Synthesis of novel conjugated oligomers for second-order nonlinear optics: incorporation of a central spacer as a conjugation modulator

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Abstract: A new series of second-order nonlinear optical chromophores has been synthesized that consists of a conjugated segment end-capped with an electron acceptor and an electron donor, respectively, and a central spacer intended to modulate the electro-optical effect. Conjugated chains have been tailored with trans-vinylene-1,5-thienylene as the building unit and \(N,N\)-dimethylamino and nitro groups as the donor-acceptor pair. Four spacers have been incorporated into the central part of the conjugated oligomers, which range from saturated to totally unsaturated functions, i.e. from methylene to vinylene units. The general strategy relies upon two consecutive Wittig or Wittig-Horner reactions between the spacer precursor and an aromatic phosphonium or phosphonate bearing the strong electron donor and the acceptor, respectively. Two synthetic pathways have been studied. The first procedure is based on the use of a symmetric precursor for the spacer. However, a reaction byproduct is formed, which must be removed and decreases the reaction efficiency. The second approach requires an asymmetric precursor for the spacer, the synthesis of which is a multistep process. In order to evaluate the effect of the spacer, a completely conjugated oligomer has been prepared by the one-step coupling of two conjugated segments end-functionalized by the electron donor and the acceptor, respectively.

Introduction

Information processing is likely to change significantly in the near future as the steadily increasing needs for speed and storage capacity of digital data rise. Interest in optical devices is rapidly growing because of their promise of extremely high speed processing, transmission and storage of data. The application of optical fibres in high speed communication is essentially devoted to a small part of modern optics: linear optics. Although design and use of optical computers are feasible on the basis of nonlinear optics (NLO) principles, the poor performance of present NLO materials limits this. Inorganic materials are known for this low NLO response, and organic NLO materials have a low degree of supramolecular organization and/or absorb strongly in the UV-VIS region.

As a result of intensive research efforts, some fundamental relationships between properties and the molecular structure of NLO organic materials have emerged. For instance, second-order NLO chromophores need a push-pull structure, which means that \(\pi\)-\(\pi\) conjugated segments must be end-functionalized by strongly electron conjugated donors and acceptors, respectively. This traditional concept emphasizes a parallel between the strength of the electron withdrawing and donating capability of the end-groups and the nonlinearity of the conjugated molecule. More recently, Marder has stated that molecular geometry is also a very important factor affecting NLO properties. Although NLO organic materials usually have a much higher NLO response than inorganic materials, their optical application is currently limited by a dramatic absorption red-shifted from the UV to the visible region. Zyss and Moylan have indicated that some interruption of chain conjugation, for instance, by the incorporation of a semi-conjugated spacer, might lead to good NLO properties and low absorption in this region.

Very few studies have dealt with conjugated chains containing a spacer other than a \(\pi\)-\(\pi\) electronic conjugated bridge. They have shown that the incorporation of the \(\sigma\)-\(\sigma\) and \(\sigma\)-\(\pi\) conjugations has no deleterious effect on NLO properties, whereas it might result in a very high damage threshold working in the off-resonance mode.

Accordingly, the NLO systems envisaged in this paper are based on the tailoring of (macro) molecules of a triblock structure in which two highly polarizable and/or conducting segments are separated from each other by a spacer. 1,4-Phenylene, 1,5-thienylene and vinylene units have been considered as building blocks for the conjugated segments, \(N,N\)-dimethylamino and nitro groups have been selected as the acceptor-donor pair. Several spacers, \(X\) in Scheme 1, will be inserted into the conjugated chain, for which electronic conjugation will be modulated from high delocalization, i.e. vinylene, to a complete break by a totally saturated group, such as...
propane-2,2-diyl. The general structure of the proposed (macro) molecules is shown in Scheme 1.

**Scheme 1**

![Scheme 1](image)

This type of molecule may be of great interest for improving our knowledge of the dependence of NLO properties on molecular structure, without disregarding potential applications. Indeed, modulation of electronic conjugation should allow electro-optical properties to be modulated by the application of an electric field of variable strength. Moreover, the spacer within the conjugated chain is expected to improve solubility in common solvents, to facilitate processing and to displace the UV absorption far away from the visible light region.

This paper reports the synthesis of the aforementioned molecules 1a-d with \( n = 1 \). A forthcoming paper will deal with the increase in length of the conjugated system (\( n = 2,3 \)) and substitution of 1,5-thienylene for the 1,4-phenylene end-groups, all these modifications being carried out in order to optimize the NLO response of the basic material (Scheme 1, \( n = 1 \)).

**Results and discussion**

**General synthetic strategy**

The general strategy relies upon the synthesis of a precursor for each spacer (2 or 3) that contains two end-groups reactive in the Wittig reaction, *i.e.* formyl 2 and/or derivatized acetal 3. Two successive Wittig-like reactions then have to be carried out to attach the donor and the acceptor groups to the precursors (Scheme 2). Benzylic phosphonium salts or phosphonates bearing the donor or acceptor will be considered depending on the starting materials available and the stability of the reaction intermediates.

