Supporting Information: Soluble Phenylenedioxythiophene Copolymers via Direct (Hetero)Arylation Polymerization: A Revived Monomer for Organic Electronics

James. F. Ponder Jr.,[a] Brian Schmatz,[a] Jeff L. Hernandez,[a] and John R. Reynolds*[a,b]

[a]School of Chemistry and Biochemistry, Center for Organic Photonics and Electronics, Georgia Tech Polymer Network, Georgia Institute of Technology, Atlanta, Georgia, 30332-0400, USA

[b]School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia, 30332-0400, USA. *E-mail: reynolds@chemistry.gatech.edu

Materials

PheDOT, biPheDOT, and PheDOT-Br_2 were prepared according to literature procedures, as mentioned in the text, and confirmed using ^{1}H-NMR and GC-MS.[1,2] AcDOT-Br_2 and biAcDOT-Br_2 were prepared as reported in the literature.[3] $Pd(OAc)_2$ (98 %, Strem Chemicals), pivalic acid (99 %, Sigma), K_2CO_3 (anhydrous, Oakwood Products), 18-Crown-6 (99 %, Acros), diethyldithiocarbamic acid diethylammonium salt (97 %, TCI America), KOH (Technical Grade, Fisher Scientific), and pTSA (monohydrate, 98 %, Alfa Aesar) were used as received. DMAc (HPLC grade, Alfa Aesar) was filtered through a pad of alumina (basic, Sigma Aldrich) and degassed by argon bubbling prior to use.

Instrument & Measurement Details

The molecular weight and dispersity of the polymer were obtained using a THF GPC at 35 °C calibrated vs. polystyrene standards and a chloroform GPC at 40 °C calibrated vs. polystyrene standards. The ^{1}H-NMR (64 scans) spectrum was collected on a Bruker 700 MHz instrument using $C_2D_2Cl_4$ as a solvent at a temperature of 323K. The electrical potential in the three-electrode cell setup was measured using either a Ag/Ag^+ reference electrode (10 mM $AgNO_3$ in 0.5 M $TBAPF_6$-ACN, $E_{1/2}$ for ferrocene: 68 mV), and the counter electrode was a platinum flag. The CV and DPV measurements were performed on an EG&G PAR (model 273A) potentiostat/galvanostatic under CorrWare control. Spectroelectrochemistry and chronoabsorptiometry were measured using an Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer under Cary WinUV control and a EG&G PAR (model 263A) potentiostat/galvanostatic under CorrWare control. All colorimetric values were quantified by converting the absorbance spectra to CIELAB L*a*b* color coordinates where the L* represents the white-black balance, a* represents the green-red balance, and the b* the blue-yellow balance of a given color. Photography was performed using a Nikon D90 SLR camera with a Nikon 18-105 mm VR lens. The photographs are presented without any manipulation apart from cropping. Grazing incidence wide angle X-ray scattering (GIWAXS) was performed at the Stanford synchrotron radiation light source (SSRL) on beamline 11-3. The polymer samples were prepared by spray casting the polymers onto silicon dioxide wafers in the same manner as described for spray casting onto glass. The beam energy was 12.7 keV. The angle of incidence was 0.13°, whereas the nominal critical angle for the films at the used energy is about 0.08°. A LaB_6 standard sample was used to calibrate the instrument and the software WxDiff version 1.20 was used for data reduction. The sample to detector distance was set to 250 mm.

