Syntheses and Substituent Effects on the Properties of Unsymmetrical Photochromic Diarylethenes Bearing a Benzothiophene Unit

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Photochromic unsymmetrical diarylethenes 1a-5a that bear different electron-donating or electron-withdrawing substitutes have been synthesized, and the structures of 2a-5a determined by single-crystal X-ray diffraction analysis. Substituent effects on their optoelectronic properties, including photochromism, fluorescence, and electrochemical properties are investigated in detail. The strong electron-donating substituents have effective contributions to the absorption maxima of the closed-ring isomers and the molar coefficients, whereas the electron-withdrawing substituents can shift significantly the absorption maxima of the diarylethenes to a longer wavelength and increase their cyclization quantum yield. Diarylethenes 2, 3, and 4 show good photochromism both in solution and in the single crystalline phase. However, diarylethenes 5 shows no photochromism in the crystalline phase. Diarylethenes 1, 2, and 3 exhibit good fluorescent switching upon alternating irradiation with UV and visible light, and their fluorescent conversions in the photostationary state are all larger than 80% in hexane. In addition, cyclic voltammogram tests show that different electron-donating and electron-withdrawing substituents have a remarkable effect on the electrochemical behaviours of these diarylethenes.

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Introduction

Photochromic compounds have been extensively studied for optoelectronic devices, such as for optical data storage, full-colour displays, and photoswitches.^[1–4] Up to date, various types of photochromic compounds, such as spirobenzopy-rans, azobenzenes, fulgides, and diarylethenes, have been developed.^[5,6] Among such compounds, diarylethenes that bear thiophene/benzothiophene rings have received the most attention because of the good thermal stability of both isomers, excellent fatigue resistance, high quantum yields, and large changes of the absorption wavelength between the two isomers.^[1,3]

The photochromic properties of the diarylethene derivatives can be improved by modifying the chemical structures upon introducing different substituents. Therefore, substituent effects on the photochromic performances of diarylethenes have attracted much attention in recent years, and many works concerning substituent effects have been reported.^[7–15] Irie and his co-workers reported that the introduction of the bulky isopropyl groups in the 2- and 2'-positions of both benzothiophene rings would increase the cyclization quantum yield.^[7] This is the first guiding principle for the increase of ring-closure quantum yield ever reported. Some reports indicate that the bulky alkoxy substituents heavily decrease the cycloreversion quantum yield and the thermal stability of the coloured closed-ring isomer at high temperature.^[8,9] Pu et al. and Irie et al. revealed 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; whereas electron-donating substituents of the bis(2-thienyl)ethane diarylethenes could increase the maxima absorption of the open-ring forms and reduce the cyclization quantum yield.^[10–14] Tanifuji et al. elucidated that diarylethene derivatives that bear imino nitroxide and nitronyl nitroxide could reduce the cyclization/cycloreversion quantum yield.^[15]

As described above, we found that most works focussed on different substituents at the 2- and 2'-positions of the thiophene rings or at different positions of the terminal phenyl groups. Investigations concerning substitution at the 5-position of the thiophene ring and their influence on the optoelectronic properties are very rare.^[16] In addition, most of the reported diarylethene derivatives hitherto are symmetrical bis(3-thienyl)perfluorocyclopentene or bis(3-benzothienyl) perfluorocyclopentene derivatives, and very little work on the unsymmetrical hybrid diarylethenes that bear both thiophene and benzothiophene moieties has been attempted with the exception of a few reports.^[17–19] However, the reports concerning this type of hybrid aryl moiety usually focussed on the applications in some specific fields when incorporating the hybrid diarylethenes into other functional groups. In this paper, one of our research goals was to develop a series of new unsymmetrical diarylethenes bearing both thiophene and benzothiophene moieties and investigate the substituent effects on the optoelectronic properties of diarylethenes that have various electron-donating or electron-withdrawing groups at the 5-position of the thiophene ring. Therefore, we have synthesized five unsymmetrical diarylethenes with



Scheme 1. Photochromism of diarylethenes 1, 2, 3, 4, and 5.

different substituents at the 5-position of the thiophene ring (Scheme 1), namely 1-(2-ethyl-3-benzothienyl)-2-(2-*n*-pentyl-5-hydroxymethyl-3-thienyl)perfluorocyclopentene (**1a**), 1-(2ethyl-3-benzothienyl)-2-{2-*n*-pentyl-5-[2-(1,3-dioxolane)]-3thienyl}perfluorocyclopentene (**2a**), 1-(2-ethyl-3-benzothienyl)-2-{2-*n*-pentyl-5-[2-(1,3-dithiolpentane)]-3-thienyl}perfluorocyclopentene (**3a**), 1-(2-ethyl-3-benzothienyl)-2-(2-*n*-pentyl-5formyl-3-thienyl)perfluorocyclopentene (**4a**), and 1-(2-ethyl-3benzothienyl)-2-[2-*n*-pentyl-5-(2,2'-dicyanovinyl)-3-thienyl] perfluorocyclopentene (**5a**). In addition, the crystal structures of **2a–5a** were determined by single-crystal X-ray diffraction analysis, and their photochromic performances in the single crystalline phase were also investigated in detail.

