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

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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.

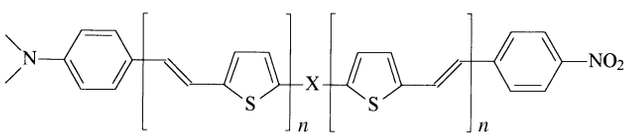
Introduction

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,[1] the poor performance of present NLO materials limits this. Inorganic materials are known for this low NLO response,[2] and organic NLO materials have a low degree of supramolecular organization and/or absorb strongly in the UV–VIS region.[3]

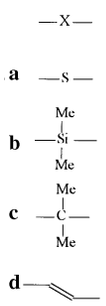
As a result of intensive research efforts, some fundamental relationships between properties and the molecular structure of NLO organic materials have emerged. For instance, second-order NLO chromophores need a push–pull structure, which means that π–π conjugated segments must be end-functionalized by 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[4] 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.[5] Zyss[6] and Moylan[7] 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[8,9] have dealt with conjugated chains containing a spacer other than a π–π electronic conjugated bridge. They have shown that the incorporation of the σ–σ and σ–π conjugations has no deleterious effect on NLO properties, whereas it might result in a very high damage threshold working in the off-resonance mode.[10]

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.



1 ***a–d***



Scheme 1

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

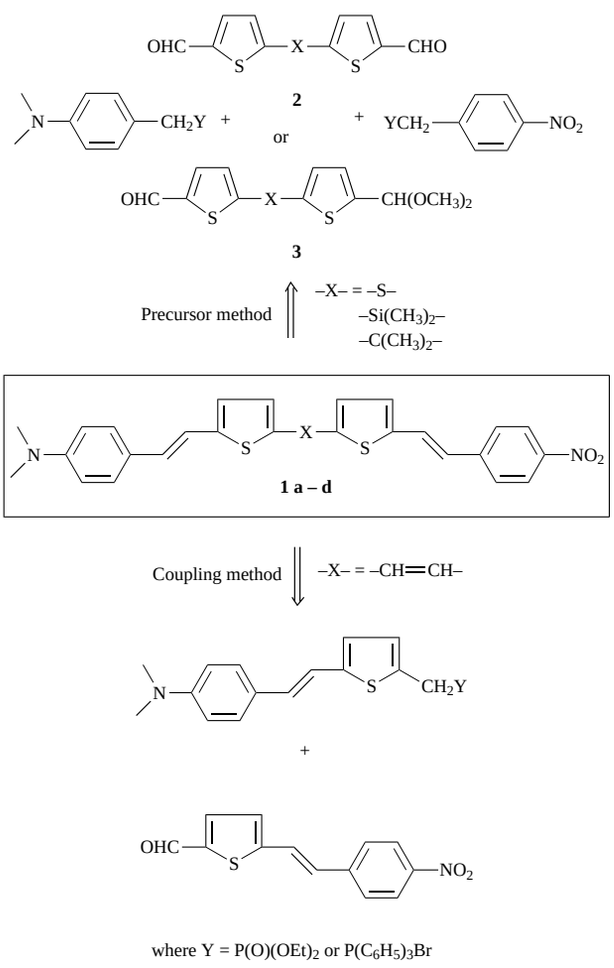
within the conjugated chain is expected to improve solubility in common solvents, to facilitate processing and to displace the UV absorption far away from the visible light region.

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.



