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Photochromism of new unsymmetrical isomeric diarylethenes bearing a methoxyl group

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Three new unsymmetrical isomeric diarylethenes having a methoxyl substituent at *ortho-*, *meta-*, and *para-*position of the terminal benzene ring, namely 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-methoxylphenyl)-3-thienyl]perfluorocyclopentene (**1o**), 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-methoxylphenyl)-3-thienyl]perfluorocyclopentene (**2o**), and 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]perfluorocyclopentene (**3o**), have been synthesized. The substituent position effect of methoxyl group on their properties, including photochromism and fluorescence both in hexane solution and in PMMA film, and their electrochemical properties, were investigated in detail. These diarylethenes showed good photochromism both in solution and in PMMA film. For the same photochromic diarylethene backbone, the electron-donating methoxyl substituent can effectively depress the cyclization quantum yields and increase the cycloreversion quantum yields compared to those of diarylethenes bearing chlorine atoms reported previously. Diarylethenes **1o-3o** showed that the electron-donating methoxyl group at different position on the terminal benzene ring had a significant effect on the electrochemical properties of these isomeric diarylethenes. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: photochromism; diarylethene; methoxyl substituent position effect; property

Introduction

Photochromism is defined as a photoinduced reversible photocoloration in a single chemical species between two forms having different absorption spectra, which is brought about by the action of electromagnetic radiation in one direction at least.^[1] Among various photochromic molecules, diarylethenes with heterocyclic rings have been developed as a new type of thermally stable and fatigue-resistant photochromic compound.^[2–4] Nowadays, these diarylethene derivatives bearing two thiophene/benzothiophene rings are regarded as the best candidates for photonics applications, such as optical memories^[5–8] and photoswitches,^[9,10] because of their excellent thermal stability, remarkable fatigue resistance, and rapid response.^[11–13]

It is well known that the photochromic property of diarylethenes depends on several factors, such as the nature of the heteroaryl moieties, the conformation of the open-ring isomer, electron donor/acceptor substituents, π -conjugation length of the heteroaryl groups, and so forth.^[14] Among these factors, the effect of electron donor/acceptor substituent is the most important one that is useful for the design efficient photoactive diarylethene derivatives with tunable properties. For instance, some reports elucidated that electron-donating substituents attached bis(3-thienyl)ethane diarylethenes could be effective to increase the absorption coefficient of the closed-ring forms and to decrease the cycloreversion guantum yield. But, those attached bis(2-thienyl)ethane diarylethenes could be an effective way to increase the maxima absorption of the open-ring forms and to reduce the cyclization quantum yield.[15-18] Morimitsu et al. suggested that the introduction of the ethynyl groups at 2- and 2'-position of both thiophene and benzothiophene rings would increase the cycloreversion quantum yields.^[19] Morimitsu *et al.* and Takami and Irie reported that bulky alkoxy substituents at 2- and 2'-position of thiophene rings would extraordinarily decrease the cycloreversion quantum yield and the thermal stability of the colored closed-ring isomers at high temperature.^[20,21] In previous publications, we demonstrated that different substituents in different photochromic systems had a significant effect on the properties of diarylethene derivatives, including photochromism, fluorescence and electrochemical features.^[22–24] The majority of these works has been devoted to the development of these photochromic molecules and investigative studies of their fundamental properties, and they have contributed to a broad understanding of the substituent effects on the photochromic characteristics of diarylethene derivatives.

Although there are many reports concerning the substituent effect on the properties of diarylethenes, studies on the substituent position effect are extremely rare. As far as we are aware, there are only a few publications concerning the substituent position effect on the optoelectronic properties of diarylethenes, all reported by our research group.^[25–29] Previously, we mainly focused on the effect of electron-withdrawing groups, such as fluorine atom and chlorine atom, and we found that the fluorine/chlorine atoms and their substituted positions

