Electronic Supplementary Information

Quantifying Internal Charge Transfer and Mixed Ionic-Electronic Transfer in Conjugated Radical Polymers

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Faradaic vs. non-faradaic analysis for cyclic voltammetry

We have investigated the charge transfer mechanism in P3HT, P3HT-TEMPO-25, and P3HT-TEMPO-100 by deconvoluting the cyclic volammogram into faradaic and non-faradaic portions. The current response at a single voltage can be aexpressed by

$$\mathrm{i(V)} = a_1 v^{0.5} + a_2 v \qquad \text{(S1)}$$

where i(V) is the current response at a given potential, v is scan rate, and a_1 and a_2 are constants. The faradaic current is expressed as $a_1 v^{0.5}$, and the non-faradaic portion is $a_2 v$.

By deviding $v^{0.5}$ on both sides, the above equation is re-arranged to

$$\frac{i(V)}{v^{0.5}} = a_1 + a_2 v^{0.5} \qquad \text{(S2)}$$

The values of a_1 and a_2 can be determined by plotting $\frac{i(V)}{v^{0.5}}$ vs. $v^{0.5}$ and fitting with linear regression, where the slope is a_2 and the intercept is a_1.

Thus, the faradaic current ($a_1 v^{0.5}$) and non-faradaic current ($a_2 v$) were deconvoluted from the raw cyclic voltammogram.

The two figures below are a representation of the $\frac{i(V)}{v^{0.5}}$ vs. $v^{0.5}$. In the real calculation, our voltage increment was 0.02 V. Due to the discontinuity between low and high scan rates, we fit $\frac{i(V)}{v^{0.5}}$ vs. $v^{0.5}$ only for scan rates of 10 – 50 mV/s.

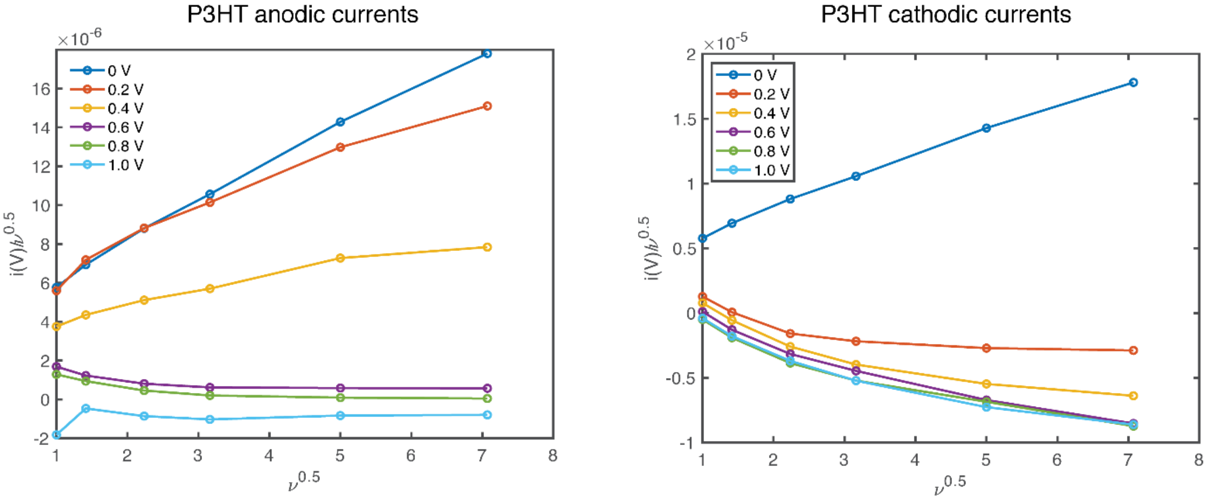

Figure S1. Example of deconvolution for the faradic and non-faradic current response.

