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Synthesis and optoelectronic properties of unsymmetrical isomeric diarylethene derivatives having a fluorine atom

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ABSTRACT

Three unsymmetrical diarylethene compounds bearing a fluorine atom at either ortho-, meta-, or parapositions of the terminal phenyl ring, namely 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-fluorophenyl)-3-thienyl]perfluorocyclopentene (10), 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-fluorophenyl)-3-thienyl]perfluorocyclopentene (**20**). and 1-(2.5-dimethyl-3-thienyl)-2-[2-methyl-5-(4fluorophenyl)-3-thienyl]perfluorocyclopentene (30), have been synthesized. Their structures were determined by single-crystal X-ray diffraction analysis. The fluorine atom position effect on their properties, such as photochromism, fluorescence, and their electrochemical properties, were investigated in detail. The results elucidated that the fluorine atom and its substituted position had a significant effect on the optoelectronic properties of these compounds. For diarylethenes 1-3, the ortho-substituted derivative 1 had the biggest cyclization and cycloreversion quantum yields; while the meta-substituted derivative 2 showed the biggest extinction coefficient and the absorption maxima both in hexane and in PMMA film. The emission peaks of diarylethenes **10–30** displayed an increasing trend along with the fluorine atom from the ortho- to meta- to the para-position of substitution both in hexane and in PMMA film, but their intensities showed a reverse changing trend. The oxidation waves of diarylethenes 1c-3c were clearly observed at 1.44, 1.27 and 1.42 V by performing the cyclic voltammograms, and those of 10-30 were observed at 1.29, 1.12 and 1.41, respectively.

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1. Introduction

Photochromism is a reversible transformation in a chemical species between two forms by means of photoexcitation [1,2]. The quick property change arising from the cyclization–cycloreversion reaction via photoexcitation 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 apparatuses such as rewritable optical recording and photo-switches [3]. Various types of photochromic compounds, such as spirobenzopyrans [4], furylfulgides [5], azobenzenes [6,7] and diarylethenes [8,9], etc., have been developed. Among these compounds, diarylethenes with heterocyclic aryl rings are regarded as the most promising candidates for optical memory and switch because of their excellent thermally irreversibility, high fatigue resistance, and rapid response [8–15].

In general, different substituents linked to photochromic diarylethene system can inevitably influence the optoelectronic properties of corresponding diarylethene derivatives. By far, many publications concerning substituent effects on the photochromic properties of diarylethene compounds have been reported [16–

* Corresponding author. Tel./fax: +86 791 3831996. E-mail address: pushouzhi@tsinghua.org.cn (S. Pu). 20]. The majority of the research work reported to date has been devoted to the development of these molecules and investigative studies of their fundamental properties, and the results obtained have contributed to a broad understanding of the substituent effect on the photochromic property of diarylethene compounds. Although many publications concerning the substituent effect on the property of diarylethene are reported, reports on the substituent position effect are extremely rare. To the best of our knowledge, only a few publications concerning the substituent position effect on the optoelectronic properties of diarylethenes are hitherto reported by our research group [21–25]. Previously, we mainly focused on the effect of electron-withdrawing groups such as cyano group and chlorine atom, and we found that these substituents and their substituted positions had a significant effect on the properties of these diarylethene compounds [21-24]. The results are very important and interesting, and they also give us valuable insight.

In previous publications, we reported the electron-donating methoxyl group position effect on the properties of diarylethenes with a pyrazole unit and found that introduction of methoxyl group at different positions of the terminal phenyl ring could significantly influence the optical and electrochemical properties [26,27]. We also reported the substituent position effect on the properties of symmetrical diarylethenes with fluorine atoms of both terminal phenyl rings [25]. As far as we are aware, this is a un-





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ique example of the fluorine atom position effect on the properties of diarylethenes hitherto reported. However, the fluorine atom position effects on the properties of unsymmetrical dithienylethene derivatives have not been reported. In this work, in order to elucidate the fluorine atom position effect on the optoelectronic characteristics of unsymmetrical diarylethenes, we have synthesized three unsymmetrical isomeric diarylethenes, namely 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-fluorophenyl)-3-thienyl]perfluorocyclopentene (10), 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-fluorophenyl)-3-thienyl]perfluorocyclopentene (20), and 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**30**), which bearing a fluorine at either the ortho-, meta-, or para-positions on the terminal phenyl ring. The three compounds showed good photochromism in solution, in PMMA film, as well as in the single crystalline phase. The photochromic scheme of diarylethenes **1–3** is shown in Scheme 1. Among these diarylethene derivatives. 10 and 20 are new compounds. Although the crystal structure of diarylethene **30** was reported by us [28], its property is not reported. We present its property data here for comparison with those of other two diarylethene compounds.

