JOC Article

Challenging the Auxiliary Donor Effect on Molecular Hyperpolarizability in Thiophene-Containing Nonlinear Chromophores: X-ray Crystallographic and Optical Measurements on Two New Isomeric Chromophores

Christopher R. Moylan,*,† Brian J. McNelis,*,‡ Lawrence C. Nathan,‡ Michael A. Marques,‡
Eric L. Hermstad,‡ and Benjamin A. Brichler‡

*Department of Electrical Engineering, University of California, 1156 High Street,
Santa Cruz, California 95064, and Department of Chemistry, Santa Clara University,
500 El Camino Real, Santa Clara, California 95053*

bmcnelis@scu.edu

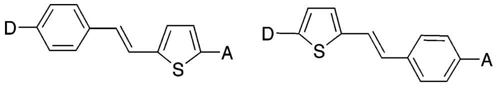
Received May 6, 2004

To reexamine the established “auxiliary donor” effect of thiophene in nonlinear optical (NLO) chromophores, we have prepared two isomeric donor−acceptor azo dyes, differing only in the position of the thiophene. Experimental analysis of these chromophores, including electric field-induced second harmonic generation (EFISH) and X-ray crystallography, contradicts previous experimental findings on similar chromophores but is consistent with the majority of computational precedents. We have found that the thiophene on the donor side produces a compound with a larger dipole moment; however, the isomer with the thiophene on the acceptor side is more nonlinear and has a higher figure of merit for NLO device applications.

Introduction

Nonlinear optical (NLO) chromophores (dyes with large molecular hyperpolarizabilities) represent the active ingredients of the electrooptic polymers that will be required for photonic switching at frequencies of 100 GHz and above. The inevitability of the need for such fast switching in the foreseeable future as demand for increased bandwidth accelerates and the difficulty of synthesizing some of the most promising candidates have prompted intense study of structure−function relationships for NLO chromophores.

Thermal stability as well as nonlinearity requirements, which often constitute a tradeoff,[1] have led to structures featuring strong electron donors and acceptors connected by a conjugated system. The conjugated system typically consists of two aromatic rings linked by an unsaturated moiety. Stilbene and azobenzene dyes containing strong electron donors and acceptors have been investigated; however, replacement of phenyl rings with heterocyclic rings has resulted in chromophores with improved values of the hyperpolarizability β, albeit lower thermal stability.[1] Of the heterocyclic rings studied, thiophene has been most effective in providing chromophores with excellent molecular hyperpolarizabilities.[2] In these chromophores, the thiophene ring can be located on the donor or acceptor side of the compound yielding two isomeric compounds **1** and **2** (Figure 1). While thiophene-containing chromophores have been the focus of numerous experimental and theoretical studies, surprisingly only one experimental study has been reported in which both isomers have been prepared and the NLO properties measured.



1a-c **2a-c**

	Donor (D)	Acceptor (A)
a	$-N(CH_3)_2$	$-NO_2$
b	$-NH_2$	$-NO_2$
c	$-NEt_2$	$-CHC(CN)_2$

FIGURE 1. Previously reported NLO chromophores containing thiophene.

In their study, Wong et al.[3] reported NLO data on chromophores **1a** and **2a**, which contain dimethylamino donor and nitro acceptor groups. Isomer **2a** was found to have greater nonlinearity and Wong proposed that the thiophene, through electron donation by the sulfur atom, functions as an auxiliary donor when positioned on the donor side of the chromophore. Surprisingly, **2a** had a smaller λ_{max}, which normally correlates with a smaller value of β in similar NLO chromophores.

The auxiliary donor effect has been examined in three recent computational studies. Varanasi et al.[4] and Albert et al.[5] performed calculations on a variety of stilbene

---

† University of California, Santa Cruz.

‡ Santa Clara University.

(1) Moylan, C. R.; McComb, I.-H.; Miller, R. D.; Lee, V. Y.; Twieg, R. J. *Mol. Cryst. Liq. Cryst.* **1996**,*283*, 115−118.

(2) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *J. Chem. Soc., Chem. Commun.* **1993**, 90−92.

(3) Wong, K. Y.; Jen, A. K.-Y.; Rao, V. P.; Drost, K. J. *J. Chem. Phys.* **1994**, *100*, 6818−6825.

