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Synthesis, Photochromism, and Thermal Stability of Two New Diarylethenes Based On Spirobifluorene

Caihua Li and Heping Zeng*

Institute of Functional Molecules, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou 510641, China
*E-mail: hpzeng@scut.edu.cn

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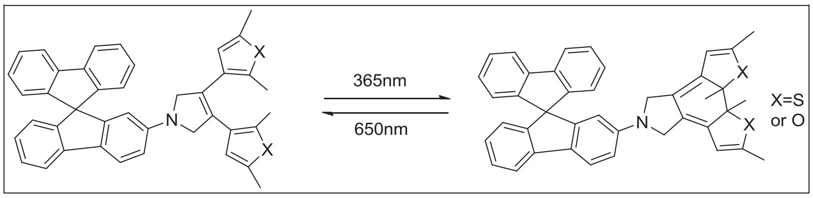

Two novel spirobifluorene-diarylethenes compounds with furan **(9a)** and thiophen **(8a)** as heterocyclic aryl groups were successfully synthesized, and their structures were fully characterized with FTIR, NMR, mass spectra (MS), and elemental analysis. Their photochromic properties were examined. The results indicated that they showed good photochromic behaviors in hexane and acetonitrile. The fluorescence emission was quenched along with the photochromism from open ring to closed ring. Large fluorescence emission blue-shift was clearly observed in polar solvents. Furthermore, the thermal stability of **8a** and **9a** was greatly improved by introducing spirobifluorene group into the molecules. The 5% loss weight temperature of **9a** was 59°C higher than that of 10**a** without spirobifluorene.

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INTRODUCTION

Photochromic materials can reversibly switch color when irradiated at different wavelengths [1–3]. This property is relevant for materials applications such as optical switching, sensing, and logic gates [4,5]. Among all the photochromic compounds, diarylethene derivatives are the most promising for practical applications. It is because of their highly desirable photochromic properties such as excellent fatigue resistance, short response time, high quantum yields, absence of thermal isomerization, and large changes in the absorption wavelength between the two isomers [6–10].

Despite of expedience, diarylethene derivatives still have not been explored for practical applications. The limitations related to these derivatives were thermal stability, rapid response, and so on. Among all, the most important one was thermal stability of both isomers. Various attempts have been carried out to stabilize the photogenerated unstable isomers by dispersing them in high T_g polymer matrices [11–13]; nevertheless, the stability is not enough for practical applications. Therefore, it was strongly desired to develop photochromic compounds in which both isomers are intrinsically stable.

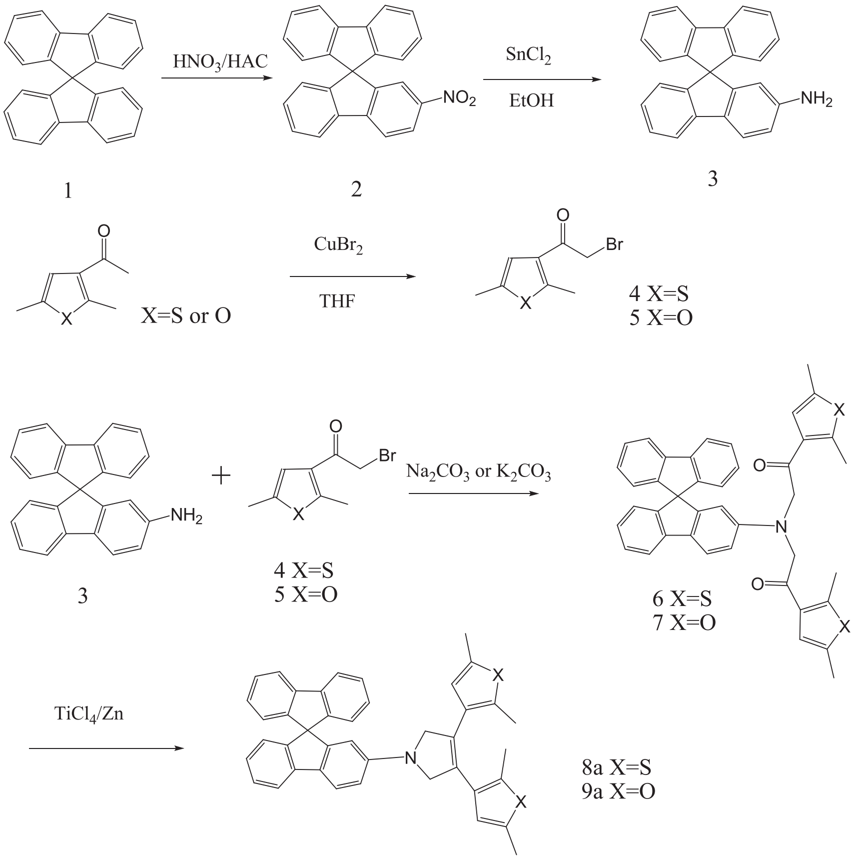
In order to improve the thermal stability of photochromic material, we have designed and synthesized two kinds of new diarylethenes compound **8a** and **9a** based on spirobifluorene(Scheme 1). In case of spirobifluorene, the bifluorene rings were orthogonally arranged through a tetracoordinated carbon. The specific, orthogonally fused structure of the spiro-type molecules entitles them the desired steric demand, reduce the crystallization tendency, enhance the rigidity, and consequently improve their thermal stability [14–17]. Therefore, spiro-type molecules are promising as functional material to improve their thermal stability. The molecular design strategy of introducing spirobifluorene into **8a** and **9a** rendered to obtain new photochromic materials. These molecules displayed good fluorescence emission, stable and reversible color changes with ultraviolet and visible light. Most importantly, they showed high thermal stability.

