Electronic Supplementary Information (ESI)

for

Functionalizable and electrically conductive thin films formed by oxidative chemical vapor deposition (oCVD) from mixtures of 3-thiopheneethanol (3TE) and ethylene dioxythiophene (EDOT)

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UV-vis-NIR SPECTROSCOPY

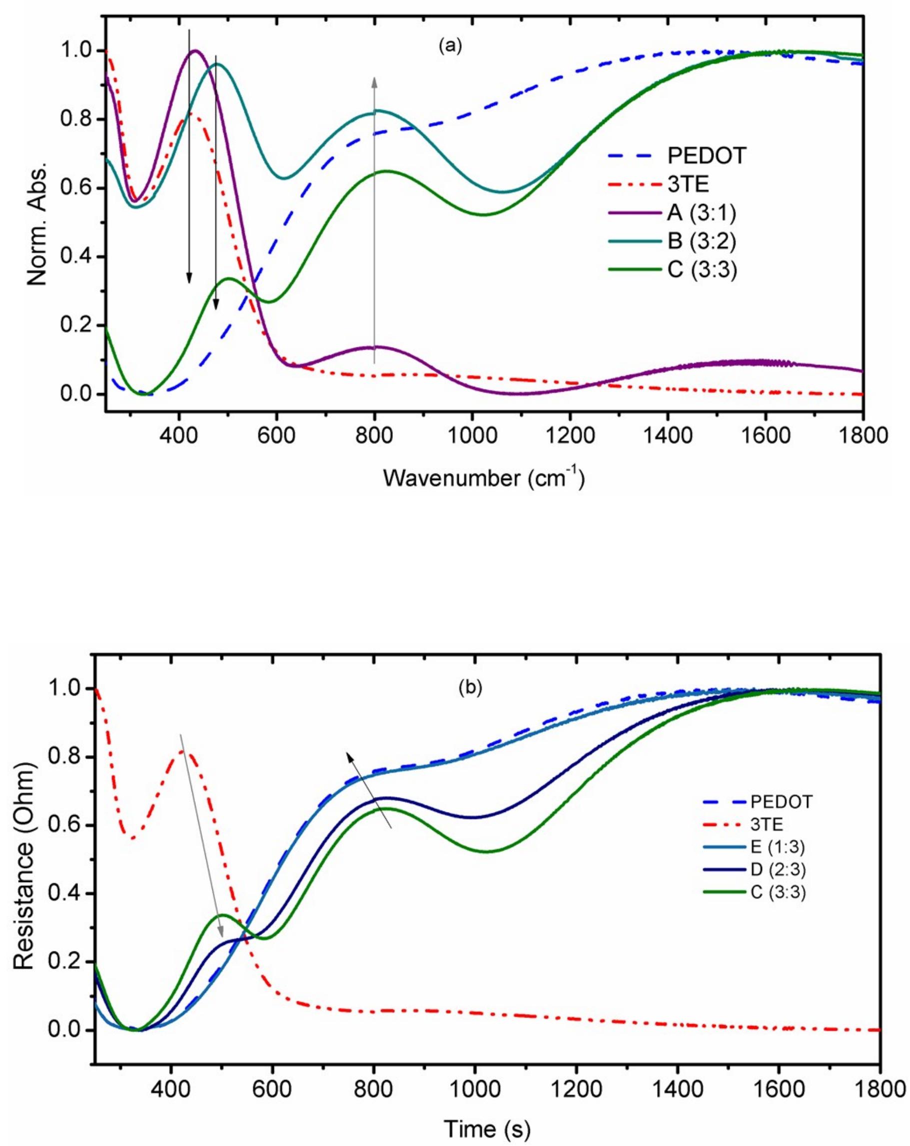

Figure S1. Thickness normalized UV-vis-NIR spectra (a) PEDOT, 3TE, A, B, and C samples; (b) for A, B, C, D, and E samples, and their optical images.

