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A new soluble poly(bithiophene)-co-3,4-di(methoxycarbonyl)methyl thiophene for LED

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Abstract

The regioregular polyalkylthiophene reported in this contribution has been electrochemically synthesised starting from a 3,4-bis-methoxyacetyl-terthiophene and carefully characterised. Photoluminescence analysis gave, both in solution and in films, very appreciable quantum yield values and LED devices realised with Ca cathode provided a value of red electroluminescence comparable with those of regioregular poly(3-alkylthiophene)s in the monolayer active material architecture, while if a blend with poly-*N*-vinylcarbazole and 2-(4-t-butyl-phenyl)-5-(4-biphenyl)-1,3,4-oxadiazole constitutes the active layer a white emission is observed.

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1. Introduction

The easy of synthesis of a large variety of functionalized polythiophenes, particularly with an heteroatom in side chains, has offered the possibility to engineer intelligent properties in conjugated polymers. Specifically, the use of carboxylate derivatives should allow the change of substitution after polymerisation: Bäuerle proposed the use of *N*-hydroxysuccinimide ester function as an easily replaceable leaving group for the preparation under mild conditions of polythiophenes having all types of amines in the side chains [1], for example lysine to fabricate amperometric biosensors [2]. Another possibility is the hydrolysis of the carboxylate group in order to generate a self-assembled conducting polymer aggregate [3].

In this view it seemed to us useful to polymerize a thiophene, easy to prepare, with two esteric

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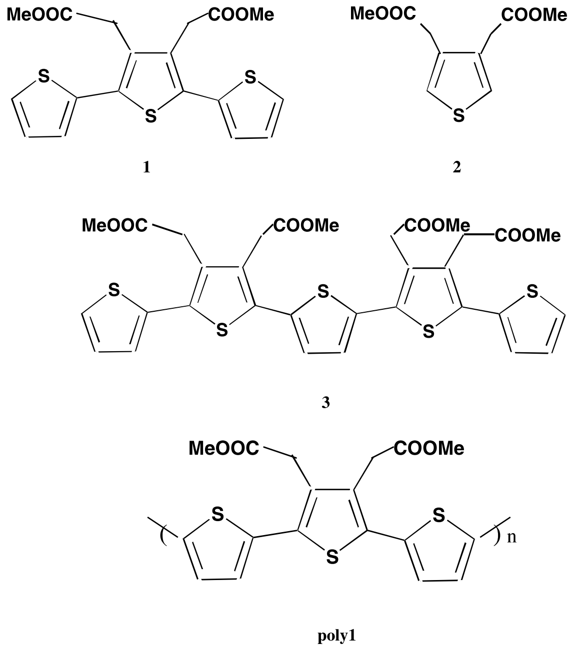
functions in the side chains and try to employ it in LED fabrication. The best results, in this regard, have been reached using regioregular polymers, particularly head-to-head/tail-to-tail [4], as active layer. The preparation of regioregular ester of any type is usually achieved by means of chemical routes using McCullough modification to Stille reaction [3], starting from an oxazoline precursor monomer. An excellent way to prepare poly(alkylthiophene-3-carboxylates) using the Ullmann coupling reaction was reported by Pomerantz who improved the molecular weight and polydispersity of the materials employing Rieke nickel or copper instead of Ni(0) catalyst [5,6]. As reported earlier for Ullmann couplings the materials were regio-random but showed efficiencies of 0.018%, which were much better than those reported for irregular poly(3-alkylthiophenes) (5×10^{-5}%) and even for regioregular head-to-tail polymers (1×10^{-4}%) [7].

Irregular polyalkylthiophenes bearing carboxylic groups have been prepared electrochemically [8]. In these thiophene derivatives the heterocycle is attached to the acylic segment, through an oligomethylenic spacer, varying from 4 to 10 units; contrariwise the moiety carrying on the thiophenic ring should be the alcohol which will give rise to the ester function. Irregular ester-functionalized polyalkylthiophenes of the latter type have been obtained both via electrochemistry [9] and by using $FeCl_3$ as catalyst; here the regioregularity of the polymer is governed by the length of the oligomethylenic spacer between the ester group and the thiophene ring [10].

