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Synthesis, linear & non linear optical (NLO) properties of some indoline based chromophores

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ABSTRACT

A series of indoline- π -acceptor chromophores has been synthesized and the members first hyperpolarizabilities measured to investigate the effect of conjugation length, the use of various substituents and configurational locking on the nonlinear optical response. While increasing the length of the conjugated interconnect enhances the optical nonlinearity, ring locking was found to have little effect, although this is thought to be due to the electronic properties of the substituent groups, rather than structural factors. Nonetheless, all of the compounds were found to have high molecular hyperpolarizabilities with values of up to 1485×10^{-30} esu when measured in chloroform at 1300 nm, findings which confirm that these chromophores are excellent candidates for further study. X-ray crystallographic studies were performed on three of the compounds and bond length alternation values obtained; these were found to correlate well with the observed molecular responses.

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1. Introduction

Organic nonlinear optical (NLO) chromophores containing donor(D) $-\pi$ -acceptor(A) units have been widely reported in the literature as the enabling materials for a range of photonic devices [1-4]. The fundamental measure of a molecule's NLO response, and therefore potential for incorporation into NLO materials, is its figure-of-merit, μ , β , where μ is the molecular dipole moment, and β is the first hyperpolarizability. In order to be considered a viable candidate for further study a molecule should have a first hyperpolarizability greater than approximately 500 \times 10^{-30} esu and an overall figure-of-merit greater than 5000×10^{-48} esu. Furthermore, in order to obtain an optimal and usable electro-optic response, it is necessary to incorporate a high weight percent of a given chromophore into either a host polymer matrix, or by covalently attaching it to a suitable polymer substrate [5–12]. In addition, for a macroscopic NLO response to be observed it is necessary for the molecular dipoles of the embedded chromophores to be aligned acentrically, and this is usually achieved via either contact or corona poling [3]. However, due to the tendency of the dipoles of the active chromophores to relax back to an isotropic state (thereby reducing

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the observed NLO response) it is often necessary to employ techniques such as cross-linking in order to preserve the requisite noncentrosymmetry [6].

Chromophores with highly polar (i.e., zwitterionic) ground states often exhibit poor solubilities as well as a tendency to readily form aggregates. This is clearly problematic when considering their use in NLO materials as this means they cannot be incorporated into host polymers at high loadings. Furthermore, the presence of significant aggregation will lower the overall poling efficiency of the final NLO material as well as increase the propensity for deleterious post-poling relaxation of the aligned dipoles. As a result, further structural modifications are often required to the active chromophores to minimise aggregation and the inclusion of bulky, "arene-rich" substituents has been shown to be particularly effective in achieving this, thereby greatly increasing the observed macroscopic response in NLO materials [8].

We have previously reported a synthetic methodology [13-17] that allows entry to a number of high figure-of-merit NLO chromophores with aromatisable donors, (e.g., 1,4-dihydropyridinylidene, 1,4-dihydroquinolinylidene), and containing the powerful acceptor 4,5,5-trimethyl-3-cyano-2(5*H*)-furanylidenepropane dinitrile (TCF) e.g., compounds **1** and **2**. While this approach allowed for ease of synthesis and for a controlled increase in the extent of conjugation in the molecules, the resultant "parent" merocyanines are prone to significant amounts of aggregation [16], and this is due to their highly

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polar, zwitterionic ground states. Evidence for H-aggregation in these compounds was routinely observed via the appearance of a high energy shoulder when UV–Vis absorption spectra were obtained in solvents of low polarity such as dioxane and chloroform. Given that the dielectric constants of these solvents resemble those found for polymer systems, *viz.* ε <10, this is clearly problematic as it suggests these molecules will resist alignment and be prone to relaxation after poling.



As a continuation of this work, we describe here further developments to our synthetic methodology, and extend the series to include chromophores with a *non-aromatisable* indoline donor group. Furthermore, we will also discuss structural modifications that are designed to increase their NLO figure-of-merit – these include ring locking of the π -conjugated system along with the incorporation of bulky substituents, e.g., diphenyl groups, onto this central ring system. In addition, we have substituted a halogen atom in middle of the conjugated interconnect with a variety of substituents in order to assess the impact from both a steric and electronic point of view.

2. Experimental

2.1. Reagents and procedures

Commercially available reagents were obtained from Aldrich and were used without additional purification. The solvents used were of analytical grade and were also used without further purification. Column chromatography was carried out using gravity feed column techniques on Merck silica gel type 9385 (230–400 mesh) with the stated solvent systems. Analytical thin-layer chromatography (TLC) analyses were performed on pre-coated plates (Merck aluminium sheets, silica gel 60F 254, 0.2 mm). Visualisation of compounds was achieved by illumination under ultraviolet light (254 nm).

2.2. Measurements and instrumentation

Melting points were recorded with a EZ-Melt automated melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were recorded on a Bruker AVANCE 300 MHz or 500 MHz spectrometer and proton multiplicities are defined by the usual notations. Accurate mass measurements were made on a Micromass Q-Tof Premier Mass Spectrometer operating in the positive ion mode. The UV-Visible (UV-Vis) absorption spectra were recorded by a Perkin-Elmer Lambda 900 spectrometer at room temperature. Hyper-Rayleigh scattering (HRS) measurements were conducted at 1300 nm for all of the compounds. For these measurements a tsunami-pumped OPO (model OPAL, Spectra-Physics) was used. The HRS measurements of compounds 7–9, 17–18 and 22–25 were performed in chloroform. Due to their limited solubility in chloroform, the HRS measurements of compounds 26-28 were conducted in dimethylformamide (DMF). The dipolar compound Disperse Red 1 (DR1, $\beta_{zzz} = 54 \times 10^{-30}$ esu in chloroform) was used

as external reference. Additional HRS measurements for compound 7 were conducted using a 800 nm fs system and using a series of solvents with a broad range of dielectric constants, (ε) ; (DMSO, ε = 47; DMF, ε = 36.7; MeOH, ε = 32.6 and CHCl₃ ε = 4.81). Crystal violet dissolved in methanol was used as an octupolar external reference ($\beta_{xxx} = 338 \times 10^{-30}$ esu) for the 800 nm measurements. For all of the HRS measurements, a series of dilute solutions were measured and compared to the reference concentration series. To correct for the differences in the solvent between the chromophores and the reference compound, local field correction factors were applied $[(n^2 + 2)/3]^3$ where n is the refractive index of the solvent at the sodium D line, with n(DMSO) = 1.48, n(DMF) = 1.43, n(MeOH) = 1.32 and $n(CHCl_3) = 1.44$. The calculations of the dynamic first hyperpolarizability were performed by taking the ratio of the slopes of the sample and the reference compound. For the dynamic first hyperpolarizability values obtained at 800 nm it is necessary to consider the appropriate tensor components (dipolar versus octupolar geometry) as the reference compound crystal violet is octupolar whereas the chromophores under investigation are dipolar. The static first hyperpolarizability is derived from the simple two-level model as previously described [18,19]. The apparatus and experimental procedures for the femtosecond HRS measurements at 800 nm and 1300 nm are exactly the same as described before [20,21].

