

Supporting Information

Thiophene-based aldehyde derivatives for functionalizable & adhesive semiconducting polymers

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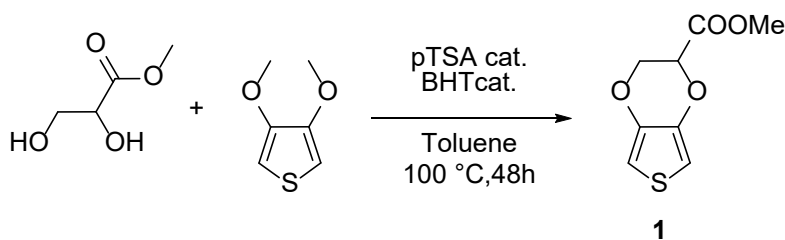
1. Materials and Methods

Deuterated solvent and NMR tubes were bought from Eurisotop. (S)-Methyl 2,3-dihydroxypropanoate (Methyl glycerate **1**) was bought from Combi-blocks via Sigma-Aldrich. 3,4-dimethoxythiophene was bought from ABCR. 3,4-ethylnediothiophene (EDOT) was bought from TCI. Poly(sodium 4-styrenesulfonate) solution average Mw 200k 30% w-w in water was bought from Sigma Aldrich. All other chemicals were supplied from Fisher Scientific. NMR spectra were recorded at ambient temperature with a 400 MHz Bruker Avance. TLC were carried out on aluminum precoated plates (silica gel 40-60Å 400mesh, F254, Aldrich) using hexane:ethyl acetate (Hex:AcOEt) as eluent. Silica gel high-purity grade, pore size 60 Å, 230-400 mesh particle size 40-63 µm was use for flash column chromatography. Fourier Transform Infrared Spectroscopy (FTIR) measurements were performed on a Brüker Alpha-p FTIR spectrometer. Spectra were collected from 4000 to 250 cm⁻¹ with the following settings: 42 scans per sample and spectral resolution: 4 cm⁻¹. The UV-Vis-NIR measures were obtained using a Perkin Elmer Lambda 950 between 200 nm and 1200 nm using quartz cuvette and preparing PEDOT:PSS suspensions diluted 1:10. The electrochemical polymerization and characterization were

performed on Princeton Applied Research VersaSTAT 3 potentiostat/galvanostat using three-electrode configuration where platinum/titanium wire used as counter, ITO used as working electrode (with an area of 1.5 cm²) and Ag/AgCl (3 M KCl) used as reference electrode. 0.1 M solution of tetrabutylammonium hexafluorophosphate in dichloromethane was also used as electrolyte. For electropolymerization reactions, 1 mM of monomer were used. Contact angle has been measured on a Krüss DSA100S at 22°C using 2 μL drop of DI water, testing 3 different films in 3 different positions.

2. Synthesis & NMRs

2.1 EDOT-Methyl ester (**1**)



Scheme S1. Synthesis of (**1**)

The synthesis has been performed as the literature. Briefly: 3,4-Dimethoxythiophene (1 eq), Methyl glycerate(5 eq) were dissolved in Toluene with of p-toluenesulfonic acid monohydrate (0.05 eq) and butylated hydroxytoluene (0.05 eq) and the mixture heated at 100 °C for 48 hours. Flash chromatographic column afford EDOT-Methyl ester (**2**) as a colorless oil in 73% yield. ¹H-NMR (400 MHz, Chloroform-d) δ 6.47 (d, J = 3.7 Hz, 1H), 6.36 (d, J = 3.7 Hz, 1H), 4.79 (t, J = 3.9 Hz, 1H), 4.45 – 4.20 (m, 2H), 3.82 (s, 3H). ¹³C-NMR (101 MHz, Chloroform-d) δ 168.31, 141.07, 140.23, 100.63, 100.55, 72.32, 65.61, 52.99.

2.2 EDOT-CHO (2)

^1H 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.

