

Second-harmonic generation from alternate-layer and Z-type Langmuir–Blodgett films: optimisation of the transparency/efficiency trade-off†

Geoffrey J. Ashwell,* Rakesh Ranjan, Anne J. Whittam and Daniel S. Gandolfo

The Nanomaterials Group, Centre for Photonics and Optical Engineering, Cranfield University, Cranfield, UK MK43 0AL. E-mail: g.j.ashwell@cranfield.ac.uk

Received 14th April 1999, Accepted 24th May 1999

Langmuir–Blodgett (LB) films of (*E*)-4-[(*N*-octadecyl-5,6,7,8-tetrahydro-5-isoquinolylidene)methyl]-*N,N*-dialkylaniline octadecyl sulfate, where the donor group is dimethylamino (**1a**), diethylamino (**1b**), dibutylamino (**1c**) and dihexylamino (**1d**), have optimum susceptibilities when the dyes are co-deposited in a 1:1 mole ratio with octadecanoic acid. Alternate-layer structures of the mixed films, interleaved with poly(*tert*-butyl methacrylate), are non-centrosymmetric and the second-harmonic intensity increases with thickness as $I_{(N)}^{2\omega} \approx I_{(1)}^{2\omega} N^2$ to $N > 100$ bilayers. Furthermore, when the dialkylamino group is sufficiently hydrophobic, *i.e.* for **1c** and **1d**, the dyes form non-centrosymmetric Z-type structures without interleaving spacer layers. The optimum susceptibilities, chromophore tilt angles, thicknesses and refractive indices of the interleaved and non-interleaved mixed films are as follows: alternate-layer (**1b**), $\chi_{zzz}^{(2)} = 67 \text{ pm V}^{-1}$ at $1.064 \mu\text{m}$ for $\varphi = 37^\circ$, $l = 4.08 \text{ nm bilayer}^{-1}$, $n^\omega = 1.50$ and $n^{2\omega} = 1.58$; Z-type (**1c**), $\chi_{zzz}^{(2)} = 76 \text{ pm V}^{-1}$ for $\varphi = 33^\circ$, $l = 3.15 \text{ nm layer}^{-1}$, $n^\omega = 1.52$ and $n^{2\omega} = 1.58$. The moderately high susceptibilities arise from an optimised transparency/efficiency trade-off, the films in this series being transparent at the fundamental wavelength ($1.064 \mu\text{m}$) and having a very slight absorbance of 5×10^{-4} per active layer at 532 nm .

Donor-(π -bridge)-acceptor materials have larger second-order nonlinear optical coefficients and provide an attractive alternative to their inorganic counterparts.¹ Also, when substituted with a hydrophobic alkyl tail, the Langmuir–Blodgett (LB) technique may be used to fabricate non-centrosymmetric structures for second-harmonic generation (SHG). The molecules align at the air/water interface but, in the deposited film, tend to adopt a centrosymmetric arrangement with successive interfaces being hydrophilic (head-to-head) and hydrophobic (tail-to-tail).² This may be overcome by alkylating both ends of the chromophore ($\text{C}_n\text{H}_{2n+1}\text{-D-}\pi\text{-A-C}_m\text{H}_{2m+1}$), thereby rendering the upper and lower surfaces hydrophobic,^{3–5} or by alternating the LB layers with complementary spacer materials, the interleaving molecules being hydrophobically substituted in the opposite sense.^{6–9}

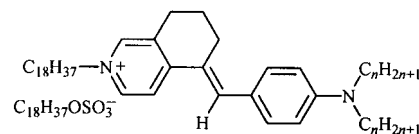


When both component layers are SHG-active and the interfacial interactions are sterically unhindered,² the second-order properties are disadvantaged by the fact that the intralayer and interlayer dipoles are opposed. Passive spacers may be preferable^{10–14} but they have the drawback of diluting the optically nonlinear component in alternate-layer films. Thus, the interleaving layer should be carefully chosen and, for this purpose, poly(*tert*-butyl methacrylate) is an ideal candidate.¹⁵ It readily deposits on the downstroke and is, therefore, compatible with the preferred transfer of the active dye layer on the upstroke. Furthermore, it is transparent throughout the visible and near infrared regions of the spectrum and has a thickness of only 1.03 nm per layer. Penner *et al.*^{16,17} have reported low-loss waveguide structures, with an optical attenuation of 1 to 2 dB cm^{-1} , for alternate-layer structures of polymeric dyes and poly(*tert*-butyl methacrylate), and have demonstrated efficient

phase-matched blue light generation with a normalised conversion efficiency of $150\% \text{ W}^{-1} \text{ cm}^{-2}$ for 819 nm radiation.

In this work, we report alternate-layer structures of a cationic hemicyanine dye interleaved with poly(*tert*-butyl methacrylate) and demonstrate a quadratic SHG dependence, $I_{(N)}^{2\omega} = I_{(1)}^{2\omega} N^2$, to more than 100 bilayers. There have been several previous studies on interleaved films of hemicyanine derivatives, both monomeric^{11,12} and polymeric,¹³ but most have failed to show the theoretically expected SHG enhancement to thicknesses of more than a few bilayers.^{18,19} This suggests a structurally disordered arrangement and recently, Han *et al.*²⁰ have reported a susceptibility enhancement from 16 pm V^{-1} , when freshly deposited, to 50 pm V^{-1} when poled by a field of 1.3 MV m^{-1} . The hemicyanine derivatives are also highly coloured and thus, combined with the difficulty of controlling the long-range structural order, they are not suitable for nonlinear optical applications.

