

Morphological characteristics of J-aggregate films of bisazomethine dyes

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Surface morphology of vapor deposited films of two bisazomethine dyes was investigated. These dyes are known to form J-aggregates or to exhibit a J-aggregate-like absorption band in vapor deposited films depending on film thickness. AFM measurement on the J-aggregate films and non-aggregate films of the diethylamino derivative showed that the J-aggregate films are composed of sub-micron crystal grains and the further crystallization is promoted by a chloroform vapor treatment. Several morphological differences were also recognized between the J-aggregate and non-aggregate films. On the basis of these observations, a model for the J-aggregate formation was proposed in terms of a nucleation process in crystallization. In the dimethylamino derivative, a thickness dependent J-aggregate-like absorption band was also found to appear in vapor deposited films. The observed similar morphological characteristics as those of the diethyl derivative is considered to support the model for the J-aggregate formation.

Key words: J-aggregates, vapor deposited film, atomic force microscopy, morphology, bisazomethine dyes

1. INTRODUCTION

Bisazomethine dyes derived from diaminomaleonitrile together with dialkylaminobenzaldehydes [1] have been studied as a material for opto-electronic applications because of their red fluorescence and high molecular absorption coefficient [2-5]. These dyes are also known to form J-aggregates or to exhibit a J-aggregate-like absorption band in vapor deposited films. In the case of dye **1**, shown in Fig. 1, a stable J-aggregate band appears

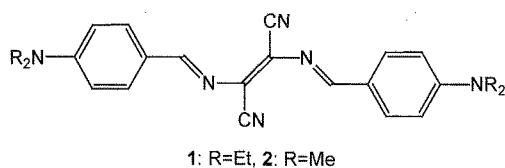


Fig. 1 Chemical structure of bisazomethine dyes.

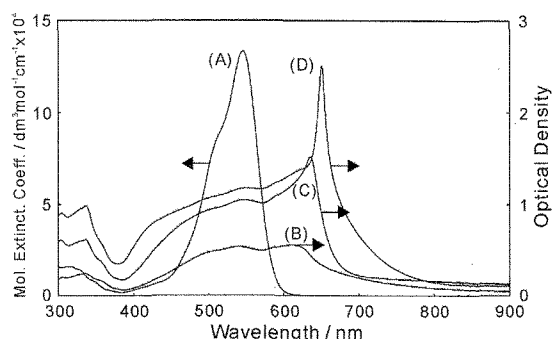


Fig. 2 Absorption spectra of **1** (A) in chloroform and vapor deposited films: film thickness (B) 600 Å, (C) 1200 Å and (D) 1500 Å.

around 650 nm depending on film thickness [6]. Fig. 2 illustrates the absorption spectra of **1** in chloroform as well as in vapor deposited films with various thickness. **1** exhibits its absorption maximum at around 550 nm in chloroform. A new sharp absorption band appears at around 650 nm depending on the film thickness. This band was characterized by J-aggregates by several optical properties including electroabsorption spectra [6]. The J-aggregate band was also found to be stable against both moisture and heat treatment [7]. However the intensity of the J-aggregate band decreases by exposing chloroform vapor; whereas the intensity of the diffraction peaks of the film increases. These results suggest that the J-aggregates are considered as a meta-stable phase.

In this study, the formation mechanism of the J-aggregates of **1** was explained based on morphology of the vapor deposited films by means of atomic force microscopy (AFM). The vapor deposited films of **2** were also investigated in absorption spectra and film morphology.

2. EXPERIMENTS

Bisazomethine dyes **1** and **2** were obtained by the reported procedure [1]. Vapor deposited films were prepared onto a glass substrate using a conventional vacuum deposition equipment under high vacuum condition (about 3.0×10^{-4} Pa). A deposition rate and film thickness were monitored by a Ulvac CRTM-6000 quartz crystal deposition controller and film thickness was confirmed by a Sloan Dektak IIA surface profiler. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 20 spectrophotometer. Vapor treatment

was performed in a sealed beaker using chloroform as a solvent. AFM images were recorded on a SII SPI-3800 probe station with a SPA-400 multi-function unit. The scan was carried out in the DFM mode with a SI-DF-20 microcantilever.

3. RESULTS AND DISCUSSION

3.1 Morphology of the vapor deposited films of **1**

Fig. 3 shows AFM images of 1500 Å-thick J-aggregate films as well as 600 Å-thick non-aggregate films of **1**. They were found to be quite different in morphology. In the J-aggregate films, there are prismatic grains of which surfaces appear to be soft and curved. On the other hand, many small grains in a block shape were recognized in the 600 Å-thick non-aggregate films. Their surfaces appear to be solid as compared with those of the J-aggregate films. The difference was also observed in grain boundaries. The J-aggregate films exhibited the unclear grain boundaries in comparison with that of the 600 Å-thick non-aggregate films.

