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Unusual Photochromic Behavior of C3-Methoxy-Substituted Bis(2-thienyl)perfluorocyclopentene

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A bis(2-thienyl)perfluorocyclopentene having methoxy groups at both reactive carbon atoms was synthesized and the quantum yields of cyclization and cycloreversion reactions were found to be 0.29 and 0.27, respectively. Usual bis(3-thienyl)perfluorocyclopentenes with methoxy groups at both reactive carbon atoms show much lower cycloreversion quantum yields. The unusual large yield was explained by theoretical methods. Additionally the compound did not show any coloration in crystalline state upon UV irradiation, even though the distance between both reactive carbon atoms is less than 4 Å. The reason was discussed by using the crystallographic data.

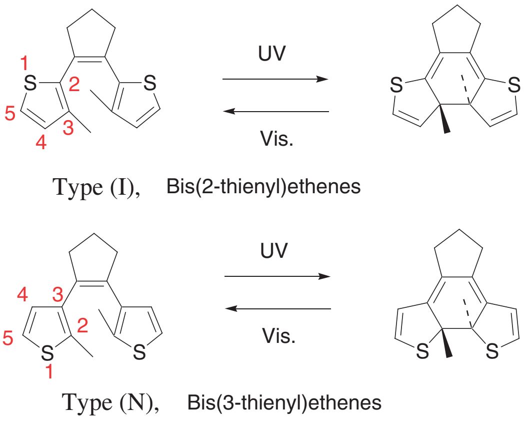
Diarylethenes are well-known photochromic compounds that show reversible color change upon alternate irradiation of UV and visible light.[1] In the family of diarylethenes, there are two groups: Normal (N) type,[2] such as bis(3-thienyl)ethenes whose thiophene rings are connected to ethene moiety at the 3-positions of both thiophene rings, and another type (Inverse (I)),[3] such as bis(2-thienyl)ethenes whose thiophene rings are connected at the 2-positions. Both types of diarylethene derivatives show excellent properties, including thermal stability of open- and closed-ring isomers and fatigue resistance on the photochromic performance. Property changes associated with their photoreversible structural changes are reported. For example, the absorption bands of the open-ring isomers of derivatives of type (I): bis(2-thienyl)ethenes have the absorption bands at longer wavelengths compared with those of type (N): bis(3-thienyl)ethenes. On the contrary, the closed-ring isomers of bis(2-thienyl)ethenes have the bands at shorter wavelengths compared with those of bis(3-thienyl)ethenes. The results were attributed to the longer conjugate chain length of the open-ring isomers of bis(2-thienyl)ethene derivatives and the shorter conjugate chain length of the closed-ring isomers of the derivatives (Scheme 1).

Here, we report new photochromic properties of type (I) bis(2-thienyl)ethenes in the substituent effect and photochromic reactivity in the crystalline state. These properties are neither observed nor expected in type (N) derivatives. We discuss these interesting properties with the aid of X-ray structural data and theoretical results.

Results and Discussion

Synthesis of Bis(3-methoxy-2-thieyl)perfluorocyclopentene (3o). Diarylethene **3** (Scheme 2) was newly synthesized and its photochromic properties were compared with those of other derivatives. Although the synthesis of **3o** was attempted in the usual method described in the literature,[3] the yield was low with low reproducibility. Therefore, we used the microreactor[4] for the synthesis and the apparatus is illustrated in Figure 1. Owing to this reactor, we could obtain constant yield and stable reproducibility which enabled us to carry out the current study.

Substituent Effect on the Photochromic Reactions. We examined photochromic behavior of the newly synthesized **3** compared with other known derivatives. The spectral changes of **3** in hexane solution are shown in Figure 2. Open-ring isomer **3o** shows the absorption maximum at 327 nm ($1.3 \times 10^4\,\mathrm{M^{-1}\,cm^{-1}}$). Upon UV (366 nm) irradiation to the solution, the intensity of the band decreased, the new band



Scheme 1.

