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Supporting Information

The Importance of Sulfonate to the Self-doping Mechanism of Water-Soluble Conjugated Polyelectrolyte PCPDTBT-SO3K

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	C 1s	N 1s	O 1s	S 2p	K 2p
w/ H_2SO_4	39.9 ± 9.2 %	3.0 ± 1.3 %	39.1 ± 9.0 %	12.9 ± 1.9 %	1.1 ± 0.7 %
Self-doped	59.4 ± 5.0 %	3.9 ± 0.5 %	21.2 ± 2.5 %	11.5 ± 1.6 %	4.1 ± 1.1 %
Un-doped	48.6 ± 2.5 %	3.7 ± 0.6 %	28.8 ± 2.8 %	9.1 ± 1.0 %	9.7 ± 2.4 %

Table S1. Summary of XPS integrations from survey spectra of CPE-K doped w/ H_2SO_4, self-doped, and un-doped averaged over four different samples for each condition

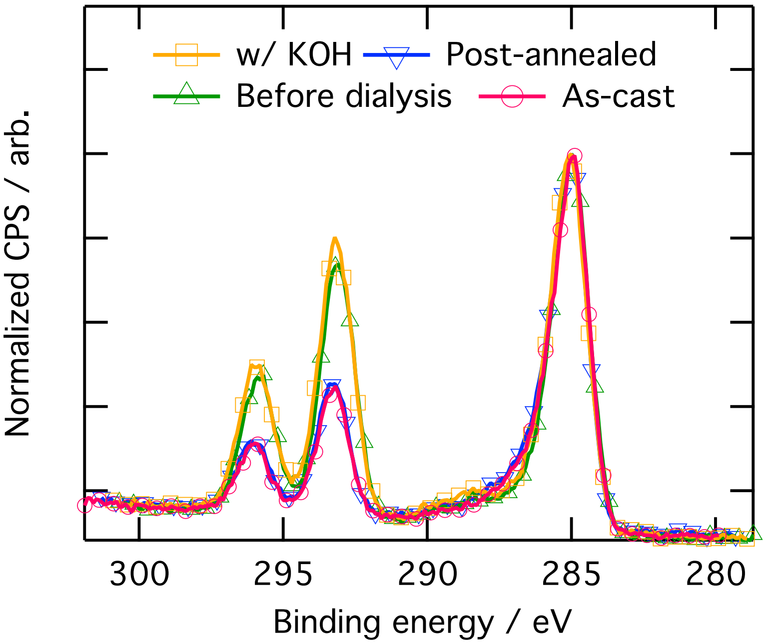


Figure S1. Normalized (to C 1s peak at 285.0 eV) XPS spectra of CPE-K under different conditions. A table with the percentage of K and C in the high-resolution spectra is included below.

CPE-K condition	Atomic % C	Atomic % K
As-cast	91.30	8.70
Post-annealed	90.67	9.33
Before dialysis	80.88	19.12
w/ KOH	81.56	18.44

Table S2. Atomic percentages of C and K in the high-resolution C 1s XPS spectra shown above in **Figure S7**.

