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Substituent effects on the properties of photochromic diarylethenes

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Abstract

Photochromic symmetrical diarylethenes **1o**–**5o** bearing different electron-donating or electron-withdrawing substitutents have been synthesized, and the structures of **1o**, **2o**, **4o**, and **5o** were determined by single-crystal X-ray diffraction analysis. Substitutent effects on their optoelectronic properties, including photochromism, fluorescence, and electrochemical properties were investigated in detail. The electron-withdrawing substituents can shift significantly the absorption maxima of the diarylethenes to a longer wavelength and increase their cyclization quantum yield, while the molar absorption coefficients increased with an increasing electron-donating ability. Diarylethenes **1**, **2**, and **4** show good photochromism both in solution and in the single crystalline phase; however, diarylethenes **5** show no photochromism in the crystalline phase because the distance between the reactive carbons become larger than 4.2 Å. Diarylethenes **1**–**3** exhibited good fluorescent switching upon alternating irradiation with UV and visible light, and their fluorescent conversions in the photostationary state were all larger than 80% in hexane. In addition, cyclic voltammetry tests showed that different electron-donating and electron-withdrawing substituents had a remarkable effect on the electrochemical behaviors of these diarylethenes.

Keywords: Diarylethene; Photochromism; Substituent effects; Optoelectronic properties

1. Introduction

Photochromic materials have been extensively investigated for their potential applications in erasable optical memories, displays, and optical switches.[1] Considerable interest has been focused on photochromic diarylethenes because of their high conversion efficiency in reversible photochromic reactions, excellent thermal stability of both isomers, and good fatigue resistance.[2] Upon photoirradiation, diarylethene derivatives can undergo photochromic cyclization/cycloreversion reactions either in solution or in the solid state. The photogenerated closed-ring isomers of diarylethenes showed some colors with broad absorption bands in the visible region, and they could regenerate their open-ring isomers upon irradiation with appropriate wavelength visible light. The reversible photochromic cyclization/cycloreversion reactions upon photoirradiation can also lead to global changes of the bulk materials characteristics, such as UV–vis absorption spectra, fluorescence spectra, oxidation/reduction potentials, and refractive indices, etc.[3] The most important difference is that the π-systems of two aryl rings are separated in the open-ring isomer, while the π-conjugation is delocalized throughout the molecule in the closed-ring isomer.[4]

Although many photochromic diarylethene compounds have been reported to date, compounds which show strong photochromic reactivity in the crystalline phase are quite rare.[2a,5] Diarylethene crystals also exhibit good thermal stability and remarkable fatigue resistance, and can reversibly turn to various colors (yellow, red, blue or green) from colorless depending on their molecular structure upon irradiation with UV and appropriate wavelength visible light. They are very useful for optical memories and nonlinear optical devices with switching properties. Therefore, investigation of diarylethene crystals has attracted much attention today, and many diarylethene crystal structures and their properties have already been reported.[6]

To date, several publications concerning substituent effects on the photochromic performances of diarylethenes have been

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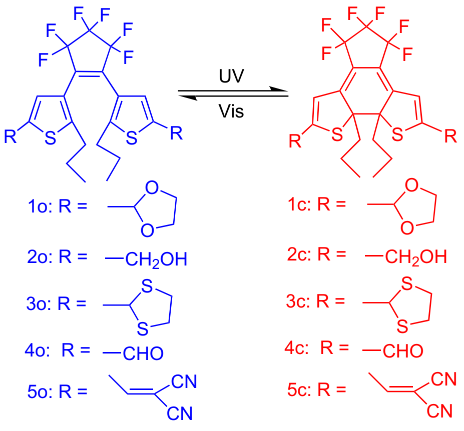
reported.[4a,7] These publications elucidated that electron-donating substituents of the bis(3-thienyl)ethane diarylethenes could be effective to increase the absorption coefficient of the closed-ring forms and decrease the cycloreversion quantum yield; while electron-donating substituents of the bis(2-thienyl)ethane diarylethenes could increase the maxima absorption of the open-ring isomers and reduce the cyclization quantum yield.[7] In addition, Morimitsu et al. presented that the introduction of the ethynyl groups at 2- and 2′-position of both thiophene and benzothiophene rings would increase the cycloreversion quantum yields.[3b] Morimitsu et al. and Takami and Irie revealed that bulky alkoxy substituents at 2- and 2′-position of thiophene rings would extraordinarily decrease the cycloreversion quantum yield and the thermal stability of the colored closed-ring isomer at high temperature.[8]

In summary, although the substituent effect on photochromic reactivity of diarylethenes is of great interest, very little work on the substituent at 5- and 5′-position of the thiophene rings affecting their optoelectronic properties has been reported. In this paper, one of our research goals was to investigate the substituent effects on the optoelectronic properties of diarylethenes bearing various electron-donating or electron-withdrawing groups at 5-position of the two thiophene rings. Therefore, we have synthesized five symmetrical diarylethenes with different substituents at 5-position of the two thiophene rings (Scheme 1), namely 1,2-bis{2-*n*-propyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (**1o**), 1,2-bis(2-*n*-propyl-5-hydroxymethyl-3-thienyl)perfluorocyclopentene (**2o**), 1,2-bis{2-*n*-propyl-5-[2-(1,3-dithiol-pentane)]-3-thienyl}perfluorocyclopentene (**3o**), 1,2-bis(2-*n*-propyl-5-formyl-3-thienyl)perfluorocyclopentene (**4o**), and 1,2-bis[2-*n*-propyl-5-(2,2′-dicyanovinyl)-3-thienyl]-perfluorocyclopentene (**5o**). Among the five compounds, **1o**, **2o**, **3o**, and **5o** are new compounds. Although diarylethene **4o** was reported by us in a previous paper,[9] it is presented here for comparison with those of other four diarylethene compounds.



Scheme 1. Photochromism of diarylethenes **1**–**5**.

