Chemistry Proceedings

Proceedings

Anionic Low Band Gap Conjugated Polyelectrolytes as Hole Transporting Layer in Optoelectronics Devices †

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† Presented at the 24th International Electronic Conference on Synthetic Organic Chemistry, 15 November–15 December 2020; Available online: https://ecsoc-24.sciforum.net/.

Received: date;

Abstract: In the last years, interfacial engineering has played a critical role in promoting the performance of optoelectronic devices as organic solar cells (OSC) and organic light emitting diodes (OLEDs) since interfacial layers help to form an ohmic contact between the electrodes and the active layers, which is of great importance for charge collection/injection. Conjugated polyelectrolytes (CPEs), which are conjugated polymers bearing side-chain ionic functionalities likes anionic, cationic or zwitterionic groups, have emerged as new class of interfacial materials in thin film based electronic devices thanks to their ability to reduce the barrier between electrode and active layer. In this view, we have designed and synthesized two novel low bandgap anionic copolymers with different anionic pendant groups and different conjugated backbones to obtain hole-transporting layer (HTL) materials as alternative to commonly used poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate). The functional behavior of these copolymers as anode modifiers is herein preliminary investigate in an OLED prototype.

Keywords: conjugated polyelectrolytes; self-doped polymers; interfacials materials; OLEDs

1. Introduction

The control of the interfaces has proved to be one of the crucial elements for the engineering of different types of optoelectronic devices such as OLED (Organic Light Emitting Diodes), OSC (Organic Solar Cells) and OFET (Field Effect Transistor) which are based on organic and inorganic multilayer systems [1,2].

There are different strategies for the engineering of the interfaces but certainly conjugated polyelectrolytes [3] are playing an increasingly important role in organic [4] and hybrid systems including colloidal semiconductor nanocrystals [5,6] and perovskites [7,8].

The conjugated polyelectrolytes are formed by an organic semiconductor backbone and by polar side pendants which can be either anionic or cationic or neutral.

Similarly, in traditional semiconductor polymers, it is possible to modify the main conjugated chain and consequently modulate the energy bandgap of the system. The presence of polar groups on the side chains, on the other hand, ensures solubility in polar solvents such as water.

The CPEs have proved to be particularly effective in solid state optoelectronic applications. In fact, as solution processed materials with respect to the evaporated counterpart, they are ideal for low-cost, large-scale technologies such as roll-to-roll or ink-jet printing; their orthogonal solubility simplifies the preparation procedures of the devices preventing re-dissolution of the hydrophobic semiconducting layer during device fabrication; they are compatible with flexible devices; they are environmental friendly thanks to water solubility, they have unique solid-state-interface properties, which increase the adhesion between organic and metallic layers and have the ability to reduce the barrier between electrode and active layer thanks to the formation of an aligned interfacial dipole at the metal/organic semiconductor interface.

There are mainly two kinds of interfacial materials which are commonly used in optoelectronic devices: if they are at the interface with the anode are called anode interfacial layer, or AIL, and cathode interfacial layer, or CIL, when they are at the interface with the cathode (Figure 1).

