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Photochromism of Metal Complexes Composed of Diarylethene Ligands and $ZnCl_2$

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Metal complexes composed of $ZnCl_2$ and bidentate 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene (**1a**) and monodentate 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene (**2a**) photochromic ligands were prepared. X-ray crystallographic analyses showed the formation of a coordination polymer and a discrete 2:1 complex for **1a**·$ZnCl_2$ and **2a**$_2$·$ZnCl_2$, respectively. While the **2a**$_2$·$ZnCl_2$ crystal underwent photochromic reaction in the crystalline state by alternate irradiation with UV and visible light, the **1a**·$ZnCl_2$ crystal did not show any photoreactivity. The difference in the photochromic behavior was explained by the difference in the conformation of the diarylethenes in the crystals.

Photochromic compounds have attracted remarkable attention because of their potential ability for optical memory media and optical switching devices.[1] Among them diarylethenes with heterocyclic aryl groups are the most promising candidates for the applications because of their fatigue resistant and thermally irreversible photochromic properties.[2] Moreover, it has recently been found that some diarylperfluorocyclopentenes having thiophene or benzothiophene rings undergo photochromic reactions even in the single-crystalline phase.[3]

Coordination-driven self-assembly is an important strategy to construct supramolecular architecture.[4] Geometrical structures of organic ligands and coordination numbers of the core metals control the two- and three-dimensional assembled structures. Several diarylethene metal complexes have been synthesized, and their structure−reactivity relationship has been studied.[5,6]

In this paper we have prepared complexes composed of monodentate and bidentate diarylethene pyridyl ligands and four-coordinated tetrahedral $ZnCl_2$ and examined the reactivity in solution as well as in the crystalline phase.

Pyridyl groups are widely used for constructing extended structures by means of metal coordination. We prepared bidentate 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene (**1a**)[7] and monodentate 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl)perfluorocyclopentene (**2a**)[8] photochromic ligands by incorporating one and two pyridyl groups in the diarylethene backbone (Scheme 1). The phenyl derivative, such as, 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, is known to exhibit photochromism in the crystalline phase. Zn^{2+} complexes have no absorption in the visible region because of fully occupied d^{10} electronic structure.

The complexation was carried out by mixing anhydrous $ZnCl_2$ and diarylethene pyridyl ligand **1a** or **2a**. Successive recrystallization from methanol gave crystals of **1a**·$ZnCl_2$,[9] and **2a**$_2$·$ZnCl_2$.[10] Confirmation of the structure was finally

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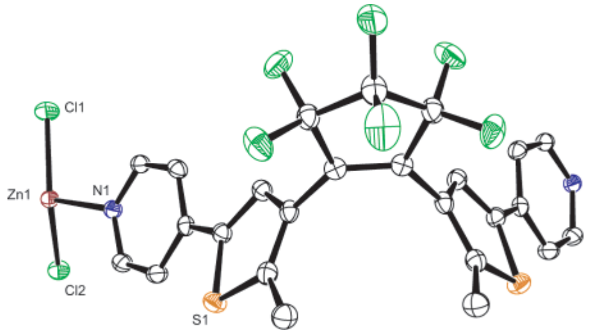


Figure 1. ORTEP drawings of X-ray crystallographic structure of the linear chain complex **1a**·$ZnCl_2$ (50% probability). Hydrogen atoms are omitted for clarity. Only one repeating unit is shown.

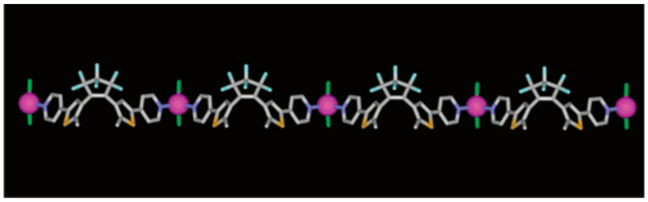
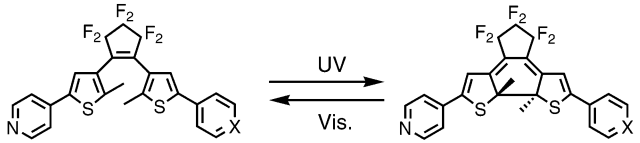


Figure 2. Linear chain structure of coordination polymer **1a**·$ZnCl_2$.

