

Alkali Metal Ion Effect on the Photochromism of 1,2-Bis(2,4-dimethylthien-3-yl)-perfluorocyclopentene Having Benzo-15-Crown-5 Moieties

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Abstract: The photocyclization quantum yield of 1,2-bis(2,4-dimethylthien-3-yl)perfluorocyclopentene having two benzo-15-crown-5 ethers was decreased by the addition of potassium and rubidium perchlorates, and the decrease is ascribed to the increase of the photoinactive parallel conformation ratio by the intramolecular interaction of the two crown ether moieties with a metal ion. © 1998 Elsevier Science Ltd. All rights reserved.

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Control of the photochromic reactions by external stimuli has been studied as ‘gated photochromism’,^[1–3] which enables us to perform non-destructive read-out of photomemory.

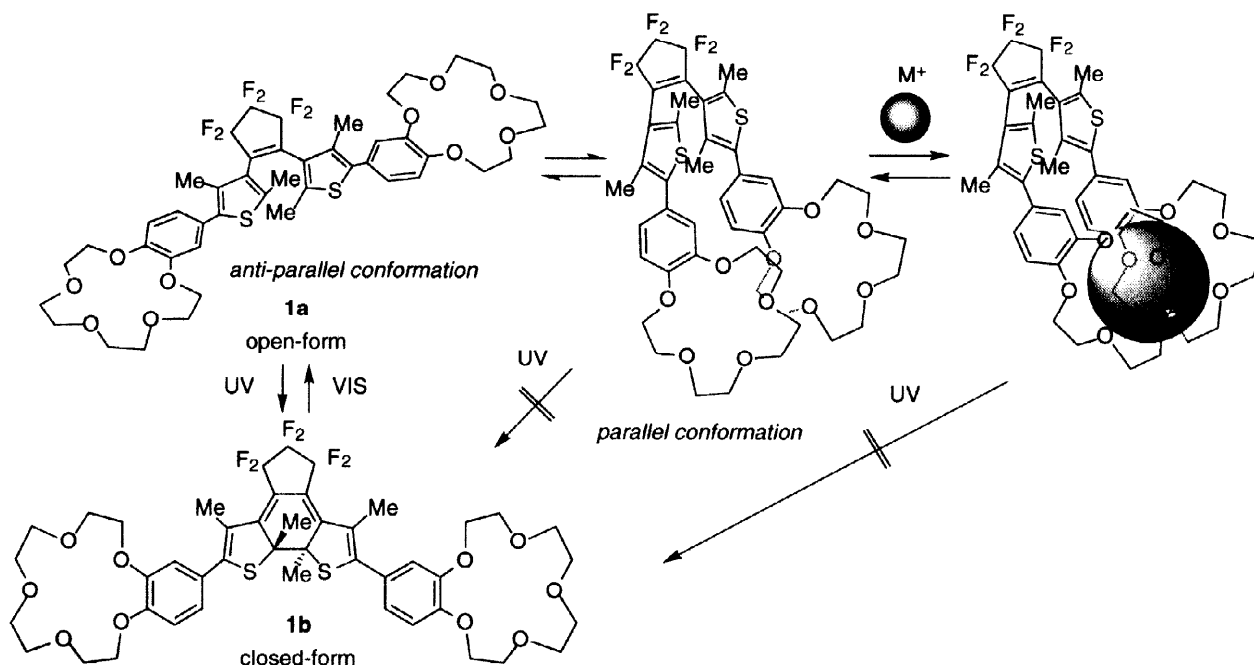


Fig. 1. Photochromic reaction of dithienylethene having two crown ethers **1**.