Results and Discussion

Synthesis of Diarylethenes

The synthetic route for diarylethenes 1a-5a is shown in Scheme 2. First, 4-bromo-2-*n*-pentyl-5-(1,3-dioxolane)thiophene derivatives (4c) were prepared according to the procedure described in a previous paper.^[20] 2-Ethylbenzothiophene (1c) was then obtained by reacting benzothiophene with ethylbromide in the presence of *n*-BuLi/tetrahydrofuran (THF) solution at -78° C. Compound 2c was obtained by brominating compound 1c with *N*-bromosuccinimide. Lithiation of 2c followed



Scheme 2. Synthetic route for diarylethenes 1, 2, 3, 4, and 5.

by the addition of excess octafluorocyclopentene simultaneously generated compounds 3c, which could be further treated with the anion generated from 4c to yield compound 2a. Compound 4a was prepared by hydrolyzing compound 2a in the presence of pyridine and *p*-toluenesulfonic acid in acetone/water. Diarylethene 1a was prepared by the reduction of diarylethene 4a with sodium borohydride. Finally, diarylethene 3a was synthesized by the condensation reaction of diarylethene 4a with ethane-1,2-dithiol, and diarylethene 5a was synthesized by the Knoevenagel condensation reaction of diarylethene 4a with malonodinitrile. The structures of 1a-5a were confirmed by NMR, IR, and elemental analysis (see the Experimental section). The crystals of 2a-5a have been determined by single-crystal X-ray diffraction analysis.

Photochromism in Solution

The photochromic behaviours of diarylethenes 1-5 were investigated in hexane ($c 2.0 \times 10^{-5} \text{ mol L}^{-1}$). Diarylethenes 1–5 showed good photochromic properties and could be toggled between their colourless open-ring isomers (1a-5a) and coloured closed-ring isomers (1b-5b) by alternating irradiation with UV light and appropriate wavelength visible light, as monitored using UV-Vis absorption. The absorption spectroscopic change of diarylethene 1 induced by photoirradiation at room temperature is shown in Fig. 1. The absorption maximum of the colourless open-ring isomer (1a) was observed at 236 nm $(\varepsilon 2.1 \times 10^4 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1})$ in hexane. Upon irradiation with 254 nm light, the colourless solution turned red with a new broad absorption band centred at 529 nm (ε 5.2 × 10³ L mol⁻¹ cm⁻¹). The red colour is a result of the formation of the closed-ring isomer (1b). The red coloured solution returned to colourless upon irradiation with visible light (>450 nm), which indicates that 1b returned to the initial open-ring isomer (1a). The colourationdecolouration cycles could be repeated more than 30 times and a clear isosbestic point was observed at 271 nm. The spectroscopic changes of diarylethenes 2-5 were similar to that of diarylethene 1. In hexane, upon irradiation with UV light, diarylethenes 2a and 3a turned purple, the absorption maxima of which were observed at 538 and 542 nm, respectively, as the closed-ring isomers 2b and 3b were generated: whereas diarylethene 4a turned blue and the absorption maximum was observed at 582 nm. Upon irradiation with 365 nm UV light, diarylethene 5a turned



Fig. 1. Absorption spectroscopic change of diarylethene 1 in hexane solution ($c \ 2.0 \times 10^{-5} \text{ mol L}^{-1}$) at room temperature.

green and the absorption maximum developed at 677 nm in hexane. All solutions of **2b–5b** can be decolourized by irradiating them with visible light of wavelength greater than 450 nm, which induces the cycloreversion reactions and reproduce **2a–5a**. After repeating 30 colouration–decolouration cycles, the isosbestic points for diarylethenes **2–5** were observed at 272, 274, 311, and 383 nm, respectively.

The colour changes of diarylethenes 1-5 upon photoirradiation in hexane are shown in Fig. 2. The absorption spectroscopic properties and the cyclization/cycloreversion quantum yields of these compounds are summarized in Table 1. The results indicate that different substituents at the 5-position of the thiophene ring had a significant effect on the photochromic behaviours of diarylethenes 1-5. For compounds 1-3, the absorption maxima of their open-ring isomers only fluctuate over a very small numerical value range (229-236 nm), which indicates that the electron-donating substituents do not significantly influence the absorption maxima of diarylethenes 1a-3a. However, the electron-donating substituents have an efficient contribution to the molar absorption coefficient of the open-ring isomers of diarylethenes 1-3. For compounds 1a-3a, the molar absorption coefficient increased remarkably when replacing the hydroxymethyl group with the strong electron-donating 1,3-dioxolane group. Meanwhile, the molar absorption coefficient decreased to some extent when replacing the 1,3-dioxolane group with the stronger electron-donating 1,3-dithiolpentane group, but it was still higher than that of compound 1a. For the closed-ring isomers of diarylethenes 1-3, the electron-donating substituents have a significant effect on



Fig. 2. Colour changes of diarylethenes 1, 2, 3, 4, and 5 upon alternating irradiation with UV and visible light in hexane.

Table 1. Absorption spectroscopic characteristics and photochromic reactivity of diarylethenes 1, 2, 3, 4, and 5 in hexane at 2.0×10^{-5} mol L⁻¹

Compound	Absorptio	Quantum yield ^C		
	$\lambda_{o, max} [nm]^A$ ($\varepsilon [L mol^{-1} cm^{-1}]$)	$\begin{array}{l} \lambda_{c, \ max} \ [nm]^{B} \\ (\varepsilon \ [L \ mol^{-1} \ cm^{-1}]) \end{array}$	$\Phi_{\text{o-c}}$	Φ_{c-0}
1	$236 (2.1 \times 10^4)$	$529 (5.7 \times 10^3)$	0.22	0.32
2	$229(3.3 \times 10^4)$	$536(5.1 \times 10^3)$	0.29	0.31
3	$231 (2.6 \times 10^4)$	$542 (5.0 \times 10^3)$	0.16	0.19
4	$257 (2.2 \times 10^4)$	$582 (4.7 \times 10^3)$	0.33	0.17
5	$358~(1.6 \times 10^4)$	668 (5.5×10^3)	0.30	0.11

^AAbsorption maxima of the open-ring isomers.

