Synthesis and characterization of end-functionalized oligo-(vinylthiophenes) with liquid crystal properties

Christophe Maertens, Jian-Xin Zhang, Philippe Dubois and Robert Jérôme

Centre for Education and Research on Macromolecules (C.E.R.M.), University of Liège, Sart Tilman B6, B-4000 Liège, Belgium

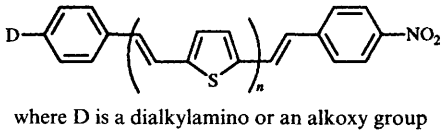
A general scheme for the synthesis of end-functionalized conjugated (*E*)-vinylthiophene oligomers with liquid crystal and potential second-order non-linear optical properties is described. These push–pull thiophene-containing aromatic molecules show mesogenic properties over different temperature ranges depending on the chain length and the functional end-groups.

Introduction

During the last decade, increasing attention has been paid to the design of new organic molecules with a high second order molecular non-linearity, for original applications in electro-optics. In this respect, π-conjugated chains capped at both ends with an electron-donor and an electron-acceptor, respectively, have been studied.[1] For instance, incorporation of a five-membered heterocycle, such as thiophene, to a π-donor–acceptor conjugated chain greatly enhances its non-linear optical (NLO) properties,[2] due mainly to a higher hyperpolarizability. However, production of useful NLO materials requires the supramolecular organization of the individual molecules,[1] which is currently carried out by electric poling techniques. Providing NLO materials with liquid crystal properties might also be a way of triggering well-defined supramolecular organization.[3] Lehn and co-workers were the first to report mesophases formed by push–pull stilbene derivatives for NLO applications.[4] Polymalonates containing liquid crystal pyridine heterocycle derivatives in the side-chains were described by Griffin *et al.* for the same applications.[5] Until now, only Kossmehl and Hoppe referred to mesophases for thiophene containing molecules.[6]

Results and discussion

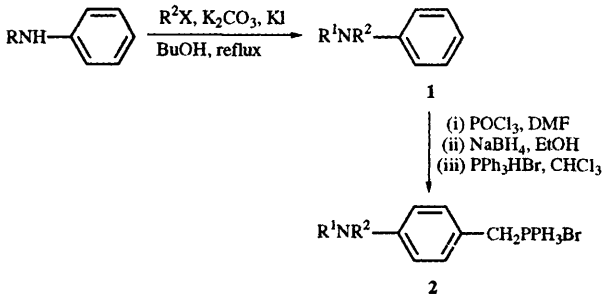
This paper describes the controlled synthesis and the characterization of end-functionalized oligo(vinylthiophenes) endowed with both potential NLO properties and liquid crystal behaviour. In agreement with the general structure reported for active NLO organic molecules,[1] compounds investigated in this study consist of an oligo[(*E*)-vinylthiophene] chain selectively capped with a nitro acceptor group at one end and an alkylamino or a butoxy donor group at the other. The choice of the donor substituents relies upon their well-known ability to promote, or at least to favour, formation of mesophases. The general formula of the synthesized conjugated chains is shown below.



where D is a dialkylamino or an alkoxy group

These NLO-mesogens have been synthesized by Wittig or Wittig–Horner reactions. Before discussing the synthesis of the short poly[(*E*)-vinylthiophene] chains, it is worthwhile reporting on the synthesis of the precursors of the functional end-groups, *i.e.* an aromatic aldehyde *para*-substituted by the nitro acceptor group and either an aromatic phosphonium salt or the phosphonate counterpart *para*-subsituted by the electron donor group.

N,*N*-Dialkylanilines **1** were prepared by alkylation of *N*-methylaniline or aniline with a selected bromide or chloride[7] as described in Scheme 1. They were then formylated by a



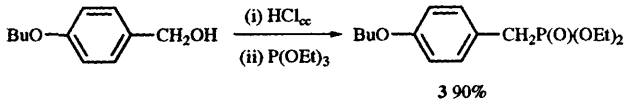
Substituents and yields:

R	X	R^1	R^2	Yield **1** (%)	Yield **2** (%)
CH_3	Br	CH_3	C_8H_{17}	**1a** 64	**2a** 32
CH_3	Cl	CH_3	$HO(CH_2)_6$	**1b** 72	**2b** 24
H	Br	Bu	Bu	**1c** 88	**2c** 33

Scheme 1

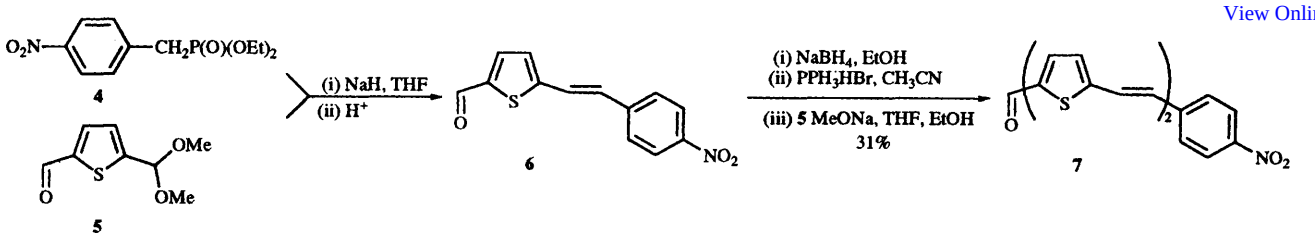
Vilsmeier reaction. The resultant aldehydes were further reduced with sodium borohydride in ethanol and the corresponding benzyl alcohols were directly transformed into phosphonium salts **2** by means of triphenylphosphonium hydrobromide in refluxing chloroform.[8]

In the case of the butoxy electron donor, phosphonate **3** was selected as the reactive intermediate. Butoxybenzyl chloride was prepared easily by treatment of concentrated hydrochloric acid with the commercially available 4-butoxybenzyl alcohol and transformed into phosphonate **3** by an Arbusov reaction with a 90% overall yield (Scheme 2).

