The Photochromism and Fluorescence of Diarylethenes with a Imidazole Bridge Unit: A Strategy for the Design of Turn-on Fluorescent Diarylethene System

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A class of diarylethenes with a imidazole bridge unit has been synthesized and shows photochromic properties with UV/vis light irradiation. It is found that electronic properties of substituent in the imidazole bridge unit have a great effect on both photochromism and fluorescence of diarylethenes because of intramolecular charge transfer. Both "turn-on" and "turn-off" fluorescent diarylethenes systems can be achieved by simple modification of molecular structure and electronic properties of substituent, which provides a strategy for the design of new fluorescent diarylethene systems to be used as switches.

1. Introduction

Diarylethenes are one class of the most important photochromic compounds for photoelectronic applications.[1] The 1,2-bis(thien-3-yl) system containing perfluorocyclopentene[2] and cyclopentene[3] units (Figure 1) is well-known as the most popular and investigated class of photochormic diarylethenes. Many studies on the photochromism and photoswitching properties of diarylethene derivatives have focused on the substituent in the thiophen moiety.[4−6] In such a molecule system, both substituents (R) in the two-thiophene moiety are usually designed to be same due to the synthetic protocol, and the same electronic properties (electron-donator or electron-acceptor) of the substituents allow diarylethenes to form D-π-D or A-π-A molecular systems (D = donator, A = acceptor) instead of so-called "push-pull" (D-π-A) systems. Therefore, the electronic properties of the substituent have no significant effect on the photochromic behavior of diarylethenes, and the marked changes of photochromism of diarylethenes mainly resulted from the extent of π-conjugation of the thiophene moiety.

Fluorescent photochormic diarylethenes have attracted considerable attention during recent years because they afford promising optoelectronic devices such as molecular switches[7] and optical memories.[8] The 1,2-bis(thien-3-yl) fragment has no emission, a fluorescent diarylethene is usually prepared by attaching covalently a fluorescent group to diarylethene molecule. In most instances,[9] the system shows turn-off fluorescence: ring-open isomers exhibit fluorescence, but the fluorescence is quenched during the photocyclization of diarylethenes, and ring-closed isomers have no or very weak fluorescence because of efficient energy transfer between the excited fluorescent chromophore group and the ring-closed diarylethene fragment.[10] Up to now, no one diarylethene system that shows turn-on fluorescence (the fluorescence is increased during photocyclization of diarylethenes) has been reported.

Recently, photochromic diarylethenes with a different bridge unit have been successfully developed for the photomodulation of chemical reactivity[11] and exhibit near-infrared photochromic behavior.[12] In this paper, we report a kind of photochromic diarylethene system containing a imidazole bridge unit (Figure 2). Because of π-conjugation between the imidazole bridge unit and the thiophene moiety, the "push-pull" molecular system is produced by introducing different substituents in the imidazole bridge unit, which exhibits intramolecular charge transfer. It is well-known that electron transfer or charge transfer has great influenced on absorption[13] and fluorescence[14] of molecules. Then, by modifying the molecular structure and electronic properties of the substituent, both turn-on and turn-off fluorescence of diarylethenes can be modulated and manipulated.

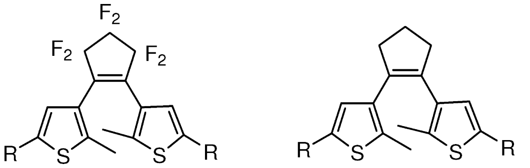
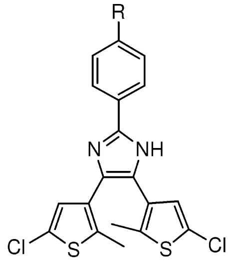


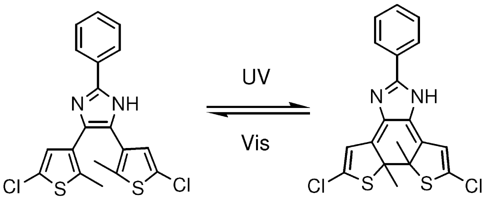
Figure 1. Diarylethenes with perfluorocyclopentene and cyclopentene units.