Diarylethenes with furan as heterocyclic aryl groups have rarely been studied in detail [18,25]. According to previous reports [19], the thermal stability of the diarylethene-type photochromic compounds can be improved by introducing aryl groups having low aromatic stabilization energy. Keeping in view, **9a** with furan unites was designed to improve the thermal stability of photochromic material because furan has lower aromatic stabilization energy than thiophen. In this study, we have investigated not only the different photochromic performance of **8a** and **9a** but also their thermal stabilities by thermogravimetry.

EXPERIMENTAL

Materials. 3,4-Bis(2,4,5-trimethylthiophen-3-yl)-1H-pyrrole-2,5-dione (**10a**) was purchased from Tokyo

Scheme 1



Chemical Industry Co. Ltd. (TCI, Shanghai). All organic solvents were commercially available, distilled, and dried by appropriate methods. Column chromatography was carried out on silica gel (200–300mesh; Qingdao Haiyang Chemical Co. Ltd, China).

Characterization and measurements. Fourier transform infrared (FTIR) spectra were recorded on a Perkin-Elmer FTIR spectrometer (Waltham, MA) using KBr pellets. ^{1}H NMR and ^{13}C NMR spectra were performed on BRUKER DRX-400 (Billerica, MA) with $CDCl_3$ as solvents. Chemical shifts (*d*) were given relative to tetramethylsilane (TMS). The coupling constants (J) were reported in Hz. The mass spectra were obtained on Esquire HCT PLUS. Ultraviolet-visible (UV/Vis) absorption and fluorescence spectra were recorded on Hitachi U-3010 and Hitachi F-2500 fluorescence spectrophotometers (Tokyo, Japan). The UV light source was a high-pressure mercury lamp through a filter (365 and 650 nm, 10 mW/cm^2). Thermal gravimetric analysis (TGA) thermograms were recorded on the STA449C thermal analysis system. Differential scanning calorimeter (DSC) measurements were performed at a heating rate of 10°C/min up to 400°C on samples taken in an aluminum pan with a pierced lid, in a dry nitrogen atmosphere with an empty pan as reference.

Synthetic procedures. The synthetic procedure for compounds **8a** and **9a** was outlined in **Scheme** 1. 9, 9′-Spirobifluorene (**1**) and 2-nitro-9,9′-spirobi[fluorene](**2**) were obtained as described in reported literatures [20–22]. For **8a** and **9a**, the central 2,5-dihydro-1H-pyrrole was formed by a ring-closure reaction of a 1,5-diketone via McMurry reaction [23].

9,9′-Spirobi[fluoren]-2-amine (3). A suspension of 2-nitro-9,9-spirobifluorene 0.72 g(1 mmol) and $SnCl_2$ $2H_2O$ 2.26g (5 mmol)in EtOH (100 mL) was refluxed under Ar for 5 h. The reaction mixture was concentrated, and residue was poured into ethyl acetate (50 mL) and water (50 mL), followed by filtering through celite pad. The organic layer was separated, washed with water, and dried over anhydrous $MgSO_4$. The residue was purified by column chromatography with CH_2Cl_2/petroleum ether (from 0.5 to 1), which gave the title compound **3 (**0.68 g) as colorless solid. The yield was 68% and mp was 227–229°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.96 (d, 1H, J=7.6 Hz), 7.94–7.81 (m, 2H), 7.86 (d, 2H, J=7.6 Hz), 7.48–7.34 (m, 3H), 7.26(s, 1H), 7.22 (t, 1H, J= 7.6 Hz), 7.12 (t, 2H, J=7.6 Hz), 6.76(d, 1H, J=7.6 Hz), 6.71(d, 2H, J=7.6 Hz),5.18(s, 2H); IR(KBr)ν: 3440, 3359, 1615, 1582, 1453, 756 cm^{-1}. Atmospheric pressure chemical ionization (APCI)-MS m/z (%): 332.1 (M$^+$, 100).

2-Bromo-1-(2,5-dimethylthiophen-3-yl)ethanone (4) [24]. 1-(2,5-Dimethylthiophen-3-yl)ethanone 0.15 g (1 mmol) and copper bromide 0.45 g (2 mmol) were suspended in dry tetrahydrofuran (THF) (20 mL). The mixture refluxed for 6 h under Ar until all of the starting materials were consumed. The reaction was monitored by thin layer chromatography (TLC). The solution was filtered hot, and the filtrate was concentrated to blue viscous oil. The oily product was dissolved in 20 mL CH_2Cl_2 and washed three times with water. The crude product was purified by column chromatography to afford compound **4 (**0.17 g) as a colorless transparent solid. The yield was 72%, and mp was 42–43°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.00(s, 1H), 4.25(s, 2H), 2.69(s, 3H), 2.42(s, 3H); IR(KBr)ν: 1659, 1546,1447, 1428, 845, 619, 591 cm^{-1}. APCI-MS *m/z* (%): 234.5 (M^+, 100).

2-Bromo-1-(2,5-dimethylfuran-3-yl)ethanone (5). The synthetic approach was similar to compound **4**, just employing 1-(2,5-dimethylfuran-3-yl)ethanone instead of 1-(2,5-dimethylthiophen-3-yl)ethanone. Yield of compound **5** was 78%, and its mp was 53–55°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.23(s, 1H), 4.12(s, 2H), 2.56(s, 3H), 2.27(s, 3H); IR(KBr)ν: 1682, 1570, 1377, 954, 670 cm^{-1}. APCI-MS *m/z* (%): 216.6 (M^+, 100).