2. Results and discussion

2.1. Photochromism in solution

Diarylethenes **1**–**5** showed good photochromism and could be toggled between their colorless open-ring isomers (**1o**–**5o**) and colored closed-ring isomers (**1c**–**5c**) by alternating irradiation with UV light and appropriate wavelength visible light, as monitored using UV–vis absorption, and their absorption spectral changes in hexane upon photoirradiation were shown in Figure 1. The absorption maximum of diarylethene **1o** was observed at 239 nm in hexane (ε=2.7×10^4 L mol^{-1} cm^{-1}). Upon irradiation with 254 nm light, the colorless solution of **1o** turned purple, in which the absorption maximum was observed at 544 nm (ε=5.7×10^3 L mol^{-1} cm^{-1}). The purple color is due to the formation of the closed-ring isomer (**1c**). Alternatively, the purple solution returned colorless upon irradiation with visible light (λ>450 nm) because **1c** reverted to the initial state **1o**. The coloration–decoloration cycles could be repeated more than 50 times and a clear isosbestic point was observed at 311 nm.

Just as diarylethene **1o**, **2o**–**5o** also showed good photochromism in hexane (Fig. 1). In hexane, upon irradiation with 254 nm light, **2o** and **3o** turned red and purple for which the absorption maxima were observed at 526 and 559 nm, as the closed-ring isomers **2c** and **3c** were generated; while **4o** turned blue and the absorption maximum was observed at 632 nm. Upon irradiation with 365 nm UV light, **5o** turned green and the absorption maximum developed at 739 nm in hexane. The color changes of diarylethenes **1**–**5** upon photoirradiation in hexane were shown in Figure 2. All the solutions of **1c**–**5c** can be decolorized by irradiating them with visible light of appropriate wavelength which induced the cycloreversion reactions to reproduce **1o**–**5o**. After repeating 50 coloration–decoloration cycles, the isosbestic points for diarylethenes **2**–**5** were observed at 313, 279, 317 and 378 nm, respectively. The absorption spectral properties of these compounds were summarized in Table 1. The result showed that the absorption maxima and the molar coefficients of diarylethenes **2**, **1**, and **3** increased with the increasing electron-donating ability. The electron-withdrawing substituents (formyl and cyano groups) significantly shifted the absorption maxima of diarylethenes **4** and **5** to a longer wavelength, but their molar absorption coefficients did not increase with the increasing electron-withdrawing ability. The results are in agreement with those reported by Irie et al.[4a]

The cyclization and cycloreversion quantum yields of diarylethenes **1**–**5** were determined in hexane at room temperature. Both cyclization and cycloreversion quantum yields were found to depend on the substituents, as shown in Table 1. All the cyclization quantum yields of diarylethenes **1**–**5** are less than 0.5, which are generally lower than those of diarylethene derivatives with phenyl groups on the end.[7b] However, the quantum yields are much higher than the values so far measured for photochromic bis(2-thienyl)perfluorocyclopentene derivatives.[7d] On the one hand, when strong electron-donating 1,3-dithiolpentane groups were substituted at the 5-position of the two thiophene rings such as compound **3**, the cyclization quantum yield decreased to some extent. On the other hand, electron-withdrawing formyl and cyano substituents increased the cyclization quantum yield, and the cyclization quantum yield decreased with the increasing electron-withdrawing ability. The result is in agreement with that reported by Irie et al.[4a] The cycloreversion

