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## Simple full-color rewritable film with photochromic fulgide derivatives

Yoshiumi Kohno, Yuuki Tamura, Ryoka Matsushima\*

Materials Science and Chemical Engineering, Faculty of Engineering, Shizuoka University, Johoku 3-5-1, Hamamatsu 432-8561, Japan

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### ABSTRACT

A trial full-color rewritable film has been prepared by mixing fulgide derivatives as three primary-coloring dyes in a polymer, giving practically colorless or black form upon irradiation with white light or UV light. A good color image was obtained by a simple, one-shot irradiation with white light above the positive-color mask attached on the black film. The image could be erased and rewritten with another positive mask though degraded after many erase–write cycles.

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### 1. Introduction

In order to reduce the wastes of paper and ink, a monochrome rewritable paper has been developed with leuco dyes [1]. In response to the increasing use of color paper documents, realization of full-color rewritable media is a challenging subject. Despite the increasing spread of electric color documents, familiar paper-like document seems still popular. Photochromic rewritable color media seem prospective and attractive [2,3], whereas the system of the leuco dyes is not applicable to rewritable full-color media since it includes thermal processes where selective erasing or writing a specific color is difficult. Thus, rewritable multi-color single crystals [4,5] and a dye-vapor doped rewritable multi-layered film [3,6] have been developed with photochromic diarylethenes since a photon-mode rewritable multi-color image has been demonstrated by Fernandez-Acebers and Lehn [7], while multi-color silver nanoparticles deposited on the TiO<sub>2</sub> surface [8,9] and electrochromic full-color film [10] have also been developed.

Regarding to the fulgide derivatives, full-color rewritable film with fulgides [2], and a dual-wavelength nondestructive-readout optical memory [11] have been demonstrated, while remarkable improvements in the thermal and photochemical stabilities [12], improved synthesis of fulgimides with microwave have been

explored [13]. The present paper reports a preliminary trial of a full-color rewritable film with fulgide derivatives (Scheme 1) for use as a temporary document, by a simpler writing method. Since color quality is essential in full-color media, dibenzyl fulginate **2** has been adopted as a yellow dye demonstrating excellent photochromic properties as reported [14,15].

### 2. Experimental details

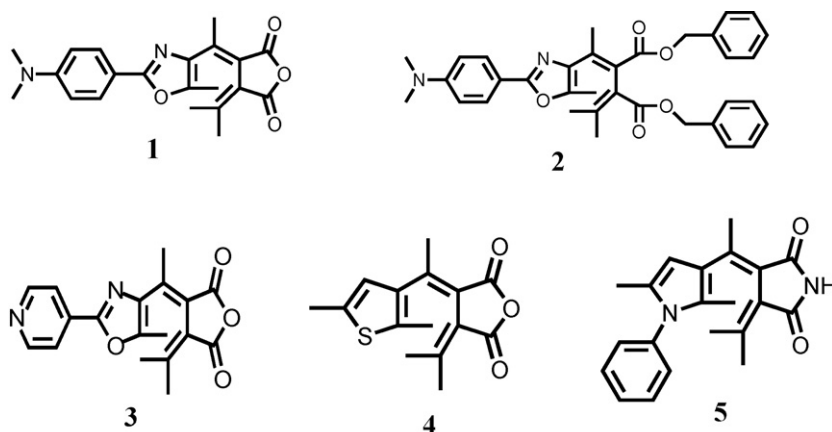
#### 2.1. Materials

Commercially available reagents and solvents of purest grade (Wako) were used without further purification. Phenoxy resin: poly(bisphenol A-co-epichlorohydrin) with average molecular weight of 40,000 (Aldrich), poly(vinyl alcohol) (PVA) with  $n = 1500$ –1800 (Wako), and poly(methyl methacrylate) (PMMA) (Wako) were used as received.