(4) Varanasi, P. R.; Jen, A. K.-Y.; Chandrasekhar, J.; Namboothiri, I. N. N.; Rathna, A. *J. Am. Chem. Soc.* **1996**, *118*, 12443−12448.

10.1021/jo049230c CCC: $27.50

analogues in which $-NH_2$ was used as the electron donor and $-NO_2$ served as the acceptor group. While focusing on the effect of replacing phenyl rings with various heterocycles, these studies provided a direct comparison between compounds **1b** and **2b** (Figure 1). The calculations indicated that electron-rich ring systems such as furan and pyrrole can act as auxiliary donors and result in higher nonlinearities when placed on the donor side of the compound. Interestingly, these general rules held for all auxiliary donor heterocycles except thiophene; compound **1b** yielded higher computed values of the hyperpolarizability β than compound **2b** in both studies. MacMahon and co-workers calculated the hyperpolarizability of two isomeric thiophene-substituted stilbene analogues **1c** and **2c**, with a diethylamine donor and a dicyanovinyl acceptor, for a comparison study with a thiazole auxiliary donor.[6] Chromophore **1c**, with thiophene located on the acceptor side, was found to be more nonlinear, consistent with the previous calculations. Interestingly, MacMahon found that the dipole moment for **1c** was actually larger as well, in contrast with both Wong's dipole moment measurements for **1a**,**b** and the previously mentioned calculations.

Results and Discussion

Given this clear contradiction between theory and experiment and the lack of corroborating experimental data for thiophene as an auxiliary donor, we sought to provide a definitive experimental measure of the auxiliary donor effect by preparing two novel, isomeric, thiophene-containing chromophores and determining their hyperpolarizabilities. In the construction of these compounds, we chose to utilize moieties that have been shown to increase hyperpolarizability while maintaining the thermal stability required for EO applications. Azo dyes have been shown to have improved nonlinear performance and thermal stability[7] as compared to stilbene analogues. Tricyanovinyl[8] accepting groups have also been determined to increase hyperpolarizability. Although dialkylamine donating groups generally have lower thermal stability than do diarylamino donors,[9] we chose to incorporate a diethylamine donor into both isomeric chromophores to facilitate the synthesis of these compounds for this initial study. Therefore, our goals were to prepare compounds **3** and **4** and determine which would exhibit the higher EO figure of merit (Figure 2).

The chromophore figure of merit for EO applications,[10] also called the molecular nonlinearity, is $\mu\beta/M$, where μ is the dipole moment, β the hyperpolarizability at the wavelength in question, and M the molecular weight. Optical signals are sent through the transmission windows of glass fiber, so the nonlinearity should be evaluated at the application wavelengths of 1300 and 1550 nm. The higher the nonlinearity, the higher the EO coefficient of a polymer containing the chromophore, and the lower the voltage required to activate a switch made from the polymeric material.

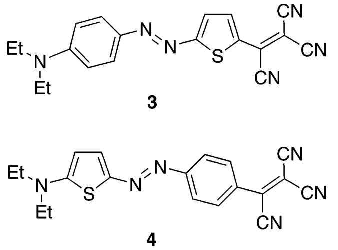
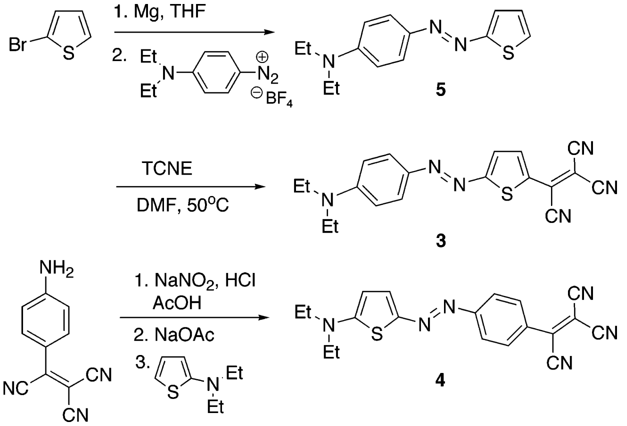


FIGURE 2. Novel isomeric NLO chromophore targets **3** and **4**.

