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Radiation-Induced Coloration of Photochromic Dithienylethene Derivatives

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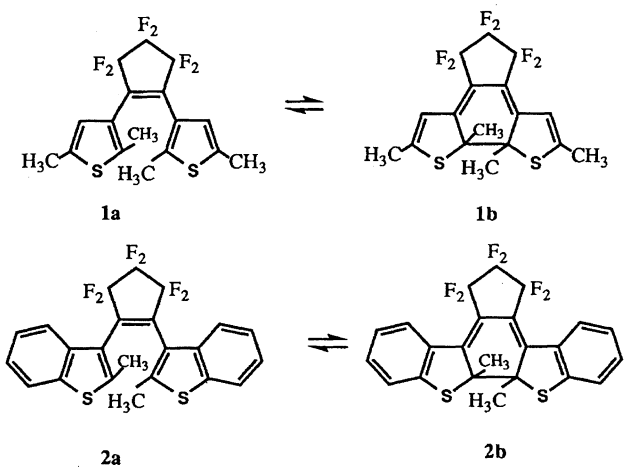
The radiation sensitivity of photochromic 1,2-dithienylethenes was studied with the aim to develop a new reusable color dosimeter. Upon γ-irradiation, crystalline colorless 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene turned red, and the absorption intensity increased linearly with the absorbed dose. The red color was bleached by visible-light irradiation and the crystal could be reused. On the other hand, crystalline 1,2-bis(2-methyl-1-benzothiophen-3-yl)perfluorocyclopentene did not show any radiation-induced coloration. The radiation sensitivity in solution was also examined to understand the possible applications to solution and film color dosimeters. Although radiation-induced coloration of the above two compounds was observed in benzene, no color change was detected in hexane, 2-methyltetrahydrofuran and *n*-butyl chloride. Excitation energy migration and transfer mechanism is considered to play a role in the coloration process in benzene.

Photochromism has attracted considerable attention because of its potential ability for applications to molecular devices, such as optical memories and switches.[1—3] Photochromic compounds, in general, undergo thermally reversible reactions. The photogenerated colored forms are thermally unstable and return to the initial colorless forms in the dark. Recently, a new type of thermally irreversible photochromic compounds has been developed.[4—8] The photogenerated colored forms are stable and never return to the colorless forms in the dark, while they return to the initial states by photoirradiation. Among the thermal irreversible photochromic compounds, diarylethenes with heterocyclic aryl groups are most promising. They undergo thermally irreversible and fatigue resistant photochromic reactions, even in the crystalline phase.[7,8]

Various types of color dosimeters are conveniently used for estimating absorbed dose in the radiation sterilization of biomedical materials.[9] A typical dosimeter is a vinyl chloride-vinyl acetate copolymer film containing 4-(dimethylamino)azobenzene.[10] Upon γ-irradiation the yellow film turns red. The red color is due to the reaction of the 4-(dimethylamino)azobenzene with acid produced by γ-irradiation. The drawback of the dosimeter is low sensitivity. The detectable dose is higher than 10 kGy. It is desired to develop a highly sensitive color dosimeter.

In the present study we attempted to develop a new highly sensitive dosimeter using photochromic diarylethenes. The colored forms of the diarylethenes with heterocyclic aryl groups, such as furan or thiophene rings, are thermally stable. Therefore, we can apply them to radiation-sensitive color dosimeters if they undergo coloration by γ-irradiation. We have examined the radiation sensitivity of two dithienylethenes, 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**1**) and bis(2-methyl-1-benzothiophen-3-yl)-perfluorocyclopentene (**2**), in solution as well as in crystal in order to determine the feasibility (Scheme 1). The photochromic dosimeter is advantageous over the present chemical dosimeters regarding sensitivity and the reusable characteristic.



Scheme 1.

CREST, Japan Science and Technology Corporation.

Experimental

Details of the synthetic procedures of dithienylethene derivatives (**1**) and (**2**) have been reported elsewhere.[5,6] The absorption spectral changes of single crystals were measured with a microscopic spectrophotometer (Nikon Optiphot 2-pol combined with Hamamatsu PMA-11). The thickness of the single crystal was measured by a micrometer. Irradiation was carried out with ^{60}Co γ-rays. The solvents used were spectrograde. All samples in solution were prepared using the freeze-thaw cycle method. Absorption spectra in solution were measured with an absorption spectrophotometer (Shimadzu UV-3100PC).

The colored product generated by γ-irradiation was isolated using a HPLC (Hitachi L-6250 HPLC system, silica-gel column, hexane as the eluent). ^{1}H NMR spectra were recorded on a Varian Gemini 200 spectrometer (200 MHz).

