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Second-harmonic generation from Langmuir–Blodgett films of centrosymmetric squaraines with heterocyclic donor groups

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Langmuir–Blodgett (LB) monolayers of squaraine dyes of general formula D—(C_4O_2)—D, where D is a heterocyclic donor, exhibit second-harmonic generation (SHG) with, for example, $\chi_{zzz}^{(2)}=100$–150 pm V^{-1} at 1.064 µm for 2,4-bis[(3,3-dimethylindolin-2-ylidene)methyl]squaraine. The behaviour is not an inherent property of the molecule and the second-order susceptibility is too high to arise from polarisation of the molecular film at the interface. Instead, the SHG is attributed to non-centrosymmetric aggregation with intermolecular charge transfer between the donor (heterocycle) and acceptor (C_4O_2) groups of adjacent molecules playing a significant role and contributing to the susceptibility. The nonlinear optical properties are discussed with reference to films of 1,4-bis(pyrrol-2-yl)squaraine derivatives which show either very weak or no SHG. The behaviour is dependent upon the type of aggregation and the extent of the donor–acceptor interaction.

The second-order nonlinear optical properties of squaraine dyes have been generally ignored because the donor–acceptor–donor molecule is centric and a prerequisite for SHG is a bulk structure which lacks inversion symmetry. Nonetheless, non-centrosymmetry can result and strong SHG from LB films of anilino squaraines,[1–5] including the *N*-alkyl-2,3,4-trihydroquinoloyl,[3] 9-julolidinyl[3,4] and hydroxy-substituted[4] analogues, has been observed at Cranfield. The chromophore is both linear and planar and, from X-ray structural analysis, the dimensions of one half of the molecule are symmetry generated across an inversion centre by the atomic coordinates of the other.[5–7] There are two crystallographic modifications: (*a*) the molecules of the purple triclinic phase adopt a parallel alignment with intermolecular overlap of the donor and acceptor groups; (*b*) those of the blue–green monoclinic phase show a similar arrangement within layers but, parallel to the third axis, they adopt a repetitive T arrangement with the terminal donor group pointing towards the central acceptor. Their Langmuir and LB films are also polymorphic and have at least three distinct forms: (*a*) an SHG-inactive H-aggregate phase with $\lambda_{max}\approx 530$ nm (ref. 2); (*b*) an SHG-active intermediate phase with $\lambda_{max}=660$–730 nm (ref. 1,2); (*c*) a J-aggregate phase with a sharp absorption maximum at 770 to 850 nm (ref. 3,4). The SHG-activity implies non-centrosymmetry suggesting that adjacent molecules probably adopt a T arrangement with closest contacts between the donor and acceptor groups.[8] In contrast, the molecules of the H and J phases pack in a parallel arrangement with face-to-face and donor-to-acceptor overlaps respectively.[9]

The most interesting example to date, 2,4-bis[4-(*N*-methyl-*N*-hexylamino)phenyl]squaraine, has a high second-order susceptibility of $\chi_{zzz}^{(2)}\approx 720$ pm V^{-1} at 1.064 µm for the monolayer.[1b] Spun-coated films of this dye in poly(vinyl acetate) are also SHG-active and, because the molecular structure is centric, the anomalous second-order behaviour is attributed to an association of the molecules in dilute solution. Evidence for this has been provided by the electrospray mass spectrum which shows *m*/*z* values corresponding to the fragmentation pattern of a dimeric aggregate.[10] The molecules adopt an acentric arrangement with the second-order properties being dependent upon the extent of the intermolecular donor–acceptor interaction.[8] This concept has since been confirmed from a theoretical study on the second-order activity of centric molecules by Brédas and Brouyère.[11]

In this paper we report the second-order nonlinear optical properties of LB films of squaraine dyes. The indolinylidene and quinolylidene derivatives (**1**–**3**) show strong SHG whereas for 1,2-bis(*N*-octadecylpyrrol-2-yl)squaraine (**4**) there is no discernible signal above the background noise. This refutes the recently published work of Lynch *et al.*[12] who reported SHG albeit very weak, for dye **4**. Close scrutiny of their published analytical data explicitly implies that their sample is heavily contaminated with an acentric 1,2-squarate. In contrast, the second-harmonic intensity for dyes **1** to **3** is too strong for impurity-induced or interfacial effects to apply and, therefore, the behaviour is attributed to the aggregate.