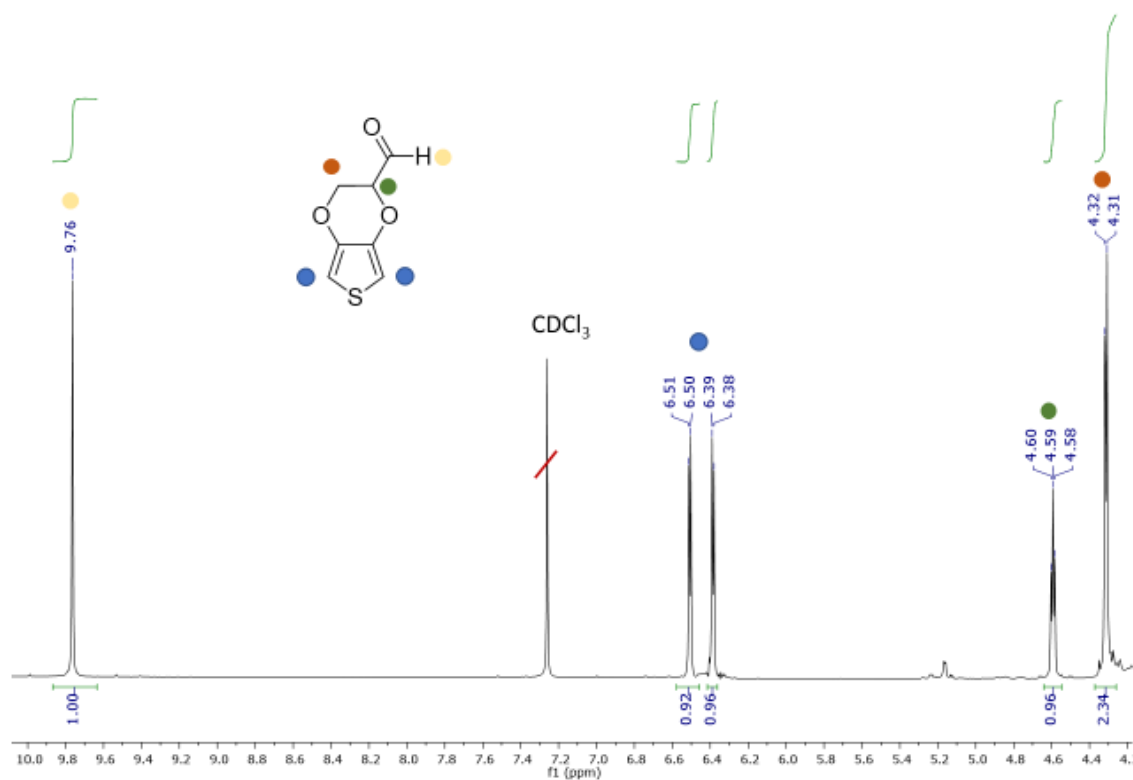


Figure S1. ^1H NMR spectrum of EDOT-CHO (1) in CDCl_3

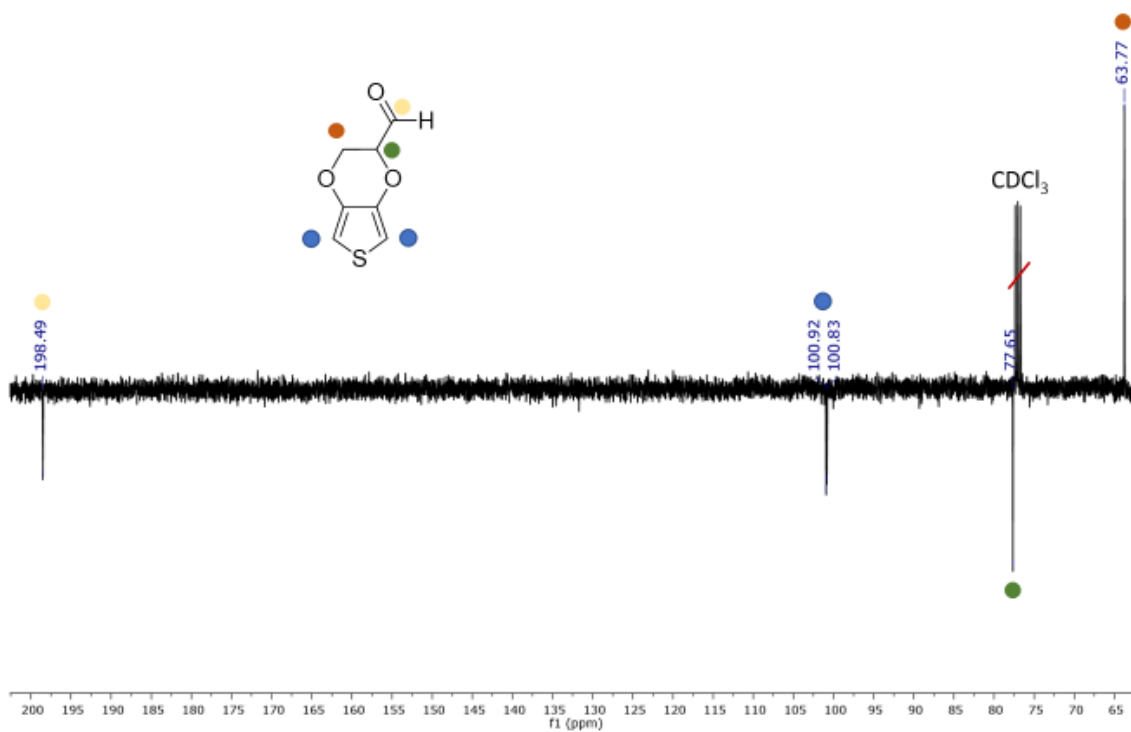
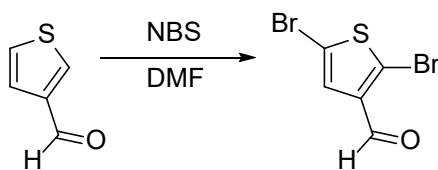


Figure S2. ¹³C NMR spectrum of EDOT-CHO (**1**) in CDCl₃

2.3 Synthesis of 2,5-dibromo-3-thiophene aldehyde (**4**)



Scheme S2. Synthesis of (**4**)

3-Thiophenecarboxaldehyde (0.672 g, 6 mmol) dissolved in 20 ml anhydrous N,N'-dimethylformamide (DMF). Then, 3.2 g (18 mmol) N-Bromosuccinimide (NBS) dissolved in 10 ml DMF were added dropwise under nitrogen flow at room temperature. The reaction mixture was then stirred for overnight at room temperature. For purification, the reaction mixture poured

onto the water and extracted with dichloromethane (CH₂Cl₂) (3x50 ml). Collected organic phase dried over MgSO₄, filtered and evaporated under vacuum. The crude product further purified by column chromatography on silica gel CH₂Cl₂. The pure 2,5-dibromo-3-thiophene aldehyde obtained as a yellowish solid. ¹H NMR (400 MHz, CDCl₃) δ 9.73 (s, 1H), 7.19 (s, 1H)

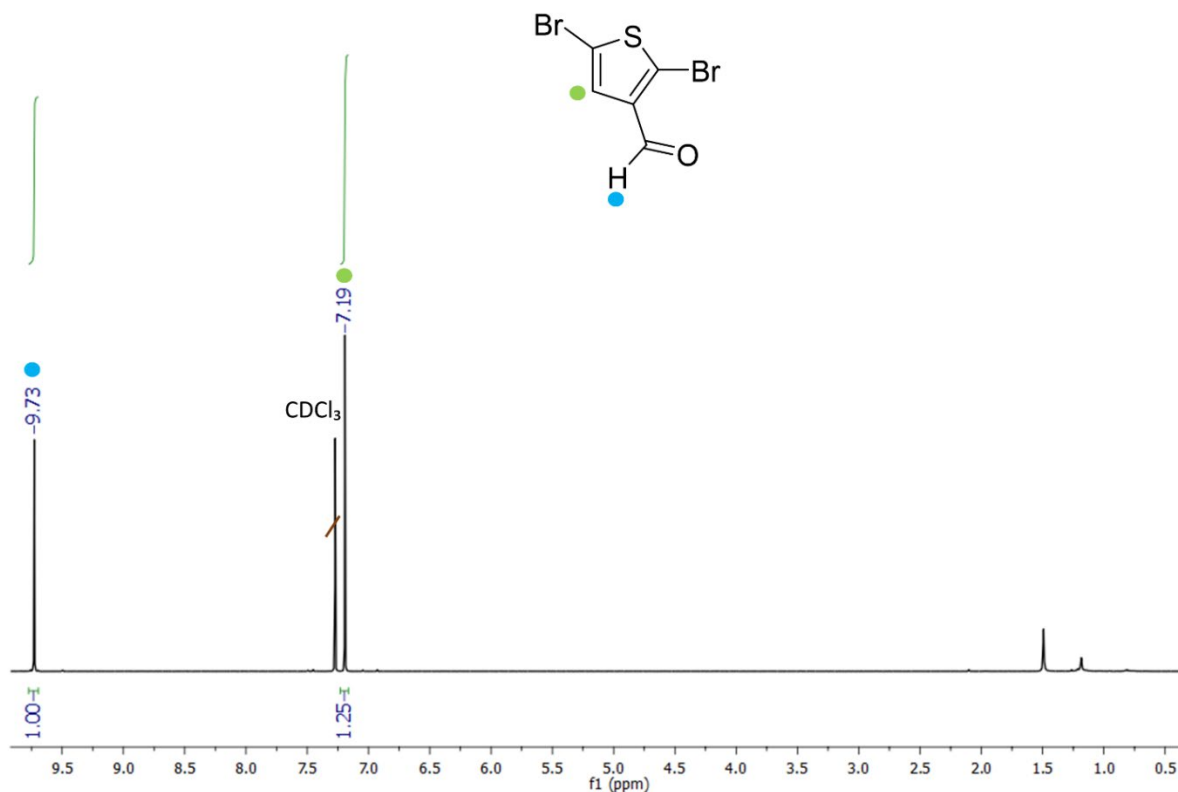
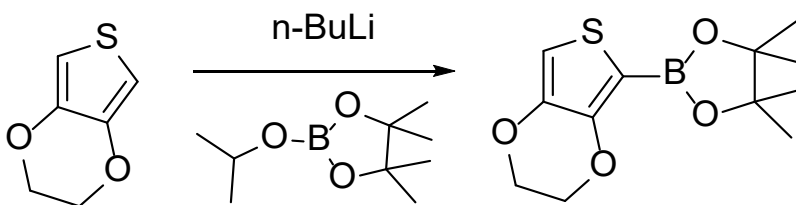


Figure S3. ¹H NMR spectrum of 2,5-dibromo-3-thiophene aldehyde (**4**) in CDCl₃

2.4 Synthesis of 2-(2,3-dihydrothieno[3,4-b][1,4]dioxin-5-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5**)



Scheme S3. Synthesis of (**5**)

In a flame dried schlenk flash, a solution of 3,4-ethylenedioxythiophene (EDOT) (1 g, 7 mmol) in dry THF (15 mL) was introduced under an argon flow. After cooling the solution to $-78\text{ }^{\circ}\text{C}$ (with ethanol-liquid nitrogen bath) a solution of n-BuLi 2.5 M in hexane (3.1 mL, 7.7 mmol) was added dropwise through the septum via syringe. Then, the temperature was slowly increased to $0\text{ }^{\circ}\text{C}$ with an ice bath and the mixture stirred 30 min. After cooling again the temperature at $-78\text{ }^{\circ}\text{C}$, 2.8 ml (14 mmol) 2-isopropoxy-4,4,5,5'-tetramethyl-1,3,2-dioxaborolane were added. The reaction mixture was slowly reach room temperature and the mixture was stirred for further overnight. For purification, the reaction mixture was quenched with saturated NH_4Cl aqueous solution and the mixture was extracted with diethyl ether (Et_2O) (3x100 mL). The collected organic phases were washed with water and dried over anhydrous MgSO_4 . After removal of the solvent under reduced pressure, crude oily product was dried under vacuum. Lastly, trituration of it with methanol gave pure EDOT boronic acid pinacol ester. ^1H NMR (400 MHz, CDCl_3) δ 6.56 (s, 1H), 4.25 – 4.20 (m, 2H), 4.13 – 4.08 (m, 2H), 1.27 (s, 12H).

