

Study of a thiophene-based polymer for optoelectronic applications

S. Cheylan^{a,*}, A. Fraleoni-Morgera^b, J. Puigdollers^c, C. Voz^c, L. Setti^b, R. Alcubilla^c,
G. Badenes^a, P. Costa-Bizzarri^b, M. Lanzi^b

^a ICFO, Institut de Ciències Fotòniques, Edificio NEXUS II, c. Jordi Girona 29, 08034 Barcelona, Spain

^b Department of Industrial and Materials Chemistry, University of Bologna, V. Risorgimento 4, 40136 Bologna, Italy

^c Departamento de Ingeniería Electrónica, Universidad Politécnica de Cataluña, UPC, Campus Nord Edifici C4, c/ Jordi Girona 1-3, 08034 Barcelona, Spain

Received 18 May 2005; received in revised form 14 September 2005; accepted 14 September 2005

Available online 21 October 2005

Abstract

A thiophene-based conjugated polymer bearing a cyano group (–CN) as a side chain substituent was successfully synthesized. The polymer evidences an excellent filmability from various organic solvents as well as an enhanced photoluminescence. The polymer has been characterized optically (Fourier Transformed Infrared spectroscopy, absorption and photoluminescence) in solution and in film, while X-ray diffraction measurements (XRD) of thin films were performed to investigate its bulk morphological features. From the absorption edge of the spectrum of a thin polymer film, the optical band gap of the polymer is estimated to be 2.0 eV, which corresponds to orange emission. Furthermore, a single layer light emitting diode (LED) was fabricated. The device produced bright stable electroluminescence at room temperature. All of the results indicate that this polymer is a promising emissive material for application in polymeric LEDs.

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Keywords: Electroluminescence; Conjugated polymer; Optical properties; Thiophenes

1. Introduction

Since the discovery of conductivity in polymers and certain organic molecules, remarkable progress has been made in synthesizing organic materials, in understanding their properties and in developing them for use in electronic and optical devices [1,2]. Currently, polymer and organic light-emitting diodes (LEDs) [3], photovoltaic cells [4] and field effect transistors [5] are being pushed towards commercialization.

So far, a wide range of conjugated polymer systems has been developed, such as poly(1,4-phenylenevinylene) (PPV) [6,7], poly(*p*-phenylene) (PPP) [8], polyfluorene (PF) [9] and polythiophene (PT) [10], and their derivatives. Among these, polythiophenes are being regarded as one of the most promising materials for practical applications because of their good thermal and chemical stability, as well as for the tunability of their electronic and optical properties [11–14]. Indeed, by attaching different functional groups as a side chain substituent and controlling their regioregularity, light emission

ranging from blue to near-infrared has been demonstrated [11,12]. Among the possible substituents attachable to the main polythiophenic chain, the cyano group (–CN) is very interesting, since it has been found that its presence in a conjugated polymer may be of help in enhancing the PL [15]. Also, it has been widely demonstrated that the presence of a cyano group may be very helpful for the tuning of the electronic properties of conjugated polymers, as in the case for example in CN-PPVs, or in CN-substituted polyfluorenes [16–18].

In this view, we present here a novel –CH₂CH₂OPhCN substituted thiophenic copolymer, poly{[3-hexylthiophene]-co-3-[2-(*p*-cyano-phenoxy)ethyl]thiophene} (in brief PTOPhCN), in an effort to develop efficient thiophene-based light-emitting polymers. The copolymer may be easily and cheaply prepared by oxidative polymerization and evidenced an excellent filmability from various organic solvents, exhibiting notable photoluminescence in solution and in solid, spin coated films. Finally, we present preliminary results on the electrical properties of this copolymer, which shows promise for its use in optoelectronic devices. Indeed, a single layer LED based on the polymer was fabricated, and showed bright and stable orange electroluminescence at high bias voltages.

* Corresponding author. Tel.: +34 93 413 7942; fax: +34 93 413 7943.