Scheme 2

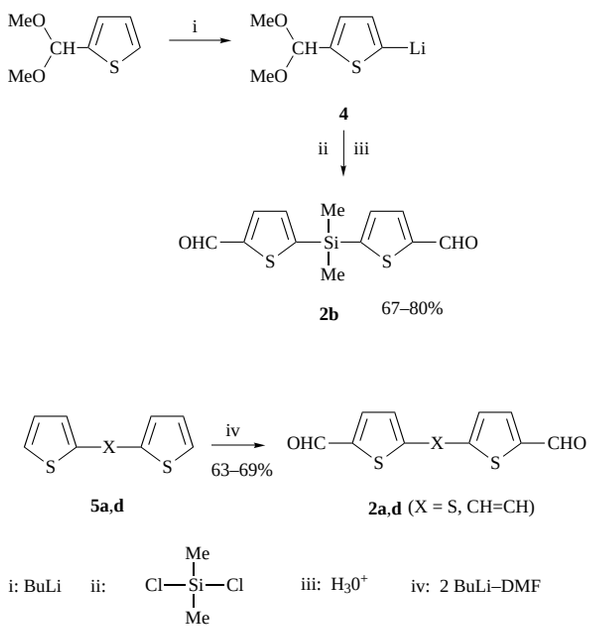
The spacer precursors are just the spacer attached to two thiophene rings. The symmetrical precursors **2** are substituted by two identical formyl groups and are easy to prepare. However, their use in the first Wittig reaction might lead to the formation of symmetrical byproducts. In order to prevent 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.

Symmetrical spacer precursors

Bis-(5-formyl-2-thienyl) sulfide **2a** was prepared according to Fedorov's procedure[11] (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).



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 acidity.[13]

(*E*)-1,2-Bis(5-formyl-2-thienyl)ethylene **2d** was prepared by metallation of (*E*)-1,2-di-2-thienylethylene **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(vinylenethienylene) 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

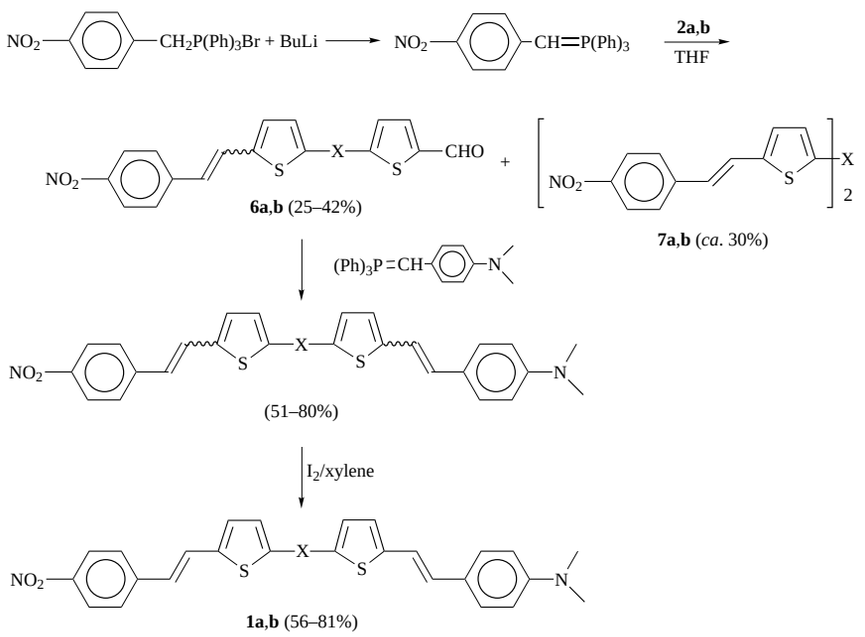
Chromophores **1a**,**b** were first prepared by two successive Wittig reactions from the symmetrical precursors **2a**,**b** (Scheme 4). In order to limit the undesired formation of the symmetrical compounds **7** in the first Wittig reaction, the ylide of 4-nitrobenzyl(triphenyl)phosphonium bromide 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,[16] no side reaction was observed, possibly due to the much lower pK_a value of the phosphonium salt compared to that of thiophene.[17]

