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Synthesis and second order nonlinear optical properties of new chromophores containing 1,3,4-oxadiazole and thiophene rings

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Received (in Cambridge, UK) 25th July 2002, Accepted 10th September 2002
First published as an Advance Article on the web 14th October 2002

We report the synthesis and physico-chemical characterization, including molecular second order nonlinear optical properties by the EFISH technique, of three new heterocycle based push–pull chromophores. Two chromophores contain the five membered 1,3,4-oxadiazole ring, the third a thiophene ring. The chromophores also contain azo or stilbene bridges between conjugated aromatic rings and are functionalized for covalent incorporation into polymer chains. The maximum observed $\mu_g\beta$ is 1350×10^{-48} esu for the thiophene chromophore in conditions far from resonance enhancement (fundamental laser wavelength 1.907 µm). The crystal structure of one oxadiazole chromophore is also discussed.

Introduction

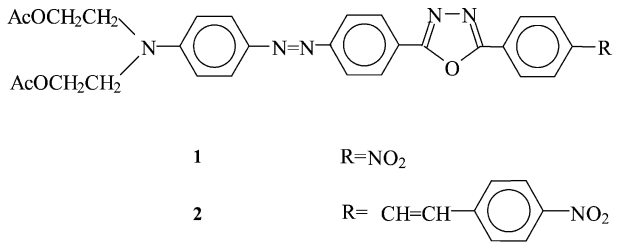
Nonlinear optical (NLO) poled polymer films have become a major focus of scientific and engineering research because of their potential applications in optical communication technology devices such as electro-optic (EO) modulators, switches, and filters as well as frequency doubling devices.[1–3] The large, nonresonant optical nonlinearity of pure electronic origin, the very high bandwidth, the low relative permittivity, the ease of processing into thin films (spin-coating technique), and low material costs are the major advantages of these organic materials.

Second order nonlinearity in polymers arises in most cases from the microscopic optical nonlinearity of the chromophores incorporated into the polymer structure. The nonlinear response of these NLO-chromophores is expressed in higher order contributions to the induced dipole moment when the molecule interacts with external electric fields.

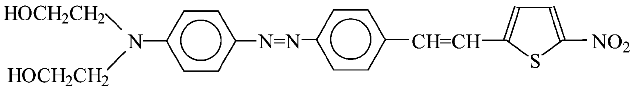
Prevalently donor–acceptor-substituted π-conjugated elongated molecules have been synthesized as NLO chromophores because of their high hyperpolarizability. In such dipolar molecules, the first order hyperpolarizability depends on the conjugated π-electronic structure, *e.g.* its length and shape, and on the specific character of the donor and acceptor groups. The introduction of aromatic heterocyclic rings along the conjugation path results in increased hyperpolarizability as compared to all benzenoid systems.[4] Chromophores containing aromatic pentaatomic heterocycles or their derivatives such as thiophene,[5–7] thiazole,[8] benzothiazole,[9] benzoxazole[10–11] are among the most studied systems.

Besides a high hyperpolarizability, NLO-chromophores should also possess a thermal stability high enough to survive in the surrounding matrix even at processing temperatures of the order of the glass transition temperature of high T_g polymers; furthermore, in the case of chromophores to be covalently incorporated in polymers, a suitable chemical functionalization is required as an additional feature that may strongly reduce (and in some cases eliminate) the chemical routes necessary for building in the chromophore.

In this paper we report the synthesis and physico-chemical characterization, including NLO properties, of three new conjugated chromophores, properly functionalized for polymerization. The first two contain a 1,3,4-oxadiazole ring in the backbone (Scheme 1), while the third contains a thiophene ring (Scheme 2).



