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Fine Tuning of the Electronic Properties of Linear π-Conjugated Oligomers by Covalent Bridging

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Abstract: A series of oligothienylenevinylenes, π-conjugated oligomers rigidified by ethylene bridges attached at different sites of the conjugated backbone, have been constructed by multistep synthetic methodologies. Electronic absorption spectra show that the rigidification of the conjugated system produces a bathochromic shift of the absorption maximum and a narrowing of the HOMO–LUMO energy gap, as compared to the spectra of an open-chain reference compound. The cyclic voltammograms of all oligomers show that these compounds can be reversibly oxidized into their cation radicals and dications and that rigidification produces a large negative shift of the first oxidation potential, which is indicative of a considerable increase of the HOMO level. Electrochemical data confirm that covalent bridging strongly affects the HOMO and LUMO levels and these data demonstrate that the sites of fixation of the bridges on the π-conjugated backbone exert a determining effect on the relative stability of the cation radical and dication. Examination of these various results in the light of theoretical calculations shows that in addition to a local control of bond length alternation, and hence of the HOMO–LUMO gap, the fixation of covalent bridges at selected positions of the π-conjugated system limits the deformation of the π-conjugated structure upon oxidation to the charged states.

Keywords: conjugation · electronic properties · oligomers · structure–property relationships · thiophene chemistry

Introduction

The control of the electronic properties of thiophene-based π-conjugated systems is currently subject to high interest motivated by the applications of these systems in organic devices such as field-effect transistors (OFETs), light-emitting diodes (OLEDs), and solar cells.[1–3] In this context, the structural control of quantities such as absorption and emission spectra, oxidation and reduction potentials, or luminescence efficiency represents a key issue. Since most of these parameters depend on the levels of the frontier orbitals and their energy gap, synthetic approaches aimed at the control of the HOMO–LUMO gap of conjugated polymers and oligomers and hence of the band gap of the resulting materials have received considerable research efforts during the past two decades.[4–8]

The HOMO–LUMO gap of linear π-conjugated systems containing (hetero)aromatic units is governed by various structural factors such as bond length alternation, planarity, aromatic resonance energy, and electronic effects of eventual substituents.[4] On these grounds, band-gap engineering has been developed along different approaches, such as the increase of the quinonoid character of the ground state as in poly(benzo[*c*]thiophene),[5] the introduction of electron-withdrawing groups on the π-conjugated backbone,[6] or the synthesis of conjugated systems containing alternant donor and acceptor groups.[7] Although this latter approach has led to conjugated polymers with the smallest optical band gaps known to date,[7] bulk heterojunction solar cells in which such low-band-gap polymers serve as donor material are still less efficient than those based on more "classical" polymers of the poly(*p*-phenylenevinylene) or poly(thiophene) series.[8] This limited success clearly underlines the need to pursue research aimed at the parallel development of strategies for band-gap engineering based on different synthetic principles.

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Supporting information for this article (^{1}H NMR spectra of compounds **3**, **4**, and **16c**, ^{13}C NMR spectrum of compound **3**) is available on the WWW under http://www.chemeurj.org/ or from the author.

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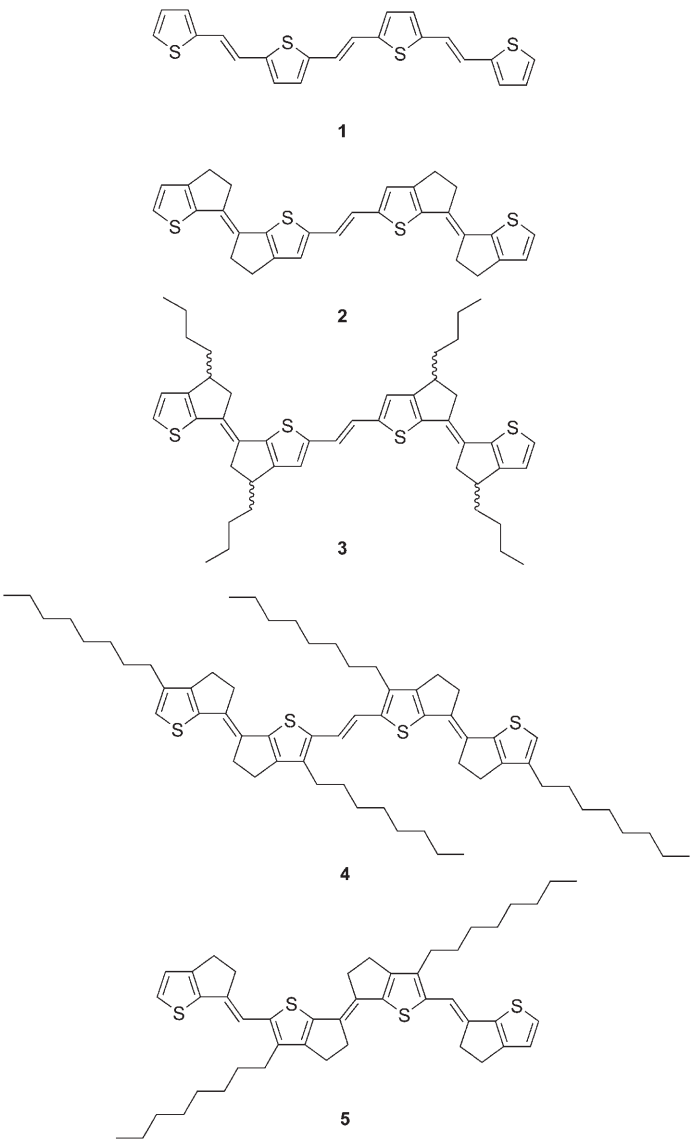
Extensive studies on oligothienylenevinylenes (nTVs) have shown that the limitation of rotational freedom and the reduction of overall aromaticity associated with the insertion of double bonds between thiophene rings confer on these systems the smallest HOMO–LUMO gap (ΔE) among extended π-conjugated oligomers.[9] On such as basis, nTVs represent a particularly interesting basic structure for the development of synthetic approaches aimed at fine control of the electronic properties of π-conjugated systems and of the corresponding molecular materials.

We have shown already that covalent bridging of the central double bond of dithienylethylene (DTE) leads to a significant reduction of the HOMO–LUMO gap of the molecule and of the band gap of the resulting polymers.[10] A particularly demonstrative illustration of the interest of this approach is provided by the threefold increase of the second-harmonic-generation efficiency of push–pull NLO-phores based on bridged-DTE conjugating spacers as compared to their open-chain analogues.[11]

As a further step, we describe here the synthesis of extended nTVs in which covalent fasteners have been introduced at various sites of the conjugated structure (**2**–**5**). Despite its conceptual simplicity, such a task requires the development of rather complex and tedious chemistry due to the need to 1) increase the solubility of the intermediate and final compounds and 2) define synthetic approaches allowing the fixation of the covalent bridges at various defined sites of the conjugated system.

The optical and electrochemical properties of these oligomers have been analyzed by UV/Vis spectroscopy and cyclic voltammetry and the relationships between the geometry of the π-conjugated structures and their electronic properties are discussed with the aid of theoretical calculations. It is shown that, through a proper choice of localization of the molecular fasteners and solubilizing side chains, it is possible to achieve fine tuning of the HOMO and LUMO levels and of their energy gap.



Results and Discussion

Synthesis: The reference open-chain compound **1** was synthesized as already reported.[9,12] Depending on their solubility, the various bridged oligothienylenevinylenes (**2**–**5**) were synthesized by either McMurry dimerization or Horner–Wadsworth–Emmons olefination with cyclic ketones **14a**–**c** as starting materials. The synthesis of **14a** and **14b** has already been described,[10c] while that of **14c** is depicted in Scheme 1. Bromination of 3-*n*-octylthiophene with bromine in the presence of a catalytic amount of iron powder gave 2,4,5-tribromo-3-octylthiophene (**6**) in 94% yield. 3-Bromo-4-*n*-octylthiophene (**7**) was obtained in 94% yield by treatment of **6** with two equivalents of *n*BuLi followed by addition of water. Reaction of **7** with CuCN in refluxing DMF[13] gave the nitrile derivative **8** in 97% yield. Aldehyde **9** was obtained in 93% yield by reduction of the nitrile group with DIBAl-H followed by hydrolysis. The carboxylic acid **13** was synthesized by two routes. Knoevenagel condensation of aldehyde **9** with malonic acid gave the acrylic acid derivative **10**, which was subsequently reduced to **13** in the presence of sodium amalgam. However, due to the hazards inherent in the large-scale use of this reagent, an alternative route was developed. Horner–Wadsworth–Emmons olefination of **9** with triethylphosphonoacetate in the presence of *n*-butyllithium gave ester **11**, which was then hydrogenated to give compound **12**. Saponification of the ester group followed by acidification gave acid **13** in an overall yield of 91%, based on **9**. The cyclic ketone **14c** was prepared from **13** either by direct intramolecular Friedel–Crafts acylation or by intermediate conversion of **13** into the corresponding acid chloride, with the latter two-step method giving better yields.

