

Supporting Information

Absorption coefficient and optical contrast modulation through side chain engineering of electrochromic polymers

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This file includes:

General synthetic procedures, Polymer solution and thin film characterization, DFT calculations for n=6 oligomers, Absorption coefficient calculations, Spectroelectrochemical measurements, In-situ nanoindentation measurements, Comparison of experimental and modelled optical contrast, Cycling stability data.

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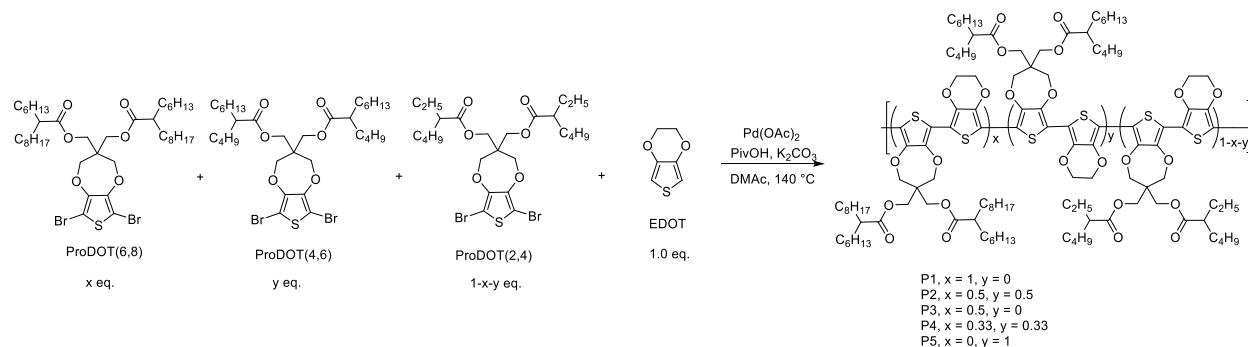
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01. General Synthetic Procedures

All reagents and EDOT monomer were purchased from commercial suppliers and used without further purification. ProDOT monomers were synthesized according to previously reported literature¹. All reactions were carried out under a N₂ atmosphere, unless otherwise noted.

1.1 Polymer synthesis

ProDOT(6,8) (x eq.), ProDOT(4,6) (y eq.), ProDOT(2,4) (1-x-y eq.), EDOT (1.0 eq.), K₂CO₃ (2.6 eq.), PivOH (0.3 eq.) and Pd(OAc)₂ (0.02) were added to a Schlenk flask, kept under vacuum for about 15 min and purged with nitrogen, three times. Then, nitrogen degassed solvent DMAc (30 ml of solvent for 1.0 g of EDOT) was added to the flask and heated in an oil bath at 140 °C for 6 h under nitrogen. The hot reaction mixture was transferred to a 1:1 mixture of CH₃OH and 1 M HCl while stirring. The resulting mixture was filtered to obtain a solid. This solid was dissolved in chloroform and washed with 1 M HCl solution. The organic phase was concentrated and precipitated with acetone, filtered, and dried to obtain the polymer.

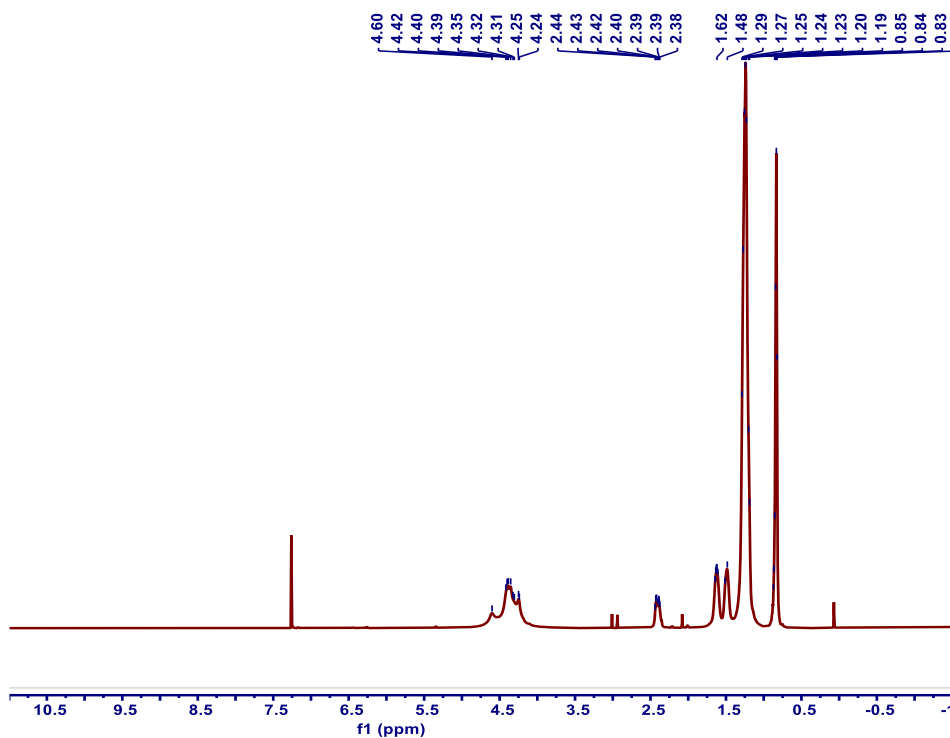


Scheme S1 Direct heteroarylation polymerization for the synthesis of polythiophenes **P1–P5**.

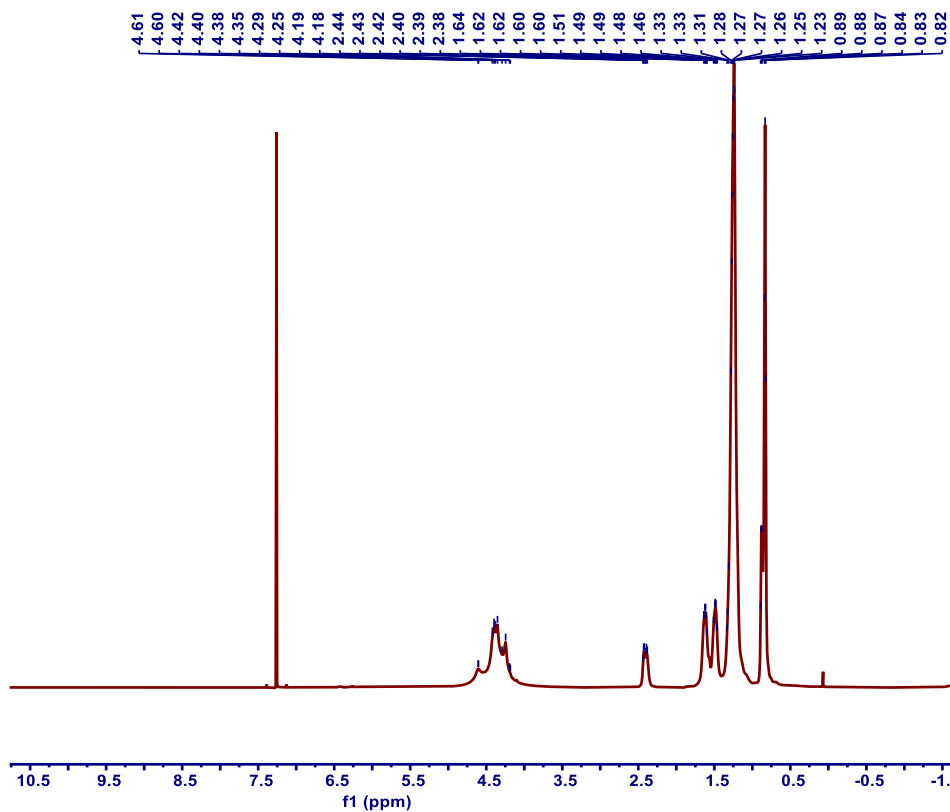
1.2 ^1H NMR spectra

^1H spectra were recorded using a Bruker ARX 400 MHz spectrometer in deuterated chloroform at 293 K.

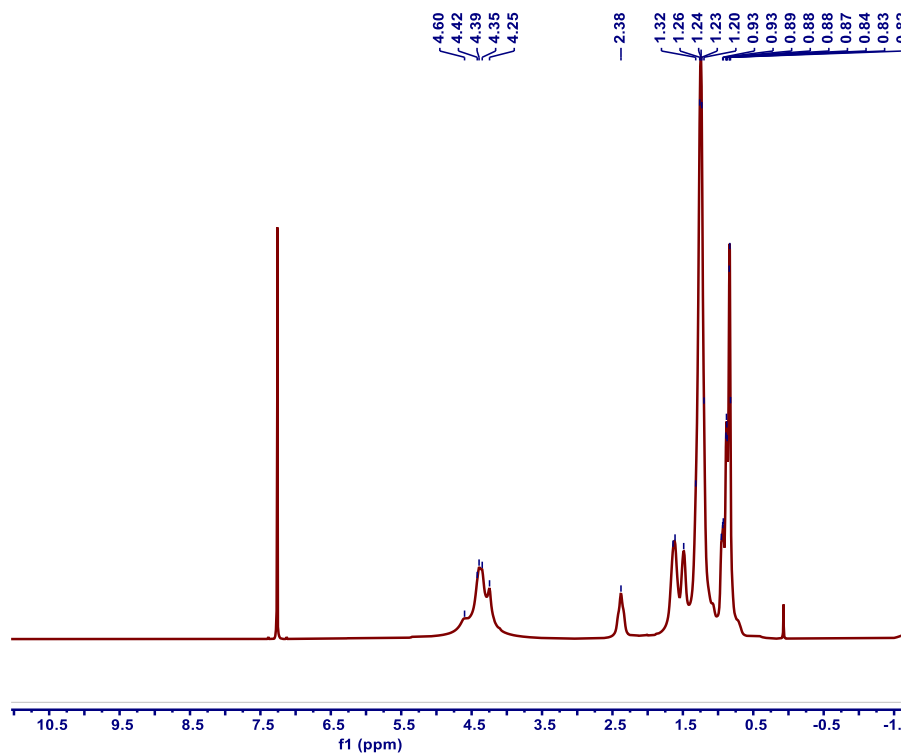
(a)



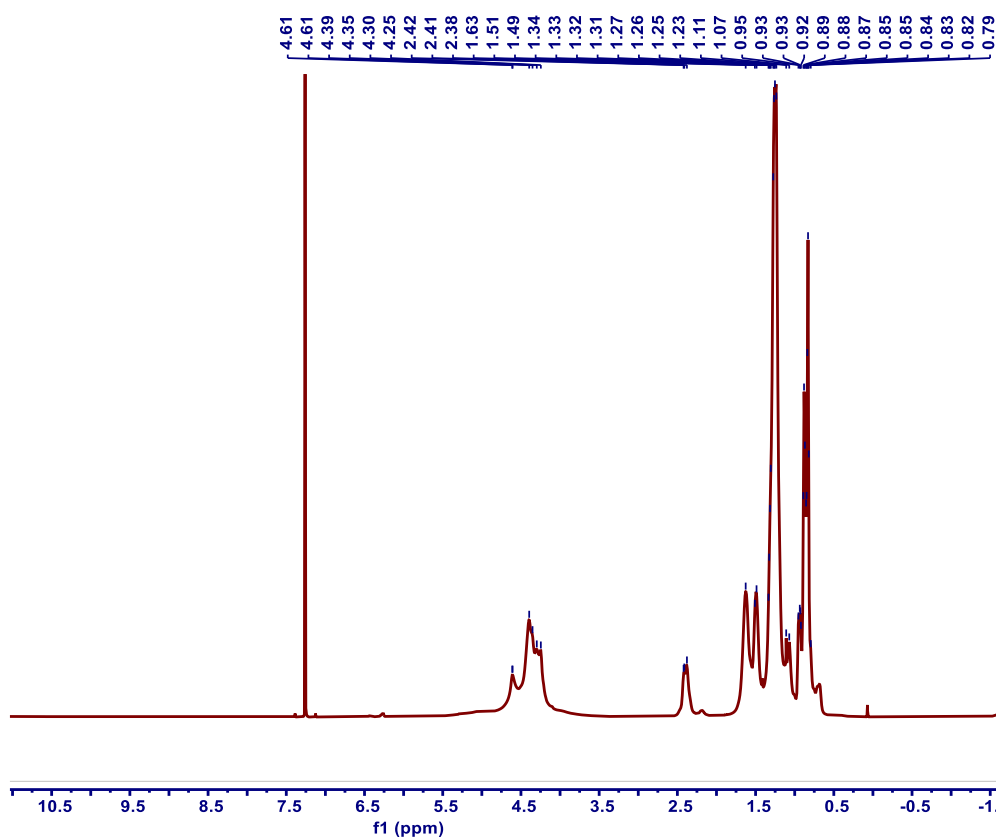
(b)



(c)



(d)



(e)

