

Supporting Information to

Electrochemical Investigations of the N-type Semiconducting Polymer P(NDI2OD-T2) and Its Monomer: New Insights in the Reduction Behavior

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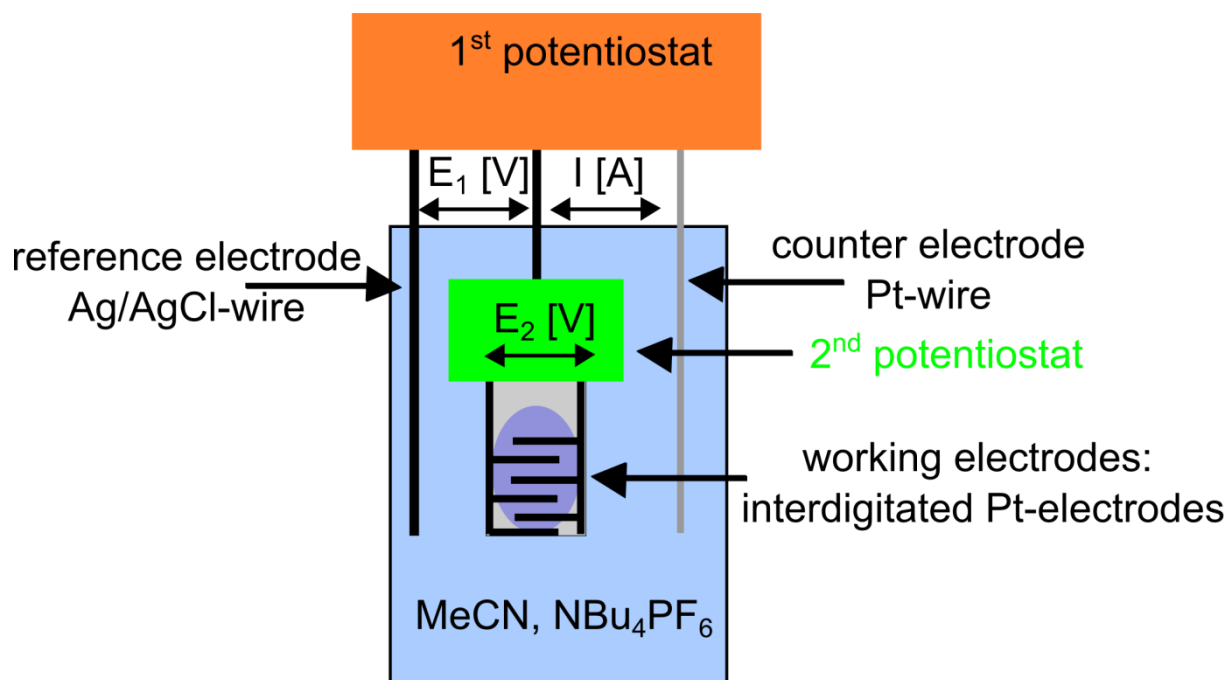


