Push–pull chromophores based on 2,2′-bi(3,4-ethylenedioxythiophene) (BEDOT) π-conjugating spacer

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Abstract—Replacement of 2,2′-bithiophene by BEDOT in push–pull NLO-phores produces a red shift of the absorption maximum accompanied with a large increase of the quadratic nonlinear optical susceptibility. © 2001 Elsevier Science Ltd. All rights reserved.

Push–pull chromophores for 2nd order nonlinear optics involve electron-donor and -acceptor groups interacting through a π-conjugating spacer.[1] Whereas the optimization of the donor[2] and acceptor[3] groups has led to considerable progress in the development of stable and efficient systems, the relationships between the structure of the spacer and 2nd order hyperpolarizability seem to have attracted less attention. Polyenic spacers allow high nonlinearities to be reached as they provide the most effective way to achieve charge redistribution between the donor and the acceptor.[4] As shown in recent work, thiophene-based spacers can lead to stable NLO-phores with large second order nonlinearities.[2,3,5–8] These high performances can be related to the moderate aromatic resonance energy of thiophene which allows a better π-electron delocalization than e.g. benzene-containing spacers.

Thus, NLO-phores built around thiophene-based conjugating spacers such as thiophene and its oligomers,[2,3,6] fused ring systems,[7] and oligothienylenevinylenes,[5,8] have been synthesized. Recently, we have shown that the covalent bridging of a dithienylethylene (DTE) spacer leads to a considerable
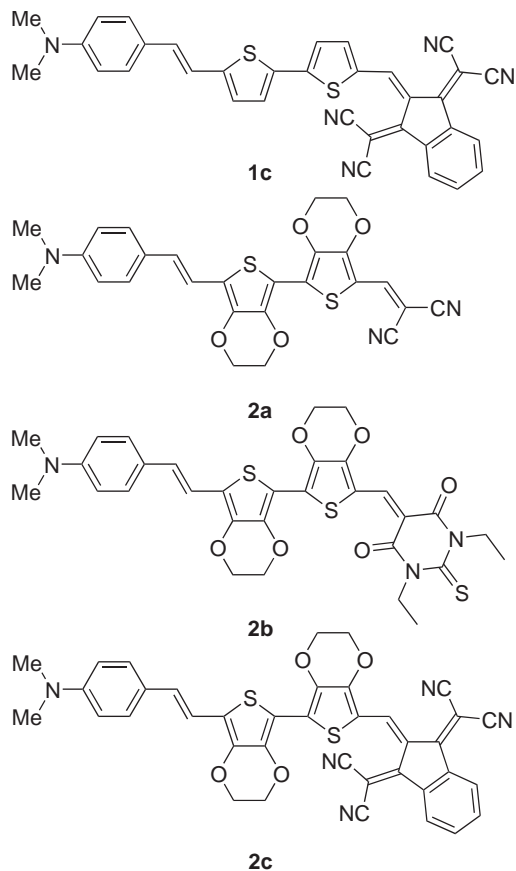
1c

2a

2b

2c

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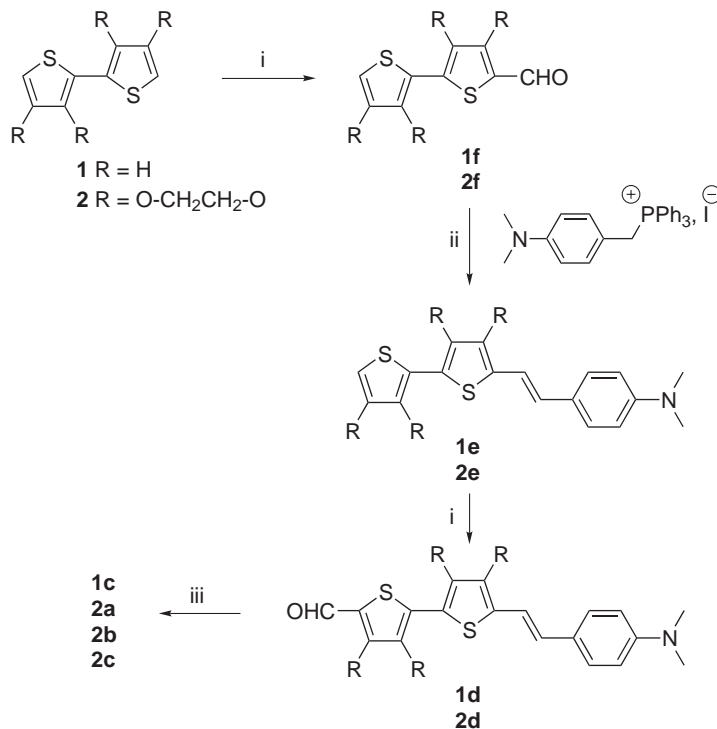
Scheme 1. *Reagents and conditions*: (i) $POCl_3$/DMF; (ii) *t*-BuOK/MeCN–THF; (iii) **1c**, **2c** bis(dicyanomethylidene)indane, Ac_2O, reflux 1 h and 1.5 h. **2a** malononitrile, $CHCl_3$, reflux 18 h. **2b** diethylthiobarbituric acid, Ac_2O, 80°C, 24 h.

