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Effects of Water/Alcohol Soluble Cationic Polythiophenes as Cathode Interlayers for Eco-Friendly Solar Cells

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*Effects of water/alcohol soluble cationic polythiophenes as cathode interlayers for eco-friendly solar cells*

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## **Abstract**

Three new ionic polythiophene derivatives, soluble in polar solvents, are synthesized with good yields using simple, low-cost, and straightforward procedures. They are investigated as interfacial cationic conjugated polyelectrolyte (CPE) layers for halogen-free bulk heterojunction (BHJ) polymeric solar cells, based on a water-soluble electron-donor polymer (poly[3-(6-diethanolaminohexyl)thiophene]) and a water-soluble electron-acceptor fullerene derivative (malonodiserinamide fullerene). The simple insertion of the CPE interlayer between the active layer and the aluminium cathode dramatically increases the power conversion efficiency (PCE) of the final device up to near 5%, resulting from a decrease of the electrode work-function, improved electron extraction and optimization of the morphology of the layers. The obtained results demonstrate that the incorporation of CPE layer is a powerful and convenient methodology for the development of highly efficient and eco-friendly processable polymeric solar cells.

## **1. Introduction**

In the burgeoning field of photovoltaic, conjugated polymer solar cells (PSCs) have drawn attention and have been widely studied for their features and advantages, such as structural versatility of the organic material, light weight, flexibility, and low cost.<sup>[1]</sup> These devices can convert sunlight into electrical energy through a mechanism that provides light absorption, the

generation of charged carriers, and their subsequent separation and transport with final collection to the respective electrodes.<sup>[2]</sup>

In the last decades, different types of devices with several architectures have been developed, obtaining the best results using bulk-heterojunction (BHJ) solar cells.<sup>[3]</sup> In this model, the photoactive layer - placed between an anode (ITO) and a cathode (Al) - is made of an electron-donor (ED, a  $\pi$ -conjugated polymer) and an electron-acceptor (EA, usually a fullerene derivative) material mixed in the same bulk. The main feature of a BHJ device is indeed the possibility to combine easy processability with high final efficiency, as the enhanced interface area between the two components promotes an efficient generation and transport of free-charge carriers.

To avoid oxidation phenomena and improve hole extraction and collection, the photoactive layer is typically not placed in direct contact with the anode, but a hole transport layer (HTL) is commonly deposited between the ITO and the active layer. The most used HTL is made of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) due to its eco-friendly solution processability, high conductivity, stability, and high light transmittance.<sup>[4]</sup>

Otherwise, in common BHJ solar cells, the photoactive layer is directly in contact with the cathode surface, with possible migration of metal atoms into the active layer during deposition and subsequent decrease of the open-circuit voltage ( $V_{oc}$ ).<sup>[5]</sup> Therefore, to avoid these drawbacks and increase the power conversion efficiency (PCE) and  $V_{oc}$  of BHJ devices, several polymeric electrolytes (i.e., polythiophene<sup>[6]</sup> and polyfluorene<sup>[7]</sup> derivatives) with different pendant cationic moieties (i.e., trimethylammonium group) have been used as interlayers between the photoactive and cathode films to modify the interface.<sup>[8,9]</sup> The presence of an ionic moiety on the conjugated polyelectrolyte – acting as an electron transporting layer (ETL) – seems to improve the final performance of the device by changing the interactions at the cathode interface due to the increase of polarity. In fact, the consequently modified dipole moment<sup>[10]</sup> – which generates a capacitive double layer – allows an easier charge transport and collection.<sup>[11,12]</sup> The reduction of the work-function of the cathode results in a lower resistance at the interface, thus leading to a higher fill factor (FF), short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), and, consequently, power conversion efficiency (PCE). Moreover, the recombination is reduced due to better charge carriers' mobility.<sup>[13]</sup>

Another interesting feature is the solubility of polymer electrolytes in environmental-friendly polar solvents such as alcohols – usually methanol, ethanol, isopropanol – and water. The possibility to process both the photoactive layer and the interlayer from more green solvents means that the sustainability of the final device considerably increases. For this reason, in recent years, the attention has been widely focused on water/alcohol soluble conjugated polymers (WSCPs)<sup>[14,15]</sup> and

their application in several fields such as biosensors,<sup>[16]</sup> chemical sensors,<sup>[17]</sup> PLEDs,<sup>[18]</sup> and PSCs.<sup>[19]</sup>

In view of the foregoing, we here report the synthesis and study of three different thiophene-based cationic interlayers soluble in green polar solvents (PT6buP<sup>+</sup>Br<sup>-</sup>, PTO6buP<sup>+</sup>Br<sup>-</sup> and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)). Besides, we compare the photoconversion efficiencies of completely eco-friendly BHJ devices, obtained by testing the prepared materials as ETL, in the presence of a non-ionic photoactive layer which is also processable from alcohols and water (blend of PT6N(EtOH)<sub>2</sub>:C<sub>60</sub>-Ser). PT6N(EtOH)<sub>2</sub> was chosen as the photoactive polymer since it has been recently reported that the presence of ionic groups in the photoactive blend may induce disorder at the macromolecular level in the solid state or act as traps for charges, thus leading to unsatisfactory PCE values.<sup>[20]</sup>

The structural and photo-physical properties of the synthesized precursor and alcohol-soluble polymers were investigated using nuclear magnetic resonance (NMR), infrared (FT-IR) and ultraviolet-visible (UV-Vis) spectroscopy, in addition to thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), cyclic voltammetry (CV), X-ray diffraction (XRD), atomic force microscopy (AFM), and external quantum efficiency (EQE). The final materials were tested in organic solar devices prepared with halogen-free solvents, obtaining an increase of photoconversion efficiency value up to 55% when PT6N(EtOH)<sub>2</sub>:C<sub>60</sub>-Ser and PTO6buP<sup>+</sup>Br<sup>-</sup> were used as a photoactive layer and CPE, respectively, in comparison with the same cell devoid of any interlayer.

## 2. Experimental section

### 2.1. Materials

Tributylphosphine (97%), 1,6-hexandiol (99%), tetrahydrofuran (THF, >99.9%), toluene (C<sub>7</sub>H<sub>8</sub>, >99.9%), diethyl ether (Et<sub>2</sub>O, >99.5%), ethyl acetate (EtOAc, >99.5%), hydroxymethyl EDOT, 3-methoxythiophene (98%) and chloroform (CHCl<sub>3</sub>, 99.0-99.4%) were purchased from Sigma Aldrich Chemical Co. (USA). Petroleum ether (Etp, >90%) was purchased from Sigma Aldrich (Israel). N,N-Dimethylformamide (≥99.8%) and sodium hydroxide (NaOH, ≥98%), were purchased from Sigma Aldrich (Germany). Hexane (≥99%) and dichloromethane (≥99.9%) were purchased from Sigma Aldrich (France). Nitromethane (CH<sub>3</sub>NO<sub>2</sub>, ≥98.5%), Tetrabutylammonium bromide (TBAB, ≥99%), hydrobromic acid (HBr, 48%), hydrochloric acid (HCl, ≥37%) and ferric chloride (FeCl<sub>3</sub>, ≥98%) were purchased from Fluka (Switzerland). Diethanolamine (DEA, 99%) was purchased from Aldrich. 1,6-Dibromohexane (B6B, >97%) was purchased from TCI (Tokyo). p-Toluenesulfonic acid monohydrate was purchased from Carlo Erba (Italy). Sodium sulfate

(Na<sub>2</sub>SO<sub>4</sub>, anhydrous) and sodium bicarbonate (NaHCO<sub>3</sub>) were purchased from Riedel-de Haën (Poland). Methanol (MeOH, >99.8%) was purchased from Honeywell (Germany). 6-bromo-1-hexanol (B6OH) was synthesized as reported in J. Chang et al. work.<sup>[21]</sup> Regioregular poly[3-(6-bromohexyl)thiophene] (rrPT6Br) was synthesized through Grignard Metathesis Polymerization (GRIM).<sup>[22]</sup> 3-(6-Bromohexyl)thiophene (T6Br) synthesis and subsequent oxidative polymerization with FeCl<sub>3</sub> to give non-regioregular poly[3-(6-bromohexyl)thiophene] (PT6Br) were performed according to the previously reported methods.<sup>[23]</sup> Poly[3-(6-diethanolaminoethyl)thiophene] (PT6N(EtOH)<sub>2</sub>) was synthesized according to the procedure reported in literature (95% HT, M<sub>n</sub> = 9.9 kDa, PDI = 1.3).<sup>[24]</sup> Synthesis of 6-bromohexyl-1-oxymethyl-EDOT (EDOT-MeO6Br) and purification of P(EDOT-MeO6Br) were carried out accordingly to the procedure reported in literature.<sup>[25,26]</sup> Malonodiserinolamide fullerene (C<sub>60</sub>-Ser) was prepared according to previously reported literature methods.<sup>[27]</sup> To remove the stabilizer, diethyl ether and THF were freshly distilled before the use. The procedures involving air/moisture-sensitive reagents were performed under argon atmosphere.