SCHEME 1. Synthesis of Chromophores 3 and 4



To synthesize compound **3**, we sought to prepare **5** and then append the requisite tricyanovinyl group by using the known procedure for electrophilic substitution with tetracyanoethylene (Scheme 1). A diazonium coupling approach to the synthesis of **5** by reaction of thiophene with the diazonium salt of diethylaminoaniline proved to be problematic, yielding a complex mixture of products. To increase the reactivity of the thiophene moiety, 2-thienyllithium was used in reaction with 1-diazo-4-diethylaminobenzene at −78 °C in THF. Compound **5** was isolated as an orange solid in good yield (43%). This process proved to be capricious on scale-up, however, providing **5** in much lower yield (~20%). In contrast, reaction of 2-thienylmagnesium bromide[11] with 1-diazo-4-diethylaminobenzene provided **5** in improved yield (51%) and the process was effective in gram-scale synthesis. As expected, reaction of compound **5** with tetracyanoethylene at 50 °C in DMF provided **3**.

Compound **4** was synthesized by utilizing standard diazonium coupling procedures (Scheme 1). Diethylaminothiophene[12] and tricyanovinylaniline[13] were prepared by using adaptations to the literature procedures. Diazotization[14] of tricyanovinylaniline and coupling with diethylaminothiophene provided **4** in modest yield (34%).

---

(5) Albert, I. D. L.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1997**, *119*, 6575−6582.

(6) Breitung, E. M.; Shu, C.-F.; McMahon, R.J. *J. Am. Chem. Soc.* **2000**, *122,* 1154−1160

(7) Moylan, C. R.; Swanson, S. A.; Walsh, C. A.; Thackara, J. I.; Twieg, R. J.; Miller, R. D.; Lee, V. Y. *SPIE Proc.* **1993**, *2025*, 192−201.

(8) Katz, H. E.; Singer, K. D.; Sohn, J. E.; Dirk, C. W.; King, L. A.; Gordon, H. M. *J. Am. Chem. Soc.* **1987**, *109*, 6561−6563.

(9) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Swanson, S. A.; Betterton, K. M.; Miller, R. D. *J. Am. Chem. Soc.* **1993**, *115*, 12599−12600.

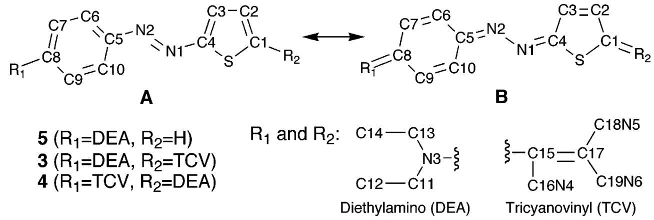
(10) Moylan, C. R.; Twieg, R. J.; Lee, V. Y.; Miller, R. D.; Volksen, W.; Thackara, J. I.; Walsh, C. A. *SPIE Proc.* **1994**, *2285*, 17−30.

(11) Garst, M. E.; Lukton, D. *Synth. Commun.* **1980**, *10*, 155−160.

(12) (a) Marder, S. R.; Bedworth, P. V.; Cai, Y.; Jen, A. K.-Y. *J. Org. Chem.* **1996**, *61*, 2242−2246. (b) King, F. D.; Walton, D. R. M. *J. Chem. Soc., Chem. Commun.* **1974**, *7*, 256−7.

(13) McKusick, B. C.; Heckert, R. E.; Cairns, T. C.; Cofman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* **1958**, *80*, 2806−2815.

TABLE 1. X-ray Crystallography Data of 5, 3, and 4: Bond Length (Å)



5 (R_1=DEA, R_2=H)
3 (R_1=DEA, R_2=TCV)
4 (R_1=TCV, R_2=DEA)

	5	**3**	**4**
thiophene			
C(1)−S	1.700(5)	1.737(4)	1.744(3)
C(4)−S	1.716(5)	1.730(4)	1.765(3)
C(1)−C(2)	1.331(8)	1.385(6)	1.414(5)
C(3)−C(4)	1.253(7)	1.391(6)	1.402(5)
C(2)−C(3)	1.547(6)	1.374(6)	1.359(5)
azo bridge			
C(4)−N(1)	1.410(6)	1.379(5)	1.328(4)
N(1)−N(2)	1.226(6)	1.297(4)	1.314(4)
N(2)−C(5)	1.435(6)	1.389(5)	1.380(4)
phenyl			
C(5)−C(6)	1.401(6)	1.393(6)	1.405(5)
C(5)−C(10)	1.386(6)	1.399(6)	1.402(5)
C(6)−C(7)	1.379(6)	1.360(6)	1.368(5)
C(9)−C(10)	1.360(6)	1.372(6)	1.363(5)
C(7)−C(8)	1.406(5)	1.431(6)	1.407(5)
C(8)−C(9)	1.415(5)	1.402(6)	1.405(5)