enhancement of the molecular 2nd order hyperpolarizability of the derived push–pull NLO-phores.[8] We now report new NLO-phores (**2a–c**) in which BEDOT is used as π-conjugating spacer.

The synthesis of the NLO-phores is depicted in Scheme 1. Vilsmeier formylation of 2,2′-bithiophene (BT) (**1**), and BEDOT (**2**),[9] gave aldehydes **1f** and **2f** in 94 and 80% yields, respectively. Wittig olefination of **1f** and **2f** with a phosphonium iodide bearing the *N,N*-dimethylaniline group led to compounds **1e** and **2e** as a mixture of *E* and *Z* isomers (∼7/3) (yields 93 and 73%). After separation of the *Z* isomer, a second Vilsmeier formylation gave aldehydes **1d** and **2d** in 60 and 66% yields and the target compounds **1c**, **2a–c** were obtained in 60–90% yield by Knoevenagel condensation of **1d** and **2d** with malononitrile, diethylthiobarbituric acid and 1,3-bis(dicyanomethylidene)indane.[10]

Table 1 lists the UV–vis absorption maxima (λ_{max}), second order nonlinear hyperpolarizabilities ($\mu\beta$), and decomposition temperatures (T_d) of the new BEDOT based NLO-phores and of compound **1c** synthesized as reference compound.

As expected, the increase of the acceptor strength induces a bathochromic shift of the λ_{max} accompanied by an increase of $\mu\beta$. Comparison of the data for compound **2a** to those of other systems having the same donor/acceptor pair but a different spacer, shows that the BEDOT spacer leads to an efficiency comparable to that of DTE[5] but inferior to that of bridged DTE[8] or

dithienothiophene.[7b] On the other hand, comparing the data for compounds **1c** and **2c** which bear the same acceptor group clearly shows that replacement of BT by BEDOT produces a 118 nm bathochromic shift of λ_{max} and more than a twofold increase of $\mu\beta$, up to 11600× 10^{-48} esu. However, this high $\mu\beta$ value may be, in part, related to resonance effect.

While these results suggest that BEDOT is a more effective electron relay than BT, the evaluation of the relative contribution of electronic[11] and geometric effects on the enhancement of $\mu\beta$ is not straightforward. Whereas theoretical work in progress should contribute to clarify the role of electronic factors, further insights on the effects of the ethylenedioxy group

Table 1. Absorption maxima,[a] quadratic hyperpolarizabilities[b] and decomposition temperatures[c] of chromophores **1**–**2**

Compd	λ_{max} (nm)[a]	$\mu\beta$ (10^{-48} esu)[b]	T_d (°C)[c]
1c	712	5000 (1900)	215
2a	588	2120 (1200)	308
2b	649	2000 (950)	300
2c	830	11600 (2400)	206

[a] In CH_2Cl_2.
[b] Measured in $CHCl_3$ at 1.9 μm by the electric field-induced second harmonic generation (EFISH) technique, values in parentheses represent the zero-frequency hyperpolarizability product $\mu\beta_0$.
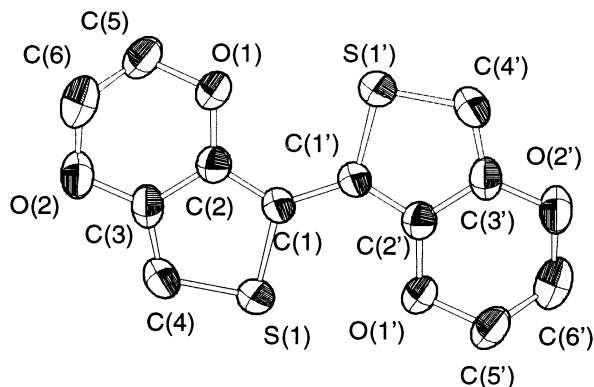[c] Determined by differential scanning calorimetry at a rate of 10°C/min.

