Fine Tuning of the Photochromic Absorption Band of Heteromolecular Langmuir–Blodgett Films of Zwitterionic Donor-π-Acceptor Molecules

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Mixed Langmuir–Blodgett films of *Z*-β-(1-hexadecyl-4-pyridinium)-α-cyano-4-styryldicyanomethanide ($C_{16}H_{33}$-P3CNQ) and *Z*-β-(1-hexadecyl-4-quinolinium)-α-cyano-4-styryldicyanomethanide ($C_{16}H_{33}$-Q3CNQ) exhibit a single charge-transfer band that may be tuned within the range 495 to 565 nm; the films are photochromic and exhibit second-harmonic generation.

The quest for molecular electronic materials has spawned several new classes of organic compounds which show second-harmonic generation,[1] superconductivity,[2] optical bistability,[3] ferromagnetism[4] and also, possibly molecular rectification.[5,6] Interest in such materials is usually confined to one area whereas Langmuir–Blodgett (LB) films of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ (Fig. 1) show exceptional multifunctional behaviour: (*a*) rectification across Pt|(LB monolayer)|Mg structures;[6] (*b*) a high second order molecular hyperpolarisability and a second harmonic intensity which increases quadratically with the number of LB layers;[7] (*c*) for optical data storage, sharp photochromic bands which, with other analogues, may be independently addressed in a multilayer device to store a multiplicity of bits per pixel.[8,9] The P3CNQ and Q3CNQ chromophores taper in opposite directions and, thus, their geometries make them susceptible to integration in heteromolecular LB films. Here we report a novel method of tuning the absorption band by varying the composition of the mixed LB monolayer.

Mixed solutions of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ in Aristar grade dichloromethane were spread on the pure water subphase (MilliQ, 18 MΩ cm) of a Nima Technology LB trough, compressed to 25 mN m^{-1} and transferred to hydrophilically treated glass slides at 0.15 mm s^{-1}. The mixed LB film structures are *Z*-type. Our second-harmonic genera-

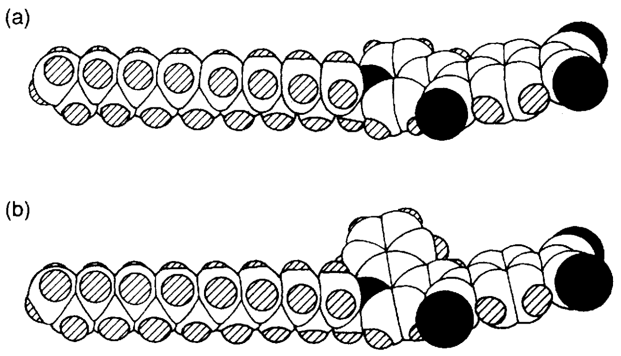

Fig. 1 van der Waals structures of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ

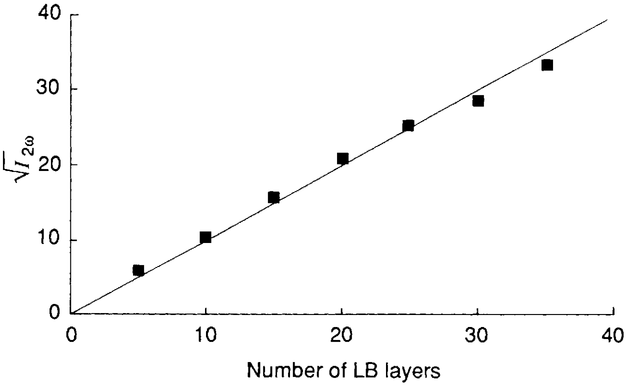

Fig. 2 Square root of the second harmonic intensity (arbitrary units) *vs.* the number of LB layers of a 1 : 2 mixed film of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ; the intensity is corrected for film absorbance at 532 nm

