

SUPPORTING INFORMATION

Radical Polymer-based Organic Electrochemical Transistors

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Materials and Methods

Materials

All chemicals were purchased from Sigma-Aldrich, and they were used as received unless otherwise stated. Poly(3-hexylthiophene) (P3HT) ($M_w \sim 36.6 \text{ kg mol}^{-1}$; 95.2% regioregularity) was purchased from Ossila Ltd. Glass wafers were purchased from Mark Optics.

Synthesis of 4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl (TEO)

PTEO was synthesized according to the literature with minor modifications.¹⁻⁴ For the synthesis of the TEO monomer, 8.25 g of 4-hydroxy-2,2,6,6-tetramethylpiperidin-*N*-oxyl (TEMPO-OH) dissolved in THF (at a concentration of 275 mg mL^{-1}) were added dropwise into the mixture containing 20 mL of epichlorohydrin, 3 g of tetrabutylammonium hydrogen sulfate (TBAHS), and aqueous sodium hydroxide (28 mL of total volume where it was 50% NaOH, by weight). The resulting mixture was stirred at room temperature for 16 h. After the reaction, the mixture was poured into 200 mL of water. The product was extracted with ethyl acetate, washed with deionized water three times, and dried with anhydrous magnesium sulfate. The monomer was dried, and it was further purified using a silica gel column chromatography (hexane:ethyl acetate

= 8:1, v/v). The monomer was recovered as needle-shaped red crystals, when the temperature was at or below room temperature, and it was stored in inert atmosphere until further use.

Synthesis of Poly(4-glycidyloxy-2,2,6,6-tetramethylpiperidine-1-oxyl) (PTEO)

The polymerization of TEO into PTEO was carried out by adding 1 g of TEO into a mixture containing 0.3 mL of diglyme, 102 μ L of 1 M potassium *tert*-butoxide in THF, and 80 mg of 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6 ether) in a glass vial. The resulting mixture was then heated at 40 °C and stirred for 40 h in an inert atmosphere. After cooling to room temperature, 200 mL of dichloromethane was added to the reaction mixture, and the organic solution was washed with water three times and dried with anhydrous magnesium sulfate. The organic phase was concentrated to 5 mL of solvent and then precipitated in hexanes. The PTEO was stored inside N₂-filled glovebox prior to use.

Electrochemical Characterization

All electrochemical analyses were carried out using 0.1 M NaCl in ultrapure (18.2 M Ω ·cm) water. The cyclic voltammetry (CV) measurements were performed using a three-electrode set-up with Ag/AgCl as the reference electrode, a platinum coil as the counter electrode, and gold as the working electrode with an active area of 10 mm² on a VersaSTAT 3 Workstation. The voltage was swept from –0.1 V to +0.9 V relative to the reference electrode. The spectroelectrochemical measurements were recorded using a custom-built system combining a Biologic SP-150 potentiostat and an Agilent Cary 5000 UV/Vis-NIR spectrophotometer, and tin-doped indium oxide-coated (ITO-coated) glass was used as the working electrode.

Surface Characterization

Atomic force microscopy (AFM) images were acquired with a Veeco Dimension 3100 atomic force microscope operating in tapping mode. The probe tips were fabricated by

Budget sensors (Tap150AI-G), and they had a resonant frequency of 150 kHz and a force constant of 5 N m^{-1} .

Organic Electrochemical Transistor (OECT) Device Fabrication and Characterization

OECT devices were fabricated following previously reported processes with minor adjustments.⁵ Briefly, the Ti/Au electrodes were patterned on a glass substrate using photolithography using LOR 3A and AZ1518 bilayer resists. Two $1 \text{ }\mu\text{m}$ -thick Parylene C (PaC) conformal coatings were deposited using the SCS Labcoater (PDS 2010) with A-174 silane and 1.5% Micro-90 aqueous solution as an adhesion promoter between the first PaC layer and the glass and as an anti-adhesion promoter between PaC layers, respectively. The PaC layers were patterned with a reactive ion etcher (March Jupiter II) using photolithographically patterned AZ9260 photoresist mask to expose the active channel area. Polymer solutions were prepared by mixing stock solutions of PTEO and P3HT dissolved in chloroform at predetermined ratios. PTEO-OH was prepared by quenching PTEO with a phenyl hydrazine solution overnight. For the OECT characterization of the P3HT-PTEO-OH films, 1% (by weight) 3-glycidoxypolytrimethoxysilane (GOPS) was added to prevent dissolution of PTEO-OH during OECT operation. The polymer thin films were deposited using a spin coater by coating at 2,000 rpm for 60 s. Then, the second layer of PaC was removed, and the devices were rinsed with water.

