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Nonlinear optical chromophores containing dithienothiophene as a new type of electron relay

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Nonlinear optical (NLO) donor–acceptor (D–A) chromophores containing a fused terthiophene, namely dithienothiophene (DTT) as electron relay, and various strength acceptors were synthesized to evaluate the relay's role in the solvatochromism as well as in the molecular nonlinearity, $\mu\beta(0)$. Their solvatochromic behavior, which is dependent on acceptor strength, is correlated to their $\mu\beta(0)$. The static quadratic hyperpolarizability, $\beta(0)$, of DTT-containing chromophores was determined by EFISH measurements. From the comparison of $\mu\beta(0)$ values of D–A chromophores based on oligothiophenes, it was assessed that DTT as relay is significantly more efficient compared to bithiophene (the same number of conjugated double bonds) and terthiophene. An additional merit of DTT is that chromophores containing DTT have a noticeably high thermal stability.

It has been well recognized that nonlinear optical (NLO) activity of chromophores is determined not only by donor–acceptor (D–A) strength but more subtly by conjugated electron relays. This can be understood from the difference in relay activities between typical relays such as a polyene and oligophenylene or oligothiophene which bear the same D–A pair and the same conjugation length; a more pronounced red-shift (in a given solvent) is commonly observed with polyenes in the low energy absorption maximum, $\lambda_{\max}$, compared with the oligophenylenes and oligothiophenes, indicative of efficient electron transmission. Such a tendency is even more intensified with an increase of solvent polarity. Positive solvatochromism has been regarded as an indication of molecular nonlinearity ($\mu\beta$) of NLO chromophores.[1–3] It was reported recently that some polyenes attached to a strong D–A pair display an inverted solvatochromism;[4,5] their $\lambda_{\max}$ exhibits a red-shift with an increase of solvent polarity up to a certain polarity limit, then reverses this trend with a further increase of solvent polarity beyond that limit. Such a peculiar solvent effect on optical nonlinearity is manifested by the observations that experimental $\mu\beta(0)$ values show a marked decrease with increasing solvent polarity, resulting in a negative value in strongly polar solvents.[5,6] Clearly, such behavior is not a simple attribute of the D–A strength but is also associated with the electronic properties of relays. It is rather surprising that no electron relays except polyenes have been known so far for displaying such behavior.

Oligothiophenes are known to be very efficient relays almost comparable to polyenes. This is attributable to the lower resonance energy compared to benzene. In fact, their conjugation effect could be more pronounced than that of polyenes due to the rigid structure and facile coplanar conformation. Such a comparison can be made, for instance, by inserting each of these conjugation units between two pyridinium units of the viologen molecule.[7] D–A molecules based on thiophenes as relay have been actively sought recently, exploiting interesting results indicating that the incorporation of a thienylene or thienylvinylene unit by replacing the phenylene moiety in D–A chromophores enhances $\mu\beta(0)$ significantly.[2,8–11] Examination of the results from various studies investigating relay efficiencies of oligothiophenes[2] and oligophenyls[12,13] indicates that oligothiophenes give a larger contribution to the $\mu\beta(0)$ compared to oligophenylenes which attain a rapid saturation beyond the terphenyl unit, while oligothiophenes have a strong tendency to increase $\mu\beta(0)$ with an increasing number of thiophene units. In this respect, an interesting question is whether fused thiophenes are more efficient compared to the oligothiophenes of corresponding number unit or π-electrons. This question is partly answered by a couple of recent reports[14,15] regarding thienothiophene, whose relay role is somewhat greater than that of bithiophene. However, it is not certain whether a similar relationship exists between terthiophene and its fused counterpart, but it could be the case from the fact that the rigidification of thiophenes (by cyclization) favors π-conjugation and thus more effective charge-transfer in push–-pull chromophores, as indicated by a bathochromic shift[16–18] of absorption bands and a strong solvatochromism compared to the flexible counterpart. A further implication for the effectiveness of fused thiophenes as relays is demonstrated by the fact that the longest wavelengths of fused thiophenes exhibit an excellent linear correlation with the number of the thiophene rings up to five.[19] To the best of our knowledge, D–A chromophores containing a dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT) relay have not been reported with respect to the molecular nonlinearity.

Aside from the electronic features, another merit of thiophenes is their inherent thermal stability from which thiophene-containing chromophores will benefit.[10,14] DTT is an outstanding example of this.