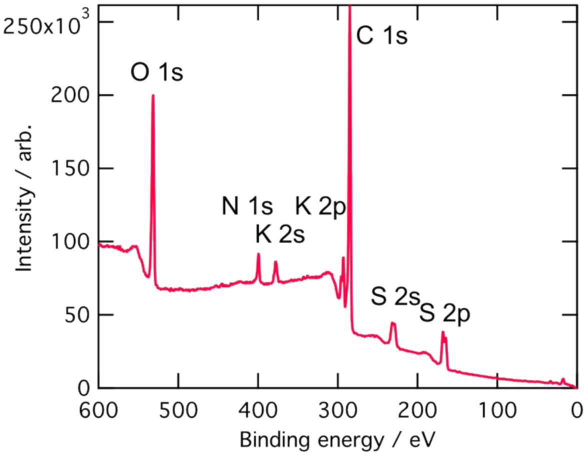
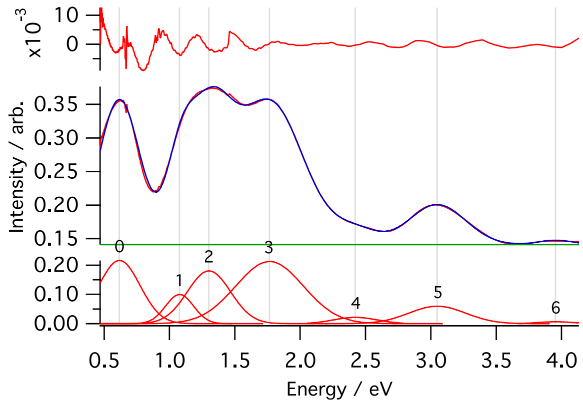
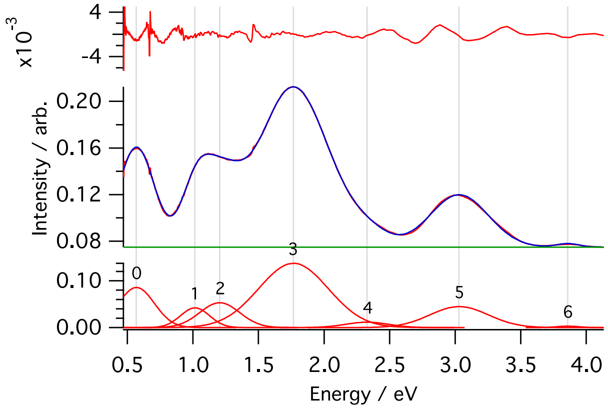


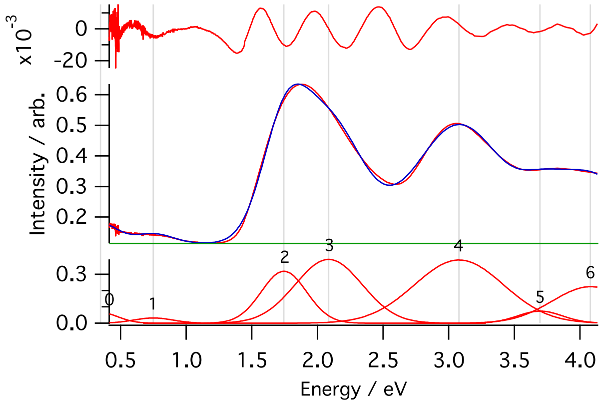
Figure S2. Survey XPS spectrum of self-doped CPE-K showing no elements other than those expected from the chemical structure.



w/ H_2SO_4



Self-doped w/ H_2O



Un-doped

Figure S3. Gaussian peak fits to the main UV-vis-nIR envelope.

Peak %	w/ H_2SO_4	As-cast	Un-doped
Electronic structure	49.3 %	76.4 %	92.3 %
Polaron bands	50.7 %	23.6 %	7.7 %

Table S3. Peak area percentages for the electronic structure and polaron band peaks. The film thickness does not change between the doped and un-doped states of the polymer as measured by a profilometer.

