

Supplementary Information

Broad Spectrum Absorption and Low-Voltage Electrochromic Operation from Indacenodithieno[3,2-*b*]thiophene-Based Copolymers

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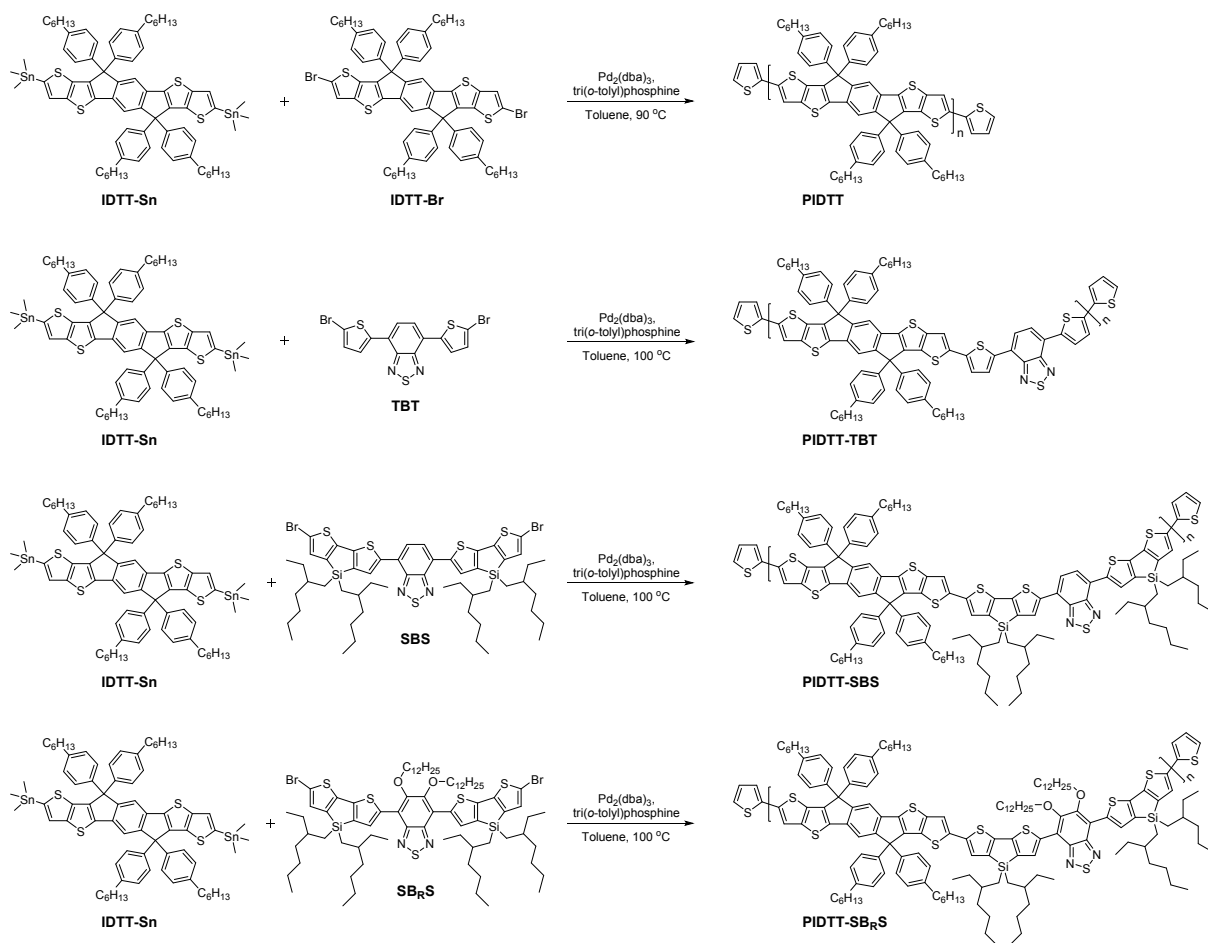
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Polymer synthesis and characterization



Scheme S1 Synthesis of PIDTT, PIDTT-TBT, PIDTT-SBS and PIDTT-SB_RS copolymers.

The 4,7-bis(5-bromothiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (TBT), the 4,7-bis(6-bromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole (SBS) and the 4,7-bis(6-bromo-4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole (SB_RS) monomers were synthesized as published previously.¹ The bis(trimethylstannyl)-substituted indacenodithieno[3,2-*b*]thiophene monomer (IDTT-Sn) and the dibromo-substituted indacenodithieno[3,2-*b*]thiophene monomer (IDTT-Br) were purchased from Solarmer Energy, Inc. and used as received. All other reagents and solvents were obtained from Sigma-Aldrich and VWR, and used as received.

Poly[indacenodithieno[3,2-*b*]thiophene-2,8-diyl] (PIDTT): To a dry 25 mL 2-neck flask was added IDTT-Sn (0.2690 g, 0.200 mmol), IDTT-Br (0.2355 g, 0.200 mmol), Pd₂(dba)₃ (0.0037 g, 0.004 mmol) and tri(*o*-tolyl)phosphine (0.0049 g, 0.016 mmol). The flask was subjected to 5 vacuum/nitrogen backfill cycles before 10 mL of dry toluene was added. The flask was lowered to a preheated oil bath at 90 °C and the mixture was stirred vigorously for 15 min. To stop the polymerization and end-cap the polymer chains, 2-(tributylstannyl)thiophene (0.0896 g, 0.240 mmol) was added and the reaction was continued for 30 min. Then, 2-bromothiophene (0.0456 g, 0.280 mmol) was added and the reaction was continued for another 1 h. The bright orange mixture was cooled to room temperature, diluted with toluene (200 mL) and extracted with 1% (aq) sodium diethyldithiocarbamate solution (300 mL) for 24 h. The organic phase was washed with water (6 × 200 mL), concentrated and precipitated by dropping slowly into acetone. The polymer was collected by filtration through a Soxhlet thimble and washed with Soxhlet extraction using acetone, hexane and DCM as solvent (24 h each step). The remaining polymer was dissolved in CB and further purified by passing the mixture through a short silica gel column, and then precipitated again, directly into acetone. The polymer was collected by filtration through a 0.45 μm Teflon filter. Finally, PIDTT (0.324 g, 79%) was obtained as orange/red solid after drying under vacuum at 40 °C overnight. ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 7.54 (br, 2H), 7.41 (br, 2H), 7.18–7.11 (m, 16H), 2.57 (br, 8H), 1.59 (br, 8H), 1.29 (br, 24H), 0.88 (m, 12H); GPC: *M*_n = 85.1 kg/mol, PDI = 2.5.

