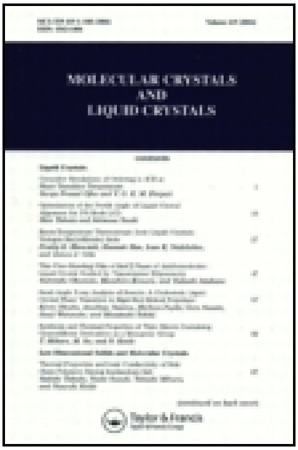

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Photochromism of Diarylethene Zinc Complexes

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To cite this article: Kenji Matsuda, Kohsuke Takayama, Yoshihiro Shinkai & Masahiro Irie (2005): Photochromism of Diarylethene Zinc Complexes, Molecular Crystals and Liquid Crystals, 431:1, 429-432

To link to this article: http://dx.doi.org/10.1080/15421400590947009

Mol. Cryst. Liq. Cryst., Vol. 431, pp. 129/[429]–132/[432], 2005
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400590947009

Photochromism of Diarylethene Zinc Complexes

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*Zinc complexes composed of bidentate 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)-perfluorocyclopentene (**1a**) or monodentate 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl) perfluorocyclopentene (**2a**) photochromic ligands and* $Zn(hfac)_2$ *or* $ZnCl_2$ *were prepared and their photochromic properties were studied.*

Keywords: metal complex; photochemistry; photochromism

INTRODUCTION

Among various types of photochromic compounds [1], diarylethenes have advantages from the viewpoints of thermal stability of both isomers and the reactivity in the crystalline phase [2].

Coordination-driven self assembly [3] is an important strategy to construct supramolecular architecture. Predesigned geometry of the metal core and organic ligands determine the final assembled structure, which can be two- or three-dimensional. An assembled structure can have unique physical properties, such as magnetism or gas adsorption. Recently optical properties of the metal complexes also attract increasing attention because of their unique optical properties [4].

Herein, the photochromism of the metal complexes composed of diarylethene ligand and transition metal will be reported.

This work was partly supported by PRESTO of Japan Science and Technology Corporation (JST).

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RESULTS AND DISCUSSIONS

Preparation of the Complexes

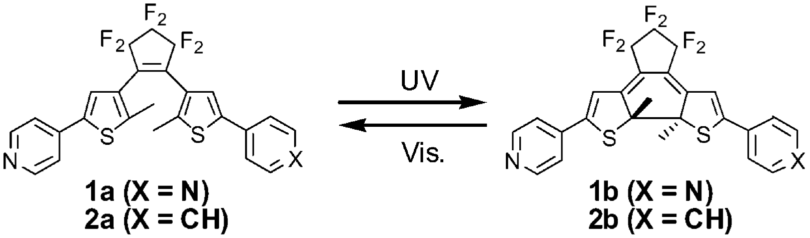
We have synthesized bidentate 1,2-bis(2-methyl-5-(4-pyridyl)-3-thienyl)-perfluorocyclopentene (**1a**) and monodentate 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methyl-5-(4-pyridyl)-3-thienyl) perfluorocyclopentene (**2a**) photochromic ligands (Scheme 1).

Complexation was carried out by mixing dehydrated Zn(hfac)$_2$ or anhydrous ZnCl$_2$ and diarylethene pyridyl ligand **1a** or **2a**. Successive recrystallization from appropriate solvents gave crystals of the complexes, $\mathbf{1a \cdot Zn(hfac)_2}$, $\mathbf{2a_2 \cdot Zn(hfac)_2}$, $\mathbf{1a \cdot ZnCl_2}$, and $\mathbf{2a_2 \cdot ZnCl_2}$ [5–7]. X-ray crystallographic analyses showed the formation of coordination polymers and discrete 1:2 complexes for bidentate and monodentate ligands, respectively (Fig. 1). $\mathbf{2a_2 \cdot Zn(hfac)_2}$ crystal contained hexane in the crystal lattice.

Photochromic Reaction

The complexes underwent reversible photochromic reactions by alternate irradiation with UV and visible light in ethyl acetate. Upon irradiation with UV light, the colorless solutions turned strongly blue. The absorption maxima of the colored isomers were observed around 590 nm which is the same as the maxima of **1b** itself in ethyl acetate.

Upon irradiation with 313 nm light, the crystals of $\mathbf{1a \cdot Zn(hfac)_2}$, $\mathbf{2a_2 \cdot Zn(hfac)_2}$, crystal turned blue. Absorption maxima were both 620 nm. Upon irradiation with 578 nm light, the blue color disappeared. The color of the crystals was observed under polarized light. Upon rotation of the crystal sample, the absorption maxima did not change, but the intensities dramatically changed, indicating that the closed-ring isomers are regularly oriented in the crystals. In other words, the photochromic reactions proceed in the crystal lattice.



SCHEME 1 Photochromic ligands **1a** and **2a**.

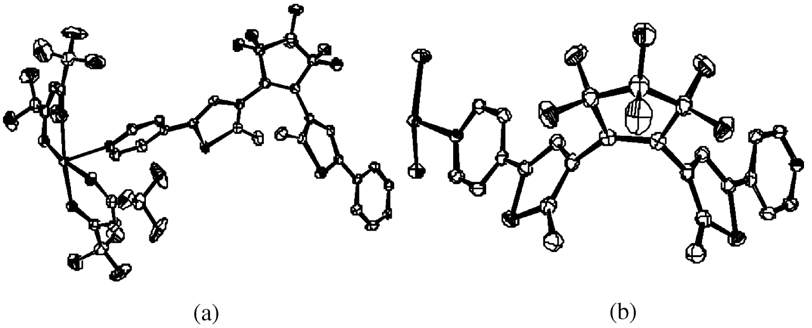

(a) (b)

FIGURE 1 ORTEP drawing of one repeating unit of the coordination polymer: a) **1a·Zn(hfac)$_2$**; b) **1a·ZnCl$_2$**.

In the case of ZnCl$_2$ complex, while the crystal of **2a$_2$·ZnCl$_2$** showed photochromism in the single-crystalline phase, the crystal of **1a·ZnCl$_2$** did not show photochromism. The X-ray structure revealed that in the crystals of **1a·Zn(hfac)$_2$**, **2a$_2$·Zn(hfac)$_2$**, and **2a$_2$·ZnCl$_2$**, the diarylethene ligand adopted the antiparallel conformation, but in the crystal of **2a$_2$·ZnCl$_2$**, the diarylethene ligand adopted the parallel conformation. Parallel conformation prohibits the photocyclization judging from Woodward-Hoffmann rule. The absorption maximum of the colored crystal of **2a$_2$·Zn(hfac)$_2$** was 625 nm at the angle of maximum intensity. Upon rotation as much as 90°, the absorption maximum was blue-shifted to 595 nm and the absorption intensity decreased. The spectral shift was as much as 30 nm. The spectral shift is due to the difference in the conformation of the diarylethene in the crystal. The photoreactivity and the absorption maximum depended on the structure of the diarylethene ligands, which are determined by the crystal structure of the complexes.

CONCLUSION

Photochromic zinc complexes were synthesized from bidentate and monodentate diarylethene ligands. The photoreactivity and the absorption maximum depended on the structure of the diarylethene ligands.

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