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Monolayer films of U-shaped molecules: suppression of the aggregation-induced second-harmonic generation of squaraine dyes by guest–host interactions

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Langmuir–Blodgett (LB) monolayers of 2,4-bis[4-(*N*-methyl-*N*-docosylamino)phenyl]squaraine† (**I**), which has a centric donor–acceptor–donor chromophore, exhibit strong second-harmonic generation (SHG) with an effective susceptibility of 26 pm V^{-1} at 1.064 μm. The squaraine molecule adopts an acentric U-conformation, with the chromophore parallel to the substrate and the docosyl groups contributing to the layer thickness of 2.41 nm. However, the SHG is attributed to non-centrosymmetric aggregation rather than the molecule itself and is suppressed when the dye is co-deposited with 2-{4-[4,5-bis(octadecylsulfanyl)[1,3]dithiol-2-ylidene]cyclohexa-2,5-dienylidene}malononitrile (**II**). The latter adopts a piggyback arrangement and is partially enclosed by the two docosyl tails of the squaraine: the areas in contact with the substrate are 0.63 ± 0.05 nm^2 $molecule^{-1}$ for **I** and 0.67 ± 0.05 nm^2 $unit^{-1}$ for $(\mathbf{I})(\mathbf{II})_n$, the combined molecular area being independent of composition for $0 < n < 0.5$. Thus, the suppression of the second-order properties may be explained by an altered film structure with self-aggregation of the squaraines being inhibited by competitive heteromolecular interactions with the adjacent acceptor group of **II**. The electron acceptors, 2-methyl-3-phytyl-1,4-naphthoquinone (**III**) and *N*,*N*′-bis(docosyl)-4,4′-bipyridinium dibromide (**IV**), affect the second-order properties in a similar manner.

Introduction

X-Ray crystallographic analysis[1–3] of the 2,4-bis[4-(*N*,*N*-dialkylamino)phenyl]squaraines has confirmed that the chromophore is both planar and centric with the dimensions of each half being symmetry generated across an inversion centre. Nonetheless, moderately strong SHG has been observed from LB monolayers[4–8] of centric squaraines as well as from solid solutions of the dyes in poly(vinyl acetate).[7–10] The molecules readily associate in solution, as shown by their electrospray ionisation mass spectra which have mass/charge peaks which conform to the dimeric species for each of the SHG-active dyes.[10] Thus, to satisfy the structural requirement, the behaviour may be explained by acentric aggregation in which the two chromophores adopt a T-arrangement with the electron-donor of one being directed towards the central electron-acceptor of the other. The concept of an SHG-active aggregate, proposed in our original publication,[4] has since been verified by the theoretical analysis of Brédas and Brouyère[11] and Honeybourne.[12] Furthermore, the T-motif has been corroborated by the scanning tunnelling microscopy data of Parkinson and coworkers[13] and, for such an arrangement, large second-order coefficients can result from intermolecular charge transfer providing the LB film structure is non-centrosymmetric. Relevant to this, Bjørnholm *et al.*[14] have demonstrated SHG from the interface between LB layers of an amphiphilic acceptor and an amphiphilic donor and have shown that the second-harmonic intensity increases quadratically with the number of bilayers. In addition, at Cranfield, we have recently demonstrated reduced SHG[15] from the interface between donor–(π-bridge)–acceptor dyes with the alkyl tails attached in the opposite sense, *i.e.* $C_{18}H_{37}$-D-π-A and D-π-A-$C_{18}H_{37}$. When the packing is head-to-head, rather than tail-to-tail, interlayer charge-transfer interactions between the facing donor and acceptor moieties result in an interlayer dipole which is significant and opposed to the molecular dipoles within the film.

The SHG from LB monolayers of squaraine dyes[4–8] is comparable with the intensity from films of conventional optically nonlinear dyes[16,17] and, to account for this anomalous behaviour, an intermolecular charge-transfer contribution to the bulk second-order susceptibility has been assumed.[4] In this work we demonstrate that the SHG may be suppressed by incorporating electron-acceptors within the 2,4-bis[4-(*N*-methyl-*N*-docosylamino)phenyl]squaraine film as well as a D-π-A material, hydrophobically substituted at the donor end. The latter adopts a piggyback arrangement with the squaraine and the SHG data suggest that the guest affects the second-order properties of an encircling region of ten host molecules which corresponds to an area of *ca.* 7 nm^2.

