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Modulation of absorption and fluorescence of photochromic diarylethene by intramolecular hydrogen bond

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Photochromic diarylethenes bearing an intramolecular hydrogen bond in bridge moiety have been prepared. It is found that intramolecular hydrogen bonding has a great effect on both absorption and fluorescence of diarylethenes. The color change of diarylethenes in a wide range (purple, blue and green) can be achieved by simple modification of the electronic properties of substituents in bridge moiety, and fluorescent diarylethenes are also obtained when diarylethenes bear an intramolecular hydrogen bond in bridge moiety. Copyright © 2011 John Wiley & Sons, Ltd.

Keywords: color change; diarylethene; fluorescence; intramolecular hydrogen bond; photochromism

INTRODUCTION

The importance of the hydrogen bond in chemistry and biology is highlighted in numerous books published, and it plays a prominent role in both biology and chemistry.[1–3] The hydrogen bond enables an extraordinary range of physiological processes such as the inhibition of enzymes,[4–6] functionalization of peptides and activation of proteins,[7–9] and chemical processes such as catalytic reactions,[10–12] assembly, and supermolecular and template chemistry.[13–15]

Switches at the molecular level have attracted considerable attention during recent years because they afford promising devices such as machines, sensors and memories. Molecule switches are, usually, based on a system in which properties and molecular conformation of the bistable chemical species are capable of interconversion under the action of various external sources. Among various external sources, phototriggered switches are the most promising for applications because they are simple to handle and easy to control.

Photochromic diarylethenes have attracted considerable attention from both fundamental and practical points of view.[16,17] Although photochromic diarylethenes are being extensively explored for application as optical switch devices based on the change of magnetic properties,[18,19] electrochemical behavior[20,21] and chemical reactivity,[22,23] the major applications of photochromic diarylethenes are based on the following two aspects: one is to take advantage of their inherent ability to produce switches between two isomers with distinct color change;[24,25] another is to create a fluorescent diarylethene that shows an on/off fluorescent switch between two isomers by UV–Vis phototrigger.[26–28]

In general, diarylethenes show very large spectral shifts upon photocyclization of open isomers (absorption bands at UV region, colorless) to closed isomers (absorption bands at visible light region, colored) because of π-electron delocalization throughout the two condensed thiophene rings and further extension of the substituents (Scheme 1). Usually, the modulation of the absorption bands (color) of closed isomers is achieved by either the extension of π-conjugation linked to thiophene rings[29,30] or the modification of the electron properties of substituents.[31–33]

It is known that the 1,2-bis(thien-3-yl) fragment has little or weak emission. A strong fluorescent diarylethene is usually constructed by covalently attaching a fluorescent group to a diarylethene molecule,[34,35] and in most instances, the open isomers have strong emission, while the closed isomers have little or very weak emission because of the efficient energy transfer between the excited fluorescent chromophores group and the closed diarylethene fragment.[36,37] Although many elegant diarylethene systems have been developed by covalently attaching a fluorescent group to a diarylethene fragment, development of a fluorescent diarylethene system that has a common structure that can be modified easily using similar synthesis methods would be useful.

Recently, photochromic diarylethenes with a different bridge moiety have been successfully developed for the photomodulation manipulation of various properties of molecular and polymer materials[38–40] and exhibit interesting photochromic behavior.[26,41,42] Herein, we describe a novel photochromic diarylethene system (**1a–3a**) containing an intramolecular hydrogen bond bridge moiety (Scheme 2). With such a system, both color change in a wide range and fluorescence emission can be obtained by simply changing the substituent group of the bridge moiety. This may be beneficial for providing a simple and efficient strategy for the design of photochromic diarylethenes with fluorescence emission and large color change in the visible light region.

