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Divalent Cation Dependent Spectral Change in Merocyanine Monolayer

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The effect of divalent cation on chromophore aggregation in a merocyanine monolayer was studied by means of spectroscopic measurements. The absorption spectra for J-aggregates were found to be controlled by the nature of metal cation.

Recently, merocyanine dyes have attracted increasing attention as potential materials for memory devices because of their sharp absorption band (J-band) in aggregate forms.[1] It is of practical importance to artificially control the structure of J-aggregate in order to construct high-density optical memory devices with dyes having different absorption peaks.

A surface-active merocyanine (MS) shown in Fig.1 has been studied both in solution and in mixed LB film, where the absorption spectra of the J-aggregates depend strongly on solvents[2] and matrices,[3] respectively. However, few attempts have been made so far to control the chromophore aggregation in the dye monolayer at air-water interface. We focussed our attention on the effect of metal cations in the subphase, which are known to promote the J-aggregate formation, and investigated cation-dependent spectral changes of J-aggregates. Here we report some preliminary results.

A chloroform solution of MS was spread on an aqueous subphase containing divalent metal chloride (pH 6.7, 25 °C) and the absorption spectra of the monolayers were measured in situ with a multichannel spectrometer of Otsuka Electronics. Figure 2 shows typical spectra on various metal ion-containing subphases (10^{-4} mol dm^{-3}) measured immediately after spreading at a low surface pressure (< 1 mN m^{-1}). The spectra on neutral subphases with no metal ions and with 10^{-4} mol dm^{-3} $LaCl_3$ are also plotted for comparison. Each spectrum was stable for several minutes except for the one with Cd^{2+}, where the absorption peak gradually shifted from 590 nm to 607 nm with time.[4] Thus, it is clear that the absorption spectra are closely correlated with the nature of metal cation. Especially, it should be noticed that J-band shifts to lower wavelength as the ionic radius of the metal increases,[5] which suggests that the absorption spectra for J-aggregates may be controlled by the size of metal cation.

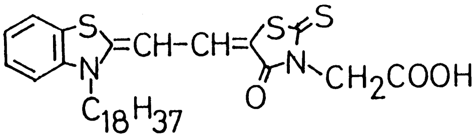

Fig.1. Chemical structure of the merocyanine dye (MS).

The effects of metal concentration and

surface pressure on the absorption peak were also examined. For each divalent cation, a clear J-band was observed when the metal concentration was above 10^{-6} mol dm^{-3} and the peak wavelength was independent of the concentration, while for La^{3+}, J-band tended to appear at 607 nm at low concentration (10^{-7} mol dm^{-3}). With increasing surface pressure, the absorption peak shifted to 607 nm for Mg^{2+}, Zn^{2+}, and Mn^{2+}. No noticeable change was observed for other metal ions on film compression.

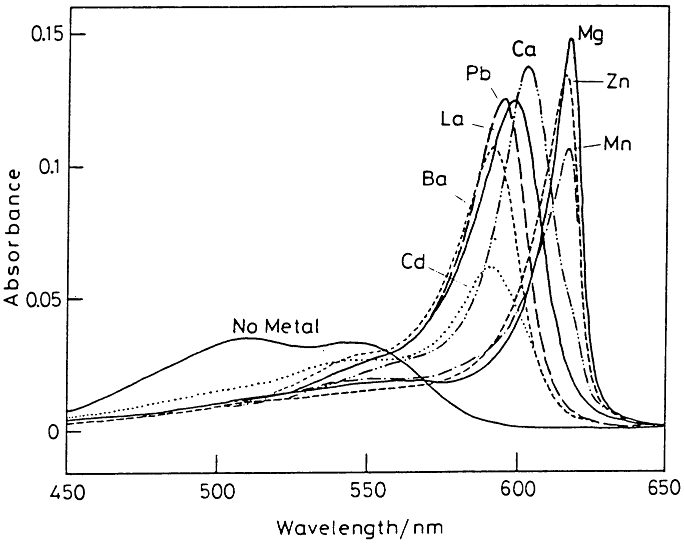

Fig.2. Absorption spectra of merocyanine monolayer on various metal ion-containing subphases.

These results indicate that the structure of chromophore aggregation in the dye monolayer is formed immediately after spreading the dye solution, responding to the metal cation in the subphase. Presumably, several types of J-aggregate exist in equilibrium in the dye monolayer, and the equilibrium constants between them depend strongly on the nature of metal cation. The surface pressure-dependent spectral shift observed for Mg^{2+}, Zn^{2+}, and Mn^{2+} is attributable to some change in such equilibrium by film compression. In any event, the present finding opens a way to control the structure of J-aggregate by using appropriate cations in the subphase. However, the mechanism of the change in aggregate structure (geometry and aggregation number) caused by the nature of metal cation cannot be decisively interpreted so far, and detailed studies, including theoretical calculation with explicit consideration on the effect of metal ion, are now in progress.

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5) Absorption maximum for each spectrum; 617 nm (Mg^{2+}), 615 nm (Zn^{2+}), 617 nm (Mn^{2+}), 590 or 607 nm (Cd^{2+}), 603 nm (Ca^{2+}), 598 nm (La^{3+}), 595 nm (Pb^{2+}), 590 nm (Ba^{2+}).

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