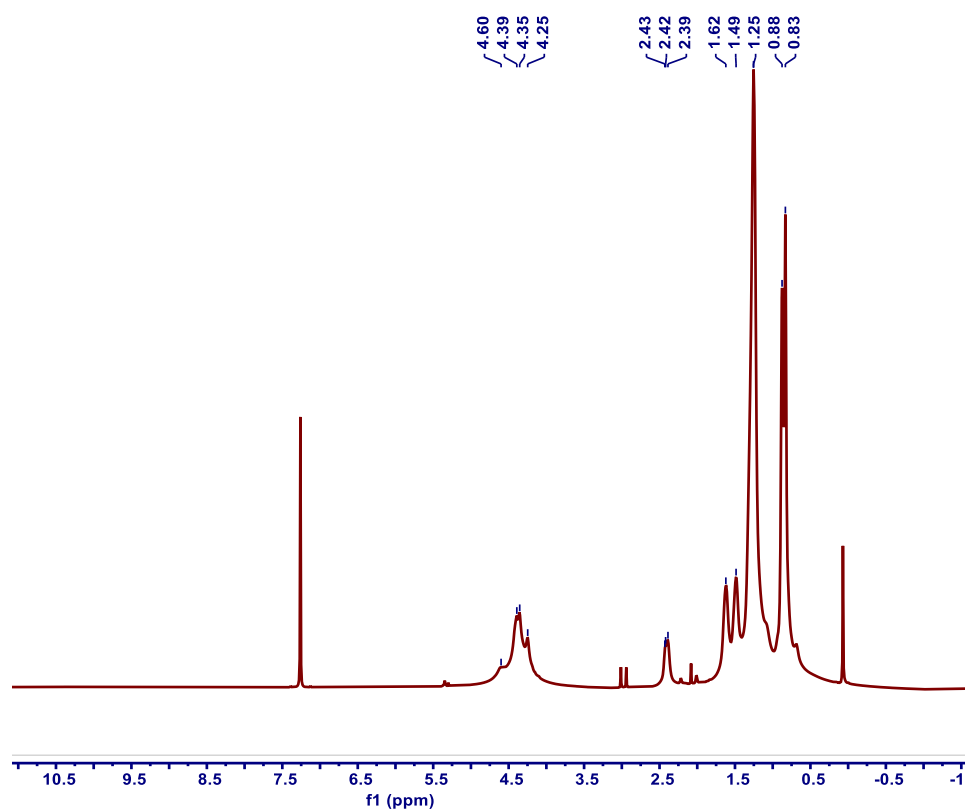
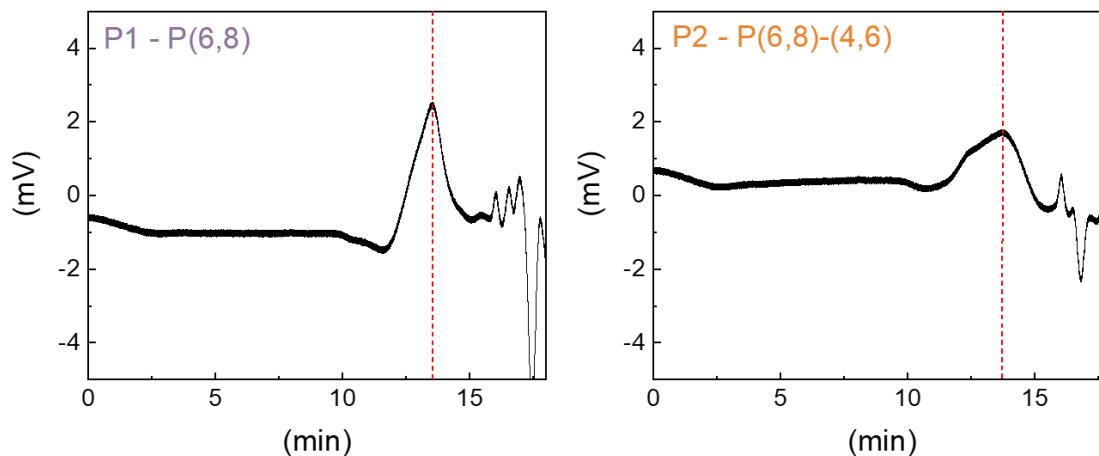


Figure S1 ^1H NMR spectra of (a) P1 = P(6,8), (b) P2 = P(6,8)-(4,6), (c) P3 = P(6,8)-(2,4), (d) P4 = P(6,8)-(4,6)-(2,4), and (e) P5 = P(4,6).

1.3 Molecular weight determination from GPC

Polymer solutions (1 mg/mL) prepared in THF were used for Gel Permeation Chromatography (EcoSEC GPC – Tosoh) at 40 °C, and flow rate of 0.35 mL/min, against polystyrene standard.



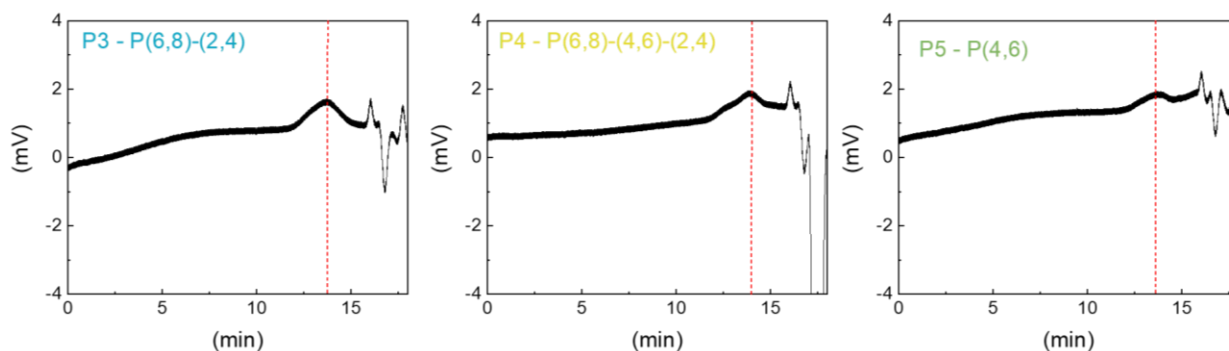


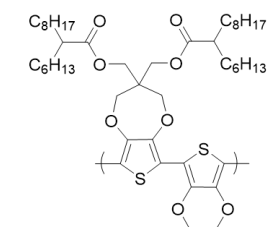
Figure S2 GPC traces of ProDOT-EDOT polymers dissolved in THF.

Table S1 Summary of GPC results

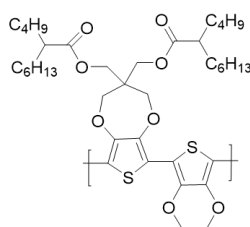
	Mn (kDa)	Mw(kDa)	PDI
P1	15.20	23.11	1.52
P2	14.13	27.92	2.01
P3	10.91	18.33	1.68
P4	(11.09)	(18.78)	(1.69)
P5	12.68	20.62	1.56

1.4 MALDI-TOF measurements

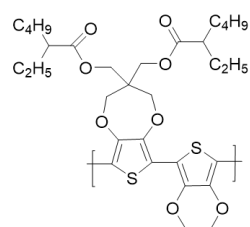
Measurements were performed at the Metabolite Profiling Facility (MPF) at the Purdue Bindley Bioscience Center, on an Applied Biosystems/MDS SCIEX 4800 MALDI TOF/TOF Analyzer, using a trans-2-[3-(4-tert-Butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) matrix (purchased from Santa Cruz Biotechnology, catalog # sc-255670).



Monomer mass = 830 amu



Monomer mass = 718 amu



Monomer mass = 606 amu

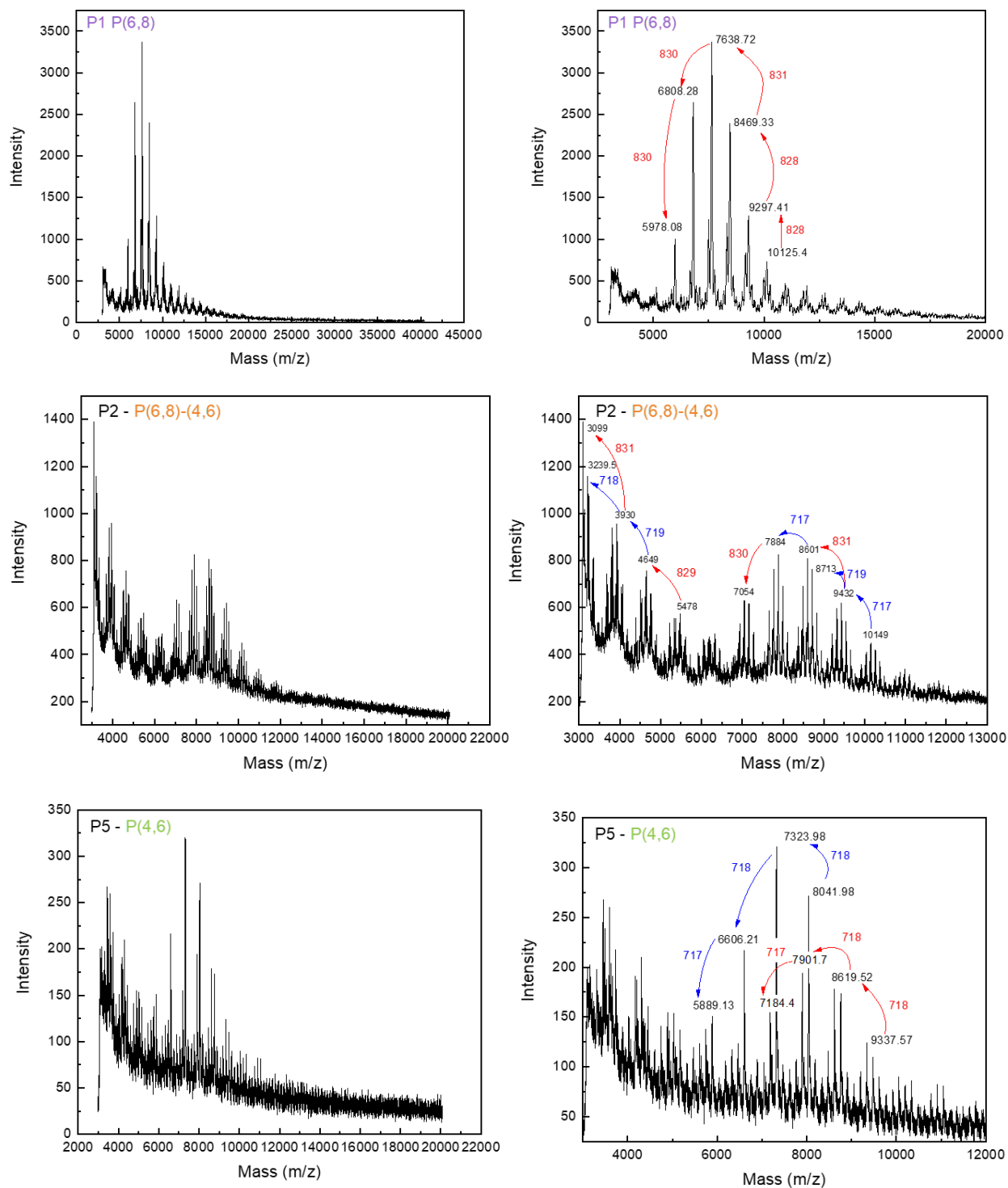


Figure S3 MALDI-TOF traces of ProDOT-EDOT polymers.

Calculated Mw: P1 – 8.5 kDa, P2 – 8.3 kDa, and P5 - 7.9 kDa.

02. Polymer solution characterization

2.1 Viscosity measurements

Polymer stock solutions (2 mg/mL) were prepared in CHCl_3 , sonicated for 30 minutes, left overnight to dissolve completely, and filtered through a 1 μm filter before further dilution. Viscosity was measured using Anton-Paar viscometer in the multi-concentration mode using solution concentrations of 0.8, 1.2, 1.6 and 2.0 mg/mL. The absolute concentration of the solutions were obtained by measuring the absorbance of a diluted solution and calculating the concentration using a Beer-Lambert plot.

Table S2 Intrinsic viscosity of ProDOT-EDOT polymers

Polymer	Intrinsic Viscosity (mL/g)
P(6,8)	40
P(6,8)-(4,6)	48
P(6,8)-(2,4)	51
P(6,8)-(4,6)-(2,4)	162
P(4,6)	147

2.2 Absorption spectra

To make the Beer-Lambert plots of polymer solutions, a stock solution of 1 mg/mL were prepared in CHCl_3 , sonicated for 30 minutes, and left overnight to ensure complete dissolution. Without further filtration, this stock solution was used to prepare a dilution series from 0.015 to 0.045 mg/mL and absorbance of each solution was measured with respect to the solvent.

