New 3D Supramolecular Framework: Photocatalytic Property and Therapeutic Activity on Orbital Wall Fracture

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1. Introduction

The clinical manifestations of orbital wall fractures are complex and diverse. The mild cases may not have any clinical manifestations, and the severe cases seriously affect the patient’s appearance and function [1]. The β-catenin signaling pathway in the osteoblast exerts a principal effect in the recovery process of orbital wall fracture [2]. Thus, new candidates for the orbital wall fracture therapy targeting the β-catenin signaling pathway were developed in this study.

As the acceleration of industrialization, global water pollution is a very serious problem facing mankind. The pollutants in wastewater mainly include heavy metal ions, organic dyes, pharmaceuticals, and oil spills [3, 4]. As one type of highly hazardous contaminant, organic dyes, such as methyl violet (MV) and methyl orange (MO), together with methyl blue (MB), have been widely used in the dyeing, dyestuffs, and the textile industry, and the dye wastewater from these plants was discharged into the environment with any treatment to reduce the dye contaminants [5, 6]. Such organic dyes are chemically stable and poorly biodegradable in a short time. In order to protect human safety and ecological environment, it is imperious to develop a green, conver-
successfully obtaining a new compound of \([Cu_4OCl_6(H\text{-bim})_4\cdot n(H_2O)\cdot 2n(EtOH)]\) with isolated 0D framework (Scheme 1). X-ray structural analysis revealed that this isolated 0D framework features a tetrahedral \([Cu_4O]\) core. These isolated frameworks are connected together via the interactions of hydrogen bonds and \(\pi\ldots\pi\) resulting in the creation of a 2-dimensional layer. Final stacking of these 2D layers induced by the weak Van der Waals interactions resulted in a new 3D supramolecular framework. The exploration of photocatalytic performance suggested that this complex reveals excellent photocatalytic efficiency of MB can reach up to 87.6% after 180 min exposure of ultraviolet light. A sequence of biological studies was implemented in this experiment to test the above complex’s application values against orbital wall fracture.

2. Experimental

2.1. Materials and Instrumentation. In this paper, the solvents together with chemical reagents applied were acquired from the commercial sources with analytical grade, which are directly employed. For exploring the elements of carbon, nitrogen, and hydrogen, the elemental Vario EL III analyzer are directly employed. For exploring the elements of carbon, nitrogen, and hydrogen, the elemental Vario EL III analyzer were employed. The PANalytical X’Pert Pro was utilized for recording the PXRD analysis with 1.54056 Å Cu Kα radiation at 0.05° step size. The complex 1’s thermal behavior was investigated through the thermoanalyzer of NETSCHZ STA-449C with 10°C per min heating rate between 30 and 800°C under nitrogen flow. The ultraviolet-visible diffuse-reflectance spectrum in solid state was determined via a Lambda 950, where BaSO4 plate was utilized as a reflectance standard.

2.2. Synthesis of \([Cu_4OCl_6(H\text{-bim})_4\cdot n(H_2O)\cdot 2n(EtOH)]\) (1). The mixture of 0.100 mmol CuCl2·2H2O, 0.1 mmol Hbim, 0.5 mmol NaCl, 3 mL EtOH, and 5.0 mL H2O was added into a reactor (25 mL) lined by Teflon, which was in-depth stirred for half an hour, and the reactor was subsequently sealed and heated for 3 days under a temperature of 135°C. After cooling this mixture gradually to RT, the green massive crystals 1 were produced with 28% yield according to CuCl2·2H2O. Elemental analysis calcld.: for \(C_{32}H_{38}Cl_6Cu_4N_8O_4\) (1065.55): N, 10.51; C, 36.04; and H, 3.57%. Found: N, 10.48; C, 36.01.44; and H, 3.61%. IR (KBr, selected bands, cm\(^{-1}\)): 3334vs, 3195vw, 3083w, 3037w, 2998m, 2954w, 2915m, 2747w, 2083w, 2009w, 1926w br, 1831w br, 1606m, 1482m, 1462m, 1444m, 1425m, 1389m, 1382m, 1335w, 1249m, 1173m, 1151s, 1111s, 1032s, 970s, 945m, 880s, 772s, 708s, 620s, 600s, 548m, and 423w.

