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Novel photoswitching dithienylethenes with ferrocene units

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Two novel dithienylethenes with ferrocene units were synthesized by Wittig reaction. The structure of 2a has been established by X-ray diffraction studies. They could reversibly interconvert between two thermally stable forms, an open and a closed one, using light of different wavelengths as triggers.

KEYWORDS: photochromism; dithienylethene; ferrocene

INTRODUCTION

Photochromic compounds have attracted increasing attention because of the potential application to optical memory media and switching devices.[1–6] The two isomers of photochromic compounds differ from one another not only in their absorption spectra but also in various physical and chemical properties, such as refractive index,[7–10] dielectric constant,[11] luminescene,[12–19] optical rotation,[20–22] electronic conductivity,[23–25] oxidation–reduction potential and geometrical structure.[26,27]

Among a number of photochromic compounds, dithienylethenes are the most promising candidates for practical applications, owing to (1) their high efficiency of reversible conversion of ring-open and ring-closed isomers upon irradiation with appropriate wavelengths of light (Scheme 1 shows the photochromic reaction by photoirradiation), (2) sufficient thermal stability of both the open and closed forms, (3) very high resistance to photofatigue and (4) large differences in ability of the transmission of electronic interactions (electronic π-conjugated ion is extended over the closed form).[28–32] In addition, many interesting characters can be introduced to the functional sites labeled R in Scheme 1.[33]

Dithienylethenes with transition metal fragments probably provide new advanced molecular functions and show novel behaviors which are not observed for organic dithienylethenes and their derivatives: MLCT (metal-to-ligand change transfer) photoisomerization, metal–metal electron transfer reaction, and isomerization-promoted photoluminescence switching.[19,34] It is possible that photoinduced cyclization of the switching unit can be promoted via an efficient energy transfer from the excited metal center to the dithienylethene switch, resulting in a very high photocyclization quantum yield and thermal stability.[35] Although there are a few reports on the synthesis of metal complexes of photochromic diarylethenes,[36–58] to our knowledge, no dithienylethenes with ferrocene units have been reported. In the present study, two novel photoswitching dithienylethenes with ferrocene units have been synthesized by Wittig reaction. Their characterization, photoisomerization and other properties will be discussed here.

RESULT AND DISCUSSION

Photochromic dithienylethenes (**1a** and **2a**) with ferrocene units were prepared by Wittig reaction, as shown in Scheme 2. Compound **3** was made from cheaper starting materials according to the previous procedure.[59,60] A THF solution of **3** (1.0 equiv.) was added to Wittig reagent **4** (2.0 equiv.) in the presence of sodium bis (trimethylsilyl)amide

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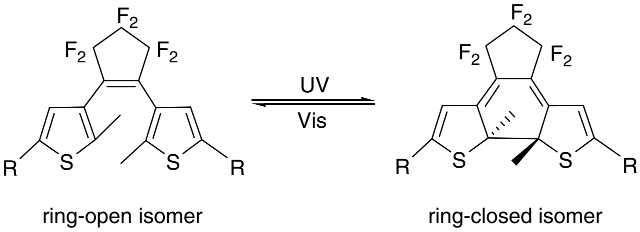


