

Single-crystalline photochromism of a linear coordination polymer composed of 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene and bis(hexafluoroacetylacetonato)zinc(II)

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A linear coordination polymer composed of diarylethene and bis(hexafluoroacetylacetonato)zinc(II) has been synthesized and its photochromism in the single-crystalline phase studied by polarized absorption spectroscopy.

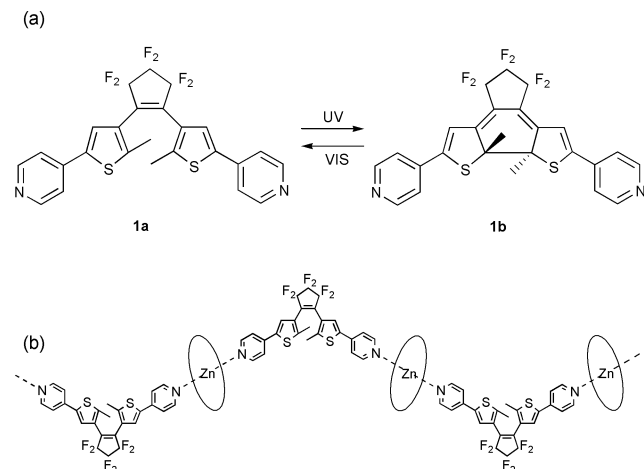
Photochromic compounds have attracted much attention because of their potential ability for photonic switching devices.¹ Among them diarylethenes with heterocyclic aryl groups are the most promising compounds for such applications. Diarylethenes undergo fatigue resistant and thermally irreversible photochromic reactions.² In addition, it has recently been found that some diarylperfluorocyclopentenes undergo photochromic reactions in the single crystalline phase.³

When metal ions are located at both ends of the aryl groups of the diarylethenes, the interaction between metal ions can be switched by photoirradiation, because the π -conjugated bond structures between the two aryl groups are different in the two isomers.⁴ Therefore, the use of a diarylethene as a photoswitching bridging ligand is of interest. The synthesis and photochromism of metal complexes of diarylethenes was first reported in 1996 by Munakata *et al.*⁵ They prepared a linear polymer, bridged by cyano groups, of *cis*-1,2-dicyano-1,2-bis[2,4,5-trimethyl-3-thienyl]ethene and copper(I) ions. In the present work we report on the synthesis of a linear chain polymer complex of 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene **1a**⁶ with $\text{Zn}(\text{hfac})_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate) and its photochromic reaction in the single-crystalline phase (Scheme 1).

Rhombus-shaped single crystals of **1a** were obtained by recrystallization from hexane. An X-ray crystallographic study showed that two independent molecules were present in the asymmetric unit.⁷ The distances between the reactive carbons of **1a** were 3.570 and 3.546 Å, short enough to react in the

crystalline phase. Single crystals of **1a** turned blue upon irradiation with 366 nm light whilst retaining their shape. The blue color is considered to arise from the closed-ring form isomer **1b**.^{3,6} The blue color disappeared upon irradiation with 578 nm light. The color of a crystal was observed under polarized light. Fig. 1(a) and (b) show the polarized absorption spectra and the polar plot. The polarized absorption spectrum at a selected angle showed its maximum at 610 nm. The absorption maximum in the crystal showed a bathochromic shift as much as 20 nm in comparison with the maximum in ethyl acetate solution ($\lambda_{\text{max}} = 589$ nm). The absorption intensity was strongly dependent on rotation, which indicates that the colored form isomers were regularly oriented in the crystal lattice. The order parameter $[(A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})]$ was as high as 0.72.

$\text{Zn}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ was chosen as the metal source for complexation because of its high affinity for pyridyl ligands.⁸ A solution of **1a** (200 mg) in dichloromethane (2 mL) was mixed with a solution of $\text{Zn}(\text{hfac})_2 \cdot 2\text{H}_2\text{O}$ (197 mg) in methanol-dichloromethane (1:1, 2 mL) to afford a pale green powder. Recrystallization from methanol-dichloromethane (1:1) gave



Scheme 1 (a) Photochromism of ligand **1a**. (b) Schematic drawing of the linear chain polymer composed of **1a** and $\text{Zn}(\text{hfac})_2$.