2,2'-(9,9'-Spirobi[fluorene]-2-ylazanediyl)bis(1-(2,5-dimethyl thiophen-3-yl)ethanone) (6). Compound **4** 0.28 g (1.2 mmol), Na_2CO_3 0.106 g (1 mmol), and Compound **3** 0.16 g (0.5mmol) were dissolved in ethanol (20 mL; 95%). The mixture was stirred for 0.5 h at ambient temperature and then refluxed for 4 h. The reaction mixture was cooled and diluted with water. Solid mass was obtained and purified through recrystallization from ethanol to obtain yellow solide (0.2 g) [25,26]. Yield and mp of compound **6** were 64%, 207–210°C, respectively; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.99–7.91 (m, 3H), 7.88 (d, 2H, *J*=7.6 Hz), 7.46–7.38 (m, 3H), 7.29(s, 1H), 7.23 (t, 1H, *J*=7.6 Hz), 7.12 (t, 2H, *J*=7.6 Hz), 6.81(d, 1H, *J*=7.6 Hz), 6.71(d, 2H, *J*=7.6 Hz);6.52(s, 2H), 4.28(s, 4H), 2.46(s, 3H), 2.29(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:191.5, 155.5, 149.2, 148.4, 147.6, 146.9, 136.0, 130.3, 129.5, 128.6, 128.1, 128.0, 126.5, 126.2, 125.3, 124.4, 123.9, 122.6, 121.2, 120.4, 120.2, 110.5, 65.71, 62.3, 14.7, 13.6; IR(KBr)ν: 1679, 1569, 1400, 1357,936, 658; APCI-MS *m/z* (%): 634.3 (M^+, 100); *Anal.* Calcd for $C_{41}H_{33}NO_2S_2$: C 77.45, H 5.23, N 2.20, S 10.09; found: C 77.48, H 5.22, N 2.18, S 10.07.

2,2'-(9,9'-Spirobi[fluorene]-2-ylazanediyl)bis(1-(2,5-dimethyl furan-3-yl)ethanone) (7). The synthetic procedure was similar to compound **6**; K_2CO_3 was used instead of Na_2CO_3, which rendered compound **7.** The yield was 68% and mp was 216–219°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.92–7.89 (m, 3H), 7.82 (d, 2H, *J*=7.6 Hz), 7.57–7.42 (m, 3H), 7.26(s, 1H), 7.21 (t, 1H, *J*=7.6 Hz), 7.19 (t, 2H, *J*=7.6 Hz), 6.78(d, 1H, *J*=7.6 Hz), 6.70(d, 2H, *J*=7.6 Hz); 6.46(s, 2H), 4.36(s, 4H), 2.38(s, 3H), 2.23(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:190.5, 159.5, 158.2, 154.4, 149.6, 143.9, 143.8, 143.2, 129.3, 128.9, 128.6, 128.0, 126.9, 126.7, 125.0, 124.3, 123.7, 122.5, 121.1, 120.3, 120.1, 112.5, 66.8, 62.3, 15.6, 14.5; APCI-MS *m/z* (%): 603.9 (M^+, 100). IR(KBr)ν: 1682, 1557, 1449, 1377, 928, 653; *Anal.* Calcd for $C_{41}H_{33}NO_4$: C 81.57, H 5.51, N 2.32, C 69.04; found: C 81.53, H 5.50, N 2.34.

1-(9,9'-Spirobi[fluorene]-2-yl)-3,4-bis(2,5-dimethylthiophen-3-yl)-2,5-dihydro-1H-pyrrole (8a). To a suspension of zinc powder 1.3 g (20 mmol) in THF (30 mL) under nitrogen, $TiCl_4$ (1.2 mL) was added very slowly at 0°C by syringe. The mixture was refluxed for 1 h. Then compound **6** 0.1 g (0.16 mmol) in THF (60 mL) was also added very slowly at ambient temperature. The reaction mixture was stirred for another 24 h in darkness followed by quenching with K_2CO_3 (40%, 8 mL). The solid was filtered and washed with diethyl ether (50 mL). The combined organic phases were concentrated to 5 mL and water (5 mL) was added to the residue. The product was extracted with diethyl ether (5 mL) and dried over $MgSO_4$, filtered, and concentrated. The residue was purified by column chromatography over silica gel using hexane(100%) as eluent to afford compound **8a** (47 mg) as a colorless transparent solid. The yield was 49%, and mp was 195–196°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89–7.82 (m, 5H), 7.43 (d, 2H, *J*=8.0 Hz), 7.40–7.36 (m, 3H), 7.15–7.11 (m, 4H), 6.77 (d, 1H, *J*=8 Hz), 6.18(s, 2H), 4.38(s, 4H), 2.32(s, 6H), 2.04(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:150.6, 148.8, 148.3, 141.8, 140.9, 140.0, 139.3, 136.0, 134.5, 131.7, 131.5, 129.2, 127.9, 127.7, 125.2, 124.1, 121.3, 120.9, 120.2, 119.9, 119.6, 117.8, 115.7, 66.0, 60.4, 15.2, 13.8; IR(KBr)ν: 1737, 1497, 1450, 752; APCI-MS *m/z* (%): 602.3 ($[M+1]^+$, 100). *Anal.* Calcd for $C_{41}H_{33}NS_2$: C 81.55, H 5.51, N 2.32, S 10.62; found: C 81.51, H 5.50, N 2.34, S 10.65.

