

Two-Dimensional Copper(I) Coordination Polymer Materials as Photocatalysts for the Degradation of Organic Dyes

Tian Wen, De-Xiang Zhang, and Jian Zhang*

State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences (CAS), Fuzhou, Fujian 350002, People's Republic of China

Supporting Information

ABSTRACT: Two isomeric two-dimensional copper(I) coordination polymer materials based on an in situ generated 5-(3-pyridyl)tetrazole ligand show similar layer structures but distinct photoluminescent and photocatalytic properties, which present an interesting comparative study on the structure–property correlation between isomeric materials.

Coordination polymers (CPs) or metal–organic frameworks have attracted great interest in recent years because of their diverse structures and potential applications in gas sorption, separation, and catalysis.^{1–3} A new emerging application of CPs is photocatalysis, and some results have demonstrated that CPs are efficient photocatalysts on the degradation of organic dyes, water splitting, or photoreduction of CO₂.^{4,5} However, such kinds of applications of CPs on visible-light-driven photocatalysis are just beginning to emerge. How to achieve inexpensive, stable, efficient, and band-gap-tunable photocatalysts based on CPs is still a big challenge.

In this work, we report two isomeric two-dimensional copper(I) CPs with interesting photocatalytic properties on the degradation of organic dyes. Remarkably, two isomers show similar layer structures and have the same formula Cu(ptz) [**1** and **2**, ptz = 5-(3-pyridyl)tetrazole], but they exhibit totally different appearances and physical properties including luminescence and photocatalytic efficiency. Compound **1** with a band-gap size of 1.65 eV shows much higher photocatalytic efficiency on the degradation of methylene blue (MB), rhodamine B (RhB), and methyl orange (MO) than compound **2** does with a band-gap size of 2.24 eV. It is notable that both materials can be used several times without decreasing the photocatalytic efficiency.

Both isomeric materials **1** and **2** were solvothermally synthesized through “click” reactions of Cu₂O, 3-cyanopyridine, and NaN₃ in different mixed solvents (e.g., **1** in *N,N*-dimethylformamide (DMF)/ethanol and **2** in DMF/toluene).⁶ The ptz ligand is in situ generated from a “click” reaction between 3-cyanopyridine and NaN₃. Such in situ “click” solvothermal synthesis of a tetrazolate ligand has been well introduced in a number of tetrazolate-based CPs.⁷ Single-crystal X-ray diffraction measurements reveal that both isomers crystallize in the same triclinic *P* $\bar{1}$ space group and feature identical wavelike layer structures, but their unit cells are distinct.⁸ The pure phase of each compound has been demonstrated by powder X-ray diffraction (PXRD). Both

compounds are stable in air and insoluble in common solvents. Because they are structural isomers, compounds **1** and **2** have very similar thermal behaviors. Thermogravimetric analyses (TGA) indicate that there is no obvious weight loss before 250 °C for both isomers (Figure S6 in the Supporting Information, SI). It is notable that no solvent molecules have been trapped in the structures of **1** and **2**. However, the formation of these two isomers with slight structural differences must be closely associated with the solvent environment during synthesis. The intermolecular interactions between solvent molecules (ethanol for **1** and toluene for **2**) and the coordination framework might induce two isomeric frameworks.

In the structure of **1**, each Cu^I center is coordinated by three N atoms from three tetrazole groups and one N donor from a pyridyl group, showing a distorted tetrahedral coordination geometry (Figure 1a). Each ptz ligand links four Cu^I centers

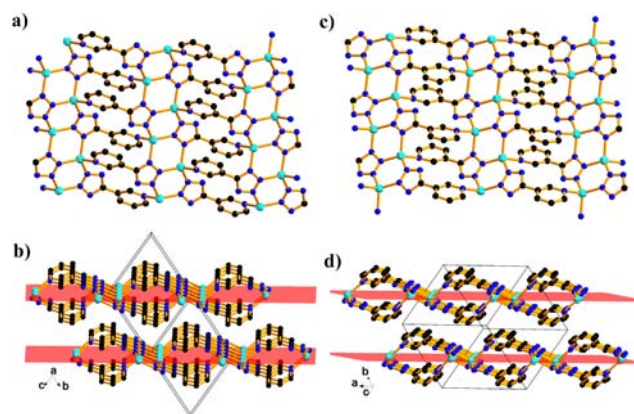


Figure 1. (a) Layer structure in **1**. (b) Two stacking layers in **1**. (c) Layer structure in **2**. (d) Two stacking layers in **2**.