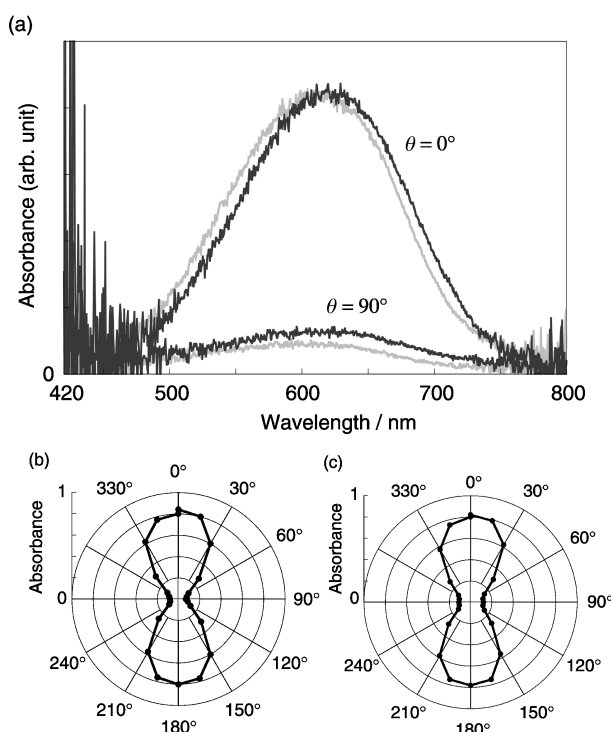


Fig. 1 (a) Polarized absorption spectra of single crystals of **1a** (grey line) and **1a**· $\text{Zn}(\text{hfac})_2$ (black line) after irradiation with 366 nm light. (b) Polar plot at the absorption maximum of **1a**. (c) Polar plot at the absorption maximum of **1a**· $\text{Zn}(\text{hfac})_2$. The angle of maximum intensity of the absorption is defined as $\theta = 0^\circ$ for **1a** and the direction of the linear chain was defined as $\theta = 0^\circ$ for **1a**· $\text{Zn}(\text{hfac})_2$.

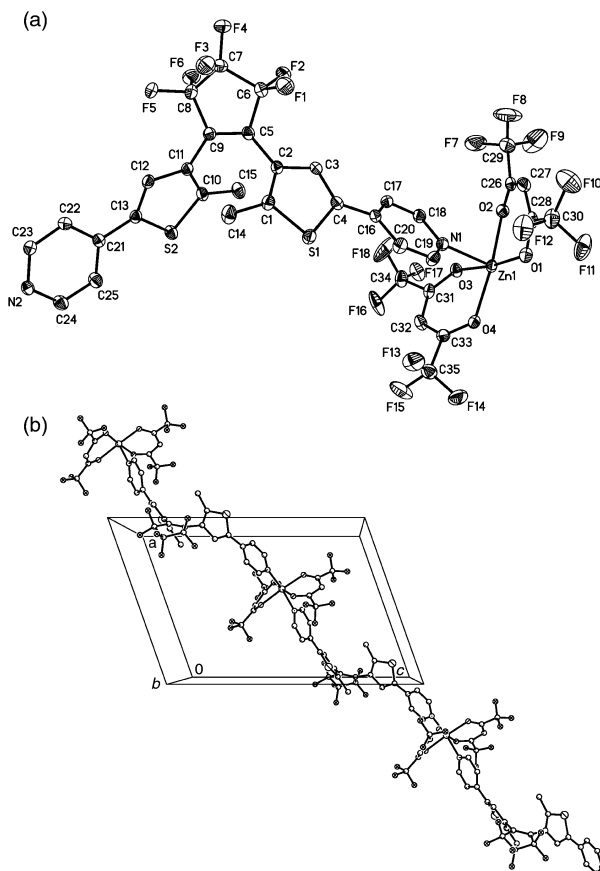


Fig. 2 (a) ORTEP drawing of the molecular structure of **1a**-Zn(hfac)₂ for one unit (50% probability) with hydrogen atoms omitted for clarity. (b) Ball-and-stick model of the linear polymer chain of **1a**-Zn(hfac)₂ viewed normal to the (010) face.

pale yellow block crystals.⁹ The IR spectrum of the crystal was a superposition of **1a** and Zn(hfac)₂·2H₂O, indicating formation of the complex. X-Ray crystallography revealed the formation of a linear chain polymer complex composed of **1a** and Zn(hfac)₂ (Fig. 2).¹⁰ The two pyridyl nitrogens of two different molecules of **1a** are coordinated with Zn(hfac)₂ in a *trans* configuration to produce a linear chain structure parallel to the [2 0 -1] direction. The molecular structure of **1a** in the complex is almost identical to that of **1a** itself. The distance between reactive carbons was 3.557 Å, again short enough to react.

