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## A multi-state fluorescence switch based on a new photochromic diarylethene with a di-(ethyl-1,8-naphthalimidyl)amine unit



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## ABSTRACT

A novel asymmetrical diarylethene with a di-(ethyl-1,8-naphthalimidyl)amine unit was synthesized. Its fluorescence can be effectively modulated by UV–vis, TFA/TEA, and Sn<sup>2+</sup>. The fluorescence intensity of the title compound was enhanced upon addition of TFA or Sn<sup>2+</sup>, which was ascribed to the blocked PET process by protonation of the tertiary amine or complexation with Sn<sup>2+</sup>. As a result, the diarylethene can serve as a fluorescence chemosensor for highly selective recognition of Sn<sup>2+</sup> in THF. Moreover, a logic circuit was designed with one optical output responding to three inputs.

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### 1. Introduction

To date, much progress has been made to develop diarylethenes due to their excellent thermal stability and notable fatigue resistance [1–3]. The molecules with both photochromic and fluorescent properties have attracted increasing interest because of their potential applications as molecular switches and biological markers [4–10]. However, most diarylethene molecules are not appreciably fluorescent. One effective strategy for fluorescence modulation is to combine the diarylethene unit with a fluorophore [11–14], and the fluorescence of fluorophore can be controlled by external stimuli [15–18]. In our previous research, we developed a series of diarylethenes with a rhodamine unit and demonstrated their multiple responsive photoswitching properties induced by light, proton, and metal ions [15]. Zou et al. reported two dithienylethene-based fluorescence sensors, which responded to UV–vis light and mercury(II) and fluoride ions [16].

Among the fluorophore moieties, naphthalimide has attracted much research interest due to its unique photophysical properties [19]. Recently, diarylethene derivatives with 1,8-naphthalimide unit have been designed and synthesized. Giordano et al. utilized naphthalimide as a donor in photochromic fluorescence resonance

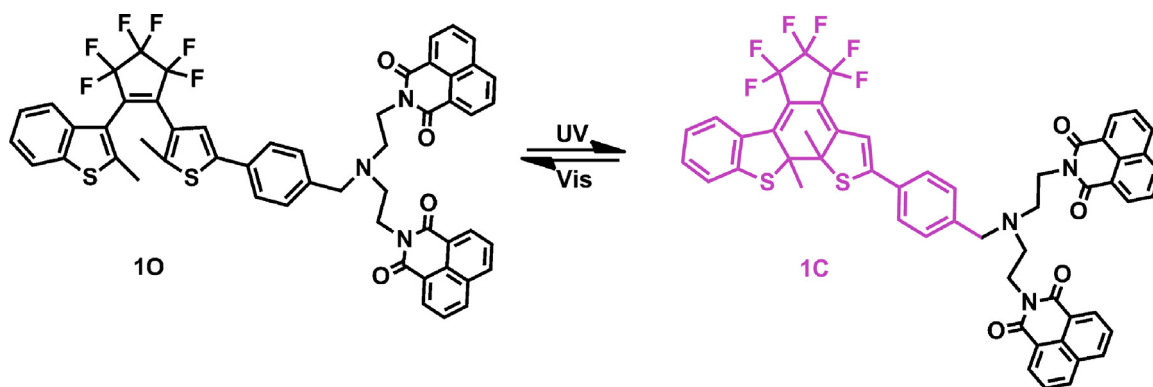
energy transfer (pcFRET), and the fluorescence emission of the donor was modulated by cyclical transformation of the photochromic acceptor [20]. Jiang et al. reported a fluorescence switch based on a bisthiénylene-naphthalimide dimer [21]. Its fluorescence showed dual responses to photo and proton. Meng et al. reported novel diarylethenes containing naphthalimide as the central ethene bridge, which showed high cyclization quantum yield and good fatigue resistance [22]. They also reported a new multi-state 1,8-naphthalimide-piperazine-tethered dithienylethene, whose fluorescence can be modulated by alternative UV–vis irradiation, protonation/deprotonation, and Cu<sup>2+</sup> ion complexation/dissociation [23]. These achievements were helpful for us to explore novel diarylethene derivatives with a naphthalimide moiety. In this report, a novel asymmetrical diarylethene with di-(ethyl-1,8-naphthalimidyl)amine unit was synthesized. As expected, a multi-addressable switch triggered by proton, light, and Sn<sup>2+</sup> ion was achieved. The photochromism of **10** is shown in Scheme 1.

### 2. Experimental

#### 2.1. General methods

Chemical reagents were purchased from Aldrich and used without further purification. TLC plates were visualized by 254 nm UV irradiation. All solvents used were of spectro-grade and purified

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**Scheme 1.** Photochromism of diarylethene **10** by photoirradiation.

by distillation prior use. NMR spectra were collected on a Bruker AV400 (400 MHz) spectrometer with  $\text{CDCl}_3$  as the solvent and tetramethylsilane (TMS) as the internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Elemental analysis was carried out with a PE CHN 2400 analyzer. Mass spectra were measured with an Agilent 1100 ion trap MSD spectrometer. UV-vis spectra were measured on an Agilent 8453 UV-vis spectrophotometer. Fluorescence spectra were recorded with a Hitachi F-4600 fluorescence spectrophotometer. Melting point was measured with a WRS-1B melting point apparatus. Photo-irradiation experiments were performed using an SHG-200 UV lamp, CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. The light intensity was  $25 \mu\text{W}/\text{cm}^2$  and  $13.5 \text{ mW}/\text{cm}^2$ , respectively.