MASS SPECTROMETRY

Table S1. Proposed assignments based on exact mass measurements of the main ions (dimer to pentamer species) detected by AP-MALDI-HRMS analysis of the films obtained from the oCVD of EDOT and 3TE for the different monomer feeding ratios (samples **B** to **E** and **PEDOT**). The detailed analysis of the films shows an increasing number of P(EDOT-co-3TE) co-polymers and 3TE units with increase of the EDOT to 3-TE ratio.

Assignment	Theory $(m/z)_{calc.}$	PEDOT $(m/z)_{exp.}$	E $(m/z)_{exp.}$	D $(m/z)_{exp.}$	C $(m/z)_{exp.}$	B $(m/z)_{exp.}$
$[H(C_6H_6SO)_2CS]^+$	297.00777	-	-	297.00644	297.00544	297.00729
$[H(C_6H_4SO_2)_1(C_6H_6SO)_1CS]^+$	310.98704	-	310.98473	310.98495	310.98505	310.98581
$[H(C_6H_4SO_2)_2CS]^+$	324.96630	324.96515	324.96396	324.96419	324.96430	324.96506
$[Cl(C_6H_6SO)_2CS]^+$	330.96880	-	330.96549	330.96831	330.96842	330.96919
$[Cl(C_6H_4SO_2)_1(C_6H_6SO)_1CS]^+$	344.94806	-	344.94545	344.94571	344.94582	344.94659
$[Cl(C_6H_4SO_2)_2CS]^+$	358.92733	358.92651	358.92379	358.92406	358.92419	358.92641
$[H(C_6H_6SO)_3CS]^+$	423.02171	-	423.01205	423.01985	423.01814	423.02075
$[H(C_6H_4SO_2)_1(C_6H_6SO)_2CS]^+$	437.00097	-	436.97917	436.99714	436.99729	436.99999
$[H(C_6H_4SO_2)_2(C_6H_6SO)_1CS]^+$	450.98024	-	450.97694	450.97734	450.97750	450.97823
$[H(C_6H_4SO_2)_3CS]^+$	464.95950	464.95758	464.95614	464.95656	464.95672	464.95744
$[Cl(C_6H_6SO)_3CS]^+$	456.98274	-	456.98349	456.98389	456.98197	456.98269
$[Cl(C_6H_4SO_2)_1(C_6H_6SO)_2CS]^+$	470.96200	-	470.94106	470.96116	470.95914	470.95986
$[Cl(C_6H_4SO_2)_2(C_6H_6SO)_1CS]^+$	484.94127	-	484.93750	484.93794	484.93812	484.94110
$[Cl(C_6H_4SO_2)_3CS]^+$	498.92053	498.91974	498.91587	498.91634	498.91652	498.91959
$[H(C_6H_6SO)_4CS]^+$	549.03565	-	-	-	-	549.03495
$[H(C_6H_4SO_2)_1(C_6H_6SO)_3CS]^+$	563.01491	-	-	-	563.01400	563.01459
$[H(C_6H_4SO_2)_2(C_6H_6SO)_2CS]^+$	576.99418	-	576.96997	576.99131	576.98857	576.99507
$[H(C_6H_4SO_2)_3(C_6H_6SO)_1CS]^+$	590.97344	-	590.96636	590.97004	590.97026	590.97081
$[H(C_6H_4SO_2)_4CS]^+$	604.95271	604.95117	604.94640	604.94703	604.94726	604.95415
$[Cl(C_6H_6SO)_4CS]^+$	582.99667	-	-	-	582.99716	582.97965
$[Cl(C_6H_4SO_2)_1(C_6H_6SO)_3CS]^+$	596.97594	-	-	596.97734	596.97757	596.97810
$[Cl(C_6H_4SO_2)_2(C_6H_6SO)_2CS]^+$	610.95520	-	-	610.95277	610.95301	610.95674
$[Cl(C_6H_4SO_2)_3(C_6H_6SO)_1CS]^+$	624.93447	-	-	624.92988	624.93012	624.93394
$[Cl(C_6H_4SO_2)_4CS]^+$	638.91373	638.91264	638.90758	638.90827	638.91197	638.91242
$[H(C_6H_6SO)_5CS]^+$	675.04958	-	-	-	-	675.02759
$[H(C_6H_4SO_2)_1(C_6H_6SO)_4CS]^+$	689.02885	-	-	-	-	689.02489
$[H(C_6H_4SO_2)_2(C_6H_6SO)_3CS]^+$	703.00811	-	-	703.00678	703.00706	703.01533
$[H(C_6H_4SO_2)_3(C_6H_6SO)_2CS]^+$	716.98738	-	-	716.98374	716.98814	716.96786
$[H(C_6H_4SO_2)_4(C_6H_6SO)_1CS]^+$	730.96664	-	-	730.96724	730.96331	730.96775
$[H(C_6H_4SO_2)_5CS]^+$	744.94591	744.94255	744.94091	744.94614	744.94210	744.95097
$[Cl(C_6H_6SO)_5CS]^+$	709.01061	-	-	-	-	-
$[Cl(C_6H_4SO_2)_1(C_6H_6SO)_4CS]^+$	722.98988	-	-	722.96750	722.96779	-
$[Cl(C_6H_4SO_2)_2(C_6H_6SO)_3CS]^+$	736.96914	-	-	-	736.96920	736.98652

