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Construction of multi-level fluorescent switch using photochromic diarylethene and fluorescent dye

Huan-Huan Liu [a,b], Yi Chen [a,*]

[a] Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, The Chinese Academy of Sciences, Beijing 100190, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

A new photochromic diarylethene **2a** is synthesized and undergoes excellent ring-opening and ring-closing photoisomerization with UV/Vis light irradiation. The absorption of ring-closing isomer **2b** ($\lambda_{max} = 615$ nm, in dichloromethane) is found to match well with the fluorescence emission of dye **1** ($\lambda_{em} = 610$, $\phi_f = 0.76$, in dichloromethane). By mixture of **1** and **2a** in the ratio of 1:2.5 equiv., a simple and efficient fluorescence switching system is built. The fluorescence intensity of **1** is modulated easily with the photoisomerization of diarylethene **2a**/**2b** by controlling irradiation time. With detecting fluorescence change, a readout method for multi-level optical storage is demonstrated.

1. Introduction

The need for huge information storage and high speed input and retrieval of information is becoming mandatory in nowadays [1–4]. The quantity of digital storage being used has increased dramatically over the last decade. One way to increase the storage density is multi-level optical storage [5–7]. It has been described in electron trapping optical memory that M-ary runlength-limited (RLL) codes can greatly increase the code density, and multi-code amplitude modulation for phase-change optical storage has been developed by Calimetrics [8,9] For two-level recording, such as CDs or DVDs, being used in current, the unrecorded and recorded dots are coded by 0 and 1, respectively. Therefore, there are just two code states (0, 1) and (1, 0) to be used for recording information. For N-level recording, however, there are $[N \times (N-1) \times (N-2) \times \ldots \times 2 \times 1]$ code states to be used for recording information. It is known that the density (ρ) of optical memory depends on N-value and relationship between ρ and N is represented as following formula $\rho = \log_2 N$. Therefore, the density of memory and data capacity are increased with increase of code number of recording media. Multi-level recording can greatly increase the storage capacity with advanced signal processing and coding techniques [10,11].

Photochromic diarylethenes [12–14] exhibit reversible variations in their physicochemical properties when stimulated by light and are amongst the most promising candidates for photoelectronic applications such as optical memory [15–20] and switching [21–26] because of their thermally-irreversible and fatigue-resistant photoisomerization performances. It is well known that photochromic materials are photon-mode recording media, the absorption or reflectivity of recording media can be modulated by controlling the exposure energy or exposure time of laser beam. Therefore, all photochromic materials, in principle, can be used as multi-level recording media, and how many levels recording of materials can be obtained depends on both materials properties and recording strategies. In general, the larger the signal to noise ratio (SNR) or the smaller the sigma to dynamic range (SDR) is, the more the levels obtained are. In our previous report [27], we demonstrated that photochromic fulgide could be used for multi-level recording media and readout by detecting the reflectivity. Herein, we report a new strategy of readout for multi-level recording by employing a simply and efficient fluorescent switching system. The system is built by combination of a fluorescent dye and a photochromic diarylethene in ratio of amount, and the fluorescence intensity is easily modulated by controlling the photoisomerization of diarylethene. Readout by (detecting) fluorescence has some advantages such as high sensitivity, high resolution, and high contrast. Moreover, fluorescence readout can also efficiently prevent recording information from destruction due to the excitation wavelength being photochemically

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* Corresponding author. Tel.: +86 10 82543595; fax: +86 10 62564049.
E-mail address: yichencas@yahoo.com.cn (Y. Chen).

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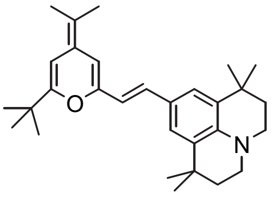
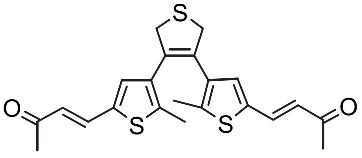


1

Fluorescent dye



2a

Photochromic diarylethene

Scheme 1. Molecular structure of model compounds.

inactive or low activity for photo-transformation between both isomers, which is the key drawback of photochromic diarylethenes used as recording media [28–33]. Both fluorescent dye **1** and photochromic diarylethene **2a** employed as model compounds are presented in Scheme 1.

