

# Synthesis, photochromism and fluorescence of new diarylethene bearing a benzofuran unit

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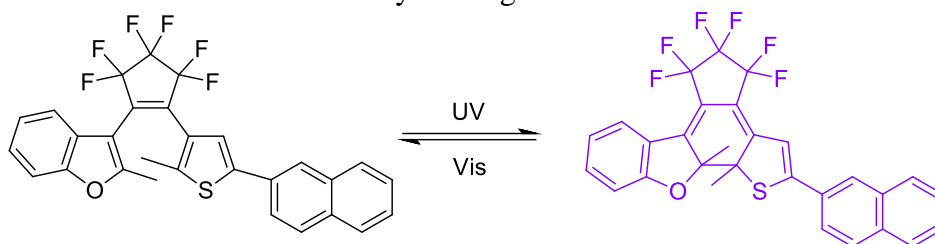
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**Abstract.** A new asymmetrical photochromic diarylethene, 1-(2-methyl-3-benzofuryl)-2-(2-methyl-5-naphthyl-3-thienyl)perfluorocyclopentene (**10**) was synthesized, and its photochromism and fluorescence properties were studied in detail. Upon irradiation with 297 nm UV light, the colorless **10** changed to violet both in solution and solid state. In addition, **10** had favourable fatigue resistant, which could be potential use for practical application in optical devices. Finally, a remarkable fluorescence switching was observed along with the photocyclization reaction of **10**.

## Introduction

Photochromic diarylethene compounds have received intense interest because of their potential applications in the area of optoelectronics such as optical recording, photo-switching, and full-color display devices [1-6]. Among the numerous reported photochromic compounds, diarylethene derivatives have been achieved much attention because of their outstanding fatigue resistance and thermally irreversible photochromic behavior [7-9]. During past decades, a huge number of works were focused on design, synthesis and investigation of novel photochromic diarylethene with different heterocyclic aryl rings in order to develop good performance diarylethene [10]. Generally, the photochromic character of diarylethene was strongly dependent on the aryl moieties. For example, diarylethenes with thiophene/benzothiophene moieties had good thermal stability and remarkable fatigue-resistance [1,11,12], whereas diarylethenes bearing two pyrrole groups was thermally unstable and returns to the open-ring isomers even in the dark [13]. Benzofuran, which belongs to a series of benzo-five heterocyclic aryl ring system like benzothiophene, and thiophene moiety. Therefore, we thought diarylethenes containing benzofuran unit will still display the same excellent properties like other five-membered heterocyclic ring.



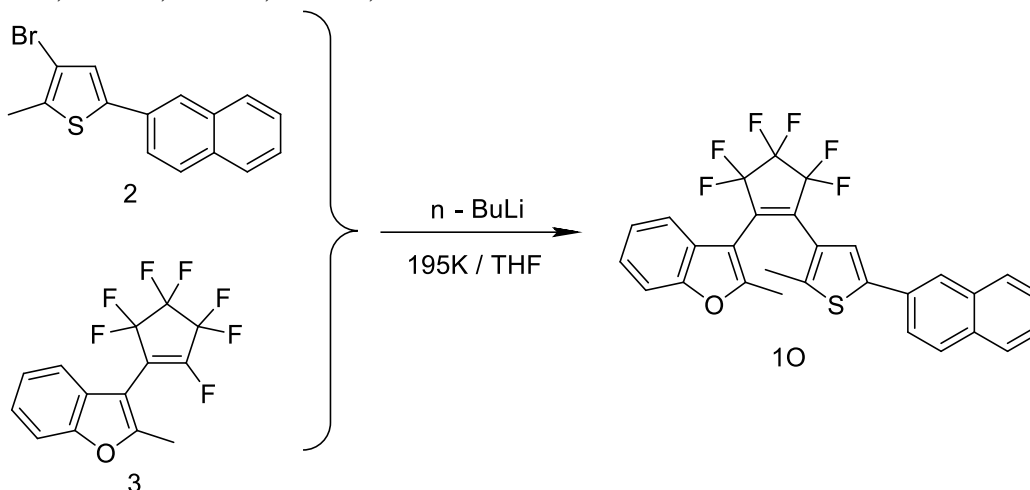
Scheme 1. Photochromism of dithienylethene **10**.

In this paper, a new photochromic diarylethene containing a benzofuran ring was designed and synthesized, *i.e.*, 1-(2-methyl-3-benzofuryl)-2-(2-methyl-5-naphthyl-3-thienyl)perfluorocyclopentene (**10**). Its photochromic reactivity, fatigue resistant and fluorescence switching were investigated in detail. The photochromic reaction of diarylethenes **10** was shown in Scheme 1.