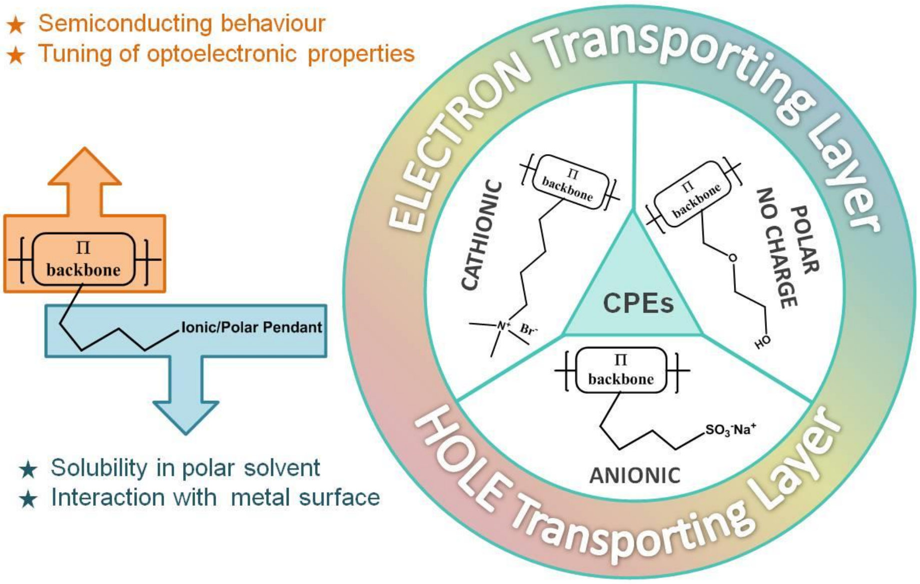

Figure 1. General structure of conjugated polyelectrolytes and their main characteristics.

Considering a traditional direct geometry device, several CILs have been developed which generally have a fluorenic, phenylene or benzodithiazole-based backbone with cationic ammonium or polar substituent groups such as amine [9,10] or phosphonates [11], while the development of AILs is lagging behind.

The most common used AIL material in OSCs is acidic poly (3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS), thanks to his high optical transparency in the visible-NIR regime, suitable energy level, and sufficient conductivity. However his hygroscopic and acidic nature induces the etching of the indium from the ITO/PEDOT:PSS interface, then causing the diffusion of indium and ultimately leading to fast deterioration of the devices [12,13].

Recently, Bazan and coworkers [14] have demonstrated an anionic low bandgap CPEs copolymer based on the acceptor (A) benzodithiazole (BT) and on the donor (D) cyclopentadithiophene (CPDT) bearing sulfonated side groups. This copolymer can be easily doped after dialysis in water and, thanks to its pH-neutral nature, is a promising alternative to acidic PEDOT:PSS.

Although this material has been successfully incorporated in different types of devices [5,15–17] however from a chemical point of view it is important to understand the role of the backbone and of the lateral anionic substituents.

Herein we present the synthesis and preliminary optoelectronic characterization of two new low bandgap D-A anionic CPEs as a possible anternative to PEDOT.PSS. We copolymerize the BT monomer with a dithienopyrrolo (DTP) unit that is reported to be a stronger donor with respect to CPDT moiety. DTP has never been used, to our knowledge, in CPE and for comparison we synthetize a CPDT-BT polymer with only a lateral substituent. The DTP-BT polymer has a carboxylate lateral group with a lower acidity then sulfonate group but with a stronger donor [18] in the backbone (polymer P1, Figure 2), the CPDT-BT polymer is similar to the CPE proposed by Bazan, but bearing only one sulfonate group. We aim to understand the combined role of the backbone, and in particular of the corresponding energy bandgap, and the lateral polar groups in the self doping process of these materials.