DEA	R_1	R_1	R_2
C(8 or 1)-N(3)	1.363(5) (C8)	1.352(5) (C8)	1.322(4) (C1)

TCV	$R_2 = H$	R_2	R_1
C(1 or 8)-C(15)		1.437(6) (C1)	1.444(5) (C8)
C(15)−C(17)		1.321(6)	1.374(5)
C(15)−C(16)		1.490(6)	1.466(5)
C(17)−C(18)		1.414(7)	1.417(5)
C(17)−C(19)		1.477(7)	1.441(5)
C(16)−N(4)		1.127(5)	1.128(4)
C(18)−N(5)		1.132(6)	1.138(5)
C(19)−N(6)		1.137(6)	1.136(4)

The structures of compounds **3**, **4**, and **5** were determined by X-ray crystallography.[15]

The X-ray structures of compounds **3** and **4** provided a unique opportunity to examine the direct evidence for the ground-state polarization of these donor−acceptor chromophores through the observed differences in bond lengths. Compound **5** serves as a base system to compare with acceptor-containing chromophores **3** and **4**. As shown in Table 1, each component of **3** and **4** (thiophene ring, azo bridge, tricyanovinyl (TCV) substituent, diethylamino (DEA) substituent), with the exception of the phenyl ring, exhibits bond lengths that are consistent with an increased contribution of the bipolar resonance form **B**. We observe, as did Marder,[16] that the magnitude of the changes in bond length is not consistent throughout all the components of such chromophores. For example, the thiophene ring in **4** exhibits the largest changes in bond lengths while the phenyl rings in all three compounds exhibit nominal changes but show significant quinoidal character.

Compound **4**, with the longest C(1)−C(2), N(1)−N(2), C(3)−C(4), and C(15)−C(17) bonds and the shortest C(2)−C(3), C(4)−N(1), N(2)−C(5), and N(3)−C(8) bonds, should be more polar than **3**, a prediction that is borne out by our dipole moment measurements. There is evidence that the sulfur functions as an auxiliary donor in **4**. In **3**, C(1)−S and C(4)−S bond lengths are nearly identical. In **4**, the C(1)−S distance is shorter than C(4)−S as would be expected if the sulfur behaves as an electron donor. As expected, both the C(15)−C(16) and C(17)−C(19) bonds are shorter in **4** than in **3**. The C(17)−C(18) bond length, however, is nearly identical in **3** and **4**, suggesting that the nitrile cis to the phenyl ring is not contributing significantly to the increased polarity of **4**.

Compounds **3** and **4** were characterized by electric field-induced second harmonic generation (EFISH), UV/vis spectroscopy, and dielectric measurements in chloroform solution (Table 2) as previously described.[17,18] Nonlinear susceptibilities of solutions were referenced to the pure solvent value of 3.3×10^{-14} esu, obtained by repeated calibration against quartz, whose susceptibility of 6.7×10^{-10} esu at the experimental wavelength of 1.9 μm is in turn based on a literature calibration against potassium dihydrogen phosphate (KDP).[19,20] The B convention of Willetts et al.[21] was used to define the hyperpolarizability β. Experimental values of $\beta(-2\omega;\omega,\omega)$ were extrapolated to zero frequency with the dispersion relationship for second harmonic generation derived from the two-level model of Oudar and Chemla.[22] The dispersion function for $\beta(-\omega;\omega,0)$ derived from the same model was used to determine electrooptic figures of merit at 1300 and 1550 nm. The absorption spectroscopy experiments were carried out between 300 and 860 nm, the latter representing the upper limit of our instrumentation. When nonlinear chromophores are to be incorporated into electrooptic polymers for use in devices, the optical loss at the application wavelength must be determined as well. In general, absorptive loss due to both chromophores and host polymers is negligible near 1300 nm, and is dominated by overtone and combination bands of the host polymers near 1550 nm.