Figure S1: Schematic of the in-situ conductance and CV measurement setup.¹

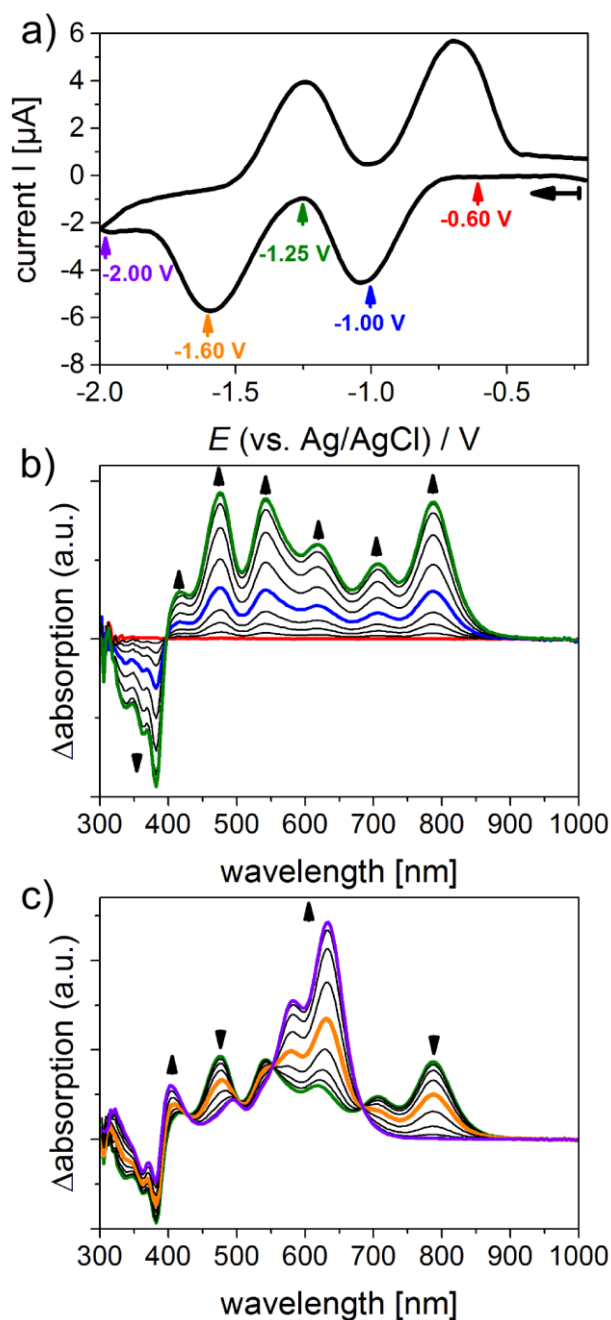


Figure S2: In-situ spectroelectrochemical characterization of the monomer Br-NDI2OD-T2-Br corresponding to Fig 1 in the main manuscript. a) Cyclic voltammogram of the in-situ spectroelectrochemistry on Br-NDI2OD-T2-Br ($c = 0.97$ mM) in 0.1 M $\text{NBu}_4\text{PF}_6/\text{THF}$ at a Pt disk electrode under thinlayer conditions (scan rate = 20 mV s^{-1}). Colors of arrows in a) indicate the potential at which the UV-vis spectra in b) and c) are recorded. b) and c) Difference UV-vis absorption spectra recorded during the forward scan in potential windows of -0.60 V to -1.25 V (b, first reduction) and -1.25 V to -2.00 V (c, second reduction). The spectra were taken every 0.05 V .

