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Photochromic reaction and fluorescence of dithienylethenes in the solid state

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Abstract

Photochromic cyclization reaction efficiency and fluorescence of two dithienylethenes in two solid states, colloidal solutions and amorphous films, were studied. Colloidal solutions of dithienylethenes were prepared by dilution of concentrated methanol solution into hot water. The diameter of particles of the colloidal solutions was about 1 μm according to observation by a scanning electron microscope. Photochromic cyclization reaction efficiency of colloidal solution of *cis*-1,2-dicyano-1,2-dithienylethene (**1**) was as high as that of hexane solution of **1**. An amorphous film of **1** also shows high efficiency. On the other hand, neither colloidal solution nor polycrystal of 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (**2**) was photochromic; only an amorphous film of **2** was colored very slightly by UV irradiation. For the dithienylethenes in the solid states, long-wavelength fluorescence which can be assigned to the colored closed-ring form was observed, while deeply colored hexane solution did not give any long-wavelength fluorescence. Fluorescence spectra and fluorescence decay curves indicated the existence of efficient energy transfer from the open-ring form to the closed-ring form of dithienylethenes in the solid states. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: 1,2-diarylethenes; 1,2-dithienylethenes; Photochromism; Colloidal solution: amorphous film; Fluorescence

1. Introduction

Recently, *cis*-1,2-diarylethene derivatives have been attracting much attention from the viewpoint of application to photonics devices, because of their high conversion efficiencies of reversible photochromic reactions, excellent thermal stability of both isomers, and good fatigue resistant characteristics [1–16].

If photochromic reactions occur efficiently in a solid state, vapor–deposited films or single crystals of photochromic molecules can be used as optical memory media. Some of diarylethenes undergo photochromism in the single crystalline phase [7,9]. An efficient photochromic reaction of *cis*-1,2-dicyano-1,2-dithienylethene (**1**) has been reported in amorphous state [10]. Munakata et al. reported that even copper (I) coordination polymer with **1** showed reversible photoreactivity in the crystalline phase [11]. Recently, rewritable near-field optical recording has been demonstrated on an amorphous diarylethene film [12]. Doped polymer films are not suitable for the near-field optical recording because of their low absorption intensity of the colored state in diluted polymer film. Bulk photochromic crystals or amorphous films are required to get high sensitivity.

Generally, quantitative absorption measurements of solids are difficult, while absorption measurements for colloidal solution are easy. In the present study, photochromic cyclization reaction efficiency, fluorescence spectra, and fluorescence lifetimes of two dithienylethenes in two solid states, colloidal solutions and amorphous films, were measured and compared with those of hexane solutions.

2. Experimental

Dithienylethenes, *cis*-1,2-dicyano-1,2-bis(2,4,5-trimethyl-3-thienyl)ethene (**1**) and 2,3-bis(2,4,5-trimethyl-3-thienyl)-maleic anhydride (**2**) were purchased from Tokyo-kasei, and used without further purification. Fig. 1 shows structural formula of **1** and **2**. Water was distilled twice, and methanol and hexane were distilled four times before use.

A little amount of concentrated methanol solution of dithienylethenes was poured into pure water at 90°C; typi-

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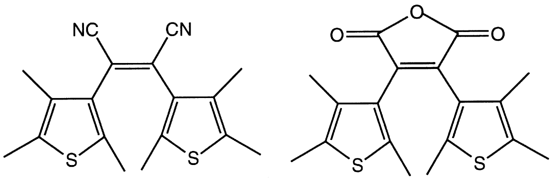

1 **2**

Fig. 1. Structural formulae of dithienylethenes studied.

cally, methanol solution of 4×10^{-3} mol dm^{-3} was diluted to colloidal solution of 1×10^{-4} mol dm^{-3}. The colloidal solutions obtained were left in a supersonic cleaner for 10 min. Without this treatment, colloidal solutions were unstable and deposited within several hours. Colloidal solutions of **1** were very stable, while those of **2** were unstable; the latter deposited within a day. The fine particles of the stable colloidal solutions were dispersed well on a glass plate and their diameter was found to be about 1 μm using a scanning electron microscope. Particles of colloidal solutions diluted in water at room temperature and without ultrasonic treatment were aggregated. Though it has been reported that the diameters of colloidal particles of some organic molecules depend strongly on the temperature of water for dilution [17], we could not find such dependence for the dithienylethenes. Particles of the colloidal solution of **1** seem to be amorphous, because external form of the particles lacked regularity, and polarizing microscopic observation indicated that the particles were optically isotropic. On the other hand, observation using a polarizing microscope suggested that those of **2** were crystalline.

