Photosynergetic response on cycloreversion reaction of a diarylethene nanoparticle induced by ns-pulse excitation

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When organic microcrystals are irradiated with intense laser pulses, excited molecules are formed densely, leading to unconventional photophysical and chemical phenomena[1-3]. In this study, we examined photoinduced cycloreversion (ring-opening) reaction of colloidal nanoparticles of a diarylethene derivative, TTP (Figure 1a) by using the second harmonics (532 nm) of a nanosecond YAG laser as the excitation light. The conversion yield from closed to open forms showed a nonlinear increase with the excitation intensity, while that in solution increases linearly with the intensity. We will discuss the mechanism from the viewpoints of laser heating effects and the mutual interaction of densely formed excited state.

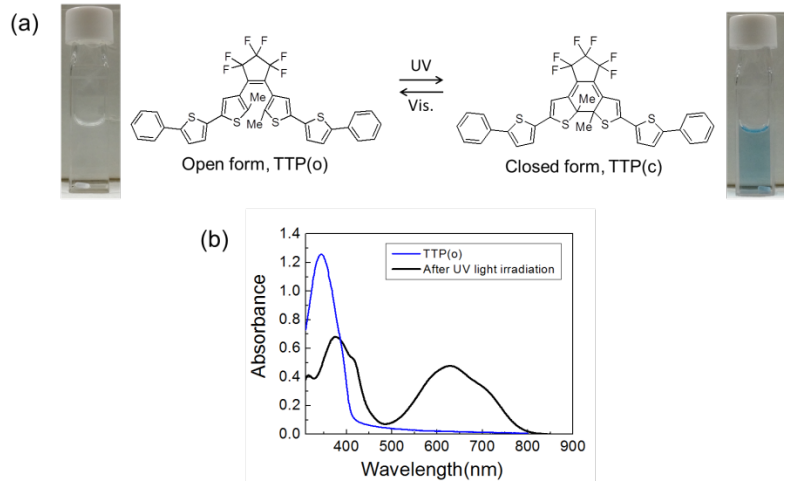

Figure 1. (a)Photochromic reactions of sample TTP. (b) Steady-state absorption spectra of aqueous nanoparticle of TTP

Aqueous nanoparticles of TTP were prepared with the reprecipitation method. The mean size was estimated to be 100 nm from the DLS measurement. Figure 1b shows the steady-state absorption spectra of TTP nanoparticles. TTP(o) nanoparticles have the absorption band in the UV region. Upon UV light irradiation, new absorption band around 620 nm originated from the TTP(c) appeared. Upon visible light irradiation, the blue color of nanocolloids disappeared, and the absorption band in the UV region due to the TTP(o) appeared again. These indicated that TTP nanocolloids showed reversible photochromic reactions as well as the solution. The conversion yield from open to closed forms in TTP nanoparticles was 70% at 360-nm light irradiation. The quantum yield of the cycloreversion reaction in the nanoparticles was estimated to be 0.36×10^{-4} at 298K and is by five times lower than that of the solution (1.4×10^{-4}) [4].

We examined the photo-density dependent cycloreversion reaction of TTP(c) nanoparticle by

532-nm ns laser excitation (8 ns fwhm). First, the conversion yield from TTP(c) to TTP(o) as a function of the number of laser shot at various laser fluences of 0.38 to 20 $mJcm^{-2}$ was observed. Next, from the conversion yield by single ns pulse excitation, we estimated the cycloreversion quantum yield at each fluence. Figure 2 shows the laser fluence dependence of the reaction yield of TTP(c) nanoparticle. The intense ns pulse laser excitation led to the increase of the reaction yield of nanoparticle. The reaction yield of the nanoparticle increased nonlinearly to the excitation intensity, while that of the ethanol solution was constant. The increase was explained as the effect of laser heating. Because the cycloreversion reaction yield is low (10^{-5}) and the excited-state lifetime is short (<10 ps), efficient photothermal conversion takes place. That is, most excitation energy converts into heat in a few tens of ps through the vibrational relaxation, resulting in a transient temperature elevation of the nanoparticle. In fact, the cycloreversion reaction yield of TTP(c) nanoparticles increased with increasing in temperature. Therefore, the photothermal conversion will lead to the rapid temperature elevation of TTP(c) nanoparticles, and accelerate the cycloreversion reaction. The present results could be considered as a photosynergetic response characteristic to laser-induced reactions of solid materials, where synergetic interactions between multi-photons and multi-chromophores are important. In the case of TTP nanoparticle, single shot of ns-laser pulse plays two roles; one is heating the nanoparticles through photothermal conversion, and second is to induce the cycloreversion reaction of molecules in the heated nanoparticle.

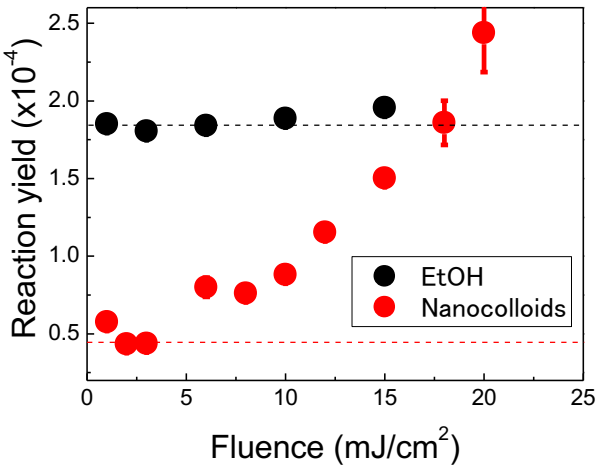

Figure 2. Laser fluence dependence of the cycloreversion reaction quantum yield of TTP(c) nanocolloids, together with that of the solution.

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References:

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