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Synthesis and the optoelectronic properties of diarylethene derivatives having benzothiophene and *n*-alkyl thiophene units

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ABSTRACT

Six new unsymmetrical diarylethenes having both benzothiophene and *n*-alkylthiophene units have been synthesized. The structures of diarylethenes **2a–6a** were determined by single-crystal X-ray diffraction analysis. The results showed that the alkyl chain length had a significant effect on the optoelectronic properties of these diarylethenes, including photochromism, fatigue resistance, fluorescence and electrochemical properties. The long alkyl chains can increase the cyclization/cycloreversion quantum yields but decrease the absorption maxima of diarylethenes **1–6**. The long alkyl chains can also induce a remarkable bathochromic shift for the absorption maxima of the closed-ring isomers **1b–6b** both in solution and in PMMA film. All these diarylethene derivatives showed good fluorescent switching (quench to *ca*. 10%) in hexane. The emission intensities and the fluorescent quantum yields of diarylethenes **1–6** decreased gradually with the alkyl chain length becoming longer. In addition, cyclic voltammetry tests showed that the alkyl chain length had a remarkable effect on the electrochemical behaviors of these diarylethenes. © 2008 Elsevier B.V. All rights reserved.

1. Introduction

Photochromic diarylethenes undergo reversible photoisomerization between two isomers with different absorption spectra upon irradiation with light of appropriate wavelength [1]. The instant property change arising from the chemical-bond reconstruction via photo-excitation has been attracting much attention not only from the viewpoint of the fundamental chemical reaction processes but also from the viewpoint of the application to optoelectronic devices, such as rewritable optical memories and photoswitches [2]. So, there has been ever-growing interest in the synthesis, property and application of photochromic diarylethenes materials in the past decade [3].

To date, a large number of publications concerning diarylethene derivatives with different aryl moieties, such as thiophene [4–8], benzothiophene [9–14], furan [15], thiazole [16,17], indole [18], pyrazole [19,20], and pyrrole [21], etc., have been reported. Among these compounds, diarylethenes bearing two thiopheneor benzothiphene-derived groups have received the most attention since they are particularly well suited as switching units. As a class of thermally irreversible photochromic diarylethenes, they have been found to display excellent photochromic properties both in solution and in solid state, including excellent thermal stability [22], outstanding fatigue resistance [23,24], short response time [25,26], and high quantum yields [27]. In fact, they have been considered as the most promising photochromic compounds due to these outstanding photochromic performances. Based on the effective contribution of the thiophene and benzothiophene rings to the photochromism of diarylethenes, we supposed that the unsymmetrical diarylethenes derivatives bearing both thiophene and benzothiophene moieties may have some new properties. However, just a few reports concerning this unsymmetrical system have hitherto been reported, and these reports usually focused on the applications in some specific fields when incorporating this unsymmetrical diarylethenes into some groups [28–30].

Quantum yield (ϕ) is a very important parameter for evaluating the photo-reactivity of diarylethene. One of the most basic requisites for various applications of photochromism is to achieve high quantum yield in photochromic reaction [31]. It is well known that the open-ring isomer of diarylethene has two conformations, i.e., anti-parallel and parallel conformers, and only the anti-parallel conformers undergo the photocyclization reaction. To some extent, the population of the photoactive anti-parallel controls the photocyclization quantum yield. When the ratio of the anti-parallel conformation increased, the photocyclization quantum yield increased as one's expecting [2]. Irie and his co-workers [32] reported that 1,2-bis(2-isopropylbenzothiophen-3-yl)perfluorocyclopentene (**7a**) having bulky isopropyl groups on both reacting carbon atoms showed a high cyclization quantum yield, owing to the high popu-

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lation of the anti-parallel conformers. This is the first guiding principle for the increase of ring-closure quantum yield ever reported, and the result showed that the quantum vield increased with increasing the anti-parallel population. However, this guiding principle is void for 1,2-bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene (8a) [31]. The quantum yield was also found to increase by incorporating dithienylethene into a polymer backbone or including the diarylethene molecule in confined space [2]. Recently, Yamaguchi and Irie [33,34] have reported the effect of alkyl chain length on the photochromic properties of symmetrical diarylethenes bearing two benzothiophene or benzofuran rings. The results indicated that the long alkyl chains could increase the cyclization quantum yield whereas could not change the cycloreversion guantum yield. The reason is that the long alkyl chains at 2-position of benzothiophene or benzofuran rings can increase the population of the anti-parallel conformers. However, Pu et al. [35] demonstrated that the long alkyl chain did not affect significantly the cyclization/cycloreversion quantum yields of bis(2-alkyl-5-fomyl-1-thien-3-yl)perfluorocyclopentene derivatives. The big difference of the long alkyl chain effect on the quantum yield between symmetric bisbenzothienyl and bisthienyl system attracted our attention. So, we supposed that the long alkyl chain effect on the unsymmetrical diarylethene derivatives bearing both thiophene and benzothiophene rings maybe showed distinctly different properties.

In order to explore further the mechanism of the alkyl chain length effect, we have designed and synthesized a series of new diarylethene derivatives bearing both benzothiophene and *n*-alkylthiophene moieties, i.e., 1-(2-ethyl-3-benzothienyl)-2-{2methyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (1a), 1-(2-ethyl-3-benzothienyl)-2-{2-ethyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (2a), 1-(2-ethyl-3-benzothienyl)-2-{2*n*-propyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (3a), 1-(2-ethyl-3-benzothienyl)-2-{2-n-butyl-5-[2-(1,3-dioxolane)]-3thienyl}perfluorocyclopentene (4a), 1-(2-ethyl-3-benzothienyl)-2-{2-n-pentyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (**5a**). and 1-(2-ethyl-3-benzothienyl)-2-{2-*n*-hexyl-5-[2-(1,3dioxolane)]-3-thienvl}perfluorocvclopentene (**6a**) (Scheme 1). We have introduced the different long alkyl chains at 2-position of the thiophene rings of diarylethenes **1a-6a**, and investigated the effect of the alkyl chains length on their photochemical and electrochemical properties. All these diarylethene compounds have a dioxolane substituent attached at 5-position of the thiophene ring, which can be easily hydrolyzed to formyl group and be changed further to many other functional groups by some simple reactions [36]. In addition, the crystal structures of 2a-6a were determined by single-crystal X-ray diffraction analysis, and their photochromic performances in single crystalline phase were also investigated in detail.

