COUNTERION EFFECTS ON THE STRUCTURE OF LANGMUIR–BLODGETT FILMS OF A BENZOTHIAZOLIUM DYE

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Dedicated to Professor Krzysztof Pigoń on the occasion of his 70th birthday[‡]

Langmuir–Blodgett films of salts of the two-legged cationic dye, E-N-hexadecyl-2-[2-(4-docosylaminophenyl)ethenyl]benzothiazolium, are Z-type. The molecular configuration within the Langmuir–Blodgett film is either "U-shaped" or "stretched" depending upon the nature of the anion, the thickness per layer being 35.1 Å for the octadecylsulphate and 54.1 Å for the iodide. For the Langmuir–Blodgett monolayers the principal components of the second order susceptibility ($\chi^{(2)}_{zzz}$) are 70 pm V^{-1} and 34 pm V^{-1} respectively at 532 nm. In the case of the octadecylsulphate salt it was possible to fabricate thick multilayer Langmuir–Blodgett films; the second harmonic intensity increased with the number of Z-type layers, albeit subquadratically, and this may be ascribed to a progressive variation in the chromophore tilt angle.

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1. Introduction

Long-range order within molecular films is a prerequisite for a diverse range of solid state applications. For example, both pyroelectricity and second harmonic generation (SIIG) require the structure to be non-centrosymmetric. In addition, sensing strategies require preferred orientation of the response elements to both reduce diffusive processes and facilitate analyte binding mechanisms. Thus, the alignment and packing of molecular materials is of paramount importance when considering the deposition characteristics of a particular species. The Langmuir–Blodgett

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(LB) technique provides an effective tool whereby such ordering can be controlled at the molecular level.

Successive deposition of floating Langmuir films can be controlled to produce LB multilayers with sustained Y-type (centrosymmetric) and X-type or Z-type (non-centrosymmetric) packing arrangements. Asymmetry can be induced by tailoring the materials to force X-type or Z-type deposition [1–7] or be acquired by interleaving Y-type layers with optically inactive spacers [8–12]. For homomolecular films in excess of 100 layers such long range non-centrosymmetry has only been realised for a modicum of materials, namely 2-docosylamino-5-nitropyridine (DCANP) [13], a quinolinium zwitterion ($C_{16}H_{33}$-Q3CNQ) [4] and a series of unconventional LB dyes comprising a chromophore with hydrophobic chains at opposing ends [5–7].

The nature of the counterion can also affect the film properties and packing arrangement [11–16]. For example, the use of octadecylsulphate instead of bromide has dramatically improved the SHG from stilbazolium dyes [17] and the presence of primary amines or metal ions (Co^{2+} or Ba^{2+}) has been shown to control the extent of J-aggregation in merocyanine dyes [18]. In this study we investigated the effect of iodide and octadecylsulphate counterions on the film-forming and nonlinear optical properties of a benzothiazolium dye (Fig. 1). The smaller iodide
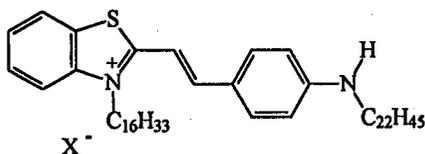

Fig. 1. Molecular structure of E-N-hexadecyl-2-[2-(4-docosylaminophenyl)ethenyl]-benzothiazolium X^-, where X^- is either iodide or octadecylsulphate.

anion gave rise to an extended molecular configuration in which the hydrophobic chains are oriented in opposite directions from the chromophore. By contrast, the octadecylsulphate anion resulted in an altered packing motif in which the molecule adopts a "U-shaped" configuration whereby all of the alkyl chains point in the same direction.

2. Langmuir–Blodgett films

The iodide and octadecylsulphate salts of the benzothiazolium dye were spread, from chloroform and methanol/chloroform solutions respectively, at concentrations of 0.1 mg ml^{-1} onto the pure water subphase of an alternate layer LB trough (Nima Technology). The films were compressed at 0.5 cm^2 s^{-1} to a surface pressure of 35 mN m^{-1} and deposited, on the upstroke, onto hydrophilically treated glass substrates and silver coated slides at a rate of 0.08 mm s^{-1}.