## 2.2. Synthesis of cationic polythiophene interlayers

### 2.2.1. General procedure for oxidative polymerization with FeCl<sub>3</sub>

In a three-neck flask, the monomer was dissolved in anhydrous chloroform under inert atmosphere, and a solution of FeCl<sub>3</sub> in CH<sub>3</sub>NO<sub>2</sub> was added dropwise to the system (10 minutes) and the mixture was allowed to react under a flux of argon for 40 minutes at room temperature. Afterward, THF was added, and the system stirred for further 50 minutes.

The mixture was poured into 300 mL of MeOH/HCl (5% v/v), and the precipitated product was recovered by filtration on a PTFE membrane (0.45 μm pore size). The obtained solid was then dissolved in CHCl<sub>3</sub>, washed with HCl 2% up to exhaustive extraction of the iron (III) ion (negative NH<sub>4</sub>SCN test), and several times with water up to neutrality. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and the solvent was removed under reduced pressure.

In the case of P(EDOT-MeO6Br) the darkish solid was recovered in CHCl<sub>3</sub> (5 mg/mL), added to a solution of NH<sub>4</sub>OH (1:1), and heated until reflux conditions for 2 h. The organic phase was washed several times with distilled water until neutrality, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure.

#### 2.2.1.1. Poly[3-(6-bromohexyl)thiophene] (PT6Br)

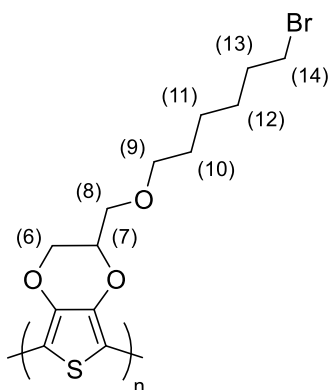
Starting from 450 mg (1.82 mmol) of 3-(6-bromohexyl)-thiophene (T6Br) in 25.0 mL of anhydrous CHCl<sub>3</sub>, the addition of 1.18 g (7.28 mmol) of FeCl<sub>3</sub> in 7.50 mL of CH<sub>3</sub>NO<sub>2</sub> gave 250 mg

(1.02 mmol) of PT6Br as a reddish solid (yield 56%, 85% HT, Mn = 9.8 kDa, PDI = 1.9).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  6.98 (s, 1H, Th  $H_4$ ), 3.43 (bt, 2H,  $\text{CH}_2\text{Br}$ ), 2.82, 2.58 (bt, 2H, Th $\text{CH}_2$ ), 1.96-1.80 (m, 2H,  $\text{CH}_2\text{CH}_2\text{Br}$ ), 1.80-1.64 (m, 2H, Th $\text{CH}_2\text{CH}_2$ ), 1.60-1.36 (m, 4H,  $(\text{CH}_2)_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  143.71, 143.01, 141.03, 140.28 (Th C3), 136.94, 135.88, 134.61, 134.77 (Th C5), 131.32, 130.85, 130.23, 129.85 (Th C2), 129.04, 128.65, 128.32, 127.63 (Th C4), 34.55 ( $\text{CH}_2\text{Br}$ ), 33.81 ( $\text{CH}_2\text{CH}_2\text{Br}$ ), 30.94 (Th $\text{CH}_2$ ), 29.96, 29.15, 28.53 (aliphatic  $\text{CH}_2$ ). FT-IR (Ge,  $\text{cm}^{-1}$ ): 3055, 2929, 2854, 1509, 1457, 1259, 1090, 827, 727, 645, 562.

### 2.2.1.2. Poly[3-(6-bromohexyloxy)thiophene] (PTO6Br)

Starting from 300 mg (1.14 mmol) of 3-(6-bromohexyl-1-oxy)thiophene (TO6Br) in 25.0 mL of anhydrous  $\text{CHCl}_3$ , the addition of 755 mg (4.65 mmol) of  $\text{FeCl}_3$  in 4.73 mL of  $\text{CH}_3\text{NO}_2$  gave 133 mg (0.509 mmol) of a reddish solid (yield 45%, 68% HT, Mn = 2.3 kDa, PDI = 1.8).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  7.03-6.70 (b, 1H, Th  $H_4$ ), 4.16, 3.93 (2bm, 2H, Th $\text{OCH}_2$ ), 3.42 (bm, 2H,  $\text{CH}_2\text{Br}$ ), 2.12-1.74 (bm, 4H, Th $\text{OCH}_2\text{CH}_2$  and  $\text{CH}_2\text{CH}_2\text{Br}$ ), 1.73-1.27 (bm, 4H, aliphatic  $\text{CH}_2$ ).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  154.82 (Th C3), 136.32 (Th C5), 107.99 (Th C4), 106.72 (Th C2), 68.00, 67.78 (Th $\text{OCH}_2$ ), 32.67 ( $\text{CH}_2\text{Br}$ ), 29.85 (Th $\text{OCH}_2\text{CH}_2$ ), 30.04, 28.14, 24.16, 23.04 (aliphatic  $\text{CH}_2$ ). FT-IR (Ge,  $\text{cm}^{-1}$ ): 3079, 2937, 2860, 1520, 1456, 1222, 1191, 1071, 829, 734, 645, 562.

### 2.2.1.3. Poly(6-bromohexyl-1-oxymethyl-EDOT) [P(EDOT-MeO6Br)]



Starting from 262 mg (0.782 mmol) of 6-bromohexyl-1-oxymethyl-EDOT (EDOT-MeO6Br) in 13.0 mL of anhydrous  $\text{CHCl}_3$ , the addition of 517 mg (3.13 mmol) of  $\text{FeCl}_3$  in 2.36 mL of  $\text{CH}_3\text{NO}_2$  gave 80.0 mg (0.240 mmol) of a dark purple solid (yield 31%, 81% HT, Mn = 4.3 kDa, PDI = 1.7).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm):  $\delta$  4.76-3.93 (bm, 3H, H7 and H6), 3.92-3.62 (b, 2H, H8), 3.49 (bs, 2H, H9), 3.41 (bs, 2H, H14), 1.85 (bs, 2H, H13), 1.59 (bs, 2H, H10), 1.50-1.24 (bm, 4H, H11 and H12).  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ , ppm): 143.87 (Th C3+C4), 121.70 (Th C2+C5), 82.70 (C7), 81.89 (C8), 77.57

(C9), 72.18 (C6), 34.22 (C14), 32.99, 29.74, 28.28, 25.57 (aliphatic CH<sub>2</sub>). FT-IR (Ge, cm<sup>-1</sup>): 2935, 2862, 1460, 1438, 1305, 1240, 1225, 1117, 1057, 913, 841, 751, 643, 561.

### 2.2.2. General procedure for the post-functionalization of brominated polymers with tributylphosphine

The brominated polymeric precursor was dissolved in toluene in a three-neck flask and then tributylphosphine was added to the system under stirring and in an inert atmosphere. After reacting at 90°C for 24 h, the supernatant was removed, and the film formed on the flask surface was recovered with methanol. The solvent was evaporated under reduced pressure, and the product was washed several times with diethyl ether and dried under vacuum to give the final cationic polymer.

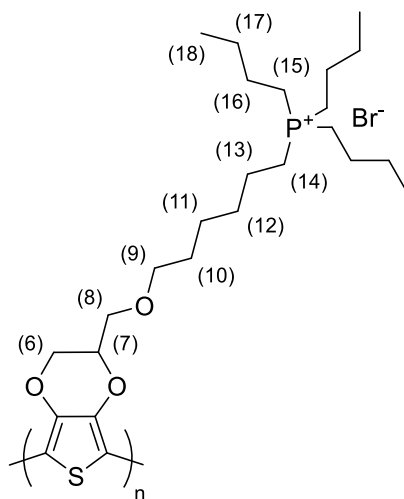
#### 2.2.2.1. Poly[3-(6-tributylphosphoniumhexyl)thiophene]bromide (PT6buP<sup>+</sup>Br<sup>-</sup>)

Starting from 360 mg (1.47 mmol) of PT6Br in 20.0 mL of toluene, the addition of 3.60 mL (14.6 mmol) of tributylphosphine gave 636 mg (1.42 mmol) of PT6buP<sup>+</sup>Br<sup>-</sup> as a dark red solid (yield 97%). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, ppm): δ 7.14 (s, 1H, Th H4), 2.90, 2.64 (bs, 2H, ThCH<sub>2</sub>), 2.25 (bs, 8H, CH<sub>2</sub>P<sup>+</sup>CH<sub>2</sub>), 1.85-1.71 (bm, 2H, ThCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.43 (bm, 18H, (CH<sub>2</sub>)<sub>n</sub>) 0.98 (bt, 9H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CD<sub>3</sub>OD, ppm): δ 141.62 (Th C3), 134.92 (Th C5), 131.67 (Th C2), 130.28 (Th C4), 31.49, 30.18, 29.74, 25.10, 24.94, 24.50, 22.49 (aliphatic CH<sub>2</sub>), 19.54 (CH<sub>2</sub>P<sup>+</sup>), 19.08 (P<sup>+</sup>CH<sub>2</sub>), 13.88 (CH<sub>3</sub>). <sup>31</sup>P-NMR (CD<sub>3</sub>OD, ppm): δ 33.86. FT-IR (Ge, cm<sup>-1</sup>): 3053, 2957, 2929, 2870, 1513, 1463, 1410, 1378, 1232, 1099, 833, 723. Elemental analysis: calcd for [(C<sub>22</sub>H<sub>40</sub>BrPS)]<sub>n</sub> C 59.05, H 9.01, S 7.17, P 6.92, Br 17.85. Found: C 59.09, H 8.89, S 7.80, P 6.88, Br 17.94.

