Photochromic Diarylethenes with Intralocking Arms

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Abstract: 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentenes with carboxyalkyl or alkyl mercaptan groups at 6 and 6′ positions of the benzothiophene rings were synthesized with the aim of controlling the photochromic reactivity by external stimulation, such as chemicals or heat treatment. 1,2-Diarylethenes with heterocyclic five-membered rings have two atropisomers, and the photochromic reactivity depends on the conformation. When the molecule was fixed in a parallel conformation with intramolecular hydrogen bonds or an intramolecular disulfide linkage, the photochromic reactivity was completely inhibited. The molecule again became photoactive when the intramolecular lock was unclasped by the addition of hydrogen bond breaking or reducing agents. The diarylethene with carboxyethyl groups showed a thermal reaction threshold in decalin. At temperatures below 50 °C the molecule was photochemically inactive, while the photochromic property was recovered upon heating above 100 °C, at which temperatures the intramolecular hydrogen bonds are broken.

Introduction

Most photochromic compounds change their color by photoirradiation and return to their initial state while kept in the dark. Recently thermally irreversible photochromic compounds, which never return to the initial state thermally but undergo reversible photoisomerization, have been developed.[1-3] Among the compounds, 1,2-diarylethenes with heterocyclic rings have the potential ability for many applications owing to additional characteristics, namely, the fatigue resistant property. The compounds continue to display this phenomenon even after 10^4 times of coloration/decoloration operations.[4,5]

Although the compounds satisfy the minimum requirements for applications to optoelectronic devices, some problems still remained unsolved. A property that is strongly desired but still lacking is a gated photochromic reactivity. Gated reactivity is the property that irradiation with any wavelength causes no color change, while the color change is induced when additional external stimulation, such as another photons, chemicals, or heat, is present. Such a threshold reactivity is indispensable for the application to optical memory media.

One of the approaches to gain access to the property is to seek compounds which undergo two-step two-photon photoisomerizations.[6] The color changes of the compounds are scarcely induced when the light intensity is weak, while the photoreactions readily occur by illumination with high intensity light. Although several irreversible two-photon reaction systems have been reported,[7-10] compounds which show multiphoton reversible photochromic reactions are limited. Another approach is to use the reactivity change of photochromic compounds by protonation. An indolyl fulgide derivative with a dimethylamino substituent at the 5-position of the indole ring was found to change the ring-opening quantum yield by the addition of acid.[11] Electron-donating ability of the dimethylamino substituent was lost by the protonation and altered the reactivity.

In this paper we described our effort to control the reactivity of diarylethenes on the basis of their conformation. 1,2-Diarylethenes show two atropisomers and the reactivity depends on the conformation.[12] The relative population of the two conformers was controlled by introducing intralocking arms, which are able to form hydrogen bonds or a disulfide (S—S) linkage.

Results and Discussion

1. 1,2-Diarylethenes with Hydrogen Bonding Arms. The photochromic reaction of 1,2-diarylethene derivatives belongs to a 1,3,5-hexatriene to cyclohexadiene type reaction. According to the Woodward–Hoffmann rule the photocyclization reaction proceeds in a conrotatory mode. When the aryl groups are five-membered heterocyclic rings, the compound has two conformations, with the two rings in mirror and C_2 symmetries,[12] and the conrotatory cyclization is allowed only from the conformation with the rings in C_2 symmetry.[13] This means that the photocyclization is inhibited if the heterocyclic rings are fixed to the mirror symmetry, or parallel orientation, while the reaction can proceed when the conformation converts to the C_2 symmetry, or antiparallel orientation. The parallel conformation can be fixed by introducing substituents into the aryl groups that show the ability of hydrogen bonding (Scheme 1).

Carboxyalkyl groups were used as substituents. 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene derivatives with carboxyethyl or -methyl or carboxy at 6 and 6′ positions of the benzothiophene rings, **1**, **2**, and **3**, respectively, were synthesized, and the photochromic reactions were measured in cyclohexane.[14]

Figure 1, parts a and b, shows the absorption spectra of **1** and **2** in cyclohexane upon irradiation with 313 nm light, respectively. The absorption band around 525 nm is due to the closed-ring form.[4] Although photocyclization of **2** proceeds to some extent, the reaction of **1** is completely suppressed. In nonpolar cyclo-

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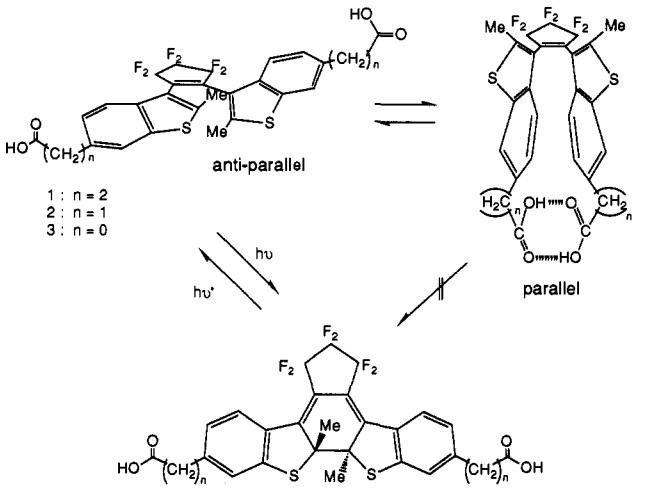
Scheme 1



hexane the carboxy groups of **1** and **2** are considered to make intramolecular hydrogen bonds. Because of the short chain length of the carboxymethyl groups, the intramolecular hydrogen bonds of **2** are incomplete, and some of **2** are still in the antiparallel conformation. The antiparallel conformers undergo photocyclization to produce the colored closed-ring forms. On the other hand, carboxyethyl groups can make stable intramolecular hydrogen bonds, and all of **1** is fixed in the photochemically inactive parallel conformation.

It is worthwhile to note that **3** underwent a normal photochromic reaction in nonpolar benzene, as shown in Figure 1c. The intramolecular hydrogen bonds are no longer produced when the carboxylic acid groups are directly connected to the benzothiophene rings.

