# The irreversible thermo-bleaching function of a photochromic diarylethene having trimethylsilyl groups†

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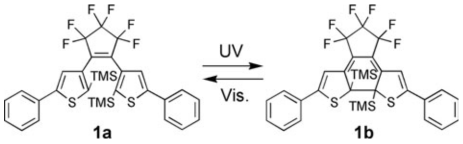
A new function of a photochromic diarylethene, having trimethylsilyl groups at the reactive positions, has been developed. Upon alternating ultraviolet and visible light irradiation, the diarylethene showed photoreversible photochromism in a polymer film, as well as in solution. The colored state changed to colorless immediately upon heating at 100 °C. The colorless state, which is different from the open-ring isomer, was stable under both ultraviolet and visible light irradiation. Such photochromic materials could potentially be used in applications as secret display materials.

## Introduction

Photochromism is referred to as a photoinduced reversible transformation reaction between two isomers with different absorption spectra upon irradiation with light of an appropriate wavelength.[1,2] Photochromic compounds exhibit changes to various chemical and physical properties, such as their absorption spectra, refractive indices, dielectric constants, oxidation–reduction potentials and geometrical structures. They are typically classified into two types, P-type (thermally stable photogenerated isomer) and T-type (thermally unstable photogenerated isomer).[1,3] Among the various photochromic compounds, diarylethenes with heterocyclic aryl rings have been developed as P-type photochromic compounds because of some excellent characteristics, such as the thermal stability of both isomers and fatigue-resistant properties.[4–8] Such materials could potentially be used in applications such as optical memory media,[9–11] switching devices,[12–14] display materials[15,16] and photomechanical actuators.[17–20]

We have recently designed and synthesized diarylethenes for novel material applications. P-type photochromic diarylethenes containing a diethylamino group can switch to a T-type photochromic system by the addition of an acid as an external stimulus.[21] The electron donating character of the substituent varied the electron accepting character by protonation, resulting in a T-type photochromic system.[22,23] Enhancement of the thermal cycloreversion reaction was realized by the introduction of bulky substituents at the reactive 2- and 2′-positions of the thiophene rings.[24–26] The photodecoloration quantum yield was strongly suppressed by the introduction of methoxy groups at the reactive positions.[27] Cyano groups contributed to a large photocycloreversion quantum yield.[28] The photostable colored isomers returned to their initial colorless isomers thermally at high temperatures above 100 °C by the introduction of cyclohexyloxy groups instead of methoxy groups.[29,30]

The introduction of substituents at the reactive positions gave us encouragement to make novel photochromic functions. For the purpose of developing new functionalized photochromic diarylethenes, we have designed and synthesized a diarylethene having trimethylsilyl (TMS) groups at the reactive positions (**1a**) (Scheme 1). In this work, we show a new reaction system, in addition to the usual photochromic reactions of diarylethenes. Diarylethene **1a**, prepared in this work, showed reversible photoisomerizations upon alternating irradiation with ultraviolet (UV) and visible light, and the colored isomer was thermally bleached to give other photostable molecules. The chemical and physical properties of the diarylethene were examined in a polymer film, as well as in solution.



**Scheme 1** Photochromic reactions of diarylethene **1a**.

## Results and discussion

### Synthesis of diarylethene 1a

Diarylethene **1a** was synthesized according to the synthetic route described in Scheme 2. 2-Bromo-5-phenylthiophene was prepared in 83% yield by the bromination of 2-phenylthiophene.[31] 3-Bromo-5-phenyl-2-trimethylsilylthiophene was synthesized in 87% yield by the Halogen dance reaction[32,33] of 2-bromo-5-phenylthiophene using lithium diisopropylamide

