Supporting Information

Effects of Linear and Branched Side Chains on the Redox and Optoelectronic Properties of 3,4-Dialkoxythiophene Polymers

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Materials

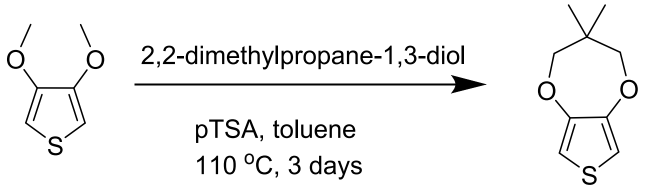
Dimethoxythiophene (98%, Oxchem), pivalic acid (99%, Sigma), $Pd(OAc)_2$ (98%, Strem Chemicals), K_2CO_3 (anhydrous, Oakwood Products), 18-Crown-6 (99%, Acros), 2-ethylhexanol (≥99.0%, Sigma), n-octanol (≥99%, Sigma), 2,2-dimethylpropane-1,3-diol (99%, Sigma), and diethyldithiocarbamic acid diethylammonium salt (97%, TCI America) were all used as received. Tetra(n-butylammonium) hexafluorophosphate ($TBAPF_6$, ≥99.0%, Sigma) was recrystallized from ethanol and dried under vacuum prior to use. DMF (anhydrous) was purchased from EMD and used as received. Acetonitrile (ACN, HPLC grade, Sigma) and propylene carbonate (PC, anhydrous, 99.7%, Sigma) were used as received. DMAc (HPLC grade, Alfa Aesar) was filtered through a pad of basic alumina (Sigma Aldrich) prior to use. Methanol, acetone, toluene, and chloroform were purchased from Fisher chemicals and used without purification. Hexanes were purchased from VWR chemicals and used as received. 3,3-Dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4] (DMP),[1] 3,4-(2-ethylhexyloxy)-thiophene,[2] 2,5-dibromo-3,4-(2-ethylhexyloxy)-thiophene,[3] and P(BAcDOT)[2] were prepared using published methods and confirmed by ^{1}H-NMR.

Instrumental and measurements details

Structural characterization: ^{1}H-NMR and ^{13}CNMR spectra were collected on either a Varian Mercury Vx 300 MHz or Bruker Corporation DRX 700 MHz instruments using $CDCl_3$ as a solvent. The ^{1}H and ^{13}C NMR spectra of monomers were collected using 300 MHz spectrometer. ^{1}H NMR spectra for the polymers were collected using the Bruker Corporation DRX 700 MHz spectrometer. The chemical shift was set based on residual $CHCl_3$ (in the $CDCl_3$ solvent) as an internal standard set to 7.26 ppm. The molecular weight and dispersity of the polymers were obtained using either a chloroform GPC at 40 °C or a THF GPC at 35 °C, both calibrated *vs.* polystyrene standards. Differential pulse voltammograms (DPV) and Cyclic voltammograms (CV) were obtained using an EG&G Princeton Applied Research model 273A potentiostat/galvanostat under CorrWare control using a three-electrode cell with a platinum flag as a counter electrode and a Ag/Ag^+ reference electrode (filled with 10 mM $AgNO_3$, 0.5 M $TBAPF_6$/ACN as the electrolyte). The working electrode consisted of a thin film of polymer drop-casted from a 0.5-1 mg/mL toluene solution onto a platinum button electrode (0.02 cm^2) or a glassy carbon electrode (0.07 cm^2). The electrolyte solution was 0.5 M $TBAPF_6$ in PC. Absorbance spectra were acquired using a Varian Cary 5000 Scan dual-beam UV−vis−near-IR spectrophotometer. For the spectroelectrochemistry measurements, the working electrode was a thin film of polymer sprayed from a 0.5-1 mg/mL toluene solutions onto ITO glass slides (7 × 50 × 0.7 mm, sheet resistance, R_s 8–12 Ω/sq, Delta Technologies, Ltd.) using a commercial airbrush sprayer (Iwata Eclipse, Revolution Series). Prior to spraying the films, the ITO glass slides were dipped into a 10mM solution of 1-dodecylphosphonic acid (95%, Alfa Aesar) for 5 to 10 minutes. Colorimetry measurements were obtained by converting the absorbance spectras to CIELAB L*a*b* color space using Star-Tek colorimetry software using a D50 illuminant, 2-degree observer. Photography was performed in a light booth designed to exclude outside light with a D50 lamp located in the back of the booth providing illumination, using a Nikon D90 SLR camera with a Nikon 18-105 mm VR lens. Photos of the films were taken as-sprayed, after break-in at -0.5 V, and at the most transmissive oxidized state (+0.8V). The photographs are presented without any manipulation apart from cropping. Thermogravimetric analysis (TGA) was carried out on a PerkinElmer Pyrus 1 to determine the decomposition temperature (T_d) at which chemical decomposition of the material occurs (5%). DSC was performed using a TA Instruments Q200 to determine where morphological or phase changes occur.

Monomer synthesis

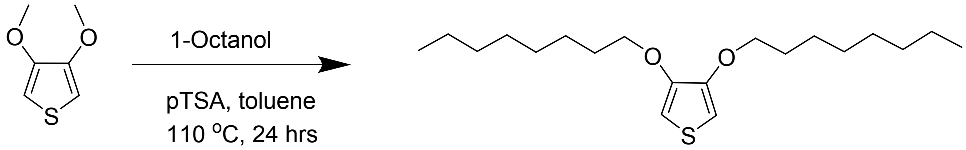
Synthesis of 3,3-dimethyl-3,4-dihydro-2H-thieno[3,4-b][1,4]dioxepine



In a dry 1 L round bottom flask with a magnetic stir bar, dimethoxythiophene (20.0 g, 0.138 mol) and 2,2-dimethylpropane-1,3-diol (144.0 g, 1.38 mol) were added under argon followed by anhydrous toluene (600 mL). While the solution was stirring, *p*-toluenesulfonic acid (2.6g, 0.015

