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A tricyanopyrroline-based nonlinear optical chromophore bearing a lateral moiety: A novel steric technique for enhancing the electro-optic effect

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Abstract

Tricyanopyrroline-based nonlinear optical chromophores bearing a thienyl or phenyl group perpendicular to the long molecular axis, so as to separate the conjugation planes of the parent chromophore, were synthesized. The incorporation of such a lateral group into the molecular backbone of the colorant, together with the use of a strong tricyano-based acceptor moiety influenced nonlinear optical character. The compounds displayed significantly improved electro-optical properties within a polymer host after poling; values of the electric-optic coefficient of amorphous polycarbonate samples imbibed with the chromophores bearing a phenyl and a thienyl moiety were 32 and 40 pm/V, respectively, which were significantly greater than those of the polymer host bearing the chromophore which did not contain a lateral moiety (∼19 pm/V). The attachment of a lateral group to the chromophore increases electro-optic character after poling by suppressing electrostatic interactions.

Keywords: Tricyanopyrroline chromophore; Nonlinear optics; Electro-optic effect; Electrostatic interaction; Lateral moiety; X-ray crystallography

1. Introduction

Organic chromophores having large molecular hyperpolarizability (β) values, as well as polymeric composites containing them have attracted considerable attention over the past two decades [1–4].

Factors such as high nonlinear optical (NLO) susceptibility, fast response time, low dielectric constant, small dispersion in the refractive index, structural flexibility, and ease of material processing are advantageous in organic NLO materials systems [5–9]. To achieve good device functionality, NLO chromophores have to possess the following criterion simultaneously: high microscopic molecular nonlinearity ($\mu\beta(0)$), good thermal stability and photostability, low absorption, and weak molecular electrostatic interaction in the polymer matrix [10,11].

Recently, very large microscopic nonlinearities were achieved by employing a tricyanopyrroline (TCP) acceptor to synthesize highly efficient planar NLO chromophores [12]. When the dipole moment of a chromophore is sufficiently high to align itself in an antiparallel manner, the planar chromophore molecules do not dissociate easily and get aligned even under a poling field. By reducing the energy required for the chromophore aggregation of highly polar NLO chromophores, different alkyl substituents in the chromophore have been designed and their effect has been reported [13,14]. In order to disturb the intermolecular aggregation of chromophores and reduce the electrostatic attraction among the chromophores, a bulky substituent is usually tethered to the secondary amine in the TCP acceptor.

In this report, we suggest the method to reduce the electrostatic attraction by adding a lateral moiety to the planar chromophore including the synthesis of the TCP-based chromophores. Compared to the chromophore, **4a**, the other chromophores (**4b–e**) all contain the lateral moiety in the

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structure, which can aid the noncentrosymmetric arrangement during electric poling by reducing the electrostatic interaction between them. Three TCP chromophores were synthesized for thin-film electro-optics (EO). A thienyl or a phenyl unit perpendicular to the long molecular axis was employed as the lateral moiety to separate the conjugation planes of the TCP chromophore. After selecting the chromophore bearing a thienyl unit, we attached two different bulky substituents into the amine group of pyrroline ring. The EO properties of guest–host system using amorphous polycarbonate (APC) were investigated by a modified reflection technique. Here, we show that the intermolecular chromophore aggregation can be significantly suppressed by using this synthetic strategy.

2. Experimental

2.1. Instrumentation and EO measurements

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 MHz spectrometer using deuterated chloroform or dimethyl sulfoxide (DMSO) (Cambridge Isotope Laboratories, Inc.). Elemental analyses were performed using an EA1112 (Thermo Electron Corp.) elemental analyzer. Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821e instrument. Absorption analysis was performed with UV–VIS spectrometer (HP 8453, PDA type, $\lambda = 190$–1100 nm). The X-ray data were collected on a Bruker SMART APEXII diffractometer. The structure was solved and refined by least-squares analysis using anisotropic thermal parameters for non-hydrogen atoms with the WinGX package. H atoms were calculated at idealized positions. The final refinement on F^2 gave $R1 = 0.0709$ and $wR2 = 0.2041$ using 6917 reflections with the condition $I > 2\sigma(I)$. CCDC 618080.

The mixed solution of chromophore and APC was prepared in cyclopentanone/cyclohexanone (1:1). The same number of chromophore (e.g. 4.56×10^{19} molecules in 0.1 g of APC) was doped in all APC samples. For studying EO effect, thin films (thickness: 2.2–2.5 μm) were fabricated on indium tin oxide (ITO) precoated glass with a filtered solution (0.2 μm Acrodisc syringe filter). For reflection measurement of EO coefficient, we deposited the gold electrode on the surface of the film (thickness: 100 nm) to fabricate the sandwiched samples. The thickness of the film was measured by using Surface Profilometer (KOSAKA, ET-3000).

