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Alignment of chevron-shaped molecules for photonic and electronic applications†

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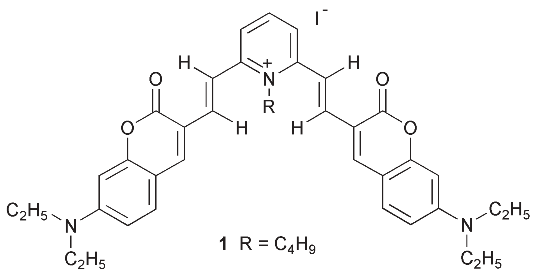
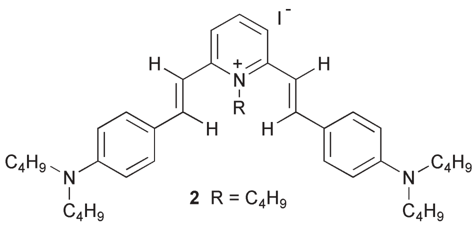
A novel method is reported whereby unconventional molecules without aliphatic tails may be non-centrosymmetrically aligned by the Langmuir–Blodgett technique, the molecules in this case having a central cationic acceptor and two π-bridged donor groups with an angle of *ca.* 120° between the charge-transfer axes of the chevron-shaped D-π-(A$^+$)-π-D unit. Their LB films exhibit second-harmonic generation and molecular rectification.

Conventional wisdom dictates that LB film-forming materials should be linear to facilitate packing and amphiphilic to permit spontaneous alignment at the air–water interface. Consequently, there have been numerous studies on chromophores with hydrophobic tails, typically dodecyl to docosyl, where the application necessitates a non-centrosymmetric structure: *e.g.* second-order nonlinear optical effects,[1,2] molecular rectification[3–6] and pyroelectricity.[7] In such cases, the properties are limited because the alkyl tail acts as an insulating barrier and frequently occupies a greater volume than the active chromophore. This is exaggerated in multilayer films where, to control alignment, the chromophore should be alkylated at both ends[8,9] to prevent centric head-to-head and tail-to-tail arrangements or where the layers are interleaved with inactive spacers.[10–12] There have been attempts to reduce the effective volume of the alkyl tail by interdigitating the layers, initially at one interface (molecular zips[13]) and then at both (molecular Lego[14]). Furthermore, molecules without alkyl tails have also been non-centrosymmetrically aligned, albeit only two to date,[15,16] by utilising D-π-A molecules with an extended π-electron bridge which acts as the hydrophobic component.

In this work, we break from convention and report two chevron-shaped dyes for alignment by LB deposition: 1-butyl-2,6-bis[2-(7-diethylamino-2-oxo-*2H*-chromen-3-yl)vinyl]-pyridinium iodide (**1**) and 1-butyl-2,6-bis[2-(4-dibutylamino-phenyl)vinyl]pyridinium iodide (**2**). They have no significant aliphatic tail but spontaneously align when spread from dilute chloroform solution (0.1 mg cm^{-3}) onto the pure water subphase of an LB trough. To obtain ordered films, the floating monolayers are left for *ca.* 5 min before compression at 0.5 cm^2 s^{-1}, the isotherms being shown in Fig. 1, and then deposited on the upstroke at a surface pressure of 20 mN m^{-1} and a rate of 5 mm min^{-1}. The areas in contact with the substrate, determined by a Sauerbrey analysis[17] of the frequency data when deposited onto 10 MHz quartz crystals, are 0.88 ± 0.05 nm^2 molecule^{-1} for **1** and 0.95 ± 0.05 nm^2 molecule^{-1} for **2**. The calculation assumes that the iodide counterion is retained in the deposited film whereas, in fact, the concentration of OH$^-$ in the neutral aqueous subphase is significantly higher than that of the I$^-$, arising from the spread solution. Furthermore, XPS studies have shown that the counterion is partially replaced unless KI is added to the subphase and it is noted that an assumed 50% replacement of I$^-$ by OH$^-$ would cause the derived areas to decrease by *ca.* 0.07 nm^2. Nonetheless, the values approximate to the molecular footprint of the long axis between the two limbs of the chevron indicating that the apex points either towards or away from the surface.



