

Comprehensive study of a novel thiophene-based polymer

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ABSTRACT

We report here on the results of the characterization of a novel –OPhCN substituted thiophenic monomer, and of the obtained copolymers between the latter and the plastifying comonomer 3-hexylthiophene. The polymer evidences an excellent filmability from various organic solvents as well as an enhanced photoluminescence. The characteristics of the polymer were characterized by FTIR and XRD as well as photoluminescence. A bandgap of 2.0eV was obtained which corresponds to orange emission. Furthermore, a single layer organic device was fabricated and resulted in bright stable electroluminescence at room temperature. All of the results indicate that this polymer is a promising emissive material for application in light-emitting devices (LEDs).

Keywords: polymer, thiophene, cyano group, optical, electrical, LED

1. INTRODUCTION

Conjugated polymers have received a great deal of attention in the last decade or so due to their potential for applications in optoelectronic devices. Currently, polymer and organic light-emitting diodes (LEDs) [1], photovoltaic cells [2] and field effect transistor [3] are being pushed towards commercialization. So far, a wide range of conjugated polymer systems have been developed, such as poly(1,4-phenylenevinylene) (PPV) [4,5], poly(p-phenylene) (PPP) [6], polyfluorene (PF) [7] and polythiophenes (PT) [8], and their derivatives. Among them, polythiophenes are being regarded as one of the most promising materials because of their good thermal and chemical stability, as well as for their electronic and optical properties, such as for example enhanced luminosity and very pure colours [9-12]. Moreover, it is possible to modify their main characteristics by the introduction of a functional group as a side chain substituent. 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 [9,10]. Among the possible substituents attachable to the main polythiophenic chain, the cyano group (-CN) is very interesting, since it has been demonstrated that its presence in a conjugated polymer may be of help in enhancing the PL [13]. 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 [14,15]. In these cases, however, the cyano group is grafted directly to the main backbone, contributing to increase the electron affinity of the polymer, hence to vary the band gap and the valence and conduction band edges level through electronic effect. Moreover, the cyano group is quite bulky, and the direct grafting on the main chain influences the polymer properties also in terms of steric hindrance. It is then interesting to explore the effect of the cyano group on the properties of conjugated polymers when the former is not directly grafted to the main chain.

In this view, we present here a novel *n*-ethylPhCN substituted thiophenic copolymer, poly{[3-hexylthiophene]-co-3-[2-(*p*-cyano-phenoxy)]thiophene} (in brief PTCN), in an effort to developing highly efficient thiophene-based light-emitting polymers. The copolymer may be easily and cheaply prepared by oxidative polymerization [16], and evidence an excellent filmability from various organic solvents, exhibiting notable photoluminescence in solution and in solid, spin-coated films. As a final point, a single layer LED based on the polymer was fabricated. Such device exhibited a diode behaviour working in forward bias. But most importantly, such simple device showed bright and stable orange electroluminescence at remarkably high bias voltages.

2. METHODOLOGY

Poly{[3-hexylthiophene]-co-3-[2-(*p*-cyano-phenoxy)]thiophene} (PTCN) 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 [18]. The polymer molecular weight was 73.900, with a polydispersity index (M_w/M_n) of 3.75, upon GPC measurements in CHCl₃ based on commercial monodispersed polystyrenic standards. The amount of cyanophenoxy-substituted monomer in the copolymer is 47% in a molar ratio with 3-hexylthiophene, as calculated from ¹HNMR.

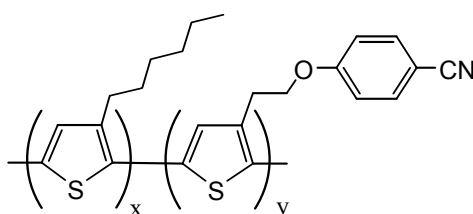


Figure 1: Chemical structure of poly{[3-hexylthiophene]-co-3-[2-(*p*-cyano-phenoxy)]thiophene} or PTCN.

For the device fabrication, indium-tin-oxide (ITO) glasses 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 mins each, and then dried with high quality nitrogen gas. To finish, the wafers were exposed during 10 mins to an ozone lamp. The layer of PTCN was spin coated from a chloroform solution at 20mg/mL at 1500 rpm for 80s. Finally, Al electrodes were thermally evaporated in a vacuum system at a deposition rate of about 1Å/s, on top of the organic layer. The thickness of such electrodes is about 350nm.

