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Application of Photochromic 5-Dimethylaminoindolylfulgide to Photon-Mode Erasable Optical Memory Media with Non-Destructive Readout Ability Based on Wavelength Dependence of Bleaching Quantum Yield

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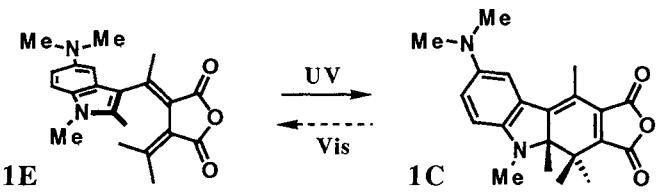
Bleaching quantum yield of 5-dimethylaminoindolylfulgide in a PMMA film decreased as the wavelength of irradiating visible light became longer, and the quantum yield was close to zero at the wavelength longer than 750 nm, where the colored species of the fulgide still has the absorption. By taking advantage of this observation, a photon-mode erasable optical memory media having non-destructive readout ability was constructed. Continual readout was possible for more than one hundred thousand times.

The vast amount of information is now requiring fast and high-density rewritable optical recording media. One of the candidates is the organic photochromic compounds.[1] As photoreactions occur in a photon-mode manner, the resolution of stored information can theoretically be higher than heat-mode recording. Thermally irreversible photochromic compounds are suitable for rewritable optical memory. Organic photochromic compounds, however, should have the following properties simultaneously for that purpose: (1) thermal stability of the recorded and unrecorded state; (2) fatigue resistivity toward the write/erase repetition; (3) responsibility for diode laser lights; (4) capability of non-destructive readout; (5) high sensitivity (large photoreaction quantum yields and large absorption coefficients); (6) rapid responsibility toward write/erase procedures (fast photoconversion speeds with regard to a molecule); (7) feasibility to make a photochromic thin polymer film.

Spiropyrans,[2] fulgides,[3] and diarylethenes[4] have been attempted to apply to such memory media. We have already reported the synthesis and photochromism of 5-dimethylaminoindolylfulgide (**1**),[5] and construction of a model of the non-destructive readout method using **1** in the presence of trichloroacetic acid in toluene.[6] We here report the application of another, more direct non-destructive readout method in polymer films, using **1**.



1E **1C**

The fundamental idea of the new non-destructive readout method based on the finding of the wavelength dependency of the bleaching quantum yield (Φ_{CE})[7–9] of **1C** in a PMMA film, which is shown in Fig. 1. The method, used in this experiment, of determination of quantum yields of photoreaction will be published elsewhere.[10,11] The quantum yield of bleaching of 550-nm light irradiation is about 0.00043, and the quantum yields in Fig. 1 are normalized with the bleaching quantum yield at 550 nm. Above 750 nm where Φ_{CE} of **1C** is almost zero ($\leq 10^{-5}$) within the limit of experimental error, **1C** still has certain absorption. Therefore 784-nm diode laser light, which would not induce photobleaching, was found to be suitable for readout.

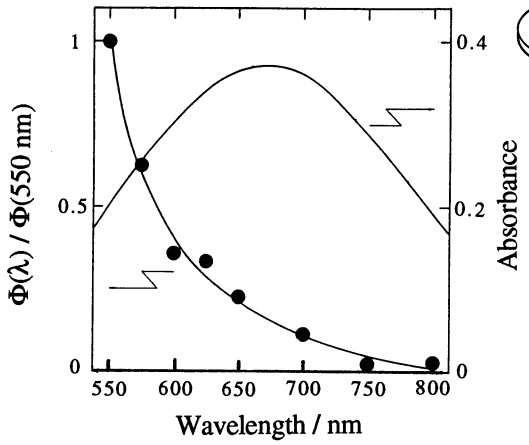


Fig. 1. Relative bleaching quantum yield of **1C** in a PMMA film (*ca.* 10 μm).

Dots: Ratio of bleaching quantum yield with regard to the quantum yield at 550 nm.
Line: Absorption spectra of a sample (**1C** in PMMA).

