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Langmuir–Blodgett Alignment of Zwitterionic Optically Non-linear D–π–A Materials

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The synthesis, Langmuir–Blodgett (LB) deposition and charge-transfer spectra of Z-β-(1-alkyl-4-quinolinium)-α-cyano-4-styryldicyanomethanide (R-Q3CNQ where R = C_6H_{13} to $C_{20}H_{41}$) and four substituted analogues are described. The deposition is Z-type and the properties are dependent upon the hydrophobic chain length. C_6H_{13}-Q3CNQ to $C_{14}H_{29}$-Q3CNQ form green LB films ($\lambda_{max} = 614 \pm 4$ nm; HWHM = 37 ± 2 nm) and occupy 28–34 Å^2 per molecule at 25 mN m^{-1}. In contrast, $C_{15}H_{31}$-Q3CNQ to $C_{20}H_{41}$-Q3CNQ occupy 40–50 Å^2 per molecule; their films are purple with $\lambda_{max} = 565 \pm 4$ nm and HWHM = 22 ± 1 nm. The shift is attributed to a change in molecular tilt which causes the transition to alter from an intermolecular to an intramolecular process. Multilayer films of $C_{16}H_{33}$-Q3CNQ exhibit strong second-harmonic generation (SHG) and the intensity increases quadratically with the number of LB layers.

The burgeoning interest in molecules which consist of a donor part linked *via* an extended π-electron bridge to an acceptor part stems from their potential non-linear optical applications.[1–3] They are capable of exhibiting second-harmonic generation (SHG), but for their second-order molecular hyperpolarisabilities (β) to be preserved as a bulk property ($\chi^{(2)}$) it is necessary to suppress the tendency of the molecules to stack centrosymmetrically. Polar molecules often overlap in a head-to-tail manner,[4,5] the arrangement arising from dipole–dipole interactions between opposite ends of adjacent molecules. Few even show close intermolecular contacts and properties similar to those of the semiconducting, mixed-stack, heteromolecular complexes.[5] Nevertheless, for amphiphilic D–π–A molecules, non-centrosymmetric alignment and bulk second-order optical effects can be realised by LB deposition.[6–16]

In this work, the synthesis and properties of R-Q3CNQ, a new LB-film-forming material, and four substituted analogues are reported (see fig. 1). They were synthesised as part of our non-linear optics programme, and our interest was stimulated by (i) the exceptionally high second-order molecular hyperpolarisability of the pyridinium analogue, Z-β-(1-alkyl-4-pyridinium)-α-cyano-4-styryldicyanomethanide, R-P3CNQ,[17] and (ii) the potential use of the materials as components of a high density multifrequency memory.[17–20]