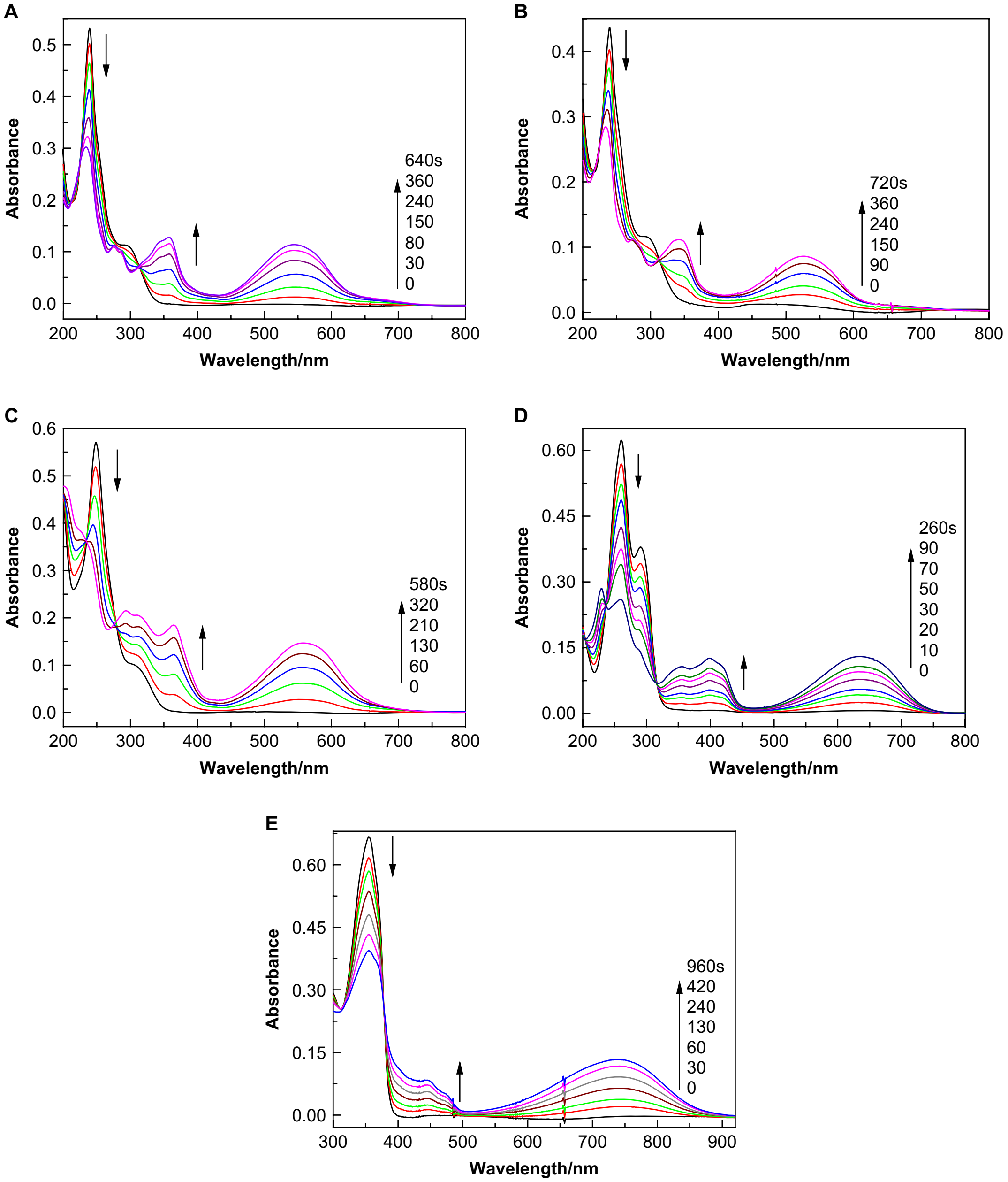


Figure 1. Absorption spectra changes of diarylethenes **1**–**5** in hexane solution (c=2.0×10^{-5} mol L^{-1}) at room temperature: (A) **1**, (B) **2**, (C) **3**, (D) **4**, and (E) **5**.

quantum yields of diarylethenes **1**–**3** having electron-donating substituents are 0.26, 0.24, and 0.12, respectively. The results indicated that the cycloreversion quantum yield was significantly dependent on the electron-donating substituents, and it was further decreased by substituting the 5-position of the two thiophene rings with electron-donating groups. Furthermore, the cycloreversion quantum yield of diarylethene **4** (Φ_{c-o}=0.078) was almost equal to that of **5** (Φ_{c-o}=0.071). This result suggested that the ability of the electron-withdrawing substituents did not affect remarkably the cycloreversion quantum yield.[4a] From Table 1, it can be easily found that the cycloreversion quantum yields of diarylethenes **1**–**3** having electron-donating substituents are much higher than those of diarylethenes **4** and **5** having electron-withdrawing substituents. The main reason is that the cycloreversion quantum yield of diarylethenes is dependent on the π-conjugation length of the aryl groups. The cycloreversion quantum yield decreases with the extension of π-conjugation in the molecules.[2a,10] For diarylethenes **4** and **5**, the electron-withdrawing formyl and dicyanovinyl groups can participate in the conjugation system, resulting in the larger extension of π-conjugation in the molecules of **4** and **5**. As a result, diarylethenes **4** and **5** exhibit more marked π-conjugation lengths than **1**–**3**, which are consistent with the red-shifted absorption maxima and the lower cycloreversion quantum yields.

In addition, the thermal stabilities of diarylethenes **1**–**5** were examined in hexane both at room temperature and at 60 °C. The result showed that no decomposition was detected when diarylethenes **1**–**5** were exposed to air for more than 10 days at room temperature. At 60 °C, diarylethenes **1**–**4** still

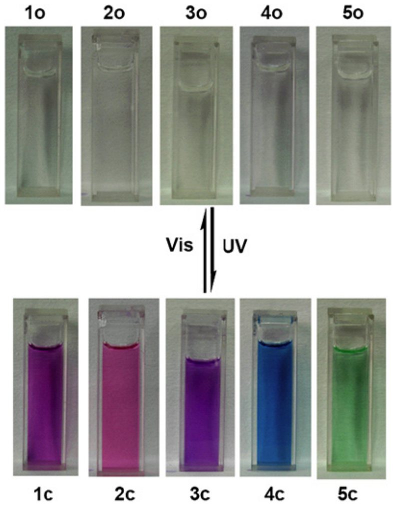


Figure 2. Color changes of diarylethenes **1**–**5** upon alternating irradiation with UV–vis light in hexane.

Table 1
Absorption spectral characteristics and photochromic reactivity of diarylethenes **1**–**5** in hexane at 2.0×10^{-5} mol L^{-1}

Compound	Absorption spectra		Quantum yield[c] (Φ)	
	$\lambda_{o,max}$[a]/nm (ε/L mol^{-1} cm^{-1})	$\lambda_{c,max}$[b]/nm (ε/L mol^{-1} cm^{-1})	Φ_{o-c}	Φ_{c-o}
1	239 (2.7×10^4)	544 (5.7×10^3)	0.31	0.26
2	239 (2.2×10^4)	526 (4.3×10^3)	0.29	0.24
3	249 (2.8×10^4)	559 (7.3×10^3)	0.19	0.12
4	261 (3.1×10^4)	632 (6.5×10^3)	0.38	0.078
5	354 (3.4×10^4)	739 (6.6×10^3)	0.22	0.071

[a] Absorption maxima of open-ring forms.
[b] Absorption maxima of closed-ring forms.
[c] Quantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

showed good thermal stabilities for more than 24 h, but the green color of **5b** disappeared completely after 2 min. The thermal instability of **5b** is ascribed to the fact that the photogenerated central carbon–carbon bond in the closed-ring isomer is weakened by the dicyanovinyl groups.[2a]