We herein describe the synthesis and characterization of DTT-based chromophores bearing various acceptors and a fixed donor (see Scheme 1), and study the correlation between their solvatochromism and their static quadratic hyperpolarizability. Discussions are made by comparing $\mu\beta$ values of chromophores based on DTT with those based on various

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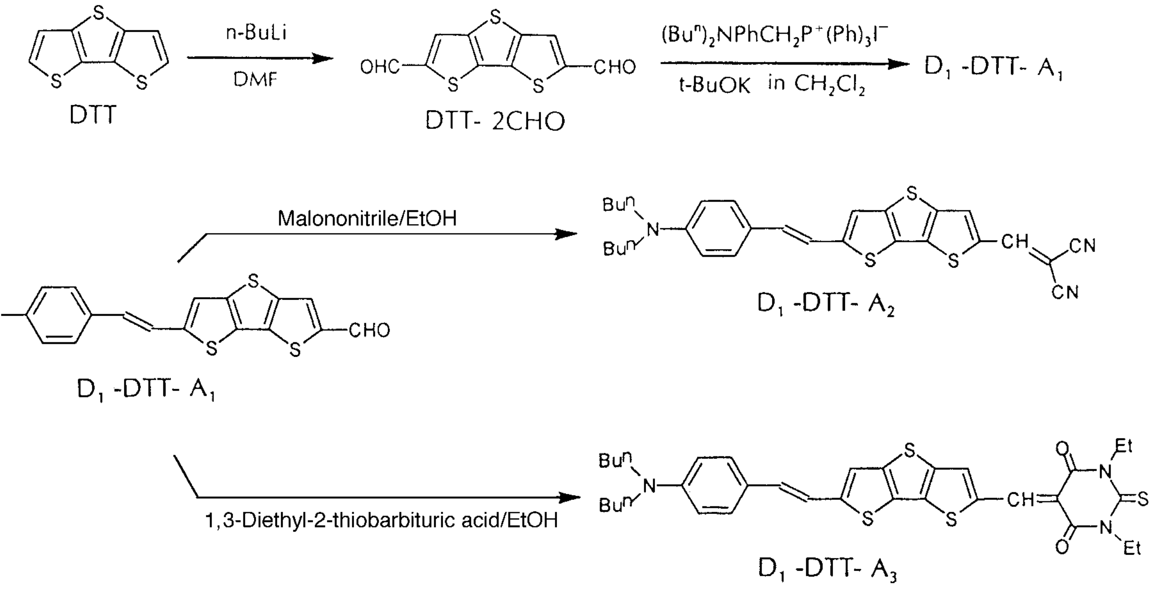


Scheme 1

relays such as polyenes and other oligothiophenes attaching the same or a similar D–A pair.

Results and discussion

Absorption spectra of DTT-containing D–A chromophores in dichloromethane (the best solvent) are shown in Fig. 1. As expected, their longest absorption maxima, λ_{max}, are shifted to the lower energy side with increasing acceptor strength, reflecting the difference in the electronic transition associated with intramolecular charge-transfer between the D–A groups. Among the three acceptors, A_3 is the strongest such that the electronic ground-state structure of D_1-DTT-A_3 is, relatively speaking, the most polarized and that of D_1-DTT-A_1 the least polarized. In other words, the contribution of the charge-separated form to the ground-state structure is largest with D_1-DTT-A_3 and smallest with D_1-DTT-A_1.

Comparison of the spectra of DTT-containing chromophores in various solvents of different polarity suggests a solvatochromic behavior pattern which is somewhat different from the typical positive solvatochromism. As shown in Fig. 2, the transition energy plot as a function of solvent polarity (E_T^N) based on the empirical relationship[20] decreases linearly with increasing solvent polarity. The declining transition energy with increasing solvent polarity is indicative of an increase of the dipole moment upon excitation ($\mu_g < \mu_e$), suggesting the predominance of the neutral form in the ground-state structure.[21] As compared to D_1-DTT-A_1, D_1-DTT-A_2 and D_1-DTT-A_3 show a somewhat different tendency; both the slope and the correlation coefficient of the latter are much smaller relative to those of the former. Although it is not unambiguously clear, an inversion of solvatochromism (positive solvatochromism followed by negative solvatochromism) could be involved in these cases. Such a phenomenon would be possible if, whereas in apolar solvents the neutral form predominates (and therefore $\mu_g < \mu_e$), increasing the solvent polarity could induce an enhanced contribution of charge-separated resonance structure in the ground state and thus, the zwitterionic form becomes predominant in highly polar solvents (and therefore $\mu_g > \mu_e$). This has been observed with short polyene-based chromophores bearing a strong D–A pair directly attached to the ends of the polyenic relay.[4–6] A similar situation is likely to occur with push–pull DTT chromophores bearing strong D–A pairs.