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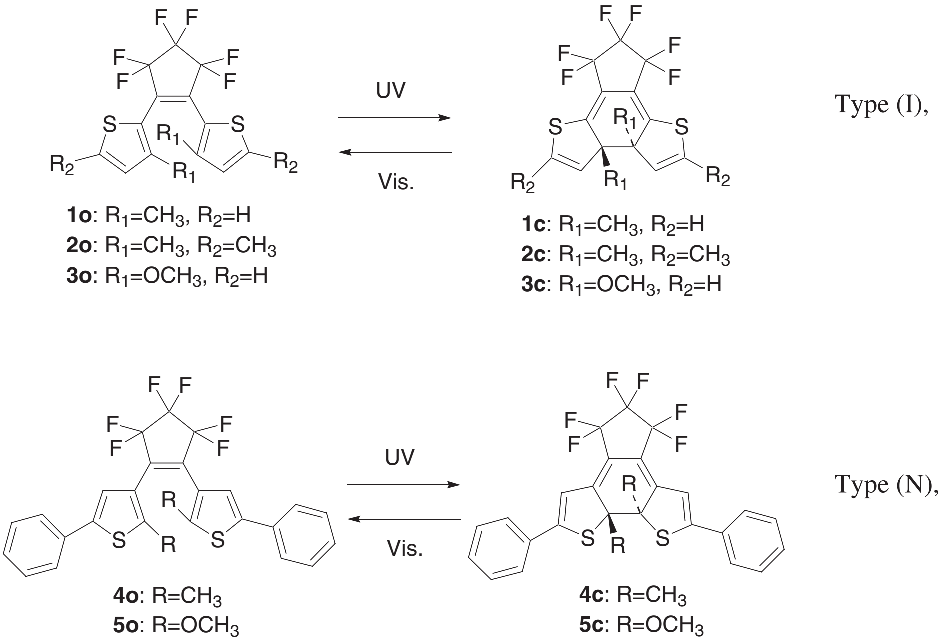


Scheme 2.

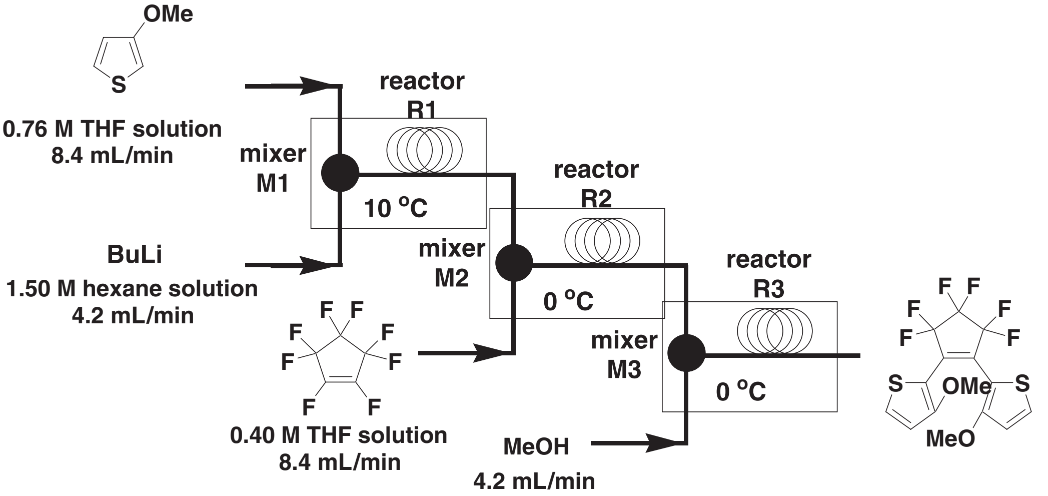


Figure 1. Microflow system for synthesis of diarylethene **3**.

appeared at 480 nm and the color of the solution turned orange. The band was attributed to the closed-ring isomer **3c**, whose absorption coefficient was $4.2 \times 10^3\,M^{-1}\,cm^{-1}$ at the wavelength. At the photostationary state, the ratio of the **3o** to **3c** was 2:8. It indicates that the photocyclization was reached at 80% conversion. Upon visible light irradiation, the original band was restored, accompanied by the disappearance of the orange color.