Device performance measurements were carried out with a three-point geometry on a Keysight B2902A sourcemeter where 200 μL of 0.1 M aqueous NaCl was drop cast on top of the channel to serve as the electrolyte. A pellet-type Ag/AgCl reference electrode (E205, Warner Instruments) was used as gate electrode immersed in the electrolyte. The transconductance of the device (g_m) was extracted by taking the first derivative of the drain current-gate voltage (I_D - V_G) transfer curves and normalizing these data using the channel dimensions.

Scheme S1. Synthetic route for the creation of PTEO.

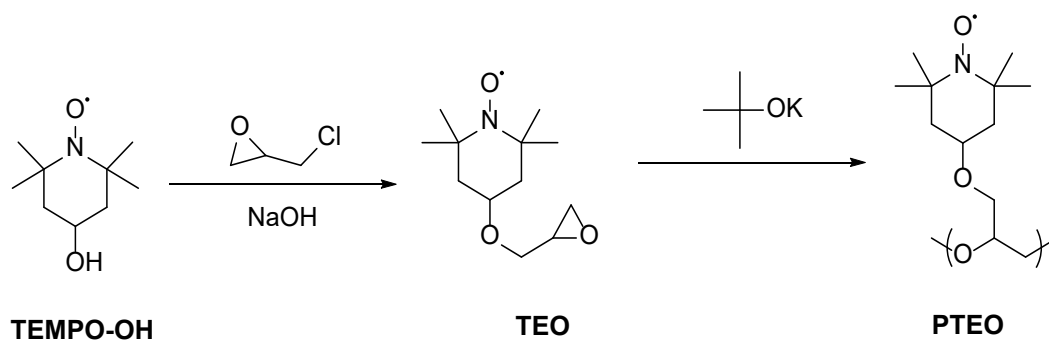
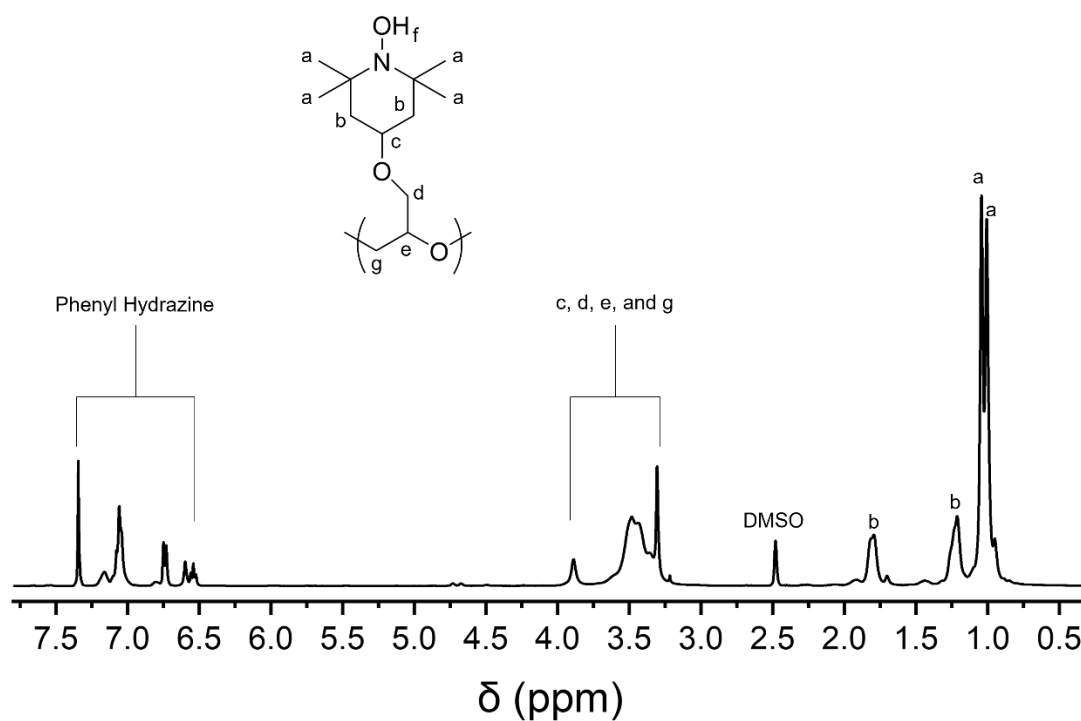


Figure S1. ^1H NMR spectrum of PTEO quenched with phenyl hydrazine. Deuterated DMSO was used as solvent.