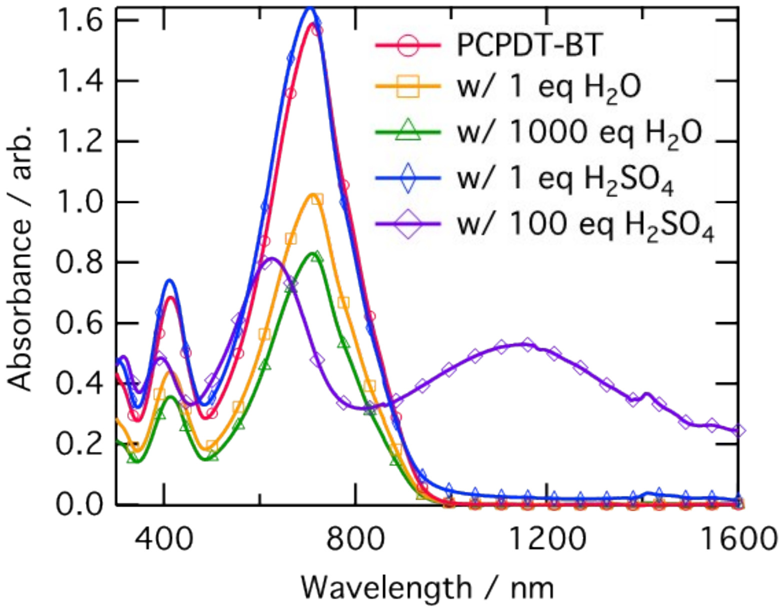


Figure S4. Solution UV-vis-nIR spectra in THF of PCPDT-BT with the alkyl-sulfonate side chains substituted for two linear C_{16} alkyl side chains. Even with the addition of 1 and 1000 equivalents of MilliQ water, there is no polaron peak at 1100 nm. Addition of 1 equivalent of H_2SO_4 shows the presence of a very small polaron peak, which does not become pronounced until the addition of 100 equivalents of H_2SO_4.

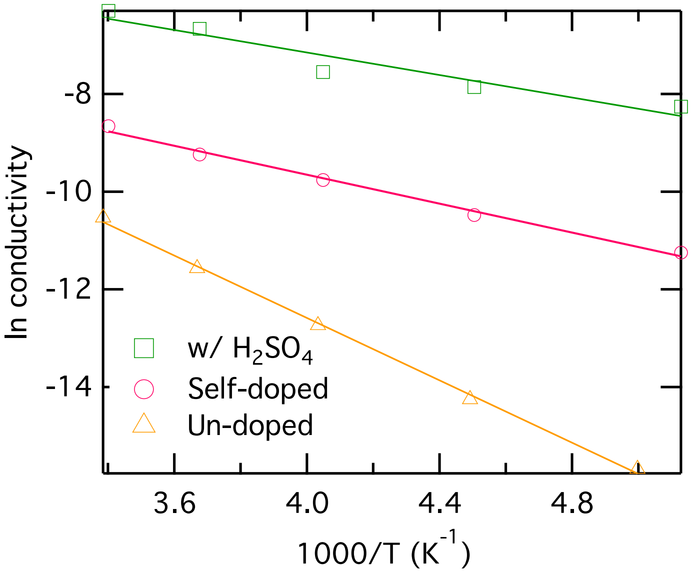
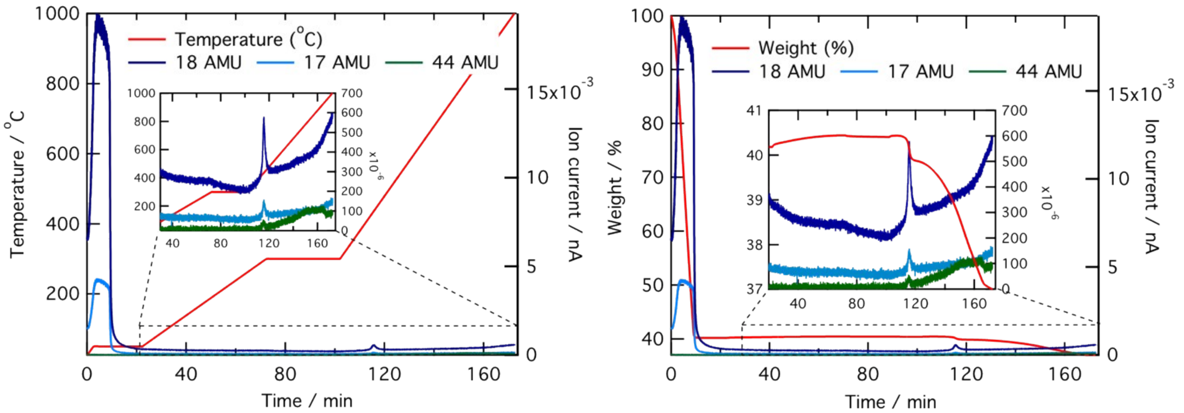


Figure S5. Arrhenius plot of CPE-K films at different doping levels



Mass (AMUs)	18	17	44
Compound	H_2O	^-OH	CO_2

Figure S6. TGA-MS of self-doped CPE-K showing the loss of water during heating by TGA-MS. Axes of insets are the same as the larger graph and show the stability of CPE-K at temperatures of up to 300 °C

