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Synthesis of Novel Thermally Irreversible Photochromic 1-Aryl-1,3-butadiene Derivatives

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A new thermally irreversible photochromic compound, 3,3,4,4,5,5-hexafluoro-1-(1-isopropylidene-1-phenylmethyl)-2-(2,4,5-trimethyl-3-thienyl)cyclopentene **3O**, was synthesized and its photochromic properties were examined. It showed thermally irreversible photochromism. While **3O** is colorless, it turned yellow (λ_{max} 445 nm) upon the irradiation of 313-nm light, caused by the generation of **3C** as the result of photochemical 6π-electrocyclization. It returned to the initial colorless state by 405-nm light irradiation. The coloration and decoloration quantum yields with 313-nm light were 0.43 and 0.14, respectively, and the decoloration quantum yield with 405-nm light was 0.16. The colored form **3C** in a PMMA film did not fade when stored at 80 °C for more than one month, and the fatigue resistivity in the PMMA film for iterative irradiation was excellent.

Although a number of families of thermally reversible photochromic compounds are known, few are known to be thermally irreversible photochromic compounds.[1–3] As far as we know, only fulgides,[4] diarylethenes,[5] and phenoxynaphthacenequinones[6] are known to be thermally irreversible to date. Thermally reversible photochromic compounds have already been applied to the auto-regulator of sunlight as ophthalmic lenses. On the other hand, thermally irreversible photochromic compounds have long been said to be potential candidates of materials for rewritable optical recording media, though they have not been realized. It is therefore invaluable to develop new thermally irreversible photochromic compounds.

Fulgides and diarylethenes undergo the 6π-electrocyclization. When fulgides have fully substituted carbon atoms at both ends of the hexatriene moiety[7] and diarylethenes have aromatic rings with rather low aromaticity,[8] they may show a thermally irreversible photochromism. With these precedents in mind, we designed a 1-aryl-1,3-butadiene system **A** (Chart 1) as a part of our project to develop new thermally irreversible photochromic compounds. The terminal aryl group and the butadiene moiety consist of a hexatriene system, and the additional aryl group on C-3 will extend the conjugation after electrocyclization.

In a preceding paper,[9] we reported on a new thermally reversible photochromic compound. We show here new structurally closely related, but thermally irreversible photochromic compounds.

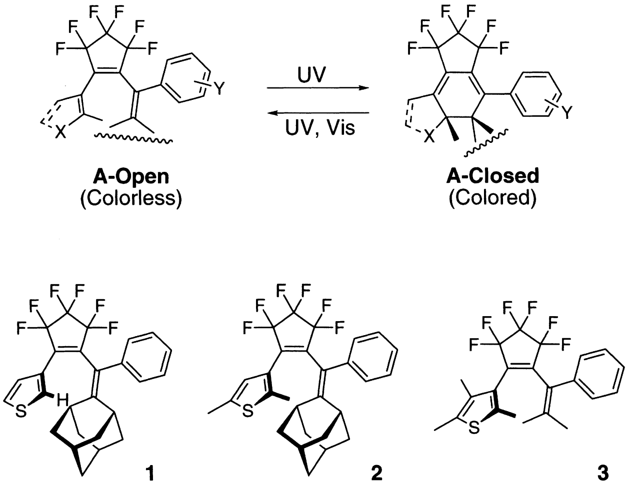


Chart 1.

Results and Discussion

Design of the Molecules. In a preceding paper, we showed that the 6π-electrocyclization of **1** followed by the thermal sigmatropic rearrangement of the hydrogen on the ring-closing carbon atom gave a thermally reversible photochromic compound.[9] If the rearranging hydrogen atom would be an alkyl substituent, a sigmatropic rearrangement would hardly occur, and it would give a thermally irreversible photochromic compound.

Consequently, the structure of the novel thermally irreversible photochromic compound to be prepared is depicted as **2**.

