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Thiophene-based aldehyde derivatives for functionalizable & adhesive semiconducting polymers

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Keywords

EDOT-Aldehyde, thiophene-Aldehyde, PEDOT, conductive polymers, adhesion, electrode materials

Abstract

The pursuit for novelty in the field of (bio)electronics demands for new and better performing (semi)conductive materials. Since the discovery of poly(3,4-ethylenedioxythiophene) (PEDOT) – the ubiquitous golden standard – many studies have focused on its applications, but only few on its structural modification and/or functionalization. This lack of structural variety strongly limits

the versatility of PEDOT, thus hampering the development of novel PEDOT-based materials. In this paper, we present a short and simple strategy for introducing an aldehyde functionality in thiophene-based semiconducting polymers. First, through a two steps synthesis, an EDOT-aldehyde derivative was prepared and polymerized, both chemically and electrochemically. Next, to overcome the inability of thiophene-aldehyde to be polymerized by any means, we synthesized a trimer, in which thiophene-aldehyde is enclosed between two EDOT groups. The successful chemical and electrochemical polymerization of this new trimer is presented. The polymers suspensions were characterized by UV-Vis-NIR spectroscopy, while the corresponding films by FT-IR and four-point-probe (FPP) conductivity measurements. Afterwards, insoluble semiconducting films were formed by using ethylenediamine as crosslinker, demonstrating in this way the suitability of the aldehyde group for the easy chemical modification of our material. The efficient reactivity conferred by aldehyde groups was also exploited for grafting fluorescent polyamine nanoparticles on the films surface, creating a fluorescent semiconducting polymer film. The films prepared by electropolymerization, as shown by means of a sonication test, exhibit strong surface adhesion on pristine indium tin oxide (ITO). This property paves the way for the application of these polymers as conductive electrodes for interfacing with living organisms. Thanks to the high reactivity of the aldehyde group, the aldehyde-bearing thiophene-based polymers prepared herein are extremely valuable for numerous applications requiring the facile incorporation of a functional group on thiophene, such as the functionalization with labile molecules (thermo-, photo- and electro-labile, pH sensitive, etc.).

1. Introduction

In modern world new materials are continuously introduced targeting a plethora of applications that range from technology-relevant ones to healthcare to food industry. This evolution requires a fast response from the scientific community, which should be able to quickly prepare and scale-up easy-functionalizable materials, ready to be easily implemented and to satisfy several ecological and economical requirements. Since their discovery in the late 70s, conductive polymers revolutionized material science.[1] Among them, poly(3,4-ethylenedioxythiophene) (PEDOT) is by far the most widely used, notably the blue aqueous suspension of PEDOT:PSS (polystyrene sulfonate), which is considered as a golden standard.[2] Thanks to its amazing mechanical, electrical and biological properties, which are supplemented by the ease to process and post-treat, this commercially available polymer became the material of choice in many bioelectronics and biomedical devices.[3–5]

Research devoted to the optimization of the PEDOT:PSS suspension spans into almost three decades,[2,6,7] resulting in a performing "black box": while PEDOT:PSS is used in a wide range of applications as-is, only a while at the state of the art there are very few studies focusing on the opportunities provided by the chemical modification of the polymer's structure and the multi-functionalities that could be achieved.[8] The introduction of functional groups allowing the preparation of more versatile materials or conferring additional properties to the existing ones is strongly desired. Up to now, this has been generally pursued starting from commercial or easily synthesized EDOT derivates, such as the chlorine-[9–12] and the hydroxy-[13–17] methyl EDOT. There are only few examples of more reactive moieties that have been attached to EDOT, such as the carboxylic acid group, which has been directly connected to the oxygenated ring.[18–22] The advantages offered by an easily functionalizable moiety have been clearly shown by several

studies, for instance in case of a carboxylic group connected on a aliphatic chain[23,24] or in case of a click reaction via azide.[25–28] The carboxylic and the amine functional groups are particularly interesting thanks to the outstanding adhesion properties they exhibit,[19,29] mainly due to their high reactivity. Functionalizing EDOT with these groups would allow avoiding further crosslinking steps of PEDOT-based suspensions, otherwise necessary for the preparation of bioactive devices.[22,30–32] The group of Prof. Martin extensively studied the adhesion properties of EDOT-Acid[19] and EDOT-NH_2[29] on inorganic solid electrodes and demonstrated via XPS the chemisorption of the carboxylic acid of EDOT-Acid on activated oxide substrates.

In this framework, the aldehyde group could provide an alternative to carboxylic acid. Thanks to its strong interaction with ITO,[33] aldehyde could enhance films adhesion, while its carbonyl group could concomitantly provide a highly reactive moiety for the functionalization of EDOT. However, to the best of our knowledge, there are no studies in literature reporting the synthesis and characterization of PEDOT bearing aldehyde functional groups. This is probably due to synthetic drawbacks, including an excessive number of synthetic steps along with the high reactivity of the aldehyde group that renders it sensitive to reaction conditions.