In this contribution, we report on a polyalkylthiophene 3,4-dimethoxyacetyl substituted on every third ring, electrochemically synthesised. Because of the impossibility of polymerising the disubstituted monomer in an electrochemical way, we started from a terthiophene (**1**) (see Scheme 1) bearing substitutions on the central ring only, thus preparing a regular copolymer constituted by alternated 3,4-bis[(methoxycarbonyl)methyl]thiophene (**2**) and bithiophene units. Finally we report on the studies of this polymer including photoluminescence and electroluminescence results of LED displays prepared with this material used as monolayer, multilayers, and blends.



Scheme 1.

2. Results and discussion

2.1. Synthesis and characterisation

Tentative electropolymerisation of **2** failed as well as the chemical polymerisation using $FeCl_3$ also employing a modified procedure suggested by Costa Bizzarri et al. [10], the latter method producing a cross-linked material only. As a matter of fact, the cyclic voltammogram of monomer **2** in $CH_3CN + 0.1$ M Bu_4NClO_4 shows a two electron irreversible oxidation process at a peak potential E_p of 1.7 V. Polymer is not produced even in highly concentrated solutions (0.5 M), because this high potential value causes nucleophilic attack to the oxidised monomer by water content of the medium. The oxidation potential of **2** is higher than those of monosubstituted 3-(ω-carboxyalkyl)thiophenes which vary only sparingly depending on the methylenic spacer length [8]. In contrast to **2** all these thiophenes undergo electroxidative polymerisation. Hence to take advantage of the lower oxidation potential of oligomers, we have prepared 3′,4′-bis[(methoxycarbonyl)methyl]-2,2′:5′,2″-

terthiophene (**1**) using Stille coupling between 2-(tributylstannyl) thiophene and **2** which was for this purpose brominated at 2 and 5 positions using bromine in glacial acetic acid [11]. Following a similar procedure, through two subsequent Stille reactions, quinquithiophene **3** (see Scheme 1) was also prepared. The former Stille reaction takes place between a monobromo derivative of **2** and 2,5-bis(tributylstannyl)thiophene, while the latter occurs between the dibrominated tetrasubstituted terthiophene resulting from the former reaction and 2-(tributylstannyl)thiophene [11].

The cyclovoltammetrical response of **3** shows an irreversible oxidation process at $E_p = 0.75$ V with n_{app} higher than two. Potential cycling beyond this value produces a fast built-up of a polymer as a brittle film which tends to detach from the electrode. The electrochemical characterisation of this polymer reveals a twin reversible oxidation process at $E^0 = 0.30$ and 0.65 V and a reversible reduction process at $E^0 = -2.2$ V, hence an energy gap of 2.5 eV was calculated to be compared with the optical one (2.75 eV) derived from absorption spectrum maximum. Polymer films show the usual electrochromic behaviour being orange in neutral form and blue in the oxidised one. The neutral polymer is completely soluble in chlorinated solvents as chloroform ($CHCl_3$) and tetrachloroethane (TCE) and partially in THF. $CHCl_3$ solution of the material shows a solvatochromic shift in the absorption spectra, the maximum being centred at 3.03 eV. MALDI mass spectroscopy shows a wide distribution of oligomers up to dodecamer with a maximum peak of the tetramer (20 thiophene rings).

Similarly, the electropolymerisation of **1** was performed in acetonitrile by potential cycling beyond $E_p = 0.85$ V, above this value the irreversible oxidative coupling process takes place. The polymerisation was ended before full consumption of monomer in order to avoid cross-links formation. The polymer was wholly obtained in the neutral state by reducing the oxidised deposit at the electrode and completing the dedoping process with hydrazine, followed by washing with CH_3CN and drying.