^BAbsorption maxima of the closed-ring isomers.

^CQuantum yields of cyclization reaction (Φ_{o-c}) and cycloreversion reaction (Φ_{c-o}), respectively.

both the absorption maximum and the molar absorption coefficient. The absorption maxima of the closed-ring isomers 1b-3b increased remarkably (from 529 nm to 542 nm) with increasing electron-withdrawing ability. However, the molar absorption coefficients of the closed-ring isomers 1b-3b decreased gradually with increasing electron-withdrawing ability. Among diarylethenes 1-3, the molar absorption coefficient of the closed-ring isomers 1b (ε 5.7 × 10³ Lmol⁻¹ cm⁻¹) is the biggest, whereas that of **3b** (ε 5.0 × 10³ L mol⁻¹ cm⁻¹) is the smallest. The result is contrary to that reported by Irie et al., which indicated that the molar absorption coefficient increased gradually with increasing electron-donating ability.^[12] The electron-withdrawing substituents (formyl and cyano groups) significantly shifted the absorption maxima of the diarylethenes 4 and 5 to a longer wavelength, and the molar absorption coefficients of 4b and 5b increased with increasing electron-withdrawing ability. The result is in agreement with that reported previously.[10-14,16]

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 also shown in Table 1. The cyclization quantum yield of diarylethene 1 was 0.22. When a strong electron-donating 1,3-dioxolane group was substituted at the 5-position of the thiophene ring such as in compound 2, the cyclization quantum yield increased significantly (Φ_{0-c} 0.29). However, when the 1,3-dithiolpentane group was substituted at the same position of the thiophene ring such as in compound 3, the cyclization quantum yield decreased to some extent (Φ_{0-c} 0.16). However, electron-withdrawing formyl and dicyanovinyl groups increased the cyclization quantum yield, and the cyclization quantum yield was observed at 0.33 for 4 and 0.30 for 5, respectively, both of which were then higher than those of compounds 1-3 bearing electron-donating groups. The result is also in good agreement with that reported by Irie and co-workers.^[12] The cycloreversion quantum yields of diarylethenes 1, 2, and 3 that have electron-donating substituents are 0.32, 0.31, and 0.19, respectively. The results indicate that the cycloreversion quantum yield was significantly dependent on the electron-donating substituents. Furthermore, the cycloreversion quantum yield of diarylethene 4 and 5 were 0.17 and 0.11, which suggests that the cycloreversion quantum yield decreased upon increasing the strength of the electron-withdrawing substituents.^[12,16] From Table 1, it can be easily seen that the cycloreversion quantum yields of diarylethenes 1, 2, and 3 that have electron-donating

substituents are much higher than those of diarylethenes 4 and 5 that have electron-withdrawing substituents. The results may be ascribed to the substituent position effect on the π -conjugated system in diarylethene molecules. The cycloreversion quantum yields decreased with an increase in the π -conjugation length of the aryl groups.^[1] For diarylethenes 4 and 5, the electron-withdrawing formyl and dicyanovinyl groups can participate in the conjugation system, which results in a larger extension of the π -conjugation in the molecules of 4 and 5. As a result, diarylethenes 4 and 5 exhibit more marked π conjugation lengths than 1, 2, and 3, which is consistent with the red-shifted absorption maxima and the lower cycloreversion quantum yields. For diarylethenes 1-5, all the cyclization quantum yields are less than 0.5, and are generally lower than those of diarylethene derivatives bearing phenyl groups on the end.^[10] However, the quantum yields are much higher than those of photochromic bis(2-thienyl)perfluorocyclopentene derivatives.^[14]

The thermal stabilities of diarylethenes 1-5 were examined in hexane both at room temperature and at 80°C. The results show that no changes in their UV-vis spectra were observed, and no decomposition was detected when these compounds were exposed to air for more than 20 days at room temperature. At 80°C, diarylethenes 1-4 still showed good thermal stabilities for more than 24 h, but the green colour 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.^[1]