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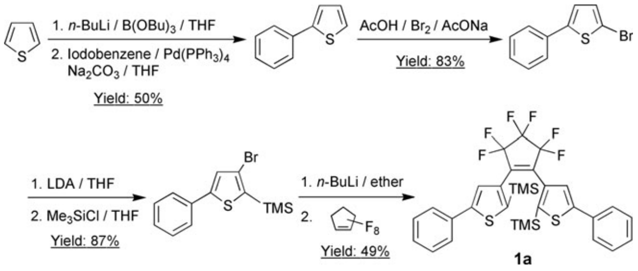
† CCDC 719459 (**1a**), 719460 (**1c**) and 719461 (**1d**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b822372f



**Scheme 2** Synthetic scheme leading to diarylethene **1a**, having TMS groups.

(LDA). Diarylethene **1a** was obtained by a coupling reaction between 3-bromo-5-phenyl-2-trimethylsilylthiophene and octafluorocyclopentene. The structure of the product was identified by its $^1$H NMR spectrum, mass spectrum and X-ray crystallographic analysis (see Experimental section).

### Photochromism of diarylethene 1a

Upon irradiation with UV light, a hexane solution of **1a** turned blue. Fig. 1(a) shows the UV-visible absorption spectral changes in hexane upon irradiation with 254 nm light. Upon irradiation with UV light, the new absorption band of the closed-ring isomer appeared at 615 nm. The blue-colored solution returned to colorless by irradiation with visible light, and the photobleached colorless solution was confirmed to be due to open-ring isomer **1a**. This indicates that diarylethene **1a** shows photoreversible photochromism in hexane. The absorption spectral changes were also observed in acetonitrile, as shown in Fig. 1(b). Upon irradiation with 254 nm light, the solution turned blue and a new peak appeared at 625 nm. The colored solution returned to colorless by irradiation with visible light at a rate similar to that seen in hexane. Such photochromic behavior was also observed in a poly(methyl methacrylate) (PMMA) film, as shown in Fig. 1(c).

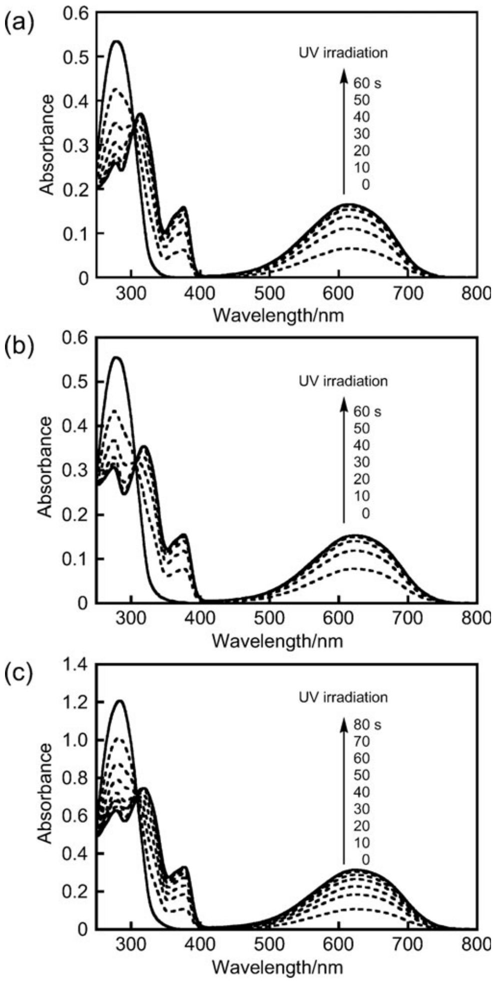


**Fig. 1** Absorption spectral changes of **1a** in (a) hexane, (b) acetonitrile and (c) a PMMA film upon irradiation with 254 nm light.

