Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Inducing Planarity in Redox-Active Conjugated Polymers with Solubilizing 3,6-Dialkoxy-thieno[3,2-*b*]thiophenes (DOTTs) for Redox and Solid-State Conductivity Applications

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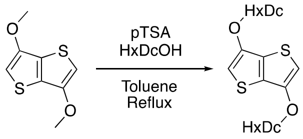
Synthetic Details:

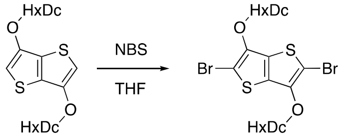
Materials. Pd(OAc)$_2$ (98 %, Strem Chemicals), pivalic acid (99 %, Sigma), K$_2$CO$_3$ (anhydrous, Oakwood Products), 18-crown-6 (99 %, Acros), diethyldithiocarbamic acid diethylammonium salt (97 %, TCI America), 2-hexyldecyl alcohol (97%, Sigma), and *p*-toluenesulfonic acid monohydrate (*p*TSA, >98.5%, Sigma) were used as received. DMAc (HPLC grade, Alfa Aesar) was filtered through a pad of alumina (basic, Sigma Aldrich) and degassed by argon bubbling before use. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$, 98%, Alfa Aesar) was purified by recrystallized from hot ethanol. Propylene carbonate was used as the electrolyte solvent (PC, Acros Organics, 99.5 %) and was purified and dried using a solvent purification system from Vacuum Atmospheres. EDOT (97%) was obtained from Alfa Aesar and vacuum distilled prior to use. DMP-Br,[1] EDOT-Br,[2] and 2-2'-BiEDOT[3] were prepared via previously reported methods. DOTT-Me was prepared by tetrabromination of thieno[3,2-*b*]thiophene followed by zinc reduction to yield 3,6-Dibromo-thieno[3,2-*b*]thiophene.[4] This unit was then converted to DOTT-Me via a previously reported Ullmann type reaction.[5]

3,6-Di(2-hexyldecyloxy)-thieno[3,2-*b*]thiophenes (DOTT-HxDc)



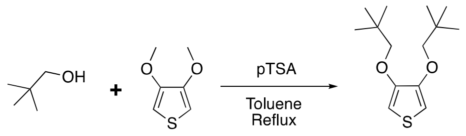
Into a 250 mL round bottom flask with a stir bar was added distilled 3,4-dimethoxythiophene (0.910 g, 4.5 mmol), 2-hexyldecanol (7.0 mL g, ~23 mmol), PTSA (86 mg, 0.5 mmol), and toluene (90 mL). The solution, after placing under argon, was heated to 100 °C for overnight and was then cooled to room temperature. The mixture was then extracted with Et_2O and deionized H_2O (washing several times). The organic solvent was removed in vacuo and the product was purified via column chromatography (5% EtOAc in Hexanes) to afford a clear viscous oil in 86% yield (2.4 g). ^{1}H NMR ($CDCl_3$, ppm): δ 6.23 (s, 2H), 3.93 (d, 4H),1.82 (m, 2H) 1.47-1.40 (br, 4H), 1.40-1.19 (br, 48H), 0.88 (m, 12H); ^{13}C NMR ($CDCl_3$, ppm): δ 150.4, 128.6, 97.6, 73.5, 37.82, 31.92, 31.86, 31.38, 31.37, 30.01, 29.67, 29.59, 29.34, 26.82, 22.69, 14.14. MALDI, $C_{38}H_{68}O_2S_2$ Calculated m/z: 620.4642, Measured m/z: 620.4661.

2-5-Dibromo-3,6-di(2-hexyldecyloxy)-thieno[3,2-*b*]thiophenes (DOTT-HxDc-Br)



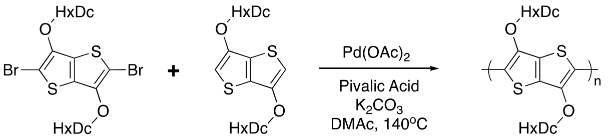
Into a 100 mL round bottom flask with a stir bar was added DOTT-HxDc (1.184 g, 1.9 mmol) and 50 mL of anhydrous THF and the mixture was placed under argon. NBS (0.753 g, 4 mmol) was then added to this solution all at once. The mixture was cover with foil to block light and was allowed to mix overnight. The reaction was extracted with Et_2O and H_2O, followed by washing with saturated $NaHCO_3/H_2O$. The organic solvent was removed in vacuo and the product was purified via column chromatography with hexanes to afford a colorless viscous oil in 93% yield (1.4 g). ^{1}H NMR ($CDCl_3$, ppm): δ 4.09 (d, 4H), 1.73 (p, 2H), 1.52-1.44 (br, 4H), 1.41-1.19 (br, 47H), 0.88 (m, 12H); ^{13}C NMR ($CDCl_3$, ppm): δ 147.79, 126.52, 96.31, 75.41, 38.53, 31.92, 31.85, 31.01, 31.00, 29.67, 29.58, 29.34, 26.77, 26.75, 22.71, 14.15. MALDI, $C_{38}H_{66}O_2S_2Br_2$ Calculated m/z: 776.2820, Measured m/z: 776.2871.

3,4-Bis(neopentyloxy)thiophene (NeoDOT)



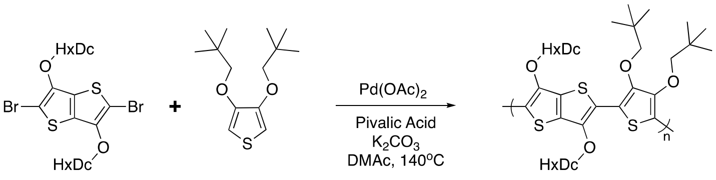
Into a 250 mL round bottom flask with a stir bar was added freshly distilled 3,4-dimethoxythiophene (1.50 g, 10.4 mmol), neopentyl alcohol (2.75 g, 31.2 mmol), PTSA (0.179 g, 1.04 mmol), and toluene (100 mL). A soxhlet condenser with a cellulose thimble filled with 3 Å molecular sieves was attached to the head of the flask. Solution was refluxed for 24 hours then cooled to room temperature. Et_2O (50mL) was added to the mixture and was washed with H_2O (3 x 100 mL). The organic solvent was removed in vacuo and the product was purified via column chromatography (1:9 EtOAc:Hexanes) to afford a white crystalline solid in 74% yield (1.97 g). Melt point: 58-59 °C. ^1H NMR ($CDCl_3$, ppm): δ 6.14 (s, 2H), 3.60 (s, 4H),1.03 (s, 18H); ^{13}C NMR ($CDCl_3$, ppm): δ 148.14, 97.76, 79.98, 32.01, 26.54. HRMS, $C_{14}H_{24}O_2SNa$ Calculated m/z: 279.1389, Measured m/z: 279.1390

Homo DOTT



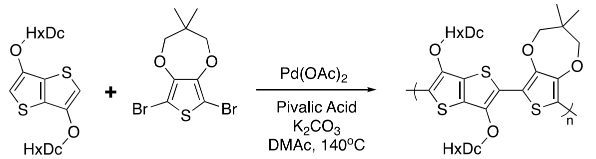
To a 38 mL Schlenk tube with stir bar, DOTT-HxDc-Br (0.6193 g, 1.0 eq.), DOTT-HxDc (0.4937 g, 1.0 eq.), palladium acetate (0.004 g, 2 mol%), pivalic acid (0.030 g, 0.3 eq.), and potassium carbonate (0.281 g, 2.5 eq.) were added. 8 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents 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, and finally dissolved into hexanes. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the hexanes were 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 90% yield (882 mg). ^{1}H NMR (700 MHz, $CDCl_3$, 50 ^{o}C) δ 4.35 (m, 4H), 1.98 (m, 2H), 1.64 (m, 4H), 1.45-1.19 (br), 0.86 (m, 12H). Anal. calcd. for $C_{38}H_{66}O_2S_2$ C 73.49, H 11.04, S 10.32, Found C 73.68, H 10.94, S 10.18. M_n: 7.6 kDa, *Đ*: 1.7, vs. PS in $CHCl_3$ at 40 °C.