This paper concerns a subtle modification to the molecular structure of the cationic dye compared with the previously reported hemicyanine,^{11–13,18–20} the suitability of its counterion, and co-deposition with octadecanoic acid to optimise local field effects and absorption in the vicinity of the second-harmonic wavelength. LB films of the modified dyes (**1a–d**) show improved SHG when the anion is amphiphilic, *i.e.* octadecyl sulfate rather than iodide, and the intensity is enhanced when the dye is diluted in a 1:1 ratio with octadecanoic acid. The second-harmonic intensity from alternate-layer films of the dye and poly(*tert*-butyl



1a $n = 1$
1b $n = 2$
1c $n = 4$
1d $n = 6$

†Basis of a presentation given at Materials Chemistry Discussion No. 2, 13–15 September 1999, University of Nottingham, UK.

methacrylate) increases quadratically with the number of active layers and, furthermore, a similar dependence has been realised to in excess of 200 Z-type layers for analogues with hydrophobically substituted donor groups.

Experimental

Synthesis

To a solution of *N*-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide (0.51 g, 1 mmol) and 4-(*N,N*-dimethylamino)benzaldehyde (0.15 g, 1 mmol) in methanol (20 cm³) was added piperidine (2 drops) and the resultant mixture heated at reflux for 12 h. Upon cooling, a red microcrystalline product of the iodide salt of **1a** was collected and recrystallised from methanol. Several batches were synthesised: typical yield *ca.* 70%. δ_{H} (200 MHz; CDCl₃, *J*/Hz): 0.90 (t, *J* 6, 3H, CH₃), 1.21 (br s, 32 H, CH₂), 1.95–2.03 (m, 2H, CH₂), 2.93–3.12 (m, 4H, C=C-CH₂), 3.13 (s, 6H, NCH₃), 4.68 (t, *J* 6, 2H, CH₂N⁺), 6.74 (d, *J* 4, 2H, Ar-H), 7.43 (s, 1H, C=C-H), 7.47 (d, *J* 4, 2H, Ar-H), 8.08 (d, *J* 4, 1H, Ar-H), 8.67 (d, *J* 4, 1H, Ar-H), 8.87 (s, 1H, Ar-H). UV–VIS (CHCl₃): λ_{max} , 487 nm. Found, C, 66.8; H, 8.8; N, 4.2%. C₃₆H₅₇N₂I requires: C, 67.05; H, 8.91; N, 4.34%.

The diethylamino to dihexylamino analogues, **1b** to **1d**, were obtained in a similar manner by the reaction of *N*-octadecyl-5,6,7,8-tetrahydroisoquinolinium iodide and the appropriate 4-(*N,N*-dialkylamino)benzaldehyde, the NMR and elemental data being satisfactory in each case. Salts with amphiphilic anions were obtained by metathesis of the cationic dye and sodium octadecyl sulfate at the air/water interface of the LB trough (see below). The water soluble ions, Na⁺ and I⁻, dissolve into the aqueous subphase and are not incorporated into the film.

LB Deposition

Dilute solutions of the dye in chloroform and sodium octadecylsulfate in methanol were spread in a 1:1 mole ratio onto the pure water subphase of one compartment of an alternate-layer LB trough (Nima Technology, model 622), left for 5 min and then compressed at 0.5 cm² s⁻¹ (*ca.* 0.1% s⁻¹ of compartment area). The surface pressure versus area (π -*A*) isotherms of the four dyes show a limiting area of *ca.* 150 to 170 Å² molecule⁻¹ at $\pi=0$, a broad plateau region and a steeply rising section with an area of *ca.* 40 Å² molecule⁻¹ just prior to collapse (*e.g.* see Fig. 1 for **1b**). The data suggest that the chromophores initially reside face down on the aqueous subphase but are tilted upwards during compression, with the limiting area in the high-pressure regime corresponding to the sum of the van der Waals cross-sectional areas of the two octadecyl chains.

Mixed films of the dye and octadecanoic acid were obtained in a similar manner, for example, by co-spreading the three components (dye:Na⁺ODS⁻:ODA) in a ratio of 1:1:*n* where 1 ≤ *n* ≤ 5. The general shape of the isotherm remains the

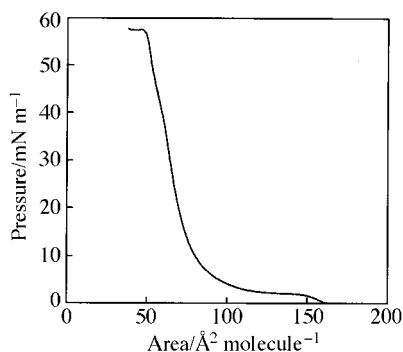


Fig. 1 Surface pressure versus area isotherm of **1b**.

same, when the dye is mixed with octadecanoic acid, but the combined area is progressively shifted by *ca.* 19 Å² per ODA molecule for mole ratios of 1:1 to 1:5. Monolayer films were deposited onto hydrophilically treated glass substrates, on the upstroke, at a rate of 80 μm s⁻¹ and at optimum surface pressures of 40 mN m⁻¹ for **1a** and 32 mN m⁻¹ for **1b–d**.