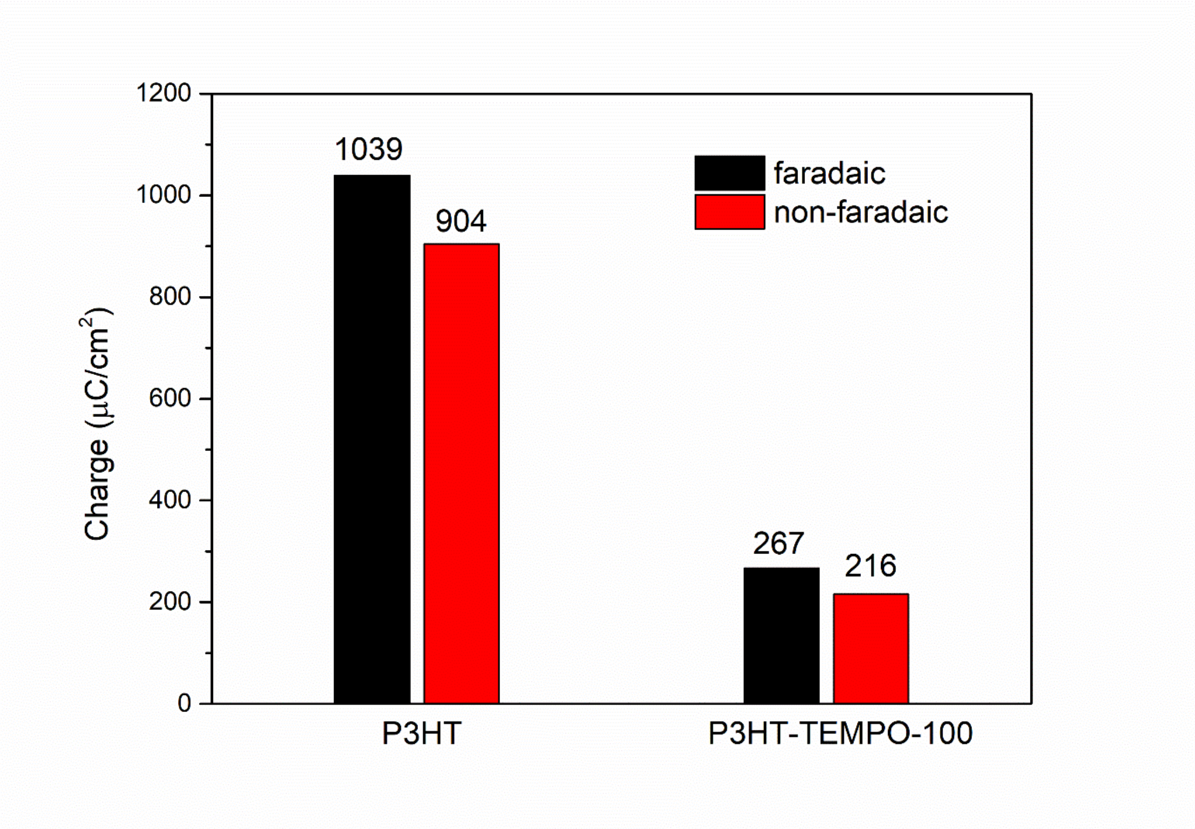

Figure S2. Faradaic vs. non-faradaic contributions to charge transfer for P3HT and P3HT-TEMPO-100 thin film electrodes.

