Optimization of Thermal Stability and Second-order Nonlinear Optical Properties of Thiophene Derived Chromophores

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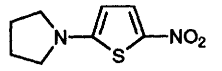
Based on the 'unconventional' dithiolyldinemethyl type donors and tricyanovinyl acceptor; a new series of highly efficient ($\beta\mu$ = 940–2400 × 10^{-48} esu) and thermally stable (275–315 °C) thiophene derived nonlinear optical chromophores have been developed.

Donor-acceptor substituted organic compounds possessing large molecular second-order nonlinear optical (NLO) responses and good thermal stability are of current interest because of their applications in electro-optic devices.[1] In spite of numerous classes of chromophores that have been explored in recent years,[2–5] limited success has been achieved in the development of efficient NLO compounds that possess a good combination of desirable properties.[6,7] This is partially due to the nature of the highly electron delocalized systems that tends to become very reactive to environments at high temperatures. We have reported previously several series of donor–acceptor substituted thiophene stilbene compounds[8–10] and demonstrated the importance of the thiophene ring in enhancing nonlinear response. Although these compounds offer excellent molecular nonlinearities ($\beta\mu$ value as high as 6200 × 10^{-48} esu at 1.9 μm), their stability at higher temperatures is limited by the thermally induced *cis–trans* isomerization of the olefinic linkage. To find a mechanism to enhance the thermal stability, and still maintain good nonlinearity of the molecule, we have designed and synthesized a series of highly efficient and thermally stable NLO chromophores by optimizing the electron donor–acceptor strengths of the single thiophene derived chromophores.

Compound **1** which was studied only for comparison purpose, possesses dialkylamino and nitro substituents. It was synthesized by the nucleophilic substitution reaction between piperidine and 2-bromo-5-nitrothiophene. The dialkylamino functional group is one of the most commonly used efficient electron-donating groups for NLO chromophores. In a search for a more efficient electron-donating group, we have investigated a series of 'unconventional' electron-donating functional groups based on the derivatives of the dithiolyldinemethyl group. The use of this group as an efficient electron donor in benzenoid type NLO chromophores has been reported previously by Katz *et al.*[11] More recently, Lehn and coworkers[12] in their studies on push–pull carotenoids, have discussed the role of 1,3-benzodithiolyldinemethyl group as an efficient electron donor. However, neither paper reported any data relating to the thermal stability of the chromophores. In this connection, we have synthesized several chromophores using analogues of the dithiolyldinemethyl group as electron donors and nitro and tricyanovinyl groups as electron acceptors to compare their molecular hyperpolarizabilities and thermal stability. Two synthetic routes were used to synthesize the nitro derivatives **2–4** (Scheme 1) and the tricyanovinyl derivatives **5–8** (Scheme 2). Compounds **2–4** were prepared by reacting 5-nitrothiophene-2-carbaldehyde with the ylides formed from the 1,3-dithian-2-yl triphenylphosphonium chloride **9**[13] and the corresponding diethylphosphonates of dithiolyl **11**[14] and 1,3-benzodithiolyl compounds **10**[15] in THF at −78 °C. The tricyanovinyl derivatives were prepared by using a two-step process reported in the literature.[10] 2-Thiophenecarbaldehyde was first condensed with ylides generated from **9–12**. [16] The resulting donor substituted thiophenes were reacted with tetracyanoethylene (TCNE) to yield the tricyanovinyl derivatives **5–8**. All the compounds were fully characterized by NMR, IR and elemental analysis.

Electronic absorption spectra of these compounds were obtained to compare their intramolecular charge-transfer properties (Table 1). The tricyanovinyl derivatives **5–7** have a substantially red shifted charge-transfer band when compared to the corresponding nitro compounds **2–4** indicating the stronger electron-accepting nature of the tricyanovinyl group. Second-order hyperpolarizabilities of these compounds were determined by using the EFISH technique described earlier.[17] In order to minimize possible resonance enhancement which would exaggerate the measured NLO responses, measurements were performed at a fundamental wavelength of 1.9 μm in dioxane solvent. At this juncture, no attempts were made to separate the quantity β from $\beta\mu$ which requires the evaluation of ground state dipole moment. However, as these molecules are likely candidates to be used as guests or pendant side chains in poled polymer films, the product $\beta\mu$ is a relevant



