The synthesis and non-linear optical properties of (*N*-alkylpyrrol-2-yl)squaraine derivatives. Part 1

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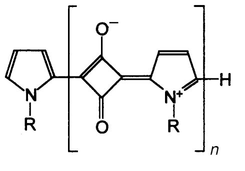
The synthesis of a soluble poly(pyrrolylsquaraine) was achieved by *N*-alkylation of the pyrrole nucleus with 1-bromooctadecane and subsequent condensation with squaric acid. Bis(1-octadecylpyrrol-2-yl)-squaraine was also produced and found to exist in a variety of inseparable isomeric forms. When deposited as Langmuir–Blodgett monolayers on hydrophilic substrates, these dyes exhibit second harmonic generation (SHG) with $d_{\mathrm{eff}} = 0.5 \pm 0.1$ pm V^{-1} for both. For comparison, bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine was synthesised and revealed a higher SHG activity of $d_{\mathrm{eff}} = 1.8 \pm 0.2$ pm V^{-1}. Poly(1-octadecylpyrrolylsquaraine) is the first alternating donor–acceptor polymer to give SHG.

Introduction

3,4-Dihydroxycyclobut-3-ene-1,2-dione, commonly known as squaric acid, condenses with two molar equivalents of an electron rich aromatic compound, such as an aniline or phenol,[1] to form intensely coloured squaraine dyes. Bis(anilino)squaraines and bis(benzothiazolium)squaraines, in particular, have been studied for a whole range of photophysical applications. The most recent discovery has been that Langmuir–Blodgett monolayers of the bis(anilino)squaraines deposited on hydrophilic glass substrates exhibit a strong second-order non-linear optical (NLO) effect when irradiated with near-infrared light.[2,3] When such electron rich compounds reveal two active sites, polycondensation can take place and polysquaraines are formed.[4,5] These alternating donor–acceptor polymers have been studied as small-band-gap semiconducting polymers with band gaps reported down to 0.5 eV and conductivity levels of 10^{-5}–10^{-9} S cm^{-1}.

Squaric acid is also known to condense with pyrroles whereby the reaction occurs over the highly reactive α-position to give violet dyes.[6] If both α-positions are free then blue to blue–green insoluble polymers are formed, **1**, for which first reports[6] gave $n = 3$ repeating units. More recent synthetic methods in butanol,[7] as opposed to originally ethanol, give a compound with the chemical formula **2**, where $n > 5$. The product was also found to have one associated water molecule per squaraine unit. This dark blue polymer was partially soluble in dimethylformamide (DMF) and *m*-cresol while χ^3 measurements were made as 10% dispersions in polycarbonate. Apart from this and fluorescence studies on bis(4-acetyl-3,5-dimethylpyrrol-2-yl)squaraine,[8,9] no other physical properties, excluding the common chemical analyses supporting the synthetic work, have been reported on either bis(pyrrolyl)squaraine or poly(pyrrolylsquaraines). Insolubility of the polymer system has been a large deterrent for such studies. However, introducing a long alkyl chain to a polyarylene backbone is a general route to enhance the solubility of this material.[10] *N*-Substitution of the pyrrole with an octadecyl chain not only aids solubility but it also allows possible deposition onto solid substrates using the Langmuir–Blodgett (LB) technique. For this, chloroform or the like are the preferred solvents.



where R = H, CH_3

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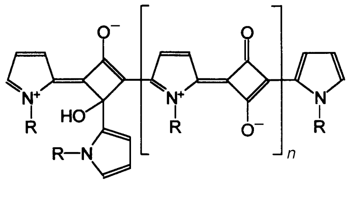
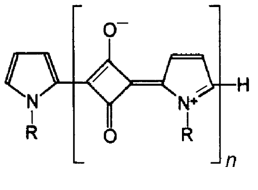


where R = CH_3

2

In this current work we report the synthesis and second-order NLO intensity of chloroform soluble poly(1-octadecylpyrrol-2-ylsquaraine) **3** as well as the separation, identification and subsequent second-order properties of bis(1-octadecylpyrrol-2-yl)-squaraine **4**, and its comparison with bis(3,5-dimethyl-1-octadecylpyrrole-2-yl)squaraine **5**. Poly(1-octadecylpyrrol-2-



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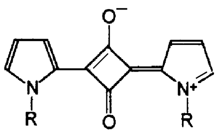

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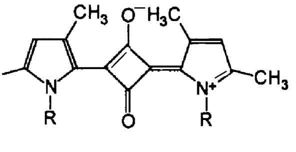
where R = $C_{18}H_{37}$