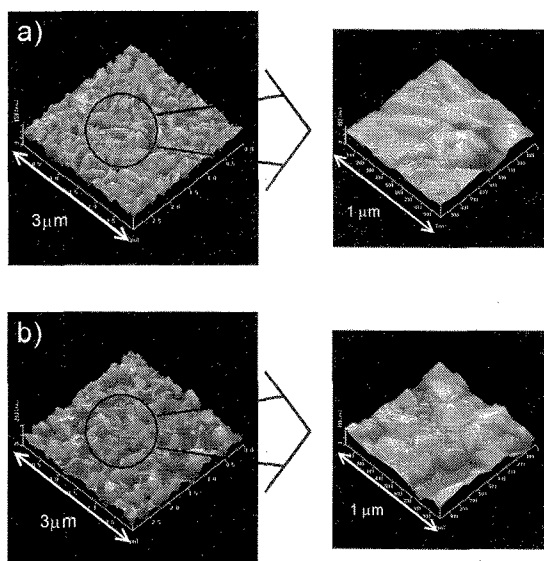


Fig. 3 AFM images of (a) J-aggregate films (1500 Å) and (b) non-aggregate films (600 Å) of **1**.

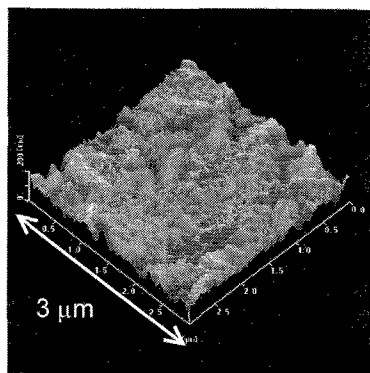


Fig. 4 An AFM image of non-aggregate films (1500 Å) of **1**.

Fig. 4 shows the morphology of 1500 Å-thick non-aggregate films of **1**. The thick non-aggregate films

can be prepared at a deposition rate of more than 25 Å/s. The remarkable difference was observed in the grain size. The grain size in the J-aggregate films was found to be in the range of 150 to 500 nm, but quite small grain texture was recognized in the thick non-aggregate films.

The effect of a chloroform vapor treatment on the film morphology is described in Fig. 5. The J-aggregate band decreases by a chloroform exposure and the further crystallization of the film is simultaneously promoted [6]. The grain surface of the film after vapor treatment was clearly characterized by a solid appearance with clear-cut grain boundaries. The significant difference was also obtained in the texture. The J-aggregate films showed heterogeneous texture composed of the prismatic grains and the unclear grain boundaries, but after vapor treatment, it changes to fine-grained texture. These morphological changes are in good agreement with the experimental result that the promotion of crystallization was performed by a chloroform vapor treatment.

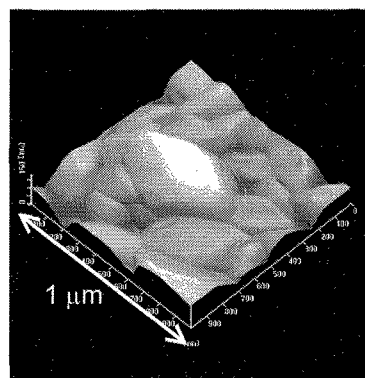


Fig. 5 An AFM image of J-aggregate films (1500 Å) of **1** after a chloroform vapor treatment.

The present AFM observation revealed that the J-aggregate films showed heterogeneous film texture with soft and curved grains and unclear grain boundaries. On the other hand, fine-grained and homogeneous texture with the solid grain surface was observed in the non-aggregate films. On the basis of these findings, the formation mechanism of the present J-aggregates is considered in terms of the nucleation mechanism of crystallization in the next section.