2.3. Synthetic methodology

The methods used to synthesis the chromophores are shown in Schemes 1 and 2. Compounds **4**–**6**, **10**, **13**, **14**, **20**, **21** and TCF were prepared according to the literature [15,22].

2.4. General procedure for the synthesis of chromophores **7–9** and **11**

1,3,3-Trimethyl-2-methyleneindoline (**3**) (1.5 eq) and the appropriate acceptor precursor (**4**–**6** or **10**) (1 eq) were dissolved in a mixture of methanol and acetic acid (4:1 ratio). A catalytic quantity of piperidine acetate was then added and the mixture refluxed for 12 h. The solution was cooled to ambient temperature, the product collected by filtration and washed with copious quantities of hot water, followed by 2–3 small portions of cold methanol to afford the crude product as a coloured solid. The chromophore was obtained pure following recrystallization.

2.4.1. 2-{3-[2-(1,3,3-Trimethyl-1,3-dihydroindol-2-ylidene) propenyl]-5H-furan-2-ylidene]malononitrile (7)

Black solid (55%). Recrystallization (ethyl acetate:hexanes, 1:1) afforded a dark green powder, m.p. 254–256 °C. (Found: MNa⁺ *m/z* 405.1694 C₂₄H₂₂N₄O requires MNa⁺ *m/z* 631.2048; $\Delta = 0.7$ ppm). ¹H NMR (500 MHz, *d*₆-DMSO) δ 8.25 (1H, app. s, CH), 7.60 (1H, m, ArH), 7.39–7.43 (1H, m, ArH), 6.30 (1H, d, *J* 15.0 Hz, CH), 6.13 (1H, d, *J* 15.0 Hz, CH), 3.69 (3H, s, N–CH₃), 1.65 (6H, s, 2 × CH₃), 1.58 (6H, s, 2 × CH₃). ¹³C NMR (75 MHz, *d*₆-DMSO) δ 177.4, 174.5, 143.7, 143.3, 142.5, 140.9. 128.4, 125.1, 122.3, 114.3, 111.3, 107.0, 102.1, 95.6, 48.9, 31.2, 26.3. λ_{max} (CHCl₃) 602 nm, log₁₀ ε 5.23.

2.4.2. 2-{3-Cyano-5,5-dimethyl-4-[5-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)penta-1,3-dienyl]-5H-furan-2-ylidene} malononitrile (**8**)

Green powder (68%). Recrystallization (ethyl acetate) afforded a green powder, m.p. 270–272 °C. (Found: MNa⁺ m/z 431.1844 C₂₆H₂₄N₄O requires MNa⁺ m/z 431.1848; Δ = 0.9 ppm). ¹H NMR (300 MHz, d_6 -DMSO) δ 8.12 (1H, t, J 12.0 Hz, CH), 7.88 (1H, t, J 12.0 Hz, CH), 7.58–7.60 (1H, m, ArH), 7.36–7.40 (2H, m, ArH), 7.21–7.27 (1H, m, ArH), 6.47 (1H, t, J 15.0 Hz, CH), 6.26 (1H, d, J



Scheme 1. Synthetic method used to prepare the parent chromophores. Reagents and Conditions. (i). MeOH: Acetic acid (4:1), piperidinium acetate, reflux 12 h.

15.0 Hz, CH), 6.04 (1H, d, *J* 12.0 Hz, CH), 3.59 (3H, s, N–CH₃), 1.70 (6H, s, 2 × CH₃), 1.64 (6H, s, 2 × CH₃). ¹³C NMR (75 MHz, *d*₆-DMSO) δ 176.1, 172.8, 169.2, 152.8, 150.8, 142.7, 140.9, 128.3, 125.4, 124.7, 122.2, 115.2, 114.4, 113.4, 110.9, 107.9, 103.9, 95.1, 48.7, 31.0, 26.9, 26.5. λ_{max} (CHCl₃) 698, log₁₀ ε 5.21.

2.4.3. 2-{3-Cyano-5,5-dimethyl-4-[7-(1,3,3-trimethyl-1,3dihydroindol-2-ylidene)hepta-1,3,5-trienyl]-5H-furan-2-ylidene} malononitrile (**9**)

Green powder (70%). Recrystallization (dichloromethane) afforded a green powder, m.p. 238–240 °C. (Found: MNa⁺ *m/z* 457.1999C₂₈H₂₆N₄O requires MNa⁺ *m/z* 457.2004; Δ = 1.1 ppm). ¹H NMR (500 MHz, *d*₇-DMF) δ 8.01–8.21 (1H, m, ArH), 7.74–7.89 (3H, m, ArH & CH), 7.60–7.71 (2H, m, ArH), 7.40–7.55 (1H, m, ArH), 6.72–6.80 (2H, m, CH), 6.60 (1H, d, *J* 15.0 Hz, CH), 6.40 (1H, d, *J* 12.0 Hz, CH), 3.88 (3H, s, N–CH₃), 1.89 (6H, s, 2 × CH₃), 1.85 (6H, s, 2 × CH₃). ¹³C NMR (125 MHz, *d*₇-DMF) δ 176.8, 171.7, 167.9, 154.0, 150.0, 148.1, 143.5, 141.3, 130.4, 128.9, 128.5, 126.2, 124.5, 122.3, 115.4, 114.7, 114.4, 110.7, 109.5, 104.2, 95.4, 48.9, 30.8, 26.9, 26.1, 25.3. λ_{max} (CHCl₃) 794, log₁₀ ϵ 5.12.

2.4.4. 2-{2-{2-Chloro-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2ylidene)ethylidene]cyclohex-1-enyl}-vinyl}-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**11**)

Green powder (36%). Recrystallization (dichloromethane:hexanes, 2:1) afforded a green solid, m.p. 252–255 °C. (Found: MNa⁺ m/z 661.304 C₄₁H₄₂N₄OS requires MNa⁺ m/z 661.294; $\Delta = 0.4$ ppm). ¹H NMR (300 MHz, d_6 -DMSO) δ 8.29 (1H, d, J 15.0 Hz, CH), 8.15 (1H, d, J 15.0 Hz, CH), 7.60 (1H, d, J 7.5 Hz, ArH), 7.39–7.44 (2H, m, ArH), 7.24–7.30 (1H, m, ArH), 6.27 (1H, d, J 15.0 Hz, CH), 5.92 (1H, d, J 15.0 Hz, CH), 3.69 (3H, s, N–CH₃), 2.67 (2H, m, CH₂), 2.62 (2H, m, CH₂), 1.66 (6H, s, 2 × CH₃), 1.62 (6H, s, 2 × CH₃). ¹³C NMR (125 MHz, d_6 -DMSO) δ 176.9, 167.9, 140.5, 128.5, 126.9, 126.6, 124.0, 122.3, 114.7, 111.5, 106.6, 102.3, 95.5, 48.7, 45.5, 31.4, 27.1, 26.3. λ_{max} (CHCl₃) 802, $\log_{10}\varepsilon$ 5.08.