### Thermal bleaching reaction

The blue-colored solution, produced by irradiating with UV light, was gradually bleached to colorless in hexane, even at room temperature. The bleaching rate was accelerated by increasing the temperature. Fig. 2(a) shows the absorption spectral changes of the blue-colored solution in hexane when heated at 50 °C. After heating for 60 min at this temperature, the solution became colorless. The thermo-bleached product

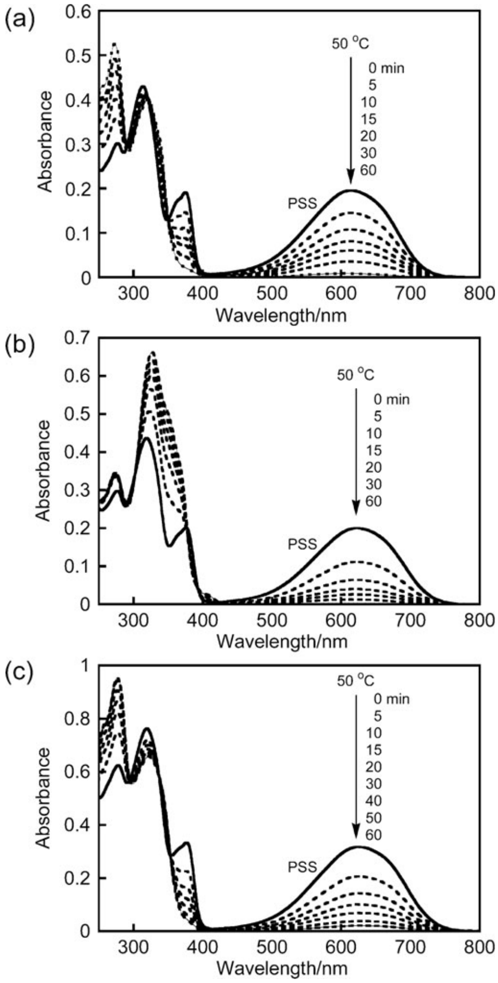


**Fig. 2** Absorption spectral changes of the blue-colored solution in (a) hexane, (b) acetonitrile and (c) a PMMA film when heated at 50 °C. The blue-colored solution was obtained by irradiation of **1a** with 254 nm light.

had a spectrum different to that of **1a**. The colorless solution was stable upon irradiation with either UV or visible light. This indicates that **1b** changed to products distinct from **1a**.

The thermal bleaching was also examined in acetonitrile. After heating for 60 min at 50 °C, the solution became colorless; the spectral changes are shown in Fig. 2(b). It was found that the bleaching rate depended on the solvent used, and that a polar solvent accelerated the thermal reaction.

It was noticed that the absorption spectra of the thermal bleaching products in hexane and acetonitrile were different, as can be seen in Fig. 2. This means that the thermal bleaching products may consist of more than two kinds of compound, and that their content depends on the solvent. Fig. 2(c) shows the absorption spectral changes of the thermal bleaching of a PMMA film. After thermal bleaching, the spectrum was similar to that in hexane.

## Identification of thermal products

In order to identify the thermal bleaching products, the bleached solution was checked by HPLC. The acetonitrile solution at the photostationary state was analyzed by HPLC with a reversed phase column, using acetonitrile as the eluent; **1a** and **1b** eluted at 31 and 29 min, respectively. Closed-ring isomer **1b** could be separated by HPLC and was used immediately in the next experiment. Fig. 3 shows chromatographs of **1b** and the solution after heating at 60 °C in acetonitrile and hexane. As can be seen from the charts, we realized that **1b** was converted to two different structures, referred to as **1c** and **1d**, and that **1a** was not produced upon heating. In acetonitrile, the main product was **1d**, the formation of which was preferred in this polar solvent. On the other hand, **1c** was mainly produced from a hexane solution. Compounds **1c** and **1d** are thermally stable and did not change upon heating or photoirradiation. The reaction mechanism leading to the formation of **1c** and **1d** may be different.

In order to determine the molecular structures of the thermally-produced materials, we isolated them by separative HPLC connected with a reversed phase column using acetonitrile. Isolated **1c** and **1d** were analyzed by $^1$H NMR, mass spectroscopy and X-ray crystallographic analysis.

