Supporting Information

Synthesis of Multifunctional PEDOT-block Copolymers by Combining Controlled and Chemical Oxidative Polymerizations for Bioelectronics

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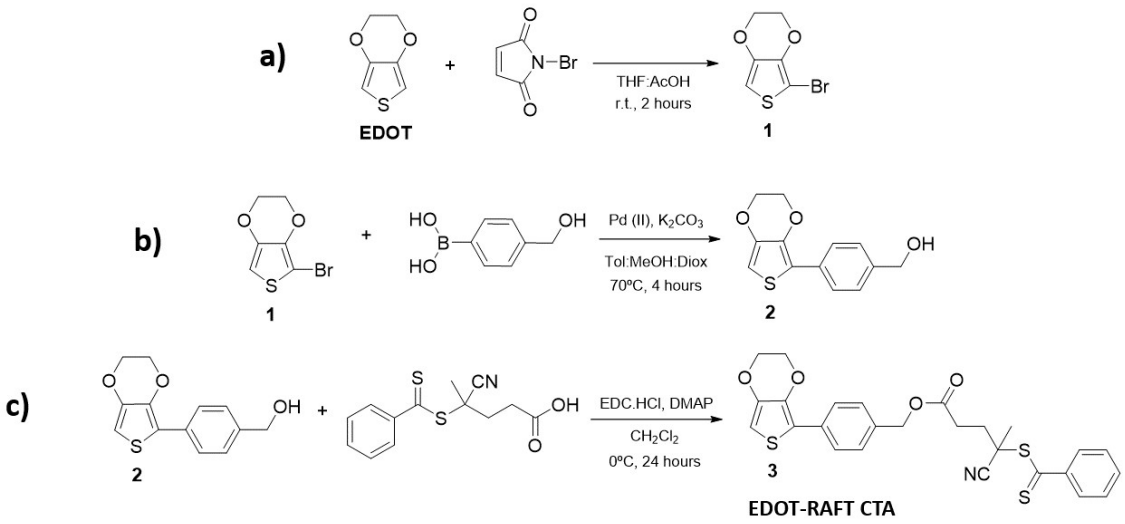


Scheme S1. Reaction scheme to synthetize EDOT-RAFT CTA. a) Bromination of EDOT, b) Suzuki cross-coupling reaction and c) Condensation reaction to obtain the EDOT-RAFT CTA (**3**).

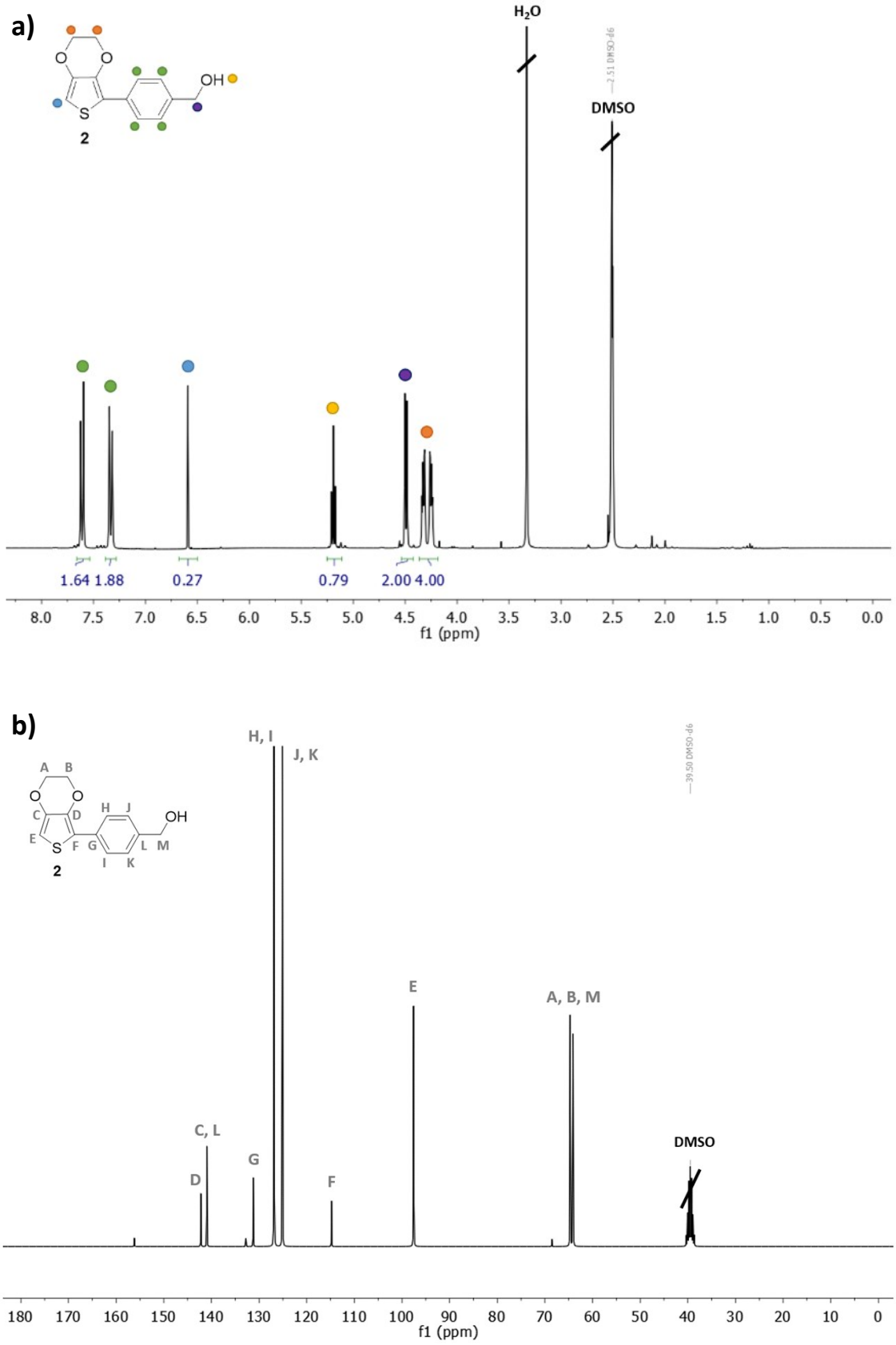


Figure S1. a) ^{1}H-NMR and b) ^{13}C-NMR of **2** in DMSO-d_6.

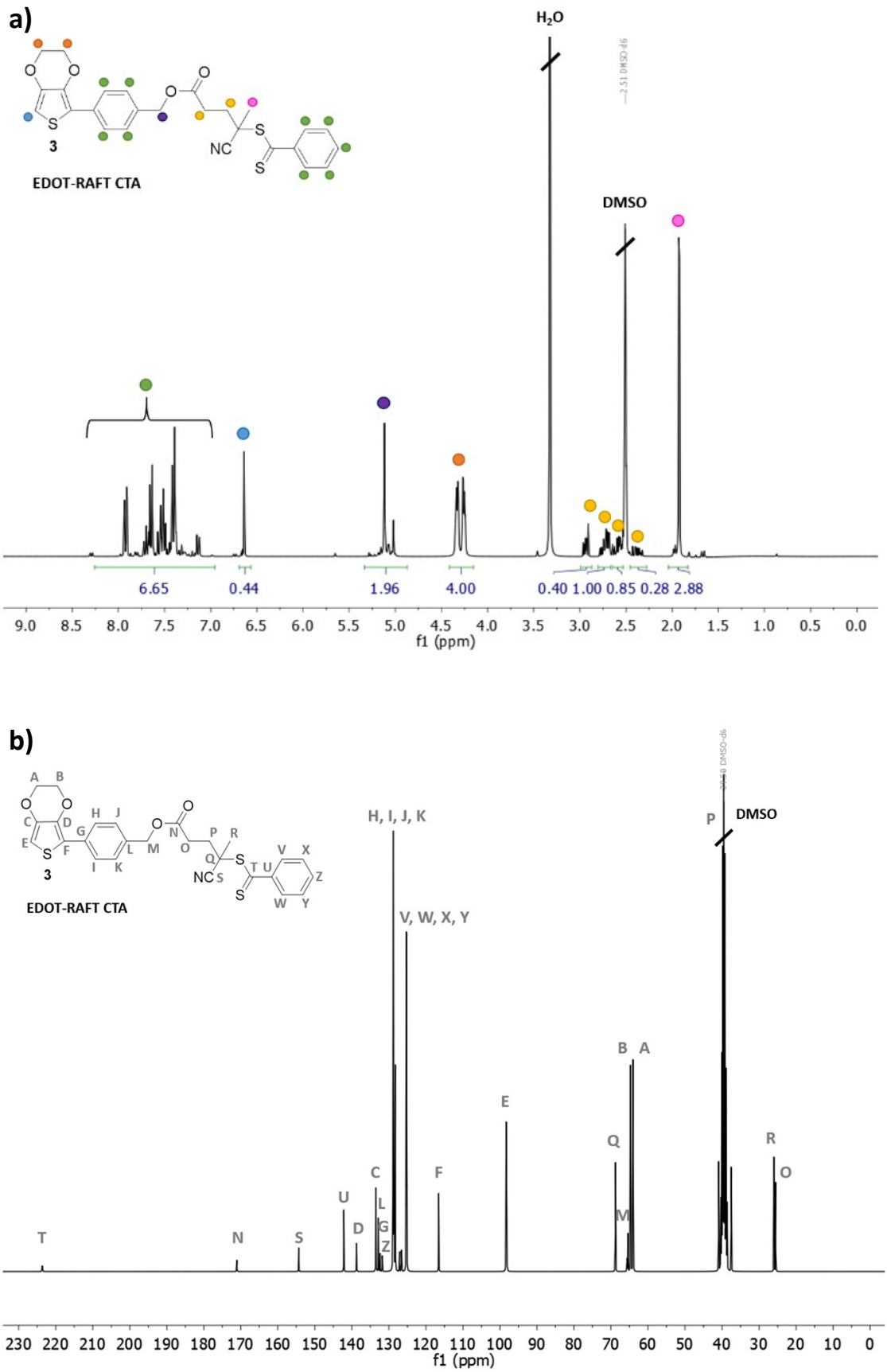


Figure S2. a) ^{1}H-NMR and b) ^{13}C-NMR of EDOT-RAFT CTA (**3**) in DMSO-d_6.