Amorphous films were made by cooling molten samples between two glass plates [10]. The films were optically isotropic based on observation using a polarizing microscope. Amorphous films of **1** were very stable as reported by Kawai et al. [10], while those of **2** crystallized in several days.

Monochromated light from a Xe lamp was used to irradiate the samples. Exciting wavelengths were 330 nm for **1**, and 400 nm for **2**. Relative photochromic reaction efficiency was calculated from absorbance change in visible region before and after UV irradiation.

Fluorescence spectra were obtained using a spectrofluorimeter (JASCO FP-777) with a red-sensitive photomultiplier tube (Hamamatsu R928) at the excitation wavelength of 362 nm. An interference filter was inserted before the sample in order to eliminate stray light in the excitation beam. Without this filter, week fluorescence from the closed-ring form could not be detected.

Fluorescence lifetime measurements were carried out at the Instrument Center, Institute for Molecular Science. A sample was irradiated by the second harmonic (ca. 300 nm) from a synchronously pumped, cavity-dumped dye laser (Spectra Physics DL-375). The repetition rate was 4 MHz. Monochromated fluorescence from a sample was detected by an MCP photomultiplier tube (Hamamatsu R3809), and analyzed by the time-correlated single-photon counting method. Fluorescence decay curves were analyzed using a nonlinear least-squares iterative convolution method based on the Marquardt algolism [18,19].

All of the measurements were made at room temperature (20–22°C).

3. Results and discussion

3.1. Photochromic cyclization reaction efficiency

Colloidal solutions of **2** were not photochromic. In this section, we explain experimental results for colloidal solution of **1**, and for amorphous films of both compounds.

Fig. 2 shows absorption spectra of colloidal solution and hexane solution of **1** before and after UV irradiation. Relative amount of UV absorption was estimated from the value of the absorbance at excitation wavelength (330 nm). Maximum change at visible region of differential spectrum between absorption spectra before and after UV irradiation was divided by the amount of absorbed excited light to calculate relative photochromic reaction efficiency. To avoid influence of reverse photochromic reaction and energy transfer from the open-ring form to the closed-ring form, we stopped UV irradiation at conversion from the open-ring to the closed-ring form of several percents. Wavelengths at the maximum value of differential spectra of **1** were about 550 nm for colloidal solution and about 510 nm for hexane solution. We assumed that the molar extinction coefficients of both solutions were the same at the maxima. Fig. 3 shows the dependence of the absorbance change of **1** on UV irradiation time. Though absorbance of the colored form increases with UV irradiation time, the photochromic reaction rate (increment of absorbance in visible region per unit time) decreases gradually with UV irradiation time for both solutions. Comparison of the photochromic reaction efficiencies for both solutions at short UV irradiation time (ca. 30 s) indicated that the coloring efficiency of the colloidal

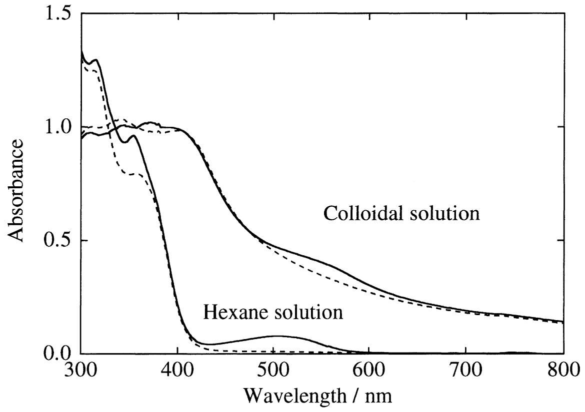

Fig. 2. Absorption spectra of colloidal solution and hexane solution of **1** before (broken line) and after (solid line) UV irradiation.

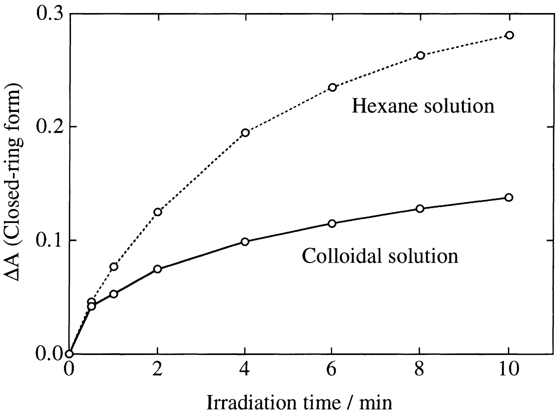

Fig. 3. Dependence of absorbance change in visible of colloidal solution and hexane solution of **1** upon UV irradiation time. The abscissa is absorbance difference between samples before and after UV irradiation, and the axis is UV irradiation time.

solution of **1** was as high as that of the hexane solution (see Table 1). However, the coloring rate of the colloidal solution decreased more rapidly than that of the hexane solution probably because of energy transfer from open-ring to the closed-ring form of **1** in a colloidal particle. Energy transfer occurs very little in a dilute organic solution because the efficiency of Förster type energy transfer depends on the reciprocal of the sixth power of the distance between an energy donor and an energy acceptor. An efficient energy transfer in a solid state could be a problem for a practical use of optical memory devises because it lowers the efficiency of photochromic reaction [13].