<u>DOTT-NeoDOT</u>



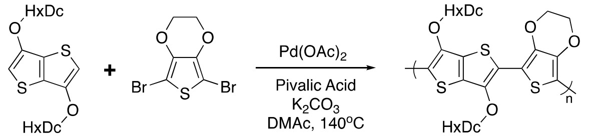
To a 38 mL Schlenk tube with stir bar, DOTT-HxDc-Br (0.4125 g, 1.0 eq.), NeoDOT (0.1357 g, 1.0 eq.), palladium acetate (0.002 g, 2 mol%), pivalic acid (0.017 g, 0.3 eq.), and potassium carbonate (0.180 g, 2.5 eq.) were added. 5.3 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and 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, and finally dissolved into hexanes. The washings were conducted until color was no longer observed during extraction. After dissolution from the thimble, the hexanes were removed using a rotary evaporator. The material was transferred into a vial and dried under vacuum. The polymer was obtained as a tacky orange solid in 77% yield (356 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50 ^{o}C) δ 4.57-3.55 (br, 18H), 1.88 (m, 4), 1.51-0.95 (br), 0.87 (m, 12H). Anal. calcd. for $C_{52}H_{88}O_4S_3$ C 71.38, H 10.36, S 14.23, Found C 71.41, H 10.17, S 10.98. M_n: 12 kDa, *Đ*: 1.8, vs. PS in $CHCl_3$ at 40 °C.

DOTT-DMP



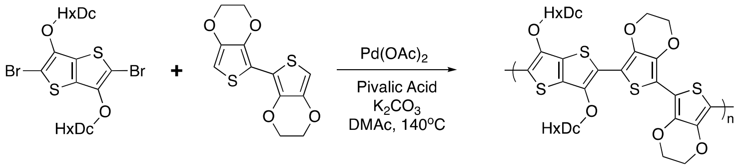
To a 38 mL Schlenk tube with stir bar, DMP-Br (0.2483 g, 1.0 eq.), DOTT-HxDc (0.4464 g, 1.0 eq.), palladium acetate (0.004 g, 2 mol%), pivalic acid (0.025 g, 0.3 eq.), and potassium carbonate (0.262 g, 2.5 eq.) were added. 7.2 mL of DMAc (N,N-dimethylacetamide) was added to dissolve the contents and 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 87% yield (502 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50 ºC) δ 1.96, (br s, 6H), 1.82-1.02 (br), 0.87 (s, 12H). Anal. calcd. for $C47H_{76}O_4S_3$ C 70.27, H 9.79, S 11.0, Found C 70.47, H 9.75, S 11.42. M_n: 44 kDa, *Đ*: 2.8, vs. PS in $CHCl_3$ at 40 °C.

DOTT-EDOT



To a 38 mL Schlenk tube with stir bar, EDOT-Br (0.2142 g, 1.0 eq.), DOTT-HxDc (0.4435 g, 1.0 eq.), palladium acetate (0.004 g, ~2 mol%), pivalic acid (0.033 g, ~0.3 eq.), and potassium carbonate (0.246 g, 2.5 eq.) were added. 7.5 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 blue solid in 52% yield (294 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50 ^{o}C) δ 1.97 (br s, 2H), 1.70-1.20 (br), 0.88 (s, 12H). Anal. calcd. for $C_{44}H_{70}O_4S_3$ C 69.42, H 9.53, S 12.63, Found C 69.16, H 9.38, S 12.43. M_n: 30 kDa, *Đ*: 1.8, vs. PS in $CHCl_3$ at 40 °C.

DOTT-BiEDOT



To a 38 mL Schlenk tube with stir bar, DOTT-HxDc-Br (0.4431 g, 1.0 eq.), biEDOT (0.1607 g, 1.0 eq.), palladium acetate (0.003 g, 2 mol%), pivalic acid (0.022 g, 0.3 eq.), and potassium carbonate (0.197 g, 2.5 eq.) were added. 5.8 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 dark blue solid in 82% yield (418 mg). ^{1}H NMR (700 MHz, $C_2D_2Cl_4$, 50 ^{o}C) δ 4.38 (m, 10H), 1.97, (s, 2H), 1.70 (s, 4H), 1.62-1.20 (br), 0.90 (m, 12H). Anal. calcd. for $C_{50}H_{74}O_6S_4$ C 66.62, H 8.50, S 14.23, Found C 65.86, H 8.21, S 13.79. M_n: 6.0 kDa, *Đ*: 1.7, vs. PS in $CHCl_3$ at 40 °C.

