Unconventional Langmuir–Blodgett films: alignment of an optically nonlinear dye where the donor and π-electron bridge are hydrophobic and the acceptor is hydrophilic

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The optically nonlinear dye, 5-{4-[2-(4-dibutylaminophenyl)vinyl]benzylidene}-2-(1-ethylpropyl)-5,6,7,8-tetrahydroisoquinolinium bromide (**1a**), differs from other Langmuir–Blodgett (LB) film-forming materials. The molecule is amphiphilic and, therefore, may be aligned at the air–water interface but, instead of a conventional aliphatic tail, has an extended π-electron bridge. It forms non-centrosymmetric LB films which exhibit second-harmonic generation (SHG) and have a high second-order susceptibility: $\chi^{(2)}_{zzz} = 40$ pm V^{-1} at 1.064 μm for a monolayer thickness of 1.8 nm and chromophore tilt angle of 55° from the substrate normal. The octadecyl sulfate salt (**1b**) also forms non-centrosymmetric films but with improved properties: $\chi^{(2)}_{zzz} = 90$ pm V^{-1} at 1.064 μm for $d = 2.4$ nm and $\varphi = 33°$. Both films exhibit charge-transfer bands at 360 nm but with absorbance cut-off above 560 nm for **1a** and 530 nm for **1b**. The latter is fully transparent at the fundamental and harmonic wavelengths and its susceptibility is the highest to date for such a film. This results from an optimised packing arrangement, a conjugation enhanced molecular hyperpolarisability of $\beta = 4.3 \times 10^{-38}$ m^4 V^{-1}, and the proximity of the absorption band, albeit non-overlapping at 532 nm. The properties are compared with those of conventional long alkyl tailed materials (**2** and **3**) of the same chromophore.

Introduction

Progress in the design of materials for SHG[1] necessitates a trade-off in efficiency for transparency as well as a dilution of the active component when supramolecular organisation is realised by electric field poling[2] or LB deposition.[3,4] The effective volume of the optically nonlinear chromophore is limited to *ca.* 15% in poled films, to avoid phase separation from the polymer matrix, and is only slightly better in LB monolayers where the occupancy is typically 40–50% with the remainder taken up by hydrophobic alkyl groups. These are necessary for alignment at the air–water interface but tend to disrupt the non-centrosymmetry by enforcing head-to-head (hydrophilic) and tail-to-tail (hydrophobic) arrangements in multilayer films. Interleaving the layers with inactive spacers[5–8] may give the necessary alignment but reduces the chromophore occupancy to *ca.* 20–25%. An alternative approach is to substitute opposite ends of the chromophore with alkyl groups,[9–11] which results in hydrophobic surfaces, both top and bottom, and retention of the initial alignment throughout the multilayer structure. In such films, an effective volume of the chromophore layer of *ca.* 50% arises when either the alkyl groups of adjacent layers interdigitate ("molecular Lego")[12] or the lengths are optimised.[13]

In this work, we now focus upon improving the chromophore occupancy within the LB layer and demonstrate alignment of a donor–(π-bridge)–acceptor molecule without long alkyl groups (**1a** and **1b**). The donor and conjugated electron-bridge act as the hydrophobic component and the acceptor as the hydrophilic component for alignment at the air–water interface. The second-order susceptibility of **1b**, $\chi^{(2)}_{zzz} = 90$ pm V^{-1} at 1.064 μm, is the highest value to date for a transparent film and confirms optimum non-centrosymmetric alignment within the monolayer. The high value is attributed, in part, to the extended π-electron bridge connecting the donor and acceptor moieties and, in part, to a greatly improved occupancy compared with conventional amphiphilic dyes.
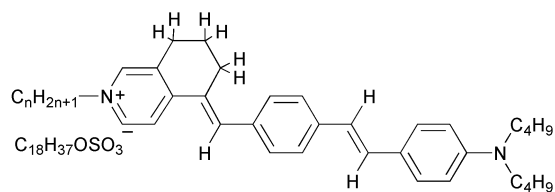
Experimental

Synthesis

4-[2-(4-Dibutylaminophenyl)vinyl]benzonitrile. To a solution of 4-dibutylaminobenzaldehyde (3.5 g, 15 mmol) in methanol (100 cm^3) was added (4-cyanobenzyl)triphenylphosphonium chloride (6.2 g, 15 mmol) and potassium *tert*-butoxide (1.7 g, 15 mmol). The mixture was heated at reflux for 24 h and then cooled. The resultant yellow precipitate was purified by column chromatography on silica gel, eluting with chloroform, to yield
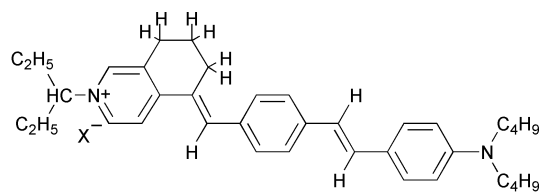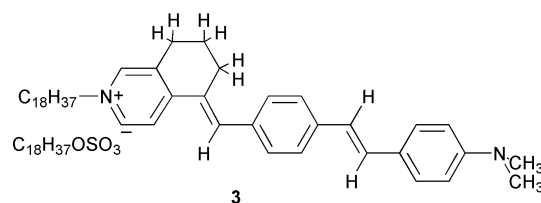