2. Result and discussion

2.1. Synthesis of diarylethenes

The synthetic route for diarylethenes **1a–6a** is shown in Scheme 2. First, 4-bromo-2-alkyl-5-(1,3-dioxolane)thiophene derivatives (**4c–4h**) were prepared according to the procedure described in a previous paper [35]. 2-Ethylbenzothiophene (**5c**) was obtained by reacting benzothiophene with ethyl-bromide in the presence of *n*-Buli/THF solution at -78 °C. Then, 3-bromo-2-ethylbenzothiophene (**6c**) was obtained by brominating compound **5c** with *N*-bromosullirimide. Lithiation of **6c** followed by the addition of excess octafluorocyclopentene simultaneously generated compounds **7c**, which could be further treated with the anion generated from **4c–4h** to yield a series compounds **1a–6a**. The structures of **1a–6a** were confirmed by NMR, IR, and elemental analysis (see Section 4). The structures of **2a–6a** were also determined by single-crystal X-ray diffraction analysis.

2.2. Photochromism of diarylethenes 1-6 in solution and in PMMA film

The photochromic behaviors of diarylethenes **1–6** were investigated both in hexane ($c = 2.0 \times 10^{-5}$ mol/L) and in PMMA film (10% w/w). The absorption spectral change of diarylethene **1** induced by photo-irradiation at room temperature is shown in Fig. 1. As shown in Fig. 1a, the absorption maximum of colorless open-ring isomer (1a) was observed at 229 nm ($\varepsilon = 4.29 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) in hexane. Upon irradiation with UV light, the colorless solution turned red with a new broad absorption band centered at 519 nm ($\varepsilon = 6.65 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$). The red color is due to the formation of the closed-ring isomer (1b). The red colored solution returned to colorless upon irradiation with visible light (>450 nm) indicating that **1b** returned to the initial open-ring isomer **1a**. The spectral changes of diarylethenes 2-6 were similar to that of diarylethene 1. Upon irradiation with 254 nm light, absorption bands in the visible region appeared and the solutions turned purple as a result of the cyclization reactions to produce **2b-6b**; all solutions of **2b-6b** can be decolorized by irradiating them with visible light of wavelength greater than 450 nm to induce the cycloreversion reaction and reproduce **2a–6a**. The color changes of diarylethenes **1–6** upon photo-irradiation in hexane are shown in Fig. 2. The absorption spectral properties and the cyclization/cycloreversion quantum yields of these compounds are summarized in Table 1.

From Table 1, we can see that the effect of alkyl chain length on the absorption maxima of open-ring isomers **1a–6a** are not

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5c (4c-4h) -78°C n-BuLi.-78°C 70 1a: R=CH₃ 4c: R=CH3 2a: R=C₂H₅ 4d: R=C₂H₅ 3a: R=n-C₃H₇ 4e: R=n-C₃H₇ 4a: R=n-C₄H₉ 4f: R=n-C₄H₀ 5a: R=n-C₅H₁₁ 4g: R=n-C₅H₁₁ 6a: R=n-C₆H₁₃ 4h: R=n-C₆H₁₃

Scheme 1. Photochromism of diarylethenes 1-6.

Scheme 2. Synthetic route for diarylethenes 1a-6a.



Fig. 1. Absorption spectral changes of diarylethenes **1** both in hexane and in PMMA film at room temperature: (a) in hexane ($c = 2.0 \times 10^{-5} \text{ mol/L}$); (b) in PMMA film (10% w/w).



Fig. 2. Color changes of diarylethenes **1–6** upon alternating irradiation with UV/vis light in hexane.

significant; the values only fluctuate in a very small numerical range (229–230 nm). However, the alkyl chain length effect on

the absorption maxima of closed-ring isomers, molar absorption coefficients of both open-ring and closed-ring isomers and the cyclization/cycloreversion quantum yields are much remarkable. It should be noted here that the absorption maxima showed evident red-shift from 1b to 2b (519-532 nm) when replacing the methyl group at 2-position of the thiophene ring with ethyl one. The significant red-shift of the absorption maximum was almost not observed even if the alkyl chains become longer (533-538 nm). This phenomenon is well coincided with the previous papers [33,35]. However, the molar absorption coefficients of both open- and closed-ring isomers showed a contrary changing against the absorption maxima of the closed-ring isomers. The values had a significant decrease when replacing the methyl group with ethyl one, and further decrease was evidently observed if the alkyl chain become longer. The trend of the cyclization quantum yield change was contrary to that described above. All of the cyclization guantum yields were clearly increased compared to that of diarylethene **1** ($\Phi_{c-0} = 0.18$). When replacing the *n*-propyl groups at the 2-position of thiophene ring with *n*-butyl one, the cyclization quantum yield had a significant increase (from 0.19 to 0.27). The cycloreversion quantum yields of diarylethenes 1-6 also showed an increasing tendency, and the values were gradually increased with the exception of compound 6 when the carbon numbers of alkyl chains increased. The result is different from that reported previously [33-35].

In order to explore the mechanism of the alkyl chain length effect on the quantum yields of diarylethene derivatives, we summarized some previous publications [33-35]. We found that the quantum yields of diarylethenes bearing one or two benzothiophene rings were controlled significantly by the alkyl chain length, but those of diarylethenes bearing two thiophene rings were almost ignored. As mentioned previously, the bulky isopropyl group had a significant effect on the cyclization quantum yield of bis(3benzothienyl)perfluorocyclopentene, but it had a void effect on that of bis(2,4-dimethyl-5-phenyl-3-thienyl)perfluorocyclopentene [31]. The authors calculated the potential energy of these diarvlethene compounds by *ab initio* MCSCF calculation method. They explained that the quantum yield of the photochromic ringclosure reaction depends on whether or not an extra minimum exists on the excited state potential surface. They also proved that only when this extra minimum is taken into account, the principle that the population of the photoactive anti-parallel controls the photocyclization quantum yield is valid. We considered that the alkyl chian length effect on the quantum yield of diarylethene was similar to that of the bulky isopropyl group effect. The excited state potential energy surface possesses two extra minima in the proximity of the open-ring isomer. One corresponds to a small internuclear distance between the two reactive carbon atoms, and can be considered as the reactive minimum. The other unreactive minimum corresponds to a large distance. Upon replacing the methyl groups with the longer alkyl chains at the reactive carbons of diarylethenes bearing one or two benzothiophene rings, the ratio of anti-parallel conformers increased in its ground state, and the photocyclization quantum yield is also expected to increase if the distance of two reactive carbons is small enough. But for diarylethenes bearing two thiophene rings, no significant increase of the quantum yield was observed when the methyl groups were replaced by the longer alkyl chains at the reactive carbons, the reason may be ascribed to be the presence of the unreactive minimum in the excited state of the open-ring isomer.

