

Electrophoretic Deposition of Copper Phthalocyanine from Trifluoroacetic Acid-Dichloromethane Mixed Solution

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The formation of a copper phthalocyanine (**1**) thin film was carried out using a trifluoroacetic acid (**2**)/dichloromethane mixed solution containing protonated copper phthalocyanines. A blue film was formed on the cathodic plate with short time deposition by electrophoretic deposition using this solution. Scanning electron micrographs showed that this film is composed of fibrous crystallites.

Ever since their synthesis in early this century, phthalocyanines continue to be the subject of numerous studies due to the following reasons: (1) They are chemically stable and yield brilliant turquoise shades. (2) Therefore, they have been used as dyes and pigments.^{1,2} (3) They function as catalysts, photovoltaic materials, sensitizers, and so on.² However, the studies and applications of their film formation by a wet process are limited because of their poor solubility in aqueous and organic solvents. Recently, we reported electrochemical formation of phthalocyanine (**1**) films using redox active surfactants^{3,4} and by electrophoretic deposition.⁵ These films were formed by depositon of the particles used for preparation of the dispersion. However, formation of a **1** thin film by an electrophoretic deposition of monomeric **1** has not been reported.

Recently, it was reported that some unsubstituted phthalocyanines are soluble in an organic solvent containing trifluoroacetic acid (**2**)^{6,7} due to the coordination of protons to periferic aza nitrogen atoms of the phthalocyanines.⁷ The preparation of the powders of the phthalocyanines^{6,7} and Langmuir-Blodgett films of **1**⁸ have been reported using this solution. In this paper, we report the formation of **1** films by an electrophoretic deposition of monomeric **1** from dichloromethane solution containing **2** and protonated **1**, which gives mechanically stable films having fibrous crystallites within a few seconds.

As a copper phthalocyanine, β -type **1** (Dainichiseika Color & Chemicals) was used. A dichloromethane solution containing **2** and protonated **1** was prepared by stirring the mixture for 30 min. The ITO and glassy carbon plates were used as the cathodic and anodic electrodes, respectively. The distance between these two electrodes was kept at 1.0 cm. Experiments were done at 25 °C.

The dependence of the electronic absorption spectrum of the solution of protonated **1** on the concentration of **2** (Figure 1) shows the existence of one isosbestic point at 680 nm and existence of two protonated species of **1**. The bathochromic shift of the long-wavelength band of this absorption spectrum has been ascribed to the protonation of **1**.⁷ Such a spectroscopic behavior is similar to that of tetrakis(*tert*-butylphthalocyaninate)copper(II) in nitrobenzene containing **2**.⁷ Based on the equilibrium analysis of the first and second steps using the dependence of the absorbance of the protonated species on the

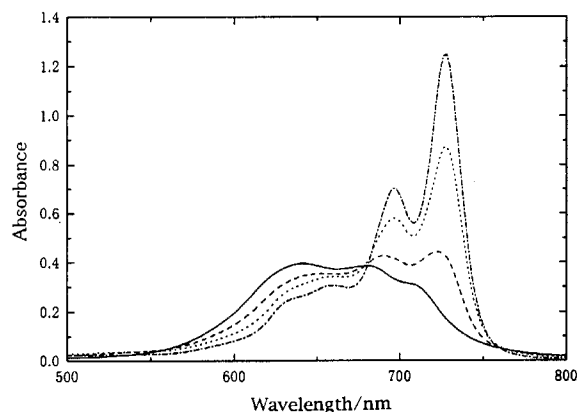
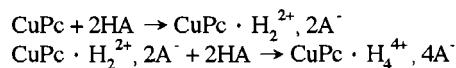


Figure 1 The electronic absorption spectrum of 0.1 mM **1** dichloromethane solution on the concentration of **2**. Concentration of **2**: 0.25 M (—), 1.0 M (---), 2.0 M (····), 4.0 M (- · - ·).

concentration of **1**, the following equilibrium reaction may occur:⁹



where CuPc and HA indicate **1** and **2**, respectively. A blue film was formed on the cathodic plate (ITO) by application of 100 V cm⁻¹ between the two plates in a dichloromethane solution containing 1 M **2** and 1 mM **1** for 5 seconds.¹⁰ The adhesive force between the film and the ITO was as strong as the film prepared by the vacuum sublimation technique. The film was not broken by touch with a finger. The amount of the film increases with applied potential, which supports the mechanism that the film formation proceeds via the electrophoretic migration of the charged species.¹¹ The electronic absorption spectrum of a 1-chloronaphthalene solution prepared by dissolving this film was the same as that of previously reported.¹² This agreement indicates that the film is mainly made of **1**.