The spacer precursors are just the spacer attached to two thiophene rings. The symmetrical precursors 2 are substituted by two identical formyl groups and are easy to prepare. However, their use in the first Wittig reaction might lead to the formation of symmetrical byproducts. In order to prevent this side-reaction from occurring, precursors 3 have been synthesized, that bear one protected formyl group and one aldehyde selectively reactive in the first of the two Wittig reactions.

As an alternative approach, a direct coupling reaction has been proposed that forms the final molecule together with the central spacer. For instance, the molecule 1d is poorly soluble in common organic solvents, so that its synthesis according to the proposed precursor method is quite a problem. The coupling method, which requires a unique Wittig reaction, is then a straightforward method to synthesise 1d, as shown in Scheme 2.
Scheme 2

Symmetrical spacer precursors

Bis-(5-formyl-2-thienyl) sulfide 2a was prepared according to Fedorov’s procedure11 (Scheme 3). Di-2-thienyl sulfide 5a was formylated by metallation with BuLi in tetrahydrofuran (THF) and finally reacted with dimethylformamide (DMF).

Silane precursor 2b was prepared by the general method of carbon-silicon bond formation,12 i.e. coupling of organometallic compounds with chlorosilane derivatives (Scheme 3).

Dichlorodimethylsilane was reacted with compound 4 followed by in situ hydrolysis of the acetal with dilute HCl. It is worth pointing out that hydrolysis must be carried out carefully because of the very high sensitivity of the aromatic C-Si bond to high acidity13.

(E)-1,2-Bis(5-formyl-2-thienylethylene 2d was prepared by metallation of (E)-1,2-di-2-thiénylethylene 5d followed by reaction with dry DMF according to the procedure used for the synthesis of 2a. This result shows that the double bond (X: -CH=CH-) does not react with BuLi at low temperature, in spite of activation of the conjugation effect. It also appears that formylation of oligo(vinylidithiénylene) should be an efficient method for attaching a functional end-group and for increasing the length of conjugated segments by a Wittig-type condensation. This increase in chain length might be of interest for applications in the electronic and photonic domains, such as polymer conductors, organic light emitting diodes (LEDs) and third-order NLO materials.14,15
Chromophores from symmetrical spacer precursors

Chromophores 1a,b were first prepared by two successive Wittig reactions from the symmetrical precursors 2a,b (Scheme 4). In order to limit the undesired formation of the symmetrical compounds 7 in the first Wittig reaction, the ylide of 4-nitrobenzyl(triphenyl)phosphonium bromide was reacted with a twofold excess of spacer precursors 2a,b. In the case of silane spacer 2b, the ylide was first prepared by reaction with BuLi, since in situ generation of these ylides by lithium ethoxide is responsible for the rupture of the silane bond during the Wittig reaction. The resulting byproduct with the Si-OH moiety was characterized by a broad IR absorption band at 3400 cm$^{-1}$. For this reason, the ylide was prepared separately using BuLi, which is less reactive towards silane than alcoholate. Although BuLi can react with the nitro group as previously mentioned, no side reaction was observed, possibly due to the much lower pK$_a$ value of the phosphonium salt compared to that of thiophene.

Although 2 equiv. of 2a,b were used, the expected final product was contaminated by ca. 30% of the symmetrical product 7. It is also worth noting that the Wittig reaction applied to a ylide stabilized by conjugation is poorly stereoselective. Contaminant 7 was separated from 6 by chromatography on a silica gel column; the ratio of the cis/trans isomers of 6 remained unchanged. This ratio was measured by $^1$H NMR spectroscopy and found to be close to 3:2 in agreement with values currently reported for Wittig reactions in case of stabilized phenyl ylides (trans content: 50 ± 30%).

The second Wittig reaction was performed similarly, i.e. preparation of the ylide, which was then added to the aldehyde solution. Four geometrical isomers, trans-trans, trans-cis, cis-trans and cis-cis, were obtained even after purification by chromatography on silica gel. Characterization of the mixture by $^1$H NMR is quite a problem due to the overlapping of the signals of the aromatic and unsaturated protons [Fig. 1 (a) for X = -SiMe$_2$-].

The chromophore containing a central vinylene spacer 1d is actually a chromophore without any spacer, since the vinylene unit does not perturb the electronic conjugation all along the chain. In this case, the product formed by the first Wittig reaction is of a very limited solubility in common organic solvents, which prevents further purification and characterization.
Since the pure trans-isomer has the highest NLO response,\textsuperscript{19} it is important to transform the original cis/trans mixture into completely the trans configuration. To this end, the isomerization reaction by iodine deserves interest. This reaction is usually carried out in nitrobenzene.\textsuperscript{20,21} Due to the low thermal stability of the silane derivative, 1 was refluxed in the presence of a trace of iodine in nitrobenzene for only 5 min. Nevertheless, decomposition occurs with formation of a hydroxy compound as proved by IR spectroscopy. Substitution of xylene for nitrobenzene allows the olefin isomerization to take place after 1 h of reflux with no evidence of decomposition. Chromophores containing silane and sulfide spacers 1a, 1b have been isomerized to pure trans-olefins.

