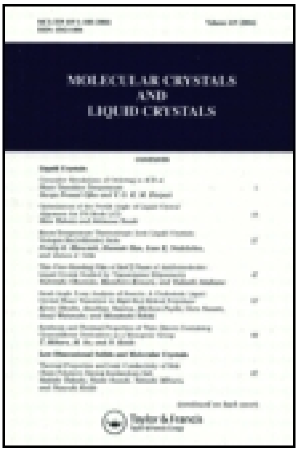

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Reversible Change Between Monomeric Form and J-Aggregate in Vapor-Evaporated Merocyanine Film

Yohei Aritoshi [a], Kuniyuki Nitta [a], Yasukiyo Ueda [a] & Zhenguo Ji [b]

[a] Fac. Eng., Kobe Univ., Rokko, Nada, Kobe, 657-8501, Japan
[b] Mat. Sci. Eng., Zhejiang Univ., Hangzhou, 310024, China

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Reversible Change Between Monomeric Form and J-Aggregate in Vapor-Evaporated Merocyanine Film

YOHEI ARITOSHI, KUNIYUKI NITTA, YASUKIYO UEDA and ZHENGUO JI*

Fac. Eng. Kobe Univ., Rokko, Nada, Kobe 657-8501, Japan and
**Mat. Sci. Eng. Zhejiang Univ. Hangzhou 310024, China*

Merocyanine (MD18) film prepared by vapor-evaporation formed J-aggregate (JA) by exposuring to dimethyl amine (DMA) aqueous vapor and/or soaking into aqueous solution containing various metallic ions. The reversible change between JA and monomeric/dimeric forms was observed by heat-treatment and acid treatment in HCl aqueous solution.

Keywards merocyanine film; J-aggregate; reversible aggregation

INTRODUCTION

Recently, self-organizing organic dyes, which can form various molecular aggregates from the simple dimer to three-dimensional structure, have attracted interesting attention both from the basic and application researches. Among them, merocyanine dyes (MD) form unique molecular aggregates, so-called J-aggregate (JA). JA is characterized by narrow absorption band (J-band) red-shifted from that of a monomeric dye. The wide researches are carrying out on its application of optical recording medium and non-linear optical materials. Nowadays, artificial control of J-band has been very important.

In this work, we prepared MD film by vapor evaporation method and investigated the reversible change between monomeric form and J-aggregate in film.

EXPERIMENTAL

3-Carboxy-methyl-5-[2-(3-octadecyl-2-benzothiazolinylidene) ethylidene]-2-thioxo-4thia-zolidinone (MD18) was used as MD dye. MD18 was evaporated onto a pyrex glass substrate from a fused silica glass crucible in a vacuum of 1.33 x 10^{-3} Pa. MD18 films were exposed to a vapor of 10 v/v% dimethyl amine (DMA) aqueous solution and/or were soaked into 0.5 mol/l various metallic salt solution such as KCl, $CaCl_2$, $SrCl_2$, $MgSO_4$ and $AlCl_3$. The structure and absorption characters of the films were investigated by atomic force microscope (AFM) and visible absorption spectrometer.

RESULTS AND DISCUSSION

Figure 1(a) shows the spectral change of MD18 film during DMA aqueous vapor treatment. Broad absorption peaks with maximum at 480 nm and 550 nm appear in the absorption spectrum of as-deposited film. These are assigned to dimeric and monomeric bands, respectively. By DMA aqueous vapor treatment, the intensity of these peaks decreased gradually and new red-sifted absorption peak with narrow half width appeared at 620 nm. This is assigned to JA band of MD18 because the fluorescence spectrum of the film excited at 550 nm indicated a single emission peak with a small Stokes shift. When the JA film prepared by DMA aqueous vapor treatment was heat-treated at the temperature below 40 ℃ in atmosphere, there was no spectral change in the absorption spectrum. When the temperature of heat-trreatment elevated at above 50 ℃, on the other hand, the intensity of J-band decreased and monomeric and dimeric bands appeared as shown in Fig.1(b). It is obvious that JA is decomposed to monomeric and dimeric forms by heat-treatment. XPS measurement of the

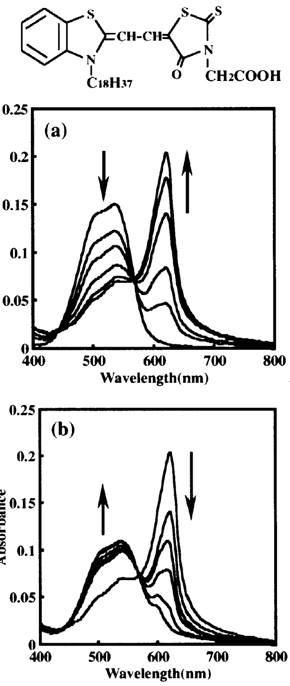

FIGURE 1 Molecular structure of MD18 and spectral change during DMA vapor treatment (a) and thermal treatment(b).