We measured the EO signal (I_m/I_c) of the samples by way of reflection technique after poling the sample following the conventional way [15–17]. An a.c. voltage (10 V_{rms} at 1 kHz) was applied to each sample to observe the modulated signal (I_m). The EO coefficient, "r_{33}" of the poled APC (poly(bisphenol A carbonate-*co*-4,4′-(3,3,5-trimethylcyclohexylidene)diphenol with $T_g = 202$ °C) film was calculated by the following equation. The r_{33} value is directly proportional to I_m/I_c in Eq. (1).

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{\left(n^2 - \sin^2\theta\right)^{1/2}}{\sin^2\theta} \sim I_m/I_c \qquad (1)$$

where n is the refractive index at 1300 nm and I_m is the amplitude of EO modulation. V_m is the a.c. voltage applied to the sample and I_c is the intensity of the incident light where phase retardation is 90° between TE and TM mode. Spectroscopic ellipsometry measurement to determine the refractive indices at various wavelengths was performed on the thin film with incidence angles of 65, 70, and 75° using a Woollam VASE model with autoretarder in the spectral range of 310–1550 nm (0.8–4.0 eV).

For *in-situ* EO study, the sample was placed on the heater to apply the voltage combined of d.c. and a.c. components ($V(t) = V_{d.c.} + V_o \sin \omega t$). An a.c. voltage ($V_o \sin \omega t$) was added to the d.c. voltage ($V_{d.c.}$) for the simultaneous poling and probing of the EO signal (I_m/I_c).

2.2. Synthesis

All commercially available starting materials were purchased from Aldrich or Acros Co. and used without further purification unless otherwise stated. All solvents used in this study were freshly dried under the standard distillation method.

2.2.1. Synthesis of dibutyl-(4-vinyl-phenyl)-amine (**2a**)

The suspension of methyltriphenylphosphonium iodide (14.15 g, 35.00 mmol) in tetrahydrofuran (THF) (100 mL) was prepared and THF solution of potassium *tert*-butoxide (3.92 g, 35.0 mmol) was slowly added over 0.5 h at room temperature. Then, **1** (7.00 g, 30.0 mmol) in THF (50 mL) was added into the mother solution and was allowed to stir for 2 h. Methanol (10 mL) was added and the solvent was evaporated. The resulting product was purified by silica-gel column chromatography (EtOAc: *n*-hexane = 1:20) to yield 3.76 g (54%) of a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.26 (d, $J = 8.4$ Hz, 2H), 6.60 (dd, $J_1 = 17.7$ Hz, $J_2 = 10.8$ Hz, 1H), 6.58 (d, $J = 8.4$ Hz, 2H), 5.49 (d, $J = 17.7$ Hz, 1H), 4.96 (d, $J = 10.8$ Hz, 1H), 3.25 (t, 4H), 1.50–1.60 (m, 4H), 1.27–1.37 (m, 4H), 0.94 (t, 6H).

2.2.2. Synthesis of 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**3a**)

Compound **5** (2.30 g, 10.00 mmol), **2a** (3.46 g, 15.00 mmol), and acetic anhydride (1.02 g, 10.00 mmol) were dissolved in 50 mL of dimethylformamide (DMF) under argon gas. The reaction mixture was cooled in an ice bath. $POCl_3$ (4.59 g, 30.00 mmol) was added dropwise over 0.5 h. The mixture was allowed to stir for 6 h at room temperature. The precipitate was collected into ice water by pouring the reaction mixture. The solid was filtered and dried to yield 1.84 g (46%) of a green solid. m.p. = 271 °C. ^{1}H NMR (300 MHz, DMSO): δ (ppm) 12.40 (s, 1H), 8.37 (d, $J = 15.0$ Hz, 1H, $-CH{=}CH-$), 7.68 (d, $J = 8.7$ Hz, 2H), 6.93 (d, $J = 15.0$ Hz, 1H, $-CH{=}CH-$), 6.80 (d, $J = 8.7$ Hz, 2H), 3.45 (t, 4H), 1.50–1.60 (m, 4H), 1.29–1.39 (m, 4H), 0.91 (t, 6H). Molecular formula: $C_{24}H_{25}N_5O$. Exact mass + H calculated, 400.22137, observed 400.2240.