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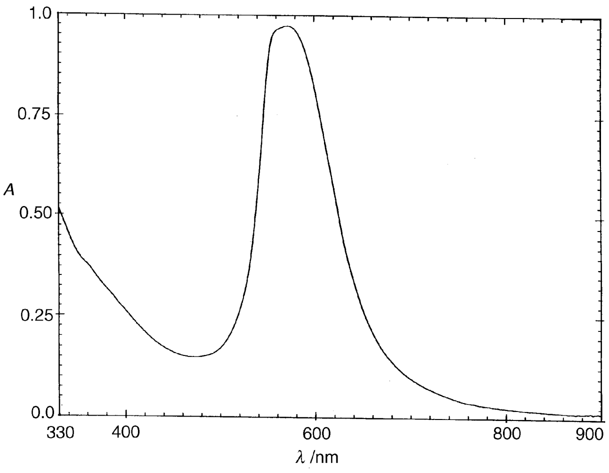


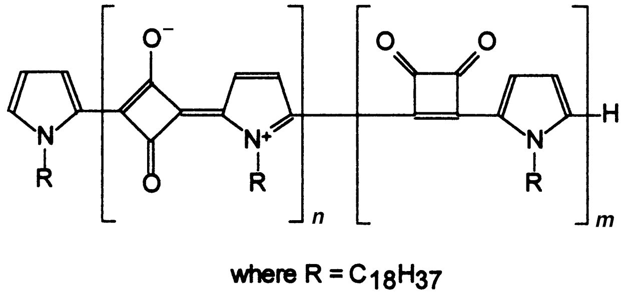
Fig. 1 Visible absorption spectrum of poly(1-octadecylpyrrol-2-ylsquaraine) **3a** in chloroform (1.8×10^{-4} M)

ylsquaraine) represents the first example of second harmonic generation (SHG) from a centrosymmetric, alternating donor–acceptor polymeric chain.

Results and discussion

Poly(1-octadecylpyrrol-2-ylsquaraine)

Fig. 1 shows the visible absorption spectrum of poly(1-octadecylpyrrol-2-ylsquaraine) in chloroform. Interestingly, two maxima are observed at 562 and 574 nm. Infrared analysis of this compound indicated that the polymer was primarily a 1,3-substituted squaraine system (as shown for **3**) from a strong $\nu_{C\text{-}O}$ peak at 1620 cm^{-1}; but a weak $\nu_{C=O}$ peak at *ca.* 1750 cm^{-1} also indicated that a percentage of 1,2-squarate substitutions were present, hence the chemical formula for this compound becomes **3a**. Generally, 1,2-squarates are produced by using acid-catalysed squaryl dichloride instead of squaric acid although the polycondensation of squaric acid with *N*-alkylcarbazole[7] is another example where 1,2-squarate units (36–43%) were formed. Gel permeation chromatography (GPC) results for **3a** showed a broad distribution of polymer chain lengths with repeat unit lengths of *ca.* 5–20. As is typical for a polymeric system, the solution ^{1}H NMR spectrum for **3a** showed a broad multiplet of peaks where the expected proton shifts usually occur but a comparison of the integration value for the end pyrrole protons (δ_H = 7.5–8.1 ppm) with the integration values of both the chain pyrrole protons (δ_H = 6.0–7.2 ppm) and the NCH_2 protons (δ_H = 3.0–5.0 ppm) suggested an average repeat length of *ca.* 35. Thus the average polymer chain lengths are only in the order of 10s of units as opposed to 1000s or 10 000s for other more common polymers. Differential scanning calorimetry (DSC) results for the bulk polymer gave a melting range of 29–89 °C.



3a

A representative surface–area isotherm (π–*A* curve) for **3a** is shown in Fig. 2, where the molecular areas are distinctly smaller than expected for LB monolayers. Atomic force microscopy (AFM) studies of Langmuir films of **3a** deposited on hydrophilic substrates showed that islands of squaraine bilayers were formed on top of the first monolayer. The film thicknesses were determined by AFM to be 16 ± 3 Å for the monolayer and 39 ± 2 Å for the bilayer islands. The islands showed no sharp edges yet distinct steps could clearly be recognised. Such evidence suggests that **3a** does not form a typical ordered LB monolayer even with the added octadecyl chains. For this reason the *N*-alkyl chains are only required to enhance solubility and there may be a relationship between the alkyl chain length and inherent solubility. This will be the subject of further studies.