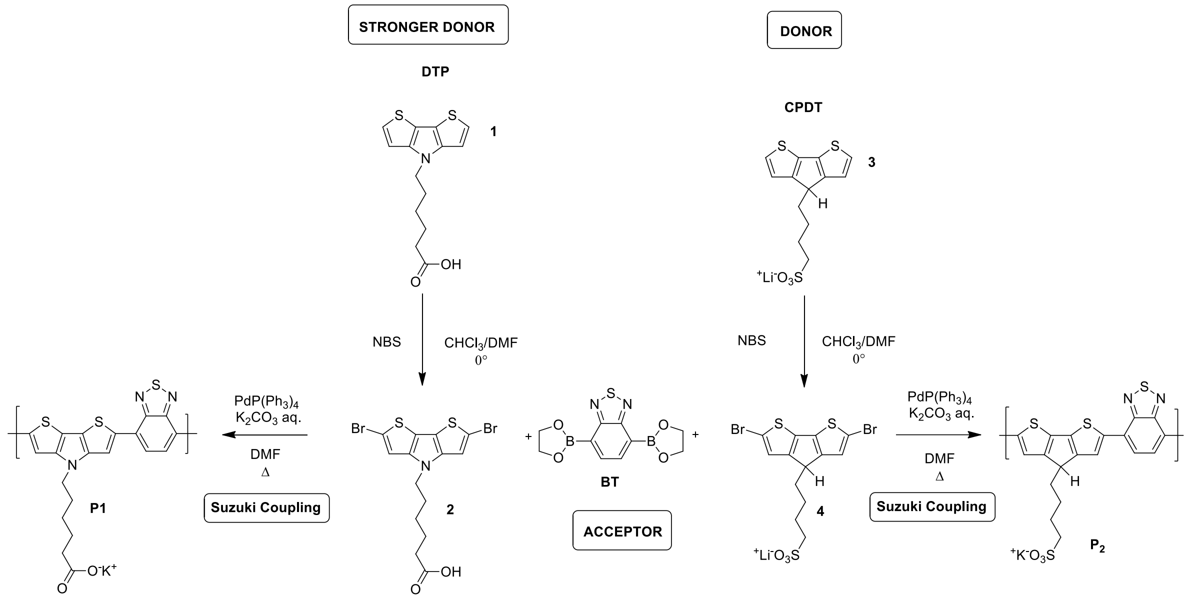

Figure 2. Synthesis of polymers P1 and P2.

The UV-vis-NIR optical characterization combined with the electron paramagnetic resonance (EPR) showed that, regardless of the bandgap and the strength of the donors, the sulfonate group seems to have a fundamental role in the self doping process of the polymer.

Finally, P2 has also been tested in a very preliminary OLED prototype.

2. Materials and Methods

All glassware has been oven-dried. Unless specifically mentioned, all chemicals are commercially available and have been used as received.

Ethyl 6-(4H-dithieno[3,2-b:2′3′-d]pyrrole-4-yl)hexanoate (**1**) has been synthesized following the procedure reported by Zecchin et al. [19].

The dialysis membrane (MWCO: 3500–5000 Da) has been purchased from Membrane Filtration Products Inc. NMR spectra were recorded at 600 MHz.

*Dibromo-ethyl 6-(4H-dithieno[3,2-b:2′3′-d]pyrrole-4-yl)hexanoate (*__2__*).* Compound 1 (150mg, 0.511 mmol, 1 eq.) has been suspended in DMF (1 mL) and cooled down at 0 °C. A solution of. N-bromosuccinimide (NBS, 182 mg2, 1.022 mmol, 2 eq.) in chloroform ($CHCl_3$, 5.11 mL) has been added dropwise under stirring. The reaction has been allowed to reach room temperture in dark by shielding the flask with aluminum foil. After 1 h at room temperature, the crude product has been diluited with $CHCl_3$ and washed three time with water. The organic solvent has been removed under reduced pressiond and the product used without further purification. ^{1}H NMR (D_2O) δ: 7.00 (s, 2H), 4.05 (t, 2H), 2.30 (m, 2H), 1.85 (m, 2H), 1.65 (m, 2H), 1.35 (m, 2H).

Polymer P1. A mixture of compound **2** (230.5 mg, 0.511 mol, 1 eq.) 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (198.32 mg, 0.511 mmol, 1 eq.) and tetrakis(triphenylphosphine)Palladium(0) ($Pd(PPh_3)_4$, 11.8 mg, 2% mol) has been added in a pre-degassed schlenk, followed by three vacuum/nitrogen cycles. Then degassed DMF (4.8 mL) and degassed potassium carbonate aqueous solution (1.2 mL) have been added. The mixture has been stirred at 110 °C for 3 h. The reaction mixture has been poured in acetone and the dark blue precipitate has been collected by filtration and washed with copious amounts of acetone and. The precipitate has been all dissolved in deionized H_2O and transferred into a dialysis tube (MWCO: 3500–5000). The dialysis tube has been placed in a large beaker with H_2O stirring for 3 days, and the H_2O has been changed every 12 h. Evaporation of H_2O has provided the title product as a dark blue solid (109 mg, 50%) after drying under vacuum overnight.

