Pergamon

Tetrahedron, Vol. 53, No. 36, pp. 12263-12271, 1997

0040-4020/97 $17.00 + 0.00

PII: S0040-4020(97)00558-9

Photochromism of Diarylethenes Having Thiophene Oligomers as the Aryl Groups

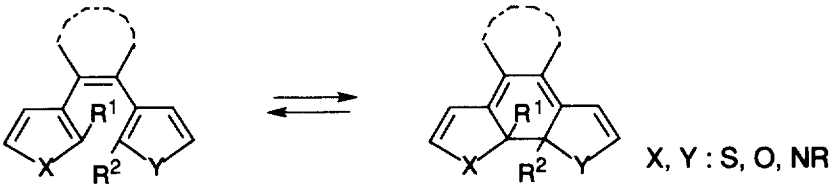
Masahiro Irie*, Takeshi Eriguchi, Toshiyuki Takada and Kingo Uchida

Department of Applied Chemistry, Faculty of Engineering
Kyushu University, Hakozaki 6-10-1, Fukuoka 812, Japan

Abstract: Diarylperfluorocyclopentenes having thiophene oligomers as the aryl groups were synthesized and their photochromic reactivity was examined. The cylization quantum yields were scarcely affected by the oligomer chain length, while the ring-opening quantum yields dramatically decreased with the increasing number of the thiophene rings. The low quantum yield of a 1,2-bis(5"-cyano-2,4-dimethyl-5,2': 5',2"-terthiophen-3-yl)perfluorocyclopentene closed-ring form was increased as large as 34 times by raising the reaction temperature from 25 °C to 150 °C. © 1997 Elsevier Science Ltd.

INTRODUCTION

Photochromism is defined as a reversible transformation of a chemical species between two forms having different absorption spectra by photoirradiation.[1] The two isomers differ from one another not only in the color but also in refractive indices, dielectric constants, oxidation / reduction potentials, and geometrical structures. The instant property change by photoirradiation without processing leads to their use in various optoelectronic devices, such as optical memory, photo-optical switching and display.[2-9] Fundamental requirements for such applications are thermal stability of both isomers and fatigue resistant characteristics. In general, photogenerated colored forms are thermally unstable and return to the initial states in the dark. Recent theoretical as well as synthetic studies[10,11] revealed the molecular design principle of thermally irreversible photochromic compounds, and new stable compounds have been synthesized.[12-20] Among the compounds, 1,2-diarylethenes with heterocyclic rings are promising candidates for the optoelectronic devices because of their thermal irreversibility and fatigue resistant characteristics. The photochromism of diarylethenes with heterocyclic rings is expressed as follows.



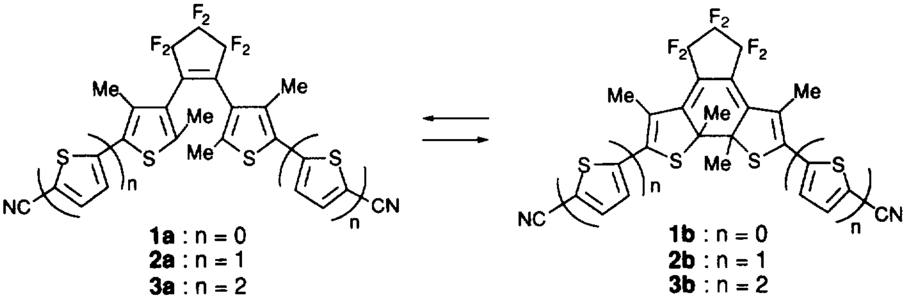
In the open-ring form the π-electrons are localized in each heterocyclic ring, and there is no π-conjugation interaction between the two rings. On the other hand, π-electrons delocalize throughout the molecule in the closed-ring form.This is the reason why the absorption maxima shift to longer wavelengths in the closed-ring forms. The diarylethene chromophore which changes the π-electron delocalization length by photoirradiation was proposed to be used as a photoswitch unit which converts from a unconjugated switched-off state to a conjugated switched-on state.[21] This kind of photoswitch was demonstrated for dithienylethenes having pyridinium ion groups [16, 21] or thiophene oligomers [18, 22] as the aryl groups.

