

Electrical Properties of Doped Conjugated Polyelectrolytes with Modulated Density of Ionic Functionalities

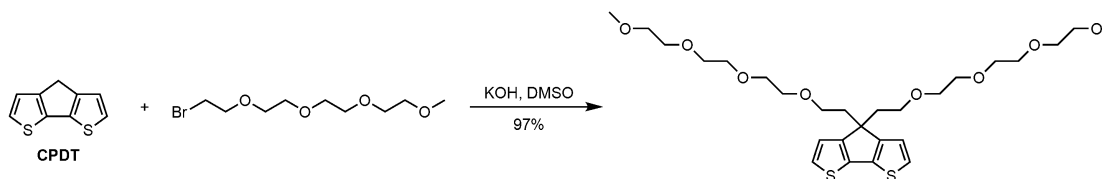
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General Information

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. ¹H NMR spectra were recorded at 500 MHz, and ¹³C NMR spectra were recorded at 126 MHz in D₂O, DMSO-d₆ or pyridine-d₅. Chemical shifts are reported in ppm referenced to residual solvent peaks as follows: D₂O, 4.79 ppm for ¹H NMR; DMSO, 2.50 ppm for ¹H NMR. Mass spectrometry was performed using electron spray as the ionization method. Gel Permeation Chromatography (GPC) was measured in Waters[®] system using DMF with 0.1% LiBr as the solvent and calibrated versus polystyrene standards. Atomic force microscopy was performed on an Asylum MFP-3D system on tapping mode.

4H-Cyclopenta[2,1-b:3,4-b']dithiophene (**CPDT**) was purchased from AstarPharma and used without further purification. 2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl bromide was purchased from TCI America and used without further purification. 2,6-dibromo-4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b:3,4-b']-dithiophene ¹ and 2,1,3-benzothiadiazole-4,7-bis (boronic acid pinacol ester) ² were synthesized according literature procedures. *N*-bromo-succinimide was purchased from Sigma Aldrich and recrystallized from water before use. Pd(PPh₃)₄ was purchased from Strem Chemicals and used as received.

Synthesis of 4,4-bis(2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene



CPDT (1.0 g, 5.6 mmol) was dissolved in DMSO (30 mL), and the solution was purged with Ar for 10 min. KI (0.03 mg, 0.2 mmol) and KOH (1.26 g, 22.4 mmol) were added and stirred for another 10 min. 2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl bromide (3.2 g, 11.8 mmol) was added and stirred at room temperature for 24 h in dark. The mixture was then poured into 1 M HCl (aq. 200 mL), and the resulting mixture was extracted with Et₂O (100 mL × 4). The organic layers were combined and washed with brine (100 mL), dried over MgSO₄, filtered, and concentrated in reduced pressure. The resulting crude brown oil was purified by flash chromatography using ethyl acetate/hexane as eluent to give a yellow oil (3.1 g, 97%). ¹H NMR (CDCl₃, 500MHz): δ (ppm) 2.25 (t, *J* = 7.0 Hz, 4H), 3.00 (t, *J* = 7.5 Hz, 4H), 3.31 (t, *J* = 5.0 Hz, 4H), 3.37 (s, 6H), 3.47 (t, *J* = 5.0 Hz, 4H), 3.53 (q, *J* = 5.0 Hz, 2.5 Hz, 4H), 3.60 (m, 12H), 6.96 (d, *J* = 5.0 Hz, 2H), 7.15 (d, *J* = 5.0 Hz, 2H). ¹³C NMR (CDCl₃, 60 MHz): δ (ppm) 37.7, 49.3, 59.2, 67.7, 70.2, 70.4, 70.5, 70.6, 70.7, 72.1, 121.8, 125.1, 136.7, 156.6. MS (ESI) *m/z* calcd for C₂₇H₄₂O₈S: 558.23; found: 581.24 (M-Na⁺).