It has been observed that a high content of trans-isomer 1 can be obtained by isomerization of the crude reaction product independently of the addition of iodine, in the case where the aldehyde 6 has been isomerized with iodine just after the first Wittig reaction. This observation merely indicates that the catalytic amount of iodine has a masked affinity for the olefinic oligomers, since it is still active beyond the synthesis and purification of 6.
Although there is no report on the possible effect of additives on the second-order NLO response, evidence for the possible effect of iodine on the excited state energy might be found in the UV spectrum of the silane-containing chromophore \(1b\), in which an additional small absorption at 650 nm characteristic of the oligomer doped with iodine is recorded after isomerization by iodine.

The only way of avoiding the iodine treatment is the direct synthesis of the all-\(\text{trans}\) isomer chromophores, which is reported in the next section, together with the improvement of the efficiency of the first Wittig reaction.

**Fig. 1** \(^1\)H NMR spectra of the Wittig reaction products \(1b\). (a) Before isomerization, and (b) after isomerization with iodine. Assignment of the resonance peaks can be found in the Experimental section.

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**Synthesis of asymmetrical spacer precursors**

The use of asymmetrical precursors substituted by a protected formyl group \(3a-c\) instead of the previously used symmetrical precursors would prevent the final product from being contaminated by the symmetric oligomer 7.

The two first steps for the synthesis of the sulfide precursor \(3a\) (Scheme 5) are the same as for the synthesis of \(2a\), i.e. the symmetrical counterpart. Di-2-thienyl disulfide was reacted with 5-lithiothiophene-2-carbaldehyde dimethyl acetal 4 in order to reduce the disulfide to sulfide 8a. The yield of the recovered sulfide 8a is very low (18%), and may result from a secondary reaction between the acetal and the RS\(^-\) anion formed as a byproduct.\(^{22}\)

Since the disulfide reduction yield is low, a new strategy has been proposed for the synthesis of the precursor \(3a\). Sulfide 5a is first synthesized by reaction of 2-lithiothiophene with bis(phenylsulfonyl) sulfide as a coupling agent.\(^{23}\) Sulfide 5a can be converted to the mono-formyl compound by Vilsmeier reaction,\(^{11}\) followed by acetalization of the aldehyde by reaction with trimethyl orthoformate in the presence of toluene-P-sulfonic acid with formation of 8a. This second strategy uses easily controlled reactions and gives quite high yields.

**Scheme 6**

\[
\begin{align*}
\text{Scheme 6} & \\
\begin{array}{l}
\text{4} \quad \text{Li} + \text{Cl} \quad \text{Si-Cl} \quad \rightarrow \\
\downarrow \\
\text{8a} \\
\text{deacetalization}
\end{array}
\end{align*}
\]
Silane precursor 3b was synthesized in a two-step process. First, a threefold molar excess of dichlorodimethylsilane was reacted with 2-lithiothiophene. The monochlorosilane 9b was then separated from the starting materials and the symmetrical dithienyl silane by distillation in vacuo. The same coupling reaction was repeated, in which the monochlorosilane 9b is reacted with 5-lithiothiophene-2-carbaldehyde dimethyl acetal 4 in dry THF. Although the order of these two reactions might be reversed, the extreme instability of 5-chlorodimethylsillylthio-phene-2-carbaldehyde dimethyl acetal 10b in the presence of air makes this modification of no practical use. Indeed, the acetals 10b are easily prepared (Scheme 6) but they are rapidly decomposed with formation of HCl.

Scheme 7. Reagents: i: HCl ii: POCl₃, MFA iii: HC(OMe)₃/ H⁺ iv: BuLi

In addition to the spacers X able to modulate the chain conjugation, special attention was also paid to a completely saturated spacer that would completely prevent the electronic conjugation from being propagated. The methylene group (X = -CH₂-) was chosen for this purpose.

The general strategy proposed for the preparation of the methylene precursor consists of the preliminary synthesis of 11 (Scheme 7) followed by metallation with BuLi and reaction of the lithio derivative with DMF. However, metallation of the thiophene ring does not occur as desired. Actually, the methylene protons of 11 are expected to be acidic enough to react with BuLi and form an anion stabilized by the two thienyl substituents. For comparison, diphenylmethane has a pKₐ of 35. Thus a proton abstraction from the methylene spacer by BuLi competes the desired metallation of thiophene.

This acidity of the methylene spacer decreases the interest in any chromophore that contains it. Indeed, an electronic delocalization may occur with formation of a thiophene quinoidal structure (Scheme 8).

2,2-Di-2-thienylpropane 5c was prepared from thiophene and acetone with H₂SO₄ as a catalyst. Then, classical formylation and aldehyde protection led to 8c with very good yields (71 and 92%, respectively) (Scheme 5).

