Oligothiophene *S,S*-Dioxides. Synthesis and Electronic Properties in Relation to the Parent Oligothiophenes

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Oligothiophene *S,S*-dioxides from dimers to pentamers were obtained in good yields by reaction of mono- and dibrominated thiophene *S,S*-dioxides with the appropriate thienyl stannanes in the presence of $Pd(AsPh_3)_4$ generated in situ. The reaction rate with brominated thiophene *S,S*-dioxides is greatly accelerated compared to that employing thienyl bromides to obtain the parent oligothiophenes. HF/6-31G*ab initio calculations on 2,2′-bithiophene and the corresponding mono- and bis-*S,S*-dioxides show that the functionalization of the thienyl sulfur to the *S,S*-dioxide does not affect the π,π^* nature of the frontier orbitals, decreases the energy of the LUMO much more than that of the HOMO, increases the degree of planarity of the molecular skeleton, and leads to higher syn anti rotation barriers about the carbon−carbon bond.

It is well-known that di- or higher alkylated thiophenes are oxidized to the corresponding thiophene *S,S*-dioxides by peroxides such as *m*-chloroperoxybenzoic acid (*m*-CPBA) or dimethyldioxirane.[1] Recently, it has been reported that thiophenes substituted with electron-withdrawing groups can be efficiently oxidized to *S,S*-dioxides using the complex $HOF{\cdot}CH_3CN$, obtained by passing F_2 through a mixture of CH_3CN and H_2O.[2] Even more recently, the synthesis and the low-temperature characterization of unsubstituted thiophene *S,S*-dioxide, which dimerizes at ambient temperature, has been described.[3] The interest in polysubstituted thiophene *S,S*-dioxides stems from the fact that they are useful synthetic intermediates for the preparation of various types of organic compounds, since they may undergo Diels−Alder or other diene reactions.[1b]

We have extended the oxidation with *m*-CPBA to α,ω-bissilylated oligothiophenes from bi- to quaterthiophene and showed that incorporation of a thiophene *S,S*-dioxide moiety into an oligothiophene increases dramatically the electron delocalization and the electron affinity of the molecule.[4a,b] This result was encouraging in relation to the possibility of transforming oligothiophenes—which are p-type (hole-transporting) semiconducting materials applied in a variety of organic based devices[5]—into n-type (electron-transporting) semiconductors.

However, in the course of our study of oxidation of oligothiophenes with *m*-CPBA, we observed an accentuated decrease of the rate of formation of the *S,S*-dioxides upon increasing the length of the oligomer, probably due to increasing aromatic stabilization. Moreover, with the longer oligothiophenes, mixtures of partially oxidized oligothiophenes were obtained, which became difficult to separate by chromatography or crystallization.[4a] As a consequence, we decided to explore different synthetic pathways to obtain oligothiophene *S,S*-dioxides.

We report here results showing that the coupling of brominated thiophene *S,S*-dioxides with thienyl stannanes in the presence of a palladium(0) catalyst (Stille reaction[6]) allows for the easy and selective insertion of thiophene *S,S*-dioxide moieties into the skeleton of bi-, ter-, quater- and quinquethiophenes. We also report an ab initio HF/6-31G* study of the changes caused by this chemical modification in the HOMO and LUMO frontier orbitals compared to those of the parent oligothiophenes and in the energy barriers to rotation around the inter-ring carbon−carbon bonds.

Results

Synthesis of the Materials. The pattern followed to synthesize dimers, trimers, tetramers, and pentamers

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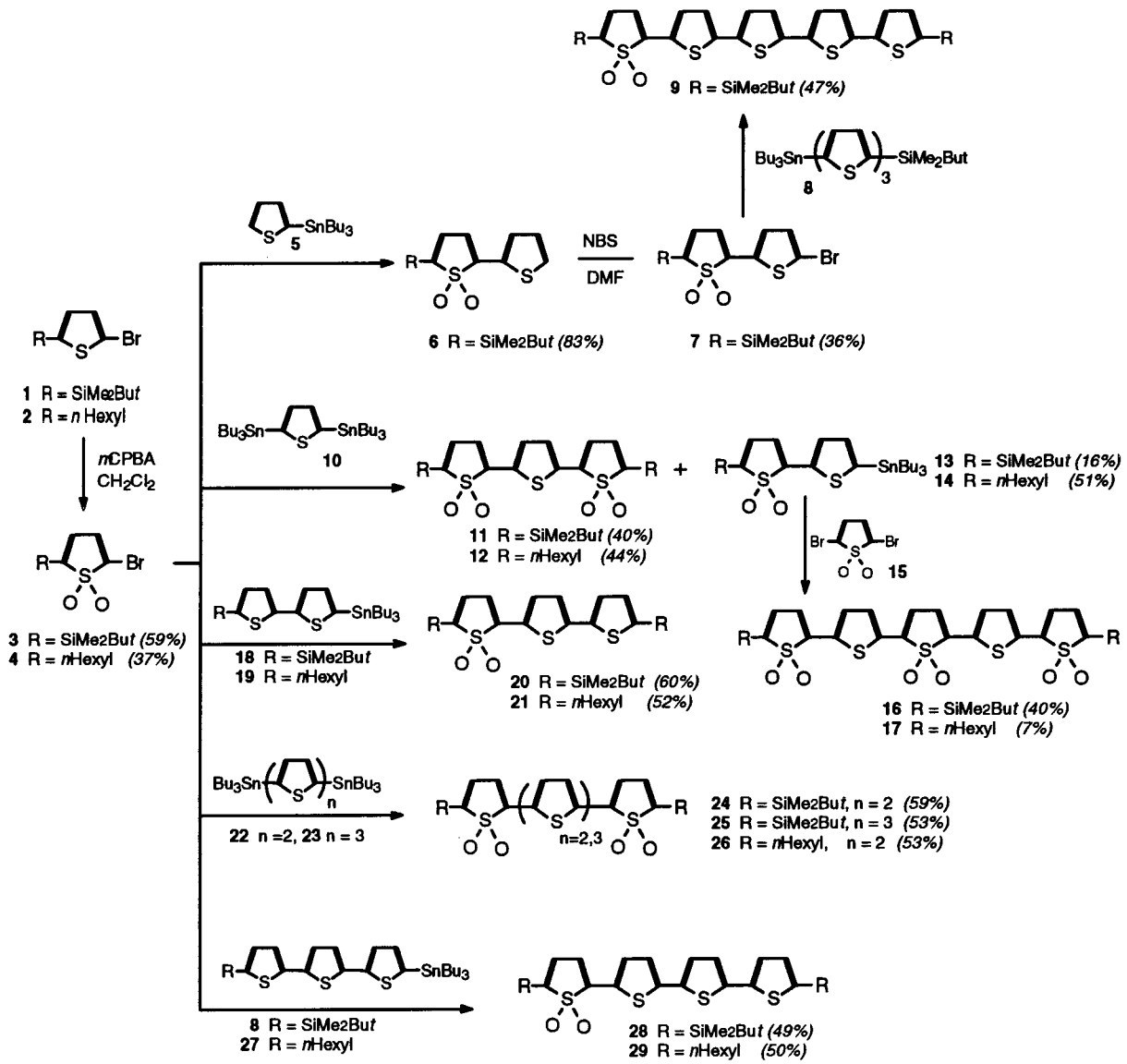
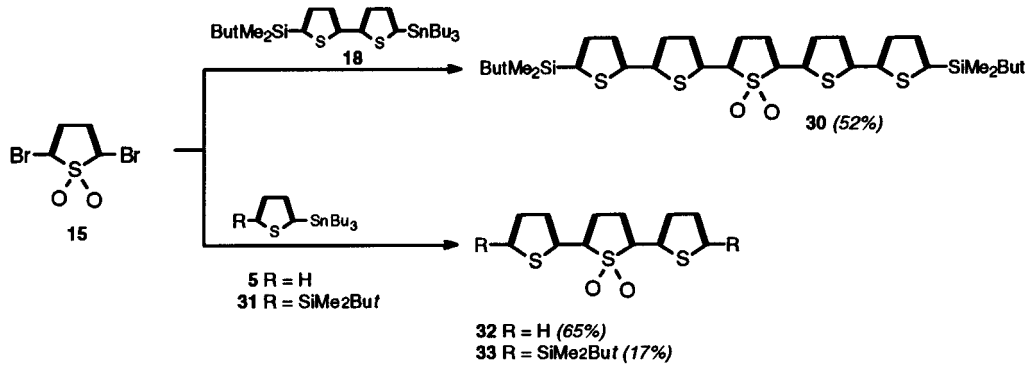
Scheme 1



Scheme 2



containing from one to three thiophene *S*,*S*-dioxide units is illustrated in Schemes 1−3. Scheme 3 also gives the synthetic pathway followed to obtain some oligothiophenes never described so far and useful to compare their electronic properties to those of the corresponding *S*,*S*-dioxides. Most products were α,ω-functionalized to prevent reactivity at the terminal positions. Dimethyl-*tert*-butylsilyl and *n*-hexyl were chosen as end-capping groups on the grounds that they favor a very ordered molecular arrangement in the solid state.[7]

2-(Dimethyl-*tert*-butylsilyl)-5-bromothiophene 1,1-dioxide (**3**), the corresponding 2-(*n*-hexyl) derivative (**4**), and

