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Three Bits Eight States Photochromic Recording and Nondestructive Readout by Using IR Light

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Abstract: A photochromic polymer film containing three different diarylethene derivatives, that is, 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, the 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 the IR spectral region. Upon irradiation with visible light of appropriate wavelengths, each closed-ring isomer was selectively bleached, and three bits eight states recording was performed. The eight states could be read out nondestructively by using IR light of appropriate wavenumbers.

Keywords: diarylethene • multi-frequency recording • nondestructive readout • photochromism • polymers

Introduction

Photochromic molecules attract much attention from both fundamental as well as practical point of views 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 for the applications, because of the thermal stability of both isomers and the fatigue resistant property.[2] For the practical application to optical memory media, nondestructive readout capability is indispensable. When the recorded information is readout by light, which electronically excites the photochromic compounds, the information is lost during the reading process. To avoid this, several attempts have been proposed. One is to use gated photochromic systems in which two different kinds of stimuli manage to read the memory without destruction.[3,4] Another approach is to use readout light, which can not cause any photoreaction. Infrared,[5] Raman,[6] and fluorescence[7–12] spectral changes along with the photochromism can be successfully readout without alternation of the ratio of the two isomers. Zerbi et al. found that 1,2-bis[5′-(4″-methoxyphenyl)-2′-methylthien-3′-yl]perfluorocyclopentene has a strong infrared absorption band at 1495 cm^{-1} in the closed-ring isomer, while it is absent in the open-ring isomer;[5] the difference can be readout nondestructively by IR light. Bisbenzothienylethene derivatives also show remarkable IR spectral changes upon alternate UV and visible light irradiation and the images recorded by UV light irradiation can be nondestructively readout by IR light.[13] Although the use of long wavelengths light such as IR light is disadvantageous for high density data storage because the light spot diameter cannot be focused shorter than the wavelength of the used light, multi-addressable recording system[14,15] may solve the problem by multiplying the data in the same spot. In usual one-component photochromic systems, interconvert between only two states, “colorless” and “colored”, is used for recording. On the other hand, in addressable recording system interconvert between more than two states have higher density data storage in a recording spot. Some photochromic compounds having multi-photochromic states are already reported.[14] Besides these molecules, in multi-component systems composed of different kinds of photochromic compounds, reversible multi-mode switching between more than two states

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can be realized by the combination of two states of each component.[15] We have already reported the two bit four states recording and nondestructive readout by IR light.[16]

We have investigated the multi-frequency recording using three diarylethene derivatives, 1,2-bis(3,5-dimethyl-2-thienyl)perfluorocyclopentene (**1**)[17] 1,2-bis(2,5-dimethyl-3-thienyl)perfluorocyclopentene (**2**),[18] and 1,2-bis(2-methyl-5-phenyl-3-thienyl)perfluorocyclopentene (**3**),[19] having different absorption bands not only in the UV/Vis region but also in the IR region. In the system, writing and erasing the data are carried out by using UV and visible light of appropriate wavelengths, and the data of eight states ($2^3=8$) are read by IR light.

Results and Discussion

UV/Vis spectral changes of the diarylethene derivatives in polymer matrix: The polymer film containing diarylethene **1** was prepared according to the Experimental Section.

Diarylethenes **1**, **2** and **3** show the photochromism even in the polymer matrix as shown in Figure 1a–c, respectively. And their spectral changes are similar to those observed in the hexane solutions.

The open-ring isomer **1o** has the absorbance maximum at 341 nm. Upon irradiation with UV light (313 nm), the closed-ring isomer **1c** with an absorption maximum at 432 nm appeared. The colored-isomer **1c** returned to the open-isomer **1o** by visible light irradiation. Diarylethene **2o** has the absorption band at 239 nm, and the closed-ring isomer **2c** has the band at 507 nm. The spectral difference of **1** and **2** is due to the difference in the π-conjugation length of open- and closed-ring isomers of the dithienylethenes.[17] The connecting positions on thiophene rings to the ethene moiety change the π-conjugation structure.[17] The open-ring isomer **3o** has the absorbance at 291 nm, while the closed-ring isomer has the absorption maximum at 588 nm. Spectral difference between **2c** and **3c** is also due to the difference in the conjugation length of the substituted thiophenes (Scheme 1).[21] Although the absorption bands of the **1o** and **2o** are well separated, the absorption bands of **2o** and **3o** overlap each other. Therefore, it is possible to selectively excite **1o** in the film containing **1o** and **2o** by choosing the wavelength of UV light. But it is hard to excite only one component chromophore from the film containing the three compounds **1o**, **2o**, and **3o**.

