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Diarylethenes with intramolecular donor–acceptor structures for photo-induced electrochemical change

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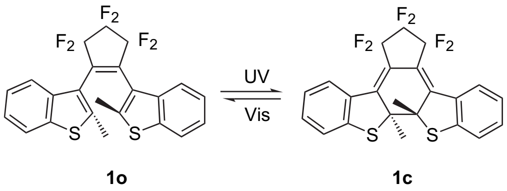
Abstract—Diarylethenes with donor–acceptor groups were synthesized to induce electrochemical switching by light. Photoisomerization was induced by 1,2-bis(2-methyl-1-benzo[*b*]thiophen-3-yl)perfluorocyclopentene (BTF, **1**) unit, while the 3,4-ethylenedioxythiophene (T) and nitro (N) groups were directly connected to BTF, to extend π-electron delocalization. Spectral change to a longer wavelength through photochromism was significant in the donor–acceptor structures (**6**), accompanied by an increase in the molar absorption coefficients, than those of the unsubstituted BTF (**1**) or the BTF substituted with only acceptor group (**2c** and **3c**). A significant peak shift toward lower redox energy was observed when the molecules were converted from an open isomer to a closed isomer. The plot of the reduction potentials (($E_{1/2}^{\mathrm{red}}$, V vs Ag/AgCl) vs LUMO energy eV) for the diarylethenes indicates that the reduction potential is strongly dependent on the nature of the substituents around the diarylethene unit. When **6** was applied to a photocell of Au/PC/ITO glass, in which PC is the polystyrene containing **6**, it became possible to switch the conductivity of the cell through the film by UV–vis irradiation, as estimated by the I–V plot on a photocell. The conductivity of the cell exposed to UV light was three times larger than that of the cell exposed to visible light, and 10 times larger than that of the cell containing **3**, indicating the importance of the push–pull structure for π-electron connectivity through the donor–BTF–acceptor.

1. Introduction

Light-induced reversible transformations of physical properties of two isomers are attracting strong interest in molecular switching.[1] In particular, the photochromic conversion of diarylethene, stimulated by irradiation with light at an appropriate wavelength,[2–8] makes it possible to switch the properties of molecules not only in electronic absorption but also for various physical and chemical properties, such as geometrical structure, refractive index, dielectric constant, and oxidation–reduction potential.[8–12] The most remarkable difference between diarylethene isomers is that the π-system of two aryl rings are separated in the open-ring isomer, whereas they are connected throughout the molecule in the closed-ring isomer. Therefore, any π-electron perturbation on the two aryl rings can modify the electrical switching properties arising from the interaction of the aryl rings through the conjugated pathway.

The diarylethenes with heterocyclic aryl rings have high application potentials due to additional characteristics, namely, the fatigue-resistant property and thermal irreversibility.[13–17] The coloration–decoloration cycle of benzothiophene derivatives such as BTF (**1**, Eq. 1) could be repeated more than 10^4 times while the thermally irreversible photochromic performance is kept in a solution.[13,17] Because of these advantages, researches on the optoelectronic application of diarylethene based on **1** are attracting strong interest.[8–18]



(1)

Substitution of the 6,6′-position on the benzothiophene ring of **1** with an electron acceptor and donor group could change the π-electron density and thus, the electronic properties and electrical conductivity of diarylethene through the conjugated pathway. In particular, introduction of the electron-donating and electron-accepting groups to the diarylethene units could stimulate intramolecular charge transfer along the closed isomer. Although many symmetrical diarylethene compounds have been reported, reports on nonsymmetrical derivatives and donor–acceptor structures are rare.[19–23]

Keywords: Photochromism; Diarylethene; Ring cyclization; Ring opening; Donor–acceptor; Photo-electrical switching.

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This paper reports on the synthesis and photo-induced electrical property change of the 6,6′-substituted nonsymmetrical diarylethenes. The nitro (N) and 3,4-ethylene-dioxythiophene (T) groups were substituted at the 6- and 6′-positions of **1** as the electron acceptor and donor group, respectively.