Experimental

Materials and deposition

2,4-Bis[4-(*N*-methyl-*N*-docosylamino)phenyl]squaraine (**I**) and 2-{4-[4,5-bis(octadecylsulfanyl)-[1,3]dithiol-2-ylidene]cyclohexa-2,5-dienylidene}malononitrile (**II**) were synthesised as previously described.[5,18] They were spread from dilute chloroform solutions (dye **I**, 0.1 mg cm^{-3}; dye **II**, 0.01 mg cm^{-3}) onto the pure water subphase of an LB trough (Nima Technology, model 622), left for 10 min at *ca.* 20 °C and then compressed at

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† The IUPAC name for 2,4-bis[4-(*N*-methyl-*N*-docosylamino)phenyl]squaraine is 2,4-bis[4-(*N*-methyl-*N*-docosylamino)phenyl]cyclobutane-1,3-diolate.

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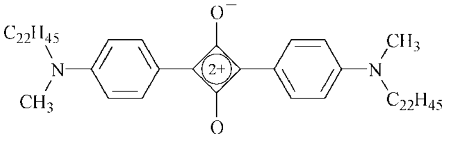
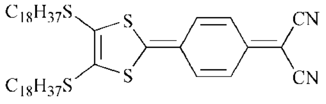
0.5 cm^2 s^{-1} (*ca.* 0.1% s^{-1} of compartment area). The pure dyes and heteromolecular films were deposited on the upstroke by passing a glass substrate (for SHG) or a 10 MHz quartz crystal (for gravimetric studies) through the floating monolayer at 30 μm s^{-1} and a surface pressure of 15 mN m^{-1}.



I



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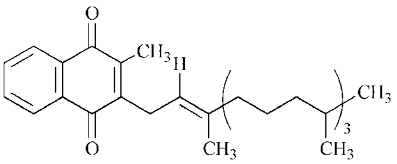
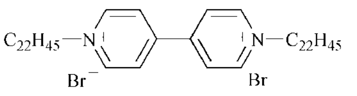


III



IV

Quartz crystal microbalance (QCM)

The change in frequency (ΔF) of a 10 MHz AT-cut quartz crystal plate, coated on each side with overlapping 0.206 cm^2 gold electrodes, was obtained for deposition at 15 mN m^{-1}. Reproducibility was investigated for 60 samples of dye **I** and five samples each of dye **II** and the mixed LB films. An oscillator circuit was used to drive the crystal at its resonance frequency (F_o) and the changes were monitored using a Hewlett Packard HP53131A frequency counter. The molecular areas in contact with the electrodes were obtained using the Sauerbrey equation [eqn. (1)]:[19]

$$A=\frac{4F_o^2M_r}{\Delta F(\rho\mu)^{1/2}L} \tag{1}$$

where ρ is the density of the quartz crystal (2.65 g cm^{-3}), μ is the shear modulus (2.95 x 10^{11} dyn cm^{-2}) and M_r and L are the molar mass and Avogadro's constant respectively. Areas were obtained for the fractional molecular unit, $(\mathbf{I})_x(\mathbf{II})_{1-x}$, and the squaraine plus all associated molecules, $(\mathbf{I})(\mathbf{II})_n$.

SHG characterisation

SHG studies on the deposited films were performed in transmission using a *p*-polarised Nd : YAG laser ($\lambda=1.064$ μm) with the beam incident at 45° to the film, there being no discernible signal at normal incidence. The second-harmonic intensity was calibrated by comparison with the first Maker fringe of a Y-cut quartz reference ($d_{11}=0.5$ pm V^{-1}) and the effective susceptibility calculated.

Results and discussion

Film structure

The surface pressure *versus* area (π–A) isotherms of the optically nonlinear material and the mixed LB films with the squaraine dye are shown in Fig. 1, the curves being generally featureless throughout the compression range. The molecular areas obtained from the isotherms at 15 mN m^{-1} match those determined from the change in frequency of an AT-cut 10 MHz quartz crystal upon deposition at this pressure (Fig. 2). Dye **I** has an area of 0.63 ± 0.05 nm^2 molecule^{-1} (*cf.* 0.67 nm^2 from the isotherm). This relates to the long edge of the chromophore, which has van der Waals dimensions of *ca.* 1.9 × 0.34 nm, and indicates that the squaraine adopts a U-shaped configuration, both at the air–water interface and in the deposited LB film, with the alkyl groups pointing upwards. This is corroborated by the previously reported[5] layer thickness of 2.41 nm from grazing incidence X-ray synchrotron diffraction. In contrast, dye **II** shows a corresponding area of 0.41 ± 0.05 nm^2 molecule^{-1} (*cf.* 0.43 nm^2 from isotherm) which relates to the molecular cross-section of the 4,5-bis(octadecylsulfanyl)-[1,3]dithiole unit.

