



New photochromic diarylethenes with a six-membered aryl unit

Shouzhi Pu*, Congbin Fan, Wenjuan Miao, Gang Liu

Jiangxi Key Laboratory of Organic Chemistry, Jiangxi Science & Technology Normal University, Nanchang 330013, China

ARTICLE INFO

Article history:

Received 31 May 2008

Received in revised form 17 July 2008

Accepted 18 July 2008

Available online 23 July 2008

ABSTRACT

A new class of photochromic diarylethenes bearing a six-membered aryl unit has been developed. They underwent reversible cyclization and cycloreversion reactions upon alternating irradiation with UV and visible light both in solution and in PMMA film. However, diarylethenes **1**, **2**, and **4** showed no photochromism in the crystalline phase although they packed with an anti-parallel conformation and the distances between the two reactive carbon atoms were both less than 4.2 Å.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

Photochromic diarylethenes have been extensively studied for optoelectronic applications because of their notable thermally irreversible photochromic behavior and remarkable fatigue resistance.¹ Up to date, design and synthesis of new photochromic compounds is an active area of research, and many publications concerning synthesis and investigation of the properties of diarylethenes with the heterocyclic aryl rings have been reported. Among diarylethenes hitherto reported, most of the heteroaryl moieties have been thiophene or benzothiophene rings,² with just a few reports concerning other heteroaryl moieties, such as furan,³ thiazole,⁴ indole,⁵ benzofuran,⁶ pyrrole,⁷ and pyrazole,⁸ etc. The photochromic performance of each kind of diarylethene is strongly dependent on the nature of the aryl moieties. For example, diarylethenes with thiophene or benzothiophene moieties exhibit excellent thermal stability and outstanding fatigue resistance,¹ whereas diarylethenes with pyrrole rings are thermally unstable and return to the opening isomers even in the dark.^{7b} Moreover, Kawai et al.⁹ reported the triangular terthiophene derivatives that showed reversible photochromic reactions with high cyclization quantum yields. Yamaguchi et al.¹⁰ developed a new type of 6π conjugated photochromic system with a bis(2,3'-benzothienyl) unit showing efficient photochromism and thermal stability for the colored isomers. Peters et al.¹¹ synthesized a new class of photochromic compounds based on a modified hexatriene skeleton. This novel molecular scaffold offers the chance to decorate photoresponsive systems with a wide range of functional groups without sacrificing photochromic behavior.

As described above, it can be easily concluded that these reports have a common merit, i.e., the hexatriene backbone of all photochromic perfluorocyclopentene systems is composed of five-membered heterocyclic rings or the combination of a five-

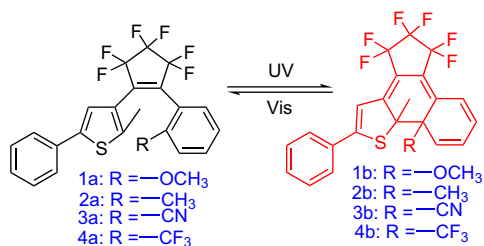
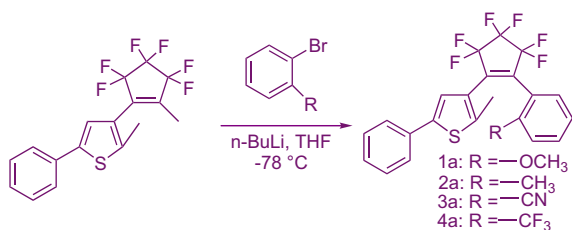
membered aryl ring and a vinyl group. The results are very interesting and important, and they contribute to a broad understanding of the photochromism of diarylethene derivatives with various aryl groups. At the same time, the results have also given us some good suggestions to design some new photochromic diarylethene systems. We predicted that diarylethene would have some novel characteristics when replacing a five-membered heterocyclic ring with a six-membered aryl ring. As far as we are aware, there are many reports on diarylethene derivatives with heteroaromatic rings as both thermally irreversible and reversible photochromic compounds, but in the case of six-membered rings as aryl moieties, only a few diphenyl-perfluorocyclopentene derivatives have been reported.¹² The majority of these compounds are thermally reversible with poor photochromism. To the best of our knowledge, photochromic hybrid diarylethene derivatives bearing both five-membered and six-membered moieties have not been reported. Herein, using a benzene ring as an aryl moiety, we have designed and prepared a new class of photochromic diarylethene derivatives, i.e., 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methoxyphenyl)perfluorocyclopentene (**1a**), 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-methylphenyl)perfluorocyclopentene (**2a**), 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-cyanophenyl)perfluorocyclopentene (**3a**), and 1-(2-methyl-5-phenyl-3-thienyl)-2-(2-trifluoromethylphenyl)perfluorocyclopentene (**4a**). All of these diarylethenes showed good reversible photochromism both in solution and in PMMA amorphous film. They are, to the best of our knowledge, the first class example of photochromic diarylethene derivatives bearing both five-membered and six-membered moieties. The photochromic scheme of **1a–4a** is shown in Scheme 1.

2. Results and discussion

2.1. Synthesis of the diarylethenes 1a–4a

The synthetic route for diarylethenes **1a–4a** is shown in Scheme 2. Compounds **1a–4a** were prepared from 2-methyl-5-phenyl-3-

* Corresponding author. Tel./fax: +86 791 3805212.
E-mail address: pushouzhi@tsinghua.org.cn (S. Pu).

Scheme 1. Photochromism of diarylethenes **1a–4a**.Scheme 2. Synthetic route of diarylethenes **1a–4a**.

thienyl-perfluorocyclopentene^{11,13} in a one-step coupling reaction with 2-bromoanisole, 2-bromotoluene, 2-bromobenzonitrile, and 2-bromobenzotrifluoride, respectively. Their structures were confirmed by NMR, MS, elemental analysis, and IR (see Section 4). Compounds **1a**, **2a**, and **4a** were also confirmed by X-ray single-crystal diffraction.

2.2. Photochromic reactions both in solution and in PMMA amorphous film

The photochromic behaviors of diarylethenes **1–4** induced by photoirradiation at room temperature were measured both in hexane and in PMMA amorphous film. In hexane, the absorption spectral and color changes of diarylethenes **1–4** induced by alternating irradiation with UV light and visible light with appropriate wavelength are shown in Figure 1. As shown in Figure 1A, compound **1a** exhibited a sharp absorption peak at 275 nm in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition.¹⁴ Upon irradiation with 297 nm light, a new visible absorption band centered at 581 nm emerged while the original peak at 275 nm decreased, indicating the formation of the closed-ring isomer **1b**. Correspondingly, the colorless solution of **1a** turned blue owing to produce the closed-ring isomer **1b**. The blue colored solution turned colorless by irradiation with visible light ($\lambda > 500$ nm), indicating that **1b** returned to the initial state **1a** and a clear isosbestic point was observed at 309 nm.

