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# Electrochemical Formation of a Phthalocyanine Thin Film by Disruption of Micellar Aggregates

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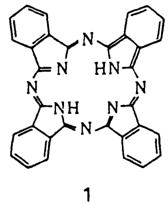
Phthalocyanine (1) was dissolved to the micellar solution formed by non-ionic surfactants with ferrocenyl moiety. A 1 thin film was prepared on an indium tin oxide (ITO) electrode by the controlled-potential electrolysis of this solution. This film consisted of rod-like crystals of 500 nm in length.

Phthalocyanine compounds continue to be the subject of numerous researches.[1)] As thin films, the area of current interests includes application of these compounds as catalysts,[2)] electrochromic materials,[1)] sensitizer,[3)] and photovoltaic materials.[4)] The technique for the preparation of unsubstituted phthalocyanine thin films is limited to only a vacuum sublimation[5)] except for the LB film of this compound from the dilithium complex,[6)] because of their insolubility in most organic solvents.

Recently, we presented a novel technique for the electrochemical formation of an organic thin film by disruption of micelles formed by cationic surfactants having a ferrocenyl moiety.[7)] Utilization of this technique requires the solubilization of the film forming compound in a micellar solution. However, phthalocyanine compounds do not dissolve in the micellar solution.[8)] Here we found the solubilization of phthalocyanine (1) in the micellar solution formed by non-ionic surfactants with ferrocenyl moiety (2), and the preparation of a 1 thin film by using this technique.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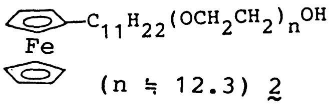
$\text{Fc}{-}C_{11}H_{22}(OCH_2CH_2)_nOH$

(n ≒ 12.3) 2

The surfactant used was (11-ferrocenyl-undecyl)polyethyleneglycol(average molecular weight ≒ 900) (2). Compound 2 was prepared by the reaction of sodium alcholate of polyethylene glycol (average molecular weight = 600) with 11-bromoundecylferrocene.[9,10)] Electrochemical measurements were carried out at 25 °C under a nitrogen atmosphere.

The micellar solution of **2** solubilized water-insoluble **1**. Compound **1** was dissolved in a 2.0 mM (1 M = 1 mol dm$^{-3}$) aqueous solution of **2** at a concentration of 4.4 mM.[11)]

Figure 1 shows the electronic absorption spectra of **1** in 1.0 mM **2** aqueous solution (A), and the 1-chloronaphthalene solution (B) prepared by dissolving the residue after evaporation of the solution (A). The absorption peaks in spectrum (B) are the same as those previously reported[12)] and have been attributed to the monomer.[13)] The spectrum of (A) consists of a broad peak at 606 nm accompanied by a shoulder band at about 680 nm. Such a broad absorption may be attributed to the formation of aggregates.[13)]

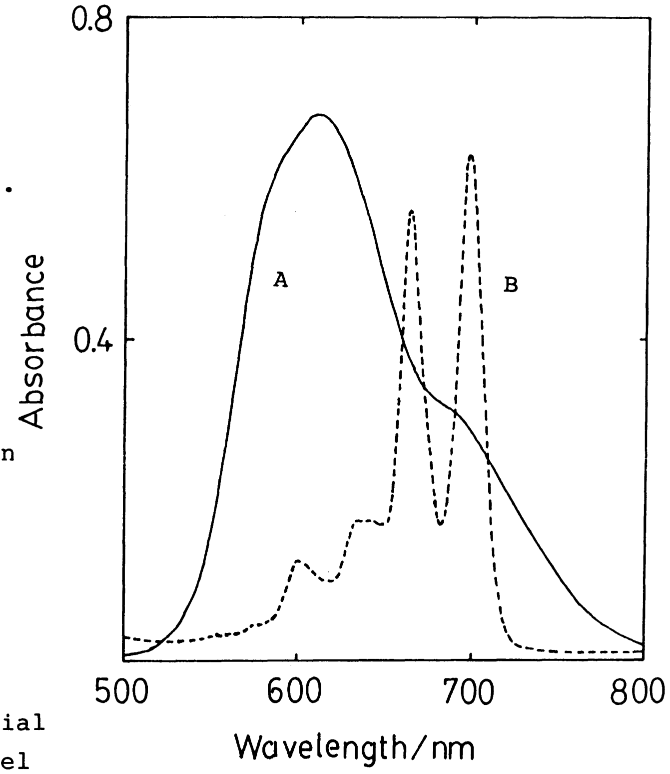

Fig. 1. Electronic absorption spectra of **1** in 1 mM **2** aqueous solution (A), the 1-chloronaphthalene solution (B) prepared by dissolving the residue after evaporation of solution (A).