*2.2.3. Synthesis of 2-{1-allyl-3-cyano-4-[2-(4-dibutylamino-phenyl)-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**4a**)*

Compound **3a** (1.00 g, 2.50 mmol) and sodium carbonate (0.13 g, 1.25 mmol) were mixed in 50 mL of DMF under argon. After heating the solution at 70 °C, allyl bromide (0.36 g, 3.00 mmol) was added dropwise and the reaction mixture was stirred for 0.5 h. It was poured into ice water to obtain the greenish solid product. The solid was filtered and dried at 60 °C *in vacuo*. The resulting product was purified by silica-gel column chromatography (EtOAc: chloroform = 1:15) to yield 0.73 g (66%) of a green solid. m.p. = 177 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.53 (d, J = 15.0 Hz, 1H, −CH═CH−), 7.61 (d, J = 8.7 Hz, 2H), 7.04 (d, J = 15.0 Hz, 1H, −CH═CH−), 6.69 (d, J = 8.7 Hz, 2H), 5.83−5.93 (m, 1H, −CH═CH_2), 5.31 (d, J = 10.2 Hz, 1H, −CH═CH_2), 5.14 (d, J = 17.1 Hz, 1H, −CH═CH_2), 4.69 (d, J = 4.8 Hz, 2H), 3.43 (t, 4H), 1.59−1.69 (m, 4H), 1.34−1.46 (m, 4H), 0.99 (t, 6H). Molecular formula: $C_{27}H_{29}N_5O$. Exact mass + H calculated, 440.2450, observed 440.2438; Anal. $C_{27}H_{29}N_5O$ (439.55) Calcd C 73.78, H 6.65, N 15.93, Found C 74.32, H 6.46, N 15.45.

*2.2.4. Synthesis of dibutyl-(4-styryl-phenyl)-amine (**2b**)*

Compound **2b** was synthesized by following the similar procedure for **2a**. Instead of methyltriphenylphosphonium iodide, benzyl-phosphonic acid diethyl ester was used in this synthesis. The resulting product was purified by silica-gel column chromatography (EtOAc: *n*-hexane = 1:15) to yield 46% of a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.38 (d, J = 8.7 Hz, 2H), 7.29−7.39 (m, 5H, phenyl), 7.03 (d, J = 16.2 Hz, 1H, −CH═CH−), 6.87 (d, J = 16.2 Hz, 1H, −CH═CH−), 6.62 (d, J = 8.7 Hz, 2H), 3.28 (t, 4H), 1.52−1.62 (m, 4H), 1.31−1.41 (m, 4H), 0.95 (t, 6H).

*2.2.5. Synthesis of 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-1-phenyl-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**3b**)*

Compound **3b** was synthesized by following the similar procedure for **3a**. Yield 31%. m.p. = 206 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.21 (s, 1H), 8.88 (s, 1H, ═C═CH−), 7.52−7.56 (m, 3H, phenyl), 7.29−7.33 (m, 2H, phenyl), 7.01 (d, J = 9.0 Hz, 2H), 6.43 (d, J = 9.0 Hz, 2H), 3.32 (t, 4H), 1.50−1.60 (m, 4H), 1.27−1.37 (m, 4H), 0.94 (t, 6H). Molecular formula: $C_{30}H_{29}N_5O$. Exact mass + H calculated, 472.2446, observed 472.2446.

*2.2.6. Synthesis of 2-{1-allyl-3-cyano-4-[2-(4-dibutylamino-phenyl)-1-styrylphenyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**4b**)*

Compound **4b** was synthesized by following the similar procedure for **4a**. The resulting product was purified by silica-gel column chromatography (EtOAc: chloroform = 1:20) to yield 0.74 g (58%) of red solid. m.p. = 180 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.73 (s, 1H, ═C═CH−), 7.50−7.54 (m, 3H, phenyl), 7.28−7.32 (m, 2H, phenyl), 6.95 (d, J = 9.0 Hz, 2H), 6.41 (d, J = 9.0 Hz, 2H), 5.86−5.96 (m, 1H, −CH═CH_2), 5.33 (d, J = 10.2 Hz, 1H, −CH═CH_2), 5.19 (d, J = 17.1 Hz, 1H, −CH═CH_2), 4.75 (d, J = 4.8 Hz, 2H), 3.31 (t, 4H), 1.49−1.59 (m, 4H), 1.27−1.37 (m, 4H), 0.94 (t, 6H). Molecular formula: $C_{33}H_{33}N_5O$. Exact mass + H calculated, 516.2763, observed 516.2770; Anal. $C_{33}H_{33}N_5O$ (515.65) Calcd C 76.87, H 6.45, N 13.58, Found C 78.02, H 6.40, N 13.65.

*2.2.7. Synthesis of dibutyl-[4-(2-thiophen-2-yl-vinyl)-phenyl]-amine (**2c**)*

Compound **2c** was synthesized by following the similar procedure for **2a**. Tributyl-thiophene-2-ylmethyl-phosphonium bromide was used in this synthesis. The resulting product was purified by silica-gel column chromatography (EtOAc: *n*-hexane = 1:15) to yield 67% of colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.33 (d, J = 8.7 Hz, 2H), 7.09 (d, J = 3.3 Hz, 1H), 7.01 (d, J = 15.9 Hz, 1H, −CH═CH−), 6.96 (d, J = 3.3 Hz, 1H), 6.95 (d, J = 3.3 Hz, 1H), 6.84 (d, J = 15.9 Hz, 1H, −CH═CH−), 6.64 (d, J = 8.7 Hz, 2H), 3.31 (t, 4H), 1.53−1.63 (m, 4H), 1.32−1.42 (m, 4H), 0.96 (t, 6H).

