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Synthesis, crystal structure and photochromism of new diarylethenes with a benzene moiety

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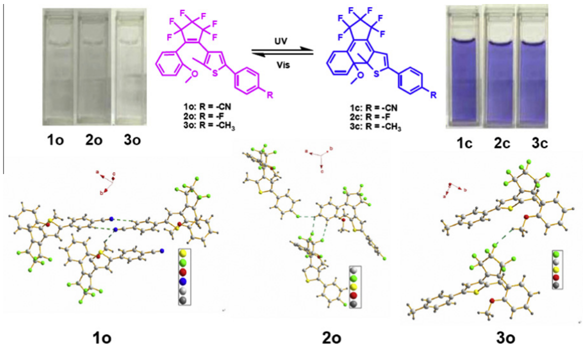
HIGHLIGHTS

- Three new diarylethenes with thiophene and benzene moieties were synthesized.
- Their crystal structures and photochromic features were investigated systematically.
- Computational studies were performed.

GRAPHICAL ABSTRACT



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ABSTRACT

Three unsymmetrical diarylethenes with both thiophene and benzene moieties were synthesized. Their crystal structures and photochromic features were investigated systematically to elucidate the substituent effects of the terminal phenyl group on photochromism. Computational studies were performed to provide further insight into their frontier molecular orbitals and spatial distributions of electronic density. Each compound exhibited favorable photochromism in hexane and functioned as notable fluorescent photo-switches with fluorescence quenching efficiency of ~96% induced by the intensity change of UV/vis light. Among the three diarylethenes, the cyano group on the terminal phenyl group significantly decreased the distance of the two reactive carbon atoms and strengthened the intermolecular hydrogen bond stacking interactions, resulting in improved stability in crystal state. Furthermore, it exhibited a red-shifted absorption maximum, an enhanced molar absorption coefficient, cyclization quantum yield, and fluorescence quantum yield in solution.

Introduction

In the past several decades, various types of photochromic compounds have been synthesized for applications in multifunctional optoelectronic fields [1,2], such as optical switch devices, optical data storage [3–9], fluorescence sensing of specific ions [10–13], photo-switchable probe for imaging living cells [14], organic memory [15], and solar cells [16]. Diarylethene derivatives are the most promising candidates for such applications because of their excellent photochromic characteristics [17]. In addition, the photochromic properties of diarylethene can be predictably improved by structure variation to meet a special functional requirement.

Two structural features strongly influence the photochromic properties of diarylethene, including the heteroaryl moieties and the terminal aryl moieties. There are a number of reports on the effect of the heteroaryl moieties [17,18–22]. For example, diarylethenes bearing thiophene/benzothiophene moieties exhibited

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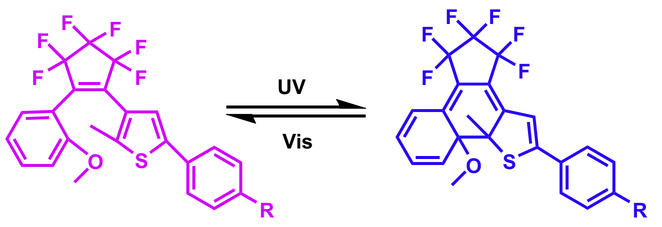
notable thermal stability and remarkable fatigue resistance [23–25], whereas diarylethenes bearing two pyrrole groups were thermally unstable and returned to the open-ring isomers even in the dark [26]. It was found by our group that diarylethenes bearing both thiazole and benzene moieties had poor fatigue resistance with 88% of closed ring isomers destroyed after 10 repeat cycles [27]. This result was in agreement with the explanation that the heteraryl groups of aromatic stabilization energy (ASE) level determined the thermal stability of the closed-ring isomers [17,22]. However, diarylethene with thienyl group, which has low ASE, and the other aromatic heterocyclic moieties also exhibited good photochromic properties [28–34]. For instance, diarylethenes bearing thiophene and isoxazole moieties exhibited remarkable photochromism which functioned as a fluorescent photoswitch in solution. Diarylethenes bearing both thiophene and benzofuran showed good thermal stability as well [31,32]. Another example is diarylethene containing thiophene moiety and six-membered pyridine unit, which exhibited good photochromism both in solution and in the crystalline phase by permitting the pyridine unit to participate in the photoinduced cyclization reaction [33]. In our previous research, it was found that diarylethenes based on thiophene moiety and a hybrid structure of six-membered naphthalene exhibited good photochromism and notable fatigue resistance, which was applied as fluorescent photoswitches in solution [34]. Based on these results, it is postulated that unsymmetrical diarylethenes containing thiophene moiety of low ASE should be able to effectively improve the properties of photochromism.

The effect of the other structural feature, i.e. the electron-donating/withdrawing substituents at the terminal groups in the aryl moieties, has also been studied, including its impact on the diarylethene absorption peaks, cyclization and cycloreversion quantum yields, and the fluorescence emission peaks [35,36]. Jeong et al. reported that the introduction of acetyl groups at the 6,6′-positions and heptyl groups at the 2,2′-positions in disulfonyl diarylethene gave rise to an increase in the fluorescence quantum yield and fluorescence lifetime [37]. In the study of a series of diarylethenes containing different electron-donating/withdrawing groups, it was found that the electron-donating groups significantly increased the cyclization quantum yield, depressed the cycloreversion quantum yield, red-shifted the emission peak, and decreased the fluorescence quantum yield in solution; while the electron-withdrawing groups functioned as an inverse action for these diarylethene derivatives [28–32].