2. Results and discussion

2.1. Synthesis

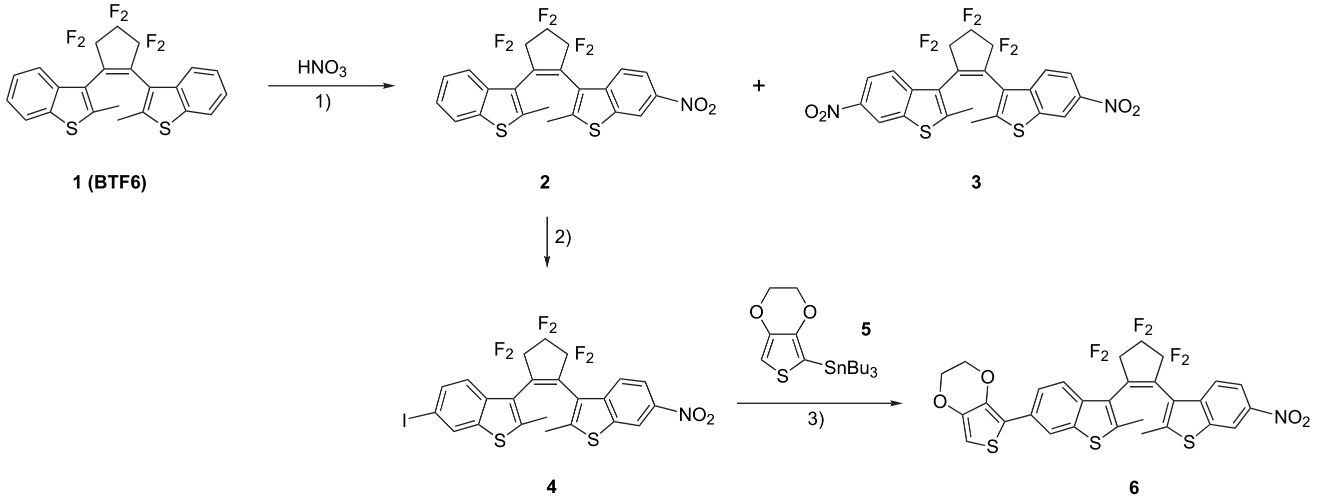
The known compound, 1,2-bis(2-methyl-1-benzo[*b*]thiophen-3-yl)perfluorocyclopentene (BTF, **1**),[24] was prepared from the reactions of perfluorocycloalkene with the organolithium compound.[8a,17] Nitration of **1** with fuming nitric acid yielded **2**. Dinitro compound **3** was synthesized using the same procedure used for **2**, but with excess nitric acid.[12,23] Then compound **2** was subjected to iodination with iodine and periodic acid in an acetic acid solution to yield **4**. Compound **6** was synthesized as a pale green powder through palladium-catalyzed Stille coupling of **4** with **5**[25] in the presence of a $Pd(PPh_3)_2Cl_2$ catalyst (Scheme 1).

The products were confirmed using the spectroscopic method and elementary analysis. The ^1H NMR spectrum of the unsymmetrical compounds **2**, **4**, and **6** showed four different methyl protons at δ 2.20–2.60, which arose from the two unsymmetric aryl groups with *anti*-parallel and parallel structures. The ratio of the *anti*-parallel structure to the parallel structure was about 65:35, as determined from the peak integration, in a solution (Supplementary data). The FTIR spectra of the nitrated compound (**2**, **3**, and **6**) showed characteristic asymmetric stretching vibration frequencies for the nitro group at 1500 and 1340 cm^{-1}.

2.2. Photochromic properties

Figure 1 shows the UV–vis spectral change upon the photochromic conversion of the diarylethenes in chloroform (1.0×10^{-5} M) through their exposure to a 365-nm light. A colorless solution that contained the open-ring isomer **2o** showed an absorption tail reaching 400 nm. Upon irradiation with UV light, new absorption bands appeared at longer wavelengths, which are ascribed to the closed-ring isomers. Most of the diarylethenes showed very large spectral shifts upon their photoisomerization from the open- to the closed-ring isomers (>6500 cm^{-1}).

In the closed-ring isomers, π-electrons were delocalized throughout the two benzothiophene rings and further



Scheme 1. Synthesis of **6**. (1) Acetic anhydride/acetic acid. (2) I_2, H_5IO_6/acetic acid, H_2SO_4, 70 °C. (3) $PdCl_2(PPh_3)_2$/toluene, reflux, 24 h.

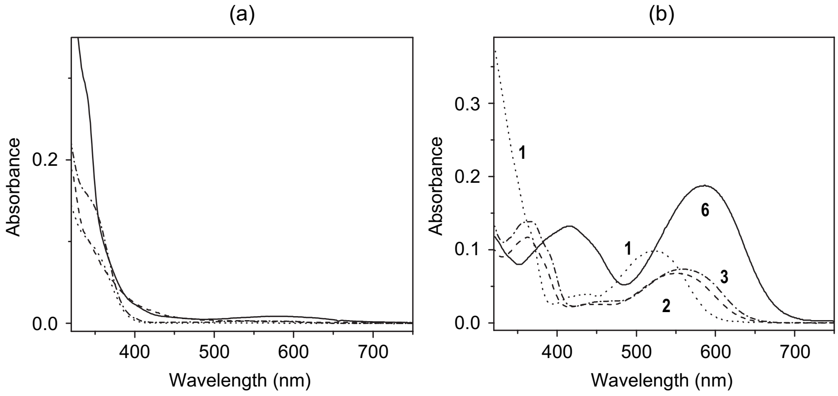


Figure 1. UV–vis spectra of compounds (1.0×10^{-5} M) in chloroform: (a) before and (b) after irradiation with 365 nm light for 2 min for compound **1** (dotted line), **2** (dashed line), **3** (dash–dotted line), and **6** (solid line).

extended to the donor and acceptor substituents. The absorption spectra of the closed-ring isomers thus depended on the substituents of the benzothiophene rings. The closed-form **2c** showed new bands at 362 nm (3.42 eV, ε=1.7×10^4 cm^{-1} M^{-1}) and 552 nm (2.24 eV, ε=7×10^3 cm^{-1} M^{-1}). Compared to the unsubstituted diarylethene (**1**), the absorption bands of **2** were red-shifted in both the open and closed isomers, indicating that the 6-nitro group affected the electronic transition of the diarylethenes. In particular, the red shift in the closed isomer (**2c**) was more significant than in the open isomer. Thus, compared to the unsubstituted diarylethene, **1c** (λ_{max}=534 nm, 2.32 eV, ε=1×10^4 cm^{-1} M^{-1}), the electronic transition of **2** was lowered to 0.08 eV in the closed form, in which the π-electrons were delocalized throughout the entire molecule. On the other hand, the ε value was decreased to 70% of **1c**. The di-nitrated **3c** showed a visible band at a similar position (559 nm) as that of **2c** with a similar ε value, indicating that the electronic transition of diarylethene was hardly modified by the second nitro group.

