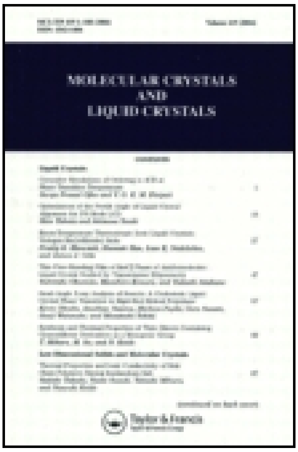

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Langmuir–Blodgett Films of Mixtures of Oxotitanium Phthalocyanine and Copper Tetrakis(hexyloxycarbonyl)phthalocyanine; Preparation and Properties

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A new method was developed for the preparation of Langmuir–Blodgett (LB) films of oxotitanium phthalocyanine (TiOPc)/copper tetrakis(hexyloxycarbonyl)phthalocyanine (C6CuPc) mixtures, based on the finding that almost insoluble TiOPc becomes soluble in chloroform upon mixing with C6CuPc. Surface pressure-area isotherms of the mixed phthalocyanines suggested that the two phthalocyanines are miscible in the monolayers. Visible absorption spectra and photoconductive properties of the mixed LB films were studied.

Keywords: Langmuir–Blodgett film, phthalocyanine, oxotitanium phthalocyanine, photoconduction.

INTRODUCTION

Among a variety of phthalocyanine (Pc) compounds, oxotitanium phthalocyanine (TiOPc) is well known as a sensitive organic photoconductor that has been practically used in electrophotographic photoreceptor.[1] Meanwhile, Langmuir–Blodgett (LB) technique can provide a promising method for the fabrication of ultrathin organic films with highly ordered molecular orientation. However, the application of this method to peripherally unsubstituted Pcs, including TiOPc, can hardly be achieved, mainly because their solubilities in usual organic solvents are generally too low for preparation of spreading solutions. Even in some exceptional cases where fairly soluble unsubstituted Pcs were used, it seems difficult yet to obtain LB films in good quality.[2,3] Therefore, in most studies, peripherally substituted Pcs which are soluble in common organic solvents have been preferably employed as LB film materials.

In previous studies on LB films of copper tetrakis(alkoxycarbonyl)phthalocyanines, the authors reported highly anisotropic molecular orientation in the films,[4,5,6] especially, surprisingly strong in-plane dichroism in the LB films of copper tetrakis(hexyloxycarbonyl)phthalocyanine (abbreviated as C6CuPc hereafter).[6] Nevertheless, the photoconduction observed in our preliminary experiment for a C6CuPc LB film was not high (vide infra), possibly implying unfavorable effects of the substituents and/or the central metal atom upon electronic properties of the film. If an effective method is available to prepare LB films containing TiOPc and C6CuPc, investigation on the photoconductivity of the films might provide rich information about roles of molecular orientation, the substituents, and/or the central metal atoms. However, the solubility of TiOPc in solvents, e.g. chloroform, is not sufficient at all for preparation of spreading solutions. In the present work, we have found that the solubility of TiOPc in chloroform can be enhanced if it is dissolved as mixtures with C6CuPc. This finding enabled us to prepare spreading solutions for LB films containing peripherally unsubstituted TiOPc with the aid of C6CuPc as a matrix molecule. Surface pressure-area isotherms of the monolayers, UV-visible absorption spectra of the spreading solutions and the multilayers of the mixed Pcs are presented, together with a preliminary result of photoconduction experiment.