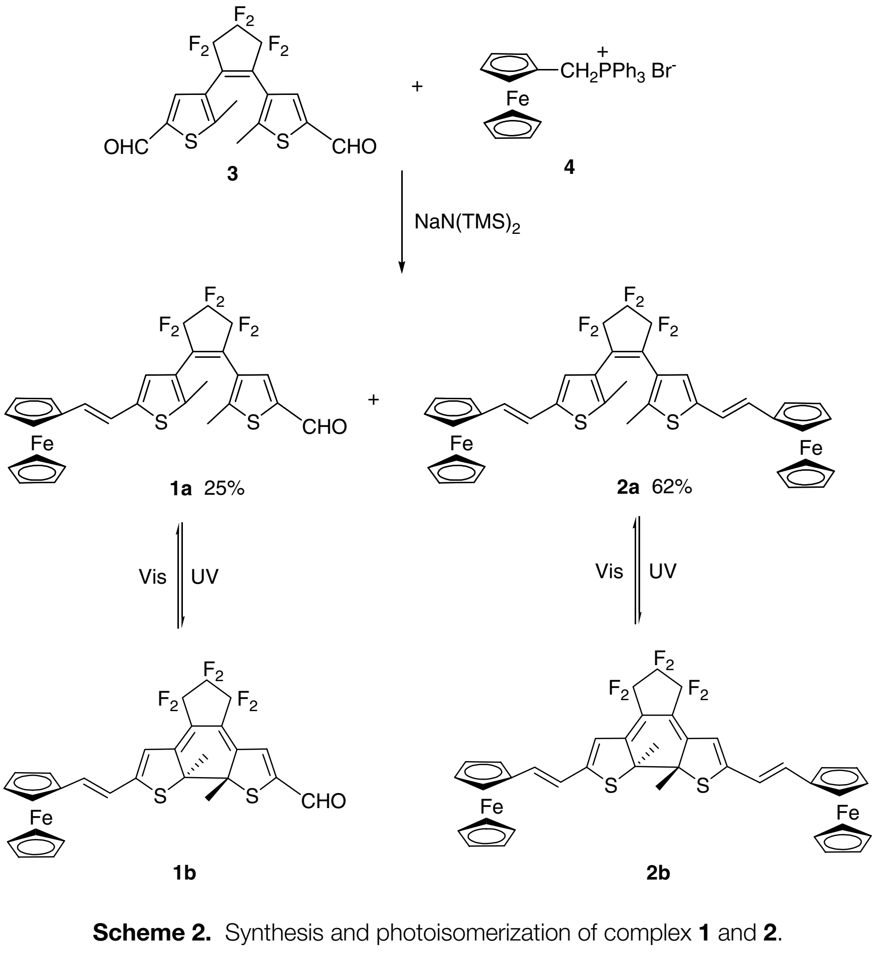
Scheme 1. Reversible photocyclizatin reactions of dithienylethene.

base. The reaction mixture was stirred for 30 min at room temperature and quenched with water, resulting in formation of monometallic complex **1a** in 25% yield and bimetallic complex **2a** in 62% yield, respectively. The two products could be purified further by column chromatography. The structures of the two compounds were confirmed by ^{1}H NMR and X-ray. The ^{1}H NMR spectra of the open form **2a** showed clearly that this compound has C_2 symmetry.

The single crystals of **2a** were grown from a dichloromethane solution layered with hexane in the absence of UV light. Figure 1 shows ORTEP drawings of the ring-open isomer **2a**; the X-ray data are listed in Table 2, while the selected bond angles and distances are given in Table 3. The dihedral angle between thiophene ring and perfluorocyclopentene ring is 52.5(1)°, suggesting the presence of some π-conjugation between the thienyl ring and the ethene unit.[61] The distance between the two reactive carbons C16–C16a is 3.864(5) Å, which is short enough, less than 4.2 Å, for the reaction to take place.[62,63] The bond distance of C11–C12 is 1.323(5) Å. The data clearly indicate that the C11–C12 bond is a double bond, being significantly shorter than the carbon–carbon single bond.[64]

Figure 2(a) shows the absorption spectra change of **1a** induced by photoirradiation in CH_2Cl_2. Upon irradiation with UV light, a new absorption band due to the closed form **1b** appeared at 460 nm. Upon irradiation with light of a wavelength longer than 450 nm, the closed form **1b** reverted to the opened form **1a**.