On the other hand, the absorption edge of the closed-ring isomers **1c**, **2c**, and **3c**, are located at 510, 605, and 705 nm. By using visible light of appropriate wavelengths (λ = 605–705 nm), it is possible to bleach only **3c** in the film containing the three closed-ring isomers **1c**, **2c**, and **3c**. Upon visible light (520 nm) irradiation, only **2c** can be bleached to regenerate the open-ring isomer **2o**. This is due to the large difference of the cyclo-reversion reaction quantum yields of the closed-ring isomers **2c** (ϕ =0.12 at 533 nm) and **3c** (ϕ =0.013 at 492 nm).[21] By 403 nm light irradiation, **1c** is se-

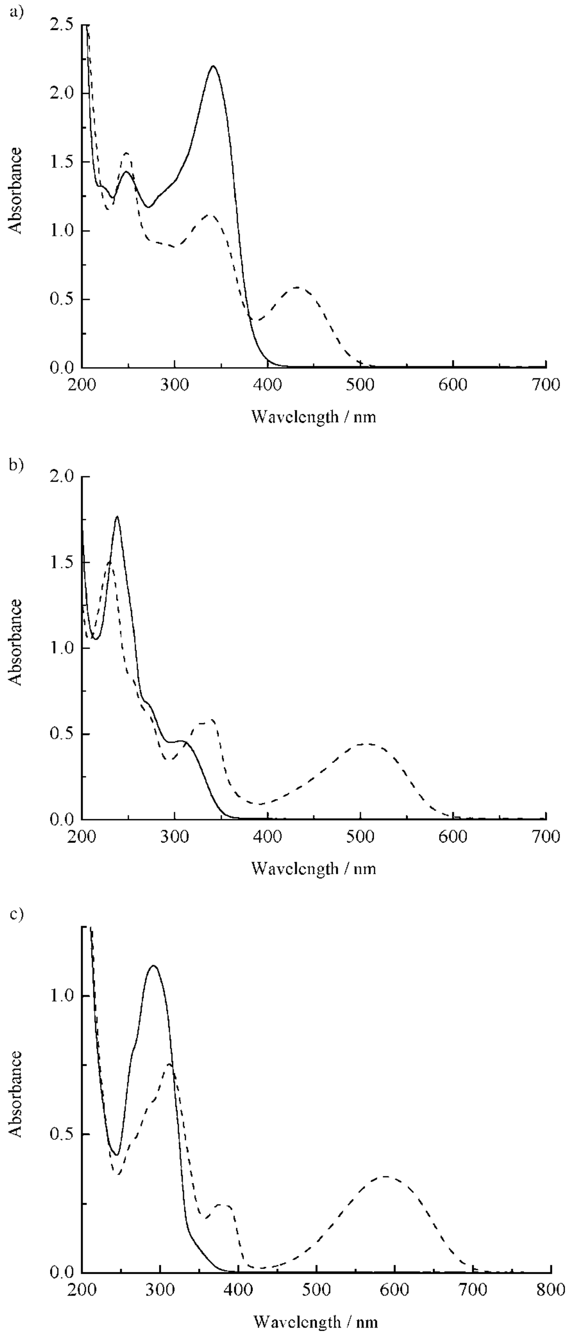
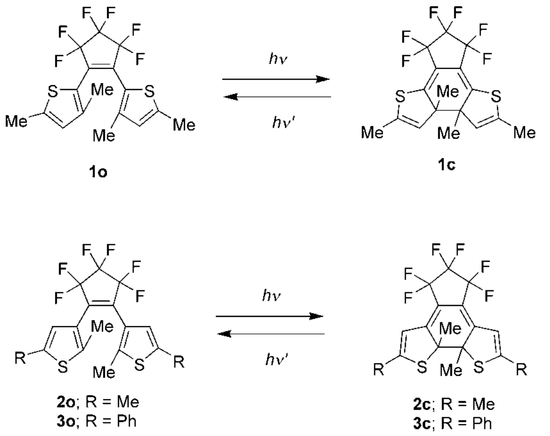


Figure 1. Absorption spectral changes of the poly(cyclopentene) (Zeonex) films. a) Absorption spectral changes of the polymer film containing diarylethene **1** (——: before UV irradiation; -----: after UV irradiation; in this photostationary state, the ratio of **1o** and **1c** was estimated to be 44:56 from the spectra). b) Absorption spectral changes of the Zeonex polymer film containing diarylethene **2** (——: before UV irradiation; -----: after UV irradiation, in this photostationary state, the ratio of **2o** and **2c** was estimated to be 36:64 from the spectra). c) Absorption spectral changes of the Zeonex polymer film containing diarylethene **3** (——: before UV irradiation; -----: after UV irradiation, in this photostationary state, the ratio of **3o** and **3c** was estimated to be 29:71 from the spectra). The thickness of all films are 15 μm. And dye contents of the photochromic films of a), b), and c) are 6.5, 4.4, and 1.5 wt %, respectively.



Scheme 1.

lectively excited to form **1o**, because **2c** and **3c** have little absorbance at the wavelength.[16]

However, it is difficult to readout the ratio of open- and closed-ring isomers of **1**, **2**, and **3** from the UV and visible absorption spectral changes, because of the overlapping of the spectra of these isomers. Therefore we tried selective readout the information on the photochromic film by IR light after writing the information by UV/Vis light and selective bleaching by visible light. IR light irradiation does not cause any photochromic reactions and half widths of the IR bands are commonly narrower than those of UV/Vis bands, therefore the crosstalk of the bands is negligible.

Computational analysis of the IR spectra and assignment of the observed IR bands of diarylethenes 1–3: The IR spectra of open- (o) and closed-ring (c) isomers of the diarylethenes **1**, **2**, and **3**, measured in carbon tetrachloride solution, are shown in Figures 2–4. The spectra calculated by the Hartree-Fock method with 6-31G basis in Gaussian 98[20] are also shown.

