-type $\{\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})\}$ cluster with the average Cu–Cu distance of 3.13 Å, and four terminal 4-NH₂-py ligands occupied the remaining coordination sites of Cu(II) ions, generating an isolated tetranuclear cluster-based 0D framework. It can be observed that four terminal 4-NH₂-py ligands point in four different directions. Interestingly, the H donors of amino groups from the terminal 4-NH₂-py ligands were just suitably accepted by the $\mu_2\text{-Cl}$ anions from the adjacent isolated tetranuclear clusters to form intermolecular H-bonds of N–H...Cl

Table 1: Crystallographic details of the compound

Formula	$\text{C}_{20}\text{H}_{24}\text{Cl}_6\text{Cu}_4\text{N}_8\text{O}$
Fw	859.37
Crystal system	Tetragonal
Space group	$I4_1/a$
a (Å)	15.918 (8)
b (Å)	15.918 (8)
c (Å)	12.200 (6)
α (°)	90
β (°)	90
γ (°)	90
Volume (Å ³)	3,091 (3)
Z	4
Density (calculated)	1.847
Abs. coeff. (mm ^{−1})	3.264
Total reflections	11,763
Unique reflections	1,766
Goodness of fit on F^2	1.109
Final R indices [$I > 2\sigma(I^2)$]	$R = 0.0587$, $wR_2 = 0.1354$
R (all data)	$R = 0.0726$, $wR_2 = 0.1450$

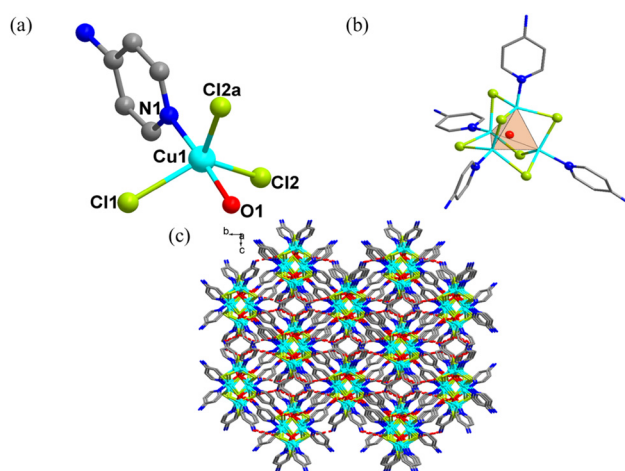


Figure 1: (a) Coordination ring view of the Cu(II) ion in complex **1**. (b) The 0D isolated framework with tetrahedral $\{\text{Cu}_4(\mu_2\text{-Cl})_6(\mu_4\text{-O})\}$ cluster. (c) A 3D supramolecular framework formed by isolated 0D clusters connected through N–H...Cl intermolecular hydrogen bonds (red dashed lines represent hydrogen bonds).

(N–H $\cdots$ Cl = 3.353 and 3.388 Å, $\angle$ NHCl = 139° and 163°). Such intermolecular hydrogen bonds finally connected these isolated 0D clusters into a 3D supramolecular framework (Figure 1c).

3.2 PXRD and TGA analysis

In this work, the analysis of PXRD was employed to confirm the bulk products' phase purity. As shown in Figure 2a, for the bulk product, the experimental results are like the simulated results and agree with the single-crystal diffraction figures. This good agreement indicates that the bulk product is in pure state.

For the sake of the **1**'s thermal behavior, the analysis of TGA was conducted under nitrogen atmosphere from 30 to 800°C (Figure 2b). In TGA curve, no weightlessness can be found from 30 to 289°C, showing that the structure of **1** could be stable up to 289°C, and then, significant weightlessness appeared on account of the framework decomposition.

3.3 Photocatalytic property of **1**

Based on the literature reports on Cu(II)-based MOFs, it can be found that these Cu-based MOFs have prominent photocatalytic activities for the photo-degradation of organic dye pollutants by UV irradiation [24,25]. Therefore, in this

work, MB was picked as the model dye to achieve evaluation of the **1**'s photocatalytic information. The detailed photocatalytic experiments were performed in a typical process as below: The finely ground samples of **1** were dispersed into the solution of MB (100 mL) with 10 mg L⁻¹ concentration, and the suspension subsequently was in-depth treated with ultrasound in darkness for 30 min, and after that, the mixture was irradiated by UV light under constant stirring conditions. At a given interval, 2 mL reaction mixed solution was taken out periodically and analyzed through an ultraviolet-visible spectrophotometer after centrifugal separation. In order to prove the photocatalytic activity of **1**, a control study excluding compound **1** was accomplished under the same circumstances. As shown in Figure 3a, when **1** as used as photocatalyst, the absorption peaks of MB solution at about 665 nm decreased significantly with the increase in the irradiation time, and after 150 min, the degradation efficiency of MB is 87.4% (Figure 3b). When the photocatalytic reaction was conducted without **1** as photocatalyst, the degradation efficiency of MB is only 8.80% after 150 min (Figure 3b). Such result indicates that compound **1** as photocatalyst shows good catalytic activity for MB degradation, that are comparable with that of previously reported MOFs-based photocatalysts [26]. After the photo-catalyzed reaction, the specimen of **1** was centrifuged and isolated and further used to perform PXRD tests as illustrated in Figure 2a, indicating that **1** was structurally intact during the photocatalytic experiments.