The cyclization and the cycloreversion reaction quantum yields of **3** in hexane were determined to be 0.29 and 0.27, respectively. The results were compared with other derivatives of the same type (I): bis(2-thienyl)perfluorocyclopentenes **1** and **2**, and are summarized in Table 1. It has been reported that in type (N) derivatives the introduction of methoxy groups at both reactive carbon atoms drastically reduced the quantum yield of the cycloreversion reaction.[5] For example, the cycloreversion quantum yield for **4c** was 1.3×10^{-2}, while that for **5c** with methoxy substituents was less than 2.0×10^{-5}.[5a] The reason for this decrease was interpreted by CASSCF level theoretical calculation on the basis of the excited state potential energy surface. It is concluded that the barrier exists on the excited state potential energy surface and its height depends on the substituent, thus the quantum yield is correlated with the height of the barrier.[6] We believe that the theoretical explanation of quantum yield is very valuable because it is very difficult to predict without the aid of theoretical calculation. On the other hand, such a remarkable substituent effect of the methoxy group was not observed for the type (I) bis(2-thienyl)perfluorocyclopentene derivatives. As shown in Table 1, it is from 0.37 of **1** with methyl substituents to 0.27 of **3**, with only a small decrease. As suggested by the theoretical study for the type (I) derivatives that we have previously reported,[7] it is, in fact, possible to understand these experimental results through the potential surfaces for both shown in Figure 3, which is

Table 1. Spectroscopic Properties of Bis(2-thienyl)perfluorocyclopentenes in Hexane

	λ_{max}/nm (ε/M^{-1} cm^{-1})	$\phi_{o \to c}$		λ_{max}/nm (ε/M^{-1} cm^{-1})	$\phi_{c \to o}$
1o	316 (1.2×10^4)	0.54 (313 nm)	**1c**	432 (6.87×10^3)	0.37 (432 nm)
2o	336 (1.3×10^4)	0.40 (366 nm)	**2c**	425 (5.8×10^3)	0.58 (425 nm)
3o	327 (1.3×10^4)	0.29 (280 nm)	**3c**	481 (4.2×10^3)	0.27 (492 nm)

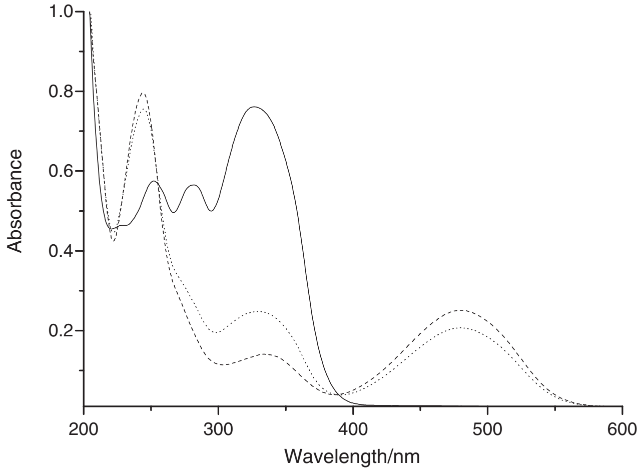
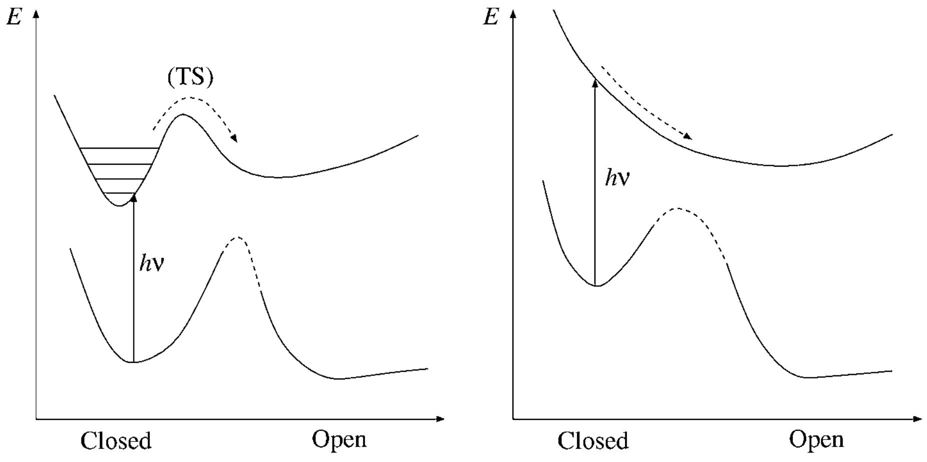