In this manuscript, we present the synthesis of two thiophene-based aldehyde derivates: an EDOT-based one and a thiophene-based one. Concerning the first, following the synthetic pathway already reported by our group for carboxyl-functionalized EDOT,[22] we prepared the aldehyde derivate of EDOT in two steps. In the same way, a thiophene derivate was obtained. The commercially available 3-aldo-thiophene could be the perfect candidate for this synthesis. However, this monomer proved to be impossible to electropolymerize. Therefore, a new trimer was designed and synthesized, consisting of a thiophene-aldehyde molecule enclosed between two EDOT molecules. The two derivatives were polymerized both chemically and electrochemically.

The chemical polymerization was performed in the presence of polystyrene sulfonate (PSS). The aldehyde reactivity in the polymerized material was demonstrated in solution and in film, by crosslinking with ethylenediamine in the former case, and by grafting fluorescent polyamine nanoparticles in the latter. We proved, thus, that the aldehyde group supplies an effective tool for functionalizing PEDOT. Moreover, by means of dedicated sonication tests in phosphate buffer saline (PBS) solution as well as by XPS measurements, it was concluded that the aldehyde functionality improves significantly the adhesion of the electropolymerized films on ITO, obviating the need for chemical crosslinking.

2. Experimental section

Deuterated solvent and NMR tubes were bought from Eurisotop, 3,4-ethylenedioxothiophene (EDOT) was bought from TCI. A 30 wt% aqueous dispersion of poly(sodium 4-styrenesulfonate) with an average Mw of 200 kg/mol was bought from Sigma Aldrich. All other chemical products were purchased from Fisher Scientific. NMR spectra were recorded at ambient temperature with a 400 MHz Bruker Avance Spectrometer. Thin Layer Chromatography (TLC) was carried out on aluminum pre-coated plates (silica gel 40-60Å 400 mesh, F254, Aldrich) using hexane:ethyl acetate (Hex:AcOEt) (1/1) (v/v) as eluent. High-purity grade silica gel with a pore size 60 Å, 230-400 mesh particle size 40-63 μm was used for flash column chromatography. The electrochemical polymerizations and characterizations were performed with a Princeton Applied Research VersaSTAT 3 potentiostat/galvanostat using a three-electrode configuration where a platinium/titanium wire was used as the counter electrode, ITO coated glass substrate (with an area of 1.5 cm^2 and resistance of 10 Ω/sq) was used as the working electrode, and Ag/AgCl (3 M KCl) was used as the reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate

in dichloromethane was used as the electrolyte. 1 mM of monomer was used for each electropolymerization reaction.

*Synthesis of EDOT-CHO **(2)*** A solution of EDOT-Methyl ester 0.3g (1.5 mmol, 1 eq) in 80 mL of dry toluene, was cooled at -80 ºC with an ethanol/liquid nitrogen bath. 1.52mL of a solution of DIBAL-H 1M in toluene was added dropwise at the same temperature and stirred for 15 minutes. Few drops of acetone were added to quench the possible residue of reductant and the solution was diluted with diethyl ether 150mL and washed gently, to avoid emulsion, three times with DI water (3x100mL). After a last wash with brine (100mL) the organic solution was dried with Na_2SO_4. Then the mixture was filtered on folded paper and the solvent removed under vacuum. The oily residue was purified via flash column chromatography using a mixture of Hexane:Ethyl acetate (EtOAc) 7:3 (Rf=0.26) affording **2** as a white solid (0.223g, 87%). ^{1}H NMR (400 MHz, Chloroform-d) δ 9.76 (s, 1H), 6.45 (dd, J = 49.0, 3.7 Hz, 2H), 4.59 (t, J = 4.1 Hz, 1H), 4.38 – 4.27 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-d) δ 198.49, 100.92, 100.83, 77.65, 63.77.

*Synthesis of Trimer-CHO (**6**)* 0.3 g EDOT boronic ester (**5**) (1.1 mmol) and 0.14 g (0.51 mmol) 2,5-dibromo-3-thiophene aldehyde (**4**) were dissolved in THF (12 ml) in a flame dried Schlenk flask. The solution was degassed (through the septum by needle) with slight flow of argon for 15 minutes. Then a solution of potassium phosphate tribasic (K_3PO_4) (1 ml of 1M water solution) was added in one portion. Lastly, 18 mg of bis(triphenylphosphine)palladium(II) dichloride ($PdCl_2(PPh_3)_2$) (0.025 mmol, 5% mol of 2,5-dibromo-3-thiophene aldehyde) were added, the flask was sealed and the reaction temperature increased to 65 ºC. The reaction was performed under stirring at 65 ºC for 24h. The reaction mixture was then poured onto the water and extracted with dichloromethane (CH_2Cl_2) (3x50 ml). The collected organic phases were dried over $MgSO_4$ and evaporated under vacuum. The crude product was purified by flash column chromatography on

