

Synthesis of second-order nonlinear optical chromophores with enhanced thermal stability and nonlinearity: a conformation-locked *trans*-polyene approach

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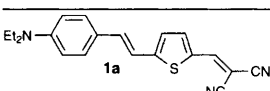
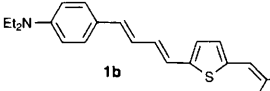
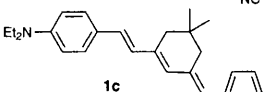
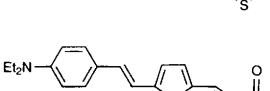
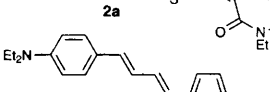
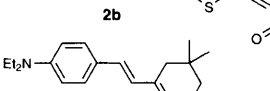
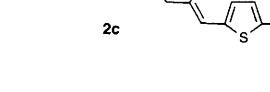
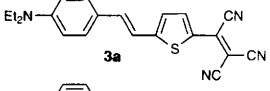
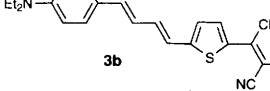
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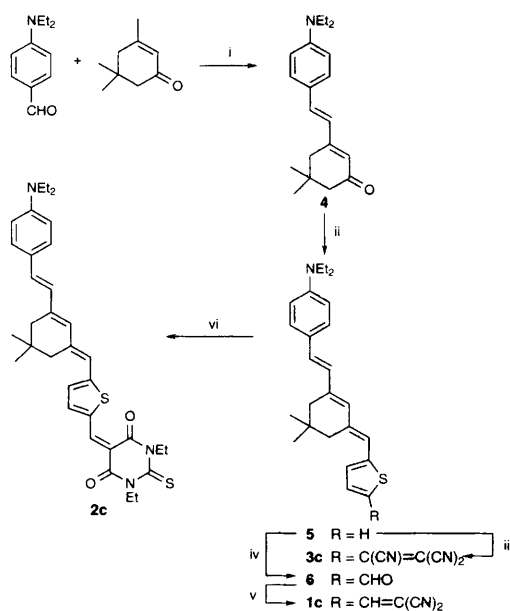
A facile synthesis that combines the use of an easily polarizable thiophene ring and a ring-locked triene as efficient conjugating moieties is employed to simultaneously enhance molecular nonlinearity (as high as $13\,000 \times 10^{-48}$ esu) and thermal stability; incorporating this highly nonlinear chromophore in polyquinoline results in high electro-optic activity and long-term alignment stability at 100 °C for more than 1000 h.

The growing interest in organic polymeric materials for electro-optic (E-O) device applications has led to the development of various classes of asymmetric π -conjugated molecules.^{1–6} In poled E-O polymer systems, the alignment of the polar order is preserved either by using host polymers with high glass transition temperatures (200–300 °C),⁷ or by cross-linking the chromophore polymer-composite.⁸ In either case, it poses a challenge for chemists in this field to develop highly nonlinear chromophores with thermal stabilities exceeding 200 °C in order to survive the material processing and device fabrication conditions. Recently, it has been shown that very large nonlinearities can be achieved by employing heteroaromatic rings which have lower aromatic stabilization energy upon charge separation,^{9–10} or by using extended polyene π -bridge systems that have strong electron acceptors.¹¹ Incorporation of these guest chromophores into host polymer matrices and their subsequent alignment by an electric field have demonstrated very large electro-optic coefficients ($r_{33} = 45\text{--}55 \text{ pm V}^{-1}$) at a wavelength of 1.3 μm .^{12,13} These values are significantly larger

than the value of 31 pm V^{−1} for commercially available LiNbO₃. However, the long-term alignment stability of these E-O polymer systems was limited due to the low inherent thermal stability (<175 °C) of these chromophores that prevents them from being processed and poled at higher temperatures. We have recently developed a facile approach to the synthesis of NLO chromophores with both enhanced nonlinearity and thermal stability. This synthetic method combines the advantages of using a thiophene ring and a triene as efficient conjugating moieties for easier charge separation, and the use of

Table 1 Electronic absorption and the first molecular hyperpolarizability obtained for nonlinear optical compounds 1a–3c

	$\mu_{\text{max}}/\text{nm}$ in dioxane	$\beta\mu/10^{-48} \text{ esu}$ at $\lambda = 1.907 \mu\text{m}$
 1a	513	1300
 1b	545	2700
 1c	559	3450
 2a	578	2400
 2b	597	4200
 2c	611	5380
 3a	640	6200
 3b	662	9800
 3c	684	13000



Scheme 1 Reagents: i, Bu^oOK–Bu^oOH; ii, diethyl 2-thienylmethylphosphonate; iii, BuLi, TCNE; iv, BuLi, DMF; v, CH₂(CN)₂; vi (from 6), diethylthiobarbituric acid

a 2,2-dimethylpropane-1,3-diyl moiety attached to the triene to give a 6-membered ring system that provides a configuration-locked geometry of *trans*-triene to prevent the thermally induced *cis*-*trans* isomerization. This allows us to synthesize a series of NLO chromophores with broad variation of electron acceptors to fine tune the linear absorption property (λ_{max}) and $\beta\mu$. We also report the preliminary results of the E-O coefficients and thermal stability.