When the T group (3,4-ethylenedioxythiophene) was substituted at the 6′-position of the diarylethene, the spectral shift became more significant in the closed form. Thus, **6c** showed an absorption band at 587 nm (2.11 eV, ε=1.9×10^4 cm^{-1} M^{-1}), which corresponds to the lowering of the first electronic transition energy of 0.21 and 0.13 eV, compared to that of **2c** and **1c**, respectively. The π-electrons could be delocalized through the electron-donating T group to the electron-accepting nitro group in **6c** with a push–pull structure, which led to significant photo-induced polarization. These results correlate well with the previous observation of dithienyl derivatives.[26,27] UV–vis spectral data for diarylethenes in this study are summarized in Table 1.

Table 1. UV–vis spectral data for diarylethenes **1**, **2**, **3**, and **6** in chloroform

Compound	λ_{max} [nm] (ε×10^3 [cm^{-1} M^{-1}])	Energy (eV)
1o	300 (sh)[a]	4.14
1c	534 (10)	2.32
2o	300 (18)	4.14
2c	289 (18), 362 (17), 552 (7)	4.29, 3.43, 2.25
3o	304 (28)	4.08
3c	288 (23), 367 (14), 559 (7)	4.31, 3.38, 2.22
6o	322 (32)	3.85
6c	279 (27), 419 (13), 587 (19)	4.48, 2.96, 2.11

[a] Shoulder.

A diarylethene with five-membered heterocyclic rings have two conformations with the two rings in mirror symmetry (parallel conformation) and in C_2 symmetry (*anti*-parallel conformation).[7,13,28] The population ratio of the parallel to the *anti*-parallel conformations in **2** and **6** was 35:65, from the ^{1}H NMR study described above. The quantum yields of **2**, **3**, and **6** were determined as 0.34, 0.36, and 0.52, respectively, from the plot of the absorbance against the irradiation time.[29] The quantum yields of **6** were close to the maximum value, i.e., almost all the photo-excited *anti*-parallel conformations underwent the cyclization reaction. In other words, the actual quantum yields were close to 1.

On the other hand, the quantum yields of the cycloreversion of **6** dramatically decreased to 0.01 compared to those of **2** (0.07). The cycloreversion quantum yields of the dithienylethenes were reported to be dependent on the π-conjugation length of the aryl groups.[30] When the electron conjugative groups were attached to the aryl groups, the quantum yield of the cycloreversion reaction dramatically decreased due to the significant extension of the π-conjugation throughout the diarylethene molecule. Such a long extension of the π-conjugation in the donor–diarylethene–acceptor push–pull structure of **6** could enhance the photo-induced electrical switching between the open and closed isomers, as described below.

2.3. Photochromic electrochemical change

The open form of the nitro-substituted compounds (**2o** and **6o**) showed reduction peaks at −1.0 V in the cyclic voltammogram (CV), as shown in Figure 2. The nitro-thiophene compounds[31–33] and compound **3**[12] showed reduction potentials at about −1.5 to −1.0 V. Thus, the redox potential at −1 V (vs Ag/AgCl) could be assigned as the redox potential of the nitrated diarylethenes, **2o** and **6o**. The reduction potential of **6o** is almost the same as that of **2o**, indicating that the electron-donating T group does not affect the reduction process of **6o** because it is separated in the open form. In the anodic region, **2o** showed only an irreversible peak at >1.5 V, which can be ascribed to the oxidation of the diarylethene unit.[34] In general, there were no remarkable oxidation or reduction waves in the region from −2.2 to +1.6 V for *o*-BTF6 (unmodified) in acetonitrile (0.1 M TBAP) on a platinum electrode (vs Ag/Ag+) using cyclic voltammetry.[35] Similarly, no clear oxidation waves for **2o** and **3o** below 1.5 V were observed.

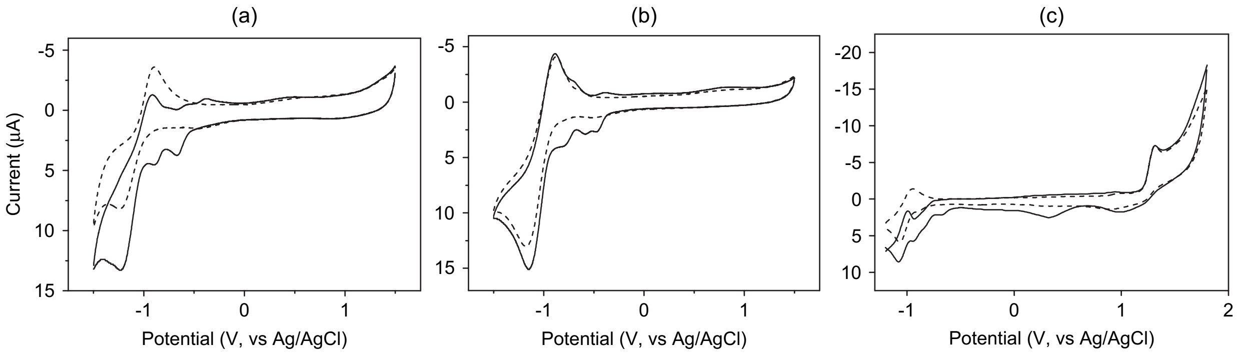


Figure 2. Cyclic voltammogram of diarylethenes (1×10^{-3} M) in dichloromethane containing 0.1 M of n-Bu$_4$NClO$_4$ before (dashed line) and after (solid line) irradiation with 365 nm light for 2 min for (a) **2**, (b) **3**,[12] and (c) **6**.