Experimental

The squaraines were obtained by established procedures[13,14] and purified by recrystallisation and column chromatography, spectral data being shown in Table 1. The dyes were spread from dilute chloroform solutions (0.1 mg ml^{-1}) onto the pure water subphase of one compartment 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). Monolayer films were deposited on the up-stroke by passing a hydrophilically treated glass substrate (for SHG) or silver coated substrate (for SPR) through the floating monolayer at 4 to 5 mm min^{-1}.

SHG measurements on the deposited monolayers were performed in transmission with the p-polarised laser beam (Nd:YAG, $\lambda=1.064$ µm) incident at an angle of 45 ° to the LB film. The data were calibrated against the Maker fringes of a Y-cut quartz reference plate ($d_{11}=0.5$ pm V^{-1}) and compared with the mean signal from an LB monolayer of the hemicyanine dye, (*E*)-4-[2-(4-dimethylaminophenyl)ethenyl]*N*-docosylpyridinium bromide.[15]

Surface plasmon resonance (SPR) studies were carried out using an attenuated total reflection geometry in the Kretschmann configuration.[16] Silver was vacuum deposited to a thickness of 45 nm onto one face of a glass substrate which

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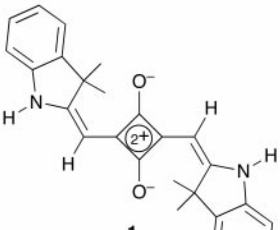

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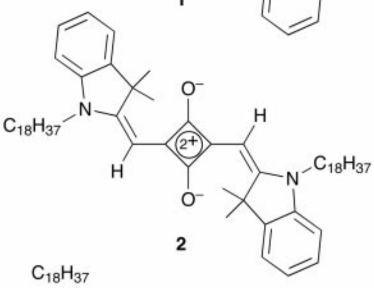

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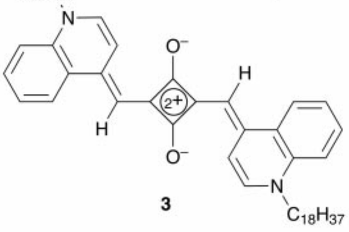

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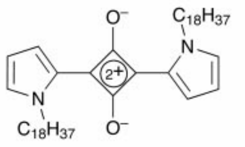

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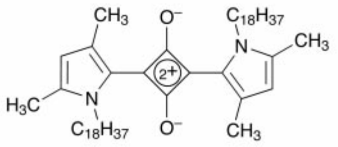

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Table 1 Selected data for the squaraine dyes

dye	VIS ($CHCl_3$) λ_{max}/nm	ν_{co} (KBr) /cm^{-1}	mass spec. *m*/*z*	mass spec. assignment
1	651	1624	397	$[M+H]^+$
2	634	1619	901	$[M+H]^+$
3	843	1602	869	$[M+H]^+$
4	544	1626	717	$[M+H]^+$
5	580	1615	773	$[M+H]^+$

was then index matched to a 60° BK7 crown glass prism. Reflectivity data were collected as a function of the incident angle using a p-polarised HeNe laser ($\lambda = 632.8$ nm) and subsequently corrected for reflections at the entrance and exit faces of the prism prior to analysis using the Fresnel reflection formulae.[17] The real (ε_r) and imaginary (ε_i) parts of the relative permittivity and thickness (l) obtained for the silver film were used in the analysis of the data obtained for the glass |Ag| monolayer structures. An acceptable analysis of the reflectivity data, using the curve fitting routine, requires the LB films to be absorbing at the excitatory wavelength and, therefore, studies on the transparent films of dyes **3** and **4** were not carried out.

Results and Discussion

Indolinylidene dyes

The pressure–area (π–A) isotherms of the indolinylidene dyes are dependent upon the substituent group (Fig. 1). For example, the octadecyl analogue (**2**) has a limiting area of 140 Å^2 molecule^{-1} at $\pi = 0$ which decreases to 80 Å^2 molecule^{-1} at 22 mN m^{-1}, the transition, the former approximating to the face area of the chromophore and the latter to the area of its side. The molecules adopt a U-shaped configuration with the alkyl chains pointing away from the surface whereas, upon compression, the chromophore is progressively tilted onto its edge. In contrast, the isotherm of 2,4-bis[(3,3-dimethylindolin-2-ylidene)methyl]squaraine (dye **1**) shows a reduced area of 65 Å^2 molecule^{-1} decreasing to *ca.* 45 Å^2 molecule^{-1} at the onset of the transition (Fig. 1). The two steep regions are separated by a broad plateau at *ca.* 12–14 mN m^{-1} and, from the extrapolation of the upper and lower sections of the curve to $\pi = 0$, the ratio of areas is *ca.* 0.5. This is probably indicative of the formation of a bilayer structure whereas, in the low-pressure regime, the chromophore initially resides with its long edge parallel to the subphase and is tilted upwards as the pressure increases.

