Effects of the substituents on 4′-position on the photon-mode erasable photochromic system of 2-hydroxychalcone derivatives

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ABSTRACT

To establish a photon-mode erasable optical memory system with non-destructive readout ability, photochemistry of the intermediate(s) of photochromic reaction between *trans*-2-hydroxychalcones and flavylium cations has been studied. The photochromic intermediates in acetonitrile have been assigned to be flav-3-en-2-ol for 4′-cyano as in the case of non-substituted one and equilibrated mixture of flav-3-en-2-ol and *cis*-form for 4′-methoxy derivative, and *cis*-form for 4′-dimethylamino derivative. The absorption spectra of flavenol derivatives have been almost independent of the substituent at 4′-position. Although photochemical formation quantum yield of flav-3-en-2-ol into *trans*-2-hydroxychalcone were independent of the substituent at 4′-position, 4′-OMe derivative has shown the highest conversion yield in the photostationary state. The reaction mechanism of photochromic intermediate(s) to give *trans*-2-hydroxychalcone has been also clarified by nanosecond transient absorption technique. By making use of this photochemical reaction, we demonstrated the indirect photon-mode erasing of photochemically stable flavylium cation in both solution and polymer film of 4′-methoxy derivative. Reversibility has been also studied.

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1. Introduction

Recently, organic photochromic molecules have attracted much attention [1–7]. Optical memory is one of the expected applications of organic photochromic molecules. For a high density optical memory, photon-mode writing, readout, and erasing are more desirable than heat-mode ones [6], because the spatial resolution of the former is higher. In the usual photochemically reversible systems composed of two compounds (Scheme 1a), the recording information is easily destroyed by the light irradiation to readout. Thus for the application to the optical memory devices, photochromic system should have both non-destructive readout and photon-mode erasable abilities. One of the strategies to satisfy both abilities, photochromic system composed of more than three compounds can be proposed as shown in Scheme 1b [6,8,9]. **B** is photochromic intermediate(s) and is in equilibrium with **C**. If **C** is photochemically stable and **B** can be photochemically returned to **A**, non-destructive readout ability is consistent with photon-mode erasable ability. To the best of our knowledge, only a few systems

with both photon-mode erasing and readout abilities were reported [6,8,9].

2-Hydroxychalcone derivatives are known to be one of organic photochromic compounds [10–35]. By the light irradiation to *trans*-2-hydroxychalcones under acidic condition, flavylium cations are produced via photochromic intermediates (*cis*-2-hydroxychalcones and/or flav-3-en-2-ols) as shown in Scheme 1c. One of authors reported that this photochromic reaction is favorable for a chemical actinometer [13,15], and the photochromic system can work not only in solution but also in solid state such as polymer [12] and hydrogel [18]. Pina et al. demonstrated that this system can be available to a light-switchable pH indicator. They also reported that flavylium cations are photochemically stable and thus this photochromic system is applicable to the "Write–Lock–Read–Unlock–Erase" molecular switching system [22]. In their consideration, "Lock" and "Unlock" are induced by adding an acid or base. To add an acid or base in the writing or erasing process has little practical value for the application to devices such as optical memory. Flavylium cations are known to be in acid-base equilibrium with flav-3-en-2-ols (and *cis*-2-hydroxychalcones). We have reported that flav-3-en-2-ol can be photochemically changed to *trans*-2-hydroxychalcone with a good quantum yield (0.29) [36]. Therefore it is expected that non-destructive readout ability can be compatible with photon-mode erasable ability in the photochromic system between

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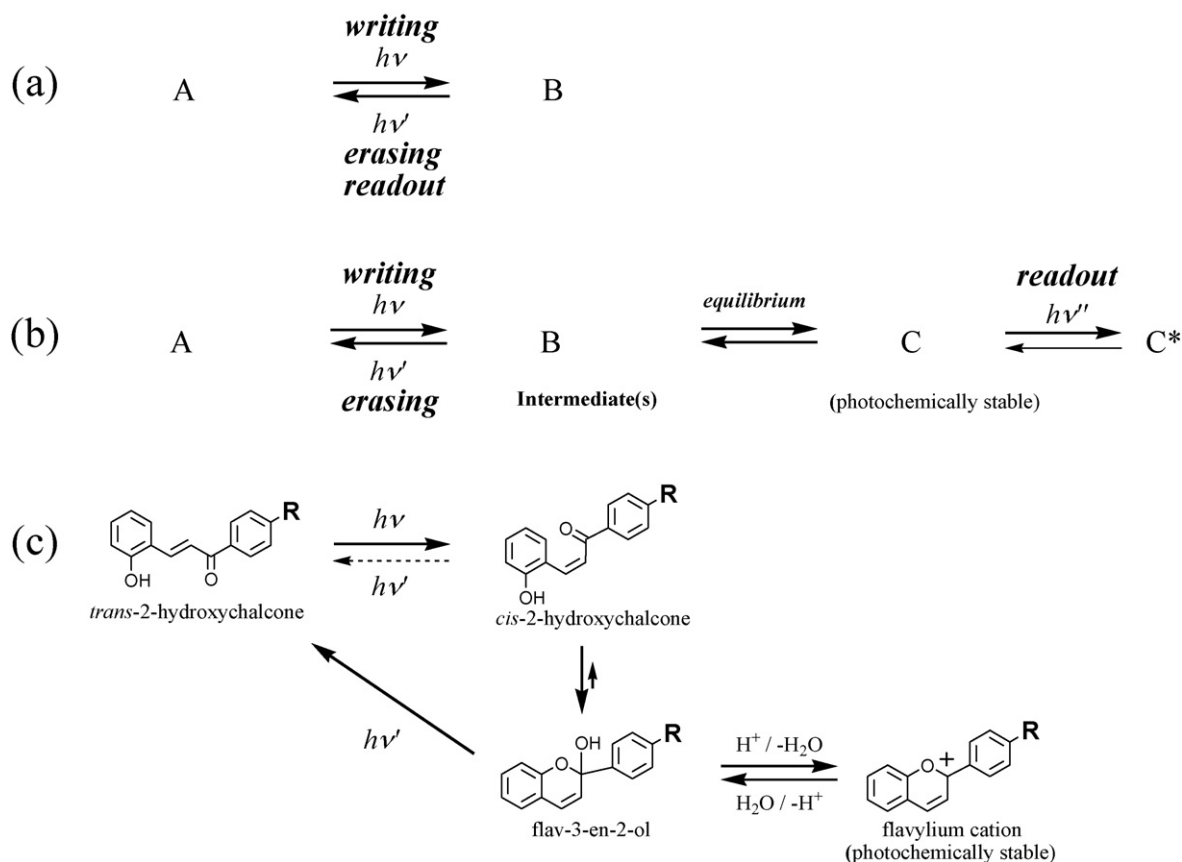
Scheme 1. Photochromic reaction mechanism of *trans*-2-hydroxychalcone derivatives and model of the photon-mode erasable optical memory system with non-destructive readout ability.