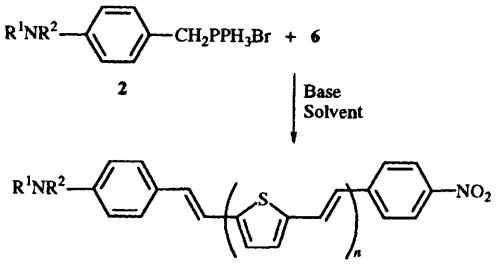


Scheme 2

One or two (*E*)-vinylthiophene unit(s) (n = 1 or 2) were end-capped with an aldehyde and the nitro acceptor group, respectively, by the reaction pathway shown in Scheme 3.



Scheme 3



Reaction conditions and yields:

Phosphonium	Aldehyde	Solvent	Base	Yield 8 (%)	*n*
2a	**6**	THF	BuLi	**8a** 70	1
2b	**6**	THF	LDA	**8b** 25	1
2b	**7**	EtOH–THF	EtOLi	**8c** 44	2
2c	**7**	THF	BuLi	**8d** 70	1

Scheme 4

4-Nitrobenzylphosphonate **4**† was treated with **5**‡ with formation of aldehyde **6** in a 75% yield.[8] Further extension of **6** by one vinylthiophene unit into **7** was achieved by a Wittig reaction of **5** with the phosphonium salt of **6**, that was previously prepared by the selective reduction of the aldehyde and reaction of the obtained alcohol with triphenylphosphonium hydrobromide.[8]

The NLO-mesogens bearing a dialkylamino substituent were finally synthesized in a one-step condensation between phosphonium salts **2** and aldehyde **6** or **7** under the conditions reported in Scheme 4. Pure all-*trans* isomers of **8a–d** were isolated by recrystallization from EtOH–H_2O, as attested by ^1H NMR analysis. Yields are shown in the caption to Scheme 4.

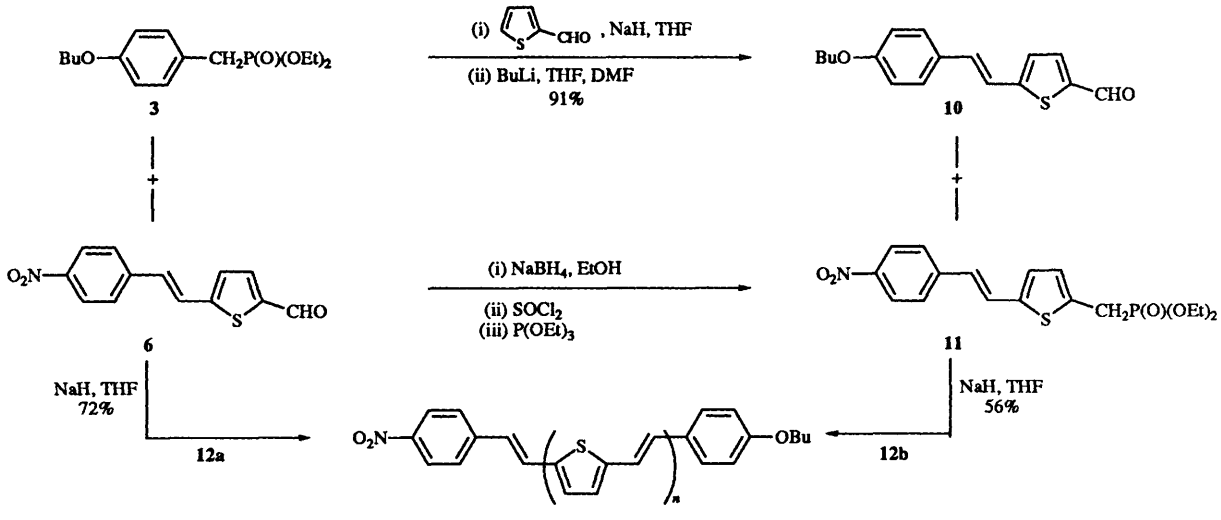
This reaction path was also used to prepare the counterpart of **8** in which the alkylamino group is substituted by a butoxy group. In contrast to the conjugated molecule with one (*E*)-vinylthiophene unit **12a** ($n = 1$) that was prepared in a good yield (72%, Scheme 5), this Wittig–Horner reaction did not yield the expected dimer **12b** ($n = 2$). In order to overcome this drawback, the reaction path has been reversed as shown in Scheme 5.

Thus, thiophene-2-carbaldehyde was treated with phosphonate **3**, followed by lithiation and DMF quenching, leading to the aldehyde **10**. Compound **6** was transformed into the phosphonate **11** by a three-step synthesis (Scheme 5). The Wittig–Horner reaction between phosphonate **11** and aldehyde **10** gave **12b** ($n = 2$) in 56% yield.[8]

Compounds **8a–d** and **12a,b** have been characterized by polarization optical microscopy and differential scanning calorimetry (DSC). Table 1 lists the liquid crystal behaviour and the transition temperatures observed by these two techniques, together with the UV–VIS maximum absorption frequency (for a 10^{-5} mol dm^{-3} solution in $CHCl_3$). It is worthwhile pointing out that all transitions observed by DSC are first order and do not permit us to distinguish the nature of the mesophase.

