Supporting Information

The Key Role of Side Chain Linkage in Structure Formation and Mixed Conduction of Ethylene Glycol Substituted Polythiophenes

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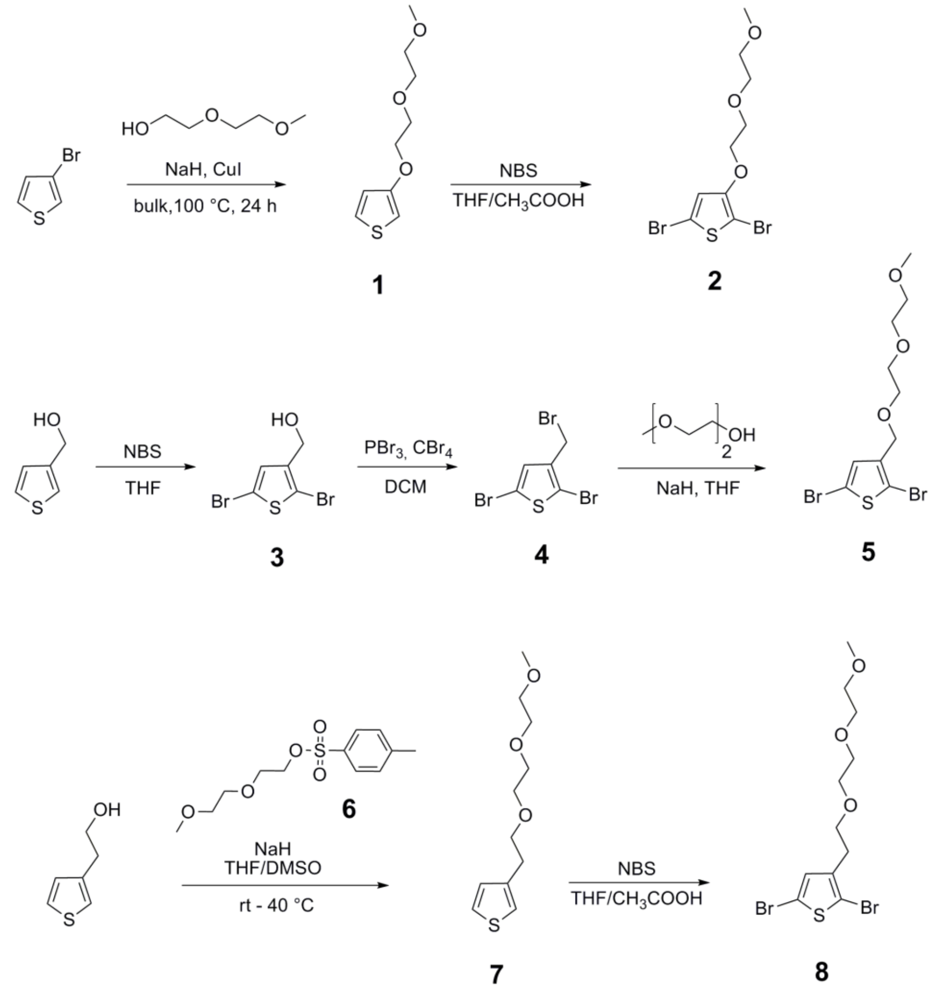
SYNTHESIS



Scheme S1: Complete synthetic route of the used ethylene glycol thiophene monomers.

Synthesis of 3-[2-(2-methoxyethoxy) ethoxy] thiophene (**1**)

A dry 250-mL Schlenk tube, was flushed with N_2 and charged with sodium hydride (6.0 g (60% in mineral oil), 0.15 mol) and anhydrous DMF (25 mL). The reaction flask was cooled down to 0 ◦C, whereupon anhydrous 1-DEGMME (60 mL, 0.48 mol) was added dropwise from the addition funnel over a 30-minute time period. The solution was allowed to stir for additional 1 hour to assure complete consumption of NaH, while the temperature was maintained at 0 ◦C. To this reaction mixture, 3-bromothiophene (16.3 g, 0.10 mol) and CuBr (1.44 g, 0.01 mol) were added. The ice bath was replaced with an oil bath and the solution was heated up to ~ 110 °C. After 30 minutes at the elevated temperature, an aliquot was taken out, quenched with a 1 M aqueous solution of NH_4Cl, extracted with diethyl ether (Et_2O), and subjected to NMR analysis. Note, if a relative abundance of the starting material was detected, an equimolar amount of CuBr was added and the reaction was allowed to proceed for an additional 30 minutes at the elevated temperature. The material was then poured into a 1 M aqueous solution of NH_4Cl (100 mL) and stirred for 10 minutes. The organic phase was extracted with hexane and dried over anhydrous magnesium sulfate ($MgSO_4$). After the product was filtered, the solvent was removed by rotary evaporation. The crude product was purified via column chromatography with hexane: ethylacetate 7:3 as eluent to yield 17.1 g (93%) of 3-[2-(2-methoxyethoxy) ethoxy] thiophene as a yellow oil.

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 3.40 (s, 3H), 3.60 (t, 2H), 3.73 (t, 2H), 3.86 (t, 2H), 4.15 (t, 2H), 6.27 (dd, 1H), 6.78 (dd, 1H), 7.19 (dd, 1H)

Synthesis of 2,5-dibromo-3-[2-(2-methoxyethoxy)ethoxy]thiophene (**2**)

14.7 g 3-[2-(2-methoxyethoxy) ethoxy] thiophene (72.6 mmol) and 29.7 g N-bromosuccinimide (166.7 mmol) were dissolved under argon and under the exclusion of light at RT in a mixture of dry THF and acetic acid (74 mL/74 mL). The reaction mixture was stirred for 3 h. Afterwards, the solvent was removed by rotary evaporation. The resulting residue was washed with hexanes, filtered, and purified using column chromatography on silica gel with hexanes/ ethyl acetate 9:1 as the eluent ($R_f = 0.16$). The product was dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. The compound was dried under vacuum (yield 78 %).

