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An improved efficiency/transparency trade-off for second-harmonic generation by extending the π-electron bridge of an optically nonlinear dye

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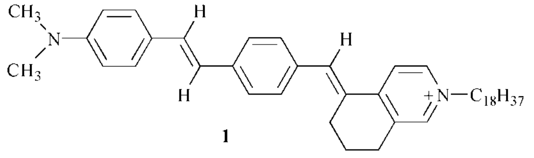
The second-harmonic intensity from Langmuir–Blodgett films of 5-{4-[2-(4-dimethylaminophenyl)vinyl]benzylidene}-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecyl sulfate(**1**), interleaved with poly(*tert*-butyl methacrylate), increases quadratically with thickness to more than 100 bilayers. The susceptibility, molecular hyperpolarisability, thickness, refractive indices and chromophore tilt angle, relative to the substrate normal, are $\chi_{zzz}^{(2)} = 45 \pm 5$ pm V^{-1} at 1064 nm, $\beta = 8 \times 10^{-38}$ m^4 V^{-1}, $l = 3.65 \pm 0.12$ nm bilayer^{-1}, $n^{\omega} = 1.53 \pm 0.01$, $n^{2\omega} = 1.56 \pm 0.01$ and $\varphi = 44 \pm 2°$. The moderately high susceptibility arises from an optimised transparency/efficiency trade-off, the alternate-layer LB film being transparent at 1064 nm and having a very slight absorbance of 3.5×10^{-4} bilayer^{-1} at 532 nm. In contrast, alternate-layer films of the corresponding 7-diethylamino-2-oxo-2*H*-chromen-3-ylmethylene (**2**) and 3-(dimethylaminophenyl)prop-2-enylidene (**3**) derivatives, also reported, have absorbances of 1.1×10^{-3} and 1.5×10^{-3} bilayer^{-1} at 532 nm and resonantly enhanced susceptibilities of 60 and 95 pm V^{-1} respectively.

Introduction

Molecules with a hydrophilic head and a hydrophobic tail spontaneously align at the air–water interface but, when deposited to form a multilayer structure, the amphiphilic layers tend to adopt centric head-to-head and tail-to-tail arrangements at successive interfaces.[1–3] This may be overcome by tailoring the molecular structure to suppress realignment: for example, (i) by utilising terminally charged C_nH_{2n+1}–D–π–A$^-$ dyes and thereby relying on Coulomb repulsion to suppress head-to-head packing;[4,5] (ii) by alkylating both ends of the hydrophilic chromophore, C_nH_{2n+1}–D–π–A–C_mH_{2m+1}, and thereby enforcing a hydrophobic film surface.[6–9] Alternatively, the LB layers may be simply interleaved to give non-centrosymmetric structures for second-harmonic generation (SHG), the spacers being complementary dyes with the alkyl tail attached at the opposite end to effect the required alignment,[10–13] amphiphilic donors which alternate with amphiphilic acceptors[14] or, in fact, any amphiphile[15–22] including polymeric materials[15,16] and those with compatible interlocking geometries.[17,18]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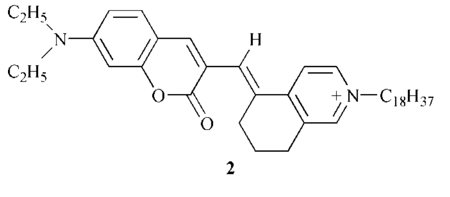
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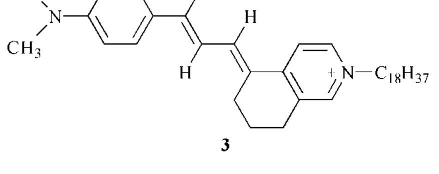
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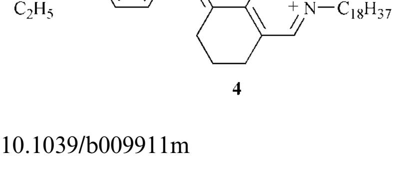
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Among the extensively studied dyes, 4-[2-(4-dimethylaminophenyl)vinyl]-1-docosylpyridinium bromide[23,24] and its derivatives,[17,18,25] including several polymeric analogues,[16,26,27] have attracted much attention for LB alignment. They have an absorbance of *ca.* 2×10^{-3} layer^{-1} at 532 nm and are unfavourable for waveguiding applications but slight modification of the molecular structure can cause a shift of the overlapping charge-transfer band. For example, films of 5-(4-diethylaminobenzylidene)-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium octadecyl sulfate(**4**) have a reduced absorbance of 5×10^{-4} layer^{-1} at the harmonic wavelength and, when interleaved with poly(*tert*-butyl methacrylate), exhibit a high second-order susceptibility of 67 pm V^{-1} at 1064 nm.[8] This may be compared with an optimum value of 50–70 pm V^{-1} for the hemicyanine derivatives above.[17,18]