Poly[indacenodithieno[3,2-*b*]thiophene-2,8-diyl-*alt*-4,7-bis(thiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-5,5'-diyl] (PIDTT-TBT): To a dry 25 mL 2-neck flask was added IDTT-Sn (0.2690 g, 0.200 mmol) and TBT (0.0916 g, 0.200 mmol) monomers. The flask was subjected to 5 vacuum/nitrogen backfill cycles, after which 15 mL of dry toluene was added and the mixture was heated at 100 °C to obtain fully dissolved solution. To start the polymerization, Pd₂(dba)₃ (0.0037 g, 0.004 mmol) and tri(*o*-tolyl)phosphine (0.0049 g, 0.016

mmol) were dissolved in 2 mL of dry toluene and added to the flask. The dark purple, nearly black mixture was stirred vigorously for 10 min, then end-capped and purified following the procedure described above for PIDTT. Finally, PIDTT-TBT (0.089 g, 34%) was obtained as black solid. ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 8.05 (br, 2H), 7.87 (br, 2H), 7.58 (br, 4H), 7.22–7.14 (m, 18H), 2.59 (br, 8 H), 1.61 (br, 8H), 1.29 (br, 24H), 0.88 (m, 12H); GPC: M_n = 78.4 kg/mol, PDI = 1.8.

Poly[indacenodithieno[3,2-*b*]thiophene-2,8-diyl-*alt*-4,7-bis(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)benzo[*c*][1,2,5]thiadiazole-6,6'-diyl] (PIDTT-SBS): To a 30 mL crimp-cap vial was added IDTT-Sn (0.1345 g, 0.100 mmol) and SBS (0.1127 g, 0.100 mmol) monomers, together with Pd₂(dba)₃ (0.0018 g, 0.002 mmol) and tri(*o*-tolyl)phosphine (0.0024 g, 0.008 mmol). The vial was subjected to 5 vacuum/nitrogen backfill cycles and 8 mL of dry toluene was added. The vial was lowered to a preheated oil bath at 100 °C and the mixture was stirred vigorously for 18 h. The polymer was end-capped by adding 2-(tributylstannyl)thiophene (0.0448 g, 0.120 mmol) and continuing the reaction for 1 h. Then, 2-bromothiophene (0.0228 g, 0.140 mmol) was added and the reaction was continued for another 2 h. The dark purple polymer solution was purified following the procedure described for PIDTT, but the Soxhlet extraction was done using acetone, hexane and chloroform (24 h each step). The chloroform fraction was concentrated and further purified by passing through a silica gel column, and precipitated into acetone. Finally, PIDTT-SBS (0.179 g, 90%) was obtained as black solid after drying under vacuum at 40 °C overnight. ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 8.01 (br, 2H), 7.50 (br, 4H), 7.22–7.14 (m, 20H), 2.59 (br, 8H), 1.65–1.52 (m, 12H), 1.30–1.06 (m, 64H), 0.88–0.83 (m, 36H); GPC: M_n = 109.1 kg/mol, PDI = 2.8.

Poly[indacenodithieno[3,2-*b*]thiophene-2,8-diyl-*alt*-4,7-bis(4,4-bis(2-ethylhexyl)-4*H*-silolo[3,2-*b*:4,5-*b'*]dithiophen-2-yl)-5,6-bis(dodecyloxy)benzo[*c*][1,2,5]thiadiazole-6,6'-diyl] (PIDTT-SB_RS): IDTT-Sn (0.1345 g, 0.100 mmol) and SB_RS (0.1496 g, 0.100 mmol)

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monomers and $\text{Pd}_2(\text{dba})_3$ (0.0018 g, 0.002 mmol) and tri(*o*-tolyl)phosphine (0.0024 g, 0.008 mmol) in a 30 mL crimp-cap vial was subjected to 5 vacuum/nitrogen backfill cycles, after which 8 mL of dry toluene was added. The polymerization was run at 100 °C for 18 h, followed by end-capping and purification of the dark blue/purple polymer solution as described above for PIDTT-SBS. Finally, PIDTT-SB_RS (0.205 g, 87%) was obtained as dark purple, nearly black solid. ¹H NMR (400 MHz, C₂D₂Cl₄, δ): 8.49 (br, 2H), 7.56–7.36 (m, 4H), 7.22–7.14 (m, 18H), 4.17 (br, 4H), 2.59 (br, 8H), 2.01 (br, 4H), 1.66–1.53 (m, 16H), 1.30–1.06 (m, 96H), 0.88–0.83 (m, 42H); GPC: $M_n = 81.7$ kg/mol, PDI = 2.8.

^1H NMR spectra

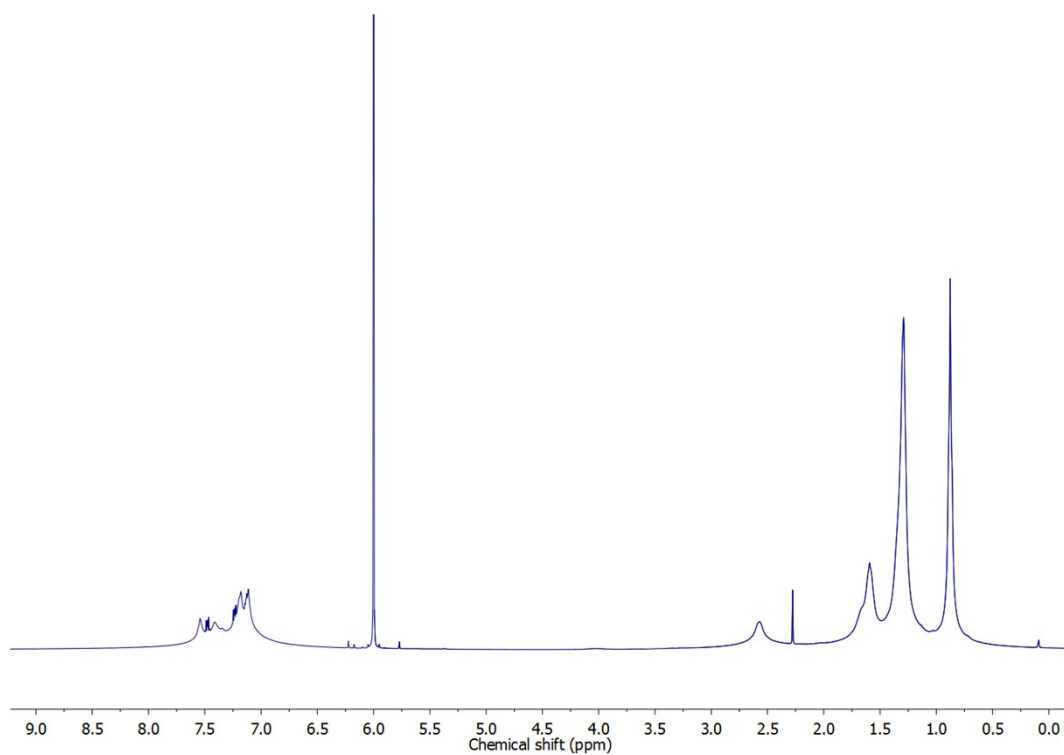


Fig. S1 ^1H NMR (400 MHz) spectrum of PIDTT in $\text{C}_2\text{D}_2\text{Cl}_4$ (^1H : 6.00).