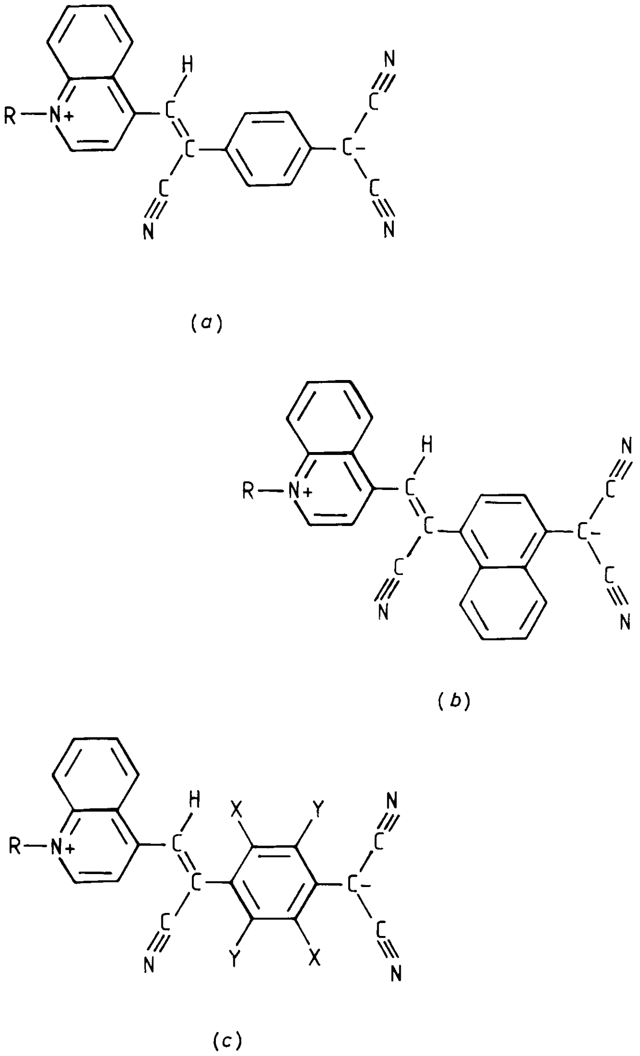

Fig. 1. Molecular structures of (*a*) R-Q3CNQ, (*b*) a benz analogue and (*c*) dichloro (X = H, Y = Cl), dibromo (X = H, Y = Br) and tetrafluoro (X = Y = F) analogues.

Experimental

The R-Q3CNQ zwitterions were synthesised from the reaction of a lepidinium halide with *either* neutral TCNQ (7,7,8,8-tetracyano-*p*-quinodimethane) and piperidine *or* Li^+TCNQ^- using procedures described previously for materials of general formula $D^+{-}CH{=}C(CN){-}C_6H_4{-}C(CN)_2^-$.[17] For example, a methanol solution of 1-n-octyl-4-methylquinolinium bromide (0.38 g, 1 mmol), TCNQ (0.20 g, 1 mmol), and piperidine (0.1 cm^3) was heated at reflux for 24 h. After cooling

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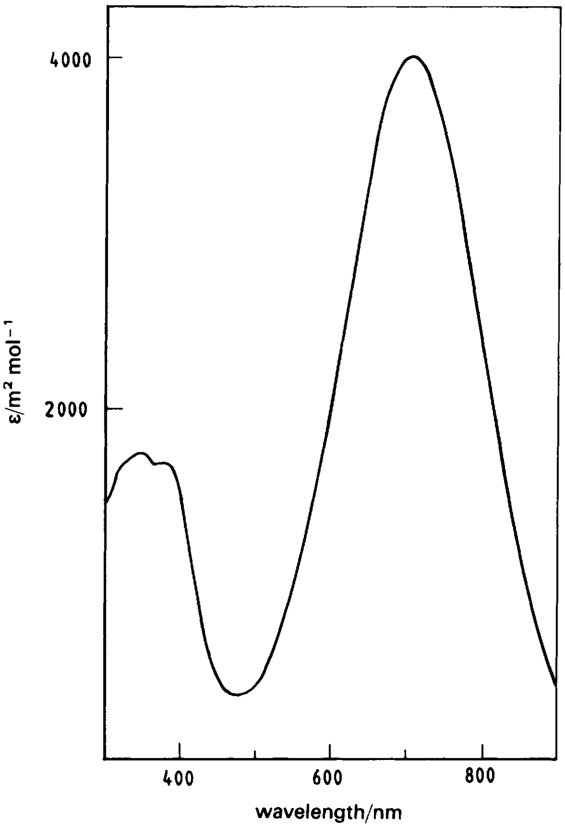

Fig. 2. Absorption spectrum of C_8H_{17}-Q3CNQ in acetonitrile.

