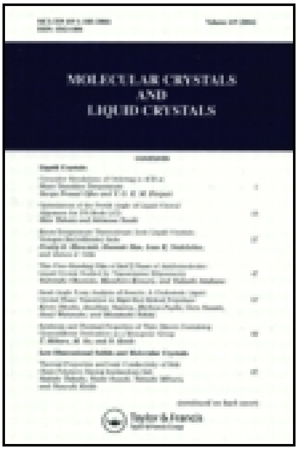

Molecular Crystals and Liquid Crystals

Molecular Ordering in Self-Organized Dye Particles

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Molecular Ordering in Self-Organized Dye Particles

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Self-organized rhodamine 6G particles prepared by wetting/dewetting process of an ethanol solution on a hydophilic glass surface did show fluorescence without quenching. Polarized evanescent field excitation showed that the molecule's transition moment within dye particles was oriented unidirectionally and parallel to the substrate surface. The deduced dye orientation showed correlation between adjacent particles, which implies a simultaneous aggregate growth from a common crystal seed grown in a possible "arm" region connecting the adjacent droplets just before these droplets were disconnected upon solvent evaporation. The dye orientation of most particles pointed about 45° off the dewetting direction. In contrast, the particles of another π-conjugated NK1420 dye, J-aggreagates of which grows easily from an oversaturated solution, showed dye orientation along the dewetting direction preferably, still indicating the effect of self-organization, however based on a different mechanism.

Keywords: dewetting process; evanescent field; J aggregate; molecular orientation; pi conjugated dye; self assembled

INTRODUCTION

Much attention has been paid to organic materials in recent years for their potential applications in electronics and photonics [1]. The main

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We express our gratitude to Professor Futao Kaneko of Niigata University for a discussion of characteristic evanescent electric field induced by a p-polarized laser reflection.

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advantage of organic materials is that they can be fabricated onto almost any type of substrate (including flexible ones) by inexpensive techniques, like spin coating and inkjet printing, in contrast to the more elaborate and sophisticated processing used with inorganic materials. For nanostructure fabrication, dewetting process of a solution specimen on a solid substrate is favorable for fabricating self-organized nanostructure because it provides a very rapid processing over huge surface area in an ambient condition.

For photonic applications π-conjugated dyes are major concerns due to its superior optical responses: high oscillator strength and 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 photoluminesence, although others get completely quenched when placed in a solid state. Investigation of how dye aggregation affects these optical behaviors is, therefore, of importance not only for application purpose but also from a fundamental point of views: The knowledge of how the molecular interaction leads to the optical behavior of the aggregates would produce a novel design of dye aggregates with efficient optical properties.

Here we present a fabrication of self-organized aggregates of two types of π-conjugated dyes, one is known to produce a two-dimensional J-aggregate [3,4] and the other is thought to get quenched in a solid. Mode of aggregation and the distribution of dye orientation are investigated leading to the discussions on possible dye aggregation mechanism.

MATERIALS AND METHODS

We adopted the π-conjugated organic dyes rhodamine 6G (Rh6G) 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 both have a static positive charge so that they are expected to interact strongly with a hydrophilic glass surface with an exposed O^- group. The hydrophilic glass surface also promoted a wetting/dewetting process [5] of polar organic solvent upon it, which is the primary motive force realizing the self-organizing formation of submicrometer-sized particle arrays of the dye [6]. When a glass rod slid over a 100 µl ethanol solution (Fig. 1), a very thin film of Rh6G solution was formed. Thickness of the solution film became thinner while the solvent ethanol evaporated naturally from it. At certain thickness the solution film became separated into droplets, and then dye particles were formed as precipitates after the solvent further evaporated. Since the particle size would be determined by

