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

Supporting Information

Side-chain Engineering of Self-Doped Conjugated Polyelectrolytes for Organic Electrochemical Transistors

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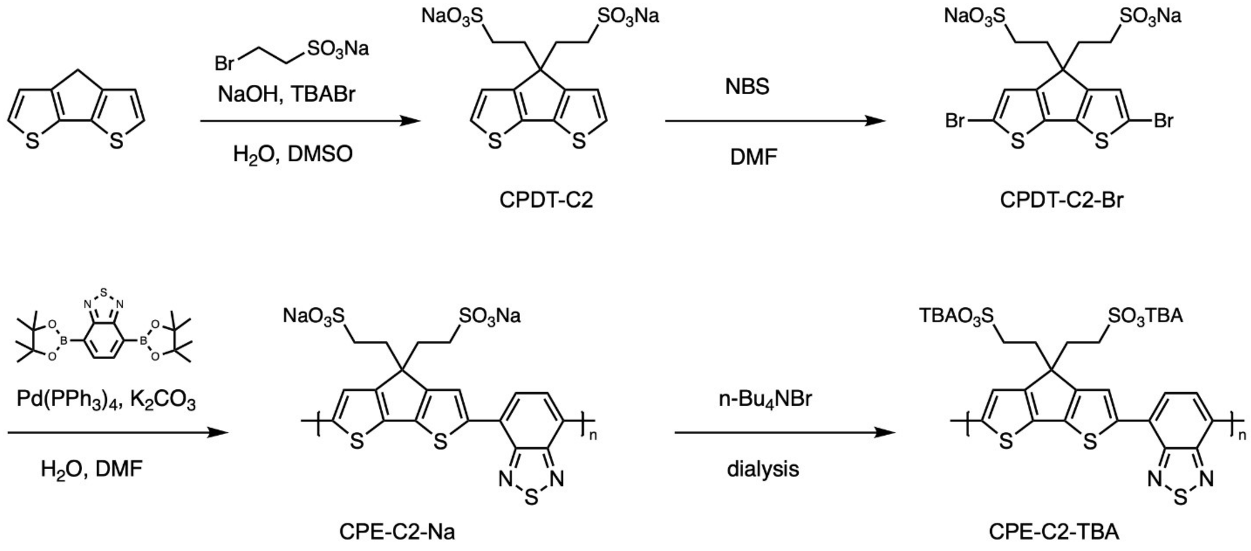
1.0 Experimental section

1.1 Materials and methods

All glassware was oven-dried or flame-dried. Unless specifically mentioned, all chemicals are commercially available and were used as received. Thin layer chromatography (TLC) was performed using EM Science Silica Gel 60 F254 glass plates. Flash chromatography was performed using 60 Å silica gel (37-75 μm). The dialysis membrane (MWCO: 3500–5000 Da) was purchased from Spectrum® Laboratories Inc. Unless otherwise mentioned, Milli-Q® was used for synthesis and dialysis. ^{1}H NMR spectra were recorded at either 500 MHz or 600 MHz, and ^{13}C NMR spectra were recorded at 500 MHz. Chemical shifts are reported in ppm referenced to residual solvent peaks as follows: $CDCl_3$, 7.26 ppm; D2O, 4.79 ppm and DMSO, 2.50 ppm ^{1}H NMR, no reference for ^{13}C NMR. Mass spectroscopy was performed using electron spray as ionization methods. Gel Permeation Chromatography (GPC) was measured in Waters® system using DMF with 0.1% LiBr as the solvent and calibrated versus polystyrene standards.

1.2 Synthesis

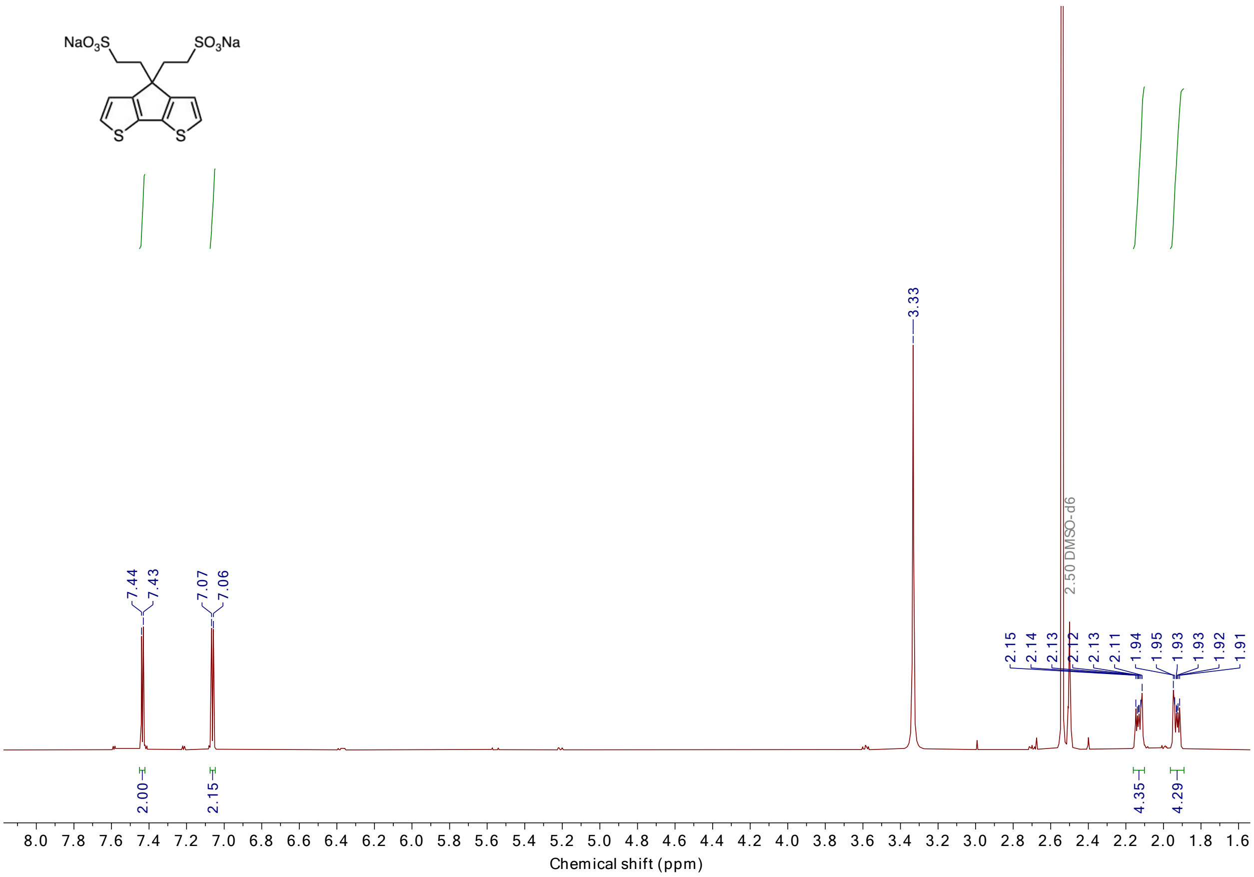
1.2.1 Synthesis of 2,2'-(2-methyl-6-(7-methylbenzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(ethane-1-sulfonate) - CPE-C2-Na



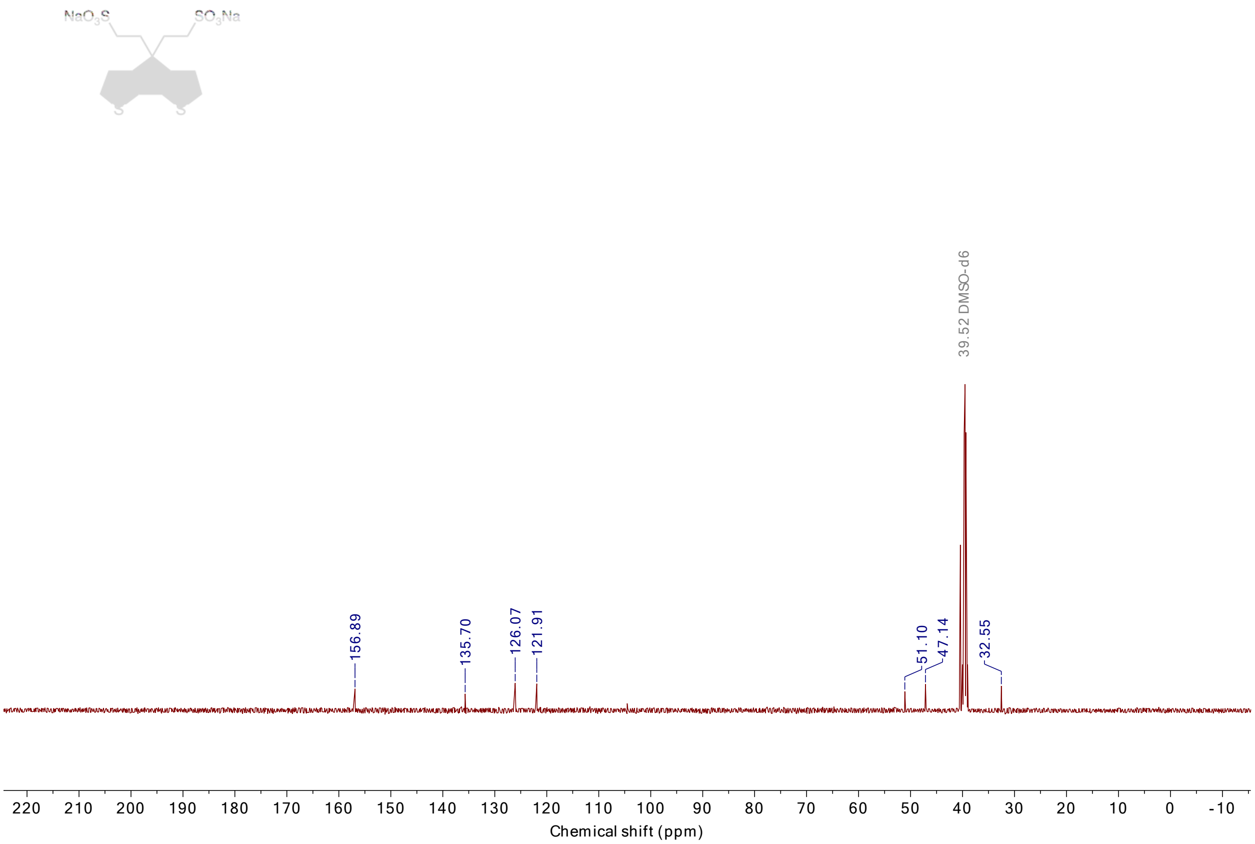
Scheme S1. Synthesis of CPE-C2-Na and conversion to CPE-C2-TBA

CPDT-C2

In a round bottom flask was added DMSO (6.5 mL) and H_2O (0.5 mL) and the mixture was purged for 30 min. In a second round bottom flask was added 4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (CPDT, 230.6 mg, 1.3 mmol, 1.0 equiv), tetrabutylammonium bromide (21 mg, 0.06 mmol, 0.05 equiv) and NaOH (517.4 mg, 13.0 mmol, 10eq), followed by 3 cycles of vacuum/argon. The solvent mixture was cannulated to the second flask and stirred. Sodium 2-bromoethanesulfonate (1.637 g, 7.8 mmol, 6.0 eq) was added quickly. The reaction mixture was heated to 80 ^{o}C and stirred overnight. Then, it was concentrated until the water was removed. The crude material in DMSO was then poured into acetone and filtered. Purification by flash chromatography (reversed phase silica gel C-18), gradient 5% MeOH/H_2O to 100% MeOH, provided CPDT-C2 (226.2 mg, 40% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.43 (d, J = 4.9 Hz, 2H), 7.06 (d, J = 4.9 Hz, 2H), 2.16 – 2.10 (m, 4H), 1.96 – 1.89 (m, 4H). ^{13}C NMR (126 MHz, dmso) δ 156.89, 135.70, 126.07, 121.91, 51.10, 47.14, 32.55. (ESI): [(M-2Na+H)$^-$] calcd: 392.9595; found: 392.9603.



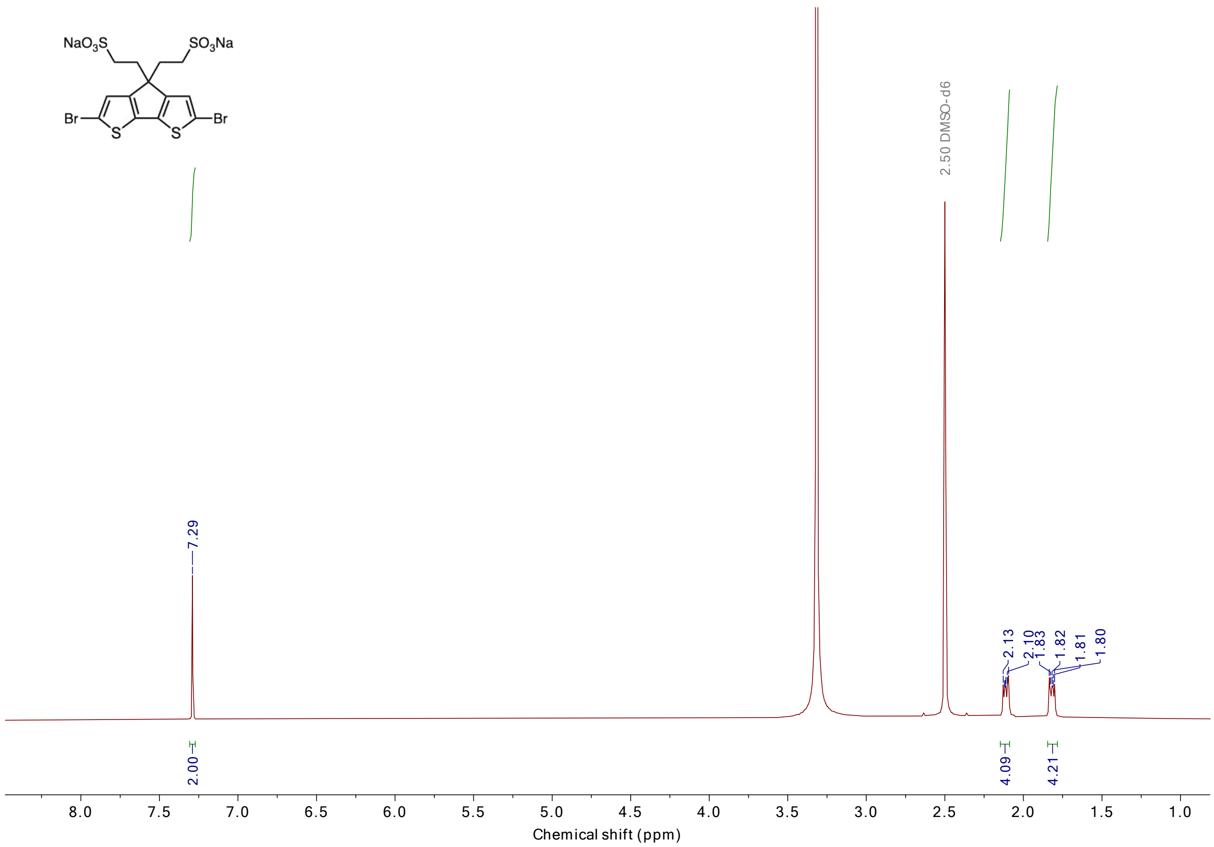
^{1}H NMR spectrum of CPDT-C2 (500 MHz, DMSO-d_6)



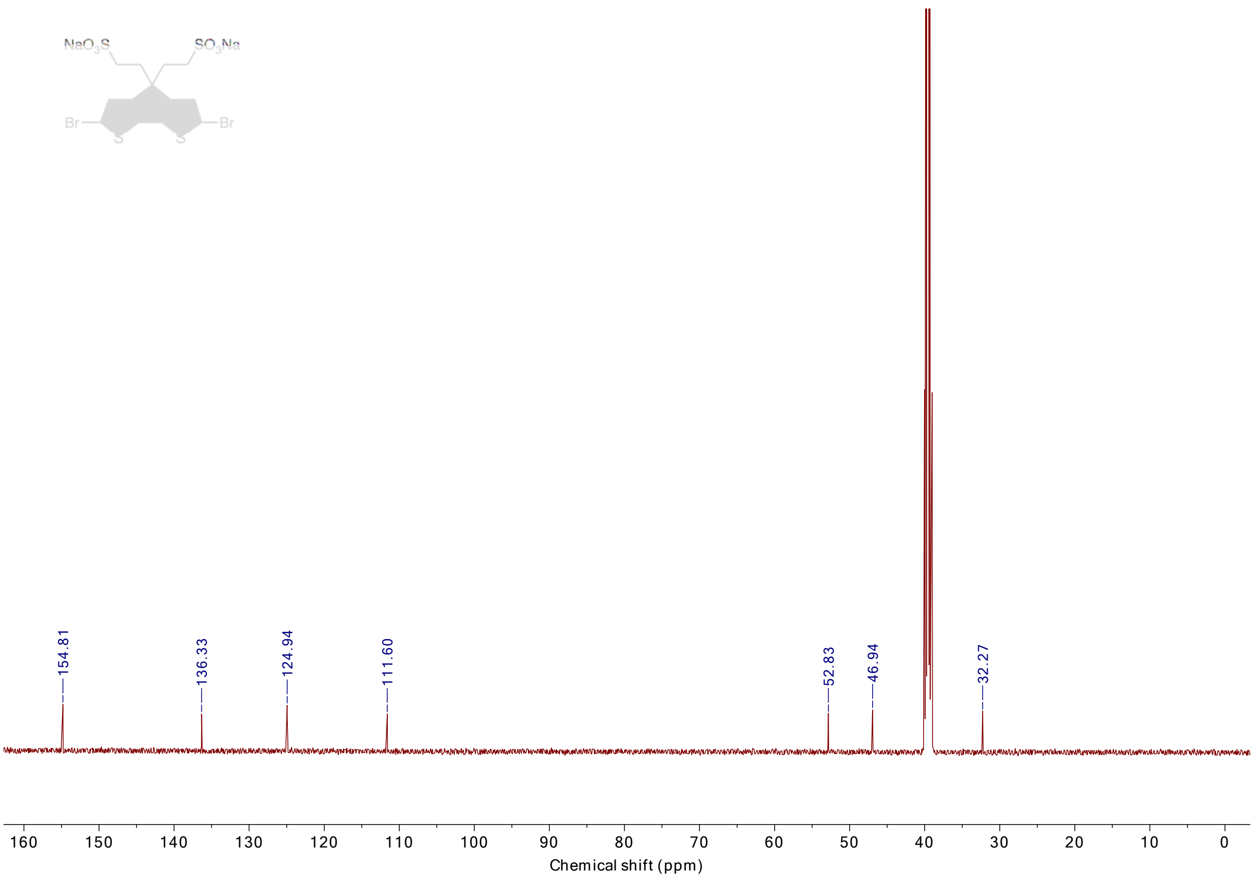
^{13}C NMR spectrum of CPDT-C2 (126 MHz, DMSO-d_6)

CPDT-C2-Br

CPDT-C2 (226.2 mg, 0.51 mmol, 1 eq) was then suspended in DMF (2.7 mL), and H_2O (0.35 mL) was added in small increments until CPDT-C2 dissolved. The solution was purged for 15 min with argon. The reaction was cooled to 0^{o}C in an ice bath. Then, NBS (226.9 mg, 1.27 mmol, 2.5 equiv) was quickly added in dark by shielding the flask with aluminum foil. The reaction was warmed up to room temperature and stirred overnight. The reaction was quenched with water and then concentrated. Purification by flash chromatography (reversed phase silica gel C-18,) gradient 5% MeOH/H_2O to 100% MeOH, provided CPDT-C4-Br (238.2 mg, 42% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29 (s, 2H), 2.14 – 2.09 (m, 4H), 1.84 – 1.79 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.81, 136.33, 124.94, 111.60, 52.83, 46.94, 32.27. MS (ESI): $[(M\text{-}Na)^-]$ calcd: 572.7603; found: 572.7611.