1a X = Br$^-$
1b X = C$_{18}$H$_{37}$OSO$_3$$^-$

2a n = C$_{12}$H$_{25}$
2b n = C$_{18}$H$_{37}$

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4-[2-(4-dibutylaminophenyl)vinyl]benzonitrile as a 1 : 1 mixture of the *cis* and *trans* forms: combined yield, 60%; mp 110–112 °C; λ_{max} (CHCl$_3$), 403 nm. Found: C, 82.8; H, 8.2; N, 8.4%. C$_{23}$H$_{28}$N$_2$ requires: C, 83.09; H, 8.49; N, 8.43%. The two forms were partially separated by preparative plate chromatography, eluting with chloroform–hexane (1 : 1 *v/v*).

trans form. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 0.96 (t, J 7.3, 6H, CH$_3$); 1.37 (sextet, J 7.3, 4H, CH$_2$); 1.59 (quintet, J 7.5, 4H, CH$_2$); 3.30 (t, J 7.6, 4H, CH$_2$N); 6.62 (d, J 9.2, 2H, Ar-H); 6.83 (d, J 16.2, 1H, C=C-H); 7.13 (d, J 16.3, 1H, C=C-H); 7.43 (d, J 8.5, 2H, Ar-H); 7.51 (d, J 8.4, 2H, Ar-H); 7.57 (d, J 8.5, 2H, Ar-H). *m/z* (FAB): 332 (M$^+$, 100%).

cis form. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 0.96 (t, J 7.3, 6H, CH$_3$); 1.37 (sextet, J 7.3, 4H, CH$_2$); 1.59 (quintet, J 7.5, 4H, CH$_2$); 3.24 (t, J 7.6, 4H, CH$_2$N); 6.29 (d, J 12.2, 1H, C=C-H); 6.47 (d, J 8.9, 2H, Ar-H); 6.58 (d, J 12.2, 1H, C=C-H); 7.06 (d, J 8.9, 2H, Ar-H); 7.38 (d, J 8.9, 2H, Ar-H); 7.50 (d, J 7.5, 2H, Ar-H). *m/z* (FAB): 332 (M$^+$, 100%).

4-[2-(4-Dimethylaminophenyl)vinyl]benzonitrile. This was prepared from 4-(dimethylamino)benzaldehyde by adapting the procedure described above. *cis* and *trans* forms, in a ratio of *ca.* 1 : 1, were obtained: combined yield 60%; mp 255–256 °C (161 °C darkens); λ_{max} (CHCl$_3$): 386 nm. Found: C, 82.3; H, 6.5; N, 11.1%. C$_{17}$H$_{16}$N$_2$ requires: C, 82.22; H, 6.49; N, 11.28%.

trans form. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 3.02 (s, 6H, N(CH$_3$)$_2$); 6.72 (d, J 8.7, 2H, Ar-H); 6.88 (d, J 16.2, 1H, C=C-H); 7.16 (d, J 15.8, 1H, C=C-H); 7.44 (d, J 8.4, 2H, Ar-H); 7.52 (d, J 8.8, 2H, Ar-H); 7.59 (d, J 8.4, 2H, Ar-H). *m/z* (FAB): 248 (M$^+$, 100%).

cis form. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 2.97 (s, 6H, N(CH$_3$)$_2$); 6.36 (d, J 12.1, 1H, C=C-H); 6.60 (d, J 8.4, 2H, Ar-H); 6.63 (d, J 12.0, 1H, C=C-H); 7.11 (d, J 8.4, 2H, Ar-H); 7.41 (d, J 8.0, 2H, Ar-H); 7.51 (d, J 8.8, 2H, Ar-H). *m/z* (FAB): 248 (M$^+$, 100%).