The inactive conformers became photoactive upon the addition of a small amount of ethanol, which breaks the intramolecular hydrogen bonds. Figure 2 shows the absorption spectra of **1** in mixed solvents of cyclohexane and ethanol in the photostationary state under irradiation with 313 nm light. The addition of 0.5 vol % of ethanol activates the photoreactivity. The increase in the content of ethanol further increases the conversion to the closed-ring form, and the conversion is as much as 64% at the content of 15 vol %. **1** became photoactive not only by the addition of ethanol but also other hydrogen bond breaking agents such as propylamine. These results suggest that the fixed parallel conformers are loosened by the agents and convert to the photoactive antiparallel conformers.

The mechanism was confirmed by ^{1}H NMR measurement in the mixed solvents of cyclohexane-d_{12} and ethanol-d_6. The methyl protons at the 2-positions of benzothiophene rings gives us information concerning the relative population of the two conformers. The signal at around 2.4 ppm is assigned to methyl protons in the parallel conformation, while the signal at around 2.1 ppm results from the antiparallel conformation.[12,14] In cyclohexane the upper field signal was not observed, which clearly indicates that **1** is in the parallel conformation. No antiparallel conformer exists in cyclohexane. The absence of antiparallel conformer explains the inactivity of **1** in cyclohexane. Intramolecular hydrogen bonds fix the molecule to the inactive conformation. The absence of an upper field signal also indicates that the contribution of intermolecular hydrogen bonding is negligible in dilute conditions.

Upon the addition of ethanol-d_6 the upper field signal at 2.1 ppm appeared, indicating the conversion from the parallel to the antiparallel conformer. Ethanol acts as a switch to unclasp the system. The population of the antiparallel conformer was increased with an increasing ethanol concentration and the compound became photoactive. The dimethyl ester derivative of **1** did not show such a strong solvent dependence.

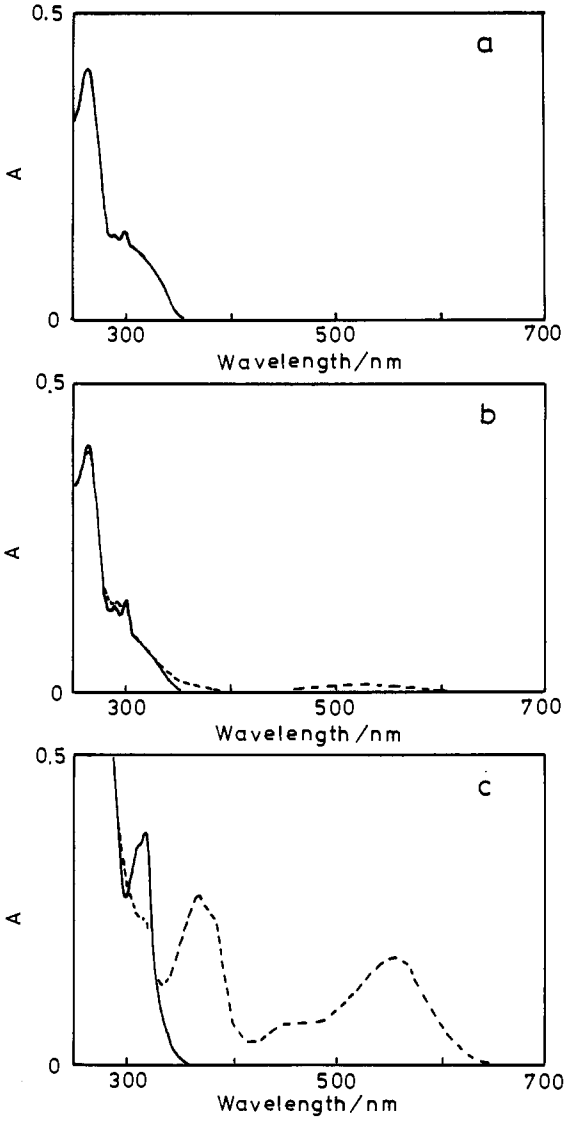


Figure 1. Absorption spectra of (a) **1** (2.5×10^{-5} mol/L) in cyclohexane, (b) **2** (2.5×10^{-5} mol/L) in cyclohexane, and (c) **3** (3.0×10^{-5} mol/L) in benzene (—) before and (- - -) after irradiation with 313 nm light. The spectra (- - -) were taken in the photostationary state.

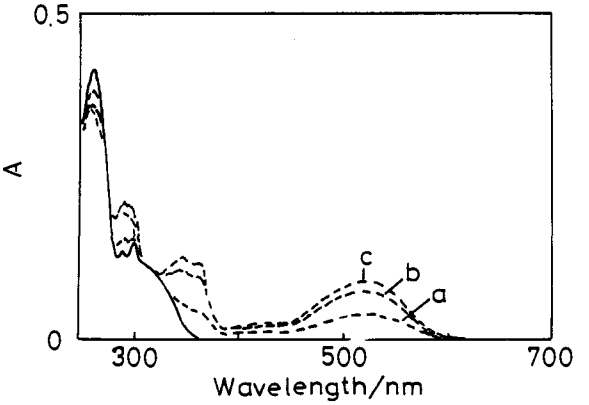


Figure 2. Absorption spectra of **1** (2.5×10^{-5}) upon irradiation with 313 nm light in (—) cyclohexane and (- - -) mixed solvents of cyclohexane and ethanol: (a) cyclohexane/ethanol = 99.5/0.5 (volume ratio); (b) cyclohexane/ethanol = 98/2; (c) cyclohexane/ethanol = 95/5.

The correlation between the relative population of the two conformers and the photocyclization quantum yield of **1** was measured, as shown in Figure 3. Both increase upon the addition of a small amount of ethanol and reach plateau values at the

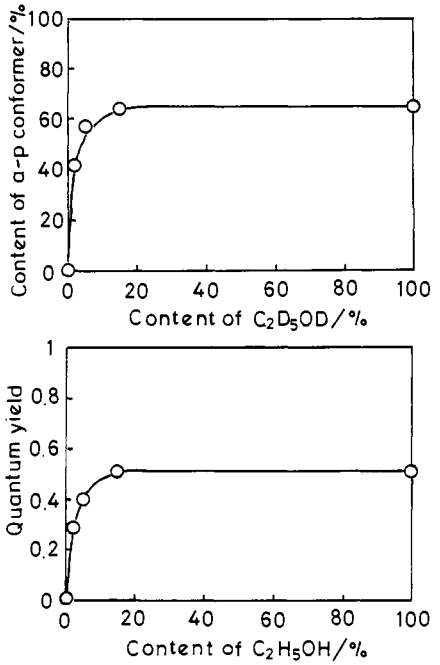


Figure 3. Dependence of the relative population of the antiparallel conformer and the photocyclization quantum yield of **1** by irradiation with 313 nm light on the content of ethanol in cyclohexane.