1-(9,9'-Spirobi[fluorene]-2-yl)-3,4-bis(2,5-dimethylfuran-3-yl)-2,5-dihydro-1H-pyrrole (9a). The synthetic procedure was similar to compound **8a**, just employing compound **7** instead of compound **6**. The yield of Compound **9a** was 42% and its mp was 183–185°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86–7.79 (m, 5H), 7.51 (d, 2H, *J*=8.0 Hz), 7.45–7.39 (m, 3H), 7.21–7.18 (m, 4H), 6.78(d, 1H, *J*=8 Hz), 6.05(s, 2H), 4.08(s, 4H), 2.51(s, 6H), 2.32(s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ:156.7, 148.8, 146.9, 142.6, 141.5, 140.0, 138.3, 135.7, 134.9, 132.0, 131.7, 129.8, 127.1, 126.7, 125.9, 124.3, 121.9, 121.0, 120.7, 119.6, 119.0, 118.0, 115.9, 68.0, 61.5, 14.6, 11.9; IR (KBr)ν: 1726, 1485, 1455, 740;APCI-MS *m/z* (%): 602.3 ($[M+1]^+$, 100). *Anal.* Calcd for $C_{41}H_{33}NO_2$: C 86.13, H 5.82, N 2.45, O 5.60; found: C 86.10, H 5.83, N 2.44.

RESULTS AND DISCUSSION

Synthesis. In the preparation of compounds **8a** and **9a**, the synthesis of compounds **6** and **7** were considered as key steps (Scheme 1). The reactions were carried out by taking a 12:5 mole ratio mixture of compounds **4** (or **5**) and **3** in the presence of some alkaline salt [25,26]. To investigate the influence of the solvent, temperature, and alkaline salt, synthesis of compound **9a** was carried out under different conditions (Table 1). The optimum conditions were achieved by using K_2CO_3 in ethanol at 80°C (Table 1, entry 4).

Photochromic behavior of compounds 8a and 9a. Photochromic reactivity of **8a** and **9a** was examined in hexane and acetonitrile through UV-Vis spectra. Absorption spectral changes of **9a** in hexane (Fig. 1a) and acetonitrile (Fig. 1b) were shown. Upon irradiation at 365 nm, the color of the solution turned into red, both in hexane and acetonitrile. The absorption bands of **9a** at 305–320 nm gradually weakened, and at the same time, new absorption bands appeared at 495 and 485 nm, which correspond to **9b** in hexane and acetonitrile, respectively. These phenomena indicated that **9a** underwent photocyclization as illustrated in **Scheme** 2.

The colorations of **8a** in hexane and acetonitrile irradiation at 365 nm were shown in Figure 2. Similar to **9a,** new absorption bands appeared at 463 (in hexane) and 448 (in acetonitrile) nm after irradiation corresponding to **8b**.

Absorption maxima of **8a** and **9a** before and after irritation in hexane and acetonitrile were shown in **Table** 2**.** It is clear that the absorption bands of **8a–9a** were shifted to hypsochromic by the solvent polarity, which is usually called “negative solvatochromism” [27]. This effect **of 8a–9a** revealed that by increasing solvent polarity, the ground-state molecules **of 8a–9a** was better stabilized by solvation than the molecules in the excited state [28]. Compared with **9a** containing furan moieties, **8a** with thiophen moieties were more sensitive to solvent polarity. Because solvatochromism came from the interaction between the dipole moments of the solvent and the molecule, the more sensitivity to solvent polarity of **8a** means larger differences in the dipole moment at the ground states and the excited states [29].

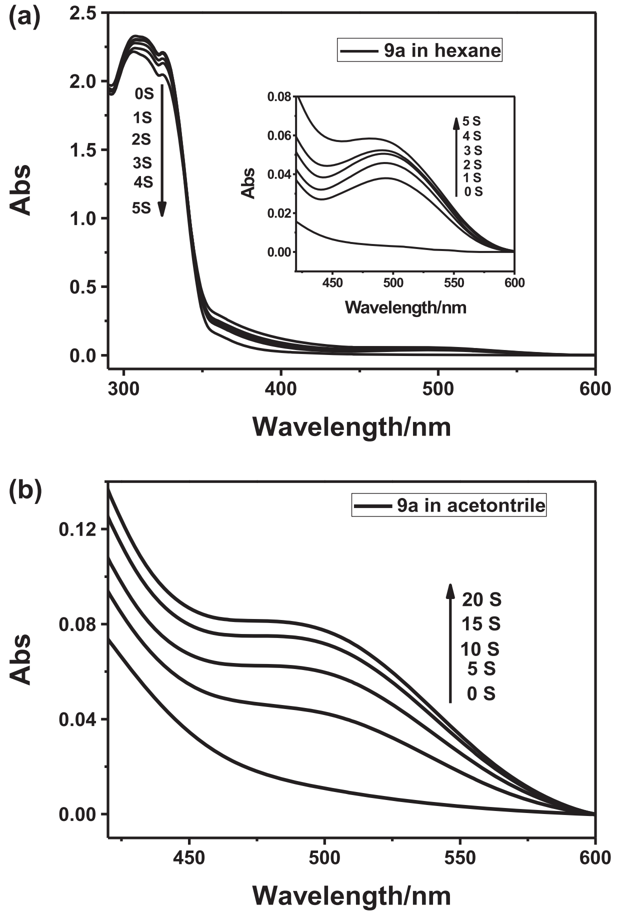


Figure 1. Absorption changes of **9a** in hexane (a) and acetonitrile (b) upon irradiation with 365 nm light.