As observed for **1a**, complex **2a** also underwent photochromism upon irradiation with UV and visible light in CH_2Cl_2 solution. Figure 2(b) shows the spectral change of complex **2a** in CH_2Cl_2. In the photostationary state, the opened form **2a** converted to the closed form **2b** upon irradiation with UV light with an absorption maximum at 458 nm. Upon irradiation with light of a wavelength longer than 450 nm, the closed form **2b** reverted to the opened form **2a**. In



Scheme 2. Synthesis and photoisomerization of complex **1** and **2**.

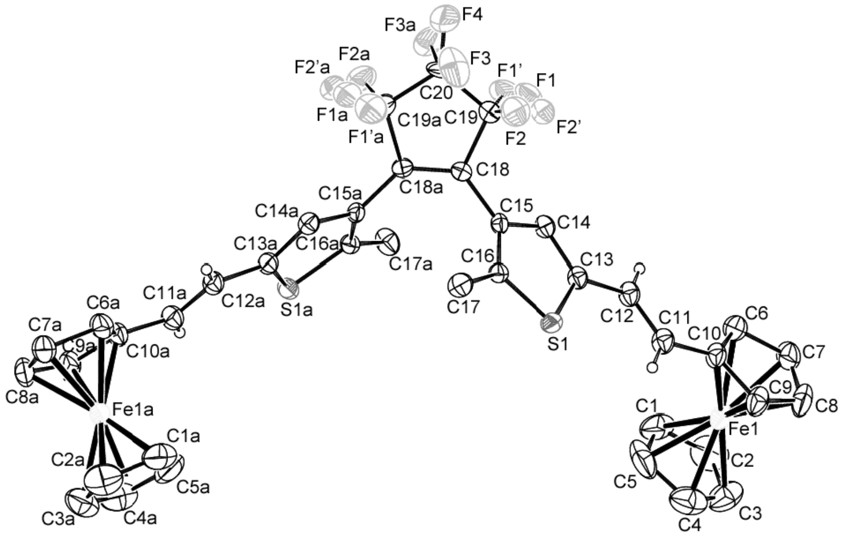


Figure 1. ORTEP drawing of molecular structure of the open-ring isomer **2a**.

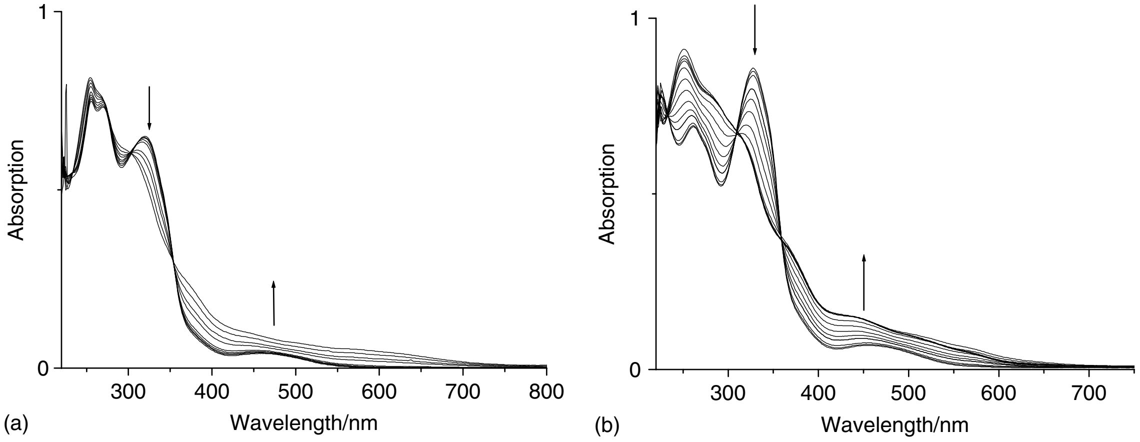


Figure 2. (a) UV–vis absorption spectra change of complex **1** (5.0×10^{-5} mol l^{-1}) in CH_2Cl_2 upon irradiation with UV light at 0, 30, 60, 90, 120 s, etc. (b) UV–vis absorption spectra change of complex **2** (5.0×10^{-5} mol l^{-1}) in CH_2Cl_2 upon irradiation with UV light at 0, 20, 40, 60, 80 s, etc.

addition, a well-defined isosbestic point was observed at 309 and 360 nm in Fig. 2(a) and 312 and 355 nm in Fig. 2(b), which indicated that complexes **1** and **2** were cleanly converted to a photocyclized product, respectively.