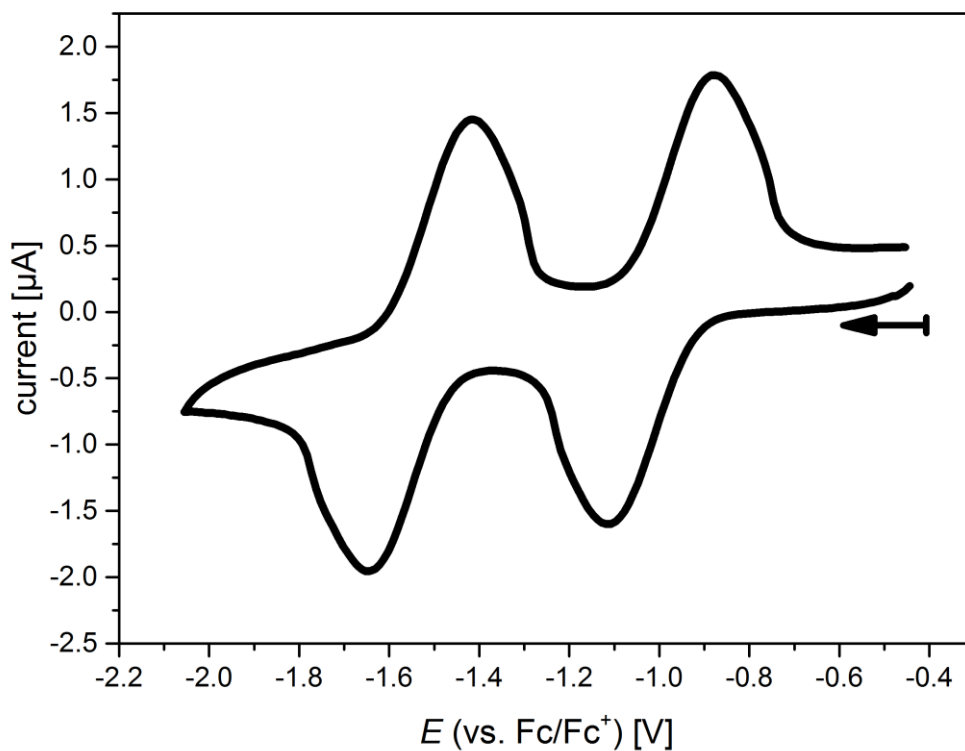


Figure S3: Cyclic voltammogram recorded during the in-situ spectroelectrochemistry of Br-NDI2OD-T2-Br ($c = 0.97$ mM) in 0.1 M NBu₄PF₆/THF at a Pt disk electrode under thin layer conditions (scan rate = 20 mV s⁻¹) corresponding to Fig. 1 in the main manuscript.