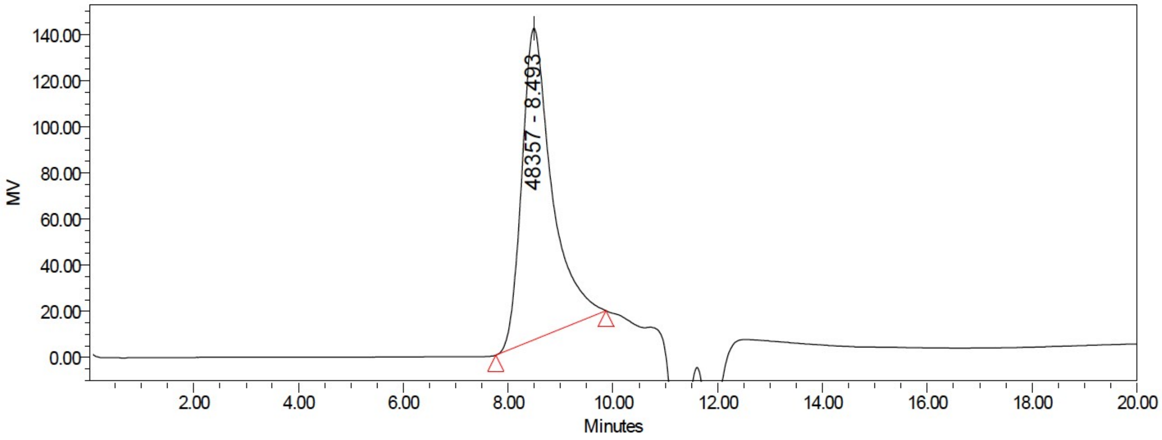
^{1}H NMR spectrum of CPDT-C2-Br (500 MHz, DMSO-d_6)



^{13}C NMR spectrum of CPDT-C2-Br (126 MHz, DMSO-d_6)

CPDT-C2-TBA

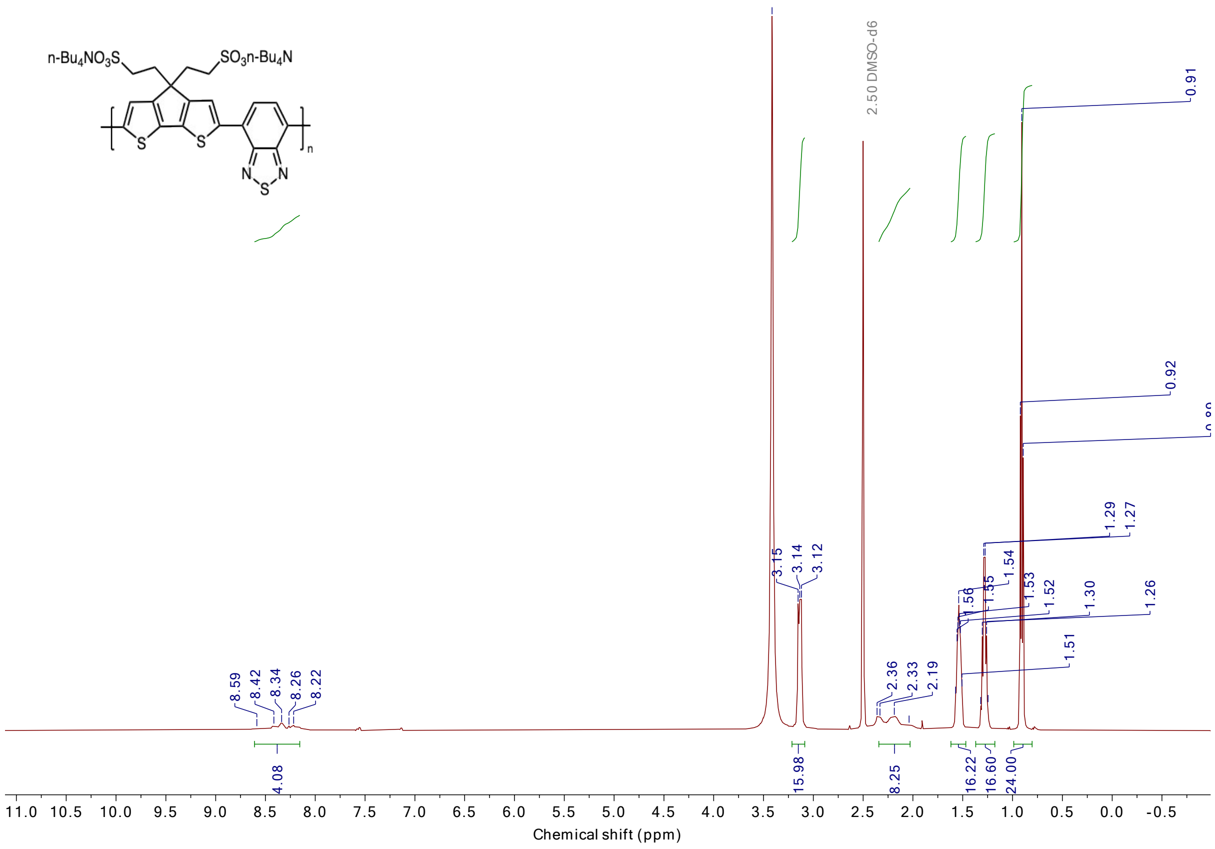
For the polymer preparation, CPDT-C2-Br (112.6 mg, 0.189 mmol, 1.0 equiv), 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) (73.3 mg, 0.189 mg, 1.0 equiv), Na_2CO_3 (100.1 mg, 0.944 mmol, 5.0 equiv) were added into a microwave tube equipped with a stir bar and transferred to the glove box. There $Pd(PPh_3)_4$ (4.4 mg, 2 mol%) was added, the tube sealed with a rubber septa and taken out of the glove box. A mixture of DMF (1.7 mL) and H_2O (0.4 mL) was degassed by sparging with argon for 30 min and cannulated into the microwave tube. The septum on the tube was removed quickly under positive pressure of argon, and the tube was resealed with a special cap for the microwave tubes. The suspension was placed into an oil bath, and heated to 90 °C, at which temperature the reaction mixture turned dark blue in about 15 min. The reaction was allowed to stir at 90 °C for 24 hrs after which it was allowed to cool down to room temperature and poured into acetone (50 mL). The dark blue precipitate was collected by filtration and washed with copious amounts of acetone and MeOH until the filtrate was almost colorless. The precipitate was all dissolved in H_2O (~25 mL), and transferred into a dialysis tube (MWCO: 3500 – 5000). The dialysis tube was placed in a large beaker with H_2O (2 L) stirring for 3 days, and the H_2O was changed every 12 hrs. Evaporation of H_2O provided the title product as a dark blue solid (92.4 mg, 89%) after drying under vacuum overnight. The NMR of the title polymer in D_2O only showed non informative broad peaks, probably due to the presence of paramagnetic radical cations. The molecular weight was not able to be determined directly due to unavailability of gel permeation chromatography (GPC) eluting with H_2O. Therefore, ion exchange with excess tetrabutylammonium bromine provided a DMF-soluble polyelectrolyte with tertbutylammonium as the counterions, of which molecular weight can be determined by GPC (DMF). Mn = 18188, Mw = 46539, PDI = 2.56. ^{1}H NMR (500 MHz, dmso) δ 8.61 – 8.15 (m, 4H), 3.18 – 3.09 (m, 15H), 2.41 – 1.98 (m, 8H), 1.62 – 1.47 (m, 16H), 1.37 – 1.18 (m, 17H), 0.91 (t, *J* = 7.3 Hz, 24H).



GPC Results

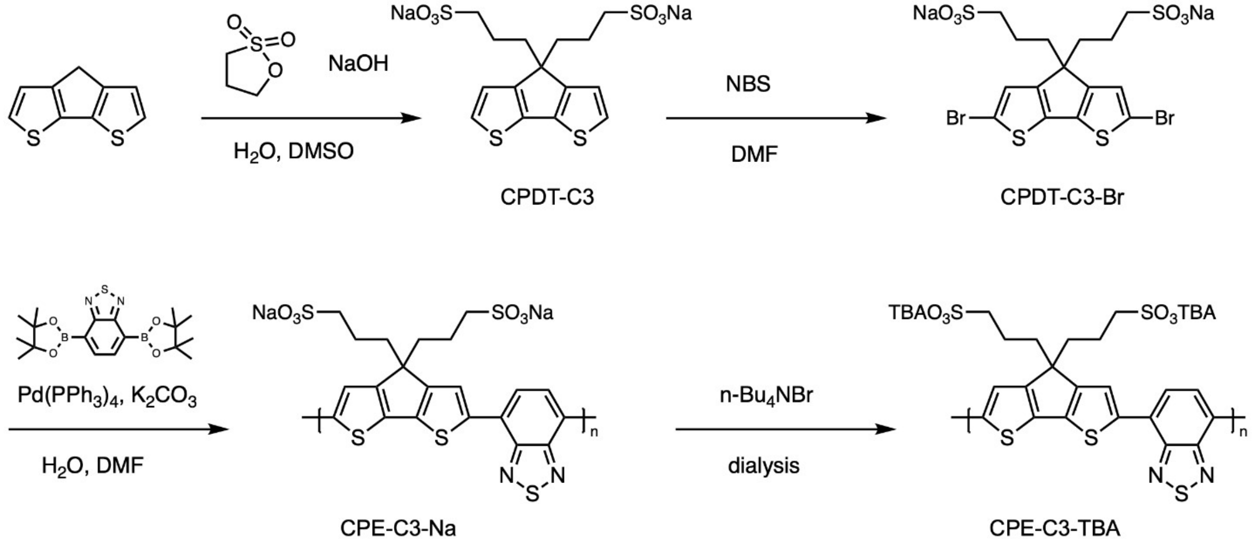
	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	18188	46539	48357	73155	98432	2.56

GPC plot of CP2-C2-TBA



^{1}H NMR spectrum of CPDT-C2-TBA (500 MHz, DMSO-d_6)

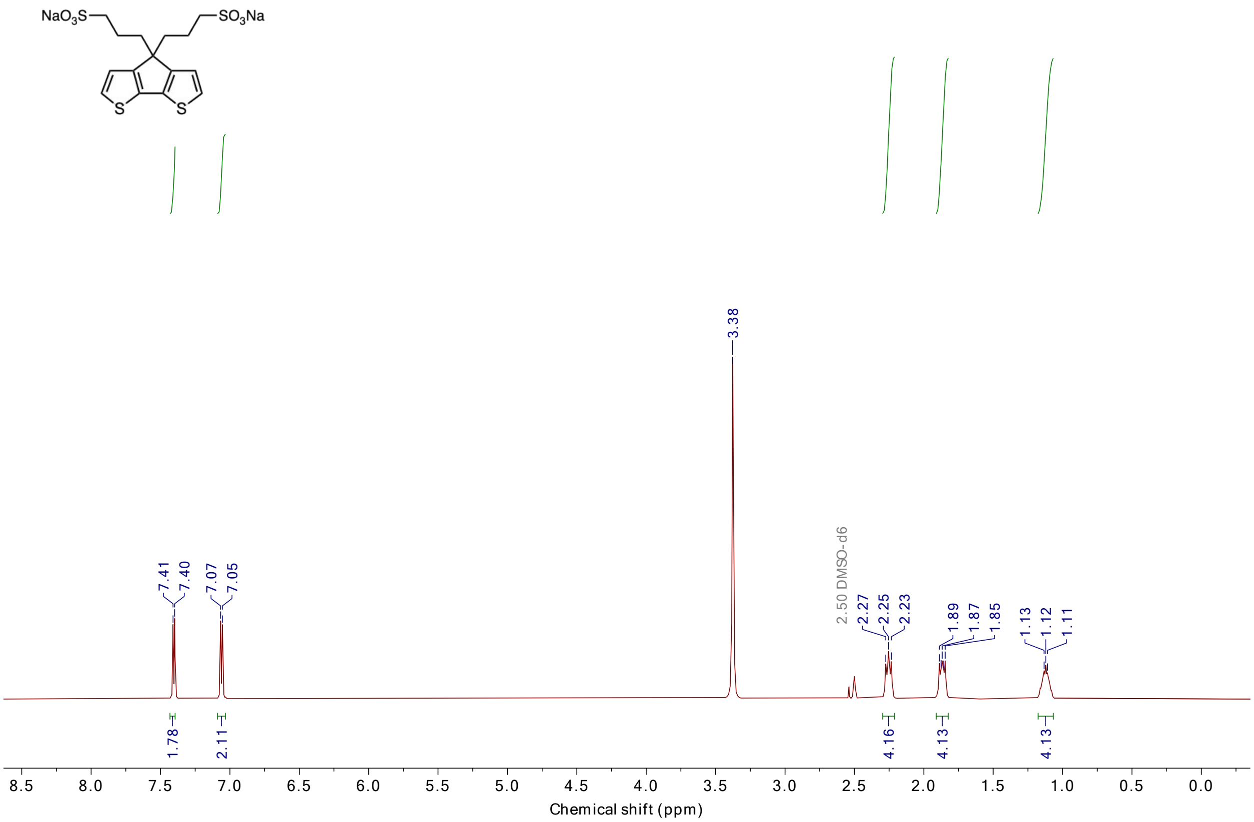
1.2.3 3,3'-(2-methyl-6-(7-methylbenzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(propane-1-sulfonate) – CPE-C3-Na



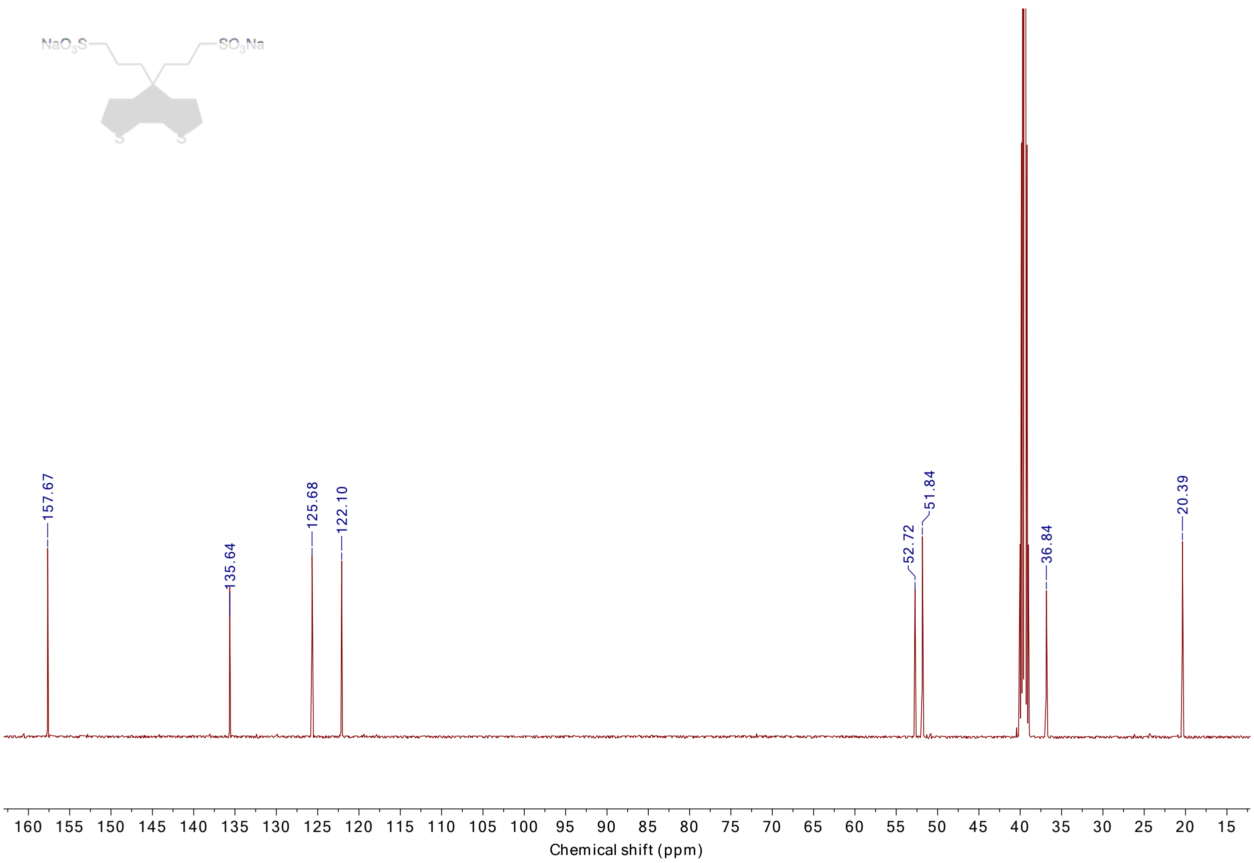
Scheme S2. Synthesis of CPE-C3-Na and conversion to CPE-C3-TBA

CPDT-C3

In a round bottom flask was added DMSO (4.9 mL) and water (0.45 mL). The solution was purged for 10 min with argon. In a second round bottom flask was added 4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (CPDT, 202.4 mg, 1.13 mmol, 1.0 equiv), tetrabutylammonium bromide (18.3 mg, 0.056 mmol, 0.05 equiv) and NaOH (454.1 mg, 11.3 mmol, 10 eq), followed by 3 cycles of vacuum/argon. The solvent was cannulated to the second flask, followed by the addition of 1,3-propanesultone (347.0 mg, 2.838 mmol, 2.5 eq). The reaction was stirred at room temperature overnight. Then, the reaction mixture was poured into acetone (100 mL), and the precipitate was collected by filtration, and washed with acetone. The crude product (CPDT-C3) was used in the next step without further purification. Analytical sample was purified by flash chromatography (reversed phase silica gel C-18), gradient 5% MeOH/H_2O to 100% MeOH, to provide a yellowish solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (d, J = 4.8 Hz, 2H), 7.06 (d, J = 4.8 Hz, 2H), 2.25 (t, J = 8.0 Hz, 4H), 1.91 – 1.82 (m, 4H), 1.18 – 1.07 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.67, 135.64, 125.68, 122.10, 52.72, 51.84, 36.84, 20.39. MS (ESI): [$(M+Na)^+$] calcd: 488.9523 ; found: 488.9530.