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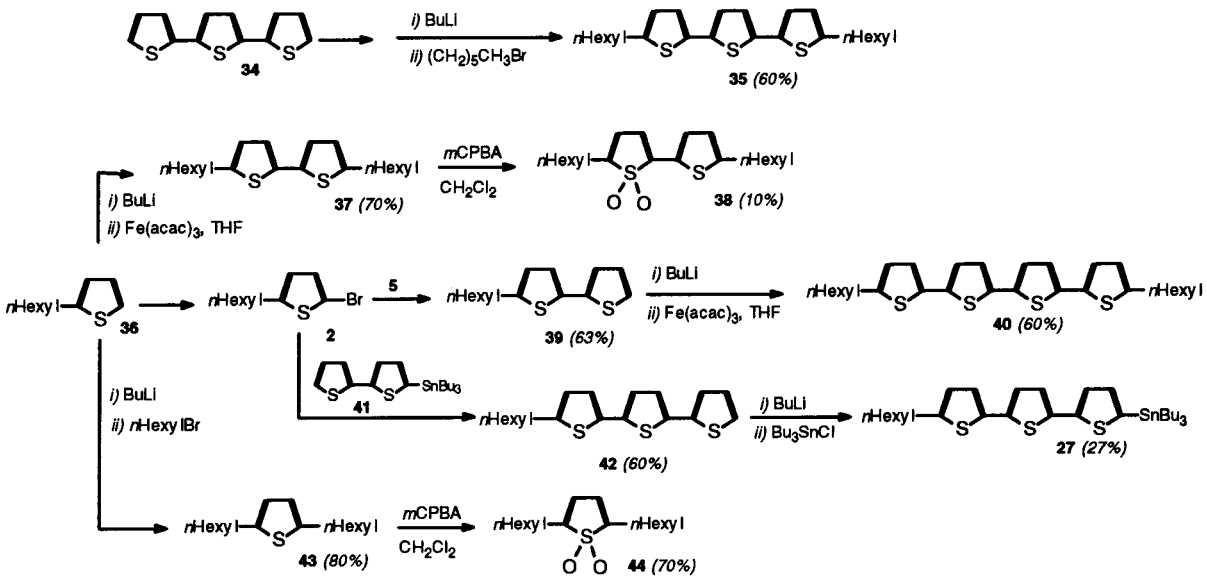
Scheme 3



2,4-dibromothiophene 1,1-dioxide (**15**) were used for the Stille coupling with the appropriate thienylstannanes in the presence of $Pd(AsPh_3)_4$ generated in situ. The choice of $Pd(AsPh_3)_4$ was motivated by the fact that this is the catalyst leading to the best reaction yields in the synthesis of oligothiophenes.[4c]

Thiophene *S,S*-dioxides **3** and **4** were obtained by action of 2 molar equiv of *m*-CPBA on the 2-bromothienyls **1** and **2**. The yield of the reaction depends largely on the ability to separate the mixture of unreacted *m*-CPBA and *m*-chlorobenzoic acid from the *S,S*-dioxide that is formed. In our case, the bissilylated compound **3** (59% yield) was more easily separated than its dialkylated counterpart **4** (37% yield).

2,5-Dibromothiophene 1,1-dioxide **15** was prepared from 2,5-bis(trimethylsilyl)thiophene 1,1-dioxide by action of bromine in the presence of $AgBF_4$, according to the procedure described by Furukawa et al.[1d] This reaction affords compound **15** in high yield (70%). We were able to identify one of the byproducts of this reaction (~5% yield), namely 2,3,5-tribromothiophene 1,1-dioxide, which was obtained in the form of colorless crystals suitable for X-ray structure determination (see below).

Brominated thiophene *S,S*-dioxides **3**, **4**, and **15** reacted with thienylstannanes in the presence of $Pd(AsPh_3)_4$ generated in situ to form carbon−carbon bonds in yields up to 65%. The reaction rate was much faster than that between thienyl bromides and thienylstannanes in the presence of the same catalyst.[4c,6] Carrying out detailed kinetic measurements was beyond the aim of the present work, but, qualitatively, we estimated the reaction rate of brominated thiophene *S,S*-dioxides with thienyl stannanes as being of about 2 orders of magnitude greater than that of thienyl bromides with thienylstannanes. This decreases from hours to minutes the reaction time required for the formation of the C−C bond and makes oligothiophene *S,S*-dioxides easier to prepare than some of the parent oligothiophenes, particularlly the longer ones.

As shown in Schemes 1 and 2, the reaction of monobrominated thiophene *S,S*-dioxides **3** and **4** with thienylmono- and -distannanes allows the insertion of thiophene *S,S*-dioxide units at the terminal positions of oligothiophenes, whereas the coupling of dibrominated dioxide **15** with thienylmonostannanes allows the insertion of a thiophene *S,S*-dioxide unit in the central position of the molecular skeleton. It is worth noting that the coupling of **15** with stannanes **13** and **14**, which already contained a thiophene *S,S*-dioxide moiety, allowed the preparation of quinquethiophenes **16** and **17** characterized by alternating aromatic and nonaromatic units (Scheme 1). The yield of formation of stannanes **13** and **14** depends largely on the reaction conditions and in particular on the rate of addition of thienyldistannane **10**. When **10** was added very slowly (dropwise, in more than 1 h), a yield increase from 13% to 52% was observed for compound **14**.

Scheme 3 gives the synthetic pathways to obtain a few oligothiophenes and thiophene *S,S*-dioxides bearing *n*-hexyl groups at the terminal positions. Bis(*n*-hexyl) bi- and quaterthiophenes **37** and **40** were obtained in high yield by coupling of lithiated 2-(*n*-hexyl)thiophene and 2-(*n*-hexyl)-2,2′-bithiophene in the presence of iron acetilacetonate, $Fe(acac)_3$. As we have already found in other cases,[4d] this reaction[8] affords highly pure compounds in rather good yields and appears a very useful way to obtain even-numbered α,ω-substituted oligothiophenes.

The oxidation of 2,5-bis(*n*-hexyl)thiophene (**43**) with *m*-CPBA affords the corresponding *S,S*-dioxide (**44**) in 70% yield. On the contrary, the oxidation of 2,5′-bis(*n*-hexyl)-2,2′-bithiophene (**37**) is difficult, the monodioxide (**38**) is obtained in low yield (10%), and no bis-*S,S*-dioxide is formed. It is worth noting that the oxidation of 2,5′-bis(dimethyl-*tert*-butylsilyl)-2,2′-bithiophene with *m*-CPBA is easier and that the 1,1,1′,1′-tetraoxide derivative can be prepared in this way.[4a]

Table 1 gives the UV−vis maximum wavelength absorption (λ_{max}) of oligothiophene *S,S*-dioxides of Schemes 1−3, compared to that of the parent oligothiophenes. The table shows that both 2-(*n*-hexyl)- and 2-(dimethyl-*tert*-butylsilyl)thiophene *S,S*-dioxide are red shifted (by 69 and 46 nm) with respect to the parent thiophenes and that this trend is mantained with the oligomers up to the pentamers. The insertion of the *S,S*-dioxide moieties

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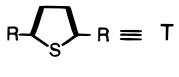
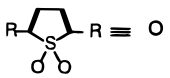
Table 1. Maximum Wavelength Absorption (λ_{max}, nm)[a] of *S,S*-Dioxides and of the Parent Oligothiophenes





R[b]	H	Sil	Hex
T	231	245[4a]	254 (**43**)
O		314[4a]	300 (**44**)
TT	302	344[4a]	340 (**37**)
OT		408[4a]	402 (**38**)
OO		406[4a]	
TTT	352	370[4a]	380 (**35**)
TOT	426 (**32**)	440 (**33**)	
OTT		460 (**20**)	430 (**21**)
OTO		460 (**11**)	442 (**12**)
TTTT	390	412[4a]	400 (**40**)
OTTT		470 (**28**)	448 (**29**)
TOTT		480[4a]	
OTTO		492 (**24**)	480 (**26**)
TTTTT	416	420	
OTTTT		470 (**9**)	
TTOTT		512 (**30**)	
OTTTO		520 (**25**)	
OTOTO		542 (**16**)	526 (**17**)

[a] In $CHCl_3$. [b] R = α,ω substituents. Sil = $SiMe_2$(*t*-Bu). Hex = $(CH_2)_5CH_3$.

affects more the λ_{max} of the longer oligomers, which in turn depends on the position and on the number of sulfonyl groups present in the molecular skeleton. Regioisomers such as trimers **33** and **20** or pentamers **9** and **30** display different λ_{max} values. The pentamer containing one terminal thiophene *S,S*-dioxide moiety (OTTTT, **9**) is red shifted by 50 nm with respect to quinquethiophene TTTTT, whereas the pentamer containing alternate aromatic and nonaromatic units (OTOTO, **16**) is red shifted by 122 nm with respect to TTTTT. As far as we know, **16** has the largest value of the maximum wavelength absorption (λ_{max} = 542 nm) ever measured for short thiophene-based oligomers.

Single-Crystal X-ray Structure of 2,3,5-Tribromothiophene 1,1-Dioxide.[9] This compound was obtained as a byproduct of the reaction of 2,5-bis(trimethylsilyl)thiophene with bromine in the presence of $AgBF_4$[1d] in the form of colorless crystals suitable for X-ray structure determination (see above). Since only very few structural data on thiophene *S,S*-dioxides are available so far,[1a] we report in Figure 1 the molecular structure of this compound together with the values of the bond angles and bond lengths.

The molecule is characterized by close coplanarity of all atoms of the five-membered ring (the maximum atomic deviation from mean plane is 0.005(8) Å). The oxygen atoms of the SO_2 moiety lie, roughly at the same distance, above and below the pentaatomic ring, and the plane through the O−S−O atoms is nearly pependicular (89.5(4)°) to that through the ring atoms. The Br atoms deviate slightly (maximum 0.11 Å) from such a plane.

Despite the limited accuracy due to the presence of three heavy Br atoms, C−C and C−S bond distances are consistent with two fully localized double bonds between C2−C3 and C4−C5 atoms (1.30(2) and 1.25(2) Å, respectively). With respect to the thiophene molecule, the loss of the aromatic conjugation by the S atom implies C−S and C3−C4 bond lengthening. Their values (1.75(1), 1.77(1), and 1.48(2) Å, respectively) in the present compound compare well with the reported mean single-bond length in parent derivatives.[10] It is of interest to

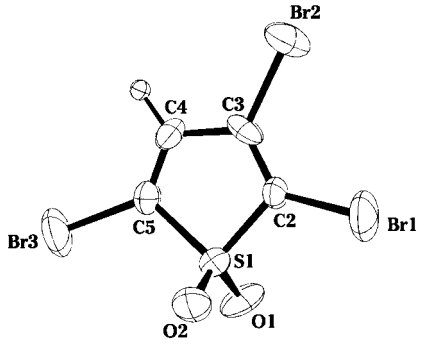


Figure 1. Molecular structure of 2,3,5-tribromothiophene 1,1-dioxide with atom numbering scheme. Thermal ellepsoids for non-H atoms enclose 60% probability. Bond lengths (Å): S1−O1, 1.414(8); S1−O2, 1.415(9); S1−C2, 1.752(12); S1−C5, 1.773(12); C2−C3, 1.30(2); C2−Br1, 1.838(10); C3−C4, 1.48-(2); C3−Br2, 1.866(10); C4−C5, 1.25(2); C5−Br3, 1.864(12). Bond angles (deg): O1−S1−O2, 116.8(6); O1−S1−C2, 110.5-(6); O2−S1−C2, 112.3(6); O2−S1−C2, 112.3(6); O1−S1−C5, 111.4(6); O2−S1−C5, 111.8(6); C2−S1−C5, 91.3(5); C3−C2−S1, 109.6(8); C3−C2−Br1, 130.3(9); S1−C2−Br1, 119.9(6); C2−C3−C4, 114.0(10); C2−C3−Br2, 125.8(9); C4−C3−Br2, 120.2(9); C5−C4−C3, 114.2(11); C4−C5−S1, 110.9(10); C4−C5−Br3, 131.3(10); S1−C5−Br3, 117.7(7).

note that the dimensions of the molecule are in close agreement with those previously found for the 2,5-di-*tert*-butyl analogue.[1a] The molecular packing is characterized by a number of extremely short van der Waals separations, all involving sulfonic O atoms. There are seven contacts less than 3.60 Å, four of them being less than 3.20 Å.