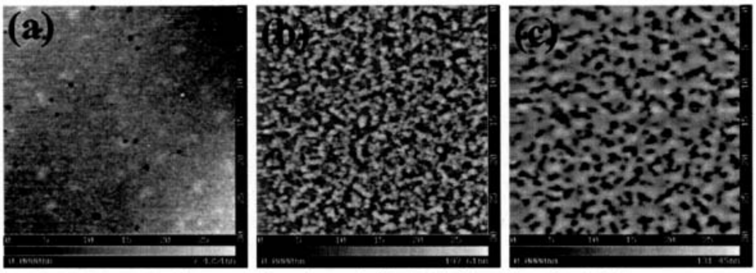

FIGURE 2 AFM images of as-deposited MD18 film (a), after DMA vapor treatment (b) and after thermal treatment(c).

film indicated that MD18 film included both DMA and H_2O molecules after treatment[1]. Therefore, it is considered that the decomposition of JA is caused by the vaporation of DMA. It is noteworthy that an isosbestic point is observed at 570 nm in both spectra during DMA vapor treatment and heat-treatment. This indicates that the formation and decomposition of JA by these treatment is reversible. In fact, the reversible process between the formation and decomposition is investigated over ten times.

As-deposited MD18 film is composed of an amorphous layer and its surface is very smooth shown in Fig.2(a). On the other hand, there are small granules with about 100 nm in height and 3 μm in diameter in the film after DMA vapor treatment, as shown in Fig.2(b). Each granule is corresponding to JA of MD18. When the film composed of JA is heat-treated at 50 ℃, its surface roughness decreases but is different from that of as-deposited film as shown in Fig.2(c). However, the morphological change between re-treatment by DMA vapor and spontenious heat-treatment is reversible as well as the change of optical character.

It is well known that metallic ion was added to sub-phase when JA was formed in LB film. In this work, we tried to form JA by soaking vapor-evaporated film into the metallic salt solution. Prior to soaking the film, the ability of JA formation from solution is checked using five kinds of metallic salt. When the metallic salt aqueous solution with 0.5 mol/l is added into MD18 methanol solution (0.5×10^{-5} mol / 50 ml), small precipitates appears in the solution. The absorption properties of the solution containing precipitates are dependent on the kind of metallic ions shown in Fig.3. In the case of KCl and $AlCl_3$, there are monomeric and dimeric bands in the spectra. On the other hand, J-band appears sharply by the addition of $MgSO_4$, $CaCl_2$ and $SrCl_2$ solution. These findings indicate that divalent metallic ion is effective in JA formation of MD18 and that the absorption peaks of JA are controllable by the choice of metallic ions

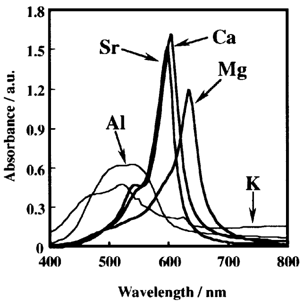

FIGURE 3 Absorption spectra of MD18 methanol solution added various metallic ions.

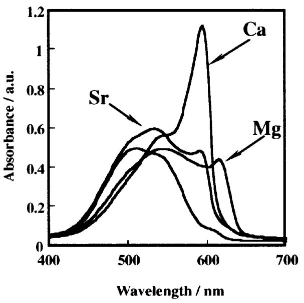

FIGURE 4 Absorption spectra of MD18 film after soaking into various metallic salt solution.

added. Reffering above results, MD18 film is soaked into $MgSO_4$, $CaCl_2$ and $SrCl_2$ solution with same concentration. Figure 5 shows the absorption spectra of the films after soaking. The absorption spectra of the films after soaking into $MgSO_4$ or $SrCl_2$ solution show the co-existence of monomeric, dimeric forms and JA. JA formation is inperfect in this case. On the other hand, J-band appears sharply at 600 nm after soaking into $CaCl_2$ solution. It seems that JA formation in solid state such as film depends on the size of metal ion , maybe hydrated, which penetrates into the film. JA film prepared by soaking into $CaCl_2$ solution was stable thermally even if it was heat-treated at 80 ℃ for 30 min. Structural change from JA to monomeric/dimeric forms was performed by acid treatment of the film. When the JA film was soaked into 5 mol/l HCl aqueous solution, J-band in the spectrum disappeared. Formation and decomposition of JA in this system was also revercible because J-band appeared again after re-soaking into $CaCl_2$ solution. It is believed that carboxy-methyl group of MD18 is dissociated to carboxyanion and counter cation such as metallic ions combines neibouring MD18 molecules each other when JA is formed. Therefore, we concluded that decomposition of JA by acid treatment is caused by exchange from metallic ion to hydrogen ion

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