So far, there have been a few examples of photochromic diarylethenes bearing thiophene moieties and aryl moieties [38]. To the best of our knowledge, for these diarylethenes bearing thiophene moieties and aryl moieties, the effects of the electro-donating or electro-withdrawing groups on their photochromism and crystal packing properties have not been reported.

Herein, we have designed and synthesized a new class of photochromic diarylethene derivatives, with different groups at the terminal of diarylethenes and a benzene ring as an aryl moiety, i.e., {1-[2-methyl-5-(4-cyanophenyl)-3-thienyl]-2-(2-methoxylphenyl)}perfluorocyclopentene (**1o**), {1-[2-methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-methoxylphenyl)}perfluorocyclopentene (**2o**), and {1-[2-methyl-5-(4-methylphenyl)-3-thienyl]-2-(2-methoxylphenyl)}perfluorocyclopentene (**3o**), all of which showed good reversible photochromism in hexane solution. The scheme showing the photochromism of **1**–**3** is presented in Scheme 1.



1o:R=-CN
2o:R=-F
3o:R=-CH$_3$

1c:R=-CN
2c:R=-F
3c:R=-CH$_3$

Scheme 1. Photochromism of diarylethenes **1–3**.

Results and discussions

Photochromism in solution

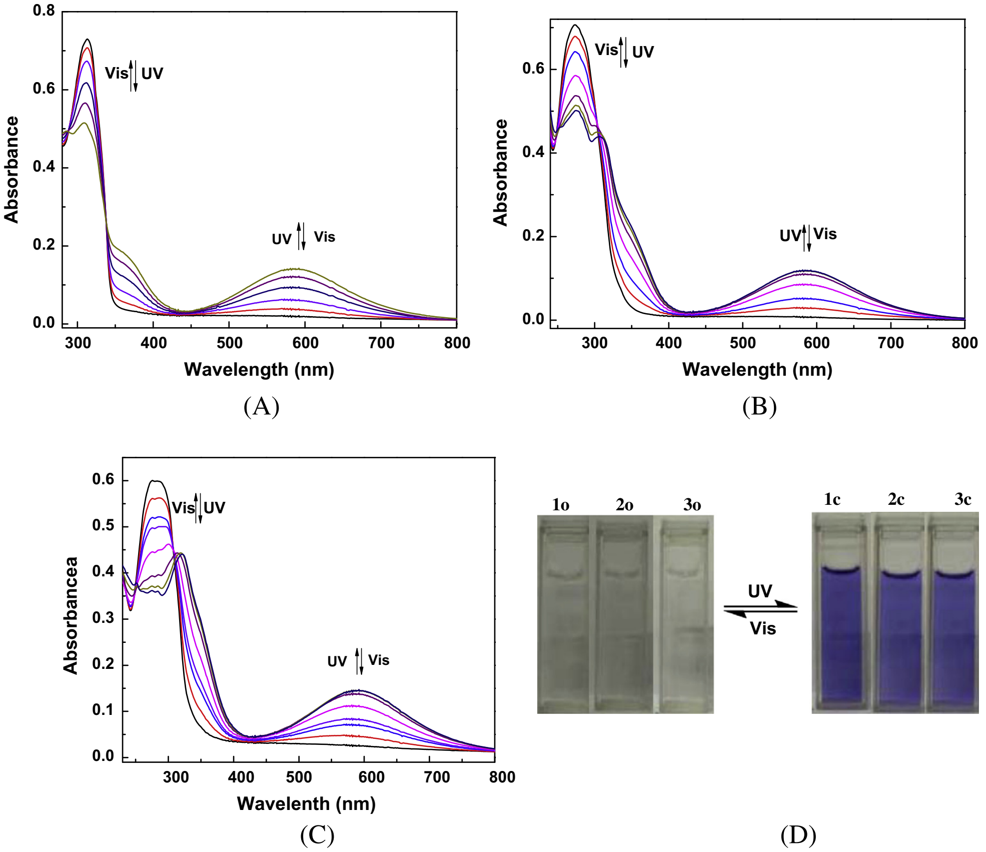
The photochromic behaviors of diarylethenes **1**–**3** were examined in solution ($c = 3.0 \times 10^{-5}$ mol/L) at room temperature. The changes in the absorption spectra of **1**–**3** induced by alternating irradiation with UV and visible light in hexane are shown in Fig. 1.

In hexane, the colorless solution of diarylethene **1o** exhibits a sharp absorption peak at 313 nm corresponding to a $\pi \rightarrow \pi^*$ transition [39]. Upon irradiation with 313 nm light, a new absorption band in the visible region centered at 591 nm emerged with a color change from colorless to blue due to the formation of the closed-ring isomer **1c** for S_0–S_1 transition [40]. Alternatively, the blue solution could bleach to colorless upon irradiation with visible light ($\lambda > 450$ nm), and the absorption spectrum return to the initial state **1o** (Fig. 1A and D). The coloration-decoloration cycles could be repeated many times and a clear isosbestic point was observed at 337 nm. Just like diarylethene **1**, diarylethenes **2** and **3** also show good photochromism in hexane (Fig. 1B and C). Upon irradiation with 297 nm light, absorption bands in the visible region appeared and the solutions of **2o** and **3o** turned blue due to the cyclization reactions leading to the closed-ring isomers **2c** and **3c**, respectively. These compounds had absorption maxima in the visible region at 584 and 589 nm, respectively. The blue solutions of **2c** and **3c** could be decolorized upon irradiation with visible light ($\lambda > 450$ nm), indicating the return to initial state of **2o** and **3o**.