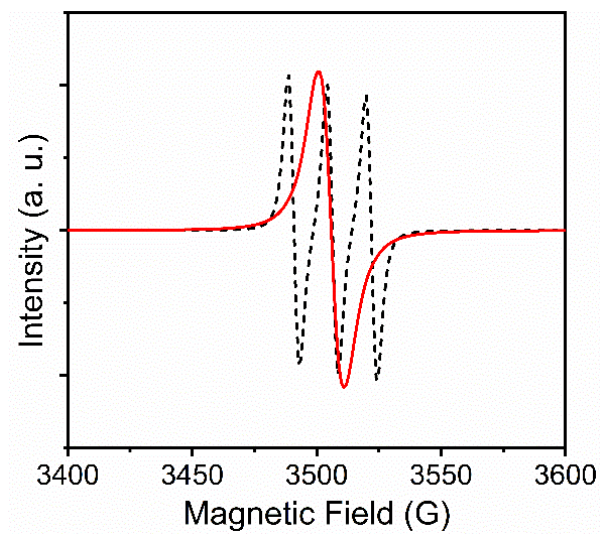


Figure S2. EPR spectra of the starting reagent, TEMPO-OH (black dashed line), and PTEO (red solid line) in chloroform. The final radical density of PTEO with respect to TEMPO-OH was 95% of the total possible repeat units.

