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STRUCTURAL FEATURES OF A CLAY FILM HYBRIDIZED WITH A ZWITTERIONIC MOLECULE AS ANALYZED BY SECOND-HARMONIC GENERATION BEHAVIOR

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Abstract—Hybrid Langmuir-Blodgett (LB) films of a single clay layer and a donor-(π-electron system)-acceptor (D^{δ}-π-$A^{\delta-}$) zwitterionic molecule (ind-TCNQ), prepared from 1,3,3-trimethyl-2-methyleneindoline (donor) and 7,7,8,8-tetracyanoquinodimethane (acceptor) were prepared. The characteristics of the electrostatic interaction between the clay layer and the ind-TCNQ molecules were investigated. The amount of ind-TCNQ molecules spread onto the air-water interface was increased systematically so that mono- and multi-layers of the molecules could be formed on the clay layer. The hybrid LB films, which were deposited onto a solid substrate, were characterized by means of UV-vis absorption spectroscopy and optical second-harmonic generation measurement. The amount of ind-TCNQ molecules adsorbed on the clay layer increased with an increase in the amount of ind-TCNQ molecules spread onto the air-water interface. On the other hand, the SHG intensities of the films did not change with the change in amount of ind-TCNQ spread. The results indicate that the electrostatic interaction between the clay layer and the ind-TCNQ molecules operates only in the region where the ind-TCNQ molecules are in direct contact with the clay layer.

Key Words—Clay, Hybrid Langmuir-Blodgett Film, Second-harmonic Generation, Sodium Montmorillonite, TCNQ Derivatives, Zwitterionic Molecules.

INTRODUCTION

Inorganic-organic hybrid films possess characteristics such as an easily changeable layer-by-layer structure or a precisely controllable film thickness, or a variety of physical properties that are not present in each of the separate components. It should therefore be possible to create new materials with novel functionalities, by utilizing these characteristics. Also, certain physical properties of these hybrid films only exist when a non-centrosymmetric molecular alignment and/or an oriented molecular alignment in the film is present (Burn *et al.*, 1999; Chemla and Zyss, 1987). However, the orientation of the organic molecules in inorganic-organic hybrid films that are produced via layer-by-layer assembly is antiparallel or random in most cases. This situation prevents utilization of these hybrid films for such practical applications as second-order non-linear optics and magnetics because the desirable physical properties are not present.

One of the most widely used techniques for controlling the alignment and orientation of molecules is the Langmuir-Blodgett (LB) technique (Ulman, 1991; Petty, 1996; Ashwell *et al.*, 1990, 1992, 1994; Ashwell, 1999). An amphiphilic molecule, which consists of a hydrophilic head group(s) and a long hydrophobic tail group(s), is used as the component molecule of the film. The amphiphilic molecule is dissolved in a volatile solvent like chloroform and is spread onto an ultra-pure water surface. The hydrophilic group is immersed in the water surface, while the hydrophobic group remains outside. This results in the formation of a monomolecular layer with an ordered molecular orientation at the air-water interface. After evaporation of the solvent, the barrier is moved and the molecules are compressed on the air-water interface. The surface pressure (π) is defined as:

$$\pi = \gamma_0 - \gamma$$

where γ_0 is the surface tension of the pure liquid and γ is the surface tension of the film-covered surface. Since we know the total number of molecules and the total area that the monolayer occupies, we can calculate the area occupied by each molecule and construct a π-A isotherm that describes the surface pressure as a function of the area per molecule (Ulman, 1991; Petty, 1996).

We have applied the LB technique for preparing inorganic-organic hybrid films (Kawamata *et al.*, 2000a) using an aqueous suspension of clay particles as the subphase instead of ultra-pure water. A clay mineral exfoliates into a single layer when stirred in water. The layer bears a negative charge, which is balanced in the precursor material by interlamellar Na^+ cations that can undergo ion-exchange reactions with other cationic materials (Kim *et al.*, 2001a, 2001b; Kleinfeld *et al.*, 1994, 1995, 1996).

