

Coordination-Driven Self-Assembly Directs a Single-Crystal-to-Single-Crystal Transformation that Exhibits Photocontrolled Fluorescence

Giannis S. Papaefstathiou, Zhenming Zhong, Lei Geng, and Leonard R. MacGillivray*

Department of Chemistry and Optical Science and Technology Center, University of Iowa, Iowa City, Iowa 52242

Received April 15, 2004; E-mail: len-macgillivray@uiowa.edu

Coordination-driven self-assembly,¹ wherein the coordination geometry of a metal is propagated in space using a di- or multitopic ligand to form a discrete metallomacrocyclic,¹ is emerging as a means, as compared to many metal–organic coordination networks,² to control bulk physical properties (e.g., porosity) of solid-state materials. One property of the solid state that such coordination-driven self-assembly has not been employed to control, however, is reactivity.^{3–8}

Inspired by work of Lewis,³ Alcock,⁴ and Foxman⁵ involving mononuclear metal complexes that facilitate dimerizations,^{3–5a} as well as polymerizations,^{5b} of olefins, and related work of Foxman,⁶ Mallouk,⁷ and others⁸ involving coordination networks that facilitate dimerizations,^{8a} oligomerizations,^{6a} and polymerizations^{6b,7,8b,c} of olefins^{6,8} and acetylenes,⁷ we report here an application of coordination-driven self-assembly to direct a photoinduced [2 + 2] cyclodimerization⁹ in the solid state. Specifically, a dinuclear Zn complex has been used to assemble 4,4'-bpe [where 4,4'-bpe = *trans*-1,2-bis(4-pyridyl)ethylene] within a tetranuclear rectangular assembly, in [Zn₄L₂(OH)₂(4,4'-bpe)₂](ClO₄)₄·4H₂O (**1**) (where LH = 2,6-bis[*N*-(2-pyridylethyl)formimidoyl]-4-methylphenol), wherein the two bipyridines react to give 4,4'-tpcb, in [Zn₄L₂(OH)₂(4,4'-tpcb)](ClO₄)₄·4H₂O (**2**) (where 4,4'-tpcb = *rac*-tetrakis(4-pyridyl)-cyclobutane), in up to 100% yield. We show that the reaction occurs via a rare single-crystal-to-single-crystal (SCSC) transformation¹⁰ that exhibits a red shift in fluorescence^{11,12} from blue to green. Our observations make the solid an attractive candidate as a high-density data storage and imaging material.^{13–15}

The tetranuclear assembly that directs the [2 + 2] photoreaction is based on dinuclear Schiff-base complexes first described by Robson and Okawa (Scheme 1).¹⁶ In these complexes, two transition-metal-ions fall within the range for [2 + 2] photoreaction in a solid (i.e., <4.2 Å).⁹ Additionally, the metals possess two parallel coordination axes that can be occupied by neutral (e.g., pyridines) and/or anionic ligands (e.g., ClO₄⁻). We reasoned that two such complexes could be used, as linear templates,¹⁷ to juxtapose two molecules of 4,4'-bpe in a discrete tetranuclear rectangular assembly in the solid state for a stereocontrolled [2 + 2] photodimerization to produce 4,4'-tpcb.

Ditopic LH was synthesized from reaction of 2-hydroxy-5-methyl-isophthalaldehyde (0.84 g) with 2-aminoethyl-pyridine (1.24 g) (1:2 ratio) in MeOH (15 mL).¹⁸ Dissolution of Zn(ClO₄)₂·6H₂O (0.37 g) to the above solution followed by addition of LiOH·H₂O (0.03 g) in H₂O (5 mL) (2:3 ratio) produced a yellow solution. Diffusion of a MeOH solution (10 mL) of 4,4'-bpe (0.90 g) into the H₂O/MeOH solution (ratio = 4:2:3) gave yellow crystals of **1** (yield = 76%) within two weeks.

A view of the crystal structure of **1**¹⁹ reveals that two dinuclear [Zn₂L(OH)]²⁺ units assemble with two molecules of 4,4'-bpe to a form tetranuclear rectangular assembly, [Zn₄L₂(OH)₂(4,4'-bpe)₂]⁴⁺, sustained by four Zn–N bonds [Zn–N (Å): Zn(1)–N(5) 2.090(3), Zn(2)–N(6)*a* 2.105(3) (*a*: -*x* + 1, -*y* + 2, -*z* + 2)] (Figure

