# Photochromism of a Protonated 5-Dimethylaminoindolylfulgide:[†] a Model of a Non-destructive Readout for a Photon Mode Optical Memory

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The 5-dimethylaminoindolylfulgide–trichloroacetic acid (1 : 1.4) system in toluene was found to constitute a photochromic system having a non-destructive readout ability applicable to rewritable photon mode optical memories.

Rewritable photon mode optical memories[1] using organic photochromic compounds are long awaited because of their potentially superior properties to those of heat mode optical memories,[2] but a number of problems must be solved for a practical realization.[2,3] There has been some progress with specific organic photochromic compounds,[2,4] but an ideal candidate has not yet appeared. The most challenging unsolved problem is the development of a non-destructive readout method.[5,6] Since photoreactions usually do not have a threshold energy, although some photochromic reactions have temperature-dependent quantum yields,[7] any readout irradiation in the absorption band usually gives rise to the corresponding amount of photoreaction to cause a reduction of the carrier to noise ratio of the record. *The record must be erasable when necessary, but should not be destroyed by the readout.*

Recently we have reported the synthesis of 5-dimethylaminoindolylfulgide **1**.[4c] It has two distinctive characteristics: (*i*) the absorption maximum of the coloured form is at 673 nm, and it has absorption at 780 nm (in the AlGaAs diode laser region); (*ii*) the bleaching quantum yield of the coloured form is negligibly small ($4 \times 10^{-5}$ at 608 nm).

In this communication, we report a photochromic system which could be a model of a non-destructive readout method. This system takes advantage of the above characteristics of **1**, together with a Brönsted acid–base equilibrium.

In the presence of a large excess (152 equiv.) of trichloroacetic acid, the absorption maximum of the coloured form **1C** in toluene shifted from 673 nm ($\varepsilon_{max}$ 6200) to 554 nm ($\varepsilon_{max}$ 6790). Among the acids tested, including Lewis acids such as trimethylsilyl trifluoromethanesulfonate, trichloroacetic acid gave the best results. Weak acids like benzoic acid did not change the spectra, and strong acids like methanesulfonic acid did not give a stable photochromic system. The species obtained was assigned structure **1CH**. That the protonation

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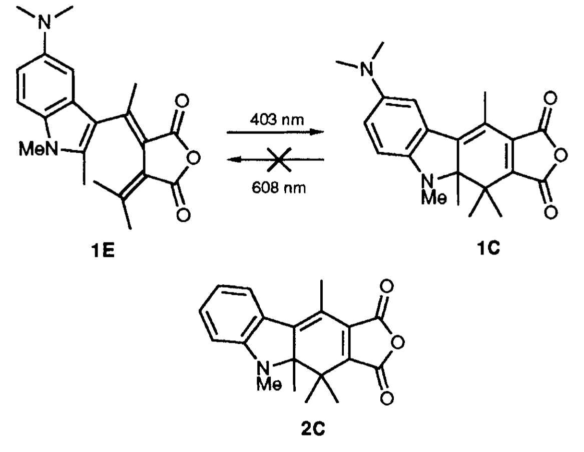
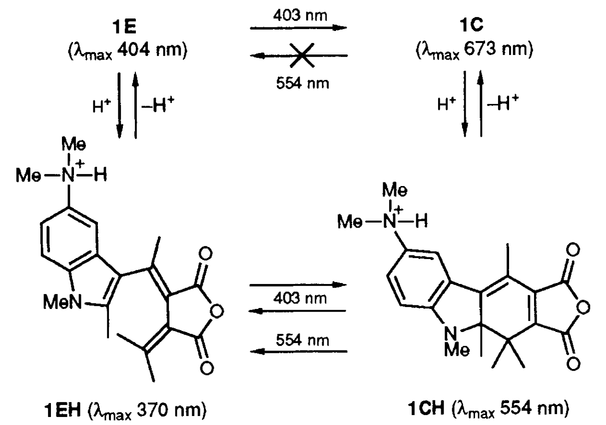
[†] 3-[2-(5-Dimethylamino-1,2-dimethylindol-3-yl)ethylidene]-4-isopropylidene-3,4-dihydrofuran-2,5-dione