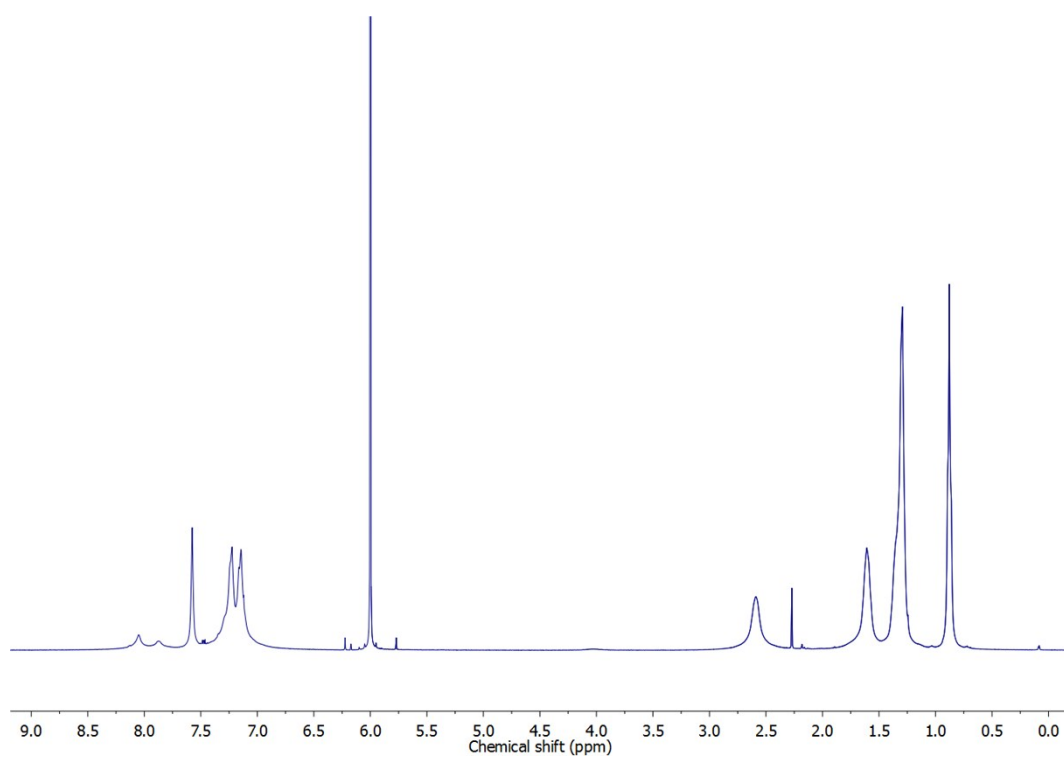


Fig. S2 ^1H NMR (400 MHz) spectrum of PIDTT-TBT in $\text{C}_2\text{D}_2\text{Cl}_4$ (^1H : 6.00).

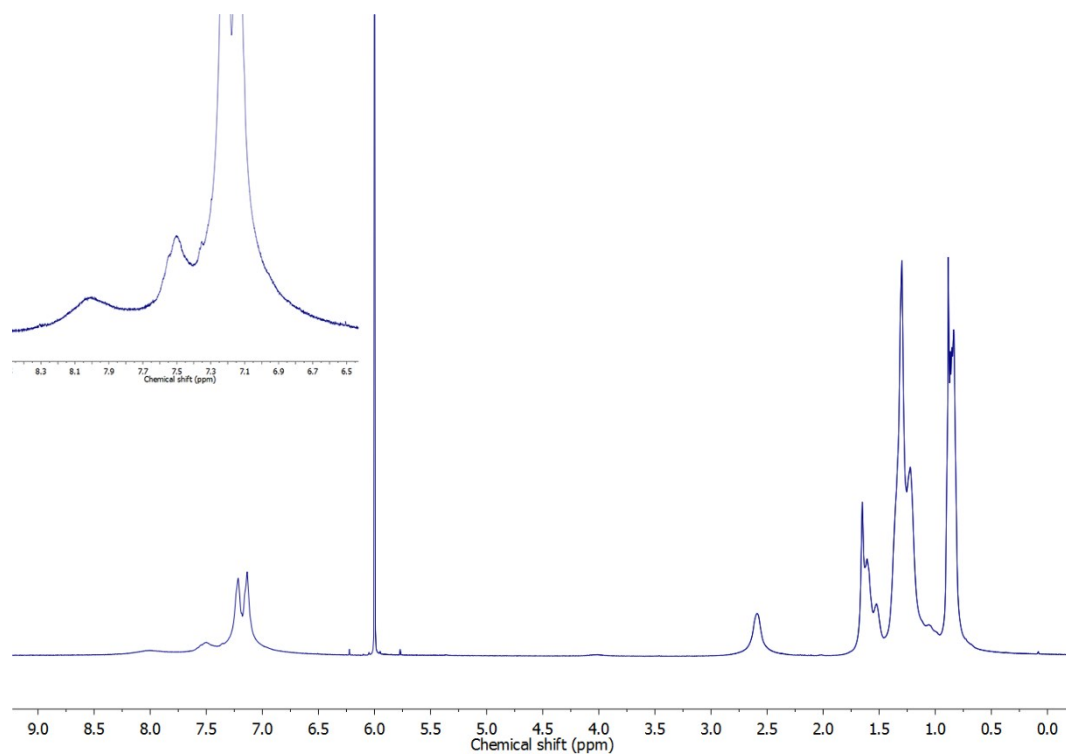


Fig. S3 ^1H NMR (400 MHz) spectrum of PIDTT-SBS in $\text{C}_2\text{D}_2\text{Cl}_4$ (^1H : 6.00).

