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J-Aggregates in vapor deposited films of a bisazomethine dye†

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This is the first report of J-aggregate formation of a non-ionic bisazomethine dye in vapor deposited films; this dye allows us to prepare easily large homogeneous and very stable J-aggregate thin films and to investigate intrinsic properties of low-dimensional Frenkel excitons.

J-Aggregates are low-dimensional aggregates of molecules, where intermolecular interactions based on a certain arrangement of molecules lead to a characteristic narrow and intense absorption band,[1] a large optical nonlinearity[2] and an ultrafast decay of photoexcitations.[3] Because of these optical properties they have attracted considerable attention as materials for electro-optical devices,[4] as well as photographic sensitizers.[5] For any kind of applications, it is of great importance that large homogeneous and stable films can be easily obtained. Of course, these features are favorable for fundamental research on J-aggregates as well. In most reports on J-aggregates in the solid state, films were prepared from a mixed solution of dye and other matrix materials using spin-coated or Langmuir–Blodgett techniques. Recently, Dähne *et al.* reported J-aggregate formation in spin-coated films prepared from a dye solution without any other materials.[6,7] Plekhanov *et al.* pointed out that the spin-coating of a cyanine dye solution is a suitable method for stable and homogeneous J-aggregate films.[8] On the other hand, J-aggregate formation of merocyanine dyes in vapor deposited films was also reported. However, the vapor deposited films have to be immersed in phosphate solution[9] or be exposed to amine vapor[10] in order to form J-aggregates. All dyes mentioned above are ionic or in ionic states in J-aggregate films. Counter ions were found to affect molecular aggregation and/or the electronic structures of J-aggregates.[6,11] Unfortunately, these effects have not been clearly understood. In this communication, we report the successful formation of J-aggregates of a non-ionic dye in vapor deposited films without any other treatment, and characterization of their optical properties including an electroabsorption measurement.‡

A bisazomethine dye **1** derived from diaminomaleonitrile together with 4-diethylaminobenzaldehyde[12] has been studied as a material for organic electroluminescent devices because of its red fluorescence in solution as well as in the solid state.[13] Dye **1** shows a remarkable spectral change from solution to the solid state. Fig. 1 depicts absorption spectra of **1** both in chloroform and in vapor deposited films with various thicknesses. 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 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. This band was found to shift towards 657 nm at 80 K. Since the intermolecular interactions are strongly dependent on the distance between molecules,[14] the present shift is considered to result from contraction of the intermolecular distance. Furthermore, the vapor deposited films are characterized by almost the same crystalline phase as that of single crystals of **1**[15] by X-ray diffraction measurements. These experimental results are in good agreement with the characteristics caused by Frenkel excitons. These J-aggregate films are extremely stable so that no significant change in absorption spectra is observed even after one year's preservation at ambient conditions or after thermal treatment at 373 K for 1 hour. Intensity of the present J-band was, however, found to decrease with several isosbestic points by exposing to chloroform vapor as shown in Fig. 2, whereas intensity of the diffraction peaks increased on exposure. Therefore, we consider that the aggregate is ascribed to a metastable crystalline state, and that the J-aggregate films consist of a stable single crystal phase and a metastable crystalline phase. However, the mechanism of J-aggregate formation is not yet clear, but will be the subject of future investigations. The emission spectrum of 1500 Å thick films has a peak in the red light region: it is found at around 660 nm with a shoulder at around 690 nm. The spectral shape is slightly dependent on the excitation intensity. A similar dependence is also observed in ionic J-aggregates, and was attributed to a strong exciton–exciton interaction.[16]

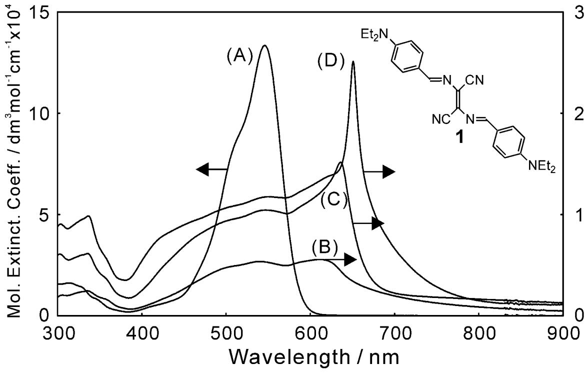

Fig. 1 Absorption spectra of **1** (A) in chloroform and vapor deposited films: film thickness (B) 600 Å, (C) 1200 Å and (D) 1500 Å.

