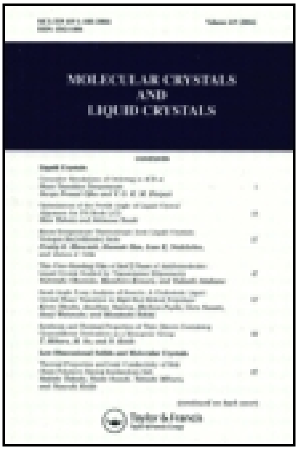

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Dewetting-Assisted Formation of Novel Dequenched Aggregates of Rhodamines: Comparison with J- and H-Aggregates

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Dewetting-Assisted Formation of Novel Dequenched Aggregates of Rhodamines: Comparison with J- and H-Aggregates

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Self-organized rhodamine aggregates prepared by wetting/dewetting process of an ethanol solution on a hydrophilic glass surface consistently exhibited fluorescence without quenching. Upon annealing, the aggregates exhibited an irreversible transition to quenched state, similar to H-aggregate, whereas the fluorescence spectrum was unchanged. The as grown highly fluorescent aggregate is a novel aggregate, neither a J-aggregate nor an H-aggregate, showing a blue-shifted excitation spectrum whereas the emission spectrum is similar to that of molecularly dispersed solution. This fluorescent aggregate was only realized in nonequilibrium by the rapid dewetting process.

Keywords: dewetting process; H aggregate; J aggregate; molecular orientation; pi conjugated dye; quasi-stable; self assembled

INTRODUCTION

Much attention has been paid to organic materials in recent years for their potential applications in electronics and photonics [1]. For photonic applications, π-conjugated dyes are major concerns due to its superior optical responses: high oscillator strength of the π-π^* transition of the conjugated π orbital and its wide tunability in wavelength via molecular design. Some dye species, e.g., those providing J-aggregates [2], of π-conjugated dyes show high quantum efficiency of photoluminescence, although others get completely quenched when placed in a solid state,

We express our gratitude to Professor Kenjiro Miyano of the University of Tokyo for a discussion of temperature dependence of dye fluorescence quantum efficiency due to phonon scattering and to Professor Nobuhito Ohno for a usage of annealing chamber.

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or even in a concentrated solution [3]. Among the latter quenched dyes, rhodamine 6G (Rh6G) is one of the most popular: both dilution and circulation of the solution are inevitable to avoid dye quenching and to induce a laser emission under photoexcitation.

There were only few reports on partial existence of fluorescent dimers of Rh6G [4] so far, where the mode of Rh6G aggregation was hypothetically discussed that brought about the dequenched state. In the present study, a reliable procedure is described to selectively yield a novel fluorescent Rh6G aggregate, demonstrating an in situ switching, for the first time, from this novel fluorescent state to a quenched state, during which every aggregate traced the identical change of fluorescence efficiency. The quasi-stable nature of the aggregate is discussed in line with the mode of dye ordering inside the aggregate, and is compared with the case of cyanine dye NK1420 J-aggregate [5,6].

MATERIALS AND METHODS

We adopted the π-conjugated organic dyes indicated in Figure 1, Rh6G, rhodamine B (RhB), rhodamine 101 (Rh101) and NK1420 (5,6-dichloro-2-[3-(5,6-dichloro-1,3-diethyl-2(3H)-benzimidazolylidene)-1-propenyl]-1,3-diethylbenzimidazolium iodide) for the present study because each dye has a static positive charge so that they are expected to interact strongly with a hydrophilic glass surface with an exposed SiO^- group [7]. The hydrophilic glass surface promoted a wetting/

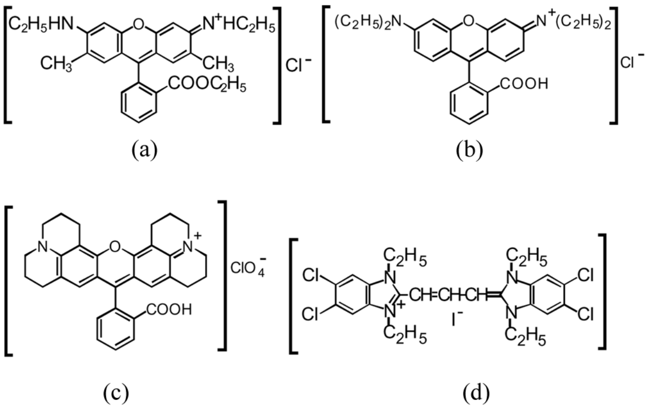


FIGURE 1 The molecular structure of (a) Rh6G, (b) RhB, (c) Rh101, and (d) cyanine dye NK1420. Note that each molecule has a positive charge in either of the NH groups (or N atoms).

