Chemically and thermally stable photo and electroluminescent thiophene-based materials

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ABSTRACT

We present a new class of thiophene-based oligomers and polymers with widely tunable photo and electroluminescence properties and which offer great potential for many different areas of application. We were able to synthesize materials displaying high solid-state fluorescence efficiency across the entire visible range. Electroactive polymers emitting ligth in the near IR were obtained by chemical and/or electrochemical polymerization of oligomers of different length. The polymers also displayed electrochromism, i.e. colour change when electric current flowed through the material. All compounds were characterized by great thermo and photooxidative stability. With some of these materials efficient electroluminescent devices were fabricated and characterized.

Keywords: thiophene, oligomers, polymers, synthesis, electron affinity, photoluminescence, electroluminescence, UV-Vis, near IR, electrochromism

1. INTRODUCTION

One of the most appealing characteristics of organic materials is the easy tunability of properties through small changes in molecular structure and appropriate functionalization, a challenge for the development of efficient and low cost technologies in various fields of application.

Conjugated oligomers and polymers are currently the most investigated semiconductor organic materials for application in electrooptical devices.[1] Among conjugated materials those derived from thiophene are known for their good electrical characteristics[2] and, more recently, also for their photo and electroluminescent properties.[3]

The aim of this report is to present a new class of electroactive thiophene-based materials displaying tunable photo and electroluminescence as well as electrochromism.

The materials in question are thiophene-based dioxides - oligomers and polymers - corresponding to the following structures:

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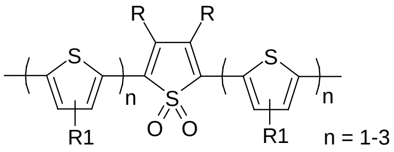
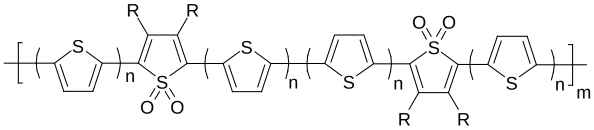


Oligo(thiophene-S,S-dioxides)



Poly(thiophene-S,S-dioxides)

2. RESULTS

The synthetic methodologies for the preparation of oligo- and poly(thiophene-S,S-dioxides) are reported in references 4a,b.

Starting from oligomers of different size (n = 1-3), several polymers with alternating oxigenated and non-oxigenated thienyl units were synthesized. These polymers can be viewed as copolimers in which the relative proportion of thienyl and thienyl-S,S-dioxide moieties allows for the control of properties. Their electronic and electrochromic properties were characterized using cyclic voltammetry and spectroelectrochemistry.[4b,c]

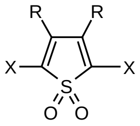
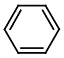
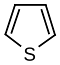
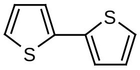
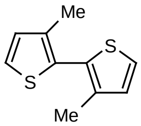
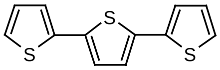
With respect to conventional oligo and polythiophenes, the presence of the oxigenated units allows for:

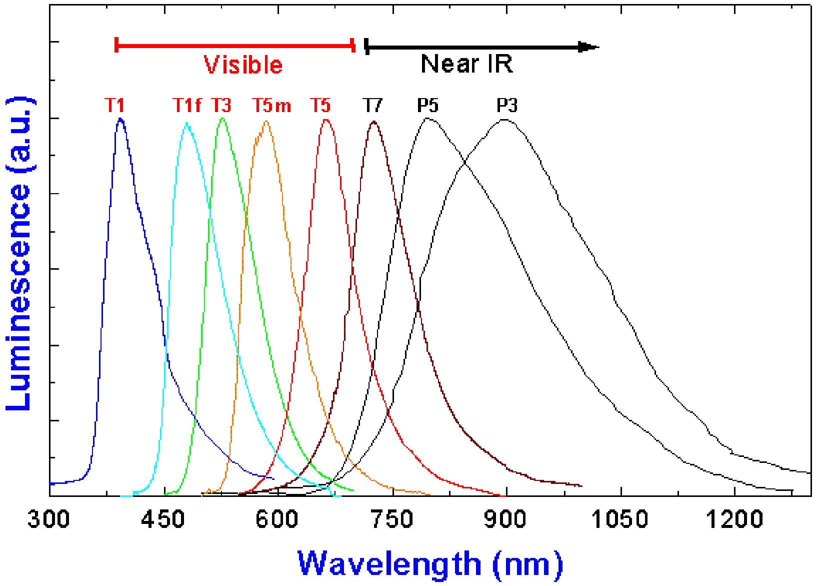
- increased photochemical stability in the solid state
- increased solid-state photoluminescence efficiency
- increased electron affinity
- increased electroluminesce efficiency
- tuning of the solid-state photoluminescence frequencies from blue to deep red (oligomers) and to near IR (polymers)

