



Article Efficient Molecular Aggregation of Rhodamine 6G and Pseudoisocyanine by Light-Induced Force

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Featured Application: One can generate by irradiation of light an exotic aggregation state of molecules that cannot exist in thermal equilibrium.

Abstract: A highly efficient light-induced aggregation of porphyrin molecules in solution was recently reported for 4-[10,15,20-tris(4-sulfophenyl)-21,24-dihydroporphyrin-5-yl]benzenesulfonic acid (TPPS). Here, we demonstrate that rhodamine 6G (R6G) and pseudoisocyanine (PIC) also show efficient light-induced aggregation in unsaturated aqueous solution, being detected with a multichannel lock-in amplifier as the absorbance decrease/increase in the monomers/aggregates, induced by a laser at 633 nm, which is non-resonant off their main monomer absorption wavelengths. The light-induced aggregation states are H-aggregates that are hardly formed in the thermal equilibrium. The similar absorbance changes are absent in the monomer molecules fixed in polyvinyl alcohol (PVA) films. The aggregation efficiency defined as $(\Delta A/A)/(U_{trap}/k_BT)$, where A is the absorbance of the monomers, ΔA is the absorbance increase in the aggregates, U_{trap} is the optical gradient force potential, and k_BT is the thermal energy at room temperature, is approximately 100 for R6G and 500 for PIC, which are much smaller than that of TPPS.

Keywords: light-induced force; gradient force; J-aggregate; H-aggregate; pseudoisocyanine; rhodamine 6G; aqueous solution; polyvinyl alcohol film; Frenkel exciton; pump-probe spectroscopy

1. Introduction

The molecular aggregation is a complex phenomenon because aggregate formation is affected by various factors such as molecular concentration [1], pH of solution [2], temperature [3], etc. There is a collaborative effect among the molecular hydrophobicity or hydrophilicity, and solute-solvent and intra-molecular hydrogen bonding [4–6]. This causes various phenomena relevant to aggregation. "J-aggregates" is one of the molecular aggregation phenomena that is accompanied by the red shift in molecular absorption peaks [7,8]. A J-aggregate was first reported by Jelley [9] as a narrow molecular absorption band associated with fluorescence of slightly longer wavelength and named after E. Jelley.

Self-assembly such as the molecular aggregation phenomenon is applied to nanodevice development [10,11], and especially J-aggregates that have an excitonic energy transfer ability that may be used for photovoltaic devices [12]. For the wider application of the aggregation phenomenon, it is important to control the aggregation process and structure of resulting aggregates. However, because the formation of molecular blocks of aggregates occurs spontaneously, it is difficult to control the size and structure of aggregates actively [3,13]. Pang at el. demonstrated that the structure of aggregates can

be controlled by replacing functional groups of the molecule that affect the intermolecular hydrogen bond [14]. Another method is to apply the photochemical process on molecules that are in the aggregation process [15]. Either way, how to affect intermolecular interaction is essential.

Light-induced force is a possible means to control intermolecular interaction. The laser-induced crystallization has been studied since the late 1990s [16] and, for molecular aggregation, there are reports of laser-induced aggregation [17,18]. These studies have been applied for preparing protein crystal samples required for X-ray structural analysis of proteins [19–22]. On the other hand, optical manipulation was demonstrated for microparticles in 1970s–1980s [23,24] and the optical trap of nanoparticles has been achieved by other groups as well [25–28]. In general, the manipulation of nanoparticles is challenging because of its weak optical trapping (gradient force) potential ($U_{trap} = \alpha E^2/2$; α is the polarizability of a trapped particle, E is the electric field of irradiated laser light) against thermal energy ($k_B T$; k_B is the Boltzmann constant, T is the environmental temperature, which, in the present study, is room temperature 293 K). The weak trapping potential comes from the small polarizability of nanoparticles and the diffraction-limited finite focal spot-size. Furthermore, heating by laser irradiation disturbs the trapping.

In spite of the difficulties, expectations are growing for the application of light-induced force for manipulating nanomaterials and controlling nano-structural order [29–32]. Through the optical manipulation studies, researchers make their efforts on improving the efficiency of optical trapping. Exploiting the surface plasmonic effect is a major way to achieve an efficient optical trap by enhancing the electric field of an irradiated laser beam [33,34]. In many cases, a metallic nano-gap structure is employed for those attempts [30,33–36]. Some researchers contrive how to utilize optically generated heat, which often disrupts optical trapping, by proposing for example the opto-thermoelectric effect due to ions' redistribution by opto-thermoplasmonic fluidics [37].

