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Formation of Magnesium and Chloroaluminium Phthalocyanine Thin Films Exhibiting an Intense Near-Infrared Absorption by Electrolysis of Surfactants with Ferrocenyl Moiety

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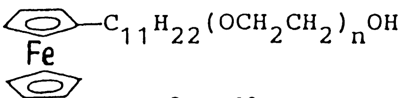
Synopsis. Magnesium or chloroaluminium phthalocyanine (**1** and **2**) was dispersed to the micellar solution formed by a non-ionic surfactant with ferrocenyl moiety (**3**). The thin films prepared by the controlled-potential electrolysis of the micellar solution exhibited an intense near-infrared absorption.

In recent years extensive researches have been carried out on organic compounds for laser recording materials.[1] The sublimed films of phthalocyanine compounds usually exhibit no strong absorption in the wavelength region over 800 nm of use for a laser diode light source.[2] After acid, organic solvent, or thermal treatments, the sublimed films of magnesium, aluminium, and vanadyl phthalocyanines show strong absorption in the near-infrared region.[3-6]

Recently, we have presented a novel technique for electrochemical formation of an organic thin film by electrolysis of cationic surfactants with ferrocenyl moiety (micelle disruption method).[7] We further reported thin films of phthalocyanine compounds MPc (M=H_2, Cu) by electrolysis of non-ionic surfactants with a ferrocenyl moiety (**3**), and showed that crystalline forms of CuPc thin films prepared by this technique are identical with those of CuPc powders dispersed in an aqueous solution of the surfactant.[8,9] The author will report the preparation of thin films of magnesium and chloroaluminium phthalocyanines (**1** and **2**) using this technique, which have an intense absorption peak in the near-infrared region and have been proposed as candidates for laser recording materials.[1]

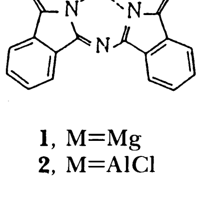
Experimental



$\mathrm{C_{11}H_{22}(OCH_2CH_2)_nOH}$

3, $n≒13$

1 was obtained from Tokyo Kasei Co. **2** was given by Nippon Shokubai Kagaku Kogyo Co. The surfactant used was poly(oxyethylene) (**13**) 11-ferrocenylundecyl ether (average molecular weight≒900) (**3**).[10] The micellar solution of **1** was prepared in the following manner: An aqueous solution containing 1 mM **3**, 0.1 M LiBr, and 5 mM **1** was sonicated for 10 min and stirred for three days. This solution was allowed to stand for overnight. The supernatant of this solution was used for preparing the films. The test solution for electronic absorption measurements was prepared by diluting this solution. The micellar solution of **2** was prepared in the same manner as that of **1**.



1, M=Mg
2, M=AlCl

Controlled-potential electrolysis was done for of an aqueous solution containing 3.2 mM **1**, 1.0 mM **3**, and 0.1 M LiBr by indium tin oxide (ITO) electrode maintained at +0.50 V vs. SCE with slow stirring. When 2.0 mM **3** solution was used, **1** film did not grow up. If **3** is present in the solution which is unadsorbed on the surfaces of **1** particles, the film formation seems to be disturbed. After a definite amount of current passed through ITO electrode, the electrode was air-dried at room temperature overnight, then rinsed with distilled water. Electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere.

Results and Discussion

Figure 1 shows the electronic absorption spectrum of 1.0 mM (1 M=1 mol dm^{-3}) aqueous solution of **1** (a), and that of **1** in ethanol solution (b). The absorption peaks in spectrum (b) are the same as those previously reported[11] and are attributable to the

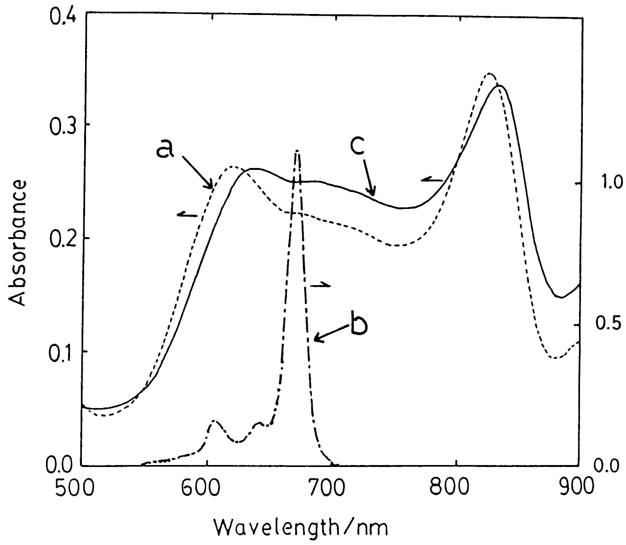


Fig. 1. Electronic absorption spectra of **1** in 1 mM **3**, and 0.1 M LiBr aqueous solution (a), in ethanol solution (b), and **1** film prepared by electrolysis of an aqueous solution containing 1 mM **3**, 3.2 mM **1**, and 0.1 M LiBr at ITO electrode maintained at +0.5 V vs. SCE for 1 h (c).

