

Highly Efficient, Thermally and Chemically Stable Second Order Nonlinear Optical Chromophores Containing a 2-Phenyl-tetracyanobutadienyl Acceptor

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Received October 7, 1998

Organic second-order nonlinear optical (NLO) polymers, with their large electro-optic (E–O) coefficients, fast response speed, and good processibility for multilayer integration into large-area devices, show promise in optoelectronic applications.^{1,2} The performance of polymeric E–O devices for information processing and telecommunications relies on exceptional E–O property, low optical loss, and temporal stability of the poling-induced polar order. In general, the large long-term E–O coefficient of a NLO polymer can be realized by aligning the dipole moment of the efficient chromophore. This is achieved by applying a strong electric field (1–2 MV/cm) at a temperature that is above the glass-transition temperature (T_g) of the high-temperature polymer. Because of the high-temperature processing of multilayer E–O devices (200–300 °C) and the very polar environment of the surrounding polymer matrix, NLO chromophores need to possess both excellent thermal stability and chemical stability.

Recently, a series of highly hyperpolarizable heteroaromatic NLO chromophores using thiophene as the conjugating moiety and tricyanovinyl as the electron acceptor have been reported to exhibit large molecular hyperpolarizability ($\beta\mu$ as high as 9800×10^{-48} esu).^{3–5} The large hyperpolarizability of these chromophores was attributed to the easily polarizable thiophene moiety (29 kcal/mol for aromatic stabilization energy), where the very strong dialkylamino and tricyanovinyl groups were used as donors and acceptors, respectively. Although these chromophores possessed very promising $\beta\mu$ values, several deficiencies were associated with these molecules, such as low thermal stability and chemical sensitivity to the nucleophiles; these traits are detrimental to materials during device fabrication. To overcome these deficiencies associated with the tricyanovinyl group, modifications by replacing the most reactive CN group in the tricyanovinyl moiety with a series of aryl groups have been reported.^{6,7} Although excellent chemical stability (to both acids and bases) and thermal stability (>300 °C) were achieved, the nonlinearity of these molecules was dramatically reduced. In this paper, we report the synthesis and characterization of a series of highly efficient, thermally and chemically stable chromophores using the 2-phenyl-tetracyanobutadienyl (Ph-TCBD) group as the electron acceptor. These compounds were synthesized via a simple

reaction between electron-rich bis-aryl acetylenes and tetracyanoethylene (TCNE).

The general methodology for the synthesis of Ph-TCBD-containing chromophores is shown in Scheme 1, using a similar approach developed by Barton et al.⁸ Phenyl acetylene was coupled with iodides **1a–f** in diethylamine at 25 °C using CuI/Pd(Ph₃P)₂Cl₂ as the catalyst. This resulted in the chromophore precursors, electron-rich bis-aryl acetylenes **2a–f**. A [2 + 2] cycloaddition of TCNE with **2a–f** followed by a ring-opening reaction resulted in Ph-TCBD containing chromophores **3a–f** (Table 1).¹⁰ All of the compounds studied here were fully characterized using ¹H NMR and elemental analysis.

On the basis of the molecular structure, a Ph-TCBD functional group could be viewed as a modified tricyanovinyl acceptor. The α -cyano in the tricyanovinyl group is “substituted” with an α -Ph-dicyanovinyl group which is a strong electron withdrawing group, but not a good leaving group. Preliminary results have demonstrated that chromophores with the Ph-TCBD group as acceptor are much more stable to amine nucleophiles than their tricyanovinyl-substituted counterparts (Figure 1).

X-ray single-crystal structure of **3a** (Figure 2) reveals that the dicyanovinyl moiety is linked coplanarly to the donor-substituted aryl segment and forms an efficient push–pull system. In the meantime, the “substituent”, α -Ph-dicyanovinyl is twisted out of the plane. The dihedral angle between two dicyanovinyl planes is 78.3°. Even though α -Ph-dicyanovinyl is a much stronger electron acceptor than a cyano group, the λ_{\max} of **3a** demonstrated a 39-nm blue-shift when compared to its tricyanovinyl-substituted analogue. Nevertheless, the α -Ph-dicyanovinyl group still strengthens the Ph-TCBD electron-acceptor through the inductive effect. Compared to its dicyanovinyl analogue, the absorption λ_{\max} of **3d** has a red-shift of 90 nm.⁷ This indicates that the α -Ph-dicyanovinyl on the Ph-TCBD group has a strong electron-withdrawing effect on the adjacent planar push–pull segment. In addition, the “stuck-out” α -Ph-dicyanovinyl group increases the intermolecular steric hindrance among the chromophores which may help prevent molecules from stacking up on each other, and thus, reduce chromophore aggregation. This, in turn, may improve the poling efficiency and lower the optical loss caused by light scattering, which are the most challenging issues for optical device applications.