Theoretical Calculations. To have an idea of the effects caused by the functionalization of the thienyl sulfur on the frontier orbitals and on the energy barriers to rotation around the inter-ring C−C bonds, we carried out ab initio HF/6-31G* calculations[11] on 2,2′-bithiophene (TT), 2,2′-bithiophene 1,1-dioxide (OT), and 2,2′-bithiophene 1,1,1′,1′-tetraoxide (OO).

In agreement with the results of other authors for thiophene *S,S*-dioxide,[12] we found that the oxygen lone pairs of the SO_2 group do not interact with the adjacent unsaturated system and that the frontier orbitals of the dioxide and of the tetraoxide mantain the π,π^* character.

Figure 2 gives the HOMO and LUMO energies and the coefficients pattern of TT, TO, and OO. It is seen that the sulfur atoms are strongly involved in the LUMO (but not in the HOMO) of 2,2′-bithiophene. Thus, as shown in Figure 2, the transformation of the thienyl sulfur into the corresponding dioxide, which decreases the energy of both the HOMO and the LUMO, affects the energy of the latter much more than that of the former.

(9) The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

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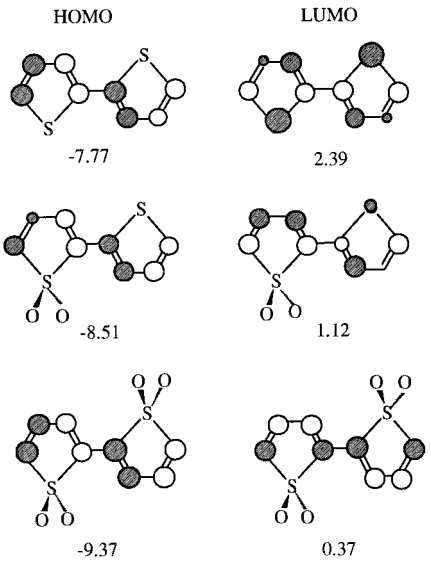

Figure 2. Coefficient patterns and energies (eV) of frontier orbitals of 2,2′-bithiophene, 2,2′-bithiophene-1,1-dioxide and 2,2′-bithiophene-1,1,1′,1′-tetraoxide as calculated at the HF/6-31G* level.

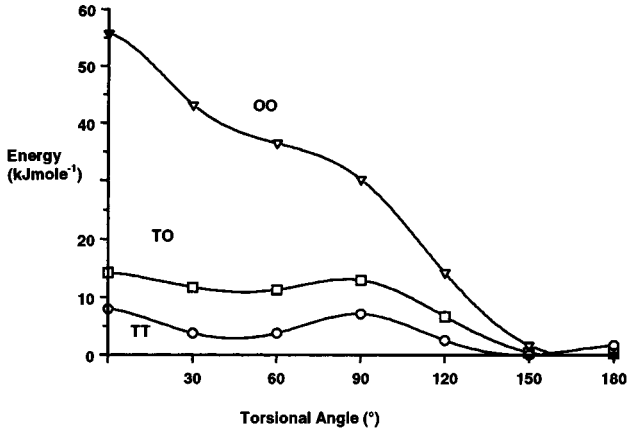

Figure 3. HF/6-31G* ab initio calculated torsional potential energies (kJ mol^{-1}) of 2,2′-bithiophene (TT), 2,2′-bithiophene-1,1-dioxide (TO), and 2,2′-bithiophene-1,1,1′,1′-tetraoxide (OO) vs inter-ring torsional angles (deg).

According to the calculations, there is a progressive decrease of the inter-ring bond distance on passing from TT (1.464 Å) to TO (1.453 Å) to OO (1.448 Å).

Figure 3 gives the ab initio HF/6-31G* calculated potential energies (kJ mol^{-1}) of TO and OO as a function of the torsional inter-ring angle ϕ (°) for ϕ varying from 0° (fully planar syn conformation) to 180° (fully planar anti conformation). For comparison, the potential energies of TT, calculated with the same basis set,[13] are also reported.

Fully relaxed geometry minimization of syn-like and anti-like TO forms leads to two minima at $\phi = 46.3°$ and 160.8°, with the latter being 10.46 kJ mol^{-1} lower in energy than the former. Qualitatively, the energy profile of TO is similar to that of TT, for which also two minima are found at $\phi = 43.9°$ and 147.4°.[13] However, the energy difference between the preferred syn and anti conformations of TT is smaller than that of OT. In particular, the energy of the anti conformation of TT is only 3.14 kJ mol^{-1} smaller than the corresponding syn one.

When both thienyl sulfurs of bithiophene are converted to the *S,S*-dioxide, the energy of the syn forms increases to a such extent that no energy minimum is found between 0° and 90°. Indeed, only a single energy minimum at $\phi = 169.6°$ is found for OO, indicating also in this case that the molecule is forced to exist entirely in the anti-quasiplanar conformation.

Discussion

The present results show that the palladium(0)-catalyzed reaction of brominated thiophene *S,S*-dioxides with thienylstannanes leads to the formation of new carbon−carbon bonds in relatively high yields. This reaction, which is a particular case of the well-known Stille reaction,[6] allows for the synthesis of oligothiophenes containing a variable number of dearomatized thiophene *S,S*-dioxide moieties in different positions of the molecular skeleton. Indeed, as shown in Schemes 1−3, depending on whether a mono- or a bisthienylstannane is used, thiophene *S,S*-dioxide moieties can be inserted in the external or in the internal position of a given oligomer. The appropriate choice of the stannanes and of the bromides makes also possible to vary the length of the aromatic residue between two adjacent nonaromatic thiophene *S,S*-dioxide moieties and even the synthesis of compounds having alternating aromatic and nonaromatic rings. This versatility is interesting in view of the fact that the redox properties[4a,b] and the optical gaps (see Table 1) of oligothiophene *S,S*-dioxides depend on the number and on the position of the dearomatized units and that in this way a fine modulation of the properties of this new class of compounds can be achieved.

The coupling reaction between thienylstannanes and thienyl bromides requires extreme conditions such as use of refluxing toluene as the solvent.[4c] On the basis of our previous experience with the synthesis of oligothiophenes, we employed extreme conditions also for the preparation of oligothiophene *S,S*-dioxides. However, the much greater reaction rate of brominated thiophene *S,S*-dioxides compared to the corresponding thienyl bromides suggests that these compounds could be synthesized in much milder conditions, such as refluxing or even room-temperature THF, as in the case of the coupling of arylstannanes with vinyl triflates.[14b]

There is much experimental evidence that thiophene *S,S*-dioxide and its polysubstituted counterparts are very reactive compounds that afford a variety of derivatives in the presence of Grignard reagents, organolithium compounds, amines, etc. through ring opening and subsequent rearrangements.[1b] Thus, the question arises whether and to what extent the reactivity of a thiophene *S,S*-dioxide moiety is changed upon insertion within the aromatic skeleton of an oligothiophene. In our experience, oligothiophene *S,S*-dioxides are very stable microcrystalline compounds. Their higher oxidation potentials[4a,b] make them less sensitive than the parent oligothiophenes to attack by moisture or oxygen.[15] They

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are apparently also less sensitive than oligo- and polythiophenes to photodegradation.[16]

Oligothiophene *S,S*-dioxides display smaller optical energy gaps than the parent oligothiophenes. Table 1 shows that their λ_{max} values are red shifted by 50 to 122 nm, depending on the number and on the position of the sulfonyl moieties. Pentamers **16** and **17**, having alternating aromatic and nonaromatic units, display unusually high λ_{max} values in chloroform (542 and 526 nm, respectively), even larger than those observed for regioregular functionalized polythiophenes.[17] The results of ab initio calculations on 2,2′-bithiophene and its mono- and bis-*S,S*-dioxides indicate that a contribution to such large λ_{max} values also comes from the more planar conformations of the bithiophene subsystems containing thiophene *S,S*-dioxide moieties and from the smallerr inter-ring carbon−carbon distances.

Figure 3 shows that the energy difference between the more stable anti conformation and the less stable, more puckered, syn conformation of 2,2′-bithiophene (TT) amounts to only 3.14 kJ mol^{-1}. Thus, in solution, TT exists as a family of syn and anti conformers of very similar energies. On the contrary, for 2,2′-bithiophene 1,1-dioxide (TO) and *a fortiori* for 2,2′-bithiophene 1,1,1′,1′-tetraoxide (OO), the difference in energy between the syn and anti conformation is such that only the latter is populated. These results indicate that the functionalization of the thienyl sulfur to the corresponding *S,S*-dioxide leads to the rigidification of the molecular skeleton. The rigidification of the backbone of oligo- and polythiophenes through the insertion of ethylene bonds is a strategy that has been pursued by several authors, since it leads to the lowering of the optical gap by decreasing the rotational disorder.[18] Clearly, the oxidation of the thienyl sulfur is an alternative way to achieve the same result, since the structural data reported in Figure 1 indicate that, in the end, this amounts to the insertion of a butadiene moiety rigidly held in the cis configuration by the sulfonyl group.

