Photochromism of 2-Hydroxy-4'-methoxychalcone: A Novel Photon-Mode Erasable Optical Memory System with Nondestructive Readout Ability

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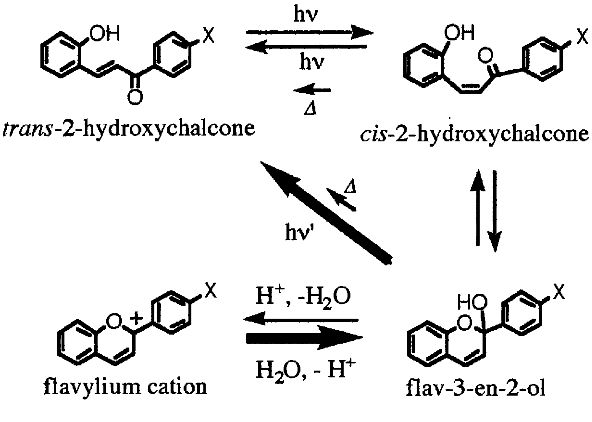
The photochromic system of 2-hydroxy-4'-methoxychalcone was found to be a novel photon-mode erasable system with nondestructive readout ability. The fatigue resistant property of the photochromic system of 2-hydroxy-4'-methoxychalcone has been confirmed at least up to 10 write-and-erase cycles.

Organic photochromic molecules are expected to be available for optical data storage media. For a high density memory, photon-mode writing, readout, and erasing are more desirable than heat-mode ones,[1,2] because the spatial resolutions of the former are theoretically higher. Some photochromic systems with nondestructive readout ability were reported,[1-6] but to the best of our knowledge, only a few systems with both photon-mode erasing and readout abilities were reported.[1,2,4] In this letter, we report the novel photon-mode erasable photochromic system of 2-hydroxy-4'-methoxychalcone with nondestructive readout ability.

2-Hydroxychalcone derivatives are one of plant pigments and are known as photochromic compounds.[6-10] *trans*-2-Hydroxychalcone derivatives are photochemically converted to their *cis*-forms. The *cis*-forms are in thermal equilibrium with the corresponding flav-3-en-2-ols. Cis forms and flav-3-en-2-ols can further be converted to the corresponding flavylium cations (colored-form) by an acid-base equilibrium reaction as shown in Scheme 1.[6,10] Flavylium cations are known to be stable for photo-irradiation and therefore the photochromic system of 2-hydroxychalcone derivatives are expected to constitute the basis for an optical memory with non-destructive readout capacity.[6] For the erasing process, however, much attention has been paid to the thermal erasing process because of the photochemical stability of flavylium cations.[7,8,10] We have recently found out that the photo-ring-opening reaction of flav-3-en-2-ol (Fl) to *trans*-2-hydroxychalcone (*t*-C) takes place with a good quantum yield of 0.29.[9] By utilizing the photo-ring-opening reaction, an indirect erasing of the flavylium cation (Fl^+) is expected to be induced by photo-irradiation of Fl (indirect photo-decoloration process) as shown in Scheme 1 (bold arrows). The opposite reaction of the indirect photo-decoloration can be suppressed when the absorption band of *trans*-2-hydroxychalcones is well-separated from that of corresponding flav-3-en-2-ols. The absorption band of *t*-C considerably overlaps with that of Fl and the indirect photodecoloration process of Fl^+ should be inefficient.



Scheme 1.

In the case of the 4'-methoxy derivative, the absorption band of *trans*-2-hydroxy-4'-methoxychalcone (*t*-MC) is rather well-separated from those of MFl and *c*-MC, which are in thermal equilibrium with each other. Therefore the system of *t*-MC is more favorable for the photon-mode erasing process than that of *t*-C.

Absorption spectrum of *t*-MC in water at pH 4.5 shown in Figure 1a by the full line shows a broad band with a maximum around 345 nm. Upon irradiation with 345-nm light, the absorption spectral change of *t*-MC was observed as shown in Figure 1a.[11] The 435-nm absorption band attributed to 4'-methoxyflavylium cation (MFl^+) increased with isosbestic

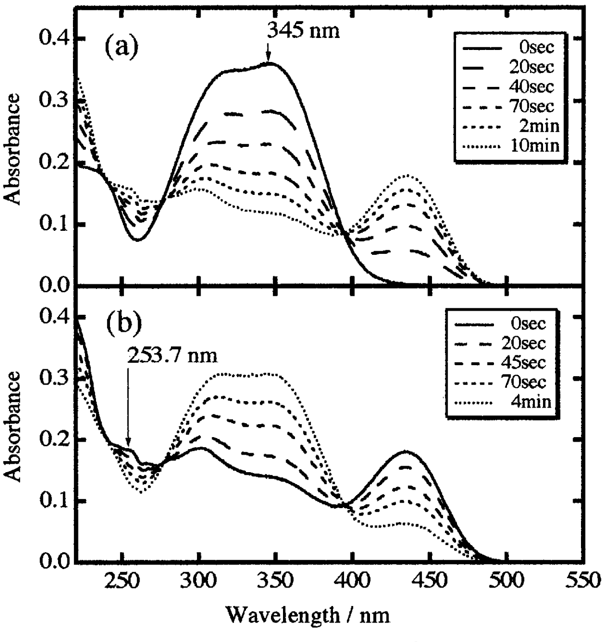
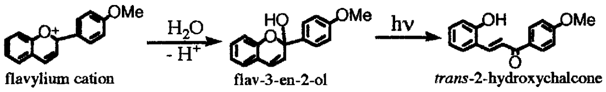