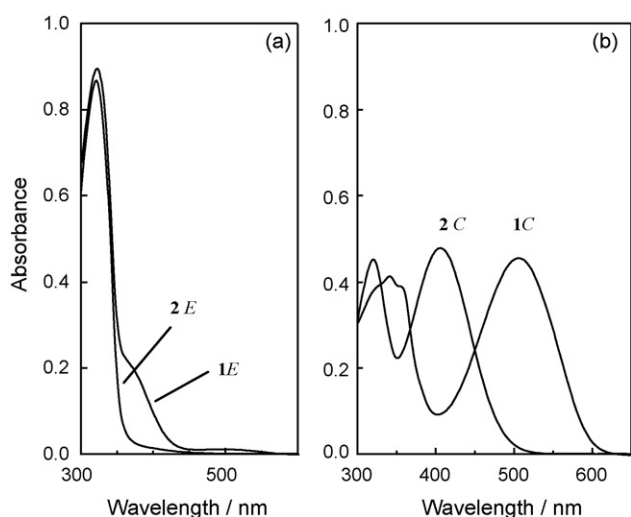
Fulgides **1** [16], **3** [17], **4** [18], and fulgimide **5** [19] were prepared according to the reported methods, while the dibenzyl fulginate **2** was prepared as described below. The <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$ /ppm were fulgide **1**: 2.00 (3H, s), 2.34 (3H, s), 2.37 (3H, s), 2.46 (3H, s), 3.05 (6H, s), 6.70–6.73 (2H, d), 7.85–7.88 (2H, d); fulginate **2**: 1.85 (3H, s), 1.88 (3H, s), 1.98 (3H, s), 2.27 (3H, s), 3.04 (6H, s), 4.91 (2H, s), 5.12 (2H, s), 6.70–6.73 (2H, d), 7.04–7.34 (10H, m), 7.81–7.84 (2H, d); GC–MS ( $m/z$ ) calcd for **2** [M<sup>+</sup>]: 564.3, found: 564.4; fulgide **3**: 2.04 (3H, s), 2.31 (3H, s), 2.38 (3H, s), 2.47 (3H, s), 7.82, (2H, d), 8.69 (2H, d); fulgide **4**: 2.01 (3H, s), 2.11(3H, s), 2.31 (3H, s), 2.41 (3H, s), 2.44 (3H, s) 6.55 (1H, s); fulgimide **5**: 1.33 (3H, s), 1.70 (3H,

\* Corresponding author.

E-mail address: [tcrcrats@ipc.shizuoka.ac.jp](mailto:tcrcrats@ipc.shizuoka.ac.jp) (R. Matsushima).



Scheme 1. Structures of fulgide derivatives.

Fig. 1. Absorption spectra of fulgide **1** (0.50  $\mu\text{M}$ ) and fulgenate **2** in ethyl acetate. (a) Erased forms and (b) colored forms at PSS.

s), 2.00 (3H, s), 2.31 (3H, s), 2.67 (3H, s), 6.02 (1H, s), 7.10–7.13 (2H, m), 7.40–7.51 (3H, m), 7.57 (1H, s).

The dibenzyl fulgenate **2** (as yellow dye) was prepared by mixing 0.52 g (1.4 mmol) of fulgide **1** and 0.37 g (2.2 mmol) of

Table 1  
Spectral properties of yellow derivatives of fulgides<sup>a</sup>.

FG	$\lambda_{\text{max}}^E$ (nm)	$\epsilon_{\text{max}}^E$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )	$\lambda_{\text{max}}^C$ (nm)	$\epsilon_{\text{max}}^C$ ( $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ )
<b>1</b>	322	3.5	506	1.9
<b>2</b>	322	2.9	405	1.7
<b>3</b>	280	1.9	444	0.75

<sup>a</sup> Measured in ethyl acetate solution.

benzyl bromide in 100 mL acetonitrile solution in the presence of 1.0 g of potassium carbonate at 80 °C for 33 h. After removal of the solvent and benzyl bromide, ethyl acetate was added and washed with water. Condensation of the organic layer followed by column-chromatographic separation gave a colorless oil in 29% yield (0.41 mmol). Thin layer chromatography on silica-gel with ethyl acetate showed a single spot. The <sup>1</sup>H NMR signals at 4.91 (2H, s), 5.12 (2H, s), and 7.04–7.34 (10H, m) are assigned to the methylene and phenyl protons of the benzyl group, respectively.