#### 2.2.2.2. Poly-[3-(6-tributylphosphoniumhexyloxy)thiophene]bromide (PTO6buP<sup>+</sup>Br<sup>-</sup>)

Starting from 120 mg (0.458 mmol) of PTO6Br in 8.00 mL of toluene, the addition of 1.14 mL of tributylphosphine gave 198 mg (0.428 mmol) of PTO6BuP<sup>+</sup>Br<sup>-</sup> as a dark-red solid (yield 93%). <sup>1</sup>H-NMR (CD<sub>3</sub>OD, ppm): δ 7.08 (b, 1H, Th H4), 4.24-4.05 (2bm, 2H, ThOCH<sub>2</sub>), 2.31-1.99 (bm, 8H, CH<sub>2</sub>P<sup>+</sup>), 1.98-1.82 (bm, 2H, ThOCH<sub>2</sub>CH<sub>2</sub>), 1.70-1.29 (bm, 18H, (CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>P<sup>+</sup>), 1.01-0.82 (bm, 9H, CH<sub>3</sub>). <sup>13</sup>C-NMR (CD<sub>3</sub>OD, ppm): δ 140.76 (Th C3), 133.45 (Th C5), 129.82 (Th C2), 127.96 (Th C4), 66.90 (ThOCH<sub>2</sub>), 28.16, 27.52, 25.27, 25.12, 24.91, 24.62 (aliphatic CH<sub>2</sub>), 19.49 (CH<sub>2</sub>P<sup>+</sup>), 18.89 (P<sup>+</sup>CH<sub>2</sub>), 13.90 (CH<sub>3</sub>). <sup>31</sup>P-NMR (400 MHz, ppm): δ 33.88. FT-IR (Ge, cm<sup>-1</sup>): 3028, 2957, 2932, 2871, 1536, 1463, 1407, 1379, 1229, 1194, 1078, 831, 727. Elemental analysis: calcd for [(C<sub>22</sub>H<sub>40</sub>BrOPS)]<sub>n</sub> C 57.01, H 8.70, O 3.45, S 6.92, P 6.68, Br 17.24. Found: C 57.07, H 8.67, O 3.43, S 6.89, P 6.71, Br 17.23.





Starting from 100 mg (0.300 mmol) of P(EDOT-MeO6Br) in 11.0 mL of toluene, the addition of 750  $\mu$ L of tributylphosphine gave 142 mg (0.266 mmol) of a red cherry solid (yield 88%).  $^1\text{H-NMR}$  ( $\text{CD}_3\text{OD}$ , ppm):  $\delta$  4.36-4.02 (b, 2H, H7 and H6), 3.95-3.65 (bm, 2H, H8), 3.64-3.36 (b, 2H, H9), 2.24 (bs, 8H, H14 and H15), 1.90-1.72 (bm, 2H, H10), 1.70-1.33 (bm, 18H, aliphatic  $\text{CH}_2$ ), 0.98 (m, 9H, H18).  $^{13}\text{C-NMR}$  ( $\text{CD}_3\text{OD}$ , ppm): 137.82 (Th C3+C4), 115.57 (Th C2+C5), 72.80 (C7), 70.29 (C8), 64.98 (C9), 60.76 (C6), 31.63, 30.51, 28.10, 27.45, 25.07, 22.46 (aliphatic  $\text{CH}_2$ ), 19.48 (C14), 19.04 (C15), 13.90 (C18).  $^{31}\text{P-NMR}$  ( $\text{CD}_3\text{OD}$ , ppm):  $\delta$  33.90. FT-IR (Ge,  $\text{cm}^{-1}$ ): 2957, 2932, 2870, 1462, 1439, 1379, 1311, 1231, 1226, 1115, 1052, 916, 835, 749. Elemental analysis: calcd for  $[(\text{C}_{25}\text{H}_{44}\text{BrO}_3\text{PS})]_n$  C 56.07, H 8.28, O 8.96, S 5.99, P 5.78, Br 14.92. Found: C 56.12, H 8.22, O 8.95, S 5.94, P 5.74, Br 15.03.

### 2.3. Measurements

NMR spectra ( $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$ , and  $^{31}\text{P-NMR}$ ) were recorded on a Varian Mercury Plus 400 spectrometer using TMS as a reference. IR spectra were taken on KBr or Ge disks using a Perkin Elmer Spectrum One spectrophotometer. UV-Vis spectra were recorded on a Perkin Elmer Lambda 19 spectrophotometer using  $10^{-5}$  M polymer solutions in spectroquality solvents in Suprasil quartz cuvettes ( $1 \times 1$  cm) or films on quartz slides. Elemental analyses were performed by Redox Laboratories, Monza, Italy.

The molecular weight of precursor polymers was determined by gel permeation chromatography (GPC) using THF solutions on a HPLC Lab Flow 2000 apparatus equipped with a Rheodyne 7725i

injector, a Phenomenex MXL 5  $\mu\text{m}$  mixed bed column, and an RI K-2301 KNAUER detector. The calibration curve was recorded using monodisperse polystyrene standards. Thermogravimetric analyses were recorded on NETZSCH TG 209 F1 Libra operating in air flux, which was used to determine the sample decomposition temperatures by heating from 30°C to 600°C with a ramp of 10°C  $\text{min}^{-1}$ .

A TA Instruments Q2000 differential scanning calorimeter (DSC) was used for the thermal analysis by varying the temperature from -20 to 200°C with a heating and cooling ramp of 10°C  $\text{min}^{-1}$  in a nitrogen atmosphere.

Cyclic voltammetry (CV) was performed at 0.1 V  $\text{s}^{-1}$  in acetonitrile/toluene (25:75) v/v solutions added with  $(\text{C}_4\text{H}_9)_4\text{NClO}_4$  (0.1 mol  $\text{L}^{-1}$ ) on polymer films deposited on Pt disc electrode (diameter 1 mm) by drop casting from methanol solutions. SCE absolute potential was 4.24 V.

X-ray diffraction data were recorded at room temperature by using a  $\text{CuK}\alpha$  ( $\lambda = 1.5406 \text{ \AA}$ ) radiation source (Philips PW 1050) and a Bragg-Brentano diffractometer (Philips PW 1710) equipped with a graphite monochromator in the diffracted beam. The  $2\theta$  range between 2.0 and 90.0° was scanned by 881 steps of 0.1° with a counting time of 15 s for each step. The XRD characterization was carried out on polymer films on glass slides deposited by doctor blading (100 nm average thickness) after an annealing procedure (heating at 120°C for 30 min under vacuum).

The sample surface topography was evaluated with an atomic force microscope (AFM, Ntegra, NT-MDT) equipped with a silicon cantilever (HA\_NC, NT-MDT, tip radius of 10 nm, and spring constant of 12 N/m). Measurements were performed in a semi-contact mode with a resonance frequency of around 150 kHz; the scanning rate was 0.5 Hz, while the size of the scanned sample was 10  $\mu\text{m} \times 10 \mu\text{m}$  per image.

### 2.3.1. Solar cells

Photovoltaic devices were prepared by the following procedure: the ITO glass substrate (2.0  $\times$  2.0 cm, surface resistance 21  $\Omega/\text{sq}$ ) was etched on one side using a 10% wt aqueous solution of HCl at 60°C to obtain an area of 1.5  $\times$  1.0 cm covered by indium tin oxide. The glass was then cleaned with distilled water and 2-propanol and dried with a nitrogen flow giving a final resistance of the ITO glass of 12  $\Omega/\text{sq}$ . Poly(3,4-ethylenedioxythiophene):polystyrene sulfonic acid (PEDOT:PSS, 2.8 wt% dispersion in water, viscosity 20 cps) was diluted 1:1 v/v with 2-propanol, sonicated for 15 min using an ultrasonic bath (Elmasonic S 30H), filtered on a Gooch G2, and the resulting solution (viscosity 12 cps) deposited over the previously treated ITO glass with the doctor blading technique using a Sheen Instrument Model S265674, leaving only a small (0.5  $\times$  1.0 cm) area uncovered at the opposite side of the previously etched area.