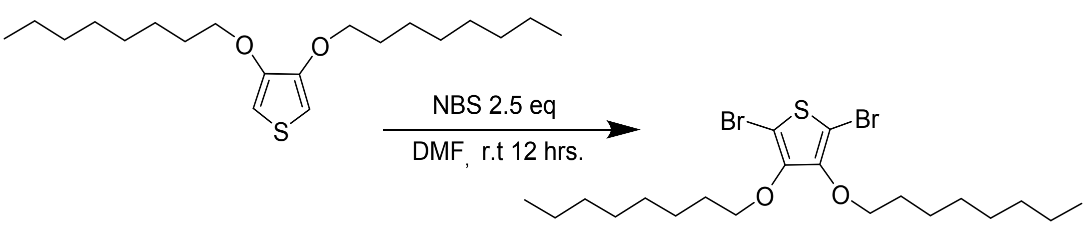
mol) was added slowly. The reaction was refluxed for three days at 110 °C. After completion, the flask was cooled to ambient temperature and quenched with 200 mL of a saturated $NaHCO_3$ solution. The organic layer was extracted 3 times with diethyl ether and dried using magnesium sulfate ($MgSO_4$). The solvent was concentrated and the crude product was purified by silica gel chromatography using pure hexanes to obtain 14.30 g (56%) of a white solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.47 (s, 2H), 3.73 (s, 4H), 1.03 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 149.96, 105.50, 80.07, 38.87, 21.66. NMR consistent with previous reported spectrum.[1]

Synthesis of 3,4-bis(octyloxy)thiophene



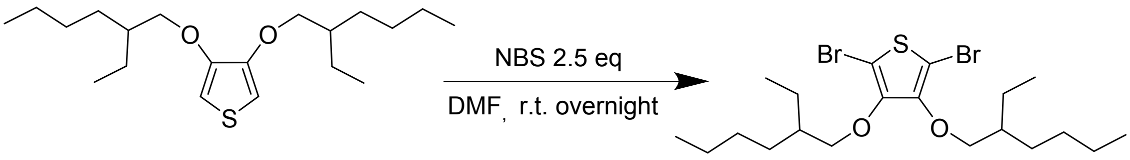
In a dry 500 mL round bottom flask with a magnetic stir bar, dimethoxythiophene (10.0 g, 0.069 mol) and n-octanol (24.0 g, 0.185 mol) was added under argon followed by anhydrous toluene (300 mL). *p*-Toluenesulfonic acid (1.3g, 0.006 mol) was added while the solution was stirring. The reaction was refluxed overnight at 110 °C. After completion, the flask was cooled to ambient temperature and quenched with 100 mL of a saturated $NaHCO_3$ solution. The organic layer was extracted 3 times with DCM and dried using $MgSO_4$. The solvent was concentrated and the crude was purified by silica gel chromatography using hexanes to obtain 17.800 g of a clear white solids (75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 6.15 (s, 2H), 3.97 (t, J = 6.8 Hz, 4H), 1.81 (p, 4H), 1.49 – 1.37 (m, 4H), 1.31 (b, J = 12.7, 9.5 Hz, 16H), 0.96 – 0.81 (m, 6H).^{13}C NMR (75 MHz, $CDCl_3$) δ(ppm) 147.67, 96.93, 70.72, 31.96, 29.51, 29.41, 29.14, 26.12, 22.82, 14.26. NMR consistent with previous reported spectrum.[4]

Synthesis of 2,5-dibromo-3,4-bis(octyloxy)thiophene.



In a dry 250 mL round bottom flask with a magnetic stir bar, 3,4-bis(octyloxy)thiophene (1.000 g, 0.0029 mol) was added. The flask was then degassed before 100 mL of anhydrous DMF was added via syringe. The solution was stirred for ten minutes at 0 °C under argon. While stirring at 0 °C, a solution of 1.340 g of N-bromosuccinimide (NBS) (0.0075 mol, 2.5 eq) in anhydrous DMF was added dropwise. The vessel was brought to room temperature and then allowed to stir for 12 hrs while covered with aluminum foil. After completion, the product was washed with brine and extracted with 200 mL of 1:1 ethyl ether/ethyl acetate. The organic layer was then washed three times with deionized water and then dried over magnesium sulfate. The solvent was removed under reduced pressure. The resulting crude oil was purified by column chromatography using hexanes on neutral silica resulting in a clear, colorless oil 1.160 g (80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.05 (t, *J* = 6.6 Hz, 4H), 1.72 (p, 4H), 1.53 – 1.39 (m, 4H), 1.39 – 1.21 (m, 16H), 0.94 – 0.82 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 147.75, 95.40, 74.10, 31.98, 30.08, 29.49, 29.42, 26.01, 22.81, 14.26. NMR consistent with previous reported spectrum.[4]

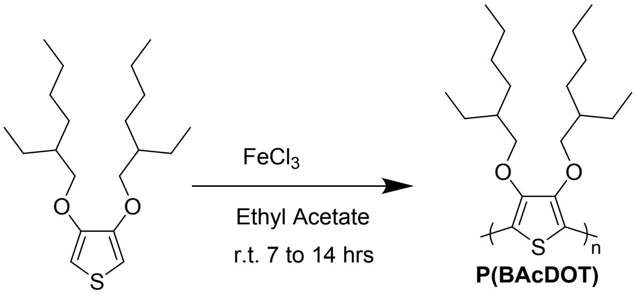
Synthesis of 2,5-dibromo-3,4-bis((2-ethylhexyl)oxy)thiophene



In a dry 250 mL round bottom flask with a magnetic stir bar, 3,4-bis(octyloxy)thiophene (5.000 g, 0.014 mol) was added. The flask was then degassed before 100 mL of anhydrous DMF was added. The solution was stirred for ten minutes at 0 °C under argon. While stirring at 0 °C, a solution of 6.53 g of NBS (0.036 mol, 2.5 eq.) in anhydrous DMF was added dropwise. The vessel was brought to room temperature and then allowed to stir overnight while covered with aluminum. After completion, the product was washed with brine and extracted with 200 mL of 1:1 ethyl ether/ethyl acetate. The organic layer was then washed three times with deionized water and then dried over magnesium sulfate ($MgSO_4$). The solvent was removed under reduced pressure. The resulting crude oil was purified by column chromatography using hexanes on neutral silica resulting in a clear, colorless oil 5.05 g (70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 3.96 (d, 2H), 1.65 (dt, J = 17.8, 6.0 Hz, 2H), 1.41 (b, 16H), 1.01 – 0.81 (m, 12H). NMR consistent with previous reported spectrum.[3]

Polymer Synthesis

Oxidative polymerization procedure for P(BAcDOT)

