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Gated Photochromism of 1,2-Diarylethenes

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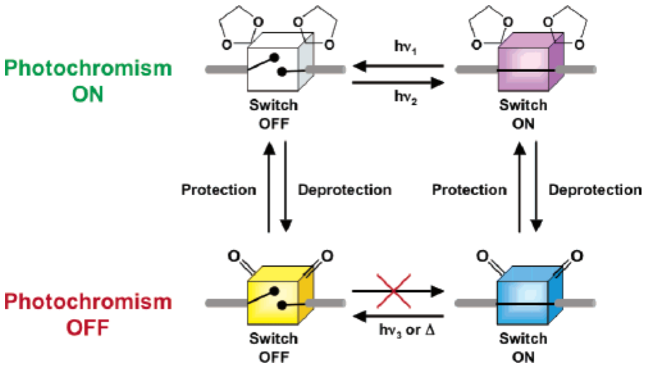
ABSTRACT



A dithienylethene derivative containing a cyclobutene-1,2-dione skeleton does not exhibit photochromic properties. However, when both ketone functions are protected with cyclic acetal groups, photochromic behavior is observed.

The properties of organic switches have been widely detailed in the literature.[1] One of the main challenges in employing these photochromic compounds for applications in optical memory media is to establish nondestructive readout capability. One of the ways to induce this property is to introduce gated photochromic reactivity into the system.

A compound is said to possess the property of gated reactivity if it converts from a photoinert state at a particular wavelength to a photoactive state by the application of external stimuli such as reactive chemicals,[2−6] heat,[7,8] or multiphoton absorption.[9]

Several gated diarylethene photochromic systems have been reported. Strategies such as esterification reactions,[2] [4 + 2] cycloaddition reactions,[3] acid/base reactions,[4] redox processes,[6] and hydrogen bondings[6,8] have been employed to manipulate the photochromic reactivity. Previously, a derivative similar to **1a**, wherein methyl groups were present in lieu of phenyl substituents, was found to be photoinert.[10] The absence of any photochromic reaction was attributed to the apparent rigidity of the structure.[10] In contrast, cyclobutene-1,2-dione derivatives can perform a photochemical

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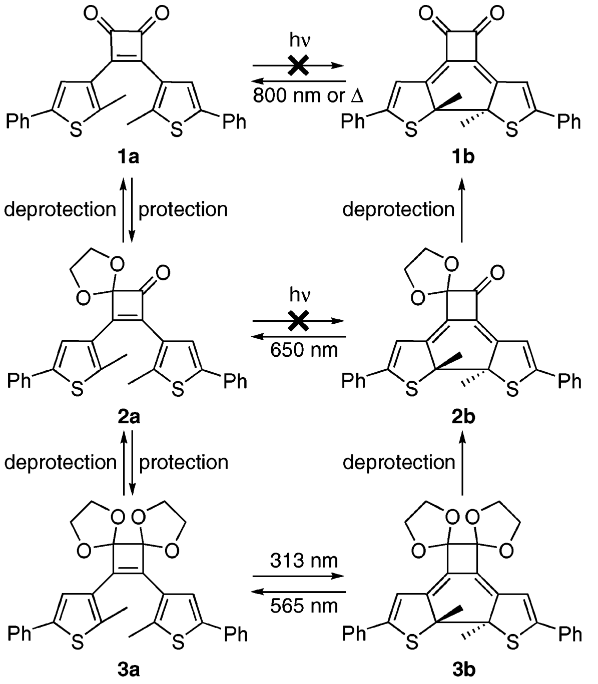
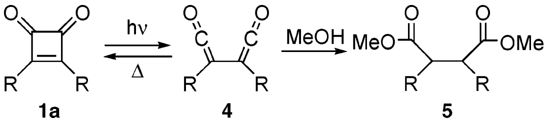
ring opening reaction yielding 1,2-bisketenes (see **4** in Scheme 2).[11] At room temperature a fast thermal back reaction takes place and the photochemical transformation to **1b** is not observed. 1,2-Bisketenes are not directly observed but rather proposed as reactive intermediates from trapping experiments.[12]

The aim of this work is to activate the photochromic property of **1a** by protecting the ketone functionality, which actually causes the suppression of the photochemically induced opening reaction of cyclobutene-1,2-dione. We have designed and synthesized a chemically gated diarylethene derivative containing a cyclobutene-1,2-dione skeleton (Scheme 1). Compound **1a** was prepared from diethyl squarate, and the diethoxy groups were substituted by thiophene moieties; compounds **2a** and **3a** were synthesized by a typical protecting reaction of ketones.[13] The absorption spectrum of **1a** was measured in acetonitrile at room temperature; **1a** did not undergo any photochromic reaction during irradiation at 365 nm. The excited state of **1a** was efficiently quenched by the ring-opening reaction yielding **4** (Scheme 2). In the absence of a trapping agent, thermal back reaction occurs very fast and **4** cannot be observed at room temperature. Nevertheless, the highly reactive intermediate **4** can be trapped with methanol, forming the moiety **5**.[13] This observation does not exclude the possibility of the absence of photochromism due to rigidity of the system. Compound **2a** with only one ketone functionality does not display any photochromic behavior.