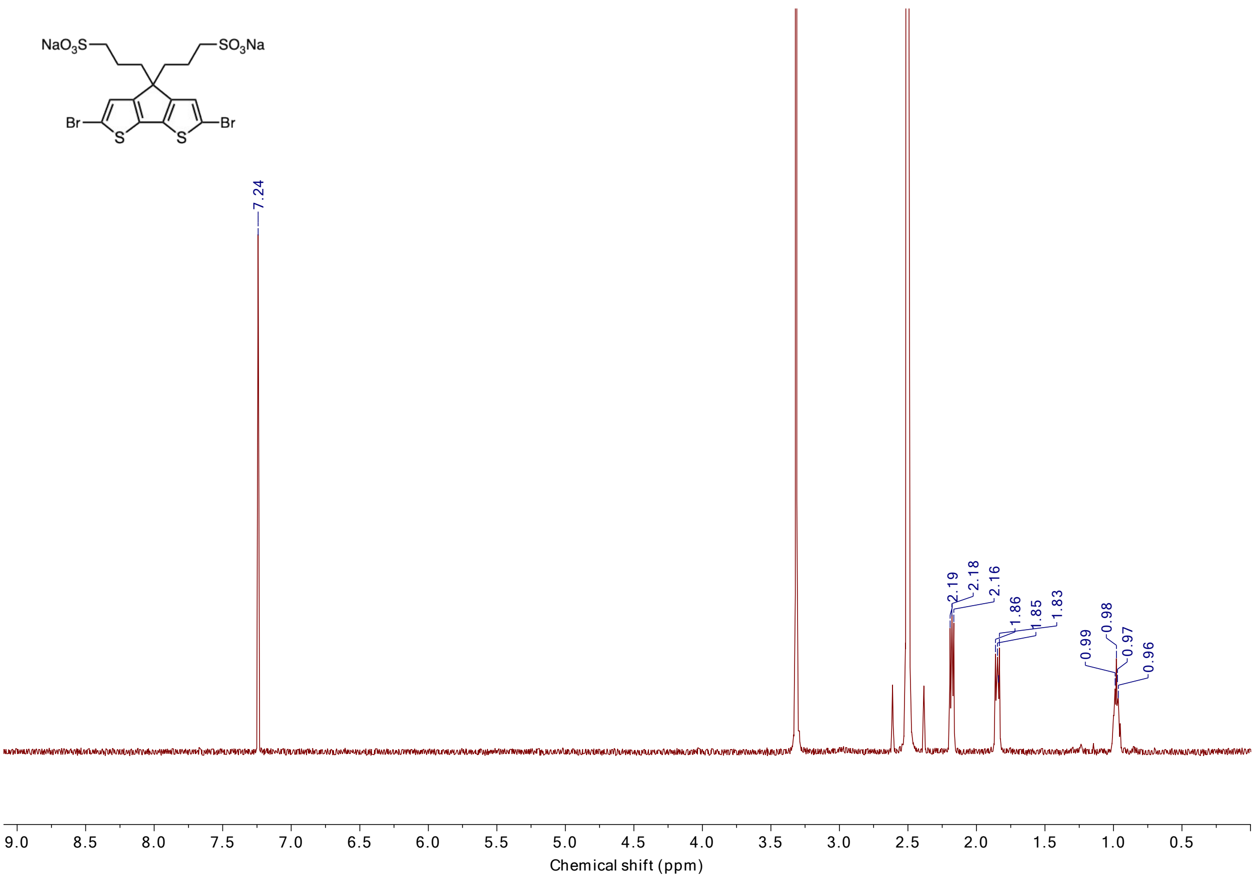
^{1}H NMR spectrum of CPDT-C3 (500 MHz, DMSO-d_6)



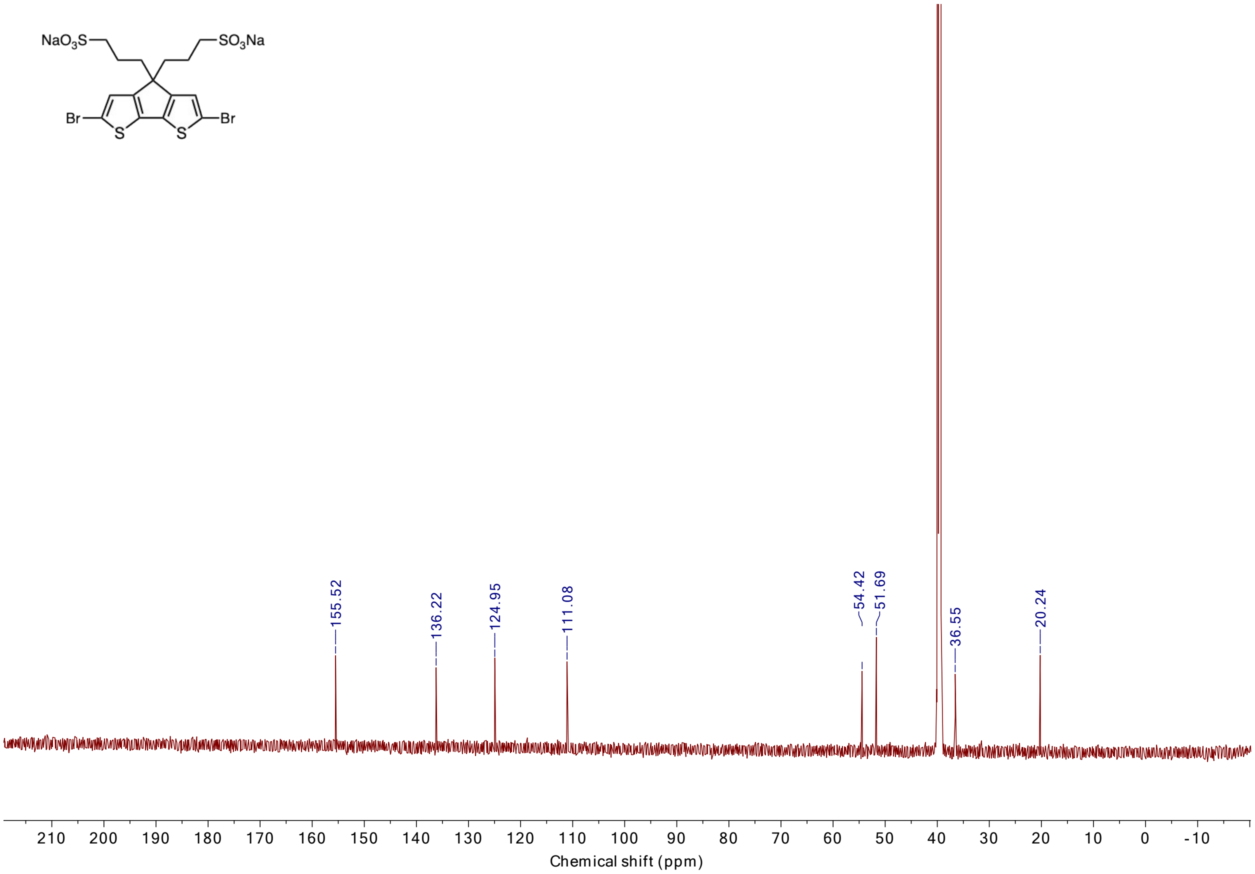
^{13}C NMR spectrum of CPDT-C3 (126 MHz, DMSO-d_6)

CPDT-C3-Br

The crude product CPDT-C3 was suspended in DMF (6 mL), and H_2O (~1.5 mL) was added in small increments until CPDT-C3 dissolved. The solution was purged for 10 min with argon. NBS (505.0 mg, 2.8 mmol, 2.5 equiv) was added in dark by shielding the flask with aluminum foil. The reaction was stirred at room temperature overnight and poured into acetone. The precipitate was collected by filtration and washed with acetone. Purification by flash chromatography (reversed phase silica gel C-18,) gradient 5% MeOH/H_2O to 100% MeOH, provided CPDT-C3-Na (164.2 mg, 31 yield%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.24 (s, 2H), 2.19 (t, J = 8.1 Hz, 4H), 1.86 – 1.82 (m, 4H), 1.00 – 0.95 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.52, 136.22, 124.95, 111.08, 54.42, 51.69, 36.55, 20.24. MS (ESI): [(M-Na)$^-$] calcd: 600.7916; found: 600.7925.



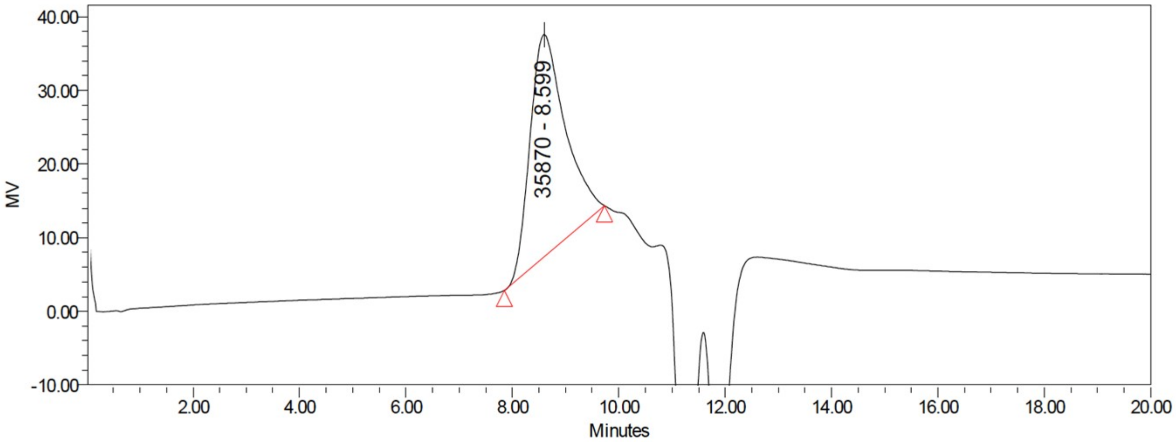
^{1}H NMR spectrum of CPDT-C3-Br (500 MHz, DMSO-d_6)

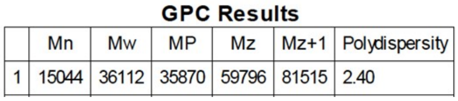


^{13}C NMR spectrum of CPDT-C3-Br (126 MHz, DMSO-d_6)

CPE-C3-TBA

CPE-C3-Na was synthesized using CPDT-C3-Na and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) via the same procedure as CPE-C2-Na to provide the desired polymer as a dark blue solid (85%), which was found to be doped after dialysis in water for 3 days. Ion exchange with tetrabutylammonium bromine provided a DMF-soluble polyelectrolyte CPE-C3-TBA with tetrabutylammonium as the counterions, of which molecular weight can be determined by GPC (DMF). Mn = 15044, Mw = 36112, PDI = 2.40. ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.78 – 7.92 (m, 4H), 3.17 – 3.07 (m, 16H), 2.45 – 2.17 (m, 10H), 1.61 – 1.47 (m, 16H), 1.46 – 1.35 (m, 2H), 1.32 – 1.24 (m, 16H), 0.91 (t, J = 7.3 Hz, 24H), 0.82 – 0.69 (m, 2H).

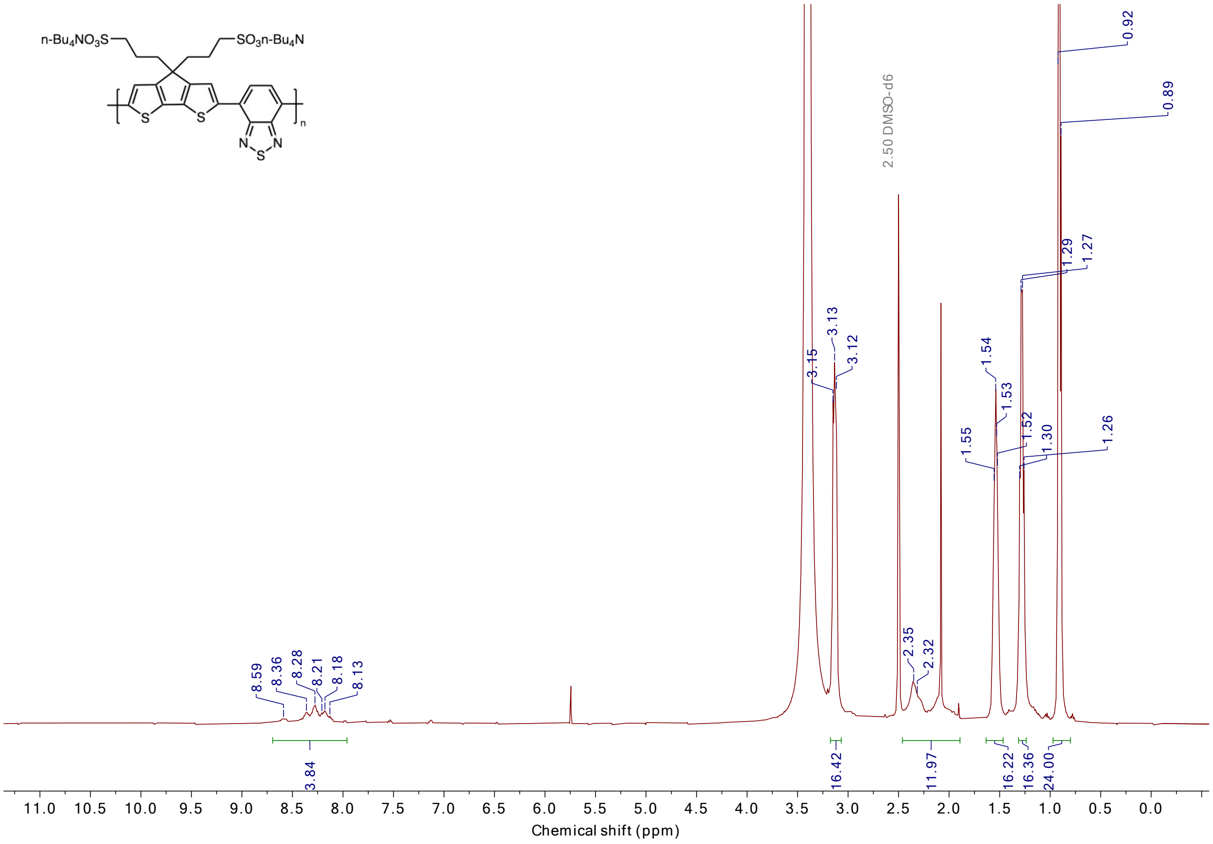




GPC Results

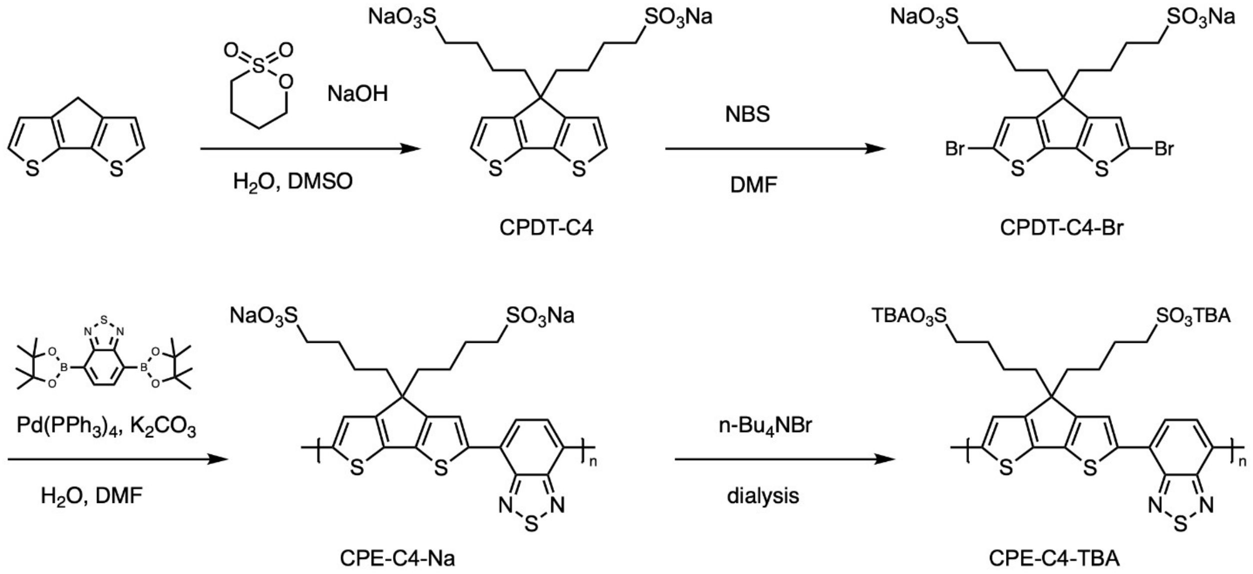
	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	15044	36112	35870	59796	81515	2.40

GPC plot of CPE-C3-TBA



^{1}H NMR spectrum of CPDT-C3-TBA (500 MHz, DMSO-d_6)

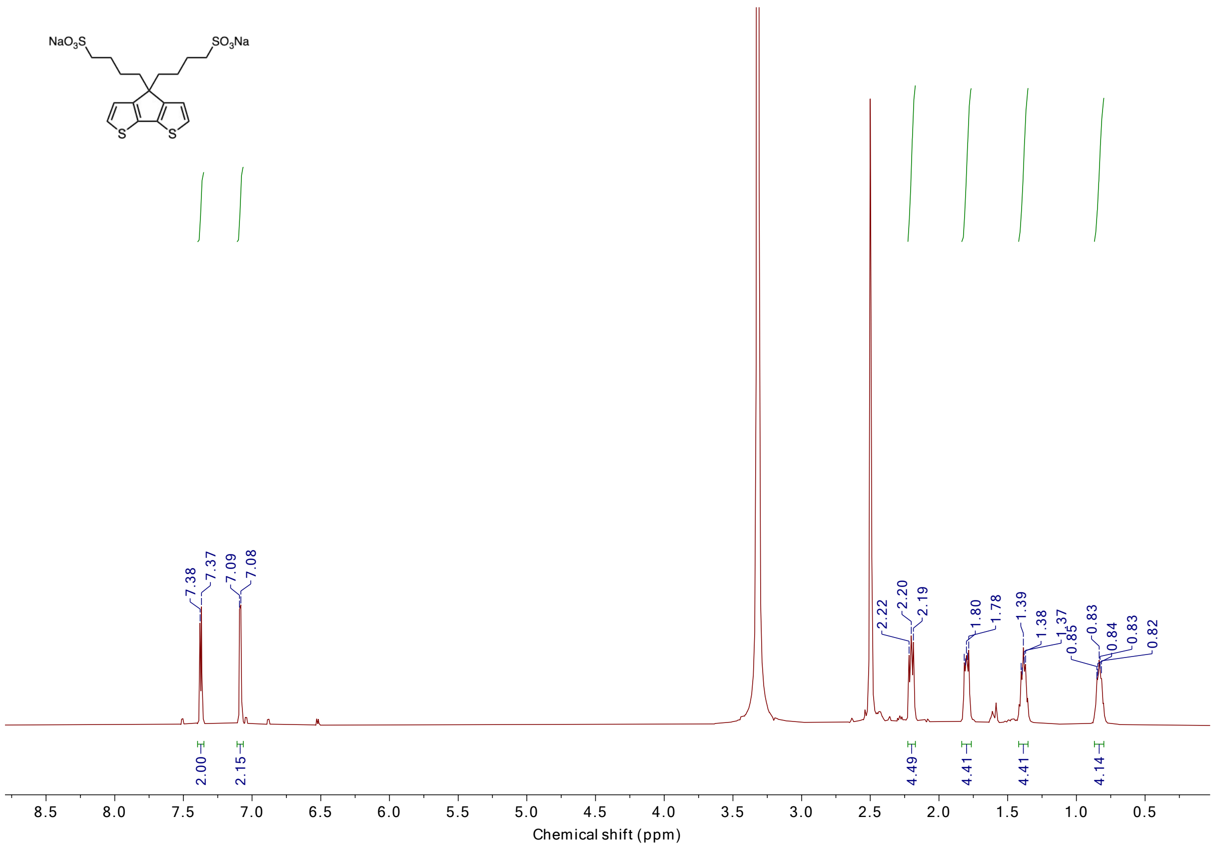
1.2.3 4,4'-(2-methyl-6-(7-methylbenzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(butane-1-sulfonate) – CPE-C4-Na



