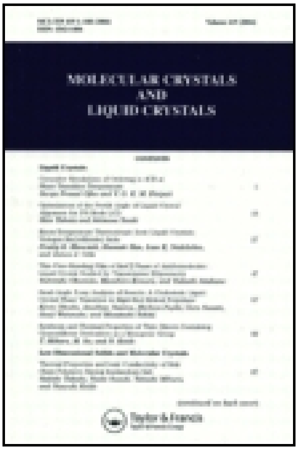

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G. J. Ashwell [a], N. D. Rees [a], G. S. Bahra [b] & C. R. Brown [b]

[a] Centre for Molecular Electronics, Cranfield University, Cranfield, MK43 OAL, UK

[b] Defence Evaluation Research Agency, Fort Halstead, Kent, TN14 7BP, UK

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2,4-Bis[6-(*N*-Octyl-2,3,4-Trihydroquinoloyl)] Squaraine: Nonlinear Optical Properties of a Centrosymmetric Dye

G.J. ASHWELL[a*], N.D. REES[a], G.S. BAHRA[b] and C.R. BROWN[b]

[a]*Centre for Molecular Electronics, Cranfield University, Cranfield MK43 OAL, UK and* [b]*Defence Evaluation Research Agency, Fort Halstead, Kent TN14 7BP, UK*

The electrospray ionisation mass spectrum of the title compound, 2,4-bis[6-(*N*-octyl-2,3,4-trihydroquinoloyl)]squaraine, shows peaks which correspond to the monomer ($m/z = 569$, $[2M + H]^+$) and aggregate ($m/z = 1137$, $[2M + H]^+$). It associates in dilute solution and the nonlinear optical behaviour is attributed to the aggregate, which must be non-centrosymmetric, rather than the molecule. The second-harmonic intensity from solid solutions of the dye in poly(vinyl acetate) increases with concentration. Its homomolecular Langmuir-Blodgett (LB) films also exhibit second-harmonic generation (SHG) and have an effective monolayer susceptibility of 50 pm V^{A1} at 1.064 μm. The thickness and real and imaginary components of the dielectric permittivity, derived from an analysis of the surface plasmon resonance at 632.8 nm, are $l = 0.6$ nm layer^{-1}, $e_r = 1.9$ and $e_i = 1.0$. The thickness suggests that the chromophore and the hexyl groups align parallel to the substrate.

Keywords: Langmuir-Blodgett; second-harmonic generation; squaraine dye

INTRODUCTION

Since the initial discovery [1] of SHG from LB films of the centric squaraine dye, 2,4-bis[4-(*N*-methyl-*N*-*alkyl*amino)phenyl]squaraine, we have investigated the film structure using neutron and X-ray synchrotron

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* To whom correspondence should be addressed (fax 44-01234-750875; e-mail g.j.ashwell@cranfield.ac.uk).

diffraction.[2,3] The packing is dependent upon the alkyl chain length. The lower analogues, butyl to dodecyl, have short interlayer spacings of 0.82-0.89 nm and pack with the chromophore and alkyl groups parallel to the substrate. In contrast, the tetradecyl to docosyl analogues adopt U conformations with the hydrophobic alkyl groups pointing upwards and the X-ray lattice spacing increases from 2.16 to 2.79 nm. The SHG is not an inherent property of the molecule, which is centric, and is too strong to be associated with the interface. Thus, to satisfy the structural requirement, it is conjectured that adjacent donor-C_4O_2-donor squaraine molecules adopt an acentric T conformation with charge transfer interactions between the terminal donor of one and the central acceptor of the other. This concept has since been verified by the theoretical analysis of Brédas and Brouyère. [4] Their work provides a theoretical basis for the second-order activity and demonstrates that strong second-order nonlinear coefficients can result from such an arrangement.

In this work, we report the deposition and properties of a heterocyclic analogue, 2,4-bis[6-(*N*-octyl-2,3,4-trihydroquinoloyl)]squaraine (Figure 1). Surface plasmon resonance (SPR) and quartz crystal microbalance (QCM) techniques have been used to characterise the LB film and SHG studies have been performed on both LB and spun coated films.