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Scheme 1. Photochromism of diarylethenes 1-3

had a significant effect on the properties of these diarylethene compounds.^[25-28] The results are very important and interesting, and they also give us some good suggestions and valuable insights. For the methoxyl group, it is a strong electron-donating substituent and has a main role on the photochromic diarylethene system. The introduction of methoxyl groups to the reactive positions renders the cycloreversion reaction quantum yield extraordinarily small.^[20,30] To the best of our knowledge, the electron-donating methoxyl substituent position effect on the properties of photochromic dithienylethene derivatives has not hitherto been reported. We considered that dithienylethene derivatives bearing a methoxyl group at the different position of the terminal benzene ring would have some new distinguishable properties. In this work, in order to better understand the methoxyl substituent position effect on the photochromic properties of diarylethene derivatives, we have synthesized three new unsymmetrical isomeric diarylethene derivatives, namely 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(2-methoxylphenyl)-3- thienyl]perfluorocyclopentene (10), 1-(2,5-dimethyl-3-thienyl)-2-[2-methyl-5-(3-methoxylphenyl)-3-thienyl]perfluorocyclopentene (20), and 1-(2,5-dimethyl-3-thien-yl)-2-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]perfluorocyclopentene (30), which have a methoxyl group at ortho-, meta-, and para-positioin of the terminal phenyl ring. The molecular structures and photochromic schemes of diarylethenes 1-3, which are discussed in this work, are shown in Scheme 1.

RESULTS AND DISCUSSION

Synthesis of diarylethenes

The synthetic route for diarylethenes **10–30** is shown in Scheme 2. At first, three bromobenzene derivatives coupled with thiophene boronic acid (**4**)^[31,32] by Suzuki reaction to give methoxylphenylthiophene derivatives (**5a–5c**). Then, 2,5-dimethyl-3-thienylperfluorocyclpentene (**7**) was prepared according to the same procedure described previously.^[33,34] Finally, compounds **5a–5c** was separately lithiated and then coupled with compound **7** to give diarylethenes **10–30**, respectively. The structures of **10–30** were confirmed by mass spectrometry, elemental analysis, NMR, and IR (Section 'Experimental').

Photochromism of diarylethenes

The photochromic properties of diarylethenes **1–3** were measured at room temperature both in hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and in PMMA medium (10%, w/w). In hexane, the absorption spectral and color changes of diarylethenes **1–3** induced by alternating irradiation with UV and visible light with appropriate wavelength are shown in Fig. 1. As shown in Fig. 1A, the colorless solution containing the open-ring isomer 10 showed a sharp absorption peak at 273 nm ($\varepsilon = 1.98 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1}$) in hexane, which was arisen from $\pi \rightarrow \pi^*$ transition.^[35] Upon irradiation with 297 nm UV light, the colorless solution turned purple and a new visible absorption band centered at 551 nm ($\epsilon\!=\!7.5\times10^3\,L\,mol^{-1}\,cm^{-1})$ emerged while the original peak at 297 nm decreased, indicating the formation of the closed-ring isomer 1c. The conversion from 1o to 1c was 93% in the photostationary state, separated and detected by LC chromatography. Alternatively, the purple colored solution returned to their original colorless upon irradiation with visible light $(\lambda > 450 \text{ nm})$, indicating that **1c** returned to the initial state **1o**. Similarly, compounds 20 and 30 also showed good photochromism in hexane, and their absorption spectral changes are shown in Fig. 1B and C. Upon irradiation with 297 nm UV light, absorption bands in the visible region appeared and the solutions of 20 and 30 turned purple as a result of the cyclization reaction to produce 2c and 3c, which the absorption maxima of them were observed at 539 and 543 nm, respectively. The color changes of diarylethenes 1-3 by photoirradiation in hexane are shown in Fig. 1D. Both the solutions of 2c and 3c can be decolorized upon irradiation with visible light $(\lambda > 450 \text{ nm})$ attributable to reproduce the open-ring isomers **20** and 30. The coloration-decoloration cycles can be repeated more than 100 times and no observable degradation can be observed. In the photostationary state, the conversion from the open-ring isomer to the closed-ring isomer was 91% for 2 and 85% for 3, respectively.