*2.2.8. Synthesis of 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-1-thiophen-2-yl-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**3c**)*

Compound **3c** was synthesized by following the similar procedure for **3a**. Yield 28%. m.p. = 224 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.55 (s, 1H), 8.90 (s, 1H, ═C═CH−), 7.59 (d, J = 5.1 Hz, 1H), 7.22 (dd, J_1 = 3.6 Hz, J_2 = 5.1 Hz, 1H), 7.10 (d, J = 9.3 Hz, 2H), 7.07 (d, J = 3.6 Hz, 1H), 6.50 (d, J = 9.3 Hz, 2H), 3.36 (t, 4H), 1.53−1.63 (m, 4H), 1.30−1.40 (m, 4H), 0.95 (t, 6H). Molecular formula: $C_{28}H_{27}N_5OS$. Exact mass + H calculated, 482.2015, observed 482.2021.

*2.2.9. Synthesis of 2-{1-allyl-3-cyano-4-[2-(4-dibutylamino-phenyl)-1-thiophen-2-yl-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**4c**)*

Compound **4c** was synthesized by following the similar procedure for **4a**. The resulting product was purified by silica-gel column chromatography (EtOAc: chloroform = 1:20) to yield 58% of a red solid. m.p. = 178 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.76 (s, 1H, ═C═CH−), 7.58 (d, J = 5.1 Hz, 1H), 7.21 (dd, J_1 = 3.6 Hz, J_2 = 5.1 Hz, 1H), 7.05 (d, J = 3.6 Hz, 1H), 7.04 (d, J = 9.0 Hz, 2H), 6.47 (d, J = 9.0 Hz, 2H), 5.85−5.95 (m, 1H, −CH═CH_2), 5.33 (d, J = 10.2 Hz, 1H, −CH═CH_2), 5.19 (d, J = 17.1 Hz, 1H, −CH═CH_2), 4.74 (d, J = 4.8 Hz, 2H), 3.34 (t, 4H), 1.52−1.62 (m, 4H), 1.30−1.40 (m, 4H), 0.95 (t, 6H). Molecular formula: $C_{31}H_{31}N_5OS$. Exact mass + H calculated, 522.2328, observed 522.2331; Anal. $C_{31}H_{31}N_5OS$ (521.67) Calcd C 71.37, H 5.99, N 13.42, Found C 71.23, H 5.47, N 13.13.

*2.2.10. Synthesis of 2-{1-benzyl-3-cyano-4-[2-(4-dibutylamino-phenyl)-1-thiophen-2-yl-vinyl]-5-oxo-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**4d**)*

Compound **4d** was synthesized by following the similar procedure for **4a**. Instead of allyl bromide, benzyl bromide was used in this synthesis. The resulting product was purified by silica-gel column chromatography (EtOAc: chloroform = 1:20) to yield

78% of a red solid. m.p. = 193 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.81 (s, 1H, =C=CH–), 7.31–7.42 (m, 3H, phenyl), 7.20–7.26 (m, 3H), 7.08 (d, $J = 3.6$ Hz, 1H), 7.04 (d, $J = 9.0$ Hz, 2H), 6.47 (d, $J = 9.0$ Hz, 2H), 5.37 (s, 2H, –CH$_2$–), 3.34 (t, 4H), 1.52–1.62 (m, 4H), 1.28–1.41 (m, 4H), 0.95 (t, 6H). Molecular formula: $C_{35}H_{33}N_5OS$. Exact mass + H calculated, 572.2479, observed 572.2510; Anal. $C_{35}H_{33}N_5OS$ (571.73) Calcd C 71.37, H 5.99, N 13.42, Found C 72.64, H 5.55, N 11.51.

*2.2.11. Synthesis of 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-1-thiophen-2-yl-vinyl]-5-oxo-1-pentafluorophenyl-methyl-1,5-dihydro-pyrrol-2-ylidene}-malononitrile (**4e**)*

Compound **4e** was synthesized by following the similar procedure for **4a**. Instead of allylbromide, we used 1-bromo-methyl-2,3,4,5,6-pentafluoro-benzene. The resulting product was purified by silica-gel column chromatography (EtOAc: chloroform = 1:20) to yield 62% of a red solid. m.p. = 185 °C. ^{1}H NMR (300 MHz, CDCl$_3$): δ (ppm) 8.70 (s, 1H, =C=CH–), 7.58 (d, $J = 5.1$ Hz, 1H), 7.21 (dd, $J_1 = 3.6$ Hz, $J_2 = 5.1$ Hz, 1H), 7.06 (d, $J = 3.6$ Hz, 1H), 7.02 (d, $J = 9.0$ Hz, 2H), 6.46 (d, $J = 9.0$ Hz, 2H), 5.46 (s, 2H, –CH$_2$–), 3.35 (t, 4H), 1.52–1.62 (m, 4H), 1.28–1.41 (m, 4H), 0.95 (t, 6H). Molecular formula: $C_{35}H_{28}F_5N_5OS$. Exact mass + H calculated, 662.2007, observed 622.1993; Anal. $C_{35}H_{28}F_5N_5OS$ (661.68) Calcd C 63.53, H 4.27, N 10.58, Found C 63.43, H 4.20, N 10.39.