2.3. X-Ray Structural Determination. Rigaku Mercury CCD diffractometer was exploited to record the 1’s crystallographic data at 293 K utilizing graphite-monochromated Mo-Kα radiation. SADABS was employed for implementing empirical absorption correction [19]. All calculations were performed by using the teXsan crystallographic software package from the Molecular Structure Corporation. SHELXS program and SHELXL refinement package were, respectively, utilized to solve and refine the structure [20]. The lattice solvents were squeezed out by the PLATON program [21]. All of the atoms except for H atoms were anisotropically refined, and the H atoms were created in their desired positions. The compound 1’s refinements and specific crystallographic data are exhibited in Table 1, and the chose bond parameters around Cu(II) ions are revealed in Table S1.

2.4. Photocatalytic Experiments. The photocatalytic performance of 1 was tested at room temperature, and the experimental process referenced from the reported literature [22]: the compound 1’s samples (50 mg) were added into a solution of MB (100 mL and 10 mg/L), and then, the suspension was stirred magnetically for half an hour in darkness to reach adsorption-desorption equilibrium of MB. With a continuous stirring, mixture was subsequently exposed to mercury lamp irradiation (125 W) with a distance of 37.5 mm from the liquid surface. With a given time interval (30 min), the reaction mixture (3 mL) was taken out and centrifuged immediately to remove the solid samples. Finally, the obtained supernatant was analyzed by the UV-Vis spectrometer. The comparison experiments (without catalyst and with catalyst in the dark) were also carried out at the same conditions.

2.5. Alkaline Phosphatase Staining Kit Method. To measure the content of alkaline phosphatase in the osteoblast after compound treatment, the alkaline phosphatase staining kit was used in the study. This implementation was finished completely following the instructions with slight change. Shortly, the SD rats (between 6 and 8 weeks, 220 g) applied in this experiment were provided by Nanjing University. All the researches were conducted strictly authorized through the Animal Ethics Committee of Nanjing University. The animal model of orbital wall fracture was created and the treatment of compound was finished with 1, 2 together with 5 mg/kg concentration. The osteoblast was gathered, which was rinsed through using PBS for three times, and a reaction solution involving diethanolamine
(25 mmol/L), magnesium chloride (1 mmol/L), and PNPP (6.7 mmol/L) was added for incubation. The cells were incubated in an incubator at the condition of 37°C for half an hour, and then, sodium hydroxide (0.1 mol/L and 100 μL) was added into the cells to stop the above reaction. The value of optical density (OD) was tested with a microplate reader at a wavelength of 405 nm.

2.6. Real-Time RT-PCR. Real-time RT-PCR was exploited for the detection of the β-catenin signaling pathway activation in osteoblast after treating with compound. This research was conducted completely following the instructions. Briefly, the animal model of orbital wall fracture was created and the treatment of compound was finished. Afterward, the osteoblast was gathered in the cells, TRIzol reagent was utilized for extracting the total RNA. After testings its concentration, it was subsequently reverse-transcribed into the cDNA. The β-catenin signaling pathway activation in osteoblast was detected through exploiting real-time RT-PCR, and gapdh was employed as an internal control gene. This experiment was conducted at least three times and the outcomes were expressed with mean ± SD.