We previously reported molecular aggregation induced by continuous wave (cw) laser irradiation, which is non-resonant from the main absorption peak of porphyrin molecules, 4-[10,15,20-tris(4-sulfophenyl)-21,24-dihydroporphyrin-5-yl]benzenesulfonic acid (TPPS) [38,39]. In the reports, we observed laser-induced absorbance change spectra $\Delta A(\omega)$, which are associated with molecular aggregation with the maximum "aggregation efficiency" as high as 10^5 . Here, the aggregation efficiency is defined as $(\Delta A/A)/(U_{trap}/k_BT)$, where A is the peak monomer absorbance and ΔA is the absorbance increase in the aggregate. As the absorbance is proportional to the molecular concentration, $\Delta A/A$ is a good measure for the experimental aggregation ratio. The theoretical aggregation ratio due to the light gradient force can be estimated to be U_{trap}/k_BT . (This is an order-of-magnitude estimate, because the molecular polarizability α is evaluated from the polarizability volume and the thermal energy used is not the three-dimensional translational kinetic energy $\frac{3}{2}k_BT$ but k_BT .) Thus, the aggregation efficiency shows how efficient the experimental aggregation ratio is against the theoretical one. In this paper, we studied absorbance change spectra of the laser-induced molecular aggregation in "unsaturated" aqueous solutions of rhodamine 6G (R6G) and pseudoisocyanine (PIC). R6G is one of the laser dyes [40], which has a xanthene skeleton and forms an H dimer, whose name comes from the hypsochromic shift (blue-shift in the absorption peak) as the molecular concentration is increased in its aqueous solution [41]. PIC is known as dye molecules that form J-aggregates [42] and for which light-induced molecular aggregation is observed in the former research with the saturated solution [17].

2. Materials and Methods

2.1. Experimental

To observe absorbance change spectra, we used a multichannel lock-in amplification system to detect the transmitted light intensity and modulated component of its signal by an irradiated cw laser, which was chopper-modulated. We used a Xe light source (EQ-99, Energetiq Technology) for a white probe light and a diode laser (MRL-III-633-500mW, Changchun New Industries Optoelectronics Tech. Co.) for irradiation light. The 633 nm cw laser having no overlap with molecular absorption

was used for irradiation. The collimated probe light was focused on a sample, and, after transmitted through the sample, it entered a spectrometer through a fiber bundle. The spectrometer dispersed the incident light and its intensity was detected with 128 avalanche photodiodes for each wavelength in the multichannel system. Our multi lock-in amplifier detected the modulated signal at frequency f_1 (227 Hz) by an optical chopper for every 128 channels. The normalized transmittance change $\frac{\Delta T}{T}$ (to be converted into ΔA) was obtained from the transmitted spectrum *T* of the probe light detected by chopping the probe light and from the transmittance change ΔT detected by chopping the irradiation light. For detecting ΔT , the tandem lock-in technique was applied by periodically blocking the probe light with an optical shutter at a lower frequency f_2 (47 mHz) to avoid the apparent absorbance change from the fluorescence signal, which was dependent only on the irradiation light. These setups were the same for our former reports [38,39] and detailed information about the multi lock-in amplification system is in Ref. [43,44].

2.2. Sample Preparation

Rhodamine 6G (Sigma-Aldrich Co.) and pseudoisocyanine chloride (Hayashibara Co.) were prepared as organic molecular samples and dissolved in deionized water (San-ei Chemical Co.). As for the R6G aqueous solution sample, 0.0021 g of R6G was measured with an electronic balance dissolved in 6 mL of deionized water for its molecular concentration to be 0.75 mmol/L. As for the PIC aqueous solution sample, we measured 0.0041 g of PIC-Cl and dissolved it in 6 mL of deionized water for a high-concentration sample of 1.88 mmol/L. In our experiment, we diluted this PIC aqueous solution to 75 μ mol/L for an experiment sample. The prepared aqueous samples were preserved in sample vials. In this experiment, the aqueous solutions were made to flow in order to avoid decolorization similarly to the preceding reports [38,39].