To further investigate the optical properties of **1o**–**3o**, molecular orbital calculations at the B3LYP/6-31G(d) level of density functional theory (DFT) were used [41,42]. Fig. 2 shows the calculated spatial distributions of the HOMO and LUMO levels of diarylethenes **1o**–**3o**. It could be easily seen that the HOMO levels of **1o**–**3o** are π orbitals concentrated on the central thiophene–phenyl moiety. For LUMO levels, **1o** with a strong electron-withdrawing cyano group is not concentrated on the central active part, but **2o** and **3o** are still concentrated on the central active part. The result is well consistent with that of the reported diarylethenes [43].

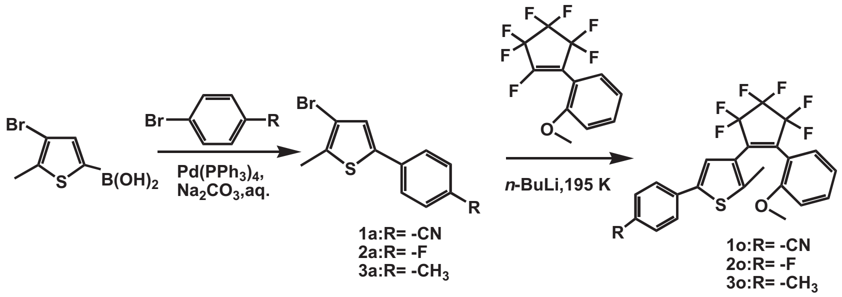
The DFT results indicate that the features of the frontier molecular orbital change significantly with different substituents. The calculated HOMO–LUMO gaps of **1o**–**3o** follow the decending order of **2o** (397.78 kJ/mol) > **1o** (395.35 kJ/mol) > **3o** (390.83 kJ/mol), indicating that the HOMO–LUMO gap of **3o** is the smallest among the three diarylethene derivatives. The possible reason is that the electron-withdrawing groups as in compound **1o** and **2o** tend to induce broader energy gaps, thus can stabilize the molecule significantly. On the contrary, the electron-donating groups as in **3o** lower the HOMO–LUMO energy gap resulting in weakened chemical stability.

The absorption spectral parameters of diarylethenes **1**–**3** in hexane solution are summarized in Table 1. The cyclization and cycloreversion quantum yields of **1**–**3** were measured by comparison of them to 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene [44] under identical conditions (Table 1). As shown in Table 1, cyano terminated diarylethene **1** in the open-ring isomer state has the largest maximum absorption wavelength of 313 nm among the three diarylethenes. The molar absorption coefficient of the



(A) (B) (C) (D)

Fig. 1. Absorption spectral and color changes of diarylethenes **1–3** by photoirradiation in hexane solution ($C = 3.0 \times 10^{-5}$ mol L^{-1}) at room temperature: (A) absorption spectral of **1**, (B) absorption spectral of **2**, (C) absorption spectral of **3**, and (D) color changes of **1–3**. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 2. Synthetic route for diarylethenes **1o**–**3o**.

open-ring isomers follows a descending order of **1o** > **2o** > **3o**. For the closed-ring isomers, diarylethene with a strong electron-donating group (**3**) has stronger molar absorption coefficient than diarylethenes with an electron-withdrawing group (**1** and **2**). Cyano terminated diarylethene **1** has the largest cyclization quantum yield ($\Phi_{o-c} = 0.46$). The results show that the electron-withdrawing/donating substituent group has a significant effect on the photochromic features of diarylethenes, including the absorption maxima, molar absorption coefficients, and quantum yields.

Diarylethenes in the single-crystal state

Single crystals of **1o**–**3o** suitable for X-ray crystallographic analysis were obtained by evaporating a hexane solution of the respective compound at room temperature. The X-ray crystallographic analysis data are listed in Table 2. It was found that the crystal system of **1o** or **3o** was triclinic with space group $P-1$, while that of **2o** was monoclinic with space group $P21/n$, which may be attributed to the coordinating effects of the fluorine atom with hexafluorocyclopentene moiety. The ORTEP drawings of the single crystals **1o**–**3o** showing 35% probability displacement ellipsoids are shown in Fig. 3. In Fig. 3A, the molecule of **1o** is a photoactive *anti*-parallel conformation in the crystalline phase, which can be expected to undergo photocyclization reaction [45]. The methyl and methoxyl groups are located on different sides of the perfluorocyclopentene plane and *trans*-direction of the thiophene and benzene ring planes, respectively. The intramolecular distance between the two active carbon atoms (C1—C13) of **1o** is 3.622 Å. The corresponding dihedral angles and the distances between the reactive carbon atoms of **1o**–**3o** are summarized in Table 3.

For the crystal of **1o**, molecules are arranged by the intermolecular C—H···F hydrogen bonds with an average H···F distance of 2.61 Å, and C—H···F angle of 140.85°. Interestingly, weak C—H···N interactions exist between methyl, benzene ring units and N atom,