2.2. Photochromic reactions in the crystalline phase

Among diarylethenes **1o**–**5o**, single crystals of diarylethenes **1o** and **4o** were obtained by recrystallization from the diethyl ether, and those of diarylethenes **2o** and **5o** were obtained by recrystallization from the mixture of diethyl ether and hexane. To know better the relation between the conformation and the photochromic behaviors of diarylethenes **1o**, **2o**, **4o** and **5o** in the crystalline phase, their final structural confirmations were provided by X-ray crystallographic analysis. The ORTEP drawings of the single crystals of **1o**, **2o**, **4o** and **5o** are shown in Figure 3, and the X-ray crystallographic analysis data are listed in Table 2. As shown in Figure 3, for compound **2o**, there are two independent molecules in the asymmetric unit and both of them adopt an approximate C_2 symmetry, while packing in a photoactive *anti*-parallel conformation in the crystalline phase, which can undergo photocyclization reaction.[5d,11] The two planar thiophene ring systems have similar geometries in each molecule, with dihedral angles between the cyclopentene ring and the adjacent thiophene rings of 53.7(7)° (S1/C1–C4) and 50.5(7)° (S2/C14–C17) in one molecule and 52.3(4)° (S3/C22–C25) and 53.6(4)° (S4/C35–C38) in the other one. The distances between the potentially photoactive C atoms (C4···C14 and C25···C35) in each molecule were 3.647(3) and 3.766(5) Å, respectively, which are close enough for the cyclization reaction.[12] Besides diarylethene **2o**, there are two independent molecules in the asymmetric unit for diarylethene **4o** (Fig. 3), the corresponding values for the dihedral angles between the central cyclopentene ring and the thiophene rings are 55.5(6)° and 59.4(6)° in one molecule and 54.2(6)° and 55.3(6)° in the other one. The corresponding distances between the potentially photoactive carbon atoms (C5···C15 and C26···C36) in each molecule are 3.732 (5) and 3.773(5) Å, respectively.[9] The distance between the potentially photoactive carbon atoms (C4···C16) in crystal **1o** is 3.802(6) Å, and that (C8···C18) in crystal **5o** is 4.226(4) Å (Table 3).

As described above, it can be concluded that all molecules of crystals **1o**, **2o**, and **4o** were fixed in an anti-parallel mode in the crystalline phase and the distances of the two reactive carbon atoms were less than 4.2 Å, which were close enough for the photocyclization reaction, indicating that they could be expected to undergo photochromism in the single crystalline phase. However, although the molecule of crystal **5o** was fixed in an anti-parallel mode, the distance of the two reactive carbon atoms was larger than 4.2 Å, which was too far to undergo photochromism in the crystalline phase.[12] In fact, the photochromic behaviors of diarylethenes **1o**, **2o**, **4o** and **5o** in the single crystalline phase were consistent with the theoretical analysis. Their color changes upon photoirradiation are shown in Figure 4. Upon irradiation with 254 nm light, the colorless crystal of **1o**, **2o**, and **4o** turned quickly carmine, carmine, and blue, respectively. When the colored crystal was dissolved in hexane, the solution turned to a corresponding color and the absorption maximum was observed at the same as that of the closed-ring isomer **1c**, **2c**, and **4c**, respectively. The color disappeared upon irradiation with visible light and the absorption spectrum of the solution containing the colorless crystal was the same as that of the **1o**, **2o**, and **4o**. However, crystal **5o** showed no photochromism in the single crystalline phase. This is verified by the fact that irradiating single crystal of **5o** with UV light for 2 h resulted in no any observable color change. When the crystal was dissolved in hexane, the solution showed colorless and the absorption spectrum was the same as that of **5o**. Furthermore, crystals **1o**, **2o**, and **4o** exhibited more than 100 times of coloration–decoloration cycles by alternate irradiation with UV and visible light. So, these crystals will be good candidates for optoelectronic applications.[6b]

2.3. Fluorescence of diarylethenes *1o*–*5o*

The fluorescence spectra of diarylethenes **1o**–**5o** in hexane (c=2.0×10^{-4} mol L^{-1}) at room temperature are illustrated in Figure 5. Because diarylethene **4o** showed almost no fluorescence and **5o** showed very weak fluorescence (Fig. 5), we