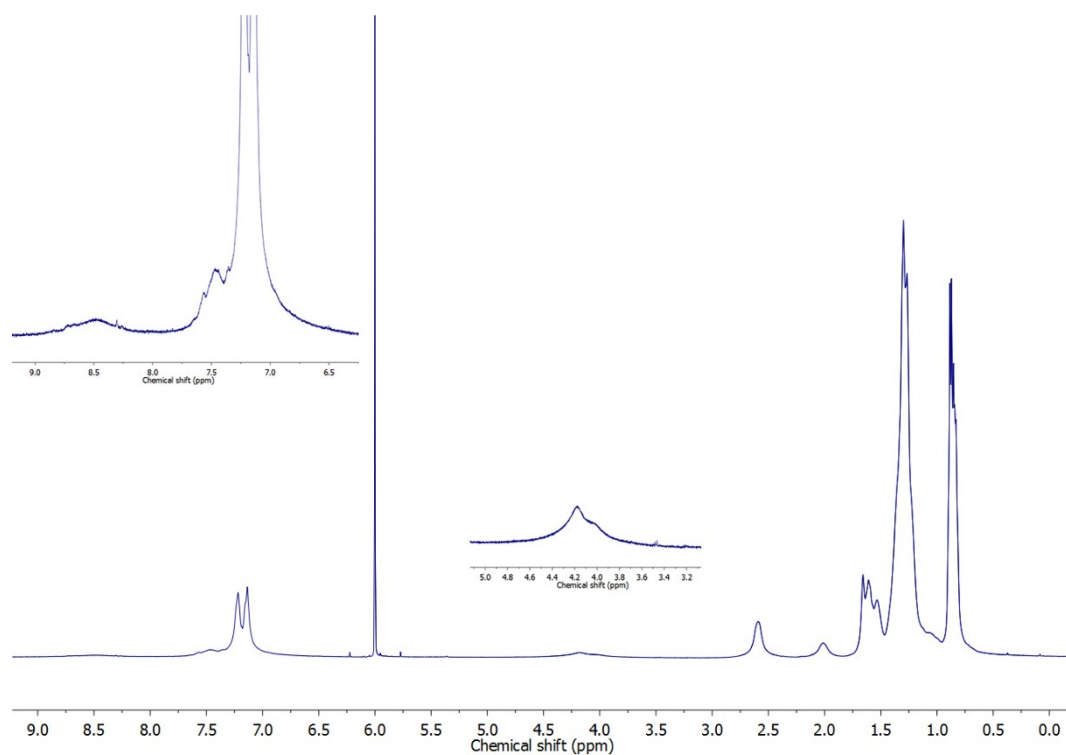
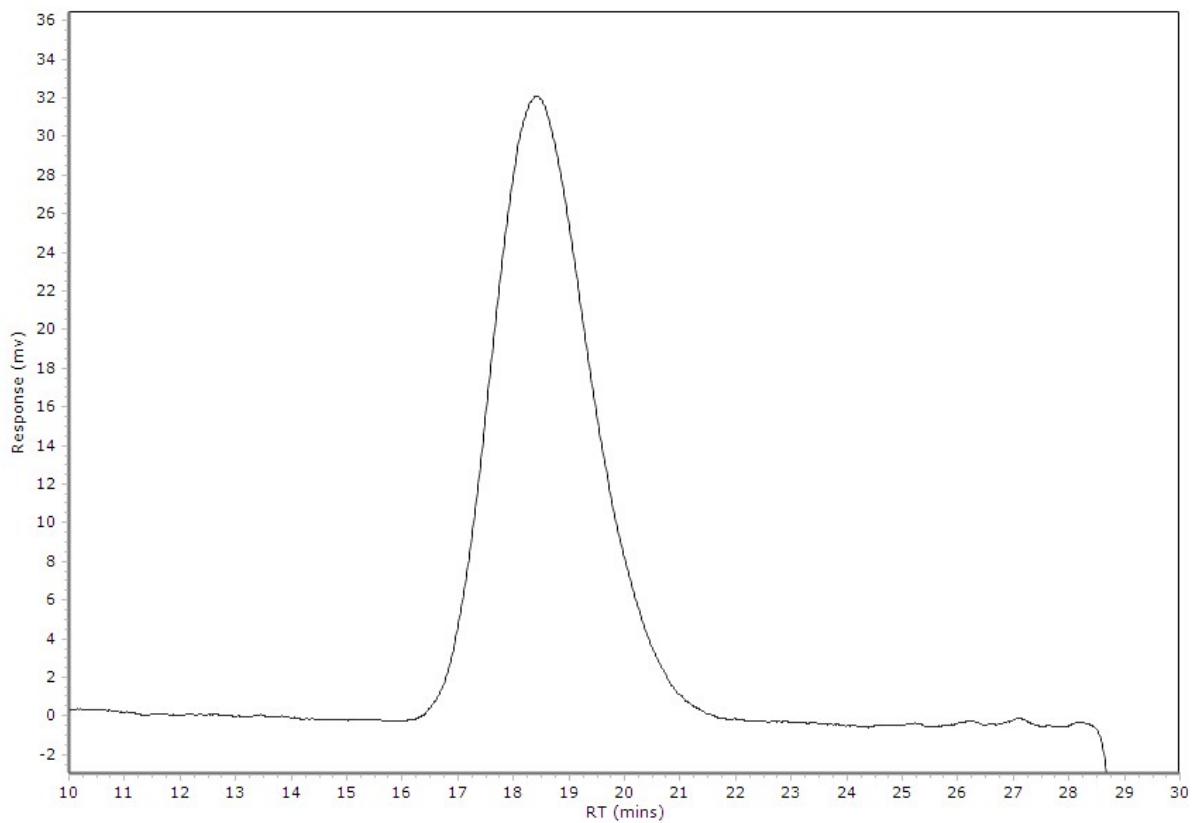


Fig. S4 ^1H NMR (400 MHz) spectrum of PIDTT-SBRs in $\text{C}_2\text{D}_2\text{Cl}_4$ (^1H : 6.00).