trans-2-hydroxychalcone and flavylium cation. We have reported preliminary results that indirect photon-mode erasing of photochemically stable 4′-methoxyflavylium cation is possible in aqueous solution [37]. It is reported that photochromic properties such as absorption spectra of both 2-hydroxychalcones and flavylium cations strongly depend on the substituent at 4′-position [12,38].

In this paper, we studied the photochemistry of the photochromic intermediate(s) of 4′-substituted *trans*-2-hydroxychalcone derivatives to establish the photon-mode erasable optical memory system with non-destructive readout ability. Photon-mode erasing of flavylium cations was also examined in both solution and solid polymer film.

2. Experimental

2-Hydroxychlacone derivatives were synthesized by condensation of the corresponding acetophenone derivatives with 2-hydroxybenzaldehyde [31]. They were purified by repeated recrystallizations from aqueous ethanol. Acetonitrile (MeCN: Wako Pure Chemical, >99.5%,) was used after drying with magnesium sulfate anhydrous. All other chemicals used were the best available commercial grade. To prepare poly(vinyl alcohol) (PVA) film, PVA powder (Koso Chemical, M_w = 1400) was dissolved in water at 100 °C. This solution was cast on a flat glass plate and kept for 10 days for drying. PVA films were about 200 μm thick. *trans*-2-Hydroxy-4′-methoxychalcone was doped into PVA film as follows. A PVA film was swelled in water containing sulfuric acid (pH 3) at 30 °C for 3 h. The swelled PVA film was soaked into aqueous ethanol (1:1, v/v) of *trans*-2-hydroxy-4′-methoxychalcone containing sulfuric acid (pH 3) for 3 min. After the soaking, the doped PVA film was washed with ethanol and dried for 1 day.

Steady-state photolysis was carried out by using outputs from a 500 W Xe short-arc lamp (Ushio UXL-500DO) passed through a monochromator (266 and 355 nm; JASCO CT-10). The intensity (I_0) of the irradiation light (266 nm) was determined to be 1.5×10^{-9} Einstein/s by using tris(oxalato)ferrate(III) as a chemical actinometer. The quantum yield of photo-ring-opening reaction was determined by monitoring the absorbance of *trans*-2-hydroxychalcone derivatives around 340 nm. ^{1}H NMR spectrum was determined on a JEOL α-50 spectrometer at 500 MHz. Transient absorption spectra were measured at room temperature by a Unisoku TSP601H nanosecond laser photolysis system with photolysis light of 266 nm (fourth harmonic) from an Nd^{3+}:YAG laser with 20 ns pulse width (Spectra Physics, Quanta-Ray GCR-130), and was monitored with a Xe lamp perpendicular to the photolysis light. Sample solutions were flowed through a cell of 10 mm light-pathlength with a flow-rate faster than 20 mL min^{-1} to ensure that the sample was always fresh for an excitation light pulse. Sample concentrations used for steady-state and time-resolved photolyses were $(1–2) \times 10^{-4}$ M.

Molecular orbital calculations were performed by WinMOPAC 3.9 Pro (Fujitsu Ltd.). Molecular structures were optimized by the PM3 method and electronic absorption spectra were calculated by the CNDO/S-CI method.

3. Results and discussion

3.1. Assignment and absorption spectra of photochromic intermediates

Absorption spectrum of *trans*-2-hydroxychalcone (*t*-H) in neutral acetonitrile (MeCN) is shown in Fig. 1b by the broken line. Three
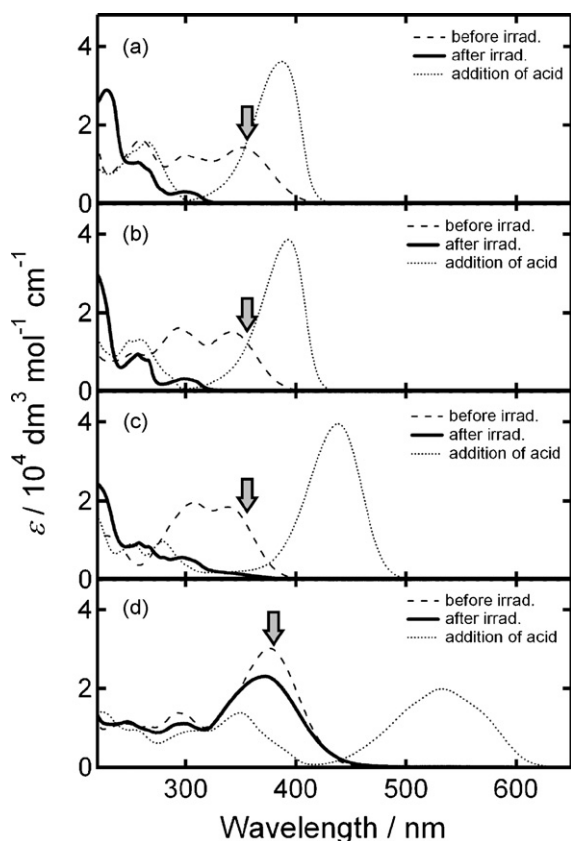
Fig. 1. Absorption spectral change of *t*-CN (a), *t*-H (b), *t*-OMe (c), and *t*-NMe$_2$ (d) observed upon irradiation, and that observed by the successive addition of acid.