Theoretical calculations show (Figure 2) that on passing from TT to TO to OO there is a progressive decrease of the energy of both frontier orbitals and that the energy of the LUMO is decreased much more than that of the HOMO. Figure 2 shows that the latter effect is a consequence of the much greater contribution of sulfur lone pair to the LUMO of 2,2′-bithiophene. Thus, the calculations predict that the insertion of a thiophene *S,S*-dioxide moiety into the skeleton of an oligothiophene should lead to the increase of the electron affinity of the system.

The trend predicted by the calculations has been confirmed experimentally through the electrochemical determination of the reduction ($E_{c,p}$) and oxidation ($E_{a,p}$) potentials of 2,5′-bis(dimethyl-*tert*-butyl)-2,2′-bithiophene (SiTT) and of the corresponding mono- (SiTO) and bis-*S,S*-dioxides (SiOO).[4b] On going from SiTT to SiTO to SiOO, there is a progressive increase of the electron affinity of the system, as shown by the reduction potential that changes from <-2.1 V to -1.34 V to -0.85 V while the oxidation potential increases from 1.29 V to 1.6 V to 1.84 V. Electrochemical data also show that the trend is maintained with the longer oligothiophene *S,S*-dioxides. For example, while quinquethiophene TTTTT has $E_{c,p} = -2.13$ V and $E_{a,p} = 0.92$ V, pentamer OTOTO (**16**) characterized by alternating aromatic and nonaromatic units has $E_{c,p} = -0.82$ V and $E_{a,p} = 1.46$ V. In general, the selective insertion of a variable number of thiophene *S,S*-dioxide units according to the synthetic pathways described in Schemes 1−3 allows a fine-tuning of the redox properties of oligothiophenes, and the electron affinity can be increased to the point that the compounds are more easily reduced than oxidized.[4a,b]

Conclusion

We have shown that brominated thiophene *S,S*-dioxides can be successfully coupled to thienylstannanes in the presence of palladium(0) catalysts to afford oligomers bearing a variable number of thiophene *S,S*-dioxide moieties in different positions of the molecular skeleton.

The regioselective insertion of such units into the backbone of oligothiophenes permits us to achieve a continuous modulation of the electronic and redox properties of the system. The possibility for the thienyl sulfur atom to deconnect its lone pair from the aromatic system through the formation of the dioxide leads to smaller optical gaps, as shown by the large red shifts of the maximum wavelength absorption of oligothiophene *S,S*-dioxides with respect to that of the parent oligothiophenes. This also leads to a dramatic decrease of the LUMO energy and to the consequent increase of the electron affinity. In this way, it is possible to go from easily oxidized oligothiophenes to easily reduced oligothiophene *S,S*-dioxides containing alternating aromatic and non aromatic moieties.

Experimental Section

General Methods. Pd_2dba_3, $AsPh_3$, BuLi, 2-(tributylstannyl)thiophene, 2,2′-bithiophene, *n*-hexyl bromide, and Bu_3SnCl were purchased from Aldrich. *m*-Chloroperoxybenzoic acid (*m*-CPBA) and 2-(*n*-hexyl)thiophene were purchased from Fluka and Lancaster, respectively. All solvents used in reactions and chromatographies were dried by standard procedures. Flash chromatographies were carried out using silica gel (230−400 mesh ASTM) and analytical thin-layer chromatographies (TLCs) using 0.2 mm silica gel plates (Merck). The visualization in TLC was accomplished by UV light.

The synthesis of 2,5-bis(tributylstannyl)thiophene (**10**),[19] 2,5-dibromothiophene 1,1-dioxide **15**),[1d] 2,5′-bis(tributylstannyl)-2,2′-bithiophene (**22**),[19] and 2,5″-bis(tributylstannyl)-2,2′:5′,2″-terthiophene (**23**),[19] has already been described.

2,3,5-Tribromothiophene 1,1-dioxide (Figure 1) was obtained as a byproduct of the preparation of compound **15** according to ref 1d. The product was isolated as a colorless crystalline compound (from pentane): mp 120−122 °C; MS *m/e* 350 ($M^{\bullet+}$); $\lambda_{max}(CHCl_3)$ 330 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 6.95 (s, 1H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 131.2, 124.2, 120.5, 118.8. The crystals were suitable for X-ray structure determination.

2-(Dimethyl-*tert*-butylsilyl)-5-bromothiophene, 1. To a solution of 4.95 g (0.025 mol) of 2-(dimethyl-*tert*-butylsilyl)-thiophene[4a] in 15 mL of DMF at room temperature were added 4.37 g (0.025 mol) of *N*-bromosuccinimide.The mixture was stirred for 12 h at 80 °C. Then 50 mL of distilled water was added, followed by 50 mL of ethyl ether. The organic phase

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was separated, dried over $MgSO_4$, and evaporated. After distillation (95 °C, 18 mmHg), 4.1 g (59% yield) of a mixture of two products, identified as **1** and the isomeric 2-(dimethyl-*tert*-butylsilyl)-3-bromothiophene **1′**, was obtained. GC measurements gave a ratio 9:1 for **1**:**1′**. Further attempts to separate the isomers by distillation were unsuccessful, and the mixture was used as such in the subsequent steps.

1: MS *m/e* 276 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.09 (d, ^3J = 3.5 Hz, 1H), 6.99 (d, ^3J = 3.5 Hz, 1H), 0.92 (s, 9H), 0.28 (s, 6H).

1′: MS *m/e* 276 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.22 (d, ^3J = 4.5 Hz, 1H), 6.90 (d, ^3J = 4.5 Hz, 1H), 0.92 (s, 9H), 0.36 (s, 6H).

2-(*n*-Hexyl)-5-bromothiophene, 2. To a solution of 2.9 g (0.017 mol) of *2-n*-hexylthiophene **36** in 10 mL of DMF was added stepwise 3.03 g (0.017 mol) of *N*-bromosuccinimide. The mixture was stirred at room temperature for 4 h, 30 mL of distilled water was added, and then the organic compounds were extracted twice with 25 mL of methylene chloride. After the usual workup, the crude product was distilled (110 °C, 760 mmHg), and 2.53 g (84% yield) of pure **2** as a white oil was obtained: MS *m/e* 247 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 246 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 6.84 (d, ^3J = 3.6 Hz, 1H), 6.53 (doublet of triplets, ^3J = 3.6 Hz, ^4J = 1.8 Hz, 1H), 2.75 (t, 2H), 1.65 (m, 2H), 1.30 (m, 6H), 0.90 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 147.8, 129.4, 124.3, 108.5, 31.5, 31.4, 30.3, 28.7, 22.5, 14.0. Anal. Calcd for $C_{10}H_{15}BrS$: C, 48.59; H, 6.12. Found: C, 48.69; H, 6.11.

2-(Dimethyl-*tert*-butylsilyl)-5-bromothiophene 1,1-Dioxide, 3. A 3.34 g (0.012 mol) portion of the 9:1 mixture of **1** and **1′** dissolved in 30 mL of CH_2Cl_2 was added dropwise to a suspension of 7.41 g (0.03 mol) of *m*-CPBA 70% in CH_2Cl_2. After being stirred for 2 days at room temperature, the mixture was cooled to −50 °C, and the precipitate containing unreacted *m*-CPBA and *m*-chlorobenzoic acid was filtered. After evaporation of the solvent, the residue was crystallized from pentane to yield 2.19 g (59% yield) of **3** as a white solid: mp 94 °C; MS *m/e* 308 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) δ 6.88 (d, ^3J = 4.8 Hz, 1H), 6.73 (d, ^3J = 4.8 Hz, 1H), 0.98 (s, 9H), 0.31 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) δ 147.7, 138.5, 126.7, 125.5, 26.2, 17.3. Anal. Calcd for $C_{10}H_{17}BrO_2SSi$: C, 38.83; H, 5.54. Found: C, 38.71; H, 5.52.

2-(*n*-Hexyl)-5-bromothiophene 1,1-Dioxide, 4. A 2.05 g (8.3 mmol) portion of **2** was dissolved in 10 mL of methylene chloride and the solution added to a mixture of 5.1 g (21.0 mmol) of *m*-CPBA (70%) in 20 mL of methylene chloride. The mixture was stirred overnight at room temperature and then filtered and washed twice with a 10% solution of $NaHCO_3$, and the product was crystallized from pentane. A total of 0.85 g (37%) of a white crystalline product, mp 48 °C, was obtained: MS *m/e* 278 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 308 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 6.76 (d, ^3J = 4.8 Hz, 1H), 6.36 (doublet of triplets, ^3J = 4.8 Hz, ^4J = 2.0 Hz, 1H), 2.50 (m, 2H), 1.65 (m, 2H), 1.30 (m, 6H), 0.90 (m, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 145.5, 127.5, 122.5, 119.2, 31.3, 28.6, 26.3, 25.3, 22.4, 13.9. Anal. Calcd for $C_{10}H_{15}BrO_2S$: C, 43.02; H, 5.42. Found: C, 42.96; H, 5.43.

5-(Dimethyl-*tert*-butylsilyl)-2,2′-bithiophene 1,1-Dioxide, 6. To a solution of 0.05 mmol of $Pd(AsPh_3)_4$ in 10 mL of toluene prepared in situ[4c] was added 0.515 g (1.67 mmol) of **3** and 0.621 g (1.67 mmol) of 2-(tributylstannyl)thiophene at room temperature. After being heated at reflux for 1 h, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl, extracted with ethyl ether, dried over $MgSO_4$, and evaporated. The residue was crystallized from pentane to give 0.42 g (83% yield) of yellow crystals: mp 75−76 °C; MS *m/e* 312 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 376 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.65 (m, 1H), 7.44 (m, 1H), 7.13 (m, 1H), 6.97 (d, ^3J = 4.1 Hz, 1H), 6.63 (d, ^3J = 4.1 Hz, 1H), 0.99 (s, 9H), 0.35 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 142.8, 140.7, 138.7, 129.9, 129.0, 128.6, 128.5, 117.3, 26.4, 17.2. Anal. Calcd for $C_{14}H_{20}O_2S_2Si$: C, 53.80; H, 6.45. Found: C, 53.73; H, 6.43.