Conventional LB films are mechanically unstable because the component molecules are held together primarily by van der Waals forces (Ulman, 1991). On the

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other hand, hybrid LB films are mechanically stable (Kawamata *et al.*, 2000a, 2000b; Ogata *et al.*, 2002, 2003; Yamagishi *et al.*, 2002). The reason for this difference is thought to be because the negatively charged single clay layer and the ionic-organic molecules or metal complex cations in hybrid LB films are bound via electrostatic attractive forces. In addition, we found that the ionic-organic molecules or metal complex cations in the hybrid LB films adopted a non-centrosymmetric molecular alignment by utilizing the electrostatic interaction even if the molecules did not possess a long alkyl chain (Kawamata *et al.*, 2000a, 2000b; Ogata *et al.*, 2002, 2003; Yamagishi *et al.*, 2002).

In this study, we made further investigations into the electrostatic interaction between the components of a hybrid LB film by examining some of the characteristics of the long-range cohesion interaction between the inorganic and organic components. In order to understand the effective distance of electrostatic interaction between a clay layer and an ionic molecule, we prepared hybrid LB films where the ionic molecules form a multilayer region while the clay remains a single layer. For the ionic molecule, a donor-(π-electron system)-acceptor (D^{δ}-π-$A^{\delta-}$) zwitterionic molecule (ind-TCNQ; Figure 1) prepared from 1,3,3-trimethyl-2-methyleneindoline (donor) and 7,7,8,8-tetracyanoquinodimethane (acceptor) was employed. The resulting films were characterized by UV-vis absorption spectroscopy and optical second-harmonic generation (SHG) measurements. We found that only the ind-TCNQ molecules in the monolayer region that are in direct contact with the clay layer maintain a non-centrosymmetric molecular alignment.

EXPERIMENTAL

Preparation of the clay LB film

Figure 2 is a schematic representation of a film preparation involving the combination of a clay and ind-TCNQ molecules. Instead of ultra-pure water, which is commonly used as the sub-phase in the conventional LB technique, an aqueous suspension of clay particles (Na-montmorillonite, 0.01 g/L) was employed. Previous work on the hybridization of an alkyl amine monolayer with a clay showed that the clay particles were present as single layered platelets under the conditions used here (Takahashi *et al.*, 2002). Thus, in this study, the clay should be exfoliated as single-layered particles in the sub-phase, so the obvious conclusion is that the Na^{+} ions of the clay particles remain as interlayer cations.

The ind-TCNQ molecules were dissolved in chloroform (2.0×10^{-4} mol/L). The solubility of the molecules in chloroform was roughly estimated to be 6.0×10^{-3} mol/L. The solution was then spread onto the clay-dispersed sub-phase (Figure 2a). Since the clay layer is negatively charged, the positively charged moiety of the ind-TCNQ molecules should be attracted to the clay

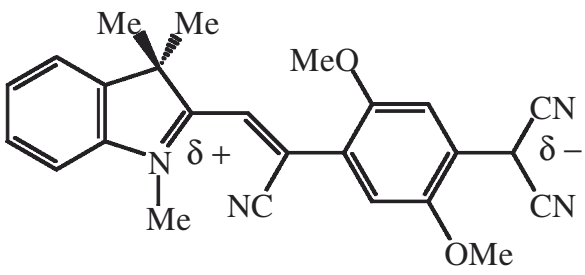


Figure 1. Molecular structure of ind-TCNQ.