On the other hand, the CV of **6o** showed a reversible peak at 1.1 V and an irreversible peak at >1.5 V. The oxidation potentials of thiophene-containing molecules are reported as 0.8–1.6 V.[31–33,36] Thus, the CV waves of **6o** at 1.1 and >1.5 V can be considered as one-electron and two-electron oxidation of diarylethene, respectively. Substituted with the electron-donating T unit, **6o** can be oxidized at a lower potential than the unsubstituted analogues.

Interestingly, the CV of the solution that contained **2** after UV irradiation showed a significant current increase plus new redox peaks at −0.82, −0.61, and −0.4 V. It has been reported that the open-ring isomer of BTF does not show redox peaks, although the closed-ring isomer shows quasi-reversible redox potentials at −1.33 and +1.05 V.[35] Thus, the new peaks in CV could be ascribed to the reduction process of diarylethene containing the nitro group. The reduction peaks of **3c** shifted toward a positive potential,[12] thus lowering the energy for the reduction processes, possibly due to the additional nitro groups in **3c**, which facilitated the reduction process by the electron-withdrawing N group.

In the CV of **6c**, the reduction peak was observed at −0.84 V and shifted to a more negative potential than did the peaks of **2c** and **3c**, due to the presence of the electron-donating T group. The reduction current for the closed isomers (**2c**, **3c**, and **6c**, formed upon UV exposure) is higher than that of the open isomer because the π-electron conjugation is extended in the closed isomer to facilitate the electron transport in the closed form.[12,35]

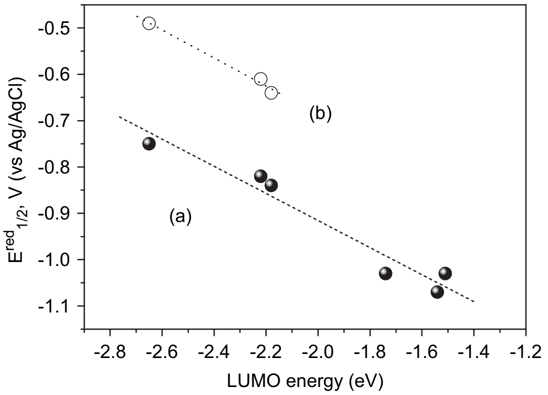


Figure 3. Plot of reduction potentials ($E^{red}_{1/2}$, V vs Ag/AgCl) versus LUMO energy (calcd, eV) for the diarylethenes, calculated using AM1 semi-empirical methods. (a) The correlations of the first reduction potential at the −1 V region for both closed and open isomers. (b) The second reduction potential from −0.7 to +0.4 V region of the closed isomers in Figure 2 against the LUMO energy of the corresponding molecules.

The addition of electron-donating groups has been reported to lower the oxidation potential, whereas the addition of electron-withdrawing groups has been reported to increase the oxidation potential.[37] Analogously, the addition of electron-donating groups will increase the reduction potential of diarylethene. The plot of the reduction potentials ($E^{red}_{1/2}$, V vs Ag/AgCl) versus LUMO energy of the diarylethenes, calculated using AM1 semi-empirical methods, indicates that the reduction potential is indeed strongly dependent on the nature of the substituents around the diarylethene molecular backbone (Fig. 3). The slopes of the plot for the first (Fig. 3a) and second reduction potentials (Fig. 3b) against the LUMO energy of diarylethene were almost identical (0.29 and 0.30, respectively) and indicate the sensitivity of these relationships, which decreases proportionally with decrease in the LUMO energy.

Compared to the reduction, the oxidation potential change through the ring closure was rather small in **2** and **3**. The CV of **6c** showed a new peak at 0.89 V (quasi-reversible) with an irreversible peak at 0.36 V, which arose from the one-electron oxidation of the BTF unit and the reduction of the diarylethene dication generated from the two-electron oxidation of the closed form according to the ECE mechanism, respectively.[34a] Furthermore, there was a significant current increase in the potential range above 1.5 V from the ring closure reaction upon UV exposure. This indicates that the electron transport becomes facile in the closed form as observed for the reduction current increase described above.

The potential shifts and the decrease in the potential difference between the oxidation and reduction peaks were more significant in **6** compared to those in **2** and **3**, indicating the importance of the push–pull structure for charge transfer. From the calculation using AM1 semi-empirical methods, the HOMO–LUMO energy difference was smallest in **6c** (Table 2), implying that the charge transfer must be faster in **6c** compared to that in others.

