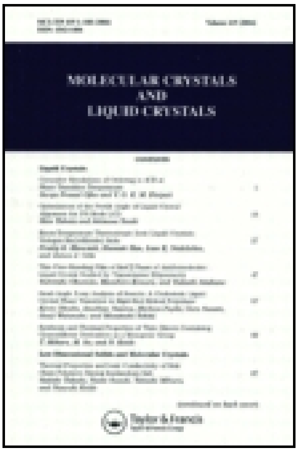

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Synthesis, Structural and Nonlinear Optical Properties of 2-(3-Cyano-4-{5-[1-(2-Hydroxyethyl)- 3,3-Dimethyl-1,3-Dihydro-Indol-2-ylidene]-Penta-1,3-dienyl}-5,5-Dimethyl-5H-Furan-2-ylidene)-Malononitrile

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Synthesis, Structural and Nonlinear Optical Properties of 2-(3-Cyano-4-{5-[1-(2-Hydroxyethyl)-3,3-Dimethyl-1,3-Dihydro-Indol-2-ylidene]-Penta-1,3-dienyl}-5,5-Dimethyl-5*H*-Furan-2-ylidene)-Malononitrile

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A chromophore for nonlinear optics with extended conjugation has been synthesized, and its structure determined from X-ray diffraction data. The compound crystallizes in the monoclinic system with the space group $P2_1/n$ *and* $Z = 4$*. The unit cell parameters are* $a = 10.7826(4)$ Å, $b = 14.5943(5)$ Å, $c = 15.3792(5)$ Å *and beta* $= 96.213(2)°$*. A thin film containing 5% of the chromophore in amorphous polycarbonate when poled at 180°C and 60 V/μm yields a maximum* r_{33} *value of 206 pm/V. This is seven times higher than the value found for the archetypical inorganic material, lithium niobate.*

Keywords Electro-optic coefficient; nonlinear optical chromophore; X-ray crystallography

Introduction

There is an ongoing interest in developing device quality organic nonlinear optical (NLO) materials as the underpinning technology for a number of photonic and electro-optic (EO) devices in industries such as telecommunications, sensing, and computing. Consequently, recent attention has focused increasingly on new organic solid-state materials as they are expected to offer extremely high optical nonlinearities [1, 2] and will allow EO devices to operate efficiently at relatively low power levels [3]. This is because most of the existing EO devices are based on inorganic compounds such as crystalline lithium niobate ($LiNbO_3$) [4]. However, inorganic materials such as this have moderate EO coefficients (32 pm/V) and yield devices with a high drive voltage (*c.* 5V). Furthermore, inorganic substrates are not processable and therefore are not able to be cast or spun as thin films, which limits their ability to be fully integrated. Organic materials offer a number of significant advantages such as low-drive voltages (<1V), higher EO coefficients (>300 pm/V), and the ability to be dissolved and therefore processed into a number of different configurations. Indeed

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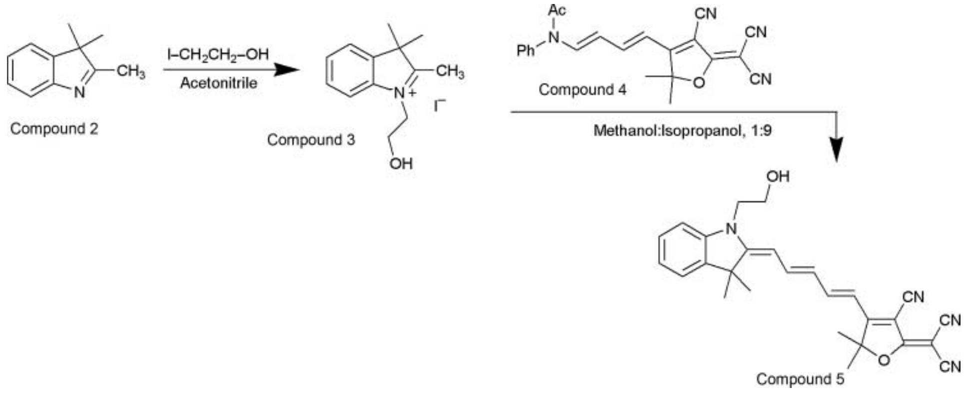


Scheme 1. Synthetic methodology used to prepare the chromophore (Compound 5).

modern synthetic methodologies have permitted access to a vast range of organic NLO compounds and allowed photonics researchers the opportunity to design, synthesize, test, and continually improve these new materials at the molecular and macromolecular levels. In order to observe a macroscopic NLO response in an organic material, it is necessary to align the dipole moments of the embedded chromophores, and this is readily achieved by heating a polymer film containing the material to its glass transition temperature and then applying an electric field – a process known as poling.

