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# Donor−Acceptor-Substituted Phenylethenyl Bithiophenes: Highly Efficient and Stable Nonlinear Optical Chromophores

**Chengzhi Cai,*[†,§] Ilias Liakatas,[†] Man-Shing Wong,[†,||] Martin Bösch,[†]
Christian Bosshard,*[†] Peter Günter,[†] Simona Concilio,[‡,⊥] Nicola Tirelli,[‡,#] and
Ulrich W. Suter[‡]**

*Nonlinear Optics Laboratory, Institute of Quantum Electronics, Swiss Federal Institute
of Technology (ETH), CH-8093 Zurich, Switzerland, and Institute of Polymers,
Department of Materials, ETH, CH-8092 Zurich, Switzerland.*

*bosshard@iqe.phys.ethz.ch*

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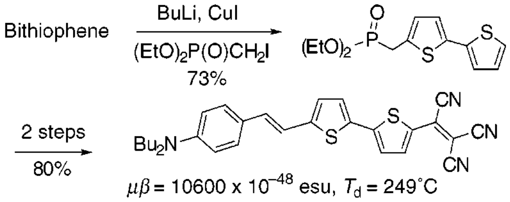
## ABSTRACT



**For practical applications of poled electrooptic polymers, highly efficient and thermally stable nonlinear optical (NLO) chromophores are required. We describe here a concise synthesis and characterization of a series of donor−acceptor chromophores incorporating a bithiophene moiety in the conjugated bridge. They display a suitable thermal stability and significantly enhanced molecular nonlinearity as compared to their monothiophene analogues and are among the most efficient yet stable NLO chromophores prepared so far.**

The continuous interest in poled electrooptic (EO) polymers[1] for device applications in information processing and telecommunications has resulted in the development of several types of second-order nonlinear optical (NLO) chromophores that are highly efficient, as characterized by their high scalar product of the dipole moment ($\mu$) and the molecular second-order polarizability ($\beta$).[2] To obtain a macroscopic order, these dipolar chromophores are usually aligned by poling with a high electric field at the glass transition temperature ($T_g$) of the polymer. To reduce randomization of the order after the poling, it is necessary to use high $T_g$ polymers[3] such as polyquinolines,[2f] and the chromophores should be stable

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[†] Nonlinear Optics Laboratory.

[‡] Institute of Polymers.

[§] Future address: Department of Chemistry, University of Houston, Houston, TX 77204-5641. Current e-mail: cai@iqe.phys.ethz.ch.

[||] Current address: Department of Chemistry, Hong Kong Baptist University, Hong Kong.

[⊥] Current address: Dipartimento di Chimica, Universitá degli Studi di Napoli “Federico II”, Via Mezzocannone 4, 80134 Napoli, Italy.

[#] Current address: Institute of Biomedical Engineering, Department of Materials, ETH, CH-8044 Zürich, Switzerland.

(1) (a) Dalton, L. R. *Chem. Ind.* **1997**, 511. (b) Bosshard, C.; Sutter, K.; Prêtre, P.; Hulliger, J.; Flörsheimer, M.; Kaatz, P.; Günter, P. *Organic Nonlinear Optical Materials*; Gordon & Breach: Amsterdam, 1995; Chapter 6.

(2) (a) Jen, A. K.-Y.; Rao, V. P.; Wong, K. Y.; Drost, K. J. *Chem. Commun.* **1993**, 90. (b) Marder, S. R.; Gorman, C. B.; Meyers, F.; Perry, J. W.; Bourhill, G.; Bredas, J.-L.; Pierce, B. M. *Science* **1994**, *265*, 632. (c) Wu, X.; Wu, J.; Liu, Y.; Jen, A. K.-Y. *J. Am. Chem. Soc.* **1999**, *121*, 472. (d) Rao, V. P.; Jen, A. K.-Y.; Wong, K. Y.; Drost, K. J. *Chem. Commun.* **1993**, 1118. (e) Jen, A. K.-Y.; Cai, Y.; Bedworth, P.; Marder, S. *Adv. Mater.* **1997**, *9*, 132. (f) Cai, Y.; Jen, A. K. Y. *Appl. Phys. Lett.* **1995**, *67*, 299. (g) Blanchard-Desce, M.; Alain, V.; Bedworth, P. V.; Marder, S. R.; Fort, A.; Runser, C.; Barzoukas, M.; Lebus, S.; Wortman, R. *Chem. Eur. J.* **1997**, *3*, 1091.

