Mixed Conductive Soft Solids by Electrostatically Driven Network Formation of a Conjugated Polyelectrolyte

Scott P. O. Danielsen,[a,b] Gabriel E. Sanoja,[a,b,c,†] Samantha R. McCuskey,[a,b] Boualem Hammouda,[d] Guillermo C. Bazan,[b,e,f] Glenn H. Fredrickson,[a,b,e,*] Rachel A. Segalman[a,b,e,*]

[a]Department of Chemical Engineering, [b]Materials Research Laboratory, [e]Materials Department, and [f]Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106

[c]Department of Chemical and Biomolecular Engineering, University of California, Berkeley, CA 94720

[d]Center for Neutron Research, National Institute of Standards and Technology, 100 Bureau Drive, Gaithersburg, MD 20899

[†]Present Address: Sciences et Ingénierie de la Matière Molle, CNRS UMR 7615, École Supérieure de Physique et de Chemie Industrielles de la Ville de Paris (ESPCI), ParisTech, PSL Research University, 10 Rue Vauquelin, F-75231- Paris Cedex 05, France

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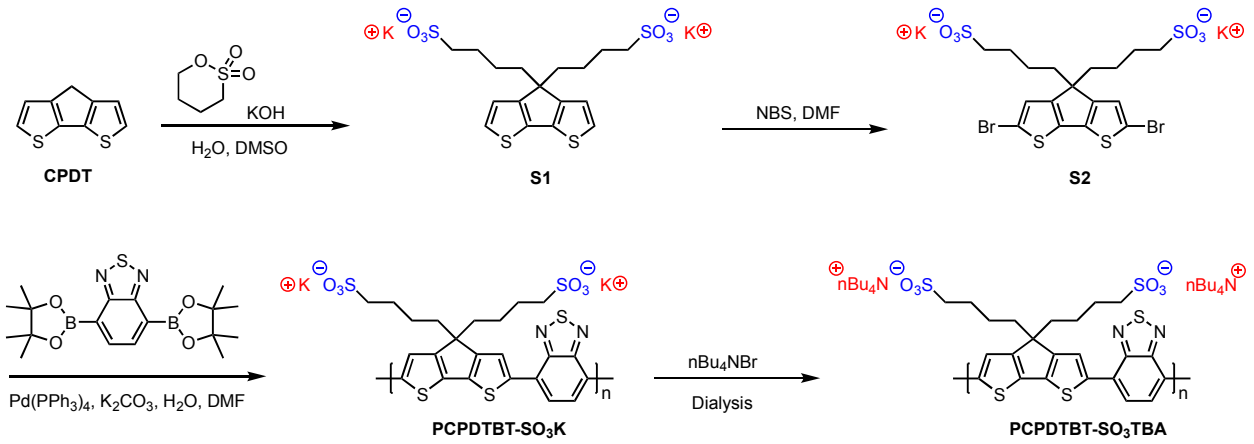
1. SYNTHESIS OF PCPDTBT-SO_3K



Scheme S1. Synthesis of **PCPDTBT-SO_3K** and conversion to **PCPDTBT-SO_3TBA**.

Synthesis of 4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (S1)
4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (**CPDT**, 510 mg, 2.86 mmol, 1.0 equiv) and tetrabutylammonium bromide (46 mg, 0.143 mmol, 0.05 equiv) were dissolved in anhydrous DMSO (14 mL), and the solution was degassed by sparging with Ar for 5 min. 50% KOH in H_2O (3.2 g) was added via syringe, followed by the addition of 1,4-butanesultone (700 µL, 6.68 mmol, 2.4 equiv). After stirring at room temperature for 3 h, the reaction mixture was poured into acetone (100 mL), the yellowish precipitate was collected by filtration, washed with acetone, and used in the next step without further purification. An analytical sample was purified by flash chromatography (reversed phase silica gel C-18, 6:5 H_2O:MeOH, R_f = 0.75) to provide a yellow solid. **^{1}H NMR** (500 MHz, D_2O) δ 7.32 (d, *J* = 4.8 Hz, 1H), 7.11 (d, *J* = 4.9 Hz, 1H), 2.70 (t, *J* = 5.8 Hz, 4H), 1.95 (t, *J* = 6.8 Hz, 4H), 1.53 (m, 4H), 0.95 (m, 4H). **^{13}C NMR** (126 MHz, D_2O) δ 158.0, 136.4, 125.4, 122.1, 52.8, 50.9, 36.5, 24.3, 23.1. **MS (ESI)** m/z calculated for $C_{17}H_{20}K_2O_6S_4$: 525.9; found: 487.0 $(M-K)^-$, 224.0 $(M-2K)^{2-}$.