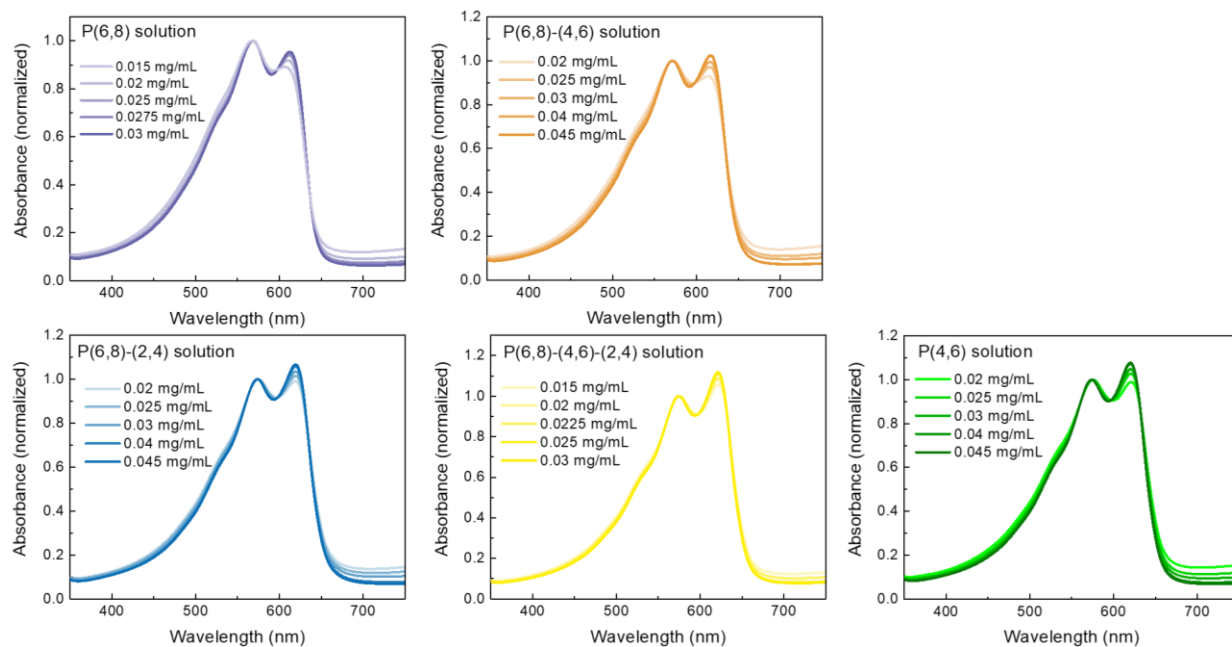


Figure S4 Absorption spectra of polymer solutions at different concentrations.

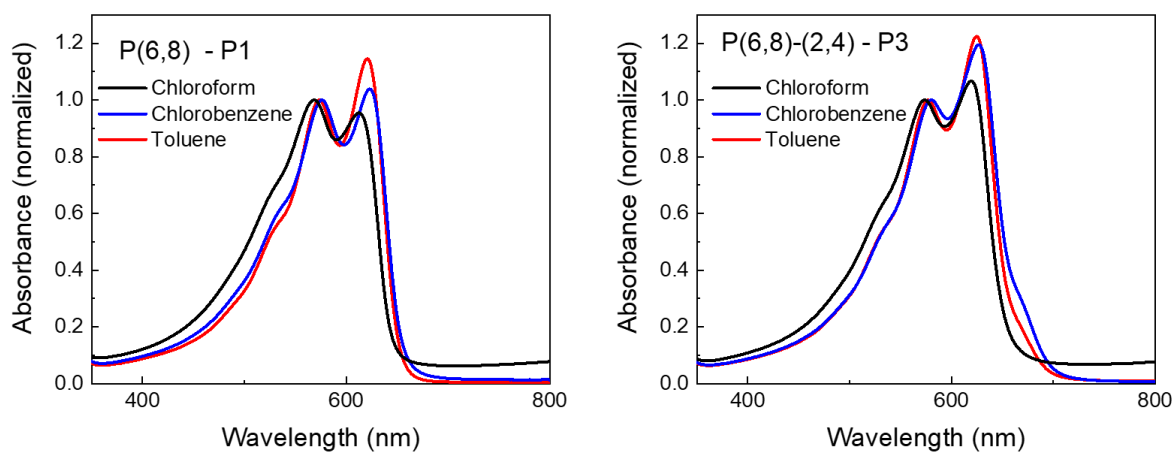


Figure S5 Solution state absorption spectra for P1 and P3 in different solvents. The relative height of the low-energy peak increases as the solubility decreases.

2.3 Temperature-dependent absorption spectra of polymer solutions

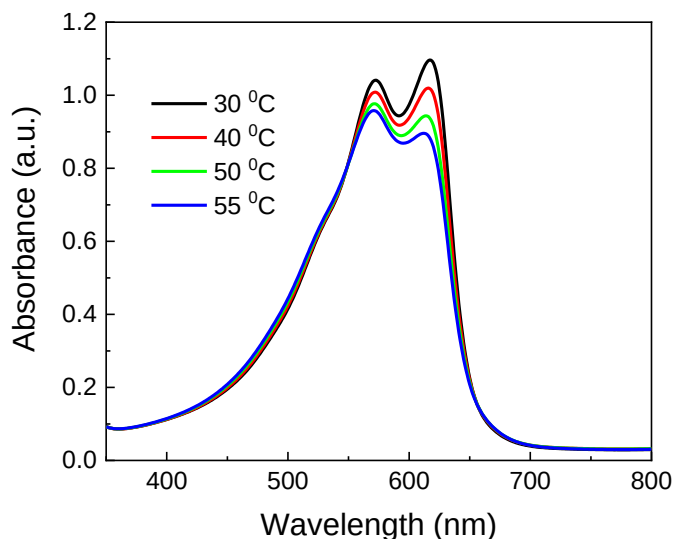


Figure S6 Peak evolution for P(6,8)-(2,4) with temperature, in chloroform

03. DFT calculations

The computational assessment of the impact of the sidechain densities on the absorption properties of the copolymers was done by time-dependent DFT (TDDFT) at the B3LYP/6-31G(d,p) level of theory. We chose this level of theory for consistency with past reports of the TDDFT calculations of conjugated polymers^{2,3}. Also, the non-local correlation effects introduced into the exchange potential in B3LYP through the Hartree potential makes it a good choice of Functional for a conjugated polymer study⁴. All calculations were carried out with Gaussian 16 (Revision B.01) software suite⁵. To ensure that the effect of the sidechain densities was investigated on an equal footing, $n = 6$ oligomers were used for both the geometry optimization (gaseous phase) and the excited states calculations (chloroform in polarizable continuum model).

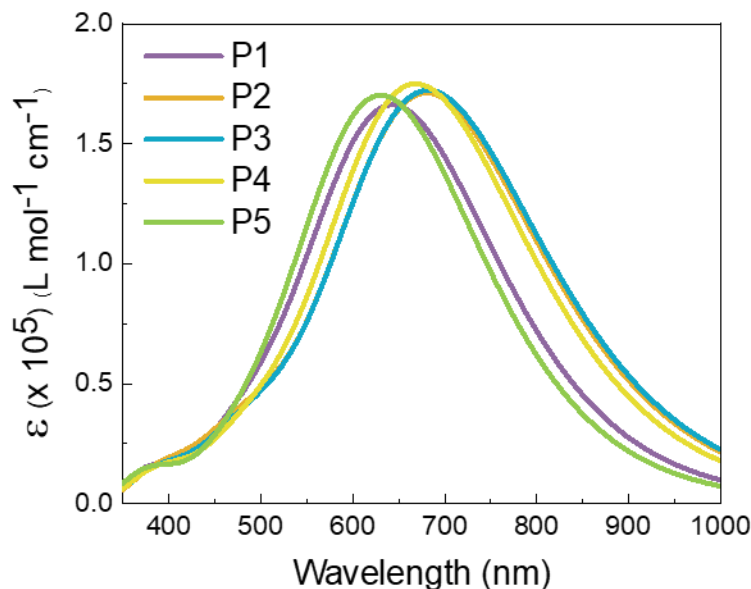


Figure S7 Molar extinction coefficients of ProDOT-EDOT oligomers (n=6) calculated using TD-DFT.

04. Thin film characterization

Polymer stock solutions (40 mg/mL) were prepared in CHCl_3 and filtered through a 1 μm pore-size filter prior to further dilution. Polymer solutions in the range of 10-35 mg/mL were used to fabricate films of different thicknesses. Thin films were prepared on FTO-glass substrates by adding 75 μL of the respective polymer solution and spin coating at a speed of 1500 rpm for 1 minute using a Laurell spin coater. Electrochemical and in-situ optical characterization were carried out in a 3-electrode setup assembled in a quartz cuvette by using the polymer coated FTO substrate as the working electrode (WE), a leakless Ag/AgCl reference electrode (eDAQ), a Pt wire counter electrode, and 0.2 M LiTFSI in propylene carbonate as the electrolyte. Electrochemical measurements were performed using Biologic SP150 and analyzed using EC-Lab software. Absorbance, transmittance and color measurements were made using Cary 5000 UV-Vis-NIR spectrophotometer. The electrochromic performance of polymer films were tested using the following general procedure. The transmittance profile of the as-cast polymer film immersed in the electrolyte (prior to any electrochemical treatment) was recorded with respect to a blank FTO-glass substrate, followed by electrochemical conditioning by ten CV cycles in the potential range -0.4 V – +1.0

V. The transmittance profile of the colored and transmissive states of electrochemically-films were recorded while applying a potential of -0.4 V and +1.0 V respectively (+1.2 V was applied only in the case of P1). The optical contrast of the polymers was measured through stepwise potential fast chronoamperometry (SPFC) by applying reducing and oxidizing potentials, -0.4 V and +1.0 V (+1.2 V for P1) respectively, for 30 s each and recording the transmittance changes in-situ at 550 nm and the respective λ_{max} of the polymer (w.r.t. blank FTO glass).

4.1 Absorption spectra

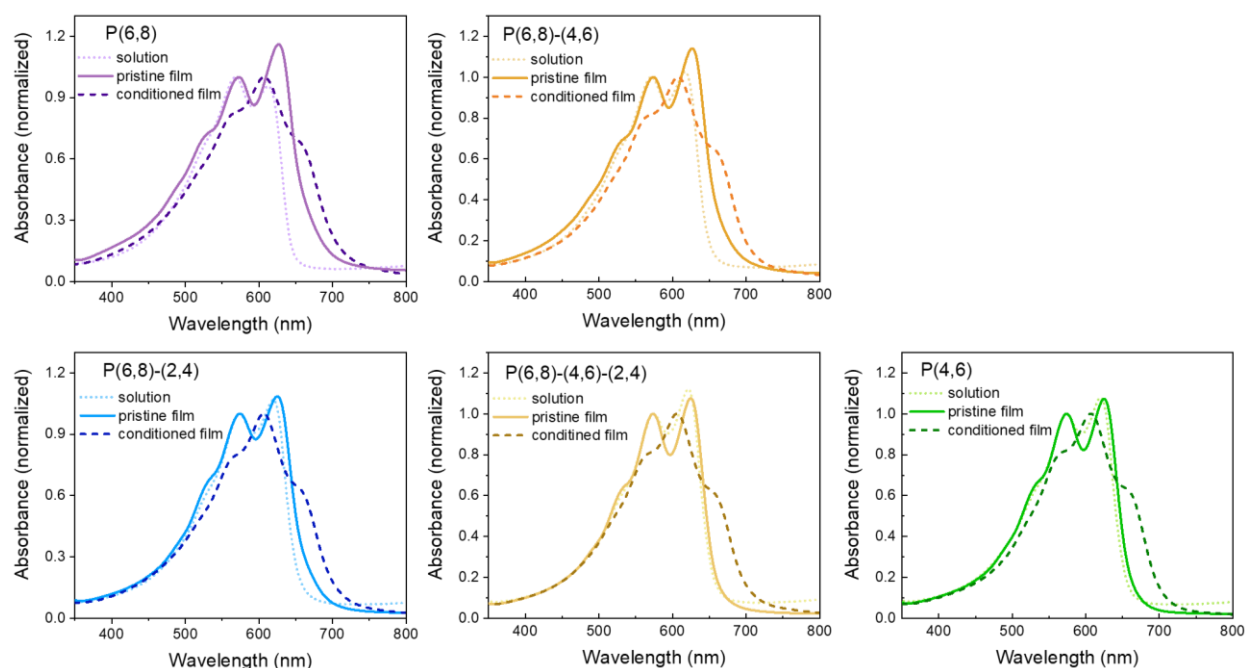


Figure S8 Comparison of solution, as-cast and electrochemically conditioned thin films of ProDOT-EDOT polymers

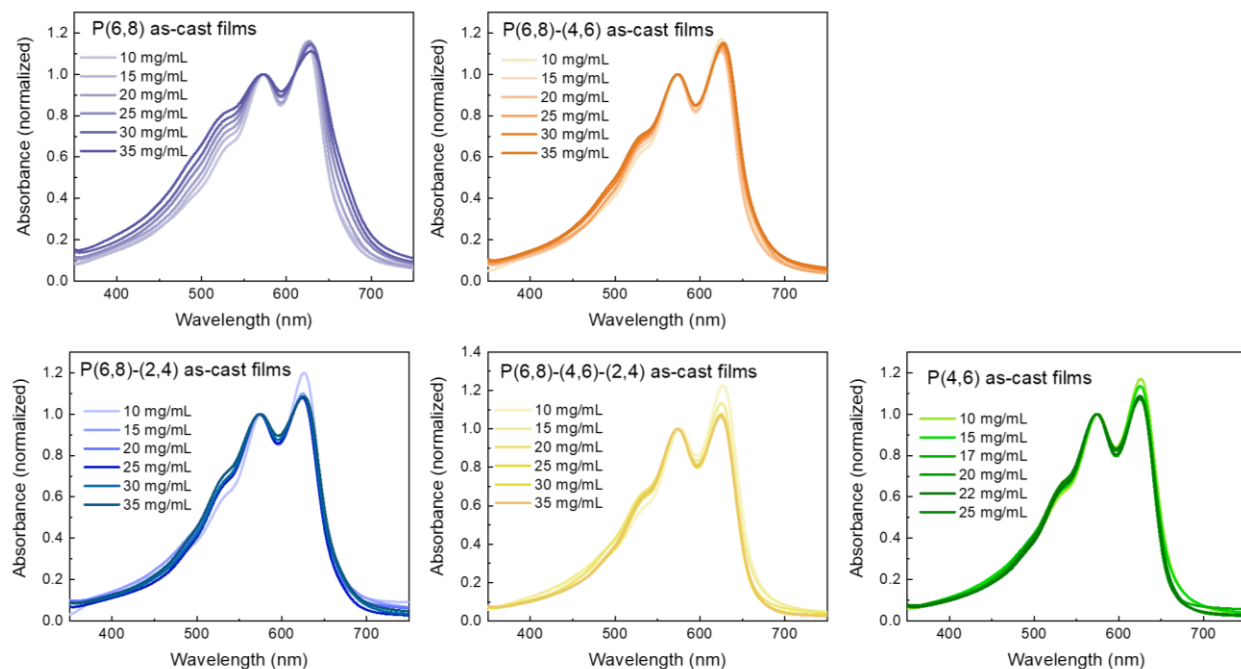


Figure S9 Absorption spectra of as-cast polymer films spin coated from precursor solutions of different concentrations