In this work, we have synthesized and characterized a new NLO chromophore containing an indoline donor, an acceptor based on the well-known moiety (2-(3-cyano-4,5,5-trimethyl-5*H*-furan-2-ylidene)-malononitrile) – hereafter CTF – and a conjugated chain of five carbon atoms between the donor and acceptor (Compound 5, Scheme 1). The chromophore also contains a hydroxyethyl substituent on the donor nitrogen atom which will allow for covalent attachment of the molecule to a polymer backbone, if needed, in the future. Compound 5 is an analogue of another NLO chromophore that we have previously studied – (Compound 1, Fig. 1) – and which was found to have a very high molecular first hyperpolarizability, β, of approximately 1200×10^{-30} esu at 1300 nm [5]. Consequently, derivatives of Compound 1 were deemed worthy of a more detailed study. To this end, we report here on the structure of Compound 5 (via X-ray crystallographic studies) and provide details on the behavior of Compound 5 in solution using nuclear magnetic resonance (NMR) and UV-Visible (UV-Vis) spectra. Furthermore, host–guest thin films containing

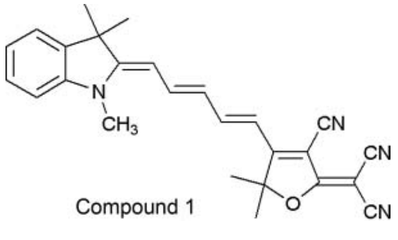


Figure 1. Structure of an NLO chromophore previously studied and with a molecular hyperpolarizability (β) of 1200×10^{-30} esu.

5% of Compound 5 in amorphous polycarbonate (APC) have been prepared and their EO coefficients (r_{33} values) measured.

Experimental

Materials

Commercially available reagents were obtained from Aldrich and were used without additional purification. Compound 4 – (*N*-[4-(4-cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydro-furan-3-yl)-buta-1,3-dienyl]-*N*-phenyl-acetamide) – was prepared according to the literature [6].

General Methods and Measurements

Melting points were recorded with an *EZ-Melt* automated melting point apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were recorded on a Bruker AVANCE 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 positive-ion mode. The UV-Vis absorption spectra were recorded by a Perkin-Elmer Lambda 900 spectrophotometer at room temperature. Column chromatography was carried out using the gravity-feed column technique on Merck silica gel type 9385 (230–400 mesh). Crystallographic data for Compound 5 have been deposited at the Cambridge Crystallographic Data Centre under reference 783,961. Copies of this information can be obtained free of charge at http://www.ccdc.cam.ac.uk.

1-(2-Hydroxyethyl)-2,3,3-Trimethyl-3H-Indolium Iodide (Compound 3)

A mixture of 2,3,3-trimethyl-3*H*-indole (Compound 2, 5.0 g, 31.4 mmol) and 2-iodoethanol (8.2 g, 47.7 mmol) was dissolved in 30-ml acetonitrile and the solution refluxed for 6 h. The reaction mixture was then cooled to room temperature and 20 ml of diethyl ether was added. The crude product precipitated and was collected by filtration and washed with 2–3 small portions of ether to give Compound 3 as brown crystals (8.3 g, 80%) [m.p. 163°C–165°C; ^{1}H-NMR (500 MHz, d$_6$-DMSO) δ 1.57 (6H, s, 2 × CH_3), 2.85 (3H, s, CH_3), 3.90 (2H, t, *J* 5.0 Hz, CH_2), 4.62 (2H, t, *J* 5.0 Hz, CH_2), 5.01 (1H, br s, –OH), 7.64–7.62 (2H, m, ArH), 7.88–7.86 (1H, m, ArH), 7.99–7.89 (1H, m, ArH); ^{13}C-NMR (125 MHz, d$_6$-DMSO) δ 14.5, 21.9, 50.3, 54.2, 57.7, 115.5, 123.5, 128.7, 129.2, 141.0, 141.7].

