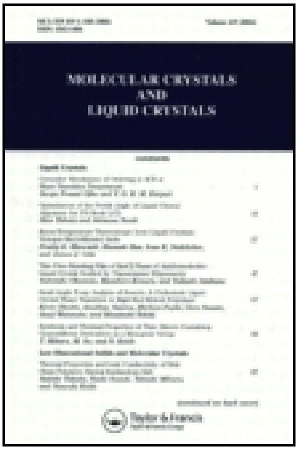

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Multi-States Photochromic Recording and Nondestructive Readout Using IR Light

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Multi-States Photochromic Recording and Nondestructive Readout Using IR Light

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*A photochromic polymer film containing three different kinds of diarylethene derivatives 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1**), 1,2-bis(2,5-dimethyl-3-thienyl)-perfluorocyclopentene (**2**), and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**) was prepared. Upon UV irradiation, these three derivatives changed to their closed-ring isomers having different colors, yellow, red, and blue. They showed different spectra not only in UV-vis. region but also in infrared (IR) spectral region. Upon irradiation with visible light of appropriate wavelengths, each closed-ring isomer was selectively bleached, and 3 bits 8 states recording was performed. The 8 states could be read out non-destructively by using IR light of appropriate wavenumbers. The technique will be applicable for near-field IR readout.*

Keywords: diarylethene; infra-red; multi-frequency recording; non-destructive readout; near-field

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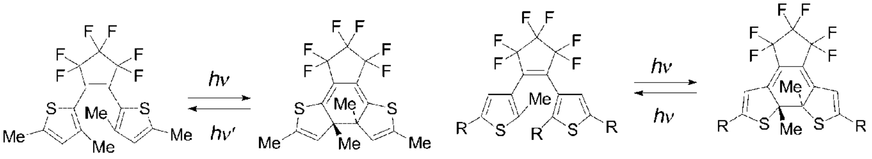
INTRODUCTION

For the practical application of photochromic materials to optical memory media, non-destructive read-out capability is indispensable [1]. Zerbi et al. have proposed to use IR light as the readout light which can not cause any photoreaction [2]. We have demonstrated that some of the diarylethene derivatives show remarkable IR spectral changes accompanied with the photochromism, and the images recorded on a polymer film containing the diarylethene by UV light irradiation can be nondestructively readout by IR light [3–5]. In the present study, we have prepared the recording film containing three diarylethenes **1**, **2**, and **3**. Each closed-ring isomers shows its distinct absorption in 1500–1700 cm^{-1} wavenumber region. By using these bands for IR readout, three bits eight states recording on the film was non-destructively observed. They are the demonstrations of non-destructive readout of multiple recording using IR light. This technique is useful for reversible high-density recoding with non-destructive readout.

EXPERIMENTAL

Diarylethene derivatives **1**, **2**, and **3** were prepared according to the literatures [6–8]. Poly(cyclopentene) polymer (Zeonex 480) was purchased by ZEON Corporation. Diarylethene **1** (3.8 mg) and 52.5 mg of poly(cyclopentene)polymer (Zeonex 480), which has no absorption in 1500–1700 cm^{-1}, were dissolved in 2 ml of chloroform, and the solution was casted on the glass plates. After the removal of the solvent, a photochromic film was obtained. The polymer films containing **2** and **3** were prepared similarly. Film thickness of these polymer films was measured by use of micrometer (Mitutoyo Corporation, M110-25) and they were found to be 15 μm. For the preparation of a polymer film containing three diarylethene derivatives, 4.4 mg of **1**, 3.1 mg of **2**, 3.7 mg of **3,** and 86.7 mg of poly(cyclopentene)polymer were dissolved in 2 ml of chloroform, and the solution was casted on the glass plates. After



1a **1b** **2a**; R = Me **3a**; R = Ph **2b**; R = Me **3b**; R = Ph

SCHEME 1

the removal of the solvent, the film was obtained. The polymer film was peeled off before the measurement. Film thickness was measured and found to be 25 μm. The letter size of the alphabetical masks was around 2.5 mm. IR images were monitored on Perkin Elmer Spectrum Spotlight 300. Transparency imaging mode was selected for the measurements. The resolving power was 4 cm^{-1}, and observing pixel size was 25 μm × 25 μm. Scanning times were 4 scans per pixels. Fourier transfer near-field infra-red spectrometer (JASCO NFIR-200) was used for near field observations. The diameter of the top of the probe was less than 1 μm. The distance separating the sample and probe was regulated by the uncontacted physical force interaction and was maintained at approximately 30 nm.

