Reversible Reduction and Reoxidation of Langmuir–Blodgett Films of Octacyanophthalocyanine Dilithium Complex

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Langmuir–Blodgett film of octacyanophthalocyanine dilithium complex with strong electron-withdrawing substituents was first prepared and its redox behavior was studied by cyclic voltammetry. The LB film exhibited excellent redox reversibility in an acid electrolyte. In contrast to the case of a solution-casting film, two couples of redox peaks were clearly discerned on the voltammetric curve. Also, the linear dependence of cathodic current on scan rate was kept up to 4000 mV s^{-1}, which was 10 times larger than that of the solution-casting film.

Langmuir–Blodgett (LB) films of phthalocyanine (Pc), due to the high thermal and chemical stabilities and non-localized charge distribution of Pc molecules, are attractive candidates for photovoltaic cells, molecular metals, chemical sensors, non-linear optics, and electrochromic display devices.[1] Thus far soluble Pc derivatives with various substituents have been synthesized to prepare LB films and their physical properties have been extensively explored. Of these Pcs, a family of derivatives with bulky alkyl groups is most studied because of their good amphiphilic character and exhibits p-type semiconductivity.[2,3] On the other hand, Pc derivatives with electron-withdrawing substituents such as cyano and nitro groups would show different physical behaviors. Especially, the phthalocyanine substituted by eight cyano groups shows strong n-type semiconductivity rather than the p-type and ready reduction at more positive potentials.[4] Strong electron-withdrawing substituents on the phthalocyanine ring increase the ionization potential and electron affinity of the film. Such features give rise to drastic sensitivity to electron-donating gases and extremely polarized structure in alternating LB films, which are of particular interest in chemical sensors, photovoltaic cells, and non-linear optics.[1,3a] Nevertheless, little study has been done for LB films of Pc derivatives with electron-withdrawing substituents owing to their poor solubility in common organic solvents.

The purpose of this study is therefore to prepare the LB film of a phthalocyanine derivative with eight strongly electron-withdrawing groups, octacyanophthalocyanine dilithium complex (Li_2PcOC), and study its redox behavior based on cyclic voltammetry.

Li_2PcOC was synthesized through the lithium propoxide catalyzed cyclotetramerization of 1,2,4,5-tetracyanobenzene in refluxing *n*-propanol.[5] As mentioned above, the solubility of Li_2PcOC into a common spreading solvent for the monolayer preparation is poor on account of its polar nature. Hence, the mixed solvent composed of benzene and dimethylformamide (DMF), which was a good solvent for Li_2PcOC, was used as a spreading solvent. When Li_2PcOC solution of 0.1 mmol dm^{-3} in benzene/DMF (2/1 v/v) was spread onto the surface of Millipore Milli-Q grade water, a monolayer was successfully formed. Surface pressure (π) vs molecular occupied area (A) isotherm of Li_2PcOC was obtained at a constant compression speed of 0.08 mm min^{-1}. The π was determined by the Wilhelmy balance technique. Since the π abruptly increased in the vicinity of the limiting area, which was specified by extrapolation to π = 0 of the straight portion of the π–A curve, it is plausible that the solid monolayer was formed on the water surface, as sshown in Figure 1. Also, the limiting area of Li_2PcOC was evaluated to be 0.52 nm^2. The cross-sectional areas of an unsubstituted Pc and tetra-*tert*-butyl-substituted one taking an edge-on configuration were reported to be 0.40 and 0.47 nm^2, respectively.[2,3c] Since the Li_2PcOC has eight small cyano groups as substituents, the occupied area of Li_2PcOC should be an intermediate value between those of unsubstituted and tetrabutyl-substituted Pcs, if the Li_2PcOC molecules are densely packed with an edge-on configuration. Thus, it can be envisaged that the Li_2PcOC are in a tilted arrangement at the air/water interface.

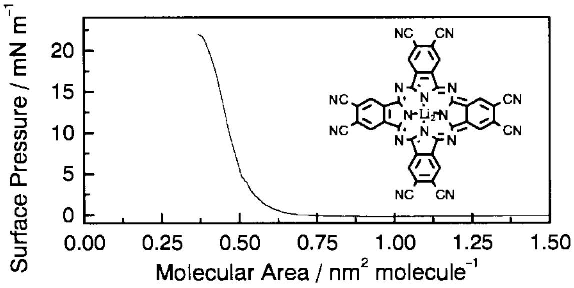

Figure 1. π–A isotherm for Li_2PcOC monolayer.