*Synthesis of 4-Potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b′]-dithiophene (***3***).* 4H-cyclopenta-[2,1-b;3,4-b′]-dithiophene (CPDT, 300 mg, 1.68 mmol, 1.0 eq.) and tetrabutylammonium bromide (27 mg, 0.084 mmol, 0.05 eq.) have been dissolved in anhydrous DMSO (8.2 mL), and the solution has been degassed by bubbling with Ar for 5 min. 50% KOH in H_2O (1.8 g) has been added via syringe, followed by the addition of 1,4-butanesultone (924 μL, 9.02 mmol, 1.2 eq.). After stirring at room temperature for 3 h, the reaction mixture has been poured into acetone (50 mL), the yellowish precipitate has been collected by filtration and washed with acetone. The crude has been used in the next step without further purification. ^{1}H NMR (D_2O) δ: 7.05 (d, 2H), 6.95 (d, 2H), 3.42 (t, 1H) 2.73 (t, 2H), 1.63 (m, broad, 2H), 1.56 (m, broad, 2H), 1.3 (m, broad, 2H).

*Synthesis of 2,6-Dibromo-4-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b′]-dithiophene (***4***).* The crude product 3 has beens suspended in DMF (6.7 mL), and H_2O (~1 mL) has been added while stirring until it was all dissolved. NBS (747 g, 4.2 mmol, 2.5 eq.) has been added in dark by shielding the flask with aluminum foil. The brown solution has been stirred at room temperature for 1 h, and poured into acetone. The yellowish precipitate has been collected by filtration, and washed with acetone (640 mg, 75% yield). ^{1}H NMR (D_2O) δ 7.23 (s, 2H), 3.74 (t, broad, 1H), 2.80 (m, broad, 2H), 2.60–2.50 (m, broad, 2H), 1.85–1.80 (m, broad, 2H), 1.55–1.45 (m, broad, 2H).

Synthesis of polymer P2. A mixture of compound **4** (117 mg, 0.230 mol, 1 eq.), 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (89 mg, 0.230 mmol, 1 eq.) and $Pd(PPh_3)_4$ (5.2 mg, 2% mol) have been added in a pre-degassed schlenk, followed by three vacuum/nitrogen cycles. Then degassed DMF (2.2 mL) and degassed potassium carbonate aqueous solution (0.55 mL) have been added. The mixture has been stirred at 110 °C for 3 h. The reaction mixture has been poured in acetone and the dark blue precipitate has been collected by filtration and washed with copious amounts of acetone.The precipitate has been all dissolved in deionized H_2O and transferred into a dialysis tube (MWCO: 3500–5000). The dialysis tube has been placed in a large beaker with H_2O stirring for 3 days, and the H_2O has been changed every 12 h. Evaporation of H_2O provided the title product as a dark blue solid (65 mg, 60%) after drying under vacuum overnight.

OLED fabrication and characterization. Glass substrates covered with indium tin oxide (ITO) pattern have been washed ultrasonically in distilled water, acetone and isopropyl alcohol. On the substrates a water solution (2 mg/mL) of P2 has been spincoated using 1400 rpm rotation and subsequently the substrates have been annealed at 100 °C for 10 min inside nitrogen filled glovebox. Emissive layer has been prepared from poly(9,9-dioctylfluorene-alt-benzothiadiazole) (F8BT, American Dye Source) dissolved in toluene at concentration 10 mg/mL and deposited with rotation 1000 rpm. Then the devices have been transferred to an evaporator where 7 nm of barium and 100 nm of aluminum have been deposited through a shadow mask at 10^{-6} mbar pressure.

Electroluminescence (EL) spectra have been recorded with liquid nitrogen cooled CCD combined with a monochromator (Spex 270M) and applying a constant bias. Keithley 2602 source meter has been employed during current density-voltage-luminance measurements. Light emitted in forward direction from the devices has been collected by a photodiode with known spectral response. In efficiency calculations Lambert distribution has been assumed. All characterization has been performed in nitrogen atmosphere.

3. Results and Discussion

Chemical characterization. The syntheses of compounds 1 and 2 are shown in Figure 2 and confirmed by ^{1}HNMR spectra (Figure 3). In particular the monosubstitution of monomer 2 is confirmed by the presence of a triplet at 3.74, attributable to H in 4 position in cylopenta-[2,1-b:3,4-b′]dithiophene [20].