absorption peaks were observed at 340, 295, and 255 nm. By the 355 nm light irradiation to this solution, these absorption bands decreased and a different absorption spectrum was observed with peaks at 300, 265, and 255 nm at the photostationary state (the bold line in Fig. 1b). These bands were assigned to the flav-3-en-2-ol (flavenol: Fl-H) [36]. By adding perchloric acid to this solution, new absorption bands were observed at 395, 260, and 250 nm (the dotted line). These bands can be ascribable to flavylium cation (FC-H) [12]. Similar experiments were carried out for 4′-cyano (4′-CN), 4′-methoxy (4′-OMe) and 4′-dimethylamino (4′-NMe$_2$) derivatives. The absorption spectra of *trans*-2-hydroxy-4′-cyanochalcone (*t*-CN), *trans*-2-hydroxy-4′-methoxychalcone (*t*-OMe), and *trans*-2-hydroxy-4′-dimethylaminochalcone (*t*-NMe$_2$) are shown in Fig. 1a, c and d. The molar absorption coefficient around 260 nm decreased with increase of electron-donating ability of the substituent at 4′-position except for *t*-NMe$_2$. In the case of *t*-NMe$_2$, absorption spectral shape is quite different from the others (red-shifted) as reported by Matsushima et al. [12]. By the 355 nm light irradiation to the neutral solution of *t*-CN, an absorption spectral change similar to that of *t*-H was observed. The photoproduct can be assigned to 4′-cyanoflavenol (Fl-CN) based on the absorption and NMR spectra. By adding perchloric acid to the solution of Fl-CN, an absorption band attributable to its flavylium cation (FC-CN) grew up at 387 nm as shown by the dotted line in Fig. 1a.

By the 355 nm light irradiation to the neutral solution of *t*-OMe, an absorption spectrum with maxima around 300 and 260 nm was observed as in the case of *t*-H and *t*-CN. This spectral change is similar to that in water [22]. However, absorption band around 350 nm did not disappear even in the photostationary state. By adding perchloric acid to the irradiated solution of *t*-OMe, absorption band attributable to 4′-methoxyflavylium cation (FC-OMe) grew up at 438 nm as shown by the dotted line in Fig. 1c, indicating

that the precursors to FC-OMe were produced by the irradiation of *t*-OMe. We tried to assign the photoproduct by NMR measurements. NMR spectra of *t*-OMe in CD$_3$CN were measured before and after the 355 nm irradiation and resulting spectra are shown in the supporting information. The signal due to the proton of the methoxy group of *t*-OMe was observed at 3.887 ppm. After the irradiation, new signals appeared at 3.840 and 3.805 ppm, indicating that two photoproducts were produced upon the irradiation. In the photostationary state, mole fraction of *t*-OMe was determined to be 0.02 by using integrated value of the signals due to the methoxy group observed around 3.8 ppm. Major signals of the photoproduct are similar to those of Fl-H and Fl-CN, indicating that F-OMe was produced by the irradiation. Some minor signals also observed. McClelland and Gedge reported that the precursors to FC-OMe in water are the equilibrated mixture of *cis*-2-hydroxy-4′-methoxychalcone (*c*-OMe) and 4′-methoxyflavenol (Fl-OMe) [11]. They carried out stopped-flow measurements and observed the fast and slow formation processes of FC-OMe by adding acid to the solution of the precursors. The latter and former have been assigned to the process of *c*-OMe → Fl-OMe → FC-OMe and Fl-OMe → FC-OMe, respectively. They also determined the equilibrium constant *K* between *c*-OMe and Fl-OMe ([*c*-OMe]/[Fl-OMe]) in water to be 0.50 by comparing the concentrations of FC-OMe produced in each process. To assign the photoproducts of *t*-OMe in MeCN, therefore, we carried out the stopped-flow measurement followed McClelland and Gedge. The irradiated solution of *t*-OMe was mixed with equivalent volume of MeCN containing 1.8×10^{-4} M perchloric acid, and absorbance change was measured as a function of time. Fig. 2 shows the absorbance change monitored at 440 nm. There are two steps in the formation processes of FC-OMe in MeCN as in the case in water, indicating that fast and slow processes can be assigned to reaction of Fl-OMe → FC-OMe and *c*-OMe → Fl-OMe → FC-OMe, respectively. This indicates that the photoproducts of *t*-OMe are the equilibrated mixture of *c*-OMe and Fl-OMe as in the case in water. This absorbance change was well analyzed by the equation $A = C - B \exp(-kt)$ with the rate constant *k* of 0.17 s^{-1}. This slow rate constant corresponds to the conversion from *c*-OMe to Fl-OMe and is similar to that in water (0.46 s^{-1}) [11]. We also measured the time profile with faster time resolution and evaluated the rate constant of the fast formation process of FC-OMe to be 8.5 s^{-1} (not shown). From this rate constant and concentration of acid, the second-order rate constant of the formation process of FC-OMe from Fl-OMe was determined to be 9.4×10^4 M^{-1} s^{-1}. This value is similar to that reported in water (1.4×10^4 M^{-1} s^{-1} [11]), by considering the difference in the diffusion-controlled rate constant in MeCN (1.9×10^{10} M^{-1} s^{-1}) and in water (7.4×10^9 M^{-1} s^{-1}).[39] We also estimated the equilibrium constant *K* to be 0.25 in MeCN fol-
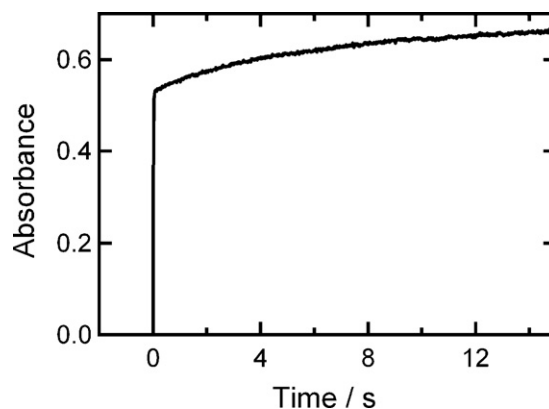

