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Synthesis and characterization of thiazole-containing chromophores for second-order nonlinear optics

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Push–pull thiazole-containing nonlinear optical chromophores with dicyanovinyl and tricyanovinyl acceptors, along with their thiophene analogs, have been synthesized and characterized. The onset temperatures of thermal decomposition of these chromophores determined by DSC are above 240 °C. The redox properties of the chromophores were studied by cyclic voltammetry and the results reveal the electron-deficient (thiazole) and electron-excessive (thiophene) nature of the heterocycles. Experimental measurements of second-order nonlinear optical response ($\mu\cdot\beta$) indicate that the combination of either a thiazole or thiophene conjugating unit and a tricyanovinyl acceptor results in a nonlinear optical chromophore exhibiting substantial molecular hyperpolarizability ($\mu\cdot\beta$ *ca.* 7000×10^{-48} cm^6 at 1907 nm).

Introduction

The electronic and structural properties of donor–acceptor substituted π-conjugated organic compounds are of considerable interest because of their applicability to electro-optic devices.[1] A wide variety of structural modifications on the donor, acceptor and π-conjugated moieties have been carried out.[2] Synthetic studies have demonstrated that replacing the benzene ring of a chromophore π bridge with easily delocalizable five-membered heteroaromatic rings, such as thiophene and thiazole, results in an enhanced molecular hyperpolarizability.[3,4] Recent theoretical calculations, however, suggest that heteroaromatic rings play a subtle role in influencing the second-order NLO response properties of donor–acceptor compounds.[5] While the aromaticity of heteroaromatics affects electronic transmission between donor and acceptor substituents, the electron-excessive or electron-deficient nature of the heterocyclic ring systems may also play a major role in determining the overall electron-donating and -accepting ability of the substituents. The electron-deficient heterocycle will act as an auxiliary acceptor.[5b,6] Thus, attaching a strong electron acceptor to an electron-deficient heteroaromatic, such as thiazole,[7] may yield chromophores with significantly enhanced NLO responses. In this report, we present the synthesis, UV–VIS absorption spectrum, thermal stability, redox properties, and second-order nonlinear optical properties of new thiazole-containing chromophores with dicyanovinyl and tricyanovinyl acceptors.

Experimental

General methods

NMR spectra were recorded with a Varian Unity 300 MHz or a Bruker-DRX-300 spectrometer. UV–VIS absorption spectra were taken on a Hewlett-Packard 8453 UV–VIS diode array spectrophotometer. Mass spectra were recorded on a JEOL JMS-HX 110 with EI ionization. Cyclic voltammetric data were obtained on a BAS 100 B/W electrochemical analyzer (1×10^{-3} M solution of chromophore in CH_2Cl_2, 0.1 M Bu_4NPF_6 supporting electrolyte, platinum working and counter electrode). All potentials are referenced to the Ag/Ag$^+$ (0.01 M $AgNO_3$, 0.1 M Bu_4NPF_6, CH_3CN) reference electrode. Differential scanning calorimetry (DSC) was performed on a SEIKO SSC 5200 DSC using a heating/cooling rate of 10 °C min^{-1}. Analytical TLC was performed on commercial Merck plates coated with silica gel GF254. Silica gel for column chromatography was Merck kieselgel 60 (70–230 mesh). All reagents were of commercial quality and used as supplied. Thiazol-2-ylmethyltriphenylphosphonium chloride was prepared by the method of Dondoni.[8] Solvents were dried where necessary using standard procedures.

2-{(*E*)-2-[4-Diethylaminophenyl]ethen-1-yl}thiazole, 2

To a solution of thiazol-2-ylmethyltriphenylphosphonium chloride[8] (4.0 g, 10.1 mmol) in benzene (150 ml) was added t-BuOK (1.5 g, 12.1 mmol). The mixture was stirred at room temperature under nitrogen for 3 h, and a solution of 4-diethylaminobenzaldehyde (2.3 g, 15.2 mmol) in benzene (50 ml) was added. The resulting mixture was stirred at room temperature for 18 h, then the solvent was removed under vacuum. The residue was chromatographed (hexane–ethyl acetate 7:1) to give **2** (2.0 g, 77%). ^{1}H NMR($CDCl_3$) δ 1.12 (t, 6 H, $J = 6.9$ Hz), 3.32 (q, 4 H, $J = 6.9$ Hz), 6.59 (d, 2 H, $J = 9.0$ Hz), 7.03 (d, 1 H, $J = 16.2$ Hz), 7.07 (d, 1 H, $J = 3.6$ Hz), 7.27 (d, 1 H, $J = 16.2$ Hz), 7.33 (d, 2 H, $J = 9.0$ Hz), 7.65 (d, 1 H, $J = 3.6$ Hz); ^{13}C NMR ($CDCl_3$) δ 12.5, 44.3, 111.3, 116.2, 116.5, 122.6, 128.6, 134.8, 142.9, 148.1, 168.4; MS (*m*/*z*) 258.1190, calcd 258.1191 for $C_{15}H_{18}N_2S$.