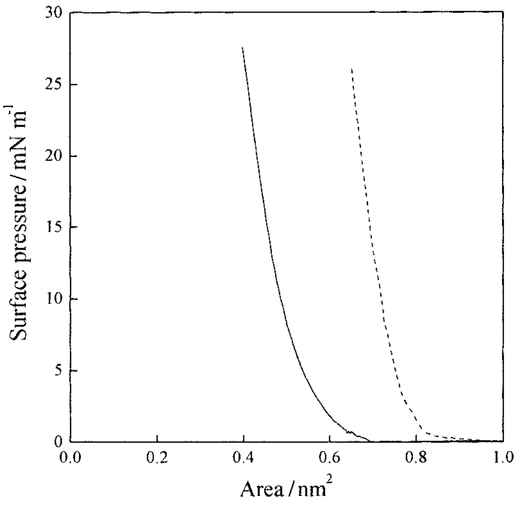


Fig. 1 Surface-pressure *versus* area isotherms of 2-{4-[4,5-bis(octadecylsulfanyl)-[1,3]dithiol-2-ylidene]cyclohexa-2,5-dienylidene}malononitrile (dye **II**, solid line) and a mixed film (broken line) where the unit area corresponds to $(\mathbf{I})(\mathbf{II})_n$, *i.e.* the squaraine plus all associated molecules. The isotherm corresponds to $n=0.5$ but almost identical behaviour has been obtained for $0<n<0.5$.

For mixed LB films, the area of the $(\mathbf{I})_x(\mathbf{II})_{1-x}$ unit in contact with the substrate is significantly less than the combined fractional areas of the individual moieties as reported above. Furthermore, the combined area of the squaraine plus all

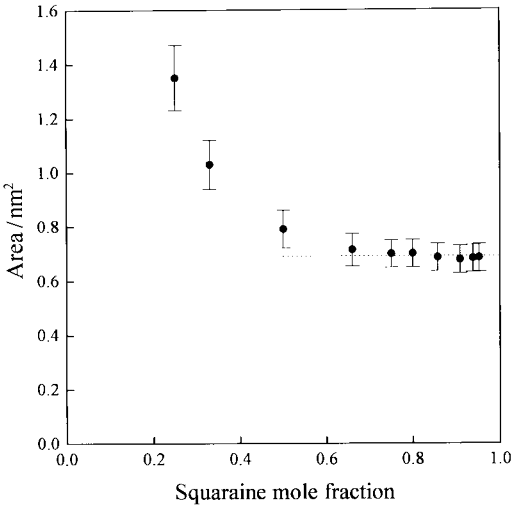


Fig. 2 Molecular area of $(\mathbf{I})(\mathbf{II})_n$ in contact with the substrate *versus* the mole fraction of squaraine. The areas, determined by the QCM technique, are identical with those obtained from the isotherms at the deposition pressure and, in each case, relate to the squaraine plus all associated molecules. The areas of the pure dyes are 0.63 ± 0.05 nm^2 molecule^{-1} for **I** and 0.41 ± 0.05 nm^2 molecule^{-1} for **II**, the former being similar to the area obtained for $(\mathbf{I})(\mathbf{II})_n$ where $0<n<0.5$.

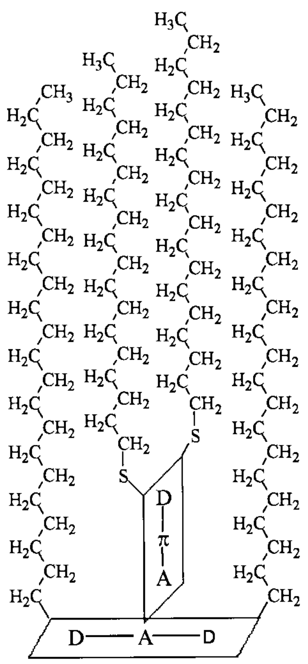


Fig. 3 Schematic representation of the U-shaped squaraine host (**I**) partially enclosing the optically nonlinear guest (**II**). The hollow cavity of the squaraine has a cross-sectional area of *ca.* 0.25 nm^2, consistent with that of the D-π-A chromophore, and the two octadecylsulfanyl tails are accommodated in the open surface structure when **I**:**II**$>2:1$.

associated molecules, *i.e.* 0.67 ± 0.05 nm^2 molecule^{-1} for $(\mathbf{I})(\mathbf{II})_n$ where $0<n<0.5$, is characteristic of the contact area of the pure squaraine, 0.63 ± 0.05 nm^2 molecule^{-1}. Therefore, the molecules overlap and it is assumed that the guest species is enclosed within the hollow cavity of the U-shaped squaraine (Fig. 3). This concept is supported by the spectra of the mixed LB films. The peak absorbance of the squaraine host is 0.015 ± 0.003 and independent of composition for $0<n<0.5$ whereas the absorbance of the guest increases linearly with concentration (Fig. 4). Thus, both sets of data are consistent with the squaraine forming a monolayer, adjacent to the substrate, with the minority component being incorporated within the hollow surface structure.