5-(Dimethyl-*tert*-butylsilyl)-5′-bromo-2,2′-bithiophene 1,1-Dioxide, 7. To a solution containing 0.312 g (1.0 mmol) of **6** in 5 mL of DMF was added stepwise 0.178 g (1.0 mmol) of *N*-bromosuccinimide at room temperature. After 2 days of heating at 80 °C, the mixture was cooled at room temperature, hydrolyzed with a saturated solution of NH_4Cl, extracted with ethyl ether, dried over $MgSO_4$, and evaporated. The residue was chromatographed on silica gel using petroleum ether/methylene chloride 5:1 as the eluent, and 0.142 g (36% yield) of **7** as a yellow oil was recovered: MS *m/e* 390 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.36 (d, ^3J = 3.9 Hz, 1H), 7.08 (d, ^3J = 3.9 Hz, 1H), 6.94 (d, ^3J = 4.5 Hz, 1H), 6.55 (d, ^3J = 4.5 Hz, 1H), 1.00 (s, 9H), 0.33 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 143.1, 139.6, 138.5, 131.6, 129.4, 127.7, 123.7, 117.2, 26.2, 17.2. Anal. Calcd for $C_{14}H_{19}BrO_2S_2Si$: C, 42.96; H, 4.89. Found: C, 43.02; H, 4.91.

5-(Dimethyl-*tert*-butylsilyl)-5″-(tributylstannyl)-2,2′:5′,2″-terthiophene, 8. To a solution containing 0.28 g (0.773 mmol) of 5-(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″-terthiophene[4a] was added 0.31 mL (0.773 mmol) of a 2.5 M solution of BuLi in hexane. After 1 h, 0.21 mL (0.773 mmol) of Bu_3SnCl was added dropwise. The reaction mixture was stirred overnight, hydrolyzed with a saturated solution of NH_4Cl, extracted with ethyl ether, dried over $MgSO_4$, and evaporated. A total of 0.471 g (94% yield) of pure **8** as a dark green oil was recovered: MS *m/e* 650 ($M^{\bullet+}$): ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.28 (d, ^3J = 3.8 Hz, 1H), 7.22 (d, ^3J = 3.6 Hz, 1H), 7.14 (d, ^3J = 3.6 Hz, 1H), 7.08 (s, 2H), 7.07 (d, ^3J = 3.8 Hz, 1H), 1.56 (m, 6H), 1.33 (m, 6H), 1.12 (t, 6H), 0.98 (s, 9H), 0.86 (t, 9H), 0.3 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 142.9, 142.5, 136.8, 136.7, 136.5, 136.3, 136.0, 135.9, 124.8, 124.5, 124.3, 124.2, 29.0, 27.2, 26.4, 16.9, 13.7, 10.9.

5,5‴-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene 1,1-Dioxide, 9. To a 10 mL toluene solution containing 0.006 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] was added 0.138 g (0.212 mmol) of **8** and 0.081 g (0.212 mmol) of **7**, and the solution was refluxed during 4 h. The reaction mixture was then hydrolyzed with a saturated solution of NH_4Cl, and after usual workup the residue was washed with ethyl ether. A total of 0.069 g (47% yield) of **9** as a red polycrystalline solid, mp 216−217 °C, was recovered: MS *m/e* 672 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 470 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.56 (d, ^3J = 4.0 Hz, 1H), 7.26 (d, ^3J = 4.0 Hz, 1H), 7.19 (d, ^3J = 4.0 Hz, 1H), 7.16 (d, ^3J = 3.5 Hz, 1H), 7.15 (d, ^3J = 3.5 Hz, 1H), 7.11 (s, 2H), 7.10 (d, ^3J = 4.0 Hz, 1H), 6.99 (d, ^3J = 4.6 Hz, 1H), 5.57 (d, ^3J = 4.6 Hz, 1H), 1.02 (s, 9H), 0.97 (s, 9H), 0.36 (s, 6H), 0.32 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm): 142.6, 141.9, 140.4, 140.2, 138.8, 138.6, 137.7, 137.5, 136.9, 136.1, 135.3, 134.8, 130.2, 125.8, 124.9, 124.8, 124.4, 124.3, 116.4, 26.3, 26.2, 17.3, 16.9. Anal. Calcd for $C_{32}H_{40}O_2S_5Si_2$: C, 57.10; H, 5.99. Found: C, 56.98; H, 6.01.

5,5″-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″-terthiophene 1,1,1″,1″-Tetraoxide, 11, and 5-(Dimethyl-*tert*-butylsilyl)-5′-(tributylstannyl)-2,2′-bithiophene 1,1-Dioxide, 13. To a 10 mL toluene solution containing 0.018 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.28 g (0.9 mmol) of **3** and 0.597 g (0.9 mmol) of 2,5-bis(tributylstannyl)thiophene **10**.[19] After being heated at reflux for 1 h, the toluene was evaporated and the residue was chromatographed on silica gel. Petrolueum ether was used as the first eluent, and 0.087 g (16%) of **13** as a yellow oil was recovered. Subsequent elution with petroleum ether/CH_2Cl_2 5:1 gave 0.097 g (40%) of a compound corresponding to tetradioxide **11**.[4a]

13: MS *m/e* 602 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.73 (d, ^3J = 3.3 Hz, 1H), 7.18 (d, ^3J = 3.3 Hz, 1H), 6.96 (d, ^3J = 4.3 Hz, 1H), 6.69 (d, ^3J = 4.3 Hz, 1H), 1.55 (m, 6H), 1.30 (m, 6H), 1.12 (t, 6H), 0.99 (s, 9H), 0.87 (t, 9H), 0.32 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 143.3, 141.8, 140.6, 139.1, 136.8, 134.8, 129.6, 116.6, 27.2, 27.0, 26.2, 17.2, 13.6, 11.0.

5,5″-Bis(*n*-hexyl)-2,2′:5′,2″-terthiophene 1,1,1″,1″-Tetraoxide, 12. To a 12 mL toluene solution containing 0.018 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] was added 0.30 g (0.45 mmol) of 2,5-bis(tributylstannyl)thiophene **10**,[19] and 0.25 g (0.90 mmol) of *2-n*-hexyl-5-bromothiophene 1,1-dioxide **4** was then added. The mixture was refluxed for 5 h, treated with a saturated solution of NH_4Cl, and washed with water, and the organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was chromatographed on silica gel using petroleum ether/methylene chloride 80:20. A total of

96 mg (44% yield) of **12** as a deep orange polycrystalline compound, mp 191−192 °C, was separated: MS *m/e* 480 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 442 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.53 (s, 2H), 6.67 (d, ^3J = 4.8 Hz, 2H), 6.44 (doublet of triplets, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 2H), 2.55 (t, 4H), 1.70 (m, 4H), 1.30 (m, 12H), 0.9 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 144.8, 134.2, 131.5, 128.8, 122.3, 119.8, 31.3, 28.8, 26.6, 24.5, 22.5, 14.0. Anal. Calcd for $C_{24}H_{32}O_4S_3$: C, 59.97; H, 6.71. Found: C, 59.88; H, 6.69.

5-(*n*-Hexyl)-5′-(tributylstannyl)-2,2′-bithiophene 1,1-Dioxide, 14. To a solution of 0.84 g (0,003 mol) of *2-(n*-hexyl)-5-bromo-thiophene 1,1-dioxide **4** and 0.17 g (0.15 mmol) of commercial $Pd(PPh_3)_4$ in 20 mL of toluene was added stepwise 2.00 g (0.003 mol) of 2,5-bis(tributylstannyl)thiophene **10**[19] dissolved in 8 mL of toluene over 1 h. The solution was refluxed for 1 h. After usual workup, 0.87 g (51% yield) of a yellow oil was obtained. The product was used as such: MS *m/e* 572 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 360 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.67 (d, ^3J = 3.5 Hz, 1H), 7.15 (d, ^3J = 3.5 Hz, 1H), 6.59 (d, ^3J = 4.8 Hz, 1H), 6.41 (doublet of triplets, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 1H), 2.52 (t, 2H), 1.6 (m, 8H), 1.3 (18H), 0.85 (m, 12H).

5,5′′′′-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene 1,1,1′′,1′′,1′′′′,1′′′′-Hexaoxide, 16. To a 10 mL toluene solution containing 0.003 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 15.1 mg (0.055 mmol) of **15**[1a] and 67 mg (0.11 mmol) of **13**. After being refluxed for 4 h, the reaction mixture was filtered through silica gel. A first fraction was collected using petroleum ether as the eluent. A second fraction was obtained using petroleum ether/CH_2Cl_2 1:1 as the eluent. After evaporation of the solvent and washing with ethyl ether, the second fraction afforded 16 mg (40% yield) of **16** as a brown solid, mp > 340 °C (upper limit of our apparatus). The solid did not show any sign of decomposition at 340 °C and was not soluble in most organic solvents: MS *m/e* 736 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 542 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.64 (s, 4H), 7.00(d, ^3J = 4.6 Hz, 2H), 6.87 (s, 2H), 6.71 (d, ^3J = 4.6 Hz, 2H), 1.00 (s, 18H), 0.34 (s, 12H). Anal. Calcd for $C_{32}H_{40}O_6S_5Si_2$: C, 52.14; H, 5.47. Found: C, 52.21; H, 5.46.

5,5′′′′-Bis(*n*-hexyl)-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene 1,1,1′′,1′′,1′′′′,1′′′′-Hexaoxide, 17. To a 15 mL toluene solution containing 0.007 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 514 mg (0.90 mmol) of **14** and 166 mg (0,45 mmol) of 2,5-diiodiothiophene 1,1-dioxide.[1d] After being refluxed for 4 h, the solution was stirred overnight at room temperature. After usual workup, the crude product was repeatedly washed with freshly distilled pentane. Then the product was purified by filtering on silica gel with CH_2Cl_2/CH_3COCH_3 1:1 as the eluent and subsequent Soxlet extraction with toluene.

A total of 21 mg (7% yield) of a brown powder, mp > 340 °C (upper limit of our apparatus), was obtained. The solid did not show any sign of decomposition at 340 °C and was not soluble in most organic solvents: MS *m/e* 676 ($M^{\bullet+}$); λ_{max}-($CHCl_3$) 526 nm. Anal. Calcd for $C_{32}H_{36}O_6S_5$: C, 56.78; H, 5.36. Found: C, 56.92; H, 5.38.