2-(3-Cyano-4-{5-[1-(2-Hydroxyethyl)-3,3-Dimethyl-1,3-Dihydro-Indol-2-ylidene]-Penta-1,3-Dienyl}-5,5-Dimethyl-5H-Furan-2-ylidene)-Malononitrile (Compound 5)

1-(2-hydroxyethyl)-2,3,3-trimethyl-3*H*-indolium iodide (Compound 3, 1 g, 3.2 mmol) and the acceptor precursor *N*-[4-(4-cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydro-furan-3-yl)-buta-1,3-dienyl]-*N*-phenyl-acetamide (Compound 4, 789 mg, 2.1 mmol) were dissolved in a mixture of methanol and isopropanol (30 ml, 1:9 ratio) and two drops of triethylamine were added. The mixture was refluxed for 3 h, allowed to cool to ambient temperature, and the crude product collected by filtration and washed with copious quantities of hot water, followed by 2–3 small portions of cold isopropanol. The crude product was purified by column chromatography (silica gel, ethyl acetate:dichloromethane 1:9) to afford Compound 5 as a brown solid (930 mg, 78%) [m.p. 258°C (decomp.); ^{1}H-NMR (500 MHz, d$_6$-DMSO) δ 1.66 (6H, s, 2 × CH_3), 1.70 (6H, s, 2 × CH_3), 3.74 (2H, q, J 5.3, 12.0 Hz, CH_2), 4.17 (2H, t, J 5.3 Hz, CH_2), 5.01 (1H, t, J 5.6 Hz, –OH), 6.01 (1H, d, J 14.4 Hz, CH), 6.36 (1H, d, J 14.4 Hz, CH), 6.44 (1H, t, J 12.5 Hz, CH), 7.21–7.29 (1H, m, ArH), 7.38 (2H, d, J 3.9 Hz, ArH), 7.58 (1H, d, J 7.5 Hz, ArH), 7.58 (1H, t, J 7.5 Hz, CH), 7.87 (1H, t, J 13.0 Hz, CH); ^{13}C-NMR (125 MHz, d$_6$-DMSO) δ 26.5, 27.1, 44.1, 46.5, 48.9, 58.1, 95.0, 104.4, 107.8, 111.6, 113.5, 114.5, 115.3, 122.1, 124.6, 125.4, 128.1, 141.1, 142.5, 150.6, 152.9, 168.9, 173.4, 176.1; HRMS (ESI$^+$): For $C_{27}H_{27}N_4O_2$ [MH]$^+$, *m/z* calc. 439.2134. Found 439.2130, Δ 0.9 ppm].

Thin-Film Fabrication, Poling, and EO Coefficient Measurements

Solutions for thin-film fabrication (5% by weight) were made by mixing the chromophore (Compound 5) (50 mg) and APC (950 mg) in cyclohexanone (5 g). The resulting solution was warmed in a water bath at ~40°C for 3 h with continual stirring. The resultant solution was then passed through a 0.45-μm syringe filter and then through a 0.22-μm syringe filter. The thin films were made by placing 0.6 ml of the filtered host–guest polymer solution on to a 25 mm × 25 mm ITO-coated glass slide and spinning at 1200 revolutions per minute for 12 s. The films were then dried in a vacuum oven at 150°C and 110 mmHg to evaporate any residual solvent. The film thicknesses and refractive indices were measured at 1300 nm and 1550 nm using a Metricon prism coupler. The thin films were poled under an inert atmosphere using a parallel plate electrode poling technique, with an applied DC field of 60V/μm of thin-film thickness (viz. 300 V across a 5-μm film). The samples were poled for 30 min at 180°C and then allowed to cool to room temperature while keeping the electric field on in order to help maintain the alignment of the poled chromophores. The observed current drops through the films were of the order of 0.12~0.14 μA throughout the poling process, which indicates that no dielectric breakdown occurred during the poling process. The EO coefficients (r_{33} values) of the films were evaluated using the Teng–Man modulation ellipsometry technique at 1310 nm [7].

Results and Discussion

Synthesis and Characterization

The synthesis of the chromophore (Compound 5; Scheme 1) builds on a method we have previously used to prepare compounds containing the CTF acceptor unit and conjugated spacers of varying length between the donor and the acceptor units [5, 6, 8, 9]. The *N*-2-hydroxyethyl indolinium iodide salt (Compound 3) was synthesized by reaction of 2,3,3-trimethyl-3*H*-indole with 2-iodoethanol in acetonitrile following the general procedure reported by Wang et al.[10]. From our prior work, we know that for NLO chromophores with an indoline donor, the optimal NLO response is found when there are five carbon atoms in the interconnect [5], and this therefore dictates the use of *N*-[4-(4-cyano-5-dicyanomethylene-2,2-dimethyl-2,5-dihydro-furan-3-yl)-buta-1,3-dienyl]-*N*-phenyl-acetamide, Compound 4, as the appropriate synthon to introduce the acceptor ring and the conjugated interconnect to the molecule. Thus, coupling of Compound 4 with the *N*-2-hydroxyethyl indolinium salt (Compound 3) in alcohol containing a catalytic amount of base yielded the target chromophore (Compound 5). As noted earlier Compound 5 is almost identical to Compound 1, except that there is a hydroxyethyl group on the donor nitrogen atom rather than a

