

## New light-emitting functionalized oligothiophenes

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### Abstract

We present a new class of highly photo and electroluminescent oligomers based on the presence of one inner thienyl-*S,S*-dioxide unit as the luminophore. The light emission frequency of the new compounds, which are characterized by greater electron affinities than the corresponding oligomers bearing an unmodified thienyl ring, was tuned over the entire visible range by changing the nature of the alkyl or aryl groups attached in the  $\alpha$ - and/or in the  $\beta$ -positions of the thienyl-*S,S*-dioxide moiety. A few aspects of the solid state supramolecular organization of the new compounds are reported. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Thiophene-*S,S*-dioxide; Synthesis; X-ray; Photoluminescence; UV–VIS

### 1. Introduction

Thiophene oligomers display high photoluminescence quantum efficiencies in solution but not in the solid state [1]. The low photoluminescence quantum yield in the solid state, together with the low electron affinity of these compounds, which are p-type, hole transporting, semiconductor materials [2–5], are the main causes of the poor efficiency of light emitting devices based on oligothiophenes [6,7].

The great current interest in organic electroluminescent materials [8–10] prompted us to investigate the possibility of engineering the molecular structure of oligothiophenes in such a way as to enhance at the same time their light emission efficiencies and their electron affinities.

We have already shown that the chemical transformation of thiophene into the corresponding thiophene-*S,S*-dioxide leads to a remarkable increase in electron affinity [11]. An example of this effect is given in Fig. 1.

We report here a new class of oligomers characterized by the presence of one inner thienyl-*S,S*-dioxide moiety, which exhibit both high photoluminescence efficiencies and high electron affinities.

### 2. Results and discussion

The structure and the synthetic pattern of a representative group of the compounds in question are reported in Schemes 1 and 2.

All compounds were prepared by the heterocoupling of the appropriate bromides and stannanes in the presence of palladium(0) catalysts [11].

All compounds are soluble and processable materials and were purified by silicagel chromatography using standard organic solvents as the eluants. All compounds were very stable and did not show any sign of decomposition after several months from their preparation. The reaction yields (in pure compound, after chromatography) varied in the range 30–70%.

All oligomers of Schemes 1 and 2 are characterized by more positive oxidation potentials and less negative reduction potentials than those of the corresponding oligomers containing an unmodified thiophene ring instead of the thienyl-*S,S*-dioxide unit.

A representative example of the trend of variation of the oxidation and reduction potentials of the new compounds is given in Table 1. For comparison, Table 1 also gives the oxidation and reduction potentials of some oligothiophenes.

All compounds of Schemes 1 and 2 are characterized by absolute fluorescence quantum yields varying in the range 10–40%, as measured for the microcrystalline powders using an integrating sphere [14]. Contrary to unsubstituted

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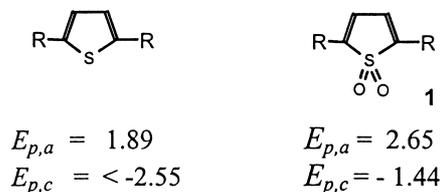
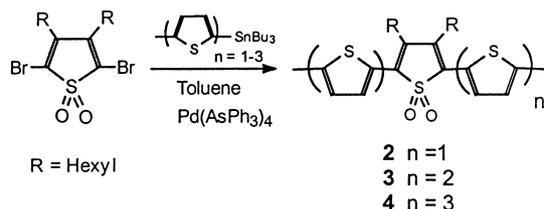


Fig. 1. Oxidation ( $E_{p,a}$ ) and reduction ( $E_{p,c}$ ) potentials of bissilylated thiophene and thiophene-*S,S*-dioxide. By cyclic voltammetry, V vs. saturated calomel electrode (SCE) [12]. R = Si(Me<sub>2</sub>tBu).



Scheme 1.

oligothiophenes [1], the new compounds displayed very low photoluminescence efficiencies in solution. For example, pentamer **6** with X = Hexyl and R = Methyl, which is characterized by a high quantum efficiency ( $\eta$ ) in microcrystalline powder ( $\eta = 37\%$ ) [14] has  $\eta < 1\%$  in chloroform solution. For unsubstituted quinquethiophene in the same solvent, photoluminescence quantum efficiencies in the range 40–50% have been reported [15,16].

Changing the oligomer length and/or the nature of the substituents allows to cover the entire visible range of light emission for the new compounds in the solid state. An example of this behavior is reported in Fig. 2, which gives the fluorescence spectra of the microcrystalline powders of compounds **1–4**. Fig. 2 shows that on increasing the number of thienyl units attached to the thienyl-*S,S*-dioxide moiety, the light emission frequency increases progressively from 400 nm (monomer **1**) to 550 nm (trimer **2**) to 650 nm (pentamer **3**) to 750 nm (heptamer **4**) in the near infrared region. We have found that only when the thienyl-*S,S*-

Table 1  
Oxidation ( $E_{p,a}$ ) and reduction ( $E_{p,c}$ ) potentials<sup>a</sup> of compounds **2–4** and **6** (X = Hexyl, R = Methyl) and of selected oligothiophenes

Compound	$E_{p,a}$	$E_{p,c}$
<b>2</b>	1.59	–1.35
<b>3</b>	1.33	–1.24
<b>4</b>	0.94	–1.36
<b>6</b>	1.09	–1.25
Terthiophene <sup>b</sup>	0.95	–2.07
Quaterthiophene <sup>b</sup>	0.80	–1.91
Quinquethiophene ( $\alpha,\omega$ -bissilylated) <sup>c</sup>	0.92	–2.13

<sup>a</sup> By cyclic voltammetry, V vs. SCE.