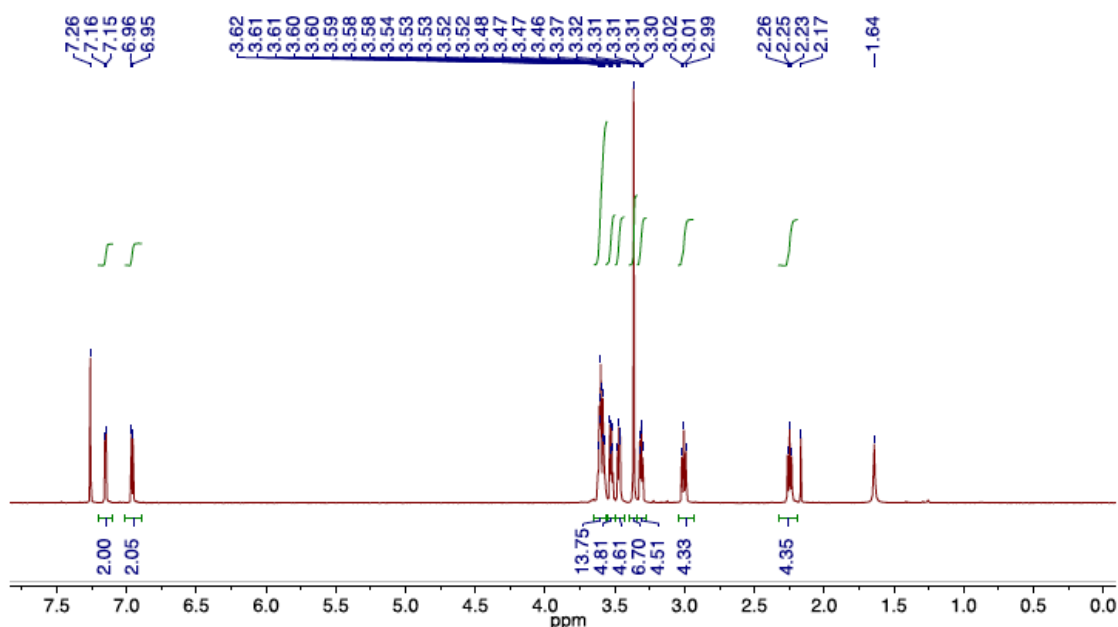
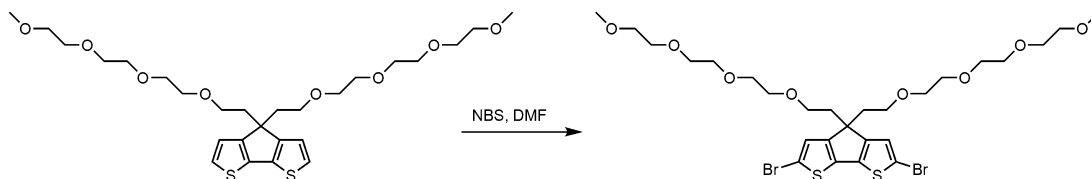


Fig. S1 ¹H-NMR of 4,4-bis(2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene.

Synthesis of 2,6-dibromo-4,4-bis(2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene



To a mixture of 4,4-bis(2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene (1.00 g, 1.79 mmol) in DMF (25 mL) was added *N*-bromosuccinimide (0.650 g, 3.67 mmol). The reaction was stirred in dark for 12 h. The mixture was then poured into water (200 mL), and the resulting mixture was extracted with Et₂O (100 mL × 4). The organic layers were combined and washed with brine (100 mL), dried over MgSO₄, filtered, and concentrated in reduced pressure. The resulting crude dark brown oil was purified by flash chromatography using ethyl acetate/hexane as eluent to give a yellow oil (0.779 g, 61 %). ¹H NMR (500 MHz, CDCl₃): δ 2.17 (t, *J* = 7.0 Hz, 4H), 3.03 (t, *J* = 7.0 Hz, 4H), 3.32 (t, *J* = 5.0 Hz, 4H), 3.48 (t, *J* = 5.0 Hz, 4H), 3.53 (t, *J* = 5.0 Hz, 4H), 3.60 (m, 12H), 6.99 (s, 2H). ¹³C NMR (151 MHz, CDCl₃): δ 37.5, 51.3, 59.2, 67.6, 70.4, 70.6, 70.7, 70.8, 70.9, 72.1, 111.7, 125.2, 136.5, 154.9. MS (FD) *m/z* calcd for C₂₇H₄₀Br₂O₈S₂: 714.05; found: 714.06 (M).