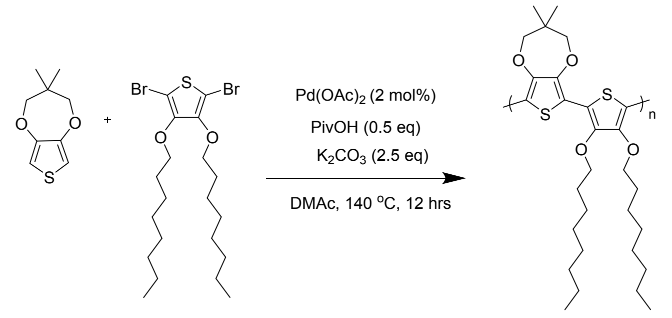


In a round-bottomed flask equipped with a stir bar, iron (III) chloride (4.290 g, 3.0 eq.) was dissolved in 20 ml of ethyl acetate for ten minutes in an ice bath. 3,4-Di(2-ethylhexyloxy)thiophene (3.000 g, 1.0 eq) was dissolved in ethyl acetate (40 mL) and added to the stirring solution of iron (III) chloride. The reaction mixture immediately turned dark green and was stirred for an additional 10 minutes in the ice bath. The solution was then removed from the ice bath and allowed to stir overnight at room temperature. Once the reaction was complete, the solution was precipitated into a beaker containing 250 mL of methanol and the mixture was stirred for 5 min. The doped polymer was collected by suction filtration using a Nylon pad (with a pore size of 20 µm) and washed with methanol (2 x 80 mL). The doped polymer was suspended in chloroform (50 mL) and hydrazine monohydrate (2 mL) was added dropwise, effecting a change in color of the mixture to light-orange/brown. The mixture was concentrated to ~10 mL and precipitated into a stirring solution of methanol (100 mL). The mixture was concentrated again to ~10 mL and precipitated into a stirring solution of methanol (100 mL). The precipitate was vacuum filtered, using a Nylon pad (with a pore size of 20 µm) as the filter. The dried polymer was collected into a vial and left to dry under high vacuum for two to three days. The polymer was obtained as a orange solid in 43% yield (1.300 g). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 3.92 (d, *J* = 4.5 Hz, 4H), 1.81 – 1.70 (m, 2H), 1.59 – 1.49 (m, 2H), 1.45 – 1.36 (m, 4H), 1.35 – 1.21 (m, 11H), 0.91 – 0.80 (m, 12H). Anal. calcd. for $C_{20}H_{34}O_2S$ C 70.96, H 10.12, S 9.47, Found C 70.85, H 10.05, S 9.48. M_n: 44 kDa, M_w/M_n: 3.0, *vs.* PS in THF at 35 °C. NMR consistent with previous reported spectrum.[2]

General direct arylation polycondensation procedure

To a 50 mL Schlenk tube equipped with a stir bar the dibromo monomer (1.0 eq.), the dihydrogen monomer (1.0 eq.), palladium(II) acetate (2 mol%), pivalic acid (0.5 eq.), and potassium carbonate (2.5 eq.) were added. ~20 mL of DMAc was added to dissolve the contents and the tube was sealed under a blanket of argon. The reaction mixture was premixed for 5 minutes before it was lowered into an oil bath heated to 140 °C. The solution was left to stir vigorously overnight (~12 hours). After the flask was removed from the oil bath and allowed to cool to room temperature, the polymer was precipitated into methanol and stirred for one hour. The precipitate was filtered into a Soxhlet extraction thimble and washed with methanol, acetone, hexanes, toluene, and finally dissolved into chloroform. The washings were conducted until the color was no longer observed during extraction. ~20 mg of a palladium scavenger (diethylammonium diethyldithiocarbamate) and ~20 mg of 18- crown-6, was added to the chloroform fraction and then stirred for 2 hours at 50 °C. The chloroform was reduced under reduced pressure and polymer was precipitated into ~300 mL of methanol. The precipitate was vacuum filtered using a nylon pad (with a pore size of 20 μm) and washed with a large volume of methanol before letting it air dry. The dried material was collected into a vial and dried under vacuum for two days.

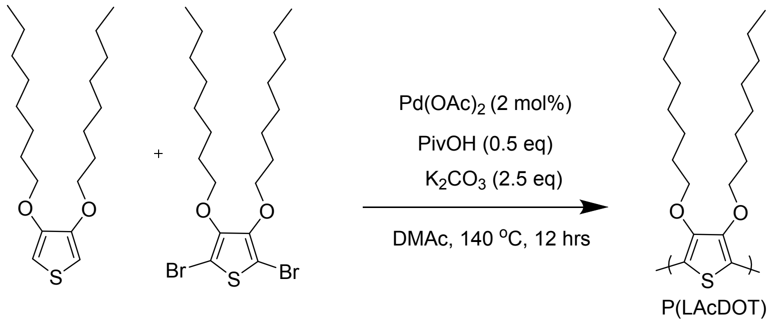
P(LAcDOT-DMP)



P(LAcDOT-DMP)

The polymer was obtained as a black solid in 68% yield (0.7048 g). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 4.08 (s, 4H), 3.79 (s, 4H), 2.04 – 1.79 (m, 4H), 1.57 – 1.18 (m, 30H), 0.87 (s, 6H). Anal. calcd. for $C_{29}H_{44}O_4S_2$ C 66.88, H 8.52, S 12.31, Found C 66.61, H 8.47, S 12.06. M_n: 5 kDa, M_w/M_n: 1.4, vs. PS in $CHCl_3$ at 40 °C.

