

메로시아닌 색소 LB 단분자막의 광메모리 특성에 관한 정성적 연구

論文

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A Qualitative Study of Photomemory Characteristics of the LB Monolayer Films of Merocyanine Dye

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Abstract - The structural changes of the merocyanine monolayer LB(Langmuir Blodgett) films were investigated. These changes were compared with the typical changes of the molecular structures of merocyanine solutions. The structural changes of quinoid/benzenoid were attained by exposure to atmosphere gases(HCl gas, NH₃ gas). The photoisomerization was not observed for the monolayer LB film due to their state of M_{trans}. But we could obtain the cis/trans photoisomerization characteristics reversibly, after the films were changed to MH⁺_{trans} structure by exposure to HCl gas. We also found that the cis/trans photoisomerization of the LB monolayer films show the memory characteristics.

Key Words : Monolayer LB(Langmuir Blodgett) Film, Merocyanine Dye, Solvatochromism, Gas Sensor, Photomemory

1. Introduction

The concept of molecular electronic device is a familiar one to the researchers in various fields. Especially, those in the electronic field who have much interest in finding the functional behavior of organic molecules, which can be aggregated as a monolayer film by using the Langmuir-Blodgett(LB) deposition method.

In this paper, we chose merocyanine dye molecule which is photosensitive organic material to find the photomemory characteristics at the state of LB monolayer films. Merocyanine dyes of the stilbazolium betain type(abbreviated as M) have been extensively studied because of their extreme solvatochromic properties.[1] The molecular structure of this type of merocyanine M can be easily changed by solvents. And this structural change can be observed by its color change. This phenomena is called the solvatochromic property. In a non-polar solvent the dye has the quinoid structure like Fig.1(a), whereas in a highly polar solvent it is changed to the benzenoid structure like Fig.1(b). Moreover the oxygen is easily be protonated by taking H⁺ ion from the solvent which changes it to the MH⁺ structure as in Fig.1(c).[2] It is known that the main reason of these solvatochromic properties is the hydrolic bondings between the dye molecules and the solvents.[3]

The paper of Tsukada shows the M in the water or in the alcohol both of which have the benzenoid structure

(Fig.1(b)) and their point of the maximum absorption wavelength(λ_m) moves to the short wavelength region(blue shift), but in chloroform which has weak hydrolic bonding with molecules, the point of the maximum absorption wavelength(λ_m) moves to the long wavelength region(red shift).[4] Kuder found that M in the solvent of pH 10 shows quinoid structure where maximum absorption wavelength(λ_m) was 440[nm], but as the pH value decrease, the benzenoid structure increase, and the maximum absorption wavelength(λ_m) moves to 370[nm].[5] According to Steiner, it was found that the merocyanine molecule at the MH⁺_{trans} state,(Fig.1(c)) which was obtained by protonation of oxygen can be changed to MH⁺_{cis} isomer state by the irradiation of light. And also this MH⁺_{cis} molecule can be changed to M_{cis} state by deprotonation in a solvent with high pH. This M_{cis} state can be changed again to M_{trans} state by irradiation of light or by application of heat. But the reverse process of isomerization from the M_{trans} to the M_{cis} state is impossible.[6]

Fig.2 shows the schematic diagram of the changes of the molecular structure of merocyanine dye. If these changes can be obtained at the state of solid films, it can stimulates interests for their application to the photo-active devices on the electronic fields.