Scheme 1



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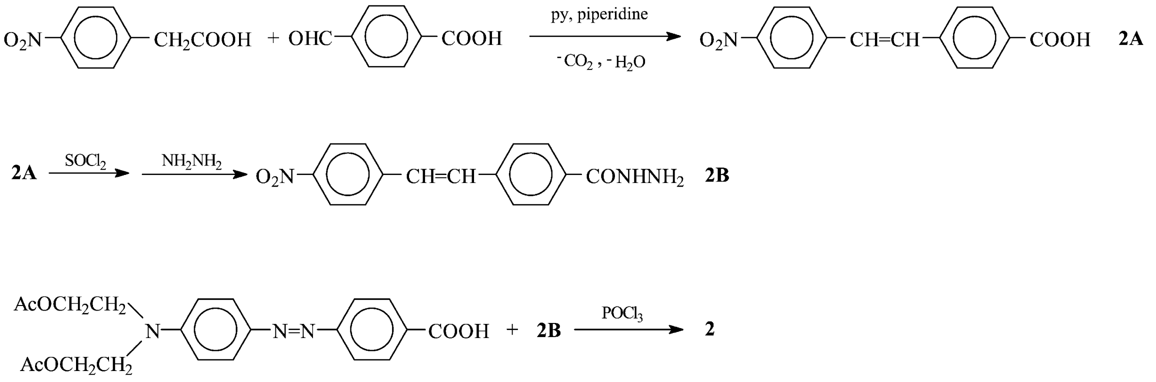
Scheme 2

The choice of the azo bridge along the conjugated path was suggested by recent application-oriented investigations[3] that have shown it offers better combined features of optical transparency and hyperpolarizability as compared with other possible bridges (*e.g.* ethenylene, imino *etc.*). The oxadiazole heteroaromatic ring was chosen on account of its well known features of thermo-chemical stability.[12,13]

Some researches on the NLO properties of oxadiazole systems have been reported, both experimental[14] and theoretical.[15–17] However, compounds **1** and **2** are, to our knowledge, the first examples of 1,3,4-oxadiazole containing chromophores specifically designed for polymers.

DOI: 10.1039/b207230k



Scheme 3

Experimental

Synthesis

A similar synthetic procedure was followed for chromophores **1** and **2** and is shown in Scheme 3 for **2**. The key step consists in the cyclization between a suitable monohydrazide and 4-{4-[*N*,*N*-bis(acetoxyethyl)amino]phenylazo}benzoic acid whose synthesis has been already described.[18]

The synthesis of **2** is given in detail.

4-Carboxy-4′-nitrostilbene (2A). The synthesis was performed through a Knoevenagel–Döbbner condensation. *p*-Carboxybenzaldehyde (30 g, 0.19 mol) and *p*-nitrophenylacetic acid (37.5, 0.21 mol) were dissolved in a solution of 100 mL of dry pyridine and 4.2 mL of piperidine, contained in a 250 mL round bottomed flask fitted with a reflux condenser protected by a calcium chloride tube, and heated to reflux for 2 h with stirring. The resulting solution was cooled to room temperature, filtered and the yellow crystalline product obtained was washed successively with 200 mL of cold ethanol; mp 363 °C, yield 20.46 g (40%).

^{1}H NMR dimethyl sulfoxide (DMSO-d$_6$): δ 7.55 (s, 2H), 7.75 (d, 2H), 7.85 (m, 4H), 8.24 (d, 2H), 12.9 (s, 1H).

4-Carboxy-4′-nitrostilbene monohydrazide (2B). The synthesis was performed by treatment of the chloride of **2A** with excess hydrazine hydrate. **2A** (10 g, 37 mmol) was refluxed with thionyl chloride ($SOCl_2$, 50 mL) in a round bottomed flask equipped with a condenser. After gas evolution ceased the mixture was further refluxed for 30 min; the excess thionyl chloride was removed by distillation at reduced pressure and the chloride was obtained as a yellow microcrystalline solid. This was added, in portions, under stirring to a boiling solution obtained by mixing 60 mL of 95% ethanol and hydrazine monohydrate (18.5 g, 370 mmol). A yellow precipitate of the monohydrazide immediately formed. The mixture was further allowed to boil for 15 min, while adding ethanol so as to keep constant the mixture volume, then cooled to room temperature. The solid was filtered, washed with ethanol and dried in an oven; mp 232 °C. Yield 9.47 g (90%).

^{1}H NMR dimethyl sulfoxide (DMSO-d$_6$): δ 4.62 (s, br, 2H), 7.59 (s, 2H), 7.79 (d, 2H, $J = 8.8$ Hz), 7.91 (s, 2H), 7.95 (s, 2H), 8.30 (d, 2H, $J = 8.8$ Hz), 9.87 (s, 1H).

IR (KBr, cm^{-1}): 3310 (w, ν_s NH_2), 3275 (w, ν_{as} NH_2), 2908 (vw), 1660 (s), 1628 (s), 1591 (s), 1505 (vs), 1339 (vs), 1184 (w), 1108 (m).