Isotherms of the iodide and octadecylsulphate salts were obtained at *ca.* 20°C (Fig. 2). At zero pressure both isotherms exhibit similar molecular areas of 110 Å^2 molecule^{-1} suggesting a "U-shaped" conformation with the chromophore
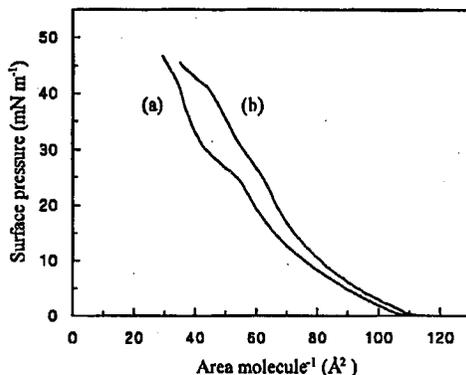
Fig. 2. Surface pressure versus area isotherm of the benzothiazolium dye spread from 0.1 mg ml^{-1} solutions at *ca.* 20°C and compressed at 0.5 cm^2 s^{-1}, where (a) is the iodide salt and (b) the octadecylsulphate salt.

adjacent to the water surface. However, just prior to collapse the areas reduce to 29 Å^2 molecule^{-1} with iodide and 44 Å^2 molecule^{-1} with octadecylsulphate suggesting an altered configuration. Based on the surface plasmon resonance (SPR) analysis of deposited films of the iodide salt there is evidence that, in this case, the molecule has a stretched motif. Although the existence of a hydrophobic chain juxtaposed to the interface is unusual, such alignments have previously been confirmed by neutron reflectivity studies on Langmuir films of Z-β-(N-decyl-4-quinolinium)-α-cyano-4-styryldicyanomethanide ($C_{10}H_{21}$-Q3CNQ) which forms antiparallel dimers at the air–water interface [4].

3. Surface plasmon resonance

SPR studies were carried out using an ATR geometry in the Kretschmann configuration [19]. An approximately 460 Å thick silver film was vacuum deposited onto a clean glass substrate and index matched to one face of an equilateral BK7 glass prism. Reflectivity data were obtained as a function of incidence angle using a p-polarised incident beam from a 532 nm Nd:YAG laser.

SPR reflectivity data were first corrected for reflections at the entrance and exit faces of the prism and analysed by comparison to the Fresnel reflection formulae by a method previously described [4, 20, 21]. The thickness (typically *ca.* 460 Å) and the real (ε_r) and imaginary (ε_i) parts of the dielectric permittivity were initially obtained for silver ($\varepsilon_r = -10.8 \pm 0.1$, $\varepsilon_i = 0.51 \pm 0.03$ at 532 nm) and these values fixed in the subsequent analysis of the reflection data for overlaid LB films. This gave rise to curves of the type illustrated in Fig. 3. The real and imaginary parts of the dielectric permittivity were similar for the two salts, the values being 2.98 and 0.426 respectively for the iodide and 2.62 and 0.452 for the octadecylsulphate. Interestingly the thicknesses are markedly different, being 54.1 Å layer^{-1} for the iodide and 35.1 Å layer^{-1} for the octadecylsulphate. The former complies with a fully stretched motif and may be compared with the van der Waals length of
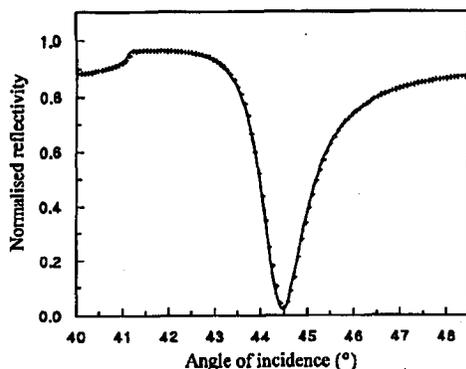
Fig. 3. Normalised theoretical (solid line) and experimental (crosses) SPR reflectivity data for a monolayer of a 1:1 molar ratio of benzothiazolium iodide and sodium octadecylsulphate. The water soluble sodium iodide, formed by metathesis, dissolves into the subphase.