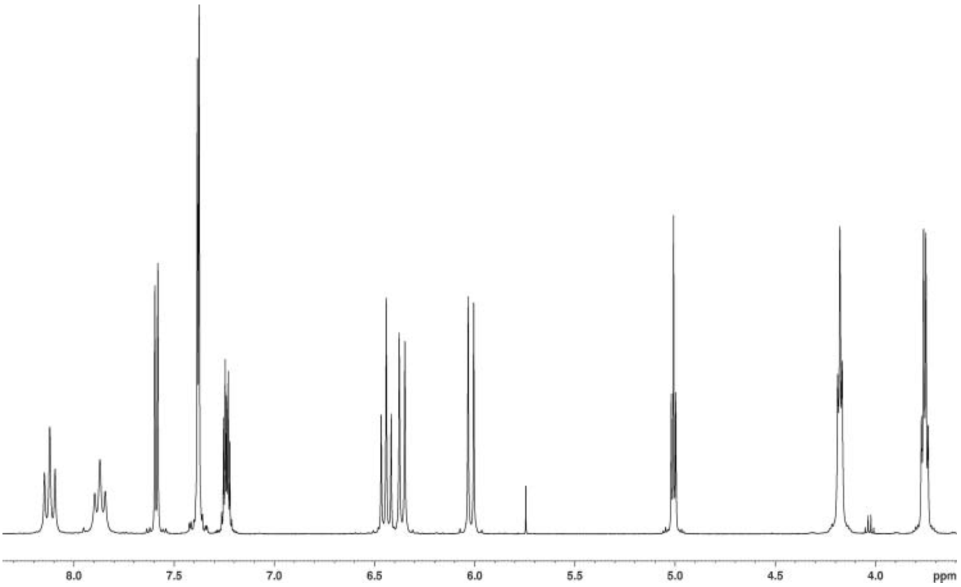
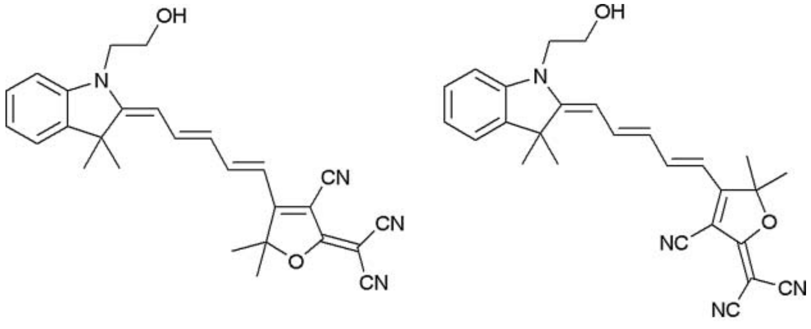


Figure 2. Partial ^{1}H-NMR spectrum of Compound 5, illustrating that a single isomer is present in solution.

methyl substituent, and this will allow for covalent attachment of Compound 5 to a polymer backbone. In addition, it also makes Compound 5 more soluble in low-polarity solvents than Compound 1, and through the introduction of strong hydrogen bonding interactions, it allowed for the growth of high-quality crystals for X-ray crystallography.

The ^{1}H-NMR spectrum of Compound 5 shows that only one isomer is present in solution, and this is evident upon examining the resonances and splitting patterns in the olefinic and aryl regions (Fig. 2). Our previous work has shown that *zwitterionic* chromophores containing the CTF acceptor exhibit two isomers in solution, and a detailed NMR study confirmed that these were due to the two rotational isomers that can occur around the acceptor ring and the terminus of the conjugated interconnect [6]. That there is only one isomer present is most likely a reflection of the fact that Compound 5 does not have significant



Transoid *Cisoid*

Figure 3. Two possible geometrical (rotational) isomers for Compound 5.

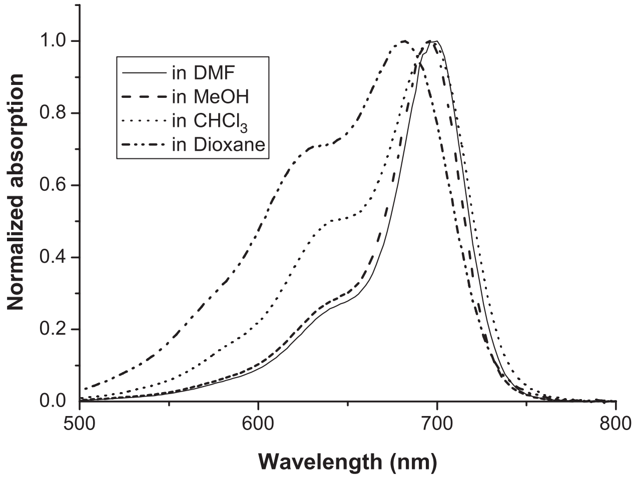


Figure 4. UV-Vis spectra of Compound 5 in a range of solvents.