The last step in the synthesis of the spacer precursors 3a-c consists of the formylation of the thiophene ring of 8a-c by BuLi (Scheme 5). The intermediate product in the reaction of the organometallic compounds with DMF is easily hydrolysed by water with formation of a strongly basic solution. It is the reason why a careful neutralization with a dilute aqueous HCl solution is recommended for precursor 3b, so as to avoid the risk of breaking the C-Si bonds. Precursors 3a-c are finally isolated by chromatography on silica gel and characterized by ¹H NMR spectroscopy (see Experimental).
Chromophores from asymmetrical spacer precursors

The Wittig-Horner reaction has been proposed to build up the desired conjugated chains with high *trans* double bond content. Nevertheless, due to the exceedingly high stability of the intermediate compound formed by the addition of diethyl 4-dimethylaminobenzylphosphonate on the aldehyde in the Wittig-Horner reaction, the alkene linking the donor group to the thiophene-based chromophore must be formed by a classical Wittig reaction with the phosphonium derivative of the donor (Scheme 9). Recrystallization has proved to be a very efficient method for the separation of the *trans*- and *cis*-isomers of compounds 12a-c. Compounds 12a and 12c with the sulfide and the propane-2,2-diyl spacer, respectively, were easily recrystallized from ethanol-water, so that the pure *trans*-intermediates were easily isolated. For compounds with a silane spacer 12b, recrystallization was carried out from light petroleum and hexane at a low temperature (-20 °C) after chromatography on silica gel in order to eliminate the triphenylphosphine oxide byproduct.

Hydrolysis of the acetal is currently performed in an aqueous HCl solution at pH = 2-3. These conditions are suitable for chromophores containing stable spacers, such as sulfide and propane-2,2-diyl. The reaction is very rapid and complete within 5 min. In the presence of the carbon-silicon bonds, mild hydrolysis conditions must be used. For instance, aldehyde 12b was obtained in a 96% yield by using pyridinium toluene-**P**-sulfonate as catalyst for the hydrolysis.

In contrast to the synthesis of the NLO chromophores from the symmetrical precursors 2a,b, a Wittig-Horner reaction is now proposed to attach the nitro acceptor group to the oligomers 12a-c in mainly the *trans*-configuration. An excess of phosphonate anion is prepared separately by reaction of parent phosphonate with BuLi in dry THF. The aldehyde 12a-c is then transferred into the anion solution. Most often, the chromophore is easily recovered by precipitation of the crude reaction product into water, while the phosphonate salt remains soluble in water. In the particular case of chromophore 1b, the silane spacer could be decomposed by the basic solution of the excess of phosphonate anions. This explains why the chromophore containing a silane-type spacer 1b was purified differently, i.e. first by chromatography on silica gel in order to remove the phosphonate and other highly polar impurities, and then by recrystallization from light petroleum-hexane mixture.

All three synthesized NLO chromophores 1a-c have an excellent stereochemical purity, since the *cis*-isomer cannot be detected by 1H NMR analysis. In spite of a large number of protons in the aromatic region, all the protons were identified from the observed chemical shifts and coupling constants. The experimental chemical shifts and their assignments are given in the Experimental section.

Synthesis of the chromophore 1d by the coupling method

The NLO chromophore with a central vinylene ‘spacer’ 1d was synthesized as a standard for a completely conjugated chromophore. The strategy based on the asymmetrical precursor was first applied to the synthesis of 1d. The starting material was (E)-1,2-di-2-thienylethylene, which was prepared by the Wittig reaction of thiophene-2-carbaldehyde with thienyltriphenyl-phosphonium bromide in the presence of lithium ethoxide as a catalyst.28 Formylation by 1 mol of BuLi and DMF mainly forms the mono-substituted aldehyde 13. Whatever the experimental conditions, the acetalization of 13 has repeatedly failed. Upon the addition of a small amount (0.05 mol%) of an acid, i.e. toluene-*P*-sulfonic acid, no reaction occurs even at 50 °C for 2 h, although a rapid decomposition of the aldehyde is observed when the acid amount is increased up to ca. 1 mol%. Formation of a less stable quinoid-like structure by a proton addition could favour the occurrence of side reactions (Scheme 10).

This drawback has been avoided by using the coupling method illustrated in Scheme 11. 5-[(4-Dimethylaminophenyl)-(E)-vinyl]thienylmethyltriphenylphosphonium bromide 14 was synthesized as an electron donor containing a conjugated segment, according to the improved reaction of a phosphonium bromide with an alcohol as previously reported.29 5-[(4-Nitrophenyl)-(E)-vinyl]thiophene-2-carbaldehyde 1516 was...
considered as the reactive counterpart bearing the electron acceptor segment.

**Scheme 9**

The coupling reaction, which is nothing but a Wittig reaction, has led to the deep-red compound 1d. Due to the long conjugated chain and the trans double bond in each of the original conjugated segments, the solubility of 1d in common organic solvents is limited even for a chromophore containing the cis-isomer of the central vinylene spacer. Accordingly, recrystallization from ethanol or diethyl ether cannot be used as an efficient method for the separation of the cis- and trans-isomers. "H NMR shows two unsaturated signals with a 12 Hz coupling constant that corresponds to a cis: trans ratio of 2:3.