3. Results and Discussion

3.1. Crystal Structure of 1. The compound 1’s structure was crystallized in the triclinic space group of P-1 and reveals a 0D skeleton with separated tetrahedral cluster of [Cu₄O]. Its fundamental unit is constructed from four crystallographically separated Cu(II) ions, four ligands of Hbim, six μ₄-Cl, one μ₃-O ligand, two free EtOH molecules, and a free H₂O molecule. As displayed in Figure 1(a), all of the Cu(II) ions are 5-coordinated in the slightly twisted trigonal bipyramidal coordination polyhedron, which is defined through three μ₂-Cl ligands in the equatorial plane and one μ₄-O ligand and one nitrogen donor of Hbim ligand in the axial positions. Around the Cu(II) ions, the bond parameters are listed in Table S1. Guided via the N-H…Cl H-bonds (the N-H…Cl is 3.321 and 3.504 Å, z(NHCl = 119° and 147°), adjacent isolated tetrahedral clusters are linked into an extended 1D infinite chain (Figure 1(b)). Further, between Hbim ligands, the π…π interactions (the distance of centroid-to-centroid is 3.558 Å) from the adjacent chains extended these 1-dimensional chains into the 2-dimensional layer (Figure 1(c)). Ultimately, these 2-dimensional layers are stacked together under weak Van der Waals interactions, affording a 3D supramolecular framework (Figure 1(d)). The free solvent molecules containing EtOH and H₂O were squeezed out by the PLATON program.

3.2. Powder X-Ray Diffraction Pattern (PXRD) and Thermogravimetric Analysis (TGA). To check the phase purity of the products, powder X-ray diffraction (PXRD) experiments have been carried out for 1 (Figure 2(a)). The peak positions of the experimental and simulated PXRD patterns are in good agreement with each other, indicating that the crystal structure is truly representative of the bulk crystal products.

The thermogravimetric analysis result for 1 is shown in Figure 2(b). In the TGA curve, the framework of 1 displays a two-step weight process between 30 and 800°C. The first weight loss appeared in the temperature range of 62-105°C, which is associated with the departure of lattice H₂O and EtOH molecules (the observed and calculated value is 10.27% and 10.34%, respectively), and the second weight loss occurred from 280 to 450°C, which is related to the decomposition of the organic ligand. The final residues may be the copper powder (the observed and calculated value is 23.96% and 24.03%, respectively).

3.3. Optical Band Gap of 1. The compound 1’s solid-state ultraviolet-visible absorption spectrum was detected at RT. As shown in Fig. S1a, it has an absorption band from 250 nm to 360 nm, which can be attributed intraligand charge transfer. According to $F = (1 - R)^2/2R$, a Kubelka-Munk function, the optical band gap ($E_g$) of 1 was calculated to be 3.21 eV (Fig. S1b), indicating that 1 may be served as a good conductive material using in the area of photocatalysis. Furthermore, the solid fluorescent property of 1 has been also studied at room temperature, and it shows weak fluorescent emission at $\lambda_{em} = 330$ nm corresponding to excitation wavelength of 270 nm (Fig S2).

3.4. Photocatalytic Property of 1. In view of the suitable band gap of 1, its photocatalytic performance was examined by photocatalytic degrading MB under UV light irradiation. As shown in Figure 3(a), it can be seen obviously that the intensity of the characteristic absorption peaks for MB gradually attenuated with the increase of the exposure time in the presence of 1. After 180 min, the degradation efficiency of MB was up to 87.6% (Figure 3(b)), whereas the degradation