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 then obtained by cycling a hydrophilically treated glass substrate (for SHG) or a silicon wafer (for reflectance studies), from below the surface, to deposit the mixed film (dye:Na⁺ODS⁻:ODA = 1:1:1) on the first upstroke, as above, and poly(*tert*-butyl methacrylate) on the subsequent downstroke at 10–12 mN m⁻¹. Multilayer films were fabricated by repeating the process with a deposition rate of 80 μm s⁻¹ in both directions. In contrast, multilayer Z-type structures of **1c** and **1d** were obtained on the upstroke by cycling the substrate *via* the air/water interface of the second compartment, in this case, with no floating layer.

SHG Measurements

The second-harmonic intensity was measured in transmission as the angle of incidence (θ) of the laser beam (Nd:YAG, $\lambda=1.064$ μm, p-polarised), relative to the LB film, was altered from 0 to 75° and the polarisation of the fundamental beam was rotated using a half-wave plate. The SHG is negligible at normal incidence (*e.g.* see Fig. 2) and, therefore, its variation with the number of deposited layers was investigated at a fixed angle of 45°. The intensity was calibrated against the Maker fringe envelope of a Y-cut quartz reference ($d_{11}=0.5$ pm V⁻¹) and the data analysed as described previously.^{4b}

Results and discussion

Monolayer films

The linear and nonlinear optical properties of **1a** to **1d** are listed in Table 1. They exhibit significantly different susceptibilities but, from the SHG polarisation dependence, the chromophore tilt angles are quite similar. The second-harmonic wavelength barely overlaps the trailing edge of the absorption band and the

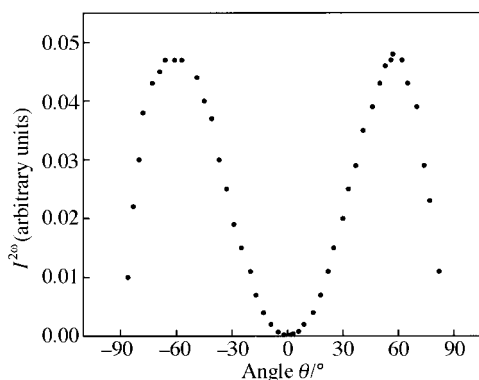


Fig. 2 Typical dependence of the second-harmonic intensity on the angle of incidence of the laser beam, relative to the LB film, for the dyes in this series. The data correspond to a Z-type film of **1d**.

Table 1 Properties of monolayer films of the pure dyes

Dye	λ_{max} /nm	A_{max} /layer ⁻¹	$\chi_{zzz}^{(2)}$ /pm V ⁻¹	$\phi/^\circ$
1a	417	3×10^{-3}	70	32
1b	425	5×10^{-3}	120	30
1c	425	5×10^{-3}	100	31
1d	415	4×10^{-3}	50	30

different nonlinearities are attributed to slight variations in the resonant enhancement. The diethylamino and dibutylamino analogues exhibit the highest susceptibilities, $\chi_{zzz}^{(2)} = 100\text{--}120 \text{ pm V}^{-1}$ at $1.064 \mu\text{m}$, and these coincide with an absorption maximum at *ca.* 425 nm and a film absorbance, albeit very weak, of *ca.* $5 \times 10^{-4} \text{ layer}^{-1}$ at the harmonic wavelength. In contrast, lower susceptibilities of $50\text{--}70 \text{ pm V}^{-1}$ for **1a** and **1d** relate to a slight blue shift of the absorption maximum to *ca.* 415 nm and a reduced absorbance of *ca.* $3 \times 10^{-4} \text{ layer}^{-1}$ at 532 nm .

The linear and nonlinear optical properties are also dependent upon the film composition and optimum SHG arises when the dyes are mixed in a 1 : 1 ratio with octadecanoic acid. The behaviour is similar in each case and, therefore, we report the SHG dependence of the diethylamino analogue which is representative of the series. Films of **1b** exhibit absorption maxima at 425 nm for the pure dye, 450 nm for the 1 : 1 mixed film and 480 nm for dye : ODA ratios of 1 : 2 to 1 : 5. The SHG polarisation dependence is independent of composition and, using the method of Kajikawa *et al.*,²¹ corresponds to a chromophore tilt angle of $30 \pm 1^\circ$ relative to the substrate normal. In contrast, the susceptibility is strongly dependent upon the ratio of dye to octadecanoic acid with an optimum value of $\chi_{zzz}^{(2)} = 145 \text{ pm V}^{-1}$ for the 1 : 1 mixed film (*cf.* 120 pm V^{-1} for the pure dye). The enhancement is unlikely to be associated with resonance effects because the residual absorbance at the harmonic wavelength, albeit very small, is almost identical for each of the films of **1b**. Therefore, it probably relates to improved non-centrosymmetric ordering and, as reported by Hayden²² and McGilp *et al.*,²³ to changes in the local field effects upon dilution.

The films are almost transparent at 532 nm and thus, it may be assumed that Kleinman's symmetry is valid and that the susceptibility components are limited to $\chi_{zzz}^{(2)}$ and $\chi_{zxx}^{(2)}$. Furthermore, as the hyperpolarisability is probably dominated by the component along the molecular charge transfer axis, the relation between $\chi^{(2)}$ and β is as shown in eqn. (1) and (2).

$$\chi_{zzz}^{(2)} = Nf^{2\omega}(f^\omega)^2\beta\cos^3\varphi \quad (1)$$

$$\chi_{zxx}^{(2)} = 1/2Nf^{2\omega}(f^\omega)^2\beta\cos\varphi\sin^2\varphi \quad (2)$$

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. The hyperpolarisability is suppressed in films with a high surface density of dye and, for **1b**, saturates to a constant