through three tetrazole N donors and one pyridyl N donor. The dihedral angle between pyridyl and tetrazole rings in a ptz ligand is 40.9° (Figure S1 in the SI). Every tetrazole group bridges three Cu^I centers together, and the adjacent Cu···Cu distances are 3.651 and 3.661 Å, respectively. A copper tetrazole chain running along the *a* axis is thus formed. These resulting chains further connect each other into a layer through the pyridyl groups of the ptz ligands (Figure 1a). The layers further stack into a three-dimensional structure. No obvious

Received: October 17, 2012

Published: December 17, 2012

interactions were observed between adjacent layers. In each layer, all Cu^I centers almost fall in one plane. The distance between such adjacent copper planes is 6.50 Å (Figure 1b).

The coordination environment in **2** is very similar to that in **1**, where the μ^4 -ptz ligands link those tetrahedral Cu^I centers into a wavelike layer (Figure 1c). However, there are three crystallographically different Cu^I centers and three 3-ptz ligands in the asymmetric unit of **2**. The dihedral angles in three 3-ptz ligands are 37.0°, 41.9° and 43.4°, respectively, which are totally different from those in **1** (Figure S4 in the SI). Moreover, the shortest Cu...Cu distance in the copper tetrazole chain is 3.684 Å. The distance between two adjacent copper planes in **2** is 6.57 Å (Figure 1d), which is a little longer than that in **1**.

One breakthrough achieved in this work was to discover distinct properties in these two isomers with such close structural features. Actually, they have totally different performances on photoluminescent emissions and photocatalysis. The solid-state photoluminescent properties of two isomers were investigated at room temperature (Figure 2). Upon irradiation

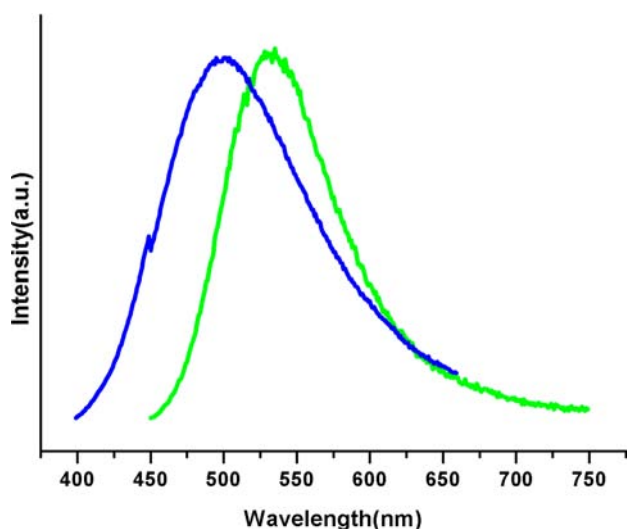


Figure 2. Emission spectra of **1** (blue line, maximum 501 nm) and **2** (green line, maximum 533 nm) in the solid state at room temperature.

of ultraviolet light at 360 nm, the emission maximum wavelengths for **1** and **2** are 501 and 533 nm, respectively. The difference in the emission spectra of two isomers implies that the properties of their excited states are mainly related to the local coordination factors, such as the torsion of the ptz ligand, the coordination between Cu^I and N atoms, or other intramolecular interactions. The emission of the ptz ligand is 455 nm upon irradiation of ultraviolet light at 295 nm. Compared to **1**, the ptz ligands in **2** are closely packed and show much stronger $\pi\cdots\pi$ interactions between adjacent layers. Such strong $\pi\cdots\pi$ interactions probably lower the π^* energy of the ptz ligand. Thus, the emission energy level of **2** is lowered, and longer wavelength emission is found. The emissions of **1** and **2** can be tentatively assigned to the Cu $\rightarrow \pi^*(3\text{-ptz})$ metal-to-ligand charge transfer, which are similar to those observed in some documented copper(I) compounds.⁹ Furthermore, Cu...Cu interactions in the same layer, probably involving with Cu...Cu [3d \rightarrow 4s] cluster-centered excited states, might also contribute to photoemission, as evidenced in other copper(I) tetrazolate compounds.¹⁰