2-{(*E*)-2-[4-Diethylaminophenyl]ethen-1-yl}thiazole-5-carbaldehyde, 3

To a solution of **2** (1.2 g, 4.65 mmol) in THF (15 ml) at −78 °C under nitrogen was added n-BuLi (2.2 ml, 5.6 mmol, 2.5 M in hexane). The solution was warmed to −10 °C, stirred for 1 h, and then cooled to −78 °C. To the mixture was added DMF (2.2 ml). The resulting solution was stirred at −78 °C for 30 min, warmed to room temperature, and stirred for 2 h. The mixture was then poured into water (10 ml), neutralized with 5% HCl, and extracted with CH_2Cl_2 (3×20 ml). The combined extracts were dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was purified by column chromatography (CH_2Cl_2) to give **3** (0.8 g, 66%). ^{1}H NMR(CD_2Cl_2) δ 1.09 (t, 6 H, $J = 7.0$ Hz), 3.31 (q, 4 H, $J = 7.0$ Hz), 6.58 (d, 2 H, $J = 8.7$ Hz), 6.97 (d, 1 H, $J = 15.9$ Hz), 7.35 (d, 2 H, $J = 8.7$ Hz), 7.47 (d, 1 H, $J = 15.9$ Hz), 8.19 (s, 1

H), 9.84 (s, 1 H); ^{13}C NMR (CD_2Cl_2) δ 13.1, 45.2, 112.1, 115.7, 122.4, 130.5, 137.4, 139.9, 150.0, 153.6, 176.3, 182.5; MS (*m*/*z*) 286.1138, calcd 286.1140 for $C_{16}H_{18}N_2OS$.

2-{(*E*)-2-[4-Diethylaminophenyl]ethen-1-yl}-5-(dicyanovinyl)thiazole, 4

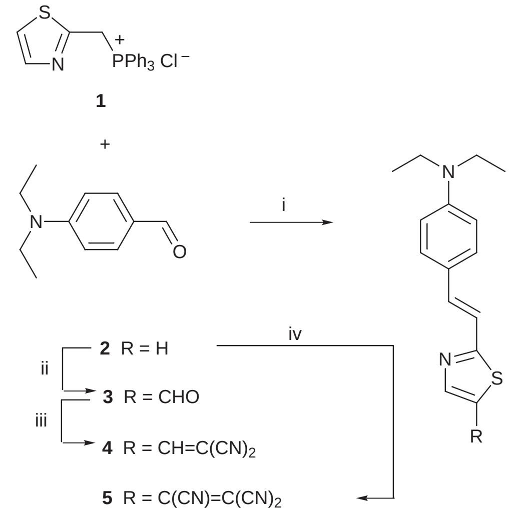
A solution of **3** (0.50 g, 1.74 mmol), malononitrile (0.17 g, 2.61 mmol), pyridine (3.8 ml) in propan-2-ol (15 ml) was stirred under nitrogen and heated to reflux for 2 h. The reaction mixture was poured into water (10 ml) and extracted with CH_2Cl_2 (3×20 ml). The combined extracts were dried over $MgSO_4$ and the solvent was removed under vacuum. The residue was recrystallized from ethyl acetate to give **4** (0.5 g, 85%). ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 6 H, $J = 6.9$ Hz), 3.43 (q, 4 H, $J = 6.9$ Hz), 6.67 (d, 2 H, $J = 9.0$ Hz), 7.08 (d, 1 H, $J = 15.9$ Hz), 7.47 (d, 2 H, $J = 9.0$ Hz), 7.65 (d, 1 H, $J = 15.9$ Hz), 7.84 (s, 1 H), 8.16 (s, 1 H); ^{13}C NMR ($CDCl_3$) δ 12.6, 44.6, 111.5, 113.3, 114.1, 114.3, 121.7, 128.6, 130.4, 141.5, 148.5, 149.8, 155.8, 177.4; MS (*m*/*z*) 334.1250, calcd 334.1252 for $C_{19}H_{18}N_4S$; UV–VIS λ_{max} (dioxane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 528 (3.9×10^4).