Synthesis of 2,6-dibromo-4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene (S2)
The crude product **S1** was suspended in DMF (15 mL), and H_2O (5 mL) was added while stirring until it was all dissolved. NBS (1.27 g, 7.15 mmol, 2.5 equiv) was added in dark by shielding the flask with aluminum foil. The brown solution was stirred at room temperature for 1 h, and poured into acetone. The yellowish precipitate was collected by filtration, and washed with acetone. Purification by flash chromatography (reversed phase silica gel C-18, 6:5 H_2O:MeOH, Rf = 0.35) to provide **1** as a yellowish solid (1.41 g, 72%). **^{1}H NMR** (500 MHz, D_2O) δ 7.15 (s, 2H), 2.72 (t, *J* = 8.0 Hz, 4H), 1.82 (t, *J* = 7.3 Hz, 4H), 1.54 (m, 4H), 0.88(m, 4H). **^{13}C NMR** (126 MHz, D_2O) δ 155.4, 136.6, 124.8, 111.7, 53.9, 51.1, 35.8, 24.5, 23.2. **MS (ESI)** m/z calculated for $C_{17}H_{18}Br_2K_2O_6S_4$: 681.8; found: 644.8 $(M-K)^-$, 302.9 $(M-2K)^{2-}$.

Synthesis of Poly[2,6-(4,4-bis-potassium butanylsulfonate-4H-cyclopenta-[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT-SO_3K)

Dibromide **S2** (145 mg, 0.212 mmol, 1.0 equiv), 4,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzothiadiazole (82 mg, 0.212 mg, 1.0 equiv), K_2CO_3 (147 mg, 1.06 mmol, 5.0 equiv), and $Pd(PPh_3)_4$ (5.0 mg, 2 mol%) were combined in a microwave tube with a stir bar in a glove box. The tube was sealed with a septum, and taken out of the glove box. A mixture of DMF (2.0 mL) and H_2O (0.5 mL) was degassed by sparging with Ar for 5 min, and cannulated into the above microwave tube. The septum on the tube was removed quickly under positive pressure of Ar, and the tube was resealed with a special cap for the microwave tubes. The brown suspension was placed into an oil bath, and heated to 90°C, allowed to stir at 90°C for 24 hrs, and poured into acetone (50 mL). The dark blue precipitate was collected by filtration, and washed with acetone and MeOH until the filtrate was colorless. The precipitate was dissolved in H_2O (25 mL), and transferred into a dialysis tube (MWCO: 3500 – 5000 Da). The dialysis tube was placed in H_2O stirring for 3 days, and the H_2O was changed every 12 h. Evaporation of H_2O provided the title product as a metallic looking dark blue solid (117 mg, 84%) after drying under vacuum overnight. NMR of the title polymer in D_2O only showed non-informative broad peaks.
Elemental Analysis: C: 40.5%; H: 3.33%; N: 4.33%. Ion exchange with excess tetrabutylammonium bromine provided a DMF-soluble polyelectrolyte **PCPDTBT-SO_3TBA** with tetrabutylammonium as the counterion, of which molecular weight can be determined by **GPC** (DMF). M_n = 7190, M_w = 7800, Đ = 1.1.