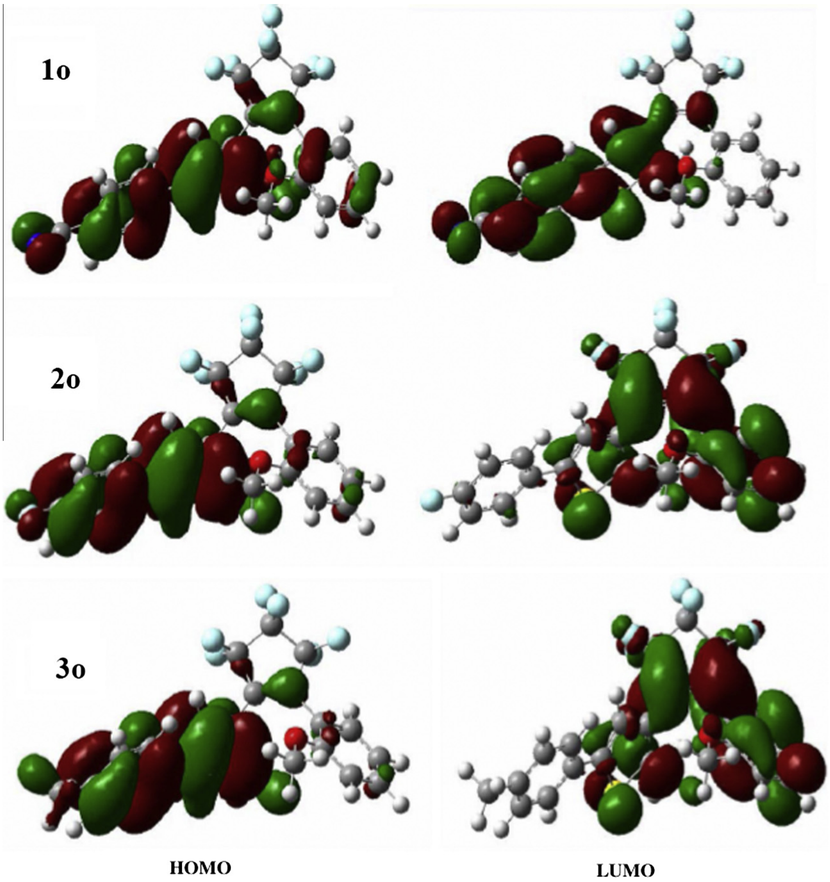


Fig. 2. Calculated spatial distributions of the HOMO and LUMO levels of diarylethenes **1o**–**3o**.

Table 1
Absorption characteristics and photochromic reactivity of diarylethenes **1–3** in hexane at 3.0 × 10^{-5} mol/L.

Compound	$\lambda_{max,\ o}$[a] (nm (ε/dm^3 mol^{-1} cm^{-1}))	$\lambda_{max,\ c}$[b] (nm (ε/dm^3 mol^{-1} cm^{-1}))	Φ[c]	
			Φ_{o-c}	Φ_{c-o}
1	313 nm (2.43 × 10^{-4})	591 nm (3.67 × 10^{-3})	0.46	0.098
2	273 nm (2.36 × 10^{-4})	584 nm (4.00 × 10^{-3})	0.21	0.11
3	276 nm (2.00 × 10^{-4})	589 nm (5.00 × 10^{-3})	0.28	0.069

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.
[c] Quantum yields of cyclization (Φ_{o-c}) and cycloreversion (Φ_{c-o}), respectively.

with an average H(7A)···N1 and H(20)···N1 distances of 2.64 Å and 2.72 Å, respectively (Fig. 4A). The special C—H···N interactions are responsible for the improved stability of diarylethene as shown by the relatively high melt points (417.5–418 K for **1o**, 403.1–403.7 K for **2o** and 395.2–395.5 K for **3o**). The inherent forces of the C—H···N interactions might be electrostatic interactions between the electron-rich N atom and the electron-deficient carbon atom. For the crystals of **2o** and **3o**, the intermolecular hydrogen bonds between C—H and F connected molecular each other (Table 4 and Fig. 4). These molecular interactions together with hydrogen bonding may strengthen the stability of these crystals.

Non-photochromism in the crystalline phase

As mentioned above, for the crystals of **1o–3o**, all the distances of the two reactive carbon atoms are less than 4.2 Å and they packed in photoactive *anti*-parallel conformations in their respective crystalline phase. Therefore, **1o–3o** may be expected to undergo photochromism in the single crystalline phase

Table 2
Crystal data for diarylethenes **1o**–**3o**.

	1o[a]	**2o**[b]	**3o**[c]
Formula	$C_{24}H_{15}F_6NOS$	$C_{23}H_{15}F_7OS$	$C_{24}H_{18}F_6OS$
Formula weight	479.43	472.41	468.44
Temperature	293(2)	291(2)	273(2)
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P* – 1	*P*21/*n*	*P* – 1
Unit cell dimensions			
a (Å)	7.5057(9)	7.8240(7)	9.4505(11)
b (Å)	9.1626(11)	20.8712(17)	10.4163(12)
c (Å)	16.685(2)	12.8403(11)	11.4299(14)
α (°)	82.0360(10)	90.00	87.3230(10)
β (°)	80.9930(10)	90.9330(10)	76.3910(10)
γ (°)	77.9380(10)	90.00	82.005(2)
Volume (Å^3)	1101.6(2)	2096.5(3)	1082.8(2)
Z	2	4	2
Density (calcd.) (g/cm^3)	1.445	1.497	1.437
Reflections collected	8039	15777	7400
Unique reflections	3990	3898	3914
Goodness-of-fit on F^2	1.016	1.059	1.031
Final R indices [I/2σ(I)]			
R_1	0.0377	0.0503	0.0472
wR_2	0.0977	0.1276	0.1166
R indices (all data)			
R_1	0.0453	0.0626	0.0627
wR_2	0.1047	0.1385	0.1289

[a] $w = 1/[\sigma^2\left(F_o^2\right) + (0.0522P)^2 + 0.3308P]$ where $P = \left(F_o^2 + 2F_c^2\right)/3$.
[b] $w = 1/[\sigma^2\left(F_o^2\right) + (0.055P)^2 + 1.3232P]$ where $P = \left(F_o^2 + 2F_c^2\right)/3$.
[c] $w = 1/[\sigma^2\left(F_o^2\right) + (0.0559P)^2 + 0.5061P]$ where $P = \left(F_o^2 + 2F_c^2\right)/3$.