McMurry dimerization[14] of cyclopenta[*b*]thiophen-6-ones **14a**–**c** gave the various bridged DTEs **16a**–**c** (Scheme 2). Whereas compounds **16a** and **16b** were obtained as pure *E* isomers,[10c] compound **16c** was obtained as a mixture of *E*

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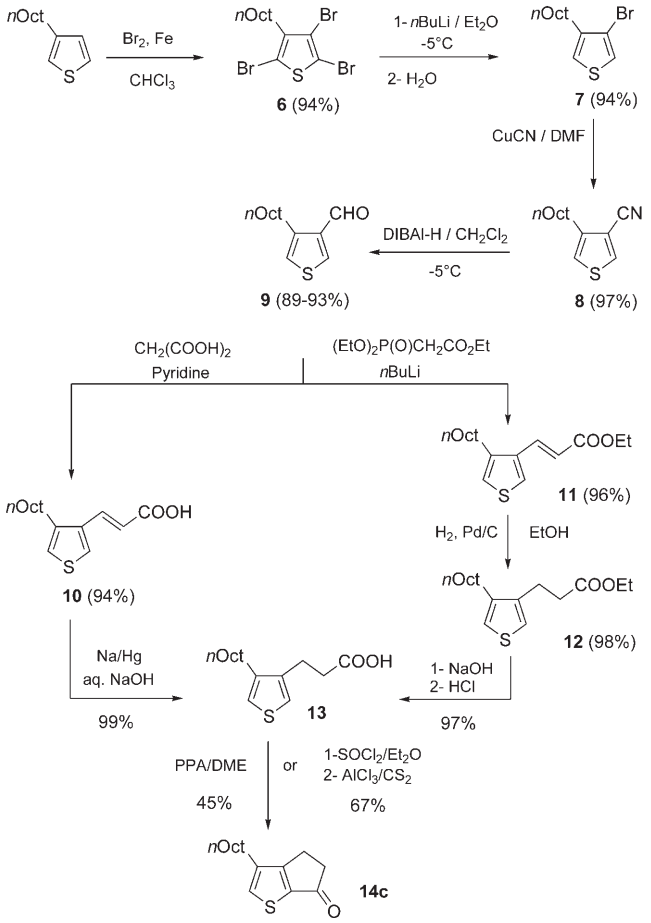
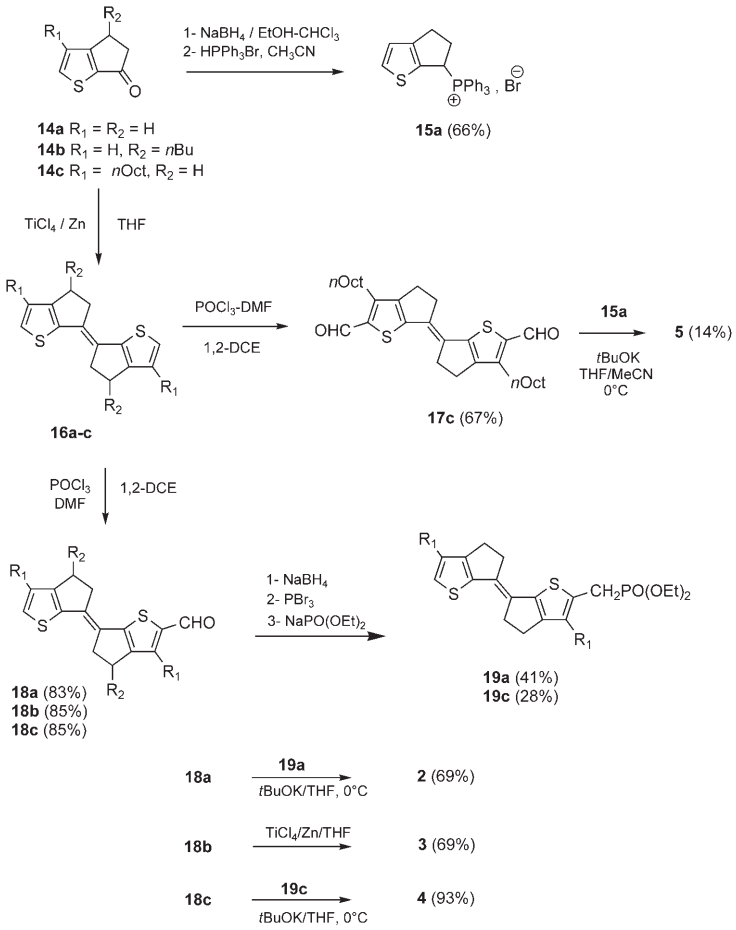


Scheme 1. Synthesis of cyclic ketone **14c**. Oct = octyl, DMF = *N*,*N*-dimethylformamide, DIBAl-H = diisobutylaluminum hydride, PPA = polyphosphoric acid, DME = dimethoxyethane.



Scheme 2. Synthesis of compounds **2**–**5**. 1,2-DCE = 1,2-dichloroethane.

and *Z* isomers which were separated by recrystallization and column chromatography. The target compounds **2**–**5** were synthesized according to two different routes depending on the solubility of the final compound. The most soluble compound **3** was prepared by McMurry coupling of aldehyde **18b** and purified by column chromatography. Due to the creation of a stereogenic center consecutive to the grafting of the butyl chains at the ethylene bridge, compound **3** was obtained as a mixture of stereoisomers.

Owing to their poor solubility, compounds **2** and **4** were prepared by an alternative route based on the Horner–Wadsworth–Emmons olefination. Aldehydes **18a**–**c** were obtained by Vilsmeier formylation of the corresponding derivatives **16a**–**c**. Dialdehyde **17c** was prepared from **16c** by the same method by using an excess of DMF and $POCl_3$. Reduction of **18a** and **18c** with $NaBH_4$ gave the intermediate alcohols. Reaction of the latter compounds with PBr_3 produced the corresponding highly unstable bromo derivatives which were immediately treated with the anion of diethyl phosphate to give phosphonates **19a** and **19c**. Compounds **2** and **4** were then prepared in 69% and 93% yields, respectively, by Horner–Wadsworth–Emmons olefination of **18a** and **18c** with phosphonates **19a** and **19c**, respectively. Compound **5** was synthesized by Wittig olefination of dialdehyde **17c** with phosphonium salt **15a**. The cyclic Wittig reagent **15a** was obtained by reduction of ketone **14a** into the related alcohol with $NaBH_4$,[15] followed by reaction with triphenylphosphonium hydrobromide[16] in acetonitrile.

UV/Vis spectroscopy: Table 1 lists the UV/Vis spectroscopic data for compounds **1**–**5**. As generally observed for nTVs,[9] all the spectra exhibit a well-resolved vibronic fine structure with three maxima in the 430–530 nm region (Figure 1). The quasi constant energy spacing of these maxima ($\approx$0.16 eV) is consistent with a coupling of the vibronic C=C stretching mode to the electronic structure.[17]

Table 1. Optical data of compounds **1**–**5** in dichloromethane.

Compound	λ_{0-2} [nm]	λ_{0-1} [nm]	λ_{0-0} [nm]	ΔE [eV]
1	429	458	487	2.55
2	456	485	520	2.38
3	460	489	523	2.37
4	466	495	531	2.34
5	450	478	513	2.42

Comparison of the electronic absorption data of the bridged compound **2** to those of the open-chain reference

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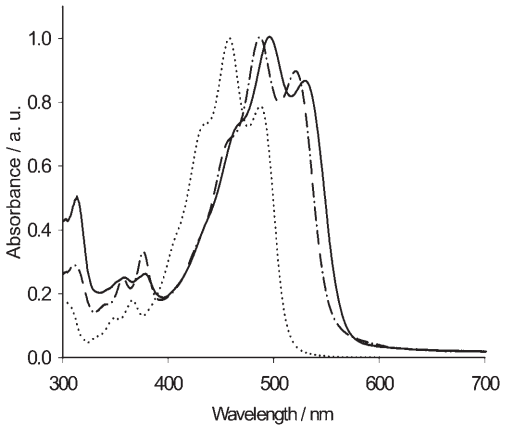

Figure 1. Electronic absorption spectra of the oligomers in CH_2Cl_2. Dotted line: **1**; dotted and dashed line: **2**; solid line: **4**.

compound **1** reveals a 27 nm bathochromic shift of the absorption maximum (λ_{0-1}) and a 33 nm shift of the maximum of the 0–0 transition (λ_{0-0}), which corresponds to a 0.17 eV decrease of the HOMO–LUMO gap (ΔE; Table 1). It is worth noting that this decrease of ΔE is two times larger than that observed between dithienylethylene and its bridged analogue **16a**,[10] but smaller than the 0.40 eV band-gap reduction observed between the corresponding polymers.[10] This result confirms that, as expected, the effects of rigidification are cumulative and effective on extended oligomers.

Introduction of butyl chains at the ethylene bridge (in **3**) produces a further 3–4 nm red shift of the band maxima. A slightly larger red shift ($\approx$10 nm) is observed for compound **4** due to the stronger inductive electron-releasing effect of the alkyl chain when attached at the 3 position of thiophene. The combined effects of rigidification and inductive effects result in an overall decrease of the HOMO–LUMO gap of 0.21 eV between oligomers **1** and **4**.

Although the structures of all the bridged compounds **2**–**5** contain four ethylene bridges, the data in Table 1 show that the red shift of the absorption maxima and the decrease of ΔE are noticeably smaller for **5** than for compounds **2**–**4**. This result clearly evidences the major influence of the position of the covalent bridges along the π-conjugated structure on the delocalization of the π electrons.

Cyclic voltammetry: The electrochemical properties of the oligomers were analyzed by cyclic voltammetry in methylene chloride with tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A low substrate concentration (approximately 5×10^{-5} M) was used for all compounds because of the low solubility of compounds **2** and **4**.

The cyclic voltammetry results of all oligomers exhibit two reversible one-electron oxidation processes corresponding to the successive generation of the cation radical and dication at redox potentials E^0_1 and E^0_2 (Figure 2). Comparison of the electrochemical data for compounds **1** and **2** (Table 2) shows that covalent bridging of the open-chain compound **1** induces negative shifts in the E^0_1 and E^0_2 values of 330 and 340 mV, respectively. The similarity of the E^0_1 and E^0_2 values for compounds **2** and **3** shows that alkyl substituents at the ethylene bridge have little effect on the HOMO level of the π-conjugated system. By contrast, introduction of octyl chains at the β positions of thiophene as achieved in compound **4** produces a further 120 mV negative shift of the E^0_1 value compared to the unsubstituted bridged compound **2**. However, the E^0_2 value shifts only by 90 mV, which results in an increase of the potential difference $E^0_2-E^0_1$ from 150 to 180 mV.

Comparison of the data for compound **4** and **5** shows that, despite the removal of two octyl chains, movement of the ethylene bridges from the outer to the inner sides of the two median thiophene rings induces a further negative shift of

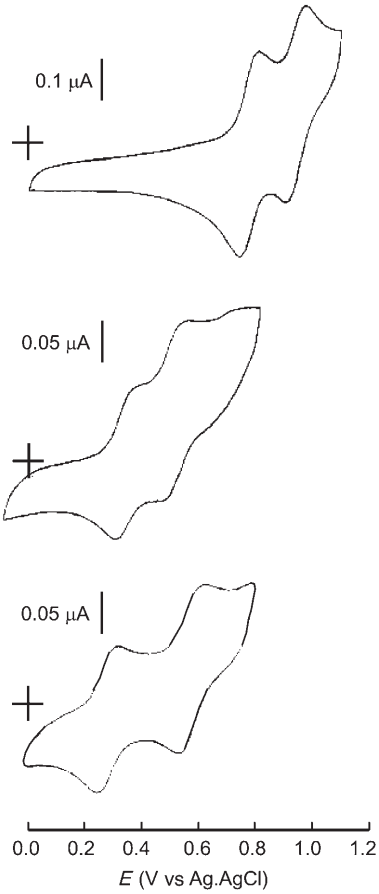

Figure 2. Cyclic voltammograms of compounds **1** (top), **4** (middle), and **5** (bottom). Concentration: approximately 0.05 mM in 0.10 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, scan rate 100 mV s^{-1}.