***trans* 4-[2-(4-Dibutylaminophenyl)vinyl]benzaldehyde.** Diisobutylaluminium hydride (1.5 M in toluene: 18 cm^3, 27 mmol) was added dropwise to a solution of 4-[2-(4-dibutylaminophenyl)vinyl]benzonitrile (3.0 g, 9 mmol) in chloroform (100 cm^3) at −78 °C and the temperature maintained for 1 h. Upon reaching room temperature, the solution was poured into acidified water and the organic layer extracted, washed with water (3 × 50 cm^3) and dried (MgSO$_4$). The solvent was removed *in vacuo* and the crude product purified by column chromatography on silica gel, eluting with chloroform, and then by preparative plate chromatography, eluting with a mixture of chloroform and hexane (1 : 1 *v/v*). The *trans* form was obtained as a yellow solid: yield, 40%; mp 68–69 °C; λ_{max} (CHCl$_3$), 409 nm. Found: C, 82.0; H, 8.5; N, 4.0%. C$_{23}$H$_{29}$NO requires: C, 82.34; H, 8.71; N, 4.18%. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 0.97 (t, J 7.2, 6H, CH$_3$); 1.37 (sextet, J 7.4, 4H, CH$_2$); 1.59 (quintet, J 7.5, 4H, CH$_2$); 3.30 (t, J 7.5, 4H, CH$_2$N); 6.63 (d, J 8.9, 2H, Ar-H); 6.89 (d, J 16.2, 1H, C=C-H); 7.19 (d, J 16.2, 1H, C=C-H); 7.40 (d, J 8.9, 2H, Ar-H); 7.58 (d, J 8.3, 2H, Ar-H); 7.82 (d, J 8.3, 2H, Ar-H); 9.95 (s, 1H, CHO). *m/z* (FAB): 335 (M$^+$, 100%).
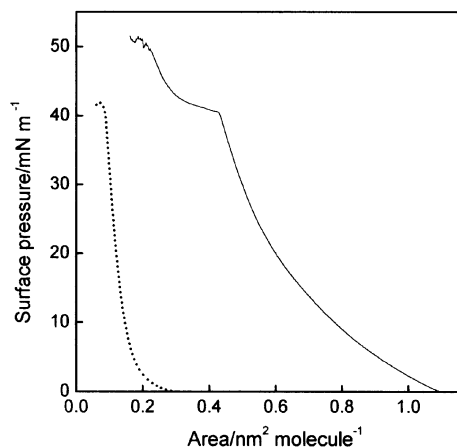
***trans* 4-[2-(4-Dimethylaminophenyl)vinyl]benzaldehyde.** This was obtained from 4-[2-(4-dibutylaminophenyl)vinyl]benzonitrile by adapting the procedure described above: yield 50%; mp 247–250 °C; λ_{max} (CHCl$_3$), 401 nm. Found: C, 81.1; H, 6.8; N, 5.6%. C$_{17}$H$_{17}$NO requires: C, 81.24; H, 6.82; N, 5.57%. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 3.02 (s, 6H, NCH$_3$); 6.73 (d, J 8.2, 2H, Ar-H); 6.94 (d, J 16.2, 1H, C=C-H); 7.22 (d, J 16.3, 1H, C=C-H); 7.45 (d, J 8.3, 2H, Ar-H); 7.60 (d, J 8.2, 2H, Ar-H); 7.84 (d, J 8.1, 2H, Ar-H); 9.96 (s, 1H, CHO). *m/z* (FAB): 251 (M$^+$, 100%).

5-{4-[2-(4-Dibutylaminophenyl)vinyl]benzylidene}-2-(1-ethylpropyl)-5,6,7,8-tetrahydroisoquinolinium bromide. To a solution of 4-[2-(4-dibutylaminophenyl)vinyl]benzaldehyde (0.20 g, 0.6 mmol) and 2-(1-ethylpropyl)-5,6,7,8-tetrahydroisoquinolinium bromide (0.17 g, 0.6 mmol) in methanol (100 cm^3) was added piperidine (0.1 cm^3) and the resultant mixture heated at reflux for 100 h. The solvent was removed *in vacuo* and the crude product purified by column chromatography on silica gel, eluting with chloroform–methanol (90 : 10 *v/v*), followed by recrystallisation from chloroform–diethyl ether (1 : 50 *v/v*), and then repeated by preparative plate chromatography: yield, 20%; mp 135–137 °C (decomp.). λ_{max} (CHCl$_3$): 395 and 490 nm. Found: C, 74.1; H, 8.4; N, 4.6%. C$_{37}$H$_{49}$N$_2$Br requires: C, 73.86; H, 8.21; N, 4.66%. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 0.90 (t, J 7.3, 6H, CH$_3$); 0.95 (t, J 7.2, 6H, CH$_3$); 1.36 (sextet, J 7.3, 4H, CH$_2$); 1.59 (quintet, J 7.4, 4H, CH$_2$); 1.92 (quintet, J 6.5, 2H, CH$_2$); 2.11 (quintet, J 7.2, 4H, CH$_2$); 2.96 (t, J 5.7, C=C-CH$_2$); 3.12 (t, J 6.0, 2H, C=C-CH$_2$); 3.31 (t, J 6.8, 4H, CH$_2$N); 4.77 (quintet, J 7.1, 1H, N$^+$CH); 6.65 (d, J 8.2, 2H, Ar-H); 6.89 (d, J 15.9, 1H, C=C-H); 7.12 (d, J 16.1, 1H, C=C-H); 7.39–7.50 (m, 6H, Ar-H); 7.60 (s, 1H, C=C-H); 8.33 (d, J 6.6, 1H, Qn-H); 9.00 (d, J 6.5, 1H, Qn-H); 9.23 (s, 1H, Qn-H). *m/z* (FAB): 521 (M$^+$ − Br$^-$, 100%).

