Reversible Photochromism of a Crystalline Dithienylethene Copper(I) Polymer

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Received December 20, 1995

Study of photochromic compounds, which undergo thermally irreversible and fatigue-resistant photochromic reactions, is one of the key points in the current revival of interest in designing light-triggered molecular and supramolecular devices.[1,2] A series of novel dithienylethene-based molecules have been found in solution to exhibit the reversible photoinduced cyclization/ring-opening process.[1−4] In contrast, photochromic dithienylethene in the solid state has rarely been reported,[5] and photochromism of a solid coordination polymer of these species, in particular, remains unknown. Although a few metal complexes with other organic photochromic compounds have been reported, origins of the photomechanical effects in solid state are not fully understood.[6,7] Here we describe the first crystallographically characterized copper(I) coordination polymer with a dithienylethene ligand, *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (*cis*-L), which shows reversible photoreactivity in the crystalline phase. The results are compared with the corresponding complex of the *trans*-L.

Reduction of $Cu(ClO_4)_2{\cdot}6H_2O$ by a copper metal sheet under ethylene atmosphere affords a colorless copper(I) solution, which reacts at ambient temperature with *trans*-L and *cis*-L in THF and acetone, respectively, yielding orange crystals in both cases. X-ray structure determination of complex **1**[8] with *trans*-L reveals that it contains [Cu(*trans*-L)(THF)(ClO_4)] units bridged sequentially by the two *trans* CN groups of each dithienylethene to form polymeric zigzag chains running parallel to a diagonal axis of the triclinic cell as shown in Figure 1. The coordination environment around the copper ions can be better described as a distorted tetrahedral comprising one CN group of two distinct dithienylethene molecules, one THF, and one perchlorate oxygens. The structure of complex **2**[9] with *cis*-L is composed of noninteracting ClO_4^- anions and macrocations $[Cu(cis\text{-}L)_2]^+$ in which each metal center is coordinated with one CN group of the four dithienylethene molecules (Figure 2a). Each *cis*-L in turn bridges two copper(I) ions with two cyano groups, leading to an infinite network of metal cations as illustrated in Figure 2b. Bond distances and angles within the polymers of **1** and **2** are as much as expected. Over the course of data collection for **2**, the single crystal was found to be sensitive to the X-ray beam and deteriorated over several hours of irradiation, which causes appreciable reduction of intensities. Thus, the high *R* value for this complex is a direct consequence of the light-sensitive nature of the material. Nevertheless, the framework and the *cis* arrangement of the two thiophene rings it generates are the aspects of major interest, and the overall chemical features of the compound are beyond any doubt.

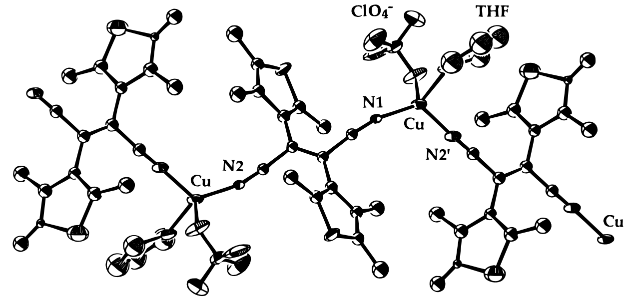

Figure 1. Portion of an infinite chain structure in **1**.