P(LAcDOT)

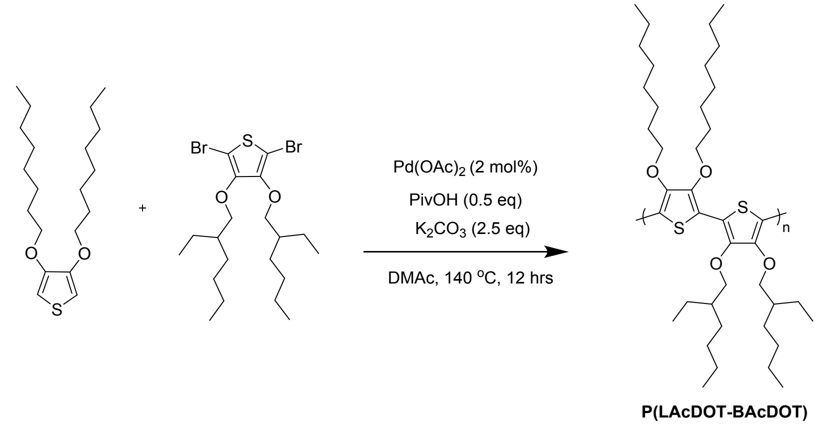


P(LAcDOT)

The polymer was obtained as a metallic looking purple solid in 50% yield (0.4938 g). ^{1}H NMR

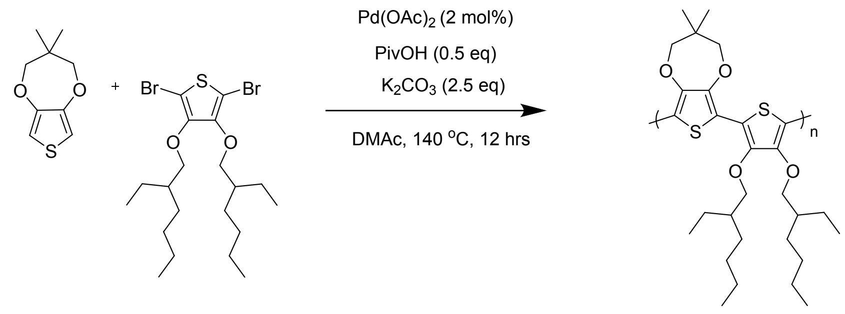
(700 MHz, $CDCl_3$) δ 4.16 (Br, 4H), 1.91 (s, 4H), 1.31 (dd, *J* = 13.6, 6.3 Hz, 18H), 0.89 (t, *J* = 6.9 Hz, 6H). Anal. calcd. for $C_{20}H_{34}O_2S$ C 70.96, H 10.12, S 9.47, Found C 70.69, H 10.03, S 9.48. M_n: 15 kDa, M_w/M_n: 2.2, *vs.* PS in $CHCl_3$ at 40 °C.

P(LAcDOT-BAcDOT)



The polymer was obtained as a red tacky material in 56% yield (0.5531 g). ^1H NMR (700 MHz, $CDCl_3$) δ (ppm) 4.07 (br, 4H), 3.95 (br, *J* = 17.0 Hz, 4H), 3.66 (s, 3H), 1.82 (br, 6H), 1.62 – 1.50 (m, 2H), 1.42 (dt, *J* = 32.8, 23.2 Hz, 10H), 1.28 (br, 28H), 0.94 – 0.82 (m, 18H). Anal. calcd. for $C_{34}H_{52}O_6S_2$ C 70.96, H 10.12, S 9.47, Found C 70.09, H 10.31, S 9.16. M_n: 16 kDa, M_w/M_n: 2.6, *vs.* PS in $CHCl_3$ at 40 °C.

P(BAcDOT-DMP)



P(BAcDOT-DMP)

The polymer was obtained as a reddish solid in 55% yield (0.5598 g). ^{1}H NMR (700 MHz, $CDCl_3$) δ (ppm) 3.96 (s, 4H), 3.83 (s, 4H), 1.63 – 1.23 (m, 18H), 1.08 (d, *J* = 30.1 Hz, 6H), 0.99 – 0.82 (m, 10H). Anal. calcd. for $C_{29}H_{44}O_4S_2$ C 66.88, H 8.52, S 12.31, Found C 66.38, H 8.35, S 12.44. M_n: 15 kDa, M_w/M_n: 2.1*, vs.* PS in $CHCl_3$ at 40 °C.