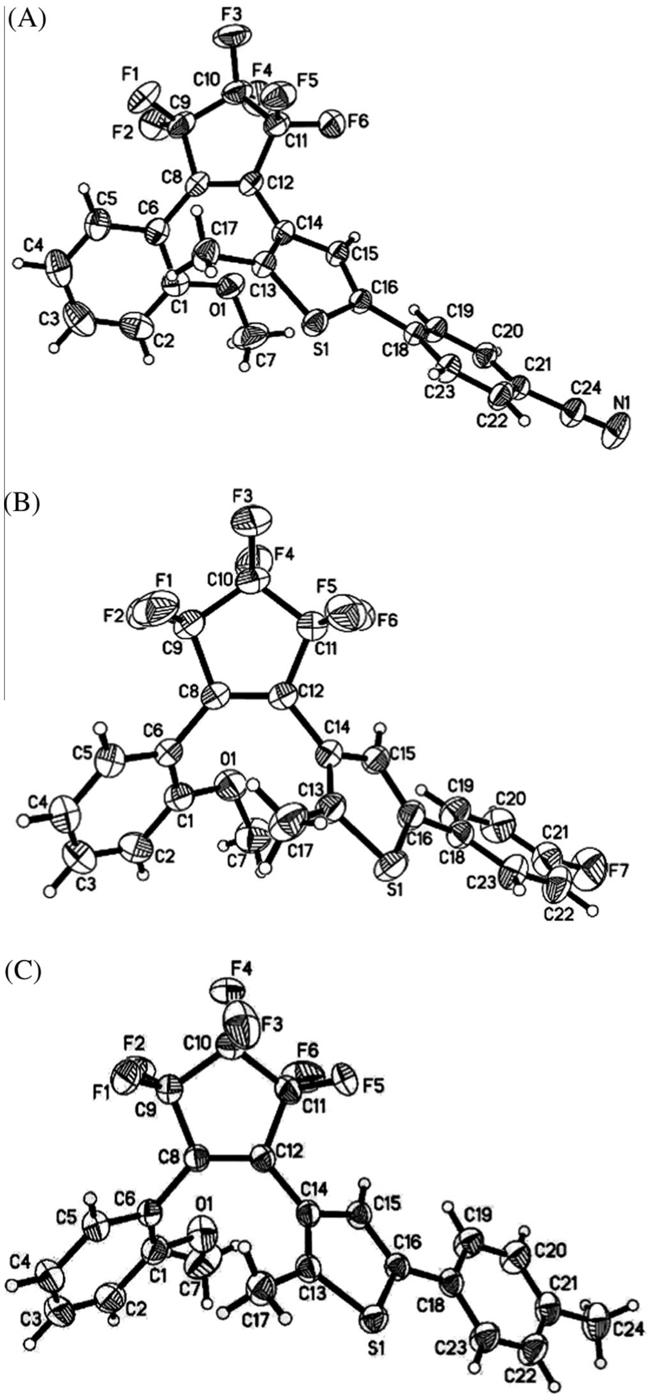


Fig. 3. ORTEP drawings of **1o**–**3o**, showing 35% probability displacement ellipsoids: (A) **1o**, (B) **2o**, and (C) **3o**.

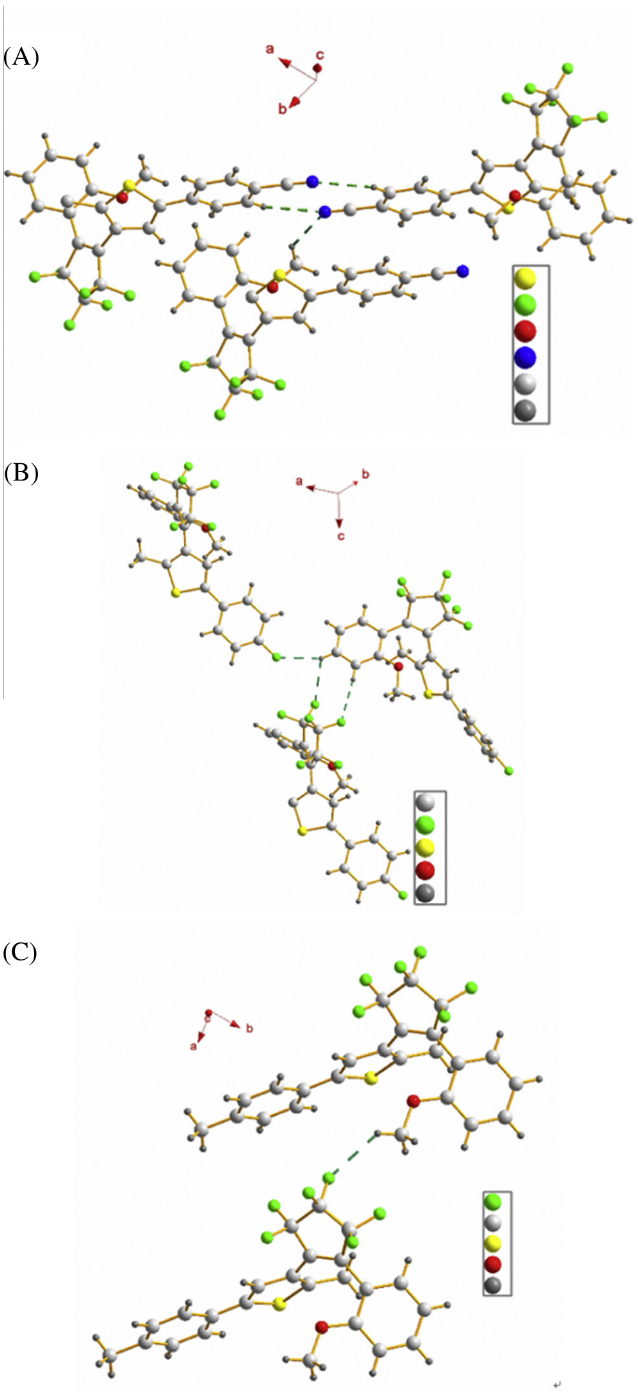


Fig. 4. The crystal packing fragments linked with H bonds: (A) **1o**, (B) **2o**, and (C) **3o**.