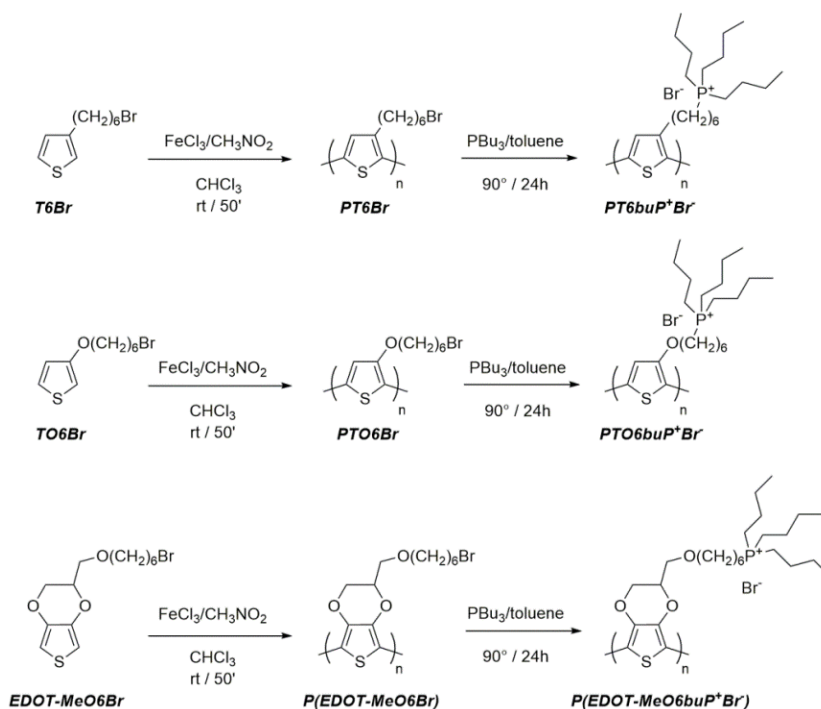
The PEDOT:PSS film was heated in a Buchi GKR-50 glass oven at 120°C for 90 min under vacuum ( $10^{-3}$  mmHg). A solution made by mixing 2.5 mg of PT6N(EtOH)<sub>2</sub> and 2.5 mg of C<sub>60</sub>-Ser in 0.5 mL of methanol was sonicated and deposited by doctor blading on the slide in order to cover the PEDOT:PSS layer. Subsequently, the sample was annealed in the glass oven under vacuum ( $10^{-3}$  mmHg) at 120°C for 30 minutes. A solution of 1.0 mg of cationic polymer (CPE) in 0.5 mL of ethanol was deposited on the photoactive layer by spray coating (Gohelper Mini Kit Airbrush, nozzle diameter 0.3 mm) and annealed at 120°C for 15 minutes. Finally, a 50 nm-thick Al electrode was deposited over the polymeric layer through a shadow mask using an Edwards 6306A coating system operating at  $10^{-6}$  mmHg. The active area of the cell was  $1.0 \times 1.0$  cm<sup>2</sup>. The current-voltage characteristics were measured in air using a Keithley 2401 source meter under the illumination of an Abet Technologies LS150 Xenon Arc Lamp Source AM 1.5 Solar Simulator (100 mW/cm<sup>2</sup>) calibrated with an ILT 1400-BL photometer. The structure of the final devices was: ITO (80 nm)/PEDOT:PSS (100 nm)/active layer (150 nm)/cationic interlayer (20 nm)/Al (50 nm). The solar cell spectral response was measured using a 7-SC Spec III Modularized Solar Cell Spectral Test System (SevenStar Optics, Beijing, PRC). Layer thicknesses were measured with a FTPAdvances FTPadv-2 Film Thickness Probe (Sentech GmbH, Germany) equipped with the FTPExpert software.

### 3. Results and Discussion

#### 3.1. Synthesis

The electron-donor material (ED) was synthesized through the post-functionalization of regioregular poly[3-(6-bromohexyl)thiophene] (rrPT6Br) with diethanolamine (see Supporting Information), giving the corresponding poly[3-(6-diethanolaminoethyl)thiophene] (PT6N(EtOH)<sub>2</sub>) as a neutral water/alcohol-soluble polymer.<sup>[28]</sup> The choice of this photoactive material - instead of the most used poly(3-hexylthiophene) (P3HT) - has been made with the aim to prepare a completely eco-friendly photovoltaic device (photoactive blend and interlayers) avoiding the use of harmful solvents. For this purpose, the electron-acceptor material (EA) C<sub>60</sub>-Ser – a fullerene derivative soluble in polar solvents - was synthesized according to a previous work.<sup>[27]</sup>

The synthetic approach followed to prepare ionic materials was based on two main strategies: polymerization of monomers in the same conditions through oxidative reaction with FeCl<sub>3</sub> and subsequent post-functionalization with the same substituent (tributylphosphine) as depicted in Scheme 1.



**Scheme 1.** Synthetic routes to obtain the CPE interlayers (PT6buP<sup>+</sup>Br<sup>-</sup>, PTO6buP<sup>+</sup>Br<sup>-</sup> and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)).

In detail, monomers 3-(6-bromohexyl)thiophene (T6Br), 3-(6-bromohexyl-1-oxy)thiophene (TO6Br) and 6-bromohexyl-1-oxymethyl-EDOT (EDOT-MeO6Br) were reacted with FeCl<sub>3</sub> in dry chloroform for 50 minutes under inert conditions.

The average molecular weight was determined by GPC analysis of the soluble fraction of the synthesized precursor polymers (Table 1). The comparison between PT6Br and the other two polymers shows the obtaining of lower molecular weights for the latter, and this can be ascribed to the presence of alkoxy-groups grafted on the thiophene ring. In this case, the electron-donating effect of the oxygen stabilizes the radicals involved in the oxidative polymerization thus favoring the formation of shorter polymeric chains.<sup>[29]</sup>

Finally, the post-functionalization reaction of precursors (PT6Br, PTO6Br, and P(EDOT-MeO6Br)) with tributylphosphine of the bromoalkylic side chains was carried out at 90°C for 24 hours leading to the complete post-functionalization of side-chain substituents.<sup>[30]</sup> The reaction of precursor polymers with tributylphosphine has been chosen since phosphine usually leads to the complete post-functionalization of bromine in the side chains, giving an optimal solubility of the resulting materials in polar solvents.<sup>[31]</sup> Then the prepared cationic polymers have been employed as interlayers for polymeric solar cells since several recent studies report the use of conjugated polyelectrolytes (CPEs) - which combine the presence of a delocalized  $\pi$ - $\pi^*$  conjugated backbone with pendant ionic groups - as promising cathode interface modifiers.<sup>[32]</sup>

**Table 1.** Polymer characteristics.

<i>Sample</i>	<i>Reaction</i>	<i>Post-functionalization</i>	<i>M<sub>n</sub></i> ( <i>kDa</i> )	<i>Đ</i>
	<i>Yield (%)</i>	<i>Yield (%)</i> <sup>a</sup>		
<i>PT6Br</i>	56	-	9.8 <sup>b</sup>	1.9 <sup>b</sup>
<i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	97	100	17.9 <sup>c</sup>	1.9 <sup>c</sup>
<i>PTO6Br</i>	45	-	2.3 <sup>b</sup>	1.8 <sup>b</sup>
<i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	93	100	4.1 <sup>c</sup>	1.8 <sup>c</sup>
<i>P(EDOT-MeO6Br)</i>	31	-	4.3 <sup>b</sup>	1.7 <sup>b</sup>
<i>P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	88	100	6.9 <sup>c</sup>	1.7 <sup>c</sup>

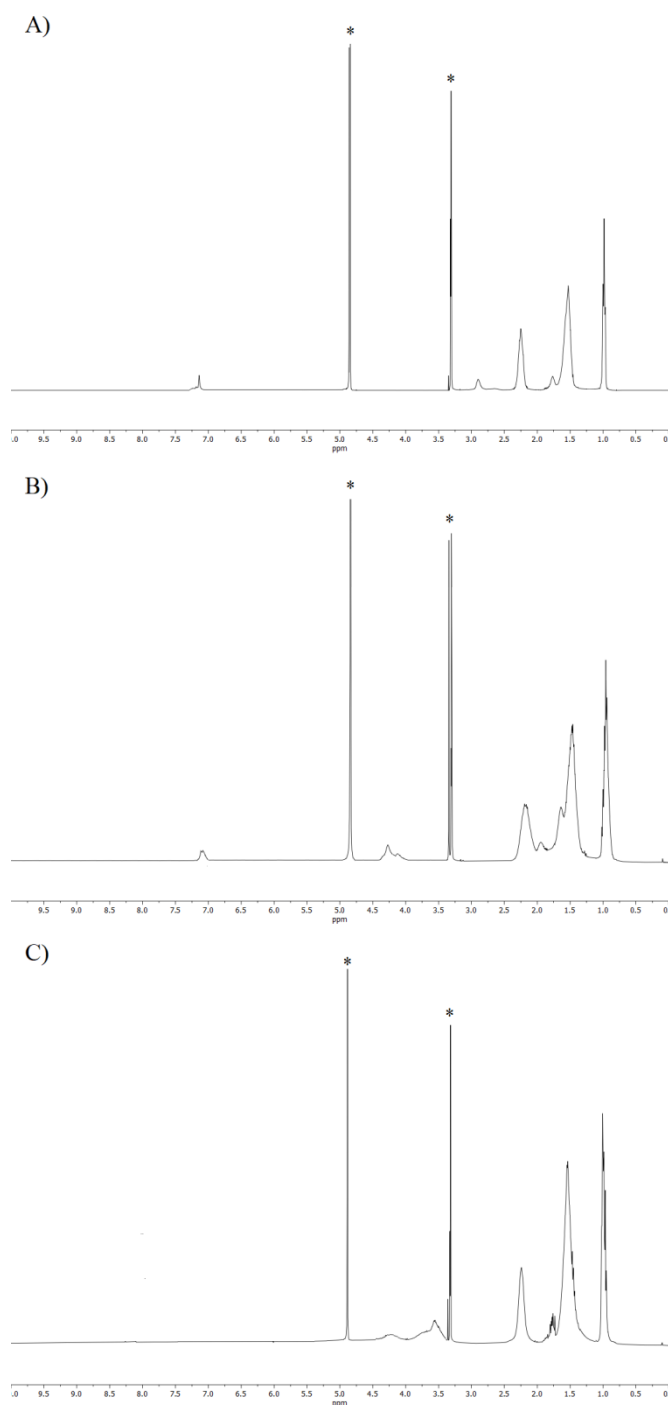
<sup>a</sup> Determined by <sup>1</sup>H-NMR; <sup>b</sup> Determined by GPC chromatography relative to polystyrene standards; <sup>c</sup> Calculated from the molecular mass of the corresponding precursors.