**Scheme 11**

Preliminary analysis of NLO properties

The NLO response of the four synthesized chromophores was measured in CHCl₃ solution by hyper-Rayleigh scattering (HRS)³⁰ (Table 1). The range of β modulation by the spacer effect varies from 150×10⁻³⁰ to 218×10⁻³⁰ esu, which suggests that the first hyperpolarizability can be improved by choosing a proper spacer with a moderate red-shift in UV absorption. The large difference in β values between, e.g. the sulfide-spacer-based chromophore and the completely conjugated chromophore (more than ten times higher than the sulfide spacer) indicates that the NLO properties could be modulated by spacers. The four chromophores under investigation have higher β values than that of P-nitroaniline (PNA, β_HRS = 23×10⁻³⁰ esu)³⁰. The β_HRS value of the NLO chromophore ‘without spacer’ (X: -CH=CH-) is very high. This effect may be explained by the complete conjugation that increases the hyperpolarizability, and by the resonance mode since the doubled frequency of the laser used for measurements (1064-532 nm) is rather close to the chromophore absorption (λ_max 487 nm). The NLO properties will be discussed in detail in another paper, in parallel with theoretical calculations according to the INDO/CI-SOS methods.

**Conclusions**

Various synthetic strategies all based on a Wittig-type condensation reaction have allowed four NLO chromophores to be synthesized with a high stereoselectivity. In this respect, superiority of the asymmetric precursor method must be outlined. Thanks to their solubility in common organic solvents, separation of the cis-trans-isomers 1a-c, as prepared by a Wittig reaction, was successfully carried out by a selective recrystallization
except for the completely conjugated chromophore 1d, the solubility of which is intrinsically limited. This chromophore 1d was synthesized in a one-step coupling reaction of two mutually reactive segments, one bearing the electron donor group and the second one the electron acceptor group. The NLO properties of the novel chromophores were also measured and the preliminary results have demonstrated the possibility of modulating the NLO properties by the insertion of central spacers. The increase in conjugated length by the incorporation of additional thienylene-(E)-vinylene units on both sides of the spacer will be the topic of the forthcoming papers.

### Table 1. Properties of NLO chromophores with spacers 1a-d

<table>
<thead>
<tr>
<th>Spacer</th>
<th>-C(Me)₂</th>
<th>-Si(Me)₂</th>
<th>-S-</th>
<th>-CH=CH-</th>
</tr>
</thead>
<tbody>
<tr>
<td>µ/Debye</td>
<td>6.1</td>
<td>5.0</td>
<td>7.1</td>
<td>6.4</td>
</tr>
<tr>
<td>βHRS(10⁻³ esu)</td>
<td>150</td>
<td>180</td>
<td>218</td>
<td>2980</td>
</tr>
<tr>
<td>λ_max/nm</td>
<td>377</td>
<td>376</td>
<td>388</td>
<td>487</td>
</tr>
<tr>
<td>(eV)</td>
<td>(3.29)</td>
<td>(3.30)</td>
<td>(3.19)</td>
<td>(2.54)</td>
</tr>
</tbody>
</table>

*1064 nm, in CHCl₃ solution.

### Experimental

#### Materials

Thiophene (99+%), thiophene-2-carbaldehyde (98%), BuLi (2.5 M in hexane) and dichlorodimethylsilane (99%) were purchased from Janssen Chimica, Belgium. THF was refluxed over sodium-benzophenone and distilled just before use. Di-2-thienyl sulfide, di-2-thienyl disulfide, thiophene-2-carb-aldehyde dimethyl acetal, 4-dimethylaminobenzyl(triphenyl)-phosphonium bromide, 4-nitrobenzyl(triphenyl)phosphonium bromide, diethyl 4-nitrobenzylphosphonate, di-2-thienylethylene and bis(phenylsulfonyl) sulfide were prepared according to the cited references.

#### Characterization and purification

The new compounds were characterized by ¹H NMR and FTIR. NMR spectra were recorded in CDC1₃ using tetramethylsilane (TMS) as a reference with Bruker AM400 apparatus; J values in Hz. IR spectra were recorded with a Perkin-Elmer FT-1600 spectrometer, and samples were prepared by solvent casting on a KBr crystal. Purification was achieved by chromatography on silica gel: 0.5 g samples were eluted through a column filled with 25 g of silica gel (Merck 63-200 µm ref. 7734). The final purity was ascertained by thin-layer chromatography (TLC) and high performance liquid chromatography (HPLC) (Waters 600 with detector 486).

#### General procedure for preparation of acetals

The aldehyde (0.5 g) was added to trimethyl orthoformate (10 ml) at room temp. A catalytic amount of toluene-p-sulfonic acid monohydrate (5 to 10 mg) was then added slowly. The reaction medium was neutralized with Na₂CO₃ after 1 h reaction at the same temperature. The acetal was recovered by distillation under vacuum within high yields (>90%).

#### General procedure of formylation via metallation

This formylation procedure has been reported. The thiophene derivatives were dried by azeotropic distillation (∗3) with previously dry toluene under N₂. Dry THF was added as solvent and cooled down to -60 °C. BuLi (0.8 M) was transferred to the reaction medium with a syringe. Then dry DMF or N-formylpiperidine (200% based on thiophene derivatives) was added to the solution at 0 °C. After 1 h, the aldehyde was recovered by precipitation into water. Due to their high molecular mass, the synthesized molecules could not be purified by distillation in vacuo. Chromatography on silica gel was successfully used for a purification method of the precursors usually by using an ethyl acetate-hexane (1:4 v/v) mixture as eluent.

