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Solvent effect on photochromism of a dithienylperfluorocyclopentene having diethylamino group

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ABSTRACT

Some photochromic diarylethenes having polar substituents were synthesized, and their photochromic behavior was examined. They exhibited photochromism with the similar photoreactivity in a non-polar solvent. However, the photocyclization quantum yield of dithienylperfluorocyclopentene having diethylamino group was found to decrease in polar solvents. The yield in acetonitrile was estimated to be 60 times smaller than that in hexane. The yields determined in various solvents were found to be correlated with the solvent polarity parameter $E_T(30)$. Such an effect was not observed in dithienylfluorocyclopentenes bearing methoxy or acetoxy group and in non-fluorinated dithienylcyclopentene bearing diethylamino group.

1. Introduction

Photochromic compounds have attracted much attention to cause reversible property changes of not only coloration but also geometrical structure, dielectric constant, refractive index, and fluorescence by photoirradiation.[1,2] Photochromic compounds are classified into two types, thermally unstable type (T-type) and thermally stable type (P-type) of the photogenerated isomers.[1,3] Azobenzene and spiropyran belong to T-type photochromic compounds. Among various photochromic compounds, diarylethenes with heterocyclic aryl rings have been developed as a P-type photochromic compound because of some excellent characteristics such as thermal stability of both isomers and fatigue-resistant property.[4–8] The diarylethenes can be potentially used for application to optical memory media,[9–11] switching devices,[12–14] display materials,[15,16] and photo-mechanical actuators.[17–20]

The solvent effects on the reactivity and the absorption band of photochromic compounds have been reported for spiropyrans,[21–24] spirooxazines,[25] furylfulgides,[26] and diarylethenes.[27–31] In most cases the dipole moment of the molecules plays an important role of the solvent effects. Diarylethenes having maleic anhydride and maleimide at the ethene part have high reactivity in non-polar solvents and low reactivity in polar solvents.[27] It has been reported to be due to the formation of a twisted intramolecular charge transfer (TICT) state in the open-ring isomer in polar solvents at the excited state, which has a photoinactive conformation.[32]

We have recently designed and synthesized some diarylethenes for novel material applications. Diarylethene molecules that show photochromism and acidichromism were designed.[33] P-Type photochromic diarylethenes with diethylamino group can switch to T-type photochromic system by the addition of an acid as the external stimuli.[33] Introduction of substituents to photochromic diarylethenes may give us new possibility of novel properties.[34] In this work, we have investigated the photochromic reactivities of diarylethene **1a** in various solvents and found that the photocyclization quantum yield of **1a** is strongly dependent on the solvent polarity. The effect was unique in comparison with other diarylethenes **2a**–**5a** (Scheme 1). The solvent effect was correlated with the solvent polarity parameter $E_T(30)$, which represents the molar electronic transition energies of a betaine as the overall polarity of solvents.[35]

2. Results and discussion

2.1. Photochromic behavior

Photochromic reactivity of **1a** was examined in various solvents. Figure 1 shows absorption spectral changes of **1a** in hexane and acetonitrile. Upon irradiation with 313-nm light, the color of

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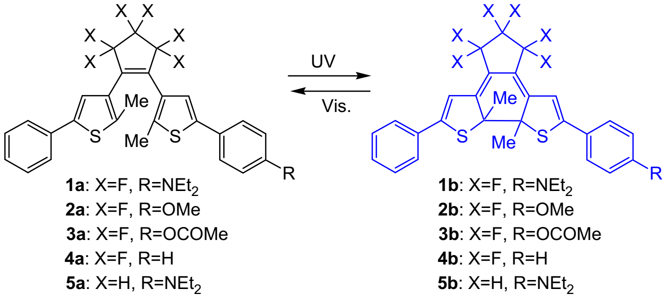


Scheme 1. Photochromic reactions of diarylethenes **1a**–**5a**.