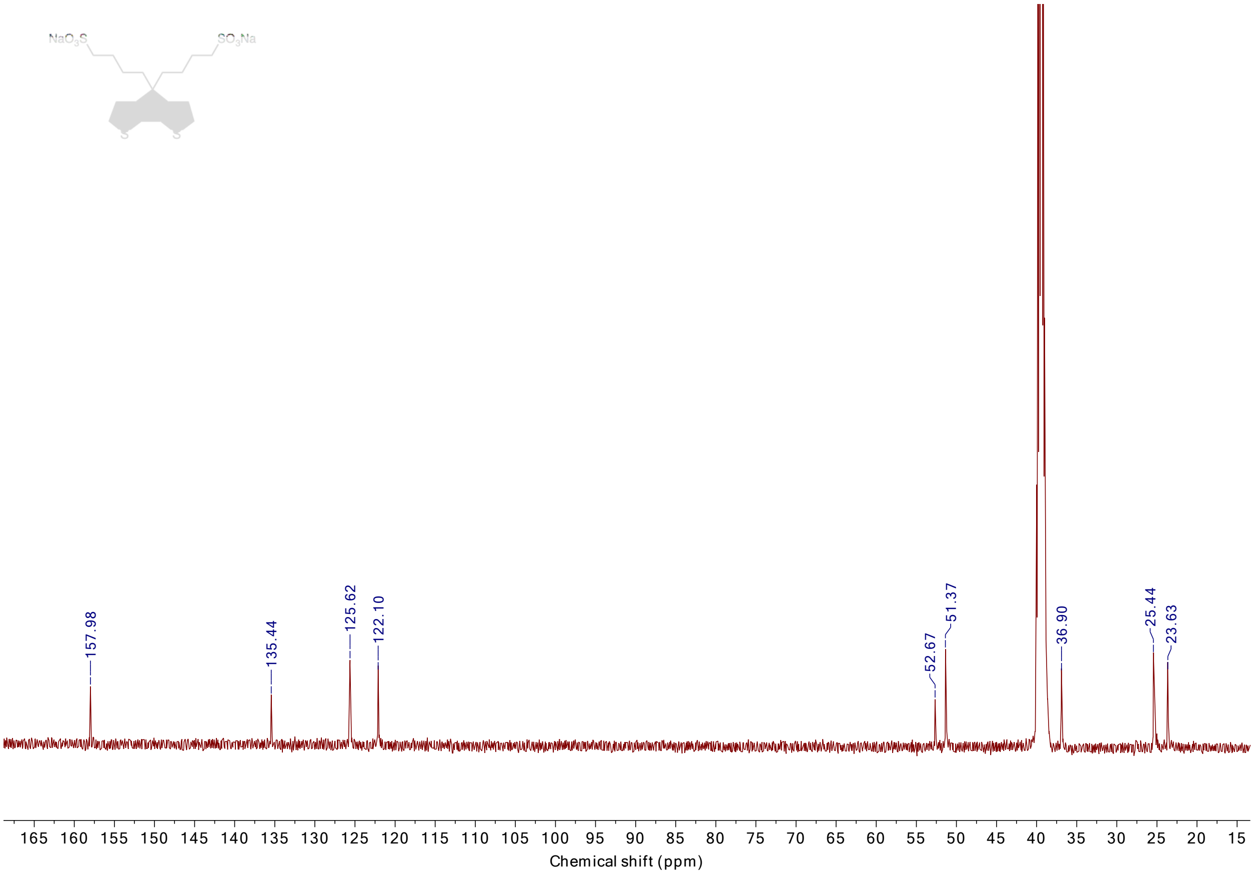
Scheme S3. Synthesis of CPE-C4-Na and conversion to CPE-C4-TBA.

CPDT-C4

This compound was synthesized under similar conditions as CPDT-C3. Analytical sample of CPDT-C4 was purified by flash chromatography (reversed phase silica gel C-18), gradient 5% MeOH/H_2O to 100% MeOH, to provide a yellowish solid. ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.37 (d, J = 4.8 Hz, 2H), 7.09 (d, J = 4.8 Hz, 2H), 2.20 (t, 4H), 1.83 – 1.76 (m, 4H), 1.42 – 1.35 (m, 4H), 0.87 – 0.80 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 157.98, 135.44, 125.62, 122.10, 52.67, 51.37, 36.90, 25.44, 23.63. MS (ESI): [(M-2Na+H)$^-$] calcd: 449.0221; found: 449.0235.



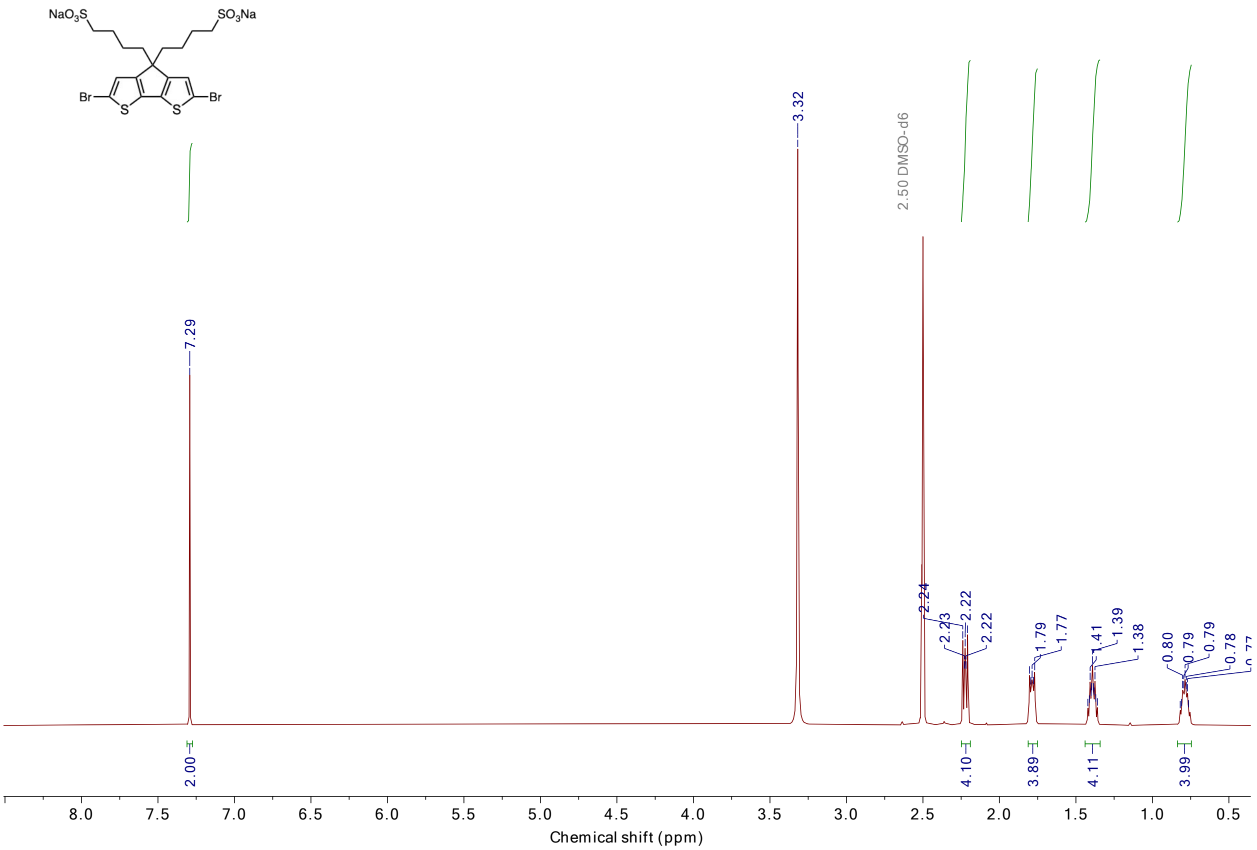
^{1}H NMR spectrum of CPDT-C4 (500 MHz, DMSO-d_6)



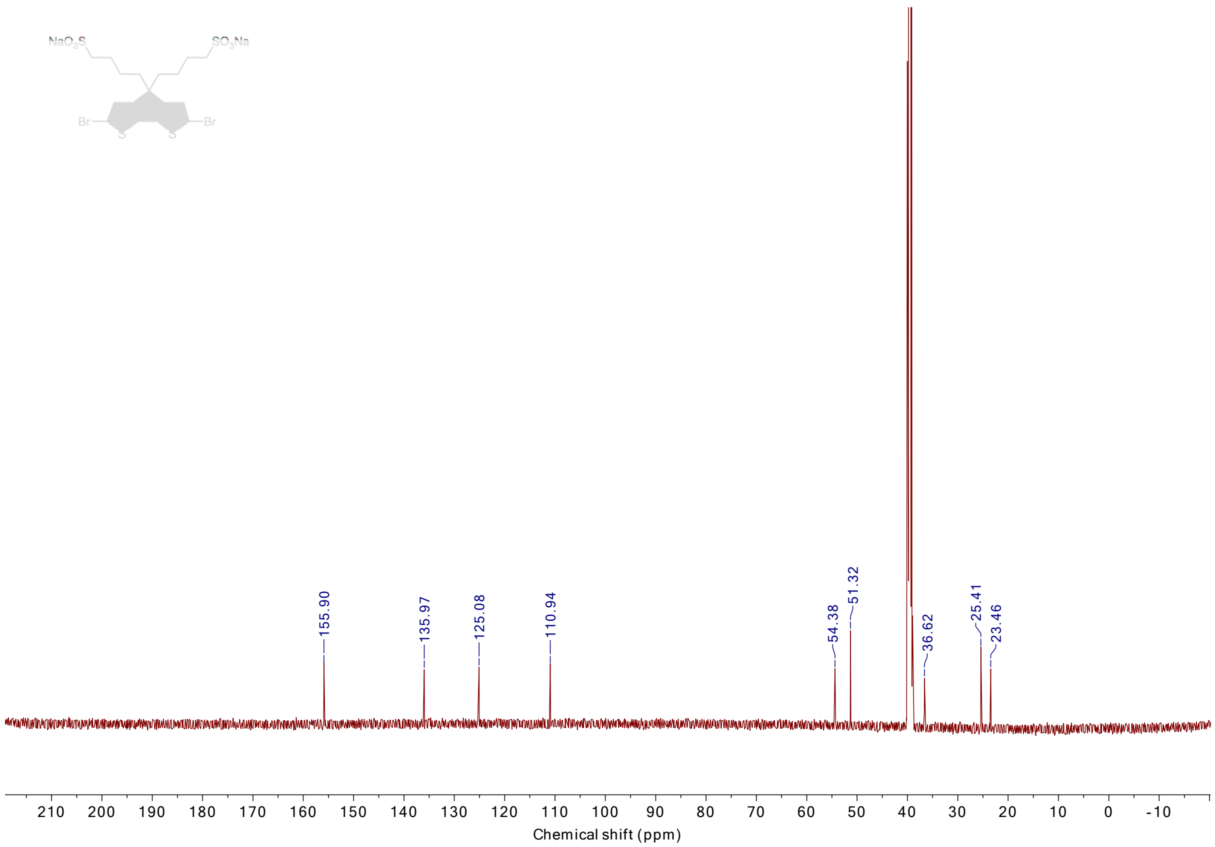
^{13}C NMR spectrum of CPDT-C4 (126 MHz, DMSO-d_6)

CPDT-C4-Br

CPDT-C4-Br was synthesized under similar conditions as CPDT-C3-Br. The crude solid was purified by flash chromatography (C18-reversed phase), gradient 5% MeOH/H_2O to 100% MeOH, subsequently freeze-dried overnight (25% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.29 (s, 2H), 2.25 – 2.19 (m, 4H), 1.81 – 1.75 (m, 4H), 1.44 – 1.34 (m, 4H), 0.84 – 0.75 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.90, 135.97, 125.08, 110.94, 54.38, 51.32, 36.62, 25.41, 23.46. MS (ESI): [(M-Na)$^-$] calcd: 628.8229; found: 628.8220.



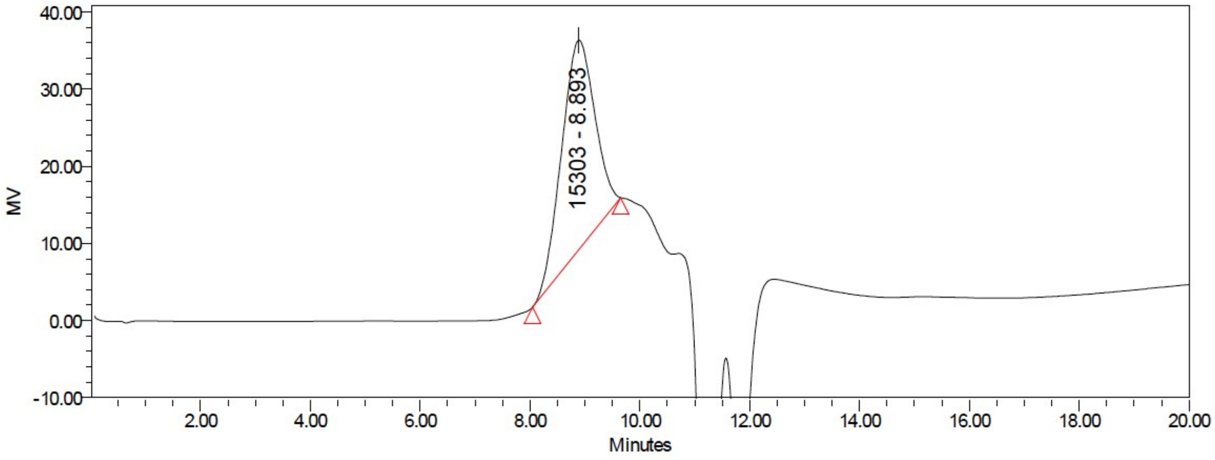
^{1}H NMR spectrum of CPDT-C4-Br (500 MHz, DMSO-d_6)



^{13}C NMR spectrum of CPDT-C4-Br (126 MHz, DMSO-d_6)

CPDT-C4-TBA

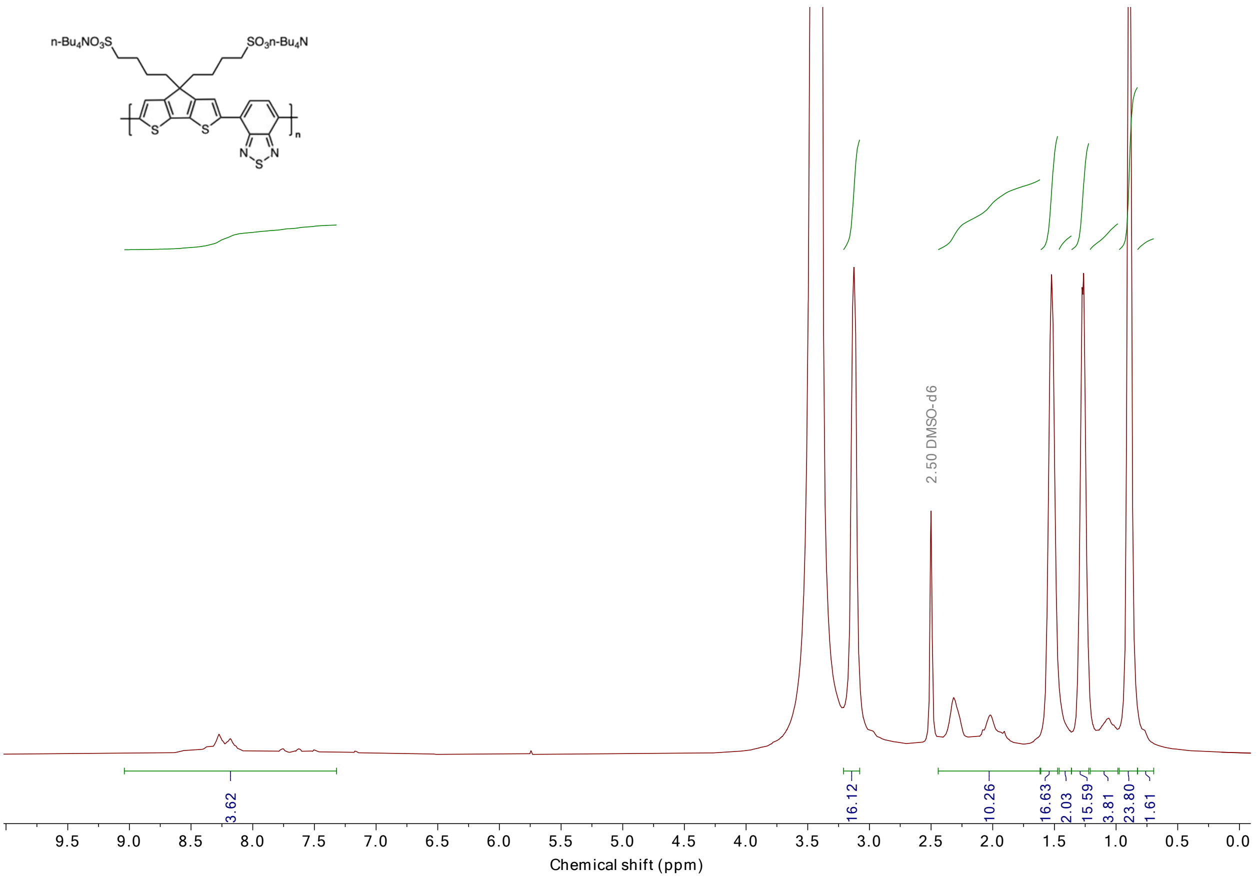
CPE-C4-Na was synthesized using CPDT-C4-Na and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) via the same procedure as CPE-C2-Na to provide the desired polymer as a dark blue solid (85%), which was found to be doped after dialysis in water for 3 days. Ion exchange with tetrabutylammonium bromine provided a DMF-soluble polyelectrolyte CPE-C4-TBA with tetrabutylammonium as the counterions, of which molecular weight can be determined by GPC (DMF). Mn = 11393, Mw = 21326, PDI = 1.87. ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.04 – 7.32 (m, 4H), 3.24 – 3.03 (m, 16H), 2.43 – 2.19 (m, 4H), 2.16 – 1.87 (m, 4H), 1.64 – 1.41 (m, 16H), 1.36 – 1.19 (m, 16H), 1.19 – 0.97 (m, 4H), 0.89 (t, J = 7.5 Hz, 24H).