Just as diarylethene **1**, diarylethenes **2–4** also showed photochromism in hexane. Upon irradiation with 297 nm light, absorption bands in visible region appeared and all solutions containing **2a**, **3a**, and **4a**, respectively, turned magenta as a result of the cyclization reactions to produce the closed-ring isomers **2b**, **3b**, and **4b**, which the absorption maxima of them were observed at 554, 545, and 544 nm, respectively (Fig. 1B). The color changes of diarylethenes **1–4** upon photoirradiation in hexane are shown in Figure 1C. All the solutions of **2b**, **3b**, and **4b** can be decolorized upon irradiation with visible light ($\lambda > 450$ nm) attributable to reproduce the open-ring isomers **2a**, **3a**, and **4a**. In the photostationary state, the isosbestic points for diarylethenes **2**, **3**, and **4** were observed at 300, 301, and 297 nm, respectively. The absorption spectral features of these compounds are summarized in Table 1.

The cyclization and cycloreversion quantum yields of diarylethenes **1–4** were measured in hexane at room temperature, and the results are also summarized in Table 1. As can be seen from these data, different substituents at 2-position of the benzene ring

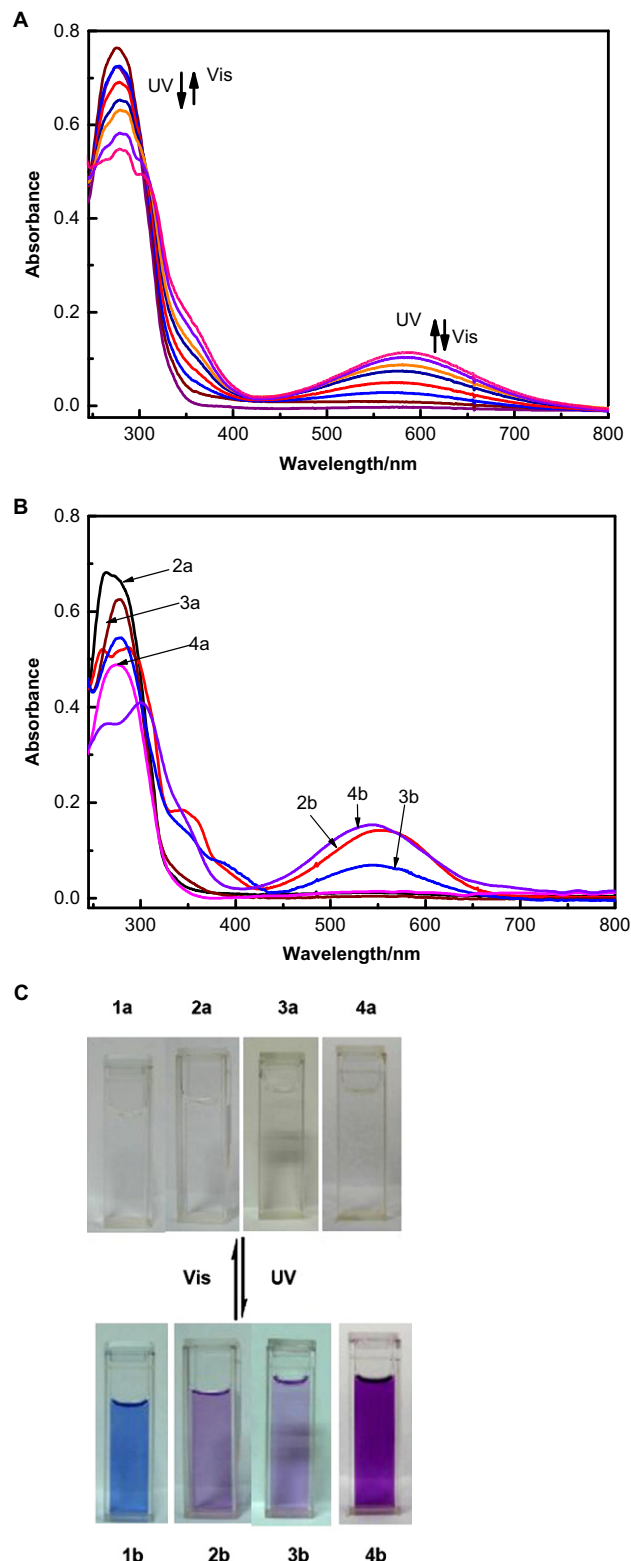


Figure 1. Absorption spectral and color changes of diarylethenes **1–4** upon alternating irradiation with UV and visible light in hexane (3.0×10^{-5} M) at room temperature; (A) spectral changes for compound **1**; (B) spectral changes for compounds **2–4**; (C) color changes for compounds **1–4**.

had a significant effect on the photochromic features of diarylethenes **1–4**, including the absorption maxima, molar absorption coefficients, and quantum yields. The results indicated that the cycloreversion quantum yields enhanced significantly when the electron-donating groups were substituted at the 2-position of

Table 1
Absorption spectral properties of diarylethenes **1–4** in hexane at 3.0×10^{-5} mol/L

Compound	$\lambda_{o,max}^a$ (nm) ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)		$\lambda_{c,max}^b$ (nm) ($\epsilon/L \text{ mol}^{-1} \text{ cm}^{-1}$)		Φ^c	
	Hexane	PMMA film	Hexane	PMMA film	Φ_{o-c}	Φ_{c-o}
1	275(2.5×10^4)	333	581(3.8×10^3)	585	0.26	0.15
2	264(2.3×10^4)	312	552(4.8×10^3)	564	0.25	0.31
3	278(2.1×10^4)	329	548(2.3×10^3)	554	0.64	0.019
4	274(1.6×10^4)	290	539(4.7×10^3)	560	0.65	0.011

^a Absorption maxima of open-ring forms.

^b Absorption maxima of closed-ring forms.

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

the benzene ring of these diarylethenes, while the cyclization quantum yields improved remarkably when the electron-withdrawing groups were substituted at the same position. The absorption maxima of diarylethenes **1–4** displayed a well regular change in hexane, i.e., they showed a remarkable blue shift ($581 \text{ nm} \rightarrow 539 \text{ nm}$) with the increase of electron-withdrawing ability. On the one hand, the absorption maxima of both open-ring and closed-ring isomers of diarylethene **1** are much longer than those of diarylethene **2**, as a result of the electron-donating ability of methoxyl group is larger than that of methyl group;¹⁵ but the molar absorption coefficient of **1b** is smaller than that of **2b**. The cyclization quantum yields of the two compounds are almost equal. However, there is a relatively big difference of the cycloreversion quantum yield between compounds **1** and **2**. The cycloreversion quantum yield of **2** ($\Phi_{c-o}=0.31$) is two-fold larger than that of **1** ($\Phi_{c-o}=0.15$), indicating that the cycloreversion quantum yield was remarkably dependent on the electron-donating substituents and it was dramatically increased with the decrease of electron-donating ability. On the other hand, the electron-withdrawing substituents (cyano and trifluoromethyl groups) significantly shifted the absorption maxima of diarylethenes **3b** and **4b** to a shorter wavelength, and their molar absorption coefficients increased with the increasing electron-withdrawing ability. The result is contrary to those reported previously.^{15a,16} In addition, electron-withdrawing groups can also enhance notably the cyclization quantum yield and depress heavily the cycloreversion quantum yield. From Table 1, it can be easily found that the cyclization quantum yields of diarylethenes **3** and **4** bearing electron-withdrawing groups are much higher than those of diarylethenes **1** and **2** bearing electron-donating groups, but a reverse case for the cycloreversion quantum yields. Furthermore, the cycloreversion quantum yield of **3** ($\Phi_{c-o}=0.019$) was almost equal to that of **5** ($\Phi_{c-o}=0.011$). The result suggested that the ability of the electron-withdrawing substituents did not influence remarkably the cycloreversion quantum yield.^{15a}

