

Monomer Blended Electrochemical Polymerization in Chiral Liquid Crystals to Produce Electro-Optically Active Copolymer

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Experimental section

Materials

3,4-Ethylenedioxythiophene (EDOT), *N*-bromosuccinimide (NBS), *N,N*-dimethylformamide (DMF), 5-(tributylstannyl)thiophene, toluene, tetrakis(triphenylphosphine)palladium(0) (Pd(PPd₃)₄), tributyltin chloride, *n*-butyllithium (*n*-BuLi, 1.6M in hexane), tetrahydrofuran (THF) and 5-bromothiazole were obtained from Tokyo Chemical Industry Co., Ltd., and used as supplied. As the composition of the electrolyte solution, 4-cyano-4'-pentylbiphenyl (5CB) as a LC host, cholesterol pelargonate (CP) as a chiral inducer and tetrabutylammonium perchlorate (TBAP) as a supporting salt were obtained from Tokyo Chemical Industry Co., Ltd. and used as supplied.

Instrument section

Optical texture observations were carried out by using an ECLIPS LV 100 high-resolution polarizing microscope (Nikon, Tokyo). ¹H NMR spectra were measured in CDCl₃ using a JEOL JNM-ECS-400 NMR spectrometer (JEOL, Tokyo). Chemical shifts were recorded in parts per million downfield from tetramethylsilane (TMS) as an internal standard. Absorption spectra were obtained using a V-630 spectrometer (JASCO, Tokyo). CD and optical rotation measurements were performed using a Jasco J-720 spectrometer with an ORDE-307W ORD unit. Electron spin resonance (ESR) measurements were conducted using a JEOL (Tokyo) JES TE-200 spectrometer with 100 kHz modulation (X-band). Electrochemical measurements of polymers were conducted using an electrochemical analyzer (μAutolab III, Autolab, the Netherlands). Electrolyte solution contained 0.1 M TBAP in acetonitrile. Cyclic voltammetry (CV) with these polymers drop-casted on ITO glass was conducted using 0.1 M TBAP in CH₃CN as an electrolyte, Ag/Ag⁺ as the reference electrode, and Pt wire as the counter electrode. Ferrocene ($E_{1/2} = 0.20$ V) was used as an external standard. Scanning electron microscopy (SEM) observations were carried out using an Advantest SEM TM4000Plus (Hitachi high technologies, Tokyo).

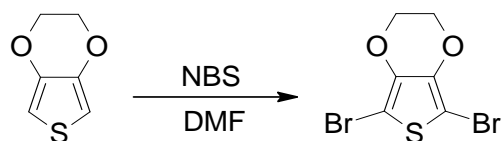
Calculation

The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy level and the optimized geometry for these monomers (2T-BT and 2T-ITN)

were calculated by density functional theory (DFT) method at Becke's three-parameter set with Lee-Yang-Parr correlation functional (B3LYP) with 6-31G* basis set, which is implemented in Spartan '04 package.

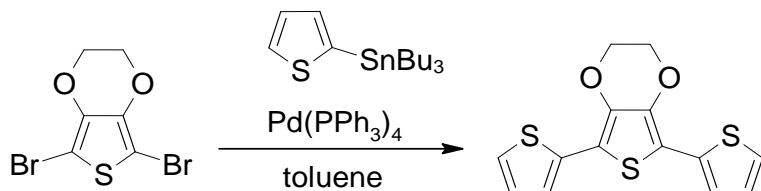
Synthesis of monomers

Synthesis of 2,5-dibromo-3,4-ethylenedioxythiophene:



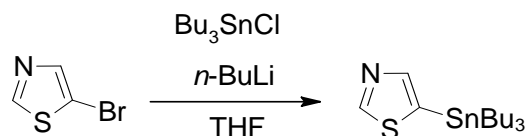
Under argon atmosphere, EDOT (100 mg, 0.703 mmol, 1equiv) and NBS (313 mg, 1.76 mmol, 2.5equiv) in DMF (5.0 mL, 7VR) were stirred at ambient temperature for 1 hour. The reaction mixture was poured into saturated sodium thiosulfate aqueous solution, and the crude product was extracted with hexane. The combined organic layer was washed with saturated sodium chloride aqueous solution several times, dried over anhydrous sodium sulfate and filtered. The filtrate was concentrated under reduced pressure and purified by silica gel chromatography with hexane eluent. The collected fraction was concentrated, and the residue was recrystallized from hexane. The desired compound was isolated as colorless crystal (86% yield: 0.606 mmol, 182 mg/211 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 4.255 (s, 4H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 139.8, 85.6, 65.0.

Synthesis of 2,6-bis(thiophene-2-yl)-3,4-ethylenedioxythiophene (2T-EDOT):



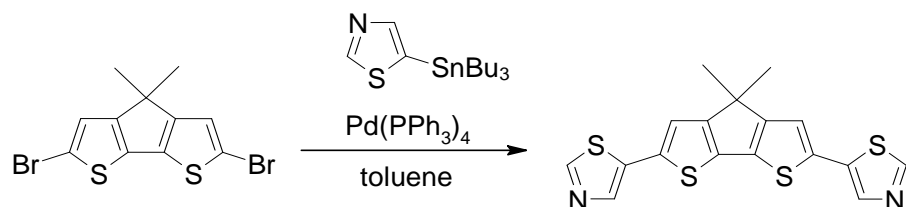
Under argon atmosphere, 2,5-dibromo-3,4-ethylenedioxythiophene (100 mg, 0.333 mmol, 1equiv) and 5-(tributylstannyl)thiophene (311 mg, 0.833 mmol, 2.5equiv) in toluene (3.3 mL, 10VR) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 30 min. Then, $\text{Pd}(\text{PPh}_3)_4$ (38.54 mg, 0.0333 mmol, 0.1equiv) was added to this solution and stirred under reflux at 90 °C for 48 hours. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 90:10) to afford the desired product (33% yield: 0.111 mmol, 34 mg/102 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 7.226–7.206 (m, 4H), 7.029–6.998 (m, 2H), 4.382 (s, 2H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 137.5, 134.5, 127.3, 124.0, 123.0, 109.6, 65.0.

Synthesis of 5-(tributylstannyl)thiazole:



Under argon atmosphere, a $n\text{-BuLi}$ (1.6 M in hexane, 4.6 mL, 7.43 mmol) was added to the flask containing a solution of 5-bromothiazole (1.06 g, 7.43 mmol) dissolved in 15 ml anhydrous THF at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 1 hour, followed by adding tributyltinchloride (2.43 g, 7.43 mmol) dissolved in 10 ml anhydrous THF at $-78\text{ }^\circ\text{C}$. The mixture was stirred for 1 hour at room temperature and then terminated by adding brine. The crude product was extracted with CH_2Cl_2 , and dried over anhydrous sodium sulfate. After removing the CH_2Cl_2 , crude product was obtained (83.8% yield: 6.24 mmol, 3.10 g/3.22 g). This material was used in the following procedure without further purification. ^1H NMR (CDCl_3 , 400 MHz): δ = 9.07 (s, 1H), 7.87 (s, 1H), 1.58–1.50 (m, 6H), 1.36–1.27 (m, 6H), 1.15–1.11 (m, 6H), 0.896–0.859 (t, 9H, J = 7.4 Hz). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 157.5, 149.9, 127.5, 28.9, 27.2, 13.7, 11.1.

Synthesis of 2,6-bis(thiazole-5-yl)-4,4-dimethyl-4*H*-cyclopenta[2,1-b:3,4-b']dithiophene (2Tz-CPDT):



Under argon atmosphere, 2,6-dibromo-4,4-dimethylcyclopenta[2,1-b:3,4-b']dithiophene (100 mg, 0.275 mmol, 1equiv) and 5-(tributylstannyl)thiazole (257 mg, 0.687 mmol, 2.5equiv) in toluene (2.7 mL, 10VR) were added to an over-dried 50 mL round-bottom flask equipped with a stir-bar and stirred for 30 min. Then, $\text{Pd}(\text{PPd}_3)_4$ (31.7 mg, 0.0275 mmol, 0.1equiv) was added to this solution and stirred under reflux at $90\text{ }^\circ\text{C}$ for 24 hours. After that, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated. The product was purified by column chromatography (silica gel, eluent: hexane/ethyl acetate = 80:20) to afford the desired product (72% yield: 0.198 mmol, 73 mg/102 mg). ^1H NMR (CDCl_3 , 400 MHz): δ = 8.67 (s, 2H), 7.96 (s, 2H), 7.11 (s, 2H), 1.50 (s, 6H). ^{13}C NMR (CDCl_3 , 100 MHz): δ = 161.3, 151.1, 138.7, 135.4, 133.6, 133.4, 119.9, 45.9, 25.1.