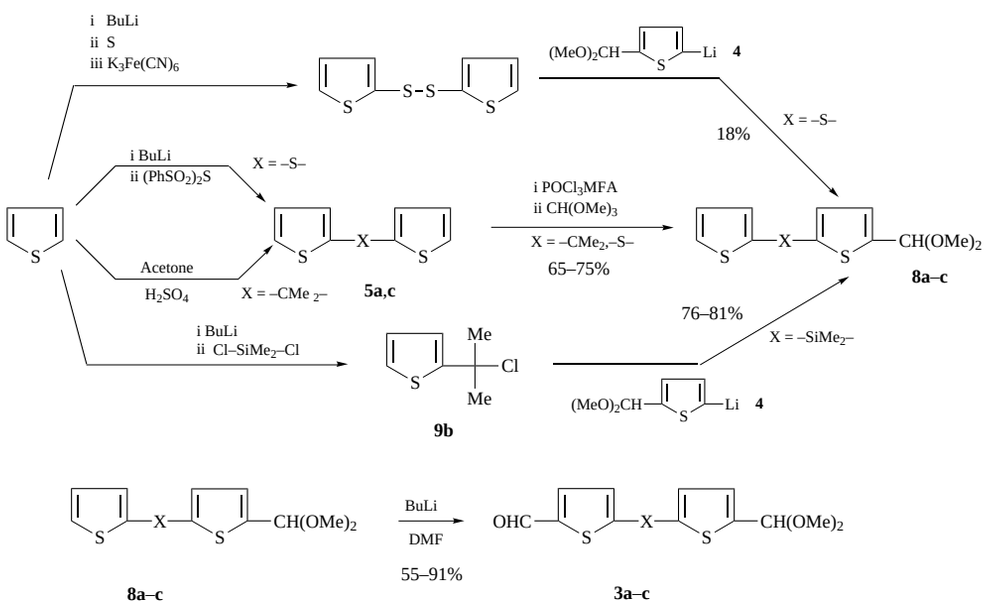
Although 2 equiv. of **2a**,**b** were used, the expected final product was contaminated by *ca.* 30% of the symmetrical product **7**. It is also worth noting that the Wittig reaction applied to a ylide stabilized by conjugation is poorly stereoselective.[18] Contaminant **7** was separated from **6** 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%).[18]

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.



Scheme 4



Scheme 5

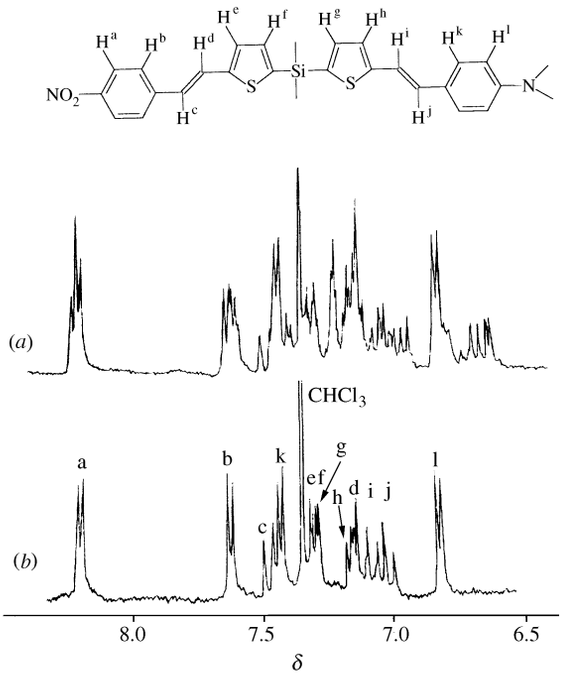


Fig. 1 ^{1}H NMR spectra of the Wittig reaction products **1b**. (*a*) Before isomerization, and (*b*) after isomerization with iodine. Assignment of the resonance peaks can be found in the Experimental section.

Since the pure *trans*-isomer has the highest NLO response,[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.[20,21] Due to the low thermal stability of the silane derivative, **1b** 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-*trans* isomer chromophores, which is reported in the next section, together with the improvement of the efficiency of the first Wittig reaction.