Fig. 2. Rise time profile of FC-OMe monitored at 440 nm in acetonitrile after the addition of perchloric acid.
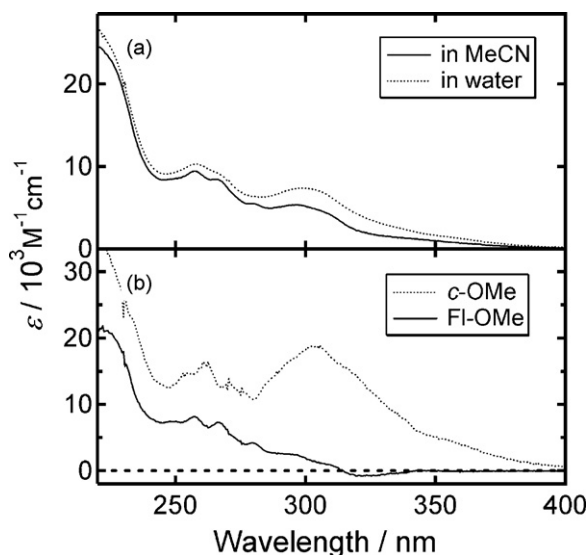
Fig. 3. Absorption spectral of irradiated solution of t-OMe in MeCN (full line) and water (dotted line) (a), and the estimated spectra of c-OMe and Fl-OMe (b).

lowed the analysis made by McClelland and Gedge. This value is half of that in water (0.50) [11]. We tried to estimate pure absorption spectra of Fl-OMe and c-OMe from the absorption spectra of equilibrated mixture of Fl-OMe and c-OMe. The apparent molar absorption coefficient ($\varepsilon_{apparent}$) of the equilibrated mixture of c-OMe and Fl-OMe is defined by the following equation,

$$\varepsilon_{apparent} = \frac{K}{1+K}\varepsilon_{c\text{-OMe}} + \frac{1}{1+K}\varepsilon_{Fl\text{-OMe}} \tag{1}$$

where $\varepsilon_{c\text{-OMe}}$, and $\varepsilon_{Fl\text{-OMe}}$ are the molar absorption coefficients of c-OMe and Fl-OMe, respectively. As mentioned above, small amount of t-OMe remained in the photostationary state, indicating that c-OMe absorbed the 355 nm light to give t-OMe by the photoisomerization. To obtain the mixture of c-OMe and Fl-OMe without t-OMe, the solution of FC-OMe was neutralized. Fig. 3a shows absorption spectra of the equilibrated mixture of c-OMe and Fl-OMe in MeCN (full line) and in water (dotted line). By assuming the molar absorption coefficients of c-OMe and Fl-OMe in MeCN are the same as those in water, the absorption spectra of c-OMe and Fl-OMe were estimated by using Eq. (1), and the estimated spectra are shown in Fig. 3b. The estimated spectrum of Fl-OMe is similar to the observed spectra of Fl-H and Fl-CN (Fig. 1a and b).

By the 380 nm light irradiation of neutral MeCN solution of t-NMe₂, the absorption band decreased with an isosbestic point around 350 nm, but deviated from this isosbestic point by further irradiation. The absorption spectrum of the moderately irradiated solution is shown by the bold line in Fig. 1d. By adding perchloric acid to this irradiated solution the absorption band at 533 nm grew up (the dotted line in Fig. 1d). This absorption band is attributable to that of 4'-dimethylaminoflavylium cation (FC-NMe₂), [12,15,29,40] indicating that the precursor of FC-NMe₂ was produced by the irradiation of t-NMe₂. This precursor is assigned to its cis-form (c-NMe₂) based on the NMR spectrum. Therefore the equilibrium constant K is considered to be almost infinity. Deviation from the isosbestic point mentioned above is interpreted in term of the photodecompositions; the photochemical reaction of c-NMe₂ is not only the cis → trans photoisomerization but also the photodecomposition. Thus reversibility of photochemical reaction of 4'-NMe₂ derivative is considered to be low.

As described above, it was clarified that photoproduct(s) of trans-2-hydroxychalcone derivatives strongly depends on the substituent at 4'-position. These results can be well explained by the results of semi-empirical molecular orbital calculation. Molecular
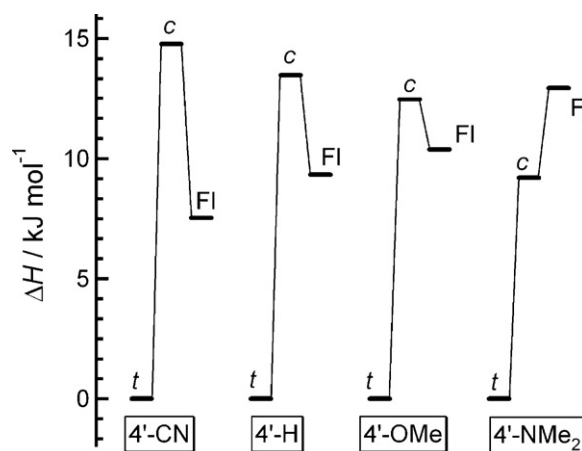

