Pergamon

Tetrahedron Letters 41 (2000) 4025–4028

TETRAHEDRON
LETTERS

A dual-mode molecular switch based on a chiral binaphthol-coumarin compound

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Received 23 March 2000; revised 5 April 2000; accepted 6 April 2000

Abstract

A dual-mode, efficient molecular switching system based on photomodulation of optical rotational power and fluorescence emission of a chiral binaphthol-coumarin compound is presented.

Keywords: binaphthol; coumarin; chiral; fluorescence; molecular switch.

Molecular switches are based on bistability of a molecule and the ability of reversible interconvertion between two isomeric forms by external stimuli. Among many requirements the two isomers should be at least switchable and detectable by non-destructive means.[1] Between a single-mode and a dual-mode molecular switch, the latter offers more advantages such as 'writing' by light at one wavelength and 'reading' by light at another wavelength that does not destroy the bistability. Lehn and co-workers reported a dual-mode molecular switch based on photochromic and electrochromic properties that are regulated and integrated in a single structure.[2] Another interesting dual-mode switching system reported by Feringa and Huck employs chiral helical alkenes in which chirality and fluorescence can be reversibly modulated by light.[3]

We report here a dual-mode switching system that is based on the photomodulation of fluorescence and optical activity of a chiral binaphthol-coumarin compound (**2**). The system is designed to have two functional moieties, chiral binaphthol and photoactive coumarin, incorporated in a single molecule which can be switched in two modes based on the changes in the fluorescence intensity and optical rotation. Photodimerization of coumarin and its derivatives has been intensively studied in solution,[4] self-assembled monolayer[5] and polymeric film,[6] as well as a pendant group in a polymer.[7] It is well known that upon irradiation at 350 nm in solution coumarin forms [2+2] dimers. These photodimers can be cleaved upon irradiation at wavelengths shorter than 300 nm. Another important feature associated with the photodimerization of coumarin is the change in its emission intensity.[8] Coumarin fluoresces upon excitation at 320 nm while its dimers do not.[5,8] If the chiroptical property and fluorescence of

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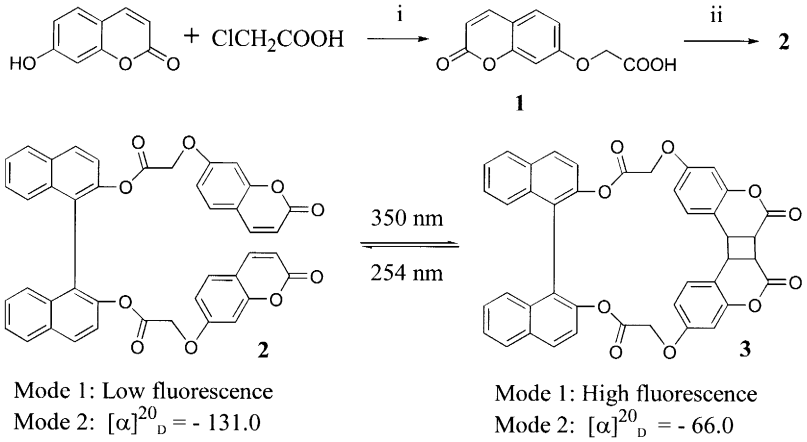
0040-4039/00/$ - see front matter
PII: S0040-4039(00)00576-1

the newly designed system **2** are distinctly different at the two photostationary states (open and closed forms), it could in principle be used as a dual-mode molecular switch.