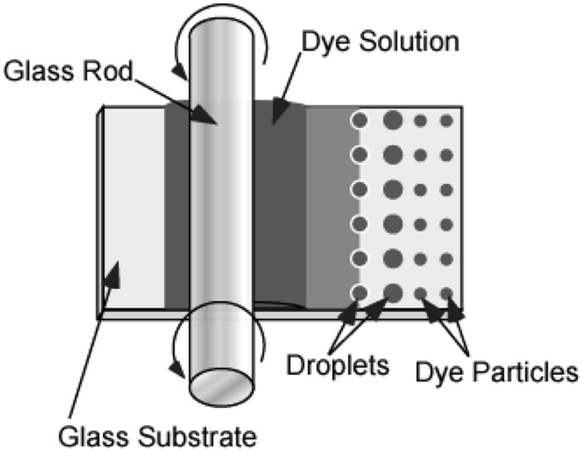


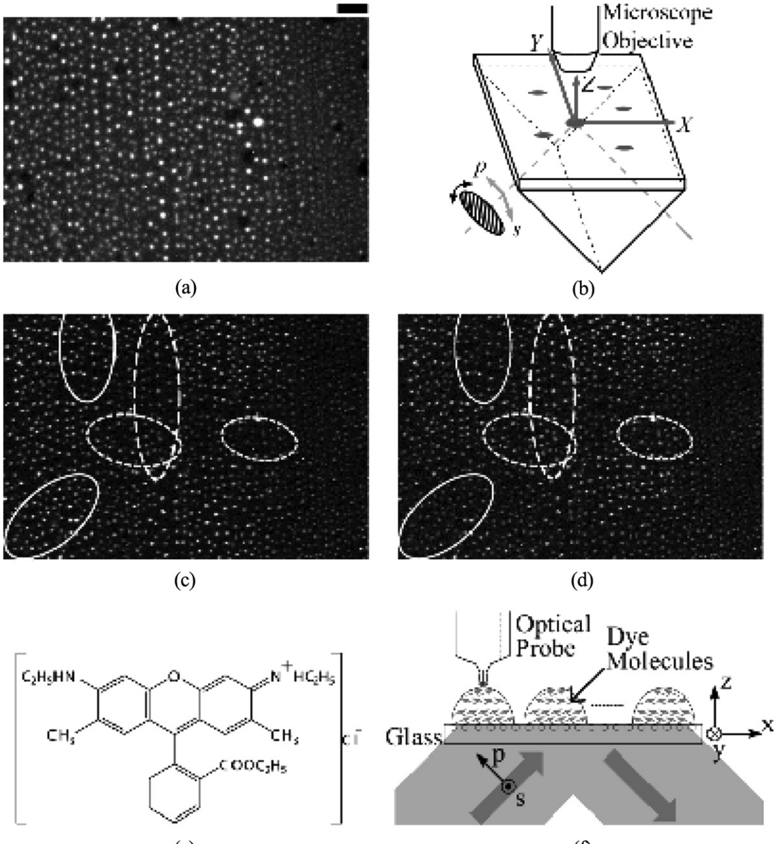
FIGURE 1 (a) Schematic diagram showing the wetting/dewetting procedure to prepare self-organized dye particles. To control the thickness of the ethanol solution of the Rh6G dye, a glass rod was pressed against a glass substrate surface and rolled over it. At a critical solution film thickness during the evaporation of ethanol, the solution film becomes separated into droplets and then dye particles are precipitated. The critical solution film thickness was controlled by the hydrophilicity of the substrate surface, which is accomplished by a prior ozone processing.

the number of dye molecules which is proportional to the droplet size left on the surface, and therefore by the wetting/dewetting process of the organic solvent, the size was controlled by the degree of the surface hydrophilicity and by changing the retraction velocity of the solvent boundary when it evaporated [6]. The same dewetting procedure was used to prepare NK1420 dye particles, but the dye was dissolved in methanol for solubility.

RESULTS

Far-Field Fluorescence of Rh6G Particles Excited by *s*- and *p*-Polarized Evanescent Field

Under an epifluorescence microscope, all the self-organized particles showed fluorescence as shown in Figure 2(a), which is a unique characteristic of the present specimen, because Rh6G fluorescence is generally regarded to be quenched in a solid state. How the dyes are stacked in the particle should be different from that in conventional



(a) (b) (c) (d) (e) (f)

FIGURE 2 (a) Conventional epifluorescence image and (c) and (d) far-field fluorescence of Rh6G particles when excited with *p*- or *s*-polarized evanescent field, respectively, at the substrate glass surface. Rolling direction of the glass rod was from right to left in these, and subsequent, figures consistently while the specimen was prepared. Corresponding regions are marked by solid and dotted ellipses in (c) and (d). Scale bar in (a) indicates 20 μm and common to (c) and (d). (b) Geometry of the incident laser, and its polarization, with respect to the specimen surface for evanescent-field observation. Microscope objective was used for both excitation and observation in the case of conventional epifluorescence. (e) The molecular structure of Rh6G molecule with single positive charge in either of the two NH group, (f) a model of alignment of dye molecules inside each particle with correlation between adjacent particles.