In this study, we report the linear and nonlinear optical properties of three analogues of dye **4**, each with an extended π-electron bridge. Of these, **1** has the weakest absorbance of 3.5×10^{-4} layer^{-1} at 532 nm and the LB absorption maximum

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is shifted to *ca.* 350 nm. Its alternate-layer films with poly(*tert*-butyl methacrylate) exhibit the theoretically predicted quadratic dependence of the second-harmonic intensity with the number of active layers, *i.e.* $I_{(N)}^{2\omega} = I_{(1)}^{2\omega}N^2$ and a moderately high susceptibility of 45 ± 5 pm V^{-1}. The compatible spacer readily deposits on the downstroke, the preferred direction when interleaving with optically nonlinear dyes,[3] and is transparent throughout the visible and near infrared regions. It has a thickness of 1.00 ± 0.03 nm layer^{-1} compared with 3.65 ± 0.12 nm bilayer^{-1} for the alternate-layer structure and, therefore, reduces the apparent second-order susceptibility of the dye in the interleaved film by only *ca.* 30%.

Experimental

Synthesis

4-[2-(4-Dimethylaminophenyl)vinyl]benzonitrile. To a solution of 4-(dimethylamino)benzaldehyde (3 g, 20 mmol) in methanol (100 cm^3) was added (4-formylbenzyl)triphenylphosphonium bromide (8.3 g, 20 mmol) and potassium *tert*-butoxide (2.45 g, 20 mmol). The mixture was heated under reflux for 24 h and then cooled. The resultant yellow precipitate was purified by column chromatography on silica gel (eluent: CHCl$_3$) to afford 4-[2-(4-dimethylaminophenyl)vinyl]benzonitrile: yield 4.9 g, 100%; mp 197–198 °C (dec). δ_H (CDCl$_3$, 200 MHz, *J*/Hz): 3.03 (s, 6H, N(CH$_3$)$_2$), 6.35 (d, *J* 10, 2H, Ar–H), 6.64 (d, *J* 10, 2H, Ar–H), 6.74 (d, *J* 7, 2H, Ar–H), 6.89 (d, *J* 13, 1H, C=C–H), 7.12 (d, *J* 7, 2H, Ar–H), 7.15 (d, *J* 13, 1H, C=C–H). *m*/*z* (FAB): 249 (M$^+$, 100%).

4-[2-(4-Dimethylaminophenyl)vinyl]benzaldehyde. To a cooled solution of 4-[2-(4-dimethylaminophenyl)vinyl]benzonitrile (0.5 g, 2 mmol) in chloroform (100 cm^3) was added diisobutylaluminium hydride (1.5 M in toluene: 4 cm^3, 6 mmol). The resultant solution was maintained at −78 °C for 1 h and then, after attaining room temperature, was poured into acidified water (150 cm^3). The organic layer was extracted and the aqueous phase repeatedly washed with chloroform (3 x 50 cm^3). The combined organic layers were then washed with water (50 cm^3), extracted and dried (MgSO$_4$), and the solvent removed *in vacuo* yielding 4-[2-(4-dimethylaminophenyl)vinyl]benzaldehyde as a yellow solid: 0.35 g, 70%. δ_H (CDCl$_3$, 200 MHz, *J*/Hz): 3.03 (s, 6H, NCH$_3$), 6.75 (d, *J* 7, 2H, Ar–H), 6.95 (d, *J* 13, 1H, C=C–H), 7.22 (d, *J* 13, 1H, C=C–H), 7.46 (d, *J* 7, 2H, Ar–H), 7.61 (d, *J* 7, 2H, Ar–H), 7.84 (d, *J* 7, 2H, Ar–H), 9.96 (s, 1H, CHO). *m*/*z* (FAB): 251 (M$^+$, 100%).

