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Carbon dioxide and water as a key for unlocking photochromism of diarylethene derivative

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ABSTRACT

A photochromic diarylethene derivative with 4-(ethylideneamino) phenol group (**1a**) is prepared, and **1a** exhibits ring-opening and ring-closing photoisomerization with UV/vis light irradiation in solution. Addition of base to both solution of ring-open isomer **1a** and ring-closed isomer **1b** produces deprotonated compounds **2a** and **2b**, respectively, and both **2a** and **2b** are photo-inactive and no photochemical reaction is detected in solution in the absence of carbon dioxide and water. Both **2a** and **2b** are, however, converted back to **1a** and **1b** when the solution contains carbon dioxide and water, and photochromic reaction is recovered. This may provide a means to generate a gate for non-destructive readout. Meanwhile, the conversion between species is accompanied color change in a wide range by combination of photo-trigger and chemical trigger. The system endowed with multi-responsive functionality for multi-color change is beneficial for applications such as display and camouflage.

1. Introduction

Typical bistable molecules are the so-called photochromic compounds, which is defined as a reversible change induced by light radiation, between two states of a molecule having different absorption spectra [1]. Great interest is currently devoted to bistable molecules presenting two forms whose inter-conversion can be modulated by an external stimulus. Molecules with switchable properties are of considerable practical and fundamental interest as the development of robust systems will open up new avenues and possibilities for applications to drug delivery systems, optical devices and sensor.

Photochromic diarylethenes are one of the most promising candidates for photoelectronic applications because of their thermo-irreversible and fatigue-resistant photoisomerization performances [2,3]. A host of applications exist for photochromic diarylethenes that take advantage of their inherent ability to produce switches between two isomers by UV–vis photo-trigger [4–7]. Currently, development of diarylethenes that integrate several switchable functions into a single molecule are of considerable interest [8–10] due to miniaturize the components of machinery and electronic down to the molecular level. To reach these goals, it is essential to transform molecular structures between two or more states in response to external signals such as photonic [11–15], chemical [16,17], electrochemical [18,19], or magnetic [20,21] stimuli and to tailor readable output state. Although there are some impressive examples of multi-addressable switching systems, which composed of different kinds of photochromic diarylethenes, have been reported [22–24], multi-input/multi-output response systems with a photochromic diarylethene are reported rarely [25,26], they have attracted considerable attention from the viewpoint of potential applications in molecular sensing and switches. Since multi-input systems are prototypes of molecular-level logic operators [27,28], the addition of a multi-output response would endow such systems with the ability to act as parallel operating logic elements.

Destructive readout is main disadvantage of photochromic materials [29,30]. Photochromic reactions, in general, proceed in proportion to the number of photons absorbed the compounds. Such a linear-response characteristic cannot be used as the basis of memory media because information is destroyed after many readout operations. Several methods have been proposed to avoid the destructive readout of diarylethenes such as fluorescence [31–35], infrared absorption [36–38], and optical rotation [39–41]. These methods are demonstrated to be efficient to non-destructive readout, but the destructive readout cannot be dismissed completely because diarylethenes are photo-active material and have more or less two-photon or multi-photon absorption. One possible way for non-destructive readout is to introduce gated reactivity to diarylethene systems [42,43], in which diarylethenes are photo-inactive, therefore, the photochromic reaction was prohibited and the non-destructive readout was achieved completely.

In this paper, we design an artificial gated photochromic diarylethene system. It is found that the system exhibits pho-

