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4-Octadecylamino-4'-nitro-tolan (ANT-18) and stilbene (ANS-18) formed stable condensed monolayers with the chromophores nearly vertical at the air/water interface. Applying the horizontal lifting method by rotation of the substrate with respect to the monolayer compression, a considerable in-plane anisotropy of the SHG for the ANT films was observed, whereas the ANS films showed relatively weak isotropic SHG intensities.

Keywords: anisotropic SHG; push-pull tolan; push-pull stilbene; monolayer assemblies; lifting method

INTRODUCTION

Non-centrosymmetric arrangements of amphiphilic polar molecules with donor and acceptor groups could be formed in the monolayer at the air/water interface. [1, 2] The Langmuir-Blodgett films with non-centrosymmetric structures could be obtained from some amphiphiles with azobenzene,[3] nitrostilbene,[4] and also nonlinear optical chromophores such as 2-docosylamino-5-nitropyridine and N-docosanoyl-4-nitroaniline.[5] It is well known that the tolan skeleton, diphenylacetylene has an advantage without chemically or photochemically *cis* →*trans* isomerization which can occur in the corresponding stilbenes.[4] The NOL properties of several push-pull tolans have been studied.[5-9] In the present work, for a long-chain push-pull toalan derivative the monolayer assemblies were prepared by the horizontal lifting method through rotation of a solid substrate with respect to the monolayer compression, and polarization dependence of the SHG intensity of the multilayer has been examined, as compared with that of a long-chain push-pull stilbene.

EXPERIMENTAL

A push-pull tolan derivative, 4-octadecylamino-4'-nitrotolan (ANT-18) was synthesized by coupling of octadecylaminoiodobenzene with 4-ethynylnitrobenzene using $Pd(PPh_3)_2Cl_2$ /CuI as a catalyst and triethylamine as a base. The chemical structure was identified by IR, MS and NMR spectra together with elemental analysis, and its melting point was 101.4 °C. 4-Octadecylamino-4'-nitrostilbene (ANS-18) was purchased from Lambda Probes & Diagnostics and its melting point was 120.1 °C. The monolayers were spread from toluene solution (10^{-5} M) onto the distilled water surface, and the surface pressure – area (π – A) isotherms were measured by a Lauda film balance. The monolayer assemblies were built up on microscope glass plates at 10 mN/m by the horizontal lifting method to form the nonalternating X-type films. Second-order NLO susceptibilities $\chi^{(2)}$ for the films were obtained at 532 nm by irradiation with a Q-switched Nd:YAG laser (Spectra-Physics Model GCR-170); repetition rate, 10 Hz; pulse width, 9 ns); the polarizer and the analyzer were set up in front of and behind the film, respectively; and the sample was rotated around the axes along the direction of monolayer compression and/or the axis perpendicular to both the surface normal and the monolayer compression. The SHG signal from the film was normalized relative to the second-harmonic Marker fringes from a 5 mm thick glass plate (d_{11}= 0.46 pm/V).

RESULTS AND DISCUSSION

Both ANT-18 and ANS-18 formed rigid condensed monolayers with the limiting areas (extrapolated from the linear part to zero pressure, $A_{\pi \to 0}$) of 26 and 24 Å^2/molecule respectively, on the water surface at 20 °C, as shown in Fig.1. Taking account of the X-ray crystal analysis[10] as well as the Corey-Pauling-Koltum model for tolan and stilbene, it is considered that long-axes of the chromophores stand nearly vertically in the condensed monolayers. As previously reported,[11] the ANT-18 monolayer could be transferred onto a solid substrate at 10 mN/m by the Langmuir-Blodgett (vertical dipping) method to form the alternating head-to-head and tail-to-tail Y-type multilayer which showed the anisotropic SHG due to the herring-bone structure induced by the transferring process. While the ANS-18 monolayer couldn't be deposited by the LB method. By applying the horizontal lifting method to these monolayers which were spread on the water surface in the long and narrow trough (180 cm x 6 cm) and compressed with a unidirection at 10 mN/m, the nonalternating head-to-tail X-type multi-

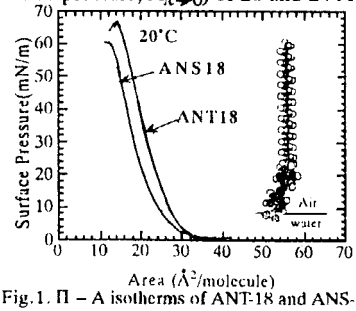

Fig.1. Π – A isotherms of ANT-18 and ANS-18.