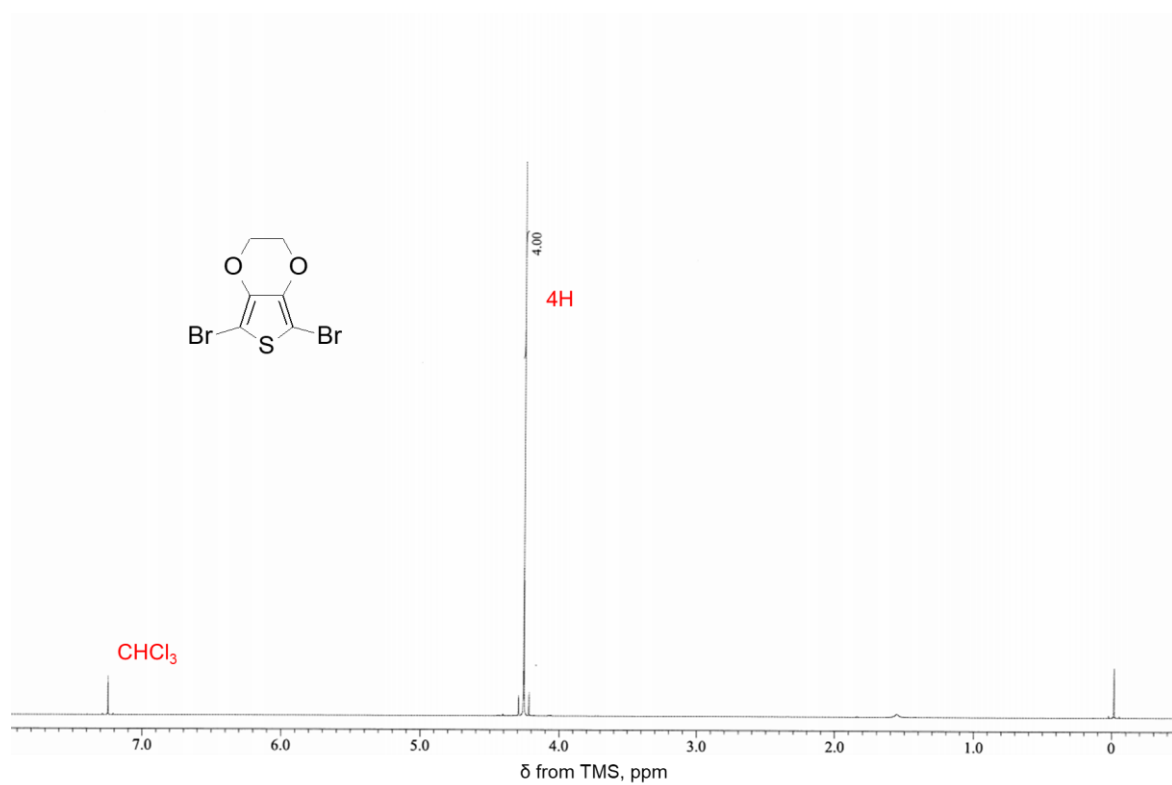


Figure S1. ^1H NMR of 2,5-dibromo-3,4-ethylenedioxythiophene.

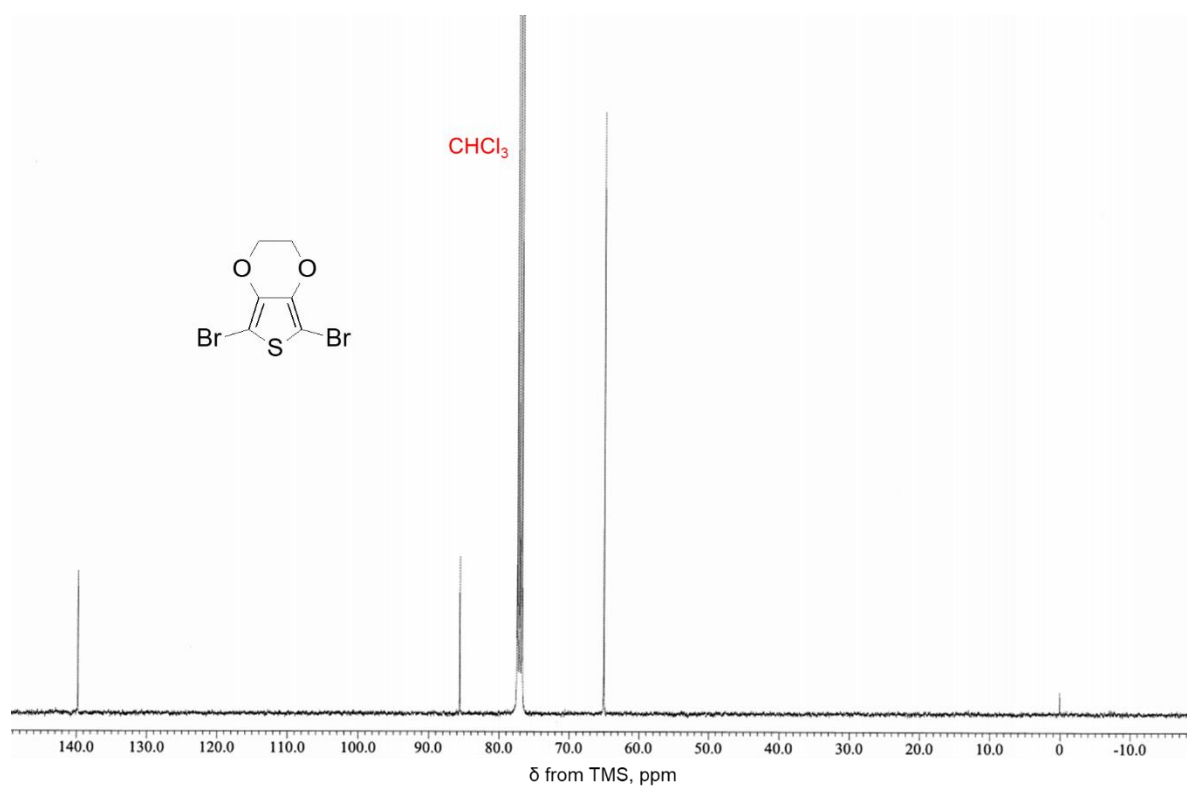


Figure S2. ^{13}C NMR of 2,5-dibromo-3,4-ethylenedioxythiophene.

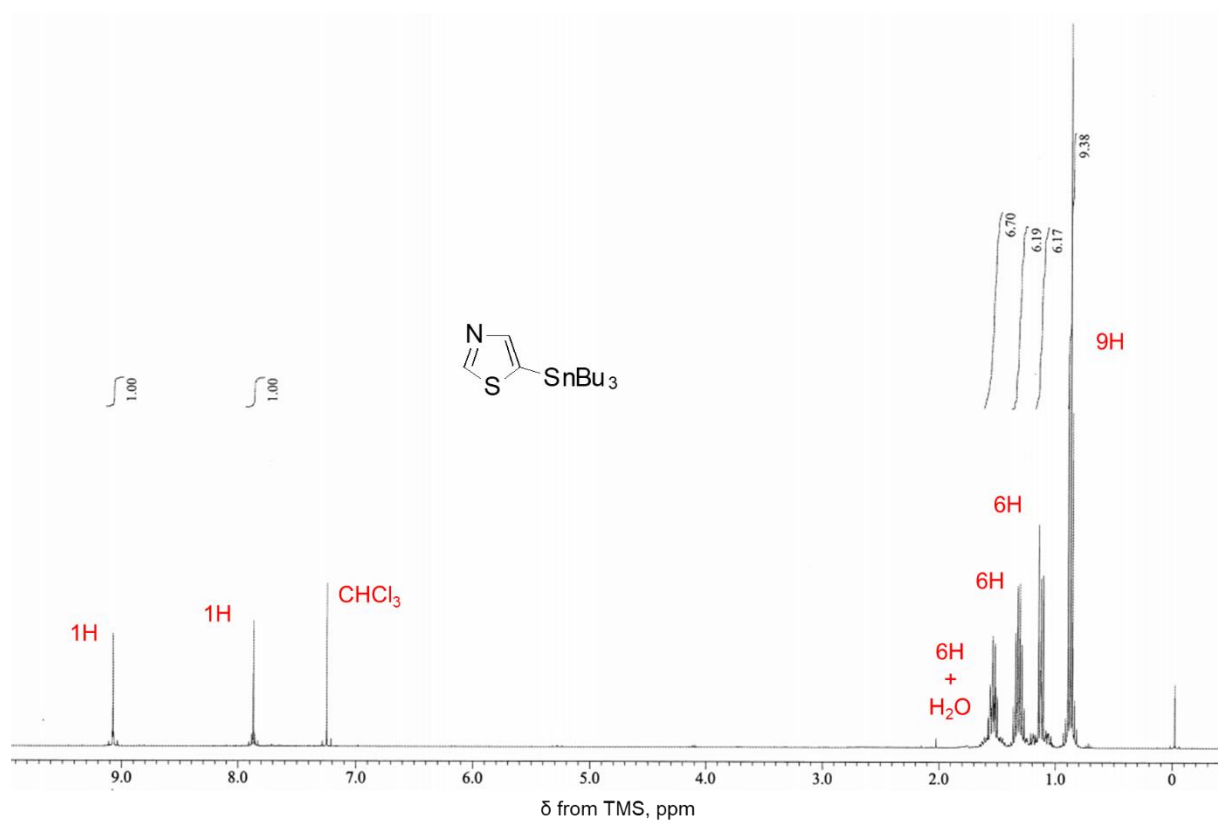


Figure S3. ¹H NMR of 5-(tributylstannyl)thiazole.