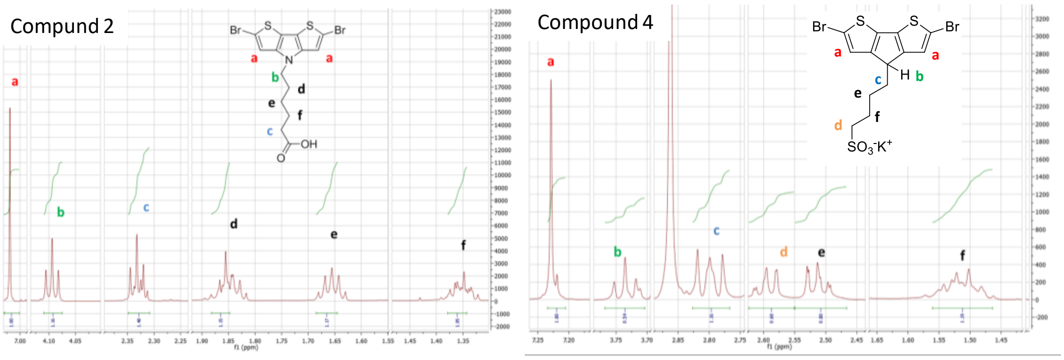

Figure 3. H NMR spectra of compound 2 and compound 4.

Polymer P1 and P2 have been synthesized through Suzuki cross-coupling of a dibromide- of the donor unit and the bis-boronic ester of benzothiadiazole, with $Pd(PPh_3)_4$ as catalyst and K_2CO_3 as base in degassed DMF as solvent. The polymers have been purified via dialysis membrane with a cutoff of 3500–5000 Da.

Differently from what reported earlier [15] where the pendant anionic moieties ensure CPEs solubility in polar organic solvents (e.g., ethanol) or water, both P1 and P2 polymers show poor solubility both in traditional organic solvents and in polar solvents probably due to the amphiphilic character given by the combination of the apolar backbone and the polar side chains.

The NMR spectra of the polymers show only non-informative broad peaks due probably to their paramagnetic characteristic, but the formation of the polymers was assured by the strong change of the color of the solution from colorless to blue/violet.

Cyclic voltammetry (Figure 4) has been applied to investigate the electrochemical properties. The HOMO levels of the polymer P1 and P2 (−4.8 eV and −4.92 eV respectively) are in agreement with the one reported by Bazan et al. [14] for a similar polymer and are comparable to the one of PEDOT:PSS (~−5 eV) reported in literature.

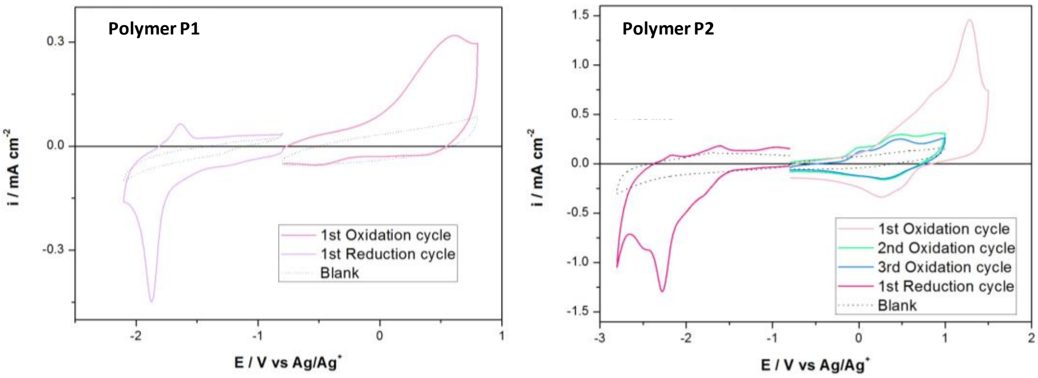

Figure 4. Voltammograms of polymer P1 and polymer P2.