## Experiment

**Synthesis of diarylethene 10.** To a stirred anhydrous THF (50.0 ml) containing 3-bromo-2-methyl-5-naphthylthiophene **2** (0.91 g, 3.0 mmol) was added dropwise to a 2.4 mol/L n-BuLi hexane solution (1.3 ml) at  $-78^{\circ}\text{C}$  under argon atmosphere. Stirring was continued for 30min

and (2-methyl-3-benzofuryl)perfluorocyclopentene **3** (1.03 g, 3.6 mmol) was slowly added and stirred for 2h at this temperature. The reaction was quenched with 10 ml water. The mixture was warmed to room temperature and extracted with dichloromethane, then the organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtrated and evaporated. The silica gel used hexane as eluent resulting in 1.0 g of **10** being obtained in 66% yield. M.p. 124–125°C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 1.91 (s, 3H, –CH<sub>3</sub>), 2.31 (s, 3H, –CH<sub>3</sub>), 7.22 (s, 3H, thiophene–H), 7.29 (d, 1H, benzofuran–H *J* = 8.0 Hz), 7.42 (s, 1H, naphthalene–H, ), 7.45 (s, 1H, naphthalene–H), 7.49 (t, 3H, benzofuran–H, *J* = 8.0 Hz), 7.65–7.67 (q, 1H, naphthalene–H, *J* = 8.0 Hz), 7.82–7.86 (q, 3H, naphthalene–H, *J* = 8.0 Hz) 7.95 (s, 1H, naphthalene–H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS): δ 14.67, 15.14, 119.42, 121.98, 123.11, 123.66, 123.94, 124.03, 125.00, 125.30, 125.76, 126.90, 127.34, 128.09, 128.45, 129.30, 130.33, 132.88, 133.58, 137.87, 138.12, 141.84, 142.17, 143.67.



Scheme 2. Synthetic route for the compound **10**.

## Results and discussion

**Photochromism of diarylethene **10**.** Figure 1 displayed the absorption spectral changes of diarylethene **10** in hexane (Figure 1A,  $C = 2.0 \times 10^{-5}$  mol/L) and in solid state Figure 1B by alternating irradiation with UV and visible light ( $\lambda > 500$  nm), respectively. Diarylethene **10** exhibited a sharp absorption peak at 266 nm ( $\epsilon = 2.67 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>) in hexane, which was due to a  $\pi$ - $\pi^*$  transition [14]. Upon irradiation with 297 nm UV light, the colorless solution of **10** gradually changed to violet. Meanwhile, a new absorption band was observed in the visible region centered at 529 nm ( $\epsilon = 1.34 \times 10^4$  L mol<sup>-1</sup> cm<sup>-1</sup>), which was attributed to the formation of the closed-ring isomer (**1c**). When the violet solution was irradiated with visible light ( $\lambda > 500$  nm), the violet colored solution of **1c** could be decolorized completely and its the absorption band at 547 nm was decreased. The photoconversion ratio of **1** was determined to be 67% by <sup>1</sup>H NMR method.

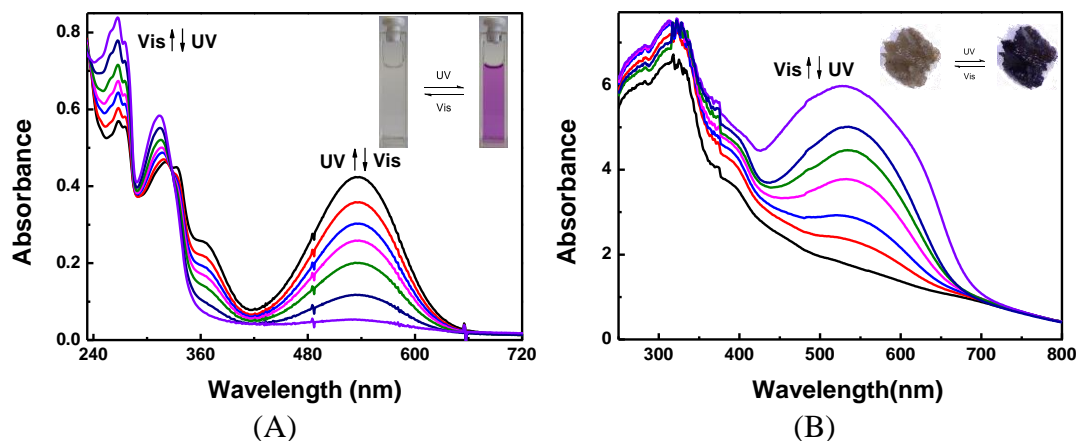


Figure 1. Absorption spectral and color changes of **1** in hexane (A) and in solid state (B).

Just like in hexane solution, **10** also showed good photochromism properties in solid powder. As shown in Figure 1B, the absorption maximum of open-ring isomers was 322 nm and the absorption

maxima of closed-ring isomers was observed at 533 nm in the photostationary state (PSS). Accompany with the photocyclization reaction, the gray solid powder became purple due to the formation of closed-ring isomer **1c**. Compared to that in hexane solution, the absorption maxima wavelength of **1c** in solid powder was red-shifted 4 nm. The stabilization of molecular arrangement in solid state may account for the bathochromic effect [15].