The material hereafter indicated as **poly1** is completely soluble in hot $CHCl_3$ and in TCE. GPC measurements performed on the THF soluble part of the sample, show a distribution of oligomers centred on the heptamer, while NMR analysis fully accounts for a polymer of this molecular weight, because an amount of terminal thiophene protons was detected corresponding to 14%, i.e., 1/7. MALDI mass spectroscopy is in agreement with this picture, in fact low molecular weight oligomers, particularly these with DP three and four prevail, although a very large distribution up to 24 is present.

Moreover ^1H and ^{13}C-NMR spectra indicate an alternated copolymer structure. Two quasi overlapped doublets centred at 7.12 and 7.15 ppm due to thiophenic protons and two singlets at 3.8 and 3.7 ppm attributable to methylene and carboxymethyl protons respectively are present in the ^1H spectrum, while the ^{13}C spectrum shows the six expected signals in the aromatic range 136–122 ppm and the carboxy, methylene and methyl carbon signals at 170.5, 50.5 and 31.7 ppm, respectively. **Poly1** as a film shows a twin reversible oxidation process at $E^0 = 0.40$ and 0.65 V and a reversible reduction at $E^0 = -2.05$ V (see Fig. 1).

As reported in the literature [12], from the potentials E^0_{ox} and E^0_{red}, the ionisation potential (IP) and the electronic affinity (EA) can be estimated: $IP = E_{ox} + 4.4 = 4.8$ eV and $EA = E_{red} + 4.4 = 2.35$ eV, and the E_g value of 2.45 eV to be compared with the optical one (2.33 eV) as derived from absorption spectra maximum of spin coated films. In Fig. 2 both the absorption and emission

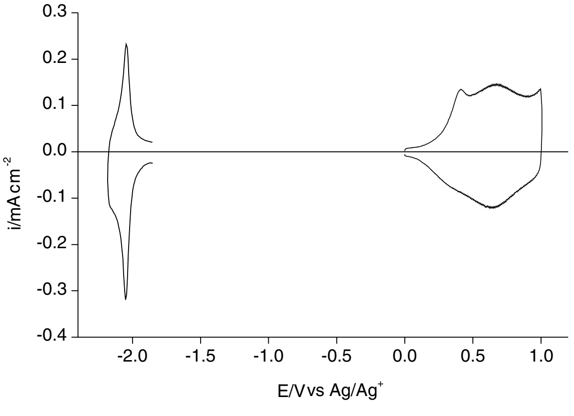


Fig. 1. Cyclic voltammogram of **poly1** in acetonitrile + 0.1 M Bu_4NClO_4 with Ag/Ag$^+$ electrodes. Scan rate: 0.1 V s^{-1}.

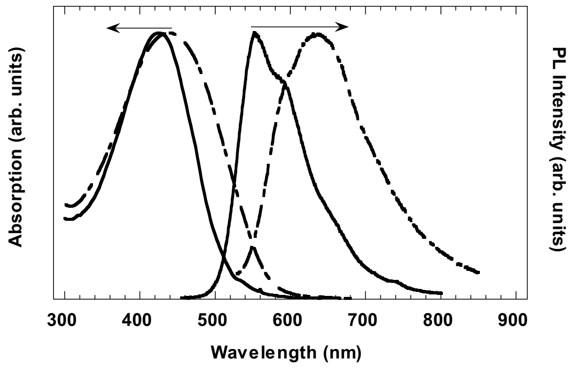


Fig. 2. Solution (——) and film (– – –) absorption and emission of **poly1**.

spectra of **poly1** $CHCl_3$ solution and thin films are presented.