The diarylethenes **1**–**3** showed a remarkable difference in the spectra of the two isomers around 1500–1700 cm^{-1} wavenumber region. All open-ring isomers **1o**, **2o** and **3o** have almost no absorption bands, while the closed-ring isomers **1c**, **2c** and **3c** have strong absorption bands in the region, and their bands appeared at different wavenumbers. The closed-ring isomer **1c** showed three absorption bands at 1655, 1631, and 1595 cm^{-1}. Their absorption coefficients are 2.5×10^{2}, 1.9×10^{2}, and $2.6\times10^{2}\,\text{M}^{-1}\text{cm}^{-1}$, respectively. The peaks correspond to the calculated peaks at 1654, 1645, 1635, and 1620 cm^{-1}, and are attributable to the symmetric and asymmetric coupling of the C=C bond in the central six member ring and C=C bond of the thiophene rings, which are formed by the ring closing reaction as shown in Table 1 and Figure 5.

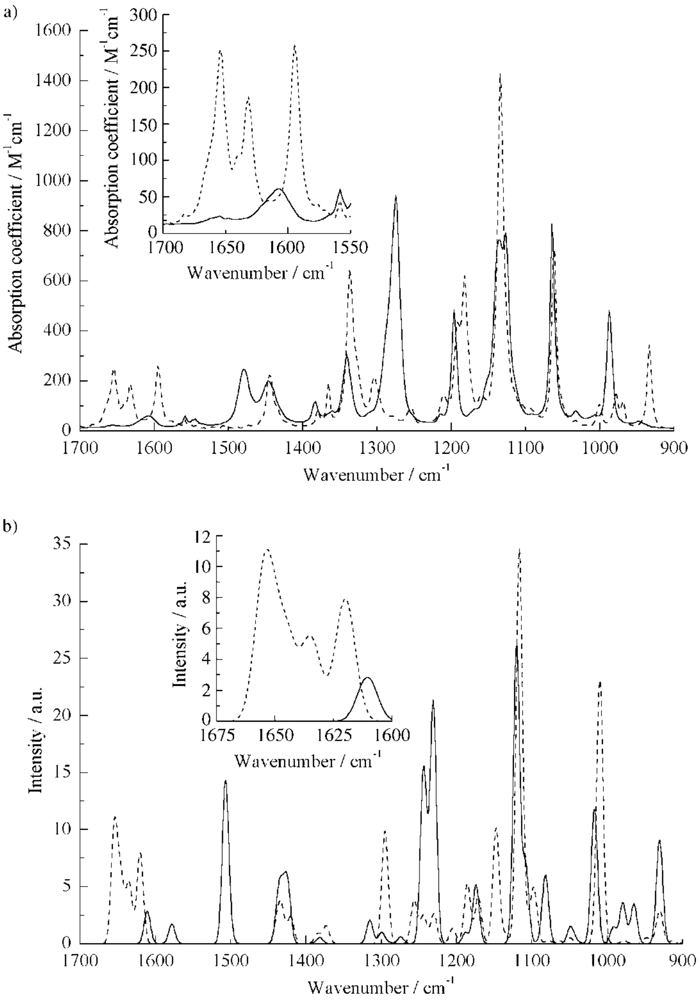


Figure 2. Observed infrared spectra a) of open-ring isomer **1o** (——) and closed-ring isomer **1c** (-----) in CCl_4 solution (1.59×10^{-2} M), and calculated spectra b) of **1o** (——) and closed-ring isomer **1c** (-----).

For the closed-ring isomer **2c**, the bands at 1639 cm^{-1} (ε $3.1\times10^{2}\,\text{M}^{-1}\text{cm}^{-1}$), 1587 cm^{-1} ($\varepsilon$ $1.1\times10^{2}\,\text{M}^{-1}\text{cm}^{-1}$), and 1549 cm^{-1} ($\varepsilon$ $5.4\times10^{2}\,\text{M}^{-1}\text{cm}^{-1}$) were observed. The observed strongest band at 1549 cm^{-1} is assigned to the two calculated vibrational modes 1578, 1584 cm^{-1}. They are asymmetric stretching of double bond of the thiophene rings and symmetric stretching of double bond of the thiophene rings, respectively. The bands appeared at 1587 and 1639 cm^{-1} are assigned to the calculated vibrational mode at 1608 and

Table 1. Wavenumbers and absolute intensities of the main IR absorption bands in the C=C stretching region of diarylethene **1**. Observed values were obtained in carbon tetrachloride solutions.