### 3.2. NMR and FT-IR spectroscopy

All the synthesized polymers were characterized by NMR spectrometry (<sup>1</sup>H-NMR, <sup>13</sup>C-NMR, and <sup>31</sup>P-NMR for materials with phosphonium side group) to confirm their chemical structure (see Supporting Information, Figure S1-S14).

The analysis of <sup>1</sup>H-NMR spectra (Figure 1), recorded in CD<sub>3</sub>OD, shows the total absence of methylenic protons in  $\alpha$  position to -Br group, evidencing the successful post-functionalization of precursors with tributylphosphine. In particular, the presence of a broad multiplet at 2.36-2.15 ppm, 2.31-1.99 ppm, and 2.24 ppm, for PT6buP<sup>+</sup>Br<sup>-</sup>, PTO6buP<sup>+</sup>Br<sup>-</sup> and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>), respectively, can be ascribed to the eight methylenic protons near to the phosphine moiety, thus confirming the substitution of bromide group.

The occurrence of the post-functionalization of precursors was further verified by both <sup>13</sup>C-NMR and <sup>31</sup>P-NMR spectroscopy. Moreover, the <sup>31</sup>P-NMR spectra evidence the absence of unreacted tributylphosphine and the complete substitution with phosphonium as previously verified by <sup>1</sup>H-NMR.



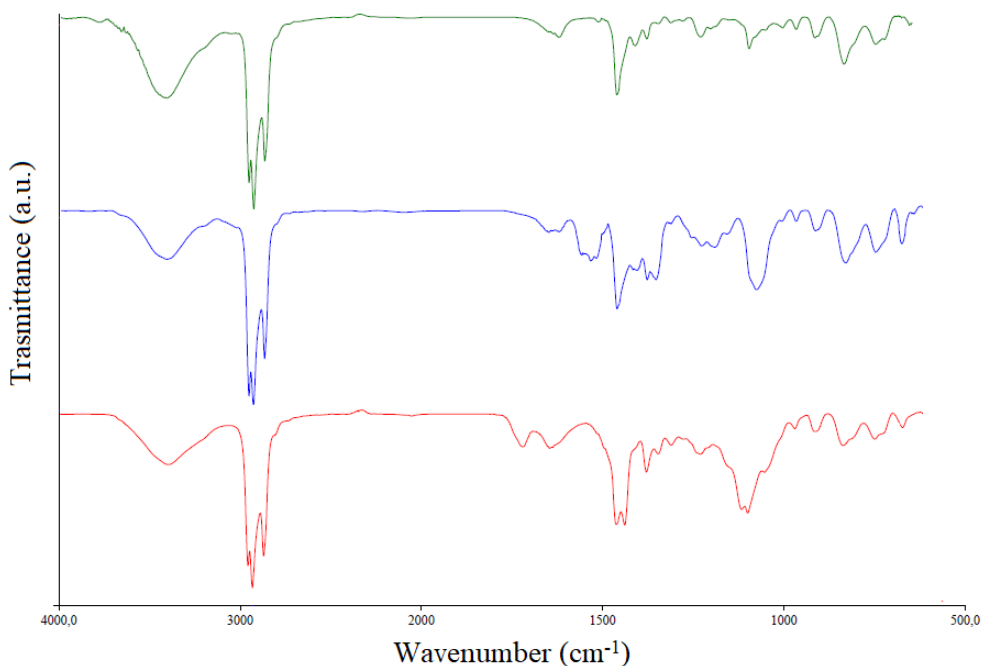
**Figure 1.**  $^1\text{H-NMR}$  spectra of: A)  $\text{PT6buP}^+\text{Br}^-$ , B)  $\text{PTO6buP}^+\text{Br}^-$  and C)  $\text{P(EDOT-MeO6buP}^+\text{Br}^-)$ . Asterisk: solvent resonance ( $\text{CD}_3\text{OD}$ ).

FT-IR spectroscopy further confirms the chemical structure of all synthesized materials. The FT-IR bands of interlayers ( $\text{PT6buP}^+\text{Br}^-$ ,  $\text{PTO6buP}^+\text{Br}^-$ ,  $\text{P(EDOT-MeO6buP}^+\text{Br}^-)$ ) and photoactive material ( $\text{PT6N(EtOH)}_2$ ) with their assignments are shown in Table S1-S4 (See Supporting Information).

In detail, the presence of bands ascribable to phosphonium group ( $\sim 1379\text{ cm}^{-1}$ ) in IR spectra of  $\text{PT6buP}^+\text{Br}^-$ ,  $\text{PTO6buP}^+\text{Br}^-$  and  $\text{P(EDOT-MeO6buP}^+\text{Br}^-)$  (Figure 2) and the absence of peaks

ascribable to -Br terminal group ( $\sim 640$  and  $560\text{ cm}^{-1}$ ) confirm the successful reaction of post-functionalization with the tributylphosphine group.

The broad band at  $\sim 3400\text{ cm}^{-1}$  (O-H stretching) is due to the high hygroscopicity of synthesized polymers thus confirming their high affinity for polar solvent (water).

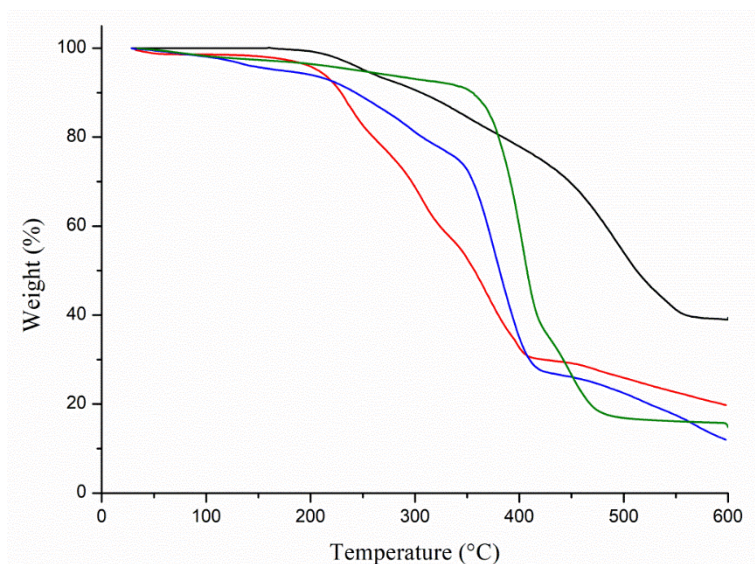


**Figure 2.** FT-IR spectra of  $\text{PT6buP}^+\text{Br}^-$  (green line),  $\text{PTO6buP}^+\text{Br}^-$  (blue line) and  $\text{P(EDOT-MeO6buP}^+\text{Br}^-)$  (red line).

### 3.3. Thermal properties

The thermal stability of interlayers and photoactive polymer have been evaluated by TGA analysis under oxidizing atmosphere (air), at a heating scan rate of  $10^\circ\text{C min}^{-1}$  and up to  $600^\circ\text{C}$  (Figure 3 and Table 2).

In the TGA curves of all cationic interlayers, the three main weight losses can be ascribed to the elimination of phosphonium group (up to  $200^\circ\text{C}$ ), to the aliphatic side chain scission ( $280\text{-}310^\circ\text{C}$ ) and to the macromolecular backbone combustion (up to  $370^\circ\text{C}$ ), respectively. In the case of  $\text{PT6N(EtOH)}_2$ , the first loss of weight is ascribable to diethanolamine group in pendant chain. The synthesized samples, however, may be considered stable enough to be used as photoactive materials in organic photovoltaic devices.



**Figure 3.** Thermograms of PT6N(EtOH)<sub>2</sub> (black line), PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (red line).

Thermal properties of polymers have been evaluated by DSC analyses which were carried out under nitrogen atmosphere with a heating ramp of 10 °C min<sup>-1</sup> from -20 °C up to 200 °C (Table 2 and Figure S15).

All the examined samples show an endothermic flexure, ascribable to the glass transition temperature ( $T_g$ ). The absence of melting and crystallization phenomena is due to the amorphous nature of the polymers: the tributylphosphonium group linked to the side chains decreases the conformational order of the polymeric chains with a consequent loss of crystallinity.

Moreover, the possibility to form inter- or intra-chain hydrogen bonds when the hydroxylamine substituent is employed increases the  $T_g$  value of PT6N(EtOH)<sub>2</sub> sample, even if any clear endothermic melting peak can not be found.