Chromophore 2. 4-{4-[*N*,*N*-bis(acetoxyethyl)amino]phenylazo}benzoic acid[18] (8.0 g, 19 mmol) and **2B** (4.9 g, 17 mmol) were refluxed under stirring with 80 mL phosphorus oxychloride ($POCl_3$) in a round bottomed flask equipped with a condenser, for 3 hours. The excess phosphorus oxychloride was removed by distillation at ambient pressure and a deep purple paste was obtained. This was transferred, in small portions, in a vessel containing a stirred cold aqueous solution of sodium acetate. The pH was maintained not below 4–5 by addition, if necessary, of solid sodium acetate. A red-orange solid was obtained. The mixture was stirred for 2 hours then the solid was filtered, washed repeatedly with water and dried. The raw product was treated with boiling *N*,*N*-dimethylformamide, filtering off the insoluble part; on cooling the hot DMF solution, **2** was obtained as a red-orange powder. Further purification by column chromatography (silica gel and chloroform as eluent) gave 3.51 g (28% yield) of pure **2** as red-orange needles.

Anal. Calc. for $C_{36}H_{32}N_6O_7$: C 65.45, H 4.88, N 12.72%. Found: C 65.28, H 4.99, N 12.62%.

^{1}H NMR chloroform ($CDCl_3$): δ 2.07 (s, 6H), 3.71 (t, 4H, $J = 5.86$ Hz), 4.31 (t, 4H, $J = 5.86$), 6.86 (d, 2H, $J = 8.79$ Hz), 7.28 (2H, partially sup. with solvent), 7.69 (m, 4H), 7.93 (d, 2H, $J = 8.79$ Hz), 8.00 (d, 2H, $J = 8.79$ Hz), 8.23 (m, 6H).

For the synthesis of **1** the monohydrazide of 4-nitrobenzoic acid was used in the last step.

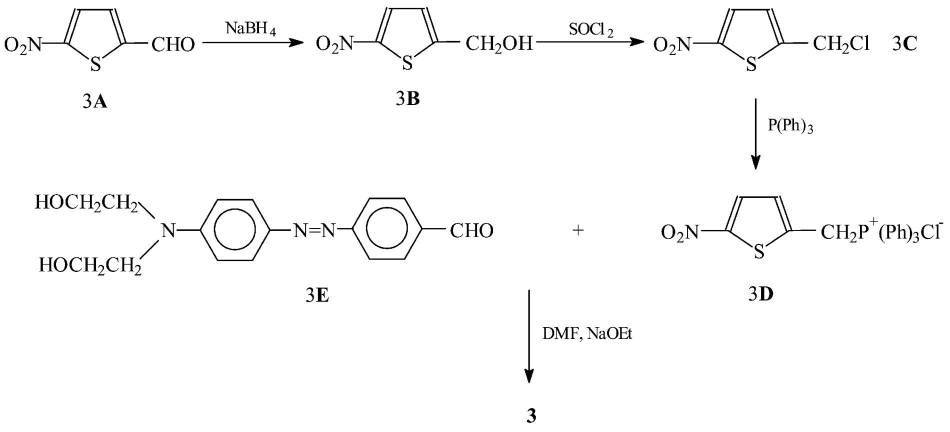
4-Nitrobenzoic acid monohydrazide. Commercial 4-nitrobenzoyl chloride (25 g, 135 mmol) was added in portions to 300 mL of boiling ethanol. The solution was allowed to boil till the volume reduced to about 50 mL. 300 mL of water were added and a white solid precipitate of the ethyl ester formed which was collected by filtration (mp 169 °C). The ester was added in portions to a boiling solution obtained by mixing 200 mL of ethanol and hydrazine monohydrate (67.5 g, 1350 mmol). The color of the solution turned from yellow to red. Boiling was continued for about 10 min, then the solution was allowed to cool in a water bath and a yellow precipitate of the monohydrazide formed which was collected by filtration, washed with ethanol and dried in oven; mp 218 °C, yield 17.1 g (70%) (lit.[19] mp 218 °C).

Chromophore 1. The synthesis was performed in an analogous way to **2** starting from 4-{4-[*N*,*N*-bis(acetyloxyethyl)amino]phenylazo}benzoic acid and 4-nitrobenzoic acid monohydrazide.