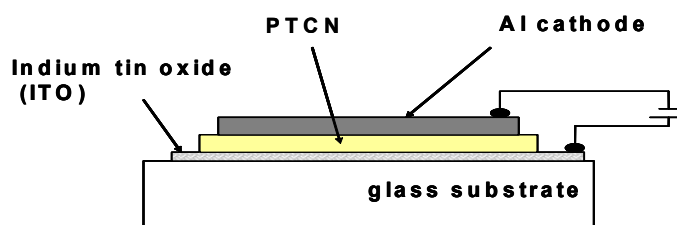


Figure 2: Schematic of a single organic layer LED device based on a PTCN layer of about 250nm thick. The device layout is ITO/PTCN/Al.

The current-voltage (I/V) characteristics were measured with an 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 500nm. The collection of the emission was done through an objective with 100X magnification, then into an optical fiber coupled to a spectrometer (OCEAN OPTICS) onto a CCD camera, connected to a computer.

3. DATA

According to the ^1H NMR analysis, the amount of $-\text{OPhCN}$ -substituted thiophenic unit in the copolymer is about the 50% in a molar ratio, hence the cyano group exerts a considerable influence on the polymer properties. The hexylic side chains in the copolymer ensures a high processability from organic solvents, which is confirmed by the observed excellent filmability of PTCN from a number of solvents, such as for example THF, CHCl_3 , and chlorobenzene. Actually, free-standing films upon casting or spin-coating glass substrates from solution of concentrations ranging from 6 to 20 mg/mL W/W 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 PTCN 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 [19]. The FT-IR characterization conducted on PTCN, both in KBr pellets and in film (by ATR FT-IR) permitted to confirm that the polymer was completely dedoped at the moment of the optical and electronic measurements.

XRD measurements were conducted on a thin 300 nm layer of PTCN deposited on glass (fig. 4). No sharp peaks due to the diffraction by a crystalline structure of the Xrays were present, leading to conclude that the PTCN layer is amorphous.

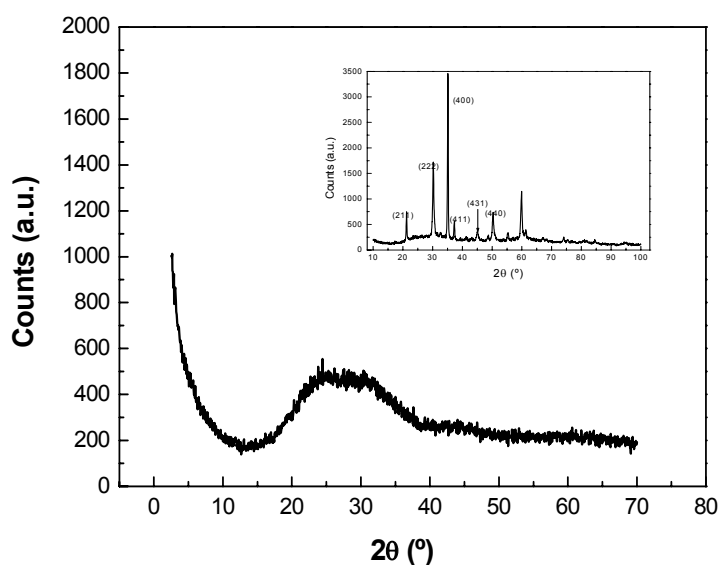


Figure 3: XRD measurements of a 300nm layer of PTCN. The broad peak observed is an artifact of the experiment. The inset is the XRD measurements conducted on the ITO substrate to show the typical peaks observed for an ITO crystalline structure.

Fig. 4 shows the absorption and photoluminescence spectra of PTCN both in solution (curves a and b) and for a layer about 250 nm thick (curves c and d). The absorption of the polymeric film evidences a marked red shift with respect to the solution, indicating an increase of the conjugation length upon chain desolvation, which could be attributed to an appreciable degree of self-organization experienced by the polymer in the solid state, although the PTCN is far from being regioregular.