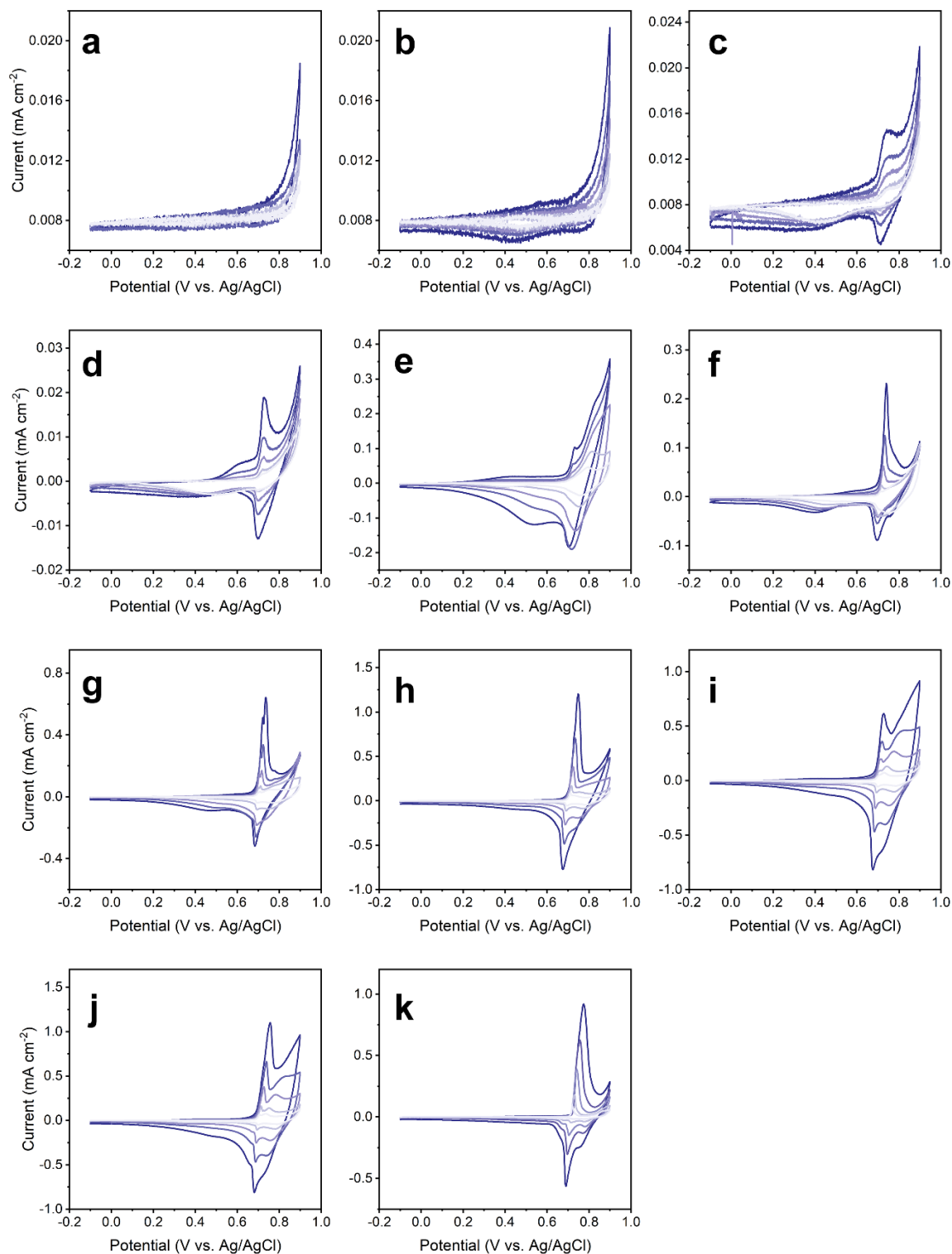


Figure S3. Cyclic voltammograms of the polymer blends containing PTEO weight percentages of: (a) 0% (i.e., pristine P3HT), (b) 1%, (c) 2.5%, (d) 5%, (e) 7.5%, (f) 10%, (g) 20%, (h) 30%, (i) 40%, (j) 50%, and (k) 100 % (i.e., pristine PTEO) at scan rates of 5, 10, 25, 50, and 100 mV s^{-1} . Here, the darker the line color indicates an increasing scan rate.

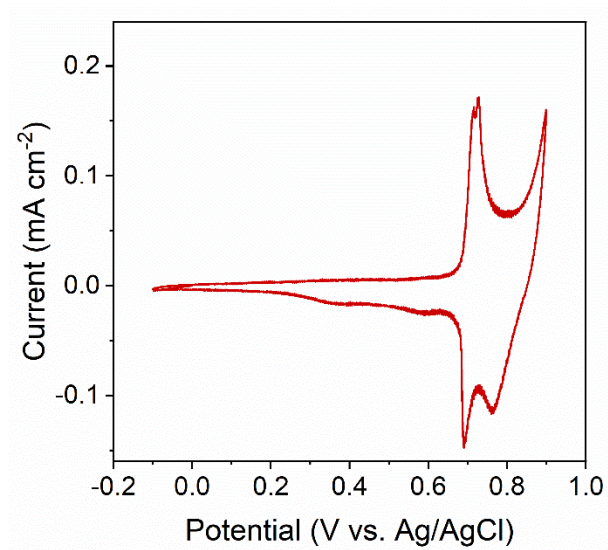


Figure S4. Representative cyclic voltammogram of an 80% PTEO (by weight) thin film where the sweeping rate was 25 mV s⁻¹.

