

A multi-responsive diarylethene system based on the structure transformation by chemical and light stimuli



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ARTICLE INFO

Article history:

Received 3 January 2014
Received in revised form 4 March 2014
Accepted 10 March 2014
Available online 21 March 2014

Keywords:

Photochromism
Diarylethene
Schiff base
Deprotonation
Benzoxazole
Multiple response

ABSTRACT

A novel diarylethene with a Schiff base unit was successfully synthesized and its multi-responsive photochromism could be effectively modulated by chemical and light stimuli. By the stimulation of sodium hydroxide, the absorption maximum of its closed-ring isomer showed extraordinarily large redshift of 134 nm, accompanied with a notable color change from purple to green. Subsequent irradiation with 420 nm visible light further caused a dramatic change in its color from green to cyan due to the formation of the benzoxazole moiety. Moreover, the deprotonated open-ring isomer exhibited typical photochromism via the diarylethene intermediate with a benzoxazole unit.

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1. Introduction

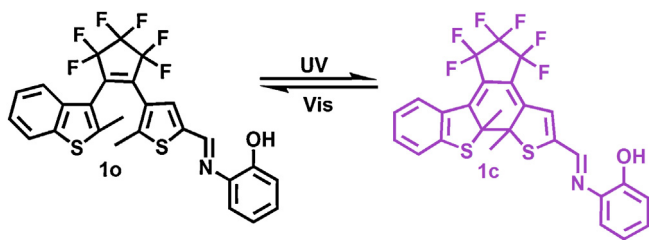
Benzoxazoles are an important class of heterocycles in many natural products and pharmaceutical agents, which exhibit a variety of biological activities including antimicrobial and antitumor properties [1–4]. Benzoxazoles are also applied in material science as photochromic agents and laser dyes [5]. Both of the two conventional methods for the construction of benzoxazole ring employ 2-aminophenols as the substrates [6,7]. One approach is the coupling of 2-aminophenols with carboxylic acid derivatives under strong acidic/high temperature conditions [8] or microwave-assisted conditions [9]. The other uses the reaction of 2-aminophenols with an aldehyde via the oxidative cyclization of phenolic Schiff base intermediates [10–12]. In these reactions, oxidants are required in stoichiometric or excess amounts relative to their respective substrates. Therefore, development of a more effective route to benzoxazole ring formation is needed.

Recently, 2-haloanilides and benzanilides are frequently used to synthesize 2-arylbenzoxazoles via copper-catalyzed intramolecular oxidative cyclization [13–15] due to their commercial availability. Under an oxygen atmosphere in the presence of activated carbon (Darco KB) [16] or $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ [17], 2-arylbenzoxazoles were synthesized directly without preparing

Schiff bases in advance. A general method for preparation of 2-arylbenzoxazoles from derived phenolic Schiff bases in the conditions of sodium hydroxide (NaOH) and phototrigger in acetonitrile (CH_3CN) was presented. Moreover, the phenolic Schiff base moiety in diarylethene could easily transformed to 2-arylbenzoxazoles in the same conditions [18]. The result provided a useful strategy for constructing a multi-responsive photochromic diarylethene.

Diarylethenes have attracted remarkable research interests by taking advantage of their excellent thermal stability and outstanding fatigue resistance [19,20]. They have potential applications in photonic switch device and optical memory media [21–23]. In previous reports [24–28], the Schiff base moiety in a diarylethene skeleton was found capable of modulating the photochromic properties by base or metal ion stimuli. Tian et al. [24] reported a novel diarylethene with phenolic Schiff base moiety. The diarylethene showed fluorescence enhancement in the presence of Cu^{2+} due to the C=N isomerization [25], which was inhibited through complexation with Cu^{2+} . Pu et al. [26] synthesized a diarylethene with a salicylic aldehyde Schiff base unit, which could be used as a multi-addressable fluorescence switch triggered by light, acid and metal ions. Liu et al. [27] revealed that diarylethenes containing Schiff-base moieties showed polychromic behavior. Chen et al. [28] suggested that the phenolic Schiff base moiety could increase the absorption maximum of the closed-ring isomer. All these results showed that diarylethenes with Schiff base moieties have versatile applications due to their unique physicochemical properties. In this work, a novel asymmetrical diarylethene with phenolic Schiff base

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Scheme 1. Photochromism of diarylethene **1**.

(**1o**) was synthesized and its multi-responsive behavior was investigated. The absorption maximum of its closed-ring isomer showed extraordinarily large redshift upon deprotonation. The deprotonated closed-ring isomer could be converted to a diarylethene with a benzoxazole moiety upon irradiation with 420 nm light. Moreover, the open-ring isomer of diarylethene with benzoxazole moiety exhibited favorable photochromism upon 297 nm UV photoirradiation. The photochromism of **1o** is shown in Scheme 1.

2. Experimental

2.1. General methods

NMR spectra were recorded on a Bruker AV400 (400 MHz) spectrometer using CDCl₃ as solvent and tetramethylsilane (TMS) as an internal standard. Infrared spectra (IR) were recorded on a Bruker Vertex-70 spectrometer. Mass spectra were measured with an Agilent 1100 ion trap MSD spectrometer. UV–visible spectra were recorded on an Agilent 8453 spectrometer. Photo-irradiation was carried out using an SHG-200 UV lamp, a CX-21 ultraviolet fluorescence analysis cabinet, and a BMH-250 visible lamp. Lights of appropriate wavelengths were isolated using different light filters. Fluorescence spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer. Melting points were measured with a WRS-1B melting point apparatus. All solvents used were of spectrograde and were purified by distillation prior to use. All other reagents were obtained from J&K Scientific Ltd. without further purification. Dissolved ultrasonically 10 mg diarylethene sample and 100 mg PMMA into 1.0 mL chloroform, the films were prepared by spin-coating method.