In PMMA film, diarylethenes **1–6** also showed good photochromism as similar as those in solution. As shown in Fig. 1b, the colorless of **1a**/PMMA films turned red with the appearance of a new broad absorption brand centered at 532 nm upon irradiation with 313 nm UV light. The red color is due to the formation of the close-ring isomer **1b**. The colored **1b**/PMMA film can revert

Compound	$\lambda_{\max,o}^{a}/nm (\epsilon/dm^{3} mol^{-1})$	$\lambda_{\max,o}^{a}/nm (\epsilon/dm^{3} mol^{-1} cm^{-1})$		$\lambda_{\max,c}^{b}/nm \ (\epsilon/dm^{3} \ mol^{-1} \ cm^{-1})$		Φ^{c}	
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	$\Phi_{ ext{c-o}}$	
1	$229~(4.29 imes 10^4)$	323	519 (6.65×10^3)	532	0.18	0.26	
2	$229(3.46 \times 10^4)$	323	$532(5.64 \times 10^3)$	535	0.22	0.26	
3	$230(3.60 \times 10^4)$	319	533 (5.72×10^3)	543	0.19	0.28	
4	$230(3.49 \times 10^4)$	320	533 (5.42×10^3)	544	0.27	0.29	
5	$230(3.31 \times 10^4)$	323	538 (5.05×10^3)	551	0.29	0.31	
6	$230(3.38 \times 10^4)$	321	540 (4.70×10^3)	545	0.31	0.26	

Absorption spectral properties of diarylethenes **1–6** both in hexane ($c = 2.0 \times 10^{-5}$ mol/L) and in PMMA film (10% w/w)

^a Absorption maxima of open-ring isomers.

Table 1

^b Absorption maxima of closed-ring isomers.

 $^{\rm c}\,$ Quantum yields of cyclization ($\varPhi_{\rm o-c})$ and cycloreversion ($\varPhi_{\rm c-o})$, respectively.

to colorless by irradiation with visible light (>450 nm), indicating that **1b** returned to the initial open-ring isomer **1a**. The similar spectral changes were observed for diarylethenes **2–6**. The absorption spectral properties of diarylethenes 1-6 in PMMA film are also summarized in Table 1. From these data, it can be clearly seen that the trends of maxima absorption of diarylethenes 1-6 in PMMA film are as similar as those in solution. The long alkyl chains did not affect the maxima absorption of open-ring isomers significantly, but induced a remarkably bathochromic shift for the absorption maxima of the closed-ring isomers when replacing the methyl group with ethyl one. The maximum absorption peaks of both the open- and closed-ring isomers of diarylethenes 1-6 are much longer than those in hexane solution. The red shifts of the absorption maxima for diarylethenes 1a-6a are 64, 64, 59, 61, 65 and 64 nm, respectively, and those for 1b-6b are 13, 3, 10, 11, 18 and 5 nm, respectively. The red shift may be ascribed to the stabilization of molecular arrangement in solid state [37,38].

2.3. Fatigue resistance of diarylethenes 1, 3 and 6

The fatigue resistances of diarylethenes 1, 3 and 6 were examined in air at room temperature. Fig. 3 shows the fatigue resistant behaviors of the three compounds both in hexane and in PMMA film. Solutions of **1**. **3** and **6** in hexane were alternately irradiated with 297 nm UV light and visible light. As shown in Fig. 3a, it can be easily seen that 90% of each of 1b, 3b and 6b was remained after 10 repeat cycles. However, there was only remained 39% for 1b, 84% for 3b and 68% for 6b after 100 repeat cycles. This may be ascribed to degradation resulting from the formation of an epoxide [24]. The result indicated that the alkyl chain length had a significant effect on the fatigue resistances of diarylethenes in hexane. Among the three compounds, diarylethene **3** showed the strongest fatigue resistance. When replacing the *n*-propyl group at 2-position of the thiophene ring with methyl or hexyl group, the fatigue resistance decreased remarkably. Compared to those of diarylethenes 1, 3 and 6 in solution, the fatigue resistant behaviors of the three compounds were much stronger in PMMA film. After 500 repeat cycles, the three compounds still showed good photochromism with only ca. 20% degradation of each compound in PMMA film (Fig. 3b). This remarkable improvement may result from suppressing effectively the oxygen diffusion in the solid medium [2,21]. It was well known that the solid state thin films containing photochromic chromophores are the promising media for optical memories and other optoelectronic devices. So, the remarkable fatigue resistant behaviors of diarvlethenes 1, 3 and 6 in PMMA amorphous medium are very useful for rewritable optical recording or photoswitches.

2.4. Photochromism of diarylethenes 2-6 in the crystalline phase

Single crystals of **2a–6a** were obtained by recrystallization from the mixture solvents of diethyl ether and hexane. To know better



Fig. 3. The fatigue-resistances of diarylethenes **1**, **3** and **6** both in hexane and in PMMA film at room temperature: (a) in hexane; (b) in PMMA film.

the relation between the conformation and the photochromic behaviors of diarylethenes **2a–6a** in the crystalline phase, 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–6a** are shown in Fig. 4 and their packing diagrams are shown in Fig. 5. As shown in Fig. 4a, the molecule of **2a** occupied approximately in C_2 symmetry, and it was packed in a photoactive *anti*parallel conformation in the crystalline phase which can undergo photocyclization reaction [39]. For compound **2a**, it was found that the perfluorocyclopentene is planar which is the average of two envelope conformations and the C9, C10, C11 atoms disordered

	2a	3a	4a	5a	6a
Formula	$C_{24}H_{20}F_6O_2S_2$	$C_{25}H_{22}F_6O_2S_2$	C ₂₆ H ₂₂ F ₆ O ₂ S ₂	C27H26F6O2S2	C ₂₈ H ₂₈ F ₆ O ₂ S ₂
Formula weight	518.52	532.55	544.56	560.60	574.62
Temperature (K)	291(2) K	291(2) K	293(2) K	291(2) K	291(2) K
Crystal system	Triclinic	Triclinic	Monoclinic	Triclinic	Triclinic
Space group	P-1	P-1	P2(1)	P-1	P-1
Unit cell dimensions					
a (Å)	10.0360(11)	8.1976(9)	13.5537(10)	10.2996(11)	10.3324(15)
b (Å)	10.5560(12)	12.0429(13)	12.8880(9)	10.7924(11)	11.4622(16)
c (Å)	12.0375(13)	12.9696(14)	15.3872(11)	13.3082(14)	12.6789(18)
α (°)	78.4080(10)	86.0250(10)	90	106.6800(10)	107.479(2)
β(°)	68.6770(10)	72.2840(10)	108.5880(10)	100.8440(10)	95.022(2)
γ (°)	84.4730(10)	82.5330(10)	90	105.1640(10)	101.956(2)
Volume (Å ³)	1162.8(2)	1208.7(2)	2547.6(3)	1311.1(2)	1383.0(3)
Ζ	2	2	4	2	2
Density (Calcd.) (g/cm ³)	1.481	1.463	1.420	1.420	1.380
Goodness-of-fit on F ²	1.043	1.031	1.037	1.058	1.067
Final R indices $[I/2\sigma(I)]$ R ₁	0.0507	0.0352	0.0518	0.0488	0.0748
wR ₂	0.1296	0.0887	0.1402	0.1258	0.2142
R indices (all data) R ₁	0.0596	0.0451	0.0653	0.0615	0.1147
wR ₂	0.1375	0.0958	0.1560	0.1355	0.2519

