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Orientation of Optically Nonlinear Chromophores at the Air-Water Interface

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The isotherms of *E-N-alkyl-4-[2-(4-(N-octadecyl-N-ethylaminophenyl))-ethenyl]-pyridinium* halide, represented here by $C_mH_{2m+1}-D-\pi-A^+-C_nH_{2n+1}X^-$, suggest that this two-legged molecule initially adopts a "U-shaped" conformation at the air-water interface but becomes "stretched" as the surface pressure is increased. The area of $0.25 \pm 0.05 \text{ nm}^2 \text{ molecule}^{-1}$, prior to collapse, is independent of the second alkyl group and approximates to the molecular cross-section. When deposited, the area in contact with the substrate is $0.25 \pm 0.05 \text{ nm}^2 \text{ molecule}^{-1}$ and the layer thickness compares favourably with the molecular length. The second-harmonic intensity is strong when the alkyl chain lengths are sufficiently different, i.e. $|m - n| \geq 4$, but is suppressed when $m \approx n$. In this limiting case, the second-order properties suggest a centrosymmetric arrangement and, therefore, a random orientation of the molecular dipoles, up and down, within the monolayer film.

Keywords: Langmuir-Blodgett; second-harmonic generation

INTRODUCTION

The majority of optically nonlinear dyes investigated by the Langmuir-Blodgett (LB) technique have a single hydrophobic tail and spontaneously align with the chromophore adjacent to the aqueous subphase.^[1] The floating monolayer is non-centrosymmetric but, when transferred to a solid substrate, the molecules frequently realign to give centrosymmetric multilayers in which the interfaces are alternately hydrophobic (tail-to-tail) and hydrophilic (head-to-head). This may be suppressed by substituting opposite ends of the chromophore with alkyl groups.^[2] Then, as each surface is hydrophobic, the

molecules retain their orientation adopted at the air-water interface throughout the deposition process. Using this technique, we have fabricated stable non-centrosymmetric structures to thicknesses suitable for waveguiding^[3] and, furthermore, the second-harmonic intensity increases quadratically with the number of Z-type layers.^[2-5]

In this work we comment upon the molecular orientation at the air-water interface and report the second-order nonlinear optical properties of the dye, $C_mH_{2m+1}-D-\pi-A^+-C_nH_{2n+1}$ halide, where $m = 18$ and $8 \leq n \leq 22$ (Figure 1). Second-harmonic generation (SHG), quartz crystal microbalance (QCM) and surface plasmon resonance (SPR) studies were performed on the deposited films.

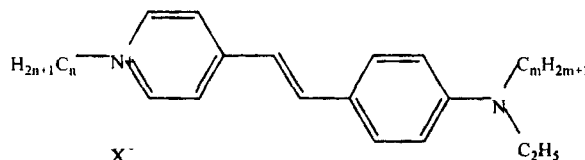


FIGURE 1 Molecular structure of the two-legged stilbazolium dye where $m = 18$ and $8 \leq n \leq 22$.

EXPERIMENTAL

The dye was spread from chloroform solution (0.1 mg cm^{-3}) onto the pure water subphase of a Nima Technology LB trough (model 622), left for 5 min at *ca.* 20°C and then compressed at $0.5 \text{ cm}^2 \text{ s}^{-1}$. LB films were obtained by passing a glass substrate (for SHG), a 10 MHz AT-cut quartz crystal (for QCM) or a gold coated slide (for SPR), through the floating monolayer at a rate of 2 mm min^{-1} . The films were deposited, on the upstroke, from the high pressure regime of the isotherms.

RESULTS AND DISCUSSION

The pressure-area (π -A) isotherms of the different alkyl analogues have limiting areas of $1.0 \pm 0.4 \text{ nm}^2 \text{ molecule}^{-1}$ at $\pi = 0$ which decrease to $0.25 \pm 0.05 \text{ nm}^2 \text{ molecule}^{-1}$ prior to collapse (Figure 2). The values match the van der Waals areas of the chromophore face and cross-section respectively. Similar isotherms have been obtained for other two-legged dyes and X-ray diffraction studies on the floating monolayers have indicated a stretched

molecular conformation in the high-pressure regime.^[5] Consequently, the molecules align with an alkyl group adjacent to the aqueous subphase and, although somewhat controversial, it may be assumed that the repulsion between the fatty chain and subphase is, in part, compensated by van der Waals interactions between hydrophobic groups with a side-by-side packing arrangement.