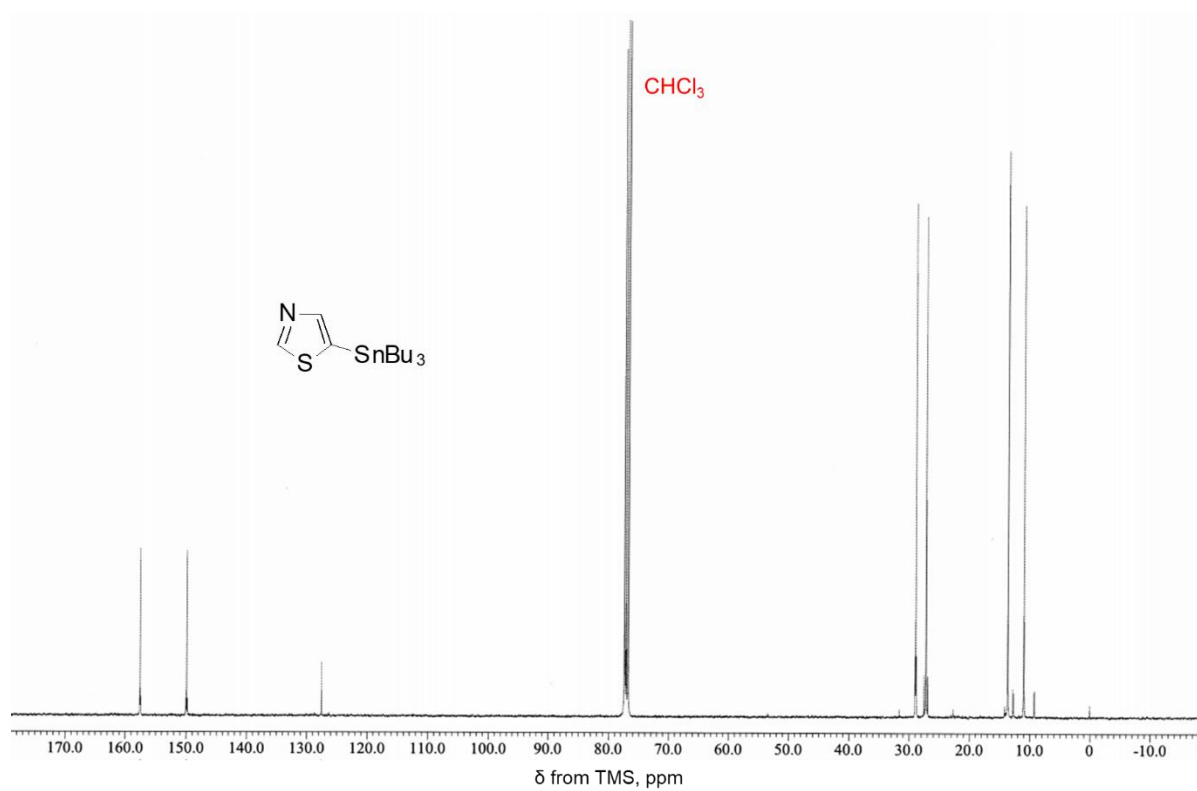


Figure S4. ¹³C NMR of 5-(tributylstannyl)thiazole.

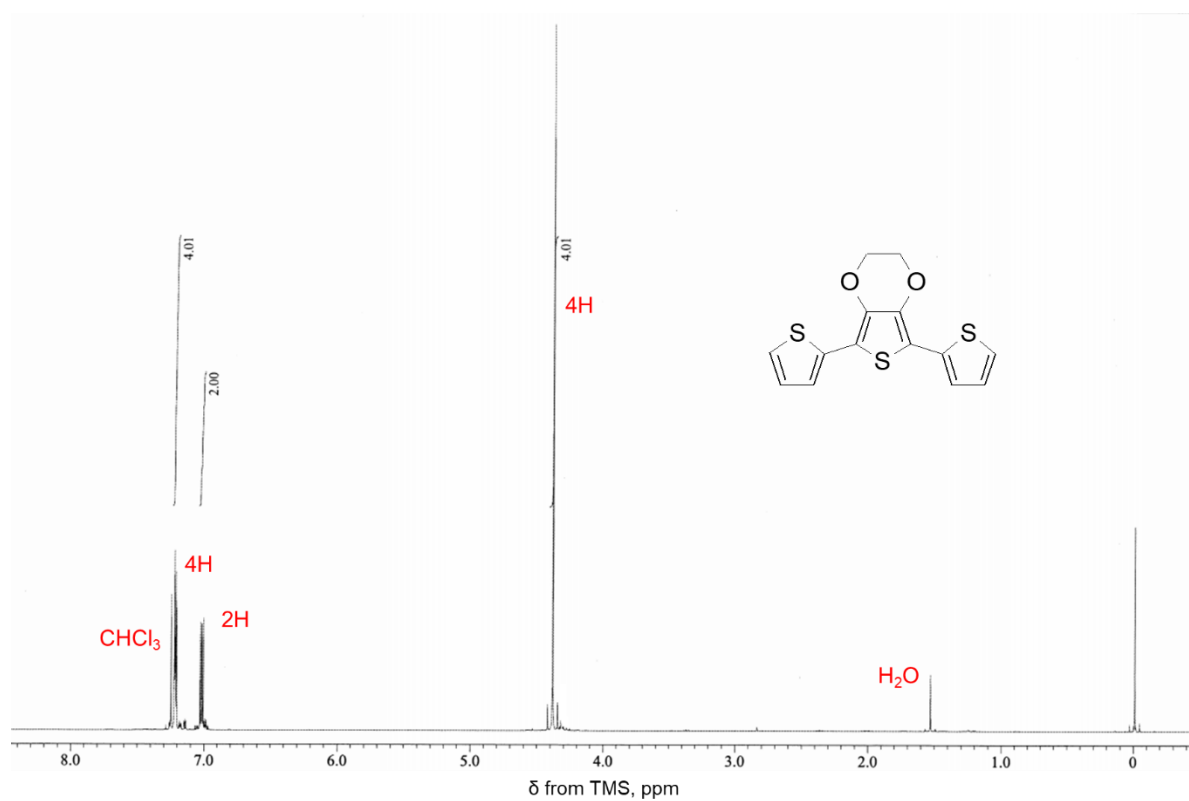


Figure S5. ¹H NMR of 2,6-bis(thiophene-2-yl)-3,4-ethylenedioxythiophene (2T-EDOT).