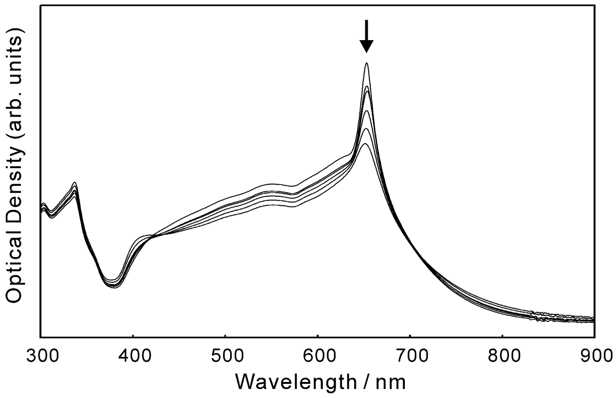

Fig. 2 Spectral change of 1500 Å thick films of **1** on chloroform vapor treatment. The spectra show in order from the top (indicated by the arrow), as deposited, treatment after 10 min, 1 h, 2 h, 4 h and 19 h.

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† Dedicated to the great dye chemist, the late Professor Masaru Matsuoka

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Electroabsorption (EA) spectra, measured using an electric field to modulate the absorption, are usually compared with the first and the second derivative of the absorption spectra to determine the character of excited states; the first and the second derivative-like features correspond to Frenkel excitons and charge-transfer (CT) states, respectively.[17] Fig. 3 (a) and (b) show the EA spectrum of the 1500 Å thick film of **1** and the first derivative of the absorption spectrum, respectively. Obviously the EA spectrum over 550 nm consists of only the first derivative component, and is evidence that the J-band originates from Frenkel excitons. In Fig. 3(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, the intensity of the EA signal due to Frenkel excitons is dependent on the angle between the 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 the J-band.[18,19] The feature is not due to CT excitation, but due to Frenkel excitons coupled with the motion of counter ions.[19] Therefore, it is impossible to investigate the nature of the excited states in ionic J-aggregates by means of EA spectroscopy. The EA spectrum in Fig. 3 demonstrates that J-aggregates of a non-ionic dye are very suitable for investigation of the intrinsic properties of low-dimensional Frenkel excitons because obscurity due to counter ions can be completely eliminated.

In conclusion, a non-ionic dye **1** allows us to prepare large homogeneous and stable J-aggregate films and to investigate the intrinsic properties of Frenkel excitons by EA spectroscopy. Furthermore, an easy synthesis of **1** and easy preparation of the films by conventional vapor deposition should be a great advantage for various applications and fundamental research on J-aggregates. The characterization of structures and electronic states of the present J-band will be reported in detail elsewhere.

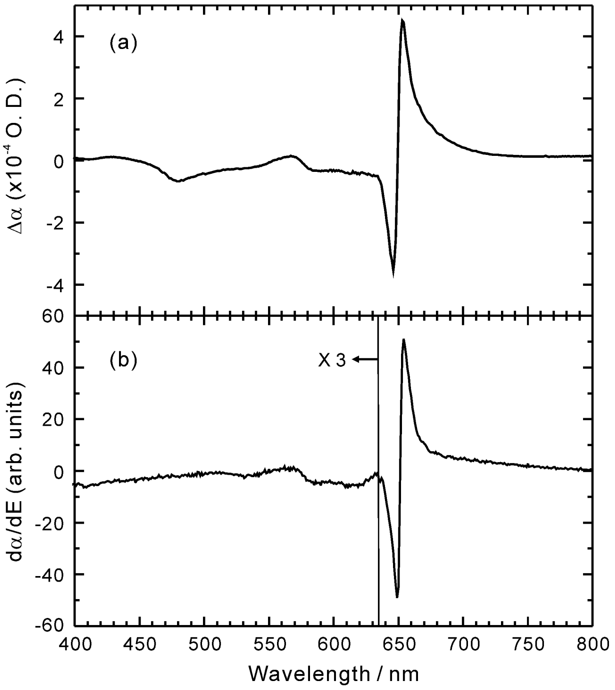

Fig. 3 (a) Electroabsorption and (b) the first derivative of absorption spectra of the 1500 Å thick film of **1**.

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Notes and references

‡ Dye **1** was synthesized by the reported procedure.[8] Vapor deposited films were prepared on a glass substrate by conventional vacuum deposition equipment. Film thickness was measured by Sloan Dektak IIA. UV/Vis and emission spectra were recorded on a Shimadzu UV-3100PC spectrophotometer and a Shimadzu RF-5301PC spectrofluorophotometer, respectively. X-Ray diffraction was measured by Rigaku RAD-IIIB (Cu–Kα, 1.8 kW). EA measurements were carried out using a homemade setup that consists of a Si photodiode, a Xe lamp, a JASCO CT-25 monochromator, a SRS SR810 Lock-in-Amp, 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 6.0×10^4 V cm^{-1} was applied between ITO and the electrode.

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