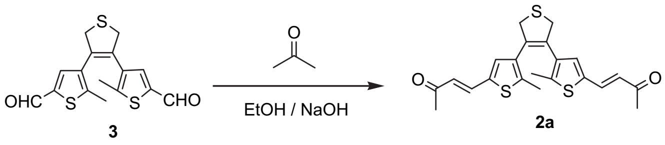
2. Experimental

2.1. General

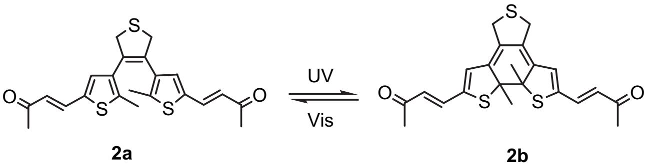
^{1}H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and $CDCl_3$ as solvent. MS spectra were recorded with TOF − MS spectrometer. Absorption and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (Hitachi F − 2500), respectively. 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 (6 W) and a Xeon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.

2.2. Chemical

*Synthesis of **2a***. The synthesis route for **2a** is presented in Scheme 2 and the details of preparation are as follows: To a solution of acetone (120 mg, 3.0 mmol) in EtOH (10 mL) was added NaOH (120 mg). The mixture was stirred for 1 h at room temperature. To the above solution was added slowly a solution of **3** [34] (500 mg, 1.5 mmol) in THF (60 mL). The mixture was stirred at room temperature and the reaction was detected by TLC plate. After no **3** was detected by TLC plate, the mixture was poured into water (50 mL). The product was extracted with DCM, and combined organic phase was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by flash column chromatography with petroleum/ethyl acetate (2:1) as eluent to afford target compound **2a** (375 mg, 31% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.48 (d, J = 15.8 Hz, 2H, CH=), 6.94 (s, 2H, Ar H), 6.40 (d, J = 15.8 Hz, 2H, CH=), 4.11 (s, 4H, CH_2), 2.31 (s, 6H, CH_3), 2.04 (s, 6H, CH_3). HRMS (ESI, m/z) [M^+] calcd. for $C_{28}H_{22}$ N_4S_3: 414.0659, found: 414.0656.



Scheme 2. Photoisomerization of diarylethene **2a** with UV/Vis light irradiation.



Scheme 3.

Preparation of a diarylethene − fluorescence − PMMA thin film: dye **1** (1.0 mg) and diarylethene **2a** (2.3 mg) was dissolved in a 1.0 mL PMMA–cyclohexanone solution (10%, w/w). The film was obtained by spin coating on an optical glass (25 mm × 25 mm × 1.5 mm) with a gradient of 700 rpm (10 s) followed 1200 rpm (30 s) (25 °C) and dried in air and kept in the darkness at room temperature. The thickness of the film was about 10 μm measured on Ambios Technology XP-1 Profilometer. The film was irradiated by UV light for 10 min before used to information recording test.

3. Results and discussion

3.1. Photochromism of diarylethene **2a**

The photoisomerization of ring-open isomer **2a** and ring-closed isomer **2b** with UV/Vis light irradiation was illustrated in Scheme 3. The absorption bands of **1a** in dichloromethane (DCM) appeared at 334 nm ($\varepsilon = 2.7 \times 10^4$ L mol^{-1} cm^{-1}). Upon irradiation with 365 nm light, the colorless solution of **1a** was converted into a blue–green solution of **1b** with an absorption band at 615 nm, and **1b** could be bleached completely back to **1a** with visible light ($\lambda \geq 480$ nm), resulted in the color change of the solution from blue–green to colorless. As shown in Fig. 1, it showed the typical absorption spectra changes of diarylethene derivatives in solutions and it could also be seen clearly that an isosbestic point appeared in the absorption spectra changes of photocyclization, indicating only two