2-{(*E*)-2-[4-Diethylaminophenyl]ethen-1-yl}-5-(tricyanovinyl)thiazole, 5

To a solution of **4** (0.8 g, 3.10 mmol) in THF (9.6 ml) at −78 °C under nitrogen was added n-BuLi (1.5 ml, 3.7 mmol, 2.5 M in hexane). The solution was stirred slowly, warmed to −10 °C, and then cooled to −78 °C. To the resulting solution was added a solution of tetracyanoethylene (0.6 g, 4.6 mmol) in THF (3.0 ml). The reaction solution was stirred for 5 min, poured into water (10 ml), neutralized with 5% HCl, and extracted with CH_2Cl_2 (3×20 ml). The combined extracts were dried over $MgSO_4$ and the solvent was removed under vacuum. The crude product was recrystallized from ethyl acetate to give **5** (0.7 g, 61%). ^{1}H NMR(CD_2Cl_2) δ 1.14 (t, 6 H, $J = 7.0$ Hz), 3.37 (q, 4 H, $J = 7.0$ Hz), 6.62 (d, 2 H, $J = 9.0$ Hz), 7.03 (d, 1 H, $J = 15.3$ Hz), 7.43 (d, 2 H, $J = 9.0$ Hz), 7.73 (d, 1 H, $J = 15.3$ Hz), 8.45 (s, 1 H); ^{13}C NMR (CD_2Cl_2) δ 12.3, 44.7, 80.9, 111.7, 112.37, 112.4, 112.5, 113.3, 121.6, 129.7, 131.3, 143.8, 150.6, 157.5, 178.9; MS (*m*/*z*) 359.1199, calcd 359.1204 for $C_{20}H_{17}N_5S$; UV–VIS λ_{max} (dioxane)/nm (ε/dm^3 mol^{-1} cm^{-1}) 628 (6.3×10^4).

NLO Measurements

Molecular hyperpolarizabilities were measured *via* the EFISH method at 1907 nm using a series of solutions (0.1–1.0 mM) in $CHCl_3$. Other experimental details of the hyperpolarizability measurements have been described previously.[9] A reference channel was not used due to power limitations at 1907 nm. Ground state geometries and dipole moments were calculated using the AM1 semi-empirical method as implemented in the MOPAC 6.0 software package.[10]



Scheme 1 *Reagents*: i, t-BuOK; ii, n-BuLi, DMF; iii, $CH_2(CN)_2$; iv, n-BuLi, TCNE.

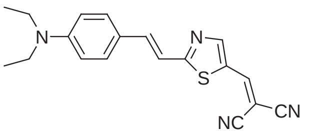
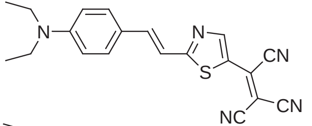
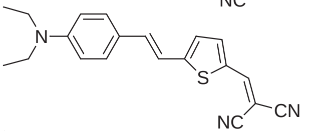
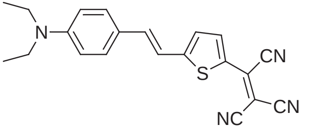
Results and discussion

The key intermediate **1**, thiazol-2-ylmethyltriphenylphosphonium chloride, was prepared by following the method previously reported in the literature.[8] Commercially available 2-bromothiazole was treated with n-BuLi at −78 °C, and the halogen–lithium exchange product was quenched with *N*-formylmorpholine to give 2-formylthiazole.[11] Reduction of the formyl group with $NaBH_4$ yielded 2-hydroxymethylthiazole, which was then transformed into 2-chloromethylthiazole upon chlorination. The reaction of 2-chloromethylthiazole with triphenylphosphine produced the corresponding phosphonium chloride **1**. The synthesis of these thiazole-containing NLO chromophores was carried out according to Scheme 1. Thus, the Wittig reaction of 4-(diethylamino)benzaldehyde with the phosphonium salt **1** in t-BuOK–benzene led to compound **2**. Compound **2** was lithiated with n-BuLi and subsequently quenched with *N*,*N*-dimethylformamide to give the formyl derivative **3**. A further Knoevenagel reaction of **3** with malononitrile produced the dicyanovinyl chromophore **4**. In contrast to the thiophene analogue of **2**, in which the thiophene ring is electron-rich and reacts with tetracyanoethylene (TCNE) readily, the thiazole ring in compound **2** is electron-deficient and can not react with TCNE directly. Therefore, compound **2** was lithiated with n-BuLi and subsequently quenched with TCNE to give tricyanovinyl-substituted chromophore **5**. For the purpose of comparison, the corresponding chromophores containing thiophene, **6** and **7**, were also prepared using literature procedures.[3b,c] All of the chromophores studied here were characterized by electronic absorption, ^{1}H NMR, and ^{13}C NMR, as well as high-resolution mass spectroscopy.