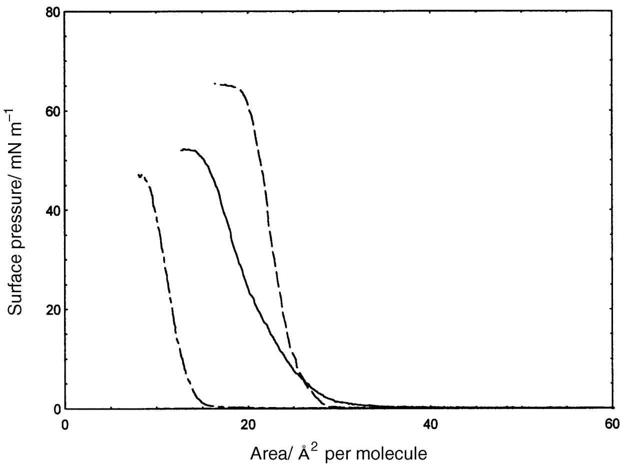


Fig. 2 π–*A* isotherms for poly(1-octadecylpyrrol-2-ylsquaraine) **3a** (– – – –), bis(1-octadecylpyrrol-2-yl)squaraine **4**+ (——) and bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine **5** (– – –)

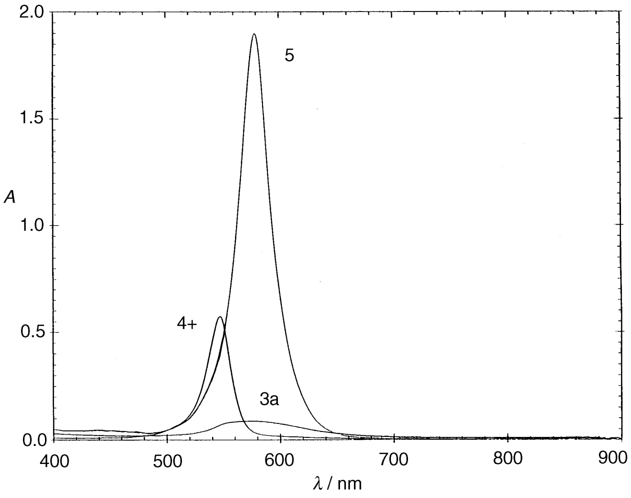


Fig. 3 Visible absorption spectra of poly(1-octadecylpyrrol-2-ylsquaraine) **3a,** bis(1-octadecylpyrrol-2-yl)squaraine **4**+ and bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine **5** in chloroform (1×10^{-5} M)

Bis(1-octadecylpyrrol-2-yl)squaraine and bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine

In our initial attempts to synthesise compound **3** it was noticed that the reaction colour started as red–violet, slowly darkening to the required blue. This reaction was then repeated in ethanol, which as expected increased the reaction time and prolonged the presence of the red–violet phase. For this reason a reaction time of 2 h in ethanol was used to produce the dye responsible for this phase. Subsequently, this dye was identified as bis(1-octadecylpyrrol-2-yl)squaraine whose absorption spectrum is shown in Fig. 3. Bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine **5** was chosen for comparison with bis(1-octadecyl-