charge separation in its ground state. Consequently, the bond order in this compound will be the opposite of that found in the zwitterionic analogues reported earlier. As a result, there will be more single bond character in the conjugated polyene-acceptor ring bond, which should make the more thermodynamically favored rotamer more accessible in solution. X-ray crystallographic studies done here (discussed later) and our earlier work [11] suggest that for indoline-π-CTF chromophores, it is the *transoid* rotamer (Fig. 3) that is energetically favored, as it is the only isomer ever observed in the crystalline state.

The UV-Vis absorption spectra of Compound 5 in a number of different solvents are shown in Fig. 4 and the results summarized in Table 1. This compound exhibits only a mild degree of solvatochromism, with a difference in the absorption maximum of only 8 nm across the range of solvents studied. Furthermore, with the highest energy absorption (690 nm) observed in the lowest-polarity solvent – dioxane – and the lowest energy absorption (698 nm) seen in the highest-polarity solvent – DMF – confirmation is given that Compound 5 exhibits positive solvatochromism and is expected to have only a moderate degree of charge separation in the ground state.

X-Ray Crystallography

A crystal of Compound 5 was obtained by the vapor diffusion method with dichloromethane as the solvent and ether as the precipitant. The X-ray structure is shown in Fig. 5, its unit cell packing is shown in Fig. 6, and key crystallographic data is given in Table 2. It is found

Table 1. UV-Vis data of Compound 5 in different solvents

Solvent	ε	λ_{max} (nm)	Log$_{10}$€
Dioxane	2.2	690	–
Chloroform	4.8	697	–
Methanol	33.0	693	5.34
Dimethyl formamide	38.0	698	–

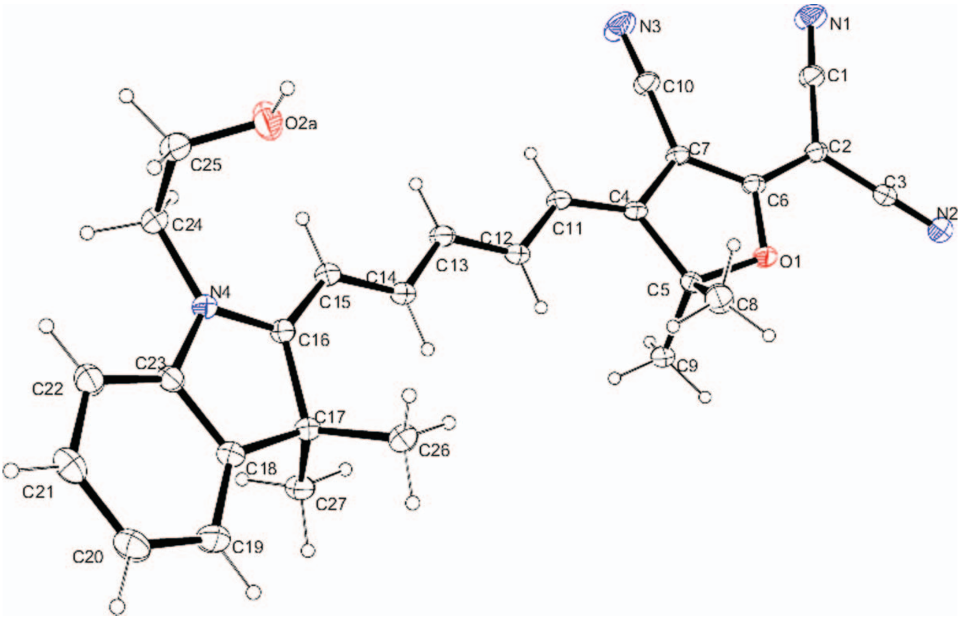


Figure 5. Structure of Compound 5 with 20% probability thermal ellipsoids [14].