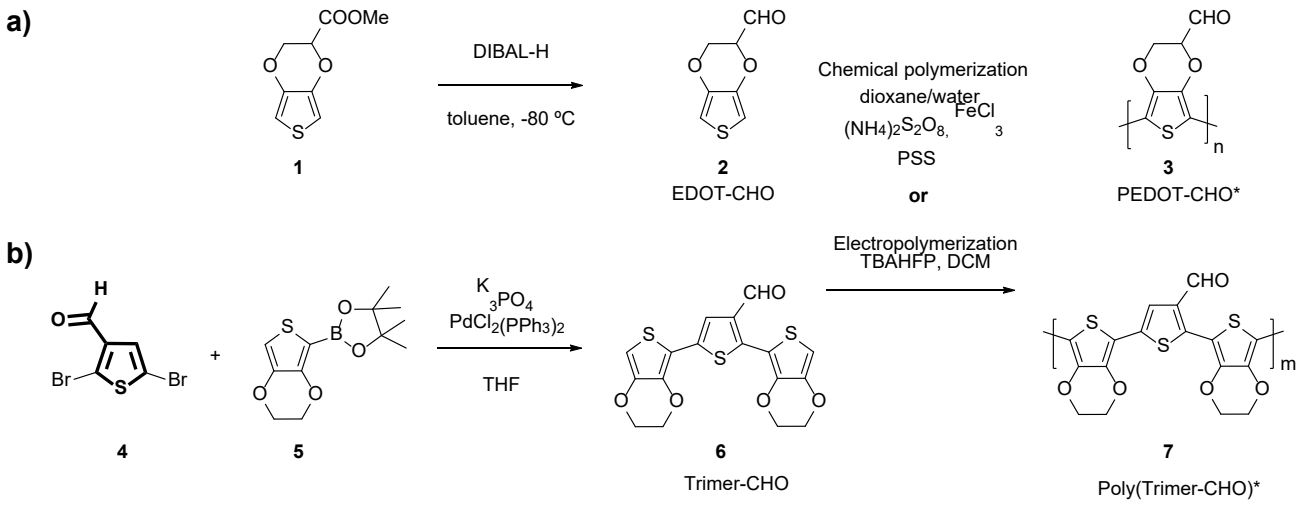
silica gel Hexane:EtOAc (1:1) and gave pure Trimer-CHO (**6**) as orange solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 9.96 (d, J = 7.2 Hz, 1H), 7.49 (m, 1H), 6.43 (m, 1H), 6.21 (m, 1H), 4.27 – 4.13 (m, 8H).^{13}C NMR (101 MHz, Chloroform-d) δ 186.08, 142.45, 140.59, 141.82, 139.68, 138.59, 136.83, 134.86, 120.86, 110.79, 101.96, 98.21, 65.08, 64.46.

*Oxidative Polymerization of EDOT-CHO (**3**) and Trimer Aldehyde (**7**)* 10 mg of Trimer-CHO or EDOT-CHO were dissolved in 2 ml of 1,4-dioxane and diluted to 10 ml with deionized (DI) water. 25 mg of polystyrene sulfonate sodium salt (PSS), 20 mg of ammonium persulfate $(NH_4)S_2O_8$ and catalytic amount of $FeCl_3$ were added to this solution and the mixture was stirred for 15 minutes. Then, the reaction mixture was let at room temperature for 10 hours without stirring. The appearance of dark green dispersions indicated that the polymerization was accomplished.

*Electropolymerization of EDOT-CHO (**2**) and Trimer Aldehyde (**6**)* A solution of 0.1M of tetrabutylammonium hexafluorophosphate (TBAHFP) in dichloromethane (CH_2Cl_2) was used, with a 50 mVs^{-1} scan rate, between 0 V and 1 V for the polymerization of trimer-CHO and between 0 V and 1.5 V for the polymerization of EDOT-CHO; both at 1 mM concentration, using ITO on glass plate with an area of 1.0 cm^2.

3. Results and discussion

3.1 Synthesis



Scheme 1. Synthesis of monomers and polymers of a) EDOT-Aldehyde (EDOT-CHO) and, b) Trimer-Aldehyde (Trimer-CHO). *The PSS used in case of chemical polymerization has been omitted from this Scheme for clarity.

The importance of EDOT as a building block for conducting organic materials is well recognized by the community, along with the need of attaching on EDOT a highly functionalizable pendant group.[34] EDOT-COOH (EDOT-Acid) can be easily functionalized thanks to the reactive carboxyl group. Nevertheless, its preparation suffers from many tedious synthetic steps.[18] Hence, our group recently reported a new synthetic pathway that allows to accomplish the synthesis of EDOT-COOH in only two steps by the use of a glycerate derivative.[22] Similarly, herein we target to push up the reactivity of the functional group which is attached to EDOT, by exploiting at the maximum the intermediate products of the EDOT-COOH synthesis. Thus, we opt for the aldehyde moiety.

To do so, the protected methyl ester (**1**), product of the condensation between 3,4-dimethoxythiophene and methyl glycerate, was treated with diisobutylaluminium hydride (DIBAL-H), a well-known esters reductant, leading to EDOT-CHO (**2**) in 87% yield. The overall two-steps yield is 63% (Scheme 1 and Scheme S1) and the facile purification (only one flash chromatographic silica column) provides an effortless and straightforward procedure.