4.2 AFM images

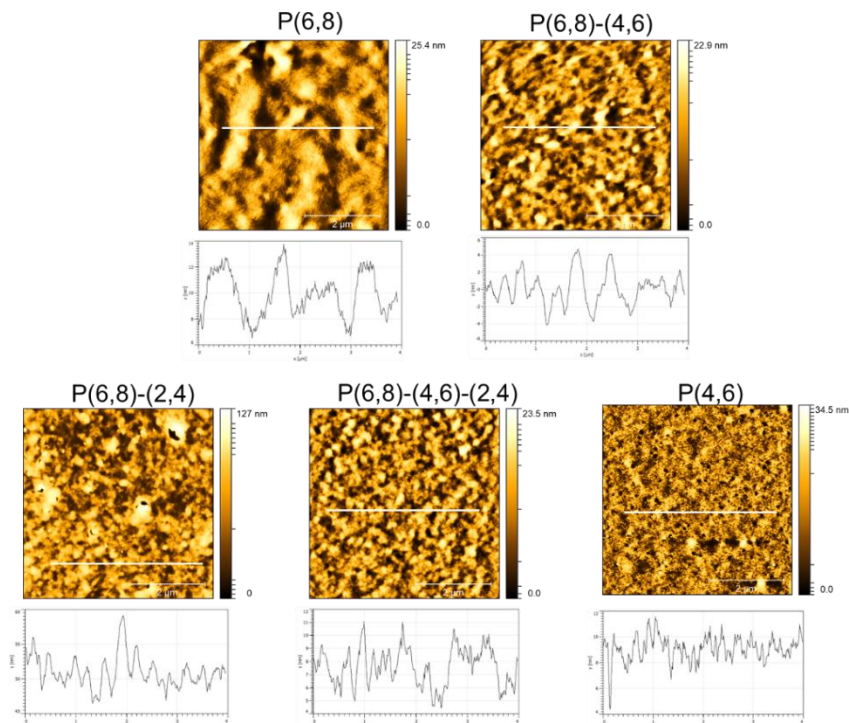


Figure S10 AFM images and height variations showing feature sizes of polymer thin films

4.3 GIXD Analysis

Polymer films spin coated on Si substrates were analyzed using GIXD, in the as-cast state, at the Advanced Photon Source at Argonne National Laboratory. Incident beam energy of 10.92 keV was used to collect the diffraction data on a 2D detector, with sample-to-detector distance of 217 mm. Samples were scanned with exposure time of 5 s with an incidence angle of 0.14° in two directions. The images obtained were combined to eliminate most of the inactive pixels using the GIXSGUI package written for MATLAB⁶. The in-plane peaks and out-of-plane peaks were obtained using linecuts in the ranges $-88^\circ < \chi < -83^\circ$ and $-15^\circ < \chi < -10^\circ$, respectively, from the geometrically corrected image. Using the same package, the 2D data were reshaped into the representation q_z versus q_r .

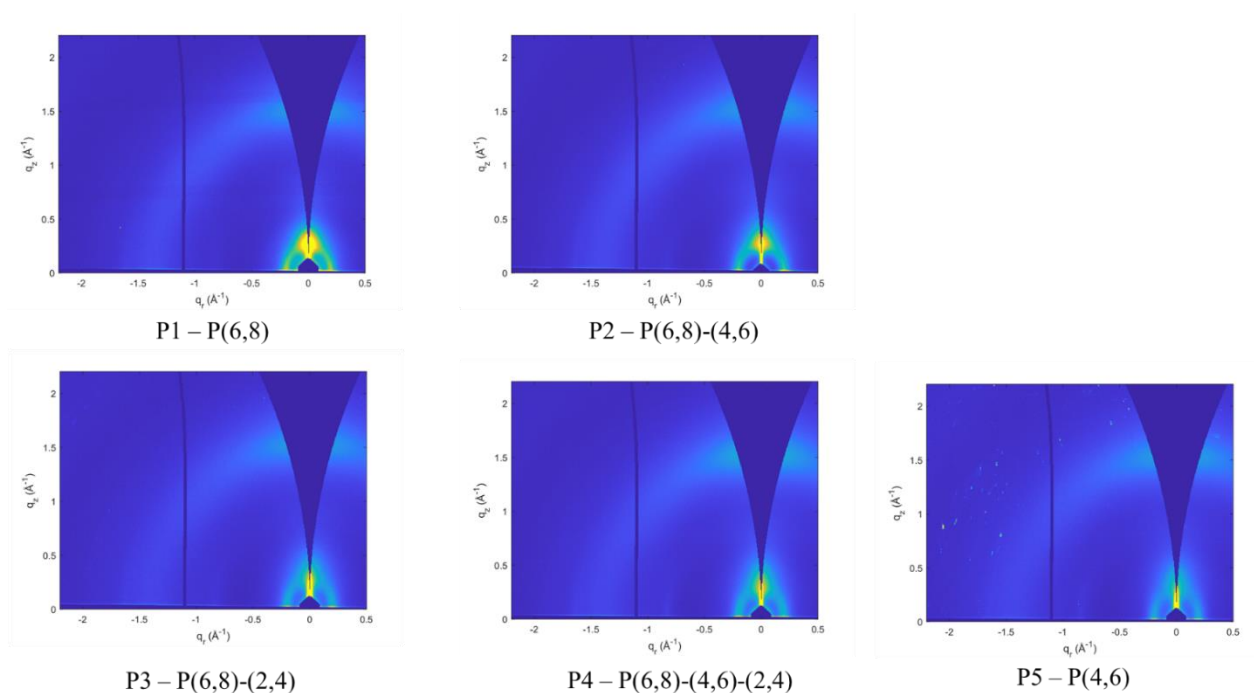


Figure S11 Reshaped 2D GIXD images of ProDOT-EDOT polymer films coated on Si substrates

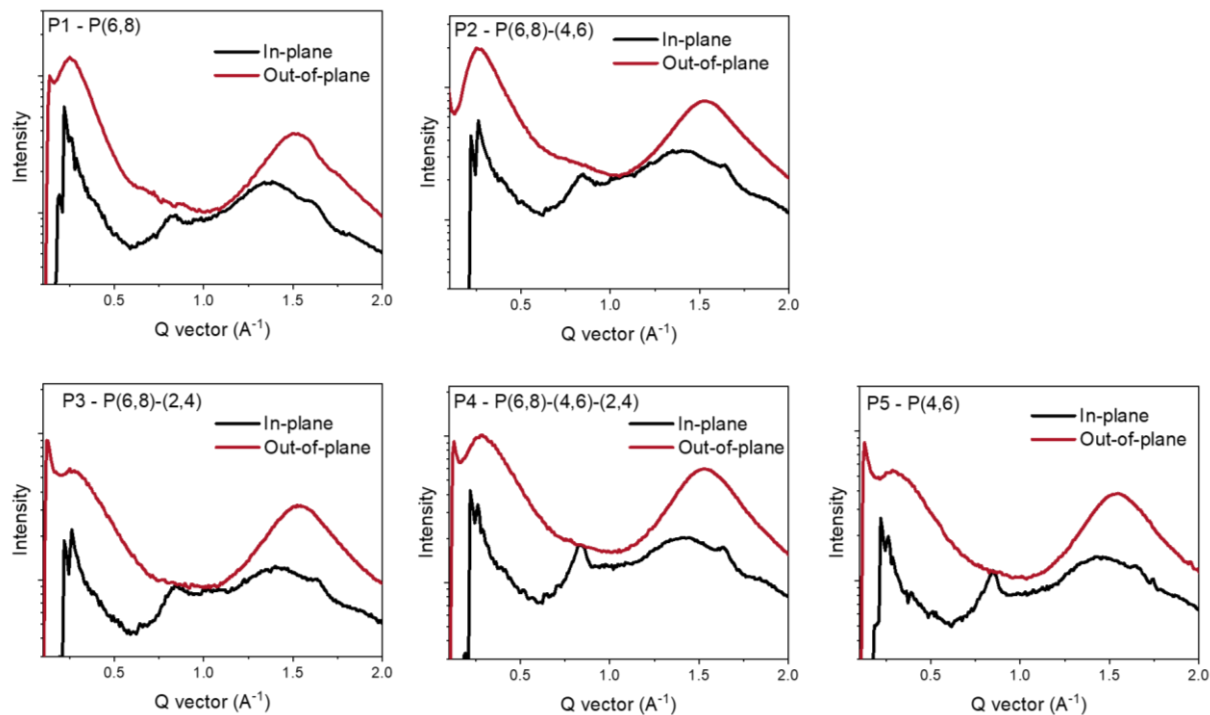


Figure S12 Linecuts performed parallel ($-88 < \chi < -83$) and perpendicular ($-15 < \chi < -10$) to the substrate

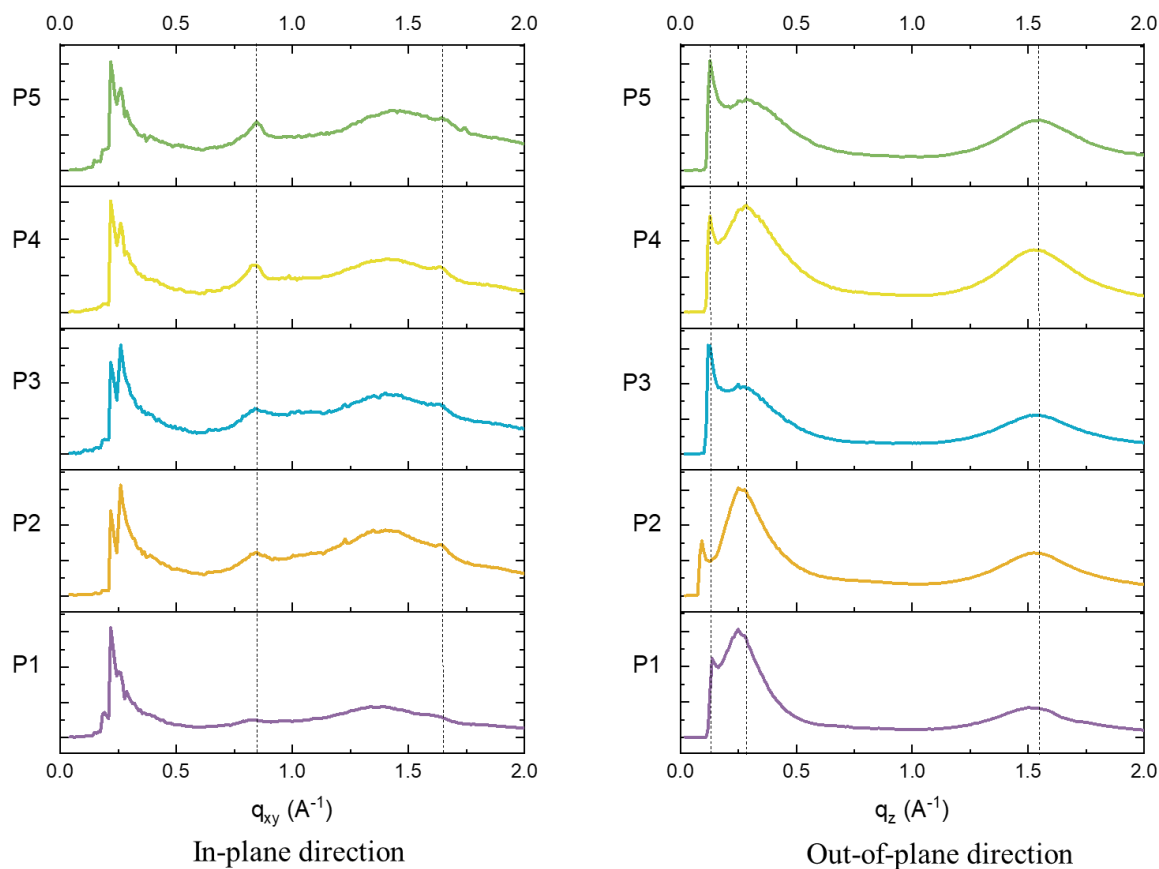


Figure S13 Comparison of peaks in the in-plane and out-of-plane directions

Table S3 Peak positions and d-spacing of the π - π and alkyl stacking features

	In-plane (q_{xy})				Out-of-plane (q_z)			
	π - π stacking		Alkyl-chain stacking		Lamellar stacking		π - π stacking	
	$\text{\AA}^{-1}$	$\text{\AA}$	$\text{\AA}^{-1}$	$\text{\AA}$	$\text{\AA}^{-1}$	$\text{\AA}$	$\text{\AA}^{-1}$	$\text{\AA}$
P1	1.63	3.85	0.82	7.7	0.25	25	1.52	4.1
P2	1.65	3.81	0.84	7.5	0.26	24	1.53	4.1
P3	1.64	3.83	0.84	7.5	0.27	23	1.53	4.1
P4	1.64	3.83	0.83	7.6	0.28	22	1.53	4.1
P5	1.66	3.78	0.85	7.4	0.29	22	1.54	4.1