(3) Pretre, P.; Meier, U.; Stalder, U.; Bosshard, C.; Günter, P.; Kaatz, P.; Weder, C.; Neuenschwander, P.; Suter, U. W. *Macromolecules*, **1998**, *31*, 1947.

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under the poling conditions. Jen et al. showed that incorporation of thiophene rings into the conjugated units in e.g. **1a**−**f** (Figure 1) can greatly enhance $\mu\beta$ while permitting a high thermal stability.[2a] According to the general guideline for optimization of $\mu\beta$,[2b] we reason that using bithiophene moieties in e.g. **2a**−**f** (Figure 1), having a longer conjugation length than **1a**−**f**, should further increase $\mu\beta$. Also, the robust bithiophene moiety may maintain the thermal, chemical, and photochemical stability. In this letter, we present the synthesis and characterization of **2a**−**f** and the comparison with their analogues **1a**−**f**.

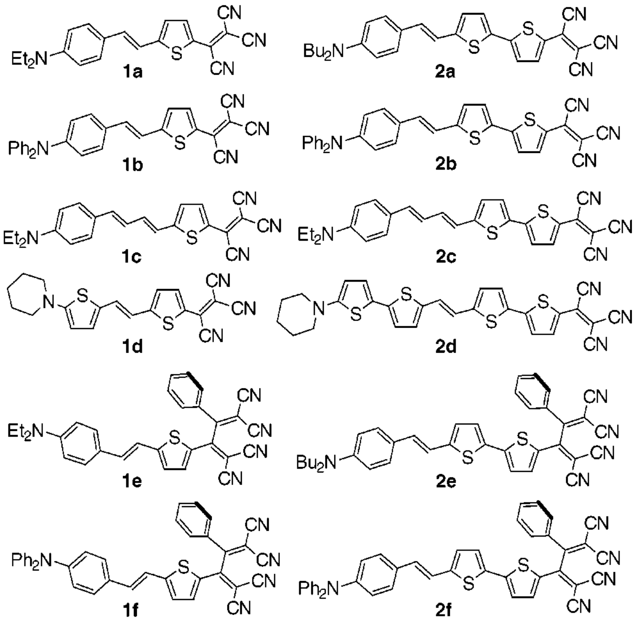
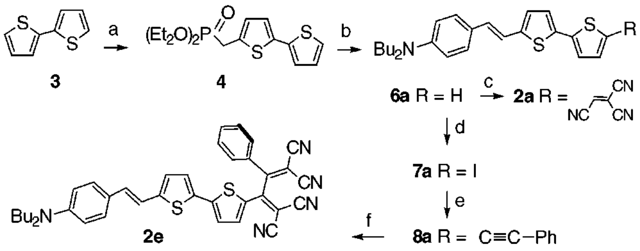


**Figure 1.**

The tricyanovinyl-substituted dyes **2a**−**d** were synthesized in three steps from bithiophene (**3**) through the common intermediate **4**, as demonstrated with **2a**[4] in Scheme 1.

**Scheme 1**[a]



[a] Conditions: (a) (1) BuLi, THF; (2) CuI; (3) $ICH_2PO(OEt)_2$, DMSO, 73%. (b) *p*-$Bu_2N-C_6H_4-CHO$ (**5a**), NaH, 15-crown-5 (cat.), THF, 100%. (c) BuLi, THF, $(CN)_2C{=}C(CN)_2$, 80%. (d) BuLi, THF, $I_2$, 93%. (e) HCCPh, $Pd_2(dba)_3$/CuI (cat.), $Et_3N$, THF, 98%. (f) $(CN)_2C{=}C(CN)_2$, $CHCl_3$, 80%.

