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Organic light emitting diodes based on functionalized oligothiophenes for display and lighting applications

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1. Introduction

The electroluminescence properties of oligothiophenes are here reviewed. It is shown that thanks to joint molecular engineering and device improvement remarkable results have been achieved in recent years in terms of device operational stability and lifetime. These results open new perspectives in the search for tailor-made oligothiophenes with improved EL properties. Since the first report on the phenomenon of organic electroluminescence by M. Pope et al. in 1963 (Pope et al., 1963) and the description of the first organic light-emitting diode based on 8-hydroxyquinoline aluminum (Alq₃) as emissive and electron-transporting material by C. W. Tang et al. in 1987 (Tang et al., 1987), astonishing progress has been made in the field of Organic Light Emitting Diodes (OLEDs) owing to improved materials and device design (Burroughes et al., 1990; Greenham et al., 1993; Kraft et al., 1998; Friend et al., 1999; Pei & Yang, 1996; Yu et al., 2000; Scherf & List, 2002; Hung et al., 2005; Müllen & Scherf, 2006; Kalinowski, 2005; Shinar, 2004; D'Andrade, 2007; Misra et al., 2006; Baldo et al., 1998; Baldo et al., 2000; D'Andrade & Forrest, 2004; Kawamura et al., 2005; Yang et al., 2006; Chou & Chi, 2007). The promise of low-power consumption and excellent emissive quality with a wide viewing angle has prompted the interest for application to flat panel displays. High-efficiency OLEDs in various colours have been demonstrated and a few commercial products are already in the market, like displays for cell phones and digital cameras. Today much research is being carried out on white OLEDs for lighting applications, in order to attain lifetimes and brightness that would allow replacing current indoor and outdoor light sources at costs competitive with those of existing lighting technologies (D'Andrade, 2007; Misra et al., 2006).

One of the key developments in the advance of organic LED technology was the discovery of electrophosphorescence which lifts the upper limit of the internal quantum efficiency of devices from 25% to nearly 100% (Kawamura et al., 2005). Indeed, one of the factors contributing to device efficiency is the ratio of the radiatively recombining excitons (from

injected holes and electrons) to the total number of excitons formed. With fluorescent emitters, statistically (parallel spin pairs will recombine to triplet excitons while antiparallel spin pairs will recombine to singlet and triplet excitons) only 25% of the generated excitons can recombine through a radiative pathway, causing an intrinsic limitation on the external quantum efficiency of the OLED. In phosphorescent materials - complexes containing heavy metals - strong spin-orbit coupling leads to singlet-triplet state mixing which removes the spin-forbidden nature of the radiative relaxation from the triplet state. Thus, when phosphorescent emitters are used, an internal quantum efficiency up to 100% can in principle be achieved since in phosphorescent emitters both singlet and triplet excitons can radiatively recombine. The synthesis of phosphorescent triplet emitting materials (phosphors) has led to remarkable improvements in EL quantum efficiencies and brightness (D'Andrade, 2007; Misra et al., 2006; Baldo et al., 1998; Baldo et al., 2000; D'Andrade & Forrest, 2004; Kawamura et al., 2005; Yang et al., 2006; Chou & Chi, 2007). Nevertheless, although much research is focused today on the synthesis of new phosphorescent emitters, a great number of laboratories are still working on fluorescent compounds. The reason for this lies in the higher chemical and electrical stability shown by many of these compounds. Another advantage is that most fluorescent materials can be deposited without dispersing them in a matrix. While indeed the phosphors need to be deposited into a wide gap material to avoid self quenching, there are numerous fluorescent compounds, including thiophene oligomers, which do not suffer this problem. Moreover, the problem of self-quenching together with the wide absorption band of phosphors implies that the host material must have a gap wider than those of the emitters, so the minimum voltage that it is possible to apply to the device is high compared to the voltage of devices based on fluorescent compounds.

So far, thiophene materials have played a little role in the development of organic LEDs compared to other materials such as polyphenylenevinylenes (Burroughes et al., 1990; Greenham et al., 1993; Kraft et al., 1998; Friend et al., 1999), polyfluorenes (Pei & Yang, 1996; Yu et al., 2000; Scherf & List, 2002; Hung et al., 2005), or phosphorescent complexes (D'Andrade, 2007; Misra et al., 2006; Baldo et al., 1998; Baldo et al., 2000; D'Andrade & Forrest, 2004; Kawamura et al., 2005; Yang et al., 2006; Chou & Chi, 2007) and the research in this field has mainly been confined to the understanding of basic properties. The electroluminescence of thiophene materials is a poorly investigated field, probably due to the fact that in the early days of OLEDs the most investigated thiophene materials displayed low electron affinities and photoluminescence quantum yields in the solid state and were believed to be mainly suited for application in field-effect transistors (Garnier, 1999). Moreover, the few investigations carried out later on phosphorescence in thiophene materials afforded rather disappointing results (Wang et al., 2004). Nevertheless, the finding that appropriate functionalization of thiophene oligomers and polymers may increase both electron affinity (Barbarella et al., 1998 a) and photoluminescence efficiency in the solid state (Barbarella et al., 2000), allows to achieve high *p*- and *n*-type charge carrier mobilities (Yoon et al., 2006), may lead to white electroluminescence via spontaneous self-assembly of a single oligomer (Mazzeo et al., 2005), may allow the realization of optically pumped lasers (Zavelani-Rossi et al. 2001) and very bright electroluminescent diodes (Mazzeo et al., 2003 a), has risen again the interest on the potentialities of these compounds, also in view of the next generations of organic devices like light-emitting transistors or diode-pumped lasers. This paper reviews the various approaches used to obtain electroluminescence from oligomeric

thiophene materials and recent progress with various device designs and synthetic products. In section 2, electroluminescence from linear oligothiophenes is discussed focusing on bilayer device structures realized by spin coating. Section 3 presents the results obtained using V-shaped thiophene derivatives and section 4 describes the different approaches employed to achieve white electroluminescence with oligothiophenes. Section 5 reports new results obtained in heterostucture devices using a thermally evaporated compound.

The choice to focus on the electroluminescence of oligomeric thiophene materials is due to the fact that there has been little progress in polythiophenes as electroluminescent materials from earlier studies (Braun et al., 1992; Berggren et al., 1994; Barta et al., 1998) to more recent investigations (Charas et al., 2001; Pasini et al., 2003; Cheylan et al., 2007; Melucci et al., 2007).

2. Linear thiophene oligomers

The first attempt to get electroluminescence from thiophene oligomers dates back to 1994 (Horowitz et al., 1994). A detailed study was reported three years later based on an end capped sexithiophene (EC6T) used as emissive and hole transporting layer in a single layer device (Väterlein et al., 1997). The molecular structure and the photoluminescence and electroluminescence spectra of EC6T at various temperatures are shown in Figure 1. The I - V and EL - V curves measured for an ITO/EC6T-/Ca-OLED at forward bias for temperatures in the range 30-270 K (thickness 65 nm) are also reported in the figure. The photoluminescence and electroluminescence spectra were virtually the same, indicating that the radiative recombination of excitons proceeded from the same excited states in both cases. The current-voltage (I - V) curves exhibited strong temperature and thickness dependence. External quantum efficiencies in the range $1\text{--}8 \times 10^{-5}$ at room temperature were measured. The orange electroluminescence generated by the device could be observed with the naked eye but lasted only for a few seconds.

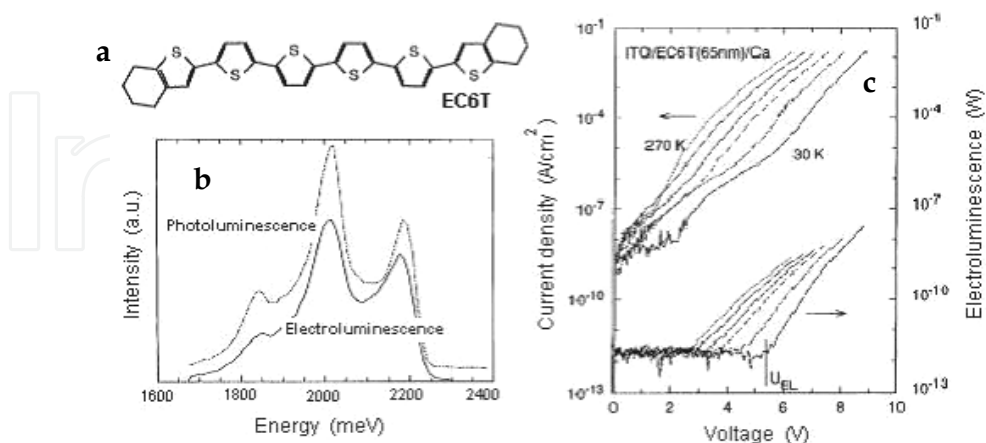


Fig. 1. a) Molecular structure of EC6T; b) photoluminescence and electroluminescence spectra at 4 and 20 K, respectively; c) I - V curves (top, left-hand scale) and EL - V curves (bottom, right-hand scale) of a ITO/EC6T/Ca OLED (thickness 65 nm) as a function of temperature (30, 90, 120, 150, 210, and 270 K from right- to left).