To compare the light-induced absorption spectra and distinguish molecular aggregation from other effects such as absorption saturation, we prepared the sample of dispersed molecules in polyvinyl alcohol (PVA) film on microscope slides. For R6G, we measured 0.0022 g of R6G and 0.0856 g of PVA to be dissolved in 2 mL of deionized water while heating them. The prepared R6G/PVA solution was dropped on a microscope slide and spin-coated. For PIC, we measured 5.5 mg of PIC-Cl and 6.31 g of PVA to be dissolved in 13 mL of deionized water and spin-coated similarly to R6G. In the PVA film samples, the molecules are fixed at specific positions and cannot move under the optical gradient force. Hence, the absorbance change due to aggregation-state change should be absent.

2.3. Aggregation Phenomenon

When the concentration of molecules increases or the condition of the solution changes such as pH, molecules form aggregates with van-der-Waals interaction, hydrogen bonds, or electrostatic interaction between molecules. The aggregation induces changes in absorption and fluorescence spectra due to the energy shift by inter-molecular interaction. For J-aggregation, the energy of the aggregation state under the interaction between the molecular transition moments, E_k , is given as follows under the point-dipole approximation [45].

$$E_k = E_0 + 2J\cos\left(\frac{k\pi}{N+1}\right) \tag{1}$$

$$J = \frac{M^2}{4\pi\varepsilon r^3} \left(1 - 3\cos^2\theta_0\right) \tag{2}$$

where E_0 is the electronic excitation energy of the monomer, k is the state number of the exciton, N is the aggregation number, M is the transition dipole moment, ε is the permittivity of the surrounding medium, r is the aggregation distance, and θ_0 is the aggregation angle. The sign of the energy shift given by 2 J changes at the aggregation angle of 54.7 according to Equation (2). With these equations, we can discuss the arrangement of the constituent molecules in the aggregate from the absorbance spectrum [46]. When the energy shift is negative, aggregates are called "J-aggregates" and when it is positive, aggregates are called "H-aggregates." This energy shift can appear as an absorbance change in the relevant spectral range. In our experiment, we detected a small absorbance change upon laser irradiation, which suggests the aggregation-state change induced by the laser light.

3. Results and Discussion

3.1. Rhodamine 6G

For the aqueous solution sample, absorption was increased by $\Delta A \sim 10^{-5}$ on the shorter-wavelength side of the absorption resonance by irradiation of the cw laser at 633 nm, where the light-induced force should act on the molecule as an attractive force if it is dominated by the gradient force (Figure 1a). On the other hand, for the PVA film sample (Figure 1b), no absorbance change was observed. We reserve discussion about another absorbance increase seen from 540 to 570 nm in the longer-wavelength side of the monomer absorption, because the reproducibility of this absorbance increase is not fully confirmed. In the PVA film, molecules are fixed in polymers and can cause a difference in the absorbance change spectrum between the aqueous and PVA samples, as discussed in Ref. [38]. According to Ref. [47], R6G forms H-aggregates in an aqueous sample, and its absorption wavelength with respect to the aggregation number is analyzed with a singular value decomposition of the absorption spectrum of R6G, as shown in Table 1.



Figure 1. The absorbance change (solid line) and absorbance (dashed line) spectra of (**a**) rhodamine 6G (R6G) aqueous solution in 0.3 mm-thick cell, where the irradiation intensity is 640 W/cm², and of (**b**) R6G in PVA, where the irradiation intensity is 360 W/cm². Both the absorbance and its change were measured with the multi lock-in amp. system.

Table 1. The absorption wavelength and aggregation number for R6G in aqueous solution.