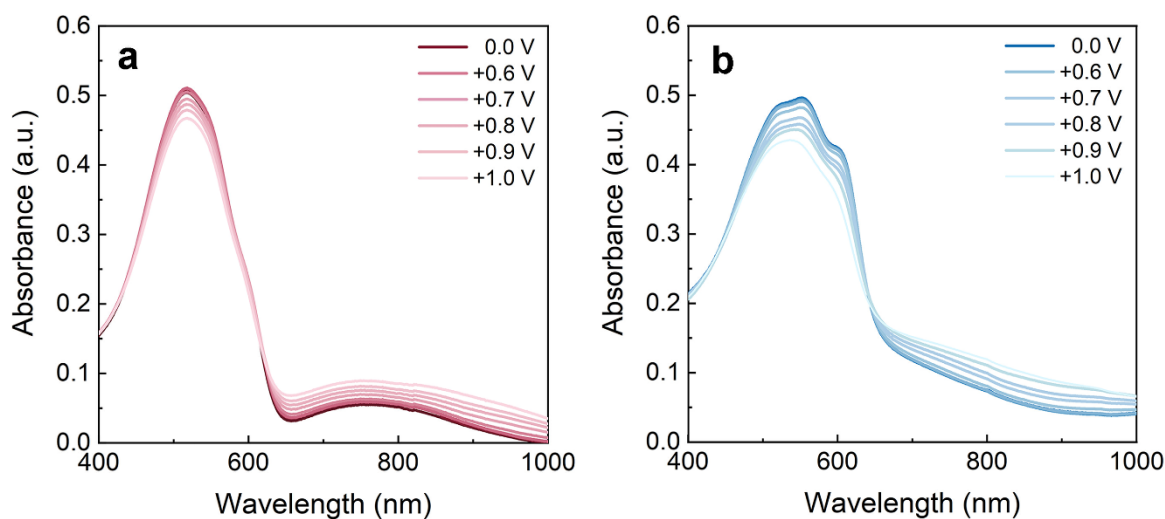


Figure S5. Absorbance spectra of (a) a P3HT thin film and (b) a thin film containing 5% PTEO (by weight) in 0.1 M $\text{NaCl}_{(\text{aq})}$ with varying applied potentials ranging from 0 V to +1 V (vs. Ag/AgCl).

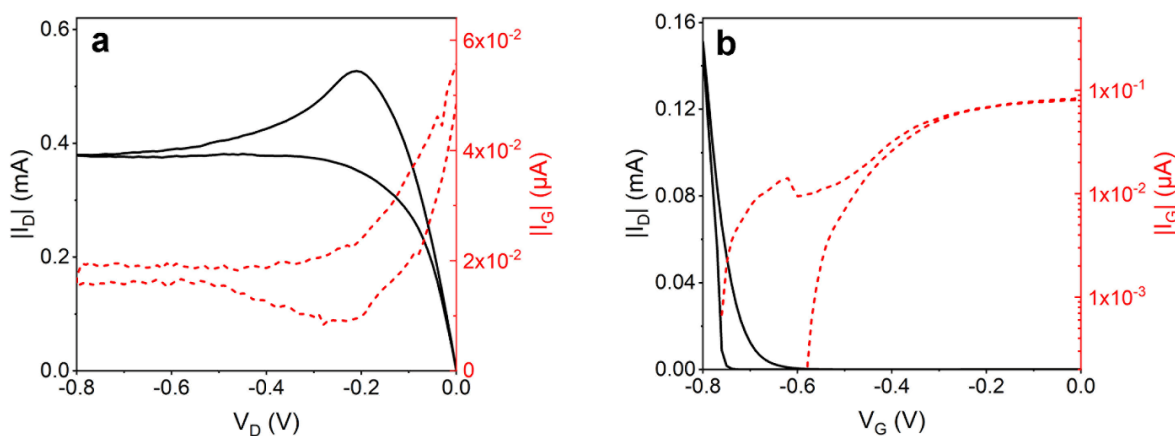


Figure S6. I_D (black, left axis) and I_G (red, right axis) as a function of (a) drain voltage ($V_G = -0.8$ V) and (b) gate voltage ($V_D = -0.8$ V) for 5% PTEO (by weight) OECT thin films.

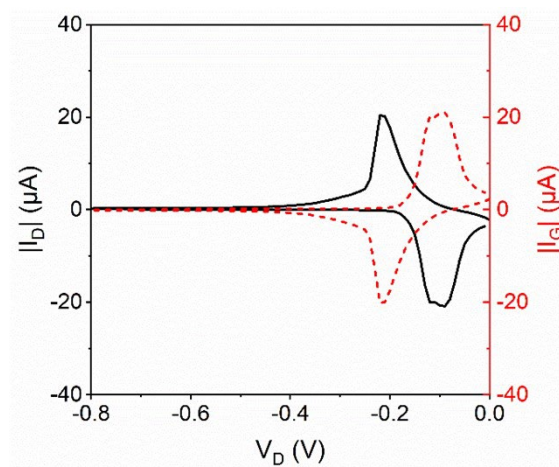


Figure S7. Output curve of pristine PTEO OEET at a gate voltage of $V_G = -0.8$ V. The I_D (black, left axis) and the I_G (red, right axis) were equal in magnitude but opposite in direction, suggesting the recorded current was due to ionic conduction.