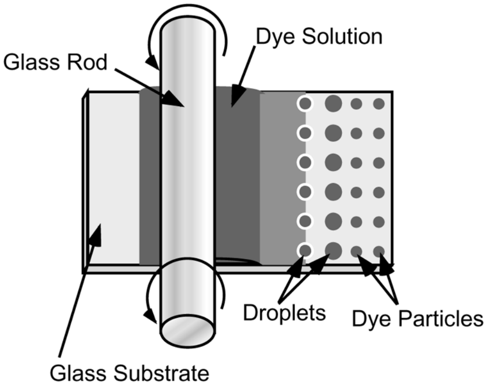


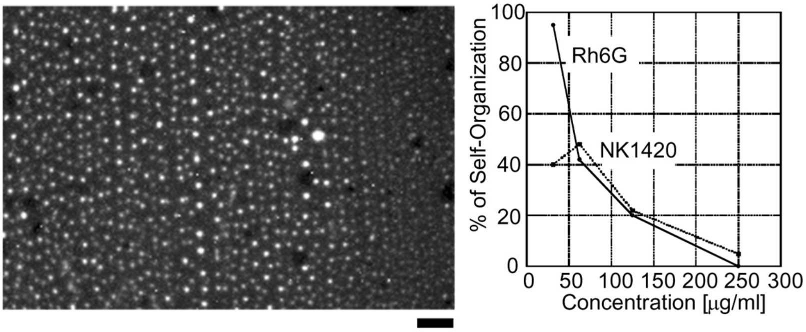
FIGURE 2 Schematic diagram showing the wetting/dewetting procedure to prepare self-organized dye particles. To control the thickness of the ethanol solution of the rhodamine dye, a glass rod was pressed against a glass substrate surface and rolled over it. At a critical solution layer thickness during the evaporation of ethanol, the solution layer becomes separated into droplets and then dye particles are precipitated. The critical solution layer thickness was controlled by the hydrophilicity of the substrate surface, which is accomplished by a prior ozone processing.

dewetting process [8] of polar organic solvent upon it, which was the primary motive force realizing the self-organizing formation of submicrometer-sized particle arrays of the dye [9]. When a glass rod slid over a 100 μl ethanol solution of typically 30 μg/ml Rh6G, a very thin layer of Rh6G solution was formed (Fig. 2). The solution layer became separated into droplets, while the solvent evaporated naturally, and then dye particles were formed as precipitates. The size was controlled by the degree of the surface hydrophilicity and by changing the retraction velocity of the solvent boundary via the glass rod movement [9]. The same dewetting procedure was used to prepare other rhodamines and NK1420 particles, but NK1420 was dissolved in methanol for solubility.

RESULTS AND DISCUSSION

Fluorescent Self-Organized Particles of Rh6G and NK1420

Under an epifluorescence microscope, all the self-organized particles showed fluorescence as shown in Figure 3(a), which is a unique characteristic of the present specimen: for example, Rh6G fluorescence is generally regarded to be quenched in a solid state. How dyes are ordered in the particle should be different from that in conventional



(a) (b)

FIGURE 3 (a) Conventional epifluorescence image of the self-organized Rh6G particles. Scale bar indicates 20 μm. (b) Molar ratios of self-organized particles of circular shape and of diameter less than 2 μm, with the dependence on the original dye concentration.

quenched Rh6G precipitates. When the dewetting process was started with higher concentration of rhodamine solution, number of particles with regular shape decreased and large irregular precipitates increased.[1] In contrast NK1420 dye gave rise to regular large particles even in higher concentrations, manifesting a red-shifted fluorescent spectrum similar to that of the two-dimensional J-aggregates grown from over-saturated solution [5,6]. In contrast to parallelogram shaped NK1420 J-aggregates with straight edges observed preferentially in precipitates [5], circular shapes of the dewetted NK1420 particles suggests that these particles are made of stacks of aggregates similar to J-aggregates with random orientation (no fluorescence dependence was observed on the direction of polarized excitation).

