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

Supporting Information for "Advances in Electropolymerization of NIR Emitting and Electronically Conducting Block Copolymers"

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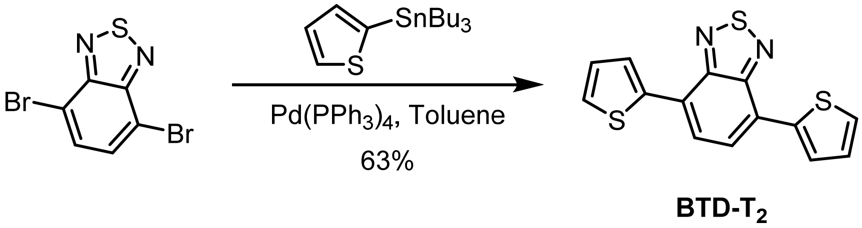
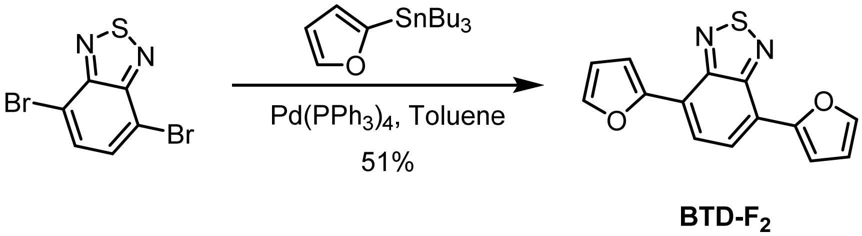
SI-I: SYNTHESIS DETAILS OF MONOMERIC UNITS

General Summary: Reagents and solvents were purchased from commercial sources and used without further purification unless otherwise specified. Thin layer chromatography (TLC) was performed on SiO2-60 F254 aluminum plates with visualization by UV light or staining. Flash column chromatography was performed using Purasil SiO2-60, 230–400 mesh from Fisher. ^{1}H NMR spectra were recorded on a Bruker Avance DRX-500 (500 MHz spectrometer) and were reported in ppm using solvent as an internal standard ($CDCl_3$ at 7.26 ppm for ^{1}H NMR). Data reported as: s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, b = broad, ap = apparent; coupling constant(s) in Hz; integration.



Scheme 1. Synthesis of **BTD-T$_2$**



Scheme 2. Synthesis of **BTD-F$_2$**

4,7-Di(thiophen-2-yl)benzo[c][1,2,5]thiadiazole (BTD-T$_2$). Under nitrogen, dry toluene (14 mL) was added to the degassed mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.009 g, 3.4 mmol) and $Pd(PPh_3)_4$ (0.079 g, 0.068 mmol). After the reaction mixture was stirred at room temperature for 15 minutes, 2-tri-*n*-butylstannylfuran (2.3 mL, 7.14 mmol) was added dropwise. The resulting solution was then heated to reflux for 24 hours. After being cooled to room temperature, the mixture was quenched with Na_2HCO_3 and extracted with diethyl ether. The organic layer was separated, dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The product was purified via flash column chromatography (chloroform/hexanes, 1:2) and obtained an orange solid in 63% yield (0.640 g): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.14 – 8.11 (m, 2H), 7.89 (s, 2H), 7.48 – 7.45 (m, 2H), 7.22 (dd, *J* = 5.1, 3.6 Hz, 2H).

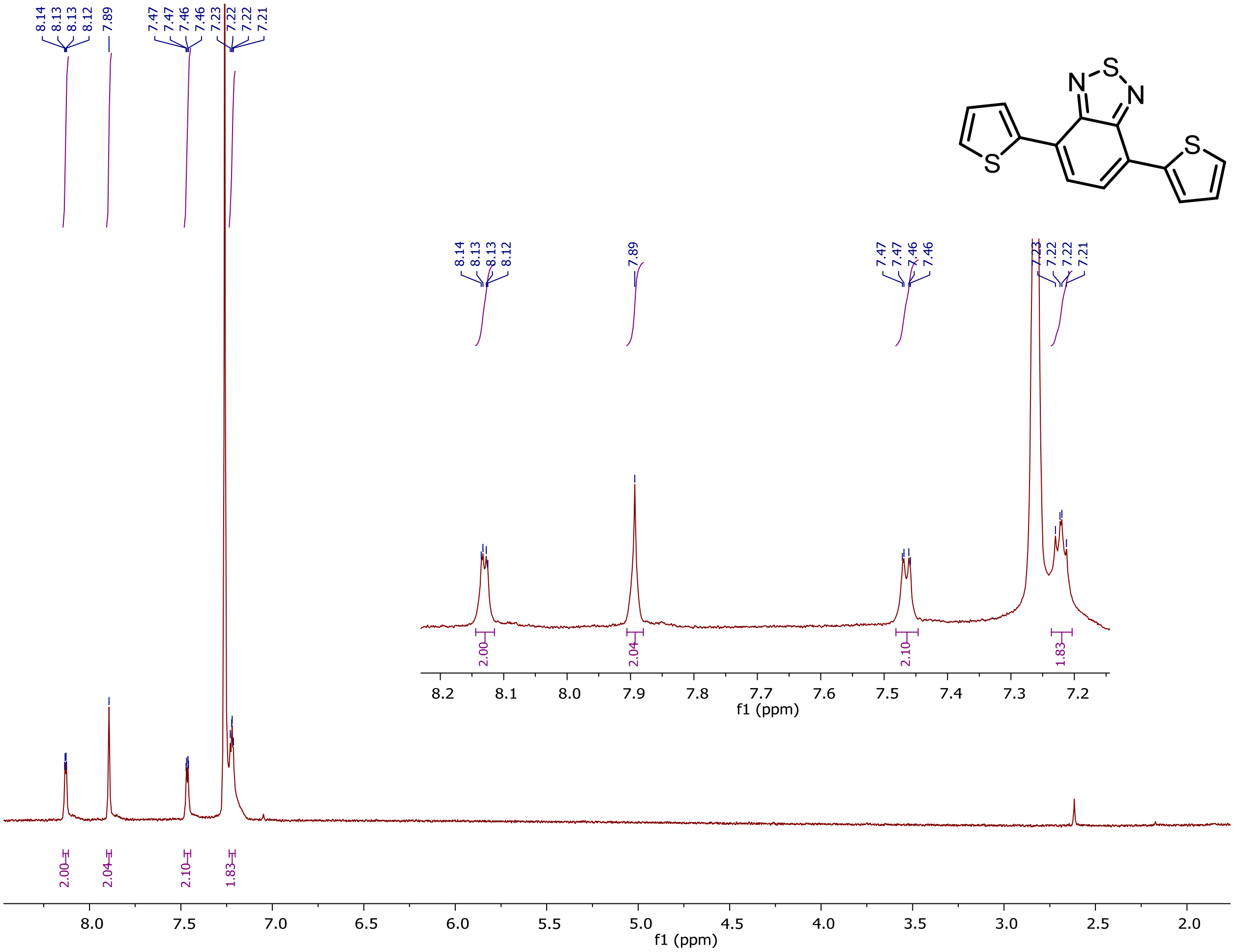


Figure SX. ^{1}H NMR spectrum of **BTD-T$_2$** (CDCl$_3$, 500 MHz).

4,7-Di(furan-2-yl)benzo[c][1,2,5]thiadiazole (BTD-F$_2$). Under nitrogen, dry toluene (18 mL) was added to the degassed mixture of 4,7-dibromobenzo[c][1,2,5]thiadiazole (1.3 g, 4.42 mmol) and Pd(PPh$_3$)$_4$ (0.30 g, 0.25 mmol). After the reaction mixture was stirred at room temperature for 10 minutes, 2-tri-*n*-butylstannylfuran (3.1 mL, 9.8 mmol) was added dropwise. The resulting solution was then heated to reflux for 24 hours. After being cooled to room temperature, the mixture was quenched with Na$_2$HCO$_3$ and extracted with dichloromethane. The organic layer was separated, dried over anhydrous Na$_2$SO$_4$, and concentrated under reduced pressure. The crude was purified by dissolving in 10 mL of DCM and 20 mL of hexane. The solution was cooled in an ice bath and filtered to collect the precipitate. Pure product was obtained as an orange solid in 51% yield (0.601 g): ^{1}H NMR (500 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 1.1 Hz, 2H), 7.70 – 7.68 (m, 2H), 7.59 (dd, *J* = 1.9, 0.9 Hz, 2H), 6.63 (dd, *J* = 3.4, 1.8 Hz, 2H).

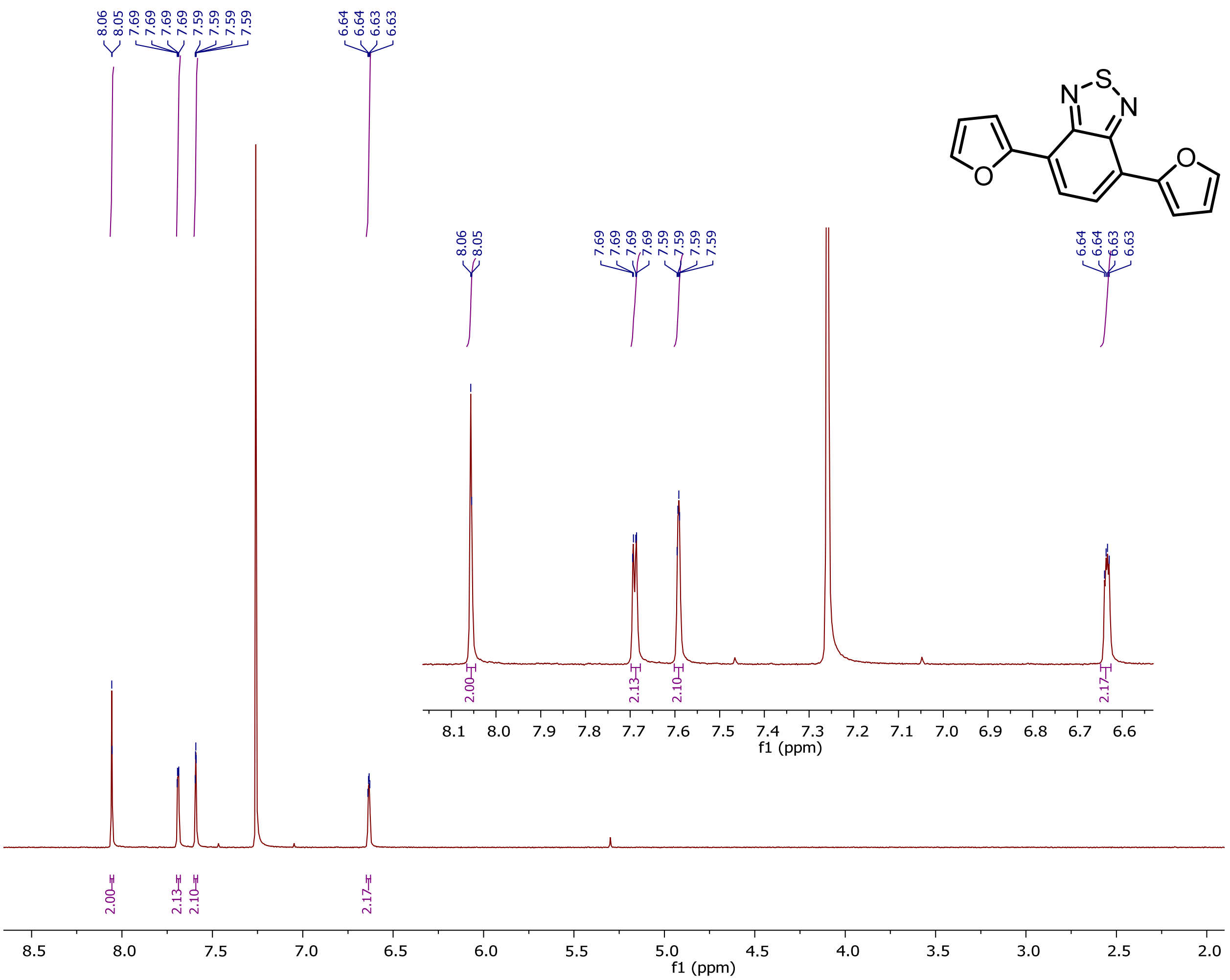


Figure SX. ^{1}H NMR spectrum of **BTD-F$_2$** (CDCl$_3$, 500 MHz).