For practical applications in optical devices, it is very important that photochromic materials can keep good photochromism in a polymer film, such as the PMMA film.¹⁷ Dissolved ultrasonically 10 mg diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the film was prepared by spin-coating method. In PMMA amorphous film, diarylethenes **1–4** also showed good photochromism (Fig. 2) as similar to those in solution. The photochromic properties of diarylethenes **1–4** in PMMA film are also summarized in Table 1. Upon irradiation with 313 nm light, the colorless diarylethene **1a**/PMMA film turned blue for which the absorption maxima were observed at 585 nm, as the closed-ring isomer **1b** was generated; while the colors of other three diarylethene/PMMA films changed from colorless to magenta with the appearance of a new broad absorption band at 564, 554, and 560 nm, respectively, which was assigned to the formation of the closed-ring isomers **2b**, **3b**, and **4b**. All colored diarylethene/PMMA films can revert to colorless upon irradiation with visible light ($\lambda > 450 \text{ nm}$). As has

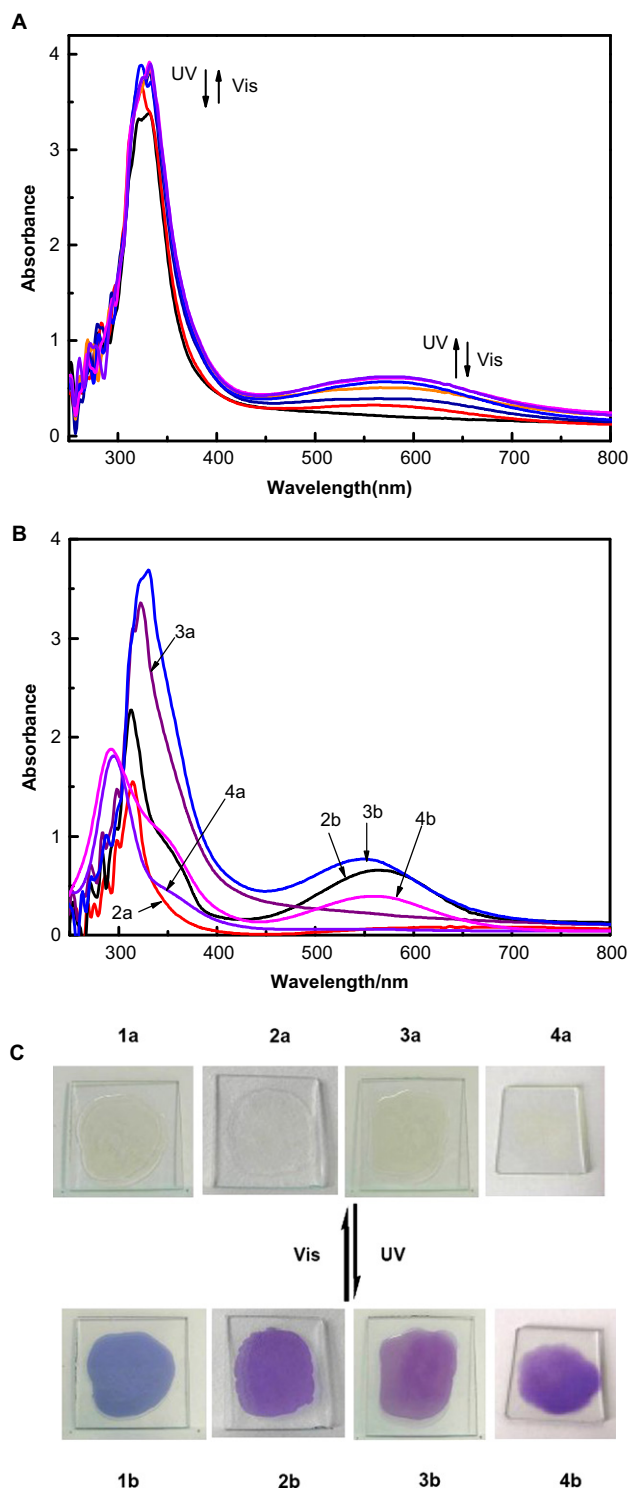


Figure 2. Absorption spectral and color changes of diarylethenes **1–4** upon alternating irradiation with UV and visible light in PMMA film (10% w/w) at room temperature; (A) spectral changes for compound **1**; (B) spectral changes for compounds **2–4**; (C) color changes for compounds **1–4**.

been observed for most of the reported diarylethenes,¹⁸ the maximum absorption peaks of both the open-ring and the closed-ring isomers in PMMA film are longer than those in hexane solution. The red shift values of the absorption maxima of the open-ring isomers are 58 nm for **1a**, 48 nm for **2a**, 51 nm for **3a**, and 16 nm for **4a**, and those of the closed-ring isomers are 4 nm for **1b**, 12 nm for **2b**, 6 nm for **3b**, and 21 nm for **4b**, respectively. The red shift phenomena

may be ascribed to the stabilization of molecular arrangement in solid state.¹⁹

The thermal stabilities of the open-ring and closed-ring isomers of diarylethenes **1–4** were tested in hexane both at room temperature and at 80 °C. Storing these solutions in hexane at room temperature in the dark and then exposing them to air for more than 10 days, we found that no changes in the UV/vis spectra of diarylethenes **2–4** were observed and, indeed, no decomposition was detected when the three compounds were exposed to air for more than a year. For diarylethene **1**, no decomposition was also detected for the open-ring isomer **1a** when exposed to air for more than a year, but its closed-ring isomer **1b** returned to **1a** when exposed to air in the dark for only 10 days. That is to say, the thermal stability of **1b** is very weak. At 80 °C, diarylethenes **2–4** still showed good thermal stabilities for more than 100 min, but the blue color of **1b** disappeared completely after 3 min. The result suggests that the thermal stability of diarylethenes with a six-membered ring is very different from that of photochromic dithienylethene derivative.^{1a,16} In general, dithienylethene derivatives bearing electron-donating substituents show good thermal stability, but those with strong electron-withdrawing substituents, such as dicyanovinyl group,^{1a,16} show thermal instability. The possible reason is that the strong electron-donating ability of methoxyl group leads to the high-density electron cloud distribution of the cyclohexadiene moiety in **1b** system, resulting in its thermal instability.