Table 3
Distances between the reacting carbon atoms (*d*, Å) and dihedral angles (*θ*, °) of **1o**–**3o**.

Compound	*d* (Å)		*θ* (°)[a]		
			θ_1	θ_2	θ_3
1o	C1···C13	3.622	48.5	57.1	23.5
2o	C1···C13	3.654	126.8	54.5	29.7
3o	C1···C13	3.751	51.3	50.0	2.1

[a] θ_1, dihedral angle between the cyclopentene ring and cyclopentene ring linked up with the benzene ring; θ_2, dihedral angle between the cyclopentene ring and the thiophene ring; θ_3, dihedral angle between the thiophene ring and the adjacent benzene ring.

[46,47]. But, in fact, the color changes of crystals **1o**–**3o** are not visible by the naked eye upon photoirradiation. This non-photochromism behavior may be attributed to the relatively high aromatic energy and the rigidity of the benzene ring in the crystal structure. However, when the crystals of **1o**–**3o** were dissolved in hexane, the solutions turned blue upon irradiation with UV light. The absorption maxima were observed at 591, 584, and 589 nm, respectively, which were the same as those of the closed-ring isomers **1c**–**3c**. The colored solutions were bleached completely and their absorption spectra recovered to those of the open-ring isomers **1o**–**3o** upon irradiation with appropriate wavelength visible light (λ > 450 nm).

Table 4
Hydrogen bond lengths (Å) and bond angles (°) of **1o**–**3o**.

Compounds	D—H···A	D—H	H···A	D···A	D—H···A
1o	C(3)—H(3)···F(3)[a]	0.93	2.61	3.38	140.85
	C(7)—H(7A)···N(1)[b]	0.96	2.64	3.39	135.16
	C(20)—H(20)···N(1)[c]	0.93	2.72	3.57	151.67
2o	C(3)—H(3)···F(7)[d]	0.93	2.58	3.44	153.84
	C(3)—H(3)···F(2)[e]	0.93	2.65	3.20	119.03
	C(2)—H(2)···F(4)[f]	0.93	2.56	3.48	166.78
3o	C(7)—H(7B)···F(3)[g]	0.96	2.57	3.32	134.70

Symmetry operation code.
[a] $-1+x, 1+y, z$.
[b] $2-x, 2-y, -z$.
[c] $3-x, 2-y, -z$.
[d] $1.5+x, 0.5-y, -0.5+z$.
[e] $0.5+x, 0.5-y, 0.5+z$.
[f] $0.5+x, 0.5-y, 0.5+z$.
[g] $1+x, y, z$.

Fluorescence of diarylethenes

The fluorescence emission spectra of the diarylethenes **1**–**3** are measured in hexane (1.0×10^{-3} mol/L) (Fig. 5). In hexane, the emission peaks of **2o** and **3o** were observed at 414 and 417 nm when excited at 346 and 354 nm, respectively. Double peaks at 413 and 434 nm were observed when the hexane solution of **1o** was excited at 360 nm. This may attribute to the strong electron-withdrawing cyano group that affected on the fluorescence emission peak in hexane solution at room temperature. Moreover, **1o** shows the strongest fluorescence emission among the three diarylethenes, which may be attributed to the strong electron-withdrawing nature of the cyano group. In hexane, the fluorescence quantum yields of **1o**–**3o** are 0.053, 0.015, and 0.017, respectively, using anthracene (0.27) as a reference.

Compared to most of the reported diarylethenes [48–50], diarylethenes **1**–**3** in hexane exhibited relatively large fluorescence changes in the photoisomerization process as shown in Fig. 5. When irradiated with 297 nm UV light, the fluorescence of the samples was effectively quenched. Irradiation by visible light of appropriate wavelength regenerated the open-ring isomers **1o**–**3o** and recovered the original emission spectra. Upon irradiation with 297 nm UV light, the emission intensity of **1**–**3** could be quenched to *ca.* 2.2%, 4.2%, and 4.4%, respectively. In addition, the "on" and "off" state of the fluorescence was measured by varying the power of the UV and visible light. The average "on" and "off" times were shortened with increasing power, indicating that the switching effect is indeed photochemical [39]. Therefore, these diarylethene compounds could be potentially applied as optical memory with fluorescence readout or as a fluorescence-modulated switch [51,52]. Furthermore, the electron-withdrawing/donating terminal group can be varied to select specific fluorescence properties for desired applications.

Conclusions

A new class of unsymmetrical photochromic diarylethenes based on a skeleton of thiophene and six-membered benzene were synthesized. These compounds exhibited notable photochromism and functioned as fluorescence-modulated switches. The different electron-donating/withdrawing substituents at the *para*-position of the terminal phenyl group had a significant effect on their photochromic and fluorescence properties. Furthermore, the electron-donating/withdrawing group affected the hydrogen bonding in crystal-packing to strengthen the stability of the framework structure. These results are helpful for the understanding of the substituent effects on the crystal structure and photochromic properties of diarylethenes with thiophene and benzene moieties.