1 R = C_4H_9



2 R = C_4H_9

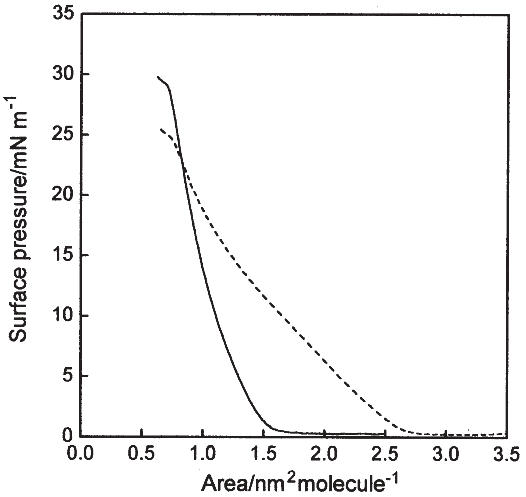


Fig. 1 Surface pressure *versus* area isotherms: dye **1** (solid line); dye **2** (broken line).

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†Electronic supplementary information (ESI) available: synthetic details and analytical data for three chevron-shaped molecules. See http://www.rsc.org/suppdata/jm/b2/b201801m/

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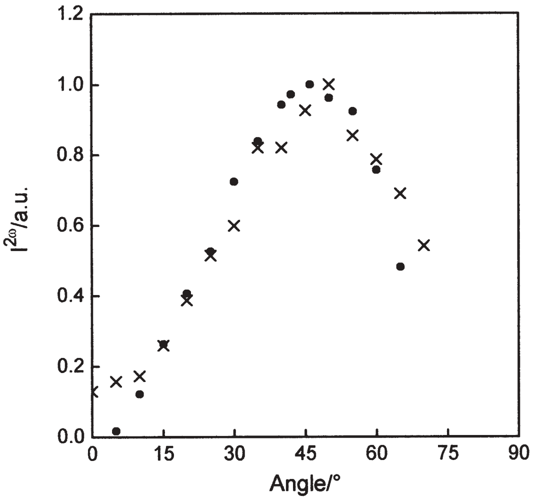

Fig. 2 Second-harmonic intensity *versus* the angle of incidence of the laser beam relative to the film where 0 corresponds to normal incidence: (●) monolayer of dye **1**; (x) monolayer of dye **2**.

Monolayer thicknesses were determined from surface plasmon resonance data, obtained from glass/Au/monolayer structures using a Kretschmann configuration[18] and *p*-polarised monochromatic radiation. The attenuated total reflection was measured both before and after deposition and the data analysed by one and two-layer models respectively using Fresnel reflection formulae. Analysis provided a thickness of 1.23 ± 0.05 nm for **1** and 1.16 ± 0.05 nm for **2**. These compare favourably with the height assuming that the chevron-shaped molecule rests symmetrically on the long axis connecting the two limbs and is upright. The density obtained from the molecular mass and product of thickness and area is consistent for both dyes: $\rho = 1.1 \pm 0.1$ Mg m^{-3}. The value is independent of the assumed counterion and slightly higher than obtained for LB films of conventional materials with long aliphatic tails.