Closed-ring isomer **1c**				Open-ring isomer **1o**			
Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]	Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]
1595	2.6×10^{2}	1620	84			1500	6
1631	1.9×10^{2}	1635	56	1606	0.6×10^{2}	1507	151
1655	2.5×10^{2}	1645	57			1578	18
		1654	110			1610	30

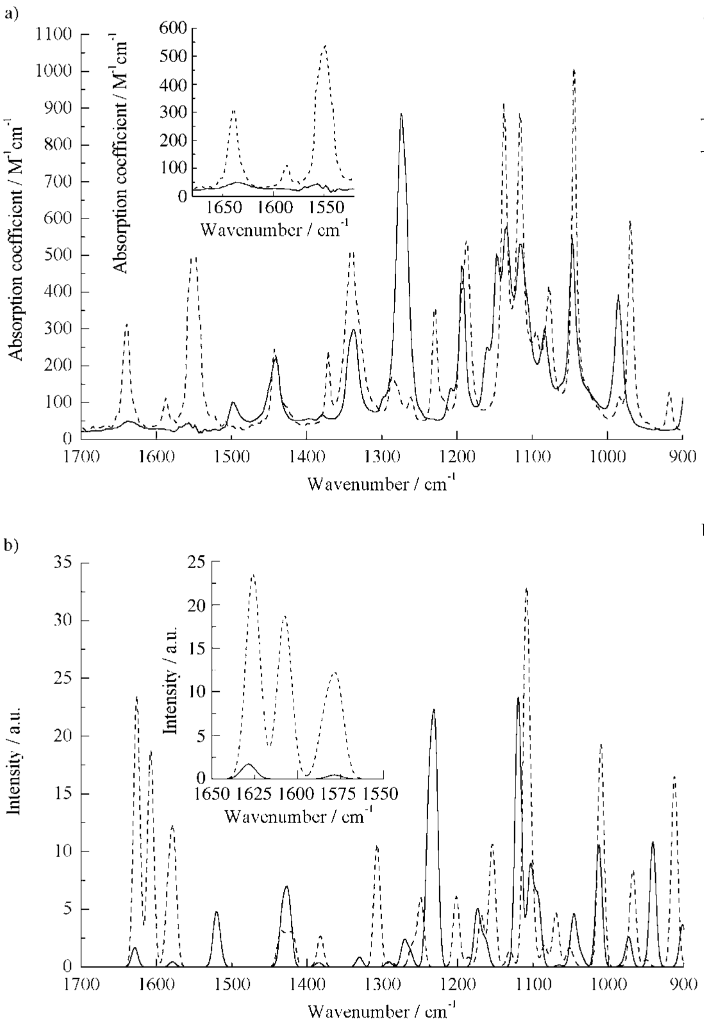


Figure 3. Observed infrared spectra (a) of open-ring isomer **2o** (——) and closed-ring isomer **2c** (-----) in CCl_4 solution (8.25×10^{-3} M), and calculated spectra (b) of **2o** (——) and closed-ring isomer **2c** (-----).

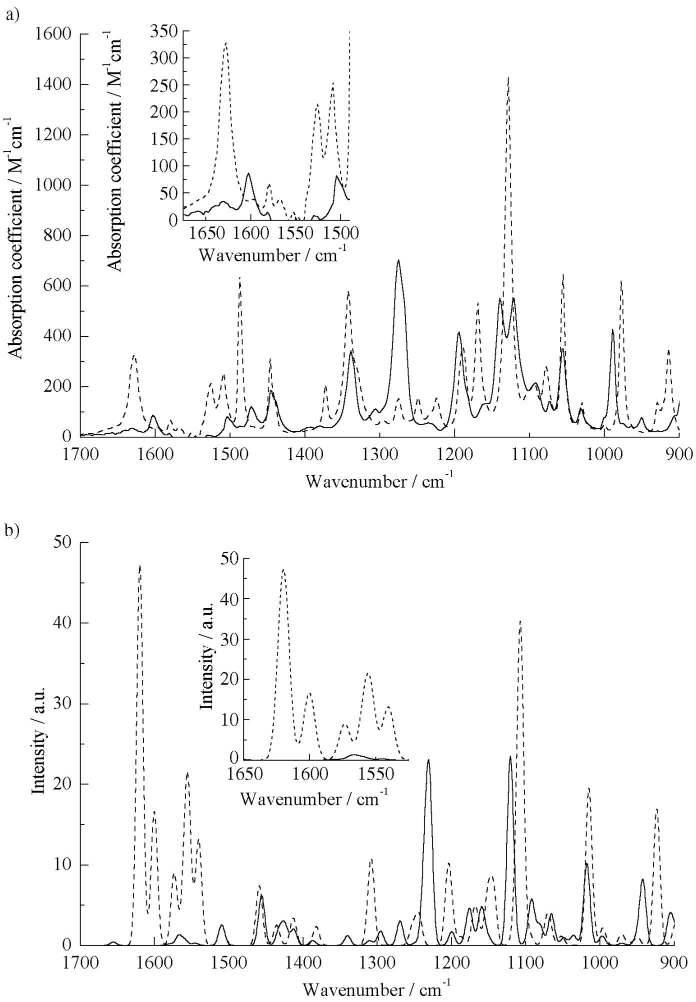


Figure 4. Observed infrared spectra (a) of open-ring isomer **3o** (——) and closed-ring isomer **3c** (-----) in CCl_4 solution (1.14×10^{-2} M), and calculated spectra (b) of **3o** (——) and closed-ring isomer **3c** (-----).

1626 cm^{-1}, respectively. They are attributable to symmetric and asymmetric stretching of double bonds of the central part of cyclohexadiene moiety. The results are summarized in Table 2 and Figure 6.