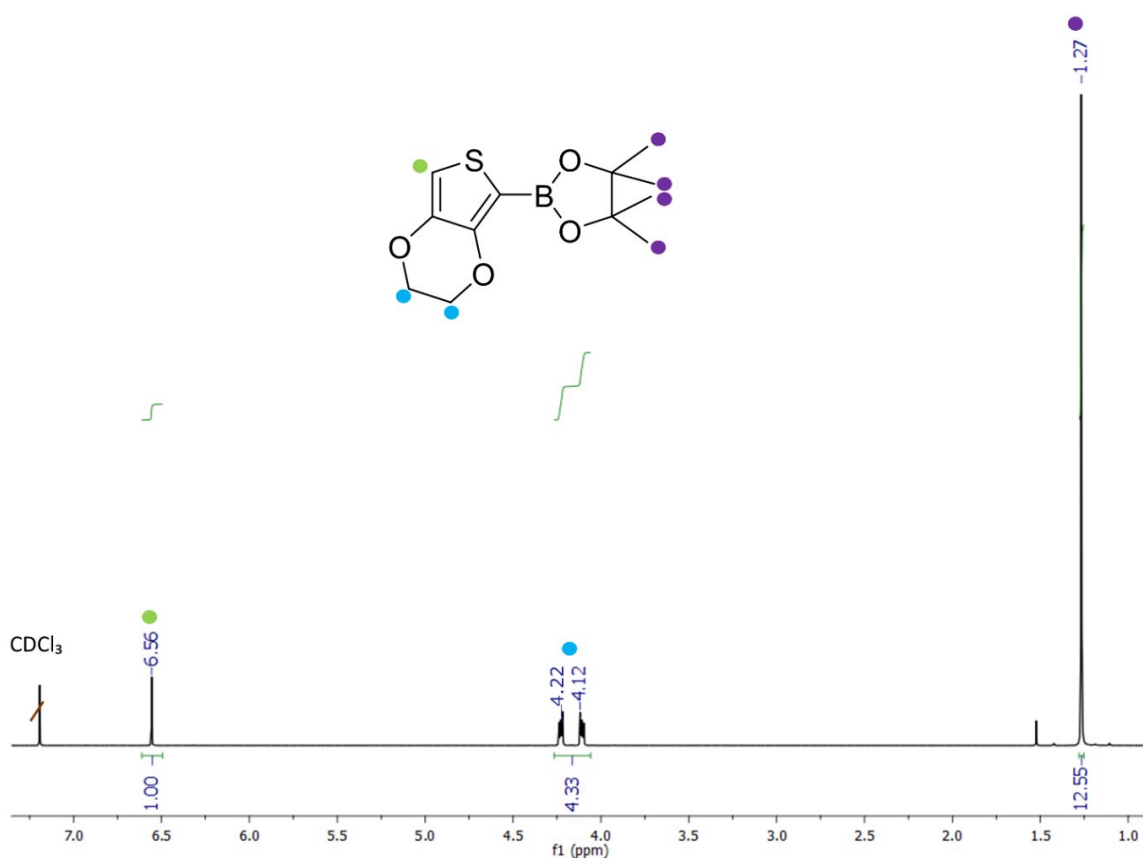
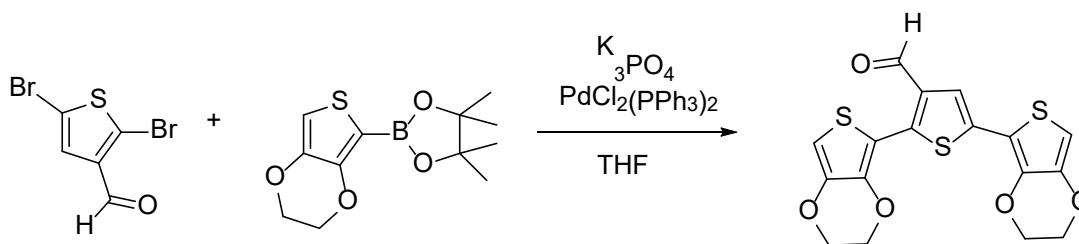


Figure S4. ^1H NMR spectrum of EDOT boronic ester (**5**) in CDCl_3

2.5 Synthesis of Trimer-CHO (6)



Scheme S4. Synthesis of (6)

1H NMR (400 MHz, $CDCl_3$) 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, $CDCl_3$) 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.