Concerning the synthesis of aldehyde-bearing conductive polythiophenes, commercially available 3-aldo-thiophene (Scheme 1b, structure in bold) could be a perfect candidate for the synthesis of the aldehyde-bearing monomer. Despite our numerous efforts to electropolymerize this derivate, changing different conditions, this polymerization was not successful, due to the oxidation side-reaction of the aldehyde group. Thus, we designed a new trimer, in which the thiophene aldehyde ring is enclosed between two EDOT moieties (called herein Trimer-CHO, **6**). In this way we managed to obtain a compound that can be easily polymerized (Scheme 1b).[35–38]

The Trimer-CHO was synthesized via Suzuki coupling reaction between 2,5-dibromo-3-thiophene aldehyde (**4**) and EDOT boronic acid pinacol ester (**5**) in presence of palladium catalyst. The coupling between the two reagents was achieved with a good yield and the product (**6**) was characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (SI, Section 2). The UV-Vis-NIR absorption spectrum of the Trimer-CHO exhibits a very broad absorption band between 250 nm and 450 nm, while EDOT-CHO absorbs only below 275nm (SI, Figure S7a). The emission peak of Trimer-CHO is located between 450 nm and 650 nm, with a peak at 510 nm (Figure S7b). The different absorption of the two aldehyde-bearing molecules indicates a larger extent of conjugation for Trimer-CHO with respect to EDOT-CHO.

3.2 Chemical polymerization

The chemical oxidative polymerizations were performed using EDOT-CHO or Trimer-CHO with polystyrene sulfonate sodium salt (PSS) in water. With the aim to mimic the commercially available dispersion of PEDOT:PSS (Clevios P®) and reach a broader audience, we chose a concentration in solid content of 1.3% m-m and a ratio between the conductive polymer and PSS of 1 to 2.5.[3] Since the aldehyde-bearing monomers were not soluble in water, 1,4-dioxane was used as co-solvent. Dioxane was preferred to DMSO due to its ease of removal. The reaction was performed *via* oxidative chemical polymerization using commercially available PSS as the anionic counterpart, ammonium persulfate as the oxidant and iron (III) as the catalyst, and it was carried out for 10 h at room temperature. Dark green dispersions were obtained and subsequently characterized by UV-vis-NIR spectroscopy. The absorption spectrum of PEDOT-CHO (SI, Figure S8) exhibits a polaron band at around 750 nm while that of poly(trimer-CHO) is located at around 850 nm, proving that the chemical polymerization was successful for both monomers.[39] The FT-IR spectra (Figure S9) show a strong signal at 1400 cm^{-1} that corresponds to the aldehyde bending. The carbonyl stretching appears as a small shoulder around 1700 cm^{-1} but it is not clearly distinguishable, as already reported.[22] Finally, the contact angle of DI water on PEDOT-CHO:PSS and poly(Trimer-CHO):PSS films was measured and compared to on the one of commercially available PEDOT:PSS (SI, Section 6 and Figures S10 - S12). The impact of the aldehyde moiety is clear: the addition of the carbonyl group increases hydrophobicity, resulting in contact angle values of 50.3º and 67.8º for PEDOT-CHO:PSS and poly(Trimer-CHO):PSS respectively, versus 44.1º for PEDOT:PSS.

It is noteworthy that no bipolaron band is observed in the UV-vis spectrum above 1100 nm (SI, Figure S8), in consistence with the relative low conductivity measured for the films of the two

polymers, *i.e.* 48 S/cm for PEDOT-CHO:PSS and 5 S/cm for poly(Trimer-CHO):PSS. These values are lower than the conductivity measured for the film prepared by a dispersion of commercial PEDOT:PSS (88 S/cm, Table S1), where 5%v-v of dioxane was added in order to mimic the dispersions of PEDOT-CHO:PSS and poly(Trimer-CHO):PSS. Note that conductivity of EDOT-based materials is known to improve significantly upon addition in the dispersion of high-boiling, polar solvents,[40,41] such as 1,4-dioxane. Moreover, the polar aldehyde side group is expected to have a positive impact on the conductivity of our EDOT:CHO-containing material, since such hydrogen-bonding side groups are reported in literature to enhance the conductivity of PEDOT-based materials.[42]

3.3 Functionalization of the films

Thanks to its high reactivity, the aldehyde moiety of EDOT-CHO and Trimer-CHO can act as a reaction center for further chemical modification, supplying an easy approach for the modification of the polymer physico-chemical properties and its implementation in applied materials. To demonstrate this, we provide herein proof-of-concept for two applications: a) the easy crosslinking of PEDOT-CHO:PSS and Poly(Trimer-CHO):PSS films, that is particularly interesting in biological applications and bioelectronics, and b) the post-functionalization of the two polymers with fluorescent nanoparticles.