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 3.40 (s, 3H), 3.60 (t, 2H), 3.73 (t, 2H), 3.86 (t, 2H), 4.15 (t, 2H), 6.78 (dd, 1H).

Synthesis of 2,5-dibromo-3-thiophenemethanol (**3**)

3-Thiophenemethanol (5.0 g, 44 mmol) was dissolved in THF (40 mL) in a dried 100 mL round bottom flask. The flask was degassed with nitrogen for 15 min before being sealed under a nitrogen atmosphere. NBS (16.445 g, 92.4 mmol) was added gradually to the reaction mixture (over 10 minutes) and the reaction was run at room temperature overnight. The solution was passed through a plug of Celite to remove residual NBS, then THF was removed by rotary evaporation. The product was dissolved in diethyl ether, then rinsed with 1M sodium hydroxide solution and water. The organic layer was concentrated and the product was eluted over silica gel using hexane:ethyl acetate (80:20). The solvent was removed by rotary evaporation to yield the desired product (10.0 g, 85% yield) as a white solid.

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 4.60 (s, 2H) and 6.70 (s, 1H).

Synthesis of 2,5-dibromo-3-bromomethylthiophene (**4**)

8 g 2,5-Dibromo-3-thiophenemethanol (29.9 mol) in dry methylene chloride (100 mL) was added to a 250 mL flask and sealed under a nitrogen atmosphere. The flask was placed in an ice water bath, and the mixture stirred for 20 min. Phosphorus tribromide (2.9 mL, 30.5 mmol) was added dropwise to the solution over a 15 min period. The reaction was run at room temperature for 5 hours, then quenched with a 10% sodium bicarbonate solution. The organic solution was passed through a plug of Celite, rinsed with water, and dried over magnesium sulfate. The solution was filtered and dried using rotary evaporation to yield the product (5.8 g, 94% yield) as a light yellow solid.

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 4.80 (s, 2H) and 6.7 (s, 1H).

Synthesis of 2,5-dibromo-3-{2-[2-(2-methoxyethoxy)ethoxy]ethoxymethyl} thiophene (**5**)

Diethylene glycol monomethyl ether (4.4 g, 36.5 mmol) was dissolved in THF (125 mL) in a 2-neck 250 mL flask and equipped with an addition funnel and septum with nitrogen inlet. Sodium hydride (0.92 g, 23.1 mol) was added, and after hydrogen gas evolution had ceased, the flask was sealed under a nitrogen atmosphere. 2,5-dibromo-3-bromomethylthiophene (6.8 g, 20.3 mol) was dissolved in THF (25 mL) and added dropwise to the reaction mixture at room temperature over the course of 10 minutes. Stirring was continued for 4 hours. The mixture was then run through a plug of Celite and the solvent was removed by rotary evaporation. The crude product was eluted over silica gel with a 7:3 hexane:ethyl acetate mixture. The second of two UV active spots, seen by TLC, was collected and dried to provide the product (9.1 g, 75% yield) as a yellow liquid.

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 3.40 (s, 3H), 3.58 (m, 2H), 3.66 (m, 6H) 4.60 (s, 2H), 6.70 (s, 1H).

Synthesis of 2-(2-methoxyethoxy)ethyl tosylate (**6**)

A solution of 25.0 g diethylene glycol monomethyl ether (208 mmol) in 70 mL pyridine was cooled down to 0 °C and 37.6 g *p*-toluene sulfonyl chloride (197 mmol) was added and stirred at room temperature for 4 h. Water was added, and the product was extracted with dichloromethane. The organic phase was washed with hydrochloric acid (1 M) and water. The solution was dried over Na_2SO_4 and the organic solvents was removed by evaporation. The colourless product was obtained after purification by a silica plug with hexane/EtoAc (1:1) as eluent (41.2 g, 73 % Yield).

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 2.45 (s, 3H), 3.36 (s, 3H), 3.49 (m, 2H), 3.59 (m, 2H), 3.70 (m, 2H), 4.19 (m, 2H), 7.35 (d, 2H), 7.81 (d, 2H)

Synthesis of 3-(2-(2-(2-Methoxyethoxy)ethoxy)ethyl)thiophene (**7**)

4.92 g 3-thiophene ethanol (38.40 mmol) were dissolved in 75 mL THF and 25 mL DMSO and 1.77 g NaH (46.08 mol) were added portion wise under stirring. After 30 min of stirring a solution of 11.03 g 2-(2-methoxyethoxy) ethyl tosylate (40.32 mmol) in 50 mL THF was added under stirring. The beige solution changed to red/orange and was stirred for 2 h at room temperature and afterwards for 17 h at 40 °C. To quench the solution 50 mL of a saturated NH_4Cl solution was added. The colour shifted from beige to red/brown and the grey precipitate was dissolved. The organic phase was separated, and the water phase was washed tree times with EtOAc, afterwards the organic phase was washed two times with a saturated NH_4Cl solution and two times with a saturated NaCl solution. The product was obtained by drying over Na_2SO_4 and evaporation of the organic solvents. After purification with a silica plug and hexane/EtOAc (7:3) as eluent, the first and only UV-active fraction was collected (7 g, 79 % Yield).

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 7.24 (d, 1 H), 7.03 (m, 1 H), 6.98 (d, 1 H), 3.69 (t, 2 H), 3.65 – 3.61 (m, 6 H), 3.56 (m, 2 H), 3.39 (s, 3 H), 2.93 (t, 2 H).

Synthesis of 2,5-Dibromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)thiophene (**8**)

Under the exclusion of light 7.0 g of 3-(2-(2-(2-methoxyethoxy)ethoxy)ethyl)thiophene (30.4 mmol) was dissolved in 125 mL THF and 11.4 g of *N*-bromo succinimide (63.8 mmol) was added stepwise at room temperature. After stirring for one hour the product was extracted with EtOAc and washed with water and saturated NaCl solution. The organic phase was dried over Na_2SO_4 and the solvent was evaporated. The product was obtained after purification by a silica plug with hexane/EtoAc (7:3) as eluent (7.95 g, 68 % Yield).