Figure 1. ORTEP view of BEDOT (H atoms omitted). Selected bond lengths: S(1)–C(1) 1.732(2); S(1)–C(4) 1.715(3); O(1)–C(2) 1.368(3); O(1)–C(5) 1.435(3); O(2)–C(3) 1.374(3); O(2)–C(6) 1.450(4); C(1)–C(2) 1.373(3); C(2)–C(3) 1.421(3); C(3)–C(4) 1.347(4); C(5)–C(6) 1.483(4).

on the geometry of the BT system have been gained by analyzing the crystallographic structure of a single crystal of BEDOT (Fig. 1).[12] Examination of the distances between the sulfur and the oxygen S(1)···O(1′) and O(1)···S(1′) (2.92 Å) shows that these distances are significantly shorter than the sum of the van der Waals radii of sulfur and oxygen (3.25 Å), which evidences the occurrence of strong intramolecular interactions. An interesting consequence of this spontaneous rigidification is that contrary to oligothiophenes,[13] the π-conjugated system of BEDOT adopts a perfectly planar geometry. Such a planarization of the structure can be expected to provide a significant contribution to the superior electron relay properties of the BEDOT spacer compared to the BT one. Such a conclusion is in agreement with the enhanced π-electron delocalization recently observed in thiophene–EDOT hybrid oligomers incorporating a median BEDOT system.[14]

The compounds exhibit decomposition temperatures (T_d) ranging from 200°C to more than 300°C. Compounds **1c**, **2c** containing the bis(dicyanomethylidene)indane acceptor group have comparable T_d (210–230°C) suggesting that the stability of these molecules is essentially limited by the nature of the acceptor. In contrast, the high T_d of compounds **2a** and **2b** (≥300°C) clearly shows that stable NLO-phores can be synthesized from BEDOT spacers.

To summarize we have shown that the use of a BEDOT π-conjugating spacer allows stable NLO-phores with enhanced quadratic hyperpolarizability to be developed. As suggested by X-ray data, this effect could be related to the non-covalent rigidification of the conjugating spacer by intramolecular S···O interactions. Covalent fixation of these chromophores into high Tg polyimides is in progress and the resulting materials will be described in future publications.

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10. All final compounds were characterized by NMR, mass spectrometry and elemental analysis. Selected data for **2c** black powder, mp 206°C (dec.), IR (KBr): 2220 cm^{-1} (CN), 1603 cm^{-1} (C=C), 1168 cm^{-1} (C-O-C). ^{1}H NMR (CDCl$_3$) 8.62 (s, 1H, =C$\underline{H}$-C$_{thio}$), 8.57 (m, 2H, =C$\underline{H}_{Ar}$), 7.78 (m, 2H, =C$\underline{H}_{Ar}$), 7.38 (d, 2H, ^3J=8.8 Hz, 2 C$\underline{H}_{Ar}$=C$_{sp2}$-CH$_E$), 6.98 (s, 2H, C$\underline{H}_E$=C$\underline{H}_E$), 6.70 (d, 2H, ^3J=8.8 Hz, 2 C$\underline{H}_{Ar}$=C$_{sp2}$-NR$_2$), 4.45–4.32 (m, 8H, 4 C$\underline{H}_2$O), 3.00 (s, 6H, C$\underline{H}_3$N). Anal. calcd C, 67.09 (67.14), H, 3.77 (3.71), N, 9.93 (10.30), O, 9.01 (9.41), S, 9.29 (9.43). MS (MALDI-TOF) calcd for C$_{38}$H$_{25}$N$_5$O$_4$S$_2$ 679.1348, found 679.1418 (M$^{+\bullet}$).

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12. *Crystal data* for C$_{12}$S$_2$O$_4$H$_{10}$. C$_{12}$S$_2$O$_4$H$_{10}$ (M_W=282.34) is monoclinic $P2_1/c$, Z=2, a=9.284(5), b=8.165(1), c=7.7706(9) Å, β=90.43(2)°, V=589.1(5) Å^3, calculated density 1.59 g cm^{-3}.
Data collection: Data collection was carried out at 293 K using the zig-zag ω–2θ scan technique in the 2–30° θ range, on an Enraf-Nonius MACH3 four-circles diffractometer. From 1948 measured reflections ($\lambda_{MoK\alpha}$= 0.71069, h 0,10; k 0,11; l −13,13), 1062 independent reflections with $I/\sigma(I)$>3 were available for structure refinement.
Structure refinement: After Lorentz-polarization corrections and absorption correction (psi-scan procedure), the structure was solved by direct methods (SIR) which

reveal all the non-hydrogen atoms. Refinement of structure did not allow hydrogen atoms to be located which were then fixed at 0.95 Å from carbon atoms (Hydro program). Finally, refinement of all atomic coordinates, anisotropic thermal factors (non-H atoms) lead to $R = 0.043$, $R_w = 0.060$ (use of F magnitude, 97 parameters for 1062 reflections). All calculations were performed using the MolEN package.

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