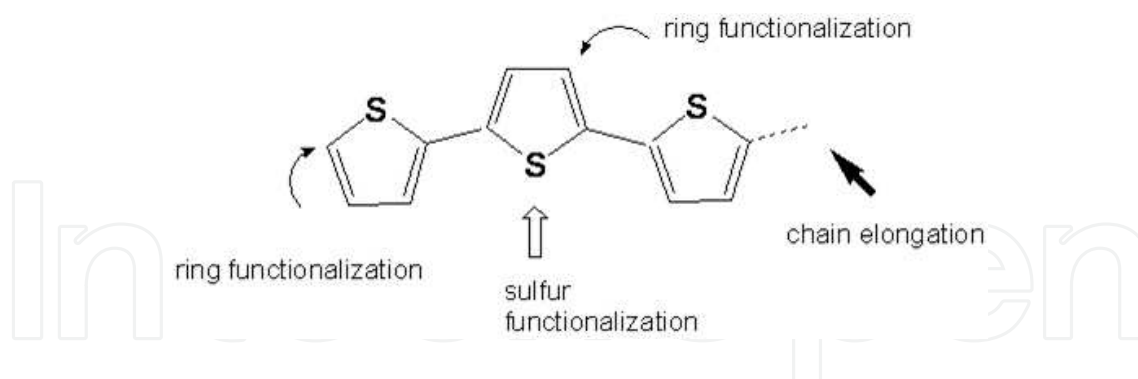
Two of the main drawbacks of conventional thiophene oligomers such as EC6T for applications in OLEDs are the low electron affinity (EA) and the non-radiative phenomena induced by packing causing the quenching of photoluminescence (PL) in the solid state.

Conventional oligothiophenes are easy to oxidize but difficult to reduce, as demonstrated by cyclovoltammetry (CV) measurements (Meerholiz & Heinze, 1996; Barbarella et al., 1998 a). In light emitting devices the low electron affinity generates a huge energy barrier between the cathode and the organic layer. In consequence, only a small number of electrons are injected, resulting in poor electron-hole balancing.

The low PL efficiency in the solid state is largely determined by the intermolecular interactions governing the supramolecular organization. The analysis of conformation and packing modalities in oligothiophene single crystals has pointed out the existence of numerous intra- and intermolecular interactions, such as van der Waals, π - π stacking, weak CH...S and CH... π hydrogen bondings and S...S contacts (Marseglia et al., 2000). Intermolecular interactions induce additional non-radiative channels so that the photoluminescence efficiency of oligothiophenes is lower in the solid state than in solution. For example, a photoluminescence quantum yield of about 40% was reported by several authors for solutions of quinquethiophene, which, however, dropped by several orders of magnitude in thin films of the same compound (Oelkrug et al., 1996; Kanemitsu et al., 1996; Ziegler, 1997). Owing to low photoluminescence efficiency caused by non-radiative phenomena induced by packing and to intrinsically low electron affinities, conventional oligothiophenes display very poor electroluminescence characteristics.

2.1 Achieving the simultaneous increase of electron affinity and solid-state PL via chemical modification

There are several ways to modify the molecular structure of oligothiophenes via chemical synthesis, as indicated in Scheme 1:

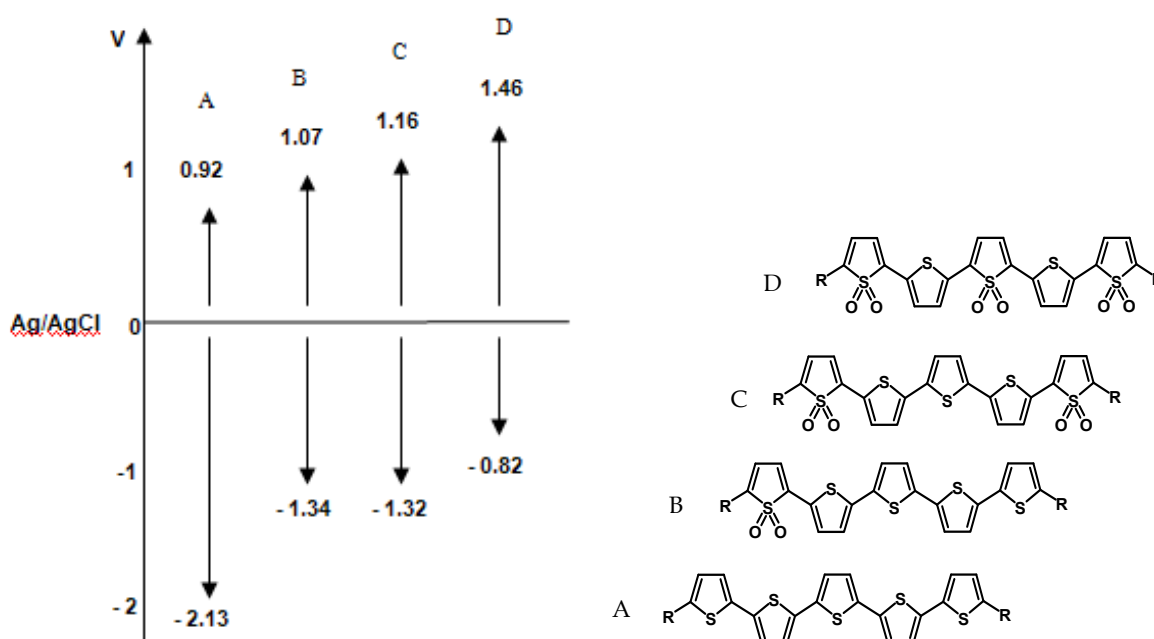


Scheme 1. Functionalization modalities in oligothiophenes

A considerable improvement in solid-state PL and electron affinity values was achieved via chemical modification of the thiophene rings through functionalization of the sulphur atom with oxygen (Barbarella et al., 1998 a). Indeed, in thiophene, sulphur has unshared lone-pair electrons which can be exploited to form chemical bonds with oxygen. In this way, a new class of oligomeric thiophene materials - namely oligothiophene-S,S dioxides, in which two oxygen atoms are linked to one or more thienyl sulphurs - was synthesized (Barbarella et al., 1998 b). By using this approach, compounds with greater electron affinities and

photoluminescence efficiencies in the solid state became available and proved to be useful for applications in electroluminescent diodes (Barbarella et al., 1999) and photovoltaic devices (Camaioni et al., 2004).

Scheme 2 shows the molecular structure of a few quinquethiophenes with one or more oxidized thienyl units and the variation of the corresponding redox peak potentials measured by cyclic voltammetry (Barbarella et al., 1998 a). Oxidation and reduction potentials are related to HOMO and LUMO orbital energies hence to ionization energies and electron affinities, respectively. The oxygen atoms cause the de-aromatization of the thiophene ring and allow the frontier orbitals to shift towards lower energies, causing in particular a sizeable increase in electron affinities (Barbarella et al., 1998 a). The scheme shows that the reduction and oxidation potentials of quinquethiophene can be tuned by changing the number and the position of the oxygenated units. In particular, it can be seen that the oligomer with alternating oxidized and non-oxidized thiophene rings is easier to reduce than to oxidize, opposite to the precursor quinquethiophene.



Scheme 2. Reduction and oxidation potentials of selected quinquethiophene-S,S-dioxides. R= Si(CH₃)₃C(CH₃)₃.

Figure 2 shows an example of cyclic voltammogram of a quinquethiophene-S,S-dioxide, namely compound B in Scheme 2. The CV in the oxidation region shows two reversible waves with E_{p,a1} = 1.00 V and E_{p,a2} = 1.30 V. The CV in the reduction region shows two reversible waves with E_{p,c1} = -1.28 V and E_{p,c2} = -1.63 V, the first of which probably corresponds to the formation of the radical anion. It should be noted that the first oxidation potential is 0.15 V larger than that of the parent unmodified quinquethiophene, while the first reduction potential is shifted by 0.79 V towards less negative values, indicating a remarkable increase of the electron affinity of the molecule.

Since the first report in 1998 (Barbarella et al., 1998 a), the increase in molecular electron affinity upon inclusion of a thienyl-S,S-dioxide unit into the aromatic skeleton of conjugated oligomers and polymers has been observed by several authors (Hughes & Bryce, 2005;

Beaupré & Leclerc, 2002; Berlin et al., 2003; Perepichka et al., 2005; Casado et al., 2006; Liu et al., 2008).