Figure 1. Absorption spectral change of *trans*-2-hydroxy-4'-methoxychalcone in water (pH=4.5) observed upon irradiation with 345-nm light (a) and that observed upon the successive irradiation with 253.7-nm light (b).

points at 277 and 394 nm, and the solution became yellow. At 435 nm *t*-MC, *c*-MC and MFl do not show any absorption band, and therefore nondestructive readout is possible by use of the 435-nm light because of the photochemical stability of MFl$^+$.

Since MFl$^+$ is in thermal equilibrium with *c*-MC and MFl at pH 4.5, the conversion from *c*-MC and MFl to MFl$^+$ was incomplete. At this pH, the ratio of the concentration of MFl$^+$, MFl, and *c*-MC was estimated to be *ca.* 2:2:1 by using the values of pK_1^a (-log ([MFl][H$^+$] / [MFl$^+$]) = 4.47) and K_2 ([*c*-MC] / [MFl] = 0.50) reported by McClelland and Gedge.[10] The molar fraction of MFl$^+$ was 0.22 at pH 4.5 by use of the molar absorption coefficient of MFl$^+$ ($\varepsilon_{435\ \mathrm{nm}}$ = 42000 M^{-1}cm^{-1})[6], and therefore the molar fraction of *t*-MC, *c*-MC, and MFl were estimated to be *ca.* 0.45, 0.11, and 0.22. It is noted that there is an absorption band of *c*-MC at 345 nm and *cis* → *trans* photo-isomerization occurs upon the 345-nm light irradiation.

The absorption maximum of the mixture of MFl and *c*-MC is observed at 255 nm.[6] The colored solution obtained by the 345-nm light irradiation was photolyzed by irradiation with 253.7-nm light. The spectral change observed is shown in Figure 1b.[12] The absorption bands of MFl$^+$ decreased with increase of that of *t*-MC with isosbestic points at 277 and 394 nm. This indicates that the indirect photo-decoloration of photochemically stable MFl$^+$ takes place by the irradiation with 253.7-nm light as shown in Scheme 2.[13] To the best of our knowledge, this is the first example to show the indirect photo-decoloration of MFl$^+$.



Scheme 2.

The photochemical reversibility of this system has been examined by the alternate irradiations with 345-nm light for the photo-coloration and 253.7-nm light for the photo-decoloration. The absorption change of MFl$^+$ at 435 nm is shown in Figure 2. It is apparent that the photochromic system of the 4'-methoxy derivative is photochemically reversible at least up to 10 write-and-erase cycles.

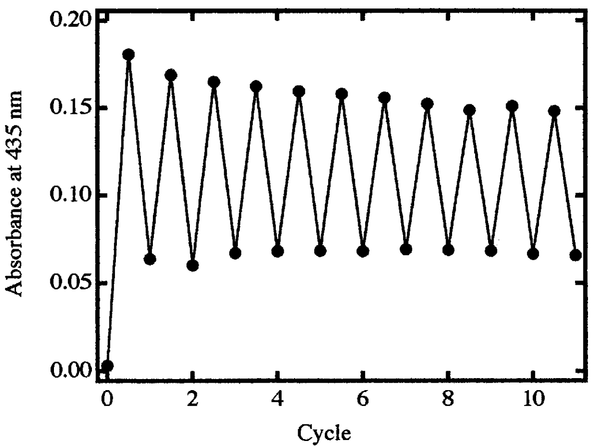


Figure 2. Reversibility of *trans*-2-hydroxy-4'-methoxychalcone toward the photo-coloration and the indirect photo-decoloration at pH 4.5.

In conclusion, we found out that the system of 2-hydroxy-4'-methoxychalcone constitutes a photon-mode erasable system with non-destructive readout ability. In this system, 345-, 435-, and 253.7-nm lights are used for writing, readout, and erasing, respectively. The fatigue resistant property of the system of 2-hydroxy-4'-methoxychalcone was confirmed at least up to 10 write-and-erase cycles.

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11 The irradiation light for the photo-coloration is outputs from a 500 W Xe short-arc lamp (Ushio UXL-500) passed through a monochromator (345 nm, Japan Spectroscopic Co., Ltd. CT-10).
12 The 253.7-nm light for the photo-decoloration was outputs of a 100 W low pressure mercury lamp with vycol glass filters.
13 Nanosecond laser flash photolysis of the solution of *c*-MC and MFl was performed in acetonitrile at room temperature. The absorption bands attributable to the corresponding enol-form were observed and the absorption bands of *t*-MC increased with decrease of those of the enol-form as in the case of *t*-C. This indicates that the predominant formation process of *t*-MC is not the *cis* → *trans* photoisomerization of *c*-MC but the photo-ring-opening reaction of MFl.