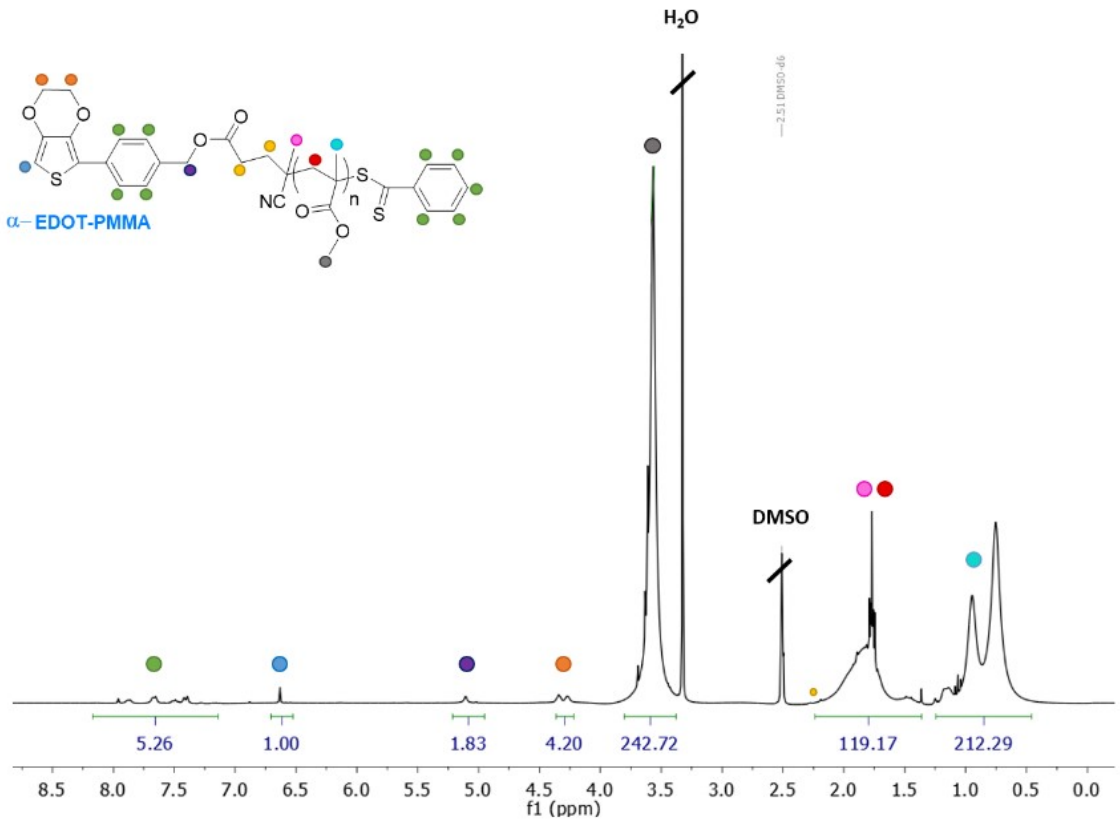


Figure S3. ^{1}H-NMR spectrum of α–EDOT-PMMA (M_n 5000 g mol^{-1}) macromonomer in DMSO-d_6.

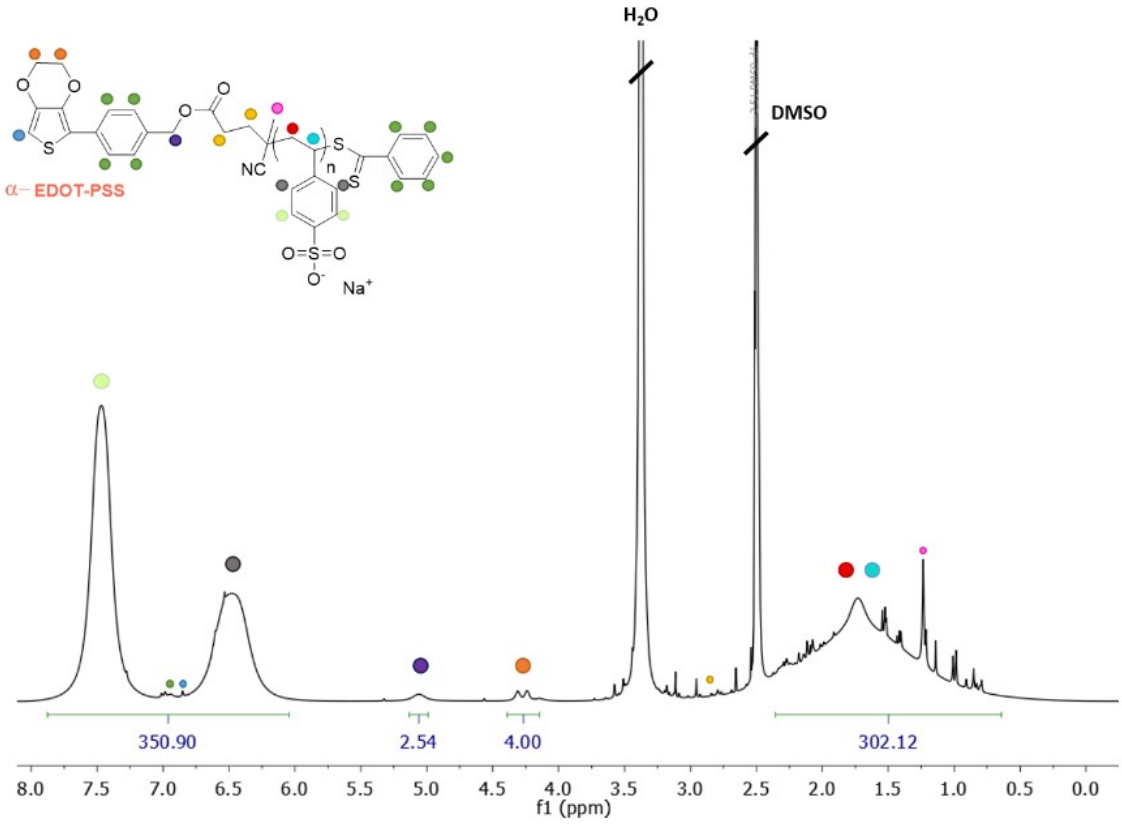


Figure S4. ^{1}H-NMR spectrum of α–EDOT-PSS (M_n 10000 g mol^{-1}) macromonomer in DMSO-d_6.

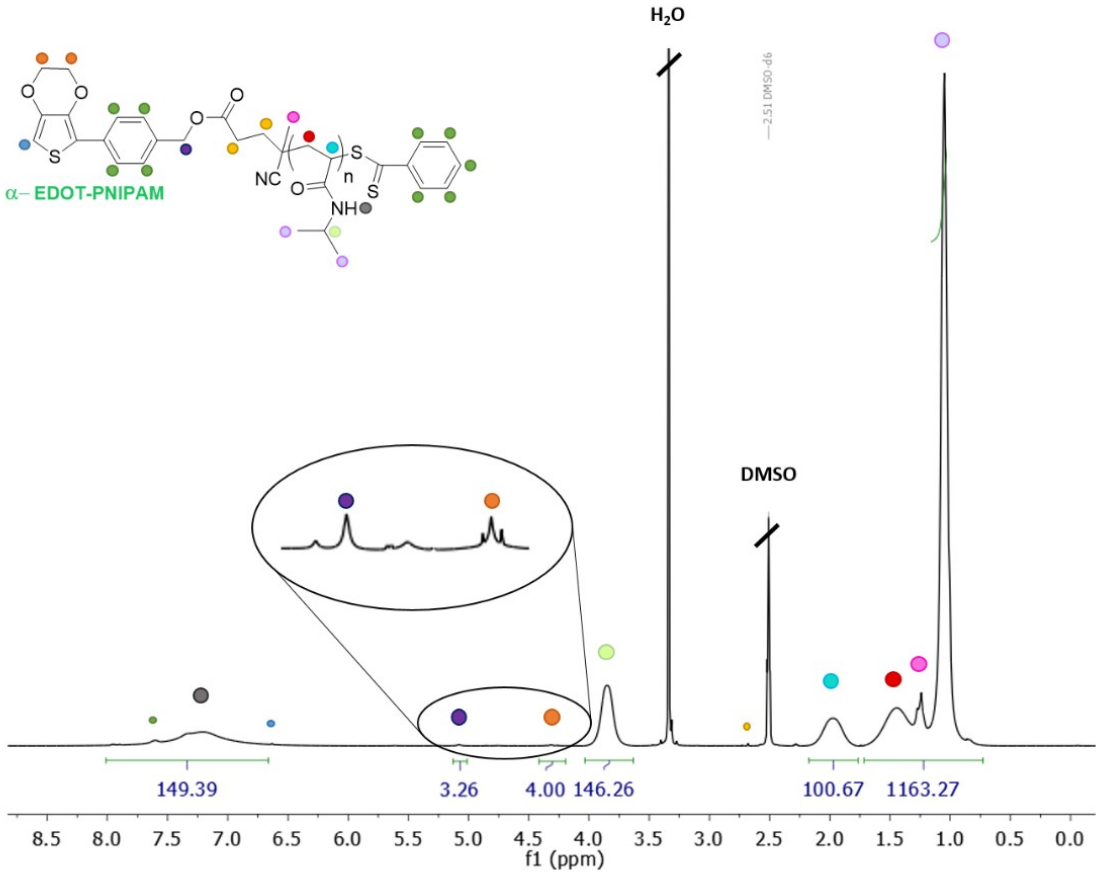


Figure S5. ^{1}H-NMR spectrum of α–EDOT-PNIPAM (M_n 20000 g mol^{-1}) macromonomer in DMSO-d_6.

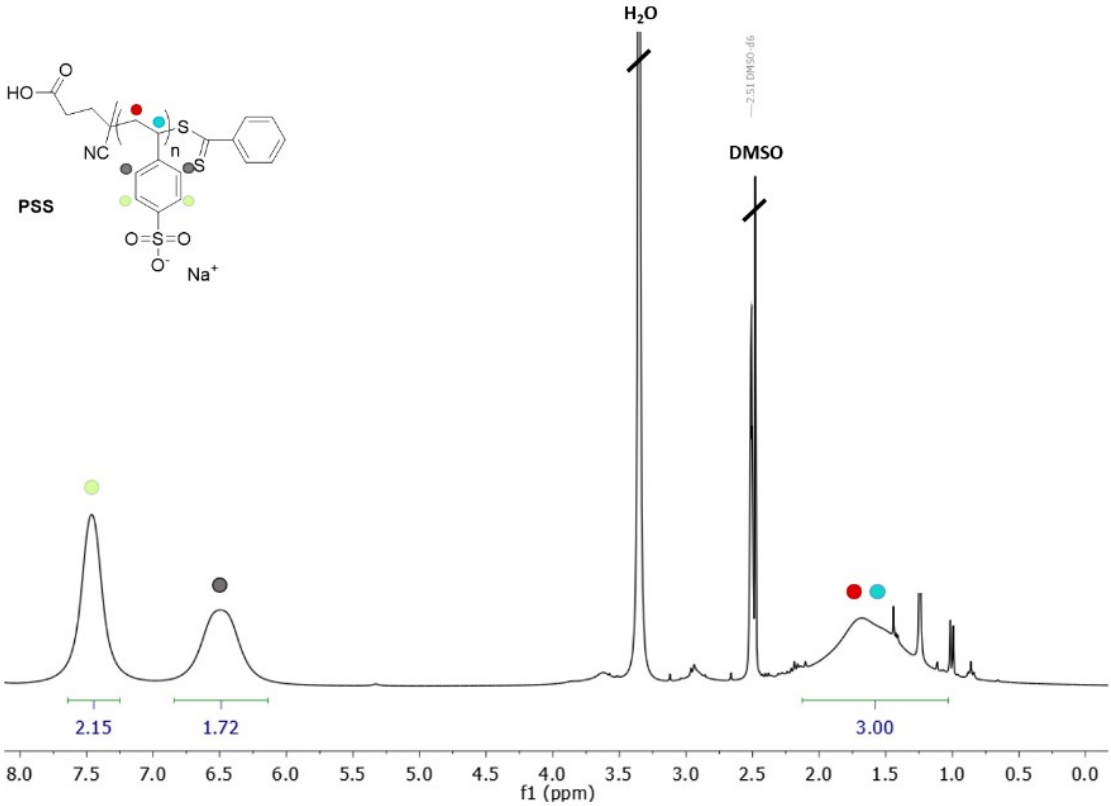


Figure S6. ^{1}H-NMR spectrum of PSS (M_n 20000 g mol^{-1}) macromonomer in DMSO-d_6.