Diethyl thienylmethyl phosphonate, analogue of **4**, was previously prepared in two steps by chloromethylation of thiophene followed by Arbuzov reaction with $P(OEt)_3$.[2b] However, all our attempts to prepare 2-(chloromethyl)-bithiophene failed probably due to its instability. To circumvent this problem, we prepared **4** in 73% yield by nucleophilic substitution of $ICH_2PO(OEt)_2$ with 2-bithienylcopper generated in situ by treatment of bithiophene (**3**) with BuLi followed by CuI. The relatively low reactivity of bithienylcopper was overcome by addition of a polar aprotic solvent (DMPU or DMSO) and running the reaction at elevated temperatures. Conversion of phenyl and naphthyl bromides to the arylmethylphosphonates via the arylcoppers has been described by Poindexter and Katz.[5] Here, we extended this method to the preparation of electron-rich thienylmethylphosphonates that are useful intermediates for the synthesis of low band gap thienylvinylene derivatives. Wittig−Horner reaction of **4** with 4-(dibutylamino)benzaldehyde (**5a**) afforded exclusively the (*E*)-alkene **6a** in quantitative yield. The tricyanovinyl group was easily introduced to provide **2a** in 80% yield.

The 2-phenyl-tetracyanobutadienyl-substituted dyes **2e** and **2f** were synthesized according to the reported procedure[2d] for **1e** and **1f**. For example, iodination of **6a** (Scheme 1) led to **7a** in 93% yield. Sonogashira reaction of **7a** readily afforded the electron-rich acetylene **8a** in 98% yield. A [2 + 2] cycloaddition of tetracyanoethylene with **8a** followed by ring opening gave rise to chromophore **2e** in 80% yield.

The molecular nonlinearity ($\mu\beta$) of the dyes **2a**−**f** were determined by electric field induced second-harmonic generation (EFISH) at a fundamental wavelength of 1907 nm using a quartz reference (nonlinear optical coefficient $d_{11}$ = 0.27 pm/V).[6] The decomposition temperature ($T_d$) of the chromophores was measured by thermal gravimetric analysis