<sup>b</sup> From Ref. [13].

<sup>c</sup> From Ref. [11].

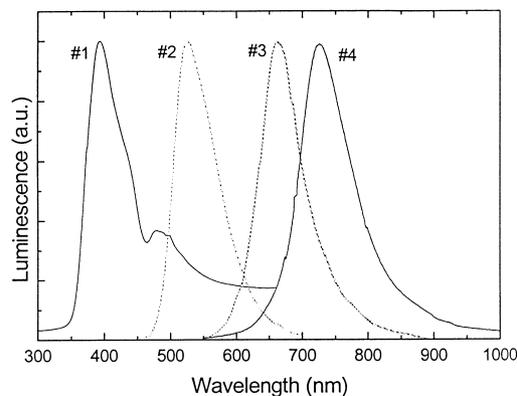
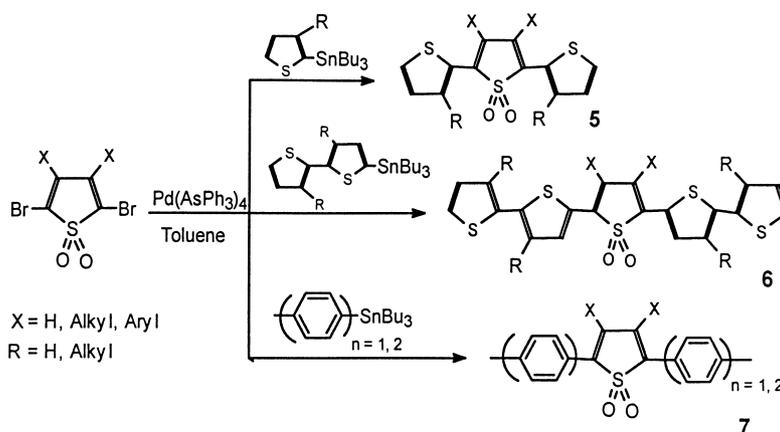


Fig. 2. Photoluminescence spectra of the microcrystalline powders of compounds **1–4**. The spectra were obtained exciting the samples by an Argon laser operating at 363 nm and detecting the signal by a 2 m double monochromator equipped with cooled photon counter.

dioxide moiety bears very bulky substituents at the  $\beta$ -position (X = *t*-butyl) no fluorescence is observed.

X-ray structure determination from single crystal and powder diffraction has allowed to relate the photoluminescence efficiency of the new class of compounds to their peculiar supramolecular organization in the solid state. An



Scheme 2.

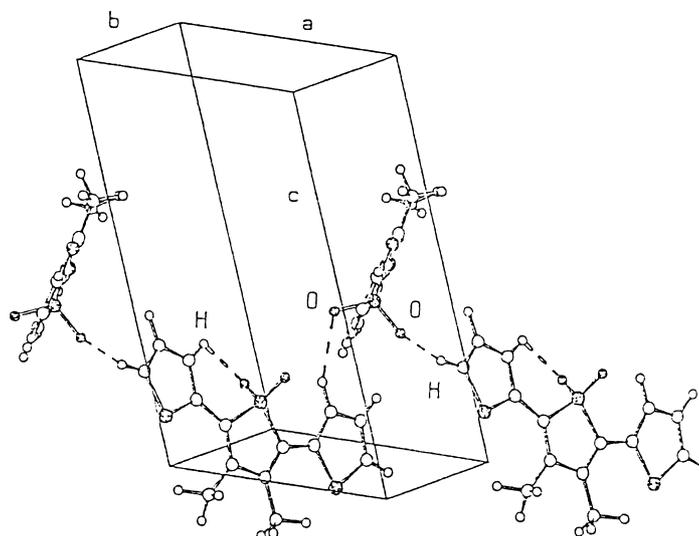


Fig. 3. Crystal packing of compound **5** ( $X = \text{Me}$ ,  $R = \text{H}$ ) showing short intramolecular and intermolecular  $\text{C-H}\cdots\text{O}$  interactions.

example is given in Fig. 3 showing the solid state arrangement of compound **5** ( $X = \text{Methyl}$ ,  $R = \text{H}$ ). The crystal packing is characterized by  $\text{C-H}\cdots\text{O}$  hydrogen bonding [17] between the thiophene  $\text{C-H}$  donors and the oxygen atoms. Molecules of **5** present either short intramolecular  $\text{H}\cdots\text{O}$  contacts of 2.594 and 2.580 Å, which cause a slight tilt of one of the thiophene rings (dihedral angle of  $12.0^\circ$ ), or  $\text{H}\cdots\text{O}$  intermolecular interactions ranging from 2.3 to 2.6 Å. Therefore the introduction of a good hydrogen bond acceptor like oxygen influences the supramolecular organization of these materials and allows better control of their solid state design and properties.

Thanks to joint effects of the increased photoluminescence efficiencies and increased electron affinities of the new compounds, light emitting devices could be fabricated displaying much greater electroluminescence efficiencies than that observed with oligothiophenes [14,18]. Significant aspects of these LED devices were the low turn-on voltage and reasonably good electroluminescence efficiency.

### 3. Conclusion

The thienyl-*S,S*-dioxide moiety provides a building block allowing the synthesis of oligomers which display higher solid-state photoluminescence efficiency and greater electron affinity than those of conventional thiophene oligomers. These results extend the prospect for the use of thiophene-based compounds as active materials in light emitting diodes.

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