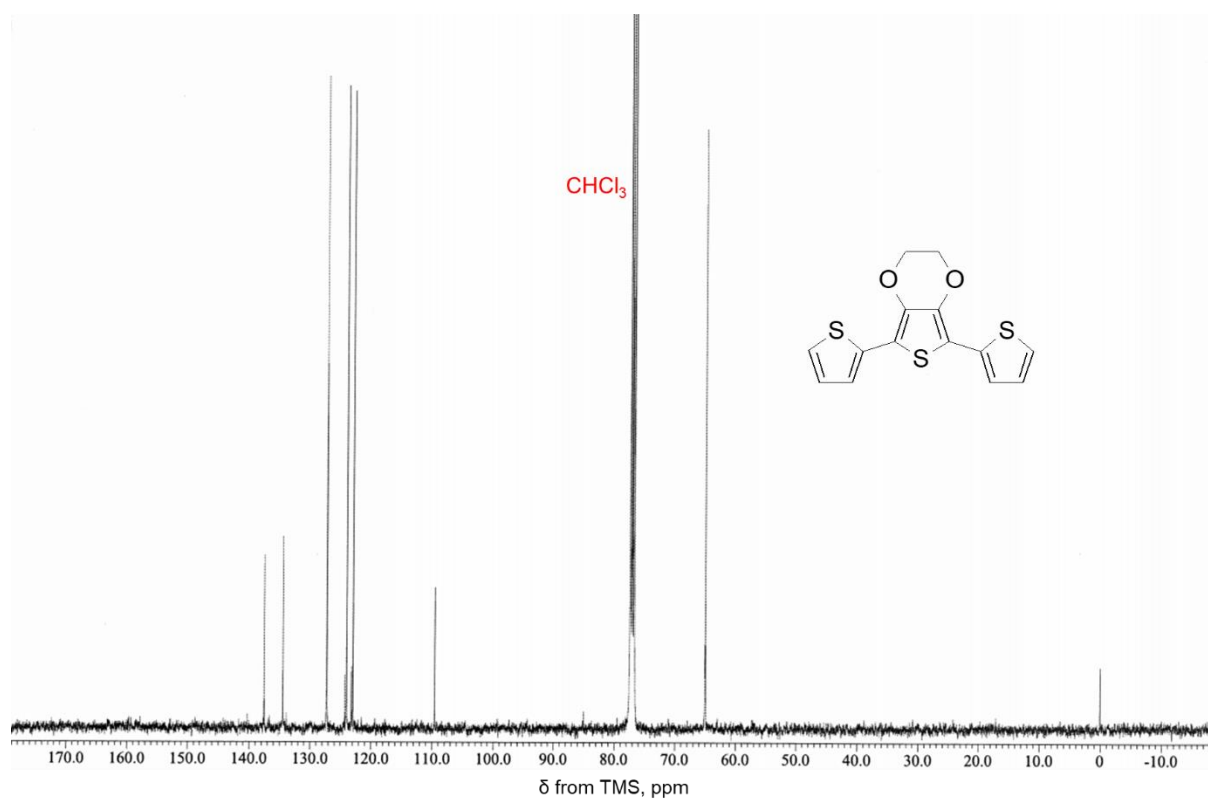


Figure S6. ¹³C NMR of 2,6-bis(thiophene-2-yl)-3,4-ethylenedioxythiophene (2T-EDOT).

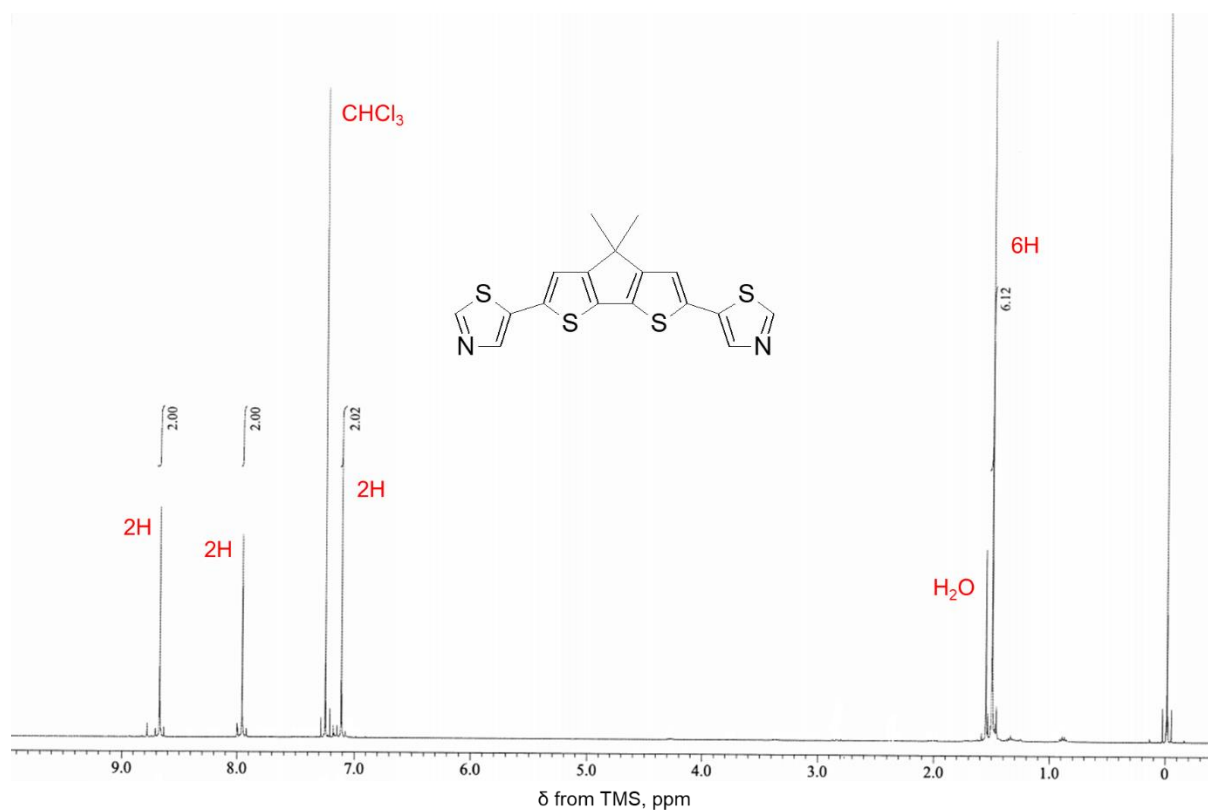


Figure S7. ^1H NMR of 2,6-bis(thiazole-5-yl)-4,4-dimethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (2Tz-CPDT).

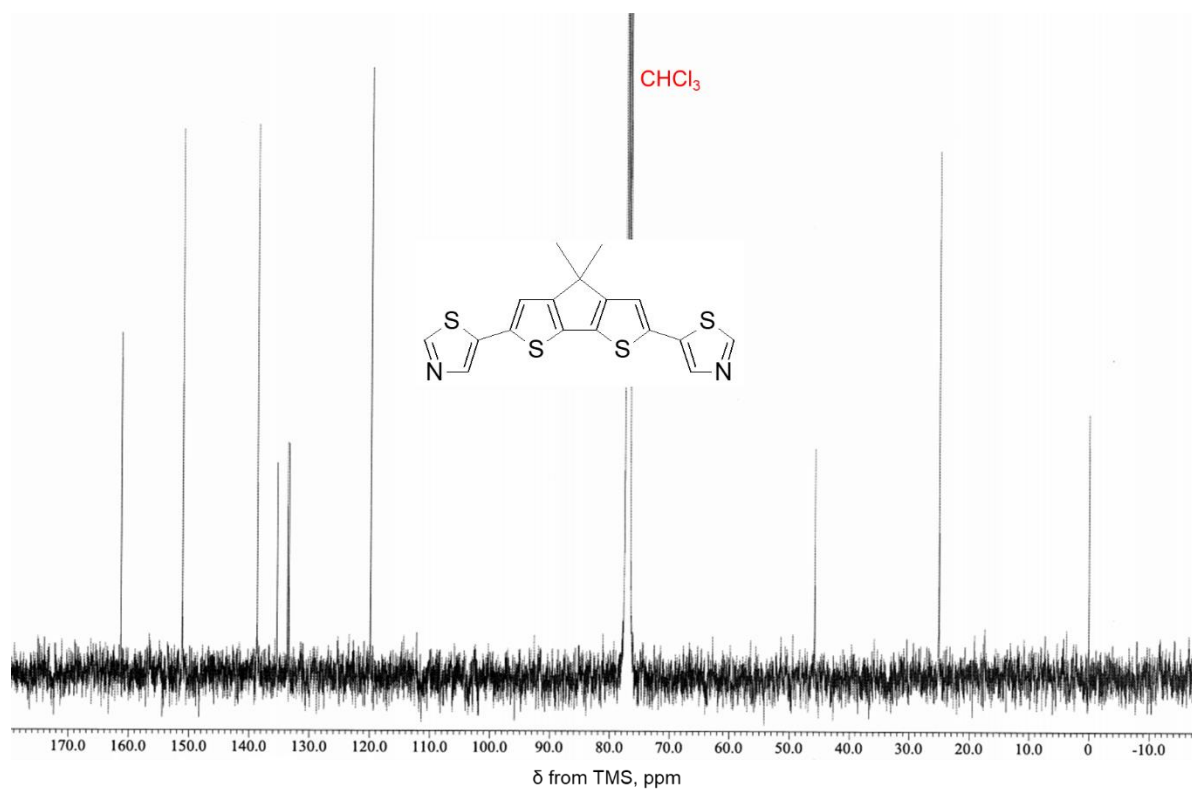


Figure S8. ^{13}C NMR of 2,6-bis(thiazole-5-yl)-4,4-dimethyl-4H-cyclopenta[2,1-b:3,4-b']dithiophene (2Tz-CPDT).