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(4) **Synthesis of 2a** (more details are in Supporting Information): At −76 °C, *n*-BuLi (2.35 M in hexane, 35 mmol) was slowly added to bithiophene (**3**, 6 g, 35 mmol) in THF (140 mL) under $N_2$. After 1.5 h of stirring at −76 °C, the solution was added to a suspension of CuI (6.67 g, 35 mmol) in THF (4 mL) at ca. −40 °C. The mixture was stirred at 0 °C for 1 h, treated with diethyl iodomethylphosphonate (8.757 g, 31.5 mmol) and DMSO (30 mL), and stirred at 56 °C for 20 h. Workup and FC (AcOEt) afforded **4** (7.32 g, 73%). A solution of **4** (1.142 g, 3.609 mmol) and 4-(dibutylamino)benzaldehyde (**5a**, 720 mg, 3.085 mmol) in THF (25 mL) was added to NaH (4.15 mmol) and 15-crown-5 (40 mg, 0.18 mmol) at room temperature. The suspension was stirred for 4 h. Workup and FC (toluene) afforded **6a** (1.22 g, 100%). To obtain **2a**, BuLi (2.1 M in hexane, 0.63 mmol) was added to **6a** (239 mg, 0.604 mmol) in THF (5 mL) at −76°. The solution was stirred at −76 °C to 0 °C for 1.5 h, recooled to −76 °C, treated in one portion with tetracyanoethylene (94.48 mg, 737 mmol) in THF (1.3 mL), stirred at −76 °C to room temperature for ~2 h. After workup and FC (toluene), **2a** was obtained as a dark green solid (242 mg, 80%). $^1H$ NMR (300 MHz, $CDCl_3$): 7.94 (d, $J$ = 4.4, 1 H); 7.42 (d, $J$ = 4.0, 1 H); 7. 34 (d, $J$ = 8.9, 2 H); 7.28 (d, $J$ = 4.4, 1 H); 6.98 (d, $J$ = 4.0, 1 H); 6.97 (d, $J$ = 16.0, 1 H); 6.92 (d, $J$ = 16.0, 1 H); 6.62 (d, $J$ = 9.0, 2 H); 3.31 (t, $J$ = 7.6, 4 H); 1.65−1.54 (m, 4 H); 1.43−1.31 (m, 4 H); 0.97 (t, $J$ = 7.3, 6 H). $^{13}C$ NMR (75 Hz, $CDCl_3$, DEPT): 152.99 (s), 150.99 (s), 148.81 (s), 141.59 (d), 133.13 (d), 131.72 (s), 131.11 (s), 130.77 (s), 130.22 (d), 128.58 (2d), 126.41 (d), 124.67 (d), 122.89 (s), 115.25 (d), 112.97 (s), 112.91 (s), 112.60 (s), 111.66 (2d), 79.13 (s), 50.80 (t), 29.49 (t), 20.33 (t), 13.99 (q). EI-MS *m*/*z*: 496 (1.6, $M^+$), 471 (1.7), 453 (1.9), 428 (1.6), 149 (3.9), 86 (56), 84 (86), 49 (100). Anal. Calcd for $C_{29}H_{28}N_4S_2$: C, 70.13; H, 5.68; N, 11.28; S, 12.91. Found: C, 70.28; H, 5.86; N, 11.04; S, 12.78.

(5) Poindexter, M. K.; Katz, T. J. *Tetrahedron Lett.* **1988**, *29*, 1513.

(6) Bosshard, C.; Knopfle, G.; Prêtre, P.; Günter, P. *J. Appl. Phys.* **1992**, *71*, 1594.

(TGA) in air and differential scanning calorimetry (DSC) in $N_2$, both with a heating rate of 20 °C/min. The results of these measurements and the electronic absorption data are summarized in the Table 1. Also listed for a comparison are the data of their monothiophene analogues **1a**−**f** and the standard NLO chromophore Disperse Red 1 (DR1). Indeed, the bithiophene-based chromophores display considerably higher $\mu\beta$ values than their monothiophene analogues, probably due to the longer and more polarizable $\pi$-conjugation. Significantly, except **2d**, the thermal stability remains nearly the same; **2d** dissolved only in polar solvents such as DMSO and DMPU, and decomposed in the presence of day light and air.

**Table 1.** Electronic Absorption, Molecular Nonlinear Optical Properties, and Thermal Stability of Selected Compounds[a]

| compound | $\lambda_{\max}$ (nm) | $\mu\beta$ ($10^{-48}$ esu) | $T_d$ (°C) |
|---|---|---|---|
| **1a** | 640 | 6 700 | 240 |
| **2a** | 661 | 10 600 | 249 |
| **1b** | 601 | 3 510 | 315 |
| **2b** | 611 | 3 940 | 308 |
| **1c** | 662 | 10 600 | − |
| **2c** | 655 | 14 300 | 238 |
| **1d** | 718 | 7 450 | 200 |
| **2d** | 712 | − | − |
| **1e** | 604 | − | 245 |
| **2e** | 623 | 6 840 | 250 |
| **1f** | 566 | − | 340 |
| **2f** | 575 | 4 120 | 343 |
| **DR1** | 473 | 1 130 | 308 |

[a] $\lambda_{\max}$ and $\mu\beta$ at $\lambda = 1907$ nm were measured in dioxane. $\lambda_{\max}$ and $T_d$ values of **1a**, **1b**, and **1d** are from ref 2e, **1c** from ref 2f, **1e** and **1f** from ref 2c. The $\mu\beta$ values of **1a**−**d** in these references were adjusted using the same value for the quartz reference ($d_{11} = 0.27$ pm/V) and the power series definition to enable comparison with our results. $T_d$ is the onset temperature of TGA in air with a scanning rate of 20 °C/min.

