Tricyanoquinodimethane derivatives with extremely large second-order optical nonlinearities

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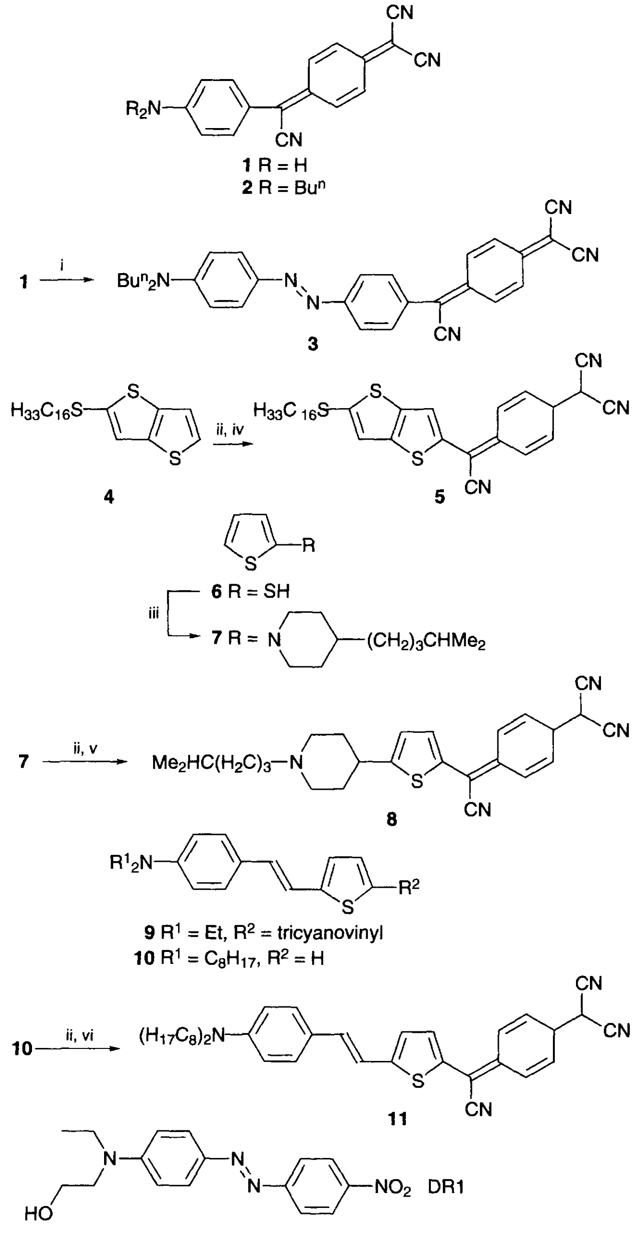
Chromophores containing the tricyanoquinodimethane acceptor moiety possess substantially larger second-order optical nonlinearities than, and similar thermal stabilities to, analogous chromophores bearing the strong tricyanovinyl acceptor.

Organic chromophores displaying both large second-order optical nonlinearities and thermal stabilities are required for optical data transmission, manipulation and storage.[1] Given the prerequisite of macroscopic and molecular asymmetry for dipolar second-order nonlinear optical (NLO) effects, such as the linear electro-optic (EO) effect, prototypical devices have been doped polymers containing dipolar chromophores of the form D–π–A, where D (A) is an electron donor (acceptor) group and π is a π-electron-conjugated bridge linking D/A moieties. Macroscopic asymmetry is normally induced *via* thermo-poling[2] the dipolar molecules at the polymer glass transition temperature, T_g. To minimize the subsequent dipolar relaxation and the decrease in second-order NLO properties after removal of the thermo-poling field, polymers with $T_g > 180\,°C$ are normally used, requiring dyes with sufficient thermal stability. For doped polymers, it is acknowledged that for some applications, EO coefficients greater than that of $LiNbO_3$ (30 pm V^{-1} at 1300 nm) are required,[3] necessitating highly (moderate) nonlinear chromophores present in small (large) amounts.

Ground rules for optimizing the chromophore second-order polarizability, β, responsible for second-order NLO effects, are now well understood and involve optimizing the ground-state polarization *via* the correct combination of D/A pairs for a given π bridge, where the ground-state polarization is related to the degree of mixing of two limiting charge-transfer forms of the molecule.[4] It has been shown theoretically[5] and experimentally[4] that β, as a function of ground-state polarization and thus mixing, exhibits positive and negative maxima.