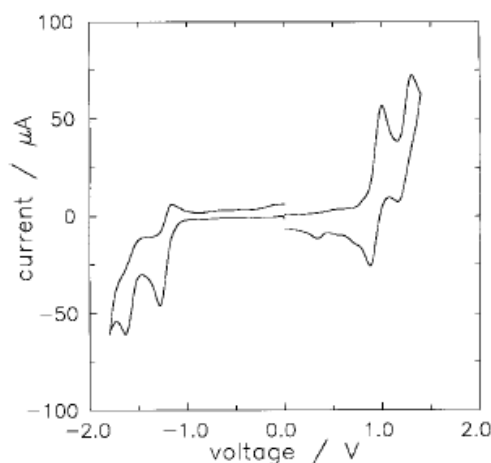
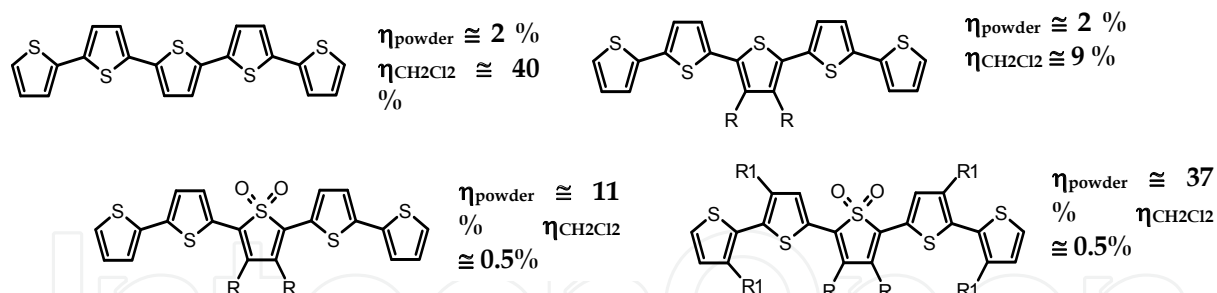


Fig. 2. Cyclic voltammogram (200 mV/s, 1 mM in $\text{CH}_2\text{Cl}_2/\text{Et}_4\text{NBF}_4$ 0.2 M. V vs. Ag/AgCl) of quinquethiophene-S,S-dioxide B depicted in Scheme 2.

Recently, the redox potentials of fully oxidized (conjugated but no more aromatic) bi- and terthiophene have also been reported, showing that complete oxidation of the thienyl rings has a dramatic effect on both redox potentials and may cause a marked energy gap increase (Amir & Rozen, 2005).

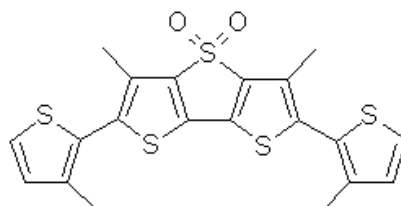
Time-Dependent Density Functional Theory (TD-DFT) simulations in adiabatic approximation, carried out on a prototype terthiophene oxidized in the inner position (Raganato et al., 2004), indicated that the oxidation of the thiophene ring leads to the formation of new interactions in the LUMO orbital. The kinetic energy of the electrons in this orbital is lowered, while the energy of the electrons in the HOMO orbital is almost unchanged. As a consequence, the electron affinity of the whole molecule is increased.

The functionalization with oxygen obliges the molecules to pack far apart from each other in the solid state thus preventing the photoluminescence quenching caused by the close packing of non oxidized thiophene oligomers (Antolini et al., 2000). Consequently, the PL quantum yield (η , the number of photons re-emitted radiatively as a percentage of the number of photons absorbed) is increased, by an amount up to one order of magnitude (Barbarella et al., 1999). Scheme 3 illustrates the trend of variation of photoluminescence quantum yield (PLQY) in solution and in the solid state of α -quinquethiophene upon introduction of different chemical modifications in the aromatic skeleton (Barbarella et al., 1999). Upon insertion of alkyl chains, there is a dramatic decrease in PLQY in solution, from 40% to 9%, while in the solid state the PLQY value remains unchanged. Modification of the inner ring with oxygen atoms causes the PLQY in solution to drop to less than 1% but increases remarkably the PLQY value in the solid state, from 2% to 11%. Further functionalization of the thienyl groups with methyl substituents in the head-to-head orientation does not modify the PLQY value in solution, but further enhances that in the solid state, which reaches a very significant 37%.



Scheme 3. Trend of variation of the photoluminescence quantum yield ($\eta\%$) of α -quinquethiophene in solution and in the solid state following different chemical modifications. R= Hexyl, R1 = Methyl.

One of the highest PLQY values, measured in the solid state for an oligothiophene-S,S-dioxide was shown by the 'rigid-core' oligomer 3,5-dimethyl-2,3'-bis(3-methylthiophene)-dithieno[3,2-b;2',3'-d]thiophene-4,4-dioxide, DTTOMe4:



3,5-Dimethyl-2,3'-bis(3-methylthiophene)-dithieno[3,2-b;2',3'-d]thiophene-4,4-dioxide (DTTOMe4)

This 'rigid core' compound displayed a PLQY value in the microcrystalline powder of $\eta = 48\%$ (Barbarella et al., 2001). DTTOMe4 belongs to a class of oligothiophene-S,S-dioxides characterized by high photoluminescence efficiency both in solution and in the solid state, contrary to conventional thiophene oligomers and conformationally flexible oligothiophene-S,S-dioxides (Barbarella et al., 2001). The conformation and the crystal-packing modalities of DTTOMe4 could be established directly from microcrystalline powder diffraction data (Tedesco et al., 2003). Semiempirical Intermediate Neglect of Differential Overlap with Single Configuration Interaction (INDO/SCI) theoretical investigations then allowed to obtain semiquantitative correlations between the structural characteristics of the compound and the main intermolecular factors that are known to affect the solid-state photoluminescence of organic molecules (Tedesco et al., 2003). The energy of the first singlet excited state and the oscillator strength of the optical transition, the exciton resonance interactions and the electron and hole transfer integrals for each pair of molecules were calculated using molecular geometries from the crystal structure. The calculations showed that there was very good agreement between the singlet excitation energies and the experimental maximum energy values of the absorption spectra in the solid state and in solution, indicating that the INDO/SCI approximation reproduces well the optical properties of this type of molecules. This result also suggested that exciton resonance interactions in the solid state (i.e., the interactions between the neutral excited states generated by photoexcitation) were weak. In agreement with this, the calculated exciton resonance interactions, which are proportional to the rate of excitation transfer between

molecules, were small. According to the calculations, the intermolecular interactions play a major role in determining the solid-state photoluminescence efficiency, which correlates well with the rate of formation of non radiatively decaying charge-transfer pairs upon photoexcitation. The theoretical results obtained with DTTOMe4 indicated that a similar mechanism may also explain the very different photoluminescence quantum yields measured for ter-, quinque-, and heptathiophene-*S,S*-dioxides in the solid state (45, 12, and 2%, respectively) (Antolini et al., 2000). The trend in the PLQY values of these conformationally flexible molecules was first tentatively ascribed to the different orientations of the long molecular axes in single crystal structures: markedly tilted in the trimer, strictly parallel in the heptamer, with the pentamer in an intermediate situation. However, the theoretical and experimental data obtained for DTTOMe4 - in which the molecules pack with their long molecular axes parallel - show that, even when oligothiophene-*S,S*-dioxide molecules pack with their long molecular axes parallel, the photoluminescence efficiency can be quite high if the molecules are sufficiently distant from each other.

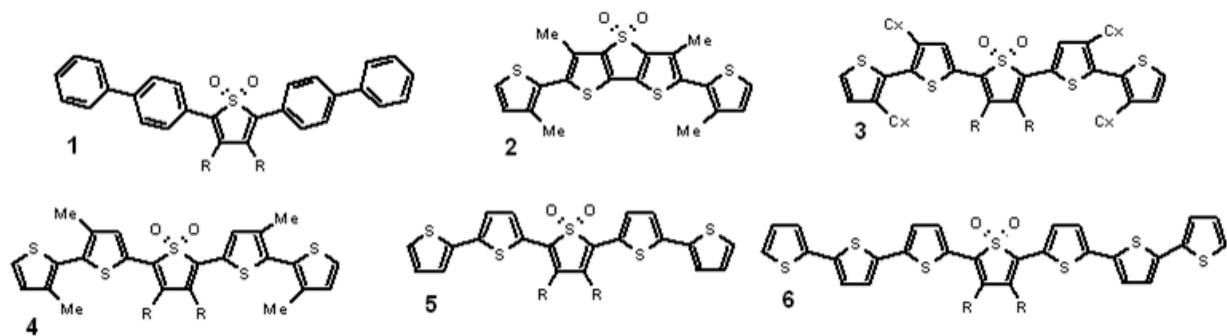
It is worth noting that first-principles Time-Dependent Density-Functional Theory (TD-DFT) calculations on terthiophene-*S,S*-dioxide have also shown that another important result of the functionalization of the thienyl ring with oxygen atoms is that the separation between the triplet state T2 and the singlet state S1 is enhanced with respect to the parent unmodified terthiophene (Della Sala et al., 2003; Anni et al., 2005). In this way, the probability of intersystem crossing from singlet states to optically forbidden triplet states is reduced, advantaging further the PL efficiency.

2.2 Electroluminescence in linear oligothiophene-*S,S*-dioxides

The increased electron affinities and PL quantum efficiencies of oligothiophene-*S,S*-dioxides in the solid state, combined with the optical and chemical stability of these compounds, allowed the fabrication of electroluminescent devices with much better characteristics than those obtained with conventional thiophene oligomers. The lifetime of the devices went from seconds to days and the characterization could be carried out in ambient atmosphere. The characteristics of the devices were well retained after a few hours of operation in air atmosphere, showing a good stability of the device.

Scheme 4 shows the molecular structure of a series of oligomers (compounds 1-6) containing a central thiophene-*S,S*-dioxide that were used as active materials in light emitting diodes (Gigli et al., 2001). The LEDs were prepared by spin coating onto indium-tin-oxide (ITO) coated glass substrates an hole transporting material, namely poly(3,4-ethylenedioxythiophene), PEDOT, doped with poly(styrene sulphonate), PSS, and then a dichloromethane (CH_2Cl_2) solution of the oligothiophene-*S,S*-dioxide. The deposition of the PEDOT-PSS layer was aimed at increasing the hole injection from the ITO anode into the oligothiophene-*S,S*-dioxide layer. The cathode was Ca capped with Al and prepared by thermal evaporation. The devices were characterized in air.