The cyclic voltammogram of the aqueous solution containing 2.0 mM **2**, and 0.2 M $Li_2SO_4$ at a glassy carbon electrode showed a reversible one-electron step with a half-wave potential ($E_{1/2}$) of +0.28 V vs. saturated calomel electrode (SCE). This step may be assigned to the redox system, **2**/**2**$^+$. Most of **2** may exist in the form of micelles under these conditions, owing to its very small critical micelle concentration (below 0.2 mM[14)]). The cyclic voltammogram of 2.0 mM **2**$^+$ showed a reversible one-electron step with a $E_{1/2}$ of +0.28 V. The solution of **2**$^+$ was prepared by controlled-potential bulk electrolysis of the solution of **2**. The peak current for this step was 1.9 times that for the solution of **2**. Since the peak current is proportional to the square root of the diffusion coefficient of **2** or **2**$^+$,[15)] respectively, this large difference between **2** and **2**$^+$ suggests that most of **2** exist in the form of micelles, whereas all of **2**$^+$ are in the monomeric form.

Controlled-potential electrolysis of an aqueous solution containing 4.4 mM **1**, 2.0 mM **2**, and 0.2 M $Li_2SO_4$ at indium tin oxide (ITO) electrode maintained at +0.50 V, was done while stirring the solution. After a definite amount of electricity, Q(C/cm$^2$), passed through the ITO electrode, the electrode was air-dried at room temperature overnight, then rinsed with distilled acetone and distilled water.[16)] The absorption spectrum of the film on the ITO electrode prepared by electrolysis for 15 min ($Q = 0.0028$ C/cm$^2$) consisted of a broad absorption peak at 615 nm and was very similar to that for the film prepared by vacuum sublimation.[5)] Figure 2 shows the electron micrographs of the film on ITO. Rod-like crystals of 500 nm in length were formed as shown in this figure. The SEM micrographs of other sections of this film were almost identical to that in Fig. 2. No defect was observed in these micrographs. Such film formation without defects may be attributable to the electrical resistance of the deposit. The electrolysis of micelles starts on the electrically most conductive part of electrode surfaces. Since the deposit exhibits marked electrical resistance, the current seeks the nearest available path. Eventually the electrode surfaces are evenly coated with the deposit. The film thickness was determined by the usual interference technique.[17)] A plot of the film thickness (d) from 0.1 to 0.6 µm vs. Q showed that the value of d increases linearly with Q. This result indicates that the film thickness can be easily controlled by the amount of current passed through the electrode.