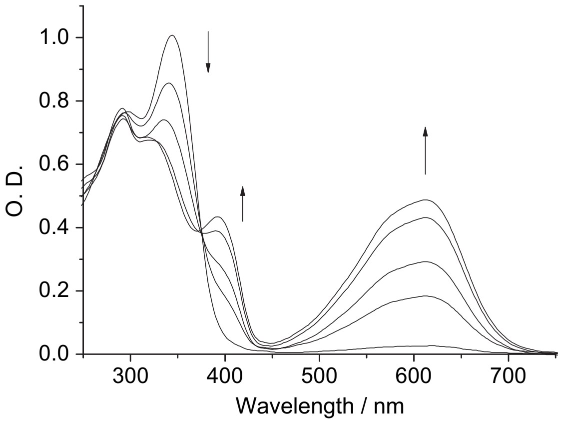


Fig. 1. Absorption changes of **2a** upon irradiation with 365 nm light (3.8×10^{-5} M, DCM).

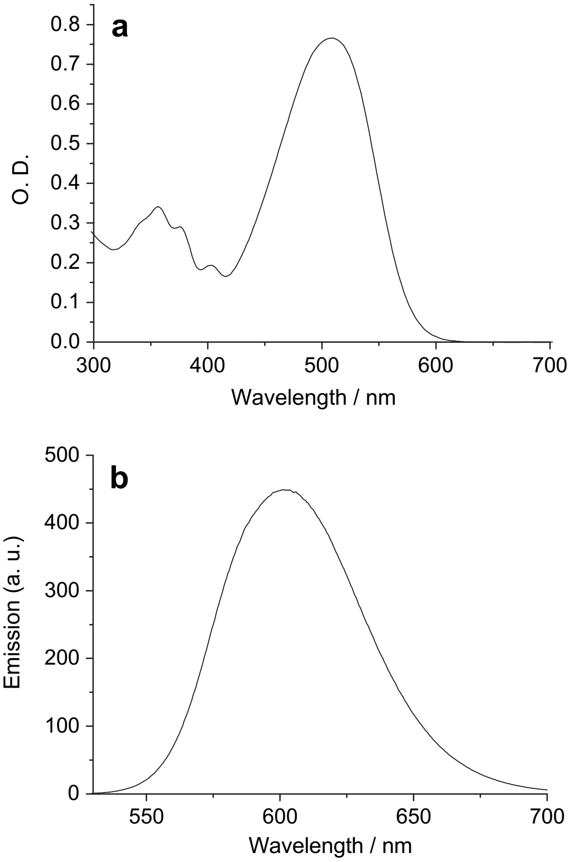


Fig. 2. Absorption (a) and fluorescence (b) of **1** (3.0×10^{-5} mol L^{-1}, DCM, $\lambda_{ex} = 510$ nm).

isomers existed when **2a** underwent the photoisomerization reaction. Both **2a** and **2b** exhibit no fluorescence emission with the excitation wavelengths of 334 nm, 402 nm, and 615 nm, respectively (Fig. 2).

3.2. Fluorescence of dye *1*

Fluorescence dye **1** was synthesized according to the literature [35,36]. The absorption and fluorescence spectra of **1** in dichloromethane (DCM) showed the maximum absorption and fluorescence bands are at 510 nm and 610 nm, respectively (Fig. 2). No significant absorption and fluorescence spectra changes of **1** were detected with 365 nm light or visible light irradiation, indicating that dye **1** is photostable under both 365 nm light and visible light. The fluorescence quantum yield of dye **1** ($\varphi_f = 0.76$) is obtained by using fluorescein as the reference.

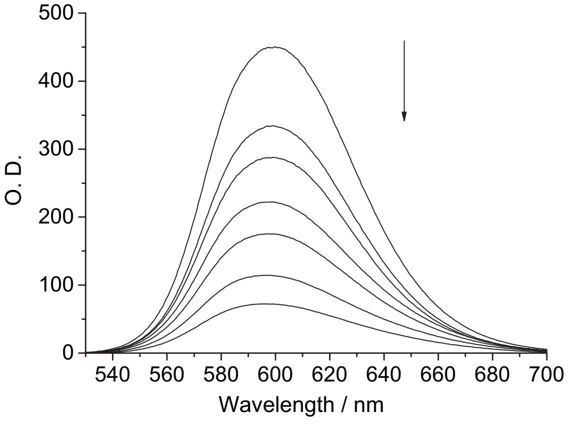


Fig. 3. Fluorescence changes of 1 blended with **2a** (**1**:**2a** = 1:2.5 equiv., 3.0×10^{-5} M, DCM) with 365 nm light irradiation (periods: 0, 20, 40, 60, 80, 100, 120 s), $\lambda_{ex} = 510$ nm.

