



A multiple switching diarylethene dimer with a bis(benzylene)amine-linked naphthalimide unit

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ABSTRACT

A novel photochromic diarylethene dimer with a bis(benzylene)amine-linked naphthalimide unit was synthesized, and its photochemical properties were systematically studied. Upon irradiation with ultraviolet light, a singly-closed isomer and a fully-closed isomer were reversibly formed, which were confirmed by the results of Nuclear Magnetic Resonance spectroscopy (NMR) and High-Performance Liquid Chromatography (HPLC). Additionally, the diarylethene dimer could be used as a multi-addressable fluorescence switch when triggered by light, proton, and metal ions. Moreover, a logic circuit was constructed with the unimolecular platform by using the fluorescence intensity at 445 nm as output and appropriate combinational stimuli of UV light, Al^{3+} , and EDTA as inputs.

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1. Introduction

Photochromic compounds, which change their color upon irradiation with light of the appropriate wavelength, have attracted increasing attention because of their potential applications to optical memory media and switching devices.¹ Among various photochromic compounds, diarylethenes are the most promising candidates for practical applications due to their high fatigue resistance and thermal stability.² In recent years, dithienylethene dimers are particularly appealing due to their remarkably reversible multimode switching and multicolor displays between the states.³ Several bi-component diarylethene based systems have been reported, which employed a bridging single bond or functional group. For example, Feringa et al. reported that multicomponent dithienylethene with a very short Me_2Si spacer underwent ring closing and opening between three distinct photochromic states.⁴ Similarly, Matsuda et al. synthesized diarylethene derivatives having a pyrene moiety and studied their reversible photoinduced molecular ordering changes at a solution-HOPG interface by STM.⁵ Ortica et al. investigated photochromic bisdiarylethene containing a benzobis(imidazole) core substituted with

two aniline moieties, which displayed highly efficient light emission in organic solvents.⁶

Since naphthalimide is an excellent fluorescent chromophore with superior photostability, high fluorescent quantum yield, and multi-responses to chemical input,⁷ diarylethene compounds containing naphthalimide moiety have been widely exploited for applications related to molecular switches and light-emitting devices in recent years. For example, Tian et al. reported a novel compound consisting of *n*-butyl-1,8-naphthalimide, piperazine, and dithienylethene units with the fluorescence that could be tuned by Cu^{2+} , proton, and light.⁸ Song et al. reported a photo- and proton-dual-responsive fluorescence switch based on a bisthienylethene-naphthalimide dimer.⁹ However, photochromic diarylethene dimer linked by an *N,N'*-bis(benzylene)amine spacer containing a naphthalimide moiety has rarely been reported in the literature. Based on the characteristics of diarylethene dimer and *N,N'*-bis(benzylene)amine spacer containing a naphthalimide moiety, we designed a novel photochromic compound **100**. The structure of **100** is shown in Fig. 1, which possesses a symmetrical molecular architecture that can be synthesized readily under mild conditions. Our results demonstrated that both diarylethene units can convert to closed-ring forms by photoirradiation. Moreover, a multi-addressable switching was achieved by triggers including proton, light, and ions.

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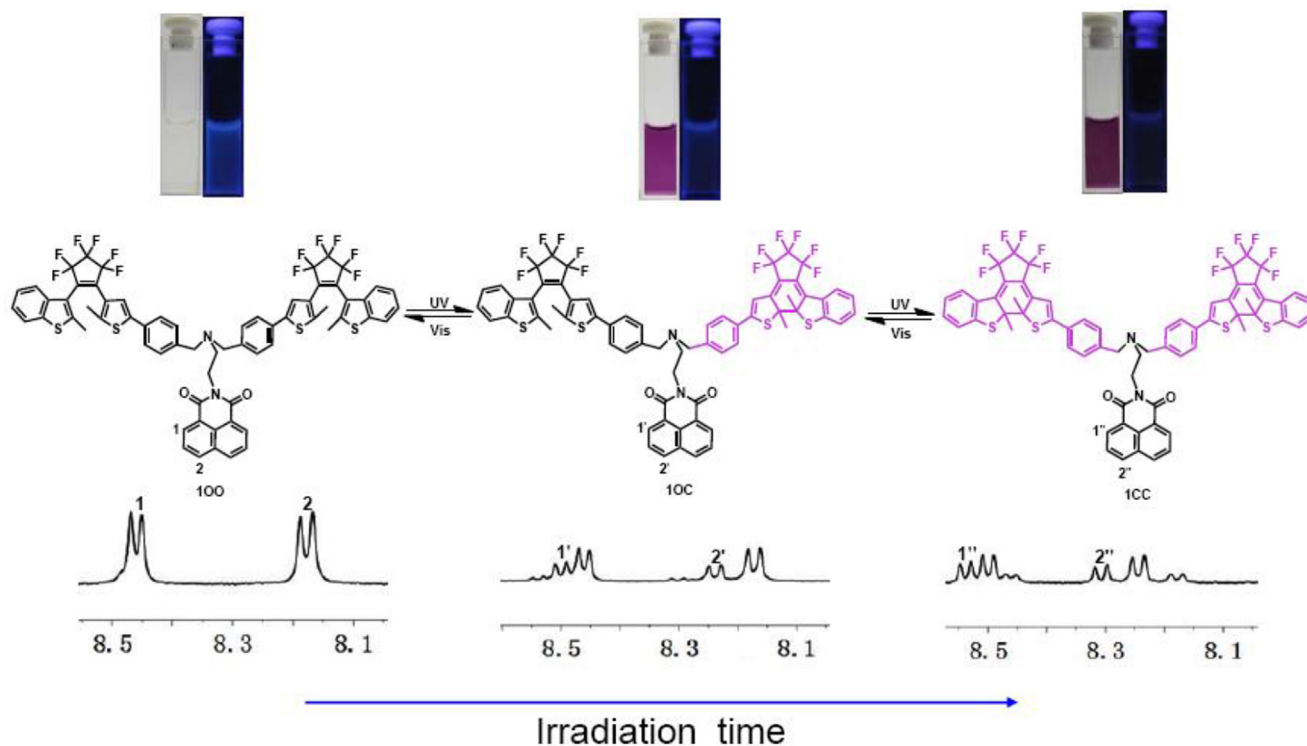


