

## Optical Properties of J-aggregates in Vapor Deposited Films of a Bisazomethine Dye<sup>†</sup>

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A bisazomethine dye derived from diaminodicyanomaleonitrile with 4-diethylaminobenzaldehyde has attracted attention as a red emitter for organic electroluminescent devices. We found J-aggregate formation in vapor deposited films of this non-ionic dye although it is widely believed that the ionicity is essential for J-aggregate formation. In this report, we present a characterization of the films using X-ray diffraction technique and their optical properties including an electroabsorption measurement, which confirms that its sharp absorption peak (J-band) arises from Frenkel excitons. The stability of the J-aggregates was also demonstrated by time dependence and heat treatment, but a degree of the J-aggregates can be easily controlled by an exposure to chloroform vapor.

Key words: J-aggregates, vapor deposited film, optical properties, electroabsorption spectroscopy, bisazomethine dye

### 1. INTRODUCTION

A bisazomethine dye **1** shown in Fig. 1 is derived from diaminodicyanomaleonitrile together with 4-diethylaminobenzaldehyde [1, 2]. Since **1** exhibits an intense red fluorescence in solution as well as in solid state, it has been studied as a material for organic electroluminescent devices [2, 3]. **1** has been known to show drastic color and spectral changes from solution to solid state. We found the dye forms J-aggregates in vapor deposited films although it is widely believed that the ionicity is essential for J-aggregate formation. This dye has several advantages for fundamental research as well as application of J-aggregates: (1) it is possible to prepare large films of J-aggregates using a vapor deposition technique. (2) the films are very stable against both moisture and heat treatment. (3) a degree of J-aggregates can be easily controlled by an exposure to chloroform vapor. In this report, we investigated the optical properties and stability of J-aggregates of **1** as well as a characterization using X-ray diffraction technique.

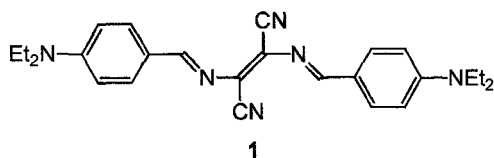


Fig. 1 Chemical structure of **1**.

### 2. EXPERIMENTAL

Dye **1** was obtained by the reported procedure [2]. Vapor deposited films were prepared on a glass substrate using a conventional vacuum deposition equipment. Film thickness was measured by Sloan Dektak IIA. UV/Vis absorption spectra were recorded on a Shimadzu UV-3100PC spectrophotometer. Heat treatment on vapor deposited films was carried out in the

conventional oven. Vapor treatment was performed in a sealed beaker using chloroform as a solvent. X-ray diffraction measurement was carried out by a Rigaku RAD-IIIB diffractometer using CuK $\alpha$  radiation (1.8 kw). Electroabsorption measurements were performed using a homemade setup consist of a Si photodiode, a Xe lamp, a JASCO CT-25 monochromator, a SRS SR810 Lock-in amplifier, a HP 8116A function generator and a Matsusada Precision HCOR-10B2 amplifier. The sample for electroabsorption measurement was prepared on an ITO glass substrate and then deposited semi-transparent Al electrode (200 Å). An electric field of  $6.0 \times 10^4$  Vcm<sup>-1</sup> was applied between ITO and the electrode.

### 3. RESULTS AND DISCUSSION

#### 3.1 J-aggregate formation in vapor deposited films

Fig. 2 shows absorption spectra of **1** in chloroform and in vapor deposited films with various thicknesses. **1** has its absorption maximum at around 550 nm in chloroform solution. In the 600 Å thick film a broad and bathochromic absorption band as compared with that in solution is observed in the visible region. A new sharp absorption band appears at longer wavelength depending on the film thickness. The absorption maximum of this new band is found at around 650 nm in the 1500 Å thick film. The shape and location of the band suggest J-aggregate formation in the vapor deposited films of **1**.

J-aggregates are low-dimensional aggregates of molecules known to exhibit extraordinary optical properties as compared to those of an isolated molecule [4, 5]. The most typical optical property of J-aggregates is its characteristic narrow and intense absorption band in the longer wavelength region. The electronic states of J-aggregates are generally explained using low-dimensional Frenkel excitons, result from intermolecular interactions based on a certain arrangement of molecules [6-8].

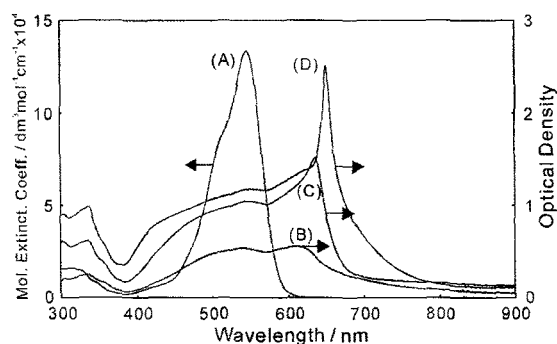


Fig. 2 Absorption spectra of 1 (A) in chloroform and vapor deposited films: film thickness (B) 600 Å, (C) 1200 Å and (D) 1500 Å.