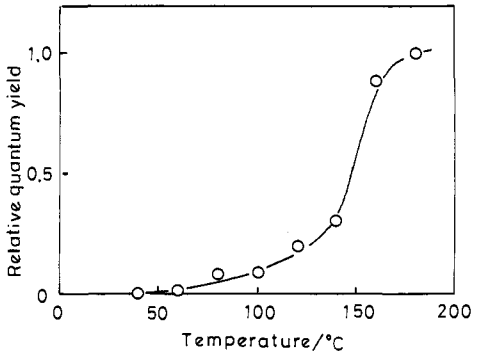


Figure 4. Temperature dependence of the relative quantum yield of cyclization of **1** by irradiation with 313 nm light in decalin.

concentration of 15 vol %. The good correlation between the two values clearly indicates that the quantum yield is dependent on the content of antiparallel conformer. When the content increases, the quantum yield concomitantly increases.

The interconversion rate between the two conformers is considered to be slower than 1 ms.[12] Therefore, both conformers are excited independently by photoirradiation, and only the photoexcited antiparallel conformer has a chance to be converted to the closed-ring form. The closed-ring form is not produced from the excited state of the parallel conformer. It is possible to estimate the actual quantum yield of photocyclization of the antiparallel conformer from its content and the total quantum yield, because both conformers have almost similar spectra. The content of antiparallel conformer at the ethanol concentration of 15 vol % is 64%, while the total quantum yield is 0.51. The actual quantum yield is calculated to be as high as 0.80. Most of the photoexcited antiparallel conformers convert to the closed ring forms.

The hydrogen bondings can be loosened not only by chemicals but also by heat treatment. A decalin solution of **1** did not undergo photocyclization at room temperature when irradiated with 313 nm light, while the solution turned red above 60 °C. Figure 4 shows the temperature dependence of the relative quantum yield of photocyclization. It increases dramatically above 100 °C and shows saturation above 170 °C. The heat treatment is also

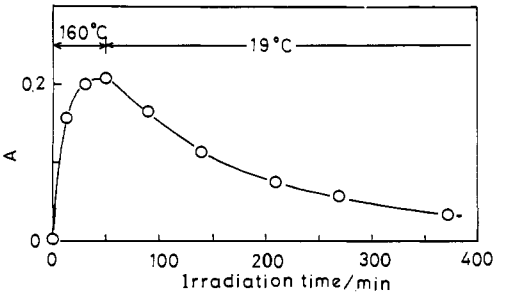
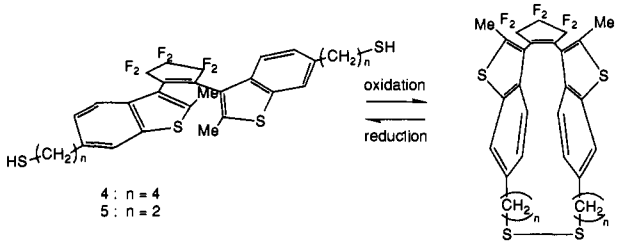


Figure 5. A reversible photocoloration/photodecoloration cycle of **1** in decalin by irradiation with 313 nm light. The temperature was kept at 160 °C during the initial 50 min and then decreased to 19 °C.

Scheme 2



effective to unclasp the intralock. The molecule has a thermal reaction threshold.

The measurement of vapor phase dissociation in a low pressure range revealed that acetic acids form hydrogen-bonded dimers (the hydrogen bonding energy of 15 kcal/mol).[15] At 51.2 °C only 18.1% of the dimers dissociate, while at 150.5 °C they dissociate as much as 90% (initial pressure at 0 °C, 18.52 mm). Although the data may not be applied directly to the present intramolecular hydrogen bonding system, it is safe to say that the heating treatment loosens the hydrogen bonds, and photoactive antiparallel conformers are produced above 100 °C.

The temperature dependence of the quantum yield indicates the possibility of inducing the reversible photochromic reaction with single wavelength light by changing the temperature. Upon irradiation with 313 nm light the decalin solution of **1** turned red at 160 °C, indicating the ring-closure reaction. The same wavelength light, on the contrary, bleached the red color at 19 °C, as shown in Figure 5. At 313 nm both the open- and the closed-ring forms have absorption. Below 50 °C photoexcitation of the open-ring form results in no reaction, while the photoexcited closed-ring form converts to the open-ring form. This is the reason why 313 nm light induces the decoloration reaction at 19 °C. The strong temperature dependence of the reactivity made it possible to induce both coloration/decoloration reactions by the same wavelength light. Such a thermal threshold system is useful for nondestructive readout operation.[16]

2. 1,2-Diarylethenes with Disulfide Bonding Arms. Another possible chemical lock can be made by the introduction of mercaptoalkyl groups, which reversibly form a disulfide linkage by oxidation/reduction cycles. Mercaptoalkyls with different alkyl chain lengths were introduced at the 6 and 6′ positions of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentene instead of carboxyalkyl groups, and their photoreactivity was examined in the presence of oxidation/reduction agents (Scheme 2).