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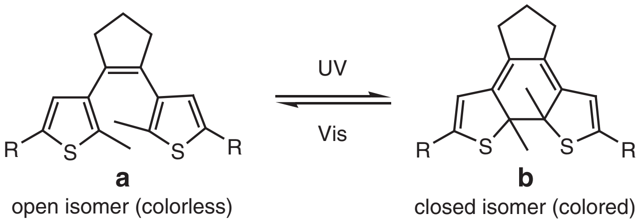


Scheme 1. Illustration of photochromism of diarylethene with UV–Vis light irradiation

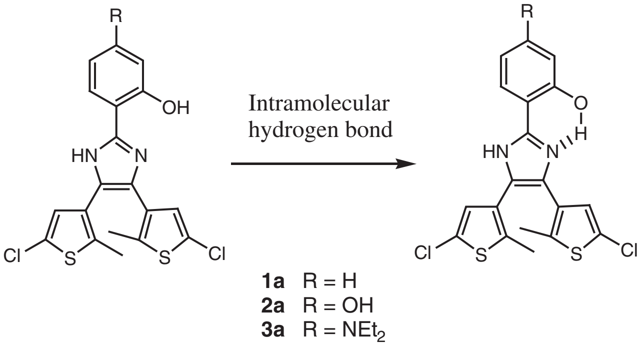
EXPERIMENTAL

General methods

^{1}H-NMR spectrum was recorded at 400 MHz with tetramethylsilane as an internal reference and DMSO-d$_6$ as solvent. HRMS spectra were recorded with matrix-assisted laser desorption/ionization mass spectrometry. Absorption spectra and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi U-3010) Hitachi High-Technologies Corporation, Japan and a fluorescence spectrophotometer (F-2500) Hitachi High-Technologies Corporation, Japan., respectively. All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reaction was monitored by thin layer chromatography silica gel plates (60 F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh) Merck Chemicals Co. Ltd., Shanghai, China. A 360-nm lamp (36 W) and a Xenon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.

Synthesis of diarylethenes 1a–6a

Target compounds **1a–6a** were prepared according to the synthetic route presented in Scheme 3. Diketone was obtained starting from commercially available 2-methylthiophene, which was chlorinated at the 5-position with N-chlorosuccinimide in AcOH,[43] followed by acylation with oxalyl chloride in dichloromethane. Treatment of diketone with salicylaldehyde in the presence of NH$_4$Ac afforded target compounds. The details of the procedure are as follows: to a solution of diketone (100 mg, 0.31 mmol) in acetic acid (10 ml) was added substituted benzaldehyde derivatives (0.37 mmol) and NH$_4$Ac (143 mg, 1.86 mmol), and the mixture was heated at reflux until the starting material disappeared (thin layer chromatography detection). The mixture solution was then slowly poured into a NaHCO$_3$ solution (10%, 50 ml), and the product was extracted with CHCl$_3$ (3 ×00A020 ml). The combined organic phase was washed with water and dried over MgSO$_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography (elute: petroleum ether / ethyl acetate = 20:1) to afford target compounds



Scheme 2. Structure of photochromic diarylethenes **1a–3a**

1a: 70 %. ^{1}H-NMR (DMSO-d$_6$) δ: 13.06 (s, 1H), 12.66 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.37 (t, *J$_1$* = 7.2 Hz, *J$_2$* = 7.1 Hz, 1H), 7.27 (s, 1H), 7.06–7.02 (m, 2H), 6.92 (s, 1H), 2.31 (s, 3H), 2.13 (s, 3H). ^{13}C-NMR (101 MHz, DMSO) δ: 157.22, 146.54, 137.30, 134.68, 131.76, 130.85, 129.01, 127.72, 127.46, 125.46, 125.19, 124.62, 122.58, 119.58, 117.47, 113.41, 14.54, 14.13. HRMS (*m/z*): calcd. for $C_{19}H_{14}Cl_2N_2OS_2$: 419.9925, Found: 420.0016.

2a: 75 %. ^{1}H-NMR (DMSO-d$_6$) δ: 12.73 (s, 1H), 12.66 (s, 1H), 9.75 (s, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.12 (s, 1H), 6.78 (s, 1H), 6.35 (d, *J* = 9.2 Hz, 1H), 6.32 (s, 1H), 2.48 (s, 3H), 2.01 (s, 3H). ^{13}C-NMR (101 MHz, DMSO) δ: 160.09, 158.94, 147.25, 136.94, 134.37, 132.12, 131.15, 129.38, 129.02, 127.74, 126.57, 125.05, 124.48, 121.59, 107.76, 105.47, 103.55, 14.54, 14.14. HRMS (GC - TOF) (*m/z*): calcd. for $C_{19}H_{14}Cl_2N_2O_2S_2$: 435.9874, Found: 435.9847.