Table 2. Cyclic voltammetry data for compounds **1**–**5**.[a]

Compound	E^0_1 [V]	E^0_2 [V]	$E^0_2-E^0_1$ [mV]	log K
1	0.78	0.94	160	2.71
2	0.45	0.60	150	2.54
3	0.44	0.59	150	2.54
4	0.33	0.51	180	3.05
5	0.29	0.60	310	5.25

[a] Conditions: Concentration = 0.05 mM in 0.10 M Bu_4NPF_6/CH_2Cl_2, Pt electrodes, scan rate 100 mV s^{-1}, reference electrode Ag/AgCl.

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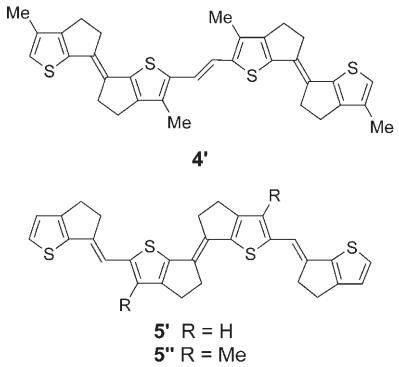
the E^0_1 value from 0.33 V for **4** to 0.29 V for **5**, thereby indicating a further increase of the HOMO level. To the best of our knowledge, the oxidation potential of compound **5** is the lowest reached for a π-conjugated chain of comparable length in the absence of electronic effects due to electron-donating substituents. For example, this potential is approximately 0.60 V lower than that of 3′,3‴″-dialkylsexithiophene[18] although this latter compound contains 12 double bonds versus the 11 in compounds **1**–**5**. On the other hand, further comparison of the data for compounds **4** and **5** shows that moving two ethylene bridges from the outer to the inner sides of the two median thiophene rings leads to a 90 mV positive shift of the E^0_2 value. The two opposite shifts of the E^0_1 and E^0_2 values result in an increase of the difference $E^0_2-E^0_1$ from 180 to 310 mV. This result shows that the position of the bridging groups exerts a considerable influence on the relative stability of the cation radical versus the dication. In fact, the increase in the $E^0_2-E^0_1$ value corresponds to an increase of more than two orders of magnitude in equilibrium constant K corresponding to the disproportionation of the cation radical into the neutral and dication states (expressed as log $K=0.059/E^0_2-E^0_1$; Table 1).[19,20]

Examination of the values of the HOMO–LUMO gap determined from optical data in the light of the cyclic voltammetry data clearly shows that the reduction of the ΔE value induced by covalent bridging is associated with a considerable increase (≈0.40–0.50 V) of the HOMO level. However, the fact that this increase is larger than the corresponding reduction of the ΔE value (≈0.20 eV) implies that the covalent bridging of the conjugated system simultaneously increases the HOMO and LUMO levels, with the net reduction of the ΔE value resulting from a faster increase of the HOMO level.

Theoretical calculations: To gain more detailed information on the electronic properties of the bridged compounds, the geometry of oligomers **1**–**5** was optimized at the DFT// B3LYP/6-31G** level[21] by using the Gaussian 98 program.[22] When not imposed by covalent bridging, an s-*trans* conformation was initially chosen for all single bonds connecting a thiophene ring to a double bond. In all cases, an *E* configuration was also imposed for all ethylenic linkages. In fact, these geometrical features precisely correspond to those found in the crystal structure of several related compounds.[9d,10b,10c,23] In order to reduce the computing time while taking into account the inductive effect of the alkyl groups in compounds **4** and **5**, calculations were performed on their methyl-substituted analogues (**4′** and **5″**, respectively), while an unsubstituted analogue of **5** (**5′**) was also computed for comparison with compound **2** (Scheme 3). After optimization, all computed molecules retain a fully planar geometry with an *E* configuration and s-*trans* conformation.



Scheme 3. Structures of the methyl-substituted analogues **4′** and **5′** and the unsubstituted analogue **5″**.

Figure 3 summarizes the computed energies of the frontier molecular orbitals. These results show that covalent bridging of the open-chain compound **1** produces an increase of both the HOMO and LUMO levels. However, the larger increase of the HOMO level results in a narrowing of the HOMO–LUMO gap.

The calculated values agree well with those derived from optical and electrochemical data and they confirm that the lowest ΔE value is reached for compound **4′**, whereas the alternative localization of the ethylene bridges in compound **5** induces a larger upshift of the LUMO level.

Whatever the position of the ethylene bridges, the introduction of alkyl substituents at the β position of thiophene produces a further upshift of all frontier orbitals. As expected, the largest effects are observed for **4′** in which four alkyl groups are added instead of the two in compound **5″**. On

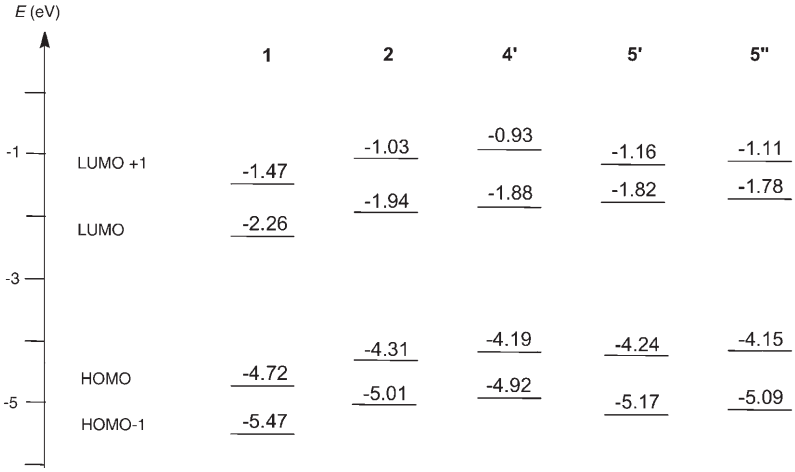


Figure 3. B3LYP/6-31G** one-electron energy diagram around the frontier molecular orbitals of **1**, **2**, **4′**, **5′**, and **5″**.

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the other hand, compound **5″** shows the highest HOMO level, a result in agreement with the lowest E^0_1 value found for compound **5**.

Previous crystallographic data have shown that the covalent bridging of DTE into **16b** produces a decrease of bond length alternation (BLA; defined as the difference between the average length of single and double bonds) from 0.095 to 0.078 Å.[10b,c] As confirmed by experimental and theoretical results, this reduced BLA is associated with a decrease of the HOMO–LUMO gap, with an important increase of the HOMO level.

Optimization of the geometry of DTE and **16b** with the procedure already used for compounds **1**–**5** leads to calculated BLA values of 0.063 and 0.061 Å for DTE and **16b**, respectively. These results show that the B3LYP/6-31G** level leads to a substantial underestimation of the BLA. With this reservation in mind, BLA values of 0.055, 0.053, and 0.054 Å have been calculated for compounds **1**, **2**, and **5′**, respectively. The values are lower than those found for DTE and **16b**, a finding in agreement with previous results showing that chain-length extension tends to reduce the BLA value.[23] On the other hand, these BLA values are, as expected, intermediate between those based on crystallographic data for polyenes (≈0.100 Å)[24] and oligothiophenes (0.051 Å for sexithiophene).[25] Although modest, the calculated BLA differences between the open-chain and bridged oligomers are in qualitative agreement with previous results and confirm that the reduction of the ΔE value produced by covalent bridging of the open-chain system **1** results from a decrease of bond length alternation.

Oxidation of linear π-conjugated systems with a nondegenerated ground state, such as poly(*p*-phenylene) or poly(thiophene), into their cation-radical and dication states is accompanied by a transition from an aromatic to a quinonoid structure of the aromatic benzene or thiophene ring.[26] Of course, such a transition implying the inversion of BLA is accompanied by a major reorganization of the geometry of the conjugated structure. From this viewpoint, the covalent fastening of several single and double bonds of the conjugated backbone can be expected to significantly affect the geometrical relaxation of the structure. In order to analyze this question, the geometry of the cation-radical and dication states of compounds **1**, **2**, and **5′** has been optimized by using the same base as for the neutral state.

The energy of the singly occupied molecular orbital (SOMO) of the cation radical increases from −7.62 eV for compound **1** to −7.07 eV for compounds **2** and **5′**. This result, which is consistent with a decrease of the E^0_2 value from 0.94 V for **1** to 0.60 V for **2** and **5** (Table 2), confirms that, as for the cation radical, the formation of the dication is easier for the bridged compounds.

Examination of the bond lengths of the neutral and charged states (Table 3) shows that oxidation to the cation radical and dication leads to a shortening of the single bonds and a stretching of the double bonds, which results in a progressive inversion of BLA in the dication. However, the structure of the cation radical remains essentially aromatic and full transition to a quinonoid structure occurs only for the dication, as recently demonstrated in the case of oligothiophenes.[27] Interestingly, further examination of the changes of bond lengths upon oxidation shows that covalent bridging contributes to limit the overall deformation of the conjugated system. Thus, the average absolute value of bond-length changes upon oxidation to the cation radical decreases from 0.0185 Å for compound **1** to 0.0179 and 0.0175 Å for compounds **2** and **5′**, respectively.

Figure 4 shows the variation of the absolute value of the bond-length difference $|\delta l|$ between the neutral and dication states versus bond number for the three compounds (Scheme 4). In every case the largest deformation occurs in the median part of the molecule while the bond lengths of the external thiophene rings remain practically unchanged. For the open-chain compound **1**, the magnitude of deformation progressively increases toward the middle of the molecule and the largest bond-length contraction involves the exocyclic median bonds 10 and 12, which decrease in length by 0.07 Å when converted into double bonds.

For the bridged compound **2**, the largest changes also involve bonds 10 and 12 but the bond-length contraction decreases from 0.07 to 0.05 Å. Another noticeable difference is that upon conversion into single bonds, the two lateral ethylenic double bonds 5 and 17 in **2** undergo a larger stretching than those in compound **1**. For compound **5′**, bonds 9, 10, 12, and 13 undergo large deformations; however, the largest stretching is now observed for the median double bond 11.

