Available online at www.sciencedirect.com

SCIENCE DIRECT®

Tetrahedron Letters 46 (2005) 9009–9012

Tetrahedron Letters

A multi-photo responsive photochromic dithienylethene containing coumarin derivative

Shuzhang Xiao, Tao Yi,* Fuyou Li and Chunhui Huang*

Laboratory of Advanced Materials, Fudan University, Shanghai 200433, China

Received 19 August 2005; revised 21 October 2005; accepted 21 October 2005
Available online 9 November 2005

Abstract—A complex photochromic diarylethene derivative containing photo-responsive coumarin groups was synthesized by an efficient method. The dimerization of coumarin groups and photochromism of diarylethene can be controlled respectively to produce the four corresponding states, which were verified by ^{1}H NMR, fluorescent, UV–vis spectroscopy and mass spectrometry. This compound gives a unique example for the controllable switch of both optical properties and chemical composition by light and chemical stimuli.

Research on photochromic materials has aroused much interest for their potential applications on optical memories and photonic switching devices, where each isomer of the photochromic compound can represent '0' or '1' of a digital code.[1–3] However, for practical applications, thermal irreversibility of the switching units is required in most cases. As a thermally irreversible system, diarylethenes may be the most promising compounds for these applications due to the good thermal stability and high fatigue resistance of both isomers.[4,5] In the field of photochromism, development of complex systems that integrate several switchable functions into a single molecule is a key aspect in the progress of molecular switches. Various new approaches to material engineering for multi-addressable switching systems based on diarylethenes have been proposed in recent years, including the design of nonsymmetric fused dithienylethene dimers or trimers,[6,7] the combination of two or more types of photochromic components into one molecule,[8–10] and the crystal engineering of several photochromic molecules into a full-colored single crystal.[11–14] Almost all of these strategies only devoted photo-induced color change, a few examples also related to the proton-induced acidichromism.[15] The photo-induced or chemical-induced mass switch such as reversibly photodimerization and subsequent photocleavage is also worth exploring, especially in biological application such as a possible controlled drug release mechanism.[16] Coumarin derivatives, another kind of optical active material which can undergo photochemical 2π+2π dimerization upon photo irradiation, is a very nice candidate for this purpose.[16,17]

Coumarin derivatives are widely used in the fields of biology, medicine and polymer science and have already been well documented as therapeutic agents.[17] The dimerization of coumarin would produce various different signals on UV–vis, fluorescent, NMR, and mass spectra.[17–25] The combination of coumarin with dithienylethene should not only involve a multi-addressed memory system, but also entail the possibilities of biological application. In this letter, we designed and prepared a complex multi-addressable compound (**1o**) containing both coumarin and diarylethene. Compound **1o** undergoes reversible photochromism and photodimerization upon irradiation of light (Scheme 1). This novel structure represents a unique example of a multi-addressable system where both controllable optical properties and chemical changes are realized using light as stimuli, assisted with catalyst.

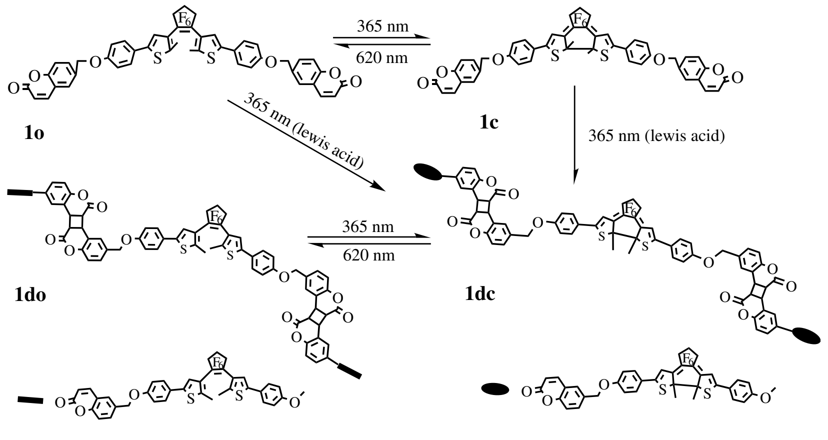
Compound **1o** was synthesized by the reaction of 1,2-bis[5′-(4″-hydroxyphenyl)-2′-methylthien-3′-yl]-perfluorocyclo pentene[26] with 6-bromomethyl coumarin in the presence of K_2CO_3 and 18-crown-6 in acetone in 80% yield (Scheme 2), and characterized by NMR, mass