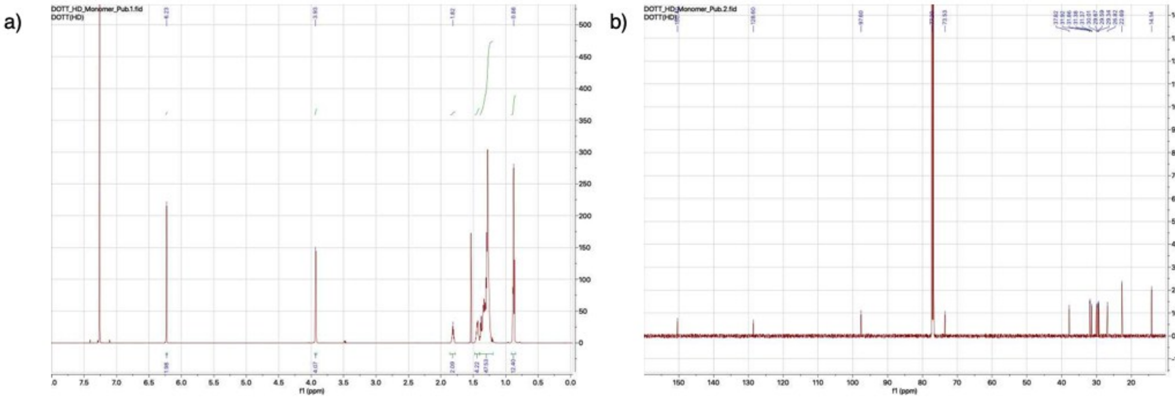


Figure S1: a) Proton and b) carbon NMRs of DOTT-HxDc

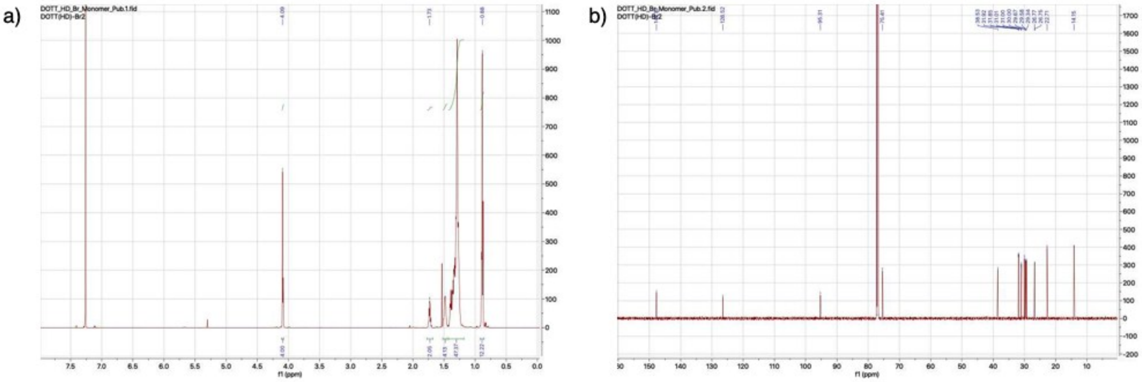


Figure S2: a) Proton and b) carbon NMRs of DOTT-HxDc-Br

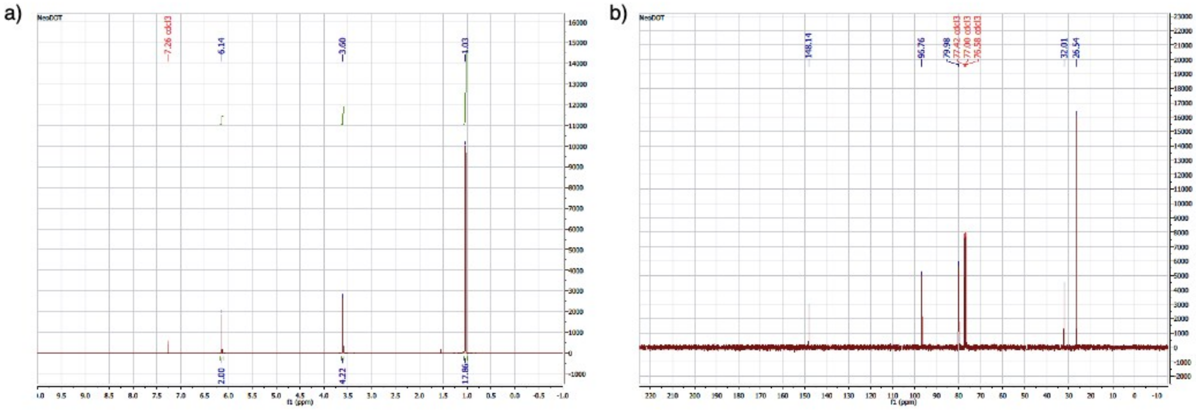


Figure S3: a) Proton and b) carbon NMRs of NeoDOT

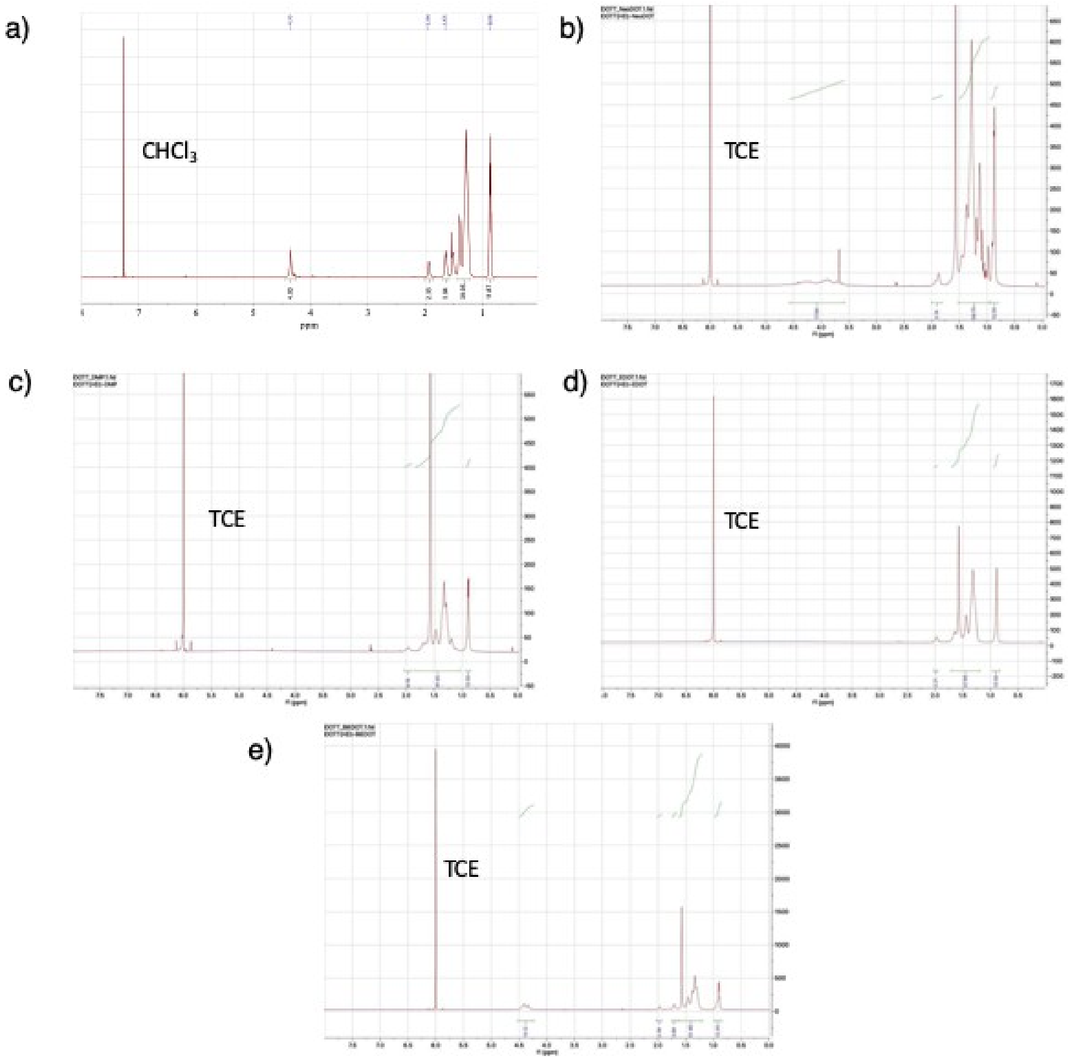


Figure S4: Proton NMRs of a) HomoDOTT, b) DOTT-NeoDOT, c) DOTT-DMP, d) DOTT-EDOT, and e) DOTT-EDOT$_2$. All spectra collected on a 700 MHz NMR in TCE-D$_2$ at 50 ^{o}C with the exception of HomoDOTT, which was found to be more soluble in CDCl$_3$.

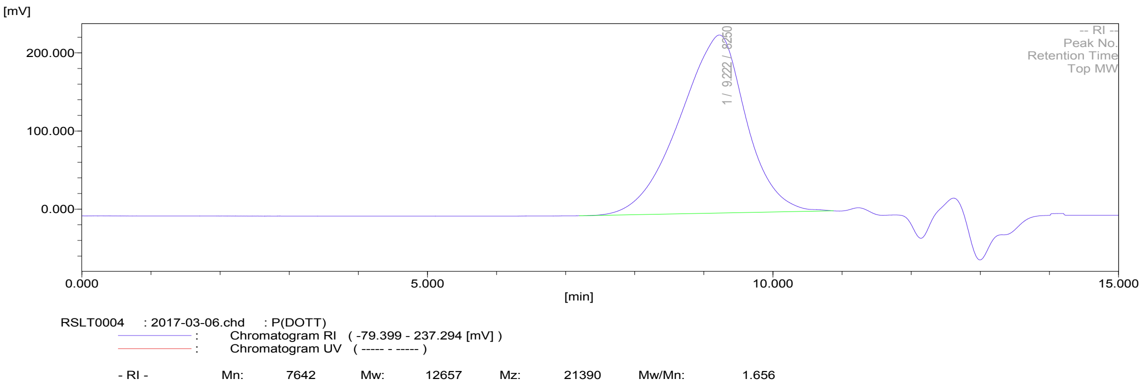


Figure S5: Gel permeation chromatogram for Homo DOTT in $CHCl_3$ at 40°C calibrated vs. polystyrene standards. M_n = 8 kg/mol and $Đ$ = 1.7.