Compound **2** was synthesized from 7-hydroxycoumarin in two steps (Scheme 1). The acid **1**[9] was first derived from 7-hydroxycoumarin and subsequently reacted with (*R*,*S*)-1,1′-bi-2-naphthol to afford the corresponding racemic **2** as a white solid (23.5%, mp 183–186°C).[10] When (*S*)-1,1′-bi-2-naphthol was used in the reaction, the optically active **2** was obtained ($[\alpha]^{20}_{D}=-131$, c=0.01, chloroform). The photochemical studies of both racemic and enantiomeric **2** and the corresponding cyclic dimers **3** were carried out in the chloroform solution (1.6×10^{-5} M) in a quartz cell and in the solid state (in KBr matrix). Using a mercury lamp (300 W, 350 nm), the photocyclization in solution was complete in about 10 min and the cyclic dimers **3** (as two regioisomers) were formed in quantitative yield as determined by HPLC (Scheme 1). The complete photocleavage occurred in 2 min at 250 nm. This reversible switching process could be repeated in many cycles similar to other reported coumarin systems (e.g. 100 on/off cycles)[6] and easily monitored by UV–vis spectroscopy. Upon irradiation with 350 nm UV light the absorption peak at 297 nm (ε=130 000 M^{-1} cm^{-1}) for the lactone double bond in **2** decreased significantly while the same peak went back to the initial intensity after irradiation at 250 nm (Fig. 1). The coumarin dimers **3** did not go back to the starting compound **2** for 4 days in chloroform solution at ambient temperatures. In the solid state (2 mg of **2** in 200 mg of KBr as a pellet) the photodimers were also formed readily (10 min) in quantitative yield. Interestingly, the racemic **3** formed in KBr matrix did not go back to the initial compound **2** after UV irradiation at 254 nm for 5 h, irradiation with white light for 1 h, or when kept in a dark environment at 22°C for weeks. Thus, once the compound **3** is formed in the solid state, it could potentially be detected or read many times, similar to a WORM memory system.



Scheme 1. Synthesis and photochemistry of (*R*,*S*)- and (*S*)-**2**. (i) K_2CO_3, acetone, 18-crown-6, reflux, 48 h; (ii) DMAP, DCC, (*R*,*S*) or (*S*)-1,1′-bi-naphthol, CH_2Cl_2, 36 h, 22°C

It was observed that before photocyclization compound **2** showed little fluorescence, due to the quenching between the binaphthol and coumarin moieties. After photocyclization, its fluorescence increased significantly (Fig. 1). This increase in fluorescence is solely contributed by the binaphthol moiety, thus modulation of fluorescence emissions between the two states (**2** and **3**) can be achieved by selective photoirradiation.

Optical rotations of optically active **2** in chloroform (10 mg in 1 mL) before and after photoirradiation also changed noticeably. Typically, the specific optical rotation of **3** is half of that of enantiomeric **2** at a given wavelength (Table 1). It is known that the more planar (or conjugated) a chiral binaphthyl molecule is, the higher its optical rotation will be.[11] Molecular modeling (HyperChem, version 4.0) showed that

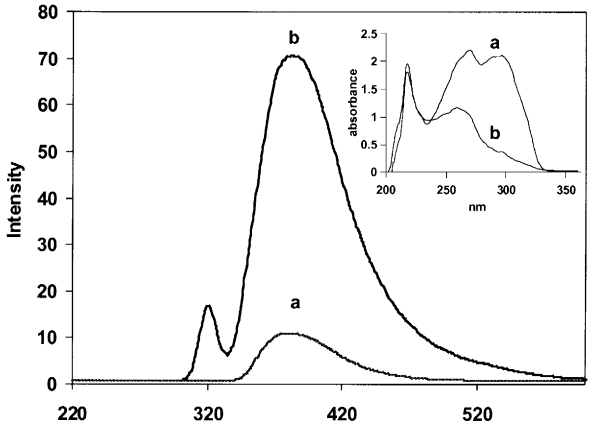


Fig. 1. Fluorescence spectra and UV–vis spectra (inset) in chloroform (1.6×10^{-5} M) of: (a) racemic **2**; and (b) racemic **3**

the cyclic dimer is more twisted and hence less conjugated than the starting compound (open form), which supports our result that after photodimerization the optical rotation is decreased.