Table 2		
Crvstal data	for diarvlethenes	2a-6a

which were named as C9 and C9', C10 and C10', C11 and C11', respectively. The dihedral angles between the least-squares plane of the atoms of the central cyclopentene ring and the two thiophene rings are 64.9(5)° for S1/C1/C6-C7/C13 and 52.3(5)° for S2/C16–C19. The dihedral angle between the left thiophene ring (S1/C1/C6-C7/C13) and the adjacent benzene ring (C1-C6) is $2.6(5)^{\circ}$ and that between the right thiophene ring (S2/C16-C19) and the 1,3-dioxolane ring (C22/O1/C23-C24/O2) is 92.6(5)°. In the perfluorocyclopentene ring of 2a, distances of C8-C9, C9-C10, C10-C11, C11-C12 and C8-C12 are 1.523(5), 1.526(5), 1.537(5), 1.521(5) and 1.347(3) Å, respectively. These data clearly indicated that C8–C12 bond is a double bond, being significantly shorter than the other carbon-carbon single bonds. The thiophene and benzothiophene moieties were linked by the C8=C12 double bond, with both of them attached to the ethylene via the 3-position. The two ethyl groups located on different sides of the double bond and trans-direction of the thiophene and benzothiophene planes. This kind conformation was crucial to its photochromic and photoinduced properties [40]. The intramolecular distance between the two active C atoms (C13-C16) is 3.890(6) Å. In the structure of the propyl analogue, the corresponding values for dihedral angles between the central cyclopentene ring and the two thiophene rings were 61.4(7)° for S1/C1/C6/C7/C8 and 56.9(7)° for S2/C16-C19, respectively, resulting in a reactive C-atom separation of 3.693(3) Å. The corresponding dihedral angles and the distances between the reacting carbon atoms for 4a-6a were also calculated, and these data were summarized in Table 3. From these data, it could be clearly seen that the distance between the two reactive carbon atoms decreased significantly (from 3.890(6) to 3.693(3) Å) replacing the ethyl group with *n*-propyl one, but then the distances were gradually increased with the further increase of the alkyl chain length. As shown in Fig. 5 and Table 3, all molecules of crystals 2a-6a were packed 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 was close enough for the cyclization reaction to take place, indicating that they could to expected to undergo photochromism in the single crystalline phase [41,42].

In fact, crystals of **2a–6a** showed photochromic reaction coincident with the theoretical analysis. Their color changes upon photoirradiation are shown in Fig. 6. The colorless crystals of **2a–6a** turned purple upon irradiation with 254 nm UV light. When the purple crystals were dissolved in hexane, the solution turned purple, and the absorption maxima were observed at 532, 533, 533, 533, and 540 nm, respectively, which were the same as those of the closed-ring isomers **2b–6b**. The purple color disappeared upon irradiation with appropriate wavelength visible light and the absorption spectrum of the solution containing the respective colorless crystal was the same as that of the open-ring isomer 2a-6a. Furthermore, the diarylethene crystals exhibited 200 times of coloration/decoloration cycles by alternate irradiation with UV and visible light. So, the crystals of diarylethenes 2a-6a will be good candidates for optoelectronic applications [43]. The result also differs from that reported in the reference [33]. In that paper, the crystals of diarylethenes bearing benzothiophene systems lack of photochromic reactivity when replacing the methyl groups with pentyl or hexyl groups. The reason is that the long pentyl/hexyl chain length leads to the long distance (larger than 4.2 Å) between the reactive carbons of the two rigid benzothiophene planes in the crystalline phase [33].

2.5. Fluorescence of diarylethenes 1-6

The fluorescence spectra of diarylethenes **1a–6a** both in hexane $(c = 2.0 \times 10^{-5} \text{ mol/L})$ and in PMMA amorphous film (10% w/w) at room temperature are illustrated in Fig. 7. The result illustrated that all of them showed good fluorescence both in hexane and in PMMA film. The emission intensities of compounds **1a–6a** changed dramatically with increasing the alkyl chain length both in hexane and in PMMA film. The fluorescence quantum yields **1a–6a** in hexane were examined by using anthracene in acetonitrile as a reference ($\Phi_f = 0.27$) [44]. The fluorescence properties of the six diarylethenes are summarized in Table 4.

As shown in Table 4, it could be clearly seen that the emission peaks of diarylethenes **1a–6a** were observed at 406, 405, 405, 406, 406 and 404 nm in hexane, while those of the six compounds were observed at 407, 404, 403, 401, 401 and 403 nm in PMMA film. These data indicating that the effect of the alkyl chain length on emission peaks were not significant. However, the alkyl chain length effect on their emission intensity was very remarkable. In hexane, the emission intensity of compounds **1a–6a** decreased rapidly from methyl-substituted to hexyl-substituted diarylethene derivatives, i.e., they decreased with the increase in alkyl chain length. Among the six compounds, the emission intensity of **1a** is the strongest, and that of **6a** is the weakest in hexane. In PMMA amorphous film, their emission intensities had a slight fluctuation because of uneven distributable concentration in the solid



(a)
$$2a$$



(b) 3a



(c) **4a**



(d) 5a



(e) 6a

Fig. 4. ORTEP drawings of crystals 2a-6a: (a) 2a; (b) 3a; (c) 4a; (d) 5a; (e) 6a.

medium, but the values still showed a clearly decreasing tendency. Compared the fluorescence quantum yields of diarylethenes **1–6** with their cyclization quantum yields (Table 4), it could be easily concluded that the fluorescence quantum yields of diarylethenes **1–6** decreased gradually with the cyclization quantum yields increased. The result is well coincided with that reported by Irie et al. [45], which they explained this phenomenon by two different mechanisms. One explanation is that the increase in the ratio of the photoactive anti-parallel conformations in the ground-state results in the increase of the cyclization quantum yield and the decrease of the florescence intensity and the fluorescence quantum yield because of the decrease of the ratio of fluorescent parallel conformers. Another explanation is the competition in the excited state. A part of excited molecules, which can not enter the cyclization reaction channel, deactivate to the relaxed fluorescence state and emit the fluorescence. The numbers of unreacted excited molecules decreases when the cyclization quantum yield increases, resulting in diminishing the fluorescence intensity and the fluorescence quantum yield [45].

As has been observed for most of the reported diarylethenes [46–51], diarylethenes **1–6** exhibited relatively strong fluorescence switches along with the photochromism from open-ring isomer to close-ring isomer. Upon irradiation with UV light, the photocyclization reaction was carried out, and the non-fluorescence close-ring isomers were produced. The back irradiation by appropriate wavelength visible light regenerated their open-ring isomers and recovered the original emission intensity. Fig. 8 shows the fluorescence spectral changes of diarylethene **1** both in hexane ($c = 1.0 \times 10^{-4}$ mol/L) and in PMMA film (10% w/w) at room temperature. As shown in Fig. 8a, it could be clearly seen that







(c) **4a**

(d) **5a**



(e) 6a

Fig. 5. Packing views of crystals 2a-6a along the *a* direction, with the exception of crystal 4a (along the *b* direction).