2. Experimental

2.1. General

All solvents used were spectrograde and were purified by distillation before use. NMR spectra were recorded on 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. The elemental analysis was measured with PE CHN 2400. Melting point was determined by WRS-1B melting point determination apparatus. The absorption spectra were measured using a Agilent 8453 UV/VIS spectrometer. Photo-irradiation 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. The quantum yields were determined by comparing the reaction yields of the diarylethenes in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane [14]. Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. Crystal data of diarylethenes 10-30 were collected by Bruker SMART APEX2 CCD area-detector. 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 quasireference electrode. It was calibrated using the ferrocene (Fc/Fc+) redox couple which has a formal potential $E_{1/2}$ = + 0.35 V versus platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol/L tetrabutylammonium tetrafuoroborate $((TBA)BF_4)$ and 4.0×10^{-3} mol/L dithienylethene. All solutions



Scheme 1. Photochromism of diarylethenes 1-3.

were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

2.2. Synthesis of diarylethenes 10-30

The synthesis method of diarylethenes **10–30** is shown in Scheme 2 and experimental details are carried out as following.

2.2.1. 3-Bromo-2-methyl-5-(2-fluorophenyl)thiophene (5a)

Compound **5a** was prepared by reacting 3-bromo-2-methyl-5thienylboronic acid **(4)** [27] (3.0 g; 13.6 mmol) with 1-bromo-2fluorobenzene (2.38 g; 13.6 mmol) in the presence of Pd(PPh₃)₄ (0.4 g) and Na₂CO₃ (6.40 g; 60 mmol) in tetrahydrofuran (THF) (80 mL containing 10% water) for 15 h at 70 °C. The product **5a** was purified by column chromatography on SiO₂ using hexane as the eluent and 4.48 g obtained as baby yellow solid in 57.0% yield. ¹H NMR (400 MHz, CDCl₃) δ 2.43 (s, 3H, –CH₃), 7.14 (d, 2H, *J* = 8.8 Hz, phenyl-H), 7.25 (s, 1H, thienyl-H), 7.27 (s, 1H, phenyl-H), 7.53 (d, 1H, *J* = 8.0 Hz, phenyl-H).

2.2.2. 3-Bromo-2-methyl-5-(3-fluorophenyl)thiophene (5b)

Compound **5b** was prepared by a method similar to that used for **5a** and obtained as buff solid in 62.4% yield. ¹H NMR (400 MHz, CDCl₃) δ 2.42 (s, 3H, –CH₃), 6.98 (t, 1H, *J* = 8.0 Hz, phenyl-H), 7.12(s,1H), 7.20 (d, H, *J* = 5.6 Hz, phenyl-H), 7.29 (s, 1H, phenyl-H), 7.32 (t,1H, *J* = 6.8 Hz, phenyl-H).

2.2.3. 3-Bromo-2-methyl-5-(4-fluorophenyl)thiophene (5c)

Compound **5c** was prepared by a method similar to that used for **5a** and obtained as buff solid in 57.0% yield. ¹H NMR (400 MHz, CDCl₃) δ 2.41 (s, 3H, –CH₃), 7.03 (s, 1H, thienyl-H), 7.04–7.08 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.45–7.48 (t, 2H, *J* = 6.2 Hz, phenyl-H).

2.2.4. (2,5-Dimethyl-3-thienyl)perfluorocyclopentene (7)

The compound was prepared by the same method as that reported in Ref. [21].

2.2.5. 1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(2-fluorophenyl)-3-thienyl]perfluorocyclopentene (**10**)

To a stirred anhydrous THF containing **5a** (2.1 g, 7.7 mmol) was added dropwise a 2.5 mol/L n-BuLi solution (3.1 mL) at -78 °C under argon atmosphere. After the mixture has been stirred for 30 min at -78 °C, compound 7 (2.36 g, 7.7 mmol) in solvent of anhydrous THF was added. The reaction was further stirred at -78 °C for 1 h, and the reaction was allowed to slowly warn to the room temperature and stirred there for 1 h. The reaction was quenched with distilled water. The product was extracted with ether, dried with MgSO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography petroleum ether to afford to 1.57 g (43%) of **1a** as white solid. M.p. 83.3-84.0 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.90 (s, 3H, -CH₃), 1.98 (s, 3H, -CH₃), 2.46 (s, 3H, -CH₃), 6.75 (s, 1H, thienyl-H), 7.15 (d, 1H, J = 8.0, phenyl-H), 7.19 (t, 1H, J = 8.0, phenyl-H), 7.29 (d, 1H, J = 5.6, phenyl-H), 7.43 (s, 1H, thienyl-H), 7.58 (t, 1H, J = 7.6, phenyl-H); ¹³C NMR (400 MHz, CDCl₃): δ 14.53, 15.00, 55.59, 111.8, 121.0, 121.8, 124.8, 127.9, 128.7, 130.1, 131.5, 136.6, 137.5, 139.7, 141.4, 155.6; IR (KBr, cm⁻¹): 753, 826, 840, 897, 938, 987, 1050, 1113, 1190, 1272, 1336, 1439, 1498, 1519, 1628, 2925; Calcd for C₂₂H₁₅F₇S₂ (%): Calcd C, 55.46; H, 3.17. Found C, 55.49; H, 3.16.