E-mail address: Stephanie.cheylan@icfo.es (S. Cheylan).

2. Experimental details

Poly {[3-hexylthiophene]-co-3-[2-(*p*-cyano-phenoxy)ethyl]thiophene} (PTOPhCN) was prepared as follows. Under a dry nitrogen atmosphere, 2.0 mmol of comonomers were placed in an oven dried, three-necked round flask, put under dry nitrogen flow and dissolved in 45 mL of CH₃NO₂, under stirring. Solid FeCl₃ (8 mmol) was then added to the system all at once by means of a navel. The reaction was allowed to proceed for 60'. After that, CCl₄ (180 mL) was added to the system, and the mixture was kept under stirring for an additional 190'. The reaction was hence quenched with a mixture of CH₃OH/HCl (5% in HCl). The solid copolymer was filtered off and washed with CH₃OH until no iron(III) was detectable by means of the NH₄SCN test, and washed again with distilled water until neutrality of the water was detected by means of pH indicator paper. It was then extracted with CH₃OH in a Soxhlet apparatus until the solvent was colorless and dried under vacuum to give the raw polymer. The raw material was extracted in a Soxhlet apparatus with CHCl₃ until the solvent was colorless. The recovered CHCl₃ solution was concentrated and dried under vacuum. A more exhaustive description of the synthetic procedure is given elsewhere [19]. The polymer molecular weight was 73.900, with a polydispersity index (Mw/Mn) of 3.75, upon Gel Permeation Chromatography (GPC) measurements in CHCl₃ based on commercial mono-dispersed polystyrenic standards. The amount of cyanophenoxy-substituted monomer in the copolymer is 47% in a molar ratio with 3-hexylthiophene, as calculated from Proton Nuclear Magnetic Resonance Spectroscopy (¹H NMR).

For the device fabrication, indium–tin–oxide (ITO) coated glass slides were used as substrates. The surface of the ITO was cleaned by using in sequence acetone, ethanol, methanol and de-ionized water in an ultrasonic bath for 10 min each, and then dried with high quality nitrogen gas. To finish, the slides were exposed for 10 min to an ozone UV lamp. The layer of PTOPhCN was spin coated from a chloroform solution at 20 mg/mL at 1500 rpm for 80 s. Finally, aluminium (Al) electrodes were thermally evaporated in a vacuum system on top of the organic layer, for a thickness of about 350 nm.

The current–voltage (*I*/*V*) characteristics were measured with a HP4156C Agilent Parameter Analyzer and were conducted in the dark and in vacuum. Photoluminescence (PL) measurements were carried out using an epifluorescence setup from an Olympus Microscope (model BX51M). Filters were used so as to select the 470–490 nm wavelength region of the spectra of a tungsten white light as the excitation source and so as to collect emission signal above 500 nm. The collection of the emission was done through an objective with 100× magnification, then into an optical fibre coupled to a HR2000 spectrophotometer from OCEAN OPTICS, integrated with a SONY ILXS11 linear CCD array detector, connected to a computer by a USB 2.0 port. Finally the structural characterisation was done by performing X-ray diffraction (XRD) measurements, using a Siemens D500 diffractometer in the Bragg–Brentano geometry. The standard method was θ/θ

scan. The radiation wavelength used is of the CuK α_1 line at 0.15406 nm.