Table S1. OEET Steady-state Performance and Film Thickness at Various PTEO Loadings.

PTEO weight loading (%)	g_m (mS) ¹	d (nm) ²	μC^* (F cm ⁻¹ V ⁻¹ s ⁻¹)	V_T (V)
0	0.15 ± 0.03	50 ± 1	7.6 ± 1.3	-0.62
1	0.16 ± 0.04	50 ± 2	8.1 ± 1.5	-0.62
2.5	0.3 ± 0.09	51 ± 2	15 ± 4	-0.71
5	3.1 ± 0.1	51 ± 2	151 ± 7	-0.72
7.5	2.8 ± 0.1	52 ± 2	135 ± 7	-0.72
10	2.8 ± 0.2	62 ± 2	113 ± 8	-0.73
20	3.5 ± 0.2	89 ± 5	97 ± 9	-0.73
30	3.2 ± 0.3	90 ± 5	90 ± 10	-0.73
40	3.1 ± 0.4	98 ± 8	80 ± 12	-0.72
50	3.7 ± 0.7	152 ± 14	61 ± 13	-0.72

¹ The reported values represent the average and error across three distinct devices.

² The film thickness, as determined using profilometry.

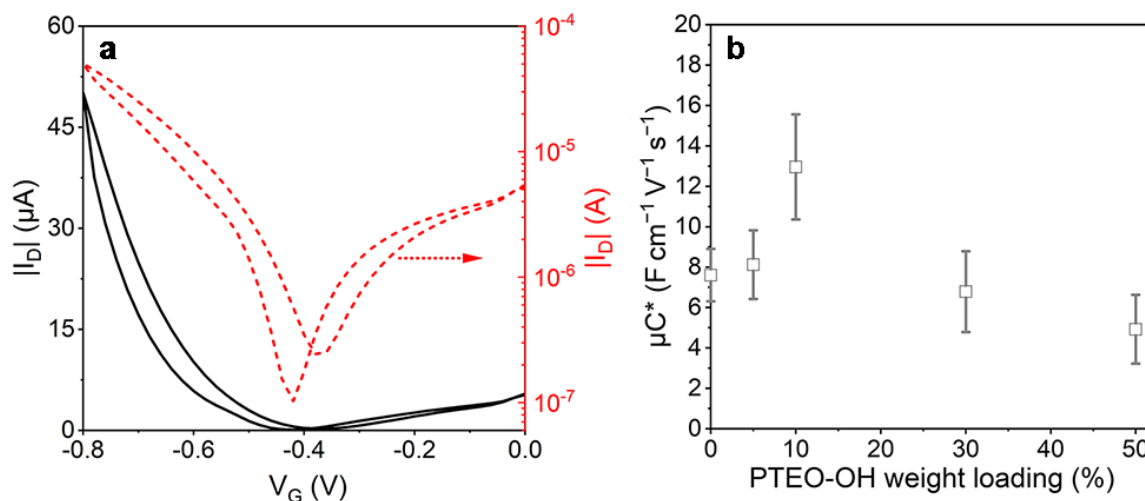


Figure S8. (a) Transfer curve recorded for a 5% PTEO-OH (by weight) OECT thin film at $V_D = -0.8\text{V}$. (b) Calculated μC^* as a function of PTEO-OH loading as extracted from respective transfer curves. The data points represent the averaged values over three devices.

Table S2. OECT Steady-state Performance and Film Thickness at Various PTEO-OH Loadings.

PTEO-OH weight loading (%)	g_m (mS) ¹	d (nm) ²	μC^* ($\text{F cm}^{-1} \text{V}^{-1} \text{s}^{-1}$)	V_T (V)
0	0.15 ± 0.03	50 ± 1	7.6 ± 1.3	-0.62
5	0.38 ± 0.08	52 ± 2	8.1 ± 1.7	-0.44
10	0.76 ± 0.15	62 ± 4	13 ± 2.6	-0.42
30	0.68 ± 0.21	106 ± 15	6.8 ± 2.0	-0.42
50	0.67 ± 0.12	142 ± 17	4.9 ± 1.7	-0.42

¹ The reported values represent the average and error across three distinct devices.