RESULTS AND DISCUSSION

The IR spectral changes accompanied the photochromism of diarylethenes **1** and **2** are already reported [5], and **3** in carbon tetrachloride solutions were shown in Figure 1. The diarylethenes **1**, **2**, and **3** showed a remarkable difference in the spectra of the two isomers around 1500–1700 cm^{-1} wavenumber region. All open-ring isomers **1a, 2a** and **3a** have almost no absorption bands, while the closed-ring isomers **1b, 2b** and **3b** have strong absorption bands in the region, and

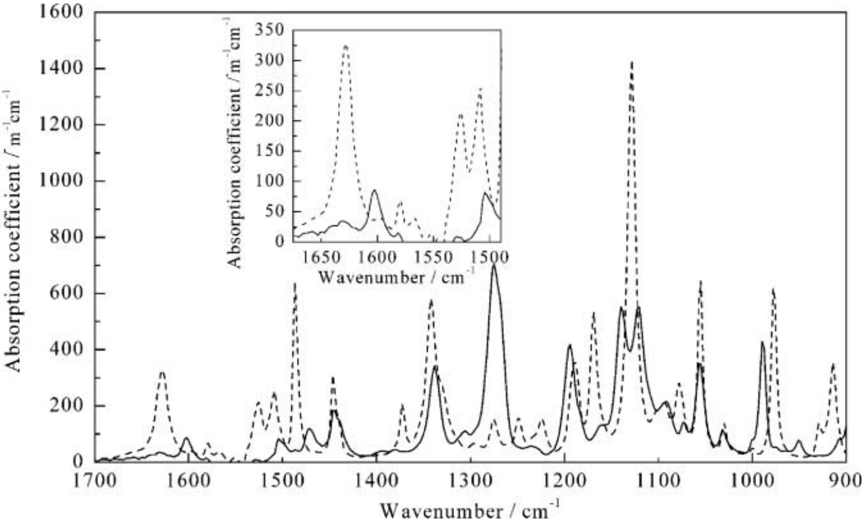


FIGURE 1 Observed infrared spectra of open-ring isomer **3a** (solid line) and closed-ring isomer **3b** (broken line) in CCl$_4$ solution (1.14 × 10^{-2} M).

their bands appeared at 1655, 1549, and 1527 cm^{-1}, respectively. Diarylethenes **1, 2** and **3** show the photochromism even in the polymer matrix, and the IR spectral changes were also observed.

The photochromic recording system containing three different diarylethene derivatives have eight ($2^3 = 8$) recording states. Using the expression of binary the eight states of the recording on the films can be expressed as follows. A (0, 0, 0), B (0, 0, 1), C (0, 1, 0), D (0, 1, 1), E (1, 0, 0), F (1, 0, 1), G (1, 1, 0), H (1, 1, 1). Here 0 means the open-ring isomer, while 1 means the closed-ring isomer. For example, in the B state, the film contains **1a**, **2a**, and **3b**, and the film in F state contains **1b**, **2a**, and **3b**. All diarylethene derivatives are in the closed-ring isomers in State H (1 ,1, 1).