5-{4-[2-(4-Dimethylaminophenyl)vinyl]benzylidene}-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide. To a solution of 2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide (1.0 g, 2.0 mmol) and 4-[2-(4-dimethylaminophenyl)vinyl]benzaldehyde (0.5 g, 2 mmol) in methanol (100 cm^3) was added piperidine (0.1 cm^3) and the resultant mixture heated under reflux for 72 h. Upon cooling, the iodide salt of **1** was obtained as dark microcrystals. The product was recrystallised from methanol: 0.42 g, 28%; mp 190 °C (dec.). λ_{max} (CHCl$_3$): 343, 455 nm. δ_H (200 MHz, CDCl$_3$, *J*/Hz): 0.88 (t, *J* 5, 3H, CH$_3$), 1.25 (br s, 32H, CH$_2$), 1.90–2.01 (m, 2H, CH$_2$), 2.43–2.51 (m, 4H, C=C–CH$_2$), 3.04 (s, 6H, N(CH$_3$)$_2$), 4.72 (t, *J* 5, 2H, CH$_2$N$^+$), 6.72 (d, *J* 7, 2H, Ar–H), 6.90 (d, *J* 13, 1H, C=C–H), 7.13 (d, *J* 13, 1H, C=C–H), 7.45–7.57 (m, 7H, Ar–H and C=C–H), 8.16 (d, *J* 5, 1H, Qn–H), 8.73 (d, *J* 5, 1H, Qn–H), 8.98 (s, 1H, Qn–H). *m*/*z* (FAB): 604 (M$^+$−2CH$_3$−I$^-$, 6%), 619 (M$^+$−CH$_3$−I$^-$, 100%), 634 (M$^+$−I$^-$, 6%).

5-(7-Diethylamino-2-oxo-2*H*-chromen-3-ylmethylidene)-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide. To a solution of 2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide (1.61 g, 3.2 mmol) and 7-diethylamino-2-oxo-2*H*-chromene-3-carbaldehyde (0.77g, 3.2 mmol) in methanol (70 cm^3) was added piperidine (0.1 cm^3) and the resultant mixture heated under reflux for 48 h. Upon cooling, the iodide salt of **2** was filtered and recrystallised from methanol: 1.42 g, 60%; mp 170–171 °C. λ_{max} (CHCl$_3$): 374, 493 nm. δ_H (200 MHz, CDCl$_3$, *J*/Hz): 0.88 (t, *J* 5, 3H, CH$_3$), 1.24 (br s, 32H, CH$_2$), 1.73 (br s, 6H, N(CH$_2$**CH$_3$**)$_2$), 1.98–1.90 (m, 2H, CH$_2$), 3.08 (t, *J* 5, 2H, C=C–CH$_2$), 3.11 (t, *J* 5, 2H, C=C–CH$_2$), 3.42–3.48 (m, 4H, N(**CH$_2$**CH$_3$)$_2$), 4.71 (t, *J* 5, 2H, CH$_2$N$^+$), 6.49 (s, 1H, Ar–H), 6.64 (d, *J* 7, 1H, Ar–H), 7.39 (d, *J* 7, 1H, Ar–H), 7.57 (s, 1H, Ar–H), 7.83 (s, 1H, Ar–H), 8.06 (d, *J* 5, 1H, Qn–H), 8.43 (d, *J* 5, 1H, Qn–H), 9.36 (s, 1H, Qn–H). *m*/*z* (FAB): 613 (M$^+$−I$^-$, 100%).

5-[3-(4-Dimethylaminophenyl)prop-2-enylidene]-2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide. To a solution of 2-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide (1.0 g, 2.0 mmol) and 4-dimethylaminocinnamaldehyde (0.35 g, 2 mmol) in methanol (60 cm^3) was added piperidine (0.1 cm^3) and the resultant mixture heated under reflux for 12 h. Upon cooling, the iodide salt of **3** was filtered and recrystallised from methanol: 0.8 g, 60%; mp 63–64 °C. λ_{max} (CHCl$_3$): 385, 495 nm. δ_H (200 MHz, CDCl$_3$, *J*/Hz): 0.87 (t, *J* 5, 3H, CH$_3$), 1.23 (br s, 32H, CH$_2$), 1.93 (br s, 2H, CH$_2$), 2.76 (t, *J* 5, 2H, C=C–CH$_2$), 2.97 (t, *J* 5, 2H, C=C–CH$_2$), 3.04 (s, 6H, N(CH$_3$)$_2$), 4.60 (t, *J* 6, 2H, CH$_2$N$^+$), 6.67 (d, *J* 7, 2H, Ar–H), 6.97 (d, *J* 6, 2H, Ar–H), 7.34–7.47 (m, 3H, C=C–H), 8.08 (d, *J* 6, 1H, Qn–H), 8.65 (d, *J* 7, 1H, Qn–H), 8.85 (s, 1H, Qn–H). *m*/*z* (FAB): 543 (M$^+$−I$^-$, 100%).