GENERAL SUMMARY OF SOLID-STATE POLYMER CHARACTERIZATION

X-ray Photoelectron spectra (XPS) of the samples were obtained on samples deposited on FTO substrates. The samples were cleaned with acetone and dried in a vacuum oven at 50°C prior to obtaining XPS, ultra violet-visible (UV-vis) spectra and scanning electron microscopy (SEM) images to remove any residual solvents. X-ray photoelectron spectroscopy (XPS) analysis of the polymers were carried out using a vacuum generator scientific 100 mm hemispherical analyser and a physical electronics Mg Kα X-ray source operating at 280 W. Peaks obtained for S, N, C and O atoms were de-convoluted with CASA XPS software. SEM images were obtained with a FEG Quanta 450 FEG Electron Microscope, operated at an acceleration voltage of 5 kV. A low acceleration voltage of 5 keV was chosen since polymers usually undergo burning when highly energetic electrons are incident on them at high acceleration voltages of 10 keV or 20 keV normally used for robust inorganic materials. Energy Dispersive X-ray Spectra (EDS) and elemental maps were obtained with an X-Max^{N} 50 spectrometer (Oxford Instrument) mounted on the SEM. UV−vis−NIR spectra were measured with a Cary 5000 spectrophotometer on the samples deposited on FTO substrates. Solid-state Raman and fluorescence emission spectra were obtained using a LabRAM HR Evolution spectrometer with a 532 nm laser as the excitation source. Fluorescence emission spectra were acquired using a 600 grooves/mm grating; higher resolution Raman spectra were collected using an 1800 grooves/mm grating. Simulated Raman spectra were calculated for BTDF$_2$ and BTDT$_2$ using the Gaussian 09 software package with the B3LYP method and the 6-311+G(*d*,*p*) basis set.

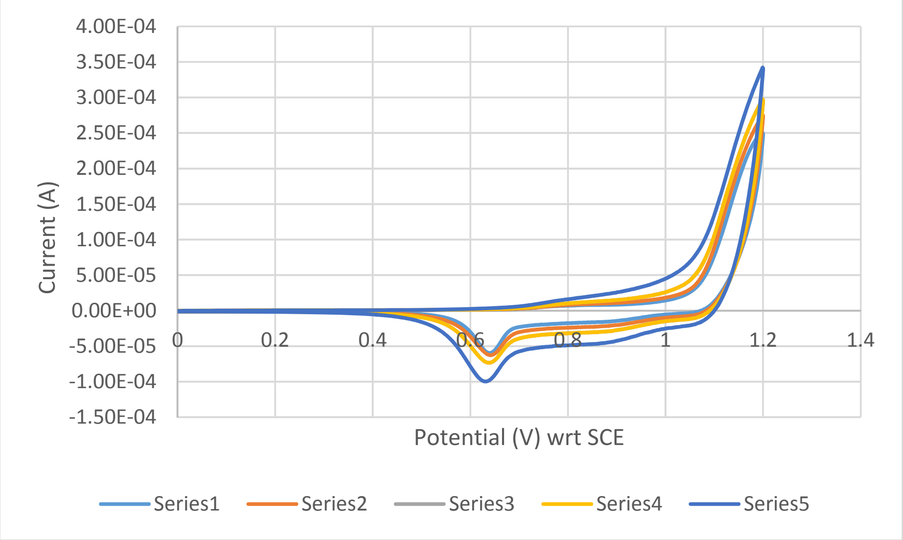
All electrochemical experiments including AC impedance analysis were carried out using CH Instruments CHI6109E Electrochemical Analyser upgraded to include AC Impedance Analysis. FTO slides were purchased from Sigma and all other electrodes from CH Instruments: Electrodes used are Saturated Calomel Reference Electrode (SCE) CHI150, Glassy carbon (GC) Working Electrode CHI104 and Pt-wire Counter Electrode CHI115. SCE was rinsed thoroughly with distilled water, wiped with paper tissue. GC was polished using 0.05 micron alumina powder on CHI polishing pad. Pt-wire CE was cleaned with conc. nitric acid and rinsed thoroughly with distilled water and air dried. In the electrocopolymerization for BTDT$_2$ and BTDF$_2$ taken in desired millimolar ratio of m:n and dissolved in acetonitrile containing 0.1 mol dm-3 tetrabutylammonium hexafluorophosphate background electrolyte (BGE). The 10.0 mL solution was purged with high purity argon gas for 30 min prior to study. The one-compartment cell consists of 3-electrodes: glassy carbon (GC) or fluoride-doped tin oxide coated glass (FTO, Sigma Sheet resistance < 1 Ω cm-2) working electrode (WE), Pt-gauze counter electrode (CE) and saturated calomel reference electrode (SCE, all potentials reported here are wrt SCE unless otherwise stated).

SI-II: ELECTROCHEMICAL DATA FOR HOMO-POLYMERS AND 2:5 BLOCK CO-POLYMERS

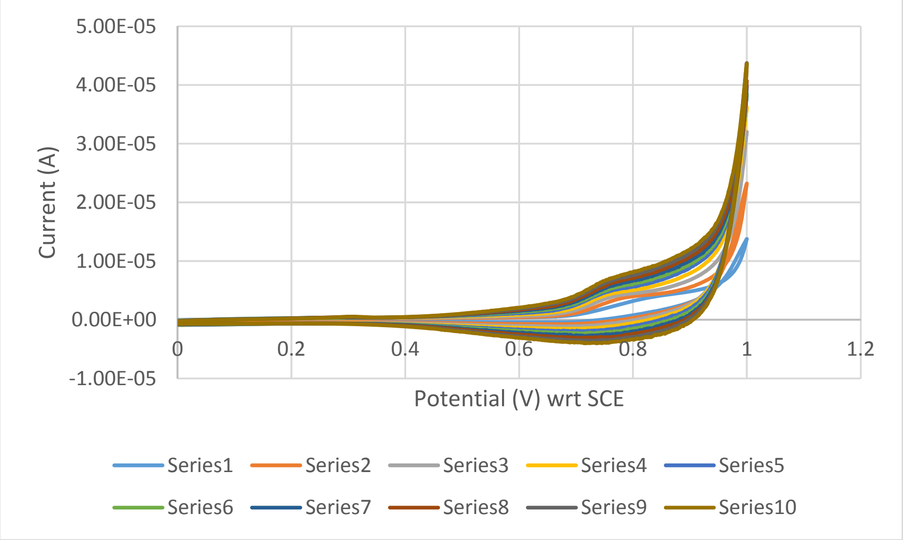
Electropolymerization of homo-polymers and 2:5 block copolymers

Successive CVs representing electropolymerization of $BTDT_2$, $BTDF_2$ and 2:5 mole ratio $BTDT_2$ and $BTDF_2$ in argon purged 0.1 mol dm^{-3} tetrabutylammonium hexafluorophosphate in acetonitrile electrolyte at 100 mV $s^{-}1$ scan rate. Three electrode configuration: Glassy carbon working electrode, saturated calomel reference electrode and Pt counter electrode. Monomer concentration used in homopolymerformation is 5 mmol dm^{-3}. For the preparation of 2:5 molar ratio copolymer 2 mmol dm^{-3} $BTDT_2$ and 5 mmol dm^{-3} $BTDF_2$ were used.

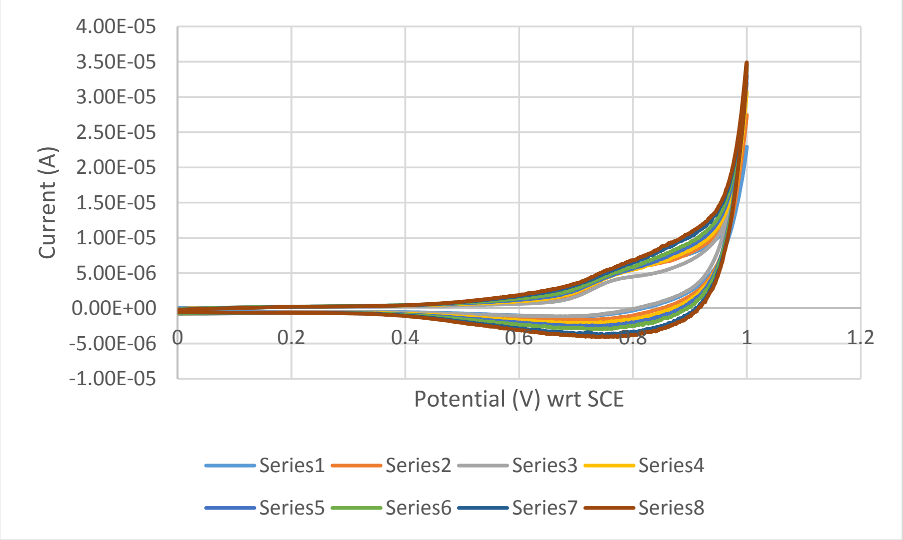
Electro-polymerization of $BTDT_2$



Electro-polymerization of $BTDF_2$



Electro-polymerization of $BTDT_2$ and $BTDF_2$ in 2:5 mole ratio

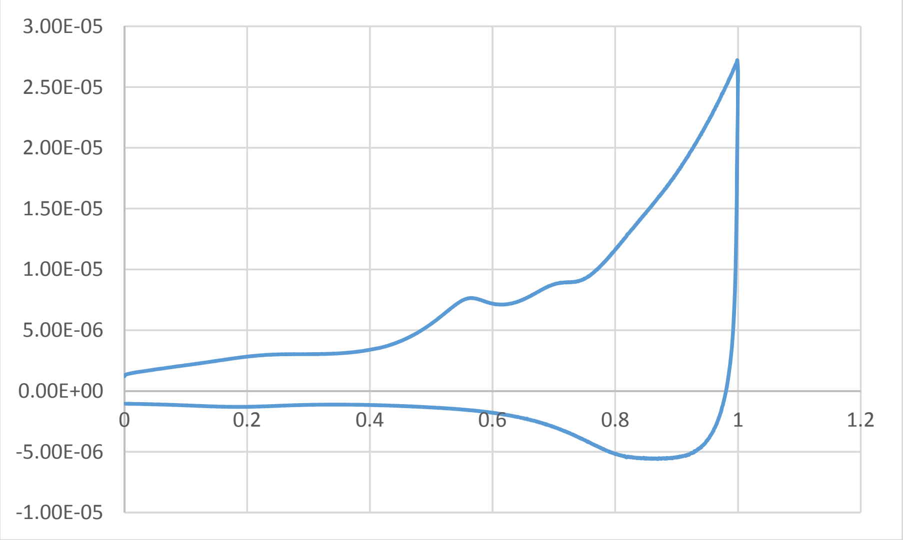


Electrochemistry of $BTDT_2$ and $BTDF_2$ homo-polymers

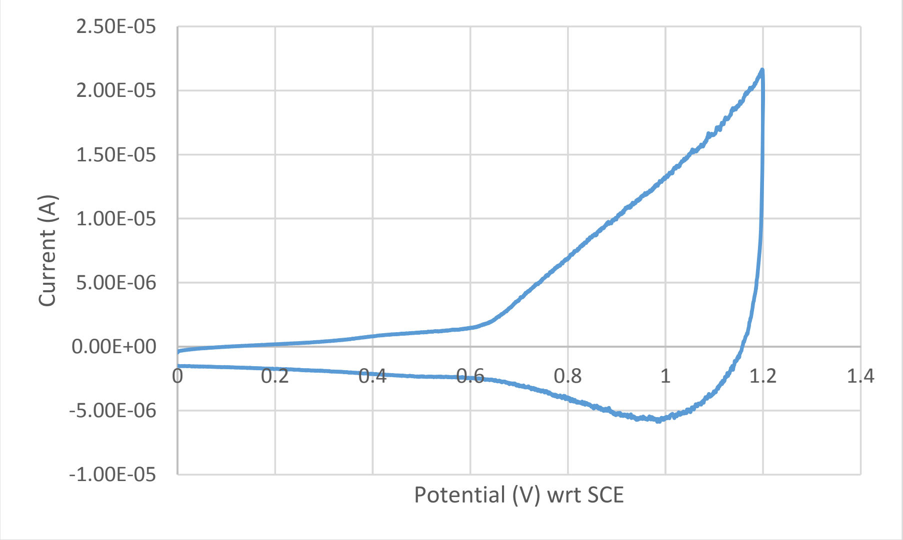
SI-IIa: In the positive potential range from 0 V wrt SCE

Note that similar behaviour of progressive charging of the polymer backbone as the potential is increased in the positive direction from 0 V wrt SCE and fast discharge of the supercapasitive behaviour of the polymer upon reversal of potential is observed in this potential range for both homopolymers and all copolymers synthesized in this work.