Ion Exchange of PCPDTBT-SO_3K

PCPDTBT-SO_3K (18 mg, MW = 658.94n g/mol, 0.027/n mmol) was dissolved in H_2O (5 mL), and tetrabutylammonium bromide (1.76 g, 200n equiv, 5.4 mmol) was dissolved in H_2O (10 mL). The two aqueous solutions were mixed, and stirred for 30 min. The solution was placed in a dialysis tube (MWCO: 3500 – 5000 Da), which was soaked in H_2O for three days. Fresh water was exchanged every 12 h. The CPE was finally dried under vacuum overnight to provide a dark blue solid **PCPDTBT-SO_3TBA** (27 mg, 93%). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 8.49 – 7.97 (m, 4H), 3.25 – 2.96 (m, 16H), 2.41 – 2.14 (m, 4H), 2.05 – 1.77 (m, 4H), 1.54 (p, *J* = 7.5 Hz, 20H), 1.29 (q, *J* = 7.4 Hz, 16H), 1.20 – 0.95 (m, 4H), 0.91 (t, *J* = 7.3 Hz, 24H).

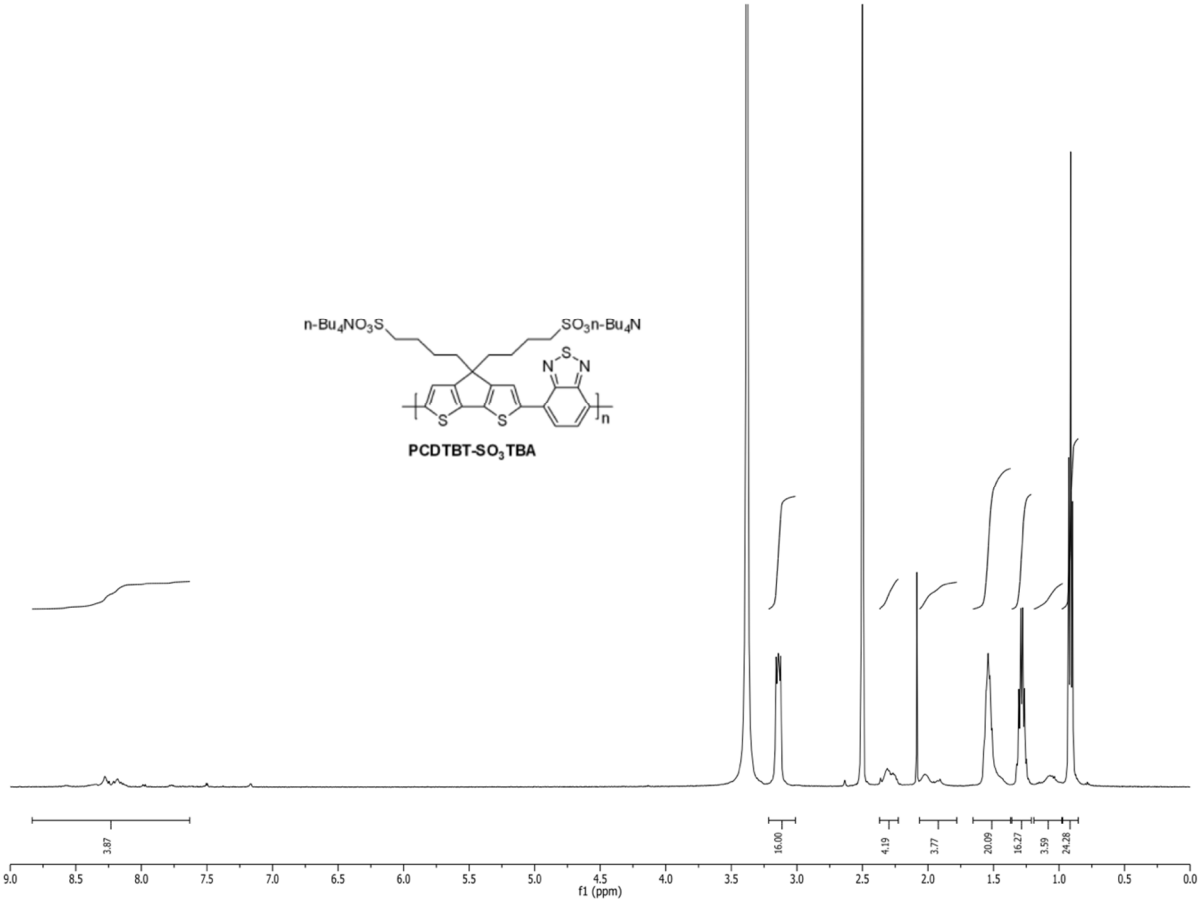


Figure S1. ^{1}H NMR spectrum of **PCPDTBT-SO$_3$TBA** in DMSO-d$_6$.