^{1}H NMR chloroform ($CHCl_3$-d$_1$): δ 2.08 (s, 6H), 3.76 (t, 4H, $J = 5.6$ Hz), 4.32 (t, 4H, $J = 5.6$ Hz), 6.88 (d, 2H, $J = 8.9$ Hz), 7.95 (d, 2H, $J = 8.9$ Hz), 8.04 (d, 2H, $J = 8.5$ Hz), 8.26 (d, 2H, $J = 8.5$ Hz), 8.40 (m, 4H).

The synthesis of chromophore **3** is based on the synthetic scheme shown in Scheme 4, whose key step is the Wittig-type reaction between aldehyde **3E** and phosphonium salt **3D**.

Commercial 5-nitro-2-thenaldehyde (**3A**) was converted into (5-nitro-2-thienyl)methanol (**3B**) and this, in turn, into 2-chloromethyl-5-nitrothiophene (**3C**) according to a procedure already described in the literature.[20]



Scheme 4

(5-Nitro-2-thienyl)methyltriphenylphosphonium chloride (3D). **3C** (1.7 g) was dissolved in 5 mL benzene. Separately, one equivalent of triphenylphosphine was dissolved, under nitrogen atmosphere, in 20 mL benzene. The solution of the chloride was slowly added, under nitrogen and stirring, to the solution of triphenylphosphine at 80 °C. After some minutes a clear green solid was obtained which was filtered and recrystallized from chloroform–ethyl ether, giving 1.6 g of a white solid (mp 240 °C).

Anal. Calc. for $C_{23}H_{19}NO_2SPCl$: P 7.04, S 7.29%. Found: P 7.08, S 7.21%.

4-{4-[*N*,*N*-Bis(hydroxyethyl)amino]phenylazo}benzaldehyde (3E). The synthesis was performed according to the diazotization–coupling scheme between 4-aminobenzaldehyde (prepared by basic hydrolysis of 4-acetamidobenzaldehyde according to ref. 21) and commercial 4-[*N*,*N*-bis(hydroxyethyl)-amino]aniline. The procedure (and yield) is analogous to that we have already described for a similar compound[18] (mp 150 °C).

^{1}H NMR chloroform ($CHCl_3$-d_1): δ 3.98 (m, 8H), 4.5 (s, 2H), 8.05 (m, 8H), 10.1 (s, 1H).

Chromophore 3. **3D** (2.0 g, 4.94 mmol) and **3E** (1.6 g, 4.94 mmol) were dissolved in 60 mL anhydrous DMF in a two necked round bottomed flask under stirring and nitrogen atmosphere. Separately, a solution of sodium ethoxide in ethanol was prepared by adding metallic sodium (148 mg, 6.42 mmol) in 10 mL absolute ethanol under nitrogen. This solution was slowly added, under nitrogen, to the DMF solution. The system was allowed to react at 120 °C under nitrogen and stirring for 78 h, then the solution was poured into 200 mL water. A red solid was obtained which was recovered by filtration, dried and treated with boiling chloroform two times to extract the unreacted aldehyde. Finally 0.43 g of **3** were obtained as a dark red solid. Yield 20%.

Anal. Calc. for $C_{22}H_{22}N_4O_4S$: C 60.26, H 5.06, N 12.78%. Found: C 59.85, H 4.65, N 12.36%.

^{1}H NMR (pyridine-d_5): δ 3.87 (t, 4H, J = 5.6 Hz), 4.09 (t, 4H, J = 5.6 Hz), 4.99 (s, br, 2H), 7.04 (d, 2H, J = 9.2 Hz), 7.12 (d, 1H, J = 4.4 Hz), 7.37 (d, 1H, J = 2.2 Hz), 7.56 (d, 1H), 7.75 (d, 2H, J = 8.6 Hz), 7.92 (d, 1H, J = 4.4 Hz), 8.12 (d, 2H, J = 8.6 Hz), 8.16 (d, 2H, J = 9.0 Hz).

MS (*m*/*z*) 439.42 (M + H$^+$, 100%) (*M* calc. 438.5).