The spectra of films deposited at pressures corresponding to the upper and lower regions of the isotherms are similar, the maximum typically being bathochromically shifted with increasing pressure and achieving higher absorbance. This has been interpreted as further evidence of film collapse, the reported data referring to films deposited from the low pressure regime, *i.e.* 10 mN m^{-1} for **1** and 20 mN m^{-1} for **2**. The LB film spectra show a principal absorption band with $\lambda_{max} =$ 640–660 nm and a distinct shoulder at *ca.* 600 nm which is particularly well developed for dye **1** (Fig. 2). Differences in the solid state spectra of the two dyes are due to variations in the molecular alignment and intermolecular interactions. The isotherms of the dioctadecyl and unalkylated analogues suggest the chromophores align with their long axes parallel and perpendicular to the substrate respectively. The thicknesses obtained from an analysis of the SPR curves, *i.e.* 17.9 Å for dye **1** and 27.4 Å for dye **2** (Fig. 3), support this hypothesis and may be compared with van der Waals dimensions of *ca.* 18 × 10 × 4 Å for the chromophore and *ca.* 24 × 5 Å for the octadecyl chains. The real and imaginary components of the relative permittivity are listed in Table 2. The absorption coefficients (k), derived from these data, are in agreement with the values calculated from the spectra.

The LB films exhibit strong SHG which is polarisation dependent. The intensities, relative to the mean signal from

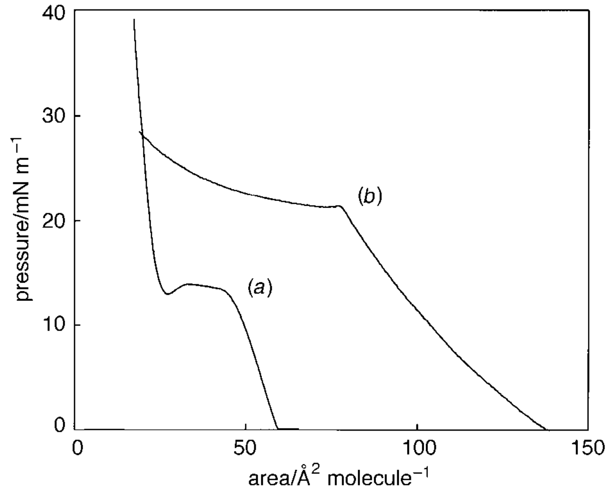

Fig. 1 Surface pressure *vs.* area isotherms of the indolinylidene dyes (*a*) **1** and (*b*) **2**

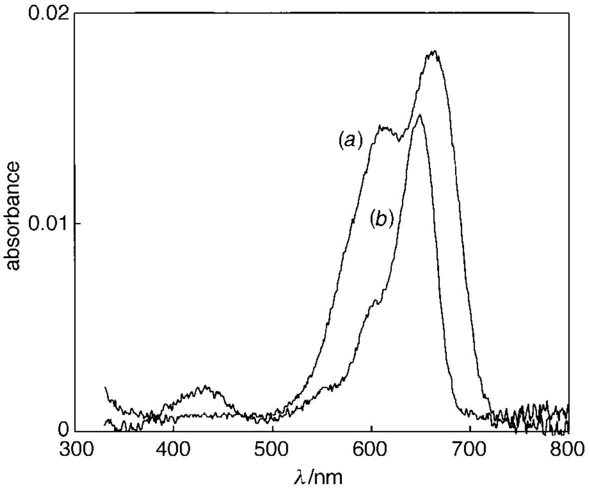

Fig. 2 Visible spectra of LB monolayers of (*a*) **1** deposited at 10 mN m^{-1} and (*b*) **2** deposited at 20 mN m^{-1}