^{1}H-NMR: δ_H (300 MHz; ppm, $CDCl_3$): 6.89 (s, 1 H), 3.67-3.61 (m, 8 H), 3.58-3.54 (m, 2 H), 3.39 (s, 3 H), 2.81 (t, 2 H).

General procedure for Kumada catalyst transfer polymerization of the ethylene glycol monomers

The ethylene glycol thiophene monomer (1 equ.) was added to a dry flask under argon and the vessel was evacuated once again and flushed with nitrogen. Then the concentration was set with dry THF to 0.5 mol/l and *t*-butylmagnesiumchloride (1.22 M in THF, 0.96 eq.) was added dropwise. The reaction mixture was stirred for 20 h under the exclusion of light. Then the reaction mixture was diluted with dry THF to 0.1 mol/l. The respective amount of Ni(dppp)Cl_2 (suspension in 2-3 ml dry THF) was added in one portion to start the polymerization. After 4 h the polymerization was quenched with water. The mixture was concentrated, and the polymer was precipitated in methanol. Furthermore, the polymer was purified by Soxhlet extraction with methanol, hexane and chloroform and dried under vacuum.

SEC: P3MEET: M_n = 10 kg/mol, Đ = 1.43, P3MEEMT: M_n = 12 kg/mol, Đ = 1.21, P3MEEET: M_n = 13 kg/mol, Đ = 1.08.

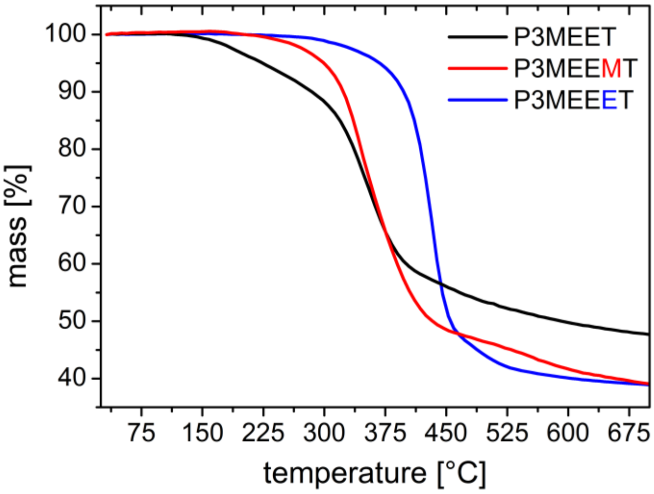


Figure S1: Thermogravimetric analysis (TGA) measurement P3MEET, P3MEEMT and P3MEEET under nitrogen atmosphere with a heating rate of 10 K/min in a temperature range from 30 °C to 700 °C.

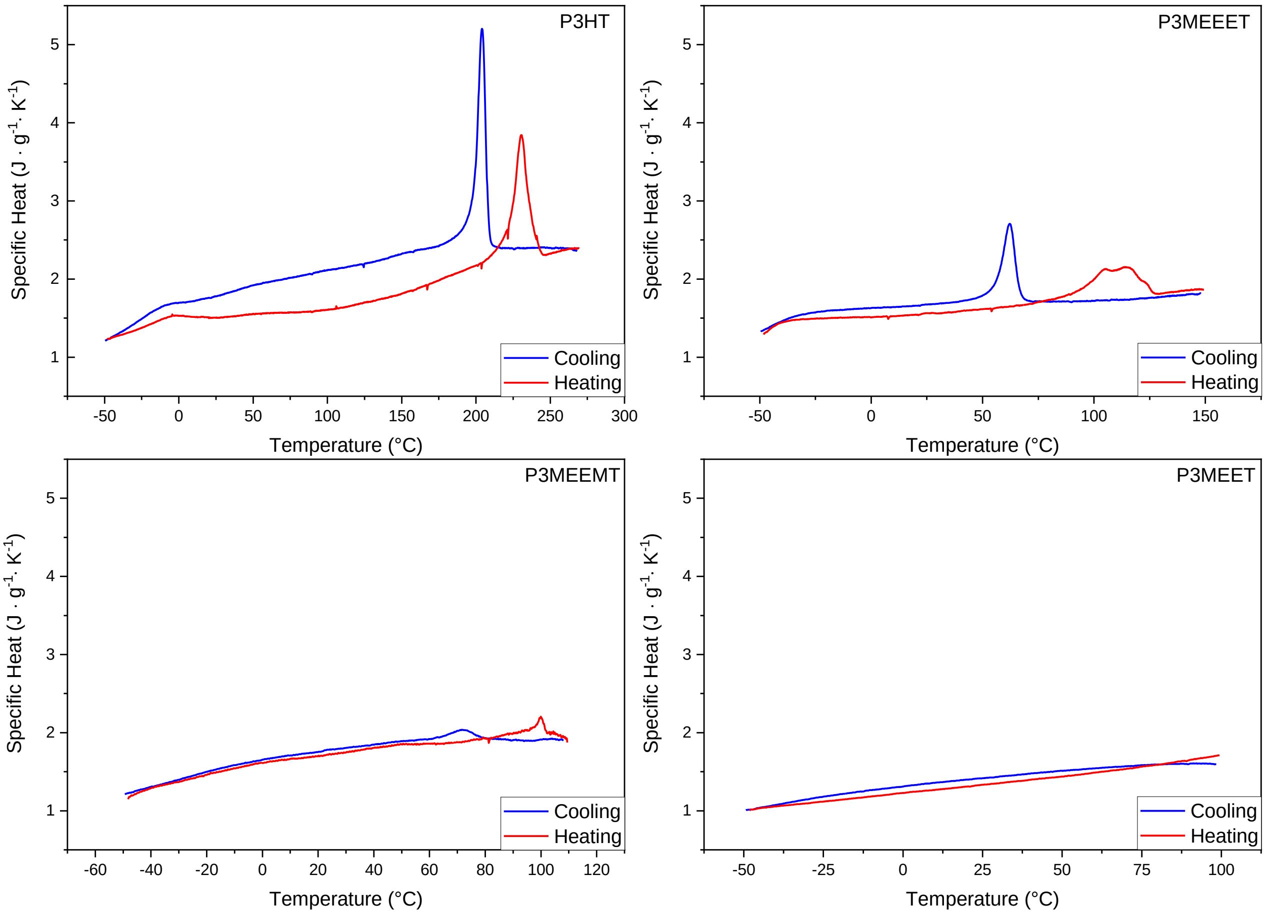


Figure S2: Differential scanning calorimetry (DSC) scans of P3MEET, P3MEEMT and P3MEEET under nitrogen, with a heating and cooling rate of 10 K/min. In all samples the 1st cooling and the 2nd heating run are shown.

