Supporting Information

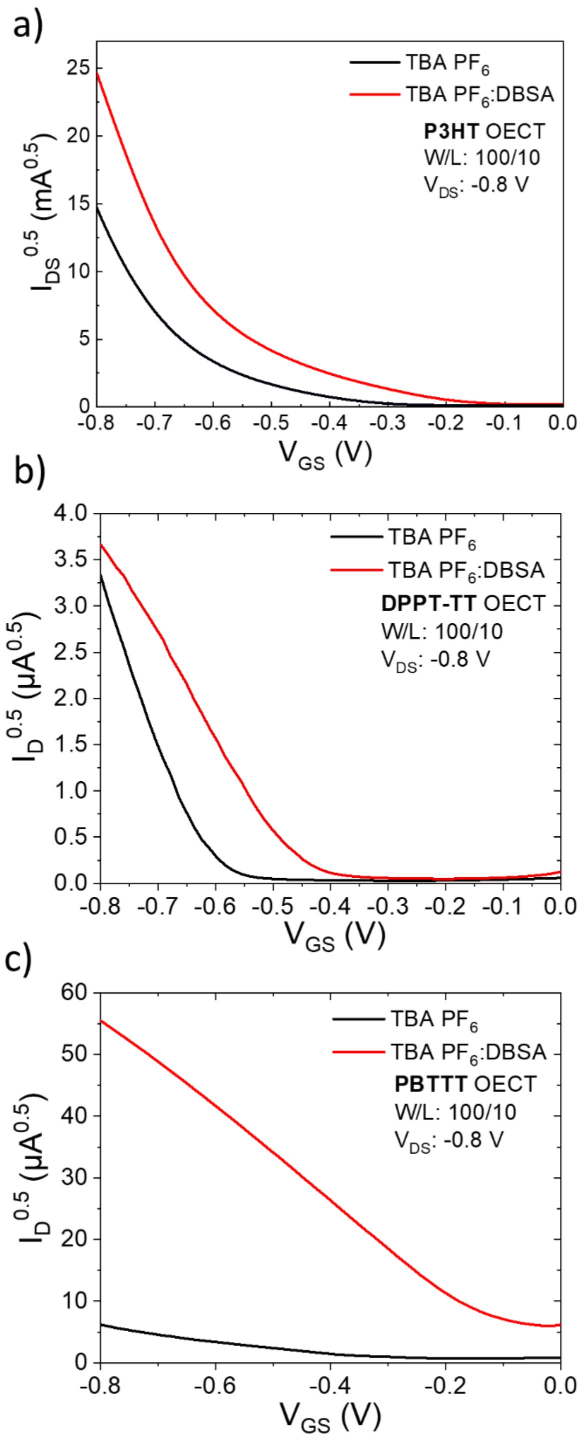

Figure S 1. Transfer curves with square root of I_{DS} to estimate the V_{ON} values.

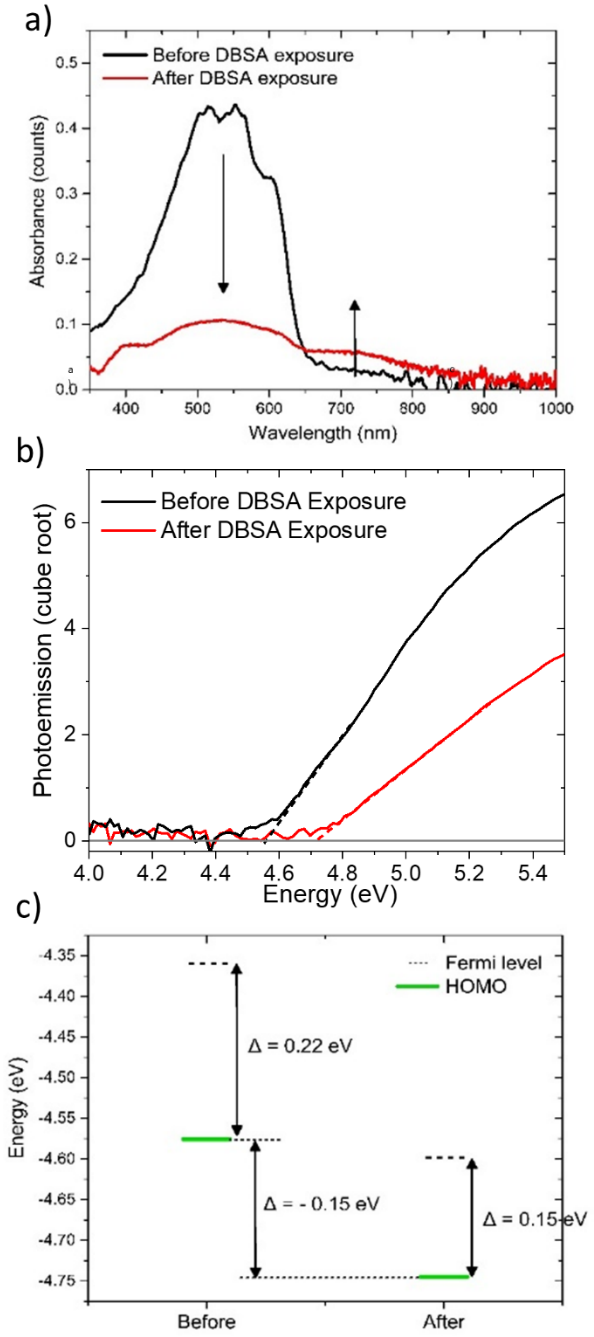

Figure S 2. Irreversible chemical doping of DBSA in ACN electrolyte. (a) Absorbance spectra of the P3HT thin film before (black) and after (red) DBSA exposure. Arrows indicate quenching of the ground state and presence of a polaron absorption band. (b) APS spectra of the P3HT thin film before (black) and after (red) DBSA exposure. (c) Energy level diagram of the P3HT thin film before and after DBSA exposure. Fermi levels were measured using a Kelvin Probe.