Detailed GIXD analysis

From the two-dimensional GIXD images of as-cast polymer thin films coated on silicon substrates (Figure S11), all polymers remain mostly amorphous with weakly diffracting crystallites and no long-range ordering, as evidenced by the arc-shaped diffraction pattern and the lack of higher order diffraction peaks. The in-plane linecuts (Figures S12, S13, Table S3) reveal a slight edge-on π - π stacking peak (010) around $q_{xy} = 1.65 \text{ \AA}^{-1}$ ($\approx 3.8 \text{ \AA}$). Moving from P1 to P5, this peak becomes more prominent and shifts to larger q_{xy} values. The most prominent difference between the polymers is observed in the lamellar spacing (100), which gets constrained from 25 $\text{\AA}$ to 22 $\text{\AA}$ in the out-of-plane direction (q_z) with the introduction of shorter side chains. Another interesting feature is observed in the q_{xy} linecuts around 0.84 $\text{\AA}^{-1}$. This peak becomes more prominent and shifted to higher q_{xy} as the side chain density is decreased. While the origin of this peak remains unclear, we hypothesize it could arise from a form of alkyl stacking⁷. Previous GIWAXS studies of dioxothiophene polymers have reported both face-on and edge-on orientation of the π -stacks⁸⁻¹¹. Even though a higher scattering intensity is observed close to 1.5 $\text{\AA}^{-1}$ in the q_z direction for all polymers (Figure S11), it is morphed together with the amorphous peak typically associated with disordered side chains.

Table S3 lists all diffraction peak positions and the corresponding d-spacing values. The data demonstrate how lowering side-chain density facilitates closer-packing of the polymer crystallites.

05. Absorption coefficient calculations for as-cast thin films

5.1 Beer-Lambert plots

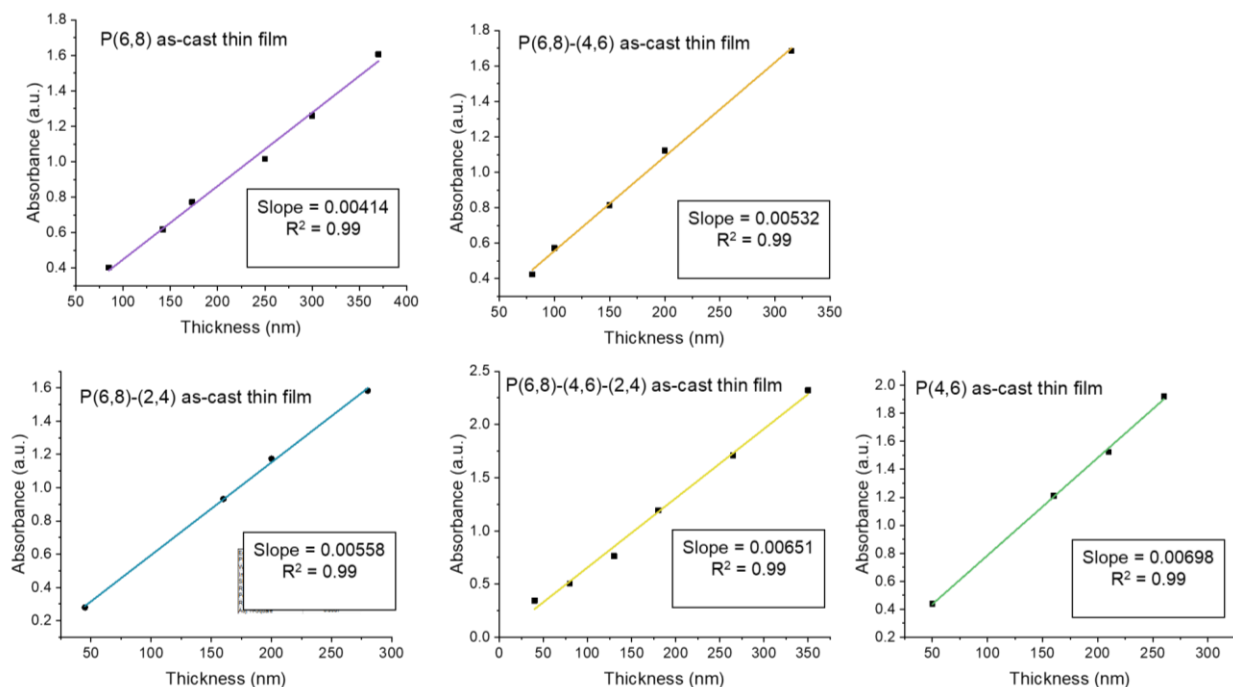


Figure S14 Beer-Lambert plots using absorbance (UV-Vis) and film thickness (AFM) data for as-cast polymer films

Film thickness of pristine polymer films coated on FTO-glass substrates were measured using Atomic Force Microscopy (AFM) (Veeco Dimension 3100). The thickness at 3 different spots were measured and the average was used for calculation of linear absorption coefficients from Beer-Lambert plots of absorbance vs. film thickness.

Table S4 Slopes of the Beer-Lambert plots of as-cast films and conversion to absorption coefficient

Polymer	Slope of the Beer-Lambert plot ($\times 10^5 \text{ cm}^{-1}$)	Absorption coefficient $\times 2.303$ ($\times 10^5 \text{ cm}^{-1}$)
P(6,8)	0.414	0.95
P(6,8)-(4,6)	0.532	1.22
P(6,8)-(2,4)	0.558	1.30
P(6,8)-(4,6)-(2,4)	0.651	1.50
P(4,6)	0.698	1.61

Slope from the Beer-Lambert plots need to be multiplied by a factor of 2.303 to be compared to calculations from spectral reflectance measurements.

$$I = I_0 e^{-\alpha t}$$

$$\alpha = \frac{\ln(I_0/I)}{t}, \quad \alpha = \frac{2.303 \log(I_0/I)}{t}, \quad \alpha = 2.303 \left(\frac{A}{t} \right)$$

06. Electrochemical and optical characterization of thin films

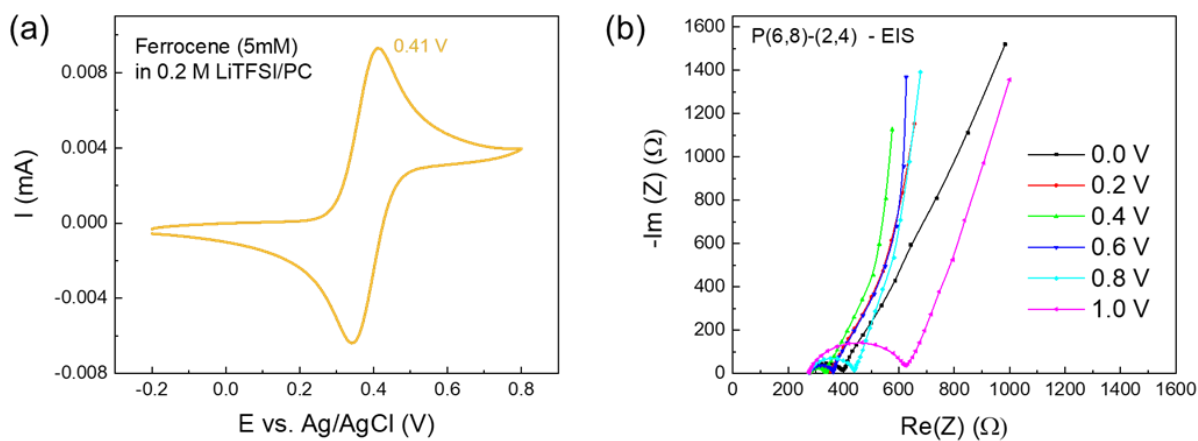


Figure S15 (a) Cyclic voltammetry of ferrocene (5 mM) in 0.2 M LiTFSI/PC for calibrating the Ag/AgCl reference electrode (b) Impedance spectra of P(6,8)-(2,4) thin films.

6.1 Spectroelectrochemical measurements and L*a*b* values

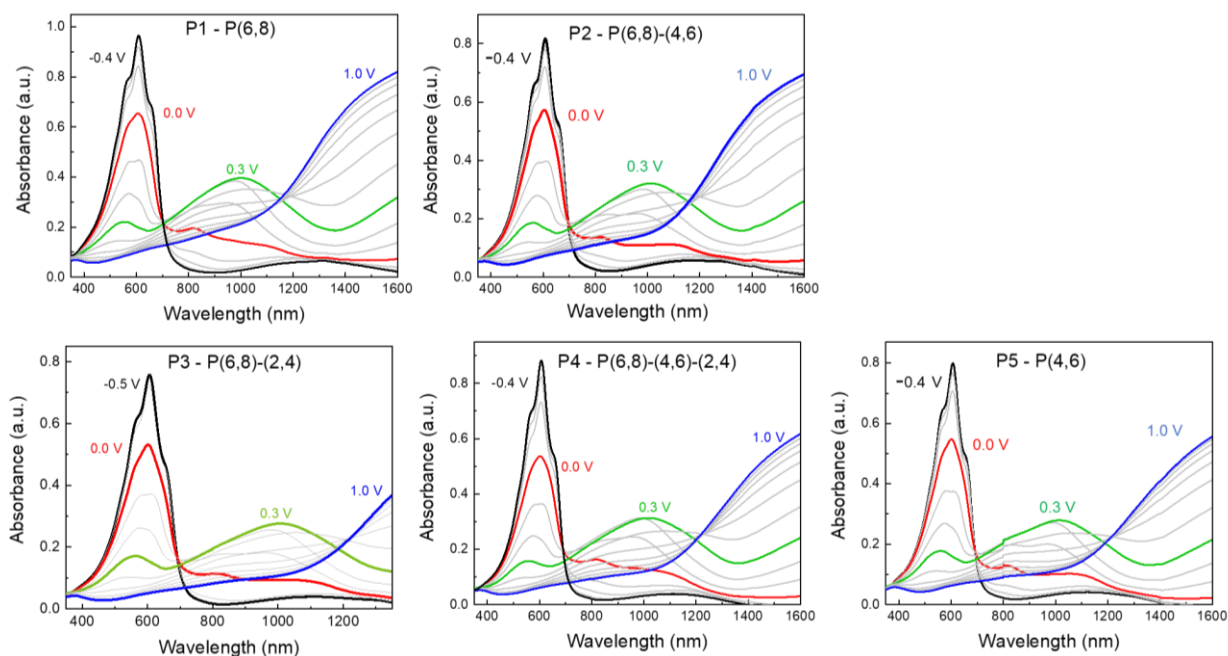


Figure S16 Spectroelectrochemical measurements of electrochemically conditioned polymer films, showing the gradual decrease of absorbance in the visible region accompanied with increased absorbance in the NIR, as the voltage is increased.

