Combination of fluorescent switch and electrochemical switch based on a photochromic diarylethene†

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A new photochromic diarylethene with oligothiophene side arm substituents has been synthesized. This diarylethene undergoes excellent photoisomerization with UV/Vis light irradiation, and shows fluorescence emission and electrochemical behavior. Both the fluorescence emission and oxidation/reduction potential are reversible based on the ring-opening and ring-closing photoisomerization of diarylethene with UV/Vis light irradiation, which may be used as a fluorescent and electrochemical switch. In addition, a combination of photochromism and electrochromism is observed for the diarylethene: the ring-closing reaction can be triggered by electrochemical oxidation while the ring-opening reaction must be photochemically driven.

Introduction

Efficient light-driven molecular switching materials are targets of increasing interest for electronics and optical memory devices.[1] The current interest in miniaturizing the components of machinery and electronics down to the molecular level is a major impetus to developing molecular systems that display switchable properties.[2] One key aspect in the progress of molecular switching technology is the development of more complex systems that integrate several switchable functions into a single molecule.

Photochromic diarylethenes exhibit reversible variations in their physicochemical properties when stimulated by light and are amongst the most promising candidates for photoelectronic applications such as memory and switching because of their thermally-irreversible and fatigue-resistant photoisomerization performances.[3] Changes in spectroscopy,[4] refractive index,[5] oxidation/reduction potential,[6] magnetic properties[7] and chiroptical properties[8] based on photoisomerization of diarylethenes have been studied widely because they can be potentially applied to molecular switch devices. A few impressive examples of multi-addressable switching systems have been reported recently,[9] which are focused on changes of absorption bands and fluorescence emission. Examples of dual- or multifunctional switching systems based on a single photochromic diarylethene molecule have, however, been reported rarely.

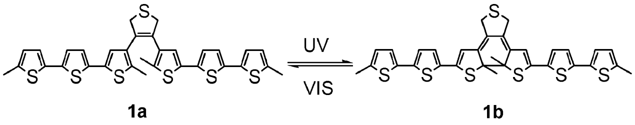
Herein, we present a multifunctional switch of a photochromic diarylethene with oligothiophene substituents, **1a** (Scheme 1), based on its photoisomerization properties. It was found that both fluorescence and electrochemical properties of diarylethene **1a** are reversible, induced by ring-opening and ring-closing photoisomerization of the molecule upon UV/Vis irradiation.

Besides, it was also observed that the cyclization reaction of the diarylethene from the ring-opened isomer **1a** to the ring-closed isomer **1b** could be triggered not only by photoirradiation but also by electrochemical oxidation. The main advantages of such a molecular switching system are: (1) multifunctionality: the system can be used not only as a fluorescent switch but also as an electrochemical switch; (2) miniaturization: fluorescence and electrochemical switching are integrated into a single molecule; and (3) photon mode system: the system benefits from the fast response time and the ease at which monochromatic light can be tuned and focused when it is used as the switching stimulus.

Experimental

General

^{1}H and ^{13}C NMR spectra were recorded at 300 MHz with TMS as an internal reference and $CDCl_3$ as solvent. Mass spectra were recorded with a Trio-2000 GC-MS spectrometer. UV absorption spectra and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (F-2500), respectively. All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reactions were monitored using TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). A low-pressure mercury lamp (30 W) and a Xenon light (500 W), with different wavelength



Scheme 1 Structure of diarylethene **1a** and its photoisomerization upon UV/Vis irradiation.

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filters, were used as light sources for photocoloration and photobleaching, respectively.

Electrochemistry

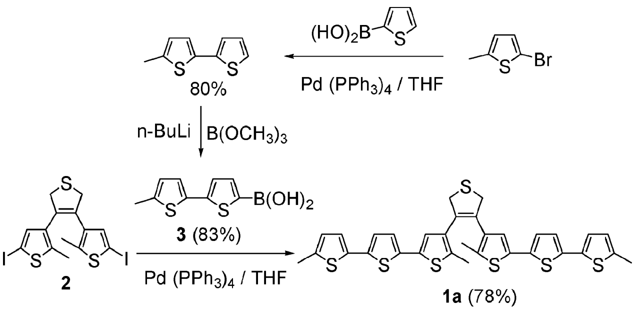
Electrochemical cyclic voltammetry experiments were performed in a three electrode single-compartment cell using a platinum disk working electrode, a platinum wire counter electrode and a Ag/AgCl reference electrode. Typically, the electrochemical reaction vessel was charged with 4–5 ml of an acetonitrile solution of the photochromic compound (1×10^{-3} M) and tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte. The solutions were deoxygenated by bubbling nitrogen through them for approximately 15 minutes. All results were referenced against ferrocene (0.4 V *vs.* SCE).

