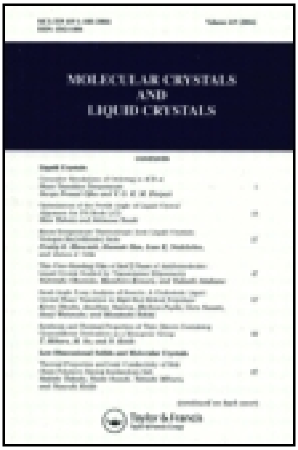

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Second Harmonic Generation in Langmuir-Blodgett Films of a Novel Phenylhydrazone Dye

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The LB films of a new phenylhydrazone dye, 4-hexadecanoxynaphthyl-4'-nitro phenylhydrazone, were prepared. The second harmonic generation (SHG) from monolayer and multilayers of the dye was measured. The dependence of SHG on number of layers is weaker than the expected square law.

Keywords: Naphthyl-ether; phenylhydrazone; LB film; SHG

INTRODUCTION

Recently, the desire to utilize the nonlinear optical (NLO) properties of materials in applications such as optical communications and data processing has created a need for the new materials with large nonlinear susceptibilities. The principal requirement for second harmonic generation (SHG) is a non-centrosymmetric structure. For optically active organic compounds, it can be offered by the Langmuir-Blodgett (LB) technique which is especially important as a means of imposing a noncentrosymmetric structure onto a material that forms centrosymmetric crystals.

In the families of molecules with NLO properties, phenylhydrazone is a new class of nonlinear dyes and is more particular compared with other systems. The smaller energy gap between ground and excited states in the molecules makes the charge transfer easier and relatively high molecular hyperpolarizability (β) could be produced. Lupo et al[1,2] reported the SHG results in LB films of several amphiphilic phenylhydrazone derivatives. This paper describes the LB films formation of a new phenylhydrazone dye with naphthyl-ether group and its SHG response.

EXPERIMENTAL

4-Hexadecanoxynaphthyl-4'-nitrophenylhydrazone (dye A) shown in Figure 1 was synthesized through condensation of 4-hexadecanoxy-naphthaldehyde with p-nitrophenylhydrazine. 2-Hexadecanoxynaphthyl-4'-nitrophenyl-hydrazone (dye B) was also prepared in order to compare the monolayer behavior with dye A. The products were characterized by elemental analysis, IR, ^{1}H-NMR and mass spectroscopy.

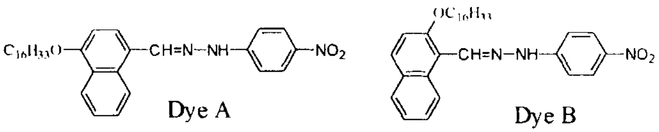

FIGURE 1 Chemical structures of dye A and dye B

Surface pressure-area isotherm measurements and deposition experiments were carried out on a KSV 5000 instrument at 21±1°C. A known amount of the compounds dissolved in chloroform (0.5-0.6 mM) was spread onto pure water. At a constant pressure of 19 mN m^{-1}, the monolayer on the subphase was transferred to quartz plates by the vertical dipping method in a speed range of 0.5-1 mm min^{-1}.

UV-Vis spectra of the LB films were recorded on a HP 8451A spectrometer. SHG of LB films was measured in transmission with a Y-cut quartz plate as reference and with a Nd:YAG laser beam ($\lambda=1.06\mu m$) at an angle of 45° to the film surface.

RESULTS AND DISCUSSION

Figure 2 shows the surface pressure-area isotherms of two phenylhydrazone dyes. Dye A exhibits a steep solid analog phase and the collapse pressure higher than 39 mN m^{-1}. The limiting molecular area is 0.37 nm^2 and only a little difference smaller than 0.01 nm^2 per molecule was observed between the first and subsequent compressions, suggesting the good monolayer behavior of dye A at the air-water interface. The monolayers could be transferred onto various substrates with a transfer

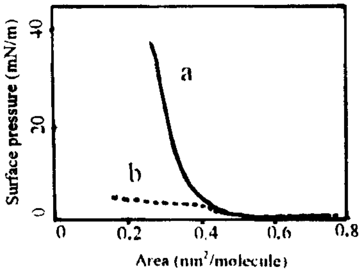

FIGURE 2 π-A isotherms of (a) dye A and (b) dye B

ratio of 0.9, forming Z-type films. The area per molecule at the deposition pressure is ca. 0.32 nm^2, implying that the hydrocarbon tails of the amphiphile can not be packed densely within the monolayer due to existence of naphthalene ring with larger dimensions. The isotherm of dye B is different from that of dye A, having a very low collapse pressure of 5 mN m^{-1}. This compound is obviously not suitable for formation of LB film maybe because the separation between hydrophilic and hydrophobic groups in molecule B is not far enough. This fact indicates that different substitution positions to the bridged group of the same substituted component would effect the monolayer behavior significantly.

The SH intensities of monolayer of dye A relative to a Y-cut quartz wedge $I_{2\omega}^{p,p}$ and $I_{2\omega}^{s,p}$ are 1.39×10^{-4} and 1.86×10^{-5} respectively. We assume that the refractive indices and thickness per layer of dye A are similar to those of phenylhydrazone derivative reported[1] ($n_\omega \approx n_{2\omega}=1.61$, $=2.75$nm). Using the known method[3], the second-order susceptibility $\chi^{(2)}$, molecular hyperpolarizability β and tilt angle φ for the molecules on a substrate are 1.64×10^{-7} esu, 4.66×10^{-30} esu and 26° respectively. Compared with the result of 4-hexadecanoxyphenyl-4'-nitrophenyl hydrazone[2], the β value is not very sensitive to the length of the conjugated system in this case.

The UV-Vis spectrum of dye A LB films exhibits a characteristic band at 446 nm and has a 32 nm red-shift of the absorption peak compared with that of the corresponding solution. As shown in Figure 3, the absorbance is additive with the

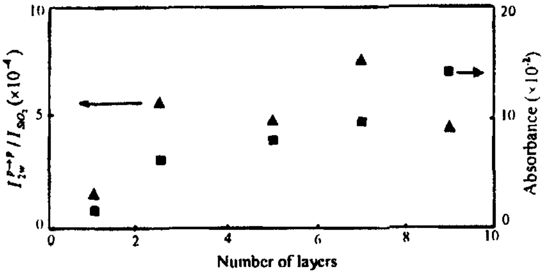

FIGURE 3 Dependence of SHG (▲) and absorbance at 446 nm (■) of dye A LB films on the number of layers

number of layers which is proportional to the amount of dye A transferred to substrate. The superposition of SH intensity depends on the geometrical sum of dipole moments of the molecules. Unfortunately, we failed to see the expected increase in SHG with the number of layers indicating disordering of the multilayer. The ideally quadratic relationships are not often observed in practice. This is due to that molecular dipoles prefer an antiparallel alignment. the molecules in Z-type films may rearrange in part to Y-type structure during or shortly after deposition. In addition, disorder could also result from the cumulative defects in films especially in our case. since the molecules are in a tilted arrangement on the substrate. In order to solve these problems. we plan to use alternating layers of dye A with arachidic acid or other molecules as a passive layer which can reduce the tendency of the molecules to invert during deposition and avoid the cancellation of SHG between the successive layers.

Acknowledgements

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