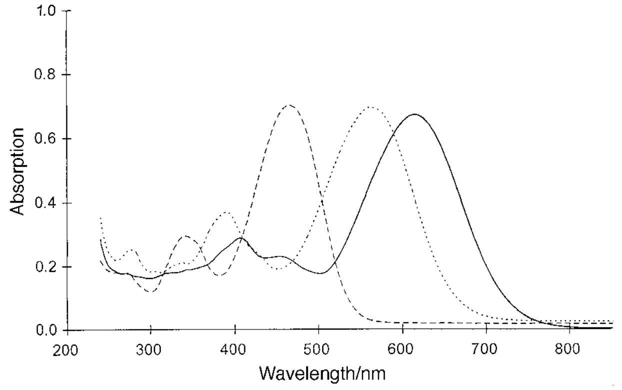


Fig. 1 UV–Vis spectra of D_1-DTT-A_1, 1.56×10^{-5} M (---); D_1-DTT-A_2, 1.46×10^{-5} M (.....); and D_1-DTT-A_3, 2.14×10^{-5} M (——) in CH_2Cl_2.

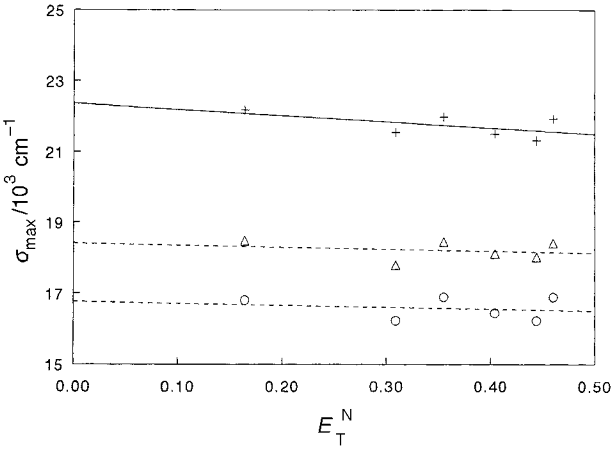


Fig. 2 Solvatochromism of D_1-DTT-A_1 (+), D_1-DTT-A_2 (open triangles), and D_1-DTT-A_3 (open circles) as a function of solvent polarity (the order of increasing polarity: dioxane, CH_2Cl_2, acetone, DMF, DMSO and MeCN).

A positive solvatochromic behavior is commonly seen with push–pull chromophores based on different relays. A chromophore based on a short rigidified polyene bearing a strong D–A pair such as D_1–A_2 shows a strongly positive solvatochromism.[3] The same holds for push–pull polyenes[5] with identical donor and acceptor groups as in D_1-DTT-A_3. Push–pull chromophores containing a bithiophene[2] or a cyclized dithienylethene relay[18] also show marked positive solvatochromism. When comparing the relay role of D_1-DTT-A_3 and its polyenic counterpart with a comparable conjugation length and the same D–A pair, a more pronounced solvatochromism is noted in the case of the latter. This seems to suggest that D_1-DTT-A_3 shows a smaller change of dipole moment between the ground state and excited state ($\Delta\mu = \mu_e - \mu_g$) as compared to its polyenic counterpart. Such a phenomenon could be explained by a larger ground-state polarization, meaning that DTT-based push–pull chromophores have a comparatively larger contribution (relative to the polyenic counterpart) of the zwitterionic form in the ground-state structure.

Another feature observed with the present DTT-containing chromophores is their solubility and spectral properties in high polarity solvents, depending on the acceptor strength. With D_1-DTT-A_3 (which is very sparingly soluble) in acetonitrile ($E_T(30) = 45.6$), in particular, there is a sharp decrease in the absorbance at the longest wavelength (Fig. 3), which is smaller than in DMF ($E_T(30) = 43.2$) and seems to be associated with the very poor solubility in this solvent. This situation is further aggravated in methanol ($E_T(30) = 55.4$) in which the chromophore is almost insoluble, although there is no solubility problem at all with D_1-DTT-A_1 in these solvents. The solubility problem of D_1-DTT-A_3 in high polarity solvents is seemingly associated with dipole–dipole interactions between strongly dipolar chromophores. As represented in Fig. 3, D_1-DTT-A_3 shows an extraordinarily strong absorption around 425 nm in DMF, which is likely to be due to aggregation, possibly as a dimeric pair that is favored by the rigid and planar structure of DTT. A similar behavior of dimeric association was reported recently for some highly polar chromophores, tertiary ethylamine–TCNQ adducts, which exhibit a very large negative second-order nonlinearity.[22] While they do not appear to dimerize in low polarity solvents such as dichloromethane, they readily associate into dimers or a higher order (causing a solubility problem) in polar solvents such as DMF and acetonitrile, as a result of their zwitterionic nature. The situation seems to be quite different for the weaker-acceptor chromophore, D_1-DTT-A_1 which is the least polar species such that it is markedly soluble in the highly-polar solvents, and exhibits fluorescence emission while D_1-DTT-A_2 and D_1-DTT-A_3 do not.[23]