$BTDT_2$ homo-polymer

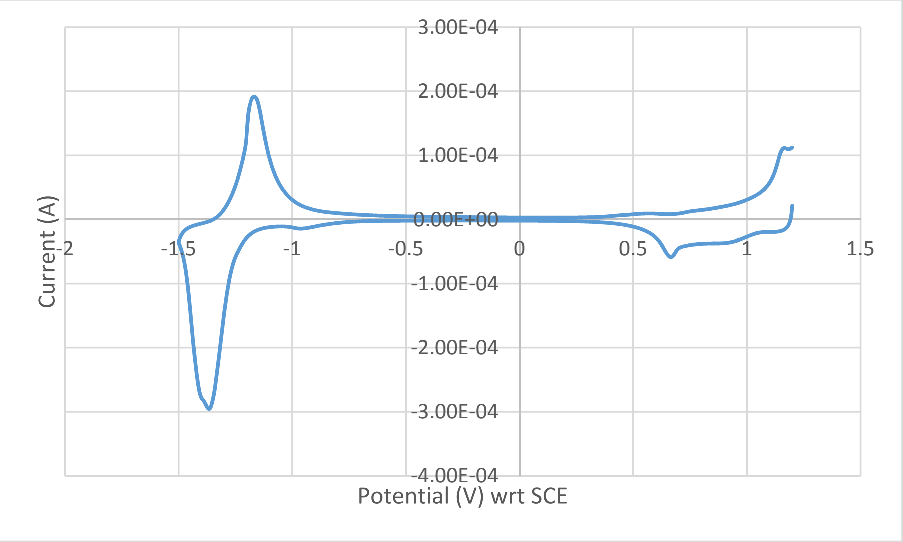


BTDF$_2$ homo-polymer



SI-IIb: CVs of homo-polymers from -1.5 V to + 1.2 V wrt SCE at 100 mV s^{-1}

BTDT$_2$ homo-polymer



Segment 1:

Ep = 0.665 V ip = -2.069e-5 A Ah =- 8.086e-6 C

Ep = -0.964V ip = -7.252e-6 A Ah = -7.097e-6 C

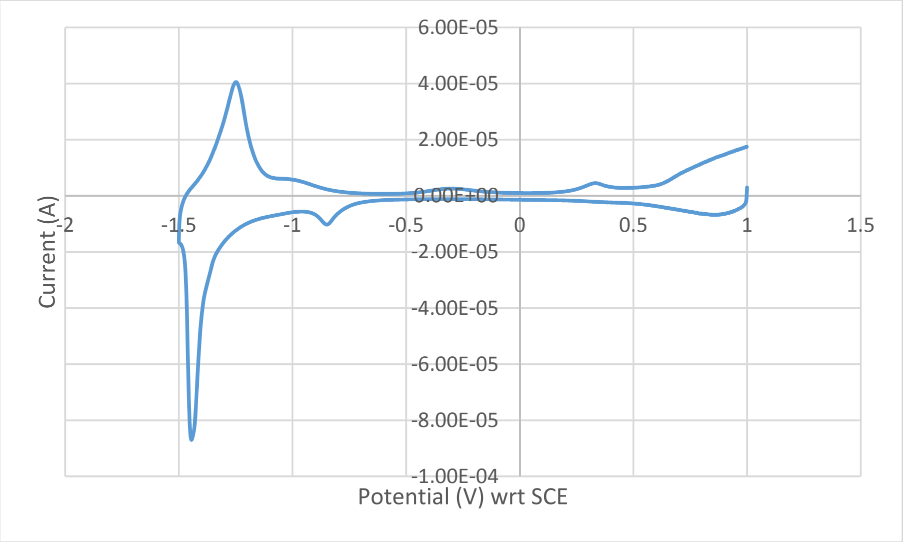
Ep = -1.366V ip = -2.659e-4 A Ah = -1.885e-4 C

Segment 2:

Ep = -1.167 V ip = 1.770e-4 A Ah = 1.096e-4 C

Note that in BTDT$_2$, BTD unit reduces at -1.336 V wrt SCE and that there is only one reduction peak between -1.0 V and -1.5 V. The peak at + 0.605 V corresponds to the first oxidation of the polymer which corresponds to the HOMO level. The corresponding reduction peak centred at -0.964 V corresponds to the LUMO level of the polymer. The HOMO-LUMO Gap is therefore 1.57 eV.

$BTDF_2$ homo-polymer



Segment 1:

Ep = -0.849 V ip = -7.599e-6 A Ah = -4.772e-6 C

Ep = -1.444 V ip = -6.818e-5 A Ah = -3.380e-5 C

Segment 2:

Ep = -1.248 V ip = 1.887e-5 A Ah = 1.246e-5 C

Ep = -0.300 V ip = 1.473e-6 A Ah = 1.575e-6 C

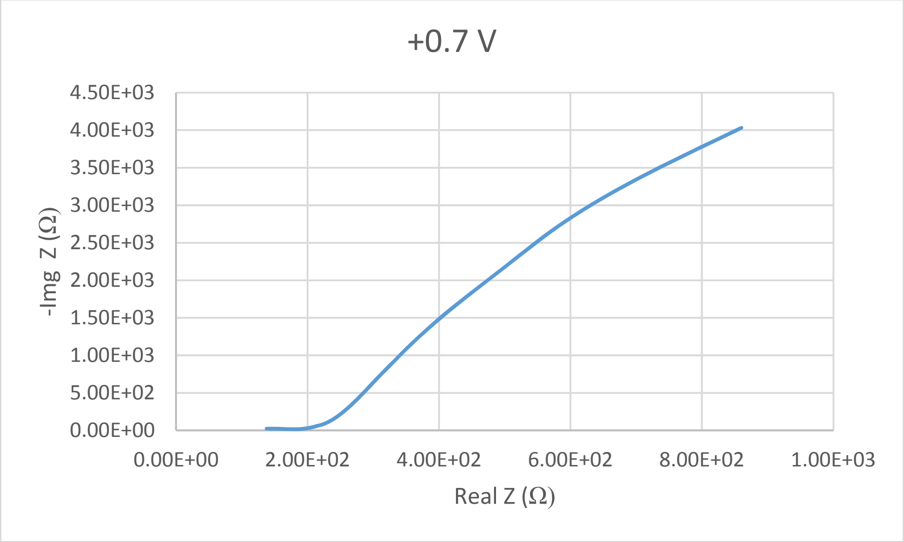
Ep = 0.331 V ip = 3.185e-6 A Ah = 2.313e-6 C

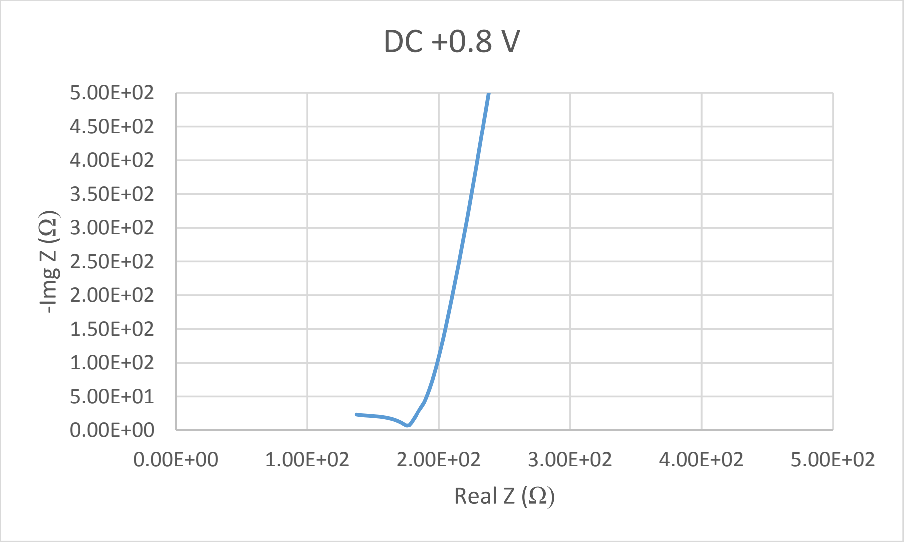
In $BTDF_2$, the BTD unit reduces at -1.444 V wrt SCE and that there is only one reduction peak between -1.0 V and -1.5 V. The HOMO level corresponds to the peak at +0.331 V and the LUMO level to -0.849 V peak. The HOMO-LUMO Gap is therefore, 1.18 eV.

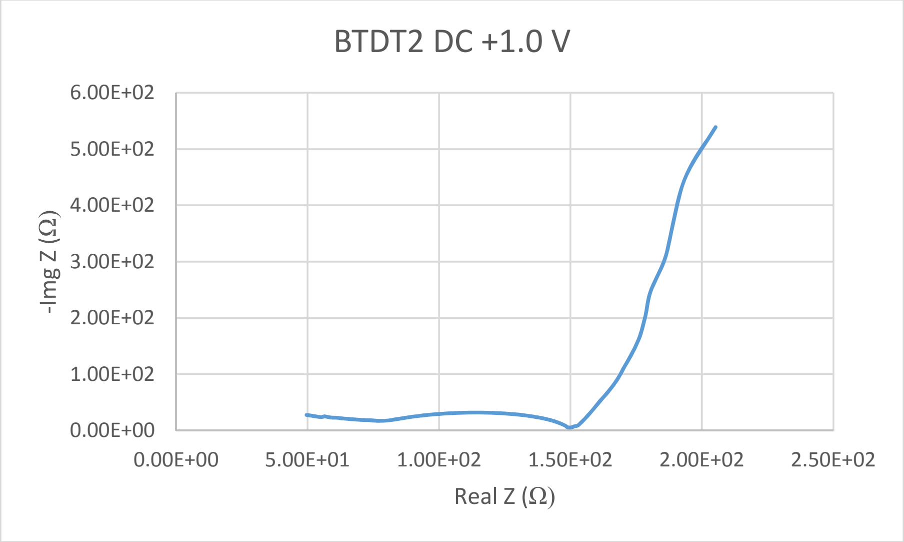
Note that there are two reduction peaks of equal size (peak current) in 1:1 $BTDT_2$-$BTDF_2$ polymer. Comparison of the BTD reduction peak positions of $BTDT_2$ and $BTDF_2$ suggest that in the copolymer the BTD reduction peak at less negative potential is due to the reduction of BTD unit attached to $BTDT_2$ and the other one at more negative potential is the reduction of BTD in $BTDF_2$ unit. Note also that in the other compositions used the ratio of the peak currents of the two reduction peaks correspond to the m:n ratio of the block copolymers $[(BTDT_2)_m(BTDF_2)_n]_p$ which is simply equal to the mole ratio of the two monomers used in copolymerization.

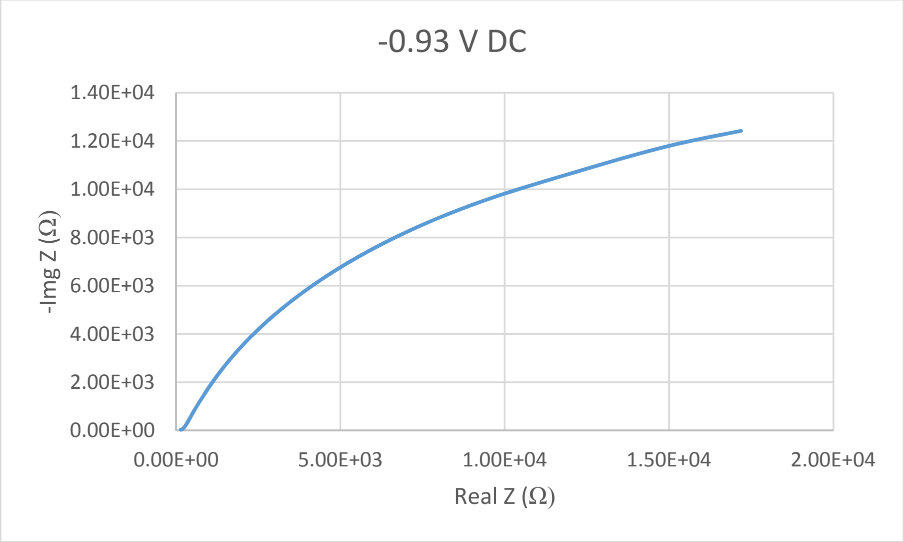
SI-IIc: AC Impedance Nyquist Plots at Different Applied DC Potentials wrt SCE for Two Homo-polymers, 1:1 Alternating Block Copolymer and 2:5 Block Copolymer

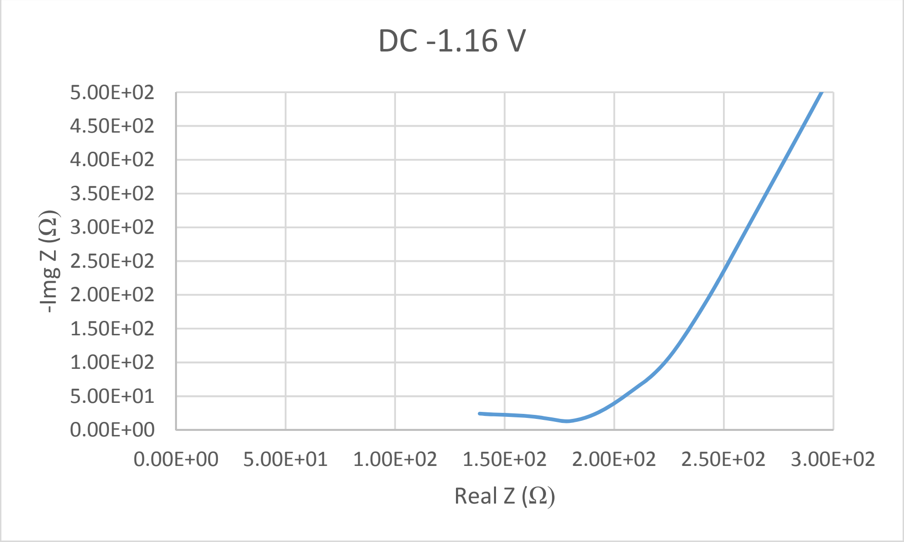
AC Impedance Data for BTDT$_2$ Homo-polymer