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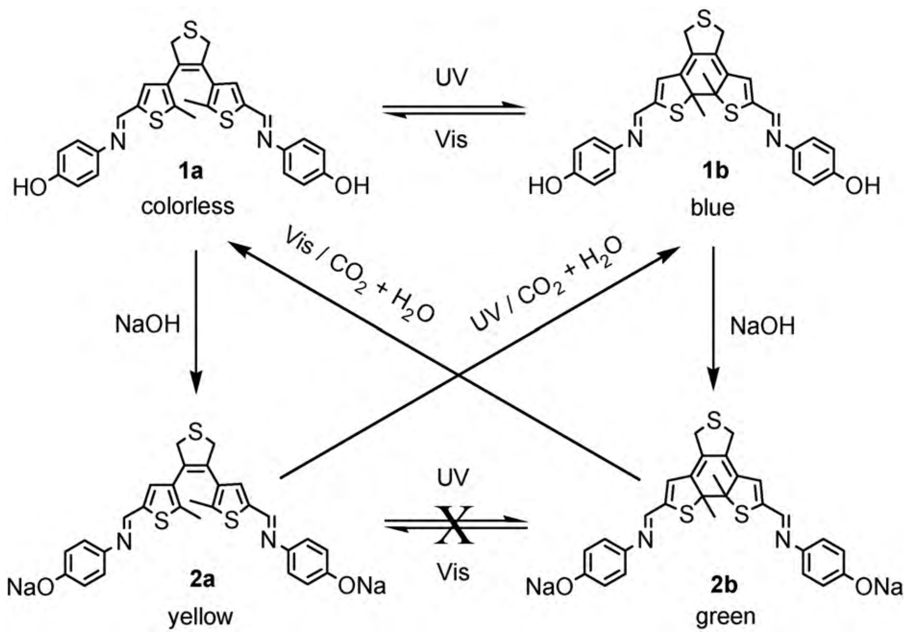


Scheme 1. Outline for the concept of inter-conversion and gated reactivity of photochromic diarylethene system.

tochromic reaction with UV/vis light irradiation. With addition of base, both ring-open isomer (**1a**) and ring-closed isomer (**1b**) converted to deprotonated compounds **2a** and **2b**, respectively. Both **2a** and **2b** are photo-inactive in absence of carbon dioxide and water, and the photoconversion between **2a** and **2b** is inhibited. In presence of carbon dioxide and water, both **2a** and **2b** are converted to **1b** and **1a**, respectively, with UV light and visible light irradiation. The inter-conversion and gated reactivity concept is outlined in Scheme 1.

2. Experimental

2.1. General methods

^{1}H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with TOF-MS spectrometer. 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. Reaction monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh). 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.

2.2. Chemical

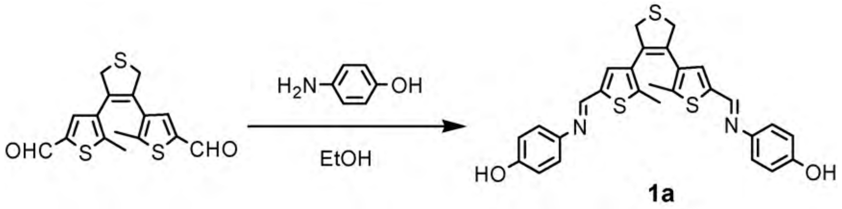
Diarylethene **1a** was prepared according to synthetic route shown in Scheme 2, and the detailed procedures and spectra data were as follows: a mixture of 3,4-bis(5-formyl-2-methylthien-3-yl)-2,5-dihydrothiophene [44] (100 mg, 0.3 mmol) and 4-aminophenol (72 mg, 0.66 mmol) in anhydrous ethanol (10 ml) was refluxed. After no starting material was detected by TLC plate, the mixture was cooled, and the yellow product was filtered off, washed with EtOH, pure diarylethene **1a** was obtained after vacuum drying. Yield: 45% (70 mg). M.p. = 210–211 °C. ^{1}H NMR (400 MHz, DMSO-d_6): 9.48 (s, 2H), 8.58 (s, 2H), 7.43 (s, 2H), 7.14 (d, 4H, J = 8.7 Hz), 6.76 (d, 4H, J = 8.7 Hz), 4.15 (s, 4H), 1.98 (s, 6H). ^{13}C NMR: 156.2, 149.8, 141.9, 139.9, 139.5, 134.3, 133.0, 132.7, 122.5, 115.7, 42.1, 14.6. TOF-MS EI (m/z) calcd. For $C_{28}H_{24}N_2O_2S_3$: 516.1000, found: 516.1000 (100%).

2.3. Measurement of the ratio of *1a* and *1b* at photostationary state

The ratio of **1a** and **1b** at photostationary state was measured by comparing the integral of proton of **1a** and **1b** in ^{1}H NMR spectroscopy. Partial ^{1}H NMR spectroscopy of both **1a** and photostationary state (PPS) is presented in Fig. 1.