5-{4-[2-(4-Dibutylaminophenyl)vinyl]benzylidene}-2-dodecyl-5,6,7,8-tetrahydroisoquinolinium iodide. The dye was obtained from 1-dodecyl-5,6,7,8-tetrahydroisoquinolinium iodide by adapting the procedure described above: yield 12%; mp 162–163 °C; λ_{max} (CHCl$_3$), 360 and 492 nm. Found: C, 70.4; H, 8.6; N, 3.8%. C$_{44}$H$_{63}$N$_2$I requires: C, 70.76; H, 8.50; N, 3.75%. ^{1}H NMR (400 MHz, CDCl$_3$, J/Hz): δ_H 0.88 (t, J 6.3, 3H, CH$_3$); 0.97 (t, J 7.1, 6H, CH$_3$); 1.26 (br s, 18H, CH$_2$); 1.33–1.43 (m, 4H, CH$_2$); 1.53–1.60 (m, 4H, CH$_2$); 1.94–2.05 (m, 4H, CH$_2$); 2.99 (t, 2H, J 6.3, C=C-CH$_2$); 3.07 (t, J 6.3, 2H, C=C-CH$_2$); 3.31 (t, J 7.5, 4H, N(CH$_2$)$_2$); 4.74 (t, J 7.2, 2H, CH$_2$N$^+$); 6.64 (d, J 8.5, 2H, Ar-H); 6.88 (d, J 16.5, 1H, C=C-H); 7.14 (d, J 16.5, 1H, C=C-H); 7.39–7.53 (m, 7H, Ar-H & C=C-H); 8.16 (d, J 6.7, 1H, Qn-H); 8.77 (d, J 6.0, 1H, Qn-H); 8.96 (s, 1H, Qn-H). *m/z*(FAB): 620 (M$^+$ − I$^-$, 100%).

5-{4-[2-(4-Dibutylaminophenyl)vinyl]benzylidene}-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide. The dye was obtained from 1-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide by adapting the procedure described above: yield 20%; mp 108–110 °C; λ_{max} (CHCl$_3$), 360 and 492 nm. Found: C, 71.8; H, 9.2; N, 3.3%. C$_{50}$H$_{75}$N$_2$I requires: C, 72.26; H, 9.10; N, 3.37%. ^{1}H NMR (400 MHz, CDCl$_3$, J/Hz): δ_H 0.85 (t, J 6.8, 3H, CH$_3$); 0.95 (t, J 7.3, 6H, CH$_3$); 1.23 (br s, 30H, CH$_2$); 1.35 (sextet, J 7.5, 4H, CH$_2$); 1.57 (quintet, J 6.9, 4H, CH$_2$); 1.89 (quintet, J 5.8, 2H, CH$_2$); 1.98 (quintet, J 7.6, 4H, CH$_2$); 2.91 (t, 2H, J 5.4, C=C-CH$_2$); 3.03 (t, J 5.9, 2H, C=C-CH$_2$); 3.28 (t, J 7.5, 4H, N(CH$_2$)$_2$); 4.68 (t, J 7.3, 2H, CH$_2$N$^+$); 6.62 (d, J 8.2, 2H, Ar-H); 6.85 (d, J 16.1, 1H, C=C-H); 7.09 (d, J 16.2, 1H, C=C-H); 7.36–7.41 (m, 4H, Ar-H); 7.43 (s, 1H, C=C-H); 7.48 (d, J 8.8, 2H, Ar-H); 8.19 (d, J 6.8, 1H, Qn-H); 8.77 (d, J 6.5, 1H, Qn-H); 9.05 (s, 1H, Qn-H). *m/z* (FAB): 704 (M$^+$ − I$^-$, 100%).