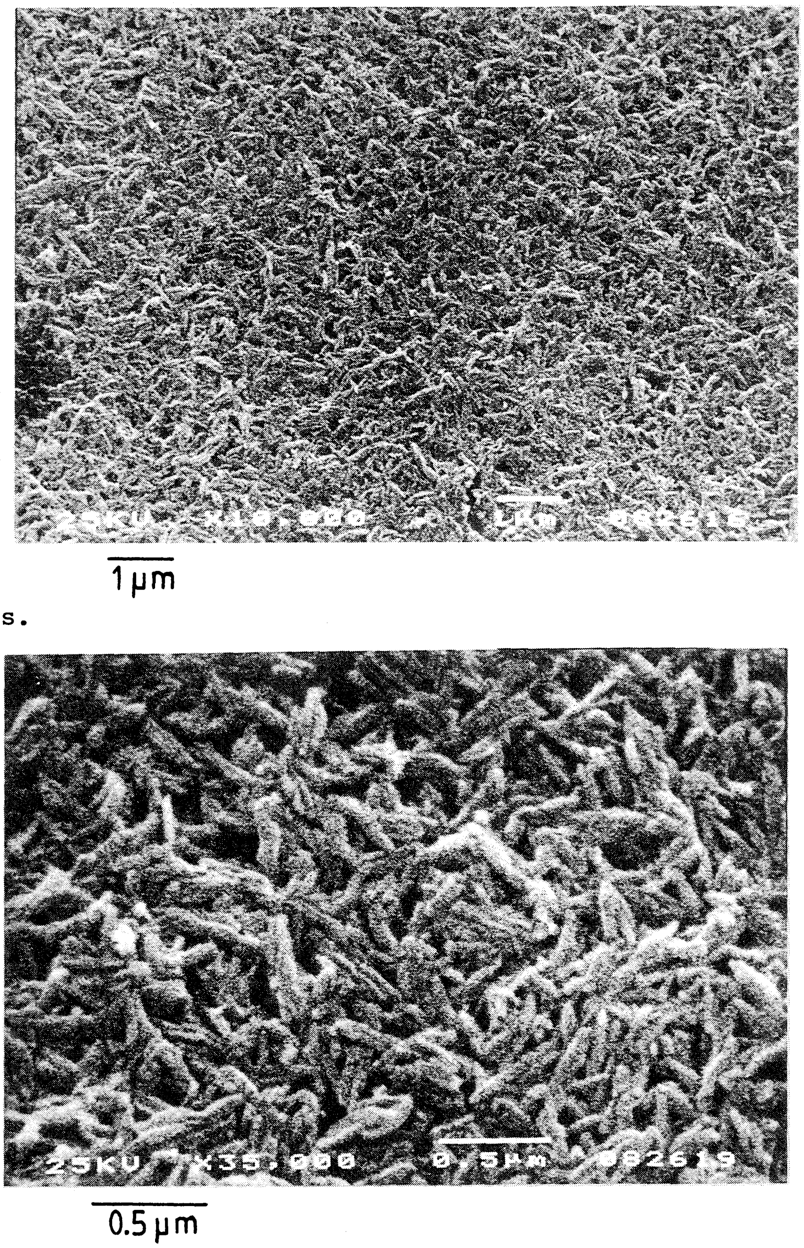

Fig. 2. Scanning electron micrographs of the film prepared by the electrolysis of an aqueous solution containing 4.4 mM **1**, 2.0 mM **2**, and 0.2 M $Li_2SO_4$ at ITO electrode maintained at +0.5 V vs. SCE for 1 h ($Q = 0.0163$ C/cm$^2$).

Using the non-ionic surfactant **2**, we demonstrated the utility of our technique for preparation of the **1** thin film. We are currently extending this technique to preparing thin films of phthalocyanine metal complexes, organic polymers,[18)] and biological compounds.

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## References

1) K. Kasuga and M. Tsutsui, Coord. Chem. Rev., 32, 67 (1980).
2) L. J. Boucher, "Coordnation Chemistry of Macrocyclic Compounds," ed by G. A. Melson, Plenum, New York (1979), p. 461.
3) A. Giraudeau, F. Fan, and A. J. Bard, J. Am. Chem. Soc., 102, 5137 (1980).
4) A. M. Hor and R. D. Loutfy, Thin Solid Films, 106, 291 (1983).
5) P. S. Vincett, Z. D. Popovic, and L. McIntyre, Thin Solid Films, 82, 357 (1981).
6) S. Baker, M. C. Petty, G. G. Roberts, and T. V. Twigg, Thin Solid Films, 99, 53 (1983).
7) K. Hoshino and T. Saji, J. Am. Chem. Soc., 109, 5881 (1987); Chem. Lett., 1987, 1439.
8) K. Hoshino and T. Saji, unpublished data.
9) T. Saji, K. Hoshino, and S. Aoyagui, J. Chem. Soc., Chem. Commun., 1985, 865
10) Elemental analysis data for 2; Found: C, 60.21; H, 9.46; N, 0.00%, Calcd for $C_{45.4}H_{80.8}O_{13.2}Fe$; C, 61.0; H, 9.04; N, 0.00%. $^1H$ NMR data (ppm) for 2 ($CDCl_3$, 25 °C): 1.27 (s, 16H, $-CH_2C\underline{H}_2CH_2-$), 1.6 (t, 2H, $-CH_2C\underline{H}_2CH_2O-$), 2.27 (t, 2H, fc-$C\underline{H}_2-$), 3.5-3.7 (m, 51H, $-OC\underline{H}_2C\underline{H}_2O-$, $-(CH_2)_2C\underline{H}_2O-$), 4.0-4.1 (m, 9H, FcH). The number of ethyleneoxide in 2 was determined from this NMR data.
11) The micellar solution of 1 was prepared in the following manner. An aqueous solution containing 2 mM 2, 0.2 M $Li_2SO_4$, and excess 1 was sonicated for 10 min and stirred overnight. These treatments were repeated. Undissolved 1 was removed by centrifugation (2000 rpm, 1 h). This solution was stable for more than eight months. The test solution for electronic absorption measurements was prepared by diluting this solution.
12) G. H. Heilmer and G. J. Warfield, Chem. Phys., 38, 893 (1963).
13) K. Bernauer and S. Fallab, Helv. Chim. Acta, 44, 1287 (1961).
14) J. H. Fendler and E. J. Fendler, "Catalysis in Micellar and Macromolecular Systems," Academic, New York (1975), p. 19.
15) For example, see: A. J. Bard and L. R. Faulkner, "Electrochemical Methods," Wiley, New York (1980), p. 218.
16) The film just after preparation was partially destroyed by washing with water. Later, we found that the film was more stable when 0.2 M LiBr was used as the supporting electrolyte.
17) S. Tolansky, "Multiple-Beam Interferometry of Surfaces and Films," Oxford University, London (1948).
18) K. Hoshino and T. Saji, submitted to Chem. Lett.

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