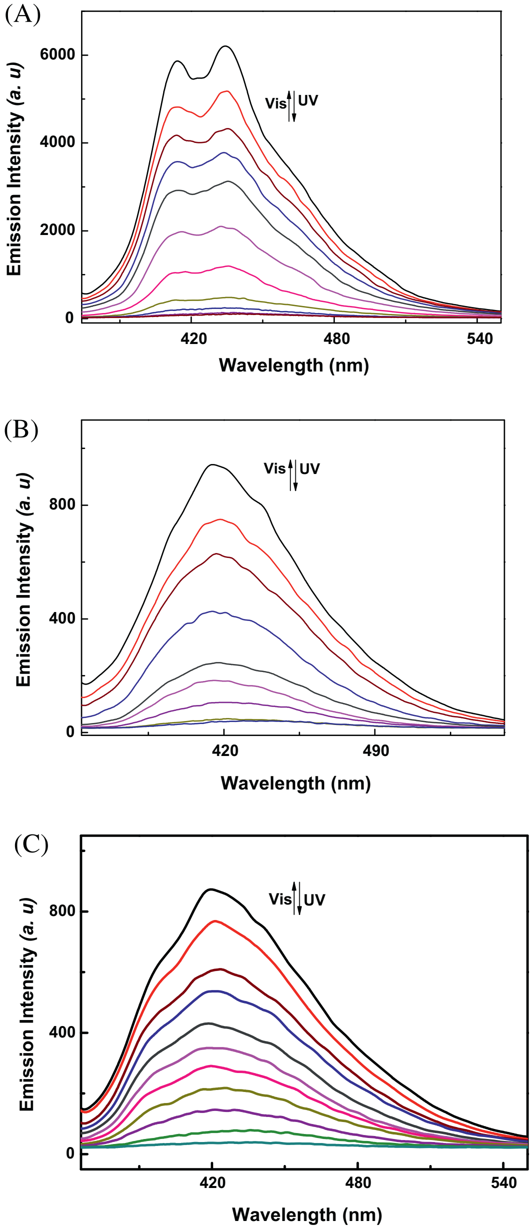


Fig. 5. Emission intensity changes of diarylethene **1**–**3** in hexane ($c = 1.0 \times 10^{-3}$ mol L^{-1}) upon irradiation with 297 nm UV light at room temperature: (A) **1**, (B) **2**, and (C) **3**.

Materials and methods

Experimental section

General: All solvents used were spectrograde and were purified by distillation before use. NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer with $CDCl_3$ as the solvent and tetramethylsilane as an internal standard. IR spectra were performed by a Bruker Vertex-70 spectrometer. Melting point was determined by a WRS-1B melting point determination apparatus. The elemental analyses were measured with a PE CHN 2400 analyzer. The absorption spectra were measured using an Agilent 8453 UV/vis spectrometer. Photo-irradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 Visible lamp. Light of appropriate wavelength 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 [44]. Fluorescent spectra were measured using a Hitachi F-4500 spectrophotometer. Suitable crystals of **1o**–**3o** were obtained by slow evaporation of a hexane solution. All the measurements were made on a Bruker SMART APEX II CCD diffractometer using a MULTI scan technique and Mo Kα radiation. The structures were solved by direct methods and refined by full-matrix least-squares procedures on F^2 by full-matric least-aquares techniques using SHELXTL-97 program. All nonhydrogen atoms were refined anisotropically. Crystallographic data for the structure **1o**–**3o** have been deposited with the Cambridge Crystallographic Data Centre as supplemental publication CCDC 729699, 729600, and 729697, respectively. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 0 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk)].

Synthesis

The synthesis route for diarylethenes 1o–3o is shown in Scheme 2.

*3-Bromo-5-(4-cyanophenyl)-2-methylthiophene (**1a**)*

Compound 3-bromo-5-(4-cyanophenyl)-2-methylthiophene was prepared by reacting 3-bromo-2-methyl-5-thienylboronic acid [53] (2.21 g, 10.00 mmol) with 1-bromo-4-cyanobenzene (1.82 g, 10.00 mmol) in the presence of $Pd(PPh_3)_4$ (0.27 g, 0.23 mmol) and Na_2CO_3 (6.36 g, 60.00 mmol) in tetrahydrofuran (THF) (80.0 mL containing 10% water). After refluxing for 15 h, the product was extracted with ether, dried over $MgSO_4$, filtrated, and evaporated. The crude product was purified by column chromatography on silica gel using hexane as the eluent to yield a white solid 2.32 g, in 83.50% yield. ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.44 (s, 3H, —CH_3), 7. 22 (s, 1H, thiophene-H), 7.58 (d, J = 8.0 Hz, 2H, benzene-H), 7.65 (d, J = 8.0 Hz, 2H, benzene-H).

*3-Bromo-5-(4-methylphenyl)-2-methylthiophene (**3a**)*

3-Bromo-5-(4-methylphenyl)-2-methylthiophene was prepared by the method similar procedure to 3-bromo-5-(4-cyanophenyl)-2-methylthiophene by Suzuki coupling between 3-bromo-2-methyl-5-thienylboronic acid and 1-bromo-4-methylbenzene (1.71 g, 10.00 mmol) (1.82 g yellow solid, yield: 68.20%). ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 2.29 (s, 3H, —CH_3), 2.34 (s, 3H, —CH_3), 6.99 (s, H, thiophene-H), 7.10 (d, J = 8.0 Hz, 2H, benzene-H), 7.33 (d, J = 8.0 Hz, 2H, benzene-H).