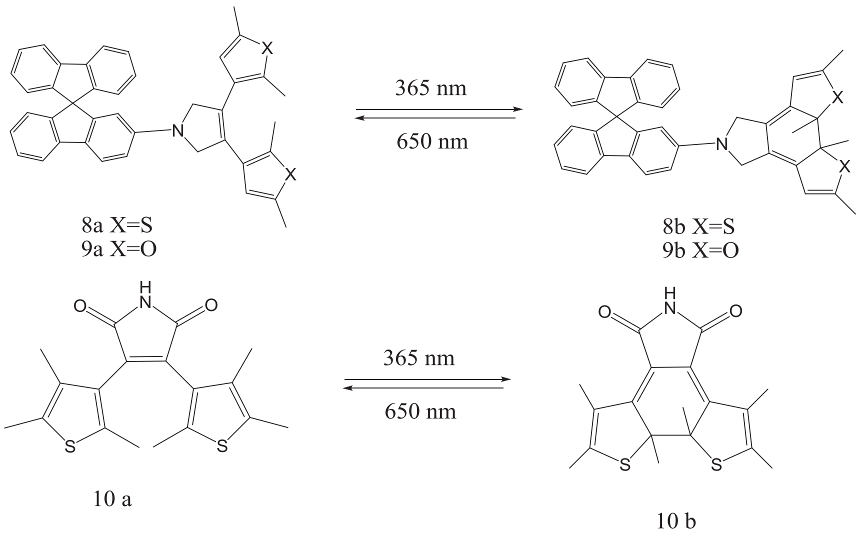
The photocycloreversion of **8b** and **9b** were also investigated in hexane using UV-Vis spectroscopy. A hexane solution of **8a** ($1{\times}10^{-5}$ mol/L) was irradiated at 365 nm for 1 min to reach photostationary state (PSS), and then the resulting colored solutions could be decolorized by irradiating the solution with 650 nm light (Xenon light 500 W, with filter), which lead to disappearance of absorption bands in the visible region (Fig. 3). It was found that the reactive time of coloration was very short for both **8a** and **9a** in solution ($1{\times}10^{-5}$ mol/L). Coloration was completed in about 5–20 s at 365 nm light (Table 2). However, the reactive time of bleaching for **8b** and **9b** was

Table 1

Synthesis of **9a** under different conditions.

Entry	Solvent	Temperature (°C)	Alkaline salt	Reaction time (h)	Yield (%)
1	Ethanol	80	Na_2CO_3	4	56
2	Ethanol	80	$NaHCO_3$	7	34
3	Ethanol	80	NaOH	1	0
4	Ethanol	80	K_2CO_3	4	68
5	THF	65	K_2CO_3	6	47

Scheme 2



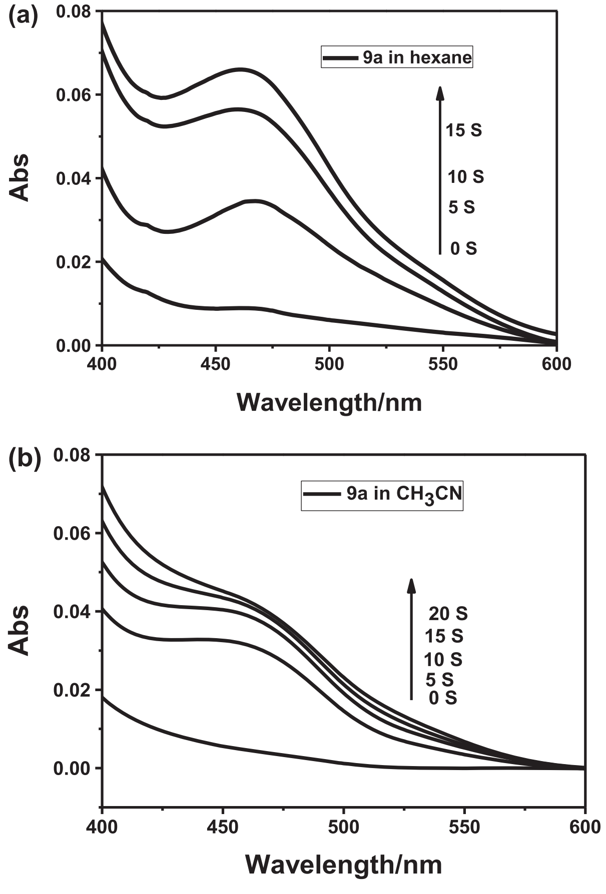


Figure 2. Absorption changes of **8a** in hexane (a) and acetonitrile (b) upon irradiation with 365 nm light.

found to be much longer than coloration. As depicted in Figure 3, the photocycloreversion of **8b** and **9b** required 30 min, although they could be shifted completely back to ring-open isomers.

The reactive time of coloration for **8a** and **9a** in hexane and acetonitrile was measured with 365 nm light and results were presented in Figure 4. It was found that the reactive time of coloration was very short for both **8a** and **9a** in solution (1×10^{-5} mol/L). Especially for **9a** in hexane, it was about only 10 s to complete the coloration. In addition, it was worth noting that the solvent polarity had significant effect on photoreactions of **8a** and **9a**. As depicted in Figure 4 and Table 2, absorbance of **9a** no longer changed with the irradiation time after 10 s in the hexane, indicating that cyclization has completed. In contrast, it took about 20 s to complete the coloration of **9a** in acetonitrile solution. This shows that photoreaction rate of **9a** in hexane was faster than in acetonitrile. So, solvent polarity had significant impacts on the rate of cyclization, because hexane is a non-polar solvent and acetonitrile is a typical large polar solvent. Similar result was obtained for **8a** that cyclization rate in non-polar hexane was faster than in large polar acetonitrile.

In addition, the photochromic cyclization kinetics of **8a** and **9a** in hexane and in acetonitrile were also presented in Figure 4. It can be seen that the relationships between the absorbance and exposal time have good linearity upon irradiation with 365 nm UV light before reaching PSS, suggesting that the cyclization processes of **8a** and **9a** belong to zeroth order reaction [30].