5-{4-[2-(4-Dimethylaminophenyl)vinyl]benzylidene}-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide. The dye was obtained from 1-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide and 4-[2-(4-dimethylaminophenyl)vinyl]benzaldehyde by adapting the procedure described above: yield 28%; mp 181–183 °C; λ_{max} (CHCl$_3$), 355 and 472 nm. Found: C, 70.3; H, 8.5; N, 3.6%. C$_{44}$H$_{63}$N$_2$I requires: C, 70.76; H, 8.50; N, 3.75%. ^{1}H NMR (CDCl$_3$, 250 MHz, J/Hz): δ_H 0.87 (t, J 6.4, 3H, CH$_3$); 1.24 (br s, 32H, CH$_2$); 1.85–2.01 (m, 2H, CH$_2$); 2.91 (t, J 6.0, 2H, C=C-CH$_2$); 3.00 (s, 6H, N(CH$_3$)$_2$); 3.04 (t, J 6.0, 2H, C=C-CH$_2$); 4.68 (t, J 7.2, 2H, CH$_2$N$^+$); 6.71 (d, J 8.7, 2H, Ar-H); 6.89 (d, J 16.2,

Fig. 1 Surface pressure *versus* area isotherms of **1**: bromide salt (broken line); octadecyl sulfate salt (solid line). The bromide salt is partially water soluble and this accounts for the unrealistic molecular area.

1H, C=C-H); 7.12 (d, *J* 16.2, 1H, C=C-H); 7.40–7.48 (m, 6H, Ar-H); 7.51 (s, 1H, C=C-H); 8.18 (d, *J* 6.7, 1H, Qn-H); 8.76 (d, *J* 6.5, 1H, Qn-H); 9.06 (s, 1H, Qn-H). *m/z*(FAB): 619 (M^{+} − I^{-}, 100%).

Deposition and film characterisation. LB films were deposited onto hydrophilically treated glass slides and gold-coated glass substrates for SHG and surface plasmon resonance (SPR) studies respectively. The specific conditions for LB deposition and details relating to the film characterisation are provided below. Additional information concerning these techniques can be found in early publications[5,11] and references therein.
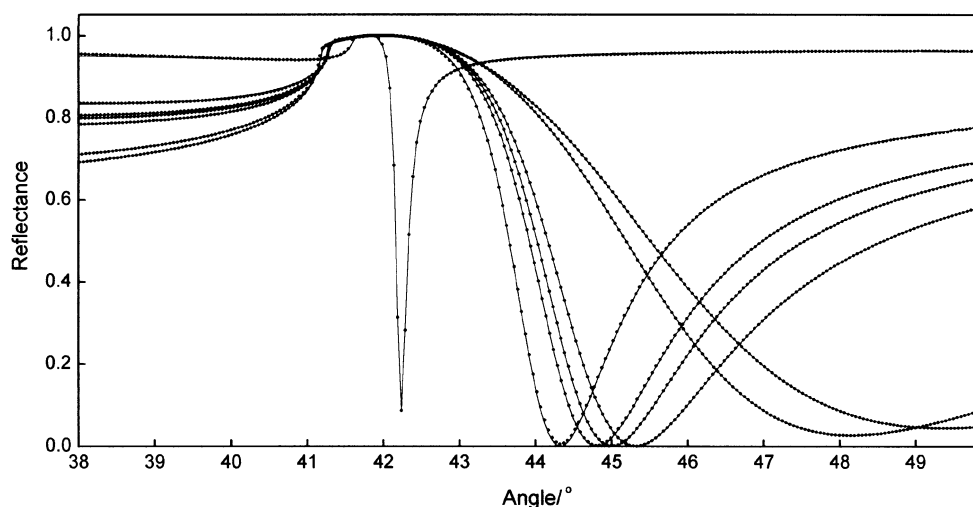
Results and discussion

Unconventional amphiphiles

The bromide salt of dye **1** was spread from dilute chloroform solution (1 × 10^{-4} M) onto the pure water subphase of a Nima Technology LB trough, left for 10 min, and then compressed at 0.5 cm^2 s^{-1}, which corresponds to a change of *ca.* 0.1% s^{-1} of the compartment area. The isotherm is featureless with collapse occurring at 41 ± 2 mN m^{-1} but, for this unconventional amphiphile, the area is less than the molecular cross-section (Fig. 1). The monolayer film is probably partially soluble in the aqueous subphase but this does not influence its deposition. Furthermore, it may be overcome by co-spreading the dye and
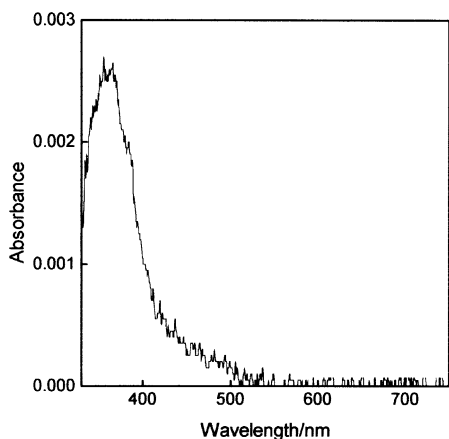
sodium octadecyl sulfate, in a 1 : 1 mole ratio, from chloroform and methanol respectively. The inorganic counterions, Na^{+} and Br^{-}, dissolve and leave the octadecyl sulfate salt of the dye at the surface. When compressed as above the isotherm exhibits areas consistent with the expected cross-sections: the film undergoes collapse at 42 mN m^{-1} with an onset area of 0.40 nm^2 molecule^{-1} and then shows a second transition at 51 mN m^{-1} and 0.20 nm^2 molecule^{-1}, which probably corresponds to collapse of the resultant bilayer structure (Fig. 1). In this study, the film was deposited on the upstroke at a surface pressure of 35 mN m^{-1} and a rate of 0.1 mm s^{-1}, this giving an optimum second-harmonic intensity. The bromide salt shows optimum behaviour when deposited at 30 mN m^{-1}.