BTDT2 DC +1.0 V
6.00E+02
5.00E+02
4.00E+02
3.00E+02
2.00E+02
1.00E+02
0.00E+00
-Img Z (Ω)
0.00E+00
5.00E+01
1.00E+02
1.50E+02
2.00E+02
2.50E+02
Real Z (Ω)


-0.93 V DC
1.40E+04
1.20E+04
1.00E+04
8.00E+03
6.00E+03
4.00E+03
2.00E+03
0.00E+00
-Img Z (Ω)
0.00E+00
5.00E+03
1.00E+04
1.50E+04
2.00E+04
Real Z (Ω)


DC -1.16 V
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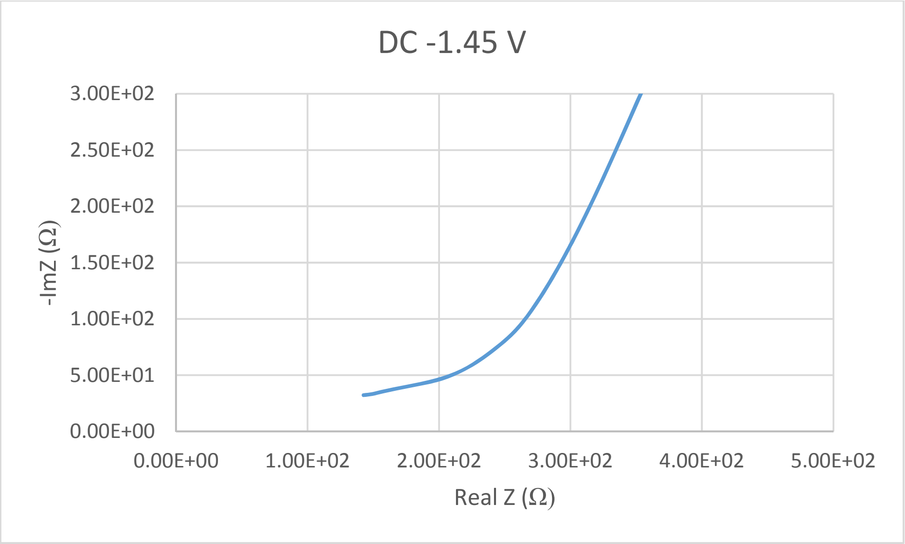
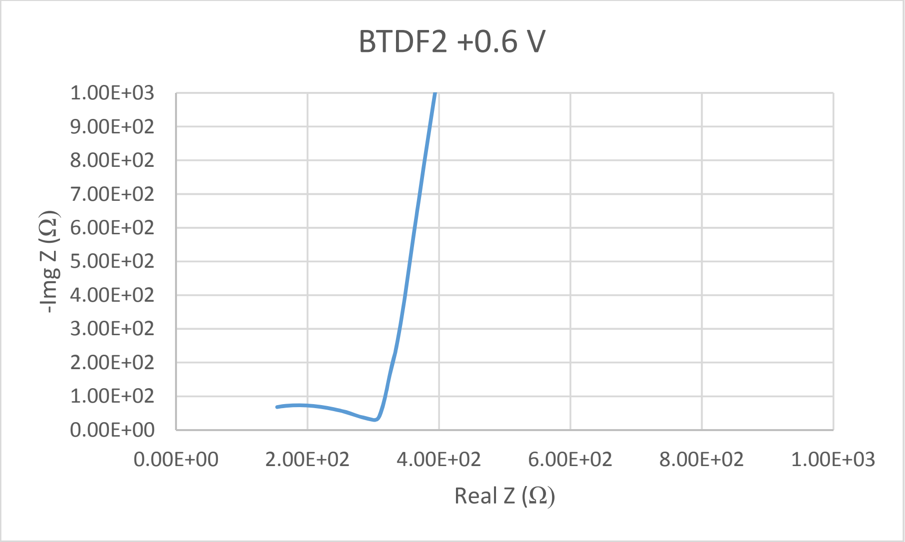
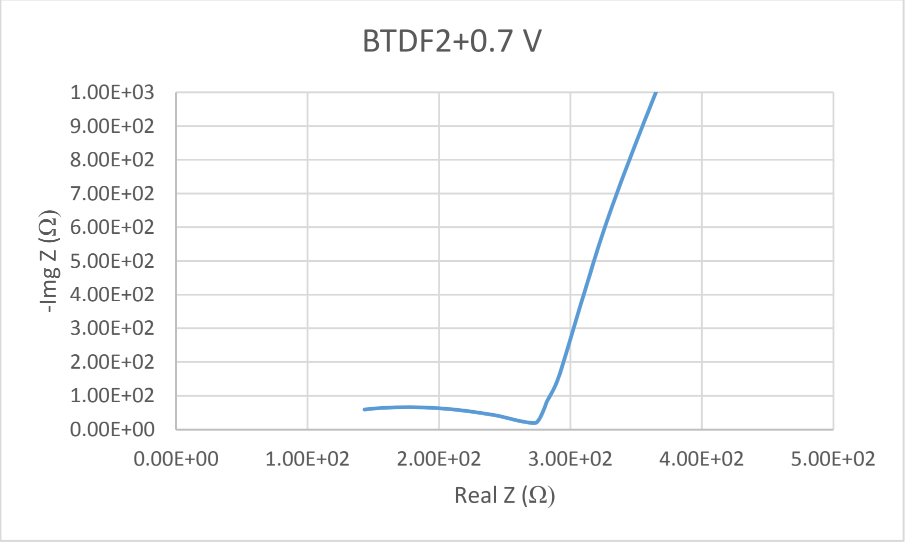
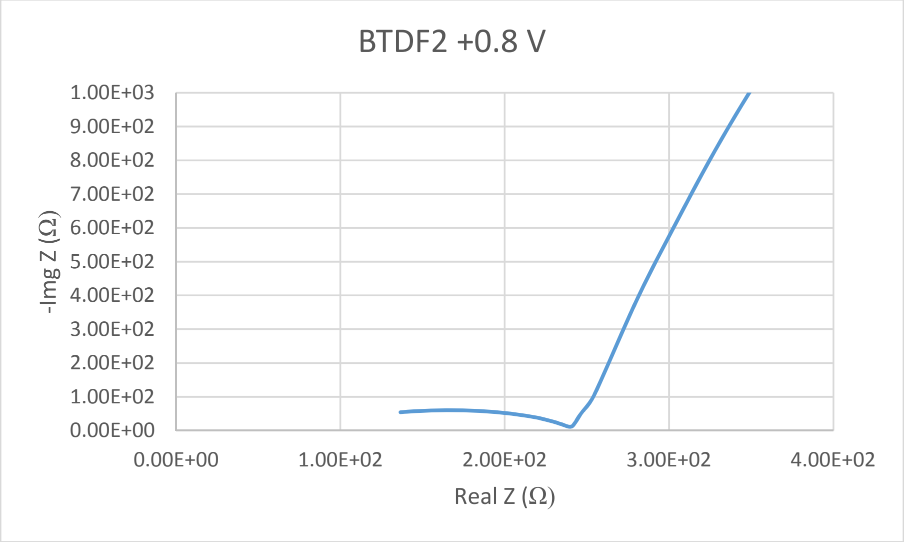
4.50E+02
4.00E+02
3.50E+02
3.00E+02
2.50E+02
2.00E+02
1.50E+02
1.00E+02
5.00E+01
0.00E+00
-Img Z (Ω)
0.00E+00
5.00E+01
1.00E+02
1.50E+02
2.00E+02
2.50E+02
3.00E+02
Real Z (Ω)



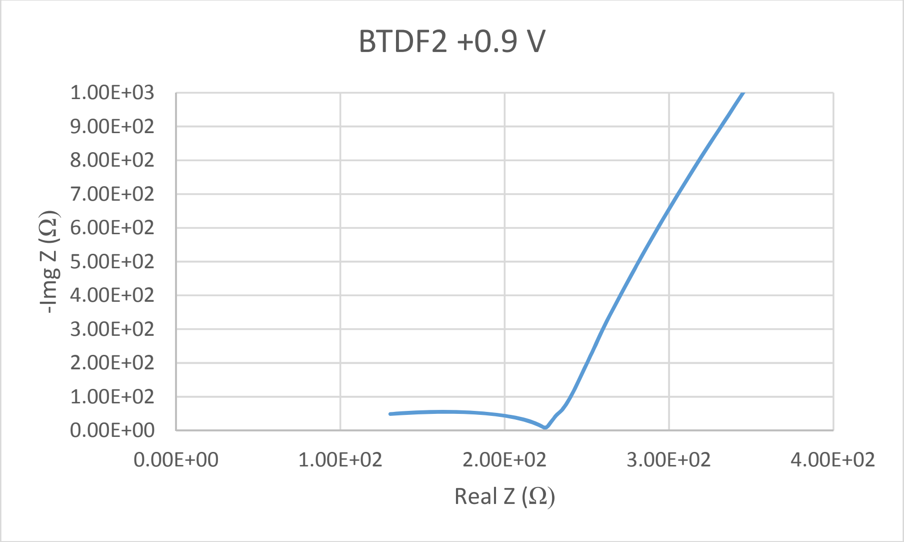
AC Impedance Data for BTDF$_2$ Homo-polymer







BTDF2 +0.8 V
-Img Z (Ω)
1.00E+03
9.00E+02
8.00E+02
7.00E+02
6.00E+02
5.00E+02
4.00E+02
3.00E+02
2.00E+02
1.00E+02
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
Real Z (Ω)



BTDF2 +0.9 V
-Img Z (Ω)
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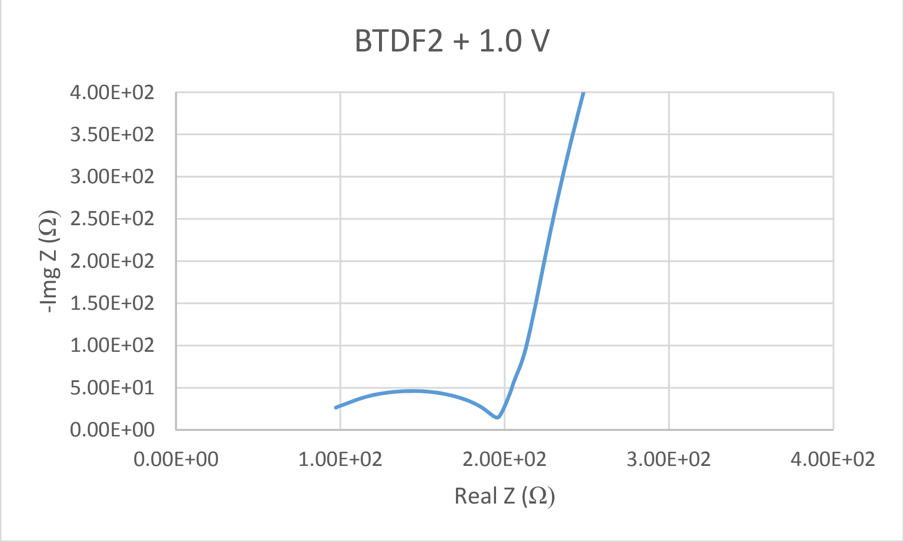
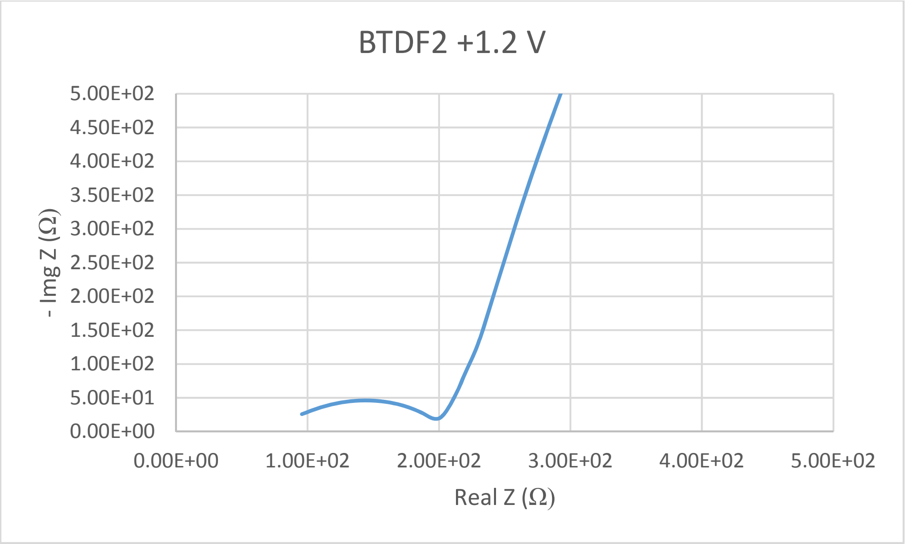
8.00E+02
7.00E+02
6.00E+02
5.00E+02
4.00E+02
3.00E+02
2.00E+02
1.00E+02
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
Real Z (Ω)



