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Synthesis of nonlinear optical chromophores containing electron-excessive and -deficient heterocyclic bridges. The auxiliary donor–acceptor effects

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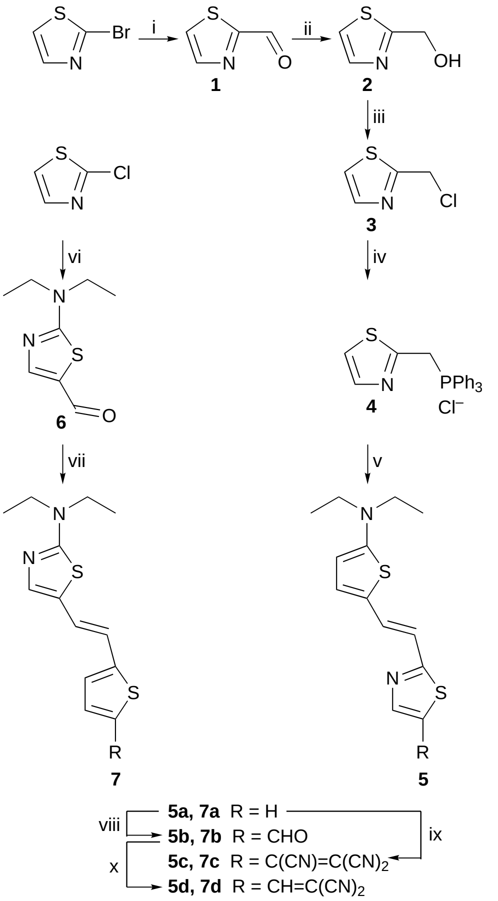
Push-pull substituted nonlinear optical chromophores with thiazole and thiophene rings and interposed ethylene units as π-conjugated bridges were synthesized. The effects of the nature and location of the heterocycles on the energy of the charge transfer transition for the chromophores are discussed.

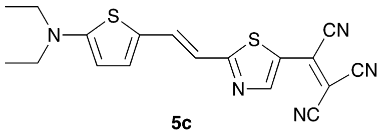
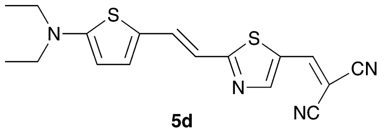
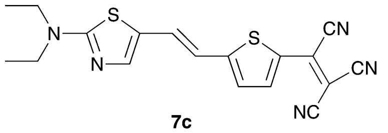
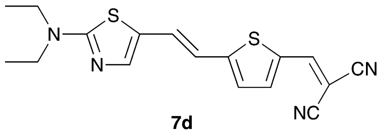
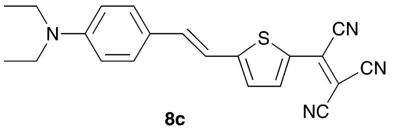
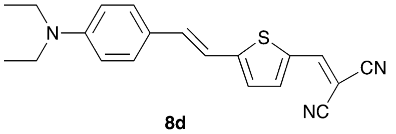
Dipolar chromophores of the form D-π-A, where D (A) is an electron donor (acceptor) group and π is a conjugated bridge possessing large molecular second-order nonlinear optical (NLO) responses and good thermal stability, are currently of interest because of their applicability to electro-optic devices.[1] In such molecules, the donor and acceptor substituents provide the requisite ground-state charge asymmetry, whereas the π-conjugation system provides a pathway for the redistribution of electric charges under the influence of electric fields. Benzene rings are widely used in combination with polyenes in π-conjugated bridges because of their thermal and oxidative stability, synthetic availability and substituent positional selectivity. However, the barrier resulting from the aromatic delocalization energy of the benzene ring leads to diminution of β values.[2] Synthetic studies have demonstrated that replacing the benzene ring of a chromophore π bridge with easily delocalizable five-membered heteroaromatic rings, such as thiazole and thiophene, results in enhanced molecular hyperpolarizability.[3] Recently, computational studies have suggested that heteroaromatic rings play a subtle role in influencing the second-order NLO response properties of donor–acceptor compounds.[4] While the aromaticity of heteroaromatics affects electronic transmissions between donor and acceptor substituents, the electron-excessive or electron-deficient nature of the heterocyclic ring systems also plays a major role in determining the overall electron-donating and -accepting ability of the substituents: electron-excessive heterocycles act as auxiliary donors and electron-deficient heterocycles act as auxiliary acceptors.[4b] Thus, attaching a strong donor to an electron-excessive heteroaromatic, such as thiophene,[5] and a strong electron acceptor to an electron-deficient heteroaromatic, such as thiazole,[5] will yield chromophores with significantly enhanced NLO responses. Contrarily, reversing the architecture of the heterocyclic rings in the π-conjugated system will lead to chromophores with diminished NLO responses.