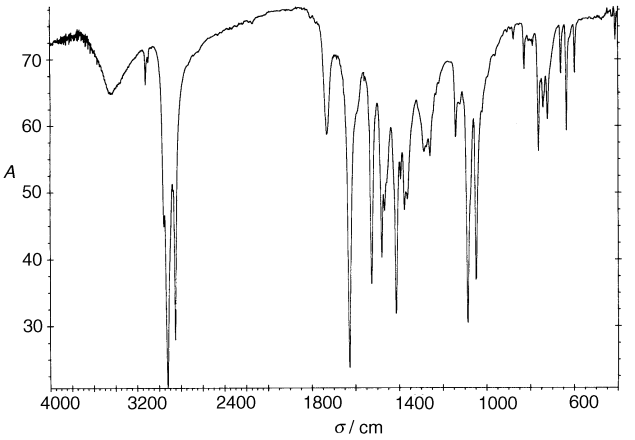


Fig. 4 IR spectrum of bis(1-octadecylpyrrol-2-yl)squaraine **4**+

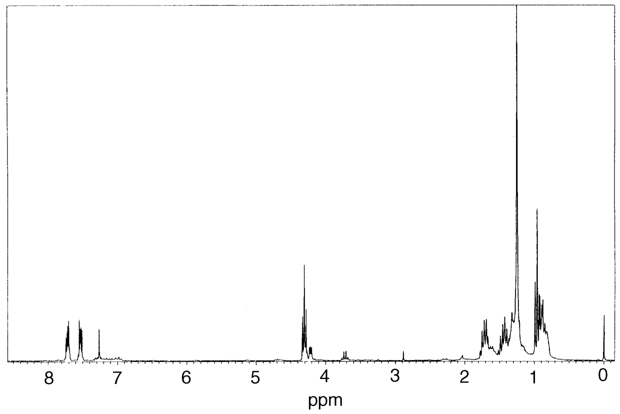
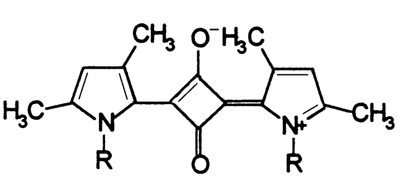
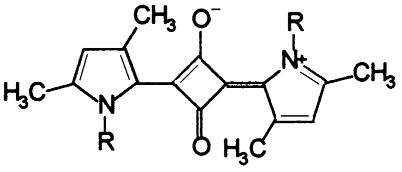


Fig. 5 Solution ^{1}H NMR of bis(1-octadecylpyrrol-2-yl)squaraine **4**+

pyrrol-2-yl)squaraine because it is one of the simplest known bis(pyrrolyl)squaraines. However, as well as the apparent absorption intensity differences (Fig. 3) the two dyes have very different aggregational states. Certain squaraine dyes are known to exist both in solution and solid-state as isomers.[11] Yet, even though **5** has two possible conformations (*cis* and *trans*), it

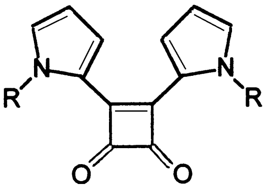


cis



trans

most likely exists only in the *trans* form due to steric hindrance of the 4-methyl groups and *N*-alkyl chains around the squarate oxygens. Both the ^{1}H and ^{13}C NMR spectra for **5** indicate only one conformation. Compound **4** however has no such restraints and can freely exist in either form. Additionally, the IR spectrum of **4** (Fig. 4) indicates the presence of the 1,2-squarate **4a**



where R = $C_{18}H_{37}$

4a

with a $\nu_{C=O}$ peak at 1750 cm^{-1}, adjacent to the expected ν_{C-O} stretch at 1625 cm^{-1}. This concurs with the presence of the 1,2-squarate units in the polymer system **3a**. Unfortunately, neither the different isomers nor the 1,2-squarate form could be isolated. This, coupled with the presence of a single symmetrical absorption peak, indicates that this red–violet fraction is a complex, or possibly aggregated micelles of both **4** and **4a**. An inspection of the ^{1}H NMR spectrum (Fig. 5) of the fraction reveals that the alkyl chain peak areas are not what would usually be expected. A possible reason for this phenomenon could be that CH_2 protons are being both shielded and deshielded due to ring current effects, as in the case of [1.8]paracyclophane.[12] This could certainly be the case if the alkyl chains are assembling as micelles. However, this theory is still only speculative and requires further study. Not knowing the exact form in which **4** and **4a** exist does not detract from the major purpose of this work, hence, this mixture of materials will for the rest of this report be referred to as **4**+.

Differential scanning calorimetry results for **4**+ and **5** are also interesting and indicate very different thermal properties. When first heated, **4**+ underwent a solid–solid endothermic phase change from 31–42 °C during which the sample reduced in size. The sample then remained stable until 57 °C where it started shrinking again, then melting *ca.* 67–75 °C. Upon cooling and reheating the sample melted at the first phase change (31–42 °C). Compound **5** upon heating released a small amount of energy (exothermic) from 46–61 °C with no visible change. The sample then shrank and melted from 67–90 °C. This process was repeatable upon cooling and reheating. It has already been noted that **4**+ exists in a variety of states. What is not currently known is how these states change or even undergo polymerisation upon heating, which may be the reason for differing thermal characteristics during the second scan.