Materials

Diarylethene **1a** was synthesized according to the synthetic route presented in Scheme 2, and the detailed procedures and spectral data are presented as ESI.† 5-Methyl-2,2′-bithiophene-5′-boronic acid **3** was obtained from 2-methyl-5-bromothiophene,[10] which was coupled with thiophene-2-boronic acid by a Suzuki coupling reaction in THF, followed by boronation with *n*-BuLi and $B(OCH_3)_3$ in THF. 3,4-Bis(5-iodo-2-methylthien-3-yl)-2,5-dihydrothiophene **2**,[11] which was synthesized by our laboratory before, was coupled with **3** in THF using $Pd(PPh_3)_4$ as the catalyst to afford the target compound 3,4-bis[5-(5′-methyl-2,2′-bithiophene)-2-methylthien-3-yl]-2,5-dihydrothiophene **1a** in 78% yield.

Results and discussion

The ring-opening and ring-closing isomerization of the diarylethene with oligothiophene substituents upon UV/Vis irradiation is illustrated in Scheme 1. Upon irradiation with UV light, the absorption band (λ_{max} = 365 nm, $\varepsilon = 9.5 \times 10^3$ in CH_3CN), which is attributed to the ring-opened isomer **1a**, decreased in intensity, and a new band (λ_{max} = 595 nm), which was assigned to the ring-closed isomer **1b**, appeared at the same time (Fig. 1); this process was accompanied by a color change of the solution from colorless to green-blue. The photostationary state (**1PSS**) was reached only after 1 minute of irradiation of **1a** (2×10^{-5} M, 30 W UV light) and the conversion was *ca.* 90%. The green-blue solution could be bleached completely back to a colorless solution under visible light (≥ 450 nm) irradiation for 10 minutes, and the original absorption spectrum was recovered quantitatively.



Scheme 2 Synthetic route to diarylethene **1a**.

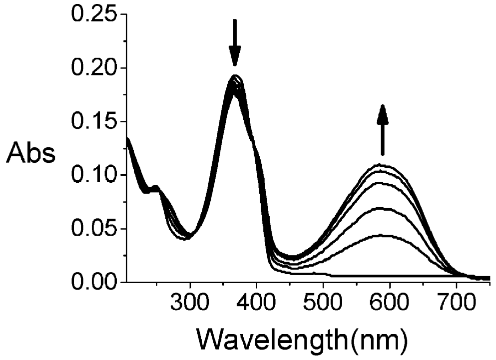


Fig. 1 Absorption changes of diarylethene **1a** (2×10^{-5} M, CH_3CN) upon irradiation at 360 nm (irradiation periods are 10, 20, 30, 40, and 50 s).

The fluorescence emission changes of **1a** are presented in Fig. 2. Upon excitation at 380 nm, **1a** exhibited a fluorescent emission (λ_{em} = 457 nm in CH_3CN), and the fluorescence quantum yield (ϕ_f = 0.028), which is rather small but high enough to be detected, was calculated by using fluorescein (ϕ = 0.90) as the reference. As shown in Fig. 2, the fluorescence intensity of **1a** decreased upon irradiation at 360 nm until the photostationary state **1PSS** was reached, the ratio of fluorescence intensities for **1a** and **1PSS** being 5 : 1. The original emission spectrum could be recovered completely when the solution of the photostationary state was bleached by visible light (≥ 450 nm) irradiation. It is worth noting that no emission of **1b** was detected at longer wavelength excitation (λ_{ex} = 600 nm), which probably results from an efficient energy transformation from the excited 2-substituted bithiophene unit to the ring-closed dithienylethene units, because of spectral overlapping of the emission band of **1a** with the absorption band of **1b**. Besides, it was found that fluorescent switching between the ring-opened isomer and the photostationary state performed well and a very small decrease in fluorescence intensity (*ca.* 5%) was detected after 10 cycles in solution.