Recent studies[4–6,24] indicate that the degree of mixing between neutral and charge-separated resonance structures, which depends on the D–A pair strength can be correlated with the ground-state polarization (dipole moment) and bond length alternation (BLA), and that the magnitude of β of D–A chromophores depends on the BLA. The validity of such a relationship was proved for polyenic chromophores with various D–A pair strengths in solvents of different polarity. Depending on the D–A pair (that determines the ground-state polarization), different regions of the β *versus* BLA curve could be mapped by changing the solvent polarity.[24] This picture can be generalized to all other push–pull systems by using a simple two-state two-level model based upon the two-level approximation (taking into account only the ground and the first excited states) introduced by Oudar,[25] and a two valence bond states (corresponding to the neutral and zwitterionic structures) description of the push–pull system.[26,27] This model allows us to correlate[27,28] both the ground-state dipole and the (hyper)polarizabilities with a parameter MIX (measuring the degree of mixing between the neutral and zwitterionic resonance forms) of the DTT-chromophores in the ground state. As shown in Fig. 4, the magnitude of β declines for major predominance of either the neutral (MIX ≈ -1) or the zwitterionic form (MIX $\approx +1$) and vanishes for equal contributions of both forms (MIX = 0). In contrast it peaks positively (or negatively) for MIX values corresponding to the intermediate situation. It is interesting to note that negative MIX values corresponding to the predominance of the neutral form in the ground state, correspond to positive $\Delta\mu$ values and therefore, to positive solvatochromism,[26] whereas positive MIX values corresponding to the predominance of the zwitterionic form in the ground state, correspond to negative $\Delta\mu$ values and therefore, to negative solvatochromism. Reversal of solvatochromism would thus correspond to MIX values changing from negative to positive with increasing solvent polarity. By this simple description, the influence of solvent polarity on the β can be rationalized since increasing solvent polarity is expected to increase MIX *via* increased stabilization of the zwitterionic form in the ground state.[29]

As seen in Table 1, the $\mu\beta(0)$ values of DTT-chromophores are markedly influenced by solvent polarity as well as by the acceptor strength. This tendency parallels the observed results of push–pull polyenes bearing D–A pairs of different strength.[6,24] For D_1-DTT-A_1, the $\mu\beta(0)$ value determined in a high polar solvent such as DMF is similar (but slightly smaller), given the experimental accuracy, to that measured in a weakly polar solvent, CH_2Cl_2. This seems to suggest that this compound lies close to an optimum negative MIX which leads the β value close to a positive maximum, being to the left of the peak in an apolar solvent and to its right in polar solvents (Region I in Fig. 4).

Increasing the acceptor strength commonly brings about an increase of zwitterionic ground state that leads to less negative (or even positive) MIX values, resulting in a different solvent dependency. This is actually the case for chromophores D_1-DTT-A_2 and D_1-DTT-A_3. Compound D_1-DTT-A_2 shows a significant decrease of the $\mu\beta(0)$ value upon changing the solvent from CH_2Cl_2 to DMF. This suggests that the MIX

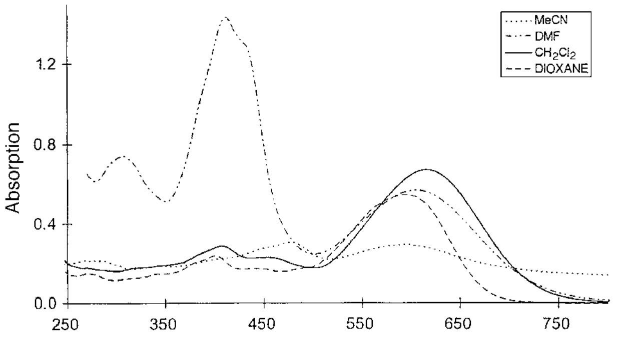


Fig. 3 UV–Vis spectra of D_1-DTT-A_3 (2.14×10^{-5} M) in various solvents.