Photochromism in the Single Crystalline Phase

Single crystals of 2a-5a were obtained by recrystallization from a mixture of diethyl ether and hexane. To gain a deeper understanding of the relation between the conformation and the photochromic behaviours of diarylethenes 2a-5a in the crystalline phase, the final structural conformations of these compounds were provided by X-ray crystallographic analysis. The X-ray crystallographic analysis data are listed in Table 2. The ORTEP drawings of the single crystals 2a-5a are shown in Fig. 3 and their packing diagrams are shown in Fig. 4. As shown in Fig. 3, the molecule of 3a occupied approximately a C_2 symmetry, and it was packed in a photoactive anti-parallel conformation in the crystalline phase, which can undergo a photocyclization reaction.^[21] The molecule has five planar rings, which can form four dihedral angles between every two adjacent planar rings. The dihedral angles between the hexafluorocyclopentene ring and the two thiophene rings are $59.9(3)^{\circ}$ for S1/C1–C3/C8 and $52.2(3)^{\circ}$ for S2/C16–C19. The dihedral angles between the left thiophene ring (S1/C1-C3/C8) and the adjacent benzene ring (C3–C8) is $1.0(3)^{\circ}$, and that between the right thiophene ring (S2/C16-C19) and the 1,3-dithiolpentane ring (C25/S3/C26-C27/S4) is $89.0(3)^{\circ}$. In the perfluorocyclopentene ring of **3a**, the distances of the bond lengths for C11-C12, C12-C13, C13-C14, C14–C15, and C11–C15 are 1.504(5), 1.523(5), 1.513(5), 1.508(4), and 1.348(4) Å, respectively. These data clearly indicate that the C11–C15 bond is a double bond, being significantly shorter than the other carbon-carbon single bonds. The two thiophene moieties were linked by the C11=C15 double bond, with both of them attached to the ethylene by the 3-position. The pentyl and ethyl groups are located on different sides of the double bond and are in a trans-direction to the two thiophene planes. This kind of conformation was crucial to its photochromic and photoinduced properties.^[22] The intermolecular distance

Parameter	2a	3a	4a	5a
Formula	$C_{27}H_{26}F_6O_2S_2$	C27H26F6S4	C25H22F6OS2	C ₂₈ H ₂₂ F ₆ N ₂ S ₂
Formula weigh	560.60	592.72	516.55	564.60
Temperature [K]	291(2)	294(2)	293(2)	291(2)
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	P-1	<i>P</i> -1	<i>P</i> -1	P-1
a [Å]	10.2996(11)	10.2169(13)	9.8868(12)	10.930(5)
b [Å]	10.7924(11)	11.0204(14)	10.1076(12)	11.525(6)
c [Å]	13.3082(14)	13.4245(17)	12.6866(15)	13.715(6)
α [°]	106.6800(10)	67.0280(10)	86.8120(10)	65.218(6)
β [°]	100.8440(10)	84.732(2)	75.5780(10)	67.338(6)
γ [°]	105.1640(10)	89.163(2)	80.7620(10)	64.912(6)
Volume [Å ³]	1311.1(2)	1385.4(3)	1211.8(3)	1374.5(11)
Ζ	2	2	2	2
Density (calcd.) $[g cm^{-3}]$	1.420	1.421	1.416	1.052
Goodness-of-fit on F^2	1.058	1.032	1.057	1.058
Final <i>R</i> indices $[I/2\sigma(I)]$				
R_1	0.0488	0.0555	0.0521	0.0743
wR_2	0.1258	0.1386	0.1365	0.2086
R indices (all data)				
R_1	0.0615	0.0867	0.0717	0.1220
wR_2	0.1355	0.1623	0.1544	0.2482

 Table 2.
 Crystal data for diarylethenes 2a, 3a, 4a, and 5a





(d)



Fig. 3. ORTEP drawings of crystals 2a, 3a, 4a, and 5a, showing 35% probability displacement ellipsoids: (a) 2a, (b) 3a, (c) 4a, (d) 5a.



Fig. 4. Packing views of crystals 2a-5a along the *a* direction: (a) 2a, (b) 3a, (c) 4a, (d) 5a.

Table 3. Distances between the reacting carbon atoms (d, A) dihedral angles (θ, \circ) of 2a, 3a, 4a, and 5a

Compound	<i>d</i> [<i>A</i>	Å]	θ [°]			
2a	C8···C16	3.938(7)	S1/C1/C6-C8	62.9(5)	S2/C16-C19	53.5(5)
3a	$C1 \cdots C16$	3.766(7)	S1/C1-C3/C8	59.9(3)	S2/C16-C19	52.2(3)
4a	$C1 \cdots C16$	3.914(3)	S1/C1-C3/C8	65.1(5)	S2/C16-C19	59.9(5)
5a	$C8 \cdot \cdot \cdot C17$	3.979(4)	S1/C1/C6–C8	70.6(6)	S2/C16-C17/C23-C24	60.0(6)

between the two active C atoms $(C1\cdots C16)$ is 3.766(7) Å. The corresponding dihedral angles and the distances between the reacting carbon atoms for **2a**, **4a**, and **5a** were also calculated, and these data are summarized in Table 3. All molecules of crystals **2a–5a** were packed in an anti-parallel mode in the crystalline phase and the distance between the two reactive carbon atoms was less than 4.2 Å, which was close enough for the reaction to take place, which indicates that they could by expected to undergo photochromism in the single crystalline phase.^[23,24]

In fact, crystals of 2a, 3a, and 4a showed a photochromic reaction coincident with the theoretical analysis. The colour changes upon photoirradiation are shown in Fig. 5. The

colourless crystals of **2a**, **3a**, and **4a** turned purple, purple, and blue upon irradiation with 254 nm UV light, respectively. When the coloured crystals were dissolved in hexane, the solution turned to the corresponding colour and the absorption maximum was observed at the same wavelength as that of the closed-ring isomer **2b**, **3b**, and **4b**, respectively. The colour disappeared upon irradiation with visible light and the absorption spectrum of the solution that contained the respective colourless crystal was the same as that of the open-ring isomer **2a**, **3a**, and **4a**. However, although the crystal of **5a** was fixed in an anti-parallel mode, and the distance of the two reactive carbon atoms was less than 4.2 Å, it cannot undergo photochromic reaction in the single