Polymer synthesis

PheDOT-ProDOT

To a 38 mL Schlenk tube with stir bar, PheDOT-Br_2 (0.4185 g, 1.0 eq.), ProDOT(HxDec) (0.800 g, 1.0 eq.), palladium acetate (0.006 g, 2 mol%), pivalic acid (0.036 g, 0.3 eq.), and potassium carbonate (0.4159 g, 2.5 eq.) were added. 12 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and the tube was sealed under argon. The reaction mixture was premixed for 2 minutes. The tube was then lowered into an oil bath and heated to 140°C and allowed to stir vigorously overnight (~14 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 obtained was filtered into a soxhlet extraction thimble and washed with methanol, acetone, hexanes, and finally dissolved into chloroform. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the chloroform was removed using a rotary evaporator and then ~50 mL of chloroform was added followed by ~20 mg of a palladium scavenger (diethylammonium diethyldithiocarbamate) and ~20 mg of 18-crown-6 and then stirred for 2 hours at 50°C. This solution was then precipitated into ~250 mL of methanol. The precipitate was vacuum filtered, using a Nylon pad (with a pore size of 20 μm) as the filter, and washed with a large volume of methanol and allowed to dry. The dried material was collected into a vial and dried under vacuum. The polymer was obtained as a purple solid in 46% yield (471 mg). ^1H NMR (700 MHz, $C_2D_2Cl_4$, 50°C) δ 7.11 (d, 4H), 4.28 (br, 2H), 3.65 (br, 4H), 3.38 (br, 4H), 1.30 (br), 1.01-0.84 (br). Anal. calcd. for $C_{51}H_{78}O_6S_2$ C 71.96, H 9.24, S 7.53, Found C 71.66, H 9.12, S 7.73. M_n: 68.2 kDa, M_w/M_n: 3.7, vs. PS in THF at 35°C. M_n: 69.6 kDa, M_w/M_n: 3.3, vs. PS in $CHCl_3$ at 40°C.

PheDOT$_2$-ProDOT

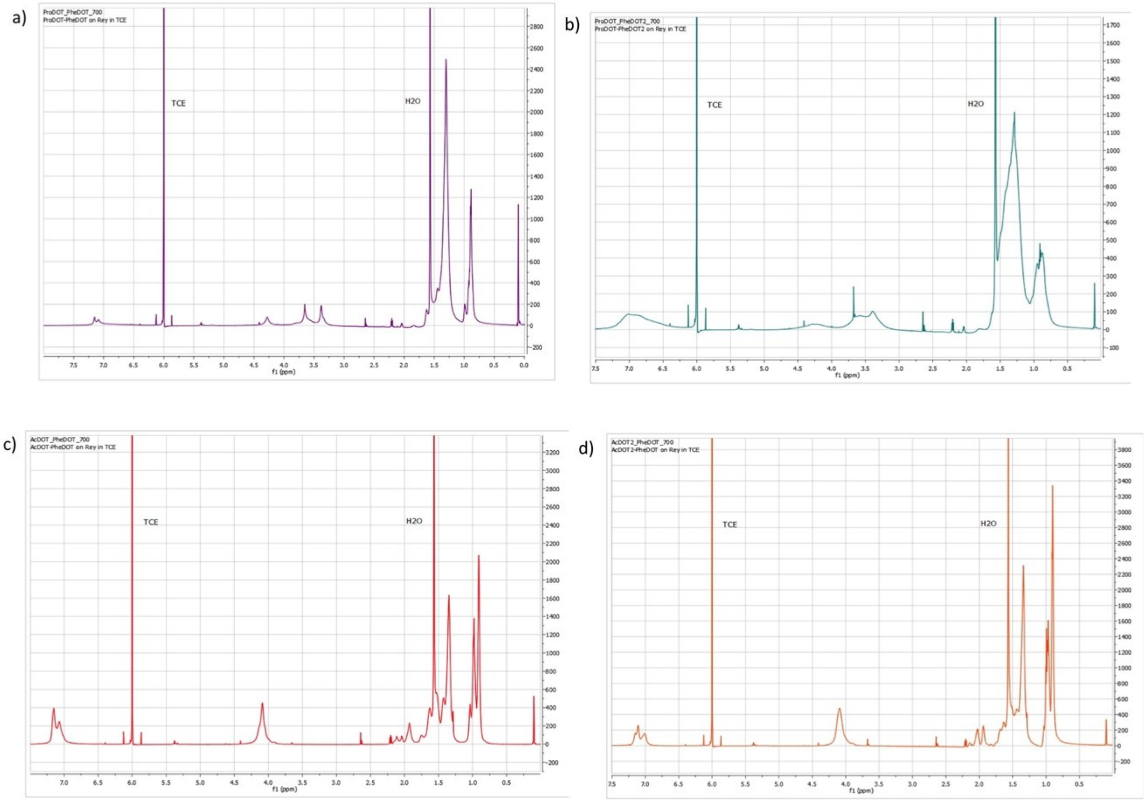
To a 38 mL Schlenk tube with stir bar, ProDOT-Br_2 (0.2129 g, 1.0 eq.), biPheDOT (0.0978 g, 1.0 eq.), palladium acetate (0.0025 g, 2 mol%), pivalic acid (0.086 g, 0.3 eq.), and potassium carbonate (0.096 g, 2.5 eq.) were added. 2.6 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and the tube was sealed under argon. The reaction mixture was premixed for 2 minutes. The tube was lowered into an oil bath and heated to 140°C and allowed to stir vigorously overnight (~14 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, and finally dissolved into chloroform. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the chloroform was removed using a rotary evaporator and then ~50 mL of chloroform was added followed by ~20 mg of a palladium scavenger (diethylammonium diethyldithiocarbamate) and ~20 mg of 18-crown-6 and then stirred for 2 hours at 50°C then precipitated into 250 mL of methanol. The precipitate was vacuum filtered, using a Nylon pad (with a pore size of 20 μm) as the filter, and washed with a large volume of methanol and allowed to dry. The dried material was collected into a vial and dried under vacuum. The polymer was obtained as a purple/blue solid in 64% yield (171 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50°C) δ 7.25-6.55 (br, 8H), 4.25 (br, 2H), 3.50 (br, d, 8H), 1.65-1.10 (br), 1.05-0.70 (br). Anal. calcd. for $C_{61}H_{82}O_8S_3$ C 70.48, H 7.95, S 9.25, Found C 69.67, H 7.42, S 9.88. M_n: 33.8 kDa, M_w/M_n: 1.4, vs. PS in THF at 35°C. M_n: 22.0 kDa, M_w/M_n: 3.0, vs. PS in $CHCl_3$ at 40°C.