In this study we synthesized 1,2-dithienylethenes having mono-, bi-, and terthiophene as the aryl groups, and compared their photochromic reactivity to evaluate the fundamental ability as the photoswitch unit.

RESULTS and DISCUSSION

Absorption Spectra:

Following three dithienylperfluorocyclopentenes having cyano substituents in the end thiophene rings were synthesized. The cyano group was introduced to the dithienylethenes to protect the reactive 5-position of the thiophene ring.



1a : n = 0
2a : n = 1
3a : n = 2

1b : n = 0
2b : n = 1
3b : n = 2

Figure 1 shows a typical spectral change of the photochromic reaction. 1,2- Bis (5''-cyano-2,4-dimethyl-5,2' : 5',2''-terthiophen-3-yl)perfluorocyclopentene (**3a**) has the absorption maximum at 374 nm (ε, 4.7 x 10^4 M^{-1} cm^{-1}) in toluene. Upon irradiation with 366 nm light the pale yellow solution of the open-ring form turned green, in which the absorption maximum was observed at 653 nm (ε, 2.5 x 10^4 M^{-1} cm^{-1}). The green color is due to the closed-ring form (**3b**). The green color disappeared again by irradiation with visible (> 550 nm) light. The conversion from the open- to the closed-ring form by irradiation with 366 nm light was almost 100%. In the ^1H NMR (200MHz) spectrum of the open-ring form signals of methyl protons at 4- and 2-positions of the thiophene rings appeared as doublet at 2.21 and 2.37 ppm, respectively. The doublet signals indicate dymamic equilibrium of two conformations.[11, 12, 15] Upon irradiation with 366 nm light a new singlet signal appeared at 2.29 ppm, which is assigned to methyl protons attached photogenerated sp^3 carbons, along with the decrease of the 2.37 ppm signal.

The absorption maximum of the closed-ring form was dependent on the number of thiophene rings. Figure 2 shows the spectra of the three compounds **1b**, **2b** and **3b**. The maximum at 588 nm of the closed-ring form of 1,2-bis(5-cyano-2,4-dimethylthiophen-3-yl)perfluorocyclopentene (**1b**), a monothiophene derivative, shifted to 653 nm when terthiophene was used as the aryl groups such as **3b**. At the same time the absorption coefficient increased. The coefficient of the terthiophene derivative (**3b**) was four times larger than that of the monothiophene derivative (**1b**). The absorption maximum and coefficient of the bithiophene derivative(**2b**) was in between the mono- and terthiophene derivatives. The absorption maximum (630 nm) of the bithiophene derivative (**2b**) is much longer than the maximum (570 nm) of 1,2-bis (2,4-dimethyl-5-(4-cyanophenyl)thiophen-3-yl)perfluorocyclopentene(TPCN), which has phenyl groups instead of thiophene rings of **2b**.[15] The large shift is ascribable to the good coplanarity of the two thiophene rings, which favors the delocalization of π-electrons. Table 1 summarizes the absorption maxima and coefficients of the close-ring forms in toluene.

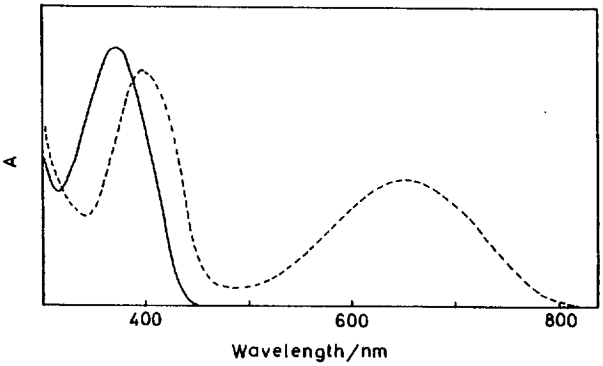


Figure 1. Absorption spectra of **3** in toluene (—) before photoirradiation and (- - -) after irradiation with 366 nm light at room temperature.