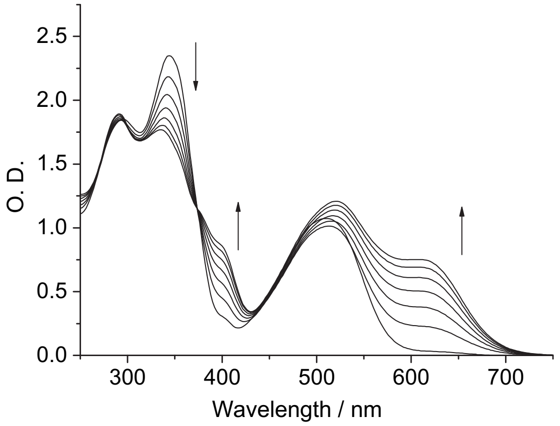


Fig. 4. Absorption changes of **2a** blended with **1** (1:2a = 1:2.5 equiv., 7.5×10^{-5} M, DCM) with 365 nm light irradiation (periods: 0, 20, 40, 60, 80, 100, 120 s).

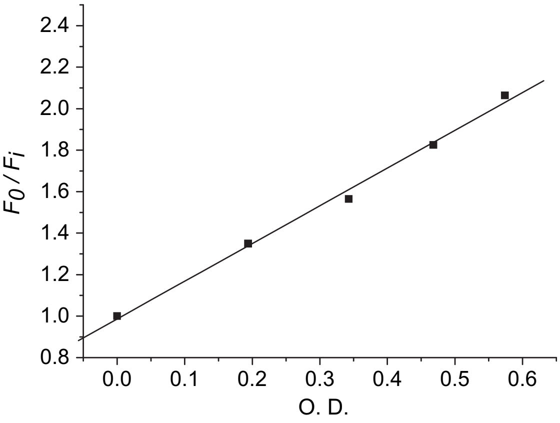


Fig. 5. Stern–Volmer plot of fluorescence quenching in dichloromethane. F_o: the initial fluorescence of dye 1, F_i: fluorescence of the mixture.

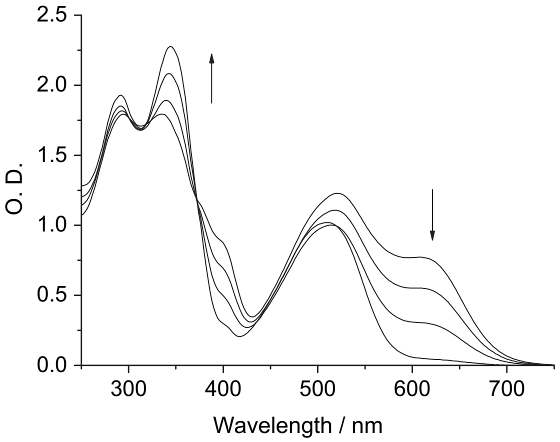


Fig. 6. Absorption changes of ring-closing isomer of **2a** in PMMA film (**1**:**2a** = 1:2.5 equiv.) by controlling the irradiation time (irradiation periods: 0, 60, 120, 180 s) with visible light ($\lambda \geq 480$ nm).

Fig. 7. Fluorescence images of **1** in PMMA film (**1**:**2a** = 1:2.5 equiv.) by controlling the irradiation time (from left to right, irradiation time: 0, 60, 120, 180 s), $\lambda_{ex} = 510$ nm.