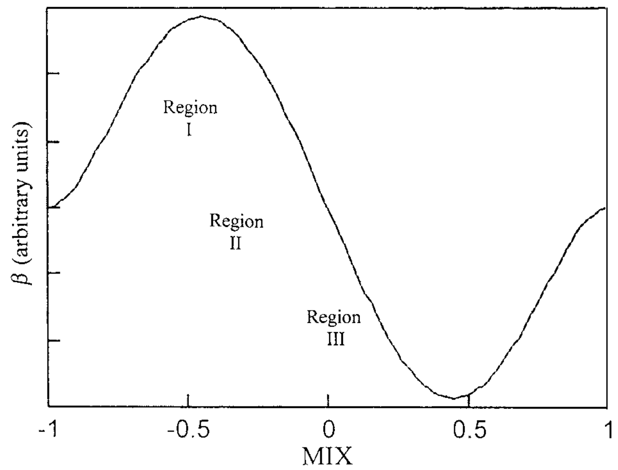


Fig. 4 Hyperpolarizability (β) *versus* degree of mixing (MIX) of ground state structures of push–pull chromophores based on the two-state two-level model.[27,28] Regions I, II, and III represent MIX boundaries of D_1-DTT-A_1, D_1-DTT-A_2 and D_1-DTT-A_3, respectively.

Table 1 UV–Vis, molecular polarizability and thermal stability of DTT-containing NLO chromophores

Compound	λ_{max} (solvent)/nm	$\mu\beta(2\omega)/10^{-48}$ esu[a]	$\mu\beta(0)/10^{-48}$ esu[b]	T_d/°C[c]
D_1-DTT-A_1	464 (CH_2Cl_2)	950	680	348
	465 (DMF)	850	610	
D_1-DTT-A_2	558 ($CHCl_3$)	3900	2300	344
	562 (CH_2Cl_2)	4000	2350	
	552 (DMF)	2800	1700	
D_1-DTT-A_3	616 (CH_2Cl_2)	5000	2600	252
	608 (DMF)	−3500	−1900	

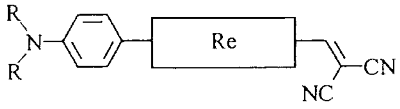
[a] Measured at a fundamental wavelength of 1.907 μm. [b] The zero-frequency values were derived from the experimental $\mu\beta(2\omega)$ data by use of the two-level model dispersion factor.[25] Experimental accuracy on $\mu\beta(0)$ is ±10%. [c] Onset of decomposition temperature was determined from the TGA thermogram taken at a heating rate of 10 °C min^{-1}.

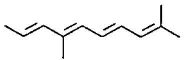
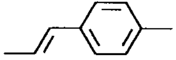
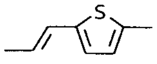
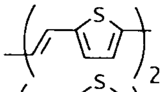
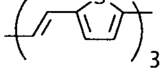
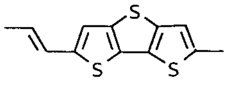
value of this compound lies between the optimum negative (brings the β to the positive peak) and 0 (Region II in Fig. 4), where the positive solvatochromism is significantly weak (MIX and $\Delta\mu$ getting closer to 0). Compound D_1-DTT-A_3, which has the strongest D–A pair and is thus expected to have the largest MIX value among the DTT-based chromophores in this study, shows an even more striking behavior: the $\mu\beta(0)$ value changes from a positive value in CH_2Cl_2 to a negative value in DMF. This indicates that for D_1-DTT-A_3, MIX turns from negative to positive upon increasing the solvent polarity (Region III in Fig. 4). In other words, the zwitterionic contribution to the ground state becomes predominant in highly polar solvents. Such behavior is consistent with the reversal of solvatochromism discussed above, although an aggregation effect cannot be excluded.