layers could be obtained. Comparing to the normal horizontal lifting method, the lifting method with rotation of the substrate was used. That is, after the first two layers were transferred, then the substrate was rotated with an angle of 30^0 and the following two layers were transferred successively. After the first four layers were transferred (4 L), then the substrate was rotated with an angle of 180^0 and the second four layers (4 L*) were transferred in an antiparallel fashion to the previous 4 layers (total of 8 layers). The SHG intensity as well as the linear dichroism of polarized UV-vis. spectra for the (4 L + 4 L*) film of ANT-18 on only one side, deposited at 10 mN/m, was reduced in comparison with the (8 L) film, as reported in the previous paper.[12] In the case of the normal (8 L) film of ANS-18 deposited at 10 mN/m by the lifting method, the linear dichroism was observed very little. The optical density *v.s.* the number of layers for both ANT- and ANS-18 films prepared by the lifting method had a good linear relationship. Figure 2 shows the polarized UV-vis. spectra of the ANT- and ANS-18 films at 45^0 incidence, prepared by the lifting method, as compared with the solution spectra. From dichroisms of the bands at visible region of which the transition moment can be assigned to the direction along the long axis of tolan and stilbene, respectively, the tilted orientation of the long axis of the chromophores is suggested in the films. And also the red shifts of the film spectra from the solution supprted the chromophore orientation with some inclination as well as the aggregate formation in the films.[12]

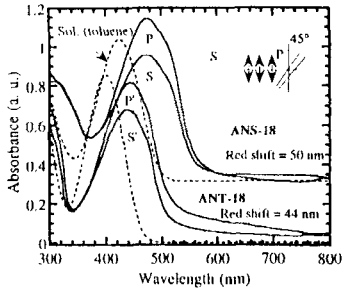

Fig. 2. Polarized UV-vis. spectra of ANT- and ANS-18 films prepared by HL method at 10 mN/m, in comparison with solution spectra.

Figure 3 shows the polarization dependence of the SHG signal for the ANT-18 (A) and ANS-18 (B) films (16L on one side) prepared at 10 mN/m by the lifting method. When both the polarizer and the analyzer were aligned along the direction of the monolayer compression and the film was rotated about the axis perpendicular both the surface normal and the monolayer compression, the (P-P) trace was obtained, and the bottom trace (S-P) indicates the SHG signal for the same rotation at the S-polarized input and the P-polarized output. From that a significant anisotropy in the SHG intensity was observed for the ANT-18 film, it is considered that the in-plane anisotropy of $\chi^{(2)}$ is probably due to enhancement of the $\chi^{(2)}_{xxx}$ and $\chi^{(2)}_{yyy}$ tensors caused by the monolayer compression through the transferring procedure in which the long axis of the NLO chromophore was preferentially oriented nearly perpendicular to the monolayer compression in the very long and narrow trough. On the other hand, the different orientation of the NLO chromophore was observed for the ANS-18 film in which the component of $\chi^{(2)}_{xxx}$ and $\chi^{(2)}_{yyy}$

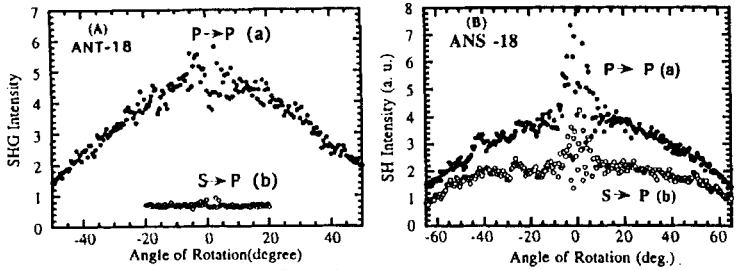

Fig.3. Polarization dependence of SHG for (A) ANT-18 and (B) ANS-18 films prepared by HL method at 10 mN/m; (a) p-polarized input, p-polarized output, (b) s-input, p-output.

tensors were almost same. This result is well consistent with that of the polarized UV-vis. spectra. As previously reported,[12] from the *in situ* observation with a Brewster angle microscopy the two-dimentional domains were shown in the ANT monolayer, which is considered to be effective on the in-plane anisotropic orientation rather than the single chromophore. Plots of the square root of the SHG intensity against the number of layers for the ANT-18 and the ANS-18 films prepared at 10 mN/m by the lifting method, gave a good linear relationship as expected. Figure 4 shows the polarization dependence of the SHG signals for the ANT-18 film prepared by the normal lifting (A) method, in compari-son with that by the rotational lifting(B) the substrate with respect to the monolayer compression (each 2L at the 30° interval rotation). The considerable anisotropy of the SHG signals was observed which is probably due to the long axis of the NLO chromophore with preferential orientation nearly perpendicular to the monolayer compression, resulting in the noncentro-symmetric self-assembly of ANT-18 at the air/water interface.

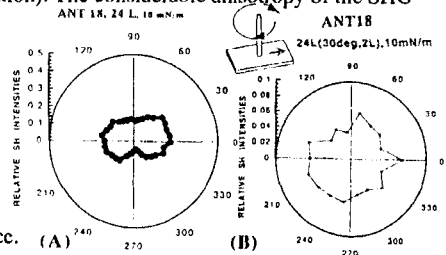

Fig.4. Polarization dependence of ANT-18 films prepared by the different HL methods at 10 mN/m.

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