*1-[2-Methyl-5-(4-cyanophenyl)-3-thienyl]-2-(2-methoxylphenyl)} perfluorocyclopentene (**1o**)*

Used (2-methoxylpheny)perfluorocyclopentene (1.35 g, 4.50 mmol) [54] and solution of 3-bromo-2-methyl-5-(4-cyanophenyl)thiophene (**1a**) (1.25 g, 4.50 mmol) [55] with *n*-butyl lithium (2.5 M, 1.80 mL, 4.50 mmol), at 195 K under a nitrogen atmosphere. After an hour, the reaction was quenched by the addition of water. The solid product was purified by column chromatography on silica with petroleum ether as the eluent to obtain 0.92 g (1.90 mmol) of solid **1o** in 42.2% yield. Anal. Calcd. for $C_{24}H_{15}F_6NOS$ (%): C, 60.12; H, 3.13; Found C, 61.15; H, 3.15; ^1H NMR (400 MHz, $CDCl_3$, TMS): z 1.94 (s, 3H, —CH_3), 3.51 (s, 3H, —OCH_3), 6.85 (d, J = 8.0 Hz, 1H, benzene-H), 7.01 (t, J = 8.0 Hz, 1H, benzene-H), 7.34 (s, 1H, thiophene-H), 7.36–7.41 (m, 2H, benzene-H), 7.61 (d, J = 8.0 Hz, 2H, benzene-H), 7.66 (d, J = 8.0 Hz, 2H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 13.7, 54.7, 110.3, 111.0, 116.6, 118.2, 120.4, 124.7, 125.1, 126.8, 129.4, 131.5, 132.3, 137.4, 138.3, 141.6, 156.5. IR (ν, KBr, cm^{-1}): 760 (1,2-disubstituted benzene), 819 (1,4-disubstituted benzene), 1269 (C—O), 1602 and 1642 (benzene), 2227 (—C≡N), 2847 (—OCH_3), 2982 (—CH_3). m.p.: 417.5–418.0 K.

*{1-[2-Methyl-5-(4-fluorophenyl)-3-thienyl]-2-(2-methoxylphenyl)} perfluorocyclopentene (**2o**)*

The compound **2o** was synthesized from the reaction of (2-methoxylpheny)perfluorocyclopentene (1.20 g, 4.0 mmol) [54] and 3-bromo-2-methyl-5-(4-fluorophenyl)thiophene (**2a**) (1.08 g, 4.00 mmol) [55] with 2.5 M *n*-butyl lithium (1.60 mL, 4.00 mmol) at 195 K under a nitrogen atmosphere. After an hour, the reaction was quenched by the addition of water. The solid product was purified by column chromatography on silica with petroleum ether as the eluent to give **2o** 0.62 g (1.31 mmol) in 32.8% yield. Anal. Calcd. for $C_{23}H_{15}F_7OS$ (%): C, 58.47; H, 3.20; Found C, 58.45; H, 3.19; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.90 (s, 3H, —CH_3), 3.51 (s, 3H, —OCH_3), 6.84 (d, J = 8.0 Hz, 1H, benzene-H), 6.99 (t, J = 8.0 Hz, 1H, benzene-H), 7.20 (s, 1H, thiophene-H), 7.35 (t, J = 9.4 Hz, 4H, benzene-H), 7.44 (t, J = 8.4 Hz, 2H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.0, 55.2, 111.5, 115.8, 116.1, 117.4, 120.9, 123.0, 126.7, 127.2, 127.2, 130.0, 131.8, 131.8, 139.8, 140.1, 157.1. 161.2, 163.6. IR (ν, KBr, cm^{-1}): 762 (1,2-disubstituted benzene), 822 (1,4-disubstituted benzene), 1269 (C—O), 1341 (—C—F), 1601 and 1652 (benzene), 2838 (—OCH_3), 2924 (—CH_3). m.p.: 403.1–403.7 K.

*{1-[2-Methyl-5-(4-methylphenyl)-3-thienyl]-2-(2-methoxylphenyl)} perfluorocyclopentene (**3o**)*

Compound **3o** was prepared by a method similar to that used for **1o** and used (2-methoxylpheny)perfluorocyclopentene (1.20 g, 4.00 mmol) [54] and 3-bromo-5-(4-methylphenyl)-2-methylthiophene (**3a**) (1.07 g, 4.00 mmol) with 2.5 M *n*-butyl lithium (1.60 mL, 4.00 mmol), then 0.59 g (1.26 mmol) of **3o** was obtained as solid in 31.5% yield. Anal. Calcd. for $C_{24}H_{18}F_6OS$ (%): C, 61.53; H, 3.87; Found C, 61.49; H, 3.90; ^1H NMR (400 MHz, $CDCl_3$, TMS): δ 1.89 (s, 3H, —CH_3), 2.36 (s, 3H, —CH_3), 3.50 (s, 3H, —OCH_3), 6.83, (d, J = 8.0 Hz, 1H, benzene-H), 6.99 (t, J = 8.0 Hz, 1H, benzene-H), 7.18 (d, J = 8.0 Hz, 2H, benzene-H), 7.18 (s, 1H, thiophene-H), 7.37 (t, J = 8.0 Hz, 2H, benzene-H), 7.41 (d, J = 8.0 Hz, 2H, benzene-H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.1, 21.2, 55.2, 111.4, 117.4, 120.8, 122.4, 125.4, 126.6, 129.6, 129.9, 130.9, 131.7, 137.6, 139.18, 141.3, 157.1. IR (ν, KBr, cm^{-1}): 757 (1,2-disubstituted benzene), 809 (1,4-disubstituted benzene), 1262 (C—O), 1599 and 1634 (benzene), 2843 (—OCH_3), 2915 (—CH_3). m.p.: 395.2–395.5 K.

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