5-(dimethyl-*tert*-butylsilyl)-5′-(tributylstannyl)-2,2′-bithiophene, 18. To a solution of 6 mL of THF containing 0.56 g (2.0 mmol) of 5-(dimethyl-*tert*-butylsilyl)-2,2′-bithiophene[4a] was added 0.8 mL (2.0 mmol) of a 2.5 M solution of BuLi in hexane. After 1 h, 0.65 g (2.0 mmol) of Bu_3SnCl was added and the mixture stirred overnight at room temperature. After addition of a saturated solution of NH_4Cl and extraction with ethyl ether, the organic phase was dried over $MgSO_4$ and evaporated. A total of 0.90 g (78% yield) of **18** as a dark green oil was obtained: MS *m/e* 570 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.31 (d, ^3J = 3.4 Hz, 2H), 7.25 (d, ^3J = 3.5 Hz, 2H), 7.13 (d, ^3J = 3.5 Hz, 2H), 7.06 (d, ^3J = 3.4 Hz, 2H), 1.55 (m, 6H), 1.34 (m, 6H), 1.10 (t, 6H), 0.92 (s, 9H), 0.87 (t, 9H), 0.30 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 142.9, 142.8, 136.6, 136.2, 136.1, 135.8, 125.0, 124.5, 29.0, 27.2, 26.3, 16.9, 13.7, 10.9.

5-(*n*-Hexyl)-5′-(tributylstannyl)-2,2′-bithiophene, 19. A 1.82 g (7.28 mmol) portion of *2-(n*-hexyl)-2,2′-bithiophene **39** was dissolved in 40 mL of anhydrous ethyl ether, and 3.20 mL (8.00 mmol) of BuLi 2.5 M in hexane was added dropwise. After 30 min, 2.16 mL (8.00 mmol) of Bu_3SnCl was added and the mixture stirred overnight. After usual workup, 3.70 g (94%) of **19** as a yellow oil was isolated, which was used as such: MS *m/e* 540 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.26 (d, ^3J = 3.3 Hz, 1H), 7.11 (d, ^3J = 3.3 Hz, 1H), 7.02 (d, ^3J = 3.5 Hz, 1H), 6.72 (d, ^3J = 3.5 Hz, 1H), 2.82 (t, 2H), 1.7 (m, 8H), 1.4 (m, 10 H), 1.2 (m, 6H), 0.9 (m, 12H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 145.5, 143.8, 136.6, 136.3, 135.5, 125.2, 124.6, 123.5, 32.1, 30.6, 29.5, 29.3, 27.8, 23.1, 14.4, 13.9, 11.3.

5,5′′-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2′′-terthiophene 1,1-Dioxide, 20. To a 25 mL toluene solution containing 0.018 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.68 g (1.2 mmol) of **18** and 0.37 g (1.2 mmol) of **3**. The mixture was refluxed for 2 h and then hydrolyzed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. After usual workup, the residue was repeatedly washed with ethyl ether, and 0.36 g (60% yield) of **20**[4a] was recovered.

5,5′′-Bis-(*n*-hexyl)-2,2′:5′,2′′-terthiophene 1,1-Dioxide, 21. To a 15 mL toluene solution containing 0.011 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.4 g (0.74 mmol) of **19** and 0.2 g (0.74 mmol) of **4**. After being refluxed for 2 h, the reaction mixture was filtered through aluminum oxide. After usual workup, 0.17 g (52% yield) of an orange red, polycrystalline compound, mp 105−106 °C, was obtained: MS *m/e* 448 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 430 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.46 (d, ^3J = 3.9 Hz, 1H), 7.07 (d, ^3J = 3.9 Hz, 1H), 7.03 (d, ^3J = 3.6 Hz, 1H), 6.69 (d, ^3J = 3.6 Hz, 1H), 6.53 (d, ^3J = 4.9 Hz, 1H), 6.42 (doublet of triplets, ^3J = 4.9 Hz, ^5J = 1.0 Hz, 1H), 2.77 (t, 2H), 2.52 (t, 2H), 1.65 (m, 4H), 1.3 (m, 12H), 0.9 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 147.2, 143.4, 140.4, 136.4, 133.7, 128.9, 127.8, 125.1, 124.7, 123.9, 122.7, 116.7, 31.5, 31.4, 30.2, 28.8, 28.7, 26.7, 24.4, 22.5, 22.4, 14.0. Anal. Calcd for $C_{24}H_{32}O_2S_3$: C, 64.24; H, 7.19. Found: C, 64.39; H, 7.21.

5,5′′′-Bis[(dimethyl-*tert*-butylsilyl)]-2,2′:5′,2′′:5′′,2′′′-quaterthiophene 1,1,1′′′,1′′′-Tetraoxide, 24. To a 6 mL toluene solution containing 0.01 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.24 g (0.32 mmol) of 5,5′-bis(tributylstannyl)-2,2′-bithiophene **22**[19] and 0.19 g (0.64 mmol) of **3**. After being refluxed for 6 h, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated, and filtered through silica gel. After evaporation of the solvent, the residue was washed with ethyl ether, and 0.118 g (59% yield) of **24**[4a] was obtained.

5,5′′′′-[Bis(dimethyl-*tert*-butylsilyl)]-2,2′:5′,2′′:5′′,2′′′:5′′′,2′′′′-quinquethiophene 1,1,1′′′′,1′′′′-Tetraoxide, 25. To an 8 mL toluene solution containing 0.016 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.31 g (1.0 mmol) of **3** and 0.41 g (0.50 mmol) of 5,5′′-bis(tributylstannyl)-2,2′:5′,2′′-terthiophene **23**.[19] After being refluxed for 6 h, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated, and filtered through silica gel. After evaporation of the solvent, the residue was washed with ethyl ether, and 0.186 g (53% yield) of **25** as a red polycrystalline solid, mp 199−200 °C, was obtained. The product was insoluble in most organic solvents: MS *m/e* 704 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 520 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.56 (d, ^3J = 3.9 Hz, 2H), 7.22 (d, ^3J = 3.9 Hz, 2H), 7.17 (s, 2H), 6.98 (d, ^3J = 4.6 Hz, 2H), 6.59 (d, ^3J = 4.6 Hz, 2H), 1.01 (s, 18H), 0.35 (s, 12H). Anal. Calcd for $C_{32}H_{40}O_4S_5Si_2$: C, 54.51; H, 5.72. Found: C, 54.47; H, 5.73.

5,5′′′-Bis(*n*-hexyl)-2,2′:5′,2′′:5′′,2′′′-quaterthiophene 1,1,1′′′,1′′′-Tetraoxide, 26. To an 11 mL toluene solution containing 0.016 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] was added 270 mg (0.50 mmol) of 5,5′-bis(tributylstannyl)-2,2′-bithiophene **19**, and 300 mg (1.00 mmol) of *2-(n*-hexyl)-5-bromothiophene **2** in 11 mL of toluene was then added dropwise. The mixture was refluxed for 5 h, treated with a saturated solution of NH_4Cl, and washed with water, and the organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was chromatographed on silica gel using pentane/ethyl acetate 90:10. A total of 150 mg (53% yield) of an orange polycrystalline compound, mp 233 °C, was recovered: MS *m/e* 562 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 480 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.49 (d, ^3J = 4.0 Hz, 2H), 7.20 (d, ^3J = 4.0

Hz, 2H), 6.60 (d, ^3J = 4.7 Hz, 2H), 6.45 (doublet of triplets, ^3J = 4.7 Hz, ^4J = 1.8 Hz, 2H), 2.56 (t, 4H), 1.70 (m, 4H), 1.30 (m, 12H), 0.9 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 144.1, 138.3, 135.9, 129.7, 128.9, 125.9, 122.5, 118.1, 31.4, 28.8, 26.7, 24.5, 22.5, 14.0. Anal. Calcd for $C_{28}H_{34}O_4S_4$: C, 59.75; H, 6.09. Found: C, 59.83; H, 7.00.

5-(*n*-Hexyl)-5″-(tributylstannyl)-2,2′:5′,2″-terthiophene, 27. A solution containing 4.0 g (0.024 mol) of commercial 2,2′-bithiophene and 4.5 mL (0.03 mol) of TMEDA in 80 mL of THF was cooled to −70 °C, and 9.6 mL (0.024 mol) of BuLi 2.5 M in hexane was added. After being stirred for a few minutes, the solution was allowed to reach room temperature and then stirred for 3 h. Then the solution was again cooled to −70 °C, and 8.12 mL (0.03 mol) of Bu_3SnCl was added dropwise. The solution was allowed to reach rt and stirred overnight. After usual workup, the yellow oil obtained was distilled (170 °C, 3 × 10^{-3} mmHg), and 8.74 g (80% yield) of a white oil identified as 5-(tributylstannyl)-2,2′-bithiophene (compound **41** of Scheme 3) was recovered: ^{1}H NMR (acetone-d_6, TMS/ppm) 7.39 (q, ^3J = 5.0, ^4J = 1.1 Hz, 1H), 7.36 (d, ^3J = 3.3 Hz, 1H),7.24 (q, ^3J = 3.6, ^3J = 3.3 Hz, 1H), 7.15 (d, ^3J = 3.3 Hz, 1H), 7.06 (q, ^3J = 3.6, ^3J = 3.3 Hz, 1H), 1.60 (m, 6H), 1.30 (m, 6H), 1.15 (m, 6H), 0.90 (t, 9H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 137.5, 129.0, 126.1, 125.9, 125.8, 125.4, 124.9, 124.6, 29.9, 28.0, 13.6, 11.1.

To a solution of 1.00 g (2.22 mmol) of **41** in 8 mL of toluene was added dropwise 1.08 g (4.39 mmol) of **2** dissolved in 10 mL toluene. After the mixture was stirred for a few minutes, 0.20 g (0.17 mmol) of commercial $Pd(PPh_3)_4$ was added and the mixture refluxed overnight. After usual workup, 0.44 g (60%) of a yellow powder identified as 5-(*n*-hexyl)-2,2′:5′,2″-terthiophene (compound **42** of Scheme 3), mp 48 °C, was obtained: ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.21 (doublet of doublets, ^3J = 4.9 Hz, ^4J = 1.1 Hz, 1H), 7.13 (doublet of doublets, ^3J = 3.6 Hz, ^4J = 1.1 Hz, 1H), 7.02 (d, ^3J = 3.5 Hz, 1H), 7.00 (doublet of doublets, ^3J = 3.6 Hz, ^3J = 4.9 Hz, 1H), 7.00 (d, ^3J = 3.5 Hz, 1H), 6.98 (d, ^3J = 3.5 Hz, 1H), 6.64 (d, ^3J = 5.0 Hz, 1H), 2.78 (t, 2H), 1.66 (t, 2H), 1.3 (m, 6H), 0.9 (t, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 145.6, 137.3, 136.8, 135.5, 134.4, 127.8, 124.8, 124.3, 123.5, 123.4, 31.5, 30.2, 28.7, 22.5, 14.1.