3. Results and discussion

According to the ¹H NMR analysis, the amount of –OPhCN-substituted thiophenic unit in the copolymer is about 50% in a molar ratio, hence the cyano group exerts a considerable influence on the polymer properties. The hexylic side chains in the copolymer ensure a high processability from organic solvents, which is confirmed by the observed excellent filmability of PTOPhCN from a number of solvents, such as for example tetrahydrofuran (THF), CHCl₃, and chlorobenzene. Actually, free-standing films upon casting or spin-coating glass substrates from solution of concentrations ranging from 6 to 20 mg/mL were obtained. Such an enhanced processability may be ascribed also to the remarkable molecular weight (around 70.000 as Mw) and the large polydispersity (3.75) of the utilized PTOPhCN batch. Again ¹H NMR spectroscopy permitted to exclude a complete head-to-tail regioregularity, while the exact degree of head-to-tail couplings is yet to be determined due to experimental reasons. The Fourier Transformed Infrared spectroscopy (FT-IR) conducted on PTOPhCN, both in KBr pellets and in film (by Attenuated Total Reflection FT-IR) permitted to confirm that the polymer was completely de-doped at the moment of the optical and electronic measurements.

The presence of the cyanophenoxy functionality in the polymer is of particular interest in view of possible practical applications as optically emitting material, being known that the cyano group is beneficial for increasing the photoluminescence (PL) and electroluminescence (EL) yield in conjugated PPVs. Ramos et al. [15] have shown by calculations that the CN group permits an electron–hole recombination with lower electrical fields applied, and this effect was attributed to a modification of the polymer electronic levels, on the basis of the electron-withdrawing effect exerted by the cyano group on the conjugated backbone. It is then interesting to explore the effect of the cyano group when this latter is supposed to be electronically decoupled from the main conjugated chain, as is the case for PTOPhCN, which holds an ethylic spacer chain between the backbone and the –OPhCN functionality. Moreover, the polar donor/□-bridge/acceptor structure of the cyanophenoxy group may play some role in establishing built-in local electric fields in the bulk of optoelectronic devices, additionally facilitating the recombination of holes and electrons injected in the device. This latter possibility is presently object of further work and will not be discussed here.

Fig. 1 shows the absorption and photoluminescence spectra of PTOPhCN both in solution (curves a and b) and for a layer about 220 nm thick (curves c and d). The absorption and emission of the polymeric film evidence a red shift with respect to the solution, from 30 (for the absorption spectra) to 40 nm (for the emission spectra), indicating an increase of the conjugation length upon chain desolvation. This evidence may be attributed to an appreciable degree of self-organization

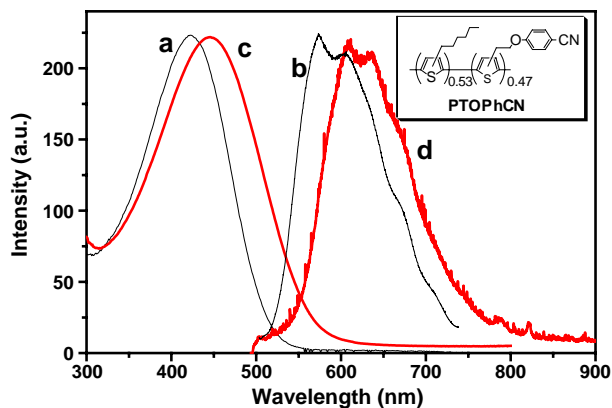


Fig. 1. Optical absorption and photoluminescence spectra of PTOPhCN in solution (respectively curves a and b), and from a 220 nm thin spin coated film (respectively curves c and d). Inset: structural formula of PTOPhCN.

experienced by the polymer in the solid state, although the PTOPhCN is far from being regioregular. From the absorption edge of the polymer in the solid phase, an optical band gap of 2.0 eV may be estimated, which corresponds to orange emission. In order to qualitatively evaluate the PL intensity of the PTOPhCN in film, an equally thick layer of 2-methoxy-5-(2-ethylhexyloxy)-*p*-phenylenevinylene (MEH-PPV) was prepared and measured. Upon this measurement, the thin 220 nm layer of PTOPhCN resulted to produce 50% less PL than the MEH-PPV one at room temperature.

