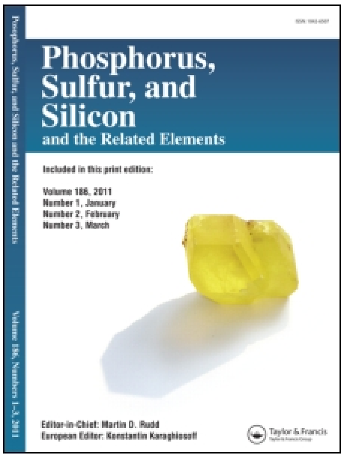

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Switching from 'Fully Aromatic' to 'Polyene-Like' Thiophene-Based Materials

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The synthesis and the redox properties of oligo and poly(thiophene-S,S-dioxides) – a new class of thiophene based materials - are reported and discussed.

Keywords: thiophene-S,S-dioxide; Stille reaction; electron affinity

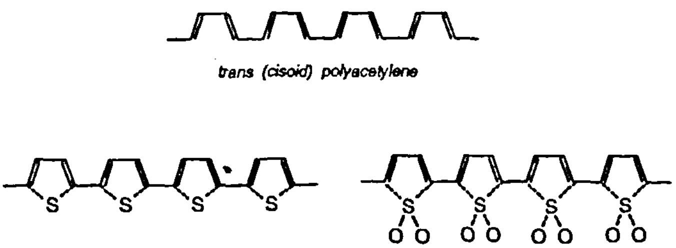
There are many sulfur derivatives, organic as well as inorganic, which are of great current interest in the field of materials research. Elemental sulfur itself has very recently raised a lot of interest for its superconductive properties, which had not been correctly predicted by previous theories.[1]

Polythiophene belongs to the class of functional conjugated materials, including polypyrrole and poly(*p*-phenylenevinylene), which are currently being investigated for applications in a variety of devices ranging from field effect transistors[2] to luminescent diodes[3], supercapacitors[4], and sensing devices.[5]

As polypyrrole or polyfuran, polythiophene can be viewed as consisting of a backbone of sp^2 hybridized carbon atoms similar to that of the cisoid form of trans(polyacetylene) but stabilized by the heteroatom which contributes to the formation of the π electron system through one of its lone pair electrons (see *Scheme 1*).

Compared to the other heterocyclic polymers, polythiophene is characterized by greater chemical stability and ease of functionalization. There is great current interest in exploiting the easy functionalization of polythiophene (as well as that of the shorter and structurally better

Scheme 1



trans (cisoid) polyacetylene

polythiophene

poly(thiophene-S,S-dioxide)

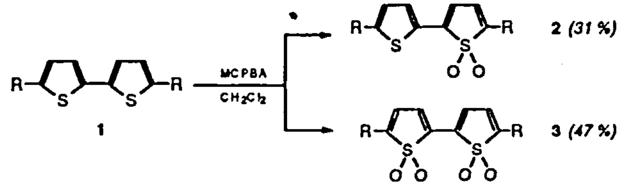
defined oligothiophenes) with groups capable of increasing the electron affinity of the material. Polythiophene - which is a so-called '*p*-type' (hole transporting) semiconductor material - has indeed poor electron affinity and is unstable in its reduced form. Increasing its electron affinity would make the material more stable in the reduced form and, possibly, would transform it into an '*n*-type' (electron transporting) semiconductor material. So far, attemps to reach this goal have focused on the functionalization of polythiophenes with electron withdrawing groups grafted at the β-positions, but few of such attempts have succeded. It is worth noting that there are very few '*n*-type' semiconductor organic materials, which are instead greatly needed for application in most of the above mentioned devices.[6]

Based on a few theoretical studies indicating that the greatest effect on the electron affinity should come from altering the nature of the heteroatom,[7] our approach to increase the electron affinity of oligo and polythiophenes has consisted in the functionalization of the thienyl sulfur to the corresponding S,S-dioxide. Work by Gronowitz *et al.*[8] and by other groups[9] have indeed shown that polysubstituted thiophene gives rise to stable S,S-dioxide derivatives.