2. RHEOLOGY

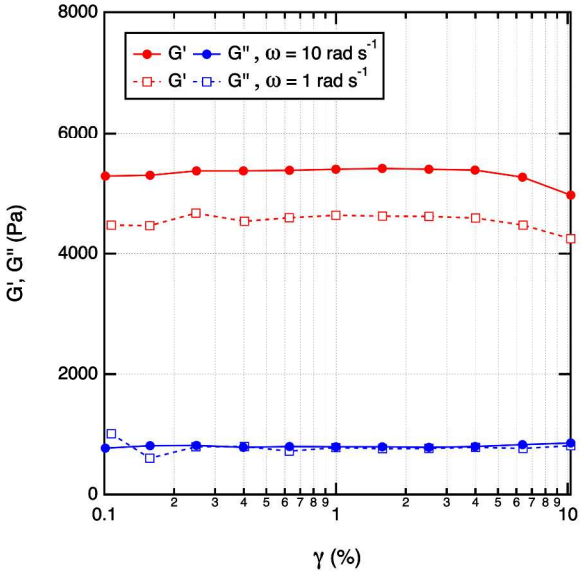


Figure S2. Strain sweeps at constant frequency, $\omega = 10\ s^{-1}$ [●] and $\omega = 1\ s^{-1}$ [□] for **PCPDTBT-SO_3K** (4.0 % *w/v*, D_2O) at 25°C, showing a critical strain of approximately 5%.

3. SANS DATA ANALYSIS: WORMLIKE CHAIN MODEL DETAILS

The scattering function, $I_{WLC}(q, L_c, b, R_{CS})$, for the Flexible Cylinder model, a Wormlike Chain model, is given by:[1, 2]

$$I_{WLC}(q) = \frac{cM_w}{\rho N_A} \Delta\rho^2 S_{WLC}(q, L_c, b) P_{CS}(q, R_{CS}) + I_{inc}$$

where c is the solution concentration, M_w is the absolute weight averaged molecular weight, $\Delta\rho$ is the difference in scattering length density between the polymer and the solvent, ρ is the mass density, N_A is Avogadro's number, b is the Kuhn length, L_c is the contour length, R_{CS} is the circular cross-sectional radius, and I_{inc} is the q invariant incoherent background scattering. $P_{CS}(q, R_{CS})$ is the scattering function accounting for the finite cross section of a rigid rod and is given by:

$$P_{CS}(q, R_{CS}) = \left[\frac{2J_1(qR_{CS})}{qR_{CS}}\right]^2$$

where $J_1(x)$ represents the first-order Bessel function of the first kind. $S_{WLC}(q, L_c, b)$ is the scattering function of a single semi-flexible polymer chain with excluded volume effects given by:

$$\begin{aligned} S_{WLC}(q, L_c, b) = {} & [1 - w(qR_g)] S_{Debye}(q, L_c, b) \\ & + w(qR_g)\left[1.22(qR_g)^{-\frac{1}{0.585}} + 0.4288(qR_g)^{-\frac{2}{0.585}} - 1.651(qR_g)^{-\frac{3}{0.585}}\right] \\ & + \frac{C(L/b)}{L/b}\left\{\frac{4}{15} + \frac{7}{15u} - \left(\frac{11}{15} + \frac{7}{15u}\right)\exp[-u(q, L, b)]\right\} \end{aligned}$$

where R_g is the radius of gyration including excluded volume effects and $w(x)$ is an empirical crossover function derived from Monte Carlo simulations:

$$w(x) = \frac{1}{2}\left\{1 + \tanh\left[\frac{x - 1.532}{0.1477}\right]\right\}$$