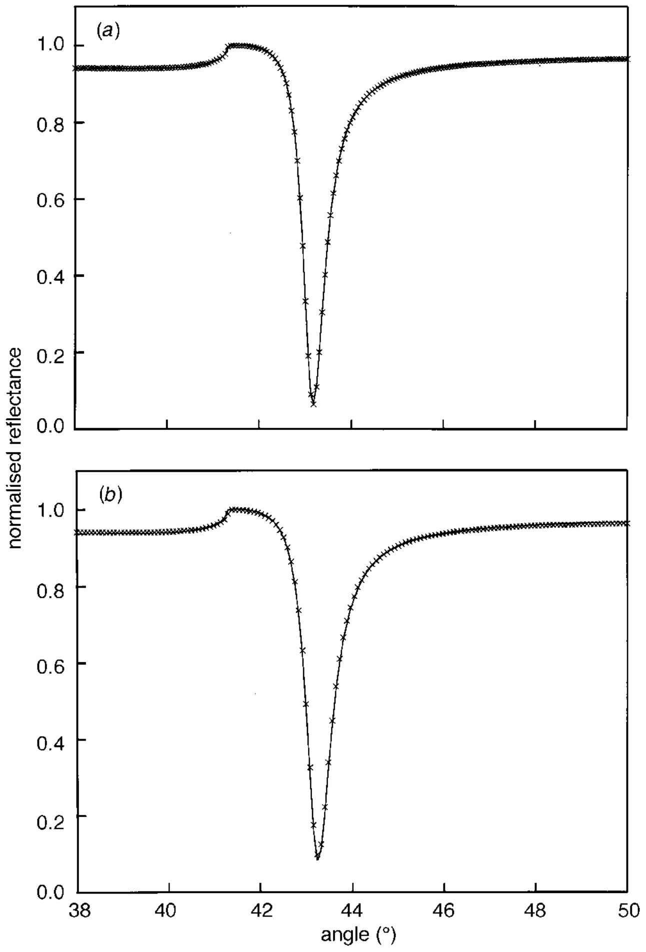

Fig. 3 Normalised reflectance *vs.* incident angle for glass |Ag| monolayer structures at 632.8 nm showing the theoretical fits (solid lines) and experimental data: (*a*) dye **1** and (*b*) dye **2**

Table 2 Data obtained from an analysis of the SPR data at 632.8 nm

dye	l/Å	ε_r	ε_i	n^a	k^a
1	17.8	2.54	3.24	1.82	0.89
2	28.8	2.47	1.78	1.66	0.54
5	27.4	3.45	0.39	1.86	0.11

$^a\varepsilon_r = (n^2 - k^2)$; $\varepsilon_i = \pm 2nk$.

monolayer films of the hemicyanine dye,[15] are $I_{2\omega}(\text{p}\rightarrow\text{p}) = 0.3$–$0.7$ and 0.03–0.1 for **1** and **2** respectively, whereas $I_{2\omega}(\text{s}\rightarrow\text{p})$ was undetectable. The different nonlinear optical properties of these dyes may be easily understood by comparing their spectra. The former has a broader optical absorption with significant resonant enhancement at the second harmonic wavelength, the susceptibility being $\chi_{zzz}^{(2)} = 100$–150 pm V^{-1} at 1.064 μm. Dye **2** has a much lower value of 20–35 pm V^{-1} but this can be partly attributed to the volume occupied by the octadecyl chains, the layer thicknesses being 28.8 Å compared with 17.8 Å for **1**. Nevertheless, these values still compare favourably with those reported for conventional donor–(π-bridge)–acceptor dyes.[16]

The X-ray crystal structure of the *N*-methyl analogue, 2,4-bis[(1,3,3-trimethylindolin-2-ylidene)methyl]squaraine, was reported by Kobayashi *et al.*[17] The crystal has a centrosymmetric space group ($P2_1/c$) within which the molecules are twisted with dihedral angles of 7.8 and 24.6° between the central ring and the terminal donor groups. However, the high susceptibility of **1** is unlikely to arise from a slight distortion of the donor–acceptor–donor structure. Furthermore, this unalkylated analogue is less sterically hindered and it may well adopt a centric arrangement similar to that of the related quinolylidene dye, 2,4-bis[(*N*-butyl-2,4-dihydroquinolin-2-ylidene)methyl]squaraine.[18] Instead, the second-order properties are attributed to an acentric aggregate structure and it is assumed that adjacent molecules adopt an acentric T arrangement with close contacts between the central acceptor and terminal donor. This was initially suggested for the SHG activity of the anilino squaraines[1,8] and has since been corroborated by the theoretical treatment of Brédas and Brouyère.[11] Furthermore, supporting experimental evidence is provided by the electrospray mass spectrum of **1** in acetonitrile (Fig. 4). This displays peaks which correspond to the monomer ($m/z = 397$, $[\text{M+H}]^+$) and dimeric aggregate ($m/z = 791$, $[\text{2M}-\text{H}]^+$).