Figure 2. Absorption spectral changes of diarylethene **3** in hexane solution (5.8×10^{-5} M; solid line: **3o**, broken line: **3c**, and dotted line: photostationary state under 366 nm irradiation).

Table 2. Calculated Excitation Wavelengths, Oscillator Strengths, and Energy Differences between Closed- and Open-Ring Isomers

	$\lambda^{a)}$/nm (Oscillator strength)		$\lambda^{a)}$/nm (Oscillator strength)	$E_c - E_o$$^{b)}$ /kcal mol^{-1}	$G_c - G_o$$^{b)}$ /kcal mol^{-1}
1o	336 (0.309)	**1c**	444 (0.082)	28.5	30.2
2o	352 (0.382)	**2c**	437 (0.087)	26.1	28.3
3o	356 (0.317)	**3c**	507 (0.057)	29.7	31.6
4o	351 (0.037)$^{c)}$	**4c**	606 (0.424)	14.3	16.4
5o	357 (0.230)	**5c**	688 (0.339)	12.3	14.6

a) The excitation wavelengths and oscillator strengths of the first excited states are shown. b) E_c (G_c) and E_o (G_o) are the ground state energies with zero point energy corrections (the ground state free energies) for open- and closed-ring isomers, respectively. c) The 4th and 5th excited states of **4o** have large oscillator strengths. The excitation wavelengths (oscillator strengths) of the 4th and 5th excited states are 294 (0.386) and 286 (1.056), respectively.



Normal-type (N) Invert-type (I)

Figure 3. Schematic potential surfaces for type (N) and type (I).

schematized from the previous CASSCF level results.[7] In the case of type (N), there is a barrier on the excited state potential surface: therefore, it is expected that this barrier height of transition state (shown as (TS) in Figure 3) can change depending on substituents, and then the quantum yield of cycloreversion can be influenced. By contrast, in case of the type (I), as we have reported previously, there is no effective barrier on the excited state potential surface.[7] Reflecting the monotonous down-hill property of the potential surface, no substituent effect will be expected. This situation is shown schematically in the right side of Figure 3.

As further supporting information, we have compared the relative stability of the ground state open- and closed-ring isomers. For **3o**, we obtained a value of 29.7 kcal mol^{-1} (31.6 kcal mol^{-1}) (1 kcal mol^{-1} = 4.184 kJ mol^{-1}) more stable relative to **3c**, where the calculation was carried out by B3LYP/6-31G(d) level with zero point energy correction (free energy at room temperature, 298.15 °C) (Table 2). In contrast, **5o** is only 12.3 kcal mol^{-1} (14.6 kcal mol^{-1}) more stable relative to **5c**. This is consistent with our previous report that in the case of type (I), the closed-ring isomer is less stable than the open-ring isomer.[7] As far as we have investigated, $\Delta E = E_c - E_o$ of Type