In this report, we present novel NLO chromophores with π-conjugating moieties that contain thiazole and thiophene, with an ethylene segment in between, and show that the location of the heterocyclic rings indeed has a pronounced effect on the energy of charge-transfer (CT) transition of the chromophores, as was predicted in previous theoretical calculations.[4] The synthetic routes used to prepare the NLO chromophores **5c–d** and **7c–d** containing thiazole and thiophene are shown in Scheme 1. The thiazole parts of compounds **5** were synthesized starting from 2-bromothiazole, which was treated with Bu^{n}Li at −78 °C, and the halogen–lithium exchange product was quenched with *N*-formylmorpholine to produce 2-formylthiazole **1**.[6] Reduction of the formyl group of **1** with $NaBH_4$ gave 2-hydroxymethylthiazole **2**, which was transformed into 2-chloromethylthiazole **3** upon chlorination with carbon tetrachloride–triphenylphosphine. The reaction of chloromethyl derivative **3** with triphenylphosphine yielded the corresponding phosphonium salt **4**.[7] Wittig reaction of 2-diethylamino-5-formylthiophene[8] with the phosphonium salt **4** in Bu^{t}OK–benzene led to compound **5a**. The thiazole portions of compounds **7** were prepared from 2-chlorothiazole,[9] which was allowed to react with Bu^{n}Li yielding 2-chloro-5-lithiothiazole. Adding *N*,*N*-diethylformamide to the 2-chloro-5-lithiothiazole solution and quenching with water yielded 2-diethylamino-5-formylthiazole **6**.[10] Wittig–Horner condensation of diethyl 2-thienylmethylphosphonate with the thiazole aldehyde derivative **6** produced compound **7a**. Compounds **5a**



Scheme 1 *Reagents*: i, Bu^{n}Li, *N*-formylmorpholine; ii, $NaBH_4$; iii, CCl_4, PPh_3; iv, PPh_3; v, 2-diethylamino-5-formylthiophene, Bu^{t}OK; vi, Bu^{n}Li, *N*,*N*-diethylformamide; vii, diethyl 2-thienylmethylphosphonate, Bu^{t}OK; viii, Bu^{n}Li, DMF; ix, Bu^{n}Li, TCNE; x, $CH_2(CN)_2$

Table 1 Electronic absorptions and thermal stabilities

chromophore	λ_{max}/nm in dioxane	$\varepsilon/10^4$ M^{-1} cm^{-1}	T_d/°C[a]
 **5c**	702	5.84	217
 **5d**	590	4.18	237
 **7c**	622	4.97	242
 **7d**	514	2.94	268
 **8c**	640[b]		245 (240[b])
 **8d**	513[c]		

[a]DSC, 10 deg min^{-1}. [b]Ref 13. [c]Ref 3(*d*).

and **7a**, which lack electron-withdrawing groups at the ends of their conjugating moieties, were lithiated with Bu^{n}Li and subsequently quenched with tetracyanoethylene and *N*,*N*-dimethylformamide to give formyl derivatives **5b** and **7b**, and tricyanovinyl-substituted **5c** and **7c**. A further Knoevenagel reaction of **5b** and **7b** with malononitrile afforded the dicyanovinyl-substituted chromophores **5d** and **7d**. All the compounds studied here were characterized using conventional spectroscopic techniques.[11]