2.2.6. 1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(3-fluorophenyl)-3-thienyl]perfluorocyclopentene (**20**)

Compound **20** was prepared by a method similar to that used for **10** and obtained as solid in 51% yield. M.p. 88.1–89.0 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.90 (s, 3H, –CH₃), 1.97 (s, 3H, –CH₃),



Scheme 2. Synthetic rout for diarylethenes 10-30.

2.45 (s, 3H, –CH₃), 6.75 (s, 1H, thienyl-H), 7.01 (t, 2H, *J* = 8.0 Hz, phenyl-H), 7.24 (d, 1H, *J* = 8.0, phenyl-H), 7.28 (s, 1H, thienyl-H), 7.31–7.37(m, 2H, phenyl-H); ¹³C NMR (400 MHz, CDCl₃): δ 14.25, 14.41, 15.07, 112.4, 114.5, 121.2, 123.4, 124.5, 126.1, 130.5, 135.5, 137.9, 139.8, 140.5, 141.8, 161.9, 164.4; IR (KBr, cm⁻¹): 734, 774, 821, 855, 866, 901, 983, 1053, 1117, 1189, 1272, 1336, 1442, 1494, 1586, 1612, 2926; Calcd for C₂₂H₁₅F₇S₂ (%): Calcd C, 55.46; H, 3.17. Found C, 55.51; H, 3.20.

2.2.7. 1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(4-fluorophenyl)-3-thienyl]perfluorocyclopentene (**30**)

Compound **30** was prepared by a method similar to that used for **10** and obtained as solid in 52% yield. M.p. 92.3–93.1 °C; ¹H NMR (400 MHz, CDCl₃): δ 1.80 (s, 3H, –CH₃), 1.85 (s, 3H, –CH₃), 2.35 (s, 3H, –CH₃), 6.65 (s, 1H, thienyl-H), 7.00 (d, 2H, *J* = 8.0, phenyl-H), 7.10(s, 1H, thienyl-H), 7.40–7.43 (m, 2H, phenyl-H); ¹³C NMR (400 MHz, CDCl₃): δ 14.25, 14.35, 15.07, 115.8, 116.1, 122.5, 124.5, 126.1, 127.3, 129.7, 137.8, 139.7, 140.9, 141.1, 161.3, 163.7; IR (KBr, cm⁻¹): 743, 830, 843, 893, 984, 1049, 1049, 1118, 1139, 1186, 1232, 1265, 1335, 1439, 1511, 1555, 1626, 1739, 2919; Calcd for C₂₂H₁₅F₇S₂ (%): Calcd C, 55.46; H, 3.17. Found C, 55.41; H, 3.15.

2.3. Determination of the crystal structures of diarylethenes

Crystal data of diarylethenes 10-30 were collected by a Bruker SMART APEX2 CCD area-detector equipped with graphite monoradiation at room temperature chromatized Мо Κα (= 0.71073 Å). The linear absorption coefficients, μ , of the three diarylethenes for Mo K radiation were 3.21, 3.17 and 3.14 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 0.93–0.96 Å according to criteria described in the SHELXTL manual. They were included in the refinement with Uiso (H) = 1.2 Ueq (C) or 1.5 Ueq (methyl C). Further details on the crystal structure investigation have been deposited with The Cambridge Crystallographic Data Centre as supplementary publication number CCDC 615591, 615592 and 6615593 for diarylethenes 10-30, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax:+44 1223-336033.

3. Results and discussion

3.1. Photochromism of diarylethenes 1-3

The photochromic reactivity of diarylethenes **1–3** was examined in hexane $(2.0 \times 10^{-5} \text{ mol/L})$. Their absorption spectra and