3. Results and discussion

3.1. Synthesis and materials

Although the microscopic nonlinearity ($\mu\beta(0)$) of the planar and highly polar chromophore, **4a**, is relatively high [12], the macroscopic nonlinearity in the polymer matrix cannot be high at a high loading level (>25%) into the host polymer. Thus, we have designed new chromophore structures for improving the poled alignment by reducing the dipole–dipole interaction in the polymer host.

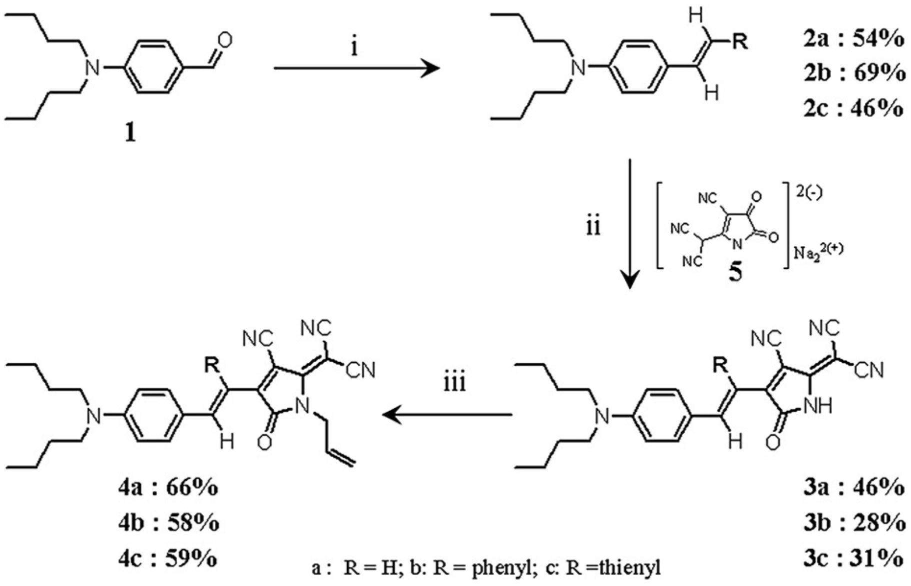
We suggest the syntheses of TCP chromophores bearing a bulky substituent in the ethylenic double bond. The syntheses of the NLO chromophores are shown in Scheme 1.

The incorporation of a phenyl or thienyl lateral group into the molecular backbone and the use of a strong tricyano-based acceptor moiety may influence the molecular NLO property. In order to prepare **4a–c**, compounds **2a** and **2c** were firstly prepared by the Wittig reaction of **1** with methyltriphenylphosphonium iodide and 2-thienylmethyltributylphosphonium bromide, respectively.

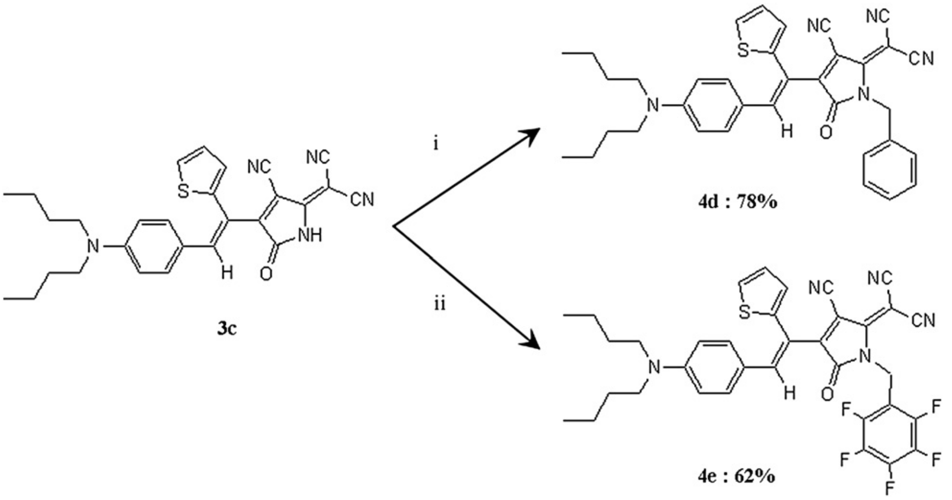
Further, **2b** was prepared by the Horner–Emmons condensation of **1** with benzyl-phosphonic acid diethyl ester. 3-Amino-2-cyano-pent-2-ene dinitrile and oxalic acid diethyl ester were reacted to yield **5**, a yellow shiny crystal [18]. Then, **5** and compounds **2a–c** were condensed to yield **3a–c**. The reaction mechanism was already well described in the literature [19]. Allyl bromide was firstly reacted with a secondary amine in the pyrroline ring to yield **4a–c**, which is a green (**4a**) and reddish green (**4b**,**c**) crystal powder.