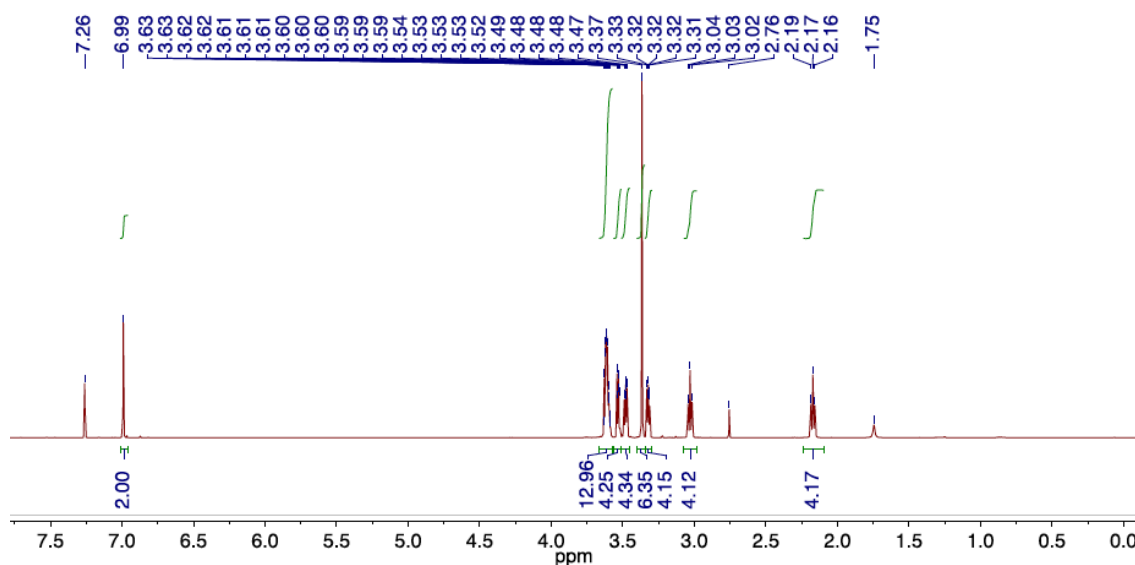
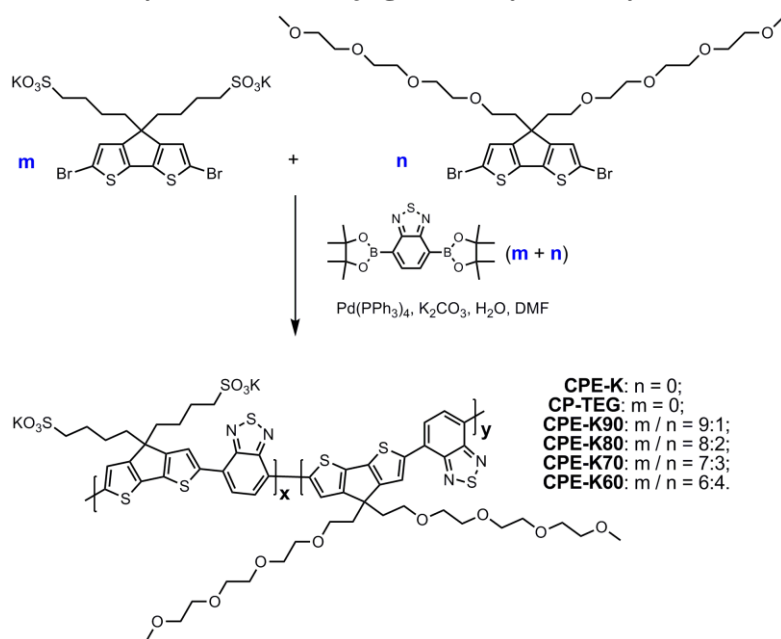


Fig. S2 ¹H-NMR of 2,6-dibromo-4,4-bis(2-[2-[2-(2-Methoxyethoxy)ethoxy]ethoxy]ethyl)-4H-cyclopenta-[2,1-b:3,4-b']dithiophene.

General Synthesis of Conjugated Polyelectrolytes



Synthesis of CPE-K was reported previously.¹ The molecular weight of CPE-K cannot be determined directly by GPC. Ion exchange of CPE-K with excess tetrabutylammonium bromide (TBABr) provided a DMF-soluble polyelectrolyte, of which molecular weight was determined by GPC (DMF): $M_n = 7.7$ K, PDI = 1.1.

Synthesis of CP-TEG

To a 5 mL microwave reaction vial were added 2,6-dibromo-4,4-bis(2-[2-(2-methoxyethoxy)ethoxy]ethoxy)-ethyl)-4H-cyclopenta-[2,1-b:3,4-b'] dithiophene dibromide (190 mg, 0.265 mmol, 1 equiv), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (103 mg, 0.265 mmol, 1.0 equiv), K_2CO_3 (110 mg, 0.795 mmol, 3.0 equiv) and $Pd(PPh_3)_4$ (31 mg, 10 mol%) in a nitrogen glove box. The tube was sealed with a septum and taken outside the glovebox. A mixture of DMF/ H_2O (4:1, 5.5 mL in total) was degassed by sparging with Ar for 15 min, and cannulated into the above microwave tube under Ar. The septum on the microwave tube was removed quickly under positive Ar pressure and sealed with a cap desired specifically for the microwave tubes. The reaction was allowed to stir in a 90 °C oil bath for 48 hrs. The reaction mixture were poured into MeOH and filtered. The collected dark blue solid was washed by Soxhlet extraction (MeOH, acetone, hexane), collected with $CHCl_3$, concentrated, and dried under vacuum to provide the title polymer as a blue solid (149 mg, 81%). 1H NMR (CD_2Cl_2 , 600 MHz) δ 8.4-8.1 (4H, aromatic), 4.7-3.2 (32H, OCH_2), 3.2-2.2 (6H, OCH_3). GPC ($CHCl_3$): $M_n = 28$ K, PDI = 2.38.