Thicknesses were obtained from SPR studies, which were performed on glass/Au/monolayer structures using a Kretschmann configuration[14] and *p*-polarised monochromatic radiation at the following excitatory wavelengths (Fig. 2): 1.064 μm and 532 nm (Nd : YAG); 632.8, 611.9, 604.0, 594.1 and 543.5 nm (multi-line He : Ne). The attenuated total reflection was measured before and after deposition and the data analysed by one and two-layer models respectively using Fresnel reflection formulae. Analysis provided thicknesses of 1.75 ± 0.06 nm and 2.43 ± 0.06 nm for the bromide and octadecyl sulfate salts respectively, the values being confirmed by atomic force microscopy. The refractive indices of both films are almost identical and independent of wavelength throughout the visible range: *n* = 1.69 ± 0.05 for 532 nm ⩽ λ ⩽ 632.8 nm and 1.62 ± 0.10 at 1.064 μm. This is expected from the spectrum, the films having a peak absorbance at 360 nm with cut-off above *ca.* 560 nm for **1a** and 530 nm for **1b** (Fig. 3). The latter is transparent at both the fundamental and harmonic wavelengths for SHG, the monolayer absorbance being less than the detection limit of the spectrophotometer and estimated at <10^{-4}.
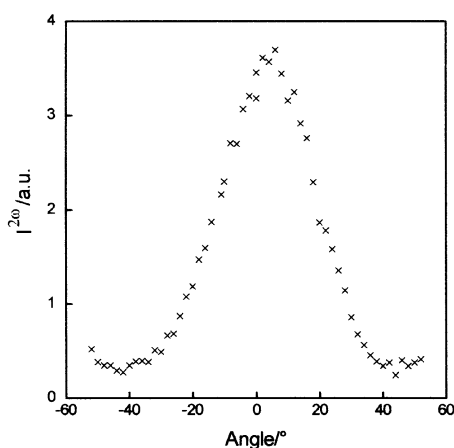
The second-harmonic intensity was measured in transmission using a *p*-polarised Nd : YAG laser and half-wave plate to alter the polarisation. The intensity is negligible at normal incidence as found for most LB films and, therefore, the polarisation dependence was investigated with the laser beam incident at 45°. However, the dependence was very different for the two salts with $I^{2\omega}$(p → p)/$I^{2\omega}$(s → p) ≈ 1.5 for the bromide and 15 for the octadecyl sulfate (Fig. 4). These indicate different tilt angles and, using the method of Kajikawa *et al.*,[15] the data correspond to a tilt of the chromophore charge-transfer axis of 33° from the substrate normal for the latter. The method fails for the bromide salt but, from the ratio of the layer thickness and the theoretically modelled molecular

Fig. 2 SPR spectra from a glass/Au/monolayer structure of the octadecyl sulfate salt of **1** on a 40 nm thick gold overlay at the following excitatory wavelengths: 532 and 1064 nm (Nd : YAG); 543.5, 594.1, 604.0; 611.9 and 632.8 nm (He : Ne). The spectra broaden with decreasing wavelength and the angle for resonance increases.

Fig. 3 UV/visible spectrum of an LB monolayer of the octadecyl sulfate salt of **1** showing a peak absorbance at 360 nm and cut-off at *ca.* 530 nm, the residual absorbance above this wavelength being noise. The bromide salt shows similar behaviour but with absorption cut-off above 560 nm.