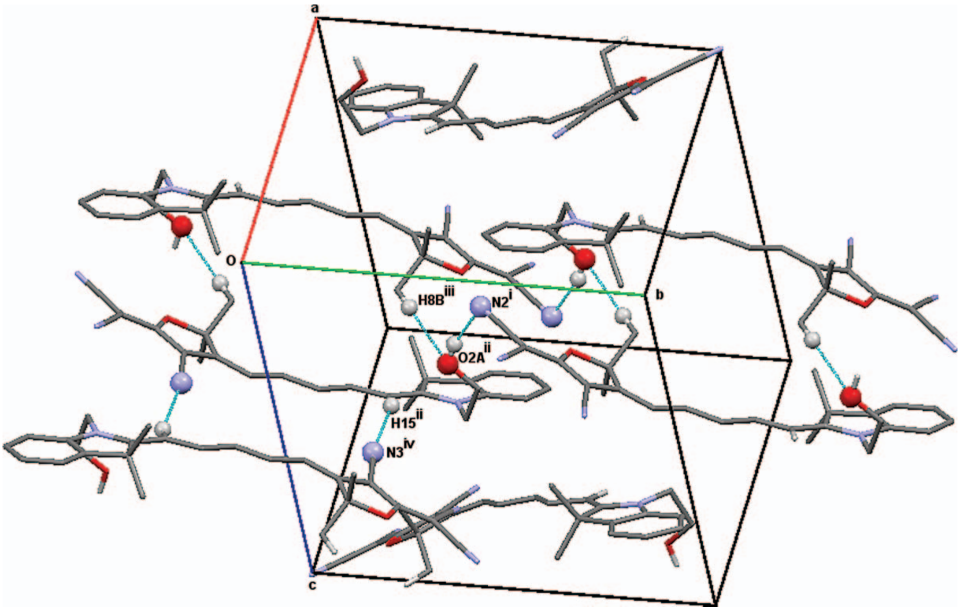


Figure 6. Unit cell packing of Compound 5, showing chain formation via hydrogen bonding and molecular twisting. Attractive contacts (atoms as balls) are shown as dotted lines. Only H atoms involved in the packing are shown for clarity. Symmetry: (i) 1/2–x, 1/2+y, 3/2–z. (ii) 1/2–x, y–1/2, 3/2–z. (iii) 1/2+x, 1/2–y, z–1/2. (iv) x–1/2, 1/2–y, z–1/2.

Table 2. Crystallographic and structure refinement data for Compound 5

Asymmetric unit	$C_{27}H_{26}N_4O_2$
MW	438.52
Temperature (K)	135(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
a (Å)	10.7826(4)
b (Å)	14.5943(5)
c (Å)	15.3792(5)
α (°)	90
β (°)	96.213(2)
γ (°)	90
Volume (Å^3)	2405.93(14)
Z	4
ρ (mg.m$^{-3)}$	1.211
μ (mm^{-1})	0.078
Crystal size (mm)	0.24 × 0.22 × 0.04
Theta range (°)	2.79–26.00
Limiting indices	$-13 \leq h \leq 13$ $-18 \leq k \leq 18$ $-18 \leq l \leq 16$
Reflections collected	28,639
No. of unique data	4715
R_{int}	0.0637
Absorption coefficient range	0.6087–0.7456
Restraints	9
No. of parameters	321
Refinement method	Full-matrix least-squares method on F^2
P1, P2 coefficients of weighting scheme[a]	0.0338, 0.93
Goodness of fit on F^2	1.002
R_1[b,c]/data number	0.044/2872
wR_2[d] (all data)	0.110
Largest differential peak and hole (e.A^{-3})	0.165 and −0.172

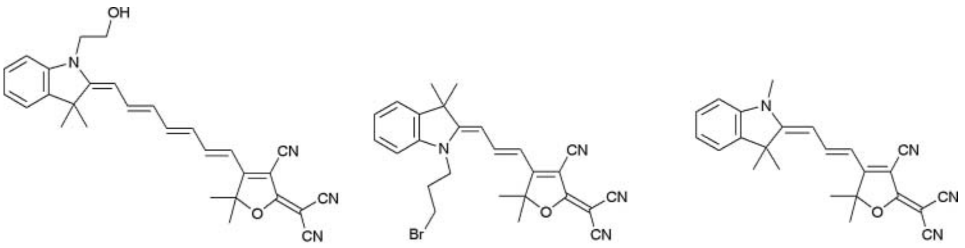
[a] Weight, $w = 1/[\sigma^2(F_o^2) + (P1 * P)^2 + P2 * P]$, where $P = (\text{Max}(F_o^2, 0) + 2 * F_c^2)/3$.

[b] Intensities two times their standard deviations (from counting statistics).

[c] $R_1 = \Sigma \| F_o | - F_c \| / \Sigma | F_o |$.