For $L_c > 10b, C\left(\frac{L_c}{b}\right) = 3.06\left(\frac{L_c}{b}\right)^{-0.44}$ and for $L_c \leq 10b, C\left(\frac{L_c}{b}\right) = 1$. S_{Debye} is the Debye function:

$$S_{Debye}(q, L_c, b) = \frac{2}{u(q, L_c, b)}\{\exp[-u(q, L_c, b)] + u(q, L_c, b) - 1\}$$

$$u(q, L_c, b) = \langle R_g^2 \rangle q^2 = \frac{L_c b}{6}\left\{1 - \frac{3b}{2L_c} + \frac{3b^2}{2L_c^2} + \frac{3b^3}{4L_c^2}\left[1 - \exp\left(-2\frac{L_c}{b}\right)\right]\right\} q^2$$

$$\langle R_g^2 \rangle = \alpha\left(\frac{L_c}{b}\right)^2 \frac{L_c b}{6}$$

where $\alpha\left(\frac{L_c}{b}\right)$is the following empirical expression:

$$\alpha(x) = \sqrt{\left[1 + \left(\frac{x}{3.12}\right)^2 + \left(\frac{x}{8.67}\right)^3\right]^{0.176/3}}$$

Finite polydispersity is accounted for by integrating the form factor over a Schulz-Zimm distribution of polydispersity index, $z = Đ - 1$, normalized by the first moment of the length distribution ensuring that the invariant is constant when the polydispersity is varied and all other structural parameters are held fixed.

$$\langle I_{WC}(Q, L_c, b, R_{CS})\rangle_{SZ} = \frac{cM_w}{\rho N_A} \Delta\rho_m^2 \langle S_{WC}(Q, L_c, b)\rangle_{SZ} P_{CS}(q, R_{CS}) + I_{inc}$$

$$\langle S_{WC}(q, L_c, b)\rangle_{SZ} = \frac{\int N_{SZ}(L_c) L_c^2 S_{WLC}(q, L_c, b) dL_c}{\int N_{SZ}(L_c) L_c^2 dL_c}$$

$$N_{SZ}(L_c) = \frac{L_c^2}{z!}\left(\frac{z+1}{\langle L_c\rangle}\right)^{z+1} \exp\left[\frac{-L_c(z+1)}{\langle L_c\rangle}\right]$$

For accurate quantification of chain conformation parameters from model fitting, it is important to account for instrument resolution. The model is resolution smeared by integrating the theoretical scattering intensity with a Gaussian resolution function:

$$I(q) = \int_{q_{min}}^{q_{max}} \frac{\langle I_{WLC}(y, L_c, b, R_{CS})\rangle_{SZ}}{\sqrt{2\pi\sigma_R^2}} \exp\left[-\frac{(q-y)^2}{2\sigma_R^2}\right] dy + I_{inc}$$

4. SANS DATA ANALYSIS: FLEXIBLE CHAIN MODEL DETAILS

The Debye function can be used to model the scattering of a single chain obeying random walk statistics:[3]

$$I_{Debye}(q) = \frac{cM_w\Delta\rho^2}{\rho N_A (qR_g)^4}\left(q^2R_g^2 - 1 + e^{-q^2R_g^2}\right) + I_{inc}$$

where c is the solution concentration, M_w is the absolute weight averaged molecular weight, $\Delta\rho$ is the difference in scattering length density between the polymer and the solvent, ρ is the mass density, N_A is Avogadro's number, R_g is the radius of gyration, and I_{inc} is the q invariant incoherent background scattering.