1a: R = H; **2a**: R = Cl; **3a**: R = OMe

Figure 2. Diarylethenes with a imidazole bridge unit.

SCHEME 1: Ring-Opening and Ring-Closing Photoisomerization of Diarylethene 1



1a **1b**

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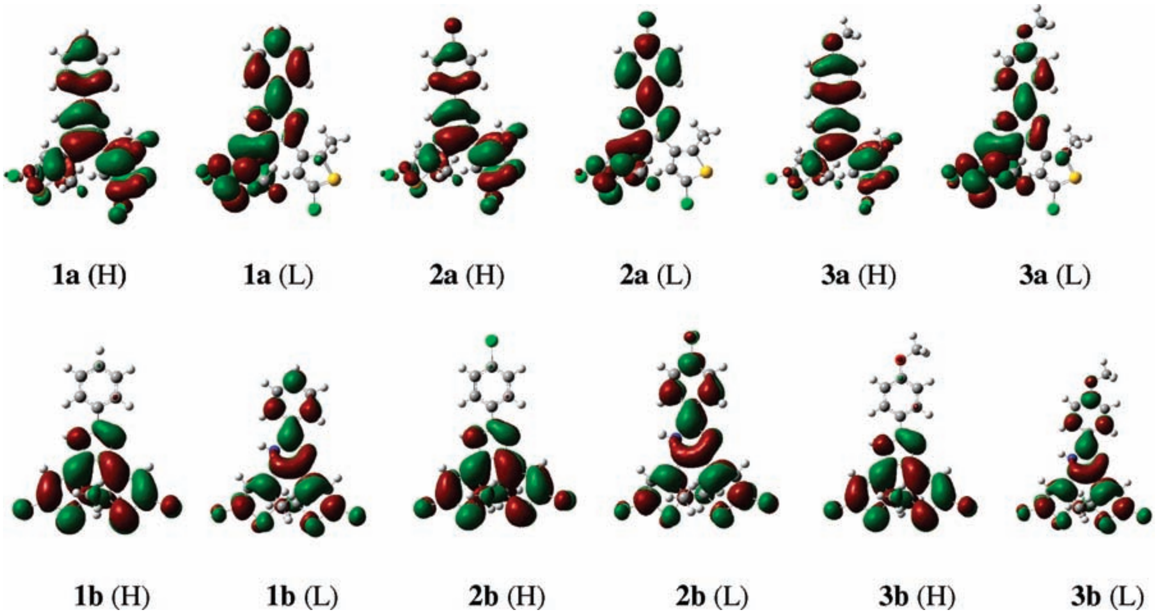

Figure 3. Optimized molecular structures and the HOMO (H) and LUMO (L) electron densities of **1**−**3** (**a**: open-isomer; **b**: closed isomer).

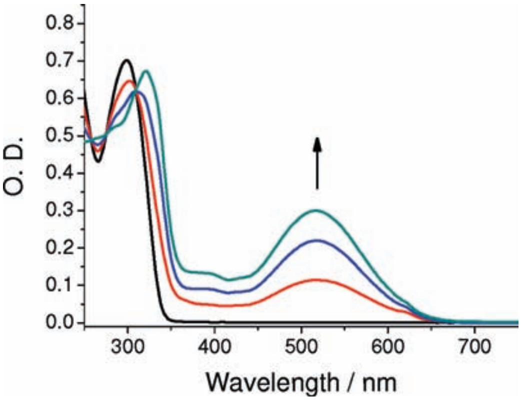

Figure 4. Absorption changes of **1a** (2.5×10^{-5} M, CH_3CN) with UV light irradiation.