The surface pressure–area isotherms (π–*A* curves) for **4**+ and **5** are shown in Fig. 2. For bis[4-(*N*-methyl-*N*-octadecylamino)-phenyl]squaraine both the experimental and calculated area per molecule are *ca.* 60 and 59.5 Å^2 mol^{-1} respectively,[13] indicating that the area per mol characteristics are dependent on the area of the chromophores. Compounds **4**+ and **5**, however, compress to cross-sectional molecular areas which are closer to those of long alkyl chains (*ca.* 20 Å^2 mol^{-1}). A possible reason for this is the fact that pyrrole squaraines have such an affinity for water, commonly precipitating with one water molecule per $-C_4O_2-$ central ring.[6,7] Attempts to spread a 0.1 mg ml^{-1} solution of bis(3,5-dimethylpyrrol-2-yl)squaraine in chloroform onto a water subphase resulted in the chromophore being dispersed into the subphase. This would further indicate that the chromophores of **4**+ and **5** could sink into the subphase allowing the surface pressure to be dependent on the compressed alkyl chains. Preliminary observations suggest that the subsequently deposited monolayers are drawn out of the subphase containing a significant amount of water. Thus, any attempts to lower the substrate back into the subphase immediately after deposition result in the monolayer pealing off the substrate back onto the subphase. Drying of the films can be seen visually on monolayers of **5** which initially appear red–violet but change to purple–blue within a few minutes of deposition. Table 1 shows that **4**+ and **5** are slightly solvatochromic with wavelength shifts of only a few nanometres.

Grazing incidence X-ray diffraction (GIXD) experiments on monolayers of **4**+ and **5** showed that **4**+ is present as randomly orientated, crystalline stacks, with no apparent orientation rela-

Table 1 Absorption maxima, ADXPS determined thicknesses and second-order non-linear optical susceptibilities for poly(1-octadecylpyrrol-2-yl-squaraine) **3a**, bis(1-octadecylpyrrol-2-yl)squaraine **4+** and bis(3,5-dimethyl-1-octadecylpyrrol-2-yl) squaraine **5**

	λ_{max}/nm		Thickness data/Å				
Dye	EtOH	$CHCl_3$	C	N	O	d_{yzz}/pm V^{-1}	d_{eff}/pm V^{-1}[a]
3a						0.15 ± 0.04	0.5 ± 0.1
4+	542.5	548.5	0.6 ± 0.6	21 ± 1	16 ± 2	0.7 ± 0.2	0.6 ± 0.1
5	573.0	579.0	19 ± 1	4 ± 1	16 ± 2	2.1 ± 0.4	2.0 ± 0.2

[a] For s polarised laser light and p polarised second-harmonic signal the experiment is sensitive to the susceptibility d_{yzz}. If both beams are p polarised then various non-linear optical coefficients contribute to an effective susceptibility. The absolute value of the effective susceptibility is given here for an angle of incidence of 45°.

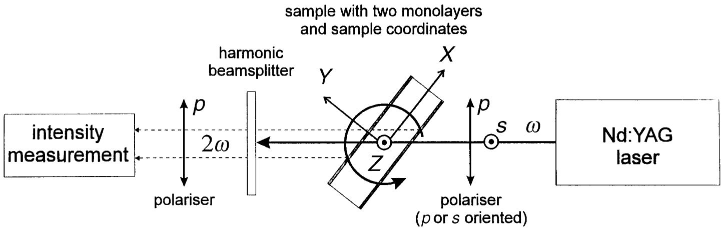


Fig. 6 Experimental geometry used for the measurement of optical nonlinearities

tionships to either the silicon surface or to the other stacks. In contrast to this, **5** forms a smooth, amorphous monolayer with average structure from the alkene groups observed at a *d*-spacing of 5.4 Å. Both films were then non-destructively depth profiled using angle dependent X-ray photoelectron spectroscopy (ADXPS) with a view to structural analysis of the monolayers. For both films XPS survey spectra showed only the presence of C, N, O and Si. The Si sweep showed two distinct peaks due to an elemental Si and a SiO_2 surface component. The isolation of the elemental and oxide components of the Si signal provided a useful check on the fitting algorithms in ensuring that sensible SiO_2 thicknesses were derived.