2.5. General procedure for the synthesis of chromophores **17**, **18**, **24** and **25**

The appropriate dialdehyde **13**, **14**, **20** or **21** (1 eq), and TCF (1 eq) were dissolved in *iso*-propyl alcohol under an argon atmosphere. A catalytic quantity of piperidine acetate was added and the solution was refluxed for 3 h. A solution of 1,3,3-trimethyl-2-methyl-eneindoline (**3**) (1 eq) in *iso*-propyl alcohol was then added and the solution refluxed for a further 3 h. The resultant solution was cooled



Scheme 2. Syntheses of the chromophores containing the either diphenylcyclohexene or *t*-butyl cyclohexene interconnect. Reagents and conditions: (i) X = Cl, POCl₃; X = Br, PBr₃, DMF, DCM, 65 °C, 3 h. (ii) TCF, Piperidinium acetate, IPA, reflux 3 h. (iii) **3**, piperidinium acetate, reflux 3 h. (iv) NaH, DMF, YH.

to room temperature and the precipitated dye filtered off. The coloured powder was washed with copious hot water and a few small portions of cold *iso*-propyl alcohol to yield the crude product as a coloured solid.

2.5.1. 2-[4-(2-{2-Chloro-5,5-diphenyl-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl}-vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**17**)

Olive green solid (30%). Recrystallization (dichloromethane:hexanes, 1:1) afforded an olive green powder, m.p. 260–262 °C. (Found: MNa⁺ m/z 683.2559C₄₃H₃₇N₄OCl requires MNa⁺ m/z 683.2554; $\Delta = 0.7$ ppm). ¹H NMR (500 MHz, d_6 -DMSO) δ 8.35 (1H, d, J 14.5 Hz, CH), 8.14 (1H, d, J 14.5 Hz, CH), 7.59 (1H, d, J 7.6 Hz, ArH), 7.41–7.43 (1H, m, ArH), 7.30–7.35 (5H, m, ArH), 7.24–7.28 (5H, m, ArH), 7.13–7.19 (2H, m, ArH), 6.55 (1H, d, J 14.5 Hz, CH), 6.36 (1H, d, J 14.5 Hz, CH), 3.74 (3H, s, N–CH₃), 3.48 (2H, br. s, CH₂), 3.44 (2H, br. s, CH₂), 1.63 (6H, s, 2 × CH₃), 1.62 (6H, s, 2 × CH₃). ¹³C NMR (125 MHz, d_6 -DMSO) δ 178.6, 168.3, 147.0, 146.7, 146.6, 146.5, 144.9, 143.8, 142.8, 141.1, 128.6, 128.5, 128.1, 126.9, 126.1, 126.0, 125.9, 125.2, 125.1, 122.2, 114.1, 111.4, 106.9, 102.1, 95.9, 48.8, 44.8, 36.8, 36.5, 31.8, 27.3, 26.1. λ_{max} (CHCl₃) 793, log₁₀ ε 5.11.

2.5.2. 2-[4-(2-{2-Bromo-5,5-diphenyl-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl}-vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**18**)

Green solid (33%). Recrystallization (dichloromethane:hexanes, 1:1) afforded a green powder, m.p. 266–268 °C. (Found: MNa⁺ *m/z* 727.2051 C₄₃H₃₇N₄OBr requires MNa⁺ *m/z* 727.2048; Δ = 0.4 ppm). ¹H NMR (500 MHz, *d*₆-DMSO) δ 8.29 (1H, d, *J* 14.5 Hz, CH), 8.17 (1H, d, *J* 14.5 Hz, CH), 7.60 (1H, d, *J* 7.4 Hz, ArH), 7.41–7.44 (1H, m, ArH), 7.30–7.34 (5H, m, ArH), 7.24–7.28 (5H, m, ArH), 7.13–7.20 (2H, m, ArH), 6.54 (1H, d, *J* 14.5 Hz, CH), 6.36 (1H, d, *J* 14.5 Hz, CH), 3.73 (3H, s, N–CH₃), 3.49 (2H, br. s, CH₂), 3.45 (2H, br. s, CH₂), 1.64 (6H, s, 2 × CH₃), 1.62 (6H, s, 2 × CH₃). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 179.1, 168.4, 155.6, 146.4, 146.3, 146.2, 144.5, 143.4, 142.9, 141.1, 128.6, 128.5, 128.3, 128.0, 127.7, 127.3, 126.9, 126.1, 125.0, 122.3, 114.6, 111.3, 107.2, 102.2, 95.9, 48.9, 44.8, 37.7, 37.5, 31.7, 27.2, 26.1. λ_{max} (CHCl₃) 793, log₁₀ ε 5.09.

2.5.3. 2-[4-(2-{5-tert-Butyl-2-chloro-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl}-vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**24**)

Green solid (40%). Recrystallization (ethyl acetate:hexanes, 2:1) afforded a green powder, m.p. 264–266 °C. (Found: MNa⁺ m/z 587.2564 C₃₅H₃₇N₄OCl. requires MNa⁺ m/z 587.2554; $\Delta = 1.7$ ppm). ¹H NMR (500 MHz, d_6 -DMSO) δ 8.32 (1H, d, J 15.0 Hz, CH), 8.19 (1H, d, J 15.0 Hz, CH), 7.60 (1H, d, J 10.0 Hz, ArH), 7.39–7.44 (2H, m, ArH), 7.24–7.30 (1H, m, ArH), 6.30 (1H, d, J 15.0 Hz, CH), 6.11 (1H, d, J 15.0 Hz, CH), 3.69 (3H, s, N–CH₃), 2.81–2.95 (2H, m, CH₂), 2.05–2.18 (2H, m, CH₂), 1.66 (6H, s, 2 × CH₃), 1.61 (6H, s, 2 × CH₃), 1.41–1.49 (1H, m, CH), 1.03 (9H, s, 3 × CH₃). ¹³C NMR (125 MHz, d_6 -DMSO) δ 176.8, 167.9, 161.1, 155.9, 153.5, 148.6, 146.9143.4, 142.9, 142.1, 141.0, 128.6, 127.4, 127.1, 125.0, 123.9, 122.3, 115.3, 114.5, 111.3, 106.6, 101.9, 95.6, 48.9, 42.0, 32.2, 31.5, 28.3, 27.2, 26.3. λ_{max} (CHCl₃) 799, log₁₀ ε 5.05.