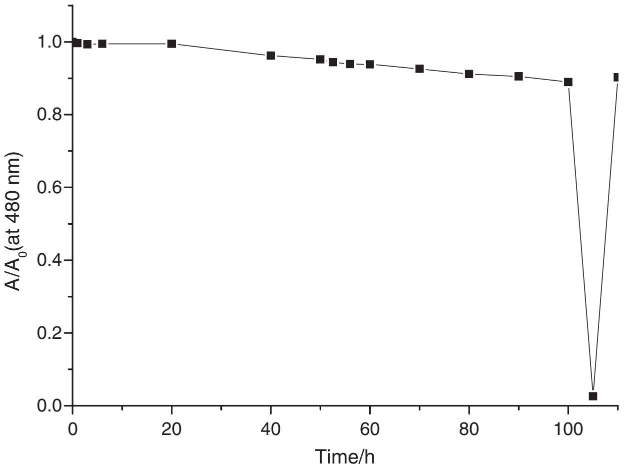


Figure 4. Thermal stability of the closed-ring isomer **3c** in hexane solution at 70 °C. After 100 h storage, visible light was irradiated to the solution, and followed by UV irradiation.

(I) is 10–15 kcal mol^{-1} larger than that of Type (N), where E_o and E_c are the ground state energy of the open- and closed-ring isomers, respectively (Table 2). Most probably, this is one of the reasons there is no effective barrier on the excited state surface (Notice that the computational results of the relative stability of the open- and closed-ring isomers in the ground state may depend on the choice of the basis sets.[6,7] The current study shows that ΔE of the type (N) derivatives show a positive value, but it could be negative.[6,7]).

Thermal Stability of 3c in Hexane Solution. In order to evaluate the above argument, we have examined the thermal stability. That is, we have confirmed that these photochromic reactions are really photochemical reactions following Woodward–Hoffmann rules, and not a mixture with thermal reactions.[8] Thermal stability of the closed-ring isomer **3c** was measured in hexane solution. The photostationary state solution of **3o** and **3c** upon UV (366 nm) irradiation was poured into a cell with a branched glass tube, and the cell was stored in an oven at 70 °C. The absorbance at the $\lambda_{\max}$ of **3c** was monitored. The intensity of the absorbance was gradually decreased and reached 90% of the initial intensity after 100 h of storage. Visible light was irradiated to the solution, the color completely disappeared indicating the formation of **3o**, and then UV light was irradiated. The absorbance recovered to 90% of the initial value (Figure 4). This result indicates the reduction of the absorbance of **3c** was not due to the thermal recovery of the closed-ring isomer, but the decomposition of **3c**. The closed-ring isomer **1c** showed high thermal stability in the same situation, and the absorbance of **1c** was kept constant after 100 h at 70 °C, indicating no thermal decomposition proceeded.

Photochromism in Crystalline State. Some diarylethenes can undergo cyclization reaction even in the crystalline state, while the other diarylethenes do not show the cyclization reaction in the crystalline state. Kobatake et al. have indicated a critical distance of 0.4 nm between the reactive carbon atoms, which is a threshold of the reaction in the crystalline state[9] (called the 0.4 nm criterion hereafter).

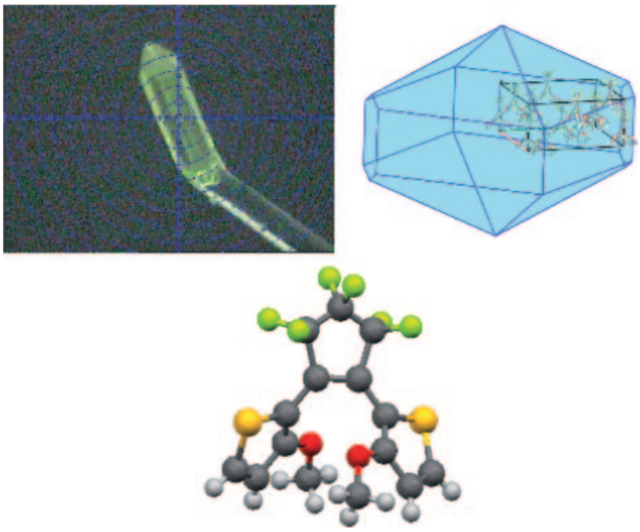


Figure 5. Pillar-shaped crystal A and molecular structure (Molecule A) in the crystal.