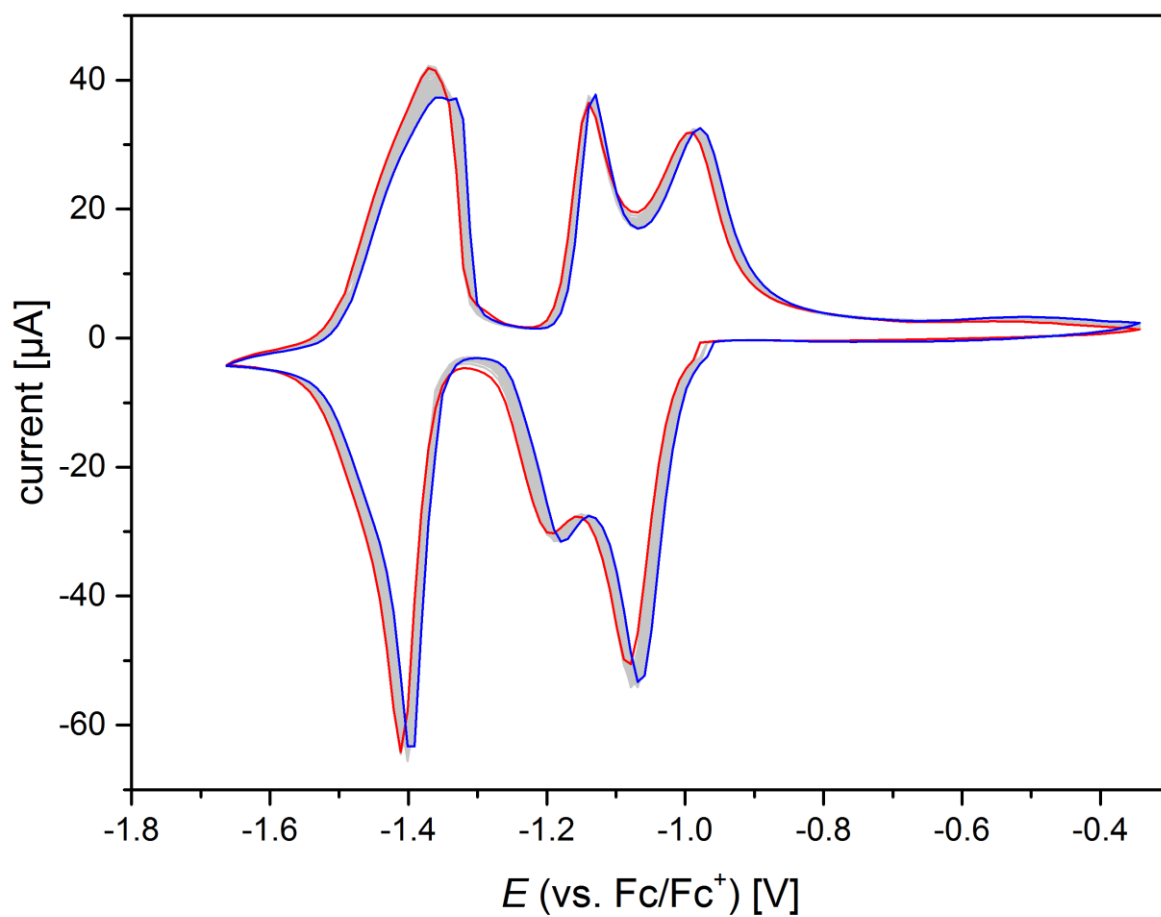


Figure S4: Multi-cyclic voltammogram (3rd cycle: red and 25th cycle: blue) of a P(NDI2OD-T2) film spincoated from 3 mg/ml CB solution on ITO in 0.1 M NBu₄PF₆/MeCN. All cycles were recorded with a scan rate of 100 mV s⁻¹ without stirring the solution between two cycles.