All synthesized compounds, except for **8d** (D = Bu_2N), are thermotropic mesogens. Nematic phases were easily identified by the Schlieren textures observed under cross-polarizers. Increasing length of the conjugated chain sharply increases the mesophase transition temperature to the point where decomposition occurs, before an isotropic liquid is formed (comparison of **8b/8c** and **12a/12b**, Table 1). The nematic phase of **12a** can be observed upon cooling down to 60 °C, although

† 4-Nitrobenzylphosphonate was prepared by the Arbusov reaction with 4-nitrobenzyl bromide and triethyl phosphite (82% yield).
‡ Compound **5** was prepared by protection of thiophene-2-carbaldehyde with trimethyl orthoformate, followed with the lithiation by BuLi–DMF in dry THF (overall yield: 77%).



12a: $n = 1$
b: $n = 2$

Scheme 5

Table 1 Absorption, optical microscopy and DSC analysis of NLO-mesogens

Donor group	Comp.	n	λ_{max}/nm	Transition temperatures/°C: Optical microscopy[a] Heating	Optical microscopy[a] Cooling	DSC[b] Heating	DSC[b] Cooling
$HO(CH_2)_6N(CH_3)$	**8b**	1	474	C 153 N N 161 I	I 160 N N 135 C	157	155 140
$HO(CH_2)_6N(CH_3)$	**8c**	2	489	C 243 N N 250 dec	—	232 242	—
BuO	**12a**	1	443	C 130 S S 133 N N 180 I	I 170 N N 60 C	115 128	70 (br) 60 55
BuO	**12b**	2	462	C 140 S S 182 dec	I 180 S S 140 C	182 (br)	182
Bu_2N	**8d**	1	489	C 175 I	I 173 C	175 (br)	
$C_8H_{17}N(CH_3)$	**8a**	1	485	C 145 I	I 140 S S 135 C	125	120

[a] C = Crystalline or glassy; N = nematic; S = smectic; I = isotropic liquid; dec = decomposition. [b] Heating rate = 10 K min^{-1}, cooling rate = 5 K min^{-1}; br = broad.

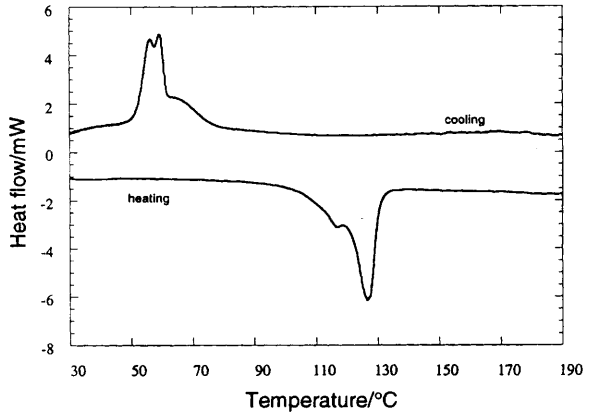


Fig. 1 DSC thermogram of **12a** (heating rate = 10 K min^{-1}, cooling rate = 5 K min^{-1})

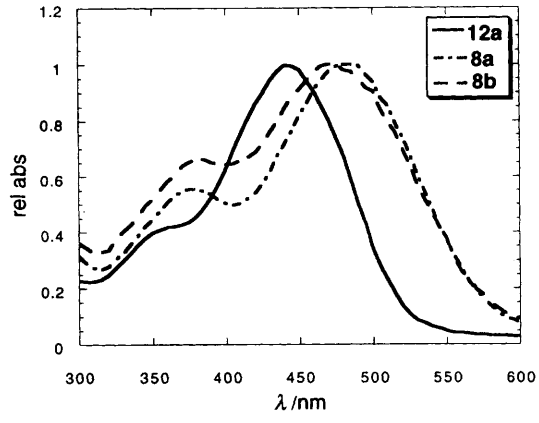


Fig. 2 Effect of the donor group on relative absorption of NLO-phores **12a**, **8a** and **8b**

this phase only appears at 130 °C when heating (Fig. 1). It is worth noting that **8a** is monotropic, the smectic phase can only be observed upon cooling.

Absorption of the NLO-phores (Table 1) is also indicative of an electronic delocalization between the donor and the acceptor groups. As expected, the nature of donor groups, *i.e.* butoxy and *N*,*N*-dialkylamino, strongly affects the relative charge-transfer absorption of the conjugated chain (Fig. 2). At the same chain length, the *N*-alkyl donor substituent on the *N*,*N*-alkylamino electron donor has also some slight effect on the absorption maximum. This charge-transfer band is red shifted upon increasing the chain length by one *trans*-vinylthiophene unit (Fig. 3).

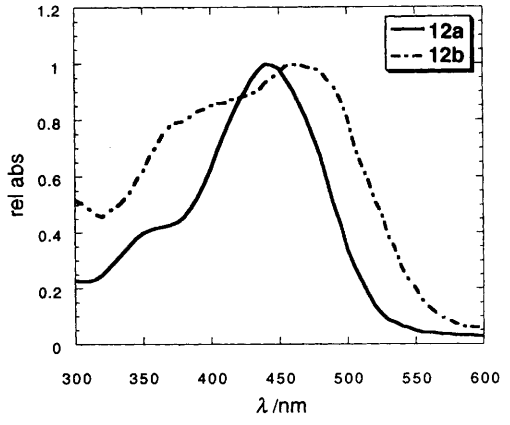


Fig. 3 Effect of chain length on relative absorption of NLO-phores **12a** and **12b**

Conclusions

An original and general scheme has been developed for the synthesis of end-functionalized conjugated (*E*)-vinylthiophene oligomers. These push–pull thiophene-containing aromatic molecules are clearly mesogenic over different temperature ranges, depending on the chain length and the functional end-groups. A more detailed analysis of the liquid crystal behaviour is under way. It must be mentioned that oligomers of poly[(*E*)-vinylthiophene] have shown an interesting second-order molecular non-linearity.[8] These NLO properties will be confirmed and quantified. The next step of this study is the incorporation of these NLO-mesogens in macromolecules, either as side-chains or parts of the main-chain.