$[Cl(C_6H_4SO_2)_3(C_6H_6SO)_2CS]^+$	750.94841	-	-	750.94944	750.94535	750.94991
$[Cl(C_6H_4SO_2)_4(C_6H_6SO)_1CS]^+$	764.92767	-	-	764.92868	764.92447	-
$[Cl(C_6H_4SO_2)_5CS]^+$	778.90694	778.90721	778.90093	778.90652	778.90219	-

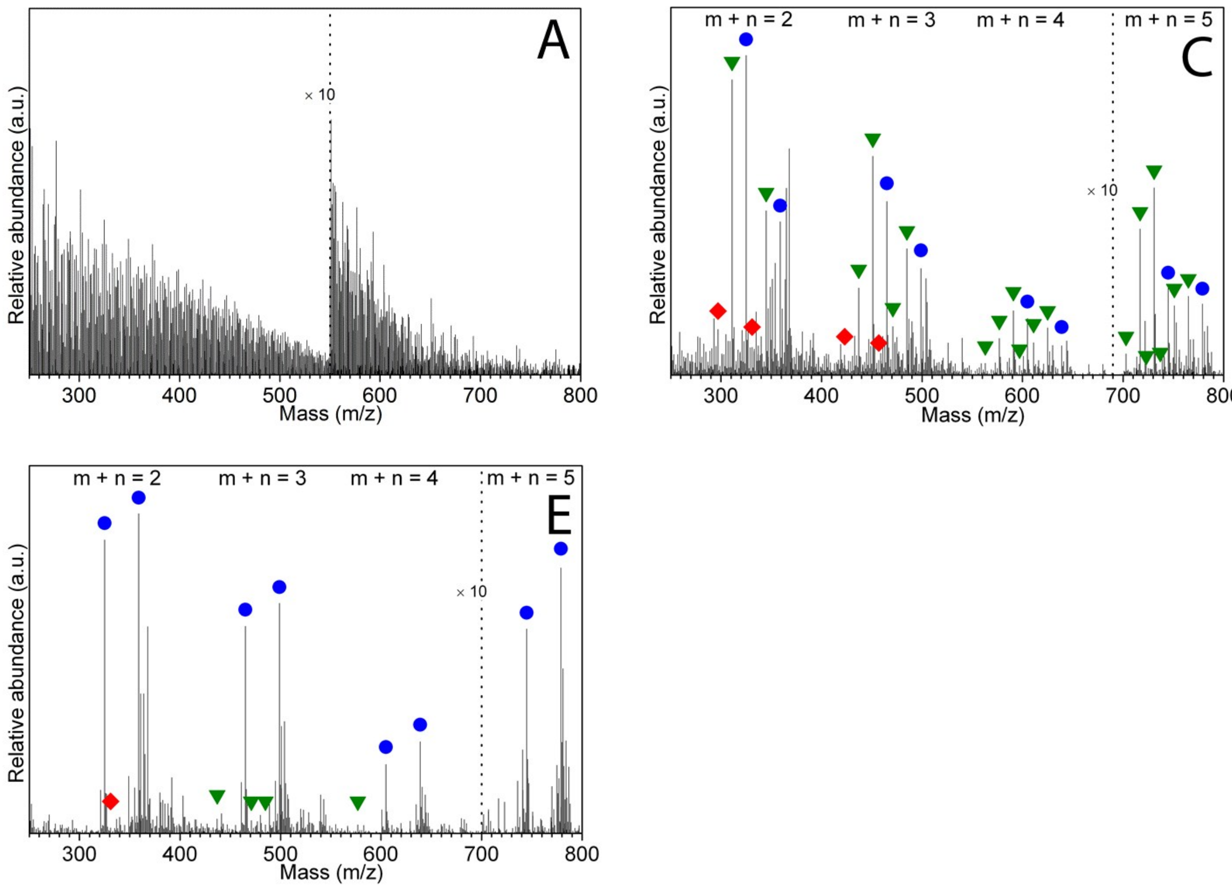

Figure S2. Detailed view of the AP-MALDI-HRMS spectra (m/z = 250−800) of the films obtained from the oCVD of EDOT and 3TE for the different monomer feeding (3TE:EDOT) ratios (3:1), (3:3), and (1:3) labelled as **A**, **C**, and **E** respectively. Two different series of ions with thioformyl and hydrogen $[H(C_6H_4SO_2)_n(C_6H_6SO)_mCS]^+$ or chlorine terminal groups $[Cl(C_6H_4SO_2)_n(C_6H_6SO)_mCS]^+$ are observed for samples **C** and **E**. For each of the ion series, different m (number of 3TE monomer units) and n (number of EDOT monomer units) combinations are detected depending on the monomer feeding ratios. Major peaks are identified either as mixed sequences of EDOT and 3TE (▼), pure sequences of 3TE (■), or pure sequences of EDOT (●).