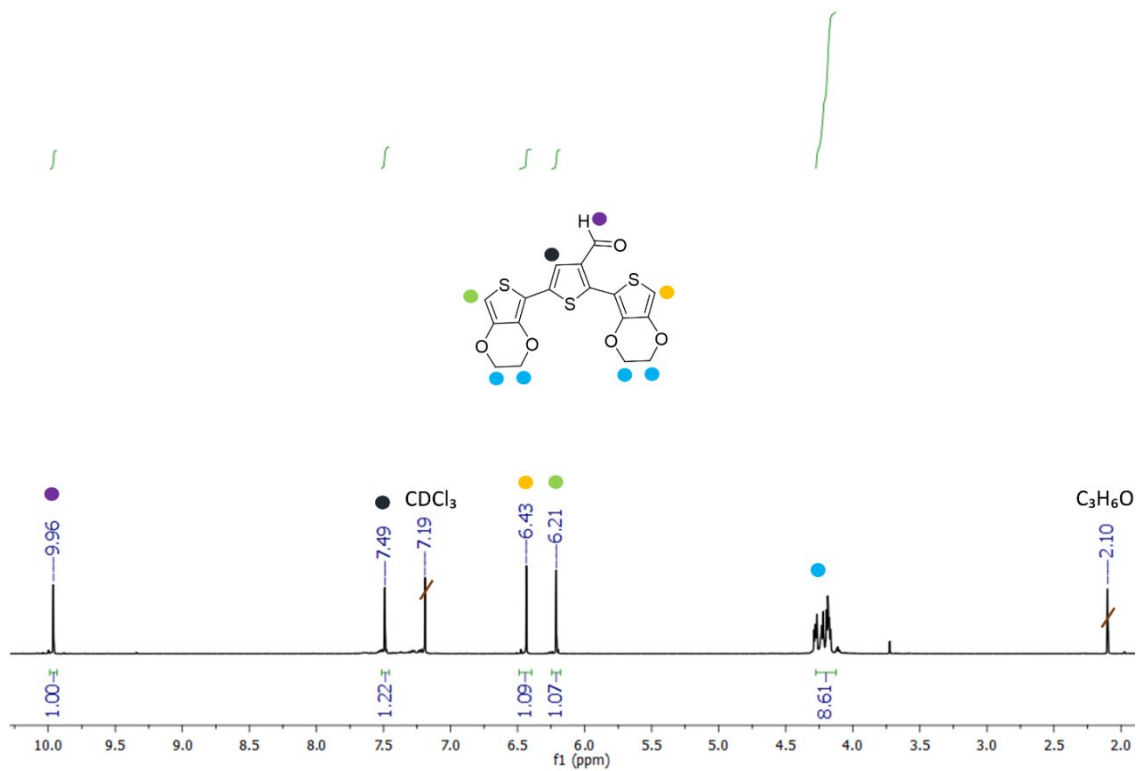


Figure S5. 1H NMR spectrum of trimer-CHO (6) in $CDCl_3$

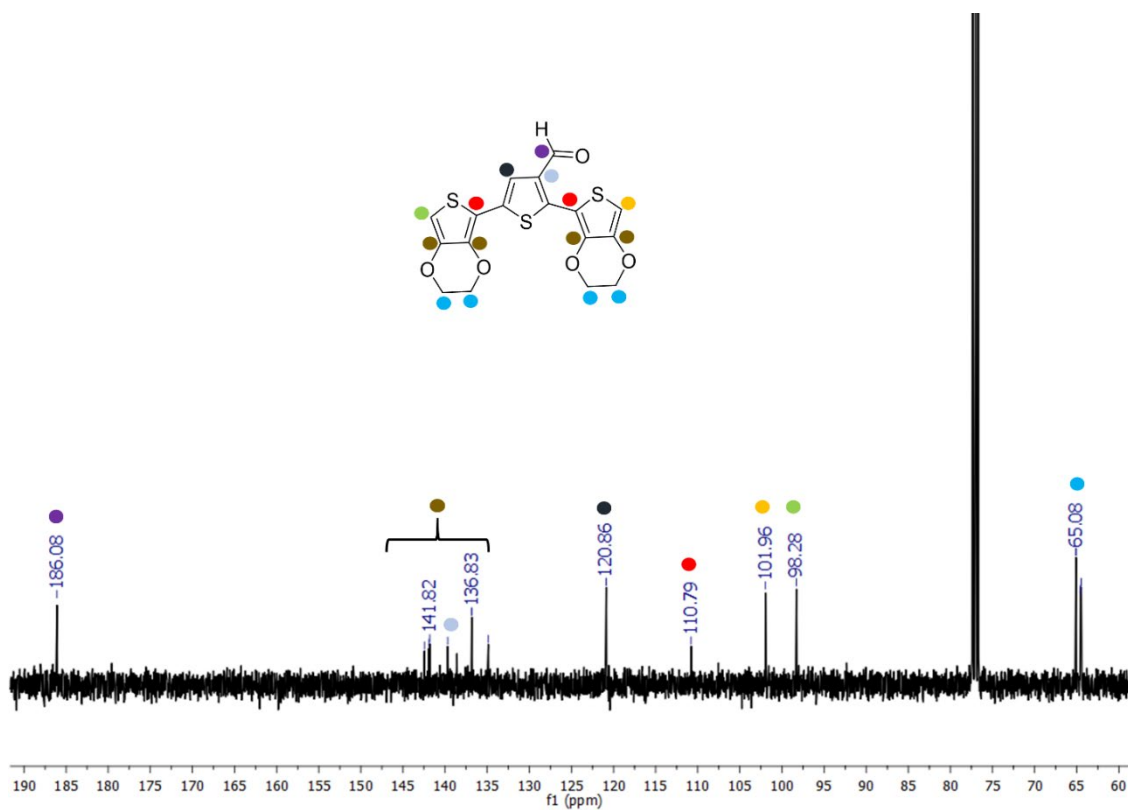


Figure S6. ^{13}C NMR spectrum of trimer- CHO (6) in CDCl_3

3. UV-Vis spectra

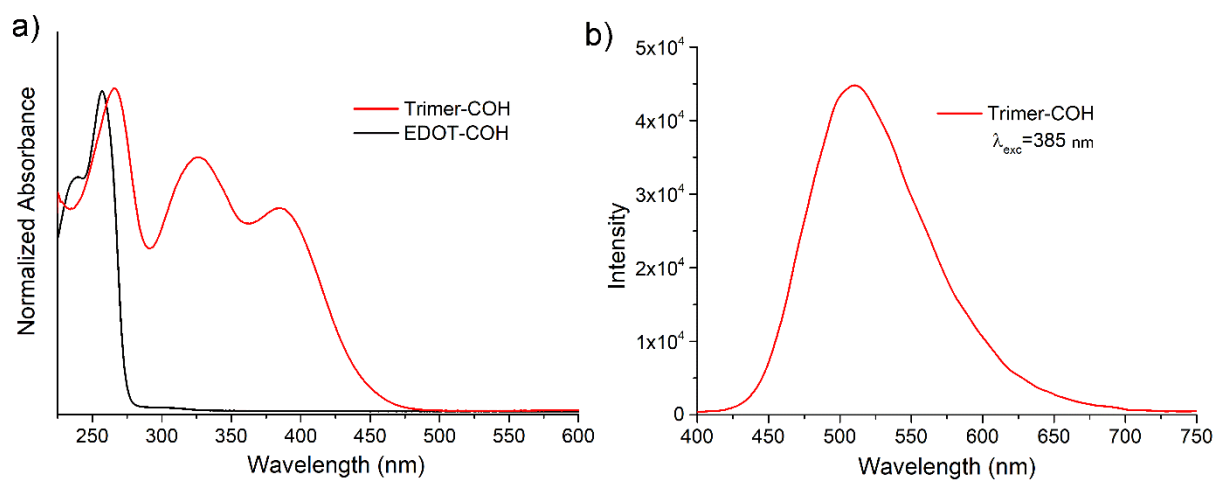


Figure S7. UV-vis spectra of the monomers in CH_2Cl_2 solution(a), emission spectrum of Trimer-CHO in CH_2Cl_2 ($\lambda_{\text{exc}} = 385$ nm)

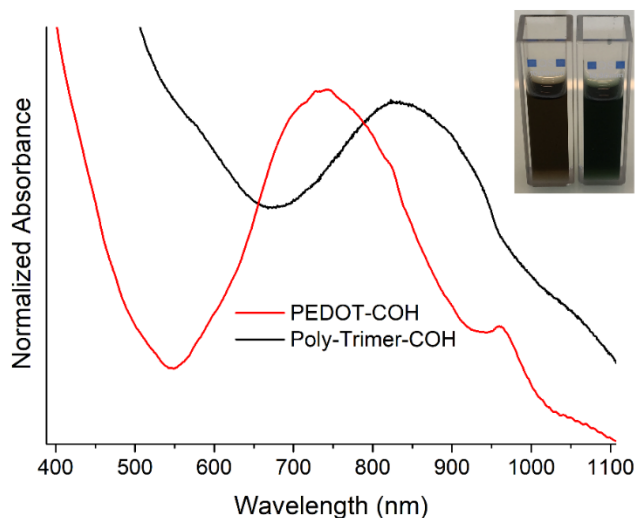


Figure S8. UV-vis spectra of PEDOT-CHO and poly(Trimer-CHO) in water. The inset figure shows the dispersion of the polymers, PEDOT-CHO (right) and poly(Trimer-CHO) (left).

4. Electrical values of chemically polymerized and cross-linked films

Table S1. Resistivity, thickness and conductivity values of drop-casted polythiophenes:PSS films.