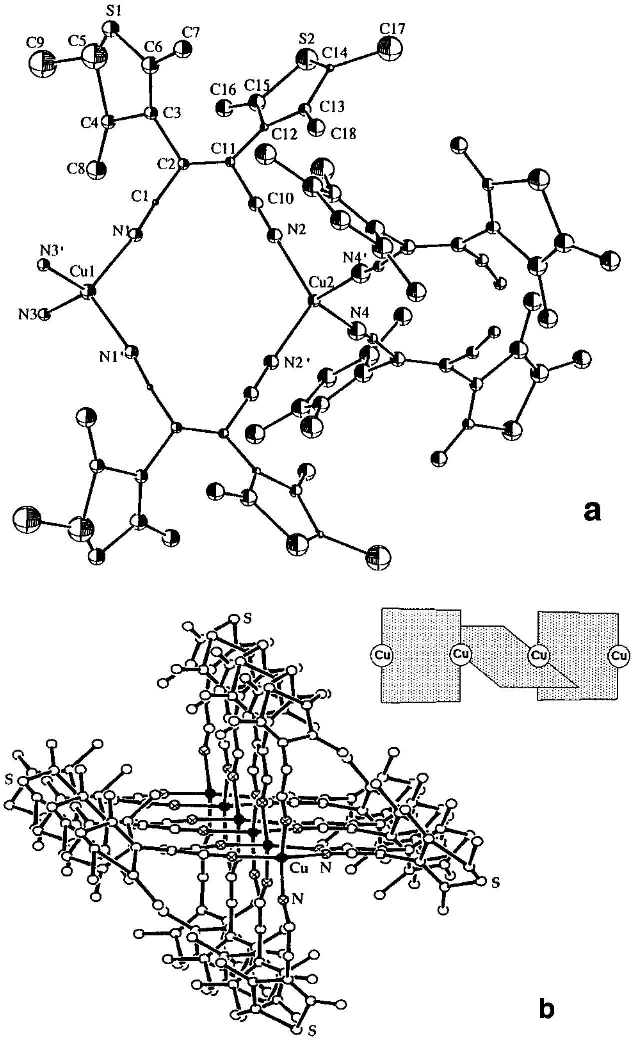

Figure 2. (a) Partial molecular structure of **2** showing the twisted ring-opened form of dithienylethene. (b) A view of the crystal packing showing a one-dimensional array of the metal ions.

The most striking feature of the two complexes is that they show a rather different photoresponsive pattern toward irradia-

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[8] Crystal data for **1**: $C_{22}H_{26}ClCuN_2O_5S_2$, $M = 561.58$, triclinic, $P\bar{1}$, $a = 11.939(6)$ Å, $b = 14.495(5)$ Å, $c = 8.271(4)$ Å, $\alpha = 87.16(4)°$, $\beta = 74.45(4)°$, $\gamma = 67.08(3)°$, $V = 1267(2)$ Å^3, $Z = 2$, $D_{calcd} = 1.471$ g/cm^3, $R = 0.092$, $R_w = 0.092$, Rigaku AFC6S diffractometer, 6131 measured reflections, Mo Kα, 5836 unique ($R_{int} = 0.100$), 187 variables [$I > 2.50\sigma(I)$].

[9] Crystal data for **2**: $C_{36}H_{36}ClCuN_4O_4S_4$, $M = 815.94$, monoclinic, $C2/c$, $a = 28.701(6)$ Å, $b = 12.273(5)$ Å, $c = 29.441(6)$ Å, $\beta = 105.98(1)°$, $V = 9969(4)$ Å^3, $Z = 8$, $D_{calcd} = 1.090$ g/cm^3, $R = 0.133$, $R_w = 0.159$, Rigaku AFC5R diffractometer, 7345 measured reflections, Mo Kα, 7129 unique ($R_{int} = 0.096$), 790 variables [$I > 5.00\sigma(I)$].

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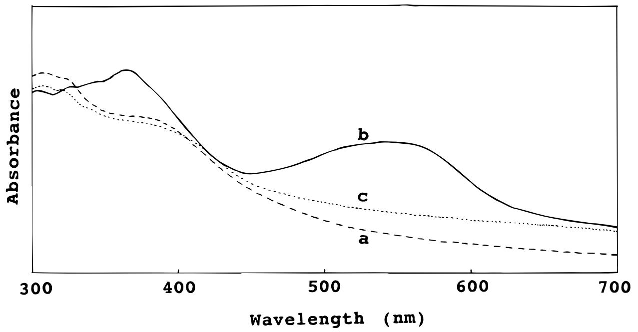
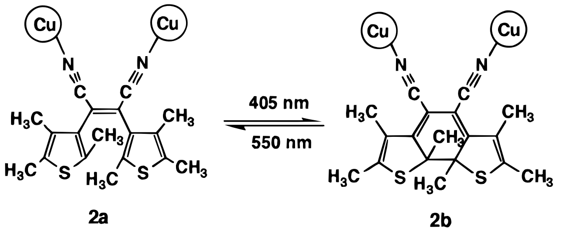