**Table 2.** Decomposition ( $T_d$ ) and glass-transition ( $T_g$ ) temperatures of polymers.

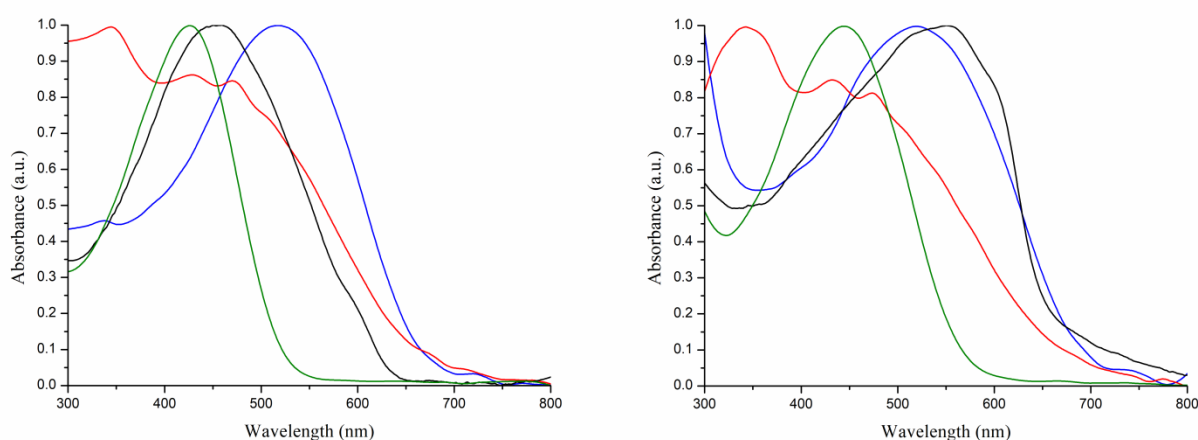
<i>Sample</i>	$T_d$ (°C) <sup>a</sup>	$T_{d,max}$ (°C) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>
<i>PT6N(EtOH)<sub>2</sub></i>	216	253	70
<i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	373	402	55
<i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	217	250	35
<i>P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	207	237	32

<sup>a</sup> Determined by the onset point of the first inflection; <sup>b</sup> calculated from the first derivative of the weight/temperature curve; <sup>c</sup> evaluated by DSC analysis.



### 3.4. Optical properties

In order to evaluate the optical properties, interlayers and photoactive material were analyzed by UV-Vis spectroscopy in solid state (film on quartz slides) and in solution of different polar solvents (i.e., alcohols and water). The normalized absorption spectra obtained in methanol are reported in Figure 4 and the maximum absorption wavelengths are reported in Table 3. UV-Vis analysis was also conducted using other polar solvents (i.e., ethanol and water), and the relative spectra and data are reported in Supporting Information (Figure S16, S17 and Table S5, S6).



**Figure 4.** Normalized UV-Vis spectra of polymers in methanol solution (left) and in film (right) from MeOH: PT6N(EtOH)<sub>2</sub> (black line), PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (red line).

The optical behavior of PT6N(EtOH)<sub>2</sub> is different in solution and in film, due to the change in the conformational order of polymeric chains. In this case, the maximum absorption wavelength shifts from 459 nm (solution) up to 551 nm (film), suggesting that this polymer can achieve highly planar conformations with a high electronic delocalization when in the solid state. Enhanced planarizing interactions can also be ascribed to inter- and intrachain hydrogen bonds, thus leading to an extended conjugation length for this polymer. This behavior is a crucial requirement in view of the final application as electron-donor material in the photoactive layer of polymeric solar cells. On the contrary, the comparison of UV-Vis spectra of cationic polymers (CPEs) in solution and in solid state shows only modest shifts of maximum absorption wavelengths.

**Table 3.** Maximum absorption wavelengths of CPEs in solution and thin film.

<i>Sample</i>	$\lambda_{max}$ (nm)		
		<i>Solution (<math>10^{-5}</math> M)</i>	<i>Solid state (film)</i>
<i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	Methanol	425	445
	Ethanol	426	444
<i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	Methanol	518	518
	Ethanol	518	514
<i>P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	Methanol	344, 428, 470	342, 432, 473
	Ethanol	348, 426, 469	337, 429, 471

The UV-Vis spectral profiles of cationic polymers are also almost independent from the solvent employed for their dissolution and subsequent deposition. In view of this, ethanol was used as the filming solvent for the preparation of cell interlayers due to its low toxicity and with the aim of obtaining more sustainable and eco-friendly devices. Furthermore, an interesting behavior can be observed for P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) sample, which shows structured profiles with three absorption maxima both in solution and in film, suggesting the coexistence of three main chromophores at different conjugation lengths.

### 3.5. Electrochemical properties

The potentials of ionic interlayers and neutral photoactive layers were evaluated by cyclic voltammetry (CV). In Table 4 are reported the electrochemical parameters of synthesized polymers in thin films obtained by drop-casting their solution in methanol on Pt electrodes.

**Table 4.** Electrochemical and optical properties of synthesized polymers in thin film.

<i>Sample</i>	$E_{ox}$ (V) <sup>a</sup>	<i>HOMO</i> (eV)	$E_{g, opt}$ (eV) <sup>b</sup>	<i>LUMO</i> (eV)
<i>PT6N(EtOH)<sub>2</sub></i>	+0.57	-4.81	1.88	-2.93
<i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	+0.56	-4.80	2.19	-2.61
<i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	+0.47	-4.71	1.80	-2.91
<i>P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	+0.50	-4.74	1.84	-2.90

<sup>a</sup> Onset potential of anodic scan. <sup>b</sup> Optical bandgap in film.

The electrochemical properties of the four synthesized polymers are quite similar between them. However, PTO6buP<sup>+</sup>Br<sup>-</sup> and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) show a lower oxidation potential when

compared to the other two polymers. In particular, PTO6buP<sup>+</sup>Br<sup>-</sup> shows the lowest oxidation potential (+0.47 V) and this can be ascribed to the conjugative effect of the oxygen atom bounded to the thiophenic ring, while the more positive potential (+0.50 V) shown by P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) is probably due to a balance of inductive and conjugative effects of the two oxygen atoms directly linked to the thiophenic ring.

While the energy levels of the highest occupied molecular orbitals (HOMO) of the four polymers were evaluated by CV according to the following equation:

$$\text{HOMO (eV)} = -e (E_{\text{ox}} + 4.24)$$

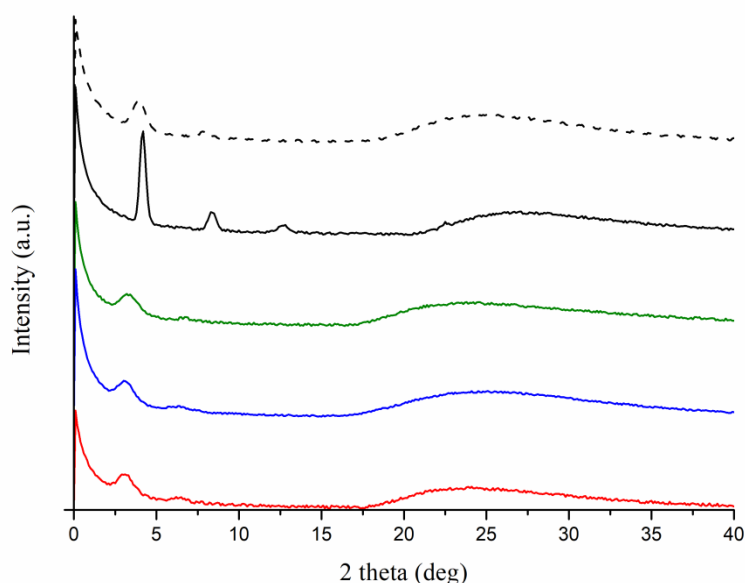
where 4.24 V is the SCE absolute potential, the energy levels of the lowest unoccupied molecular orbital (LUMO) were evaluated indirectly since the reduction potentials of the four polymers were outside the electrochemical stability window of the electrolyte. LUMO levels were then calculated from HOMO levels and the optical bandgaps ( $E_{\text{g,opt}}$ ) obtained from the UV-Vis spectra of the films with the equation:

$$\text{LUMO (eV)} = \text{HOMO} + E_{\text{g,opt}}$$

The photoactive polymer and cationic interlayers energy levels and bandgaps suggest comparable degrees of electronic delocalization over the polyconjugated backbones.

### 3.6. XRD diffraction

X-ray diffraction (XRD) patterns of polymer films cast on glass slides are shown in Figure 5.



**Figure 5.** X-ray diffractograms of PT6N(EtOH)<sub>2</sub> not annealed (dash line) and annealed (black line), PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (red line).

All the examined samples show a diffractogram pattern ascribable to an essentially amorphous polymer, according to the absence of evident melting/crystallization peaks evidenced in the thermal analysis section. They only provide for a weak diffraction peak in the  $2\theta$  range from 3.11 to 3.93 degrees (Table 5), a second one from 6.29 to 7.95 degrees, and a broad amorphous halo at wider angles.