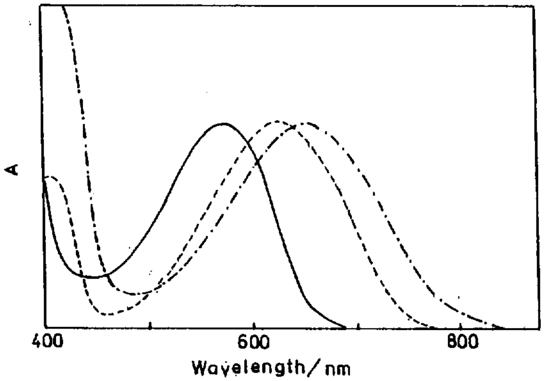


Figure 2. Absorption spectra of **1b**(—), **2b**(- - -) and **3b**(— • —) in toluene at room temperature. The absorption maximum intensity was normalized.

Table 1 Absorption Maxima (λ max) and Coefficients (ε) of the Closed-ring Forms of Dithienylethenes **1b**, **2b** and **3b** in toluene.

	1b	**2b**	**3b**
λ max/ nm	588	630	653
ε / M^{-1} cm^{-1}	6,300	15,000	25,000

Quantum Yields:

Dithienylperfluorocyclopentenes, in general, have large cylization quantum yields. The quantum yield of TPCN is as large as 0.50 in hexane.[15] The yield is larger than that of 1,2-bis(2,4-dimethylthiophen-3-yl)perfluorocyclopentene, which has no phenyl substituent. It is of significance to reveal the substituent effect at 5-position of the thiophene rings on the quantum yields from the view point of their use as photoswitch units.

The cyclization and ring-opening quantum yields of **1**-**3** were measured in toluene at 25°C. The cyclization quantum yields slightly decreased with the increasing number of thiophene rings in the aryl groups, as shown in Table 2. The quantum yield as large as 0.44 was observed for **1a**, while it decreased to 0.12 when a thiophene ring is attached to each thiophene ring of **1a**. The quantum yield (0.12) of **2a** is smaller than the yield (0.50) of TPCN. The electron donating property of the thiophene ring is considered to decrease the yield.[15] The attachment of one more thiophene ring to the aryl groups did not affect the cyclization quantum yield.

The ring-opening quantum yields dramatically decreased when the number of thiophen rings was increased. The yield of 0.075 of **1b** decreased to 0.0013 when a thiophene ring was attached to **1**. It further decreased to 0.00013 in a terthiophene derivative (**3b**). The very low ring-opening quantum yield of **3b** is ascribable to large extension of π-conjugation throughout the 6 thiophene moieties. The anti-bonding nature in the excited singlet state of the central newly photogenerated single bond decreases with the extension of π-conjugation, and the weak anti-bonding character is considered to decreases the ring-opening quantum yield. The decrease in the ring-opening quantum yield of the dithienylethenes with long π- delocalization aryl groups is unfavorable as a photoswitch unit in molecular wire systems.[16]

Table 2 Cyclization ($\Phi_{a\to b}$) and Ring-opening ($\Phi_{b\to a}$) Quantum Yields of Dithieylethenes **1**, **2** and **3** in decalin.

Compd	$\Phi_{a\to b}$ / 25 ℃	$\Phi_{b\to a}$		
		25 ℃	100 ℃	150 ℃
1	0.44	0.075	0.13	—
2	0.12	0.0013	0.0056	0.016
3	0.12	0.00013	0.0012	0.0044

Temperature Dependence:

Temperature dependence of the ring-opening quantum yield was measured in decalin, as shown in Fig.3, in which the yields at 25 °C were normalized to 1 for all three compounds. The yield of **3b** steeply increased as large as 34 times when the temperature was raised from 25 °C to 150 °C. The increase in the yield of **1b** was much smaller. The small temperature dependence of **1b** indicates that the large temperature dependence of **3b** can not be explained by the inherent activation energy of the ring-opening reaction in the excited state. The conformational change of the oligothiophene groups by heating is considered to play an important role in the ring-opening process.

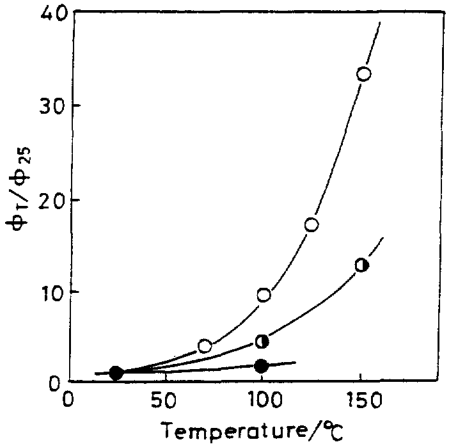


Figure 3. Temperature dependence of the ring-opening quantum yields of **1b**(●), **2b**(◑) and **3b**(○) in decalin. The yield at 25 °C of each compound was normalized to 1.