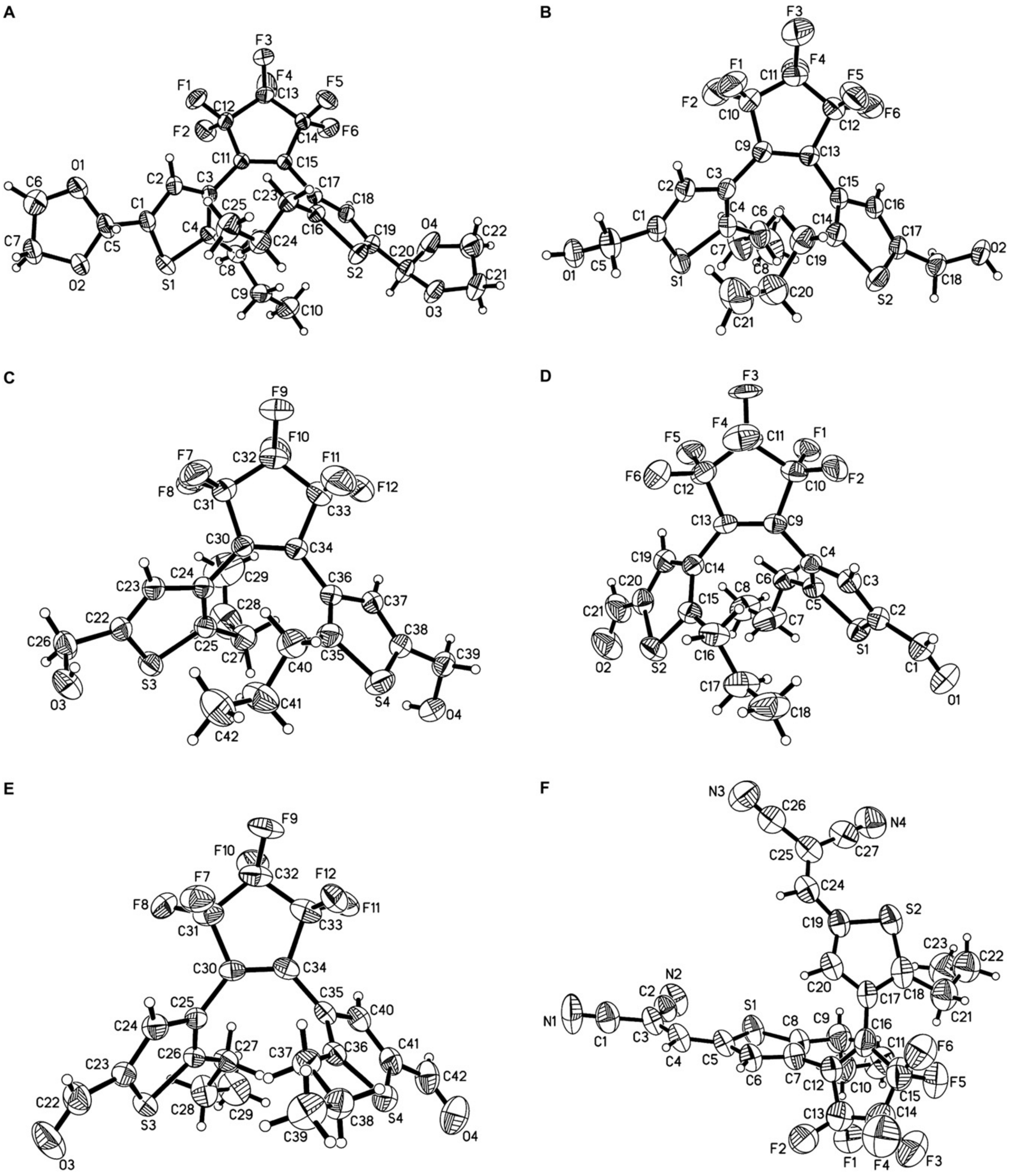


Figure 3. ORTEP drawings of crystals **1o**, **2o**, **4o** and **5o**, showing 35% probability displacement ellipsoids: (A) **1o**, (B) **2o**—molecule I, (C) **2o**—molecule II, (D) **4o**—molecule I, (E) **4o**—molecule II, and (F) **5o**.

only discuss the fluorescence properties of **1o–3o** in this work. In hexane, diarylethenes **1o–3o** showed good fluorescence at 399, 395, and 411 nm when excited at 285 nm. Their fluorescence maxima were observed between 395 and 411 nm, indicating that the electron-donating substituent effects on the emission peak was not significant. However, the emission intensity was heavily dependent on the categories of electron-donating substituents. Among diarylethenes **1o–3o**, the emission intensity of diarylethene **3o** was the weakest, and that of **1o** and **2o** was almost equal each other.

As has been observed for most of the reported diarylethenes,[13] diarylethenes **1–3** exhibited a relatively strong

Table 2
Crystal data for diarylethenes **1o**, **2o**, **4o**, and **5o**

Compound		**1o**	**2o**	**4o**	**5o**
Formula		$C_{25}H_{26}F_6O_4\ S_2$	$C_{21}H_{22}F_6O_2S_2$	$C_{21}H_{18}F_6O_2S_2$	$C_{27}H_{18}F_6N_4S_2$
Formula weight		568.58	484.23	480.47	576.57
Temperature (K)		291(2)	291(2)	294(2)	291(2)
Crystal system		Triclinic	Triclinic	Triclinic	Monoclinic
Space group		*P*-1	*P*-1	*P*-1	*C*2/*c*
Unit cell dimensions	*a* (Å)	8.4422(12)	11.5147(14)	10.6721(18)	35.398(6)
	b (Å)	12.0784(18)	14.0903(16)	14.059(2)	11.2324(19)
	c (Å)	13.2661(19)	15.4140(18)	16.532(3)	15.557(3)
	α (°)	83.945(2)	79.5930(10)	88.656(3)	90
	β (°)	79.569(2)	86.3180(10)	73.603(3)	113.127(2)
	γ (°)	75.617(2)	69.2580(10)	67.958(3)	90
Volume (Å^3)		1286.1(3)	2300.3(5)	2196.1(7)	5688.6(17)
Z		2	4	4	8
Density (calcd) (g/cm^3)		1.468	1.399	1.453	1.346
Goodness-of-fit on F^2		1.034	1.051	1.028	1.053
Final *R* indices [$I/2\sigma(I)$]	*R*1	0.0494	0.0663	0.0558	0.0960
	*wR*2	0.1304	0.1726	0.1325	0.2672
R indices (all data)	*R*1	0.0679	0.1004	0.1066	0.1932
	*wR*2	0.1460	0.2008	0.1651	0.3415

Table 3
Distances between the reacting carbon atoms (*d*, Å) dihedral angles (θ, °) of **1o**, **2o**, **4o** and **5o**

Compound	*d* (Å)		θ (°)			
1o	C4⋯C16	3.802(6)	S1/C1–C4	58.2(3)	C5/O1/C6–C7/O2	49.9(3)
			S2/C16–C19	58.3(3)	C20/O3/C21–C22/O4	49.3(3)
2o	C4⋯C14	3.647(3)	S1/C1–C4	53.7(7)	S2/C14–C17	50.5(7)
	C25⋯C35	3.766(5)	S3/C22–C25	52.3(4)	S4/C35–C38	53.6(4)
4o	C5⋯C15	3.732(5)	S1/C2–C5	55.5(6)	S2/C15/C14/C19/C20	59.4(6)
	C26⋯C36	3.773(5)	S3/C23–C26	54.2(6)	S4/C36/C35/C40/C41	55.3(6)
5o	C8⋯C18	4.226(4)	S1/C5–C8	63.7(3)	S2/C18/C17/C20/C19	47.8(4)

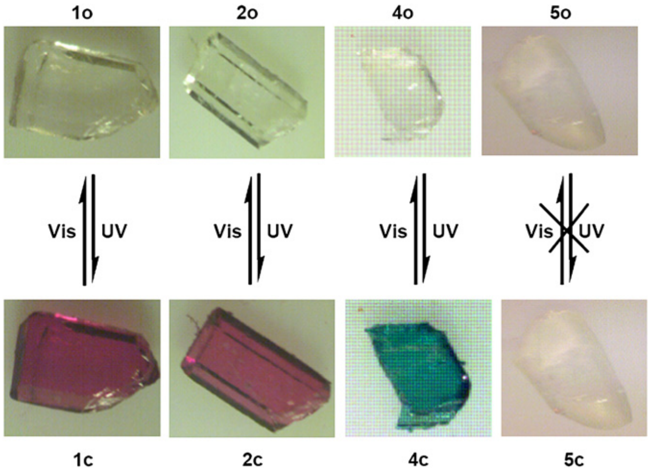


Figure 4. Photographs of photochromic processes of diarylethenes **1**, **2**, **4**, and **5** in the crystalline phase.