3. Results and discussion

The ring-opening and ring-closing photoiosmerization of **1a** with UV/vis light are presented in Scheme 1. Upon irradiation with UV light, the absorption band (λ_{max} = 353 nm, ε = 4.6 × 10^4, in CH_3CN), which attributes to the ring-open isomer **1a**, decreased in intensity, and a new band (λ_{max} = 590 nm), which corresponds to the ring-closed isomer **1b**, appeared at the same time (Fig. 2). The band at 590 nm increased in intensity with the increase of irra-



Scheme 2. Synthesis of diarylethene **1a**.

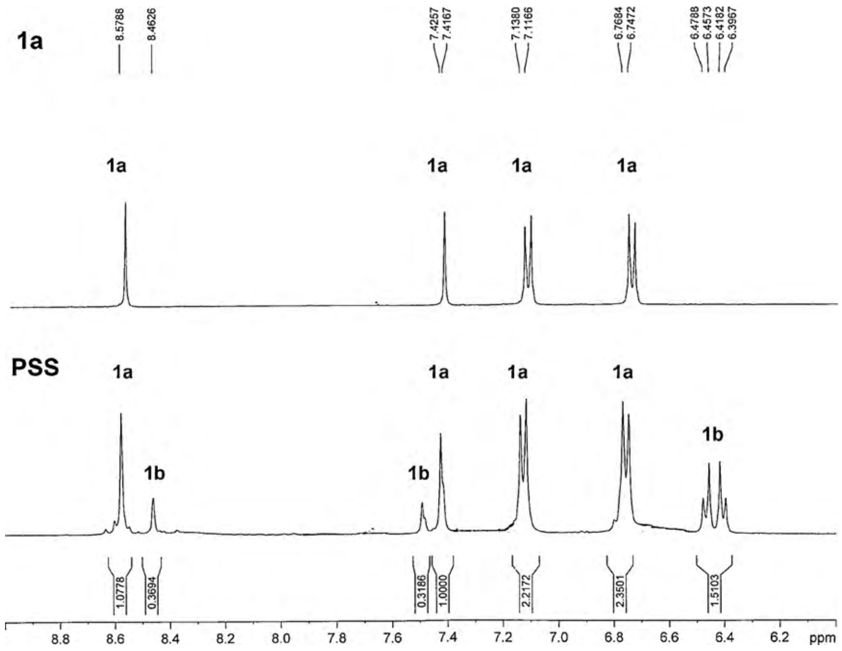


Fig. 1. Partial ^{1}H NMR spectroscopy of **1a** and photostationary state (PSS).

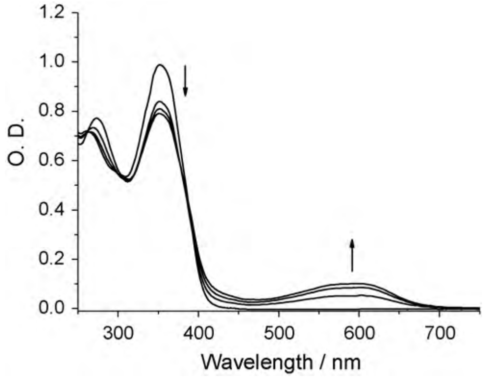


Fig. 2. Absorption change of diarylethene **1a** (25 μM, CH_3CN) with 365 nm light irradiation till to photo-trigger state (periods: 0, 2, 4, 6 min).

diation time till the photostationary state was reached, and the ratio of **1a** and **1b** at photostationary state is *ca.* 1.0:0.3 (see Section 2.3). This process was accompanied by a color change of solution from colorless to blue. As presented in Fig. 2, the figure showed the typical absorption spectra changes of photochromic diarylethene derivatives in solution, and the clear isobestic point indicated that only two isomers existed when the compound underwent the photoisomerization reaction. The blue solution was bleached completely back to colorless solution with visible light (≥400 nm) irradiation, and the coloration and decoloration can be repeated.

Addition of base (NaOH, 50 μM) to the solution of **1a** (25 μM) produced a deprotonated diarylethene **2a**, whose absorption was bathochromic shifted to 425 nm (Fig. 3a), resulting in the color change of solution from colorless to yellow. Similar result was obtained with ring-closed isomer **1b**: addition of NaOH (50 μM) to the solution of photostationary state (**1b** *ca.* 7.5 μM) produced a new absorption at 655 nm (Fig. 3b), which corresponded to ring-closed isomer **2b**. This process was accompanied by a color change of solution from blue to green.