Photochromic reaction efficiencies of amorphous films of **1** and **2** were also measured, based on the absorbance difference before and after UV irradiation (see Fig. 4). Table 1 summarizes the results of photochromic reaction efficiencies. Though the efficiency for the amorphous film of **1** was half of that for the hexane solution, the coloring reaction terminated soon after UV irradiation started (ca. 30 s). The existence of diffusion process in liquid phase lengthens the time to reach equilibrium.

Though neither polycrystal nor colloidal solution of **2** was photochromic, the color of an amorphous film of **2** turned to purple immediately by UV irradiation (Fig. 4(b)). The photochromic reaction efficiency of the amorphous film was about 3% of that of the hexane solution (Table 1); a small portion of **2** seems to become photochromic in an amorphous state. This result means that **2** is photochromic in an amorphous state, and not photochromic in the crystalline state. This property is potentially applicable to optical memories with non-destructive readout capability.

Table 1
Relative photochromic cyclization reaction efficiencies of dithienylethenes

Sample	Cyclization reaction efficiency	
	1	**2**
Hexane solution	1.00[a]	1.00[a]
Colloidal solution	0.91	0.00
Amorphous film	0.49	0.03[b]

[a] Taken to be unity as references. The absolute quantum yields for **2** is 0.13 [1].

[b] This value could be larger, because the coloring reaction of this sample terminated in several seconds while all measurements were made after UV irradiation for 30 s.

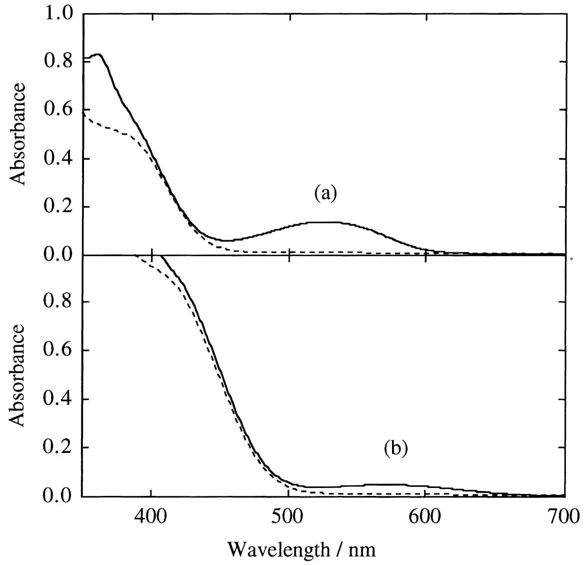

Fig. 4. (a) Absorbance spectra of amorphous films of **1** before (broken line) and after (solid line) UV irradiation. (b) Those of **2**.

Though polycrystal of **1** is photochromic, quantitative measurements were very difficult. We believe that photochromic properties of polycrystalline **1** are similar to those of colloidal solution.

3.2. Fluorescence spectra and fluorescence decay curves

Though Kawai et al. reported that colored amorphous films of **1** were not fluorescent [10], we observed long-wavelength fluorescence which can be assigned to the colored closed-ring form. Fig. 5(a) shows fluorescence spectrum of colloidal solution of **1** before UV irradiation, and Fig. 5(b) shows fluorescence after UV irradiation. Fluorescence with maximum at about 630 nm was observed for deeply colored colloidal solution. Moreover, colored amorphous film gave fluorescence at around 630 nm much stronger than that of the open-ring form (Fig. 5(c)). On the other hand, we were unable to detect any long-wavelength fluorescence of deeply colored hexane solutions of dithienylethenes. Because the long-wavelength fluorescence band was very week, we were unable to obtain its excitation spectra. Nevertheless, we assigned this red band to fluorescence from the closed-ring form, because it appeared only for colored colloidal solution and colored amorphous films; it disappeared with the colored form after green light irradiation, and was reproduced after UV irradiation. The enhanced fluorescence of the closed-ring form of **1** in solid

