

Magnetic Alignment of Fiber-Shaped Pseudoisocyanine J Aggregates in a Gelated Solution

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An aqueous solution of 1,1′-diethyl-2,2′-quinocyanine bromide (PIC-Br) containing highly concentrated counter ions provided by NaCl was prepared by heating the solution at 90 °C. Upon cooling the solution to room temperature, it transformed into a gel-like state. Optical microscopy revealed that fiber-shaped J aggregates formed a network structure in the gelated solution. By cooling the solution in a magnetic field of 10 T, highly oriented J aggregates were obtained in the gel. Without any additional treatment, the alignment of the fibers was preserved after the gelated solution was removed from the magnetic field. The absorption spectra of the gelated solution showed a strongly polarized J-band, reflecting the high degree of orientation of the magnetically aligned J aggregates.

Ionic dyes in an electrolyte solution form supramolecular aggregates, called J aggregates, which are characterized by a narrow, intense absorption band (J-band) that is redshifted with respect to the monomer absorption band.[1,2] The J-band is due to the coherent excitation of highly ordered molecules in aggregates, which leads to a delocalized excitonic state.[3] Pseudoisocyanine (PIC) dyes form fiber-shaped J aggregates; the optical properties and the internal structure of these aggregates have been intensively studied. Spectroscopic studies show that the J-band of PIC is polarized in a direction parallel to that of the fiber, indicating that the transition dipole moments of the constituent molecules align in a direction that is nearly parallel to that of the fiber.[4–13] Various models for the molecular arrangement in aggregates, such as a brickwork,[4–6,8,13] a herringbone,[5,6,8,13] and more complex 3-dimensional molecular stackings,[8] have been proposed.

Since the J-band of the PIC J aggregates is strongly polarized, it is of particular importance to align the J aggregates in a solution or in a thin film, both for fundamental science as well as potential device applications. The polarized absorption spectra of highly oriented J aggregates can reveal the direction of the transition dipole moment with respect to the direction of the orientation, thus, making it possible to investigate the internal molecular alignment of the J aggregates. The polarized J-band also enables the application of thin films of oriented J aggregates to optical devices, such as in wavelength-selective polarizing optics. A thin-film polymer, consisting of highly oriented PIC J aggregates, was prepared by Misawa et al. using a technique called vertical spin coating, in which the centrifugal force is used to align the J aggregates.[10–12] This thin film exhibited strong dichroism and a linear dichroic ratio of the J-band, defined by Absorbance(∥)/Absorbance(⊥), ranging from 5 to 10.

It has been reported that a strong magnetic field, exceeding 10 T, can be used to align molecular materials, such as liquid crystals, crystals, polymers, and J aggregates.[14–16] In a magnetic field, a diamagnetic molecule acquires magnetic energy, which is given by $E = -\chi B^2$, where χ is the diamagnetic susceptibility ($\chi < 0$) and B is the magnetic field. Since most molecules have an anisotropic molecular structure, their anisotropic diamagnetic susceptibility is expressed as $\Delta\chi = \chi_{\parallel} - \chi_{\perp}$, where $\chi_{\parallel}$ and $\chi_{\perp}$ are the diamagnetic susceptibilities along two orthogonal molecular axes. The magnetic energy difference, depending on the orientation, is therefore given by $\Delta E = -\Delta\chi B^2$. Due to ΔE, molecules tend to orient in a specific direction with respect to the applied field. Generally, ΔE is much smaller than the thermal energy ($|\Delta E| \ll kT$) for individual molecules; thus, the magnetic alignment cannot be observed for individual molecules. Since the magnetic energy difference is given by $N\Delta E$ for molecular aggregates constructed from N molecules, the magnetic energy difference can be larger than the thermal energy ($N|\Delta E| > kT$) when N is sufficiently large. Therefore, the molecular aggregates that are constructed from a large number of molecules can be magnetically aligned. The advantage of the magnetic alignment is that molecular materials can be aligned homogeneously over a wide area by using a magnet that can generate a homogeneous magnetic field. This advantage is important in fabricating oriented J aggregates that are significantly large for practical use in actual devices. However, magnetically aligned molecular materials lose their alignment immediately after the material is removed from the magnet. Therefore, for device applications, an additional treatment, such as fixing the alignment by the addition of gelatin, is necessary to preserve this alignment.[15]