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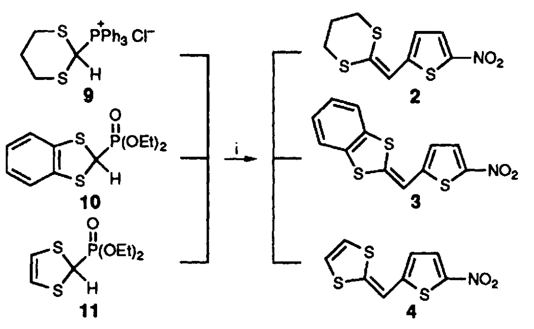
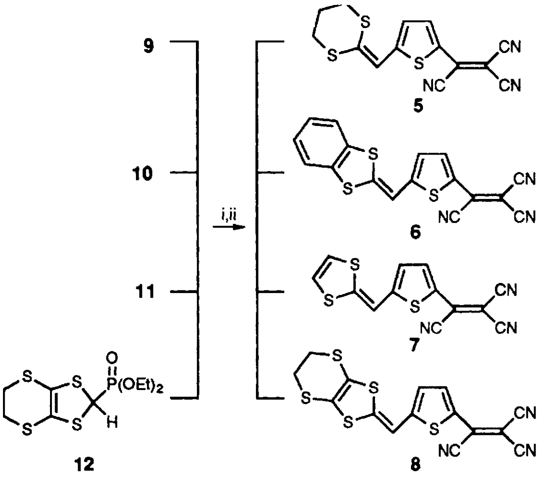


Scheme 1 *Reagents and conditions*: i, 2-thiophenecarbaldehyde, Bu^{t}OK-THF, −78 °C



Scheme 2 *Reagents and conditions*: i, 2-thiophenecarbaldehyde, Bu^{t}OK-THF, −78 °C, N_2; ii, TCNE, DMF

figure of merit combining both the nonlinearity of the molecule and the ability of the molecule to couple with a macroscopic poling field.

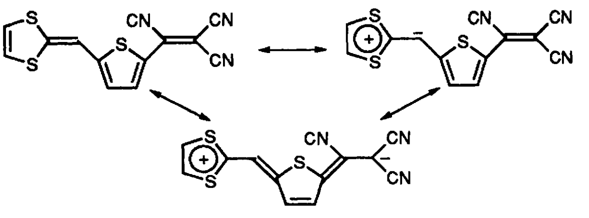
Comparison of the $\beta\mu$ values and λ_{max} peaks of the derivatives **5**–**8** reveals that the combination of the dithiolyldinemethyl type donors with the tricyanovinyl acceptor provides a very efficient mechanism to enhance molecular nonlinearity and charge-transfer properties in spite of a relatively short conjugation length. Compounds **5** with 1,3-dithiane methine as the electron-donating functional group is the least efficient, but this may be due to the inability of the lone pair electrons (4) on the sulfur atoms of the dithiane ring to form the stabilized dithiolium aromatic structure as in compounds **6**–**8** in the charge separated state (Scheme 3). The electron-donating ability of the analogues of the dithiolyldinemethyl functional group depends on the molecular framework in which the donating group is present. In **8**, the presence of two more sulfur substituents seems to enhance the electron-donating ability of the dithiolyldinemethyl group (λ_{max} red-shifted by 15 nm) and $\beta\mu$ value of the molecule (2400 $\times$ 10^{-48} *vs.* 1600 $\times$ 10^{-48} esu). On the contrary, involvement of the fused benzenoid ring in the dithiolyldinemethyl group (compound **6**) reduces the electron-donating ability (λ_{max} blue-shifted by 21 nm) which in turn decreases the $\beta\mu$ value (1350 $\times$ 10^{-48} *vs.* 1600 $\times$ 10^{-48} esu).

Inherent thermal stabilities of these compounds were determined by differential scanning calometry (DSC). All the samples were heated in a sealed pan at the rate of 20 °C min^{-1} to give a T_m (melting point) and T_d (onset of decomposition temperature given by the intercept of the tangent of the exothermic peak with adjusted baseline) (Table 1). The tricyanovinyl derivatives seem to possess much higher thermal stability than the nitro compounds. Compounds **5**, **6** and **8** possess very high thermal stability (in the range of 275–315 °C). As these T_d's vary with the rate at which the samples were heated, care must be taken in interpreting the results from these studies. For this reason, we have chosen to study the thermal stability of **6** by dissolving it in a polyamic acid PIQ-L2200 (Hitachi) in *N*-methylpyrrolidone (NMP), and curing the thin film sample at 220 °C for 30 min to complete the imidization process. The sample was then isothermally heated at 250 and 275 °C for 30 min, respectively. The π–π^* charge-transfer absorption band of the chromophore was used to monitor the decomposition temperature. No change in the intensity of the absorption due to the chromophore was observed at the above temperatures indicating the high thermal stability of this compound.

