

Synthesis of Hymecromone Derivatives Containing Chiral 1,1'-Bi-2-naphthyl Moiety for Dual-mode Molecular Switch

Zi Xing SHAN*, Chun Guang XIAO

Department of Chemistry, Wuhan University, Wuhan 430072

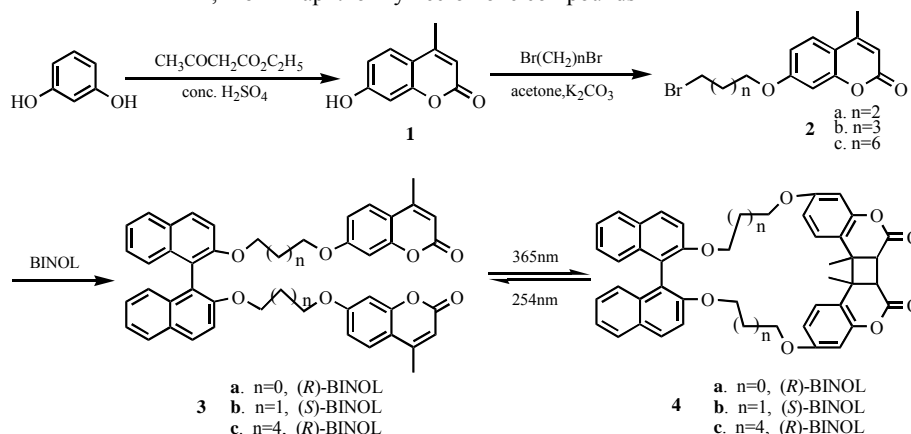
Abstract: Some hymecromone derivatives containing chiral 1,1'-bi-2-naphthyl moiety were synthesized and their photodimerizations were investigated. It was found that fluorescence intensity and optical rotation of the new chiral hymecromone derivatives could be regulated by light. This property has potential significance for developing a new type of dual-mode molecular switch.

Keywords: Hymecromone, chiral 1,1'-bi-2-naphthol, photodimerization, molecular switch.

Photodimerization of coumarins has been extensively studied in homogeneous solution and in organized media such as micelles, cyclodextrin inclusion complexes, and crystals¹. It is well known that coumarin derivatives in solutions are generally converted to dimers upon irradiation with light longer than 300 nm through a [2+2] photocycloaddition, and these dimers can be photocleaved upon irradiation with light shorter than 300 nm. Another interesting property associated with coumarin photodimerization is the modulation of fluorescence emission². Upon excitation of light at 320 nm, coumarins strongly fluoresce, whereas the corresponding dimers do not. Therefore, these simple photodimerization and photocleavage reactions represent an on-off molecular switch. Development of molecular devices requires the realization of molecular components. If the chiral element is led to a photoactive coumarin, it will have fluorescent property and optical rotation in the meantime. However, for the photodimerization of the coumarins containing chiral moiety, it has been seldom investigated up to now³. In the present letter, we will report the synthesis of a type of dual-mode molecular switch, which is based on hymecromone compounds containing chiral 1,1'-bi-2-naphthyl moiety (**Scheme 1**).

Hymecromone (7-hydroxy-4-methylcoumarin) **1** is a derivative of coumarin. In **Scheme 1**, compounds **3a**, **3b** and **3c** were designed to have two functional moieties, namely photoactive hymecromone moiety and chiral 1,1'-bi-2-naphthyl group, which were connected by the methylene chain. The investigation indicated that they could be switched into two modes as the changes in the fluorescent intensity and optical rotation, which could be reversibly modulated by light.

* E-mail: kenshan@public.wh.hb.cn

Scheme 1 Synthesis of a dual-mode molecular switch based on chiral 1,1'-bi-2-naphthol-hymecromone compounds