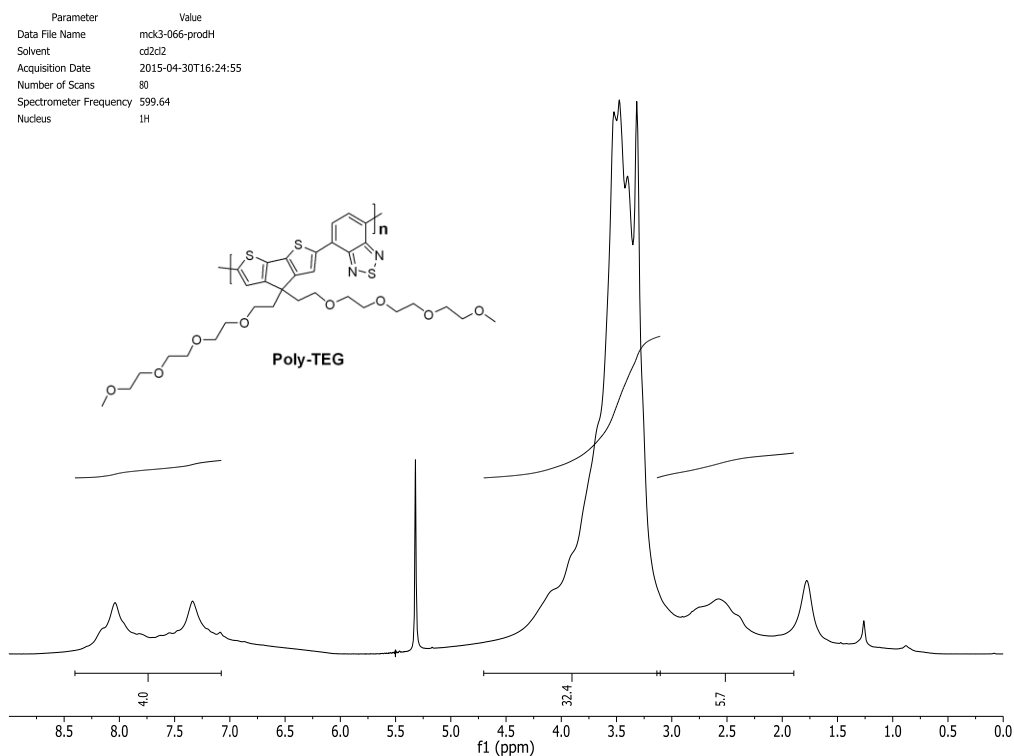


Fig. S3 ¹H-NMR of CP-TEG in CD₂Cl₂.

Synthesis of CPE-K90

To a 5 mL microwave reaction vial was added 2,6-dibromo-4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (43.0 mg, 0.063 mmol, 0.9 equiv), 2,6-dibromo-4,4-bis(2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-ethyl)-4H-cyclopenta-[2,1-b;3,4-b'] dithiophene dibromide (5.0 mg, 0.007 mmol, 0.1 equiv), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (27 mg, 0.070 mmol, 1.0 equiv), and Pd(PPh₃)₄ (4.0 mg, 5 mol%) in a nitrogen glove box. Dry DMF (1.2 mL) was added and the vial was sealed with a septum then taken out of the glove box. Aqueous 2 M K₂CO₃ (1 mL) was degassed by Ar for 15min and injected into the microwave vial. The reaction mixture was stirred at 95 °C for 48 h then poured into acetone (100 mL). The dark blue precipitate was collected by filtration, and washed with copious amounts of acetone until the filtrate was almost colorless. The precipitate was all dissolved in Millipore H₂O (25 mL), and transferred into a dialysis tube (MWCO: 3500 – 5000 Da). The dialysis tube was placed in a large beaker with H₂O (2 L) stirring for 3 days, and the H₂O was changed every 12 hrs. Evaporation of H₂O provided CPE-K90 as a dark blue solid (34 mg, 74%) after drying under vacuum overnight. The NMR of the title polymer in D₂O only showed non-informative broad peaks, probably due to the presence of paramagnetic radical cations. The molecular weight of CPE-K was not able to be determined directly due to unavailability of gel permeation chromatography (GPC) eluting with H₂O.

Therefore, ion exchange with excess tetrabutylammonium bromide provided a DMF-soluble polyelectrolyte CPE-NBu₄90 with tertbutylammonium as the counterions, of which molecular weight can be determined by GPC (DMF).

Synthesis of CPE-K80

CPE-K80 was synthesized with 2,6-dibromo-4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (38.2mg, 0.056mmol, 0.8 equiv), 2,6-dibromo-4,4-bis(2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-ethyl)-4H-cyclopenta-[2,1-b;3,4-b']dithiophene dibromide (10.0 mg, 0.014 mmol, 0.2 equiv), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (27.0 mg, 0.070 mmol, 1.0 equiv) by using the same procedure as for CPE-K90. Yield: 40 mg (86%).