For common stilbene and thiophene bridges, there is evidence[6,7] that the ground-state polarization required to optimize β in a positive sense, has not, to date, been reached, requiring stronger D/A groups than those currently used, of which the tricyanovinyl (TCV) acceptor is amongst the strongest.[8] The tricyanoquinodimethane (TCQ) acceptor is known to form a strongly hydrophilic end-group in Langmuir–Blodgett film-forming materials, consistent with a large acceptor strength.[9] Recently, a very large negative β value for a novel TCQ-containing D/A polyenic zwitterion was reported; however, questions about the chromophore stability remain.[10] In this paper, TCQ-containing chromophores are shown to possess both significantly larger nonlinearities, measured using an EO technique, and similar thermal stabilities (> 200 °C) to analogous molecules bearing the TCV moiety. Additionally, a guest–host system containing 2 mol% of one TCQ-containing chromophore, possessed a similar EO coefficient at 1550 nm as $LiNbO_3$. Finally, the degree of ground-state polarization required to optimize β in a positive sense, may have been surpassed for a D–thiophene–TCQ chromophore.

The molecules examined, with a brief synthetic description of the previously unreported chromophores, are shown in Scheme 1. Compounds **1**, **2**, **4**, **9** and **10** were synthesized using literature



Scheme 1 *Reagents and conditions*: i, *N*,*N*-dibutylaniline, H_2SO_4, AcOH, $NaNO_2$, 10 °C, 23%; ii, TCNQ, DMF, 80 °C, 2 h; iii, 4-(4-methylpentyl)-piperidine, toluene, reflux, 2 h, 40%; iv, DMF, *hv*, 25 °C, 45 min, 29%; v, DMF, *hv*, 25 °C, 45 min, 35%; vi, DMF, *hv*, 25 °C, 15 min, 38%

procedures.[8,11,12] TCQ was introduced in **5** and **8** using a modified procedure,[11] whereas **3** was obtained by azo coupling the diazotized aniline **1** with *N,N*-dibutylaniline. Disperse Red 1 (DR1), purchased commercially and used as received (Aldrich 34420-6), was studied since it (*i*) afforded comparison with **3** and (*ii*) is a common benchmark for EO polymers.[2] The purity of synthesized chromophores was checked using normal methods.

The real and imaginary components of the EO coefficient, r_{33}, of dye-doped polymers were measured at 1064 nm using an angle-dependent, modulated-intensity, ellipsometric method,[13] with sample preparation detailed previously.[14] Chromophores were dispersed in either polymethylmethacrylate (PMMA) or polycarbonate (PC), both purchased commercially (PMMA: Aldrich 18226-5, T_g = 95 °C; PC: Aldrich 18162-5, T_g = 150 °C) and used without further purification.

The r_{33} coefficients of the chromophores studied are presented in Table 1, along with the maximum absorption wavelength, $\lambda_{\max}$, in both chloroform and the appropriate polymer host. Absorption coefficients in chloroform are also given.

Comparing **9** with **11** clearly demonstrates that substitution of TCV with TCQ leads to a very large bathochromic shift in charge-transfer absorption. This may be rationalized by both the increased conjugation length of the TCQ-containing dye and by the aromatic–quinonal nature of the ground-state of **11**, where the loss of aromatic stabilization energy in the alkyl-substituted aniline ring upon charge transfer is offset by a concomitant gain in the TCQ ring, increasing the degree of ground-state polarization.[15] A similar bathochromic shift is observed by comparing (*i*) **2** with *N,N*-dimethyl-*p*-(tricyanovinyl)aniline, which has a $\lambda_{\max}$ of 516 nm[6] and (*ii*) **3** with DR1.

For all dyes studied, except **11**, the imaginary component of r_{33} at 1064 nm was negligible. The EO measurement was therefore repeated with **11** at 1550 nm, where the extremely large and purely real r_{33} of 31 pm V^{-1}, similar to $LiNbO_3$, was obtained. The lack of a significant imaginary component at 1550 nm was evidenced by (*i*) agreement between the theoretical angle-dependent modulated intensity, using a model based on transparent guest–host films,[13] and that observed experimentally (Fig. 1 ≈), and (*ii*) the extremely small absorption coefficient of 1.68 dm^3 mol^{-1} cm^{-1} in chloroform. To afford comparison between TCV- and TCQ-containing dyes, **9** was also measured at 1550 nm, with the resulting r_{33} significantly smaller than for **11**, despite **9** being one of the most promising EO dyes known.[7] This difference in r_{33}, which does not arise due to either the red-shifted $\lambda_{\max}$ of **11** [the calculated EO dispersion-enhancement factor, using a two-state quantum-mechanical model,[2] being 1.8 (1.4) for **11** (**9**) at 1550 nm] or a significantly enhanced ground-state dipole moment [12.5 D (10.1 D) for **11** (**9**) in $CHCl_3$], underscores the benefits of the TCQ acceptor. The advantage of TCQ is also highlighted by comparing the EO coefficients at 1064 nm of (*i*) **2** with *N,N*-dimethyl-*p*-(tricyanovinyl)aniline, calculated to have an r_{33} of 1.3 pm V^{-1},[6] and (*ii*) **3** with DR1.