PheDOT-AcDOT

To a 38 mL Schlenk tube with stir bar, AcDOT-Br_2 (0.700 g, 1.0 eq.), PheDOT (0.2672 g, 1.0 eq.), palladium acetate (0.007 g, 2 mol%), pivalic acid (0.045 g, 0.3 eq.), and potassium carbonate (0.485 g, 2.5 eq.) were added. 14.0 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and the tube was sealed under argon. The reaction mixture was premixed for 2 minutes. The tube was lowered into an oil bath and heated to 140°C and allowed to stir vigorously overnight (~14 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, and finally dissolved into hexanes. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the chloroform was removed using a rotary evaporator and then ~50 mL of chloroform was added followed by ~20 mg of a palladium scavenger (diethylammonium diethyldithiocarbamate) and ~20 mg of 18-crown-6 and then stirred for 2 hours at 50°C then precipitated into 250 mL of methanol. The precipitate was vacuum filtered, using a Nylon pad (with a pore size of 20 μm) as the filter, and washed with a large volume of methanol and allowed to dry. The dried material was collected into a vial and dried under vacuum. The polymer was obtained as a dark red solid in 41% yield (304 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50°C) δ 7.12 (d, 4H), 4.08 (br, 4H), 1.95 (br, 2H), 1.70-1.48 (br, m), 1.47-1.26 (br), 1.10-0.80 (br). Anal. calcd. for $C_{30}H_{38}O_4S_2$ C 68.41, H 7.27, S 12.17, Found C 68.14, H 7.08, S 12.42. M_n: 22.5 kDa, M_w/M_n: 4.4, vs. PS in THF at 35°C. M_n: 24.7 kDa, M_w/M_n: 3.8, vs. PS in $CHCl_3$ at 40°C.

PheDOT-AcDOT$_2$

To a 38 mL Schlenk tube with stir bar, biAcDOT-Br_2 (1.001 g, 1.0 eq.), PheDOT (0.2269 g, 1.0 eq.), palladium acetate (0.006 g, 2 mol%), pivalic acid (0.034 g, 0.3 eq.), and potassium carbonate (0.4181 g, 2.5 eq.) were added. 12 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and the tube was sealed under argon. The reaction mixture was premixed for 2 minutes. The tube was lowered into an oil bath and heated to 140°C and allowed to stir vigorously overnight (~14 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, and finally dissolved into hexanes. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the chloroform was removed using a rotary evaporator and then ~50 mL of chloroform was added followed by ~20 mg of a palladium scavenger (diethylammonium diethyldithiocarbamate) and ~20 mg of 18-crown-6 and then stirred for 2 hours at 50°C then precipitated into 250 mL of methanol. The precipitate was vacuum filtered, using a Nylon pad (with a pore size of 20 µm) as the filter, and washed with a large volume of methanol and allowed to dry. The dried material was collected into a vial and dried under vacuum. The polymer was obtained as a fluffy, deep red solid in 94% yield (966 mg). ^{1}H-NMR (700 MHz, $C_2D_2Cl_4$, 50^{o}C) δ 7.08 (d, 4H), 4.07 (br, 8H), 1.98 (d, 4H), 1.73-1.2 (br, m), 1.07-0.82 (br). Anal. calcd. for $C_{50}H_{72}O_6S_3$ C 69.40, H 8.39, S 11.12, Found C 69.44, H 8.25, S 11.26. M_n: 51.8 kDa, M_w/M_n: 2.4, vs. PS in THF at 35°C. M_n: 52.7 kDa, M_w/M_n: 2.4, vs. PS in $CHCl_3$ at 40°C.