BTDF2 + 1.0 V
-Img Z (Ω)
4.00E+02
3.50E+02
3.00E+02
2.50E+02
2.00E+02
1.50E+02
1.00E+02
5.00E+01
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
Real Z (Ω)


BTDF2 +1.2 V
- Img Z (Ω)
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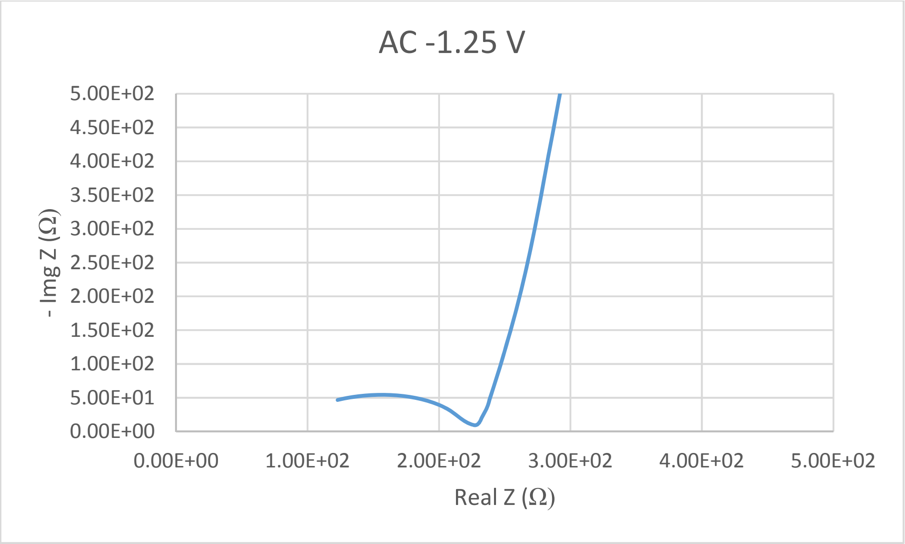
4.50E+02
4.00E+02
3.50E+02
3.00E+02
2.50E+02
2.00E+02
1.50E+02
1.00E+02
5.00E+01
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
5.00E+02
Real Z (Ω)


AC -1.25 V
- Img Z (Ω)
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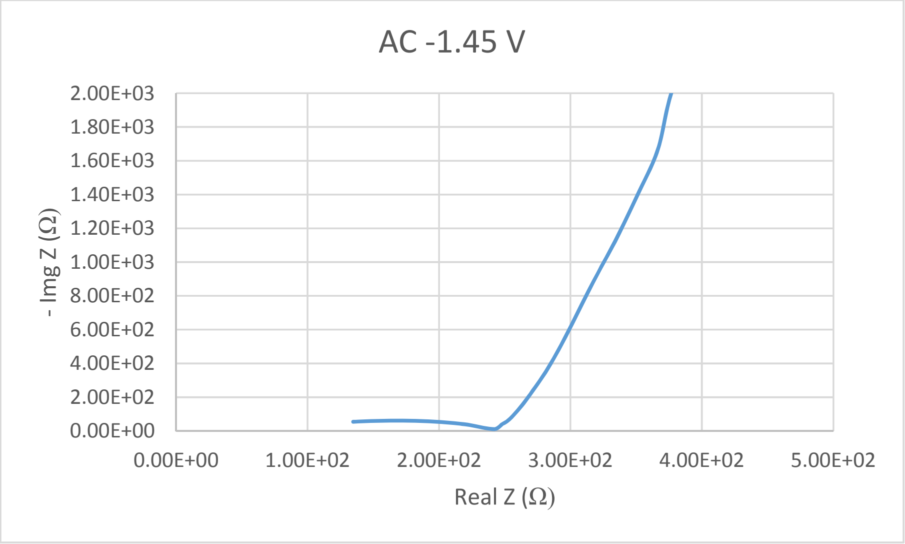
4.50E+02
4.00E+02
3.50E+02
3.00E+02
2.50E+02
2.00E+02
1.50E+02
1.00E+02
5.00E+01
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
5.00E+02
Real Z (Ω)


AC -1.45 V
- Img Z (Ω)
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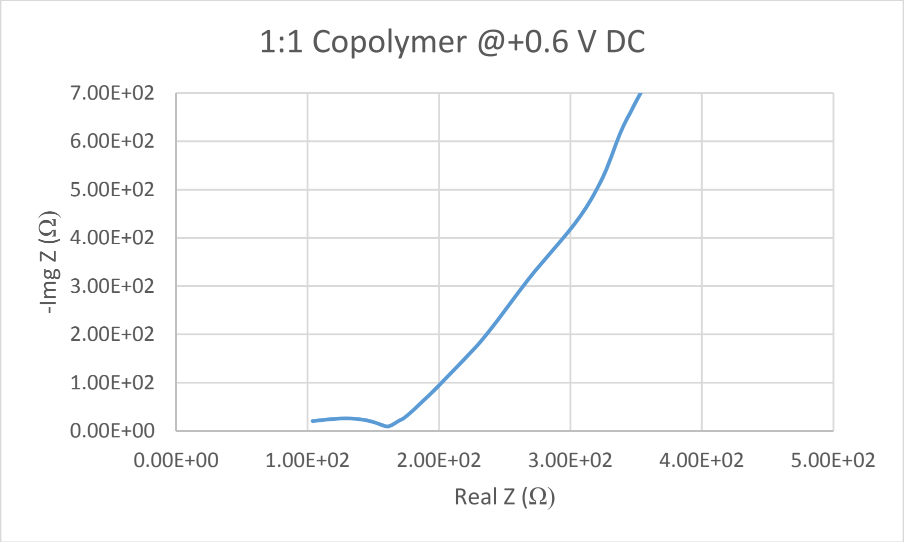
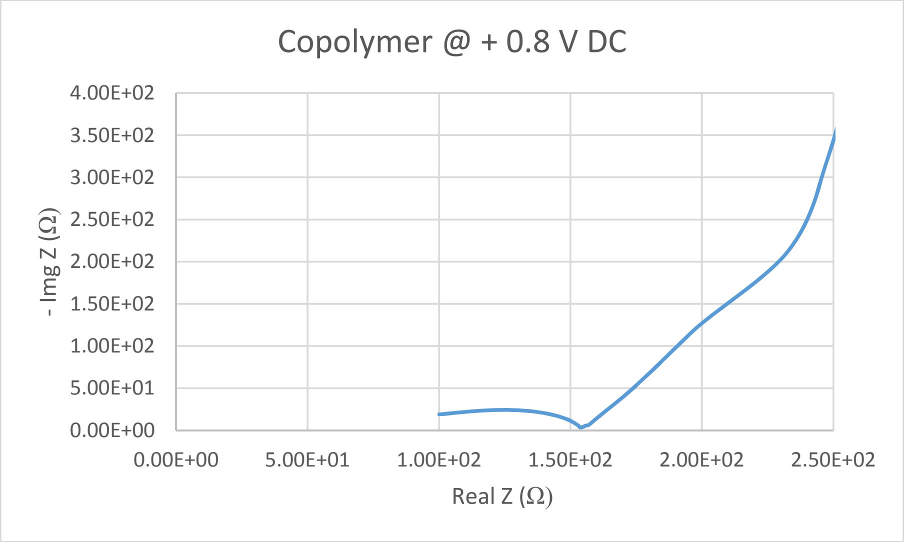
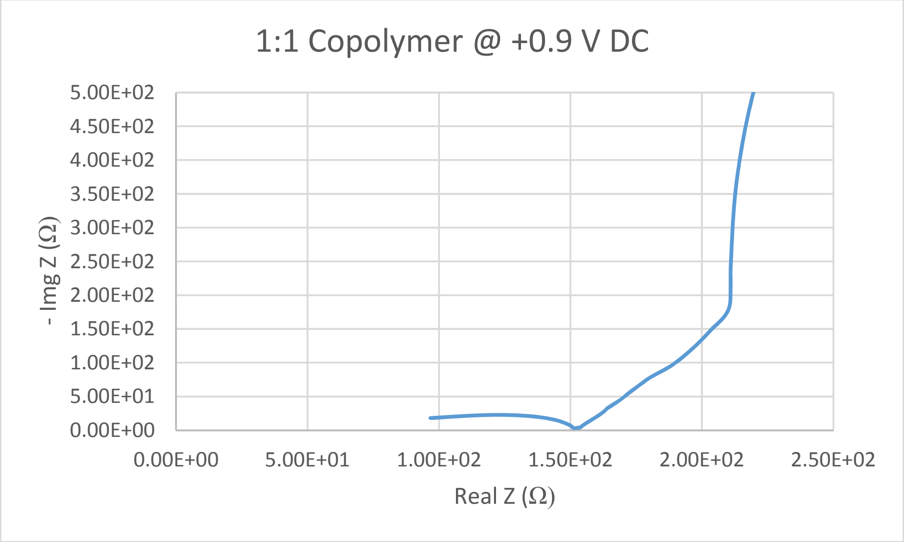
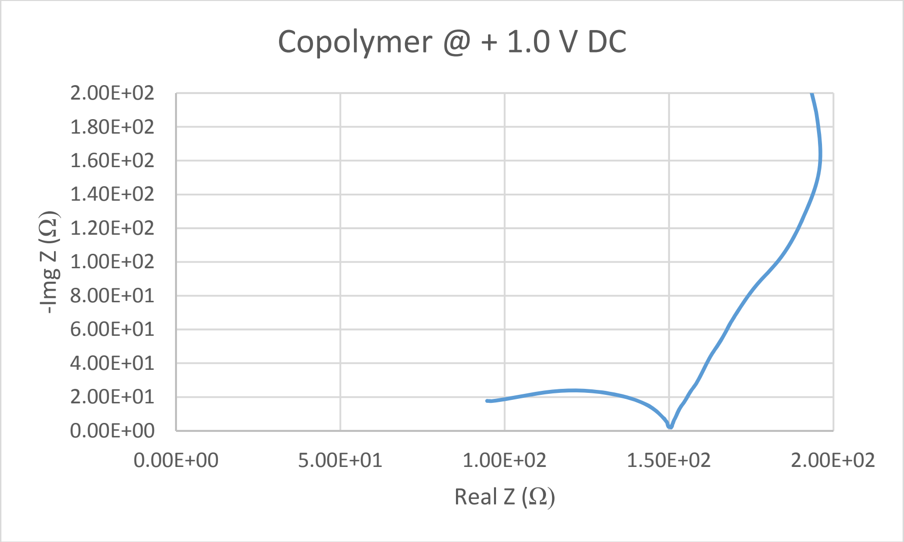
1.80E+03
1.60E+03
1.40E+03
1.20E+03
1.00E+03
8.00E+02
6.00E+02
4.00E+02
2.00E+02
0.00E+00
0.00E+00
1.00E+02
2.00E+02
3.00E+02
4.00E+02
5.00E+02
Real Z (Ω)