EXPERIMENTAL

TiOPc (Dainippon Ink & Chemicals Inc.) was used after repeated sublimation. C6CuPc used here is the same sample as that we used in our previous study.[6] A spreading solution of TiOPc/C6CuPc mixture (mole fraction of TiOPc 46%) was prepared as follows. Each 1 ml solutions of TiOPc (0.94 mmol/l) and C6CuPc (0.92 mmol/l) in concentrated sulfuric acid were admixed thoroughly and poured into ca. 40 ml of cold water to give a precipitate of mixed Pcs. The precipitate was filtered, washed with water and then with methanol, dried, dissolved in chloroform, and then filtered off. The filtrate thus obtained was used as a spreading solution. Concentrations of Ti and Cu in the spreading solution were determined by ICP (inductively coupled plasma) emission spectroscopy to be 12 μmol/l and 14 μmol/l, respectively, from which the mole fraction of TiOPc in this solution was calculated to be 46%. Similarly, other spreading solutions with different mole fractions of TiOPc were prepared by mixing the sulfuric acid solutions of TiOPc and C6CuPc in various ratios. All glassware used throughout this procedure was carefully washed prior to use by immersing into concentrated sulfuric acid containing a metal-free oxidizer (NOCHROMIX®, Godax Laboratories.) to eliminate surface-active contamination.

Measurements of surface pressure (π)-area (A) isotherms and deposition of multilayers were performed with a commercial LB trough system (KSV5000). Doubly distilled pure water was used as the subphase. Multilayers were deposited with a vertical dipping (LB) method or a horizontal lifting method, onto quartz or glass plates which were rendered hydrophobic with dimethyldichlorosilane. Multilayers prepared with the horizontal lifting method are not called LB films in a strict sense, but hereafter we call them also as LB films for convenience.

Visible absorption spectra for the sample solutions and for the LB films were recorded on a Hitachi U-3500 spectrometer, with Glan-Taylor prisms if necessary. For measurements of photoconduction, LB films were deposited on hydrophobized glass plates on which gold interdigital electrodes (ca. 700 Å; Figure 1) had been vacuum-deposited under 10^{-5} torr. The interelectrode gap for a pair of electrodes was 0.22 mm and the total gap length was 36.4 mm. During the measurements, samples were placed in a shielded box under ambient air. A bias voltage of 500V DC was applied between

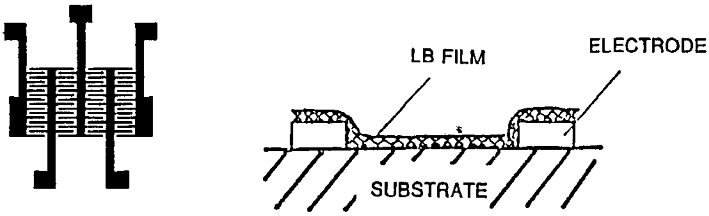

FIGURE 1 Interdigital electrodes (left) and LB film/electrode configuration (right).

two adjacent electrodes, and the response of current upon light illumination ($3.5\,mW/cm^2$) was recorded. Monochromatic light at 622 nm was obtained through an interference filter and an infrared cut filter from a 500 W xenon lamp.

RESULTS AND DISCUSSION

Table I shows TiOPc mole fractions in the sulfuric acid solutions and the chloroform (spreading) solutions of the TiOPc/C6CuPc system, which are similar to each other at $< 50\%$ mole fractions of TiOPc in H_2SO_4. At higher ($\geq 50\%$) TiOPc mole fractions in H_2SO_4, on the other hand, the TiOPc ratio in $CHCl_3$ solution does not increase but tends to become irreproducible. Consequently, we were able to obtain the mixed Pc solutions with ca. 50% of TiOPc at maximum. It should be noted that the concentrations of TiOPc in the spreading solutions are $\sim 10^{-5}$ M as determined by ICP emission spectroscopy, higher by an order of magnitude than that in a saturated $CHCl_3$ solution of neat TiOPc ($\sim 2 \times 10^{-6}$ M).

