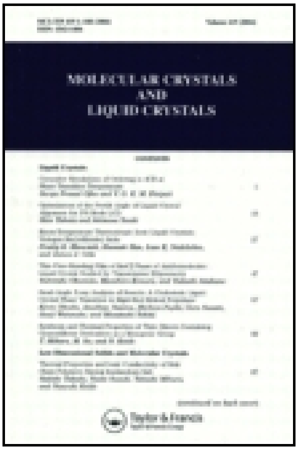

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# Z-Type Films of a Two-Legged Optically Nonlinear Dye

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# Z-Type Films of a Two-Legged Optically Nonlinear Dye

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The second-harmonic intensity from Langmuir-Blodgett (LB) films of the two-legged dye, E-N-docosyl-4-[2-(4-dodecyloxynaphthyl)ethenyl]quino-linium bromide, co-deposited in a 1:1 mole ratio with docosanoic acid (DA), increases quadratically with film thickness to more than 100 Z-type layers. The bulk second-order susceptibility, $\chi^{(2)}_{zzz}$, of the 100 layer film is *ca.* 25 pm/V at 1064 nm.

*Keywords:* Langmuir-Blodgett films; second-harmonic generation

## INTRODUCTION

Second-harmonic generation (SHG) requires a non-centrosymmetric alignment of the molecules and this may be achieved by the LB deposition.[1-5] It offers control of the packing at the molecular level but, as most amphiphiles adopt a centrosymmetric multilayer arrangement, it has been necessary to interleave the layers with suitable spacers. Recently, Ashwell *et al.*[2] discovered that a second hydrophobic tail, introduced at the opposite end of the chromophore, stabilises a Z-type structure in which the molecular dipoles are aligned. The theoretically predicted quadratic dependence of the SHG upon the number of LB layers has since been realised for several such dyes and in this work, we report a new example, E-N-docosyl-4-[2-(4-dodecyloxynaphthyl)ethenyl]-quinolinium bromide

(Figure 1), was synthesised and its deposition and nonlinear optical properties studied.

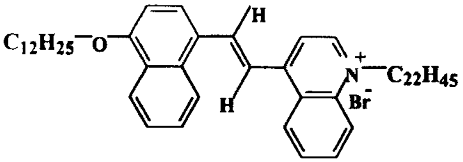

FIGURE 1 Molecular structure of the two-legged dye

## RESULTS AND DISCUSSION

Films were obtained by spreading a dilute chloroform solution of the dye and docosanoic acid (1:1 mole ratio) onto the pure water subphase of a Nima Technology trough (model 622). The isotherm was recorded at a compression rate of 0.5 $cm^2$ $s^{-1}$ and is shown in Figure 2. Allowing for the cross-section of the fatty acid, the dye molecule has a limiting area of *ca.* 1.4 $nm^2$ at $\pi = 0$ decreasing to *ca.* 0.5 $nm^2$ at collapse. The former coincides with the face area of the chromophore and suggests that the molecule initially adopts a U conformation at the air-water interface. The latter is ambiguous. It may be interpreted as a tilted arrangement but, as reported for other two-legged dyes,[2-5] the reduced area probably corresponds to a stretched conformation with the alkyl chains pointing in opposite directions.

The film was deposited on the up-stroke at a surface pressure of 40 mN $m^{-1}$ and a rate of 0.1 mm $s^{-1}$. It exhibits a blue-shifted absorption band at 470 nm relative to the solution spectrum (490 nm) of the dye in chloroform. The LB film is transparent at the excitatory wavelength for surface plasmon resonance (632.8 nm) but has a slight absorbance of $1.4\times10^{-3}$ $layer^{-1}$ at the harmonic wavelength (532 nm). The second-order properties are resonantly enhanced but the transparency-efficiency tradeoff is not significantly comprised by the absorbance.

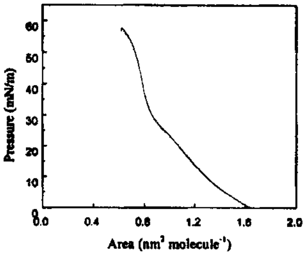

FIGURE 2 Pressure-area isotherm of the dye and docosanoic acid at 24°C in a 1:1 mole ratio

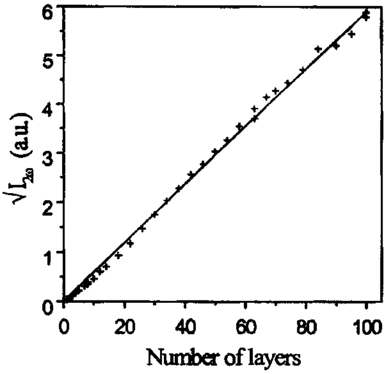

FIGURE 3 Variation of the square root of the second-harmonic intensity *vs.* the number of LB layers

The SHG was measured in transmission with the Nd:YAG laser beam (1064 nm) incident at 45° to the film, the signal being negligible at normal incidence. The second-harmonic intensity shows the theoretically predicted dependence and increases quadratically with film thickness to in excess of 100 LB layers (Figure 3). A stable non-centrosymmetric (Z-type) arrangement is maintained whereas single-legged counterparts of the cationic dye invariably form centrosymmetric structures in which the molecules pack head-to-head and tail-to-tail. For these, the SHG is modest when the number of layers is odd and negligible when the number is even.

Using the method of Kajikawa *et al.*,[6] the SHG polarisation dependence, $I_{2\omega}(p \rightarrow p)/I_{2\omega}(s \rightarrow p)$, of the multilayer structure suggests that the chromophores are inclined at an angle of *ca.* 36° to the substrate normal. The bulk layer thickness and dielectric permittivities, from SPR studies at 632.8 nm, are $l =$ 4.3 nm, $e_r = 2.5$ and $e_i = 0.0$. Combining these results with the SHG data gives a susceptibility, $\chi^{(2)}_{zzz}$, of 25 pm $V^{-1}$. Interestingly, E-*N*-dodecyl-4-[2-(4-docosyloxyphenyl)ethenyl]quinol-inium bromide shows similar behaviour[4,5] and the quadratic SHG enhancement, indicative of an ordered Z-type arrangement, is attributed to film stabilisation by the hydrophobically substituted end groups. If the molecules adopt a stretched conformation, the non-centrosymmetry results from the fact that each interface is hydrophobic and the dipole orientation is maintained during deposition.

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