Rh6G precipitates. To elucidate the mode of dye stacking we investigated the dye orientation inside the particle by observing the far-field fluorescence when the particles were photoexcited by linearly polarized evanescent field [Fig. 2(b)]. The incident laser polarization was selected by a film polarizer as *p*- or *s*-polarized for Figure 2(c) or 2(d), respectively, that had the same intensity after the laser was guided through an enough length ($>10\,\mathrm{m}$) of multimode optical fiber and was accurately collimated with an aspheric lens. Let us point out three observations: (A) Some of the particles showed strong fluorescence [enclosed in solid ellipses in Fig. 2(c)] when excited by a *p*-polarized evanescent field, indicating that dye molecules within these particles were oriented in the *zx*-plane. (The incident laser spot was larger than the field of view and was almost uniform within this picture.) (B) Figure 2(d) shows a different distribution of fluorescence intensity when the particles are excited by an *s*-polarized evanescent field. Particles enclosed in solid ellipses show weak fluorescence. In contrast, those in dotted ellipses show strong fluorescence, indicating that dye molecules within them should be oriented in the *y*-direction. (C) On the other hand, we detected no difference in Figure 2(a), even if we set the far-field excitation to be polarized in the *x*- or *y*-direction.

Observation (C) suggests that the majority of dye molecules within a particle is distributed randomly within the *xy*-plane and observations (A) and (B) indicate that only dyes near the surface have a unidirectional orientation within each particle [Fig. 2(f)]. The evanescent field was expected to extend out into the air about 100 nm from the surface at a wavelength of 532 nm, which justifies our prediction that only surface dyes would be observed in the evanescent field excitation. If the transition moment of dye molecules has a *z*-component, it should appear as a bright particle in Figure 2(c) but disappear in Figure 2(a). The fact that no candidate for this type of particle can be found in the figures suggests that surface dyes in a particle are oriented unidirectionally and dominantly within the *xy*-plane. The fluorescence in Figure 2(c) was, therefore, due to only the *x*-component of the evanescent field although its field direction was rotating in time [7,8] within the *zx*-plane when excited by a *p*-polarized light.

The unidirectional orientation of only surface dyes may be ascribed to the strong electrostatic interaction between the dye molecule's positive charge [Fig. 2(e)] and the glass surface's negative charge [Fig. 2(f)]. How this electric attractive force and the capillary force lead to the self-organization of dye aggregates in a particle is still an open question.

In Figures 2(c) and (d), the molecules in adjacent particles seem to be oriented in a similar direction because they have similar intensities. This observation suggests that the dewetting process contributed to the alignment of the molecular direction among adjacent particles, which further proves that the dye particles were formed by a self-organizing mechanism. Then what is the actual mechanism of dye orientation correlation in the course of dye aggregates formation from solution droplets?

When the solution droplets are dried up to particles composed of dye aggregates, orientation of dye molecules would be fixed and these particles becomes spatially separated. The observation in Figure 2 indicates the existence of a mechanism that orients dye molecules in the same direction among adjacent, however separated, particles. Narrow "arms" (Fig. 3) might exist to connect the solution droplets, and to connect them and the bulk solution, which are similar to the ones observed in droplets of polymer solution [5]. At these "arms", the effect of capillary force becomes stronger because the two edges of the solution surface approaches to each other, possibly forcing the dye orientation e.g. perpendicular (or parallel) to the surface. If this dye ordering at the "arm" works as a crystal seed and extends towards the adjacent droplets connected by the "arm", these droplets would lead to the same direction of dye ordering. The present model of the dye orientation correlation among adjacent particles needs a solid basis that will be obtained from an *in situ* observation of emerging dye ordering in real time while droplets and resultant dye aggregates grow.

When the capillary force plays a key role in this self-organizing mechanism, orientation of the dye molecules should be near perfect only in smaller particles because they have larger surface-to-volume ratio. Then in the near-field scanning optical microscope observation, the mode of optical coupling between the dye molecules and the probe with vertical polarization may become prohibited preferentially in smaller particles, which is consistent with our observation of near-field fluorescence [9].