The electronic absorption spectra of the chromophores are characterized by an intense, broad low-energy band that is dependent on the substituents and the nature of the heteroaromatic rings (Table 1). These chromophores appear to display a positive solvatochromism. This solvatochromic behavior is attributed to an intramolecular charge-transfer (CT) transition with an increase of the dipole moment upon excitation and is interpreted in terms of predominance of neutral form in the ground-state structure. The contribution of the zwitterionic form in the ground-state is increased upon increasing the polarity of the solvent. Fig. 1 illustrates the marked solvatochromism of compound **5**. The CT band is substantially red shifted in compound **5** as a consequence of the stronger electron-acceptor character of the tricyanovinyl substituent, in comparison with the dicyanovinyl group in compound **4**.[3c,12] Compound **4** shows a slight red shift when compared to the corresponding thiophene chromophore **6**. However, compound **5** shows a slight blue shift compared with compound **7**.

The thermal stability of these chromophores was studied using differential scanning calorimetry (DSC, 10 °C min^{-1}). The intercept of the leading edge of the thermal decomposition exotherm by the baseline of each DSC scan was assigned as the decomposition temperature (T_d). It should be noted that T_d values only provide a helpful upper limit of thermal stability.[13] All of the NLO chromophores studied in this work have T_d above 240 °C (Table 1).[14] The dicyanovinyl-substituted compounds, **4** and **6**, have a higher thermal stability than the tricyanovinyl compounds, **5** and **7**. With the same acceptor group, the thiazole-containing and the thiophene-containing chromophores have comparable thermal stabilities.

Table 1 Electronic absorption, decomposition temperature, redox potentials, dipole moment, and EFISH data for compounds **4**–**7**

Chromophore	λ_{max}/nm^a	T_d/°C	E_{ox}/V^b	E_{red}/V^b	μ_{calc}/D^c	$\mu\beta$/10^{-48} cm^{6d,e}	β_μ/10^{-30} cm^5 esu$^{-1d,e}$
4 	528	262	0.73^f	−1.07^g	10.4	1540	148
5 	628	242	0.81^f	−0.53	11.3	7300	646
6 	513	266	0.62	−1.18^g	10.7	1600	150
7 	640	245^h	0.69	−0.61	10.8	7170	664

^{a}Measured in dioxane. ^{b}In volts *vs.* Ag/Ag$^+$ reference electrode; scan rate 0.2 V s^{-1}. ^{c}Computed from AM1 geometry, 1 D = 10^{-18} esu cm. ^{d}Determined by EFISH at 1907 nm. ^{e}In CHCl$_3$. ^{f}Anodic peak potential for irreversible oxidation. ^{g}Cathodic peak potential for irreversible reduction. ^{h}T_d = 240 °C, reported in reference 14.

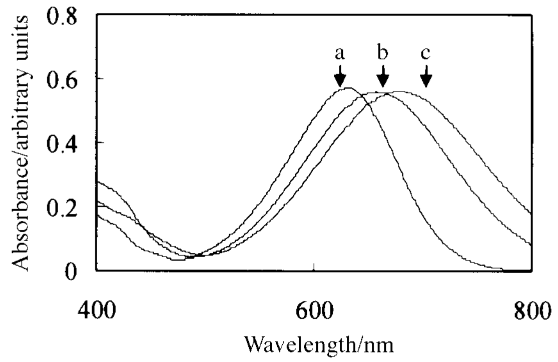


Fig. 1 UV–VIS absorption spectra for compound **5** in various solvents, demonstrating positive solvatochromism. Solvents: a, dioxane; b, CH$_3$CN; c, DMSO.