Thus, bis(dimethyl-tert-butyl)silyl-2,2'-bithiophene-1,1-dioxide (**2**) and bis(dimethyl-tert-butyl)silyl-2,2'-bithiophene-1,1,1',1'-tetraoxide (**3**) were prepared by oxidation of the corresponding bissilylated bithiophene (**1**) with *m*-chloroperbenzoic acid (see *Scheme 2*)[10a] and their oxidation ($E_{Ip,a}$) and reduction ($E_{Ip,c}$) potentials measured by cyclic voltammetry.[10b] We found that, with respect to the starting bithiophene

1 ($E_{Ip,c} = <-2.1$, $E_{Ip,a} = 1.29$ V *vs* Ag/AgCl), the corresponding mono S,S-dioxide 2 ($E_{Ip,c} = -1.34$, $E_{Ip,a} = 1.6$ V) was characterized by a large shift towards less negative values in the reduction potential (related to the LUMO energy) and by a smaller increase in thè oxidation potential (related to the HOMO energy).[10]

Scheme 2

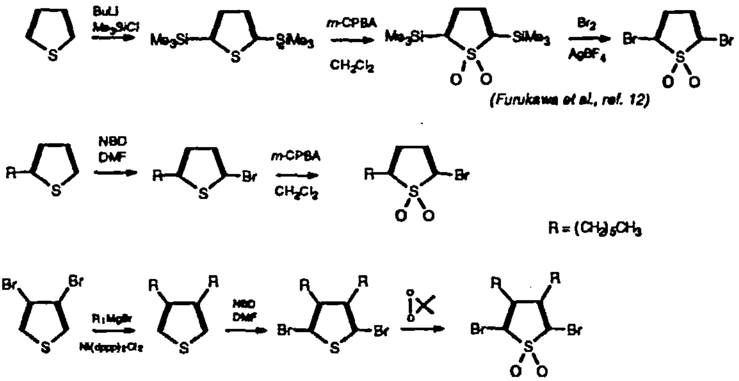


Further transformation of the second thienyl ring into the correspondig S,S-dioxide led to compound 3 having redox properties ($E_{Ip,c} = -0.85$ V, $E_{Ip,a} = 1.84$ V) markedly different from those of the starting bithiophene 1. The electron affinity of the no longer aromatic compound 3 had increased to a point where this compound became easier to reduce than to oxidize.[10]

Unfortunately, the oxidation of longer oligothiophenes with *m*-chloroperbenzoic acid led to the formation of mixtures of isomers which became increasingly difficult to separate by crystallization or silicagel chromatography. Moreover, owing to increasing aromatic stabilization, the reactivity of the oligothiophenes towards *m*-CPBA showed a marked decrease on increasing the chain length.[10a]

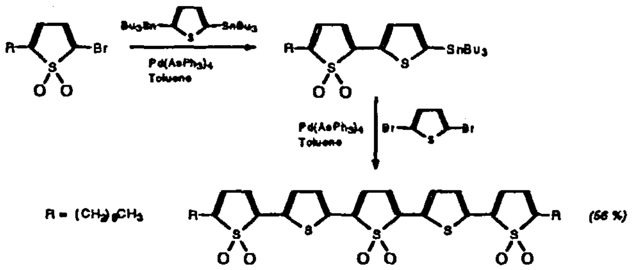
Much better results were obtained through the Stille reaction,[11] namely the palladium(0) catalyzed cross coupling of mono or dibromo thiophene-S,S-dioxides with the appropriate thienyl stannanes. In this way we synthesized a variety of oligothiophenes[7c] containing thiophene-S,S-dioxide moieties either in the inner or in the external positions, using the mono and dibromo thiophene-S,S-dioxides reported in *Scheme 3*. The Stille reaction allowed for the selective insertion of non-aromatic thiophene-S,S-dioxide moieties into the skeleton of di-, ter-, quater- and quinquethiophenes in yields which could be as high as 70%.[7a] As an example, *Scheme 4* reports the reaction pattern for the synthesis of a pentamer having alternating aromatic (thienyl) and non-aromatic (thiophene-S,S-dioxide) units. Our results showed that there is a lot of room for optimizing the reaction yields in terms of choice of catalyst, solvent, reaction temperature for controlling the metal-halogen exchange reaction, etc...