When 100 mg of iodine (an oxidizing agent) was added to the chloroform solution of **4** (60 mg in 600 mL of chloroform), 60% of **4** converted to the parallel conformer **21** by the intralocking disulfide formation. The rest of the compound formed oligomers by intermolecular disulfide formation. The parallel conformer was isolated by thin layer chromatography (silica gel, hexane/

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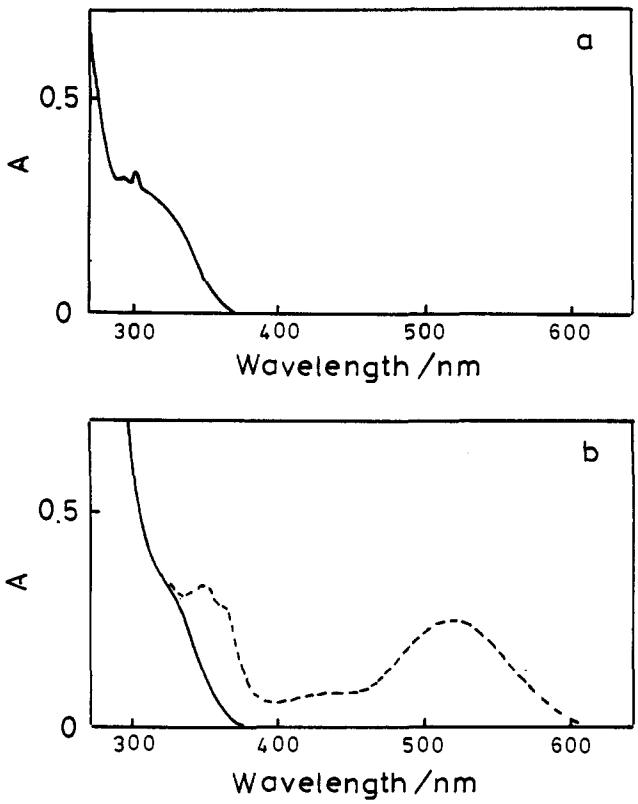

Figure 6. Absorption spectra of **21** (6.2×10^{-5} mol/L) in THF containing 0.5 vol % water (a) in the absence and (b) in the presence of tri-n-butylphosphine (—) before and (- - -) after irradiation with 313 nm light. The spectrum (- - -) was taken in the photostationary state.

chloroform = 3/2), and the photochemical reactivity was examined in tetrahydrofuran containing 0.5% water. Figure 6, parts a and b, shows the absorption spectra upon irradiation with 313 nm light in the absence and presence of tri-n-butylphosphine (a reducing agent).[17] Before adding the reducing agent the compound **21** was photochemically inactive. No absorption due to the closed-ring form was observed even after prolonged irradiation. The compound fixed in the parallel conformation with the intra-disulfide linkage cannot convert to the closed-ring form. On the other hand, red color appeared upon irradiation with 313 nm light in the presence of tri-n-butylphosphine. The reducing agent unclasped the disulfide to form thiols and made it possible for the compound to convert to the photoactive antiparallel conformer. When the disulfide linkage is broken, the compound can freely rotate around C—C bonds between the benzothiophene and perfluorocyclopentene moieties, and two conformers, antiparallel and parallel, are equally formed. The photoexcited parallel conformer converts to the closed-ring form as already mentioned for **1**.

The interconversion process from the locked parallel conformer to the freely rotating open-ring form by the chemical reduction was followed by ^{1}H NMR measurement. Figure 7 showed the time course of the NMR spectral change. Before mixing the reducing agent, no methyl proton due to the antiparallel conformation was observed. The intramolecular disulfide bonding fixes the compound to the parallel conformation. After 15 min of mixing with the reducing agent a singlet signal appeared at 2.19 ppm which can be assigned to the methyl protons of the antiparallel conformation. After 1 h the disulfide linkage was completely broken (reduced). The result confirms that the disulfide linkage is useful to control the photochemical reactivity of the diarylethene.

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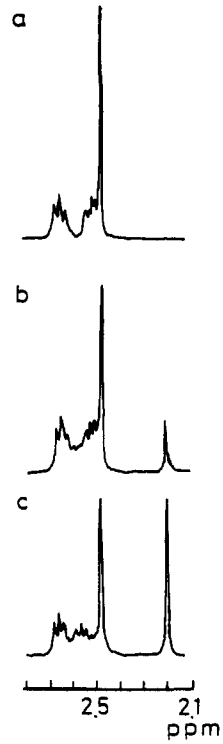

Figure 7. ^{1}H NMR spectral changes of **21** in THF-d_8 containing 0.5 vol % D_2O by the addition of tri-n-butylphosphine: (a) before the addition; (b) 15 min and (c) 1 h after the addition.

The efficiency of the intramolecular disulfide formation was dependent on the alkyl chain length of the mercaptoalkyl substituents. When the length is shortened from 4 to 2, the ratio of the intramolecular to the intermolecular bond formation decreased. Under the same oxidation conditions as described above the conversion yield of **5** to the intralocked form was only 15%. The rest converted to oligomers. In the case of only two methylene units the reaction probability to make an intramolecular disulfide bond is less likely in comparison with the four methylene units per chain.

Although the intermolecular bond formation takes place to a large extent for **4** and **5** even in very diluted solutions, it was negligible for **1** and **2**. The different behavior between mercaptoalkyl and carboxyalkyl substituents can be interpreted as follows. The disulfide linkage is a covalent bonding (bond energy, 63 kcal/mol)[18] and cannot dissociate thermally. Therefore, the ratio of the intramolecular to intermolecular linkages depends on the ratio of intramolecular to intermolecular collision frequencies of the two thiol groups. It does not depend on whether the intramolecular or the intermolecular hydrogen bonding is more favorable. In other words, the ratio is determined kinetically. On the other hand, the hydrogen bonds between carboxylic acid groups are rather weak and dissociate thermally to some extent. Both intramolecular and intermolecular bonds are in association–dissociation equilibrium and the compounds are finally stabilized in the most stable forms. The intramolecular hydrogen bond is more favorable than the bimolecular hydrogen-bond formation in dilute solutions. This is the reason why the intralocked form is dominant for **1** and **2**.