The photochromic properties of diarylethenes 1-3 in hexane are summarized in Table 1. It could be seen from these data that the methoxyl substituent position had a significant effect on the photochromic properties (including absorption maxima, molar absorption coefficients, and quantum yields) of diarylethenes 1-3. Among diarylethenes 1-3, the absorption maximum of the open-ring isomer of the *para*-substituted derivative (compound **3**) $(\lambda_{30,max} = 293 \text{ nm})$ is the biggest and its molar absorption coefficient ($\varepsilon_{30} = 1.87 \times 10^4 \,\text{Lmol}^{-1} \,\text{cm}^{-1}$) is the smallest, while the absorption maximum of the open-ring isomer of the ortho-substituted derivative (compound 1) ($\lambda_{1o,max} = 273 \text{ nm}$) is the smallest and the molar absorption coefficient of the *meta*-substituted derivatives (compound 2) ($\varepsilon_{20} = 2.15 \times$ 10^4 L mol⁻¹ cm⁻¹) is the biggest. The result indicated that absorption maxima of the open-ring isomers 1o-3o had a red shift trend along with the methoxyl group substituting hydrogen atom of the benzene ring from at ortho- to at para-position, but their molar absorption coefficients changed irregularly. For the closed-ring isomers 1c-3c, both the absorption maximum and the molar absorption coefficient of diarylethene 1 $(\lambda_{1c,max} = 551 \text{ nm}, \varepsilon_{1c} = 7.50 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1})$ are the biggest, and those of diarylethene **2** ($\lambda_{2c,max} = 539 \, nm$, $\epsilon_{2c} = 5.85 \, \times$ 10^{3} L mol⁻¹ cm⁻¹) are the smallest. As shown in Table 1, all the cyclization quantum yields diarylethenes 1-3 are greatly higher than their respective cycloreversion quantum yields. This is differing from unsymmetrical diarylethenes bearing a pyrazole unit whose cyclization quantum yields are lower than their respective cycloreversion quantum yields.^[29,31] Among diarylethenes 1-3, the cyclization quantum yield of diarylethene 1 $(\Phi_{o-c} = 0.45)$ is the biggest and that of diarylethene 2 $(\Phi_{o-c}=0.33)$ is the smallest, while the cycloreversion quantum yield of diarylethene **2** ($\Phi_{c-o} = 0.041$) is the biggest and that of diarylethene **3** ($\Phi_{c-0} = 0.015$) is the smallest. The cycloreversion quantum yield of diarylethene 1 ($\Phi_{c-o} = 0.015$) is almost equal to that of diarylethene 3. That is to say, diarylethene 1 has a large



Figure 1. Absorption spectral and color changes of diarylethenes 1–3 upon alternating irradiation with UV and vis light in hexane $(2.0 \times 10^{-5} \text{ mol } L^{-1})$ at room temperature: (A) spectral changes for 1; (B) spectral changes for 2; (C) spectral changes for 3; (D) color changes for 1-3.

cyclization quantum yield and a small cycloreversion quantum yield, indicating that it is convenient to achieve high conversion to the closed-ring isomer at the photostationary state, ^[36] which is well in agreement with the experimental result. The result is remarkably distinguished from those of diarylethenes having a chlorine atom reported in a previous paper.^[28] When replacing the methoxyl group with chlorine atom in the same diarylethene system, the cyclization quantum yields increased and the cycloreversion quantum yields decreased remarkably, and above all, the photochromic behaviors of these compounds were also significantly different.^[28] In addition, compared to the non-methoxyl group derivative (1-(2,5-dimethyl-3-thienyl)-2-(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene, **D4**), the closed-ring isomers' molar absorption coefficients and the

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

Compound	$\lambda_{ m o,max}~(m nm)^{a}(\epsilon/ m L m mol^{-1} m cm^{-1})$		$\lambda_{c,max} \; (nm)^{b} (\varepsilon/L mol^{-1} cm^{-1})$		${\it \Phi}^{\sf c}$	
	Hexane	PMMA film	Hexane	PMMA film	$\Phi_{o ext{-c}}$	$\Phi_{ ext{c-o}}$
1	273 (1.98 $ imes$ 10 ⁴)	d	551 (7.50 $ imes$ 10 ³)	557	0.454	0.017
2	286 (2.15×10^4)	_	539 (5.85 $ imes$ 10 ³)	555	0.334	0.041
3	293 (1.87 $ imes$ 10 ⁴)	—	543 (6.38 $ imes$ 10 ³)	556	0.343	0.015
^a Absorption ma	axima of open-ring isome	ers.				