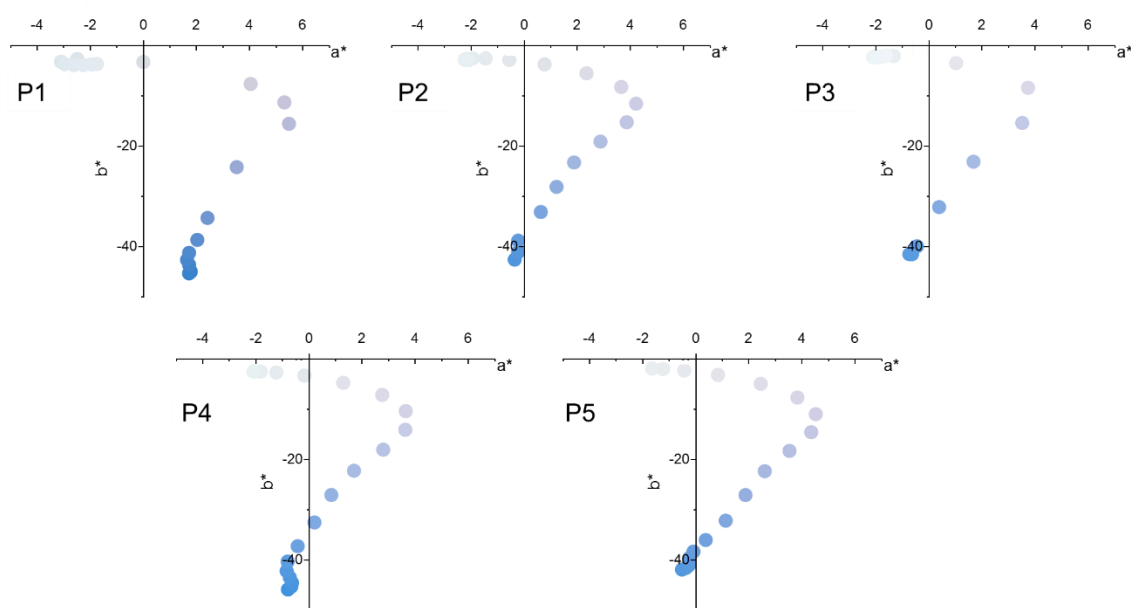
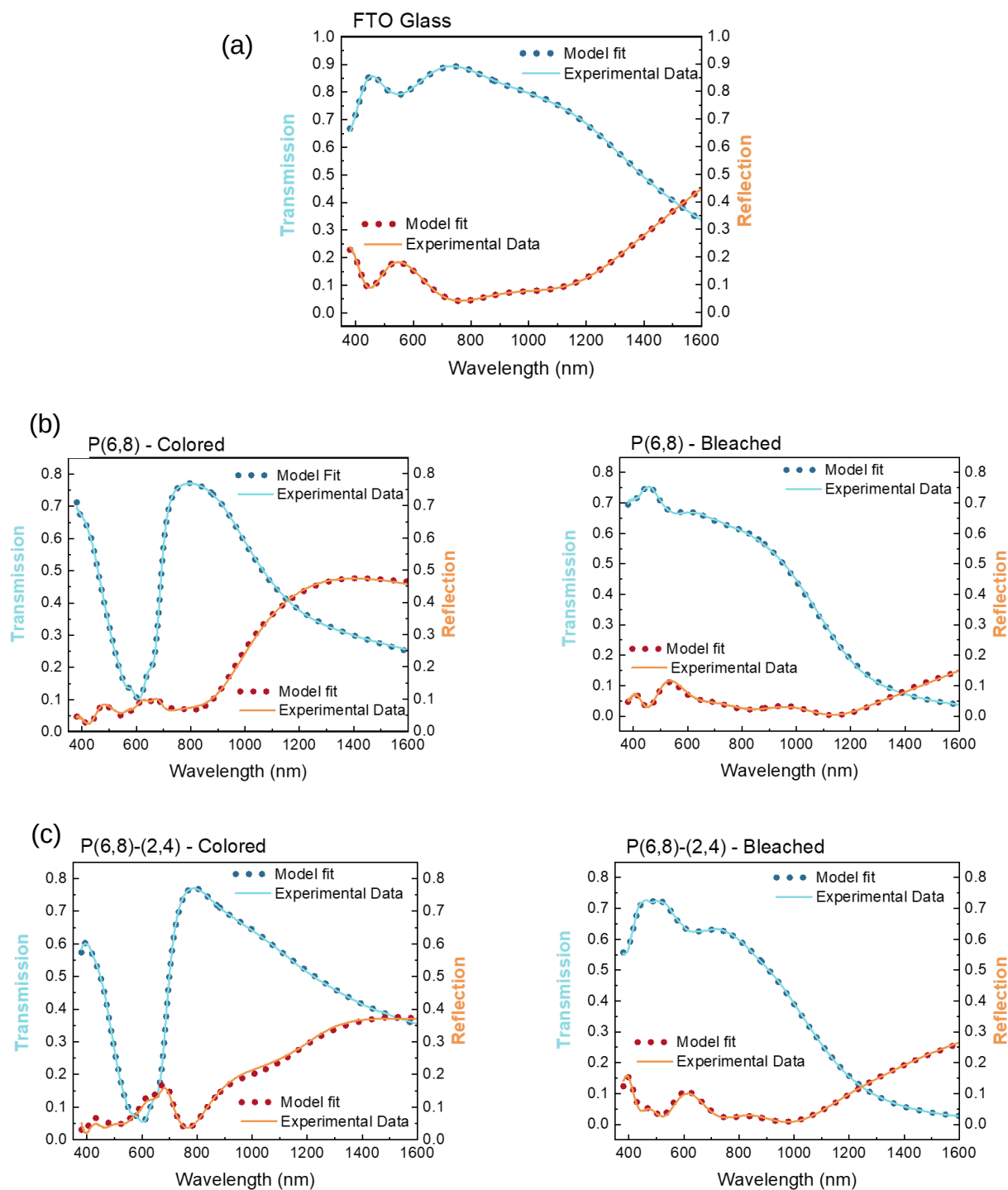


Figure S17 Color changes during electrochemical bleaching (represented using CIE L*a*b* values, D50 illuminant).

6.2 WVASE fitting for Transmittance and Reflectance



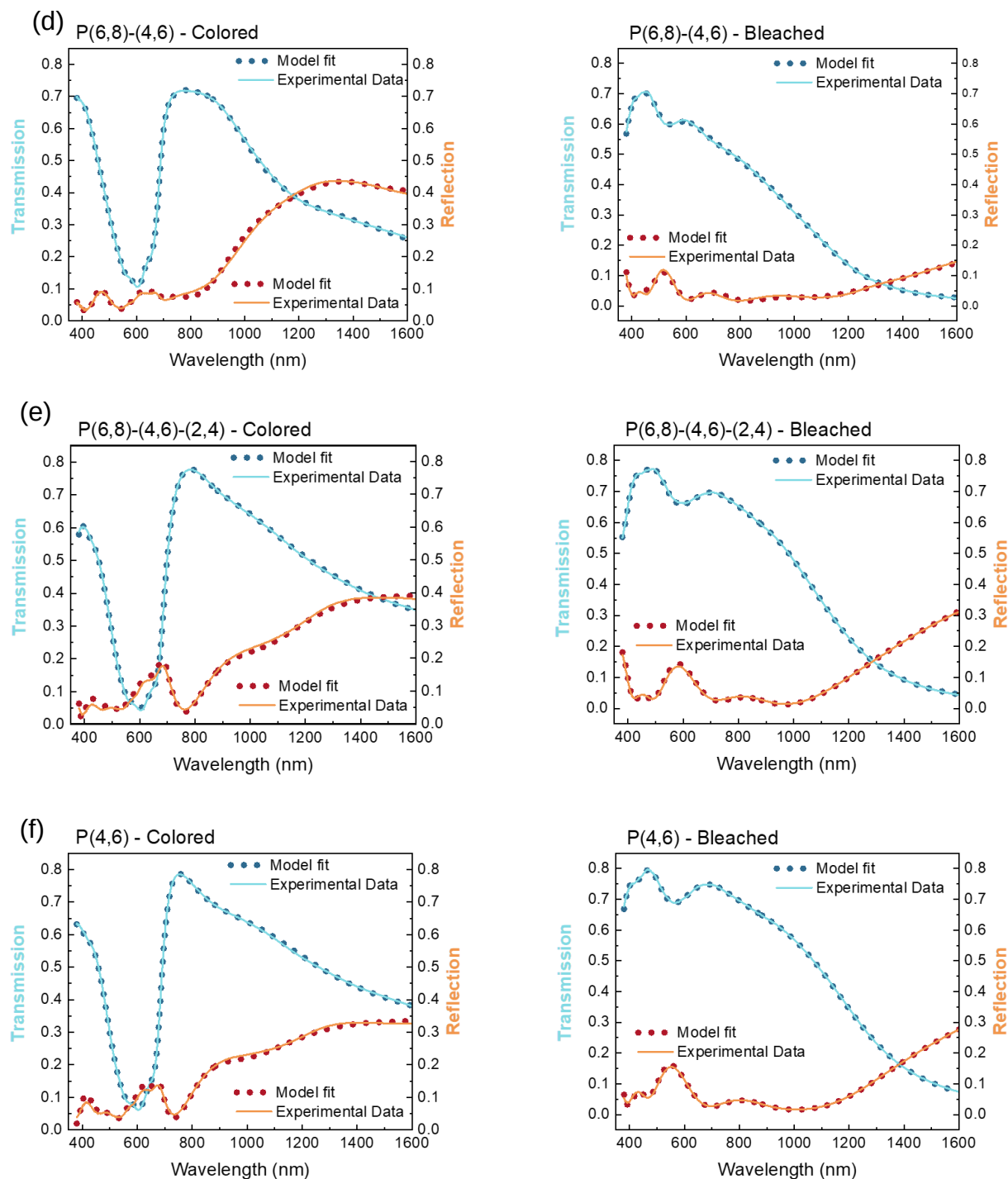


Figure S18 Generated model vs. experimental data for transmission and reflection of (a) FTO glass, (b) P(6,8), (c) P(6,8)-(4,6), (d) P(6,8)-(2,4), (e) P(6,8)-(4,6)-(2,4), and (f) P(4,6).

6.3 Optical constants of electrochemically conditioned films

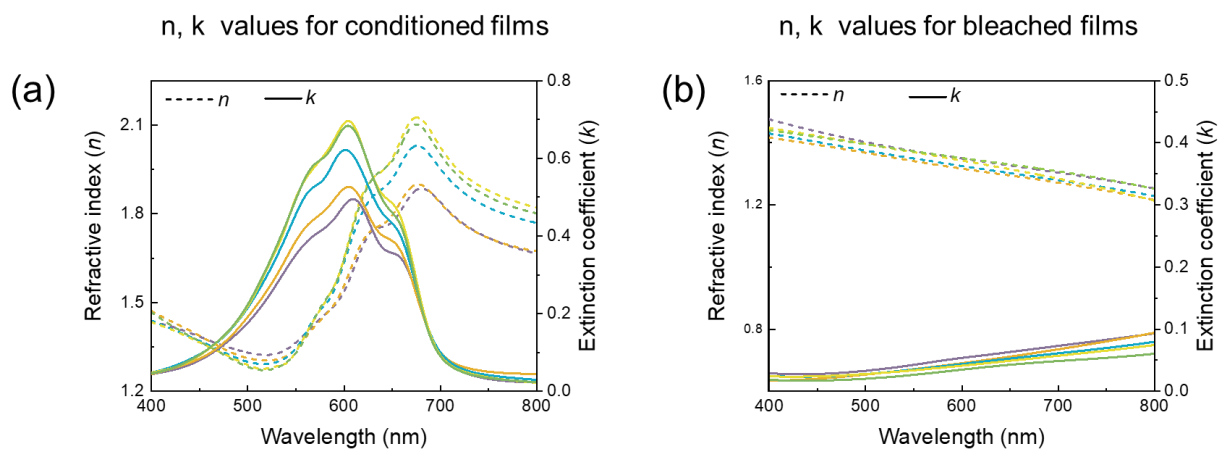


Figure S19 Refractive index (n) and extinction coefficient (k) of electrochemically conditioned colored and bleached films modeled using spectral reflectance data.

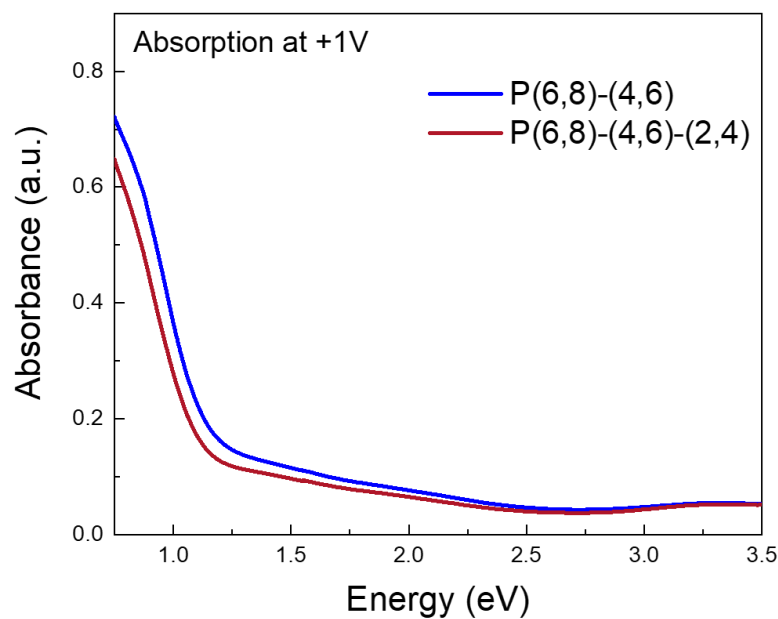


Figure S20 Slight shifting of the bipolaron peak observed for short side chain polymers