Figure 3. Absorption spectra of **2** as KBr disc: a, before irradiation; b, in the photostationary state under irradiation with 405 nm light; c, irradiation of b with 550 nm light.

tion of light by using a high-pressure mercury lamp (400 W). For **1**, there is no visible color change upon any reasonable period of irradiation. However, **2** showed normal photochromism in the single-crystalline state. On irradiation with 405 nm light for 1 h at room temperature the orange fine crystals of **2** gradually turned red. This leads to the increase of the electronic spectral absorption at 364 nm and the formation of a new band at 550 nm as illustrated in Figure 3. This spectral pattern is very similar to that observed for the ring-closed form of the free *cis*-L ligand in CCl_4 solution[3] and another dithienylethene, 1,2-bis(2,4-dimethy-3-thienyl)perfluorocyclopentene, in the solid phase.[5] The photogenerated ring-closed form is stable, and the red color hardly faded at room temperature for 2 days. It reverts to the orange ring-opened form on exposure to 550 nm light. This cycle can be repeated many times, indicative of the reversible cyclization reaction that takes place in the crystalline state. The system studied here may be used as an optical memory.[2]

The 270 MHz NMR spectrum of the methyl groups for **2** before photoirradiation was measured in acetone, and it showed three resonances at 2.09, 2.19, and 2.25 ppm. Under irradiation with 405 nm light, three new lines appeared at 2.23, 2.36, and 2.55 ppm along with a decrease of the intensity of the initial three lines. On further irradiation with 550 nm light, the original three resonances were restored. This phenomenon was observed in the previously reported light-induced dithienylethene species in CCl_4.[3]

The properties of photochromic materials in solution are dependent on solvent polarity,[10] and by comparison, the study of these compounds in solid state form with the aid of X-ray crystallography can provide direct information essential to rational designing of many other photochromic systems. The X-ray structure analysis of **2** indicates that the two thiophene rings are significantly twisted with an average dihedral angle of 48.3°. The two C atoms, C(6) and C(15) as shown in Figure 2a, where bridging occurs during cyclization, are 3.68 Å apart. During the cyclization reaction of **2a**, the two thiophene rings are required to approach each other by rotating along the C−C bond between thiophene and ethylene groups. The ring-closed form **2b** is considered to have a coplanar structure,[5] in which the C(6)−C(15) distance is expected to be in the range of 1.54−1.56 Å for a covalent C−C single bond. Inevitably, such rotation destroys the crystal, which precludes any detailed structural investigation of the ring-closed form. Although the precise mechanism for photochromic interconversion of the twisted ring-opened form and coplanar ring-closed form in the solid state is not clear at present, light-induced crystal oscillation[6] might be one possible pathway to account for the approach and rotation of the two thiophene rings. The mechanism should be a corotatory mode, but it needs to be proved in the solid state. It is noteworthy that **2** has an infinite chain structure, Figure 2b, and any rotation of thiophene rings of one *cis*-L group might cause perturbation upon others. Therefore, cooperative effects[7] of elastic coordinative behavior of a copper(I) ion cannot be ruled out. Further investigation with other metal systems such as Ag(I) and Pd(II) are underway to clarify this point.



Acknowledgment. This work was supported in part by a Grand-in Aid for Science Research [Numbers 0723226 and 07241260 (priority areas)] from the Ministry of Education, Science and Culture, Japan. We are also grateful to Kinki University for financial support (GG 1100).

Supporting Information Available: Tables of complete fractional atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles, least-squares plane calculations, and listing of observed and calculated structure factors (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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