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Thermally stable triaryl amino chromophores with high molecular hyperpolarizabilities

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Abstract—The synthesis of a series of high temperature triaryl amino chromophores with unprecedented hyperpolarizability values for potential EO applications is described. 4-(*N*,*N*-di-*p*-anisylamino)phenyl donors are for the first time bridged to powerful acceptors such as tricyanovinyldihydrofuran via vinyl thiophene linkages. The chromophores are readily soluble in common organic solvents, exhibit useful absorptions and high thermal decomposition temperatures (highest $T_d = 358\,°C$). Molecular hyperpolarizabilities (β) of the chromophores were measured by Hyper Rayleigh Scattering (HRS) at 1604 nm, which gave β values from 1000 to $20{,}000 \times 10^{-30}$ esu. The electrochemical behavior of the chromophores were studied by cyclic voltametry, and agree well with the intrinsic nonlinearities observed. These chromophores are of particular interest due to their large optical nonlinearities, transparency in the near IR, high thermal decomposition temperatures, and their potential to be incorporated into polymeric materials.

Organic electrooptic materials (EO) are of great interest due to their potential ultrafast modulation of light in telecommunications applications.[1] Organic nonlinear optical (NLO) chromophores, which exhibit and maintain in use properties such as thermal and chemical stability, high nonlinearity, and transparency as well as compatibility with polymer hosts are currently pursued for next generation high performance photonics devices.[2] Here we report the synthesis, optical, and thermal properties of a series of novel chromophores with 4-(*N*,*N*-di-*p*-anisylamino)phenyl moiety as the electron donor (Fig. 1) and their unprecedented hyperpolarizability values measured for triaryl amine EO chromophores.

In general, optimization of the electron acceptor group has led to considerable progress in achieving higher molecular hyperpolarizabilities (β).[3] Heterocyclic bridges such as thiophene and oligomers,[4] and combined thiophene–isophorone[5] have enhanced nonlinearities, and improved stability. Thiophene in particular is an appealing class of linker in optoelectronics.[6] Chromophores with the largest nonlinearity have been obtained by using the tricyanovinyldihydrofuran (TCF) acceptor.[7] Studies on donor groups, however, have attracted less attention compared to acceptor groups or bridges. Triaryl amine groups have been introduced as donors to increase the thermal stability of electrooptic chromophores and provide functionality for incorporation into polymers.[8]

In particular, chromophores with 4-(*N*,*N*-di-*p*-anisylamino)phenyl moieties as the electron donor have shown long-lived charge separated states and have been used as multiphoton absorbing materials for a large variety of potential applications in optics.[9] Coupling these triphenyl amine donors with strong acceptors for use as NLO chromophores, however, has not been reported, although similar compounds without methoxy substitution have shown increased thermal stability, but decreased $\mu\beta$ over alkyl amines.[10] In the present study, triaryl amine donors of this type are for the first time bridged to powerful acceptors via vinyl thiophene linkages and the strongest known acceptors (Fig. 1).

The syntheses of chromophores **5**–**8** are depicted in Scheme 1. Ullmann condensation of 4-iodoanisole with