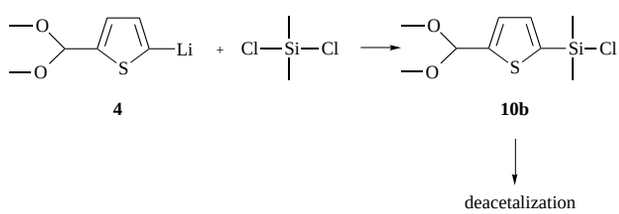
Synthesis of asymmetrical spacer precursors

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.

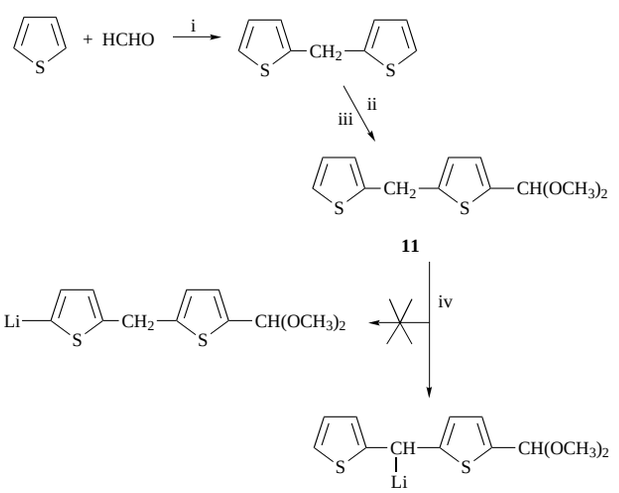
Silane precursor **3b** was synthesized in a two-step process. First, a threefold molar excess of dichlorodimethylsilane was reacted with 2-lithiothiophene. The monochlorosilane **9b** was then separated from the starting materials and the symmetrical dithienyl silane by distillation *in vacuo*. The 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-chlorodimethylsilylthiophene-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.[24]



Scheme 6

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 = $-CH_2-$) 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

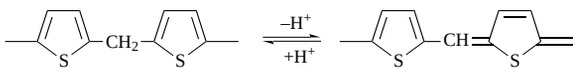


Scheme 7 *Reagents*: i: HCl ii: $POCl_3$, MFA iii: $HC(OMe)_3/H^+$ iv: BuLi

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 pK_a of 35.[25] 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).[26] A more suitable spacer for isolating the conjugated system completely could be found in a substituted methylene group, such as the propane-2,2-diyl group (X = −CMe$_2$−).



Scheme 8

2,2-Di-2-thienylpropane **5c** was prepared from thiophene and acetone with H_2SO_4 as a catalyst.[27] 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 ^{1}H 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,[16] 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.

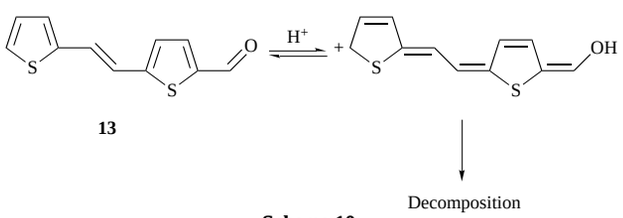
Hydrolysis of the acetal is currently performed in an aqueous HCl solution at pH = 2–3. These conditions are suitable for chromophores containing stable spacers, such as sulfide and propane-2,2-diyl. The reaction is very rapid and complete within 5 min. In the presence of the carbon–silicon bonds, mild 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 ^{1}H 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.