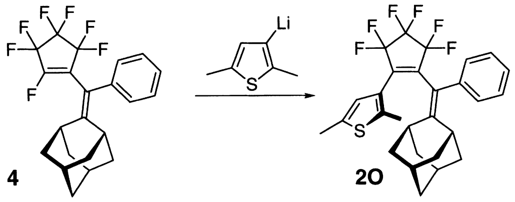
Later, some modifications were made on **2** to afford the photochemical fatigue resistivity. As shown in **3**, the thiophene group was fully methylated, and the adamantylidene group was replaced by a sterically less-demanding isopropylidene group.

Synthesis of 2. The synthesis of **2** was carried out as shown in Scheme 1. The synthesis of **4** was described in a preceding paper.[9] The reaction of 3-lithio-2,5-dimethylthiophene, generated from 3-bromo-2,5-dimethylthiophene and butyllithium, with **4** afforded **2** in 28% yield

Photoreaction of 2. When **2O** in toluene was irradiated with 313-nm light, the color of the solution turned yellow, and a new absorption band in the visible light region appeared on the UV-vis spectroscopy. The absorption maximum was 450 nm. It was attributed to the generation of the colored form **2C**. The color was retained when the colored solution was kept in the dark.

When a PMMA film doped with **2O** was irradiated with 313 nm light, the colored species also appeared. In order to assess the thermal stability of the colored form, the film was kept at 80 °C under an atmospheric environment in the dark. The absorption band showed almost no change after 30 days. Thus, **2** proved to be thermally irreversible.

However, when the irradiation of 313-nm light to the toluene solution of **2** was continued for a prolonged time, the new band in the visible region began to diminish. As can be seen in Fig. 1, the absorption in the visible region increased for 18 minutes of irradiation, and then turned to decrease. Apparently a photochemical decomposition of the compound occurred.



Scheme 1. Synthesis of **2O**.

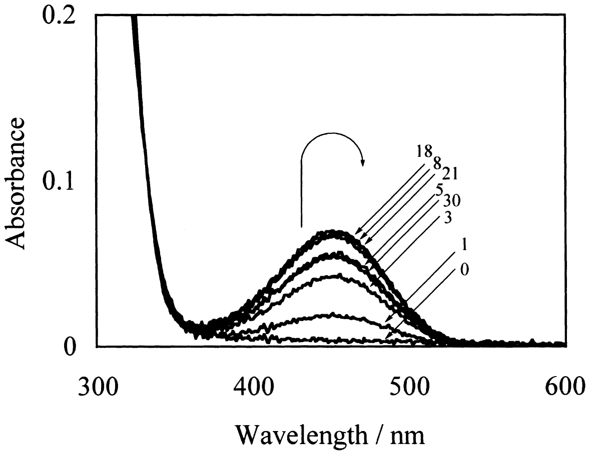
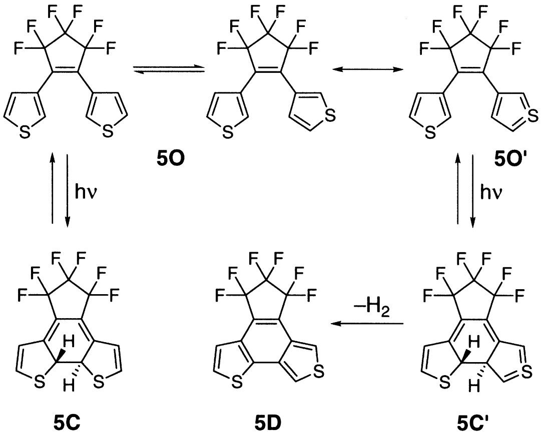
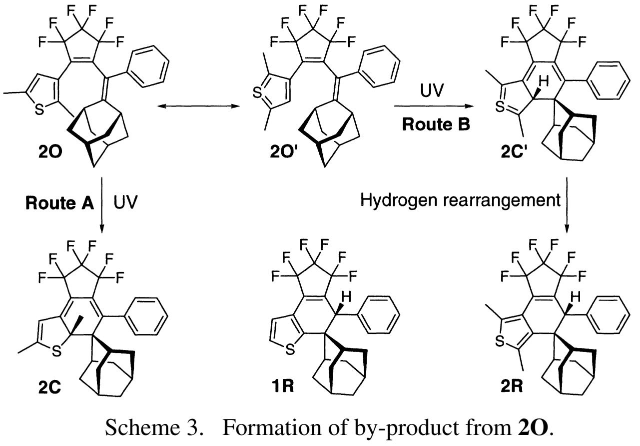


Fig. 1. Absorption spectral change of **2** during 313-nm light irradiation in toluene. Irradiation time/min; 0, 1, 3, 5, 8, 18 (largest absorbance at 450 nm), 21, 30.