their color changes induced by photoirradiation at room temperature are shown in Fig. 1. The absorption maximum of diarylethene 10 was observed at 272 nm in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition [29]. Upon irradiation with 297 nm UV light, the colorless open-ring isomer 10 induced a ring-closure reaction and evolved into the purple color of the closed-ring isomer 1c, in which the absorption maximum was observed at 539 nm. Alternatively, the purple solution returned colorless upon irradiation with visible light ($\lambda > 450$ nm) because **1c** reverted to the initial state **1o**. Just as diarylethene 1, diarylethenes 2 and 3 also showed photochromism in hexane (Fig. 1). Upon irradiation with 297 nm light, absorption bands in visible region appeared and both solutions containing 20 and 30, respectively, turned purple as a result of the cyclization reactions to produce the closed-ring isomers 2c and 3c, which their absorption maxima were observed at 542 and 538 nm, respectively. The two solutions can be decolorized upon irradiation with visible light attributable to reproducing their respect open-ring isomer. The color changes of diarylethenes 10-30 upon photoirradiation in hexane are shown in Fig. 1D. The photochromic parameters of diarylethenes 1-3 are summarized in Table 1. From these data, it can be seen that the fluorine atom position effect on the molar absorption coefficients and the cyclization/cycloreversion quantum yields are remarkable, but the effect on the absorption maxima of both open-ring and closed-ring isomers are not significant. In hexane, the molar absorption coefficients of both the open-ring and the closed-ring isomers of the meta-substituted derivative (compound 2) are the biggest; while those of diarylethenes 1 and 3 are relatively smaller and they are not significantly different each other. For diarylethenes 1-3, the cyclization and cycloreversion quantum yields of ortho-substituted derivative (compound 1) are the biggest; while those of diarylethenes 2 and 3 are relatively smaller and they are almost equal each other. Compared to those symmetric analogue diarylethenes bearing two fluorine atoms [25], the results are remarkably different. For those analogues, the cyclization and cycloreversion quantum yields of *para*-substituted diarylethene are the biggest; while those of meta-substituted diarylethene are the smallest [25].

In PMMA amorphous film (10%, w/w), diarylethenes **1–3** also showed good photochromic properties. Their absorption spectra and color changes are shown in Fig. 2. Upon irradiation with 313 nm light, the colors of the three diarylethene/PMMA films changed from colorless to violet with the appearance of a new broad absorption band at 554, 558 and 553 nm, respectively, which was assigned to the formation of the closed-ring isomers **1c–3c**. All colored diarylethene/PMMA films can invert to colorless upon irradiation with visible light of wavelength longer than 450 nm. The distortion of spectra in UV region is ascribed to absorbing UV light of the glass substrate in the PMMA film with glass substrate [30]. The photochromic properties of diarylethenes **1–3** are also displayed in Table 1. Compared to those in hexane, the maximum



Fig. 1. Absorption spectra and color changes of diarylethenes 1–3 by photoirradiation in hexane $(2.0 \times 10^{-5} \text{ mol/L})$ at room temperature: (A) spectral changes for 1, (B) spectral changes for 2, (C) spectral changes for 3, (D) color changes for 1–3. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Absorption characteristics and photochromic reactivity of diarylethenes 1–3 in hexane (2.0×10^{-5} mol/L) and in PMMA film (10%, w/w).

Compound	$\lambda_{o,max} (nm)^{a}$ ($\epsilon/L mol-1 cm^{-1}$)	$\lambda_{c,max} (nm)^{b}$ ($\epsilon/L mol^{-1} cm^{-1}$)		$arPhi^{c}$	
	Hexane	Hexane	PMMA film	$\Phi_{\mathrm{o-c}}$	$\Phi_{\rm c-o}$
1	$272\;(1.27\times 10^4)$	$539~(5.33\times 10^{3})$	554	0.63	0.072
2	$274~(1.74 imes 10^4)$	542 (8.01 \times 10 ³)	558	0.52	0.040
3	$274~(1.43\times 10^4)$	538 (5.08 \times 10 ³)	553	0.51	0.041

^a Absorption maxima of open-ring isomers.
 ^b Absorption maxima of closed-ring isomers.

^c Quantum yields of open-ring (Φ_{o-c}) and closed-ring isomers (Φ_{c-o}), respectively.

absorption peaks of the closed-ring isomers of diarylethenes 1-3 in PMMA film are much longer than those in hexane. The red shift values of the absorption maxima of the closed-ring isomers are 15 nm for **1c**, 16 nm for **2c** and 15 nm for **3c**, respectively. The red shift phenomena may be ascribed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [31].

Moreover, X-ray crystallographic studies have been carried out for diarylethenes **1o–3o**. These single crystals were obtained by the slow evaporation in hexane. The X-ray crystallographic analysis data are listed in Table 2. The ORTEP drawings of diarylethenes **1o–3o** and their color changes by photo-irradiation in the single crystalline phase are shown in Fig. 3. All molecules of diarylethenes **1o–3o** adopt the anti-parallel conformation, and the distances between the two reacting carbon atoms (*d*(C5C13)) are 3.568(4) Å for **1o**, 3.791(5) Å for **2o** and 3.572(5) Å for **3o**, respectively, which is within the range where crystalline-state photochromism is expected to occur [32-36]. Therefore, diarylethenes 10-30 can undergo photochromism in the single crystalline phase. In fact, these crystals showed photochromism in the crystalline state, in accordance with the expected ring closure, to form their respect closed-ring isomers. Their color changes upon photo-irradiation are shown in Fig. 3D. Upon irradiation with 313 nm light, the colorless crystals **10–30** turned to purple quickly. When the purple crystals were dissolved in hexane, the solutions quickly turned to purple, and the absorption maxima were the same as those of the closed-ring isomers **1c-3c**, respectively. Alternatively, these colored crystals reverted to the colorless one upon irradiation with appropriated wavelength visible light ($\lambda > 450$ nm). Furthermore, the diarylethene crystal exhibited remarkable fatigue resistance (larger than 100 cyclization/cycloreversion repeat cycles) and its closed-ring isomer remained stable for more than one year in the dark at room temperature. So, this crystal will be a promising candidate for optoelectronic applications, such as high density threedimensional optical recording medium and optical switch material [37,38].