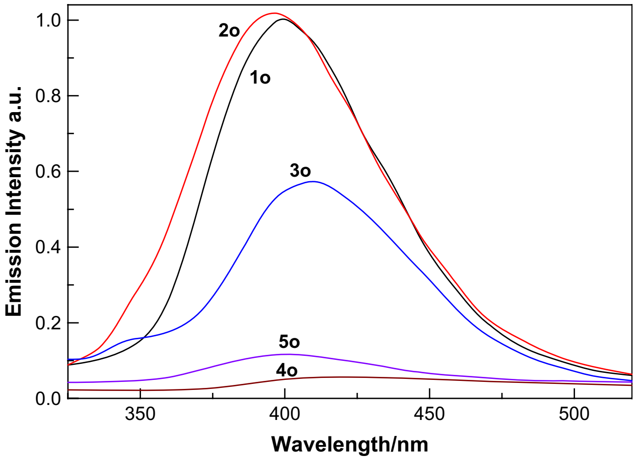


Figure 5. Fluorescence emission spectra of diarylethenes **1o**–**5o** in hexane (c=2.0×10^{-4} mol L^{-1}) at room temperature, excited at 285 nm.

fluorescence switches along with the photochromism from open-ring isomers to closed-ring isomers. When irradiated by 254 nm UV light, the photocyclization reactions were carried out and the non-fluorescent closed-ring isomers of the three compounds were produced. The back irradiation by appropriate wavelength visible light regenerated the open-ring isomers of diarylethenes **1o**–**3o** and recovered the original emission spectra. During the process of photoisomerization, diarylethenes **1o**–**3o** exhibited changes in their fluorescence in hexane as shown in Figure 6. Upon irradiation with 254 nm UV light, the emission intensities of diarylethenes **1o**–**3o** were decreased remarkably by photocyclization. When arrived at the photostationary state, their emission intensities were quenched to ca. 19, 18, and 18%, respectively, indicating that all of them

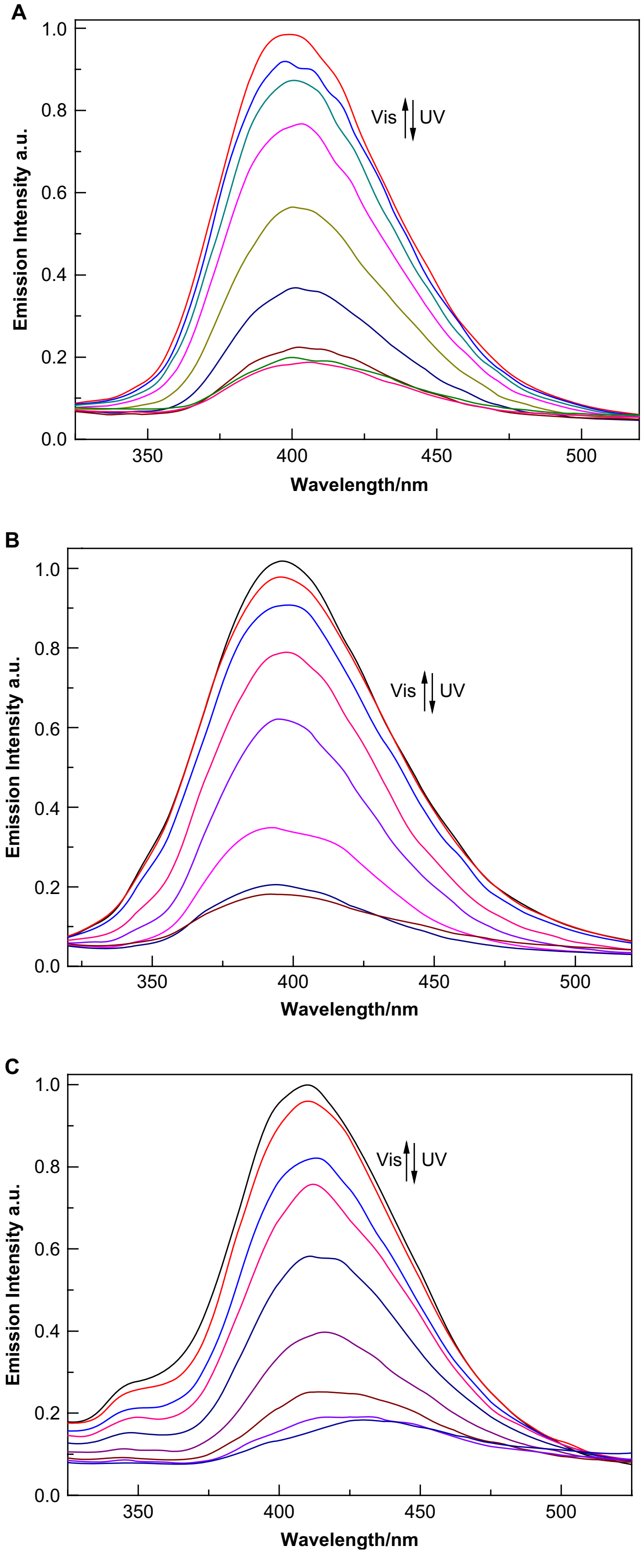


Figure 6. Emission intensity changes of diarylethenes **1–3** in hexane (c=2.0×10^{-4} mol L^{-1}) upon irradiation with 254 nm UV light at room temperature, excited at 285 nm: (A) **1**, (B) **2**, and (C) **3**.

exhibited very strong fluorescent switching in hexane. In addition, we measured the 'on' and 'off' state of the switchable fluorescence by changing the power of the UV and visible light. The average 'on' and 'off' times shortened in proportion to the reciprocal power of the radiated light, indicating that the switching effect is indeed photochemical.[14] This fluorescent characteristics, which use external photostimulation to switch the fluorescence 'on' and 'off' from open-ring isomers to closed-ring isomers are similar to those of some other diarylethene compounds reported.[6c,13,15] It has been reported that diarylethenes, which showed fluorescence in the open-ring isomer and showed no fluorescence or weak fluorescence in the closed-ring isomer could be potentially applied to optical memory with fluorescence readout method and fluorescence switches.[13e,15]