An ethyl acetate solution of **1a**-Zn(hfac)₂ underwent a photochromic reaction by alternate irradiation with 313 and 578 nm light. The absorption maximum of the colored form isomer **1b**-Zn(hfac)₂ was at 590 nm, the same as the maximum of **1b** itself in ethyl acetate solution.

Crystals of **1a**-Zn(hfac)₂ also showed photochromic reactivity in the single-crystalline phase. Upon irradiation with 366 nm light single crystals of **1a**-Zn(hfac)₂ turned blue with formation of the closed-ring isomer **1b**-Zn(hfac)₂ considered to be the origin of the blue color.³ Upon irradiation with 578 nm light the blue color disappeared. The polarized absorption spectra and the polar plot measured normal to the (010) plane of the face-indexed crystal are shown in Fig. 1(a) and (c). Here, the [2 0 -1] direction, the direction of the linear polymer chain, is defined as $\theta = 0^\circ$. The absorption intensity was strongly dependent on rotation, indicating a regular orientation of the closed-ring form isomer **1b**-Zn(hfac)₂. The transition moment was almost identical to the direction of the linear chain. The absorption maximum of **1b**-Zn(hfac)₂ in the crystal was 620 nm, 10 nm longer than that observed for crystals of **1b**.

Table 1 summarizes the absorption maxima of the colored closed-ring isomer **1b** and **1b**-Zn(hfac)₂, which are generated by irradiation with UV light in solution and in the single crystalline phase. In solution there was no difference between the free ligand and the complex, but in the single-crystalline phase the

Table 1 Absorption maxima (nm) of the closed-ring form isomers generated by irradiation with UV light

	1b	1b -Zn(hfac) ₂
In solution	589	590
In single crystal	610	620

absorption maximum of the polymer complex showed a bathochromic shift upon complexation. The absorption shift upon complexation in the single crystal can be attributed to an increase in the strain upon complexation.

In conclusion we have synthesized a linear chain polymer complex composed of 1,2-bis[2-methyl-5-(4-pyridyl)-3-thienyl]perfluorocyclopentene **1a** and Zn(hfac)₂. The complex undergoes a photochromic reaction in the single-crystalline state. While there was no shift in solution, the absorption maximum in the single crystal showed a 10 nm bathochromic shift upon complexation.

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- Crystal data for 1a*: C₂₅H₁₆F₆N₂S₂, *M* = 522.53, triclinic, *P* $\bar{1}$, *a* = 11.6091(18), *b* = 12.899(2), *c* = 15.818(3) Å, α = 76.850(2), β = 85.771(2), γ = 77.020(2)°, *V* = 2247.0(6) Å³, *Z* = 4, μ (Mo-K α) = 0.304 mm⁻¹, *R* [*I* > 2 σ (*I*)] = 0.0554, *wR*² (all data) = 0.1535, 8955 data, 635 parameters. For **1a**-Zn(hfac)₂: C₃₅H₁₈F₁₈N₂O₄S₂Zn, *M* = 1002.01, monoclinic, *P*₂/c, *a* = 12.3592(9), *b* = 18.3531(14), *c* = 17.9411(13) Å, β = 109.4780(10)°, *V* = 3836.7(5) Å³, *Z* = 4, μ (Mo-K α) = 0.879 mm⁻¹, *R* [*I* > 2 σ (*I*)] = 0.0309, *wR*² (all data) = 0.0777, 8418 data, 561 parameters. CCDC 154005 and 154006. See <http://www.rsc.org/suppdata/cc/b0/b009352/> for crystallographic data in .cif or other electronic format.
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- Analytical data for 1a*-Zn(hfac)₂: mp 274 °C (decomp.); ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.01 (s, 6H), 5.55 (s, 2H), 7.65 (d, *J* 4 Hz, 4H), 7.83 (s, 2H), 8.59 (br s, 4H); IR (KBr) ν 1130, 1230, 1500, 1600 cm⁻¹; UV-VIS (AcOEt) λ_{max} /nm (ϵ /dm³ mol⁻¹ cm⁻¹) 300 (6.0 × 10⁴). Anal. calc. for C₃₅H₁₈F₁₈N₂O₄S₂Zn: C, 41.95; H, 1.81; N, 2.80. Found: C, 42.13; H, 1.82; N, 2.95%. Corresponding closed-ring form isomer **1b**-Zn(hfac)₂: ¹H NMR (400 MHz, DMSO-*d*₆) δ 2.14 (s, 6H), 5.55 (s, 2H), 7.30 (s, 2H), 7.72 (d, *J* 6 Hz, 4H), 8.70 (br s, 4H).