Comparison of the average absolute value of bond-length changes between the neutral and dication states shows that this quantity decreases from 0.041 Å for compound **1** to 0.037 Å for the bridged compounds **2** and **5′**. This result,

Table 3. Bond lengths and BLA values for the neutral, cation-radical, and dication states of the open-chain compound **1** and the bridged compounds **2** and **5′**.

Compound	Bond number[a]											BLA
	1/21	2/20	3/19	4/18	5/17	6/16	7/15	8/14	9/13	10/12	11	
1	1.369	1.422	1.383	1.442	1.356	1.436	1.386	1.411	1.386	1.435	1.360	0.055
1$^{+\cdot}$	1.377	1.410	1.393	1.422	1.372	1.417	1.407	1.387	1.409	1.406	1.384	0.017
1^{++}	1.390	1.396	1.411	1.401	1.395	1.397	1.431	1.368	1.432	1.364	1.410	−0.026
2	1.373	1.420	1.381	1.443	1.359	1.439	1.384	1.409	1.390	1.435	1.361	0.053
2$^{+\cdot}$	1.377	1.413	1.392	1.425	1.379	1.416	1.408	1.386	1.411	1.407	1.383	0.017
2^{++}	1.384	1.403	1.409	1.406	1.403	1.396	1.432	1.368	1.432	1.383	1.410	−0.021
5′	1.372	1.422	1.377	1.444	1.360	1.437	1.392	1.408	1.384	1.438	1.362	0.054
5′$^{+\cdot}$	1.375	1.415	1.388	1.428	1.376	1.416	1.411	1.386	1.409	1.407	1.392	0.019
5′$^{++}$	1.384	1.405	1.404	1.408	1.399	1.395	1.433	1.368	1.434	1.384	1.422	−0.020

[a] Bond numbering as shown in Scheme 4.

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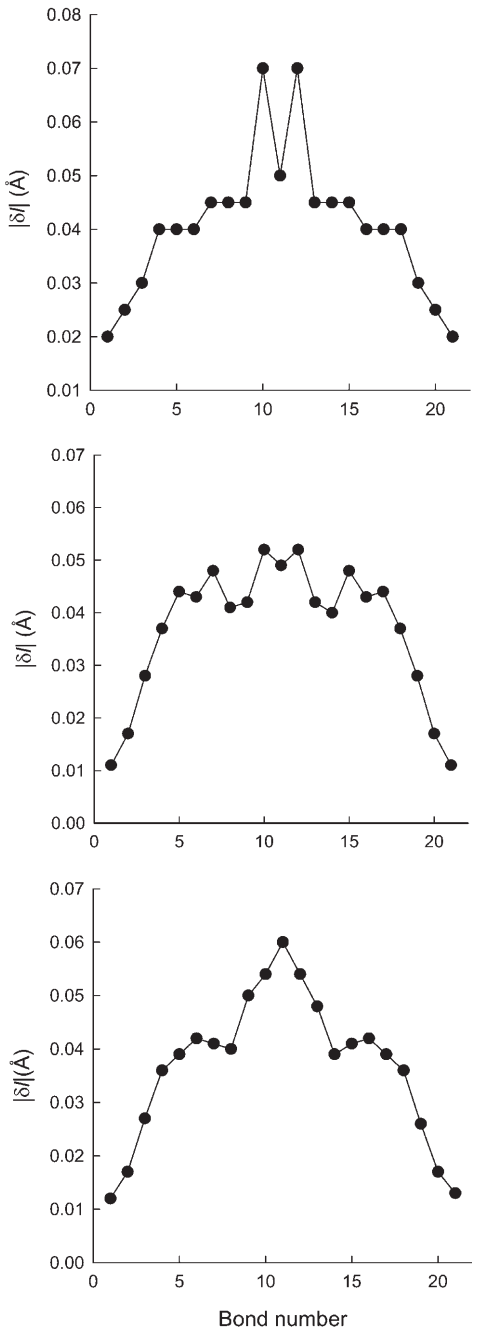
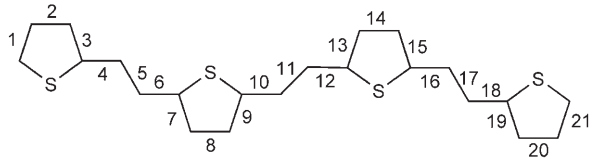


Figure 4. Variation of the absolute value of the bond-length difference between the neutral and the dication states versus bond number for compounds **1** (top), **2** (middle), and **5′** (bottom).

which confirms the smaller deformation of the bridged π-conjugated backbone, suggests that the inner-sphere reorganization energy associated with oxidation of bridged conjugated systems should be smaller than for the open-chain analogue. Since this parameter is known to play a major role in the charge-carrier mobility of the resulting organic semiconductors,[28] the above results provide a strong incitement to pursue the development of synthetic strategies aimed at the rigidification of π-conjugated systems.



Scheme 4. Bond numbering system for the oligomers.

Conclusion

Oligothienylenevinylenes with covalent fasteners attached at different positions of the π-conjugated backbone have been synthesized. The relationships between the structure and the electronic properties of these oligomers have been analyzed by UV/Vis spectroscopy, cyclic voltammetry and theoretical calculations with reference to an open-chain compound. These various investigations show that covalent bridging induces an increase of the energy levels of the frontier orbitals with a faster upshift of the HOMO, which results in a reduction of the HOMO–LUMO gap. Experimental and theoretical results have revealed the importance of the sites of fixation of the covalent bridges along the π-conjugated structure for the fine tuning of the energy levels of the neutral and charged states. An analysis of the geometrical changes associated with the oxidation processes has shown that covalent bridging limits the structural relaxation of the conjugated structure. This latter result suggests that, besides control of the energy gap, rigidification of π-conjugated systems by covalent bridging represents an interesting tool to reduce the reorganization energy associated with the charge-transport process in organic semiconductors.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker Avance DRX 500 spectrometer at 500.13 and 125.7 MHz, respectively; Chemical shift (δ) values are given in ppm (relative to TMS) and coupling constants (J) are given in Hz. IR spectra were recorded with a Perkin–Elmer 841 spectrophotometer by using samples embedded in KBr discs or thin films between NaCl plates. UV/Vis spectra were recorded with a Perkin–Elmer Lambda 2 spectrometer by using dichloromethane as the solvent (HPLC grade from SDS). Melting points are uncorrected. Elemental analyses were performed by the Service Central d'Analyses of the CNRS (Vernaison, France). Column chromatography purifications were carried out on Merck Si 60 silica gel (40–63 μm).

Mass spectrometry analyses were performed on a JMS-700 (JEOL LTD, Akishima, Tokyo, Japan) double-focusing mass spectrometer with reversed geometry, equipped with a pneumatically assisted electrospray-ionization (ESI) source. Nitrogen was used as the nebulizer gas. The sample, diluted in a chloroform solution or in a $CHCl_3/CH_3CN$ (70:30) mixture, was introduced into the ESI interface through a syringe pump (PHD 2000 infusion; Harvard Apparatus, Holliston, MA, USA) at a 40 μL min^{-1} flow rate. A 5 kV acceleration voltage was applied and the elemental composition of ions was checked by high-resolution measurements by using an electric-field scan with a mixture of poly(ethylene glycols) as the internal standard with nominal molecular weights centered around 1000. Matrix-assisted laser desorption/ionization MS was performed on a MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer with dithranol as the matrix.

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Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.1 or 0.2 M as the supporting electrolyte) was purchased from Acros and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment that was run under a nitrogen atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode ($\varnothing = 1$ mm) and a platinum wire counterelectrode. An Ag/AgCl electrode checked against the ferrocene/ferricinium couple (Fc/Fc^+) before and after each experiment was used as a reference. Electrochemical experiments were carried out with a PAR 273 potentiostat with positive feedback compensation.

DFT calculations were carried out by means of the Gaussian 98 program.[22] We used the Becke's three-parameter exchange functional combined with the LYP correlation functional (B3LYP).[21] The 6-31G* basis for carbon and sulfur atoms and 6-31G basis for hydrogen atoms were used to optimize the geometry and to compute the electronic structure at the minima found. The geometry of computed molecules was obtained by using the Molekel-4.0 program.

2,4,5-Tribromo-3-*n*-octylthiophene (6): In the absence of light, bromine (20.3 mL, 0.3962 mol) was added dropwise over a period of 1.5 h to a solution of 3-*n*-octylthiophene (25 g, 0.1275 mol) in anhydrous $CHCl_3$ (300 mL) in the presence of a catalytic amount of iron powder (0.72 g, 0.0129 mol). The reaction mixture was stirred for 2 h. After careful addition of water (50 mL), the mixture was slowly neutralized by an aqueous solution of 2 M NaOH (150 mL). The organic phase was separated by decantation and the aqueous phase was extracted with CH_2Cl_2 (2×100 mL). The organic phases were collected and washed with a saturated aqueous solution of $Na_2S_2O_3$, dried over Na_2SO_4, and concentrated to dryness to afford an orange oil (51.8 g, 94% yield): ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3H, $^3J = 7.05$ Hz), 1.28–1.32 (m, 12H), 2.73 ppm (t, 2H, $^3J = 7.5$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 14.09$, 22.65, 28.44, 29.18, 29.25, 29.68, 30.80, 31.84, 108.03, 109.71, 115.76, 141.56 ppm.

3-Bromo-4-*n*-octylthiophene (7): Under an N_2 atmosphere, 2.5 M *n*BuLi in hexane (84 mL, 0.21 mol) was slowly added over a period of 2 h to a solution of compound **6** (43.30 g, 0.10 mol) in anhydrous Et_2O (220 mL) cooled to −5 °C. After 20 min of additional stirring at −5 °C, the reaction mixture was carefully hydrolyzed at −5 °C with vigorous stirring by addition of an aqueous solution of 4 M HCl (50 mL). The mixture was diluted with Et_2O (50 mL) and slowly warmed to 20 °C. The aqueous phase was separated and extracted with Et_2O (2×100 mL). The organic phases were collected and washed with water (2×150 mL), dried over Na_2SO_4, and evaporated to dryness. The oily residue was purified by chromatography on silica gel (eluent: petroleum ether) to afford a slightly yellow oil (25.8 g, 94% yield): ^{1}H NMR ($CDCl_3$): $\delta = 0.91$ (t, 3H, $^3J = 7.05$ Hz), 1.10–1.43 (m, 10H), 1.50–1.70 (m, 2H), 2.60 (t, 2H, $^3J = 7.5$ Hz), 6.95 (d, 1H, $^3J = 3.3$ Hz), 7.22 ppm (d, 1H, $^3J = 3.3$ Hz); ^{13}C NMR ($CDCl_3$): $\delta =$ 14.09, 22.65, 29.27, 29.30, 29.36, 29.68, 29.86, 31.85, 112.80, 120.54, 122.59, 128.29 ppm.