The visible absorption spectra for chloroform solutions of neat C6CuPc (Figure 2) show that the increase in concentration results in the substantial decrease of the molar extinction coefficient at 682 nm accompanied by the increase of that at 500–600 nm, spectral changes characteristic of equilibrium between the monomeric and associated states of phthalocyanine molecules.[7–9] The absorption peak at 682 nm dominant at lower concentrations can be attributed to the monomeric species, whereas the absorption at 530–600 nm should be, at least in part, due to the associated species. On the other hand, a saturated solution of neat TiOPc in $CHCl_3$ showed an absorption spectrum with the strong absorption maximum at 690 nm (Figure 3) typical for monomeric Pc.[7–9] Because the contour of the spectrum was almost unchanged upon

TABLE I

Mole fractions of TiOPc in solutions of mixed Pcs in H_2SO_4 and $CHCl_3$

Solution	TiOPc (%)				
H_2SO_4	20	33	50	50	67
$CHCl_3$	25	33	46	16	41

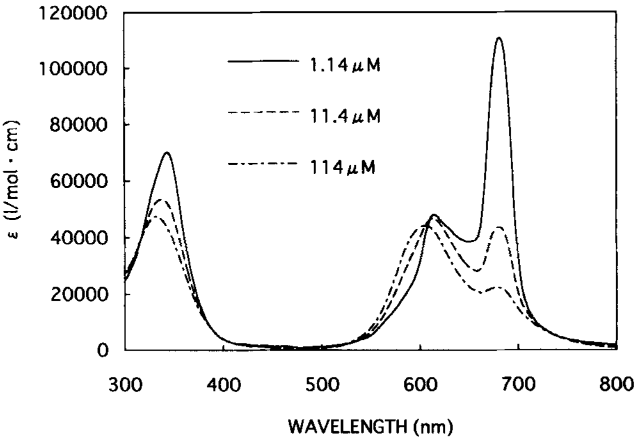

FIGURE 2 Visible absorption spectra of C6CuPc solutions in $CHCl_3$ at various concentrations.

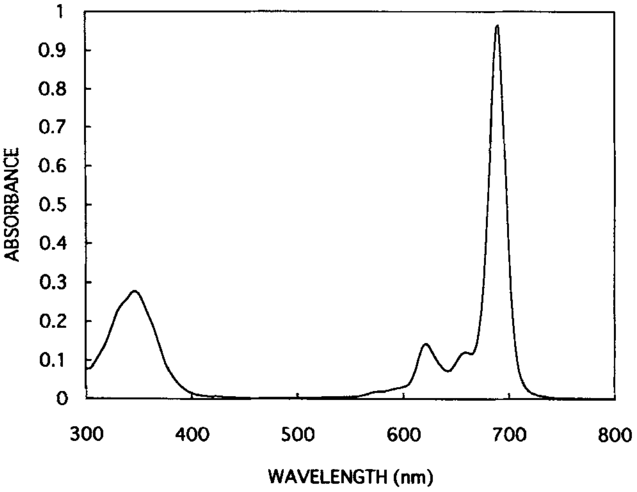

FIGURE 3 Visible absorption spectrum of a saturated TiOPc solution in $CHCl_3$.

dilution, the association of TiOPc molecules appears to be negligible at $\leq 10^{-6}$ M in $CHCl_3$.

Figure 4 shows visible absorption spectra for solutions of the mixed Pcs obtained by dilution of the spreading solutions with chloroform to 1×10^{-5} M total concentration of the Pc species (C6CuPc + TiOPc). As the mole fraction of TiOPc increases, the sharp absorption at 690 nm increases correspondingly, while absorbance between 500 nm and 620 nm slightly decreases. This behaviour is similar to that observed in Figure 2, obviously due to the increase of the ratio of monomeric Pc species accompanied by the