3. Conclusion. 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentenes with carboxyalkyl or mercaptoalkyl groups underwent photochromic reactions only when the intramolecular bondings were unclasped by switch molecules such as hydrogen bond breaking or reducing agents. The compound with carboxyalkyl groups also showed a thermal reaction threshold. The photochromic reaction was not observed at room temperature,

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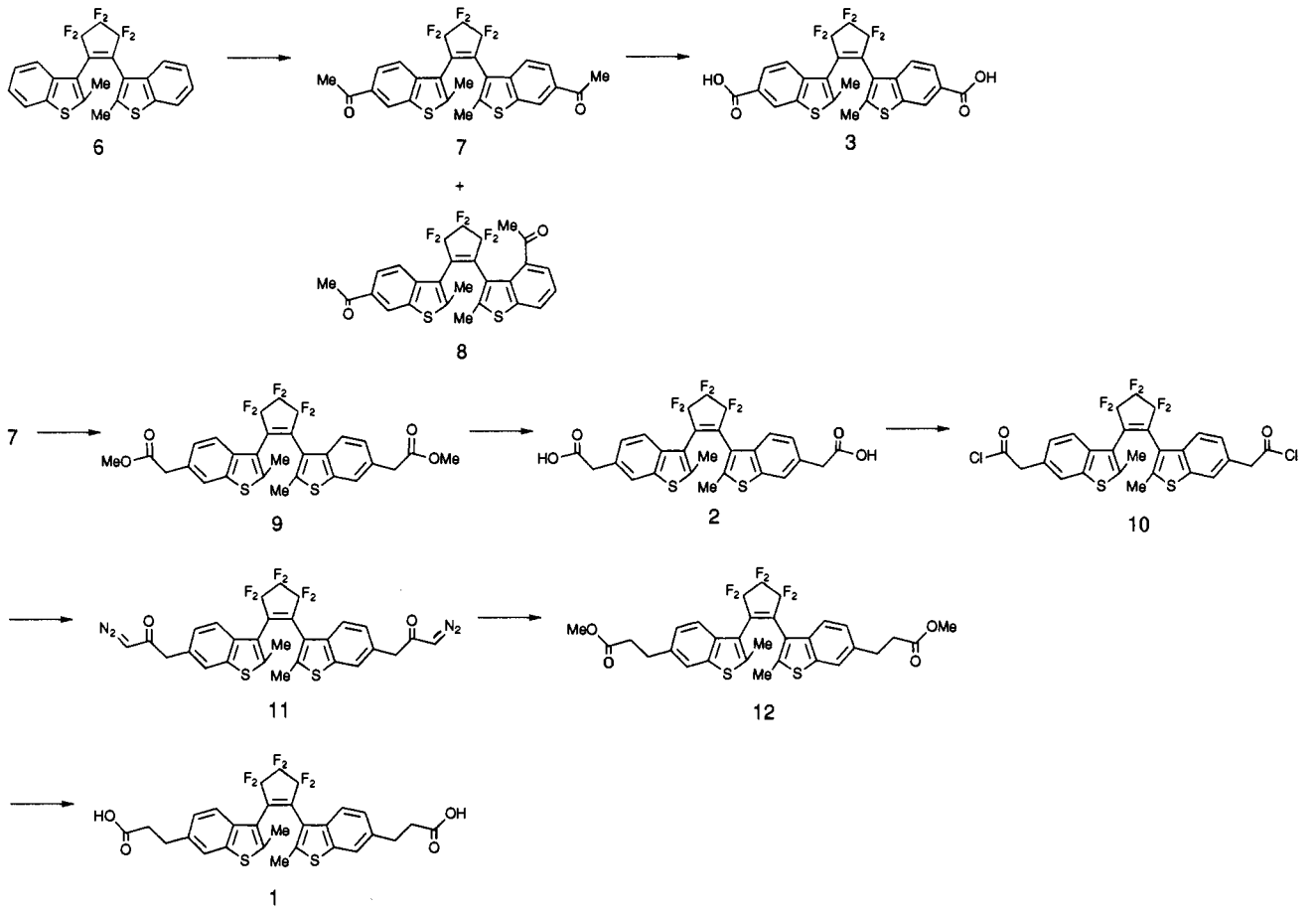
Scheme 3



while the compound became photoactive above 100 °C, at which temperatures the intramolecular hydrogen bonds are broken.

Experimental Section

General. Absorption spectra were recorded on an absorption spectrophotometer (Hitachi U-3410). ^{1}H NMR spectra were recorded on JEOL-FX 100 (100 MHz) and JEOL-GX 270 (270 MHz) spectrometers. Chemical shifts are reported in parts per million. Atropisomer assignments are p (parallel) or ap (antiparallel). Photoirradiation was carried out in the thermostat by using a USHIO 500 W high pressure mercury lamp as the excitation light source. Mercury lines of 313 and 546 nm were isolated by passing the light through a monochromater (Ritsu MC-10N). Quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against furyl fulgide in toluene.[21] The samples were not degassed.

Materials. 1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentenes with carboxyalkyl groups were synthesized according to the above reaction route (Scheme 3).

1,2-Bis(6-acetyl-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (7). To a well-stirred nitrobenzene solution (20 mL) of 1.0 g (2.1 mmol) of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**6**) and 0.86 g (11 mmol) of acetyl chloride was added 1.5 g (11 mmol) of aluminum chloride over 1 h at room temperature. The solution was stirred for an additional 1 h. To stop the reaction, dilute HCl was added. The reaction mixture was extracted twice with chloroform (2 × 20 mL). The organic layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by chromatography on silica gel (chloroform) to give 0.94 g of 1,2-bis(6-acetyl-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**7**) and a trace of 1-(6-acetyl-2-methylbenzo-[*b*]thiophen-3-yl)-2-(4-acetyl-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**8**) (yield: 80%).

7: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.27 (3H, ap Me), 2.54 (3H, p Me), 2.59 (3H, p COMe), 2.66 (3H, ap COMe), 7.58–8.33 (6H, m, aromatic protons); MS *m*/*z* 552 (M^+).

8: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.24 (3H, ap Me), 2.51 (3H, p Me), 2.53 ($^3/_2$H, p 6-COMe), 2.72 ($^3/_2$H, ap 6-COMe), 2.59 ($^3/_2$H, p 4-COMe), 2.66 ($^3/_2$H, ap 4-COMe), 7.25–8.32 (6H, m, aromatic protons); MS *m*/*z* 552 (M^+).

1,2-Bis(6-carboxy-2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (3). To a mixture of 2.80 mL of 10% sodium hypochlorite solution and 0.40 mL of dioxane was added 0.133 g (0.241 mmol) of **7** in 0.70 mL of dioxane solution with stirring at 55 °C. The solution was heated up to 80 °C and kept at the temperature for 3 h. Then aqueous sodium sulfite was added to decompose the excess sodium hypochlorite. The mixture was poured into water and extracted with chloroform. The aqueous layer was acidified with concd sulfuric acid to precipitate white crystalline diacid (**3**). The organic layer was dried, filtered, and concentrated to give white crystals. Combined crystals weight 0.112 g (85%). The crystals were recrystallized from acetone.

