Achieving excellent tradeoffs among optical, chemical and thermal properties in second-order nonlinear optical chromophores

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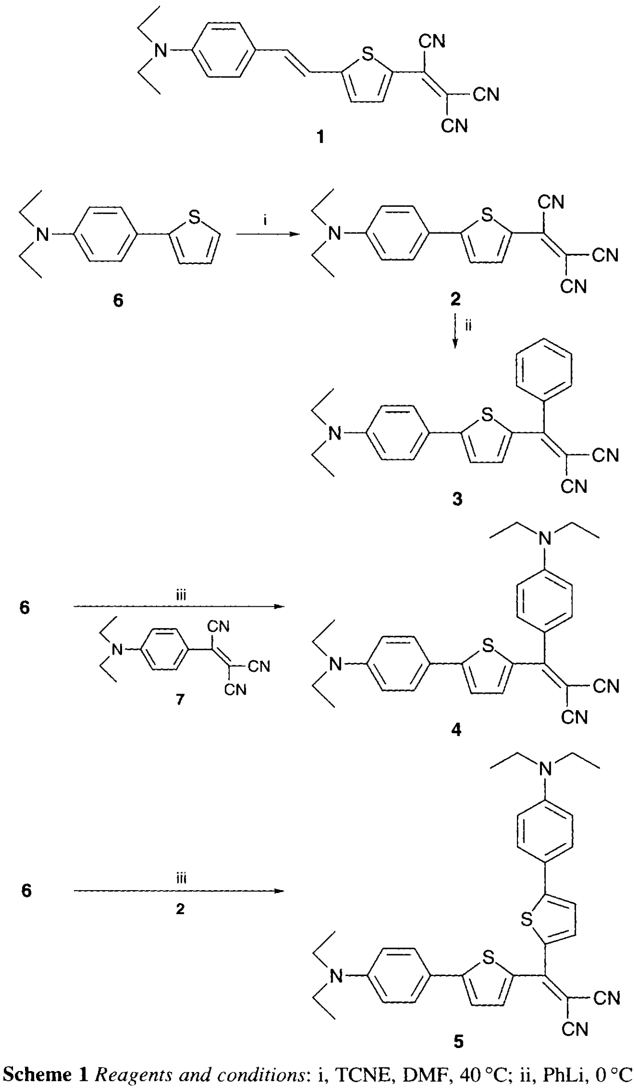
A new class of second-order nonlinear optical chromophores resulting from the replacement of the most reactive CN group in tricyanovinylthiophene derivatives with aryl units, are designed and synthesized.

Earlier research has clearly shown that large molecular nonlinearity ($\beta\mu$) can be achieved in donor–acceptor substituted stilbenes by replacing phenyl moieties with easily delocalizable thiophene moieties.[1–4] By combining thiophene conjugating units with tricyanovinyl electron acceptors, highly efficient nonlinear optical chromophores have been developed,[5] *e.g.* the measured non-linear optical activity of **1** (Scheme 1) in 1,4-dioxane was 6200×10^{-48} esu at 1.907 μm (under the same conditions, the measured activity of the standard dialkylaminonitrostilbene, DANS, was 580×10^{-48} esu). This prompted us to evaluate its secondary properties and modify further to achieve the required tradeoffs.



Scheme 1 *Reagents and conditions*: i, TCNE, DMF, 40 °C; ii, PhLi, 0 °C; iii, BuLi, THF, −78 °C

Sealed-pan DSC of **1** indicated its decomposition at 274 °C. The presence of the isomerizable alkenic bond in **1** probably resulted in its relatively low thermal stability. As a first modification, compound **2**, an analogue of **1** without the alkenic bridge, was developed.[6] This led to lowering of the $\beta\mu$ value (2700×10^{-48} esu) with respect to **1**, but enhanced the thermal stability to 300 °C as anticipated.

We then attempted to incorporate **2** into high-temperature polyimides (Hitachi PQ-2200 & Ultradel 4212) as solid solutions.[7] This revealed other limiting factors associated with compounds containing tricyanovinyl groups: the concentration of the guest in host polyimides could not be optimized beyond 10–15% because of its poor solubility, and the tricyanovinyl group was found to be very sensitive to the polyamic acid curing conditions. This decomposition process lowers the effective concentration of the chromophore in fully cured polyimides. In another control experiment, **2** was heated in some of the processing solvents of polyamic acids, such as *N*-methylpyrrolidine and *N,N*-dimethylacetamide. Ready decolouration of the chromophore occurred at the boiling temperatures of these solvents. Analysis indicated that the tricyanovinyl group was highly sensitive to these conditions, although the mechanism of the decomposition is not apparent.

To overcome these deficiencies associated with the tricyanovinyl group, **2** was further modified by replacing the most reactive CN in the tricyanovinyl group with aryl groups, as shown in Scheme 1.

Analysis of the data revealed that the replacement of the cyano group on the vinylcarbon-2 of the tricyanovinyl acceptor of **2** with a phenyl moiety resulted in a significant blue shifted charge-transfer absorption and a lower $\beta\mu$ value. However, the introduction of an electron donor such as a dialkylamino group on the benzene ring of **3** (*i.e.* **4**) caused a significant increase in $\beta\mu$. Further increase in molecular nonlinearity was obtained by extending the conjugation in **4** with thiophene (*i.e.* **5**). These $\beta\mu$ values suggest that the loss of activity caused by the replacement of the cyano group in **3** may, to some extent, be compensated for by increasing the conjugation length and

Table 1 The first molecular electronic hyperpolarizability and thermal stability data obtained for nonlinear optical compounds **1–5**

Compound[a]	λ_{max}/nm	10^{48} $\beta\mu$/esu[b]	T_d/°C[c]
1	653	6200	274
2	607	2700	296
3	514	480	346
4	467	840	369
5	513	1300	354

[a] 1,4-Dioxane was used as solvent for all the measurements. [b] EFISH experiments were done at a fundamental wavelength of 1.907 μm and the $\mu\beta$ values are as measured and not corrected for resonance effects. [c] Decomposition temperatures were estimated from DSC measurements (heating rate: 20 °C min^{-1}).

introducing stronger donor substituents. These new compounds, despite their higher molecular mass, possess much greater solubility than **2** and thus could be used to increase the chromophore density in polyimide matrices.