The Li_2PcOC monolayer on the subphase was transferred onto an indium–tin-oxide (ITO) glass substrate by a horizontal dipping method at π = 11 mN m^{-1}. The transfer ratio was approximately two, meaning that the bilayer Li_2PcOC film was prepared on the substrate. Figure 2 shows the typical cyclic voltammogram (CV) of the bilayer LB film electrode of the Li_2PcOC in 1 M HCl. Two overlapped cathodic current peaks could be distinguished at 30 and –38 mV, while two anodic peak currents appeared at 80 and –9 mV. Since little change was discerned on the voltammogram over 80 cycles, it seems reasonable to claim that this LB film possesses excellent electrochemical stability. The charge passed under the curve was calculated to be about 3.1 F mol^{-1} in either branch of the stable voltammogram, after the correction taking into account the double layer charge capacity. Takeshita et al. examined the reduction and reoxidation of the octacyanophthalocyanine film on an ITO electrode, which was prepared by a solution-casting method, and observed only one reduction peak.[6] They interpreted this result by invoking a complicated characteristic of a semi-conductive ITO electrode. However, the Li_2PcOC LB

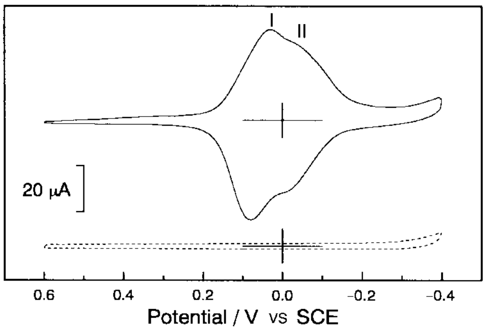

Figure 2. Cyclic voltammogram of LB film of Li_2PcOC deposited on ITO, in 1 M HCl with a platinum coil as the counter electrode and a saturated calomel electrode (SCE) the reference one, scan rate 40 mV s^{-1}, under a nitrogen atmosphere. The dash curve depicts the CV of a bare ITO substrate.

film clearly showed two distinctive reduction peaks on the CV curves, even though the same substrate was used.

Redox process of the film in HCl solution is composed of intercalation and extraction steps of electrons and charge-compensating protons. More concretely, the cathodic reaction involves the following steps; electron injection at the electrode surface, electron transport through the film and intercalation of charge-compensating protons, which produce protonated reduced Pc species with neutral character.[4] On the other hand, electrons and cations were extracted during the anodic reaction. The intercalation and extraction of charge-compensating cations are strongly dependent on aggregation states in the films.[7] In addition, the molecular orientation affects intrinsic conductivity of the film, meaning that electron transport is correlated with the molecular orientation in the film. Therefore, it is conceivable that the discrepancy of CV curves between solution-casting and LB films is arisen from the difference of aggregation states in both films. That is, Li_2PcOC molecules in the LB film are well-ordered in the two-dimensional state. Further investigation is in progress to rationalize this correlation.

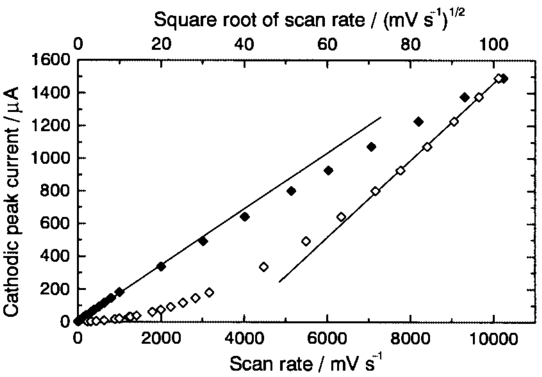

Figure 3. Dependence of cathodic peak current on the scan rate (solid symbol) and its square root (open symbol).

Dynamic character of the electrode process was further examined. Figure 3 shows the scan rate dependence of cathodic peak current for the Li_2PcOC LB film. The linear relation between peak current and scan rate was kept up to 4000 mV s^{-1}. This limiting rate was much faster than that of the corresponding solution-casting film by approximately 10 times,[4] suggesting the possibility of a rapid and sensitive response in chemical sensor applications.[1] Nernstian behavior of the electrode in such a wide scan rate range can be explained in terms of the ultra thin thickness of the LB film configuration. Beyond 6000 mV s^{-1}, the cathodic peak current increased linearly with the square root of the scan rate. This result clearly indicates that the electrode process is diffusion-controlled in this scan rate region.

Table 1. Peak potentials for reduction and reoxidation cycles of Li_2PcOC LB films in different electrolytes, scan rate 40 mV s^{-1}

	Peak potential vs SCE / mV			
Electrolyte	E_{red}^{I}	E_{ox}^{I}	E_{red}^{II}	E_{ox}^{II}
1 M HCl	30	80	−38	−9
1 M LiCl/0.1 M LiOH	−791	−732	−940	−879
1 M NaCl/0.1 M NaOH	−839	−780	−948	−894
1 M KCl/0.1 M KOH	−806	−744	−962	−899

To study an effect of charge-compensating cations on the electrode process, CV measurement was made in three alkaline electrolytes. Comparing with the acid electrolyte, the two redox peaks were more clearly separated and, as listed in Table 1, the potentials of peak currents were shifted into the negative direction in alkaline solution. A large change of the position of the first redox peak was observed when the cation changed from Li^+ to Na^+, while the position of the second redox peak was less dependent on the type of cations. This implies that the incorporation of charge-compensating cation is not simply determined by its ion radius and thus some other factors might exist to account for this phenomenon. More conclusive result about this effect will be reported in near future.

In conclusion, we have successfully prepared the Li_2PcOC LB film. Related with the ordered two-dimensional assembly at a molecular level, two couples of redox peaks were clearly observed on the CV curves for the bilayer LB film. Also, Li_2PcOC LB film showed excellent dynamic character as an electrode.

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