**Fatigue resistance of 1o.** Fatigue-resistance feature of diarylethene was an important factor for practical applications in optical devices [13-16]. The fatigue resistance of **1o** was examined both in hexane and in solid state at room temperature. As shown in Figure 2, **1o** could be repeated more than 100 times with only 9% degradation. The degradation may be ascribed to generate oxidative by-product, which was transform from closed-ring isomer by UV irradiation. Similarly, fatigue resistance of **1o** in solid state was degraded to 21% after 100 repeat cycles.

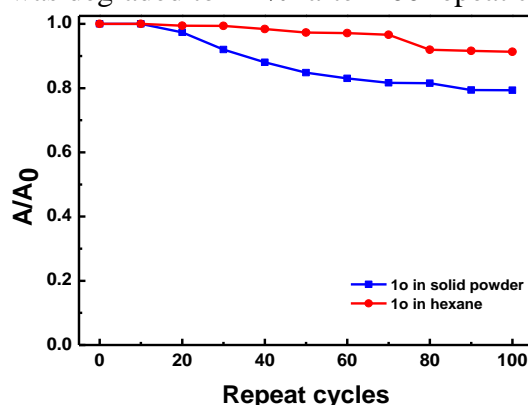


Figure 2. Fatigue resistance of **1o** in air atmosphere at room temperature.

**Fluorescence of diarylethene 1o.** The fluorescence properties of **1o** was measured by using a Hitachi F-4600 spectrophotometer, and the breadths of excitation and emission slit were selected 5.0 nm and 5.0 nm. As shown in Figure 3, the emission peak of **1o** was observed at 399 nm in hexane when excited at 315 nm, and the emission peak of **1o** was observed at 458 nm in solid powder upon exciting at 335 nm. The back irradiation by appropriate wavelength visible light regenerated its open-ring isomer and recovered the original emission intensity. Notably, the emission intensity of **1o** could be quenched only 27% in solution and 41% in solid state when the PSS arrived. The fluorescence intensity of diarylethene **1o** decreased with the photochromism, which attributed to the non-fluorescent closed-ring isomer. Compared to that in solution, the fluorescence modulation efficiency of **1** in the solid state was much higher. Therefore, **1o** could be potentially applied to optical memory with fluorescence readout method and fluorescence modulation switches [17-18].

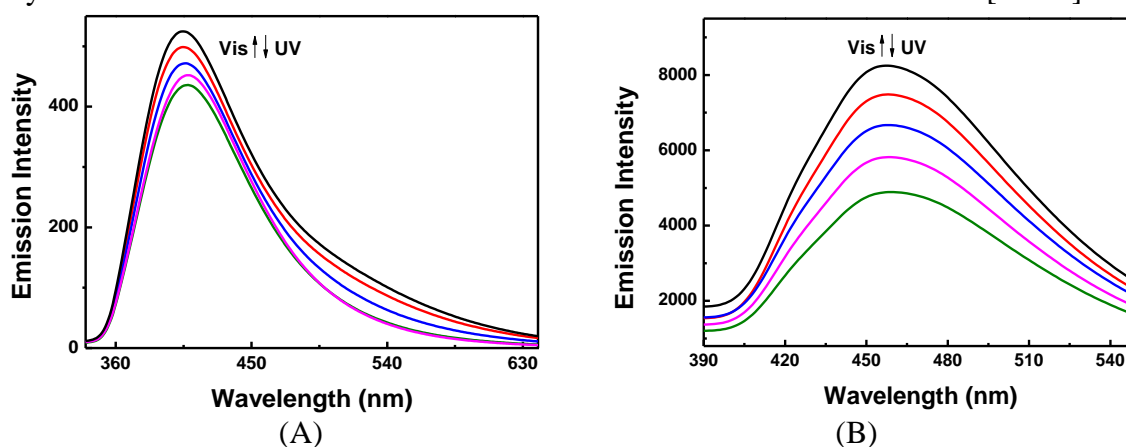


Figure 3. Fluorescence spectra of diarylethene **1o** in hexane (A) and in solid powder (B) excited at 315 nm and 335 nm, respectively.

## Conclusions

A new asymmetrical photochromic diarylethene with benzofuran ring and a naphthalene pendant was designed and synthesized. The compound exhibited good photochromic properties and fluorescent switch behavior. The fatigue resistant showed that the cycles of **10** could be repeated more than 100 times with only 9% and 21% degradation in solution and solid state, respectively. Meanwhile, the favorable fluorescent modulation in the solid state may be promising application in photoswitchable devices, such as optical memory and fluorescent modulation switches.

## Acknowledgements

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