5. SANS DATA ANALYSIS: RIGID ROD MODEL DETAILS

The rigid rod description of the single-chain scattering is modeled as a circular cylinder with uniform scattering length density. The form factor is normalized by the particle volume and averaged over all possible orientations of the cylinder:[4, 5]

$$I_{rod}(q) = \frac{cM_w\Delta\rho^2}{\pi r^2 L_c \rho N_A}\int_0^{\pi/2} f^2(q,\alpha)\sin\alpha\, d\alpha + I_{inc}$$

$$f(q,\alpha) = 2\pi r^2 L_c \,\mathrm{sinc}\left(\tfrac{1}{2}qL_c\cos\alpha\right)\frac{J_1(qr\sin\alpha)}{qr\sin\alpha}$$

where c is the solution concentration, M_w is the absolute weight averaged molecular weight, $\Delta\rho$ is the difference in scattering length density between the rod and the solvent, ρ is the mass density, N_A is Avogadro's number, $\mathrm{sinc}(x)$ is the cardinal sine function, $\mathrm{J}_1(x)$ is the first order Bessel function, I_{inc} is the q invariant incoherent background scattering, and α is the angle between the scattered wavevector and the long axis of the cylinder.

6. SANS DATA ANALYSIS: CHAIN CONFORMATION FITTING OF PCPDTBT-SO_3K (0.3 % *w/v*, D_2O)

Table S1. Debye fitting parameters for **PCPDTBT-SO_3K** (0.3 % *w/v*, D_2O).

Parameter	Debye Function
M_w (g mol^{-1})	11022.7 ± 319.593
R_g (Å)	45.0094 ± 0.742582

Table S2. WLC fitting parameters for **PCPDTBT-SO_3K** (0.3 % *w/v*, D_2O).

Parameter	WLC
M_w (g mol^{-1})	11043.1 ± 289.124
Radius (Å)	14.3325 ± 0.91047
Kuhn Length (Å)	133.852 ± 8.8837

Table S3. Rigid Rod fitting parameters for **PCPDTBT-SO_3K** (0.3 % *w/v*, D_2O).

Parameter	Rigid Rod
M_w (g mol^{-1})	11858.1 ± 213.093
Radius (Å)	13.8321 ± 0.790673
Length (Å)	175.285 ± 6.6721

7. SANS DATA ANALYSIS: MODIFIED BROAD PEAK FITTING OF PCPDTBT-SO_3K (4.0 % *w/v*, D_2O)

Table S4. Modified Broad Peak model fitting parameters for **PCPDTBT-SO_3K** (4.0 % *w/v*, D_2O) at 25°C and 75°C.

Parameter	25°C	75°C
A	$5.5801\times10^{-6} \pm 5.09\times10^{-7}$	$6.1798\times10^{-6} \pm 6.45\times10^{-7}$
B	0.64795 ± 0.0617	0.49388 ± 0.0486
C	0.12025 ± 0.0346	0.10043 ± 0.0418
I_{inc}	0.0032051 ± 0.0121	0.0094971 ± 0.0151
n	2.5481 ± 0.0163	2.5485 ± 0.0187
m	2.0639 ± 0.174	2.2384 ± 0.27
p	2.1157 ± 1.08	2.3592 ± 1.69
q*	0.045971 ± 0.000762	0.049155 ± 0.00126
q_{ion}	0.095026 ± 0.0185	0.098924 ± 0.0184
L	48.721 ± 3.69	42.765 ± 3.32
L_{ion}	19.646 ± 8.46	16.714 ± 12.4