$^1$H NMR spectroscopy and mass spectrometry of **1c** indicate that one of the two TMS groups had been eliminated during the thermal reaction of **1b**. The $^1$H NMR spectrum of **1d** indicates that both of the TMS groups had been eliminated. Furthermore, two fluorine atoms are confirmed to have been eliminated, as seen from its mass spectrum; the $^1$H NMR and mass spectroscopy data of **1c** and **1d** appear in the Experimental section. However, the structures of **1c** and **1d** could not be determined conclusively by NMR and mass spectroscopy, and they were finally established by the X-ray crystallographic analysis of single crystals.

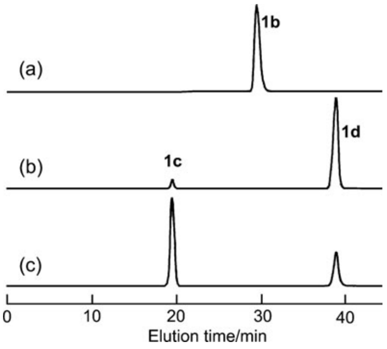


**Fig. 3** HPLC charts of (a) **1b**, and the solution after the thermal bleaching reaction of **1b** in (b) acetonitrile for 0.5 h and (c) hexane for 1 h at 60 °C. The peak intensity was detected by absorbance at 300 nm in acetonitrile.

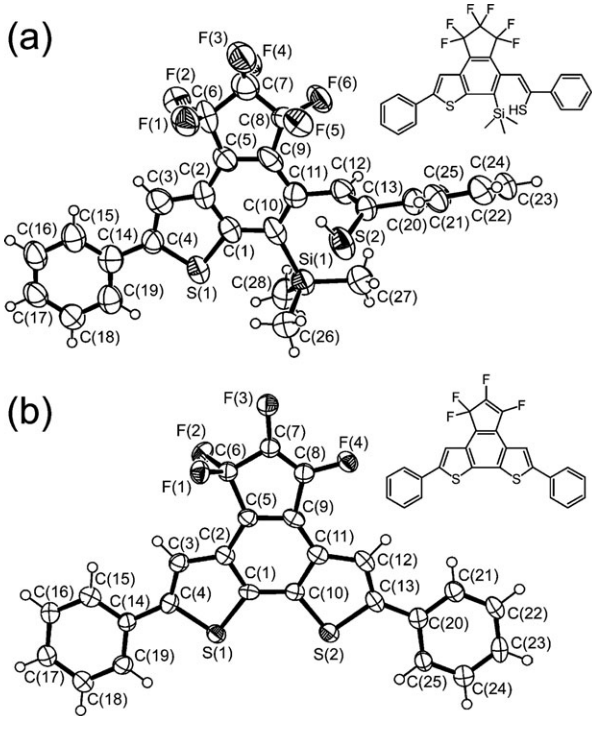


**Fig. 4** ORTEP drawings of (a) **1c** and (b) **1d**, showing 50% probability displacement ellipsoids. **1d** has a disordered structure for the cyclopentadienyl ring. Only one of these structures is illustrated for clarity.

Fig. 4 shows ORTEP drawings of **1c** and **1d**; one of the TMS groups in **1c** is no longer present, and the cleavage of the C–S bond is confirmed. On the other hand, both TMS groups in **1d** are no longer present. The mass spectra of these compounds identify them as structures **1c** and **1d**.