3-Cyano-4-*n*-octylthiophene (8): A mixture of compound **7** (25.7 g, 93.4 mmol) and CuCN (9.25 g, 103.3 mmol) in anhydrous DMF (190 mL) was refluxed for 38 h. The reaction mixture was cooled to 60 °C before a solution of $FeCl_3$ (31.9 g, 196.5 mmol) in an aqueous solution of 8 N HCl (130 mL) was added. The mixture was then cooled to 20 °C and extracted with CH_2Cl_2. The organic phases were washed with water, dried over Na_2SO_4, and evaporated in vacuo. The resulting red oil was purified by column chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether (2:8)) to afford **8** as an orange oil (20 g, 97% yield): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 3H, $^3J = 6.8$ Hz), 1.16–1.41 (m, 10H), 1.61 (m, 2H), 2.73 (t, 2H, $^3J = 7.7$ Hz), 7.01 (d, 1H, $^3J = 3.1$ Hz), 7.86 ppm (d, 1H, $^3J = 3.1$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 14.06$, 22.60, 29.04, 29.11, 29.16, 29.24, 29.71, 31.79, 111.99, 115.04, 121.74, 135.40, 144.51 pm; EI MS: *m*/*z* (%): 221 [$M^{+\cdot}$] (11), 150 (7), 136 (8), 123 (100), 57 (11); IR (NaCl): $\tilde{\nu} = 2227$ cm^{-1} (C≡N); elemental analysis calcd (%) for $C_{13}H_{19}NS$: C 70.54, H 8.65, N 6.33, S 14.48; found: C 70.44, H 8.67, N 6.25, S 14.47.

3-Formyl-4-*n*-octylthiophene (9): A solution of 1 M diisobutylaluminum hydride in CH_2Cl_2 (130 mL, 0.13 mol) was slowly added to a solution of compound **8** (22.1 g, 0.1 mol) in anhydrous CH_2Cl_2 (500 mL) cooled between −5 and −10 °C under an N_2 atmosphere. After being stirred for 2 h at −5 °C, the reaction mixture was carefully hydrolyzed at −5 °C by addition of a 2:1 mixture of an aqueous solution of 2 M HCl and MeOH (100 mL). The mixture was then warmed to 20 °C and stirred overnight. After filtration of the mixture and separation of the organic phase, the aqueous phase was extracted with CH_2Cl_2. The organic phases were collected, washed with an aqueous solution of 2 M HCl, dried over Na_2SO_4, and evaporated in vacuo. After purification by filtration on silica gel (eluent: CH_2Cl_2), compound **9** was obtained as a yellow oil (20.8 g, 93% yield): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 3H, $^3J = 6.9$ Hz), 1.30 (m, 10H), 1.59 (m, 2H), 2.89 (t, 2H, $^3J = 7.7$ Hz), 6.98 (d, 1H, $^3J = 3.3$ Hz), 8.07 (d, 1H, $^3J = 3.3$ Hz), 9.98 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 14.07$, 22.62, 29.14, 29.22, 29.36, 29.96, 31.84, 122.76, 139.39, 140.28, 143.70, 185.70 ppm; EI MS: *m*/*z* (%): 224 [$M^{+\cdot}$] (50), 139 (38), 126 (100), 97 (44); IR (NaCl): $\tilde{\nu} = 1687$ cm^{-1} (C≡O); elemental analysis calcd (%) for $C_{13}H_{20}OS$: C 69.59, H 8.98, O 7.13, S 14.29; found: C 69.89, H 9.11, O 7.85, S 13.51.

(*E*)-3-(4-*n*-Octyl-3-thienyl)propenoic acid (10): A mixture of compound **9** (6 g, 26.5 mmol) and malonic acid (5.52 g, 53 mmol) in anhydrous pyridine (30 mL) in the presence of piperidine (1.2 mL) was heated to 110 °C for 2.5 h and then refluxed for 0.5 h. When cooled to 20 °C, the reaction mixture was poured into water (100 mL) and an aqueous solution of 25% HCl was dropwise added until the pH value became lower than 7. The resulting white precipitate was recovered by filtration and dried to give **10** as a white powder (6.68 g, 94% yield). M.p. 142–143 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (t, 3H, $^3J = 7.05$ Hz), 1.31 (m, 10H), 1.61 (m, 2H), 2.68 (t, 2H, $^3J = 7.5$ Hz), 6.32 (d, 1H, $^3J = 16.0$ Hz), 6.98 (d, 1H, $^3J = 2.8$ Hz), 7.63 (d, 1H, $^3J = 2.8$ Hz), 7.76 ppm (d, 1H, $^3J = 16.0$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 14.09$, 22.65, 29.01, 29.22, 29.36, 29.97, 31.84, 117.03, 121.78, 126.48, 135.65, 139.44, 142.55, 172.57 ppm; EI MS: *m*/*z* (%): 266 [$M^{+\cdot}$] (32), 168 (100), 123 (33); IR (KBr): $\tilde{\nu} = 3000$–2400 (O−H), 1676 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{15}H_{22}O_2S$: C 67.33, H 8.32, O 12.01, S 12.03; found: C 66.88, H 8.41, O 11.70, S 11.73.

(*E*)-Ethyl-3-(4-*n*-Octyl-3-thienyl)propenoate (11): A solution of 2.5 M *n*BuLi in hexane (78 mL, 0.195 mol) was added dropwise over a period of 1 h to a solution of triethylphosphonoacetate (40 mL, 0.202 mol) in anhydrous THF (100 mL) cooled to −50 °C under an N_2 atmosphere. After additional stirring for 0.5 h at −50 °C, a solution of aldehyde **9** (22.4 g, 0.1 mol) in anhydrous THF (100 mL) was added dropwise over 1 h and then the reaction mixture was allowed to warm up to 20 °C overnight. After addition of a saturated aqueous solution of NH_4Cl (140 mL) and an aqueous solution of 1 M HCl (100 mL) and dilution with Et_2O (200 mL), the organic phase was separated, washed with water, dried (Na_2SO_4), and concentrated to dryness. The resulting oil was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give a yellow oil (28.36 g, 96% yield): ^{1}H NMR ($CDCl_3$): $\delta = 0.88$ (t, 3H, $^3J = 6.9$ Hz), 1.25–1.37 (m, 10H), 1.33 (t, 3H, $^3J = 7.1$ Hz), 1.61 (m, 2H), 2.66 (t, 2H, $^3J = 7.7$ Hz), 4.26 (q, 2H, $^3J = 7.1$ Hz), 6.29 (d, 1H, $^3J = 15.9$ Hz), 6.95 (d, 1H, $^4J = 3.2$ Hz), 7.55 (d, 1H, $^4J = 3.2$ Hz), 7.65 ppm (d, 1H, $^3J = 15.9$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 14.07$, 14.30, 22.63, 29.01, 29.21, 29.33, 29.36, 29.916, 31.81, 60.37, 118.10, 121.52, 125.37, 135.97, 137.07, 142.39, 167.18 ppm; EI MS: *m*/*z* (%): 294 [$M^{+\cdot}$] (58), 196 (100); IR (NaCl): $\tilde{\nu} =$ 1712 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{17}H_{26}O_2S$: C 69.35, H 8.91, S 10.87, O 10.87; found: C 69.17, H 8.81, S 11.87, O 10.95.

Ethyl-3-(4-*n*-Octyl-3-thienyl)propanoate (12): A mixture of compound **11** (50 g, 0.170 mol) and 10% palladium on activated carbon (5 g) in absolute EtOH (300 mL) was allowed to react with H_2 (70 bar, 15 °C) for 24 h. The mixture was filtered over celite and the solution was concentrated to dryness to afford an almost pure product. Further purification by filtration over silica gel (eluent: CH_2Cl_2) led to a pure yellow oil (49.32 g, 98%): ^{1}H NMR ($CDCl_3$): $\delta = 0.89$ (t, 3H, $^3J = 6.9$ Hz), 1.24–1.39 (m, 10H), 1.28 (t, 3H, $^3J = 7.2$ Hz), 1.59–1.65 (m, 2H), 2.52 (t, 2H, $^3J =$ 7.8 Hz), 2.64 (t, 2H, $^3J = 7.8$ Hz), 2.86 (t, 2H, $^3J = 7.8$ Hz), 4.12 (q, 2H, $^3J = 7.2$ Hz), 6.91 (d, 1H, $^4J = 3.8$ Hz), 6.92 ppm (d, 1H, $^4J = 3.8$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 14.08$, 14.18, 22.64, 23.95, 28.72, 29.25, 29.45, 29.55, 29.56, 31.85, 34.16, 60.45, 120.32, 139.73, 141.86, 172.97 ppm; EI MS: *m*/*z* (%): 296 [$M^{+\cdot}$] (27), 198 (100), 124 (77); IR (NaCl): $\tilde{\nu} =$ 1734 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{17}H_{28}O_2S$: C 68.87, H 9.52, S 10.81, O 10.79; found: C 68.48, H 9.63, S 12.11, O 10.51.