We assumed that particles with circular shape and with diameter less than 2 μm, exhibiting an orientational order [10], have grown under self-organization process on a homogeneous glass surface, whereas irregular shaped particles are random precipitates or ensemble of small crystals grown under intrinsic crystallization process: area of the circular particles with diameter less than 2 μm, which was regarded to be proportional to the number of dye molecules inside, were measured, and the ratio of the summed area to the area of total particles was plotted in Figure 3(b). Under high concentration

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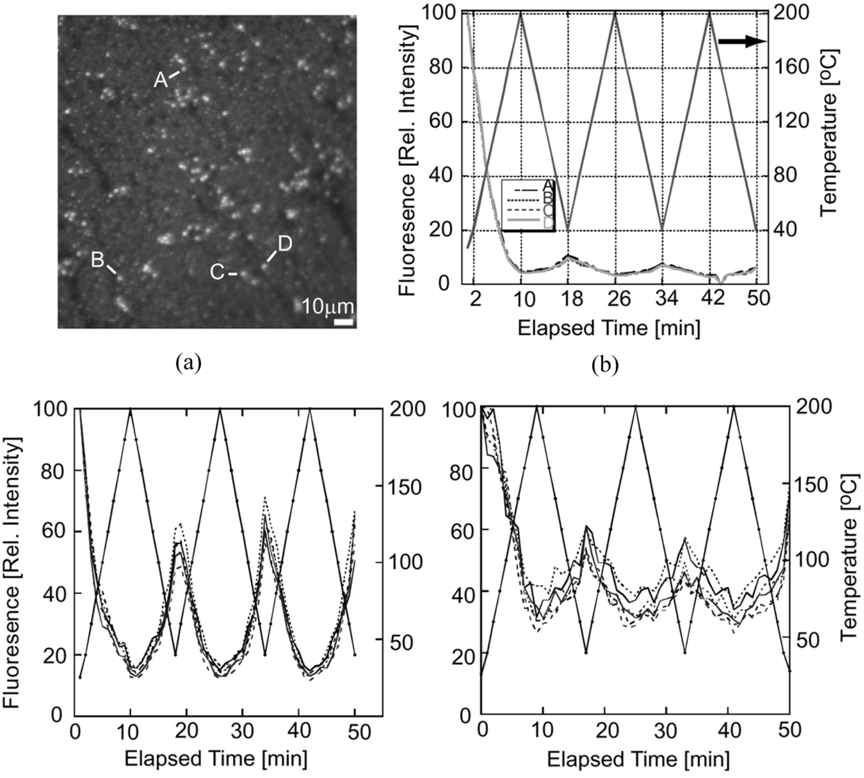
[1] Even under high concentration, dewetting process lets precipitated particles dispersed on the substrate, which is a prosperous property of the present procedure for industrial application.

(>60 μg/ml), the ratio of self-organization shows a similar tendency between Rh6G and NK1420. In contrast below 60 μg/ml, Rh6G manifests perfect self-organization, whereas NK1420 indicates a saturation of the self-organization process. Figure 3(b) indicates that the self-organization process was favored by a low concentration of target dyes, which is reverse to the fact that conventional crystallization takes place only at the dye saturation. The dewetting of a volatile solution on a glass is a rapid and efficient process in accumulating the dyes in a particle, whereas the diffusion is slow and negligible in a short time scale, which suggests that the Rh6G aggregates have grown in nonequilibrium conditions and that these aggregates are stable only under electrostatic interaction with the charged surface of the glass substrate.

Fluorescence Change Due to Annealing

To evaluate the thermal stability of the self-organized aggregate, dye aggregates on a glass was sealed in an observation chamber filled with nitrogen gas and the fluorescence was monitored while the specimen temperature was elevated from 23°C to 200°C, lowered down to 40°C, and then repeatedly changed between 40°C and 200°C. Dye particles with a diameter less than 2 μm were traced for fluorescence change since they were expected to show unidirectional dye orientation [10]. In the Rh6G case, the fluorescence intensity decreased down to 5 % irreversibly at the first temperature raise, and thereafter showed reversible fluorescence between two states (Fig. 4(b)). The latter change was essentially reversible, other than the small gradual decrease possibly due to dye bleaching by remnant oxygen. This reversible change reflected the difference of fluorescence quantum efficiency with temperature due to phonon scattering: at elevated temperature, the photoexcited state energy should be transferred to e.g., a vibration of dye molecule with higher probability, reducing the fluorescence quantum efficiency. The relative fluorescence change was identical between particles (only four particles are shown in Fig. 4(b) for clarity), which indicates that the dye aggregates are in the same electronic state and that the electronic state was changed in accordance among different aggregates along with the temperature change.