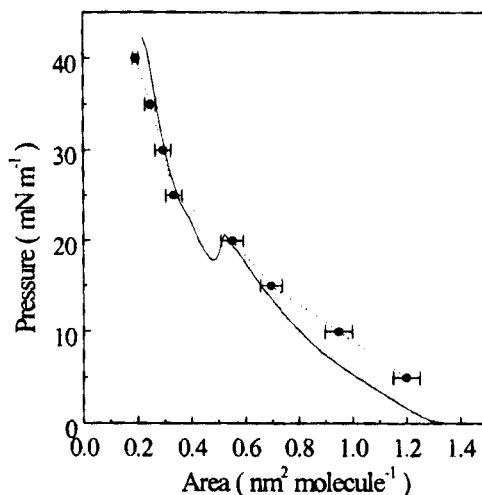


FIGURE 2 Pressure-area isotherm of the octadecyl analogue ($n = 18$) and, from QCM studies (broken line), the molecular area in contact with the substrate versus deposition pressure.

The QCM studies provide a molecular area in contact with the substrate of $0.25 \pm 0.05 \text{ nm}^2$ for the different alkyl analogues ($8 \leq n \leq 22$) deposited at pressures just prior to collapse. Furthermore, the thickness from SPR studies on glass|Au|LB structures are $5.4 \text{ nm layer}^{-1}$ ($n = 22$); $4.7 \text{ nm layer}^{-1}$ ($n = 20$) and $2.7 \text{ nm layer}^{-1}$ ($n = 1$). These data suggest that the molecule is stretched and almost vertical rather than U-shaped with the chromophore parallel to the substrate and the alkyl groups pointing upwards. This assignment is supported by a tilt angle of $35 \pm 5^\circ$ from the normal to the substrate for the D- π -A chromophore, this being obtained from the SHG polarization dependence.

SHG measurements were performed in transmission with the laser

beam (Nd:YAG; $\lambda = 1.064 \mu\text{m}$) incident at 45° to the film, there being negligible SHG at normal incidence. The optimum second-harmonic intensity, $I_{2\omega}(\text{p} \rightarrow \text{p})$, is shown as the difference between the number of alkyl carbons in the two groups for films deposited from the high-pressure regime of the isotherm (Figure 3). The SHG is strong for $|(m-n)| \geq 4$ but suppressed when $m \approx n$. From this, we infer that the molecules align with the shorter of the two alkyl chains adjacent to the aqueous subphase and that there is a random orientation of the molecular dipoles, up and down, when the hydrophobic groups are similar. Furthermore, the data support our premise that the two-legged molecules are stretched rather than U-shaped.

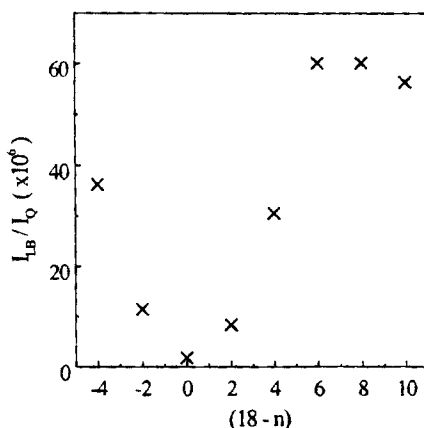


FIGURE 3 Relative second-harmonic intensity versus the difference in the number of alkyl carbons.

References

- [1] M.C. Petty, *Langmuir-Blodgett Films: an Introduction* (Cambridge University Press, Cambridge, 1996).
- [2] G.J. Ashwell, P.D. Jackson, and W.A. Crossland, *Nature*, **368**, 438 (1994).
- [3] G.J. Ashwell, G. Jefferies, C.D. George, R. Ranjan, R.B. Charters, and R.P. Tatam, *J. Mater. Chem.* **6**, 131 (1996).
- [4] G.J. Ashwell, T. Handa, and R. Ranjan, *J. Opt. Soc. Am. B*, **15**, 466 (1998).
- [5] G.J. Ashwell, P.D. Jackson, G. Jefferies, I.R. Gentle, and C.H.L. Kennard, *J. Mater. Chem.* **6**, 137 (1996).