Crosslinked conductive polymer coatings are highly desired in biological applications and bioelectronics, in order to avoid any possible re-dispersion and/or delamination of the material, which could be harmful for the biological cells.[19,43,44] Ethylenediamine was chosen as a crosslinker because it is the most simple and common commercially available diamine, and its small size does

not perturb the microstructure of the film and guarantees a decent atom economy. Ethylenediamine was added in water dispersions of Poly(Trimer-CHO):PSS or PEDOT-CHO:PSS and the as-prepared dispersions were drop-casted on glass substrates. After solvent evaporation, the drop-casted films were placed on a hot plate at 110°C for 15 minutes or they were let at room temperature overnight. The efficient crosslinking of the two polymers was demonstrated by dipping the films in a phosphate buffered saline (PBS) buffer solution. As shown in the right part of Figure 1, the crosslinked films are insoluble in PBS thanks to the reaction between the aldehyde and the amine. This reaction was confirmed by FT-IR spectroscopy that showed that the O=C-H bending related to aldehyde almost disappeared after ethylenediamine crosslinking (SI, Figure S9). Noteworthy, without ethylenediamine addition in the dispersions (left part of Figure 1) or after ethylenediamine addition in PEDOT:PSS dispersions (Figure 1, bottom right), the resulting films were readily re-dispersed when immersed in water (or buffer solution).

All films became insoluble in water and preserved their conductivity and color (SI, Table S1) for ethylenediamine amounts lower than one equivalent with respect to aldehyde. Crosslinking was also performed using a large excess of ethylenediamine, in order to check if the formed imine groups affect film properties. In this case, the PEDOT-CHO:PSS and PEDOT:PSS films almost did not change color, however the Poly(Trimer-CHO):PSS film turned from dark blue to orange. This change could be due to dedoping caused by the inclusion of imine groups in the conjugated system. This hypothesis is supported by the conductivity measurements: while PEDOT-CHO:PSS and PEDOT:PSS preserve their pristine conductivity, the one of Poly(Trimer-CHO):PSS drops by three orders of magnitude (SI, Table S1).

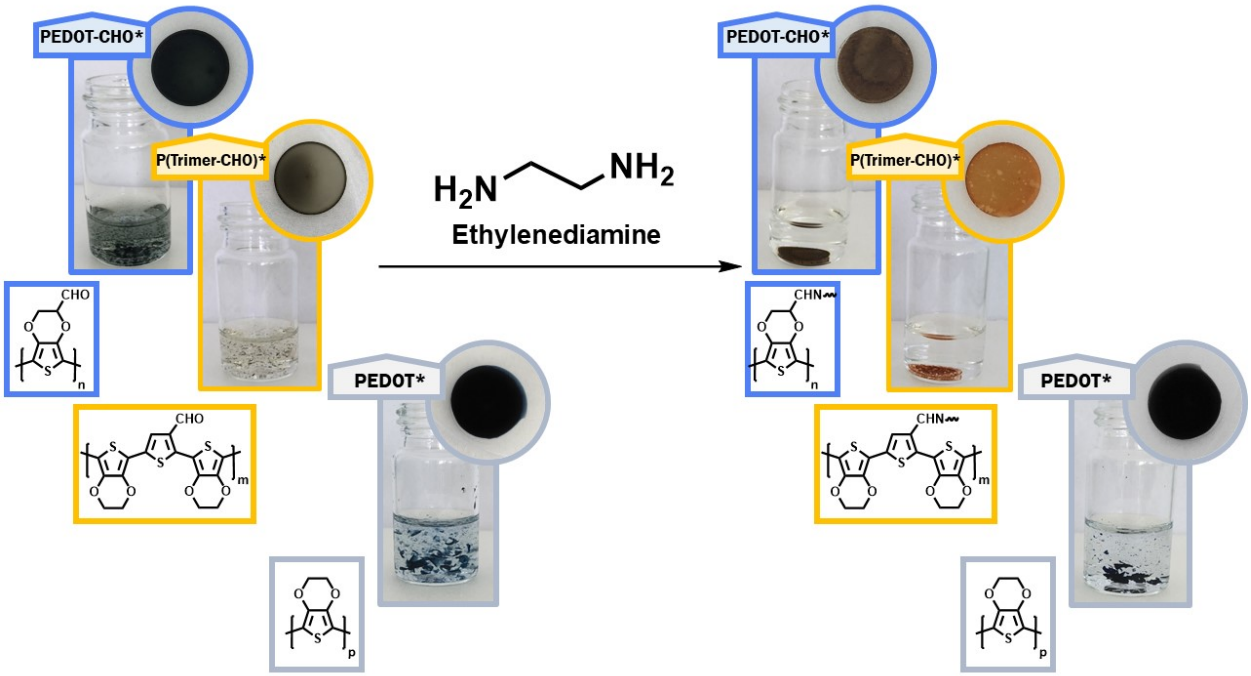


Figure 1. The molecular structures of PEDOT-CHO:PSS (blue), poly(Trimer–CHO):PSS (yellow) and PEDOT:PSS (gray) and photos of their films drop casted on glass substrates, and immersed in PBS (vials), before and after crosslinking with excess of ethylene diamine. (*PSS is omitted for clarity)

As a second example of the advantages offered by the high reactivity of the aldehyde group of these novel molecules, we performed the grafting of fluorescent polymer nanoparticles on the conducting PEDOT-CHO:PSS and Poly(Trimer-CHO):PSS films. The nanoparticles employed herein are bearing amine pendant groups and their synthesis (Scheme S4) has been reported elsewhere.[45,46] A solution containing the nanoparticles and a catalytic amount of acid was prepared and the polymer films were immersed for 30 minutes. Next, the films were thoroughly rinsed and

examined under a 365nm UV lamp. The strong blue fluorescence observed upon illumination (Figure 2, upper part) witnesses the efficient grafting of the nanoparticles, and, therefore, the efficient aldehyde-mediated functionalization of PEDOT-CHO and poly(Trimer-CHO) films. Note that the grafting of the fluorescent nanoparticles on PEDOT:PSS was unsuccessful, as shown in the upper part of Figure 2, due to the lack of the aldehyde group.