2.4. Photo-induced electrochemical switching of a photocell containing diarylethene

The diarylethene compounds in this study were homogeneously dispersed in polystyrene without phase separation to produce transparent polymer composite films. A photocell

Table 2. Electrochemical data for open- and closed-form diarylethenes obtained before and after UV irradiation, respectively

Sample	E_{red} (ΔE)[a] (V)	E_{ox} (V)	HOMO (eV)[b]	LUMO (eV)[b]	Δ (LUMO−HOMO) (eV)
2o	−1.07 (0.33)	>1.5[c]	−8.92	−1.54	7.38
2c	−0.82 (0.15), −0.61 (0.07), −0.4 (0.08)	>1.5	−8.72	−2.22	6.5
3o	−1.03 (0.28)	>1.5[c]	−9.508	−1.74	7.77
3c	−0.75 (0.11), −0.49 (0.18), −0.37 (0.21)	>1.5	−9.12	−2.65	6.47
6o	−1.03 (0.12)	0.92 (0.12), 1.1,[d] >1.5[c]	−8.64	−1.51	7.13
6c	−0.84 (0.17), −0.64 (0.07), −0.36[c]	0.89 (0.1), 1.1,[d] >1.5[c]	−8.58	−2.18	6.4

[a] Anodic–cathodic peak separation.

[b] Calculated using the AM1 semi-empirical method. Open and closed isomers are represented as **o** and **c**, formed before (dark) and after UV exposure, respectively.

[c] Irreversible process.

[d] Quasi-reversible process.

was fabricated with three layers of Au/PC/ITO glass, in which 'PC' represents the photochromic layer of **6** dispersed in a polystyrene binder. The PC layer was prepared from the solution of **6** (10 or 30 wt %) and polystyrene in a mixture of chloroform and trichloroethene (3:1, w/w). The cathode layer (Au) was in turn deposited on the photochromic film using the thermal evaporation method under the pressure of 3×10^{-6} Torr. The thickness of the Au layer and the photochromic layer were 40 and 220 nm, respectively, with an active area of 0.02 cm^2 (Fig. 4), and the prepared cell showed a color change from the UV and visible light sources (Fig. 5). Compared to the solution spectra, the band centered at 400 nm slightly changed due to the overlapping of the absorption tail with the binder.

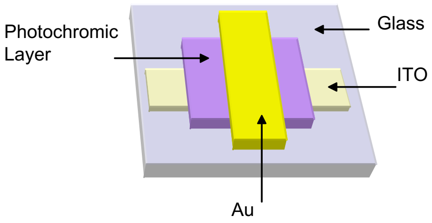
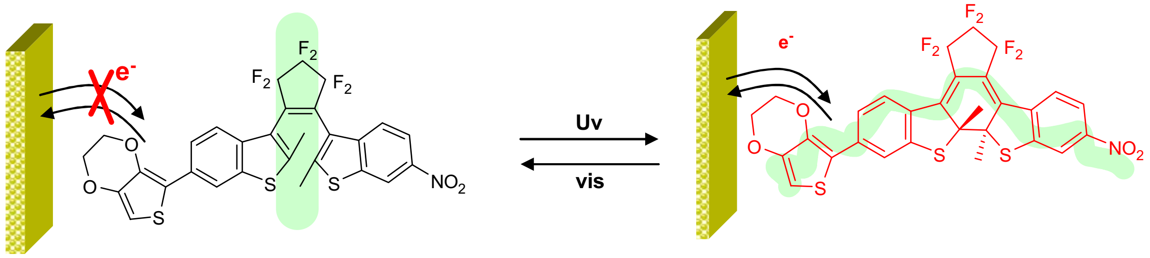


Figure 4. Structure of the thin-film photocell consisting of the Au/photochromic layer (diarylethene in polystyrene)/ITO.

The applied voltage dependence of the electric current is shown in Figure 6. It is important to note that the slope of the current–voltage (I–V) curve for the cell containing **6** significantly increased when the cell was irradiated with UV light. The current at 2 V for the colored cell, which contained closed form of **6**, was three times larger than that of the bleached cell. This demonstrates that the π-electron conjugation between the donor T and the acceptor N group in **6c** was extended, resulting in a higher current response than in the open form, in which such π-conjugation was limited. In particular, the donor–acceptor substituents could allow the electron push–pull mechanism in the closed form, in which the π-electron conjugation from the donor group through the diarylethene and then to the acceptor unit can be extended in the closed form, as schematically shown below.



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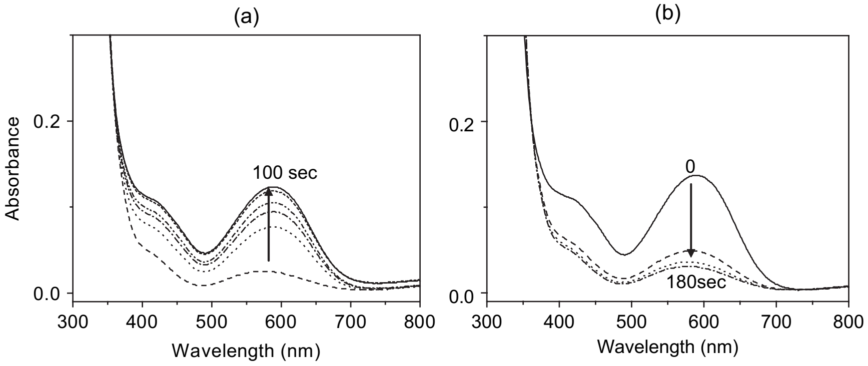

Figure 5. Spectral change in the photocell containing **6** (structured as in Fig. 4) through UV–vis irradiation. (a) UV exposure for 3, 20, 40, 60, 80, and 100 s. (b) Visible light (532 nm laser) exposure for 0, 60, 120, and 180 s.