[d] $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

that the furan-2-ylidene ring (C4–C7, O1) is planar, while the component planar rings of the indol-2-ylidene system are at 1.95(11)° to each other which is similar to the value of 1.94(6)° found for 2-(3-cyano-4-{7-[1-(2-hydroxyethyl)-3,3-dimethyl-1,3-dihydro-indol-2-ylidene]-hepta-1,3,5-trienyl-5,5-dimethyl-5*H*-furan-2-ylidene)-malononitrile – Compound 6 (Fig. 7) [12]. The indol-2-ylidene plane (N4, C16–C23) makes an angle of 5.11(17)° to the plane running through the polymethine chain atoms (C11–C15). This plane in turn subtends 16.51(18)° to the plane through the furan-2-ylidene



Compound 6 Compound 7 Compound 8

Figure 7. Structure of related chromophores for which structural parameters have previously been reported.

ring (C4–C7, O1). This reflects a twist along the molecules between the terminal groups of ~19°, which is significantly greater than the value for both Compound 6 (~8°, Fig. 8) and 2-(4-{3-[1-(3-bromo-propyl)-3,3-dimethyl-1,3-dihydro-indol-2-ylidene]-propenyl}−3-cyano-5,5-dimethyl-5*H*-furan-2-ylidene)-malononitrile – Compound 7 (also ~8°) [11].

The bond length alternation (BLA) parameter [13] for Compound 5 is 0.024 Å (Table 3), which is similar to the values found from X-ray data for the closely related compounds, Compound 6 (0.018Å), Compound 7 (0.012 Å) and 2-{3-cyano-5,5-dimethyl-4-[3-(1,3,3-trimethyl-1,3-dihydro-indol-2-ylidene)-propenyl]-5*H*-furan-2-ylidene}-malononitrile – Compound 8 (0.006Å) [5]. Nonetheless, as Compound 5 has a slightly larger BLA value, it is expected to also have the highest NLO response of these four compounds. As noted above, this is in agreement with previous work which shows that a five-carbon interconnect between the donor and the acceptor in indoline-π-CTF chromophores is optimal [5]. It is also worth noting that Compounds 5, 6, and 8 have molecular configurations in which the indoline dimethyl and CTF dimethyl groups are in a *cis* relationship with respect to the polymethine chain, whereas the corresponding relationship in Compound 7 is *trans*. The unit cell packing of Compound 5 shows that the molecules are packed head to tail, consistent with a centrosymmetric space group linked in three dimensions by three different hydrogen bond interactions (Fig. 6, Table 4). The major hydrogen bonding interaction (entry 1, Table 4) is between the hydroxyl proton and the cyano nitrogen,

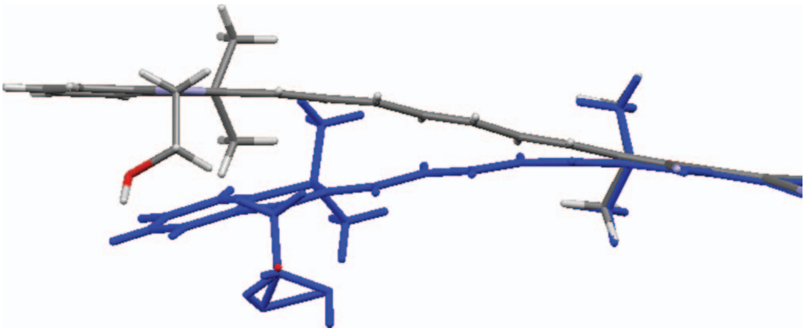


Figure 8. Comparison of the twists from planarity of Compound 5 (lower structure, dark shading) and 6 (upper structure, grey shading); see text.

Table 3. Selected bond distances (Å) and magnitude of BLA for CTF and Compound 5

Bond	CTF	Compound 5
C_2–C_6	1.358	1.389(3)
C_6–C_7	1.445	1.397(3)
C_7–C_4	1.343	1.413(2)
C_4–C_{11}	1.472	1.367(3)
C_{11}–C_{12}	—	1.402(3)
C_{12}–C_{13}	—	1.375(3)
C_{13}–C_{14}	—	1.391(3)
C_{14}–C_{15}	—	1.371(3)
C_{15}–C_{16}	—	1.391(3)
BLA	0.108	0.024

N2, with formation of chains of molecules along the *b*-axis in a C17 hydrogen bonding motif [15]. The alkene C–H···N(cyano) interactions form edge-on dimers, motif $R^2{}_2(20)$ [15] along the *a*-axis direction. Finally, a weak methyl C–H···hydroxyl O interaction is observed between approximately parallel adjacent molecules (entry 2, Table 4) in the *c*-axis direction, motif $R^2{}_2(28)$ [15]. Although unexpected, given the rigorously planar nature of Compound 8, the twisting present in Compound 5 is consistent with, and indeed can be explained by, these attractive packing interactions.