Aggregation number	1	2	3	4
Absorption wavelength	526	498	485	475

This table indicates that the R6G sample forms H dimers whose absorption spectrum is shown in Figure 1a. The laser-induced absorbance increase occurs on the shorter-wavelength side than the monomer and H-dimer absorption band. Table 1 shows that the peak wavelength of the absorbance increase is close to the tetramer's absorption wavelength, although it is broad. The ratio of the light gradient force potential ($\alpha E^2/2$) to thermal motion energy (k_BT), which is estimated from the polarizability volume (876 Å³), is 1.0×10^{-7} , and $\Delta A/A$ ($\approx 10^{-5}$) is ~100 times larger, i.e., the aggregation efficiency is about 100. When the PIC aqueous solution was irradiated with 633 nm cw laser light, an absorption increase of $\Delta A \sim 10^{-5}$ was observed around 390 nm, as shown in Figure 2a. On the other hand, the PIC/PVA sample did not exhibit the absorption change, as can be seen in Figure 2b. These results indicate that the aggregation state was changed by laser irradiation, as discussed in Ref. [38]. In general, PIC molecules form J-aggregates, which have the resonance energy peak at 573 nm [42] and do not form H-aggregates when simply dissolved in water. However, it is reported that, when surfactants are mixed, PIC molecules form H-aggregates and an absorption peak at 430 nm appears [48]. The observed state (390 nm) is much higher in energy than the H aggregates reported for PIC in Reference [48], and this result suggests that aggregate has an aggregation distance of 0.8 nm and an aggregation angle of 24.8 [49]. From Equations (1) and (2), the absorption wavelength of the H aggregate is estimated to be 438 nm (where the aggregation angle = 90°), which is close to the value in Ref. [48]. Under the same conditions, when there is an absorption resonance at 390 nm, the aggregation distance is estimated to be 0.6 nm.

For the PIC sample, the ratio of the optical gradient force potential to the thermal motion energy is 7.8×10^{-8} for the PIC's polarizability volume (671 Å³) and the irradiation intensity (1.1 kW/cm²). The peak monomer absorbance is approximately 0.25 in Figure 2a, so the experimental aggregation ratio is $\Delta A/A = 4 \times 10^{-5}$. Therefore, the aggregation efficiency is estimated to be 500.



Figure 2. The absorbance change (solid line) and absorbance (dashed line) spectra of (**a**) pseudoisocyanine (PIC) aqueous solution in 0.3 mm-thick cell, where the irradiation intensity is 1.1 kW/cm^2 , and of (**b**) PIC in PVA, where the irradiation intensity is 1.1 kW/cm^2 . Both the absorbance and its change were measured with the multi lock-in amp. system.

4. Conclusions

In this paper, we studied the laser-induced absorbance change spectra for R6G and PIC instead of TPPS, which we used in the preceding reports [38,39]. For both molecules, we compared the unsaturated aqueous solution samples and the PVA film samples about the effects of non-resonant laser-light irradiation and found the absorbance decrease and increase in the monomers and in the aggregates, respectively, for the aqueous samples and no absorbance change for the PVA samples. For R6G, which is known to form H-aggregates [41], the observed absorbance increase was expectedly located on the shorter-wavelength side of the H dimer's absorption, close to the H tetramer's absorption wavelength [47]. For PIC, which is known to form J-aggregates on the longer-wavelength side of the

monomer in the equilibrium, on the other hand, we unexpectedly observed an absorbance increase on the shorter-wavelength side of the monomer, suggesting the formation of H-aggregates. The result for the PIC sample demonstrates that aggregation states that do not exist in the equilibrium are generated by light-induced force, as we discussed in Ref. [38].

The observed absorbance increases for R6G and PIC are approximately 100 and 500 times larger, respectively, than the ratio of the optical gradient force potential to the thermal motion energy at room temperature. This magnitude (defined here as the aggregation efficiency) is much smaller than that of TPPS in our preceding report [38]. Therefore, the molecular aggregation by light-induced force occurs far more efficiently for TPPS molecules than R6G and PIC. Although the mechanism is still unknown and the efficiency is varied depending on the kinds of molecules, it is notable that the high-efficiency molecular aggregation by light-induced force is most likely a universal phenomenon.

Multichannel lock-in nonlinear spectroscopy, which can detect changes in absorption spectra on the order of 10^{-5} , was the most suitable for the discovery of this phenomenon, where an extremely small amount of specific aggregation states is formed only under light irradiation. In the future, in order to elucidate the mechanism, it is desirable to observe not only the spectroscopic signature but also the spatial image of the aggregation products. Direct imaging of molecular aggregates is realized by AFM [50], X-ray/electron diffraction [51], and cryo-TEM [52], and nanoscale structures have been observed. In particular, cryo-TEM is a powerful method that allows observation of structures as they are in aqueous solution at room temperature, which are preserved by rapid freezing, and it is promising if the samples can be rapidly frozen under irradiation light. Even for this approach, there remain many challenges to overcome, one of which is to increase the aggregation fraction $\Delta A/A$, which is 10^{-3} at its highest (TPPS).

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