#### General synthesis of the symmetrical precursors by Wittig reactions (Scheme 4)

The phosphonium salt (0.015 mol) and the precursor aldehyde (0.01 mol) were separately dried by azeotropic distillation with dry toluene. The precursor was then dissolved in dry THF and the phosphonium salt dispersed in the same solvent. BuLi (0.015 mol) was first added to the phosphonium salt at -30 to -40 °C. The temperature...
was allowed to rise to room temp. for 30 min, before the aldehyde solution in THF was added. After 2 h, the solvent was removed and the crude product was purified by chromatography on silica gel with ethyl acetate-hexane (1:4 v/v) as eluent.

The second Wittig reaction in the preparation of the NLO chromophores from the intermediate 6 was performed by the same procedure.

**Isomerization by iodine**

A small pellet of iodine (<1 mg) was added at 130 °C to a xylene solution (20 ml) containing 0.6 g of the sample to be isomerized. After 1 h reflux, the mixture was allowed to cool to room temp. and the isomerized sample was recrystallized from hexane (100 ml). The product was filtered and dried. Yields were in the range of 56-81%.

**Bis(5-formyl-2-thienyl) sulfide 2a**

Di-2-thienyl sulfide 5a (4.0 g, 0.0202 mol) was formylated by metallation with BuLi (2.5 M, 18 ml) in THF (120 ml) and then reaction with 4.0 ml of dry DMF. Ethyl acetate-hexane (1:1) was used as eluent for chromatography on silica gel. The diformyl compound was isolated in 63% yield. δ_H 9.83 (2 H, s), 7.66 (2 H, d), 7.28 (2 H, d), v/cm^-1 3080, 2821, 2733, 1668, 1650, 1412, 1220, 1196, 1066, 989, 801, 749, 665.

**Bis(5-formyl-2-thienyl)dimethylsilane 2b**

A solution of 5-lithiothiophene-2-carbaldehyde dimethyl acetal was prepared by metallation of thiophene-2-carbaldehyde dimethyl acetal (15 g, 0.095 mol) with BuLi (2.5 M, 38 ml) in dry THF at -78 °C. To this was added 5.7 g (0.0475 mol) of freshly distilled dichlorodimethylsilane at -78 °C. The temperature was allowed to increase to room temp, for 30 min. Then, the solution of the acetal was hydrolysed with 0.1 M HCl at pH 4-5 for 5 min. The product was recovered by precipitation in water and purified by chromatography on silica gel with 1:1 ethyl acetate-hexane as eluent. (Yield, 67%).

δ_H 9.96 (2 H, s), 7.82 (2 H, d), 7.39 (2 H, d); δ_H 0.724 (6 H, s), v/cm^-1 3089, 2959, 2845, 1664, 1511, 1426, 1254, 1056, 992, 813, 790, 760, 669.

**(E)-1,2-Bis(5-formyl-2-thienyl)ethene 2d**

This compound was prepared from (E)-1,2-di-2-thienylethene by metallation, followed by reaction with DMF as reported for 2a (yield, 69%), δ_H 9.89 (2 H, s), 7.69 (2 H, d), 7.24 (2 H, s), 7.22 (2 H, d), v/cm^-1 3082, 1652, 1456, 1229, 1046, 949, 808, 669.

**5-Formyl-2-thienyl 5'-dimethoxymethyl-2'-thienyl sulfide 3a**

**Method 1.** Di-2-thienyl disulfide (1.74g, 7.6 mmol), previously dried by azeotropic distillation with toluene, was added to a solution of 5-lithiothiophene-2-carbaldehyde dimethyl acetal 4 (0.0106 mol) in THF at -78 °C. The mixture was warmed to room temp., stirred for 3 h, and then poured into water. Compound 8a was recovered by extraction with diethyl ether, washed with water, dried over anhydrous Na_2SO_4 and finally distilled _in vacuo_ (125 °C, 0.1 mmHg): yield, 18%.

**Method 2.** Di-2-thienyl sulfide 5a (3.1 g, 0.016 mol) was mixed with POCl_3 (3.12 g, 0.02 mol) and N-methylformanilide (2.75 g, 0.02 mol) at 0 °C. After a slight release of HCl, the solution was heated to room temp. and stirred overnight. The viscous mixture was quenched by adding ice and extracted with diethyl ether. The extracted product was washed and dried, and the diethyl ether removed. The aldehyde was purified by distillation (yield: 82%). The acetalization procedure is the same as described above. Compound 8a was obtained in 91% yield by distillation _in vacuo_ (126 °C, 0.1 mmHg).

Compound 8a was reacted with BuLi and DMF to produce the precursor 3a following the standard procedure detailed above (yield: 55%), δ_H 9.74 (1 H, s), 7.57 (1 H, d), 7.27 (1 H, d), 7.04 (2 H, d), 5.60 (1 H, s), 3.37 (6 H, s), v/cm^-1 3086, 2934, 2829, 1666, 1414, 1223, 1179, 1094, 1055, 973, 801, 667.