² The film thickness, as determined using profilometry.

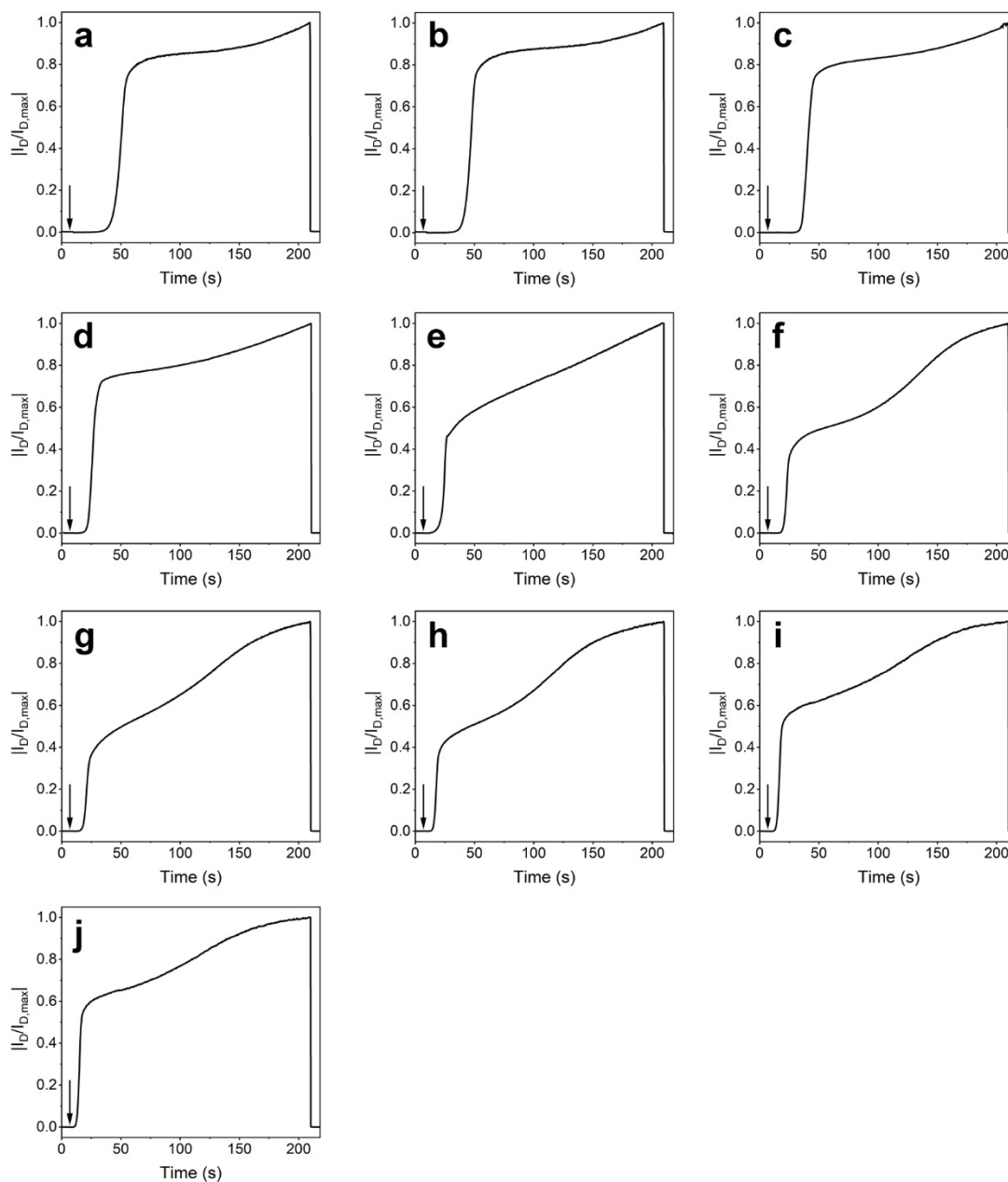


Figure S9. Normalized transient responses with a V_G of -0.8 V sourced at $t = 10$ s for 200 s at a constant $V_D = -0.8$ V of the thin films containing PTEO weight percentages of: (a) 0% (i.e., pristine P3HT), (b) 1%, (c) 2.5%, (d) 5%, (e) 7.5%, (f) 10%, (g) 20%, (h) 30%, (i) 40%, and (j) 50%.

