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Self-oriented pseudoisocyanine J-aggregates in solution

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Highly oriented fiber-shaped J-aggregates of pseudoisocyanine (PIC) molecules were prepared by simply growing the aggregates in a narrow glass cell, which allows evaporation of the solution in one direction.

J-aggregates of organic dye molecules are characterized by a narrow, intense absorption band that is red-shifted with respect to monomer absorption. This absorption band, called a J-band, is due to a highly ordered transition dipole moment of the constituent molecules that leads to a delocalization of excitons upon optical excitation. Pseudoisocyanine (PIC) molecules form fiber-shaped J-aggregates, and orientation of molecules within such aggregates has been extensively studied.[1–12] Aligning these fiber-shaped J-aggregates is important from a fundamental scientific viewpoint and for potential device applications. Due to the ordered transition dipole moment within J-aggregates, highly oriented fiber-shaped J-aggregates exhibit a large dichroism in their polarized absorption spectra. From the dichroic absorption spectra, the internal molecular orientation in the J-aggregates can be determined.[9] In turn, the large dichroic ratio and the narrow, intense J-band enable device applications, such as polarizing optics and nonlinear optical devices. It has been demonstrated that J-aggregates can be aligned by using centrifugal force,[9] solution flow,[10] and magnetic fields.[13] Here, we have developed a simple method to prepare highly oriented PIC J-aggregates in solution by using a self-orientation process.

A sample solution (1 mM) was prepared by dissolving PIC-Br (Hayashibara Kankou Shikiso Kenkyusho) into distilled water by stirring the heated solution (50 °C) for 24 h. The solution was placed in a narrow glass cell (Fig. 1). The cell was constructed from two square glass plates separated by two 3 μm-thick rectangular copper spacers placed along two sides of the upper glass plate to prevent evaporation of the solution through those two sides. The other two sides of the cell were open to the air, allowing evaporation of the solution only through those two sides.

After the cell was filled with the sample solution, an aggregation process was observed between crossed polarizers using a polarized light microscope (Olympus, BX-60). It was observed that aggregation started at the edge of the open sides, and that aggregates grew in the direction perpendicular to the edge of the cell (Fig. 2a). Fig. 3 shows images of the aggregates obtained using a high-magnification objective (100×, NA = 1.3). Individual

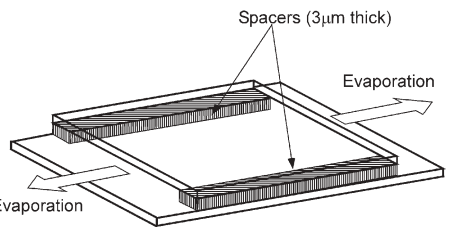

Fig. 1 Narrow glass cell for growing self-oriented J-aggregates. The upper square glass plate is 22 mm wide and 0.17 mm thick.

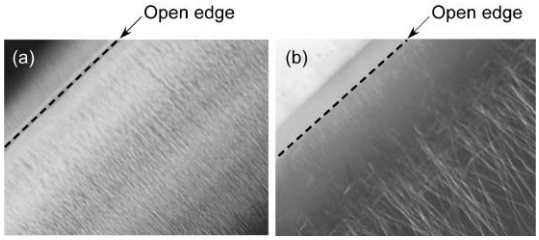

Fig. 2 (a) Cross-polarized image (150 × 200 μm^2) of oriented fiber-shaped J-aggregates prepared from a high-concentration solution (1 mM), (b) Cross-polarized image (150 × 200 μm^2) of randomly oriented J-aggregates from a low-concentration solution (0.5 mM).