In the various photochromic molecules, dithienylethenes indicate the reversible photocyclization of hexatriene structures as shown in Fig. 1.^[4] The open-ring form has two conformations, parallel and anti-parallel conformations. The anti-parallel conformation undergoes the photocyclization reaction, while the parallel conformation is photochemically inactive. Therefore, the control of the ratio of the two conformations is useful to change the photocyclization quantum yield. The idea was realized in bis(benzothieryl)ethene derivatives by using intramolecular hydrogen bonds or a dithiol bond.^[2]

It is well known that crown ether compounds form a 2:1 sandwich-type complex with an alkali metal ion which is larger than the crown ether cavity.^[5] Dithienylethenes having two crown ether moieties are expected to capture large alkali metal ions by the intramolecular cooperative interaction of the two crown ethers like tweezers.^[6] The resulting conformations of the diarylethenes are in parallel.^[2,4] The large alkali metal ion acts as a lock of the photocyclization reaction. The dithienylethene having two benzo-15-crown-5 ethers **1a**^[7] was synthesized by the reaction of 4-(3-lithio-2,4-dimethylthiophen-5-yl)benzo-15-crown-5 ether with perfluorocyclopentene. Upon irradiation with 313 nm light the initial colorless acetonitrile solution containing **1a** ($[1a] = 2.0 \times 10^{-5} \text{ mol dm}^{-3}$) turned blue and a new absorption band appeared at 597 and 370 nm, which indicates the formation of **1b**. Upon visible (>480 nm) irradiation the spectrum returned to the initial state (Fig. 2).

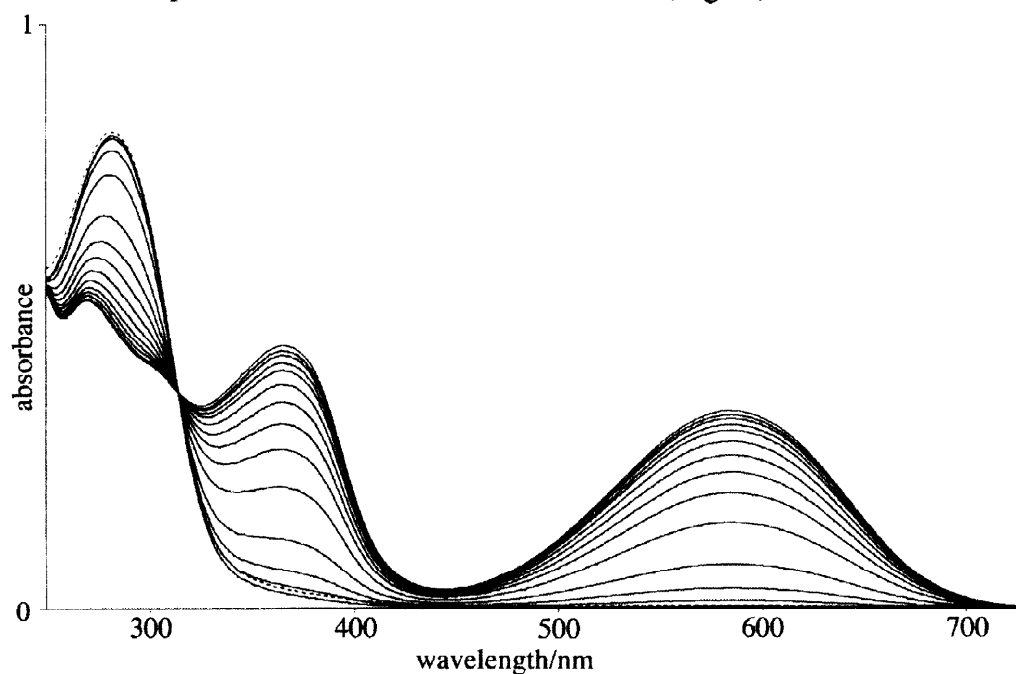


Fig. 2. Absorption spectral change of **1** in CH_3CN ($2.0 \times 10^{-5} \text{ mol dm}^{-3}$) irradiated with 313 nm light.