The large $\mu\beta$ values observed (Table 1) indicate that the DTT linker functions as an efficient relay. The magnitude of the $\mu\beta(0)$ products clearly corresponds to the acceptor strength; D_1-DTT-A_3 exhibits the largest absolute values, whereas D_1-DTT-A_1 presents the smallest. It is worthwhile to evaluate relay efficiencies by comparing the $\mu\beta$ values among chromophores bearing the same or a similar D–A pair such as *N*,*N*-dialkylanilino and dicyanoethenyl moieties based on the number of π-electrons involved in the relays. Although it is not simple to make a direct comparison due to the difference in measurement conditions and limited availability of material information in the literature, we can make a significant assessment of the conjugated relays among homologous chromophores. In Table 2, the published data for those chromophores are compared with the present results. Undoubtedly, the efficiency of DTTvinylene is smaller than that of octatetraenylene as a polyenic linker. As already discussed by Jen and his coworkers,[11] chromophores containing thienylenevinylene linker have a significantly larger $\mu\beta(0)$ compared to ones containing phenylenevinylene linker, and the $\mu\beta(0)$ increases noticeably with increasing number of the thienylenevinylene unit in the homologues.[11] Although a rigorous comparison would require measurements performed in a range of similar solvents, examination of the $\mu\beta(0)$ values shown in Table 2 indicates that DTTvinylene plays a far more efficient relay role compared to dimeric thienylenevinylene and is comparable to trimeric thienylenevinylene. From this observation, it may be inferred that DTT as relay would be significantly more efficient than bithiophene (the same number of conjugated double bonds) and terthiophene because dimeric and trimeric thienylvinylenes (Table 2) are known to have a lower bandgap relative to the corresponding oligothiophenes, namely bithiophene and terthiophene, respectively, due to the presence of the vinylene moiety.[11,30] Since fused thiophenes have a lesser number of conjugated double bonds compared to the corresponding nonfused counterpart as in the case of fused thienylthiophene *vs.* bithiophene and yet, the former is more efficient as relay relative to the latter,[14] the same analogy may exist between DTT and terthiophene. Such a superior relay efficiency of DTT can be attributable to the rigid planar structure.

As shown in Table 1, DTT-containing chromophores present

Table 2 Comparison of molecular polarizability among chromophores containing the following D–A pairs linked by various relays



R	Re	n[a]	λ_{max} (solvent)/nm	$\mu\beta(2\omega)/10^{-48}$esu[b]	$\mu\beta(0)/10^{-48}$esu[c]	Ref.
Me		4	560 ($CHCl_3$)	5500	3300	33
Et		4	468 (dioxane)	1100	785	11
Et		3	513 (dioxane)	1300	860	11
Et		6	547 (dioxane)	2300	1420	11
Et		9	556 (dioxane)	3800	2300	11
Bu^n		5	562 (CH_2Cl_2)	4000	2350	This work

[a] The number of conjugated double bonds. [b] Measured at a fundamental wavelength of 1.907 μm. [c] The zero-frequency values were derived from the experimental $\mu\beta(2\omega)$ data by use of the two-level model dispersion factor.[25]

a high thermal stability which is clearly due to the presence of the DTT moiety. Their decomposition temperatures were determined by thermogravimetric analysis (TGA). Both D_1-DTT-A_1 and D_1-DTT-A_2 exhibit a remarkably high decomposition temperature (T_d) compared with D_1-DTT-A_3. The reason for this difference is unclear but attributable to the thiobarbituric moiety. Such thermally-stable NLO chromophores can be of use for developing solid film-forming materials by making poled polymeric composites and also by incorporating chromophores into polymer chains. Such a materials study is underway. In this regard, D_1-DTT-A_2 is a particularly interesting chromophore.

Experimental

General procedure for materials synthesis

As shown in the reaction scheme, DTT-based push–pull chromophores were synthesized firstly by Wittig reaction of dithieno[3,2-*b*:2′,3′-*d*]thiophene-2,6-dicarbaldehyde (DTT-2CHO) with the donor component, (4-*N*,*N*-dibutylaminobenzyl)triphenylphosphonium iodide, which was reacted with only one aldehyde to connect D_1, the other aldehyde remaining free, yielding D_1-DTT-A_1. Further reactions leading to D_1-DTT-A_2 and D_1-DTT-A_3 involve Knoevenagel condensation of D_1-DTT-A_1 with an acceptor component, malononitrile and 1,3-diethyl-2-thiobarbituric acid, respectively. DTT-2CHO itself was prepared by formylation of DTT through dilithiation with *n*-BuLi and subsequent reaction with DMF. DTT was obtained according to the procedure described in the literature.[31] The final products were purified by chromatographic fractionations and/or recrystallizations, and the purity was confirmed by ^{1}H NMR spectra and elemental analysis.

Dithieno[3,2-*b*:2′,3′-*d*]thiophene (DTT). Synthesized according to the known procedure[31] by the oxidative reaction of 3,3′-dithienyl sulfide with anhydrous $CuCl_2$ after treatment of the sulfide with 10 M *n*-BuLi in *n*-hexane. 3,3′-Dithienyl sulfide was made by the reaction of 3-thienyllithium which was prepared from 3-bromothiophene and *n*-BuLi in *n*-hexane with bis(phenylsulfonyl) sulfide. The latter compound was prepared by modifying the literature method using CH_2Cl_2 instead of ether. The final product was pale-yellow crystals, melting at 65 °C. ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 2H, CH at 3,5-DTT), 7.36 (d, 2H, CH at 2,6-DTT).