Polymer P2 shows an interesting behavior: the first oxidation peak is at high potential, while the second and third, perfectly reproducible, are at lower potential. Most probably this behavior indicates the formation of solid state aggregates which disaggregate after the first potential application [21].

Self-doping behavior. In order to understand the self-doping properties of the polymers we have recorded absorption spectra in water solution at different pH. In fact, it has been shown for CPDT based CPE the acidic environment favors the doping of the polymers and the formation of a polaron contribute in the absorption spectrum.

In UV-vis-NIR absorption characterization (Figure 5) the peak at 410 nm corresponds to p–p* absorption from localized p orbitals, while the higher intensity peak around 700 nm corresponds to the absorption from the intramolecular charge transfer (ICT) band [14].

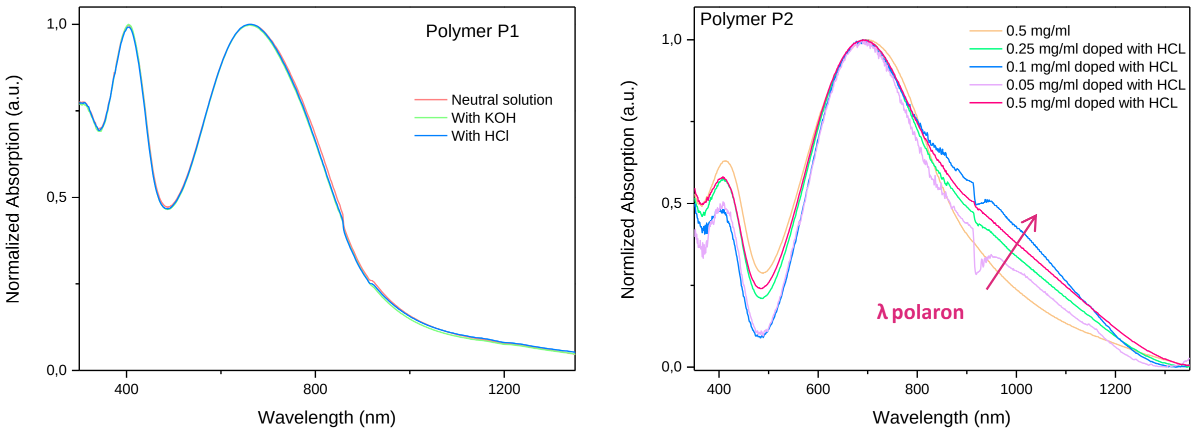

Figure 5. Absorption spectra in water solution of polymers P1 and P2.

As it can be observed in Figure 5 the absorption spectrum of polymer P1 seems to be unaffected by the addition of an acid or base to change the pH, pointing out the polymer cannot be doped in acidic conditions. On the other hand, polymer P2 show the uprising of a polaron band in the near-infrared region with the increasing of the acidity of the solution, confirming the self-doping behavior of the material [14].

A further evidence of self-doping behavior has been obtained by electron paramagnetic resonance (EPR) measurements in aqueous solution (Figure 6): strong EPR symmetric signal consistent with the presence of unpaired electrons is observed for both PEDOT:PSS and P2, while no signal has been observed for polymer P1, in agreement with the absorption spectra.

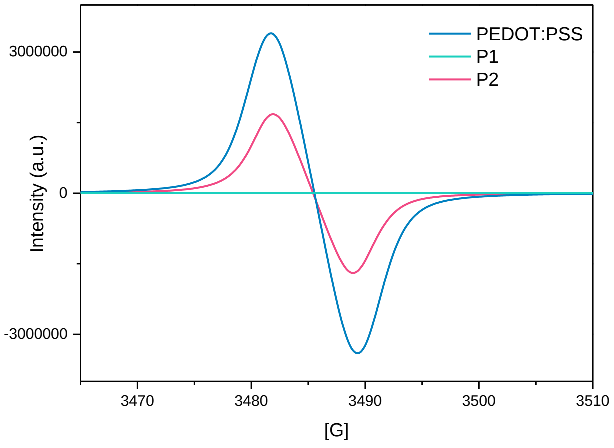

Figure 6. EPR spectra of PEDOT:PSS, P1 and P2.