To a solution of 1.00 g (0.003 mol) of **42** in 5 mL of THF and containing 0.54 mL (0.0036 mol) of TMEDA was added 1.2 mL (0.003 mol) of BuLi 2.5 M in hexane and 1.0 mL (0.0036 mol) of Bu_3SnCl at −10 °C. The temperature was then allowed to rise to ambient and the mixture stirred overnight. After solvent evaporation, the mixture was chromatographed on aluminum oxide using petroleum ether 30−40 °C as the eluent. A total of 0.51 g (27% yield) of **27** as a yellow oil was obtained. The product was used as such: MS *m/e* 622 ($M^{\bullet+}$); ^{1}H NMR (C_6D_6, TMS/ppm) 7.30 (d, ^3J = 3.3 Hz, 1H), 7.08 (d, ^3J = 3.3 Hz, 1H), 6.96 (d, ^3J = 3.7 Hz, 1H), 6.92 (d, ^3J = 3.6 Hz, 1 H), 6.88 (d, ^3J = 3.7 Hz, 1H), 6.47 (d, ^3J = 3.6 Hz, 1 H), 2.55 (t, 2H), 1.6 (m, 8H), 1.3 (m, 8 H), 1.2 (m, 10H), 0.9 (m, 12H); ^{13}C NMR (C_6D_6, TMS/ppm) 145.5, 143.4, 137.1, 136.7, 136.5, 136.4, 135.3, 125.4, 125.2, 124.6, 124.1, 123.8, 31.9, 30.4, 29.4, 29.0, 27.6, 22.9, 14.2, 13.8, 11.2.

5,5‴-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″:5″,2‴-quaterthiophene 1,1-Dioxide, 28. To an 8 mL toluene solution containing 0.017 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] were added 0.37 g (0.569 mmol) of **8** and 0.176 g (0.569 mmol) of **3**. After being refluxed for 6 h, the reaction mixture was hydrolyzed with a saturated solution of NH_4Cl and extracted with CH_2Cl_2. The organic phase was dried over $MgSO_4$, concentrated, and filtered through silica gel.

After evaporation of the solvent, the residue was washed with ethyl ether, and 0.163 g (49% yield) of **28**[1a] was recovered.

5,5‴-Bis(*n*-hexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene 1,1-Dioxide, 29. To a 9 mL toluene solution containing 0.012 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] was added 260 mg (0.42 mmol) of 5-(*n*-hexyl)-5″-(tributylstannyl)-2,2′:5′,2″-terthiophene **27**, and 120 mg (0.42 mmol) of 2-(*n*-hexyl)-5-bromothiophene 1,1-dioxide **4** in 9 mL of toluene was added dropwise. The mixture was refluxed overnight, treated with a saturated solution of NH_4Cl, and washed with water, and the organic layer was separated, dried over $MgSO_4$, and evaporated. The crude product was chromatographed on silica gel using pentane/ethyl acetate 90:10. A total of 110 mg (50% yield) of an orange powder, mp 172 °C, were recovered: MS *m/e* 530 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 448 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.48 (d, ^3J = 4.0 Hz, 1H), 7.13 (d, ^3J = 4.0 Hz, 1H), 7.10 (d, ^3J = 3.8 Hz, 1H), 7.00 (d, ^3J = 4.0 Hz, 2 H), 6.69 (d, ^3J = 3.8 Hz, 1H), 6.55 (d, ^3J = 4.9 Hz, 1H), 6.43 (doublet of triplets, ^3J = 4.9 Hz, ^4J = 1.8 Hz, 1H), 2.78 (t, 2H), 2.52 (t, 2H), 1.65 (m, 4H), 1.30 (m, 12H), 0.9 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 146.3, 143.6, 139.5, 138.4, 136.1, 134.1, 133.8, 128.8, 128.2, 125.8, 124.9, 124.3, 123.8, 123.6, 122.5, 117.0, 31.6, 31.4, 30.2, 28.8, 28.7, 26.8, 24.5, 22.6, 22.5, 14.1, 14.0. Anal. Calcd for $C_{28}H_{34}O_2S_4$: C, 63.35; H, 6.46. Found: C, 63.17; H, 6.47.

5,5‴-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗-quinquethiophene 1″,1″-Dioxide, 30. To a 5 mL toluene solution of Pd(AsPh3)4 (0.01 mmol) prepared in situ[4c] were added 0.05 g (0.18 mmol) of 2,5-dibromothiophene 1,1-dioxide **15**[1d] and 0.2 g (0.36 mmol) of 5-(dimethyl-*tert*-butylsilyl)-5′-(tributylstannyl)-2,2′-bithiophene **18**. After being refluxed for 4 h, the reaction mixture was filtered through silica gel using petroleum ether for the first fraction and petroleum ether/methylene chloride for the second one. After evaporation of the solvent from the second fraction, the residue was washed with ethyl ether, and 63 mg (52% yield) of a brown solid, mp 233−234 °C, was obtained: MS *m/e* 672 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 512 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.54 (d, ^3J = 3.7 Hz, 2H), 7.30 (d, ^3J = 3.5 Hz, 2H), 7.21 (d, ^3J = 3.7 Hz, 2H), 7.16 (d, ^3J = 3.5 Hz, 2 H), 6.72 (s, 2H), 0.95 (s, 18H), 0.34 (s, 12H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 141.3, 140.3, 139.2, 136.1, 135.8, 129.0, 128.6, 126.1, 125.1, 117.9, 26.3, 16.9. Anal. Calcd for $C_{32}H_{40}O_2S_5Si_2$: C, 57.10; H, 5.99. Found: C, 57.22; H, 6.00.

2-(Dimethyl-*tert*-butylsilyl)-5-(tributylstannyl)thiophene, 31. To 30 mL of an ethyl ether solution of 5.07 g (0.0256 mol) of 2-(dimethyl-*tert*-butylsilyl)thiophene[4a] was added 10.3 mL (0.0257 mol) of BuLi 2.5 M in hexane at −10 °C. After the mixture was stirred for 1 h, an ethyl ether solution of 6.39 mL (0.0256 mol) of Bu_3SnCl was added to the solution at room temperature and the mixture stirred overnight. After usual workup, the crude product was distilled (185 °C, 0.1 mmHg), and 10.60 g (85% yield) of **31** as a white oil was recovered: MS *m/e* 488 ($M^{\bullet+}$); ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.42 (d, ^3J = 3.6 Hz, 1H), 7.30 (d, ^3J = 3.6 Hz, 1H), 1.58 (m, 6H), 1.36 (m, 6H), 1.12 (t, 6H), 0.98 (s, 9H), 0.30 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 142.8, 142.3, 136.0, 135.8, 29.0, 27.3, 26.5, 17.0, 13.7, 10.9, −4.6.

2,2′:5′,2″-Terthiophene 1′,1′-Dioxide, 32. To a 12 mL toluene solution containing 0.024 mmol of $Pd(AsPh_3)_4$ prepared in situ[4c] was added 0.20 g (0.73 mmol) of 2,5-dibromothiophene 1,1-dioxide **15**,[1d] 0.54 g (1.50 mmol) of 2-(tributylstannyl)-thiophene **5** was added dropwise, and the mixture was stirred overnight. The solvent was evaporated, and the crude product was chromatographed on silica gel using petroleum ether/ethyl alcohol 80:20. A total of 0.13 g (65% yield) of orange-red polycrystalline powder, 155 °C, was recovered: MS *m/e* 280 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 428 nm; ^{1}H NMR ($CDCl_3$, TMS/ppm) 7.65 (doublet of doublets, ^3J = 4.0 Hz, ^4J = 1.2 Hz, 2H), 7.44 (doublet of doublets, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 2H), 7.15 (q, ^3J = 4.0 Hz, ^3J = 5.0 Hz, 2H), 6.78 (s, 2H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 136.2, 129.8, 128.7, 128.2, 128.0, 118.6. Anal. Calcd for $C_{12}H_8O_2S_3$: C, 51.40; H, 2.88. Found: C, 51.21; H, 2.87.

5,5″-Bis(dimethyl-*tert*-butylsilyl)-2,2′:5′,2″-terthiophene 1′,1′-Dioxide, 33. A 0.01 mmol (12 mg) portion of Pd_2dba_3 and 0.05 mmol (15 mg) of $AsPh_3$ were dissolved in 10 mL of THF, and the solution was stirred for 30 min. Then a solution containing 0.33 g (1.2 mmol) of 2,5-dibromothiophene 1,1-dioxide **15**[1d] and 1.16 g (2.4 mmol) of 2-dimethyl(*tert*-butylsilyl)-5-(tributylstannyl)thiophene **31** was added dropwise, and the mixture was stirred for 6 h. The solvent was evaporated, and the crude product was chromatographed on silica gel using petroleum ether/ethyl alcohol 80:20. From chromatography, two fractions were isolated. The first (105 mg, 17% yield) was a brown polycrystalline product, mp 199−203 °C, identified as trimer **33**. The second (160 mg, 34% yield) was a yellow orange powder, mp 102−103 °C, identified as 5-(dimethyl-*tert*-butylsilyl)-5′-bromo-2,2′-bithiophene 1′,1′-dioxide **33′**.

33: MS *m/e* 508 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 440 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 7.69 (d, ^3J = 3.5 Hz, 2H), 7.25 (d, ^3J = 3.5 Hz, 2H), 6.79 (s, 2H), 0.93 (s, 18H), 0.31 (s, 12H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 142.1, 136.5, 135.9, 134.4, 128.6, 118.7, 26.2, 16.9. Anal. Calcd for $C_{24}H_{36}O_2S_3Si_2$: C, 56.64; H, 7.13. Found: C, 56.76; H, 7.10.

33′: MS *m/e* 390 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 394 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 7.67 (d, ^3J = 3.5 Hz, 1H), 7.23 (d, ^3J = 3.5 Hz, 1H), 6.91 (d, ^3J = 5.0 Hz, 1H), 6.68 (d, ^3J = 5.0 Hz, 1H), 0.92 (s, 9H), 0.31 (s, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 143.0, 137.4, 136.5, 134.2, 129.7, 128.4, 118.6, 117.6, 26.2, 16.9. Anal. Calcd for $C_{14}H_{19}BrO_2S_2Si$: C, 42.96; H, 4.89. Found: C, 42.74; H, 4.91.