In this paper, the MC₁₆ molecules were synthesized which have a long alkyl chain(C₁₆H₃₃) at the site of R of the M molecule in Figure 1. Using these molecules, the monolayer LB films were deposited. And we investigated whether the structural changes of this M solution can be occurred at the state of solid films. The solvatochromic and the photoisomeric characteristics of these monolayer LB films were measured. To obtain the solvatochromic effect

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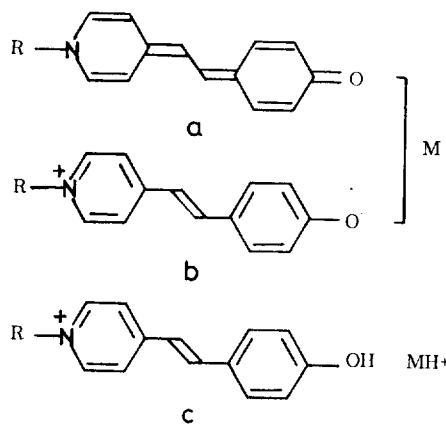


Fig. 1 The Molecular structures of the merocyanine dye.
 (a) quinoidal form (b) benzoidal form
 (c) protonated form

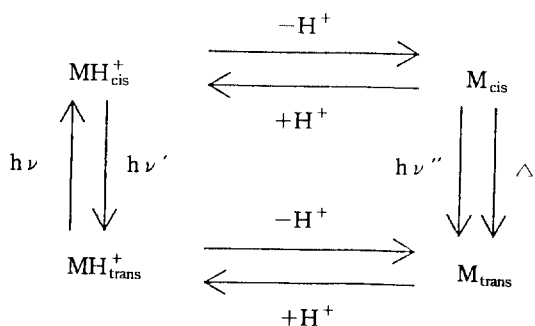


Fig. 2 The structural changes of the merocyanine molecules induced by the solvatochromism and the photoisomerization

we used the atmosphere gases instead of solvents. The spectral changes of the LB films were measured, when the atmosphere gas was changed to NH₃ gas and vice versa. In order to find the photoisomerization the spectral changes of the LB films were measured by the irradiation of light after the exposure to HCl gas.

As a result, the typical solvatochromic characteristics of M can also be obtained at the MC₁₆ monolayer LB films by using the atmosphere gases instead of the solvents. The photoisomerization was also attained by the irradiation of light after the LB films were changed to the MH_{trans}⁺ state by exposure to HCl gas atmosphere. And these films show the photomemory characteristics that each photoisomerized structure was maintained until the light of other wavelength was irradiated. This photomemory characteristic can be applied to the memory device, if it can be detected by the electrical measurement. Now we are trying to detect this photomemory characteristic by using the displacement current measuring method.[7]

2. Experiments

2.1 Materials

The MC₁₆ molecules were prepared by attaching the alkyl chain of C₁₆H₃₃ at the site of R- in Fig.1 which is the typical structure of the stilbazolium betain merocyanine(M) molecules. The solution was prepared by dissolving the MC₁₆ molecules with chloroform. The solution was spreaded on the water-surface, and the LB films were prepared by the vertical dipping method at the surface pressure of 20 mN/m. As the substrates, we used slide glasses and quartz glasses which were treated to be hydrophilic by immersing it in KOH solution. The films were made as the Y-type film at the dipping and lifting rate of 5 mm/min.. And the temperature of the water was maintained to 18 degree.

2.2 Solvatochromism

The sample cell for measuring the solvatochromic properties was prepared by using transparent acryl plate as shown in Fig.3, which has two valves, one that flows acid gas and the other basic gas, respectively. The dimension of the cell was 50x50x1 mm. The gas atmospheres were maintained during the measurements by closing the valves after flowing each gases from 30% HCl and 28% ammonia solution. Reference glass plate and the LB film were placed in the cell, and the absorption spectral changes were measured using a halogen lamp(Nikon type2) and a monochromater(Nikon G250, chopper 2 type).[8]

2.3 Photoisomerization

The absorption spectra of MC₁₆ LB films were taken just after the deposition and which were compared with the absorption spectra of the films taken after the irradiation of lights. As the light source of irradiation, we used the 500[mW] Xenon lamp(OSHIO electro mechanics ,UI-501). And the lights of 280[nm] and 400[nm] were selected through interference filters. After the irradiation MC₁₆ LB films were moved in the spectrophotometer(UV-2100, Shimadzu Co.) maintaining the dark state, and the absorption spectra were measured immediately. The protonation of the as deposited LB films were executed by exposing to acid gases, and the absorption spectra of these protonated films were measured. Also, the changes of the absorption spectra after the irradiation of lights were measured.