Scheme 1

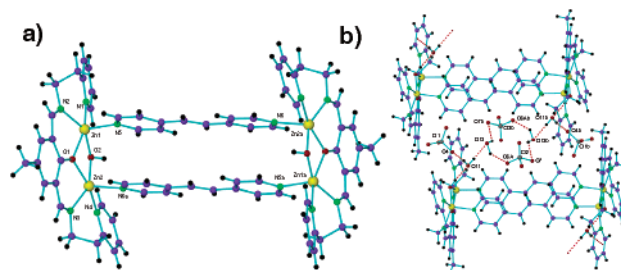
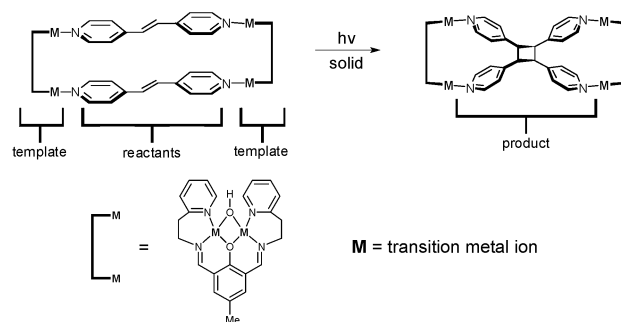


Figure 1. X-ray crystal structure of **1**: ball-and-stick views of (a) tetranuclear assembly and (b) hydrogen-bonded array. Color scheme: Zn = yellow; Cl = gray; O = red; N = green; C = blue; H = black.

1a). Each metal [Zn...Zn (Å): Zn(1)–Zn(2) 3.135(1), Zn(1)–Zn(2)*a* 13.542] adopts a square pyramidal geometry where the pyridyl N-atoms of 4,4'-bpe occupy the apical positions, while the remaining sites are occupied by a single O- and two N-atoms of L and a single O-atom of a μ_2 -OH⁻ ion. Each assembly is surrounded by two ClO₄⁻ ions, one that lies disordered across two sites A and B (occupancies: (A) 0.53, (B) 0.47), and two water molecules that assemble with the OH⁻ ligand to form a one-dimensional hydrogen-bonded array with cavities filled by four ClO₄⁻ ions and four water molecules [O...O (Å): O(2)...O(11) 2.888(5), O(11)...O(12) 2.804(6), O(11)...O(4) 2.787(5), O(12)...O(8A) 3.03(1), O(12)...O(7)*b* 3.063(8), (*b*: -*x* + 1, -*y* + 1, -*z* + 2)] (Figure 1b). In this arrangement, the C=C bonds of the assembly lie parallel and separated by 3.64 Å. This geometry conforms to the topochemical postulate of Schmidt for [2 + 2] photoreaction.⁹ C=C bonds of nearest-neighbor assemblies lie offset and separated by 9.82 Å such that the C=C bonds of the polyagonal assembly are the sole olefins organized for reaction.

Further examination of **1** suggests the tetranuclear assembly to be photoactive. Specifically, electron density consistent with a cyclobutane ring from a [2 + 2] photoreaction to produce 4,4'-tpcb is observed between the two bipyridines (yield = 8%). Moreover, exposure of either single crystals or a powdered crystalline sample of **1** to UV radiation, using either a 419 nm or

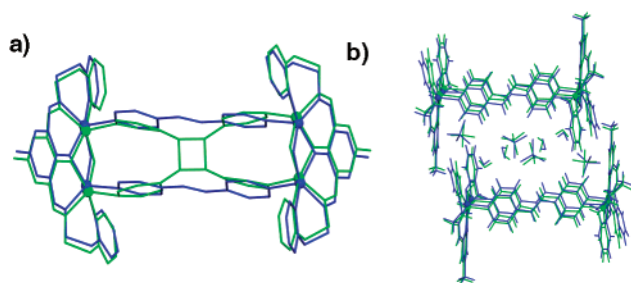


Figure 2. Overlay views of **1** (blue) and **2** (green): (a) tetranuclear assembly and (b) hydrogen-bonded array.