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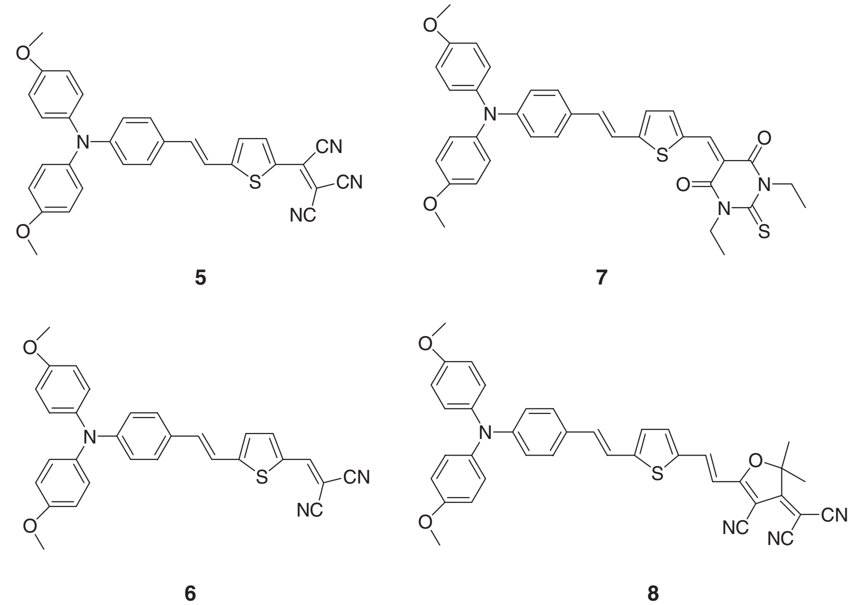
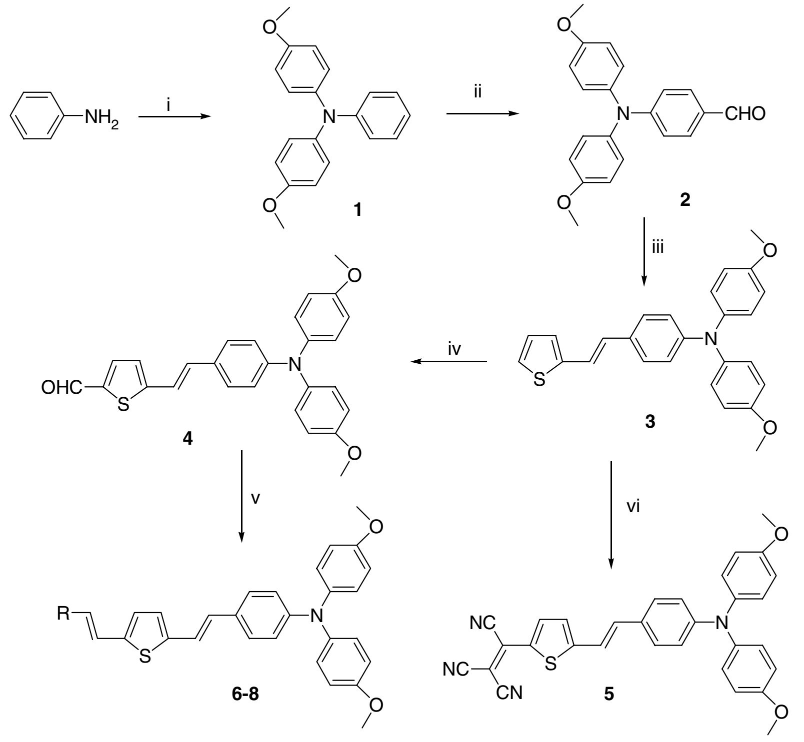


Figure 1. Triaryl amine derived chromophores **5**–**8**.

aniline yielded bis-(4-methoxyphenyl)-phenyl-amine (**1**) in 70% yield. Vilsmeier–Haack reaction of **1** afforded bis-(4-methoxy-phenyl)-aminobenzaldehyde (**2**) in 85% yield. Condensation of the aldehyde with thiophene methyl phosphonate gave the intermediate **3**. Lithiation of **3** and reaction with DMF provided the aldehyde **4** in 60% yield. The intermediate **3**, upon treatment with tetracyanoethylene (TCNE), gave the target compound **5** in 70% yield. Chromophores **6**–**8** were synthesized by condensation of the aldehyde **4** with malononitrile, diethyl thiobarbiturate, and TCF in 65%, 50%, and 35% yield, respectively.[11]

All intermediates and chromophores were isolated as pure compounds as evidenced by ^{1}H NMR, ^{13}C NMR, and high resolution MS. The compounds are soluble in common organic solvents.

Table 1 lists the UV–vis absorption maxima ($\lambda_{\max}$), second order NLO properties, and thermal decomposi-



Scheme 1. Synthesis of chromophores **5**–**8**. Reagents and conditions: (i) CuI, 4-iodoanisole, toluene-reflux, (ii) DMF, POCl$_3$, (iii) diethyl(2-thienylmethyl)phosphonate,[12] ^{t}BuOK, THF, (iv) *n*-BuLi, −78 °C, DMF, H$_2$O, (v) acceptor, Et$_3$N, reflux, (vi) TCNE, DMF.