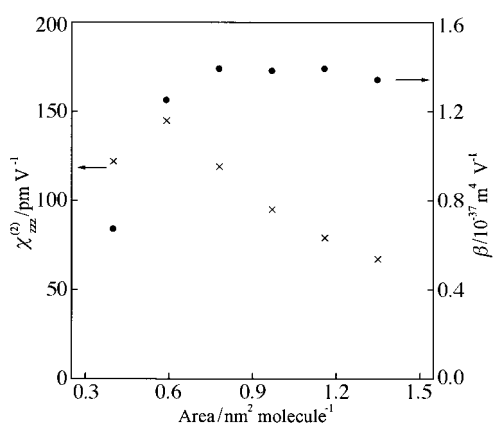


Fig. 3 Variation of the second-order susceptibility (\times) and molecular hyperpolarisability (filled circles) with the surface area occupied by **1b** and associated ODA molecules in the mixed LB monolayers. The nonlinear optical coefficients were evaluated using a monolayer thickness of 3.1 nm and a weighted average of the refractive indices of the dye ($n^\omega = 1.51$, $n^{2\omega} = 1.60$) and octadecanoic acid ($n^\omega = 1.53$, $n^{2\omega} = 1.54$) as the ratio of dye : ODA is altered from 1 : 0 to 1 : 5.

value of *ca.* $1.4 \times 10^{-37} \text{ m}^4 \text{ V}^{-1}$ ($330 \times 10^{-30} \text{ esu}$) when diluted with octadecanoic acid (Fig. 3). The apparent variation is attributed to changes in the local field correction factors and, interestingly, both β and λ_{max} remain constant for dye : ODA ratios of 1 : 2 and above. However, as optimum SHG is realised for a dilution of 1 : 1, the principal characterisation is limited to films of this composition and the following discussion only concerns this ratio.

Reflectance studies

The thickness and optical constants of films, deposited on silicon wafers, were determined using a four-layer model (air/LB/SiO₂/Si) and a procedure similar to that described by Wang.²⁴ Reflections from the multiple interfaces were analysed using a derivation based on the treatment of Heavens²⁵ and applied to absorbing biaxial surfaces. The reflectance was determined as the angle of incidence of the laser beam, relative to the film, was rotated from 10° to 83° for both p and s polarised light. The films were investigated at the four wavelengths (green, 543.5 nm ; yellow, 594.1 nm ; orange, 611.9 nm ; red, 632.8 nm) of a multiline He-Ne laser and the reflectance data fitted to theoretical equations using a Simplex curve fitting routine to minimise the sum of the least squares fit.

The thickness and refractive indices of an alternate-layer mixed film of the diethylamino analogue (**1b**) were derived from an analysis of the wavelength dependent reflection data for a 32 bilayer film (Fig. 4; Table 2). A mean thickness of 130.8 nm corresponds to $4.08 \text{ nm bilayer}^{-1}$ and, from studies on non-interleaved films of poly(*tert*-butyl methacrylate), conforms to *ca.* $3.05 \text{ nm layer}^{-1}$ for the SHG-active dye and *ca.* $1.03 \text{ nm layer}^{-1}$ for the spacer. The corresponding thickness from alternate-layer films of the dibutylamino analogue (**1c**) is $4.13 \text{ nm bilayer}^{-1}$ and conforms to $3.10 \text{ nm layer}^{-1}$ for the dye compared with $3.15 \text{ nm layer}^{-1}$ obtained from the reflectance data of a non-interleaved Z-type film of **1c**. Thus, for these analogues, a minimal difference in the layer thickness suggests that the dialkylamino groups are expanded in the horizontal rather than the vertical direction. Sufficient space is made available, at the other end, by a side-by-side packing arrangement of the three octadecyl tails of the cationic dye, the amphiphilic anion and the octadecanoic acid.

The refractive indices, obtained from the analysis of the reflectance data of the alternate-layer film of **1b**, increase with decreasing wavelength and their dispersion may be represented by eqn. (3), the Sellmeier equation (Fig. 5).

$$n^2 = A + s\lambda^2/(\lambda^2 - \lambda_0^2) \quad (3)$$

where A is a constant, s is the oscillator strength and λ_0 is the resonance wavelength of the absorbance band. The refractive

Table 2 Refractive indices (n), extinction coefficients (k) and thicknesses (l) obtained from analysis of the reflection data from 32 layers each of the 1 : 1 mixed film of dye **1b** and octadecanoic acid interleaved by poly(*tert*-butyl methacrylate)

Coefficient	Wavelength/nm			
	543.5	594.1	611.9	632.8
n_x	1.565	1.547	1.540	1.538
n_y	1.557	1.526	1.520	1.515
n_z	1.583	1.544	1.530	1.526
n_{iso}	1.568	1.539	1.530	1.526
k_x	7.0×10^{-3}	1.0×10^{-4}	0	0
k_y	0.3×10^{-3}	1.7×10^{-4}	0	0
k_z	1.5×10^{-2}	5.0×10^{-4}	0	0
l/nm	130.5	130.4	130.8	130.6
$l/\text{nm bilayer}^{-1}$	4.078	4.075	4.088	4.081