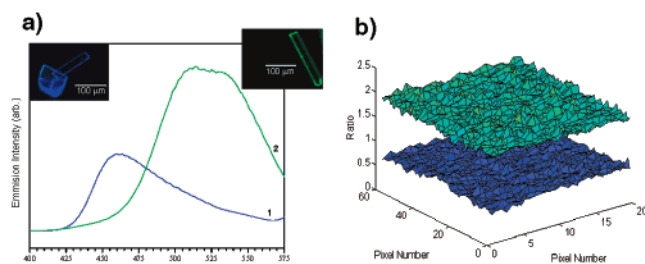


Figure 3. Spectra of **1** and **2**: (a) emission spectra (290 nm excitation) (inset: microscope images of fluorescence of single crystals of **1** and **2**) and (b) confocal fluorescence microscopy data (excitation at 454 nm with Ar ion laser) comparing ratios of intensities at 510 and 480 nm (blue = **1**; green = **2**). Each ratio image taken for $10 \times 30 \mu\text{m}$ cross section $\sim 12 \mu\text{m}$ from the crystal surface. Cross section: $\sim 1 \mu\text{m}$ thick. Spatial resolutions: 500 nm lateral and $\sim 1 \mu\text{m}$ z -axis.

broadband Hg lamp,¹⁰ for a period of approximately 5 h resulted in dimerization of 4,4'-bpe to give 4,4'-tpcb in 100% yield. The identity of 4,4'-tpcb in **2** was confirmed by ¹H NMR spectroscopy. Optical microscopy revealed that the transparency of the single crystals¹⁰ remained intact during the photoreaction, which suggested that the reaction occurred via a SCSC transformation.

An X-ray diffraction analysis of a single crystal of the photo-reacted sample of **1**²⁰ confirms that the reaction occurred via a SCSC transformation (Figure 2). Overlay views of **1** and **2** reveal that the olefins dimerized to give 4,4'-tpcb (Figure 2a). In this arrangement, 4,4'-tpcb lies within **2** such that the pyridyl groups, which adopt an unsymmetrical boat conformation and lie inclined by approximately 12° with respect to the basal planes of the metals, interact with the Schiff-base complex within a tetranuclear assembly, similar to **1**, sustained by four Zn–N bonds [Zn–N (Å): Zn(1)–N(5) 2.094(3), Zn(2)–N(6) 2.106(3)]. To accommodate 4,4'-tpcb, the distances between the metals within and between the Schiff-base ligands have slightly increased and decreased, respectively [Zn···Zn (Å): Zn(1)–Zn(2) 3.182(1), Zn(1)–Zn(2) c 13.36 ($c: -x + 1, -y + 1, -z + 1$)], while the hydrogen-bonded array has undergone a slight deformation, the most significant being a 1.15 Å displacement of the ordered ClO₄[−] ion toward the center of each inclusion cavity (Figure 2b). To our knowledge, **1** is the first example of a transition-metal-ion complex that directs a [2 + 2] photodimerization in the solid state.

Illumination of **1** and **2** at room temperature with UV energy reveals that **2** (Figure 3) exhibits a remarkably different fluorescence emission than **1**. Specifically, excitation of **1** at 290 nm gives blue emission at 464 nm, while that of **2** gives green emission at 520 nm (Figure 3a). Illumination of cleaved crystals of **1** and **2** using a handheld UV lamp demonstrates that the emissions are propagated from the bulk, an observation confirmed by laser scanning confocal fluorescence microscopy, which reveals a consistent difference in fluorescence between **1** and **2** as determined by comparing ratios of the fluorescence at 480 and 510 nm (Figure 3b) at different depths

in each single-crystalline solid. Although a related complex exhibits blue fluorescence in solution,²¹ our observations support the green emission to be the result of the photocontrolled solid-state reaction. To our knowledge, **1** is the first example of a SCSC transformation that displays such photocontrolled fluorescence.²²

In this report, coordination-driven self-assembly has been used to direct a [2 + 2] photoreaction in the solid state. Specifically, a dinuclear Zn complex has positioned two molecules of 4,4'-bpe within a tetranuclear rectangular assembly for a SCSC photodimerization that results in a dramatic red shift in fluorescence emission. We are now using such complexes to organize multiple reaction centers that may exhibit multicolor fluorescence²³ and produce complex covalent structures.^{17a} We are also developing complexes that combine additional properties of metals with the organic solid-state reactivity.

Acknowledgment. We thank the National Science Foundation (CAREER Award, L.R.M., DMR-0133138) for support.

Supporting Information Available: Crystallographic reports and ¹H NMR spectra (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