## 2.2. Apparatus and procedures

UV–vis spectra were recorded on a Hitachi U-3000 spectrometer. <sup>1</sup>H NMR spectra were recorded on a 300 MHz FT-NMR system AL-300 (JEOL), while GC–MS spectra were recorded on a GC MS-QP5050 (Shimadzu). A 0.10 g polymer (PMMA or phenoxy resin)

Table 2  
Photochromic properties of fulgide derivatives in polymer films.

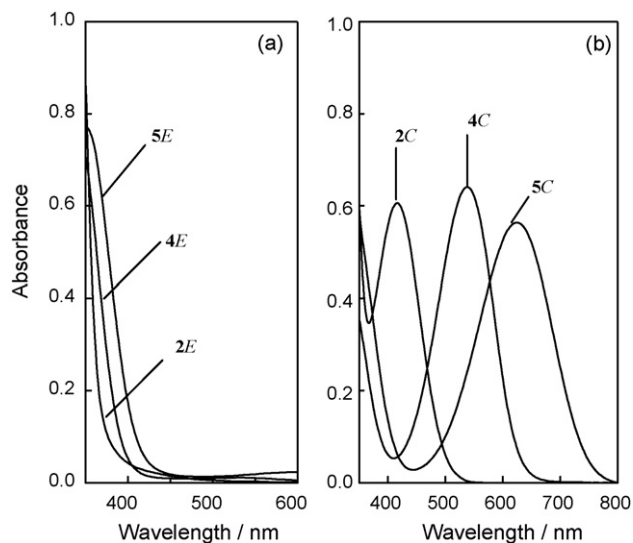
FG	Polymer medium	$\lambda_{\text{max}}^C$ (nm)	Photostability <sup>a</sup>		Thermostability at 80 °C <sup>b</sup>	
			$A_{20}/A_0$ ( $\lambda_{\text{max}}^C$ )	$A_{10}/A_0$ ( $\lambda_{\text{max}}^E$ )	$A_{10}/A_0$ ( $\lambda_{\text{max}}^C$ )	
<b>1</b>	PMMA	514	0.82	0.84	0.90	
<b>2</b>	PMMA	408	0.86	0.95	0.96	
	Phenoxy resin	416	0.71	–	–	
	Phenoxy resin/PVA <sup>c</sup>	416	0.96	–	–	
<b>3</b>	PMMA	451	0.84	0.88	0.85	
<b>4</b>	PMMA	526	0.40	–	0.65	
	Phenoxy resin	538	0.65	–	–	
	Phenoxy resin/PVA <sup>c</sup>	538	0.75	–	–	
<b>5</b>	PMMA	605	0.54	(0.87) <sup>d</sup>	(0.08) <sup>d</sup>	
	PMMA/PVA <sup>c</sup>	605	0.86	0.99	0.94	
	Phenoxy resin	625	0.13	–	–	
	Phenoxy resin/PVA <sup>c</sup>	625	0.60	–	–	

<sup>a</sup>  $A_0$  and  $A_{20}$  refer to the absorbances before and after 20 repeated cycles of photochemical coloration and decoloration, respectively.

<sup>b</sup>  $A_0$  and  $A_{10}$  refer to the absorbances of the erased ( $\lambda_{\text{max}}^E$ ) and colored ( $\lambda_{\text{max}}^C$ ) forms before and after heating for 10 days at 80 °C, respectively [20].