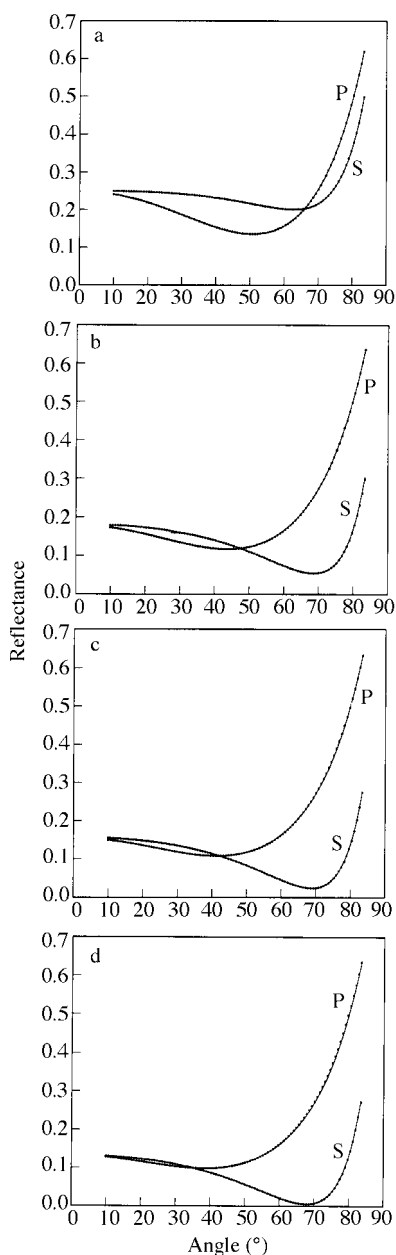


Fig. 4 Reflectance of polarised light from 32 bilayers of the 1 : 1 mixed film of **1b** and octadecanoic acid interleaved with poly(*tert*-butyl methacrylate) on a silicon wafer: (a) $\lambda = 543.5$ nm; (b) 594.1 nm; (c) 611.9 nm; (d) 632.8 nm. The curves represent the theoretical fits using the data in Table 2.

indices at the fundamental and harmonic frequencies, obtained by substitution of the experimental data into eqn. (3), are 1.495 and 1.581 respectively. The difference ($n^{2\omega} - n^\omega = 0.086$) is smaller than reported²⁶ for LiNbO₃ and substitution into the following equation provides a coherence length of *ca.* 3 μm at normal incidence for the wavelength described in eqn. (4).

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

The data obtained for the dibutylamino analogue (**1c**) are summarised in Table 3 for alternate-layer and Z-type films. The thickness and refractive indices of the alternate-layer structure are similar to those obtained for **1b**.

SHG From alternate-layer films

Non-centrosymmetric multilayer structures are readily fabricated by interleaving the SHG-active layers with those of poly(*tert*-butyl methacrylate), the films showing a nearly

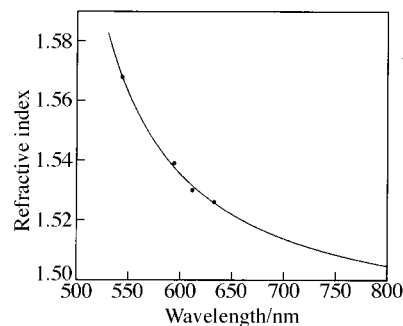


Fig. 5 Variation of the isotropic refractive index with wavelength of a 1 : 1 mixed film of **1b** and octadecanoic acid interleaved with poly(*tert*-butyl methacrylate). The points represent the experimental data from Table 2 and the solid line is the theoretical fit using the Sellmeier equation.

quadratic increase in the second-harmonic intensity with the number of active layers. This was achieved to thicknesses in excess of 100 bilayers for the pure dyes, **1a** to **1c**, as well as for 1 : 1 mixed films of the dyes and octadecanoic acid. Optimum intensities were obtained for the latter and, therefore, the following discussion is limited to the mixed LB films.

The apparent quadratic SHG dependence of the 1 : 1 mixed films of **1a** and **1b** is shown in Fig. 6 but, if viewed as $I_{(\text{N})}^{2\omega} / N^2$ vs. N , there are discrepancies in the normalised intensities. These probably result from variable deposition conditions. The multilayer structure was fabricated in several stages, throughout a period of two weeks, this tedious and unnecessary procedure resulting from our enforced requirement to monitor the linear and nonlinear optical behaviour throughout the entire deposition process. The diethylamino analogue (**1b**) exhibits the strongest SHG but the normalised intensity decreases by a factor of two throughout the early stages of deposition. However, it is constant for $N > 55$ bilayers and the deviation is also accompanied by a slight shift of the peak wavelength, from an initial value of 455 nm to 447 nm for thicknesses greater than 60 bilayers. Furthermore, the SHG polarisation dependence, $I^{2\omega}(\text{p} \rightarrow \text{p}) / I^{2\omega}(\text{s} \rightarrow \text{p})$, indicates that the chromophores modify their tilt from *ca.* 30° in the monolayer to 37° in the thick alternate-layer film, both values being relative to the normal to the substrate.

The second-order susceptibility decreases from $\chi_{\text{zzz}}^{(2)} \approx 110 \text{ pm V}^{-1}$ for the first bilayer to a steady state of *ca.* 67 pm V^{-1} for structures in excess of 55 bilayers. Despite this, the properties are extremely encouraging and optimisation of the deposition conditions should result in improved second-order coefficients. The normalised SHG, $I_{(\text{N})}^{2\omega} / N^2$, from the thick multilayer film is significantly greater than the signal obtained from LB films of the extensively studied hemicyanine, (*E*)-*N*-docosyl-4-[2-(4-dimethylaminophenyl)ethenyl]pyridinium bromide, first reported by Girling and co-workers.²⁷ In addition, whereas the hemicyanine dye has an absorbance of *ca.* 0.002 layer^{-1} at 532 nm, the interleaved films of **1b**, reported in this study, are almost transparent and have a corresponding absorbance of *ca.* $5 \times 10^{-4} \text{ bilayer}^{-1}$ (Fig. 7).