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

^dNo absorption peak because of being absorbed UV light by glass substrate.

cycloreversion quantum yields of isomeric diarylethenes **1–3** bearing a electron-donating methoxyl group are much bigger than those of compound **D4** ($\varepsilon_{\text{D4,c}} = 3.68 \times 10^3 \text{ Lmol}^{-1} \text{ cm}^{-1}$, $\Phi_{\text{D4,c-o}} = 0.119$).^[28] The possible reason is that electron-donating methoxyl group changes effectively the charge distribution and can be effective to increase the absorption coefficient and to decrease the cycloreversion quantum yield.^[16] Compared to symmetric analogue, 1,2-bis[2-methyl-5-(4-methoxylphenyl)-3-thienyl] perfluorocyclopentene (**D5**),^[37] the cycloreversion quantum yields of these isomeric derivatives increase remarkably, but their cyclization quantum yields and molar absorption coefficients decrease significantly.

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.^[6,23] Dissolved ultrasonically 10 mg diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the films were prepared by spin-coating method. In PMMA film, diarylethenes 1-3 also showed good photochromism (Fig. 2) as similar to those in hexane. The photochromic features of diarylethenes 1-3 are also summarized in Table 1. The distortion of spectra in UV region is ascribed to absorbing UV light of the glass substrate.^[38] The coloration–decoloration cycles could be also repeated more than 100 times, and the result showed that no clear photodegradation for these compounds was detected. As described above, the maximum absorption peaks of the closed-ring isomers of diarylethenes 1-3 in PMMA film are much longer than those in hexane solution. The red shift values of the absorption maxima of the closed-ring isomers are 6 nm for **1c**, 16 nm for **2c** and 13 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.^[39]

Fluorescence of diarylethenes

Fluorescent properties can be useful in molecular scale optoelectronics,^[40] digital fluorescence photoswitches,^[41,42] ion-sensors,^[43-46] and so on. In the present work, the fluorescence properties of diarylethenes 1-3 both in solution and in PMMA film were measured using a Hitachi F-4500 spectrophotometer. The fluorescence emission spectra of diarylethenes **10–30** both in hexane $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and in PMMA film (10%, w/w) at room temperature are shown in Fig. 3. When excited at 300 nm, diarylethenes 1o-3o showed an obvious fluorescent emission bands peaked at 350, 346, and 348 nm, respectively, which were attributed to the $\pi \rightarrow \pi^*$ transfer of the phenyl-thiophene or thienyl-cyclopentene moiety. However, a remarkable bathochromic shift of the fluorescent emission were observed for 1o-3o when doped in PMMA matrix. The maximal emission peaks of **10–30** were measured to be 408, 401, and 399 nm, that shifts to the longer wavelength direction, with 58 nm for 10, 55 nm for 20, and 51 nm for 30, respectively, compared to those in hexane solution. For diarylethenes 1-3, the emission intensity and emission peak are distinguishable different both in hexane and in PMMA film, indicating that the electron-donating the methoxyl group attached at different position on the terminal benzene ring had a significant effect



Figure 2. Absorption spectral and color changes of diarylethenes 1-3 upon alternating irradiation with UV and vis light 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.



Figure 3. Fluorescence emission spectra of diarylethenes **1–3** both in hexane solution $(2.0 \times 10^{-5} \text{ mol L}^{-1})$ and in PMMA film (10%, w/w) at room temperature; (A) emission spectra in hexane, excited at 300 nm; (B) emission spectra in PMMA film, excited at 300 nm. This figure is available in color online at www.interscience.wiley.com/journal/poc

not only on the emission peak but also on the emission intensity.