Figure 3 shows the ^1H NMR spectral change of **1a** in the presence of large excess of sodium (b), potassium (c) and rubidium picrates (MPic) (d) in $\text{CDCl}_3\text{-CD}_3\text{CN}$ (3:1) at 20°C ($[1a] = 2.0 \times 10^{-3} \text{ mol dm}^{-3}$, 600 MHz). In the absence of the metal ions (Fig. 3(a)), the ratio of anti-parallel / parallel conformations is 1:1, which was determined by integrating the methyl protons which appear between δ 2.0 and 2.2. No appreciable change is observed in the ratio of

the two conformations by the addition of NaPic (Fig. 3(b)). On the other hand, the methyl protons at 4-position of the thiophene ring in the parallel conformation are shifted to higher magnetic field (1.61 ppm) by the addition of RbPic as shown in Fig 3(d). The EXSY spectrum at 20°C indicated that the methyl protons in Fig. 3 (circles and triangles) exchanges each other. The shift to higher magnetic fields of the methyl protons (from 2.05 to 1.61 ppm) and aromatic protons (from 6.87 to 6.25 ppm) are due to proximity of each aromatic ring in the sandwich-type parallel conformation. By the addition of RbPic, the parallel conformation becomes dominant and the ratio of anti-parallel / parallel conformations changes from 1:1 to 1:6. When KPic (Fig. 3(c)) was added, the spectrum was broadened and the aromatic and methyl protons shifted to higher magnetic field. This indicates that the sandwich-type complex does not form by the addition of small Na^+ , while it forms by the addition of K^+ and Rb^+ .⁵