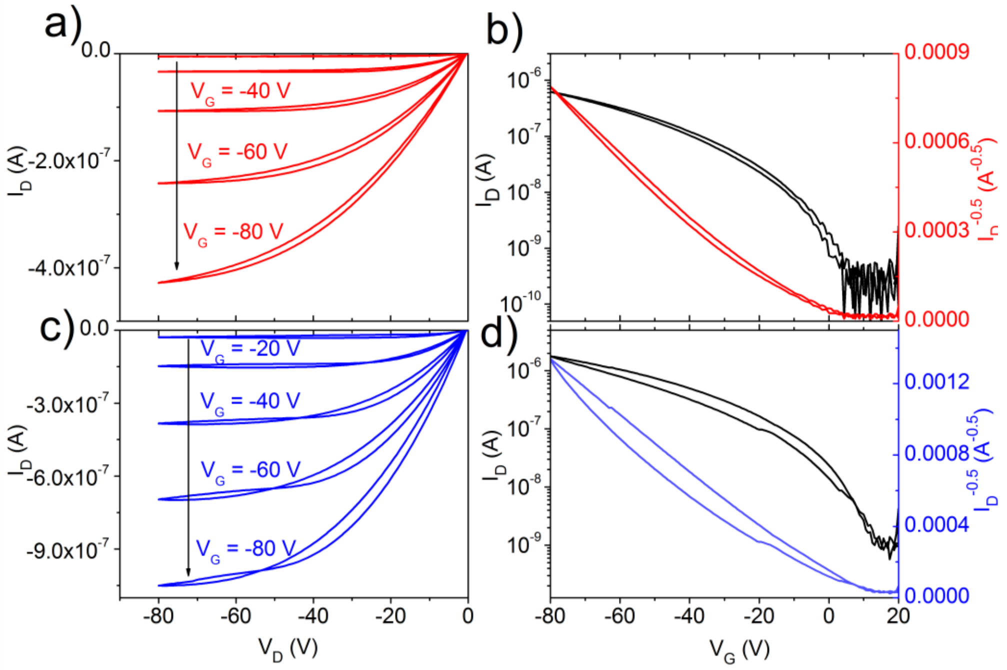


Figure S3: a) and c): Output curve of P3MEEMT (red) and P3MEEET (blue). b) and d): p-transfer curves of P3MEEMT (red) and P3MEEET (blue). With P3MEET no transistor characteristics were observed.

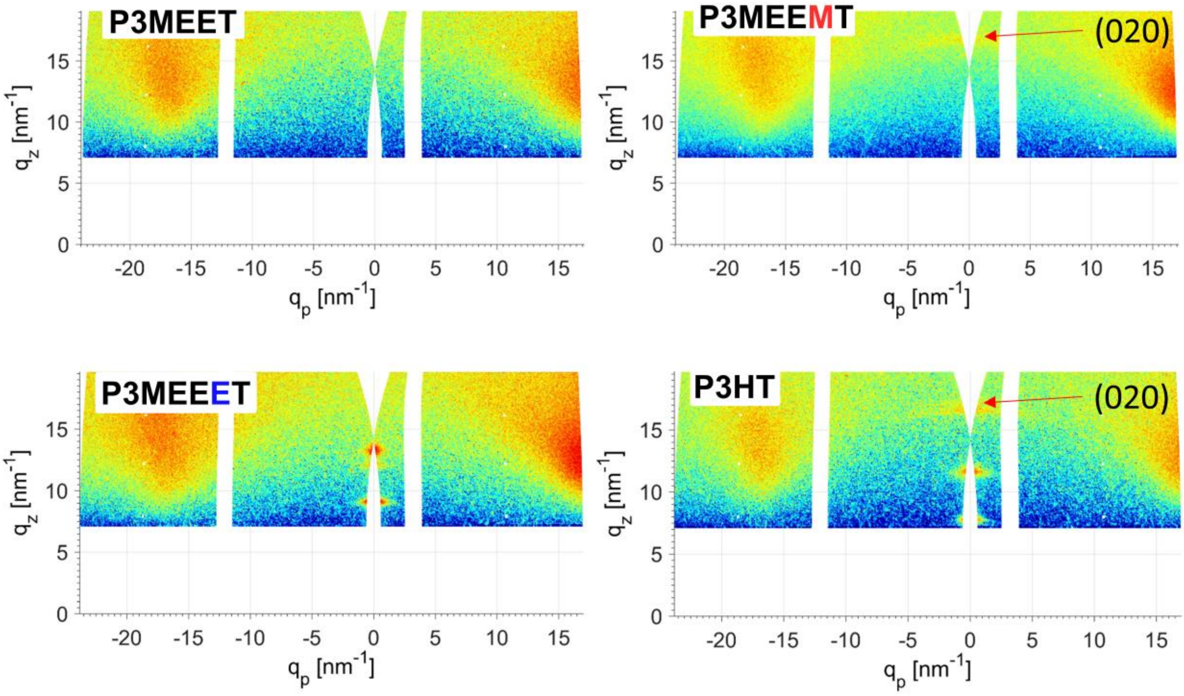


Figure S4: Reciprocal space maps from GIWAXS of thin films of P3MEET, P3MEEMT, P3MEEET and P3HT measured at an incident angle $\alpha_i = 10°$. After spin coating, the polymer films except P3MEET were melt-crystalized in vacuo (P3HT, P3MEEET), respectively annealed (P3MEEMT at 70 °C).