GPC Results

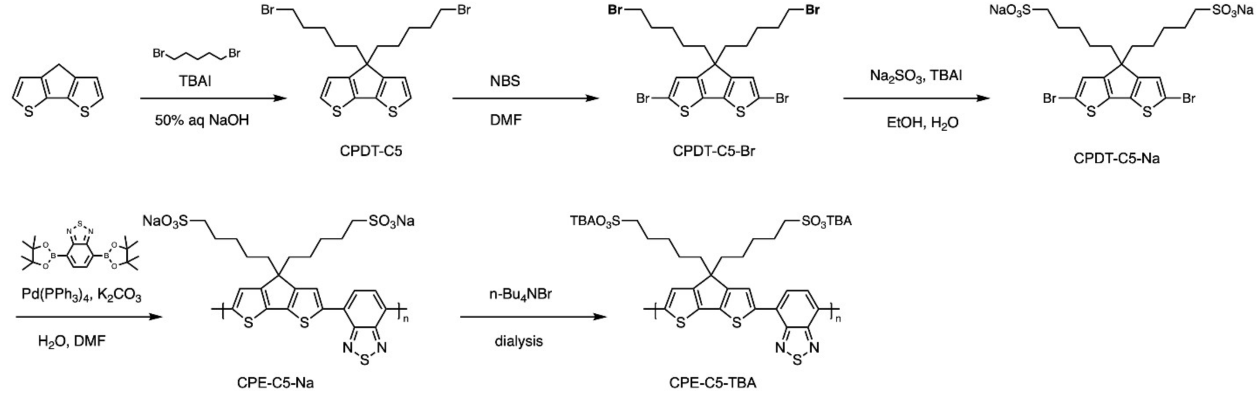
	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	11393	21346	15303	35976	52423	1.87

GPC plot of CPE-C4-TBA



^{1}H NMR spectrum of CPDT-C4-TBA (500 MHz, DMSO-d_6)

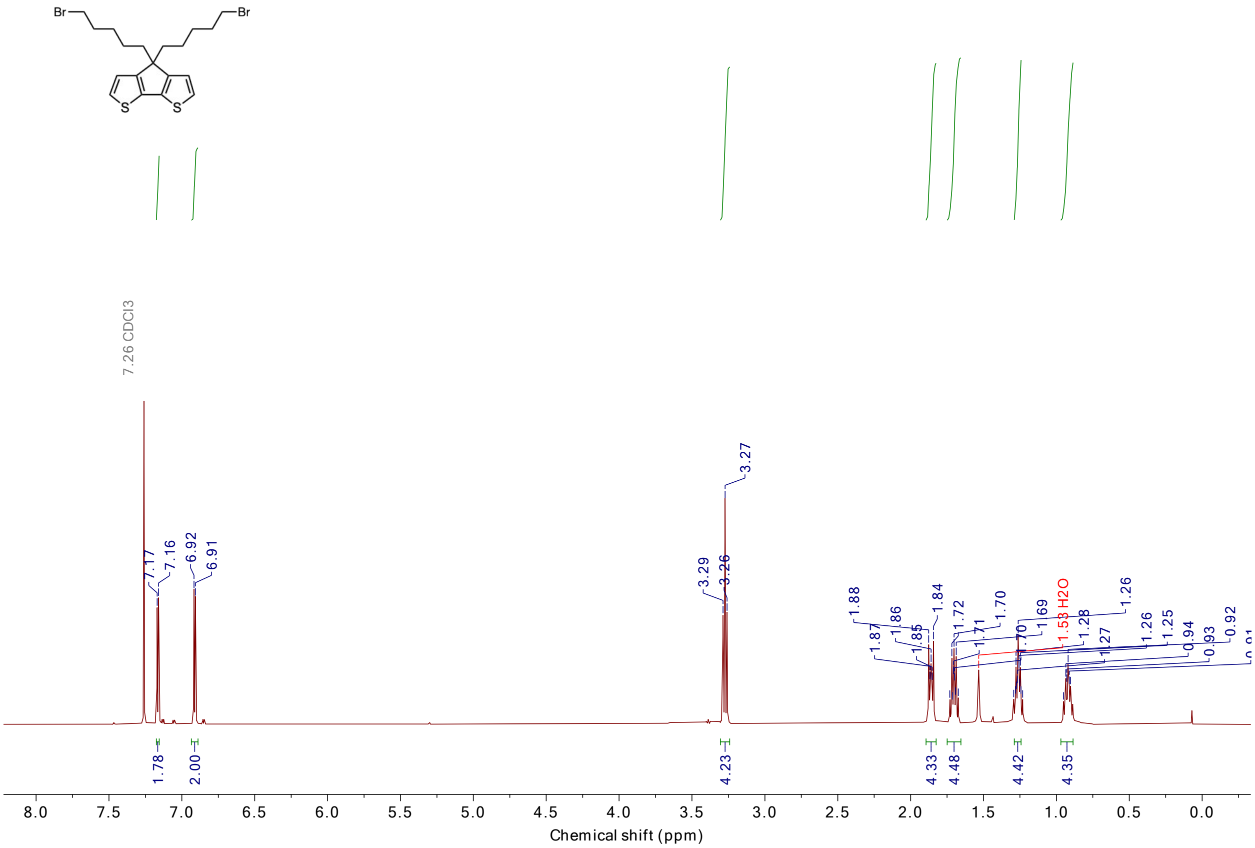
1.2.4 Synthesis of sodium 5,5'-(2-methyl-6-(7-methylbenzo[c][1,2,5]thiadiazol-4-yl)-4H-cyclopenta[2,1-b:3,4-b']dithiophene-4,4-diyl)bis(pentane-1-sulfonate) – CPE-C5-Na



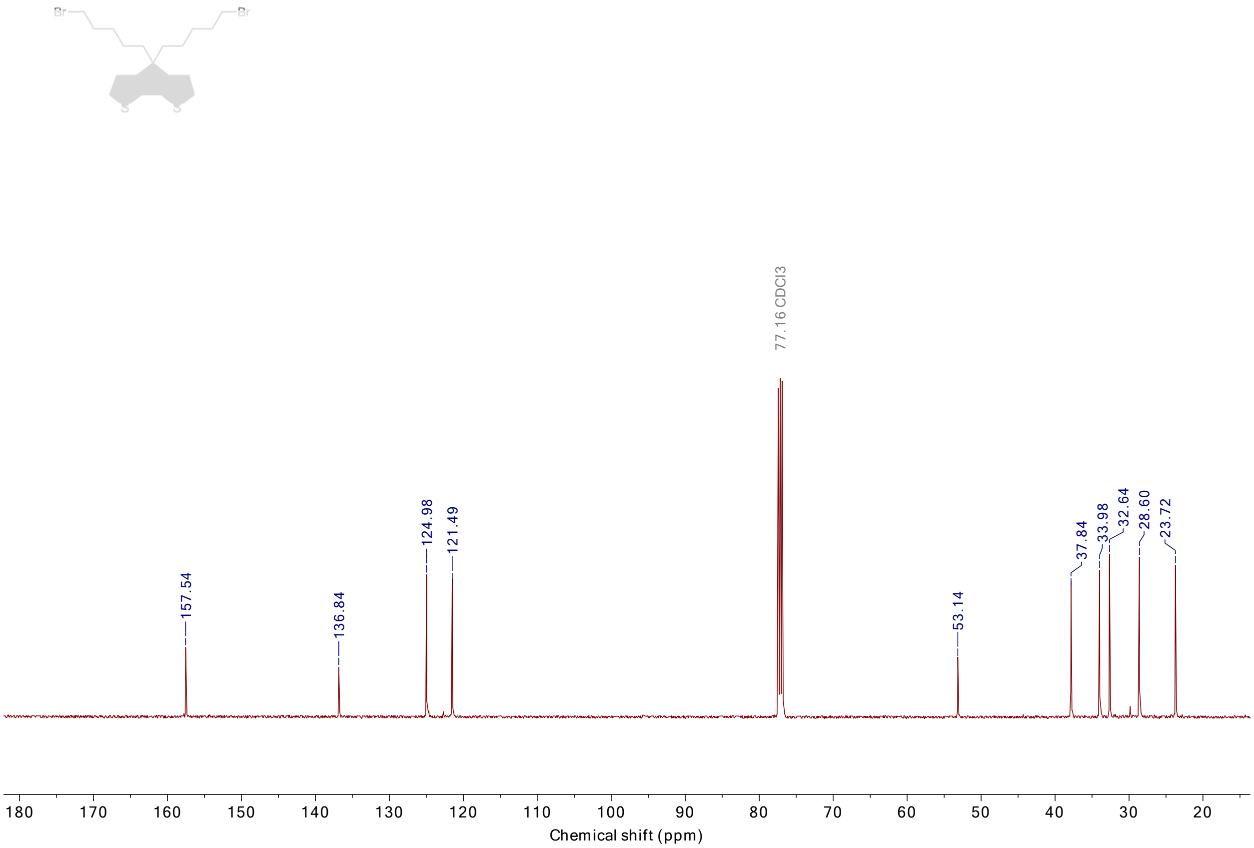
Scheme S4. Synthesis of CPE-C5-Na and conversion to CPE-C5-TBA.

CPDT-C5

In a round bottom flask was added NaOH (7.6 g) and water (7.6 mL). The solution was purged for 30 min with argon. In a second round bottom flask was added 4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (CPDT, 300.3 mg, 1.68 mmol, 1.0 equiv) and tetrabutylammonium iodide (124.4 mg, 0.33 mmol, 0.2 equiv) followed by 3 cycles of vacuum/argon. The solvent was cannulated to the second flask, followed by the addition of 1,5-dibromopentane (3.87 g, 16.8 mmol, 10.0 equiv). The reaction was stirred at 75^{o}C for 3h. Then, the reaction was cooled to room temperature and extracted with ethyl acetate. The organic layer was washed with H_2O, dried over Na_2SO_4 and concentrated. The material was dried loaded onto a column and eluted with hexane, followed by 10% EtOAc/Hex affording 595.7 mg of CPDT-C5, in a 74% yield. ^{1}H NMR (500 MHz, cdcl$_3$) δ 7.16 (d, *J* = 4.9 Hz, 2H), 6.91 (d, *J* = 4.8 Hz, 2H), 3.27 (t, *J* = 6.9 Hz, 4H), 1.89 – 1.83 (m, 4H), 1.75 – 1.66 (m, 4H), 1.31 – 1.21 (m, 4H), 0.97 – 0.89 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 157.54, 136.84, 124.98, 121.49, 53.14, 37.84, 33.98, 32.64, 28.60, 23.72. MS (ESI): [(M)$^+$] calcd: 475.9666; found: 475.9653.



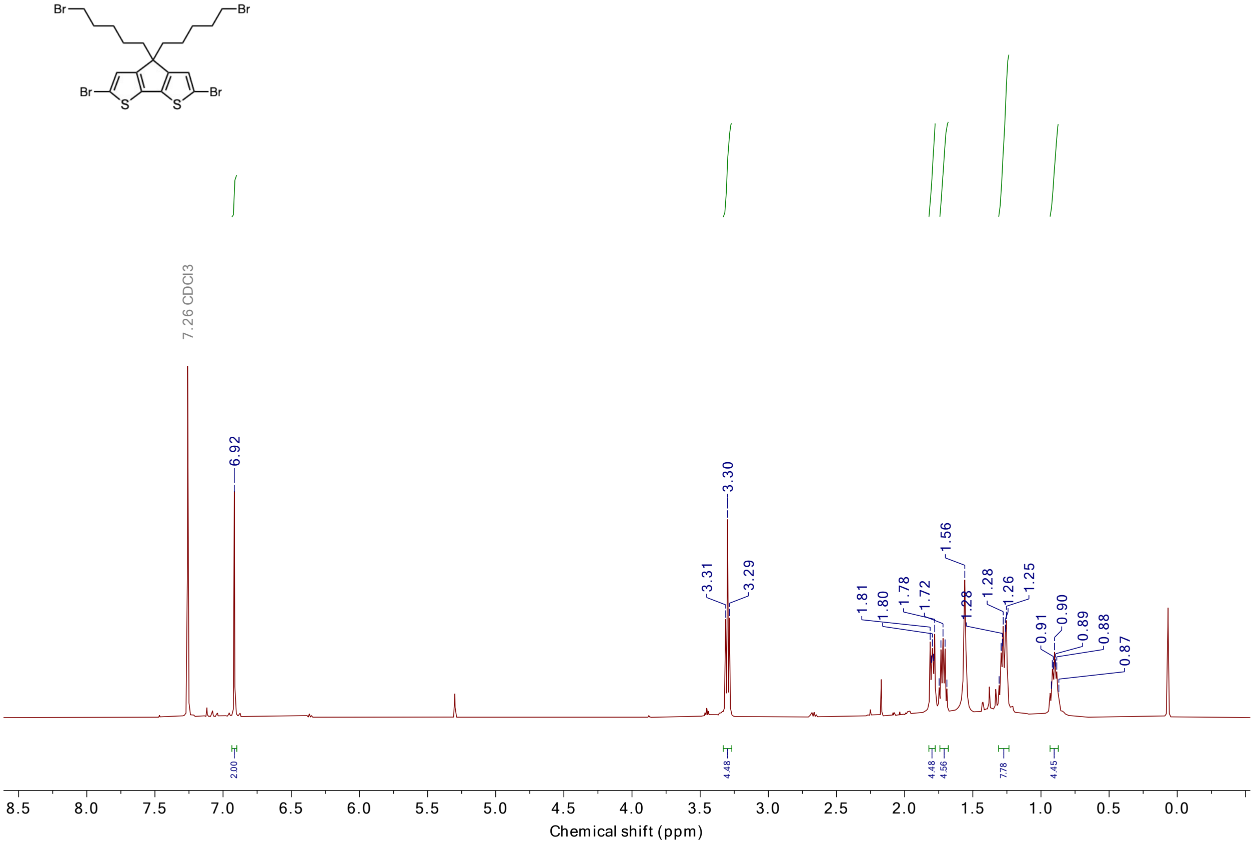
^{1}H NMR spectrum of CPDT-C5 (600 MHz, Chloroform-*d*)



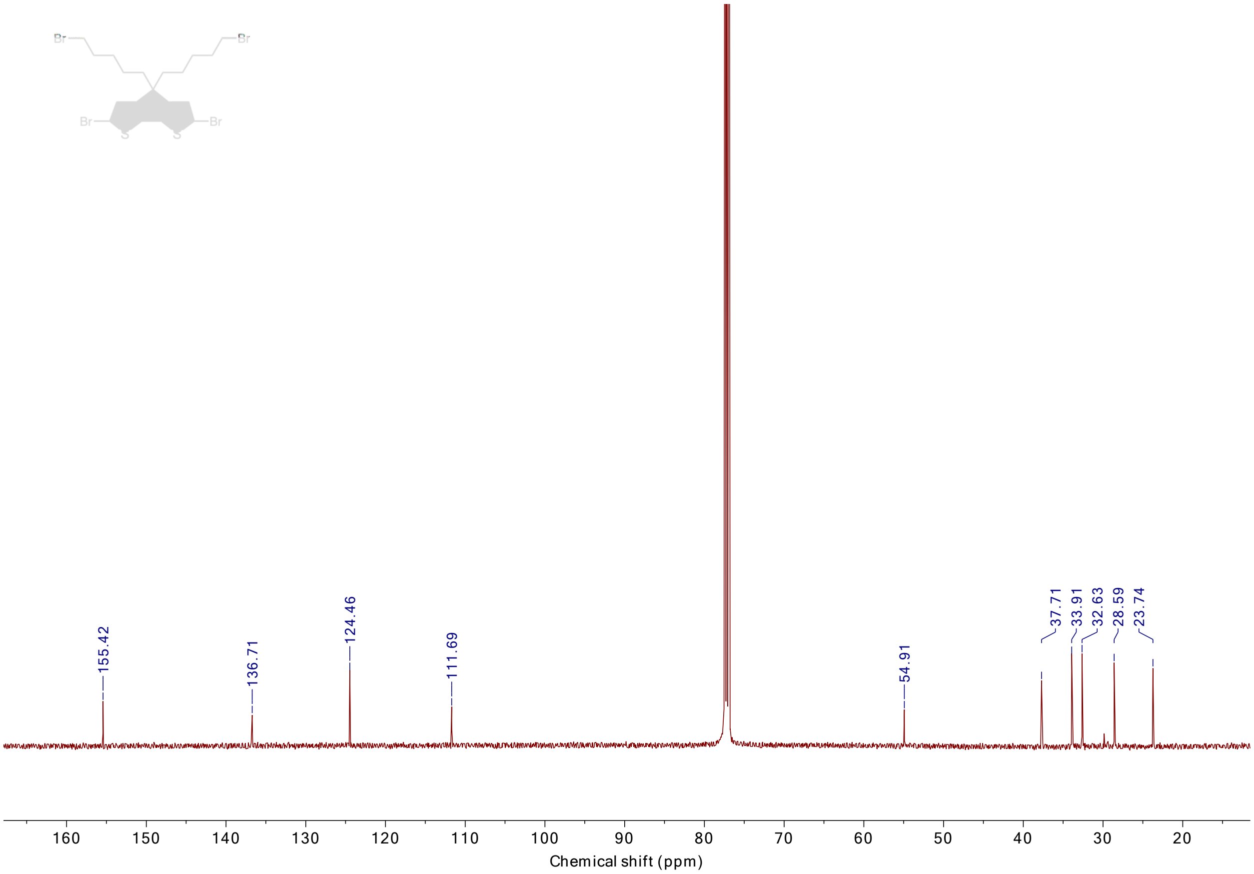
^{13}C NMR spectrum of CPDT-C5 (126 MHz, Chloroform-*d*)

CPDT-C5-Br

CPDT-C5 in a round bottom flask was subjected to an argon atmosphere (3 cycles vacuum/argon) and suspended in dry DMF (31 mL). NBS (467.4 mg, 2.6 mmol, 2.5 equiv) was added in dark by shielding the flask with aluminum foil. The reaction was stirred at room temperature overnight and quenched with water (DI). The reaction mixture was dissolved in ether and washed with brine, dried over Na_2SO_4 and concentrated. Flash chromatography was pursued using hexane as the eluent and the crude material was dry loaded onto the column. After purification, 667.4 mg of CPDT-C5 was purified, in a 84% yield. ^{1}H NMR (600 MHz, Chloroform-*d*) δ 6.92 (s, 2H), 3.30 (t, J = 6.8 Hz, 4H), 1.82 – 1.78 (m, 4H), 1.74 – 1.68 (m, 5H), 1.31 – 1.26 (m, 4H), 0.93 – 0.87 (m, 4H). ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.42, 136.71, 124.46, 111.69, 54.91, 37.71, 33.91, 32.63, 28.59, 23.74. MS (ESI): [(M)$^+$] calcd: 633.7856; found:633.7844.