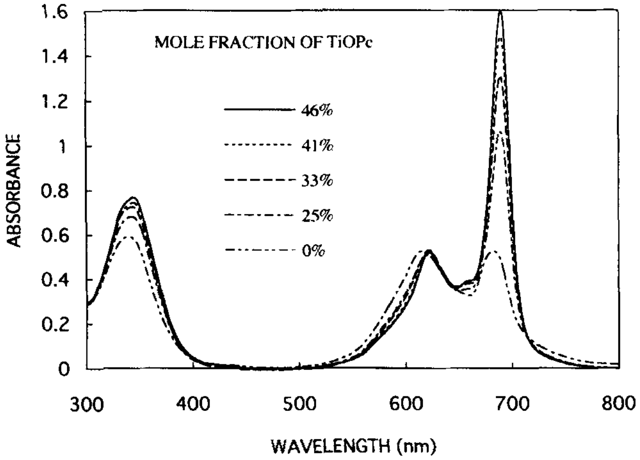

FIGURE 4 Visible absorption spectra of TiOPc/C6CuPc solutions in $CHCl_3$; [TiOPc] + [C6CuPc] $\cong 1 \times 10^{-5}$ M.

decrease of associated Pc species. The increments of the monomeric absorption should arise from the increased TiOPc content, as indicated by the ICP emission spectroscopy. The association should occur mainly with C6CuPc molecules and conceivably between TiOPc and C6CuPc molecules. The formation of this mixed associated species in the association equilibrium might explain the reason why the solubility of TiOPc is remarkably enhanced upon mixing with C6CuPc. On the other hand, the association of TiOPc molecules seems to be still negligible in the mixed solutions, as is in neat TiOPc solution.

The $\pi - A$ isotherms (20°C) for the monolayers of the mixed phthalocyanines are shown in Figure 5. In all cases, the limiting area per one Pc molecule fell within a range of 70–80 Å^2, which seems reasonable if Pc molecules take so-called 'edge-on' style molecular orientation, i.e., the molecular planes oriented nearly perpendicularly to the water surface. Another significant feature is the lack of a plateau region in the isotherm of the mixed Pcs, in sharp contrast to that of neat C6CuPc at ca. 20 mN/m.[6] This fact suggests that TiOPc and C6CuPc are miscible in the monolayers. If the two Pcs were immiscible and phase-separated, the same type of plateau should have appeared in the isotherms for the mixed monolayers.

The deposition of LB films of the mixed Pcs was achieved with the vertical dipping method at $\leq 20\%$ mole fractions of TiOPc and with the horizontal lifting method at higher mole fractions. Probably the inclusion of TiOPc having no flexible side chains might render the monolayer rigid to make the vertical dipping deposition difficult at high TiOPc content. The LB films obtained with either the horizontal lifting or vertical dipping method were visually uniform.

As reported previously,[6] the LB films of neat C6CuPc exhibit a very strong in-plane dichroism with respect to the dipping direction. In the case of the TiOPc-C6CuPc mixed system, the polarized UV-visible absorption spectra also show substantial dichroism at $\leq 20\%$ mole fractions of TiOPc (Figure 6). However, the dichroic ratio observed for the as-deposited film is 2.9 at 610 nm, considerably smaller than that for

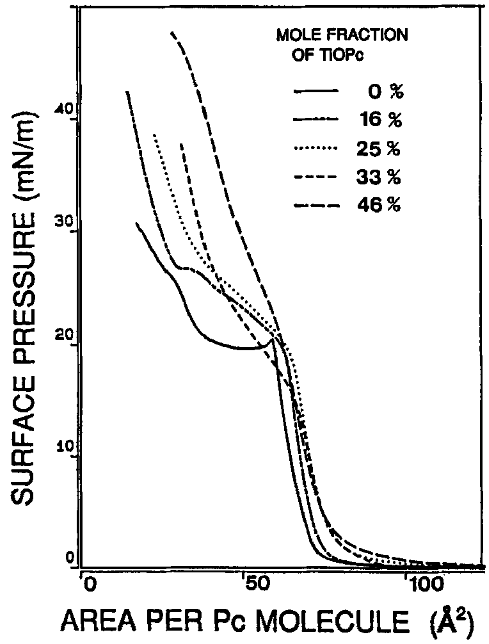

FIGURE 5 Surface pressure-area isotherms (20°C) for the TiOPc-C6CuPc mixed monolayers.