Scheme 2. Formation of by-product from **5O**.

Recently, Irie et al. reported on the formation of photochemical by-products of diarylethene **5**.[10] They reported that the photochemical cyclization of **5O** occurred not only from the *s-cis-s-cis* conformation around the hexatriene moiety to afford **5C**, but also from the *s-trans-s-cis* conformation. They explained, as depicted in Scheme 2, that the latter may have occurred from the electrocyclization of **5O′** containing the isoelectronic structure of the thiophene moiety, followed by dehydrogenation from **5C′** to form the light-insensitive colorless final product **5D**. In the case of **2O**, a similar reaction is possible. In addition to the regular electrocyclization to lead **2C** (route A in Scheme 3), an abnormal electrocyclization (route B) to give **2C′** could be possible from **2O′** that is isoelectronic with **2O**. If the thermal 1,5-hydrogen shift, as we described in the preceding paper,[9] may have followed on **2C′**, the resulting compound **2R** would restore the aromaticity of the thiophene ring. To confirm this hypothesis, we took ^{1}H NMR after photoirradiation. After **2O** in $CDCl_3$ was irradiated with light longer than 300 nm (Pyrex filter) from a high-pressure Hg lamp for 40 min, the solution was colorless. All of **2O** was consumed, and no signals attributable to **2C** were observed by ^{1}H NMR. Instead, a new set of signals attributed to the new compound appeared. The most characteristic signal was the doublet at δ 4.58, with J = 2.97 Hz (probably a coupling with one of the adamantane proton), attributed to the hydrogen adjacent to the phenyl group. As we showed in the preceding paper, the hydrogen under a similar situation of **1R** appeared as a doublet at δ 4.57, with J = 8.91 Hz. The difference of the coupling constants may reflect the slight difference in the conformation of the compounds. In addition, because the mass spec-



Scheme 3. Formation of by-product from **2O**.

trum of **2R** showed the same molecular ion peak (508) as **2O**, neither dehydrofluorination nor dehydrogenation occurred. We therefore concluded that an irreversible side reaction occurred by way of the abnormal electrocyclization of **2O**, followed by a thermal sigmatropic 1,5-hydrogen rearrangement to give **2R**.

Synthesis of Improved Compound 3. Because of the hydrogen atom on C-4 of the thiophene group of **2O**, that can migrate after abnormal photocyclization, a thermally as well as photochemically inert by-product **2R** was generated. In order to avoid the formation of **2R**, we decided to introduce a methyl group at C-4. The trimethylthiophene has often been used for diarylethenes as aromatic rings.[5] However, the sterically more demanding 3-lithio-2,4,5-trimethylthiophene than the 3-lithio-2,5-dimethylthiophene did not react with **4**. The introduction of trimethylthiophene to the octafluorocyclopentene, followed by the introduction of the right half (1-adamantylidene-1-phenylmethyl group), was also not successful. We then decided to reduce the steric bulkiness of the adamantylidene group by replacing it with the isopropylidene group, which has been frequently used in fulgides.[4]

A synthesis of the right half **6** was carried out using similar procedures to obtain **4**, which was described in the preceding article.[9] Starting with 2-methyl-1-phenyl-1-propene, bromination, dehydrobromination, and lithiation followed by a reaction with octafluorocyclopentene, afforded **6** in 66% yield in three steps. The reaction of 3-lithio-2,4,5-trimethylthiophene with **6** afforded **3O** in 64% yield (Scheme 4).