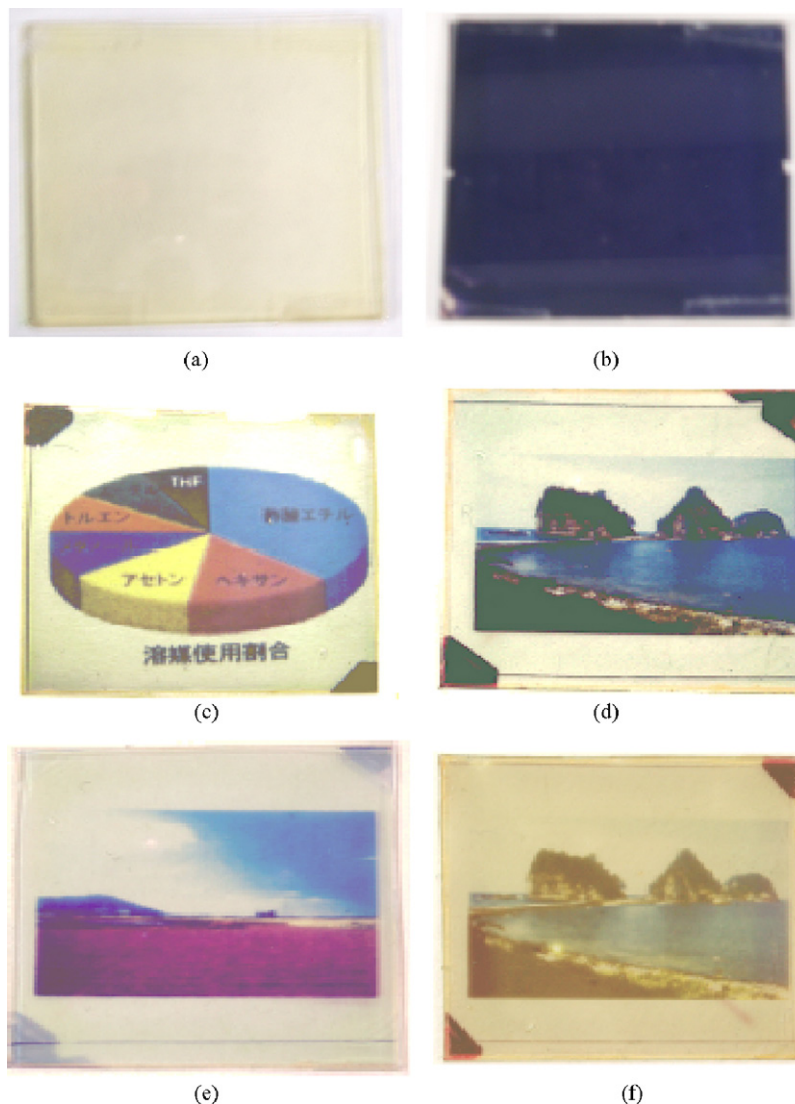
<sup>c</sup> The surface was further covered with PVA film to keep air-tight.

<sup>d</sup> After heating for 5 days.



was dissolved in a 0.45 g cyclohexanone at 80 °C, after cooling to room temperature a 5–12 mg of each fulgide derivative was added and stirred. The mixture solution was spin-coated on a sheet of PET (25 cm × 25 cm) with spin rate of 350 rpm for 20 s, followed by 1100 rpm for 20 s. In the experiments of full-color rewritable images, the surface of the photochromic layer was further covered with a 15 wt.% aqueous PVA solution and spin-coated to minimize oxidative degradations. In order to convert the *Z*-isomers substantially into the *E*-isomers, UV and vis light beams were alternately irradiated twice, before use. A 400-W high-pressure mercury lamp (Riko) was used as UV and visible light source in the experiments of photochemical reversibility. In the experiments of full-color rewritable images, on the other hand, UV light beams were irradiated with a 27-W black light (Sankyo Denki) for 7 min and with a 6-W UV-B lamp (Sankyo Denki) for 3 min, to form a black film. Full-color image was formed by irradiation of white light with a 100-W Mega Light 100 (Shot Japan) for 10 min, at a 5-cm distance above the positive mask attached on the black film.

**Fig. 2.** Absorption spectra of (a) erased forms and (b) colored forms at PSS. A mixture of **2** (12.5 wt.%), **4** (7.5 wt.%), and **5** (5 wt.%) in phenoxy resin was spin-coated.



**Fig. 3.** Full-color images in a spin-coated film covered with PVA film. (a) Erased colorless film, (b) black film after UV irradiation, (c) a full-color image obtained by white light irradiation of the black film above a positive-color mask, (d) fifth-rewritten image, (e) tenth-rewritten image, and (f) eighteenth-rewritten image, after repeated erase-write cycles. Irradiation times of visible light and UV light were both 10 min, in each write-erase cycle.