3.2. Fluorescence of diarylethenes 1-3

Fluorescent properties can be useful in molecular-scale optoelectronics [39], digital fluorescence photo-switches [40–42], as well as ion-sensors [43–47]. In this work, the fluorescence properties of diarylethenes **10–30** were measured both in solution and in PMMA film using a Hitachi F-4500 spectrophotometer. Fig. 4 shows the fluorescence emission spectra of diarylethenes **10–30** both in hexane solution $(2.0 \times 10^{-5} \text{ mol/L})$ and in PMMA film



Fig. 2. Absorption spectra and color changes of diarylethenes **1–3** by photoirradiation in PMMA film (10%, w/w) at room temperature: (A) spectral changes for **1**, (B) spectral changes for **2**, (C) spectral changes for **3**, (D) color changes for **1–3**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2		
Crystal data f	or diarylethenes	1-3.

	10	20	30
Formula	$C_{22}H_{25}F_7S_2$	$C_{22}H_{25}F_7S_2$	$C_{22}H_{25}F_7S_2$
Formula weight	476.46	476.46	476.46
Temperature (K)	294(2)	294(2)	294(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	P2(1)/c	C2/c	P-1
Unit cell dimensions			
a (Å)	13.693(2)	23.916(7)	8.602(2)
b (Å)	18.547(3)	11.889(3)	11.709(3)
c (Å)	8.6042(14)	15.826(4)	11.984(3)
α (°)	90.00	90.00	105.472(4
β (°)	106.099(2)	109.073(5)	94.977(4)
γ (°)	90.00	90.00	109.737(4
Volume (Å ³)	2099.4(6)	4253(2)	1074.1(5)
Ζ	4	8	2
Density (calcd.) (g/cm ³)	1.507	1.488	1.473
Goodness-of-fit on F^2	1.045	1.022	1.074
Final R indices $[I/2\sigma(I)]$			
R ₁	0.0385	0.0726	0.0459
wR ₂	0.1006	0.1744	0.1300
R indices (all data)			
R ₁	0.0616	0.1617	0.0706
wR ₂	0.1167	0.2379	0.1469

(10%, w/w) at room temperature. The emission peaks of diarylethenes **10–30** were observed at 341, 343 and 348 nm when excited at 300 nm in hexane; while those of the three compounds were observed at 391, 393 and 400 nm when excited at 300 nm in PMMA film. The result showed that the emission peaks of diarylethenes **10–30** displayed a minor increasing trend along with the fluorine atom substituting hydrogen atom of the benzene ring from the *ortho-* to *meta-* to the *para-*positions both in hexane and in PMMA film. Compared to those in hexane, the emission peaks of the three isomeric diarylethene derivatives show a remarkable red shift in PMMA film, and the red shift values are 50 nm for **10**, 50 nm for **20**, and 52 nm for **30**, respectively. For diarylethenes **10–30**, the changing trend of emission intensity is reverse to that of emission peak, which was accompanied by appreciably decreasing of emission intensity when the fluorine atom was joined into the benzene ring from the *ortho*- to *meta*- to the *para*-positions both in hexane and in PMMA film.

Upon exposure to 313 nm UV light, diarylethenes **10–30** were photocyclized to the closed-ring isomers **1c-3c**, along with a significant decrease in the fluorescence intensities in PMMA film, as shown in Fig. 5. When reaching the photostationary state, the fluorescence efficiency of diarylethenes 1-3 was distinctly quenched to ca. 47, 40 and 41%, respectively. This is resulted from the -electron delocalization enlargement of the closed-ring isomers as a fluorescence quencher in the possible channel of Föster resonance energy transfer [48,49]. Upon irradiation, each of the generated closed-ring isomers 1c-3c has a broad absorption which covers the majority of the visible area (Fig. 2), thus resulting in an efficient overlap between the absorption (400-650 nm) and emission band (350–550 nm). Upon irradiation with visible light, the emissions were completely converted into their respective open-ring isomers according to the spectral change, showing the classical switchable property of diarylethene. In PMMA solid medium, the incomplete cyclization reaction and the existence of parallel conformation of diarylethenes 10-30 may be the main cause for the moderate change in fluorescence induced by photoirradiation. Unexpectedly, diarylethenes 1-3 showed almost no fluorescence modulation in hexane, which may be attributed to the solvent polar effect.