Fig. 5. Photographs of photochromic processes of diarylethenes **2**, **3**, **4**, and **5** in the crystalline phase.

crystalline phase. This was verified by the fact that irradiating a single crystal of **5a** with UV light for 5 h resulted in no observable colour change. When the crystal was dissolved in hexane, the solution remained colourless and the absorption spectrum was the same as that of diarylethene **5a**. The reason for this is currently not clear and further work is still in progress. To the best of our knowledge, this is another special diarylethene example that shows no photochromism in the crystalline phase although it satisfies the two conditions, with the exception of those diarylethene crystals with a six-membered unit.^[25] Furthermore, the diarylethene crystals of **2a**, **3a**, and **4a** exhibited 200 colouration–decolouration cycles by alternating irradiation with UV and visible light. So, the crystals of diarylethenes **2a**–**4a** are good candidates for potential optoelectronic applications.^[26]

Fluorescence of Diarylethenes 1a-5a

Fluorescent photochromic materials attract strong interest for their possible applications in optical memories as well as in fluorescent probes. In particular, fluorescent diarylethenes, which show a reversible change in fluorescence intensity with photochromic reaction, are useful for non-destructive optical read-out systems.^[3] To date, many diarylethene derivatives and their fluorescent properties have been reported.^[17,27,28] In this paper, the fluorescence spectra of diarylethenes 1a-5a in hexane $(c \ 1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ at room temperature are illustrated in Fig. 6. The results illustrate that 1a, 2a, and 3a show good fluorescence in hexane, whereas diarylethenes 4a and 5a showed very weak fluorescence. Therefore, we only discuss the fluorescence properties of 1a-3a in this paper. As shown in Fig. 6, it can be clearly seen that the emission peaks of diarylethenes 1a-3a are observed at 405, 407, and 410 nm in hexane. These data indicate that the effect of electron-donating groups on the emission peak is not significant and the values undergo a minor red-shift with increasing electron-donating ability. However, the effect of electron-donating substituents on their emission intensity are very remarkable. Among diarylethenes 1a-3a, the emission intensity of diarylethene 3a was the weakest, and that of 1a and 2a were almost equal to each other.

As has been observed for most of the reported diarylethenes, [29-31] diarylethenes 1-3 exhibited a relatively strong



Fig. 6. Fluorescence emission spectra of diarylethenes 1a, 2a, 3a, 4a, and 5a in hexane $(c \ 1.0 \times 10^{-4} \ \text{mol } \text{L}^{-1})$ at room temperature, excited at 312 nm.

fluorescence switch along with the photochromism from openring isomers to closed-ring isomers. When irradiated by 254 nm UV light, photocyclization reactions occurred and the emission intensities of diarylethenes 1, 2, and 3 decreased significantly, which is attributed to the production of the non-fluorescent closed-ring isomers. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers and recovered the original emission intensity. During the process of photoisomerization, the three compounds exhibited changes in their fluorescence in hexane ($c \ 1.0 \times 10^{-4} \text{ mol } \text{L}^{-1}$) as shown in Fig. 7. Upon irradiation with 254 nm light, the emission intensities of diarylethenes 1a, 2a, and 3a were decreased by photocyclization. The emission intensities of 1, 2, and 3 in a photostationary state were quenched to $\sim 17\%$, 12%, and 11%, respectively, which indicates that all of them exhibit a very strong fluorescent switching in hexane. We also measured the 'on' and the 'off' state of the switchable fluorescence by changing the power of the UV and visible light, respectively. The results show that the average 'on' and 'off' times shortened in proportion to the reciprocal power of the radiated light, which indicates that the switching effect is indeed photochemical.^[32] Therefore, these diarylethene compounds can be potentially applied to optical memories with a fluorescence readout method and photomodulation switches.^[33-35]

Electrochemical Properties of Diarylethenes 1-5

Reversible modulation of electrochemical properties by photoirradiation is of basic importance for the development of molecular electronic devices. To date, many diarylethene derivatives and their electrochemical properties have been reported.^[11,20,36-38] In this work, the electrochemical properties of 1-5 were investigated using cyclic voltammetry (CV) methods under the same experimental conditions. The typical electrolyte was acetonitrile (5 mL) that contained $0.10 \text{ mol } \text{L}^{-1}$ tetrabutylammonium tetrafluoroborate ((TBA)BF₄) and 4.0×10^{-3} mol L⁻¹ diarylethenes 1–5. The experimental methods and conditions are described in a previous paper.^[20] Fig. 8 shows the CV curves of diarylethene 1 with a scanning rate of 50 mV s^{-1} . From the anodic polarization curves, it can be clearly seen that the oxidation of the ring-open isomer 1a is initiated at 1.47 V and that of the ring-closed isomer **1b** is at 1.39 V. According to the same method described in pre-vious publications, [20,39,40] the values of the ionization potential



Fig. 7. Emission intensity changes of diarylethenes 1, 2, and 3 in hexane $(c \ 1.0 \times 10^{-4} \text{ mol } \text{L}^{-1})$ upon irradiation with 254 nm UV light at room temperature, excited at 312 nm: (a) 1, (b) 2, and (c) 3.