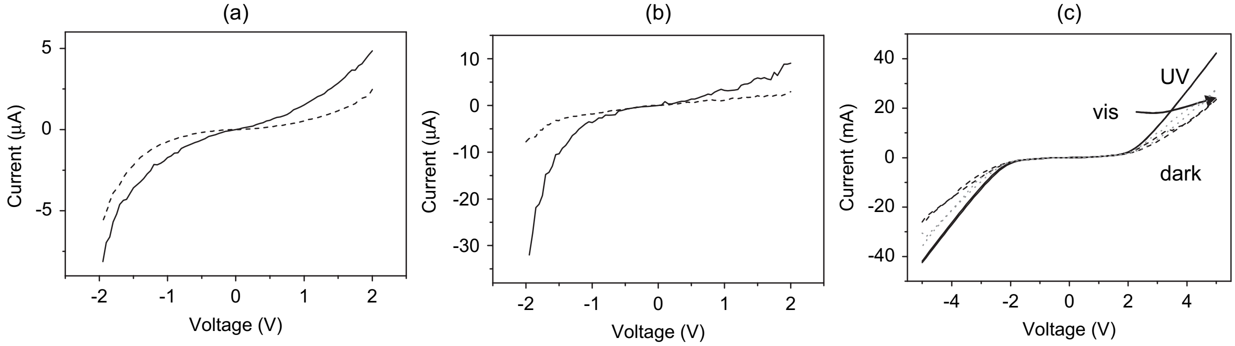

Figure 6. I–V plot for the cell containing (a) PS (90)/**6** (10) and (b) PS (70)/**6** (30) in the potentials between −2 and +2 V, before (dashed) and after (solid line) and (c) PS (70)/**6** (30) in the potentials between −5 and +5 V irradiation with 365 nm light, in dark (dashed) and after UV (solid), and then after visible light excitation (dotted line).

The conductivity was determined from the linear region of the I–V plot as 0.54×10^{-9} and 1.60×10^{-9} S cm^{-1} for the cell containing 10 wt % of **6**, before and after UV irradiation, respectively. The I–V curve was reversibly returned to the dark state upon irradiation with a visible light, allowing conductivity modulation through alternative irradiation with UV and visible lights. The switching efficiency, as defined by the ratio of the conductivities of the cells irradiated with UV and visible lights, was 2.9.

The conductivities of the cells increased to 1.51×10^{-9} and 3.52×10^{-9} S cm^{-1} before and after UV irradiation, respectively, when the content of **6** increased from 10 to 30 wt % in the PC layer. This shows that the conductivity of the photocell originated from the diarylethene molecules, which can act as active charge carriers. Similar I–V experiments were carried out on a photocell containing **3** (10 wt % in PS). The conductivity of the colored cell of **3** was lower than 10^{-10} S cm^{-1}. Moreover, the conductivity of the colored cell of 1 was 10^{-11} S cm^{-1}.[38] The conductivity of the PS binder without diarylethene was lower than 10^{-12} S cm^{-1}.[37] This implies that the charge transport must be facilitated in a donor–acceptor structure such as **6** that can push–pull the carrier during the transport between the molecules. In a doped system, in which a nonconductive binder (PS) is surrounded by diarylethene compounds, the content of the diarylethene and the donor–acceptor structure are important in carrier transport. Typically, carrier transport occurs through hopping of the charge carriers between active sites, and thus, is facilitated when the distance between the donor and the acceptor becomes shorter with the increased contents of the active carrier.

Although the I–V curve was reversible in the potentials' cycle between −2 and +2 V, it became less stable when the potential range was wider (from −5 to +5). There is a large current increase (40 mA at 5 V) by the UV excitation in the high potential range, however, the current drop by the visible light excitation was not completely overlapped to that of the dark and the I–V curve (visible in Fig. 6c) showed some hysteresis, possibly due to electrochemical decomposition at high voltage. Thus, working voltage for a stable switching effect of the photocell should be low (−2 to +2 V).

Such a reversible light-induced control of the electroactivity by means of the photoisomerization in a polymeric film allows the application of the functionalized electrode as an active interface to photostimulate selective electrochemical transformations: photon-mode actuation, electrochemical, and photochemical storage of information,[40] and in photoelectrode patterning for biological and nonbiological systems.[38,41] Furthermore, conductivity switching from an organic photochromic film could be utilized for injection control at the metal–organic interface of the photon mode.

3. Conclusions

A new diarylethene, with T and N as the electron donor and acceptor group, respectively, was synthesized to achieve photochromic and electrochemical switching with UV and visible light irradiation. The donor–acceptor structure **6** showed a significant shift in electronic transition, which resulted in spectral and redox potential changes. The closed form of **6**, generated through UV exposure, showed a higher current-to-voltage response, which resulted in a higher conductivity than that of the open form. Thus, conductivity switching was possible with UV and visible light switching. Such conductivity switching from an organic photochromic film opens up a new application potential in injection control at the metal–organic interface of the photon mode.