Fig. 3 shows X-ray diffraction diagram of the vapor deposited films of 1. Several diffraction peaks were clearly observed and these peaks were well indexed by the data of single crystals of 1 [9]. This indicates that the vapor deposited films of 1 is characterized by almost the same crystalline phase as that of the single crystals. Fig. 4 illustrates temperature dependence of the absorption spectrum of the 1500 Å thick films. The band was found to shift toward 657 nm at 80 K. This spectral shift is considered to result from contraction of the intermolecular distance at low temperature, because the intermolecular excitonic interactions are significantly dependent on the distance between molecules [6]. These experimental results are in good agreement with the band characteristics caused by Frenkel excitons. We then made an attempt to determine the band character directly by the experiment described in the next section.

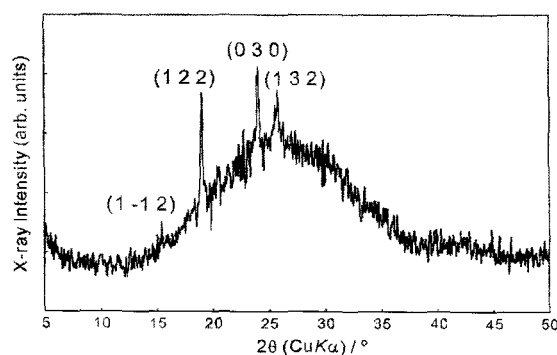


Fig. 3 X-ray diffraction diagram of 4100 Å thick films of 1.

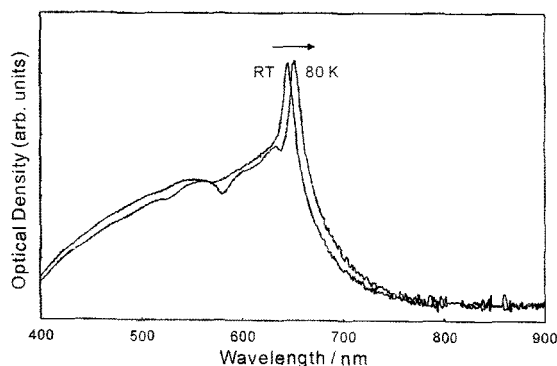


Fig. 4 Temperature dependence of the absorption spectra of 1500 Å thick films of 1.

### 3.2 Electroabsorption measurements

Electroabsorption (EA) spectroscopy, measured using an electric field to modulate the absorption, is usually used to determine the character of the excited states: the first and the second derivative-like features of the spectrum correspond to Frenkel excitons and charge-transfer (CT) excitons, respectively [10, 11]. Fig. 5 (a) and (b) show the EA spectrum of the 1500 Å thick film and the first derivative of the absorption spectrum, respectively. The EA spectrum around 650 nm consists of only the first derivative component of the absorption spectrum. This is direct evidence that the present J-band arises from Frenkel excitons. In Fig. 5 (b), a part of the spectrum under 635 nm is enlarged for easy comparison between the EA and the first derivative spectra. Although they qualitatively agree with each other well, there is a quantitative difference in the relative intensities between the J-band and the band around 600 nm. Generally, intensity of EA signal due to Frenkel excitons is dependent on an angle between transition dipoles and the applied field. Therefore, it is expected that the transition dipoles of the band around 600 nm are more tilted to the substrate than that of the J-band.

On the other hand, in EA measurements on ionic J-aggregates, the second derivative-like spectrum is known to appear around J-band [12-15]. The feature is not due to CT excitation, but due to Frenkel excitons coupled with a motion of counter ions [15]. Therefore, it is impossible to investigate a nature of the excited states in ionic J-aggregate by means of EA spectroscopy. The EA spectrum in Fig. 5 demonstrates that J-aggregates of a non-ionic dye is by far suitable for investigation of the intrinsic properties of low-dimensional Frenkel excitons because obscurity due to counter ions can be perfectly eliminated.

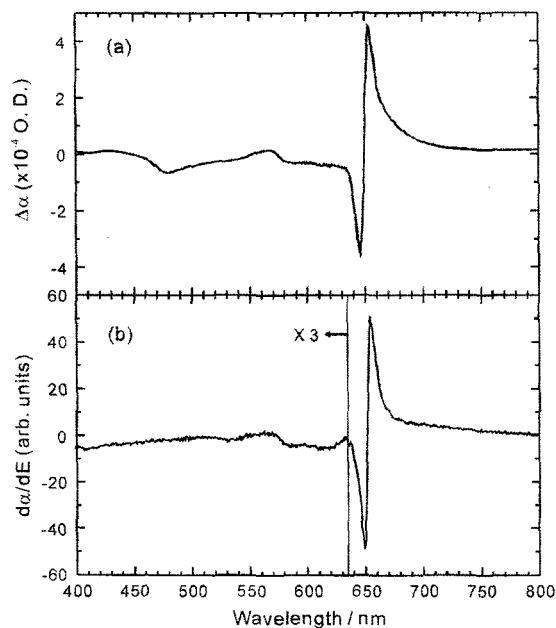


Fig. 5 (a) Electroabsorption and (b) the first derivative of absorption spectra of the 1500 Å thick film of 1.