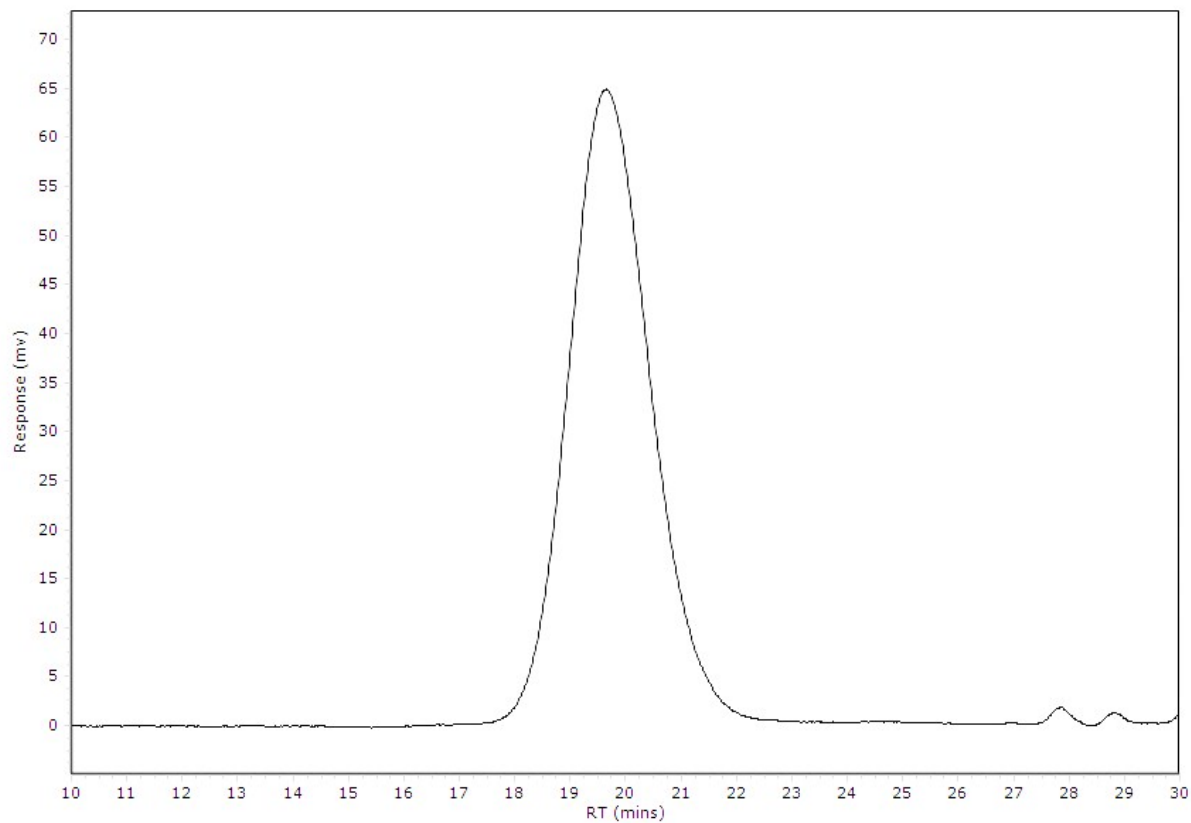
GPC Traces



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	173613	85083	208560	382607	580103	355790	2,451

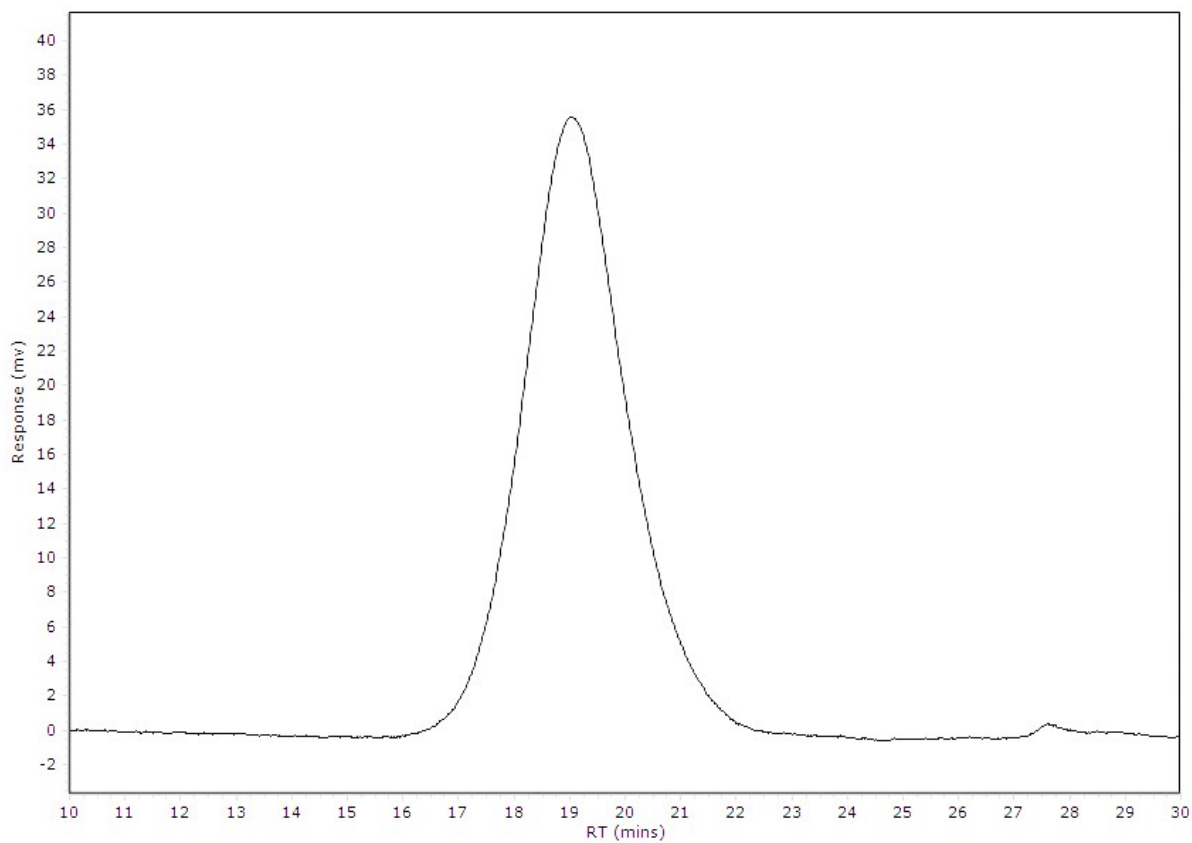
Fig. S5 GPC trace and molecular weight data of PIDTT relative to polystyrene standards.