**5-Formyl-2-thienyl-(5 '-dimethoxymethyl-2 '-thienyl )-dimethylsilane 3b**

Thiophene (2.6 g, 0.031 mol), distilled from CaH_2, was metallated with BuLi (2.5 M, 12.5 ml) in dry THF (65 ml) under N_2 at 0 °C for 30 min. The solution was added dropwise to dichlorodimethylsilane (12 g, 0.09 mol) under vigorous stirring at room temp. The reaction was very rapid and followed by distillation of solvent and
unreacted reagents under reduced pressure. The monochlorosilane 9b was finally purified by distillation (37 °C, 0.1 mmHg): yield, 58%.

5-Lithiothiophene-2-carbaldehyde dimethyl acetal (0.025 mol) in THF (60 ml) was added to the monochlorosilane 9b (4.5 g, 0.025 mol) at -78 °C. The temperature was first increased to room temp., and the solution was then poured into water and extracted with diethyl ether. The ethereal phase was washed with water and dried over anhydrous Na$_2$SO$_4$. After solvent removal, the acetal 8b was distilled in vacuo (105 °C, 0.1 mmHg): yield, 70%. $\delta_H$ 7.60 (1 H, d), 7.20 (2 H, d), 7.16 (1 H, d), 7.09 (1 H, d), 5.65 (1 H, s), 3.37 (6 H, s), 0.62 (6 H, s), v/cm$^{-1}$ 3062, 2930, 2885, 1530, 1400, 1251, 1210, 1187, 1090, 1061, 981, 832, 786, 671.

Compound 3b was prepared by the standard formylation procedure via metallation of 8b (final yield: 91%). $\delta_H$ 9.91 (1 H, s), 7.79 (1 H, d), 7.36 (1 H, d), 7.20 (1 H, d), 7.13 (1 H, d), 5.65 (1 H, s), 3.36 (6 H, s), 0.663 (6 H, s), v/cm$^{-1}$ 3070, 2972, 2801, 1667, 1527, 1436, 1436, 1216, 1038, 850, 811, 760, 700, 666.

**2-(2-Thienyl)-2-(5'-dimethoxymethyl-2'-thienyl) propane and 2-(5-formyl-2-thienyl)-2-(5'-dimethoxymethyl-2'-thienyl) propane 8c and 3c**

The same procedure as used for the synthesis of 3a (method 2) was implemented with 2,2-di-2-thienylpropane instead of di-2-thienyl sulfide.

8c: yield, 92%, $\delta_H$ 7.31 (1 H, d), 6.89 (1 H, d), 6.86 (2 H, m), 6.73 (1 H, d), 5.54 (1 H, s), 3.35 (6 H, s), 1.83 (6 H, s), v/cm$^{-1}$ 3072, 2969, 2829, 1682, 1478, 1348, 1186, 1095, 1053, 975, 904, 850, 802, 698.

3c: yield, 70%, $\delta_H$ 9.82 (1 H, s), 7.59 (1 H, d), 6.97 (1 H, d), 6.89 (1 H, d), 6.80 (1 H, d), 5.56 (1 H, s), 3.36 (6 H, s), 1.85 (6 H, s), v/cm$^{-1}$ 3103, 2972, 2801, 1667, 1527, 1446, 1366, 1216, 1038, 850, 811, 760, 700, 666.

**Wittig reaction for the synthesis of intermediates 12a-c**

The Wittig reaction previously used for the synthesis of the symmetrical precursors 2a-c was considered. A typical preparation of the intermediates 12a-c was as follows for the particular case of the silane spacer 12b. The precursor 3b (0.5 g, 0.0016 mol) and 4-dimethylaminobenzyl(triphenyl)phosphonium bromide (0.00234 mol, 1.0 g) were separately dried under vacuum and dissolved in dry THF. BuLi (1.3 M, 1.3 ml) was added to the phosphonium suspension at -30 to -40 °C, and the ylide solution formed was slowly warmed in vacuo at 40 °C for 30 min., and then added to 80 ml of dry THF. The ylide solution was transferred to the ylide solution with vigorous stirring. After 2 h, the solvent was removed and the crude product was purified by chromatography on silica gel with ethyl acetate-hexane (1:4 v/v) as eluent. Final hydrolysis in acetone (40 ml) containing pyridinium toluene-sulfonate (50 mg in 10 ml water) for 2 h at room temp. released the almost completely essentially trans-2a-c: yield, 60%. $\delta_H$ 9.74 (1 H, s), 7.58 (1 H, d), 7.35 (2 H, d), 7.22 (1 H, d), 7.04 (1 H, d), 6.95 (1 H, d), 6.91 (1 H, d), 6.86 (1 H, d), 6.69 (2 H, d), 3.00 (6 H, s), v/cm$^{-1}$ 3080, 2885, 2806, 1651, 1601, 1526, 1418, 1359, 1227, 1200, 1063, 949, 810, 752, 666.

5-Formyl-2-thienyl-5-[4-(dimethylaminophenyl)-(E)-vinyl]-2-thienyl sulfide 12a: yield, 47%. $\delta_H$ 9.95 (1 H, s), 7.80 (1 H, d), 7.39 (2 H, d), 7.33 (1 H, d), 7.20 (1 H, d), 7.12 (1 H, d), 7.09 (1 H, d), 7.07 (2 H, d), 6.90 (1 H, d), 3.01 (6 H, s), 0.67 (6 H, s), v/cm$^{-1}$ 3054, 2954, 1673, 1605, 1524, 1425, 1358, 1252, 1202, 1061, 990, 948, 833, 806, 781, 761.