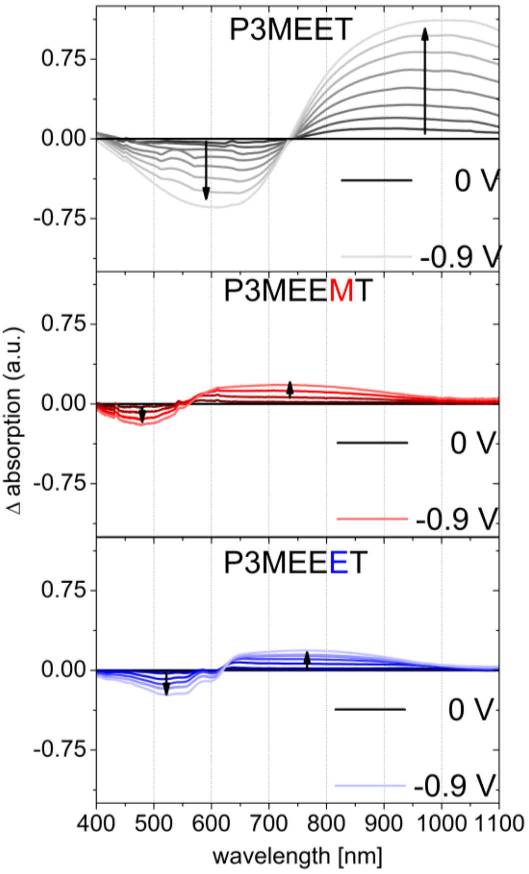


Figure S5: Difference spectra obtained by subtracting the absorption spectra of the copolymers in the neutral state (0 V) from the absorption spectra under different applied potentials during the in situ electrochemical oxidation of P3MEET, P3MEEMT and P3MEEET by applying a potential from 0 to -900 mV.

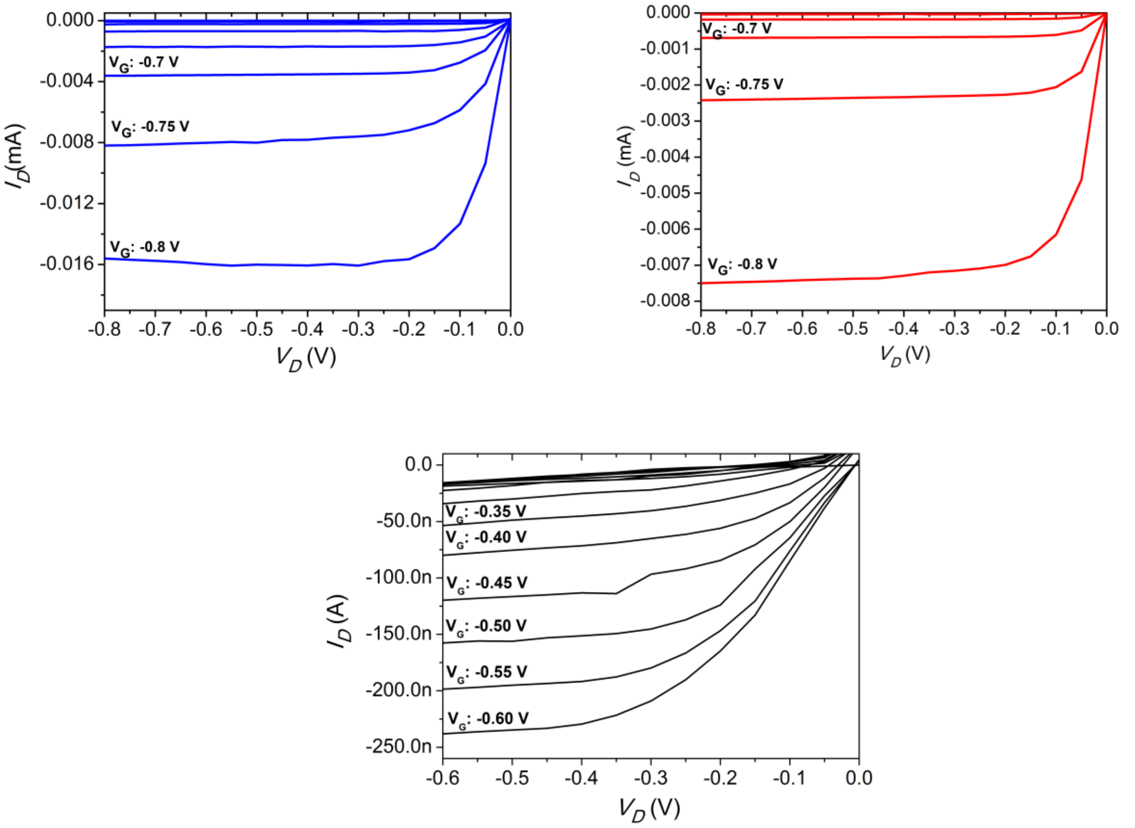


Figure S6: Output curves of P3MEEET (blue), P3MEEMT (red) and P3MEET (black) for gate voltages ranging from 0 V to -0.80 V (ΔV= -0.05 V) and 0 V to -0.60 V respectively.

