

Laser Ablation of Micro-sized Organic Dye Particles in Solvents with Limited Solubility for the Dye: Formation of a Supersaturated Solution

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Solvents with limited solubility for *N,N'*-di(octyl)perylene-3,4,9,10-tetracarboxylic diimide (PTCDI-C8) were used for laser ablation in liquid. Laser irradiation of the suspension induced an absorption spectral change of the solution. The absorbance of free PTCDI-C8 molecules in the solution obtained by laser irradiation was unusually larger than that of the suspension before laser irradiation, suggesting that a supersaturated solution was formed by laser irradiation of PTCDI-C8 nanoparticles prepared by laser ablation.

Organic nanoparticles have attracted considerable research interest from the viewpoints of both fundamental science and industrial applications. Pulsed laser ablation in liquid is a common method used to prepare organic nanoparticles. The method was developed by Masuhara et al.,^{1–4} and recently their results were reviewed together with results achieved by single nanoparticle spectroscopy.² The laser ablation method was applied to micrometer-sized organic dye crystals dispersed in poor solvents, which never dissolve target organic dye compounds. As a result, a suspension of a target material was directly converted into a colloidal solution, consisting of a mixture of organic nanoparticles and the poor solvent.^{1–4} Herein, we for the first time, used solvents with limited solubility for the target materials. In this case, the obtained solution consisted of a mixture of free molecules of the target materials, their nanoparticles, and the solvent. As a result, we observed a very interesting phenomenon in the laser ablation. That is, exposing PTCDI-C8 (Figure S1) microcrystals dispersed in solvents with limited solubility for PTCDI-C8 to a nanosecond laser light, we found that a supersaturated solution of PTCDI-C8 is formed via its nanoparticles. This phenomenon was not attributed to an accelerated dissolution rate due to nanoparticle formation, although dissolution rates of nanoparticles are enhanced by an increase in their surface area.

The perylenetetracarboxylic diimide (PTCDI) used in the present study is a unique class of *n*-type semiconductors.^{5,6} Because of both strong π - π interactions between the planar aromatic skeletons and the noncollapsible structure, PTCDI molecules form self-assembled one-dimensional nanostructures.⁷ In addition, due to their high thermal- and photo-stability, PTCDI molecules have attracted interest for the fabrication of single-molecule devices such as fluorescence switches⁸ and sensors.⁹ Hence, the present investigation on the formation of PTCDI nanoparticles and the supersaturated solution is of interest.

Laser ablation of a compound bearing a PTCDI group was reported by Asahi et al.³ In this work, nanosecond laser ablation was applied to micrometer-sized powders of dendronized PTCDI dispersed in water containing sodium dodecyl sulfate

(SDS). In this case, due to the bulky dendron groups, the π - π interactions between PTCDI groups are very weak. However, there has been no report on the laser ablation of PTCDI molecules capable of stacking.

PTCDI-C8 crystalline powders were ground in a mortar. The ground powders were weighed and suspended in solvent. The PTCDI-C8/solvent suspension was warmed up at 50 °C for 15 min and cooled down to 20 °C, in order to saturate the solvent with free PTCDI-C8 molecules.¹¹ The suspension (4 mL) was placed in a 1 × 1 × 5 cm³ quartz cell with a 1-cm optical path length and stirred during irradiation. The second-harmonic output (532 nm) of a Nd³⁺:YAG laser (8 ns FWHM, 10 Hz) was used.

n-Butyl acetate, ethyl acetate, and methyl methacrylate (MMA) were used as solvents with limited solubility for PTCDI-C8.¹¹ For reference, we used methanol and water containing SDS as poor solvents. Typical absorption spectra of PTCDI-C8/*n*-butyl acetate suspensions brought about by laser irradiation with a fluence of 50 mJ cm⁻² are shown in Figure 1. The absorption spectrum before irradiation (0 min) is ascribed mainly to PTCDI-C8 free molecules (400–530 nm) and micrometer-sized crystals over the entire wavelength region. In the latter, scattering would also contribute to the spectrum. Laser irradiation for 1 min induces the appearance of a new absorption peak at ca. 569 nm and a large spectral change in the wavelength region of 400–530 nm. Further irradiation results in an increase in the new absorption peak, the spectral change in the wavelength region of 400–530 nm, and a decrease in the scattering in the longer wavelength. For an irradiation time from 3 to 10 min, the spectral change is almost not observed. Further irradiation results in both a decrease in the new absorption peak at ca. 569 nm and an increase in the absorption peak at ca. 525 nm.