Dithieno[3,2-*b*:2′,3′-*d*]thiophene-2,6-dicarbaldehyde (DTT-2CHO). To a solution of DTT (0.98 g; 5.0×10^{-3} mole) in 40 ml dry THF at room temp. with stirring (the reaction vessel has to be completely purged with dry argon before the reaction and the atmosphere maintained until finishing the *n*-BuLi addition), was added 6.25 ml of 1.6 M *n*-hexane solution of *n*-BuLi (0.064 g; 1.0×10^{-2} mole) dropwise. The orange-colored solution became completely turbid upon finishing the addition of *n*-BuLi. Stirring was continued another hour at room temp. While keeping the resulting yellow-colored slurry stirring at −78 °C, 2 ml DMF were added in several portions. Stirring was continued for another 1.5 h at the same temperature which was then allowed to rise to room temp. in 2 h. The yellow suspension was neutralized with dil. HCl solution, filtered off, washed thoroughly with water and then air-dried overnight. After drying *in vacuo* at 35 °C for 8 h it weighed 1.20 g (95% yield); the product was a yellow–brown solid (decomp. starts at 270 °C). This product was quite pure (by ^{1}H NMR) and used for the subsequent reactions without recrystallization. Recrystallization was carried out by dissolving the product in a minimum amount of DMF and a large excess of methanol. ^{1}H NMR (DMSO-d_6) δ 8.52 (s, 2H, CH at 3,5-DTT), 10.04 (s, 2H, CHO).

2-(4-*N*,*N*-Dibutylaminostyryl)dithieno[3,2-*b*:2′,3′-*d*]thiophene-6-carbaldehyde (D_1-DTT-A_1). To the suspension of 4-(*N*,*N*-dibutylbenzyl)triphenylphosphonium iodide (0.729 g; 1.2×10^{-3} mole) and potassium *tert*-butoxide (0.27 g; 2.4×10^{-3} mole) in 60 ml methylene chloride with vigorous stirring at room temp. were added 18-crown-6 ether (10 mg) and DTT-2CHO (0.30 g; 1.2×10^{-3} mole). The red-colored suspension became an orange-colored solution. The reaction was complete within 2 h but contaminated significantly by D_1-DTT-D_1 (a major by-product). The reaction mixture was filtered on Celite, and the residue was brought to dryness by removing the solvent. The solid mixture was chromotographed through a silica column using methylene chloride as eluent. Fractions containing the pure product were collected, the solvent removed and the residue was treated with petroleum ether to solidify the product. A red solid product, D_1-DTT-A_1 was separated by filtration (the by-product, D_1-DTT-D_1, is difficult to solidify) and dried overnight *in vacuo*, yielding 0.52 g (48.1% yield). This product had a minor contamination by the *cis*-isomer, which was then eliminated by filtration after treatment with *n*-pentane (which dissolves the *cis*-isomer well). ^{1}H NMR ($CDCl_3$) δ 0.96 (t, $J = 7.1$ Hz; 6H, CH_3), 1.39 (m, 4H, CH_2), 1.57 (m, 4H, CH_2), 3.30 (t, $J = 7.5$ Hz; 4H, CH_2N), 6.62 (d, $J = 8.9$ Hz; 2H, ArH), 6.97 (d, $J = 4.8$ Hz; 2H, –CH=CH–), 7.15 (s, 1H, CH at 5-DTT), 7.35 (d, $J = 8.8$ Hz; 2H, ArH), 7.92 (s, 1H, CH at 3-DTT), 9.92 (s, 1H, CHO). Anal. Calcd for $C_{25}H_{27}NOS_3$: C, 66.19; H, 6.00; N, 3.09. Found: C, 65.96; H, 6.17; N, 3.08%.