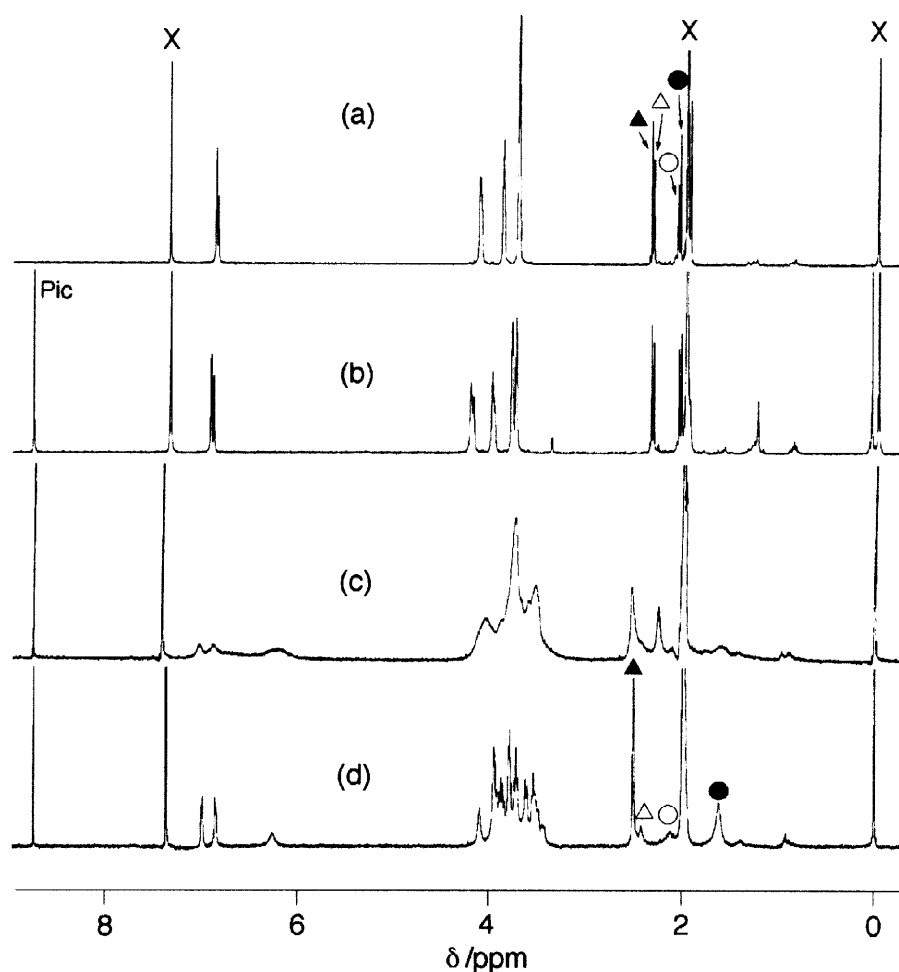


Fig. 3. ^1H NMR spectra of **1a** ($2.0 \times 10^{-3} \text{ mol dm}^{-3}$, 600 MHz) in $\text{CDCl}_3\text{-CD}_3\text{CN}$ (3:1) at 20 °C; (a) in the absence of metal and in the presence of (b) NaPic, (c) KPic and (d) RbPic ($5 \times 10^{-3} \text{ mol dm}^{-3}$). The methyl protons at 4-position and 2-position of the thiophene rings are denoted as circles and triangles, and those of the parallel and anti-parallel conformations are denoted in black and white, respectively.

The quantum yields for the photocyclization reaction of **1a** in $\text{CH}_3\text{CN-CHCl}_3$ (1:4) in the presence of alkali metal perchlorates are shown in Table 1. The absorbance of **1a** in

$\text{CH}_3\text{CN}-\text{CHCl}_3$ at 313 nm did not change by the addition of KClO_4 , while the absorption maximum of **1a** was shifted from 284 nm to 287 nm.

Table I. Photocyclization Quantum Yields of **1a** in the Presence of Alkali Metal Perchlorates^a

System	1a	1a + NaClO_4	1a + KClO_4	1a + KClO_4 +18C6 ^b	1a + RbClO_4
Quantum yield	0.21	0.17	0.02	0.17	0.02

^a **1a** (1.0×10^{-5} mol dm^{-3}) and MClO_4 (ca 5×10^{-3} mol dm^{-3}) in $\text{CH}_3\text{CN}-\text{CHCl}_3$ (1:4). Irradiated with 313 nm. ^b In the presence of both KClO_4 and 18-crown-6 ether (5.0×10^{-2} mol dm^{-3}).

Although no change in the photocyclization quantum yield was observed by addition of sodium perchlorate, the quantum yield dramatically decreased in the presence of potassium and rubidium perchlorate. The quantum yield changes agree with the result of NMR experiments. Addition of 18-crown-6, which forms a stable complex with K^+ , to a mixture of **1a** and KClO_4 restored the cyclization quantum yield. This result confirmed that the decrease in the quantum yield by the addition of KClO_4 is due to the formation of a complex with KClO_4 . Additionally, the positive FAB mass spectrum (3-nitrobenzylalcohol matrix) of a mixture of **1a** and RbPic showed a 1:1 complex ($[\text{1a} \cdot \text{Rb}^+]$) peak at m/z 1013 and no peak corresponding to the 1:2 complex was observed. A small alkali metal ion like sodium is captured by a single crown ether moiety. Therefore, the addition of a small metal ion does not affect the ratio of parallel / anti-parallel conformations and the cyclization quantum yield does not change dramatically. On the other hand, large alkali metal ions like potassium and rubidium form the photoinactive parallel conformation and decrease the quantum yield of photocyclization.

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- [7] Synthesis of **1a** and two-phase extraction of alkali metal picrates with **1a** and **1b** will be published elsewhere; **1a** (100% open form): colorless prisms (hexane). mp 137.0-138.0 °C; δ_{H} (200 MHz, 20 °C, CDCl_3) 2.05 (s, 3H), 2.08 (s, 3H), 2.33 (s, 3H), 2.35 (s, 3H), 3.76 (s, 16H), 3.89-3.92 (m, 8H), 4.12-4.16 (m, 8H), 6.86-6.87 (m, 6H); Calc. for $\text{C}_{45}\text{H}_{50}\text{F}_8\text{O}_{10}\text{S}_2$: C, 58.18; H, 5.42. Found: C, 58.38; H, 5.49 %; MS (FAB+) m/z = 928 [M^+].