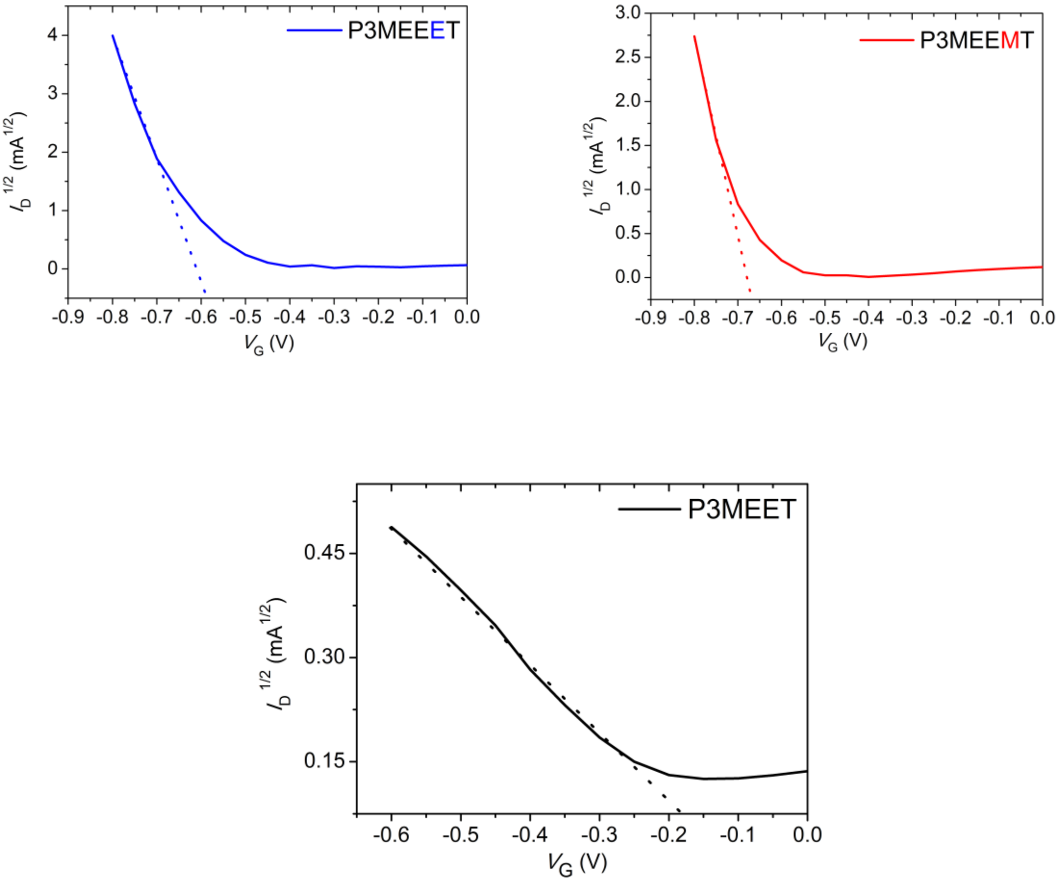


Figure S7: √I$_D$ vs. V$_G$ plots of the OECTs comprising of P3MEET, P3MEEMT and P3MEEET. The threshold voltage, V$_{th}$, was determined by extrapolating the linear region of the curves. The intersection of the x-axis corresponds to the V$_{th}$.

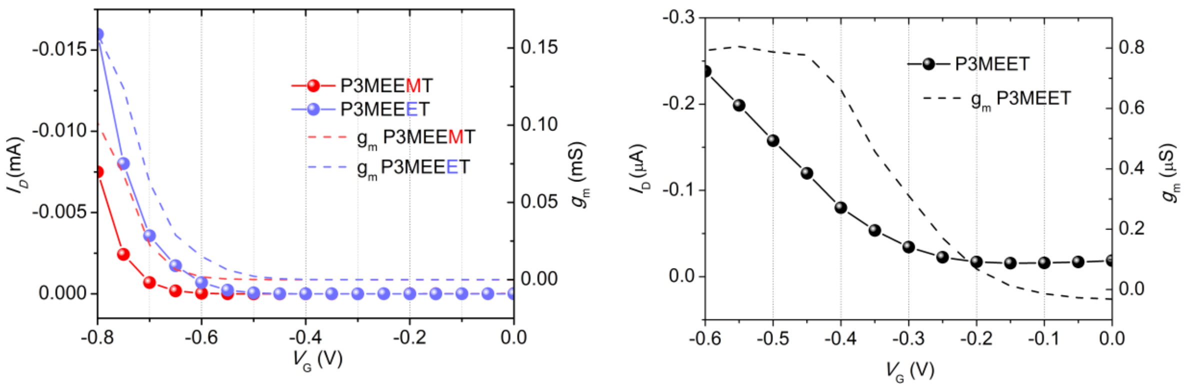


Figure S8: Transfer curve of P3MEEMT, P3MEEET (left) and P3MEET (right) with corresponding transconductance values (right).