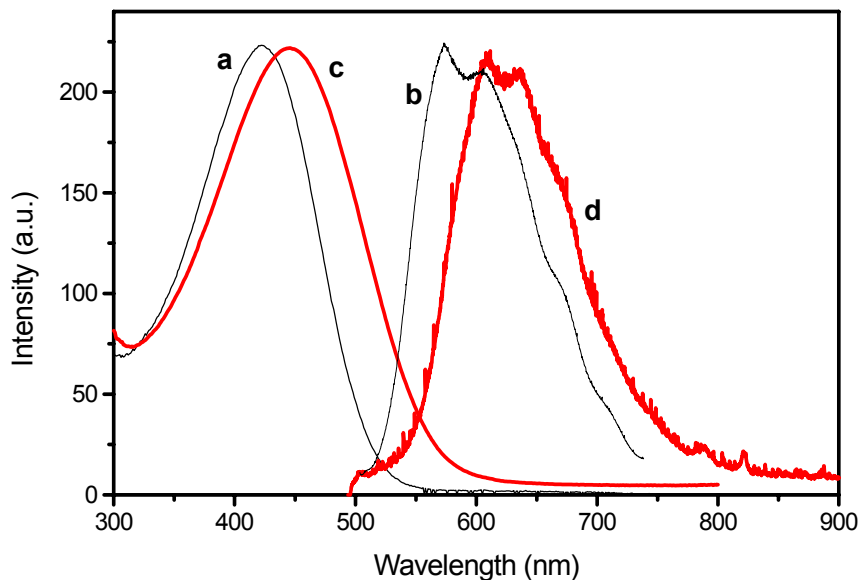


Figure 3: Optical absorption and emission characteristics of PTCN: absorption and photoluminescence in solution (respectively curves a and b), and from a 250nm thin spin coated film (respectively curves c and d).

The photoluminescence spectra for the polymer solution and the spin coated thin film are very similar to each other, although a clear PL redshift of about 40nm can be observed, passing from the solution to the solid state. The absorption edge of the sample in film is at 2eV and corresponds to orange emission. The photoluminescence shows two sharp peaks at 600 nm and 650 nm with the presence of a bump around 670 nm.

The current-voltage (I/V) characteristics obtained for the device based on PTCN as described in Fig 2 is shown in Fig. 5. The graph in fig. 5a shows a typical I/V while the graph in fig 5b shows the analysis of the I/V curve being plotted as a log-log. Current densities of the order of 300 mA/cm² were typically reached for our single layer device at room temperature at 40V (see Fig. 4).

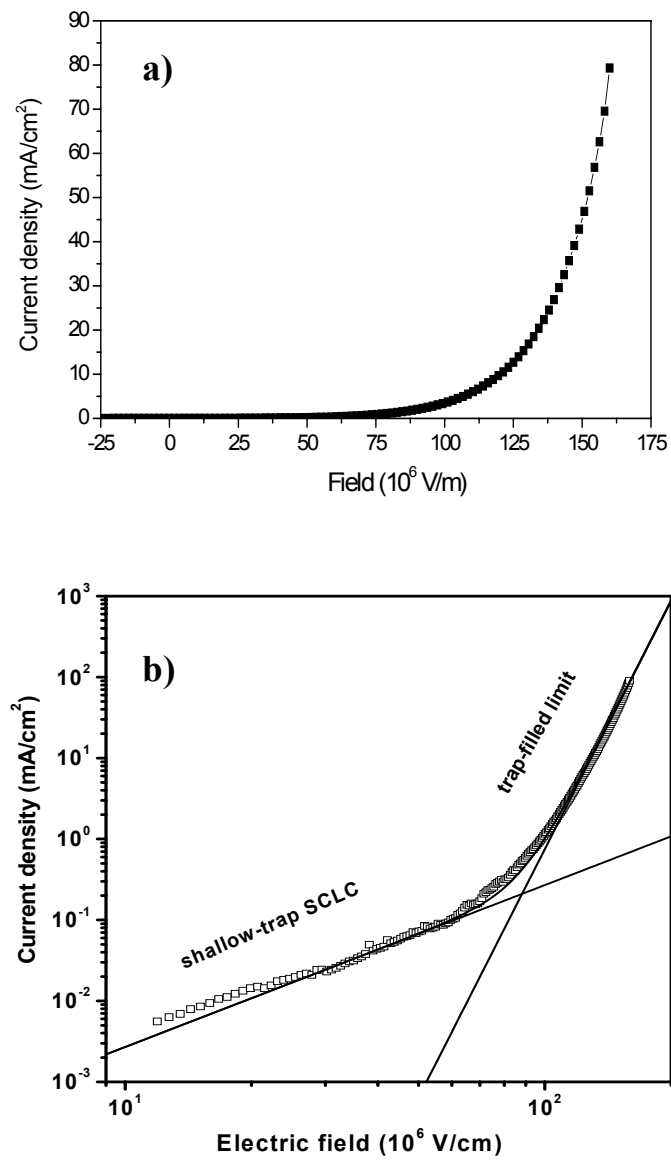


Figure 5: I/V curves of the thiophene-based diode structure: ITO / PTCN / Al. a) Normal plot and b) with log-log plot. The layer of PTCN is around 250 nm.

Bright orange electroluminescence was observed at room temperature for bias voltages above the threshold voltage of 24V. Such LED structure is stable up to the maximum range of voltages studied here, that is 40V (as can be seen in the I/V curve in Fig. 5a). The reason for such interesting characteristic is not known for the moment.