2.5.4. 2-[4-(2-{2-Bromo-5-tert-butyl-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl}-vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**25**)

Dark green solid (45%). Recrystallization (ethyl acetate:hexanes, 2:1) afforded a dark green powder, m.p. 254–256 °C. (Found: MNa⁺ *m*/*z* 631.2039 C₃₅H₃₇N₄OBr. requires MNa⁺ *m*/*z* 631.2048; Δ = 1.4 ppm). ¹H NMR (500 MHz, *d*₆-DMSO) δ 8.25 (1H, d, *J* 15.0 Hz, CH), 8.20 (1H, d, *J* 15.0 Hz, CH), 7.60 (1H, d, *J* 10.0 Hz, ArH), 7.39–7.46 (2H, m, ArH), 7.24–7.31 (1H, m, ArH), 6.30 (1H, d, *J* 15.0 Hz, CH), 6.13 (1H, d, *J* 15.0 Hz, CH), 3.69 (3H, s, N–CH₃), 2.77–3.00 (2H, m, CH₂), 2.05–2.25 (2H, m, CH₂), 1.68 (6H, s, 2 × CH₃), 1.64 (6H, s, 2 × CH₃), 1.41–1.51 (1H, m, CH),

1.03 (9H, s, 3 × CH₃). ¹³C NMR (125 MHz, d_6 -DMSO) δ 176.9, 168.0, 160.9, 156.6, 153.2, 148.5, 145.5, 143.7, 143.3, 142.9, 141.0, 129.3, 128.9, 128.5, 125.1, 122.3, 115.2, 114.3, 111.3, 107.0, 102.1, 95.6, 48.8, 42.1, 32.2, 31.6, 28.2, 27.2, 26.3. λ_{max} (CHCl₃) 799, $\log_{10}\epsilon$ 5.17.

2.6. General procedure for the synthesis of chromophores 26-28

Under a nitrogen atmosphere and at 0 °C, a slurry of NaH (1.2 eq) (60% in mineral oil, washed with hexane) in anhydrous DMF (5 mL) was added to a stirring solution of the appropriate phenol or thiophenol derivative (1.1 eq) in anhydrous DMF (10 mL). After 30 min the reaction was allowed to warm up to ambient temperature. This mixture was added to a solution of **24** or **25** (1 eq) in anhydrous DMF (10 mL). The reaction was stirred for 5 h, then quenched with water. The solvent was evaporated under vacuum and the resulting dye conjugate was purified by column chromatography to yield a coloured solid.

2.6.1. 2-[4-(2-{5-tert-Butyl-2-(2,6-di-tert-butyl-4-

methylphenoxy)-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene) ethylidene]cyclohex-1-enyl}vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (**26**)

Green powder (55%, from **24**) (2,6-di-*tert*-butyl-4-methylphenol derivative). Purification by column chromatography on silica gel (dichloromethane) afforded a green solid, m.p. 223–226 °C. (Found: MNa⁺ *m/z* 771.4566 C₅₀H₆₀N₄O₂ requires MNa⁺ *m/z* 771.4554; $\Delta = 0.6$ ppm). ¹H NMR (300 MHz, *d*₆-DMSO) δ 8.31 (1H, d, *J* 15.0 Hz, CH), 8.17 (1H, d, *J* 15.0 Hz, CH), 7.60 (1H, d, *J* 10.0 Hz, ArH), 7.39–7.44 (5H, m, ArH), 7.24–7.30 (1H, m, ArH), 6.27 (1H, d, *J* 15.0 Hz, CH), 6.08 (1H, d, *J* 15.0 Hz, CH), 3.68 (3H, s, N–CH₃), 2.81–2.95 (2H, m, CH₂), 2.30 (3H, s, CH₃), 2.05–2.18 (2H, m, CH₂), 1.68 (18H, s, 2 *o*-*tert*-butyl), 1.64 (6H, s, 2 × CH₃), 1.61 (6H, s, 2 × CH₃), 1.41–1.49 (1H, m, CH), 1.03 (9H, s, 3 × CH₃). ¹³C NMR (125 MHz, *d*₆-DMSO) δ 176.7, 167.7, 161.0, 155.8, 153.6, 149.2, 148.3, 147.2, 143.4, 142.6, 142.0, 141.0, 136.6, 131.9, 128.5, 127.3, 125.3, 124.8, 123.9, 122.5, 115.7, 114.7, 111.5, 106.4, 102.0, 95.4, 48.5, 42.0, 33.3, 32.2, 31.2, 28.5, 27.2, 26.3, 26.0, 23.1. λ_{max} (DMF) 896, log₁₀ ϵ 4.18.

2.6.2. 2-[4-(2-{5-tert-Butyl-2-phenylsulfanyl-3-[2-(1,3,3trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl} vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene]malononitrile (27)

Green powder (62%, from **24**) (thiophenol derivative). Purification by column chromatography on silica gel (3% MeOH in dichloromethane) afforded a green solid, m.p. 252–255 °C. (Found: MNa⁺ m/z 661.304 $C_{41}H_{42}N_4OS$ requires MNa⁺ m/z 661.294; $\Delta = 0.4$ ppm). ¹H NMR (300 MHz, d_6 -DMSO) δ 8.29 (1H, d, J 15.0 Hz, CH), 8.15 (1H, d, J 15.0 Hz, CH), 7.60 (1H, d, J 10.0 Hz, ArH), 7.39–7.44 (2H, m, ArH), 7.24–7.30 (1H, m, ArH), 7.20 (5H, m, ArH), 6.6.12 (1H, d, J 15.0 Hz, CH), 5.92 (1H, d, J 15.0 Hz, CH), 3.69 (3H, s, N–CH₃), 2.81–2.95 (2H, m, CH₂), 2.05–2.18 (2H, m, CH₂), 1.66 (6H, s, 2 × CH₃), 1.62 (6H, s, 2 × CH₃), 1.41–1.49 (1H, m, CH), 1.03 (9H, s, 3 × CH₃). ¹³C NMR (125 MHz, d_6 -DMSO) δ 176.9, 167.9, 161.1, 153.6, 156.0, 148.5, 147.0, 143.5, 142.8, 142.1, 141.0, 135.7, 133.7, 132.5, 128.7, 127.8, 127.3, 125.0, 124.0, 122.6, 115.7, 114.7, 111.5, 106.6, 102.3, 95.5, 48.7, 42.1, 32.3, 31.6, 28.3, 27.1, 26.3. λ_{max} (DMF) 907, log₁₀ ε 5.02.

2.6.3. 2-[4-(2-{5-tert-Butyl-2-pentafluorophenylsulfanyl-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1enyl}-vinyl)-3-cyano-5,5-dimethyl-5H-furan-2-ylidene] malononitrile (**28**)

Greenish brown solid (65%, from **24**) (pentafluorothiophenol derivative). Purification by column chromatography on silica gel (3% MeOH in dichloromethane) afforded a greenish brown powder, m.p. 242–246 °C. (Found: MNa⁺ m/z 751.2562 C₄₁H₃₇F₅N₄OS

requires MNa⁺ m/z 751.2454; $\Delta = 0.2$ ppm). ¹H NMR (300 MHz, d_{6} -DMSO) δ 8.35 (1H, d, J 15.0 Hz, CH), 8.23 (1H, d, J 15.0 Hz, CH), 7.68 (1H, d, J 10.0 Hz, ArH), 7.40–7.46 (2H, m, ArH), 7.26–7.32 (1H, m, ArH), 6.20 (1H, d, J 15.0 Hz, CH), 6.15 (1H, d, J 15.0 Hz, CH), 3.70 (3H, s, N–CH₃), 2.81–2.95 (2H, m, CH₂), 2.05–2.18 (2H, m, CH₂), 1.69 (6H, s, 2 × CH₃), 1.63 (6H, s, 2 × CH₃), 1.41–1.49 (1H, m, CH), 1.03 (9H, s, 3 × CH₃). ¹³C NMR (125 MHz, d_{6} -DMSO) δ 177.0, 167.8, 141.2, 156.2, 153.7, 149.8, 149.0, 147.2, 143.6, 143.0, 142.2, 141.1, 139.1, 136.1, 128.9, 127.5, 125.2, 124.0, 122.8, 115.9, 114.9, 111.5, 106.9, 106.6, 102.1, 95.6, 48.9, 42.5, 32.5, 31.2, 28.3, 27.4, 26.5. λ_{max} (DMF) 906, log₁₀ ϵ 4.55.

