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Nanoparticle Formation of Vanadyl Phthalocyanine by Laser Ablation of Its Crystalline Powder in a Poor Solvent†

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Water suspension of micrometer-sized vanadyl phthalocyanine (VOPc) crystals was converted into VOPc colloidal solution by irradiation with an excimer laser (351 nm, 30 ns, 5 Hz). VOPc nanoparticles with nearly equilateral triangular and hexagonal shapes were obtained from the colloidal solution, and the mean width and height are 60 and 19 nm for triangular nanoparticles, respectively, and 49 and 17 nm for hexagonal ones, respectively. Laser fluence dependence was examined and laser ablation of the microcrystals in water is considered to be responsible for the nanoparticle formation. A threshold laser fluence of the conversion was determined to be ∼20 mJ/cm^2. Nanoparticle formation processes and their phase transition during standing were analyzed by electronic absorption spectroscopy.

Introduction

In recent years, studies on organic nanoparticles consisting of aromatic and dye molecules have gradually been increasing.[1−13] It is fascinating to design electronic and optical properties of nanoparticles, to synthesize organic molecules, and to prepare their nanoparticles for realizing the properties. It is expected that organic nanoparticles can be used as sensors, bioprobes, devices, and so on. We consider it essential and important to establish how to prepare nanoparticles, and indeed about half of the published studies deal with preparation method.[1−7] Until now, two approaches have been done based on deposition and reprecipitation of organic molecules. In the deposition method, organic molecules are evaporated in a chamber under vacuum[1] and inert gas atmosphere[2], and nanometer-sized organic aggregates are deposited on a substrate. In the reprecipitation method, a solution of organic molecule is added to a poor solvent with[3] and without[4−7] surfactant, and nanometer-sized precipitates of the molecule are produced. Although these two methods are interesting and useful, it is strongly requested to develop more simple and versatile methods to prepare organic nanoparticles.

Recently, we have applied a laser ablation technique to preparation of organic nanoparticles, where some phthalocyanines and aromatic hydrocarbons were adopted as the first example.[8] Phthalocyanine and its metal derivatives are known to possess useful photoconductive and semiconductive properties and, interestingly, size reduction of VOPc nanoparticles enhances its photoconductivity.[3] As absorption spectra of phthalocyanines in the solid state strongly depend on mutual molecular orientation and intermolecular distance,[14−16] spectroscopic analysis is useful to elucidate morphological and electronic properties of formed particles. In this method, organic crystalline powders suspended in a poor solvent are exposed to a laser beam, which induces fragmentation of the initial crystals. Consequently, the opaque suspension is converted into a transparent colloidal solution. In the case of VOPc dispersed in water, nanoparticles with a size of ∼ 100 nm were formed. For copper phthalocyanine (CuPc) with ϵ phase, the molecular aggregation structure of the initial crystals was changed to an α-like phase by laser irradiation. Namely, laser irradiation of organic crystals in a poor solvent is regarded not only as a nanoparticle formation method but also as a way to control its solid phase. Furthermore, the method is simple compared to two preceding methods and will give a new way to control the size and molecular aggregation structure of nanoparticles by adjusting optical parameters and chemical conditions.

To establish the laser ablation method it is necessary to examine preparation conditions of nanoparticles in solution and to elucidate the formation mechanism. As a typical sample we choose VOPc, as its colloidal solution formed by the laser method is most stable.[8] This is quite helpful for spectroscopic analysis of formation processes of colloidal VOPc nanoparticles. In this study, a conversion of VOPc aqueous suspension into colloidal solution is conducted by excimer laser irradiation, its processes are analyzed by observing absorption spectra of initial and irradiated solution, and its laser fluence dependence is made clear. Morphology of formed VOPc nanoparticles was examined in detail by AFM observation. On the basis of these experiments, we consider the formation mechanism of VOPc nanoparticles and related phase transition.

