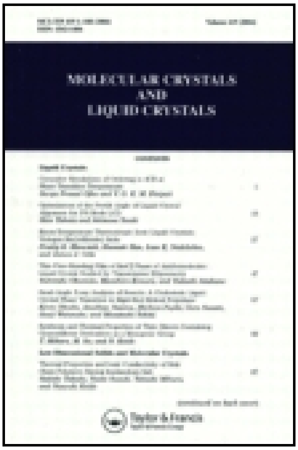

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Novel Thermochromism of Merocyanine J-Aggregate Monolayers

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Novel Thermochromism of Merocyanine J-Aggregate Monolayers

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A new thermochromic transition was observed in merocyanine dye (MD)/arachidic acid mixed monolayers with the subphase which contained cadmium and magnesium ions. Special cells were fabricated to observe the phenomenon. By heating the cell above 27.8 °C, the J-band at 620 nm changed to 595 nm irreversibly with an isosbectic point around 600 nm.

Keywords: merocyanine dye; J-aggregate; thermochromism; monolayer at the solid-water interface

INTRODUCTION

At the air-water interface, the amphiphilic merocyanine dye (MD) forms two dimensional J-aggregate assembly [1-3], which is characterized by the red-shifted sharp absorption band in comparison with the monomer band [4]. The formation of J-aggregate assembly is influenced by the counter-ion of MD which is contained in the subphase and the magnitude of the shift depends on the kind of counter-ion [2,5]. For example, cadmium ion induces the J-band at 595 nm, and magnesium at 620 nm.

This paper reports a new finding of the thermochromic transition from J-band at 620 nm (J620) to 595 nm (J595) when the subphase contained both cadmium and magnesium ions. We investigated this phenomenon in a newly-designed cell for further application to memory device or so on. In this cell, the counter-ions have enough mobility to exchange the interaction between MD-Cd and MD-Mg, which cannot be realized in the usual Langmuir-Blodgett films.

EXPERIMENTAL

We prepared mixed solution of MD and arachidic acid (AA) for 1 mM spreading solution. AA was mixed for the structure stabilization. The molar ratio of MD and AA were 2:3 and the chloroform was used as a solvent. A Kuhn type trough was used to deposit monolayers by the vertical dipping method [6]. All deposition processes were performed on two slide glasses simultaneously at 30 mN/m. As subphases, the solution of 0.5 mM $CdCl_2$ with 0.05 mM $NaHCO_3$ was used for AA monolayer, and of 1.5 mM mixture of $CdCl_2$ and $MgCl_2$ with 0.15 mM $NaHCO_3$ for MD/AA mixed monolayer. The molar ratio of $CdCl_2$ and $MgCl_2$ was 1:4. These subphases were kept at 17 °C. To make the slide glass surface hydrophobic, one AA monolayer was deposited by the up stroke. For a second layer, MD/AA mixed monolayer was deposited by the down stroke. Without taking out the slide glasses from the subphase, the subphase surface was cleaned up, and the subphase was sandwiched by the two slide glasses with a 0.12 ~ 0.17 mm thickness spacer. After this process, it is possible to take out the set of three glasses from the subphase, without leaking the subphase from the gap due to the capillarity. The subphase was bound with paraffin and the glasses were fixed together to form a cell. The schematic illustration of the cell is indicated in Fig. 1. From these procedures, we can obtain the cell with only J620 at room temperature (20 °C).

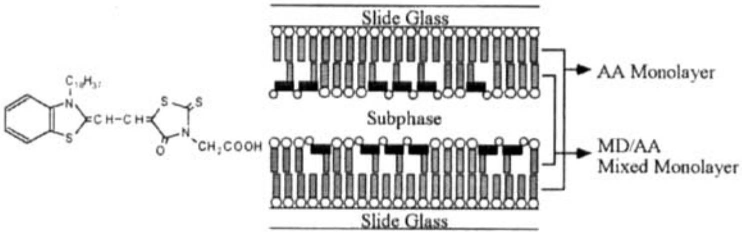

FIGURE 1 Amphiphilic merocyanine dye and the newly-designed cell for observing the thermochromic transition.

Soon after the preparation of the sample, the absorption spectrum was measured by Shimadzu UV-2100 equipped with a heating stage.