Results and Discussion

1. Coloration in Crystals. Figure 1 shows the absorption spectrum of a single crystal of 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene **1** γ-irradiated with a dose of 10 kGy. Before γ-irradiation, the crystal was colorless, and no absorption was detected in the 400—800 nm region. Upon γ-irradiation, the crystal turned red and the absorption maximum was observed at 535 nm. The color change suggests that γ-irradiation induced a cyclization reaction of the open-ring form **1a** to the closed-ring form **1b**. The reaction was confirmed by measuring the absorption spectrum in hexane. The red-color crystal was dissolved in hexane and the spectrum was compared with that of a hexane solution containing photogenerated **1b**. Both spectra, the absorption maximum (505 nm) and the spectral shape, were identical. This result indicates that the red color of the crystal is due to the closed-ring form **1b**. Upon irradiation with visible light ($\lambda > 450$ nm light) the color disappeared. The coloration/decoloration cycles by γ-irradiation/visible light irradiation could be repeated many times (more than 10 times) without destruction of the crystal shape. γ-Irradiation causes the cyclization reaction of **1a** to **1b** and visible irradiation converts **1b** to **1a**.

A single crystal of 1,2-bis(2-methyl-1-benzothiophen-3-yl) perfluorocyclopentene **2a** was also exposed to γ-irradiation. In this crystal, no color change was observed.

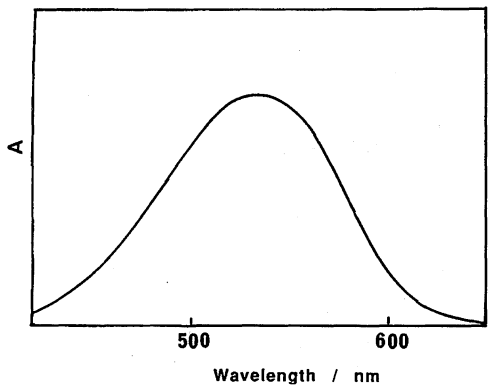


Fig. 1. Absorption spectrum of a single crystal of **1** γ-irradiated with a dose of 10 kGy. Before γ-irradiation the crystal had no absorption longer than 400 nm.

In order to obtain information concerning the dose dependence, the absorption-intensity change of polycrystalline **1** upon γ-irradiation was measured. The most convenient way to measure the color change of the polycrystalline compound is to measure the absorption spectrum changes of solutions containing dissolved γ-irradiated crystals. Figure 2 shows the dose-response curve of polycrystalline **1**. Polycrystalline **1** (0.5 mg) was γ-irradiated, and dissolved into hexane (4 ml). The dose rate was 5 kGy h^{-1}. The optical density linearly increased with the irradiation time. A linear dependence is essential for applications to dosimeters. The detectable minimum color change (Abs. = 0.001) corresponds to an absorbed dose of 10 kGy. When the amount of polycrystalline **1** is increased to 5 mg, the minimum detectable dose decreases to 1 kGy.

The dose dependence was also measured for a single crystal, itself. The absorption spectra of the colored single crystal was directly measured by using a microscopic spectrophotometer. Figure 3 shows the dose dependence. The absorption intensity linearly increases with the irradiation time. The absorption intensity correlates with the crystal thickness. When the crystal thickness is large, a small dose can induce a color change. An optical density as large as 0.16 was detected for a crystal with a thickness of 1.75 mm irradiated at a dose of 7.5 kGy. A dose as small as 160 Gy can be easily detected (Abs. = 0.01) using a single crystal with

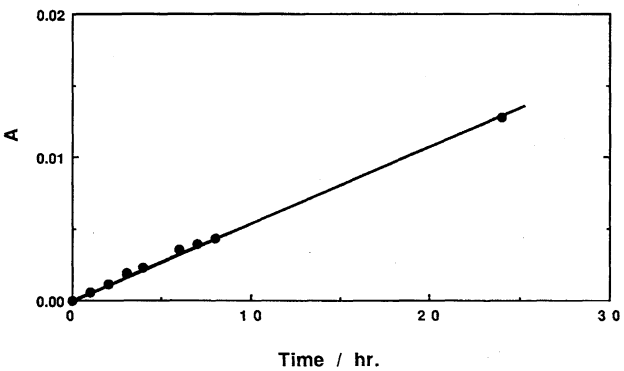


Fig. 2. Dose response curve of polycrystalline **1**. Dose rate was 5 kGy h^{-1}. 0.5 mg of polycrystalline **1** was γ-irradiated, and it was dissolved and diluted to 10 ml hexane.

