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

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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 metallomacrocycles,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,5−7 as well as polymerizations,3,9 of olefins, and related work of Foxman,6 Mallouk,7 and others8 involving coordination networks that facilitate dimerizations,8a oligomerizations,8b and polymerizations8b,7,8c of olefins6,8 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, [Zn4L2(OH)2(4,4′-bpe)](ClO4)4 within a tetranuclear rectangular assembly, [Zn4L2(OH)2(4,4′-bpe)](ClO4)4 (where LH = 2-bis[4-(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 = rcr-tetakis(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 fluorescence11,12 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] photo reaction 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.9 C=O bonds of nearest-neighbor assemblies lie offset and separated by 2.8 Å such that the C=C bonds of the polygonal assembly are parallel (Figure 1). In this arrangement, the C=C bonds of the assembly lie parallel and separated by 3.6 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 9.8 Å such that the C=C bonds of the polygonal 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 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 = red; O = green; N = blue; H = black.

1a). Each metal [Zn⋯Zn (Å): Zn(1)⋯Zn(2) 3.135(1), Zn(1)⋯Zn(2) 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 μ2-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) 2.885(8), O(11)⋯O(12) 2.804(6), O(11)⋯O(4) 2.787(5), O(12)⋯O(8A) 3.03(1), O(12)⋯O(7b) 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 3.6 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 9.8 Å such that the C=C bonds of the polygonal assembly are the sole olefins organized for reaction.

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

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 fluorescence and produce complex covalent structures. 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

(19) X-ray data for 1: triclinic, space group PI, a = 10.7509(1) Å, b = 10.9233(1) Å, c = 18.5582(2) Å, Û = 97.531(5°) β = 101.758(5°), Û = 110.933(5°), Û = 1942.7(4) Å2 for Z = 1 and R = 0.046.
(20) X-ray data for 2: triclinic, space group PI, a = 10.9641(1) Å, b = 11.2922(1) Å, c = 17.6367(18) Å, Û = 96.933(5°) β = 101.342(5°), γ = 113.218(5°), Û = 1914.9(3) Å2 for Z = 1 and R = 0.044.

J. AM. CHEM. SOC. ■ VOL. 126, NO. 30, 2004 9159