Using the compound **3c**, we also attached a bulky substituent to the amine of pyrroline ring. As can be seen in Scheme 2, instead of allylbromide, benzyl bromide and 1-bromomethyl-2,3,4,5,6-pentafluoro-benzene were used for this synthesis. Therefore, **4d** and **4e** were found to contain two bulky substituents in one molecule.

The solubility of chromophore, **4b–e** in some organic solvents, such as chloroform, tetrahydrofuran, and cyclohexanone was observed to be considerably better than that of **4a**. In addition, when **4a** was doped into host APC polymer whose



Scheme 1. Synthetic procedure of the chormophores **4a–c**. Reagents and conditions: (i) (a) $[CH_3\text{-}PPh_3]^+I^-$, KO^{t}Bu, THF, rt; (b) 2-thienylmethyltributylphosphonium bromide, KO^{t}Bu, THF, rt; (c) benzyl-phosphonic acid diethyl ester, KO^{t}Bu, THF, rt; (ii) disodium salt(5), POCl$_3$, DMF, Ac$_2$O, 0 °C, (iii) allyl bromide, Na$_2$CO$_3$, DMF, 70 °C.



Scheme 2. Synthetic procedure of the chormophores **4d** and **4e**. Reagents and conditions: (i) benzyl bromide, Na_2CO_3, DMF, 70 °C, (i) 1-bromomethyl-2,3,4,5,6-pentafluoro-benzene, Na_2CO_3, DMF, 70 °C.

concentration is higher than 25 wt%, severe crystallization occurs to ruin the optical quality of a spin cast film. However, the chromophores of **4b–e** can be doped into APC without crystallization even if the doping concentration is higher than 40 wt%. In short, they are so miscible with APC to maintain good optical quality of thin films.

UV–VIS absorption spectroscopy revealed that **4a** had a λ_{max} value of 741 nm in chloroform (see Fig. 1). Further, **4b** and **4c** exhibit the absorption maximum at 740 and 735 nm, respectively. However, **4a** exhibits a relatively shorter absorption edge wavelength ($\lambda_{abs.\ edge}$) of approximately 820 nm, which implies a slightly larger HOMO–LUMO energy gap ($\Delta E_g = 1.51$ eV). The chromophore **4e** exhibited highest λ_{max} at around 752 nm, which is due to additional electron withdrawing effect from pentafluorobenzyl moiety.

Using the absorption edge wavelength ($\lambda_{abs.\ edge}$) of each spectrum, we determined the optical bandgap ($\Delta E_g^{opt.}$) that implies the approximate value of highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gap. Briefly, no significant changes in the electronic and optical properties are observed although a lateral moiety is placed along the molecule. When we tether the pentafluorobenzyl moiety into the amine group of pyrroline ring, chromophore **4e** shows lowest HOMO–LUMO energy gap to be around 1.47 eV, which is smaller than the others (see Table 1).

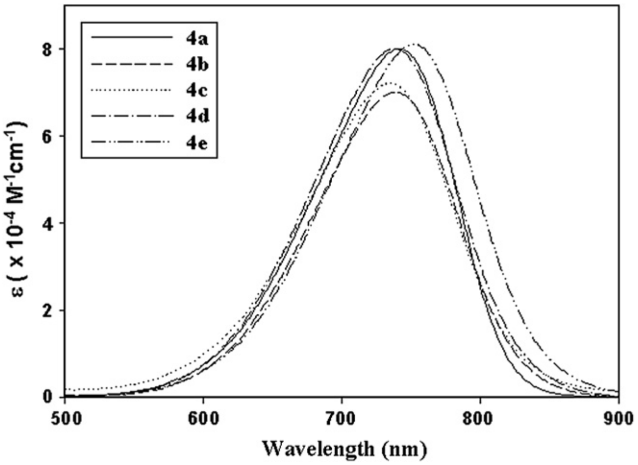


Fig. 1. Absorption spectra of five chromophores in solution states (solvent: chloroform).