and electron affinity were calculated to be -6.27 and -3.53, respectively. Based on the highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level, the band-gap E_g of **1a** and **1b** can be determined to be 2.74 eV and 2.70 eV, respectively. The corresponding values for diarylethenes **2–5** are summarized in Table 4. As shown in 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 **1a–5a** is initiated at 1.47, 1.80, 1.81, 1.46, and 1.75 V, and that of **1b–5b** is initiated at 1.39, 1.79, 1.40, 1.44, and 1.67 V, respectively. The results show that the oxidation potential onsets of the open-ring isomers are



Fig. 8. Cyclic voltammetry (second scan) of diarylethene 1 in acetonitrile with a scanning rate of 50 mV s^{-1} .

clearly higher than those of the closed-ring isomers. This is in accordance with the theory that longer conjugation length generally leads towards lower positive potentials, with the addition of each heterocyclic ring. During the ring-closed reaction, the π conjugation lengths of 1b, 2b, 3b, 4b, and 5b was much longer than those of 1a, 2a, 3a, 4a, and 5a, thus leading to lower oxidation onset. The difference of oxidation onset between the openand closed-ring isomers of diarylethenes 1-5 was 0.08 V for 1, 0.01 V for 2, 0.41 V for 3, 0.02 V for 4, and 0.08 V for 5, respectively. For the band-gap of diarylethenes 1–5, all the values of E_{g} of the open-ring isomers were higher than those of the closedring isomers, with the exception of diarylethene 2. Among these compounds, the E_g of **3b** was the smallest, which implies that the charge transfer of 3b must be faster compared with those of the others. All the data described above suggest that different electron-donating and electron-withdrawing substituents have a remarkable effect on the electrochemical behaviours of these diarylethenes. It should be noted here that the absolute HOMO and LUMO levels in combination with the energy gap calculated by electrochemical data is still under debate. $[^{39,40}]$

Conclusions

In summary, five new unsymmetrical diarylethenes that have different substituents at the 5-position of the thiophene ring were synthesized and the substituent effects on their optoelectronic properties were investigated. The results showed that the absorption characteristics, photochromic reactivity, fluorescence, and electrochemical properties were significantly dependent on the substituents attached at the 5-position of thiophene ring, which may be attributed to the different electron-donating or electronwithdrawing substituent effects. The result of this study is useful for the efficient design and synthesis of photoactive diarylethene derivatives with excellent characteristics.

Experimental

General Methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with CDCl₃ 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 a PE CHN 2400. The absorption spectra were measured using an Agilent 8453 UV/VIS spectrometer. Photo-irradiation was carried out using a SHG-200 UV lamp and a

Compound	Oxidation		Reduction		Band gap
	E_{onset} [V]	Ionization potential [eV]	E_{onset} [V]	Electron affinity [eV]	E_{g}
1a	+1.47	-6.27	-1.27	-3.53	2.74
1b	+1.39	-6.19	-1.31	-3.49	2.70
2a	+1.80	-6.60	-1.62	-3.18	3.42
2b	+1.79	-6.59	-1.68	-3.12	3.47
3a	+1.81	-6.61	-0.91	-3.89	2.72
3b	+ 1.40	-6.20	-1.22	-3.58	2.62
4a	+1.46	-6.26	-1.76	-3.04	3.22
4b	+1.44	-6.24	-1.71	-3.09	3.15
5a	+1.75	-6.55	-1.01	-3.79	2.76
5b	+1.67	-6.47	-1.13	-3.67	2.68

Table 4. Electrochemical properties of diarylethenes 1, 2, 3, 4, and 5 in acetonitrile

BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. Electrochemical examinations were performed in a one-compartment cell 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 of diarylethenes **2a**, **3a**, **4a**, and **5a** 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 661184, 676246, 676245, and 676247 for **2a**, **3a**, **4a**, and **5a**. These data can be obtained free of charge at http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis

The syntheses of diarylethenes 1a-5a is shown in Scheme 2. The experimental details were carried out as follows.

2-Ethylbenzothiophene (1c)

To a stirred THF solution (60 mL) that contained benzothiophene (5.00 g, 37.26 mmol) was slowly added 15.60 mL of *n*-BuLi (2.5 mmol) at -78° C under a nitrogen atmosphere, and the solution was stirred for 45 min. Ethylbromide (3.05 mL, 40.98 mmol) was then added slowly to the reaction mixture, and left to stand with stirring at -78° C to room temperature for 18 h. The reaction mixture was then poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether) to give 5.70 g of **1c** in 94% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 1.38 (t, 3H, *J*7.4, $-CH_3$), 2.91–2.97 (m, 2H, $-CH_2$), 7.01 (s, 1H, thienyl-H), 7.22–7.28 (m, 1H, phenyl-H), 7.30–7.35 (m, 1H, phenyl-H), 7.74 (t, 2H, phenyl-H). (Found: C 74.11, H 6.23. Calc. for C₁₀H₁₀S: C 74.03, H 6.21.)

3-Bromo-2-ethyl-benzothiophene (2c)

Although this compound was reported,^[13] its synthetic method was not described. To a stirred THF solution (60 mL) that contained compound **1c** (5.70 g, 37.26 mmol) was slowly added 6.88 g of *N*-bromosuccinimide (38.64 mmol) at 5°C. The reaction mixture was stirred for 22 h, and was then poured into sodium thiosulfate solution and extracted with diethyl ether. The organic layer was dried, filtered, and concentrated. The residue was purified by column chromatography on silica gel (petroleum

ether) to give 7.5 g of **2c** in 89% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 1.38 (t, 3H, *J* 7.4, -CH₃), 2.91–2.97 (m, 2H, -CH₂), 7.22–7.28 (m, 1H, phenyl-H), 7.30–7.35 (m, 1H, phenyl-H), 7.74 (t, 2H, phenyl-H). (Found: C 49.85, H 3.81. Calc. for C₁₀H₉BrS: C 49.81, H 3.76.)