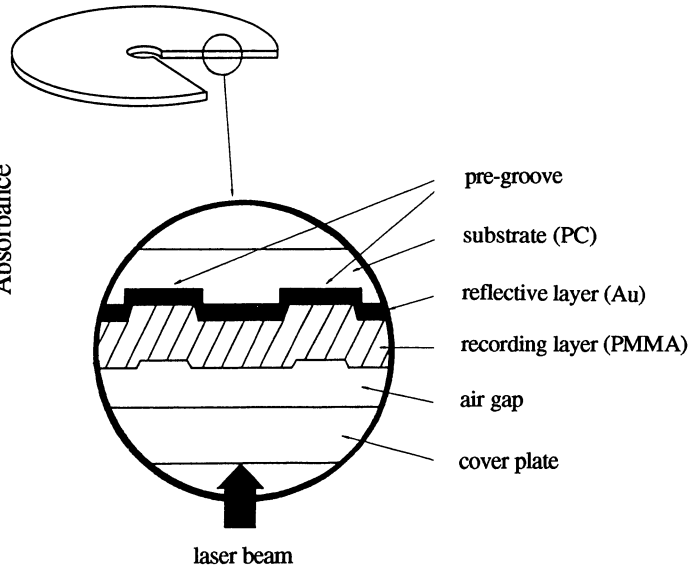


Fig. 2. Schematic diagram of cross-section of a sample disk.

A memory media containing **1** was prepared as follows: Onto a polycarbonate substrate having a spiral groove (width: 0.35 μm, depth; 0.1 μm) and a reflection layer of deposited gold (0.1 μm), about 2 ml of a solution of **1E** and poly(methyl methacrylate) (PMMA) in cyclohexanone (1:2:97 by weight) was dropped and spin-coated. After drying the disk at 70 °C for 10 min, the surface of the disk was covered with a PMMA plate (Fig. 2). Using He-Cd laser (325 nm, 2 mm diameter of the beam spot), the fulgide **1E** in the two one fourths of arc-shape part (35 mm radius) of the disk, opposite to each other, were changed to the colored form **1C** (*i. e.*, two recorded portions were made in one rotation of the disk). Reproduction of the record was carried out by detecting the reflecting light intensity, using a pick-up with an AlGaAs diode laser (784 nm). As only **1C** absorbs 784-nm light, the reflection light intensity from the unrecorded part (containing **1E**) is stronger than from the recorded part (containing **1C**). Change in the reflected light intensity from the recorded and unrecorded part during the continual reproduction of the same track of the recorded disk was examined. Reproduction conditions are; (1) linear velocity: 1.83 m s^{-1} (500 rpm), light power of reproduction: 0.3, 0.5, 0.7, and 1.0 mW, and (2) linear velocity 4.56 m s^{-1} (1250 rpm), light power of reproduction: 0.5 mW. The numerical aperture of the pick-up lens was 0.5.

The value ΔLr(n) is defined as the difference of the reflected light intensity between that from the recorded part and from the unrecorded part when N_R is n, where N_R is the number of repetition of reproduction. As N_R increased, the ratio of ΔLr(n) with regard to ΔLr(0) decreased (Fig. 3). That the decrease in ΔLr(n)/ΔLr(0) is

due to the photochromic bleaching reaction was confirmed by the fact that the reflection-light intensity recovered to the original level with the UV laser irradiation. The reproduction carried out with 0.3 mW laser power was possible for more than 10^5 times with keeping $\Delta Lr(n)/\Delta Lr(0)$ more than 80% of the initial.

Table 1 shows N_R values for $\Delta Lr(n)/\Delta Lr(0)$ with two different linear velocities of the disk rotation and the ratio of N_R with these linear velocities, when 0.5 mW laser power was used for reproduction. As the average of the numbers of ratio $N_R(4.56)/N_R(1.83)$ for each $\Delta Lr(n)/\Delta Lr(0)$ is 2.73 and the ratio of linear velocity is 2.5, the photochromic bleaching reaction governs the destruction of the record. This phenomenon will again be discussed later.

Table 1. Reproduction number for different linear velocity of disk rotation

$\Delta Lr(n)/\Delta Lr(0)$	N_R(1.83 m s^{-1})	N_R(4.56 m s^{-1})	$N_R(4.56)/N_R(1.83)$
0.9	1300	4000	3.08
0.85	2200	6000	2.73
0.8	4500	10800	2.40
0.75	6800	17500	2.57
0.7	8500	24200	2.85

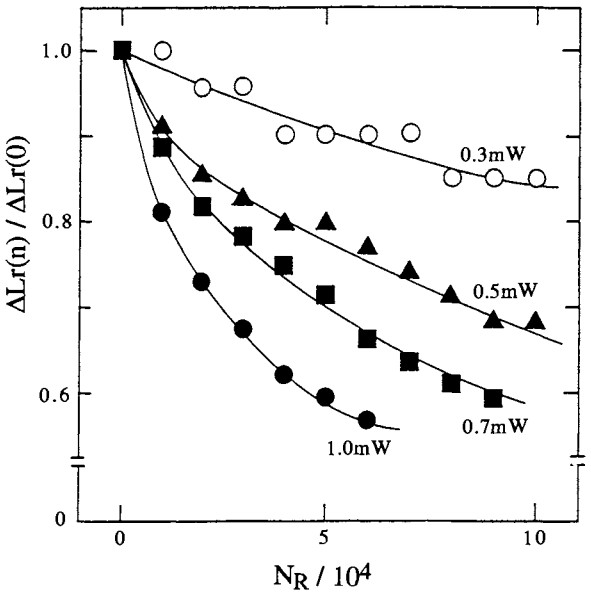


Fig. 3. Change in $\Delta Lr(n) / \Delta Lr(0)$ *vs.* the reproduction number N_R.