The PL spectra for the polymer solution and the spin coated thin film, while being very similar in shape to each other, show evident structuration and differ markedly from the absorption ones, which are broad and miss any trace of sharp peaks and/or shoulders. In particular, for the thin film, two sharp peaks at 609 and 636 nm, with the presence of a bump around 665 nm, are visible, while for the solution PL spectrum these values are 575, 605 and 666 nm, respectively. Such a behaviour is well known and reported for a variety of thiophene-based emitting polymers [20], and is ascribed to the increased conjugation assumed upon photoexcitation by PTOPhCN, which, due to a more quinoid conformation of the polymer, originates a stiffening of the backbone that permits energy transfer to tail states, and consequent emission from the latter ones. However, eventual formation of excimers may in principle also account for such a behaviour, since these states are known to present a higher conjugation degree than the ground state single chromophores from which they are originating. Phenomena of this kind have been reported previously for cyano-substituted PPVs [21]. In fact the cyano group, being highly polar, is likely to produce strong interchain interactions, decreasing hence the intermolecular distance and favoring the possibility of formation of local aggregations of excited chromophores. More work is underway to elucidate this point. As a final observation on the absorption and emission properties of PTOPhCN, from Fig. 1 a large Stokes' shift of 0.75 eV between the PL and the absorption (in both solution and film) is evident, with a low self-absorption, which makes this material a promising candidate also for laser applications.

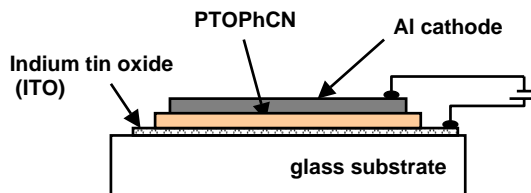


Fig. 2. Schematic of the single layer LED device: ITO/PTOPhCN/Al.

XRD measurements were conducted on a thin 300 nm layer of PTOPhCN spin coated on glass (not shown here), measured as-deposited. No sharp peaks due to the diffraction by a crystalline structure of the X-rays were present, leading to conclude that the PTOPhCN layer as deposited is amorphous.

Fig. 2 represents the schematic of a single layer LED structure. In this work, the organic active layer of PTOPhCN is sandwiched between two electrodes on a glass substrate. The bottom electrode is an ITO layer, which serves as the anode, and the top electrode is an Al layer, which is used as the cathode. In forward bias condition, the positive voltage was applied to the ITO layer with respect to the metal electrode. The current–voltage (I/V) characteristics obtained for our device correspond to a typical I/V characteristic from a single layer device and are shown in Fig. 3. Analysis of these curves in general reveals that various regimes can be discriminated, following the power law $I \sim V^{(m+1)}$ [22,23], namely the space charge limited current (SCLC) model. SCLC theory predicts the crossover from the Ohmic regime ($m=0$) at low voltages to the SCLC regime governed by a shallow-trap ($m=1$) and to a trap-filled regime ($m \gg 1$). For our case, it can be seen in Fig. 3b that the Ohmic regime is not visible, probably due to a low intrinsic conductivity of our polymer. We do observe a good fit of the curve to the shallow-trap SCLC model at low applied voltage with $m=1$. Then as the applied voltage increases, a gradual increase in current density can be seen and for this region, the fitting of the curve with the SCLC model gives $m=9$. The fact that the change in current density with voltage is gradual and not abrupt points to broad distribution of trap-level energies, which is what one would expect from a highly disordered system such as a polymer [23,24].

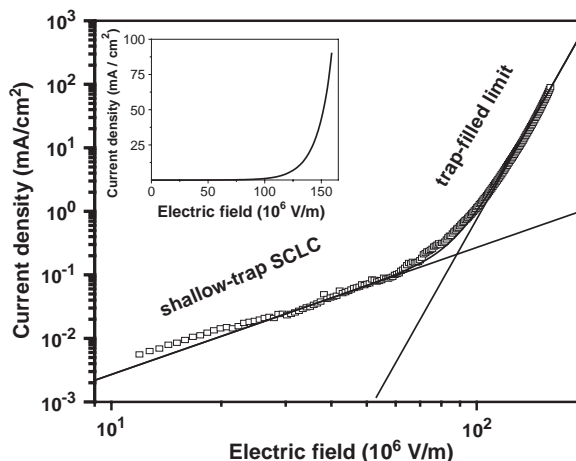


Fig. 3. I/V curves of the thiophene-based diode structure: ITO/PTOPhCN/Al, with a PTOPhCN layer of around 220 nm, fitted by the SCLC model.