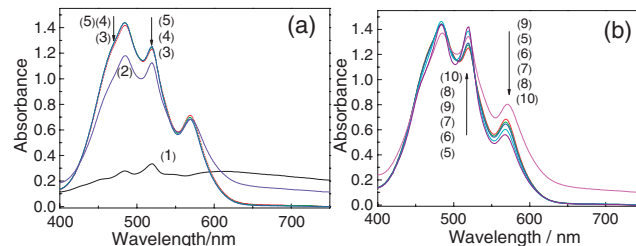


Figure 1. Change in absorption spectra of PTCDI-C8/*n*-butyl acetate (0.16 mg/4 mL) suspension caused by irradiation with laser light with a fluence of 50 mJ cm⁻². Total irradiation periods: (a) (1) 0, (2) 1, (3) 3, (4) 6, and (5) 10 min, and (b) (5) 10, (6) 20, (7) 30, and (8) 60 min. (9) After storage for 92.5 h with stirring after irradiation for 90 min and (10) after irradiation for 10 min after (9).

The new absorption with a peak at ca. 569 nm and absorption at the shorter wavelength are similar to those of aggregates and thin films of PTCDI compounds with different alkyl chain lengths linked at the two imide positions.⁵ This indicates that PTCDI-C8 is dispersed as aggregates in the irradiated solutions. Because the irradiated solutions were optically transparent, the sizes of the main aggregates were smaller than the wavelength of light. Hence, laser irradiation of PTCDI-C8/*n*-butyl acetate suspensions causes fragmentation of micrometer-sized crystals into nanometer-sized particles.

To obtain information on the threshold for nanoparticle formation, the absorption spectra obtained by irradiation with various fluences for 6 min were examined. The appearance of the absorption around 569 nm was observed at 18 mJ cm⁻², indicating that the threshold for the nanoparticle formation is ca. 18 mJ cm⁻².

In an effort to confirm the formation of PTCDI-C8 nanoparticles in *n*-butyl acetate, AFM observation was carried out.¹¹ In the AFM image with the irradiation time showing the largest absorbance at ca. 569 nm (Figure S3a), plate-like rectangular nanoparticles were observed, with a mean height, width, and length of ca. 17, 160, and 310 nm, respectively. The width and length of the plate-like rectangular nanoparticles shortened with increasing irradiation time. After irradiation for 60 min, the width and length reached ca. 140 and 250 nm, respectively, and plate-like round nanoparticles were also observed (Figure S3b).¹¹

To confirm that the spectral change observed in Figure 1 is ascribed to the formation of nanoparticles by laser ablation, we laser-irradiated micrometer-sized PTCDI-C8 crystals in methanol (poor solvent), measured the absorption spectra of the irradiated sample, and observed the AFM images. The spectral change of the PTCDI-C8/methanol suspension induced by laser irradiation is shown in Figure 2. Laser irradiation for 1 min results in the appearance of a new absorption in the wavelength region of 400–600 nm (two peaks at 489 and 569 nm and two shoulders around 470 and 525 nm) and slight scattering in the wavelength region longer than 600 nm. Further irradiation induces both an increase in the new absorption and a decrease

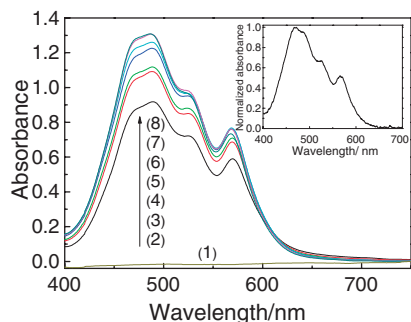


Figure 2. Change in absorption spectra of PTCDI-C8/methanol (ca. 0.16 mg/4 mL) suspension caused by laser irradiation with a fluence of 50 mJ cm⁻². Total irradiation periods: (1) 0, (2) 1, (3) 2, (4) 3, (5) 6, (6) 10, (7) 20, and (8) 35 min. The figure inserted is the absorption spectrum of PTCDI-C8 nanoparticles in water prepared by reprecipitation [200 μ L of THF solution of PTCDI-C8 (0.025 mM) was injected into 10 mL of water while stirring].¹⁰