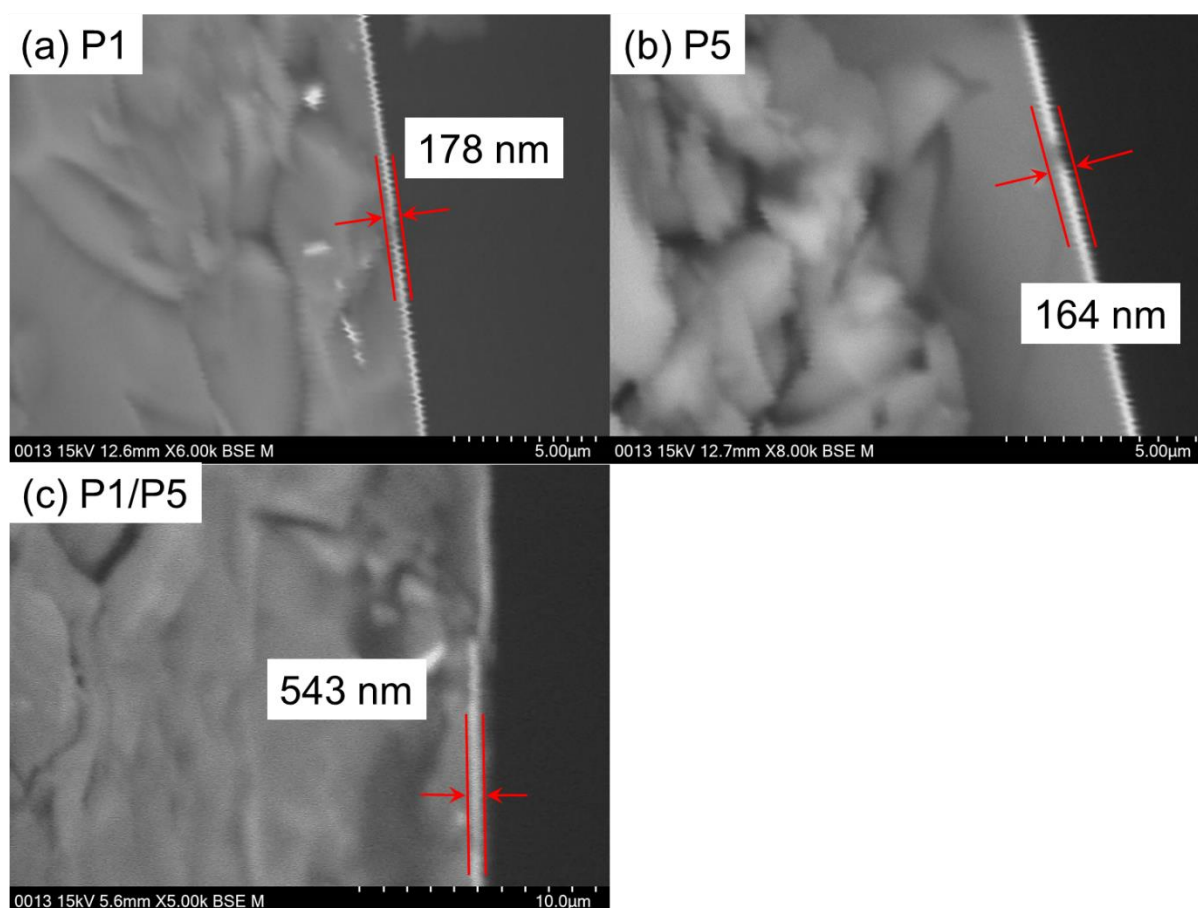


Figure S9. The thickness of polymer films of (a) P1, (b) P5, and (c) P1/P5 were measured by scanning electron microscopy (SEM) images.

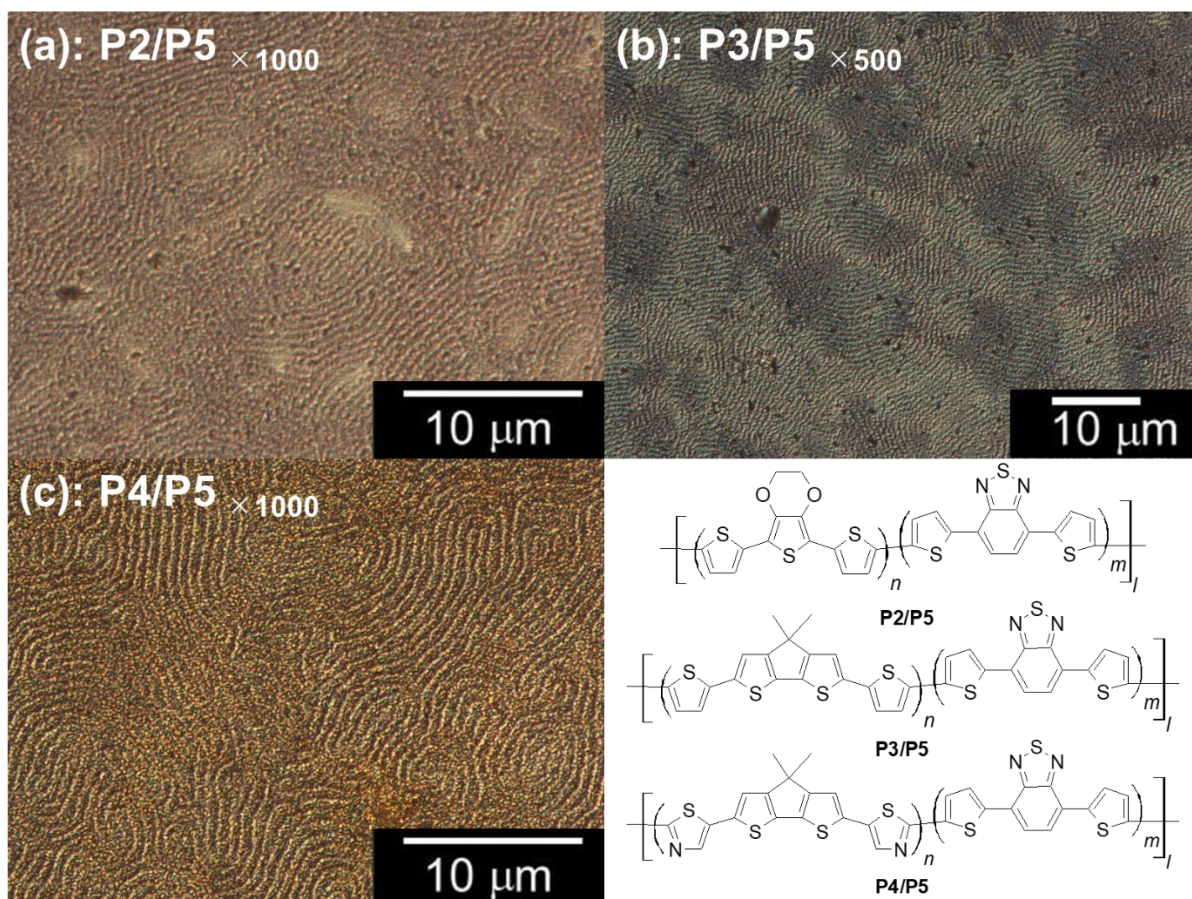


Figure S10. Polarizing optical microscopy (POM) image of the electrochemically prepared polymer films of (a) P2/P5 of 1000 magnifications, (b) P3/P5 of 500 magnifications and (c) P4/P5 of 1000 magnifications transcribed from CLC morphology.