Scheme 1



1a (X = N)
2a (X = CH)

1b (X = N)
2b (X = CH)

performed by elemental analysis and X-ray crystallography. The complexes showed photochromism in methanol solution by irradiation with UV and visible light. The absorption maxima were exactly same as the absorption maxima of the ligands.[8,11]

The complexes of bidentate ligand **1a** were chainlike structures.[12] The crystal structure of the repeating unit and the chain structure are shown in Figures 1 and 2, respectively. Two pyridyl nitrogens of two different molecules are coordinated with $ZnCl_2$ to form a linear coordination polymer. All diarylethenes in the complex adopt parallel conformation, in which photocyclization reaction is prohibited. In fact, the crystal did not show any photochromic reactivity.[13]

A discrete 2:1 complex was formed from monodentate ligand **2a**.[14] Figure 3 shows the discrete structures of **2a**$_2$·$ZnCl_2$. In this crystal there are two independent **2a** molecules in the asymmetric unit (**A** and **B** in Figure 3). **A** and **A′**, **B** and **B′** are crystallographically equivalent by C_2 axis on Zn atoms. The dihedral angles between the pyridine ring and the thiophene ring are quite different (−11° for **A** and 22° for **B**). The distances between reactive carbons are 3.56 and 3.67 Å for **A** and **B**, respectively, suggesting that photocyclization in the crystal lattice is possible.

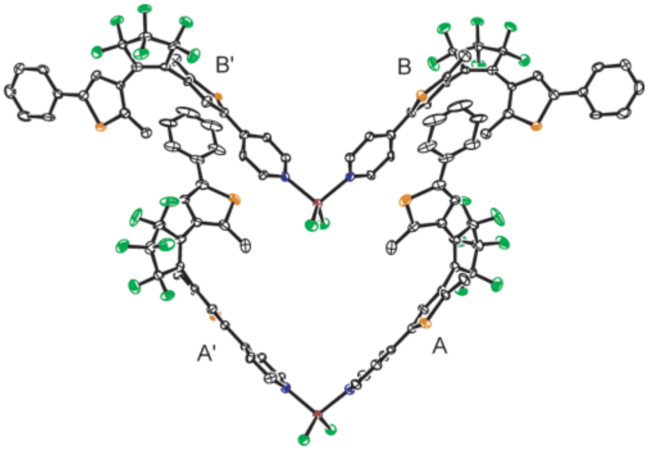


Figure 3. ORTEP drawing of X-ray crystallographic structure of discrete complex **2a**$_2$·$ZnCl_2$ (50% probability). Hydrogen atoms are omitted for clarity.

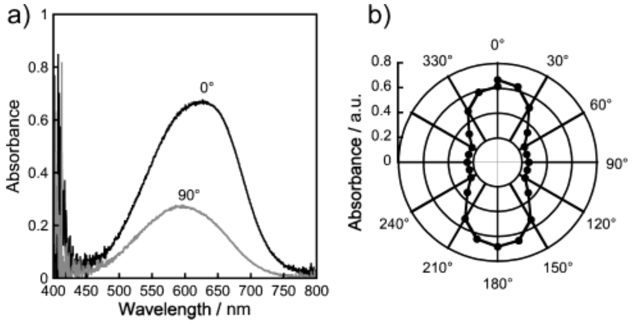


Figure 4. (a) Polarized absorption spectra of **2a**$_2$·$ZnCl_2$ single crystal. The direction of the maximum intensity was defined as 0°. The absorption maxima at 0° and 90° were 625 and 595 nm, respectively. (b) Polar plots measured at 625 nm.

Although the bidentate complex **1a**·$ZnCl_2$ did not show any photochromic reactivity, the monodentate complex **2a**$_2$·$ZnCl_2$ showed a photochromic reaction in the crystalline phase. Upon irradiation with 365 nm light the single crystals turned blue. Upon irradiation with visible light ($\lambda > 500$ nm) the blue color disappeared. The origin of the blue color is the closed-ring isomer **2b**.

The color of the crystals was observed under polarized light on the (001) plane of the face-indexed crystal of **2a**$_2$·$ZnCl_2$. Figure 4a shows the polarized absorption spectra of **2a**$_2$·$ZnCl_2$ crystals. The direction of the maximum intensity was defined as 0°. At 0° the absorption maximum of the spectrum was 625 nm. Upon rotation as much as 90°, the absorption maximum was blue-shifted to 595 nm and the absorption intensity increased. The spectral shift is as much as 30 nm. The decrease of the blue color intensity on rotation

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(9) Elemental anal. for **1a**·$ZnCl_2$. Calcd for $C_{25}H_{16}F_6N_2S_2Cl_2Zn$: C, 45.58; H, 2.45; N, 4.25. Found: C, 45.73; H, 2.48; N, 4.19.

(10) Elemental anal. for **2a**$_2$·$ZnCl_2$. Calcd for $C_{52}H_{34}F_{12}N_2S_4Cl_2Zn$: C, 52.96; H, 2.91; N, 2.38. Found: C, 52.67; H, 2.87; N, 2.34.