Experimental

General

The ^{1}H NMR spectra were measured at 400 MHz using a Bruker AM 400 spectrometer, the chemical shifts are given relative to tetramethylsilane (TMS) and J values are given in Hz. The IR spectra were recorded using a Perkin-Elmer 1600 FT spectrometer. The phase transitions were determined calorimetrically using a Dupont 9000 instrument, under a nitrogen atmosphere. Optical investigations were carried out with a Leitz Wetzlar polarizing microscope coupled with a Mettler heating regulation system.

Synthetic procedures

Synthesis of *N*-methyl-*N*-octylaniline 1a

Freshly distilled *N*-methylaniline (5.35 g, 0.05 mol), octyl bromide (9.65 g, 0.05 mol), potassium carbonate (6.9 g) and potassium iodide (0.041 g) in 100 cm^3 of dry BuOH were stirred under nitrogen at 110 °C for 24 h. The solution was then allowed to cool to room temperature, filtered and the BuOH was distilled under vacuum. The residue was dissolved in 100 cm^3 of diethyl ether and washed three times with 30 cm^3 of water. The organic layer was dried over $MgSO_4$ and the solvent removed under reduced pressure. Fractional distillation *in vacuo* gave 7.08 g (64%) of *N*-methyl-*N*-octylaniline **1a** as a colourless oil, bp 105 °C, 10 mmHg; $\delta_H(CDCl_3)$ 7.25 (3 H, t, *J* 7.2, 3-, 4-, 5-H), 6.72 (2 H, t, *J* 7.2, 2-, 6-H), 3.32 [2 H, t, *J* 7.3, $CH_2CH_2N(CH_3)$], 2.95 [3 H, s, $N(CH_3)$], 1.60 [2 H, m, $CH_2CH_2CH_2N(CH_3)$], 1.33 [10 H, m, $CH_3(CH_2)_5CH_2$] and 0.92 [3 H, t, *J* 6.8, $CH_3(CH_2)_5$]; ν_{max}/cm^{-1} 3048, 2919, 2855, 1600, 1504, 1461, 1370, 747 and 688.

Synthesis of *N*-(6-hydroxyhexyl)-*N*-methylaniline 1b

Freshly distilled *N*-methylaniline (5.35 g, 0.05 mol), 6-chlorohexan-1-ol, (6.8 g, 0.05 mol), potassium carbonate (6.9 g) and potassium iodide (0.041 g) in 100 cm^3 of dry BuOH were stirred under nitrogen at 110 °C for 72 h. After the treatment described for **1a** fractional distillation *in vacuo* gave 7.45 g (72%) of *N*-(6-hydroxyhexyl)-*N*-methylaniline **1b** as a colourless oil, bp 145 °C, 0.1 mmHg. Spectral data correspond to the reported values.[7]

Synthesis of *N*,*N*-dibutylaniline 1c

Freshly distilled aniline (4.65 g, 0.05 mol), butyl bromide (13.7 g, 0.10 mol), potassium carbonate (13.8 g) and potassium iodide (0.082 g) in 100 cm^3 of dry BuOH were stirred under nitrogen at 110 °C for 24 h. After the treatment described for **1a**, fractional distillation *in vacuo* gave 6.95 g (88%) of *N*,*N*-dibutylaniline **1c** as a colourless oil, bp 120 °C, 10 mmHg; $\delta_H(CDCl_3)$ 7.17 (3 H, t, *J* 7.4, 3-, 4-, 5-H), 6.62 (2 H, m, 2-, 6-H), 3.24 [4 H, m, $(CH_2CH_2)_2N$], 1.31 {8 H, m, $[CH_3(CH_2)_2CH_2]_2N$} and 0.95 [6 H, t, *J* 2.6, $CH_3(CH_2)_2$]; ν_{max}/cm^{-1} 3091, 2956, 2871, 1601, 1505, 1465, 1368, 744 and 691.

Synthesis of 4-(*N*-methyl-*N*-octylamino)benzaldehyde

N-Methyl-*N*-octylaniline **1a** (5.47 g, 0.025 mol) was formylated with $POCl_3$ (2.6 cm^3, 0.028 mol) and DMF (10 cm^3, 0.1 mol). After the treatment described above the brown residue was distilled *in vacuo* to provide 2.8 g (45%) of 4-(*N*-methyl-*N*-octylamino)benzaldehyde, bp 152 °C, 0.1 mmHg; $\delta_H(CDCl_3)$ 9.71 (1 H, s, CHO), 7.70 (2 H, d, *J* 7.0, 2-, 6-H), 6.66 (2 H, d, *J* 7.2, 3-, 5-H), 3.38 [2 H, t, *J* 7.3, $CH_2CH_2N(CH_3)$], 2.95 [3 H, s, $N(CH_3)$], 1.60 [2 H, m, $CH_2CH_2CH_2N(CH_3)$], 1.33 [10 H, m, $CH_3(CH_2)_5CH_2$] and 0.92 [3 H, t, *J* 6.8, $CH_3(CH_2)_5$]; ν_{max}/cm^{-1} 2923, 2853, 2723, 1681, 1596, 1555, 1528, 1386, 1313, 1240, 1166 and 814.