3. Result discussion

3.1. Synthesis

The chromophores used in this study (7-9, 11, 17-18 and 24-28) were prepared as outlined in Schemes 1 and 2. The methodology used to prepare 7–9 and 11 relies on an approach previously described by us [14] and which utilizes the N-phenylacetamide precursors 4-6 and 10. Reaction of these precursors with 1,1,3-trimethyl-2-methyleneindoline, 3, in alcohol afforded chromophores 7-9 and 11 as colored solids in yields of 36-87%. Notably the crude dyes readily precipitated from solution and were obtained essentially pure following washing with water and methanol. The hydroxymethylene-cyclohexenecarbaldehydes 13, 14, 20 and 21 were prepared by formylation of the appropriate cvclohexanone via the Vilsmeier reaction [22]. Condensation of these compounds with the TCF acceptor in refluxing isopropyl alcohol containing catalytic quantities of piperidinium acetate yielded the cyclic enol intermediates 15, 16, 22 and 23 which were reacted in situ with 3 to give chromophores 17, 18, 24, and 25. As with the compounds above the final products readily precipitated from solution. Conversion of 24 or 25 to phenylether 26 and the thiophenylethers 27 and 28 was effected by displacement of the vinylic halogen atoms in the precursor compounds by the appropriate nucleophile - presumably via a tetrahedral intermediate as this anion would be allylic and therefore readily formed. These substitution reactions proceeded smoothly with either chlorine or bromine as the leaving group, although the reactions with bromide 25 were found to take place slightly faster.

It is important to note that the ¹H NMR spectra of all of the chromophores prepared indicate only one isomer to be present. Furthermore as the coupling constants observed for the vinylic protons of the conjugated interconnects are of the order of 12–15 Hz this confirms that they are in an all-trans configuration [23]. This is in contrast to our previous observations for zwitterionic compounds such as 1 and 2, where detailed NMR studies showed two isomers to be present and that these were due to rotational isomerisation about the acceptor ring and conjugated interconnect [14]. The absence of such rotamers in the present compounds is likely due to them being far less charge separated in their ground states (confirmed from X-ray crystallographic studies discussed later in the work), than, for example, 1 and 2. This, in turn, affects bond order throughout the indoline containing molecules and leads to more single bond character in the crucial bond connecting the conjugated backbone and the acceptor when compared to their zwitterionic analogues. This allows for more freedom of rotation about this bond and therefore, presumably, easier conversion to the thermodynamically favored transoid rotamer.

3.2. UV-vis spectroscopy

The UV-vis absorption spectra of NLO chromophores in solution can give important information about the propensity for the



Fig. 1. Uv-Vis absorption spectra of compounds 7-9, 11, 17, and 24 in chloroform.

compounds to aggregate and in particular in environments of low polarity such as those encountered in polymers (i.e., $\varepsilon = 1-7$). Indeed it is worth noting that although a given chromophore may show no aggregation and an excellent NLO response (*viz.* high β value) in a highly polar solvents such as DMF ($\varepsilon = 38$) or DMSO ($\varepsilon = 46.7$), this is no indicator of how it will perform in a polymer, or in a low polarity solvent such as chloroform ($\varepsilon = 4.8$) or THF ($\varepsilon = 7.5$). Consequently, in order to best replicate the response expected in a polymer matrix the UV–Vis absorption spectra and extinction coefficients of the chromophores were measured – where possible – in chloroform. This proved feasible for all of the compounds except **26–28** which were found to have poor solubility in chloroform and their extinction coefficients were therefore obtained in DMF; the results are presented in Figs. 1 and 2 and Table 1.

It is seen from Fig. 1 that for this series of compounds the UV–Vis absorption spectra obtained in chloroform all contain an intense main absorption band accompanied by a blue shifted, i.e., high energy, shoulder. As the relative intensities of both the high energy shoulder and the main absorption band showed no variation across a range of concentrations this confirms that the shoulder is not due to H-aggregation. Rather as Leng et al. reported for compounds **29** and **30** [24] and as Smith et al. demonstrated for compounds **2** and **31** [17], the blue-shifted shoulders observed in low polar solvents are associated with excited vibronic states. It is



Fig. 2. Uv-Vis absorption spectra of compounds 26-28 in DMF.

therefore concluded that the high energy shoulders observed in chloroform are also due to excited vibronic states, and not to aggregation. As identical absorption maxima and band shapes were observed for **17**, **18**, **24** and **25** in both DMF and chloroform it implies that substituting the vinylic chlorine for bromine is ineffective in tuning either the ground states or excited states of this particular suite of compounds.

twisted out of the plane of the chromophore backbone, and hence is unable to efficiently transfer charge.

3.3. X-ray crystallography

We have managed to obtain X-ray crystallographic data for three of the compounds -7, 17 and 24, and the relevant results are pre-



An analysis of the linear optical data shows that shifts in the absorption maxima are mainly related to variations in the conjugation length (e.g., 7 vs 8 vs 9), ring locking (c. 30 nm increase in λ_{max} , i.e., **9** vs **11**, **17–18** and **24–25**), and replacement of chlorine or bromine with either 2,6-di-t-butyl-4-methylphenoxy (26), thiophenoxy (27) or pentafluorothiophenoxy (28) leads to an approximate 60 nm increase in the wavelength of the absorption maxima. The moderate increase in the absorption maximum with configuration locking likely reflects improved planarity in the chromophores as well as more efficient electron delocalisation. This should also translate to improved NLO responses in these compounds. A previous study by us demonstrated that configurational locking across the donor-polyene unit improved the linear optical response by up to 50% [16]. When the halogen on the cyclohexene ring is replaced by either a 2,6-di-tert-butyl-4-methylphenoxy (26), thiophenoxy (27) or pentafluorothiophenoxy (28) substituent a sizable red-shift in absorption maxima occurs, and this is to be expected as these auxochromes are in direct conjugation with the π -system. It is also worth noting that the extinction coefficient of 26, which contains two bulky substituents in close proximity to the polyene chain, is around one order of magnitude less than the value for 27. This would suggest that the tert-butyl groups cause some degree of twisting in the polyene unit and/or that the phenoxy group is