2.2. Synthesis of

1-(2-methyl-3-benzothienyl)-2-(5-(2-methyleneaminophenol)-2-methyl-3-thienyl)perfluorocyclopentene (**1o**)

The synthesis method of the diarylethene **1o** was shown in Scheme 2 and experimental details were carried out as followed. Compound **2** was prepared according to the reported method [29].

To a stirred solution of compound **2** (0.22 g, 0.50 mmol) in ethanol (2.5 mL), 2-aminophenol (0.056 g, 0.50 mmol) was added and continuously stirred. After refluxing for 5 h, the mixture was

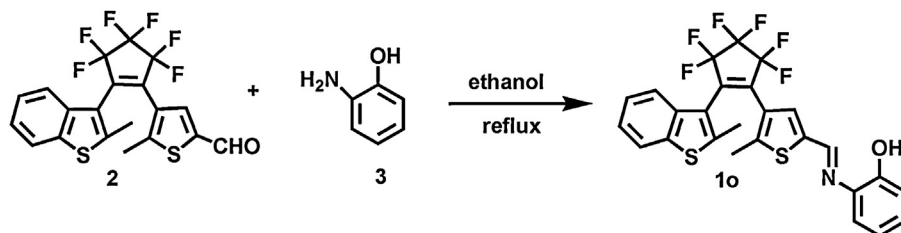
cooled to room temperature and concentrated under vacuum. The crude product was purified by recrystallization with ethanol to give the compound **1o** (0.090 g, 1.71 mmol) as a yellow solid in 35% yield. M.p. 403–404 K; ¹H NMR (CDCl₃, 400 MHz, TMS), δ (ppm): 1.98 (s, 3H, –CH₃), 2.30 (s, 3H, –CH₃), 6.86 (s, 1H, thiophene-H), 6.88–7.24 (m, 4H, phenyl-H), 7.31–7.76 (m, 4H, benzothiophene-H), 8.61 (s, 1H, –CH=N); ¹³C NMR (CDCl₃, 100 MHz), δ (ppm): 14.8, 15.38, 115.15, 115.66, 119.94, 120.10, 121.98, 122.16, 124.64, 125.04, 125.36, 129.18, 131.80, 134.54, 137.98, 138.27, 140.53, 142.59, 147.63, 148.40, 152.24; IR (KBr, ν, cm⁻¹): 759, 833, 845, 896, 989, 1033, 1056, 1097, 1114, 1038, 1183, 1278, 1366, 1377, 1486, 1560, 1599, 2223, 2891, 3412. LRMS, ESI⁺ *m/z* 538.1 (MH⁺, C₁₈H₁₄BrF₆NS requires 537.5); Anal. Calcd for C₂₆H₁₇F₆NOS₂ (%): Calcd C, 58.09; H, 3.19; N, 2.61. Found C, 59.12; H, 3.15; N, 2.58.

3. Results and discussion

3.1. Photochromism of **1**

Upon alternative irradiation with UV and visible light, diarylethene **1o** underwent a reversible reaction in both acetonitrile (2.0 × 10⁻⁵ mol L⁻¹) and a PMMA film (10%, w/w) at room temperature. The changes in the absorption spectra and color of **1o** induced by photoirradiation are shown in Fig. 1. In acetonitrile, the open-ring isomer **1o** showed a sharp absorption peak at 264 nm (ε = 2.64 × 10⁴ L mol⁻¹ cm⁻¹). Upon irradiation with 297 nm UV light, a new absorption band centered at 566 nm (ε = 3.52 × 10³ L mol⁻¹ cm⁻¹) emerged due to the formation of the closed-ring isomer **1c**, accompanied with a color change from colorless to purple. The purple color was bleached to colorless upon irradiation with visible light (λ > 450 nm), and the absorption spectrum returned to the initial state of **1o**. The absorption spectral change upon photoirradiation was accompanied by an isosbestic point at 390 nm, which clearly indicated a two-component photochromic reaction [30–32]. Similarly, diarylethene **1o** showed favorable photochromism in a PMMA film. Irradiation of **1o**/PMMA film with 297 nm UV light resulted in the appearance of new absorption band at 576 nm, accompanied with a color change from colorless to purple. The purple color was faded to colorless by irradiation with visible light (λ > 450 nm). Compared to that in acetonitrile, the maximum absorption peak of **1c** in a PMMA film was redshifted by 10 nm. The redshift phenomena may be ascribed to the polar effect of the polymer matrix and the stabilization of molecular arrangement in solid state [33].

The maximum absorbance for **1c** as a function of time was determined by alternating irradiation with 297 nm UV light and visible light (λ > 450 nm) in acetonitrile and a PMMA film, and the result is shown in Fig. 2. After 10 repeat cycles, 38% degradation in acetonitrile and 13% degradation in a PMMA film were observed for **1c**. This remarkable improvement may result from effective suppression of the oxygen diffusion in the solid state [21]. The observation could be testified by the following experiment. In a degassed acetonitrile solution of **1o**, the coloration and decoloration cycles of **1** could repeat 10 times with only the degradation of 11% for **1c**.



Scheme 2. Synthetic route for diarylethene **1o**.

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