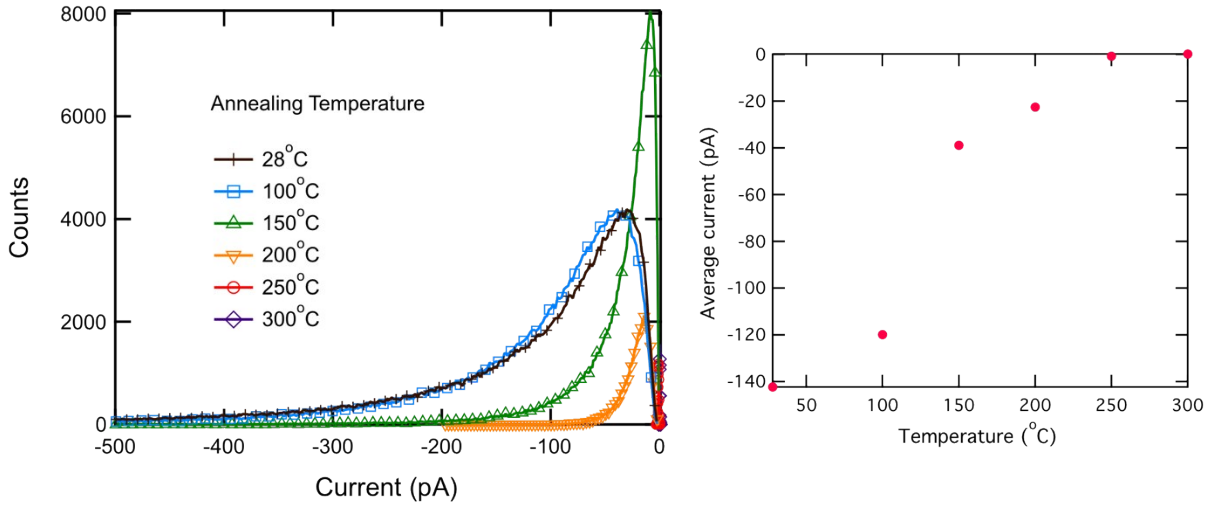


Figure S7. Graphical distribution showing the current of each pixel for each 5 x 5 µm image plotted as a histogram (left). On the right, the average current across the CPE-K film as a function of annealing for thirty minutes at the specified temperatures. All cAFM measurements were taken at a bias of -500 mV applied to the substrate