Suspension	Resistivity (Ω/\square)	Thickness (nm)	Conductivity (S/cm)
PEDOT:PSS (Clevios PH1000) pristine	17000	760	0.77
PEDOT:PSS (Clevios PH1000) In the same condition (Dioxane 5% v-v)	314	360	88
PEDOT-CHO:PSS	255	815	48
Poly(Trimer-CHO):PSS	4580	402	5

PEDOT:PSS Ethylenediamine	15500	760	0.84
PEDOT-CHO:PSS Ethylenediamine	156	815	78
Poly(Trimer-CHO):PSS Ethylenediamine	7805	402	3.2
PEDOT:PSS Ethylenediamine excess	16200	760	0.81
PEDOT-CHO:PSS Ethylenediamine excess	212	815	57
Poly(Trimer-CHO):PSS Ethylenediamine excess	813000	402	0.03

5. FTIR spectra of chemically polymerized and cross-linked films

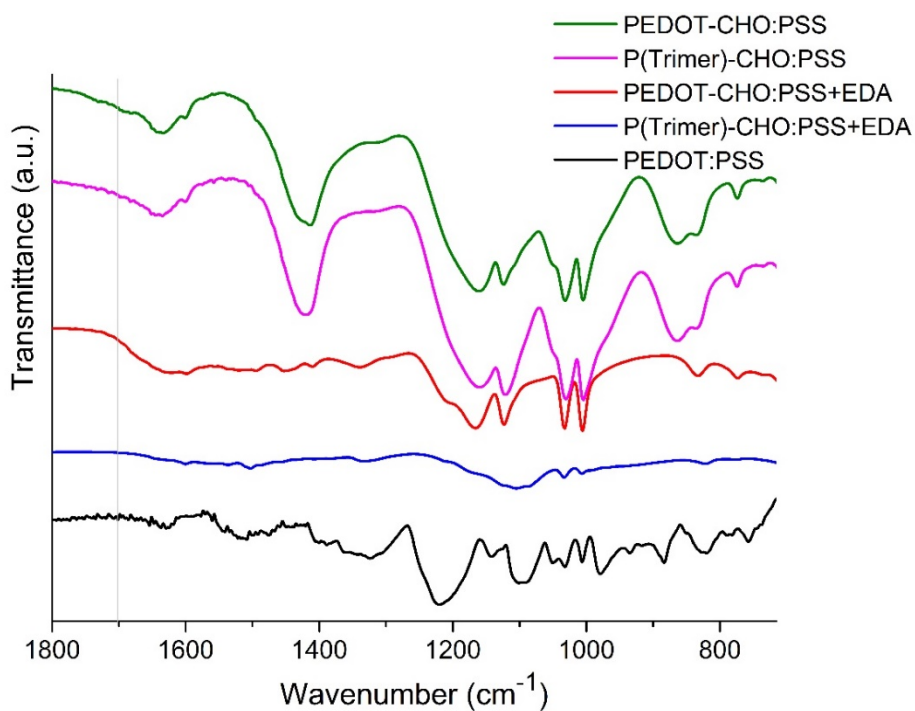


Figure S9. FT ATR-IR of PEDOT-CHO:PSS pristine and after crosslinking (green and red), polymerized Trimer-CHO:PSS pristine and after crosslinking (pink and blue) and pristine PEDOT:PSS.

6. Contact angles of chemically polymerized films

The contact angle has been measured using 2 μ L of DI water directly on the films, testing with more than 3 measures in different part of the films, using 3 substrates: for the chemical polymerized film using a drop casted film on a coverslip and for the electropolymerized film using directly the glass supported ITO electrode.

Table S2. Contact angle values of chemically polymerized films

Material	Contact angle [°]
PEDOT:PSS (Clevios PH1000)	44.1
PEDOT-CHO:PSS	50.3
poly(Trimer-CHO):PSS	67.8