6.4 Beer-Lambert plots for electrochemically conditioned films

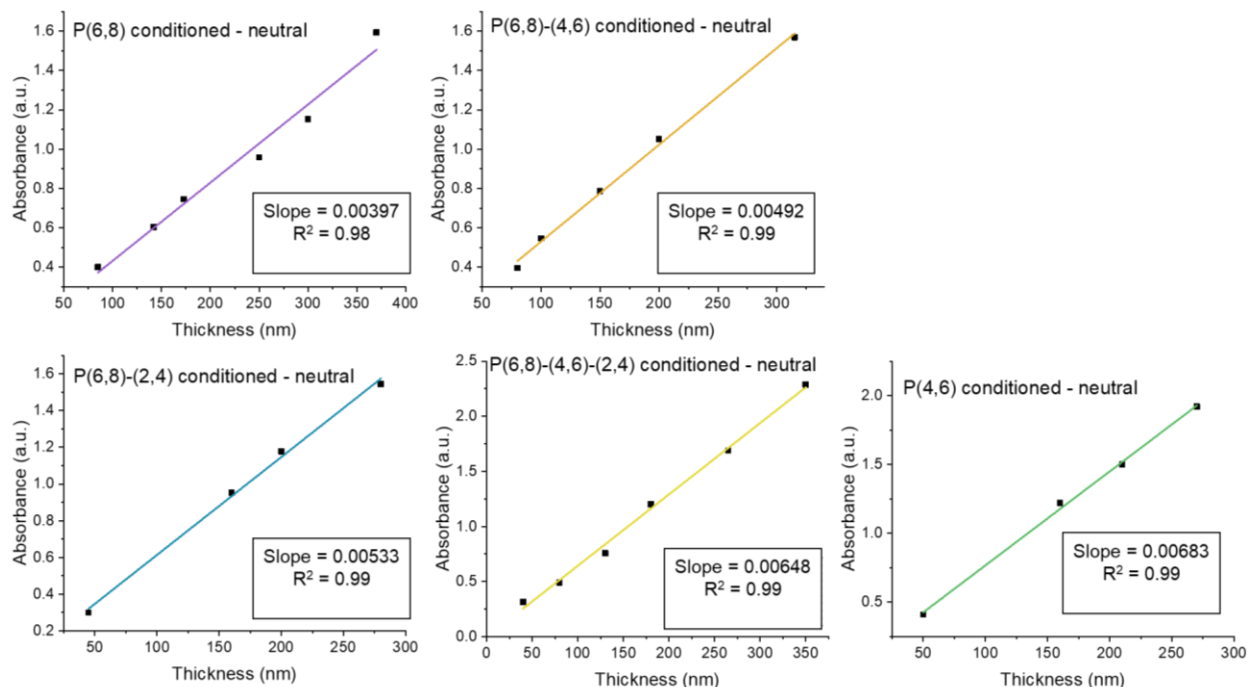


Figure S21 Beer-Lambert plots of electrochemically conditioned polymer films in neutral state

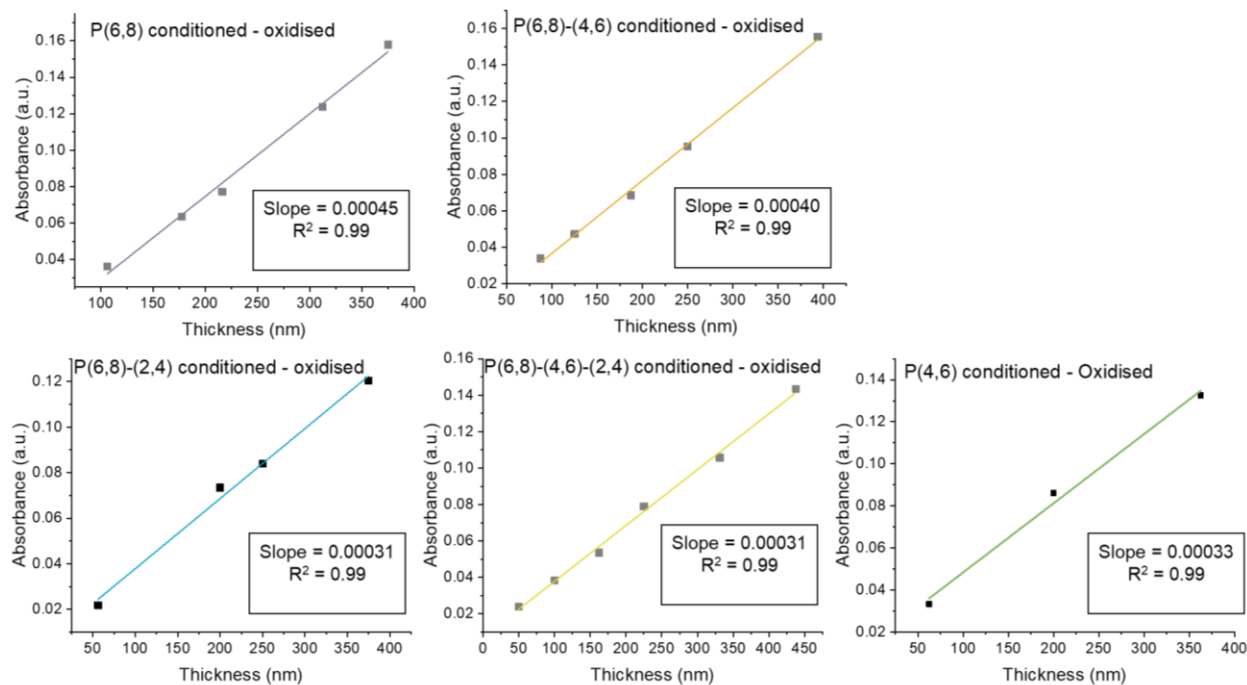


Figure S22 Beer-Lambert plots for oxidised polymer films, assuming a swelling factor of 25%

07. In-situ nano-indentation measurements

Polymer film coated on FTO-glass substrates was mounted in a home-made fluid cell¹². LiTFSI salt (Sigma-Aldrich) was dissolved into propylene carbonate solvent (Sigma-Aldrich) and stirred for 12 h to form a 0.2 M liquid electrolyte. Using Pt wire as the counter electrode and Ag/AgCl as the reference electrode, the electrochemical test was conducted using VersaSTAT 3 station. Instrumented nanoindentation (G200 Nanoindenter, KLA) was used to track the surface of the film using a very gentle contact force ($<1 \mu\text{N}$)^{13,14}. The indenter tip displacement, i.e., thickness change of the film, is recorded.

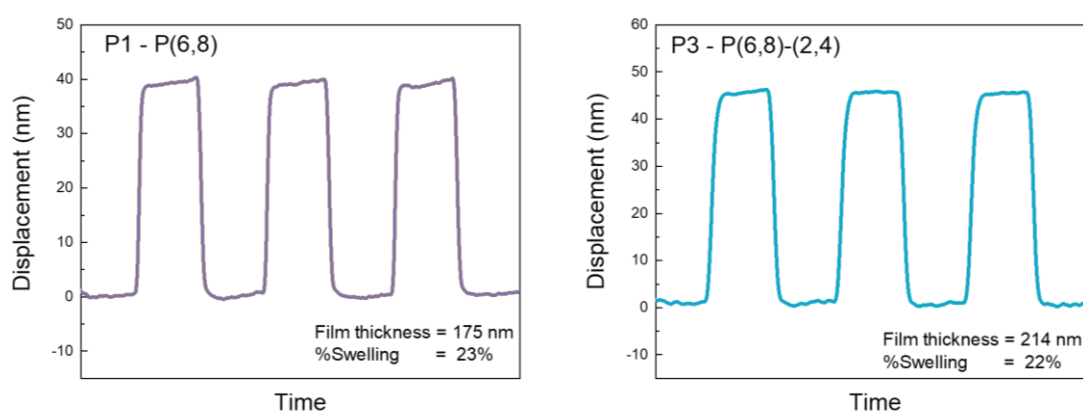


Figure S23 Film swelling measurement using nano-indentation

08. Comparison of experimental and modelled optical contrast

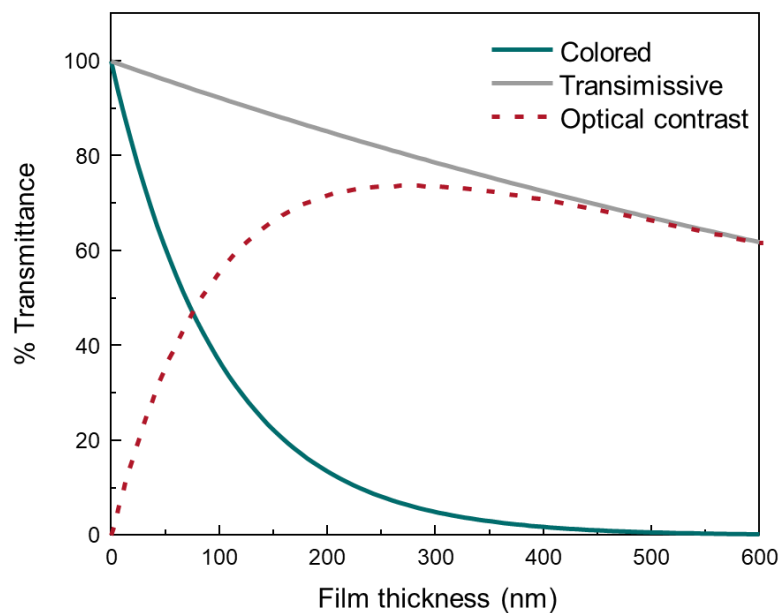


Figure S24 Variation of optical contrast as a function of film thickness, based on the transmittance of colored and transmissive states.

Table S5: The maximum optical contrast and corresponding thickness, calculated using the absorption coefficients in the colored and bleached states

Polymer	% $\Delta T_{\text{max,predicted}}$	$t_{\text{max,predicted}}$ (nm)
P(6,8)	68	245
P(6,8)-(4,6)	73	235
P(6,8)-(2,4)	76	215
P(6,8)-(4,6)-(2,4)	78	206
P(4,6)	81	210

$$t_{\text{max}} = \frac{\ln\left(\frac{\alpha_C}{\alpha_B}\right)}{\alpha_C - \alpha_B} \quad \%T_{\text{max}} = 100(e^{-\alpha_B t_{\text{max}}} - e^{-\alpha_C t_{\text{max}}})$$

Table S6: Experimentally derived values for maximum optical contrast, switching time and coloration efficiency

Polymer	$\% \Delta T_{\max}$	Thickness (nm)	Switching time (t_{95}, s)	Coloration Efficiency ($C^{-1} \text{ cm}^2$)
P(6,8)	68	224	1.4	624
P(6,8)-(4,6)	72	204	1.1	621
P(6,8)-(2,4)	77	178	1.0	673
P(6,8)-(4,6)-(2,4)	78	188	1.5	805
P(4,6)	79	147	1.7	702

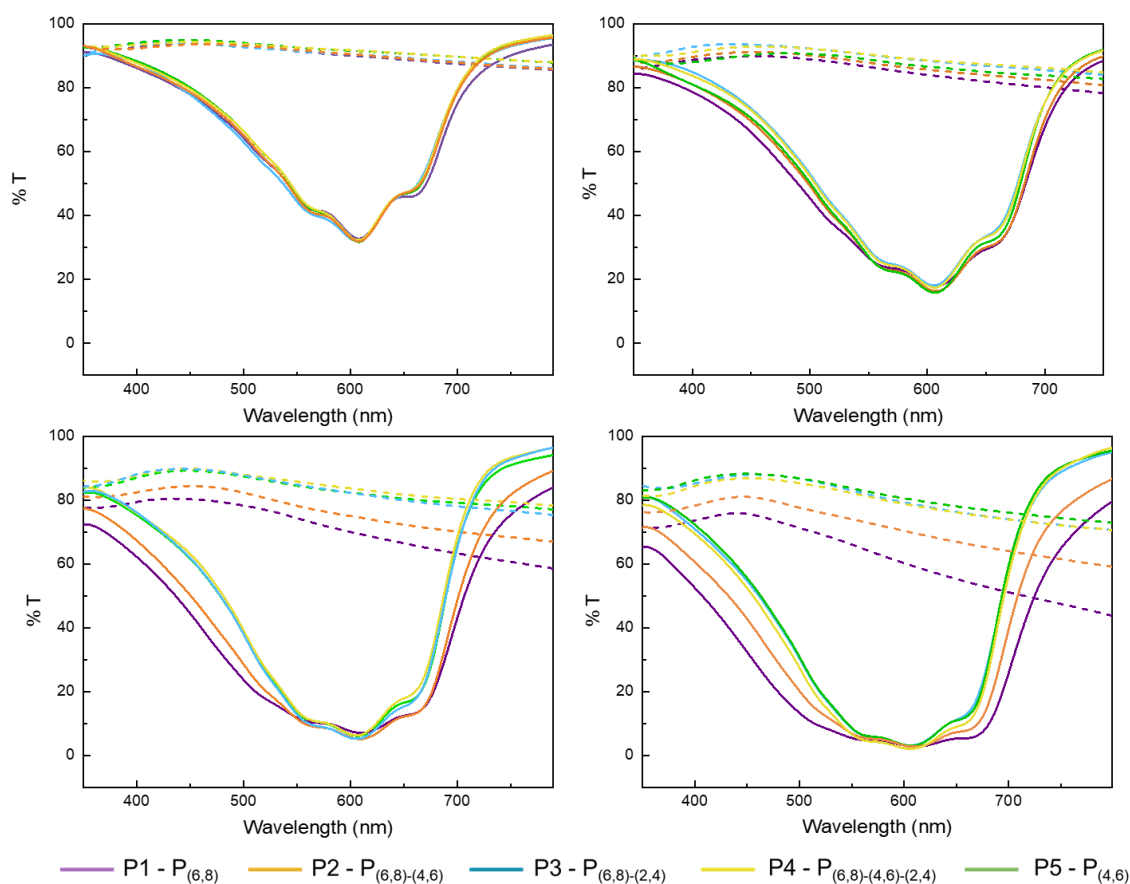


Figure S25 Comparison of bleached state transmittance for films of similar colored state transmittance