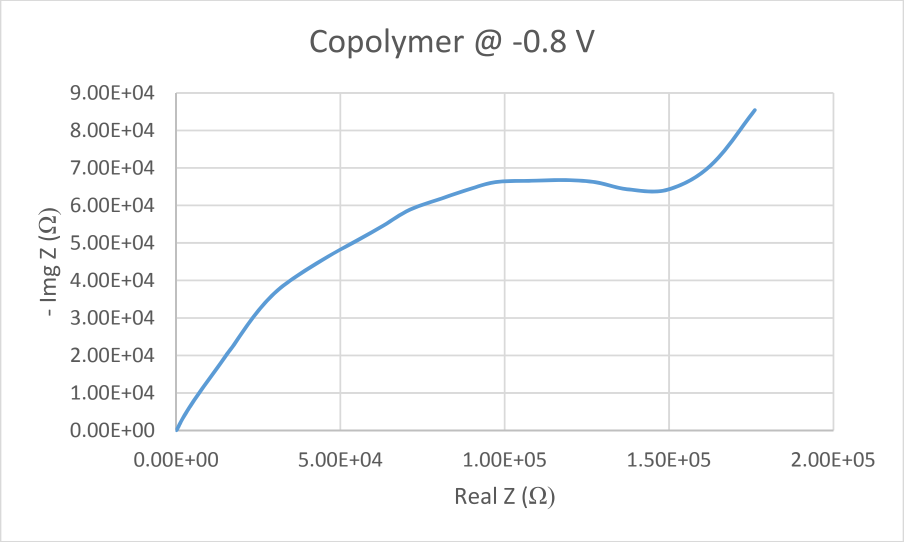
AC Impedance Data of 1:1 Copolymer

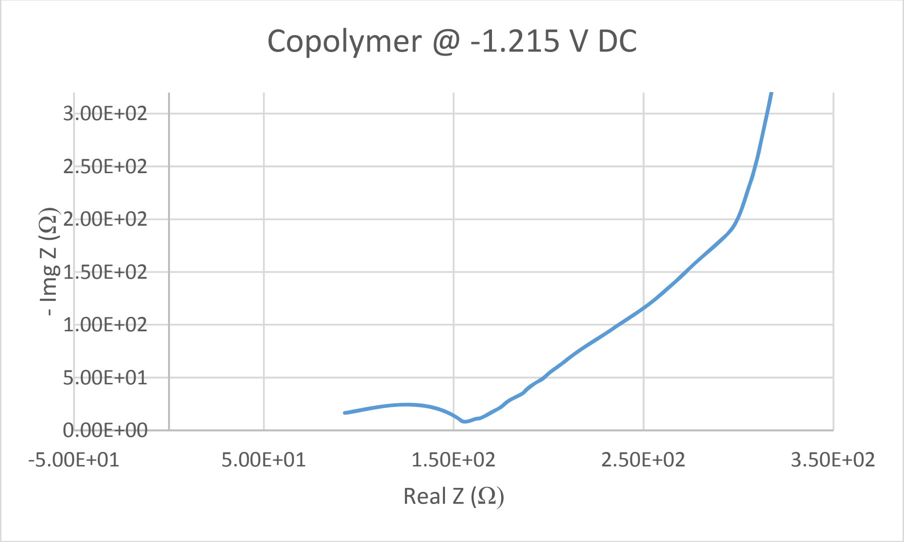


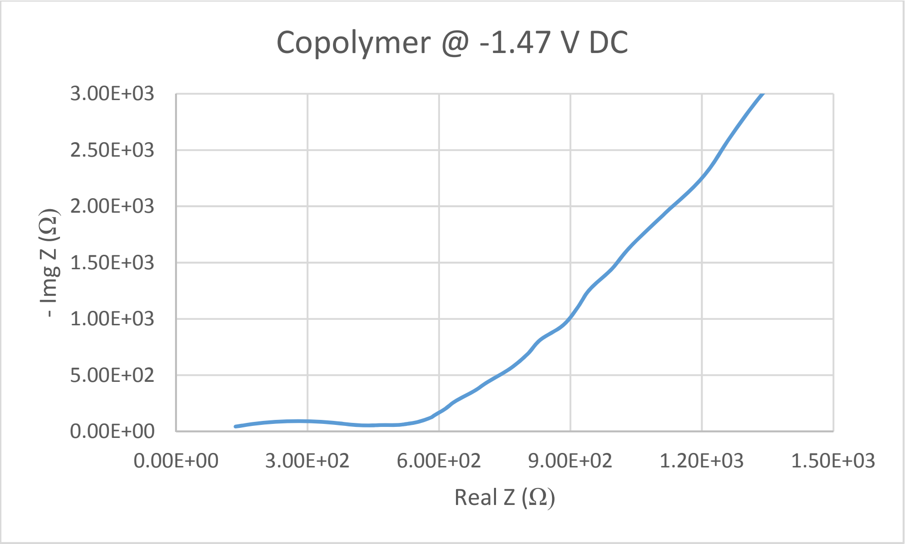




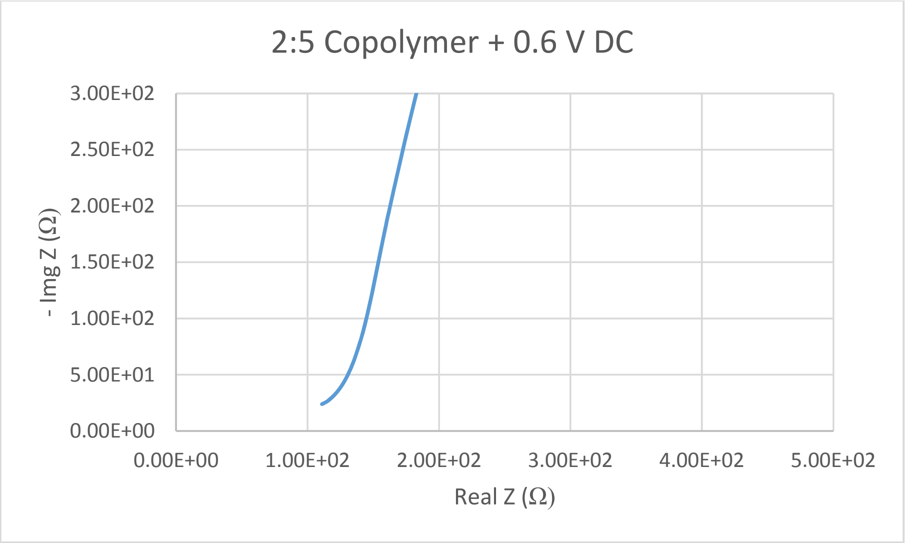

Copolymer @ + 1.0 V DC
2.00E+02
1.80E+02
1.60E+02
1.40E+02
1.20E+02
1.00E+02
8.00E+01
6.00E+01
4.00E+01
2.00E+01
0.00E+00
-Img Z (Ω)
0.00E+00
5.00E+01
1.00E+02
1.50E+02
2.00E+02
Real Z (Ω)

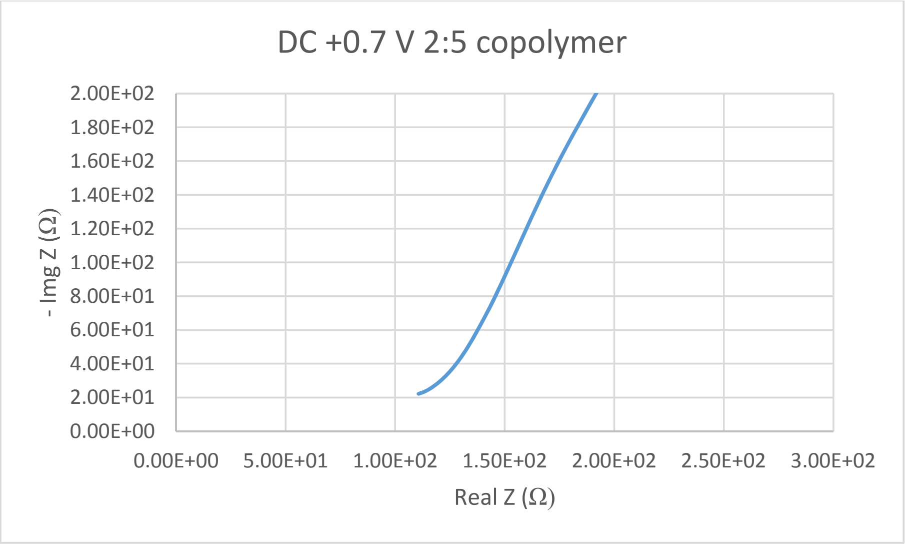

Copolymer @ -0.8 V
9.00E+04
8.00E+04
7.00E+04
6.00E+04
5.00E+04
4.00E+04
3.00E+04
2.00E+04
1.00E+04
0.00E+00
- Img Z (Ω)
0.00E+00
5.00E+04
1.00E+05
1.50E+05
2.00E+05
Real Z (Ω)

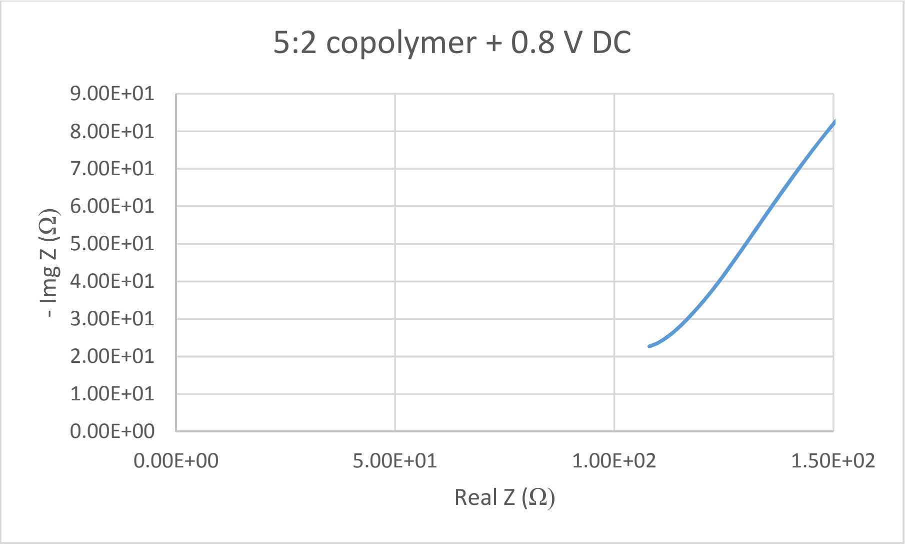

Copolymer @ -1.215 V DC
3.00E+02
2.50E+02
2.00E+02
1.50E+02
1.00E+02
5.00E+01
0.00E+00
- Img Z (Ω)
-5.00E+01
5.00E+01
1.50E+02
2.50E+02
3.50E+02
Real Z (Ω)



AC Impedance data of BTDT2:BTDF2 2:5 Block Copolymer






5:2 copolymer + 0.8 V DC
9.00E+01
8.00E+01
7.00E+01
6.00E+01
5.00E+01
4.00E+01
3.00E+01
2.00E+01
1.00E+01
0.00E+00
- Img Z (Ω)
0.00E+00
5.00E+01
1.00E+02
1.50E+02
Real Z (Ω)

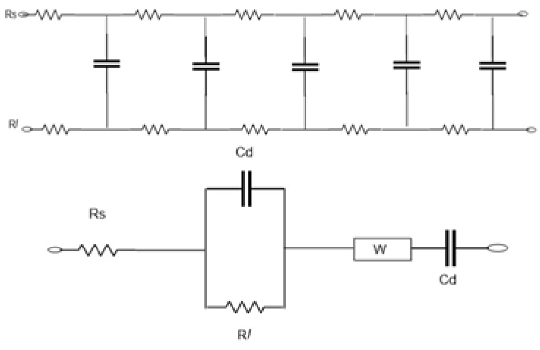
SI-Table 1: Resistance values for electron (R_e) and ion (R_I) transport of homo- and co-polymers at selected DC bias potentials.

BTDT2 Homo-polymer

Applied DC potential (V) vs SCE	**R_e (Ω)**	**R_I(Ω)**
+ 0.7	>1 M Ω	>1 M Ω
+0.8	52	14
+ 1.0	70	13
-0.93	>1 M Ω	>1 M Ω
-1.16	100	4
-1.45	100	75
BTDF2 Homo-polymer		
+0.6	209	27
+0.7	170	7
+0.8	140	5
+0.9	101	5
+1.0	105	6
+1.2	102	6
-1.25	100	5
-1.45	120	24
1:1 BTDT2:BTDF2 Copolymer		
+0.6	50	33
+0.8	62	29
+0.9	59	20
+1.0	70	27
-0.8	> 1 MΩ	> 1 MΩ
-1.215	80	33
1.47	380	133
2:5 BTDT2:BTDF2 Copolymer		
+0.6	10	8
+0.7	9	9
+0.8	8	9
-1.5	200	105

Note that copolymers have much lower resistance for electron transport along the polymer backbone than those of homo-polymers. Ion ingress and egress through diffusion in and out the polymer also appear to be more efficient in the copolymer than the respective homo-polymers. The copolymer also shows electro-activity in a wider potential range than the homo-polymers possibly due to possession of more charge carriers in the copolymer than in homo-polymers. The XPS analysis described below shows that the copolymer indeed possesses more charge carriers than respective homo-polymers.

Dual rail transmission line circuit (top) and simplified equivalent circuit (bottom) used to extract data are also shown. [1, 2]



SI-III: XPS Analysis

SI-Table 2: XPS data of S2p and N1s regions of $BTDT_2$ and $BTDF_2$ monomers, $BTDT_2$ and $BTDF_2$ homo-polymers and 1:1 mole ratio $BTDT_2$:$BTDF_2$ p-type and n-type copolymer (N_{quat} refers to N atoms from quaternary ammonium salt).