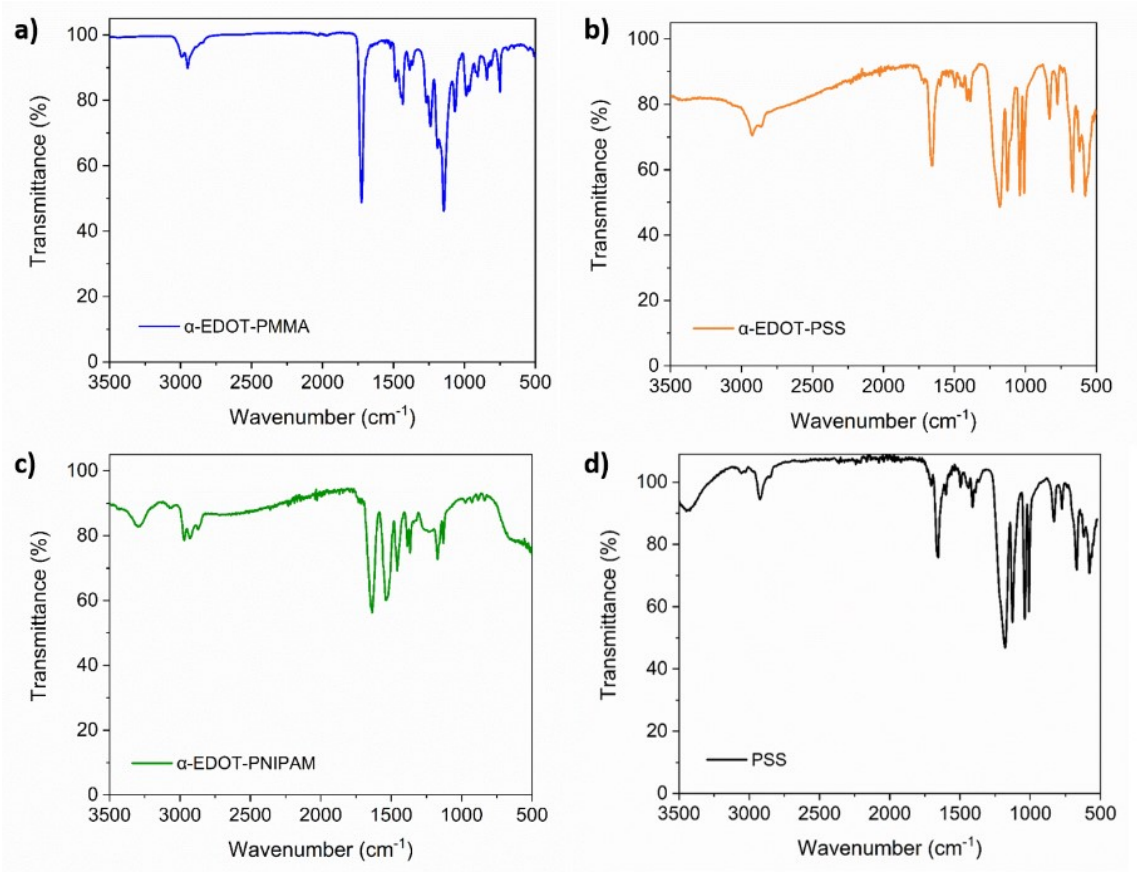


Figure S7. FTIR spectra of a) α–EDOT-PMMA, b) α–EDOT-PSS, c) α–EDOT-PNIPAM and d) PSS macromonomers.

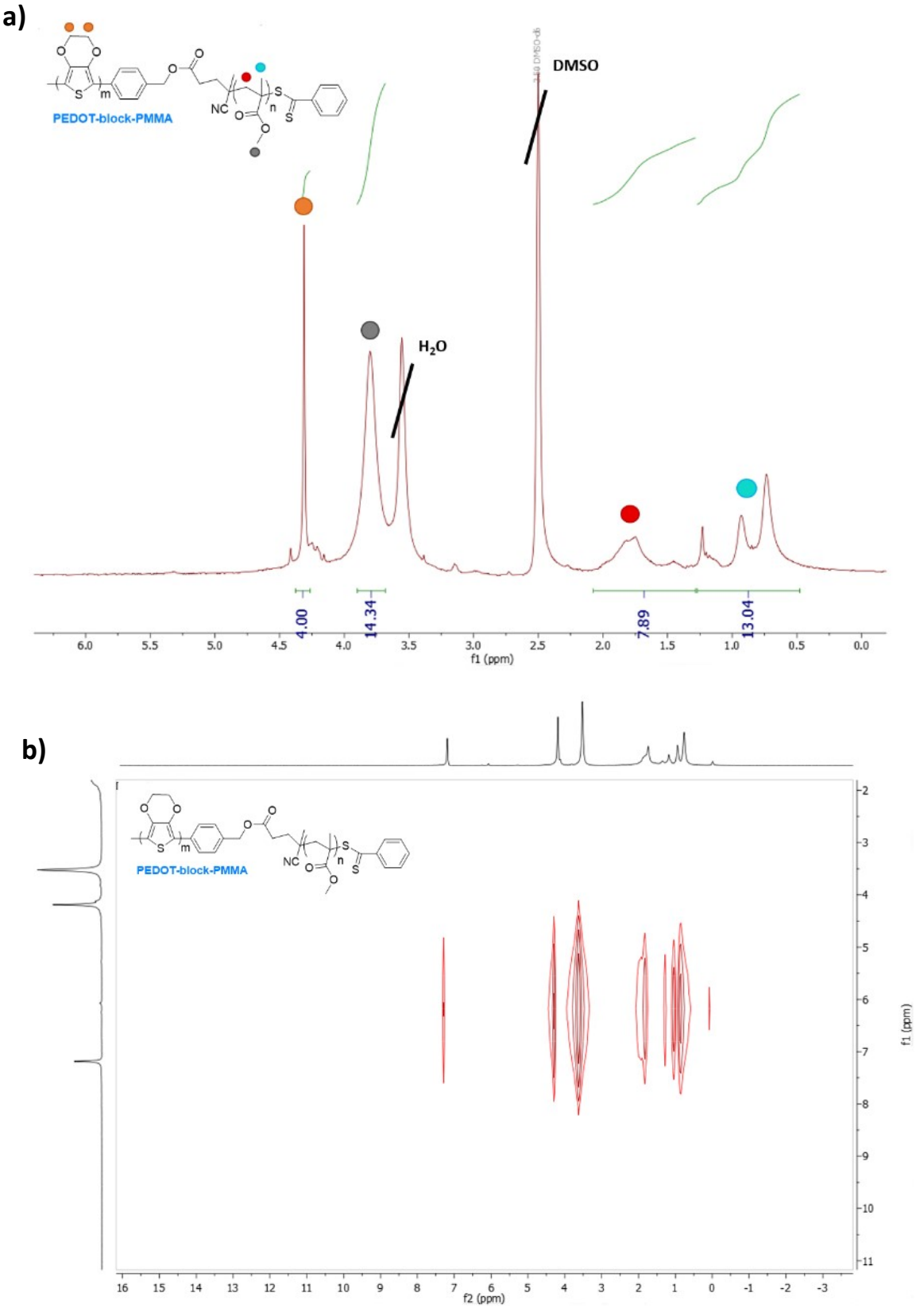


Figure S8. a) ^{1}H-NMR and b) DOSY-NMR of PEDOT-*b*-PMMA (M_n 10000) 50-50 block copolymer in Chloroform-*d.*

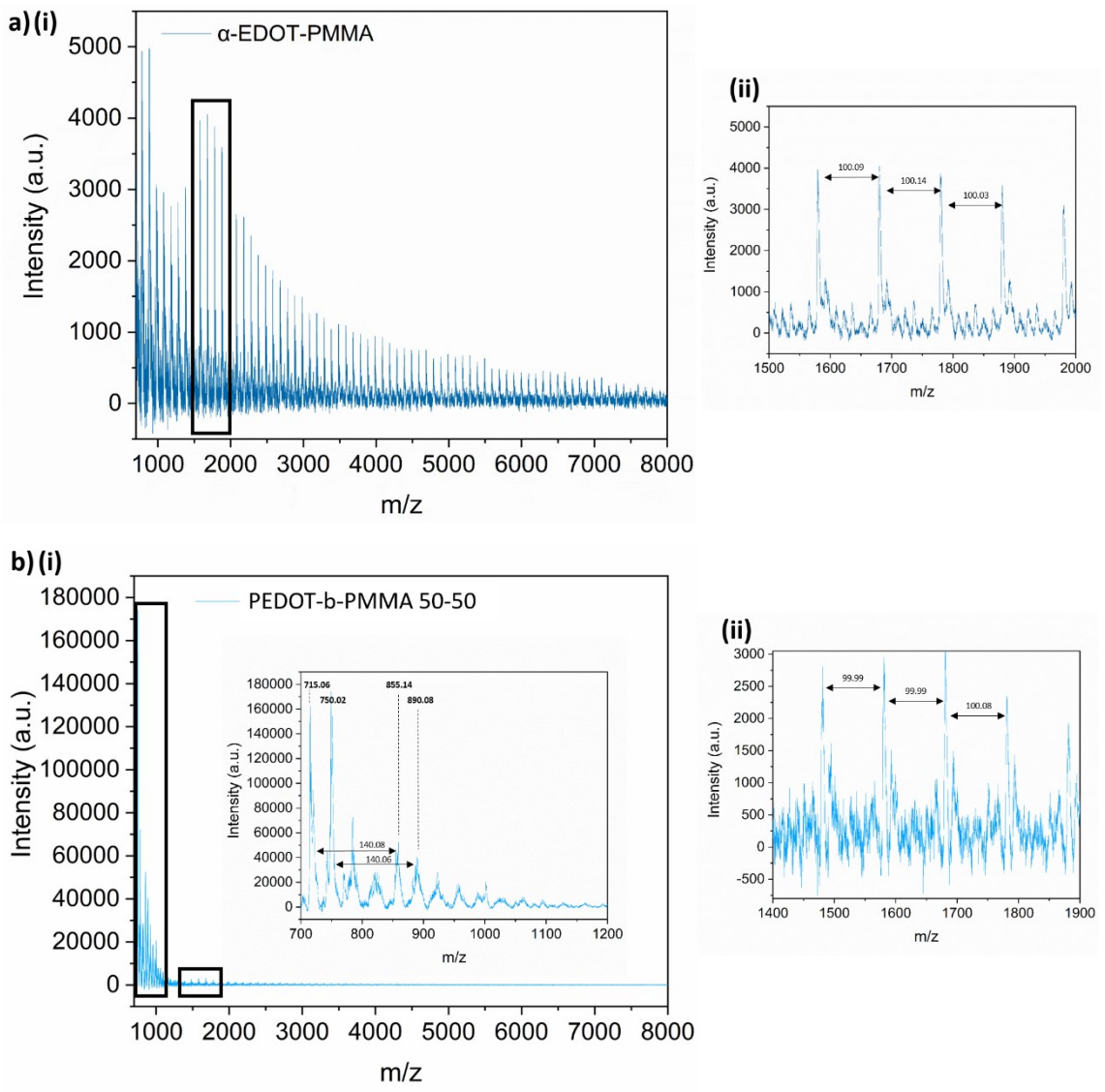


Figure S9. MALDI-TOF of a) α–EDOT-PMMA (M_n 10000 g mol^{-1}) macromonomer and b) PEDOT-*b*-PMMA (M_n 10000) 50-50 block copolymer. (i) Full scale and (ii) zoom of the spectra.

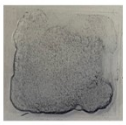
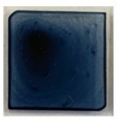
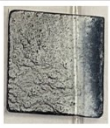
Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Conductivity (S cm^{-1})	Film
1	30	70	α-EDOT-PMMA (Mn 5000)	-	
2	50	50	α-EDOT-PMMA (Mn 5000)	-	
3	70	30	α-EDOT-PMMA (Mn 5000)	-	
4	30	70	α-EDOT-PMMA (Mn 10000)	-	
5	50	50	α-EDOT-PMMA (Mn 10000)	$7.5 \pm 0.3\ 10^{-7}$	
6	70	30	α-EDOT-PMMA (Mn 10000)	$1.2 \pm 0.4\ 10^{-6}$	
7	30	70	α-EDOT-PMMA (Mn 20000)	-	
8	50	50	α-EDOT-PMMA (Mn 20000)	$8.3 \pm 0.2\ 10^{-7}$	
9	70	30	α-EDOT-PMMA (Mn 20000)	$3.3 \pm 0.3\ 10^{-6}$	

Table S1. Electrical conductivity and film images of PEDOT-*b*-PMMA block copolymers.