TABLE 1: UV/Vis Data of Ring-Open Isomer (a) and Ring-Closed Isomer (b) of Diarylethene 1−3 in CH_3CN Solvent (λ_{max} nm)

isomers	1	2	3
A	298	309	295
B	322, 520	327, 516	337, 533

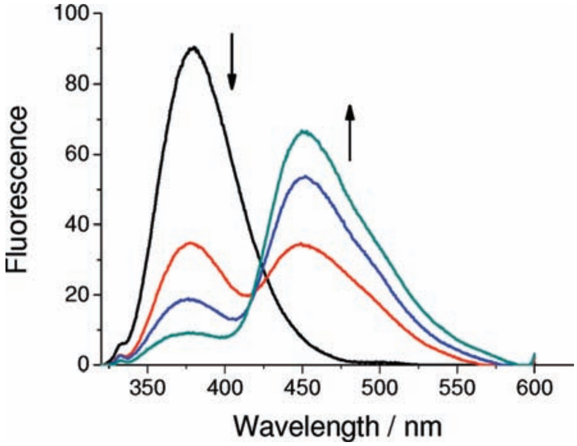

Figure 5. Fluorescence changes of **1a** (2.5×10^{-5} M, CH_3CN) with UV light irradiation ($\lambda_{ex} = 300$ nm).

2. Experimental Section

2.1. General Methods. ^1H NMR spectra were recorded at 400 MHz with TMS as an internal reference and DMSO-d_6 as solvent. HRMS spectra were recorded with a GC-TOF MS spectrometer. UV absorption spectra were measured with an absorption spectrophotometer (Hitachi U-3010). All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reactions were monitored by TLC silica gel plate (60F-254). Column chromatography was performed on silica gel (Merck, 70−230 mesh). A low-pressure mercury lamp (30 W) and a Xeon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.

2.2. General Procedure and Characteristic Data of Compounds 1a−3a. Target compounds **1a**−**3a** were prepared according to the synthetic route presented in Scheme 1. Diketone was obtained starting from commerically avaliable 2-methylthiophene, which was chlorinated at the 5-position with NCS in AcOH,[15] followed by acylation with oxalyl chloride in DCM. Treatment of diketone in acetic acid with substituted benzaldehyde in the presence of NH_4Ac afforded target compounds **1a**−**3a** in yields of 60−70%. The details of the procedures for **1a**−**3a** are as follows: To a solution of diketone (100 mg, 0.31 mmol) in acetic acid (10 mL) was added substituted benzaldehyde (0.37 mmol) and NH_4Ac (143 mg, 1.86 mmol), then the mixture was heated at reflux until the starting material disappeared (TLC detection). The mixture was then slowly poured into $NaHCO_3$ solution (10%, 50 mL) and the product was extracted with $CHCl_3$ (3×20 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 **1a**−**3a**.

1a: yield 61%; ^1H NMR (DMSO-d_6) δ 12.72 (s, 1H), 8.02 (d, $J = 7.5$ Hz, 2H), 7.47 (t, $J_1 = 7.4$ Hz, $J_2 = 7.7$ Hz, 2H), 7.38 (t, $J_1 = 7.2$ Hz, $J_2 = 7.3$ Hz, 1H), 7.12 (s, 1H), 6.81 (s, 1H), 2.21 (s, 3H), 2.02 (s, 3H); HRMS (GC-TOF) (m/z) calcd for $C_{19}H_{14}Cl_2N_2S_2$ 405.9640, found 405.9640 (100%). Anal. Calcd for $C_{19}H_{14}Cl_2N_2S_2$: C, 56.29; H, 3.48. Found: C, 56.62; H, 3.54.

2a: yield 60%; ^1H NMR (DMSO-d_6) δ 12.79 (s, 1H), 8.01 (d, $J = 8.6$ Hz, 2H), 7.54 (d, $J = 8.6$ Hz, 2H), 7.10 (s, 1H),

TABLE 2: Fluorescence Data of Ring-Open Isomer (a) and Ring-Closed Isomer (b) of Diarylethene 1−3 in CH_3CN Solvent (λ_{max} nm)

compd	$^a\lambda_{em}$	$^a\phi_f$	$^b\lambda_{em}$	$^b\phi_f$
1	381	0.017	452	0.014
2	390	0.114	449	0.009
3	378	0.002	489	0.130

6.79 (s, 1H), 2.19 (s, 3H), 2.00 (s, 3H); HRMS (GC-TOF) (*m*/*z*) calcd for $C_{19}H_{13}Cl_3N_2S_2$ 439.9261, found 439.9261 (100%). Anal. Calcd for $C_{19}H_{13}Cl_3N_2S_2$: C, 51.89; H, 2.98. Found: C, 52.56; H, 3.04.