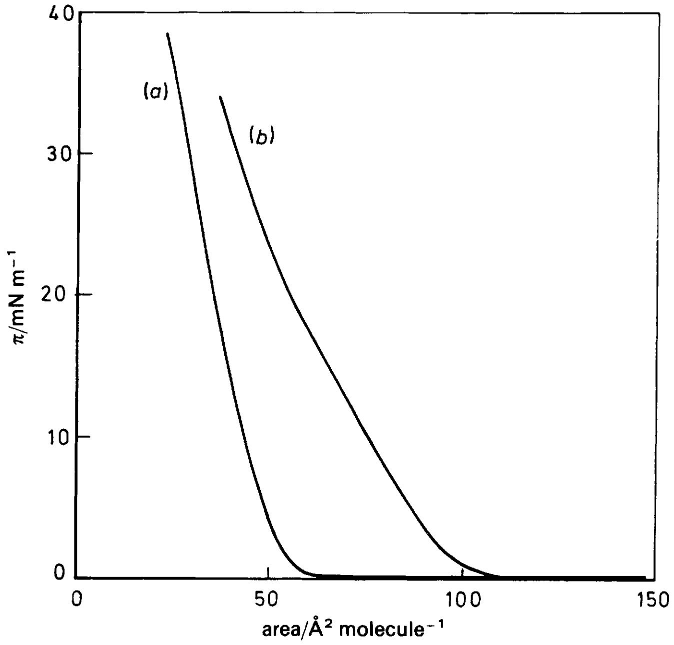

Fig. 3. Surface pressure (π) vs. surface area isotherms of (a) C_8H_{17}-Q3CNQ and (b) $C_{16}H_{33}$-Q3CNQ.

to room temperature a microcrystalline product of C_8H_{17}-Q3CNQ was obtained by filtration (0.19 g, 44%). Crystallisation from acetonitrile gave fine green needles. ^{1}H NMR (DMSO): 0.88 (3H, t, $J = 5.5$ Hz, CH_3—); 1.26 (12H, s, —$(CH_2)_6$—); 4.97 (2H, broad s, —N^+CH_2—); 6.86 (2H, d, $J = 8.1$ Hz, acceptor-H); 7.73 (2H, d, $J = 8.4$ Hz, acceptor-H); 7.95–8.85 (6H, m, donor-H); 9.43 (1H, d, $J = 6.2$ Hz, donor-H). MS: m/z 432 (M^+, 45%); 320 (M^+—C_8H_{16}, 80%); 255 (M^+—C_8H_{17}—$C(CN)_2$, 100%). IR (KBr): 2137, 2177 cm^{-1} (C≡N). UV–VIS (CH_3CN): λ_{max} 348, 378, 710 nm. Calcd for $C_{29}H_{28}N_4$: C, 80.5; H, 6.5; N, 13.0%. Found: C, 80.6; H, 6.4; N, 12.9%.

Other *N*-alkyl homologues were synthesised in a similar manner and the substituted 2,5-dichloro, 2,5-dibromo, 2,3,5,6-tetrafluoro and 2,3-benz analogues were obtained from derivatives of TCNQ[21] using the procedures described for the unsubstituted zwitterion. The materials were characterised by ^{1}H NMR, elemental analysis and mass spectrometry and by comparison of their UV–VIS and IR data with those of the alpha-bridged pyridinium analogue, *Z*-β-(1-methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide, CH_3-αP3CNQ, whose crystal structure is known.[4]

Table 1. Molecular areas and spectroscopic data (wavelength, absorbance and half-width at half-maximum) of the R-Q3CNQ LB films

alkyl group (R)	area/Å² at 25 mN m^{-1}	λ_{max} /nm	absorbance per layer	HWHM /nm
n-hexyl	29	610	0.014	37
n-heptyl	28	614	0.017	39
n-octyl	32	616	0.020	37
n-nonyl	30	617	0.018	35
n-decyl	34	616	0.017	39
n-undecyl	30	616	0.018	38
n-dodecyl	30	613	0.018	37
n-tridecyl	31	615	0.022	36
n-tetradecyl	28	614	0.020	37
n-pentadecyl	40	561	0.016	22
n-hexadecyl	47	565	0.020	22
n-octadecyl	50	565	0.020	23
n-eicosyl	48	568	0.020	21