(11) The solution phase reactivity of the related compound, 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)cyclopentene zinc complex, has been reported: Qin, B.; Yao, R.; Tian, H. *Org. Biomol. Chem.* **2003**, *1*, 2187−2191.

(12) Crystal data for **1a**·$ZnCl_2$: $C_{25}H_{16}F_6N_2S_2Cl_2Zn$, fw = 658.83, monoclinic $P2_1/n$, $a = 7.3867(16)$ Å, $b = 13.969(3)$ Å, $c = 12.949(3)$ Å, $\beta = 100.089(3)°$, $V = 1315.5(5)$ Å^3, $Z = 2$, $R1$ ($I > 2\sigma$) = 0.0251, $wR2$ (all data) = 0.0682.

(13) For the notation of parallel and antiparallel, see: (a) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305−8309. (b) Matsuda, K.; Irie, M. *Tetrahedron Lett.* **2000**, *41*, 2577−2580.

(14) Crystal data for **2a**$_2$·$ZnCl_2$: $C_{52}H_{34}F_{12}N_2S_4Cl_2Zn$, fw = 1179.32, monoclinic $C2/c$, $a = 15.865(3)$ Å, $b = 15.734(3)$ Å, $c = 40.755(7)$ Å, $\beta = 92.113(5)°$, $V = 10167(3)$ Å^3, $Z = 8$, $R1$ ($I > 2\sigma$) = 0.0559, $wR2$ (all data) = 0.1541.

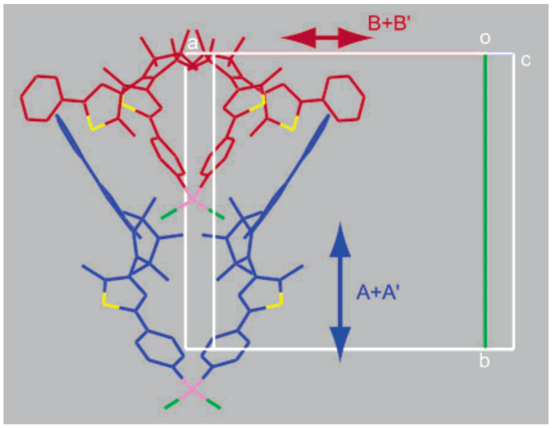

Figure 5. Crystal structure viewed normal to (001) plane. Blue molecules are **A** and **A′** (cf. Figure 3), and red molecules are **B** and **B′**. Blue and red arrows indicate the transition moment of the corresponding closed-ring isomers.

indicates that the closed-ring isomers are regularly oriented in the crystals. In other words, the photochromic reactions proceed in the crystal lattice.

The relation between the transition moment and the crystal structure was examined. Figure 4b shows the polar plot measured normal to the (001) plane. A weak absorption perpendicular to the main absorption was observed. The absorption at 625 nm corresponds to the main transition, and the absorption at 595 nm corresponds to the minor transition. The crystal structure viewed normal to the (001) plane is shown in Figure 5. **A** and **A′** molecules (cf. Figure 3) are indicated in blue, and **B** and **B′** molecules are indicated in red. Upon cyclization there appear two orthogonal transition moments of the corresponding closed-ring isomers, which are indicated by blue (from **A** and **A′**) and red (from **B** and **B′**) arrows. The long axes of the closed-ring isomers of **A** and **A′** molecules are aligned almost parallel to the (001) plane, while the long axes of the closed-ring isomers of **B** and **B′** are aligned almost perpendicular to the (001) plane. Therefore, when viewed normal to the (001) plane, the electronic transition moment of the **A** molecule is larger than that of the **B** molecule. The main transitions correspond to **A** molecules, and the minor transitions correspond to **B** molecules.

The dihedral angles between the pyridine ring and the thiophene ring are 11° for **A** and 22° for **B**, and the direction of the torsion is opposite in molecules **A** and **B**. Upon cyclization the **A** molecule becomes planar, while in the **B** molecule the pyridine ring is twisted to the central cyclohexadiene part. Therefore, the π-conjugation length is longer in the **A** molecule. The difference in absorption maxima in **A** (625 nm) and **B** (595 nm) is ascribed to the difference in coplanarity between the thiophene ring and the pyridine ring.[15]

In conclusion we have synthesized metal complexes composed of bidentate and monodentate diarylethene pyridyl ligands and $ZnCl_2$. The photochromic reactivity and the absorption anisotropy of the colored crystal are well explained by the crystal structure.

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Supporting Information Available: X-ray crystallographic data of $\mathbf{1a}\cdot ZnCl_2$ and $\mathbf{2a_2}\cdot ZnCl_2$ (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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