While the nonlinearities of both of these compounds are outstanding (the largest of the more than 250 compounds measured with our apparatus), they are not equal. Molecular hyperpolarizabilities for similar chromophores with varying donor and acceptor groups are typically proportional to $\lambda_{\max}$ to the sixth power.[23] The ordering of the absorption maxima and hyperpolarizabilities here are consistent; compound **3** is red-shifted

---

(14) Schilling, M. L.; Katz, H. E.; Cox, D. I. *J. Org. Chem.* **1988**, *53*, 5538−5540.

(15) Crystallographic data: **3**, $C_{19}H_{16}N_6S$, monoclinic, $P2_1/c$, yellow-green prism, a = 9.130(1) Å, b = 14.984(2) Å, c = 13.598(2) Å, β = 94.62(2)°, Z = 4, R = 0.0644, GOF = 1.012; **4**, $C_{19}H_{16}N_6S$−0.691$CHCl_3$−0.309CH_2Cl_2, triclinic, $P\bar{1}$, green-gold pillar, a = 9.471(2) Å, b = 10.193(2) Å, c = 12.338(2) Å, α = 69.970(9)°, β = 88.88(2)°, γ = 83.96(1)°, Z = 2, R = 0.0555, GOF = 0.998; **5**, $C_{14}H_{17}N_3S$, orthorhombic, $P2_12_12_1$, orange irregular block, a = 7.5253(7) Å, b = 9.059(1) Å, c = 20.415(3) Å, Z = 4, R = 0.0639, GOF = 1.075.

(16) Marder, S. R.; Cheng, L.-T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoj, J. *Science* **1994**, *263*, 511−514.

(17) Moylan, C. R.; Miller, R. D.; Twieg, R. J.; Betterton, K. M.; Lee, V. Y.; Matray, T. J.; Nguyen, C. *Chem. Mater.* **1993**, *5*, 1499−1508.

(18) Moylan, C. R.; Miller, R. D.; Twieg, R. J.; Lee, V. Y. *ACS Symp. Ser.* **1995**, *601*, 66−81.

(19) Jerphagnon, J.; Kurtz, S. K. *Phys. Rev. B* **1970**, *1*, 1739−1744.

(20) Roberts, D. A. *IEEE J. Quantum Electron.* **1992**, *28*, 2057−2074.

(21) Willetts, A.; Rice, J. E.; Burland, D. M.; Shelton, D. P. *J. Chem. Phys.* **1992**, *97*, 7590−7599.

(22) Oudar, J. L.; Chemla, D. S. *J. Chem. Phys.* **1977**, *66*, 2664−2668.

TABLE 2. Hyperpolarizability and Thermal Data for 3 and 4[a]

compd	$\lambda_{\max}$	m	β_{SHG}	β_0	$\mu\beta_{\mathrm{EO}}$/M		T_d	μ_{ex}	f
					1300 nm	1550 nm			
3	719	10.8 ± 0.1	867 ± 35	321 ± 13	17.9	14.5	213	18.2	0.726
4	708	12.2 ± 0.1	686 ± 21	265 ± 8	16.3	13.3	208	19.2	0.658

[a] Optical characterization data for compounds **3** and **4**. Thermal decomposition data (T_d values) obtained for solid material by differential scanning calorimetry at 5 deg/min; all other data obtained in chloroform solution. Wavelengths are given in nm, dipole moments in debye, and hyperpolarizabilities in 10^{-30} esu. $\beta(-2\omega;\omega,\omega)$ values (abbreviated β_{SHG}) obtained from EFISH measurements at 1.9 μm as described above. Excited-state dipole moments (μ_{ex}), zero-frequency hyperpolarizabilities (β_0), and $\beta(-\omega;\omega,0)$ values (abbreviated β_{EO}) were calculated with the two-level model.[18,22] Oscillator strengths (f) were determined by estimation of the area under spectral peaks.

and clearly more nonlinear even though the thiophene auxiliary donor is located on the acceptor side of the azo bridge. Compound **4** does have a larger dipole moment in the ground state, but its hyperpolarizability is smaller. Because the product of μ and β (divided by molecular weight, which in this case is the same for both compounds) represents the figure of merit for electrooptic applications, chromophore **3** has a higher nonlinear figure of merit at both application wavelengths, 1300 and 1550 nm.