The UV–VIS solution spectra of the unsubstituted R-Q3CNQ homologues are independent of chain length. In acetonitrile they show a broad-top transition with slight maxima at *ca.* 348 and 378 nm and a charge-transfer band at 710 ± 5 nm with $\varepsilon = 4000 \pm 400$ m² mol^{-1} (fig. 2). The high-wavelength band is solvatochromic and is shifted bathochromically with decreasing solvent polarity, from 710 ± 5 nm in acetonitrile ($\mu = 3.92$ D†) to 760 ± 5 nm in acetone ($\mu = 2.88$ D). The behaviour is consistent with a transition from an ionic ground state to a neutral excited state[22] and the band may be assigned to a transition involving back charge transfer from the negatively charged dicyanomethanide group to the positively charged quinolinium heterocycle. The ionic ground state is also indicated by the IR spectra. A comparison of the C≡N stretching frequencies of the R-Q3CNQ homologues, a doublet at 2137 ± 3 cm^{-1} and 2177 ± 3 cm^{-1}, with those of TCNQ° and TCNQ$^-$ [23,24] suggests a zwitterionic structure. For the pyridinium analogue, CH_3-αP3CNQ, the zwitterionic ground state has been confirmed by X-ray crystallography.[4]

Langmuir–Blodgett Films of R-Q3CNQ

A systematic investigation of the film-forming properties of the R-Q3CNQ alkyl homologues was carried out for R = CH_3 to $C_{20}H_{41}$ using a two-compartment Nima Technology LB trough. Solutions of the zwitterions, in Aristar grade dichloromethane, were spread on the pure-water subphase of one compartment (A) which was isolated from the second compartment (B) by a surface barrier. LB films were obtained by cycling the substrate (a hydrophilically treated quartz slide) *via* B, under the barrier, to deposit in A on the upstroke only. In this way *Z*-type deposition is imposed and, for the zwitterions, interlayer repulsions between the negatively

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† 1 D = 3.33564 × 10^{-30} C m.

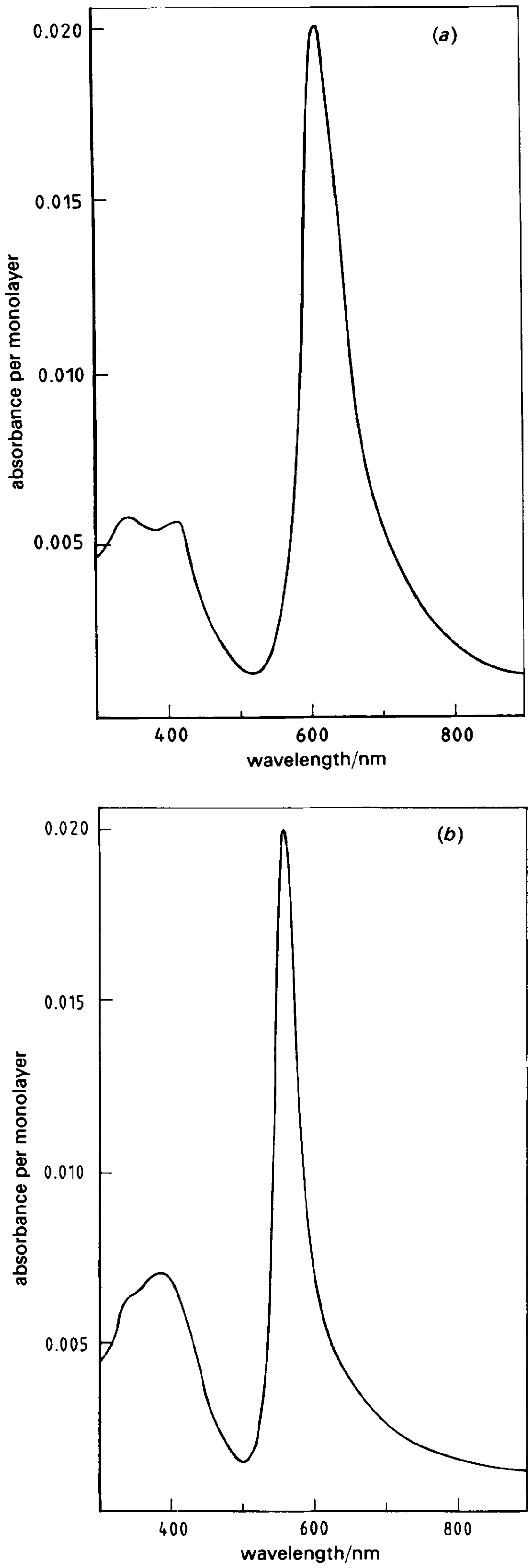

Fig. 4. Absorption spectra of LB films of (*a*) C_8H_{17}-Q3CNQ and (*b*) $C_{16}H_{33}$-Q3CNQ.

charged $-C(CN)_2^-$ groups stabilise the films against molecular rearrangement to a centrosymmetric *Y*-type structure. During deposition the surface layer was maintained at 25 mN m^{-1}.