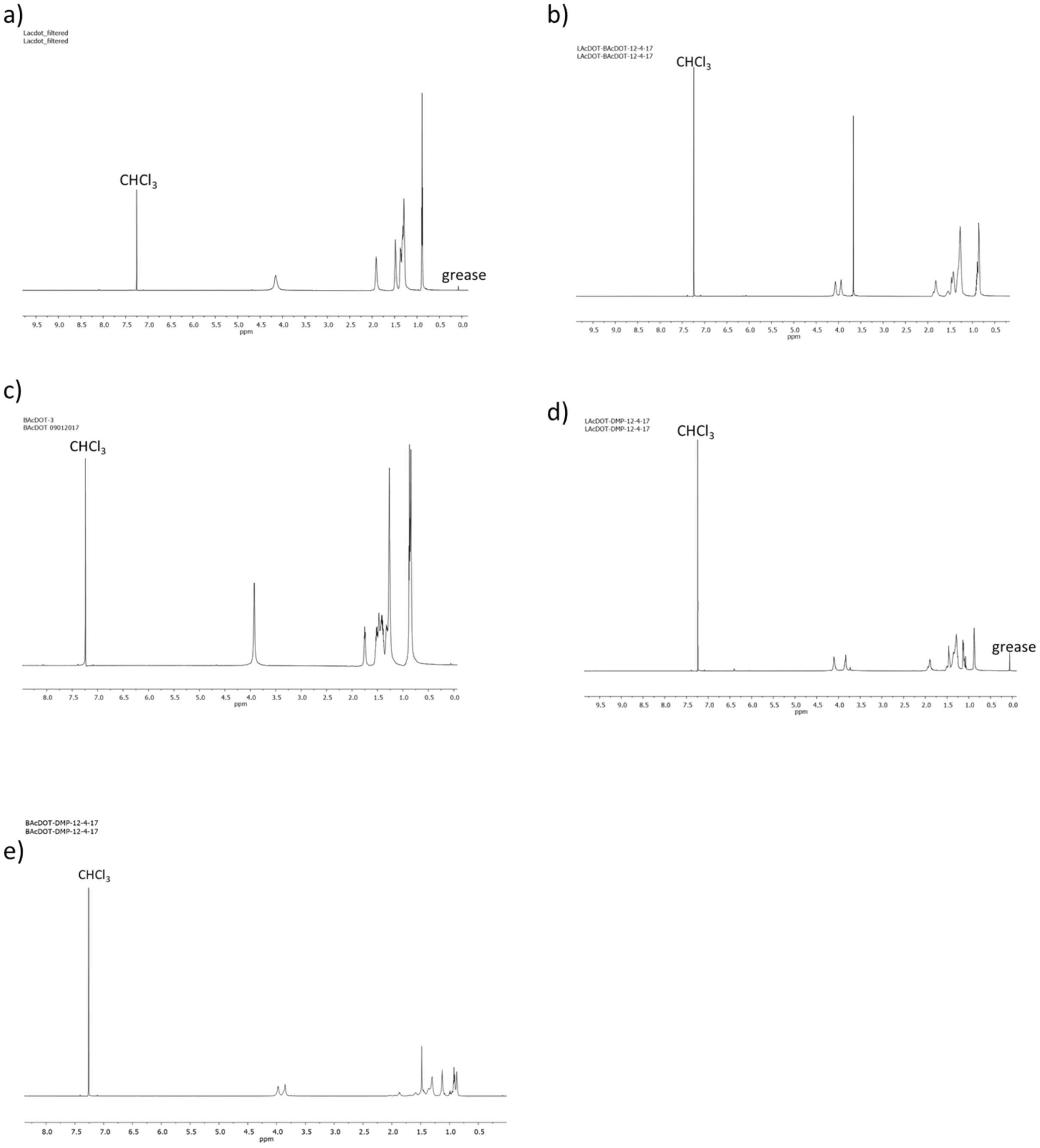


Figure S1. ^{1}H-NMR spectra (700 MHz in $CHCl_3$ at 50 °C) of a) P(LAcDOT), b) P(LAcDOT-BAcDOT), c) P(BAcDOT), d) P(LAcDOT-DMP), and e) P(BAcDOT-DMP.

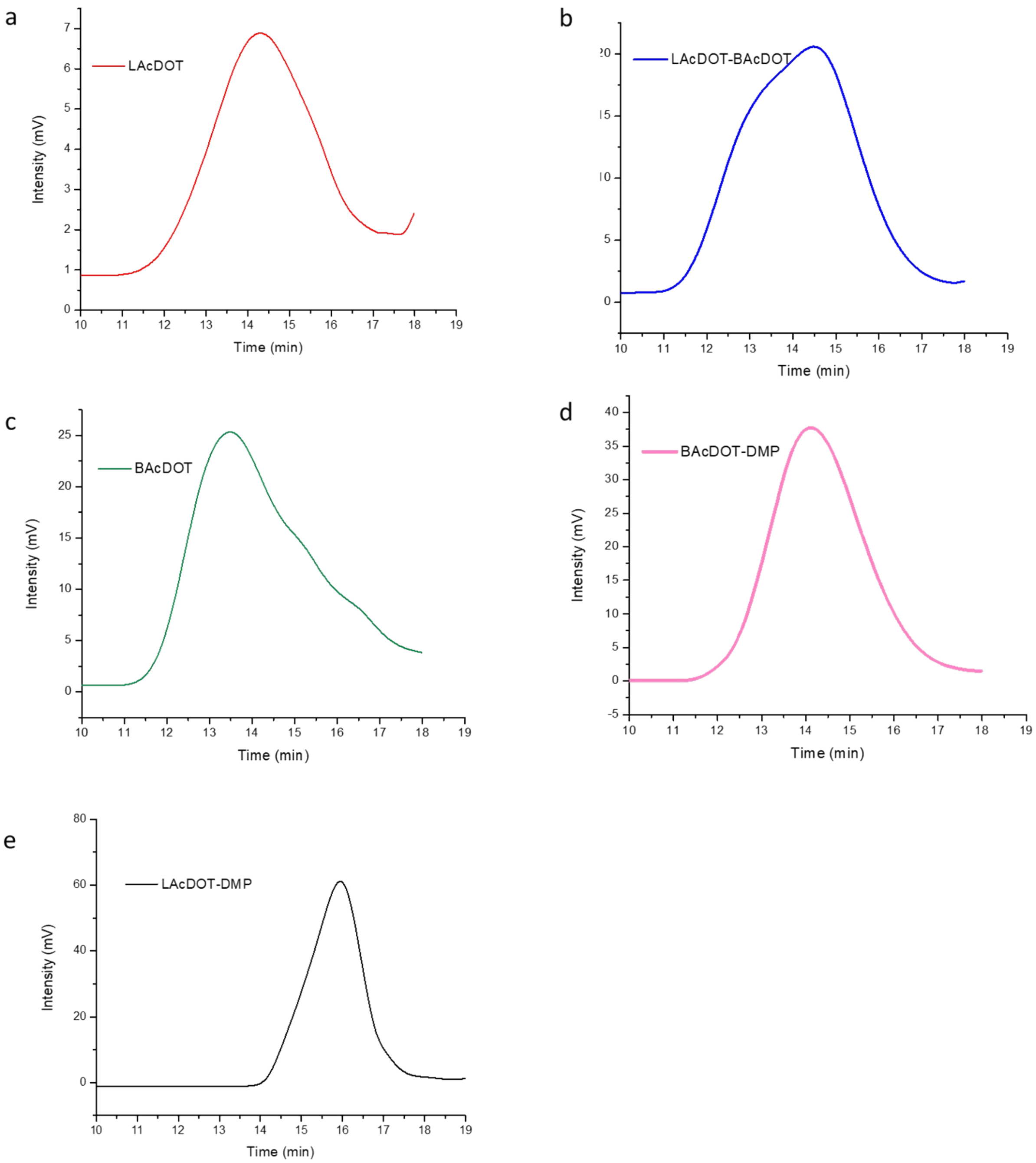


Figure S2. GPC traces of a) P(LAcDOT), b) P(LAcDOT-BAcDOT), c) P(BAcDOT), d) P(BAcDOT-DMP), and e) P(LAcDOT-DMP). All polymers measured using $CHCl_3$ at 40 °C (calibrated *vs.* polystyrene standards) except for P(BAcDOT), which was measured using THF at 35 °C (calibrated *vs.* polystyrene standards) due to the higher solubility of this polymer in ethereal solvents.