Fatigue-resistant property, i.e., how many times photocyclization and cycloreversion reaction cycles can be repeated without loss of performance,^{1a,7b} is an very important factor for practical applications in optical devices.^{1a,20} The fatigue resistances of diarylethenes **1–4** were examined both in hexane and in PMMA amorphous film at room temperature, as shown in Figure 3. In hexane, diarylethenes **1–4** were irradiated alternatively with 297 nm and visible light ($\lambda > 450$ nm), respectively. The irradiation time was long enough for coloration to reach the photostationary state and for the color to be completely bleached. As shown in Figure 3A, the fatigue-resistant characteristics of **1** and **2** in solution indicated that ~70% of each of **1b** and **2b** was destroyed after 10 repeat cycles, but only 27% of **3b** and 12% of **4b** were destroyed after 11 repeat cycles at the same condition. This may be ascribed to degradation resulting from the formation of an epoxide.²¹ Similarly, the fatigue resistances of diarylethenes **1–4** were tested in PMMA film by alternatively irradiating with 313 nm and visible light, respectively. As shown in Figure 3B, the fatigue resistances of diarylethenes **1–4** in the solid state (PMMA amorphous film) are much stronger than those in solution. After 200 repeated cycles, these compounds still showed good photochromism with only ~37% degradation of **1b**, 22% of **2b**, 9% of **3b**, and 7% of **4b**, respectively. This remarkable improvement may result from effectively suppressing the oxygen diffusion.^{1a} As described above, it can be easily concluded that the fatigue resistances of **3** and **4** are much stronger than those of **1** and **2**, both in solution and in PMMA amorphous film, which may be attributed to the different electron-withdrawing/electron-donating substituent effects.

2.3. Non-photochromism in the crystalline phase

Among diarylethenes **1a–4a**, single crystals of diarylethenes **1a**, **2a**, and **4a** were obtained by recrystallization from diethyl ether. To know better, the relation between the conformation and the photochromic behaviors of diarylethenes **1a**, **2a**, and **4a** in the crystalline phase, their final structural conformations were provided by X-ray crystallographic analysis. The ORTEP drawings of diarylethenes **1a**, **2a**, and **4a** are shown in Figure 4, and the X-ray crystallographic analysis data are listed in Ref. 22. As shown in Figure 4, these three molecules were packed in anti-parallel conformations²³

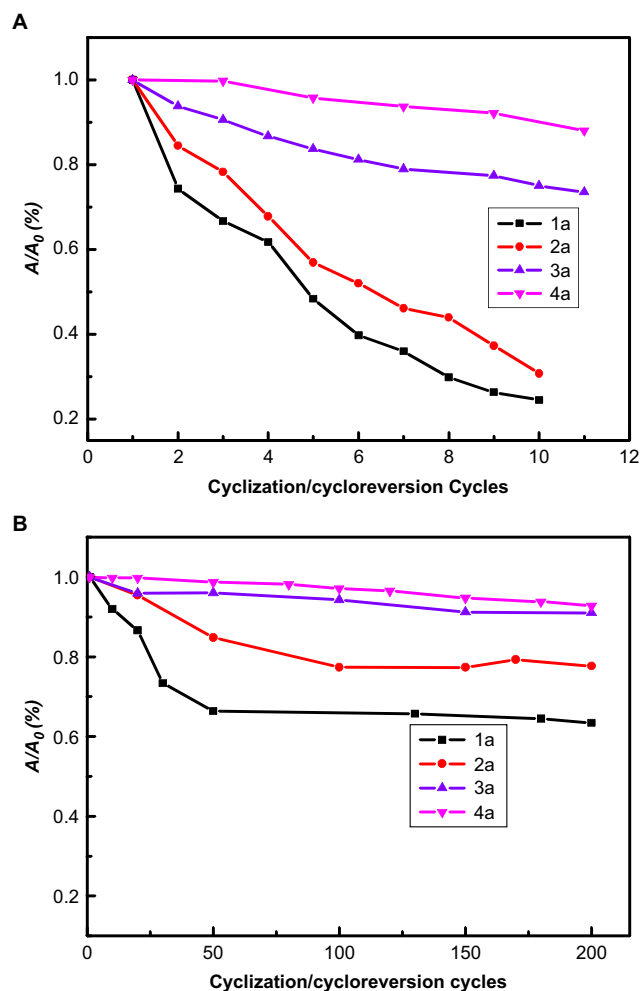


Figure 3. Fatigue resistance of diarylethenes **1–4** in hexane and in PMMA film in air atmosphere at room temperature. Initial absorbance of the sample was fixed to 1.0; (A) in hexane; (B) in PMMA film.

in the crystalline phase. The distances between the two reactive carbons of **1a** (C10···C22), **2a** (C4···C21), and **4a** (C1···C18) were 3.672(4), 3.817(3), and 4.089(7) Å, respectively. In general, the molecule undergoes the photocyclization reaction if the molecule is fixed in an anti-parallel mode and the distance between reacting carbon atoms on the aryl rings is less than 4.2 Å.²⁴ Therefore, **1a**, **2a**, and **4a** should undergo photochromism in the crystalline phase. However, the fact is contrary to the above analysis. All of the three compounds showed no photochromism in the crystalline phase. This is verified by the fact that irradiating single crystals of **1a**, **2a**, and **4a** with UV light for 12 h resulted in no observable color change. When these crystals were dissolved in hexane, the solutions showed colorless and their absorption spectra were the same as those of the open-ring isomers **1a**, **2a**, and **4a**. Thus, the important rule described above²⁴ should restrict its applied condition: it wasn't applicable to diarylethene systems bearing a six-membered aryl ring reported in this paper at least.

2.4. Fluorescence of diarylethenes 1–4

The fluorescence spectra of diarylethenes **1a–4a** both in hexane and in PMMA amorphous film at room temperature are illustrated in Figure 5. All of them showed good fluorescence both in hexane and in PMMA film. As shown in Figure 5, we could clearly see that the fluorescent emissions of **1a**, **2a**, **3a**, and **4a** were at 353, 409,