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	120447	78406	139808	231490	430057	213823	1,783

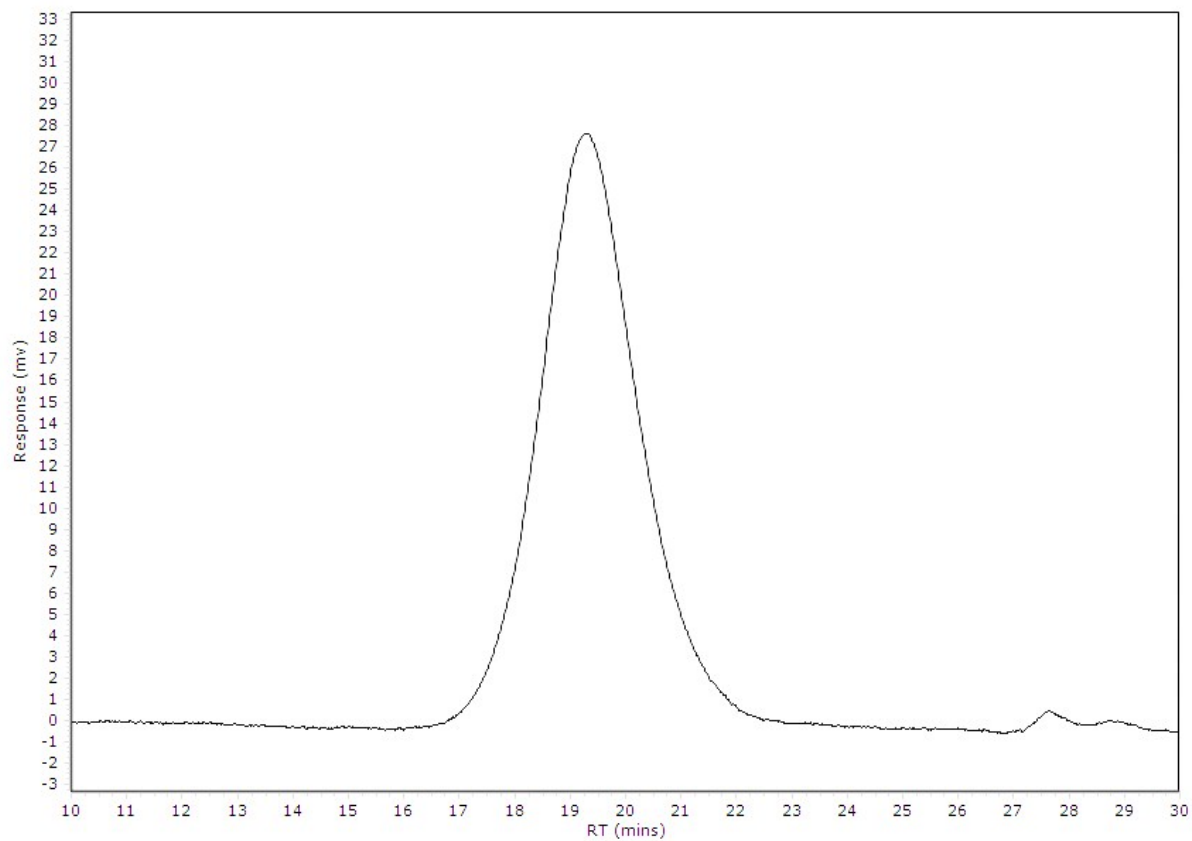
Fig. S6 GPC trace and molecular weight data of PIDTT-TBT relative to polystyrene standards.



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	214794	109133	304716	700159	1368896	624879	2,792

Fig. S7 GPC trace and molecular weight data of PIDTT-SBS relative to polystyrene standards.



Molecular Weight Averages

Peak	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
Peak 1	162524	81656	230701	513755	1014317	459388	2,825

Fig. S8 GPC trace and molecular weight data of PIDTT-SB_RS relative to polystyrene standards.

Additional electrochemical characterization

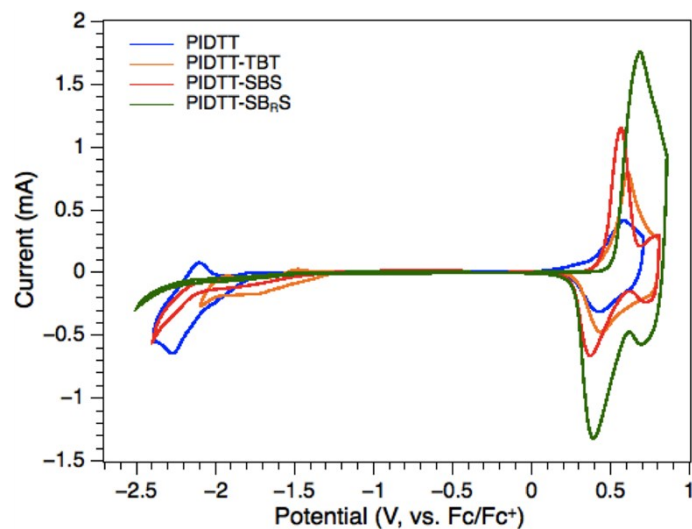


Fig. S9 Cyclic voltammograms of the polymers at the scan rate 100 mV/s.