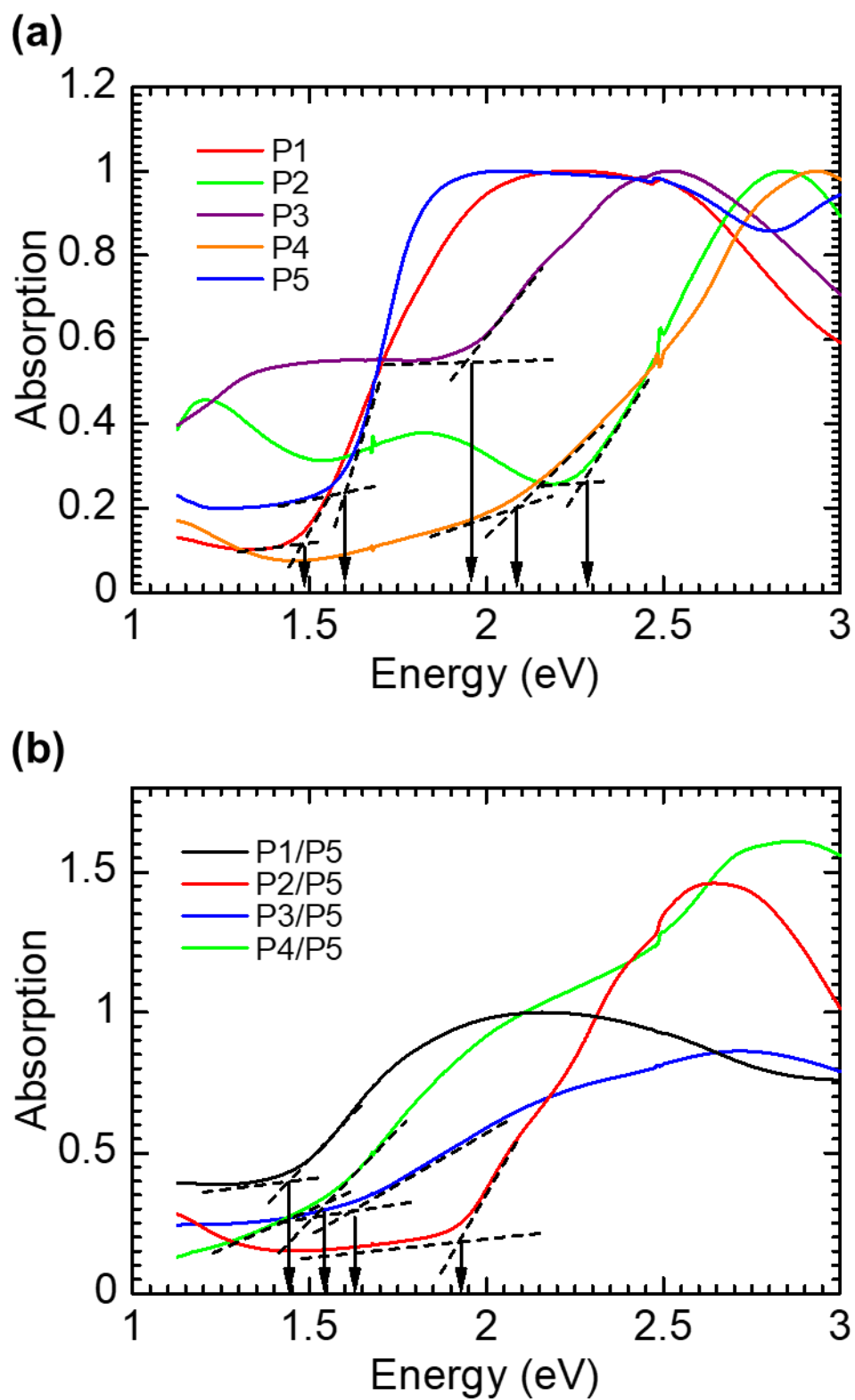


Figure S11. Energy level estimated from onset absorption wavelength on the low energy side.

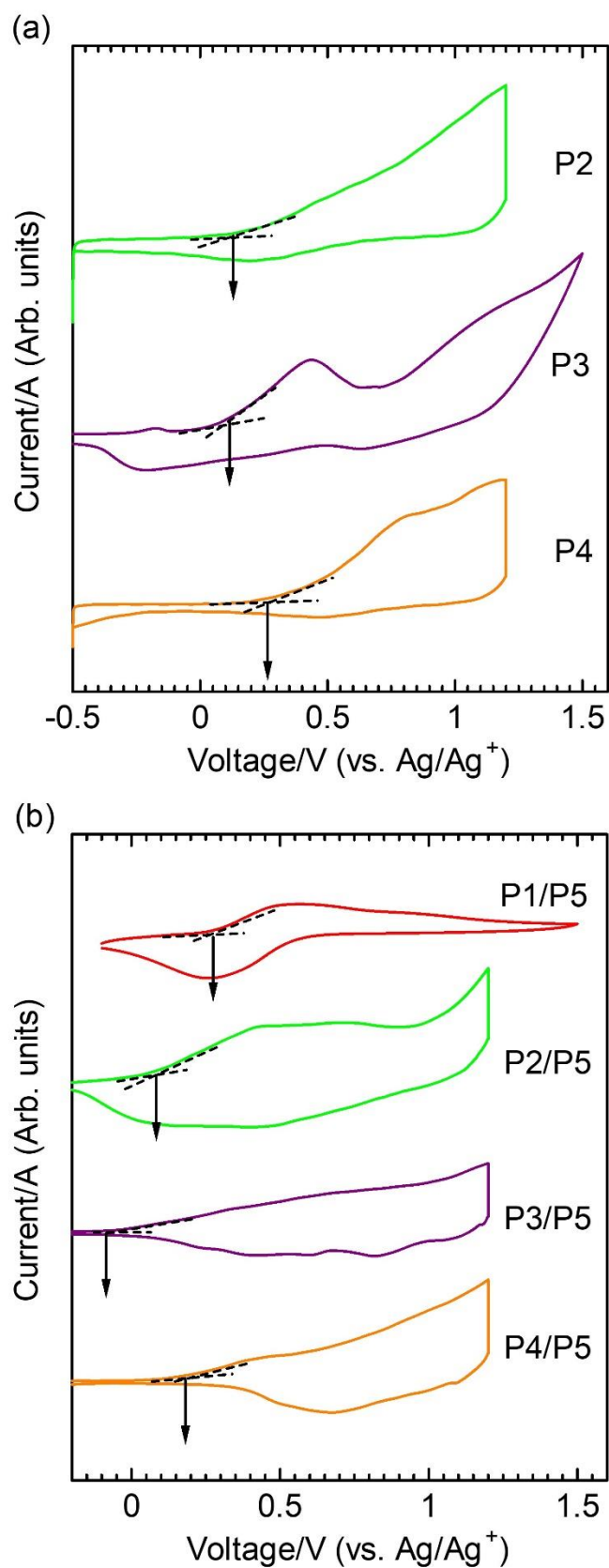
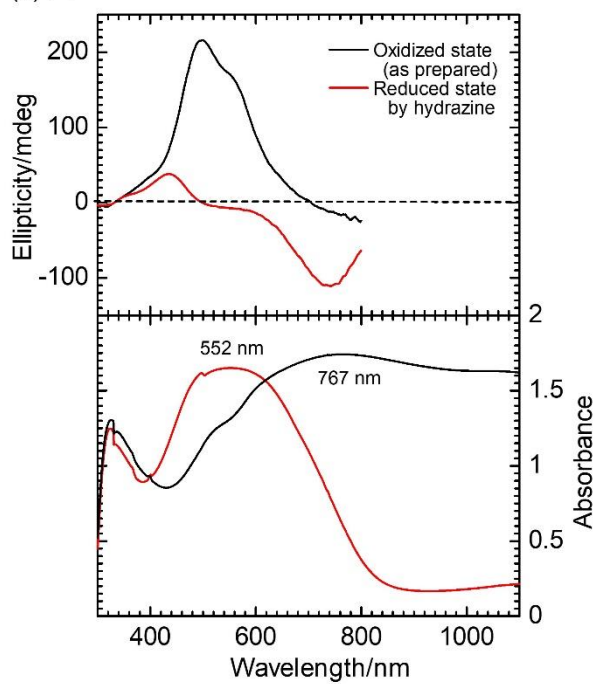
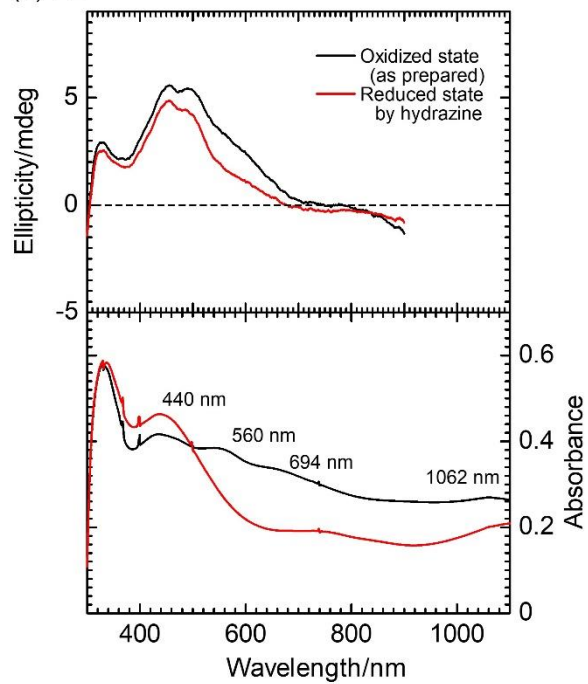


Figure S12. Cyclic voltammetry (CV) results at scan rate of 50 mV/s vs. Ag/Ag⁺ reference electrode in 0.1 M/TBAP acetonitrile solution. TBAP: tetrabutylammonium perchlorate.