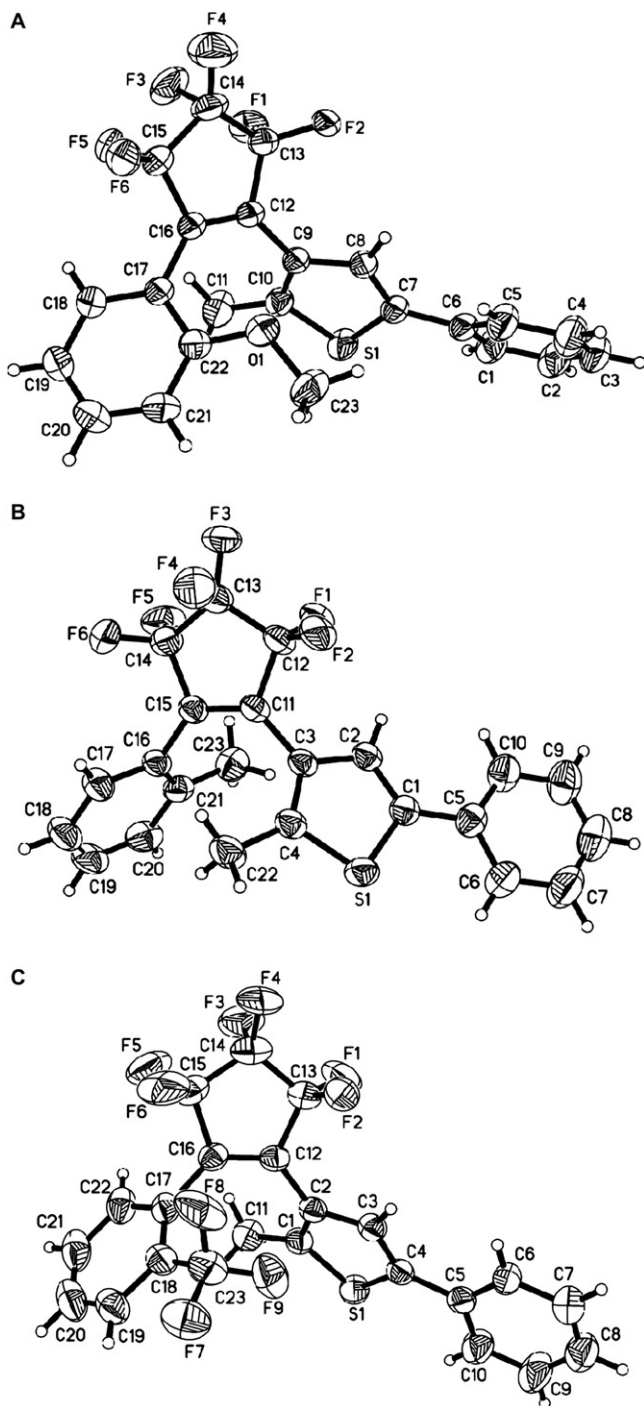


Figure 4. ORTEP drawings of crystals **1a**, **2a**, and **4a** showing 35% probability displacement ellipsoids: (A) **1a**, (B) **2a**, and (C) **4a**.

475, and 436 nm when excited at 285 nm; while those of them were observed at 435, 417, 471, and 445 nm when excited at 295 nm in PMMA film. By using anthracene (0.27 in acetonitrile) as the reference, the fluorescence quantum yields of **1a**, **2a**, **3a**, and **4a** were determined to be 0.047, 0.021, 0.010, and 0.041, respectively. Thus, it is clear that the introduction of methoxyl group at 2-position of benzene ring of diarylethene system can significantly enhance the fluorescence quantum yield. Compared to those in hexane, the emission peaks of diarylethenes **1a**, **2a**, and **4a** showed a remarkable bathochromic shift in PMMA film, which is well consistent with those of their maxima absorption wavelengths. Compared to that in hexane, the emission peak of **3a** is almost

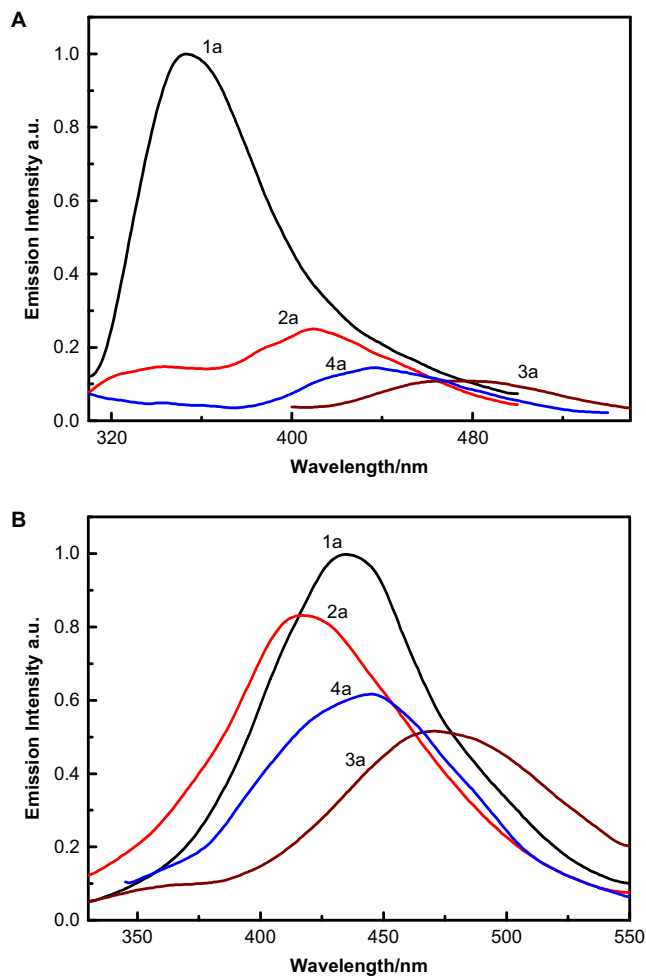


Figure 5. Fluorescence emission spectra of diarylethenes **1–4** both in hexane solution (2.0×10^{-5} mol/L) and in PMMA film (10% w/w) at room temperature; (A) emission spectra in hexane, excited at 285 nm; (B) emission spectra in PMMA film, excited at 295 nm.

constant in PMMA film. Among compounds **1a**, **2a**, **3a**, and **4a**, the emission intensity of **1a** is the strongest and that of **3a** is the weakest both in hexane solution and in PMMA film. The result suggests that different substituents attached at the 2-position of the benzene ring has a significant effect not only on the emission peak but also on the emission intensity.

Generally, the open-ring isomers of diarylethenes have been known to exhibit fluorescence, while the fluorescence of the closed-ring isomers of diarylethenes is inactive.²⁵ As has been observed for most of the reported diarylethenes,²⁶ diarylethenes **1–4** exhibited fluorescent switches during the process of photoisomerization both in solution and in PMMA film. When irradiated by UV light, the photocyclization reaction occurred and the emission intensity of diarylethenes **1–4** decreased gradually, because of forming the non-fluorescence closed-ring isomers. The back irradiation by visible light with an appropriate wavelength regenerated their open-ring isomers and the original emission intensity. In hexane, the emission intensity of diarylethenes **1–4** was decreased upon irradiation with 297 nm light, and it was quenched to ca. 90% for **1**, 47% for **2**, 65% for **3**, and 29% for **4**, respectively, when arrived at a photostationary state. The existence of parallel conformations and weakly fluorescent anti-parallel conformations of diarylethenes **1a**, **2a**, and **3a** in hexane may be the main cause for the lower fluorescent change induced by photoirradiation.^{18a,b} Similarly, upon irradiation with 313 nm light, the emission

intensity of diarylethenes **1–4** was also decreased remarkably in PMMA film. When arrived at its photostationary state, the emission intensity of diarylethenes **1–4** was quenched to ca. 15%, 28%, 58%, and 22%, respectively. The result showed that the fluorescent switchable efficiencies of diarylethenes **1–4** in PMMA film were much bigger than those in solution. For example, the fluorescent switchable efficiency of diarylethene **1** in PMMA film was enhanced about 75% more than that in hexane solution, and those of other three compounds increased remarkably in PMMA film. Among these compounds, diarylethene **4** showed a big fluorescent switchable efficiency both in solution and in PMMA film, suggesting that it is the most promising candidate for application on photoswitchable devices, such as optical memory and fluorescent modulation switches.²⁷

3. Conclusion

In conclusion, we have succeeded in preparing four new photochromic diarylethenes based on a six-membered aryl ring skeleton and investigated their spectral properties both in solution and in solid media. This new photochromic system showed good photochromism, strong fatigue resistance, and remarkable fluorescent switch in PMMA film. The result indicated that the substituents at 2-position of the benzene ring had a significant effect on the properties of these diarylethene derivatives. The six-membered aryl moiety induced some new dramatic properties differing from other diarylethenes with five-membered aryl moieties reported so far. The results provide a useful design strategy for the tuning of photochromic properties for further potential applications.