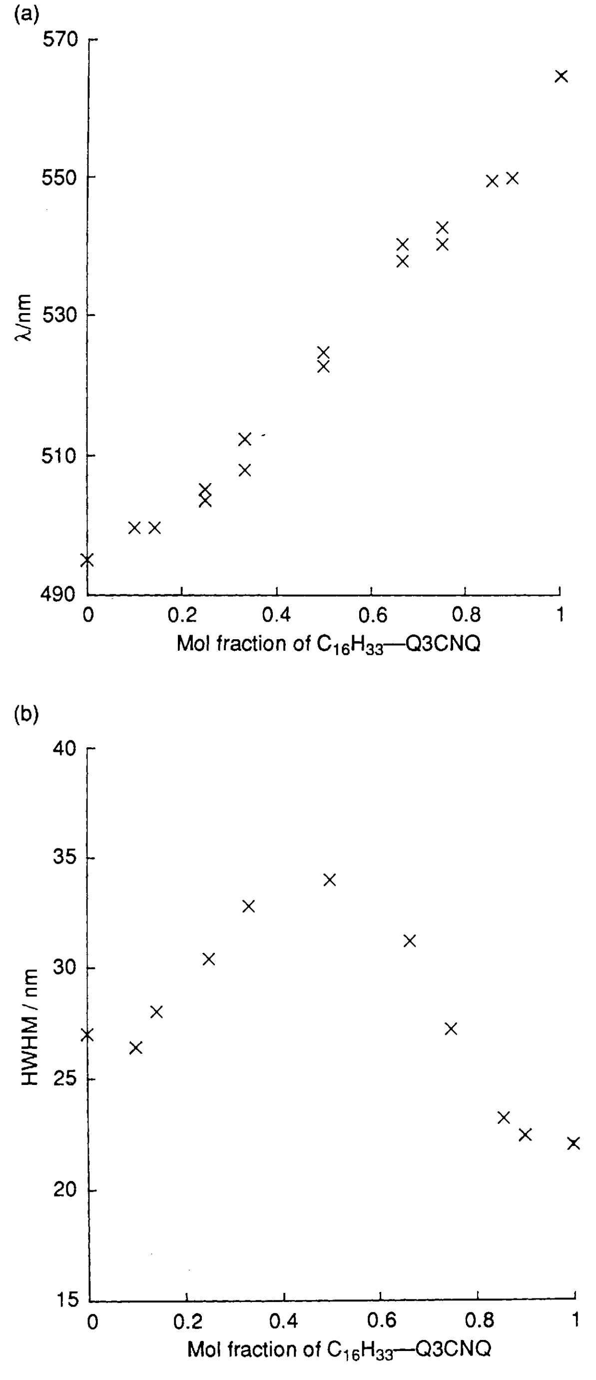

Fig. 3 Charge-transfer band: (*a*) peak wavelength and (*b*) half width at half maximum *vs.* mole fraction of $C_{16}H_{33}$-Q3CNQ in the mixed LB films

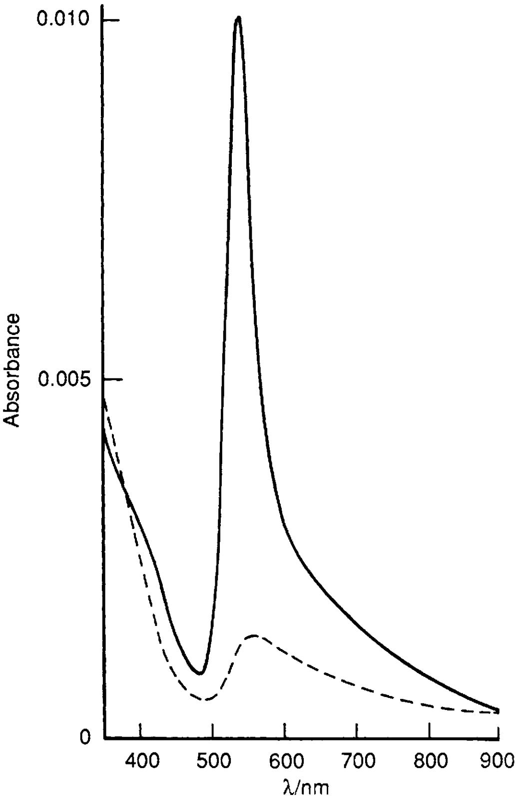

Fig. 4 UV–VIS spectrum of a 1 : 2 mixed LB film of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$Q3CNQ before (solid line) and after (broken line) bleaching by a quartz halogen source fitted with a 532 nm bandpass filter

tion studies† corroborate the non-centrosymmetric alignment, the second-harmonic intensity increasing quadratically with the number of layers (Fig. 2).

Homomolecular LB films of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ show sharp charge-transfer bands at 495 and 565 nm respectively with half widths at half maximum (HWHM) of 27 and 22 nm. Heteromolecular LB films of these chromophores also show a single charge-transfer band, the peak wavelength being dependent upon mole fraction, *x*, and varying from 503 to 550 nm for $C_{16}H_{33}$-P3CNQ : $C_{16}H_{33}$-Q3CNQ = 3 : 1 to 1 : 3 (Fig. 3). The charge-transfer band is very sharp, the broadest being for the 1 : 1 film with HWHM = 34 nm compared with the solution value of 110 nm. It should be noted that the LB absorption band is not a simple combination of the separate spectra of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ which, for $x = \frac{1}{2}$, would give a broad top band with two slight maxima and HWHM *ca.* 60 nm.

The single charge-transfer band implies that the zwitterionic components do not phase separate but, instead, form an organic alloy. This is facilitated by their compatible molecular geometries. Although not obvious from the van der Waals structures (Fig. 1), the P3CNQ and Q3CNQ chromophores widen at opposite ends, the cross-sectional areas of the pyridinium and quinolinium cation groups being 20 and 30 Å^2 respectively. Their mean is similar to that of the $-C(CN)_2$ swallowtail (24 Å^2) and, thus, for effective space filling it should be necessary for the chromophores to integrate.

The $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ zwitterions are photochromic and their properties have been described elsewhere.[8,9] The mixed LB films show similar behaviour and bleach when irradiated at frequencies which overlap the charge-transfer bands (see Fig. 4). The mechanism has not been elucidated but the bleaching may result from one or more of the following: (i) *cis–trans* isomerisation; (ii) dimerisation (or polymerisation) or, more probably, (iii) intramolecular charge transfer followed by molecular rearrangement from the zwitterionic form $[D^+$-CH=C(CN)-C_6H_4-$C(CN)_2^-]$ to the neutral quinonoid

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† SHG studies were carried out on mixed LB films of $C_{16}H_{33}$-P3CNQ and $C_{16}H_{33}$-Q3CNQ, irradiated using a Nd : YAG laser (λ 1.064 μm) at an incident angle of 45°.

form [$D=CHC(CN)=C_6H_4=C(CN)_2$].[9] The bleached films do not thermally recolour and, thus, they have potential applications for optical data storage as write once read many (WORM) memories and, utilising the sharpness of the absorption bands, as components of multifrequency memory devices.[8]

In conclusion this is the first example of an LB film to exhibit a tunable peak wavelength for photochromic and non-linear optical applications. As the photochromic band is tunable within the range 495 to 565 nm it is accessible to available laser wavelengths, for example, the Nd:YAG second harmonic at 532 nm.

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