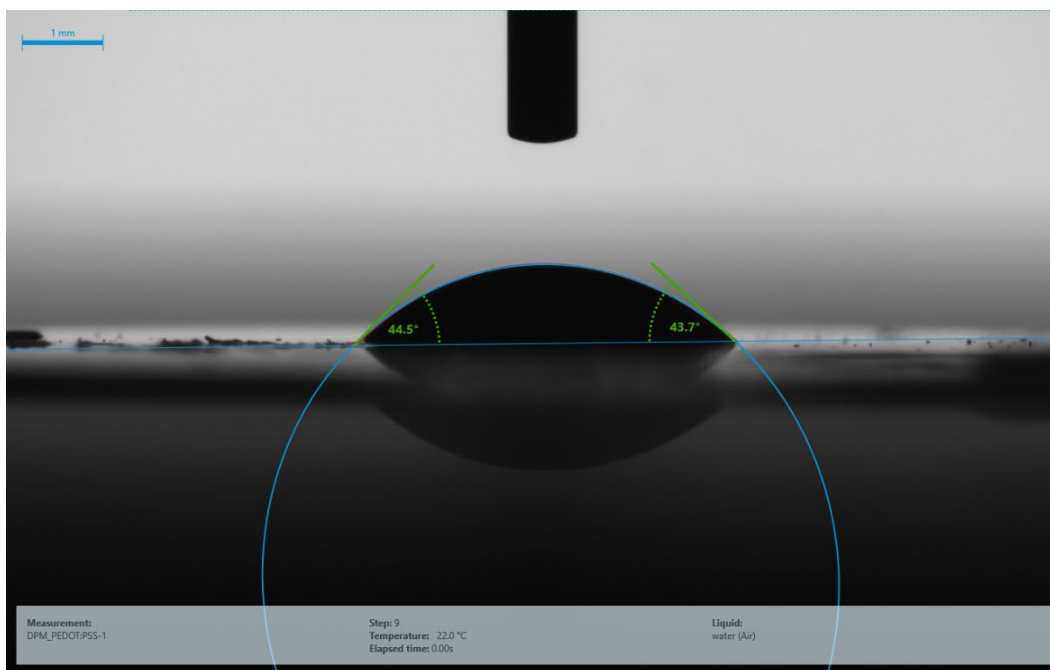


Figure S10. Contact angle measurement of chemical polymerized PEDOT:PSS

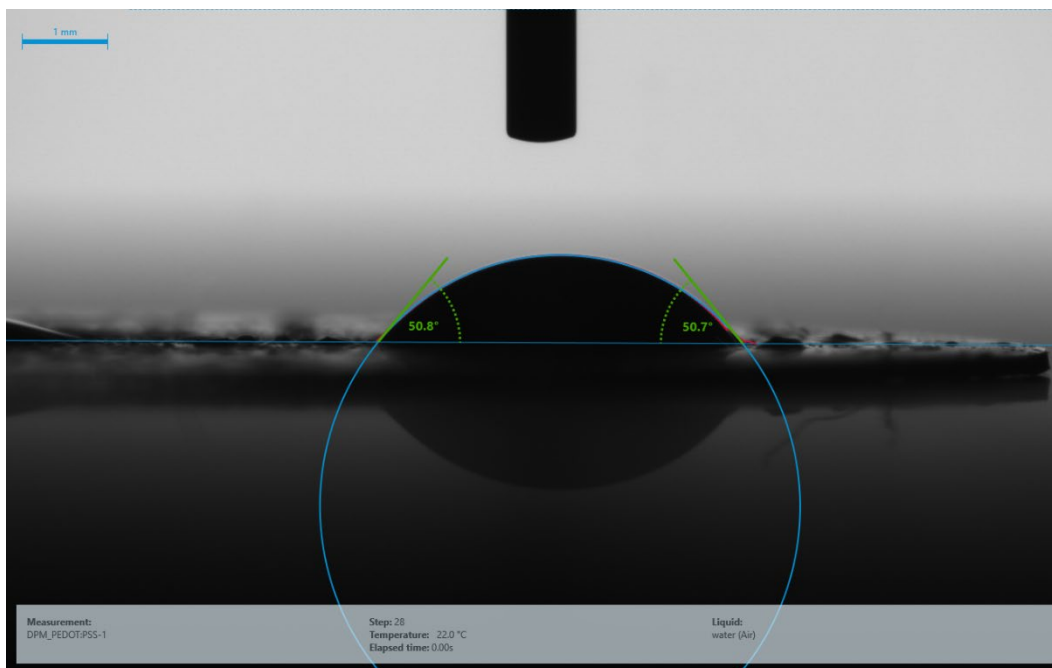


Figure S11. Contact angle measurement of chemical polymerized PEDOT-CHO:PSS

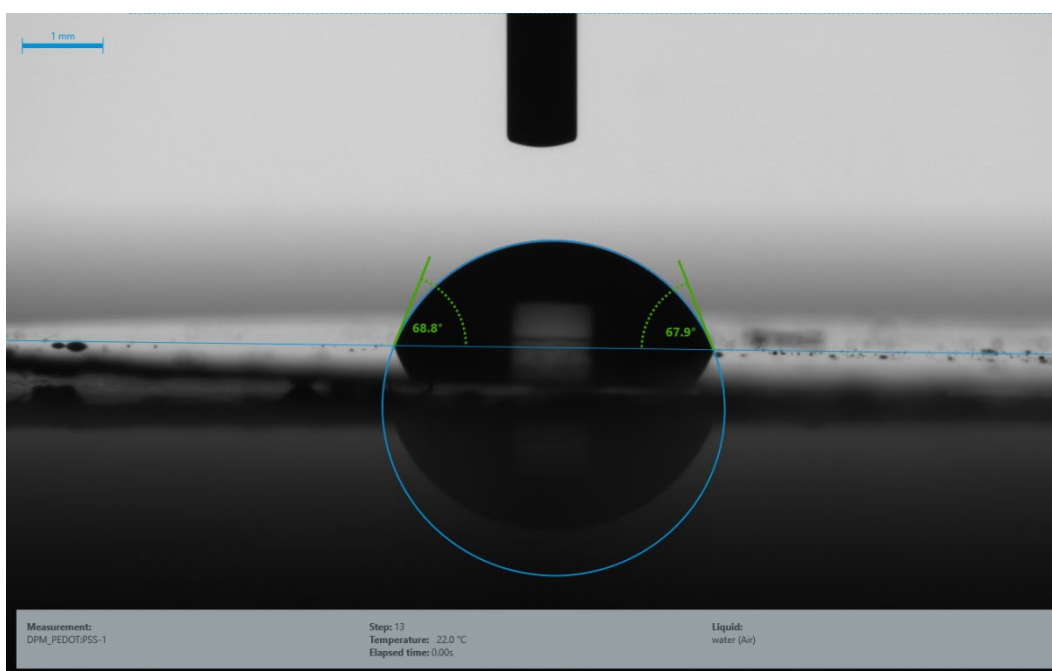
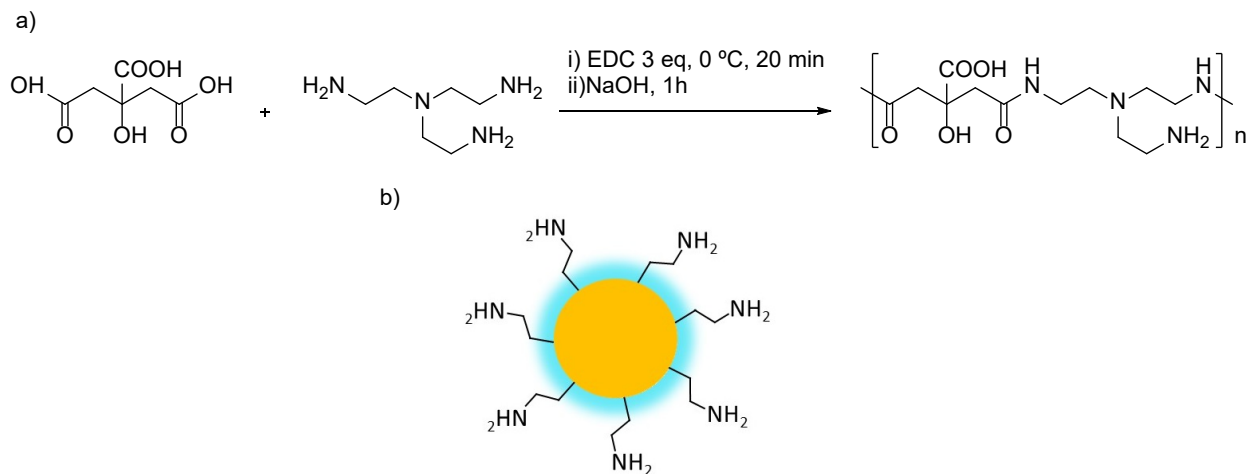


Figure S12. Contact angle measurement of chemical polymerized Trimer-CHO:PSS

7. Films post-functionalization with a fluorescent polymer

7.1 Synthesis and structure of the polymer



Scheme S5. a) synthetic scheme of non-conjugated fluorescent polymer, b) schematic representation of fluorescent nanoparticle.

A fluorescent non-conjugated polymer dots bearing amine pending groups has been used. The synthesis was repeat as already reported in literature, briefly:

0.650 mg of anhydrous citric acid (3.4 mmol, 1 eq.) and 0.510 ml of tris(2-aminoethyl)amine (1 eq.) were dissolved in 10 ml of water and the solution was cooled in an ice bath. Subsequently, 1.95 g of N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride (EDC, 3 eq.) were added under stirring and the reaction was removed from the ice bath. In 20 minutes the solution becomes intense yellow, at this point a NaOH solution was added until reaching pH=10. The reaction was stirred for 1 hour. Afterwards the crude was washed with ethyl acetate 3 times. Finally the water phase was adjusted to pH=7 with a diluted HCl solution and dialyzed against ultrapure water (MWCO = 0.5-1.0 KDa, 4 days, twice a day). After filtration on a 0.22 μ m pore-size filter, the water was removed by freeze-drying, obtaining 785 mg of product (yield in mass of 68 wt. %).

7.2 Functionalization

Round-shaped glass coverslips with size 1.3 cm of diameter were used. The different dispersion of PEDOT were drop casted and let completely dry overnight at room temperature or in oven at 50 °C for 2 hours. The resulting dark coverslips were soaked in an ethanol solution of primary-amine rich fluorescent polymer 1.5 M (in respect to the free amine) and a catalytic amount of trifluoroacetic acid 0.01 M. The films were let react 2 hours without stirring or shaking. After, gently pull out from the solution, dry at air and rinsed three time with ethanol, by soaking and let some minute in fresh solvent.

8. Cyclic voltammetry

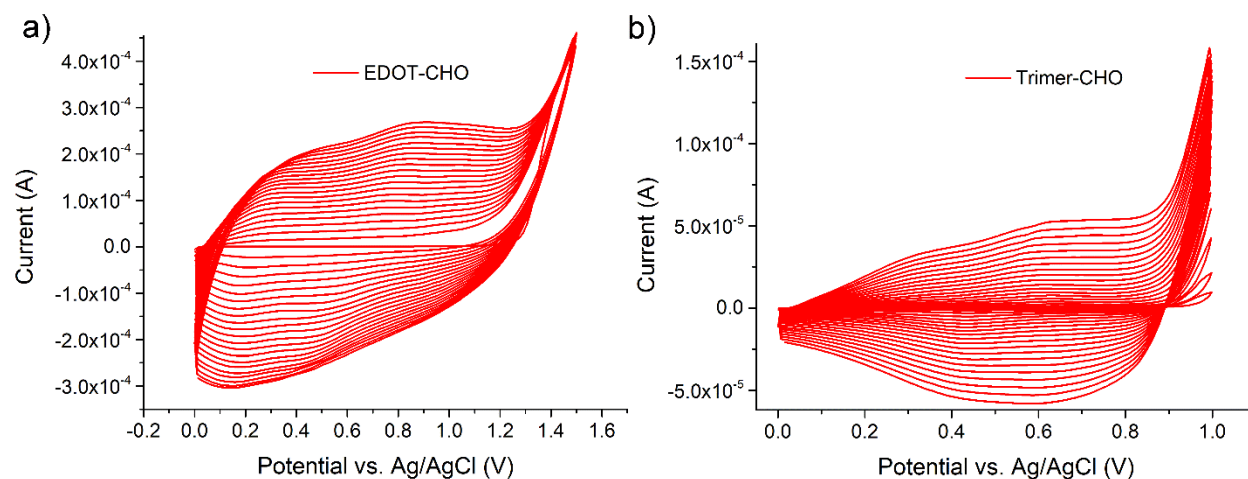


Figure S13. Electropolymerization of EDOT-CHO (a) and Trimer –CHO (b)