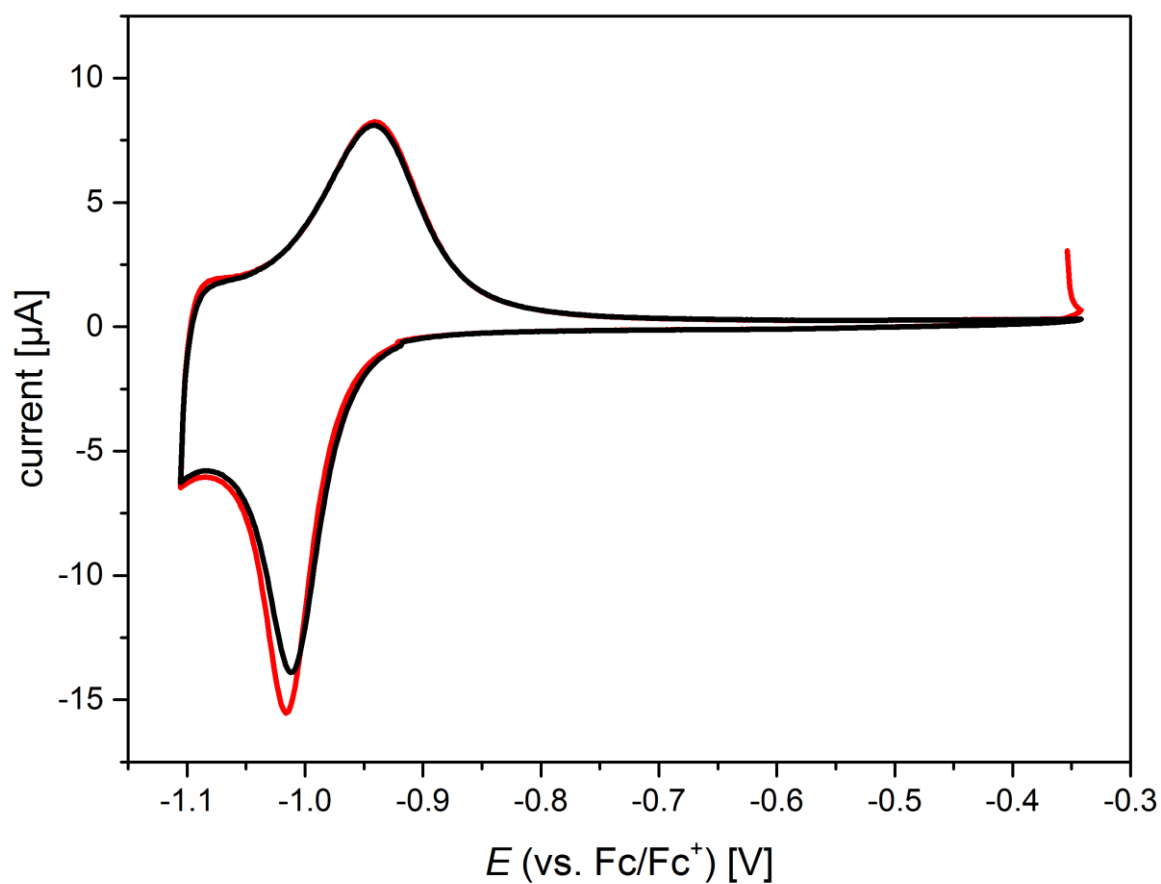


Figure S5: 1st (red) and 2nd (black) cycle of a P(NDI2OD-T2) film spincoated from 3 mg/ml CB solution on ITO in 0.1 M NBu₄PF₆/MeCN showing only the very first redox wave. All cycles were recorded with a scan rate of 20 mV s⁻¹.