Characterization

The thermal behaviour was examined by differential scanning calorimetry (Perkin Elmer DSC-7, nitrogen atmosphere, scanning rate 10 K min^{-1}). Temperature controlled polarising microscopy was used for optical observations (Zeiss microscope combined with Mettler FP5 micro furnace). Thermogravimetric analysis was performed with Mettler TG50 apparatus. Proton NMR spectra were recorded on Varian XL 200 and Bruker AC 250 spectrometers. The mass spectrum of **3** was recorded with a MALDI TOF DE-PRO apparatus on an α-cyano-4-hydroxycinnamic acid matrix. UV–VIS spectra were recorded with a Perkin Elmer Lambda 7 UV–VIS spectrophotometer and IR spectra on a Jasco FT-IR spectrometer.

X-Ray analysis of 1 †

Single crystals were obtained by evaporation from a DMF solution in the form of thin elongated orange plates. Weissenberg and oscillation photographs indicated an orthorhombic system and the *Pbca* space group. Data were collected on a Nonius CAD4 diffractometer (graphite monochromated CuKα radiation). Although the crystal specimen used in data collection was single, the quality of the diffraction pattern was not high; in particular the diffraction pattern did not extend to high sinθ/λ values; therefore data were collected up to 60° of θ, this allowing a more than sufficient number of independent data for full refinement. The structure was solved by direct methods (SHELXS program of the SHELX-97 package[22]) and refined by the full matrix method (SHELXL program of the same package). During the course of refinement a high thermal motion resulted for the terminal aliphatic tails; a careful inspection of the Fourier maps allowed the discarding of a static disorder in favour of a dynamic one, and some restraints were introduced for handling the disorder. This is probably the reason for the poor quality of the diffraction pattern. Some crystal, collection and refinement data are given in Table 1.

NLO measurements

The conventional EFISH technique was used to experimentally determine the non linearity $\mu_g\beta$ of the chromophores, where μ_g stands for the ground state permanent dipole moment and β for the quadratic hyperpolarizability of the molecules. The light source was a Q-switched Nd:Yag laser whose emission at 1.06 µm was shifted to 1.907 µm by stimulated Raman scattering in a high pressure hydrogen cell. The measurements were calibrated relative to a quartz wedge: the experimental value of $d_{11}^{\text{Quartz}} = 1.2 \times 10^{-9}$ esu at 1.06 µm was extrapolated to 1.1×10^{-9} esu at 1.907 µm. Neglecting the purely electronic contribution compared to the orientational part and allowing Kleinman symmetry for rod-like molecules, one finally determines the projection β of the vector part of the tensor β_{ijk} along the direction of the dipole moment. A detailed description of the experimental apparatus has been given elsewhere.[23]

Measurements were performed in chloroform solution for **1** and **2** and in DMF solution for **3**.

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† CCDC reference number 190459. See http://www.rsc.org/suppdata/p2/b2/b207230k/ for crystallographic files in .cif or other electronic format.

Table 1 Crystal, collection and refinement data for **1** †

Temperature	293 K
Chemical formula	$C_{28}H_{26}N_6O_7$
Wavelength/Å	1.5418
Crystal system	Orthorhombic
Space group	*Pbca*
a/Å	7.171(3)
b/Å	11.543(2)
c/Å	65.146(7)
α/°	90
β/°	90
γ/°	90
V/Å^3	5392(3)
Z, D_x/g cm^{-3}	8, 1.379
μ/mm^{-1}	0.847
Theta range	1.36° to 59.94°
Data/restr./parameters	3978/2/370
R_1, on F ($I > 3\sigma(I)$)	0.072
R_1, wR_2 (all data) on F^2	0.2808, 0.2944
Max. peak − hole/e Å^{-3}	0.411, −0.361

$$R1 = \frac{\sum \left\| F_0 \right| - \left| F_c \right\|}{\sum \left| F_0 \right|}; \quad wR2 = \left\{ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right\}^{1/2}$$

Table 2 Selected bond lengths (Å), bond angles (°) and torsion angles (°) for **1** with e.s.d.'s in parentheses

N2–N3	1.416(8)
O3–C7	1.361(7)
O3–C8	1.355(8)
N2–C7	1.299(8)
N3–C8	1.281(8)
N4–N5	1.264(7)
N6–C18	1.364(9)
C7–O3–C8	103.1(5)
C7–N2–N3	106.5(6)
C8–N3–N2	105.4(6)
C18–N6–C21	121.9(8)
C18–N6–C25	122.5(8)
C21–N6–C25	115.2(8)
O3–C7–N2	111.5(7)
O3–C8–N3	113.4(6)
O3–C7–C4–C5	173.7(7)
O3–C8–C9–C14	173.9(6)
N5–N4–C12–C13	−158.0(7)
C15–N5–N4–C12	−174.3(6)
C16–C15–N5–N4	−174.2(7)