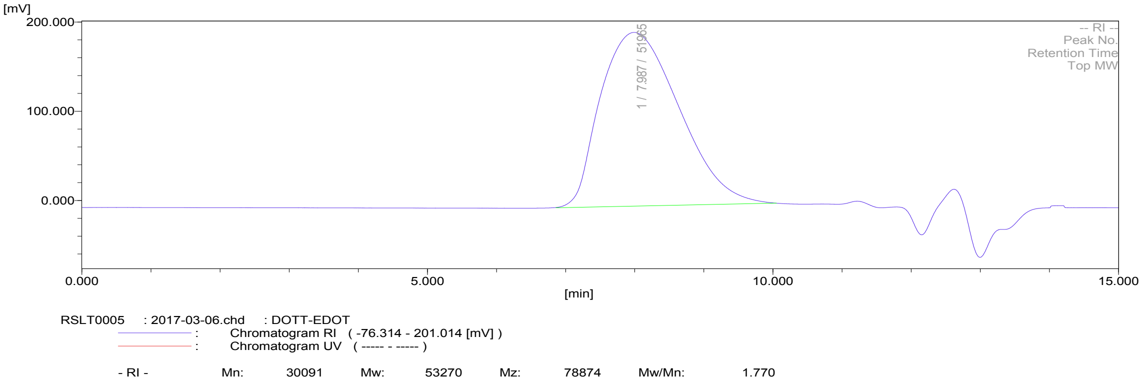


Figure S6: Gel permeation chromatogram for DOTT-EDOT in $CHCl_3$ at 40°C calibrated vs. polystyrene standards. M_n = 30 kg/mol and $Đ$ = 1.8.

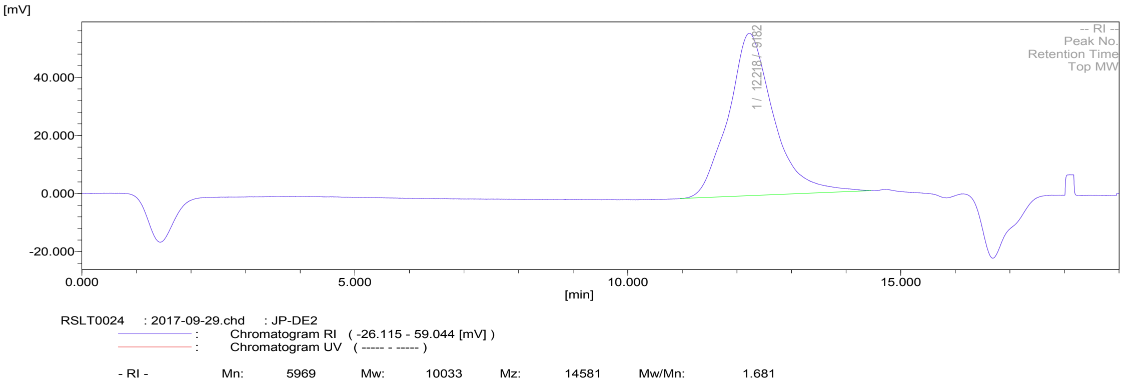


Figure S7: Gel permeation chromatogram for DOTT-BiEDOT in $CHCl_3$ at 40°C calibrated vs. polystyrene standards. M_n = 6 kg/mol and $Đ$ = 1.7.

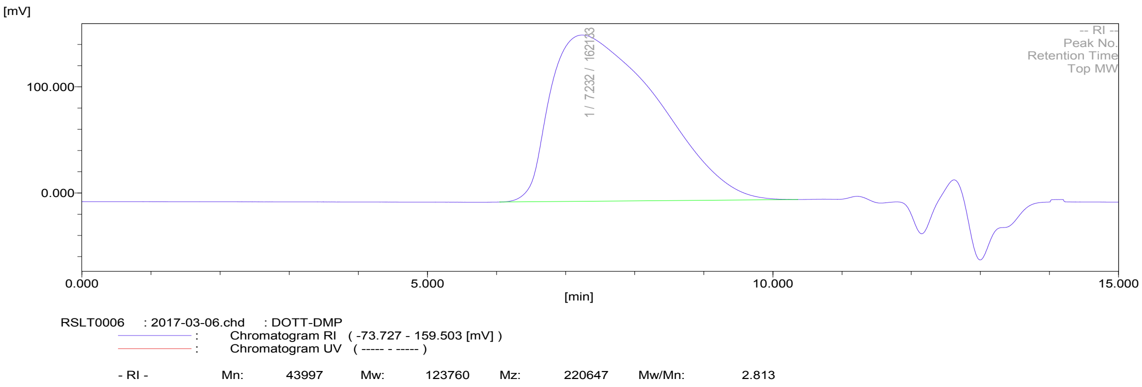


Figure S8: Gel permeation chromatogram for DOTT-DMP in $CHCl_3$ at 40°C calibrated vs. polystyrene standards. M_n = 44 kg/mol and $Đ$ = 2.8.

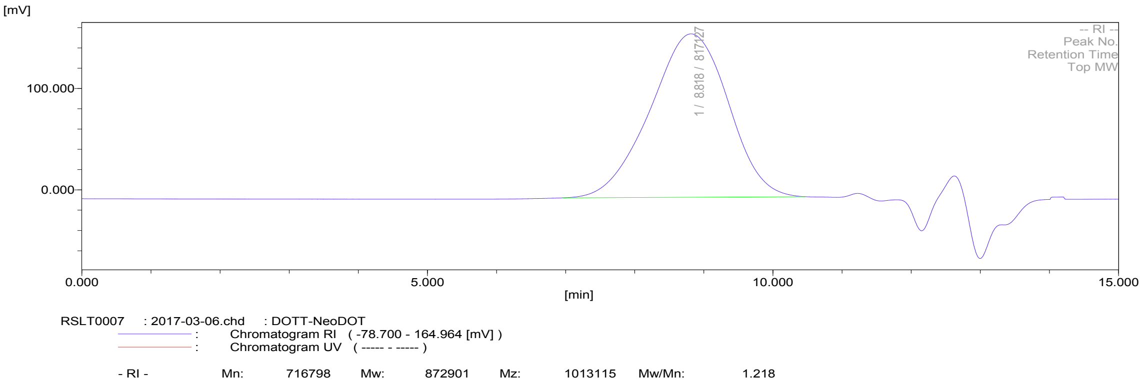


Figure S9: Gel permeation chromatogram for DOTT-NeoDOT in $CHCl_3$ at 40°C calibrated vs. polystyrene standards. M_n = 12 kg/mol and $Đ$ = 1.8.