Experimental Section

VOPc (98% purity) was purchased from Wako and used without further purification. Water was deionized, distilled, and used as a solvent. VOPc crystalline powders (33 mg) were suspended in water (50 mL) and sonicated for 30 min. The VOPc aqueous suspension (3.5 mL) was contained in a quartz cell of $1 \times 1 \times 5$ cm^3 with 1 cm optical path length and stirred during irradiation. A XeF excimer laser (Lambda Physik, LEXTRA 200, 351 nm wavelength, 30 ns fwhm, 5 Hz repetition rate) was applied as an irradiation light source. The laser beam was focused by a lens ($f = 250$ mm), where the spot size at the center of the cell was estimated to be 3.3×3.7 mm^2 by examining a laser beam pattern formed on a thermal recording paper. The laser intensity was measured by a pyroelectric joulemeter (Gentec, ED200) connected with an oscilloscope

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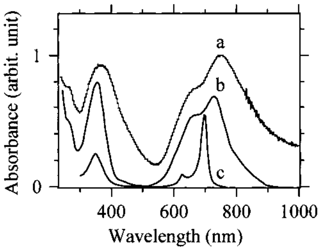


Figure 1. (a) Absorption spectra of supernatants of VOPc aqueous suspensions after irradiation, (b) VOPc vapor-deposited thin film of phase I, and (c) VOPc in pyridine. The spectra of (b) and (c) are cited from ref 14.

(Hewlett Packard 54522A). Absorption spectra were measured with a spectrophotometer (Shimadzu UV-3100PC). For examining morphologies of initial crystals and formed nanoparticles, corresponding solutions were spread on a sapphire substrate (Shinkosha, Sapphire STEP) which is hydrophobic and flat in atomic level. The particles with various sizes on the substrate were observed by a SEM (Hitachi, S-3500N) or by a tapping mode AFM (Digital Instruments, Nanoscope IIIa) using silicon probes. The size of initial VOPc crystals in aqueous suspensions prior to irradiation was in the order of 10 μm (see below). To understand the shape of nanoparticles and to determine the size distribution of nanoparticles, 420 particles were examined. All experiments were conducted at room temperature in air.

Results and Discussion

Nanoparticle Formation in Water by Excimer Laser Irradiation. VOPc crystalline powders in water were sinking on the bottom of a glass vessel during and after sonication, and its supernatant was keeping colorless. This means that VOPc molecules are hardly dissolved in water, as the compound has a strong absorption band in the visible wavelength region. The crystals were floated in water by applying a magnetic stirrer and exposed to laser pulses, then the solution became transparent and blue. With increasing irradiation time the color of the solution and the number of the floating crystals became deeper and fewer, respectively. Absorption spectra of supernatants of the irradiated solution were measured at 1 h after irradiation at the fluence of 30 mJ/cm^2 for 10 min and shown in Figure 1a. The standing time was necessary to exclude VOPc crystals remaining after irradiation from the supernatant, since the crystals were floating for a few tens of minutes after stopping the stirring.

The absorption spectrum of the blue supernatant after the irradiation is compared with absorption spectra of the VOPc molecule dissolved in pyridine[14] and a VOPc vapor-deposited thin film[14] in Figure 1. The latter is referred to phase I,[14] which is discussed later. The absorption bands of the blue supernatant around 350 and 750 nm are assigned to the Soret band and Q-band, respectively, on the bases of similarity between the supernatant spectrum and reference ones.[14] The band shape of the blue supernatant is more similar to that of the VOPc thin film than that of VOPc in solution, indicating VOPc are dispersed in water as aggregates. The solution was optically transparent, so that their sizes are much smaller than the wavelength of UV light. Thus, it is considered that fragmentation of crystals to nanometer-sized particles takes place upon intense excimer laser irradiation.

To confirm the fragmentation directly, examined was morphology of dispersoids in a VOPc colloidal solution, which was obtained by irradiating VOPc aqueous suspension at 68 mJ/cm^2 for 20 min and allowing the irradiated suspension to stand for 1 h. Figure 2 shows a SEM image of initial VOPc crystals and AFM images of the obtained VOPc nanoparticles. The crystals are bulky and have planes and arrises, while nanoparticles are rather flat and roughly classified to two types; equilateral triangle and hexagon (or circle). It is worth noting that the sizes of nanoparticles are far smaller than micrometers. For more quantitative elucidation, width and height of formed nanoparticles were analyzed. The AFM images of the nanoparticles were sectioned from side to side of the particles as shown in Figure 2C. The results on both triangle and hexagonal particles are summarized as histograms in Figure 3. The particle size is small and its distributions are narrow enough; the width and height are 60 ± 5 nm and 19 ± 5 nm for triangular nanoparticles, respectively, and 49 ± 13 nm and 17 ± 5 nm for hexagonal ones, respectively. Thus, it is clearly demonstrated that laser irradiation of VOPc crystals in water gave nanometer-sized particles.