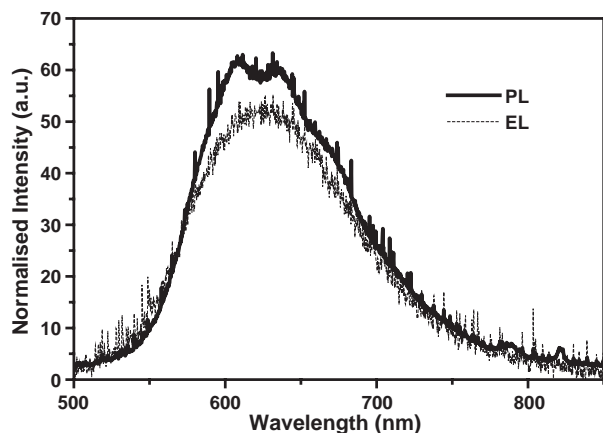


Fig. 4. Room temperature photoluminescence and electroluminescence of the thiophene-based diode structure: ITO/PTOPhCN/Al, with a PTOPhCN layer of around 220 nm. The electroluminescence was obtained for an applied bias of 28 V.

Bright orange electroluminescence was observed at room temperature in forward bias conditions with a turn on voltage of about 28 V, at a current density of 275 mA/cm². As usual, there is no light in reverse bias. Such LED structure is stable up to the maximum range of voltages studied here that is 40 V, still with visible emission, although at this voltage it evidences a fast spectral intensity decrease, pointing to polymer degradation. Optimum current densities of about 1250 mA/cm² were reached at 40 V. During the testing of other devices, the EL characteristics such as intensity and current densities were observed to increase as the thickness of the active layer of the device was lowered. More importantly, the high turn on voltage observed for our first device also showed an improvement upon using thinner active layer. These and other features of PTCN-based devices will be the subject of a separate publication.

As can be seen in Fig. 4, although the emission range of both EL and PL spectrum is overlapping, the shape of the spectrum differs. The EL spectrum does not show the peaks and shoulder structuration observed in the PL spectrum and consists in a plain broad spectrum centered around 627 nm. In general, the different spectral shape points to different exciton recombination mechanisms, but at this stage of investigation it is not possible to identify the reason for such a behaviour. More work is underway in order to clarify this point.

4. Conclusion

A new orange light emitting thiophene-based polymer (PTOPhCN) has been synthesized and characterized. The polymer is well processable from a number of solvents and may be easily synthesized. Emission centered around 590 nm has been observed for PTOPhCN in solution, while spin coated layers showed a red shift of the emission of about 35 nm with respect to the solution. A similar behaviour has been found for the optical absorption. From these last data, an optical energy bandgap of about 2.0 eV was deduced for the polymer in the

solid state. A successful electroluminescent device based on a single organic layer was achieved, which evidenced promising stability and appreciable emission intensity.

Although preliminary, these results are very interesting in view of the potential applications of thiophene-based polymers in the realization of single layer organic devices and even more complex device structures. As an outlook, the main goal now is to optimize the polymeric material itself (i.e. charge affinity, transition temperature, solubility and processability, etc.) and the device fabrication conditions. Such work is actually in progress and will be reported shortly. We believe that PTOPhCN presented here demonstrates promising qualities for future use in organic LED applications.

Acknowledgements

S. Cheylan acknowledges support from the Spanish Government from the Ramon y Cajal program.

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