The closed-ring isomer **3c** showed the band at 1628 (ε 3.3×10^2 M^{-1}cm^{-1}), 1527 (ε 2.0×10^2 M^{-1}cm^{-1}), and 1508 cm^{-1} (ε 2.5×10^2 M^{-1}cm^{-1}) in carbon tetrachloride solutions. The observed strongest peak at 1628 cm^{-1} is assigned to a calculated vibrational mode at 1620 cm^{-1}, which is attributable to asymmetric stretching of double bonds of the central part of cyclohexadiene moiety. The results are summarized in Table 3 and Figure 7.

Multi-frequency photochromic recording and the nondestructive readout: The photochromic polymer film containing three diarylethenes **1–3** was prepared by a solution casting method. The photochromic recording system containing three different diarylethene derivatives have eight ($2^3=8$) recording states. By using the expression of binary the eight

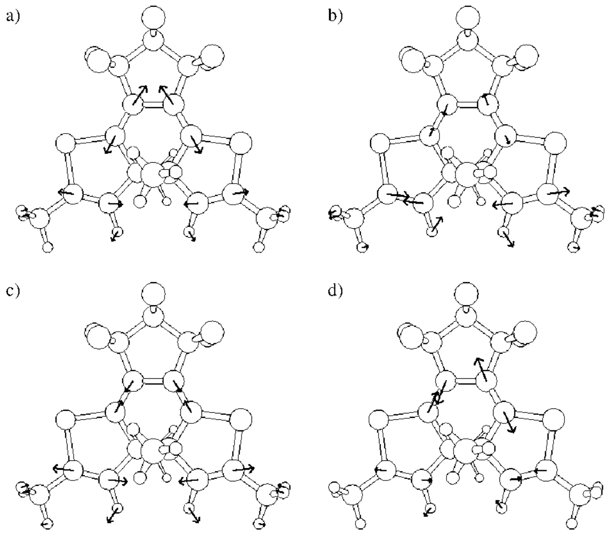


Figure 5. IR vibration modes of **1c**: a) 1620, b) 1635, c) 1645, d) 1654 cm^{-1}.

Table 2. Wavenumbers and absolute intensities of the main IR absorption bands in C=C stretching region of diarylethene **2**. Observed values were obtained in carbon tetrachloride solutions.

Closed-ring isomer **2c**				Open-ring isomer **2o**			
Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]	Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]
1549	5.4×10^2	1578	109			1517	17
		1584	69			1522	41
1587	1.1×10^2	1608	199			1579	5
1639	3.1×10^2	1626	250	1635	0.4×10^2	1629	18

Table 3. Wavenumbers and absolute intensities of the main IR absorption bands in C=C stretching region of diarylethene **3**. Observed values were obtained in carbon tetrachloride solutions.

Closed-ring isomer **3c**				Open-ring isomer **3o**			
Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]	Obsd [cm^{-1}]	ε [M^{-1}cm^{-1}]	Calcd × 0.87 [cm^{-1}]	Intensity [km mol^{-1}]
1508	2.5×10^2	1540	104			1509	27
1527	2.0×10^2	1554	189			1559	7
1628	3.3×10^2	1600	177	1603	0.9×10^2	1567	13
		1620	504				

states of the recording on the films are shown in Table 4. The state of the open-ring isomer is expressed in o or 0, while that of the closed-ring isomer is expressed in c or 1 at each wavenumber band in Table 4. All diaryletenes are in the open-ring isomer state (o or 0) in A (0,0,0) state. States B (0,0,1), C (0,1,0), and E (1,0,0) have the situation in which only one diarylethene is in the closed-ring isomer state (c or 1). The (0,0,1) of the state B means an absorption band was observed at 1527 cm^{-1}, while no bands were observed at 1655 and 1549 cm^{-1}, respectively. In states D (0,1,1), F (1,0,1), and G (1,1,0), two diarylethene derivatives are in the closed-ring isomers. All diarylethenes are in the closed-ring isomers in state H (1,1,1). Figure 8

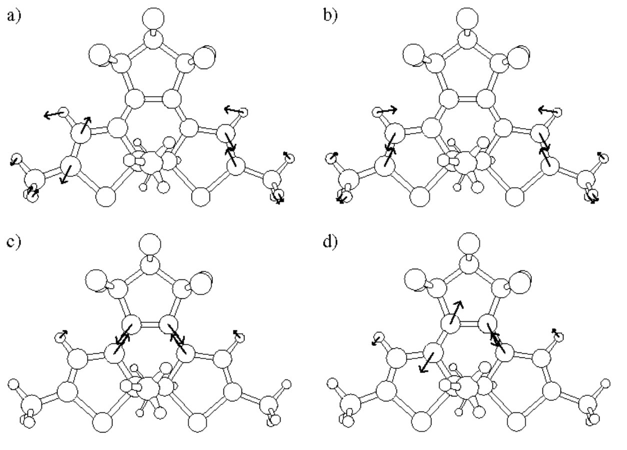


Figure 6. IR vibration modes of **2c**: a) 1578, b) 1584, c) 1608, d) 1626 cm^{-1}.

