Non-destructive Readout of the Photochromic Recording Using the IR Light in the Near Field

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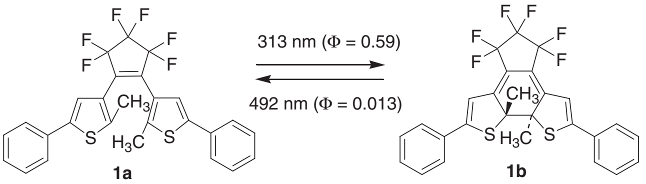
An IR spectral difference of the isomers of a photochromic diarylethene derivative was successfully observed by a near field microscope. The near-field detection can be used for non-destructive readout of high-density photochromic recording of the derivative.

Photochromic molecules attract much attention from both fundamental as well as practical points of view because of their potential for applications to optical devices such as optical memories and switches.[1] Among photochromic compounds, diarylethenes are regarded as the best candidate because of the thermal stability of both isomers and the fatigue resistant property.[2] For the practical application to optical memory media, non-destructive read-out capability is indispensable. When the recorded information is readout by UV–vis. light, which electronically excites the photochromic compounds, the information is lost during the reading process. To avoid this, several attempts have been reported. An approach is to use readout light, which can not cause any photoreaction.[3–10] Zerbi and his co-workers found that 1,2-bis[5-(4-methoxyphenyl)-2-methylthien-3-yl]-perfluorocyclopentene has a strong infrared absorption band at 1495 $\mathrm{cm^{-1}}$ in the closed-ring isomer, while it is absent in the open-ring isomer. Bisbenzothienylethene derivatives also showed remarkable IR spectral changes upon alternate UV and visible light irradiation and the images recorded by UV light irradiation could be nondestructively read out by IR light.[11] The use of IR light is, however, disadvantageous for reading the high density data because the focused readout IR light has diameter larger than μm.[12] A possible solution to decrease the spot size of the readout light is to use near-field optics.[13] In the near-field optics, recording and reading mark size depends on the tip diameter of the probe but not on the wavelength of the light. The recording density can be increased, in principle, if a tip with a small sized aperture is used.

As reported previously, some diarylethene derivatives[11,12] show the reversible IR spectral changes accompanied with the photoisomerization. We have prepared the recording films by doping the diarylethenes into Zeonex polymers, and casted on the mirror polished aluminum substrate by a solution casting method. Although the color changes of the films were observed upon UV light irradiation, any detectable IR spectral change was not observed. It is due to the low absorption coefficients of IR bands. The closed-ring isomer of bis(2-methylbenzo[b]thiophen-3-yl)perfluorocyclopentene have the absorption coefficient of $9.1 \times 10^{3}\ \mathrm{mol^{-1}cm^{-1}}$ at 517 nm in visible region in hexane,[14] while that of IR band at 1591 $\mathrm{cm^{-1}}$ is only 550 $\mathrm{mol^{-1}cm^{-1}}$.[11] Therefore the photochromic film with high dye concentration is desired for the near field IR observation. For preparing such films, bulk photochromic systems, such as single crystalline[15] or amorphous films,[16] and oxidation polymerization films[17] are indispensable. We have selected a diarylethene derivative showing photochromism even in the crystalline state for the recording films.

Here we report on the IR spectral changes of 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**1**)[15] accompanied by the photochromism, and the observation of the changes in the solid film state using IR diffraction type near field microscope.[18] As reported for the diarylethene derivatives,[11,12] diarylethene **1** shows reversible IR spectral changes accompanied with the photoisomerization in the carbon tetrachloride solution as shown in Figure 1.



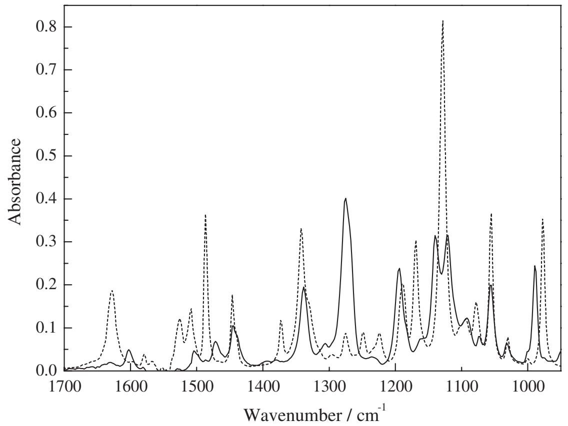


Figure 1. Infrared spectra of the open-ring isomer **1a** (solid line) and the closed-ring isomer **1b** (broken line) in the carbon tetrachloride (1.14×10^{-2} M).

Recording films were prepared as follows. Hexane solution (50 mL) containing diarylethene **1** (2.5 mg) was irradiated with UV light to form photostationary state mixture (**1a**:**1b** = 8:92). After the solvent was removed in the dark, the mixture was dissolved in 0.5 mL of chloroform. The solution was casted on the mirror polished aluminum substrate (9 × 9 mm). Blue colored photochromic layer was formed on the substrate (thickness ca. 10 μm). Quasi amorphous film was used for the recording. Half

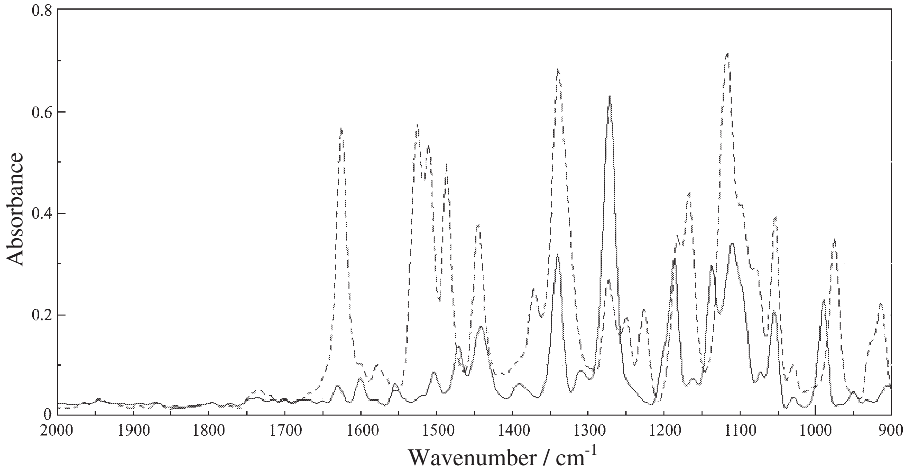


Figure 2. Obtained near field infrared spectra of the colorless domain (open-ring isomer **1a**) (solid line) and the blue colored domain (closed-ring isomer **1b**)(broken line).

of the substrate was irradiated upon visible light ($\lambda > 500$ nm) to regenerate the colorless isomer **1a**. The colored and colorless domains were observed by Fourier transfer near-field infrared spectrometer (JASCO NFIR-200). 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.[19]

The near field IR point spectra of both domains for 2000–900 cm^{-1} (wavelength: 5–11 µm) were obtained using the probe with 100 scanning times and 8 cm^{-1} resolution. The obtained spectra are shown in Figure 2. As compared with Figures 1 and 2, IR spectra of both isomers are similar, consequently near field IR measurement is effective for nondestructive readout of the photochromic recordings of diarylethene derivatives. If the observing wave number is locked on 1626 cm^{-1}, for example, a large change in absorbance should be observed by the alternative irradiation of UV and visible lights. Therefore, in principle, the nondestructive readout of a submicrometer-sized record has been realized with the near-field IR absorption technique.

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