Quinolylidene dyes

The X-ray crystal structure of the 2-quinolylidene analogue, previously reported by Bernstein *et al.*,[18] has revealed a centric chromophore whereas the LB monolayer is again SHG-active.[19] As the second-order properties are not an inherent feature of the molecules themselves and the signal is too strong to be associated with the interface, the behaviour can be unambiguously assigned to interactions arising within the aggregate structure. In this work, the LB deposition and second-order properties of the related 4-quinolylidine dye, 2,4-bis[(*N*-octadecyl-2,4-dihydroquinolin-4-ylidene)methyl]squaraine **3**, are reported. The π–*A* isotherm shows an area of *ca.* 115 Å^2 molecule^{-1} at $\pi = 0$, a structural anomaly at

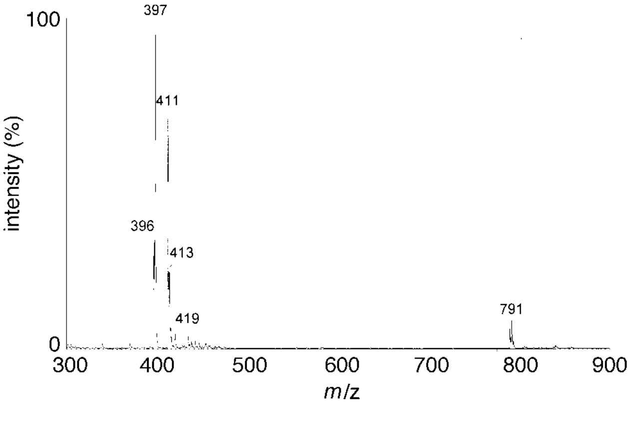

Fig. 4 Positive ion electrospray mass spectrum of a dilute solution of dye **1** in acetonitrile. Monomer: $m/z = 397$ $[\text{M+H}]^+$. Dimeric aggregate: $m/z = 791$ $[\text{2M}-\text{H}]^+$.

23 mN m^{-1} and film collapse at 50 mN m^{-1} with a limiting area of *ca.* 40 Å^2 molecule^{-1} (Fig. 5). The van der Waals dimensions of the chromophore, including the first methylene attached to each of the nitrogen atoms of the heterocyclic ring, are *ca.* 18 × 8 × 4 Å. The data suggest that the two-legged molecule initially adopts a U-shaped configuration at the air–water interface. However, at 50 mN m^{-1}, the area is only slightly larger than the molecular cross-section and this may indicate the onset of collapse at the lower transition pressure of 23 mN m^{-1}. Alternatively, there may be a change in the molecular conformation, from U-shaped to stretched with the two alkyl groups pointing in opposite directions, a consequence being that the molecules align with one of the hydrophobic groups adjacent to the water surface. Although somewhat controversial, similar isotherms have been obtained for other two-legged dyes;[20–22] for these, X-ray studies at the air–water interface have provided corroborating evidence[20,21] and this has been supported by the thickness of previously deposited LB monolayers.[22]

The LB film spectrum of the quinolylidene dye **3**, deposited at 5–25 mN m^{-1}, shows an absorption maximum at 850 nm with an absorbance of 0.006 layer^{-1} (Fig. 6). The film is transparent at the harmonic frequency. However, the second-harmonic intensity is resonantly enhanced because, at longer wavelengths, the absorption tail overlaps the fundamental frequency of the Nd : YAG laser. The SHG is dependent upon the deposition pressure with an optimum behaviour at 30 mN m^{-1}, the value being *ca.* 0.5 times the mean intensity from monolayer films of the hemicyanine standard (Table 3). For comparison, films deposited from the lower region of the isotherm show greatly reduced SHG with a relative intensity of 0.03 to 0.05.