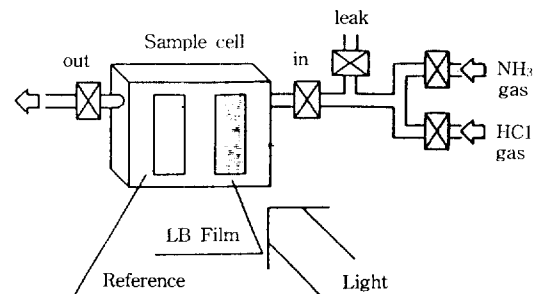


Fig. 3 A sample cell used to measure the absorption characteristics of LB films in the gas atmosphere

3. Results and Discussion

3.1 Solvatochromism of LB Films

Fig.4 shows the changes of absorption spectra of 23 layer MC₁₆ LB film by exposing to HCl gas. A solid line is taken just after deposition, which has a broad peak near 500[nm]. By exposure to HCl gas, the absorption peak near the 500[nm] was decreased and the absorption peak near the 380[nm] increased as a dotted line. These results shows almost all the merocyanine molecules of LB films were changed from the M_{trans} to the MH'_{trans} structure.[6] Furthermore, when the atmosphere gas was changed from the HCl gas to the air, the absorption spectra was not changed as a dashed line. This result means that the MH'_{trans} state is stable.

Fig.5 shows the spectral changes of the 61 layer MC₁₆ LB film. As a dotted line of the figure, when the LB film was exposed to ammonia gas, absorption peak near 500[nm] was increased. When the atmosphere gas was changed from the ammonia gas to the air the spectrum returned to the almost same form(the dashed line) of the solid line. These results show that the molecules of the LB film just after the deposition have both the M_{trans} and MH'_{trans} structure and the portion of the M_{trans} structure was increased by exposing to ammonia gas but this state is unstable.

From Fig.5 we found that the absorption of the merocyanine LB film was largely changed at the wavelength of 500[nm] by flowing the ammonia gas. Using this 500[nm] light we tried to find the possibility of the ammonia gas sensor by placing the merocyanine LB film in the sample cell of Fig.3. As in Fig.6, by flowing ammonia gas in the cell the absorption was increased, and by flowing air in the cell the absorption was decreased. Although the time response was late, this figure shows that the merocyanine LB films can be applied to the ammonia gas sensor.

3.2 Cis/Trans Photoisomerization

The changes of the absorption spectra by irradiation of light were measured. Fig.7 shows the absorption spectra of MC₁₆ monolayer LB films. The solid line is taken just after the deposition and the dotted line is taken after the irradiation of 400[nm] light. From this figure, we found that a relatively little structural changes were occurred by the irradiation. This result is coincide with the Steiner's result about the merocyanine molecules in solution that there is no structural change by irradiation of light at the state of M_{trans}. [6] It can be explained that the photoisomerization is difficult to occur because the deposited LB film has an intermediate structure of the M_{trans} and the MH'_{trans}. This intermediate state can easily be certified by it's color change. To obtain the trans-cis photoisomerization the structure of the LB film must be changed from the intermediate state to the perfect MH'_{trans}. Fig.8 shows the MH'_{trans} structure of the monolayer MC₁₆ LB film was attained by

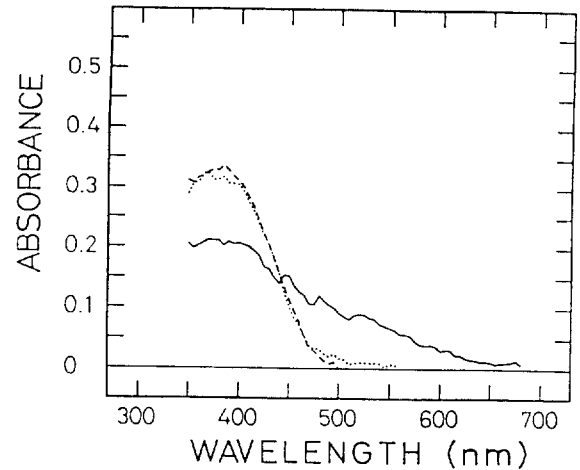


Fig. 4 Spectral changes of the MC₁₆ 23 layer LB film in HCl gas.