4. Experimental

4.1. General methodology

Methylene chloride and toluene were distilled from phosphorus pentoxide prior to use, and tetra-*n*-butylammonium perchlorate (TBAP) was purchased from TCI. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, in a $CDCl_3$ solution that contained Me_4Si as an internal standard with Bruker. IR spectra were recorded on a Shimadzu 540 spectrophotometer as KBr or film on KBr plates. An elemental analysis was performed by the Korea Basic Science Center. The FAB mass spectra were determined by the National Center for Inter-University Research Facilities. Column chromatography was performed using silica gel (200–400 mesh, Merck). All reactions were monitored for completion using thin-layer chromatography (TLC), which was performed using a precoated silica gel plate (Merck 60 F_{245}), and detection was performed with the aid of UV light. Melting points were measured on the Fisher–Jones melting point apparatus and uncorrected. The UV–vis spectra were recorded for chloroform solutions with a Jasco V-530 UV–vis spectrophotometer. Molar absorption coefficients were experimentally determined from the absorbance change at different concentrations using Lambert–Beer's law. The electrochemical properties were studied using cyclic voltammetry (CV) on a BAS 100B electrochemical analyzer (BAS, Inc.). The measurement was carried out in 10 mL methylene chloride solution that contained tetra-*n*-butylammonium perchlorate (TBAP, 0.1 M, 0.341 g) as a supporting electrolyte. Each of the photochromic compounds was dissolved under an argon atmosphere. The condition was composed of a three-electrode assembly equipped with a platinum working electrode, a platinum coil as the counter electrode, and an Ag/AgCl electrode as the reference electrode. Measurements were examined in a glass cell at room temperature. The cell was measured before and after it was irradiated with UV light and after it was blenched with visible light. The scan rate was 200 mV sec^{-1} and the voltage range was −1.5 to +1.5 V. The current–voltage (I–V) properties were measured using Agilent E5272A 2-Channel (High-power and Medium-power) Source/Monitor Units of Agilent Technologies. The measurement range was −2.0 to +2.0 V. For the study of I–V character photochromic compound (10, 30 wt %) and polystyrene (90, 70 wt %, Polysciences, Inc., 50,000 Mw) in chloroform, and the 1,1,2,2-tetrachloroethane solution was spin-coated on the ITO glass. Then the coated glass film was dried in an oven at 70 °C for more than 12 h, and gold was evaporated at a higher temperature. The thickness of the photochromic material was 220 nm and of gold was 40 nm. For coloration, the film was exposed to UV light (365 nm, 0.5 mW) for 10 min, after which its properties (I–V curve, UV) were examined. After the film was bleached with light (532 nm, 2.0 mW), its properties were again investigated. The HOMO and LUMO energy of each compound were calculated using the AM1 semi-empirical method, as implemented in HyperChem ver. 7.0.[39]

4.1.1. 1-[6-Nitro-2-methyl-1-benzothiophen-3-yl]-2-(2′-methyl-1′-benzothiophen-3′-yl)hexafluorocyclopentene (2). To a solution of 30 mL acetic acid, 3 mL acetic anhydride was added with **1** (1 g, 2.13 mmol) at 10 °C. Fuming nitrate (1 mL) was slowly added to the solution, while the temperature was kept below 10 °C. The mixture was stirred overnight at room temperature, after which cold water was added to it. The solution was neutralized and extracted with ethyl acetate (3×30 mL). The organic layer was washed with 30 mL water, dried over $MgSO_4$, filtered, and evaporated. The residue was purified using column chromatography on a silica gel using hexane–ethyl acetate (5:1) as the eluent to produce **2** [yield: 75%; parallel (p):*anti*-parallel (ap)=40:60; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.21 (s, apMe, 2H), 2.31 (s, apMe, 2H), 2.49 (s, pMe, 1H), 2.58 (s, pMe, 1H), 7.20–7.76 (m, ArH, 5H), 8.10 (d, J=7 Hz, pArH, 0.4H), 8.26 (d, J=7 Hz, apArH, 0.6H), 8.54 (s, pArH, 0.4H), 8.64 (s, apArH, 0.6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.2, 15.8, 118.4, 118.6, 119.8, 120.0, 122.0, 122.3, 124.7, 124.9, 138.0, 142.6, 144.7]. HRMS (FAB) *m*/*z* (MH+) calcd for $C_{23}H_{14}F_6NO_2S_2$: 514.0370; obsd: 514.0369.

4.1.2. 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)-perfluorocyclopentene (3).[12,23] To a solution of acetic acid (30 mL), acetic anhydride (3 mL) was added with **1** (1 g, 2.13 mmol) at 10 °C. Fuming nitrate (3 mL) was slowly added to the solution, while the temperature was kept below 10 °C. The mixture was stirred overnight at room temperature, after which cold water was added to it. The solution was neutralized and extracted with ethyl acetate (3×30 mL). The organic layer was washed with water (30 mL), dried over $MgSO_4$, filtered, and evaporated. The residue was purified using column chromatography on a silica gel with hexane–ethyl acetate (5:1) as the eluent to produce **3** [yield=75%; parallel (p):*anti*-parallel (ap) ratio=40:60; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.53 (s, apMe, 3.6H), 2.59 (s, pMe, 2.4H), 7.62 (d, J=9 Hz, pArH, 0.8H), 7.74 (d, J=9 Hz, pArH, 1.2H), 8.08 (d, J=9 Hz, apArH, 1.2H), 8.11 (d, J=9 Hz, apArH, 0.8H), 8.58 (d, J=2 Hz, pArH, 0.8H), 8.67 (d, J=2 Hz, apArH, 1.2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 14.8, 15.2, 113.0, 113.3, 114.8, 117.1, 133.0, 137.0, 140.0, 144.3, 144.7].