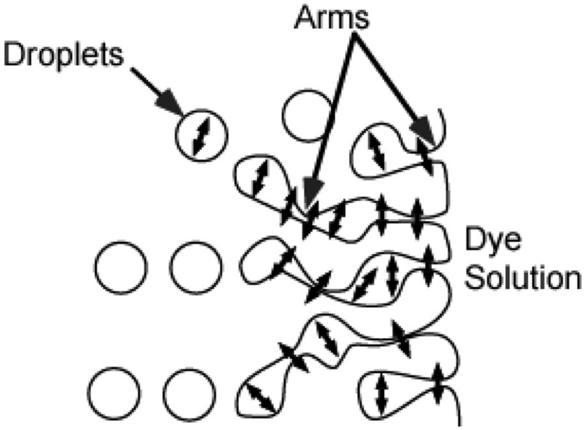
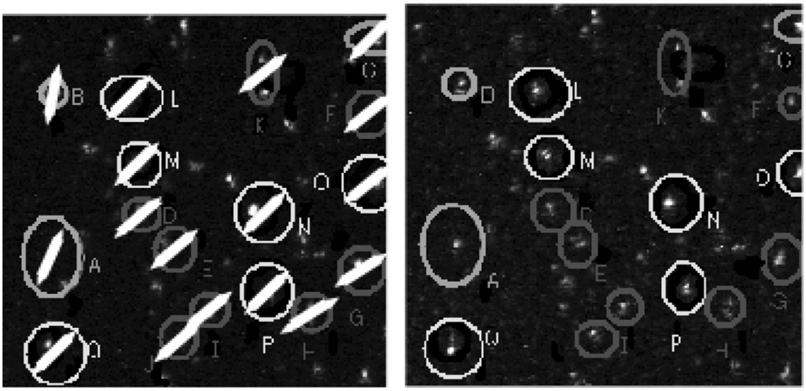


FIGURE 3 Tentative model of the origin of the dye orientation correlation due to "arms" connecting adjacent droplets just before the droplets become completely separated from the dye solution.

Estimation of Dye Orientation in Rh6G and NK1420 Particles

The orientation of surface dyes was estimated from the ratio of fluorescence intensity excited by p-polarized evanescent field and that by s-polarized evanescent field (Fig. 4). The estimated orientation shown by a white bar in the figure for each particle points to similar direction (about 45° from the x-direction in this field of view) over a region with a side $>100\,\mu$m. Only few particles showed dye orientation perpendicular to the dewetting direction. A preliminary observation during the specimen preparation indicated that the solution boundary did not move smoothly in the direction of glass rod movement, and that the boundary movement may correspond locally to the orientation, or perpendicular to the orientation, of the dyes in the resultant particles. Simultaneous real time observation of solvent boundary movement and the polarization-dependent fluorescence of the resultant particle is necessary to elucidate the detailed mechanism of the correlation of dye orientation between adjacent particles.

Then the specimen was rotated successively from 0° to 180° at 5° intervals around the axis of microscope objective [normal to the substrate, Fig. 2(b)] with the incident laser polarization fixed as s-polarization. If a dye aggregate has a unidirectional dye orientation at $-30°$ off the y-direction originally, the orientation coincides with



(a) (b)

FIGURE 4 (a), (b) Far-field fluorescence of Rh6G particles excited with p- or s-polarized evanescent field, respectively, in the same field of view. In (a), the white bar indicates the unidirectional orientation of surface dyes inside each particle that was deduced from the ratio of fluorescence intensity between (a) and (b).