Table 1
Specific optical rotations for (*S*)-**2** and corresponding cyclic **3**[a]

λ, nm	$[\alpha]^{20}$, **2**	$[\alpha]^{20}$, **3**
589	- 131.0	- 66.0
578	- 137.5	- 69.5
546	- 161.4	- 74.8

[a] Concentration: 10 mg of **2** in 1 mL of chloroform.

In conclusion, compound **2** acts as a molecular switch that can be addressed by UV light and has two stable distinct states detectable in two modes by light (fluorescence and optical rotation) at the wavelengths that will not destabilize either of the two isomeric molecules.

This work was supported by the Natural Sciences and Engineering Research Council of Canada.

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9. A suspension of 7-hydroxycoumarin (3.000 g, 0.018 mol), chloroacetic acid (1.700 g, 0.018 mol), anhydrous K_2CO_3 (7.460 g, 0.054 mol), 18-crown-6 (1.200 g) in 100 mL of dry acetone was heated to reflux for 3 days. The suspension was filtered and the yellowish precipitate was dissolved in water. The resulting solution was extracted with ethyl acetate (4×25 mL) and the organic layer was washed with saturated $NaHCO_3$ solution (4×20 mL). The washings were acidified with concentrated HCl solution until it was slightly acidic. The resulting white precipitate was filtered and dried at 100°C in an oven for 10 h to afford the pure product **1**: 2.49 g (61% yield); mp 223–226°C; ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.98 (d, J=9.52 Hz, 1H), 7.62 (d, J=9.28 Hz, 1H), 6.94 (dd, J=7.4 Hz, 2.2 Hz, 2H), 6.29 (d, J=9.48 Hz, 1H), 4.81 (d, 2H); ^{13}C NMR (100

MHz, DMSO-d_6): δ 169.7, 160.9, 160.2, 155.2, 144.3, 129.5, 112.8, 112.7, 101.5, 64.8, 54.9; HRMS calcd for $C_{11}H_8O_5$: 220.0376; found: 220.0376.

10. 1,1′-Bi-2-naphthol (1.430 g, 0.005 mol), 7-carboxymethoxycoumarin (**1**) (2.500 g 0.011 mol) and 3 spatula tips of 4-*N*,*N*-dimethylaminopyridine (DMAP) were dissolved into 50 mL of anhydrous dichloromethane. After the addition of *N*,*N*-dicyclohexylcarbodiimide (DCC) (4.726 g, 0.023 mol), the solution was stirred at room temperature for 36 h. The white suspension was filtered and the organic phase was washed first with 150 mL of 1 M HCl solution, then with 150 mL of 1 M NaOH solution and finally with distilled water (5×20 mL). The organic solution was dried over $MgSO_4$ and the solvent was removed in vacuo to afford 1.5 g of the crude product. After further washing with acetone, the pure product **2** was obtained: 0.811 g (23.5% yield); mp 183–186°C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (d, J=5.84 Hz, 1H), 7.84 (d, J=8.16 Hz, 1H), 7.54 (d, J=10.4 Hz, 1H), 7.42 (d, J=8.96 Hz, 1H), 7.38 (d, J=6.96, 1H), 7.21–7.17 (m, 1H), 7.10 (d, J=11.2 Hz, 1H), 7.04 (d, J=8.48 Hz, 1H), 6.45 (dd, J=8.6 Hz, 2.48 Hz, 1H), 6.37 (d, J=2.48 Hz, 1H), 6.2 (d, J=9.48 Hz, 1H), 4.4–4.5 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 160.9, 160.4, 155.3, 145.8, 143.2, 133.1, 131.7, 130.3, 128.8, 128.1, 127.2, 126.2, 125.9, 122.9, 121.1, 113.7, 113.3, 113.2, 101.5, 64.7; MS (FAB, *m/e*, relative intensity) 691 ($M+H^+$, 38%).
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