Confirmation of the non-centrosymmetric alignment has been obtained from second-harmonic generation (SHG) studies, the intensity being measured in transmission using a Nd:YAG laser ($\lambda = 1.064$ µm, *p*-polarised) and a half-wave plate to alter the polarisation. The two films exhibit a weak polarisation dependence with, for example, $I^{2\omega}$ (p→p)/$I^{2\omega}$(s→p) ≈ 5 for dye **1** and *ca.* 2 for dye **2** when the laser beam is incident at 45° to the film. The dependence of the second-harmonic intensity upon the angle of incidence is shown in Fig. 2. It is complicated by the fact that there are two intramolecular charge-transfer axes, which move respectively towards and away from the electric vector of the incident radiation as the film is rotated. The signal is weakest at normal incidence and optimum when the substrate is rotated *ca.* 35 to 55°, the lower limit approximating to the angle for one of the charge-transfer axes to be perpendicular to the beam. The second-harmonic intensities are similar to those previously reported for films of the extensively studied hemicyanine dyes[1,2] but, as a consequence of non-centrosymmetric alignment without the need for long aliphatic tails, the susceptibilities are significantly higher than previously obtained. By comparing the intensities with the Maker fringe envelope of a Y-cut quartz reference ($d_{11} = 0.5$ pm V^{-1}), the optimum effective susceptibilities are as follows: $\chi^{(2)}_{\mathrm{eff}} = 110$ pm V^{-1} for **1** and $\chi^{(2)}_{\mathrm{eff}} = 120$ pm V^{-1} for **2**, assuming $n^{\omega} = 1.5$ and $n^{2\omega} = 1.6$. The films exhibit broad charge-transfer bands (λ_{max}: 520 nm for **1**, 493 nm for **2**) which overlap the harmonic wavelength and, thus, the high values are resonantly enhanced. Nonetheless, the data indicate that molecules without long aliphatic tails, as shown in Fig. 3, may be aligned by the LB technique. It is also noted that of three chevron-shaped materials studied to date only 1-butyl-2,6-bis[2-(4-butoxyphenyl)vinyl]pyridinium iodide failed to give the required film structure.

This work forms the basis of an initial investigation of the alignment of unconventional molecules with enhanced second-order nonlinear optical coefficients, achieved by eliminating the SHG-inactive volume of long aliphatic tails normally associated with LB films. Furthermore, in a separate collaborative study with Metzger at the University of Alabama,[19] the alignment of dye **2** has resulted in asymmetric current-voltage characteristics from an Au/(LB monolayer)/Au device. The behaviour has been assigned to molecular rectification and, unlike all previously reported examples,[3–6] there is no insulating alkyl barrier between the chromophore and electrode.

It is concluded that chevron-shaped D-π-(A$^+$)-π-D molecules open the way for improved SHG and rectification from LB films. They may be non-centrosymmetrically aligned without extensive alkyl substitution and their unusual shape suppresses centric antiparallel arrangements, commonly associated with linear D-π-A molecules.

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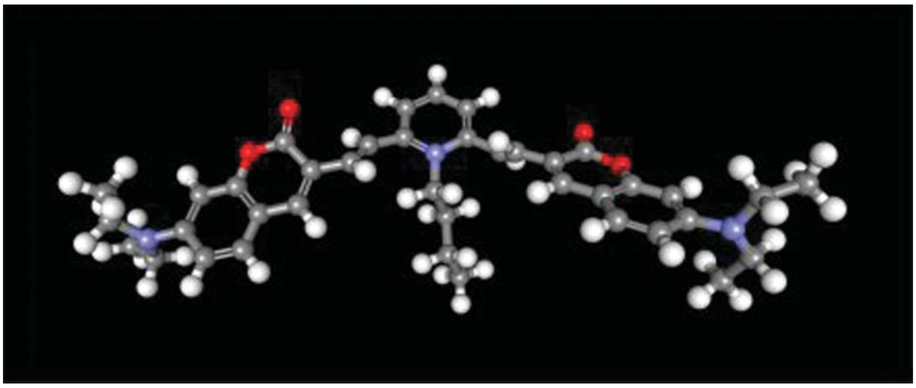

Fig. 3 Structure of dye **1**, which has been modelled using the MNDO program of Cerius^2 (Accelrys, Cambridge). For clarity the iodide counterion has been omitted. The monolayer thickness of 1.23 ± 0.05 nm, obtained by analysis of the SPR data, indicates that the molecules are probably upright and rest on the long axis connecting the two limbs.

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