Scheme 1. Protection Reactions of **1a**, Deprotection Reactions of **3a** and **3b**, and Photochromism of **3a**



Scheme 2. Trapping Reaction of 1,2-Bisketenes **4** by Methanol



Compound **3a** was obtained by protecting both ketone functionalities of **1a**. Upon irradiation at 313 nm, the colorless solution of **3a** in acetonitrile became increasingly violet, indicative of its closing process. Opening reaction takes place upon irradiation with visible light at 550 nm. UV−vis spectra of this typical photochromic behavior are shown in Figure 1 (part I). Compound **3a** has a broad absorption band at 275 nm. After closing the switching molecule, two new absorption bands appear at 361 and 565 nm, attributable to **3b**.

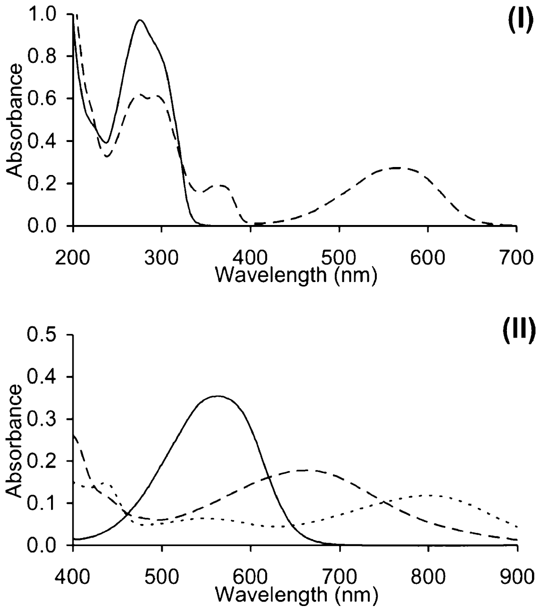


Figure 1. (I) Absorption spectra of **3** in acetonitrile solution: (—) open-ring isomer (**3a**), (- - -) closed-ring isomer (**3b**) obtained after irradiation of a solution of **3a** in acetonitrile at 313 nm. (II) Absorption spectra of closed forms in the visible region in acetonitrile. Closed isomers of **3b** (—), **2b** (- - -) and **1b** (· · · ·).

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(13) See Supporting Information for details.

Table 1. Wavelength Maxima and Absorption Coefficients of Open and Closed Isomers of Diarylethenes

compd	$\lambda_{\max}$/nm ($\epsilon_{\max} \times 10^4$ M^{-1} cm^{-1})[a]
1a	267 (3.7), 290 (4.1), 365 (0.9)
1b	292 (2.5), 436 (0.3), 548 (0.1), 800 (0.2)
2a	259 (2.7), 289 (4.1), 346[b] (0.6)
2b	294 (2.3), 400 (0.5), 666 (0.4)
3a	275 (4.2)
3b	275 (2.7), 293 (2.6), 361 (0.8), 565 (1.2)

[a] MeCN at 293 K. Solution concentration: 3×10^{-5} M. [b] Shoulder.

The deprotection of **3b** occurs easily under acidic conditions, forming **2b**. Moreover, the first deprotection is much faster than the second one. Therefore, by adding a base, it is possible to arrest the reaction after the first deprotection in order to obtain **2b**. Compound **3a** shows the same behavior as **3b**. Only the closed forms (**1b**, **2b**, and **3b**) have absorption bands above 400 nm (Table 1). The deprotection reaction[14] of **3b** can be followed by spectroscopic measurements in the visible region (Figure 1, part II). During the first deprotection, the band at 565 nm disappears while a new band is seen at 666 nm, attributable to **2b**. The second deprotection leads to a decrease in the band intensity at 666 nm with the appearance of a new band at 800 nm, attributable to **1b**. As mentioned earlier, deprotection processes of the closed forms (**2b** and **3b**) are accompanied by a strong red shift. The results of UV−vis spectra have been summarized in Table 1.