As has been observed for most of the reported diarylethenes,^[22,47-52] diarylethenes 1-3 exhibited a clear fluorescent switches along with the photochromism from open-ring isomers to closed-ring isomers by photoirradiation both in hexane and in PMMA film. Upon irradiated with UV light, the photocyclization reaction was carried out and the non-fluorescent closed-ring isomers 1c-3c were produced. The back irradiation by appropriate wavelength visible light regenerated the open-ring isomers 10-30 and recovered the original emission spectra. During the process of photoisomerization, the three isomeric compounds exhibited changes in their fluorescence in hexane as shown in Fig. 4. Upon irradiation with 297 nm UV light, the emission intensities of diarylethenes 1o-3o in hexane were clearly decreased by photocyclization. When arrived at the photostationary state, the emission intensities of diarylethenes 1–3 were guenched to ca. 58, 48, and 67%, respectively. The back irradiation with visible light ($\lambda > 450 \text{ nm}$) regenerated the open-ring forms and recovered the original emission spectra. The phenomena are useful for potential application as



Figure 4. Emission intensity changes of diarylethenes **1–3** in hexane $(C = 2.0 \times 10^{-5} \text{ mol L}^{-1})$ upon irradiation with 297 nm UV light at room temperature, excited at 300 nm; (A) **1**; (B) **2**; (C) **3**. This figure is available in color online at www.interscience.wiley.com/journal/poc

fluorescent switches.^[53,54] The fluorescence switch property of diarylethenes 1-3 in PMMA film was similar to that of in hexane solution, and their emission intensity changes in PMMA film during the process of photoisomerization are shown in Fig. 5. Upon irradiation with 313 nm UV light, the emission intensities of diarylethenes 1-3 decreased remarkably along with the



Figure 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**; (C) **3**. This figure is available in color online at www.interscience.wiley.com/journal/poc

photoisomerization from open-ring isomers to closed-ring isomers when excited at 300 nm. When arrived at the photostationary state, the emission intensities of diarylethenes **1–3** were quenched to *ca*. 50, 61, and 49%, respectively. The back irradiation with visible light ($\lambda > 450$ nm) regenerated the open-ring forms and recovered the original emission spectra.

The incomplete cyclization reaction and the existence of parallel conformation of diarylethenes **1o–3o** may be the main cause for the moderate change in fluorescence induced by photoirradiation.^[25–29] In addition, the average times of "on" and "off" state shortened in proportion to the reciprocal power of radiated light by changing the power of the UV and visible light, indicating that the switching effect is indeed photochemical.^[47]

Electrochemistry of diarylethenes

It is well known that the ring opening and closing transformation of some diarylethenes can be initiated not only by UV or visible light irradiation, but also by electrochemical or chemical oxidation, such as electrochromism.^[55,56] Therefore, besides their excellent photochromic performance, the electrochemical behaviors of diarylethenes were also attracted much attention.^[57–60] In present 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^{-1} are shown in Fig. 6. From this figure, it can be easily calculated that the oxidation onsets of the three diarylethenes were initiated at 1.30 and 1.23 V for **10** and **1c**, 1.19 and 1.04 V for **20** and **2c**, and 1.07 and 0.90 V for **30** and **3c**, respectively. The result indicated that the oxidation potential onsets of the open-ring isomers of diarylethenes **1–3** were much higher than those of the corresponding closed-ring isomers. This phenomenon is consonant with the theory that longer conjugation length generally leads to less positive potentials due to the addition of each heterocyclic ring.^[18] After cyclization reaction, the



Figure 6. Cyclic voltammetry (second scan) of diarylethenes **1–3** in acetonitrile at a scan rate of 50 mV s⁻¹; (A) **1**; (B) **2**; (C) **3**. This figure is available in color online at www.interscience.wiley.com/journal/poc