The band-gap sizes of **1** and **2** were investigated by a UV/vis diffuse-reflectance measurement method at room temperature. The results give E_g (band-gap energy) values of 1.65 and 2.24 eV for **1** and **2**, respectively (Figures S9 and S10 in the SI). Different dihedral angles presented by the ptz ligands in two isomers as well as different layer–layer distances in two structures might lead to such distinct band-gap sizes for **1** and **2**. Both **1** and **2** have absorption response to visible light because of their narrow band-gap sizes. The photocatalytic activities of both isomers were further studied. The degradation of organic dyes was selected as the reference.

Two isomers showed high photocatalytic efficiency for the degradation of MB, RhB, and MO in aqueous solution under xenon arc lamp irradiation (Figure 3). First, for the degradation

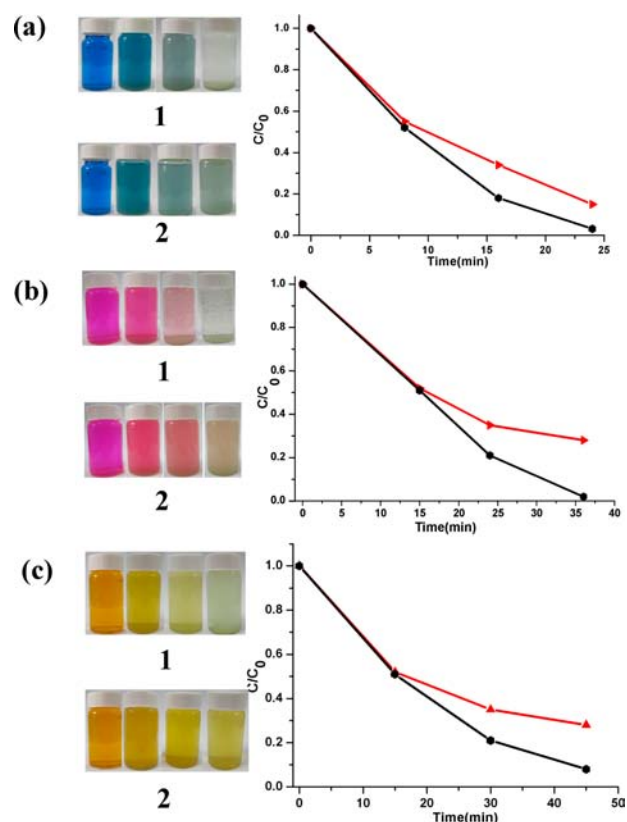


Figure 3. Photodecomposition of three dyes (a, MB; b, RhB; c, MO) in solution over two isomers. Left: color change photograph image of dye solutions. Right: time-dependent UV/vis spectra of three dyes over two isomeric photocatalysts. Black line: **1**. Red line: **2**.

of MB, the characteristic absorption of MB at about 650 nm was selected to monitor the adsorption and photocatalytic degradation process. Figure 3a shows a comparison of the photocatalytic activities of two isomers. The photocatalytic activity of each sample was gradually enhanced with time increasing from 0 to 25 min. It is obvious that **1** exhibits much higher activity. When the light application time increases to 24 min, the degradation ratio of MB reaches 98% (Figure 3a). Similar procedures were performed to check the photocatalytic activities of two isomers upon degradation of RhB and MO. For photocatalyst **1**, the full degradation time for RhB is only 35 min (Figure 3b), and the degradation of MO in 45 min also reaches 95% (Figure 3c). In contrast, photocatalyst **2** has to take a little longer time for degradation of these dyes. It is clear that **1** possessed higher activity than **2**, but the detailed reason

is difficult to explain at the current stage. It is clear that the slight structural difference between **1** and **2** leads to their discrepancy in the band-gap sizes, which might also affect their discrepancy in the photocatalytic activity.

