

一个新颖的单齿桥联羧基——金属二聚物为顶点的发光分子矩形网格

袁荣鑫^{1,2} 张 静¹ 熊仁根^{*,1} 范洪筠³

(¹ 南京大学配位化学研究所, 配位化学国家重点实验室, 南京 210093)

(² 常熟理工学院化学科学与技术系, 常熟 215500)

(³ X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia)

关键词: 水热合成 发光 分子矩形网格 一价铜配合物
分类号: O614.121

An Unprecedented Luminescent Molecular Square Grid Based on Monodentate Bridging Carboxylate-Metal Dimer as Corner Unit

YUAN Rong-Xin^{1,2} ZHANG Jing¹ XIONG Ren-Gen^{*,1} FUN Hoong-Kun³

(¹ Coordination Chemistry Institute, the State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093)

(² Department of Chemistry, Chgangshu Institute of Technology, Changshu 215500)

(³ X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800, USM, Penang, Malaysia)

The hydrothermal reaction of 4-pyridylacrylic acid (4-HPYA) with $[\text{Cu}(\text{MeCN})_4](\text{BF}_4)$ and PPh_3 gives rise to an unprecedented luminescent molecular square grid, $[\text{Cu}(\text{I})(4\text{-PYA})(\text{PPh}_3)]_n$ (**1**) which may be used as a sensor. CCDC: 236419.

Keywords: hydrothermal synthesis luminescence molecular square grid copper(I) complex

0 Introduction

Since the elegantly pioneering works of self-assembly of molecular square (or rectangle, rhombohedron or triangle) containing metal ions performed by Lehn, Robson, Stang, and Fujita in just the last decade^[1], the exploiting of novel and functional molecular architectures introducing many special functional properties, such as luminescence^[2], redox activity^[3], molecular recognition (or enantioselectivity)^[1,4], second-harmonic generation^[5], and magnetism^[6] as well as catalysis^[1d] into the structures, has been at the frontiers of

the molecular science, as demonstrated by the extremely intense interest and the near exponential growth of publication in this area. Although metallomacrocycles are being prepared from an increasing variety of metals and ligands, metal-amine coordination still remains the dominant structural motif^[7]. Recently, the molecular square grids constructed from the bifunctional multidentate anion as building block have attracted much attention, due in part to a large cavity available in the absence of anion^[5,8]. Among those bifunctional multidentate anion ligands, the end of the

收稿日期:2004-03-01. 收修改稿日期:2004-04-19.

国家重点基础研究发展规划资助项目(No.G2000077500)和国家自然科学基金资助项目。

* 通讯联系人。E-mail:xiongrg@netra.nju.edu.cn

第一作者:袁荣鑫,男,42岁,副教授,博士;研究方向:功能配位化合物。

ligand is carboxylate group in which three coordination modes of carboxylate with metal, such as syn-syn bidentate bridging, symmetric chelating and syn-monodentate terminal, have been found so far. To our surprise, the reaction of 4-pyridylacrylic acid (4-HPYA) with $[\text{Cu}(\text{MeCN})_4](\text{BF}_4)$ and PPh_3 yields $[\text{Cu}(\text{I})(4\text{-PYA})(\text{PPh}_3)]_n$ (**1**) which, to the best of our knowledge, represents an unprecedented 2D neutral molecular square grid containing a monodentate bridging carboxylate metal-dimer as corner unit^[9]. Here we report its synthesis and solid state structure as well as the fluorescent property of **1**.

1 Result and Discussion

The pale-yellow block crystalline **1** was harvested by the hydrothermal reactions of 4-HPYA and PPh_3 with $[\text{Cu}(\text{MeCN})_4](\text{BF}_4)$. In its IR spectrum, there no longer exist anion BF_4^- for **1** due to the absence of a typical peak at ca. 1023 cm^{-1} for **1** instead of two strong peaks (deprotonated carboxylate group) at 1570 and 1380 cm^{-1} for **1**.

The X-ray crystal analysis of **1** revealed that each Cu(I) ion is coordinated in a distorted tetrahedral geometry (Fig.1), although there are two crystallographically independent Cu atoms [Cu(1) and Cu(2)]. The local environment around each Cu(I) ion is composed of one N atom of pyridyl ring of 4-PYA, one P atom of PPh_3 and two O atoms from two different 4-PYA ligands. The salient structural feature of **1** is that one of two oxygen atoms of carboxylate group of 4-PYA adopts a monodentate bridging mode to connect two Cu(I) ions. Thus, 4-PYA acts as a tridentate ligand and to link three Cu(I) ions, resulting in the formation of a 2D neutral molecular square grid containing a monodentate bridging carboxylate-metal dimer (Fig.2). Four carboxylate-metal dimer corner units of each molecular square are almost perfectly planar and have a dihedral of 69.9° between two adjacent corner units. Each square cavity has a dimension of $0.9911\text{ nm} \times 1.1512\text{ nm}$. However, it is careful to investigate the cavity accessible for guest molecules, finding that two benzene rings are in parallel accommodated over the