3a: 68 %. ^{1}H-NMR (DMSO-d$_6$) δ: 12.66 (s, 1H), 12.57 (s, 1H), 7.78 (d, *J* = 8.8 Hz, 1H), 7.23 (s, 1H), 6.90 (s, 1H), 6.37 (d, *J* = 8.9 Hz, 1H), 6.23 (s, 1H), 3.48 (t, 4H), 2.28 (s, 3H), 2.21 (s, 3H), 1.21 (q, 6H). ^{13}C-NMR (101 MHz, DMSO) δ: 159.61, 150.54, 148.52, 137.34, 134.85, 132.05, 131.77, 129.73, 128.59, 128.47, 127.15, 125.65, 125.09, 121.77, 104.60, 102.22, 99.29, 44.93, 15.23, 14.84, 13.86. HRMS (GC - TOF) (*m/z*): calcd. for $C_{23}H_{23}Cl_2N_3OS_2$: 491.0660, Found: 491.0279.

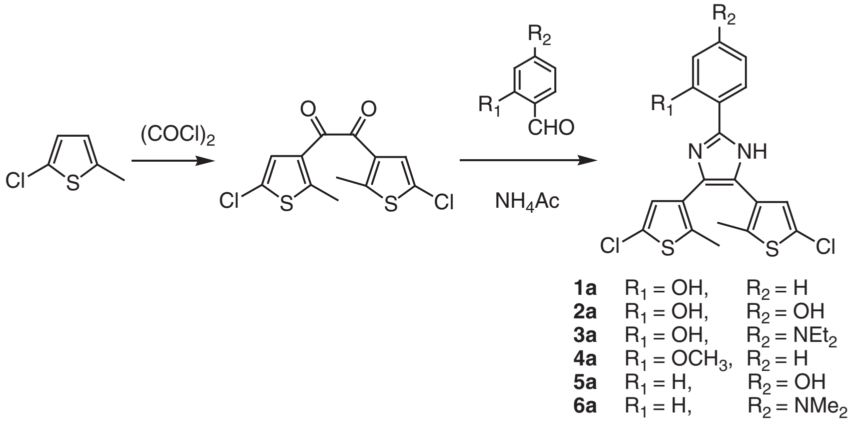
4a: 62 %. ^{1}H-NMR (DMSO-d$_6$) δ: 12.17 (s, 1H), 8.14 (d, *J* = 7.7 Hz, 1H), 7.50 (t, *J$_1$* = 8.7 Hz, *J$_2$* = 8.6 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 1H), 7.15 (t, *J$_1$* = 7.2 Hz, *J$_2$* = 7.1 Hz, 1H), 7.01 (s, 2H), 4.02 (s, 3H), 2.23 (s, 6H). ^{13}C-NMR (101 MHz, DMSO) δ: 156.47, 143.84, 134.17, 130.43, 129.19, 128.52, 128.33, 128.22, 124.32, 122.66, 119.15, 112.21, 56.09, 14.37. HRMS (GC - TOF) (*m/z*): calcd. for $C_{20}H_{16}Cl_2N_2OS_2$: 434.0081, Found: 434.0014.

5a: 72 %. ^{1}H-NMR (DMSO-d$_6$) δ: 12.42 (s, 1H), 9.69 (s, 1H), 7.81 (d, *J* = 8.6 Hz, 2H), 7.32 (s, 1H), 7.11 (s, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 2.16 (s, 3H), 2.0 (s, 3H). ^{13}C-NMR (101 MHz, DMSO) δ: 157.89, 146.19, 135.38, 133.68, 133.26, 132.13, 128.41, 127.99, 127.63, 126.74, 124.17, 123.35, 121.99, 121.46, 115.49, 13.93, 13.58. HRMS (GC - TOF) (*m/z*): calcd. for $C_{19}H_{14}Cl_2N_2OS_2$: 419.9925, Found: 420.9842.

6a: 60 %. ^{1}H-NMR (DMSO-d$_6$) δ: 12.44 (s, 1H), 7.93 (d, *J* = 8.8 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 7.18 (s, 1H), 6.88 (s, 1H), 3.06 (s, 6H), 2.27 (s, 3H), 2.10 (s, 3H). ^{13}C-NMR (101 MHz, DMSO) δ: 150.32, 146.58, 133.37, 131.86, 130.11, 128.05, 126.18, 123.65, 118.04, 111.89, 40.33, 13.72. HRMS (GC - TOF) (*m/z*): calcd. for $C_{21}H_{19}Cl_2N_2S_2$: 447.0397, Found: 447.0477.