Table 3
Distances between the reacting carbon atoms (d , Å) and dihedral angles (θ , °) of diarylethenes 2a–6a

Compound	d (Å)			θ (°)		
2a	C13-C16	3.890(6)	S1/C1/C6-C7/C13	64.9(5)	S2/C16-C19	52.3(5)
3a	C8-C19	3.693(3)	S1/C1/C6-C8	61.4(7)	S2/C16-C19	56.9(7)
4a	C1-C19	3.746(5)	S1/C1-C3/C8	56.6(1)	S2/C16-C19	52.6(1)
5a	C8-C16	3.938(7)	S1/C1/C6-C7/C8	62.9(5)	S2/C16-C19	53.5(5)
6a	C13-C17	3.833(4)	S1/C1/C6-C7/C13	56.6(3)	S2/C16-C19	54.6(3)

the fluorescence intensity decreased dramatically upon increasing the exposure time when excited at 305 nm. Upon irradiation with 297 nm UV light, the photocyclization reaction was occurred and the non-fluorescence close-ring isomer **1b** was produced, resulting in the decrease of the fluorescence intensity. When arrived at the photostationary state, the fluorescence intensity of diarylethene **1** was quenched to *ca.* 7%. Similarly, Fig. 8b shows the emission intensity changes of diarylethene **1** during the process of



Fig. 6. Photographs demonstrating the photochromic processes of diarylethenes **2–6** in the single crystalline phase.

photoisomerization in PMMA film. Upon irradiation with 313 nm light at room temperature, the emission intensity of compound **1** decreased remarkably along with the photoisomerization from open-ring isomers to closed-ring isomers when excited at 325 nm. When arrived at the photostationary state, the emission intensity was quenched to *ca.* 49%. The incomplete cyclization reaction and the existence of parallel conformation of diaryleth-

Table 4

Гhe	fluorescence	properties	of diar	vlethenes	2-6 in	hexane	and in	PMMA	film

Compound	$\lambda_{f,max}$ (intensity)		Φ		
	Hexane	PMMA film	Φ_{f}	$\Phi_{o\text{-}c}$	
1	406 (3340)	407 (3387)	0.0100	0.18	
2	405 (2892)	404 (3424)	0.0115	0.22	
3	405 (2504)	403 (2794)	0.0099	0.19	
4	406 (2240)	401 (2464)	0.0084	0.27	
5	406 (1904)	401 (2546)	0.0085	0.29	
6	404 (1584)	403 (2403)	0.0084	0.31	

 $\Phi_{\rm f}$ – fluorescence quantum vield.

 $\Phi_{\rm o-c}$ – cyclization quantum yield.

enes **1** may be the main cause for the moderate change in fluorescence induced by photoirradiation in PMMA film. For compounds **2a–6a**, the emission intensity changes are similar to that of diarylethene **1**. When arrived at the photostationary state, the emission intensities of diarylethenes **2–6** in hexane were quenched to *ca.* 9%, 10%, 11%, 12%, and 15%, respectively, and those in PMMA film were quenched to *ca.* 48%, 35%, 50%, 54%, and 39%, respectively. The result indicated that the fluorescence switches of diarylethenes **1–6** showed much more significant in hexane than those in PMMA film. We have also measured the "on" and the "off" state of the switchable fluorescence by changing the power of the UV and visible



Fig. 7. Fluorescence emission spectra of diarylethenes **1–6** both in hexane ($c = 1.0 \times 10^{-4} \text{ mol/L}$) and in PMMA film (10% w/w) at room temperature: (a) Emission spectra in hexane, excited at 305 nm; (b) emission spectra in PMMA film, excited at 325 nm.



Fig. 8. Emission intensity changes of **1** both in hexane solution ($c = 1.0 \times 10^{-4} \text{ mol}/L$) and in PMMA film (10% w/w) at room temperature: (a) Emission spectra in hexane upon irradiation with 297 nm UV light, excited at 305 nm; (b) Emission spectra in PMMA film upon irradiation with 313 nm UV light, excited at 325 nm.

light, respectively. The result showed that the average "on" and "off" times shortened in proportion to the reciprocal power of the irradiated light. So, it can be easily known that the fluorescent switching effect is indeed photochemical, which can be potentially applied to optical memory with fluorescence readout method and photo-modulation switches [52,53].

The concentration dependence on the florescence spectrum of diarylethenes 1a was measured in hexane at room temperature, as shown in Fig. 9. When the solutions at 1.0×10^{-5} , 2.0×10^{-5} , 5.0×10^{-5} , and 1.0×10^{-4} mol/L were excited at 305 nm, the maximum emission of 1a arose at 400, 403, 405, 406 nm, respectively, and the relative fluorescence intensity increased dramatically with the increase in the concentration. But when the concentration increased to 1.0×10^{-3} mol/L, the fluorescence intensity decreased remarkably. Just as for 1a, the diarylethenes 2a-6a showed similar fluorescent properties depending on the concentration employed. The results are summarized in Table 5. From this table, it could be clearly seen that all fluorescence spectra of 1a-6a showed remarkably concentration dependence. The fluorescence peaks showed a minor red shift upon increasing the concentration. However, the fluorescence intensities showed a remarkable initial increase with subsequent dramatic decrease with increasing concentration. The biggest and the smallest values were obtained at 1.0×10^{-4} and 1.0×10^{-3} mol/L, respectively. The fluorescence quench take place in high concentration may be ascribed to the molecular aggregation [54]. We also found the fluorescence intensity of diarylethenes 1-6 showed a systemic decreased with increasing the chain length in whichever concentration, and the phenomenon also can be explained with the alkyl chain length effect.

2.6. Electrochemical properties of diarylethenes 1-6

Reversible modulation of electrochemical properties by photoirradiation is of basic importance for the development of molecular electronic devices [55]. To date, many diarylethene derivatives and their electrochemical properties have been reported [56–59]. In this work, the electrochemical properties of **1–6** were investigated by cyclic voltammetry. The typical electrolyte was acetonitrile (5 mL) containing 0.10 mol/L tetrabutylammonium tetrafluoroborate ((TBA)BF₄) and 4.0×10^{-3} mol/L diarylethenes **1–6**, respectively. Experimental method and condition were described in a previous paper [35]. Fig. 10 shows the CV curves of



Fig. 9. Fluorescence emission spectra of 1 in various concentrations in hexane at room temperature, excited at 305 nm.

diarylethene **1** with the scanning rate of 50 mV/s. According to Eqs. (2) and (3) [60,61], the energy parameters EA and IP were also calculated.

$$HOMO: IP = -\{[E_{on}]^{ox} + 4.8\}$$
(2)

$$LUMO: EA = -\{[E_{on}]^{red} + 4.8\}$$
(3)

where the units of onset potentials are volts, and those of IP and EA are electronvolts; 4.8 eV is the constant of the energy level of the ferrocene/ferrocenium (Fc) below the vacuum level.