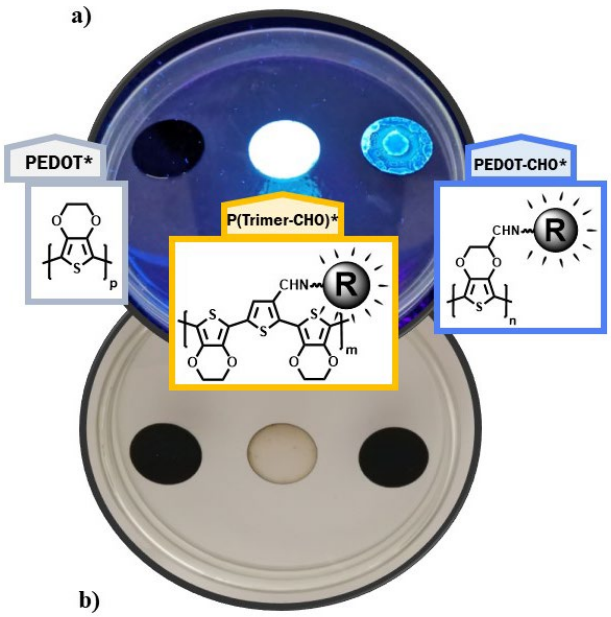


Figure 2. Drop casted films of PEDOT:PSS (gray on the left), poly(Trimer–CHO):PSS (yellow at the center), and PEDOT-CHO:PSS (blue on the right), functionalized with amine-rich non-covalent fluorescent polymer nanoparticles. The functionalized films are presented upon illumination with UV-light (365 nm) (a, upper part) or white light (b, bottom part). (*PSS is omitted for clarity)

3.4 Electropolymerization

The electrochemical polymerization of EDOT-CHO and Trimer-CHO on indium tin oxide (ITO) was investigated by means of cyclic voltammetry, in order to evaluate the potential electrodeposition of these two molecules. The voltage range employed was 0 V – 1 V for Trimer-CHO and 0 V – 1.5 V for EDOT-CHO (SI, Figure S13). This difference reflects the different oxidation potential of EDOT-CHO and Trimer-CHO, which was attributed to the different conjugation lengths of the molecules. In fact, a larger extension of conjugation, which is the case for Trimer-CHO, induces the decrease of the oxidation potential of the thiophene ring. During electropolymerization, the constant increase of current between consecutive cycles reflects the successful electrodeposition of the materials onto the ITO electrode (Figure S13). The electrodeposition is also visible by eye, thanks to the gradual appearance of the characteristic blue color, related to the polymer formation (Figure 3, 0 sec).

After electropolymerization, the resulting thin films of PEDOT-CHO and poly(Trimer-CHO) were further characterized via cyclic voltammetry, using the same experimental conditions and applying a voltage between 0 V and 1 V in both cases. The obtained voltammograms (Figure S14) exhibit the characteristic rectangular shape of PEDOT based materials.[47,48] However, a higher capacitive current is recorded in case of PEDOT-CHO with respect to poly(Trimer-CHO). This intrinsic property of PEDOT-like structure indicates that the capacitive nature of the system is not affected by the aldehyde functions The FT-IR spectra of the electropolymerized films (Figure S15) show a small carbonyl stretching peak around 1650 cm^{-1}. On the other hand, the strong signal at 1400 cm^{-1} related to the aldehyde bending is clearly visible in all the aldehyde-bearing materials. The signal at about 1100 cm^{-1} is due to the siloxane stretching of the glass substrate. Interestingly, a peak arises at around 850 cm^{-1}, which corresponds to the indium-oxygen stretching. This signal is very

strong in case of the aldehyde-bearing films deposited on ITO and almost disappears in case of bare PEDOT deposited on ITO. The appearance of the indium-oxygen stretching could be attributed to a possible interaction occurring between the oxygen of the carbonyl group and the indium atoms of the inorganic substrate.[49] Concerning the hydrophilicity of the electropolymerized films, the contact angle measurements showed that the aldehyde group is strongly affecting the wettability of the films. The contact angles of 81.9º and 88.8º measured respectively for a water drop on PEDOT-CHO and on poly(Trimer-CHO) prove that the aldehyde-bearing polymers are much more hydrophobic with respect to electropolymerized PEDOT for which the water contact angle is 12.2º (SI Section 10 and Figures S16-18).