The proposed reaction mechanism is shown in Fig. 5. Cleavage of the Si–C bond results in the formation of a benzene ring at the central position, followed by cleavage of

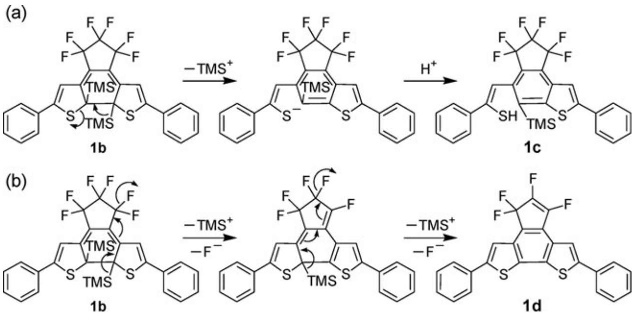


**Fig. 5** The reaction mechanism proposed for formation of **1c** and **1d**.

the C–S bond to give **1c**. Compound **1d** shows the elimination of both TMS groups and two fluorine atoms. The reaction is proposed to proceed in two steps; the first is elimination of the TMS group and one fluorine atom. It is presumed that the second step takes place at a fast rate because of the aromatic stability of the product. The intermediate product was not observed under our reaction conditions.

### Thermal bleaching reactivity

The thermal bleaching reaction of **1b** was examined in hexane, acetonitrile and on a PMMA film. The thermal bleaching reaction rates of **1b** were followed at various temperatures by absorption spectral measurements in the visible region. Fig. 6 the shows decay curves of the absorbance of **1b**; the decay curves followed first-order kinetics. The absorbance of **1b** decreased slowly at 30 °C, and the half-life time, $t_{\frac{1}{2}}$, in hexane at this temperature was estimated to be 3.3 h. The reaction in acetonitrile ($t_{\frac{1}{2}}$ = 1.8 h) was faster than that in hexane. The difference between the reactivities in hexane and acetonitrile may be ascribed to the difference in their thermal bleaching products. The reaction even proceeded in a PMMA film; at higher temperatures, the decay was accelerated. The $t_{\frac{1}{2}}$ was 5.0 and 3.3 min at 60 °C in hexane and acetonitrile, respectively.

Fig. 7 shows the temperature dependence of the bleaching reaction. From the plots, the activation energy ($E_a$) and frequency factor ($A$) were determined: $E_a$ = 103 kJ mol$^{-1}$ and $A$ = 3.3 × 10$^{13}$ s$^{-1}$ in hexane, $E_a$ = 98 kJ mol$^{-1}$ and $A$ = 7.7 × 10$^{12}$ s$^{-1}$ in acetonitrile, and $E_a$ = 102 kJ mol$^{-1}$ and $A$ = 3.0 × 10$^{13}$ s$^{-1}$ in the PMMA film; these parameters depended on the polarity of the solvent. Extrapolation of the temperature dependence indicates that the $t_{\frac{1}{2}}$ of **1b** at 100 °C is 5.6, 4.8 and 4.5 s in hexane, acetonitrile and PMMA film, respectively. This indicates that a fast thermal bleaching reaction is accomplished above 100 °C.