Photoreaction of both **2a** and **2b** was investigated. It is found that both **2a** and **2b** are photo-inactive and no photoreaction was obtained when the solution of **2a** or **2b** was irradiated with UV light and visible light in absence of carbon dioxide and water (moisture). The prohibition of photoreaction of **2a** and **2b** are probably resulted from the large energy barriers between the ground states and photoexcited states due to very strong electron-donator of oxygen anion. The strong electron donation produced a large decrease of energy of **2a** and **2b** in ground states, which was confirmed by

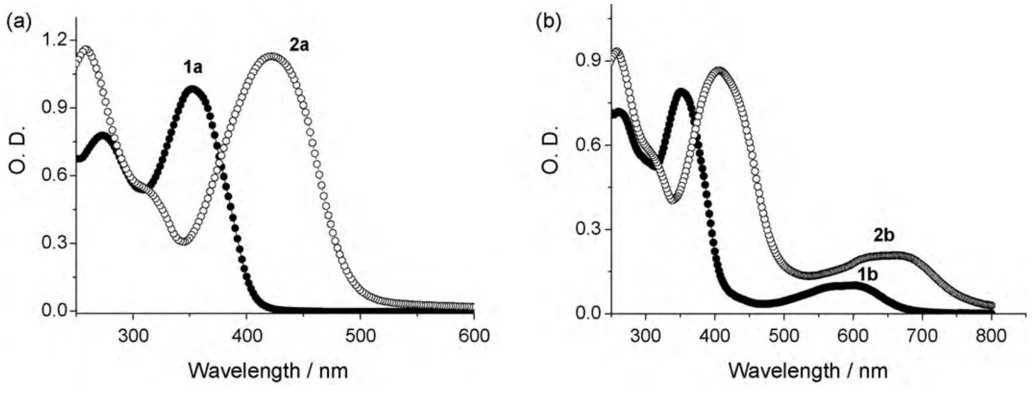


Fig. 3. Absorption change of deprotonation of **1a** (a) and **1b** (b) (25 μM, CH_3CN) with addition of NaOH (50 μM, MeOH).

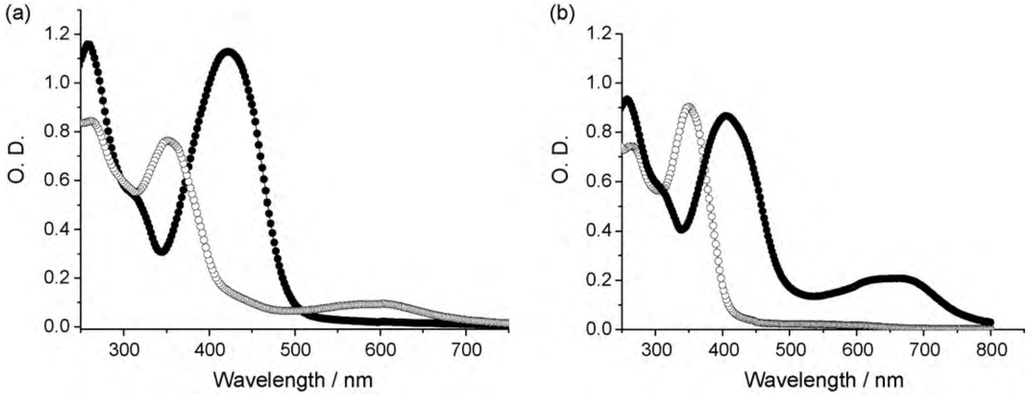


Fig. 4. Absorption change of **2a** (a) and **2b** (b) before (●) and after (○) irradiation with 365 nm light and visible light (λ ≥ 480 nm) till to photo-steady state, respectively.

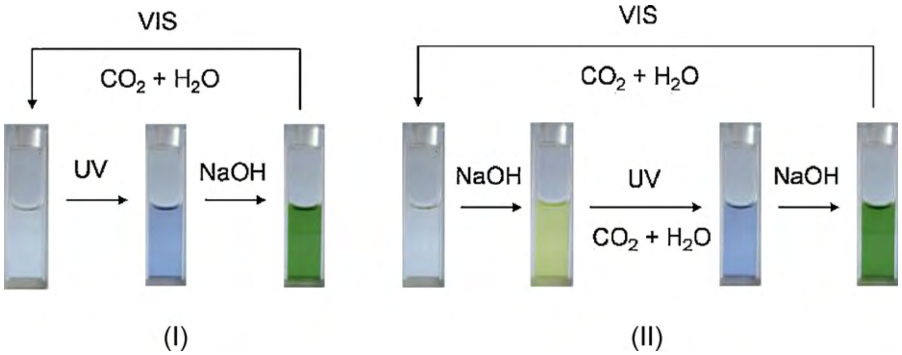


Fig. 5. Images of cascade color change patterns using photo-trigger and chemical trigger.

a large bathochromic shift (more than 60 nm) of **2a** and **2b**, and therefore it increased the energy gap between the ground states and excited states.