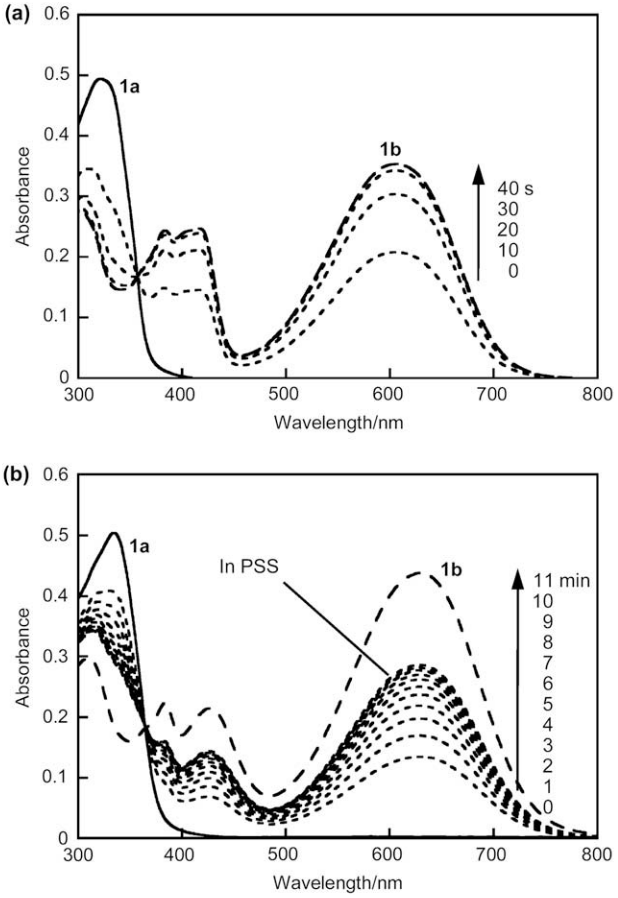


Figure 1. Absorption spectral changes of diarylethene **1a** in hexane (1.4×10^{-5} M) (a) and acetonitrile (1.5×10^{-5} M) (b) upon irradiation with 313-nm light.

the solution turned to blue and green in hexane and acetonitrile, respectively. The colored solution was bleached by irradiation with visible light ($\lambda>520$ nm) in both solutions. Table 1 shows absorption maxima and absorption coefficients of the open- and closed-ring isomers. The absorption bands of **1a** and **1b** were shifted to bathochromic by the solvent polarity. The solvent effect of the absorption band was observed in the closed-ring isomer more effectively than in the open-ring isomer. The absorption maximum of the colored isomer **1b** was observed at 607 and 630 nm in hexane and acetonitrile, respectively, depending on the solvent polarity. The absorption coefficient of **1b** increased according to the shift of the absorption band to the longer wavelength. These findings indicate that the molecule **1b** has relatively large dipole moment and the molecule at the π–π* excited state is more stable in polar solvents. This is due to π–π* excitation solvent effect called solvatochromism.[36] Solvatochromism is arised from the interaction between the dipole moments of the solvent and the molecule. As a result, solvatochromism appears to a large effect if the difference in the dipole moments at the ground state and the excited state is large.[35]

Figure 2 shows absorption spectral changes of **2a** in hexane and acetonitrile upon irradiation with 313-nm light. The absorption maximum of **2a** was not shifted by the difference in the solvents. Diarylethene **3a** also exhibited the similar photochromic behavior in hexane and in acetonitrile. The absorption maxima of the closed-ring isomers in acetonitrile were shifted to only 10 nm longer wavelength than that in hexane, whereas that of **1b** in acetonitrile was shifted to 23 nm longer than that in hexane. The results are similar to that of diarylethene without any substituent (R=H) (**4a**). Even in non-fluorinated diarylethene with diethylamino group (**5a**) and its closed-ring isomer (**5b**), the absorption maxima were not changed by the solvent in spite of having diethylamino group. These results indicate that both the strong electron-donating character of diethylamino group and the electron-accepting character of the perfluorocyclopentene play an important role of the solvent effect for solvatochromism.

The solvent effect was also observed for the photoreactivity. Upon irradiation with 313-nm light, the photocyclization of **1a** proceeded to 100% conversion in hexane, whereas in acetonitrile the conversion was only 66% in the photostationary state (PSS) at the slower rate than that in hexane. The difference of the photocyclization conversion between in hexane and in acetonitrile was not observed for other diarylethenes **2a**–**5a**. This indicates that the solvent effect of the photocyclization of **1a** is unique. The electron-donating and electron-accepting characters for diethylamino group and perfluorocyclopentene ring were also strongly affected by the solvent effect of the photochromic reaction.