Synthesis of 4-[*N*-(6-acetoxyhexyl)-*N*-methylamino]-benzaldehyde

After protection of the 6-hydroxyhexyl group in the acetate form as described,[7] 4-[*N*-(6-acetoxyhexyl)-*N*-methylaniline (4.98 g, 0.020 mol) was formylated with $POCl_3$ (2.08 cm^3, 0.022 mol) and MFA (9.56 cm^3, 0.076 mol). After the treatment described above, the brown residue was purified by chromatography on a silica gel column (ethyl acetate–hexane 7:3, v:v) to provide 4.66 g (84%) of 4-[*N*-(6-acetoxyhexyl)-*N*-methylamino]benzaldehyde; R_f 0.41 (ethyl acetate–hexane 7:3, v:v). Spectral data correspond to the reported values.[7]

Synthesis of 4-(*N*,*N*-dibutylamino)benzaldehyde

Following the described procedure,[7] *N*,*N*-dibutylaniline **1c** (5.00 g, 0.032 mol) was formylated with $POCl_3$ (3.32 cm^3, 0.035 mol) and DMF (12 cm^3, 0.15 mol). After the treatment described above and two filtrations on silica gel, the brown residue was distilled *in vacuo* to provide 2.6 g (44%) of 4-(*N*,*N*-dibutylamino)benzaldehyde, bp 135 °C, 0.1 mmHg; $\delta_H(CDCl_3)$ 9.69 (1 H, s, CHO), 7.69 (2 H, d, *J* 8.8, 2-, 6-H) 6.64 (2 H, d, *J* 8.8, 3-, 5-H), 3.34 [4 H, t, *J* 7.7, $(CH_2CH_2)_2N$], 1.58 {8 H, m, $[CH_3(CH_2)_2CH_2]_2N$} and 0.95 [6 H, t, *J* 7.3, $CH_3(CH_2)_2$]; ν_{max}/cm^{-1} 3091, 2871, 2727, 1666, 1595, 1552, 1526, 1406, 1367, 1168 and 813.

Synthesis of 4-(*N*,*N*-dialkylamino)benzyl alcohols

4-(*N*,*N*-Dialkylamino)benzaldehydes were reduced to the corresponding benzyl alcohols with reaction of an excess of sodium borohydride in ethanol (room temp., 1 h). After acidic hydrolysis (HCl 1 mol dm^{-3}), usual diethyl ether work-up, $MgSO_4$ drying and solvent evaporation, the purity of the alcohols was confirmed by the total disappearance of the C=O IR band and by ^1H NMR. 4-(*N*,*N*-Dialkylamino)benzyl alcohols were used without any further purification. Yields were quantitative. Spectroscopic data are given below.

4-(*N*-Methyl-*N*-octylamino)benzyl alcohol. $\delta_H(CDCl_3)$ 7.25 (2 H, d, *J* 8.7, 2-, 6-H), 6.71 (2 H, d, *J* 8.7, 3-, 5-H), 4.57 (2 H, s, CH_2OH), 3.32 [2 H, t, *J* 7.4, $CH_2CH_2N(CH_3)$], 2.95 [3 H, s, $N(CH_3)$], 1.90 (1 H, s, CH_2OH), 1.60 [2 H, m, $CH_2CH_2CH_2N(CH_3)$], 1.33 [10 H, m, $CH_3(CH_2)_5CH_2$] and 0.92 [3 H, t, *J* 6.7, $CH_3(CH_2)_5$]; ν_{max}/cm^{-1} 3344, 2919, 2855, 1612, 1520, 1465, 1365, 1180, 1024 and 799.

4-[*N*-(6-Acetoxyhexyl)-*N*-methylamino]benzyl alcohol. $\delta_H(CDCl_3)$ 7.25 (2 H, d, *J* 8.0, 2-, 6-H), 6.66 (2 H, d, *J* 8.0, 3-, 5-H), 4.53 (2 H, s, $PhCH_2OH$), 3.60 (2 H, t, *J* 6.6, CH_2CH_2OH), 3.29 [2 H, t, *J* 7.3, $CH_2CH_2N(CH_3)$], 2.91 [3 H, s, $N(CH_3)$], 2.03 (1 H, s, CH_2OH) and 1.77–1.36 (br) and 1.21 [9 H, $HOCH_2(CH_2)_4CH_2$ and CH_2OH]; ν_{max}/cm^{-1} 3371, 2933, 2859, 1612, 1520, 1364, 1242, 1187 and 799.

4-(*N*,*N*-Dibutylamino)benzyl alcohol. $\delta_H(CDCl_3)$ 7.22 (2 H, d, *J* 8.6, 2-, 6-H), 6.64 (2 H, d, *J* 8.6, 3-, 5-H), 4.53 (2 H, s, $PhCH_2OH$), 3.27 [4 H, t, *J* 7.6, $CH_2(CH_2)_2N$], 1.8 (1 H, br, $PhCH_2OH$), 1.58 and 1.32 {8 H, m, $[CH_3(CH_2)_2CH_2]_2N$} and 0.97 [6 H, t, *J* 7.2, $CH_3(CH_2)_2$]; ν_{max}/cm^{-1} 3349, 2956, 2871, 1614, 1595, 1521, 1455, 1366, 1183 and 794.