Table 1 UV/VIS, $\beta\mu$ values and decomposition temperatures for **1**–**8**

Compound	λ_{max}/nm in dioxane	$\beta\mu$ (10^{-48} esu at λ = 1.907 μm)[a]	T_d/°C
1	430	125 (95)	233
2	438	200 (150)	252
3	478	253 (178)	270
4	493	350 (239)	228
5	558	940 (565)	300
6	604	1350 (727)	315
7	625	1600 (815)	230
8	640	2400 (1170)	275

[a] Values in parentheses represent $\beta_0\mu$, zero-frequency hyperpolarizability product, obtained from the extrapolation of the measured $\beta\mu$ value using a two-level model.



Scheme 3

Our EFISH and thermal stability studies conclude that the combination of benzodithiolyldinemethyl or ethylenedithiothiolyldinemethyl electron-donating group with tricyanovinyl electron-accepting group on thiophene ring provides a very efficient method to optimize the molecular nonlinearity and thermal stability. These properties greatly enhance the usefulness of these chromophores in high-temperature polymer matrices for achieving large χ^2 properties.

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References

1 *Electrical, Optical and Magnetic Properties of Organic Solid State Materials*, ed. A. F. Garito, A. K-Y. Jen, C. Y-C. Lee and L. R. Dalton, *Mater. Res. Soc. Sym. Proc.*, 1994, 328.
2 C. W. Dirk, H. E. Katz, M. L. Schilling and L. A. King, *Chem. Mater.*, 1990, **2**, 700.
3 A. K-Y. Jen, K. Y. Wong, V. P. Rao, K. J. Drost and R. M. Mininni, *Mater. Res. Soc. Sym. Proc.*, 1992, **247**, 59.
4 S. R. Marder, C. B. Gorman, B. G. Tiemann and L. T. Cheng, *J. Am. Chem. Soc.*, 1993, **115**, 3006.
5 L. T. Cheng, W. Tam, S. R. Marder, A. E. Stiegman, G. Rikken and C. W. Spangler, *J. Phys. Chem.*, 1991, **95**, 10631.
6 C. R. Moylan, R. J. Twieg, V. Y. Lee, S. A. Swanson, K. M. Bettereon and D. R. Miller, *J. Am. Chem. Soc.*, 1993, **115**, 12599.
7 R. F. Shi, M. H. Wu, S. Yamada, Y. Cai and A. F. Garito, *Appl. Phys. Lett.*, 1993, **63**, 1173.
8 A. K-Y. Jen, V. P. Rao, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 90.
9 V. P. Rao, A. K-Y. Jen, K. Y. Wong and K. J. Drost, *Tetrahedron Lett.*, 1993, **34**, 1747.
10 V. P. Rao, A. K-Y. Jen, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 1118.
11 H. E. Katz, K. D. Singer, J. E. Sohn, C. W. Dirk, L. A. King and H. M. Gordon, *J. Am. Chem. Soc.*, 1987, **109**, 6561.
12 M. Blanchard-Desce, I. Ledoux, J. M. Lehn, J. Malthete and J. Zyss, *J. Chem. Soc., Chem. Commun.*, 1988, 736; F. Meyers, J. L. Bredas and J. Zyss, *J. Am. Chem. Soc.*, 1992, **114**, 2914.
13 C. G. Cruse, N. L. J. M. Broekhof, A. Wijsman and A. Van der Gen, *Tetrahedron Lett.*, 1977, 885.
14 L. R. Molley, H. D. Hartzler and W. A. Sheppard, *J. Org. Chem.*, 1974, **39**, 2456.
15 K. Ishikawa, K-Y. Akiba and N. Inamoko, *Tetrahedron Lett.*, 1976, 3695.
16 A. J. Moore and M. R. Bryce, *Synthesis*, 1991, 26.
17 K. Y. Wong, A. K-Y. Jen and V. P. Rao, *Phys. Rev.*, 1994, **49**, 3077; K. Y. Wong, A. K-Y. Jen, V. P. Rao and K. J. Drost, *J. Chem. Phys.*, 1994, **100**, 6818.