— : just after deposition
 : in the HCl gas atmosphere
 - - - : after changing the atmosphere gas from HCl to air

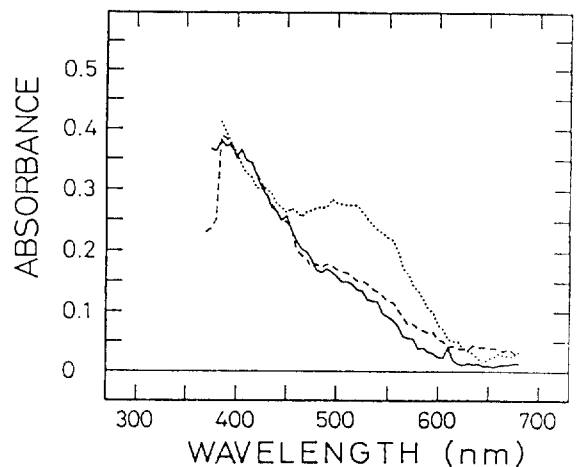


Fig. 5 Spectral changes of the MC₁₆ 61 layer LB film in NH₃ gas.

— : just after deposition
 : in the NH₃ gas atmosphere
 - - - : after changing the atmosphere gas from NH₃ to air

exposure to HCl gas. The solid line of the figure is the absorption spectrum of LB film measured just after deposition and the dotted line is for the same LB film after the exposure to HCl gas. The peak of 400[nm] was increased and the peak of 500[nm] was decreased after the exposure. From this figure, we can find the fact that the deposited merocyanine molecules is changed much closer to the MH'_{trans} state rather than the M_{trans} state by exposure to HCl gas.

This results resemble with the results of the merocyanine solution that the MH'_{trans} state which has higher possibility of photoisomerization can be obtained by using

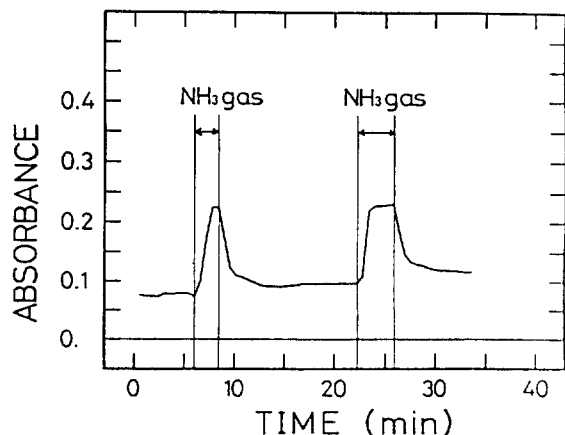


Fig. 6 Absorption change due to the injection gases(NH₃ and air), Measured at the wavelength of 500[nm] using 23 layer LB film. The vertical lines in the figure show the starting times of flowing the NH₃ gas and air

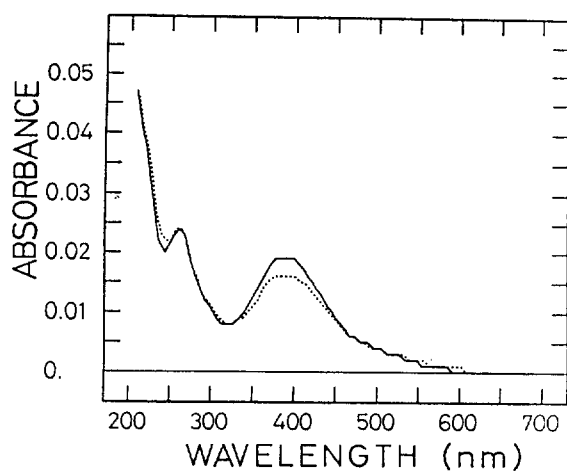


Fig. 7 Spectral changes of the MC₁₆ monolayer LB film by irradiation just after deposition
 — : just after deposition, before irradiation
 : after irradiation by 400[nm] light for 10 min