3.2. X-ray crystallographic study of chromophore **4c**

Further evidence of the formation of loosely held molecular arrangement of the chromophores is provided by the structure determination of chromophore **4c** in the solid state by using X-ray crystallography. Crystals of **4c** that are suitable for crystallographic structure analysis could be obtained by slow recrystallization from an ethanol solution under an ambient condition.

Chromophore **4c** crystallizes in the monoclinic $P2_1/n$ space group and the presence of the thiophene group plays a crucial role in altering the crystal system (see Table 2). Recently, the chromophore similar to **4a** that is 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-vinyl]-5-oxo-1-propyl-1,5-dihydro-pyrrol-2-ylidene}-malononitrile was reported in the literature except for the allyl substituent.

The crystallographic structure exhibits the triclinic $P\bar{1}$ space group with the crystal parameters of $a = 11.1230(4)$ Å, $b = 13.0450(5)$ Å, $c = 17.9940(7)$ Å, $\alpha = 100.870(2)°$,

Table 1
Measured and calculated values for five TCP-based chromophores; **4a–e** and EO samples

Compound	T_m (°C)	λ_{max} (nm)	ε ($M^{-1}\,cm^{-1}$)	ΔE_g^{opt}	λ_{cutoff} (nm)	EO sample	r_{33} (pm/V)
4a	177	741	80,000	1.51	820	Sample **I**	19
4b	170	740	72,000	1.50	825	Sample **II**	33
4c	178	735	70,000	1.50	827	Sample **III**	45
4d	193	738	80,000	1.50	828	Sample **IV**	29
4e	185	752	81,000	1.47	841	Sample **V**	22

Table 2
Crystal data and structure refinement for **4c**

Empirical formula	$C_{31}H_{31}N_5OS$
Formula weight	521.67
Temperature	130 K
Crystal system, space group	Monoclinic, $P2_1/n$
Unit cell dimensions	$a = 12.8510(3)$ Å
	$b = 11.3677(3)$ Å
	$c = 19.1196(5)$ Å
	$\beta = 94.2190(10)°$
Volume	2785.54(12) $Å^3$
Z, Calculated density	4, 1.244 Mg/m^3
Absorption coefficient	0.149 mm^{-1}
F(000)	1104
Theta range for data collection	1.85–28.31°
Reflections collected/unique	27028/6917 [*R*(int) = 0.0451]
Completeness to theta = 28.31	99.8%
Data/restraints/parameters	6917/0/345
Goodness-of-fit on F^2	1.038
Final *R* indices [$I > 2\sigma(I)$]	$R1 = 0.0709$, $wR2 = 0.2041$
R indices (all data)	$R1 = 0.1100$, $wR2 = 0.2323$

Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 618080. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

$\beta = 96.658(2)°$, and $\gamma = 102.460(1)°$ [12]. Although the thiophene unit in **4c** is tethered to C16 carbon, the overall coplanarity of the chromophore from the dialkylamine to TCP acceptor is unusually retained as expected from the conjugation through the molecular backbone. The donor and acceptor units in the dipolar chromophore are positioned in a trans mode with respect to the central double bond.

In particular, the thiophene moiety in a molecule lies almost perpendicular to the main plane with a dihedral angle of 85.09(9)° between the benzene and thiophene rings as shown in Fig. 2a. Further, Fig. 2b shows that the unit cell contains two types of non-coplanar benzene molecules tilted at 71.72(8)°. The main feature of this crystal is the shortest inter-chromophoric distance (4.333 Å) between the benzene carbons on the neighboring molecules. This value is much larger than that (3.412 Å) of 2-{3-cyano-4-[2-(4-dibutylamino-phenyl)-vinyl]-5-oxo-1-propyl-1,5-dihydro-pyrrol-2-ylidene}-malononitrile [12]. Although the allyl substituent in **4a** is slightly different from the propyl substituent in the reported chromophore, we found that this longer separation between the chromophores is definitely associated with the existence of a lateral thiophene unit. The inter-distance between the nitrogen of dibutyl amine and the nitrogen of pyrroline acceptor on adjacent chromophores is 6.091 Å, resulting in an antiparallel crystal packing between the molecules.

3.3. Electro-optic properties of the chromophore doped APC samples

In order to compare the macroscopic nonlinearities of APC samples bearing five different TCP chromophores, we doped them with an identical molar concentration (e.g. 4.56×10^{19} molecules in 0.1 g of APC) and poled the samples to measure the EO coefficient at 1300 nm [15–17]. Samples **I**, **II**, **III**, **IV**, and **V** contains the chromophores **4a**, **4b**, **4c**, **4d**, and **4e**, respectively. Spectroscopic ellipsometry measurements performed on the materials were used along with the absorption spectra of each film to accurately determine the real and imaginary part of refractive index at 1300 nm. Under identical measurement conditions, APC samples containing **4a**, **4b**, **4c**, **4d**, and **4e** all showed refractive indices to be 1.63, 1.63, 1.62, 1.64, and 1.66, respectively.