The electrooptical characteristics of 1-6 are reported in Table 1, while the electroluminescence spectra of all compounds, together with the current-voltage (*I-V*), luminance-voltage (*L-V*) characteristics and EL efficiency of the device obtained with compounds 3 are shown in Figure 3.



Scheme 4. Molecular structure of linear oligothiophene-S,S-dioxides 1-6. R = Hexyl; Me = Methyl; Cx = Cyclohexyl.

Changing oligomer size and substituents from 1 to 6 allowed to tune the electroluminescence from green to near-infrared (Gigli et al., 2001). Pentamers 1-5 emit in the green-red region, the colour tuning being obtained either by replacing the thienyls with phenyl groups or by distortion of the oligomer chain length via β -functionalization with methyls or cyclohexyl groups. Light emission in the NIR region was obtained by using compound 6 as the active material. This long oligomer, a derivative of heptathiophene, adopts a fully planar conformation in the solid state (Antolini et al., 2000), which determines a large electron delocalization and a strong decrease of the optical gap.

	η %	EA (eV)	V (Volts)	Lum _M (cd/m ²)	ϕ %
1	70	3	3.2	100	0.03
2	48	2.9	2.3	110	0.004
3	22	3.1	4.8	400	0.2
4	37	3	1.9	110	0.08
5	13	3.1	2	105	0.03
6	2	3	4.9	80	0.002

Table 1. Electro-optical characteristics of compounds 1-6^a

a) η : PL efficiency; EA: electron affinity, extrapolated from CV data; V: turn-on voltage; Lum_M: maximum luminance; ϕ : EL efficiency.

As shown in Table 1, the turn-on voltages for luminance at 0.01 cd/m² were all between 2 and 5 V, strongly reduced as compared to the values reported for poly(alkylthiophenes)-based devices (Barta et al., 1998). This was the result of the increased electron affinity of compounds 1-6 induced by the S,S-dioxide functionalizaty and to the consequent reduction of the electron injection barrier.

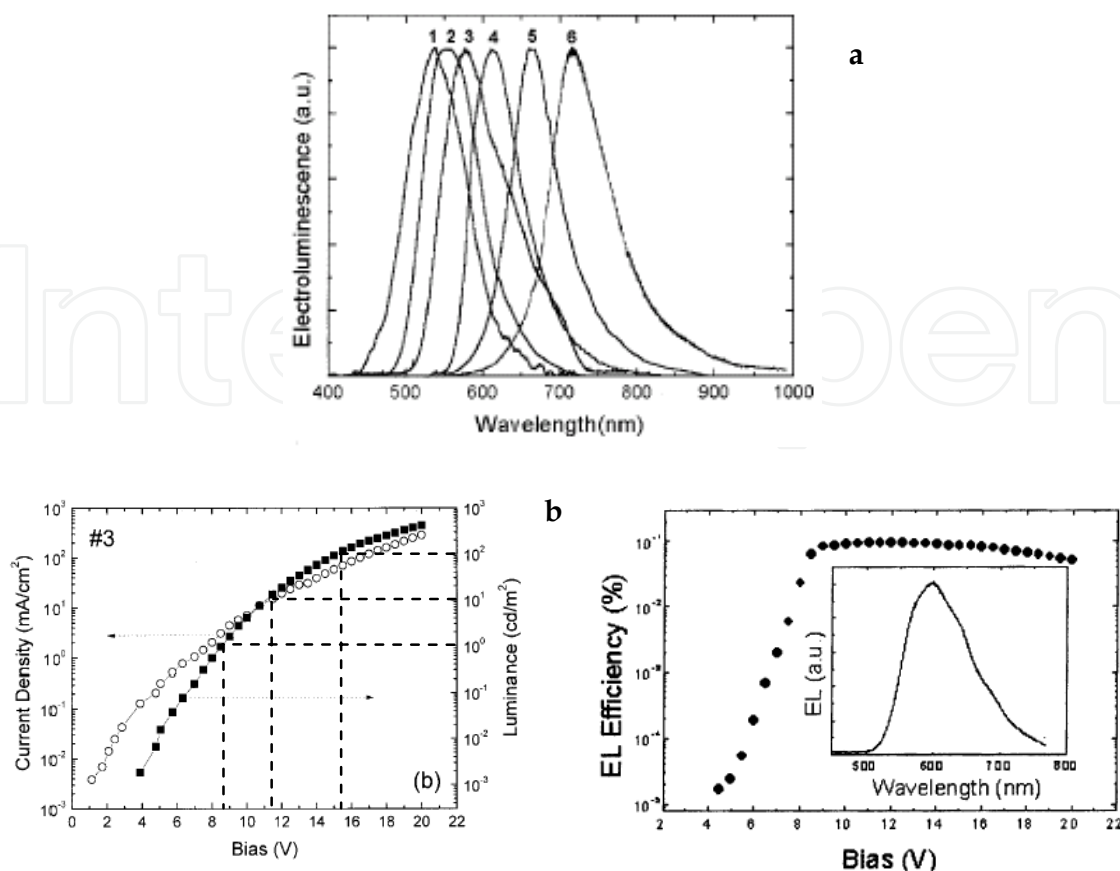


Fig. 3. a) Electroluminescence spectra of compounds 1-6 spanning from green to near IR; b) Current-voltage (I - V), luminance-voltage (L - V) characteristics (left) and EL efficiency (right) of the device obtained with compounds 3 as the active layer (120-nm-thick with a 70-nm-thick PEDOT layer).

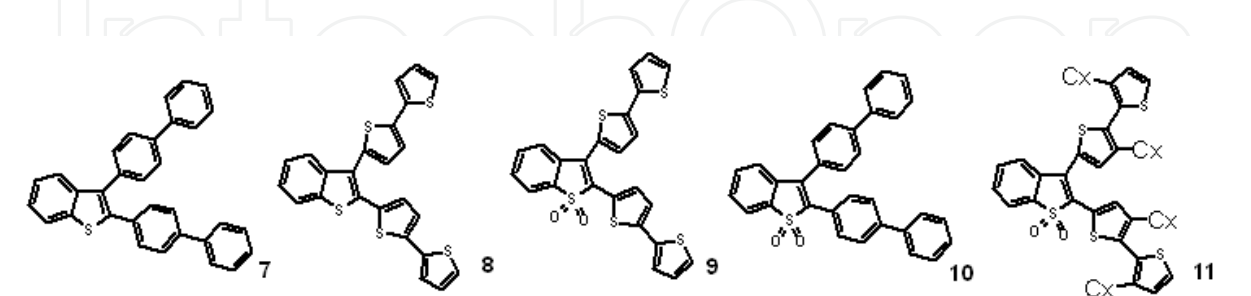
The maximum luminance reached using compound 3 (Figure 3b) was 400 cd/m² at 20 V, a value which was already good enough for display applications. The device with compound 3 displayed also the highest EL efficiency, 0.2%, which was at least one order of magnitude larger rather than those already reported for the best oligo- and polythiophene based devices. The devices obtained with compounds 1-6 showed that it was possible to obtain multicolor electroluminescence from oligomeric thiophene materials and greatly improve the electroluminescence characteristics compared to conventional oligomers.

3. V-shaped oligothiophene-S,S-dioxides with high photo and electroluminescence performance

A remarkable improvement was achieved in 2003 with a new approach based on the replacement of the conventional linear structure of oligothiophenes and oligothiophene-S,S-dioxides with branched benzo[*b*]thiophene based structures (Mazzeo et al., 2003 a; Barbarella et al. 2005). These compounds (V-shaped oligothiophenes), in combination with the oxygen functionalization of the core thienyl sulphur and the cyclohexyl substitution of the lateral thienyl rings, allowed to achieve a remarkable luminance value of 10500 cd/m², which was the highest value obtained for LEDs based on oligothiophenes. The rationale

behind the synthesis of V-shaped compounds was the need to replace crystalline by amorphous thin films in order to avoid strong intermolecular interactions and then reduce the contribution of non radiative intermolecular deactivation pathways.

The molecular structure of selected V-shaped oligothiophene-S,S-dioxides is shown in Scheme 5, while the corresponding electro-optical characteristics are reported in Table 2. The luminance vs. voltage plots and the electroluminescence spectra of the devices fabricated with 9, 10 and 11 as the active materials, are shown in Figure 4.



Scheme 5. Molecular structure of V-shaped oligothiophene-S,S-dioxides 7-11. Cx = Cyclohexyl.

	η %	Epc	Epa	Lum _M (cd/m ²)	ϕ %
7	4	<-2	1.60	35	0.001
8	2	<-2	1.35	1250	0.02
9	4	-1.26	1.43	2500	0.14
10	50	-1.45	>2	500	0.06
11	21	-1.36	1.48	10500	0.45

Table 2. Electro-optical characteristics of compounds 7-11^a
a) η : PL efficiency; Epc, Epa: reduction and oxidation peak potentials (vs calomel electrode) measured by cyclovoltammetry; Lum_M : luminance max; ϕ : EL efficiency.