Chromophore **8** differs from **2** by replacement of the benzene π-electron bridge with thiophene, which is known to increase ground-state polarization.[7] Given the red-shifted $\lambda_{\max}$, it is reasonable that the ground-state polarization of **8** is increased relative to **2**. However, this increase in $\lambda_{\max}$ was accompanied by a significant decrease in r_{33}, and thus β, suggesting that the degree of ground-state polarization required to optimize β had been surpassed.

Preliminary thermal stability data, as measured by DSC, showed **2** melted at 140 °C and decomposed at 250 °C. However DSC, depending on the heating rate, may overestimate thermal stability. We therefore examined the change in the charge-transfer absorption band of dye-doped polymers after baking, under reduced pressure, for 30 min at a specified temperature. If > 60% of the initial absorbance remained, the sample was re-baked, but at a higher temperature, with this cycle repeated until 60% of the initial absorbance remained—the final baking temperature being defined as the thermal stability (Table 1). In this test, dye decomposition and out-diffusion both play a role. The data in Table 1 show: (*i*) all dyes possess similar thermal stabilities, which may be large enough for some applications;[3] (*ii*) the greater thermal stability of the fused-thiophene analogue **5** is consistent with previous results;[7] and (*iii*) the thermal stabilities are larger than those reported previously for D/A thiophenes.[16] An improvement in thermal

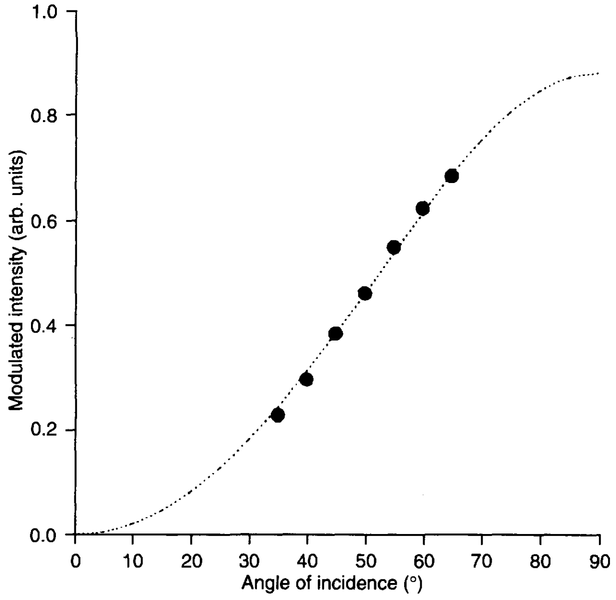


Fig. 1 Angle-dependent experimental (●) and theoretical (- - - -) modulated intensity for **11** at 1550 nm

Table 1 Physical and optical properties of the new chromophores

Dye	$\lambda_{\max}$[a]/nm (CHCl$_3$)	log (ε/dm^3 mol^{-1} cm^{-1}) (CHCl$_3$)	Polymer	$\lambda_{\max}$[a]/nm (polymer)	r_{33}[b]/pm V^{-1} (1064 nm)	r_{33}[b]/pm V^{-1} (1550 nm)	Thermal stability[c] (*T*/°C)
2	700	4.79	PMMA	690	10.6	4.7	235
9	697	4.62	PC	682	10.0	5.1	235
11	867	4.75	PC	848	—	31	210
8	738	4.83	PC	724	6.0	—	220
5	614	4.56	PMMA	588	3.6	—	240
3	679	4.46	PMMA	632	10.0	—	200
DR1	480	4.50	PMMA	488	1.3	—	210

[a] Absorption maxima, $\lambda_{\max}$, in both chloroform and a polymer host; absorption coefficient, ε, in chloroform. [b] The real part of the EO coefficient, r_{33}, at 1064 and 1550 nm. Due to differences in both chromophore solubility and polymer T_g, all EO coefficients have been 'normalized' to that of a 2 mol% dye–PMMA film, poled at 105 °C with 1 MV cm^{-1}. [c] Thermal stabilities are defined as being the temperature at which 60% of the initial chromophore absorbance remained after baking the polymer film for 30 min under reduced pressure.

stability of some dyes, without a concomitant reduction in r_{33}, may be possible by replacing dialkylamino donor groups with diarylamino moieties.[17]

Compounds **2** and **9** show both similar thermal stabilities and r_{33} values. However, **9** requires an elaborate synthesis[8] whereas **2** is obtained in a simple 'one-pot' procedure.

TCQ-containing chromophores possess second-order optical nonlinearities (thermal stabilities) which are much greater than (equivalent to) analogous compounds bearing the TCV acceptor. One guest–host film, containing 2 mol% of a TCQ-chromophore, gave an EO coefficient comparable to $LiNbO_3$ and a thermal stability of 210 °C, with further improvements in thermal stability, without degradation of the nonlinearity.

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