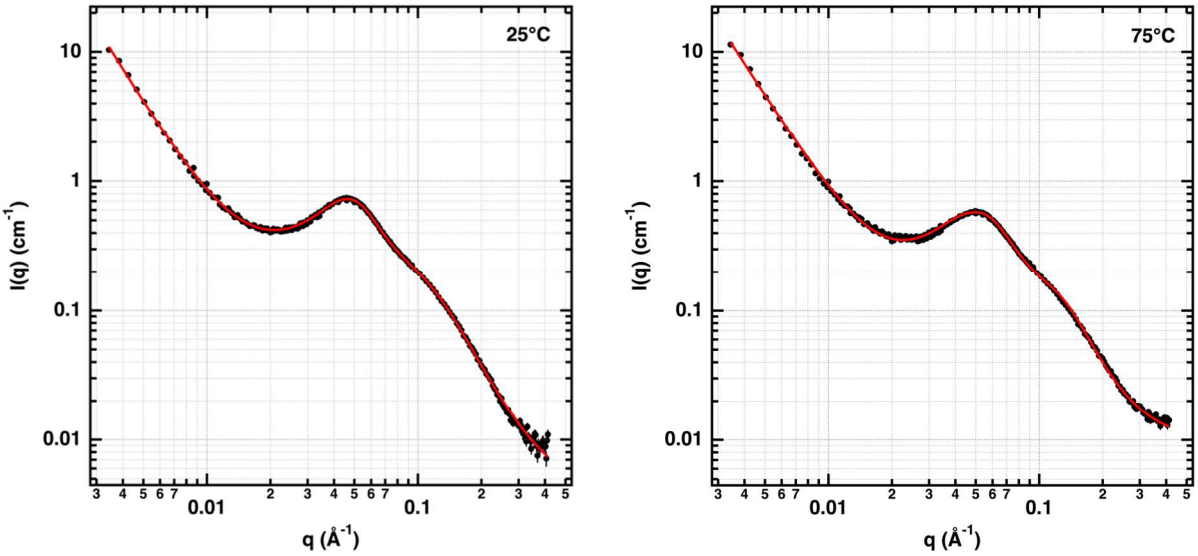


Figure S3. Small-Angle Neutron Scattering (SANS) data [**O**] for **PCPDTBT-SO_3K** gels (4.0 % *w/v*, D_2O) at 25°C [left] and 75°C [right] with fits [–] to our modified broad peak model, Equation 7. Outside of high-q data points, error bars are smaller than markers.

8. ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY OF PCPDTBT-SO_3K (4.0 % *w/v*, H_2O)

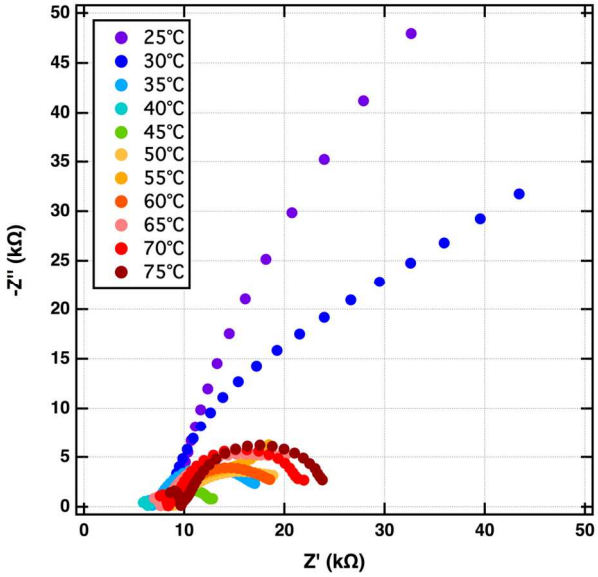


Figure S5. Nyquist plots of **PCPDTBT-SO_3K** (4.0 % *w/v*, H_2O), as a function of temperature.

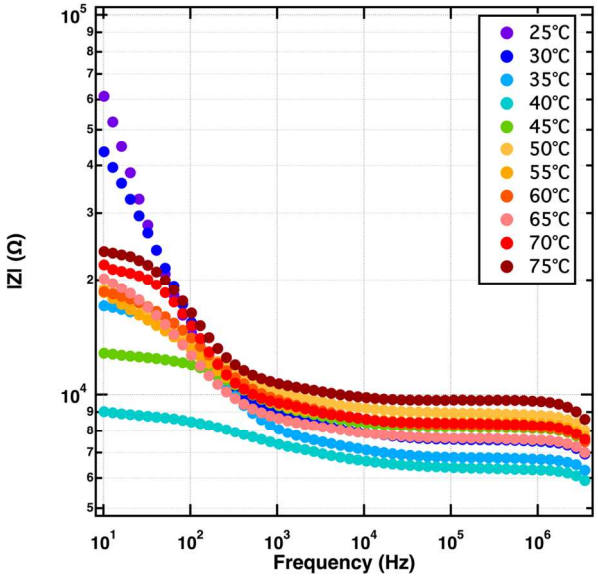


Figure S6. Bode plots of **PCPDTBT-SO_3K** (4.0 % *w/v*, H_2O), as a function of temperature.

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