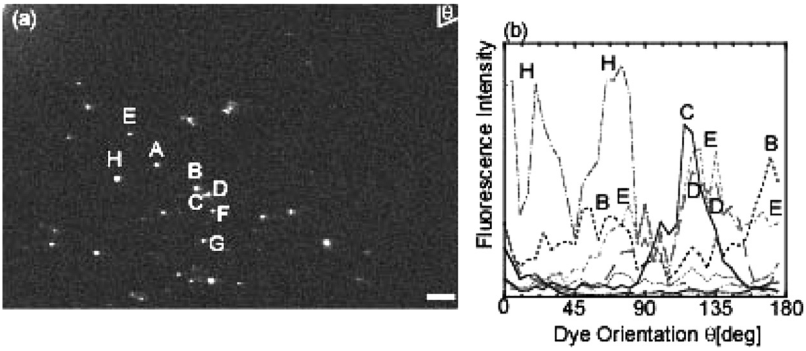


FIGURE 5 Dye orientation of Rh6G self-organized particles. (a) Epifluorescence image when excited with *s*-polarized evanescent field. Bar indicates 10 μm. (b) Fluorescence intensity of the particles indexed in (a) depending on the direction of incident laser polarization.

the y-axis when the whole specimen is rotated by 30° and the optical absorption, therefore the fluorescence also, of the aggregate is maximum at this angle. The absorption and fluorescence of the aggregate would decrease while the specimen is further rotated, and become minimum at the rotation of 120°.

More than half of the self-organized particles showed a major peak at about 45° off the dewetting direction (Fig. 5). Other than this major peak, some of the particles seemed to show a minor peak around 90° (the same as the dewetting direction) or 0° (perpendicular to the dewetting direction). Larger particles, such as those indexed as H and B, had a tendency to show multiple peaks at 0° and 90°. When self-organized particles were prepared with another dye [Fig. 6(a)], NK1420 [Fig. 6(g)], which was reported to form two-dimensional J-aggregates from over-saturated solution [3,4] half of the particles showed 90° orientation [Fig. 6(b), (e)] and only a quarter populations

FIGURE 6 Dye orientation of NK1420 self-organized particles. (a) Epifluorescence image when excited with *s*-polarized evanescent field. Bar indicates 10 μm. (b), (c) and (d) Fluorescence intensity dependence on the direction of incident laser polarization, of the particles indexed as A–D, E–I, and J–M, respectively, in (a). The major peak angles, 90° corresponding to the dewetting direction [horizontal in (a)], are indicated by arrows and showed by white bars on the corresponding particles in (a). (e) and (f) Schematics of dye aggregate and composite dye aggregate showing single and three peak angle(s), respectively. (g) Molecular structure of NK1420 dye.