4. Experimental

4.1. General methods

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 and mass spectra were measured with Agilent MS Trap VL spectrometer. The elemental analysis was measured with PE CHN 2400. The absorption spectra were measured using Agilent 8453 UV/VIS spectrometer. Photoirradiation was carried out using SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and BMH-250 Visible lamp. Light of appropriate wavelengths was isolated by different light filters. 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 (290 \pm 2 K). The fluorescent property was measured using a Hitachi F-4500 spectrophotometer, and the breadths of excitation and emission slit were selected both 10 nm.

THF was distilled over lithium aluminum hydride under argon. All other solvents were used as received. 2-Methyl-5-phenyl-3-thienyl-perfluorocyclopentene (MPTF) was synthesized according to Refs. 11 and 12. The other reagents were purchased from Shanghai Reagents Ltd.

4.2. Synthesis of diarylethenes **1a–4a**

The synthetic route for diarylethenes **1a–4a** is shown in Scheme 2.

4.2.1. Synthesis of **1a**

To a stirred THF solution (30 mL) of 2-bromoanisole (0.94 g, 5.0 mmol) was slowly added a 2.5 M *n*-BuLi/hexane solution (2.0 mL, 5.0 mmol) at -78°C under an argon atmosphere. After 30 min, MPTF (1.83 g, 5.0 mmol) was added and the mixture was stirred for 2 h at this temperature. The reaction mixture was extracted with diethyl ether, dried with anhydrous MgSO₄, filtered,

and evaporated in vacuo, then purified by column chromatography (petroleum ether/ethyl acetate mixture, *v/v*=5:1) to give **1a** (1.2 g) in 53% yield. The compound was recrystallized from diethyl ether at room temperature and produced the crystals suitable for X-ray analysis. Mp 98.3–98.7 $^{\circ}\text{C}$; ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.93 (s, 3H, $-\text{CH}_3$), 3.53 (s, 3H, $-\text{CH}_3$), 6.85, 6.87 (d, 1H, *J*=8.0 Hz, benzene-H), 7.02 (t, 1H, *J*=8.0 Hz, benzene-H), 7.25 (s, 1H, thiophene-H), 7.30 (t, 1H, *J*=8.0 Hz, benzene-H), 7.39 (t, 4H, benzene-H), 7.53, 7.55 (d, 2H, *J*=8.0 Hz, benzene-H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 13.57, 54.72, 110.98, 116.94, 120.31, 122.55, 124.98, 126.17, 127.14, 128.46, 129.45, 131.27, 133.20, 139.24, 140.67, 156.62; IR (KBr, ν , cm⁻¹): 757, 867, 894, 988, 1023, 1128, 1191, 1269, 1339, 1462, 1497, 1600, 2836, 2935. Anal. Calcd for C₂₃H₁₆F₆O₅: C, 60.79, H, 3.55. Found: C, 60.71, H, 3.46. MS *m/z* (M⁺) 455.1. Compound **1b**: ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.18 (s, 3H, $-\text{CH}_3$), 2.75 (s, 3H, $-\text{CH}_3$), 6.76, 6.78 (d, 1H, *J*=8.0 Hz, benzene-H), 7.00–7.08 (m, 3H, benzene-H), 7.14 (s, 1H, thiophene-H), 7.58–7.74 (m, 3H, benzene-H), 8.19, 8.21 (d, 1H, *J*=8.0 Hz, benzene-H), 8.29, 8.31 (d, 1H, *J*=8.0 Hz, benzene-H).

4.2.2. Synthesis of **2a**

Using 2-bromotoluene as the starting material, compound **2a** was prepared by a method similar to that used for **1a** and obtained as white solid in 57% yield. Mp 86.4–86.7 $^{\circ}\text{C}$; ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.99 (s, 3H, $-\text{CH}_3$), 2.02 (s, 3H, $-\text{CH}_3$), 7.19 (t, 2H, *J*=8.0 Hz, benzene-H), 7.28 (s, 1H, thiophene-H), 7.34, 7.36 (d, 2H, *J*=8.0 Hz, benzene-H), 7.38 (t, 3H, *J*=8.0 Hz, benzene-H), 7.49, 7.51 (d, 2H, *J*=8.0 Hz, benzene-H); ¹³C NMR (100 MHz, CDCl₃, ppm): δ 13.69, 18.65, 121.68, 124.35, 124.57, 125.09, 126.65, 126.80, 127.94, 128.05, 128.92, 129.39, 132.39, 135.96, 140.03, 140.87; IR (KBr, ν , cm⁻¹): 748, 827, 861, 895, 988, 1062, 1199, 1278, 1341, 1439, 1500, 1600, 1640, 2917. Anal. Calcd for C₂₃H₁₆F₆S: C, 63.01, H, 3.68. Found: C, 63.05, H, 3.59. MS *m/z* (M⁺) 439.3. Compound **2b**: ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.93 (s, 3H, $-\text{CH}_3$), 2.14 (s, 3H, $-\text{CH}_3$), 5.92–5.95 (m, 2H, benzene-H), 5.99 (t, 1H, *J*=8.0 Hz, benzene-H), 6.39, 6.41 (d, 1H, *J*=8.0 Hz, benzene-H), 7.12 (s, 1H, thiophene-H), 7.32 (t, 1H, *J*=7.2 Hz, benzene-H), 7.44 (t, 2H, *J*=7.2 Hz, benzene-H), 7.56–7.58 (m, 2H, benzene-H).

4.2.3. Synthesis of **3a**

Using 2-bromobenzonitrile as the starting material, compound **3a** was prepared by a method similar to that used for **1a** and obtained as yellowish oil liquid in 20% yield. ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.06 (s, 3H, $-\text{CH}_3$), 7.18 (s, 1H, thiophene-H), 7.29 (s, 1H, benzene-H), 7.35 (t, 2H, *J*=8.0 Hz, benzene-H), 7.46, 7.48 (d, 2H, *J*=8.0 Hz, benzene-H), 7.55 (t, 1H, *J*=8.0 Hz, benzene-H), 7.62, 7.64 (d, 1H, *J*=8.0 Hz, benzene-H), 7.64–7.74 (m, 2H, benzene-H); ¹³C NMR (100 MHz, CDCl₃, TMS): δ 14.51, 116.21, 125.73, 127.86, 128.91, 129.75, 130.41, 131.75, 132.91, 133.30, 133.88, 141.24, 142.18; IR (ν , KBr, cm⁻¹): 758, 863, 894, 991, 1065, 1137, 1197, 1270, 1340, 1384, 1445, 1470, 1600, 1637, 2230, 2860, 2926, 3073. Anal. Calcd for C₂₃H₁₃F₆N₅: C, 61.47, H, 2.92, N, 3.12. Found: C, 61.35, H, 2.89, N, 3.07. MS *m/z* (M⁺) 450.1. Compound **3b**: ¹H NMR (400 MHz, CDCl₃, ppm): δ 1.93 (s, 3H, $-\text{CH}_3$), 6.40, 6.42 (d, 1H, *J*=8.0 Hz, benzene-H), 6.86, 6.88 (d, 1H, *J*=8.0 Hz, benzene-H), 7.10–7.14 (m, 2H, benzene-H), 7.15 (s, 1H, thiophene-H), 7.62, 7.64 (d, 1H, *J*=8.0 Hz, benzene-H), 8.26, 8.28 (d, 1H, *J*=8.0 Hz, benzene-H), 7.73–7.90 (m, 2H, benzene-H), 8.58, 8.60 (d, 1H, *J*=8.0 Hz, benzene-H).