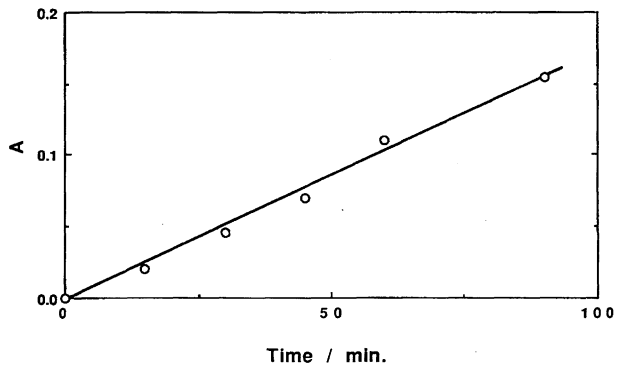


Fig. 3. Dose response curve of single crystal **1**. Dose rate was 5 kGy h^{-1}. The thickness of the single crystal was 1.75 mm.

a thickness of 5 mm. The sensitivity is 50-times higher than that of the ordinary color dosimeter.[10] The colored crystal could be reused after photobleaching. The dose dependence of the reused crystal was identical with the result of a fresh crystal as long as the total irradiation dose was less than 120 kGy.

Another important feature of the photochromic dosimeter is a linear dose dependence. The red-color absorption increased linearly up to 0.4, which corresponds to an irradiation dose of 19 kGy.

2. Coloration in Solutions. Although the crystalline photochromic material is useful as a sensitive dosimeter, the crystal can not be used for large-area detection. The development of a solution or film dosimeter is required. The radiation-induced coloration of the dithienylethenes was measured in various solvents at 20, 0, −78, and −196 °C to examine the radiation sensitivity in solution. Table 1 summarizes the results. A color change was not discerned in hexane, 2-methyltetrahydrofuran (MTHF) and *n*-butyl chloride (*n*-BuCl) solutions. It is well-known that solute radical anions and cations are dominantly produced in hexane, MTHF and *n*-BuCl solutions.[11] This result indicates that the contribution of ionic species to the coloration is negligible.

On the other hand, a benzene solution and solids containing **1** (5×10^{-5} mol dm^{-3}) turned red upon γ-irradiation at 20, 0, −78, and −196 °C. The energy transfer from γ-irradiated benzene to **1a** is considered to play an important role in coloration in a benzene solution. In benzene, the yield of the ionic species is low. At first, benzene was excited to electronically excited states by γ-irradiation, and the excited energy was migrated among benzene molecules and finally transferred to solute dithienylethene **1a**. The excited **1a** converted to the closed-ring form **1b**, which has a red color.

Figure 4 shows the absorption spectra of **1** in benzene (2×10^{-4} mol dm^{-3}) upon γ-irradiation at a total dose of 2 kGy. The irradiation was carried out at −78 °C and the spectrum was measured at room temperature. The broken curve is the spectrum before γ-irradiation. Upon γ-irradiation, a colorless benzene solution containing **1** turned to red, in which the absorption maximum was observed at 505 nm. The absorption maximum is the same as that of photogenerated **1b**, shown by dotted line in the figure. This result indicates

Table 1. Radiation Induced Coloration of **1** in Solutions and Solids

Solvent	Temperature	State	Coloration
Hexane	20 °C, 0 °C	Solution	No
Hexane	−196 °C	Solid	Yes
MTHF	−196 °C	Solid	No
n-BuCl	−196 °C	Solid	No
Benzene	20 °C	Solution	Yes
Benzene	0 °C	Solid	Yes
Benzene	−78 °C	Solid	Yes
Benzene	−196 °C	Solid	Yes

Total dose: 10 kGy, [C]: 5×10^{-5} mol dm^{-3}.

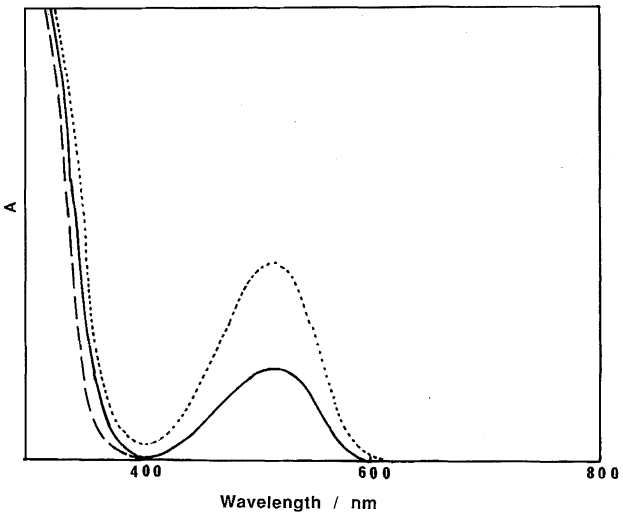


Fig. 4. Absorption spectra of benzene solution of **1** at −78 °C irradiated with a total dose of 1.5 kGy. (— —) before γ-irradiation. (—) after γ-irradiation. (····) after photoirradiation.