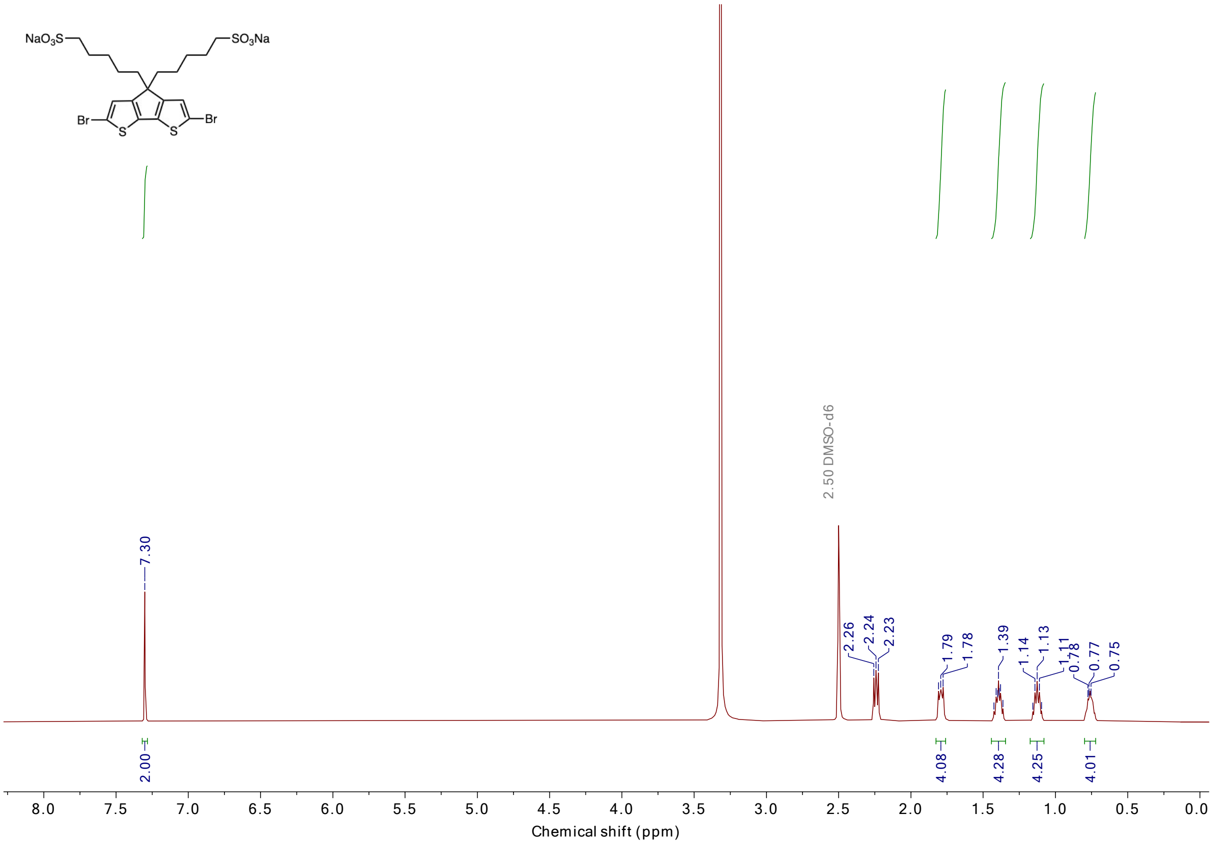
^{1}H NMR spectrum of CPDT-C5-Br (600 MHz, Chloroform-*d*)



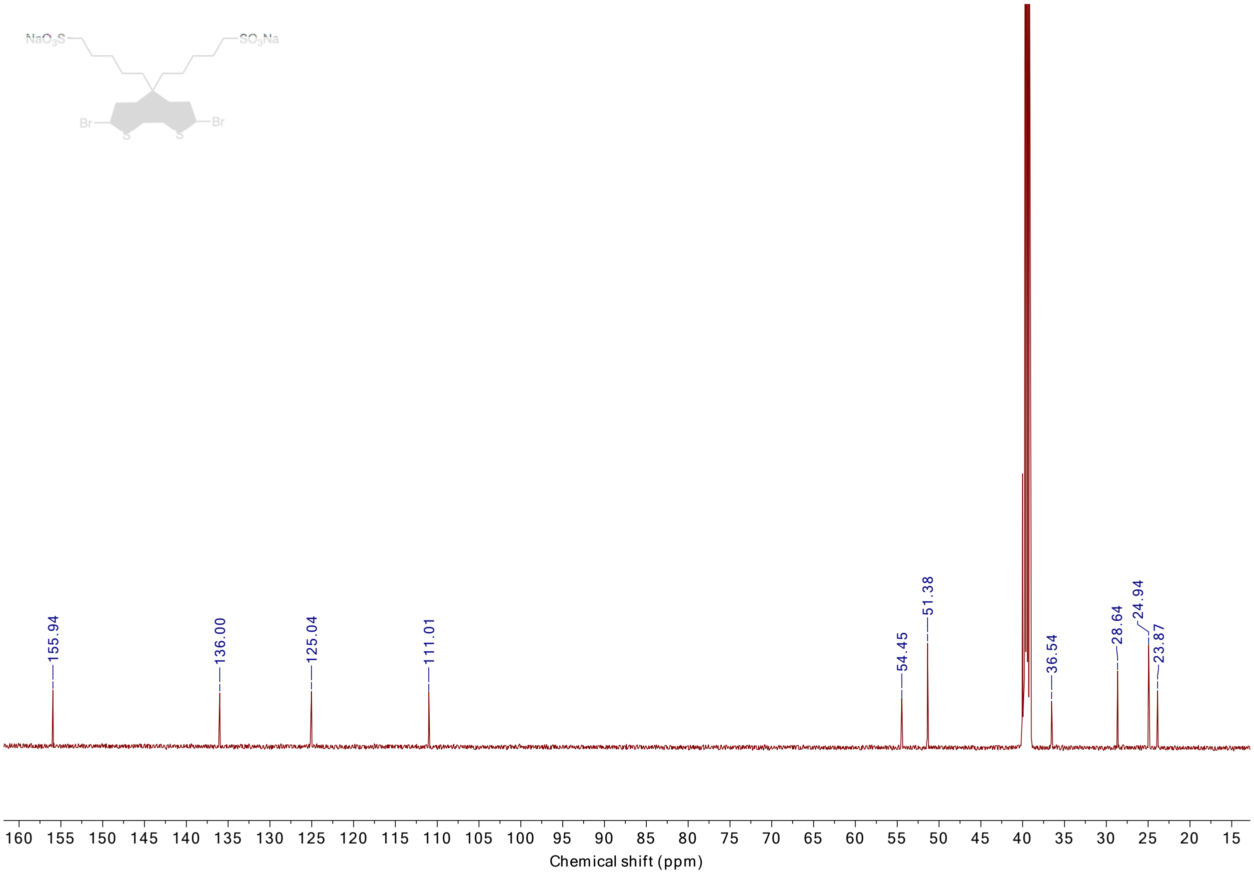
^{13}C NMR spectrum of CPDT-C5-Br (600 MHz, Chloroform-*d*)

CPDT-C5-Na

A round bottom flask containing CPDT-C5-Br (667.4 mg, 1.05mmol, 1.0 eq) was charged with a reflux condenser. The starting material was dissolved in a mixture of ethanol (10.4 mL) and water (10.4 mL) and then sodium sulfite (265.3 mg, 2.1 mmol, 2 eq) and tetrabutylammonium iodide (39 mg, 0.105 mmol, 0.1 equiv) were added. The reaction was refluxed for 24h. Then, the reaction mixture was washed with chloroform and concentrated. Purification by flash chromatography (reversed phase silica gel C-18,) gradient 5% MeOH/H_2O to 100% MeOH, provided CPDT-C5-Na (437.0 mg, 61%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 7.30 (s, 2H), 2.24 (t, J = 7.6 Hz, 4H), 1.83 – 1.76 (m, 4H), 1.44 – 1.34 (m, 4H), 1.17 – 1.08 (m, 4H), 0.81 – 0.71 (m, 4H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.94, 136.00, 125.04, 111.01, 54.45, 51.38, 36.54, 28.64, 24.94, 23.87. MS (ESI): [$(M-2Na+H)^-$] calcd: 634.8723; found: 634.8719.



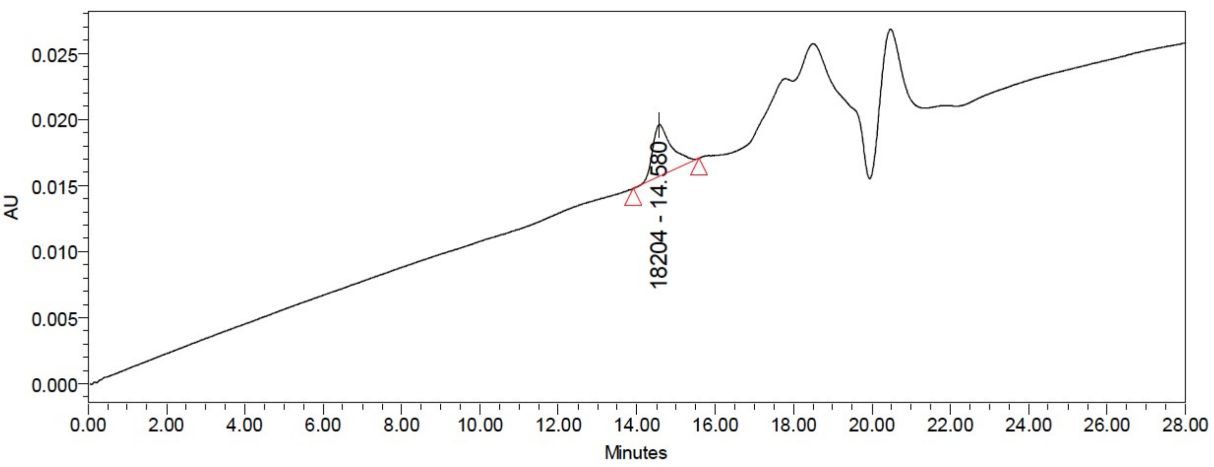
^{1}H NMR spectrum of CPDT-C5-Na (500 MHz, DMSO-d_6)



^{13}C NMR spectrum of CPDT-C5-Na (126 MHz, DMSO-d$_6$)

CPE-C5-TBA

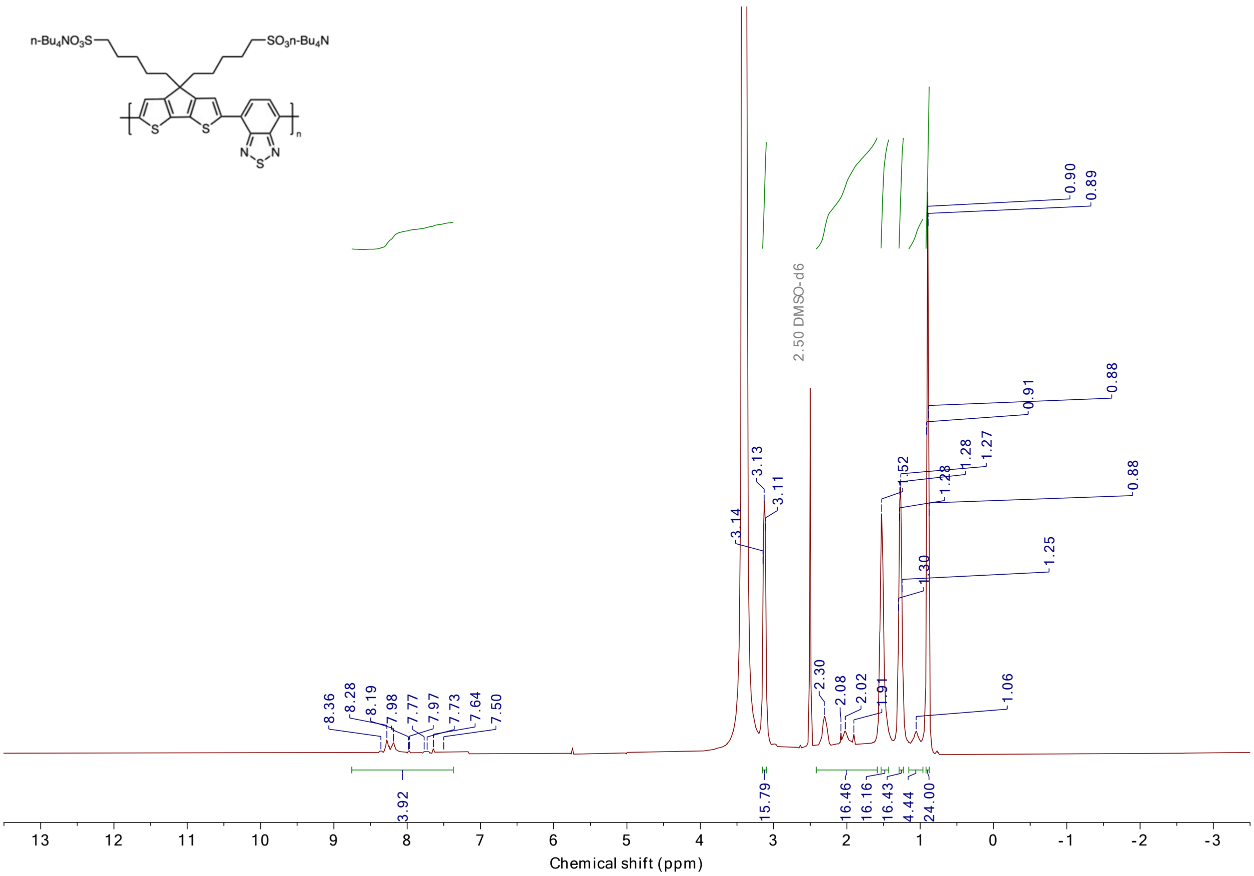
CPE-C5-Na was synthesized using CPDT-C5-Na and 2,1,3-Benzothiadiazole-4,7-bis(boronic acid pinacol ester) via the same procedure as CPE-C2-Na to provide 303.0 mg of the desired polymer as a dark blue solid (quantitative yield) ,which was found to be doped after dialysis in water for 3 days. Ion exchange with tetrabutylammonium bromine provided a DMF-soluble polyelectrolyte CPE-C5-TBA with tetrabutylammonium as the counterions, of which molecular weight can be determined by GPC (DMF). Mn = 14484, Mw = 16292, PDI = 1.12. ^{1}H NMR (500 MHz, DMSO-*d*$_6$) δ 8.74 – 7.35 (m, 4H), 3.13 – 3.08 (m, 16H), 2.42 – 1.59 (m, 16H), 2.08 – 1.88 (m, 4H), 1.53 – 1.43 (m, 16H), 1.37 – 1.25 (m, 16H), 1.20 – 0.97 (m, 4H), 0.88 (t, *J* = 5.2, 4.3 Hz, 24H).



GPC Results

	Mn	Mw	MP	Mz	Mz+1	Polydispersity
1	14484	16292	18204	17865	19193	1.12
2						

GPC plot of CPE-C5-TBA



^{1}H NMR spectrum of CPDT-C5-TBA (500 MHz, DMSO-d_6)

1.3 Thickness Measurements

The thickness of the CPE films was determined using an Ambios XP-100 profilometer. A line of CPE material was removed using the backside of a razor blade and the profilometer was scanned across multiple points along the scratch.

1.4 UV-vis-nIR

All UV-vis-nIR spectra were obtained using a Perkin-Elmer Lambda 750 UV-vis-nIR spectrometer using a tungsten lamp for the visible to near-IR region and a deuterium lamp for the UV region. CPE films for spectroelectrochemistry were prepared by drop-casting 30 μL of a solution of 10 mg/mL CPE onto a cleaned ITO-coated glass substrate. For solution measurement, 10 µL of 1mg/mL solution was dissolved in 3mL of water.

1.5 pH dependent UV-VIS measurement

pH measurements were carried out Fisher Scientific Accumet® AB150. Buffer solutions of pH = 1.1 ; 2.7; 5.1; 7.5; 9.2 and 11.3 were prepared. For pH of 1 a solution of 1M HCl was used. For pH of 3 a glycine buffer was used. For pH of 5 a citrate buffer was used. For pH of 7 a phosphate buffer was used. For pH of 9 a Tris buffer was used. For pH of 11 a sodium hydrogen phosphate/sodium hydroxide buffer was used. 10 µL of 1mg/mL CPE solution was dissolved in 3 mL of the buffer solution and left to equilibrate for 24 hours. UV-VIS measurements were performed after which the pH was measured again.

1.6 Differential Pulse Voltammetry

A Bio-Logic SP-300 potentiostat was used to perform DPV and EC-Lab software to interface with the user and treat the data. DPV traces were collected using a glassy carbon working electrode, Saturated calomel reference electrode (SCE), platinum counter electrode and 0.1M NaCl as supporting electrolyte. The working electrode was cleaned and polished before each scan by rubbing on a polishing cloth with a paste of MicroPolish Alumina particles in water. Particles sizes of 1.0 µm, 0.3 µm and 0.05 µm were used successively, rinsing with water between each particle size. The working electrode was then rinsed with water and let to air dry. The parameters for DPV scans were as follows: the scan window (low E to high E) was chosen as needed and the following parameters were kept invariant, Incr E (V) = 0.005 , amplitude (V) = 0.005, pulse width (s) = 0.05, pulse period (s) = 0.5. Voltammetry on the alkylated CPDT derivatives were performed in solution and in film. For solution measurement, $1 * 10^{-3}$ mol/L solutions were prepared and degassed for 10 min with nitrogen prior de measurement. For film measurement, solutions of $5.6 * 10^{-3}$ mol/L solutions were prepared and 10 µL drop casted on top of the working electrode. The film was dried for 20 minutes aided by N_2 flow, and the supporting electrolyte degassed for 10 min prior the measurement. Voltammetry on CPE derivatives were carried out by preparing 1 mg/mL solutions of the polymer and drop casting 5 µL on top of the working electrode. The film was dried for 20 min aided by N_2 flow and the supporting electrolyte degassed for 10 min prior the measurement.

The electrochemical cell was placed inside a Faraday cage for data collection. For the DPV redox peak, the potential measured, E_{max}, is shifted from the actual redox potentials of the redox species, $E_{1/2}$, by a value of one half the pulse amplitude, $\Delta E/2 = 5$ mV. This was corrected using the expression: $E_{1/2} = E_{max} + \Delta E/2$.[77]

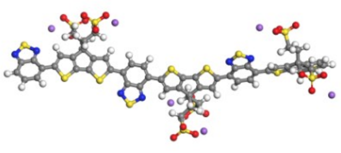
1.7 Ultraviolet-Photoelectron Spectroscopy (UPS)

UPS was carried out with a Kratos Axis Ultra X-ray Photoelectron Spectroscopy (XPS) system on drop casted films prepared from 30 μL of a solution of 10 mg/mL CPE materials on top of ITO coated glass substrates. A clean piece of silver was argon etched to get the exact zero position of the system for an accurate calibration of the energy scale. The ionization potential of each CPE material was determined by subtracting the width of the high-binding cutoff and the highest occupied state (HOS) from the 21.22 eV of the incident photon. The data was processed using CasaXPS© software.

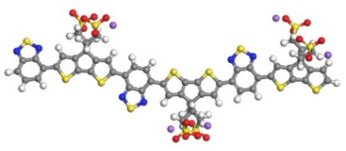
1.8 Computational details

All of the computations were accomplished using the Gaussian 09 package[78] with water as the solvent. The geometry optimizations and electronic structures calculations are performed at the ωB97XD/6-31G(d)[3] level of DFT with three repeat units of CPE. Oscillator strengths were simulated by using TD-DFT at the same level of theory, i.e., ωB97XD/6-31G(d)[79]. Restricted spin was used in the calculations for CPE, while for the CPE^+ and CPEH, the unrestricted spin calculations were performed.