Film properties

SHG from LB films of centrosymmetric squaraines was first discovered[4] at Cranfield in 1995 and the *N*-methyl-*N*-docosylamino derivative (**I**), reported in this work, has an effective second-order monolayer susceptibility of 26 pm V^{-1} with the *p*-polarised Nd:YAG laser beam incident at 45° to the LB film. The molecule is centric but, as previously demonstrated by electrospray mass spectrometry,[10] the squaraine molecules readily associate in solution and the SHG-active building block is a dimeric charge-transfer aggregate. It has been assumed that the two molecules adopt an acentric T-motif within the LB film, with the terminal donor of one directed towards the central acceptor of the other,[4] and the structure has been confirmed by scanning tunnelling microscopy.[19] The units must pack non-centrosymmetrically within an SHG-active film and, furthermore, to account for the out-of-plane second-harmonic intensity, using the *p*-polarised laser, there must be a vertical displacement of the interacting donor and acceptor groups of adjacent molecules of the repeating dimeric T-motif.

In contrast to this, dye **II** is a conventional optically nonlinear dye with an acentric D-π-A structure but the second-harmonic intensity is much weaker. The low effective susceptibility of 8 pm V^{-1} is anticipated because the LB monolayer is only weakly absorbing at the harmonic wavelength. The absorption band is extremely narrow, with

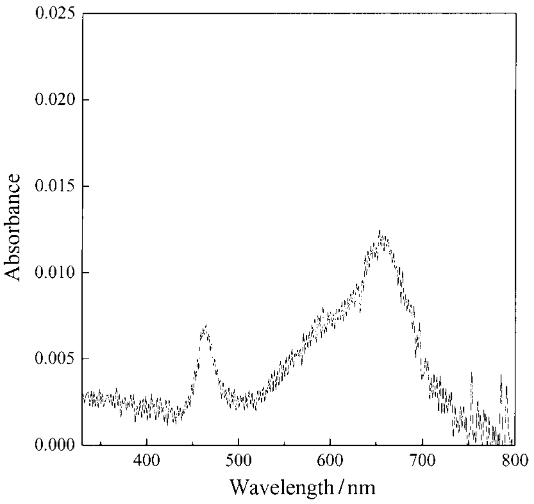


Fig. 4 Visible spectrum of a mixed LB film where the ratio of **I**:**II** is 1:0.5. The absorbance of the squaraine peak, as shown, is *ca.* 0.013 at 655 nm but for all films is typically 0.015 ± 0.003 for $\lambda_{max}=640\pm20$ nm and independent of composition for ratios of 1:0 to 1:0.5.

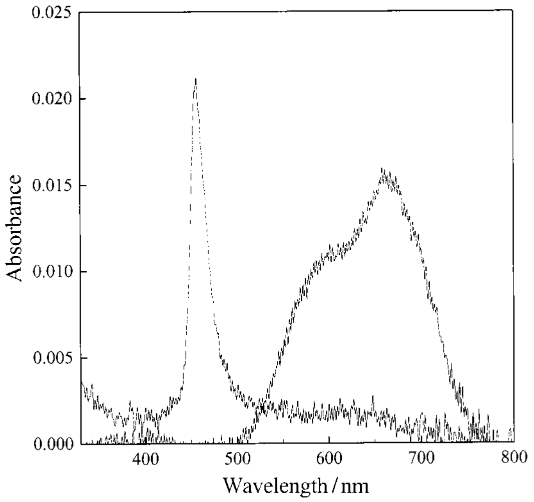


Fig. 5 Visible spectra of LB films of **I** ($\lambda_{max}=660$ nm as shown) and **II** ($\lambda_{max}=455$ nm). The peak wavelength of the former varies from film to film with $\lambda_{max}=640\pm20$ nm whereas the latter is constant to ±2 nm.