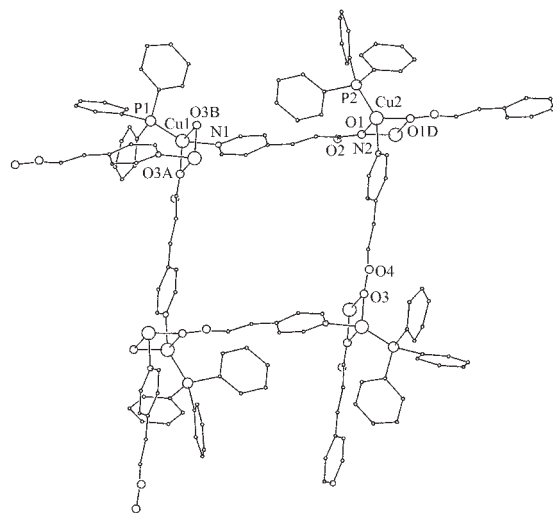


Fig.1 A molecular square representation of **1**

The increasing size circles stand for C, N, O, P and Cu atoms, respectively. H atoms are omitted for clarity. Selected bond lengths (nm) and angles ($^\circ$): Cu(1)-N(1) 0.203 0(10), Cu(1)-O(3) 0.209 2(7), Cu(1)-P(1) 0.218 1(3), Cu(1)-O(3A) 0.226 0(8), Cu(2)-N(1) 0.206 4(10), Cu(2)-O(1B) 0.208 4(7), Cu(2)-P(2) 0.217 9(3), Cu(2)-O(1A) 0.227 5(8); N(1)-Cu(1)-O(3) $103.1(4)$, N(1)-Cu(1)-P(1) $120.2(3)$, O(3)-Cu(1)-P(1) $128.5(2)$, N(1)-Cu(1)-O(3A) $96.3(4)$, O(3A)-Cu(1)-O(3B) $77.5(3)$, N(2)-Cu(2)-O(1A) $103.6(3)$, N(2)-Cu(2)-P(2) $119.2(3)$, O(1A)-Cu(2)-P(2) $129.2(2)$, N(2)-Cu(2)-O(1) $97.2(4)$, O(1A)-Cu(2)-O(1) $76.8(3)$, P(2)-Cu(2)-O(1) $119.7(2)$.

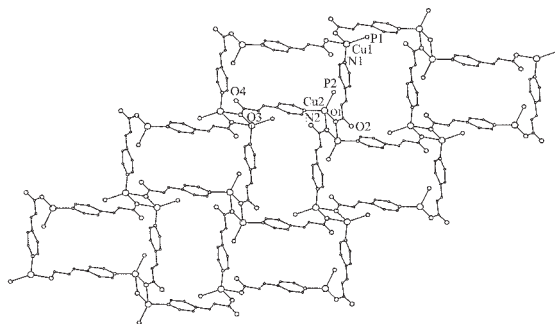


Fig.2 An extended 2D molecular square grid diagram of **1** cavity. Thus, remaining small cavity is available for guest molecule accessible.

The most interesting feature of **1** is that strong yellow fluorescent emission in the solid state at room temperature is observed (Fig.3). A maximum peak at ca. 550 nm is tentatively assigned to a metal-to-ligand charge transfer (MLCT) due to the absence of the similar peak for the free ligand (ca. 360 nm). However,

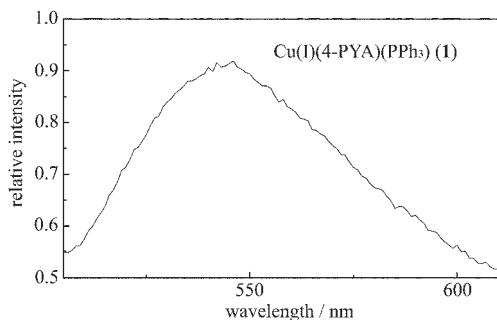


Fig.3 A fluorescent emission spectrum of **1** in the solid state at room temperature

the metal center d to s orbital transition is not ruled out^[10]. Thus, the fluorescent characteristics of the square box makes **1** a candidate for sensing applications on the basis of recognition and inclusion of appropriate guest molecules.

2 Experimental

Preparation of 1: Samples of 1 mmol of $\text{Cu}(\text{MeCN})_4\text{BF}_4$, 1 mmol of PPh_3 and 1 mmol of 4-HPYA were placed in a thick Pyrex tube (ca. 20 cm long). After addition of 0.1 mL of water and 2.5 mL of *n*-butanol, the tube was frozen with liquid N_2 , evacuated under vacuum and sealed with torch. The tube was heated at 90 °C for two days to give pale-yellow crystals with a yield of 75% based on 4-HPYA (Found(%): C, 65.74; H, 4.63; N, 3.05; Calc. C, 65.82; H, 4.57; N, 2.95). IR (KBr, cm^{-1}), 3 955(w), 1 640(w), 1 570(s), 1 480(w), 1 432(m), 1 380(s), 1 236(w), 1 090(m), 980(m), 824(w), 748(m), 698(s) and 520(m).