In this study, we observed that an aqueous solution of PIC could be transformed to a gel-like state with a high viscosity by the addition of highly concentrated counter ions, provided by NaCl. Optical microscopy revealed that the gelated solution consisted of fiber-shaped aggregates that formed a network structure. The alignment of the fibers in the gel was preserved for at least 3 days; after that time the J aggregates sometimes transformed into crystals. Therefore, if the fibers in the gel can be magnetically aligned, then without any additional treatment

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the alignment can be preserved after the material is removed from a magnet. In order to align the J aggregates in a gelated solution, we developed an alignment technique using a magnetic field. The polarized absorption spectra of the magnetically aligned J aggregates were then measured in order to investigate the degree of orientation of the J aggregates.

Experimental

1,1′-Diethyl-2,2′-quinocyanine bromide (1-ethyl-2-(1-ethylquinolin-2-ylidenemethyl)quinolinium bromide, PIC-Br, Hayashibara Kankou Shikiso Kenkyusho), sodium chloride (NaCl, Merck), and distilled water (Cica-Merck) were used as obtained. Fifty milliliters of a 0.25 mM PIC-Br solution were prepared by dissolving PIC-Br in heated distilled water (90 °C) in a beaker by stirring the solution for 3 h. After the PIC-Br was completely dissolved, 1.74 g of NaCl was dissolved in the heated stirred solution in order to provide counter ions that would induce the aggregation of PIC molecules. The amount of NaCl was more than 10-times greater than that required to induce aggregation; 0.4 mL of the solution was subsequently transferred to a glass cuvette (10 mm × 40 mm, 1 mm optical path length). The cuvette was then mounted at the center of a room-temperature bore of a superconducting magnet (Japan Magnet Technology) that could generates magnetic fields of up to 10 T (Fig. 1). After the solution in the cuvette transformed into a gel, the cuvette was removed from the magnet, and the alignment of the aggregates was investigated using a polarized light microscope (Olympus, BX-60). The polarized absorption spectra of the gelated solution were measured with a spectrometer (OceanOptics, USB2000) coupled with a microscope (Olympus, BX-51).

Results and Discussion

PIC J Aggregates in a Gelated Solution Prepared at $B = 0$ T. First, a gelated solution of PIC was prepared in the absence of a magnetic field. The heated solution in the beaker was transferred to a cuvette and then cooled to room temperature, yielding a gelated solution with high viscosity. The gelation process strongly depended on the temperature of the solution during the transfer from the beaker to the cuvette. When the heated solution at 90 °C was transferred to the cuvette, the solution transformed to a gel within 2 to 3 min. However, when the heated solution was first cooled to a moderate temperature (40 °C) in the beaker, and then transferred to a cuvette, the transition to the gel took 10 to 15 min. This temperature dependence of the gelation process can be explained as follows. Transfer of the heated solution to the small cuvette resulted in a rapid cooling of the solution. When the solution at 90 °C was transferred to the cuvette, the initial cooling rate of the solution was large due to a large temperature difference between the solution and the cuvette. This large initial cooling rate might have accelerated the gelation process. On the other hand, when the solution at a moderate temperature (40 °C) was transferred to the cuvette, the initial cooling rate of the solution was low due to a small temperature difference between the solution and the cuvette. Thus, the gelation progressed slowly.