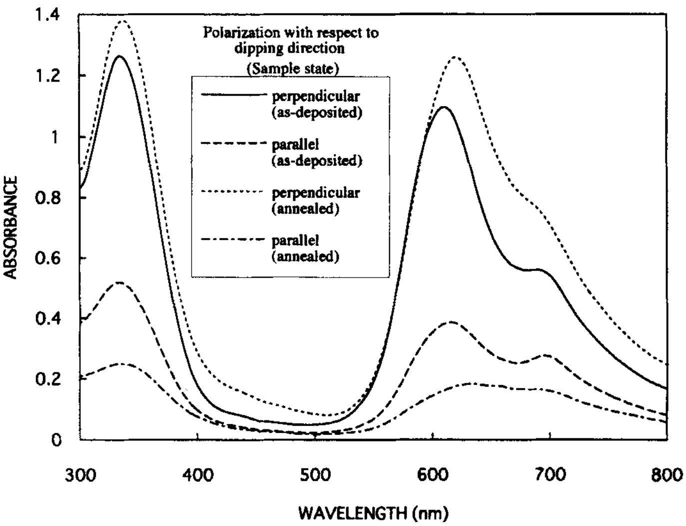

FIGURE 6 Polarized UV-visible absorption spectra for an LB film of TiOPc-C6CuPc (TiOPc 20%, 50 layers per side, deposited at 15 mN/m, 20°C).

the neat C6CuPc LB film (10.1 for as-deposited film),[6] perhaps reflecting the reduced fluidity of the monolayer caused by the inclusion of TiOPc. The dichroic ratio for the mixed LB film was able to be enhanced up to 7.2 at 620 nm by thermal annealing of the film (300°C, 1 hour), as seen in Figure 6.

Another UV-visible absorption spectrum (not polarized) is shown in Figure 7 for the LB film of TiOPc (46%)-C6CuPc mixture deposited with the horizontal lifting method. The absorption peak at 702 nm is pronouncedly recognized correspondingly to the higher mole fraction of TiOPc in the film.[10] For this sample, in-plane dichroism was negligible.

Photoconductive properties of the 10-layer LB films of TiOPc-C6CuPc in a 46:54 ratio and neat C6CuPc were measured and compared under identical conditions described in the experimental section. Photoresponses of current were clearly observed in both of the films. While dark current values for the both films were commonly of the order of 1×10^{-11} A, the magnitude of photocurrent for the mixed LB film was approximately 20 times larger than that for the neat C6CuPc film as seen in Figure 8. This preliminary result indicates that the incorporation of peripherally unsubstituted TiOPc in the LB film certainly enhances the photoconductivity. This would arise from the superior intrinsic nature of TiOPc in photoconductivity.

CONCLUSION

In the present study, the most significant point is the incorporation of *scarcely-soluble* TiOPc into LB films as mixtures with soluble C6CuPc. On the preparation of spreading solutions, C6CuPc acted as a "dissolution promoter" for TiOPc. Furthermore, in this method, the substituted phthalocyanine can be considered as a "transfer promoter" for unsubstituted TiOPc. Though typical amphiphilic molecules like long-

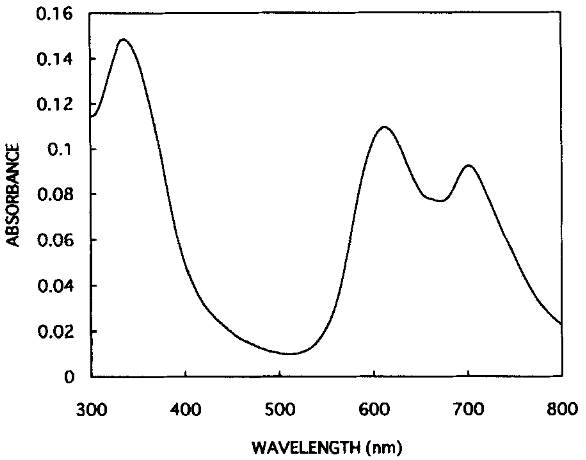

FIGURE 7 UV-visible absorption spectrum for an LB film of TiOPc-C6CuPc (TiOPc 46%, 10 layers) prepared by horizontal lifting method (10 mN/m, 20°C).