### 3.3 Stability of the J-aggregate films

The present J-aggregate films are very stable against moisture and heat treatment, whereas one of serious

problems of ionic J-aggregates is instability. Fig. 6 illustrates the time dependence of the absorption spectra of the J-aggregate films. The films were placed under dark and ambient condition for 3, 6 and 9 days after deposition. The J-band was found to shift slightly toward the longer wavelength. However the spectral shift is *not significant* and no more change was observed in the film placed under the above condition for more than 9 days. The influence of heat treatment on the J-aggregate films was also investigated. Fig. 7 depicts the absorption spectra of the film after deposition and after heat treatment at 373 K for 1 min, 10 min and 60 min. In this experiment, the J-band was also found to shift very slightly to the longer wavelength. Although the reason for the small band shifts has not been understood, these experimental results obviously demonstrate the stability of the J-aggregate films of **1**. This is an advantage of the present J-aggregate films for fundamental research as well as applications in addition to the very easy preparation method, in contrast to other J-aggregate films reported so far.

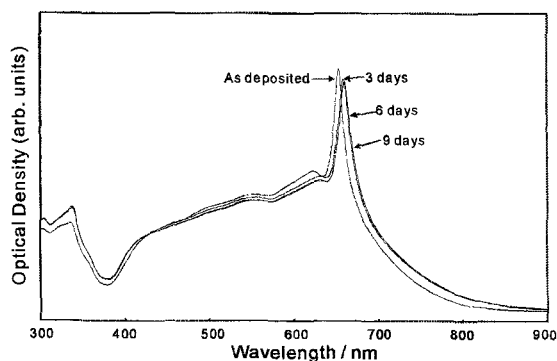


Fig. 6 Time dependence of the absorption spectra of 1500 Å thick films of **1**.

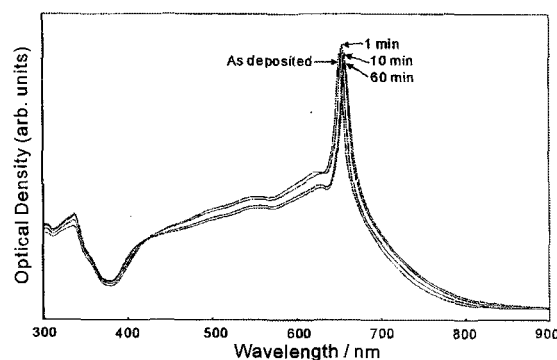


Fig. 7 Spectral change of 1500 Å thick films of **1** on heat treatment at 373 K.

Intensity of the present J-band was, however, found to decrease after an exposure of chloroform vapor as shown in Fig. 8. In this figure, several isosbestic points indicate that the vapor deposited film consists of two phases and the vapor treatment induce phase transition from one to another. At the same time, the vapor treatment improves intensity of the X-ray diffraction and peak width. Therefore, those phases can be considered to be the stable single crystal phase and the metastable crystalline phase, i.e. J-aggregates phase. Unfortunately,

the mechanism of J-aggregate formation and the structure of the J-aggregate film are not yet clear, but will be the subject of future investigations.

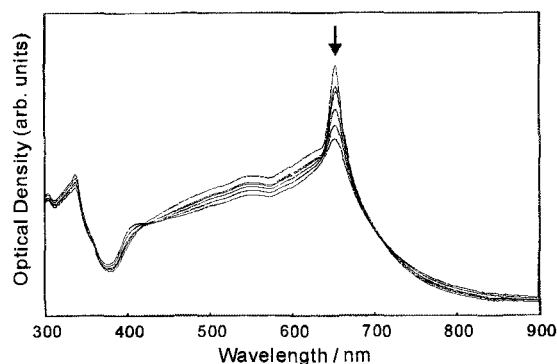


Fig. 8 Spectral change of 1500 Å thick films of **1** on chloroform vapor treatment. The spectra show in order from the top, as deposited, treatment after 10min, 1h, 2h, 4h and 19h.

#### 4. CONCLUSION

This study is summarized as follows:

- 1) We found J-aggregates formation in vapor deposited films of non-ionic dye.
- 2) Although the J-aggregate films are very stable against both moisture and heat treatment, the J-aggregates are considered to be a metastable state.
- 3) The dye **1** allows us to investigate the intrinsic properties of J-aggregates changing a degree of J-aggregates by the vapor treatment.

#### 5. ACKNOWLEDGEMENT

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<sup>†</sup>The present text and figures include a part of our paper (S. Matsumoto et al., *Chem. Commun.*, 1910-1911, 2003) and are adapted by the permission of the Royal Society of Chemistry.

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