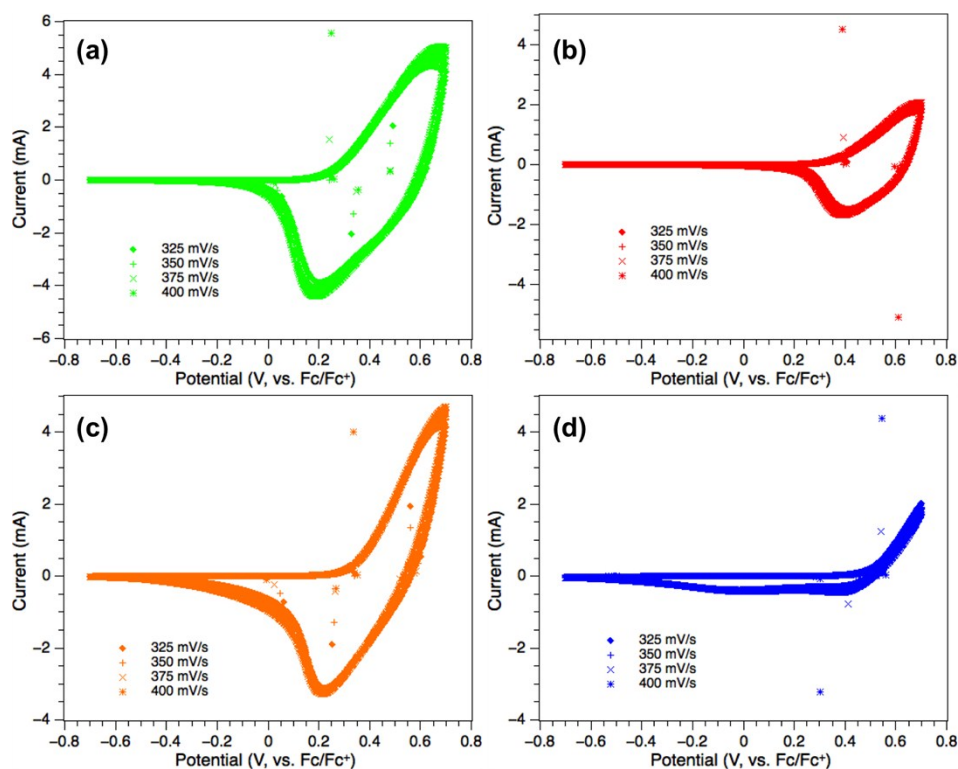


Fig. S10 Scan rate dependence of the polymer films (a) PIDTT, (b) PIDTT-TBT, (c) PIDTT-SBS and (d) PIDTT-SB_RS at the scan rates 325, 350, 375 and 400 mV/s continuing from Fig. 2 in the main manuscript. The cyclic voltammetry traces were separated from Fig. 2 due to the scatter at the higher scan rates 325–400 mV/s.

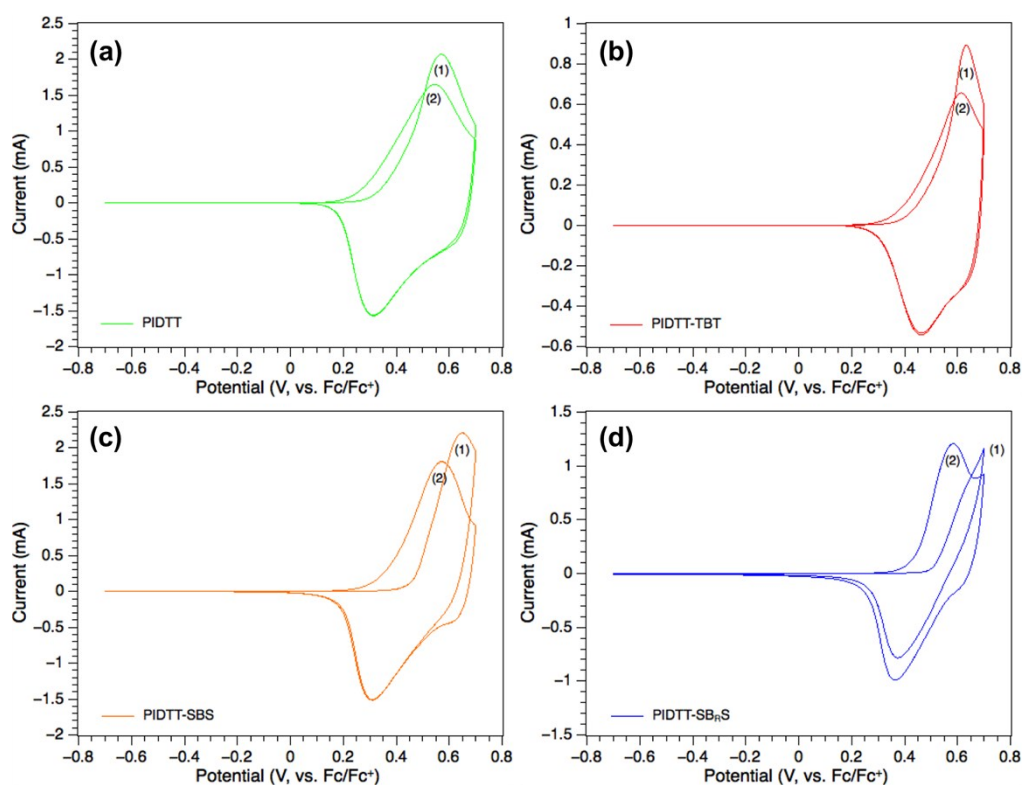


Fig. S11 First (1) and second (2) cyclic voltammetry traces of the fresh polymer films (a) PIDTT, (b) PIDTT-TBT, (c) PIDTT-SBS and (d) PIDTT-SB_RS at the scan rate 100 mV/s.

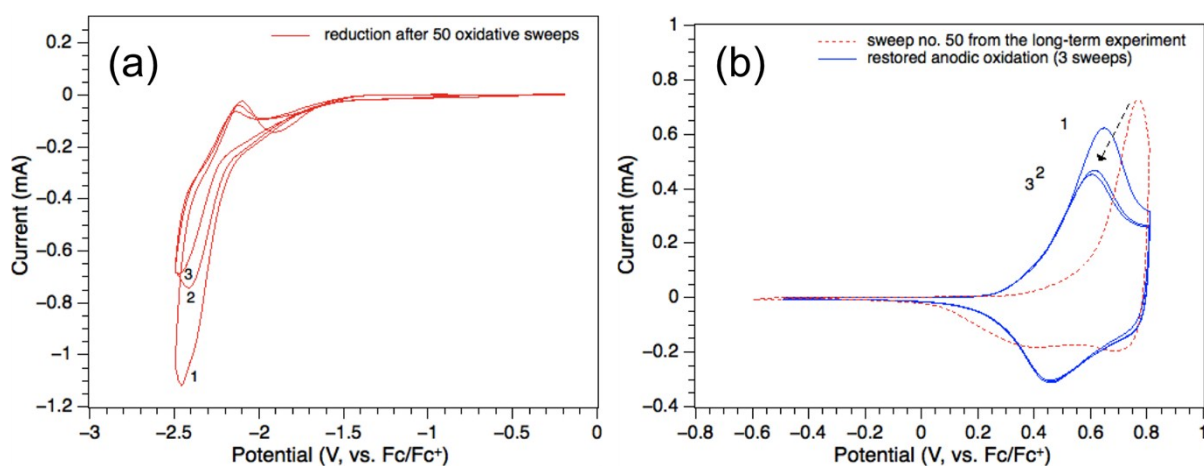


Fig. S12 (a) Cathodic reduction of PIDTT (scans 1–3) in the potential range of -0.2 to -2.5 V versus Fc/Fc^+ at a scan rate of 50 mV/s after the long-term oxidative sweeps followed by (b) fully restored reversibility of the anodic oxidation (scans 1–3), measured at the scan rate 100 mV/s; the numbers in the cyclic voltammetry traces indicate the number of the sweeps in each

experiment. For better illustration of the restored reversibility, the last sweep from the long-term oxidative sweeps is also plotted in (b) as the red dashed line.