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3-(4-*n*-Octyl-3-thienyl)propanoic acid (13): Method A: 3% sodium amalgam, prepared from sodium (1.56 g, 67.8 mmol) and mercury (50.3 g), was added portionwise to a solution of compound **10** (6.6 g, 24.8 mmol) dissolved in an aqueous solution of 2% NaOH (50 mL). After 20 h of stirring, the resulting mercury was separated by decantation, then the mixture was cooled to 0 °C and acidified with an aqueous solution of 1 M HCl. The resulting white precipitate was filtered off and dissolved in CH_2Cl_2 and the solution was dried over Na_2SO_4. After the solution was evaporated to dryness, compound **13** was obtained as white powder (6.60 g, 99% yield). Method B: An aqueous solution of 3.5 M NaOH (350 mL, 1.225 mol) was added to a solution of compound **12** (49.13 g, 0.166 mol) in EtOH (250 mL). The reaction mixture was stirred at 90 °C for 4 h and then cooled to 0 °C before concentrated HCl (100 mL) was carefully added. The resulting white precipitate was recovered by filtration, washed thoroughly with an aqueous solution of 4 M HCl, and dried. The product was dissolved in CH_2Cl_2, then the resulting solution was dried over Na_2SO_4 and concentrated to dryness to afford compound **13** as a white powder (43.03 g, 97%). M.p. 92–95 °C; ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 3H, ^3J = 7.04 Hz), 1.28 (m, 10H), 1.62 (m, 2H), 2.51 (m, 2H), 2.69 (m, 2H), 2.86 (m, 2H), 6.95 (d, 1H, ^3J = 2.6 Hz), 7.28 ppm (d, 1H, ^3J = 2.6 Hz); ^{13}C NMR ($CDCl_3$): δ = 14.09, 22.65, 23.64, 28.72, 29.25, 29.45, 29.54, 31.85, 33.82, 65.03, 120.47, 120.54, 139.33, 141.82, 178.96 ppm; EI MS: *m*/*z* (%): 268 [$M^{+\cdot}$] (22), 170 (100), 123 (30), 111 (20); IR (KBr): $\tilde{\nu}$ = 3600–2500 (O–H), 1696 cm^{-1} (C=O); elemental analysis calcd (%) for $C_{15}H_{24}O_2S$: C 67.12, H 9.01, O 11.92, S 11.94; found: C 66.68, H 9.15, O 12.21, S 11.78.

4,5-Dihydro-6*H*-3-octylcyclopenta[*b*]thiophen-6-one (14c): Method A: A mixture of compound **13** (6.6 g, 24.06 mmol) and polyphosphoric acid (6 g) in anhydrous dimethoxyethane (100 mL) was refluxed for 24 h. The reaction mixture was cooled to 20 °C and poured into water (200 mL). After extraction with Et_2O (3×200 mL), the organic phases were collected, washed with water (200 mL), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2) to afford an orange oil (2.8 g, 45% yield). Method B: A mixture of compound **13** (22 g, 82.09 mmol) and thionyl chloride (26 mL, 0.356 mol) in dry Et_2O (200 mL) was refluxed for 4 h under an N_2 atmosphere. After evaporation of the solvent and the excess thionyl chloride, the resulting oil (25.10 g), the acyl chloride, was directly engaged in the next step. Thus, a solution of the acyl chloride in CS_2 (150 mL) was added dropwise to a suspension of $AlCl_3$ (13.85 g, 0.1039 mol) in CS_2 (200 mL) under an N_2 atmosphere. The reaction mixture was refluxed for 16 h, cooled to 20 °C, and then poured into a mixture of ice (400 mL) and concentrated HCl (200 mL). After extraction of the aqueous solution with CH_2Cl_2, the organic phases were collected, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by chromatography on silica gel, with CH_2Cl_2 as the eluent for the first column and a mixture of CH_2Cl_2/petroleum ether (3:7) as the eluent for a second column, to afford a yellow oil (13.75 g, 67% yield): ^{1}H NMR ($CDCl_3$): δ = 0.87 (t, 3H, ^3J = 7.0 Hz), 1.18–1.40 (m, 10H), 1.61 (m, 2H), 2.56 (t, 2H, ^3J = 7.7 Hz), 2.90–3.00 (m, 4H), 7.48 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.10, 22.65, 23.33, 28.31, 29.22, 29.28, 29.35, 31.85, 40.91, 135.27, 139.22, 140.87, 168.72, 197.58 ppm; EI MS: *m*/*z* (%): 250 [$M^{+\cdot}$] (22), 165 (6), 152 (100), 123 (10); IR (NaCl): $\tilde{\nu}$ = 1698 cm^{-1} (C=O); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 263 nm (4.58); elemental analysis calcd (%) for $C_{15}H_{22}OS$: C 71.95, H 8.86, S 12.80; found: C 72.17, H 8.93, S 11.74.

5,6-Dihydro-4*H*-cyclopenta[*b*]thiophen-6-yl triphenylphosphonium bromide (15a): $NaBH_4$ (0.35 g, 9.2 mmol) was added in small amounts over a period of 10 min to a solution of ketone **14a** (0.55 g, 4 mmol) in anhydrous EtOH (20 mL) cooled to 0 °C and the reaction mixture was stirred at 20 °C for 7 h. After addition of Et_2O (100 mL) and water (30 mL), the aqueous phase was separated by decantation and extracted with Et_2O (2×30 mL). The organic phases were collected, washed with a saturated aqueous solution of NaCl, dried (Na_2SO_4), and concentrated to dryness. Chromatography on silica gel (eluent: CH_2Cl_2) gave the intermediate alcohol as a yellow oil (0.45 g, 80% yield): ^{1}H NMR ($CDCl_3$): δ = 2.09 (br s, 1H), 2.31–2.34 (m, 1H), 2.65–2.69 (m, 1H), 2.84–2.93 (m, 2H), 5.29 (br s, 1H), 6.81 (d, 1H, ^3J = 4.9 Hz), 7.33 ppm (d, 1H, ^3J = 4.9 Hz).[15] The relatively unstable alcohol compound was directly dissolved in hot MeCN (30 mL), then $HPPh_3Br$ (1.15 g, 3.35 mmol; prepared from a solution of 48% HBr and PPh_3[16]) was added portionwise to this solution over a period of 10 min. The reaction mixture was then cooled to room temperature. After addition of water (30 mL) and extraction with CH_2Cl_2, the organic phases were washed with water, dried ($MgSO_4$), and concentrated to dryness. Purification by chromatography on silica gel (eluent: CH_2Cl_2 and then MeOH) led to an orange foam (0.99 g, 66% yield): M.p. = 122–127 °C; ^{1}H NMR ($CDCl_3$): δ = 1.54–1.61 (m, 1H), 2.55–2.2.66 (m, 2H), 3.62–3.71 (m, 1H), 6.61 (d, 1H, ^3J = 4.9 Hz), 6.99 (dd, 1H, $^3J_{H,H}$ = 7.2, $^2J_{H,P}$ = 8.7 Hz), 7.17 (dd, 1H, $^3J_{H,H}$ = 4.9, $^5J_{H,P}$ = 3.2 Hz), 7.61–7.65 (m, 6H), 7.76–7.81 ppm (m, 9H).

6,6′-Bi(4,5-dihydro-6*H*-3-*n*-octyl-cyclopenta[*b*]thienylidene) (16c): After the dropwise addition of $TiCl_4$ (4.20 mL, 38.2 mmol) to anhydrous THF (150 mL) cooled to 0 °C under an N_2 atmosphere, zinc powder (4.99 g, 76.3 mmol) was added portionwise. The mixture was successively warmed to room temperature, refluxed for 30 min, and cooled again to 0 °C, before a solution of compound **14c** (4.83 g, 19.3 mmol) in anhydrous THF (120 mL) was added. The reaction mixture was then refluxed for 5 h. At 20 °C, the reaction mixture was filtered over celite. After washing of the cake of celite with THF, water (100 mL) was added to the solution. The organic phase was separated by decantation and the aqueous phase was extracted with CH_2Cl_2. At this step, the beige precipitate observed at the interface between the aqueous and the CH_2Cl_2 organic phase was recovered by filtration and washed with Et_2O to give a white powder (0.78 g). The previous cake of celite was also thoroughly washed with hot CH_2Cl_2 and all organic phases were collected, washed with water, dried over Na_2SO_4, and evaporated to afford a yellow solid (3.77 g). Independent recrystallizations of the two fractions from CH_2Cl_2 afforded beige needles of pure (*E*)-**16c** isomer (2.07 g). The filtered solutions were collected and concentrated to dryness and the residue was purified by chromatography on silica gel (eluent: CH_2Cl_2/cyclohexane (5:95)). The resulting fraction corresponding to an *E*/*Z* mixture was triturated with petroleum ether to afford a beige solid (0.88 g) that was a mixture of (*E*)- and (*Z*)-**16c** isomers. The overall yield of the reaction was 65%, with the *E*/*Z* ratio being approximately 5:1. It was possible to isolate the pure (*Z*)-**16c** isomer from the mixture by successive recrystallizations from CH_2Cl_2 to separate as much as possible of the (*E*)-**16c** isomer followed by chromatography on silica gel (adsorption of the mixture on silica gel and elution with cyclohexane). (*E*)-**16c** isomer: R_f = 0.62 (cyclohexane); m.p. 118–120 °C; ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6H, ^3J = 6.9 Hz), 1.25–1.35 (m, 20H), 1.56–1.61 (m, 4H), 2.52 (t, 4H, ^3J = 7.7 Hz), 2.89–2.91 (m, 4H), 3.21–3.23 (m, 4H), 6.90 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.03, 22.65, 26.76, 29.25, 29.42, 29.47, 31.88, 32.94, 34.95, 124.04, 126.29, 138.38, 143.58, 149.94 ppm; EI MS: *m*/*z* (%): 468 [$M^{+\cdot}$] (3), 235 (100), 137 (47); UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 367 (3.64), 347 (3.72), 331 nm (3.59); elemental analysis calcd (%) for $C_{30}H_{44}S_2$: C 76.86, H 9.46, S 13.68; found: C 76.78, H 9.58, S 13.23; (*Z*)-**16c** isomer: R_f = 0.51 (cyclohexane); m.p. = 65–67 °C; ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6H, ^3J = 6.9 Hz), 1.25–1.35 (m, 20H), 1.56–1.61 (m, 4H), 2.51 (t, 4H, ^3J = 7.7 Hz), 2.81–2.84 (m, 4H), 3.09–3.12 (m, 4H), 6.89 ppm (s, 2H).

Isomerization of (*Z*)-16c to (*E*)-16c: A solution of (*Z*)-**16c** isomer (1.08 g, 2.31 mmol) in CH_2Cl_2 (30 mL) in the presence of *p*-toluenesulfonic acid monohydrate (40 mg, 0.21 mmol) was stirred at 20 °C. The (*E*)-**16c** isomer slowly started to precipitate and complete conversion to the (*E*)-**16c** isomer was achieved after 2 days, as checked by TLC (SiO_2/cyclohexane). Water (50 mL) was added and the mixture was extracted with CH_2Cl_2 (4×50 mL). The organic phases were dried (Na_2SO_4) and evaporated in vacuo to give a residue, which was adsorbed on silica gel by evaporation of a CH_2Cl_2 solution and then purified by chromatography on silica gel (eluent: cyclohexane) to afford pure (*E*)-**16c** isomer (0.76 g, 70% yield).