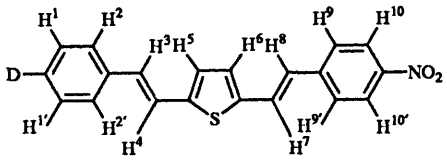
General procedure for the synthesis of 4-(*N*,*N*-dialkylamino)-benzylphosphonium bromides 2

To a 0.2 mol dm^3 solution of benzyl alcohol in $CHCl_3$ was added triphenylphosphonium hydrobromide (0.95 equiv.).[9] The solution was then refluxed for 2 h before solvent distillation. Residual solid was then dissolved in $CHCl_3$, the organic phase was washed once with saturated aqueous $NaHCO_3$, twice with water, dried over $MgSO_4$ and concentrated *in vacuo* before precipitating the phosphonium bromide in dry diethyl ether. The white powder was filtered off and dried *in vacuo* overnight.

4-(*N*-Methyl-*N*-octylamino)benzyl(triphenyl)phosphonium bromide 2a. Following the general procedure, crude 4-(*N*-methyl-*N*-octylamino)benzyl alcohol (1.1 g, 0.0044 mol) was treated with triphenylphosphonium hydrobromide (1.43 g, 0.0042 mol). After precipitation, filtration and drying, 2.12 g (82%) of 4-(*N*-methyl-*N*-octylamino)benzyl(triphenyl)phosphonium bromide **2a** was isolated as a white powder; $\delta_H(CDCl_3)$ 7.80–7.30 [15 H, m, $P(Ph)_3$], 6.84 (2 H, d, *J* 8.5, 2-, 6-H), 6.41 (2 H, d, *J* 8.5, 3-, 5-H), 5.02 [2 H, d, *J* 13, $CH_2P(Ph)_3$], 3.22 [2 H, t, *J* 7.4, $CH_2CH_2N(CH_3)$], 2.85 [3 H, s, $N(CH_3)$], 1.50 and 1.28 [12 H, br, $CH_3(CH_2)_6CH_2$] and 0.88 [3 H, t, *J* 6.7, $CH_3(CH_2)_5$]; ν_{max}/cm^{-1} 3051, 2946, 2848, 2776, 1612, 1522, 1466, 1437, 1377, 1185, 1111, 995, 850, 826, 745, 716 and 689.

4-[*N*-(6-Hydroxyhexyl)-*N*-methylamino]benzyl(triphenyl)-phosphonium bromide 2b. Following the general procedure, crude 4-[*N*-(6-acetoxyhexyl)-*N*-methylamino]benzyl alcohol (0.554 g, 0.002 mol) was treated with triphenylphosphonium

Table 2 ^{1}H NMR data for conjugated compounds **8a, 8b, 8d and 12a**



δ(CDCl$_3$)

	Assignment									
	H^1, H$^{1'}$ (2 H, d, *J* 8.5)	H^2, H$^{2'}$ (2 H, d, *J* 8.5)	H^3 (1 H, d, *J* 16)	H^4 (1 H, d, *J* 16)	H^5 (1 H, d, *J* 3.5)	H^6 (1 H, d, *J* 3.5)	H^7 (1 H, d, *J* 16)	H^8 (1 H, d, *J* 16)	H^9, H$^{9'}$ (2 H, d, *J* 8.5)	H^{10}, H$^{10'}$ (2 H, d, *J* 8.5)
8a	6.67	7.36	6.86	6.94	6.88	7.03	6.98	7.34	7.56	8.20
8b	6.67	7.36	6.86	6.90	6.90	7.03	6.98	7.34	7.56	8.20
8d	6.62	7.34	6.85	6.89	6.89	7.03	6.96	7.29	7.55	8.20
12a	6.89	7.40	6.89	6.91	6.94	7.04	7.05	7.34	7.57	8.20

hydrobromide (0.617 g, 0.0018 mol). After precipitation, filtration and drying, 0.62 g (56%) of 4-[*N*-(6-hydroxyhexyl)-*N*-methylamino]benzyl(triphenyl)phosphonium bromide **2b** was isolated as a white powder (deprotection of acetoxy group was observed to be quantitative); δ_H(CDCl$_3$) 7.75–7.25 [15 H, m, P(*Ph*)$_3$], 6.84 (2 H, d, *J* 8.5, 2-, 6-H), 6.38 (2 H, d, *J* 8.5, 3-, 5-H), 5.02 [2 H, d, *J* 13, C*H*$_2$P(Ph)$_3$], 3.60 (2 H, t, *J* 6.6, CH$_2$C*H*$_2$OH), 3.20 [2 H, t, *J* 7.3, CH$_2$C*H*$_2$N(CH$_3$)], 2.81 [3 H, s, N(C*H*$_3$)], 1.86 (1 H, s, CH$_2$O*H*) and 1.52–1.25 [8 H, br, HOCH$_2$(C*H*$_2$)$_4$CH$_2$]; ν_{max}/cm^{-1} 3327, 2927, 2854, 1610, 1520, 1436, 1364, 1110, 816, 744, 717 and 688.

4-(*N*,*N*-Dibutylamino)benzyl(triphenyl)phosphonium bromide 2c. Following the general procedure, crude 4-(*N*,*N*-dibutylamino)benzyl alcohol (1.5 g, 0.008 mol) was treated with triphenylphosphonium hydrobromide (2.61 g, 0.0072 mol). After precipitation, filtration and drying, 3.22 g (76%) of 4-(*N*,*N*-dibutylamino)benzyl(triphenyl)phosphonium bromide **2c** was isolated as a white powder; δ_H(CDCl$_3$) 7.70–7.25 [15 H, m, P(*Ph*)$_3$], 6.90 (2 H, d, *J* 8.6, 2-, 6-H), 6.30 (2 H, d, *J* 8.6, 3-, 5-H), 5.03 [2 H, d, *J* 13, PhC*H*$_2$P(Ph)$_3$], 3.27 [4 H, t, *J* 7.6, CH$_2$(C*H*$_2$)$_2$N] and 1.58 and 1.32 {8 H, m, [CH$_3$(C*H*$_2$)$_2$-CH$_2$]$_2$N}, 0.97 [6 H, t, *J* 7.2, C*H*$_3$(CH$_2$)$_2$]; ν_{max}/cm^{-1} 3051, 2956, 2871, 2776, 1614, 1521, 1455, 1437, 1366, 1185, 1111, 995, 850, 826, 745, 716 and 689.