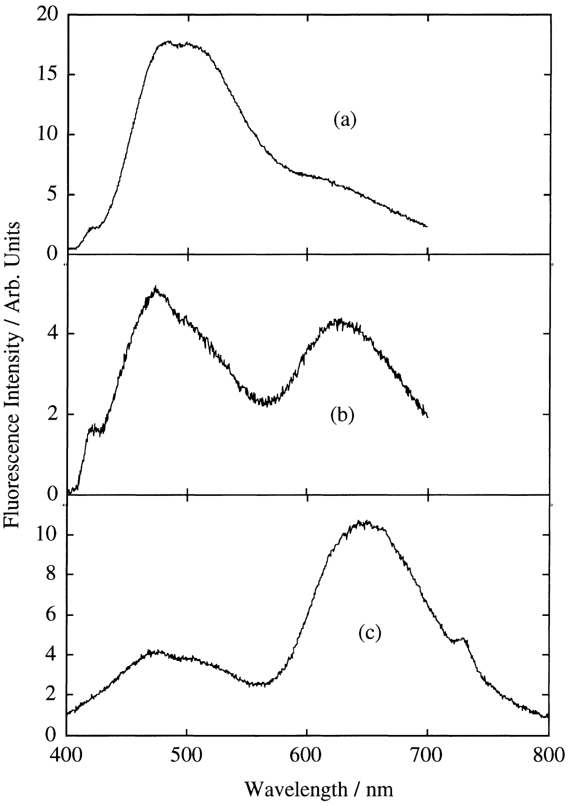

Fig. 5. (a) Fluorescence spectrum of colloidal solution of **1** before UV irradiation. (b) Fluorescence spectrum of deeply colored colloidal solution of **1** (c) Fluorescence spectrum of colored amorphous film of **1**.

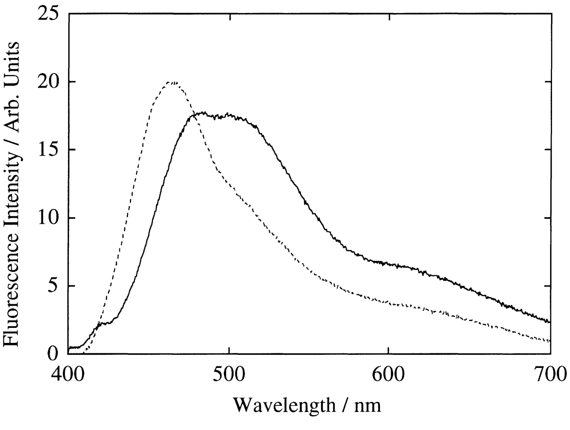

Fig. 6. Fluorescence spectrum of colloidal solution of **1** (solid line) and that of dried colloid on a glass plate (broken line).

Table 2
Fluorescence lifetimes of dithienylethenes. Double exponential response function $[a_1\exp(-t/t_1) + a_2\exp(-t/t_2)]$ was assumed. Amorphous films have not been measured

Sample	Fluorescence lifetime/ns			
	1		**2**	
	t_1 (a_1)	t_2 (a_2)	t_1 (a_1)	t_2 (a_2)
Hexane solution	0.149[a]		0.375[a,b]	
Colloidal solution	0.02 (0.79)[c]	0.23 (0.19)[c]	0.14 (0.89)	0.55 (0.11)
Polycrystal	0.39 (0.79)	1.74 (0.21)	1.03[a]	

[a] Single exponential.

[b] This value is in good agreement with previously measured values (0.34 ns [4] and 0.365 ns [5]).

[c] Deeply colored solution (see text). There existed the third component having a value of 1.33 ns (0.02).

states is probably due to the efficient energy transfer from the open-ring form to the closed-ring form.

Fig. 6 shows fluorescence spectrum of colloidal solution of **1** and that of dried colloidal particles on a glass plate. Colloidal solution gave broader spectrum than its dried particles, probably because molecules in colloidal surface are in polar circumstances and give red-shifted fluorescence. Since the number of molecules in colloidal surface is negligible in 1 μm diameter particle, energy transfer from molecules in the bulk to those in surface must be very efficient.

Table 2 summarizes the results of fluorescence lifetime measurements. It was difficult to obtain reproducible fluorescence decay curves of **1** in solid states because of rapid coloring. However, it was found that an increase of the amount of the ring-closed form enhanced rapid fluorescence decay efficiently due to energy transfer from the open-ring form to the closed-ring form for colloidal solution of **1**. Colloidal solution of **2** showed no coloration upon UV irradiation, and a little shorter fluorescence lifetime than that of hexane solution of **2** was obtained. Polycrystals of the dithienylethenes have longer fluorescence lifetimes than hexane solutions. This result may be explained in terms of rapid energy migration and fluorescence from trapped levels in polycrystals.

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