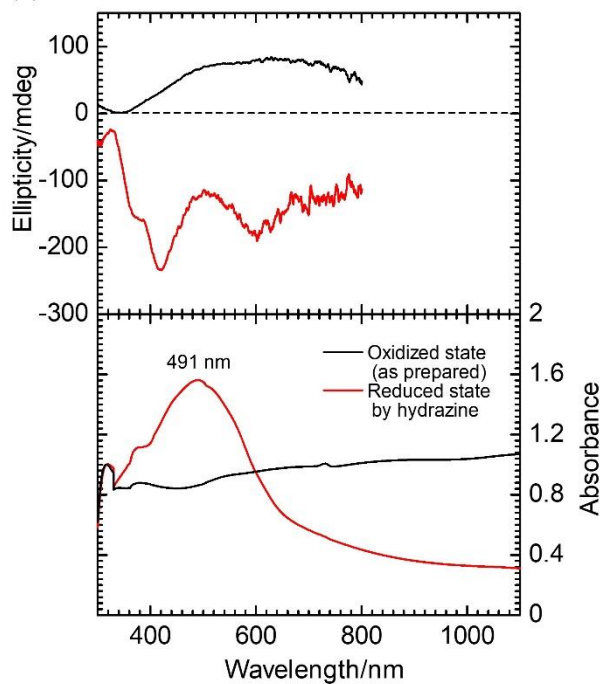
(a) P1



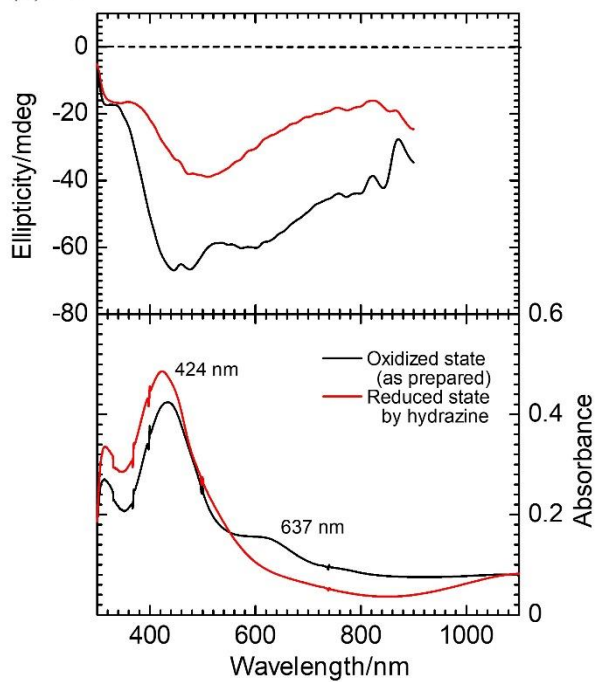
(b) P2

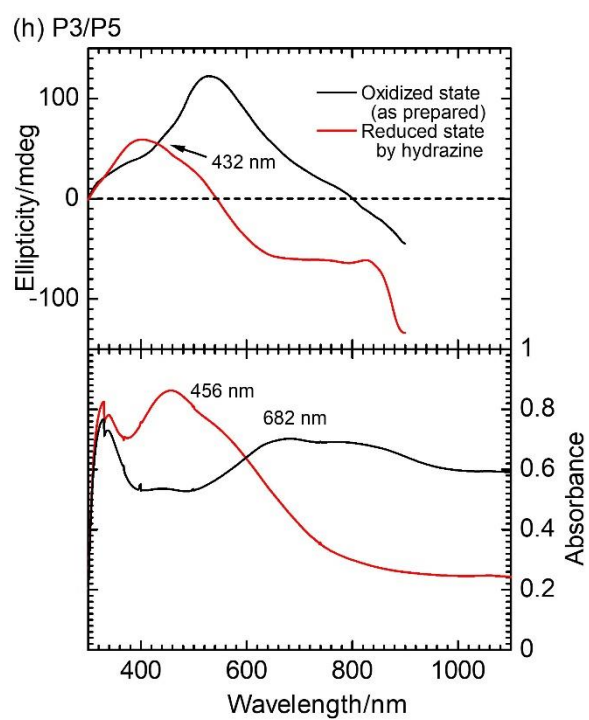
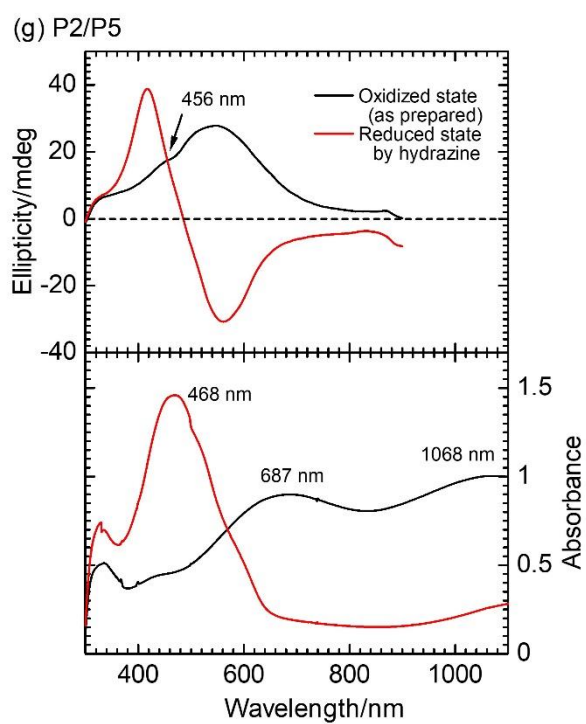
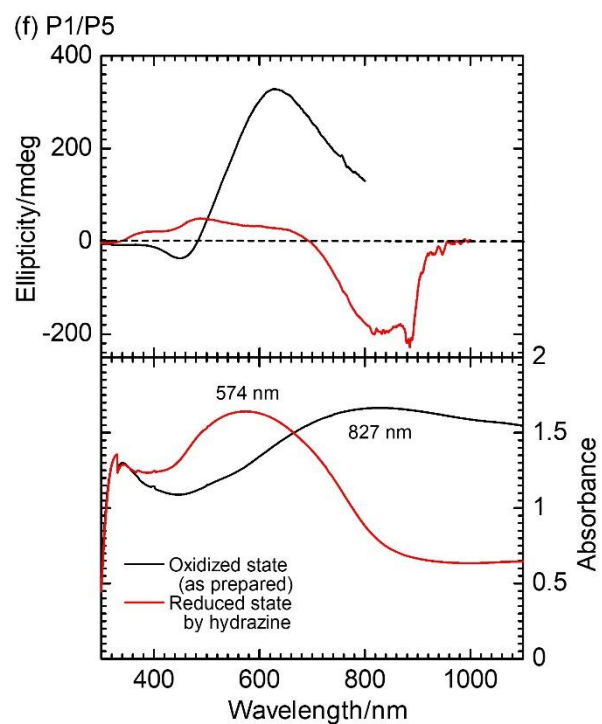
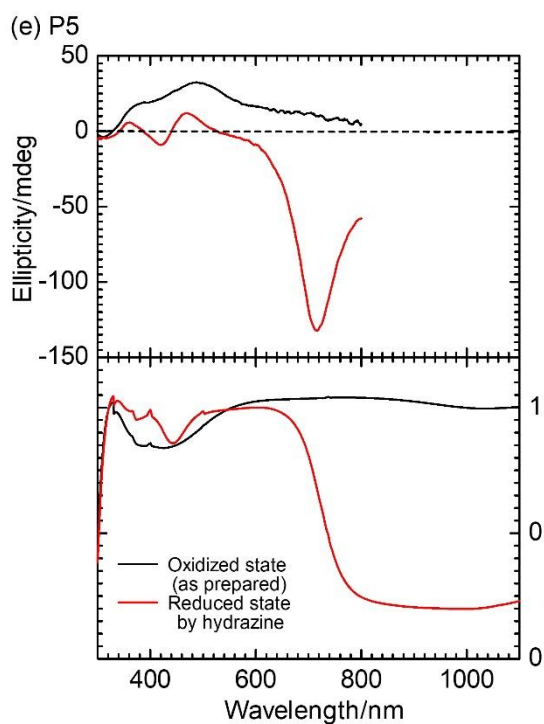