These results underscore an important point with regard to calculation of nonlinearities. A structural change can affect the dipole moment in one direction and the hyperpolarizability in the opposite direction and to a different extent, as with the interchange of the phenyl and thiophene rings discussed here. Even though the $\mu\beta$ product corresponds to the figure of merit, the two effects must be examined independently, because the change in that product cannot be directly correlated with structural modifications. To guide future synthetic efforts, structure–property relationships should include the influence of structure on each of the two properties.

For any delocalized structure, attaching a donor at one end and an acceptor at the other end polarizes the molecule to some degree, a degree that can be quantified by a parameter representing the relative contribution of the charge-transfer resonance structure $D^+{-}A^-$ to the ground electronic state. This parameter, which can be referred to as c^2, varies from 0 (completely neutral with no dipole moment) to 1 (complete charge transfer and large dipole moment).[24] While the ground-state dipole moment increases monotonically with c^2, the hyperpolarizability β, which depends on the difference between the ground- and excited-state dipole moments, vanishes[24] at $c^2 = 0$, 0.5, and 1.0, with a maximum positive value near 0.25 and a maximum negative value near 0.8. Both of the compounds in this study have positive values of β, which means that c^2 is less than 0.5. With the auxiliary donor on the donor side of the structure, the net polarization is larger (higher dipole moment), so c^2 must be greater. The observation that β is smaller indicates that these compounds are in the regime where c^2 is between 0.25 and 0.5. For either of these compounds, if a stronger donor or acceptor were used, we would expect μ to increase and β to decrease, analogous to the effect of changing from structure **3** to structure **4**, making it likely that the nonlinear figure of merit would decrease in the same manner as well.

These findings clearly demonstrate that the auxiliary donor effect primarily influences the dipole moment. More importantly for such NLO chromophores, improved hyperpolarizability *and* $\mu\beta$ product are obtained with the thiophene on the acceptor side of the chromophore. In addition, these results corroborate the previous calculations, validating the computational methods, and should focus synthetic efforts for the future design of thiophene-containing chromophores. Compound **3** has a slightly higher decomposition temperature than **4**; however, neither is thermally stable enough for use in an electrooptic polymer. Additional thermal stability can be obtained by synthesis of diarylamino analogues of these diethylamino compounds. Given the synthetic challenges of substituted amino thiophenes required for analogues of **4**, the synthetic methods described herein provide a facile preparation of **3** and related compounds.

Conclusions

We synthesized two novel azo-linked chromophores, **3** and **4**, to examine the auxiliary donor effect of thiophene. Each exhibited outstanding nonlinearity sufficient for device applications. Chromophore **3**, with the "auxiliary donor" on the acceptor side of the link, had a higher figure of merit, in conflict with both the general auxiliary donor rule and the lone previous experimental result, but in agreement with theoretical calculations on the analogous compounds. The auxiliary donor concept thus apparently applies consistently to the dipole moment (the zero-order term in a power series of molecular polarization as a function of applied electric field), but inconsistently to the molecular hyperpolarizability (the second-order term). Chromophore **3** is superior to **4** under all relevant criteria for electrooptic applications: ease and flexibility of synthesis, thermal stability, and molecular nonlinearity.

Experimental Section

4-(2-Thienylazo)-*N*,*N*-diethylaniline (5). To a solution of 2-bromothiophene (0.620 g, 15.2 mmol) in THF (15 mL) was added magnesium (0.370 g, 15.3 mmol) at room temperature. After all the magnesium was consumed (45 min), the amber solution was added via cannula to a suspension of 4-diazo-*N*,*N*-diethylaniline fluoroborate (4.00 g, 15.2 mmol) in THF (50 mL) at −78 °C. After addition, the reaction mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched with water, extracted with EtOAc, and dried (Na_2SO_4). Column chromatography (silica gel, 3:1 hexane:EtOAc) yielded **1** (2.01 g, 51%) as an orange solid; mp 136−138 °C. ^{1}H NMR ($CDCl_3$) δ 1.19 (t, $J = 6.8$ Hz, 6H), 3.41

---

[23] Moylan, C. R.; Ermer, S.; Lovejoy, S. M.; McComb, I.-H.; Leung, D. S.; Wortmann, R.; Krämer, P.; Twieg, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 12950−12955, ref 6.