1-(3-Bromo-2-n-ethyl)-1-(benzothiophene-3-yl)perflourocyclopentene (**3c**)

To a stirred THF solution (80 mL) that contained compound **2c** (6.79 g, 26.63 mmol) was slowly added 10.52 mL of *n*-BuLi (2.5 M) at -78° C under a nitrogen atmosphere. After 40 min, C₅F₈ (3.64 mL, 0.136 mL mol⁻¹) was added quickly to the reaction mixture, and left to stand with stirring at -78° C under a nitrogen atmosphere for 2 h. The reaction mixture was then extracted with diethyl ether and evaporated under vacuum. The residue was purified by column chromatography on silica gel to give 5.16 g of **3c** in 55% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 1.36 (t, 3H, *J* 7.5, -CH₃), 2.82–2.88 (m, 2H, -CH₂), 7.36–7.41 (m, 2H, phenyl-H), 7.48 (d, 1H, *J* 7.6, phenyl-H), 7.82 (d, 1H, *J* 7.6, phenyl-H). (Found: C 50.91, H 2.61. Calc. for C₁₅H₉F₇S: C 50.85, H 2.56.)

1-(2-Ethyl-3-benzothienyl)-2-{2-n-pentyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (2a)

To a stirred THF solution (30 mL) that contained 3-bromo-2-npentyl-5-(1,3-dioxolane)thiophene $(4c)^{[20]}$ (2.62 g, 8.20 mmol) was slowly added 3.31 mL of n-BuLi (1.6 M) at -78°C under a nitrogen atmosphere. After 40 min, a 10 mL THF solution that contained compound 3c (2.79 g, 8.20 mol) was added slowly to the reaction mixture, and left to stand with stirring at -78° C under a nitrogen atmosphere for 2 h. The reaction mixture was then extracted with diethyl ether and evaporated under vacuum. The residue was purified by column chromatography on silica gel to give 2.03 g of **2a** in 44% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 0.74 (t, 3H, J 7.1, -CH₃), 0.98-1.01 (m, 4H, -CH₂), 1.07 (t, 3H, J7.5, -CH₃), 1.26-1.27 (m, 2H, -CH₂), 2.03-2.28 (m, 2H, -CH₂), 2.43-2.67 (m, 2H, -CH₂), 3.96-4.05 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.03 (s, 1H, thienyl-H), 7.33-7.38 (m, 2H, phenyl-H), 7.60 (d, 1H, J 7.1, phenyl-H), 7.75 (d, 1H, J 7.8, phenyl-H). $\delta_{\rm C}$ (CDCl₃, 100 MHz, TMS) 13.70, 15.33, 22.19, 22.73, 29.23, 30.96, 31.04, 65.15, 65.21, 99.87, 118.85, 122.21, 122.40, 122.47, 122.62, 124.42, 124.83, 125.86, 138.22, 138.31, 139.66, 150.10, 150.22. ν_{max} (KBr)/cm⁻¹ 731, 754, 942, 970, 989, 1018, 1073, 1100, 1141, 1190, 1275, 1343, 1435, 1458, 1640, 2930, 2954. (Found: C 58.01, H 4.48. Calc. for $C_{27}H_{26}F_6O_2S_2$: C 57.85, H 4.67.)

1-(2-Ethyl-3-benzothienyl)-2-(2-n-pentyl-5-formyl-3-thienyl)perfluorocyclopente (**4a**)

Compound 2a (1.63 g, 2.9 mmol) and p-toluenesulfonic acid (0.55 g) were dissolved in a mixture of water (30 mL) and acetone (90 mL). Pyridine (0.23 mL) was added into the mixture and it was refluxed for 24 h. After stopping the reaction, the mixture was washed sequentially by aqueous NaHCO3 and water. The organic layer was dried, filtered, and evaporated. The residue was purified by column chromatography on silica gel to give 1.23 g of 4a in 83% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 0.74 (t, 3H, J7.0, -CH₃), 0.96-1.04 (m, 4H, -CH₂), 1.08 (t, 3H, J7.5, -CH₃), 1.26–1.27 (m, 2H, -CH₂), 2.07–2.34 (m, 2H, -CH₂), 2.43-2.68 (m, 2H, -CH₂), 7.33-7.40 (m, 2H, phenyl-H), 7.60 (d, 1H, J 7.4, phenyl-H), 7.72 (s, 1H, thienyl-H), 7.77 (d, 1H, J 7.7, phenyl-H), 9.81 (s, 1H, -CHO). δ_C (CDCl₃, 100 MHz, TMS) 13.74, 15.47, 22.16, 22.83, 29.85, 30.81, 30.89, 118.27, 122.17, 122.24, 122.42, 124.71, 124.79, 125.08, 135.96, 137.92, 138.26, 141.43, 150.46, 159.03, 182.11. ν_{max} (KBr)/cm⁻¹ 733, 757, 993, 1071, 1111, 1147, 1204, 1235, 1276, 1343, 1388, 1460, 1545, 1677, 2958. (Found: C 58.39, H 4.12. Calc. for C₂₅H₂₂F₆OS₂: C 58.13, H 3.89.)