The redox properties of the D–π–A chromophores were studied by cyclic voltammetry (Table 1). The tricyanovinyl-substituted compounds show both higher oxidation potentials and less negative reduction potential than the dicyanovinyl compounds, in agreement with the more pronounced acceptor strength which facilitates reduction and renders oxidation more difficult. Fig. 2 shows the cyclic voltammograms of compounds **5** and **7**. The cyclic voltammetric data reveal that the change from the thiazole ring to the thiophene ring leads to a decrease of the oxidation potentials as well as a shift of the reduction potentials toward more negative values. This result is consistent with the electron-deficient (thiazole) and electron-excessive (thiophene) nature of the heterocyclic ring systems.[7] The shift of the oxidation potential to less positive values upon replacement of the thiazole ring by a thiophene ring also indicates that the heterocyclic rings have a considerable interaction with the diethylaminophenyl moiety *via* the conjugated double bond.

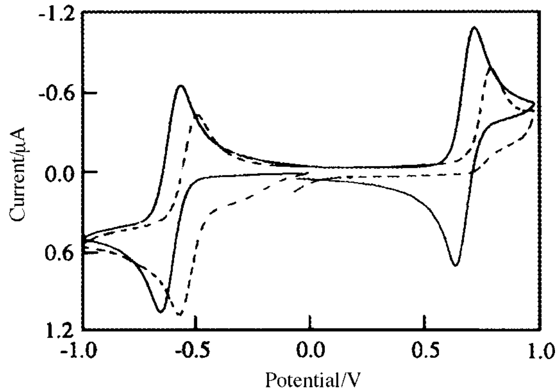


Fig. 2 Cyclic voltammograms of compounds **5** (---) and **7** (—), 1.0 × 10^{-3} M in CH$_2$Cl$_2$. Scan rate 200 mV s^{-1}.

The nonlinear optical properties of compounds **4**–**7** were determined experimentally by electric-field-induced second-harmonic generation (EFISH) (Table 1).[15] The values of the dot product $\mu\cdot\beta$ were measured experimentally at 1907 nm in chloroform. AM1 optimized geometries[16] were used to compute dipole moments, which enabled the determination of β_μ, the hyperpolarizability in the direction of the dipole moment. Hyperpolarizabilities are not corrected for resonance enhancement because the second harmonic signal (954 nm) lies far from the electronic absorptions.

EFISH experiments show that compounds with a tricyanovinyl acceptor (**5** and **7**) have significantly larger hyperpolarizabilities (β_μ) than those with a dicyanovinyl acceptor (**4** and **6**). These data further corroborate the CV and UV–VIS absorption results, which are indicative of the stronger acceptor strength of the tricyanovinyl moiety relative to dicyanovinyl. It is also apparent from the hyperpolarizability data that the nature of the heterocycle (thiazole or thiophene) does not significantly affect the magnitude of β_μ, which is likely due to the overwhelming effect of the acceptors used in the study. Further structure *vs.* nonlinear optical property relationships will be discussed in a future publication.

Summary

We synthesized dicyanovinyl- and tricyanovinyl-substituted thiazole chromophores as well as their thiophene analogs. These chromophores exhibit good thermal stability with T_d above 240 °C. The redox properties studied by cyclic voltammetry reveal the electron-deficient (thiazole) and electron-excessive (thiophene) nature of the heterocyclic rings. The result of EFISH measurements indicates that these thiazole-containing chromophores possess substantial second-order optical nonlinearities which, however, are not superior to the corresponding thiophene-containing chromophores.

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15. The experimental hyperpolarizabilities for compounds **6** and **7** correlate well to previously published values measured in 1,4-dioxane ($\mu\cdot\beta_{1907\ \mathrm{nm,\ dioxane}} = 1300\times10^{-48}$ esu and $\mu\cdot\beta_{1907\ \mathrm{nm,\ dioxane}} = 6200\times10^{-48}$ esu, respectively).[3a,b]
16. Structures **4**, **6**, and **7** (Table 1) are computed to be the lowest energy conformer for each species. Although structure **5** lies 0.4 kcal mol^{-1} above the lowest energy conformer, this conformer was used for the purpose of remaining consistent with the other compounds. It should be noted that the computed dipole moment of **5** differs from that of the lowest energy conformer by only 0.2 D.

Paper 9/00820I