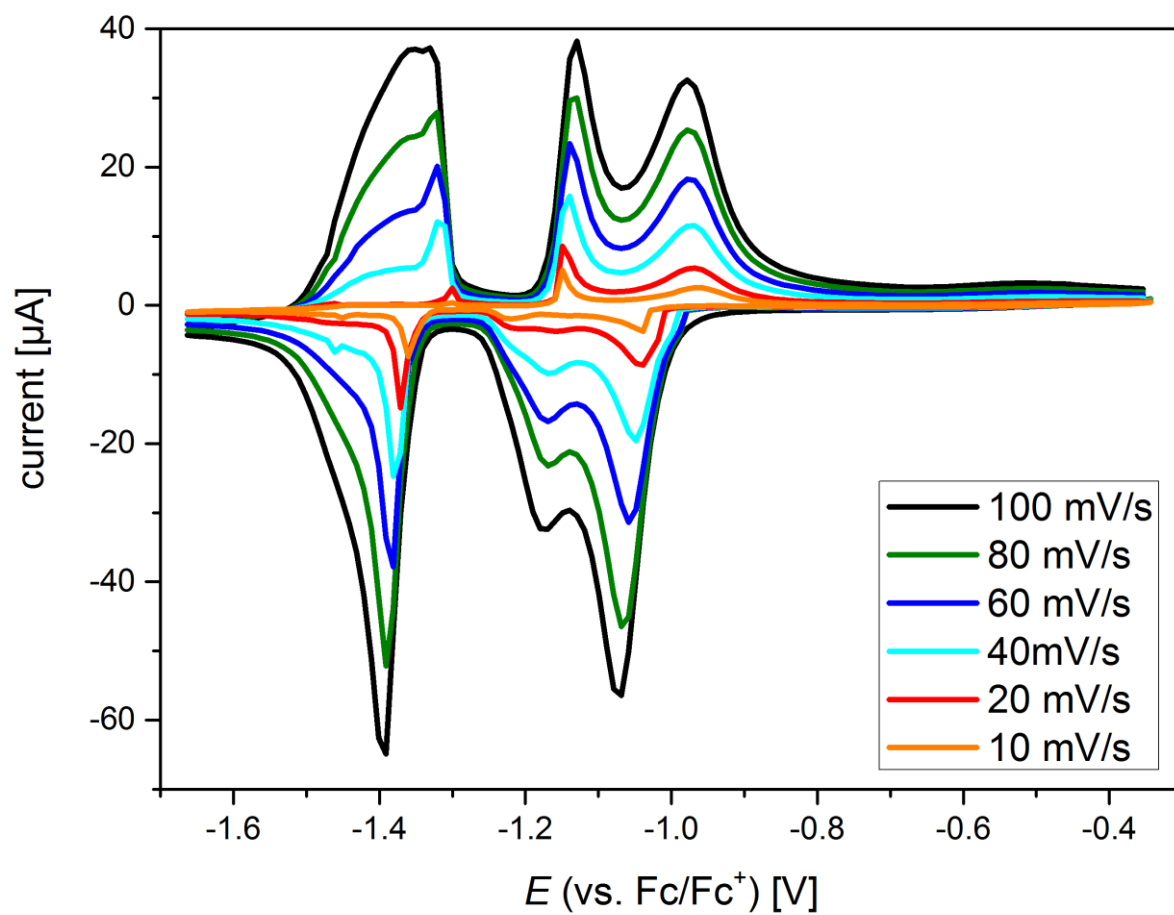


Figure S6: Cyclic voltammograms of a P(NDI2OD-T2) film spincoated on ITO from 3 mg/ml CHCl_3 at different scan rates (electrolyte: 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$).