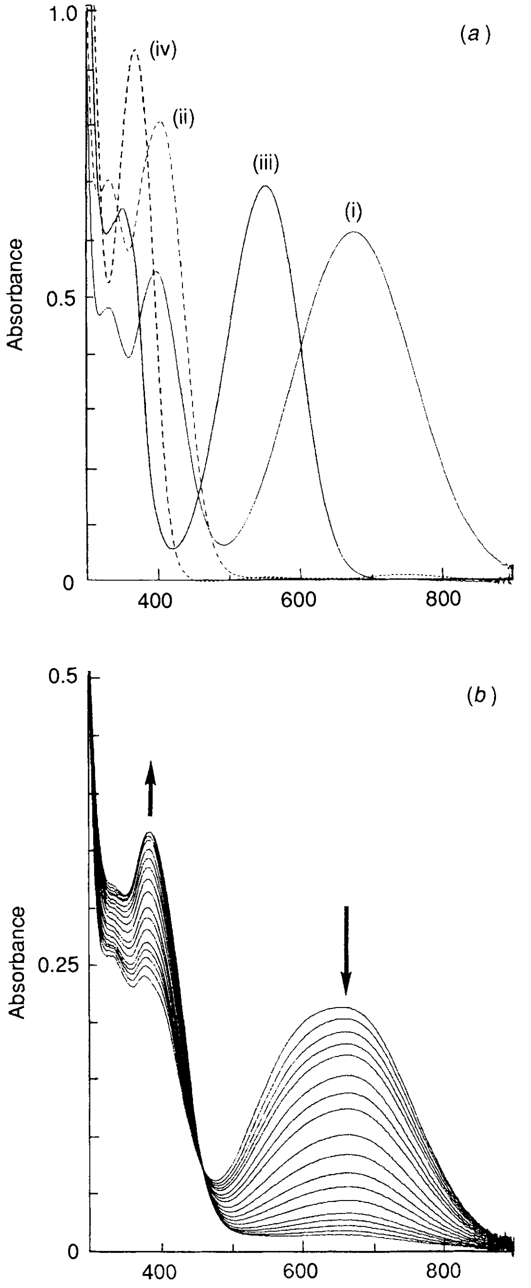


**Fig. 1** (*a*) Absorption spectra of (*i*) **1C** and (*ii*) **1E** in toluene (both $1 \times 10^{-4}$ mol dm$^{-3}$). Absorption spectra of (*iii*) **1CH** and (*iv*) **1EH** in toluene (both $1 \times 10^{-4}$ mol dm$^{-3}$ with $1.52 \times 10^{-2}$ mol dm$^{-3}$ trichloroacetic acid). (*b*) Absorption spectral change of **1C**–trichloroacetic acid mixture in toluene; [**1C**] $0.44 \times 10^{-4}$ mol dm$^{-3}$; [trichloroacetic acid] $0.62 \times 10^{-4}$ mol dm$^{-3}$. Irradiation: 554 nm light from a 250 W xenon lamp. Irradiation time/min: 0 (before irradiation), 1, 2, 3, 4, 6, 8, 10, 14, 18, 23, 28, 35, 46, 56, 71, 100 and 150 (photostationary state).

occurred on the nitrogen atom of the dimethylamino group of **1C** but not on the nitrogen of the indole ring was confirmed from the fact that no spectral change was observed when an excess of trichloroacetic acid was added to a toluene solution of the indolylfulgide **2C**.