sented in Tables 2 and 3. Table 2 contains the refinement data whereas Table 3 contains a summary of key bond lengths in the compounds, provides a comparison with the parent TCF and shows the degree of bond length alternation (BLA) in the compounds. All three crystals contain partial solvents of crystallization (Table 2) and two of the structures (7, 24) have the molecule of interest constrained to a crystallographic mirror plane. For this reason, the atom labeling is slightly different corresponding to the symmetry-related methyl atoms in the TCF moiety (e.g., C8 & C8' in 7 & 24; C8 & C9 in 17). From the bond length data in Table 3 it is seen that the bond order in the acceptor portion of all of the chromophores follows the same trend as that found in the parent TCF acceptor, meaning that these compounds should have more neutral, or non-charge-separated, ground states (as opposed to the complete reversal of bond order that would be expected in zwitterionic systems). However, paradoxically, in the case of 7 the bond order at the acceptor end of the molecule is marginally in line with what would be expected for a charged separated, or zwitterionic, species. The bond length alternation values shown in Table 3 reveal that in compound 7 (BLA = 0.006 Å) there is near equivalence in the bond lengths of the neighboring bonds in the polyene chain, but for both 17 and 24 the differences are somewhat more distinct. This suggests that of the three compounds it is 7 that will have the highest degree of charge

Table 1

Linear and nonlinear optical properties of the chromophores used in this study. λ_{max} , Wavelength of maximal absorption; $\log_{\epsilon_{10}}$, \log_{arithm} of molar extinction coefficient at λ_{max} ; β_{zzz} , dynamic first hyperpolarizability determined at a fundamental wavelength of 800 and/or 1300 nm; β_{zzz0} , static first hyperpolarizability derived from the two-level model. ϵ is the fluorescence life time obtained from the demodulation fit in nanoseconds.

Compound	λ_{max} (nm) In CHCl ₃	$\lambda_{\rm max}$ (nm) In DMF	Log ₁₀ ε	β_{zzz} (*10 ⁻³⁰ esu)	β_{zzz0} (*10 ⁻³⁰ esu)	τ (ns)	Td (°C)
7	602	599	5.23 ^a	$820\pm40^{a,e}$	90 ± 5	1	254
7	602	-	5.23	$1485\pm40^{a,f}$	815 ± 20	-	254
7	_	599	5.11	$1110\pm45^{b,f}$	610 ± 25	-	254
7	_	605 ^c	5.20 ^c	$1175 \pm 45^{c,f}$	645 ± 25	-	254
7	_	598 ^d	5.25 ^d	$1340\pm40^{d,f}$	730 ± 20	-	254
8	698	691	5.21 ^a	$1230\pm120^{a,e}$	130 ± 10	0.85 ± 0.1	280
9	794	810	5.12 ^a	$960\pm50^{a,e}$	300 ± 20	-	249
11	802	840	5.08 ^a	$1030\pm40^{a,e}$	330 ± 10	-	263
17	799	839	5.05 ^a	$880\pm 30^{a,e}$	280 ± 10	-	270
18	799	839	5.17 ^a	$930\pm 30^{a,e}$	270 ± 10	-	261
24	793	843	5.11 ^a	$950\pm50^{a,e}$	290 ± 10	-	278
25	793	843	5.09 ^a	$880\pm 30^{a,e}$	270 ± 10	-	275
26	895	896	4.18 ^b	$760 \pm 40^{\mathrm{b,e}}$	360 ± 20	1.86 ± 0.1	150
27	915	907	5.02 ^b	$610\pm40^{b,e}$	290 ± 20	$\textbf{2.03} \pm \textbf{0.3}$	205
28	907	906	4.55 ^b	$720\pm40^{\rm b,e}$	350 ± 20	1.97 ± 0.1	225

Td is taken at 5% weight loss.

^a Measured in chloroform.

^b Measured in dimethylformamide.

^c Measured in dimethyl sulfoxide.

^d Measured in methanol.

^e Measured with a 1300 nm fs operating system.

^f Measured with a 800 nm fs operating system.

Table 2

Crystallographic and structure refinement data for 7, 17 and 24.

	7	17	24
Asymmetric unit	C _{24.88} H _{23.75} Cl _{1.75} N ₄ O	C46H43CIN4O2	C ₃₅ H ₃₇ ClN ₄ O _{1.25}
Moiety formula	C24H22N4O.0.88CH2Cl2	C43H37CIN4O.C3H6O	C35H37ClN40.0.25H20
MW	456.98	719.29	569.14
Temperature (K)	107 (2)	116 (2)	112 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Hexagonal
Space group	C2/m	P-1	P6 ₃ /m
<i>a</i> , Å	24.1889 (8)	11.9943 (5)	27.2322 (8)
b, Å	6.8064 (3)	12.1474 (5)	27.2322 (8)
<i>c</i> , Å	14.8976 (6)	14.2267 (6)	7.3713 (3)
α , deg.	90	76.315 (3)	90
β , deg.	101.274 (2)	71.363 (2)	90
γ, deg.	90	77.448 (2)	120
Volume, Å ³	2405.40 (16)	1885.63 (14)	4734.1 (3)
Ζ	4	2	6
ho, Mg m ⁻³	1.262	1.267	1.198
μ , mm ⁻¹	0.266	0.146	0.155
Crystal size (mm)	$1.00 \times 0.50 \times 0.04$	$0.31\times0.21\times0.02$	0.45 imes 0.12 imes 0.09
Theta range deg.	2.79-34.94	2.28-26.50	2.90-25.21
Limiting indices	$-37 \le h \le 35$	$-15 \le h \le 15$	$-32 \le h \le 32$
	$-10 \le k \le 10$	$-14 \le k \le 15$	$-32 \le k \le 32$
	$-22 \le l \le 22$	$-17 \le l \le 17$	$-8 \le l \le 8$
Reflections collected	43 728	33 203	90 267
No of unique data	4913	7793	3074
R _{int}	0.0427	0.0741	0.1276
Absorp. Coeff. range	0.809, 1.0	0.780, 1.0	0.645, 0.745
Restraints	1	1	11
No. of parameters	197	485	281
Refinement method	Full matrix least-squares on F ²	Full matrix least-squares on F ²	Full matrix least-squares on F^2
P1, P2 coefficients of weighting scheme ^c	0.0646, 1.8954	0.040, 1.0761	0.0588, 5.4309
Goodness-of-fit on F ²	1.034	1.005	1.029
R1 ^{a,b} ,/data number	0.055, 3739	0.049, 4925	0.051, 1943
wR_2^{b} i(all data)	0.163	0.125	0.157
Largest diff. peak and hole ($e A^{-3}$)	1.008 and -0.735	0.260 and -0.349	

Intensities 2.0 times their standard deviations (from counting statistics).

b

 $R_1 = \Sigma ||F_0| - |F_c|| / \Sigma |F_0|; wR_2 = \Sigma [[w(F_0^2 - F_c^2)^2] / \Sigma [(wF_0^2)^2]]^{1/2}.$ Weight, $w = 1/[\sigma^2(F_0^2) + (P1 \times P)^2 + P2 \times P]$ where $P = (Max (F_0^2, 0) + 2 \times F_c^2)/3.$

separation across the π -conjugated backbone in the ground state, and may even be slightly zwitterionic in nature. Nonetheless as its BLA value is close to zero it is expected from theory to have the lowest molecular NLO response [25-27]. This is indeed confirmed from the HRS data which shows **7** to have a β_{1300} of only 820×10^{-30} esu, whereas the compound with the highest BLA value (**24**, BLA = 0.033) has a higher β_{1300} value, i.e., 950×10^{-30} esu.