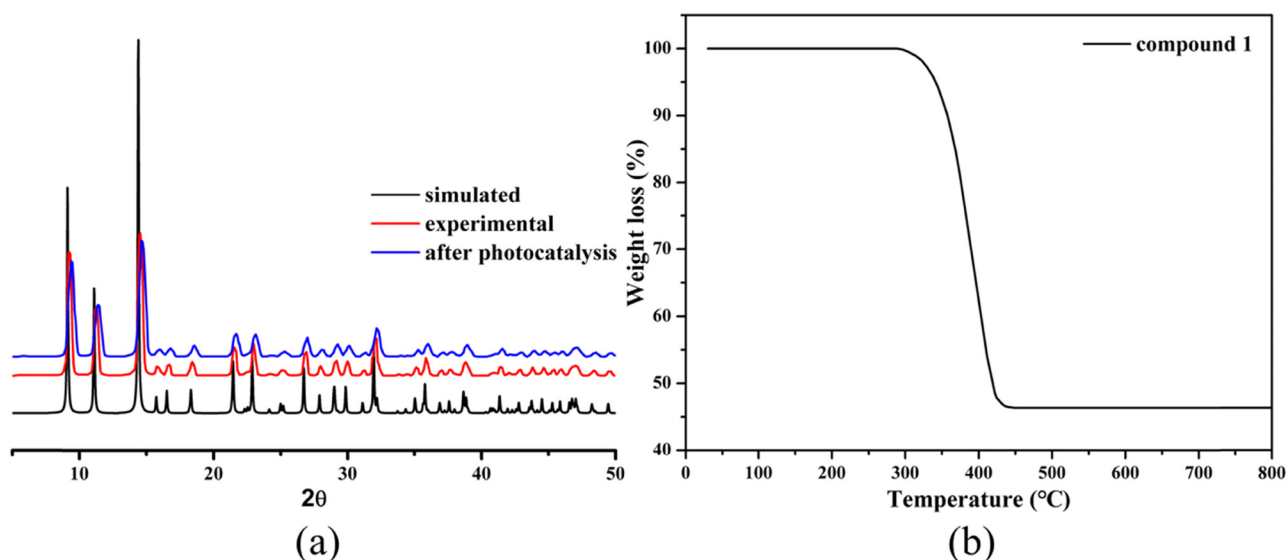


Figure 2: (a) The PXRD for the complex **1**. (b) The TGA result of complex **1**.