For the layered systems dealt with in this study, there were four layers considered. These were given nominal compositions for the purposes of calculating average electron densities and photoelectron penetration depths. These layers are described as (*a*) the alkane group, represented as $(CH_2)_n$, (*b*) the squaraine head-group, represented as $C_{12}H_4N_2O_2$, (*c*) the oxidised Si surface—the true substrate for the monolayer—and (*d*) an infinitely thick elemental Si layer. Thicknesses found for dyes **4+** and **5** are listed in Table 1. In each case there was 100% coverage of the surface by the monolayer. The larger thickness for the nitrogenous layer found in **4+**, and the very thin carbonaceous overlayer implies that the head-group is isotropically distributed throughout the organic layer, indicating that the surface is uneven. AFM studies on monolayers of **4+** confirm that the film is layered (as in **3a**), with the total film thickness being determined by this technique as 28 ± 2 Å. Again the layering is in the form of regular terraces with the most frequent step height being two but both one and three layer steps are also observed. AFM additionally confirmed that there was 100% coverage of the surface by the organic. The observed layering would certainly explain the smaller than expected molecular areas displayed in the π–A isotherm for this dye. In contrast, dye **5** has discrete C and N containing layers with the nitrogenous layer beneath the surface C layer. The thickness of the total organic monolayer for **5** is consistent with that of octadecane-type tail groups, *e.g.* 21.93 Å for stearic acid.[14] Furthermore, a thickness of 16 Å was found in both cases for the SiO_2 layer, which agrees with other published values for surface oxide layers on silicon.[15,16]

Second harmonic generation

The optical nonlinearities of the three films on hydrophilic substrates were measured using the Maker-fringe technique[17] and are listed in Table 1. By this technique the sample (experimental geometry indicated in Fig. 6) was exposed to a laser beam (frequency ω) with defined polarisation (p or s polarisation). In contrast to the bare substrate, films of **3a**, **4+** and **5** generated frequency-doubled light (2ω). The signals from each monolayer, either side of the substrate, interfered both constructively and destructively with each other as the sample was rotated (as indicated). The optical non-linearities of each sample were calculated from the second-harmonic intensities in dependence on the rotational angle and on the polariser orientations. The sample symmetry was proved to be $C_{\infty v}$ with the polar axis normal to the surface. The non-linearities of the samples were calibrated against a quartz standard with an optical susceptibility of $d_{11} = 0.4$ pm V^{-1}.[18] Additionally, relative permittivities for films of **4+** and **5** were not determined. For our calculations we used the interface model of Mizrahi and Sipe[19] which neglects the refractive indices of the monolayer for the calculation of the electric fields at the surface. The non-linearities of the three dyes are remarkably high for centrosymmetric species, such as the symmetrically substituted squaraines, with the second-harmonic light intensity increasing quadratically with increasing susceptibility.

Efficient SHG can usually be attributed to π-electron rich polar molecules that act as electric–dipole oscillators. The polymer backbone in **3a**, however, possesses no overall polarisation, *i.e.* it is centrosymmetric, although we have been unable to determine the contribution, if any, from the minor amounts of the 1,2-squarate units. A recent paper[20] has demonstrated that unsymmetrically substituted 1,2-squarates possess second-order susceptibilities but in the case of **3a**, and **4+**, all the 1,2-squarates are symmetrical. Hence, the SHG in this case could be due to a polarisation of the aromatic backbone by the underlying hydrophilic substrate. For highly extended charge distributions, however, the electric–dipole approximation may be invalid and the optical non-linearities would be due to magnetic–dipole or electric–quadrupole interactions. In such a scenario noncentrosymmetry would not be required for SHG. Closer investigation of the origin of the optical non-linearities for these systems looks highly interesting and promising. If the SHG is due to electric dipoles, the non-linearities of a monolayer could be influenced by the selection of the underlying material. LB film devices could be developed, for example, with alternating layers of squaraines and polar materials. If, on the other hand, the optical non-linearity is due to magnetic–dipole or electric–quadrupole interactions, devices could be developed that do not require a polar order of the molecules.

Conclusions

Through a variety of chemical and instrumental techniques we have shown in this work that the previously reported poly(pyrrolylsquaraines) first form as bis(pyrrolyl)squaraine dimers and that these dimers can subsequently be synthesised. The fact that pyrrolylsquaraines have a sustained dimeric form, when synthesised in a low boiling point solvent, may be due to the characteristic resonant nature of these dyes. The α-position in pyrrole is the favoured site for electrophilic substitution due to the generation of a negative charge which is stabilised by induction from the electronegative nitrogen atom.[21] After two pyrroles have condensed with squaric acid the resonance of the dye affords both nitrogen atoms to be partially electropositive, balancing the resultant zwitterionic state of the dye, and hence disrupting the possibility of a sustained negative charge on the free α-positions. Therefore, higher temperatures or prolonged reaction times are required for successful polymerisation. Furthermore, we have also shown that poly(pyrrolylsquaraines) can be made soluble in chloroform by the *N*-alkylation of the pyrrole nucleus with octadecane. This therefore provides a suitable solvent for LB purposes as well as other thin film techniques such as dip-coating and spin-coating. Comparisons between bis(pyrrolyl)squaraine and the known bis(3,5-dimethylpyrrol-2-yl)squaraine suggest that in their *N*-octadecyl alkylated forms these two chemically similar dyes have very different solid-state and solution properties which, in turn, are directly related to their aggregational states.