Table 1
Photochemical properties of **1**–**5** in hexane and acetonitrile

Diarylethene	In hexane						In acetonitrile					
	Open-ring isomer		Closed-ring isomer		$\Phi_{a\to b}$	Conversion[a]/%	Open-ring isomer		Closed-ring isomer		$\Phi_{a\to b}$	Conversion[a]/%
	λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}			λ_{max}/nm	ε/M^{-1} cm^{-1}	λ_{max}/nm	ε/M^{-1} cm^{-1}		
1[b]	323	35,100	607	25,100	0.66	100	335	32,500	630	28,300	0.011	66
2	290	41,200	580	19,500	0.57	97	291	42,000	590	21,000	0.55	99
3	284	40,500	575	19,100	0.53	92	286	39,100	585	17,700	0.50	94
4[c]	280	35,600	575	15,600	0.59	97	285	37,100	587	16,800	0.56	97
5[b]	321	32,500	538	23,400	0.51	100	329	26,600	540	22,400	0.70	100

[a] Upon irradiation with 313-nm light.
[b] Ref. 33.
[c] The results in hexane were cited from Ref. 37.

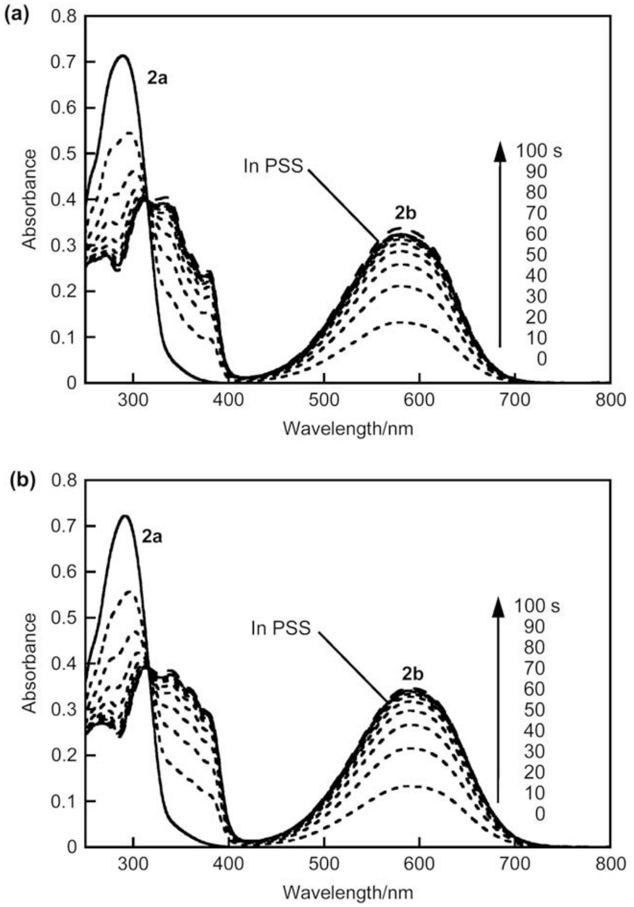


Figure 2. Absorption spectral changes of diarylethene **2a** in hexane (1.7×10^{-5} M) (a) and acetonitrile (1.7×10^{-5} M) (b) upon irradiation with 313-nm light.

2.2. Quantum yield

The photochromic conversion is related to the photocyclization and photocycloreversion quantum yields. Therefore, their yields of **1**–**5** were examined. As shown in Table 1, the photocyclization quantum yields of **1a** were largely different in hexane and acetonitrile. However, other diarylethenes **2a**–**5a** showed similar quantum yields in hexane and acetonitrile. These results indicate that only diarylethene **1a** exhibits the solvent effect to the reactivity.

To investigate the difference in the photoreactivity of **1a** by the solvent polarity in more detail, the photocyclization and cycloreversion quantum yields were examined in various solvents. Table 2 shows photocyclization and photocycloreversion quantum yields in hexane, toluene, tetrahydrofuran (THF), and acetonitrile. The photocyclization quantum yields were estimated to be 0.66 and 0.011 in hexane and acetonitrile, respectively. The value in acetonitrile was found to be 60 times smaller than that in hexane. The yields remarkably decreased in the polar solvents. When the acid was added to **1a** in acetonitrile, the photocyclization quantum yield increased to be 0.63. On the other hand, the photocycloreversion quantum yields were similar in both solutions. The slower photocoloration rate and the lower conversion in PSS in acetonitrile are due to the smaller photocyclization quantum yield.