Synthesis of CPE-K70

CPE-K70 was synthesized with 2,6-dibromo-4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (38.3mg, 0.056mmol, 0.7 equiv), 2,6-dibromo-4,4-bis(2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-ethyl)-4H-cyclopenta-[2,1-b;3,4-b'] dithiophene dibromide (17.2 mg, 0.024 mmol, 0.3 equiv), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (31.1 mg, 0.080 mmol, 1.0 equiv) by using the same procedure as for CPE-K90. Yield: 34mg (65%).

Synthesis of CPE-K60

CPE-K60 was synthesized with 2,6-dibromo-4,4-bis-potassium butanysulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (34.4mg, 0.050mmol, 0.6 equiv), 2,6-dibromo-4,4-bis(2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]-ethyl)-4H-cyclopenta-[2,1-b;3,4-b']dithiophene dibromide (24.0 mg, 0.034 mmol, 0.4 equiv), 2,1,3-benzothiadiazole-4,7-bis(boronic acid pinacol ester) (32.5 mg, 0.084 mmol, 1.0 equiv) by using the same procedure as for CPE-K90. Yield: 43 mg (77%).

Ion Exchange of CPE-K90

CPE-K90 (11 mg, MW = 661.2n g/mol, 0.017/n mmol) was dissolved in millipore water (5 mL), and tetrabutylammonium bromide (1.07g, 200n equiv, 5.4 mmol) was dissolved in Millipore water (10 mL). The two aqueous solutions were mixed, and stirred for 30 min. The solution was placed in a dialysis tube (MWCO = 3500 – 5000), which was soaked in 2 L millipore water for three days. Fresh water was exchanged every 12 hrs. The CPE solution was concentrated under vacuum, dissolved in water with the same amounts of tetrabutylammonium bromide as above, and subjected to dialysis for three days. The procedure was repeated another time. The final CPE was dried under vacuum overnight to provide a dark blue solid CPE-NBu₄90 (15 mg, 87%), which is soluble in common polar

solvents, such as water, MeOH, DMF, DMSO and pyridine. NMR was able to be taken in DMSO-d₆. NMR spectrum of CPE-NBu₄90 in DMSO-d₆ is shown below. Molecular weight of CPE-NBu₄90 was determined by GPC (DMF). M_n = 5.1k, M_w = 5.8 k, PDI = 1.13.

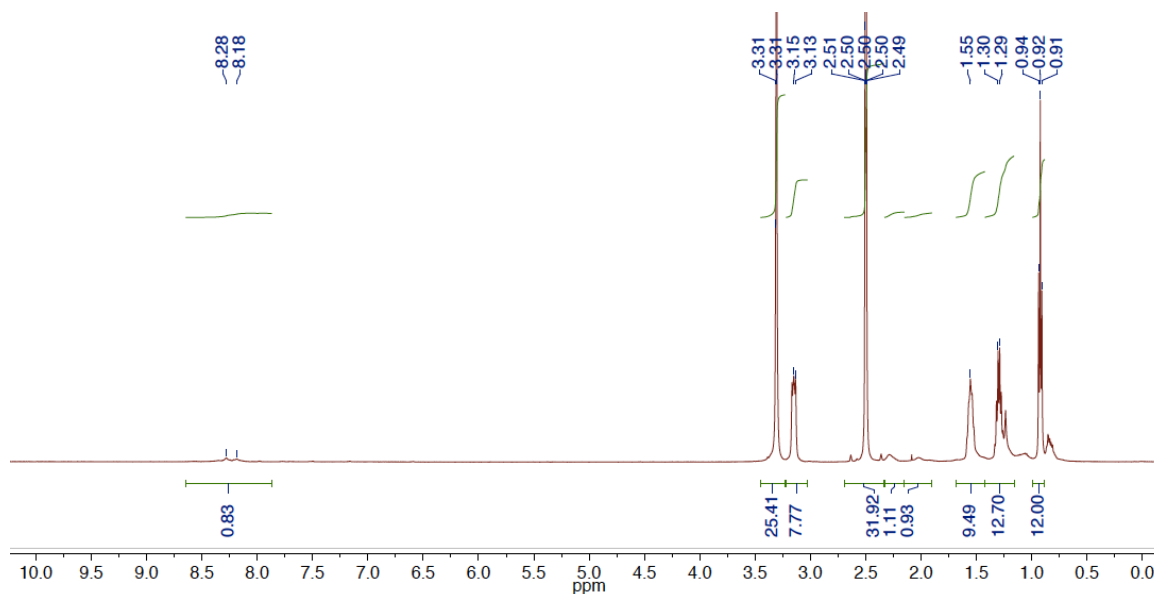


Fig. S4 ¹H-NMR of CPE-NBu₄90 in DMSO-d₆.

Ion Exchange of CPE-K80

Ion exchange of CPE-K80 (12 mg, MW = 664.5n g/mol, 0.018/n mmol) was carried out by using the same procedure as for CPE-K90. Yield: 15mg (83%). NMR spectrum of CPE-NBu₄80 in DMSO-d₆ is shown below. Molecular weight of CPE-NBu₄80 was determined by GPC (DMF). M_n = 5.2k, M_w = 5.8k, PDI = 1.11.