3.3. Electrochemistry of diarylethenes 1-3

It was well known that the ring opening and closing transformation of some diarylethenes can be initiated not only by UV or



Fig. 3. ORTEP drawings of crystals **10–30** and their color changes by photoirradiation in the single crystalline phase: (A) ORTEP drawing of **10**, (B) ORTEP drawing of **20**, (C) ORTEP drawing of **30**, (D) color changes for **1–3**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. Emission spectra of diarylethenes **1–3** both in hexane $(2.0 \times 10^{-5} \text{ mol/L})$ and in PMMA film (10%, w/w) at room temperature, excited at 300 nm: (A) in hexane, (B) in PMMA film.

visible light irradiation, but also by electrochemical or chemical oxidation, such as electrochromism [50,51]. Therefore, besides their excellent photochromic performance, the electrochemical

behaviors of diarylethenes were also attracted much attention [52,53]. The electrochemical properties of diarylethenes can be used potentially for molecular switches and molecular-scale electronic switches [54,55]. In this study, the electrochemical examinations were performed by cyclic voltammograms (CV) method under the same experimental conditions using diarylethenes **1–3**, respectively.

The CV curves of diarylethenes 1-3 with the scanning rate of 50 mV/s were shown in Fig. 6. From the figure, it can be seen that the oxidation potential onsets of the closed-ring isomers of diarylethenes 1-3 were higher than those of the corresponding openring isomers. After cyclization reaction, the π -conjugation lengths of the closed-ring isomers **1c-3c** were much longer than those of the open-ring isomers 10-30. The initiation values of their oxidation are 1.17 and 1.31 V for 10 and 1c, 0.50 and 0.60 V for 20 and 2c, 1.26 and 1.30 V for 3o and 3c, respectively. The results is reverse to that of symmetrical analogues bearing two fluorine atoms at both terminal phenyl rings [25], which their oxidation potential onsets of the open-ring isomers were higher than those of the corresponding closed-ring isomers. Furthermore, there are great differences of the electronic current and polarization curve shapes between the open- and closed-ring isomers of diarylethenes 1 and 2, with the exception of diarylethene 3. All of these diarylethene derivatives showed the distinct oxidation waves, and the values are observed at 1.29 and 1.44 V for 10 and 1c, 1.12 and 1.27 V for **20** and **2c**. and 1.41 and 1.42 V for **30** and **3c**. respectively. This is very different from those of symmetrical and unsymmetrical diarylethene analogues reported previously [21-23]. For those analogues, only the closed-ring isomers showed a distinct oxidation wave at one voltage, but all of their open-ring isomers did not [21-23].

According to the same method described in previous works [56–58], the HOMO and LUMO energy levels can be estimated by using the energy level of the ferrocene as reference. As shown in



Fig. 5. Emission intensity changes of diarylethenes **1–3** in PMMA film (10%, w/w) upon irradiation with 313 nm UV light at room temperature, excited at 300 nm: (A) **1**, (B) **2**, and (C) **3**.

Fig. 6A, the onset potentials (E_{onset}) of oxidation and reduction of **10** were observed at +1.17 and -1.25 V, respectively. So the values of IP and EA were calculated to be -5.97 and -3.55 eV. Based on the the HOMO and LUMO energy levels, the band gap (E_g , E_g = LU-MO-HOMO) of **10** can be determined as 2.42 eV. Similarly, the E_g of **1c** can be calculated as 2.65 eV. Corresponding values for diarylethenes **2** and **3** are summarized in Table 3. From these data, it can be clearly seen that the band gaps of the closed-ring isomers **2c** and **3c** are higher than those of their corresponding open-ring isomers **20** and **30**, but that of **1c** are smaller than that of **10**. The result indicated that the fluorine atom and its substituent position have a great effect on the electrochemical behaviors of these diarylethene derivatives.

4. Conclusions

Three unsymmetrical isomeric diarylethenes having a fluorine at either the *ortho-*, *meta-*, or *para-*positions of the terminal phenyl ring were synthesized and their optical and electrochemical prop-



Fig. 6. Cyclic voltammetry (second scan) of diarylethenes **1–3** in acetonitrile at a scan rate of 50 mV/s: (A) **1**, (B) **2**, and (C) **3**.

Table	3
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Electrochemical properties of diarylethenes 1-3.