- (1) (a) Seidel, S. R.; Stang, P. J. *Acc. Chem. Res.* **2002**, *35*, 972. (b) Fujita, M.; Umemoto, K.; Yoshizawa, M.; Fujita, N.; Kusakawa, T.; Biradha, K. *Chem. Commun.* **2001**, 509. (c) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 202.
- (2) (a) Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705. (b) Kesanli, B.; Lin, W. *Coord. Chem. Rev.* **2003**, *246*, 305. (c) Moulton, B.; Zaworotko, M. J. *Chem. Rev.* **2001**, *101*, 1629.
- (3) Lewis, F. D.; Quillen, S. L.; Hale, P. D.; Oxman, J. D. *J. Am. Chem. Soc.* **1988**, *110*, 1261.
- (4) Alcock, N. W.; de Meester, P.; Kemp, T. J. *J. Chem. Soc., Perkin Trans. 2* **1979**, 921.
- (5) (a) Cho, T. H.; Chaudhuri, B.; Snider, B. B.; Foxman, B. M. *Chem. Commun.* **1996**, 1337. (b) Vela, M. J.; Snider, B. B.; Foxman, B. M. *Chem. Mater.* **1998**, *10*, 3167.
- (6) (a) de Delgado, G. C. D.; Wheeler, K. A.; Snider, B. B.; Foxman, B. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 420. (b) Vela, M. J.; Buchholz, V.; Enkelmann, V.; Snider, B. B.; Foxman, B. M. *Chem. Commun.* **2000**, 2225.
- (7) Cao, G.; Mallouk, T. E. *J. Solid State Chem.* **1991**, *94*, 59.
- (8) (a) Theocharis, C. R.; Clark, A. M.; Hopkin, S. E.; Jones, P.; Perryman, A. C.; Usanga, F. *Mol. Cryst. Liq. Cryst. Inc. Nonlin. Opt.* **1988**, *156*, 85. (b) Tiekke, B.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1981**, *2*, 543. (c) Agnew, N. H.; Brown, M. E. *J. Pol. Sci.* **1971**, *9*, 2561.
- (9) Schmidt, G. M. J. *Pure Appl. Chem.* **1971**, *27*, 647.
- (10) Enkelmann, V.; Wegner, G.; Novak, K.; Wagener, K. B. *J. Am. Chem. Soc.* **1993**, *115*, 10390.
- (11) Tyson, D. S.; Bignozzi, C. A.; Castellano, F. N.; *J. Am. Chem. Soc.* **2002**, *124*, 4562.
- (12) Pistolis, G.; Boyatzis, S.; Chatzichristidi, M.; Argitis, P. *Chem. Mater.* **2002**, *14*, 790.
- (13) Koehler, W.; Novak, K.; Enkelmann, V. *J. Chem. Phys.* **1994**, *101*, 10474.
- (14) Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167.
- (15) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.
- (16) (a) Robson, R. *Inorg. Nucl. Chem. Lett.* **1970**, *6*, 125. (b) Okawa, H. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3019.
- (17) (a) Gao, X.; Friscic, T.; MacGillivray, L. R. *Angew. Chem., Int. Ed.* **2004**, *43*, 232. (b) Shan, N.; Jones, W. *Tetrahedron Lett.* **2003**, *44*, 3687. (c) Amirakis, D. G.; Garcia-Garibay, M. A.; Rowan, S. J.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Angew. Chem., Int. Ed.* **2001**, *40*, 4256. (d) Ito, Y.; Borecka, B.; Trotter, J.; Scheffer, J. R. *Tetrahedron Lett.* **1995**, *36*, 6083.
- (18) Visinescu, D.; Andruh, M.; Muller, A.; Schmidtmann, M.; Journaux Y. *Inorg. Chem. Commun.* **2002**, *5*, 42.
- (19) X-ray data for **1**: triclinic, space group $P\bar{1}$, $a = 10.7509(11) \text{ \AA}$, $b = 10.9233(11) \text{ \AA}$, $c = 18.558(2) \text{ \AA}$, $\alpha = 97.531(5)^\circ$, $\beta = 101.758(5)^\circ$, $\gamma = 110.933(5)^\circ$, $U = 1942.7(4) \text{ \AA}^3$ for $Z = 1$ and $R = 0.046$.
- (20) X-ray data for **2**: triclinic, space group $P1$, $a = 10.9644(11) \text{ \AA}$, $b = 11.2922(11) \text{ \AA}$, $c = 17.6367(18) \text{ \AA}$, $\alpha = 96.933(5)^\circ$, $\beta = 101.342(5)^\circ$, $\gamma = 113.218(5)^\circ$, $U = 1919.4(3) \text{ \AA}^3$ for $Z = 1$ and $R = 0.044$.
- (21) Ameerunisha, S.; Zacharias, P. S. *Ind. J. Chem.* **1998**, *37A*, 696.
- (22) For a related fluorescence change, see: Fukaminato, T.; Kobatake, S.; Kawai, T.; Irie, M. *Proc. Jpn. Acad. Ser. B* **2001**, *77*, 30.
- (23) Fernandez-Acebes, A.; Lehn, J.-M. *Adv. Mater.* **1999**, *11*, 910.

JA047819N