The quantum yields were also measured in mixed solvents of toluene and acetonitrile. Figure 3 shows the photocyclization quantum yields measured in the mixed solvents. The quantum yields decreased with the increasing volume fraction of acetonitrile. This indicates that the solvent polarity strongly affects the photocyclization quantum yield. A decrease in the photocyclization quantum yields with increasing solvent polarity was ascribed to the presence of the TICT state in the excited state.[27] In non-polar solvents, diarylethenes have a photoreactive planar antiparallel conformation and a photoinactive parallel conformation both in the excited state and in the ground state. However, in polar solvents, the photoinactive twisted antiparallel conformation in the TICT state has an advantage rather than the photoreactive planar antiparallel conformation in the excited state because the TICT state is more stable than the planar conformation in the excited state. As a result, the photocyclization quantum yields decreased in polar solvents. The sensitivity of the solvent effect to the quantum yields depends on the strength of electron-donating and electron-accepting characters in the molecules.

In order to correlate the relationship between the photocyclization quantum yields and the solvent polarity, we employed $E_T(30)$ as a polar parameter of solvents.[35] Figure 4 shows the relationship between the photocyclization quantum yields and $E_T(30)$. The $E_T(30)$ values for the mixed solvent of toluene and acetonitrile were cited from Ref. 23. When we used solvents, of which $E_T(30)$ is smaller than 146 kJ mol^{-1}, diarylethene **1a** exhibited the photocyclization reaction with the high cyclization quantum yield. This indicates that such solvents have no interaction with **1a** in the excited state. However, when $E_T(30)$ is larger than 146 kJ mol^{-1}, the cyclization quantum yield decreased. In such cases, the population

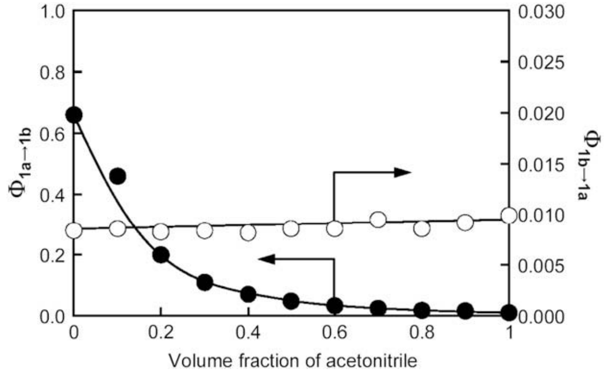


Figure 3. Photocyclization and photocycloreversion quantum yields in mixed solvents of toluene and acetonitrile. Photocyclization and photocycloreversion reactions were carried out upon irradiation with 313- and 500-nm light, respectively.

Table 2
Photochemical properties of **1a** in various solvents

Solvent	1a		$\Phi_{1a\rightarrow1b}$	1b		$\Phi_{1b\rightarrow1a}$	Conversion[a]/%
	λ_{max}/nm	ε/M^{-1} cm^{-1}		λ_{max}/nm	ε/M^{-1} cm^{-1}		
Hexane	323	35,100	0.66	607	25,100	0.0053	100
Toluene	335	30,200	0.66	626	24,500	0.0084	99
THF	334	33,600	0.32	631	28,100	0.0074	98
Acetonitrile	335	32,500	0.011	630	28,300	0.0099	66
Acetonitrile[b]	293	37,400	0.63	590	15,800	0.015	99

[a] Upon irradiation with 313-nm light.
[b] In the presence of 10 equiv of CF_3SO_3H relative to **1a**.[33]

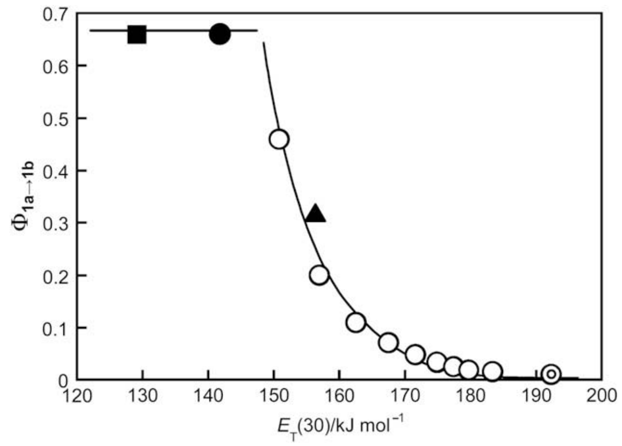


Figure 4. Relationship between photocyclization quantum yield and $E_T(30)$ of solvents (■: hexane, ●: toluene, ▲: THF, ⊙: acetonitrile, ○: mixture of toluene and acetonitrile).

