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Fluorescence Switching in Photochromic Diarylethenes

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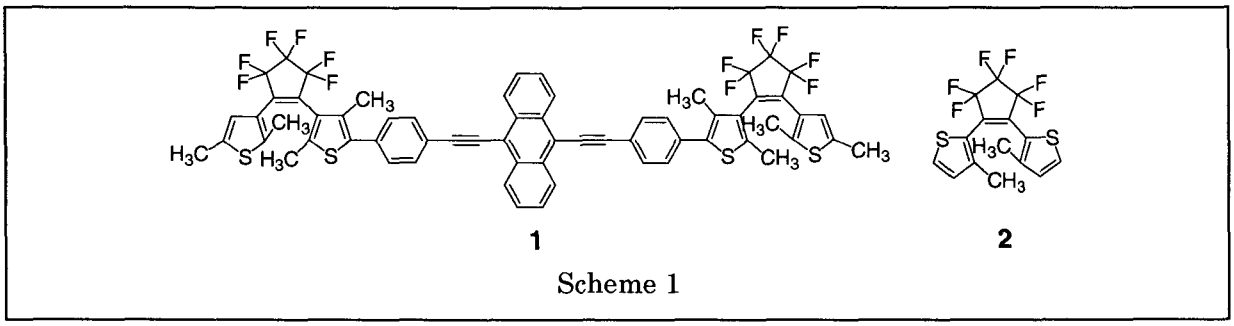
Photochromic molecular materials have been extensively studied from fundamental interests and also, recently, from technological interests. Considerable interests have been focused onto light-driven switching effects since photo excitation of molecules is one of the simple ways to manipulate molecular-based devices. Among various kinds of photo-responsive properties of the photochromic molecular materials, we have been interested in fluorescence switching properties in photochromic materials because of their possibility for apply in recording, display and various photonic devices. Among a number of photochromic dyes so far studied, only diarylethene shows thermal irreversible and fatigue resistant photochromic properties even in solid states such as single crystalline, polymer dispersed and amorphous states.

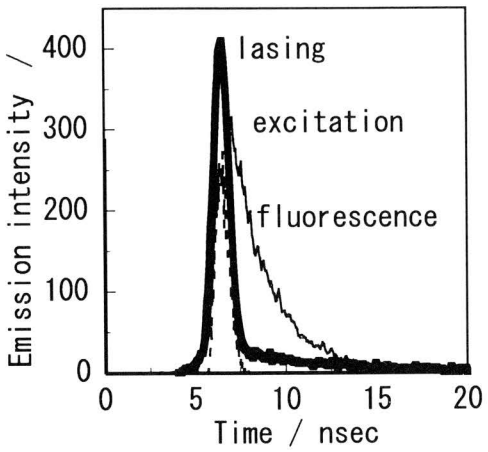
In the present paper, photo-responsive switching in fluorescence quantum yield and wavelength of diarylethenes are studied and unique laser emission control and possibility of 3D-optical recording will be demonstrated.



1 **2**

Scheme 1

Scheme 1 shows molecular structures of diarylethenes studied here. In the molecule **1**, a fluorescent unit, 9,10-bis(phenylethynyl)anthracene, and diarylethene units are linked directly. **1** showed fairly reversible photochromic properties and fluorescence switching upon irradiation with UV and visible light. The fluorescence quantum yield of ring open form isomer, **1a**, was as high as 0.83 while that of the ring-closed form, **1b** was less than 0.001. In a relating molecule, it was found that the cycloreversion reaction from the ring-closed isomer to the ring-open isomer showed no marked dependence on irradiation wavelength between 480nm and 580nm. That is, excited state formed upon excitation of fluorescent unit in the ring-closed form transfers to the ring-closed form isomer of the diarylethene unit quantitatively. This intra-molecular excited state energy transfer seems to be enough efficient to quench the fluorescence of the 9,10-bis(phenylethynyl)anthracene unit completely.



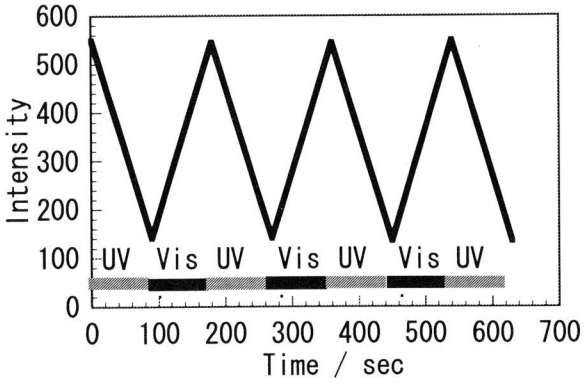


Fig. 1 Temporal emission profiles of **1** in a laser cavity and out the cavity and excitation pulse
Fig. 2 Repetitive modulation of laser emission intensity of **1**

The emission quantum yield of **1** is enough high even for laser emission as follows. Figure 1 shows temporal emission profile of **1** placed in a laser cavity composed of a grating mirror and a mirror under excitation with pulse N_2 laser (337 nm, 0.6 nsec). Profiles of spontaneous emission of **1** and of excitation pulse are also shown in Fig. 1. The spontaneous emission showed a single exponential decay with emission lifetime of 1.8 nsec while the emission from the cavity exhibited dumping profile similar as the excitation pulse. The wavelength profile of the emission also showed sharp and symmetric shape indicating laser emission. As shown in Fig. 2, the laser emission intensity was modulated repetitively for many times upon irradiation with UV and visible light.

Compound **2** also showed reversibie changes in the fluorescence emission intensity upon the photochromic reactions. Possibility of the 3D optical recording was demonstrated with a single crystal of compound **2** which showed reversible photochromic reactions and fluorescence intensity changes as well as its solution. UV laser light from an Ar-ion laser was focused into the single crystal and photocyclization was induced in the focused area. After the recording process, 3-dimensional fluorescence intensity profile was accumulated with the layer-by-layer distance of 0.4 nm under excitation with a 488 nm line of the Ar-ion laser. A confocal microscope with an objective of NA=1.4 and a pinhole of 1 μm in diameter was used in this experiments. Figure 3 shows typical 3D fluorescence profile after the recording. Fluorescence in the recording marks was bleached and each area is observed as a dark spot. The diameter in depth of the spots is about 1500nm and it in plane was about 200 nm, which corresponds to the recording density higher than 5Gbit/mm^3. These dark spots were erased by irradiation of 488 nm laser light and recording-reading-erasing cycles could be repeated for many times.

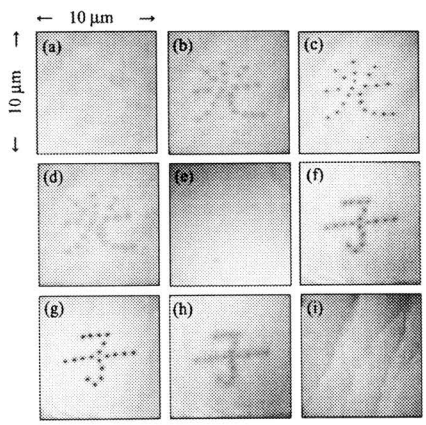


Fig. 3 3D-fluorescence image of single crystal of **1**