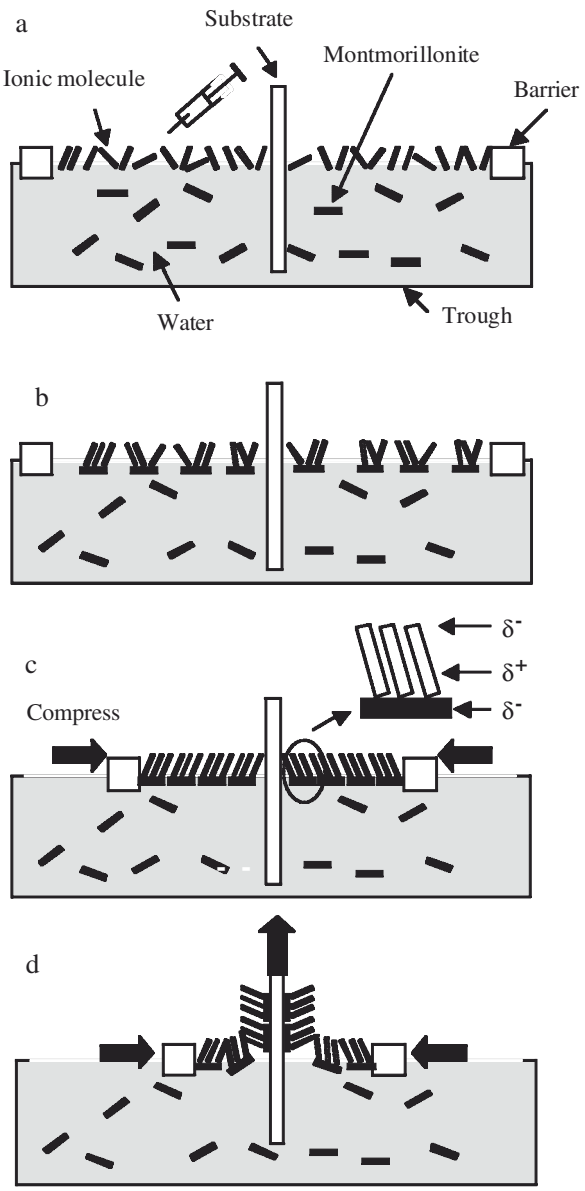


Figure 2. Schematic representation of the procedure to prepare hybridized clay-ionic molecule films.

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layer at the air-water interface (Figure 2b). It is not certain which cation is present as the exchanging cation in the clay parts of the films. It is likely that the Na^+ ions remain as the exchangeable cations in the film.

Next, we performed a common procedure for preparing a conventional LB film (Ulman *et al.*, 1991; Petty, 1996; Ashwell, 1999), as follows. After evaporation of the solvent, the resulting hybridized clay-ionic molecule layer was compressed at the rate of 5 cm^2/min by moving the barrier (Figure 2c). Figure 3 shows an example of the surface pressure-area per molecule (π-A) isotherm taken when the volume of ind-TCNQ spread was 140 μL. The compressed film was deposited onto a hydrophilic silica substrate by the vertical deposition method (Figure 2d). The preparation of a hydrophilic substrate is described elsewhere (Kleinfeld *et al.*, 1994). A trough with a maximum area of 130 cm^2 was used. The cross-section of the ind-TCNQ molecule was calculated to be 0.6 nm^2 when the molecule is viewed along the long axis. In our experimental set-up, a monolayer of the ind-TCNQ molecules should be formed when the volume spread is <180 μL, in which case one molecule occupies an area of 0.6 nm^2. A multilayer is considered to be formed when the amount of ind-TCNQ solution spread is >180 μL.

Optical measurements

The UV-vis absorption spectra of the hybrid LB films were recorded on a JASCO Ubest-30 spectrophotometer. Incident-angle dependence of the SHG intensities of the films were measured using a pulsed beam from a repetitively Q-switched Nd-YAG laser (Lee, Model 818TQ; 1 kHz) at a wavelength of 1.064 μm with a pulse duration of 100 ns, and a peak power of 5 kW. The angle of incidence of the laser beam, relative to the film, was rotated from 0 to 60º.