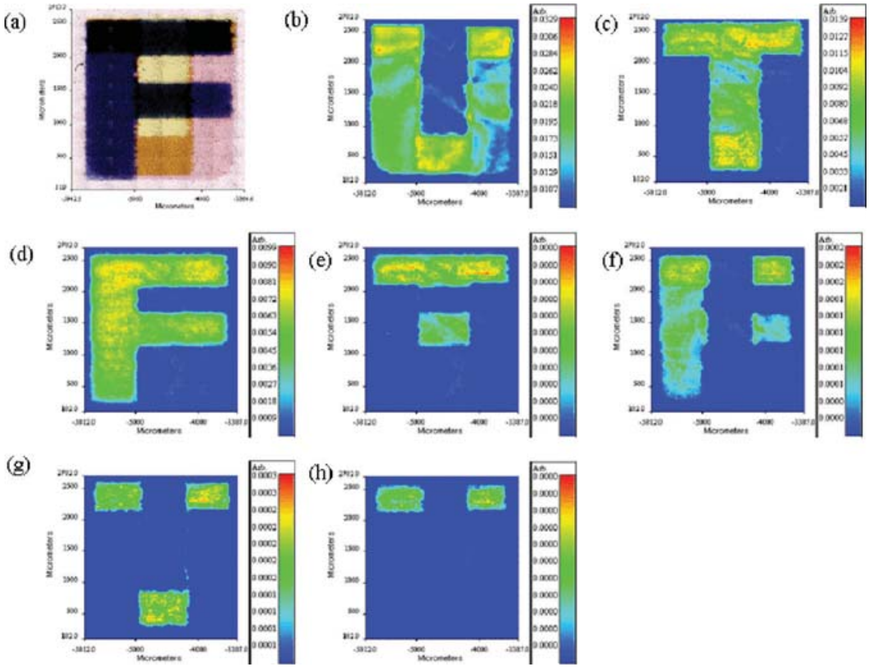


FIGURE 2 Visible (a) and IR images (b–h) of the recorded polymer film containing diarylethenes **1**, **2**, and **3**. (b) IR image detected at 1549 cm^{-1} indicating State C, (c) IR image detected at 1655 cm^{-1} indicating State E, (d) IR image detected at 1527 cm^{-1} indicating State B, (e) IR image detected both at 1655 and 1527 cm^{-1} indicating State F, (f) IR image detected both at 1549 and 1527 cm^{-1} indicating State D, (g) IR image detected both at 1655 and 1549 cm^{-1} indicating State G, and (h) IR image detected at 1655, 1549, and 1527 cm^{-1} indicating State H.

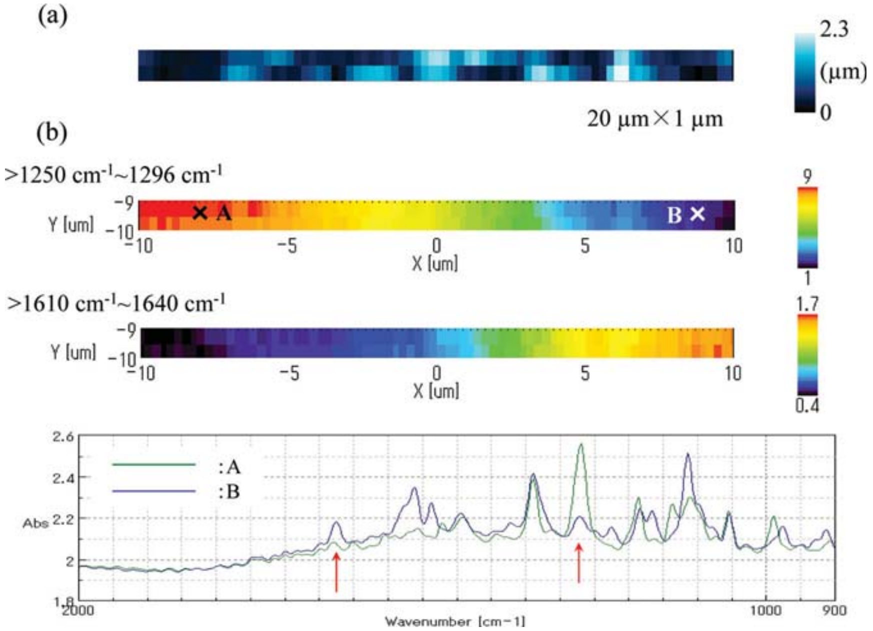


FIGURE 3 Topographic image of recorded quasi-crystalline diarylethene **3** surface (a) and the IR images (b) obtained at different wavenumber light by FT near-field infra-red spectrometer.