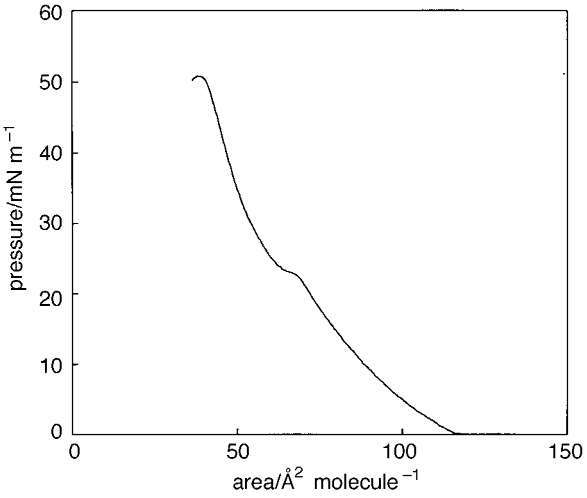

Fig. 5 Surface pressure *vs.* area isotherm of dye **3**

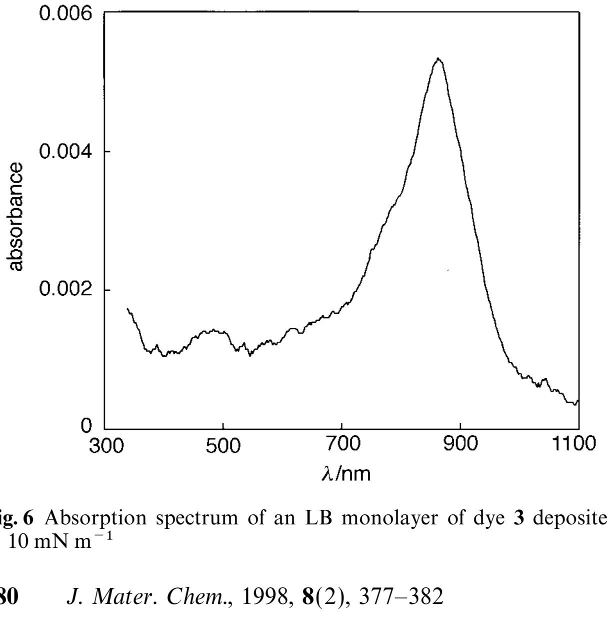

Fig. 6 Absorption spectrum of an LB monolayer of dye **3** deposited at 10 mN m^{-1}

Pyrrolyl dyes

LB films of dyes **4** and **5** have been reported by Lynch *et al.*[12] but their isotherms and LB film properties are atypical and we have not been able to reproduce the published results. Close scrutiny of their analytical data indicates that the dyes are impure. For example, they reported broad endothermic transitions at 31–42 and 67–75 °C for dye **4** whereas, from differential scanning calorimetry studies, we have observed a single melting point at 32–36 °C with an enthalpy of 62 kJ mol^{-1}. Furthermore, their published FTIR data for ν_{CO}, *i.e.* bands at 1625 and 1750 cm^{-1} with an absorbance ratio of *ca.* 3 : 1, indicate a mixture of isomeric forms. The former corresponds to dye **4** whereas, using the assignment of Triebs and Jacob,[23] the latter may be attributed to an acentric 1,2-squarate. In contrast, the Cranfield sample has a single CO band at 1626 cm^{-1}.

Isotherms have been reported by Lynch *et al.*[12] but the published areas are significantly less than the molecular cross-sections throughout the entire pressure range; they decrease from *ca.* 30 Å^2 molecule^{-1} at $\pi = 0$ to less than 20 Å^2 molecule^{-1} at collapse, whereas the van der Waals dimensions of the chromophores of dyes **4** and **5**, excluding the four methyl groups of the latter, are *ca.* 13 × 7 × 3.4 Å. In contrast, we have obtained limiting areas of *ca.* 95 Å^2 molecule^{-1} at $\pi = 0$ and extrapolation of the steep high-pressure regions yields corresponding values of *ca.* 45 and 70 Å^2 molecule^{-1} for **4** and **5** respectively (Fig. 7). Additionally, the isotherms show only a slight hysteresis when repeatedly cycled between 0 and

Table 3 Linear and nonlinear optical properties of monolayer LB films

	spectra		relative SHG[a]
dye	λ_{max}/nm	A/layer^{-1}	$I_{2\omega(LB)}/I_{2\omega(hemi)}$
1	660	0.018	0.7
2	640	0.016	0.1
3	850	0.006	0.5
4	350	0.002	0
5	585	0.007	0.01

[a] Optimum intensity relative to the mean signal from monolayer films of the hemicyanine dye, (*E*)-4-[2-(4-dimethylaminophenyl)ethenyl]-*N*-docosylpyridinium bromide.