in the photoinactive twisted antiparallel conformation increases relative to the photoreactive antiparallel conformation in the excited state. The good relationship between the cyclization quantum yield and $E_T(30)$ was observed. The linear relationship was observed by the plot of $\ln(1/\Phi)$ against $E_T(30)$, as shown in Figure 5.

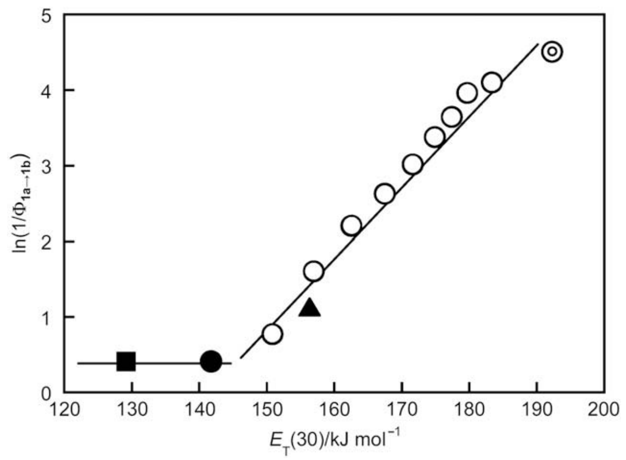


Figure 5. Relationship between $\ln(1/\Phi)$ and $E_T(30)$ of solvents (■: hexane, ●: toluene, ▲: THF, ⊙: acetonitrile, ○: mixture of toluene and acetonitrile).

3. Conclusion

We examined the photochromic property and reactivity of some diarylethenes bearing polar substituents in polar and non-polar solvents. Diarylethene **1a** and its closed-ring isomer showed solvatochromism because the excitation of diarylethene **1a** is considered to have a large dipole moment in comparison with the ground state. The solvent dependence of **2a**–**5a** was hardly observed. The photocyclization quantum yield of **1a** also showed the solvent effect and was correlated with $E_T(30)$. The solvent effect of diarylethene **1a** is due to the formation of the TICT state in the excited state by the strong electron-donating character of the diethylamino group and the strong electron-accepting character of perfluorocyclopentene ring.

4. Experimental section

4.1. General

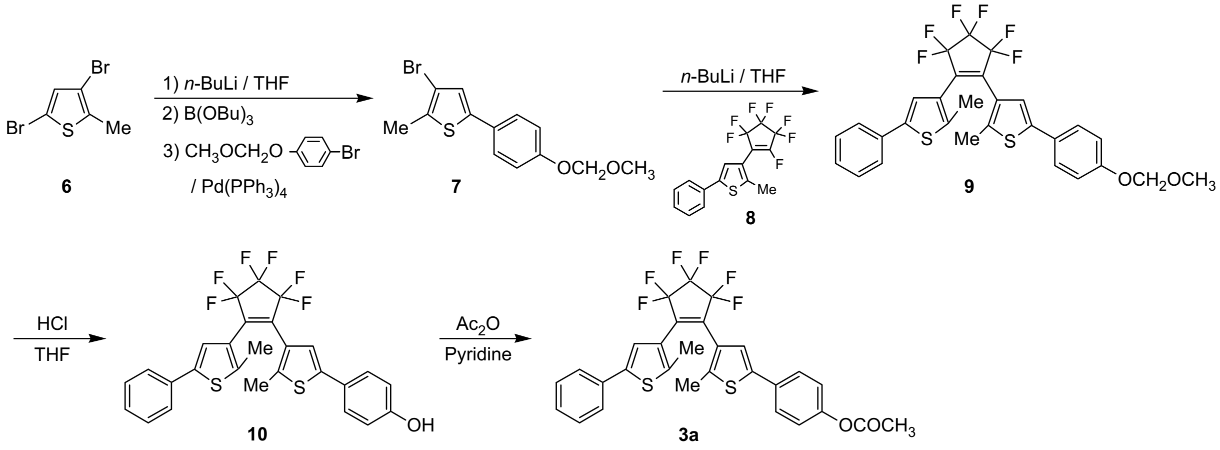
Solvents used were spectroscopic grade and purified by distillation. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AV300N NMR spectrometer. IR spectra were recorded on a JASCO FT/IR-410 spectrometer. Mass spectra were obtained on a Jeol JMS-700T (FAB) spectrometer. Elemental analysis was performed with an Elementar vario EL III. Absorption spectra were performed with a JASCO V-560 spectrophotometer. Photoirradiation was carried out using a 200 W mercury–xenon lamp (Moritex MUV-202) as the light source. Monochromic light was obtained by passing the light through a monochromator and a UV filter or a colored filter. The relative quantum yields were determined by comparing the reaction yield with a reference sample.