Table 1. Thermal and optical properties of **5–8**

Chromophore	λ_{max} (nm)[a]	T_d (°C)[b]	β (10^{-30} esu)[c]
5	683	295	—
6	547	288	1000
7	596	358	5000
8	648	320	20,000

[a] λ_{max} in $CHCl_3$.
[b] T_d=TGA onset in N_2 at 10 °C/min and confirmed by DSC.
[c] First molecular hyperpolarizability at $\lambda = 802$ nm. β for **5** could not be determined due to absorption at the second harmonic signal.

tion temperatures (T_d) of the new chromophores. An increase in acceptor strength induces a bathochromic shift of the λ_{max} as expected. The absorption properties of chromophores **5–8** are comparable to similar compounds with alkyl amine donors.[10] The UV–visible spectra in $CHCl_3$ exhibits an intense absorption band in the visible region as shown in Figure 2.

The maximum absorption wavelength depends on the strength of the donor/acceptor pair. As expected the bathochromic shift is largest for chromophores containing three cyano groups (**5**, **8**), compared to barbiturate (**7**), and malononitrile (**6**) acceptors.

The decomposition temperature T_d of the chromophores were measured by thermal gravimetric analysis (TGA) and dynamic scanning calorimetry (DSC) in N_2, with a heating rate of 10 °C/min. The chromophores **5–8** exhibit T_d ranging from 288–358 °C (Table 1). Compound **6**, containing the dicyanovinyl (DCV) acceptor has the lowest T_d value. Chromophore **7** has the highest thermal decomposition at 358 °C, maybe due to the presence of diethylthiobarbiturate as the electron acceptor.

In an effort to explore the stability and compatibility of the new chromophores within established optical polymer hosts, compound **8** was dispersed in perfluorocyclobutyl (PFCB) polymers[13] from our laboratory, cast as a thin film on glass, and heated at 200 °C for 45 min under N_2. The UV–visible spectra of the films before and after heating exhibited no significant change in peak maximum or shape as expected. This demonstrates the thermal stability of the chromophore in a commercially viable optical polymer host. The thermal decomposition temperatures are higher than those of chromophores with alkyl amine donors[10] and indicate good potential for use in high temperature polymer devices.[8]

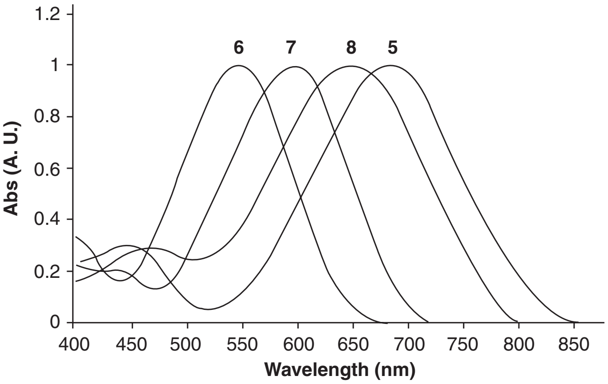


Figure 2. UV–vis spectrum ($CHCl_3$) of chromophores **5–8**.

The electrochemical properties of chromophores **5–8** have been studied by cyclic voltammetry (CV) at room temperature and are shown in Table 2. The CV of **1** (Fig. 3) shows one reversible wave for the oxidation of the triaryl amino moiety at 217 mV, corresponding to the transfer of one electron, and an additional irreversible second oxidation at 986 mV, in agreement with the electrochemical behavior previously reported in the literature.[14]

Addition of an electron-accepting fragment to the triaryl amine structure results in an increase in the redox potentials compared to those of unsubstituted triaryl amine. This effect is clearly observed in compounds **5–8**, which incorporate acceptors of different strength, and agrees with the general trend observed for other related structures.[15] The tricyano groups (**5** and **8**) show the best electron acceptor properties, whereas **6** and **7** have similar lower reduction potentials. In general, with the same electron donating group and chain length, better electron acceptor groups (Table 2) promote a bathochromic shift of the λ_{max} and an enhancement in hyperpolarizability.