2-(4-*N*,*N*-Dibutylaminostyryl)-6-(2-dicyanoethen-1-yl)dithieno[3,2-*b*:2′,3′*d*]thiophene (D_1-DTT-A_2). To the suspension of D_1-DTT-A_1 (0.2 g; 4.40×10^{-4} mole) and malononitrile (0.087 g; 1.32×10^{-3} mole) in 80 ml absolute ethanol, was added a drop of piperidine and then, the mixture was refluxed for 5 h with stirring, resulting in a dark red solution. The purple–black residue remaining upon evaporation of ethanol was chromatographed through a silica column using methylene chloride as eluent. Fractions containing the pure product were collected and the solvent evaporated. The resulting purple–black crystals gave 0.151 g (68% yield) after drying overnight *in vacuo*. ^{1}H NMR ($CDCl_3$) δ 0.97 (t, $J = 7.0$ Hz; 6H, CH_3), 1.35 (m, 4H, CH_2), 1.55 (m, 4H, CH_2), 3.31 (t, $J = 7.5$ Hz; 4H, CH_2N), 6.62 (d, $J = 9.2$ Hz; 2H, ArH), 6.98 (s, 2H, –CH=CH–), 7.15 (s, 1H, CH at 5-DTT), 7.36 (d, 2H, ArH), 7.78 (s, 1H, CH at 3-DTT), 7.82 (s, 1H, –CH=). Anal. Calcd for $C_{28}H_{27}N_3S_3$: C, 67.03; H, 5.42; N, 8.38. Found: C, 66.90; H, 5.49; N, 8.14%.

2-(4-*N*,*N*-Dibutylaminostyryl)-6-(1,3-diethyl-2-thioxo-4,6-dioxohexahydropyrimidin-5-ylidenemethyl)dithieno[3,2-*b*:2′,3′-*d*]thiophene (D_1-DTT-A_3). To the suspension of D_1-DTT-A_1 (0.60 g; 3.5×10^{-4} mole) in 80 ml absolute ethanol with stirring at room temp. were added a drop of piperidine and 1,3-diethyl-2-thiobarbituric acid (0.210 g; 1.05×10^{-3} mole), during which the color changed immediately from red to green–black and then to blue. The mixture was refluxed for 2 h and then ethanol was evaporated, resulting in a dark blue solid. The product was separated by column chromatography with silica gel, using methylene chloride as eluent. Impurities contaminating the solid product were eliminated by treatment with hot acetonitrile which dissolves unreacted thiobarbituric acid as well as other unknown impurities. The pure product was obtained after drying overnight *in vacuo*, 0.201 g (89.7% yield). ^{1}H NMR ($CDCl_3$) δ 0.95–1.59 (m, CH_3CH_2–), 3.31 (t, $J = 7.5$ Hz; 4H, CH_2N), 4.58 (t, $J = 7.1$ Hz; 4H, $CH_2N<$), 6.64 (d, $J = 8.7$ Hz; 2H, ArH), 7.03 (s, 2H, –CH=CH–), 7.20 (s, 1H, CH at 5-DTT), 7.38 (d, $J = 8.7$ Hz; 2H, ArH), 8.08 (s, 1H, CH at 3-DTT), 8.71 (s, 1H, –CH=). Anal. Calcd for $C_{33}H_{37}N_3O_2S_4$: C, 62.36; H, 5.86; N, 6.61. Found: C, 62.02; H, 5.61; N, 6.14%.

Optical measurement

UV–Vis spectra were recorded on a Beckman DU-640 spectrophotometer in a series of common organic solvents. Since the DTT-containing chromophores exhibited a very high molar absorptivity, their concentration was diluted as low as 10^{-5} M. Quadratic hyperpolarizabilities of the DTT-containing chromophores were determined using an electric field-induced second harmonic generation (EFISH) technique described elsewhere.[25,32] The EFISH $\mu\beta(2\omega)$ products were obtained in dichloromethane, chloroform or DMF solution at a fundamental wavelength of 1.907 μm.

Thermal analysis

Thermogravimetric analysis (TGA) was carried out using a Perkin-Elmer 7 Series Thermal Analysis System at a heating rate, 10 °C min^{-1}.

Conclusion

We have synthesized a new type of NLO chromophore based on fused dithienothiophene (DTT) as electron relay, studied their solvatochromism in various polarity solvents and determined their quadratic hyperpolarizability by EFISH measurements in dichloromethane, chloroform and DMF. It was found that $\mu\beta$ values of the chromophores are remarkably high in dichloromethane, increasing with the acceptor strength. The solvent effect on $\mu\beta$ is intensified by the acceptor strength: a marked decrease of $\mu\beta(0)$ observed for D_1-DTT-A_2 in DMF shifts to a large negative value for D_1-DTT-A_3. This trend suggests an increasing contribution of the zwitterionic structure (to the ground state) with increasing D–A strength and increasing solvent polarity, resulting in D_1-DTT-A_3 being predominantly zwitterionic in the highly polar DMF, although an aggregation effect cannot be excluded. From the comparisons of $\mu\beta$ values among chromophores bearing the same or a similar D–A pair, it was assessed that DTT is a superior electron relay among related oligothiophenes. Also, these DTT-containing chromophores are thermally stable so that they can be incorporated into poled polymeric systems to develop various efficient NLO materials.

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