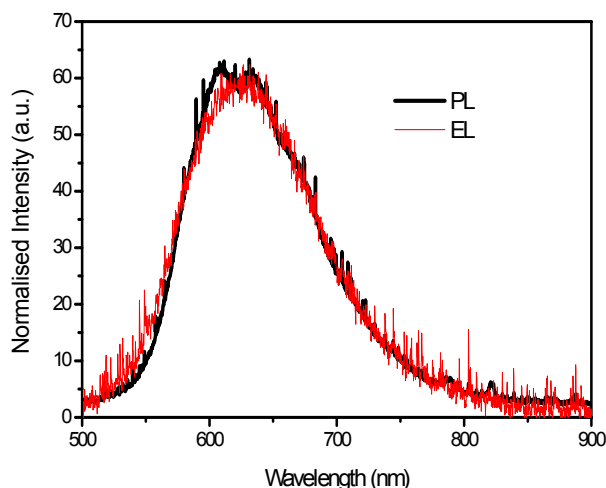


Figure 6: Photoluminescence and Electroluminescence spectra from a device of ITO/PTCN/Al. The Electroluminescence spectrum was taken at 24V at room temperature.

4. DISCUSSION

The presence of the cyanophenoxy functionality in the polymer is of particular interest in view of possible practical applications as optically emitting material. In fact the cyano group is known to enhance the recombination rate of electrons and holes, thus enhancing the PL and EL yield in conjugated PPVs. M. M. D. Ramosa *et al* [15] have demonstrated by calculation that the CN group permits an electron-hole recombination with lower electrical fields applied. Moreover, the polar donor/ π -bridge/acceptor structure $-\text{OPhCN}$ 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 possibility is presently object of further work and that will not be discussed here.

As mentioned previously, the photoluminescence shows two sharp peaks at 600 nm and 650 nm with the presence of a bump around 670 nm. The characteristic structures seen in the PL spectrum are usually associated with vibrational modes of the thiophene backbone, pointing to a good degree of order of the PTCN chains [20]. In order to evaluate the PL intensity of the PTCN, an equally thick layer of MEHPPV was prepared and measured. Upon this measurement, the thin 250 nm layer of PTCN resulted to produce 50% less PL than the MEHPPV one. In Figure 1 it is also possible to verify a large Stokes' shift of 0.69 eV between the PL and the Absorption, evidencing hence a very low self-absorption, which makes this material a promising candidate also for laser applications.

Analysis of the I/V curves reveals that two different regimes can be discriminated, following the power law given in equation 1, namely the space charge limited current (SCLC) [21]:

$$I \sim V^{(m+1)} \quad (1)$$

At low voltages, the density of injected carriers is low. The conductance is due to the polymer's own carriers and it is given by the ohmic law ($m=0$), where the current depends linearly on the bias voltage. Increasing the voltage causes additional injection of charge carriers into the polymer from the electrodes. Only a fraction of the injected carriers participate in the conductance, the rest being trapped. This is illustrated by a square law region ($m=1$) in the I/V characteristic. The fact that the change in current density with voltage is gradual and not abrupt points to a distribution of trap-level energies, which is what one would expect from a highly disordered system such as a polymer [22].

Current densities of the order of 300 mA/cm² were reached at room temperature at 40V (see Fig. 5). Fig. 6 shows the two spectrum of EL and PL being normalized. As can be seen the EL spectrum and the PL one are very similar. This feature indicates that the exciton recombination mechanism is the same for both processes. During the testing of other devices, the EL efficiency was found to be dependent on the current and the film thickness. As the film thickness decreases, the current densities achieved are higher. This preliminary observation leads to believe that the efficiency of such a device will be limited by the bulk properties of the material itself. Indeed, if the current densities increase with thinner layers, therefore the limiting factor for the mechanism is not the charges injection but the charge transport throughout the layer. These and other features of PTCN-based devices will be the subject of a separate publication.

5. CONCLUSION

A new orange light emitting thiophene-based polymer (PTCN) has been synthesized and characterized. The polymer is well processable from a number of solvents and may be easily synthesized. We have presented preliminary results of studies on the substitution of a –CN group in the main chain of the thiophene-based polymer and its effects upon its optical and electrical properties. Emission around 650 nm has been observed for such modified polymer in solution, as well as for spin coated layers, and an energy bandgap of about 2eV was deduced from the absorption data. A successful electroluminescent device based on a single organic layer was achieved, and work is in progress for a quantitative evaluation of its efficiency.

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. In particular, we believe that PTCN, as it is or with properly designed structural modifications, is a good candidate for organic LED applications.

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 the –OPhCN substituted thiophenic monomer presented here demonstrates promising qualities for future use in organic LED applications.

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