## 2.2. Synthesis of 1-(2-methyl-3-benzothiophenyl)-2-{2-methyl-5-[4-(bis(N-ethyl-1,8-naphthalimidyl)amine)methylphenyl]-3-thienyl}perfluorocyclopentene (**10**)

The synthesis method of the diarylethene **10** is shown in Scheme 2 and experimental details were carried out as followed.

Compounds **2** [24] (0.18 g, 0.30 mmol) and **3** [25] (0.12 g, 0.25 mmol) were dissolved in anhydrous  $\text{CH}_3\text{CN}$  (60 mL). Then,  $\text{K}_2\text{CO}_3$  (0.17 g, 1.20 mmol) and KI (0.050 g, 0.30 mmol) were added, and the resulting mixture was heated at 353 K for 6 h. Subsequently, the reaction mixture was cooled to room temperature, quenched with water and the solvent was removed under reduced pressure. After being extracted with dichloromethane, the organic phase was dried over  $\text{MgSO}_4$ , filtered, and evaporated. The crude compound was purified by column chromatography on silica gel using dichloromethane/methanol ( $v/v=8/2$ ) as the eluent to give 0.20 g compound **10** as a yellow solid in 86% yield. M.p. 497–498 K;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz),  $\delta$  (ppm): 1.91 (s, 3H), 2.31 (s, 3H), 2.95 (t,

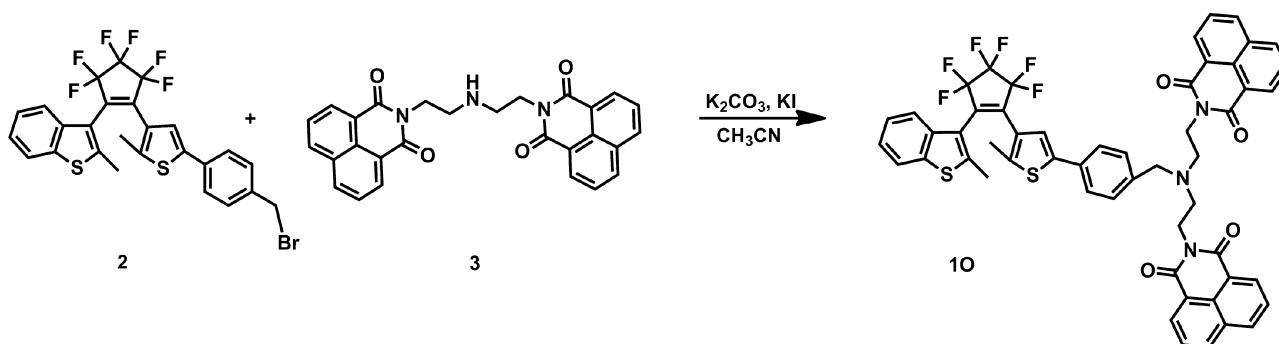
4H,  $J=5.2$  Hz), 3.66–3.77 (m, 2H), 4.32 (t, 4H,  $J=6.6$  Hz), 6.51 (d, 2H,  $J=7.6$  Hz), 6.82 (s, 1H), 6.93 (d, 2H,  $J=7.6$  Hz), 7.30–7.38 (m, 3H), 7.58 (t, 4H,  $J=7.8$  Hz), 7.76 (d, 1H,  $J=8.4$  Hz), 8.14 (d, 4H,  $J=6.8$  Hz), 8.19 (d, 4H,  $J=8.4$  Hz);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  (ppm): 14.7, 14.9, 37.9, 52.1, 57.9, 122.1, 123.0, 124.5, 124.6, 124.9, 126.7, 128.2, 129.4, 130.8, 131.5, 133.4, 140.8, 164.1; IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 1699 (C=O), 1385 (C–N); MS ( $m/z$ ): 970.01 [M–H] $^+$ ; Anal. calcd. for  $\text{C}_{54}\text{H}_{37}\text{F}_6\text{N}_3\text{O}_4\text{S}_2$  (%): C, 66.86; H, 3.84; N, 4.33, found: C, 66.98; H, 3.94; N, 4.25.

## 3. Results and discussion

### 3.1. Photochromism

The photochromic behavior of diarylethene **10** induced by photoirradiation at room temperature was investigated in dichloromethane ( $2.0 \times 10^{-5} \text{ mol L}^{-1}$ ). The changes in its absorption spectrum and color upon photoirradiation are shown in Fig. 1. The open-ring isomer **10** exhibited an absorption peak at 267 nm due to  $\pi \rightarrow \pi^*$  transition [26]. Upon irradiation with 297 nm UV light, a new absorption band centered at 552 nm was observed due to the formation of the closed-ring isomer **1C**, accompanied with the color change from colorless to purple. The colored solution was bleached entirely upon irradiation with visible light ( $\lambda > 500 \text{ nm}$ ), and the absorption spectrum recovered to its initial state. The quantum yields of cyclization and cycloreversion were 0.28 and 0.017, respectively. The fatigue resistance of **10** was tested in dichloromethane upon alternative irradiation with UV and visible light in air at room temperature. The coloration and decoloration cycles of **10** could be repeated for 100 times with only 7% degradation.

The single crystal of **10** was obtained by diffusion method from a mixture of dichloromethane and ethanol at room temperature.



**Scheme 2.** Synthetic route to diarylethene **10**.

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