3.2 Consideration of the J-aggregate formation

The crystallization process is generally understood to be divided into two steps: a nucleation step and a crystal growth step [8,9]. Before nucleation, many kinds of small aggregates are considered to exist. They are called prenucleation aggregates. These aggregates should be in equilibrium with a non-aggregate state as described in Fig. 6. One or several aggregates that can gain the activation energy for nucleation should generate nuclei. Nucleation usually occur for the thermally stable crystalline phase. But a great number of kinetic factors could also make it possible to generate meta-stable and/or un-stable polymorphic phases. In the present dye films, at the beginning of the deposition the nucleation of the stable crystalline phase and the subsequent crystal

growth would occur to give rise to non-aggregate films characterized by homogeneous and fine-grained texture. After a certain degree of the grain growth, the surface energy of the grains and boundaries would allow to exist the meta-stable state corresponding to the J-aggregates. Therefore the present J-aggregates can be ascribed to one of the prenucleation aggregates. The crystallographic analysis of **1** actually suggested that a portion of the crystal structure would contribute to the J-aggregates [10]. This is considered to support the proposed formation mechanism. The proposed mechanism was then examined by experiment. Additional deposition of the dye in 1000 Å-thick was carried out on a 500 Å-thick non-aggregate film. The resulted 1500 Å-thick film showed the same optical as well as morphological properties as the 1500 Å-thick J-aggregate films prepared in the normal condition. This result clearly indicated that the J-aggregates were generated on the non-aggregate state. But the rate of deposition to form the J-aggregates in vapor deposited films would also suggest that the aggregates correspond to a super-cooling state. We need thus further experiments and discussions for the confirmation of the proposed mechanism for the J-aggregate formation.

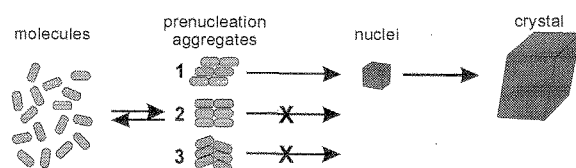


Fig. 6 Schematic representation of crystallization process.

3.3 Aggregate formation of **2** in vapor deposited films

Fig. 7 shows absorption spectra of **2** in chloroform and in vapor deposited films with various thickness. In solution, the absorption maximum is detected at around 535 nm. The absorption band was broadened in the thin deposited films. A new bathochromic band appears depending on the film thickness. In the 1500 Å-thick film the absorption maximum of the new band is found at round 608 nm. This band would also indicate the J-aggregate formation as same as **1**.

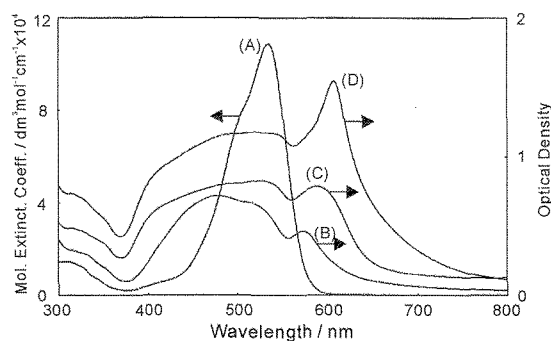


Fig. 7 Absorption spectra of **2** (A) in chloroform and vapor deposited films: film thickness (B) 500 Å, (C) 1000 Å and (D) 1500 Å.

The film morphology of 500 Å and 1500 Å-thick

films are depicted in Fig. 8. In the 500 Å-thick film, the growth of small grains were observed. On the other hand, grains in a needle shape, that resembles the habit of single crystals of **2** [10], were recognized in the 1500 Å-thick film. The grain boundaries were found to be slightly unclear. This observation is considered to support the consideration upon the aggregates formation of **1** described in 3.2.

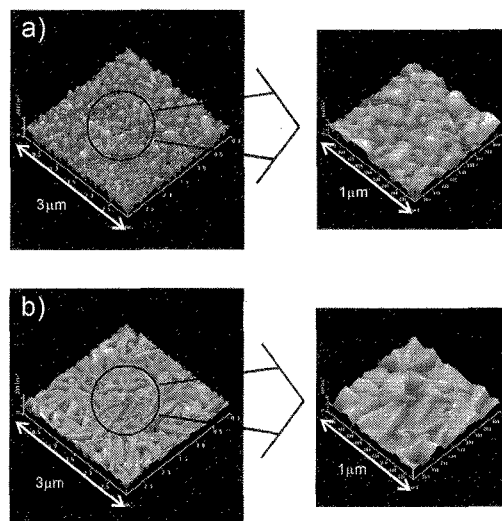


Fig. 8 AFM images of the vapor deposited films of **2**: film thickness (a) 500 Å and (b) 1500 Å.

4. CONCLUSION

This study is summarized as follows:

- 1) There is a significant difference in the film morphology of the J-aggregate films and non-aggregate films of bisazomethine dyes. The J-aggregate films exhibited heterogeneous texture composed of soft grains and unclear grain boundaries; whereas homogeneous texture was observed in the non-aggregate films.
- 2) The J-aggregates are considered to originate from one of the prenucleation aggregates and may only form on a stable crystalline phase.

5. ACKNOWLEDGEMENT

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