2.4. Electrochemical properties of diarylethenes *1–5*

The electrochemical properties of diarylethene can be potentially applied to molecular scale electronic switches.[16] The oxidative cyclization and cycloreversion and the reductive electrochemical cyclization of some diarylethene derivatives have been reported.[17] Herein, electrochemical examinations by the CV method under the same experimental conditions using diarylethene **1–5** were performed. The typical electrolyte was acetonitrile (5 mL) containing 0.10 mol L^{-1} tetrabutylammonium tetrafluoroborate ((TBA)BF_4) and 1.0×10^{-3} mol L^{-1} diarylethenes **1–5**. Platinum wire (0.5 mm) and steel electrodes were used as working and counter electrodes, respectively. Platinum wire (0.5 mm) in the supporting electrolyte solutions was used as a quasi-reference electrode, which was calibrated through the CV of ferrocene in similar electrolyte. Figure 7 showed the CV curves of diarylethenes **5** with the scanning rate of 50 mV s^{-1}. According to the same method described in previous publications,[9,18] the HOMO and LUMO energy level can also be estimated. As shown in Figure 7, the onset potentials (E_{onset}) of oxidation and reduction for **5o** were observed at +2.13 and −0.75 V, respectively. Therefore, the values of IP and EA were calculated to be −6.93 and −4.05. Based on the HOMO and LUMO energy level, the band gap E_g (E_g=LUMO−HOMO) of **5o** can be determined as 2.88 eV. Similarly, the E_g of **5c** can be easily calculated as 2.61 eV. Corresponding values for diarylethenes **1–5** were summarized in

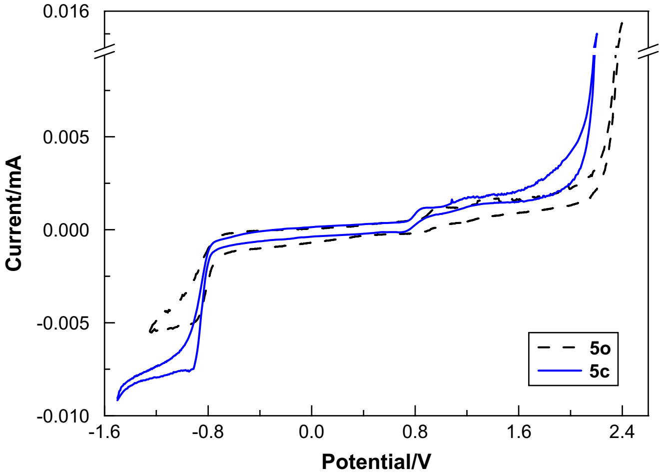


Figure 7. Cyclic voltammetry (second scan) of diarylethene **5** in acetonitrile with the scanning rate of 50 mV s^{-1}.

Table 4
Electrochemical properties of diarylethenes **1–5** in acetonitrile

Compound	Oxidation		Reduction		Band gap
	E_{onset} (V)	IP (eV)	E_{onset} (V)	EA (eV)	E_g
1o	+2.08	−6.88	−1.53	−3.27	3.61
1c	+2.06	−6.86	−0.86	−3.94	2.92
2o	+1.88	−6.68	−1.13	−3.67	3.01
2c	+1.80	−6.60	−1.22	−3.58	3.02
3o	+1.74	−6.54	−0.76	−4.04	2.50
3c	+1.67	−6.47	−0.79	−4.01	2.46
4o	+1.85	−6.65	−1.29	−3.51	3.14
4c	+1.84	−6.64	−1.08	−3.72	2.92
5o	+2.13	−6.93	−0.75	−4.05	2.88
5c	+1.82	−6.62	−0.79	−4.01	2.61

Table 4. From Table 4, it can be clearly seen that the electrochemical parameters of the five compounds are remarkably dependent on the substituent effects. The oxidation of **1o**, **1c**, **2o**, **2c**, **3o**, **3c**, **4o**, **4c**, **5o**, and **5c** was initiated at 2.08, 2.06, 1.88, 1.80, 1.74, 1.67, 1.85, 1.84, 2.13, and 1.82 V, respectively. The result indicated that the oxidation onsets of the open-ring isomers were higher than those of the closed-ring isomers. This is in accordance with the theory that longer conjugation length generally leads to less positive potentials, with the addition of each heterocyclic ring.[7b] After cyclization reaction, the π-conjugation lengths of **1c–5c** were much longer than those of **1o–5o**, respectively. Moreover, the difference of oxidation onset between the open- and closed-ring isomers of diarylethenes **1–5** ($\Delta V_{\text{o-c}}$) was 0.02 V for **1**, 0.08 V for **2**, 0.07 V for **3**, 0.01 V for **4**, and 0.31 V for **5**, respectively. For the band gap of diarylethenes **1–5**, all values of E_g of the open-ring isomers were higher than those of the closed-ring isomers, with the exception of diarylethene **2**. Among these compounds, the E_g was the smallest in **3c**, implying that the charge transfer must be faster in **3c** compared to that in others.[19] All these data described above suggested that different electron-donating and electron-withdrawing substituents have remarkable effect on the electrochemical behaviors of these diarylethenes. It should be noted here that calculation absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate.[18b]