RESULTS AND DISCUSSION

First, we studied the relationship between the spread volume of the solution of ind-TCNQ and the molecular alignments of the ind-TCNQ in the prepared films. As mentioned previously, a chloroform solution of ind-TCNQ molecules was dispersed onto an aqueous suspension of clay to form the hybrid LB film. The spread volumes of ind-TCNQ solution were varied at 140 μL, 210 μL, 280 μL and 420 μL. When the volume spread was 140 μL, deposition of the film onto the silica substrate was initiated when the surface pressure reached 20 mN/m. The surface pressure was kept constant during the deposition. When spreading volumes were >140 μL, the depositions were initiated with the barrier at the same position when the surface pressure was 20 mN/m and the spreading volume was 140 μL. For all of the depositions, the transfer ratio was close to unity. The transfer ratio is defined as the ratio of the decrease in the area of the floating film to the area of the substrate during the deposition. Continuous compression is needed to maintain surface pressure when a film is transferred to the substrate. Consequently, the area of the film at the air-water interface decreases during the deposition. The average thicknesses of the organic portion of the deposited films were expected to be a monolayer, 1.5, 2.0 and 3.0 layers thick when the spread volume of ind-TCNQ was 140, 210, 280 and 420 μL, respectively. Figure 3 shows an example of the π-A isotherm. In the case of the conventional LB technique, regions I and II are referred to as the gaseous phase and expanded phase, respectively (Ulman *et al.*, 1991; Petty, 1996). However, for the clay LB technique, regions I and II have been defined as expanded phase and condensed phase, respectively (Yamagishi *et al.*, 2002). Thus, the behavior of the π-A isotherm of the clay LB technique is a little different from that of the conventional one.

The UV-vis absorption spectra taken for these films, and the solution of ind-TCNQ in chloroform, are shown in Figure 4. The spectra show an absorption maximum at 705 nm that is assigned to a charge-transfer band, a shoulder at ~790 nm for the ind-TCNQ molecules in solution, and another shoulder at ~860 nm for the films. We also measured the dependence of the UV-vis spectra on the concentration of ind-TCNQ in chloroform solution in the concentration range between 10^{-6} and 10^{-4} mol/L (data not shown). The absorption maximum and shoulder position were essentially the same in the stated range. In addition, the absorption maximum at 705 nm for all films was identical to that of a chloroform solution. This fact suggests that the electronic states of the chromophore in the films are the same in solution. However, the position of the shoulder observed for the

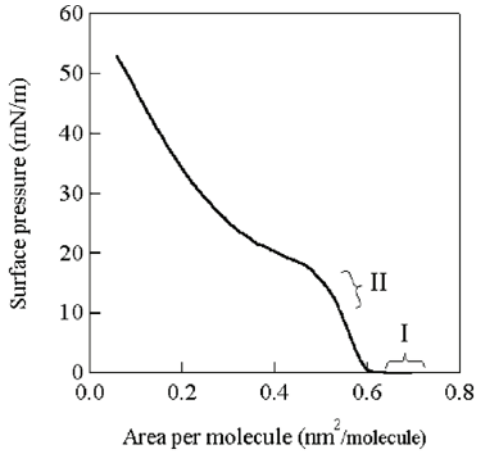


Figure 3. An example of the π-A isotherm. The isotherm recorded for a film prepared under the following conditions is shown. The concentration of the chloroform solution of the ind-TCNQ molecules was 2.0×10^{-4} mol/L and the spread volume was 140 μL. The barrier speed was 5 mm/min. The concentration of the aqueous suspension of the clay was 0.01 g/L. Region I corresponds to steps shown in Figure 2a and b, and region II corresponds to that shown in Figure 2c.

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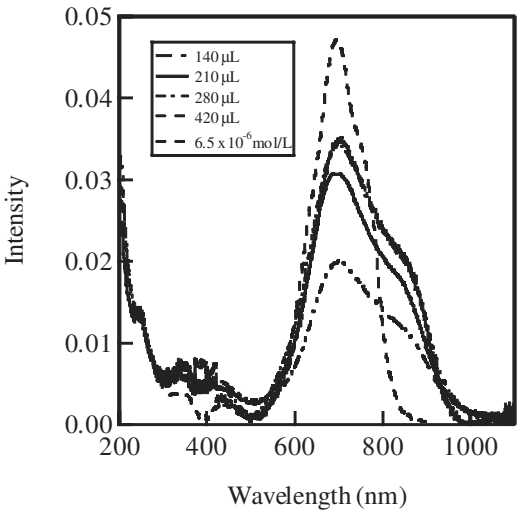


Figure 4. The UV-vis absorption spectra of hybrid LB films prepared at various spread volumes, and for the chloroform solution of the ind-TCNQ molecules.

films and that observed for the solution was different. Since the electronic nature of the species causing this shoulder has not yet been revealed, the reason for the shift is unknown.