Table 4. Three bit eight states of the photochromic film and the nondestructive readout wavenumbers.[a]

	States of diarylethenes			Detectable IR wavenumbers [cm^{-1}]		
States	**1**	**2**	**3**	1655	1549	1527
A	o	o	o	0	0	0
B	o	o	c	0	0	1
C	o	c	o	0	1	0
D	o	c	c	0	1	1
E	c	o	o	1	0	0
F	c	o	c	1	0	1
G	c	c	o	1	1	0
H	c	c	c	1	1	1

[a] o: state in the open-ring isomer, c: state in the closed-ring isomer or in the photostationary state, 0; non-detectable, 1; detectable.

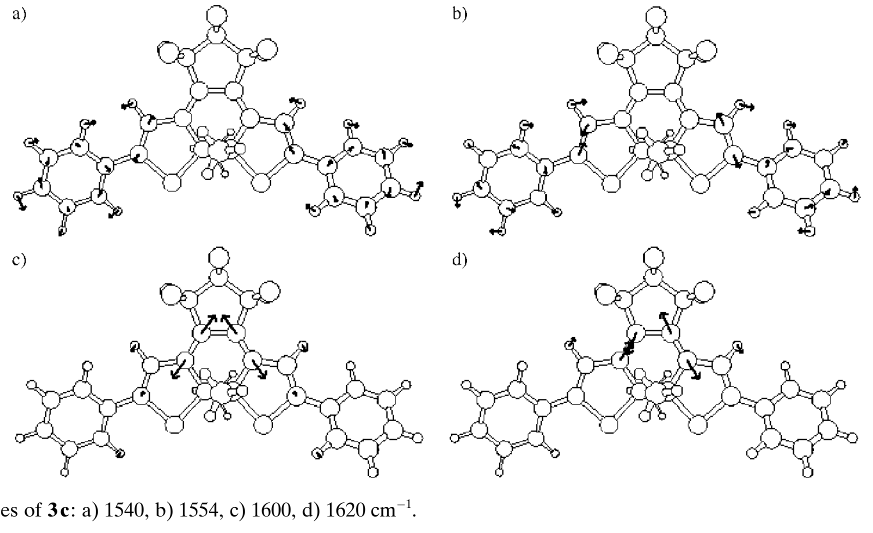


Figure 7. IR vibration modes of **3c**: a) 1540, b) 1554, c) 1600, d) 1620 cm^{-1}.

shows the UV/Vis and IR spectral changes of the photochromic composite film.

The recording operation is as follows. The absorption spectrum of the polymer film containing three open-ring isomers **1o**, **2o** and **3o** is shown as the black solid line (state A) in the figures. Upon irradiation with 313 nm light, all diarylethenes **1o**, **2o** and **3o** converted to their closed-ring isomers **1c**, **2c**, and **3c** (state H). Under the present conditions, conversion to the closed-ring isomers **1c**, **2c**, and **3c** were estimated to be 57, 55, and 52%, respectively. Upon irradiation with 403 nm light to the state, only one closed-ring isomer **1c** returns to the **1o** (state D), while upon irradiation with visible light ($\lambda > 640$ nm) only **3c** reverts to **3o** to form state G. Upon irradiation with 520 nm light to the state H in short period, only **2c** reverts to **2o** (state F) due to large difference of cycloreversion quantum yield of **2c** (0.12) and **3c** (0.013). By combination of the operations other states A, B, C, and E were formed. The recording process by using alphabetical masks **F**, **U**, and **T** on the film is illustrated in Figure 9a.