Table 2 shows that the functionalization of the benzothienyl moiety with oxygen affects slightly the oxidation potentials but causes a relevant displacement of the reduction potentials towards less negative values (by an amount up to 0.74 eV), indicating a marked increase in the electron affinity of the compounds, in line with what was observed for linear oligothiophene-S,S-dioxides. All compounds were employed as active layers in OLEDs in which ITO/PEDOT:PSS and calcium/aluminum were used as the anode and the cathode, respectively, i.e. the same conditions employed with linear oligothiophene-S,S-dioxides. Most devices showed much better performance and operational stability than those achieved using the linear oligomers.

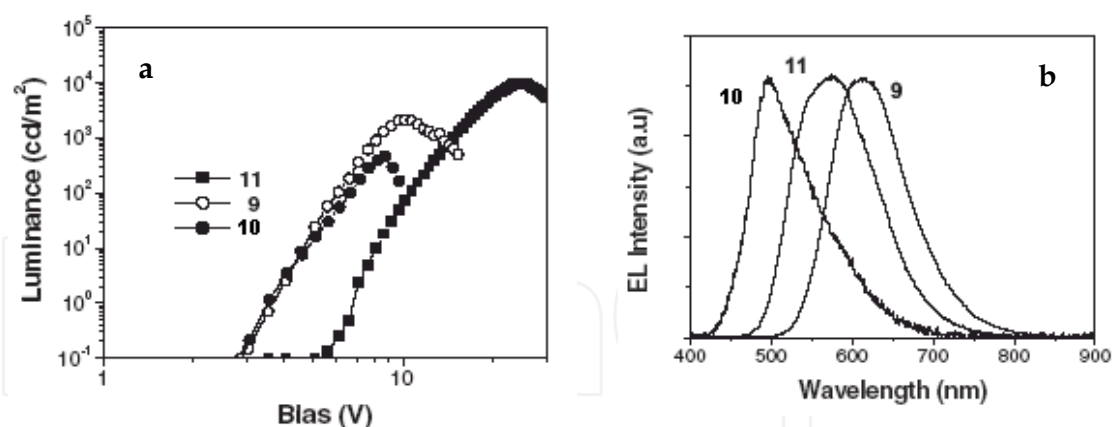


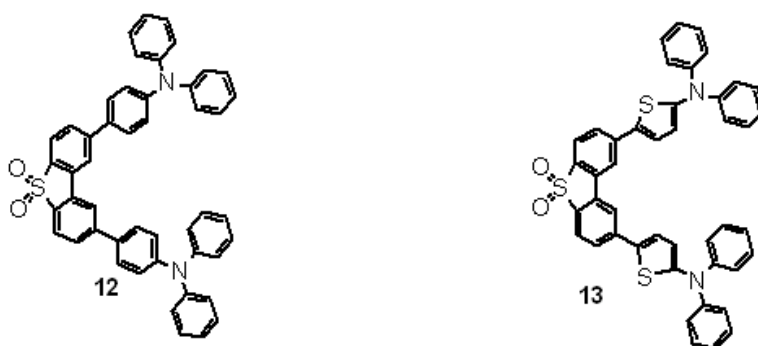
Fig. 4. a) Luminance vs. voltage and b) electroluminescence spectra of devices fabricated using compounds 9, 10 and 11.

Comparison of the the luminance values reported in tables 1 and 2, shows that the V-shaped structure was crucial to improve the brightness of the devices. For example, the non oxidized branched compound 8, shows a maximum brightness value of 1250 cd/m², three times higher than the best functionalized linear oligothiophene-S,S-dioxide reported in Table 1. While, in contrast to linear oligothiophene-S,S-dioxides, the functionalization with oxygen does not result in a substantial enhancement in photoluminescence efficiency, the EL efficiency is significantly improved. This is shown, for example, by comparison of the efficiency and luminance of the devices fabricated with compound 8 (0.02% and 1250 cd/m², respectively) and with the corresponding oxygenated derivative 9 (0.14% and 2400 cd/m²). This result is due to the fact that the oxygen atoms induce a strong reduction in the energetic barrier between the cathode and the emissive layer, as in linear oligothiophene-S,S-dioxides. The maximum luminance (10500 cd/m²) for the LED fabricated with compound 11 is more than 20 times larger than the maximum luminance displayed by the LED fabricated with the corresponding linear oligothiophene-S,S-dioxide, i.e. compound 3 (400 cd/m²). As shown by comparison of the data reported in tables 1-2, also the maximum luminance of the devices based on compounds 9 (2500 cd/m²) and 10 (500 cd/m²) are much higher than those obtained with the devices based on the corresponding linear compounds 5 (105 cd/m²) and 1 (100 cd/m²). Since theoretical calculations, optical and CV data indicate that V-shaped oligothiophene-S,S-dioxides have electronic and optical features very similar to those of the corresponding linear compounds, the reason for the improved performances was ascribed to the much better film-forming properties of V-shaped compared to linear compounds and to changes in morphology from crystalline to amorphous films. There are several studies in the literature indicating that amorphous thin films, obtained either by vapor deposition or spin coating, enhance the electroluminescence properties (Robinson et al., 2001; Su et al., 2002; Doi et al., 2003).

The good film-forming properties and the amorphous morphology of V-shaped oligomers are due to their branched structure and asymmetric molecular conformation. TD-DFT calculations showed indeed that the molecular geometry of V-shaped oligothiophenes was not planar due to the large dihedral angle (>60°) between the branch in the β -position and the rigid core (Mazzeo et al., 2003).

The best performance of OLEDs based on V-shaped oligomers was obtained with the oxygenated compound functionalized with β -cyclohexyl substituents, namely compound 11,

in which electronic de-excitation via intermolecular interactions and internal conversion processes - which are the most important non radiative relaxation channels in oligothiophene-S,S-dioxides (Lanzani et al., 2001; Della Sala et al., 2003; Anni et al., 2005) - are strongly reduced. Functionalization with the bulky cyclohexyl groups has several effects. First, the large intermolecular distances due to the bulky substituents reduce the intermolecular interactions. Second, as shown by DFT (ground state) and TD-DFT (excited state) molecular geometry optimizations (Mazzeo et al., 2003 a), the molecular distortion is increased both in the ground and in the excited state. In the first singlet excited state the thiophene branches lie in two different planes, making the formation of non radiative aggregates unlikely. Third, the flexibility of the branches is strongly reduced. The calculations show, for example, that while compounds 8 and 9 are very flexible and can exist in different conformations of similar energy, for compound 11 only one ground-state energy minimum is found. Thus, the cyclohexyl substituents stabilize the conformation and make the molecule more rigid. All factors lead to enhanced photoluminescence in the solid state. The luminance of 10500 cd/m² reached with the device based on compound 11 is one of the highest values reported so far in the literature for devices with spin coated active layers. Recently, OLEDs using as emitting layers nicely engineered branched oligomers (compounds 12-13) containing a dibenzothiophene-S,S-dioxide core and triarylamine branches, have been reported (Huang et al., 2006). The thiophene-S,S-dioxide group was introduced for its beneficial effect on the electron affinity of the molecules, while the triaryl amino groups were introduced because of their beneficial effect on charge (holes) transport and film forming properties. The molecular structure of compounds 12 and 13 is reported in Scheme 6.



Scheme 6. Molecular structure of branched oligomers 12 and 13.

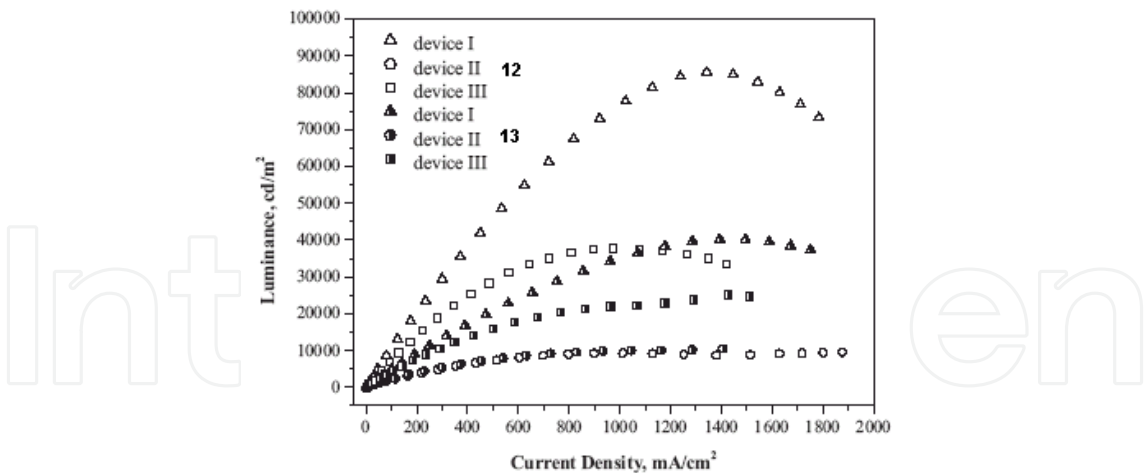


Fig. 5. Luminance versus current density characteristics for single layer devices of compounds 12 and 13. Structure of the devices: I) ITO/12 (or 13) (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al (150 nm); II) ITO/NPB (40 nm)/12 (or 13) (40 nm)/LiF (1 nm)/Al (150 nm); III) ITO/12 (or 13) (80 nm)/LiF (1 nm)/Al (150 nm).