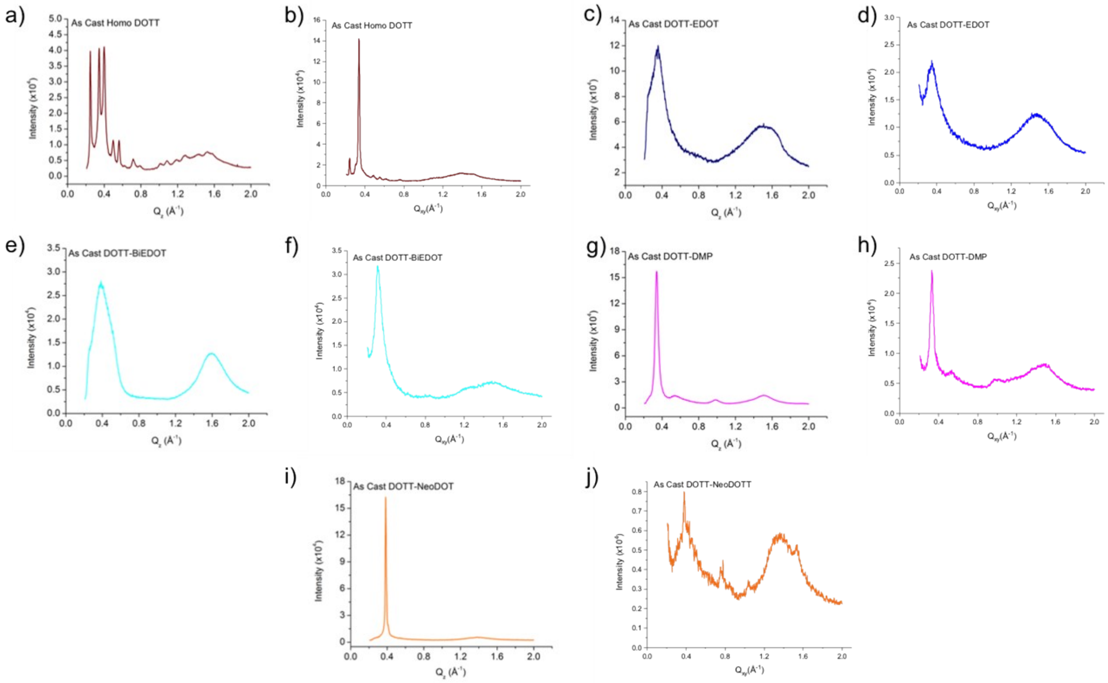


Figure S10: Line cuts along the Q_z and Q_{xy} direction for GIWAXS images of as-cast blade-coated films coated from chloroform of Homo DOTT (a-b), DOTT-EDOT (c-d), DOTT-BiEDOT (e-f), DOTT-DMP (g-h), and DOTT-NeoDOT (i-j) on glass. Films coated with a custom-built in-house blade-coater.

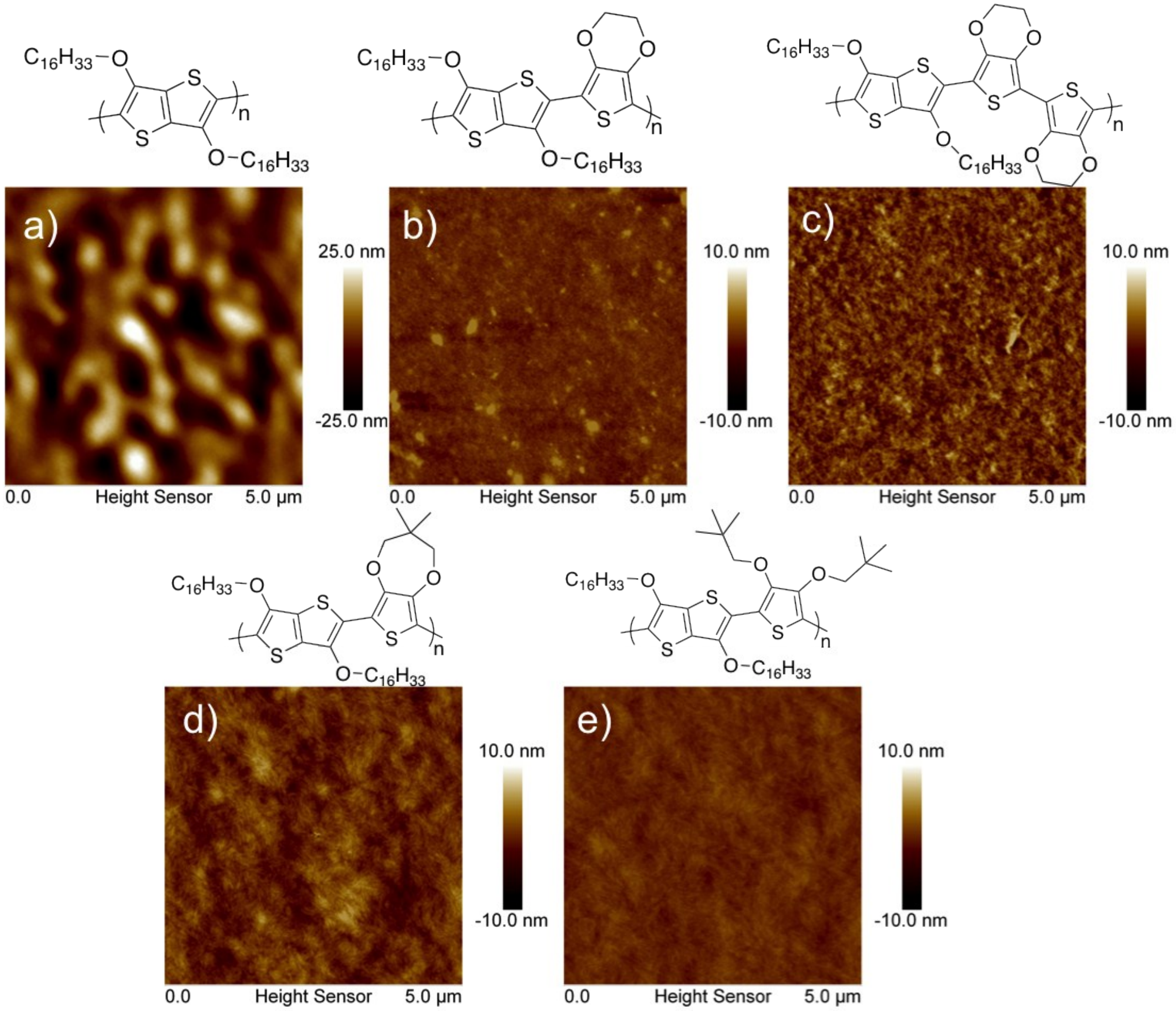


Figure S11: AFM height images of as-cast blade-coated films coated from chloroform of Homo DOTT (a), DOTT-EDOT (b), DOTT-BiEDOT (c), DOTT-DMP (d), and DOTT-NeoDOT (e) on glass. Films coated with a custom-built in-house blade-coater.

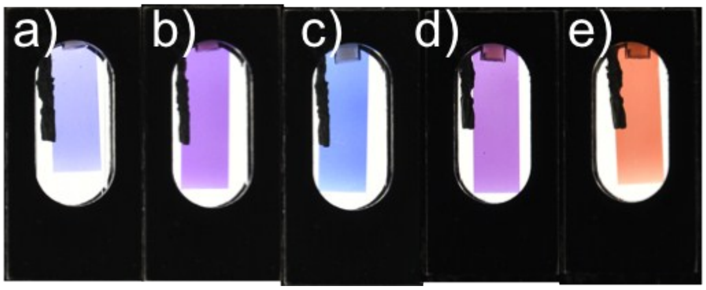


Figure S12: Photographs of polymer films Homo DOTT (a), DOTT-EDOT (b), DOTT-BiEDOT (c), DOTT-DMP (d), and DOTT-NeoDOT (e) on ITO/glass in 0.5 M TBAPF$_6$ in propylene carbonate -0.5 V versus Ag/Ag$^+$.