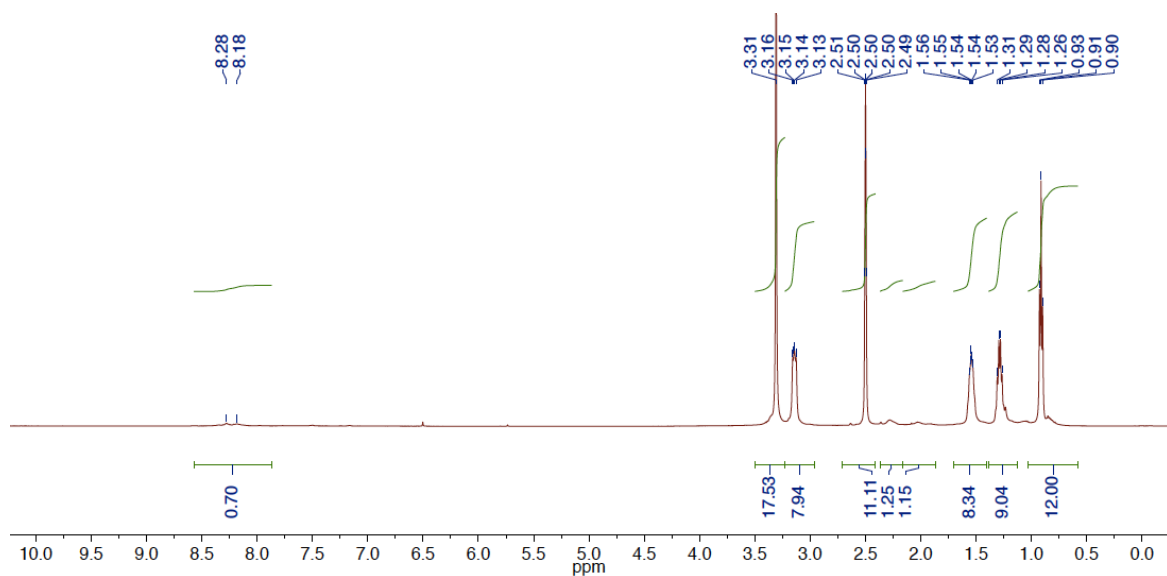


Fig. S5 $^1\text{H-NMR}$ of CPE-NBu₄80 in DMSO-d₆.

Ion Exchange of CPE-K70

Ion exchange of **CPE-K70** (12 mg, MW = 667.8n g/mol, 0.018/n mmol) was carried out by using the same procedure as for CPE-K90. Yield: 14 mg (81%). NMR spectrum of **CPE-NBu₄70** in DMSO-d₆ is shown below. Molecular weight of CPE-NBu₄80 was determined by GPC (DMF). $M_n = 6.3\text{k}$, $M_w = 7.5\text{k}$, PDI = 1.19.

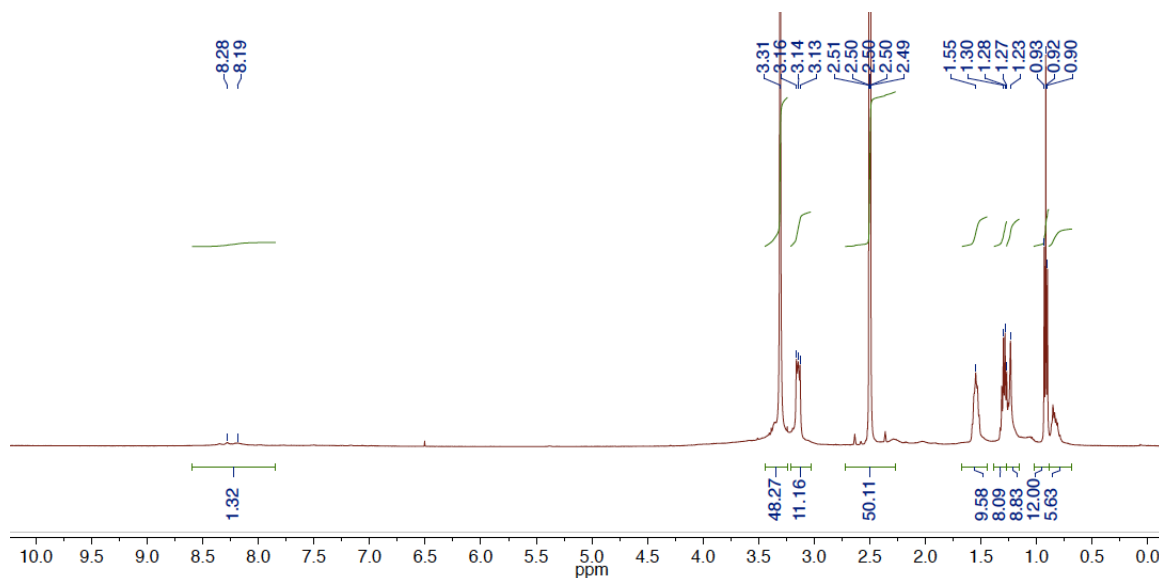


Fig. S6 $^1\text{H-NMR}$ of CPE-NBu₄70 in DMSO-d₆.