The inherent thermal stabilities of these Ph-TCBD-substituted chromophores were determined by sealed-pan differential scanning calorimetry (DSC). Each of the chromophore samples was

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(9) The synthetic procedure for precursor **2a**: a mixture of **1a** (300 mg, 0.84 mmol), phenyl acetylene (95 mg, 0.92 mmol), Pd(Ph₃P)₂Cl₂ (12 mg, 0.17 mmol), and CuI (7 mg, 0.34 mmol) in diethylamine (4 mL) was stirred under N₂ at 25 °C for 5 h. The reaction mixture was then added to H₂O (50 mL). The organic layer was first diluted with CH₂Cl₂ (30 mL) and then washed twice with H₂O. The CH₂Cl₂ solution was dried with anhydrous Na₂SO₄, and the solvent was evaporated under reduced pressure. The crude product was purified through a silica gel column using CH₂Cl₂/hexanes (20/80) as eluent to afford **2a** as a yellow powder in 89.7% yield (250 mg): ¹H NMR (300 MHz, CDCl₃) 7.60 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.8$ Hz, 2H), 7.42–7.36 (m, 3H), 7.27 (d, $J = 3.9$ Hz, 1H), 7.08 (d, $J = 3.9$ Hz, 1H), 6.69 (d, $J = 8.8$ Hz, 2H), 3.43 (q, $J = 7.0$ Hz, 4H), 1.20 (t, $J = 7.0$ Hz, 6H). Anal. Calcd for C₂₂H₂₁NS: C, 79.72; H, 6.39. Found: C, 79.57; H, 6.28.

(10) The synthetic procedure for chromophore **3a**: a mixture of **2a** (250 mg, 0.75 mmol) and TCNE (97 mg, 0.76 mmol) in CHCl₃ (10 mL) was stirred at 25 °C for 2 h. The crude product was directly concentrated onto silica gel by removing the solvent under a reduced pressure. It was then purified through a silica gel column using CH₂Cl₂/hexanes (50/50) as eluent to give **3a** as a blue solid in 72% yield (250 mg): ¹H NMR (300 MHz, CDCl₃) 7.80 (d, $J = 8.4$ Hz, 2H), 7.72 (d, $J = 4.5$ Hz, 1H), 7.67 (d, $J = 7.3$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 4H), 7.33 (d, $J = 4.5$ Hz, 1H), 6.70 (d, $J = 8.8$ Hz, 2H). Anal. Calcd for C₂₈H₂₁N₅: C, 73.17; H, 4.61. Found: C, 73.41; H, 4.83.

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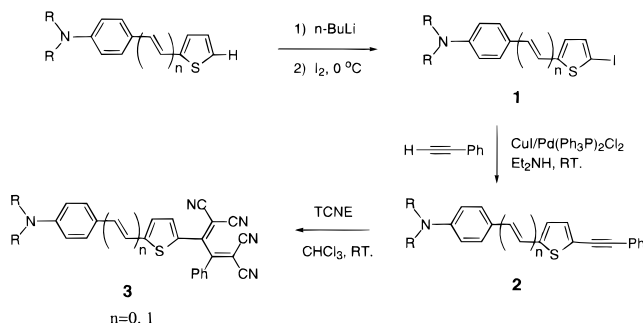
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Scheme 1. Synthetic Route for Ph-TCBD-Containing Chromophores

Table 1. Electronic Absorption and Thermal Stability of Compound **3a–f**

	R	n	λ_{max} (nm)	T_d ($^\circ\text{C}$)
3a	C ₂ H ₅	0	562	265
3b	C ₆ H ₅	0	542	350
3c	(C ₄ H ₉)C ₆ H ₄	0	561	325
3d	C ₂ H ₅	1	604	245
3e	C ₆ H ₅	1	566	340
3f	(C ₄ H ₉)C ₆ H ₄	1	589	305

heated at a rate of 20 $^\circ\text{C}/\text{min}$ in order to determine its decomposition temperature (T_d). The T_d 's of chromophores **3a–f** ranged from 240 to 360 $^\circ\text{C}$. This makes these chromophores ideal candidates for incorporation into high-temperature polymers for device applications. The data also showed that the T_d 's of the chromophores with diarylamino groups as electron donors were 60–90 $^\circ\text{C}$ higher than their dialkylamino analogues.¹¹ To determine the compatibility between the chromophores and the polymers, the thermal stability of the chromophores in a polymer matrix was also examined. For instance, a guest/host system was prepared by doping 10 wt % of **3b** into PQ-100. A spin-coated film was heated to temperatures of 150, 175, 200, and 225 $^\circ\text{C}$ under N₂ at 20-min intervals. From the absorption spectrum, the π - π^* charge-transfer band was used to monitor the degradation/sublimation of the chromophores in their polymer matrix. It was found that these chromophores were stable in the polymer at temperatures up to 225 $^\circ\text{C}$. The experiment demonstrated that the Ph-TCBD thiophene chromophores possessed higher chemical stability than their tricyanovinyl counterpart (decomposition at 180 $^\circ\text{C}$).