1-(2-Ethyl-3-benzothienyl)-2-(2-n-pentyl-5-hydroxymethyl-3-thienyl)perfluorocyclopentene (**1a**)

To a stirred THF solution (30 mL) that contained 4a (0.2 g, 0.39 mmol) was added 0.017 g of sodium borohydride (0.47 mmol) at room temperature. The reaction mixture was stirred for 22 h, and then stopped by addition of a 6% hydrochloric acid solution. The mixture was extracted with chloroform and evaporated under vacuum. The residue was purified by column chromatography on silica gel to give 0.15 g of 1a in 76% yield. δ_H (CDCl₃, 400 MHz, TMS) 0.73 (t, 3H, J 7.1, -CH₃), 0.88-0.95 (m, 4H, -CH₂), 1.06 (t, 3H, J7.5, -CH₃), 1.19-1.24 (m, 2H, -CH₂), 2.02-2.28 (m, 2H, -CH₂), 2.43-2.68 (m, 2H, -CH₂), 4.68-4.76 (m, 2H, -CH₂), 6.92 (s, 1H, thienyl-H), 7.30-7.39 (m, 2H, phenyl-H), 7.61 (d, 1H, J7.3, phenyl-H), 7.75 (d, 1H, J7.7, phenyl-H). $\delta_{\rm C}$ (CDCl₃, 100 MHz, TMS) 13.78, 15.28, 15.39, 22.25, 22.77, 29.24, 30.98, 31.16, 59.99, 118.93, 122.25, 122.43, 122.50, 122.72, 124.45, 124.70, 124.85, 138.22, 138.33, 149.35, 150.14. v_{max} (KBr)/cm⁻¹ 730, 755, 978, 1073, 1112, 1192, 1274, 1344, 1384, 1436, 1634, 2931. (Found: C 58.03, H 4.70. Calc. for C₂₅H₂₄F₆OS₂: C 57.90, H 4.66.)

1-(2-Ethyl-3-benzothienyl)-2-{2-n-pentyl-5-[2-(1,3dithiolpentane)]-3-thienyl}perfluorocyclopentene (**3a**)

Compound **4a** (0.1 g, 0.19 mmol), ethan-1,2-dithiol (0.018 g, 0.19 mmol), and *p*-toluenesulfonic acid (0.74 mg) were dissolved in benzene (160 mL). Under Dean–Stark conditions, the reaction mixture was refluxed overnight, and then washed sequentially three times with NaOH (3.0 mol L⁻¹) and water. The combined benzene layers were dried, filtered, and evaporated. The residue was purified by column chromatography on silica gel to give 0.084 g of **3a** in 74% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 0.73 (t, 3H, *J*7.1, –CH₃), 0.83–0.88 (m, 4H, –CH₂), 0.92–0.95 (m, 2H, –CH₂), 1.04 (t, 3H, *J*7.5, –CH₃), 1.98–2.27 (m, 2H, –CH₂), 2.43–2.67 (m, 2H, –CH₂), 3.29–3.36 (m, 4H, –CH₂), 5.75 (s, 1H, dithiolpentane-H), 6.93 (s, 1H, thienyl-H), 7.30–7.39 (m, 2H, phenyl-H), 7.61 (d, 1H, *J* 7.5, phenyl-H), 7.75 (d, 1H, *J* 7.8, phenyl-H). $\delta_{\rm C}$ (CDCl₃, 100 MHz, TMS) 13.78,

1-(2-Ethyl-3-benzothienyl)-2-[2-n-pentyl-5-(2,2'dicyanovinyl)-3-thienyl]perfluorocyclopentene (5a)

To a stirred solution of compound 1 (0.1 g, 0.19 mmol) and malonodinitrile (0.019 g, 0.19 mmol) in anhydrous ethanol (10 mL), a very small quantity of piperidine was added dropwise at room temperature. The reaction mixture was stirred overnight at 50°C. The mixture was then extracted with chloroform and evaporated under vacuum. The residue was purified by column chromatography on silica gel to give 0.08 g of 5a in 75% yield. $\delta_{\rm H}$ (CDCl₃, 400 MHz, TMS) 0.76 (t, 3H, J 7.1, -CH₃), 0.98-1.04 (m, 4H, -CH₂), 1.07 (t, 3H, J 7.5, -CH₃), 1.10-1.14 (m, 2H, -CH₂), 2.17-2.40 (m, 2H, -CH₂), 2.46-2.68 (m, 2H, -CH₂), 7.34-7.40 (m, 2H, phenyl-H), 7.56 (d, 1H, J 7.5, phenyl-H), 7.60 (s, 1H, thienyl-H), 7.73 (s, 1H, -CH), 7.78 (d, 1H, J 7.6, phenyl-H). δ_C (CDCl₃, 100 MHz, TMS) 13.73, 15.56, 22.13, 22.90, 30.04, 30.91, 31.01, 112.63, 113.44, 117.99, 122.02, 122.08, 122.53, 124.87, 125.21, 125.52, 133.06, 137.82, 138.30, 150.04, 150.57, $160.55. \nu_{\text{max}}$ (KBr)/cm⁻¹ 731, 757, 948, 990, 1074, 1139, 1187, 1275, 1333, 1384, 1437, 1581, 2228, 2928. (Found: C 59.83, H 3.95, N 4.87. Calc. for C₂₈H₂₂F₆N₂S₂: C 59.56, H 3.93, N 4.96.)

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