Mixed films of the dimethylamino and dibutylamino

Table 3 Thickness and refractive indices of interleaved and Z-type films

Dye	Dye: ODA	Thickness/nm layer ⁻¹	n^ω	$n^{2\omega}$	Film type
1b	1 : 1	4.08 ^a	1.50	1.58	interleaved
1c	1 : 1	4.13 ^a	1.51	1.55	interleaved
1c	1 : 1	3.15	1.52	1.58	Z-type
1c	1 : 0	3.16	1.52	1.59	Z-type

^aCorresponds to the repeating bilayer structure of the alternate-layer film interleaved with poly(*tert*-butyl methacrylate).

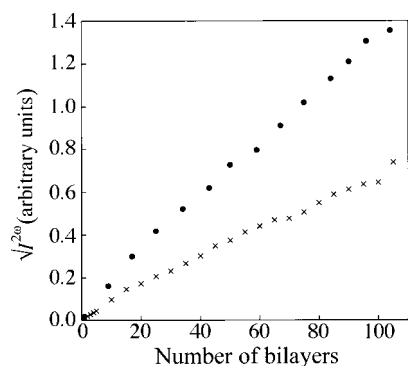


Fig. 6 Variation of the square root of the second-harmonic intensity with the number of bilayers for 1:1 mixed films interleaved with poly(*tert*-butyl methacrylate): **1a** (×); **1b** (solid circles).

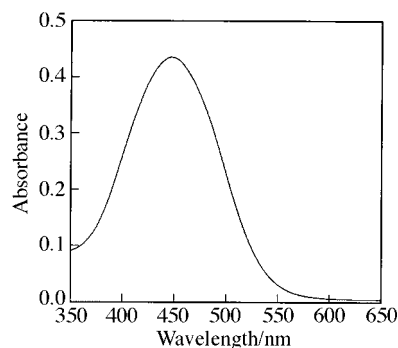


Fig. 7 Visible spectrum of 104 bilayers of the 1:1 mixed film of **1b** interleaved with poly(*tert*-butyl methacrylate). The residual absorbance at the higher wavelength end of the spectrum is attributed to the glass substrate.

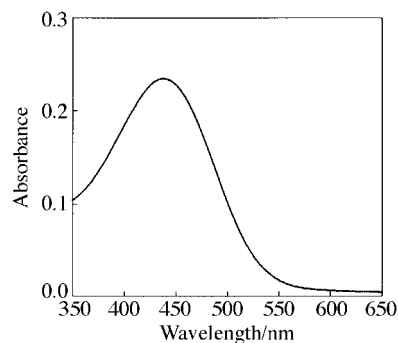


Fig. 8 Visible spectrum of 105 bilayers of the 1:1 mixed film of **1a** interleaved with poly(*tert*-butyl methacrylate).

analogues show a similar quadratic SHG dependence to more than 100 bilayers. Their linear and nonlinear optical properties are summarised in Table 4. The former has a lower second-order susceptibility of 40 pm V^{-1} (*cf.* 67 pm V^{-1} for **1b**). This coincides with a reduced absorbance of $3 \times 10^{-4} \text{ bilayer}^{-1}$ at

Table 4 Linear and nonlinear optical properties of thick multilayer films with interleaved and Z-type structures

Dye	Dye:ODA	$\lambda_{\text{max}}/\text{nm}$	$\chi_{\text{zzz}}^{(2)}/\text{pm V}^{-1}$	$\varphi/^\circ$	Film type
1a	1:0	410	26	39	interleaved
1b	1:0	420	50	33	interleaved
1c	1:0	425	31	32	Z-type
1d	1:0	410	21	30	Z-type
1a	1:1	439	40	30	interleaved
1b	1:1	447	67	37	interleaved
1c	1:1	450	52	33	interleaved
1c	1:1	450	76	33	Z-type

the harmonic wavelength and the absorption maximum being shifted to 439 nm (Fig. 8). Thus, resonant effects can explain the altered nonlinear optical properties and, although the spectra probably reflect slightly different packing arrangements, it is unclear why they are dependent upon the dialkylamino groups. Nonetheless, when interleaved with poly(*tert*-butyl methacrylate), dyes in this series form non-centrosymmetric structures. They exhibit SHG comparable with that obtained from conventional hemicyanine derivatives^{18–20} but have a greatly improved transmittance at the harmonic wavelength.

SHG From Z-type films

Unless interleaved, the dimethylamino and diethylamino analogues form centrosymmetric Y-type arrangements in which the molecules pack head-to-head and tail-to-tail. However, if the second end of the molecule is sufficiently hydrophobic, as in the case of the dibutylamino and dihexylamino analogues, a stable Z-type structure results. Quadratic enhancement of the second-harmonic intensity with the number of deposited layers has been observed for both **1c** and **1d**, the strongest SHG and most favourable packing being obtained for 1:1 mixed films of the former (Fig. 9). In this case, quadratic SHG enhancement has been realised to in excess of 200 Z-type layers and, when carefully deposited, the normalised intensity, $I_{\text{(N)}}^{2\omega}/N^2$, matches the signal obtained from monolayer films. The Z-type films have a moderately high susceptibility of 76 pm V^{-1} for $l=3.15 \text{ nm}$, $\varphi=33^\circ$, $n^\omega=1.52$ and $n^{2\omega}=1.58$ and, like other members of this series, are transparent at the fundamental wavelength and have a minimal absorbance of $5 \times 10^{-4} \text{ layer}^{-1}$ at the harmonic wavelength. The spectrum is almost identical with that of the 1:1 mixed film of **1b** (Fig. 7).