(*E*)-2,2′-Diformyl-6,6′-bi(4,5-dihydro-6*H*-3-*n*-octyl-cyclopenta[*b*]thienylidene) (17c): $POCl_3$ (0.37 mL, 4 mmol) was added dropwise to a solution of compound **16c** (0.47 g, 1 mmol) and anhydrous DMF (0.46 mL, 6 mmol) in anhydrous 1,2-dichloroethane (20 mL) under an N_2 atmosphere. The reaction mixture was refluxed for 16 h and then cooled to 20 °C before an aqueous solution of 2 M sodium acetate (30 mL) was added and the mixture was stirred for a further 3 h. After extraction with CH_2Cl_2, the organic fractions were washed with water, dried over

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Na_2SO_4, and evaporated in vacuo. The residue was purified by chromatography on silica gel (by adsorption of the residue on silica gel and elution with CH_2Cl_2/petroleum ether (1:1)). Dialdehyde **17c** was obtained as a yellow-orange solid (0.35 g, 67% yield). M.p. 191–194°C; ^{1}H NMR ($CDCl_3$): δ = 0.88 (t, 6H, ^3J = 6.9 Hz), 1.26–1.36 (m, 20H), 1.58–1.65 (m, 4H), 2.88 (t, 4H, ^3J = 7.7 Hz), 3.00 (br s, 4H), 3.28 (br s, 4H), 9.95 ppm (s, 2H); ^{13}C NMR ($CDCl_3$): δ = 14.12, 22.66, 26.62, 27.70, 29.21, 29.37, 29.42, 30.62, 31.85, 34.72, 131.82, 142.77, 147.84, 151.60, 153.65, 182.01 ppm; EI MS: *m*/*z* (%): 524 [$M^{+\bullet}$] (100), 439 (8); HRMS: calcd for $C_{32}H_{44}O_2S_2$: 524.278275; found: 524.277643; IR (KBr): $\tilde{\nu}$ = 1646 cm^{-1} (C=O).

(*E*)-2-Formyl-6,6′-bi(4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (18a): $POCl_3$ (0.23 mL, 2.46 mmol) was added dropwise to a solution of bridged DTE **16a** (0.54 g, 2.21 mmol) and anhydrous DMF (0.20 mL, 2.46 mmol) in anhydrous 1,2-dichloroethane (70 mL) at 0°C under an N_2 atmosphere. The reaction mixture was refluxed for 18 h and then cooled to 20°C before an aqueous solution of 2M sodium acetate (50 mL) was added and the mixture was stirred for a further 3 h. After extraction with CH_2Cl_2, the organic fractions were dried over Na_2SO_4 and evaporated in vacuo to give a solid, which was purified by chromatography on silica gel (eluent: CH_2Cl_2) to give a yellow-orange powder (540 mg, 83% yield): M.p. = 184–186°C; ^{1}H NMR ($CDCl_3$): δ = 3.03 (m, 4H, CH_2), 3.25 (m, 4H, CH_2), 6.95 (d, 1H, ^3J = 4.8 Hz), 7.43 (d, 1H, ^3J = 4.8 Hz), 7.51 (s, 1H), 9.77 ppm (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ = 26.8, 27.4, 34.5, 35.8, 123.2, 125.1, 131.8, 131.9, 133.3, 143.3, 146.6, 150.1, 153.3, 154.1, 182.4 ppm; EI MS: *m*/*z* (%): 272 [$M^{+\bullet}$] (100); IR (KBr): $\tilde{\nu}$ = 1642 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max} = 434 nm.

(*E*)-2-Formyl-6,6′-bi(4-*n*-butyl-4,5-dihydro-6*H*-cyclopenta[*b*]thienylidene) (18b): $POCl_3$ (0.16 mL, 1.68 mmol) was added dropwise to a solution of compound **16b** (0.50 g, 1.40 mmol) and anhydrous DMF (0.13 mL, 1.68 mmol) in anhydrous 1,2-dichloroethane (17 mL) under an N_2 atmosphere. The reaction mixture was refluxed for 18 h and then cooled to 20°C before an aqueous solution of 2M sodium acetate (30 mL) was added and the mixture was stirred for a further 3 h. After extraction with CH_2Cl_2, the organic fractions were dried over Na_2SO_4 and evaporated in vacuo to give a residue, which was purified by chromatography on silica gel (eluent: CH_2Cl_2/petroleum ether (1:1)) to give a yellow-orange oil (0.46 g, 85% yield): ^{1}H NMR ($CDCl_3$): δ = 0.89–1.10 (m, 6H), 1.30–1.82 (m, 12H), 2.79–2.93 (m, 2H), 3.25–3.51 (m, 4H), 6.97 (d, 1H, ^3J = 4.9 Hz), 7.43 (d, 1H, ^3J = 4.9 Hz), 7.55 (s, 1H), 9.79 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.04, 22.77, 29.54, 29.71, 36.19, 36.27, 40.07, 40.65, 41.53, 42.87, 124.44, 131.69, 131.72, 132.73, 142.49, 146.47, 153.51, 154.19, 157.43, 182.54 ppm; EI MS: *m*/*z* (%): 384 [$M^{+\bullet}$] (100), 327 (100); IR (KBr): $\tilde{\nu}$ = 1658 cm^{-1} (C=O); UV (CH_2Cl_2): λ_{max} (log ε) = 434 nm (4.58); elemental analysis calcd (%) for $C_{23}H_{28}S_2O$: C 71.83, H 7.34, S 16.67, O 4.16; found: C 72.01, H 7.48, S 16.61, O 4.72.

(*E*)-2-Formyl-6,6′-bi(4,5-dihydro-6*H*-3-*n*-octyl-cyclopenta[*b*]thienylidene) (18c): $POCl_3$ (0.50 mL, 5.36 mmol) was added dropwise to a solution of compound **16c** (2.20 g, 4.70 mmol) and anhydrous DMF (0.50 mL, 6.47 mmol) in anhydrous 1,2-dichloroethane (85 mL) under an N_2 atmosphere. The reaction mixture was refluxed for 4 h and then cooled to 20°C before an aqueous solution of 2M sodium acetate (50 mL) was added and the mixture was stirred for a further 3 h. After extraction with CH_2Cl_2, the organic fractions were dried over Na_2SO_4 and evaporated in vacuo to give a solid, which was purified by chromatography on silica gel (by adsorption of the solid on silica gel and elution with CH_2Cl_2/petroleum ether (1:1)). Aldehyde **18c** was obtained as yellow crystals after recrystallization from iPr$_2$O (1.99 g, 85% yield): M.p. = 128–132°C; ^{1}H NMR ($CDCl_3$): δ = 0.86–0.89 (m, 6H), 1.26–1.35 (m, 20H), 1.60–1.63 (m, 4H), 2.53 (t, 2H, ^3J = 7.7 Hz), 2.85 (t, 2H, ^3J = 7.7 Hz), 2.92–2.95 (m, 4H), 3.22–3.27 (m, 4H), 7.04 (s, 1H), 9.90 ppm (s, 1H); ^{13}C NMR ($CDCl_3$): δ = 14.13, 14.15, 22.67, 22.70, 26.3, 26.97, 27.72, 29.19, 29.22, 29.29, 29.39, 29.44, 30.63, 31.87, 31.91, 34.14, 35.64, 125.16, 126.76, 133.75, 138.69, 140.92, 142.93, 148.02, 151.04, 153.21, 153.29, 181.55 ppm; UV/Vis (CH_2Cl_2): λ_{max} (log ε): 437 nm (4.55); elemental analysis calcd (%) for $C_{31}H_{44}OS_2$: C 74.95, H 8.93, S 12.91, O 3.22; found: C 74.87, H 8.87, S 12.79, O 3.35; IR (KBr): $\tilde{\nu}$ = 1649 cm^{-1} (C=O).

Diethylphosphonate 19a: $NaBH_4$ (0.24 g, 6.32 mmol) was added in small amounts to a solution of aldehyde **18a** (0.91 g, 3.34 mmol) in a mixture of THF and MeOH (1:1; 80 mL) and the reaction mixture was stirred overnight at 20°C. After partial concentration of the solvents, an aqueous solution of 2M HCl (40 mL) was added and the mixture was extracted with CH_2Cl_2. The organic phases were thoroughly washed with water, dried (Na_2SO_4), and concentrated to dryness to give the intermediate alcohol compound as a beige solid (0.84 g, 92% yield). M.p. > 140°C (decomp.); ^{1}H NMR ($CDCl_3$): δ = 2.90–3.05 (m, 4H), 3.10–3.20 (m, 4H), 4.81 (s, 2H), 6.86 (s, 1H), 6.92 (d, 1H, ^3J = 4.7 Hz), 7.32 ppm (d, 1H, ^3J = 4.7 Hz); IR (KBr): $\tilde{\nu}$ = 3100–3600 cm^{-1} (O–H); elemental analysis calcd (%) for $C_{15}H_{14}OS_2$: C 65.66, H 5.14, S 23.37, O 5.83; found: C 65.73, H 5.32, S 21.81, O 6.11. A solution of 1M PBr_3 in CH_2Cl_2 (0.75 mL, 0.75 mmol) was added to a solution of alcohol (0.40 g, 1.46 mmol) in anhydrous THF (35 mL) cooled between −5°C and −10°C under an N_2 atmosphere. After 5 min of additional stirring at between −5°C and −10°C (the complete conversion of the alcohol was confirmed by TLC), this solution was rapidly poured onto a solution of $NaPO(OEt)_2$ in anhydrous THF at −10°C (freshly prepared by dropwise addition of a solution of $HPO(OEt)_2$ (0.75 mL, 5.81 mmol) in anhydrous THF (5 mL) to a suspension of 60% NaH dispersion in oil (0.23 g, 5.81 mmol) in anhydrous THF (10 mL) cooled to −10°C, with the reaction being stirred for 1 h between −5°C and −10°C under an N_2 atmosphere). The reaction mixture was stirred at 0°C for 2 h and was slowly warmed to 20°C overnight. After addition of water (40 mL) and extraction with CH_2Cl_2, the organic phases were washed with water, dried (Na_2SO_4), and evaporated in vacuo. The oily residue was purified by chromatography on silica gel (eluent: CH_2Cl_2/EtOAc (9:1)) to afford a beige solid (0.26 g, 45% yield). M.p. 123–126°C; ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 6H, ^3J = 7.2 Hz), 2.90–3.06 (m, 4H), 3.13–3.28 (m, 4H), 3.37 (d, 2H, $^2J_{H,P}$ = 21.1 Hz), 4.11 (m, 4H), 6.83 (d, 1H, $^4J_{H,P}$ = 3.8 Hz), 6.91 (d, 1H, ^3J = 4.9 Hz), 7.31 ppm (d, 1H, ^3J = 4.9 Hz); EI MS: *m*/*z* (%): 394 [$M^{+\bullet}$] (38), 257 (100).