2.1 Solid-state photoluminescence

2.1.1. Pure compounds

Figure 1 shows the normalized photoluminescence spectra of the microcrystalline powders of a few selected oligomers and polymers under UV excitation (λ_{exc} = 367 nm). The figure shows that by changing the oligomer length and/or the degree of π-electron delocalization by appropriate choice of substituents X, emission wavelengths are obtained which span from blue to near IR.

 	T1	T1f	T3	T5	T5m	T7
X	$SiMe_3$		 	 	 	
R	H	Hexyl	Hexyl	Hexyl	Hexyl	Hexyl



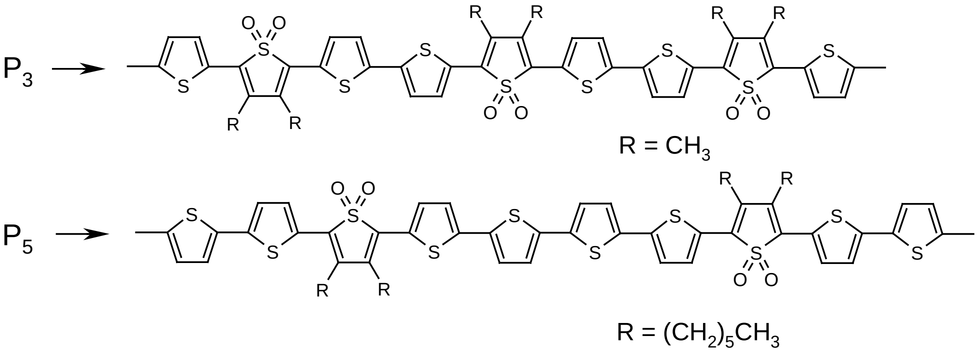


Figure 1. Chemical structure and photoluminescence spectra of selected oligo- and poly(thiophene-S,S-dioxides) under UV excitation (λ_{exc} = 367 nm)

A great variety of shades in the blue, green, yellow, orange and red regions can be obtained from the oligomers with solid-state photoluminescence efficiencies which can be as high as 70%, as shown in Figure 2. The photoluminescence efficiencies reported in figure 2 were measured by using an integrated sphere and are relative to samples in the form of microcrystalline powders. Values very similar to those reported in the figure were also obtained for samples in the form of thin films (spin-coated).

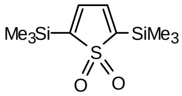
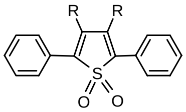
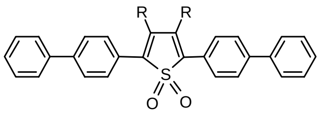
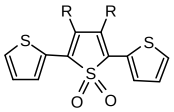
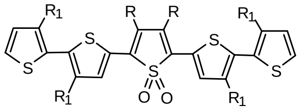
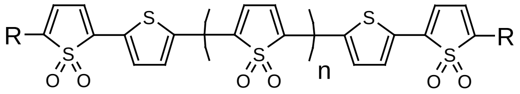
	λ_{PL}(nm)	η (%)		λ_{PL}(nm)	η (%)
	405	29	 R = Alkyl	470-510	10-60
 R = Hexyl	500	70	 R = Alkyl, Aryl	520-570	10-45
 R, R_1 = Alkyl, Aryl	600-660	10-40			