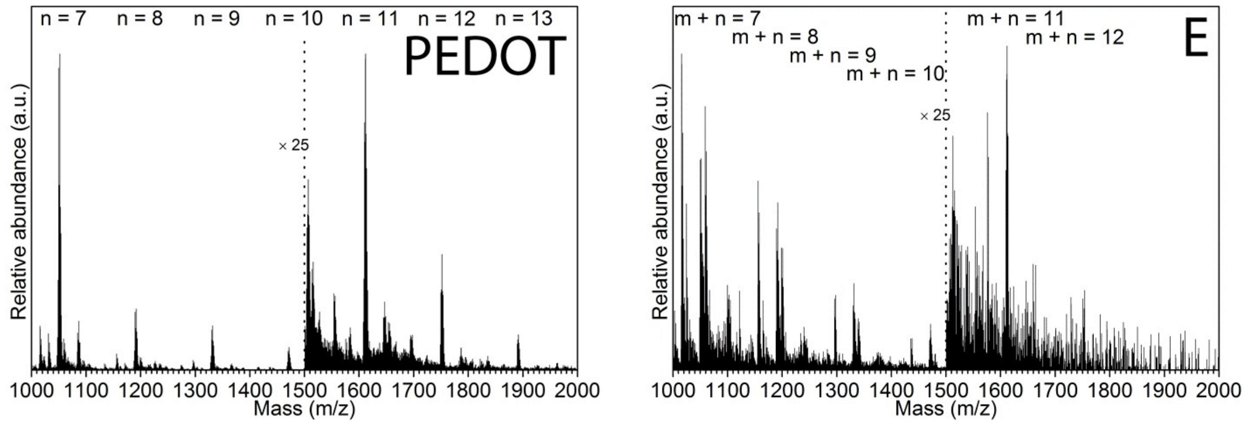

Figure S3. Detailed view of the AP-MALDI-HRMS spectra (*m/z* = 1000−2000) of the films obtained from the oCVD of EDOT (sample **PEDOT**) and from a film obtained from the oCVD of EDOT and 3TE (sample **E**). The mass spectrum is dominated by PEDOT cations with general formulae $[H(C_6H_4SO_2)_nCS]^+$ and $[Cl(C_6H_4SO_2)_nCS]^+$ with repeating units up to n = 13.

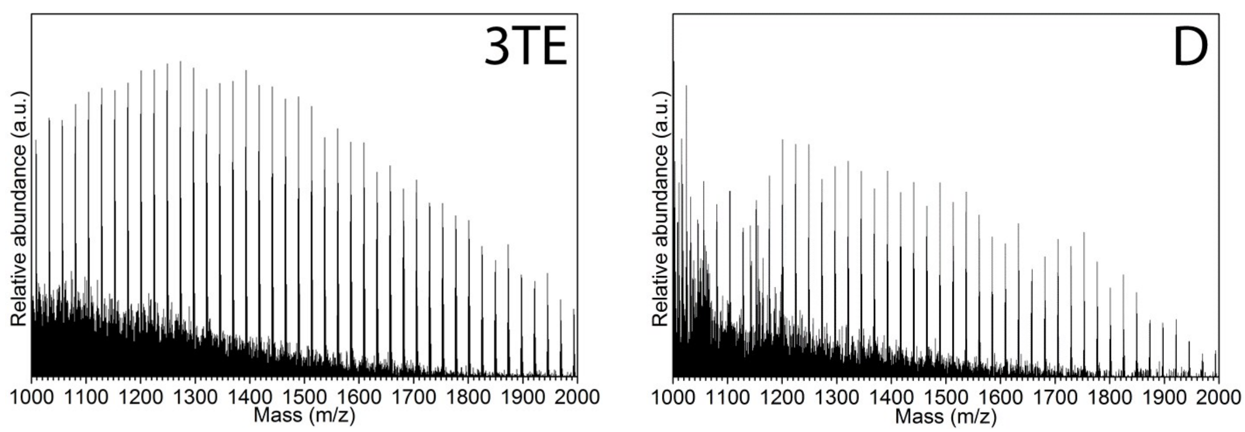

Figure S4. Detailed view of the AP-MALDI-HRMS spectra (*m/z* = 1000−2000) of a film obtained from the oCVD of pure 3TE monomer (sample **3TE**) and from a film obtained from the oCVD of EDOT and 3TE (sample **D**). The mass spectra are dominated by carbon clusters ions (C_2 repeating units) due to the excessive fragmentation of 3TE under the laser beam used for the AP-MALDI-HRMS analyses.

XPS ANALYSIS

High resolution core spectra and chemical composition of the oCVD produced pure 3TE, EDOT and their co-polymers were obtained after sputtering the surface (4.0 min) to get rid of the effect of if any adsorbed atom/molecules on the surface by using the instrument's C_{60}^{+} ion source. The ion source was rastered over 3x3 mm^2 area and operated at 10 kV and 5 nA at an angle of 70^{O} to the surface normal. The atomic composition (Table S2) was computed from photoelectron peak areas by taking into account the relative sensitivity factors provided at the PHI's Multipak software. As it's expected, the O 1s concentration is low for pure 3TE sample and increases with the addition of EDOT monomer (Table S2) while the C-O-C bonding increases as well (see Fig. S5 and Table S3). On the other hand, the C-OH concentration decreases with the increase of EDOT monomer ratio and vanishes at PEDOT sample (Table S3). No direct evidence was obtained between the chlorine (Cl 1s) concentration and the sample conductivity due to the irregular Cl 1s amount obtained for them.