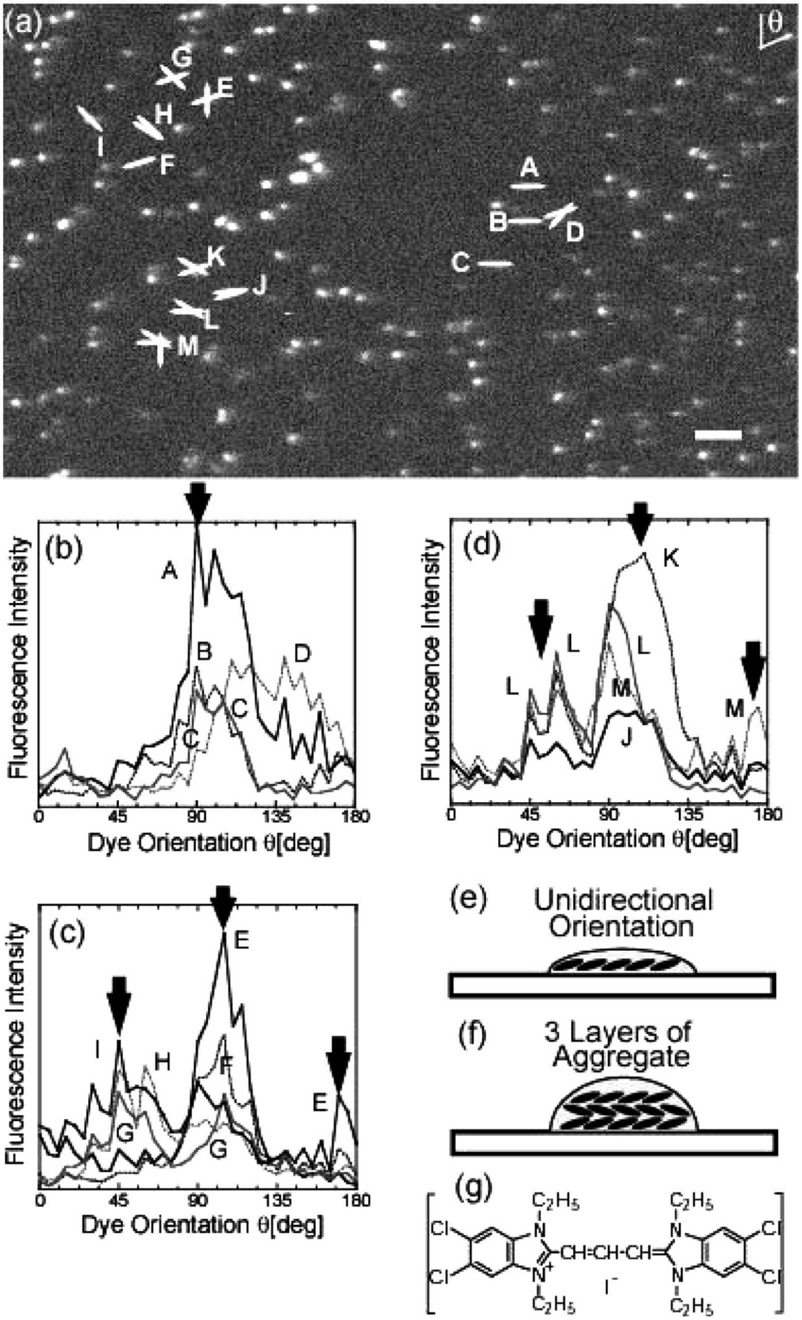
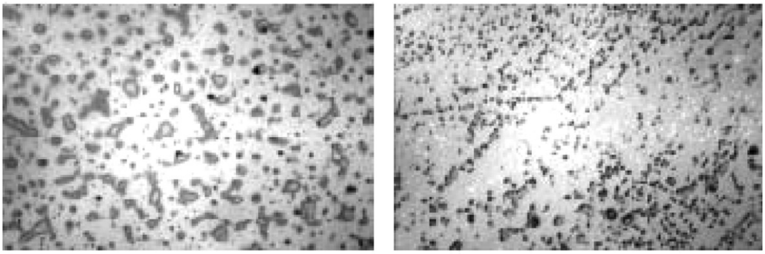
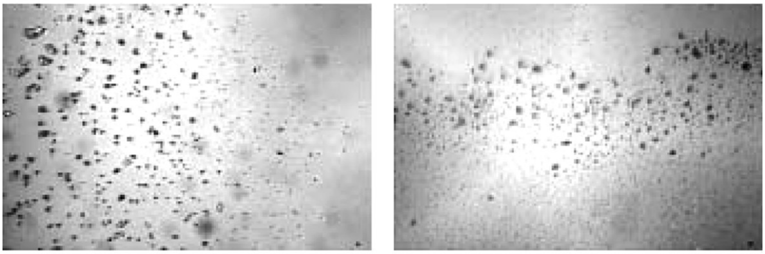


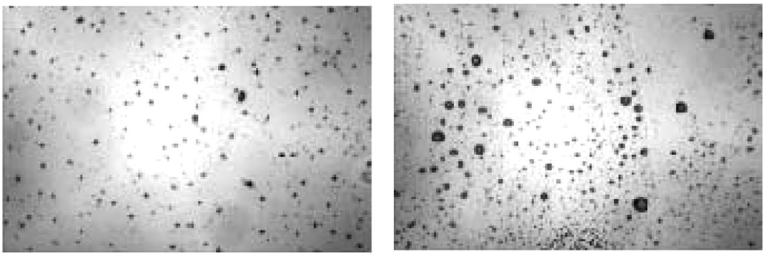
FIGURE 6 Continued.



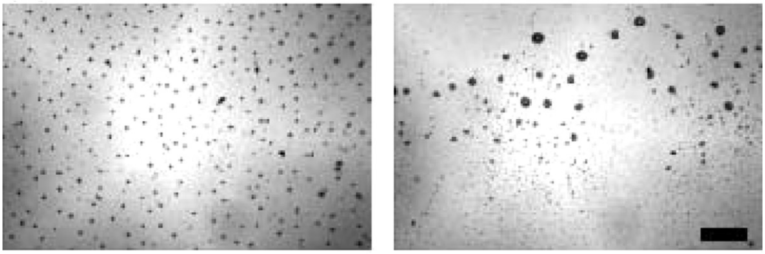
(a) 0.25 mg/ml (e) 0.25 mg/ml



(b) 0.125 mg/ml (f) 0.125 mg/ml



(c) 0.0625 mg/ml (g) 0.0625 mg/ml



(d) 0.03125 mg/ml (h) 0.03125 mg/ml

FIGURE 7 Particle morphology dependence on the dye concentration. (a)–(d) Rh6G, (e)–(h) NK1420, particles prepared at the concentrations indicated. Bar indicates 50 µm.