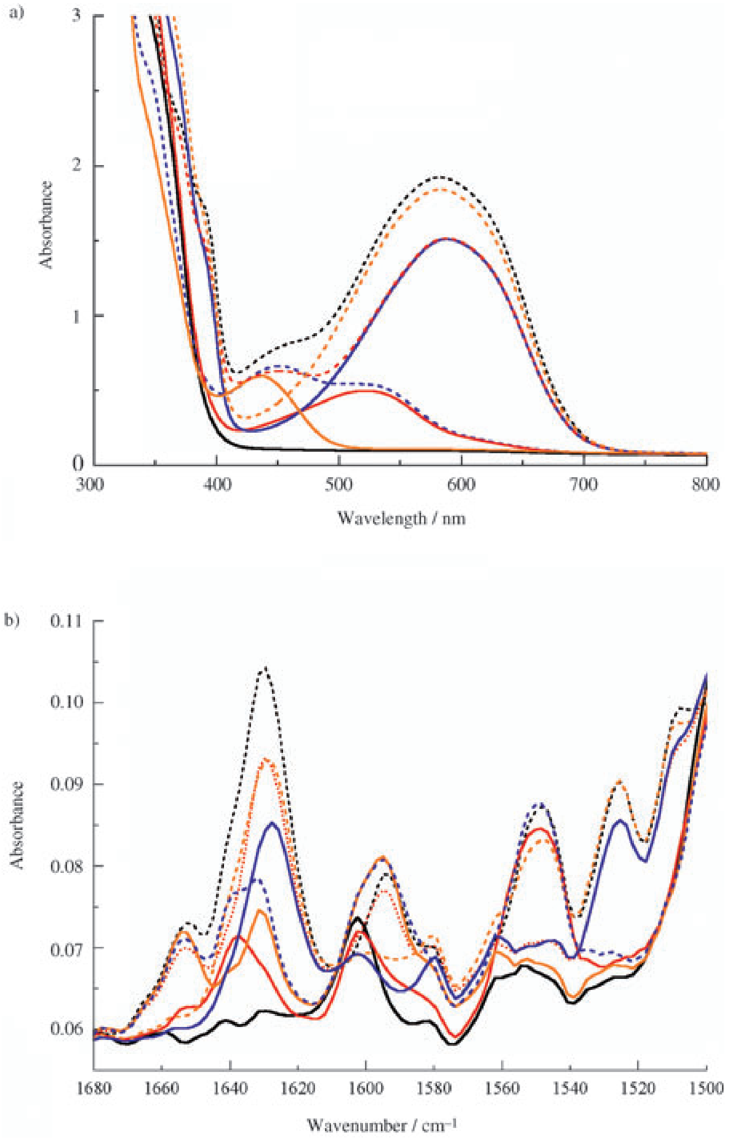


Figure 8. a) UV/Vis and b) IR spectra of the eight states of the composite film. State A (——), B (——), C (——), D (-----), E (——), F (-----), G (-----), H (-----).

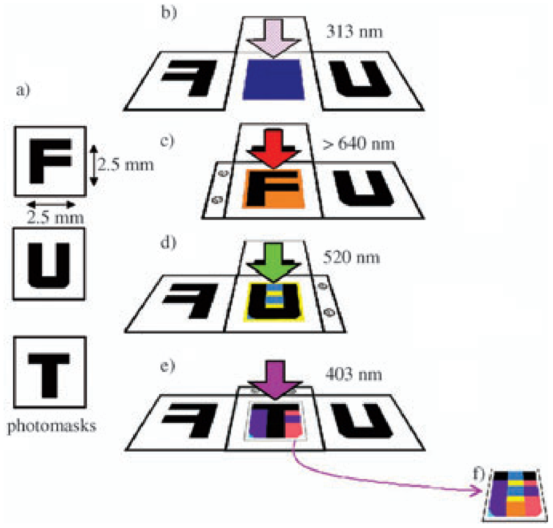


Figure 9. Schematic illustration of recording on the photochromic film with three bits eight states.

Initially the film was homogeneously irradiated with 313 nm light (b). Then, an **F** mask pattern was placed on the film and visible light ($\lambda > 640$ nm) was irradiated (c). 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 **2c** reverted to **2o**, because of large difference of the cycloreversion reaction quantum yield between **2c** and **3c** (d). Then the mask was replaced by a **T** mask followed by irradiation with 403 nm light (e). The recorded film was obtained (f) and the visible image is shown in Figure 10a. In the recorded film, closed-ring isomer **1c** remains in the domain **T**, **2c** remains in the domain **U**, and **3c** remains in the domain **F**. The images monitored by IR light at 1549, 1655, and 1527 cm^{-1} are shown in Figure 10b–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, respectively, in Table 4. 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 10g, 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 10h. The background of the letters is in the state A. Using the different wavenumber IR light, three bits eight states information was detected as the different letters and overlapping domains. Even after prolonged readout of the image using IR light, any decrease in

