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We have attempted to develop a novel Langmuir-Blodgett (LB) film with a non-centrosymmetric molecular alignment by hybridizing a clay and an organic molecule, a D-π-A zwitter ionic molecule based on amine and TCNQ derivatives. Hybridization is made by forming a monolayer of the organic molecule onto a subphase of an aqueous dispersion of a clay. Second Harmonic Generation (SHG) measurements have revealed that the hybridized LB film possesses non-centrosymmetry in spite of the fact that the used organic molecule has neither a positive charge nor a long alkyl chain. Observations with a Brewster Angle Microscope (BAM) have revealed a clear difference in film properties when pure water as opposed to and a clay suspension is used as a subphase. These facts suggest that the clay plays an important role in the organization of zwitter ionic molecules in the film.

Keywords: Clay; Zwitter ionic molecule; TCNQ derivative; LB film; Hybrid film; Second Harmonic Generation

INTRODUCTION

Organic materials are expected to be used as functional materials in the fields of electronics[1, 2], optics[3, 4] and so forth. This is because the recent development of molecular engineering has made it possible to synthesize a molecule with desired properties[3, 4]. Some interesting properties are observed only when the molecular alignment is a non-centrosymmetric array[3, 5].

The Langmuir-Blodgett (LB) technique is one of the most attractive methods to control molecular alignment and orientation[6]. Crystal structures of many organic molecules have been reported to have a centrosymmetric structure[7]. In most cases, the molecular alignments of spin-coated and cast films are random with no non-centrosymmetric organization. By using the LB technique, it is possible to align molecules in a non-centrosymmetric array. Unfortunately, however, a LB film is generally too soft to maintain its primary as-grown alignment, that is, the films have a tendency to collapse and realign[6]. This is because the aggregation force is mainly by weak intermolecular force (van der Waals force). In order to overcome these defects, we have improved the mechanical strength of the film by hybridizing it with a clay. Since the clay layer is rigid and charged negatively[8], a molecule which has a positively charged moiety is considered to be attached to the clay surface by electrostatic attractive force. Based on the above hypothesis, we have already prepared a hybrid film of a clay and [Λ-Ru (4,7-diphenyl-1,10-phenanthroline)$_3$](ClO_4)$_2$ (Λ-Ru(dpp)$_3$) by using the LB technique. As a result, we have confirmed that the film is stable enough for SHG measurements for at least one month[9, 10].

If electrostatic interaction can play a role as a cohesive force of the film, the minimum requirement for the molecule is that the molecule be equipped with a positively charged moiety. That is, the molecule need not necessarily be equipped with a long alkyl chain or even a net positive charge. Based on this, we have fabricated a hybrid film of a clay (sodium montmorillonite) and a D-π-A zwitter ionic molecule based on amine and TCNQ derivatives. In order to examine the molecular alignment of the film, we have made Second Harmonic Generation (SHG) measurements of the film. As a result, zwitter ionic molecules in the film are found to be aligned in a non-centrosymmetric array. The result of the Brewster Angle Microscopy (BAM) observation made clear the role of a clay in forming a uniform film.

SAMPLE PREPARATION

A chloroform solution of D-π-A zwitter ionic molecules (Figure1.) was spread onto an aqueous suspension of a clay (sodium montmorillonite, 0.02 g/l). After 30 minutes, the surface was compressed at the rate of 10 cm^2min^{-1}. The deposition of the hybrid film was performed on a silica substrate at 20 mN/m. The Z-type hybrid film was prepared by the vertical deposition method where the deposition was made onto both sides of the substrate. The Y-type hybrid film was prepared by the horizontal deposition method where the film was deposited onto only one side of the substrate.

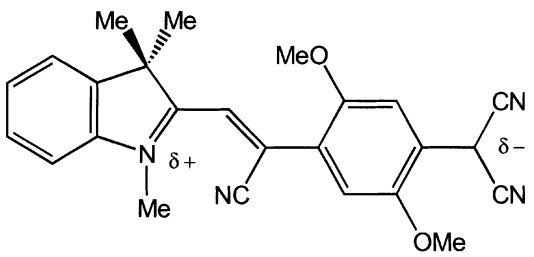

FIGURE 1. Chemical Formula of D-π-A zwitter ionic molecular based on amine and TCNQ derivative.

OPTICAL EXPERIMENT

The absorption spectrum of UV-vis on the substrate was measured with a SHIMADZU UV-160 spectrophotometer. Incident angle dependence of the SHG intensity was measured using a pulsed beam from a repetitively Q-switched Nd-YAG laser (Lee, Model 818TQ; 1kHz) at a wavelength of 1.064 μm, with a pulse duration of 100 nsec, and a peak of 1 kW.