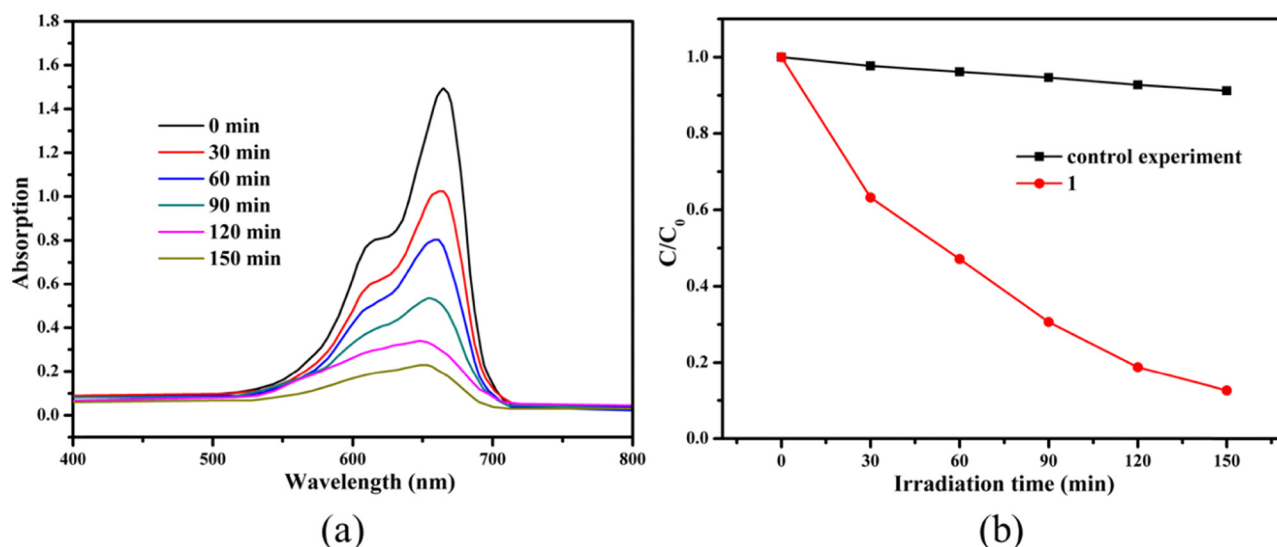


Figure 3: (a) UV-Vis absorption of MB degradation in the presence of **1** acting as photocatalyst. (b) Degradation percentage of MB under UV light in the absence or presence of compound **1** acting as photocatalyst.

3.4 Stability and recoverability of **1**

An important factor in considering solid materials as effective adsorbents in industry is their ability to be recycled. In order to investigate the reusability of the sample of compound **1**, a recycling experiment was carried out using ethanol as desorbent. For this purpose, 20 mg of the sample was added to a methyl bromide solution at an amount of 100 mg L^{-1} and stirred for 40 min. In the next step, the sample was separated using a centrifuge, washed four times with ethanol, and finally dried at 40°C for 5 h. After drying, the sample was adsorbed again under the same conditions. The findings indicated that the adsorbent can be repeated five times and there is no noticeable decrease in the activity (Figure 4). These results demonstrate that the structure of sample **1** is stable and does not change after repeated use.

3.5 Photocatalytic mechanism

The mechanism was determined based on our synthesis of former publications and results of experiments. In a photocatalytic degradation system of this photocatalytic degradation method, the adapting agent (i.e., Cu organic framework material) absorbs UV light. The light-absorbing ability and bandgap position of the photocatalytic materials are important factors affecting their degradation performance. Materials having thinner band gap energy levels have improved damage properties. Visible light absorbance is highly dependent on the band gap energy scale,

which affects the electron (e^-) mobility from the source of material to the water molecules. Materials with smaller bandgap energy levels and larger surface areas are expected to exhibit better light absorption capabilities. The band energy levels of Cu (BA) were determined using VB-xps control of valence band energy and UV-vis DRS measurements. Under UV irradiation, electrons (e^-) in the energy band of 4-aminopyridine migrated into the energy band of copper (BA) to form a heterojunction, which inhibited the complexation of photo-generated carrier and absorbed UV-visible light at wavelengths lower than 460 nm. In addition, OH moieties on the outside of the complex catalysis reacted

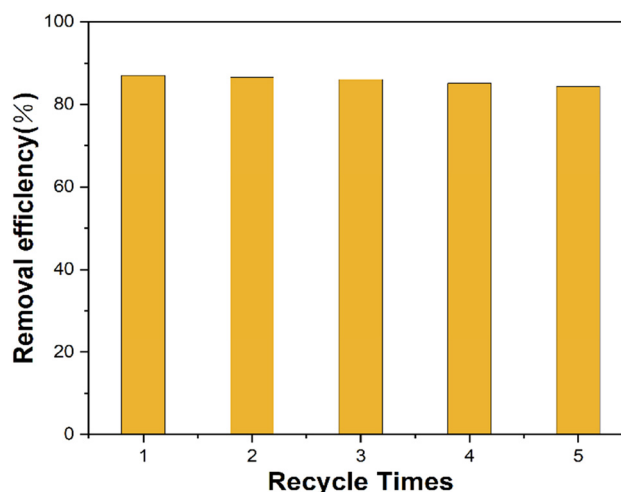


Figure 4: Reusability of catalysts **1** in MB removal.

with photo-generated holes (h^+) to form $-OH$ radicals, which resulted in the degradation of the contaminants [27,28].

4 Conclusion

In summary, a new 0D framework with isolated tetranuclear $\{Cu_4(\mu_2-Cl)_6(\mu_4-O)\}$ cluster was hydrothermal synthesized. The H donors of uncoordinated amino groups from the terminal 4-NH₂-py ligands were suitably accepted by the μ_2-Cl anions from the adjacent 0D cluster to form intermolecular hydrogen bonds, which further extended these 0D isolated clusters into a 3D supramolecular framework. Under UV light irradiation, this compound could be seen as an excellent photo-catalyst for the MB solution degradation. Mechanistic studies indicate that the catalytic process is driven by the generation of $-OH$ radicals, which play a crucial role.

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Author contributions: Jing Li and Jiangtao Li synthesized and prepared the crystals of complexes; Hongjiang Ren performed other experiments; Liuchang Wang wrote the article.

Conflict of interest: There are no conflicts to declare.

Ethical approval: The work is not relating to the use of either human or animal.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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