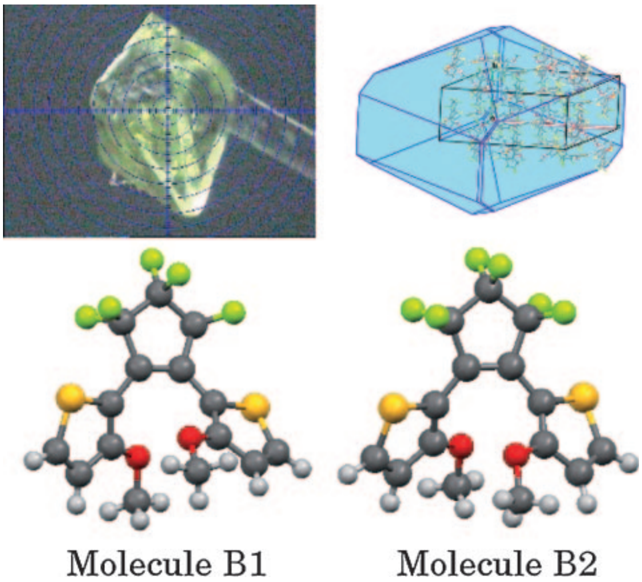


Figure 6. Prism-shaped crystal B and molecular structures (Molecule B1 and Molecule B2) in the crystal.

As for the current diarylethene, bis(2-thienyl)ethenes, this is an interesting counter example of the 0.4 nm criterion. Although we do not yet completely know the reason for this, it is noteworthy that the **3o** has two crystal structures,[10] A and B shown in Figures 5 and 6, respectively. In the pillar-like crystal, **3o** exists only in one conformation (Molecule A) where the distance of both reactive carbon atoms was 0.329 nm. On the other hand, **3o** exists in two conformers, Molecules B1 and B2 in prism-shaped crystals, where the distances were 0.335 and 0.334 nm, respectively. Molecules B1 and B2 have almost the same conformation and Molecule A is slightly different from Molecules B1 and B2 (Figure 7). In all cases, the distances between both reactive carbon atoms are shorter than the critical distance of 0.4 nm with which a cyclization reaction is expected: however, upon irradiation of both crystals, no coloration was observed.

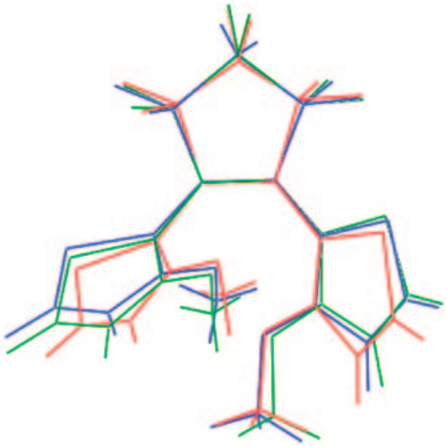


Figure 7. Superimposed molecular structures of **3o** molecules (Molecule A: red, Molecule B1: blue, and Molecule B2: green).