Laser Fluence Dependence of Nanoparticle Formation. We consider that aqueous colloidal solution is possibly prepared by laser ablation of crystals in water. Hence, it is important and indispensable to examine fluence dependence for revealing the nanoparticle formation mechanism. A series of irradiation experiments were performed, in which laser fluence was varied, irradiation time was kept 10 min, and absorption spectra of supernatants of irradiated VOPc suspensions were recorded at 1 h after the irradiation. The spectra of supernatants before and after irradiation indicate clearly whether formation of VOPc nanoparticles is achieved or not. Figure 4A shows absorption spectra of supernatants obtained at various laser fluences. A flat spectrum of the initial supernatant can be ascribed to absorption and reflection by VOPc crystals, suggesting that some crystals were suspended in the colorless supernatants. The spectral shape of the supernatants obtained above 26 mJ/cm^2 is almost independent upon laser fluence, except for UV region (see below).

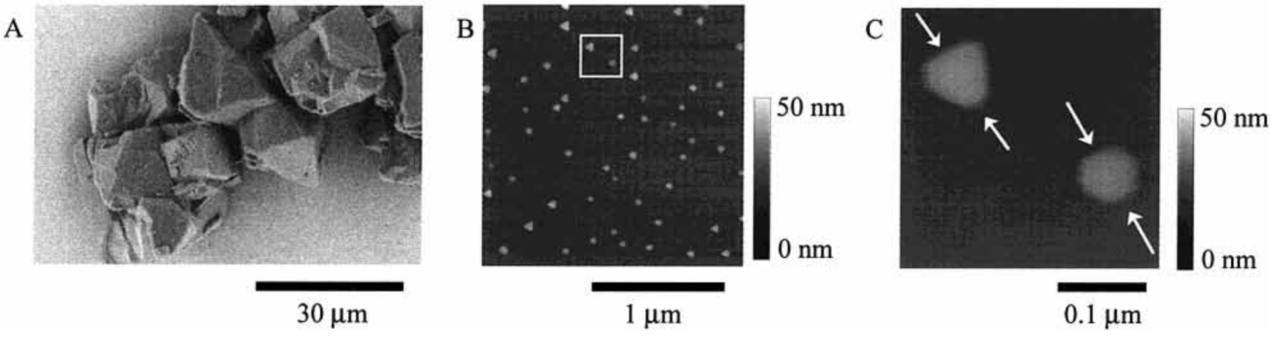
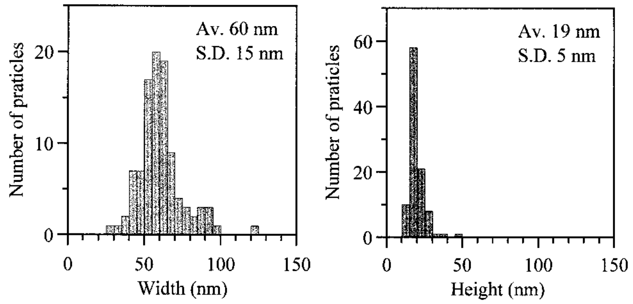


Figure 2. (A) A SEM image of initial VOPc crystals after sonication. (B) and (C) AFM images of VOPc nanoparticles formed by irradiation at the fluence of 68 mJ/cm^2 for 20 min. The image (C) corresponds to the square in (B). The arrows in (C) denote sectioning directions.

(a) Triangular particles



(b) Hexagonal particles

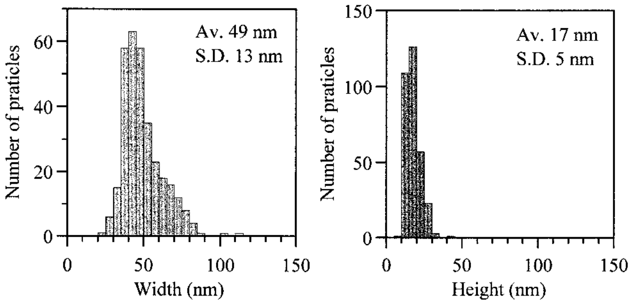


Figure 3. Histograms of width and height of VOPc triangular (a) and hexagonal (b) nanoparticles formed by irradiation at the fluence of 68 mJ/cm^2 for 20 min. The mean width and height, and their standard deviations are given in the figure.