Table 2. LB film and single-crystal[26] charge-transfer bands of the quinolinium and pyridinium zwitterions

zwitterion	intramolecular CT band/nm	intermolecular CT band/nm	form
R-Q3CNQ	565 ± 4	614 ± 4	LB film
C_6H_{13}-P3CNQ[a]	495 ± 4	634 ± 4	LB film
CH_3-αP3CNQ[b]	538	806	crystal[c]

[a] *Z*-*β*-(1-n-Hexyl-4-pyridinium)-α-cyano-4-styryldicyanomethanide.
[b] *Z*-*β*-(1-Methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide.
[c] Ref. (26).

LB films were obtained for chain lengths greater than C_5H_{11} and from the molecular areas, listed in table 1, a transition in the alignment occurs at $R = C_{15}H_{31}$. The molecular area at which the surface pressure starts to increase is 100–120 Å^2 for $R \geqslant C_{15}H_{31}$ compared with 50–70 Å^2 for the shorter-chain homologues (fig. 3), indicating a different angle of tilt within the monolayer at $\pi = 0$. A comparison of the largest cross-sectional van der Waals area† (30 Å^2) and face area‡ (114 Å^2) of the Q3CNQ chromophore clearly shows that the long-chain homologues lie face down on the water surface. It may be relevant that the molecular alignment alters at $R = C_{15}H_{31}$ and that this is the shortest chain capable of tucking back to fill the space along the full length of the chromophore.

Charge-transfer Spectra

The LB film spectra are shown in fig. 4 and the spectroscopic data are summarised in table 1. The general profile of the solution spectrum (fig. 2) is displayed by the LB spectra (fig. 4), but they differ significantly in the position and width of the charge-transfer band. In acetonitrile the transition occurs at 710 ± 5 nm for all chain lengths, whereas for C_6H_{13}-Q3CNQ to $C_{14}H_{29}$-Q3CNQ the LB band is shifted to 614 ± 4 nm with HWHM = 37 ± 2 nm and for $C_{15}H_{31}$-Q3CNQ to $C_{20}H_{41}$-Q3CNQ it is further shifted to 565 ± 4 nm with HWHM = 22 ± 1 nm.

The reason for the shift becomes clear when we compare the molecular areas at the deposition pressure of 25 mN m^{-1}, listed in table 1. For films of C_6H_{13}-Q3CNQ to $C_{14}H_{29}$-Q3CNQ, areas of 28–34 Å^2 per molecule are in close agreement with the cross-sectional van der Waals area of 30 Å^2 of the widest part of the chromophore, the quinolinium cation.[25] We deduce that the alignment is nearly perpendicular to the substrate. It follows that the transition at *ca.* 614 nm corresponds to an intermolecular charge-transfer band because the intramolecular transition moment and electric vector are orthogonal. In contrast, areas of 40–50 Å^2 per molecule at 25 mN m^{-1} for $C_{15}H_{31}$-Q3CNQ to $C_{20}H_{41}$-Q3CNQ suggest that the chromophores are tilted towards the plane of the substrate. The band at *ca.* 565 nm, therefore, probably corresponds to an intramolecular transition.

The LB spectra of $C_{15}H_{31}$-Q3CNQ provide evidence of both charge-transfer bands: when deposited at $\pi = 25$ mN m^{-1} the principal band occurs at 561 nm with a broad shoulder above 600 nm, but when deposited at $\pi \approx 40$ mN m^{-1} the main absorption may be shifted to 614 nm. Both charge-transfer bands have also been observed in the LB and single-

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† Calculated from the molecular dimensions of the 1,4-di(*N*-quinoliniummethyl)benzene cation in ref. (25).