3.5 Film adhesion

Recent literature reported that the adhesion of the PEDOT films on ITO can be enhanced by introducing carboxylic acids or amines on EDOT, *i.e.* forming EDOT-COOH or EDOT-NH_2. These moieties strongly interact with metal oxides and, thus, behave as anchoring groups.[19,29,50] Inspired by these studies, we studied the adhesion strength of the aldehyde-bearing molecules developed herein on ITO, using an ultrasonic bath. Electropolymerized films of PEDOT-CHO and Poly(Trimer-CHO) were immersed in a 20 mL vial filled with distilled water and sonicated in a 220 W ultrasonic cleaner. Interestingly, PEDOT-CHO and Poly(Trimer-CHO) films remained intact even after 5 min of sonication. On the contrary, a film of electropolymerized EDOT readily cracked after only some seconds of sonication, and it was completely detached from ITO after 5 minutes. Snapshots of the films before sonication as well as after 30 sec and 5 min of sonication are presented in Figure 3 and in the video (see SI). These results suggest strong interface interactions between ITO and the aldehyde modified polymers.[33]

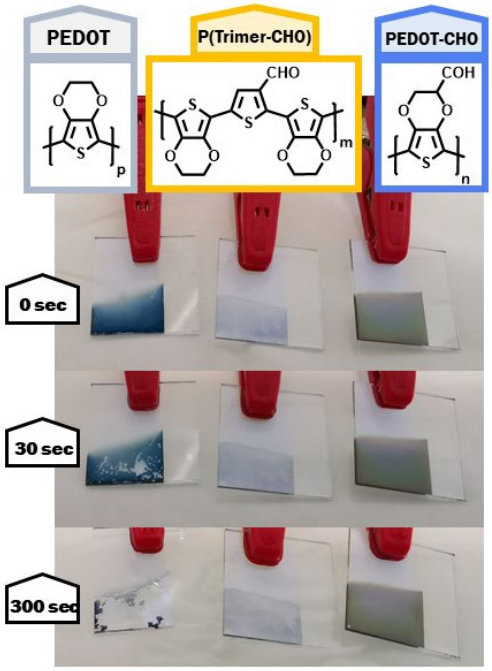


Figure 3. Films of PEDOT (left column in gray), poly(Trimer–CHO) (center column in yellow) and PEDOT-CHO (right column in blue) electropolymerized on an ITO electrode supported on glass (first row, 0 sec). The films are also presented after sonication in a PBS buffer solution for 30 seconds (2nd row) and 5 minutes (3rd row).

In order to investigate further the interaction between the aldehyde group and ITO, three ITO-coated glass substrates were immersed *i)* in ethanol, *ii)* in an EDOT-CHO ethanol solution (5 mg/ml) and, *iii)* in a Trimer-CHO ethanol solution (5 mg/ml). After 24h, the three substrates were removed from the respective solutions, thoroughly rinsed with acetonitrile, and dried under argon flow. This treatment targets the deposition of ultra-thin EDOT-CHO and Trimer-CHO films on ITO. Next, the surface of the as-prepared samples was analyzed by X-ray photoelectron

spectroscopy (XPS). The Indium In(3d) peak is apparent in all three spectra, proving that the deposited films are thin enough to allow investigation of the interface with ITO. The sulfur S(2p) signal at 169eV is absent when the ITO substrate is immersed in pure ethanol, but it is clearly detected for the other two samples, showing indirectly the affinity of both monomers towards the ITO surface (Figure S19). Additional proof is provided by the comparison between the C(1s) peak profile recorded for the bare ITO and the ITO covered by EDOT-CHO and by Trimer-CHO (Figure 4a). While in the former case the sharp carbon signal is due to external impurities, in case of EDOT-CHO and Trimer-CHO the C-O signal at 286.6 eV and the C=O at 288.2 and 289.0 eV additionally appear, in agreement with the expected spectroscopic features of EDOT-based monomers.[51] Moreover, the splitting of the C=O contribution could be attributed to different types of interactions that can take place between the aldehyde group and the oxygen of ITO, as depicted in Figure 4b, providing direct evidence on the affinity and interface interactions between the materials. This observation is in-line with the appearance of a strong indium-oxygen stretching mode at 850 cm^{-1} in the FT-IR spectra of the electropolymerized aldehyde-bearing films that, as discussed above, can be attributed to an interaction occurring between the oxygen of the carbonyl group and the indium atoms of the inorganic substrate.