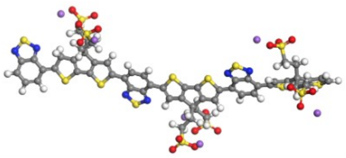
The optimized structures used in calculations are the following:



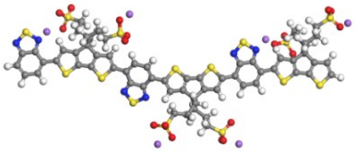
CPE-C2



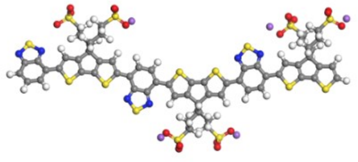
CPE^+-C2



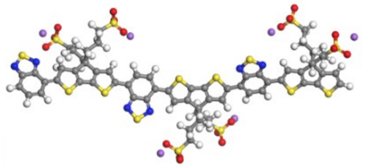
CPEH-C2



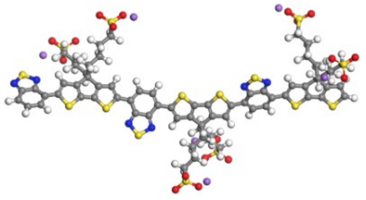
CPE-C3



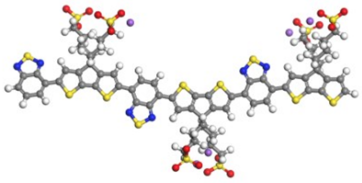
CPE$^+$-C3



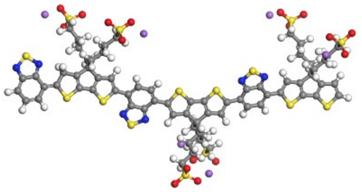
CPEH-C3



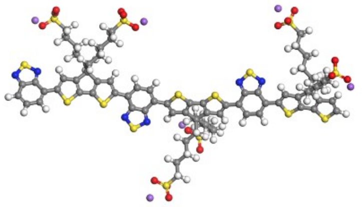
CPE-C4



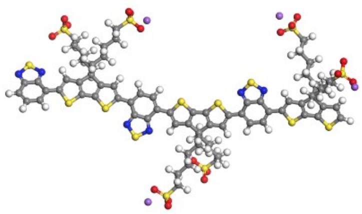
CPE$^+$-C4



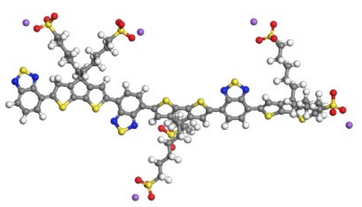
CPEH-C4



CPE-C5



CPE$^+$-C5



CPEH-C5

1.9 Synchrotron-based GIWAXS measurements

Two-dimensional (2D)-GIWAXS measurements were performed at the PLS-II 5A beamline of the Pohang Accelerator Laboratory (PAL) in Korea. 2D-GIWAXS images were collected at a 0.12 incidence angle with 11.57 keV ($\lambda = 1.07156$ Å) and a MAR345 image plate detector (sample-to-detector distance: 414.6045 mm).

1.10 AFM

All topographic images were obtained using a Multimode Atomic Force Microscope (Digital Instruments) in a nitrogen atmosphere glove box. Silicon tips with a resonant frequency of 300 kHz and a force constant of 40 N/m were used (Budget Sensors). First order image flattening was performed on the morphology images on Nanoscope Analysis 1.5 software.

1.11 OECT Fabrication

Gold electrodes were patterned on glass wafers using standard clean-room lithography protocols. Polydimethylsiloxane (PDMS) wells were used to contain the electrolyte and insulate the gold contacts from the electrolyte. PDMS was prepared from Sylgard® 184 from Dow-Corning using a mixing ratio of 10:1 between the base and the curing agent with a curing time of 4 hours at 80 ºC. Wells were cut from a sheet of PDMS and fused to the patterned glass substrates using an oxygen plasma. For the device fabrication, polydimethylsiloxane (PDMS) wells were bonded to cleaned glass substrates by exposing both surfaces to an oxygen plasma before placing the well. The purpose of incorporating the PDMS well was to confine the electrolyte above the channel area and to reduce the leakage current between the source and drain contacts and the gate electrode. CPE films were deposited by drop-casting 14 µL of 10 mg/mL solutions of CPE in Milli-Q® into the PDMS well. 2 µL of 32 %wt GOPS in 1:1 methanol:Milli-Q® water solution was added to CPE-C2-Na, CPE-C3-Na and CPE-C4-Na for cross-linking. 2 µL of 16 %wt GOPS in 1:1 methanol:Milli-Q® water solution was added to CPE-C5-Na. After dispensing the solutions into the well, the devices were heated to 80ºC for 15 minutes to drive off the solvent, followed by 110ºC for 1 hour to cross-link the film.

1.12 Electrical Characterization

Electrical characterization was performed using a Keithley® semiconductor parametric analyzer (model 4200-SCS). Transfer curves were measured with a 1 second hold time as each data point. The capacitance of CPE films were measured using a Solartron SI 1260A impedance analyzer. An AC voltage of 40 mV was applied between a Ag/AgCl electrode and the CPE film at a frequency from 0.1 Hz to 10 MHz.

The ionic conductivity of each CPE material was compared using electrochemical impedance spectroscopy on a Solartron SI 1260A impedance analyzer running ZPlot® software. The measurement were done with a two terminal configuration: the working electrode being CPE-CX-Na films, and the counter electrode as a Ag/AgCl pellet, which acted as a reference electrode. CPE films were prepared by drop casting 14 µL of a 10 mg/mL solution on interdigitated gold electrodes. Films were de-doped by annealing at 300ºC to drive off moisture in the film. In these measuremenst, AC voltage is applied at the working electrode with an amplitude of 20 mV at a frequency of 10 Hz to 10 MHz and DC bias is applied. The measured Nyquist plot was fit to a circuit shown in the Figure S8 inset using ZView® software.

2. Figures of Supporting Information

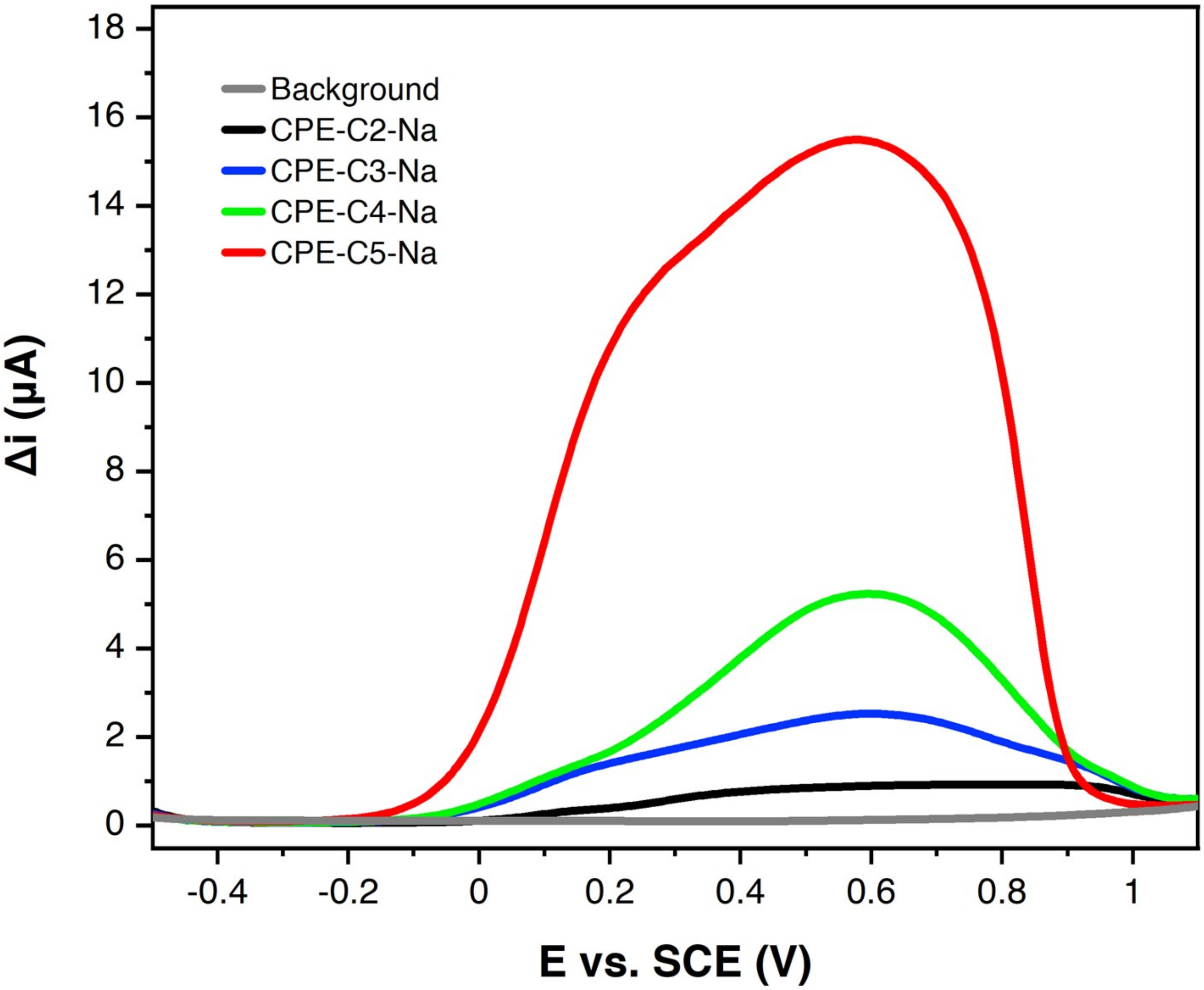


Figure S1. a) Differential pulsed voltammetry of film of CPE derivatives measured in 0.1M NaCl. A solution of 1mg/mL CPE-CX-Na in Millipore water was drop-casted on top of a glassy carbon for working electrode, Pt was used as counter electrode and SCE as reference electrode.

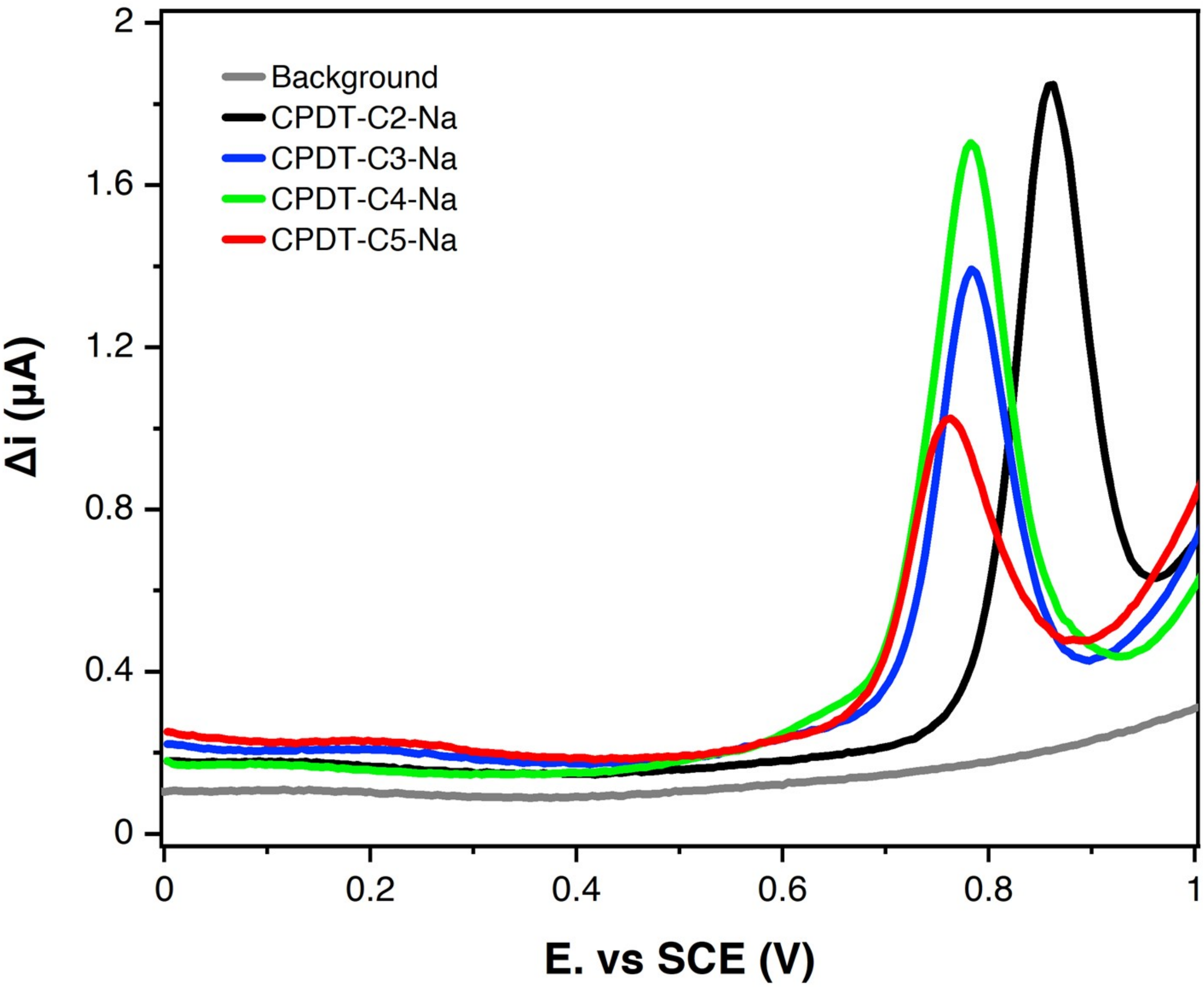


Figure S2. Differential pulsed voltammetry of alkylated cyclopentadithiophene derivatives in aqueous solution. A solution of 1mg/mL CPDT-CX-Na in 0.1M NaCl was prepared and the measurement conducted using glassy carbon for working electrode, Pt as counter electrode and SCE as reference electrode.

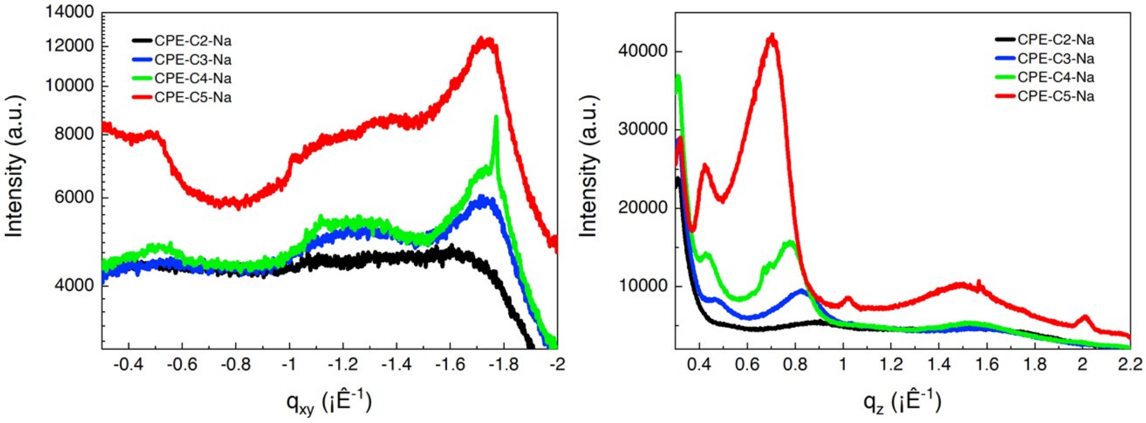


Figure S3. Line cuts extracted from the 2D images of the CPE films along with out-of-plane and in-plane directions.

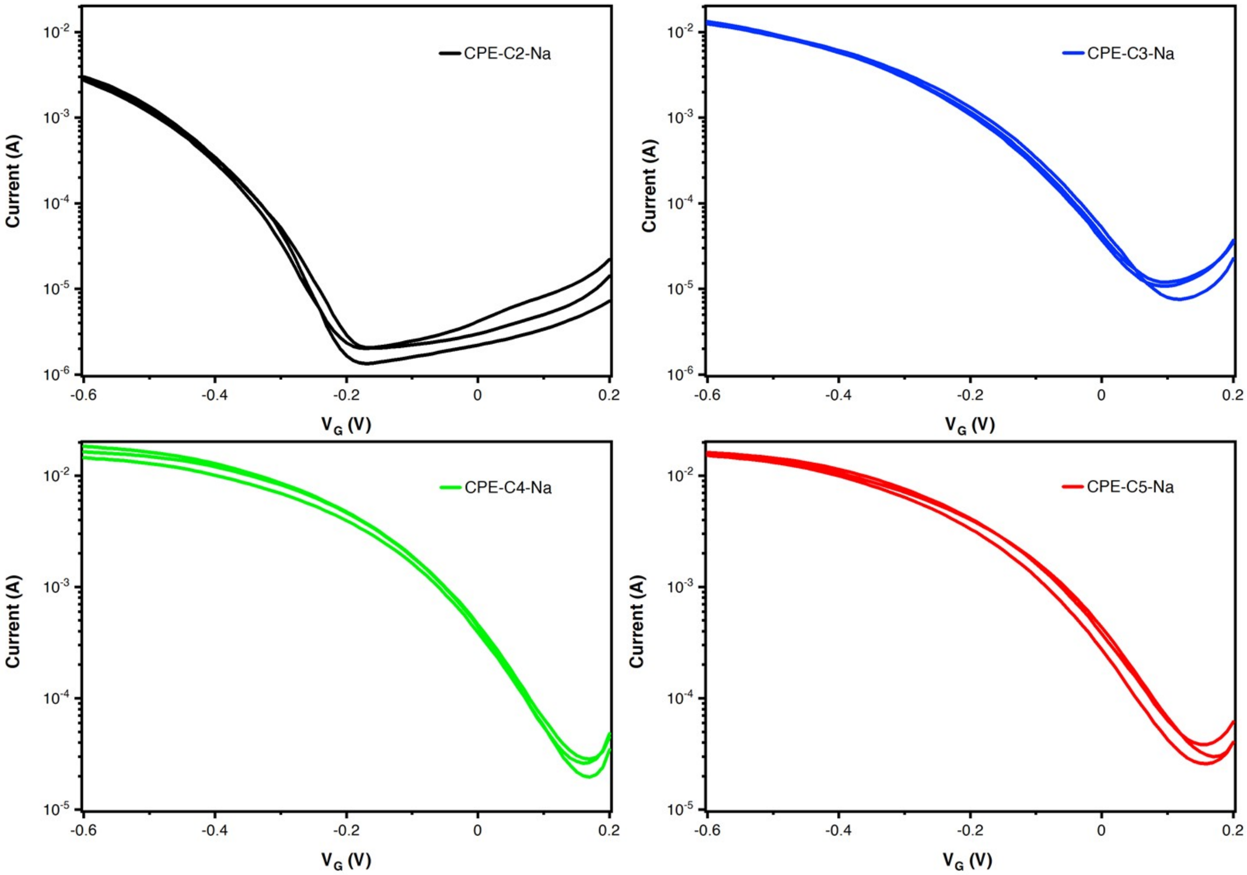


Figure S4. Transfer characteristics of all CPE-CX-Na (OECTs) with optimized amounts of GOPS cross-linker. Each plot contains the transfer curve of three devices for each CPE. CPE-2-Na, CPE-3-Na and CPE-4-Na OECTs are prepared with 32% GOPS by weight. CPE-5-Na OECTs are prepared with 16% GOPS by weight.