The synthesis of a series of configuration-locked triene chromophores **1c**–**3c** is shown in Scheme 1. Compound **4** (*trans*-*trans*) was prepared by using the Knoevenagel condensation of 4-(*N,N*-diethylamino)benzaldehyde with isophorone (3,5,5-trimethylcyclohex-2-en-1-one) in the presence of Bu^tOK–Bu^tOH. Compound **5** was derived from the Wittig–Horner condensation of diethyl 2-thienylmethylphosphonate with **4** in Bu^tOK–THF. Compound **5**, which does not have an electron-withdrawing group at the end of the conjugating moieties, was obtained as a mixture of *trans*-*trans*-*trans* and *trans*-*trans*-*cis* isomers in a ratio of 2:1, as determined by ¹H NMR spectroscopy. Lithiation of **5** (mixture of *trans*- and *cis*-isomers) with BuLi and subsequent quenching with dimethylformamide (DMF) and tetracyanoethylene (TCNE) gives **6**[†] and tricyanovinylsubstituted chromophore **3c**. Treatment of **6** (all-*trans*) with malononitrile and diethylthiobarbituric acid gave the all-*trans* **1c** and **2c** in 80–90% yields. All the double-bond linkages in **1c**–**3c** were confirmed to be *trans* by careful NMR analysis.

Electronic absorption spectra of these compounds were obtained to compare their intramolecular charge-transfer properties (Table 1). The trienes **1c**–**3c** have a substantially red shifted charge-transfer band when compared to the stilbenes **1a**–**3a** and dienes **2a**–**2c**, indicating the more efficient electron delocalization nature of the triene bridge. Second-order hyperpolarizabilities of these compounds were determined by using the electric field-induced second harmonic generation (EFISH) technique described previously.¹⁴ 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. Comparison of the $\beta\mu$ values of the compounds in Table 1 reveals that the combination of the conformation-locked *trans*-triene bridge with the tricyanovinyl acceptor provides a very efficient mechanism to enhance molecular nonlinearity. The absorption maximum (λ_{max}) for **3c** was at 684 nm and thus correcting this value for dispersive enhancement using the two-level correction¹⁵ gave a zero frequency value, $\mu\beta(0)$, of 5480×10^{-48} esu, which is 15 times greater than that for the commonly employed NLO chromophore 4-(*N,N*-diethylamino)nitrostilbene [DANS, $\mu\beta(0)$ of 370×10^{-48} esu]. Thermal stability studies were performed by dissolving **3b** and **3c** in polyquinoline PQ-100 (Maxdem) and heating the thin film samples isothermally at 175, 200 and 225 °C for 20 min, respectively. The π - π^* charge-transfer absorption band was used to monitor the decomposition

temperature. Compound **3c** with a configuration-locked *trans*-triene bridge possesses much better thermal stability at 200 °C (100%) than **3b**, which has a *trans*-diene bridge (<70%) (Fig. 1). It is well known that thermal stability of the polyene NLO chromophores decreases with an increase in the number of double bond linkages. However, by using this configuration-locked triene approach, the thermal stability of compounds with even longer chain lengths is significantly enhanced. Furthermore, when **3c** was doped (15 wt%) in a polyquinoline PQ-100 host and poled at 210 °C with a poling field of 1.4 MV cm^{-1} , the resulting polymer had an electro-optic coefficient, r_{33} , of 27 pm V^{-1} measured at 1.3 μm ,¹⁶ consistent with the large molecular nonlinearity. The thermal stability of the poled polymer was demonstrated by heating the poled sample in an oven at 100 °C for over 1000 h. The E-O activity of the sample shows an initial drop to 75% of its original value within 80 h, then remains unchanged for a similar period of time.

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Footnote

[†] Both **6** and **3c** were obtained as a mixture of *trans*-*trans*-*trans* and *trans*-*trans*-*cis* isomers. However, the *trans* isomer can be separated from the *cis* isomer by column chromatography. δ_{H} (CDCl_3 , 300 MHz) for **3c** (*trans*): 1.08 (s, 6 H), 1.19 (t, 6 H), 2.35 (s, 2 H), 2.54 (s, 2 H), 3.40 (q, 4 H), 6.33 (s, 1 H), 6.63 (s, 1 H), 6.64 (d, *J* 9.0, 2 H), 6.72 (d, *J* 16.8, 1 H), 6.78 (d, *J* 17.0, 1 H), 7.12 (d, *J* 4.8, 1 H), 7.35 (d, *J* 9.0, 2 H), 7.95 (d, *J* 4.8, 1 H); for **3c** (*cis*): 1.03 (s, 6 H), 1.22 (t, 6 H), 2.32 (s, 2 H), 2.38 (s, 2 H), 3.40 (q, 4 H), 6.37 (s, 1 H), 6.64 (d, *J* 9.0, 2 H), 6.65 (s, 1 H), 6.96 (d, *J* 15.6, 1 H), 6.80 (d, *J* 15.3, 1 H), 7.10 (d, *J* 4.8, 1 H), 7.37 (d, *J* 9.0, 2 H), 7.95 (d, *J* 4.8, 1 H).

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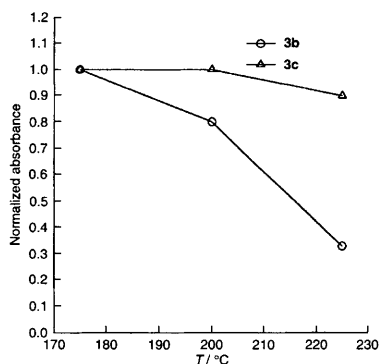


Fig. 1 Thermal stability of **3b** and **3c** heated isothermally at 175, 200 and 225 °C for 20 min each, measured by following the change in absorbance of a 20 wt% dye-doped polyquinoline thin film vs. *T*