4.2. Synthesis

Diarylethenes **1a**,[33] **2a**,[38] **4a**,[37] and **5a**[33] were prepared according to the methods in the literature. Diarylethene **3a** was prepared according to the synthetic routes as shown in Scheme 2.

4.2.1. *1-(2-Methyl-5-(4-(methoxymethoxy)phenyl)thien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene (**9**)*

Under an argon atmosphere, 1.6 M *n*-butyllithium in hexane (4.0 mL, 6.4 mmol) was added dropwise to a solution of **7**[39] (1.7 g, 5.4 mmol) in dry THF (100 mL) at −78 °C. The solution was stirred for 2 h at the same temperature. To the solution was added dropwise the mixture of 1-(2-methyl-5-phenylthien-3-yl)heptafluorocyclopentene (**8**)[40] (1.2 g, 3.3 mmol) and dry THF (10 mL) at −78 °C, and then the mixture was stirred for 4 h at the same



Scheme 2. Synthetic routes of diarylethene **3a**.

temperature. The reaction was stopped by the addition of water. The solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (9:1) as the eluent. Compound **9** was obtained as a colorless solid by further purification by HPLC (0.81 g, 42%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ=1.95 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 3.49 (s, 3H, OCH_3), 5.20 (s, 2H, OCH_2O), 7.05 (d, J=8.8 Hz, 2H, Ar), 7.17 (s, 1H, thienyl H), 7.28 (s, 1H, thienyl H), 7.30 (t, J=7.4 Hz, 1H, Ar), 7.39 (t, J=7.4 Hz, 2H, Ar), 7.46 (d, J=8.8 Hz, 2H, Ar), 7.54 (d, J=7.4 Hz, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.5, 14.6, 56.1, 94.4, 111.1 (t of quintet, J_{C-F}=271, 271, 25, 25, 25, 25 Hz), 116.2 (tt, J_{C-F}=257, 257, 24, 24 Hz), 116.7, 121.5, 122.4, 125.6, 125.7, 125.9, 126.9, 127.3, 127.9, 129.0, 133.3, 136.0, 140.5, 141.3, 142.0, 142.2, 157.1. HRMS (FAB) calcd for $C_{29}H_{22}F_6O_2S_2$ 580.0965, found 580.0985.

*4.2.2. 1-(2-Methyl-5-(4-hydroxyphenyl)thien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene (**10**)*

Into a flask containing diarylethene **9** (0.70 g, 1.2 mmol) in THF (15 mL) was added concd hydrochloric acid (2 mL), and the solution was stirred overnight at room temperature. The solution was neutralized and extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (8:2) as the eluent. Compound **10** was obtained as a solid by further purification by HPLC (0.59 g, 92%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ=1.94 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 4.90 (br, 1H, OH), 6.85 (d, J=8.1 Hz, 2H, Ar), 7.16 (s, 1H, thienyl H), 7.28 (s, 1H, thienyl H), 7.30 (t, J=7.6 Hz, 1H, Ar), 7.38 (t, J=7.6 Hz, 2H, Ar), 7.42 (d, J=8.1 Hz, 2H, Ar), 7.54 (d, J=7.6 Hz, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.5, 14.6, 111.1 (t of quintet, J_{C-F}=271, 271, 25, 25, 25, 25 Hz), 115.9, 116.2 (tt, J_{C-F}=257, 257, 24, 24 Hz), 121.3, 122.4, 125.6, 125.7, 125.9, 126.4, 127.2, 127.9, 129.0, 133.3, 136.1, 140.3, 141.3, 142.0, 142.2, 155.5. IR (KBr): ν=3380 cm^{-1} (br, OH); HRMS (FAB) calcd for $C_{27}H_{18}F_6OS_2$ 536.0703, found 536.0701.