Crystal data for 1: $\text{C}_{52}\text{H}_{43}\text{Cu}_2\text{N}_2\text{O}_4\text{P}_2$, $M_r=948.90$, triclinic, space group $P\bar{1}$, $a=1.206\ 76(3)$ nm, $b=1.404\ 75(3)$ nm, $c=1.798\ 05(1)$ nm, $\alpha=109.901\ 0(10)^\circ$, $\beta=90.163\ 0(10)^\circ$, $\gamma=103.343\ 0(10)^\circ$, $V=2.777\ 60(9)$ nm³, $Z=2$, $T=293(2)$ K, $D_c=1.135$ g·cm⁻³, MoK α radiation ($\lambda=0.071\ 073$ nm), $\mu=0.862$ mm⁻¹, $R_1=0.135\ 8$, $wR_2=0.329\ 7$ for 3 661 observed reflections from 11 969 independent reflections, GOF=0.957.

CCDC: 236419.

References

- [1] (a)Lehn J. M. *Supramolecular Chemistry: Concepts and Perspectives*, VCH Publishers: New York, **1995**;
- (b)Batten S. R, Robson R. *Angew. Chem. Int. Ed.*, **1998**,**37**, 1460 and references therein;
- (c)Leininger S., Olenyuk B., Stang P. J. *Chem. Rev.*, **2000**, **100**,853 and references therein;
- (d)Fujita M. *Chem. Soc. Rev.*, **1998**,**27**,417 and references therein.
- [2] (a)Slone R. V., Benkstein K. D., Belanger S., Hupp J. T., Guzei I. A., Rheingold A. L. *Coord. Chem. Rev.*, **1998**, **171**,221 and references therein;
- (b)Xiong R. G., Zuo J. L., You X. Z., Fun H. K., Raj S. S. *S. Organometallics*, **2000**,2061;
- (c)Zhang J., Xiong R. G., Zuo J. L., You X. Z. *Chem. Commun.*, **2000**,1495;
- (d)Fun H. K., Raj S. S. S., Xiong R.G., Zuo J. L., Yu Z., Zhu X. L., You X. Z. *J. Chem. Soc. Dalton Trans.*, **1999**, 1711;
- (e)Zhang J., Xiong R. G., Chen X. T., Che C. M., Xue Z. L., You X. Z. *Organometallics*, **2001**,**20**,4118;
- (f)Zhang J., Xiong R. G., Chen X. T., Xue Z. L., Peng S. M., You X. Z. *Organometallics*, **2002**,**21**,235;
- (g)Zhang J., Xie Y. R., Ye Q., Xiong R. G., Xue Z. L., You X. Z. *Eur. J. Inorg. Chem.*, **2003**,2572.
- [3] Jones C. J. *Chem. Soc. Rev.*, **1998**,**27**,289.
- [4] (a)Zaworotko M. J. *Chem. Soc. Rev.*, **1994**,**23**,284 and references therein;
- (b)MacGillivray L. R., Atwood J. L. *Angew. Chem. Int. Ed.*, **1999**,**38**,1018 and references therein;
- (c)Yaghi O. M., Li H., Davis C., Richardson D., Groy T. L. *Acc. Chem. Res.*, **1998**,**31**,474 and references therein;
- (d)Hagman D., Zubieta C., Rose D. J., Zubieta J., Haushalter R. C. *Angew. Chem. Int. Ed. Engl.*, **1997**,**36**,873;
- [5] (a)Lin W., Evans O. R., Xiong R. G., Wang Z. J. *Am. Chem. Soc.*, **1998**,**120**,13272;
- (b)Huang S. D., Xiong R. G. *Polyhedron*, **1997**,**16**,2315.
- [6] Solari E., Lesueur W., Klose A., Schenk K., Floriani C., Chiesi-Villa A., Rizzoli C. *Chem. Commun.*, **1996**,807.
- [7] (a)Chen H., Ogo S., Fisher R. H. *J. Am. Chem. Soc.*, **1996**, **118**,4993;
- (b)Chi X., Guerin A. J., Haycock R. A., Hunter C. A., Sarsion L. D. *J. Chem. Soc., Chem. Commun.*, **1995**,2567.
- [8] Cotton A., Daniels L. M., Lin C., Murillo C. A. *J. Am. Chem. Soc.*, **1999**,**121**,4538;
- [9] Rardin R. L., Tolman W. B., Lippard S. J. *New J. Chem.*, **1991**,**15**,417.
- [10](a)Fun H. K., Raj S. S. S., Xiong R. G., Zuo J. L., Yu Z., Zhu X L., You X. Z. *J. Chem. Soc. Dalton Trans.*, **1999**, 1711;
- (b)Li D., Yip H. K., Che C. M., Zhou Z. Y., Mak T. C. W., Liu S. T. *J. Chem. Soc. Dalton Trans.*, **1992**,2445.