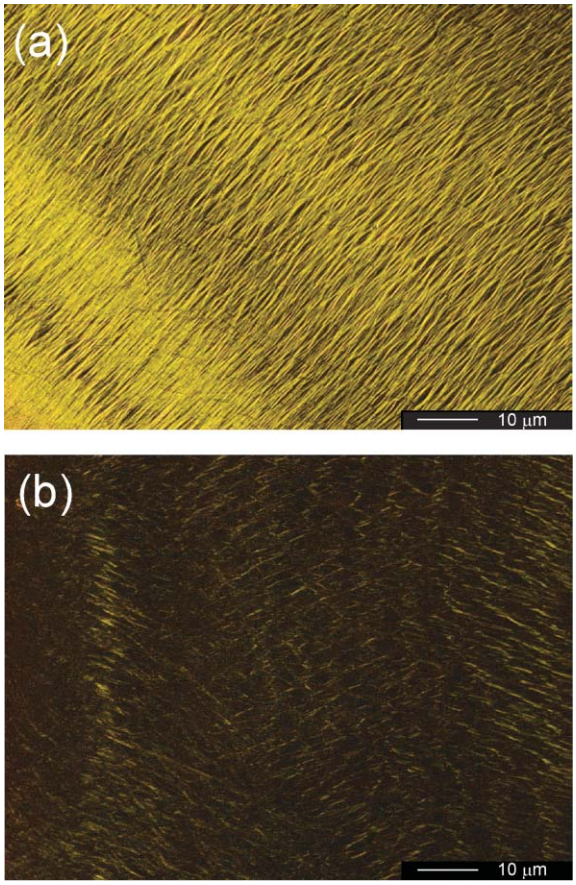

Fig. 3 (a) Cross-polarized image of self-oriented J-aggregates. The polarizer and analyzer are horizontal and vertical to the image, respectively. The microscope objective was a 100× oil immersion objective (NA = 1.3). The open edge of the cell is at the lower left of the image and perpendicular to the fiber direction. (b) Cross-polarized image after 45° clockwise rotation of the sample.

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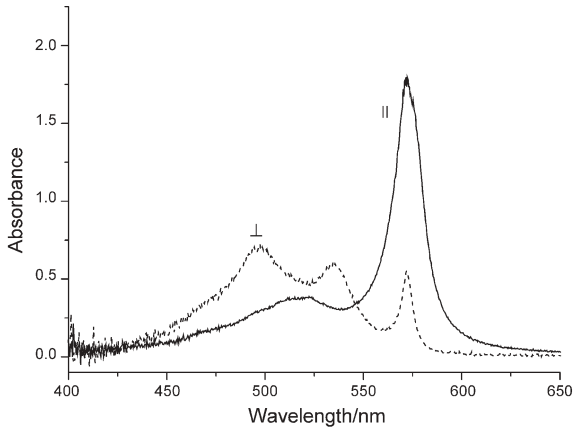

Fig. 4 Polarized absorption spectra of self-oriented PIC J-aggregates measured by using polarized light parallel (solid curve) and perpendicular (dashed curve) to the fiber direction.

fiber-shaped aggregates were observed when the fiber direction was tilted by 45° with respect to both the polarizer and analyzer (Fig. 3a). A 45° rotation of the sample resulted in a dark image, indicating a high degree of orientation of the fibers (Fig. 3b). The fibers were more than 20 μm long, and about 250 nm wide. The length and width are similar to those of fibers grown in a polymer (polyvinylsulfate) thin film prepared by spin-coating a polymer containing aqueous PIC solution on a substrate.[11,12] These highly oriented fibers were formed in the area between the edge of the cell and about 3 mm from the edge. Further evaporation of the solution induced fibers to adhere to each other. After the solution was completely evaporated, a sheet-like architecture composed of adhered fibers was formed on the surface.

Fig. 4 shows the polarized absorption spectra of the oriented fibers measured by using a spectrometer (OceanOptics, USB2000) coupled with a microscope (Olympus, BX-51). The absorption spectrum measured with light that was polarized parallel to the fiber direction showed an intense J-band at 572 nm. Rotating the light polarization by 90° (perpendicular to the fiber direction) reduced the intensity of the J-band. This polarization dependence indicates that the transition dipole moments of the constituent molecules were aligned nearly parallel to the fiber direction, as previously reported.[5–12] From these absorption spectra (Fig. 4), the estimated dichroic ratio ($Abs_{\parallel}/Abs_{\perp}$) at the J-band was 7.5. These dichroic spectra and the dichroic ratio are similar to those obtained for PIC J-aggregates oriented by using centrifugal force.[9]

The mechanism of self-orientation of the J-aggregates was considered here in terms of the solution flow and the steric interaction between the fibers. When the aggregation starts from the open edge of the cell, the dye concentration in the solution at the edge decreases, thus inducing a gradient in the dye concentration perpendicular to the edge. To compensate the gradient, the solution flows from the center of the cell to the edge. This solution flow might align the fibers in the direction perpendicular to the edge. The steric interaction between fibers also can determine the direction of fiber growth, because the density of the fibers is considerably high, as can be seen in Fig. 3a. To minimize the steric interaction, fibers grow in the same direction, namely, perpendicular to the edge of the cell.

To investigate this self-orientation mechanism, J-aggregates were then prepared from low-concentration solution (0.5 mM). Similarly to the high-concentration solution, J-aggregates grew from the edge of the cell. Reflecting the low concentration of the solution, the density of the fibers was lower than that when the high-concentration solution was used. Moreover, fibers were randomly orientated with respect to the edge (Fig. 2b). These results indicate that a high density of the fibers is essential to the self-orientation, suggesting that the steric interaction between fibers plays a dominant role in the self-orientation process.

Our results demonstrate that highly oriented fiber-shaped J-aggregates of PIC-Br in solution can be fabricated by simply evaporating the solution in one direction through the open edges of a narrow glass cell. This method will be widely applicable to align aggregates that have an anisotropic shape. Future study will include the fabrication of self-oriented aggregates of other dye molecules and an investigation of the internal molecular orientation in the aggregates by utilizing polarized absorption spectroscopy.

Notes and references

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