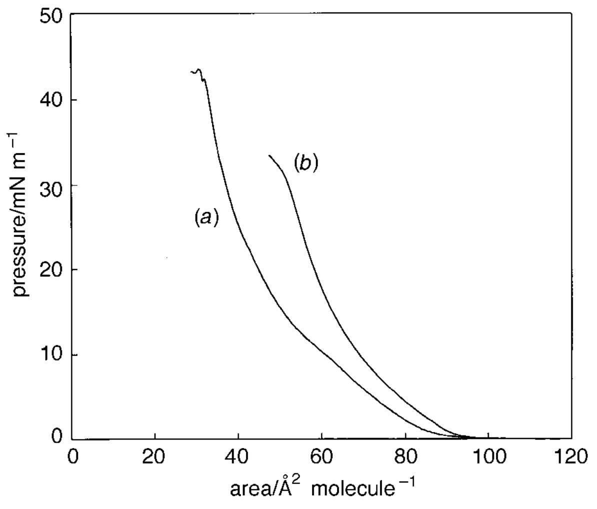

Fig. 7 Surface pressure *vs.* area isotherms of dyes (*a*) **4** and (*b*) **5**

30 mN m^{-1}. The films collapse at 45 and 33 mN m^{-1} respectively and, thus, deposition was carried out at 30 mN m^{-1}.

The LB film spectra of dye **4** show a meagre absorption maximum centred at *ca.* 350 nm and have a weak absorption throughout the visible region. SHG has not been observed whereas Lynch *et al.*[12] reported a weak signal with an effective second-order susceptibility of 1 pm V^{-1}. However, since their FTIR data indicate a high concentration of the acentric 1,2-squarate (crudely *ca.* 25% from the ratio of peaks at 1625 and 1750 cm^{-1}) the SHG may be attributed to this rather than the centric 2,4-isomer. Based on our studies of the analytically pure sample of dye **4** we conclude that the LB films are either SHG-inactive or the intensity is so weak that it is indistinguishable from the background noise. The discrepancy between the published results[12] and our data is emphasised in Table 4.

The LB film spectra of dye **5** show a broad absorbance throughout the visible region and an intense band at 585 nm (Fig. 8). Lynch *et al.*[12] have reported that the colour changes from red–violet to purple–blue within a few minutes of deposition whereas, with the exception of a slight decrease in absorbance, the colour of our films remained unchanged. Analysis of the SPR data, shown in Fig. 9, gave $l = 27.4$ Å, $\varepsilon_r = 3.45$ and $\varepsilon_i = 0.39$, the layer thickness being consistent with the van der Waals length with the octadecyl chains packing side-by-side. The films are initially SHG-active although the second-harmonic intensity is very weak compared with signals obtained from LB films of dyes **1** and **3** (Table 1) and the related SHG-active anilino squaraines.[1–4] Non-centrosymmetric aggregation may be responsible for the second-order behaviour but, if applicable, the slight SHG suggests a less favourable intermolecular donor–acceptor interaction. Furthermore, a resonantly enhanced intensity would be expected from the overlapping absorption band (Fig. 8).

The 2,4-bis(*N*-octadecylpyrrol-2-yl)squaraines were previously synthesised at Cranfield but, unlike the anilino derivatives,[1–4] the SHG is far too weak ($\chi_{\rm eff}^{(2)} = 4$ pm V^{-1} for **5**) to be unambiguously assigned to an intrinsic property of the aggregate. Lynch *et al.*[12] tentatively assigned the nonlinearities to electric–quadrupole or magnetic–dipole interactions but it is significant that we have not observed SHG from LB films of the analytically pure sample of dye **4**. Furthermore, we note that the second-harmonic intensity for dye **5** is *ca.* 100 times smaller than obtained from films of the anilino squaraines[1] and, therefore, as the molecule is centric, interfacial and impurity-induced effects cannot be excluded as the origin of the second-order behaviour. This is particularly relevant to dye **4** where the FTIR data of Lynch *et al.*[12] indicate a high concentration of an acentric 1,2-squarate which may be present as the monomer or units of an oligomer or polymer.[14,24] However, these remarks do not apply to the indolinylidene (**1**) and quinolylidene (**3**) dyes which exhibit strong SHG when deposited as LB films.