Using compounds 12 and 13, excellent luminances were obtained with single layer (spin coated) devices, as shown in Figure 5. The optical characteristics of compounds 12-13 and the relevant parametrs of the devices based on these compounds are reported in Table 3.

	12	13
V_{on} [V]	2.5, 2.3, 2.2	2.2, 2.5, 2.0
L_{max} [cdm ⁻²]	85475 (12.5), 9537 (15.0)	40140 (13.0) 10521 (11.5)
(V at L_{max} , [V])	37699 (12.5)	25159 (14.5)
λ_{em} [nm]	492, 492, 496	540, 536, 542
$\eta_{ext,max}$ [%]	4.9, 1.3, 3.1	1.4, 0.87, 1.3
$\eta_{p,max}$ [lmW ⁻¹]	9.7, 3.3, 7.2	4.9, 3.3, 5.0
$\eta_{c,max}$ [cdA ⁻¹]	11, 3.1, 7.7	5.1, 3.1, 4.7
L [cd m ⁻²] ^[a]	10778, 2107, 7529	4904, 2272, 4245
η_{ext} [%] ^[a]	4.7, 0.94, 3.1	1.4, 0.65, 1.2
η_p [lmW ⁻¹] ^[a]	6.5, 1.3, 3.9	2.8, 1.7, 2.1
η_c [cdA ⁻¹] ^[a]	10.8, 2.1, 7.5	4.9, 2.3, 4.2

Table 3. Optical characteristics of compounds 12-13 and performance of the corresponding devices^a

a) V_{on} : turn-on voltage; L_{max} : maximum luminance; $\eta_{ext,max}$: maximum external quantum efficiency; η_p,max : maximum power efficiency; η_c,max : maximum current efficiency.

[a] Measured at a current density of 100 mA/cm². V_{on} was obtained from the x-intercept of a plot of log(luminance) vs applied voltage

A maximum luminance value of about 90000 cd/m² at 1300 mA/cm² was reached for 13 and of about 90000 cd/m² at a similar current density for 2. The good performance of the devices was likely to be related to a much better balance of electron- and hole-transport properties than that achieved with linear or V-shaped oligothiophene-S,S-dioxides.

These results underline the potential impact that molecules containing thiophene-S,S-dioxide moieties could have on light emitting devices if more sophisticated device structures were realized with these materials.

4. Oligothiophenes for white OLEDs applications

Application in displays is only one among the several possible technological developments of oligomeric thiophene materials. Another important application is in the lighting sector where the replacement of standard white sources with flat organic devices is currently a matter of intense research.

One of the first approaches to realize white OLEDs (WOLEDs) using thiophene materials consisted in exploiting the high electron affinity of 2,5-bis-trimethylsilyl-thiophene-1,1-dioxide (STO) used as acceptor to generate exciplex states in combination with a very low electron affinity material (triphenyldiamine, TPD) used as donor (Mazzeo et al., 2003 b). Figure 6 shows the molecular structure of both TPD and STO. While the electron affinity of TPD is around 2,3 eV, that of STO is around 3,0 eV, i.e. close to that of longer linear oligothiophene-S,S-dioxides. The reason for this is in the fact that the LUMO state of the longer compounds is almost entirely localized in the central oxidized ring (Della Sala et al., 2003; Anni et al., 2005). Once the exciton is formed on the TPD molecule, the electron can move to a near STO molecule, with higher electron affinity. In consequence, two radiative transitions become allowed, one from the TPD molecules and the other from the transition between the LUMO level of STO and the HOMO level of TPD. As a result, a peak at 420 nm and a band at 570 nm are obtained, the two transitions resulting in white emission.

In Figure 6, PL spectra and images of blended films with different relative donor/acceptor concentrations, spin-coated on quartz substrates, are reported. It is seen that enhancing the concentration of STO a broad red-shifted emission due to exciplex states appears, in addition to the blue emission due to TPD, which is responsible for the white emission within a concentration range 17-53% of STO in TPD. The normalized EL spectra were similar to the PL spectra for the concentration used (20%), showing that the shape of the low-energy exciplex spectrum is almost independent of the applied voltage. The CIE coordinates of the EL spectra indicated a balanced white emission (0.39, 0.40) (Mazzeo et al., 2003 b).

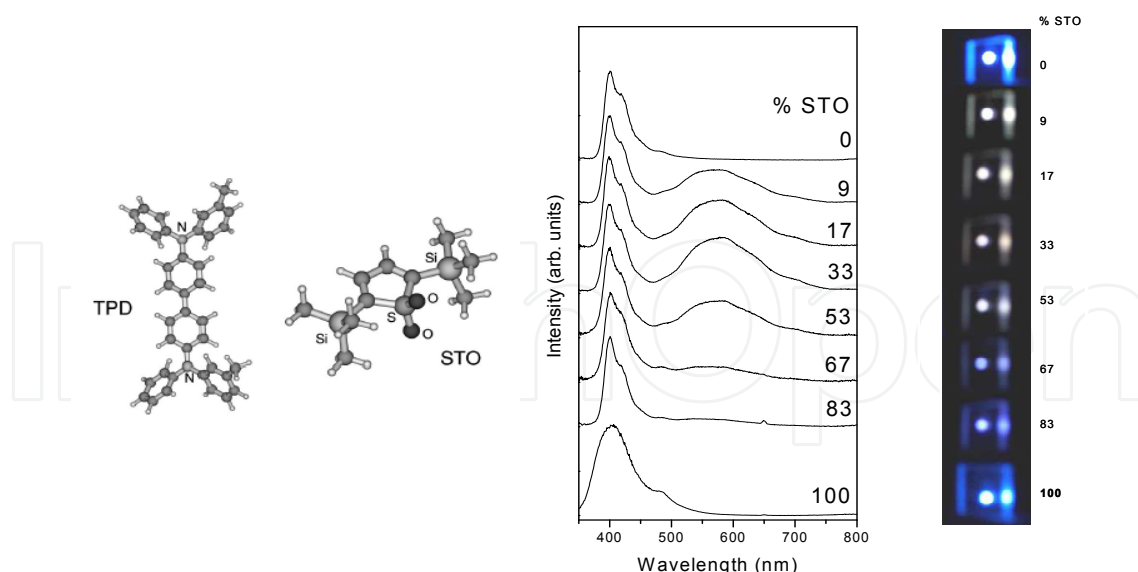


Fig. 6. Molecular structure of TPD and STO (left); PL spectra of the blends realized through TPD and STO (middle) and images of the blends in solid state films (right).

Although these results were promising for the generation of a new class of devices, their luminance was not very high. Much better results were obtained with a different approach, i.e. using a single thiophene material emitting in the white by virtue of its supramolecular organization (Mazzeo et al., 2005). The material in question is 3,5-dimethyl-2,6-bis(dimesitylboryl)-dithieno[3,2-b:2',3'-d]thiophene, whose molecular structure is reported in Figure 7.

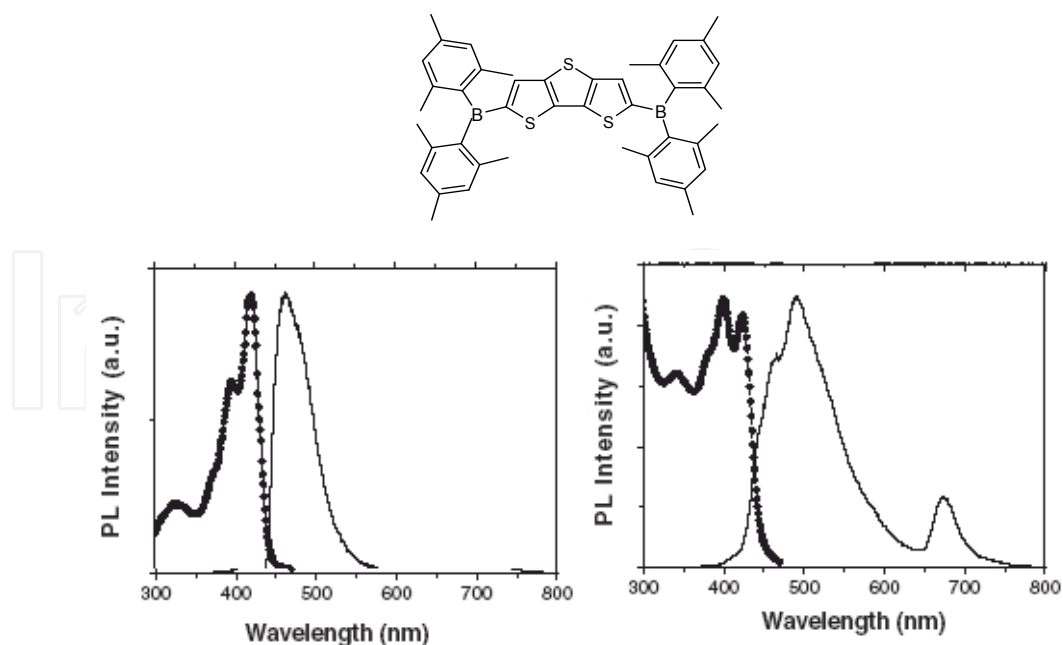


Fig. 7. Molecular structure of 3,5-dimethyl-2,6-bis(dimesitylboryl)-dithieno[3,2-b:2',3'-d]thiophene and PL spectrum in solution (left) and in the solid state (right).