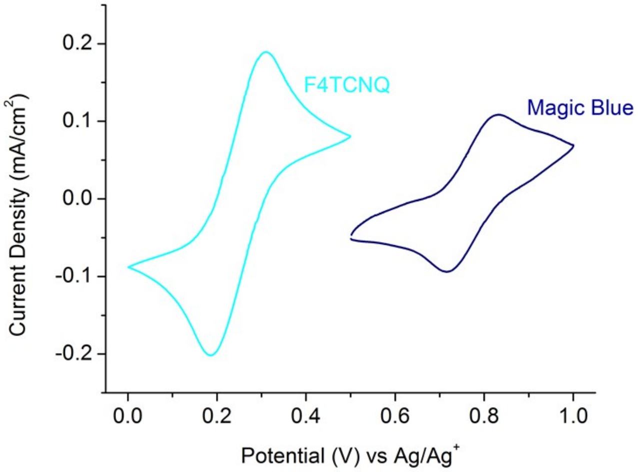


Figure S13: Cyclic voltammograms of 10 mM Magic Blue and F4TCNQ in 0.5 M TBAPF$_6$ in propylene carbonate. CVs were performed with a glassy carbon rod as the working electrode, platinum flag as the counter electrode, and a Ag/Ag$^+$ reference electrode with $E_{1/2}$ = 55 mV and a scan rate of 5 mV/s.

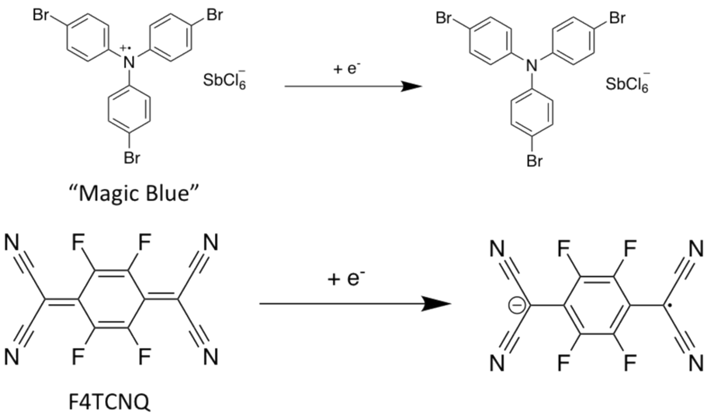


Figure S14: Electron accepting reactions for Magic Blue and F4TCNQ dopants.

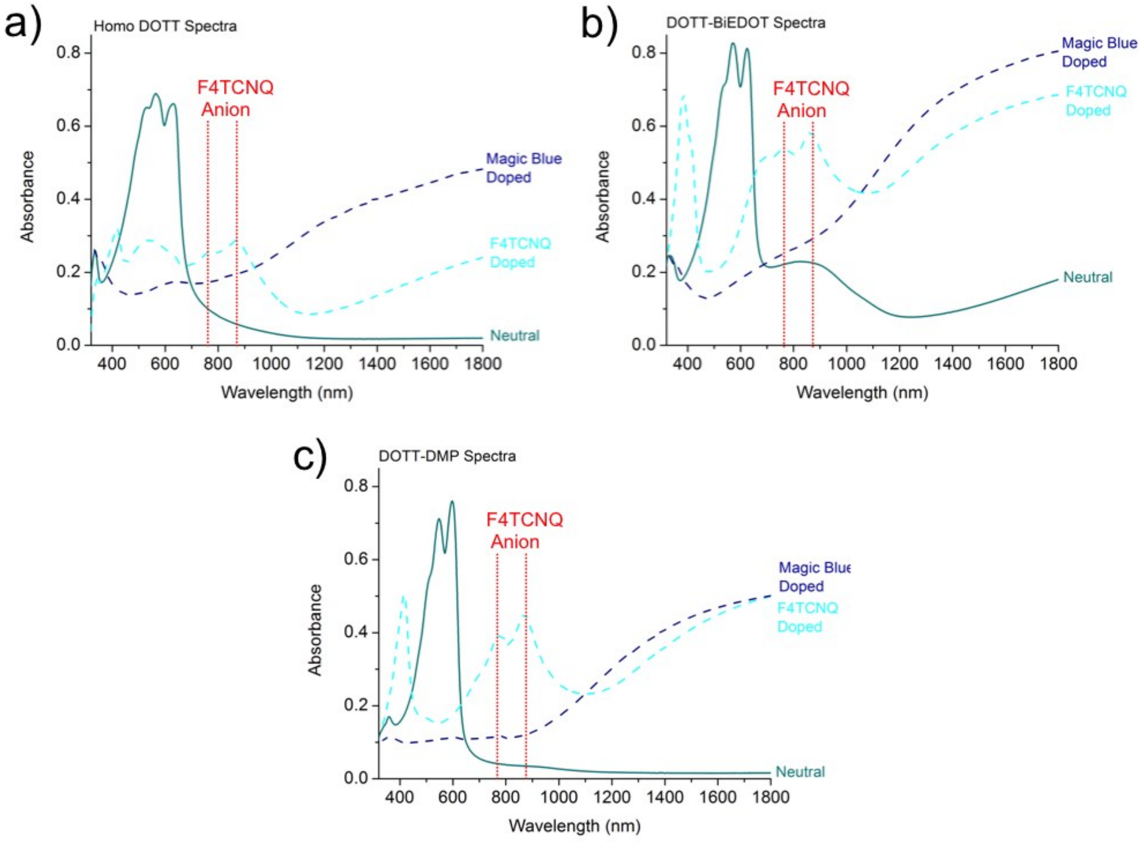


Figure S15: UV-vis absorption spectra of a blade-coated polymer film of (a) Homo DOTT, (b) DOTT-BiEDOT, and (c) DOTT-DMP on glass before and after 30 s of exposure to a 10 mM solution of either Magic Blue (dark blue curve) or F4TCNQ (dark cyan curve) in propylene carbonate and a methanol rinse. Absorbance at 400 nm corresponds to the neutral F4TCNQ molecule.

Table S1: Average Doping Ratios Calculated from XPS Atomic Abundance Values for Polymer Films Doped with 10 mM Magic Blue in Propylene Carbonate

Polymer	**Cl 2p Abundance**	**S 2p Abundance**	**S:Cl**	**Number of Rings Per Dopant**
Homo DOTT	59.3	37.1	5.8	6
DOTT-EDOT	105.1	74.7	4.7	5
DOTT-BiEDOT	155.7	62.8	2.4	2
DOTT-DMP	100.3	81.1	5.0	5
DOTT-NeoDOT	145.2	54.2	2.2	2

Table S2: Average Doping Ratios (Rings/Dopant) Calculated from XPS Atomic Abundance Values (F 1s and S 2p) for Polymer Films Doped with Various Concentrations of F4TCNQ in Propylene Carbonate

Polymer	**1 mM F4TCNQ**	**10 mM F4TCNQ**	**50 mM F4TCNQ**
Homo DOTT	46	19	9
DOTT-EDOT	32	8	8
DOTT-BiEDOT	8	5	6
DOTT-DMP	10	7	7
DOTT-NeoDOT	94	5	6

Table S3: Calculated Spacing Values from GIWAXS Images of As-Cast and Doped Polymer Films

Polymer	**Lamellar As-Cast (Å)**	**Lamellar F4TCNQ Doped (Å)**	**Lamellar Magic Blue Doped (Å)**	**Pi-Pi As-Cast (Å)**	**Pi-Pi F4TCNQ Doped (Å)**	**Pi-Pi Magic Blue Doped (Å)**
Homo DOTT	18.4	20.9	23.0	4.2	3.8	4.8
DOTT-EDOT	18.4	18.5	19.5	4.3	4.0	4.7
DOTT-BiEDOT	17.0	20.0	23.7	4.0	3.7	4.3
DOTT-DMP	18.6	18.5	17.7	4.3	3.9	4.5
DOTT-NeoDOT	16.4	18.2	19.1	4.7	4.8	4.8