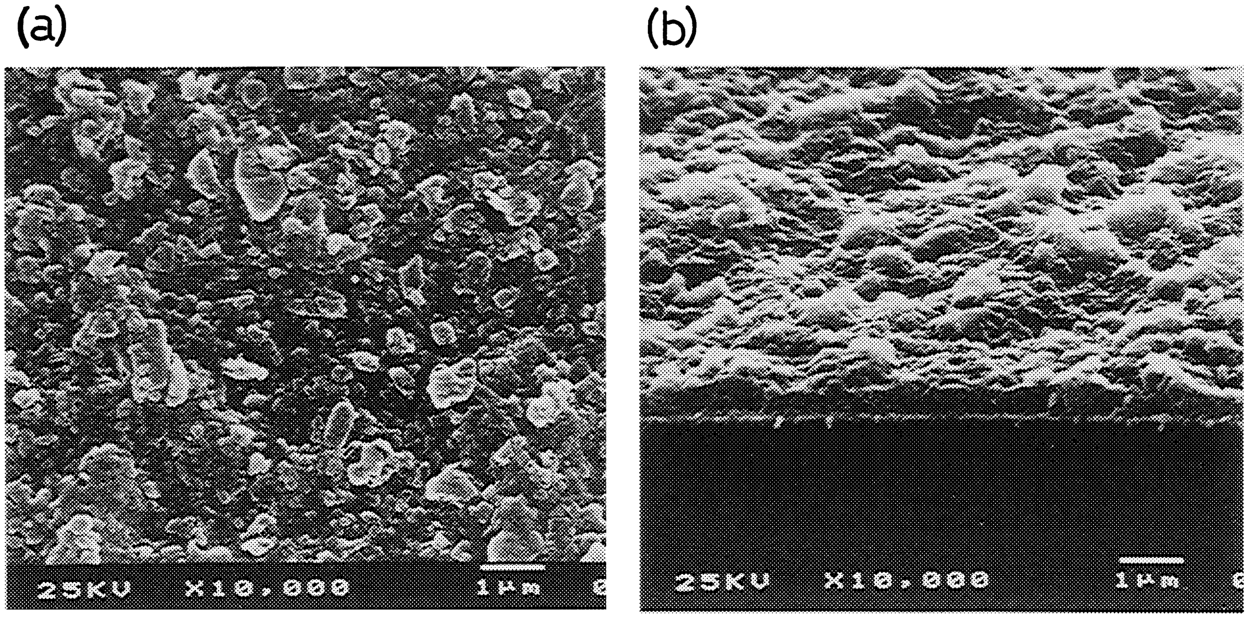


Fig. 2. SEM top (a) and cross sectional (b) views of **1** film prepared by the electrolysis of an aqueous solution containing 3.2 mM **1**, 1.0 mM **3**, and 0.1 M LiBr at ITO electrode maintained at +0.5 V vs. SCE for 14 h.

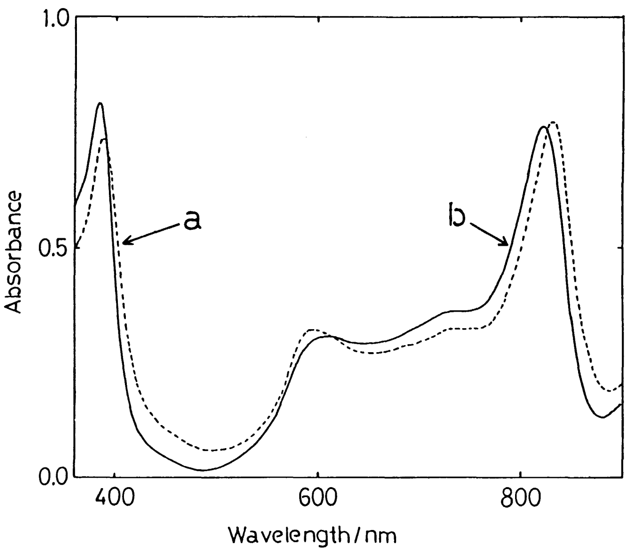


Fig. 3. Electronic absorption spectra of **2** in aqueous solution containing 2.0 mM **3** and 0.1 M LiBr (a), and **2** film prepared by the electrolysis of the same solution at ITO electrode maintained at +0.5 V vs. SCE for 3 h (b).

monomer.[12] The spectrum (a) consisting of a broad intense near-infrared peak at 827 nm suggests that the molecules of **1** in micellar solution exist in aggregates (particles).

The absorption spectrum of **1** film on the ITO electrode prepared by the electrolysis for 1 h consists of a broad intense near-infrared peak at 830 nm (Fig. 1-c).

Figure 2 shows the scanning electron micrographs (SEM) of the film on ITO. The crystals less than 1 μm in length were formed as shown in this figure. The SEM of the cross section of the film shows that the film thickness is approximately 0.5 μm (Fig. 2). This film thickness was easily controlled by changing the electrolysis time.

Figure 3-a shows the electronic absorption spectrum of **2** in 2.0 mM **3** (Fig. 3-b). The spectrum consists of an intense near-infrared peak at 828 nm. The thin film of **2** was prepared by the same method as that of **1**. The electronic absorption spectrum of **2** film (Fig. 3-b) consisted of an intense near-infrared peak at 822 nm.

Such near-infrared peaks of **1** and aluminium-phthalocyanine derivatives have been reported in the cases of treating these sublimed films with organic solvents.[3,4] These phenomena have been ascribed to a crystal form change, followed by dissolving of these compounds in the organic solvent. The formation of the films in our studies which show near-infrared peaks is relevant to the process of preparing these films: The cyrstal form of the particles dispersed in the surfactant solution is maintained in that of the film deposited on ITO electrode, because the electronic absorption spectrum of the film is similar to that of the micellar solution (Figs. 1 and 3).

The experimental results indicate that such an electrochemical method will give a technique for preparing **1** and **2** films which show near-infrared peaks without any further treatment.

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