DSC studies indicated that the inherent thermal stabilities of compounds **3–5** were 340–370 °C. Unlike **1** and **2**, these modified compounds were inert to the processing and curing conditions of polyamic acids, and their treatment with alcoholic KOH resulted in no chemical change in these compounds.

Compound **5** was shown to possess the best optical, thermal and chemical properties and, therefore, was chosen for electro-optic studies on polyimide thin films. Using Ultradel 4212 polyamic acid (solvent: diglyme), polymeric thin films were formed by spin-coating the combined dye/polymer solution on an indium tin oxide (ITO) coated glass substrate. The films were kept in a vacuum oven at 120 °C for 10 h to remove the solvent. At this stage, the films were imidized by heating at 200 °C for 30 min. A thin layer of gold was vacuum evaporated onto the imidized polymer films to serve as the top electrode for poling. The polyimide samples were poled at 220 °C for 10 min with an applied dc electric field (1.0 MV cm^{-1}). The electro-optic activity of the poled polymer films was measured at 830 nm.[8] The measured electro-optic coefficients, r_{33}, were 10–12 pm V^{-1} for polyimide films containing 20 mass% of **5**.

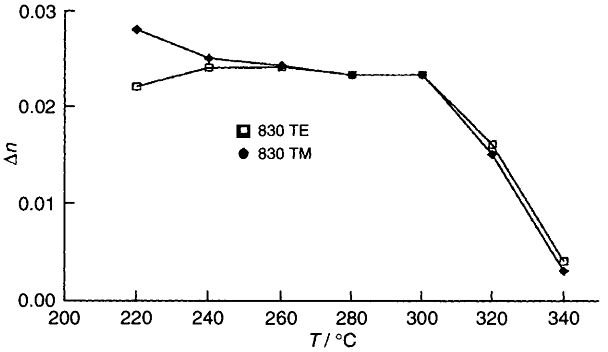


Fig. 1 Index of refraction at 830 nm for a guest (**5**)–host (PI-4212) material system *vs.* cure temperature

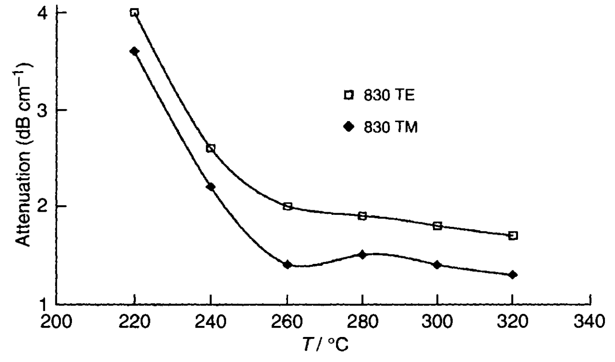


Fig. 2 Slab attenuation of guest (**5**)–host (PI-4212) material system *vs.* cure temperature

The index of refraction was measured by the prism coupling method on single layer slabs of core (**5**/PI-4212) and cladding (PI-4212) materials coated onto 3 μm thermal oxide on silicon wafers. The refractive index difference between the core and cladding as a function of cure temperature is shown in Fig. 1. The index difference between the core and clad was 0.025 and did not change up to 300 °C which clearly indicates the high thermal stability of **5** at 300 °C. Above 300 °C, a drop of index difference was noticed which reflects diffusion of the chromophore out from the single layer of the guest–host material. This was demonstrated by depositing 0.5 μm of aluminium and performing the same heating sequence, then removing the metal. In this case there was no change in index upon heating to 325 °C. Another attractive feature of this material system appeared to be the compatibility between the chromophore and polyimide. This was examined by determining the attenuation of the material system at various cure temperatures in the slab form by the prism coupling and streak method (Fig. 2). The attentuation for the fully cured sample, at 830 nm, was < 2 dB cm^{-1} which clearly reflects the compatibility of **5** with the polyimide.[9]

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References

1 K. Y. Wong, A. K. Y. Jen and V. P. Rao, *Phys. Rev. A*, 1994, **49**, 3077.
2 A. K. Y. Jen, K. Y. Wong, V. P. Rao, K. J. Drost and Y. Cai, *J. Electronic Mater.*, 1994, **23**, 653.
3 V. P. Rao, A. K. Y. Jen, K. Y. Wong and K. J. Drost, *Tetrahedron Lett.*, 1993, **34**, 1747.
4 K. J. Drost, A. K. Y. Jen and V. P. Rao, *ChemTech.*, 1995, **25**, 16.
5 V. P. Rao, A. K. Y. Jen, K. Y. Wong and K. J. Drost, *J. Chem. Soc., Chem. Commun.*, 1993, 1118.
6 V. P. Rao, Y. Cai and A. K. Y. Jen, *J. Chem. Soc., Chem. Commun.*, 1994, 1689.
7 K. Y. Wong and A. K. Y. Jen, *J. Appl. Phys.*, 1994, **75**, 3308.
8 C. C. Teng and H. A. Mann, *Appl. Phys. Lett.*, 1990, **56**, 1734.
9 J. T. Kenney, E. S. Binkley, A. K. Y. Jen and K. Y. Wong, *Mater. Res. Soc. Symp. Proc.*, 1993, **328**, 511.

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