With regard to the energy level of the ferrocene reference (4.8 eV below the vacuum level), the HOMO and LUMO energy levels can also be estimated. As shown in Fig. 10, it can be clearly seen that the onset potentials of oxidation and reduction for **1a** were observed at +1.52 V and -1.86 V, and those for **1b** were observed at +1.49 V and -1.77 V, respectively. Therefore, the values of IP and EA were calculated to be -6.32 and -2.94 eV according to Eqs. (2) and (3). Based on the HOMO and LUMO energy levels, the band gap (E_g , E_g = LUMO – HOMO) of **1a** can be calculated as 3.38 eV, and that of **1b** is 3.26 eV. Just as for diarylethene **1**, the electrochemical properties of diarylethenes **2–6** are similar to that of diarylethene **1**, and the corresponding values for them are summarized in Table 6.

As shown in Table 6, it can be clearly seen that the HOMO energy levels of the open-ring isomers **1a-6a** decreased gradually when the carbon numbers of alkyl chains increased. The HOMO energy levels of the closed-ring isomers 1b-6b also showed a decreasing tendency from methyl to *n*-butyl first. However, even if the alkyl chains become longer, further decrease were not observed. On the other hand, LUMO energy levels of the open-ring isomers 1a-6a and the closed-ring isomers 1b-6b with the exception of **2** decreased gradually when the carbon numbers of alkyl chains increased. In fact, the LUMO of compound 2 also decreased comparing to that of 1, but they decreased much faster than those of compounds 3-6. For the band gap of diarylethenes 1-6, the carbon numbers of alkyl chains have almost no effect on the band gap of open-ring isomers **1a-6a**, but they had a remarkable effect on those of closed-ring isomers **1b–6b**. The values of E_g increased from methyl to ethyl, *n*-propyl and *n*-butyl, and then decreased with the further increases of carbon chain length for the closedring isomers of these compounds. The result was contrary to that reported in Ref. 35. In that paper, the chain length have almost no effect on the band gaps of the closed-ring isomers whereas remarkable on those of the open-ring isomers. All these data described above showed that different chain lengths of alkyl substituents have a remarkable effect on the band gaps of these diarylethene derivatives. It should be noted here that the calculation of absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate [61].

3. Conclusions

In conclusion, six new unsymmetrical diarylethenes having both benzothiophene and *n*-alkylthiophene units were synthesized in order to reveal the effect of the alkyl chain length on their optoelectronic properties. All these compounds showed good reversible photochromism both in solution and in PMMA amorphous film. Introduction of the long alkyl chains at 2-position of the thiophene ring can increase the cyclization quantum yield. However, it can decrease the fluorescent quantum yield, which may be attributed to the long alkyl chains at 2-position of the thiophene ring leading to the population of the anti-parallel conformers increasing. The long alkyl chains induced bathochromic shifts of the maxima absorption of the closed-ring isomers, but they didn't affect those of open-ring isomers. In addition, cyclic voltammograms tests indicate that the alkyl chain length have a significant effect on the band

Table 5
The concentration effect on the fluorescence spectra of diarylethenes $1-6$ at room temperature in hexane, monitored at 305 nm

Concentration (mol/L)	$\lambda_{em,max}$ (relative intensity)							
	1	2	3	4	5	6		
1.0×10^{-5}	400 (667)	404 (653)	404 (575)	402 (568)	403 (534)	405 (292)		
$2.0 imes 10^{-5}$	403 (1271)	405 (1025)	403 (742)	406 (780)	403 (619)	404 (500)		
$5.0 imes 10^{-5}$	405 (2598)	405 (2326)	406 (1861)	407 (1642)	400 (1700)	404 (1241)		
$1.0 imes 10^{-4}$	406 (3340)	405 (2892)	405 (2504)	406 (2240)	406 (1904)	404 (1584)		
$1.0 imes 10^{-3}$	404 (226)	409 (360)	410 (359)	406 (322)	407 (221)	406 (227)		



Fig. 10. Cyclic voltammetry of diarylethene 1 in 0.1 mol/L ((TBA)BF_4) with a san rate of 50 mV/s.

Table 6Electrochemical parameters of diarylethenes 1–6

Compound	Oxidiation		Reduction	Reduction	
	$E_{\text{onset}}(V)$	IP (eV)	$E_{\text{onset}}(V)$	EA (eV)	
1a	+1.52	-6.32	-1.86	-2.94	3.38
1b	+1.49	-6.29	-1.77	-3.03	3.26
2a	+1.67	-6.47	-1.60	-3.20	3.27
2b	+1.74	-6.54	-1.51	-3.29	3.25
3a	+1.66	-6.46	-1.72	-3.08	3.36
3b	+1.67	-6.47	-1.76	-3.04	3.44
4a	+1.77	-6.57	-1.71	-3.09	3.48
4b	+1.84	-6.64	-1.68	-3.12	3.52
5a	+1.80	-6.60	-1.62	-3.18	3.42
5b	+1.79	-6.59	-1.68	-3.12	3.47
6a	+1.87	-6.67	-1.53	-3.27	3.40
6b	+1.70	-6.50	-1.58	-3.22	3.28

gap of these diarylethenes. The results of this study are useful for the efficient design and synthesis of photoactive diarylethene derivatives with excellent characteristics.

4. Experimental

4.1. General methods

¹H NMR and ¹³C NMR spectra were recorded on BrukerAV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. IR spectra were measured from KBr pellets using a Bruker Vertex 70 system. The elemental anaylysis 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, CX-21 ultraviolet fluorescence analysis cabinet and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. The X-ray experiment of the single-crystal was performed on Bruker Smart APEX2 CCD area-detector equipped with graphite monochromatized Mo K α radiation at room temperature (291 ± 2 K). 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. Platinum-electrodes (diameter 0.5 mm) served as working electrode and counter electrode. Platinum wire served as a quasi-reference electrode. It was calibrated using the ferrocene (Fc/Fc+) redox couple which has a formal potential $E_{1/2}$ = +0.35 V vs. platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.15 mol/L LiClO₄ and a diarylethene sample $(c = 4 \times 10^{-3} \text{ mol/L})$. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments. All solvents used were of spectrograde and were purified by distillation before use.

4.1.1. Synthesis

The synthetic method of diarylethenes **1a–6a** is shown in Scheme 2 and experimental details are carried out as following.