In comparison with similar poly(alkylthiophene 3-carboxylates) [5], the absorption spectra of this polymer show a maximum at similar wavelengths, while the emission spectrum in solid state red-shifts. There is also a noticeable blue-shift of **poly1** as compared with both head to tail polythiophenes [4] and poly(3ω-carboxyalkyl)thiophenes whose regiotacticity was not determined [8]. Moreover the absorption maximum of **poly1** in solution is quite similar to that observed in head to tail poly(alkylthiophene 3-carboxylates) spectra, when bulky Bu_4N^+ cations are incorporated hampering or breaking up aggregational self-assembly [3]. These findings are in agreement with a largely polydispersed material where the order is prevented by the presence of several oligomers of different length. As a matter of fact, through polar interactions among carboxylate groups, monodisperse oligomers can orderly aggregate [13]. PL determinations carried out in $CHCl_3$ solutions supply a quantum yield of 49%.

2.2. OLED

The electroluminescent devices were prepared by spin-coating the **poly1** solution in $CHCl_3$-TCE onto indium–tin-oxide (ITO) glass coated substrates using either Al or Ca coated by Al as the cathode. Such LEDs show electroluminescence spectra as reported in Fig. 3 together with the corresponding *I–V* and EL–*V* curves related to the Ca cathode. The turn on voltage, defined as the applied voltage at which the current reaches the value of 1 mA/cm^2, is relatively small 4V and the external efficiency measured is too low (<10^{-3}%) using Al cathode; while when Ca is used, a decade is gained. The forward light emitted was measured by a photodiode of 100 mm^2 area at a distance of 7 mm from devices of 12 mm^2 area.

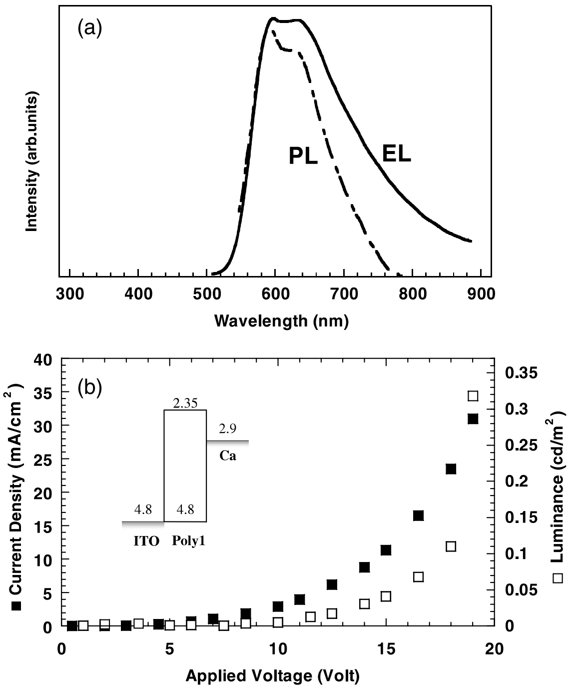


Fig. 3. PL–EL spectra of **poly1** (left-side) and corresponding *I–V* and EL–*V* curves (right-side), current (full squares), luminance (white square).

Bright red EL emission is detected (CIE (1931) chromaticity coordinates (0.575; 0.421) and a purity of 0.994) at the same wavelength of PL implying that the excited state responsible for light generation in the LED is the same as produced by photoexcitation. The external quantum efficiency η_{EL} of the device (>10^{-3}%, Ca cathode) is comparable to that found for other PT, but lower than that observed by Pomerantz for poly(3-alkyloxycarbonylthiophenes) using Al as cathode [5]. On the contrary, PL measurements carried out on fractions extracted with $CHCl_3$ and TCE reveal a decreased emission of about the same intensity for both the fractions with the respect to native polymer. Unexpectedly, solid state PL quantum yield of native sample is rather low (~1%), possibly due to some tendency to local crystallisation. Correspondingly in XRD experiments performed on native material, TCE, and $CHCl_3$ polymeric fractions, a progressive ordering from a fully amorphous (for the first and essentially the second sample) to a weak nematic organisation (for the last one) turns out. Hence polar interactions, already evidenced in structure determination of **3** [13], can be responsible for PL intensity reduction, in fact such interactions are weaker in native **poly1**, where a large distribution of oligomers is present, than in extracted fractions, especially in $CHCl_3$ one, where a small dispersity of chain length occurs. Accordingly, PL spectra of the three samples, reported in Fig. 4, show a red-shift peak position for $CHCl_3$ fraction only, indicating an aggregate formation.