*4.2.3. 1-(2-Methyl-5-(4-acetoxyphenyl)thien-3-yl)-2-(2-methyl-5-phenylthien-3-yl)perfluorocyclopentene (**3a**)*

Into a flask were added diarylethene **10** (0.27 g, 0.50 mmol), acetic anhydride (0.24 g, 2.4 mmol), and pyridine (0.080 g, 1.0 mmol). The solution was stirred overnight at room temperature. The solution was extracted with ether. The organic layer was washed with water, dried over $MgSO_4$, filtered, and concentrated. The residue was purified by silica gel column chromatography with hexane/ethyl acetate (8:2) as the eluent. Compound **3a** was obtained as a solid by further purification by HPLC (0.24 g, 83%).

^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ=1.952 (s, 3H, CH_3), 1.959 (s, 3H, CH_3), 2.32 (s, 3H, $COCH_3$), 7.11 (d, J=8.8 Hz, 2H, Ar), 7.24 (s, 1H, thienyl H), 7.28 (s, 1H, thienyl H), 7.30 (t, J=7.4 Hz, 1H, Ar), 7.39 (t, J=7.4 Hz, 2H, Ar), 7.54 (d, J=8.8 Hz, 2H, Ar), 7.54 (d, J=7.4 Hz, 2H, Ar). ^{13}C NMR (75 MHz, $CDCl_3$) δ=14.5, 21.1, 111.0 (t of quintet, J_{C-F}=271, 271, 25, 25, 25, 25 Hz), 116.2 (tt, J_{C-F}=257, 257, 24, 24 Hz), 122.2, 122.3, 122.6, 125.6, 125.8, 125.9, 126.7, 127.9, 129.0, 131.2, 133.3, 136.1, 141.3, 141.5, 142.3, 150.3, 169.4. IR (KBr): ν=1770 cm^{-1} (s, C=O); HRMS (FAB) calcd for $C_{29}H_{20}F_6O_2S_2$ 578.0809, found 578.0809. Anal. Calcd for $C_{29}H_{20}F_6O_2S_2$: C, 60.20; H, 3.48%. Found: C, 60.27; H, 3.56%.