4.2.4. Synthesis of **4a**

Using 2-bromobenzotrifluoride as the starting material, compound **4a** was prepared by a method similar to that used for **1a** and obtained as white solid in 28% yield. Mp 92.7–93.5 $^{\circ}\text{C}$; ¹H NMR (400 MHz, CDCl₃, ppm): δ 2.19 (s, 3H, $-\text{CH}_3$), 6.98 (s, 1H, thiophene-H), 7.24 (t, 1H, *J*=8.0 Hz, benzene-H), 7.32 (t, 2H, benzene-H), 7.40–7.45 (m, 3H, benzene-H), 7.54 (t, 1H, *J*=8.0 Hz, benzene-H), 7.62 (t, 1H, *J*=8.0 Hz, benzene-H), 7.67, 7.69 (d, 1H, *J*=8.0 Hz, benzene-H);

^{13}C NMR (100 MHz, CDCl_3): δ =14.70, 121.92, 123.85, 124.64, 125.55, 125.70, 127.60, 127.80, 128.95, 129.66, 129.98, 130.33, 131.03, 131.78, 133.35, 140.76, 141.60; IR (ν , KBr, cm^{-1}): 752, 859, 989, 1067, 1126, 1266, 1316, 1445, 1581, 1654, 1985, 2859, 2923. Anal. Calcd for $\text{C}_{23}\text{H}_{13}\text{F}_9\text{S}$: C, 56.10, H, 2.66. Found: C, 56.15, H, 2.73. MS m/z (M^+) 493.1. Compound **4b**: ^1H NMR (400 MHz, CDCl_3 , ppm): δ 1.96 (s, 3H, $-\text{CH}_3$), 5.66, 5.68 (d, 1H, $J=8.0$ Hz, benzene-H), 5.95 (t, 1H, $J=8.0$ Hz, benzene-H), 6.21–6.23 (m, 2H, benzene-H), 6.96 (s, 1H, thiophene-H), 7.31 (t, 1H, $J=8.0$ Hz, benzene-H), 7.40–7.45 (m, 2H, benzene-H), 7.57–7.63 (m, 2H, benzene-H).

Acknowledgements

This work was supported by the Project of National Natural Science Foundation of China (20564001), the Key Scientific Project from Education Ministry of China (208069), the Project of Jiangxi Youth Scientist, and the Science Funds of the Education Office of Jiangxi, China (GJJ08365).