The effect of substituents on the $\mu\beta$ value and thermal stability are similar for both types of chromophores. Thus, $\mu\beta$ values increase with the addition of one more ethenylene moiety into the bridge (**1c** and **2c** vs **1a** and **2a**) which, interestingly, did not lead to a red shift of the absorption $\lambda_{\max}$. However, this unfortunately results in the decrease of thermal stability (**2c** vs **2a**). The high thermal stability of **1a** and **2a** can be enhanced even further by using the diphenylamino group as the donor[7] (in **1b** and **2b**), however, at the expense of a significant reduction of $\mu\beta$ probably due to the lowering of the electron donating strength. Jen et al. reported that replacement of tricyanovinyl with 2-phenyltetracyanobutadienyl (Ph-TCBD) as the acceptor (**1a** vs **1e**, and **1b** vs **1f**) improves the thermal and chemical stability.[2c] The molecular nonlinearities ($\mu\beta$) of **1e** and **1f** have not been reported. According to our measurements, at least for the bithiophene-based chromophores, the use of Ph-TCBD as the acceptor did not bring up the $\mu\beta$ value: while the $\mu\beta$ value remains about the same for **2f** and **2b**, it decreased considerably from **2a** to **2e**. Also, the Ph-TCBD acceptor improves thermal stability only if the diphenylamino group is used as the donor (**2f** vs **2e** and **2a**). This suggests that the thermal stability of **1a**, **2a**, **1e**, and **2e** can be limited by the dialkylamino groups but not by the acceptor groups.

To address the thermal stability of the chromophores in the presence of high $T_g$ polymers such as polyquinolines, compound **2a** and **2f** were dispersed in PQ100,[8] and heated at 200 °C for 30 min under $N_2$. Thin-layer chromatography (TLC) showed no sign of decomposition for **2f**, while around 20% decomposition for **2a**. Therefore, most of the chromophores should be able to withstand poling at 200 °C that was usually completed within 10 min.

In summary, we have developed an efficient synthesis of a series of donor−acceptor substituted chromophores (**2a**−**f**) based on arylvinyl bithiophene as the conjugated unit. Nonlinear optical and thermal measurements showed that except for **2d** they are among the most efficient, yet stable, NLO chromophores reported to date. In particular, besides the high $\mu\beta$ value and thermal stability, chromophore **2a** also possesses a high photochemical stability that exceeds DR1 by a factor of 2, as indicated by our preliminary experiments. Unfortunately, the poled thin films of **2a**−**f** in PQ100 or PMMA displayed low electrooptic coefficient ($r_{33}$) values in the order of 3−10 pm/V. This is not unexpected for such rodlike chromophores with very high $\mu\beta$ values. Dalton et al. have reported that such molecules are difficult to pole due to the strong intermolecular electrostatic interaction that facilitates centrosymmetrical aggregation of the dipolar molecules.[9] Fortunately, this interaction can be greatly reduced by introducing side chains to the chromophores to separate the dipoles.[9] We expect that incorporation of side chains to the bithiophene moiety should not decrease the efficiency and stability of the chromophores. Further structural modification, e.g. replacing the dibutylamino-phenyl group in **2a** with diphenylaminothienyl group, could further improve $\mu\beta$ while keeping a good stability.[2e] Together with the need to properly bond the chromophores to a suitable polymer to ensure durability of the poling induced order, considerable synthesis efforts still lie ahead before practical EO polymers based on such promising chromophores can be developed.

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**Supporting Information Available:** Synthetic procedures and characterization for the new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) 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.

(8) We thank Hitachi Co. for providing the sample.

(9) Dalton, L. R.; Harper, A. W. *Polym. News* **1998**, *23*, 114.