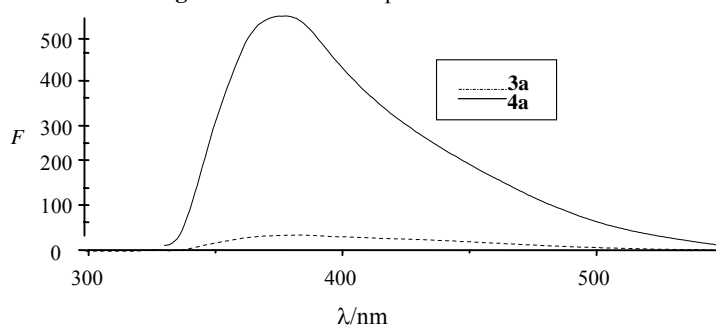
1,3-Dihydroxybenzene reacted with ethyl acetoacetate under catalysis of concentrated H_2SO_4 to give 7-hydroxy-4-methylcoumarin **1**; **1** was etherized with a α,ω -dibromo alkane in dry acetone in the presence of K_2CO_3 to furnish 7-(ω -bromoalkyloxy)-4-methylcoumarin **2**. To dry acetone solution of **2** was added enantiomerically pure 1,1'-bi-2-naphthol⁴ and refluxed for 24-48 h. After the precipitate was filtrated out, **3a**, **3b** or **3c**, a perfectly etherized product of 1,1'-bi-2-naphthol, was obtained from the acetone filtrate. We observed that the longer the methylene chain, the higher the fluorescence intensity; however, the values of optical rotation decreased with increase of the methylene chain. After photoirradiation with light at 365 nm, the fluorescent spectra of them showed that fluorescence intensity had significantly increased; however, their values of optical rotation lowered considerably. It meant that conjugated chain in the molecules of **3a**, **3b** or **3c** had reduced; in other words, **3a**, **3b** or **3c** had dimerized into **4a**, **4b** or **4c** under the photoirradiation condition. On the contrary, if **4a**, **4b** or **4c** was irradiated by light at 254 nm, its fluorescence intensity decreased and optical rotation increased. Optical rotations and the fluorescent spectra of **3a-c** and **4a-c** were shown in **Table 1** and **Figure 1** (the spectra of **3a-c** were similar, and the spectra of **4a-c** also were similar, only the spectra of **3a** and **4a** were shown for clarity).

The following preparative procedure is representative.

A mixture of hymecromone (1.76 g), anhydrous potassium carbonate (1.38 g), dibromoethane (0.9 mL) was refluxed in 70 mL of dry acetone for 24 h. Acetone was distilled off and the residual mixture was poured into an excess of water, the precipitate was filtrated off and washed with water, dried, then stirred in 50 mL of dry ether for 0.5 h. After the insoluble solid was filtrated off, the ether solution was evaporated to dryness to afford 0.65 g crude **2a**. It was recrystallized from anhydrous ethanol to give a white crystal of **2a**, m.p., 104-106 °C; IR (KBr, cm^{-1}): 3080, 2962, 2932, 1717, 1616, 1460, 1389, 1265, 1147, 1065, 847; $^1\text{H-NMR}$ (CDCl_3): δ 2.32 (s, 3H), 3.59 (t, 2H, $J=5.7$ Hz), 4.25 (t, 2H, $J=6.0$ Hz), 6.05 (s, 1H), 6.70 (s, 1H), 6.78 (dd, 1H, $J=9.0$ Hz), 7.40 (d, 1H, $J=9.0$ Hz).

Table 1 Optical rotations of compounds **3a-c** before and after photoirradiation

Compounds	Before photoirradiation ($[\alpha]_D^{20}$)	After photoirradiation ($[\alpha]_D^{20}$)
3a	+60.4 (c 0.5, CHCl ₃)	+29.2 (c 0.5, CHCl ₃)
3b	-50.0 (c 0.5, CHCl ₃)	-28.0 (c 0.5, CHCl ₃)
3c	+18.4 (c 0.5, CHCl ₃)	+12.6 (c 0.5, CHCl ₃)

Figure 1 Fluorescent spectra of **3a** and **4a**

A mixture of **2a** (0.28 g), anhydrous potassium carbonate (0.45 g), (*R*)-BINOL (0.14 g) was refluxed in 30 mL of dry acetone for 24 h, then cooled to room temperature and filtrated. The acetone filtrate was evaporated to dryness to afford 0.30 g solid. It was worked up in 20 mL CHCl₃, washed successively with 10 mL 0.05 mol/L NaOH solution, water, and then dried over anhydrous sodium sulfate, filtrated, after moving the solvent, 0.25 g white solid was afforded, recrystallized from acetone to give 0.20 g **3a**, as a white needless crystal. m. p. 170-171 °C; IR (KBr, cm⁻¹): 2930, 1720, 1617, 1509, 1444, 1394, 1281, 1241, 1155, 1070, 843, 808. ¹H-NMR (CDCl₃): δ 2.35 (s, 3H), 3.92 (m, 2H), 4.27 (m, 2H), 6.08 (s, 1H), 6.41 (d, *J*=1.8 Hz, 1H), 6.47 (m, 1H), 7.08 (m, 1H), 7.15 (m, 1H), 7.24-7.28 (m, 2H), 7.41 (d, *J*=9.3 Hz, 1H), 7.78 (d, *J*=8.1 Hz, 1H), 7.88 (d, *J*=9.0 Hz, 1H).

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