RESULTS AND DISCUSSION

The ring-opening and ring-closing photoisomerization of diarylethenes is illustrated in Scheme 1. Upon irradiation with UV light (254 nm), the ring-open isomers underwent photocyclization to ring-closed isomers. The absorption spectra also changed during photocyclization. Figure 1 represents the absorption changes of **1a** with UV light irradiation. The absorption of **1a**, appearing at λ_{max} = 314 nm, decreased and two main absorptions at 542 nm and 345 nm, corresponding to **1b**, appeared and increased until the photostationary state was reached. The clear isosbestic point showed that the photo-conversion occurred between **1a** and **1b**,



Scheme 3. Synthesis of diarylethenes **1a–6a**

and the photocyclization process was accompanied by a color change of the solution from colorless to purple. Upon irradiation with visible light, the purple solution was bleached back to colorless solution. Similar results were obtained when the solution of diarylethenes **2a** and **3a** was irradiated with UV light, and their absorption data are summarized in Table 1.

The fluorescence of **1a** in acetonitrile showed that the emission of **1a** was at $\lambda_{em} = 445$ nm with 315 nm excitation wavelength, and a moderate fluorescence quantum yield of $\varphi_f = 0.25$ (in CH_3CN) was obtained by using quinine sulfate ($\varphi_f = 0.58$, in H_2SO_4) as a reference. The fluorescence of **1a** was decreased when it photo-converted to **1b**, and the fluorescence of **1a** was completely quenched when the solution of **1a** was irradiated with 254 nm light to the photo-stationary state (Fig. 2). No fluorescence was detected when the solution of **1b** was excited with 545 nm excitation wavelength. The fluorescence quench of **1b** is due to the efficient energy transfer between the excited fluorescent chromophore unit and the ring-closed diarylethene unit. A similar result was obtained when the solution of **2a** was excited with $\lambda_{ex} = 316$ nm wavelength excitation.

Table 1. Absorption and fluorescence data of diarylethenes **1a–3a** and **3a-H** in CH_3CN solvent

Compound	λ_{max} (nm)	λ_{max} (nm)	λ_{em} (nm)	φ_f	Color
	(Open isomer)	(Closed isomer)	(Open isomer)	(Open isomer)	(Closed isomer)
1a/1b	314	542	445	0.25	purple
2a/2b	316	560	428	0.10	blue
3a/3b	338	648	448	0.002	green
3a-H$^+$	348	—	408	0.10	—

It is noteworthy that no fluorescence was detected when the solution of **3a** was excited with $\lambda_{ex} = 350$ nm wavelength excitation. This is probably because the twist intramolecular charge transfer of **3a** was formed in excited state, which resulted from a strong electro-donating group (NEt_2) in the bridge unit. The suggestion was confirmed by protonation of **3a** in a solution with the addition of acid (CF_3COOH). The twist intramolecular charge transfer of **3a** in the excited state was dismissed when the strong electron-donating group (NEt_2) was changed to a strong electron-acceptor group (HN^+Et_2) with the addition of acid, and protonated **3a-H**$^+$ showed fluorescence emission (Fig. 3). Further investigation found that protonated **3a-H**$^+$ showed no photocyclization reaction with UV light irradiation. The photocyclization of diarylethene was probably inhibited by the strong electron-acceptor group in the bridge moiety unit.

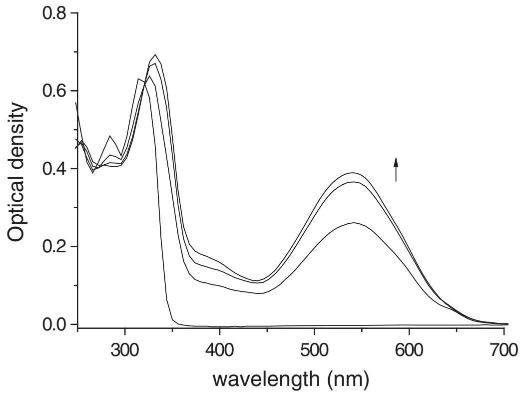


Figure 1. Absorption changes of **1a** (25 μM, CH_3CN) upon irradiation with 254-nm light (irradiation time periods: 0, 15, 30, 45 s)