UV-Vis-NIR Absorptions:

All the measurements were performed using a Perkin Elmer Lambda 750 spectrophotometer at room temperature. All solution experiments were performed using the aqueous solution. Thin film samples

were prepared by spin-coating the respective 1:1 H₂O:MeOH solution (5 mg/mL) onto quartz substrates.

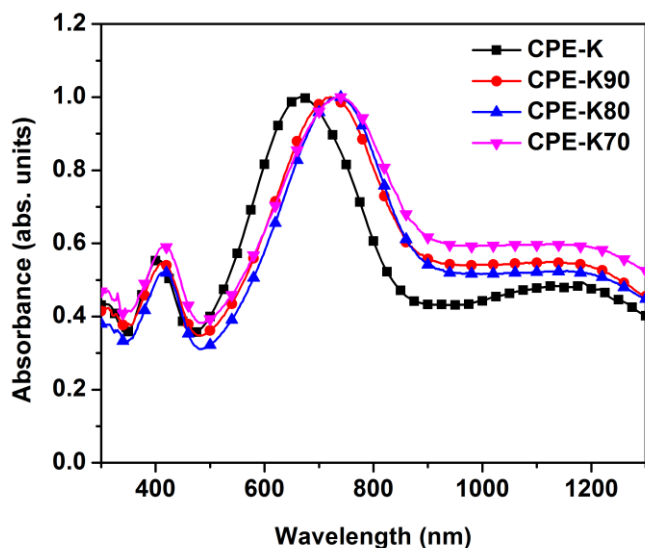


Fig. S7 UV/Vis-NIR absorption spectra of CPEs in water (0.025 mg/mL).

Infrared spectra (IR)

Infrared spectra were recorded with a Perkin Elmer FT-IR spectrum 2000 spectrometer and are reported in wavenumbers (cm^{-1}). The broad peaks of these doped CPEs at higher wavenumber are due to the polaron absorption (compared to absorptions, $4000 \text{ cm}^{-1} = 2500 \text{ nm}$).

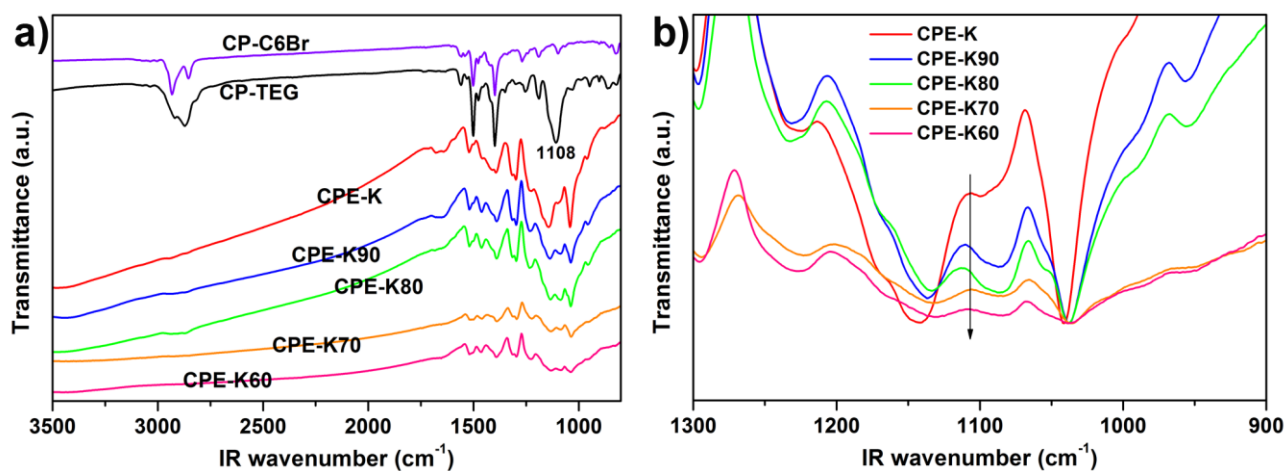


Fig. S8 FT-IR of CPE films on NaCl plates, a) full spectra; b) magnification from 1300 – 900 cm^{-1} . The strong peak (1108 cm^{-1}) is due to the C-O-C stretch. The incorporation of TEG side chain is confirmed by the appearance of this peak, and this peak intensity is consistent with the concentrations of TEG side chain incorporated. CP-C6Br (purple line)³ is a neutral polymer with the same CPDT-*alt*-BT backbone and 6-bromohexyl side chains.