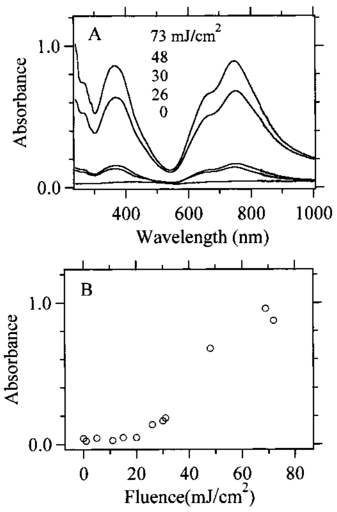


Figure 4. (A) Absorption spectra of supernatants of irradiated VOPc aqueous suspensions at various laser fluence for 10 min. The laser fluence is given in the figure. The spectrum at the fluence of zero corresponds to the supernatant of the suspension prior to the irradiation. (B) Absorbance of the supernatants at 760 nm as a function of laser fluence.

Laser fluence dependence of formation of VOPc nanoparticles can be assessed by the Q-band intensities of the supernatants after irradiation. The absorbance at 760 nm of the supernatant after 10 min irradiation is plotted as a function of the laser fluence in Figure 4B. It is clear that the absorbance increased only above 20 mJ/cm^2, indicating that the VOPc nanoparticle formation has a threshold with respect to laser fluence. To confirm thoroughly that the nanoparticle formation does not depend on total photon number but on excitation photon density, two suspensions were exposed to the same number of photons at two fluences below and above the threshold. The measured absorption spectra are presented in Figure 5. At a fluence below the threshold characteristic absorption bands of VOPc nanoparticles were not raised. The nanoparticle formation clearly requires high photon density as in laser ablation of material surface in air and vacuum environment. On the basis of these results we conclude that laser ablation of crystalline powders in water leads to the present nanoparticle formation. The absorbance ratio of the supernatants produced at various laser fluences can be regarded as relative conversion yield from VOPc crystals to nanoparticles.

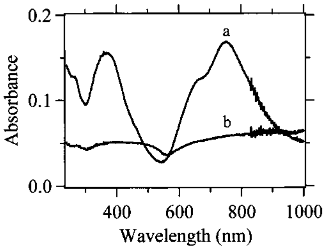


Figure 5. Absorption spectra of VOPc aqueous supernatants after irradiation. Laser fluence and irradiation time are (a) 30 mJ/cm^2 and 10 min, respectively, and (b) 11 mJ/cm^2 and 27.3 min, respectively, while total photon numbers was fixed to 1.9×10^{19}.

Sharp peaks were observed at 230 and 291 nm when prepared at 73 mJ/cm^2 as in Figure 4A. The peaks were confirmed to be due to water-soluble components, which means that they can be separated from VOPc nanoparticles. The peaks were not observed after long time irradiation at 30 mJ/cm^2 for 24.3 min where the total photon number, 4.6×10^{19}, was approximately the same as that of irradiation at 73 mJ/cm^2 for 10 min. It is considered that this degradation of VOPc molecules occurs only at higher laser fluence, forming a decomposition product exhibiting the peaks. To check other impurity formation, the colloidal solution was deposited on a glass substrate, the material left was dissolved in dichloromethane, and absorption spectra of the solution were measured. As a result unknown absorption were not observed. Thus, adjusting laser fluence just above the threshold we can suppress decomposition of molecules and prepare chemically pure nanoparticles.

Nanoparticle Formation Processes and Mechanisms. To elucidate VOPc nanoparticle formation mechanism, VOPc suspensions were irradiated at different laser fluence and their absorption spectra were monitored. The absorption spectrum of the initial suspension was measured immediately after adding the suspension to an optical cell. Then, the cell was irradiated and the absorption spectra were measured, which was repeated during pauses of less than 3 min between the irradiation. Thereby, these spectra include contribution of crystals. Absorption spectral changes showing nanoparticle formation are given for irradiated suspension at 30 and 68 mJ/cm^2 as a representative example in Figure 6. The flat spectrum of the initial suspensions is due to absorption and reflection by crystals and other spectra also include these effects to more or less extent. It is clear that absorption of the irradiated suspension is increased with the irradiation period.

