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A SIMPLE METHOD FOR THE SPECTRAL CONTROL OF MEROCYANINE FILM

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A simple method for the spectral control of merocyanine films has been developed.

The optical properties of organic dye films attract much attention in relation to their application to photoelectric device or photography. Development of a method for the spectral control of organic dye films may be essentially required. However, there have been very few reports concerned with the method.[1] The purpose of this letter is to report an attempt for the spectral control of merocyanine films recently developed.

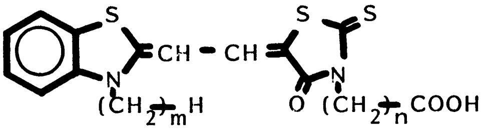

Fig. 1. General chemical structure of merocyanine dyes.

A red-shifted band such as a J-aggregate has been expected to give enhanced photoelectric effect.[2] In addition, the J-aggregate is effective for photographic sensitization of silver halide crystals.[3] The so-called J-aggregate is characterized by a red-shifted band and zero Stokes shift fluorescence.[4] Merocyanine dyes have generally been recognized as a family of dyes forming almost no J-aggregate. Recently, we have synthesized a group of photoactive merocyanine dyes (M(m,n)), whose general chemical structure is shown in Fig. 1, according to the procedures of Brooker *et al.*[5] with some modifications. The values of m are 1, 2, 3, 4, 5, 6, 7, 8, 10, 12, 14, 16, 18, and 20, and the values of n are 1, 2, and 3. The $M(10 \geqq m,1)$ are water-soluble. Substitution of a longer hydrocarbon chain in the chemical structure (see Fig. 1) allows the water-insoluble dyes to form the J-aggregate in the presence of water molecules. A solution-cast M(m,n) film was prepared according to the procedures previously described elsewhere.[6] We have found the consecutive changes in the absorption spectra of water-insoluble M(m,n) films in an alkaline or a neutral aqueous solution, probably due to the gradual formation of chromophore aggregation induced by dipping the dye film into the solution.[6] For example, Fig. 2 illustrates the typical absorption spectral changes of M(12,1) film on a glass plate (1 x 4 cm in size) immersed in doubly distilled water, whose pH was adjusted to 7.0 by addition of small quantity of KOH and periodically checked during the course of immersion, as a function of time. Buffering of water was avoided to prevent adsorption of the buffering agents on the surface of the dye film, since it has been recognized that the presence of the agents tends to inhibit the formation of an ohmic contact at dye film-metal interface in preparing the M(m,n) photodiodes. The water-soluble M(m,n) films immersed in the same aqueous solution did not show any changes in the optical absorption. Fig. 3 shows the typical fluorescence spectrum of the M(12,1) film soaked in the aqueous solution for 1 hr. As is evident, the red-shifted relatively sharp absorption at 600 nm and the almost zero Stokes shift of fluorescence are recognized in Fig. 3. These observations suggest that the absorption spectral changes of the dye film dipped into the solution are due to the formation of J-aggregate or its adducts. However, the structure of the dye aggregate in a film has not been determined.

When the M(12,1) film on a glass plate was removed from the pH-controlled aqueous solution at some intermediate stage of the spectral changes (*e.g.*, the curve (c) in Fig. 2) and was then dried in a vacuum chamber (10^{-2}Torr) for 1 hr, it was found that the absorption spectrum of the dye film was fixed. Subsequent immersion of the dye film in the solution promoted the further absorption changes (*e.g.*, from the curve (c) to the curve (d) or (e) in Fig. 2). Thus, we have carried out the spectral control of the dye film in a dry state by the simple procedures described above. As a preliminary study, these procedures were employed in preparing the organic photodiodes (*e.g.*, Al/a solution-cast M(12,1) film/Ag). It has been found7) that the spectral controlled M(12,1) photodiode achieved to collect light energy at longer wavelengths with higher light conversion efficiency as compared with the photodiode without the aqueous treatment. In addition, we have found6) that the appearance of the absorption peak at 600 nm (see Fig. 2) tends to enhance the photocurrent generation at the M(18,1)-coated electrode preserved in an alkaline solution as compared with that at the pigmented electrode without the aqueous treatment.

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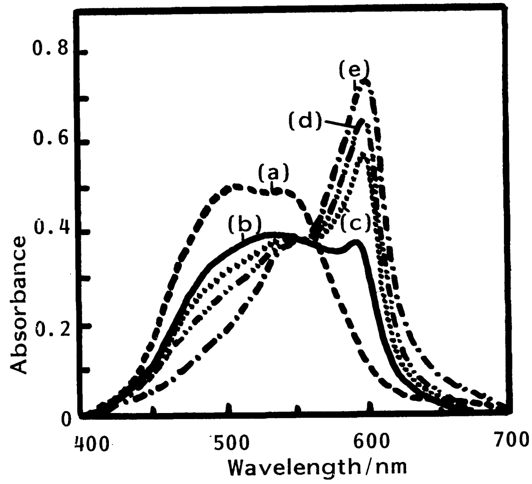

Fig. 2. Absorption spectral changes of the solution-cast film of the M(12,1) on a glass plate in doubly distilled water containing small quantity of KOH (pH 7.0) at 25°C as a function of time. The curve (a) presents the absorption spectrum of the pigmented plate before soaking in the aqueous solution. The curves (b), (c), (d), and (e) are the absorption spectra of the dye film after soaking in the solution for 10 sec, 4 min, 12 min, and 1 hr.

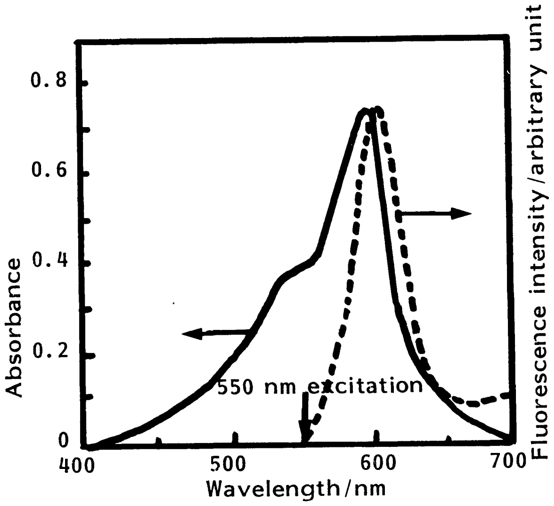

Fig. 3. Absorption and fluorescence spectra of the M(12,1) film on a glass plate held in the aqueous solution used in Fig. 2 for 1 hr. The fluorescence spectrum of the dye film held in the solution was recorded under 550 nm illumination on a Hitachi 650-10 S fluorescence spectrophotometer.

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