Among bis(2-thienyl)perfluorocyclopentenes, although **1**[11] and **2**[12] show photochromism in the crystalline state, **3o** does not show photochromism, in spite of satisfying the 0.4 nm criterion until the distance between the reacting carbons became shorter than 0.4 nm. The steric hindrance of the substituent may affect the cyclization reaction in the restricted reaction space such as the crystal. The possible explanation for no coloration is that these bulky methoxy groups require large space to react, and it is not possible in crystal. In other words, for the relatively unstable closed-ring isomer, a large geometrical change is needed to be separated with enough barriers from open-ring isomers: however, the space for necessary conformational changes is so prohibited in crystal that the reaction coordinate cannot vary sufficiently. As it has been suggested for **5o** derivative,[13] the existence of multiple local minima in ground and excited states due to the surrounding polymer may cause a quite different photoreaction process. Both **5o** and **3o** have methoxy groups at the reactive CC bond. The similarity indicates that the potential energy surface of **3o** along the reaction coordinate (the central CC bond distance) in the crystal is distorted due to the methoxy groups. In order to accomplish the complete rationalization, a careful study of the packing effect, to which the approach is not obvious, is an important subject of future theoretical study.

Conclusion

The newly synthesized bis(3-methoxy-2-thienyl)perfluorocyclopentene unexpectedly showed the large cycloreversion quantum yield in spite of the existence of methoxy groups at both reactive carbon atoms unlike bis(2-methoxy-3-thienyl)-perfluorocyclopentene. The reason was attributed to the difference in the potential surfaces in their exited state. Bis(3-thienyl)perfluorocyclopentenes have an energy barrier on the surface during cycloreversion while bis(2-thienyl)perfluorocyclopentenes have no barrier. Introduction of methoxy groups to the former would raise the barrier and reduce the quantum yields, while the substituent effect was not observed for the new derivative because of the lack of barrier. Additionally the compound showed an exception to the photoreactivity in the crystalline state. The study on the photoreactivity of bis(2-thienyl)perfluorocyclopentenes should be continued to clarify the relation between the reactivity and distance of both reactive carbon atoms in the derivatives.

Experimental

Absorption spectra were measured with an absorption spectrometer (Hitachi U-3500). ^{1}H NMR spectra were recorded on a Bruker DPX 400 (400 MHz) spectrometer at ambient temperature. Chemical shifts are denoted in δ units relative to the solvent signals $CHCl_3$ (^{1}H NMR: δ 7.26).[14] Photoirradiation was carried out using a USHIO 500 W high-pressure mercury lamp as the exciting light source. Mercury lines at 334 and 366 nm were isolated by passing the light. Quantum yields were determined by measuring the rates of isomerization in the initial stage of the reaction at low concentration.

Synthesis of 1,2-Bis(3-methoxy-2-thienyl)perfluorocyclopentene by Ordinary Methods. In a 100-mL reaction flask containing 30 mL of ether anhydrous, 3-methoxythiophene (1.00 g, 8.76 mmol) and TMEDA (*N*,*N*,*N*′,*N*′,-tetramethylethylenediamine) (1.44 mL, 9.64 mmol) were added and the flask was cooled to 0 °C in an ice bath. To this mixture, 6.0 mL (9.64 mmol) of 1.6 M *n*-BuLi hexane solution was added dropwise and stirred for 1 h at the same temperature. Then, the flask was cooled to −10 °C in a salt–ice bath followed by addition of 0.3 mL (2.25 mmol) of octafluorocyclopentene at the same temperature. After stirring for 20 min at the temperature, 5 mL of 1 M HCl was added. To the mixture, 50 mL of ether and 50 mL of 1 M HCl were added and the ether layer was separated: then the layer was washed with 10 mL of brine. The ether solution was dried over $MgSO_4$ and the solvent was removed in vacuo. The mixture was purified by silica gel chromatography to obtain 0.21 g of yellow oil. Recrystallization was carried out by using hexane to obtain 0.15 g of 1,2-bis(3-methoxy-2-thienyl)perfluorocyclopentene (**3o**) in a 16.7% yield. Mp 84.5–84.8 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (s, 6H), 6.80 (d, 2H, $J = 5.5$ Hz), 7.41 (d, 2H, $J = 5.5$ Hz); MS (m/z) 400 (M^+).