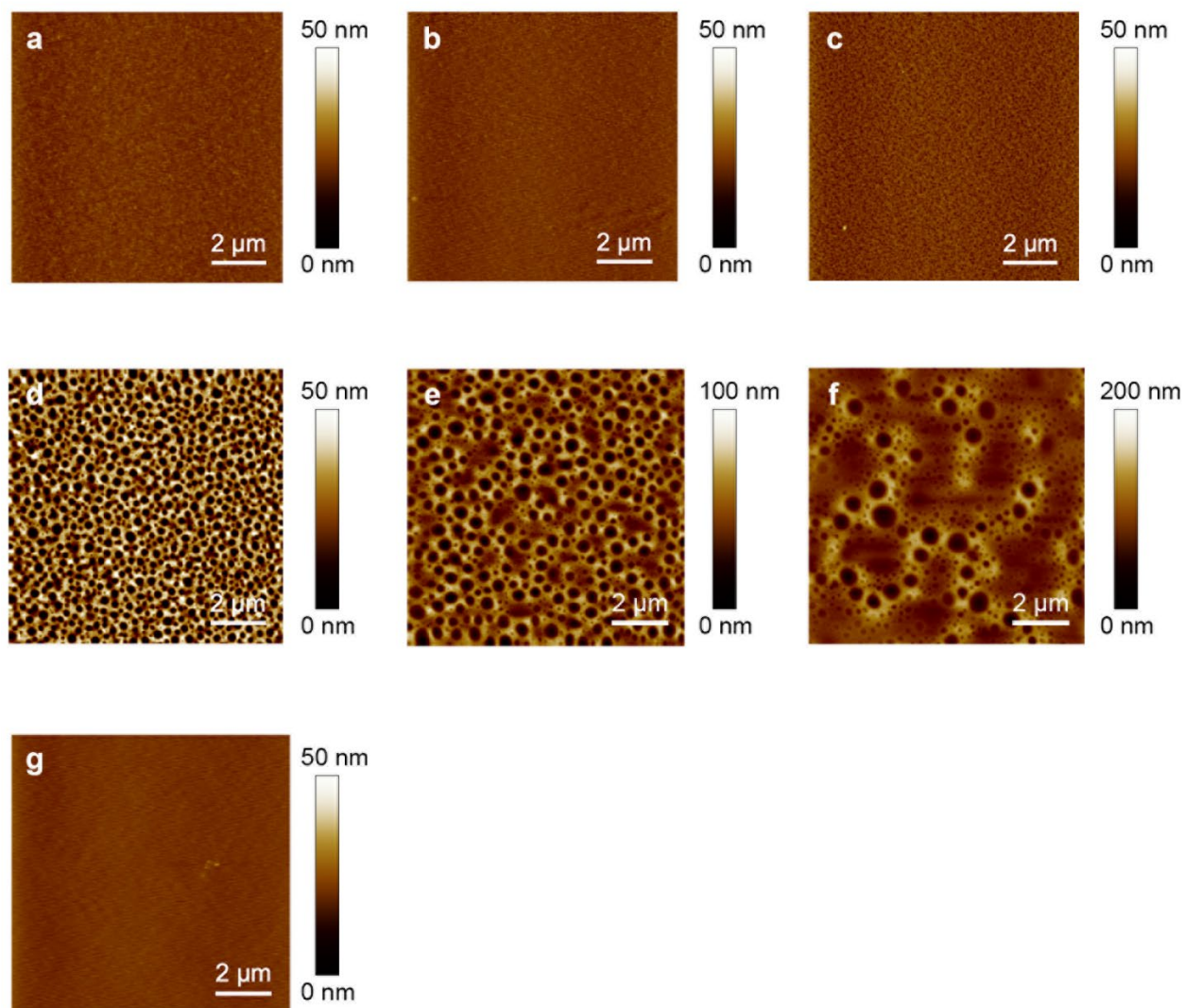


Figure S10. AFM images of the polymer blend thin films containing PTEO weight percentages of: (a) 1%, (b) 2.5%, (c) 10%, (d) 30%, (e) 40%, (f) 50%, and (g) 100% (i.e., pristine PTEO).

References

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