Fig. 4. Energy diagram of trans-2-hydroxychalcone, cis-2-hydroxychalcone, and flav-3-en-2-ol derivatives calculated by the PM3 method.

structure of trans-2-hydroxychalcones (t), cis-2-hydroxychalcones (c), and flavenols (Fl) were optimized by the PM3 method for 4'-CN, 4'-H, 4'-OMe, and 4'-NMe₂ derivatives. The resulting ΔH_f values are shown in Fig. 4. All ΔH_f values are relative to trans-2-hydroxychalcones. In the case of 4'-CN derivative, flavenol is much more stable than cis-form. With increase of electron-donating ability of the substituent at 4'-position, cis-form and flavenol stabilized and unstabilized, respectively. In the case of 4'-OMe derivative, ΔH_f of flavenol and cis-form is comparable, supporting that the photoproducts of t-OMe is the mixture of Fl-OMe and c-OMe. In the case of 4'-NMe₂ derivative, cis-form becomes more stable than flavenol, supporting that the photoproduct of t-NMe₂ is only c-NMe₂.

Fig. 5 shows absorption spectra of the flavenols for 4'-CN (a), 4'-H (b), and 4'-OMe (c) derivatives. These spectra are very similar to each other except for the small shift of the band around 220 nm, indicating that the electronic structure of flavenols is independent of the substituent at 4'-position. We also calculated the electronic absorption spectra by the CNDO/S-CI method and resulting spectra are shown by the sticks in Fig. 5. The detailed analysis for 4'-H derivative has been already reported in a previous paper [36]. The electronic structure of 4'-CN and 4'-OMe derivatives are similar to
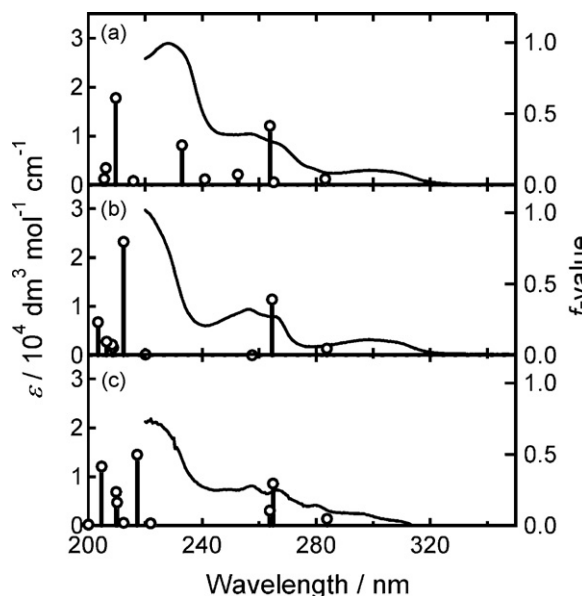

Fig. 5. Absorption spectra (full line) of Fl-CN (a), Fl-H (b), and Fl-OMe (c) and their electronic spectra calculated by the CNDO/S-CI method (sticks with circle).
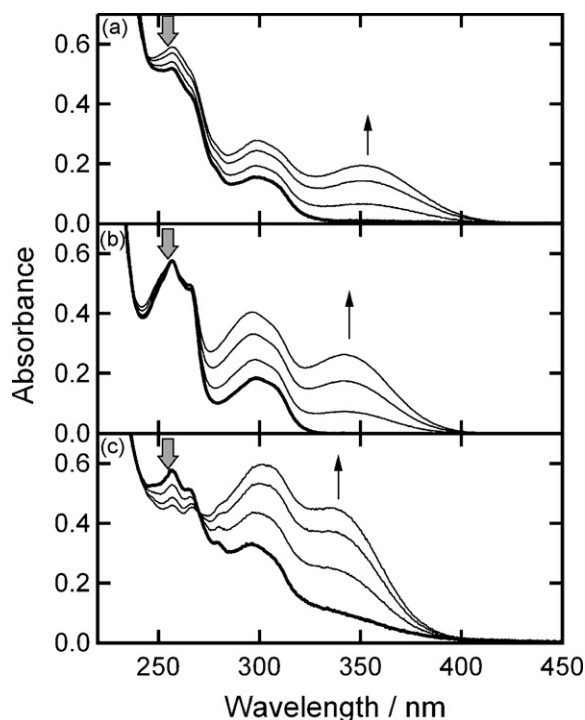
Fig. 6. Absorption spectra change of the photochromic intermediate(s) of t-CN (a), t-H (b), and t-OMe (c) observed upon 266 nm light irradiation.

that of 4′-H derivative, supporting that the absorption spectra of flavenols is independent of the substituent at 4′-position.

3.2. Photochemical processes of photochromic intermediates

To establish the photon-mode erasable optical memory system with non-destructive readout ability, photochemical processes of the photochromic intermediates are important. As mentioned above, 4′-NMe$_2$ derivative is not available for the photochemically reversible system. Thus we studied the photochemical processes of the photoproduct(s) of 4′-CN, 4′-H, and 4′-OMe derivatives.