that the open-ring form converted to the closed-ring form in polycrystalline benzene by γ-irradiation. Energy migration and transfer take place even in the polycrystalline benzene. The formation of **1b** was also confirmed by a ^{1}H NMR measurement. In the ^{1}H NMR spectrum of the isolated colored product three peaks were observed at 2.03, 2.19, and 5.99 ppm, which are assigned to two methyl protons and thienyl protons of **1b**, respectively.[12]

Figure 5 shows the dose-response curve of **1** in benzene at −78 °C. The dose rate was 0.5 kGy h^{-1}. The absorption intensity linearly increased upon γ-irradiation. The linear relationship was found to hold above 2 kGy. The result in benzene solid suggests that polystyrene film containing **1** can possibly be used as a film dosimeter.

It is worthwhile noting that the red color appeared in polycrystalline hexane upon γ-irradiation at −196 °C. The color change indicates that excited energy produced by γ-irradiation in hexane can be transferred to **1a** in the polycrystalline phase, though such energy migration and transfer are negligible in solution. The photochromic compound is potentially useful to reveal energy transfer mechanisms in alkane crystals.

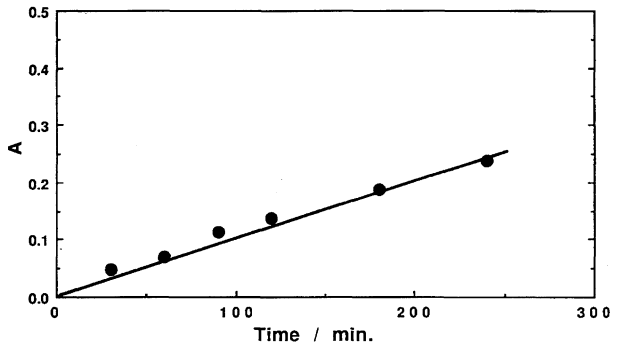


Fig. 5. Dose response curve of **1** in benzene at −78 °C. Dose rate was 0.5 kGy h^{-1}.

Table 2. Radiation Induced Coloration of **2** in Solutions and Solids

Solvent	Temperature	State	Coloration
Hexane	20 °C, 0 °C	Solution	No
Hexane	−196 °C	Solid	No
MTHF	−196 °C	Solid	No
n-BuCl	−196 °C	Solid	No
Benzene	20 °C	Solution	Yes
Benzene	0 °C	Solid	Yes
Benzene	−78 °C	Solid	Yes
Benzene	−196 °C	Solid	No

Total dose: 10 kGy, [C]: 5×10^{-5} mol dm^{-3}.

Although crystalline **2a** did not show any response to γ-irradiation, the benzene solutions and solids containing **2a** turned red upon γ-irradiation at 20, 0, and −78 °C, as shown in Table 2. Molecularly dispersed **2a** molecules in the benzene solution and solids are reactive enough to convert to the closed-ring forms **1b**, when they are excited by energy transfer from the excited benzene matrix. MTHF and *n*-BuCl solutions containing **2a** molecules did not show any discernible color change upon γ-irradiation. These results are similar to the behavior of **1a**. However, in contrast with **1a**, benzene and hexane solids containing **2a** did not show any color change at −196 °C upon γ-irradiation. At −196 °C, **2a** is considered to be phase-separated from benzene and hexane solids and polycrystalline **2a** phases are produced. Even if the excited energy is transferred from the matrices to the polycrystalline **2a**, **2a** molecules are inactive in the crystalline phase. This is the reason why **2a** did not undergo coloration by γ-irradiation at −196 °C.

Conclusion

Photochromic 1,2-bis (2,5-dimethyl-3-thienyl)perfluorocyclopentene was found to undergo coloration in the single crystalline phase as well as in a benzene solution upon γ-irradiation. No coloration was observed in hexane, MTHF and *n*-BuCl solutions. The absorption intensity due to the colored isomer linearly increased with the absorbed dose in both the crystal and the solution. The linear dependence indicates the possible application of the photochromic material to the sensitive reusable color dosimeters.

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