Compound	Oxidation		Reduction		
	E _{onset} (V)	IP (eV)	E _{onset} (V)	EA (eV)	Band gap (Eg
10	+1.30	-6.10	-0.84	-3.96	2.14
1c	+1.23	-6.03	-0.95	-3.85	2.18
2o	+1.19	-5.99	-0.91	-3.89	2.10
2c	+1.04	-5.84	-0.96	-3.84	2.00
30	+1.07	-5.87	-0.91	-3.89	1.98
3c	+0.90	-5.70	-0.99	-3.81	1.89



Scheme 2. Synthetic route for diarylethenes 1o-3o

 π -conjugation lengths of the closed-ring isomers of diarylethenes 1-3 were much longer than those of open-ring isomers, inducing to the lower oxidation potential onset. Furthermore, the oxidation onsets of the open- and closed-ring isomers of diarylethenes 1-3 decreased along with the methoxyl group substituting hydrogen atom of the benzene ring from at ortho- to at para-position, which may be attributed to the different electron-donating ability of the methoxyl group at different substituted-position. From Fig. 6, we can easily see that there are great differences of the electronic current and polarization curve shapes between the open- and closed-ring isomers of diarylethenes 1-3. The values of oxidation waves are 1.40 and 1.35 V for 1o and 1c, 1.36 and 1.47 V for 2o and 2c, and 1.46 and 1.23 V for 3o and 3c, respectively. The result suggested that the methoxyl group and its substituted position have a significant effect on the electrochemical properties of the three isomeric diarylethene derivatives.

According to Eqn (1) and (2), $^{[24,61,62]}$ the energy parameters EA and IP were calculated.

HOMO : IP =
$$-\{[E_{on}]^{ox} + 4.8\}$$
 (1)

LUMO :
$$EA = -\{[E_{on}]^{red} + 4.8\}$$
 (2)

where the units of potentials are volt, and those of IP and EA are electronvolts; 4.8 eV is the constant of the energy level of the ferrocene/ferrocenium (Fe) 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 be estimated. As shown in Fig. 6, the onset potentials (E_{onset}) of oxidation and reduction of **10** were observed at +1.30 and -0.84 V, respectively. So the values of IP and EA were calculated to be -6.10 and -3.96 eV according to Eqn (1) and (2). Based on the HOMO and LUMO energy levels, the band gap (E_{α} , $E_{q} = LUMO-HOMO$) of diarylethene **1o** can be determined as 2.10 eV. Similarly, the E_q of 1c can be calculated as 2.18 eV. Corresponding values for diarylethenes 2 and 3 are summarized in Table 2. Among these diarylethene derivatives, the E_a was the smallest in 3c, implying that the charge transfer must be faster in 3c compared to that in others.^[59] The result showed that band gap E_{α} of the open- and closed-ring isomers of diarylethenes **1**-**3** gradually decreased along with the methoxyl group substituting hydrogen atom of the benzene ring from at ortho- to at para-position. All these data in Table 2 suggested that the methoxyl group and its substituted position have a great effect on the electrochemical characteristics of these isomeric diarvlethenes. It should be noted here that calculation absolute HOMO and LUMO levels from electrochemical data in combination with the energy gap is still in debate.^[62]

Conclusions

Three new isomeric diarylethenes having a methoxyl group were prepared to study substituent position effect on optoelectronic properties. All of these compounds showed good photochromism and fluorescent switches both in solution and in PMMA film. The results suggested that the optoelectronic performances of the three isomeric diarylethenes, including absorption spectra, photochromic reactivity, fluorescent property, and electrochemical feature, were clearly dependent on the effect of substituent position. Compared to diarylethenes bearing chlorine atoms reported previously, diarylethenes with an electron-donating methoxyl group showed some new characteristics and changing trends, which would be helpful for tuning the optoelectronic properties of photochromic diarylethenes for further applications.