Fig. 6 shows the absorption spectral change of the photochromic intermediate(s) of $trans$-2-hydroxychalcones in MeCN observed upon the 266 nm light irradiation. By the irradiation of the photoproduct of t-H (Fl-H), absorption bands due to t-H increased [36]. The quantum yield of photo-ring-opening reaction Φ_{open} and yield of t-H in the photostationary state were reported to be 0.29 and 30%, respectively [36]. By the 266 nm light irradiation to the photochromic intermediate of t-CN (Fl-CN), absorption bands due to t-CN increased as in the case of 4′-H derivative. The quantum yield of photo-ring-opening reaction Φ_{open} and yield of t-CN in the photostationary state were estimated to be 0.32 and 27%, respectively. By the 266 nm light irradiation to the MeCN solution of the photoproducts of t-OMe (equilibrated mixture of Fl-OMe and c-OMe (0.79:0.21)), absorption bands due to t-OMe increased. The apparent reaction quantum yield to produce t-OMe was estimated to be 0.23. This reaction consists of the photo-ring-opening reaction of Fl-OMe and $cis \rightarrow trans$ photoisomerization of c-OMe. In the photostationary state obtained by the 355 nm light irradiation of t-OMe, the quantum yield of $cis \rightarrow trans$ photoisomerization $\Phi_{c\text{-OMe}}$ can be estimated from the following equation:

$$\varepsilon_{t\text{-OMe}} \Phi_{t\text{-OMe}} \chi_{t\text{-OMe}} = \varepsilon_{c\text{-OMe}} \Phi_{c\text{-OMe}} \chi_{c\text{-OMe}} \qquad (2)$$

where $\varepsilon_{t\text{-OMe}}$ and $\varepsilon_{c\text{-OMe}}$ are molar absorption coefficients at the excitation wavelength, $\Phi_{t\text{-OMe}}$ and $\Phi_{c\text{-OMe}}$ are quantum yield of the photochemical reaction, and $\chi_{t\text{-OMe}}$ and $\chi_{c\text{-OMe}}$ are mole fraction of

t-OMe and c-OMe, respectively. In the photostationary state, $\chi_{t\text{-OMe}}$ was 0.02 in MeCN as mentioned above, and thus $\chi_{c\text{-OMe}}$ could be estimated to be 0.2 by using the equilibrium constant K. $\Phi_{t\text{-OMe}}$ was determined to be 0.47 at 355 nm. By using these values and molar absorption coefficient shown in Fig. 3b, $\Phi_{c\text{-OMe}}$ was estimated to be 0.14. The apparent reaction quantum yield to produce t-OMe (0.23) is larger than $\Phi_{c\text{-OMe}}$, indicating that the photo-ring opening reaction of Fl-OMe also took place by the 266 nm light irradiation. The apparent reaction quantum yield to produce t-OMe $\Phi_{apparent}$ can be written by the following equation:

$$\Phi_{apparent} = \frac{\varepsilon_{\text{Fl-OMe}} \chi_{\text{Fl-OMe}}}{\varepsilon_{\text{Fl-OMe}} \chi_{\text{Fl-OMe}} + \varepsilon_{c\text{-OMe}} \chi_{c\text{-OMe}}} \Phi_{open}$$
$$+ \frac{\varepsilon_{c\text{-OMe}} \chi_{c\text{-OMe}}}{\varepsilon_{\text{Fl-OMe}} \chi_{\text{Fl-OMe}} + \varepsilon_{c\text{-OMe}} \chi_{c\text{-OMe}}} \Phi_{c\text{-OMe}} \qquad (3)$$

By using this equation, the quantum yield of the photo-ring-opening reaction Φ_{open} was estimated to be 0.27, being slightly smaller than those of Fl-H (0.29) and Fl-CN (0.32). The contribution of the photo-ring-opening reaction to the whole reaction was estimated to be 83%, indicating that the photochemical reaction of the mixture of Fl-OMe and c-OMe to give t-OMe is mainly induced by the photo-ring-opening reaction of Fl-OMe in MeCN. The yield of t-OMe in the photostationary state was estimated to be 44%. This is much higher than those of 4′-CN (27%) and 4′-H (30%) derivatives. This high yield of t-OMe is ascribable to low molar absorption coefficient of t-OMe at 266 nm (0.52 × 10^4 M^{-1} cm^{-1}). These results indicate that 4′-OMe derivative is expected to be the most suitable for the indirect photon-mode erasing of photochemically stable flavylium cation.

To clarify the mechanism of the photo-ring-opening reaction of flavenol derivatives, nanosecond transient absorption spectra were measured. We have already reported the followings by studying the transient absorption of flavenol [36]. Absorption bands of the enol-form of 2-hydroxychalcone were observed at around 530, 350, and 290 nm in MeCN just after the excitation (Fig. 7b) [36]. With decrease of these absorption bands, absorption bands at 340 and 290 nm due to t-H increased. The decay rate constant of
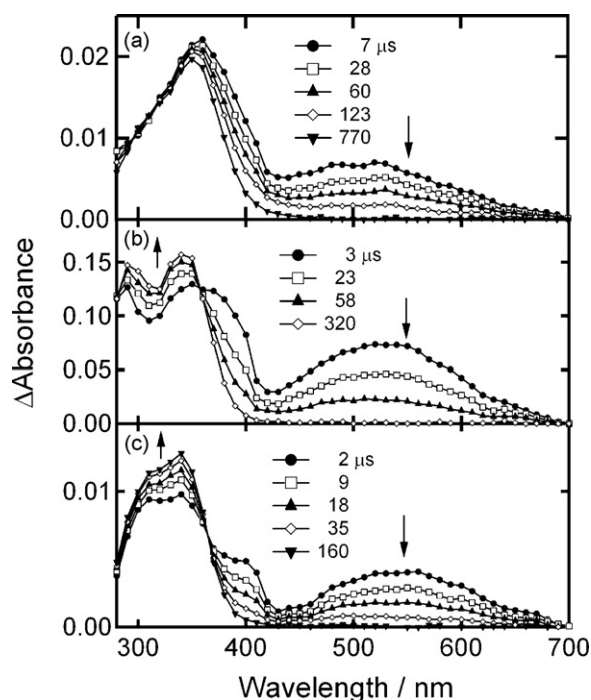

Fig. 7. Nanosecond transient absorption spectra of the photochromic intermediate(s) of t-CN (a), t-H (b), and t-OMe (c) observed upon 266 nm light irradiation.

the enol-form was $3.2 \times 10^4 \, s^{-1}$ and increased by adding of protic solvent such as water. The acceleration rate constants were $6.3 \times 10^5 \, M^{-1} \, s^{-1}$ and $12.5 \times 10^6 \, M^{-2} \, s^{-1}$ in the case of water. The tautomerization yield from the enol-form to *t*-H was almost unity even in MeCN and the molar absorption coefficients of the enol-form were 12,800, 10,300, and 5800 $M^{-1} \, cm^{-1}$ at 290, 350, and 530 nm, respectively.