Figure 2. Molecular structure and solid-state photoluminescence frequencies (λ_{PL}, nm) and efficiencies (η, %) of selected oligothiophene-S,S-dioxides

Figure 1 also shows the photoluminescence spectra of polymers P3 and P5, obtained by oxidative polymerization of the corresponding trimer (T3) and pentamer (T5).[4b] The spectra are very broad with light emission tails up to more than 1 µm. Light emission tails up to more than 1.4 µm are observed in the spectrum of polymer P6, shown in Figure 3. Although the photoluminescence efficiencies of these polymers are only of a few % - probably due to unfavorable morphology characteristics – these results and the extreme synthetic flexibility associated with the preparation of polymers containing oxigenated thienyl groups[4] looks encouraging for the search of electroactive polymers with light emission frequencies tunable in the near IR and reasonably high solid-state photoluminescence quantum efficiencies.

P_6 →



R = $(CH_2)_5CH_3$

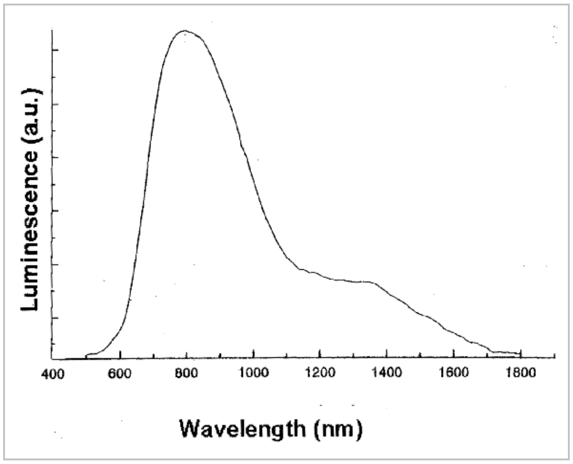


Figure 3. Photoluminescence spectrum of P6 under UV excitation (λ_{exc} = 367 nm)

2.1. 2. Binary blends of oligomers

Fully tunable binary blends have been fabricated by combining oligothiophene(S,S-dioxides) of high efficiency, covering the entire spectrum of colors according to the standards of the Commission International de l'Eclairage (CIE). Binary blends resulting in purple, red and white colors were prepared.

We have shown that the emission spectrum of the blend is determined by the Forster transfer when the energy separation between the HOMO-LUMO gap of the constituting molecules is smaller than 0.56 eV. For larger energy separation, the blend emission is just given by the superposition of the emission spectra of the constituting molecules.[5]

2.2 Frontier orbital energies

The oxidation and reduction potentials of organic molecules give information on the HOMO and LUMO energies, respectively. In the case of photoluminescent molecules, these parameters are of paramount importance for the fabrication of electroluminescent devices.

The presence of the thiophene-S,S-dioxide moiety leads to less negative reduction potentials and more positive oxidation potentials compared to those of corresponding thienylene and phenylene derivatives and, in consequence, to the decrease of the energy of both the frontier orbitals in thiophene-based as well as phenyl-based oligomers. Moreover, since the LUMO energy is more affected than the HOMO energy, there is also a significant decrease in the HOMO-LUMO energy gap.[4c]