Experimental

1-Octadecylpyrrole was synthesised using the following procedure: a solution of pyrrole (2.0 g, 30 mmol) in dry toluene (25 cm^3) was added under nitrogen to a stirred suspension of potassium *tert*-butoxide (4.0 g, 36 mmol) and dibenzo-18-crown-6 (300 mg) in dry toluene (75 cm^3). After 1 h, 1-bromooctadecane (8.0 g, 24 mmol) in dry toluene (25 cm^3) was added and the resultant mixture refluxed for 12 h. Upon cooling, water (50 cm^3) was added and the organic phase separated after which the aqueous phase was extracted with toluene (3 × 25 cm^3). The combined organic phases were then washed three times with water and then dried using anhydrous magnesium sulfate. After removal of toluene the crude 1-octadecylpyrrole was purified by column chromatography (Al_2O_3) using light petroleum (bp 40–60 °C) (yield 8.6 g, 90%). δ_H(250 MHz; $CDCl_3$; $SiMe_4$) 0.90 (3 H, t, CH_3), 1.25 (30 H, br s, CH_2), 1.75 (2 H, quintet, NCH_2CH_2), 3.86 (2 H, t, NCH_2), 6.13 (2 H, dd, 3-H), 6.65 (2 H, dd, 2-H).

Poly(1-octadecylpyrrol-2-ylsquaraine) was synthesised according to the literature procedure for the synthesis of poly(1-methylpyrrol-2-ylsquaraine)[7] by refluxing equimolar amounts of squaric acid (200 mg, 1.75 mmol) and 1-octadecylpyrrole (560 mg, 1.75 mmol) in butan-1-ol (50 cm^3) for 2 h. The crude product was collected by filtration upon cooling of the reaction solution and was purified by column chromatography (Al_2O_3) first by using incremented amounts of chloroform in light petroleum (bp 40–60 °C) to separate unreacted 1-octadecylpyrrole as well as short chain oligomeric materials, followed by THF to collect the dark blue product (yield 334 mg, 48%).

Bis(1-octadecylpyrrol-2-yl)squaraine was synthesised by refluxing squaric acid (200 mg, 1.75 mmol) and 1-octadecylpyrrole (560 mg, 1.75 mmol) in ethanol (50 cm^3) for 2 h. The crude product was collected by filtration upon cooling of the reaction solution and was purified by column chromatography (Al_2O_3) using incremented amounts of chloroform in light petroleum (bp 40–60 °C) with the major red–violet fraction being collected (yield 340 mg, 43%) (Found: C, 80.8; H, 11.4; N, 3.9%. $C_{48}H_{79}N_2O_2$ requires C, 80.5; H, 11.1; N, 3.9%; *M*, 716); *m/z* 717 (MH^+, 100%) and 739 (MNa^+, 50). GPC results showed this material to have a single molecular mass *ca.* 700.

2,4-Dimethyl-1-octadecylpyrrole was made using the same procedure (and molar amounts) as for the production of 1-octadecylpyrrole (yield 8.8 g, 85%). δ_H(250 MHz; $CDCl_3$; $SiMe_4$) 0.87 (3 H, t, CH_3), 1.25 (30 H, br s, CH_2), 1.66 (2 H, quintet, NCH_2CH_2), 2.05 (3 H, s, 2-CH_3), 2.16 (3 H, s, 4-CH_3), 3.68 (2 H, t, NCH_2), 5.67 (1 H, s, 3-H), 6.33 (1 H, s, 5-H).