3.3.1. Crystallographic features of compound 7

The asymmetric unit of 7 contains the title compound lying on a crystallographic mirror plane (Fig. 3) and containing a disordered and non-stoichiometric amount (0.88) of dichloromethane as solvent of crystallization. The methyl hydrogen atoms on C21 are disordered

Tab	le	3
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Selected Dolld distances and magnitude of DLA (A) for 7, 17 and 24	Selected bond distances	and magnitude of BLA	(Å) for	7, 17	and 24 ^a
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Bond ^b	TCF	7	17	24
C2-C6	1.358	1.386 (2)	1.380 (3)	1.363 (5)
C ₆ -C ₇	1.445	1.415 (2)	1.421 (3)	1.422 (5)
$C_7 - C_4$	1.343	1.406 (2)	1.393 (3)	1.389 (5)
$C_4 - C_{10}$	1.472	1.389 (2)	1.399 (3)	1.402 (5)
C ₁₀ -C ₁₁	_	1.397 (2)	1.387 (3)	1.371 (5)
C ₁₁ -C ₁₂	_	1.391 (2)	1.398 (3)	1.405 (5)
C ₁₂ -C ₁₃	_	1.395 (2)	1.400(3)	1.380 (5)
BLA	_	0.006	0.019	0.033
Av. β_{zzz0}	-	90	280	290

^a The BLA value is obtained by considering the average differences in bond length for the polyene interconnect and acceptor only; not all relevant bond length data for 17 and 24 is shown in the table.

^b Using the equivalent bond labels in **7**.

over the mirror plane. The alkene C12–H12...N3(cyano) interactions are aligned around a two fold axis of symmetry resulting in dimeric units, with a halogen bond at one end of the molecule between N1 and the dichloromethane chlorine Cl1 atom (Table 4). The molecules therefore lie in (010) planes with only weak interactions between the planes provided by a C10...Cl2B (dichloromethane) contacts at an interplane distance of 3.43 Å. The "angle of slippage" [28] is 16°; although this is smaller than the approximated angles in related compounds [29,30] the molecular planes in the latter crystals are not



Fig. 3. Structure of 7 (with 50% probability ellipsoids) [31].

Tuble 1					
Hydrogen	bond	geometry	/ (Å,	deg.)	for 7 .

D-HA	D-H	HA	DA	D-HA	Symmetry ^a
C12–H12N3 C32A–Cl1N1	0.95 1.784	2.53 3.160 (2)	3.462 (3)	167 173.1 (2)	1 - x, y, 1 - z x, y, z

^a Symmetry to bring the A atom into contact.

present in crystallographically-imposed parallel planes. By symmetry constraint, the TCF and indoline moieties are planar.

3.3.2. Crystallographic features of compound 17

Structure 17 contains independent molecules of 2-[4-(2-{2chloro-5,5-diphenyl-3-[2-(1,3,3-trimethyl-1,3-dihydroindol-2-ylidene)ethylidene]cyclohex-1-enyl}vinyl)-3-cyano-5,5-dimethyl-5Hfuran-2-ylidene]malononitrile (Fig. 4) and one acetone molecule of crystallization. The TCF group (atoms O1, C4–C7) and "polyene chain" (atoms C11–C15, C31 & C32) are close to coplanar with an interplanar twist of 1.2 (2) deg. The indol-2-vlidene group is close to planar with the mean planes through the 5 and 6 membered rings subtending 1.8 (1)deg.. The indol-2-ylidene mean plane is twisted with respect to the polyene chain-TCF plane by 18.8 (1) deg.: overall the molecular segments are twisted about the mean line passing through the polyene atoms. The cell packing is dominated by the head to tail C (phenyl)–H...N(cyano) H bonding link (entry 1, Table 5). This is supplemented by C–H...Cl, C–H... π and C–Cl... π interactions with the solvent acetone providing a donor O to the C9-H9B hydrogen bond (Table 5). The molecules pack into approximately parallel layers (a maximum interplanar deviation of 10 deg. is noted) which are parallel to the (-1, 2, -2) plane.

3.3.3. Crystallographic features of compound 24

In structure **24**, the target molecule (Fig. 5) lies on a crystallographic mirror plane and the crystal contains a partial (0.25) water of crystallization. Because of the imposed symmetry, the cyclohexene ring system is disordered between half-chair & half-boat forms. Packing within and between the mirror plane layers is provided by bifurcated attractive C–H...N(Cyano), two other weak C–H...N and weak halogen N2...Cl1 (3.250(6) Å), interactions (Table 6).

3.4. Hyperpolarizability

The hyper-Raleigh scattering measurements (HRS) were performed at 1300 nm due to the strong absorption at 800 nm found for those compounds with extended conjugation; the results are presented in Table 1. In the case of compounds 7, 8, 26, 27 and 28 the HRS signal at 1300 nm was convolved with multiphoton fluorescence, but the latter contribution could be extracted. By demodulating the apparent hyperpolarizability at increasing modulation frequencies, an accurate fluorescence-free hyperpolarizability could be obtained [21]. The corresponding fluorescence life time (τ in ns) obtained from the demodulation fit is tabulated in Table 1. The longer conjugation path present in shifting from compound **7** to **11** resulted in a shift of the emission away from 650 nm. The HRS signal for compounds 7-11 was constant as a function of modulation frequency and an average over these frequencies was obtained. The results are compiled in Table 1. The experimental dynamic hyperpolarizability values, $\beta_{zzz,1300}$, are affected by resonance enhancement to varying degrees, and this depends both on the proximity of the wavelength of the electronic charge-transfer resonance to the fundamental wavelength and that of the second-harmonic ($\lambda/2$). Consequently, in order to make more meaningful comparisons between the compounds the resonancefree static hyperpolarizability value $\beta_{zzz0.1300}$ is also given in Table 1.

We observe an increase in the molecular nonlinearity for all of the compounds when the degree of the conjugation between the donor and acceptor is increased (i.e., in moving from compounds **7** to **9**). This is a well documented phenomenon and, therefore,



Fig. 4. Structure of 17 showing the asymmetric unit contents (50% probability ellipsoids) [31].

Table 5 Hydrogen Bond geometry (Å, deg.) for 17.

D-HA	D-H	НА	DA	D-HA	Symmetry ^a
C39–H39N2	0.95	2.43	3.376 (4)	171	<i>x</i> , <i>y</i> + 1, <i>z</i> + 1
C9-H9BO2	0.98	2.59	3.505 (4)	155	<i>x</i> − 1, <i>y</i> , <i>z</i>
C8-H8CCl1	0.98	2.90	3.642 (3)	133	1 - x, 1 - y, -z
C14–Cl1…Cg1 ^b	1.749 (2)	3.6395 (13)	5.364 (3)	168	1 - x, 2 - y, -z
C36–H36…Cg1 ^b	0.95	2.66	3.566 (3)	159	<i>x</i> + 1, <i>y</i> , <i>z</i>

^a Symmetry to bring the A atom into contact.