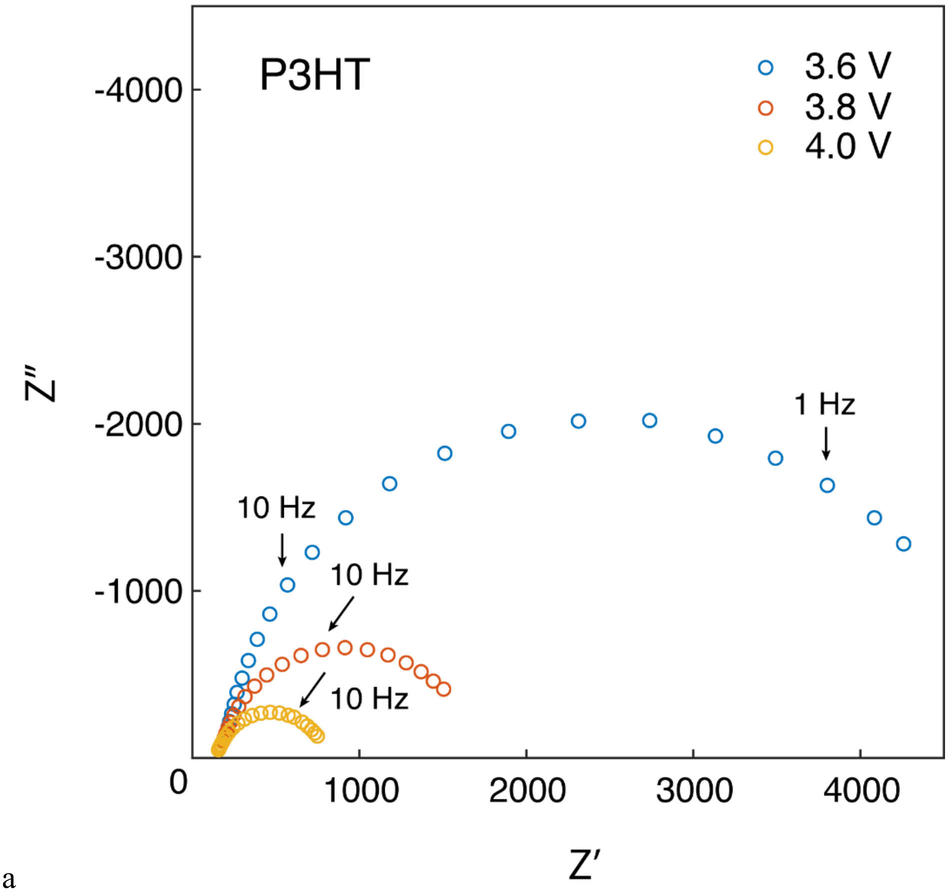

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Figure S3. Electron impedance spectrocopy of P3HT.

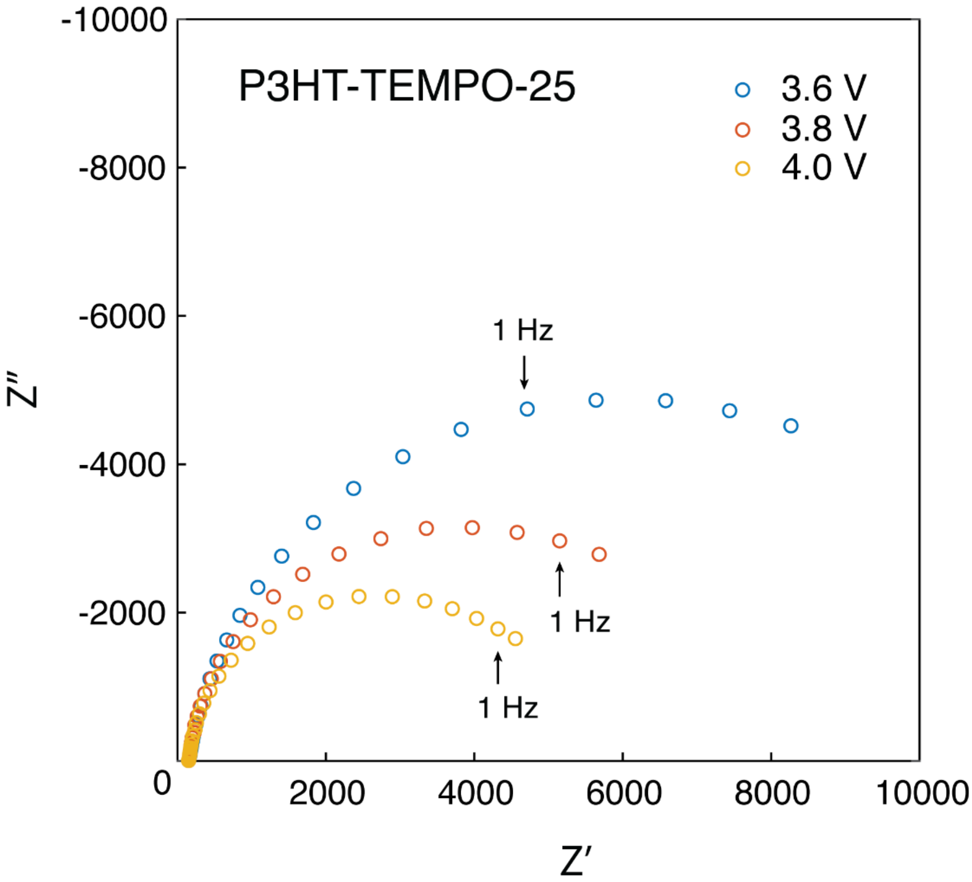

Figure S4. Electron impedance spectrocopy of P3HT-TEMPO-25.