57 Å. However, the thickness for the octadecylsulphate salt suggests a "U-shaped" molecular configuration similar to that proposed for the Langmuir isotherm at low pressures. Thus, the long chain anion alters the architecture of the deposited film.

4. Nonlinear optical effects

The measurements of SHG were carried out in transmission using a 1064 nm Nd:YAG laser incident at 45° to the normal of the LB film. The polarisation dependence of the second harmonic intensity, $I_{2\omega}(p \rightarrow p)/I_{2\omega}(s \rightarrow p)$, was analysed for the monolayer using the method of Kajikawa et al. [22]. This gave rise to chromophore tilt angles, from the normal to the substrate, of 40° for the iodide and 32° for the octadecylsulphate. These values, the thicknesses and refractive indices from SPR, and the SH intensity data provide principal second order susceptibility components of $\chi_{zzz}^{(2)} = 34$ pm V^{-1} for monolayer films of the iodide and $\chi_{zzz}^{(2)} = 70$ pm V^{-1} for monolayer films of the octadecylsulphate. This indicates that the use of a long chain anion results in an alternative packing structure giving rise to enhanced $\chi^{(2)}$ effects.

Z-type multilayer films of the octadecylsulphate salt have been successfully deposited to 200 layers, although similar results could not be obtained for the iodide analogue. The SH intensity increased with the number of layers (Fig. 4) indicating a Z-type structural arrangement, although this did not vary according to theory (i.e. $I_{2\omega} = I_{2\omega(1)}N^2$, where N is the total number of LB layers). The curvature for thicker films may be due, in part, to absorbance of the SH intensity although the dominant effect is more likely to be the variation in the tilt of the chromophores. The polarisation dependence indicates a change in tilt angle from *ca.* 32° for the monolayer to an average value of *ca.* 79° for the 200 layer film (Fig. 5).
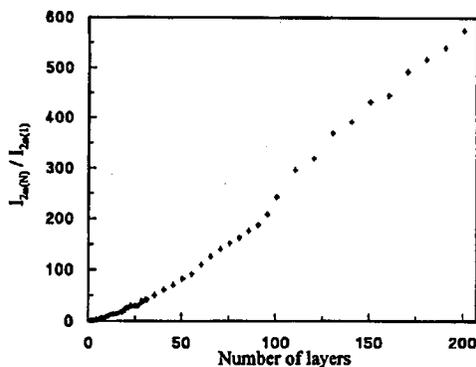
Fig. 4. Ratio of film to monolayer second harmonic intensity $(I_{2\omega(N)}/I_{2\omega(1)})$ with increasing number of LB layers showing the subquadratic behaviour of the benzothiazolium octadecylsulphate salt.
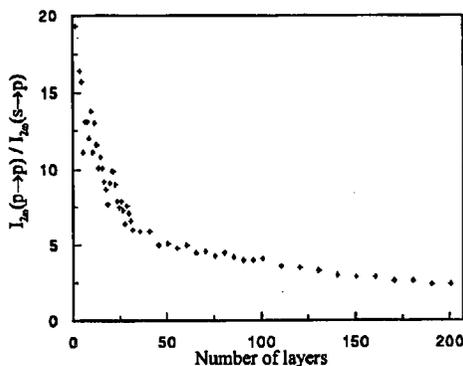

Fig. 5. Variation in the polarisation dependence $[I_{2\omega}(p \to p)/I_{2\omega}(s \to p)]$ with increasing number of LB layers of benzothiazolium octadecylsulphate.

5. Conclusion

The thin film characteristics of a two-legged benzothiazolium dye have been investigated to ascertain the impact of structurally disparate anions. The molecular configuration is dependent upon the type of anion and may adopt either a "stretched" or "U-shaped" arrangement within the film. Z-type multilayer structures have successfully been deposited to 200 LB layers, albeit with subquadratic enhancement, though this may be attributable to the variation in tilt angle as the film thickness increases.

Acknowledgments

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