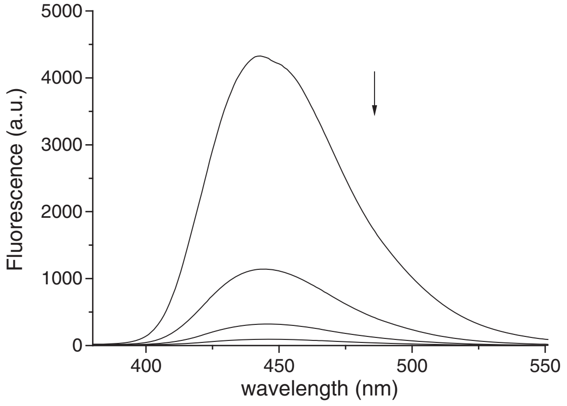


Figure 2. Fluorescence changes of **1a** (25 μM, CH_3CN, $\lambda_{ex} = 315$ nm) upon irradiation with 254-nm light (irradiation time periods: 0, 15, 30, 45 s)

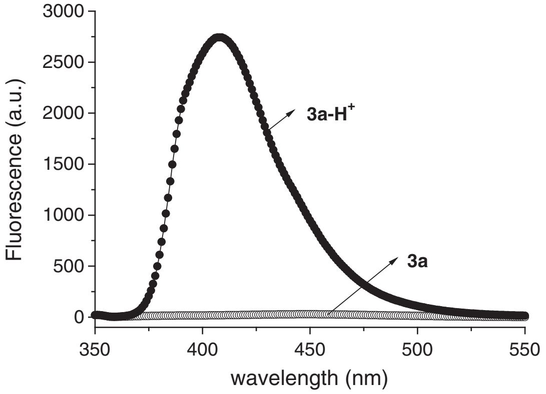


Figure 3. Fluorescence emission of **3a** and **3a**-**H**$^+$ (λ_{ex} = 350 nm, in CH_3CN)

The fluorescence data of **1a–3a** together with **3a**-**H**$^+$ are summarized in Table 1.

Control experiments were performed by using diarylethenes **4a–6a** as analogues (Scheme 3) to compare absorption and fluorescence of diarylethenes with and without intramolecular hydrogen bond. It was found that diarylethenes **4a–6a** exhibited photochromic properties with UV–Vis light irradiation, and their absorption and fluorescence data are listed in Table 2. Comparing the absorption of **4b** with that of **1b**, we found that a blue-shift of 26 nm was obtained when the OH group was replaced by the OCH_3 group, which suggested that the intramolecular hydrogen bond promoted the red-shift of the colored isomer probably because of strong intramolecular charge transfer resulting from co-planarity. This suggestion was confirmed by the comparison of absorptions of **5b** and **6b** with that of **2b** and **3b**, both a blue-shift of 28 nm (**5b**) and 40 nm (**6b**), respectively, were obtained when the OH group was replaced by the H group. Further investigation found that intramolecular hydrogen bonding is beneficial to the fluorescence emission of diarylethenes. As presented in Table 2, the fluorescence of diarylethenes was significantly decreased when the OH group was replaced by the OCH_3 group or by the H group.

CONCLUSIONS

We have developed a kind of photochromic diarylethene with an intramolecular hydrogen bond in an ethene bridge. It was demonstrated that intramolecular hydrogen bonding in the ethene bridge has a great influence on both the absorption and fluorescence of diarylethenes. The color change of diarylethenes in a wide range can be achieved by simple modification of the electronic properties of substituents in the bridge moiety. Compared with diarylethenes without intramolecular hydrogen bonding, diarylethenes bearing intramolecular hydrogen bonding in the ethene bridge show strong fluorescence emission. This may provide a simple and efficient strategy for designing photochromic diarylethenes with fluorescence emission and distinguished color change in the visible light region.

Table 2. Absorption and fluorescence data of diarylethenes **4a/4b–6a/6b** in CH_3CN solvent

Compound	λ_{max} (nm)	λ_{max} (nm)	λ_{em} (nm)	φ_f	Color
	(Open isomer)	(Closed isomer)	(Open isomer)	(Open isomer)	(Closed isomer)
4a/4b	310	516	384	0.009	red
5a/5b	294	532	408	0.006	purple
6a/6b	320	608	393	0.001	blue

Acknowledgements

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