EXPERIMENTAL

General

The solvents were purified by distillation before use. Mass spectra were measured with an Agilent MS Trap VL spectrometer. The elemental analysis was measured with a PE CHN 2400 analyzer. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with CDCl₃ as the solvent and tetramethylsilane as an internal standard. IR spectra were recorded on a Bruker Vertex-70 spectrometer. The absorption spectra were measured using an 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 guantum yields were determined by comparing the reaction yields of these dithienylethene compounds in hexane against 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene in hexane (with their respective absorption maxima visible light irradiation).^[63] Fluorescence spectra were measured using a Hitachi F-4500 spectrophotometer. 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. Platinumelectrodes (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 $E_{1/2} = +0.35 \text{ V}$ versus platinum wire. The typical electrolyte was acetonitrile (5 mL) containing 0.1 mol L⁻¹ tetrabutylammonium tetrafluoroborate ((TBA)BF₄) and 4.0×10^{-3} mol L⁻¹ dithienylethene. All solutions were deaerated by a dry argon stream and maintained at a slight argon overpressure during electrochemical experiments.

Synthesis

The synthesis method of three diarylethenes **1o–3o** is shown in Scheme 2 and experimental details were carried out as following.

3-Bromo-2-methyl-5-(2-methoxylphenyl)thiophene (5a)

Compound **5a** was prepared by reacting 3-bromo-2-methyl-5thienylboronic acid **(4)**^[35] (5.0 g; 22.6 mmol) with 1-bromo-2-methoxylbenzene (4.23 g, 22.6 mmol) in the presence of Pd(PPh₃)₄ (0.8g) 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 buff solid in 70.2% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.41 (s, 3H, —CH₃), 3.91 (s, 3H, —CH₃), 6.95–6.99 (m, 2H, phenyl-H), 7.27 (s, 1H, thienyl-H), 7.30 (s, 1H, phenyl-H), 7.54 (d, 1H, J = 8.0 Hz, phenyl-H).

3-Bromo-2-methyl-5-(3-methoxylphenyl)thiophene (5b)

Compound **5b** was prepared by a method similar to that used for **5a** and obtained as buff solid in 75.3% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.41 (s, 3H, —CH₃), 3.83 (s, 3H, —CH₃), 6.83 (d, 1H, J = 8.0 Hz, phenyl-H), 7.03 (s, 1H, thienyl-H), 7.09 (t, 2H, J = 4.0 Hz, phenyl-H), 7.27 (t, 1H, J = 8.0 Hz, phenyl-H).

3-Bromo-2-methyl-5-(4-methoxylphenyl)thiophene (5c)

Compound **5c** was prepared by a method similar to that used for **5a** and obtained as buff solid in 78.3% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.40 (s, 3H, —CH₃), 3.83 (s, 3H, —CH₃), 6.90 (d, 2H, J = 8.8 Hz, phenyl-H), 6.99 (s, 1H, thienyl-H), 7.43 (d, 2H, J = 8.8 Hz, phenyl-H).

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

To a stirred solution of 3-iodo-2,5-dimethylthiophene (6) (18.2 g, 76.5mmol) in THF was added dropwise a 1.6 mol L⁻¹ *n*-BuLi/ hexane solution (50 mL, 80 mmol) at -78 °C under argon atmosphere. Stirring was continued for 30 min at this low temperature. Perfluorocyclopentene (10.3 mL, 76.5 mmol) was added to the reaction mixture at -78 °C, and the mixture was stirred for another 2h at the temperature, then the reaction was warned to the room temperature spontaneously. The reaction was stopped by the addition of methanol (5 mL). The product was extracted with ether. The organic layer was washed with 1 M HCl aqueous solution and water, respectively. The organic layer was dried over MgSO₄, filtrated, and evaporated. The crude product was purified by column chromatography on SiO₂ using hexane as the eluent and 15.3 g of 7 obtained as yellow oil in 65.8% yield. ^{19}F NMR (376 MHz, CDCl₃): δ 108.53 (2F), 117.84 (2F), 128.22 (1F), 129.90 (2F). ¹H NMR (400 MHz, CDCl₃): δ 2.281 (s, 3H, --CH₃), 2.23(s, 3H, --CH₃), 6.54 (s, 1H, thienyl-H).