3a: yield 73%; ^{1}H NMR (DMSO-d_6) 12.54 (s, 1H), 7.95 (d, *J* = 8.6 Hz, 2H), 7.10 (s, 1H), 7.05 (d, *J* = 8.7 Hz, 2H), 6.81 (s, 1H), 3.81 (s, 3H), 2.19 (s, 3H), 2.01 (s, 3H); HRMS (GC-TOF) (*m*/*z*) calcd for $C_{20}H_{16}Cl_2N_2OS_2$ 435.9602, found 435.9602 (100%). Anal. Calcd for $C_{20}H_{16}Cl_2N_2OS_2$: C, 55.17; H, 3.70. Found: C, 55.67; H, 3.64.

2.3. Molecular Orbital Calculations. The optimized structure of the diarylethene molecule was calculated at the density functional theory (DFT) level with the hybrid B3LYP functional[16] and the 6-31G basis set. The energy levels and the electron densities of the HOMO and LUMO were calculated with the Gaussian 03 package.

3. Results and Discussion

3.1. Molecular Orbital Calculations. Optimized structures of both ring-opening isomers and ring-closing isomers of **1−3** are shown in Figure 3. It is found that **1−3** have similar structures with both ring-opening isomers and ring-closing isomers and they showed typical configurations of diarylethenes with 1,2-bis(thien-3-yl) systems. The electron densities of both HOMO and LUMO with ring-opening isomers are different from those with ring-closing isomers. With ring-opening isomers, the electron densities of HOMO localize on the whole molecule and LUMO localize on one side, which corresponds to the distribution of the electron in the charge-separated state. By contrast, the electron densities of HOMO localize on the second half of the molecule and LUMO localize on the whole molecule with ring-closing isomers, which also corresponds to the distribution of the electron in the charge-separated state.

3.2. Photoisomerization of Photochromic Diarylethenes. The two isomers **1a** (ring-open isomer) and **1b** (ring-closed isomer) undergo photoisomerization with UV/vis light irradiation as illustrated in Scheme 1. The absorption band of **1a** in CH_3CN appeared at 300 nm ($\varepsilon = 2.8 \times 10^4$). Upon irradiation with UV light, the colorless solution of **1a** was converted into a purple solution of **1b** with two absorption bands at 520 and 325 nm (Figure 4). **1b** could be bleached back to **1a** with visible light (≥400 nm), resulting in the color change of the solution from purple to colorless. Similar results were obtained when the solutions of other diarylethenes **2a−3a** in CH_3CN were irradiation with UV/vis light. Their absorption changes with UV/vis light irradiation.

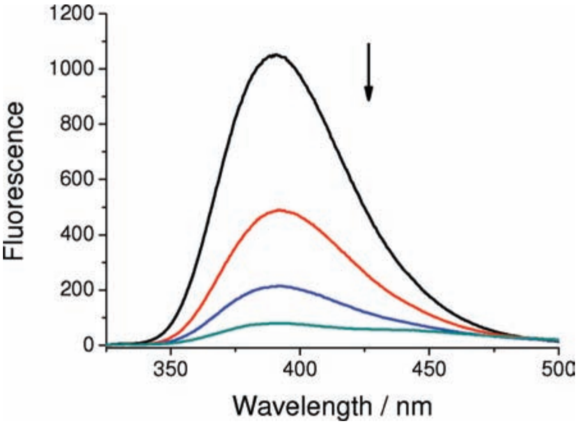

Figure 6. Fluorescence changes of **2a** (2.5×10^{-5} M, CH_3CN) with UV light irradiation (λ_{ex} = 300 nm).