in the scattering. During these changes, the solution became transparent. A very similar spectral change was also observed for laser ablation of micrometer-sized crystals in water containing 10 mM of SDS. The inset in Figure 2 shows the absorption spectrum of PTCDI-C8 nanoparticles in water prepared by reprecipitation.¹⁰ On the basis of comparison of this spectrum with the spectrum of the PTCDI-C8/methanol suspension after irradiation, the spectrum after irradiation could be primarily assigned to the absorption of PTCDI-C8 nanoparticles in methanol. AFM images of nanoparticles formed by irradiation for 10 min and prepared by reprecipitation were observed (Figure S4).^{10,11} The heights of the former nanoparticles ranged from 2 to 20 nm. The size of the nanoparticles prepared by reprecipitation was larger than those prepared by laser irradiation, and the heights ranged from 2 to 60 nm. These results also strongly indicate that the absorption band with a peak of ca. 569 nm induced by laser irradiation of PTCDI-C8/*n*-butyl acetate suspensions is ascribed to PTCDI-C8 nanoparticles and that the spectra after irradiation are ascribed to the overlap of absorptions of both PTCDI-C8 free molecules and nanoparticles.

As shown in Figure 1b, laser irradiation for longer than 10 min results in both a decrease in the new absorption with a peak at ca. 569 nm and an increase in the absorption with a peak at ca. 525 nm. The former decrement suggests a decrease in the nanoparticles and the latter increment suggests an increase in the free molecules. The presence of the isosbestic point indicates the stoichiometric transformation between the nanoparticles and free molecules. In order to examine this phenomenon in detail, difference spectra were utilized. The absorption spectrum of the PTCDI-C8/*n*-butyl acetate sample irradiated for 20 min (Figure 1b (6)) and the normalized absorption spectrum of the diluted PTCDI-C8/methanol sample (ca. 5 μ g mL⁻¹) irradiated for 10 min are shown in Figure 3a. The latter spectrum was normalized at the first absorption peak wavelength (ca. 569 nm) of the nanoparticles of the former sample, and a difference

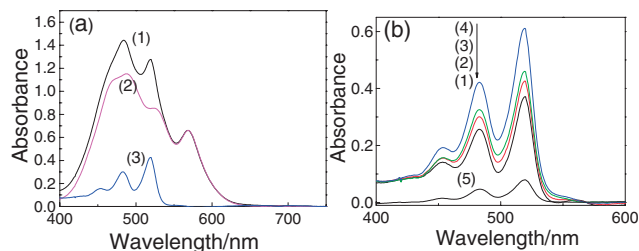


Figure 3. (a) (1) The absorption spectrum of the PTCDI-C8/*n*-butyl acetate sample irradiated for 20 min, (2) the absorption spectrum of the PTCDI-C8/methanol sample irradiated for 10 min, normalized to the first absorption peak (ca. 569 nm) of (1), and (3) difference spectrum obtained by subtracting (2) from (1). The concentration of the PTCDI-C8/methanol sample was ca. 5 μ g mL⁻¹, which was identical to that for AFM observation.¹¹ (b) Difference absorption spectra (1)–(4) obtained in a similar manner as above from the spectra of Figure 1b. Total irradiation periods: (1) 10, (2) 20, (3) 30, and (4) 60 min. (5) The absorption spectrum of a PTCDI-C8 saturated (suspended) *n*-butyl acetate solution. The concentration of this PTCDI-C8 solution was much lower than that shown in Figure 1a in order to decrease the influence of scattering due to micrometer-sized crystals in the spectrum.