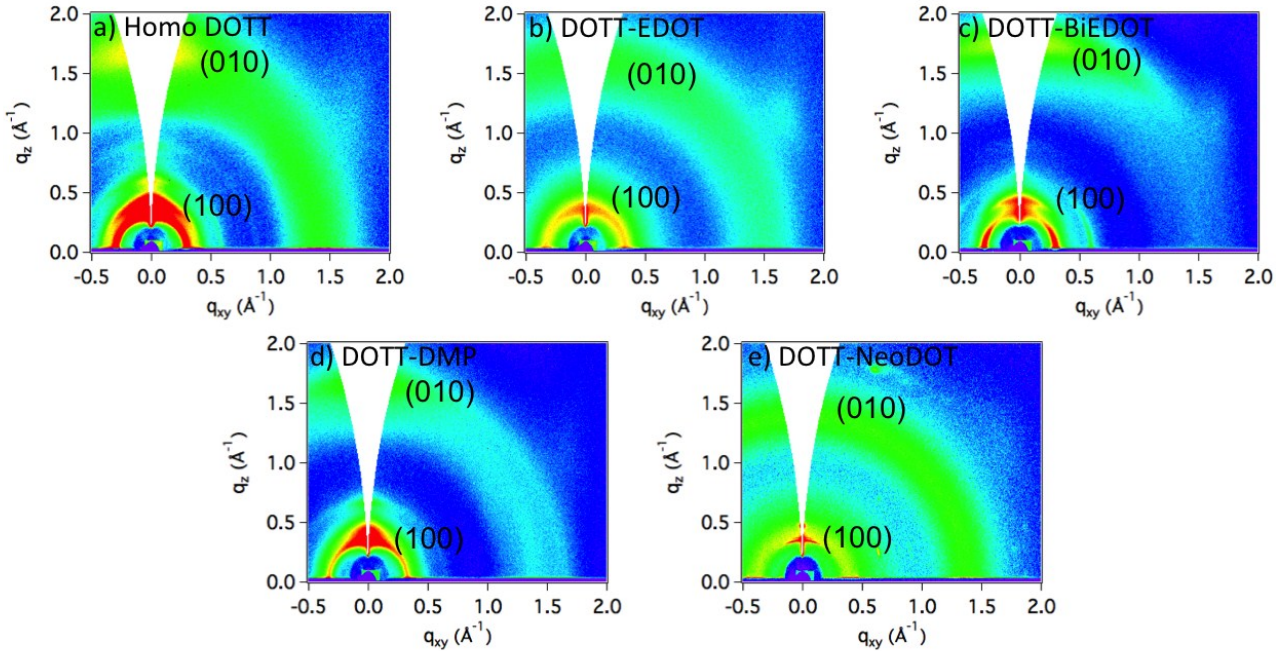


Figure S16: GIWAXS images of blade-coated films of Homo DOTT (a), DOTT-EDOT (b), DOTT-BiEDOT (c), DOTT-DMP (d), and DOTT-NeoDOT (e) on silicon wafers after 30s of exposure to a 10 mM F4TCNQ solution in propylene carbonate and rinse in clean methanol.

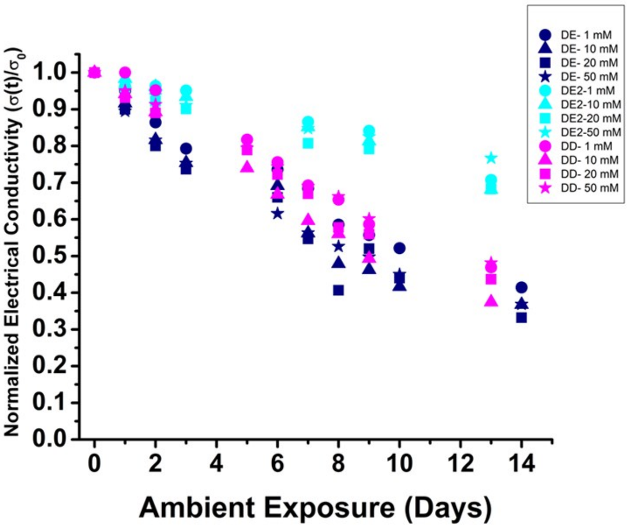


Figure S17: Normalized electrical conductivity values of blade-coated polymer films on glass after exposure to a F4TCNQ dopant solution with concentrations ranging from 1-50 mM in propylene carbonate for 30 seconds and a subsequent methanol rinse.

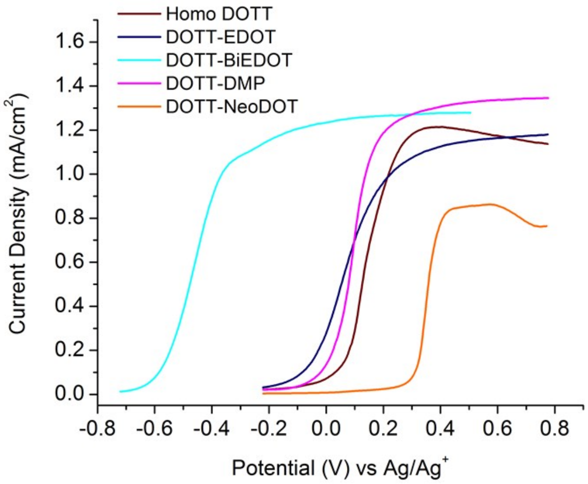


Figure S18: Differential pulse voltammograms for drop-cast films of Homo DOTT in red, DOTT-EDOT in navy blue, DOTT-BiEDOT in cyan, DOTT-DMP in magenta and DOTT-NeoDOT in orange on a glassy carbon electrode as the working electrode in a three-electrode cell in 0.5 M $TBAPF_6$ in propylene carbonate after 5 conditioning CV cycles.