As described in the previous section the ring-opening quantum yield increases with the decreasing number of thiophene rings, or the decreasing π-conjugation length. At higher temperatures the effective π-conjugation length is shortened by active rotation of the thiophene rings, and this causes the increase in the quantum yield. The decrease of effective π-conjugation length was confirmed by measuring the temperature dependence of the absorption spectrum. At 25 °C the maximum was observed at 653 nm, while it shifted to a shorter wavelength of 638 nm at 100 °C. The hypsochromic shift indicates that the effective π- conjugation was shortened at higher temperatures.

The large temperature dependence is useful for non-destructive readout of the memory when the compounds are used for optical recording media. The recorded memory can be read many times with weak laser light, which does not raise the media temperature. The memory can be erased with high intensity laser, which can raise the media temperature as high as 100-150 °C.

EXPERIMENTAL SECTION

General:

Absorption spectra were measured with an absorption spectrometer (Hitachi U-3410). ^{1}NMR spectra were recorded on a Varian-Gemini-200 (200 MHz) spectrometer. Chemical shifts were reported in parts per million. Photoirradiation was carried out in the thermostat by using a USHIO 1 kW high-pressure mercury lamp or a USHIO 500 W Xenon lamp as the exciting light sources. Mercury lines at 313 and 366 nm were isolated by passing the light through a monochrometer (Ritsu MC-10N). Quantum yields were determined by comparing the reaction yields of diarylethenes against furyl fulgide in toluene.[23,24] The cyclization quantum yields were measured at 313 nm, while the ring-opening quantum yields were measured by irradiation at the absorption maxima. The samples were not degassed.

Materials:

Compounds **1a**-**3a** were synthesized as shown in **Scheme 1**.

1,2-Bis(5-iodo-2,4-dimethylthiophen-3-yl) perfluorocyclopentene (**4**)

To a mixed solvent of 50 ml of carbon tetrachloride and 50 ml of acetic acid containing 1,2-bis(2,4-dimethylthiophen-3-yl)perfluorocyclopentene[15] (500 mg, 1.26 mmol) were added iodic acid (111 mg, 0.63 mmol) and iodine(179mg, 1.26 mmol) and the solution was refluxed for 3 h. The reaction mixture was poured into water (saturated with NaCl) and extracted with chloroform. The organic layer was washed with a sodium carbonate aqueous solution, and water three times. Iodine was eliminated by washing the chloroform layer with a sodium thiosulfate aqueous solution. The organic layer was washed with water, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 793 mg of 1,2-bis(5-iodo-2,4-dimethylthiophen-3-yl)perfluorocyclopentene (**4**) in 92% yield. **4**: ^{1}H NMR(200 MHz, $CDCl_3$, TMS) δ 1.95(s, 6H), 2.30(s, 6H); MS *m/z* 648 (M^+)