RESULTS AND DISCUSSIONS

We measured the time dependence of the absorption spectrum at various temperatures. The temperature was measured by a thermocouple located at the outside surface of the cell. Results are indicated in Fig. 2.

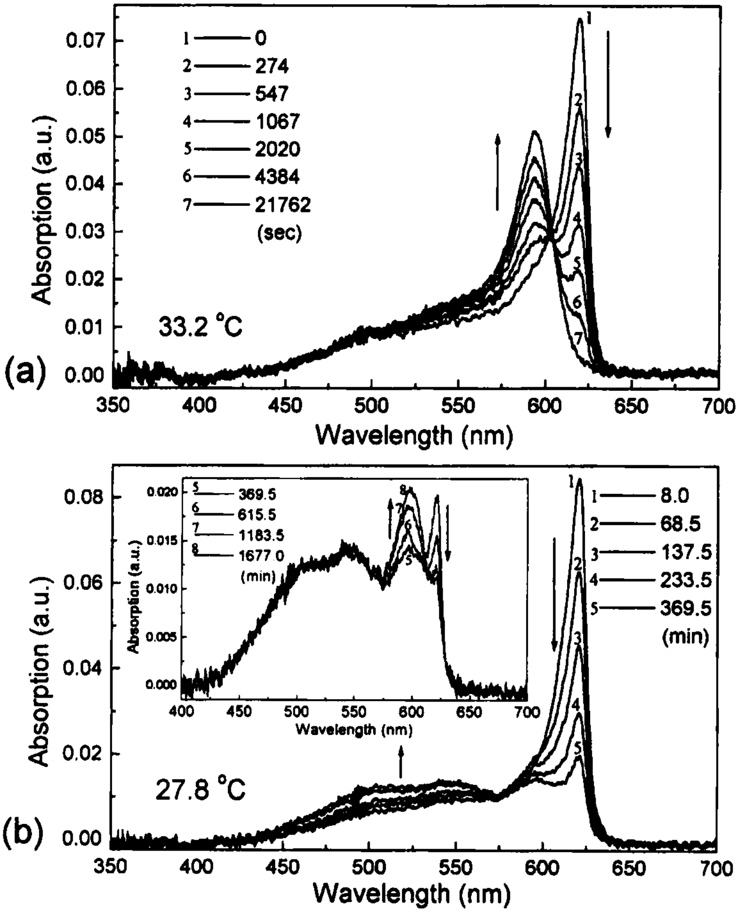

FIGURE 2 The time dependence of the absorption spectrum at (a) 33.2 and (b) 27.8 °C.

At 33.2 °C (Fig. 2 (a)), J620 changes to J595 with an isosbestic point around 600 nm. While at 27.8 °C ((b)), the dissociation of J620 to monomer (the broad band at 540 nm) is more remarkable than the J620-to-J595 transition. In this case, the transition seems to occur in two steps: The J620-to-monomer dissociation in the first step (see (b)), and the J620-to-J595 transition in the second (see the inset graph). At 20 °C, only J620 is observed and no J620-to-J595 transition occurs. After the transition, J620 was never restored again by cooling. The J620-to-J595 transition occurs above certain temperature which is located between 27.8 ~30.6 °C.

When the J620-to-J595 transition occurs, all samples show an isosbestic point around 600 nm as shown in Fig. 2 (a). This indicates that the two characteristic J-aggregate states without any other intermediate are related to this transition. The time characterizing the transition velocity was determined by extracting the J595 contribution to the whole spectra. Here the J595 contribution is assumed to be the spectrum observed at sufficiently long time, i.e. 21762 sec in Fig. 2 (a). In general case, it was observed that the characteristic time decreased with increasing temperature. It should be also pointed out that additional small transitions were obtained: One is the decrease of several tens % of the integrated spectrum from 350 to 800 nm at the beginning of the J620-to-J595 transition. The other is the transition between monomer and J595.

We reported the thermochromic transition from 620 to 595 nm of the MD/AA mixed monolayer in the newly-designed cell with the two counter-ions subphase. The origin of the thermochromism can be attributed to the change in the interaction strength between MD-Mg and MD-Cd with temperature, as the two J-bands at 620 and 595 nm coincide with the J-band of single counter-ion Mg and Cd, respectively. This mechanism is different from the heat treatment dissociation and basic vapor restoration of the MD J-aggregate in Langmuir-Blodgett films [7].

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