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Quadratic Enhancement of the Second-Harmonic Intensity from Alternate-Layer Langmuir-Blodgett Films of an Optically Nonlinear Dye and Poly(*T*-Butyl Methacrylate)

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Langmuir-Blodgett films of the optically nonlinear dye are non-centrosymmetric when the LB layers are interleaved by poly(*t*-butyl methacrylate). The second-harmonic intensity increases as $I_{2\omega(N)} = I_{2\omega(1)}\ N^2$ where N is the number of active layers, and the normalised intensity is independent of film thickness to more than 100 bilayers. The second-order susceptibility and chromophore tilt angle are as follows: $\chi^{(2)}_{zzz} = 60$ pm V^{-1} at 1.064 μm and $\varphi = 32°$ relative to the normal to the substrate. The susceptibility is resonantly enhanced but the absorbance at the harmonic wavelength is only 1.5×10^{-3} bilayer^{-1}.

Keywords: Langmuir-Blodgett; second-harmonic generation

INTRODUCTION

Interest in LB films for second-harmonic generation (SHG)[1-6] stems from the requirement that the structure must lack inversion symmetry and, consequently, from the layer-by-layer control of the deposition. Amphiphilic molecules, those with a hydrophilic head and hydrophobic alkyl tail, align

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with their hydrophilic groups adjacent to the water subphase but, when deposited, the layers tend to pack centrosymmetrically with the interfaces being alternately hydrophilic (head-to-head) and hydrophobic (tail-to-tail). This may be overcome by interleaving the layers and, for such films, long-range order has been realised by interdigitating the alkyl tails of the dye and spacer ("molecular zips"),[1,2] by utilising interlayer hydrogen bonding[3] and, in general, by simply exploiting SHG-active dyes and inactive spacers which readily deposit on the upstroke and downstroke respectively.[4-6] A useful spacer material is poly(*t*-butyl methacrylate) and, in this work, we report its deposition and the second-order properties of an alternate-layer structure with a chemically modified hemicyanine dye (Figure 1).

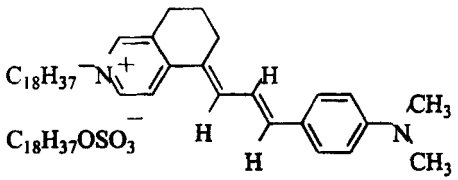

FIGURE 1 Molecular structure of the SHG-active dye.

EXPERIMENTAL SECTION

The iodide salt of the cationic dye was obtained from the condensation of *N*, *N*-dimethylaminocinnamaldehyde (175mg, 1mmol) and *N*-octadecyl-5,6,7,8-tetra-hydroisoquinolinium iodide (513mg, 1mmol) in methanol (30cm^3). Piperidine (2 drops) was added to the solution and the resultant mixture refluxed for 12 h. Upon cooling, a red microcrystalline product was collected and washed with cold methanol: yield 62%; m.p. 63-64°C. Found: C, 67.8; H, 8.9; N, 4.0%. $C_{38}H_{59}N_2I$ requires: C, 68.03; H, 8.86; N, 4.17 %. Vis ($CHCl_3$): λ_{max}, 385 nm. ^{1}H NMR (300 MHz; $CDCl_3$): δ_H 0.87 (3H, t, CH_3); 1.25 (30H, br s, CH_2); 1.7 (2H, br s, CH_2); 1.96 (2H, quintet, $CH_2CH_2N^+$); 2.79 (2H, t, C=C-CH_2); 2.97 (2H, t, C=C-CH_2); 3.06 (6H, s, $N(CH_3)_2$); 4.61 (2H, t, CH_2N^+); 6.67 (2H, d, Ar-H); 7.00 (3H, br s, CH); 7.45 (2H, d, Ar-H); 8.07 (H, d, Ar-H); 8.62 (H, d, Ar-H); 8.85 (H, s, Ar-H).

Dilute solutions of the dye in chloroform and sodium octadecylsulfate in methanol were co-spread in a 1:1 mole ratio onto the pure water subphase of one compartment of a Nima Technology LB trough (model 622), left for 5 min at 20°C and then compressed at 0.5 cm^2 s^{-1} (*ca.* 0.1% s^{-1} of compartment

area). The water soluble ions, Na^+ and I^-, dissolve into the subphase thus, leaving the octadecylsulfate salt at the interface. Poly(*t*-butyl methacrylate) was spread from chloroform solution onto the second compartment of the trough and compressed as above. Alternate-layer films were then obtained by the sequential deposition of the dye at 35 mN m^{-1} and poly(*t*-butyl methacrylate) at 10 mN m^{-1}, the substrate being cycled from below the surface to transfer the SHG-active layer on the first upstroke and the spacer on the subsequent downstroke. Thick films were obtained by repeating the process with a deposition rate of 80 μm s^{-1} in each direction.