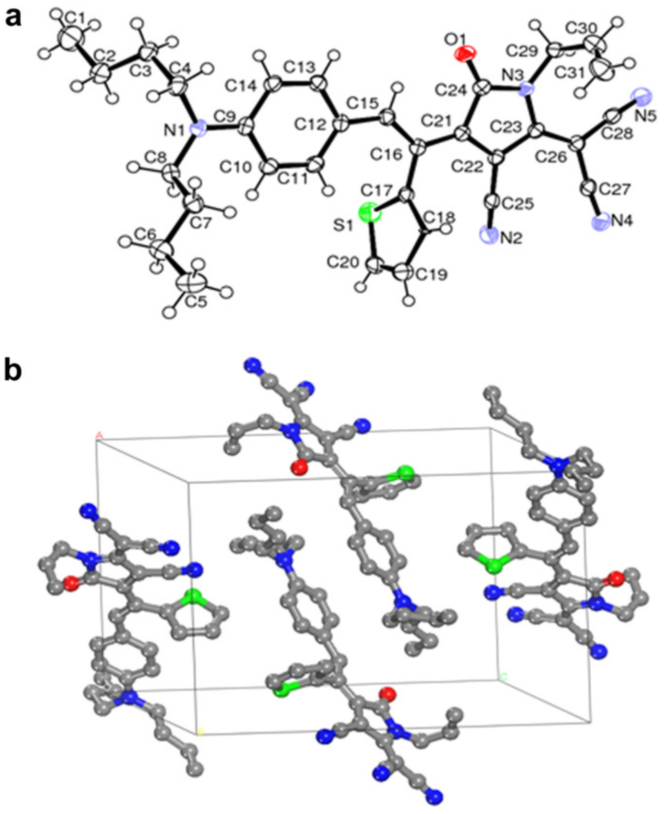


Fig. 2. (a) ORTEP representation of the asymmetric unit in **4c** showing the atom-labeling scheme and (b) crystal packing diagram in the unit cell. Colors indicate C in grey, N in blue, O in red, and S in green. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

The EO coefficient (r_{33}) values were measured by a modified reflection technique described in Section 2.

In this experiment, we applied the electric field $[E(t) = E_{d.c.} + E_o \sin \omega t]$ ($E_{d.c.} = 70$ V/μm)to the samples in order to monitor the EO signal while heating the sample. The EO signal, (I_m/I_c), increases slowly as a temperature is raised. The temperature rate was set to be 5 °C/min. As we increase the sample temperature, the signal (I_m/I_c) has a transition temperature (T_{tr}) at which the signal abruptly increases. The transition temperatures (in the vicinity of T_gs of the samples) of the five samples were observed similarly at around 108 °C. Therefore, we selected 113 °C as a poling temperature. Therefore we compared poling efficiency under an identical condition; Poling temperature, 113 °C in the presence of 70 V/μm. This optimization method of poling conditions was well described in our previous work [20].

The EO coefficients of APC samples **II** and **III** were determined as 33 and 45 pm/V, respectively, which are significantly greater than that of the sample **I** (19 pm/V). When the sample **III** was poled under 100 V/μm, the EO coefficient was determined as 54 pm/V. Although the molecular energy state, bandgap energy, and main conjugated structure are fairly similar, the sample **III** exhibited a relatively higher EO coefficient (~40–54 pm/V) only owing to the existence of the lateral group that is located almost perpendicular to the long molecular axis. The samples **IV** and **V** displayed 29 and 22 pm/V under an identical poling condition. Resulting from this comparison, the presence of bulky substituent in the pyrroline ring reduces the poling efficiency. It might require higher activation energy to align the chromophores to the poling direction. This study provides conclusive evidence that the chromophore having a lateral group has less electrostatic interaction to diminish the dimeric or multimeric aggregation rather than chromophore **4a**.

Additionally, when tethering a bulkier substituent in the pyrroline ring, lower EO coefficient, r_{33} was observed. Smaller substituent in the pyrroline ring will provide better poling efficiency to exhibit high EO coefficient when comparing the EO coefficients of samples **IV** and **V**, which is likely to be attributed to higher activation energy for aligning the chromophore (see Table 1).

4. Conclusion

We synthesized tricyanopyrroline-based nonlinear optical (NLO) chromophores either bearing a lateral moiety in the ethylenic bond or a substituent in the pyrroline ring successfully. The incorporation of a lateral group into the molecular backbone and the use of a strong tricyano-based acceptor moiety may influence the molecular NLO property. They exhibit significantly improved EO properties in a polymer host after poling. This provides clear evidence that the chromophore having a lateral group has less electrostatic interaction to diminish the multimeric aggregation rather than chromophore without it. When we tether a bulky substituent into the pyrroline ring, the poling efficiency is less than those of the chromophore bearing an allyl substituent.

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