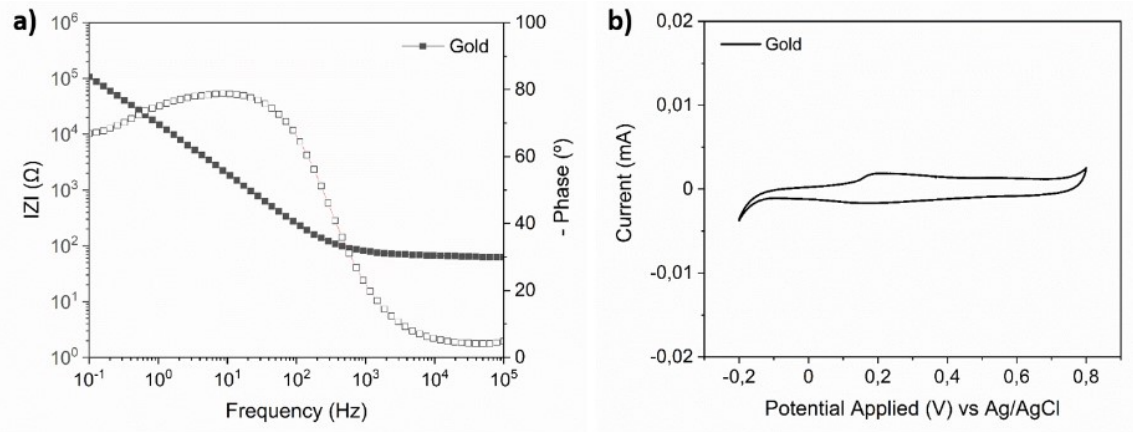


Figure S10. a) Bode plot obtained by EIS and b) CV (10 cycles, 20 mV s^{-1}) of gold electrode using PBS as the electrolyte, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

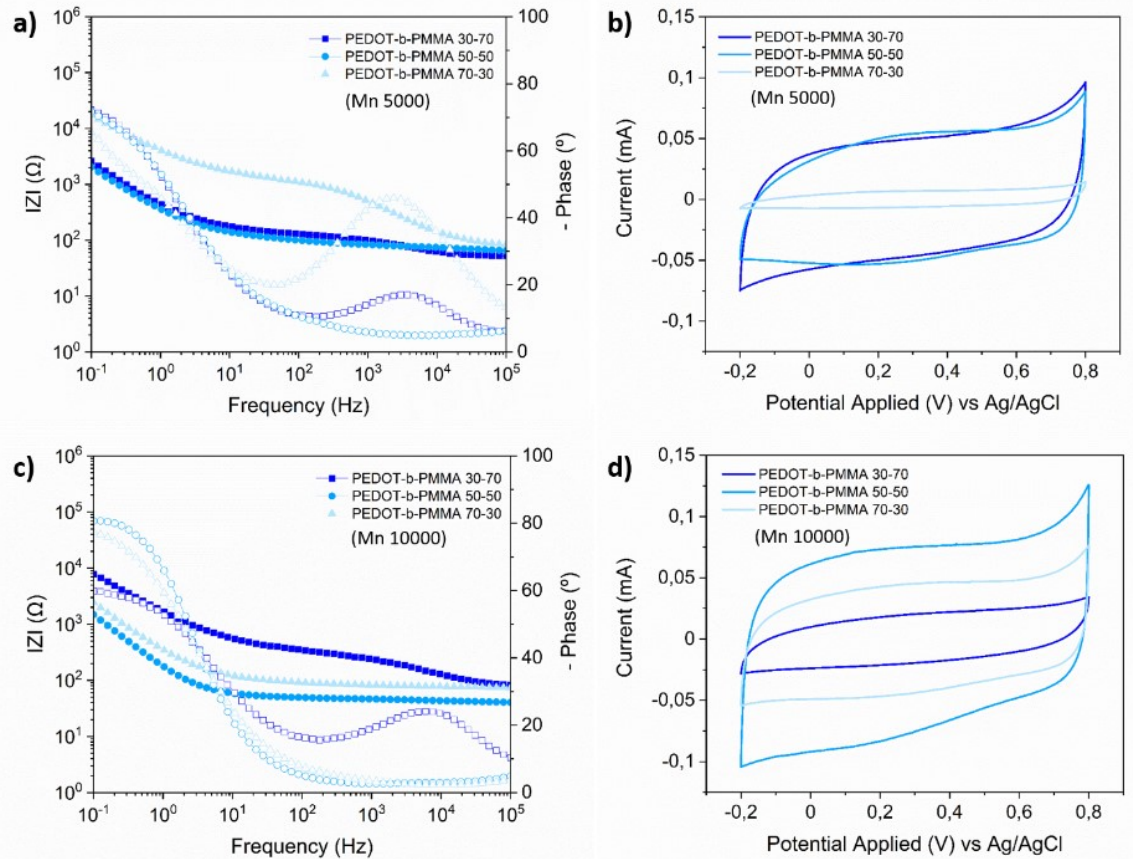


Figure S11. a) Bode plot obtained by EIS and b) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PMMA (M_n 5000) block copolymers. c) Bode plot obtained by EIS and d) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PMMA (M_n 10000) block copolymers. Conditions: PBS as the electrolyte, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Capacitance C (F)
0 (Gold)	-	-	-	$1.63 \pm 0.05\ 10^{-5}$
1	30	70	α-EDOT-PMMA (Mn 5000)	$6.40 \pm 0.07\ 10^{-4}$
2	50	50	α-EDOT-PMMA (Mn 5000)	$8.24 \pm 0.03\ 10^{-4}$
3	70	30	α-EDOT-PMMA (Mn 5000)	$1.01 \pm 0.04\ 10^{-4}$
4	30	70	α-EDOT-PMMA (Mn 10000)	$2.36 \pm 0.05\ 10^{-4}$
5	50	50	α-EDOT-PMMA (Mn 10000)	$1.09 \pm 0.04\ 10^{-3}$
6	70	30	α-EDOT-PMMA (Mn 10000)	$6.63 \pm 0.03\ 10^{-4}$
7	30	70	α-EDOT-PMMA (Mn 20000)	$1.75 \pm 0.07\ 10^{-4}$
8	50	50	α-EDOT-PMMA (Mn 20000)	$1.23 \pm 0.05\ 10^{-3}$
9	70	30	α-EDOT-PMMA (Mn 20000)	$8.71 \pm 0.03\ 10^{-4}$

Table S2. Capacitance values obtained from EIS by Equation 2 of PEDOT-*b*-PMMA block copolymers.

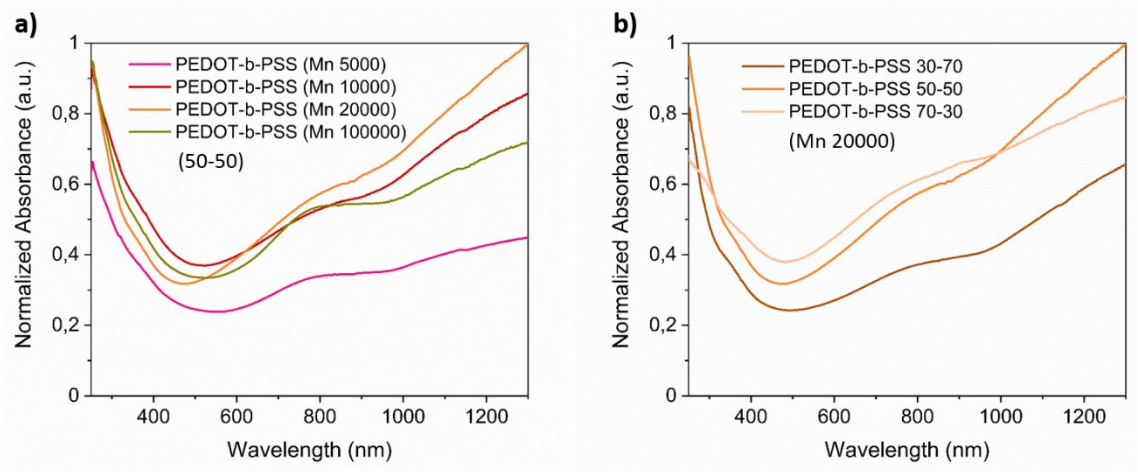


Figure S12. UV-Vis-NIR normalized absorption spectra of a) PEDOT-*b*-PSS (M_n 5000, 10000, 20000 and 100000) 50-50 block copolymer dispersions and b) PEDOT-*b*-PSS (M_n 20000) 30-70, 50-50 and 70-30 block copolymer dispersions.

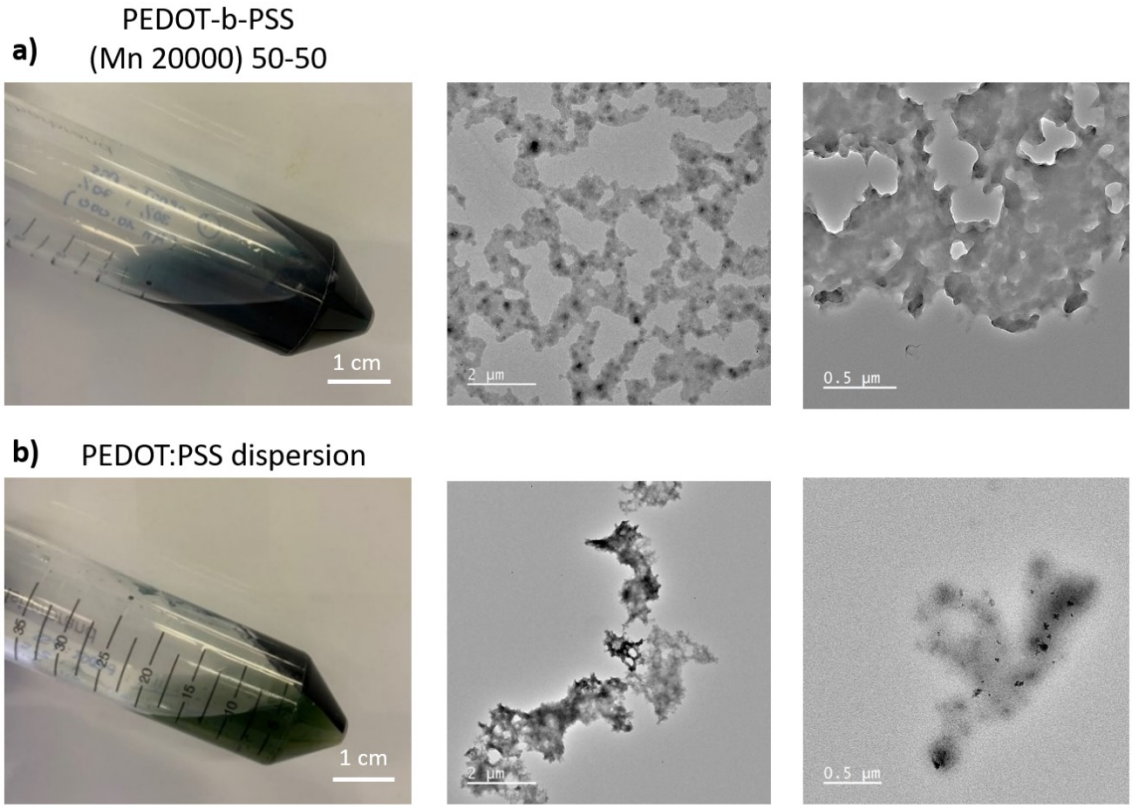


Figure S13. Dispersion stability after centrifugation and TEM images of a) PEDOT-*b*-PSS (M_n 20000) 50-50 block copolymer particles and b) synthetized PEDOT:PSS normal dispersion particles.