LB deposition

Dilute solutions of sodium octadecyl sulfate in methanol and the iodide salts of the dyes in chloroform were co-spread, in a 1 : 1 mole ratio, onto the pure water subphase of an LB trough (Nima Technology, model 622), left for 10 min and compressed at 0.5 cm^2 s^{-1} (*ca.* 0.1% s^{-1} of compartment area). The water-soluble ions, Na$^+$ and I$^-$, dissolve into the subphase and, therefore, leave the amphiphilic cation and amphiphilic anion as the floating monolayer. The dyes were deposited on the upstroke at 35 mN m^{-1}.

The inactive spacer, poly(*tert*-butyl methacrylate), used in the fabrication of the alternate-layer structures, was spread from dilute chloroform solution onto the water subphase of the second compartment of the trough. Interleaved films were obtained by cycling hydrophilically treated glass substrates (for SHG and reflectance studies) and gold coated quartz crystal (for QCM studies) from below the surface, to deposit the optically nonlinear dye on the first upstroke at 35 mN m^{-1} and poly(*tert*-butyl methacrylate) on the subsequent downstroke at

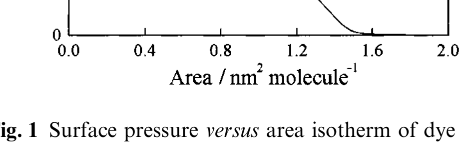

Fig. 1 Surface pressure *versus* area isotherm of dye **1**.

12 mN m^{-1}. Multilayer films were fabricated by repeating the process with a deposition rate of 80 μm s^{-1} in both directions.

Results and discussion

Dye 1

The pressure-area (π–A) isotherm shows a limiting area of *ca.* 1.6 nm^2 molecule^{-1} at $\pi = 0$ decreasing to 0.45 nm^2 molecule^{-1} just prior to collapse, the latter corresponding to the combined cross-sectional areas of the octadecyl groups of the amphiphilic cation and amphiphilic anion (Fig. 1). When transferred to a 10 MHz AT-cut quartz plate, at the deposition pressure of 35 mN m^{-1}, the frequency change (ΔF) gives an area of 0.54 ± 0.02 nm^2 molecule^{-1} in contact with the central gold electrodes. This coincides with the corresponding value at the air–water interface and is obtained from the Sauerbrey equation:[28]

$$A = -4F_0^2 M/\Delta F(\rho\mu)^{1/2}L \qquad (1)$$

F_o is the resonance frequency (10 MHz) of the quartz crystal, ρ the density of quartz (2.648 Mg m^{-3}), μ the shear modulus (2.947×10^7 Mg m^{-1} s^{-2}), and M and L are the molecular mass (969.55) and Avogadro constant (6.022×10^{23} mol^{-1}) respectively. The product of area and thickness provides a volume of 1.43 ± 0.12 nm^3 molecule^{-1} and, thus, a density of 1.1 ± 0.1 Mg m^{-3}.

The layer thickness, referred to above, was determined by analysis of the reflectance data from an alternate-layer film on glass and corrected for the thickness of the poly(*tert*-butyl methacrylate) spacer, its film characteristics being determined separately by an identical method. The reflectance was determined as the angle of incidence of the laser beam, relative to the LB film, was rotated from 10 to 83° for both p and s polarised light (Fig. 2), the film being investigated at six different wavelengths: the fundamental (1064 nm) and second-harmonic (532 nm) of a Nd:YAG and at four wavelengths (632.8, 611.9, 604.0 and 594.1 nm) of a multilane HeNe laser. The thickness and optical constants of the 105 bilayer film of **1** were derived using a three-layer (air–LB–glass) model. Reflections from the multiple interfaces were applied to the absorbing surfaces and analysed, by fitting to theoretical equations,[29] using a Simplex curve fitting routine to minimise the sum of the least squares fit. The data are summarised in Table 1, the mean thickness being 3.65 ± 0.12 nm bilayer^{-1} with the refractive index increasing from 1.53 at 1064 nm to 1.56 at 532 nm, the slight change being consistent with the fact that the peak absorbance is at *ca.* 350 nm with very little absorption at the second-harmonic wavelength. The difference ($n^{2\omega} - n^{\omega} = 0.03$) is significantly smaller than reported[30] for LiNbO$_3$ and, from the following equation, the data yield a coherence length for SHG at 1064 nm of *ca.* 8 μm at normal incidence:

$$L_{\mathrm{LB}} = \lambda/4(n^{2\omega}\cos\theta^{2\omega} - n^{\omega}\cos\theta^{\omega}) \qquad (2)$$

Table 1 Thickness and relative permittivity data obtained from 105 bilayer film of dye **1**

Wavelength/nm	Thickness/nm bilayer^{-1}	ε_r	ε_i	n
532.0	3.57	2.43	0.03	1.56
594.1	3.68	2.36	0.00	1.54
604.0	3.74	2.37	0.00	1.54
611.9	3.68	2.37	0.00	1.54
632.8	3.69	2.37	0.00	1.54
1064	3.53	2.33	0.00	1.53

[a] Mean thickness: $l = 3.65 \pm 0.12$ nm bilayer^{-1}. Standard deviations: ε_r, ± 0.04; n, ± 0.01.

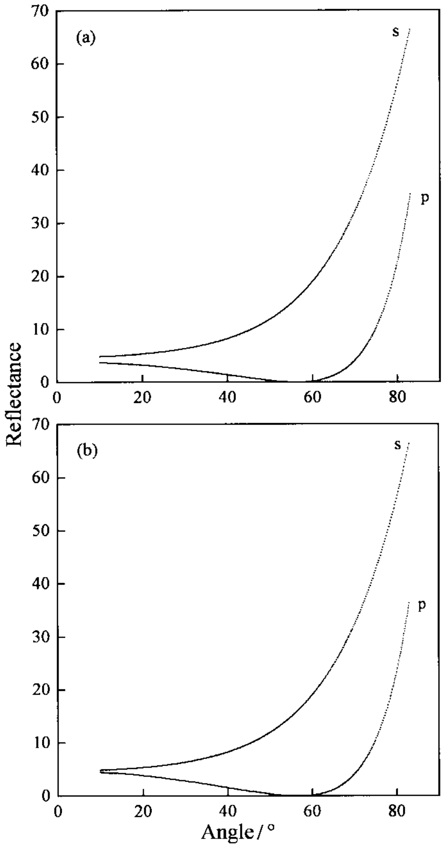

Fig. 2 Reflectance from a 105 bilayer film of dye **1** and poly(*tert*-butyl methacrylate) on a glass substrate: (a) $\lambda = 1064$ nm and (b) $\lambda = 532$ nm, p and s polarised in each case.

The second-harmonic intensity, as for the majority films, is negligible at normal incidence and, therefore, was investigated with the p-polarised laser beam (Nd : YAG, $\lambda = 1.064$ μm) at an angle of 45° relative to the LB film. The intensity increases quadratically with the film thickness, in this case to 105 bilayers (Fig. 3), indicating long-range structural order when poly(*tert*-butyl methacrylate) is alternated with the dye layers. The films exhibit moderately strong SHG with a normalised intensity, $I^{2\omega}/N^2$ where N is the number of bilayers, of 1.1×10^{-4} *versus* the optimum intensity from the Maker fringe envelope of a Y-cut quartz reference ($d_{11} = 0.5$ pm V^{-1}). The polarisation of the fundamental beam was rotated using a half-wave plate and, using the method of Kajikawa *et al.*,[31] the polarisation

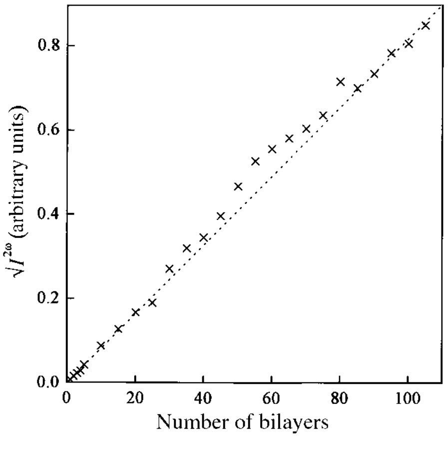

Fig. 3 Variation of the square root of the second-harmonic intensity with the number of bilayers of dye **1** interleaved by poly(*tert*-butyl methacrylate).