RESULTS AND DISCUSSION

The absorption spectra for the Z-type and Y-type hybrid films are shown in Figure 2. Since the Z-type sample has two hybrid films on

both sides of the substrate, the intensity of the absorption spectrum of the Z-type sample was expected to be twice as large as that of the Y-type sample. Comparing the intensities of the Z- and Y-type hybrid films, however, the intensity of the Z-type hybrid film is rather smaller than that of Y-type hybrid film. It was also noted that the intensity of the Z-type films depended greatly on each sample. On the other hand, those for the Y-type films do not show significant sample dependence. This fact suggests that the quality of the Y-type sample is better than that of the Z-type sample.

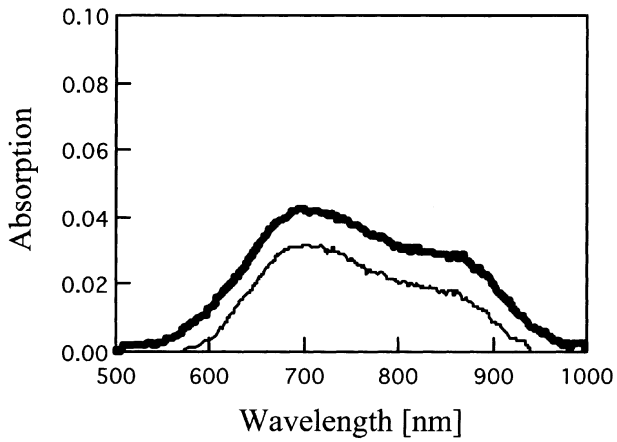

FIGURE 2. Example of the absorption spectrum of the Z-type(thin line) and Y-type(thick line) hybrid-films of a clay and zwitter molecules

The SHG intensity of the incident angle dependence from both films is shown in Figure 3. In the case of the Z-type hybrid film, the interference pattern of SHG light, which arises from both sides of the substrate, is clearly observed. As for the Y-type hybrid film, the SHG intensity tends to increase from zero angle, reaching a maximum at $\theta =$ 50° as the value of the incident angle increased from zero to 75°. These behaviors are typical for each type of thin films exhibiting SHG activity[11, 12]. It is concluded therefore that the molecules in those films are arranged in a non-centrosymmetric array. It is also certain that the signal arises from the film and not from the substrate. In a solid state,

the present compound has been found to be crystallized in a centrosymmetric array ($P\bar{1}$)[12] in order to avoid the electric repulsion between the large dipole moments. Seeing that they were aligned in a noncentrosymmetric array in the hybrid film, it is natural to consider that such an alignment is induced by the existence of the clay. In this respect, the clay plays a crucial role in forming the hybrid film.

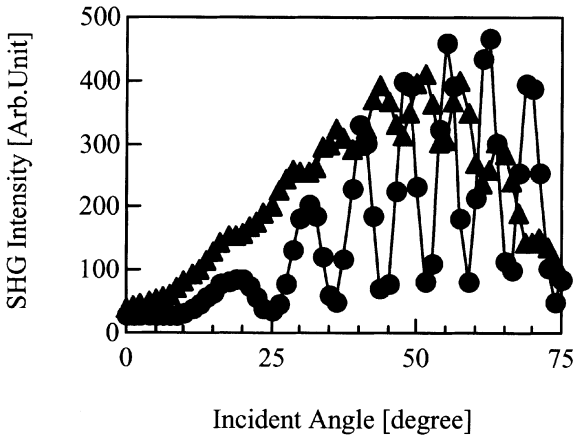

FIGURE 3. Incident angle dependence of the SHG signals from Z-type (×2;triangle) and Y-type (circle) hybrid film. The solid line serves as a guide.

Preliminary results of the BAM experiments also support the above statement. That is, it is observed that the film spread on an aqueous suspension of a clay was homogeneous, while the film spread on pure water was considerably heterogeneous.

CONCLUDING REMARKS

In this paper, we have fabricated a non-centrosymmetric LB film by hybridizing sodium montmorillonite and a D-π-A zwitter ionic molecule based on amine and TCNQ derivatives. Since the present molecules have no long alkyl chain, the method may be expected to be

effective particularly for chromophores where it such a chromophore as is difficult to introduce an alkyl chain. Thus the method should provide a means to control the molecular alignment of a wider range of functional materials. Attempts to prepare a Z-type multilayered film of high quality are now in progress.

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