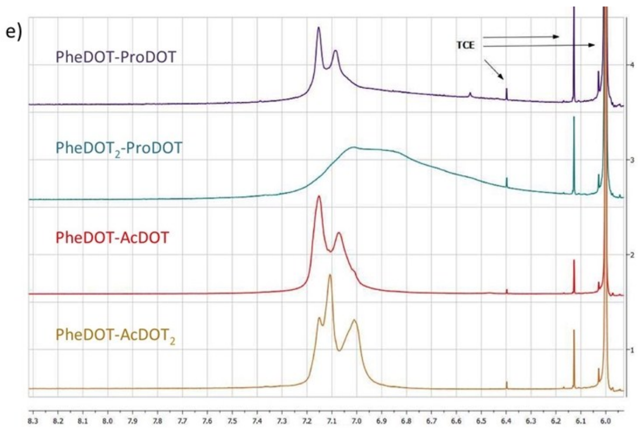


Fig. S1 ^{1}H-NMR spectra (700 MHz in TCE at 50 °C) of a) PheDOT-ProDOT, b) PheDOT$_2$-ProDOT, c) PheDOT-AcDOT, and d) PheDOT-AcDOT$_2$, and e) stacked spectra focusing on the aromatic protons.

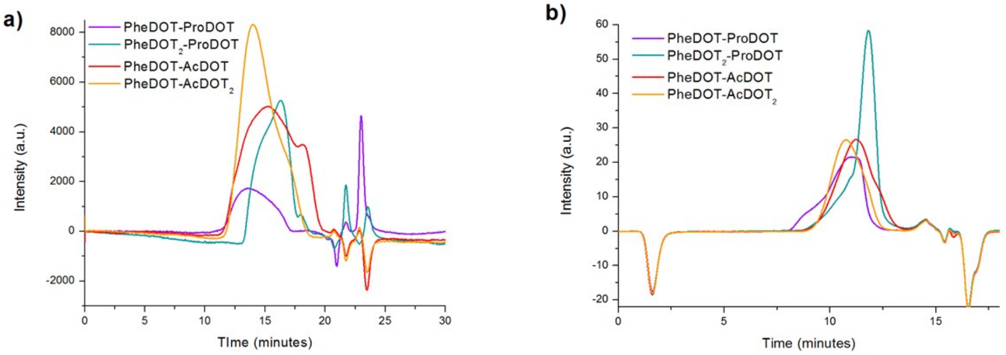


Fig. S2 GPC traces of the copolymer series in a) THF at 35 °C and b) $CHCl_3$ at 40 °C calibrated vs. polystyrene standards.

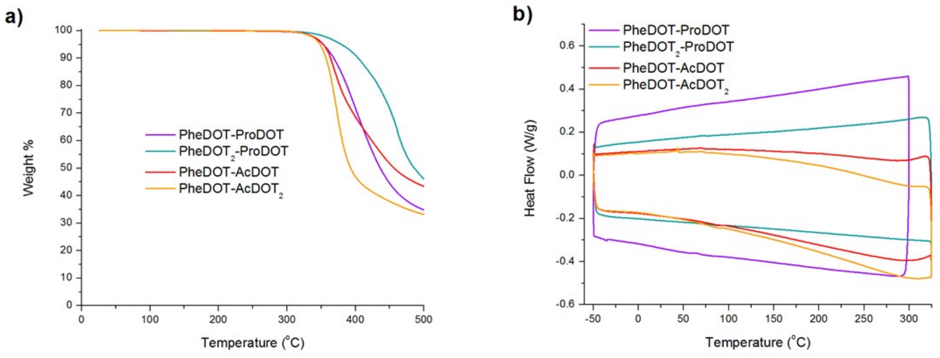


Fig. S3 a) TGA at a rate of 10 °C/minute and b) DSC of the copolymer series.