3: ^{1}H NMR (100 MHz, CD_3OD, TMS) δ 2.25 (3H, s, ap Me), 2.53 (3H, s, p Me), 7.54–8.23 (6H, m, aromatic protons); MS *m*/*z* 556 (M^+); mp >490 °C.

1,2-Bis[2-methyl-6-[[(methyloxy)carbonyl]methyl]benzo[*b*]thiophen-3-yl]hexafluorocyclopentene (9).[19] To a mixture of 3.60 mL of methanol and 0.91 mL of 60% perchloric acid aqueous solution were added successively 0.644 g (1.45 mmol) of thallium(III) nitrate and 0.400 g (0.724 mmol) of diacetyl compound **7**. After being stirred for 24 h, solvent was removed in vacuo, and then water and chloroform were added to the reaction mixture. The organic layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (chloroform) to give 0.246 g of 1,2-bis-[2-methyl-6-[[(methyloxy)carbonyl]methyl]benzo[*b*]thiophen-3-yl]hexafluorocyclopentene (**9**) (yield 56%).

9: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.18 (3H, s, ap Me), 2.47 (3H, s, p Me), 3.63 (2H, s, p CH_2), 3.67 (2H, s, ap CH_2), 3.71 (6H, s, COOMe × 2), 7.08–7.62 (6H, m, aromatic protons); MS *m*/*z* 612 (M^+).

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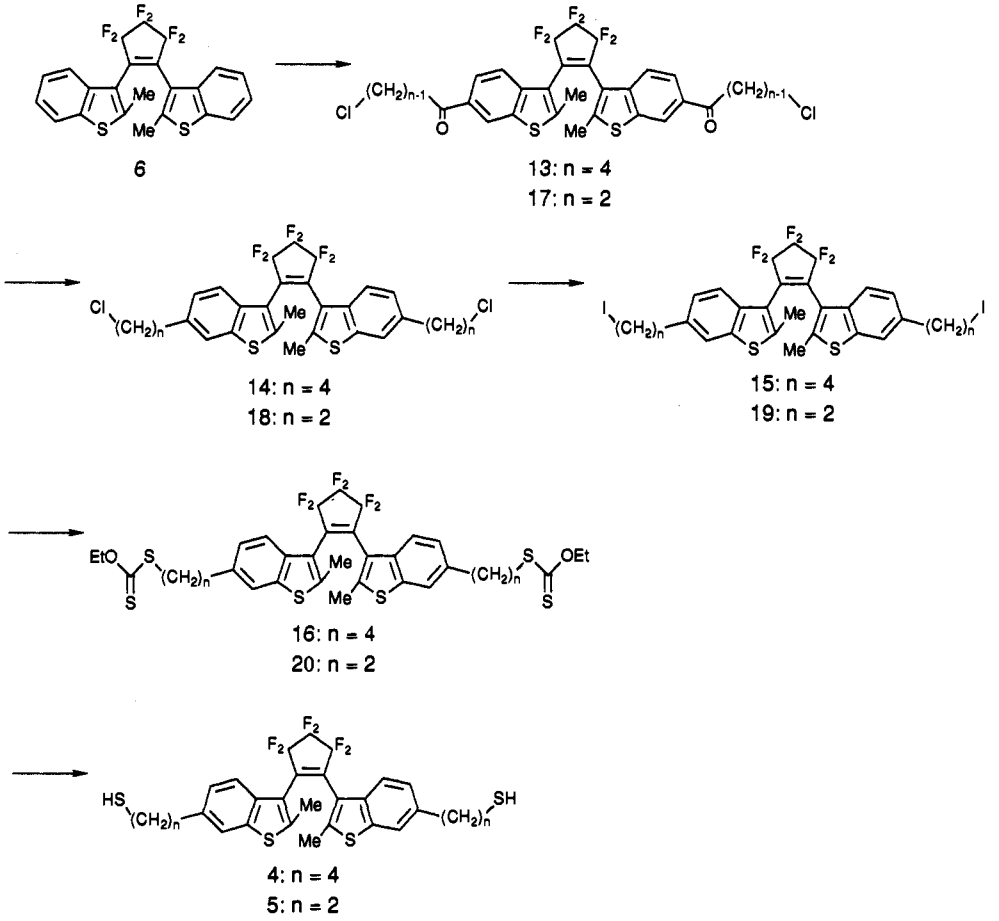
Scheme 4



1,2-Bis[6-(carboxymethyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (2). To a 74.3 mL dioxane solution containing 3.05 g (5.0 mmol) of **9** was added 111 mL of a sodium hydroxide solution (2 N). Separation into two layers was prevented by the addition of a small amount of methanol. The homogeneous solution was stirred for 4 h at room temperature. Solvents were removed in vacuo, and dilute hydrochloric acid was added to give white crystals. Recrystallization from methanol gave 1.83 g of **2** (63%).

2: ^{1}H NMR (270 MHz, CD_3OD, TMS) δ 2.21 (3H, s, ap Me), 2.49 (3H, s, Me), 3.62 (2H, s, p CH_2), 3.71 (2H, s, ap CH_2), 7.14 (1H, d, J = 8.2 Hz, p 5-H), 7.34 (1H, d, J = 8.2 Hz, ap 5-H), 7.50 (1H, d, J = 8.2 Hz, p 4-H), 7.61 (1H, d, J = 8.2 Hz, ap 4-H), 7.59 (1H, s, p 7-H), 7.69 (1H, s, ap 7-H), 219.5–220.5 °C; MS m/z 584 (M^+). Anal. Calcd for $C_{27}H_{18}O_4S_2F_6$: C, 55.48; H, 3.10. Found: C, 55.56; H, 3.40. IR (KBr; cm^{-1}) 1705 (COOH).

1,2-Bis[6-[[(diazomethyl)carbonyl]methyl]-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (11).[20] Diacid **2** (1.07 g, 1.82 mmol) was dissolved in excess amount of thionyl chloride and the solution was stirred for 2 h at 75 °C. Removal of thionyl chloride in vacuo gave diacid chloride **10**. An ether solution of diazomethane was added to **10** and stirred for 24 h at room temperature. Removal of the solvent followed by purification by column chromatography (chloroform) gave 0.419 g of **11** (yield 36%).