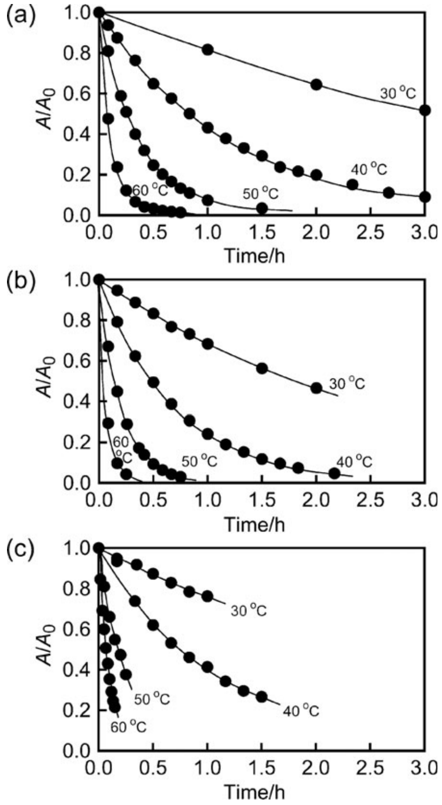


**Fig. 6** Decay curves of **1b** in (a) hexane, (b) acetonitrile and (c) a PMMA film.

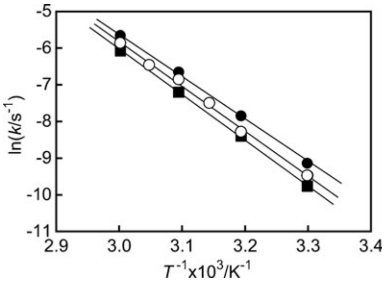


**Fig. 7** The temperature dependence of the rate constant for the thermal bleaching reaction of **1b** in hexane (■), acetonitrile (●) and a PMMA film (○).

### Secret image recordings

Diarylethene **1a** showed photoreversible photochromism and a rapid thermal bleaching reaction of the colored state (**1b**) to give the other colorless compounds (**1c** and **1d**), which are stable to both UV and visible light irradiation. This irreversible thermo-bleaching function can therefore be added to the P-type photochromic function.

Fig. 8 shows secret image recordings using the irreversible thermo-bleaching function. When a colorless state paper surface was irradiated with UV light through a photomask, a colored pattern was observed. The pattern was stable for a few hours at room temperature. When the pattern was heated for 10 s at 100 °C, it was completely bleached and the image recorded through the photomask could not be seen on the surface. In this state, the recording is secret. To see the secret image, the entire surface was irradiated with UV light. When UV light irradiation was carried out on the whole surface, the pattern appeared as the opposite image. The secret state and the image patterning state can be switched between for more than 100 cycles by alternating UV and visible light irradiation.

### Conclusions

We have synthesized a new functionalized diarylethene that has TMS groups at the reactive positions. Upon alternating UV and visible light irradiation, the diarylethene showed photoreversible photochromism in a polymer film, as well as in solution. In addition to the photochromic reactions, we found that the colored state immediately and irreversibly changed to a colorless state by heating at 100 °C, and that the colorless state was stable to both UV and visible light irradiation. Such photochromic materials could potentially be used in applications as secret display materials.

## Experimental section

### General

$^{1}$H (400 MHz) and $^{13}$C (100 MHz) NMR spectra were recorded using a JEOL JNM A400 spectrometer. Tetramethylsilane was used as an internal standard. Mass spectra were obtained with a JEOL JMS-700/700S mass spectrometer.

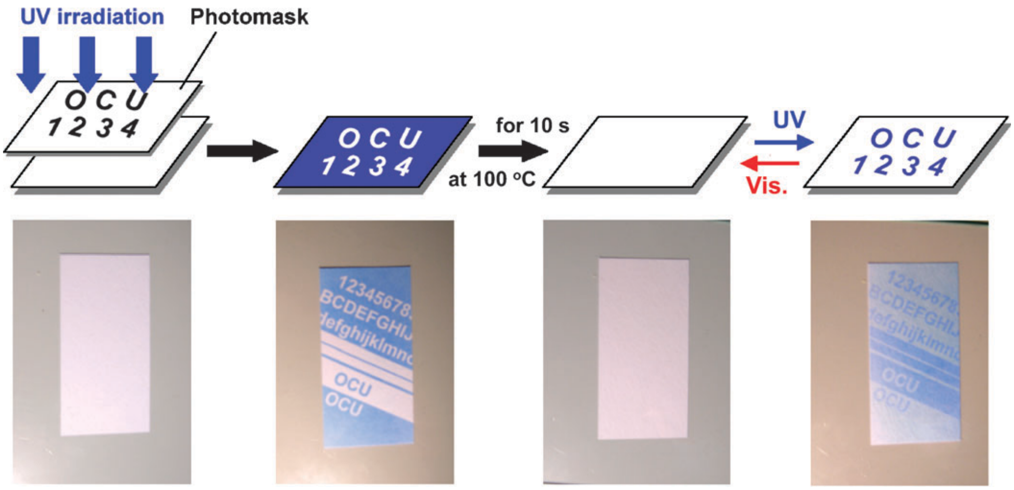


**Fig. 8** Secret image recordings using a photomask by UV irradiation and heating at 100 °C. Diarylethene **1a** is present on the paper surface.