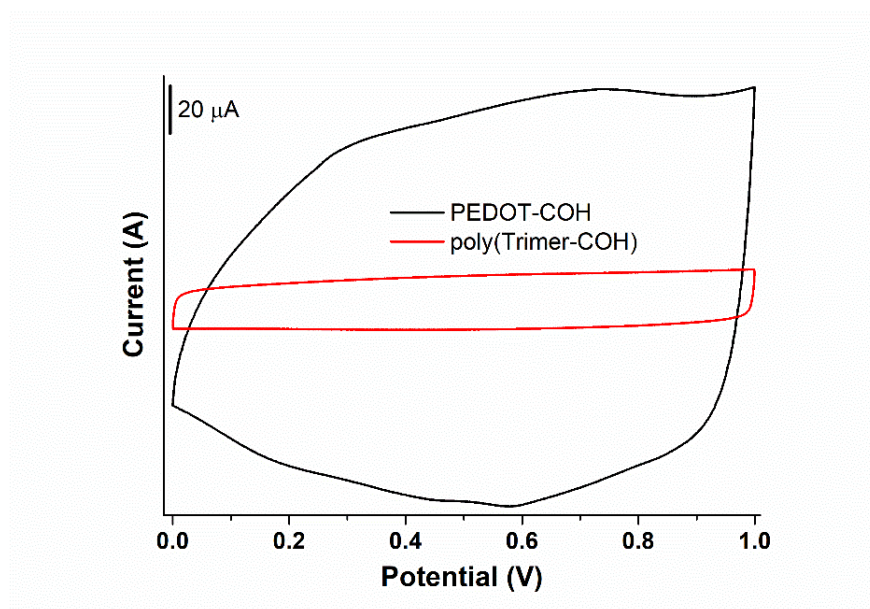


Figure S14. Cyclic voltammogram of PEDOT-CHO and poly(Trimer-CHO) in the potential range of 0-1V

9. FTIR spectra of electrochemically polymerized films

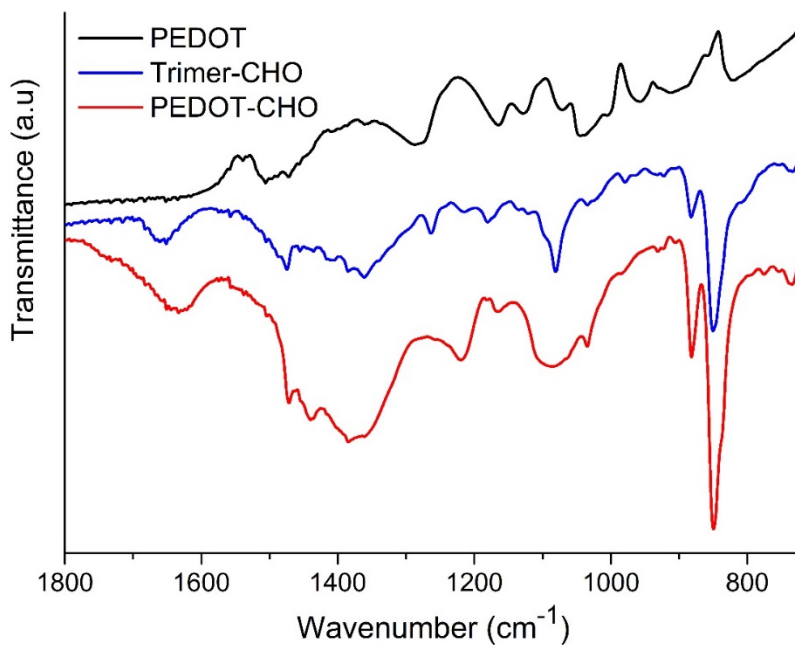


Figure S15. FT ATR-IR of electropolymerized PEDOT, P(Trimer-CHO) and PEDOT-CHO

10. Contact angles of chemically polymerized films

Table S3. Contact angle values of electrically polymerized films

Material	Contact angle [°]
Electropolymerized PEDOT	12.2
Electropolymerized PEDOT-CHO	81.9
Electropolymerized Poly(Trimer-CHO)	88.8