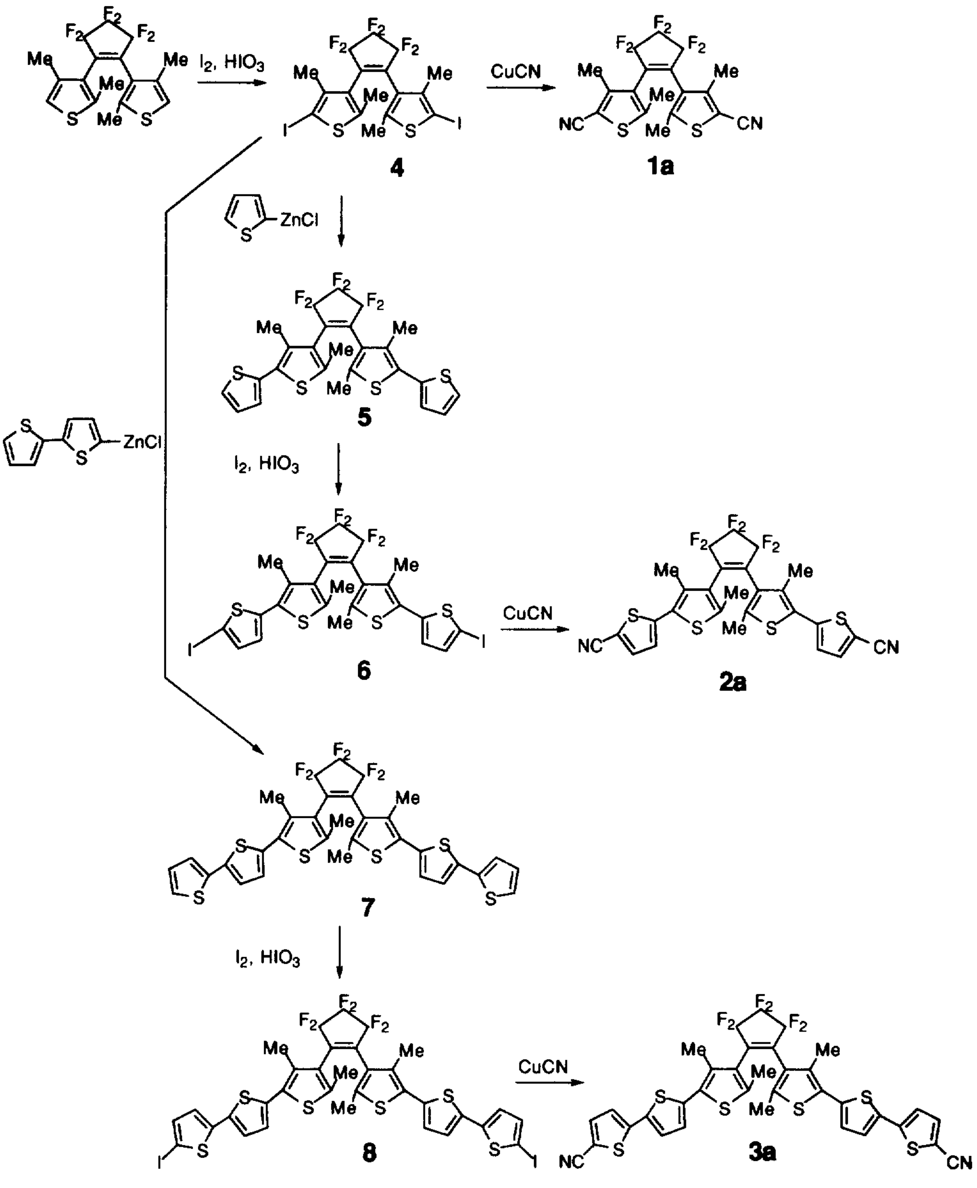
1,2-Bis(5-cyano-2,4-dimethylthiophen-3-yl) perfluorocyclopentene (**1a**)

Copper (I) cyanide (166 mg, 1.85 mmol) was dissolved in 5 ml of hexamethylphosphoramide at around 80 °C. To the solution was added **4** (400 mg, 0.62 mmol), and then the solution was heated up to 100 °C and kept at the temperature for 48 h. The solution was poured into a sodium cyanide aqueous solution and extracted with ether. The ether layer was neutralized with a dilute HCl aqueous solution, washed with water three times, dried ($MgSO_4$), filtered, and evaporated. The residue was purified by column chromatography on silica gel (hexane/ethyl acetate = 10/1) to give 113 mg of 1,2-bis(5-cyano-2,4-dimethylthiophen-3-yl) perfluorocyclopentene (**1a**) in 40% yield.

1a : mp 203-204 °C; ^{1}H NMR(200 MHz, $CDCl_3$, TMS) δ 2.23(s, 6H) 2.38(s, 6H); MS *m/z* 446 (M^+). Anal. Calcd for $C_{19}H_{12}N_2S_2F_6$: C 51.12; H, 2.71; N, 6.27. Found: C, 51.35; H, 2.94, N, 6.56.