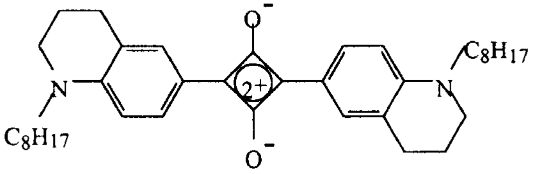

FIGURE 1 2,4-bis[6-(*N*-octyl-2,3,4-trihydroquinoloyl)]squaraine

RESULTS AND DISCUSSION

The dye was spread from dilute chloroform solutions (0.1 mg ml^{-1}) onto the pure water subphase of an LB trough (Nima Technology, 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 total area). The resultant pressure-area isotherm is almost vertical and the absorbance of the floating monolayer is independent of the surface pressure. This suggests that the molecules are closely packed at *ca.* p= 0 and consequently, when deposited, the area in contact with the substrate, 0.95 ± 0.10 nm^2 $molecule^{-1}$ from QCM studies, is independent of the surface pressure for $2 \leq p \leq 25$ mN m^{-1}. The area is consistent with the chromophores being on edge rather than face down and, similar to other squaraines, the estimated value is probably influenced by localised clustering and bilayer formation.

SPR studies were carried out using an attenuated total reflection geometry in the Kretschmann configuration[5] using a glass|Au|monolayer device structure and an excitation wavelength of 632.8 nm (Figure 2). Analysis of the data gave $e_r = 1.9 \pm 0.2$, $e_i = 1.0 \pm 0.2$ and $l = 0.6 \pm 0.2$ nm for the LB monolayer, the permittivities corresponding to a refractive index (n) and absorption coefficient (k) of 1.42 and 0.35 respectively. The mean layer thickness of 0.6 ± 0.2 nm is consistent with the value obtained for 2,4-bis[4-(*N*-methyl-*N*-*alkyl*amino)phenyl]squaraine[2] and suggests that the chromophore and octyl groups are aligned parallel to the substrate.

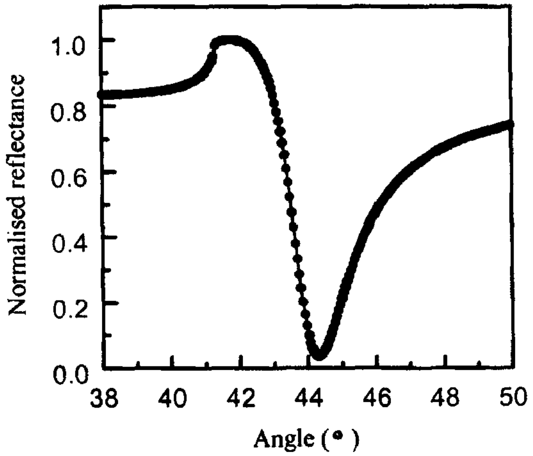

FIGURE 2 Normalised reflectance *vs.* incident angle for the glass|Au|LB device at 632.8 nm and with a thickness of 45 nm for the gold layer.

LB films exhibit SHG with an effective second-order susceptibility of 50 pm V^{-1} at 1.064 μm when the p-polarized Nd:YAG laser beam is incident at 45°. Furthermore, solid solutions of the dye in poly(vinyl acetate) are also SHG-active; the second-harmonic intensity increases, albeit subquadratically, with the squaraine concentration and is extinguished by the addition of an electron acceptor, 7,7,8,8-tetracyano-p-quinodimethane. The nonlinearity is attributed to non-centrosymmetric aggregation, even in dilute solution, and evidence has been provided by electrospray ionisation mass spectrometry. Peaks with high *m/z* values conform to the dimeric aggregate (*m/z*=1137, $[2M+H]^+$) and similar data have been obtained for other anilino squaraines.[6,7] As the SHG-active species is dimeric, the two molecules must adopt a non-parallel arrangement. An acentric T conformation is assumed with intermolecular charge transfer between the terminal donor and central acceptor of the molecules. This is supported by the fact that the SHG is suppressed when electron acceptors are incorporated into the solid solution.

Acknowledgements

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