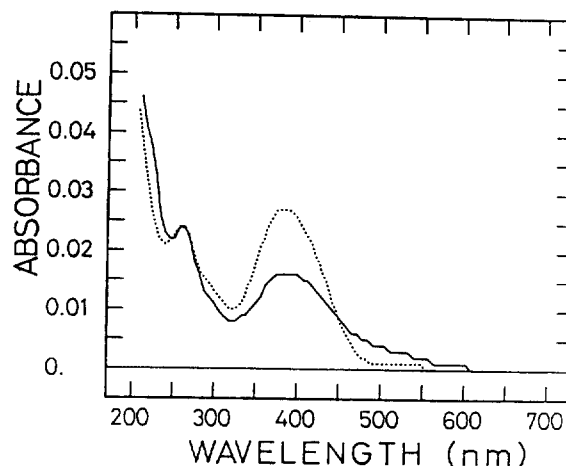


Fig. 8 Spectral changes to show the MC₁₆ monolayer LB film becomes to MH⁺_{trans} state after exposure to HCl gas.

— : just after deposition
 : pull out the film to air after exposure to HCl gas for 90 sec

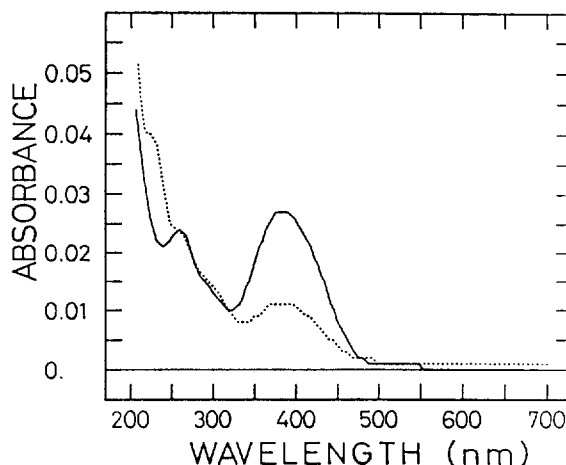


Fig. 9 Spectral changes to show the MC₁₆ monolayer LB film by irradiation of 400[nm] light

— : after pull out from HCl gas
 : after irradiation of 400[nm] light for 30 min

the solvents.[6] For the merocyanine LB films we used HCl gases instead of solvents. Fig.9 shows the spectral changes by the irradiation of 400[nm] light to the monolayer LB film which was changed to MH⁺_{trans} state as shown at Fig.8. We can know the fact that the LB films at the state of MH⁺_{trans} can easily isomerize to MH⁺_{cis} state as the same manner with solution. The peak of absorption spectrum of 400[nm] was decreased. Fig.10 shows the result of the case that the 280[nm] light was irradiated to the LB film which was changed to MH⁺_{cis} state by 400[nm] light. The peak of absorption spectrum of 400[nm] was increased again. It shows that the LB films on the state of MH⁺_{cis} is restored to MH⁺_{trans} state again by irradiation of light.

Fig.11 shows the absorption spectral changes by irradiation of lights of 400[nm] and 280[nm] alternately. The

absorption peak of 400[nm] was decreased when trans to cis isomerization was occurred partially by irradiation of 400[nm] light, and the peak was increased by irradiation of 280[nm] light reversibly. And these films show the photomemory characteristics that each photoisomerized structure was maintained until the light of other wavelength was irradiated.