Finally chromophores **6–8** were evaluated using Hyper Rayleigh Scattering (HRS)[16] as shown in Table 1.

Table 2. Selected electrochemical properties of **5–8**[a]

Chromophore	$E^1_{1/2,\mathrm{ox}}$	E^2_{ox} [b]	$E^1_{1/2,\mathrm{red}}$	$E^2_{1/2,\mathrm{red}}$
1	217	986	—	—
5	285	979	−950	−1589
6	245	957	−1513[c]	—
7	247	927	−1313[c]	—
8	232	835	−1046[c]	—

[a] Room temperature potentials versus ferrocene, CH_2Cl_2–$TBAPF_6$ at 100 mVs^{-1} with carbon as working electrode.
[b] E_{pc} reported due to electrochemical irreversibility ($\Delta E_p \gg 80$ mV).
[c] E_{pa} reported due to chemical irreversibility.

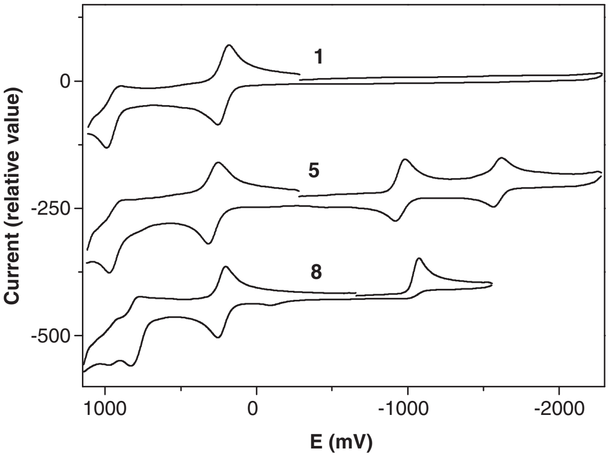


Figure 3. CV of **1**, **5**, and **8**.

β values for chromophores **6–7** were evaluated by the external reference method[17] using chromophore **6** as the reference material, the β for which was determined with that of chloroform (0.49×10^{-30} esu,[18] uncorrected for the wavelength dispersion). Chromophore **8** exhibited the highest β value of $20{,}000 \times 10^{-30}$ esu, which may represent the highest known hyperpolarizability for triaryl amine derived compounds. Note that chromophore **8** has a cut-off wavelength very close to the HRS signal wavelength (Fig. 2), so that the value might include resonance enhancement.[19]

In summary, we have synthesized a series of high temperature chromophores with high hyperpolarizability values for potential EO applications. The triaryl amine donor has been connected to powerful acceptors via vinylene thiophene bridges. The chromophores show excellent thermal stability and good absorption properties.

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11. Synthesis and characterization of **8**: To a stirred solution of aldehyde **4** (1 equiv) in dry CH_2Cl_2 (10 mL/g) was added tricyanovinyldihydrofuran (TCF) (1.2 equiv) and catalytic amount of Et_3N (0.003 equiv). The dark reaction mixture was heated to reflux for 3 h and monitored by TLC (Hexane–E.A. 4:1). After complete disappearance of the aldehyde, the reaction mixture was cooled to room temperature, poured into ice water, and extracted with excess CH_2Cl_2. The combined organic layers were washed with water, dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by chromatography (CH_2Cl_2) to afford **8** (65%) as a green solid. Mp 205–210 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, $J = 16$ Hz, 1H), 7.43 (d, $J = 4$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 1H), 7.15–7.13 (m, overlap, 4H), 7.11–7.09 (m, overlap, 2H), 6.94–6.91 (m, overlap, 8H), 3.81 (s, 6H), 1.63 (s, 6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 175.8, 173.0, 156.6, 153.6, 149.9, 139.9, 139.4, 137.9, 137.4, 134.1, 128.2, 127.5, 127.3, 127.2, 119.2, 117.4, 114.9, 112.2, 111.5, 97.1, 96.5, 56.3, 55.5, 26.6. HRMS observed for $C_{38}H_{30}N_4O_3S$: 622.2050 (calcd: 622.2039).
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