5,5″-Bis(*n*-hexyl)-2,2′:5′,2″-terthiophene, 35. To a solution containing 0.5 g (0.002 mol) of 2,2′:5′,2″-terthiophene **34** dissolved in 30 mL of anhydrous THF was added dropwise 1.72 mL (0.0043 mol) of BuLi 2.5 M in hexane. The solution was stirred for about 1 h, and then 0.74 g (0.0045 mol) of *n*-hexyl bromide was added dropwise and the solution stirred at room temperature overnight. After the usual workup, 0.50 g (60% yield) of yellow crystals, mp 79 °C, was obtained: MS *m/e* 416 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 380 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 6.97 (s, 2H), 6.96 (d, ^3J = 3.5 Hz, 2H), 6.67 (doublet of triplets, ^3J = 3.5 Hz, ^4J = 1.0 Hz, 2H), 2.75 (t, 4H), 1.65 (t, 4H), 1.3 (m, 12H), 0.85 (t, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 146.0, 136.8, 135.3, 125.4, 124.1, 123.8, 32.2, 30.8, 29.4, 23.2, 14.7. Anal. Calcd for $C_{24}H_{32}S_3$: C, 69.18; H, 7.74. Found: C, 69.23; H, 7.75.

5,5′-Bis(*n*-hexyl)-2,2′-bithiophene, 37. To a solution containing 2.00 g (0.012 mol) of 2-*n*-hexylthiophene **36** dissolved in 75 mL of anhydrous THF was added 6.4 mL (0.016 mol) of 2.5 M BuLi in hexane dropwise at −60 °C. The solution was stirred for about 2 h while the temperature was allowed to increase to 0 °C. The temperature was again decreased to −60 °C, and 8.5 g (0.024 mol) of solid $Fe(acac)_3$ was added stepwise. The solution was stirred at −60 °C for 2 h, and then the temperature was allowed to increase to room temperature overnight. The reaction mixture was first washed with a 5% HCl solution and then with a solution of 10% KOH and finally with distilled water. The organic phase was separated, dried with $MgSO_4$, and evaporated. A red oil was obtained that was redissolved in hot methanol. A total of 1.4 g (70% yield) of **37** as white crystals, mp 34 °C, was separated: MS *m/e* 334 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 338 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 6.89 (d, ^3J = 3.5 Hz, 2H), 6.64 (doublet of triplets, ^3J = 3.5 Hz, ^4J = 0.8 Hz, 2H), 2.75 (triplets of doublets, ^4J = 0.8 Hz, 4H), 1.65 (m, 4H), 1.32 (m, 12H), 0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 144.8, 135.4, 124.6, 122.7, 31.6, 30.2, 28.8, 22.6, 14.1. Anal. Calcd for $C_{20}H_{30}S_2$: C, 71.80; H, 9.04. Found: C, 71.87; H, 9.03.

5,5′-Bis(*n*-hexyl)-2,2′-bithiophene 1,1-Dioxide, 38. A 0.5 g (1.50 mmol) portion of **37** was dissolved in 5 mL of freshly distilled methylene chloride, and 0.93 g (3.74 mmol) of solid *m*-CPBA 70% was added stepwise. The solution was stirred for 3 h, filtered, and washed first with a 10% solution of $NaHCO_3$ and then with distilled water, the organic layer was separated, dried with Na_2SO_4, and evaporated, and the crude product was chromatographed on silica gel using pentane/ethyl acetate 93:7. A total of 55 mg (10% yield) of **38** as a pale yellow solid, mp 45 °C, was obtained: MS *m/e* 366 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 402 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 7.39 (d, ^3J = 3.7 Hz, 1H), 6.77 (d, ^3J = 3.7 Hz, 1H), 6.47 (d, ^3J = 4.9 Hz, 1H), 6.40 (doublet of triplets, ^3J = 4.9 Hz, ^4J = 1.9 Hz, 1H),2.80 (t, 2H), 2.50 (triplet of doublets, ^4J = 1.9 Hz, 2H), 1.65 (m, 4H), 1.35 (m, 12H), 0.90 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 149.4, 143.0, 136.7, 128.0, 127.4, 125.7, 122.6, 116.2, 31.4, 31.3, 30.2, 28.7, 28.6, 26.7, 24.3, 22.8, 14.0. Anal. Calcd for $C_{20}H_{30}O_2S_2$: C, 65.53; H, 8.25. Found: C, 65.69; H, 8.24.

5-(*n*-Hexyl)-2,2′-bithiophene, 39. A 2.11 g (12.5 mmol) portion of 2,2′-bithiophene was dissolved in 25 mL of anhydrous THF, and the mixture was cooled to −50 °C. A 5 mL (12.5 mmol) portion of BuLi 2.5 M in hexane was added dropwise followed by 1.76 mL (12.5 mmol) of *n*-hexyl bromide. The mixture was then stirred for 30 min at room temperature. After the usual workup, the crude product was chromatographed on silica gel RP 18 using CH_3OH/CH_2Cl_2 9:1. A total of 1.96 g (63% yield) of **39** as a yellow-green oil was recovered: MS *m/e* 250 ($M^{\bullet+}$); ^1H NMR ($CDCl_3$, TMS/ppm) 7.2 (m, 2H), 7.1 (m, 2H), 6.7 (m, 1H), 2.85 (t, 2H), 1.75 (m, 2H), 1.41 (m, 6H), 1.0 (t, 3H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 145.2, 137.9, 134.7, 127.6, 124.6, 123.6, 123.3, 122.9, 31.5, 30.1, 28.7, 22.5, 14.1. Anal. Calcd for $C_{14}H_{18}S_2$: C, 67.15; H, 7.25. Found: C, 67.38; H, 7.23.

5,5‴-Bis(*n*-hexyl)-2,2′:5′,2″:5″,2‴-quaterthiophene, 40. A 0.37 g (0.0015 mol) portion of **39** dissolved in 10 mL of anhydrous THF was added dropwise to a solution of 0.68 mL (0.0017 mol) of BuLi 2.5 M in hexane. The mixture was stirred for 1 h at room temperature, then 1.0 g (0.003 mol) of $Fe(acac)_3$ was added stepwise and the mixture stirred overnight. Subsequently, 20 mL of distilled water was added followed by 100 mL of HCl 3 M. After usual workup, the crude product was chromatographed on silica gel using hexane/ethyl acetate 70:30. A total of 0.22 g (60% yield) of **40** as an orange polycrystalline compound, mp 166 °C, was obtained: MS *m/e* 498 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 400 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 7.03 (d, ^3J = 4.0 Hz, 2H), 6.99 (d, ^3J = 4.0 Hz, 2H), 6.98 (d, ^3J = 3.5 Hz, 2H), 6.68 (doublet of triplets, ^3J = 3.5 Hz, ^4J = 0.8 Hz, 2H), 2.78 (t, 4H), 1.65 (m, 4H), 1.28 (m, 12H), 0.88 (m, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 145.7, 136.8, 135.4, 134.5, 124.9, 124.1, 123.6, 123.4, 31.6, 30.3, 28.8, 22.6, 14.1. Anal. Calcd for $C_{28}H_{34}S_4$: C, 67.42; H, 6.87. Found: C, 67.61; H, 6.89.

2,5-Bis(*n*-hexyl)thiophene, 43. To a solution containing 1.0 g (0.006 mol) of *2-n*-hexylthiophene **36** dissolved in 40 mL of anhydrous THF was added dropwise 3.2 mL (0.008 mol) of 2.5 M BuLi in hexane at −10 °C. The solution was stirred for about 2 h while the temperature was allowed to increase to 0 °C. Then the temperature was decreased again to −10 °C, and 1 mL (0.006 mol) of *n*-hexyl bromide dissolved in 5 mL of THF was added dropwise. After 1 night at room temperature, 50 mL of distilled water was added, and the organic phase was separated, dried over Na_2SO_4, and evaporated. A yellow oil was obtained that was chromatographed on silica gel using petroleum ether as the eluent. A total of 1.21 g (80% yield) of **43** as a white oil was obtained: MS *m/e* 252 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 254 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 6.56 (s, 2H), 2.75 (t, 4H), 1.65 (m, 4H), 1.32 (m, 12H), 0.89 (t, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 143.3, 123.3, 31.7, 31.6, 30.2, 28.9, 22.6, 14.1. Anal. Calcd for $C_{16}H_{28}S$: C, 76.12; H, 11.18. Found: C, 76.22; H, 11.16.

2,5-Bis(*n*-hexyl)thiophene 1,1-Dioxide, 44. A 0.5 g (0.002 mol) portion of **43** was dissolved in 3 mL of methylene chloride, and 1.23 g (0.005 mol) of solid *m*-MCPA 70% was added stepwise. The mixture was stirred for 2 days and filtered and washed first with 10% $NaHCO_3$ and then with distilled water, and the organic layer was separated, dried with Na_2SO_4, and evaporated. The white oil obtained in this way was chromatographed on silica gel using pentane/ethyl acetate 90:10. A total of 0.4 g (70% yield) of **44** as a white crystalline material, mp 41 °C, was obtained: MS *m/e* 284 ($M^{\bullet+}$); λ_{max}($CHCl_3$) 298 nm; ^1H NMR ($CDCl_3$, TMS/ppm) 6.25 (s, 2H), 2.46 (t, 4H), 1.62 (m, 4H), 1.30 (m, 12H), 0.89 (t, 6H); ^{13}C NMR ($CDCl_3$, TMS/ppm) 144.0, 121.6, 31.4, 28.7, 26.5, 24.3, 22.5, 14.0. Anal. Calcd for $C_{16}H_{28}O_2S$: C, 67.56; H, 9.92. Found: C, 67.63; H, 9.91.

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Supporting Information Available: Tables of crystal data and structure refinement, final fractional coordinates and equivalent isotropic thermal parameters, anisotropic displacement parameters, bond distances and angles, torsion angles, selected least-squares planes, and shortest nonbonded distances. Fully optimized geometries and energies of 2,2′-bithiophene and of the corresponding mono- and bis-*S*,*S*-dioxides (8 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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