4.1.1.1. 2-Ethylbenzothiophene (**5c**). To a stirred THF solution (60 mL) containing benzothiophene (5.00 g, 37.26 mmol) was slowly added 15.60 mL *n*-BuLi (2.5 mmol) at -78 °C under nitrogen atmosphere, and the solution was stirred for 45 min. Then the ethyl-bromide (3.05 mL, 40.98 mmol) was added slowly to the reaction mixture, and kept stirring for 18 h at -78 °C to room temperature. Then the reaction mixture was poured into concentrated sodium chloride solution and extracted with diethyl ether. The organic layer was dried, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether) to give 5.70 g of **5c** in 94.2% yields. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.38 (t, 3H, *J* = 7.4 Hz, -CH₃), 2.91–2.97 (m, 2H, -CH₂), 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).

4.1.1.2. 3-Bromo-2-ethyl-benzothiophene (**6c**). To a stirred THF solution (60 mL) containing compound **5c** (5.70 g, 37.26 mmol) was slowly added 6.88 g *N*-bromosullirimide (38.64 mmol) at 5 °C. The reaction mixture was stirred for 22 h, then was poured into sodium thiosulfate solution and extracted with diethyl ether. The organic layer was dried, filtrated, and concentrated. The residue was purified by column chromatography on silica gel (petroleum ether) to give 7.5 g of **6c** in 88.76% yields. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.35 (t, 3H, *J* = 7.6 Hz, -CH₃), 2.95–3.00 (m, 2H, -CH₂), 7.31–7.39 (m, 1H, phenyl-H), 7.41–7.45 (m, 1H, phenyl-H), 7.74 (t, 2H, *J* = 7.2 Hz, phenyl-H).

4.1.1.3. 1-(3-Bromo-2-ethyl)-1-benzothiophene-3-yl)perfluorocyclopentene (**7c**). To a stirred THF solution (80 mL) containing compound **6c** (6.79 g, 26.63 mmol) was slowly added 10.52 mL n-BuLi (2.5 M) at $-78 \,^{\circ}$ C under nitrogen atmosphere. After 40 min, the C₅F₈ 3.64 mL (0.136 mL/mol) was added quickly to the reaction mixture, and kept stirring for 2 h at -78 °C under nitrogen atmosphere. Then the reaction mixture was extracted with diethyl ether and evaporated in vacuum. The residue was purified by column chromatography on silica gel to give 5.16 g of **7c** in 54.7%. ¹H NMR (CDCl₃, 400 MHz, TMS): δ 1.37 (t, 3H, J = 7.5 Hz, -CH₃), 2.82–2.88 (m, 2H, -CH₂), 7.36–7.41 (m, 2H, phenyl-H), 7.48 (d, 1H, J = 7.6 Hz, phenyl-H), 7.82 (d, 1H, J = 7.6 Hz, phenyl-H).

4.1.1.4. 1-(2-Ethyl-3-benzothienyl)-2-{2-methyl-5-[2-(1,3-dioxolane)]-3thienyl}perfluorocyclopentene 1a. To a stirred THF solution (30 mL) containing 4-bromo-2-methyl-5-(1,3-dioxolane)thiophene (4c) [35] (2.04 g, 8.20 mmol) was slowly added 3.31 mL n-BuLi (1.6 M) at -78 °C under nitrogen atmosphere. After 40 min, 10 mL THF solution containing compound 7c 2.79 g (8.20 mol) was added slowly to the reaction mixture, and kept stirring for 2 h at -78 °C under nitrogen atmosphere. Then the reaction mixture was extracted with diethyl ether and evaporated in vacuum. The residue was purified by column chromatography on silica gel to give 1.65 g of **1a** in 40.1%. ¹H NMR $(CDCl_3, 400 \text{ MHz}, \text{TMS})$: $\delta 0.7$ (t, 3H, $I = 7.5 \text{ Hz}, -CH_3$), 1.09 (t, 3H, I = 7.5 Hz, -CH₃), 2.47-2.53 (m, 1H, -CH₂), 2.68-2.73 (m, 1H, -CH₂), 3.97-4.04 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.03 (s, 1H, thienyl-H), 7.26–7.35 (m, 2H, phenyl-H), 7.55 (d, 1H, *J* = 7.7 Hz, phenyl-H), 7.75 (d, 1H, J = 7.6 Hz, phenyl-H). ¹³C NMR (CDCl₃. 100 MHz, TMS): 8 14.37, 14.88, 22.30, 64.57, 64.65, 99.21, 118.39, 121.68, 121.80, 123.15, 123.93, 124.37, 125.78, 137.66, 139.04, 142.87, 149.61. IR (KBr, v, cm⁻¹): 731, 760, 779, 850, 898, 947, 979, 1006, 1023, 1078, 1123, 1156, 1174, 1196, 1269, 1334, 1367, 1436, 1459, 1564, 1634, 2977. Anal. Calcd for C₂₃H₁₈F₆O₂S₂ (%): Calcd C, 54.76; H, 3.60. Found: C, 55.08; H, 3.37.

4.1.1.5. 1-(2-*Ethyl*-3-*benzothienyl*)-2-{2-*ethyl*-5-[2-(1,3-*dioxolane*)]-3-*thienyl*}*perfluorocyclopentene* (**2a**). Compound **2a** were prepared by a method similar to that used for **1a** (43.50% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.72 (t, 3H, *J* = 7.5 Hz, -CH₃), 1.10 (t, 3H, *J* = 7.5 Hz, -CH₃), 2.18-2.23 (m, 1H, -CH₂), 2.36-2.41 (m, 1H, -CH₂), 2.46-2.50 (m, 1H, -CH₂), 2.66-2.70 (m, 1H, -CH₂), 3.97-4.04 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.03 (s, 1H, thienyl-H), 7.26-7.35 (m, 2H, phenyl-H), 7.56 (d, 1H, *J* = 7.9 Hz, phenyl-H), 7.75 (d, 1H, *J* = 7.7 Hz, phenyl-H). ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 15.35, 15.43, 22.64, 22.82, 65.16, 65.23, 115.90, 118.80, 122.21, 122.45, 124.44, 124.88, 125.99, 137.30, 138.29, 139.69, 150.18, 151.26. IR (KBr, v, cm⁻¹): 733, 762, 932, 991, 1082, 1138, 1190, 1271, 1340, 1433, 1458, 1560, 1633, 2893, 2978. Anal. Calcd for C₂₄H₂₀F₆O₂S₂ (%): Calcd C, 55.59; H, 3.89. Found: C, 55.74; H, 3.67.