11: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.20 (3H, s, ap Me), 2.47 (3H, s, Me), 3.61 (2H, s, p CH_2), 3.69 (2H, s, ap CH_2), 5.06 (1H, s, p CHN_2), 5.17 (1H, s, ap CHN_2), 7.04–7.58 (6H, m, aromatic protons); MS m/z 632 (M^+), 576 ($M - N_2 \times 2$).

1,2-Bis[2-methyl-6-[[(methyloxy)carbonyl]ethyl]benzo[*b*]thiophen-3-yl]-hexafluorocyclopentene (12). To a mixture of 10.0 mL of methanol anhydrous and 0.800 g (3.44 mmol) of silver oxide was added 0.191 g (0.302 mmol) of **11**, and the solution was stirred for 4 h at 50 °C. Silver oxide powder was removed by filtration. Purification by column chromatography on silica gel (chloroform) gave 85 mg of **12** (yield 44%).

12: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.17 (3H, s, ap Me), 2.46 (3H, s, Me), 2.59 (2H, t, p CH_2COO), 2.67 (2H, t, ap CH_2COO), 2.95 (2H, t, CH_2Ar), 3.04 (2H, t, CH_2Ar), 3.63 (3H, s, p COOMe), 3.67 (3H, s, ap COOMe), 7.01–7.52 (6H, m, aromatic protons); MS m/z 640 (M^+).

1,2-Bis[6-(carboxyethyl)-2-methyl-1-benzothiophen-3-yl]hexafluorocyclopentene (1). To a 8.0 mL dioxane solution containing 85 mg (0.13 mmol) of **12** were added successively 15 mL of water and 10 mL of sulfuric acid, and the solution was stirred for 6 h at 105 °C. The solution was left overnight at room temperature. Crystals precipitated from the solution were filtered and purified by recrystallization (ethyl acetate/hexane) to give 75 mg of white crystals **1** (yield 92%).

1: mp 105–106 °C; ^{1}H NMR (270 MHz, C_2D_5OD, TMS) δ 2.16 (3H, s, ap Me), 2.47 (3H, s, p Me), 2.55 (2H, t, p CH_2COO), 2.60 (2H, t, ap CH_2COO), 2.92 (2H, t, CH_2Ar), 3.01 (2H, t, CH_2Ar), 7.07 (1H, d, J = 8.1 Hz, p 5-H), 7.29 (1H, d, J = 8.1 Hz, ap 5-H), 7.44 (1H, d, J = 8.1 Hz, p 4-H), 7.56 (1H, d, J = 8.1 Hz, ap 4-H), 7.50 (1H, s, p 7-H), 7.60 (1H, s, ap 7-H); MS m/z 612 (M^+). Anal. Calcd for $C_{29}H_{22}O_4S_2F_6$: C, 56.85; H, 3.62. Found: C, 56.78; H, 3.72. IR (KBr; cm^{-1}) 1705 (COOH).

1,2-Bis(2-methylbenzo[*b*]thiophen-3-yl)perfluorocyclopentenes with mercaptoalkyl groups were synthesized according to the above reaction route (Scheme 4).

1,2-Bis[6-(2-chloro-1-oxoethyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (13). Amounts of 1.4 g (3.0 mmol) of 1,2-bis(2-methylbenzo[*b*]thiophen-3-yl)hexafluorocyclopentene (**6**) and 1.1 g (7.8 mmol) of 4-chlorobutyryl chloride was dissolved in 10 mL of distilled nitrobenzene. After the addition of 0.45 g (7.1 mmol) of anhydrous aluminum chloride, the solution was stirred for 2 h at room temperature. The solution was acidified by the addition of dilute HCl. The reaction mixture was extracted three times with chloroform (3 × 20 mL). The combined organics were washed with water, dried ($MgSO_4$), filtered, and evaporated. Nitrobenzene was removed by column chromatography on silica gel (hexane). After removal of nitrobenzene, chloroform was used to elute compound **13** as a pale yellow oil (1.56 g, 2.3 mmol) in 90% yield.

13: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.21–2.31 (3H, m, CH_2 × 2), 2.27 (3H, s, ap MeAr), 2.54 (3H, s, p MeAr), 3.17 (2H, t, J = 7 Hz, p CH_2CO), 3.24 (2H, t, J = 7 Hz, ap CH_2CO), 3.64–3.72 (4H, m, p ap CH_2Cl), 7.59–8.35 (6H, m, aromatic protons); MS m/z 677 (M^+).

1,2-Bis[6-(4-chlorobutyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (14). To a 40 mL dichloromethane solution containing 1.6

g (2.3 mmol) of **13** were added 2.3 g (26 mmol) of borane-*tert*-butylamine complex and 1.5 g (11 mmol) of anhydrous aluminum chloride at 0 °C. The reaction mixture was stirred for 24 h at room temperature followed by the addition of dilute HCl to decompose excess borane complex. The aqueous solution was extracted with chloroform (3 × 20 mL). The organic layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by chromatography on silica gel (chloroform/hexane = 1/1) to give 1.08 g (1.66 mmol) of **14** (72%) as a pale yellow oil.

14: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.70–1.90 (8H, m, $CH_2CH_2CH_2CH_2$ × 2), 2.17 (3H, s, ap MeAr), 2.46 (3H, s, p MeAr), 2.62–2.80 (4H, m, p ap CH_2Ar), 3.50–3.68 (4H, m, CH_2Cl), 6.99–7.56 (6H, m, aromatic protons); MS *m/z* 649 (M^+).

1,2-Bis[6-(4-iodobutyl)-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (15). Amounts of 1.08 g (1.66 mmol) of **14** and 1.50 g (10.0 mmol) of sodium iodide were dissolved in 50 mL of 2-butanone and the solution was refluxed for 24 h. After removal of 2-butanone in vacuo, water and benzene were added to the reaction mixture. The benzene layer was dried ($MgSO_4$), filtered, and evaporated to give a pale yellow oil. The oil was purified by column chromatography on silica gel (benzene/hexane = 2/1) to give 1.38 g (1.66 mmol) of **15** (100%).