4.1.3. 1-(6-Nitro-2-methyl-1-benzothiophen-3-yl)-2-(6′-iodo-2′-methyl-1′-benzothiophen-3′-yl)hexafluorocyclopentene (4). Iodine (37 mg, 0.15 mmol) and H_5IO_6 (16 g, 0.07 mmol) were added to a stirred solution of **2** (100 mg, 0.19 mmol) in acetic acid (20 mL), sulfuric acid (1 mL), and water (1.5 mL). The mixture was stirred for 3 h at 70 °C in open air. The reaction mixture was poured into 500 mL of ice water. The organic layer was extracted with methylene chloride (3×30 mL), dried over $MgSO_4$, filtered, and evaporated. The residue was purified using column chromatography on a silica gel with hexane–ethyl acetate (5:1) as the eluent to produce **4** [yield=85%; parallel (p):*anti*-parallel (ap) ratio=40:60; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, apMe, 2H), 2.30 (s, apMe, 2H), 2.47 (s, pMe, 1H), 2.56 (s, pMe, 1H), 7.20–8.26 (m, ArH, 5H), 8.57 (s, pArH, 0.4H), 8.64 (s, apArH, 0.6H)].

4.1.4. 2-Tri-butylstannyl-3,4-ethylenedioxythiophene (5). To a solution of 3,4-ethylenedioxythiophene (4.50 g, 320 mmol) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) (4.25 g, 370 mmol) in anhydrous diethyl ether (100 mL), a solution of *n*-butyllithium (12.7 mL, 320 mmol, 2.5 M in hexane) was slowly added using a syringe under an argon atmosphere at room temperature. The mixture was stirred at room temperature for 10 min, and then refluxed for 30 min. A pink, milk-like mixture was formed. The mixture was cooled to −25 °C, and tributyltin chloride (10.33 g, 320 mmol) was added slowly to it over 1 h. The reaction mixture was warmed up to room temperature and stirred for 3 h. After it was quenched with saturated sodium chloride solution (50 mL), its organic layer was extracted with diethyl ether (3×30 mL), dried over $MgSO_4$, and filtered. Triethylamine (10 mL) was added to the filtrate, and the solvents were evaporated. The residue was purified using column chromatography with hexane on a pre-treated silica gel (silica gel was washed with neat triethylamine, and then with hexane). The solvent was removed in a vacuum and the residue was further purified through vacuum distillation to produce a colorless liquid [yield=68%; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.90 (t, J=7 Hz, Me, 9H), 1.10 (m, –CH_2, 6H), 1.34 (m, –CH_2–, 6H), 1.56 (m, –$SnCH_2$–, 6H), 4.15 (m, –OCH_2, 4H), 6.57 (s, –CH–, 1H)].

4.1.5. 1-[6-(3′,4′-Ethylenedioxy)thienyl]-2-methyl-1-benzothiophen-3-yl-2-[6′-nitro-2′-methyl-1′-benzothiophen-3′-yl]hexafluorocyclopentene (6). Under an argon atmosphere, 2-tributylstannyl-3,4-ethylenedioxythiophene (27 mg, 0.079 mmol) and **4** (50 mg, 0.079 mmol) were dissolved in toluene (20 mL). To this was added a catalytic amount of dichlorobis(triphenylphosphine)palladium(II) ($PdCl_2(PPh_3)_2$) (5 mg, 0.028 mmol) and the mixture was refluxed for 24 h. During the reaction, the color changed from yellow to black as Pd^0 was formed. After the reaction mixture was cooled, it was poured into a saturated sodium chloride solution (50 mL). Then benzene (20 mL) was added to it. The organic layer was extracted with benzene (3×30 mL), dried over $MgSO_4$, filtered, and evaporated. The residue was purified using column chromatography on a silica gel with hexane–ethyl acetate (5:1) as the eluent to produce **6** [yield=87%; parallel (p):*anti*-parallel (ap) ratio=35:65; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.20 (s, apMe, 2H), 2.32 (s, apMe, 2H), 2.48 (s, pMe, 1H), 2.57 (s, pMe, 1H), 4.26 (m, –OCH_2, 2H), 4.32 (m, –OCH_2, 2H), 6.30 (s, –CH–, 1H), 7.68–8.55 (m, ArH, 6H), 8.64 (s, apArH, 0.4H), 8.65 (s, pArH, 0.6H). HRMS (FAB) *m*/*z* (MH+) calcd for $C_{29}H_{18}F_6NO_4S_3$: 654.0302; obsd: 653.0301].

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Supplementary data

The conductivities determined from the I–V plot in Figure 6 (Table S1), and spectra for the characterization of compounds are available upon request. The supplementary data associated with this article can be found in the online version at, doi:10.1016/j.tet.2006.04.089.

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