Photocycloreversion occurs by irradiation at 800 nm for **1b** and 650 nm for **2b**. Consequently, deprotection of cyclic acetal does not suppress ring-opening reactions. Moreover, **1b** also undergoes a spontaneous back reaction in the dark at room temperature. The reaction rate was determined by applying a first-order reaction model. The rate constant and the half-life were 0.025 h^{-1} and 28 h, respectively.[13] The rate constant for the back reaction increases drastically under acidic conditions.

However, this process can also be studied by ^{1}H NMR measurements wherein the peaks corresponding to the methyl groups of the thiophene moieties are prominent (Figure 2). Methyl groups of **3a** appear at 2.21 ppm. Upon irradiation at 313 nm, 57% of **3a** was converted into **3b** and a new peak appeared at 2.18 ppm, assignable to the methyl groups of **3b** (Figure 2, part I). Under acidic conditions,[15] the peak at 2.18 ppm (2.21 ppm) was replaced by two peaks appearing at 2.24 and 2.31 ppm (2.37 and 2.44 ppm) indicating the formation of **2b** (**2a**) (Figure 2, part II). Because of the faster reaction rate for the deprotection reaction of **2b** compared to that of **2a**, the spectrum shows the presence of **2a**, **1a**, and **1b** (Figure 2, part III). After 4 days, only the singlet of **1a** at 2.65 ppm was observed.

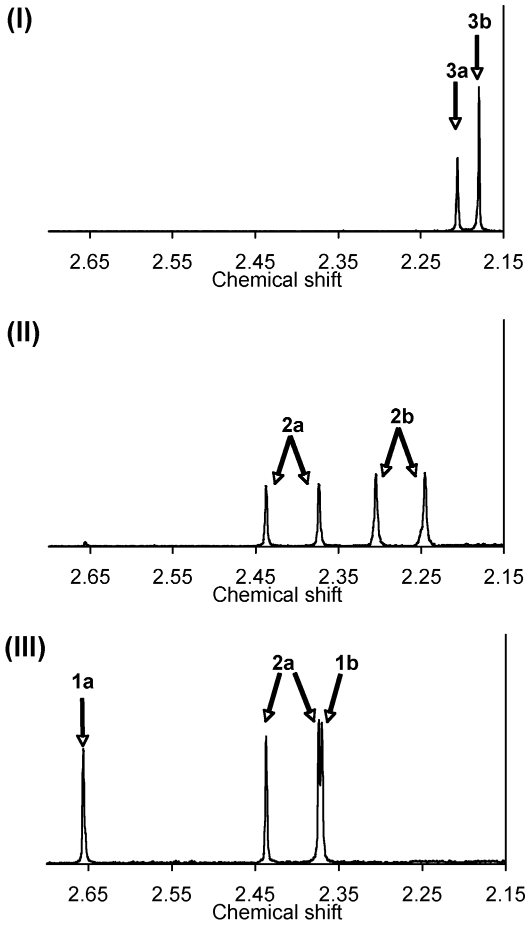

Figure 2. (I) ^{1}H NMR spectra of **3a** in chloroform solution after irradiation with light at 313 nm. (II) After the addition of methanesulfonic acid, one of the protecting groups of **3a** and **3b** is eliminated, and (III) both protecting groups of **3b** are eliminated.

Closing and opening reactions of **3** were performed several times. After only 10 irradiation cylces, there is a ca. 25% loss of photochromic activity,[13] indicating that the system is not very robust for any kind of recording/storage application. Side products were detected after the closing reaction of **3a** by ^{1}H NMR spectroscopy, and this could possibly explain the decreasing effect. Protection and deprotection reactions, however, did not show any undesired side reactions.

In summary, we have developed a new chemically gated dithienylethene switch whose photochromic reactions can be manipulated by the addition of an acid.

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Supporting Information Available: Synthetic details and characterizations for compounds, including CIF file. This material is available free of charge via the Internet at

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[14] A solution of **3a** (2.5 cm^3, 3×10^{-5} M) in acetonitrile was irradiated at 313 nm for 1 min. Methanesulfonic acid (10 μL) was added, and the deprotection processes was followed by UV−vis spectra.

[15] Forty solutions of **3a** (2.5 cm^3, 3×10^{-5} M) in acetonitrile were irradiated at 313 nm for 1 min. Solvent was removed in the dark. The residue was dissolved in deuterated chloroform. Methanesulfonic acid (10 μL) was added and deprotecting processes was followed by ^{1}H NMR spectra.

3http://pubs.acs.org. Crystal structure data for compound **1a** (CCDC 626864) can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by email to data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033.

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