1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(2-methoxylphenyl)-3-thienyl]perfluorocyclopentene (10)

To a stirred anhydrous THF containing 5a (2.0 g, 7.06 mmol) was added dropwise a 2.5 mol L $^{-1}$ n-BuLi solution (2.8 mL) at $-78\,^\circ\text{C}$ under argon atmosphere. After the mixture has been stirred for 30 min at -78 °C, compound 7 (2.15 g, 7.06 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 using petroleum ether as the eluent to yield 1.52 g (44%) of **1a** as white solid. MS *m/z* (M⁺) 487.09; Calcd for C₂₃H₁₈F₆OS₂ (%): Calcd C, 56.55; H, 3.71. Found C, 57.07; H, 3.81; ¹H NMR (400 MHz, CDCl₃): δ 1.78 (s, 3H, —CH₃), 1.86 (s, 3H, —CH₃), 2.33 (s, 3H, —CH₃), 3.83 (s, 3H, —CH₃), 6.66 (s, 1H, thienyl-H), 6.90 (t, 2H, J = 7.6 Hz, phenyl-H), 7.17 (s, 1H, phenyl-H), 7.35 (s, 1H, thienyl-H), 6.89 (d, 1H, J = 7.6 Hz, 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 (v, KBr, cm⁻¹): 739, 764, 825, 855, 893, 983, 1049, 1115, 1191, 1273, 1336, 1442, 1487, 1630, 2919.

1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(3-methoxylphenyl)-3-thienyl]perfluorocyclopentene (20)

Compound 20 was prepared by a method similar to that used for **1o** and obtained as solid in 48% yield. MS m/z (M⁺) 487.05; Calcd for C₂₃H₁₈F₆OS₂ (%): Calcd C, 56.55; H, 3.71. Found C, 56.99; H, 3.74; ¹H NMR (400 MHz, CDCl₃): δ 1.80 (s, 3H, —CH₃), 1.86 (s, 3H, --CH₃), 2.36 (s, 3H, --CH₃), 3.77 (s, 3H, --CH₃), 6.65 (s, 1H, thienyl-H), 6.77 (d, 2H, J = 7.8 Hz, phenyl-H), 6.97 (s, 1H, thienyl-H), 7.05 (d, 1H, J = 7.6 Hz, phenyl-H), 7.19 (t, 1H, J = 7.6 Hz, phenyl-H); ^{13}C NMR (400 MHz, CDCl_3): δ 14.20, 14.35, 15.02, 55.26, 111.3, 113.3, 118.2, 122.8, 124.7, 126.0, 129.8, 134.7, 137.7, 139.7, 141.2, 141.9, 160.1; IR (v, KBr, cm⁻¹): 745, 776, 823, 836, 892, 977, 1051, 1108, 1189, 1273, 1336, 1445, 1492, 1571, 1594, 2924.

1-(2,5-Dimethyl-3-thienyl)-2-[2-methyl-5-(4-methoxylphenyl)-3-thienyl]perfluorocyclopentene (30)

Compound **30** was prepared by a method similar to that used for **1o** and obtained as solid in 51% yield. MS m/z (M⁺) 487.03; Calcd for C₂₃H₁₈F₆OS₂ (%): Calcd C, 56.55; H, 3.71. Found C, 57.17; H, 3.85; ¹H NMR (400 MHz, CDCl₃): δ 1.80 (s, 3H, —CH₃), 1.83 (s, 3H, --CH₃), 2.34 (s, 3H, --CH₃), 3.75(s, 3H, --CH₃), 6.65 (s, 1H, thienyl-H), 6.83 (d, 2H, J = 7.6 Hz, phenyl-H), 7.05 (s, 1H, thienyl-H), 7.37 (d, 2H, J = 8.0 Hz, phenyl-H); ¹³C NMR (400 MHz, CDCl₃): δ 14.21, 14.27, 15.02, 55.37, 114.3, 121.5, 121.8, 124.6, 124.7, 125.9, 126.3, 127.9, 137.6, 139.7, 140.1, 142.0, 159.5; IR (v, KBr, cm⁻¹): 727, 819, 888, 984, 1049, 1103, 1187, 1265, 1336, 1440, 1489, 1550, 1622, 2922.

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