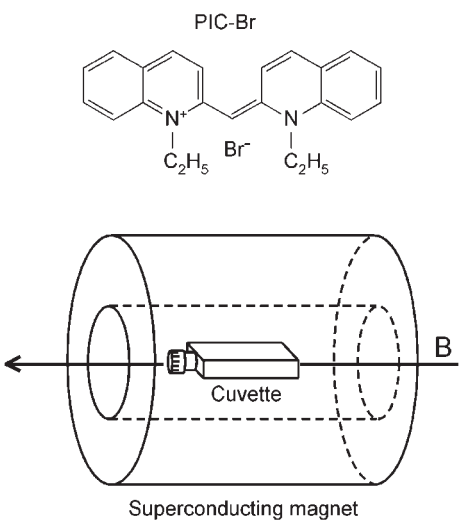

Fig. 1. Structural formula of 1,1′-diethyl-2,2′-quinocyanine bromide (PIC-Br) and experimental setup for magnetic alignment of PIC J aggregates.

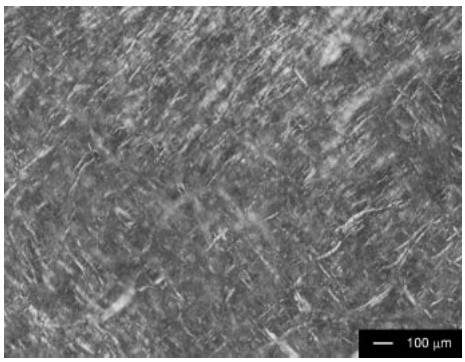

Fig. 2. Polarized light microscope images of the gelated solution of PIC prepared in the absence of a magnetic field. The polarizer and the analyzer of the microscope were horizontal and vertical to the image, respectively.

Figure 2 shows polarized light microscopy images of the gelated solution. The polarizer and analyzer were orthogonal. Randomly oriented fiber-shaped aggregates that formed the network structure are clearly evident. The alignment of the fibers in the gel was not influenced by external disturbances, such as tilting of the sample; this alignment was preserved for at least 3 days after sample preparation. The fibers were approximately 200 μm long and 3 μm wide, approximately 10-times longer and wider than fibers grown in a thin film polymer.[4–9] This difference in size is probably due to an enhancement of aggregation by the high concentration of counter ions provided by NaCl.

Figure 3 shows the absorption spectra of the gelated solution and the PIC monomer solution (prepared without the addition of NaCl for comparison), measured using unpolarized light. The gelated solution showed a narrow, intense absorption band at 573 nm. The position of this band is identical to that of the J-band of previously reported PIC J aggregates,[4–13] suggesting that the fibers that formed in the gelated solution were J aggregates.

Magnetic Alignment of J Aggregates in a Gelated Solution. In order to magnetically align fiber-shaped J aggregates, gelated solutions were prepared by using three different procedures, as follows:

(1) A heated solution at 90 °C in a beaker was transferred to a cuvette and then cooled to room temperature. After the solu-

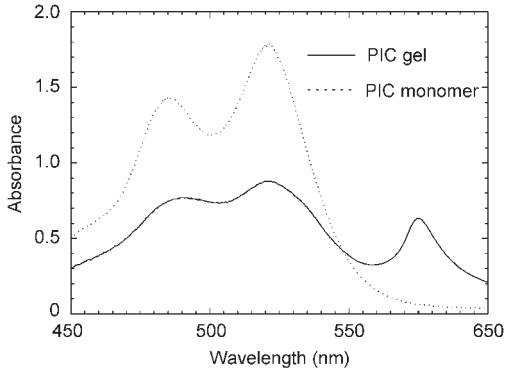

Fig. 3. Absorption spectra of the PIC gelated solution (solid curve) and the PIC monomer solution (dashed curve) prepared in the absence of a magnetic field with unpolarized light.

tion transformed into a gel, the cuvette was placed in a magnetic field of 10 T for 1 h.
(2) A heated solution at 90 °C in a beaker was cooled to a moderate temperature (40 °C). At this temperature, the solution showed gold-colored opalescence, which is distinctive of a solution containing J aggregates. However, the solution was still fluid, suggesting that the J aggregates were too small to form a network structure. The solution was then transferred to a cuvette and placed in a magnetic field of 10 T for 1 h.
(3) A heated solution at 90 °C in a beaker was transferred to a cuvette and immediately placed in a magnetic field of 10 T for 1 h. At 90 °C, the solution did not show opalescence, suggesting that J aggregates were not formed in the solution due to the high temperature of the solution.