Bis(3,5-dimethyl-1-octadecylpyrrol-2-yl)squaraine was synthesised according to the literature procedure for the synthesis of bis(3,5-dimethylpyrrol-2-yl)squaraine[6] by refluxing squaric acid (200 mg, 1.75 mmol) and 2,4-dimethyl-1-octadecylpyrrole (1.2 g, 3.5 mmol) in ethanol (50 cm^3) for 2 h and was purified by column chromatography (Al_2O_3) using incremented amounts of chloroform in light petroleum (bp 40–60 °C) (yield 582 mg, 43%) (Found: C, 80.6; H, 11.6; N, 3.6%. $C_{52}H_{88}N_2O_2$ requires C, 80.7; H, 11.5; N, 3.6%; *M*, 772); ν_{max}/cm^{-1} 1610 (C–O); δ_H(250 MHz; $CDCl_3$; $SiMe_4$) 0.87 (6 H, t, CH_3), 1.22 (60 H, br s, CH_2), 1.55 (4 H, br m, NCH_2CH_2), 2.30 (6 H, s, CH_3), 2.63 (6 H, s, CH_3), 4.63 (4 H, t, NCH_2), 6.05 (2 H, s, H); δ_C(62.9 MHz; $CDCl_3$) 176.75 (0), 175.86 (0), 146.50 (0), 138.88 (0), 127.14 (0), 117.81 (1), 47.07 (2), 32.13 (2), 31.95 (2), 29.92 (2), 29.87 (2), 29.84 (2), 29.79 (2), 29.66 (2), 29.57 (2), 26.85 (2), 22.89 (2), 15.31 (3), 14.32 (3), 13.62 (3); *m/z* 773 (MH^+, 100%) and 795 (MNa^+, 20).

IR spectra were recorded as pressed KBr disks on a Nicolet 205 FTIR spectrometer. UV–VIS measurements were made on a Shimadzu UV-2100 spectrometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 NMR spectrometer. Electrospray mass spectra were recorded in positive ion mode on a Micromass Platform mass spectrometer. Samples for gel permeation chromatography were run on a Spectra Physics Model SP 8100 attached to a Kronwald UV-detector and a Waters Model R401 differential refractometer and were calibrated *versus* polystyrene. Samples for differential scanning calorimetry were run on a Perkin-Elmer DSC 1B heated at 8 °C min^{-1} from 20–300 °C. AFM measurements were made on a Digital Instruments Nanoscope III. Images were obtained using both the tapping and contact modes while thicknesses were obtained using the contact mode with applied forces of *ca.* 10^{-8} N.

GIXD experiments were carried out using the BIGDIFF facility at BL20B at the Photon Factory, Tsukuba, Japan. The patterns were recorded on image plates at a wavelength of 1.116 34 Å with an incident angle of 0.1375°, as described by Foran *et al.*[22] The electron spectrometer employed for ADXPS studies was a Physical Electronics Industries PHI Model 560, using a model 25–270 AR Cylindrical Mirror Analyser (CMA).[23] This double-pass CMA with rotatable drum device is advantageous because the sample–analyser–source geometry remains fixed, thus avoiding errors due to misalignment which may occur by tilting the sample.[24] Multiple sweeps of the 1s peaks of C, N and O with binding energies of 285.0, 398.0 and 532.0 eV respectively from the monolayers, and the Si 2p peaks at 101.8 and 105.4 eV from the substrates were used for the analyses. Spectra relative to the sample surface were collected at 87.7, 69.9, 51.5 and 34.5° for dye **4**+ and 87.7, 34.5 and 7.7° for dye **5**. Integrated intensities were normalised for instrumental sensitivity factors. Mean free paths for the photoelectrons through each of the media were calculated according to the formulae given by Ashley.[25] Using functions of the form given by Marshbanks *et al.*,[15] a set of functions describing the angle-dependent relative intensities of each of the C, N, O and Si signals were derived for dye **4**+ and dye **5**-type monolayers. A trial-and-error least-squares fitting of the observed data was undertaken, using free variables of elemental scale factors, percent coverage of the Si surface and thickness of each layer.

Surface pressure–area isotherms for compounds **3a**, **4**+ and **5** were run on a Nima Technology, series 2000 Langmuir-Blodgett trough. Compounds **3a**, **4**+ and **5** were spread from chloroform solutions (*ca.* 0.1 mg cm^{-3}) onto a pure water subphase of a custom-built Nima 'Münster' LB trough. LB monolayers were deposited on (*a*) mica for AFM studies, (*b*) both sides of a hydrophilic fused silica substrate and (*c*) hydrophilic (111)-cut silicon wafers for GIXD and ADXPS studies at a compressed surface pressure of 30 mN m^{-1} for compound **3** and 35 mN m^{-1} for compounds **4**+ and **5** on the upstroke by passing the substrate through the floating monolayer at 25 mm min^{-1}. Frequency-doubling experiments were run using a Spectra Physics GCR 190/30 laser at a wavelength of 1064 nm and intensity of 1.5 MW cm^{-2}.

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