‡ Calculated from the molecular dimensions of *Z*-*β*-(1-methyl-2-pyridinium)-α-cyano-4-styryldicyanomethanide in ref. (4) and the quinolinium cation in ref. (25).

Table 3. Comparison of the charge-transfer bands of the $C_{16}H_{33}$-Q3CNQ analogues and the half-wave reduction potentials *vs.* SCE of the TCNQ derivatives[28,29] from which they were prepared

zwitterion	CH_3CN λ_{max}/nm (eV)	LB film λ_{max}/nm (eV)	$E_{1/2}$/V
$C_{16}H_{33}$-Q3CNQ(benz)	742 (1.67)	623 (1.99)	−0.09
$C_{16}H_{33}$-Q3CNQ	712 (1.75)	565 (2.20)	+0.17
$C_{16}H_{33}$-Q3CNQ(Cl_2)	602 (2.06)	545 (2.28)	+0.41
$C_{16}H_{33}$-Q3CNQ(Br_2)	602 (2.06)	545 (2.28)	+0.41
$C_{16}H_{33}$-Q3CNQ(F_4)	565 (2.20)	480 (2.59)	+0.53

crystal spectra of two pyridinium analogues (table 2). From the Kramers–Kronig-transformed, single-crystal absorption spectra of CH_3-αP3CNQ, Akhtar *et al.*[26] have assigned the higher-energy transition (538 nm) to an intramolecular charge-transfer band and the lower-energy transition (806 nm) to an intermolecular band. This is consistent with our assignment of the LB bands of R-Q3CNQ, but whereas the intramolecular transitions are in close agreement the intermolecular LB bands are significantly hypsochromically shifted (table 2). The shift may be explained by the more favourable molecular overlap (head-to-tail) within the crystals.[4]

Analogues of $C_{16}H_{33}$-Q3CNQ

The charge-transfer spectra of $C_{16}H_{33}$-Q3CNQ and four substituted analogues are summarised in table 3, the materials being listed in order of increasing transition energy. From Mulliken charge-transfer theory[27] the HOMO–LUMO intramolecular transition energy is given by:

$$E_{CT} = (E_{i,D} - E_{ea,A} - E_C) + 2t^2/(E_{i,D} - E_{ea,A} - E_C)$$

where $E_{i,D}$ and $E_{ea,A}$ are the ionisation energy and electron affinity of the donor and acceptor parts of the molecule, E_C is the Coulomb energy and t the transfer integral. The second term of the equation, $2t^2/(E_{i,D} - E_{ea,A} - E_C)$, is trivial compared with the first[26] unless, by chance, $E_{i,D}$ and $E_{ea,A}$ are closely matched. Also, for the materials shown in fig. 1, *substituted only at the acceptor end*, the mean intramolecular charge separation and the ionisation energy are assumed to be constant and, thus, the energy of charge transfer is mainly dependent upon $E_{ea,A}$. Values for the phenyldicyanomethane acceptor groups are not available, but as a crude approximation they may be related to the half-wave reduction potentials of TCNQ[28] and its derivatives[28,29] (see table 3). The substituent effect on the transition energy is clearly demonstrated by the progressive hypsochromic shift of the charge-transfer band with increasing reduction potential of the acceptor moiety: λ_{max} (LB film) = 623 nm for the benz analogue; 565 nm for the unsubstituted material; 545 nm for the dichloro and dibromo analogues and 480 nm for the tetrafluoro analogue. Thus, the position of the charge-transfer band may be finely tuned by substitution, for example, in non-linear optical applications, to provide a window at the frequency of the second harmonic.