The frequencies, intensities, and width of the two peaks at 500–800 nm (Q band) in the absorption spectrum of the film are quite similar to those of the α -type **1** spectra reported by earlier researchers,^{12–14} which is different from that used for the preparation of the solution for this film formation (β -type **1**). The X-ray diffraction pattern of this film also supports this conclusion.¹⁵

Figure 2 shows scanning electron micrographs (SEM) of the film. The SEM of the cross section of the film (Figure 2a) shows that the film is densely packed with **1**. The SEM of the surface (Figure 2b) shows that the film is composed of fibrous

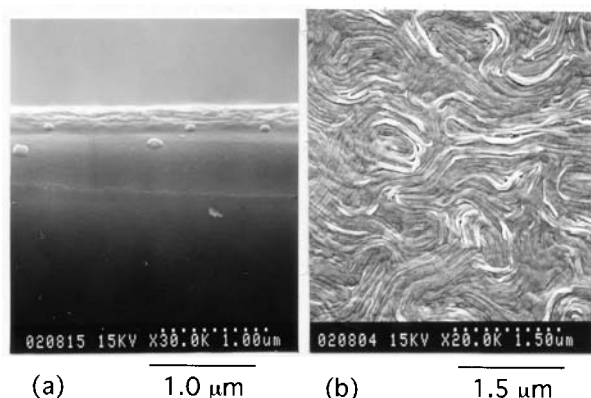


Figure 2 Scanning electron micrographs of the film prepared by application of 100 V cm^{-1} for 5 s between ITO and carbon plates in a dichloromethane solution containing 1 mM **1** and 1 M **2**. Cross section (a) and surface (b).

crystallites. The size of the crystallites increased with electrolysis time and their shape is different from those prepared by the sublimation method. In general, **1** films prepared by the sublimation method are composed of granular or columnar crystallites.¹⁶ These differences can be ascribed to the rate of the film growth and the atmosphere of the film formation. The time for preparation of the film (5 s) was much shorter than that for the sublimed one. Such a short time formation may lead to such an imperfect film crystalline structure.

The film formation may be explained by the following mechanism: **1** is dissolved as positively charged protonated species ($\mathbf{1} \cdot \text{H}_2$)²⁺ and ($\mathbf{1} \cdot \text{H}_4$)⁴⁺. These protonated species electrophoretically migrate to the cathode. The protonated species is then reduced to yield the monomer of **1** and hydrogen. Subsequently, the monomers deposit on the electrode and form the **1** film.

In conclusion, formation of the **1** film was successfully carried out using the protonated species of **1** in dichloromethane containing **2**. In this preliminary study, we confirmed that the present technique can be applied to the formation of the films of other phthalocyanines, e.g., phthalocyanines (MPC, M = H₂, Fe, Ni, Zn, VO). Such a technique provide a convenient method to prepare the films of a wide variety of phthalocyanines.

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- The equilibrium constants of the first and second steps were 2.5×10^2 and 0.30 M^{-2} , respectively, assuming most of A⁻ form ion pairs with protonated species. The number of protons coordinating to **1** was 2.0 and 4.0 for the first and the second protonated species, respectively.
- 1 mM **1** may change to $0.81 \text{ mM } \mathbf{1} \cdot \text{H}_2^{2+}$ and $0.19 \text{ mM } \mathbf{1} \cdot \text{H}_4^{4+}$ in dichloromethane containing 1 M **2** based on the equilibrium constants in Ref. 9.
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- X-Ray diffraction pattern of the **1** film prepared by application of 100 V cm^{-1} for 30 seconds showed one major peak at 6.81 together with one minor small peak at 15.70. This major peak agreed with that for the α -type of **1**: See, for example: M. Komiyama, Y. Sakakibara, and H. Shirai, *Thin Solid Films*, **151**, L109 (1987); M. Debe, R. J. K. Poirier and K. K. Kam, *Thin Solid Films*, **197**, 335 (1991); Y. Kohno, M. Masui, K. Ono, T. Wada, and M. Takeuchi, *Jpn. J. Appl. Phys.* **31**, L252 (1992).
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