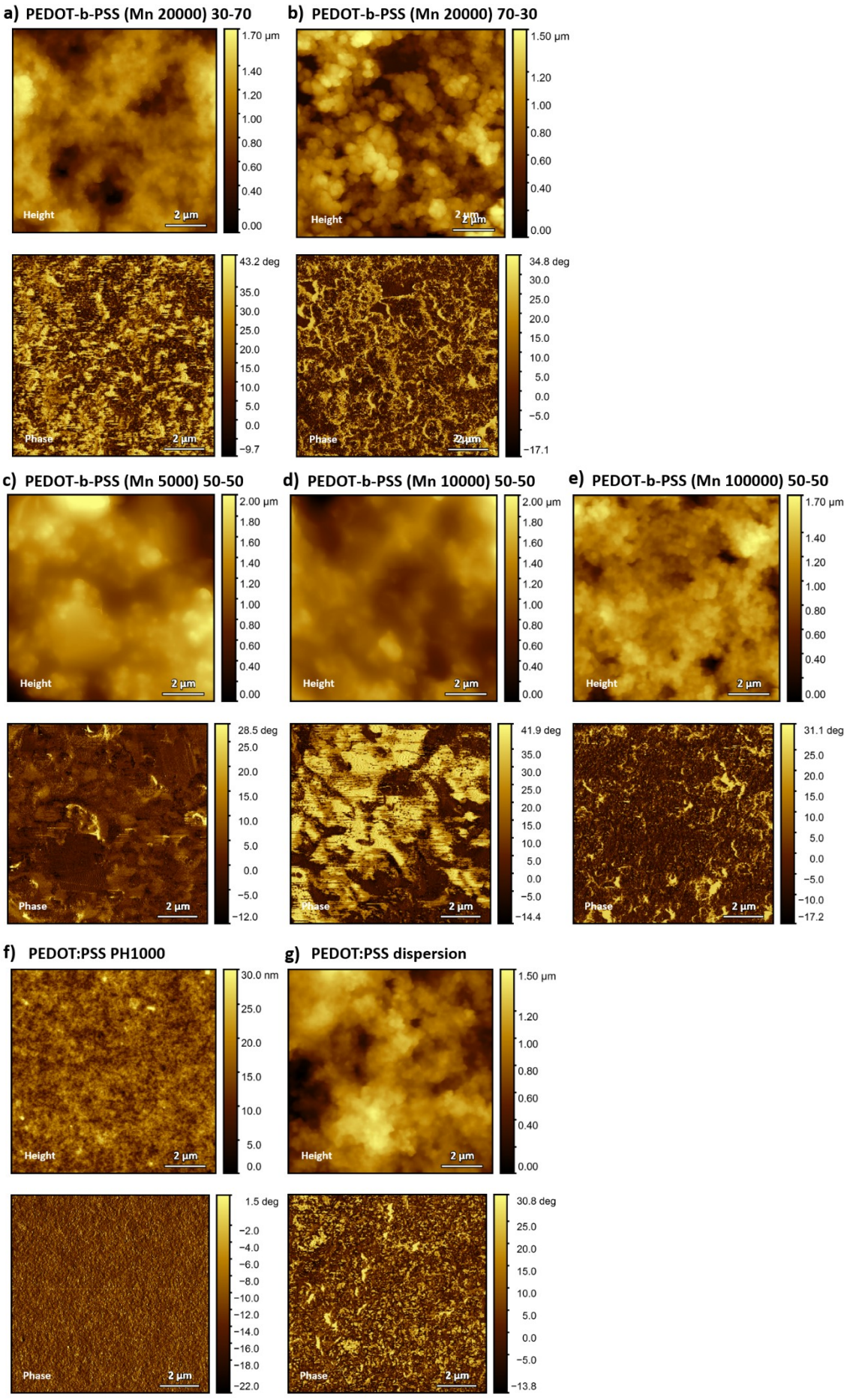

a) PEDOT-b-PSS (Mn 20000) 30-70
b) PEDOT-b-PSS (Mn 20000) 70-30
c) PEDOT-b-PSS (Mn 5000) 50-50
d) PEDOT-b-PSS (Mn 10000) 50-50
e) PEDOT-b-PSS (Mn 100000) 50-50
f) PEDOT:PSS PH1000
g) PEDOT:PSS dispersion
Height
Phase
2 µm
1.70 µm
1.50 µm
2.00 µm
30.0 nm
43.2 deg
34.8 deg
28.5 deg
41.9 deg
31.1 deg
1.5 deg
30.8 deg

Figure S14. AFM topographic height and phase images of a) PEDOT-*b*-PSS (M_n 20000) 30-70 block copolymer, b) PEDOT-*b*-PSS (M_n 20000) 70-30 block copolymer, c) PEDOT-*b*-PSS (M_n 5000) 50-50 block copolymer, d) PEDOT-*b*-PSS (M_n 10000) 50-50 block copolymer, e) PEDOT-*b*-PSS (M_n 100000) 50-50 block copolymer, f) PEDOT:PSS PH1000 commercial solution and g) PEDOT:PSS normal dispersion.

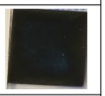
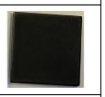
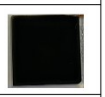
Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Conductivity (S cm^{-1}) No additives	Film No additives	Conductivity (S cm^{-1}) Additives	Film Additives
0 (PEDOT:PSS PH1000)	30	70	PSS	$4.5 \pm 0.2\ 10^{-1}$		$1.7 \pm 0.6\ 10^{+2}$	
1	30	70	α-EDOT-PSS (Mn 5000)	$3.2 \pm 0.1\ 10^{-4}$		$5.3 \pm 0.3\ 10^{-4}$	
2	50	50	α-EDOT-PSS (Mn 5000)	$3.7 \pm 0.5\ 10^{-4}$		$6.0 \pm 0.4\ 10^{-4}$	
3	70	30	α-EDOT-PSS (Mn 5000)	$5.0 \pm 0.3\ 10^{-3}$		$2.4 \pm 0.2\ 10^{-3}$	
4	30	70	α-EDOT-PSS (Mn 10000)	$5.4 \pm 0.4\ 10^{-4}$		$7.4 \pm 0.1\ 10^{-4}$	
5	50	50	α-EDOT-PSS (Mn 10000)	-		$2.7 \pm 0.2\ 10^{-1}$	
6	70	30	α-EDOT-PSS (Mn 10000)	$4.0 \pm 0.2\ 10^{-4}$		$7.8 \pm 0.5\ 10^{-1}$	
7	30	70	α-EDOT-PSS (Mn 20000)	$2.3 \pm 0.1\ 10^{-1}$		$2.0 \pm 0.2\ 10^{-1}$	
8	50	50	α-EDOT-PSS (Mn 20000)	$8.7 \pm 0.5\ 10^{-4}$		$2.8 \pm 0.4\ 10^{0}$	
9	70	30	α-EDOT-PSS (Mn 20000)	$2.9 \pm 0.3\ 10^{-1}$		$2.5 \pm 0.5\ 10^{0}$	
10	30	70	α-EDOT-PSS (Mn 100000)	$1.1 \pm 0.2\ 10^{-3}$		$4.0 \pm 0.3\ 10^{-2}$	
11	50	50	α-EDOT-PSS (Mn 100000)	$6.5 \pm 0.6\ 10^{-4}$		$2.0 \pm 0.4\ 10^{-2}$	
12	70	30	α-EDOT-PSS (Mn 100000)	-		$5.7 \pm 0.6\ 10^{-1}$	
13 (normal dispersion, no block copolymer)	50	50	PSS (Mn 20000)	$5.3 \pm 0.3\ 10^{-2}$		$1.4 \pm 0.4\ 10^{-1}$	

Table S3. Electrical conductivity and film images of PEDOT-*b*-PSS block copolymers.

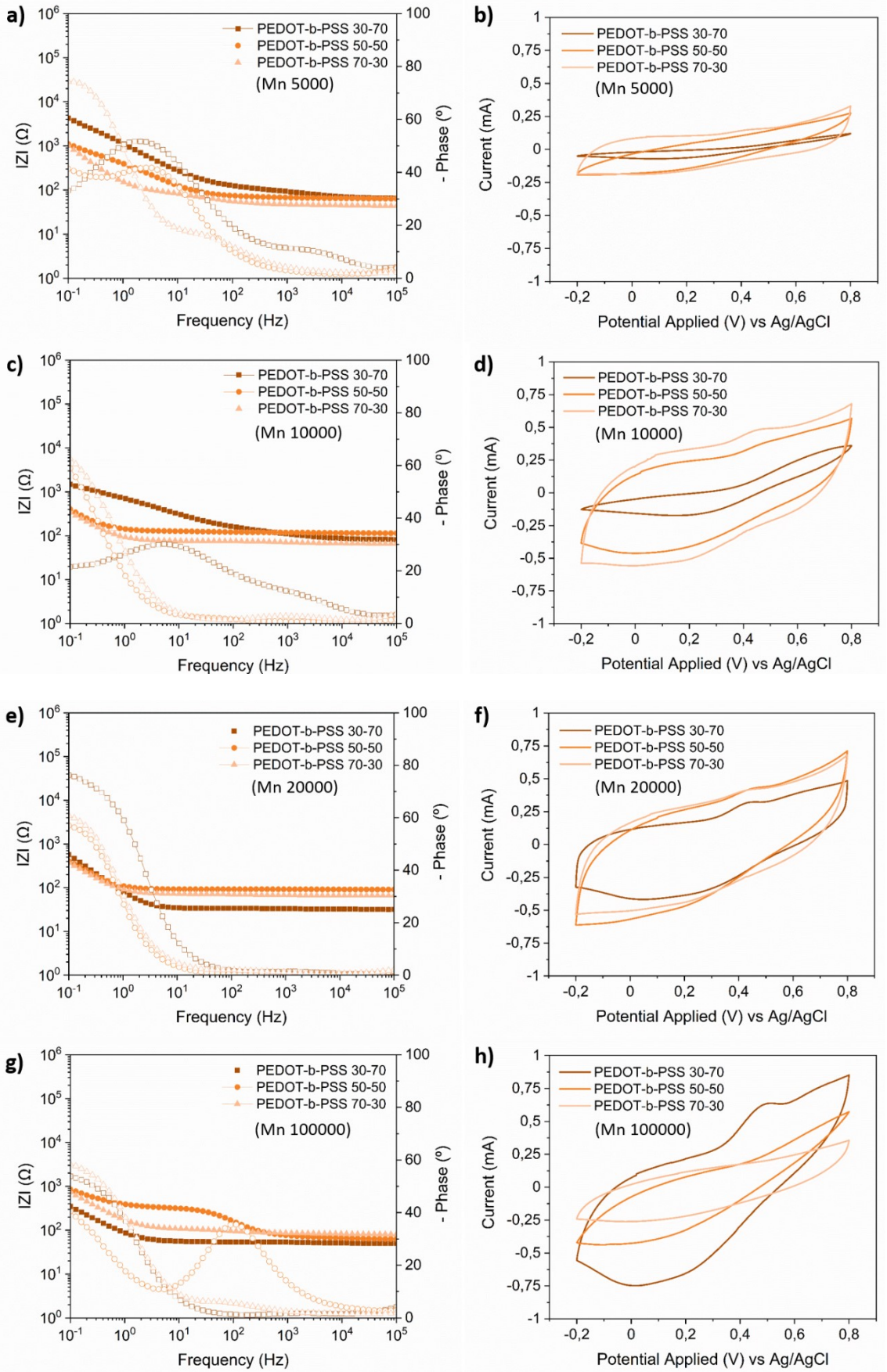

a)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 5000)
|Z| (Ω)
- Phase (°)
Frequency (Hz)
b)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 5000)
Current (mA)
Potential Applied (V) vs Ag/AgCl
c)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 10000)
|Z| (Ω)
- Phase (°)
Frequency (Hz)
d)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 10000)
Current (mA)
Potential Applied (V) vs Ag/AgCl
e)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 20000)
|Z| (Ω)
- Phase (°)
Frequency (Hz)
f)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 20000)
Current (mA)
Potential Applied (V) vs Ag/AgCl
g)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 100000)
|Z| (Ω)
- Phase (°)
Frequency (Hz)
h)
PEDOT-b-PSS 30-70
PEDOT-b-PSS 50-50
PEDOT-b-PSS 70-30
(Mn 100000)
Current (mA)
Potential Applied (V) vs Ag/AgCl