General procedure for the synthesis of dialkylamino-containing NLO-compounds 6, 8 and 12

To a suspension of dialkylaminobenzyl(triphenyl)phosphonium bromide **2** in dry THF, cooled at −78 °C and under a nitrogen atmosphere, was added a selected base (1 equiv.). After immediate dissolution of the phosphonium **2**, the dark red solution was allowed to warm to room temp. and stirred for 15 min. Aldehyde **6** (1 equiv.) in dry THF was slowly added to the ylide solution and further stirred for 2 h before quenching with water. The aqueous phase was then extracted three times with chloroform, the organic phases washed with saturated aqueous sodium hydrogen carbonate and water and then dried over MgSO$_4$. After solvent evaporation under reduced pressure, the crude product was further purified by recrystallization or chromatography on silica gel column.

2-[(*E*)-4-(*N*-Methyl-*N*-octylamino)styryl]-5-[(*E*)-4-nitrostyryl]thiophene 8a. Following the described procedure, 4-(*N*-methyl-*N*-octylamino)benzyl(triphenyl)phosphonium bromide **2a** (1.76 g, 0.003 mol) in 25 cm^3 of dry THF was treated with 15 cm^3 of a 0.2 mol dm^{-3} BuLi solution in hexane. After 15 min, aldehyde **6** (0.77 g, 0.003 mol in 25 cm^3 THF) was slowly added. After the treatment described above and recrystallization from EtOH–H$_2$O (7:3, v:v), filtration and drying, 1.0 g (70%) of **8a** was isolated as red crystals (Found: C, 73.4; H, 8.0; N, 6.05; S, 6.7. Calc. for C$_{29}$H$_{34}$N$_2$O$_2$S: C, 73.37; H, 7.22; N, 5.90; S, 6.76%); δ_H(CDCl$_3$) (for the conjugated chain, see Table 2) 3.22 [2 H, t, *J* 7.4, CH$_2$C*H*$_2$N(CH$_3$)], 2.85 [3 H, s, N(C*H*$_3$)], 1.50 and 1.28 [12 H, br, CH$_3$(C*H*$_2$)$_6$CH$_2$] and 0.88 [3 H, t, *J* 6.7, C*H*$_3$(CH$_2$)$_5$]; ν_{max}/cm^{-1} 3066, 3017, 2918, 2850, 1597, 1511, 1466, 1430, 1383, 1334, 1299, 1183, 1107, 1035, 952, 867, 805, 746 and 689.

2-{(*E*)-4-[*N*-(6-Hydroxyhexyl)-*N*-methylamino]styryl}-5-[(*E*)-4-nitrostyryl]thiophene 8b. Following the described procedure, 4-[*N*-(6-hydroxyhexyl)-*N*-methylamino]benzyl(triphenyl)phosphonium bromide **2b** (4.55 g, 0.007 mol) in 50 cm^3 of dry THF was treated with 0.014 mol of LDA in 10 cm^3 THF. After 15 min, aldehyde **6** (1.813 g, 0.007 mol) in 25 cm^3 THF was slowly added. After the treatment described above, crude **8b** was purified by chromatography on silica gel column (hexane–ethyl acetate, 1:1) to give 0.65 g (25%) of **8b** as red crystals (Found: C, 69.7; H, 7.0; N, 5.6; S, 6.5. Calc. for C$_{27}$H$_{30}$N$_2$O$_3$S: C, 70.06; H, 6.48; N, 6.05; S, 6.90%); δ_H(CDCl$_3$) (for the conjugated chain, see Table 2) 3.60 (2 H, t, *J* 6.6, CH$_2$C*H*$_2$OH), 3.20 [2 H, t, *J* 7.3, CH$_2$C*H*$_2$N(CH$_3$)], 2.81 [3 H, s, N(C*H*$_3$)], 1.86 (1 H, s, CH$_2$O*H*), 1.52–1.25 [8 H, br, HOCH$_2$(C*H*$_2$)$_4$CH$_2$)]; ν_{max}/cm^{-1} 3351, 2925, 2854, 1597, 1510, 1336, 1183, 1108, 943, 806, 746 and 689.

2-[(*E*)-(5-Formyl)-2-thienylvinyl]-5-[(*E*)-4-nitrostyryl]thiophene 7. Following the described procedure, 5-(4-nitrostyryl)thienyl(triphenyl)phosphonium bromide (1.172 g, 0.002 mol) in 10 cm^3 of dry THF was treated with 5.5 cm^3 of a 0.4 mol dm^{-3} EtOLi solution in EtOH. After 1 h, aldehyde **5** (0.372g, 0.002 mol) in 10 cm^3 THF was slowly added and the orange solution further stirred for 2 h before quenching with 5 cm^3 of 2 mol dm^{-3} HCl. After the treatment described above, crude **7** was purified by recrystallization from EtOH–H$_2$O (7:3, v:v), filtrated and dried to give 0.19g (30%) of **7** as orange crystals. Owing to product insolubility and low recoveries, no NMR spectra could be recorded; ν_{max}/cm^{-1} 1660, 1617, 1586, 1508, 1461, 1425, 1337, 1230, 1109, 1048, 938, 860, 827, 798 and 746.