Fig. 4 Second-harmonic intensity from a monolayer film of the octadecyl sulfate of **1** salt *versus* the angle of the half-wave plate, the maximum corresponding to a *p*-polarised fundamental beam and the minima to *s*-polarised. The laser beam is incident at 45° to the film.

length, an angle of 55° may be estimated. As both films are effectively transparent at the harmonic wavelength it may be assumed that Kleinman's symmetry is valid and that the components of the susceptibility are limited to $\chi^{(2)}_{zzz}$ and $\chi^{(2)}_{zxx}$. By comparison with the intensity from the Maker fringe envelope of a Y-cut quartz reference plate ($d_{11} = 0.5$ pm V^{-1}), the susceptibilities for $\lambda = 1.064$ μm are 40 pm V^{-1} and 28 pm V^{-1} respectively for the bromide salt and 90 and 19 pm V^{-1} for the octadecyl sulfate. The molecular hyperpolarisability (β) is probably dominated by the component along the molecular charge transfer axis and the relation between $\chi^{(2)}$ and β is as given below:

$$\chi^{(2)}_{zzz} = Nf^{2\omega}(f^{\omega})^2\beta\cos^3\varphi \qquad (1)$$

$$\chi^{(2)}_{zxx} = \tfrac{1}{2}Nf^{2\omega}(f^{\omega})^2\beta\cos\varphi\sin^2\varphi \qquad (2)$$

where N is the number of molecules per unit volume, f^{ω} and $f^{2\omega}$ are local field correction factors at ω and 2ω respectively, and $f = (n^2 + 2)/3$ where n is the refractive index at the corresponding wavelength. For the octadecyl sulfate salt, the molecular hyperpolarisability is 4.3×10^{-38} m^4 V^{-1} where the number density is calculated from the product of layer thickness and area from the isotherm at the deposition pressure. The pressure–area isotherm of the partially soluble
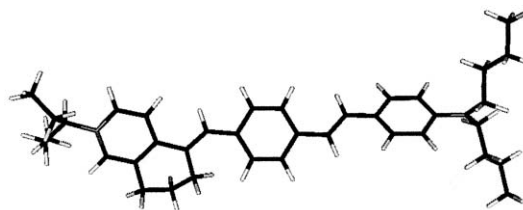
Fig. 5 Cationic dye **1** as modelled and, for clarity, omitting the counterion.

bromide salt provides unreliable data and, in this case, an area of 0.47 nm^2 molecule^{-1} at the deposition pressure was calculated by a Sauerbrey analysis[16] of the frequency change following deposition onto a 10 MHz quartz crystal. This gives a hyperpolarisability of 4.5×10^{-38} m^4 V^{-1}.

The susceptibility of the octadecyl sulfate salt is the highest to date for any transparent film and may be compared with, for example, 16 pm V^{-1} at 1.064 μm for LB films of the extensively studied 2-docosylamino-5-nitropyridine[17–19] which has a peak absorbance at 374 nm and is effectively transparent above 500 nm. In this work an optimum of $\chi^{(2)}_{zzz} = 90$ pm V^{-1} has been realised for films where $\lambda_{\text{max}} = 360$ nm with cut-off above 530 nm.

Long tailed analogues of **1b** with a shorter π-bridge, for example, 5-{4-[2-(4-dibutylamino)benzylidene]}-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecyl sulfate,[10b,13] have shown asymmetric current–voltage characteristics when sandwiched between gold electrodes, the behaviour being assigned to molecular rectification. However, the electrical properties are disadvantaged by the hydrophobic alkyl substituent which acts as a barrier and separates the active donor–(π-bridge)–acceptor component from the electrode. The novel design of dye **1** (Fig. 5) overcomes this problem, the alignment being achieved by utilising a conductive π-bridge rather than an insulating aliphatic tail. Therefore, it is anticipated that its films should rectify with improved behaviour.

Conventional amphiphiles

Dyes **2** and **3** have long aliphatic tails and spontaneously align when their iodide salts are co-spread with sodium octadecyl sulfate at the air–water interface. The dimethylamino analogue (**3**) has been reported previously.[24] Its films exhibit a quadratic increase of the second-harmonic intensity with the number of LB layers when alternated with poly(*tert*-butyl methacrylate). The second-order susceptibility and absorbance are $\chi^{(2)}_{zzz} = 45$ pm V^{-1} at 1.064 μm and $A = 3.5 \times 10^{-4}$ bilayer^{-1} at 532 nm respectively with cut-off above 600 nm. The dibutylamino analogue with a dodecyl tail (**2a**) is an isomer of dye **3** and its LB films exhibit similar behaviour, as do those of the octadecyl derivative (**2b**). In each case, the second-harmonic intensities from monolayer films are comparable to those obtained from films of **1b** and confirm optimum non-centrosymmetric alignment for this unconventional LB film-forming analogue. However, as a consequence of the long aliphatic tails of **2** and **3**, which are SHG-inactive but contribute to the film thickness, the susceptibilities are significantly lower.