RESULTS AND DISCUSSION

The pressure-area (Π-A) isotherms are generally featureless with film collapse occurring at 17 mN m^{-1} and 0.60 nm^2 $unit^{-1}$ for poly(*t*-butyl methacrylate) and 42 mN m^{-1} and 0.43 nm^2 $molecule^{-1}$ for the dye (Figure 2). The deposition of the spacer has been reported[7] and, therefore, this work focuses upon the SHG-active dye. Its area at collapse is consistent with the sum of the van der Waals cross-sections of the two octadecyl chains and suggests that these groups are vertical and closely packed. In contrast, in the low pressure regime, the limiting area of *ca.* 1.6 nm^2 $molecule^{-1}$ indicates that the chromophore aligns with its face adjacent to the subphase.

Non-centrosymmetric structures were readily fabricated by interleaving layers of the dye and poly(*t*-butyl methacrylate). The films have a broad absorption maximum at *ca.* 420 nm and exhibit a linear increase in the absorbance with the number of deposited bilayers. This corresponds to the dye with the poly(*t*-butyl methacrylate) spacer being transparent throughout the entire visible region. The films are transparent at the fundamental wavelength of 1.064 μm for SHG studies but have a slight absorbance of 1.5×10^{-3} $bilayer^{-1}$ at 532 nm. This is important because the efficiency/transparency trade-off is optimised. The second-harmonic intensity is resonantly enhanced but the loss from absorption is not too significant.

The SHG was measured in transmission with the p-polarized Nd:YAG laser beam (λ = 1.064 μm) incident at 45° to the LB film, there being negligible SHG at normal incidence. The polarization was rotated using a half-wave plate and the second-harmonic intensity ($I_{2\omega}$) calibrated against the Maker fringe envelope of a Y-cut quartz reference (d_{11} = 0.5 pm V^{-1}). The data were analyzed as described elsewhere.[7]

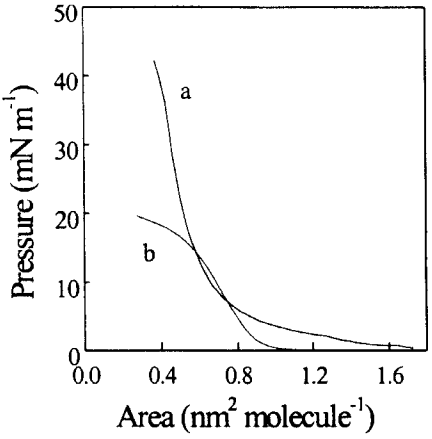

FIGURE 2 Surface pressure *vs.* area isotherms: (a) dye and (b) spacer

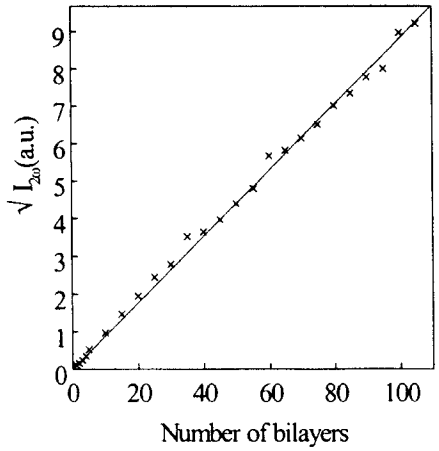

FIGURE 3 Variation of the second-harmonic intensity with the number of bilayers of the dye and poly(*t*-butyl methacrylate).

The variation of the second-harmonic intensity with the number of active layers is shown in Figure 3. It shows the theoretically predicted quadratic dependence, i.e. $I_{2\omega(N)} = I_{2\omega(1)} N^2$, and the normalised intensity, $I_{2\omega(N)}/N^2$, is identical for the monolayer and thick multilayer structure. Using the method of Kajikawa *et al.*,[8] the SHG polarization dependence, $I_{2\omega}(p\rightarrow p)/I_{2\omega}(s\rightarrow p)$, indicates that the chromophores are tilted by *ca.* 32° from the normal to the substrate. From this, and by assuming a thickness from molecular modelling of 4.0 nm bilayer^{-1}, the components of the susceptibility, $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$, are 60 and 10 pm V^{-1} respectively. The second-order coefficients are large and the study has demonstrated that, with careful deposition, quadratic SHG enhancement may be achieved to thicknesses suitable for waveguiding.

CONCLUSION

Relatively few LB films have exhibited the theoretically predicted quadratic SHG enhancement to thicknesses in excess of 100 bilayers.[1,3,9-13] The example in this work adds to the list and, together with recent studies on alternate-layer structures of poly(*t*-butyl methacrylate),[7] demonstrates the effectiveness of the spacer when deposited on the downstroke. The dye/spacer combination may be routinely used to fabricate non-centrosymmetric structures and, in this work, a moderately high second-order susceptibility and relatively weak absorbance have been demonstrated.

Acknowledgements

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