Results and discussion

The synthetic route followed for **1** and **2** belongs to the classic scheme of synthesis of oxadiazoles by one step cyclization between a carboxylic acid and a monohydrazide. The choice of the cyclizing agent ($POCl_3$) among possible others (*e.g.* polyphosphoric acid) was suggested by the need to maintain the acetate protection of the terminal hydroxy groups. Without such protection, in fact, an additional cyclization of the terminal tails with formation of a stable 4-morpholinyl six membered cycle would likely occur. The synthesis of monohydrazide **2B** is noteworthy. In fact, the most common route, *i.e.* reaction of the ethyl ester of the carboxylic acid with excess hydrazine hydrate, which is fully satisfactory for nitrobenzoic acid monohydrazide, is unsatisfactory in this case, the ethyl ester of nitrostilbenic acid being recovered substantially unaltered after even long treatments with hydrazine hydrate. Therefore the route through the more reactive chloride of the acid was chosen which afforded the desired monohydrazide in excellent yields. In particular, although reaction between the chloride and hydrazine hydrate was performed in ethanol solution, no trace of the possible by-products (the ethyl ester and the acid) was observed. This should be due to the stronger nucleophile character of hydrazine.

Chromophore **1** shows solid state polymorphism. An enantiotropic solid–solid phase transition is observed at 185 °C (ΔH = 16.1 J g^{-1}), while melting to the isotropic liquid occurs at 236 °C (ΔH = 82.6 J g^{-1}). The X-ray molecular structure of **1** is reported in Fig. 1; selected bond lengths, bond angles and torsion angles are given in Table 2. A bent, "banana"-like shape of the overall molecule is evident and is due, fundamentally, to the noncollinearity of the two bonds spanning out from the oxadiazole ring, whose directions are at about 42°. Bond lengths and angles in the molecule are close to expected values with the exception of some atoms of the (disordered) aliphatic tails; in particular a planar trigonal geometry is observed around the N amino atom, N6, as reported in other chromophores bearing the same or similar dialkylamino groups.[24] Phenyl rings bonded to the azo group are not coplanar, making a dihedral angle of 35.7(2)°. As may be inferred from Table 2 this is due mainly to torsion around the N4–C12 bond. A possible conclusion is that the torsional barrier around this bond is lower than around the N5–C15 bond and this is in agreement with crystal data and theoretical calculations on azophenylbenzoxazole chromophores we have already studied.[24] The crystal packing is very simple, Figs. 2 and 3. Molecules are piled along c forming a layered structure. Within each layer molecules are placed with a parallel orientation of their mean planes and mean elongation axes. No intercalation occurs between consecutive layers along c, this being consistent with the high thermal motion observed for some atoms of the terminal tails.

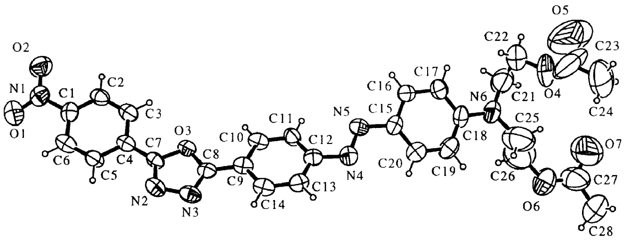

Fig. 1 Molecular drawing of **1**. Ellipsoids are drawn at 50% probability level.

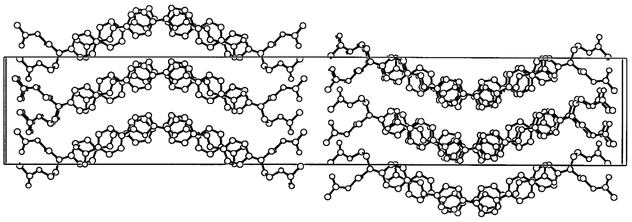

Fig. 2 Crystal packing of **1** viewed down a. H atoms are omitted for clarity.