Figure 7 shows that while in solution only a blue-green emission is observed, in the solid state an additional narrow red-shifted emission at 680 nm is also present in the PL spectrum. This red shifted absorption was peculiar to the solid state and could not be observed in solution in the concentration range 10^{-5} – 10^{-2} M. The appearance of similar red shifted absorption peaks had already been reported for several organic compounds and were assigned to triplets activated in the solid state or particular aggregation states (Lupton et al., 2003). By the aid of time-resolved photoluminescence (TR-PL) the red-shifted emission could be ascribed to the formation of aggregates or excimers. However, contrary to what it is generally observed with aggregates and excimers that are characterised by broad PL spectra (Lupton et al., 2003), the linewidth of the peak at 680 nm was narrow. In order to elucidate this point, INDO/SCI calculations were carried out. The calculations suggested that the narrow line was the result of the very peculiar supramolecular arrangement assumed by the compound in the aggregated state (Mazzeo et al., 2005). Indeed, due to the planar and rigid conformation of the inner dithienothiophene core and the presence of the bulky mesityl substituents, the molecules tend to fit together in a *cross-like* configuration as shown in Figure 8. Only very small movements of the molecules through translations along the x-y axis, or small angular (α) deviations are allowed.

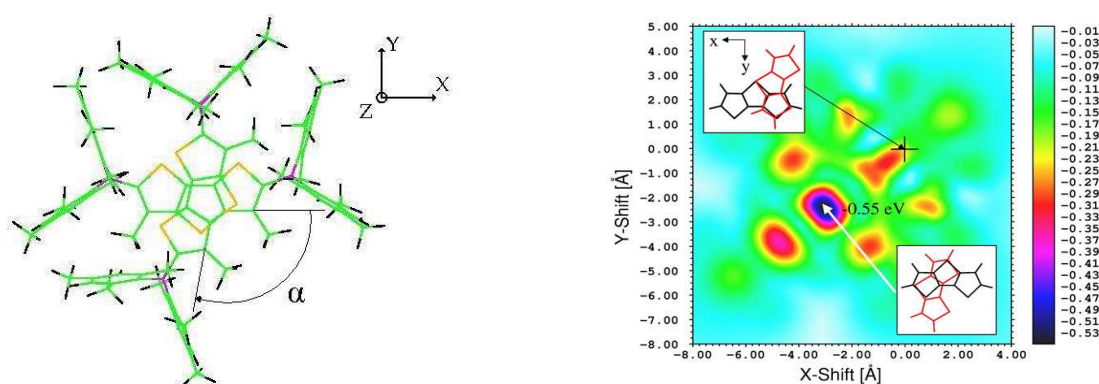


Fig. 8. Molecular structure of two interacting molecules forming a cross-like dimer (left) and (right) Intermediate neglect of differential overlap/single configuration interaction (INDO/SCI) excitation-energy shifts due to intermolecular interactions. The scale on the right corresponds to calculated excitation energy shifts.

Commonly observed *HB*-type dimeric aggregates (i.e. with $\alpha=180^\circ$) are completely forbidden for this rigid compound, due to the repulsion of the mesityl substituents. In such fixed *cross-like* configuration the peak broadening induced by supramolecular conformational dispersion is strongly reduced. The plot reported in Figure 8 shows that the excitation energy shift is indeed dominated by only one deep minimum. This means that only one single arrangement is responsible for the additional red emission observed in the solid state, leading to a very narrow emission. The calculations also showed that this kind of intermolecular arrangement induces a red-shift as high as 0.55 eV, a value which is in good agreement with the experimental result (0.7 eV).

The white emitting dithienothiophene derivative displayed good film forming properties and could be used as active material in light emitting diodes. The emissive layer was spin-coated between ITO/PEDOT:PSS and LiF/Al, used as anode and cathode, respectively. The

LiF layer was employed in order to enhance the carrier injection in the emissive layer (Hung et al., 1997). The EL spectrum at a LiF thickness of ≈ 5 nm and the device performance are shown in Figure 9.

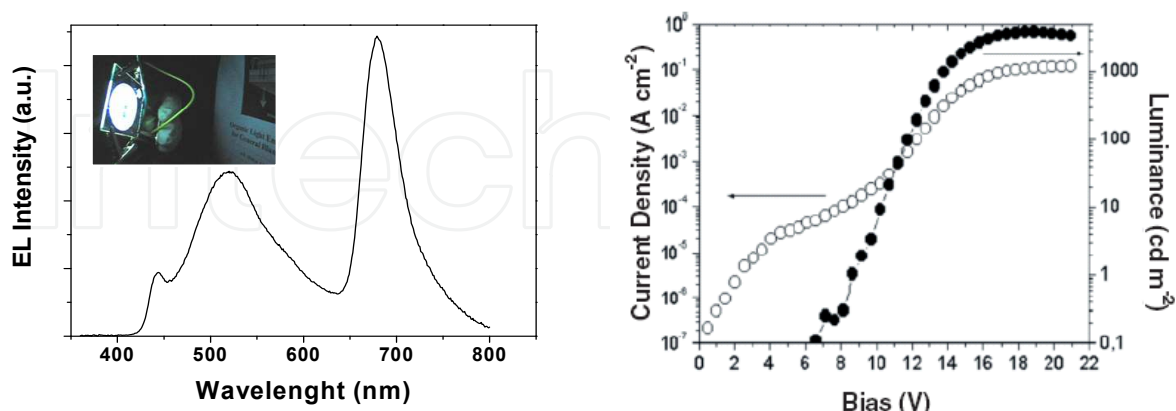


Fig. 9. EL spectrum of device with $d_{LiF} \approx 5$ nm (left) (inset: image of a large area device); Luminance-current density-voltage characteristics (right).

For 4.8 nm of LiF the performances are 50 times higher than the device in which only the Aluminium was used as cathode. In particular, a brightness of 3800 cd/m^2 at 18 V (Figure 9) and a maximum QE of 0.35% could be achieved. It is worth noting that the luminance of this device overcomes the minimum value of 1000 cd/m^2 required for lighting systems. The white electroluminescence was achieved by the superposition of the broad blue-green emission originating from the single molecule and the red-shifted narrow peak assigned to the formation of cross-like dimers in the solid-state. This was one of the first examples in the literature of white emission from a single molecular material in the solid state. The good performance of the device was due to an unusual mixing of favourable factors, i.e. the very peculiar self-organization properties of the dithienothiophene derivative, the well known electron-acceptor properties of the boron atom and the good film forming properties of the material. Nevertheless, the results obtained, indicate that the fabrication of a new class of white emitting devices combining the simplicity and low-cost of single layer spin-coated devices is achievable through appropriate molecular engineering.

5. Very low voltage and stable oligothiophene OLEDs.

As shown in the previous section, thiophene oligomeric materials have great potential for application in displays and lighting. All the devices described in the previous sections have been realized in a single-layer or bilayer configuration by depositing the active material by spin coating. This is a strong limitation for oligomeric materials since, even if the material is highly performant in terms of PL, the devices are not efficient enough due to the limits of wet deposition processes like spin coating. Polymeric materials have the same type of problems. However, while polymeric materials cannot be evaporated, this is possible for oligomeric materials owing to their small molecular weight. Thus, a possible improvement in OLEDs based on thiophene oligomeric materials can be realized if these compounds are deposited in a heterostructure system (Walzer et al., 2007; Zhou et al., 2001; Huang et al.,

2002). So far, no attempts have been made in this direction and the data shown below are the first reported to date.

We fabricated a much more sophisticated device using compound 3 (Mariano et al., 2009) and, to check the limit in brightness and stability of the compound, we realized an OLED based on electrically doped transport layers, i.e. in the so-called *p-i-n* (p-type-intrinsic-n-type) configuration (Walzer et al., 2007).

In order to obtain low driving voltages, low ohmic losses at the interface between the metal and the transport layers are an important factor. Organic light-emitting diodes are usually realized with un-doped thin organic films, requiring high operating voltages to overcome the energy barriers between the contacts and the transport layers and to drive the opposite charges into the emissive layer. Contrary to inorganic LEDs, the typical driving voltage is much higher than the thermodynamic limit, which is given by the energy gap of the active layer. Recently, controlled electrical doping in transport layers of the OLEDs has been introduced (Walzer et al., 2007; Zhou et al., 2001; Huang et al., 2002). The typical dopants explored have been the 2,3,5,6-tetrafluoro-7,7,8,8 tetracyanoquinodimethane (F4TCNQ) as donor of holes in an hole transport layer and alkali metals such as Cs or Li as donors of electrons in an electron transport layer. The doping of the transport layers leads to the formation of thin space charge layers which are formed at the interface with the metal contact layer, allowing for a good injection (ohmic) of the carriers by tunneling despite the barriers. This effect removes completely the energy barrier between the metal layers and the transport layers, thus reducing the voltage. Moreover, the high electrical conductivity of the doped layers reduces also the drop in voltage caused by the usually high resistance of the undoped organic films. The *p* and *n*-doping of the transporting layers permits to reach a conductivity of 10^{-5} S/cm, which is enough in order to have a negligible drop in the voltage across these layers. Due to the incorporation of these very conductive transporting layers, which form Ohmic contacts with the electrodes, *p-i-n* architectures supply more current density than conventional OLEDs, under the same driving voltage (Zhou et al., 2001; Huang et al., 2002). Therefore, higher brightness can be obtained at low bias.