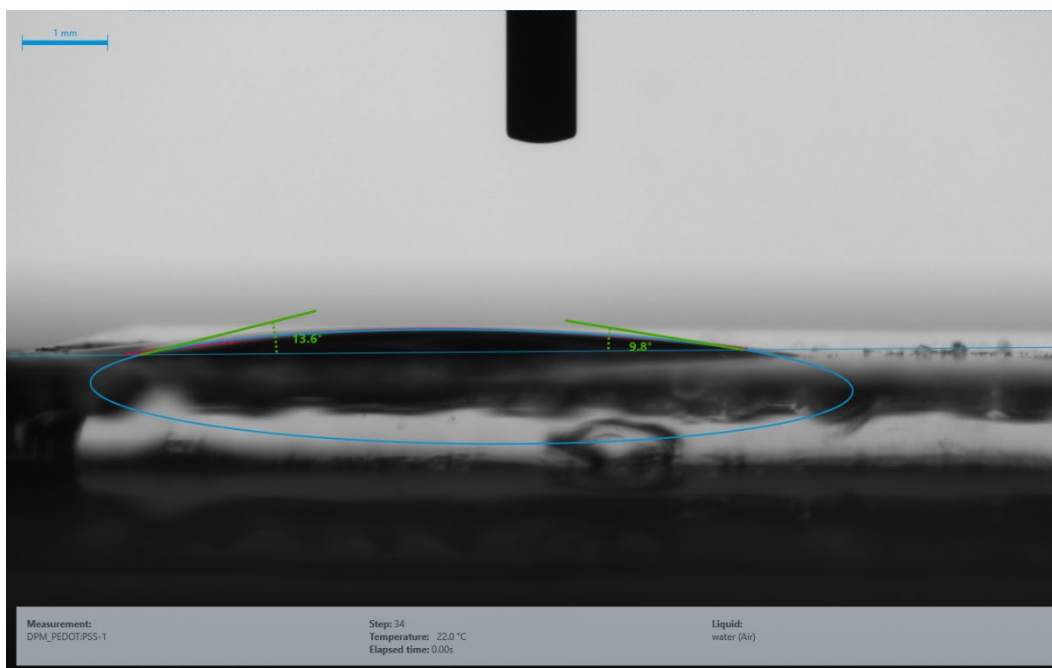


Figure S16. Contact angle measurement of electropolymerized PEDOT

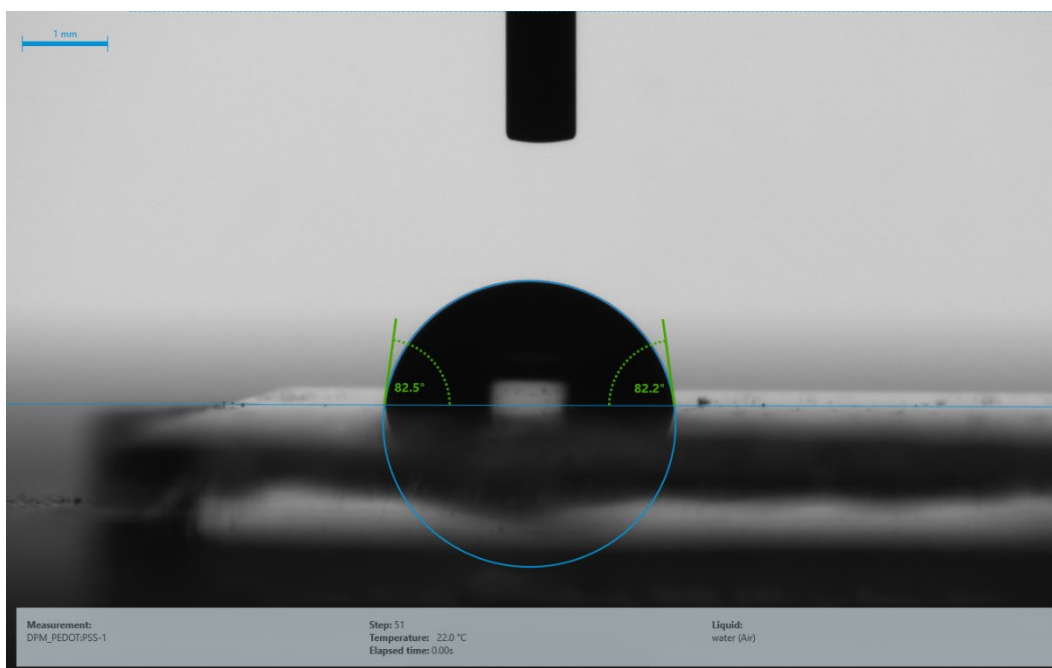


Figure S17. Contact angle measurement of electropolymerized PEDOT-CHO

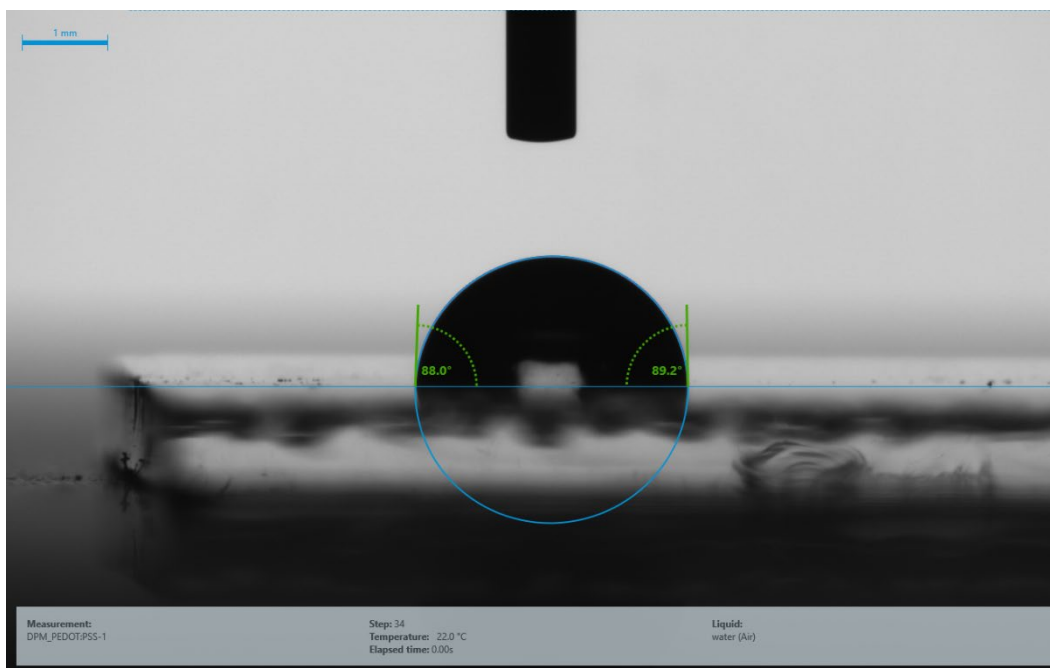


Figure S18. Contact angle measurement of electropolymerized Trimer-CHO

11. Films preparation and re-dispersibility tests

Round-shaped glass coverslips with size 1.3 cm of diameter were used. Coverslips used for the measurements were previously treated for 2 h with piranha solution which was freshly prepared mixing one part of H_2O_2 and another part of H_2SO_4 . Drop casted films were made using 0.15mL of freshly prepared dispersion and let dry at room temperature overnight.

To check re-dispersibility of the drop casted films, the resulting coverslips after crosslinking were put in a beaker with 20 mL of PBS (phosphate buffer saline) 0.01M changing this solution 3 times every 8 h.

In the case of electropolymerized films on ITO, the dried films, were sonicated for 5 minutes continuously at maximum power in DI water, as shown in the photos and in the video.

12. XPS characterization of ITO-coated glass substrates immersed in monomer solutions

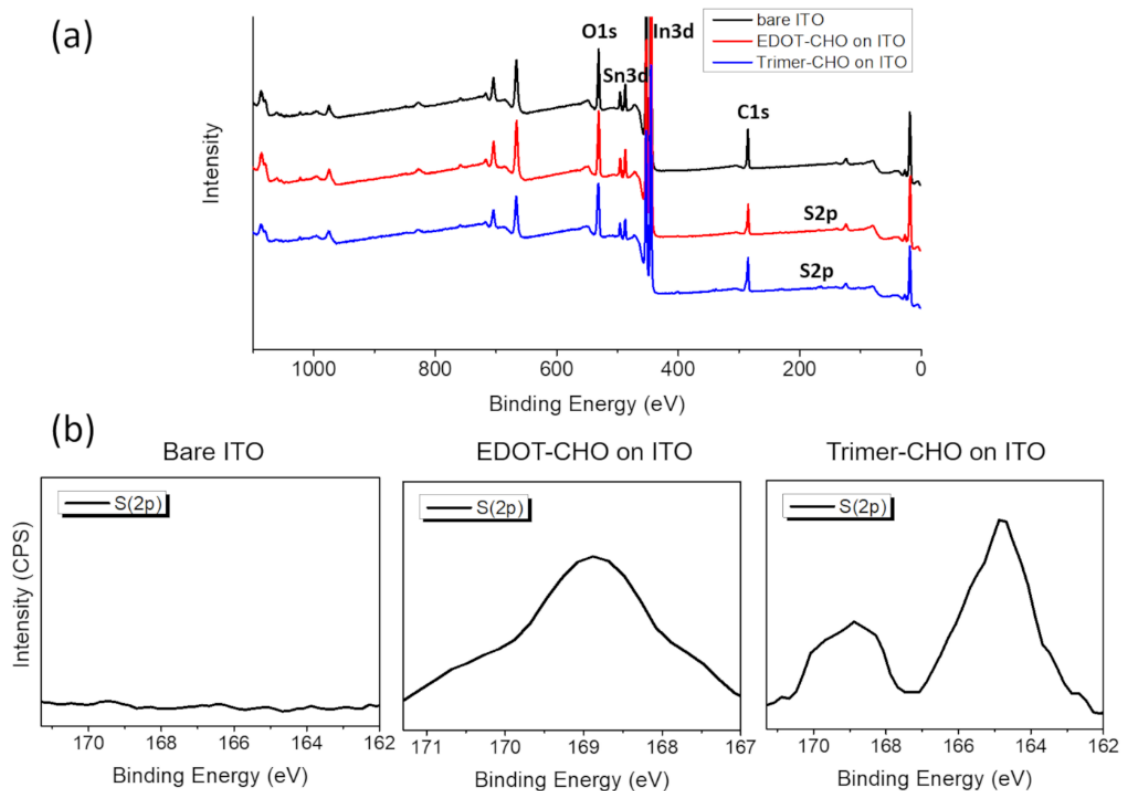


Figure S19. a) XPS surveys and b) zooms at the S(2p) binding energy range, recorded for the bare ITO substrate and those covered by EDOT-CHO and Trimer-CHO.