Supporting Information for

Disorder-to-Order Transition of Regiorandom P3HT upon Electrochemical Doping

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Figure S1: UV/Vis absorption spectra of RRa P3HT films doped at various voltages in 100 mM aqueous KTFSI, along with dedoping steps. (A) UV/Vis absorption spectra of RRa P3HT undoped, doped at 0.7 V vs. Ag/AgCl for 20 min, and doped at 0.7 V vs Ag/AgCl for 20 min then dedoped at -0.5 V vs. Ag/AgCl for 20 min. (B) and (C) are the same as (A) but with 20 min doping steps of 0.8 V vs. Ag/AgCl and 0.9 V vs. Ag/AgCl, respectively.



Figure S2: UV/Vis absorption spectra of RRa P3HT thin films undoped, doped, and dedoped. (A) UV/Vis absorption spectra of RRa P3HT undoped, doped in an aqueous 100 mM KTFSI electrolyte at 0.7 V vs. Ag/AgCl for 20 min, and doped in an aqueous 100 mM KTFSI electrolyte at 0.7 V vs. Ag/AgCl for 20 min and then dedoped at -0.5 V vs. Ag/AgCl for 20 min. (B) UV/Vis absorption spectra of RRa P3HT undoped, doped in 10 mg/mL acetonitrile F₄TCNQ in inert conditions for 20 min and then doped in F₄TCNQ followed by thermal annealing at 120 °C for 20 min to dedope the film.



Figure S3: RRa P3HT thin films spin coated on ITO glass. (A) an undoped RRa P3HT film. (B) a RRa P3HT film doped for 20 min at 0.7 V. (C) a RRa P3HT film doped for 20 min at 0.7 V followed by dedoping for 20 min at -0.5 V.



Figure S4: 50 x 50 μ m PiFM images of (A) an undoped RRa P3HT thin film, (B) a RRa P3HT thin film doped in an aqueous 100 mM KTFSI electrolyte for 20 min, and (C) a RRa P3HT thin film immersed in 10 mg/mL F4TCNQ for 20 min.



Figure S5: FTIR and PiFM spectra of RRa P3HT thin films doped with F_4TCNQ . (A) FTIR spectrum of an undoped RRa P3HT film and a thin film doped with F_4TCNQ (B) PiFM and FTIR spectra of a RRa P3HT thin film doped with F_4TCNQ .



Figure S6: EQCM measurement of two RRa P3HT thin films in 100 mM water KTFSI recorded over 50 CVs. (A) the applied potential (vs. Ag/AgCl), (B) the current during the cycling, (C) the accumulated charge during the CV cycling, and (D) the change in mass.



Figure S7: AFM thickness measurements showing the average thickness of the RRa P3HT thin film after every 10 CVs and the standard deviation of each CV sample. The error bars represent the standard deviation of the sample thickness based on surface roughness.



Figure S8: 2D GIWAXS diffractogram of a dropcast KTFSI film on an ITO-coated glass. This pattern was acquired by the tabletop GIWAXS at the Utah Nanofab.



Figure S9: 2D GIWAXS diffractogram of a RR P3HT film after performing 50 CVs in a 100 mM KTFSI electrolyte. The CVs were from -0.5 - 0.9 V vs. Ag/AgCl at a scan rate of 0.1 V/s.



Figure S10: 3 x 3 μ m PiFM images of RRa P3HT thin film after acquiring 50 CVs (non-wrinkled regions) (A) before and (B) after annealing the thin films at 120 °C for 20 min.



Figure S11: PiFM spectra of a RRa P3HT thin film after acquiring 50 CVs on a wrinkled region and a non-wrinkled region.



Figure S12: FTIR and PiFM spectra of a RRa P3HT film after acquiring 50 CVs. (A) FTIR spectra an undoped RRa P3HT film and a RRa P3HT thin film after performing 50 CVs. (B) PiFM spectrum acquired on a wrinkle and FTIR spectrum of the entire thin film.

Figure S13: Energy dispersive spectroscopy (EDS) maps and spectra of a RRa P3HT thin films on an ITO/glass substrates after 50 CVs in 100 mM NaTFSI. (A) The EDS elemental maps of fluorine (from TFSI-) and sodium (Na⁺). (B) the point spectrum of RRa P3HT off of a wrinkled region. (C) the point spectrum of RRa P3HT on a wrinkled region. In, Sn, and Si are from the ITO glass, and the rest of the peaks are attributed to NaTFSI and RRa P3HT.

Figure S14: 2D GIWAXS diffractograms after doping in each electrolyte for 20 min. (A) 100 mM KTFSI in water, (B) 100 mM KTFSI in acetonitrile, and (C) 100 mM KTFSI in propylene carbonate.

Figure S15: UV/Vis spectra of undoped RRa P3HT thin films, thin films doped for 20 min in KTFSI, and thin film doped for 20 min and then dedoped for 20 min with three different electrolyte solvents. (A) 100 mM KTFSI in water. (B) 100 mM KTFSI in acetonitrile, (C) 100 mM KTFSI in propylene carbonate.

Figure S16: AFM topography and PiFM images (50 x 50 μ m) of RRa P3HT thin films after 20 min doping in (A) water, (B) acetonitrile, and (C) propylene carbonate. In each case the KTFSI concentration is 100 mM. (D) A series of histograms representing the PiFM signal in each image, showing that ion trapping occurs most predominantly in water and least predominantly in acetonitrile.

Figure S17: 50 CVs acquired with each electrolyte solvent with 100 mM KTFSI. (A) 50 CVs in the aqueous electrolyte. (B) 50 CVs in the acetonitrile electrolyte. (C) 50 CVs in the propylene carbonate electrolyte.

Figure S18: Series of UV/Vis spectra in each electrolyte solvent (100 mM KTFSI) collected after every 5 CVs for (A) water, (B) acetonitrile, and (C) propylene carbonate. The error bars are the standard deviation of the mean for three separate measurements.

Figure S19: 50 CV acquired with each electrolyte in water. (A) 50 CVs in 100 mM KPF₆. (B) 50 CVs in 100 mM KOTf. (C) 50 CVs in 100 mM KClO₄.

Figure S20: 2D GIWAXS diffractograms after performing 50 CVs (A) KClO₄, (B) KOTf, and (C) KPF₆.

Figure S21: Comparison between different electrolyte upon performing 50 CVs. (A) The normalized absorbance of a RRa P3HT thin film in each electrolyte every 5 CVs. (B) The wavelength at the intensity maximum of the the π - π * peak during the 50 CVs in each electrolyte. The error bars show the standard deviation of the mean.