The absorption increment of the irradiated suspension can be correlated to number of VOPc molecules which are responsible to light absorption and scattering. It should be noted that absorption coefficient of VOPc at 351 nm is very large, and its skin depth is about 40 nm. The value is calculated from the absorption coefficient of VOPc vapor-deposited film of phase I at 351 nm, $\sim 2.43 \times 10^5$ cm^{-1}.[14] Thus, the effective VOPc molecules located at the crystal surface layer have an important role in absorption of irradiated suspension. Since the size of the initial crystalline powders was a few tens of micrometers,

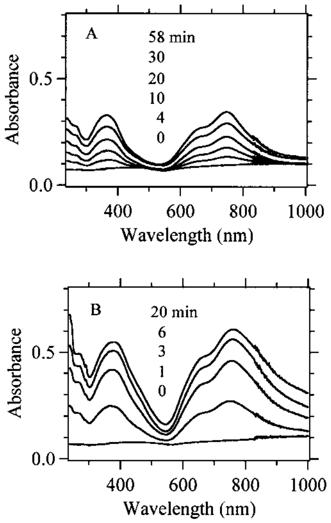


Figure 6. Absorption spectral changes of VOPc aqueous suspensions by irradiation at the fluence of (A) 30 and (B) 68 mJ/cm^2. The total irradiation periods of each spectrum are given in the figures.

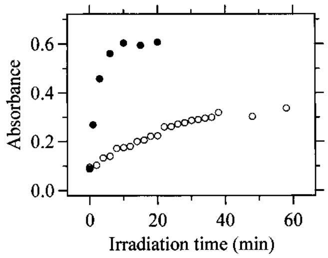


Figure 7. Temporal profiles of 760 nm absorbance of VOPc aqueous suspensions irradiated at (○) 30 and (●) 68 mJ/cm^2. The data correspond to Figure 6.

most molecules have nothing to do with absorption and reflection. Upon fragmentation by laser irradiation, effective surface layer becomes large, so that the number of probed molecules increases, giving large absorption.

Sizes of nanoparticles formed at different laser fluences are assumed here the same with each other on the basis of spectral similarity. It is well-known that some organic nanoparticles show phenomenologically a size dependence of absorption spectra,[3,5,9–13] while our result does not, as seen in Figure 4. Furthermore, we confirmed that the mean sizes of VOPc nanoparticles are almost the same at 30 and 68 mJ/cm^2. Hence absorbance of the nanoparticles are considered to be proportional to their number. Consequently, from the temporal profiles the formation rate of nanoparticles, namely, an increase of nanoparticles per laser pulse can be deduced. The absorbance profiles of the irradiated suspensions at 760 nm are summarized in Figure 7. The formation rate at 68 mJ/cm^2 is faster than that at 30 mJ/cm^2. Higher laser fluence gives a larger fragmentation rate, which is similar to laser ablation behavior. Indeed ,for CuPc[17] and its derivative[18] thin films, the ablation experiment confirms such a relation between the fluence and the etch depth.

Absorption spectra of VOPc suspensions irradiated at 30 and 68 mJ/cm^2 of Figure 6 are normalized at the Q-band peak position and shown in Figure 8. The bandwidth at 30 mJ/cm^2 is broad and becomes narrow with increasing irradiation period. The peak positions of Soret and Q-bands are almost constant through the irradiations at both fluences and correspond to that of the final irradiated suspension at 68 mJ/cm^2. Under this irradiation condition VOPc nanoparticles with size distribution around ∼50 nm are formed as shown in Figure 3. As the peak positions did not change during irradiation, nanometer-sized particles are produced even at the early stage of the irradiations. Thus, the above idea that only the surface layer of VOPc crystal is fragmented is supported by examining the absorption spectral changes of the suspension through the irradiation. Another explanation that the cracking of crystals into a few pieces and its repetitions give nanoparticles is inconsistent with the spectral changes in Figure 8.

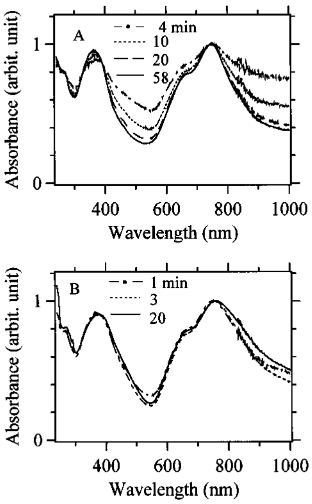


Figure 8. Absorption spectra of irradiated VOPc aqueous suspensions normalized at the Q-band peak position of each spectrum. (A) and (B) are obtained from Figure 6A and 6B, respectively. The total irradiation periods of each spectrum are given in the figures.