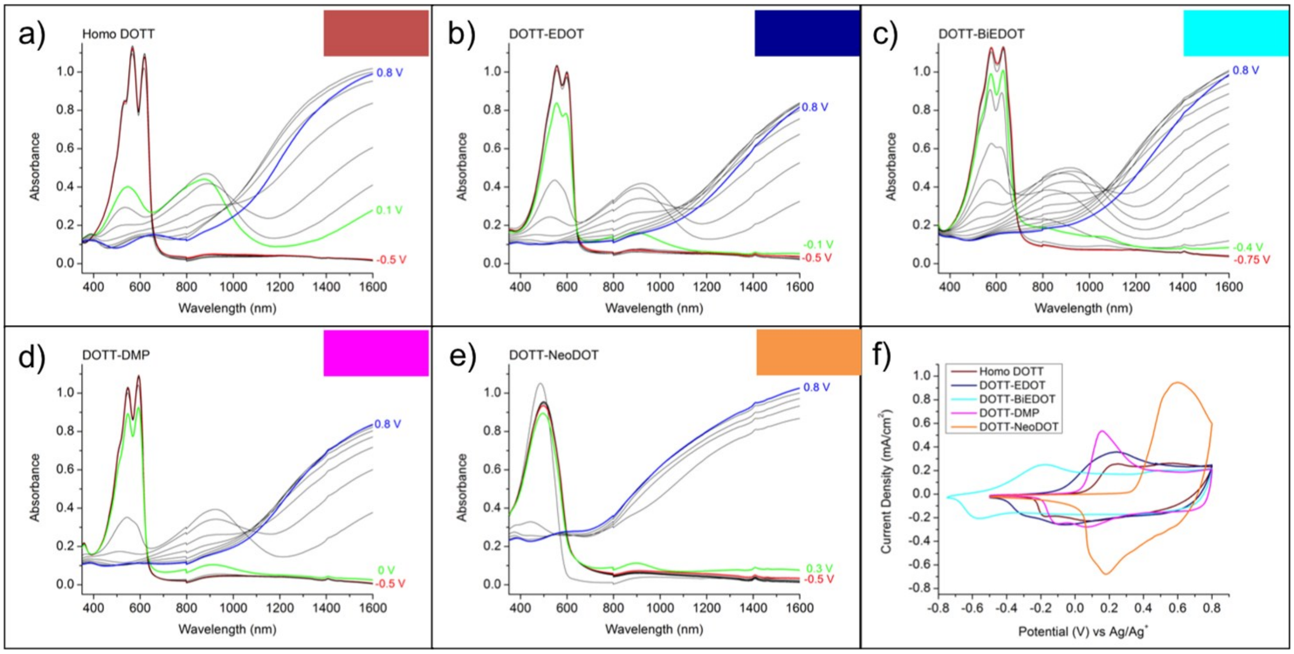


Figure S19: UV-vis absorption spectra as a function of applied potential of spray-coated polymer films Homo DOTT (a), DOTT-EDOT (b), DOTT-BiEDOT (c), DOTT-DMP (d), DOTT-NeoDOT (e) on ITO/glass in 0.5 M $TBAPF_6$ in propylene carbonate and conditioning cyclic voltammograms (f) with a scan rate of 50 mV/s.

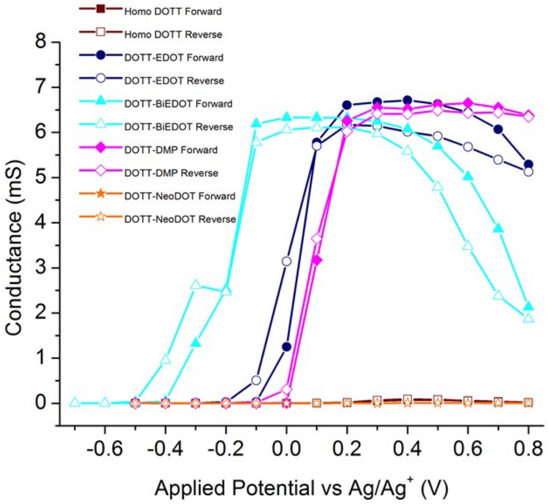


Fig. S20: In situ conductance of Homo DOTT (red), DOTT-EDOT (navy blue), DOTT-BiEDOT (cyan), DOTT-DMP (magenta), and DOTT-NeoDOT (orange) from -0.5 to 0.8 V vs Ag/Ag$^+$ in 0.5 M TBAPF$_6$ in propylene carbonate. Scans started from negative potentials.

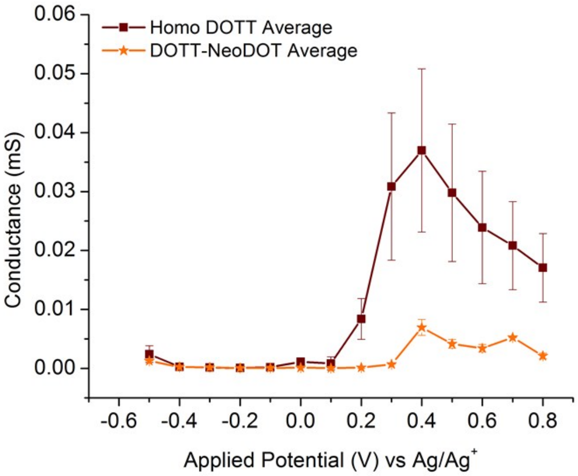


Fig. S21: In situ conductance of Homo DOTT (red) and DOTT-NeoDOT (orange) from -0.5 to 0.8 V vs Ag/Ag$^+$ in 0.5 M TBAPF$_6$ in propylene carbonate. Averages taken from values collected from three films of each polymer.

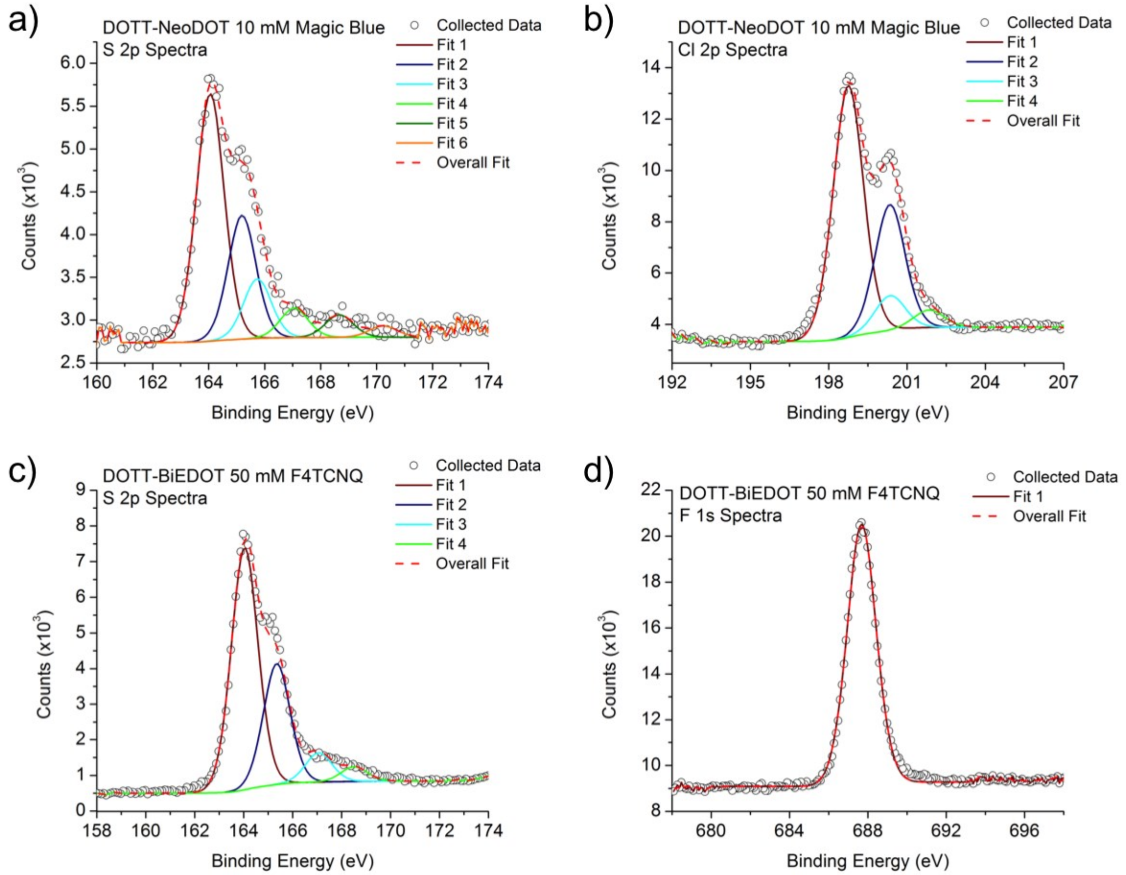


Fig. S22: Example plots of fitted XPS spectra corresponding to a polymer film of DOTT-NeoDOT [(a) and (b)] doped with a 10 mM solution of Magic Blue in propylene carbonate and a polymer film of DOTT-BiEDOT [(c) and (d)] doped with a 50 mM solution of F4TCNQ in propylene carbonate. Spectra were recorded after polymer films were rinsed with clean methanol and dried under vacuum at 50°C. Areas of fitted spectra were used to calculate relative abundance values and doping ratios for chemically oxidized polymer films.

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