Table S2. Atomic composition (%) of the oCVD produced samples.

(3TE:EDOT)	(1:0)	A (3:1)	B (3:2)	C (3:3)	D(2:3)	E(1:3)	(0:1)
C 1s	79.32	74.77	71.58	70.4	68.95	66.66	68.79
O 1s	8.66	10.88	15.42	16.77	18.19	18.45	18.52
S 2p	11.03	10.98	11.64	11.40	10.56	10.17	10.14
Cl 2s	0.90	2.15	1.19	1.22	1.83	3.39	2.15
Fe 2p	0.10	1.22	0.17	0.22	0.47	1.34	0.40
S/Cl	12.25	5.10	9.78	9.34	5.77	3.0	4.72

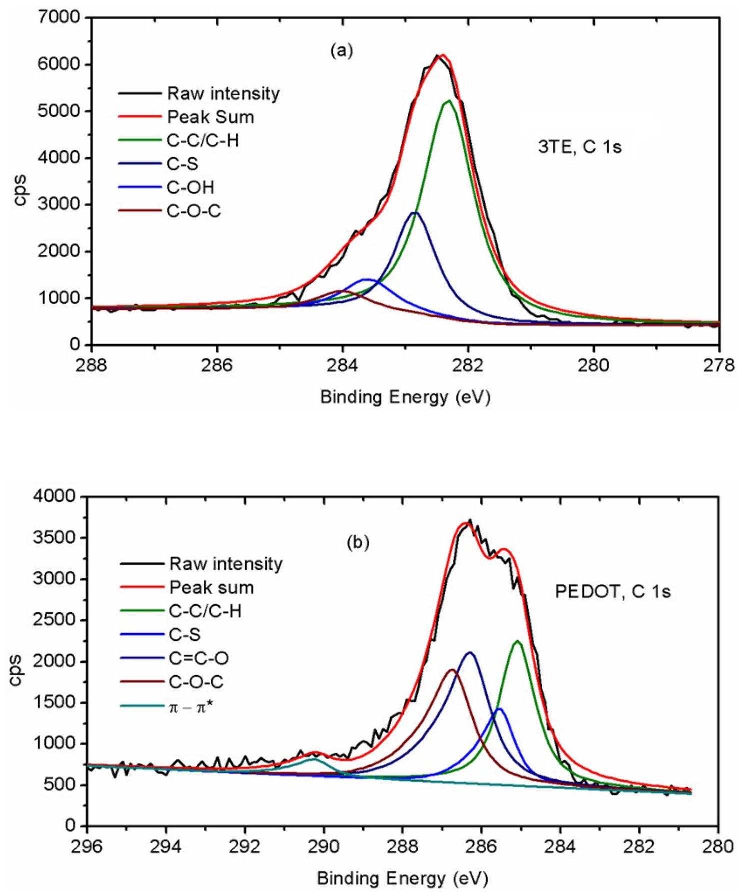

Figure S5. Deconvolution of C 1s core spectra for samples produced from a) pure 3TE and b) PEDOT monomers, respectively.

Table S3. Deconvolution (given in %) of C 1s spectra of produced from pure 3TE, EDOT monomers and their copolymer A, B, C, D, E copolymer samples.

(3TE:EDOT)	(1:0)	A	B	C	D	E	(0:1)
C-C/C-H	61.65	42.62	38.85	37.87	34.04	30.70	25.40
C-S	21.51	24.51	15.54	20.83	18.38	16.12	14.17
C=C-O	0.00	7.40	19.43	11.21	15.30	24.56	32.92
C-O-C	5.61	14.37	19.04	24.49	27.23	24.53	27.95
C-OH	11.22	11.10	7.14	5.61	5.05	4.10	0.00