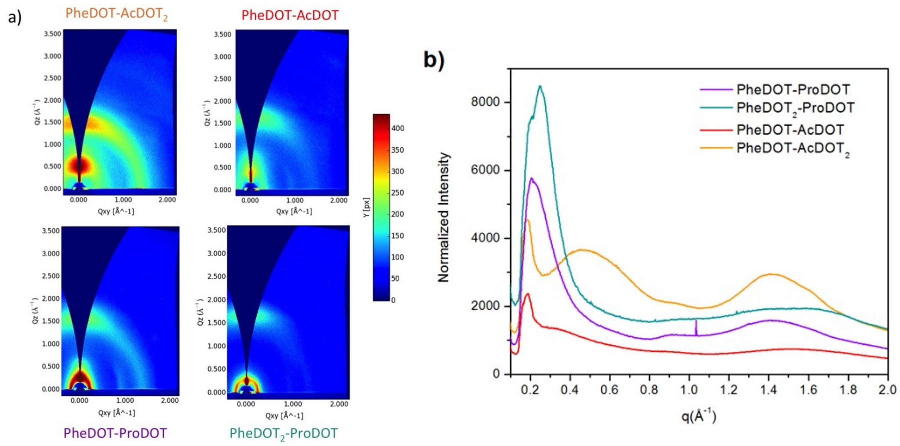


Fig. S4 a) 2D GIWAXS scattering pattern and b) 1D line cuts taken in the q_z direction of films spray cast onto Si substrates from 4 mg/mL solutions of the copolymer series. The 1D line cuts shown in S5 b) have been normalized by the film thickness, which was measured using a Dextak Profilometer