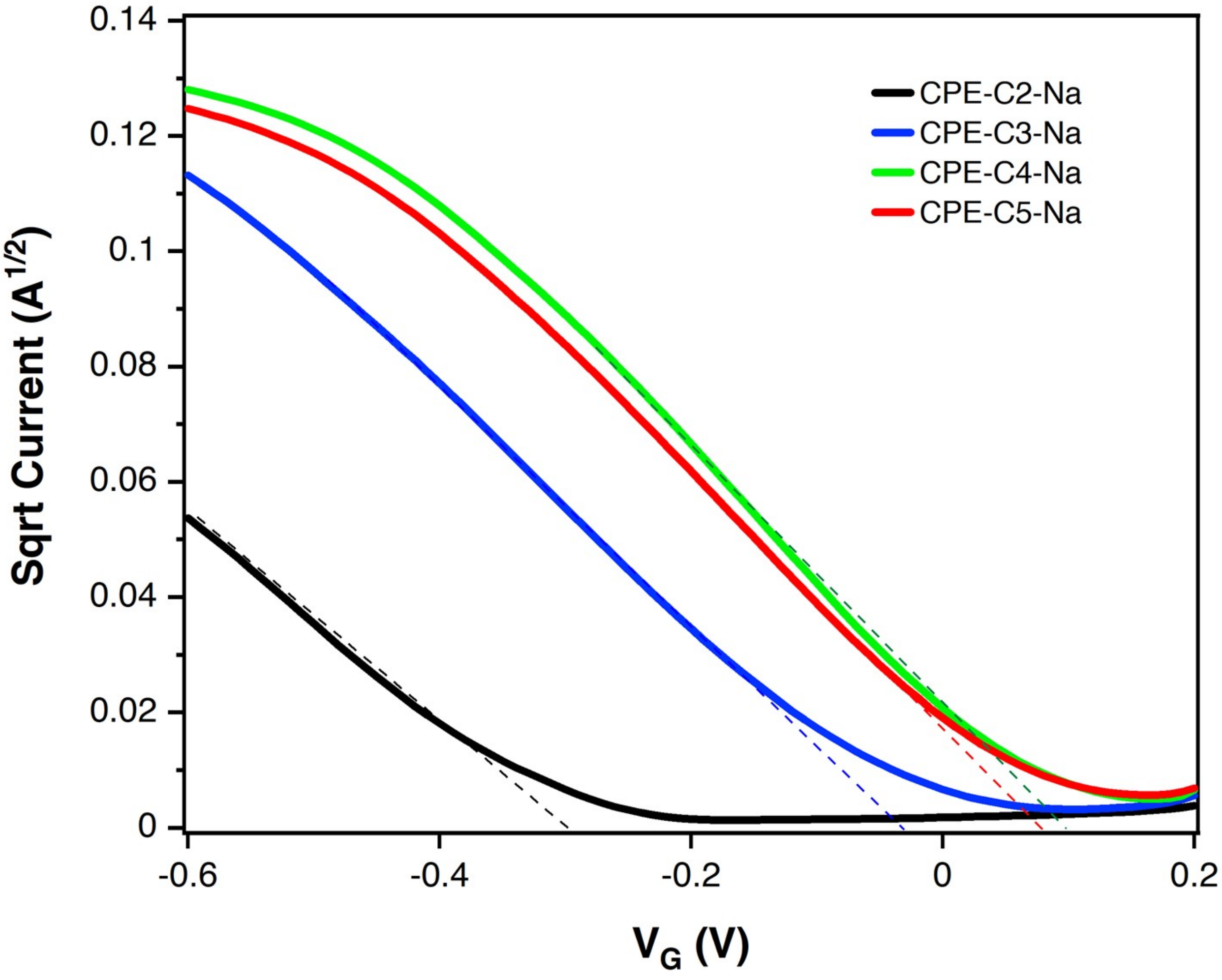


Figure S5. Square root of I_D versus gate voltage (V_G). Fits in the linear regime of the curves were used to extract the OECT threshold voltage (V_T).

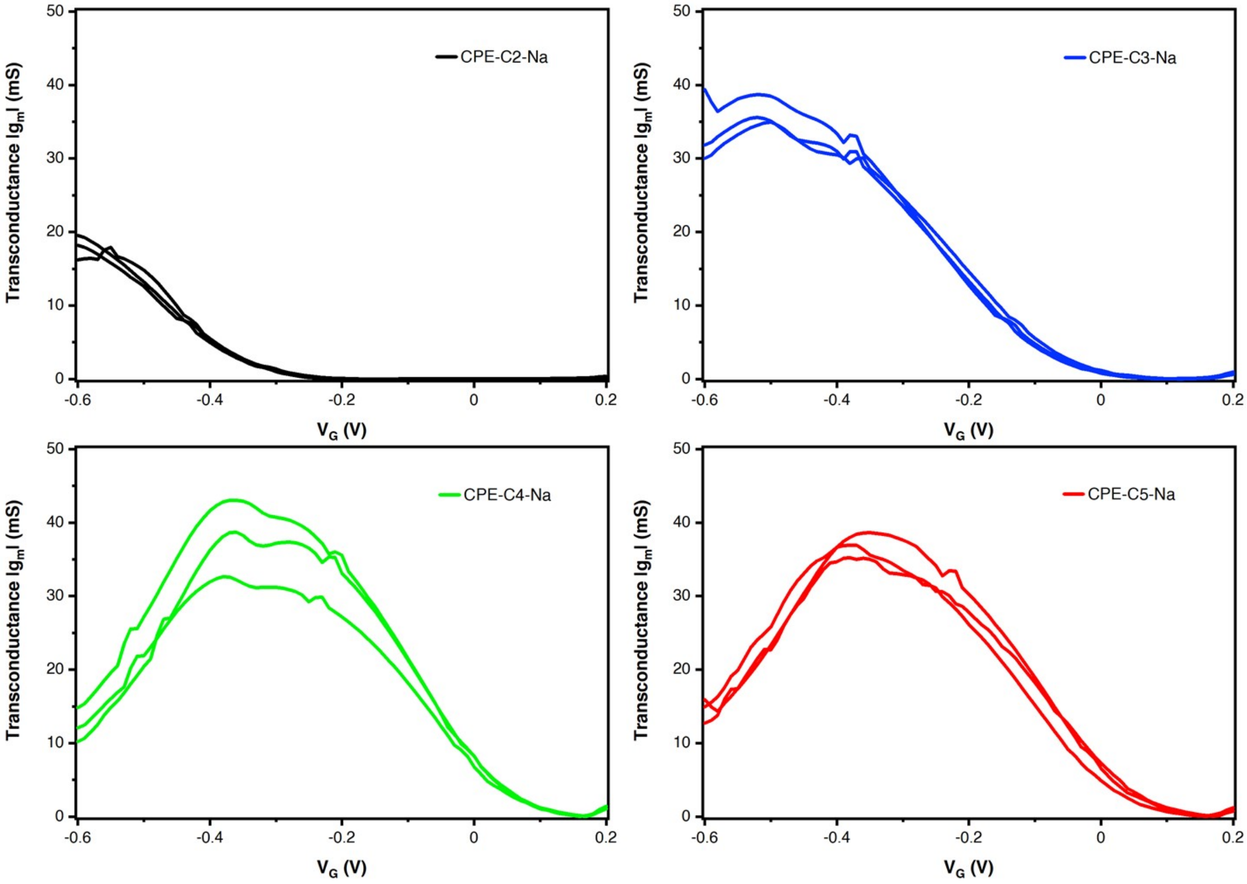


Figure S6. Transconductance versus applied gate voltage for each CPE material. The transconductance is calculated from the transfer curves from Figure S4.

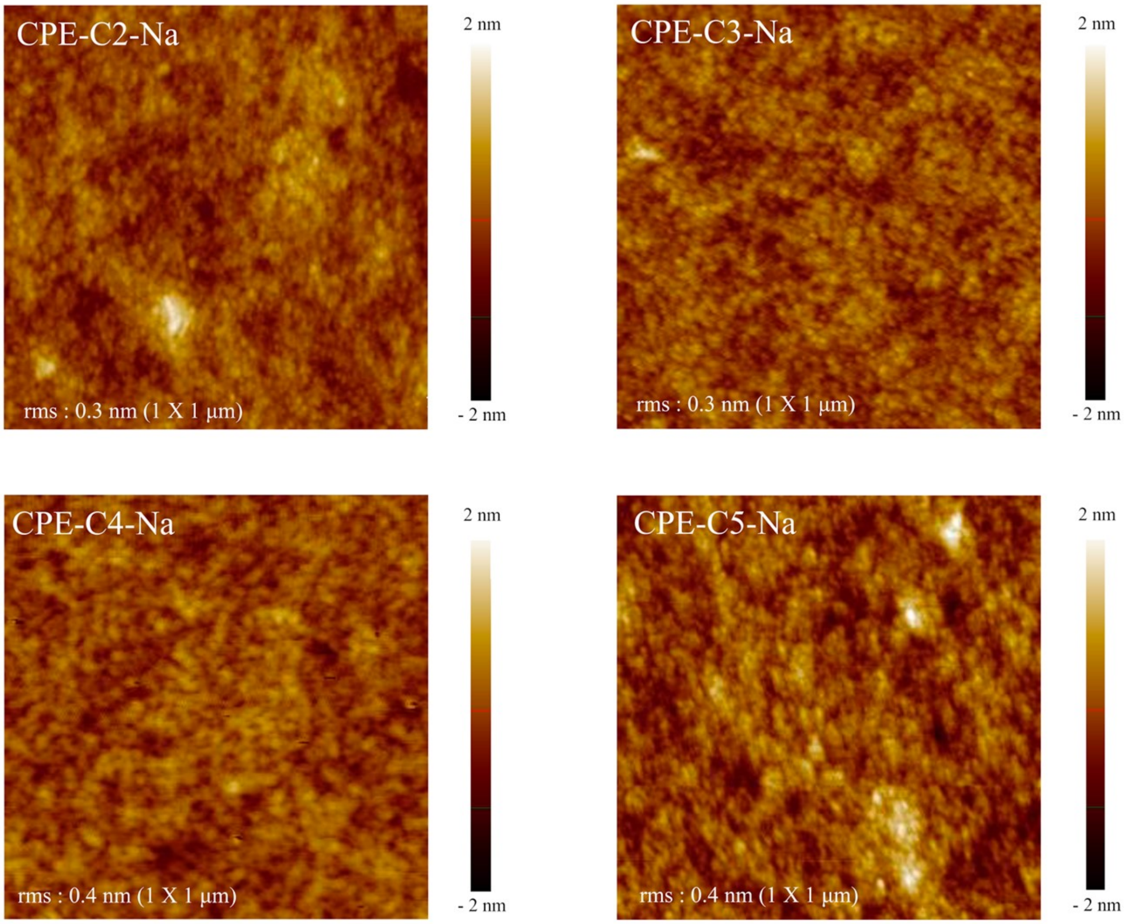


Figure S7. Morphology measured by Atomic Force Microscopy (AFM) of neat CPE-CX-Na films prepared from solution.

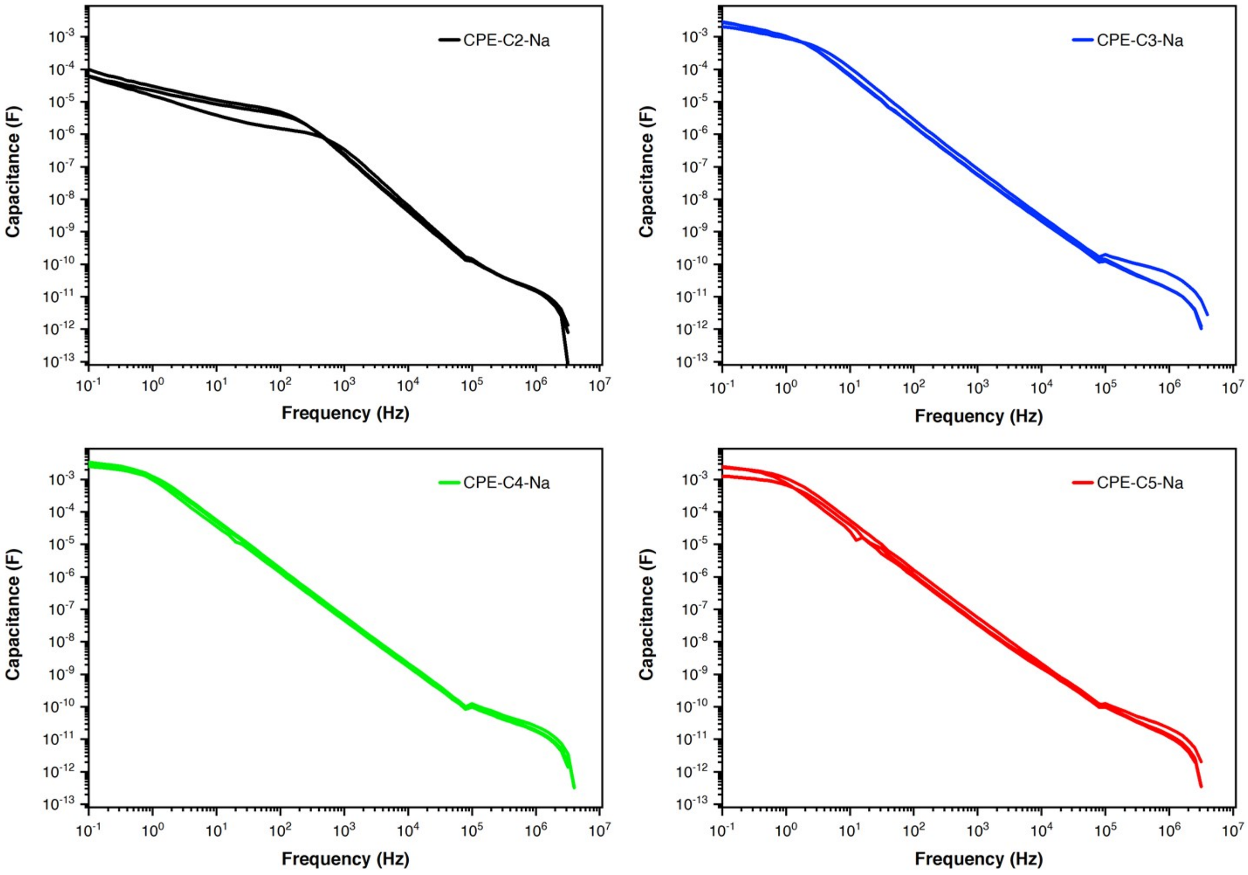


Figure S8. Capacitance as a function of frequency measured by impedance spectroscopy for each CPE material.

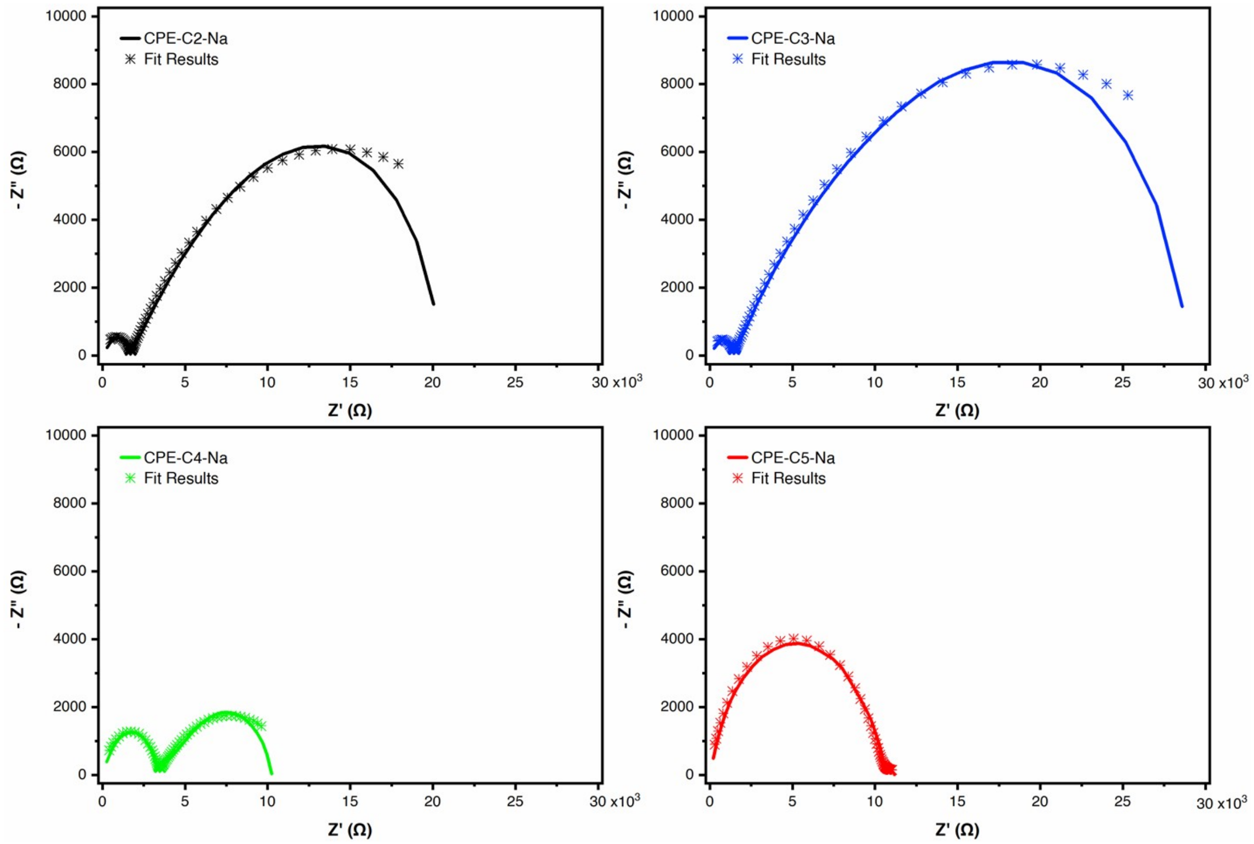


Figure S9. Nyquist plots of each CPE material generated by electrochemical impedance spectroscopy (EIS) measurements for each CPE. Each Nyquist plot is fit to the circuit shown in Figure S13 in order to estimate the ion conductivity of each CPE derivative.

The ionic conduction is represented by a constant phase element (CPE-dl) in series with an ion resistance (R-ion). These are presented in series due to the ion blocking nature of gold contacts. Since gold contacts are not hole blocking, we expect to see hole conduction presented by a constant phase element (CPE-bulk) parallel to hole resistance (R-e). Since CPE's are mixed conductors, we expect to see ionic and electronic carriers transporting simultaneously. As a result, both ion and hole circuit elements are shown parallel to each other.

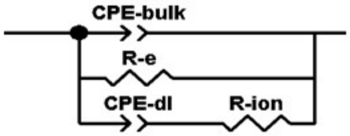


Figure S10. Circuit diagram used to fit Nyquist plots to determine ion conductivity of each CPE derivative.

3. Tables of the SI

Sample →	$\lambda_{polaron}/\lambda_{max}$			
Condition ↓	**CPE-C2-Na**	**CPE-C3-Na**	**CPE-C4-Na**	**CPE-C5-Na**
Film	0.36	0.59	0.75	0.81
Solution	0.29	0.64	0.79	0.81
pH 1.0	0.6	0.96	1.13	1.05
pH 2.6	0.38	0.76	0.94	0.93
pH 5.0	0.22	0.49	0.66	0.71
pH 7.0	0.12	0.27	0.41	0.43
pH 9.1	0.11	0.24	0.33	0.31
pH 11.1	0.06	0.11	0.2	0.19

Table S1. Summary of $\lambda_{polaron}/\lambda_{max}$

		CPE-C2	CPE-C3	CPE-C4	CPE-C5
Out-of-plane	Peak (Å^{-1})	0.882	0.821	0.787	0.721
	FWHM (Å^{-1})	0.378	0.243	0.130	0.118
	Lattice (nm)	0.712	0.765	0.799	0.872
	L_c (nm)	1.661	2.589	4.834	5.333
In-plane	Peak (Å^{-1})	1.667	1.735	1.730	1.737
	FWHM (Å^{-1})	0.406	0.253	0.246	0.170
	Lattice (nm)	0.377	0.362	0.363	0.362
	L_c (nm)	1.546	2.484	2.553	3.686

Table S2. Summary data of GIWAXS