EO Coefficient

The maximum EO coefficient we were able to measure for a thin film containing 5% of Compound 5 in APC was 206 pm/V; this measurement was obtained immediately after poling was completed. Following this initial measurement, the sample was allowed to stand at room temperature and under atmospheric conditions for 72 h and the r_{33} value regularly re-measured over this period; the results are presented in Table 5. It was found that the response gradually decreased to around half of its original value after 72 h (viz. 108 pm/V, 53%). Furthermore, the reduction was initially quite rapid, with a 20% loss in response occurring after only 8 h. The rate of decay then slowed, and it took approximately 36 h for the EO coefficient to drop by another 20%. This reduction in the observed EO coefficient is not unexpected and is due to relaxation of the chromophore molecules, and therefore a return to a random orientation. While presently beyond the scope of the current work, this is a phenomenon that can be addressed by covalent attachment of the chromophore to a

Table 4. Hydrogen bond geometry Å(°)

D–H . . . A	D–H	H . . . A	D . . . A	D–H . . . A	Symmetry[a]
O2A-H2OA . . . N2	0.82(3)	2.10(3)	2.888(3)	161(4)	x, y + 1, z
C8–H8B . . . O2A	0.98	2.40	3.273(3)	147	−x, −y + 1, −z + 2
C15–H15 . . . N3	0.95	2.51	3.363(3)	150	−x + 1, −y + 1, −z + 2

[a] Symmetry to bring the A atom into contact.

Table 5. Change in the electro-optic coefficient over 72 h for a host–guest film containing Compound 5

Time (h)	r_{33} (pm/V)	% of initial r_{33} value	Time (h)	r_{33} (pm/V)	% of initial r_{33} value
0	206	100	22	148	72
0.5	192	93	25	141	69
1	187	91	27	140	68
2	184	89	28	139	67
3	180	87	44	124	60
4	169	82	46	123	60
8	167	81	48	122	59
9	163	79	72	108	53

host polymer with a high glass transition temperature (such as a polyimide) and incorporating additives that thermally cross-link around, or just below, the final poling temperature. Nonetheless, the present work has demonstrated that a simple and readily accessible chromophore such as Compound 5 can exhibit an EO coefficient almost an order of magnitude higher than the values reported for lithium niobate (32 pm/V) [4] and potassium titanium oxide phosphate (KTP) (36.3 pm/V) [16]. Furthermore, the macroscopic response we report here for a host–guest film containing Compound 5 is considerably higher than for a number of other organic systems. For example, crystals of the well-known organic salt DAST were found to give r_{11} values of 53 pm/V at 1310 nm and 92 pm/V at 720 nm [17]. In addition, host–guest thin films containing the DEMI chromophore in polysulfone were reported to have a r_{33} value of 21 pm/V at 1550 nm [18], while a thin film containing 35% CLD in APC gave an r_{33} value of 37 pm/V at 1310 nm [19]. While variations in chromophore loading, the poling conditions and wavelength used to undertake the measurements all affect the observed macroscopic nonlinearity, it is clear that Compound 5 has an excellent EO response when compared with other materials; consequently, this is a compound worthy of more detailed studies. The reason for the high r_{33} value found for films containing Compound 5 is not readily obvious, but may stem from the fact that the chromophore (Compound 5) has a high molecular hyperpolarizability, as deduced from the value of 1200×10^{-30} esu found for the analogue (Compound 1). In addition, the weak hydrogen bonding interactions that arise from the presence of the hydroxyl group (Fig. 6) appear to occur in competition with strong dipole–dipole interactions and should make electric field poling more efficient. Thus, overall, while Compound 5 has a very high EO coefficient and is able to be easily prepared and processed (features not readily applicable to crystalline materials), it is still not a viable replacement for current inorganic crystalline materials until issues with the temporal stability of poled films have been adequately addressed.

Conclusions

For use in nonlinear optics, a simple chromophore containing an indoline donor and a CTF acceptor has been prepared using a straightforward method. X-ray crystallographic studies show that while the molecule has a gentle twist along its length, it has a higher degree of BLA than its closely related counterparts and is therefore expected to provide thin films with high macroscopic NLO responses. This was indeed the case, as the maximum

EO coefficient of a host–guest film containing the molecule was found to be some seven times higher than the value reported for lithium niobate. Further studies to both optimize the loading of the chromophore in a host–guest film and improve the temporal stability of the final poled polymers using known methods are underway. These include covalent attachment of the chromophore to a polymer with a high glass transition temperature, the use of cross-linking agents during the poling process, and the incorporation of bulky, arene-rich substituents to retard aggregation.

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