Interesting results were obtained when both solution of **2a** and **2b** with UV and visible light irradiation in presence of carbon dioxide and water (moisture). It is found that the absorption of **2a** at 425 nm was unexpectedly shifted to 590 nm upon irradiation with UV light, which is in accordance with absorption of **1b** (Fig. 4a). Similar results were obtained with solution of **2b**: upon irradiation with visible light, the absorption of **2b** at 655 nm hypochromic shifted to 353 nm, which corresponded to absorption of **1a** (Fig. 4b).

The mechanism and control experiments were also explored. It is known that sodium phenoxide can be converted to phenol in the presence of CO_2 and H_2O [45]. Based on this result, it is supposed that both **2a** and **2b** were converted to **1a** and **1b**, respectively, in the presence of CO_2 and H_2O. In order to confirm the supposal, some control experiments have been done. First, no color change was observed and no absorption change was detected by UV–vis absorption spectroscopy when both solution of **2a** and **2b**, which were under argon (CO_2 and moisture were expelled completely), were irradiated with UV light and visible light, respectively. It indicated that both **2a** and **2b** are photo-inactive in absence of CO_2 and H_2O. Second, both yellow (**2a**) and green (**2b**) were gradually changed (it took about 5 h) to colorless and blue, respectively, in moisture air without light irradiation, and the speed of color change above was significantly increased (it took about less than 5 s) when the solution was bubbled with moisture air or carbon dioxide in a gas cylinder (carbon dioxide from gas cylinder through water first before into the solution). Third, both colorless and blue solution showed photo-active, and photochromic reaction was recovered with UV/vis light irradiation. Fourth, TLC (thin layer chromatogram) plate test showed the products, resulted from the conversion of **2a** and **2b** in moisture air, appeared at the place with $R_f = 0.78$ and 0.71 (elute: ethyl acetate), respectively, where are the same as these of **1a** and **1b**. All confirmed that **2a** and **2b** were converted to **1a** and **1b**, respectively, in the presence of CO_2 and H_2O, and upon irradiation with UV light or visible light, **2a** was converted to **1b** *via* **1a** and **2b** was converted to **1a** *via* **1b**.

Cascade color change patterns were achieved using both photo-trigger and chemical trigger. Upon irradiation of **1a** with UV light, followed by deprotonation, the color changed from colorless to blue to green, the green solution was bleached back to colorless solution with visible light irradiation in the presence of CO_2 and H_2O. As represented in Fig. 5 (pattern I), the color change could be recycled by combination both photo-trigger and chemical trigger (addition of NaOH). It is worth noting that the recycle was just performed two to three times due to decompose of **1a** in solution containing water, and during this process, a white solid (Na_2CO_3) as by-product was obtained. More complicated color change patterns (colorless → yellow → blue → green), which showed in Fig. 5 (pattern II), were also obtained by changing the order of trigger: deprotonation first, followed by UV light irradiation and deprotonation again. Also, the green solution was bleached back to colorless solution with visible light irradiation in the presence of CO_2 and H_2O, and the color change could be recycled two to three times.

4. Conclusions

An artificial photochromic diarylethene system with multi-responsive functionality has been developed. The system possesses ring-opening and ring-closing photoisomerization with UV/vis light irradiation. Both ring-open isomer and ring-closed isomer are converted to deprotonated compound, respectively, with addition of NaOH, whose photochromic reaction is inhibited. The deprotonated compounds can be reversed back to original compounds in moisture air, and photochromic reaction is recovered with UV/vis light irradiation. The conversion between species is accompanied with distinct color change, and the cascade color change patterns are obtained with multi-input. The system with gate reactivity and multi-color change is beneficial for non-destructive readout and applications.

Acknowledgments

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