1,2-Bis(2,4-dimethyl-5,2'-bithiophen-3-yl) perfluorocyclopentene (**5**) :

To 20 ml of an ether solution containing 2-bromothiophene (470mg, 2.9 mmol) and *N*, *N*, *N'*, *N'*-tetramethylenediamine (410 mg, 3.5 mmol) was added 2.2 ml of a *n*-butyllithium (BuLi) hexane solution (1.6 M, 3.5 mmol) under nitrogen atmosphere, and the solution was stirred at room temperature for 2 h. To this reaction mixture was added 3.77 ml of an ether solution of zinc (II) chloride (1.0 M), and the reaction mixture



Scheme 1

was stirred for 4 h. In another reaction flask, 25 mg (0.022 mmol) of tetrakis(triphenylphosphine)palladium(0) and 470 mg (0.725 mmol) of **4** were added to 20 ml of anhydrous tetrahydrofuran (THF), and the solution was stirred. To the THF solution was added the previous ether solution dropwise at room temperature and the mixture was refluxed for 3 h. The reaction was stopped by the addition of a dilute HCl aqueous solution and the reaction product was extracted with chloroform. The organic layer was washed with water, dried ($MgSO_4$), and evaporated. The residue was purified by column chromatography on silica gel (hexane) to give 385 mg of 1,2-bis(2,4-dimethyl-5,2'-bithiophen-3-yl)perfluorocyclopentene (**5**) in 95% yield.

5 : ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.15, 2.18 (sx2, 3Hx2), 2.31, 2.33(sx2, 3Hx2) ,7.03-7.05 (m, 4H), 7.27-7.30 (m, 2H); MS *m/z* 560 (M^+)

1,2-Bis (5'-iodo-2,4-dimethyl-5,2'-dithiophen-3-yl)perfluorocyclopentene (**6**) :

5 (385 mg, 0.69 mmol) was iodized by the procedure used for **4**. The crude product was purified by column chromatography on silica gel (hexane) to give 502 mg of 1,2-bis (5'-iodo-2,4-dimethyl-5,2'-dithiophen-3-yl)perfluorocyclopentene (**6**) in 90% yield.

6 : ^{1}H NMR (200MHz, $CDCl_3$, TMS) δ 2.11, 2.14 (sx2, 3Hx2), 2.31, 2.33(sx2, 3Hx2), 6.75(d, *J* = 11 Hz, 4H), 7.18(d, *J* = 11Hz, 4H); MS *m/z* 812 (M^+).

1,2-Bis(5'-cyano-2, 4-dimethyl-5,2'-bithiophen-3-yl)perfluorocyclopentene (**2 a**):

Replacement of iodide substituents with cyano groups was carried out by the procedure used for **1a**. The yield was 26%.

2a : mp 90-91 °C, ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.18, 2.22 (sx2, 3Hx2), 2.35, 2.37(Sx2, 3Hx2), 7.05(d, *J* = 11Hz, 4H), 7.54(d, *J* = 11Hz, 4H); MS m/z 610 (M^+); Anal. Calcd for $C_{27}H_{16}N_2S_4F_6$: C, 53.10; H, 2.64; N, 4.59. Found: C, 52.83; H, 2.92; N, 4.51.

1,2-Bis(2,4-dimethyl-5,2': 5',2"-terthiophen-3-yl)perfluorocyclopentene(**7**):

7 was prepared by the procedure used for **5** using 2,2'-bithiophene instead of 2-bromothiophene. The yield was 42%.

5 : ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.18, 2.20 (sx2, 3Hx2), 2.31, 2.33(sx2, 3Hx2), 6.95-7.25 (m, 10H); MS *m/z* 724 (M^+).

1,2- Bis (5"-iodo-2,4-dimethyl-5,2': 5',2"-terthiophen-3-yl) perfluorocyclopentene(**8**):

7 (177 mg, 0.244 mmol) was iodized by the procedure used for **4**. The crude product was purified by column chromatography on silica gel (hexane) to give 150 mg of 1,2- bis (5"-iodo-2,4-dimethyl-5,2': 5',2"-terthiophen-3-yl) perfluorocyclopentene (**8**) in 63% yield.

8 : ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.18, 2.20 (sx2, 3Hx2), 2.31, 2.33 (sx2, 3Hx2), 6.95-7.25 (m, 8H); MS *m/z* 976 (M^+)

1,2-Bis (5"-cyano-2,4-dimethyl-5,2': 5',2"-terthiophen-3-yl)perfluorocyclopentene(**3 a**):

Replacement of iodide substituents with cyano groups was carried out by the procedure used for **1a**. The yield was 13%.