Most donor–acceptor substituted NLO chromophores are characterized by a long-wavelength CT transition that contributes strongly to the second-order molecular hyperpolarizability.[12] All of the chromophores in this study had strong bands in the visible region of the spectrum. Table 1 lists the positions of the absorption maxima for the chromophores in this study, and for related chromophores.[3d,13] Chromophores **5c,d**, which have an electron-excessive heterocycle (thiophene) on their donor ends, and an electron-deficient heteocycle(thiazole) on their acceptor ends, show pronounced bathochromic shifts (*ca.* 80 nm) in their CT bands as compared with chromophores **7c,d**, which have reversed heterocycle substitution patterns. This result is reasonable since in chromophores **5c,d**, the thiophene and thiazole rings act as additional donor/acceptor groups, facilitating CT transitions. In chromophores **7c,d**, the thiazole ring reduces the donation ability of the donor substituent and the thiophene ring attenuates the acceptance power of the acceptor substituent, an arrangement that impedes CT transitions. When compared to chromophores **8c,d**, chromophores **7c,d** have no red-shifted CT bands, and even have slightly blue-shifted CT bands. This result again indicates that replacing a benzene ring on the donor end with an electron-deficient heterocycle, such as thiazole, decreases the electron-donating ability of the dialkylamine group, and counteracts the effects of reduced aromaticity.

The relative thermal stabilities of the chromophores were also studied using differential scanning calorimetry (DSC). The onset temperatures (T_d) of the chromophore thermal decomposition exotherms are shown in Table 1. Although, as expected, the replacement of a benzene ring with a heterocyclic ring does not lead to substantially lower thermal stability, we note that chromophores with lower charge-transfer transitional energies tend to possess lower thermal stabilities.

In summary, compounds **5c,d** and **7c,d** represent the first example of NLO chromophores synthesized in which the conjugating moieties contain both electron-excessive heterocycles (thiophene) and electron-deficient heterocycles (thiazole).[5] As predicted by theoretical calculations, the CT transitional energies of the chromophores depends not only on the natures but also strongly on the locations of the heterocyclic rings, which in turn may have significant effects on the molecular second-order NLO response properties.[4] Experiments to measure the second-order molecular hyperpolarizabilities of these chromophores are in progress.

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11 ^{1}H NMR spectra were recorded using CD_2Cl_2 as solvent and TMS as internal standard. Chemical shifts are in ppm, coupling constants are in Hz. **5c**: δ 1.21 (t, 6H, *J* 7.1), 3.42 (q, 4H, *J* 7.1), 6.01 (d, 1H, *J* 4.6), 6.46 (d, 1H, *J* 14.3), 7.24 (d, 1H, *J* 4.6), 7.85 (d, 1H, *J* 14.3), 8.34 (s, 1H). **5d**: δ 1.17 (t, 6H, *J* 7.1), 3.33 (q, 4H, *J* 7.1), 5.82 (d, 1H, *J* 4.3), 6.48 (d, 1H, *J* 14.9), 7.05 (d, 1H, *J* 4.3), 7.69 (d, 1H, *J* 14.9), 7.71 (s, 1H), 7.99 (s, 1H). **7c**: δ 1.18 (t, 6H, *J* 7.0), 3.48 (q, 4H, *J* 7.0), 6.47 (d, 1H, *J* 15.5), 7.05 (d, 1H, *J* 4.4), 7.32 (d, 1H, *J* 15.5), 7.35 (s, 1H), 7.83 (d, 1H, *J* 4.4). **7d**: δ 1.17 (t, 6H, *J* 7.1), 3.45 (q, 4H, *J* 7.1), 6.48 (d, 1H, *J* 15.5), 6.96 (d, 1H, *J* 4.2), 7.20 (d, 1H, *J* 15.5), 7.22 (s, 1H), 7.49 (d, 1H, *J* 4.2), 7.65 (s, 1H). HRMS (*m*/*z*) **5c**: Obs. 365.0745, calc. 365.0768; **5d**: obs. 340.0810, calc. 340.0816; **7c**: obs. 365.0751, calc. 365.0768; **7d**: obs. 340.0814, calc. 340.0816.

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