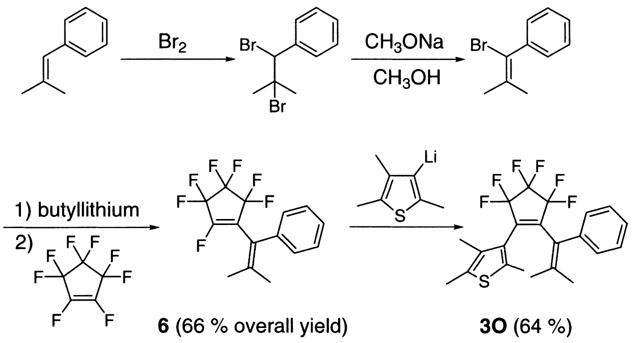
Photoreaction of 3. When the thus-prepared arylbutadiene **3O** was dissolved in toluene and the solution was irradiated with 313-nm light, a new absorption band appeared in the visible-light region. Its absorption maximum was 445 nm. Apparently **3C** was produced by photochemical 6π-electrocyclization. The colored species **3C** was stable, and was detected by HPLC. It returned to colorless **3O** upon the irradiation of visible light. The changes in the absorption spectra during photoirradiation experiments are shown in Figs. 2(a) and 2(b), and the photoreaction processes are depicted in Scheme 5.

The quantum yields of photoreactions, shown in Table 1 along with the absorption spectroscopic data, were determined by analyzing the change in the concentration of **3O** and **3C**, determined by HPLC as the function of the irradiation time.[11]

The coloration quantum yield by 313-nm light is as large as 0.43, and the decoloration quantum yields for 313- and 405-nm lights are practically the same, 0.14 and 0.16, respectively. The largeness of the molar absorption coefficient of **3C** at 313 nm suppressed the conversion ratio of **3O** to **3C** by 313-nm light irradiation to 63%.

Although the isolation of **3C** has not yet been carried out, the change in ^{1}H NMR spectrum during the photoirradiation in $CDCl_3$ was followed, and the assignment of the methyl signals of **3C** was done. Before 313-nm light irradiation, **3O** showed five singlet methyl signals (δ = 1.43, 1.59, 1.73, 1.90, 2.19), along with two (δ = 6.69 (2H, m)) and three (δ = 7.13–7.16 (3H, m)) protons on the phenyl ring. After UV irradiation for 315 min, four small new singlet peaks attributable to **3C** appeared (δ = 0.95, 1.46, 1.69, 1.99: one peak may be overlapping with the peaks of **3O**) as well as the down-field shifted aromatic protons (δ = 7.35, m) appeared, while the peaks of **3O** remained almost unchanged (**3O**/**3C** = 86/14). These new peaks disappeared upon the irradiation of visible light (405 nm) for 270 minutes. Therefore, the new peaks are assigned to the signals of **3C**.

Thermal Stability. The thermal stability is important for "thermally irreversible photochromic compounds." Therefore, we next evaluated the thermal stability of **3C**. A PMMA film containing 0.36 weight% of **3O** was irradiated with 313-nm light to make a photostationary state. This film was kept at 80 °C in the dark in the air for 30 days, and the absorption



Scheme 4. Synthesis of **3O**.

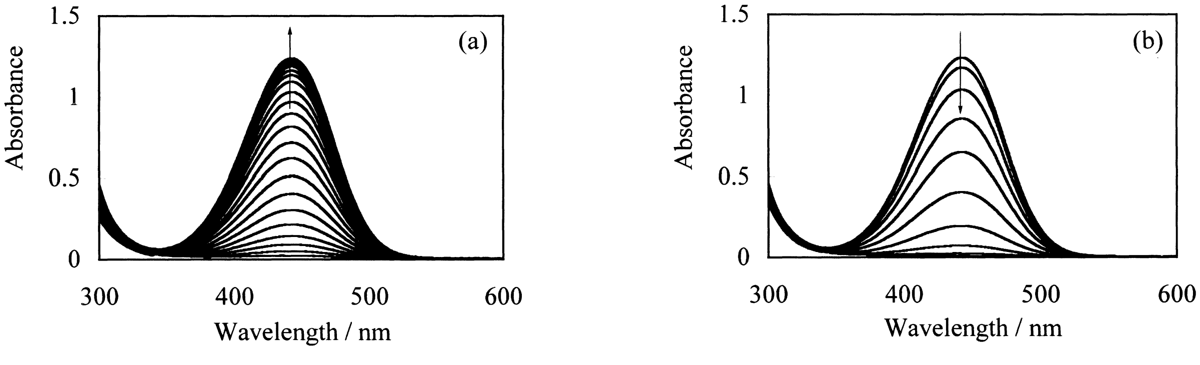
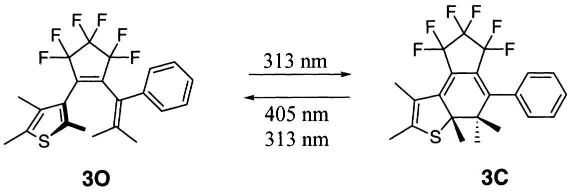