Figure S15. a) Bode plot obtained by EIS and b) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PSS (M_n 5000) block copolymers. c) Bode plot obtained by EIS and d) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PSS (M_n 10000) block copolymers. e) Bode plot obtained by EIS and f) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PSS (M_n 20000) block copolymers. g) Bode plot obtained by EIS and h) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PSS (M_n 100000) block copolymers. Conditions: PBS as the electrolyte, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Capacitance C (F)
0 (PEDOT:PSS PH1000)	30	70	PSS	$6.14 \pm 0.02\ 10^{-3}$
1	30	70	α-EDOT-PSS (Mn 5000)	$6.80 \pm 0.05\ 10^{-4}$
2	50	50	α-EDOT-PSS (Mn 5000)	-
3	70	30	α-EDOT-PSS (Mn 5000)	$1.66 \pm 0.04\ 10^{-3}$
4	30	70	α-EDOT-PSS (Mn 10000)	$2.94 \pm 0.03\ 10^{-3}$
5	50	50	α-EDOT-PSS (Mn 10000)	$4.60 \pm 0.04\ 10^{-3}$
6	70	30	α-EDOT-PSS (Mn 10000)	$5.27 \pm 0.02\ 10^{-3}$
7	30	70	α-EDOT-PSS (Mn 20000)	$2.88 \pm 0.05\ 10^{-3}$
8	50	50	α-EDOT-PSS (Mn 20000)	$4.70 \pm 0.07\ 10^{-3}$
9	70	30	α-EDOT-PSS (Mn 20000)	$4.86 \pm 0.06\ 10^{-3}$
10	30	70	α-EDOT-PSS (Mn 100000)	$5.70 \pm 0.04\ 10^{-3}$
11	50	50	α-EDOT-PSS (Mn 100000)	$2.87 \pm 0.02\ 10^{-3}$
12	70	30	α-EDOT-PSS (Mn 100000)	$2.53 \pm 0.05\ 10^{-3}$
13 (normal dispersion, no block copolymer)	50	50	PSS (Mn 20000)	$4.44 \pm 0.03\ 10^{-3}$

Table S4. Capacitance values obtained from EIS by Equation 2 of PEDOT-*b*-PSS block copolymers.

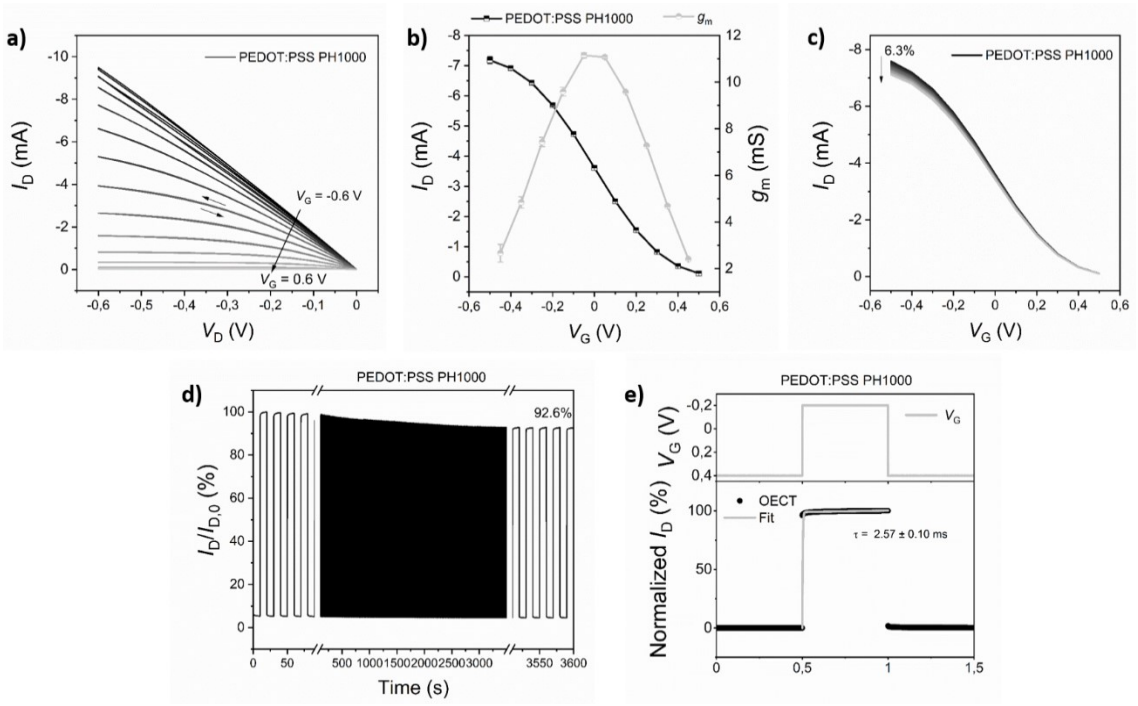


Figure S16. a) Output curve, b) transfer curve and g_m characteristics, c) repetition test (100 times), d) 1 hour operational stability test and e) pulse test response for commercial PEDOT:PSS PH1000. All characteristics were recorded at V_D = -0.5 V.

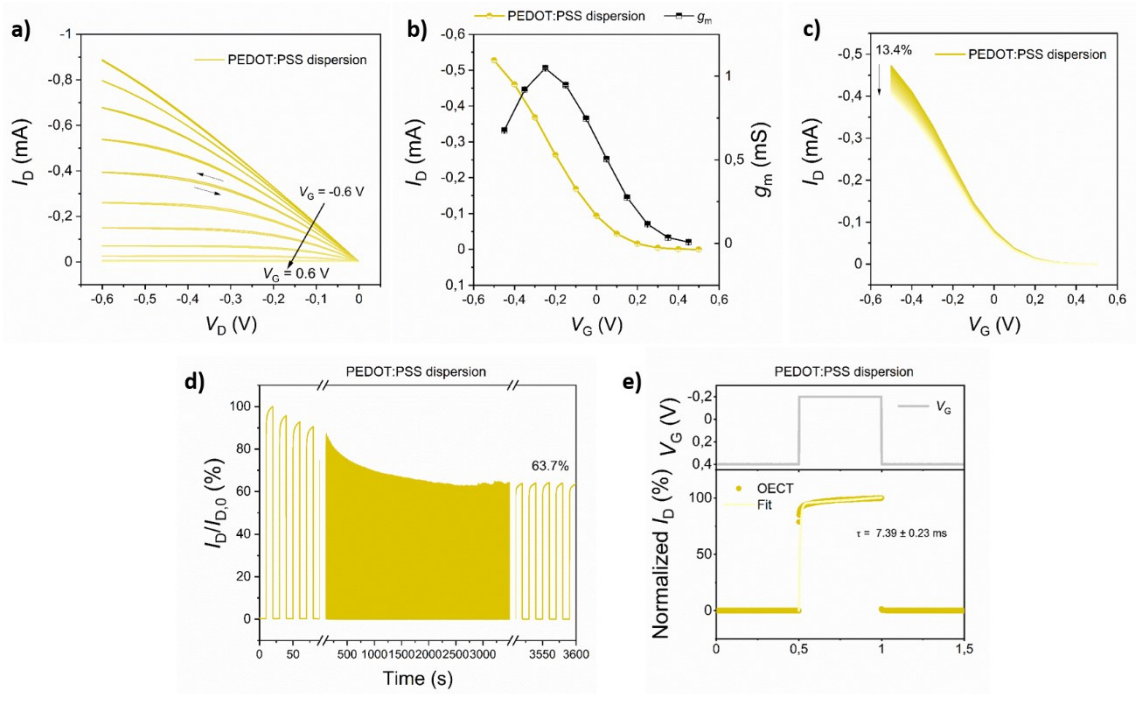


Figure S17. a) Output curve, b) transfer curve and g_m characteristics, c) repetition test (100 times), d) 1 hour operational stability test and e) pulse test response for normal PEDOT:PSS dispersion. All characteristics were recorded at V_D = -0.5 V.

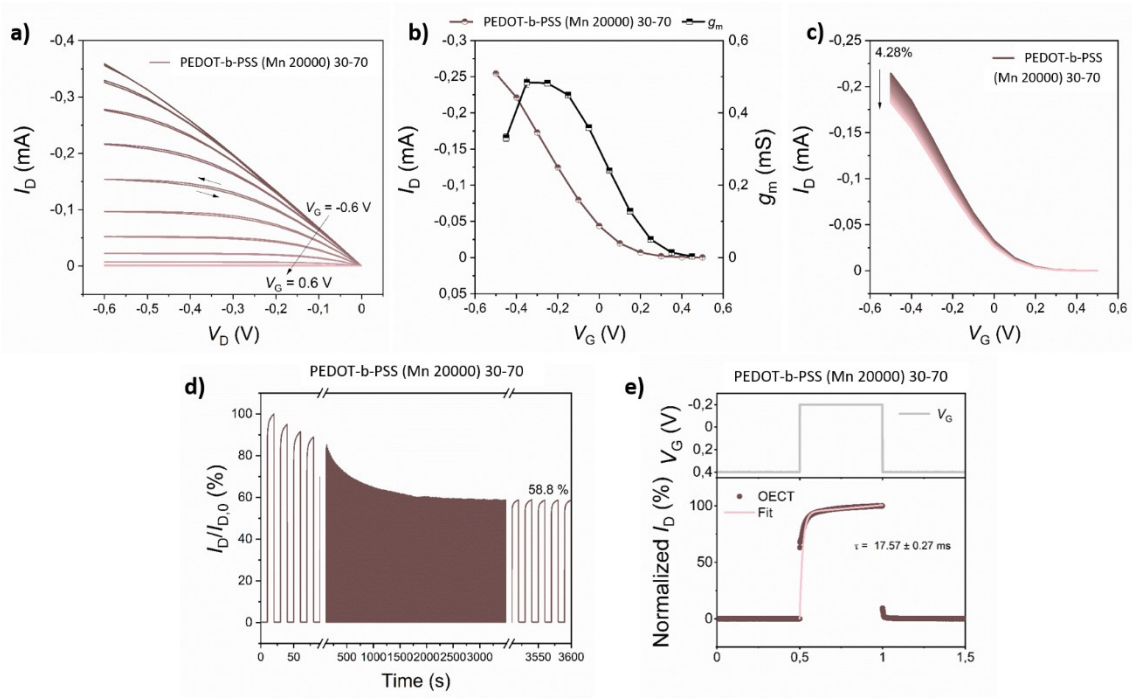


Figure S18. a) Output curve, b) transfer curve and g_m characteristics, c) repetition test (100 times), d) 1 hour operational stability test and e) pulse test response for PEDOT-*b*-PSS (M_n 20000) 30-70 block copolymer. All characteristics were recorded at V_D = -0.5 V.