Synthesis of 1,2-Bis(3-methoxy-2-thienyl)perfluorocyclopentene Using Microflow System. The reaction was carried out using a microflow system consisting of two T-shaped micromixers (M1, M2, and M3) (Swagelok Union Tee, channel width M1: $\phi = 0.5$ mm, M2: $\phi = 0.25$ mm, M3: $\phi = 0.5$ mm), and stainless microtube reactors (R1: $\phi = 1000\,\mu m \times 1.095$ m, R2: $\phi = 1000\,\mu m \times 2.49$ m, R3: $\phi = 1000\,\mu m \times 2.58$ m) as shown in Figure 1. A solution of 3-methoxythiophene (0.76 M) in THF and a solution of butyllithium (1.50 M) in hexane were introduced to the first micromixer (M1) at a flow rate of 8.4 and 4.2 mL min^{-1}, respectively. The resulting solution was mixed with a solution of octafluorocyclopentene (0.40 M) in THF in the second micromixer (M2) (the 2nd step) (flow rate: 8.4 mL min^{-1}). The resulting solution was quenched by methanol in the third micromixer (M3) (flow rate: 4.2 mL min^{-1}). The residence times were usually as follows: R1: 4.1 s, R2: 5.6 s, R3: 4.8 s. For the procedure, 17.35 g (1.37×10^{-1} mol) of 3-methoxythiophene, 100 mL of *n*-BuLi hexane solution, and 16.96 g (8.0×10^{-2} mol) of octafluorocyclopentene were applied. After a steady state was reached, an aliquot of the product solution was taken into a flask. Evaporation of the solvent followed by column chromatography on silica gel (hexane) yielded the bisthienyl compound (450 mg, 1.12 mmol, 2% yield).

Crystal Structure Determination. Intensity data of Crystals A and B of **3o** were collected by the ω scan on a Bruker SMART 1000 CCD diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structure was solved by direct methods using the program SHELXS97[15] and refined by full-matrix least squares against F^2 of the observed reflections with SHELXL97.[16] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at ideal positions and refined in isotropic approximation. Crystal data for Crystal A of **3o**: Orthorhombic, *Fdd*2, $a = 17.511(3)$ Å, $b = 20.195(4)$ Å, $c = 9.616(2)$ Å, $V = 3400(1)$ Å^3, $Z = 8$, $D_{\text{calcd}} = 1.564\,\text{Mg}\,\text{m}^{-3}$, $R((I) > 2\sigma(I)) = 0.1179$, CCDC-739850. Crystal B of **3o**: monoclinic, $C2/c$, $a = 28.355(8)$ Å, $b = 12.912(3)$ Å, $c = 17.495(5)$ Å, $\beta = 127.303(4)°$, $V = 5095(2)$ Å^3, $Z = 12$, $D_{\text{calcd}} = 1.566\,\text{g}\,\text{cm}^{-3}$, $R((I) > 2\sigma(I)) = 0.0716$, CCDC-739849. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge, CB2 1EZ, U.K.; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

Calculation of the Ground State Energies and the Excitation Wavelengths of Bis(3-thienyl)ethene Derivatives and Bis(2-thienyl)ethene Derivatives. The ground states of **1c**–**5c** and **1o**–**5o** were optimized by the density functional theory (DFT) with the B3LYP[17] exchange correlation functional. The C_2 symmetry has been imposed on all the structures. The zero point energies and the free energies at room temperature, 298.15 °C, were calculated using a rigid-body rotator and a harmonic oscillator model. The excitation wavelengths and oscillator strengths were obtained by the time-dependent DFT (TDDFT)[18] with the B3LYP. We have used the 6-31G(d) basis set both for the optimization of the structures and the calculation of the excited states. This level of calculation has reproduced the results given by a higher level of calculation.[19] All calculations were performed by Gaussian 03.[20]

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