Fluorescence of photochromism 8a and **9a** in different solvents. The fluorescence changes of **8a** and **9a** were examined in hexane and acetonitrile during photochromism(Figs. 5 and 6). The compounds **8a** and **9a** exhibited photoluminescence at 361 and 367 nm in acetonitrile solution, while in hexane, their photoluminescence peaks were at 414 and 407 nm, respectively. These photoluminescence were attributed to

Table 2

Photochemical properties of **8a–9b** and TGA date of **8a–10a**.

	In hexane				In acetonitrile				TGA	
	λ_{ab1}/nm[a]	λ_{ab2}/nm[b]	Time[c]	λ_{em}/nm	λ_{ab1}/nm	λ_{ab2}/nm	Time	λ_{em}/nm	5%	50%
8a	325	463	15 s	414	318	448	20 s	361	265°C	336°C
9a	320	495	10 s	407	315	485	20 s	367	275°C	357°C
10a	322	520	10 s	410	321	517	20 s	408	216°C	263°C

"a" refers to the absorption peak before irradiation; "b" refers to the new absorption peak after irradiation; "c" is the time of cyclization with 365 nm light.

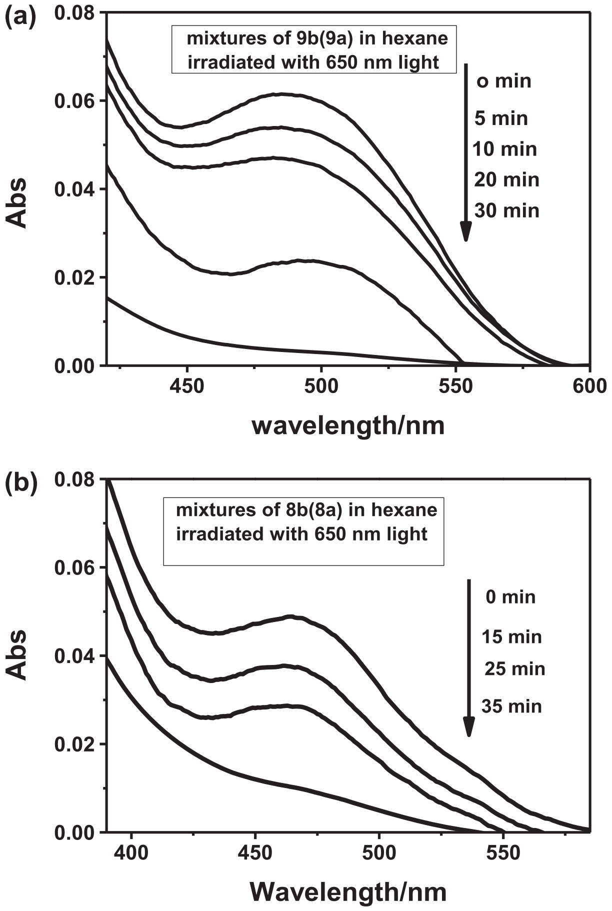


Figure 3. Absorption changes of mixtures of **9b** (**9a**) (a) and **8b** (**8a**) (b) in hexane upon irradiation with 650 nm light.

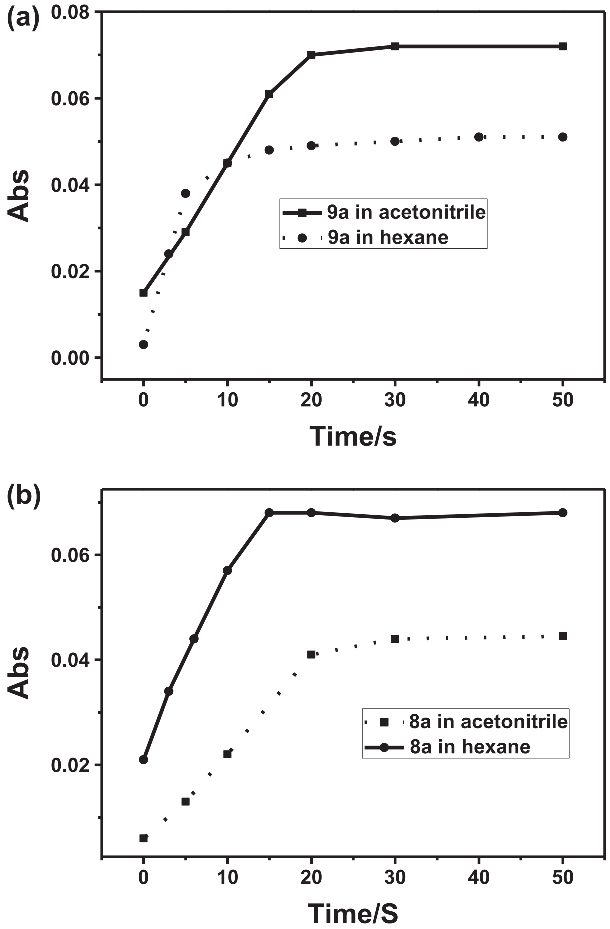


Figure 4. (a) Absorption changes of **9a** at 485 nm (hexane) and 495 nm (acetonitrile) with the irradiation time; (b) absorption changes of **8a** at 463 nm (hexane) and 448 nm (acetonitrile) with the irradiation time.

the emission of dithienylethene (DTE) (**8a**) and difuranylthene (**9a**) units [20]. The fluorescence intensity of **8a** and **9a** decreased along with the photochromism from the open ring to the closed ring upon irradiation at 365 nm. As shown in Figures 1 and 2, the ring-closed form has the second absorption band ranging 350–600 nm. The overlapping of emission and absorption bands suggested that efficient energy transfer to the ring-closed form resulting in quenching of the photoluminescence [20]. In other words, the more fluorescence were quenched, the more **8a** and **9a** were transformed into ring-closed forms. As shown in Figure 5, there were 60% fluorescence of **9a** quenched at PSS in hexne while in acetonitrile, suppression was only 44%. Therefore, the photochromic conversion of **9a** was higher in non-polar hexane than that in highly polar acetonitrile. Similar finding was found for **8a** while evaluating its fluorescence changes at PSS in different solvents.