Kinetic measurements at varied potentials

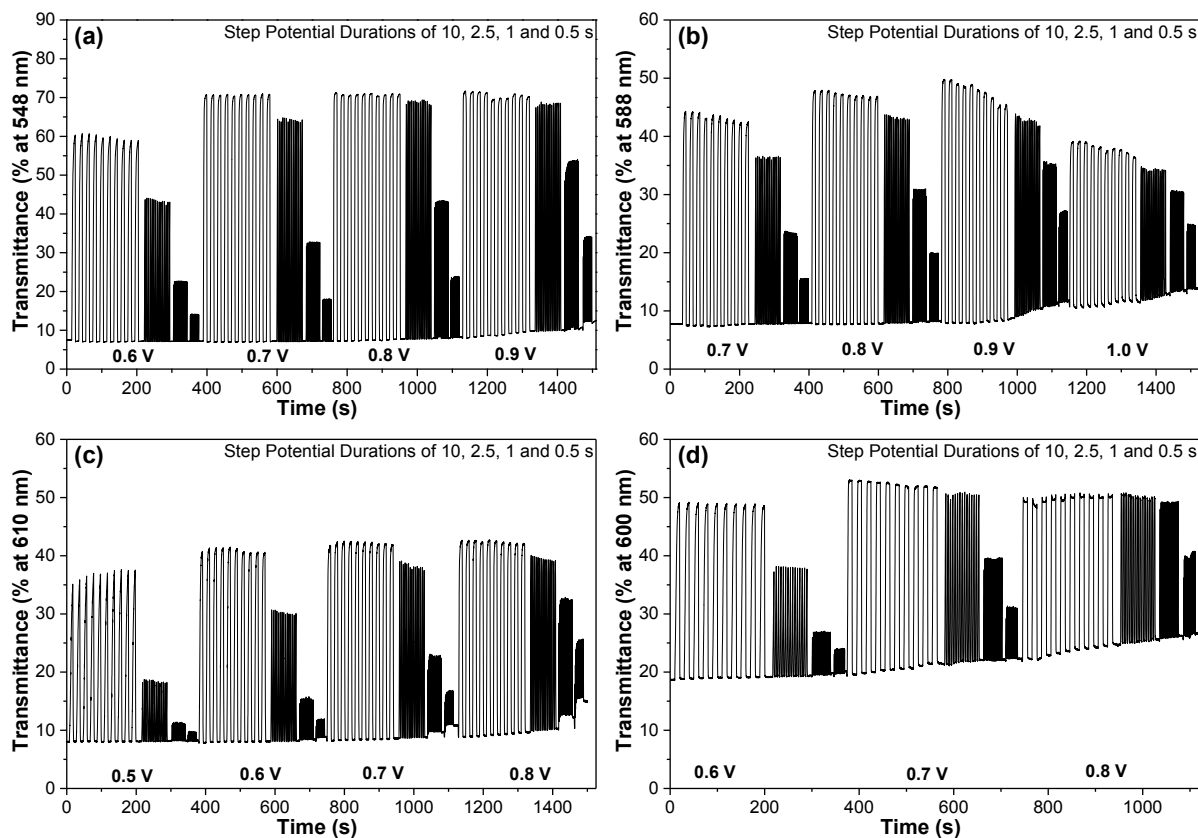


Fig. S13 Kinetic measurements at varied potentials for (a) PIDTT, (b) PIDTT-TBT, (c) PIDTT-SBS and (d) PIDTT-SB_RS thin films.

Cut-out of 10 s step potential oxidation

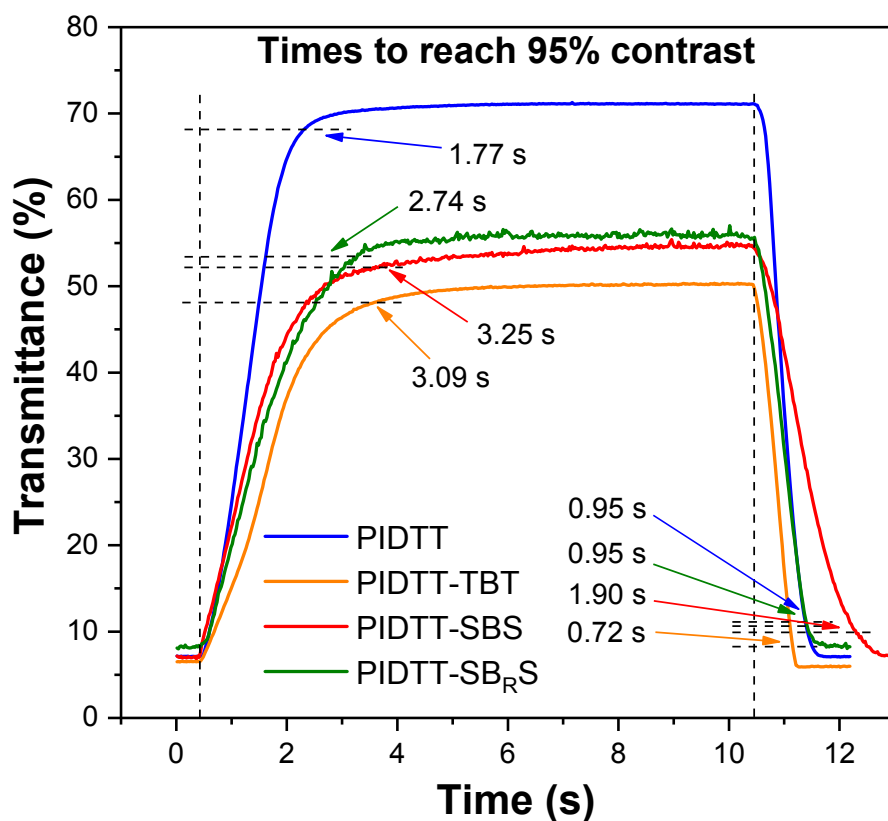


Fig. S14 Percent transmittance attained with times to reach 95% of the maximum optical contrast for both oxidation and reduction, as measured at 0.8 V for PIDTT and PIDTT-TBT, 0.6 V for PIDTT-SBS and 0.7 V for PIDTT-SB_RS.

References

- 1 P. Murto, S. Tang, C. Larsen, X. Xu, A. Sandström, J. Pietarinen, B. Bagemihl, B. A. Abdulahi, W. Mammo, M. R. Andersson, E. Wang and L. Edman, *ACS Appl. Energy Mater.*, 2018, **1**, 1753–1761.