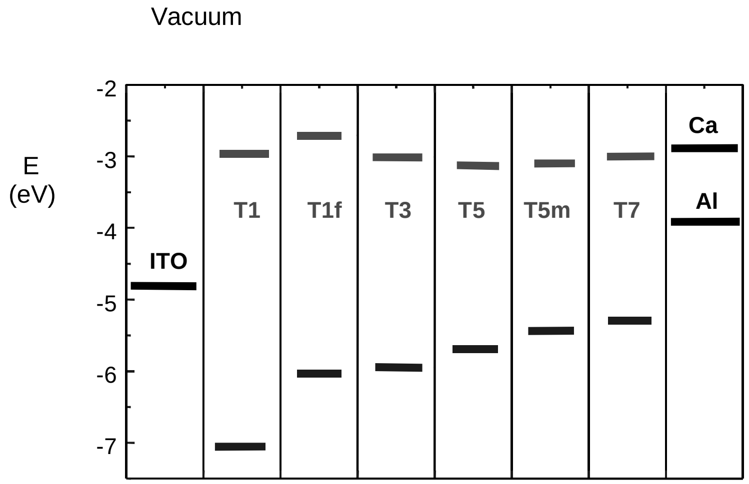


Figure 4. Ionization potentials and electron affinities of selected oligothiophene-S,S-dioxides (see figure 1) obtained from electrochemical oxidation and reduction peak potentials.

Figure 4 shows the ionization potentials and the electron affinities obtained from electrochemical oxidation and reduction peak potentials measured by cyclic voltammetry for the oligomers whose photoluminescence spectra are shown in Figure 1. For comparison, the figure also shows the work functions of aluminum and calcium and the work function of ITO which are generally used as the cathode and the anode materials, respectively, in the fabrication of electroluminescent devices.

2.3 Electroluminescence

High solid-state photoluminescence efficiencies and electron affinities are favorable conditions for obtaining high efficiency light emitting diodes. Indeed, the greater is the electron affinity of the light emitting material, the smaller is the energy barrier between the LUMO and the Fermi level of the metal used as the cathode, leading to better electron injection and increased device performance. In agreement with this, pentamer T5m was characterized by high electroluminescence efficiency (up to 1.2 Cd/A) and low turn on voltage (down to 1.9 V).[6a]

As a further example, figure 5 shows the current density and the luminance versus the applied voltage for a two layers device with a 100 nm thick active layer and a 60 nm thick PEDOT hole transporting layer under direct bias.[6b] The active material was a quinquethiophene-S,S-dioxide corresponding to the structure of pentamer T5m but with head-to-head cyclohexyl instead of methyl substituents grafted to the lateral thienyl rings. The LEDs were prepared by spin coating onto indium-tin-oxide (ITO) coated glass substrates first a hole transporting material, namely poly(3,4-ethylene dioxythiophene) doped with poly(styrene sulphonate), and then a chloroform solution of the pure active material. Cathode materials (Ca/Al) were deposited by thermal evaporation. Device characterization was carried out in air atmosphere.

The maximum value measured for EL efficiency was 0.1%, more than one order of magnitude larger than the typical values reported for non substituted oligothiophenes. These characteristics are well retained after a few hours of operating in air atmosphere, showing a good stability of the device.

It is worth noting that owing to the generally high glass transition temperatures of oligomers compared to polymers, small molecule-based devices are particularly suitable for applications in which heating of the device occurs.

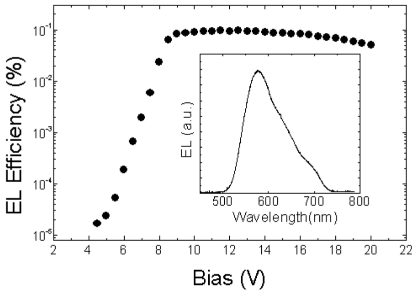


Fig. 5 Electroluminescence efficiency vs applied voltage. Inset: electroluminescence spectrum

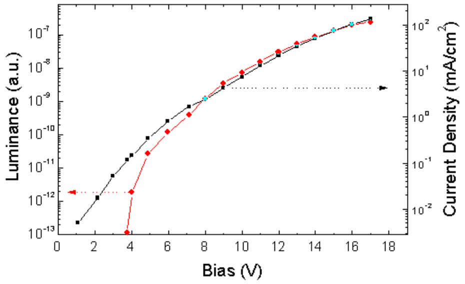


Fig. 6 Current density and Luminance vs applied voltage for ITO/PEDOT-PSS/T5c/Ca+Al LED

2.4 Electrochromism

Polymers P3 and P5 (see Figure 1) are characterized by the presence of one non-aromatic thienyl-S,S-dioxide moiety every two and four aromatic thienyl units, respectively. These kinds of polymers display remarkably greater electron affinities than those of conventional polythiophenes and can be reversibly *n*-doped at moderate potentials, while still maintaining the property of also being *p*-doped at moderate potential values.[4b]

These polymers are also characterized by electrochromism, namely they take or change color under the action of voltage applied.