From these results we can summarize the structural changes of the MC₁₆ monolayer LB films. The films just after deposition has the intermediate structure of the M_{trans} state and the MH⁺_{trans} state at which the trans to cis isomerization is difficult to occur like in Fig.7. To obtain the tran to cis photoisomerization, LB film must be changed to

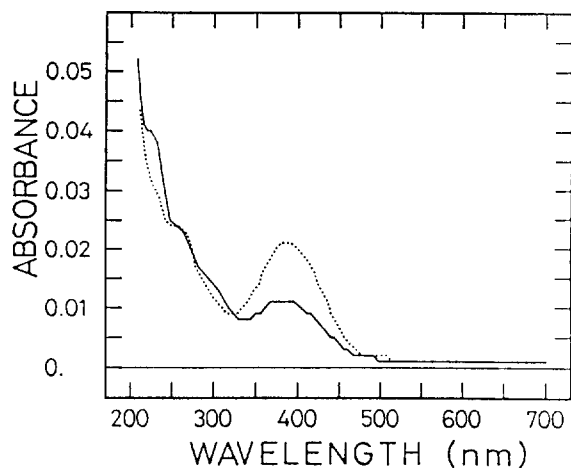


Fig. 10 Spectral changes to show the cis to trans isomerization of the MC_{16} monolayer LB film by irradiation of 400[nm] light

— : after irradiation of 400[nm] light for 30 min
 : after irradiation of 280[nm] light for 40 min

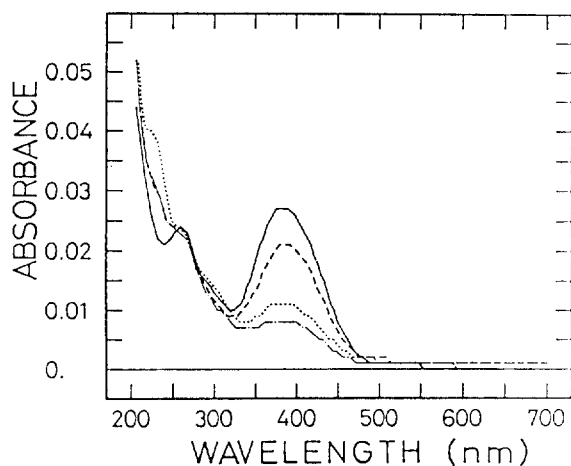


Fig. 11 Spectral changes to show the reversibility of the photoisomerization of the MC_{16} monolayer LB film

— : before irradiation
 : after irradiation of 400[nm] light for 30 min
 - - - - : after irradiation of 280[nm] light for 40 min
 - · - · - : after irradiation of 400[nm] light for 30 min

the MH'_{trans} state by using the solvatochromic property. We used HCl gas to change the LB film to the state of MH'_{trans} state like Fig.8. This MH'_{trans} state was obtained by attaching H^+ ion to LB film from HCl gas. At the MH'_{trans} state, LB film was easily changed from trans to cis by irradiation of 400[nm] light like Fig.9, and the cis to trans isomerization was also easily occurred by irradiation of 280[nm] light like Fig.10. These photoisomerizations occurred reversibly like Fig.11 and the either states has memory

characteristics in dark state.

4. Results

In this paper, the typical structural changes of the solvatochromism and the photoisomerization of the merocyanine molecules were measured in the state of monolayer LB films. The conclusions are as follow :

(1) The quinoid/benzenoid structural change of the merocyanine LB film was obtained by using the atmosphere gases, like the solvatochromism of merocyanine solutions.

(2) The possibility of an application to the ammonia gas sensor using these films was found.

(3) As-deposited LB films show a little structural changes by irradiation of lights, because it was at the intermediate state of the M_{trans} state and the MH'_{trans} state.

(4) By exposure to the atmosphere gas(HCl gas), MH'_{trans} state of the LB films were attained, and at this state LB films shows the cis/trans photoisomerization by light.

(5) Each trans and cis structure was maintained until the light of other wavelength was irradiated and this photomemory phenomena can be applied to the photomemory devices.

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