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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

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## 1. Introduction

Organic chromophores having large molecular hyperpolarizability ($\beta$) 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. $4.56 \times 10^{19}$ 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, $CDCl_3$): $\delta$ (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): $\delta$ (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.