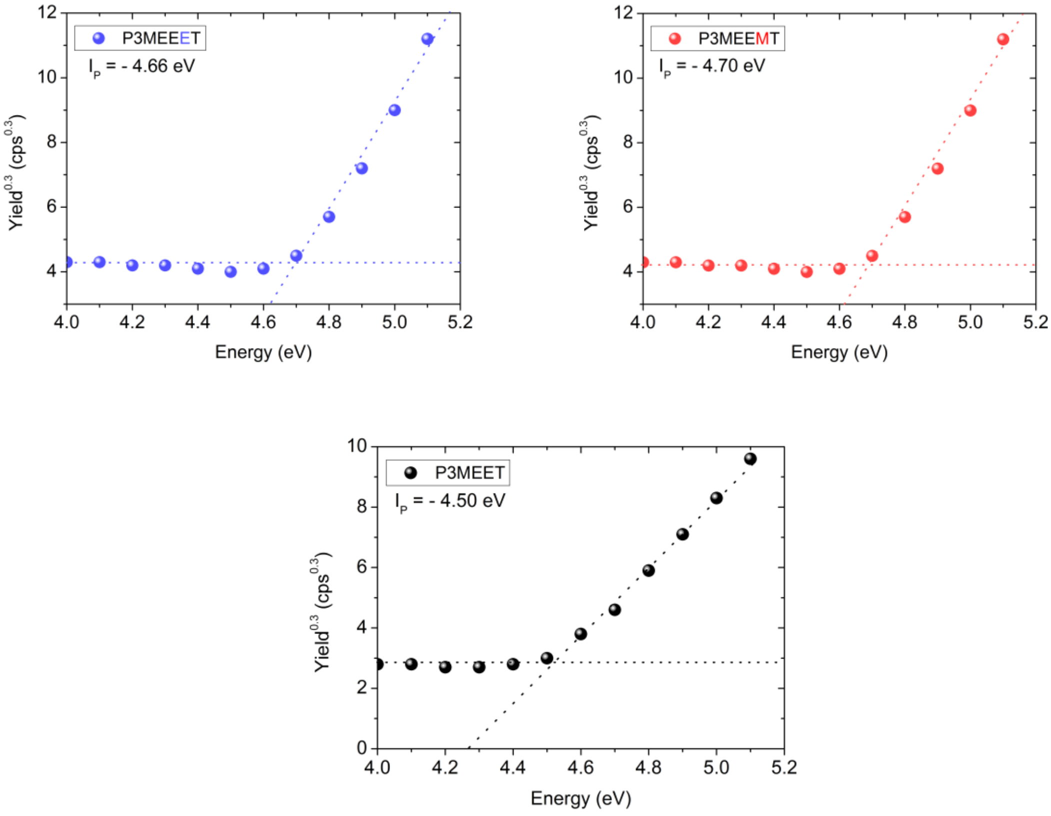


Figure S9: Photoelectron spectroscopy in air (PESA) measurements of P3MEEET (blue), P3MEEMT (red) and P3MEET (black) on thin polymer films on glass substrates. I_p values were determined by interception of the both linear fitting curves.

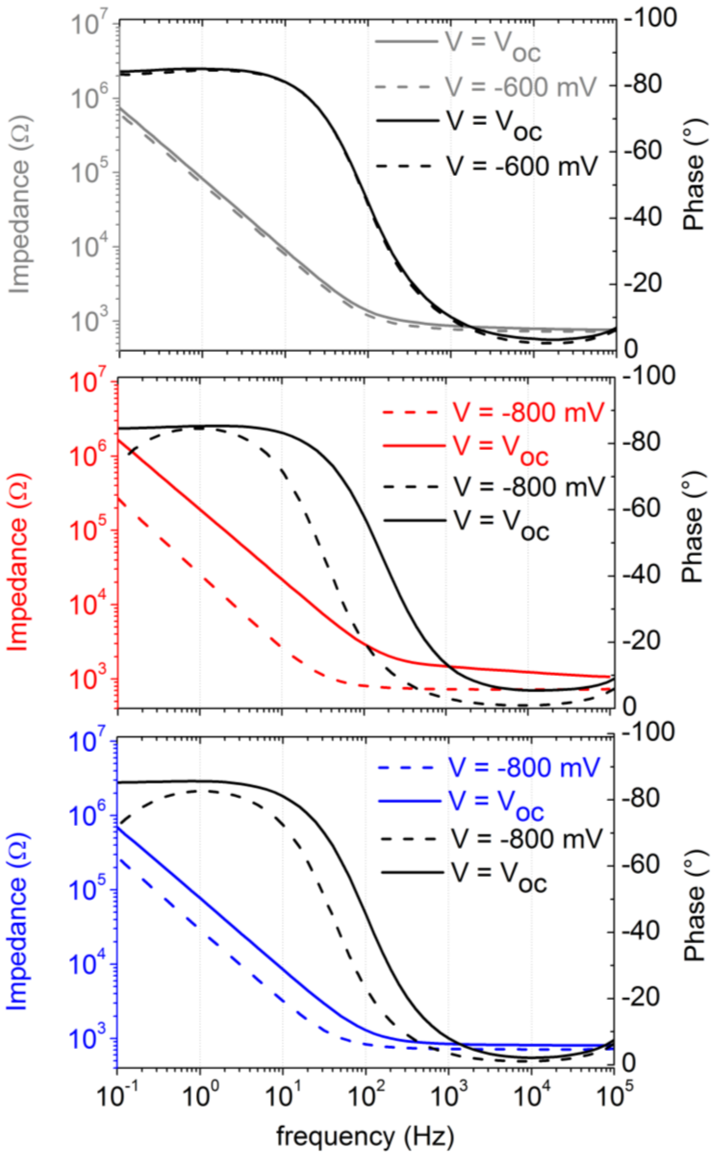


Figure S10: Electrochemical impedance spectra of P3MEEET (blue), P3MEEMT (red) and P3MEET (black) recorded at V_{oc} and at the doping potential that attains the maximum transconductance (V= -0.8 V P3MEEMT and P3MEEET and -0.6 V for P3MEET) in NaCl solution (0.1 M). Randles circuit was used for fitting the impedance and the phase spectrum, $R_{Electrolyte}(R_{Polyme}r||C_{Polymer})$ at a doping potential (V = -0.8V and -0.6 V respectively). Following chi-fitting values were noted: 0.180 (P3MEEET), 0.223 (P3MEEMT) and 0.813 (P3MEET).