In all three procedures, after the sample was removed from the magnet, the alignment of the fibers in the gelated solution was investigated by using a polarized light microscope. The gels prepared using procedures (1) and (3) exhibited randomly oriented fibers that were similar to the fibers prepared in the absence of a magnetic field, as shown in Fig. 2. In contrast, the gel prepared using procedure (2) exhibited highly oriented fibers. When the polarizer and analyzer of the microscope were tilted by 45 degrees with respect to the direction of the applied magnetic field, the oriented fibers were clearly observed (Fig. 4a); however, when the polarizer was perpendicular to the applied field, a dark image was obtained (Fig. 4b). These images indicate that the fibers were highly oriented in a direction perpendicular to the applied field. This direction of the magnetic alignment indicates that the diamagnetic susceptibility perpendicular to the fiber ($\chi_\perp$) was larger than that parallel to the fiber ($\chi_\parallel$), as expressed by $\chi_\parallel < \chi_\perp < 0$. These highly oriented fibers were observed throughout the sample, regardless of their location within the cuvette.

Figure 5 shows the polarized absorption spectra of the magnetically aligned J aggregates. The J-band at 573 nm showed a strong polarization dependence, reflecting the high degree of orientation of the J aggregates (Fig. 5a). The spectrum measured with the light polarized parallel (∥) to the fiber orientation exhibited an intense J-band; however, when the polarization was changed perpendicular (⊥) to the fiber orientation, the intensity of this J-band was reduced. This polarization dependence indicates that the transition dipole moments of the PIC

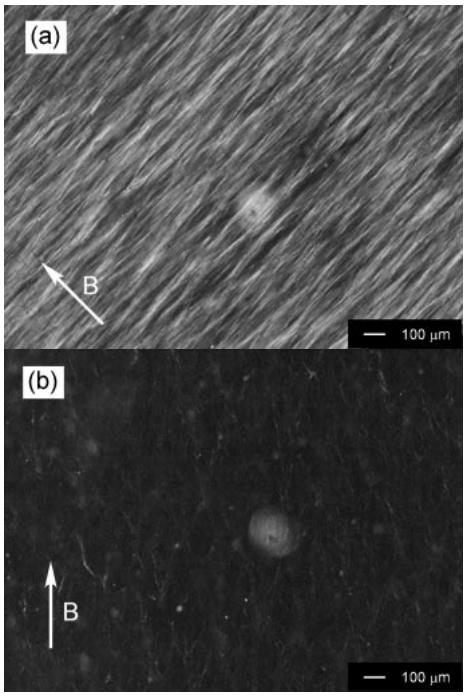

Fig. 4. Polarization microscope images of the gelated solution of PIC prepared using a magnetic field of 10 T. The direction of the applied magnetic field *B* (arrow) was tilted (a) 45 degrees with respect to both the polarizer and the analyzer and (b) perpendicular to the polarizer.

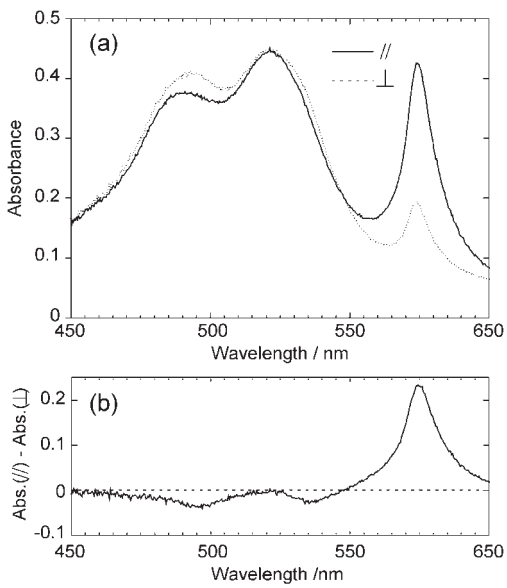

Fig. 5. (a) Polarized absorption spectra of magnetically aligned PIC J aggregates in the gelated solution measured with light polarized parallel (solid curve) and perpendicular (dashed curve) to the direction of alignment. (b) Difference in absorption spectra shown in (a).

molecules were aligned in a direction along the fiber. Based on these absorption spectra, the estimated dichroic ratio (Absorbance(∥)/Absorbance(⊥)) of the J-band was 2.5.