Fig. 2. Change in absorption spectra in toluene. (a) Irradiation of 313-nm light. Irradiation time/min; 0, 0.5, 1.5, 3, 5, 8, 12, 17, 23, 30, 38, 47, 57, 68, 80, 95, 110, 125, 140, 155, 170, 185, 200. (b) Irradiation of 405-nm light. Irradiation time/min; 0, 0.5, 1.5, 3, 5, 8, 12, 17, 23, 30, 38.



Scheme 5. Photoreaction of **3O**.

spectrum was measured at intervals. As shown in Fig. 3, the absorbance at 445 nm decreased only slightly. It is thus proved that **3C** is thermally quite stable.

Fatigue Resistivity. In order to apply to photochemical switches, the photochromic compound should be robust. Photochemical coloration and decoloration cycles should be repeated without any, or at least very few, side reactions. Some of the diarylethenes are known to show excellent fatigue resistance. Because the structure of **3** is similar to that of diarylethenes, we anticipated a high fatigue resistivity of **3**. A similar PMMA film used for thermal stability was used for the repeated irradiation of 313- and 405-nm lights. As shown in Fig. 4, after iterative irradiation was performed ten times, little decrease in the absorption of the colored form at photostationary state was observed.

Conclusion

A new thermally irreversible photochromic 1-aryl-1,3-butadiene system was established. While compound **2** with a 2,5-dimethyl-3-thienyl group exhibited a serious side reaction upon 313-nm light irradiation, compound **3** with a 2,4,5-trimethyl-3-thienyl group showed thermally irreversible photochromism. Its thermal stability and fatigue resistivity in PMMA films were shown to be excellent. Further modification of its structure is now in progress in our laboratory.

Experimental

General. ^{1}H NMR spectra were recorded with a JEOL JNM-EX-270 (270 MHz) spectrometer in $CDCl_3$. The signals are expressed as parts per million down field from tetramethylsilane, used as an internal standard (δ value). Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were measured using a Perkin-Elmer 1650 FT-IR spectrometer. Low- and high-resolution mass spectra were taken with a JEOL JMS AX-500 mass spectrometer. UV-vis spectra were recorded on a JASCO Ubest-50 UV-vis spectrophotometer. The emission line of 313 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (5-cm water filter, Toshiba UV-D35 glass filter, 5 cm aqueous $NiSO_4 \cdot 6H_2O$ solution, 1 cm aqueous K_2CrO_4–NaOH solution, and 1 cm aqueous potassium hydrogen phthalate solution). The emission line of 405 nm of a 500 W high-pressure mercury lamp (Ushio Electric) was separated by filters (5-cm water filter, a Pyrex glass filter, Toshiba UV-35, V-44, and KL-40 glass filters). The irradiation-light intensity was determined by a photometer (Newport Co., Optical Laser Power Meter, Model 1830-C). Measurements of the concentration of components during the photoreactions were made using a high-pressure liquid chromatograph (Shimadzu LC-6A) and a detector (Shimadzu SPD-6AV) using a silica-gel column (Wakosil 5-sil, 4.6 mm × 150 mm, Wako) with a mixture of ethyl acetate and hexane as an eluent. The silica-gel column chromatographic separation was carried out with a Merck Kieselgel 60 (230–400 mesh) with a mixture of ethyl acetate and hexane as an eluent. Analytical thin-layer chromatography was performed on Merck pre-coated silica gel 60 F-254, 0.25-mm thick TLC plates. All of the synthetic reactions were carried out under a dry nitrogen atmosphere. Tetrahydrofuran (THF) was freshly distilled from benzophenone ketyl, and diethyl ether and dichloromethane were distilled from CaH_2 immediately before use.