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References and notes

1. Brown, G. H. *Photochromism*; Wiley-Interscience: New York, NY, 1971.
2. Dürr, H.; Bouas-Laurent, H. *Photochromism: Molecules and Systems* Rev. Ed.; Elsevier: Amsterdam, 2003.
3. Kobatake, S.; Irie, M. *Annu. Rep. Prog. Chem., Sect. C* **2003**, *99*, 272–313.
4. Irie, M.; Uchida, K. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 985–996.
5. Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716.
6. Myles, A. J.; Branda, N. R. *Adv. Funct. Mater.* **2002**, *12*, 167–173.
7. Kobatake, S.; Irie, M. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 195–210.
8. Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792.
9. Irie, M.; Matsuda, K. Memories. In *Electron Transfer in Chemistry*; Balzani, V., Ed.; Wiley-VCH: Weinheim, 2001; Vol. 5, pp 215–242.
10. Irie, M. High-Density Optical Memory and Ultrafine Photofabrication. In *Nano-Optics*; Kawata, S., Ohtsu, M., Irie, M., Eds.; Springer: Berlin, 2002; pp 137–150.
11. Tian, H.; Feng, Y. *J. Mater. Chem.* **2008**, *18*, 1617–1622.
12. Irie, M. Photoswitchable Molecular Systems Based on Diarylethenes. In *Molecular Switchings*; Feringa, B. L., Ed.; Wiley-VCH: Weinheim, 2001; pp 37–62.
13. Matsuda, K.; Irie, M. Photoswiching of Intermolecular Magnetic Interaction Using Photochromic Compounds. In *Chemistry of Nano-molecular Systems-Toward the Realization of Molecular Devices*; Nakamura, T., Matsumoto, T., Tada, H., Sugiura, K. I., Eds.; Springer: Berlin, 2002; pp 25–40.
14. Tan, W.; Zhang, Q.; Zhang, J.; Tian, H. *Org. Lett.* **2009**, *11*, 161–164.
15. Yao, J.; Hashimoto, K.; Fujishima, A. *Nature* **1992**, *355*, 624–626.
16. Fernandez-Acebes, A.; Lehn, J. M. *Adv. Mater.* **1999**, *11*, 910–913.
17. Irie, M.; Kobatake, S.; Horichi, M. *Science* **2001**, *291*, 1769–1772.
18. Kobatake, S.; Takami, S.; Muto, H.; Ishikawa, T.; Irie, M. *Nature* **2007**, *446*, 778–781.
19. Irie, M. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 917–926.
20. Uchida, K.; Sukata, S.; Matsuzawa, Y.; Akazawa, M.; de Jong, J. J. D.; Katsonis, N.; Kojima, Y.; Nakamura, S.; Areephong, J.; Meetsma, A.; Feringa, B. L. *Chem. Commun.* **2008**, 326–328.
21. Vandewyer, P. H.; Hoefnagels, J.; Smets, G. *Tetrahedron* **1969**, *25*, 3251–3266.
22. Sueishi, Y.; Ohcho, M.; Nishimura, N. *Bull. Chem. Soc. Jpn.* **1985**, *58*, 2608–2613.
23. Wetzler, D. E.; Aramendia, P. F.; Japas, M. L.; Fernandez-Prini, R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4955–4959.
24. Wojtyk, J. T. C.; Wasey, A.; Kazmaier, P. M.; Hoz, S.; Buncel, E. *J. Phys. Chem. A* **2000**, *104*, 9045–9055.
25. Nishikiori, H.; Tanaka, N.; Takagi, K.; Hujii, T. *Res. Chem. Intermed.* **2003**, *29*, 485–493.
26. Liang, Y. C.; Dvornikov, A. S.; Rentzepis, P. M. *J. Photochem. Photobiol., A* **1999**, *125*, 79–84.
27. Irie, M.; Sayo, K. *J. Phys. Chem.* **1992**, *96*, 7671–7674.
28. Yamaguchi, T.; Uchida, K.; Irie, M. *J. Am. Chem. Soc.* **1997**, *119*, 6066–6071.
29. de Jong, J. J. D.; Lucas, L. N.; Hania, R.; Pugzlys, A.; Kellogg, R. M.; Feringa, B. L.; Duppen, K.; van Esch, J. H. *Eur. J. Org. Chem.* **2003**, 1887–1893.
30. Tanifuji, N.; Irie, M.; Matsuda, K. *Chem. Lett.* **1997**, *36*, 1232–1233.
31. Yan, S. F.; Belov, V. N.; Bossi, M. L.; Hell, S. W. *Eur. J. Org. Chem.* **2008**, 2531–2538.
32. Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136–6138.
33. Kobatake, S.; Terakawa, Y. *Chem. Commun.* **2007**, 1698–1700.
34. Kobatake, S.; Imagawa, H.; Nakatani, H.; Nakashima, S. *New J. Chem.* **2009**, *33*, 1362–1367.
35. (a) Reichardt, C. *Solvents and Solvent Effects in Organic Chemistry*; VCH: New York, NY, 1988; pp 365–371; (b) Reichardt, C. *Chem. Rev.* **1994**, *94*, 2319–2358.
36. Hantzsch, A. *Ber. Dtsch. Chem. Ges.* **1922**, *55*, 953–979.
37. Irie, M.; Lifka, T.; Kobatake, S.; Kato, N. *J. Am. Chem. Soc.* **2000**, *122*, 4871–4876.
38. Browne, W. R.; de Jong, J. J. D.; Kudernac, T.; Walko, M.; Lucas, L. N.; Uchida, K.; van Esch, J. H.; Feringa, B. L. *Chem.—Eur. J.* **2005**, *11*, 6430–6441.
39. Arai, R.; Uemura, S.; Irie, M.; Matsuda, K. *J. Am. Chem. Soc.* **2008**, *130*, 9371–9379.
40. Yamamoto, S.; Matsuda, K.; Irie, M. *Org. Lett.* **2003**, *5*, 1769–1772.