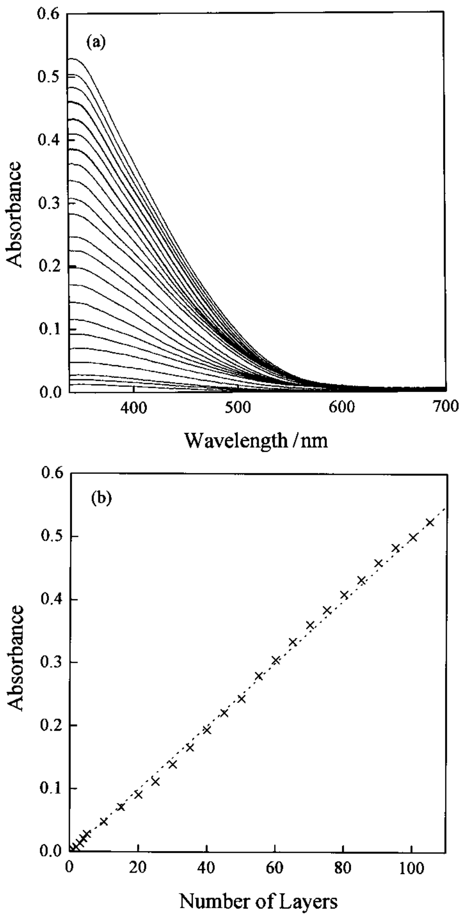

Fig. 4 Interleaved film of dye **1** and poly(*tert*-butyl methacrylate): (a) spectrum showing the gradual increase in film absorbance following the deposition of 1 to 105 bilayers and (b) the linear dependence of the absorbance at 350 nm with thickness. The peak absorbance ($\lambda_{max} = 350$ nm) is close to the lower limit of the transparency window of the glass substrate and any asymmetry, as found for dyes **2** and **3**, cannot be observed.

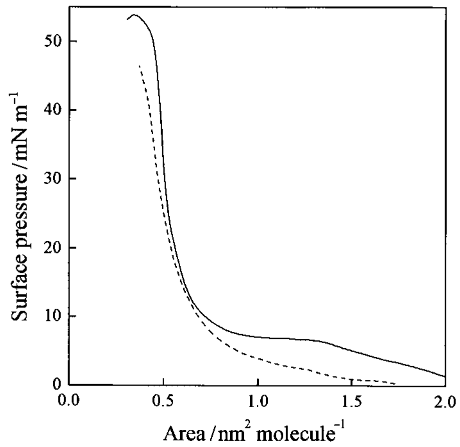

Fig. 5 Surface pressure *versus* area isotherms of dyes **2** (solid line) and **3** (broken line).

Table 2 Thickness and relative permittivity data at $\lambda = 632.8$ nm for alternate-layer films of the dyes and poly(*tert*-butyl methacrylate) (ptbm) and homomolecular films of the spacer

Film structure	Thickness/ nm repeat^{-1}	ε_r	ε_i
Alternate-layer			
1+ptbm	3.65±0.12	2.37±0.04	0.00
2+ptbm	3.90±0.12	2.31±0.04	0.00
3+ptbm	3.60±0.12	2.23±0.04	0.00
Homomolecular			
ptbm	1.00±0.03	2.18±0.04[a]	0.00

[a] Published values of ε_r: 2.13±0.03 (spun-coated films); 2.17±0.07 (LB films).[32]

dependence, $I^{2\omega}(p\rightarrow p)/I^{2\omega}(s\rightarrow p)$, indicates that the chromophore is tilted by 44±2° from the normal to the substrate.

The films are almost transparent at the harmonic wavelength. Thus, it may be assumed that Kleinman's symmetry is valid and that the susceptibility components are limited to $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$ which, from the data above, may be estimated as 45 ± 5 pm V^{-1} and 21 ± 2 pm V^{-1} respectively. Furthermore, as the hyperpolarisability is probably dominated by the component along the molecular charge-transfer axis, the relation between β and $\chi^{(2)}$ is as follows:

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

$$\chi^{(2)}_{zxx} = 1/2Nf^{2\omega}(f^{\omega})^2\beta\cos\phi\sin^2\phi \qquad (4)$$

N is the number of molecules per unit volume, $f^{2\omega}$ and f^{ω} are local field correction factors at 2ω and ω respectively where $f = (n^2+2)/3$ and n is the refractive index at the corresponding wavelength, and ϕ is the chromophore tilt angle. The molecular hyperpolarisability is *ca.* 8×10^{-38} m^4 V^{-1}.