**Table 3**

Approximate irradiation times of white light to erase the colored forms in PMMA film<sup>a</sup>.

Colored form	Concentration (wt.%)	Half-erase time (min)	Total erase time (min)
2C	12.5	1.1	5.0
4C	10.0	2.0	10.0
5C	5.0	1.3	5.0

<sup>a</sup> Initial absorbances of the colored forms were around 0.6 attained at PSS on UV irradiation.

### 3. Results and discussion

Fig. 1 compares the absorption spectra of the fulgenate **2** and oxazolylfulgide **1** while Table 1 lists the spectral data of **1–3**, in ethyl acetate solution. The colored form **2C**, attained at the photostationary state of coloration (PSS), exhibits substantial blue shift from **1C**, thus featuring pure yellow color ( $\lambda_{\text{max}}$  405 nm) and large absorption coefficient as compared with oxazolylfulgide **3C** [17]. In the erased form **2E** the shoulder of **1E** around 360–430 nm is completely disappeared. Regarding to the solvolytic resistance, fulgenate **2C** remained unchanged whereas **1C** showed substantial (85%) degradations, in aqueous methanol solution on standing for 3 h at room temperature. Photochemical and thermal properties of **1–5** in spin-coated polymer films are listed in Table 2. The thermal stabilities in the phenoxy resin, though not available, are assumed to be similar to those in the PMMA film. Fulgenate **2** revealed excellent photochemical and thermal stabilities in PMMA without protection by PVA film, as well as excellent property as a yellow dye. These favorable features of fulgenates have been reported earlier with indolylfulgenates by Yokoyama et al. [14,15]. On the other hand, photochemical and thermal stabilities of **4** and **5** were substantially poor in the bare films, but significantly improved by protection with PVA film. Though **5** featured better stabilities in PMMA/PVA, the color property as cyan seemed better in phenoxy resin/PVA.

As the three primary dyes, **2** (12.5 wt.%), **4** (7.5%), and **5** (5 wt.%) were mixed with phenoxy resin in cyclohexanone and spin-coated on a PET sheet. After trials with some polymeric films the phenoxy resin was selected as the best polymer to meet the three primary colors. Thus, the colored forms at PSS exhibit fairly pure colors as shown in Fig. 2(b), while the erased forms exhibit fair cut-off above 400 nm as shown in Fig. 2(a). A black film, formed by UV irradiation, was covered with a positive-color mask and one-shot irradiated with white light, instead of a step-wise irradiation of red, green, and blue light beams [2]. The first-written image was erased by white light and made black by UV light, then a second image was written with another positive mask and white light. Fig. 3 illustrates the real color images: (a) erased colorless film, (b) full-colored black film, and (c) a full-color image obtained by irradiation with white light above a positive mask attached on the black film. Fig. 3(d)–(f) illustrates the color images after repeated write–erase cycles: (d) at fifth-cycle, (e) at tenth-cycle, and (f) at eighteenth-cycle, respec-

tively. The image (f) reveals substantial degradations despite the protection by PVA film, as anticipated from the lower photochemical fatigue resistances of **4** and **5** in the polymer films (Table 2). Thus, substantial improvements in the fatigue resistances are necessary [12]. Another issue may be concerned with the difference in the erasing rates upon white light irradiation. Table 3 lists the approximate irradiation time taken to convert from the C- to E-isomer in PMMA film, at a similar concentration to that found in the phenoxy resin/PVA film. In order to obtain a full-color image or a colorless film, an irradiation time not less than 10 min is necessary to erase **4C** but it is excessively long to erase **2C** and **5C**. While one-shot irradiation is simple and effective for robust materials, step-wise irradiation would be more suitable for less robust materials having different erasing rates since the erasing time of individual dye can be optimized or minimized in each step.

### 4. Conclusion

A trial full-color rewritable film of a mixture of fulgide derivatives has been prepared. A colorless or black film was obtained by irradiation with white light or UV light. A full-color image almost identical to positive-color mask was obtained by a simpler, one-shot irradiation with white light rather than a step-wise irradiation with RGB light beams. Though the present color-forming method is simpler and effective, substantial improvements in the fatigue resistances are necessary.

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