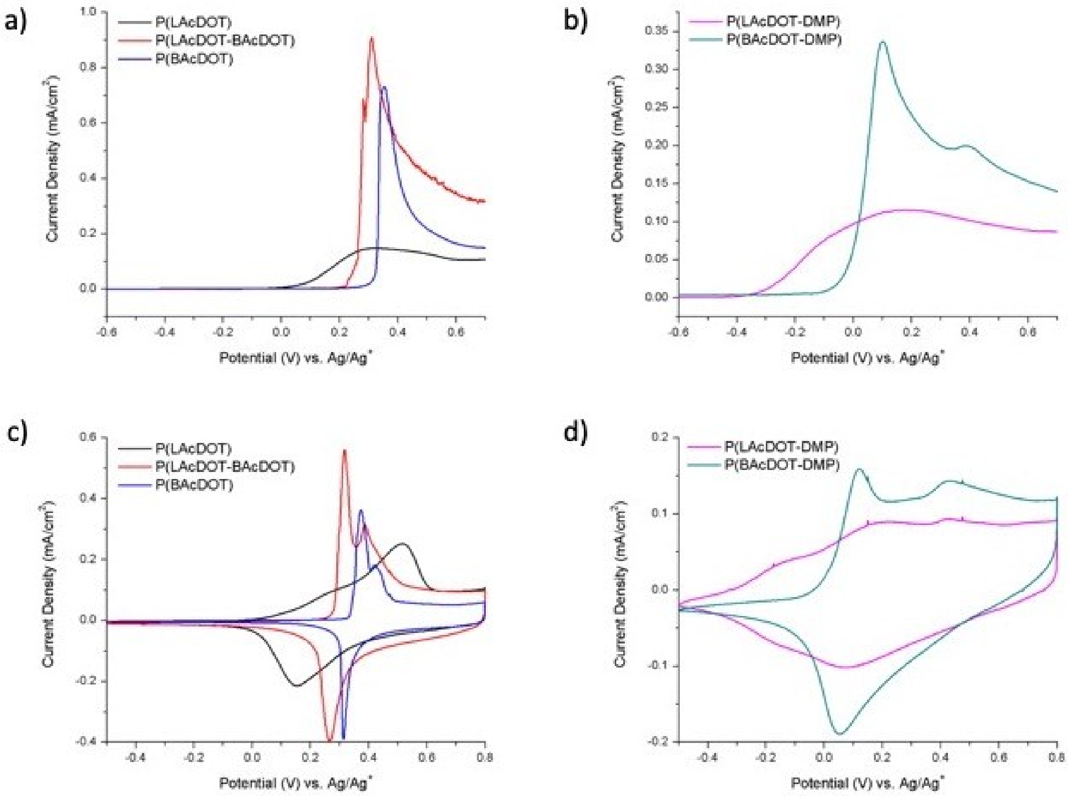


Figure S3. Differential pulse voltammetry (DPV) traces of a) P(LAcDOT), P(LAcDOT-BAcDOT), and P(BAcDOT), and b) P(LAcDOT-DMP) and P(BAcDOT-DMP). Cyclic voltammetry (CV) traces of c) P(LAcDOT), P(LAcDOT-BAcDOT), and P(BAcDOT), and d) P(LAcDOT-DMP) and P(BAcDOT-DMP). Measurements performed in an electrolyte of 0.5 M TBAPF$_6$/PC at a scan rate of 50 mV/s.

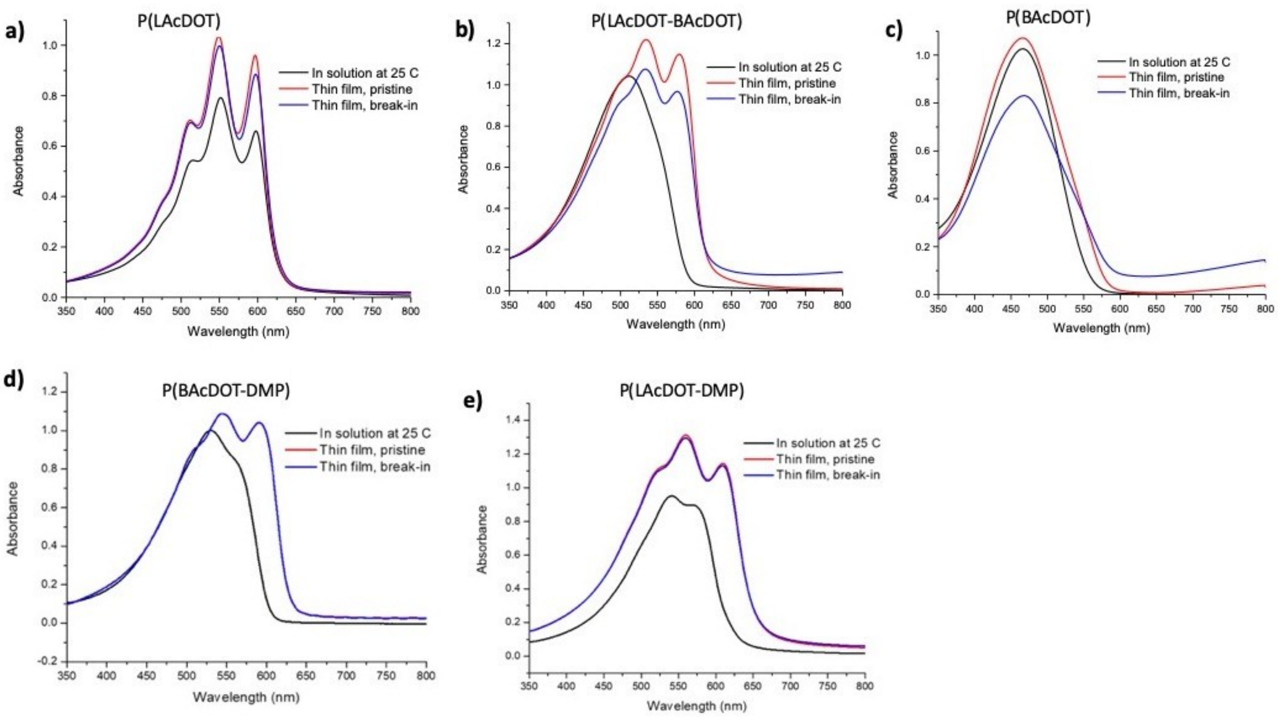


Figure S4. Solution ($CHCl_3$), pristine film, and post electrochromical break-in UV-vis spectra of a) P(LAcDOT), b) P(LAcDOT-BAcDOT), c) P(BAcDOT), d) P(LAcDOT-DMP), and e) P(BAcDOT-DMP). Pristine and broken-in films in an electrolyte of 0.5 M TBA/PF_6.