[24] Beckmann, S.; Etzbach, K.-H.; Krämer, P.; Lukaszuk, K.; Matschiner, R.; Schmidt, A. J.; Schuhmacher, P.; Sens, R.; Seybold, G.; Wortmann, R.; Würthner, F. *Adv. Mater.* **1999**, *11*, 536−541.

(q, $J = 6.8$ Hz, 4H), 6.66 (d, $J = 9.3$ Hz, 2H), 7.05 (dd, $J = 3.9$, 5.3 Hz, 1H), 7.20 (dd, $J = 1.3$, 5.3 Hz, 1H), 7.53 (dd, $J = 1.1$, 3.7 Hz, 1H), 7.74 (d, $J = 9.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.7, 44.7, 111.0, 125.3, 125.5, 127.0, 127.5, 142.3, 149.9, 161.5. Anal. Calcd for $C_{14}H_{17}N_3S$: C, 64.84; H, 6.61; N, 16.21. Found: C, 64.61; H, 6.86; N, 16.21.

4-[4-(Tricyanovinyl)-2-thienylazo]-*N,N*-diethylaniline (3). To a solution of 4-(2-thienylazo)-*N,N*-diethylaniline (**5**) (1.20 g, 4.63 mmol) in DMF (15 mL) at 50 °C was added tetracyanoethylene (0.711 g, 5.55 mmol) over 15 min, and the reaction was stirred overnight at 50 °C. The reaction mixture was diluted with water and filtered, and the solid was washed well with water. The resulting solid was purified by column chromatography on silica gel (hexane:EtOAc, 3:1) to provide **3** (0.378 g, 23%); mp 204−205 °C. ^{1}H NMR ($CDCl_3$) δ 1.21 (t, $J = 7.1$ Hz, 6H), 3.43 (q, $J = 7.1$ Hz, 4H), 6.67 (d, $J = 9.3$ Hz, 2H), 7.07 (d, $J = 4.21$ Hz, 1H), 7.27 (d, $J = 4.2$ Hz, 1H), 7.73 (d, $J = 9.3$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.8, 45.5, 79.8, 112.2 (broad, 2 carbons), 112.80, 112.86, 112.89, 126.5, 131.8, 131.9, 141.0, 143.8, 153.1, 172.8. Anal. Calcd for $C_{19}H_{16}N_6S$: C, 63.61; H, 4.48; N, 23.33. Found: C, 63.39; H, 4.40; N, 23.00. HRMS calcd for $C_{19}H_{16}N_6S$ 360.1157, found 360.1161.

4-(4-*N,N*-Diethylamino-2-thienylazo)tricyanovinylbenzene 4. To a solution of 4-(tricyanovinyl)aniline (0.250 g, 1.29 mmol) in acetic acid (5 mL) and concentrated HCl (1.2 mL, 14.8 mmol) cooled to 0 °C was added $NaNO_2$ (0.107 g, 15.4 mmol) in water (0.5 mL) over 45 min. After the solution was stirred for an additional 45 min, NaOAc (1.37 g, 16.7 mmol) was added, followed by 2-*N,N*-diethylaminothiophene (0.200 g, 1.29 mmol) in CH_2Cl_2 (2 mL). The reaction was allowed to warm to room temperature and stirred overnight. The reaction mixture was diluted with water, neutralized with $NaHCO_3$, and extracted with EtOAc. Concentration and column chromatography (tBuOMe) yielded **4** (0.160 g, 34%) as a gold solid; mp 182−183 °C. ^{1}H NMR ($CDCl_3$) δ 1.37 (t, $J = 7.1$ Hz, 6H), 3.61 (q, $J = 7.1$ Hz, 4H), 6.41 (d, $J = 5.1$ Hz, 1H), 7.62 (d, $J = 9.2$ Hz, 2H), 7.68 (d, $J = 5.1$ Hz, 1H), 8.06 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 12.5, 48.5, 83.3, 109.9, 112.97, 113.02, 114.3, 121.9, 125.4, 131.5, 138.4, 142.2, 144.2, 159.4, 168.6. HRMS calcd for $C_{19}H_{16}N_6S$ 360.1157, found 360.1156.

Acknowledgment. The authors gratefully acknowledge NSF-ILI grant DUE-9650341 for diffractometer support, as well as helpful discussions with Prof. Robert J. Twieg of Kent State University.

Supporting Information Available: X-ray crystallographic data for compounds **3**, **4**, and **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO049230C