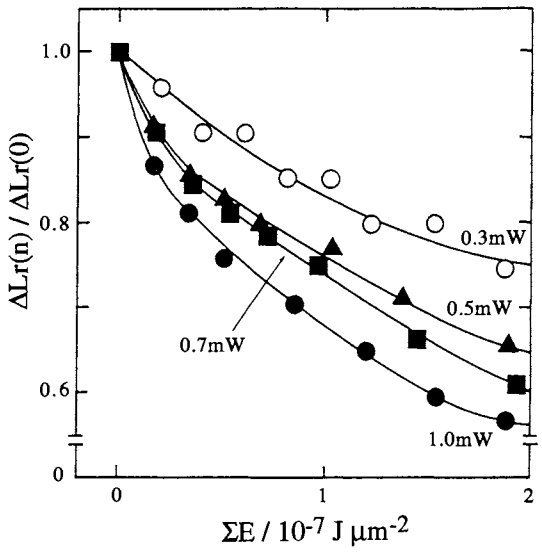


Fig. 4. Change in $\Delta Lr(n) / \Delta Lr(0)$ *vs.* the integrated reading-light energy.

Figure 4 shows the plot of $\Delta Lr(n)/\Delta Lr(0)$ as the function of the total applied light energy (ΣE) with various light powers with the linear velocity of 1.83 m s^{-1}. As the number of molecules that undergo the photochromic reaction should be proportional to the number of photons absorbed, the rate of decrease of $\Delta Lr(n)/\Delta Lr(0)$ with regard to the total applied light energy should be the same irrespective of the light power. However, as shown in Fig. 4, the rate of decrease in $\Delta Lr(n)/\Delta Lr(0)$ is faster as the light power is larger. This means that the quantum yield of photobleaching, though really small, increases as the temperature of the medium rises. The temperature-dependence of bleaching quantum yields of fulgides have been documented.[7–9]

As mentioned previously, the average of $N_R(4.56)/N_R(1.83)$ of Table 1 (2.73) is slightly greater than the ratio of linear velocities (2.5). When the linear-velocity value is smaller, the temperature of the irradiated spot rises higher due to the limited rate of diffusion of heat, resulting in the increase in the bleaching quantum yield and therefore the decrease in N_R. That is to say, the ratio $N_R(4.56)/N_R(1.83)$ should be greater than the ratio of linear velocities. Therefore the difference 0.23 should have arisen from the local raise in temperature of the medium when the linear velocity was 1.83 m s^{-1}. However, the quantitative analysis of the temperature dependence of the bleaching quantum yield was not inspected further because of the difficulty of measuring the temperature of the irradiated spot of the turning disk.[12)]

In conclusion, we have examined a new non-destructive readout method based on the wavelength dependence of bleaching quantum yield of 5-dimethylaminoindolylfulgide. The continual readout was possible for more than 10^5 times. Although the repeating write-erase cycle may be possible for many times with iterative UV-light (*e.g.* 405 nm) and visible-light (*e.g.* 550 nm) irradiation, increase in the apparent rate of coloring and bleaching photoreactions is necessary for practical use. Efforts to enlarge the quantum yields with steric effects that were effective for furylfulgides[13,14)] are now under way.

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11) The sample film was prepared as follows: A portion of dichloroethane solution containing 150 mg PMMA and 3.0 mg **1E** (6.7×10^{-2} mol dm^{-3}) was spread on a glass plate. After complete evaporation of the solvent, the film was irradiated with 400-nm light to change **1E** to **1C** completely. The film thickness was estimated by using ε_{max} value of **1C** in toluene (6200 mol^{-1} dm^3 cm^{-1}) to be *ca.* 10 μm.

12) The qualitative experiment of temperature-dependence of apparent bleaching rate of **1C** in a PMMA film with 650-nm light at the film temperature of 20°C and 60°C showed that the bleaching at 60°C is more than twice as fast as at 20°C.

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