15: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.65–1.90 (8H, m, $CH_2CH_2CH_2CH_2$ × 2), 2.17 (3H, s, ap MeAr), 2.46 (3H, s, p MeAr), 2.64 (2H, t, *J* = 7 Hz, p CH_2Ar), 2.72 (2H, t, *J* = 7 Hz, ap CH_2Ar), 3.16 (2H, t, *J* = 7 Hz, p CH_2I), 3.21 (2H, t, *J* = 7 Hz, ap CH_2I), 7.00–7.56 (6H, m, aromatic protons); MS *m/z* 832 (M^+).

1,2-Bis[6-[4-[(ethoxythiocarbonyl)thio]butyl]-2-methylbenzo[*b*]thiophen-3-yl]hexafluorocyclopentene (16). To a 30 mL acetone solution containing 1.38 g (1.66 mmol) of **15** was added 0.585 g (3.65 mmol) of potassium *O*-ethyldithiocarbonate and the solution was stirred for 8 h at room temperature. After removal of acetone, water and ether were added to the reaction mixture. The ether layer was dried ($MgSO_4$), filtered, and evaporated to give a pale yellow oil. The oil was purified by column chromatography on silica gel (hexane/benzene = 1/2) to give 1.17 g of **16** (86%).

16: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.39 (6H, t, *J* = 7 Hz, p (CH_3CH_2) × 2), 1.62–1.80 (8H, m, CH_2 × 4), 2.17 (3H, s, ap MeAr), 2.46 (3H, s, p MeAr), 2.64–2.73 (4H, m, CH_2Ar), 3.07–3.20 (4H, m, CH_2S), 4.63 (4H, q, (CH_3CH_2O) × 2), 6.99–7.55 (6H, m, aromatic protons); MS *m/z* 820 (M^+).

The procedure to prepare **17**, **18**, **19**, and **20** was the same as that of **13**, **14**, **15**, and **16**, respectively.

20: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.38 (3H, t, *J* = 7 Hz, p CH_3CH_2), 1.42 (3H, t, *J* = 7 Hz, ap CH_3CH_2), 2.19 (3H, s, ap MeAr), 2.47 (3H, s, p MeAr), 3.01 (2H, t, *J* = 7 Hz, p CH_2Ar), 3.07 (2H, t, *J* = 7 Hz, ap CH_2Ar), 3.31 (2H, t, *J* = 7 Hz, p CH_2S), 3.39 (2H, t, *J* = 7 Hz, ap CH_2S), 4.60–4.69 (4H, m, CH_3CH_2O), 7.08–7.59 (6H, m, aromatic protons); MS *m/z* 764 (M^+).

General Procedure to Prepare Dithiol Compounds 4 and 5. Preparation of 4. An amount of 0.100 g (0.122 mmol) of **16** was added to 25 mL of ethylenediamine and stirred for 30 min at room temperature. Ethylenediamine was distilled in vacuo (temperature of the bath was kept below 50 °C). To the reaction mixture were added chloroform and water. The chloroform layer was dried ($MgSO_4$), filtered, and evaporated to give a yellow oil, which was purified by silica gel chromatography-(hexane/chloroform = 8/2) to give 60 mg of **4** (76%).

4: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.55–1.90 (8H, m, CH_2-CH_2), 2.17 (3H, s, ap Me), 2.46 (3H, s, p Me), 2.41–2.68 (8H, m, CH_2-Ar, CH_2S), 6.99 (1H, d, *J* = 8 Hz, p 5-H), 7.16 (1H, d, *J* = 8 Hz, ap 5-H), 7.38 (1H, s, p 7-H), 7.45 (1H, d, *J* = 8 Hz, p 4-H), 7.46 (1H, s, ap 7-H), 7.54 (1H, d, *J* = 8 Hz, ap 4-H); MS *m/z* 644 (M^+).

5 was prepared in the same manner.

5: ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.18 (3H, s, ap Me), 2.46 (3H, s, p Me), 2.60–3.10 (8H, m, CH_2CH_2 × 2), 6.99–7.58 (6H, m, aromatic protons); MS *m/z* 588 (M^+).

General Procedure of Intramolecular Disulfide Bond Formation. A Typical Example for 4. To a 600 mL chloroform solution containing 60 mg (0.093 mmol) of **4** was added 0.1 g of iodine, and the solution was stirred for 1 h at room temperature. The chloroform solution was washed with aqueous sodium thiosulfate solution, dried ($MgSO_4$), filtered, and evaporated to give a yellow oil, which was purified by thin layer chromatography (silica gel, hexane/chloroform = 8/2) to give 36 mg of the intralocked form **21** (60%).

21: mp 128–130 °C; ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 1.48–1.73 (8H, m, CH_2 × 4), 2.46 (6H, s, p Me × 2), 2.53 (4H, t, *J* = 7 Hz, CH_2Ar × 2), 2.67 (4H, t, *J* = 7 Hz, CH_2S × 2), 7.00 (2H, d, *J* = 8 Hz, p 5-H × 2), 7.38 (2H, s, p 7-H × 2), 7.46 (2H, d, *J* = 8 Hz, p 4-H × 2). Anal. Calcd for $C_{31}H_{28}S_4F_6$: C, 57.92; H, 4.39. Found: C, 57.80; H, 4.45. MS *m/z* 642 (M^+).

Dithiol **5** was converted to the intralocked form **22** in 15% yield by the same procedure.

22: mp 243–246 °C; ^{1}H NMR (270 MHz, $CDCl_3$, TMS) δ 2.70 (3H, s, p Me), 2.71 (3H, s, p Me), 2.80–3.60 (8H, m, CH_2CH_2 × 2), 6.77 (1H, s, 7-H), 6.86 (1H, d, *J* = 8 Hz, 5-H), 7.50 (2H, d, *J* = 8 Hz, 4-H, 5′-H), 7.51 (1H, s, 7′-H), 7.98 (1H, d, *J* = 8 Hz, 4′-H). Anal. Calcd for $C_{27}H_{20}S_4F_6$: C, 55.27; H, 3.44. Found: C, 55.01; H, 3.54. MS *m/z* 586 (M^+).

General Procedure of Bond Scission of Intramolecular Disulfide. A Typical Example for 21. An amount of 4.0 mg of **21** was dissolved in 100 mL of THF containing 0.5 mL of water, 6.3 mg of tri-n-butylphosphine was added, and the solution was stirred for 1 h at room temperature to give **4**.

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