(c) P3



(d) P4





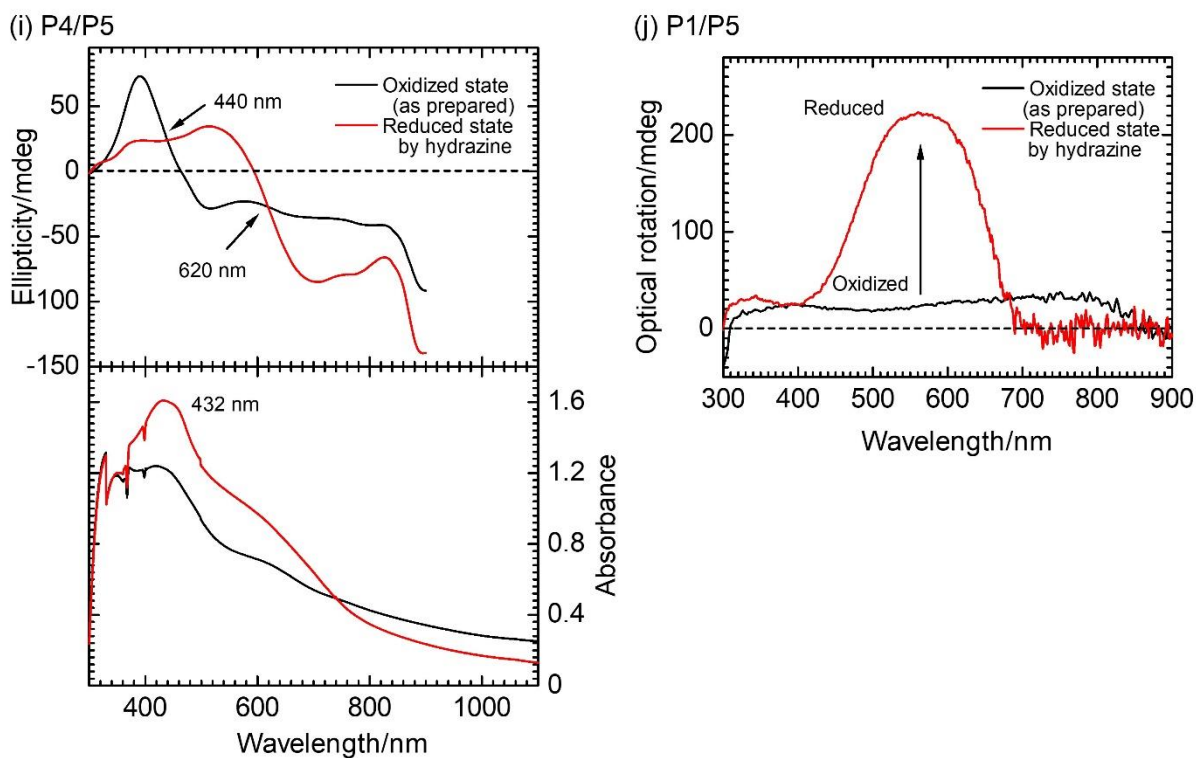


Figure S13. (a)–(i) Circular dichroism (CD) absorption spectra (upper) and UV–vis absorption spectra (below) of all homopolymer and random copolymer films. (j) Optical rotatory dispersion (ORD) spectra. Black line: oxidation state. Red line: reduction state by treatment of hydrazine vapor.

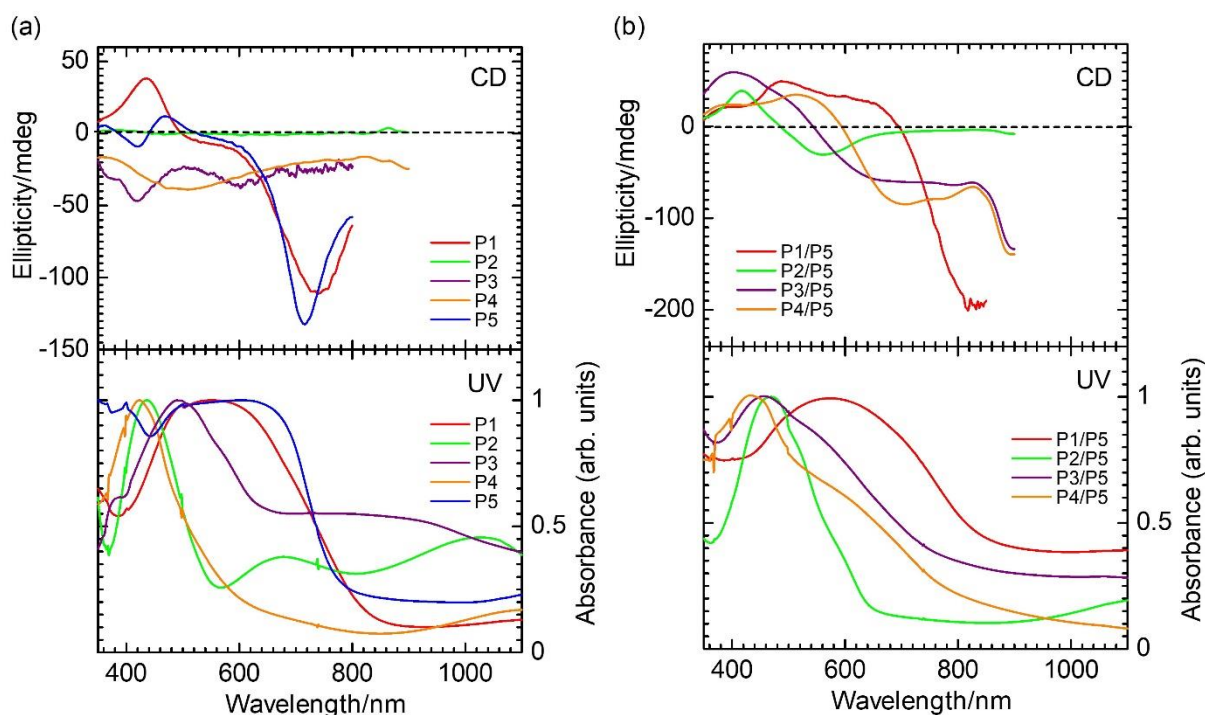


Figure S14. Circular dichroism (CD) absorption spectra (upper) and UV-vis absorption spectra (below) of (a) all homopolymer and (b) random copolymer films. All polymer films are reduced by hydrazine vapor.

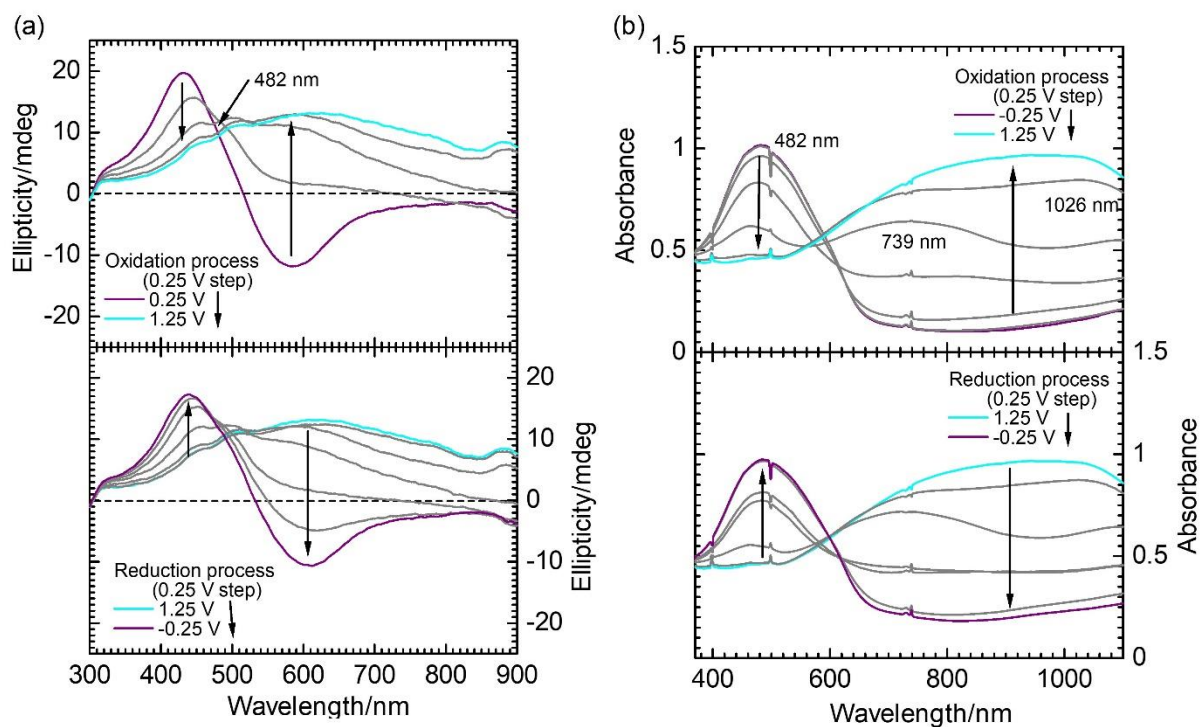


Figure S15. In-situ (a) UV-vis absorption spectra and (b) circular dichroism (CD) absorption spectra of P2/P5 film in 0.1 M TBAP/acetonitrile solution at different voltages.