In addition, there was strong solvent effect on fluorescence emission of **8a** and **9a**. As shown in Table 2, the emission wavelength of **8a** and **9a** blue-

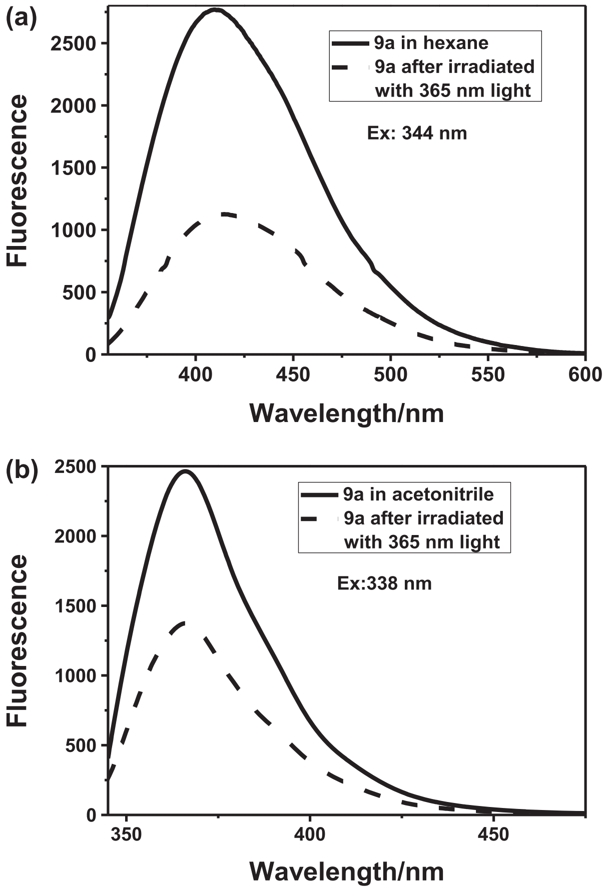


Figure 5. Fluorescence changes of **9a** in hexane (a) and acetonitrile (b) upon irradiation with 365 nm light.

shifted by 53 and 40 nm, respectively, by varying solvent polarity from hexane to acetontrile. In view of previous theoretical and experimental results [31,32], the intramolecular charge transfer (ICT) characteristic is the major mechanism responsible for the large solvent-reliant emission properties of **8a** and **9a**. The ICT compounds represent a donor–acceptor (D-A) system [33]. In **8a** and **9a**, thiophen and furan as electron-rich aryl [34], are favorable electron donor, and dihydropyrrolo group acts as electron acceptor, thus leading to D-A structures. Interestingly, **8a** and **9a** with different donor units displayed different fluorescence solvent effect. Compared with **9a**, **8a** had much larger solvent sensitivity (Table 2), which indicated more effective ICT processes. According to ICT mechanism, thiophen is a better electron donor than furan, therefore **8a** will have a higher dipolar moment than **9a** upon excitation. Thus, it can be concluded that ICT processes in **8a** are more effective.

Thermal stability of 8a–10a and their ring-closed compounds 8b–10b

The thermogravimetric analysis of 8a–10a. The TGA traces of **8a–10a** were shown in Figure 7, and the data were

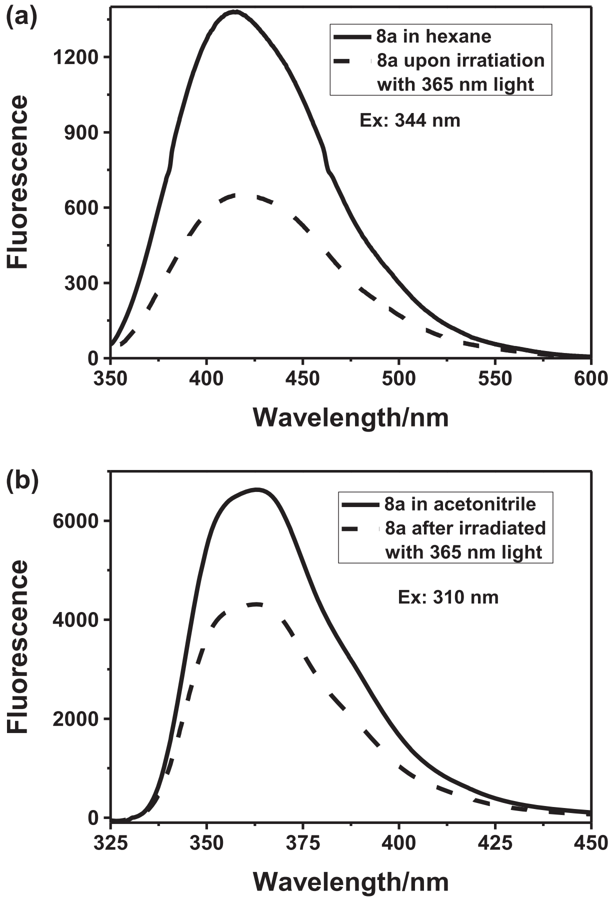


Figure 6. Fluorescence changes of **8a** in hexane (a) and acetonitrile (b) upon irradiation with 365 nm light.