Diethylphosphonate 19c: $NaBH_4$ (0.19 g, 5 mmol) was added in small amounts to a solution of aldehyde **18c** (2 g, 4.03 mmol) in a mixture of THF (120 mL) and MeOH (30 mL) cooled to 0°C and the reaction mixture was stirred overnight at 20°C. After partial concentration of the solvents, an aqueous solution of 1M HCl (40 mL) was added and the mixture was extracted with CH_2Cl_2. The organic phases were thoroughly washed with water, dried (Na_2SO_4), and concentrated to dryness. Recrystallization from iPr$_2$O gave a beige solid (1.60 g, 80% yield). M.p. 122–124°C; ^{1}H NMR ($CDCl_3$): δ = 2.90–3.05 (m, 4H), 3.10–3.20 (m, 4H), 4.81 (s, 2H), 6.86 (s, 1H), 6.92 (d, 1H, ^3J = 4.7 Hz), 7.32 ppm (d, 1H, ^3J = 4.7 Hz); EI MS: *m*/*z* (%): 498 [$M^{+\bullet}$] (32), 482 (75), 480 (85), 382 (100); IR (KBr): $\tilde{\nu}$ = 3393 cm^{-1} (O–H); elemental analysis calcd (%) for $C_{31}H_{46}OS_2$: C 74.64, H 9.29, S 12.85, O 3.21; found: C 74.38, H 9.46, S 12.56, O 3.27.

A solution of 1M PBr_3 in CH_2Cl_2 (0.33 mL, 0.33 mmol) was added to a solution of alcohol (0.50 g, 1 mmol) in anhydrous THF (20 mL) cooled to 0°C under an N_2 atmosphere. After 5 min of additional stirring at 0°C (complete conversion of the alcohol was confirmed by TLC), this solution was rapidly poured onto a solution of $NaPO(OEt)_2$ in anhydrous THF at −20°C (freshly prepared by dropwise addition of a solution of $HPO(OEt)_2$ (0.86 mL, 6.67 mmol) in anhydrous THF (10 mL) to a suspension of 60% NaH dispersion in oil (0.27 g, 6.75 mmol) in anhydrous THF(10 mL) cooled to −20°C, with the reaction being stirred successively for 1 h at −20°C and 2 h at 20°C, then cooled to −20°C under an N_2 atmosphere). The reaction mixture was stirred at −10°C for 1 h and was slowly warmed to 20°C overnight. The mixture was poured onto ice (100 mL) and Et_2O (50 mL) was added. The organic phase was separated by decantation and the aqueous phase was extracted with CH_2Cl_2. The organic phases were dried (Na_2SO_4) and evaporated in vacuo. The residue was purified by flash chromatography on silica gel (eluents: CH_2Cl_2, CH_2Cl_2/EtOAc (9:1), and CH_2Cl_2/EtOAc (7:3)) to afford a brown solid (0.22 g, 35% yield): M.p. = 116–119°C; ^{1}H NMR ($CDCl_3$): δ = 1.32 (t, 6H, ^3J = 6.9 Hz), 1.27–1.32 (m, 28H), 1.48–1.53 (m, 2H), 2.49–2.53 (m, 4H), 2.88–2.90 (m, 4H), 3.14–3.21 (m, 4H), 3.31 (d, 2H, $^2J_{H,P}$ = 21.0 Hz), 4.06–4.12 (m, 4H), 6.89 ppm (s, 1H); EI MS: *m*/*z* (%): 618 [$M^{+\bullet}$] (100), 481 (33); HRMS: calcd for $C_{35}H_{55}O_3S_2P$: 618.333028; found: 618.328264.

Compound 2: *t*BuOK (45 mg, 0.40 mmol) was added in small amounts to a solution of aldehyde **18a** (50 mg, 0.21 mmol) and freshly purified phos-

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phonate derivative **19a** (80 mg, 0.20 mmol) in anhydrous THF (15 mL) cooled to 0 °C under an N_2 atmosphere. The solution rapidly became dark red and the mixture was stirred at 20 °C for 5 h. The solvent of the reaction was partially evaporated under reduced pressure before MeOH (25 mL) was added. The resulting precipitate was recovered by filtration and successively washed with water, MeOH, and Et_2O to give a dark red-brown powder (72 mg, 69 % yield). M.p. 269–272 °C; UV/Vis (CH_2Cl_2): λ_{max} (log ε) = 456 (4.26), 485 (4.32), 520 nm (4.25); EI MS: *m*/*z* (%): 512 [$M^{+\cdot}$] (100), 482 (33), 384 (24), 257 (31); HRMS: calcd for $C_{30}H_{24}S_4$: 512.076088; found: 512.075522.

Compound 3: After the dropwise addition of $TiCl_4$ (0.16 mL, 1.43 mmol) to anhydrous THF (20 mL) cooled to 0 °C under an N_2 atmosphere, zinc powder (0.19 g, 2.86 mmol) was added in one portion. The mixture was successively warmed up to room temperature, refluxed for 30 min, and cooled again to 0 °C before a solution of compound **18b** (0.50 g, 1.30 mmol) in anhydrous THF (50 mL) was added. The reaction mixture was then refluxed for 1.5 h (completion of the reaction was checked by TLC with CH_2Cl_2/petroleum ether (1:9) as the eluent). At 20 °C, water (40 mL) was added and the mixture was extracted with CH_2Cl_2. The organic phases were washed with water, dried (Na_2SO_4), and concentrated to dryness. The residue was purified by chromatography on silica gel (deposition of the residue dissolved in pure CH_2Cl_2 or THF and elution with CH_2Cl_2/cyclohexane (4:6)). The product was then dissolved in the minimum amount of THF and precipitated with an excess of MeOH after 1 h at 4 °C to give a dark red powder (0.33 g, 69 % yield) which was a mixture of diastereomers. M.p. 229–232 °C; ^{1}H NMR ($CDCl_3$): δ = 0.90–1.00 (m, 12H), 1.25–1.85 (m, 24H), 2.70–2.94 (m, 4H), 3.15–3.52 (m, 8H), 6.85 (s, 2H), 6.94 (d, 2H, ^3J = 4.9 Hz), 7.00 (s, 2H), 7.31 ppm (d, 2H, ^3J = 4.9 Hz); ^{13}C NMR ($CDCl_3$): δ = 14.11, 22.86, 29.66, 29.71, 29.76, 36.36, 36.44, 40.52, 41.60, 42.38, 120.73, 121.80, 122.73, 125.63, 126.25, 129.39, 142.20, 143.30, 147.22, 154.63, 154.71; EI MS: *m*/*z* (%): 736 [$M^{+\cdot}$] (42), 370 (100), 313 (86); HRMS: calcd for $C_{46}H_{56}S_4$: 736.326489; found: 736.326242; UV/Vis (CH_2Cl_2): λ_{max} (log ε): 460 (4.55), 489 (4.72), 523 nm (4.67); elemental analysis calcd (%) for $C_{46}H_{56}S_4$: C 74.95, H 7.66; found: C 75.02, H 7.52.

Compound 4: *t*BuOK (90 mg, 0.80 mmol) was added in small amounts to a solution of aldehyde **18c** (170 mg, 0.34 mmol) and freshly purified phosphonate derivative **19c** (210 mg, 0.34 mmol) in anhydrous THF (15 mL) cooled to 0 °C under an N_2 atmosphere. The solution rapidly became dark red and the mixture was stirred at 20 °C for 5 h. After addition of MeOH, the resulting precipitate was recovered by filtration and successively washed with water, MeOH, Et_2O, and MeOH to give a dark red-brown powder (305 mg, 93 % yield). M.p. 202–204 °C; ^{1}H NMR (CS_2/C_6D_6): δ = 0.81 (brs, 12H), 1.20 (brs, 40H), 1.48 (brs, 8H), 2.38–2.46 (m, 8H), 2.76 (brs, 8H), 2.99–3.12 (m, 8H), 6.69 ppm (s, 4H); HRMS (ESI): calcd for $C_{62}H_{88}S_4$: 960.576890; found: 960.5821; UV/Vis (CH_2Cl_2): λ_{max} (log ε): 466 (4.46), 495 (4.61), 531 nm (4.54).

Compound 5: *t*BuOK (130 mg, 1.14 mmol) was added in small amounts to a solution of dialdehyde **17c** (100 mg, 0.19 mmol) and phosphonium salt **15a** (270 mg, 0.57 mmol) in a mixture of anhydrous THF (30 mL) and anhydrous CH_3CN (20 mL) cooled to 0 °C under an N_2 atmosphere. After concentration to dryness, the residue was purified by two successive filtrations on silica gel (eluent: CH_2Cl_2) to afford an orange-brown powder (20 mg, 14 % yield): M.p. = 130–132 °C; ^{1}H NMR (CS_2/C_6D_6): δ = 0.78–0.81 (m, 6H), 1.15–1.24 (m, 20H), 1.32–1.50 (m, 4H), 2.47 (t, 4H, ^3J = 7.6 Hz), 2.78–2.80 (m, 4H), 2.86–2.88 (m, 4H), 3.08 (brs, 4H), 3.22–3.24 (m, 4H), 6.49 (brs, 2H), 6.66 (d, 2H, ^3J = 4.7 Hz), 7.01 ppm (d, 2H, ^3J = 4.7 Hz); MALDI-TOF MS: calcd for $C_{46}H_{56}S_4$: 736.3264; found: 736.32 [$M^{+\cdot}$]; UV/Vis (CH_2Cl_2): λ_{max} (log ε): 450 (4.44), 478 (4.57), 513 nm (4.48).

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