The recording operation is as follows. The polymer film containing all open-ring isomers **1a, 2a** and **3a** is prepared at first. Upon irradiation with 313 nm light, all diarylethenes **1a, 2a** and **3a** converted to their closed-ring isomers **1b, 2b**, and **3b** (State H). Under the present conditions, conversion to the closed-ring isomers **1b, 2b**, and **3b** were estimated to be 57, 55, and 52%, respectively. Upon irradiation with 403 nm light to the state, only one closed-ring isomer **1b** returns to the **1a** (State D), while upon irradiation with visible light ($\lambda > 640$ nm) light only **3b** reverts to **3a** to form state G. Upon irradiation with 520 nm light to the State H in short period, only **2b** reverts to **2a** (State F) due to large difference of cycloreversion quantum yield of **2b** (0.12) and **3b** (0.013). By combination of the operations other States A, B, C, E were formed. The recording on the film was performed as follows. Initially the film was homogeneously irradiated with 313 nm light. Then, an F mask pattern was placed on the film and visible light ($\lambda > 640$ nm) was irradiated. Then the **F** mask is removed and replaced by a **U** mask. After the 520 nm light irradiation (10 s with monochromic light), almost only **2b** reverted to **2a**, because of large difference of the cycloreversion reaction quantum yield between **2b** and **3b**. Then the mask was replaced by a **T** mask followed by irradiation with 403 nm light. The recorded film was obtained and the visible image is shown in Figure 2a. In the recorded film, closed-ring isomer **1b** remains in the domain T, **2b** remains in the domain U, and **3b** remains in the domain F. The images monitored by IR light at 1655, 1549, and 1527 cm^{-1} are shown in Figure 2b, c, d, respectively. The green domain is the area having stronger absorption at the wavenumber. The IR images **T**, **U**, and **F** are attributable to the state E, C, and B in Figure 2, respectively. The images of the states G, D, and F are obtained as the overlap of each two letters **T** and **U**, **U** and **F**, and **T** and **F**, respectively. They are shown in Figure 2g, f, e, respectively. The image of state G in which all diarylethenes are in the closed-ring forms, was obtained as the triple overlapping of three letters **T**, **U**, and **F** as shown in Figure 2h. And background of the letters is in the State A. Using the different wave number IR light, 3 bits 8 states information was detected as the different letters and overlapping domains. Even after prolonged readout of the image using IR light, any decrease in the signal-to-noise ratio was observed. By visible light irradiation, all images in Figure 2a–g were bleached and the recording was erased. This technique is applicable for near-field IR reading. We could observe the IR spectral deference of **3a** and **3b** in near-field using IR diffraction type near field microscope [9]. The obtained spectra, shown in Figure 3, are similar to that in Figure 1, therefore near field IR measurement is effective for nondestructive readout of the photochromic recordings of diarylethene derivatives [10].

REFERENCES

[1] Irie, M. (2000). *Chem. Rev.*, *100*, 1685.

[2] Stellacci, F., Bertarelli, C., Toscano, F., Gallazzi, M. C., & Zerbi, G. (1999). *Chem. Phys. Lett.*, *302*, 563.

[3] Uchida, K., Saito, M., Murakami, A., Nakamura, S., & Irie, M. (2003). *Adv. Mater.*, *15*, 121.

[4] Uchida, K., Takata, A., Saito, M., Murakami, A., Nakamura, S., & Irie, M. (2003). *Adv. Funct. Mater.*, *13*, 755.

[5] Uchida, K., Saito, M., Murakami, A., Nakamura, S., & Irie, M. (2003). *Chem. Phys. Chem.*, *4*, 1124.

[6] Uchida, K. & Irie, M. *Chem. Lett.*, *1995*, 969.

[7] Kobatake, S., Yamada, T., Uchida, K., Kato, N., & Irie, M. (1999). *J. Am. Chem. Soc.*, *121*, 2380.

[8] Irie, M., Lifka, T., Kobatake, S., & Kato, N. (2000). *J. Am. Chem. Soc.*, *122*, 4871.

[9] Narita, Y. & Kimura, S. (2001). *Anal. Sci.*, *17*, 1685.

[10] Saito, M., Miyata, T., Murakami, A., Nakamura, S., Irie, M., & Uchida, K. (2004). *Chem. Lett.*, *33*, 786.