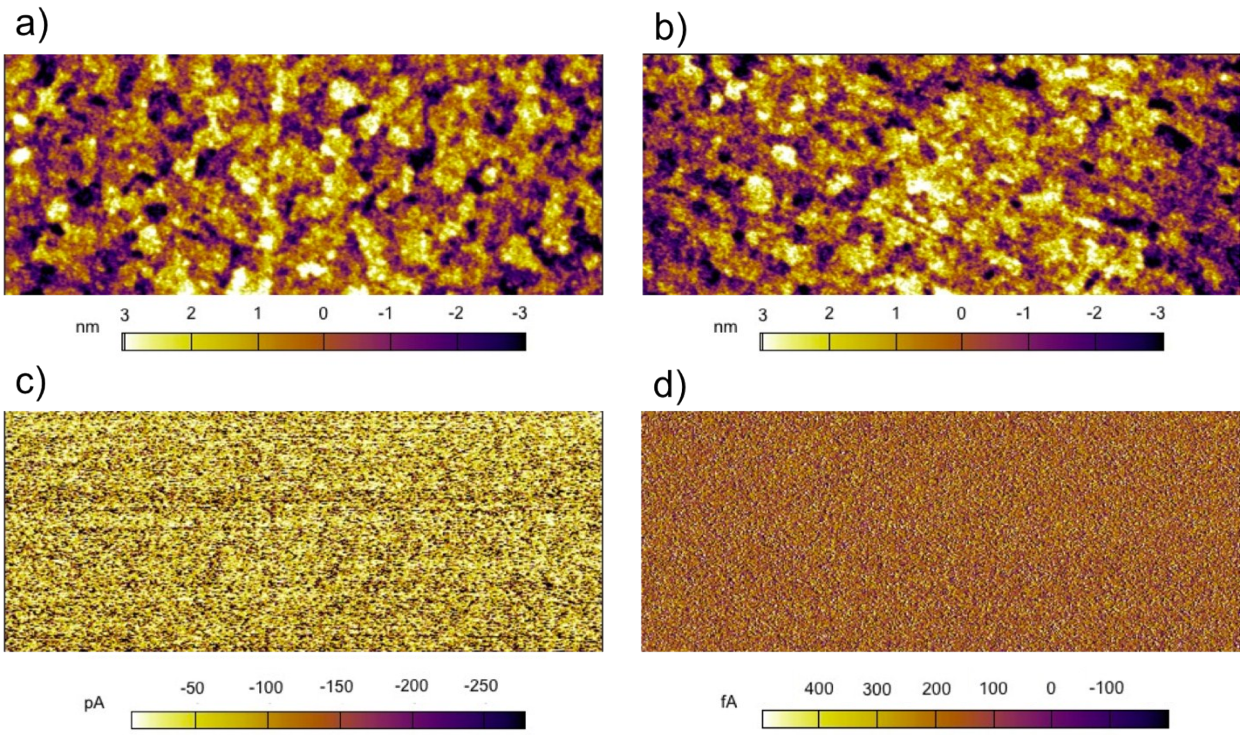


Figure S8. Film morphology of CPE-K films a) as cast and b) annealed at 300 °C for 30 minutes, showing no change in the morphology after annealing. Current images of CPE-K films c) as-cast and d) annealed at 300 °C for 30 minutes, showing dramatic reduction in current after annealing, supporting the argument that current reduction seen is due to chemical and structural changes in the polymer and not film morphology. Both samples were obtained at a bias of -500 mV applied to the substrate.

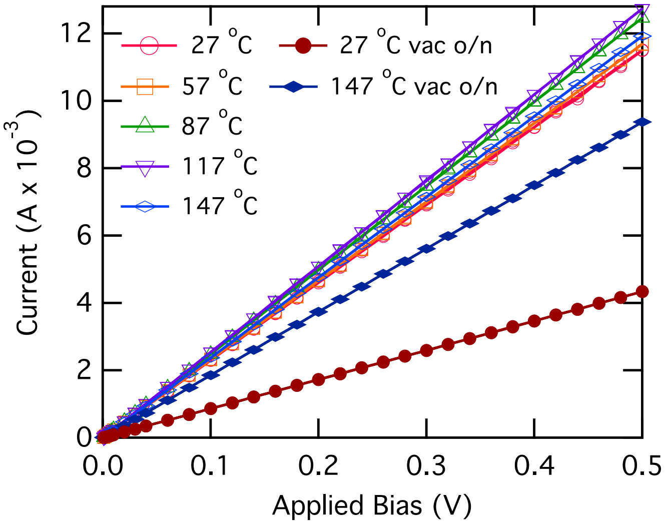


Figure S9. Current-voltage curves obtained under vacuum at different temperatures (note the units). After leaving the CPE-K film under vacuum at an elevated temperature of 147 °C overnight, there is a decrease in current which further decreases as expected when dropping the temperature of the film to 27 °C

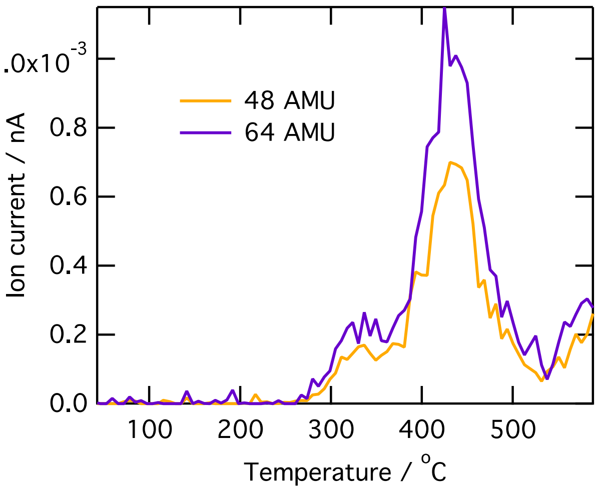


Figure S10. Zoomed-in TGA-MS of self-doped CPE-k showing formation of SO_2 and SO at a temperature of 300 °C