| Table 1: The compound 1’s crystal data. |
|---------------------------------------|
| Formula | C₁₂₅₁₈₅₃Cl₂₅₄₃Cu₄₂₅₄O₄₁ |
| Fw      | 1065.55                  |
| Crystal system | Triclinic |
| Space group | P-1               |
| a (Å)  | 12.936 (5)              |
| b (Å)  | 13.464 (6)              |
| c (Å)  | 14.961 (6)              |
| α(°)   | 70.286 (17)             |
| β(°)   | 65.353 (17)             |
| γ(°)   | 68.775 (18)             |
| Volume (Å³) | 2153.6 (15)   |
| Z      | 2                       |
| Density (calculated) | 1.473               |
| Abs. coeff. (mm⁻¹) | 2.351               |
| Total reflections | 16832              |
| Unique reflections | 9261               |
| Goodness of fit on F² | 1.013             |
| Final R indices [I > 2sigma(I²)] | R = 0.0622, wR₂ = 0.1401 |
| R (all data) | R = 0.1089, wR₂ = 0.1668 |
| CCDC   | 2117604                |
The efficiencies of the comparison experiments in the presence of 1 in the dark and in the absence of 1 under UV light were found to be 1.8% and 15.3%, respectively. The significant improvement of degradation efficiency in the existence of compound 1 under the ultraviolet light exposure suggests that complex 1 has high photocatalytic effect in the course of MB photodegradation (Table S2). Through applying \( \ln \left( \frac{C_0}{C} \right) = kt \), the pseudo-first-order kinetic equation, in which \( C_0 \) represents the original concentration of MB, \( C \) represents the concentration of MB with given irradiation.
time \( t \), and \( k \) represents the rate constant, the rate constant can be calculated to be 0.018 min\(^{-1}\) by fitting the relationship between the \( \ln \left( \frac{C_0}{C} \right) \) and irradiation time \( t \) (Figure 3(c)). After photocatalysis, the PXRD pattern shows no obvious change compared to that of the fresh samples (Figure 2(a)), demonstrating that the compound \( 1 \) stays stable in the course of photocatalytic reaction, which can be reusable as a photocatalyst for the organic dye degradation. To study the photocatalytic mechanism, we used isopropanol, benzoquinone, and ammonium oxalate in the photocatalytic experiment as scavengers for \( \cdot \text{OH} \), \( \cdot \text{O}_2^- \), and (h\(^+\)) radicals, respectively. There was no obvious decrease in the photocatalytic efficiency with benzoquinone and ammonium oxalate, indicating that \( \cdot \text{O}_2^- \) and (h\(^+\)) radicals are not reactive species. However, isopropanol greatly suppressed the process of the photocatalytic reaction (Figure 3(c)), and the degradation efficiency was only 48.2% after 180 min of irradiation. These results suggest that the photodegradation of MB solution occurs primarily through attack by \( \cdot \text{OH} \) radicals.

To understand the effect of pH on the photodegradation property of \( 1 \), we performed an independent experiment
with MB dye. All other conditions in this experiment were as described in the experimental section. A set of photodegradation tests was performed at a different pH value, ranging from 2 to 12, with compound 1 as catalyst at an ambient temperature. The pH of the mixture was adjusted using 0.1 M NaOH and 0.1 M HCl solutions. It can be seen from Figure 3(d) that, under acidic conditions, the surface of 1 becomes positively charged, causing H⁺ ions to compete with the cationic part of the dye, which hinders the degradation of MB. The degradation efficiency of 1 also decreases in basic medium as the chloride anions of MB react with NaOH to give NaCl and MBS⁺OH⁻ via a displacement reaction. The amount of NaCl salt can reduce the degradation efficiency of MBS⁺OH⁻ in aqueous medium. Therefore, the maximum degradation efficiency of MB by 1 was observed in neutral medium (pH = 7).

3.5. Compound Significantly Increases the Content of the Alkaline Phosphatase in the Osteoblast. After producing the complex containing novel architecture, the application values of the above complex against the orbital wall fractures were assessed firstly. Thus, in this present research, the content of the alkaline phosphatase in the osteoblast was measured with the alkaline phosphatase staining kit. As the outcomes revealed in Figure 4, it can be found that in contrast to control group, there existed a much lower alkaline phosphatase content level in the osteoblast. There was a significantly different differences between the above two groups, with P less than 0.005. After the complex treatment, the alkaline phosphatase content in the osteoblast was increased obviously in a dose-dependent manner.

3.6. Compound Obviously Activates the β-Catenin Signaling Pathway in the Osteoblast. In the previous experiment, we have demonstrated that the compound possesses superb promotion effect against the alkaline phosphatase content in the osteoblast, which showed a dose relationship. In addition to the alkaline phosphatase content, the β-catenin signaling pathway also exerts a principal effect in the recovery process of orbital wall fracture. So, the β-catenin signaling pathway in the osteoblast was in-depth tested through the real-time RT-PCR. The outcomes in Figure 5 showed that there was a reduced level of the β-catenin signaling pathway in the model group, which is obviously different from the control group. After treating through compound, the β-catenin signaling pathway levels in the osteoblast were upregulated significantly. The above complex’s biological activity revealed a dose- and time-dependent correlation.