Scheme 3



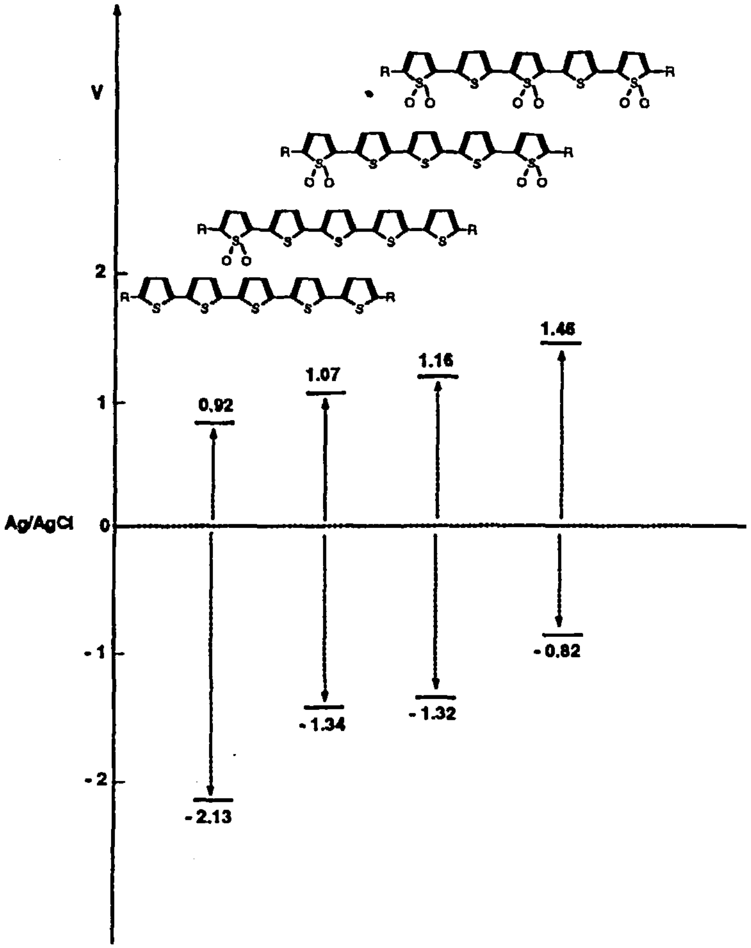
The cyclic voltammetry of these compounds showed that their electron affinity was much greater than that of the corresponding 'fully aromatic' oligothiophenes and that a fine tuning of the electron affinity (as well as of the ionization potential and of the HOMO-LUMO energy gap) could be obtained by changing the number and the position of the non-aromatic thiophene-S,S-dioxide moieties present in the molecular skeleton.[13]

Scheme 4



As an example, *Scheme 5* gives the ionization and reduction potentials of a series of pentamers (R = SiMe$_2$Bu*t*) containing the non-aromatic units at the terminal positions or having alternating aromatic and non-aromatic units, compared to those of the corresponding

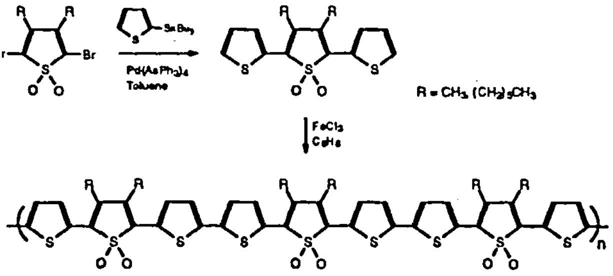
Scheme 5



quinquethiophene. The data reported in *Scheme 5* show that there is a progressive increase in the electron affinity of these compounds following the introduction of the non-aromatic units into the molecular skeleton, paralleled by a progressive but smaller increase in the ionization potential. The pentamer having alternating aromatic and non aromatic units showed reversed redox properties compared to bissilylated quinquethiophene since it was more easily reduced than oxidized. *Scheme 5* shows that the pentamers bearing terminal non-aromatic units can be reduced as well as oxidized at moderate potential values, opening the door to interesting applications such as, for example, light emitting electrochemical cells.[14]

Currently, we are analyzing the redox properties of polymers having a regular arrangement of aromatic and non aromatic units. An example of this kind of material is given in *Scheme 6*, which reports the synthesis of the polymer with one non-aromatic thiophene-S,S-dioxide moiety every two aromatic thienyl units. The electrochemical characterization of this polymer showed that it undergoes *n*-doping at a moderate potential value ($E_{Ip,c}$ = - 1.2 V *vs* Ag/AgCl), *i.e.* a potential which is about 1 V less negative than that required for *n*-doping of the corresponding 'fully aromatic' counterpart.[10c] Further work is being carried out aimed at establishing the cyclability properties of this kind of polymer in relation to the relative number of aromatic and non-aromatic units.[15]

Scheme 6



In conclusion, our work has shown that thienyl sulfur functionalization to the corresponding S,S-dioxide - which can be viewed as the disconnection of the sulfur lone pair from the aromatic system - is an efficient and versatile way to tune the electron affinity values of these materials, and, more generally, their redox properties. So far, only mixed aromatic-non aromatic structures have been synthesized but the door is open to the synthesis of derivatives made exclusively of α-linked thiophene-S,S-dioxide moieties, such as those reported in *Scheme 1*. Polymers like these can be viewed as being functionalized trans (cisoid) polyacetylenes, configurationally stable and more planar than the corresponding 'fully aromatic' counterparts.[7c] On the basis of the results of semiempirical calculations, these compounds are expected to display very low band gaps and very high electron affinity values.[7b] Preliminary results from this laboratory indicate that some of these products are also promising for their fluorescence properties.[15] The ease of functionalization characteristic of thiophene will allow the functionalization of these peculiar polyacetylene versions by a variety of groups for further tuning of electrooptical properties.

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