From the electronic structure of the isolated material it is expected a lower barrier for hole injection in **poly1** (4.8 eV) from ITO (4.8 eV) than that for electron injection in **poly1** (2.35 eV) from Ca (2.9 eV) and especially from Al (4.3 eV) (see the inset of Fig. 3). The electron donor nature of substituent groups makes **poly1** a good hole transport material.

However, devices were also prepared by adding either hole transport or electron transport materials obtaining both blend and multi-layered LED active component: poly-*N*-vinylcarbazole (PVK) or polyethylenedioxythiophene (PEDOT) which is also an efficient hole injection layer and 2-(4-t-butyl-phenyl)-5-(4-biphenyl)-1,3,4-oxadiazole (PBD) respectively, were used. By using PEDOT the optical curves do not change with respect to the behaviour observed when only **poly1** is present. In Fig. 5 the PL–EL spectra of the different architectures are reported. In particular, PL spectrum of the bilayer device with PVK shows a small emission, attributable to hole transport layer; this emission totally disappears in the EL spectrum. Hence the exciton recombination takes place in **poly1** layer only, i.e., considering the character of the substituents at the polymer, a hole transport is inferred.

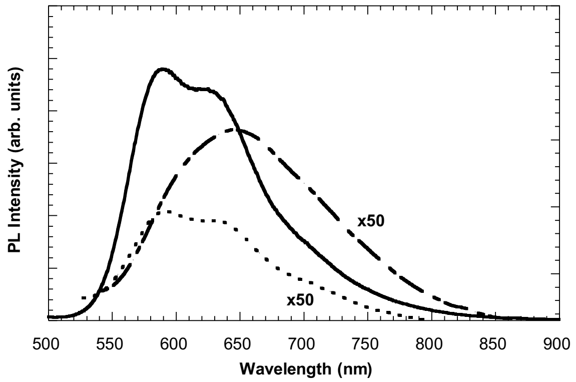


Fig. 4. PL spectra of **poly1** films: (▬) native, (····) TCE fraction, (▬ ▬) $CHCl_3$ fraction (see text).

When a blend of PVK and **poly1** (95:5 by weight) is used the emission peaks of both the polymers appear in PL and the EL spectrum is blue-shifted in comparison with the previous case because, in the device, the emission comes from both isolated **poly1** chains and aggregates, see Fig. 6 where the comparison among PL of the molecules considered are reported. More experimental work using different concentrations could confirm a resonant energy transfer from PVK to polythiophene.

In the monolayer device the current density is detected, while light emission turns on at a voltage near to 4 V, which increases up to 12 V being concomitant with the current in the bilayer architecture when PVK is employed. The use of PEDOT allows a decrease of this value, in fact the monolayer device begins to work near to 2 V, while the corresponding efficiencies are not significantly improved.

In Fig. 7 the PL and EL spectra of a three-component blend (PVK:**poly1**:PBD) as active layer and the corresponding *I*–*V* and EL–*V* curves are shown.

In the last device a light turn on voltage, near to 7 V, is observed but with a slow increase of the current density with respect to those of monolayer and two-component blend devices. The use of PEDOT on ITO with three-component blend (PVK:**poly1**:PBD) do not produce a further decrease of the turn on voltage, which on the contrary arises up to 15 V. Bright white light is