We investigate the behaviour of DBSA in an electrochemical cell with no other salts present by exposing a P3HT thin film to 0.1 M DBSA in ACN electrolyte and measuring in situ ERRS (Figure 4). Further evidence for irreversible p-type doping is provided by changes in the absorbance spectra which shows the ground state absorption band quenches and a small polaron absorption band increasing at higher wavelength in the NIR region (Figure S 2a). We measure the HOMO level by Air Photoelectron Spectroscopy and find it deepens by ~0.15 eV after DBSA exposure (Figure S 2 b & c). This is consistent with Alveroglu who also measures a deepening of P3HT HOMO level when mixed with DBSA.[40] In addition, we measure the Fermi level (using Kelvin Probe) and find it moves closer to the HOMO level by ~0.07 eV, which provides further evidence for p-type chemical doping induced by DBSA.

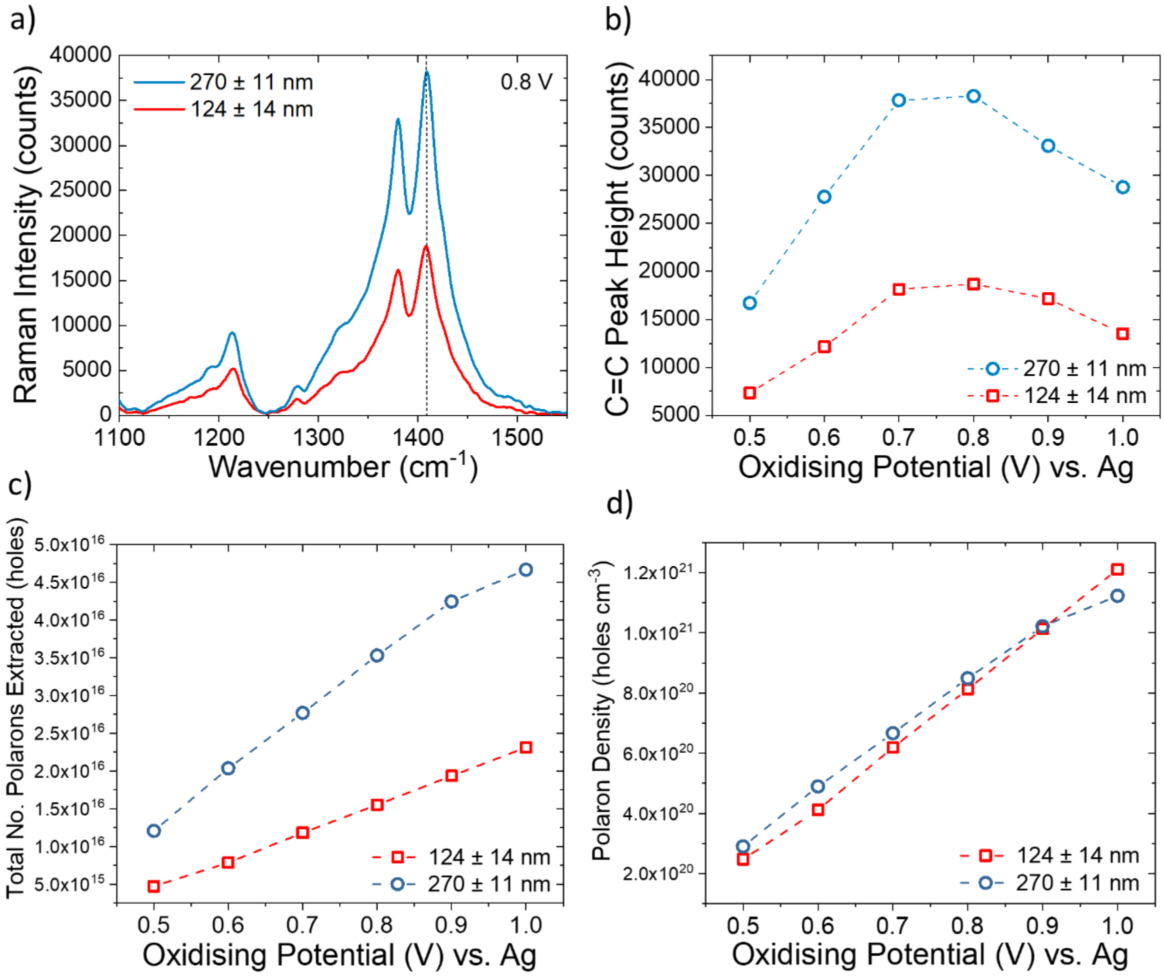

Figure S 3. Volumetric effect: electrochemical doping throughout bulk of film. (a) Comparison of ERRS spectra of thin (124 ± 14 nm) and thick (270 ± 11 nm) films of P3HT during 0.8 V oxidising potential. (b) Comparison of C=C peak height as a function of oxidising potential (V). (c) Total number of holes extracted after oxidising potential was applied. (d) Polaron density generated in each film during each oxidising potential.