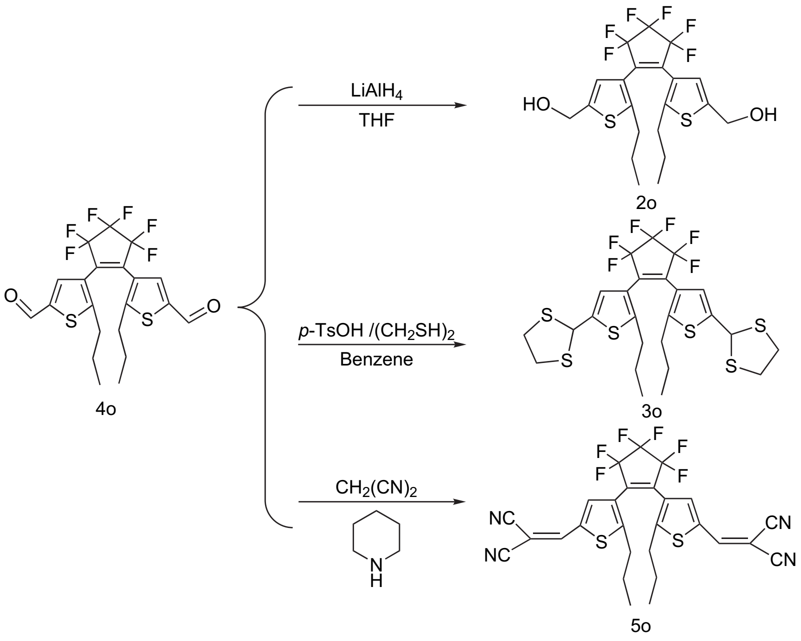
3. Conclusion

In conclusion, five symmetrical diarylethenes bearing different substitutents at 5-position of the two thiophene rings were synthesized to reveal the effect of the substitution on their optoelectronic properties. The result indicated that the substituents at 5-position of the thiophene rings had a remarkable effect on the optoelectronic properties of these diarylethene derivatives, including photochromism, fluorescence, and electrochemical properties, which may be attributed to the different electron-donating or electron-withdrawing substituent effects. The present results were useful for the design of efficient photoactive and excellent characteristic diarylethene derivatives.

4. Experimental

4.1. General methods

NMR spectra were recorded on Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were recorded on Bruker Vertex-70 spectrometer and mass spectra were measured with Agilent MS Trap VL spectrometer. The elemental analysis was measured with PE CHN 2400. The absorption spectra were measured using Agilent 8453 UV/VIS spectrometer. Photoirradiation was carried out using SHG-200 UV lamp



Scheme 2. Synthetic route for diarylethenes **2o**, **3o**, and **5o**.

and BMH-250 Visible lamp. Light of appropriate wavelength was isolated by different light filters. Electrochemical examinations were performed in a one-compartment cell by using a Model 263 potentiostat-galvanostat (EG&G Princeton Applied Research) under computer control at room temperature. All solvents used were of spectrograde and were purified by distillation before use. Crystal data diarylethenes **1o**, **2o**, **4o** and **5o** were collected by a Bruker SMART APEX2 CCD area-detector. Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication numbers CCDC 657309, 642550, 631249, and 654194 for **1o**, **2o**, **4o**, and **5o**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif.

*4.2. Synthesis of diarylethenes **1o–5o***

The synthetic method of **1o** and **4o** was described in reference.[9] Diarylethene **2o** was prepared by the reduction of diarylethene **4o** with lithium aluminum hydride. Diarylethene **3o** was synthesized by the condensation reaction of diarylethene **4o** with 1,2-ethanedithiol, and diarylethene **5o** was synthesized by the Knoevenagel condensation reaction of diarylethene **4o** with malonodinitrile. The synthetic method of **2o**, **3o**, and **5o** was described in Scheme 2 and their structure analysis data were shown in Ref. 20.

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References and notes

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20. Structure analysis data. Compound **2o**: 83% yield as colorless crystals; mp 99.4–100 °C; MS *m/z* (M^+) 483.4 (−H), 507.1 (+Na). Anal. Calcd for $C_{21}H_{22}F_6O_2S_2$ (%): C, 52.06; H, 4.58. Found: C, 52.73; H, 4.45; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.78 (t, 6H, J=7.2 Hz, −CH_3), 1.26–1.33 (m, 4H, −CH_2), 2.17 (t, 4H, J=7.6 Hz, −CH_2), 4.78 (s, 4H, −CH_2), 6.94 (s, 2H, thiophene−H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.73, 24.32, 24.42, 31.01, 60.03, 123.42, 124.71, 142.36, 148.24; IR (KBr, ν, cm^{-1}): 939, 1004, 1109, 1272, 1340, 1643, 2875, 2935, 2964, 3317. Compound **3o**: 65% yield as yellow power; mp 108.1–108.4 °C; MS *m/z* (M^+) 655.0 (+Na). Anal. Calcd for $C_{25}H_{26}F_6S_6$ (%): C, 47.45; H, 4.14. Found: C, 47.51; H, 3.94; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.86 (t, 6H, J=7.6 Hz, −CH3), 1.47–1.53 (m, 4H, −CH2), 2.34 (t, 4H, J=7.6 Hz, −CH_2), 3.34–3.48 (m, 8H, −CH_2), 7.64 (s, 2H, thiophene−H), 7.79 (s, 2H, −CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 14.00, 24.15, 31.20, 40.04, 50.62, 123.02, 124.86, 145.40, 148.40; IR (KBr, ν, cm^{-1}): 742, 943, 1021, 1101, 1191,

1267, 1336, 1460, 1552, 1626, 2875, 2929, 2964. Compound **5o**: 67% yield as colorless crystals; mp 109.3–109.7 °C; MS *m/z* (M+) 574.9 (−H). Anal. Calcd for $C_{27}H_{18}F_6N_4S_2$ (%): C, 56.24; H, 3.15; N, 9.72. Found: C, 56.60; H, 3.07; N, 9.47; ^1H NMR ($CDCl_3$, 400 MHz, TMS): δ 0.86 (t, 6H, J=7.6 Hz, $-CH_3$), 1.48–1.55 (m, 4H, $-CH_2$), 2.34 (t, 4H, J=7.6 Hz, $-CH_2$), 7.64 (s, 2H, thiophene−H), 7.79 (s, 2H, −CH); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS): δ 13.61, 24.39, 31.76, 80.00, 112.48, 113.15, 125.40, 133.82, 137.33, 149.52; IR (KBr, ν, cm^{-1}): 748, 947, 1008, 1076, 1140, 1272, 1338, 1429, 1579, 2227, 2875, 2966.