1-(5-{(*E*)-4-[*N*-(6-Hydroxyhexyl)-*N*-methylamino]styryl}-2-thienyl)-2-{5-[(*E*)-4-nitrostyryl]-2-thienyl}ethene 8c. Following the described procedure, 4-[*N*-(6-hydroxyhexyl)-*N*-methylamino]benzyl(triphenyl)phosphonium bromide **2b** (0.325 g, 0.0005 mol) in 10 cm^3 of dry THF was treated with 0.0011 mol of EtOLi in 10 cm^3 EtOH. After 15 min, aldehyde **7** (0.183 g, 0.0005 mol) in 5 cm^3 THF was slowly added. After the treatment described above, crude **8c** was purified by recrystallization from EtOH–H$_2$O (7:3, v:v), filtrated and dried to give 0.12 g (44%) of **8c** as red crystals (Found: C, 69.7;

H, 5.9; N, 4.2; S, 10.4. Calc. for $C_{33}H_{34}N_2O_3S_2$: C, 69.44; H, 6.00; N, 4.90; S, 11.23%); owing to product insolubility and low recoveries, no NMR spectra could be recorded; ν_{max}/cm^{-1} 3300, 3094, 3041, 2924, 2853, 1593, 1513, 1465, 1427, 1386, 1338, 1182, 1109, 1044, 948, 885, 811, 746 and 688.

2-[(*E*)-4-(*N*,*N*-Dibutylamino)styryl]-5-[(*E*)-4-nitrostyryl]-thiophene 8d. Following the described procedure, 4-(*N*,*N*-dibutylamino)benzyl(triphenyl)phosphonium bromide **2c** (2.104 g, 0.004 mol) in 50 cm^3 of dry THF was treated with 0.014 mol of LDA in 10 cm^3 THF. After 15 min, aldehyde **6** (1.813 g, 0.007 mol) in 25 cm^3 THF was slowly added. After the treatment described above, crude **8b** was purified by chromatography on silica gel column (hexane–ethyl acetate, 1:1) to give 0.65 g (25%) of **8b** as red crystals (Found: C, 73.5; H, 7.5; N, 6.3; S, 7.1. Calc. for $C_{28}H_{32}N_2O_2S$: C, 73.01; H, 7.00; N, 6.08; S, 6.96%); $\delta_H(CDCl_3)$ (for the conjugated chain, see Table 2) 3.27 [4 H, t, *J* 7.6, $CH_2(CH_2)_2N$], 1.58 and 1.32 {8 H, m, $[CH_3(CH_2)_2CH_2]_2N$} and 0.97 [6 H, t, *J* 7.2, $CH_3(CH_2)_2$]; ν_{max}/cm^{-1} 3071, 3015, 2954, 2868, 1588, 1512, 1402, 1336, 1222, 1183, 1107, 1034, 947, 855, 807, 745 and 688.

1-{5-[(*E*)-4-Butoxystyryl]-2-thienyl}-2-{5-[(*E*)-4-nitrostyryl]-2-thienyl}ethene 12b. A solution of 5-[(*E*)-4-butoxystyryl] thiophene-2-carbaldehyde **10** (0.45 g, 0.0015 mol) and diethyl phosphonate **11** (0.60 g, 0.0015 mol) in 30 cm^3 dry THF under nitrogen was slowly added to sodium hydride (0.08 g, 0.002 mol) under nitrogen. After immediate reaction followed by gas evolution, the reaction mixture was heated at 50 °C for 2 h, allowed to cool to room temp. and neutralized with water. Crude **12b** was obtained by precipitation in a mixture EtOH–H_2O (7:3, v:v), filtered and recrystallized from Et_2O to afford 0.45 g (50%) of **12b** as orange crystals (Found: C, 69.0; H, 4.95; N, 3.6; S, 11.9. Calc. for $C_{30}H_{27}NO_3S_2$: C, 70.0; H, 5.2; N, 2.73; S, 12.4%); owing to product insolubility and low recoveries, no NMR spectra could be recorded; ν_{max}/cm^{-1} 2955, 1588, 1511, 1336, 1248, 1172, 1108, 1022, 946 and 821.

2-[(*E*)-4-Butoxystyryl]-5-[(*E*)-4-nitrostyryl]thiophene 12a. Following the same procedure as for **12b** diethyl 4-butoxybenzylphosphonate (0.6 g, 0.002 mol) **3** and aldehyde **6** (0.518 g, 0.002 mol) in 30 cm^3 of dry THF were added to sodium hydride (0.09 g, 0.003 mol). The treatment described above gave 0.58 g (72%) of **12a** as orange crystals (Found: C, 72.1; H, 6.6; N, 3.5; S, 7.9. Calc. for $C_{24}H_{23}NO_3S$: C, 71.04; H, 5.67; N, 3.45; S, 7.89%); $\delta_H(CDCl_3)$ (for the conjugated chain, see Table 2) 3.99 (2 H, t, *J* 6.4, CH_2CH_2O), 1.78 (2 H, m, $CH_2CH_2CH_2O$), 1.51 (2 H, m, $CH_2CH_2CH_2O$), 0.99 (3 H, t, *J* 7.5, CH_3CH_2); ν_{max}/cm^{-1} 2924, 2870, 1588, 1515, 1465, 1340, 1252, 1174, 1107, 1067, 1035, 953, 867, 825, 796, 745 and 689.

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