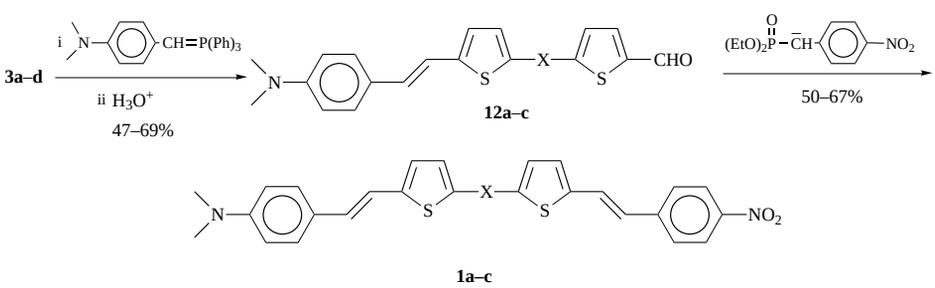
Synthesis of the chromophore 1d by the coupling method

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 thienyltriphenylphosphonium 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).

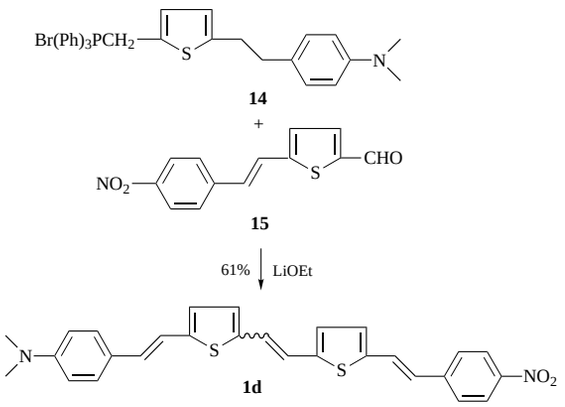


Scheme 10

This drawback has been avoided by using the coupling method illustrated in Scheme 11. 5-[(4-Dimethylaminophenyl)-



Scheme 9



Scheme 11

(*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 **15**[16] was considered as the reactive counterpart bearing the electron acceptor segment.

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. ^{1}H NMR shows two unsaturated signals with a 12 Hz coupling constant that corresponds to a *cis*:*trans* ratio of 2:3.

Preliminary analysis of NLO properties

The NLO response of the four synthesized chromophores was measured in $CHCl_3$ 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, $\beta_{HRS} = 23 \times 10^{-30}$ 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[31] 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**

Spacer	−C(Me)$_2$−	−Si(Me)$_2$−	−S−	−CH=CH−
μ/Debye	6.1	5.0	7.1	6.4
β_{HRS}[a] (10^{-30} esu)	150	180	218	2980
λ_{max}/nm (eV)	377 (3.29)	376 (3.30)	388 (3.19)	487 (2.54)

[a] 1064 nm, in $CHCl_3$ 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,[11,23] di-2-thienyl disulfide,[11] thiophene-2-carbaldehyde dimethyl acetal,[16] 4-dimethylaminobenzyl(triphenyl)-phosphonium bromide,[29] 4-nitrobenzyl(triphenyl)phosphonium bromide,[32] diethyl 4-nitrobenzylphosphonate,[33] (*E*)-1,2-di-2-thienylethylene[28] and bis(phenylsulfonyl) sulfide[23] were prepared according to the cited references.

Characterization and purification

The new compounds were characterized by ^{1}H NMR and FTIR. NMR spectra were recorded in $CDCl_3$ 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 Na_2CO_3 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.[16] The thiophene derivatives were dried by azeotropic distillation (× 3) with previously dry toluene under N_2. 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), $\tilde{\nu}$/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); 0.724 (6 H, s), ν/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), ν/cm^{-1} 3082, 1652, 1456, 1229, 1046, 949, 808, 668.

5-Formyl-2-thienyl 5′-dimethoxymethyl-2′-thienyl sulfide 3a

Method 1. Di-2-thienyl disulfide (1.74 g, 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), ν/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_2SO_4. After solvent removal, the acetal **8b** was distilled *in vacuo* (105 °C, 0.1 mmHg): yield, 70%. δ_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), ν/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%). δ_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), ν/cm^{-1} 3060, 2957, 2830, 2732, 1674, 1512, 1425, 1345, 1254, 1214, 1182, 1094, 1060, 996, 834, 808, 782, 668.