Sample	**S (eV)**		**S %**	**N 1s (eV)**	**N %**	**N 1s $_{quat}$**	**N_{quat}%**
	$2p_{3/2}$	$2p_{1/2}$					
$BTDT_2$	164.3	165.5	69	399.4	51.0		
	165.0	166.3	31				
$BTDF_2$	165.1	166.2		399.6	74.8		
$BTDT_2$ homopolymer	164.8	166.0	32.0	399.0	64.0	401.8	6.0
	165.2	166.4	68.0				
$BTDF_2$ homopolymer	165.7	166.9	100	399.4	42.8	401.8	4.1
1:1 –ve copolymer	165.0	166.2	52	399.4	60	402.3	18
	166.0	167.2	48	397.9	22		
1:1 +ve copolymer	165.2	166.4	53	399.4	59.0	402.3	15
	165.8	167.0	47	398.8	26.0		

In pure $BTDT_2$ and $BTDF_2$ monomers, N-1S appear at 399.4 eV and 399.6 eV, respectively. These peak positions are very close to each other and hence it N atoms in BTD unit in $BTDT_2$ and $BTDF_2$ seem to be at approximately the same electronic environments. $BTDT_2$ monomer contains S in two different electronic environments. Since BTD unit has accepted electrons from T unit S in BTD unit should appear at a lower binding energy than S in thiophene unit. Therefore, in the $2Sp_{2/3}$ electronic state, peaks at 164.3 eV and 165.0 eV should correspond to the binding energies of BTD S and thiophene S, respectively. Those in $2p_{1/2}$ state are 165.5 eV and 166.3 eV, respectively. $BTDF_2$ monomer has S in only one electronic environment $2p_{3/2}$ and $2p_{1/2}$ states at 165.1 eV and 166.2 eV, respectively, which is the S in BTD unit of $BTDF_2$. This S in the BTD unit of $BTDF_2$ appears at higher binding energies than that in the BTD unit of $BTDT_2$ suggesting that the former is in a more oxidized state than the latter.

All polymers contain quaternary ammonium ions. All the homopolymers are in their p-state and 1:1 copolymer in both p-and n-states are provided. All these polymers contain appreciable amounts of quaternary ammonium cations. Interestingly, the copolymer in both states have more quaternary ammonium ions than both homo-polymers. This indicates that the copolymer takes up more ions from solution than both homo-polymers. The copolymer was synthesized at positive potentials and the polymer deposited GC electrode was cycled in the negative potential range from -1.0 V to -1.5 V wrt SCE to make it n-type. In this case, the n-type copolymer should contain more negative charge carriers than the p-type copolymer and hence should take up more quaternary ammonium cations as observed experimentally from the above XPS data. Even the p-type polymers contain appreciable amounts of quaternary ammonium cations. This indicates $BTDT_2$ and $BTDF_2$ homo-polymers and the copolymer formed at positive potentials are polarized to have positive and negative ends and accompany ions from the solution to counterbalance the charges. The higher electrical conductivities observed for the copolymer when compared to homo-polymers (SI-Table 1) is therefore due to the presence of higher number of charge carriers as revealed by XPS data (SI-Table 2).

In summary, XPS analysis of these materials confirm that the copolymer indeed contains both $BTDT_2$ and $BTDF_2$ units and higher number of charge carriers than those present in the respective homo-polymers. Results are in good agreement with those obtained from CV and AC impedance analyses.

CVs show improved currents in the copolymer than in homo-polymers at a wider range of potentials indicating that the copolymer is conducting over a wider potential range than the respective homo-polymers. This is corroborated by the low resistance values obtained for electron transport along the polymer backbone in the copolymer than those in homo-polymers in AC impedance experiments. As such, the copolymers have improved electrical properties than both homopolymers.

XPS Fitting

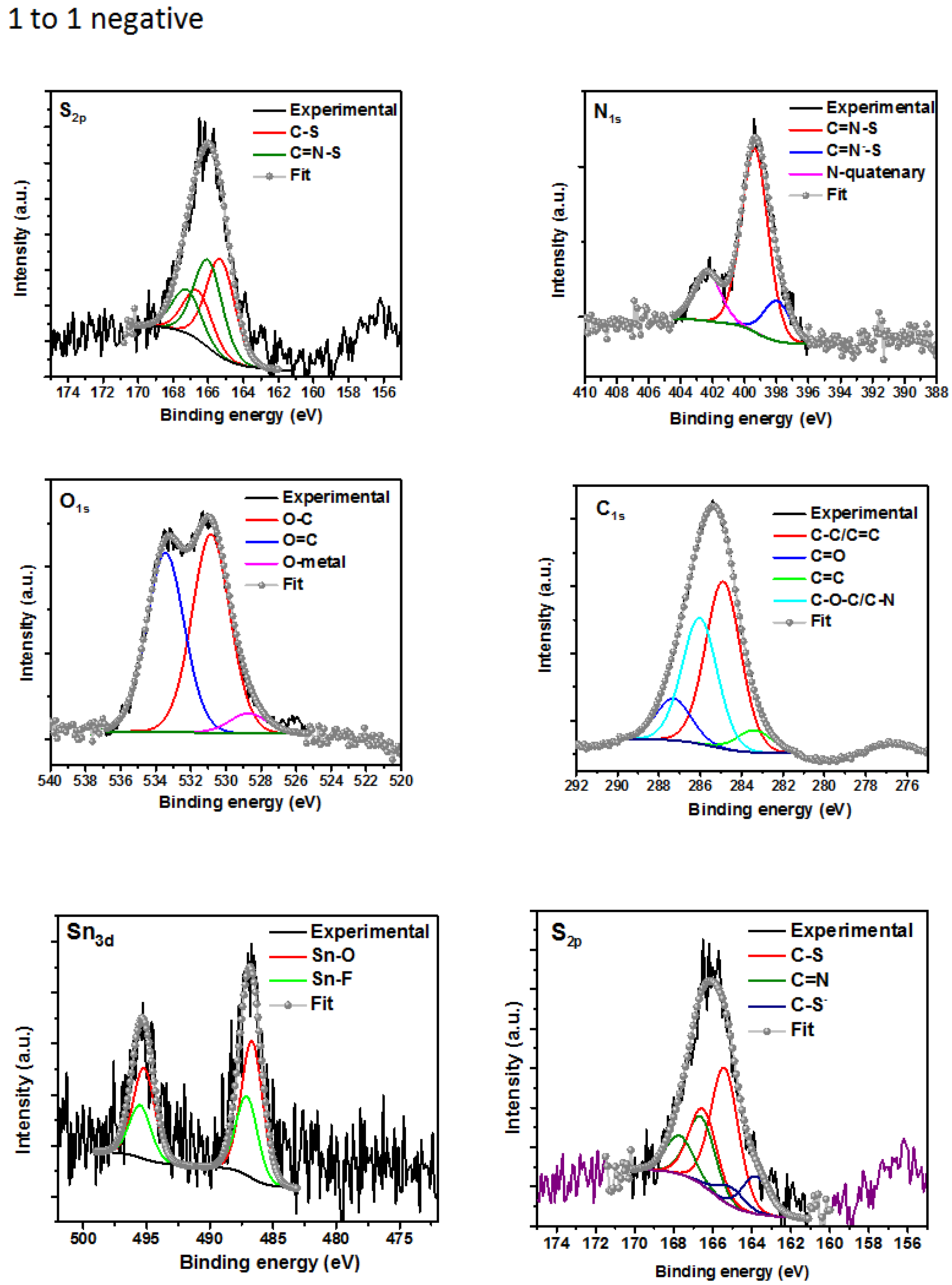


Figure S3. XPS fitting for 1:1 n-type copolymer

1 to 1 positive

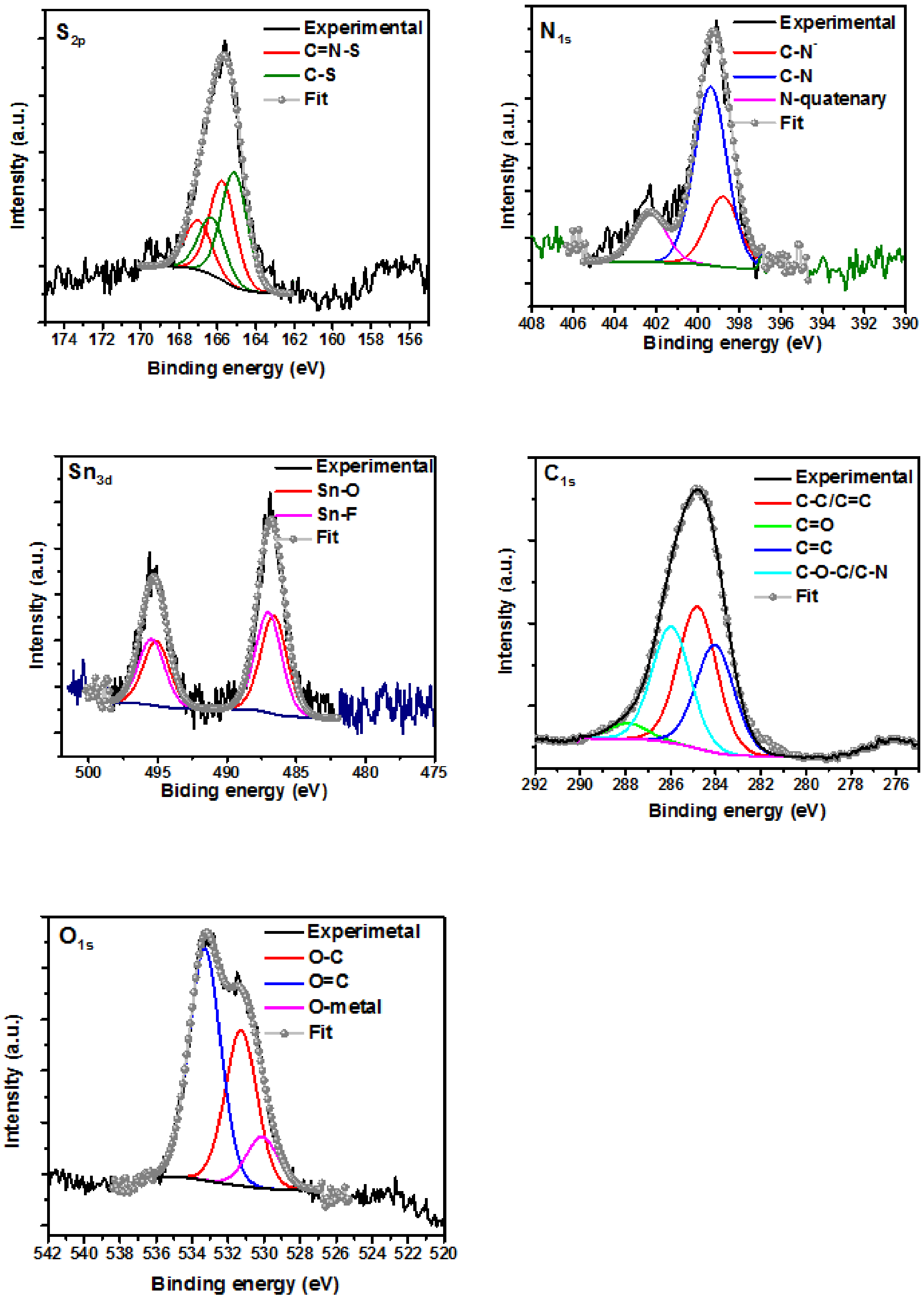


Figure S4. XPS fitting for 1:1 p-type copolymer

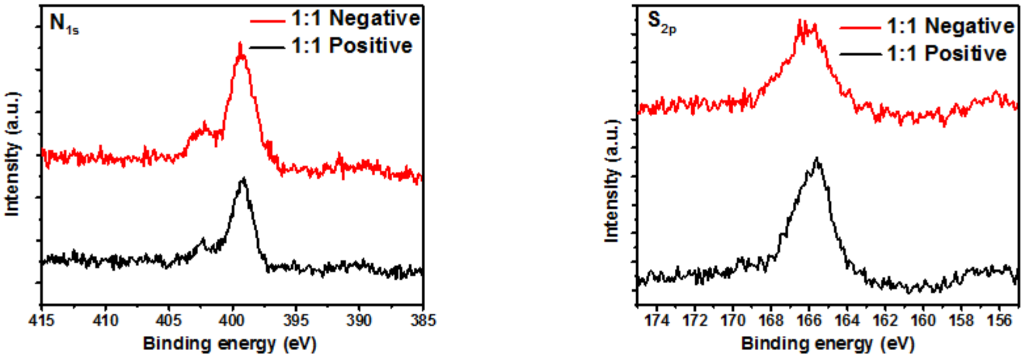


Figure S5. XPS fitting for 1:1 copolymer

In the copolymer, N is present in two different electronic environments in both p-type and n-type copolymers. In the p-type the two binding energies are 399.4 eV and 398.8 eV while those in the n-type are 399.4 eV and 397.9 eV, respectively. As evident from monomers and homo-polymers, N in the BTD unit of BTDF$_2$ is more polarized as N$^{\delta-}$S$^{\delta+}$ than that in BTDT$_2$. Therefore, the higher binding energy of 399.4 eV could be assigned for N in the BTD units of BTDT$_2$. This position is the same as that in BTDT$_2$ monomer and is slightly higher than that in BTDT$_2$ homo-polymer (399.0 eV). Peaks appearing at lower binding energies are those due to electron rich atoms and hence N in BTD in BTDF$_2$ units seems be richer in electrons than the BTD in BTDT$_2$ units. As such, peaks at binding energies of 398.4 eV and 397.9 eV, respectively, can be assigned to be N in BTD of BTDF$_2$ units of p- and n-type copolymers. Note that this N appears at much lower binding energies than that in BTDF$_2$ homo-polymer and BTDF$_2$ monomer indicating that BTD units in BTDF$_2$ are highly polarized as N$^{\delta-}$S$^{\delta+}$ than those in the respective homo-polymer and monomer.