spectrum was obtained by subtracting the latter spectrum from the former spectrum. The difference spectrum is very similar to the absorption spectrum of PTCDI-C8 free molecules in *n*-butyl acetate with limited solubility. Here, an anomalous trend can be observed; the absorbance of the difference spectrum is larger than the absorbance of free molecules prior to irradiation. Difference spectra were obtained in a similar manner as above from the spectra of Figure 1b. Figure 3b shows the difference spectra (1)–(4) and the absorption spectrum of a PTCDI-C8 saturated (suspended) solution (5). In the difference spectra, the absorption in the short wavelength region of 450–400 nm does not change irrespective of irradiation time. This means that peak-normalized spectra of these difference spectra do not overlap perfectly. However, the main absorption of the difference spectra is much larger than that of the saturated solution and increases with irradiation time. In addition, three isosbestic points are observed in the main absorption region of 475–525 nm (Figure 1b). By integrating the present results with those obtained upon AFM observation,¹¹ we can conclude that large PTCDI-C8 plate-like rectangular nanoparticles prepared by initial laser irradiation change to both small plate-like rectangular and round nanoparticles accompanied with formation of free molecules. In other words, further laser irradiation of the large plate-like rectangular nanoparticles prepared by initial laser ablation results in destruction to both plate-like round and small square nanoparticles as well as free molecules. In addition, the above results suggest anomalously large dissolution of PTCDI-C8 molecules in solvents with limited solubility.

When the sample was irradiated for 90 min and subsequently stirred without irradiation for 92.5 h, the absorption band at ca. 569 nm due to the nanoparticles increased together with the appearance of a declining band in the longer wavelength region (Figure 1b (9)). The latter declining band is likely attributable to light scattering. This spectral change is most probably attributed to the addition of free molecules to nanoparticles. When the sample irradiated for 60 min was stored for 6 days, the size of plate-like rectangular nanoparticles increased. The width and length reached ca. 170 and 270 nm, respectively. These results indicate that the solution with the anomalously large dissolution of free PTCDI-C8 molecules is not stable. Although exact evaluation of a decrement of the free molecules in the solution was difficult because of the presence of the scattering, ca. 50% of the free molecules disappeared during storing for 92.5 h. The sample was then irradiated a second time for 10 min, which induced the spectral change attributed to the formation of free molecules from the nanoparticles (Figure 1b (10)).

The above results suggest that a supersaturated solution of PTCDI-C8 is obtained from laser ablation of PTCDI-C8/*n*-butyl acetate suspensions. Laser irradiation results in PTCDI-C8 plate-like rectangular and round nanoparticles with a large specific surface area. When both the nanoparticles with a large specific surface area are irradiated repeatedly by intense laser pulses, dissolution of the nanoparticles into free molecules in the solution is enhanced due to abrupt temperature increase in the nanoparticles. Thus, PTCDI-C8 molecules are considered to be produced not only during the destruction of large nanoparticles, but also due to further irradiation of the small nanoparticles

produced by the destruction. As a result, the supersaturated solution of PTCDI-C8 is obtained for the solvents with limited solubility for it.

Additional laser irradiation experiments for the PTCDI-C8/methanol sample irradiated for 10 min are shown in Figure 2. Further irradiation was found to induce an additional increase in nanoparticles [Figure 2 (7)]. However, further irradiation for 15 min [Figure 2 (8)] almost never induced a spectral change, as observed for the solvents with limited solubility (Figure 1). This result indicates that irradiation of nanoparticles in a poor solvent never results in the formation of free molecules, and that it does not induce photodecomposition of PTCDI-C8 molecules. In addition, the latter indicates that the results obtained for the *n*-butyl acetate system could not be ascribed to photodecomposition of PTCDI-C8 molecules.

The trend observed for the *n*-butyl acetate system was also observed for MMA and ethyl acetate solvents with limited solubility for PTCDI-C8. After laser irradiation for 60 min, concentrations of PTCDI-C8 in ethyl acetate, *n*-butyl acetate, and MMA solutions were evaluated to be ca. 4.2×10^{-6} , 6.2×10^{-6} , and 8.9×10^{-6} M, respectively. That is, the present phenomenon is generally observed for solvents with limited solubility. Until now, laser ablation to prepare organic nanoparticles has been applied only to poor solvents for the target materials. Thus, the formation of supersaturated solutions induced by laser ablation has never been reported to our knowledge.

Detailed investigations on other PTCDis, as well as other organic compounds are currently underway. These results are expected to be published shortly.

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- 11 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.