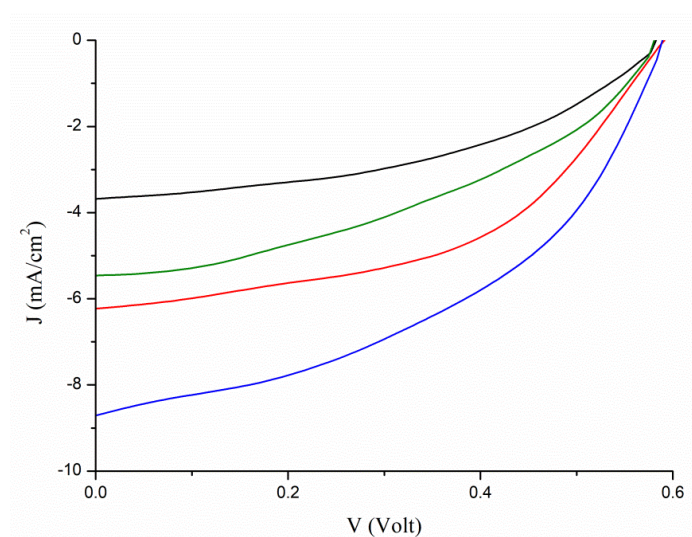
**Table 5.** Structural parameters of polymers.

<i>Sample</i>	<i>Low-angle diffractions (degrees)</i>	<i>High-angle diffractions (degrees)</i>	<i>On plane Th chains distances (Å)</i>	<i>Planes stacking distances (Å)</i>
<i>PT6N(EtOH)<sub>2</sub> not annealed</i>	3.93; 7.95	-	22.4	-
<i>PT6N(EtOH)<sub>2</sub> annealed</i>	4.17; 8.37; 12.6	22.5	21.2	3.95
<i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	3.31; 6.72	-	26.6	-
<i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	3.13; 6.33	-	28.2	-
<i>P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	3.11; 6.29	-	28.4	-

Moreover, their morphological behavior is not affected by the annealing procedure used during the preparation of the photovoltaic cell (heating at 120°C for 30 min under vacuum). Only sample PT6N(EtOH)<sub>2</sub> not annealed shows an evident increase in crystallinity after annealing (sample PT6N(EtOH)<sub>2</sub> annealed). Indeed, the XRD diffractogram of the latter shows first, second, and third-order reflections at  $2\theta = 4.17, 8.37,$  and  $12.6$  degrees, corresponding to an intermolecular spacing of polymeric chains on the XY plane of  $21.2 \text{ \AA}$  (interchain distance) as can be seen in Table 5. The small peak at  $2\theta = 22.5^\circ$  ( $3.95 \text{ \AA}$ ) can be ascribed to the  $\pi$ - $\pi$  stacking distance of PT6N(EtOH)<sub>2</sub> lamellae (Figure 6, black line). The photoactive layer can conformationally rearrange its structure towards a more compact and crystalline structure and the achieved more ordered chain conformations can be maintained at room temperature, thanks to the hydrogen bonds between hydroxy groups in the side chains. This hypothesis is also supported by the fact that, after annealing, PT6N(EtOH)<sub>2</sub> films become insoluble in alcohol/water solvents.

### 3.7. Photovoltaic properties

Cationic alcohol-soluble polymers (PT6buP<sup>+</sup>Br<sup>-</sup>, PTO6buP<sup>+</sup>Br<sup>-</sup>, P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>)) were tested as electron transport interlayers for the obtention of green BHJ solar cells based on a photoactive layer composed by PT6N(EtOH)<sub>2</sub> and C<sub>60</sub>-Ser. Photovoltaic properties were investigated by adopting the device configuration ITO/PEDOT:PSS/photoactive layer/CPE/Al. PT6N(EtOH)<sub>2</sub> was used in a 1:1 weight ratio blend with C<sub>60</sub>-Ser, while CPEs were filmed from an ethanol solution (2.0 mg/mL). Photovoltaic performance parameters are shown in Table 6, while J/V curves are reported in Figure 6.



**Figure 6.** Current density-voltage (J/V) for the best-performing cells tested under AM 1.5 one-sun illumination. PT6N(EtOH)<sub>2</sub>:C<sub>60</sub>-Ser without (black line) and with interlayer: PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (red line).

Taking as a reference the photovoltaic device composed by photoactive blend (PT6N(EtOH)<sub>2</sub>:C<sub>60</sub>-Ser) and devoid of any cationic interlayer, from Table 6 and Figure 6 is evident that the photovoltaic parameters obtained from cells prepared with CPE interlayers notably increase, and this is particularly true for the current density. The effect of CPE interlayers on the interface between the cell active layer and the Al cathode can be ascribed to the interactions between PT6N(EtOH)<sub>2</sub> and the cationic polymer, which enhances the electron injection to the Al cathode.<sup>[33]</sup> Moreover, the enhancement of V<sub>oc</sub> can be ascribed to the reduction in the electrode (Al) work function owing to the formation of an interfacial dipole between the cathode interlayer and the metal, induced by the presence of ionic salts in the side chains of the employed cationic polythiophenes. Indeed, at cathodes with an interfacial layer composed of a tetraalkylphosphonium

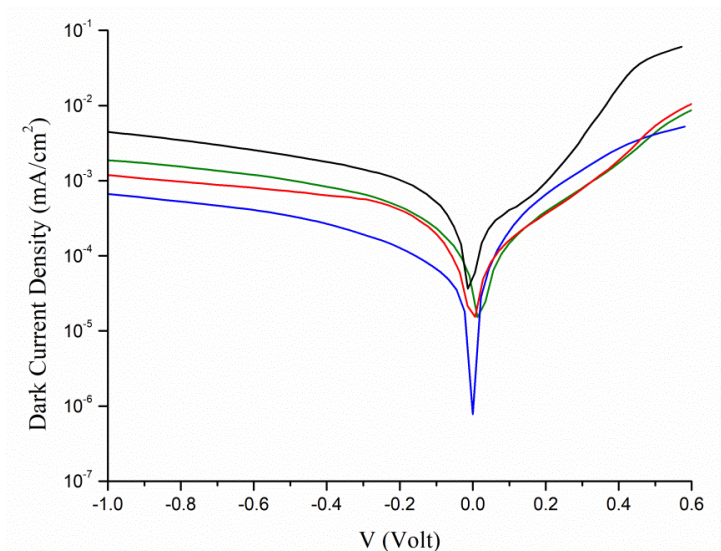
bromide polythiophene derivative, the ohmic contact with the electrons transported from the photoactive layer to the metal electrode is enhanced.<sup>[34]</sup>

Best results were obtained using the PTO6buP<sup>+</sup>Br<sup>-</sup> interlayer with an improvement of PCE of 55% with respect to the reference device. These results are particularly promising since all prepared polymers can be easily synthesized, their deposition does not require the use of toxic or harmful solvents (chlorinated and aromatics), and the simple solution process can be a wide practicable methodology for the development of efficient and sustainable OPV solar cells.

**Table 6.** Short-circuit current density ( $J_{sc}$ ), open-circuit voltage ( $V_{oc}$ ), fill factor (FF), power conversion efficiency (PCE), parallel resistance ( $R_p$ ), and series resistance ( $R_s$ ) of tested photovoltaic devices. Average performances are taken from ten devices.

<i>Sample</i>	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	<i>FF</i>	<i>PCE</i> (%)	$R_p$ (Ohm/cm <sup>2</sup> )	$R_s$ (Ohm/cm <sup>2</sup> )
<i>PT6N(EtOH)<sub>2</sub></i>	9.77±0.14	0.58±0.01	0.57±0.02	3.23±0.22	170±18	5.5±0.22
<i>PT6N(EtOH)<sub>2</sub>/</i> <i>PT6buP<sup>+</sup>Br<sup>-</sup></i>	12.1±0.15	0.60±0.01	0.58±0.03	4.21±0.18	260±22	2.2±0.16
<i>PT6N(EtOH)<sub>2</sub>/</i> <i>P(EDOT-</i> <i>MeO6buP<sup>+</sup>Br<sup>-</sup>)</i>	12.6±0.18	0.61±0.01	0.59±0.01	4.54±0.19	280±21	1.5±0.11
<i>PT6N(EtOH)<sub>2</sub>/</i> <i>PTO6buP<sup>+</sup>Br<sup>-</sup></i>	13.2±0.16	0.62±0.01	0.61±0.03	4.99±0.16	490±21	0.8±0.09

The electrical behavior of the prepared cells has also been examined in the dark, and the resulting curves are reported in Figure 7.



**Figure 7.** Semi-logarithmic current density vs. voltage curves of the prepared devices measured in the dark: PT6N(EtOH)<sub>2</sub> (black line), PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (red line).