UV-visible absorption spectra in solution were measured with JASCO V-560 or JASCO V-630 absorption spectrophotometers. The quartz cell was heated by a JASCO ETC-505 thermostatic cell holder. Spectroscopic grade solvents were used after purification by distillation. The solvents were dried over 4A molecular sieves and used without de-gassing. The absorption spectra of polymer films on quartz glass plates were measured using a Nikon E600POL microscope connected to a Hamamatsu PMA-11 photodetector. A Mettler-Toledo FP-90/FP82HT hot stage was used to maintain the constant temperature of the polymer film. Photoirradiation was carried out using a 200 W mercury–xenon lamp (Moritex MUV-202) as the light source. Monochromatic light was obtained by passing the light through a monochromator and a UV filter. Monochromatic light was also obtained by using a Keyence UV-400/UV-50 LED lamp (365 nm) or a handy TLC UV lamp (254 nm). The PMMA films were prepared by casting a toluene solution of the polymer onto a quartz glass plate. X-Ray crystallographic analyses were carried out using a Rigaku RAXIS RAPID imaging plate diffractometer with Mo-$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) (50 kV, 40 mA) monochromated by graphite. Data collections were performed by direct methods using SHELXS-97, and refined by the full-matrix least-squares method on $F^2$ using SHELXL-97, with anisotropic displacement parameters for the non-hydrogen atoms.[34] The positions of all the hydrogen atoms were calculated geometrically and refined using a riding model. The bond lengths and geometry of the disordered parts of molecules were restrained in the refinement.

## Materials

**3-Bromo-5-phenyl-2-trimethylsilylthiophene.** Into a flask containing diisopropylamine (2.70 g, 0.0267 mol) in dry THF (150 mL) was added dropwise a 1.6 M n-BuLi/hexane solution (12.7 mL, 0.0203 mol) at −30 °C under an argon atmosphere. The solution was stirred for 1 h at this temperature. To the reaction mixture was added a dry THF (30 mL) solution of 2-bromo-5-phenylthiophene[31] (4.00 g, 0.0167 mol) at −78 °C in one batch. The reaction mixture was stirred for 2 h at this temperature. A dry THF solution containing trimethylsilyl chloride (2.64 mL, 0.0209 mol) was added to the reaction mixture, and it was stirred for 30 min. The reaction mixture was then washed with water, extracted with ether and the organic layer dried over $MgSO_4$. The filtrate was concentrated and purified by column chromatography on silica gel using hexane/ethyl acetate (95 : 5) as the eluent. Yield: 4.49 g (86.8%). $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 0.42 (s, 9H, TMS), 7.28 (s, 1H, Ar-H), 7.30 (t, $J$ = 7.6 Hz, 1H, Ar-H), 7.38 (t, $J$ = 7.6 Hz, 2H, Ar-H) and 7.56 (d, $J$ = 7.6 Hz, 2H, Ar-H). MS: $m/z$ = 310 ($M^+$).