---

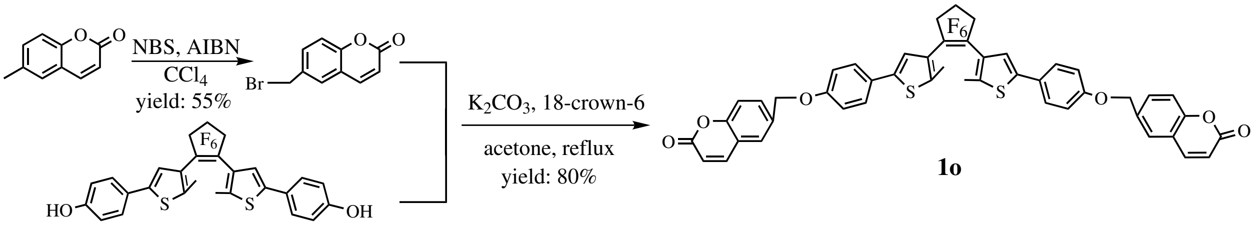
Keywords: Photochromism; Diarylethene; Coumarin; Dimerization; Multi-addressed.

* Corresponding authors. Tel.: +86 21 55664185; fax: +86 21 55664621 (T.Y.); e-mail: yitao@fudan.edu.cn

0040-4039/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2005.10.102



Scheme 1. Four states of compound **1** responding to external stimuli.



Scheme 2. Synthetic process of **1o**.

spectroscopy, and elemental analysis.[27] The 6-bromomethyl coumarin was produced from 6-methyl coumarin brominated with NBS in CCl_4 using 2,2′-azo-bis-isobutyronitrile as catalyst.

As illuminated in Scheme 1, **1o** undergoes a reversible photocyclization to **1c** upon alternate irradiation with UV and visible light. In the presence of BF_3, by taking more than 20 h of irradiation with light longer than 320 nm, the photodimerization took place to produce **1dc**. ^1H NMR measurement gives the direct evidence for photocyclization and photodimerization.[20–22] Figure 1 clearly exhibits the signals for photochemical reactions. Chemical shifts of $-CH_3$ on thienyl of **1o** appeared at 1.94 ppm (A), and it shifted to 2.13 ppm (B) upon UV light irradiation due to photocyclization reaction. In the photostationary state, the conversion value of **1c** is calculated to 69% by both HPLC analysis and NMR measurement. After photodimerization of coumarin, signals of cyclobutane on **1dc** appeared as the mutiplets in the range of 3.60–3.75 ppm (C), which indicated the formation of *anti*-hh isomer.[22] Electrospray ionization mass spectra (ESI-MS) of the photodimerization product **1dc** showed obvious signals corresponding to the trimer. The ESI mass spectrum of **1dc** contains peaks for multiplied charged cationic species. The two main peaks at *m*/*z* 869.6744 and 652.5044 are assignable to the cationic species $[\mathbf{1dc}+3H]^{3+}$ and $[\mathbf{1dc}+4H]^{4+}$, respectively. These results indicate the formation of trimer. The conversion of coumarin monomer to trimer is expected to be 21% from the integration of ^1H NMR spectrum.

The absorption spectral changes of **1o** in chloroform solution responding to light are shown in Figure 2A.

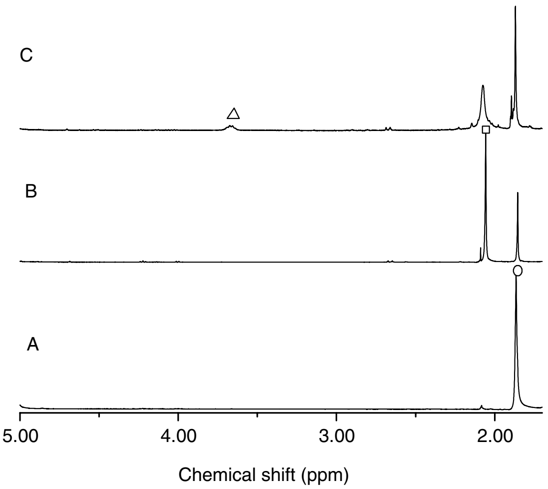


Figure 1. ^1H NMR spectra of **1o** (A); after 365 nm UV light irradiation (B); after photodimerization of coumarin derivative (C) (400 MHz, CD_3Cl). (○) CH_3- on thienyl of **1o**; (□) CH_3- on thienyl of **1c**; (△) $-CH-$ on cyclobutane for the dimer **1dc**.

Upon 3 min irradiation with 365 nm UV light, the colorless solution of **1o** turned blue referred to the close state of **1c**. The maximum absorption of **1c** was observed at 595 nm ($\varepsilon = 2.3 \times 10^4$ M^{-1} cm^{-1}), with a quantum yield ($\Phi_{o \to c}$) of 0.32. Photodimerization of **1o** would not occur in such a short time without a catalyst. The blue colored solution of **1c** returned to colorless on irradiation with visible light ($\lambda > 590$ nm). This process was completely reversible. The absorption spectral shape of **1dc** was similar to that of **1c**, only the maximum absorption at both 595 and 290 nm was reduced compared to state **1c**. This change may be due to the smaller ε value of