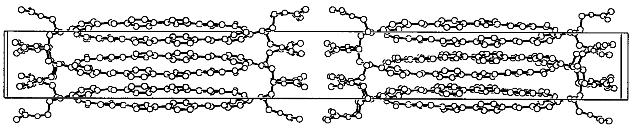

Fig. 3 Crystal packing of **1** viewed down b. H atoms are omitted for clarity.

DSC thermograms of **2** are reported in Fig. 4. Melting occurs at 244 °C (ΔH = 48.9 J g^{-1}) with formation of a liquid crystal phase of probable smectic A type as suggested by the observed morphologies: fan and focal conics textures. Isotropization occurs at 290 °C (ΔH = 7.6 J g^{-1}). The mesogenic character of chromophore **2** does not necessarily imply that polymers containing it, particularly for low molar contents, are bound to be mesogenic themselves. Therefore, the mesogenic chromophore is not in itself a possible negative feature for the polymer.

Table 3 EFISH data of chromophores

Chromophore	Solvent	λ_{max}/nm	$\mu_g\beta/10^{-48}$ esu
1	$CHCl_3$	453	900
2	$CHCl_3$	428	1250
3	DMF	465	1350

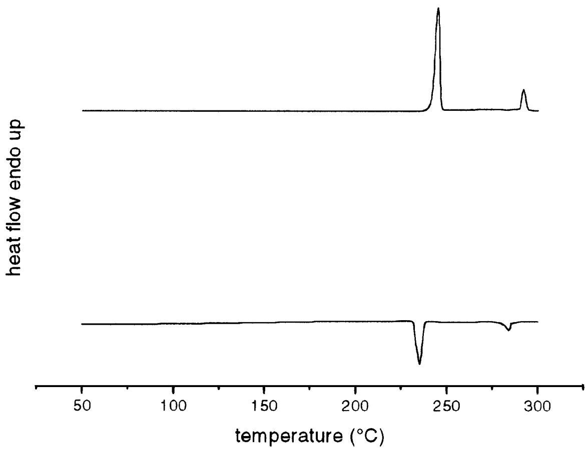

Fig. 4 DSC thermograms on heating (upper curve) and cooling (down curve) for **2**. Scanning rate 10 K min^{-1}.

The NLO activity of chromophores has been determined by the EFISH technique in solution and $\mu_g\beta$ coefficients are reported in Table 3. Owing to the absorption features of chromophores and to the fundamental laser wavelength used, the reported values may be considered as free from resonance enhancement, thus allowing safe comparisons. The three chromophores have in common the first part of the molecular skeleton, *i.e.* the 4-(4-dialkylaminophenylazo)phenyl group. To this, 4-nitrophenyl in **1** and 4′-nitrostilben-4-yl in **2** are attached through a 1,3,4-oxadiazole bridge, while in **3** 2-nitro-4-ethenylthiophene is attached. The length of the conjugation path in **1** (taken as the distance between N-aniline and N-nitro atoms) is 18.3 Å; this increases to about 24–25 Å in the case of **2**. For **3** a slightly smaller value than **1** may be derived.

The higher value measured for **2** as compared to **1** is consistent with the longer conjugation path.

On the other hand the value measured for **3** which is higher than **1** and also than **2** is indicative of the high efficiency of the thiophene heterocycle in giving highly NLO active chromophores.[1,4,6] In particular, in **3**, an important role should be played by the acceptor group (NO_2) being directly attached to the heterocycle ring. Finally, the value reported for **3** is comparable with that of chromophores having the stronger dicyanovinyl electron withdrawing group attached to thiophene ring.[25]

A fair thermal stability is observed for the chromophores. If defined as the temperature corresponding to 5% weight loss in a TGA experiment at a heating run of 10 °C min^{-1} under nitrogen atmosphere, decomposition temperatures are 337 °C for **1** and 332 °C for **2**. A lower value, 240 °C, is observed for **3**. This, however, could be also a consequence of the absence of the acetyl protective groups on the aliphatic tails.

In conclusion, the combined features of NLO activity and thermal stability make chromophores **1**, **2** and **3** interesting candidates for the synthesis of potentially second order NLO active polymer materials.

Acknowledgements

Financial support of MIUR of Italy (PRIN 2000) is gratefully acknowledged. Thanks are due to CIMCF of the Università di Napoli “Federico II” for NMR and MS facilities and to the director of the CNR Istituto di Biostrutture e Bioimmagini of Naples for kind permission to use the Nonius diffractometer.

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