The leakage current difference between the device without interlayer and those with the cationic interlayer is about one order of magnitude. The reduced dark current after the insertion of the interlayer can be attributed to the charge-blocking properties of the employed cationic-polythiophene materials, which can induce a positive shift of the cell built-in voltage (Table 6).<sup>[35]</sup> Moreover, the low dark current densities observed with the hole blocking layers indicate that the bimolecular recombination is reduced, thus leading to a higher photocurrent.<sup>[36]</sup>

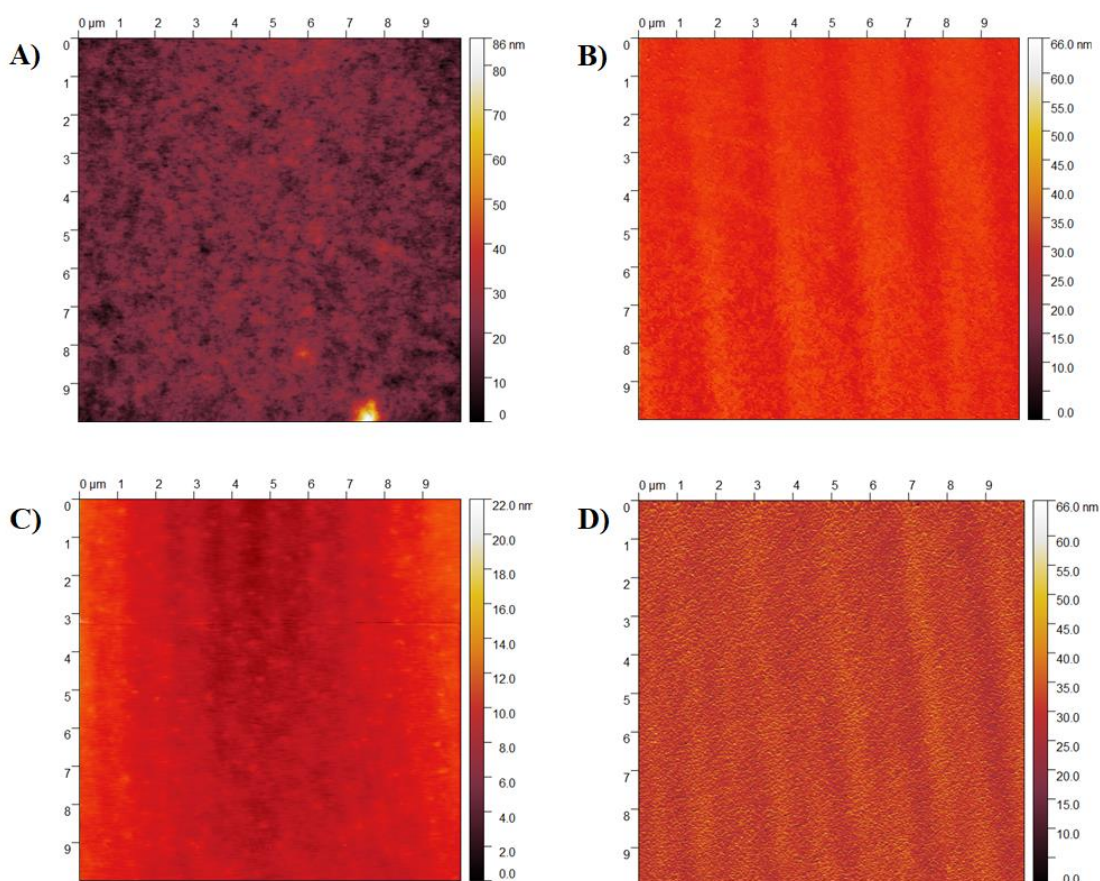
The incorporation of an interlayer in photovoltaic devices can also influence their electrical characteristics and the relevant diode parameters. Series resistance ( $R_s$ ) and parallel (shunt) resistance ( $R_p$ ) - summarized in Table 6 - were obtained by the inverse gradient of the  $J/V$  curve at the short circuit and the open circuit under illumination, respectively. After the incorporation of the cationic interlayers,  $R_s$  values decrease while  $R_p$  values increase, indicating that the ionic polythiophenes can effectively reduce the bimolecular recombination in organic solar cells.<sup>[37]</sup>

Based on the obtained results, the highest device efficiencies have been achieved with PTO6buP<sup>+</sup>Br<sup>-</sup> interlayer, which is able to positively interact with PT6N(EtOH)<sub>2</sub>, leading to a reduced hole-electron recombination in the photoactive layer as well as an increased electron extraction from C<sub>60</sub>-Ser to the cathode.

### 3.8. Morphological characterization

The morphology of the examined solar cells has been evaluated by the investigation of the surface nano-topography using AFM technique. Figure 8A shows the image of the active layer film (PT6N(EtOH)<sub>2</sub>) after the annealing procedure. The surface RMS roughness is 10.2 nm, and the

observed phase separation can be ascribed to the presence of polymer crystallites, as already evidenced by XRD measurements. The deposition of CPE layers on the active surface decreases the surface roughness leading to RMS values of 7.07, 5.08, and 6.03 nm with PT6buP<sup>+</sup>Br<sup>-</sup>, PTO6buP<sup>+</sup>Br<sup>-</sup> and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>), respectively (Figure 8B, C, D). Moreover, the high affinity of the CPE with respect to the underlying active layer leads to the complete coverage of the photoactive film, an important requisite to achieve high performance of the OPV device.<sup>[38]</sup>

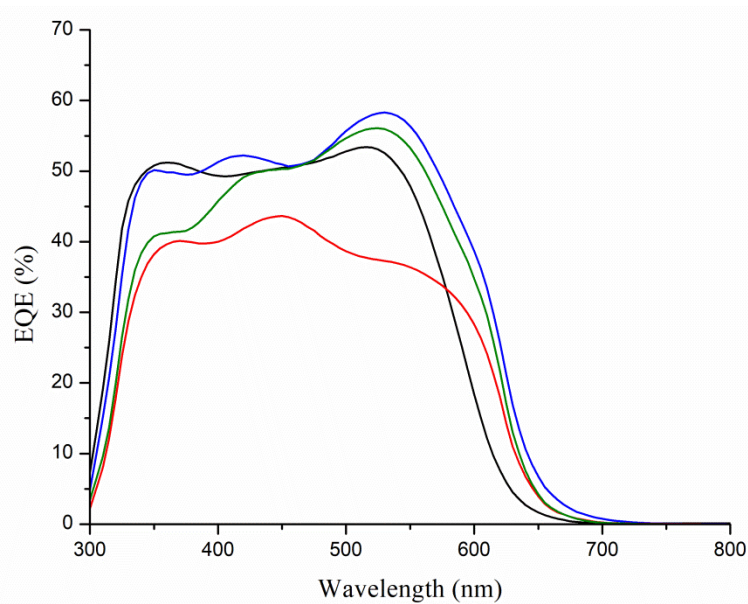


**Figure 8.** AFM topography images of PT6N(EtOH)<sub>2</sub> layer (A) and of PT6N(EtOH)<sub>2</sub> after spray-coating of PT6buP<sup>+</sup>Br<sup>-</sup> (B), PTO6buP<sup>+</sup>Br<sup>-</sup> (C), P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (D) outer layer.

### 3.9. EQE measurements

Further confirmation of the increment of electron extraction efficiency by the insertion of cathodic layers is given by the analysis of the EQE spectra reported in Figure 9. The photovoltaic cell without interfacial layer (red line) shows an EQE in the 350-650 nm range of about 40%, while those with CPE reach an EQE of about 52-58%. In particular, the cell with PTO6buP<sup>+</sup>Br<sup>-</sup> as an interfacial layer (blue line) shows a wide absorption (300-660 nm) and the higher value of quantum efficiency. The obtained results are in good agreement with the improvement in photocurrent reported in Table 6 when interlayers are employed.





**Figure 9.** EQE spectra of the tested devices: PT6N(EtOH)<sub>2</sub>:C<sub>60</sub>-Ser without (red line) and with interlayer: PT6buP<sup>+</sup>Br<sup>-</sup> (green line), PTO6buP<sup>+</sup>Br<sup>-</sup> (blue line) and P(EDOT-MeO6buP<sup>+</sup>Br<sup>-</sup>) (black line).

#### 4. Concluding Remarks

Three polythiophenes functionalized with a tetraalkylphosphonium bromide cationic group - poly[3-(6-tributylphosponiumhexyl)thiophene]bromide, poly[3-(6-tributylphosphoniumhexyloxy)thiophene]bromide and poly(6-tributylphosphoniumhexyl-1-oxymethyl-EDOT)bromide - were successfully synthesized, through a simple and effective post-polymerization functionalization reaction on the corresponding ω-alkylbrominated polymeric precursors obtained by oxidative polymerization with iron trichloride. The prepared cationic polythiophenes (CPEs), well soluble in polar solvents (water/alcohols), were then employed as cathode interlayers in BHJ photovoltaic solar cells based on the photoactive water/alcohol soluble blend made of poly[3-(6-diethanolaminohexyl)thiophene] and the serinol-functionalized fullerene derivative (C<sub>60</sub>-Ser). The comparison of photovoltaic parameters of the reference device with those of the cells with cathode interlayers showed that the insertion of the CPE improves photoconversion efficiency, and this is particularly true for the cell employing poly[3-(6-tributylphosphoniumhexyloxy)thiophene]bromide as electron-transfer polymer, achieving an efficiency increase of 55%. Electrical measurements revealed an increase in charge collection efficiency and in exciton dissociation rate, while the AFM measurements evidenced that CPEs afforded a complete coverage of the photoactive layers, owing to the high physico-chemical affinity between the two polymeric layers.

This work demonstrates that the right choice of the fundamental components of a polymeric solar cell can give promising results not only in terms of photoconversion efficiency but also regarding the environmental impact during the assembly of the final device.

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## **Conflicts of Interest**

The authors declare no conflict of interest.

## **Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon request.

## **Keywords**

CPE (conjugated polyelectrolyte), ETL (electron transport layer), water/alcohol-soluble polymer, polythiophene.

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