Similar results were obtained for 4′-CN and 4′-OMe derivatives. Absorption bands of the enol-form were also observed around 500 and 360 nm for 4′-CN derivative (Fig. 7a), and around 550 and 340 nm with two shoulders around 400 and 310 nm for 4′-OMe derivative (Fig. 7c). With decrease of these absorption bands, absorption band due to the corresponding *trans*-form increased with a maximum at 350 nm for 4′-CN derivative and at 340 nm for 4′-OMe derivative. The decay time profile of the transient band observed around 500 nm can be analyzed by a single exponential function with the decay rate constant of 1.3×10^4 and $4.2 \times 10^4 \, s^{-1}$ for 4′-CN and 4′-OMe derivatives, respectively. The decay of the enol-form was accelerated by water with the rate constants of $1.3 \times 10^5 \, M^{-1} \, s^{-1}$ and $7.6 \times 10^6 \, M^{-2} \, s^{-1}$, and $5.5 \times 10^6 \, M^{-2} \, s^{-1}$ and $3.6 \times 10^7 \, M^{-2} \, s^{-1}$ for 4′-CN and 4′-OMe derivatives, respectively. The two different rate constants for each compound are due to bimolecular (enol-form and a protic solvent) and termolecular (enol-form and two protic solvents) processes as reported before [36]. Although the tautomerization of the enol-form was accelerated by water for both 4′-CN and 4′-OMe derivatives, formation yield of *trans*-form did not change, indicating that the tautomerization efficiency is almost unity as in the case of 4′-H derivative. Therefore the molar absorption coefficients of the enol-form of *t*-CN can be estimated to be 15,700 and 5100 $M^{-1} \, cm^{-1}$ at 360 and 520 nm, respectively, by using the transient absorption spectral change and molar absorption coefficient of *t*-CN. These values are similar to those of 4′-H derivative (10,300 $M^{-1} \, cm^{-1}$ at 350 nm and 5,800 $M^{-1} \, cm^{-1}$ at 530 nm). In the case of 4′-OMe derivative, *c*-OMe was also excited to give *t*-OMe. Usually *cis* → *trans* photoisomerization is very fast, thus it is considered that the *cis* → *trans* photoisomerization completed within our time resolution (~20 ns). As mentioned above, the contribution of *cis* → *trans* photoisomerization in the formation processes of *t*-OMe was 17%. By using this value, the molar absorption coefficient of the enol-form can be estimated to be 12,000 $M^{-1} \, cm^{-1}$ at 340 nm and 6400 $M^{-1} \, cm^{-1}$ at 550 nm. These molar absorption coefficients are very similar to those of 4′-H and 4′-CN derivatives.

Based on these results, it is clarified that the electronic structure and mechanism of the photo-ring-opening reaction of flavenol derivatives are almost independent of the substituent at 4′-position. It is noted that reversible photochemical reaction between *trans*-2-hydroxychalcone and flavenol is also expected as invisible photochromic system.

3.3. Photon-mode erasing of flavylium cation

By utilizing the photo-ring-opening reaction of flavenol derivatives, the indirect photon-mode erasing of the photochemically stable flavylium cation is expected to be induced by the excitation of flavenol as shown in Scheme 1. As mentioned above, 4′-OMe derivative is promising for this photon-mode system, because it has the highest yield to produce its *trans*-form from the photochromic intermediates. To demonstrate the indirect photon-mode erasing of the flavylium cation, coexistence of both flavenol and flavylium cation is indispensable. The pK_a ($-\log$[Fl-OMe][H$^+$]/[FC-OMe]) value of FC-OMe was reported to be about 4.47.[11] Thus we selected aqueous hydrochloric acid solution at pH 4.5 as a solvent. Absorption spectrum of *t*-OMe is shown in Fig. 8a by the full line. There are broad absorption bands with maxima around
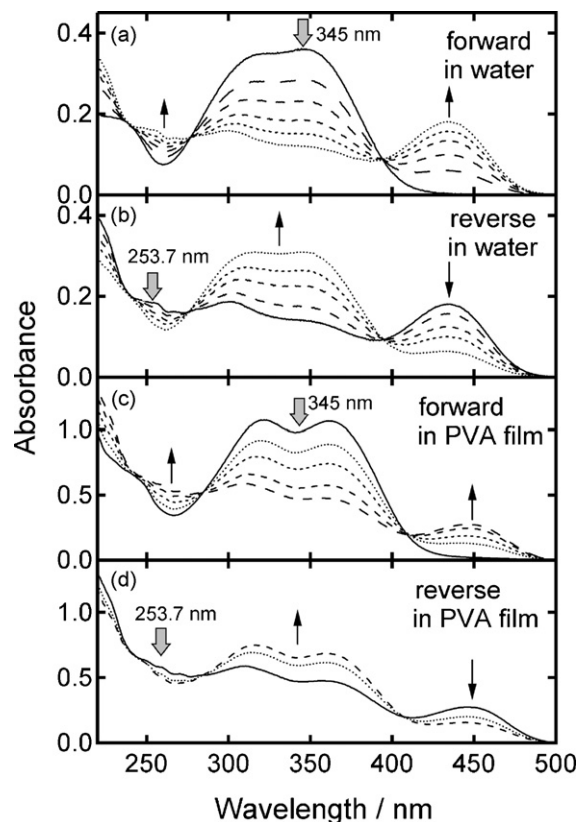

Fig. 8. Absorption spectral change of *trans*-2-hydroxy-4′-methoxychalcone in water (pH 4.5) and in a acidic PVA film observed upon irradiation with 345 nm light (a and c) and that observed upon the successive irradiation with 254.7 nm light (b and d).