Since both polymers have a low and very similar energy gap, the explanation of the different behavior has probably to be found in the different polar groups. The sulfonate group appears to have a crucial impact in the formation of self doped systems.

Preliminary OLED device. The polymer P2, showing self-doping behavior, has been tested as an HTL in a PEDOT:PSS-free OLED architecture with F8BT as emitter. In the left part of Figure 4, the EL spectrum of the diode is shown together with Commission Internationale de l'Eclairage (CIE) chromaticity coordinates (0.41, 0.58). The EL spectrym is typical from F8BT and no contribution from P2 polymer was observed.

The performance of the device are presented in the right panel of Figure 7. The J(U) and L(U) curves had forms typically observed for diodes. The device switched on at 6 V and the maximal recorded luminance approached 40 cd/m². Current density values were quite high and in combination with modest luminance lead to a weak external quantum efficiency (EQE), shown in the inset of the right panel of Figure 7. It should be underlined that performance were achieved for the device without any optimization.

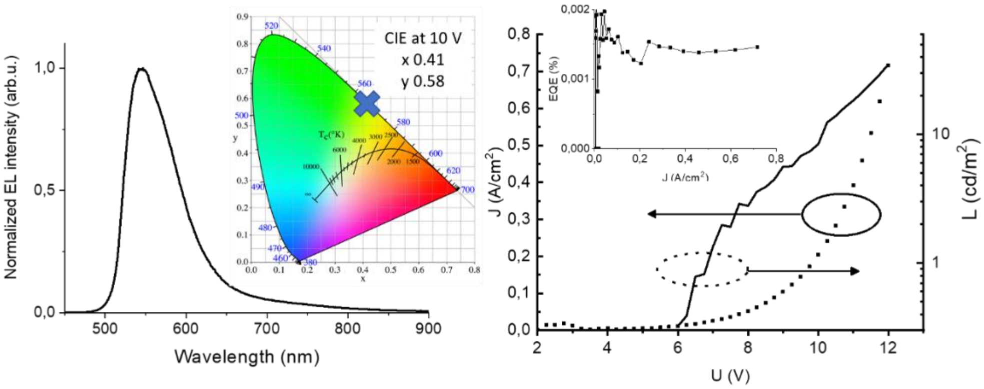

Figure 7. (**Left**) EL spectrum of F8BT-based diode with P2 as an HTL, registered at 10 V. In the inset CIE coordinates of the spectrum are shown. (**Right**) Current density (J)—voltage (U)—luminance (L) characteristics of the OLED. In the inset external quantum efficiency (EQE) is presented as a function of J.

4. Conclusions

Two new low bandgap conjugated polyelectrolytes, polymer P1 and P2, has been synthesized and characterized.

The DTP moiety, reported to be a stronger donor with respect to CPDT monomers, was used for the first time in the synthesis of a low bandgap CPE giving a material with suitable HOMO-LUMO levels. Polymer P1 did not show a self-doping behavior, as confirmed by EPR measurements. On the contrary, polymer P2 seemed to be a promising materials because it showed a self-doping behavior hence highlighting the importance of the proper combination between low bandgap conjugated backbone and suitable anionic substituent.

Very Preliminary OLEDs device using polymer P2 as HTL has been fabricated. The performance, even if modest due to the not optimized architecture and parameters, showed the potential application of P2 compound.

This work will help guide the synthetic design of new, highly conductive CPEs. Specifically, we showed the importance of incorporating an electron-rich structural unit into the polymer backbone, that can be oxidized easily, as well as the necessity of having a pendant anionic group to stabilize the resulting positively charged backbone for self-doped polymer systems.

Yet, a more comprehensive understanding of the importance of sulfonate for the self-doping mechanism of CPE and its effect on charge transport and mobility is required to improve the design and the use of this class of polymers.

Acknowledgments: The authors thanks Barbara Vercelli for cyclic voltammetry measurements and Maristella Gussoni and Simona Mrakic-Sposta for the EPR measurements.

Conflicts of Interest: The authors declare no conflict of interest.

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