Compound	Oxidation		Reduction		Band gap	
	$E_{\text{onset}}(V)$	IP (eV)	E _{onset} (V)	EA (eV)	E_{g}	
10	+1.17	-5.97	-1.25	-3.55	2.42	
1c	+1.31	-6.11	-1.34	-3.46	2.65	
20	+0.50	-5.3	-0.91	-3.89	1.41	
2c	+0.60	-5.4	-0.76	-4.04	1.36	
30	+1.26	-6.06	-1.36	-3.44	2.62	
3c	+1.30	-6.1	-1.27	-3.53	2.57	

^{*}The acetonitrile used as solvent was spectrograde and was purified by distillation before use.

erties were studied. These unsymmetrical compounds showed good photochromism in solution, in PMMA film and in the single crystalline phase. Their fluorescence and electrochemical behaviors are remarkably dependent on the fluorine atom position effect, which may be attributed to the different electron-withdrawing ability and steric effect when the fluorine atom was substituted on the different position of the terminal phenyl ring.

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References

- H. Dürr, H. Bouas-Laurent, Photochromism, Molecules and Systems, Elsevier, Amsterdam, 1990.
- [2] C.H. Brown, Photochromism, Wiley, New York, 1971.

- [3] S. Ryo, Y. Ishibashi, M. Murakami, H. Miyasaka, S. Kobatake, M. Irie, J. Phys. Org. Chem. 20 (2007) 953.
- [4] S.A. Ahmed, M. Tanaka, H. Ando, K. Tawa, K. Kimura, Tetrahedron 60 (2004) 6029.
- [5] Y.C. Liang, A.S. Dvornikov, P.M. Rentzepis, Macromolecules 35 (2002) 9377.
- [6] T. Tuuttila, J. Lipsonen, M. Lahtinen, J. Huuskonen, K. Rissanen, Tetrahedron 64 (2008) 10590.
- [7] M.V. Peters, R. Goddard, S. Hecht, J. Org. Chem. 71 (2006) 7846.
- [8] M. Irie, Chem. Rev. 100 (2000) 1685.
- [9] H. Tian, S.J. Yang, Chem. Soc. Rev. 33 (2004) 85.
- [10] M. Morimoto, S. Kobatake, M. Irie, J. Am. Chem. Soc. 125 (2003) 11080.
- [11] S.Z. Pu, F.S. Zhang, J.K. Xu, L. Shen, Q. Xiao, B. Chen, Mater. Lett. 60 (2006) 485.
- [12] H. Tian, B. Qin, R.G. Yao, X.L. Zhao, S.J. Yang, Adv. Mater. 15 (2003) 2104.
- [13] H, Tian, Y.L. Feng, J. Mater. Chem. 18 (2008) 1617.
- [14] D. Dulic, T. Kudernac, A. Puzys, B.L. Feringa, B.J. Wees, Adv. Mater. 19 (2007) 2898.
- [15] V.A. Barachevsky, Y.P. Strokach, Y.A. Puankov, M.M. Krayushkin, J. Phys. Org. Chem. 20 (2007) 1007.
- [16] M. Irie, K. Sakemura, M. Okinaka, K. Uchida, J. Org. Chem. 60 (1995) 8305.
 [17] K. Uchida, T. Matsuoka, S. Kobatake, T. Yamaguchi, M. Irie, Tetrahedron 57
- (2001) 4559. [10] 57 m TS Varg LV Vi L Chan C.7 Li O Vias D Chan Tetrahedron (1
- [18] S.Z. Pu, T.S. Yang, J.K. Xu, L. Shen, G.Z. Li, Q. Xiao, B. Chen, Tetrahedron 61 (2005) 6623.
- [19] S.Z. Pu, C.H. Zheng, Z.G. Le, G. Liu, C.B. Fan, Tetrahedron 64 (2008) 2576.
- [20] S.Z. Pu, C.B. Fan, W.J. Miao, G. Liu, Tetrahedron 64 (2008) 9464.
- [21] S.Z. Pu, L.S. Yan, Z.D. Wen, G. Liu, L. Shen, J. Photoch. Photobio. A 196 (2008) 84.
- [22] C.B. Fan, S.Z. Pu, G. Liu, T.S. Yang, J. Photoch. Photobio. A 194 (2008) 333.
- [23] C.B. Fan, S.Z. Pu, G. Liu, T.S. Yang, J. Photoch. Photobio. A 197 (2008) 415.
- [24] G. Liu, S.Z. Pu, C.H. Zheng, Z.G. Le, M.B. Luo, Phys. Scr. T129 (2007) 278.
- [25] S.Z. Pu, T.S. Yang, G.Z. Li, J.K. Xu, B. Chen, Tetrahedron Lett. 47 (2006) 3167.
- [26] S.Z. Pu, T.S. Yang, J.K. Xu, B. Chen, Tetrahedron Lett. 47 (2006) 6473.
- [27] T.S. Yang, S.Z. Pu, B. Chen, J.K. Xu, Can. J. Chem. 85 (2007) 12.
- [28] Z.D. Wen, S.Z. Pu, L.S. Yan, J.K. Xu, Acta Cryst. E62 (2006) 04372.
- [29] Z.X. Li, L.Y. Liao, W. Sun, C.H. Xu, C. Zhang, C.J. Fang, C.H. Yan, J. Phys. Chem. C 112 (2008) 5190.
- [30] T.S. Yang, S.Z. Pu, C.B. Fan, G. Liu, Spectrochim. Acta A 70 (2008) 1065.
- [31] K. Kasatani, S. Kambe, M. Irie, J. Photoch. Photobiol. A 122 (1999) 11.
- [32] M. Irie, T. Lifka, S. Kobatake, N. Kato, J. Am. Chem. Soc. 122 (2000) 4871.