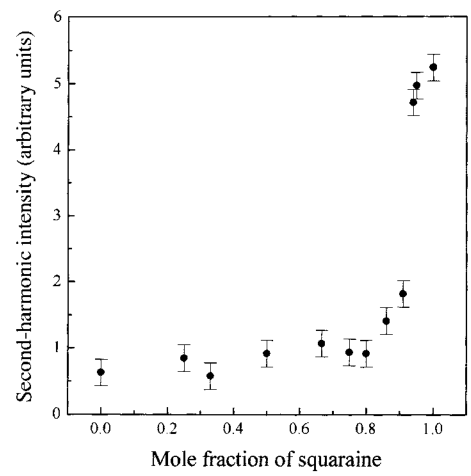


Fig. 6 Variation of the second-harmonic intensity with the mole fraction of squaraine. The strong SHG of the squaraine is only partially quenched by **II** and the intensity is independent of concentration for $0\leqslant x\leqslant0.8$. There may be partial phase separation at these concentrations.

a half width at half maximum of 10 nm centred about 455 ± 2 nm (Fig. 5). The squaraine exhibits a broad absorption between 500 and 800 nm with $\lambda_{\max} = 640 \pm 20$ nm and, although the molecule is centric, the higher susceptibility of 26 pm V^{-1} may be explained by a resonantly enhanced signal and non-centrosymmetric aggregation.

The second-harmonic intensity from the mixed LB films of **(I)(II)**$_n$ is dependent upon the composition and decreases abruptly for $n \sim 0.10$ (Fig. 6). The guest "impurity" has a cross-section of 0.41 nm^2 and, at such concentrations, the QCM data of Fig. 2 indicate that it is included in the hollow cavity of the squaraine host. The concentration dependence of the SHG suggests that the included guest suppresses the second-order nonlinear optical properties of the adjoining ten molecules, occupying a surface area of *ca.* 7 nm^2. Interestingly, the scanning tunnelling microscopy studies of Parkinson and coworkers[13] show a repeating dimeric T-motif for squaraines adsorbed on highly oriented pyrolytic graphite (HOPG). Thus, by analogy to the structure reported in ref. 19, the region of influence of the guest corresponds to the dimeric host and its four closest T-aggregate neighbours. We note that the SHG from LB films of squaraine dyes[4–10] is serendipitous and arises from an intermolecular charge-transfer induced contribution to the susceptibility of the acentric T-aggregate. Therefore, it may be assumed that either the guest modifies the aggregate structure or competitive heteromolecular interactions inhibit this contribution. Both explanations would account for the suppression of SHG within mixed films.

The second-order nonlinear optical properties of dye **I** are similarly suppressed by low concentrations of electron-acceptors, for example, 2-methyl-3-phytyl-1,4-naphthoquinone (vitamin K$_1$, **III**) and *N*,*N*′-docosyl-4,4′-bipyridinium dibromide (**IV**). The 4,4′-bipyridinium chromophore is also centric but too large to be inserted within the hollow cavity of the U-shaped squaraine. In this case, the combined molecular area of **(I)(IV)**$_n$ simply reflects the sum of the individual components and it may be assumed that charge-transfer interactions between the planar 4,4′-bipyridinium acceptor and the donor groups of the planar squaraine promote face-to-face contact. The second-harmonic intensity is quenched for $n > 0.25$ (*cf.* $n \sim 0{:}1$ for **(I)(II)**$_n$) and, in the absence of phase separation, it may be assumed that the guest molecules affect the non-centrosymmetric aggregate structure of the squaraine.

Conclusion

Homomolecular LB films of 2,4-bis[4-(*N*-methyl-*N*-docosylamino)phenyl]squaraine exhibit an area of 0.63 ± 0.05 nm^2 molecule^{-1} in contact with the substrate and a bulk layer thickness of 2.41 nm, these being consistent with a U-shaped conformation. The chromophore is centric but the LB films exhibit strong SHG, this being attributed to intermolecular charge-transfer interactions within a non-centrosymmetric aggregate structure. However, the second-order properties are influenced by guest molecules, for example, donor–(π-bridge)–acceptor materials and electron-acceptors, which either modify the aggregate structure or inhibit self-association. In particular, the data suggest that the optically nonlinear dye, 2-{4-[4,5-bis(octadecylsulfanyl)-[1,3]dithiol-2-ylidene]cyclohexa-2,5-dienylidene}malononitrile, occupies the hollow cavity of the U-shaped squaraine and suppresses the SHG when co-deposited as a mixed monolayer. The second-harmonic intensity is limited to that of the guest ($\chi^{(2)}_{\text{eff}} = 8$ pm V^{-1} at 1.064 μm) at relatively low "impurity" concentrations. In contrast, although the molecular structure of the squaraine is centric, its homomolecular LB films have a moderately high effective susceptibility of 26 pm V^{-1}.

Acknowledgements

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