Perfect On/Off Switching of Emission of Fluorescence by Photochromic Reaction of a Binaphthol-Condensed Fulgide Derivative

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While the colorless form of the propyl-substituted, binaphthol-condensed indolylfulgide did not emit fluorescence, its colored form, generated by the UV-light irradiation, emitted fluorescence in toluene at room temperature. Thus, a perfect on/off switching system of fluorescence controlled by the photochromic reaction has been exhibited.

Photochromic compounds change their absorption spectra drastically and reversibly with the photochemical mutual conversion of their structures. Besides the color change which is the origin of the term "photochromism", recent interest in materials sciences has been focused also on the changes of other chemical and physical properties of molecules associated with this phenomenon. Although one of such properties of importance is the fluorescent nature, only a few examples have appeared to date.[1-4]

Both the colorless and colored forms of fulgides, the representative of the thermally irreversible photochromic compounds,[5] are known to emit fluorescence only at low temperature[6,7] either in glassy organic solvents or in polymer matrices as far as they do not have fluorescent substituents in the molecule.[2]

We here report about a fulgide derivative which fluoresces in solution at room temperature, and the fluorescence nature is completely controlled in the on/off manner by the photochromic interconversion.

Synthesis, structural characterization including the determination of the absolute configuration of the colored form, and diastereoselective photochromic transformation of the fulgide derivative **1** having a binaphthyl moiety have been reported.[8] During the research mentioned above, we have realized that, different from other fulgide derivatives, **1C** in toluene (absorption maximum 471 nm) was fluorescent at room temperature (fluorescence maximum 610 nm) when excited within the absorption bands of both UV- and vis-region. In contrast, **1E** in toluene (absorption maximum 368 nm) was not fluorescent with the excitation light longer than 300 nm.

Figure 1 shows the absorption and the emission spectra of **1C** excited with 470-nm light in toluene. The S_1 energy obtained from them is 225 kJ mol^{-1} (18.8 x 10^3 cm^{-1}).

In order to clarify the chromophore of **1C** that is responsible for the fluorescence, we synthesized the methylene acetal of binaphthol **2**.[9] The absorption maximum wavelength of **2** was 329 nm, and the fluorescent maximum wavelength was 391 nm. While the excitation of **1E** with 300-, 320-, and 367-nm light did not result in emission of fluorescence, **1C** emitted fluorescence of 610 nm by the 320-nm light excitation. This result implies that

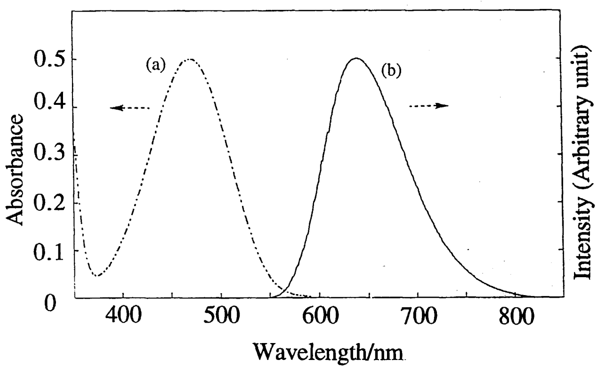


Figure 1. Absorption and fluorescence spectra of **1C** in toluene.
(a): Absorption spectrum (c: 7.58 x 10^{-5} mol dm^{-3}).
(b): Fluorescence spectrum (excitation: 470 nm, r. t.).