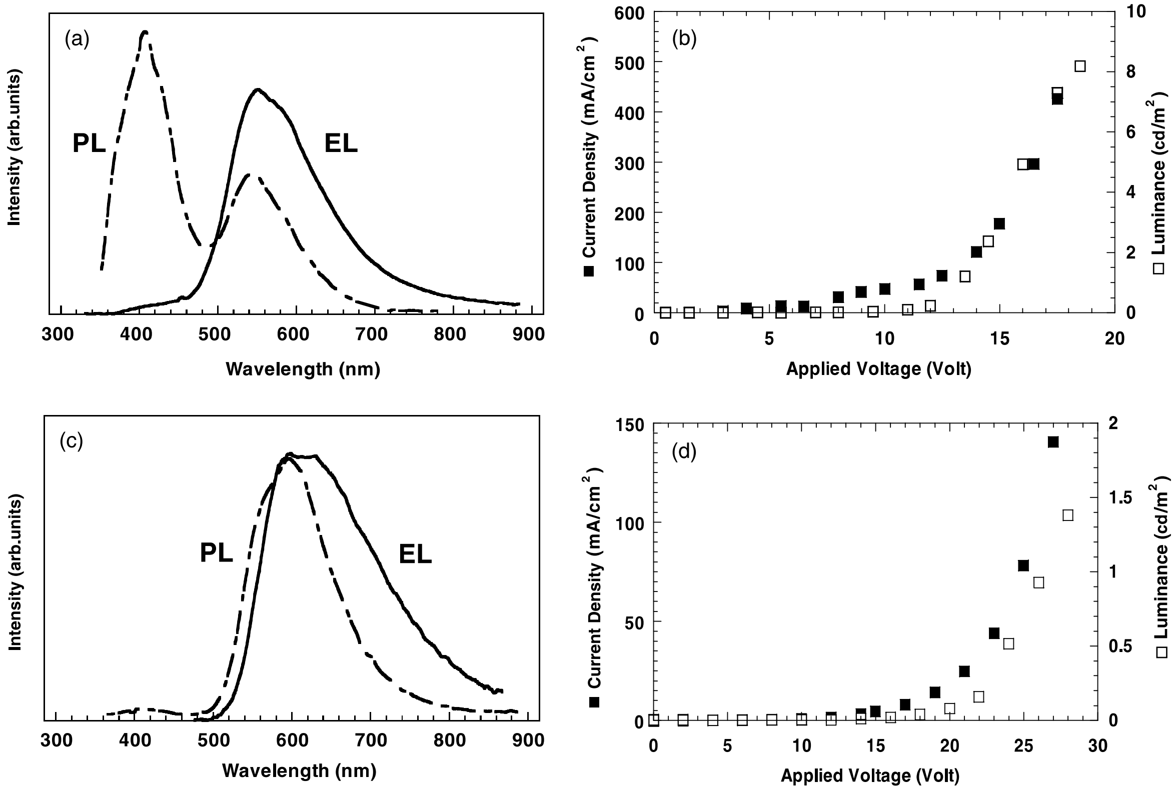


Fig. 5. PL–EL and related I/V curves of blend, (a) and (b), and bilayer, (c) and (d), of **poly1** with PVK.

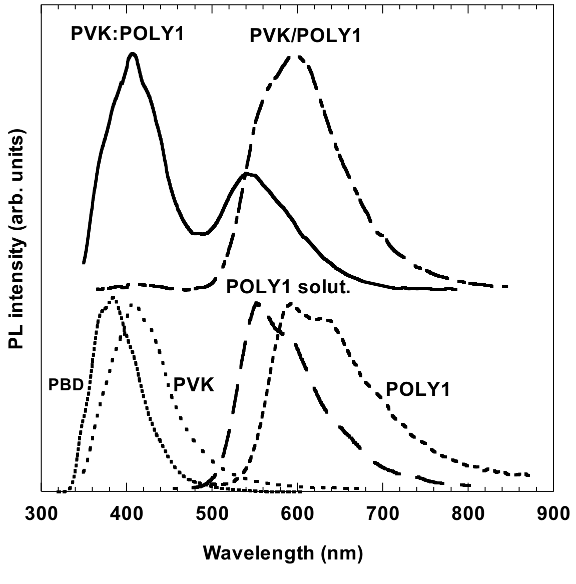


Fig. 6. Comparison among PL of the three components used in the devices.

observed from this device, due to the simultaneous emission of PVK, PBD, and **poly1** materials. Its external quantum efficiency is better than $3 \times 10^{-2}\%$.

