

# Thermochromic phase transition of merocyanine J-aggregate monolayer at the air–water interface

Noritaka Kato\*, Takeshi Araki, Yoshiaki Uesu

*Department of Physics, Waseda University 3-4-1, Okubo, Shinjuku-ku, Tokyo 169-8555, Japan*

Received 25 June 2005; received in revised form 5 October 2005; accepted 28 October 2005

Available online 5 December 2005

## Abstract

The thermochromic phase transitions of the merocyanine J-aggregate monolayers on the binary counter-ion subphases containing a pair of  $\text{Mg}^{2+}$  and  $\text{Cd}^{2+}$  ( $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase) or that of  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ( $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphase) were investigated by the visible reflection spectroscopy. The temperature of the subphase was controlled between 40 °C and a freezing temperature of the aqueous subphases. In addition to the phases of the J-band at 595 and 618 nm, a new phase of the J-band at 614 nm was found at the temperatures below 10 °C for both subphases. Although one of the ion species in the binary counter-ion subphase is different, the transition behaviors on the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  and  $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphases were almost the same, suggesting that not the atomic number but the hydrated ionic radius influences the phase transition of the merocyanine J-aggregates. © 2005 Elsevier B.V. All rights reserved.

**Keywords:** Amphiphilic dye molecule; Merocyanine; J-aggregate; Thermochromism; Phase transition; Langmuir film

## 1. Introduction

J-aggregates [1,2] are organic dye assemblies that show a bathochromic shift upon an aggregation of the dye molecules, and the shift is attributed to an exciton formation [3] in the aggregate that typically has a brick-stone work arrangement of the molecules [4,5]. The J-aggregates have been used as sensitizers of silver halide photography for long time, and various kinds of dye molecules have been found to form the J-aggregates [6]. In recent years, they attract attention as model systems for investigating the ultra-fast exciton dynamics [7], materials for ultra-fast nonlinear optical devices [8], fluorescence probes for mitochondrial membranes [9], and photoharvesting antennas for artificial photosynthesis [10].

Amphiphilic merocyanine dye (MD) molecules (Fig. 1) form a stable monolayer at the air–water interface and self-organize two-dimensional (2D) J-aggregates [11,12], resulting in a shift of the visible absorption band from 525 nm to around 600 nm. Metal ions in the subphase act as counter-ions of the hydrophilic group of MD and accelerate the formation of the J-aggregates. Various kinds of metal ions were used for assembling the

J-aggregates at the air–water interface [13–15]. Besides the intensive investigations on their fundamental properties [16], we found the thermochromic phase transition of the MD J-aggregates at the air–water interface [17–19]. The  $\text{Cd}^{2+}$  and  $\text{Mg}^{2+}$  ions in the subphase induce the J-aggregate absorption band (J-band) at 595 and 618 nm, respectively. When the MD J-aggregates are on the subphase containing both ions (binary counter-ion subphase), a reversible change in the J-band between 595 and 618 nm occurs by changing the subphase temperature, and the J-band peak wavelength exhibits a thermal hysteresis loop. The phase transition temperature depends on the molar fraction of two ions, and each phase has different molecular packing [20], i.e., this phenomenon is a structural phase transition of the 2D MD aggregate (crystal).

Our final goal is to clarify a mechanism of this phase transition, understand general requirements for controlling the molecular packing in the condensed monolayer by the counter-ions, and seek out other amphiphiles that show a similar phenomenon on the binary counter-ion subphase. So far, we have observed the phase transition using the subphase that contains  $\text{Mg}^{2+}$  and  $\text{Cd}^{2+}$  ( $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase) in a temperature range above 15 °C. The present work was devoted to the investigations of the phase transition behavior below 15 °C and the influence of the ion species to the phase transition behavior. A trough equipped with Peltier devices was made to control the subphase temperature

\* Corresponding author. Tel.: +81 3 5286 3446; fax: +81 3 5286 3446.  
E-mail address: [n.k@waseda.jp](mailto:n.k@waseda.jp) (N. Kato).

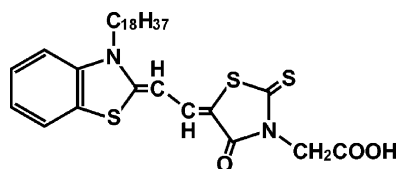


Fig. 1. Molecular structure of amphiphilic merocyanine dye.

rapidly, and the phase transitions of the MD J-aggregates on the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  and  $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphases were observed. The choice of the Zn ion was simply because the atomic number of the Zn atom is in between those of the Mg and Cd atoms.

## 2. Experimental

The MD molecules (3-caboxymethyl-5-[2-(3-octadecylbenzothiazolin-2-ylidene)-ethylidene]rhodanine, Fig. 1) were purchased from Hayashibara Biochemical Laboratory, Inc., and 1 mM of chloroform solution of MD was prepared as a spreading solution. For the counter-ions, three kinds of chlorides ( $\text{MgCl}_2$ ,  $\text{ZnCl}_2$ , and  $\text{CdCl}_2$ ) were obtained from Kanto Chemical Co., Inc. Pure water was prepared in a Milli-Q system, and its resistivity was greater than  $18\text{ M}\Omega\text{ cm}$ . Aqueous solutions of the chlorides were prepared as binary counter-ion subphases. The total concentration of the chlorides was fixed at  $0.5\text{ mM} = [\text{CdCl}_2] + [\text{MCl}_2]$ ,  $\text{M} = \text{Mg}$  or  $\text{Zn}$ , and the molar ratio  $\rho_{\text{Cd}} = [\text{CdCl}_2]/([\text{CdCl}_2] + [\text{MCl}_2])$  was fixed at 40% for both  $\text{Mg}^{2+}/\text{Cd}^{2+}$  and  $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphases. To keep the pH value of the subphases around 7, ca. 0.06 mM of  $\text{NaHCO}_3$  was added. Under this condition, after spreading the MD molecules on the subphases, the J-aggregates were formed immediately without any compression.