In order to investigate the stability of two isomers as visible-light photocatalysts, we repeated the photocatalytic degradation of MB three times. It is interesting that they still keep similar photocatalytic efficiencies and the PXRD patterns of two isomers at the end of each repeated bleaching experiment are almost identical with that of the as-prepared sample (Figures S7, S8, and S17–S19 in the SI). We analyzed the total organic carbon (TOC) of the organic residues after photocatalysis experiments of isomer **1** (Table S1 in the SI). The results reveal that the TOC decreases obviously, which infers that the dyes should degrade into carbon dioxide. Compared to other reported CPs with photocatalytic properties, both photocatalysts **1** and **2** show high visible-light-driven photocatalytic efficiency.^{4a,5,11}

In summary, through in situ “click” reactions in different solvents, two isomeric two-dimensional copper(I) materials based on an in situ generated ptz ligand were successfully synthesized. The results reveal distinct photoluminescent and photocatalytic properties presented by two such isomers with very similar structural features. This work is an interesting comparative study on the structure–property correlation between isomeric materials. Considering their high efficiency and high stability on the photocatalytic degradation of organic dyes, both isomeric materials might be good candidates for photocatalytic applications.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental details, additional figures, TGA, PXRD patterns, and a CIF file. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

■ Corresponding Author

*E-mail: zhj@fjirsm.ac.cn.

■ Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is supported by the 973 program (Grants 2011CB932504 and 2012CB821705), National Science Foundation (NSF) of China (Grants 21073191, 21221001, and 91222105), NSF of Fujian Province (Grant 2011J06005), and CAS.

■ REFERENCES

- (1) (a) Férey, G. *Chem. Soc. Rev.* **2008**, *37*, 191. (b) D'Alessandro, D. M.; Smit, B.; Long, J. R. *Angew. Chem., Int. Ed.* **2010**, *49*, 6058. (c) Zheng, S.; Wu, T.; Zuo, F.; Chou, C.-T.; Feng, P.; Bu, X. *J. Am. Chem. Soc.* **2012**, *134*, 1934. (d) Lin, Q.; Wu, T.; Zheng, S.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 11852.
- (2) (a) Cui, Y. J.; Yue, Y. F.; Qian, G. D.; Chen, B. L. *Chem. Rev.* **2012**, *112*, 1126. (b) Jiang, H. L.; Tatsu, Y.; Lu, Z. H.; Xu, Q. *J. Am. Chem. Soc.* **2010**, *132*, 5586. (c) Zhao, X.; Wu, T.; Zheng, S.-T.; Wang, L.; Bu, X.; Feng, P. *Chem. Commun.* **2011**, *47*, 5536.
- (3) (a) Caskey, S. R.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2008**, *130*, 10870. (b) Vaidyanathan, R.; Iremonger, S. S.; Dawson, K. W.; Shimizu, H. G. *Chem. Commun.* **2009**, 5230.

(c) Wang, F.; Tan, Y.-X.; Yang, H.; Zhang, H.; Kang, Y.; Zhang, J. *Chem. Commun.* **2011**, 5828.

(4) (a) Wang, F.; Liu, Z.-S.; Yang, H.; Tan, Y.-X.; Zhang, J. *Angew. Chem., Int. Ed.* **2011**, *50*, 450. (b) Das, M. C.; Xu, H.; Wang, Z.-Y.; Srinivas, G.; Zhou, W.; Yue, Y.-F.; Nesterov, V. N.; Qian, G.-D.; Chen, B.-L. *Chem. Commun.* **2011**, *47*, 11715.

(5) (a) Fu, Y.-H.; Sun, D.-R.; Chen, Y.-J.; Huang, R.-K.; Ding, Z.-X.; Fu, X.-Z.; Li, Z.-H. *Angew. Chem., Int. Ed.* **2012**, *51*, 3364. (b) Wen, L.-L.; Zhao, J.-B.; Lv, K.-L.; Wu, Y.-H.; Deng, K.-J.; Leng, X.-K.; Li, D.-F. *Cryst. Growth Des.* **2012**, *12*, 1603. (c) Mahata, P.; Madras, G.; Natarajan, S. *J. Phys. Chem. B* **2006**, *110*, 13759.