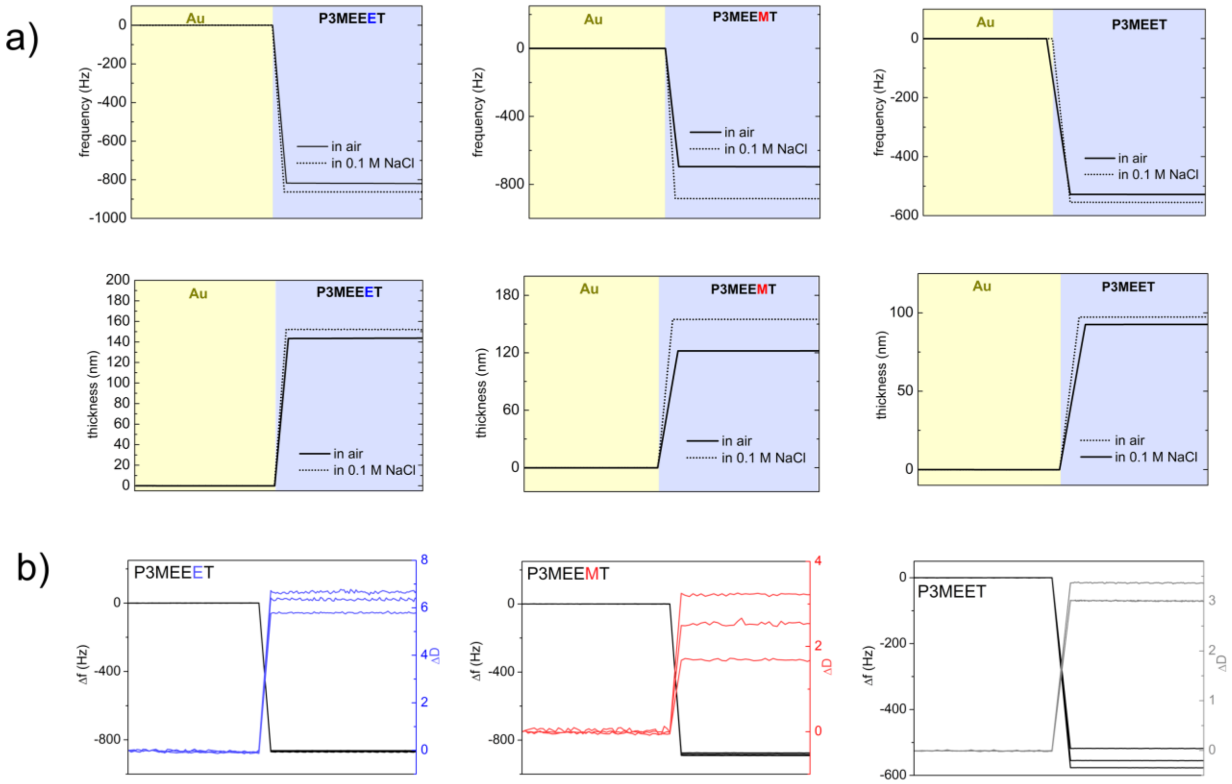


Figure S11: a) Shifts of the QCM-D frequency (Δf) and the calculated thicknesses of P3MEEET (blue), P3MEEMT (red) and P3MEET (black) films. Spectra were recorded in air and in aqueous 0.1 M NaCl solution. For all three copolymers, the 7th overtone was used for calculations based on Sauerbrey model. b) Changes in Δf as well as dissipation of energy (ΔD) for these copolymers before and during the injection of 0.1 M NaCl solution into the chambers. The 3rd, 5th and 7th overtone are shown.

Table S1: Dry and wet thicknesses of the copolymer films after swelling in 0.1 aqueous NaCl solution. The thickness was calculated using Sauerbrey equation. The 7th overtone was used for calculation.

Copolymer	Dry thickness (nm)	Thickness after swelling (nm)	Swelling (%)
P3MEET	92	97	5
P3MEEMT	122	155	26
P3MEEET	143	152	6

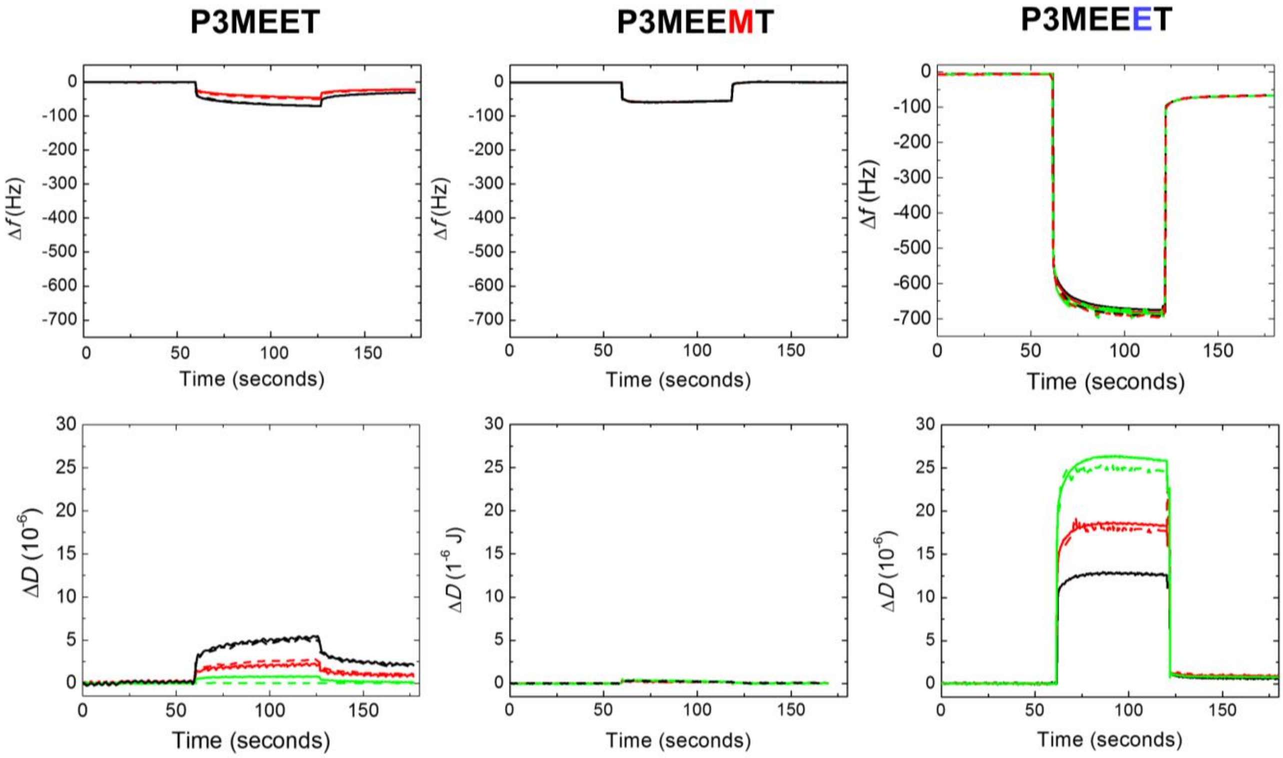


Figure S12: Raw frequency shifts and changes in dissipation (3rd, 5th and 7th overtone is shown) of the E-QCM study upon applying a doping potential of -0.6 V for P3MEET and -0.8 V for P3MEEMT and P3MEEET. The mass uptake, as well as the charge of the systems after ion injection were calculated using viscoelastic modelling.