The thermal stability of closed forms is an indispensable property for the application to optical memory media. The closed form of dithienylethene derivatives having thiophene groups is thermally stable.[3] Irie and co-worker predicted by theoretical calculation that thermal stability is dependent on the aromatic stabilization energy of the aryl group.[65] It is of interest to examine the thermal stability of our ferrocenyl complexes having a dithienylethene group. Preliminary investigations show that the thermal stability of closed-ring isomer **2b** is very good in toluene at 80 °C, and the absorption intensity remained constant even after 80 h.

CONCLUSION

Novel photoswitching dithienylethenes with ferrocene unit were synthesized by Wittig reaction and their structures were identified. They show an excellent thermal stability and photochromism properties. Further research efforts will focus on illustrating that the steric and electronic difference between the two interconverting isomers can be harnessed in practical applications. In addition, we will illustrate the effect of conjugating olefin and transition metal to the photochromic properties utilizing our previous work about conjugating olefin metallic complexes.[66–70] Because of the difference of the extent of the π-conjugated and transition metal atoms, it will have an important effect on the properties of the resulting photochromic complexes. These results will be reported in due course.

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EXPERIMENTAL

General procedures and starting materials

The manipulations were carried out at room temperature under an inert atmosphere of argon using standard Schlenk techniques. All solvents were dried using standard procedure. The starting material **3**[59,60] and Wittig reagent **4**[70] were prepared according to literature. All other chemicals were obtained from commercial sources. ^{1}H NMR (400 MHz) and ^{13}C NMR (100.6 MHz) spectra were collected on a Varian Mercury Plus 400 spectrometer (400 MHz). UV–vis spectra were recorded with Shimadzu UV-2550 spectrometer. Photoisomerization measurements were carried out under a PHK 125-W mercury lamp as an irradiation source. The ring-opening reactions were carried out using the light of a 200 W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light.

1-[5-(2-ferrocenyl-1-ethylene-yl)-2-methylthiophene-3-yl]-2(5-formyl-2-methylthiophene-3-yl) perfluorocyclopentene (1a) and 1,2-bis[5-(2-ferrocenyl-1-ethylene-yl) -2-methylthiophene-3-yl] perfluorocyclopentene (2a)

To a slurry of **4** (1.08 g, 2.0 mmol) in THF (30 ml) was added sodium bis(trimethylsilyl)amide (1.0 ml, 2.0 mmol, 2 M solution in THF) under argon atmosphere. The reaction mixture was stirred at room temperature for 30 min. Then a solution of **3** (0.44g, 1.0 mmol) in THF (30 ml) was added slowly by syringe and the resulting mixture was stirred for an additional 30 min. Water (10 ml) was added to quench the reaction and the layers were separated. The aqueous layers was extracted with diethyl ether (3 × 15 ml). The combined organic layers were washed with saturated brine and dried over magnesium sulfate anhydrous, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography (silica, eluent: hexane–CH_2Cl_2 1 : 3) to give a pale-yellow solid **1a** in 25% yield and an orange-red solid **2a** in 62% yield. Complex **1a**: ^{1}H NMR (400M Hz, $CDCl_3$): δ 1.87 (s, CH_3), 2.05 (s, 3H, CH_3), 4.15 (s, 5H, Cp), 4.30 (s, 2H, C_5H_4), 4.41 (s, 2H, C_5H_4), 6.68 [d, J(HH) = 16.0 Hz, 1H, thienyl-CH], 6.86 [d, J(HH) = 16.0 Hz, 1H, CH], 6.99 (s, 1H, thienyl-H), 7.32 (s, 1H, thienyl-H), 9.86 (s, 1H, CHO). Anal. calcd for $C_{28}H_{20}F_6FeOS_2$: C, 55.46; H, 3.32; S, 10.57. Found: C, 55.71; H, 3.45; S, 10.31. Complex **2a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.91 (s, 6H, CH_3), 4.15 (s, 10H, Cp), 4.29 (s, 4H, C_5H_4), 4.41 (s, 4H, C_5H_4), 6.59 [d, J(HH) = 16.0 Hz, 2H, thienyl-CH], 6.69 [d, J(HH) = 16.0 Hz, 2H, CH], 6.89 (s, 2H, thienyl-H). Anal. calcd for $C_{39}H_{30}F_6Fe_2S_2$: C, 59.41; H, 3.84; S, 8.13. Found: C, 59.75; H, 4.01; S, 7.86.