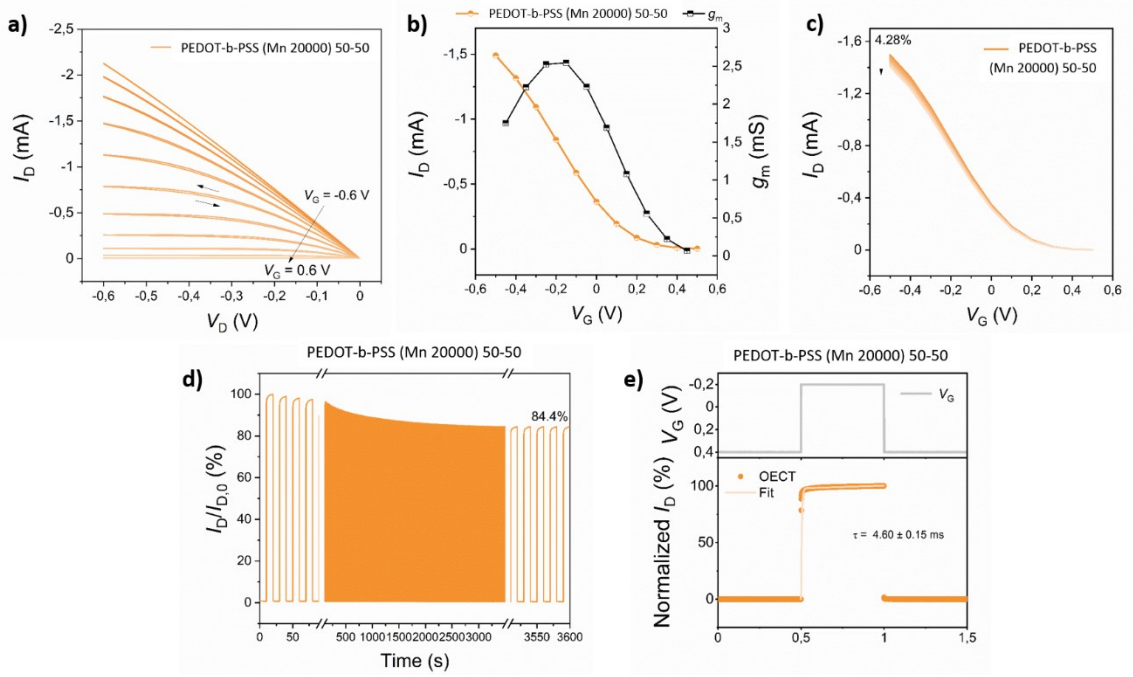


Figure S19. a) Output curve, b) transfer curve and g_m characteristics, c) repetition test (100 times), d) 1 hour operational stability test and e) pulse test response for PEDOT-*b*-PSS (M_n 20000) 50-50 block copolymer. All characteristics were recorded at V_D = -0.5 V.

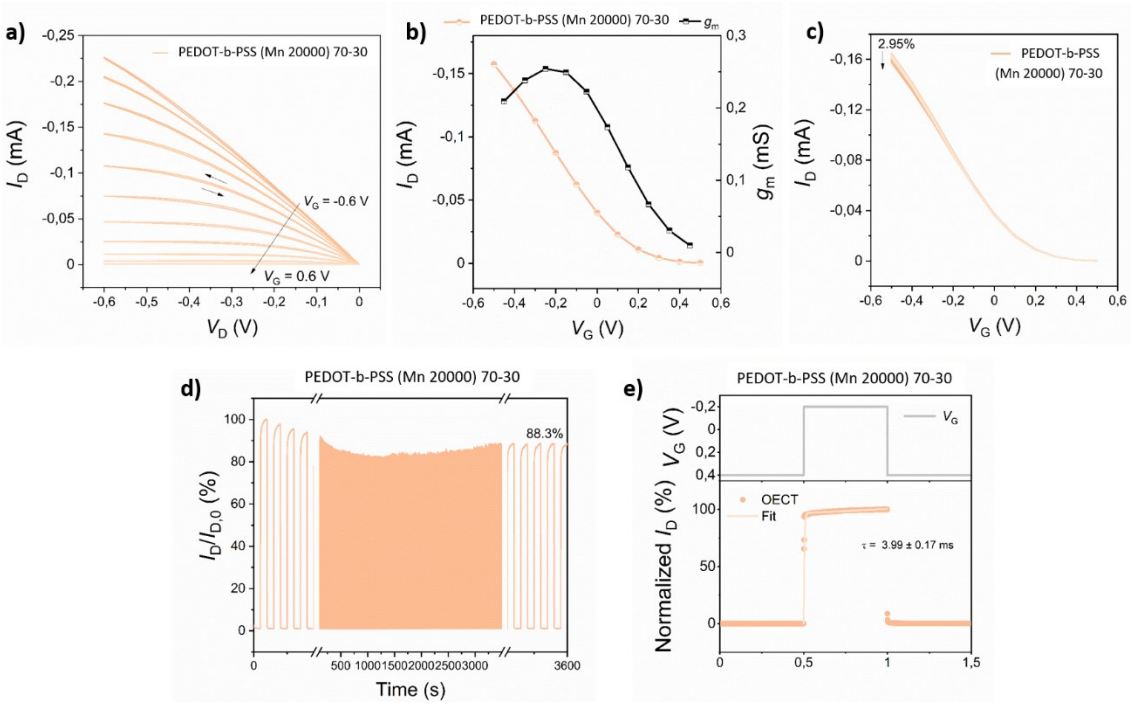


Figure S20. a) Output curve, b) transfer curve and g_m characteristics, c) repetition test (100 times), d) 1 hour operational stability test and e) pulse test response for PEDOT-*b*-PSS (M_n 20000) 70-30 block copolymer. All characteristics were recorded at V_D = -0.5 V.

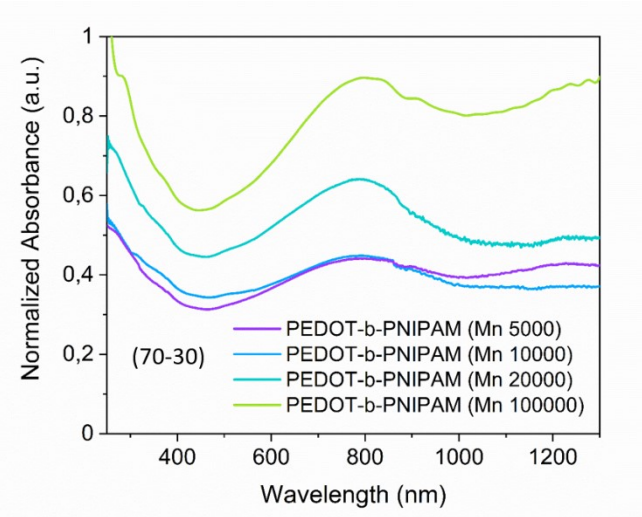
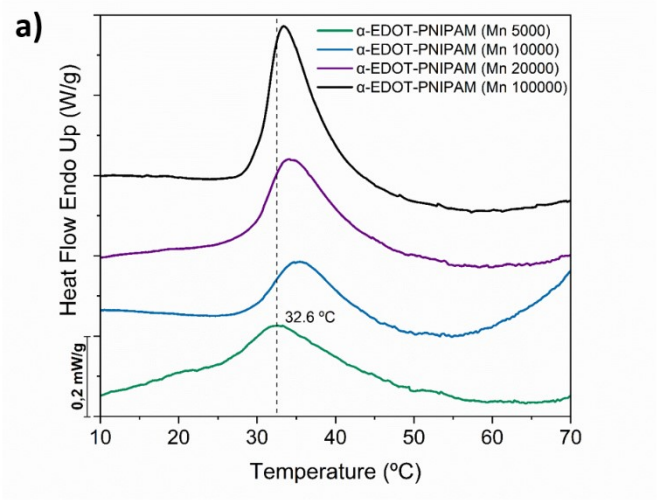


Figure S21. UV-Vis-NIR normalized absorption spectra of PEDOT-*b*-PNIPAM (M_n 5000, 10000, 20000 and 100000) 70-30 block copolymer dispersions.

a)



b)

Sample	T_{LCST} (°C)	ΔH_{LCST} (J/g)
α-EDOT-PNIPAM (Mn 5000)	33.2	38.4
α-EDOT-PNIPAM (Mn 10000)	35.6	15.5
α-EDOT-PNIPAM (Mn 20000)	34.1	30.2
α-EDOT-PNIPAM (Mn 100000)	33.4	36.9
PEDOT-b-PNIPAM (Mn 100000) 30-70	36.3	14.7
PEDOT-b-PNIPAM (Mn 100000) 50-50	37.3	8.8
PEDOT-b-PNIPAM (Mn 100000) 70-30	38.0	7.0

Figure S22. a) Micro-DSC thermograms of different α–EDOT-PNIPAM macromonomers. b) Thermal parameters obtained for the LCST transition of different α–EDOT-PNIPAM macromonomers and PEDOT-*b*-PNIPAM (M_n 100000) 30-70, 50-50 and 70-30 block copolymer dispersions.

Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Conductivity (S cm^{-1}) No additives	Film No additives	Conductivity (S cm^{-1}) Additives	Film Additives
1	30	70	α-EDOT-PNIPAM (Mn 5000)	-		$7.5 \pm 0.5\ 10^{-7}$	
2	50	50	α-EDOT-PNIPAM (Mn 5000)	-		$2.5 \pm 0.2\ 10^{-5}$	
3	70	30	α-EDOT-PNIPAM (Mn 5000)	$4.1 \pm 0.3\ 10^{-7}$		$1.3 \pm 0.4\ 10^{-4}$	
4	30	70	α-EDOT-PNIPAM (Mn 10000)	-		$9.2 \pm 0.6\ 10^{-7}$	
5	50	50	α-EDOT-PNIPAM (Mn 10000)	-		$3.3 \pm 0.2\ 10^{-5}$	
6	70	30	α-EDOT-PNIPAM (Mn 10000)	$4.4 \pm 0.1\ 10^{-7}$		$1.2 \pm 0.3\ 10^{-4}$	
7	30	70	α-EDOT-PNIPAM (Mn 20000)	-		$8.8 \pm 0.4\ 10^{-7}$	
8	50	50	α-EDOT-PNIPAM (Mn 20000)	-		$3.4 \pm 0.5\ 10^{-4}$	
9	70	30	α-EDOT-PNIPAM (Mn 20000)	$7.6 \pm 0.4\ 10^{-7}$		$2.3 \pm 0.2\ 10^{-3}$	
10	30	70	α-EDOT-PNIPAM (Mn 100000)	-		$1.7 \pm 0.4\ 10^{-6}$	
11	50	50	α-EDOT-PNIPAM (Mn 100000)	-		$6.7 \pm 0.5\ 10^{-4}$	
12	70	30	α-EDOT-PNIPAM (Mn 100000)	$1.2 \pm 0.3\ 10^{-6}$		$7.26 \pm 0.3\ 10^{-3}$	

Table S5. Electrical conductivity and film images of PEDOT-*b*-PNIPAM block copolymers.