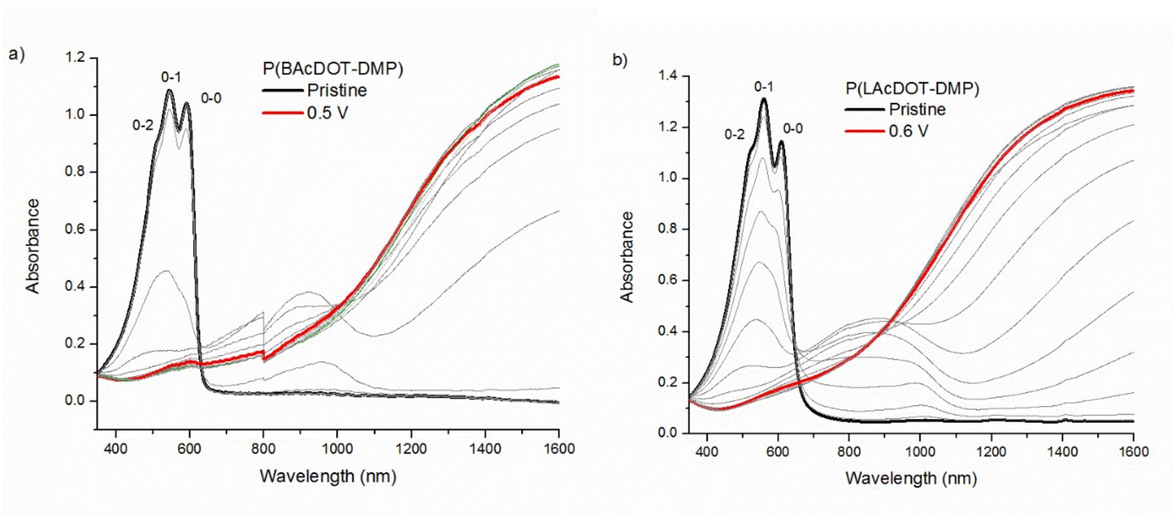


Figure S5. Spectroelectrochemistry of a) P(BAcDOT-DMP) and b) P(LAcDOT-DMP). The applied potential was increased by 100 mV steps between the fully colored and bleached states in 0.5 M TBAPF$_6$/PC.

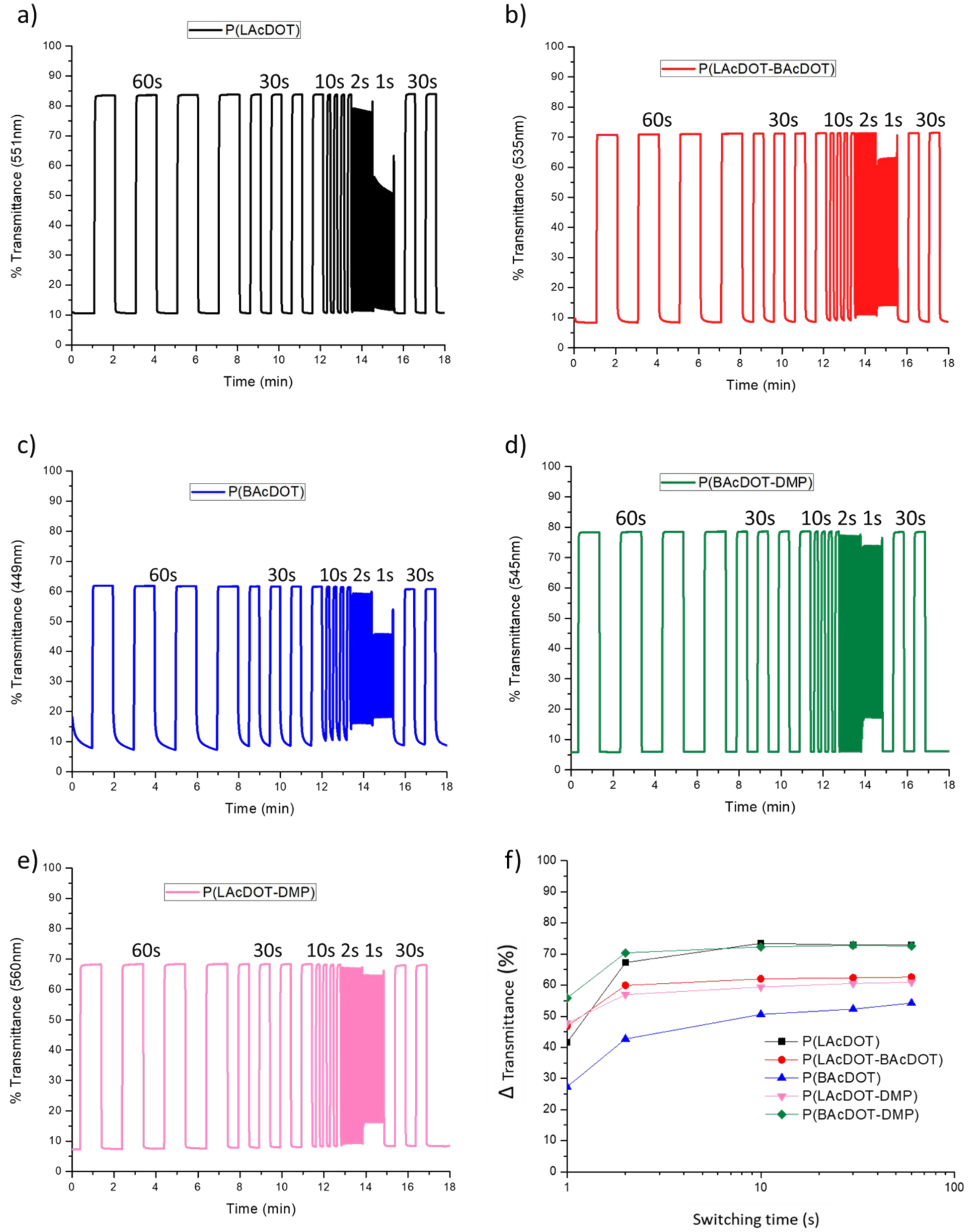


Figure S6. a) Chronoabsorptometry of all the polymers(a-e) in 0.5 M TBAPF$_6$/PC electrolyte solution measured at λ_{max}. All the polymers were switched between -0.5 V and +0.8 V for periods ranging from 60 seconds to 1 second. f) ΔT at λ_{max} of each polymer as a function of switching time from 60 seconds to 1 second.