09. Scan-rate dependent cyclic voltammetry

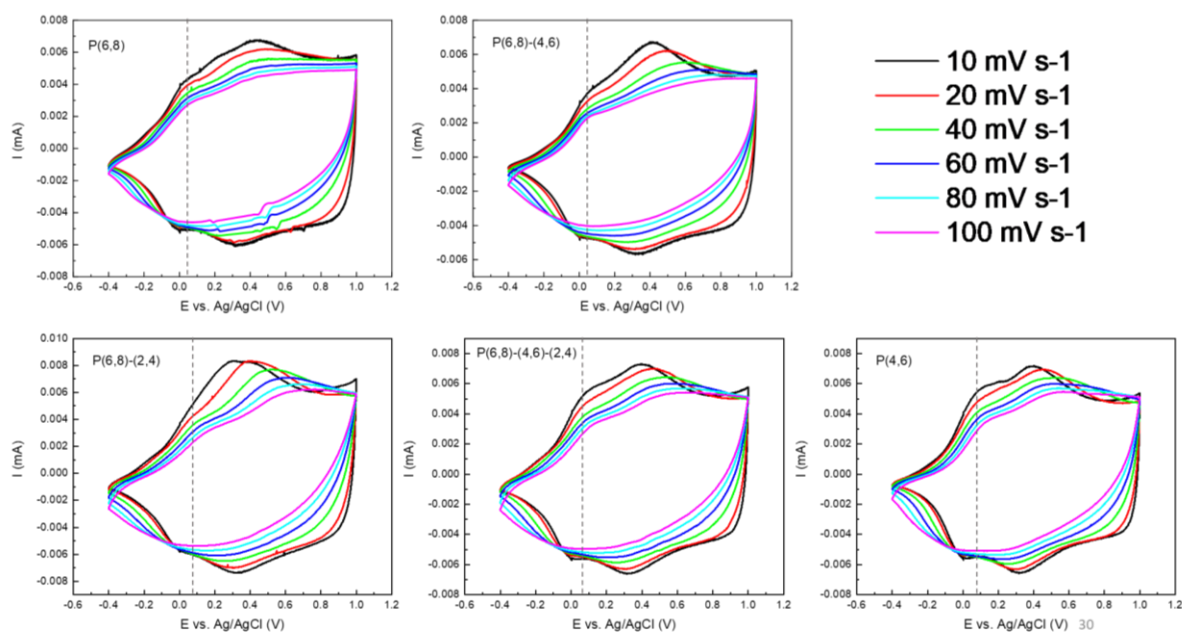


Figure S26 Scan rate-normalized cyclic voltammetry for polymer films of similar thickness

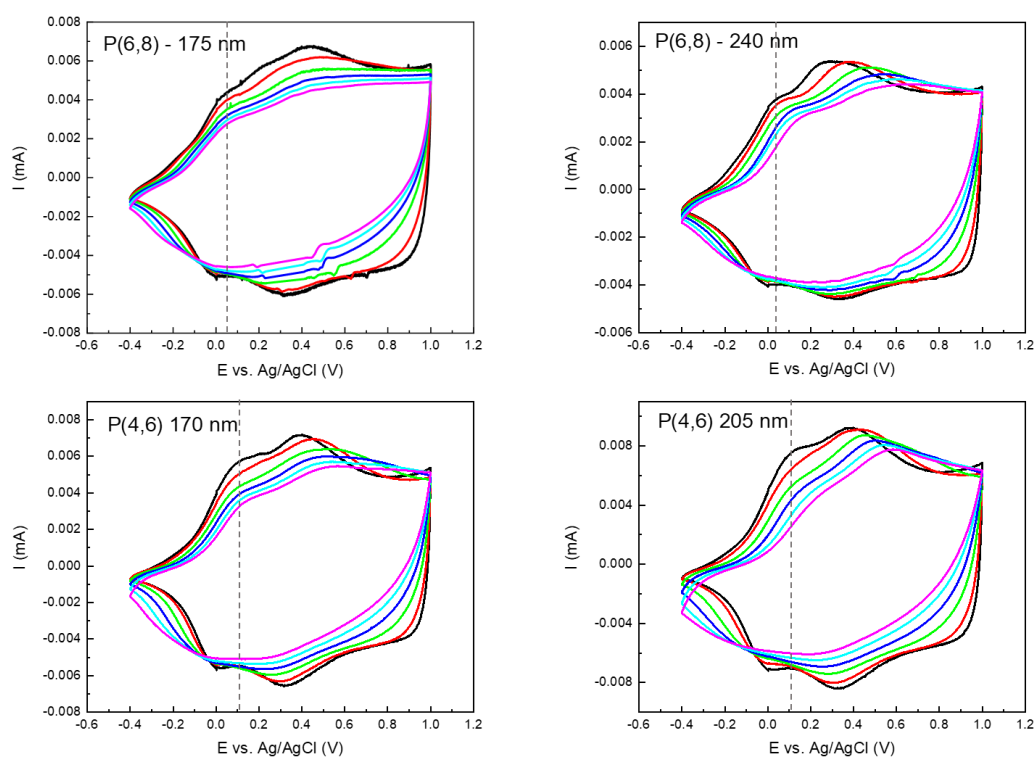


Figure S27 Scan rate-normalized cyclic voltammetry comparison for thin and thick films

10. Volumetric charge density distribution

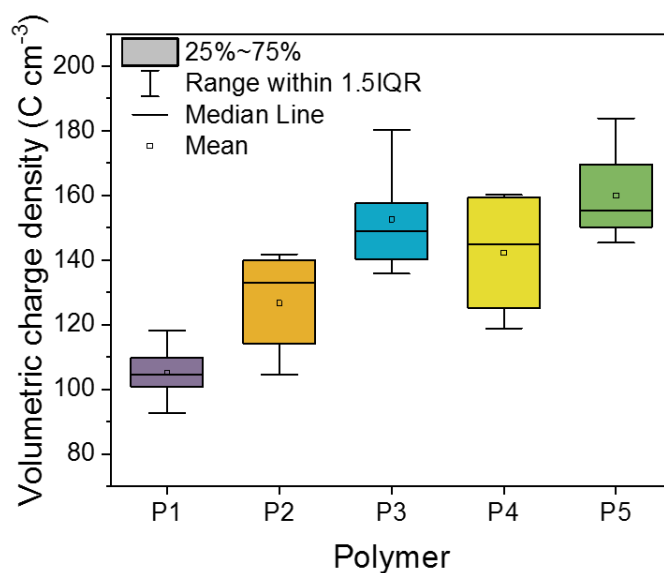
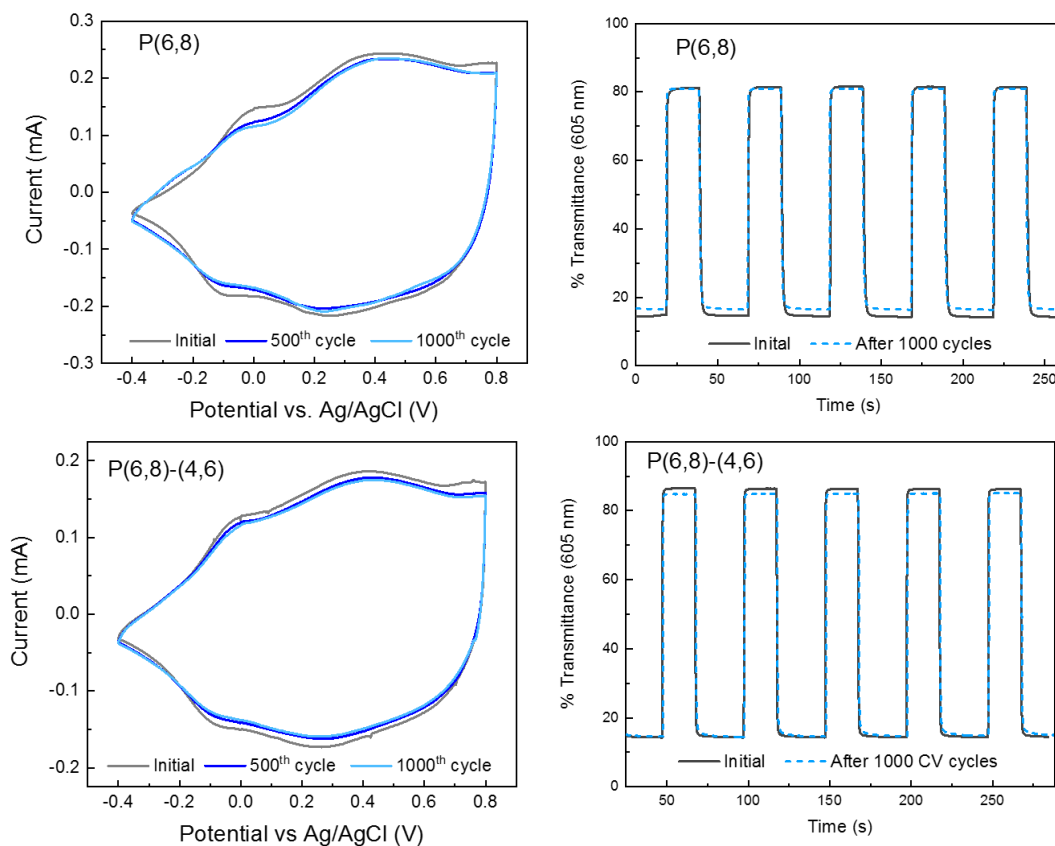


Figure S28 Volumetric charge density distribution, considering the total charge consumed during oxidation of polymer films for a range of thicknesses.

11. Cycling stability



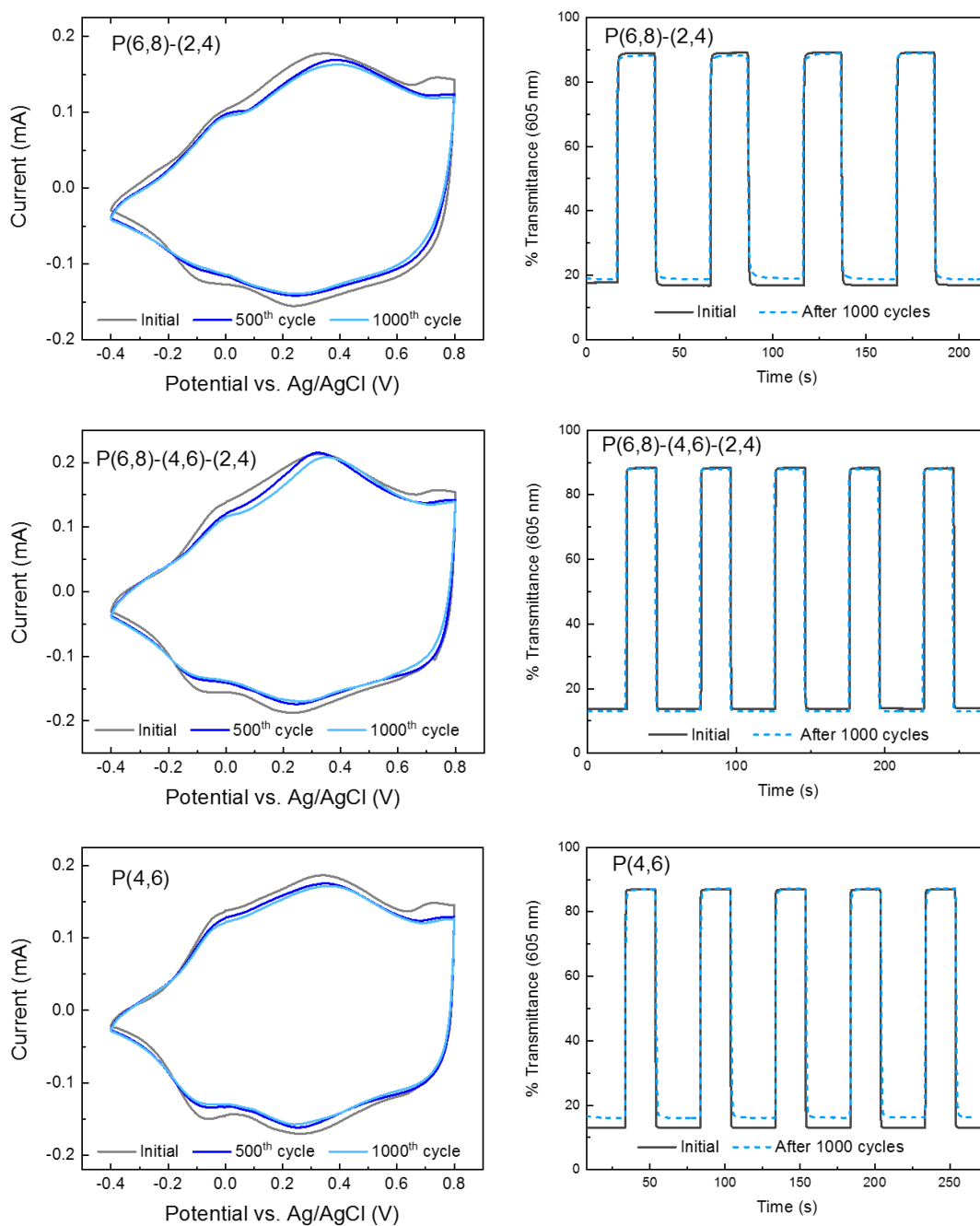


Figure S29 Cycling stability data for polymers P1 to P5. The respective cyclic voltammograms of electrochemically conditioned films during the initial, 500th and 1000th cycles are represented. Transmittance changes during electrochromic switching before and after 1000 CV cycles are also compared.

12. References

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