Interestingly, the second-harmonic intensity is similar to (or higher than) resonantly enhanced values reported for alternate-layer films of the many different hemicyanine derivatives.[13,16–18] For example, Han *et al.*[18] have reported a susceptibility of 50 pm V^{-1} for electrically poled LB films of (*E*)-*N*-octadecyl-4-{2-[4-(*N*,*N*-diethylamino)phenyl]ethenyl}pyridinium bromide interleaved with docosanoic acid (*cf.* 16 pm V^{-1} when not poled). This may be increased to 70 pm V^{-1} by substituting the inorganic anion with octadecyl sulfate and interleaving with poly(*tert*-butyl methacrylate).[13] However, the films have an absorbance of 3×10^{-3} bilayer^{-1} at the harmonic wavelength whereas, in this work, the corresponding value is an order of magnitude weaker (Fig. 4). The absorbance peaks at *ca.* 350 nm (*cf.* 343 and 455 nm in $CHCl_3$) and then decreases to 3.5×10^{-4} bilayer^{-1} at 532 nm with the films being transparent at 1064 nm. Thus, together with alternate-layer films of dye **4**,[8] which has a susceptibility of 67 pm V^{-1} and an absorbance of only 5×10^{-4} bilayer^{-1}, the susceptibility is among the highest obtained to date for an effectively transparent alternate-layer

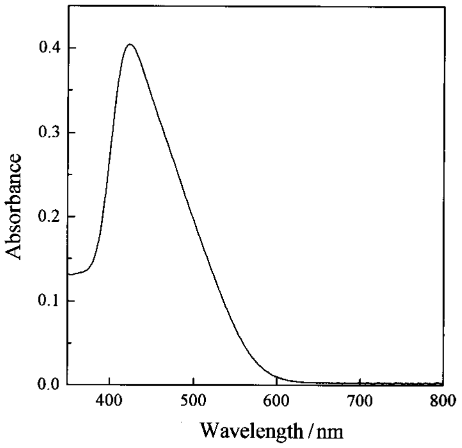

Fig. 6 Visible spectrum of the interleaved film of dye **2** and poly(*tert*-butyl methacrylate) comprising 95 bilayers. Analysis has indicated that the combined absorbance of separate symmetrical bands at 360, 420 and 470 nm can give rise to the unusual asymmetric spectrum and such values may be compared with $\lambda_{max} = 364$, 450 (sh) and 495 nm when the dye is dissolved in chloroform.

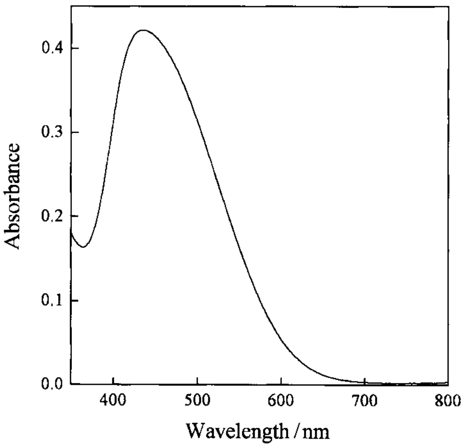

Fig. 7 Visible spectrum of the interleaved film of dye **3** and poly(*tert*-butyl methacrylate) comprising 105 bilayers.

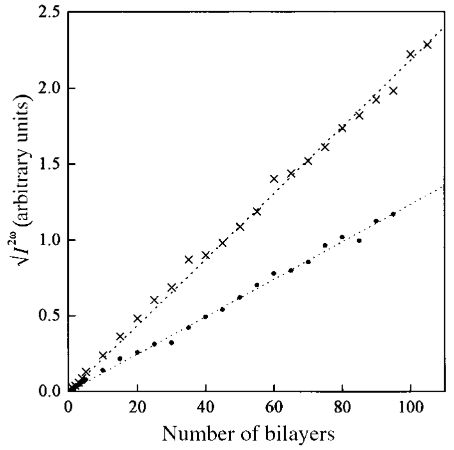

Fig. 8 Variation of the square root of the second-harmonic intensity with the number of bilayers of the dyes interleaved by poly(*tert*-butyl methacrylate): dye **2** (●); dye **3** (×).

film. The enhancement is attributed to the proximity of the charge-transfer band, which is barely overlapping but optimises the trade-off in efficiency and absorbance.