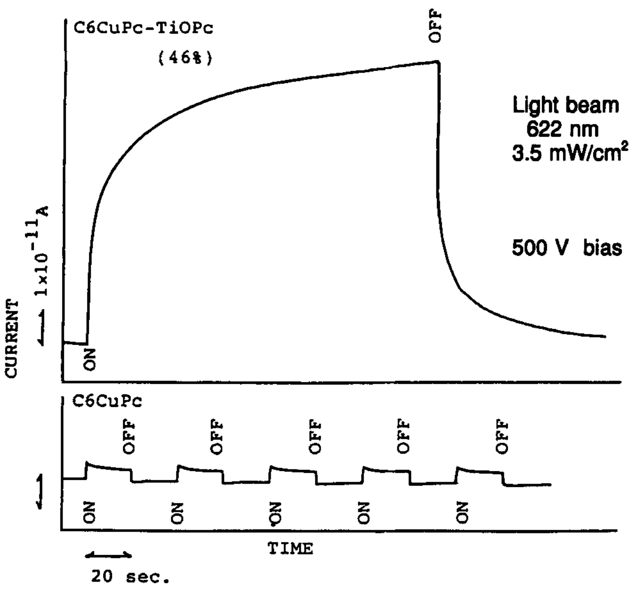

FIGURE 8 Photoresponse of current under 500 V bias voltages for LB films (10 layers); (top) TiOPc-C6CuPc in a 46:54 ratio and (bottom) neat C6CuPc without TiOPc.

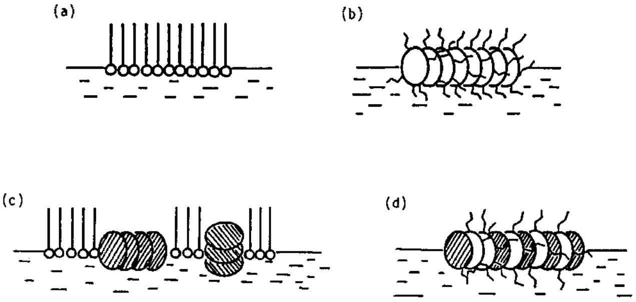

FIGURE 9 Schematic drawings for molecular arrangements of monolayers on water; (a) classical amphiphiles, (b) peripherally substituted phthalocyanine, (c) mixture of peripherally unsubstituted phthalocyanine and classical amphiphiles, and (d) mixture of peripherally unsubstituted phthalocyanine and peripherally substituted phthalocyanine.

chain fatty acids have been frequently employed as transfer promoters for LB films of Pc derivatives, immiscibility of Pcs and the amphiphiles have often been pointed out.[11,12] Many of the LB films of Pcs with these transfer promoters are considered as microscopically inhomogenious LB films. In contrast, the use of soluble and easily-transferable Pcs as transfer promoters of peripherally unsubstituted Pcs is beneficial, because of the structural similarity, to better miscibility in the monolayers. Therefore, the present method may allow the fabrication of better-quality LB films with well ordered molecular orientation. This idea is schematically represented in Figure 9.

Higher photoconductivity, than that in the neat C6CuPc LB film, was achieved by incorporating TiOPc in the film.

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10. The absorption spectrum of the TiOPc (46%)-C6CuPc film (Figure 7), is substantially different from that of the spreading solution (Figure 4), particularly in relative intensities of the absorbances at ~620 nm and ~700 nm. This difference might be attributable to stronger and more complex electronic interactions of Pc molecules in the film compared with those in solution [7]. It is reported that exciton coupling may occur even between different Pc molecules in mixed-crystal thin solid films [see E. A. Lucia and F. D. Verderame, *J. Chem. Phys.*, **48**, 2674 (1968)].
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