The absorbance at 760 nm approaches asymptotically a constant value and already saturates at 10 min of irradiation period at 68 mJ/cm^2 as shown in Figure 7. The starting crystals are consumed, while some VOPc crystals remained at the ends of the irradiations, which means formation rates of nanoparticles are significantly slowed at the late stages of the irradiation. Effective laser fluence should be lowered by formed nanoparticles, as the nanoparticles increase and absorb more incident light with increasing irradiation periods. The effective fluences at the center of the cell are estimated to be 21 and 37 mJ/cm^2 for incident fluences of 30 and 68 mJ/cm^2, respectively, at the end of each irradiation. Furthermore, it was found that the formed nanoparticles aggregate with each other and the aggregation is accelerated by stirring. The aggregates are optically deemed as something like crystals, as surface layer absorbing the light is shielded and effective absorption is reduced. It is also considered that the aggregation leads to suppression of the apparent formation rate. These effects accompanying fragmentation of crystals give the spectral changes of Figure 6 and the asymptotic curve of Figure 7.

Before closing the discussion on nanoparticle formation processes and mechanisms, we have to consider why triangular and hexagonal particles are formed in parallel. Surface energy and mechanical stability of each shape should be responsible, but we have not found any suggestive data to show the correlation between the shape and experimental conditions, so that we are now extending various experiments.

Phase Transition in Formed Nanoparticles. The VOPc colloidal solution obtained by the present laser ablation method is stable enough without surfactant at room temperature and the blue color becomes pale after some precipitation. Interesting absorption spectral changes of VOPc nanoparticles were detected while the irradiated solution stood at room temperature for 6 days. The results on the Q-band of a colloidal solution obtained

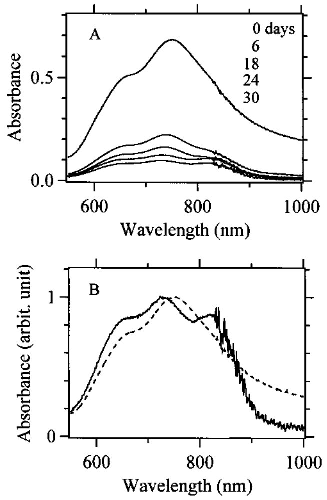


Figure 9. (A) Absorption spectral changes of an aqueous solution of VOPc nanoparticles which was formed by an irradiation at 48 mJ/cm^2 for 10 min and left at room temperature for long time. The standing time after irradiation is given in the figure. (B) Normalized absorption spectra before (−−−) and after (−) 30 days.

by an irradiation at 48 mJ/cm^2 for 10 min are given in Figure 9A and 9B. The absorbance decreased over the whole wavelength region owing to precipitation of nanoparticles, while a new absorption at 820 nm appeared. Similar spectral changes were observed for nanoparticles formed at the laser fluence of 30 and 73 mJ/cm^2. It is well-known that the Q-band is sensitive to orientation and distance of phthalocyanine rings. The peak at 820 nm is a characteristic of phase II in VOPc crystal[14] and identified by X-ray analysis.[19] Huang[20] and Minami et al.[21] reported that metastable VOPc vapor-deposited thin film with phase I, which is considered to have small amorphous character,[14] underwent slow transition to phase II at room temperature. As the X-ray analysis corresponds to absorption spectral data, the spectral change indicates that phase transition occurs in the nanoparticles at room temperature. It is general in phthalocyanine crystals that phase transition is induced by heating and treating with organic solvents, while phase transition of phthalocyanine nanoparticles is novel. It is worth noting that metastable nanoparticles are produced by the laser ablation method and their phase transition can be followed spectroscopically. This is of interest in connection with phase transition in the nanoscopic domain.

Conclusion

By examining laser irradiation phenomena of VOPc crystals in water, it is clearly demonstrated that the laser ablation method is very useful for creating nanoparticles. The method is simple enough, the formation processes can be easily followed spectroscopically, and the size distribution of produced nanoparticles is narrow enough. The nanoparticle formation can be realized only above a certain threshold of laser fluence, indicating that the method is based on laser ablation of crystals in poor solvent. It is probable to control size and molecular packing in nanoparticles by changing laser wavelength, pulse duration, fluence, repetition rate, irradiation period, solvent, temperature, and so on. It will be simple and easy to optimize irradiation and chemical conditions. We believe that the present laser ablation method will be applied to diverse organic compounds as the third method for organic nanoparticle formation, following deposition and reprecipitation methods.

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