**1,2-Bis(5-phenyl-2-trimethylsilyl-3-thienyl)perfluorocyclopentene (1a).** To a stirred solution of 3-bromo-5-phenyl-2-trimethylsilylthiophene (0.910 g, 2.92 mmol) in dry ether (12 mL) was added dropwise a 1.6 M n-BuLi/hexane solution (2.0 mL, 3.2 mmol) at −78 °C under an argon atmosphere, and stirring was continued for 1 h at this low temperature. Octafluorocyclopentene (0.20 mL, 1.49 mmol, Nippon Zeon) was slowly added to the reaction mixture at −78 °C, and the mixture was stirred for 4 h at this temperature. The reaction was stopped by the addition of water, the product extracted with ether, and the organic layer washed with a 1 N HCl aqueous solution and water. The organic layer was dried over $MgSO_4$, filtered and evaporated. The crude product was purified by column chromatography on $SiO_2$ using hexane as the eluent. Yield: 0.459 g of **1a** (49.3%) as colorless crystals. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ = 0.10 (s, 18H, TMS), 7.32 (t, $J$ = 7.2 Hz, 2H, Ar-H), 7.38 (s, 2H, Ar-H), 7.39 (t, $J$ = 7.2 Hz, 4H, Ar-H) and 7.55 (d, $J$ = 7.2 Hz, 4H, Ar-H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ = 0.13, 111.09 (t of quintet, $J_{C-F}$ = 271 and 25 Hz), 116.00 (tt, $J_{C-F}$ = 257 and 24 Hz), 126.24, 126.76, 128.35, 129.17, 133.41, 133.50, 139.33 (t, $J_{C-F}$ = 25 Hz), 142.66 and 149.77. MS: $m/z$ = 636 ($M^+$). Crystal data: $C_{31}H_{30}F_6S_2Si_2$, $M$ = 636.85, $T$ = 296(2) K, triclinic, $P$-1, $a$ = 8.959(16), $b$ = 10.52(2), $c$ = 17.69(3) Å, $\alpha$ = 97.56(9), $\beta$ = 97.02(8), $\gamma$ = 107.21(8)°, $V$ = 1556(5) Å$^3$, $Z$ = 2, $R_1$ ($I > 2\sigma(I)$) = 0.0628, w$R_2$ (all data) = 0.1682. CCDC 719459.†

**1c.** $^1H$ NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 0.57 (s, 9H, TMS), 2.90 (s, 1H, SH), 6.96 (s, 1H, Ar-H), 7.44 (t, $J$ = 7.2 Hz, 4H, Ar-H), 7.50 (t, $J$ = 7.2 Hz, 2H, Ar-H), 7.67 (d, $J$ = 7.2 Hz, 2H, Ar-H), 7.81 (d, $J$ = 7.2 Hz, 2H, Ar-H) and 7.87 (s, 1H, Ar-H). MS: $m/z$ = 564 ($M^+$). Crystal data: $C_{28}H_{22}F_6S_2Si$, $M$ = 564.67, $T$ = 123(2) K, monoclinic, $C2/c$, $a$ = 13.994(12), $b$ = 16.162(15), $c$ = 23.68(2) Å, $\beta$ = 94.73(4)°, $V$ = 5337(8) Å$^3$, $Z$ = 8, $R_1$ ($I > 2\sigma(I)$) = 0.1238, w$R_2$ (all data) = 0.3875. CCDC 719460.†

**1d.** $^1$H NMR (400 MHz, $CDCl_3$, TMS): $\delta$ = 7.41 (t, $J$ = 6.9 Hz, 2H, Ar-H), 7.48 (t, $J$ = 6.9, 8.0 Hz, 4H, Ar-H), 7.71 (s, 1H, Ar-H), 7.77 (d, $J$ = 8.0 Hz, 4H, Ar-H) and 7.80 (d, $J_{H–F}$ = 18 Hz, 1H, Ar-H). MS: $m/z$ = 452 ($M^+$). Crystal data: $C_{25}H_{12}F_4S_2$, $M$ = 452.47, $T$ = 123(2) K, orthorhombic, $Pba2$, $a$ = 19.245(10), $b$ = 24.970(11), $c$ = 3.9399(19) Å, $V$ = 1893.3(16) Å$^3$, $Z$ = 4, $R_1$ ($I > 2\sigma(I)$) = 0.0589, w$R_2$ (all data) = 0.1149, Flack $x$ = 0.11(11). CCDC 719461.†

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