Figure 5b shows the differences in the spectra measured with two orthogonal polarizations (Absorbance(∥) −

Absorbance($\perp$)) to subtract the contribution from monomers and dimers that do not exhibit a polarization dependence. The difference in the spectra reveals that in addition to the main J-band at 573 nm there are two absorption bands at 497 nm and 534 nm that show a polarization dependence. The band at 497 nm was due to the transition dipole moments that were directed in a direction perpendicular to the fiber, and the band at 534 nm was due to the phonon sideband of the J aggregates.[10–13,17]

The mechanism of magnetic alignment of the aggregates in the gelated solution can be explained on the basis of the fact that only the sample prepared using procedure (2), where the heated solution was first cooled to a moderate temperature before being subjected to a magnetic field, showed aligned fibers. As described in the introduction, molecular aggregates constructed from N molecules are magnetically aligned when the magnetic energy difference, which depends on the orientation of the aggregates in the magnetic field, is larger than the thermal energy ($N|\Delta E| > kT$). In cyanine dye J aggregates, the minimum number of molecules necessary for magnetic alignment in aggregates in a field of 20 T was estimated to be approximately 20000.[15,16] In a sample prepared using procedure (1), where the heated solution was first cooled to room temperature before being subjected to a magnetic field, the solution was gelated before the sample was placed in a magnetic field. Since the J aggregates had already formed a network structure in the gelated solution, the magnetic field did not influence the alignment of the aggregates. In contrast, in the sample prepared using procedure (2), the solution (40 °C) showed a gold-colored opalescence before it was placed in a magnetic field. This opalescence is distinctive of a solution containing J aggregates. At this moderate temperature, however, the solution was still fluid, suggesting that the size of the aggregates was smaller than that of the fibers in the gelated solution, and that they did not form a network structure. Therefore, the J aggregates could rotate in the solution. When the J aggregates grew with decreasing temperature in a magnetic field, the molecules in the aggregates were sufficient for magnetic alignment ($N \approx 20000$) and, hence, were magnetically aligned. Further growth of the fibers induced the solution to transform into a gel. As a result, the gel was constructed from highly oriented fibers. However, in the sample prepared using procedure (3), where the heated solution was immediately placed in a magnetic field without cooling, although J aggregates were grown in the magnetic field, oriented fibers were not obtained. This can be explained by the rapid gelation process induced by a rapid initial cooling rate of the solution. In this sample, therefore, the fibers grew quickly and formed a network structure before the fibers were magnetically aligned.

In conclusion, an aqueous solution of 1,1′-diethyl-2,2′-quinocyanine bromide (PIC-Br) containing highly concentrated counter ions, provided by NaCl, was prepared by heating the solution at 90 °C. Upon cooling the solution to room temperature, the solution transformed to a gel-like state. Optical microscopy revealed that fiber-shaped J aggregates formed a network structure in the gelated solution. The gelation process strongly depended on the cooling rate of the solution. By cooling the solution to room temperature in a 10 T magnetic field, highly oriented J aggregates in the gelated solution were obtained. Without any additional treatment, the alignment of the fibers was preserved after the gelated solution was removed from the magnetic field. The estimated dichroic ratio of the J-band for the magnetically oriented fibers was 2.5. In addition, because gelation is not unique to PIC-Br, the technique that we developed in this study to magnetically align the J aggregates should be applicable to other molecules. We are currently investigating similar gelation behavior in J aggregates of other cyanine dyes and porphyrin derivatives and their magnetic alignment.

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