- [33] M. Morimoto, M. Irie, Chem. Eur. J. 12 (2006) 4275.
- [34] V. Ramamurthy, K. Venkatesan, Chem. Rev. 87 (1987) 433.
- [35] [35] S. Kobatake, K. Uchida, E. Tsuchida, M. Irie, Chem. Commun. (2002) 2804.
- [36] M. Morimoto, M. Irie, Chem. Commun. (2005) 3895.
- [37] S. Kawata, Y. Kawata, Chem. Rev. 100 (2000) 1777.
- [38] [38] M. Irie, T. Fukaminato, T. Sasaki, N. Tamai, T. Kawai, Nature 420 (2002) 759.
- [39] B. Gorodetsky, H.D. Samachetty, R.L. Donkers, M.S. Workentin, N.R. Branda, Angew. Chem. Int. Ed. 43 (2004) 2812.
- [40] S.Z. Xiao, T. Yi, F.Y. Li, C.H. Huang, Tetrahedron Lett. 46 (2005) 9009.
- [41] S.Z. Xiao, T. Yi, Y.F. Zhou, Q. Zhao, F.Y. Li, C.H. Huang, Tetrahedron 62 (2006) 10072.
- [42] H.Y. Hu, M.Z. Zhu, X.M. Meng, Z.P. Zhang, K. Wei, Q.X. Guo, J. Photoch. Photobio. A 189 (2007) 307.
- [43] Z.G. Zhou, H. Yang, M. Shi, S.Z. Xiao, F.Y. Li, T. Yi, C.H. Huang, ChemPhysChem 8 (2007) 1289.
- [44] Y. Gabe, Y. Urano, K. Kikuchi, H. Kojima, T. Nagano, J. Am. Chem. Soc. 126 (2004) 3357.
- [45] Y. Liu, N. Zhang, Y. Chen, L.H. Wang, Org. Lett. 9 (2007) 315.
- [46] Y. Suzuki, K. Yokoyama, J. Am. Chem. Soc. 127 (2005) 17799.
- [47] N. Chattopadhyay, A. Mallick, S. Sengupta, J. Photoch. Photobio. A 117 (2006) 55.
- [48] Y. Zou, T. Yi, S.Z. Xiao, F.Y. Li, C.Y. Li, X. Gao, J.C. Wu, M.X. Yu, C.H. Huang, J. Am. Chem. Soc. 130 (2008) 15750.
- [49] X.L. Meng, W.H. Zhu, Q. Zhang, Y.L. Feng, W.J. Tan, H. Tian, J. Phys. Chem. B 112 (2008) 15636.
- [50] A. Peters, N.R. Branda, J. Am. Chem. Soc. 125 (2003) 3404.
- [51] M.S. Kim, H. Maruyama, T. Kawai, M. Irie, Chem. Mater. 15 (2003) 4539.
- [52] C.C. Ko, M.W. Kwok, V.W. Yam, D.L. Phillips, Chem. Eur. J. 12 (2006) 5840.
- [53] W.R. Browne, J.J. Jong, T. Kudernac, M. Walko, L.N. Lucas, K. Uchida, J.H. Esch, B.L. Feringa, Chem. Eur. J. 11 (2005) 6414.
- [54] E. Kim, M. Kim, K. Kim, Tetrahedron 62 (2006) 6814.
- [55] N. Xie, D.X. Zeng, Y. Chen, J. Electroanal. Chem. 609 (2007) 27.
- [56] C.H. Zheng, S.Z. Pu, J.K. Xu, M.B. Luo, D.C. Huang, L. Shen, Tetrahedron 63 (2007) 5437.
- [57] F.C. Tsai, C.C. Chang, C.L. Liu, W.C. Chen, S.A. Jenekhe, Macromolecules 38 (2005) 1958.
- [58] X.W. Zhan, Y.Q. Liu, X. Wu, S. Wang, D.B. Zhu, Macromolecules 23 (2002) 2529.