3a : mp 240-241 °C; ^{1}H NMR (200 MHz, $CDCl_3$, TMS) δ 2.21, 2.22 (sx2, 3Hx2), 2.37, 2.38 (sx2, 3Hx2), 7.06 (d, *J* = 11 Hz, 4H), 7.37 (d, *J* = 11 Hz, 4H); MS m/z 774 (M^+); Anal. Calcd for $C_{35}H_{20}N_2S_6F_6$: C, 54.25; H, 2.60; N, 3.61. Found: C, 54.33; H, 2.84; N, 3.91.

REFERENCES

1. Brown, G. H. Ed. Photochromism, Wiley-Interscience, New York, **1971**
2. For reviews, see: (a) Photoreactive-Materials for Ultrahigh Density Optical Memory; Irie, M. Ed; Elsevier: Amsterdam, **1994**. (b) Feringa, B.L.; Jager, W. F.; de Lange, B *Tetrahedron* **1993**,*49*, 8267. (c) Applied Photochromic Polymer Systems; McArdle, C. B., Ed.; Blackie: Glasgow, **1992**. (d) Kirkby, C. J. G.; Bennion, I. *IEE Proc.* **1986**, *133*, 98.
3. Tatezono, F.; Harada, T.; Shimizu, Y.; Ohara, M.; Irie, M. *Jpn. J. Appl. Phys.* **1993**, *32*, 3987.
4. Tsujioka, T.; Shimizu, Y.; Irie, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 1914.
5. Tanio, N.; Irie, M. *Jpn. J. Appl. Phys.* **1994**, *33*, 1550
6. Ebisawa, F.; Hoshino, M.; Sukegawa, K. *Appl. Phys. Lett.* **1994**, *65*, 2919.
7. Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys.* **1995**, *34*, 6439.
8. Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys.* **1996**, *35*, 4353.
9. Tsujioka, T.; Kume, M.; Irie, M. *Jpn. J. Appl. Phys.* **1996**, *35*, L1532.
10. Nakamura, S.; Irie, M. *J. Org. Chem.* **1988**, *53*, 6136.
11. Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 807.
12. Uchida, K.; Nakayama, Y.; Irie, M. *Bull. Chem. Soc. Jpn.* **1990**, *63*, 1311.
13. Nakayama, Y.; Hayashi, K.; Irie, M. *J. Org. Chem.* **1990**, *55*, 2592.
14. Hanazawa, M.; Sumiya, R.; Horikawa, Y.; Irie, M. *J. Chem. Soc., Chem. Commun.* **1992**, 206.
15. Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305.
16. Gilat, S. L.; Kawai, S. H.; Lehn, J-M. *Chem. Eur. J.* **1995**, *1*, 275.
17. Kawai, S. H.; Gilat, S. L.; Ponsinet, R.; Lehn, J-M. *Chem. Eur. J.* **1995**, *1*, 285.
18. a. Tsivgoulis, G. M.; Lehn, J-M. *Angew. Chem., Int. Ed. Eng.* **1995**, *107*, 1188.
    b. Tsivgoulis, G. M.; Lehn, J-M. *Chem. Eur. J.* **1996**, *2*, 1399.
    c. Tsivgoulis, G. M.; Lehn, J-M. *Adv. Mater.* **1997**, *9*, 39.
19. Darcy, P. J.; Heller, H. G.; Strydom, P. J.; Whittal, J. *J. Chem. Soc., Perkin Trans.* **1981**, *1*, 6136.
20. Buckholtz, F.; Zelichenok, K.; Krongauz, V. *Macromolecules* **1993**, *26*, 906.
21. Gilat, S. L.; Kawai, S. H.; Lehn, J-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1439.
22. Saika, T.; Irie, M.; Shimidzu, T. *J. Chem. Soc., Chem. Commun.* **1994**, 2123.
23. Yokoyama, Y.; Kutita, Y. Nippon Kagaku Kaishi **1992**, 998.
24. Yokoyama, Y.; Kutita, Y. *J. Synth. Org. Chem. Jpn.* **1991**, *49*, 364.

(*Received* 11 *March* 1997; *accepted* 8 *May* 1997)