Fig. 1. Reversible photoisomerization reactions and ^1H NMR spectra of the target compound **1** upon irradiation with different times in CDCl_3 : before irradiation (**100**), 1 min (**10C**), 22 min (**1CC**).

2. Experimental

2.1. General methods

Chemical reagents were purchased from Aldrich and used without further purification. Thin Layer chromatography (TLC) plates were visualized under 254 nm UV irradiation. All solvents used were of spectro-grade and distilled before use. ^1H NMR spectra were collected on a Bruker AV400 (400 MHz) spectrometer with 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 on 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 in a CX-21 ultraviolet fluorescence analysis cabinet and a BMH-250 visible lamp with the light intensities of $25 \mu\text{W}/\text{cm}^2$ and $13.5 \text{ mW}/\text{cm}^2$, respectively.

2.2. Synthesis

The synthetic route to the diarylethene **100** is shown in Fig. 2, and experimental details were carried out according to the following procedures.

Compounds **2**¹⁰ (0.15 g, 0.26 mmol) and **3**¹¹ (0.022 g, 0.093 mmol) were dissolved in anhydrous CH_3CN (60 mL). Then K_2CO_3 (0.043 g, 0.34 mmol) and KI (0.042 g, 0.23 mmol) were added successively, and the resulting mixture was heated at 353 K for 6 h. Subsequently, the reaction mixture was cooled to room

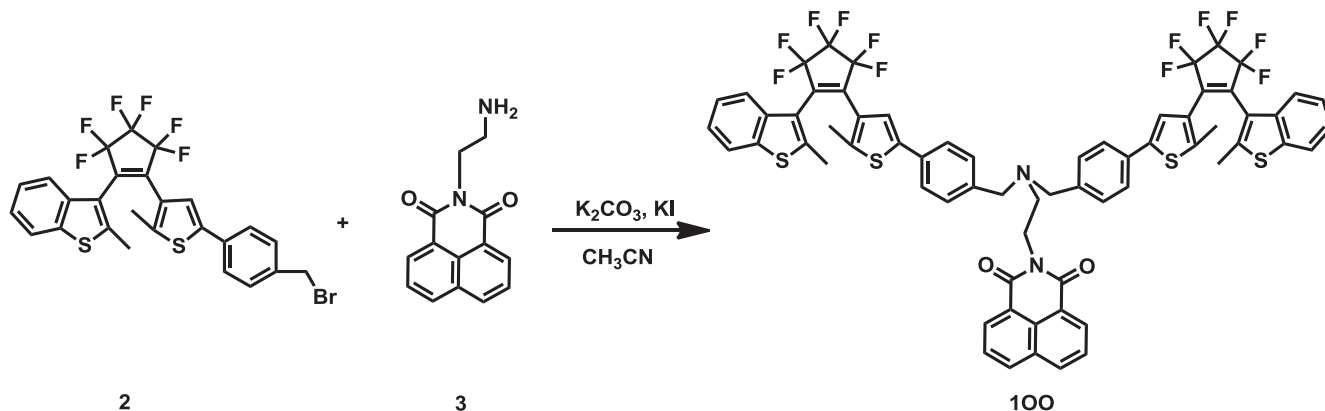


Fig. 2. Synthesis of diarylethene **100**.

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