Non-linear Optical Properties

Previously one of us reported[17] the second-order molecular hyperpolarisability of the pyridinium zwitterion, R-P3CNQ, which has a theoretical coefficient of $\beta = 1270 \times 10^{-30}$ cm^5 esu^{-1} at 1.064 μm. This exceptionally high value may be contrasted with 0.45×10^{-30} cm^5 esu^{-1} for urea[30] (against which most materials are compared), 200×10^{-30} cm^5 esu^{-1} for hemicyanine dye[9] and 1000×10^{-30} cm^5 esu^{-1} for the unstable merocyanine Gedye.[31] On a theoretical basis the quinolinium zwitterions should possess high second-order coefficients and in this work we report the non-linear optical data of $C_{16}H_{33}$-Q3CNQ LB films. SHG studies were carried out using an apparatus similar to that described by Allen and Murray.[32] The films were irradiated with a Q-switched Nd : YAG laser at an incident angle of 45° and a *Y*-cut quartz plate was used as the reference material.

The SH intensity of the $C_{16}H_{33}$-Q3CNQ film is compared in fig. 5 with the data obtained for a hemicyanine dye† which has a high β (see above). The hemicyanine films are *Y*-type and the centrosymmetric structure causes the bulk susceptibility of the bilayer (and all even numbers of layers) to be zero. In contrast, the $C_{16}H_{33}$-Q3CNQ films are *Z*-type and, consistent with theory, the SH intensity increases quadratically with the number (n) of LB layers (fig. 5). The mean reduced SH intensity, $I_{(n)}/n^2$, is similar to that observed for the hemicyanine monolayer. The result is very encouraging and the data corroborate the *Z*-type structure of the $C_{16}H_{33}$-Q3CNQ films.

Unlike the hemicyanine[9] and merocyanine Gedye[8] films, there is no need to alternate the chromophore layer with a spacer layer to realise a non-centrosymmetric alignment for SHG. Also, for the series of zwitterions reported here [and in ref. (17)] the tunability of the intramolecular charge-transfer band may be exploited to optimise the behaviour.

The results of the SHG study were reported, in part, at the Materials Research Society Fall Meeting, Boston.[20]

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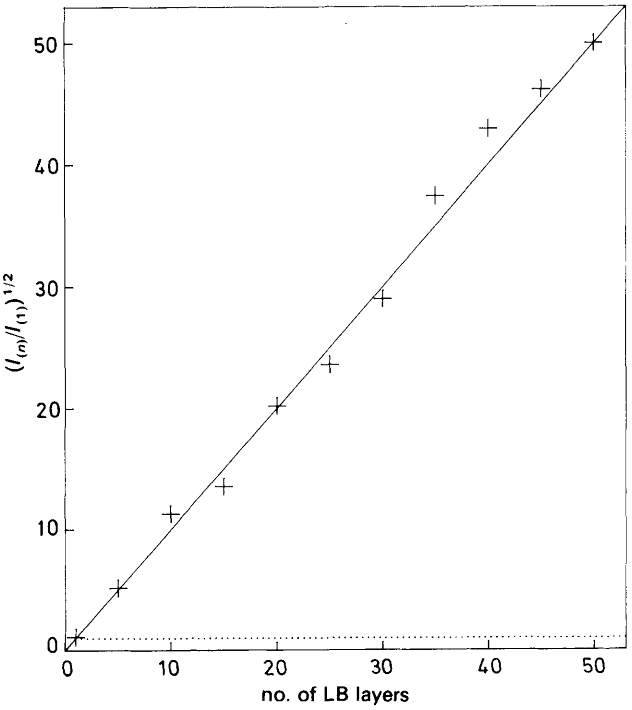

Fig. 5. Square root of the normalised SH intensity of $C_{16}H_{33}$-Q3CNQ *vs.* the number of LB layers (+). The dotted line corresponds to the maximum value obtained for multilayer films of the hemicyanine dye.

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† *E*-1-docosyl-4-{2-(4-dimethylaminophenyl)ethenyl}pyridinium bromide.

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Note added in proof:

Four *R*-Q3CNQ zwitterions described in this work have recently been reported (N. A. Bell, R. A. Broughton, J. S. Brooks, T. A. Jones, S. C. Thorpe and G. J. Ashwell, *J. Chem. Soc., Chem. Commun.*, 1990, 325). G.J.A. is listed as a co-author, but was not informed of this prior to publication. G.J.A. will produe an Addendum to be published in *J. Chem. Soc., Chem. Commun.*