A simple trough without a barrier and a pressure sensor was designed according to the literature [21]. On one side of a copper plate, a thin Teflon sheet covered and a Teflon frame was fixed to form a trough (an inner size  $80\text{ mm} \times 190\text{ mm}$  and a depth of 5 mm). On the other side of the plate, eight Peltier devices were equipped, and a Peltier controller (Cell System Co., Ltd.) was connected between a dc power source (PAN 110-10A, Kikusui Electronics Corp.) and the Peltier devices to control the subphase temperature from 0 to  $40^\circ\text{C}$  at accuracy better than  $\pm 0.3^\circ\text{C}$ . The trough was placed in a chamber and the chamber was purged with  $\text{N}_2$  gas at  $0.3 \pm 0.1\text{ L/min}$  to prevent a bleach of MD molecules due to the oxidization. The spreading amount of the MD molecules was regulated to be sure that the surface pressure was below  $0.5\text{ mN/m}$ . The subphase temperature was changed step by step. Incubation was performed for longer than 15 min after each temperature change, followed by the reflectance measurement.

Because the shapes of the absorption and reflection spectra were similar [18,19], the J-band was monitored by the reflection spectrometer that provides a simple optical setup. A bundle of two optical fibers was introduced into the chamber and placed above the monolayer to observe the vertically reflected light. One fiber is for illuminating the monolayer with white light and the other one is for transferring the reflected light to the

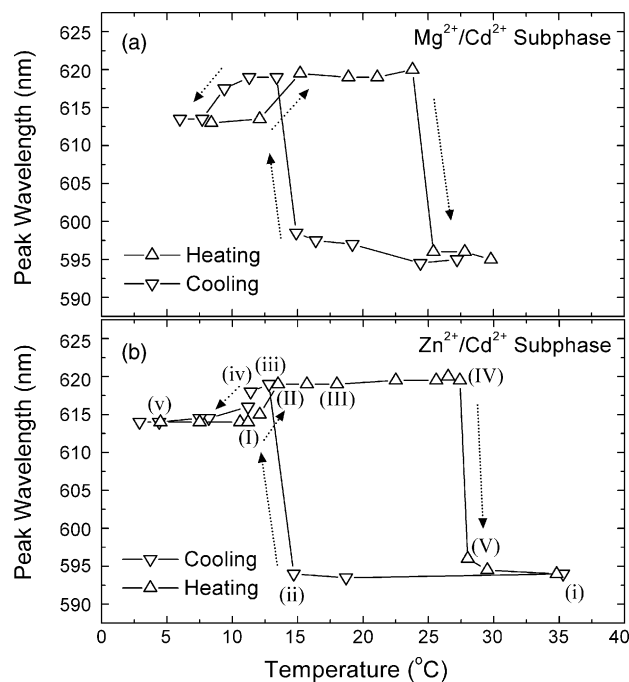


Fig. 2. Thermal hysteresis loops of the J-band wavelength of the monolayers on (a) the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase and (b) the  $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphase. Both subphases were  $\rho_{\text{Cd}} = 40\%$ . Note that the plotted wavelength was simply taken at the maximum reflectance intensity even if the different phases coexisted. Roman numerals in small letters in (b) indicate the points where the reflection spectra in Fig. 3 were observed, and those in capital letters indicate the points where the spectra in Fig. 4 were observed.

spectrometer (EPP2000, StellarNet Inc.), having a resolution of 0.7 nm.

## 3. Results and discussion

Fig. 2(a) indicates the thermal hysteresis loop of the J-band wavelength obtained from the monolayer on the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase. The MD molecules were spread at  $8.5^\circ\text{C}$ , and the J-band was observed at 614 nm, where we had not observed the J-band so far. By increasing the temperature, the J-band at 614 nm shifted to 618 nm at  $13.5^\circ\text{C}$ . Further increase of the temperature induced another J-band shift from 618 to 595 nm at  $24.5^\circ\text{C}$ . The heating of the subphase was stopped at  $30^\circ\text{C}$  and the cooling process was followed. The J-band shifted back from 595 to 618 nm at  $14^\circ\text{C}$ , and from 618 to 614 nm at  $8.5^\circ\text{C}$ . The transition temperatures of the J-aggregates on the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase are listed in Table 1. Each of the transitions ( $614\text{ nm} \leftrightarrow 618\text{ nm}$  and  $618\text{ nm} \leftrightarrow 595\text{ nm}$ ) exhibited the thermal hysteresis, resulting in a double hysteresis loop of the J-band peak position. The same double hysteresis loop was observed even if the MD molecules were spread at a high temperature, where the phase of the J-band at 595 nm was formed.

Fig. 2(b) shows the thermal hysteresis loop observed from the monolayer on the  $\text{Zn}^{2+}/\text{Cd}^{2+}$  subphase. The loop in Fig. 2(b) was observed after spreading the MD molecules at  $35^\circ\text{C}$ , but a similar loop was obtained when the MD molecules were spread at  $5^\circ\text{C}$ . In this case, the double hysteresis loop was also observed as in the case of the  $\text{Mg}^{2+}/\text{Cd}^{2+}$  subphase, and the

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