While irradiation with 554 nm light (from a filtered 250 W xenon lamp) of **1C** in toluene did not bring about photoreaction, irradiation of **1CH** in toluene caused complete bleaching to afford **1EH** ($\lambda_{max}$ 370 nm, $\varepsilon_{max}$ 8730), the protonated form of **1E** (**1E**: $\lambda_{max}$ 404 nm, $\varepsilon_{max}$ 8040), with $\Phi_{CH\text{-}EH}(554) = 0.10$. As a result of loss of the electron-donating ability of the dimethylamino group caused by the protonation, the electronic structure of **1C** changed to bring about a hypsochromic shift of the absorption maximum and a recovery of the photochromic ability.

Irradiation with 403 nm light (from a filtered 500 W high-pressure mercury lamp) of **1EH** gave a photostationary state (**1CH**:**1EH** = 38 : 62), with quantum yields $\Phi_{EH\text{-}CH}(403) = 0.026$, and $\Phi_{CH\text{-}EH}(403) = 0.20$.

When a controlled amount of trichloroacetic acid (1.4 equiv.) was added to a toluene solution of **1C**, the mixture gave a superimposed spectrum of **1C** and **1CH** (71 : 29). It was converted to a mixture of **1E** and **1EH** together with small amounts of **1C** and **1CH** (**1C**:**1CH**:**1E**:**1EH** = *ca.* 5 : 3 : 75 : 17) upon irradiation with 554 nm light. This implies that a proton exchange equilibrium exists between **1C**, **1CH**, **1E** and **1EH**. Furthermore, the constant **1C**:**1CH** ratio throughout the photoreaction suggests that the proton exchange between **1CH** and **1C**, and probably between the four species involved, occurred quite quickly. The existence of isosbestic points for four-component systems is exceptional. The acid concentration of this experiment happend to make the concentration-based average absorption coefficient of **1E** and **1EH**, the absorption coefficient of **1C**, and that of **1CH** equal at the isosbestic point (458 nm).

Irradiation with 403 nm light of the resulting **1E**–**1EH**-rich mixture gave a photostationary state with **1C**:**1CH**:(**1E** + **1EH**) = *ca.* 67 : 23 : 10. Owing to the low concentration of **1E** and **1EH** and the overlapping of the absorption of the four species, determination of the concentration of **1E** and **1EH** by analysis of the UV region of the absorption spectra was unsuccessful in this case.

Irradiation with 554 nm light of this mixture again afforded the same **1E–1EH**-rich mixture as obtained above.

We suggest that the dimethylaminoindolylfulgide **1**–trichloroacetic acid combination provides a model of a simple and efficient rewritable optical memory possessing non-destructive readout ability. Namely, 554 nm light could be used for writing (or erasing), 403 nm light for erasing (or writing), and 780 nm light for readout.

Transplantation of this system to a polymer matrix[8] is now under active investigation.

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## References

1 H. G. Heller, *IEE Proceedings*, 1983, **130**, Pt. I, 209; Y. Hirshberg, *J. Am. Chem. Soc.*, 1956, **78**, 2304.
2 M. Irie, *Jpn. J. Appl. Phys.*, 1989, **28**, Suppl. 28-3, 215.
3 H. G. Heller, *Chem. Ind. (London)*, 1978, **18**, 193.
4 (*a*) Y. Yokoyama, T. Goto, T. Inoue, M. Yokoyama and Y. Kurita, *Chem. Lett.*, 1988, 1049; (*b*) Y. Yokoyama, T. Iwai, N. Kera, I. Hitomi and Y. Kurita, *Chem. Lett.*, 1990, 263; (*c*) Y. Yokoyama, T. Tanaka, T. Yamane and Y. Kurita, *Chem. Lett.*, 1991, 1125.
5 W. J. Tomlinson, *Appl. Optics*, 1984, **23**, 4609.
6 Z. F. Liu, K. Hashimoto and A. Fujishima, *Nature*, 1990, **347**, 658.
7 *E.g.*, H. G. Heller, *New Fatigue-resistant Organic Photochromic Materials*, in *Fine Chemicals for the Electronic Industry*, ed. P. Bamfield, Royal Society of Chemistry, London, 1986, pp. 120–135.
8 Y. Yokoyama, H. Hayata, H. Ito and Y. Kurita, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1607.