2-(5-Formyl-2-thienyl)-2-[5-[4-(dimethylaminophenyl)-(E)-vinyl]-2-thienyl] propane 12c: yield, 69%. $\delta_H$ 9.83 (1 H, s), 7.60 (1 H, d), 7.32 (2 H, d), 6.99 (1 H, d), 6.95 (1 H, d), 6.78 (3 H, m), 6.68 (1 H, d), 2.97 (6 H, s), 1.86 (6 H, s), v/cm$^{-1}$ 3070, 2969, 2802, 1667, 1604, 1520, 1445, 1359, 1217, 947, 809, 668.

**Wittig-Horner reaction for the synthesis of NLO chromophores 1a-c** (Scheme 9)

As a representative example, a typical procedure for the synthesis of the silane-containing chromophore 1b is as follows. The intermediate 12b (0.48 g, 0.0012 mol) and diethyl 4-nitrobenzylphosphonate (0.50 g, 0.0018 mol) were dried separately under vacuum and dissolved in dry THF (50 ml × 2). BuLi (1.3 M, 1.3 ml) was added dropwise to the phosphonate solution at -78 °C for 5 min and the solution was then slowly warmed to room temp. (about 30 min). Compound 12b in THF was transferred into the anion solution at room temp. After 2 h,
the solvent was removed and the product was purified by chromatography on silica gel with ethyl acetate-hexane (1:4 v/v) as eluent. Compound \( \text{lb} \) was finally recrystallized from the same solvent mixture at -20 °C (yield, 67%).

5-[(4-Nitrophenyl)-(\( E \))-vinyl]-2-thienyl 5-[(4-dimethylamino-phenyl)-(\( E \))-vinyl]-2-thienyl sulfide (la): yield, 61% (Found: C, 63.64; H, 4.87; N, 5.55; S, 19.48. Calc: C, 63.65; H, 4.52; N, 5.71; S, 19.6%). \( \delta \)H 8.18 (2 H, d), 7.53 (2 H, d), 7.26 (1 H, d), 7.14 (1 H, d), 7.07 (1 H, d), 6.99 (1 H, d), 6.93 (1 H, d), 6.85 (1 H, d), 6.83 (1 H, d), 6.82 (1 H, d), 6.67 (2 H, d), 2.98 (6 H, s). v/cm\(^{-1}\) 3010, 2919, 2850, 1594, 1506, 1361, 1340, 1226, 1110, 1060, 945, 812, 792, 748, 688.

5-[(4-Nitrophenyl)-(\( E \))-vinyl]-2-thienyl-5-[(4-dimethylaminophenyl)-(\( E \))-vinyl]-2-thienyl dimethylsilane (lb): yield, 67% (Found: C, 65.12; H, 5.94; N, 5.42; S, 12.29. Calc: C, 65.08; H, 5.46; N, 5.42; S, 12.41%). \( \delta \)H 8.19 (2 H, d), 7.57 (2 H, d), 7.41 (1 H, d), 7.35 (2 H, d), 7.25 (2 H, d), 7.23 (1 H, d), 7.20 (1 H, d), 7.06 (2 H, m), 6.98 (1 H, d), 6.91 (1 H, d), 6.69 (2 H, d), 2.98 (6 H, s), 0.65 (6 H, s). v/cm\(^{-1}\) 3017, 2953, 1621, 1604, 1514, 1358, 1338, 1067, 990, 947, 830, 808, 779.

Wittig reaction for the synthesis of 1-[(5-[4-(4-nitrophenyl)-(\( E \))-vinyl]-2-thienyl)-2-5-[4-(dimethylaminophenyl)-(\( E \))-vinyl]-2-thienyl]ethene (ld)

5-[(4-Nitrophenyl)-(\( E \))-vinyl]thiophene-2-carbaldehyde (0.31 g, 0.0012 mol) and 5-[(4-dimethylamino-phenyl)-(\( E \))-vinyl]thienyl-methyl(triphenyl)phosphonium bromide (0.8 g, 0.00137 mol) were added to 50 ml of dry THF. Lithium ethoxide (0.4 M; 5.0 ml) was then added to the vigorously stirred suspension at room temp. After 2 h, the product was recovered by precipitation with ethanol, and washed with diethyl ether: yield, 61% (Found: C, 69.90; H, 5.53; N, 5.84; S, 12.76. Calc: C, 69.39; H, 4.99; N, 5.78; S, 13.23%). \( \delta \)H 8.19 (2 H, d), 7.57 (2 H, d), 7.34 (2 H, d), 7.33 (1 H, d), 7.16 (1 H, d), 7.09 (2 H, d), 7.02 (1 H, d), 7.00-6.80 (ca. 4 H, m), 6.68 (2 H, d), 2.99 (6 H, s), 1.85 (6 H, s). v/cm\(^{-1}\) 3072, 2967, 2802, 1620, 1603, 1589, 1336, 1109, 946, 863, 809, 746, 688.

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