This type of OLED has an electrically intrinsic emission layer (EML), a hole transport layer (HTL) and an electron transport layer (ETL). Additional blocking layers between the charge transport layers and the emissive layer are generally also introduced to prevent problems related to the lack of charge balance, exciton quenching by excess of charge carriers, and exciplexes formation at the interface. All these layers complicate the structure of the device but increase its efficiency and stability. The aim of *p-i-n* technology is to reduce the applied voltage in order to have a given luminance and improve power efficiency giving more stability to the device and less power consumption.

The structure of the device realized with the linear oligothiophene-S,S-dioxide 3 (whose molecular structure is shown in Scheme 4) is shown in Figure 10. It consists of the following layers: ITO transparent anode; a 35 nm thick layer of *N,N,N',N'* tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD) doped with 2.7 wt % of 2,3,5,6-tetrafluoro-7,7,8,8 tetracyanoquinodimethane (F4-TCNQ) that was evaporated as *p*-doped hole injection and transport layer; a 7 nm thick film of 2,2',7,7'-tetrakis-(diphenylamino)-9,9'-spirobifluorene (Spiro-TAD) which acts as electron blocking layer; an emitting layer consisting of 30 nm of compound 3 of Figure 5; 10 nm of 4,7-diphenyl-1,10-phenanthroline (Bphen) as hole blocking layer; 35 nm of Bphen doped with Cs as electrons injecting and transporting layer;

200 nm Al deposited as cathode. The optically thick metallic film acts as a reflector and thereby aids the output coupling of light from the device.

All films were deposited by thermal evaporation in a base pressure of about 10^{-8} mbar, at a rate in the range 0.5-1.0 Å/s. Before the deposition of the organic compounds, ITO substrates were cleaned in acetone, isopropanol and deionized water for 10 min at 60 °C in an ultrasonic bath. No plasma oxygen was performed because of the electrical doping of the transport layers.

Figure 10a shows the luminance and the current density of the device as a function of the voltage. The turn-on voltage was around 2.1 V, while the luminance reached the remarkable value of 11000 cd/m² at only 9 V. The device showed a maximum EQE of 0.55%. It is worth noting that the same material deposited by spincoating in a bilayer configuration shows a maximum luminance of about 400 cd/m² obtained at the very high voltage of 19 V (Table 1). This result obtained with the LED in *p-i-n* configuration underlines how all the properties of the device can be strongly improved thanks to the possibility of vacuum evaporating oligomeric materials.

The device reported in Figure 10 was encapsulated using a lid attached to the sample by an epoxy resin in order to carry out aging measurements and to check the stability of both the device and the material. We recall that the lifetime of OLEDs is defined as the time taken to reach half of the starting luminance.

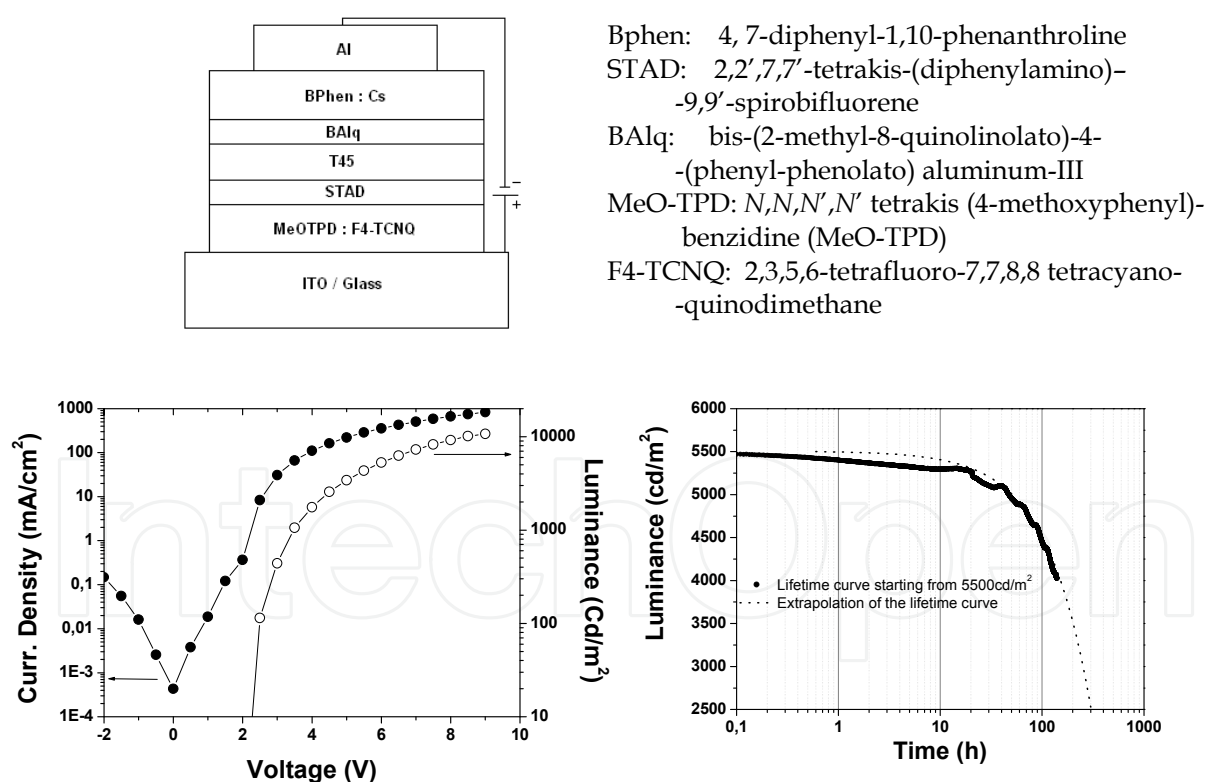


Fig. 10. Top: device structure. Bottom: (A) Luminance-Current Density vs. Voltage (left); Luminance decay time for a starting value of 5500Cd/m² at fixed current density (right).

Figure 10b shows the plot of the luminance as a function of time for a starting value of 5500 cd/m² at a fixed current density of 320 mA/cm². The black curve represents the experimental data while the dotted curve represents the extrapolated behavior. The figure

shows that a remarkable lifetime of about 270 hours was reached. This result demonstrates that heterostructure devices are the tools where thiophene oligomeric materials should be tested to reveal all their potential as emissive compounds. Moreover, the demonstration that oligothiophene-S,S-dioxides show very high stability is an important step forward that allows to classify these materials among the best so far available for electroluminescence (Mariano et al., 2009).

6. Conclusions and Outlook

Today, the field of electroluminescence of organic semiconductors is dominated by two kinds of materials: phosphorescent and fluorescent small molecules, in particular for applications where high emission power is needed, like lighting. Although phosphorescent compounds seem to be the most promising in terms of external quantum efficiency and low power consumption, fluorescent compounds show high stability and the possibility to be deposited avoiding codeposition with a host. This is particularly true for oligothiophenes which show high stability and the possibility to tune the emission wavelength in a very wide range, from green-bluish to near infrared without the need of coevaporation. The possibility to functionalize these compounds in a very flexible way and finely tailor their properties, make this class of molecules strongly competitive with respect to standard ones (also phosphorescent), although much research must still be carried out to further improve the stability and the efficiency of devices based on these materials. We are currently pushing up this research field trying to mix the best technology for OLEDs (*p-i-n* technology) with the best thiophene oligomeric materials with the aim to generate new kinds of electroluminescent devices for different purposes: from display to lighting and automotive.

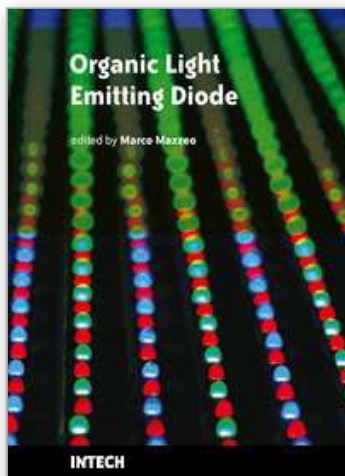
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Organic light emitting diodes (OLEDs) have attracted enormous attention in the recent years because of their potential for flat panel displays and solid state lighting. This potential lies in the amazing flexibility offered by the synthesis of new organic compounds and by low-cost fabrication techniques, making these devices very promising for the market. The idea that flexible devices will replace standard objects such as television screens and lighting sources opens, indeed, a new scenario, where the research is very exciting and multidisciplinary. The aim of the present book is to give a comprehensive and up-to-date collection of contributions from leading experts in OLEDs. The subjects cover fields ranging from molecular and nanomaterials, used to increase the efficiency of the devices, to new technological perspectives in the realization of structures for high contrast organic displays and low-cost organic white light sources. The volume therefore presents a wide survey on the status and relevant trends in OLEDs research, thus being of interest to anyone active in this field. In addition, the present volume could also be used as a state-of-the-art introduction for young scientists.

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