Although BTD S 2p$_{3/2}$ in the copolymer appears at the same binding energy (165.2 eV in p-type and 165.0 eV in n-type) as that in BTDF$_2$ monomer (165.1 eV) it is slightly higher than that in BTDT$_2$ homo-polymer (164.8 eV) and lower than that in BTDF$_2$ homo-polymer (165.7 eV) suggesting that BTD S in other polymers are in more reduced environment than that in BTDF$_2$ homopolymer. Interestingly, thiophene S in both p- (165.5 eV) and n-type (166.0 eV) copolymers are at higher binding energies than those in BTDT$_2$ homopolymer (165.2 eV) and monomer (165.0 eV). This suggests that in the copolymer more electrons are withdrawn from thiophene units to BTD units than that in the homopolymer and the monomer thus giving rise to higher positive charge on thiophene units. This fact is also in line with other observations described above where the copolymer has a much higher charge separation than the copolymers and monomers thus giving rise to increased number of charge carriers to have higher electrical conductivity. The same argument can be made by comparing the binding energies of S in 2p$_{1/2}$ state.

BTDT$_2$ homo-polymer

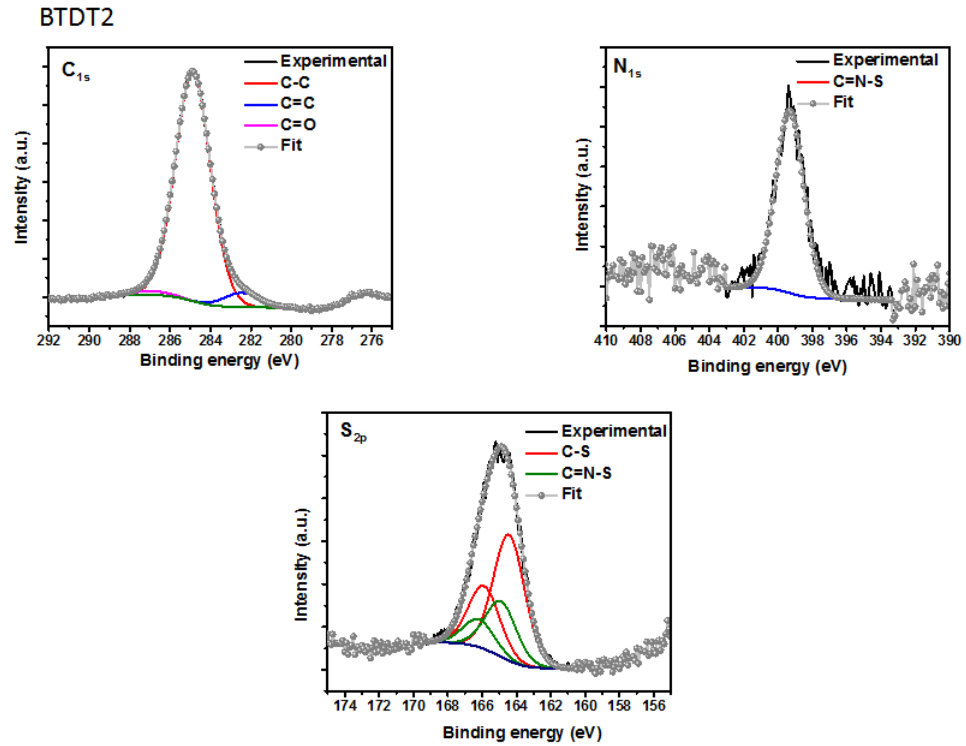


Figure S6. XPS fitting for homopolymer

In the BTDT$_2$ homopolymer, N appears at slightly lower binding energy (399.0 eV) than BTDT$_2$ monomer (399.4 eV) because N is in slightly reduced form due to electron withdrawal from thiophene units on either sides in the repetitive units of the polymer. In BTDF$_2$ N appears at binding energy 399.4 eV and is also at a slightly lower value than that of BTDF$_2$ monomer (399.6 eV) indicating that BTD units are richer in electrons in polymers than their corresponding monomers. In BTDT$_2$ homopolymer, S appears at two electronic environments; one at lower binding energy (164.8 eV in S 2p$_{3/2}$ and 166.0 eV in S 2p$_{1/2}$) is the S in BTD and the other is S in thiophene (165.2 eV in S 2p$_{3/2}$ and 166.4 eV in S 2p$_{1/2}$). Note that both S atoms appear at slightly higher binding energies than the respective S in BTDT$_2$ monomer. This indicates that both S atoms in the BTDT$_2$ polymer are slightly depleted of electrons than those in the monomer. As pointed out earlier, in BTDT$_2$ homopolymer N appears at a lower binding energy than that in BTDT$_2$ monomer. On average N is richer in electrons in the polymer than that in the monomer. That explains why S of the BTD unit in slightly oxidized compared to that of the monomer. Additionally, this may be due to two reasons: (i) electrons withdrawn from thiophene units into BTD units are concentrated on N atoms than S atoms due to higher electronegativity of N compared to S and (ii) intramolecular polarization of the BTD unit where N possessing a δ- charge and S having δ+ charge due to electron withdrawal of N from S. This effect seems to be more prominent in the polymer than in the monomer.

BTDF$_2$ homo-polymer

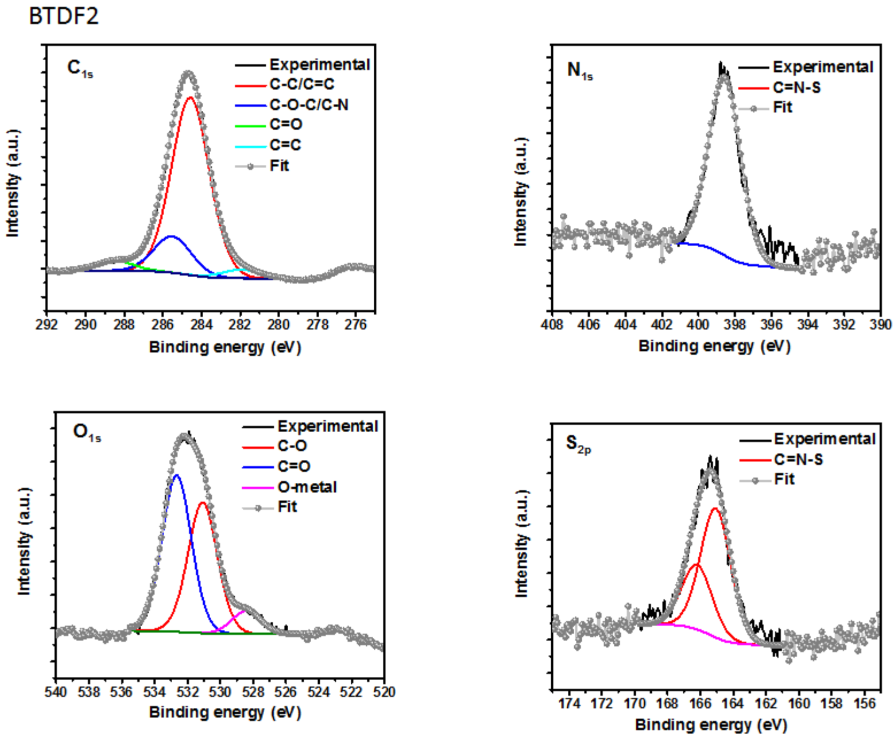


Figure S7. XPS fitting for homopolymer

In BTDF$_2$ homopolymer, N appears at 399.4 eV which is a slightly lower binding energy than 399.6 eV binding energy of N in BTDF$_2$ monomer. The difference is only 0.2 eV and may be indicating that BTD N is electron rich in the polymer than that in the monomer as in the case of BTD N in BTDT$_2$. S in both 2p$_{3/2}$ and 2p$_{1/2}$ states of the homo-polymer (165.7 eV and 166.9 eV, respectively) appear at higher binding energies than S in the BTDF$_2$ monomer (165.1 eV and 166.2 eV, respectively) indicating that S atom of the BTDF$_2$ homo-polymer is deficient in electrons than that in the monomer. These data indicate that the BTD unit in the homo-polymer is more polarized as N$^{\delta-}$S$^{\delta+}$ than that in the monomer. This is consistent with the results obtained for the BTDT$_2$ homo-polymer where BTD unit shows similar polarization. However, the effective polarization is higher in BTDF$_2$ homo-polymer than that of BTDT$_2$ homo-polymer.

SI-Table 3: Absorbance and emission data for $BTDT_2$ and $BTDF_2$ monomers, $BTDT_2$ and $BTDF_2$ homo-polymers and 1:1 mole ratio $BTDT_2$:$BTDF_2$ p-type and n-type copolymer

Polymer	**Absorbance**			**Emission**
	Peak Position (nm)	Onset (nm)	E_g^{opt} (eV)	Wavelength Maxima (nm)
1:1 block copolymer (n-type)	325, 542, 1061	753	1.65	710
1:1 block copolymer (p-type)	314, 528, 1256	745	1.66	657
$BTDF_2$	321, 488, 995	677	1.83	700
$BTDT_2$	328, 498, 1070	739	1.68	630

Electrochemical E_g values are calculated by taking the first reduction and first oxidation peak positions. Therefore, these data cannot be evaluated for the polymer in the p- and n- states. However, data can be evaluated for different polymers. Table below give the BG values calculated for $BTDT_2$, $BTDF_2$, 1:1 $BTDT_2$-$BTDF_2$ and 2:5 $BTDT_2$-$BTDF_2$ polymers.

Material	**$BTDT_2$ homopolymer**	**$BTDF_2$ homopolymer**	**1:1 $BTDT_2$-$BTDF_2$copolymer**	**2:5 $BTDT_2$-$BTDF_2$copolymer**
CV E_g (eV)	1.54	1.31	1.21	1.29

SI-IV: RAMAN SPECTRA OF 1:1 COPOLYMER

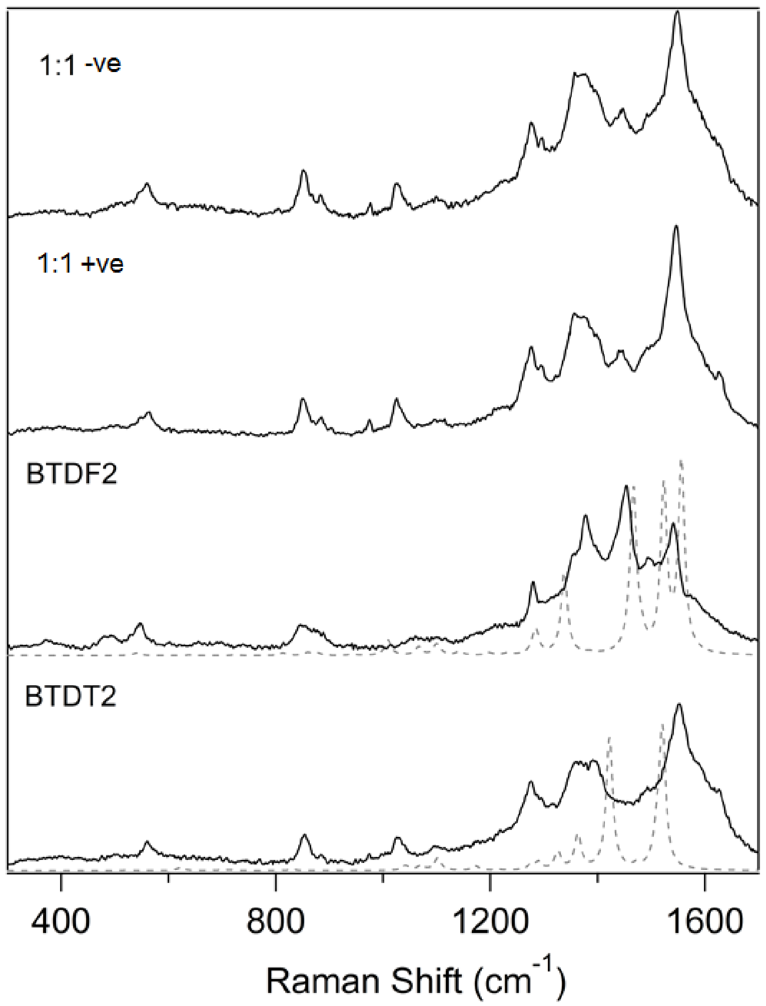


Figure S8. Raman spectroscopy employed to confirm copolymerization. Simulated Raman spectra are depicted as dashed lines; experimental data shown as solid lines.

References

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2. A. Guerrero, G. Garcia-Belmonte, I. Mora-Sero, J. Bisquert, Y. S. Kang, T. J. Jacobsson, J.-P. Correa-Baena and A. Hagfeldt, *The Journal of Physical Chemistry C*, 2016, **120**, 8023-8032.