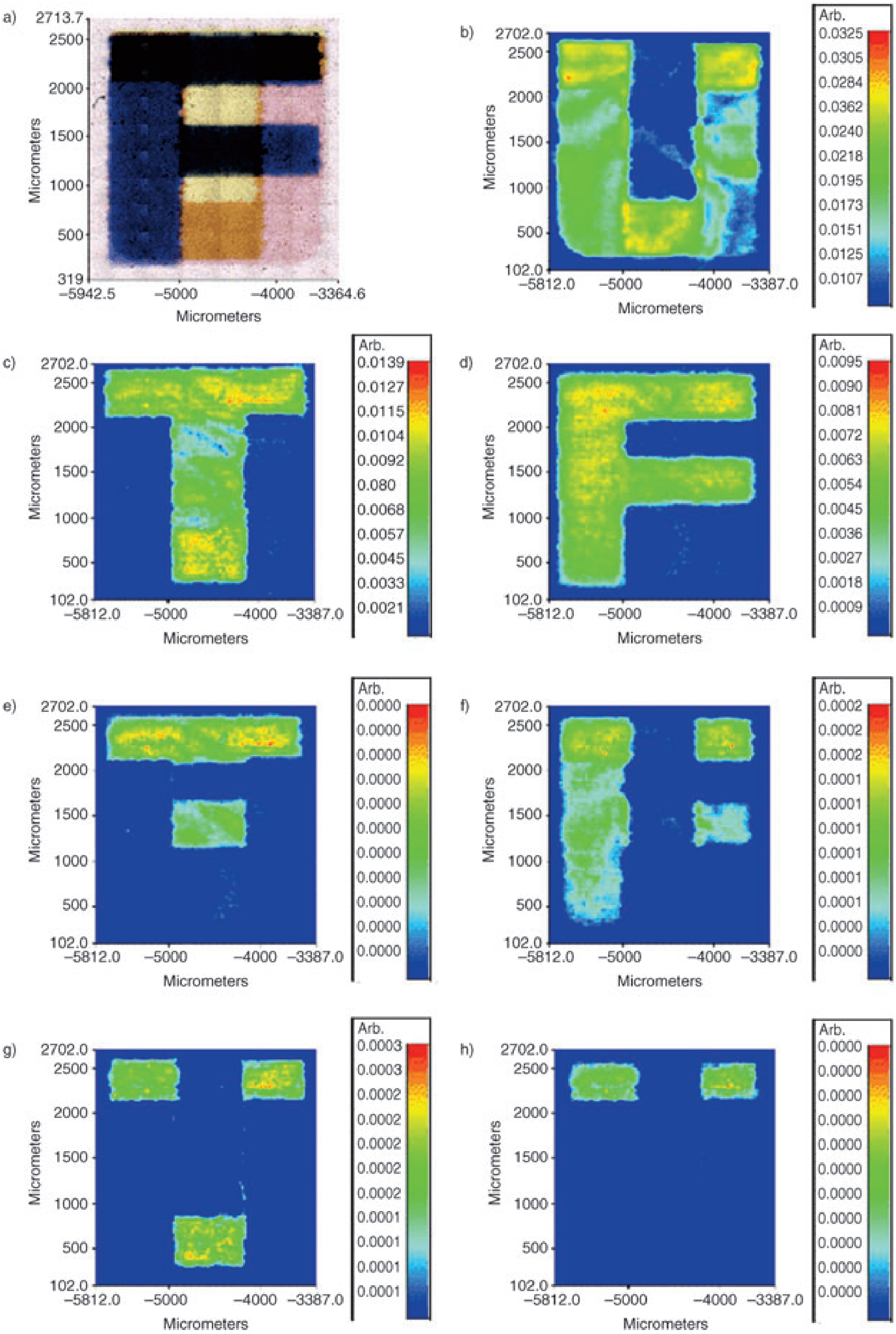


Figure 10. a) Visible and b)–h) IR images of the recorded polymer film containing diarylethenes **1** (4.4 wt %), **2** (3.1 wt %), and **3** (3.7 wt %). b) IR image detected at 1549 cm^{-1} indicating State C, c) IR image detected at 1655 cm^{-1} indicating State E, d) IR image detected at 1527 cm^{-1} 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, h) IR image detected at 1655, 1549, and 1527 cm^{-1} indicating State H.

the signal-to-noise ratio was observed. By visible light irradiation, all images in Figure 10a–g were bleached and the recording was erased. This multi-frequency technique is also applicable for near-field IR readout technique.[23]

Conclusion

In summary, a multi-frequency photochromic recording film containing three diarylethene derivatives having different

UV/Vis and IR spectra was constructed. And triple-frequency three bits eight states information was recorded on the polymer film by using UV and visible light, and the individual eight states was readout by appropriate wavenumber IR light, nondestructively. And the recording was erased by visible light irradiation. This technique is useful for reversible high-density recoding with nondestructive readout capability.

Experimental Section

Measurements: The absorption spectra were measured by using a Hitachi U-3410 spectrophotometer. Photoirradiation was carried out by using an Ushio 500 W high-pressure Hg and Xe arc lamp. Light of appropriate wavelengths was isolated by passing the arc light through a monochromator (Jobin Yvon H-10 UV).[22] Photochromic thin films were prepared using a spin quarter Mikasa 1H-D7. The IR spectra were measured using a Horiba FT-710 FTIR interferometer. UV light was irradiated by using TOPCON PU-2 black light. Visible light irradiation was carried out by using an Ushio 500 W high-pressure Mercury lamp with Toshiba Y-50 cut-off filter.

The ratios of the open- and closed-ring isomers of diarylethenes in the photostationary states in polymer matrices, were estimated from the comparison of spectral changes of the polymers to those of the molecules in the hexane solution. IR images were monitored on a Perkin–Elmer Spotlight 300 spectrometer. 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 four scans per pixels.

Computational details: The molecular structures were optimized and vibrational analysis were done by Hartree–Fock method with 6-31G basis set in Gaussian98.[20] The calculated frequencies were scaled by 0.87.

Materials: 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**) were prepared according to the literatures.[16–18] Poly(cyclopentene) polymer (Zeonex 480) was purchased by ZEON Corporation.

Preparation

Polymer films containing each of one derivative: Diarylethene **1** (3.8 mg) and poly(cyclopentene)polymer (Zeonex 480) (52.5 mg), which has no absorption in 1500–1700 cm^{-1}, were dissolved in chloroform (2 mL), 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 from a mixture containing **2** (2.5 mg), the polymer (54.3 mg), and chloroform (2 mL), and a mixture containing **3** (0.8 mg), the polymer (53.4 mg), and chloroform (2 mL), respectively. Film thickness of these polymer films was measured by use of micrometer (Mitutoyo Corporation, M110-25) and they were found to be 15 μm.

Polymer film containing three diarylethene derivatives: Compound **1** (4.4 mg), **2** (3.1 mg), **3** (3.7 mg), and poly(cyclopentene)polymer (86.7 mg) were dissolved in chloroform (2 mL), and the solution was casted on the glass plates. After the removal of the solvent, a photochromic 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.

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