Synthesis of 1-(1-Adamantylidene-1-phenylmethyl)-2-(2,5-dimethyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (2O). To a solution of 3-bromo-2,5-dimethylthiophene (274 mg, 1.43 mmol) in 10 mL THF at −78 °C was added a hexane solution of butyllithium (1.57 mol dm^{-3}, 1.0 mL, 1.57 mmol). This mixture was added dropwise to a THF (15 mL) solution of 1-(1-adamantylidene-1-phenylmethyl)perfluorocyclopentene (**4**) (560 mg, 1.34 mmol) at −78 °C, and the resulting mixture was kept stirring for 24 h. After the reaction was quenched with water, the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. After the drying agent was removed, the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **2O** (194 mg, 28%). Mp 103–105 °C. IR (KBr) ν/cm^{-1} 3056, 3033, 2965, 2916, 2851, 1614, 1493, 1446, 1340, 1272, 1187, 1133, 1101, 1074, 1038, 1020, 1001, 973, 956, 885, 858, 822, 749, 724, 700, 578, 566, 528. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.62–1.92 (12H, m), 2.05 (3H, s), 2.34 (3H, s), 2.62 (2H, br), 6.33 (1H, s), 6.95–6.98 (2H, m), 7.21–7.24 (3H, m). MS (EI, 70 eV) m/z 508 (M$^+$, 41), 507 (100), 492 (3), 488 (3), 446 (3), 386 (8), 372 (16). Found: m/z 508.1692. Calcd for $C_{28}H_{26}F_6S$: M, 508.1659.

Prolonged UV Irradiation on 2O. To a solution of **2O** in $CDCl_3$ in an NMR sample tube was irradiated light longer than 300 nm from a high-pressure Hg lamp (only a Pyrex glass filter was used) for 40 min, and the NMR spectrum was measured. Only the signals of the by-product were observed. After evaporating the solvent, the mass spectrum of the by-product was taken. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.50–2.53 (14H, m), 2.09, 2.57 (each 3H, s), 4.58 (1H, d, J = 2.97 Hz), 6.72 (2H, d, J = 7.26 Hz), 7.13–7.19 (3H, m). MS (EI, 70 eV) m/z 509 (38), 508 (M$^+$, 93), 507 (100), 492 (26), 416 (59), 388 (34), 387 (79), 386 (24).

Synthesis of 4-Bromo-2,3,5-trimethylthiophene. To a solution of 2,3,5-trimethylthiophene (1.92 g, 15.21 mmol) in 40 mL

Table 1. Absorption Spectral Data and Quantum Yields of Photoreactions of **3** in Toluene

λ_{max}/nm (ε_{max}/mol^{-1} dm^3 cm^{-1})		Quantum Yield		
		313 nm		405 nm
3O	**3C**	Φ_{OC}	Φ_{CO}	Φ_{CO}
No absorption peaks longer than 280 nm	445 (9.90 × 10^3)	0.43	0.14	0.16

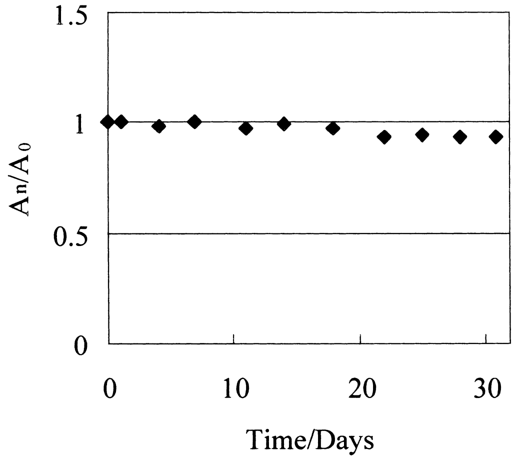


Fig. 3. Thermal stability of **3C** in a PMMA film at 80 °C.