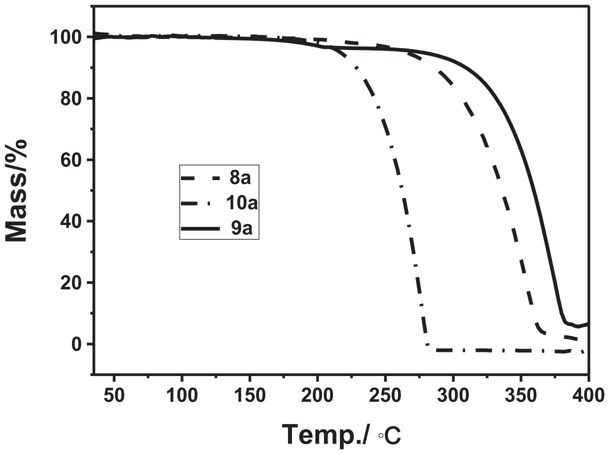


Figure 7. The TGA curves of **8a–10a**.

given in Table 2. The thermal stability was evaluated by 5% and 50% weight loss at minimum temperature. TGA revealed that **8a–10a** were stable up to 265, 275, and 216°C, respectively, in nitrogen atmosphere. After that, degradation started followed by a one-stage decomposition pattern.

As shown in Figure 7 and Table 2, **8a** with spirobifluorene group achieved higher thermal stability than **10a**. The significant gap of 50% weight loss temperature (from 336 to 263) between **8a** and **10a** may be ascribed to the spirobifluorene group. As far as spirobifluorene is concerned, the bifluorene rings are orthogonally arranged through a tetracoordinated carbon. So introduction of this component into **8a** enhanced the rigidity and consequently improved the thermal stability of this material [35–37].

For **8a** and **9a** with thiophen and furan respectively, the thermal stability of **9a** was a little higher than **8a**, which may be explained on the basis of their different heterocyclic aromatics. It has been reported that the thermal stability of the diarylethene-type photochromic compounds can be improved by introducing aryl groups having a low aromatic stabilization energy [7].Therefore, Furan, which has a lower aromatic stabilization energy than thiophene (for **8b**) according to the modified neglect of diatomic overlap calculation [7], made **9a** more stable than **8a**.

Thermal stability of 8b–10b. Thermal stability of **8b–10b** was estimated by heating a toluene solution of a mixture of **8b (8a)–10b (10a)** in the dark [38].

A toluene solution of **8a** was irradiated for 5 min by 365 nm light. The absorbance of **8b** was observed at 492 nm (A_0, in Fig. 8). The solution in a sealed tube was heated at 110°C in the dark. After 5, 10, 25, 50, 75, and 100 h, the absorbances at 492 nm (A, in Fig. 8) were observed. The similar procedures using **9a** were carried out and the absorbances at 460 nm were observed. Thermal stability of the ring-closed compounds **10b** was also measured in order to compare with **8b** and **9b** through the absorbances at 530 nm.

It was found that upon heating at 80°C for 100 h, **8b, 9b,** and **10b** were not converted to the ring-opened form**.** However, it was worthwhile that there were significant differences in their thermal stability while heating the sample to 110°C**.** After 100 h, **95%** of **9b** was recovered unchanged in contrast to only 42% **for 10b** (Fig. 8). In addition, 76% of **8b** was not transformed after heated for 100 h. So, the thermal stability sequence of 9b>8b>10b was in full accord with the sequence of 9a>8a>10a.

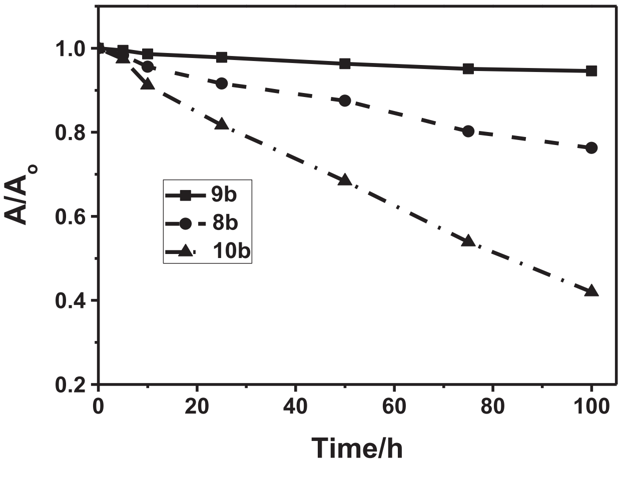


Figure 8. Thermal stability of **8b–10b** in toluene solutions at 110°C.

CONCLUSION

We have designed and synthesized two new photochromic spirobifluorene-diarylethenes with furan **(9a)** or thiophen **(8a)** as heterocyclic aryl groups and investigated their photochromism in different solvents. The results showed that both molecules showed good photochromic behaviors in hexane and acetonitrile, and the photochromic reaction rate and conversion in hexane were both higher than these in acetonitrile. The fluorescence intensity of **8a** and **9a** decreased along with the photochromism from open ring to closed ring under irradiation, and there were large fluorescence emission blue-shift in polar solvent. Furthermore, the thermal stability of **8a** and **9a** and their closed-ring forms **8b** and **9b** were greatly improved because of spirobifluorene or furan groups in the molecules. The 5% loss weight temperature of **9a** was 59°C higher than that of **10a** without being substituted by spirobifluorene and only 5% of **9b** decomposed after heating at 110°C, while decomposition of **10b** was 58%.

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