Related dyes

The π–A isotherm of dye **2** (Fig. 5) is similar to that of dye **1** but the steep high-pressure regime extends from *ca.* 8 to 52 mN m^{-1} with a limiting area of *ca.* 0.50 nm^2 molecule^{-1} just prior to collapse. In contrast, that of dye **3** is generally featureless and has a similar limiting area of 0.43 nm^2 molecule^{-1} (*cf.* 0.45 nm^2 for **1**), this common value corresponding to the combined cross-sectional areas of the octadecyl groups of the amphiphilic cation and amphiphilic anion. The areas in contact with the substrate, obtained by the quartz crystal microbalance (QCM) technique at the deposition pressure of 35 mN m^{-1}, are 0.50 nm^2 molecule^{-1}. Thus, when related to the thickness data of Table 2, the density of the dye layer is *ca.* 1.1 Mg m^{-3} and consistent with the value obtained for **1**.

Table 3 Alternate-layer films: spectroscopic data, susceptibilities and chromophore tilt angles

Dye	λ_{max}/nm	$A_{2\omega}$/bilayer^{-1}	$\chi_{zzz}^{(2)}$/pm V^{-1}	φ/°
1	350	3.5×10^{-4}	45 ± 5	44 ± 2
2	422	1.1×10^{-3}	60 ± 5	37 ± 2
3	465	1.5×10^{-3}	95 ± 5	32 ± 2

Their films are less transparent in the visible region (Figs. 6 and 7), having absorbances of 1.1×10^{-3} (**2**) and 1.5×10^{-3} bilayer^{-1} (**3**) at the second-harmonic wavelength and showing maxima at 422 and 465 nm respectively (*cf.* $\lambda_{max}=350$ nm for **1**). The transitions are strangely asymmetric and this is particularly pronounced for dye **2**. Its absorption band may be resolved as separate peaks at 470 and 420 nm and albeit shifted, as is usual for LB film spectra, the maxima relate to those of the solution ($\lambda_{max}=493$, sh 450, 374 nm in $CHCl_3$). When interleaved with poly(*tert*-butyl methacrylate), the two dyes exhibit quadratic SHG enhancement with the number of layers (Fig. 8), the second-order susceptibility, thickness and chromophore tilt angle, relative to the substrate normal, being *ca.* 60 pm V^{-1}, 3.9 nm bilayer^{-1} and 37° respectively for the 7-diethylamino-2-oxo-2*H*-chromen-3-ylmethylene analogue (**2**) and *ca.* 95 pm V^{-1}, 3.6 nm bilayer^{-1} and 32° for the 3-(diethylaminophenyl)prop-2-enylidene derivative (**3**). The higher susceptibilities, relative to 45 pm V^{-1} for dye **1** (Table 3), arise from increased resonance enhancement but are far less interesting because the dyes are more absorbing at 532 nm. Nonetheless, judicious choice of the counterion, amphiphilic rather than spherical, and the polymeric spacer has resulted in improved deposition characteristics and quadratic enhancement of the second-harmonic intensity with thickness to more than 100 bilayers. This is noteworthy, because relatively few alternate-layer films.[13–22] have exhibited long-range order to such thicknesses.

Conclusion

Alternate-layer films of the three optically nonlinear dyes exhibit second-order susceptibilities of 45 to 100 pm V^{-1} at $\lambda=1064$ nm, the most interesting of these having the weakest susceptibility but a very slight absorbance of 3.5×10^{-4} bilayer^{-1} at the harmonic wavelength. The interleaving layers readily deposit with the dye on the upstroke and the poly(*tert*-butyl methacrylate) on the subsequent downstroke, this arrangement resulting in long-range order as indicated by the quadratic SHG dependence. This study is now being extended at Cranfield to include similar dyes but where further extension of the π-electron bridge results in this being the hydrophobic substituent for alignment at the air–water interface. Such molecules then do not require the aliphatic tail and, consequently, the second-order susceptibility may be further improved.

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