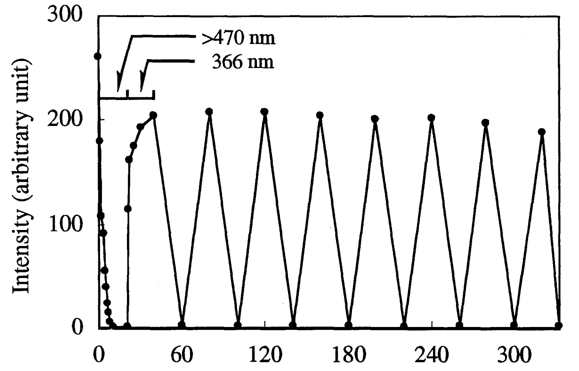
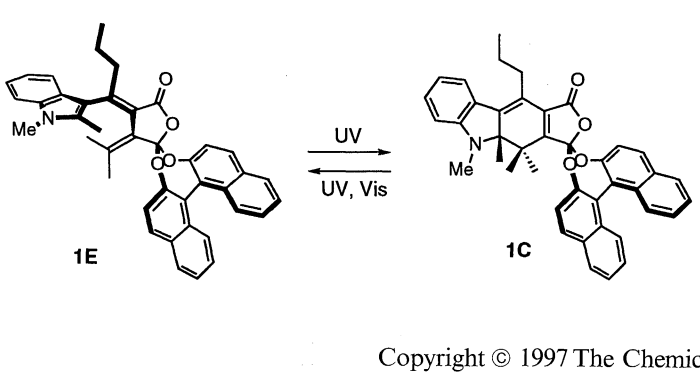
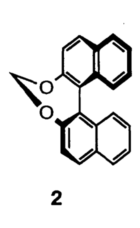


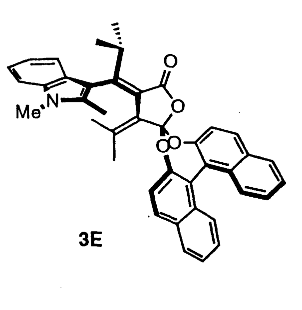
Figure 2. On/off switching of fluorescence of **1** in toluene.
Photochromic reaction: Vis light; >470 nm, UV light; 366 nm.
Excitation: 470 nm. Detection: 610 nm.



1E **1C**



2



3E

(i) the binaphthol unit in **1E** and **1C** does not emit light, and (ii) the complete energy transfer from the binaphthol unit to the fulgide core occurred for both **1E** and **1C**. While the excited core part of **1E** is deactivated without emission of light, the excited core of **1C** emits fluorescence at 610 nm.

Interestingly, the intensity of fluorescence of **3C**, the isomer having an isopropyl group instead of a propyl group of **1C**, is about 1/10 of that of **1C**, while it still shows the switching of fluorescence with photochromic structural change.

It has been reported that the deactivation of the colored form of a fulgide from S_1 excited state occurs mainly from the alkyl group on the carbon atom between the aromatic ring and the acid anhydride ring through C-H vibration.[7c] Therefore the structural difference between **1C** and **3C** may have caused the difference of their fluorescent nature. However, the fact that **1C** emits light while other colored forms of fulgides do not may be due to the absence of one of the carbonyl group. This means that the carbonyl group also plays an important role for deactivation of S_1 of the colored form of the fulgides. On the other hand, the reason of the difference of fluorescent nature between **1E** and **1C** is not clear. The flexibility of **1E** may have made its thermal deactivation easier to occur.

The quantum yield of fluorescence of **1C** when excited between 400 and 500 nm in toluene was determined to be 0.01 ± 0.001, by using *N,N*-dimethyl-3-nitroaniline to calibrate the fluorescence spectra,[10] and 9,10-diphenylanthracene and 4-dimethylamino-4'-nitrostilbene to correlate with the known fluorescence quantum yield.[11]

Figure 2 shows the change of fluorescence intensity (excited at 470 nm and detected at 610 nm) associated with the photochromic reaction in toluene (coloration with 366-nm light by high-pressure Hg lamp and decoloration with >470-nm light from xenon lamp). Because the colorless **1E** is not fluorescent while the colored **1C** which disappears by visible-light irradiation is fluorescent, and because **1E** and **1C** are thermally stable, the first example of a system with the perfect on/off switching of the fluorescence controlled by light irradiation is thus constructed.[12]

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References and Notes

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12 The reported switching phenomena of fluorescence so far are the change of strong/weak manner of the intensity of fluorescence. They are either thermally reversible[1] or that the emitting species is present at both photostationary states of light irradiation.[2-4]