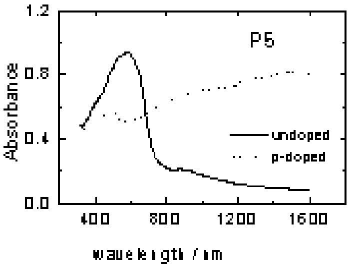


Figure 7. Absorption spectrum of polymer P5 in the undoped and *p*-doped form

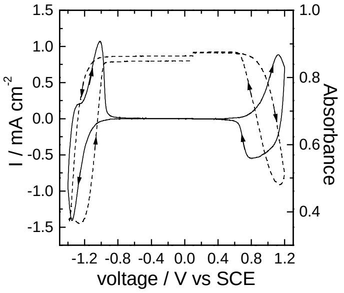


Figure 8. Cyclic voltabsorptometry of P5 in the neutral and in *p*- and *n*-doped forms

Figure 7 shows the absorption spectra of polymer P5 in the undoped and *p*-doped form, while Figure 8 shows the cyclic voltabsorptometry (CVAs) of the same polymer in the neutral and in *p*-doped and *n*-doped forms (at the maxim absorption wavelength). P5 is violet-blue in the undoped form and transparent grey in the *p*- and *n*-doped forms.

2.5 Chemical and thermal stability

In general, conventional polythiophenes display low photochemical stability in the solid state, resulting in short operation lifetimes of thin film devices based on these materials. It has been shown than in the solid state singlet oxygen adds to the polymer π-system generating radicals which may recombine or attack adjacent polymeric chains thus leading to a mixture of decomposition products.[7]

Oligo and polythiophene(S,S-dioxides), having oxygen atoms covalently attached to the thienyl rings, are much more stable than their conventional counterparts towards the action of visible light and oxygen. Thin films of the oligomers of figure 1 obtained by casting from chloroform solutions did not show any sign of photodegradation after many months from preparation. Likewise, this is also the result of the increase of oxidation potentials brought about by presence of the thienyl-S,S-dioxide moiety into the molecular backbone.[4c]

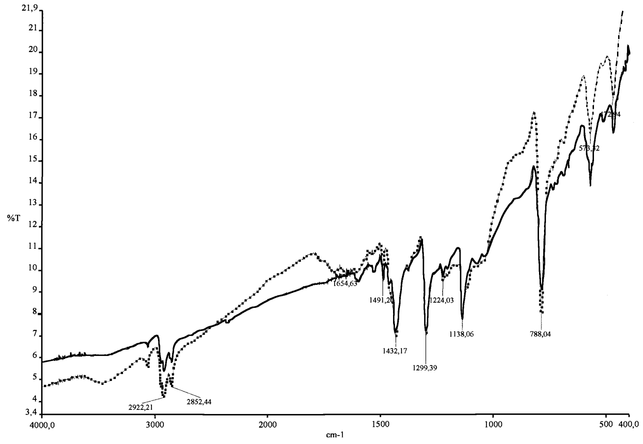


Figure 9. IR spectrum of polymer P5. The dotted line is the spectrum of the P5 after 90 h at 210 °C.

Oligo and polythiophene-S,S-dioxides are also stable towards temperature changes. Thermogravimetric analyses showed that they are stable above 300 °C in air. Long term exposition to high temperatures does not cause any decomposition of polythiophene-S,S-dioxides, as shown in figure 9 for polymer P5. The figure shows that no modifications appeared in the infrared spectrum of P5 after about four days at temperature higher than 200 °C, in particular in the region 1100-1300 cm^{-1} characterized by the intense bands pertaining to the sulphonyl groups.

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