Table 4 2,4-Bis(*N*-octadecylpyrrol-2-yl)squaraine (dye **4**)

property	Lynch *et al.*[12]	this work[a]
DSC/°C	31–42, 67–75	32–36
$\nu_{\rm CO}$/cm^{-1}	1625, 1750	1626
$\lambda_{\max}$ (CHCl$_3$)/nm	548.5	544
area at $\pi = 0$ /Å^2 molecule^{-1}	30	95
SHG-active	yes	undetectable

[a]Analytical data. $\delta_{\rm H}$ (CDCl$_3$, *J*/Hz): 7.42 (2H, t, *J* 2, pyrrole); 6.65 (2H, d, *J* 4, pyrrole); 6.13 (2H, d, *J* 4, pyrrole); 3.86 (4H, t, *J* 7, NCH$_2$); 1.8–1.7 (4H, m, NCH$_2$CH$_2$); 1.25 (60H, s, CH$_2$); 0.88 (6H, t, *J* 7, CH$_3$). MS: $m/z = 717$ [M+H]$^+$. Found: C, 80.1; H, 11.0; N, 3.7. C$_{48}$H$_{80}$N$_2$O$_2$ requires C, 80.4; H, 11.3; N, 3.9%.

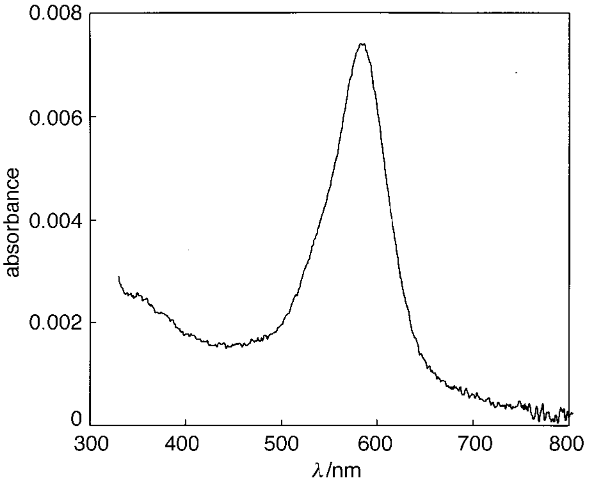

Fig. 8 Visible spectrum of an LB monolayer of dye **5**

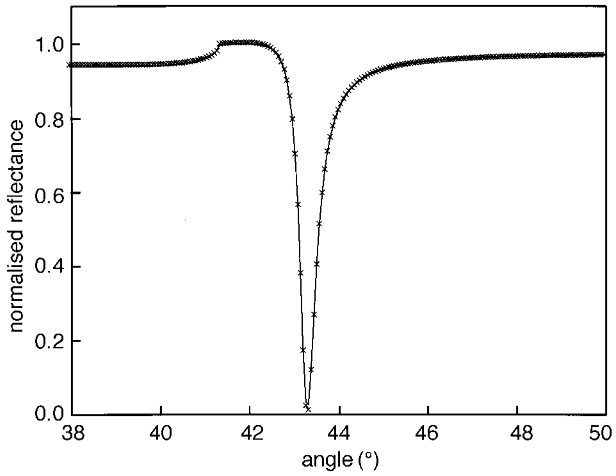

Fig. 9 Normalised reflectance *vs.* incident angle for a glass |Ag| monolayer structure of dye **5** at 632.8 nm showing the theoretical fit (solid line) and experimental data

Effect of the substrate

The second-order nonlinear optical properties of squaraines with heterocyclic donor groups (indolinylidene and quinolylidene) have demonstrated that strong SHG can result from centric chromophores. When deposited on substrates coated with cadmium icosanoate or icosanoic acid, LB films of **1** to **3** exhibit SHG but the signal is typically reduced to *ca.* 20–30% of the intensity from the LB monolayer on glass. Films of the amphiphilic acid and its cadmium salt are SHG-inactive and, therefore, only serve to provide an optically inert interface between the underlying glass substrate and the LB film. This in itself is likely to modify the SHG from the squaraine aggregate since the nature of the substrate has a profound effect on the molecular tilts in the adjacent layer. It is assumed that the surface morphology of the organic buffer is sufficiently different from glass to suppress second-order interfacial effects which undoubtedly would be very weak for the glass |squaraine interface. Furthermore, the SHG from films of dyes **1** to **3** decays with time and is immeasurable within a few days inferring that the nonlinear optical behaviour is a characteristic of the LB film and not of the interface. The SHG is also too strong to be associated with a boundary effect and, instead, is attributed to non-centrosymmetric aggregation within the film.

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