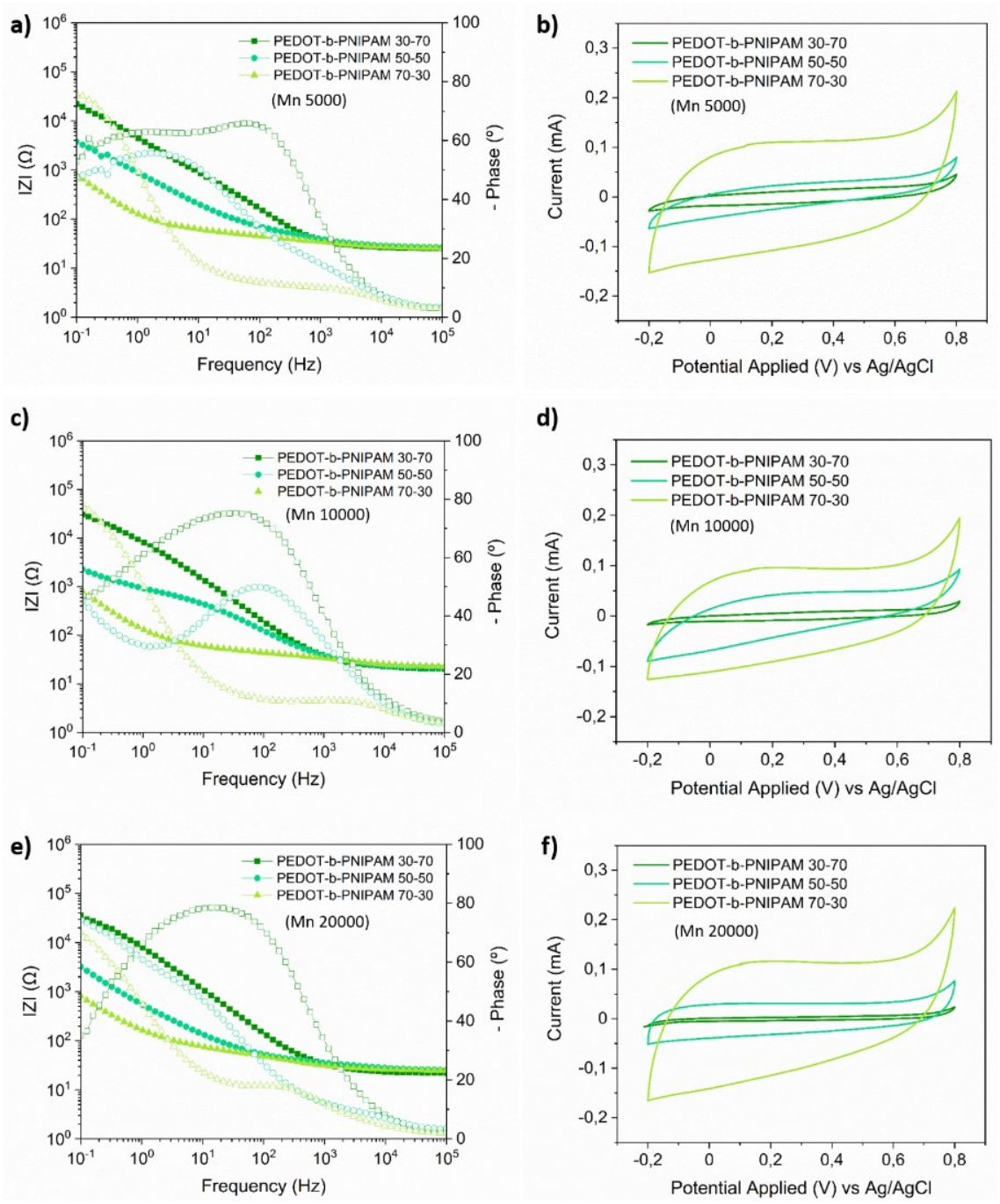


Figure S23. a) Bode plot obtained by EIS and b) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PNIPAM (M_n 5000) block copolymers. c) Bode plot obtained by EIS and d) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PNIPAM (M_n 10000) block copolymers. e) Bode plot obtained by EIS and f) CVs (10 cycles, 20 mV s^{-1}) of PEDOT-*b*-PNIPAM (M_n 20000) block copolymers. Conditions: PBS as the electrolyte, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

Code	PEDOT (wt%)	Macromonomer (wt%)	Macromonomer	Capacitance C (F) at 25 °C	Capacitance C (F) at 45 °C
1	30	70	α-EDOT-PNIPAM (Mn 5000)	$9.06 \pm 0.05\ 10^{-5}$	-
2	50	50	α-EDOT-PNIPAM (Mn 5000)	$5.77 \pm 0.03\ 10^{-4}$	-
3	70	30	α-EDOT-PNIPAM (Mn 5000)	$2.04 \pm 0.04\ 10^{-3}$	-
4	30	70	α-EDOT-PNIPAM (Mn 10000)	$7.34 \pm 0.06\ 10^{-5}$	-
5	50	50	α-EDOT-PNIPAM (Mn 10000)	$9.91 \pm 0.02\ 10^{-4}$	-
6	70	30	α-EDOT-PNIPAM (Mn 10000)	$2.03 \pm 0.04\ 10^{-3}$	-
7	30	70	α-EDOT-PNIPAM (Mn 20000)	$7.71 \pm 0.05\ 10^{-5}$	-
8	50	50	α-EDOT-PNIPAM (Mn 20000)	$5.13 \pm 0.03\ 10^{-4}$	-
9	70	30	α-EDOT-PNIPAM (Mn 20000)	$2.11 \pm 0.06\ 10^{-3}$	-
10	30	70	α-EDOT-PNIPAM (Mn 100000)	$2.34 \pm 0.07\ 10^{-4}$	$5.09 \pm 0.06\ 10^{-4}$
11	50	50	α-EDOT-PNIPAM (Mn 100000)	$1.74 \pm 0.04\ 10^{-3}$	$1.94 \pm 0.02\ 10^{-3}$
12	70	30	α-EDOT-PNIPAM (Mn 100000)	$2.08 \pm 0.05\ 10^{-3}$	$2.34 \pm 0.04\ 10^{-3}$

Table S6. Capacitance values obtained from EIS by Equation 2 of PEDOT-*b*-PNIPAM block copolymers at 25 and 45 °C.

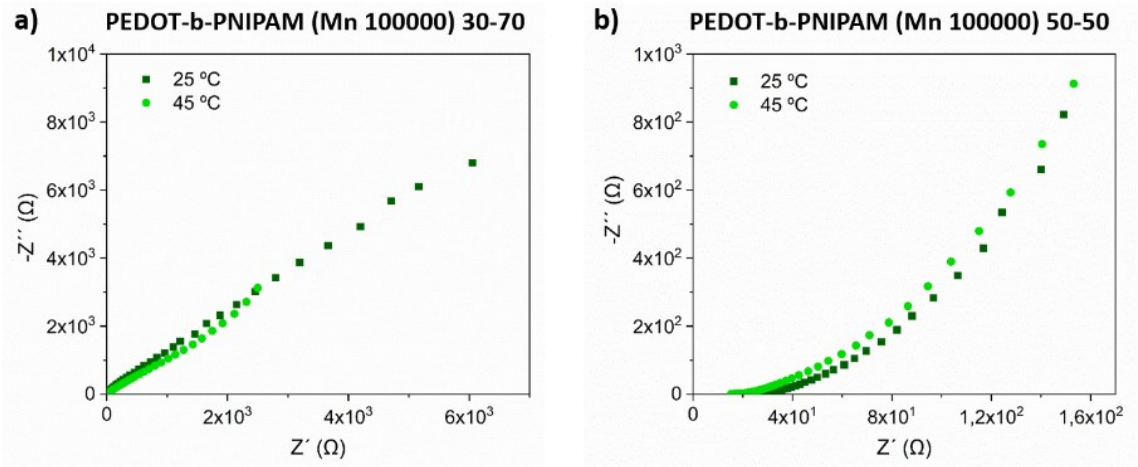


Figure S24. Nyquist plot obtained by EIS of a) PEDOT-*b*-PNIPAM (M_n 100000) 30-70 block copolymer and b) PEDOT-*b*-PNIPAM (M_n 100000) 50-50 block copolymer at different temperatures (25 and 45 °C) using PBS as the electrolyte, Pt wire as the counter electrode and Ag/AgCl electrode as the reference electrode.

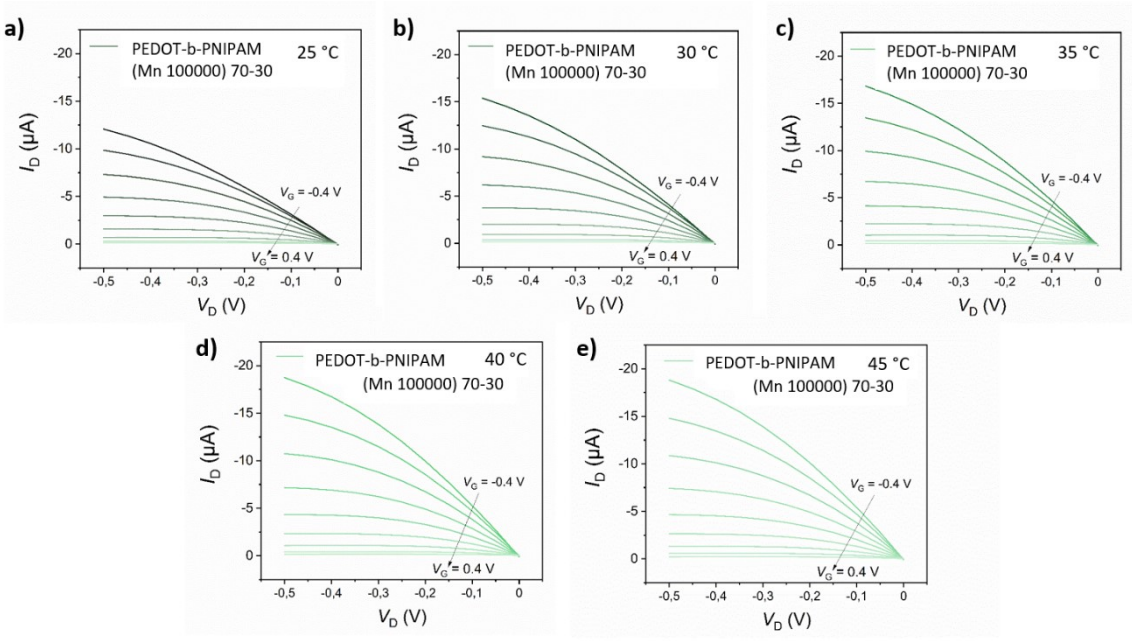


Figure S25. The OECT output curves with PEDOT-*b*-PNIPAM (M_n 100000) 70-30 block copolymer as channel material at a) 25, b) 30, c) 35, d) 40 and e) 45 °C.

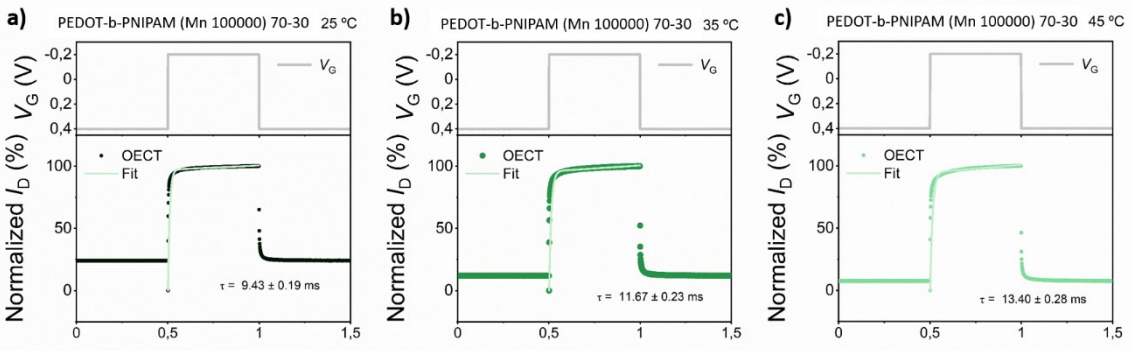


Figure S26. Pulse test response for PEDOT-*b*-PNIPAM (M_n 100000) 70-30 block copolymer OECT channel material at a) 25, b) 35 and c) 45 °C.