showed 45° orientation [Figs. 6(c) and (d)]. Some particles showed a major 90° orientation and at the same time 45° and 0° minor peak, which may reflect a stack of multiple aggregates with different orientation [Fig. 6(f)]. At the specimen preparation, if a dye is aligned to the liquid-substrate-air boundary, where the surface energy due to the capillary force is constant, the resultant dye orientation would become perpendicular to the dewetting direction. If the droplet boundary gets static charges, as is often the case with a droplet floating in the air, the polar dye may be aligned under the electric field, perpendicular to the droplet boundary in this case. If there is some mechanism for the dye to avoid the steepest curvature of the solution surface that was bent vertically by its adhesion to the glass rod, the dye should have a tendency to point away both from the dewetting direction and from the solution boundary. Simultaneous observation of solvent boundary movement and the polarization-dependent fluorescence of the resultant particle would help to elucidate how and which of these mechanism governs the self-organization of Rh6G and NK1420 particles on a hydrophilic surface.

Self-Organization of Rh6G and NK1420 Particles Under Higher Concentrations

Figure 7 shows how the specimen looked like when the dewetting process was started with higher concentration of dye solution. When the dye concentration was raised by 2, 4 and 8 times, number of self-organized Rh6G particles with regular circular shape decreased and large precipitates increased stepwisely as shown in (a) through (d). In contrast NK1420 dye gave rise to regular large particles even in higher concentrations as shown in (e) through (h), which might reflect the intrinsic capability of NK1420 to form regular aggregates. In contrast to parallelogram shaped NK1420 aggregates with straight edges observed preferentially in precipitates [3], observed circular shape of the NK1420 particles suggests that self-organization process was still favored even under high concentration. The different behavior in the higher dye concentration suggests that this NK1420 self-organization under higher dye concentration was due to different mechanism of self-organization from that under lower dye concentration which might be common to both dyes.

CONCLUSION

Polarized evanescent field excitation showed that the dye molecule's transition moment within self-organized dye particles was oriented unidirectionally and parallel to the substrate surface. The dye orientation deduced from the fluorescence intensity dependence on the direction of incident *s*-polarized laser showed correlation between adjacent particles, which is a strong indication of the self-organization of the specimen. The dye orientation distribution showed a clear difference between Rh6G and NK1420, which demonstrated that different self-organization mechanisms were responsible for the two dyes, reflecting the different intrinsic capability of aggregate formation.

REFERENCES

[1] Heeger, A. J. (2001). *Angew. Chem. Int. Ed.*, *40*, 2591–2611.

[2] Kobayashi, T. (Ed.). (1996). *J-aggregates*, World Scientific: Singapore, and references therein.

[3] Nabetani, A., Tamaru, H., Tomioka, A., & Miyano, K. (1995). *J. Chem. Phys.*, *102*, 5109–5117.

[4] Tomioka, A. & Miyano, K. (1996). *Phys. Rev.*, *B54*, 2963–2967.

[5] Karthaus, O., Grasjo, L., Maruyama, N., & Shimomura, M. (1999). *Chaos*, *9*, 308–314.

[6] Ido, Y., Tomioka, A., Itakura, Y., & Motokubota, T. (2005). *Nonlinear Opt. Quant. Opt.*, *34*, 265–269.

[7] Tojo, S. & Hasuo, M. (2005). *Phys. Rev.*, *A71*, *012508*, 1–6.

[8] Ohtsu, M. & Kobayashi, K. (2004). *Optical Near Fields – Introduction to Classical and Quantum Theories of Electromagnetic Phenomena at the Nanoscale*. Springer: New York, USA, p18.

[9] Tomioka, A., Ido, Y., Itakura, Y., & Motokubota, T. (2006). *Jpn. J. Appl. Phys.*, *45*, 417–420.