Grazing Incidence Wide Angle X-ray Scattering (GIWAXS)

GIWAXS experiments were performed at the Stanford Synchrotron Radiation Lightsource (SSRL) at beamline 11-3. Samples were prepared by spin coating solutions onto Si substrates. A MAR 2300 area detector was used for 2D diffraction pattern collection. The energy of the incident beam is 12.7 keV. The angle of incidence used was 0.12° and the sample-to-detector distance was 40 cm. Samples were kept in a helium atmosphere to minimize X-ray damage and background scattering. Exposure times were typically between 120 s and 240 s. The peak position ($d_{\pi-\pi} = 2\pi/q_{xy}$) and the full width at half maximum (FWHM) were determined by fitting the in-plane scattering with a combination of Voigt functions.

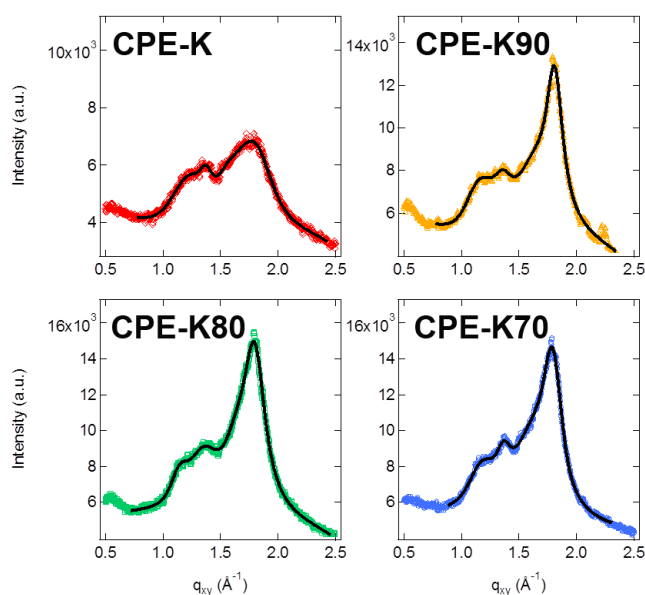


Fig. S9 One dimension in-plane GIWAXS profiles.

Table S1 Summary of q_{xy} values, d -spacings, and FWHM from in-plane GIWAXS scattering profiles.

	π - π stacking		
	q_{xy} (\AA^{-1})	d -spacing (\AA)	FWHM (\AA^{-1})
CPE-K	1.76	3.57	0.39
CPE-K90	1.81	3.47	0.17
CPE-K80	1.80	3.49	0.23
CPE-C3-K	1.80	3.50	0.17

Electrical Conductivity Measurements:

The low-ion borosilicate glass substrates (D263) were purchased from University Wafer. Prior to use,

the substrates were cleaned by sonication in soapy water, DI water, acetone, and isopropyl alcohol for 30 min each, dried with compressed air, treated with oxygen plasma for 2 min. CPE thin films were spun-cast from the respective solutions (10 mg mL⁻¹ in 1:1 H₂O:MeOH) onto glass substrates, and heated at 80 °C for 1 h on a hot plate. The thin films were transferred into a thermoevaporator to deposit gold electrodes (100 nm thick) on the top through a shadow mask.

Current-sourced four-point conductivity measurements were conducted in an N₂ glovebox. All devices measured with four-point probe conductivity had a channel length (L) of 200 μm and a channel width (w) of 1 mm. The electrical conductivity was determined by $\sigma = \frac{I}{V} \times \frac{L}{A}$, where A is the cross-sectional area of the sample between the electrodes. A was calculated as the film thickness (t , measured by AFM) times the channel width (w). At least three different samples were measured and averaged.⁴

Seebeck coefficients (S) were determined on the same samples as electrical conductivity, by linear fitting of a data series taken by imposing temperature differences across the sample and measuring the corresponding thermovoltage ($S = -\Delta V/\Delta T$) from two thermocouples contacting the sample in parallel to the two voltage probes. Thermocouples are attached to the sample via a spring force from the probe arm and good thermal contact is made with thermal paste. The system was calibrated by measuring samples of bismuth telluride, silicon, and indium tin oxide, and the uncertainty was determined to be $\pm 15\%$.⁵ At least three different samples were measured and averaged.

Table S2 Thermoelectric Properties of CPEs with Varied Density of Ionic Functionality

	σ (S cm ⁻¹)	S (μV K ⁻¹)	σS^2 (μW m ⁻¹ K ⁻²)
CPE-K	0.024 ± 0.002	232 ± 35	0.14 ± 0.05
CPE-K90	0.252 ± 0.018	216 ± 32	1.17 ± 0.09
CPE-K80	0.436 ± 0.022	231 ± 42	2.33 ± 0.12
CPE-K70	0.298 ± 0.024	237 ± 35	1.67 ± 0.13

References

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