The initial large and irreversible fluorescence decrease, therefore, strongly suggests that the original dequenched (fluorescent) self-organized Rh6G aggregate is in a quasi-stable state, which is consistent with the nonequilibrium nature of the rapid dewetting process. When the specimen chamber was evacuated keeping the temperature

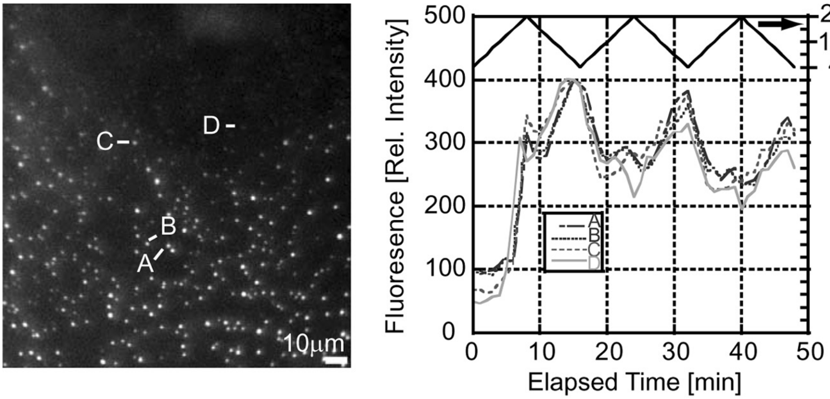


(a) (b)

(c) (d)

FIGURE 4 Fluorescence intensity change upon annealing. (a) Fluorescence image of traced four Rh6 G particles indicated as "A" through "D". (b) Time course of relative fluorescence intensities of four Rh6 G particles during repeated linear temperature increase and decrease shown by a thick line (scaled in the right ordinate). (c, d) Relative fluorescence intensity change of six RhB, and Rh101, particles upon annealing, respectively.

constant at room temperature, the fluorescence decreased only few %, which may be due to a release of solvent ethanol incorporated in the aggregate particles. The majority of the initial large fluorescence decrease should be ascribed to an irreversible change of the aggregate electronic state, further suggesting an irreversible alteration of molecular ordering in the aggregate. Other rhodamines, RhB and Rh101, also showed an initial irreversible fluorescence decrease and subsequent reversible fluorescence change upon annealing (Figs. 4(c) and (d)). Every aggregate in a microscope field of view showed similar patterns of fluorescence change, indicating that the self-organized



(a) (b)

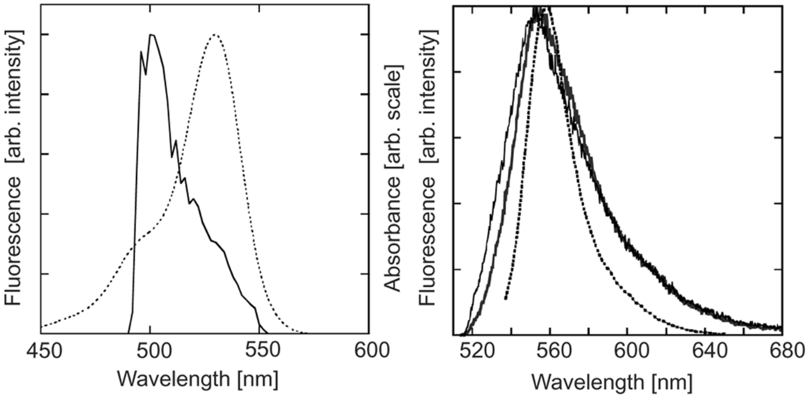
FIGURE 5 Time course of relative fluorescence intensities (b) of four NK1420 particles indicated in (a) during repeated temperature increase and decrease.

particles are composed of the identical dye aggregate with the same optical and thermodynamic property. Figure 4 indicates that the as grown aggregates are quasi-stable and that they consistently manifest a high quantum efficiency of fluorescence.

In the case of cyanine dye NK1420, the fluorescence increased to 400% irreversibly at the initial temperature raise (Fig. 5). This initial increase ruled out the possibility that the fluorescence change may be due to a thermal degradation of the dyes. The time course of the fluorescence change was also similar between particles although the initial fluorescence seemed to vary between particles, suggesting that the degree of the initial dye ordering was somewhat different between particles and may be imperfect as the broad J-aggregate peak of the specimen suggested. This imperfection is consistent with the limited self-organization of NK1420 dye (Fig. 3(b)). These observations indicate that the self-organized NK1420 aggregates were also in a quasi-stable state originally, showing a weaker fluorescence than a perfect stable J-aggregate that was attained after annealing.