4.1.1.6. 1-(2-Ethyl-3-benzothienyl)-2-{2-n-propyl-5-[2-(1,3-dioxolane)]-3thienyl}perfluorocyclopentene (**3a**). Compound **3a** were prepared by a method similar to that used for **1a** (44.20% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.51 (t, 3H, *J* = 7.3 Hz, -CH₃), 1.08 (t, 3H, *J* = 7.4 Hz, -CH₃), 1.26-1.34 (m, 2H, -CH₂), 2.00-2.06 (m, 1H, -CH₂), 2.20-2.26 (m, 1H, -CH₂), 2.45-2.49 (m, 1H, -CH₂), 2.65-2.70 (m, 1H, -CH₂), 3.96-4.03 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.03 (s, 1H, thienyl-H), 7.32-7.37 (m, 2H, phenyl-H). 7.59 (d, 1H, *J* = 7.9 Hz, phenyl-H), 7.74 (d, 1H, *J* = 7.8 Hz, phenyl-H). ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 13.20, 15.36, 22.75, 24.49, 31.17, 65.14, 65.20, 99.85, 118.82, 122.21, 122.37, 122.44, 122.68, 124.43, 124.84, 125.93, 138.22, 138.23, 139.68, 149.75, 150.19. IR (KBr, v, cm⁻¹): 729, 753, 768, 935, 986, 1016, 1073, 1099, 1120, 1137, 1191, 1271, 1338, 1384, 1438, 1571, 1677, 2889, 2972. Calcd for C₂₅H₂₂F₆O₂S₂ (%): Calcd C, 56.38; H, 4.16. Found: C, 56.47; H, 4.02.

4.1.1.7. 1-(2-Ethyl-3-benzothienyl)-2-{2-n-butyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (4a). Compound 4a were prepared by a method similar to that used for 1a (41.62% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.65 (t, 3H, *J* = 6.7 Hz, -CH₃), 0.94–0.97 (m, 2H, -CH₂), 1.24–1.26 (m, 2H, -CH₂), 1.07 (t, 3H, *J* = 7.5 Hz, -CH₃), 2.00–2.08 (m, 1H, -CH₂), 2.27–2.32 (m, 1H, -CH₂), 2.42–2.48 (m, 1H, -CH₂), 2.64–2.70 (m, 1H, -CH₂), 3.97–4.04 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.04 (s, 1H, thienyl-H), 7.32–7.35 (m, 2H, phenyl-H), 7.60 (d, 1H, *J* = 7.8 Hz, phenyl-H), 7.75 (d, 1H, *J* = 7.7 Hz, phenyl-H). ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 13.56, 15.34, 21.97, 22.75, 33.47, 38.59, 65.14, 65.20, 99.86, 118.84, 122.20, 122.36, 122.43, 122.63, 124.43, 124.85, 125.88, 136.93, 138.21, 141.12, 150.03. IR (KBr, ν, cm⁻¹): 731, 758, 783, 953, 989, 1031, 1072, 1116, 1140, 1188, 1251, 1274, 1343, 1384, 1460, 1558, 1630, 2957. Calcd for C₂₆H₂₄F₆O₂S₂ (%): Calcd C, 57.13; H, 4.43. Found: C, 57.31; H, 4.14.

4.1.1.8. 1-(2-Ethyl-3-benzothienyl)-2-{2-n-amyl-5-[2-(1,3-dioxolane)]-3-thienyl}perfluorocyclopentene (**5a**). Compound **5a** were prepared by a method similar to that used for **1a** (44.31% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.74 (t, 3H, J = 7.1 Hz, -CH₃), 0.98–1.01 (m, 4H, -CH₂), 1.07 (t, 3H, J = 7.5 Hz, -CH₃), 1.26–1.27 (m, 2H, -CH₂), 2.03–2.05 (m, 1H, -CH₂), 2.24–2.28 (m, 1H, -CH₂), 2.43–2.45 (m, 1H, -CH₂), 2.65–2.67 (m, 1H, -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 Hz, phenyl-H), 7.75 (d, 1H, J = 7.8 Hz, phenyl-H). ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 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. IR (KBr, v, cm⁻¹): 731, 754, 942, 970, 989, 1018, 1073, 1100, 1141, 1190, 1275, 1343, 1435, 1458, 1640, 3930, 2954. Calcd for C₂₇H₂₆F₆O₂S₂ (%): Calcd C, 57.85; H, 4.67. Found: C, 58.01; H, 4.48.

4.1.1.9. 1-(2-Ethyl-3-benzothienyl)-2-{2-n-hexyl-5-[2-(1,3-dioxolane)]-3thienyl}perfluorocyclopentene (6a). Compound 6a were prepared by a method similar to that used for **1a** (42.10% yield). ¹H NMR (CDCl₃, 400 MHz, TMS): δ 0.81 (t, 3H, I = 7.5 Hz, $-CH_3$), 0.93–0.98 (m, 4H, -CH₂), 1.08 (t, 3H, J = 7.6 Hz, -CH₃), 1.12-1.16 (m, 2H, -CH₂), 1.24-1.26 (m, 2H, -CH₂), 2.00-2.03 (m, 1H, -CH₂), 2.24-2.30 (m, 1H, -CH₂), 2.41–2.47 (m, 1H, -CH₂), 2.63–2.69 (m, 1H, -CH₂), 3.96–4.05 (m, 4H, dioxolane-H), 5.96 (s, 1H, dioxolane-H), 7.05 (s, 1H, thienyl-H), 7.33–7.39 (m, 2H, phenyl-H), 7.60 (d, 1H, J = 7.8 Hz, phenyl-H), 7.75 (d, 1H, J = 7.8 Hz, phenyl-H). ¹³C NMR (CDCl₃, 100 MHz, TMS): δ 12.92, 14.33, 21.38, 21.76, 27.55, 28.28, 30.33, 64.16, 64.23, 98.90, 117.89, 121.21, 121.41, 121.48, 121.66, 123.45, 123.72, 123.85, 124.87, 137.24, 137.34, 138.70, 149.10, 149.23. IR (v, cm⁻¹): 730, 754, 984, 1021, 1076, 1140, 1193, 1274, 1344, 1384, 1459, 1565, 1678, 2929, 3065. Calcd for C₂₈H₂₈F₆O₂S₂ (%): Calcd C, 58.52; H, 4.91. Found: C, 58.76; H, 4.73.

4.2. Crystallography

Crystal data of diarylethenes were collected by a Bruker SMART APEX2 CCD area-detector equipped with graphite monochromatized Mo Ka radiation at room temperature. The linear absorption coefficients, μ , of diarylethenes **2a–6a** for Mo K α radiation 2.97, 2.88, 2.75, 2.69 and 2.57 cm⁻¹. Direct phase determination yielded the positions of all non-hydrogen atoms. All non-hydrogen atoms were subjected to anisotropic refinement. All hydrogen atoms were generated geometrically with C-H bond distances of 0.93-0.97 Å according to criteria described in the SHELXTL manual. They were included in the refinement with Uiso(H) = 1.2Ueq(C) or 1.5Ueq(methyl C). Further details on the crystal structure investigation have been deposited to The Cambridge Crystallographic Data Centre as supplementary publication number CCDC 661183 for 2a, 661185 for 3a, 661186 for 4a, 661184 for 5a and 661187 for **6a.** These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/deposit, by emailing at data_deposit@ccdc.-

cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, CAMBRIDGE 1EZ, UK; Facsimile: (44) 01223, 336033.

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