Conclusion

Chromophore occupancy and alignment are significant factors when optimising the second-order susceptibility of bulk films whereas, at the molecular level, the hyperpolarizability is dependent upon the π-electron bridge[20,21] and nature of the substituent groups.[22,23] It may be enhanced by increasing the conjugation length and, in this work, we have successfully improved the bulk ($\chi^{(2)}$) and molecular (β) components by extending the π-bridge of the stilbazolium dye and utilising it

as the hydrophobic component for alignment at the air–water interface and subsequently for LB deposition. The susceptibility is the highest obtained to date for any transparent film.

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References

1 C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörsheimer, P. Kaatz and P. Günter, *Organic Nonlinear Optical Materials, Advances in Optics, Vol. 1*, ed. A. F. Garito and F. Kajzar, Gordon and Breach, Basel, Switzerland, 1995.

2 K. D. Singer, S. L. Lalama, J. E. Sohn and R. D. Small, in *Nonlinear Optical Properties of Organic Molecules and Crystals*, ed. D. S. Chemla and J. Zyss, Academic Press, Orlando, 1987.

3 M. C. Petty, *Langmuir-Blodgett Films: an Introduction*, Cambridge University Press, Cambridge, 1996.

4 G. J. Ashwell, *J. Mater. Chem.*, 1999, **9**, 1991.

5 G. J. Ashwell, E. J. C. Dawnay, A. P. Kuczynski and P. J. Martin, *Proc. SPIE – Int. Soc. Opt. Eng.*, 1991, **1361**, 589.

6 M. Era, K. Nakamura, T. Tsutsui, S. Saito, H. Niino, K. Takehara, K. Isomura and H. Tanaguchi, *Jpn. J. Appl. Phys.*, 1992, **210–211**, 163.

7 P. Hodge, Z. Ali-Adib, D. West and T. A. King, *Macromolecules*, 1993, **26**, 1789.

8 S. H. Ma, X. Z. Lu, J. H. Xu, W. C. Wang and Z. M. Zhang, *J. Phys. D*, 1997, **30**, 2651.

9 G. J. Ashwell, P. D. Jackson and W. A. Crossland, *Nature*, 1994, **368**, 438.

10 (*a*) G. J. Ashwell, R. Ranjan, A. J. Whittam and D. Gandolfo, *J. Mater. Chem.*, 2000, **10**, 63; (*b*) G. J. Ashwell and D. Gandolfo, *J. Mater. Chem.*, 2001, **11**, 246.

11 G. J. Ashwell, D. Gandolfo and R. Hamilton, *J. Mater. Chem.*, 2002, **12**, 416.

12 G. J. Ashwell, R. Hamilton, B. J. Wood, I. R. Gentle and D. Zhou, *J. Mater. Chem.*, 2001, **11**, 2966.

13 G. J. Ashwell and D. Gandolfo, *J. Mater. Chem.*, 2002, **12**, 411.

14 E. Kretschmann, *Z. Phys.*, 1971, **241**, 313.

15 K. Kajikawa, K. Kigata, H. Takezoe and A. Fukuda, *Mol. Cryst. Liq. Cryst.*, 1990, **182**, 91.

16 G. Sauerbrey, *Z. Phys.*, 1959, **155**, 206.

17 (*a*) G. Decher, B. Tieke, C. Bosshard and P. Günter, *J. Chem. Soc., Chem. Commun.*, 1988, 933; (*b*) C. Bosshard, G. Decher, B. Tieke and P. Günter, *Proc. SPIE - Int. Soc. Opt. Eng.*, 1988, **1017**, 141.

18 (*a*) M. Küpfer, M. Flörsheimer, C. Bosshard and P. Günter, *Electron. Lett.*, 1993, **29**, 2033; (*b*) M. Küpfer, M. Flörsheimer, C. Bosshard and P. Günter, *Nonlinear Opt.*, 1995, **10**, 341.

19 (*a*) N. Asai, H. Tamada, I. Fujiwara and J. Seto, *J. Appl. Phys.*, 1992, **10**, 4521; (*b*) I. Fujiwara, N. Asai and V. Howarth, *Thin Solid Films*, 1992, **221**, 285.

20 A. Dulcic, C. Flytzanis, C. L. Tang, D. Pépin, M. Fétizon and Y. Hoppilliard, *J. Chem. Phys.*, 1981, **74**, 1559.

21 R. A. Huijts and G. L. J. Hesselink, *Chem. Phys. Lett.*, 1989, **156**, 209.

22 A. Dulcic and C. Sauteret, *J. Chem. Phys.*, 1978, **69**, 3453.

23 S. R. Marder, D. N. Beratan and L.-T. Cheng, *Science*, 1991, **252**, 103.

24 G. J. Ashwell, A. J. Whittam, M. A. Amiri, R. Hamilton, A. Green and U. W. Grummt, *J. Mater. Chem.*, 2001, **11**, 1345.