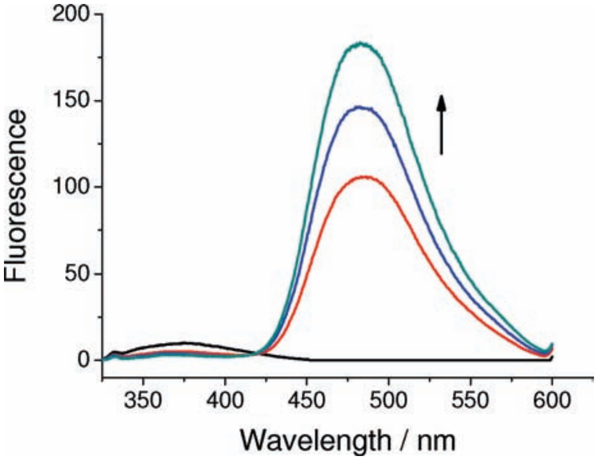

Figure 7. Fluorescence changes of **3a** (2.5×10^{-5} M, CH_3CN) with UV light irradiation (λ_{ex} = 300 nm).

3.3. The Influence of Electronic Properties of Substituent in the Bridge Unit on the Absorption of Diarylethenes. The UV/vis data of diarylethenes **1−3** were listed in Table 1. Comparing the absorption of both ring-open isomers and ring-closed isomers of **2** and **3** with those of **1** found the following interesting results. First, by comparison of the ring-open isomer of **1a**, **2a** was red-shifted ($\Delta\lambda$ = 11 nm) but **3a** was blue-shifted ($\Delta\lambda$ = 3 nm). Second, by comparison of the ring-closed isomer of **1b**, **2b** was blue-shifted ($\Delta\lambda$ = 4 nm) but **3b** was red-shifted ($\Delta\lambda$ = 13 nm). The results showed that substituents with different electronic properties (donor or acceptor) produced intramolecular charge transfer and formed a push-and-pull system, which resulted in the decrease of energy in the ground state and the absorption shift to long wavelength.

3.4. The Influence of the Electronic Property of Substituent in the Bridge Unit on the Fluorescence of Diarylethenes. The fluorescence change of **1a** in solution with UV light irradiation was presented in Figure 5. Upon excitation of **1a** in CH_3CN solution with 300 nm excitation wavelength, **1a** exhibited emission at 381 nm, and a small fluorescence quantum yield (ϕ_f = 0.017) was obtained by using coumarin 307 (ϕ_f = 0.58, in CH_3CN) as a reference. The fluorescence of **1a** quenched during photocyclization of **1a** to **1b** and a new emission at 452 nm with ϕ_f = 0.014 appeared at the same time, which was attributed to the emission of **1b** (the emission at 452 nm was also obtained by excitation of **1b** with 325 nm excitation wavelength). This is the first time it has been observed that the fluorescence increased (turn-on) during photocyclization of diarylethene. More interesting results were obtained by investigation of the fluorescence of **2a** and **3a**. It is found that the fluorescence of diarylethenes is quite different with different substituents. When the substituent in the bridge unit changed from H to Cl, the ϕ_f of **2a** increased (0.114), but the ϕ_f of **2b** decreased (0.009). On the contrary, when the substituent in the bridge unit changed from H to OCH_3, the ϕ_f of **3a** decreased (0.002), but the ϕ_f of **3b** increased (0.13) (Table 2). Moreover, the emission bands of both ring-open isomer and ring-closed isomer were 12 nm blue-shifted and 40 nm red-shifted, respectively, when theh substituent in the bridge unit changed from Cl to OCH_3 (Figures 6 and 7). These results also indicated that intramolecular charge transfer has a great effect on the fluorescence of diarylethenes, and both "turn-on" and "turn-off" fluorescence of diarylethenes can be modulated and manipulated by simple modification of molecular structure and electronic properties of the substituent.

4. Conclusions

We have developed a kind of diarylethene with a "push-pull" system in which intramolecular charge transfer has great influence on both photochromism and fluorescence of diarylethenes. Both "turn-on" and "turn-off" fluorescence during photocyclization of diarylethenes can be achieved by simple modification of molecular structure and electronic properties of the substituent in the bridge unit. By adjusting a suitable push−pull system, significant changes of absorption and strong fluorescence of diarylethene can be obtained. This study may offer insights into the link between molecular structures and functional properties and provide a new strategy for the design of fluorescent diarylethenes to be used as molecular switches.

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