Fluorescence Spectrum Change Due to Annealing

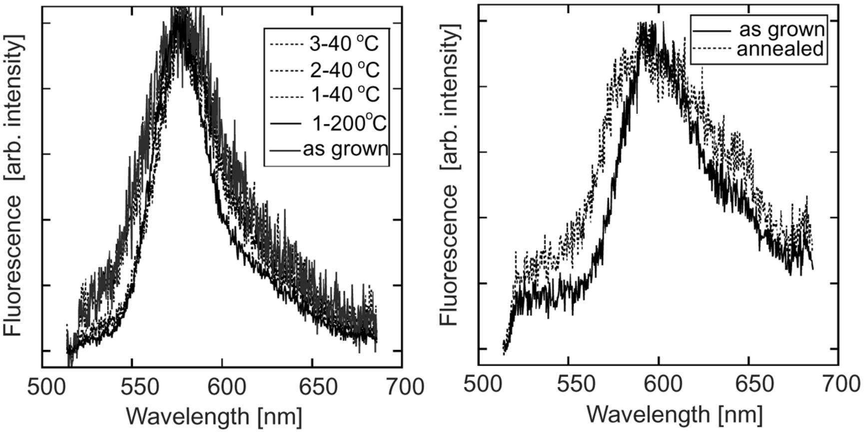
The fluorescence excitation spectrum of the self-organized Rh6G aggregates was blue-shifted by 30 nm from the absorption peak of the molecularly dispersed specimen (Fig. 6(a)), whereas the fluorescence emission spectrum was similar (Fig. 6(b)). Surprisingly the emission peak and the profile were also similar before and after the annealing.



(a) (b)

FIGURE 6 (a) Comparison of the fluorescence excitation spectrum of Rh6G self-organized particles (solid curve) and the absorption spectrum of Rh6G solution (dotted curve). (b) Comparison between three fluorescence emission spectra of Rh6G self-organized particles before (thick gray curve) and after (thin solid curve) the annealing, and of the Rh6G solution (dotted curve).

These features were consistent among other rhodamines as shown in Figure 7. Blue-shift of the absorption peak was believed to be typical to the H-aggregate of conjugated dyes: in H-aggregate, constituent



(a) (b)

FIGURE 7 Comparison between the fluorescence emission spectra of RhB (a), and Rh101 (b), self-organized particles before (black solid curve) and after (gray and dotted curve) the annealing.

rod-like dyes are aligned vertically to the substrate, with the same electric charge at the end of the rod molecules placed in proximity, elevating the energy of excitons (blue-shift). Some reports [4] argued that their Rh6G specimens were made of hypothetical H-aggregates manifesting a strong quenching of fluorescence. Contrary to these reports, our self-organized aggregates are in a dequenched state, clearly bearing a different optical property from the H-aggregates. Blue-shift of the absorption peak and the invariable emission spectrum upon annealing may suggest that the energy band of the self-organized aggregates is similar to H-aggregates both before and after the annealing. Drastic decrease in fluorescence may then be explained by two tentative models: (A) efficient relaxation processes in as grown aggregates may take the excited states from top of the band to the bottom where emission takes place, whereas the annealed aggregates do not possess these relaxation paths due to dipole-emission inhibited triplet states emerged as a result of annealing. (B) The transition moment of the band top levels decreases along with the annealing, reducing the absorbance of the aggregate.

Anyway the drastic fluorescence change along with the invariant emission spectrum may present a possibility of switching the fluorescence quantum efficiency of π-conjugated dye aggregates by a slight modification of molecular ordering. Artificial rearrangement of the substrate surface charge may trigger this fluorescence switching: this approach will open a new way to manipulate molecules to exhibit a macroscopic change of optical property. Our self-organized dye particles, manifesting both the quenched state and the dequenched state, will present a solid basis for this study.

CONCLUSION

The dewetting process on a hydrophilic surface enabled a selective formation of dequenched rhodamine aggregates with identical dye ordering, having a blue-shifted exciton band structure. Upon annealing, the band structure was preserved, whereas the fluorescence decreased drastically, suggesting an irreversible transition to quenched state. The as grown rhodamine aggregate, with high fluorescence, was quasi-stable, only realized by a rapid dewetting process.

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