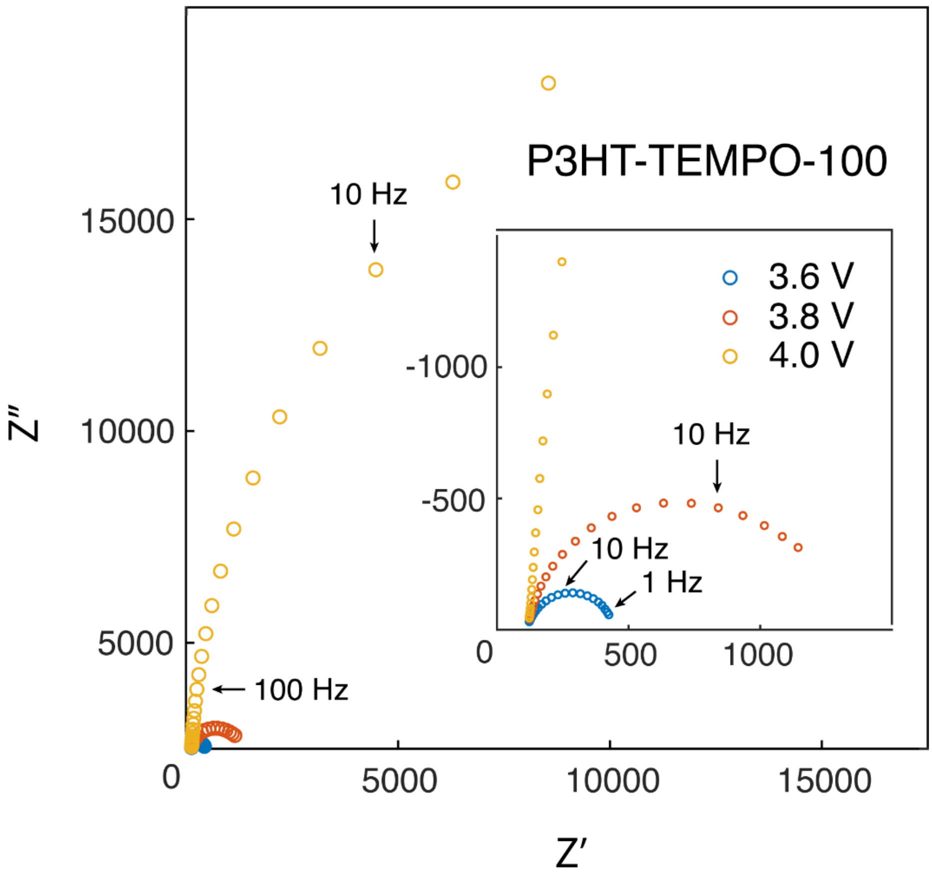

Figure S5. Electron impedance spectrocopy of P3HT-TEMPO-100.

Equivalent circuit

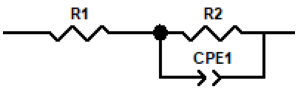

Table S1. Summary of EIS data.

	P3HT			P3HT-TEMPO-25			P3HT-TEMPO-100		
	3.6 V	3.8 V	4.0 V	3.6 V	3.8 V	4.0 V	3.6 V	3.8 V	4.0 V
R_s/Ω	164	153	142	152	153	153	114	120	121
R_{ct}/Ω	4,850	1,590	671	11,500	7,140	4,990	338	1,110	42,100
$Q_{dl}/10^{-5}$.F s^{n-1}	2.12	2.23	2.44	2.11	1.49	1.33	2.26	1.40	1.07
n_{dl}	0.89	0.87	0.86	0.90	0.93	0.94	0.88	0.93	0.96

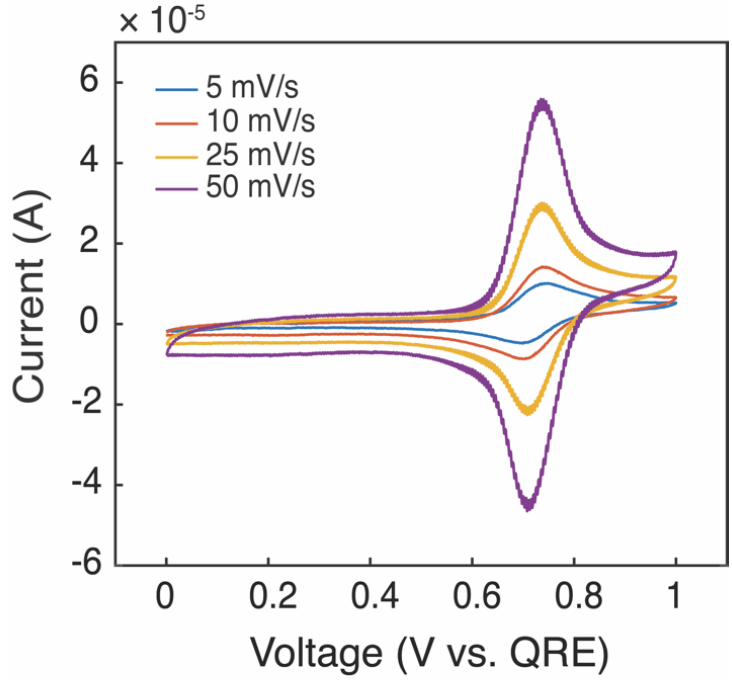

Figure S6. Cyclic voltammetry of P3HT-TEMPO-100.