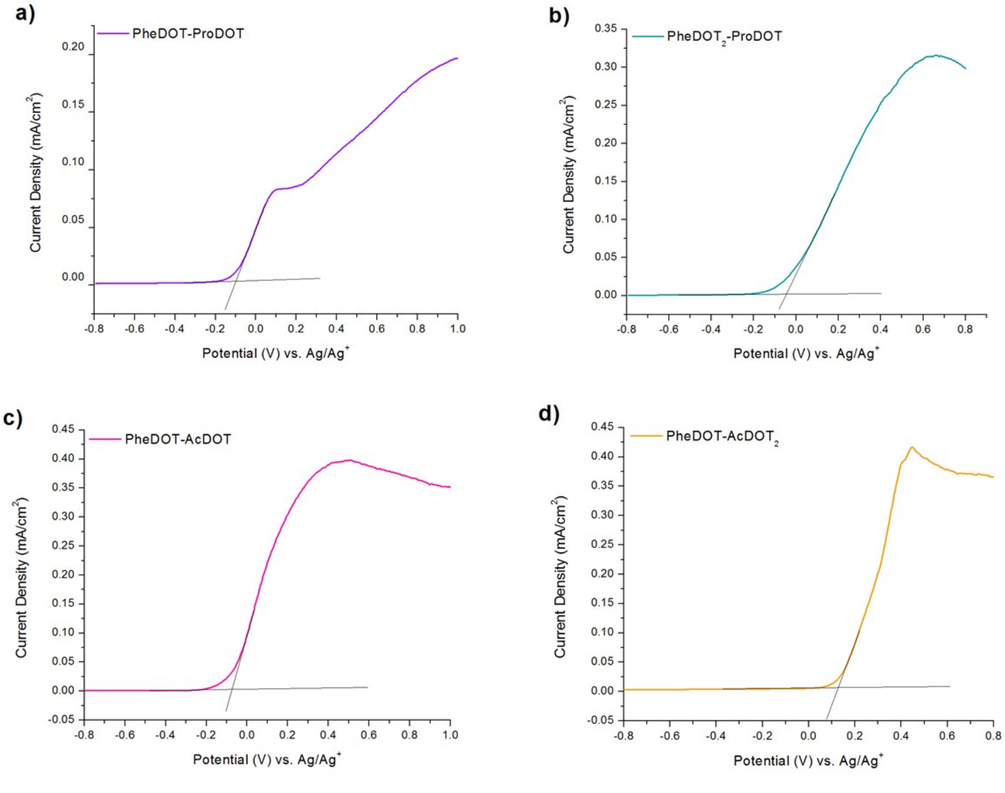


Fig. S5 DPVs of dropcast films (3μL of a 2mg/mL solution in $CHCl_3$) of the copolymer series on glassy carbon button electrodes using a Pt flag as a counter electrode and 0.5 M $TBAPF_6$/PC as the electrolyte.

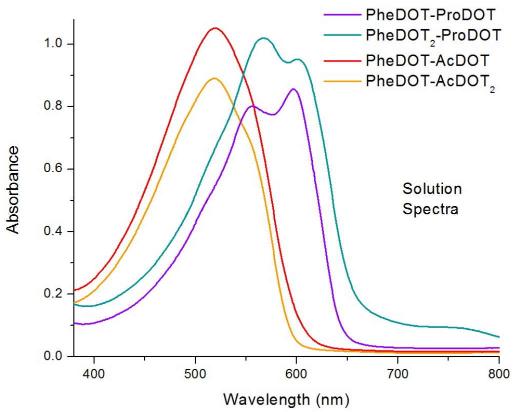


Fig. S6 Solution UV-vis spectra of the copolymer series in $CHCl_3$ at a concentration of 0.025 mg/mL.

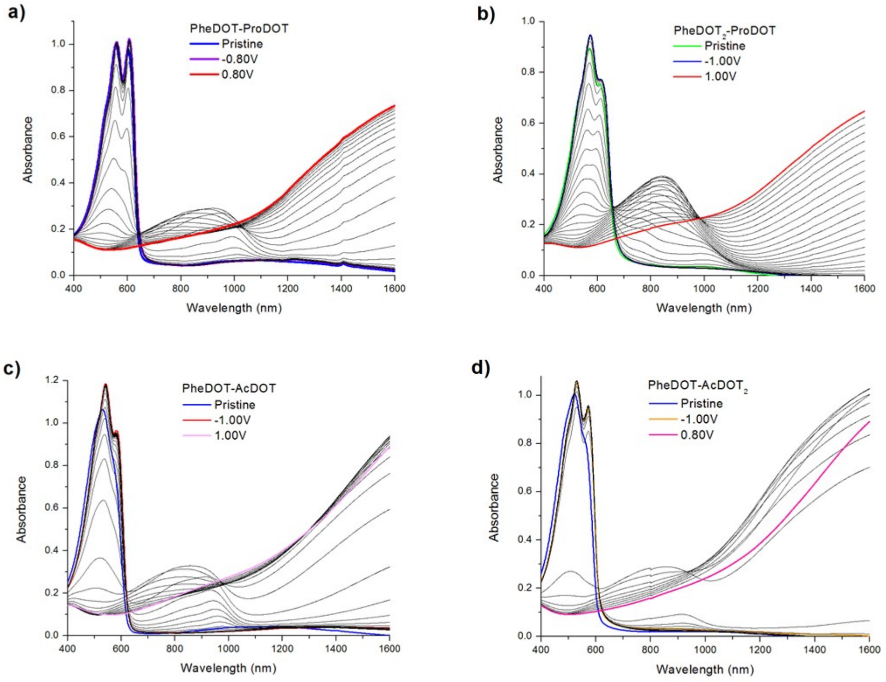


Fig. S7 Vis-NIR absorbance of the pristine polymer films on ITO glass and as a function of potential in 50 mV increments for the copolymer series recorded between -1 or -0.8 V and + 0.8 or 1 V vs. Ag/Ag^+ in 0.5 M $TBAPF_6$.