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%, δ_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), ν/cm^{-1} 3072, 2969, 2829, 1682, 1478, 1348, 1186, 1095, 1053, 975, 904, 850, 802, 698.

3c: yield, 70%, δ_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), ν/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 (0.002 34 mol, 1.0 g) were separately dried *in vacuo* at *ca.* 40 °C for 30 min., and then added to 80 ml of dry THF. BuLi (2.5 M, 1.0 ml) was added to the phosphonium suspension at −30 to −40 °C, and the ylide solution formed was slowly warmed to room temp. for 30 min. The solution of **3b** 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-*p*-sulfonate (50 mg in 10 ml water) for 2 h at room temp. released the almost completely essentially *trans*-aldehyde **12b**. Compound **12b** was finally purified by recrystallization from hexane–light petroleum (EtOH–H_2O for **12a**,**c**) at −20 °C (yield: 47%).

5-Formyl-2-thienyl 5-[(4-dimethylaminophenyl)-(*E*)-vinyl]-2-thienyl sulfide **12a**: yield, 60%. δ_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), ν/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-thienyldimethylsilane **12b**: yield, 47%. δ_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), ν/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%. δ_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), ν/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 **1b** was finally recrystallized from the same solvent mixture at −20 °C (yield, 67%).

5-[(4-Nitrophenyl)-(*E*)-vinyl]-2-thienyl 5-[(4-dimethylaminophenyl)-(*E*)-vinyl]-2-thienyl sulfide (**1a**): 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%). δ_H 8.18 (2 H, d), 7.53 (2 H, d), 7.33 (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). ν/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 (**1b**): 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%). δ_H 8.19 (2 H, d), 7.57 (2 H, d), 7.41 (1 H, d), 7.35 (2 H, d), 7.25 (1 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). ν/cm^{-1} 3017, 2953, 1621, 1604, 1514, 1358, 1338, 1067, 990, 947, 830, 808, 779.

2-{5-[(4-Nitrophenyl)-(*E*)-vinyl]-2-thienyl}-2-5-[(4-dimethylaminophenyl)-(*E*)-vinyl]-2-thienyl}propane (**1c**): yield, 50% (Found: C, 69.68; H, 6.11; N, 5.61; S, 12.89. Calc: C, 69.57; H, 5.64; N, 5.60; S, 12.81%). δ_H 8.18 (2 H, d), 7.52 (2 H, d), 7.31 (3 H, m), 6.98 (1 H, d), 6.96 (1 H, d), 6.84 (1 H, d), 6.82 (1 H, d), 6.78 (2 H, m), 6.76 (1 H, d), 6.68 (2 H, d), 2.97 (6 H, s), 1.85 (6 H, s). ν/cm^{-1} 3072, 2967, 2802, 1620, 1603, 1589, 1336, 1109, 946, 863, 809, 746, 688.

Wittig reaction for the synthesis of 1-{5-[(4-nitrophenyl)-(*E*)-vinyl]-2-thienyl-2-5-[(4-dimethylaminophenyl)-(*E*)-vinyl]-2-thienylethene (1d)

5-[(4-Nitrophenyl)-(*E*)-vinyl]thiophene-2-carbaldehyde (0.31 g, 0.0012 mol) and 5-[(4-dimethylaminophenyl)-(*E*)-vinyl]thienylmethyl(triphenyl)phosphonium bromide (0.8 g, 0.001 37 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%). δ_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), 6.58 (*ca.* 0.4 H, d, *J* 11.9) and 6.48 (*ca.* 0.4 H, d, *J* 11.8) associated with *cis*-double bond in the middle of the molecule). ν/cm^{-1} 2950, 1593, 1509, 1363, 1338, 1229, 1182, 947, 931, 865, 811, 793, 746, 688.

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