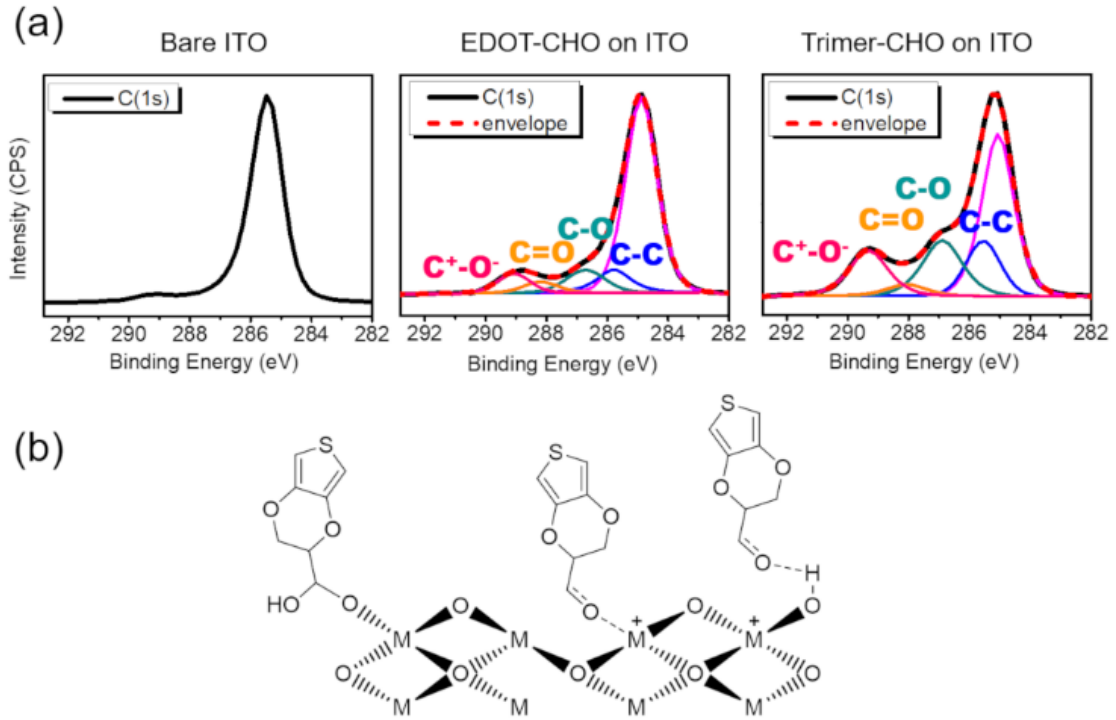


Figure 4. a) C(1s) XPS spectra of ITO-coated glasses soaked respectively in EtOH (left), PEDOT-CHO EtOH solution (center) and Trimer-CHO EtOH solution (right). b) Representation of the possible interactions between ITO surface and aldehyde.

4. Conclusions

In this work, two new aldehyde derivatives of thiophene were synthesized, and their polymerization and further functionalizations were studied in solution and in thin films. The first derivative is an aldehyde functionalized EDOT-CHO monomer. This was obtained via a facile two-steps synthesis with a yield of 64%. The second derivative, Trimer-CHO, was prepared by enclosing a 3-thiophene carboxaldehyde between two EDOT molecules, showing a lower oxidation potential as compare to EDOT-CHO for further successful electropolymerization. While the commercially available thiophene aldehyde resulted extremely hard to polymerize, the polymer

of the as-formed trimer could be easily obtained. Therefore, both PEDOT-CHO and poly(Trimer-CHO) polymers were prepared by chemical oxidative polymerization and by electropolymerization. The chemically polymerized materials were characterized by FT-IR, UV-Vis-NIR and conductivity measurements. Moreover, the suitability of the aldehyde group for introducing further chemical modifications was demonstrated both in solution and in films, in the former case performing a crosslinking reaction with ethylenediamine and, in the latter, grafting fluorescent polymeric nanoparticles on the film surface. The electropolymerized materials were characterized via cyclic voltammetry and FT-IR. In addition, XPS analysis and a visual test involving the sonication of the films revealed the presence of strong interface interaction between the aldehyde-bearing polymers and ITO, reflected in the polymers superior adhesion properties. These characteristics open a new way to the easy and quick functionalization of semiconducting polymer materials. Moreover, the mild functionalization conditions are compatible with the grafting of many labile biological compounds, either before or after film formation. Finally, thanks to the strong adhesion observed, the electropolymerized films could be suitable for a safe application in biological systems, such as *in vivo* operating devices or neuronal probes.

ASSOCIATED CONTENT

Supporting Information. Materials and methods; synthesis & NMRs of: 2.1 EDOT-Methyl ester (**1**), EDOT-CHO (**2**), 2,5-dibromo-3-thiophene aldehyde (**4**), 2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4,4,5,5-tetramethyl- 1,3,2-dioxaborolane (**5**), Trimer-CHO (**6**); UV-Vis spectra; cyclic voltammetry; films preparation and re-dispersibility tests; electrical values; FT-IR spectra; films post-functionalization and a video of sonication.

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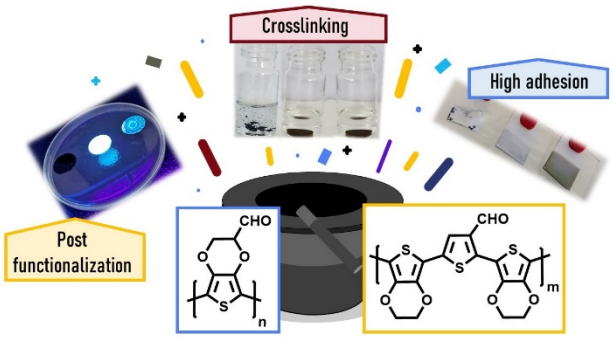
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