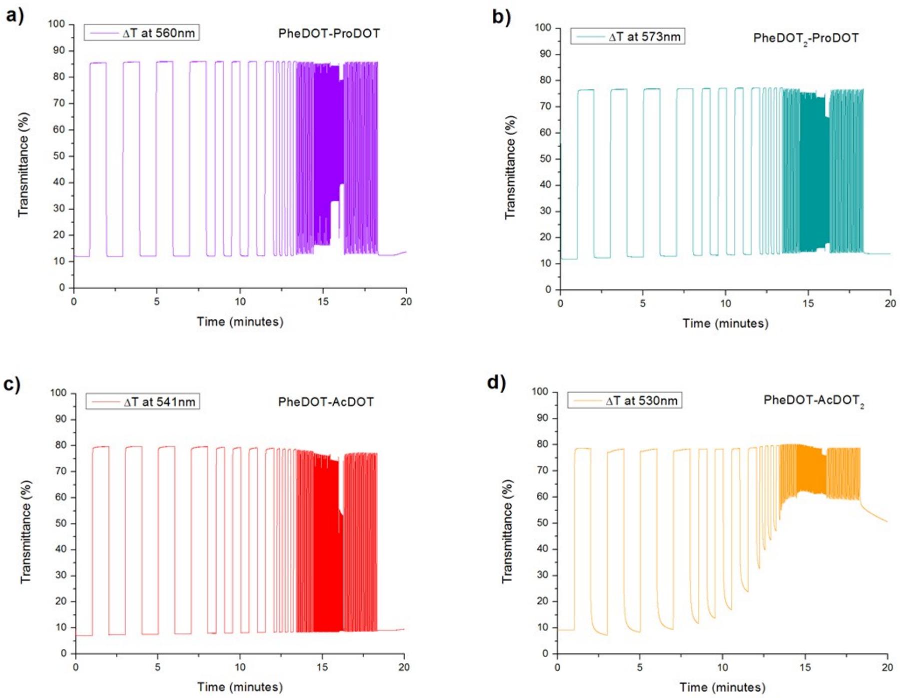


Fig. S8 Transmittance at λ_{max} as a function of time of films (on ITO glass) of the copolymers switching from the charge neutral state to the oxidized state in 0.5 M TBAPF$_6$/PC using a Pt flag as a counter electrode.

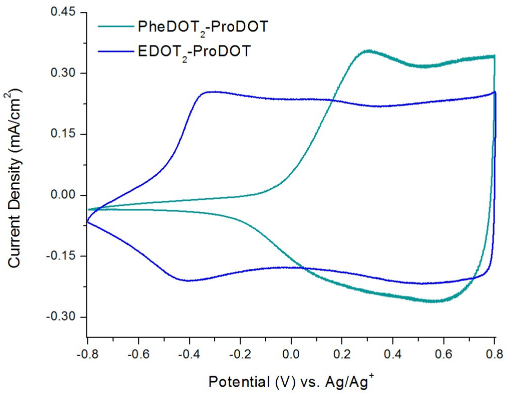


Fig. S9 CVs of dropcast films (3μL of a 2mg/mL solution in CHCl$_3$) of PheDOT$_2$-ProDOT and EDOT$_2$-ProDOT on glassy carbon button electrodes using a Pt flag as a counter electrode and 0.5 M TBAPF$_6$/PC as the electrolyte, sweeping at a scan rate of 50 mV/s.

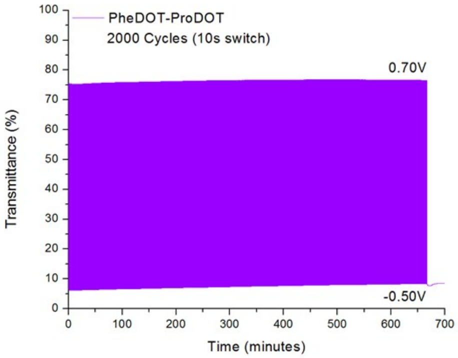


Fig. S10 Transmittance at λ_{max} as a function of time of a PheDOT-ProDOT film (on ITO glass) switching from the charge neutral state (-0.5 V) to the oxidized state (0.7 V) in 0.5 M $TBAPF_6$/PC using a Pt flag as a counter electrode for 2000 charge/discharge cycles and open to air.

References:

1. S. Roquet, P. Leriche, I. Perepichka, B. Jousselme, E. Levillain, P. Frere, J. Roncali, *J. Mater. Chem.*, 2004**, 14** (9), 1396-1400.

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3. J. A. Kerszulis, K. E. Johnson, M. Kuepfert, D. Khoshabo, A. L. Dyer, J. R. Reynolds, *J. Mater. Chem. C*, 2015, **3** (13), 3211-3218.