Another interesting feature of the 1:1 mixed films of **1c** and octadecanoic acid is that deposition on the downstroke (X-type) also results in non-centrosymmetric ordering but with the dipole orientation reversed. This has been demonstrated by X-type deposition onto a thick Z-type film, there being a suppression of the second-harmonic intensity when the

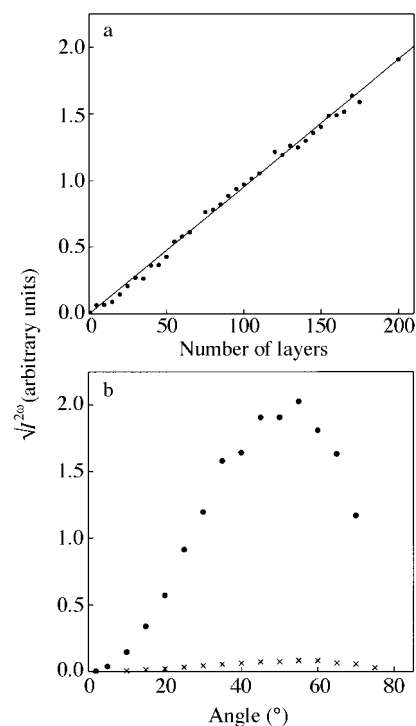


Fig. 9 Z-Type films of **1c**: variation of the square root of the second-harmonic intensity with (a) the number of deposited layers and (b) the angle of incidence of the Nd:YAG laser beam: p-polarised (solid circle) s-polarised (×) relative to the LB film.

number of layers of each type is equal. The intensity decreases quadratically with increasing film thickness and then, when the number of X-type layers is greater, it begins to increase quadratically. This is indicative of favourable LB deposition on the downstroke, as well as the upstroke, and may be used to fabricate waveguide structures with inversion symmetry in the thickness direction.^{16,28,29} The waveguiding properties of these films have not been studied but, in a parallel investigation on the 4-quinolinium analogue of **1c**, we have previously reported Cerenkov-type phase matched SHG using fibre optic coupling.^{2,30} The materials reported here are more suitable candidates for investigation.

Conclusion

We conclude that the observed quadratic SHG dependence to more than 200 Z-type layers is a consequence of improved deposition and of our recent discovery that stable non-centrosymmetric structures result when the interface is invariably hydrophobic. The 200 layer film is the thickest Z-type structure to date and the normalised intensities, $I_{(N)}^{2\omega}/N^2$, obtained for interleaved films of the diethylamino analogue (**1b**) and Z-type films of the dibutylamino analogue (**1c**), both co-deposited with octadecanoic acid, are the strongest yet from semi-transparent LB films. The enhancement results, in part, from the proximity of the charge-transfer band which optimises the trade-off in efficiency and absorbance.

Acknowledgements

The EPSRC (U.K.) is acknowledged for financial support of the nonlinear optics programme at Cranfield and for providing studentships to R.R., A.J.W. and D.G.

References

- 1 C. Bosshard, K. Sutter, P. Prêtre, J. Hulliger, M. Flörshemer, P. Kaatz and P. Günter, *Organic Nonlinear Optical Materials, Advances in Optics*, ed. A. F. Garito and F. Kajzar, Gordon and Breach, Basel, Switzerland, Vol. 1, 1995.
- 2 G. J. Ashwell, *J. Mater. Chem.*, 1999, **9**, 1991.
- 3 G. J. Ashwell, P. D. Jackson and W. A. Crossland, *Nature*, 1994, **368**, 438.
- 4 (a) G. J. Ashwell, G. Jefferies, C. D. George, R. Ranjan, R. B. Charters and R. P. Tatam, *J. Mater. Chem.*, 1996, **6**, 131; (b) G. J. Ashwell and R. Ranjan, *Proc. SPIE Int. Soc. Opt. Eng.*, 1998, **3474**, 76.
- 5 (a) G. J. Ashwell, P. D. Jackson, G. Jefferies, I. R. Gentle and C. H. L. Kennard, *J. Mater. Chem.*, 1996, **6**, 137; (b) G. J. Ashwell, T. Handa and R. J. Ranjan, *J. Opt. Soc. Am. B*, 1998, **15**, 466.
- 6 M. J. Roberts, G. A. Lindsay, K. J. Wynne, R. A. Hollins, P. Zarras, J. D. Stenger-Smith, M. Nadler and A. P. Chafin, *Polym. Prepr.*, 1997, **38**, 975.
- 7 H. R. Motschmann, T. L. Penner, N. J. Armstrong and M. C. Ezenyilimba, *J. Phys. Chem.*, 1993, **97**, 3933.
- 8 W. M. K. P. Wijekoon, S. K. Wijaya, J. D. Bhawalkar, P. N. Prasad, T. L. Penner, N. J. Armstrong, M. C. Ezenyilimba and D. J. Williams, *J. Am. Chem. Soc.*, 1996, **118**, 4480.
- 9 (a) G. A. Lindsay, K. J. Wynne, W. N. Herman, A. P. Chafin, R. A. Hollins, J. D. Stenger-Smith, J. Hoover, J. Cline and