References and notes

- (a) Irie, M. *Chem. Rev.* **2000**, *100*, 1685–1716; (b) Tian, H.; Yang, S. J. *Chem. Soc. Rev.* **2004**, *33*, 85–97.
- Higashiguchi, K.; Matsuda, K.; Tanifuji, N.; Irie, M. *J. Am. Chem. Soc.* **2005**, *127*, 8922–8923; (b) Frigoli, M.; Welch, C.; Mehl, G. H. *J. Am. Chem. Soc.* **2004**, *126*, 15382–15383; (c) Moriyama, Y.; Matsuda, K.; Tanifuji, N.; Irie, S.; Irie, M. *Org. Lett.* **2005**, *7*, 3315–3318; (d) Tanifuji, N.; Matsuda, K.; Irie, M. *Org. Lett.* **2005**, *7*, 3777–3780; (e) Zhou, Z. G.; Xiao, S. Z.; Xu, J.; Liu, Z. Q.; Shi, M.; Li, F. Y.; Yi, T.; Huang, C. H. *Org. Lett.* **2006**, *8*, 3911–3914; (f) Jeong, Y. C.; Yang, S. I.; Kim, E.; Ahn, K. H. *Tetrahedron* **2006**, *62*, 5855–5861; (g) Kim, E.; Kim, M.; Kim, K. *Tetrahedron* **2006**, *62*, 6814–6821.
- Deng, X. D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **2001**, *123*, 7703–7704.
- (a) Uchida, K.; Ishikawa, T.; Takeshita, M.; Irie, M. *Tetrahedron* **1998**, *54*, 6627–6638; (b) Takami, S.; Irie, M. *Tetrahedron* **2004**, *60*, 6155–6161.
- Yagi, K.; Soong, C. F.; Irie, M. *J. Org. Chem.* **2001**, *66*, 5419–5423.
- Yamaguchi, T.; Irie, M. *J. Org. Chem.* **2005**, *70*, 10323–10328.
- (a) Pu, S. Z.; Liu, G.; Shen, L.; Xu, J. K. *Org. Lett.* **2007**, *9*, 2139–2142; (b) Uchida, K.; Matsuoka, T.; Sayo, K.; Iwamoto, M.; Hayashi, S.; Irie, M. *Chem. Lett.* **1999**, 835–836; (c) Favaro, G.; Mazzucato, U.; Ortica, F.; Smimmo, P. *Inorg. Chim. Acta* **2007**, *360*, 995–999.
- Pu, S. Z.; Yang, T. S.; Xu, J. K.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 6473–6477.
- Kawai, T.; Iseda, T.; Irie, M. *Chem. Commun.* **2004**, 72–73.
- Yamaguchi, T.; Fujita, Y.; Irie, M. *Chem. Commun.* **2004**, 1010–1011.
- Peters, A.; Vitols, C.; McDonald, R.; Branda, N. R. *Org. Lett.* **2003**, *5*, 1183–1186.
- (a) Takeshita, M.; Ogawa, M.; Keisuke, M.; Yamato, T. *J. Phys. Org. Chem.* **2003**, *16*, 148–151; (b) Uchida, K.; Nakamura, S.; Irie, M. *Res. Chem. Intermed.* **1995**, *21*, 861–876; (c) Liu, X. D.; Tong, Q. X.; Shi, M.; Zhang, F. S. *Sci. China, Ser. B* **2006**, *49*, 517–521.
- Pu, S. Z.; Liu, G.; Chen, B.; Wang, R. J. *Acta Crystallogr.* **2005**, *C61*, o599–o601.
- Li, Z. X.; Liao, L. Y.; Sun, W.; Xu, C. H.; Zhang, C.; Fang, C. J.; Yan, C. H. *J. Phys. Chem. C* **2008**, *112*, 5190–5196.
- (a) Irie, M.; Sakemura, K.; Okinaka, M.; Uchida, K. *J. Org. Chem.* **1995**, *60*, 8305–8309; (b) Uchida, K.; Matsuoka, T.; Kobatake, S.; Yamaguchi, T.; Irie, M. *Tetrahedron* **2001**, *57*, 4559–4565.
- Pu, S. Z.; Zheng, C. H.; Le, Z. G.; Liu, G.; Fan, C. B. *Tetrahedron* **2008**, *64*, 2576–2585.
- (a) Pu, S. Z.; Zhang, F. S.; Xu, J. K.; Shen, L.; Xiao, Q.; Chen, B. *Mater. Lett.* **2006**, *60*, 485–489; (b) Pu, S. Z.; Tang, H. H.; Chen, B.; Xu, J. K.; Huang, W. H. *Mater. Lett.* **2006**, *60*, 3553–3557; (c) Pu, S. Z.; Yang, T. S.; Yao, B. L.; Wang, Y. L.; Lei, M.; Xu, J. K. *Mater. Lett.* **2007**, *61*, 855–859.
- (a) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A: Chem.* **2008**, *194*, 333–343; (b) Fan, C. B.; Pu, S. Z.; Liu, G.; Yang, T. S. *J. Photochem. Photobiol., A: Chem.* **2008**, *197*, 415–425; (c) Pu, S. Z.; Yang, T. S.; Xu, J. K.; Shen, L.; Li, G. Z.; Xiao, Q.; Chen, B. *Tetrahedron* **2005**, *61*, 6623–6629; (d) Tsujioka, T.; Kume, M.; Irie, M. *J. Photochem. Photobiol., A: Chem.* **1997**, *104*, 203–206.
- (a) Kasatani, K.; Kambe, S.; Irie, M. *J. Photochem. Photobiol., A: Chem.* **1999**, *122*, 11–15; (b) Hoshino, M.; Ebisawa, F.; Yoshida, T.; Sukegawa, K. *J. Photochem. Photobiol., A: Chem.* **1997**, *105*, 75–81.
- Tian, H.; Wang, S. *Chem. Commun.* **2007**, 781–792.
- Higashiguchi, K.; Matsuda, K.; Yamada, T.; Kawai, T.; Irie, M. *Chem. Lett.* **2000**, 1358–1359.
- Crystal data for **1a**: $\text{C}_{23}\text{H}_{16}\text{F}_6\text{OS}$; $M=454.42$, monoclinic ($P2_1/n$), $a=7.6537(15)$ Å, $b=21.900(4)$ Å, $c=12.403(2)$ Å, $\alpha=90^\circ$, $\beta=90.574(4)^\circ$, $\gamma=90^\circ$, $V=2079.0(7)$ Å³, $Z=4$, $\mu=0.221$ mm⁻¹, $R1[I>2\sigma(I)]=0.0473$, $wR2[I>2\sigma(I)]=0.1084$, $R1$ (all data)=0.0910, $wR2$ (all data)=0.1336, GOF=1.028. The CCDC number of **1a** is 615079. Crystal data for **2a**: $\text{C}_{23}\text{H}_{16}\text{F}_6\text{S}$; $M=438.42$, triclinic ($P-1$), $a=8.8308(12)$ Å, $b=10.3593(14)$ Å, $c=11.6965(16)$ Å, $\alpha=85.022(2)^\circ$, $\beta=77.405(2)^\circ$, $\gamma=76.548(2)^\circ$, $V=1014.9(2)$ Å³, $Z=2$, $\mu=0.220$ mm⁻¹, $R1[I>2\sigma(I)]=0.0787$, $wR2[I>2\sigma(I)]=0.2158$, $R1$ (all data)=0.0955, $wR2$ (all data)=0.2321, GOF=1.095. The CCDC number of **2a** is 654197. Crystal data for **4a**: $\text{C}_{23}\text{H}_{13}\text{F}_9\text{S}$; $M=492.39$, monoclinic ($P2_1/c$), $a=7.9158(9)$ Å, $b=16.6999(19)$ Å, $c=16.1145(18)$ Å, $\alpha=90^\circ$, $\beta=91.6250(10)(2)^\circ$, $\gamma=90^\circ$, $V=2129.4(4)$ Å³, $Z=4$, $\mu=0.238$ mm⁻¹, $R1[I>2\sigma(I)]=0.0578$, $wR2[I>2\sigma(I)]=0.1465$, $R1$ (all data)=0.1027, $wR2$ (all data)=0.1786, GOF=1.019. The CCDC number of **4a** is 676248.
- Irie, M.; Miyatake, O.; Uchida, K. *J. Am. Chem. Soc.* **1992**, *114*, 8715–8716.
- (a) Kobatake, S.; Uchida, K.; Tsuchida, E.; Irie, M. *Chem. Commun.* **2002**, 2804–2805; (b) Morimoto, M.; Irie, M. *Chem.—Eur. J.* **2006**, *12*, 4275–4282; (c) Masakazu, M.; Irie, M. *Chem. Commun.* **2005**, 3895–3905; (d) Shibata, K.; Muto, K.; Kobatake, S.; Irie, M. *J. Phys. Chem. A* **2002**, *106*, 209–214; (e) Ramamurthy, V.; Venkatesan, K. *Chem. Rev.* **1987**, *87*, 433–481.
- (a) Frigoli, M.; Mehl, G. H. *Chem.—Eur. J.* **2004**, *10*, 5243–5250; (b) Pu, S. Z.; Yang, T. S.; Li, G. Z.; Xu, J. K.; Chen, B. *Tetrahedron Lett.* **2006**, *47*, 3167–3171; (c) Xiao, S. Z.; Yi, T.; Zhou, Y. F.; Zhao, Q.; Li, F. Y.; Huang, C. H. *Tetrahedron* **2006**, *62*, 10072–10078.
- (a) Tian, H.; Chen, B. Z.; Tu, H. Y.; Müllen, K. *Adv. Mater.* **2002**, *14*, 918–923; (b) Kim, H. J.; Jang, J. H.; Choi, H.; Lee, T.; Ko, J.; Yoon, M.; Kim, H.-J. *Inorg. Chem.* **2008**, *47*, 2411–2415; (c) Tomasulo, M.; Giordani, S.; Raymo, F. M. *Adv. Funct. Mater.* **2005**, *15*, 787–794; (d) Fukaminato, T.; Sasaki, T.; Kawai, T.; Tamai, N.; Irie, M. *J. Am. Chem. Soc.* **2004**, *126*, 14843–14849; (e) Irie, M.; Fukaminato, T.; Sasaki, T.; Tamai, N.; Kawai, T. *Nature* **2002**, *420*, 759–760; (f) Giordano, L.; Jovin, T. M.; Irie, M.; Jares-Erijman, E. A. *J. Am. Chem. Soc.* **2002**, *124*, 7481–7489.
- (a) Tian, H.; Feng, Y. L. *J. Mater. Chem.* **2008**, *18*, 1617–1622; (b) Corredor, C. C.; Huang, Z.-L.; Belfield, K. D. *Adv. Mater.* **2006**, *18*, 2910–2914; (c) Frigoli, M.; Mehl, G. H. *Chem. Eur. J.* **2004**, *10*, 5243–5250.