A three layered device, i.e., PEDOT/**poly1**/ PBD:PMMA (2/1 by weight), deposited by dipping, shows a red emission, quite similar to that observed in bilayer device (see Fig. 5(c)), while in EL spectrum the PVK contribution previously observed is substituted by PBD component. The turn on value is measured near to 14 V, while both a satisfying charge balance and an efficiency close to $2 \times 10^{-2}\%$ are observed.

Attempts to build up three layer devices, like the previous one, using vacuum deposited PBD as third thin layer (36 nm), are presently unsatisfactory. Hence the device optimisation is in progress.

All these findings together with the consideration of the energy levels of the constituents (see the diagram reported in the inset of Fig. 7(b)) are

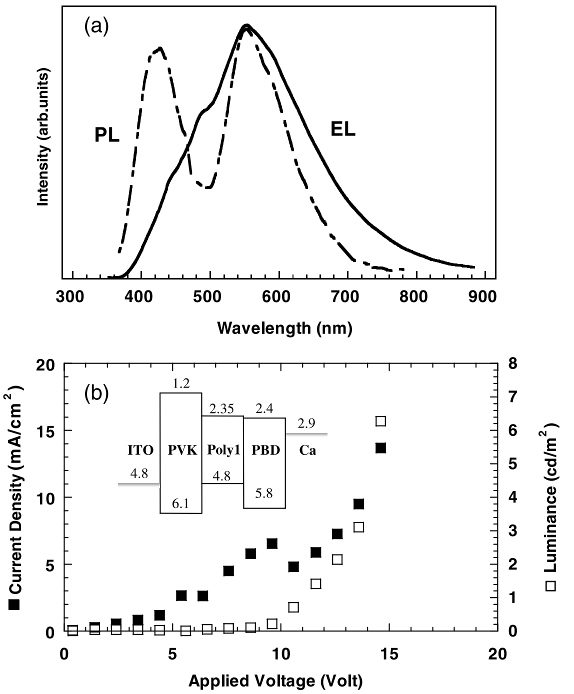


Fig. 7. PL and EL spectra of three-component blend (a) and corresponding *I–V* and EL–*V* curves (b). In the inset, the energy levels of the components are reported separately for the sake of clarity.

in agreement with a picture of the three-component device where the presence of a huge number of interfaces between PVK/PBD, PVK/**poly1**, and **poly1**/PBD, allows for the recombination on different sites near the cathode. Moreover, on the basis of PL results shown in Fig. 6, i.e., the overall peak position and the overlap of peaks of solution and blend at about 550 nm, the single-chain emission of **poly1** is prevailing.

Therefore the overlap of these different emissions results in the broad white PL reported in Fig. 7(a). Admittedly, the present efficiency values cannot be compared with up to date best values published; however it should be noted that significant efficiency improvements together with the tuning of the spectral window can be expected from salification of esteric functions with transition metals, following the recent results obtained by some authors using different metal-organic materials [14,15].

3. Conclusion

A red emitting LED with appreciable efficiency was prepared in a monolayer architecture by using electropolymerised polythiophene with regular double methoxyacetyl substitution on the same ring every third unit. Such a substitution imparts hole-injection character to the material. Colour tuning is obtained both by introducing PVK and PBD and by modifying the display architecture. In particular by blending **poly1** with PVK and PBD a white emitting diode with 0.03% efficiency was obtained.

4. Experimental

4.1. Chemicals and reagents

Acetonitrile was reagent grade (Uvasol, Merck) with a water content lower than 0.01% The supporting electrolyte tetrabutylammonium perchlorate (Bu_4NClO_4) was previously dried under vacuum at 70 °C. Quinine sulphate, PBD, PVK (Aldrich) were use without any further purification.