4. Conclusion

Overall, a new Cu(II) compound was prepared, and it exhibits a 0D isolated framework with tetrahedral [Cu₄O] cluster. These isolated tetrahedral cluster-based units are further extended into a 2D layer through the connection of hydrogen bonds and π...π interactions. The final layer-to-layer stacking affords a new 3D supramolecular framework. The band gap of the compound is 3.21 eV, and the efficiency of photocatalytic degradation of MB under ultraviolet irradiation is high. The outcomes of alkaline phosphatase staining kit suggested that this complex could remarkably upregulate...
the alkaline phosphatase content in osteoblast. Moreover, the β-catenin signaling pathway activation in osteoblast was activated through the novel complex dose dependently.

**Data Availability**

Selected bond lengths (Å) and angles (°) for 1 (Table S1). (a) The solid-state UV-Vis absorption spectrum of 1 at room temperature. (b) Diffuse reflectance spectrum of Kubelka-Munk function versus energy of for 1 (Fig S1). The information could be found in the supporting information file.

**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.

**Authors’ Contributions**

Yanxiu Qi and Siying Li synthesized and characterized the compounds; Pingping Zhou performed the activity assay experiments; Donglan Wang designed the study and prepared the manuscript. Yanxiu Qi and Siying Li contributed equally to this work.

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**Supplementary Materials**

Table S1: selected bond lengths (Å) and angles (°) for 1. Table S2: some previously reported CPs as photocatalysts in the literature. Fig. S1: (a) the solid-state UV-Vis absorption spectrum of 1 at room temperature. (b) Diffuse reflectance spectrum of Kubelka-Munk function versus energy of for 1. Fig S2: the fluorescence spectrum of 1. (Supplementary Materials)

**References**

[1] Q. N. Dong, M. Karino, T. Koike et al., “Navigation-assisted isolated medial orbital wall fracture reconstruction using an U-HA/PLLA sheet via a transcaruncular approach,” *Journal of Investigative Surgery*, vol. 33, no. 7, pp. 644–652, 2020.

[2] C. K. Hsu, M. W. Hsieh, H. C. Chang, M. C. Tai, and K. H. Chien, “Anatomic factors predicting postoperative strabismus in orbital wall fracture repair,” *Scientific Reports*, vol. 9, no. 1, p. 14785, 2019.

[3] L. Lu, J. Wang, C. Shi et al., “Four new coordination complexes prepared for the degradation of methyl violet dye based on flexible dicarboxylate and different N-donor coligands,” *Journal of Molecular Structure*, vol. 1225, p. 129181, 2021.

[4] N. Yuan, X. Gong, W. D. Sun, and C. Yu, “Advanced applications of Zr-based MOFs in the removal of water pollutants,” *Chemosphere*, vol. 267, p. 128863, 2021.

[5] W. C. Kang, Z. C. Hao, C. Han, and G. Y. Dong, “Multicomponent self-assembly of two Cd(II)-based coordination polymers: synthesis, structures and photocatalytic properties,” *Journal of Inorganic and Organometallic Polymers*, vol. 30, no. 5, pp. 1877–1885, 2020.

[6] C. L. Jin, S. J. Fang, and Z. S. Guo, “A new thermostable Cu(II) coordination polymer: photocatalytic activity and application values on diabetes,” *Designed Monomers and Polymers*, vol. 24, no. 1, pp. 136–144, 2021.

[7] D. Zhang, C. Bi, Z. Zong, and Y. Fan, “Three different Co(II) metal-organic frameworks based on 4,4’-bisimidazolyl)diphenyl ether: syntheses, crystal structure and photocatalytic properties,” *Journal of Inorganic and Organometallic Polymers*, vol. 30, no. 12, pp. 5148–5156, 2020.

[8] L. Fan, D. Zhao, B. Li et al., “Luminescent binuclear zinc(II) organic framework as bifunctional water-stable chemosensor for efficient detection of antibiotics and Cr(VI) anions in water,” *Spectrochimica Acta Part A Molecular Biomolecular Spectroscopy*, vol. 264, p. 120232, 2022.