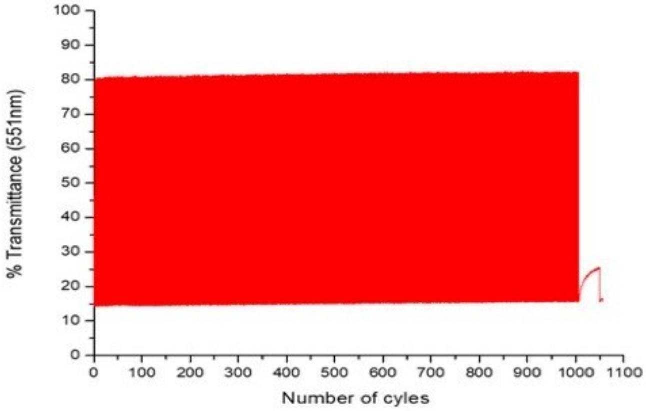


Figure S7 Chronoabsorptometry of P(LAcDOT) at λ_{max} switched from the charge neutral state (-0.5 V) to the oxidized state (+0.8 V) in 0.5 M TBAPF$_6$/PC for 1,000 cycles.

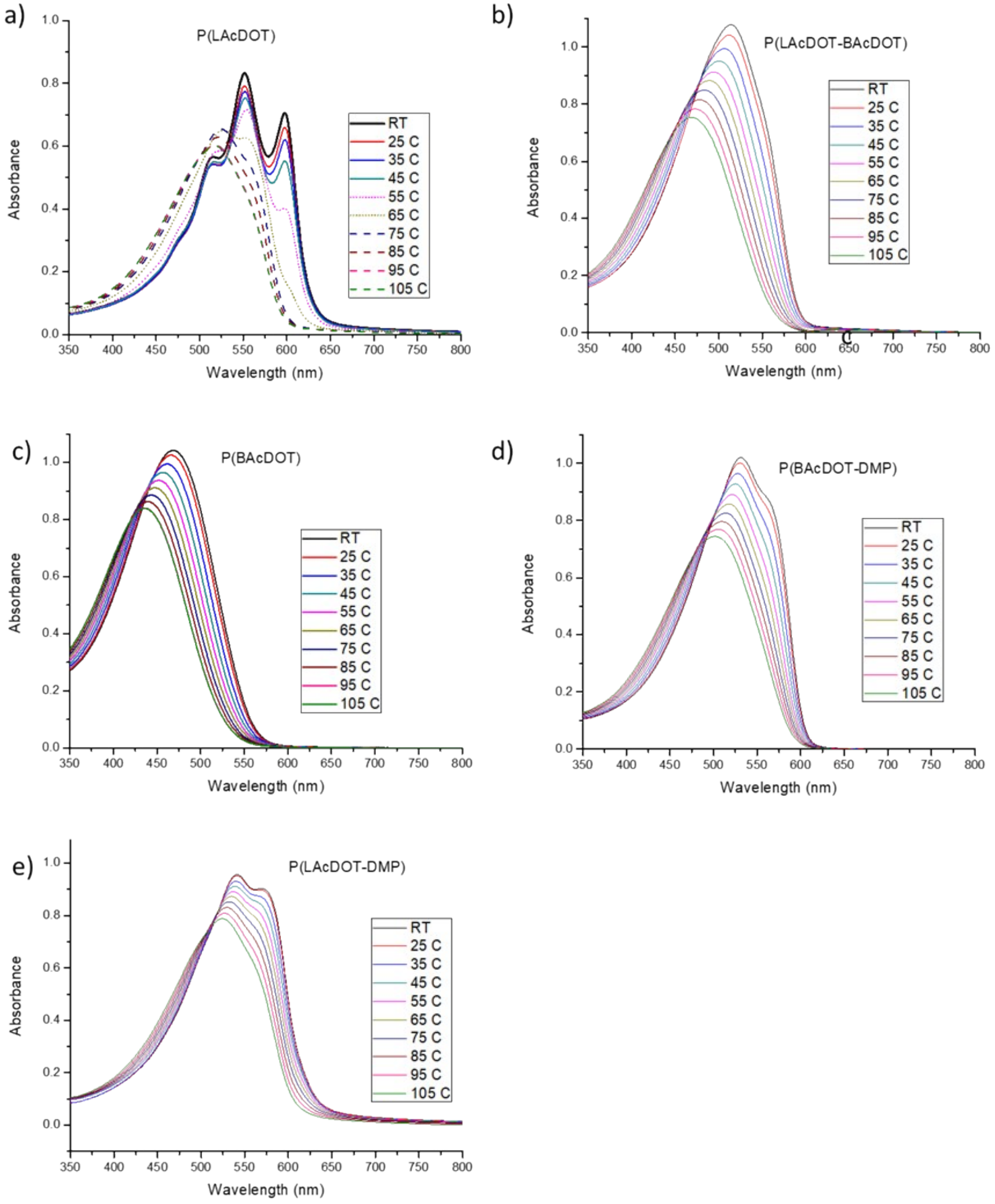


Figure S8. (a) Absorbance of P(LAcDOT) in toluene solution (~10 μg/mL). Spectra that correspond to the three different temperature ranges described in the text are indicated by dashed, dotted, and straight lines to show aggregate formation. (b-e) The absorbance of P(BAcDOT-LAcDOT), P(BAcDOT), P(BAcDOT-DMP) and P(LAcDOT-DMP) in toluene solution (~10 μg/mL), showing minimal changes with decreasing temperature.

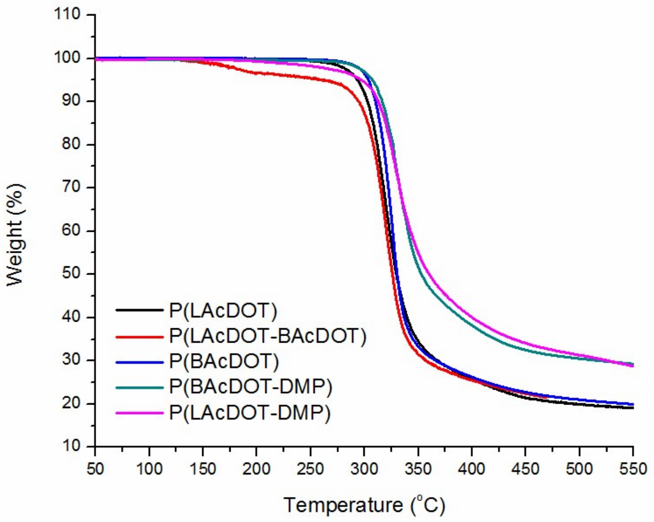


Figure S9. TGA studies performed at a rate of 10 °C/minutes.

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