$CHCl_3$ and TCE employed for spin coating were used as received.

The monomers: 3,4-bis[(methoxycarbonyl)-methyl]thiophene (**2**), 3′,4′-bis[(methoxycarbonyl)-methyl]-2,2′: 5′,2″-terthiophene (**1**) and 3′,4′,3‴, 4‴-tetra[(methoxycarbonyl)methyl]-2,2′: 5′,2″:5″, 2‴: 5‴,2⁗-quinquithiophene (**3**) were prepared according to the literature [11].

4.2. Apparatus

Electrochemistry was performed at room temperature under nitrogen in three electrode cells. The counter electrode was platinum; reference electrode was a silver/0.1 M silver perchlorate in acetonitrile (0.34 V versus SCE). The voltammetric apparatus (AMEL, Italy) included a 551 potentiostat modulated by a 568 programmable function generator and coupled to a 731 digital integrator. The working electrode for cyclic voltammetry was a platinum mini-disc electrode (0.003 cm^2). For electronic spectroscopy a 0.8 × 2.5 cm ITO sheet (ca 20 ohm/square resistance, from Balzers, Liechtenstein) was used.

500 MHz NMR spectra were obtained on a Bruker DMX 500 spectrometer: ^{1}H-NMR were recorded at 500 MHz, while ^{13}C-NMR spectrum were recorded at 125.7 MHz. For both spectra TMS was used as internal reference and TCE as a solvent.

Matrix-assisted laser desorption ionisation (MALDI) mass spectra were taken on a Reflex TOF spectrometer (Bruker) using 2,5-dihydroxybenzoic acid as a matrix.

The molecular weights were also determined by gel permeation analysis (GPC) relative to polystyrene standards. The measurements were carried out by using a SEC System Waters GPCV 2000 apparatus equipped with a differential-refractometer 410 on line detector and Waters Styragel columns at room temperature using THF as an eluent.

XRD experiments were carried out on both powders and films at room temperature using a computer controlled Siemens D-500 diffractometer equipped with Soller slits and graphite-monochromator, in Bragg–Brentano geometry.

Optical transmission measurements for both solutions and films were performed with a Lamba 900 Perkin Elmer spectrometer. CW photoluminescence spectra were recorded by using a SPEX 270 M monochromator equipped with a N_2 cooled CCD detector, by exciting with a monochromated Xe lamp. Solution PLQY measures were performed using, as reference, a quinine sulphate solution by exciting at 350 nm ($\Phi = 54.6\%$). Solid state PLQY were carried out by using an integrating sphere exciting the sample with He–Cd laser ($\lambda = 325$ nm).

PBD was deposited by sublimation in a RIAL vacuum chamber at 10^{-7} mbar maintaining the crucible at 160 °C and a deposition rate of 0.9 nm/min obtaining a film of 36 nm.

The cathodes (Al, Ca–Al, 100–150 nm thick) were deposited by thermal evaporation at 10^{-5}–10^{-6} mbar using an Edwards instrument.

Spin coated films were prepared by using a P6700 PI-KEM apparatus using different parameters depending on the samples: PVK 3000 rpm for a $CHCl_3$ solution of 4 mg/cc in the bilayer display; **poly1** 1500 rpm for a TCE-$CHCl_3$ solution of 6 mg/cc; 1500 rpm for TCE-$CHCl_3$ solutions for two-component PVK:**poly1** (15:6 mg/cc) and PMMA:PBD (10:5 mg/cc) blends in toluene or for three-component PVK:**poly1**:PBD (8:6:4 mg/cc) blends in $CHCl_3$. In three layer films, PEDOT/**poly1**/PBD:PMMA (2/1 by weight) blend, the last component was deposited by dipping the sample in the same toluene solution used for spin coating preparation, obtaining no **poly1** dissolution.

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