X-ray crystal structure analysis

Single crystal suitable for X-ray diffraction was obtained by slow diffusion of hexane into a solution of **2a** in CH_2Cl_2 at room temperature. A crystal was mounted on a glass fiber, and the diffraction intensity data were collected on a Bruker CCD 4 K diffractometer with graphite-monochromatized Mo K_α radiation ($\lambda = 0.71073$ Å). Lattice determination and data collection were carried out using SMART version 5.625 software. Data reduction and absorption corrections were performed using SAINT version 6.45 and SADABS version 2.03. Structure solution and refinement were performed using the SHELXTL version 6.14 software package. The space group C_2/c was determined based on the systematic absences and intensity statistics. All non-hydrogen atoms were refined anisotropic. All hydrogen atoms were placed in ideal positions and refined as riding atoms with relative isotropic displacement parameters. Further crystallographic details were summarized in Table 1, and selected bond distances and angles are given in Table 2.

Table 1. Crystal date and structure refinement for complex **2a**

Compound	**2a**
Empirical formula	$C_{39}H_{30}F_6Fe_2S_2$
Molecular weight	788.45
Wavelength (Å)	0.71073
Temperature (K)	292(2)
Crystal system	Monoclinic
Space group	C2/c
a (Å)	36.795(3)
b (Å)	8.0365(9)
c (Å)	12.2082(9)
ß (deg)	107.9680(10)
V (Å^3)	3433.9(4)
Z	4
D_{cala}(Mg m^{-3})	1.525
μ (mm^{-1})	1.027
F(000)	1608
θ(min − max)(deg)	1.16–26.99
Refections collected	18 771
Independent reflection	3746
R_{int}	0.1042
Crystal size (mm)	0.30 × 0.20 × 0.06
Weighting Scheme	$w = 1/[\sigma^2(Fo^2) + (0.0775P)^2 + 0.0000P]$ where $P = (Fo^2 + 2Fc^2)/3$
R indices ($I > 2\sigma$)	$R_1 = 0.0589, \omega R_2 = 0.1319$
R indices (all data)	$R_1 = 0.0900, \omega R_2 = 0.1532$
Goodness-of-fit on F^2	0.974

Table 2. Selected bond lengths (Å) and angles (deg) of compound **2a**

C(10)–C(11)	1.460(5)	C(12)–C(11)–C(10)	125.3(4)
C(11)–C(12)	1.323(5)	C(11)–C(12)–C(13)	126.4(4)
C(12)–C(13)	1.455(5)	C(14)–C(13)–C(12)	128.5(4)
C(15)–C(18)	1.476(5)	C(12)–C(13)–S(1)	121.5(3)
C(16)–C(17)	1.497(5)	C(15)–C(16)–C(17)	129.0(3)
C(16)–S(1)	1.712(4)	C(14)–C(15)–C(18)	124.2(3)
C(20)–F(3)	1.517(7)	F(4)–C(20)–F(3)	76.0(4)

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