[9] S. H. Zhou, J. Wang, Y. W. Liu et al., “Structures and photocatalytic properties of two new Zn(II) coordination polymers based on semi-rigid V-shaped multicarboxylate ligands,” *RSC Advances*, vol. 10, no. 32, pp. 18721–18727, 2020.

[10] R. Y. Zhao, R. D. Xu, G. N. Liu, Y. Sun, and C. Li, “Water stable tetracuclear copper(I) iodide cluster for visible-light driven photocatalytic application,” *Inorganic Chemistry Communication*, vol. 105, pp. 135–139, 2019.

[11] F. Wang, F. Tian, Y. Deng et al., “Cluster-based multifunctional copper(II) organic framework as a photocatalyst in the degradation of organic dye and as an electrocatalyst for overall water splitting,” *Crystal Growth & Design*, vol. 21, no. 7, pp. 4242–4248, 2021.

[12] Q. W. Xu, Q. S. Wang, S. S. Li, and X. Li, “Cu(ii)/Ni(ii)-organic frameworks constructed from the homometallic clusters by 5-(2-carboxyphenoxyl)isophthalic acid and N-ligand: synthesis, structures and visible light-driven photocatalytic properties,” *RSC Advances*, vol. 9, no. 29, pp. 16305–16312, 2019.

[13] J. Liu, Y. H. Tang, F. Wang, and J. Zhang, “Syntheses of copper-iodine cluster-based frameworks for photocatalytic degradation of methylene blue,” *CrystEngComm*, vol. 20, no. 9, pp. 1232–1236, 2018.

[14] X. F. Wang, X. Y. Guo, and T. Liu, “Two Co(II) based coordination polymers constructed from π electron rich polycarboxylate arylic ether ligand: structural insights and photocatalytic dye degradation,” *Chinese Journal of Structural Chemistry*, vol. 40, pp. 722–728, 2021.

[15] Y. Zhang, W. Hu, C. Rao et al., “Fast photocatalytic organic dye by two metal-organic frameworks with 3D two-fold interpenetrated feature,” *Journal of Molecular Structure*, vol. 1227, p. 129538, 2021.

[16] M. Shahnawaz Khan, M. Khalid, and M. Shahid, “A Co(II) coordination polymer derived from pentaerythritol as an efficient photocatalyst for the degradation of organic dyes,” *Polyhedron*, vol. 196, 2021.

[17] M. Aghaee, K. Mohammadi, P. Hayati et al., “Morphology design and control of a novel 3D potassium metal-organic coordination polymer compound: crystallography, DFT, thermal, and biological studies,” *Journal of Molecular Structure*, vol. 1228, 2021.

[18] R. K. Tiwari and J. N. Behera, “Hybrid materials based on transition metal–BTC–benzimidazole: solvent assisted crystallographic and structural switching,” *CrystEngComm*, vol. 20, no. 41, pp. 6602–6612, 2018.

[19] G. M. Sheldrick, SADABS, Version 2.03, University of Göttingen, Germany, 1996.
[20] G. M. Sheldrick, “Crystal structure refinement with SHELXL,” *Acta Crystallographica, Section C: Structure Chemistry*, vol. 71, no. 1, pp. 3–8, 2015.

[21] P. van der Sluis and A. L. Spek, “BYPASS: an effective method for the refinement of crystal structures containing disordered solvent regions,” *Acta Crystallographica, Section A: Foundations of Crystallography*, vol. 46, no. 3, pp. 194–201, 1990.

[22] X. J. Wei, D. Liu, Y. H. Li, and G. H. Cui, “New 2D and 3D Cd(II) coordination polymers from aromatic dicarboxylate and 1,3-bis(5,6-dimethylbenzimidazol-1-yl)-2-propanol ligands: syntheses, structures, photocatalytic, and luminescence sensing properties,” *Journal of Solid State Chemistry*, vol. 272, pp. 138–147, 2019.