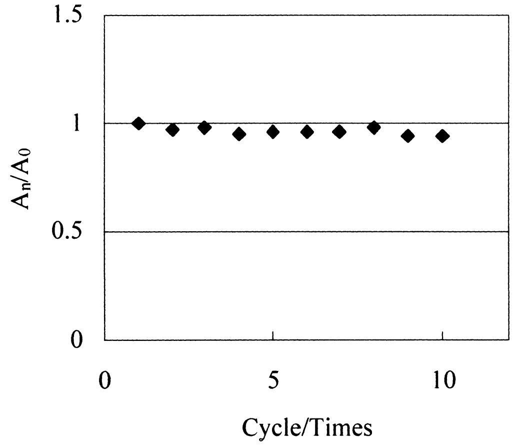


Fig. 4. Fatigue resistivity of **3** in a PMMA film by iterative irradiation of 313- and 405-nm light.

THF at 0 °C was added bromine (0.8 mL, 15.52 mmol); the resulting mixture was kept stirring for 30 min at room temperature. The reaction was quenched with aqueous sodium thiosulfate and 10% aqueous sodium hydrogencarbonate. The mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. The drying agent was filtered off and the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give 4-bromo-2,3,5-trimethylthiophene (1.357 g, 44%) as a colorless liquid. IR (neat) ν/cm^{-1} 2916, 2855, 1567, 1438, 1378, 1150, 995, 764, 508. ^{1}H NMR (270 MHz, $CDCl_3$) δ 2.08 (3H, s), 2.32 (6H, s).

Synthesis of {3,3,4,4,5,5-Hexafluoro-1-(2-methyl-1-phenyl-1-propenyl)-2-(2,4,5-trimethyl-3-thienyl)}cyclopentene (3O). To a solution of 4-bromo-2,3,5-trimethylthiophene (620 mg, 3.02 mmol) in 25 mL THF at −78 °C was added a hexane solution of butyllithium (1.56 mol dm^{-3}, 2.45 mL, 3.79 mmol). This mixture was added dropwise to a THF (20 mL) solution of **6** (980 mg, 3.02 mmol) at −78 °C, and the reaction mixture was kept stirred for 5 h with gradual warming up to room temperature. To it was added water; the mixture was extracted with ethyl acetate three times. The organic layer was washed with saturated brine, and dried with anhydrous sodium sulfate. The drying agent was filtered off and the solvent was removed in vacuo. The residue was purified by silica-gel column chromatography to give **3O** (830 mg, 64%) as a colorless liquid. IR (neat) ν/cm^{-1} 2996, 2943, 2864, 1443, 1338, 1274, 1189, 1145, 1120, 971, 744, 700, 581. ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.43, 1.59, 1.73, 1.90, 2.19 (each 3H, s), 6.69 (2H, m), 7.13–7.16 (3H, m). MS (EI, 70 eV) *m*/*z* 430 ((M^+), 100), 415 (46), 387 (30). Found: *m*/*z* 430.1154. Calcd for $C_{22}H_{20}F_6S$: M, 430.1190.

Photoreactions of 2 and 3. To the toluene solution (1.04×10^{-4} mol dm^{-3} for **2O** and 2.04×10^{-4} mol dm^{-3} for **3O**) was irradiated with 313-nm light, and the UV-vis spectra were recorded with designated time intervals until they reached the photostationary states. Also, the concentrations of the isomers were determined by HPLC. To the photostationary state solutions, 405-nm light was irradiated until they returned to the initial O-forms. The UV-vis spectra were recorded with designated time intervals to determine the concentrations of the isomers.

Preparation of a PMMA Film Containing 3. A mixture of PMMA pellets (Wako Chemicals Co., d 1.19, *n* = 1000–1500) (320.8 mg) dissolved in 2 mL of dichloromethane and **3O** (1.16 mg) dissolved in 2 mL of toluene was cast into a Petri dish (5.8 cm diameter). The cast solution was kept in the dark at room temperature for 3 days to let the solvent evaporate. The thus-obtained PMMA film was further dried under a vacuum at room temperature for 24 h. The film was cut into two, and each piece was used for a thermal-stability experiment and for a fatigue-resistivity experiment, respectively.

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