Cg1 is the centroid of the C25-C30 phenyl ring.

entirely expected [15,16]. The inclusion of ring locking in the centre of the conjugated π -system, along with either *t*-butyl or diphenyl substitution on the central cyclohexene ring (compounds 11, 17, 18, 24, 25) has a minimal effect on the second-order nonlinear response. This is interesting because configurational locking would be expected to increase planarity throughout these compounds thereby allowing for much more efficient charge transfer. One possible reason for the negligible change may be due to the presence of the vinylic halogen atoms on the cyclohexene ring. It has been predicted through DFT calculations that the placement of donor groups on the even numbered methines and acceptor groups on the odd numbered methines of a chromophore polyene backbone leads to a reduction in the NLO response [32]; the relevant numbering system is shown for compound 11, Scheme 1. Thus, as halogens are able to act as electron donor groups through resonance their presence may be off-setting any gains obtained through ring locking of the π -conjugated interconnect. This may also explain the differences in the β values between **26–28**. In the case of compound 26 it is likely the orbitals containing the non-bonding pairs on the vinylic oxygen atom are twisted orthogonally to the polyene chain, while for **28** the fluorine atoms on the thiophenoxy ring will strip electron density from the sulphur; hence in both cases the substituents are inferior donors when compared to 27 which has a comparatively unencumbered thiophenoxy as the donor group. As a result **26** and **28** have beta values approximately 20% higher than 27. From our previous work we found that in some cases ring locking across the donor ring-polyene chain led to a 50% increase in β [16]. In the present work it is apparent that ring locking across the centre of the polyene chain does not lead to a corresponding increase in the NLO response, and that electronic factors probably play an important role. While there is scope to investigate this further it must be noted that the halogen atoms present in the precursors 13-14 and 20-21 are artefacts of the

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Table 6					
D-HA	D-H	НА	DA	D-HA	Symmetry ^a
C30–H30N3 C32–H32AN3 C16–H16N1 C8–H8CN2	0.95 1.01 (6) 0.99 (2) 0.98	2.35 2.45 (6) 2.65 (3) 2.72	3.296 (7) 3.459 (8) 3.569 (8) 3.421 (5)	176 178 (4) 155 (4) 129	1 - y, x - y + 1, z 1 - y, x - y + 1, z y, -x + y, z + 1/2 y, -x + y, z - 1/2

Symmetry to bring the A atom into contact

synthetic procedures used to prepare these enol-aldehydes (i.e., via the Vilsmeier reaction on a cyclohexanone precursor) and their replacement with electron withdrawing substituents will not be necessarily straightforward.

In addition to the experimental results obtained for compound 7 at 1300 nm, solvent dependant HRS measurements were also conducted using an 800 nm fs system (Table 1). A very important observation from these measurements is that there is a modest increase in the NLO response (from 645×10^{-30} esu to 815×10^{-30} esu) as the dielectric constant of the surrounding medium is decreased (from $\varepsilon = 46.7$ to 4.8). As reported by Marder et al. [33] the reaction field model holds that the electric field exerted on a dipolar molecule by a solvent has an effect similar to that of donor/acceptor substitution. This solvent-mediated polarization results in more stabilization of a charge separated zwitterionic form in high polarity solvents (like DMSO and DMF) and in turn leads to a reduction in the observed β value. Conversely, in low polarity media such as chloroform, the solvent is very ineffective at stabilizing charge separated species and the β value is therefore increased. Therefore, the results of our solvent polarity vs NLO response study suggest that for compound **7** the charge separated form dominates the ground state, albeit to a moderate extent. Lastly, there is a significant difference in the observed molecular response for compound 7 when values obtained in chloroform at 1300 nm (β_0 , 90 × 10⁻³⁰ esu) are compared to those obtained at 800 nm (β_0 , 815 \times 10⁻³⁰ esu). The dependence of the molecular hyperpolarizability on wavelength is a known phenomenon [34]. The low static hyperpolarizability value found for 7 at 1300 nm reflects the fact that the magnitude of β_0 decreases the closer the two photon absorption wavelength (viz. 650 nm for a 1300 fundamental) is to the absorption maximum of the chromophore (602 nm). This indicates that to maximise the macroscopic response of 7, at least, electro-optic coefficients should be measured at wavelengths remote from c. 1300 nm. Overall, the observed molecular hyperpolarizabilities of the compounds used in



Fig. 5. Structure of 24 (with 50% probability ellipsoids) [31].



32: n = 1; β_{1300} = 100, β_0 = 36 **33**: n = 3; β_{1300} = 2,045, β_0 = 496 **34**: n = 5; β_{1300} = 1,200, β_0 = 224



35: β₁₃₀₀ = 500, β₀ = 220

Fig. 6. Measured molecular hyperpolarizabilities of selected chromophores obtained at 1300 nm in chloroform. Values for **32–34** are taken from ref. [35] and values for **35** obtained from ref. [16]. β values have units of 10⁻³⁰ esu.

this study range in magnitude from approximately $\beta_{1300} = 700$ to 1000×10^{-30} esu and $\beta_0 = 250$ to 350×10^{-30} esu, and these values compare quite favourably to other compounds for which data has been obtained at 1300 nm. For example, the response found for **7** is similar to that obtained for the highly extended compound **34**, but is only around 50% of the value found for **33** which has six carbon atoms in the donor–acceptor interconnect (Fig. 6). However, the value obtained for **11** is approximately twice that observed for the analogous compound **35** which contains a quinolinylidene donor and is therefore highly zwitterionic in character. Thus, given the relative ease by which the present compounds can be synthesised and modified, and their comparative NLO responses, it suggests they are worthwhile candidates for further study.

4. Summary and conclusions

A suite of chromophores containing an indoline donor and various π -conjugated interconnects between the powerful TCF acceptor were prepared. The static and dynamic molecular NLO responses of the compounds were measured and in low polarity media values of β_{800} up to 1485 \times 10⁻³⁰ esu were obtained; the magnitude of the responses confirms that these compounds are excellent candidates for further study. While extending the conjugation length between the donor and acceptor led to an increase in the first hyperpolarizability, configurational locking of the polyene interconnect did not result in the expected enhancements to β . This is probably due to electronic rather than structural factors and suggests that in order to optimize the NLO response of these, and related compounds, any configurational locking system will need to have strategically placed donor/acceptor substituents. X-ray crystallographic studies showed that while none of the three compounds studied crystallized in a non-centrosymmetric fashion, as expected it was possible to correlate the BLA values found for the crystalline materials with the magnitude of the observed hyperpolarizabilities. Further studies are underway to exploit the findings of this work including structural modifications to allow for covalent attachment of the chromophores to a polymer backbone and to induce non-centrosymmetry in the crystalline state.

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