(6) Synthesis of isomers **1** and **2**: A mixture of Cu₂O (0.0143 g, 0.1 mmol), 3-cyanopyrimidine (0.0105 g, 0.1 mmol), and NaN₃ (0.0325 g, 0.5 mmol) in a mixed DMF/ethanol solvent (3/9 mL) along with a few drops of NH₃·H₂O was stirred for 15 min. It was then transferred and sealed in a 23 mL Teflon-lined stainless steel reactor, which was heated in an oven to 160 °C for 72 h and then cooled to room temperature. Pale-yellow sheet crystals of **1** were obtained as the main product (86% yield). **2** was prepared by using a similar procedure except with toluene replacing ethanol. Pale-blue sheet crystals of **2** were collected and dried in air (80% yield).

(7) (a) Zhao, H.; Qu, Z.-R.; Ye, H.-Y.; Xiong, R.-G. *Chem. Soc. Rev.* **2008**, *37*, 84. (b) Li, Z. M.; Li, D. *Chem. Commun.* **2008**, 3390. (c) Wen, T.; Li, M.; Zhou, X.-P.; Li, D. *Dalton Trans.* **2011**, *40*, 5684. (d) Kolb, H. C.; Finn, M. G.; Sharpless, K. B. *Angew. Chem., Int. Ed.* **2001**, *40*, 2004.

(8) The diffraction data of **1** and **2** were collected on an Oxford Xcalibur diffractometer equipped with graphite-monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) at 293(2) K. Crystal data for **1**: C₆H₄CuN₃, $M = 209.68$, triclinic, $a = 5.8132(4)$ Å, $b = 7.9619(12)$ Å, $c = 8.2074(9)$ Å, $\alpha = 67.801(12)^\circ$, $\beta = 74.775(7)^\circ$, $\gamma = 83.256(8)^\circ$, $V = 339.29(7)$ Å³, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 2$, 2025 reflections measured, 1189 independent reflections ($R_{\text{int}} = 0.0531$). The final $R1$ value was 0.0594 [$I > 2\sigma(I)$]. The final $wR(F^2)$ value was 0.1568 [$I > 2\sigma(I)$]. The final $R1$ value was 0.0638 (all data). The final $wR(F^2)$ value was 0.1591 (all data). The goodness of fit on F^2 was 1.196. Crystal data for **2**: C₁₈H₁₂Cu₃N₁₅, $M = 629.08$, triclinic, $a = 9.022(3)$ Å, $b = 10.445(2)$ Å, $c = 12.295(3)$ Å, $\alpha = 71.225(19)^\circ$, $\beta = 75.08(2)^\circ$, $\gamma = 70.25(2)^\circ$, $V = 1017.9(4)$ Å³, $T = 293(2)$ K, space group $P\bar{1}$, $Z = 2$, 6030 reflections measured, 3311 independent reflections ($R_{\text{int}} = 0.1262$). The final $R1$ value was 0.1041 [$I > 2\sigma(I)$]. The final $wR(F^2)$ value was 0.2898 [$I > 2\sigma(I)$]. The final $R1$ value was 0.3096 (all data). The final $wR(F^2)$ value was 0.3555 (all data). The goodness of fit on F^2 was 0.828. The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELXTL-97 program.

(9) (a) Hu, J.-S.; Qin, L.; Zhang, D. M.; Yao, Q. X.; Li, Z. Y.; Guo, Z.-J.; Zheng, H.-G.; Xue, Z.-L. *Chem. Commun.* **2012**, *48*, 681. (b) Han, T.-Y.; Feng, X.; Tong, B.; Shi, J.-B.; Chen, L.; Zhi, J.-G.; Dong, Y.-P. *Chem. Commun.* **2012**, *48*, 416. (c) Yam, V. W.-W.; Lo, K. K.-W. *Chem. Soc. Rev.* **1999**, *28*, 323.

(10) (a) Kim, T. H.; Shin, Y. W.; Jung, J. H.; Kim, J. S.; Kim, J. *Angew. Chem., Int. Ed.* **2008**, *47*, 685. (b) Chen, D.; Liu, Y.-J.; Lin, Y.-Y.; Zhang, J.-P.; Chen, X.-M. *CrystEngComm* **2011**, *13*, 3827.

(11) Zhang, H.; Zong, R.; Zhu, Y. *J. Phys. Chem. C* **2009**, *113*, 4605.