*3.3. Fluorescence modulation of dye **1***

The fluorescence changes of **1** blended with **2a** in the ratio of 1:2.5 equiv. were investigated with UV light irradiation. No significant fluorescence change in both profile and intensity was observed *via* comparison of **1** blended with **2a** in the ratio of 1:2.5 with pure **1** under the same condition before irradiation. The fluorescence intensity of **1** blended with **2a** in the ratio of 1:2.5, however, decreased significantly with irradiation (365 nm) of the solution. As presented in Fig. 3, the fluorescence decreased with increasing exposure time and the largest decrease (90%) of the fluorescence intensity was obtained with 120 s irradiation, at this time, the photo-conversion of **2a** to **2b** reached photostationary state. As presented in Fig. 4, the presence of isosbestic point clearly stated that only two isomers existed when **2a** underwent the photoisomerization process with **1** being blended. It is worth noting that the decrease of fluorescence may result from the following two aspects: 1) intermolecular energy transfer between the fluorescence dye and photochromic diarylethene [37], which was confirmed by the Stern–Volmer plot (Fig. 5) and 2) the decrease of amount of excitation photons absorbed by the fluorescent molecules due to the increase of concentration of ring-closing isomer of diarylethene [38], whose absorption matched with the excitation wavelength of fluorescence dye (Fig. 4). The fluorescence intensity of **1** blended with **2a** in the ratio of 1:2.5 was recovered completely when the solution was bleached with visible light ($\lambda \geq 480$ nm).

3.4. Strategy of fluorescence readout for multi-level optical storage

A method of fluorescence readout for 4-level optical storage is explored by using a PMMA thin film, which contained the mixture of **1** and **2a** (**1**:**2a** = 1:2.5 equiv.), as model device. Both ring-opening isomer and ring-closing isomer are usually regarded as recorded state and unrecorded state, respectively, when photochromic diarylethenes are used as recording media, the unrecorded state (ring-closing isomer) is inverted to the recorded state (ring-opening isomer) while the information is recorded with light. In this paper, **2b** blended with **1** was acted as unrecorded state. By controlling irradiation time (0, 60, 120, 180 s) with visible light ($\lambda \geq 480$ nm), different optical density (0.75, 0.50, 0.25, 0.00) of **2b** at 610 nm (Fig. 6) and correspondent fluorescence images with different intensity (Fig. 7) were obtained, respectively. As presented in Fig. 5, it showed that **2b** could be completely bleached back to **2a** in PMMA thin film with visible light ($\lambda \geq 450$ nm), and an isosbestic point appeared in the absorption spectra changes indicated that only two isomers existed when **2b** underwent the photo-reversible transformation reaction in PMMA thin film. Companying the unrecorded state **2b** converted to the recorded state **2a**, the fluorescence of **1** changed from no emission to strong emission. As shown in Fig. 7, the difference in fluorescence intensity was large enough to be used for 4-level recording readout. It is worth emphasizing that the SNR (signal to noise ratio) by detecting fluorescence is much larger than that by detecting reflectance for readout of multi-level recording in general signal process procedure. Moreover, readout by fluorescence is also available to nondestructive readout of photochromic diarylethene by employing 510 nm as excitation wavelength instead of 610 nm since the absorption of diarylethene **2a** at 510 nm ($\varepsilon = 4.2 \times 10^3$ L mol^{-1} cm^{-1}) is smaller than that at 610 nm ($\varepsilon = 2.7 \times 10^4$ L mol^{-1} cm^{-1}).

The study described above highlights the fact that the fluorescence change of a dye can be easily modulated with photoisomerization of diarylethene by choosing a suitable combination of a fluorescent dye and a photochromic diarylethene, With controlling the exposure time, different fluorescence intensity is obtained, which can be used to readout of multi-level optical storage. This provides the flexibility to design the modulation codes, which match with the resolution and jitter characteristics of the recording system. The effect of the multi-level recording scheme depends on the number of the levels, the minimum and maximum run length, and the spacing. The optimum selection of these parameters can realize a large recording capacity close to the intrinsic potential of the multi-level recording system.

4. Conclusions

A simple and controllable fluorescent switch system has been achieved by the combination of a fluorescent dye and a photochromic diarylethene. It has demonstrated that the fluorescence of dye is easily modulated with the photoisomerization of diarylethene by controlling exposure time. Based on the fluorescence modulation, four different fluorescence images are obtained, which provides a readout method for multi-level optical storage.

Acknowledgments

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