The absorbance at $\lambda = 705$ nm for the films is plotted as a function of the spreading volume of ind-TCNQ solution in Figure 5. The data indicate that the absorbance increases with an increase in the spreading volume initially, then begins to level off at the larger spreading volumes of 280 and 420 µL. The most likely reason for the non-linear dependence exhibited is thought to be the partial crystallization of the ind-TCNQ molecules at the air-water interface, which does not take place in linear fashion. Regardless of the reason, a uniform multilayer is thought to be formed in the region where the absorbance increases linearly.

An example of the results of the SHG experiment is shown in Figure 6. A clear fringe pattern of the SHG signal was observed. This indicates that the film is attached to the substrate uniformly at least within the part used for SHG measurement. As we have already mentioned in the experimental section, the films were prepared by the vertical deposition method and therefore the films should be attached to both sides of the substrate. The fringe pattern arises as an interference of the second-harmonic light generated by the films attached on both sides of the substrate. If the films are not attached to both sides of the substrate uniformly, a clear fringe pattern of the SHG signal intensities should not be observed. Thus, the SHG measurement is a powerful tool to investigate the uniformity of the film. We also checked the dependence of the SHG intensities for the hybrid LB film on the volume of ind-TCNQ dispersed. The SHG intensities were essentially the same for the various volumes dispersed. This indicates that the monolayer region of the ind-TCNQ molecules is well

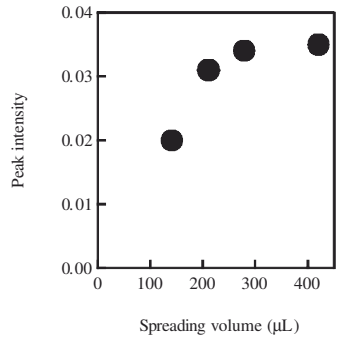


Figure 5. The dependence of the absorption peak intensity at $\lambda = 705$ nm of the hybrid LB films on the spread volumes of ind-TCNQ solution.

ordered on a clay layer and that the other regions of the ind-TCNQ molecules, *i.e.* the regions not in contact with the clay, are disordered.

CONCLUSIONS

A hybrid LB film of a single layer of a clay mineral and ind-TCNQ molecules was prepared where the thickness of the organic part of the film was changed systematically by varying the spreading volume of ind-TCNQ solution. Based on measurements of UV-vis absorption spectra and SHG signal intensity of the fabricated films, we conclude that the thickness of the ind-TCNQ layer of the hybrid LB film increases with an increase in spreading volume, and that a non-centrosymmetric structure is maintained only in the region where the ind-TCNQ molecules are directly in contact with the clay layer. In other words, electrostatic control of the ind-TCNQ layer by a negatively charged clay is restricted in this narrow region. These results should prove helpful for further studies into the development and use of hybrid LB films for practical applications.

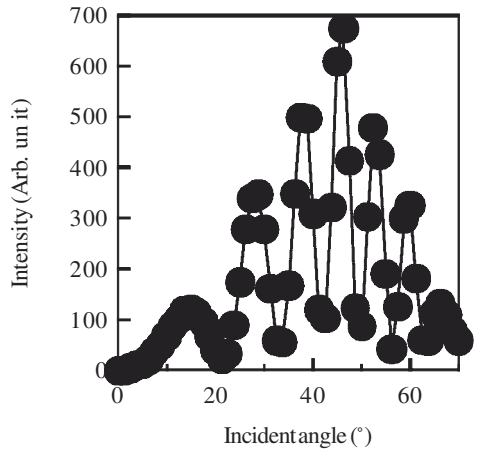


Figure 6. An example of the incident-angle dependence of the SHG signal intensities. The fringe pattern shown was taken for the hybrid LB film prepared at a spread volume of 140 µL, a 10 min waiting time for evaporation of the solvent, and a barrier speed of 5 mm/min. The solid line serves as a guide.

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