E–O studies were performed on the polymers (guest/host) in which chromophores **3a** and **3d** (25 wt %) were formulated into PQ-100. Optical quality films (optical loss < 2 dB/cm at 1.3 μm) were spin-coated onto indium-tin-oxide (ITO) glass slides using a 12% w/w solution of the resin in cyclopentanone. The films were kept in a vacuum oven at 85 $^\circ\text{C}$ for 24 h and were then briefly heated on a hot stage at 170 $^\circ\text{C}$ under nitrogen for 20 min to remove residual solvent. A thin layer of gold was sputtered onto the polyquinoline films as the top electrode for poling. The samples were then poled at 200 $^\circ\text{C}$ with an applied DC electric field of 0.9 MV/cm. The poled thin films of **3a** and **3d** in PQ-100 exhibited an r_{33} value of 18 and 36 pm/V, respectively, at 1.3 μm . These results were higher than those of their tricyanovinyl-substituted analogues (14 and 27 pm/V) that were formulated and poled under similar conditions. These results indicated that the electron-accepting strength of the Ph-TCBD group may be

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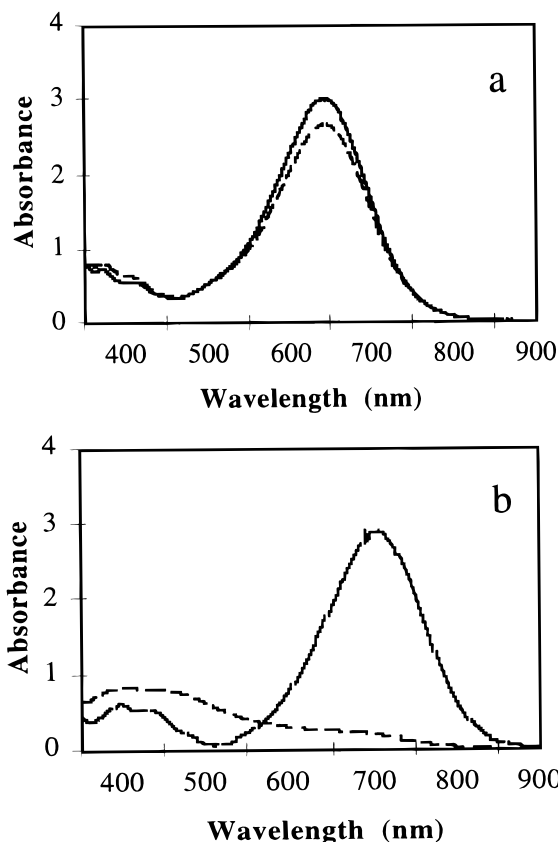


Figure 1. UV–vis absorption spectra of a Ph-TCBD-containing chromophore **3d** (a) and of a tricyanovinyl analogue (b) in dilute solution of CHCl₃, (—) untreated solution, (---) solution treated with excess diethylamine for 24 h.

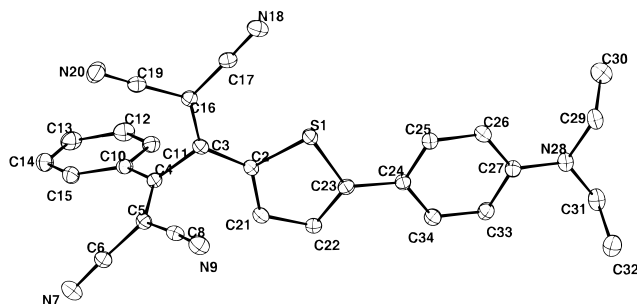


Figure 2. X-ray single-crystal structure of **3a**.

higher than that of the tricyanovinyl group. The r_{33} values of these polymers remained at ~80% of their original values at 85 $^\circ\text{C}$ for more than 1000 h.

In summary, the reaction of the TCNE with the electron-rich diaryl acetylenes provides a simple and convenient synthetic method for preparing highly efficient, thermally and chemically stable chromophores exhibiting significant blue-shifted absorption peaks. Poled polymers derived from these chromophores possess very high E–O coefficients (as high as 36 pm/V) and very good temporal stability at 85 $^\circ\text{C}$.

Acknowledgment. This work is supported by the Air Force of Scientific Research (AFOSR) under Grant F49620-97-1-0240 and Office of Naval Research (ONR) through the MURI Center CAMP.

JA983537+