345 and 320 nm. Upon irradiation with 345 nm light, the absorption spectral change shown in Fig. 8a was observed. The 435 nm absorption band due to FC-OMe increased with isosbestic points at 277 and 394 nm, and the solution changed from colorless to yellow. FC-OMe is photochemically stable, and *t*-OMe, *c*-OMe, and Fl-OMe do not show any absorption at 435 nm. Therefore nondestructive readout is possible by use of the 435 nm light. At this pH, the ratio of the concentration of FC-OMe, Fl-OMe, and *c*-OMe was estimated to be ca. 1:1.7:0.9 by using the values of pK_a and equilibrium constant K ([*c*-OMe]/[Fl-OMe] = 0.50 [11]). The molar fraction of FC-OMe was estimated to be 0.22 at pH 4.5 by use of the molar absorption coefficient of FC-OMe ($\varepsilon_{435nm} = 42,000 \, M^{-1} \, cm^{-1}$)[22], and therefore the molar fraction of *t*-OMe, *c*-OMe, and Fl-OMe were estimated to be ca. 0.22, 0.19, and 0.37. The colored solution obtained by the 345 nm light irradiation was successively irradiated with 253.7 nm light. The spectral change observed is shown in Fig. 8b. The absorption bands of FC-OMe decreased with increase of that of *t*-OMe with isosbestic points at 277 and 394 nm. This indicates that the indirect photo-decoloration of photochemically stable FC-OMe takes place by the irradiation with 253.7 nm light as shown in Scheme 1. If we assume the Φ_{open} and $\Phi_{c\text{-}OMe}$ are independent of solvent, then the contribution of the photo-ring-opening reaction of Fl-OMe in the formation processes of *t*-OMe was 63%. The absorbance change of FC-OMe at 435 nm against the repeated coloration and decoloration cycle is shown in Fig. 9 by the open circles. It is apparent that the photochromic system of the 4′-OMe derivative is photochemically reversible at least up to 10 write-and-erase cycles.

For the application to the optical memory, this photochemically reversible system should function in solid state. Therefore we studied this system in poly(vinyl alcohol) (PVA) film. *t*-OMe was doped in a PVA film on acidic condition and resulting absorp-
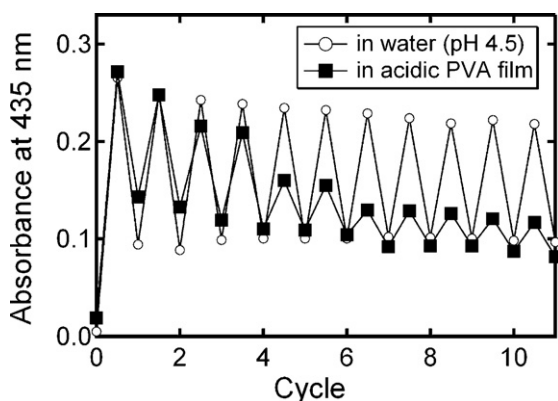
Fig. 9. Reversibility of *trans*-2-hydroxy-4′-methoxychalcone towards the photocoloration and the indirect photo-decoloration.

tion spectrum is shown in Fig. 8c by the full line. Upon irradiation with 345 nm light, the absorption spectral change shown in Fig. 8c was observed. The 450 nm absorption band attributable to FC-OMe increased with isosbestic points at 410 and 285 nm, and the film changed from colorless to yellow. This colored film was photolyzed by the irradiation with 253.7 nm light. The spectral change observed is shown in Fig. 8d. The absorption bands of FC-OMe decreased with increase of that of *t*-OMe with isosbestic points at 410 and 285 nm, indicating that the indirect photo-decoloration of photochemically stable FC-OMe takes place even in the solid state. The absorption change of FC-OMe at 450 nm is shown in Fig. 9 by the full squares. It is concluded that the photochromic system of 4′-OMe derivative is photochemically reversible even in the solid state.

4. Summary

To establish a photon-mode erasable optical memory system with non-destructive readout ability, photochemistry of the intermediate(s) of photochromic reaction between *trans*-2-hydroxychalcones and flavylium cations has been studied for 4′-cyano, 4′-methoxy, and 4′-dimethylamino derivatives as in the case of non-substituted one. The photochromic intermediates in acetonitrile have been assigned to be flavenol for 4′-cyano as in the case of non-substituted one and equilibrated mixture of flavenol and *cis*-form for 4′-methoxy derivative, and *cis*-form for 4′-dimethylamino derivative. The absorption spectra of flavenol derivatives have been almost independent of the substituent at 4′-position. For 4′-cyano, 4′-methoxy derivative and non-substituted one, the efficient formation of *trans*-2-hydroxychalcone derivatives have been observed by the irradiation with 266 nm light to the photochromic intermediates with a high quantum yield (∼0.3). The mechanism of this formation process of *trans*-2-hydroxychalcone derivatives has been studied by the nanosecond transient absorption measurements and it has been clarified that *trans*-2-hydroxychalcone derivatives are produced via their enol-forms. Although photochemical formation quantum yield of *trans*-2-hydroxychalcone were almost the same, 4′-methoxy derivative has shown the highest conversion yield of *trans*-2-hydroxychalcone in the photostationary state, because of the lower molar absorption coefficient of *trans*-2-hydroxy-4′-methoxychalcone at the peak wavelength (irradiation wavelength) of its flavenol. By making use of this photochemical reaction, we demonstrated the indirect photon-mode erasing of photochemically stable flavylium cation for 4′-methoxy derivative in both solution and polymer film. Reversibility has been also demonstrated. Thus this system is expected to apply to the photon-mode high density optical memory devices.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jphotochem.2009.05.004.

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