- M. J. Roberts, *Nonlinear Opt.*, 1996, **15**, 139; (b) G. A. Lindsay, M. J. Roberts, J. D. Stenger-Smith, W. N. Herman, P. R. Ashley and K. J. Wynne, *Nav. Res. Rev.*, 1997, **XLIX**, 21.
- 10 (a) M. Era, K. Nakamura, T. Tsutsui, S. Saito, H. Niino, K. Takehara, K. Isomura and H. Tanaguchi, *Jpn. J. Appl. Phys.*, 1990, **29**, L2261; (b) M. Era, H. Kawafuji, T. Tsutsui, S. Saito, K. Takehara, K. Takehara, K. Isomura and H. Taniguchi, *Thin Solid Films*, 1992, **210–211**, 163.
- 11 (a) G. J. Ashwell, E. J. C. Dawnay, A. P. Kuczynski and P. J. Martin, *Proc. SPIE Int. Soc. Opt. Eng.*, 1991, **1361**, 589; (b) G. J. Ashwell, P. D. Jackson, D. Lochun, P. A. Thompson, W. A. Crossland, G. S. Bahra, C. R. Brown and C. Jasper, *Proc. R. Soc. London A*, 1994, **445**, 385.
- 12 (a) S. H. Ma, K. Han, X. Z. Lu, W. C. Wang, Z. M. Zhang and Z. Q. Yao, *Opt. Commun.*, 1994, **111**, 513; (b) S. Ma, X. Lu, J. Xu, W. Wang and Z. Zhang, *J. Phys. D*, 1997, **30**, 2651.
- 13 (a) P. Hodge, Z. Ali-Adib, D. West and T. King, *Macromolecules*, 1993, **26**, 1789; (b) P. Hodge, Z. Ali-Adib, D. West and T. King, *Thin Solid Films*, 1994, **244**, 1007.
- 14 (a) W. Hickel, B. Menges, O. Althoff, D. Lupo, U. Falk and U. Scheunemann, *Thin Solid Films*, 1994, **244**, 966; (b) I. Cabrera, A. Mayer, D. Lupo, U. Falk, U. Scheunemann and W. Hickel, *Nonlinear Opt.*, 1995, **9**, 161.
- 15 G. J. Ashwell, A. J. Whittam and K. Skjonnemand, *Langmuir*, submitted for publication.
- 16 (a) T. L. Penner, H. R. Motschmann, N. J. Armstrong, M. C. Ezenyilimba and D. J. Williams, *Nature*, 1994, **367**, 49; (b) K. Clays, N. J. Armstrong, M. C. Ezenyilimba and T. L. Penner, *Chem. Mater.*, 1993, **5**, 1032.
- 17 (a) K. Clays, T. L. Penner, N. J. Armstrong and D. R. Robello, *Proc. SPIE Int. Soc. Opt. Eng.*, 1992, **1775**, 326; (b) T. L. Penner, N. J. Armstrong, C. S. Willand, J. S. Schildkraut, D. R. Robello and A. Ulman, *Nonlinear Opt.*, 1993, **4**, 191; (c) K. Clays, N. J. Armstrong and T. L. Penner, *J. Opt. Soc. Am. B*, 1993, **10**, 886.
- 18 M. C. J. Young, W. X. Lu, R. H. Tredgold, P. Hodge and F. Abassi, *Electron. Lett.*, 1990, **26**, 993.
- 19 L. Liu, J. Zheng, W. Wang, Z. Zhang, F. Tao, L. Xu and J. Hu, *Opt. Commun.*, 1992, **93**, 207.
- 20 K. Han, X. Lu, J. Xu, S. Ma and W. Wang, *Opt. Commun.*, 1998, **152**, 371.
- 21 K. Kajikawa, K. Kigata, H. Takezoe and A. Fukuda, *Mol. Cryst. Liq. Cryst.*, 1990, **182**, 91.
- 22 L. M. Hayden, *Phys. Rev. B*, 1988, **38**, 3718.
- 23 J. F. McGilp, Z. R. Tang and M. Cavanagh, *Synth. Met.*, 1993, **61**, 181.
- 24 (a) H. Wang, *Fiber Integr. Opt.*, 1994, **13**, 293; (b) H. Wang, *J. Modern Opt.*, 1995, **42**, 497; (c) H. Wang, *J. Opt. Soc. Am. B*, 1994, **11**, 2331.
- 25 O. S. Heavens, *Optical Properties of Thin Solid Films*, 2nd rev. edn., Dover Publications, Mineola, 1991.
- 26 *CRC Handbook of Laser Science and Technology*, ed. M. J. Weber, CRC Press, Boca Raton, FL, 1982.
- 27 I. R. Girling, N. A. Cade, P. V. Kolinski, R. J. Jones, I. R. Peterson, M. M. Ahmad, D. B. Neal, M. C. Petty, G. G. Roberts and W. J. Feast, *J. Opt. Soc. Am. B*, 1987, **4**, 950.
- 28 (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; (c) N. Asai, I. Fujiwara, H. Tamada and J. Seto, *Mater. Res. Soc. Symp. Proc.*, 1994, **328**, 91.
- 29 M. Küpfer, M. Flörshemer, C. Bosshard and P. Günter, *Nonlinear Opt.*, 1995, **10**, 341.
- 30 S. Johal, S. W. James, R. P. Tatam and G. J. Ashwell, *Opt. Lett.*, 1999, **24**, 1194.

Paper a902954k