Electrochemical properties of **1a** and **1b** were investigated by cyclic voltammetry. Fig. 3 shows cyclic voltammograms of **1** in CH_3CN (1×10^{-3} M) containing tetrabutylammonium tetrafluoroborate (0.1 M) at 50 mV s^{-1}. It was found that the oxidation and reduction potentials of **1a** are E_{ox} = 1.05 V and

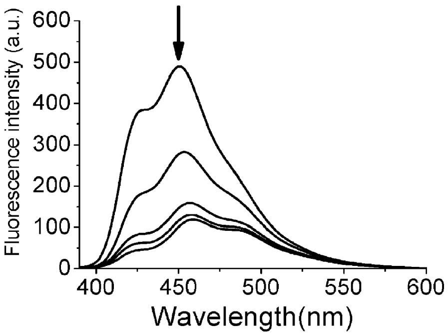


Fig. 2 Fluorescence changes of diarylethene **1a** (2×10^{-5} M, CH_3CN) upon irradiation at 360 nm (irradiation periods were 10, 20, 30, 40, and 50 s), λ_{ex} = 380 nm.

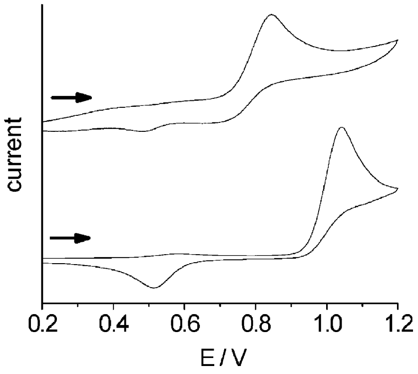
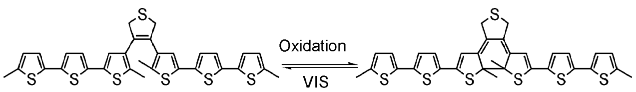


Fig. 3 Cyclic voltammograms of **1a** (bottom) and **1b** (top) in CH_3CN solution (1×10^{-3} M) at 50 mV s^{-1}.

E_{red} = 0.52 V, respectively. After 1 h of irradiation, the photostationary state was reached and was composed of more than 80% of the ring-closed isomer.

The oxidation and reduction potentials of **1b** are E_{ox} = 0.85 V and E_{red} = 0.45 V, respectively. The 0.2 V shift of oxidation potential indicates that the communication extending throughout each thiophene unit of the ring-closed isomer **1b** was more than that of the ring-opened isomer **1a**. Upon subsequent irradiation with light (≥ 450 nm) for 1 h, the cyclic voltammogram changed back to that observed for the ring-opened isomer **1a**. It was found that electrochemical switching between **1a** and **1b** performed well and no significant change was detected after 10 cycles in solution under UV/Vis irradiation (see Fig. 1S in ESI).† The clear difference in oxidation potentials between **1a** and **1b** and the observed reversibility upon UV/Vis irradiation suggests that diarylethene **1a** can be used as an electrochemical switch.

Besides photochromism, electrochromism was also observed with the ring-closing of diarylethene **1a** during electrolysis. It was found that the colorless solution of **1a** around the platinum electrode changed to green-blue during the cyclic voltammetry experiments. This indicates that the ring-opened isomer **1a** underwent oxidative cyclization to produce ring-closed isomer **1b**, although no marked changes in the absorption spectra were detected because of the too small amount of **1b** in solution. The green-blue solution of **1PSS**, which was obtained from the conversion of **1a** under UV light irradiation was, however, not decolorized back to a colorless solution during the electrolysis, suggesting that the ring-closed isomer **1b** cannot undergo oxidative cycloreversion. It has been reported[12] recently that there are two possible reactions involved in the oxidation of diarylethene derivatives: oxidative cyclization of the ring-opened isomers and oxidative cycloreversion of the ring-closed isomers, and these two cases can be distinguished from the energies of the radical cations of the ring-opened and ring-closed isomers. In our experiments, diarylethene **1a** underwent only oxidative cyclization, suggesting that the cation radical of the ring-closed isomer, $\mathbf{1b}^{+\bullet}$, is more stable than that of the ring-opened isomer, $\mathbf{1a}^{+\bullet}$, and the oxidative cyclization is thermodynamically allowed. The combination of photochromism and electrochromism of diarylethene **1a** is illustrated in Scheme 3.



1a **1b**

Scheme 3 Photoelectrochromism of diarylethene **1a**.

Conclusions

A diarylethene with oligothiophene substituents has been synthesized and its photochromic and photoswitching properties have been presented. It is demonstrated that this diarylethene with two oligothiophene side arms exhibits both fluorescent and electrochemical switching properties, based on a UV/Vis irradiation-induced photoisomerization reaction. A combination of photochromic and electrochromic properties was also observed; the ring-opened isomer undergoes oxidative cyclization, while the ring-closed isomer undergoes photochemical cycloreversion. This new system demonstrates that a multifunctional switch can be achieved with a single molecule.

Acknowledgements

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