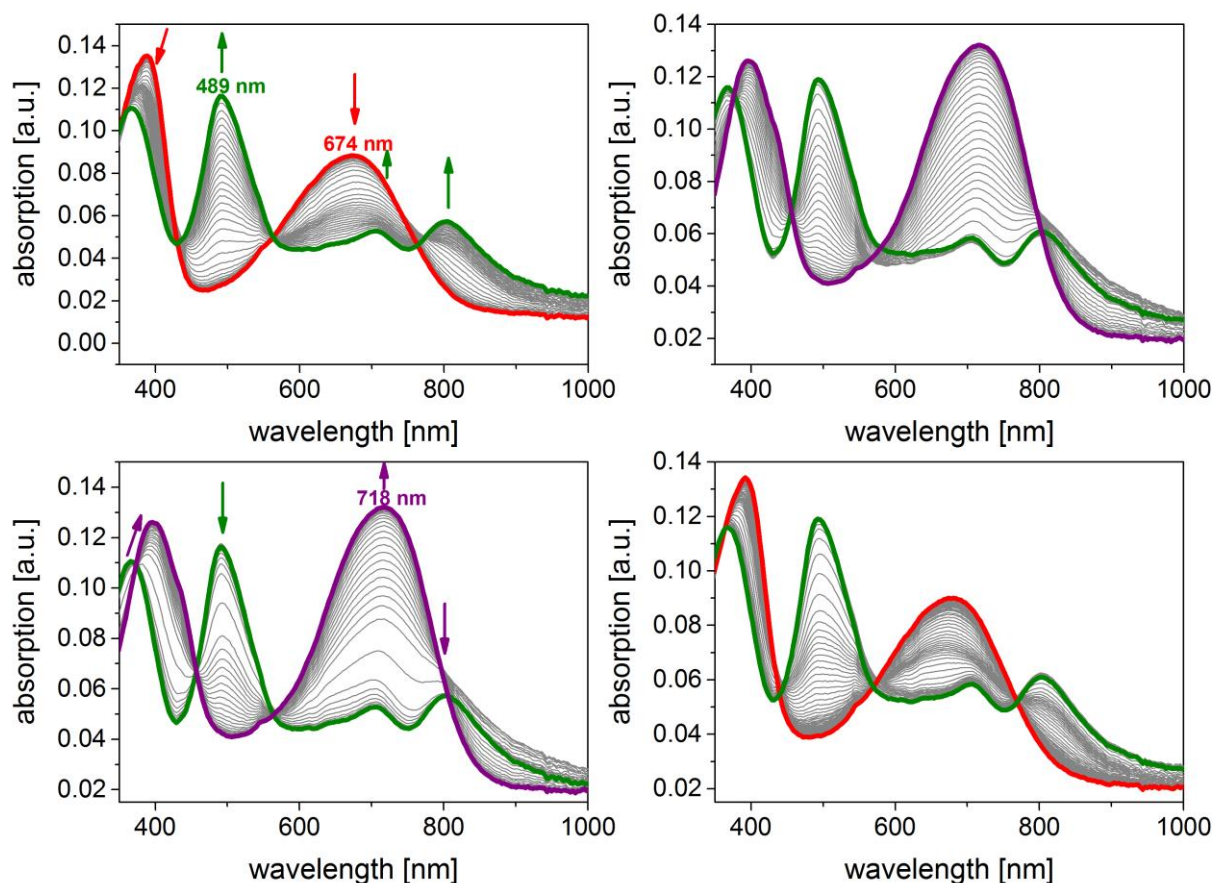


Figure S7: In-situ spectroelectrochemistry of P(NDI2OD-T2) spincoated from 3 mg/ml CB solution onto ITO, measured in 0.1 M NBu₄PF₆/MeCN. Left side: UV-vis spectra recorded during the forward scan in the cyclic voltammogram corresponding to Fig. 2 in the main manuscript. Colors of arrows in Fig 2 a) indicate the potential at which the UV-vis spectra are recorded. Right side: UV-vis spectra recorded during the backward scan in the cyclic voltammogram (purple: -1.77 V, green: -1.2 V and red: -0.37 V). The spectra were taken every 0.01 V.

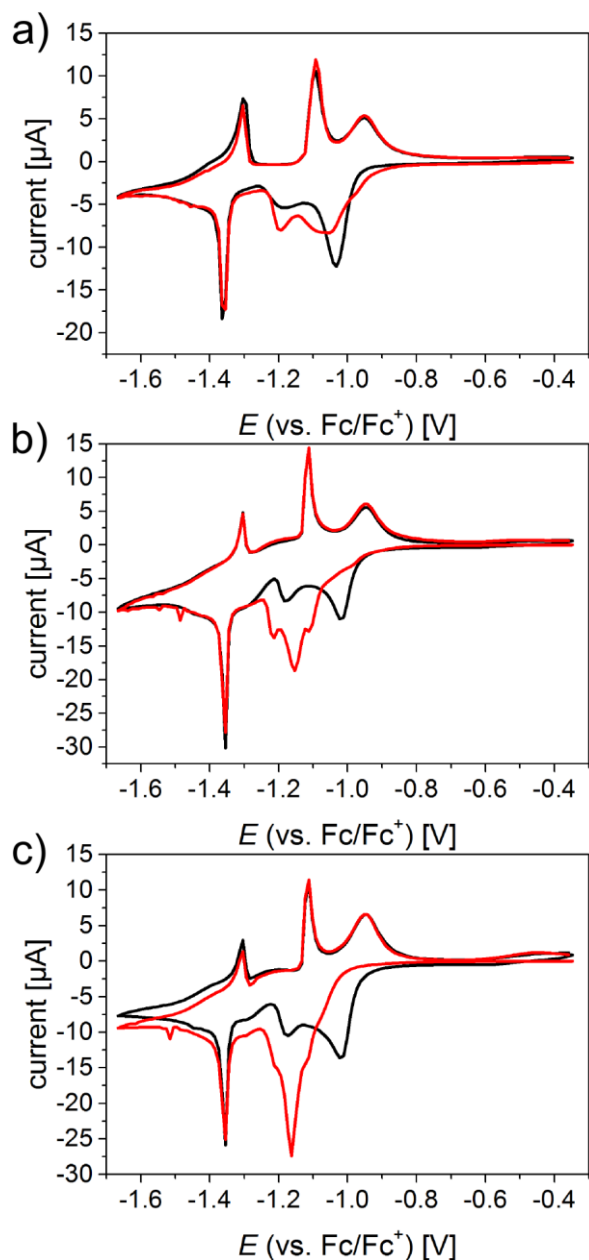


Figure S8: Cyclic voltammograms of different film morphologies of the low molecular weight P(NDI2OD-T2) on ITO in 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$. First (red) and second (black) cycles of spincoated films from a) CB as well as annealed films at 220°C b) and 300°C c). All cycles were recorded with a scan rate of 20 mV s^{-1} .

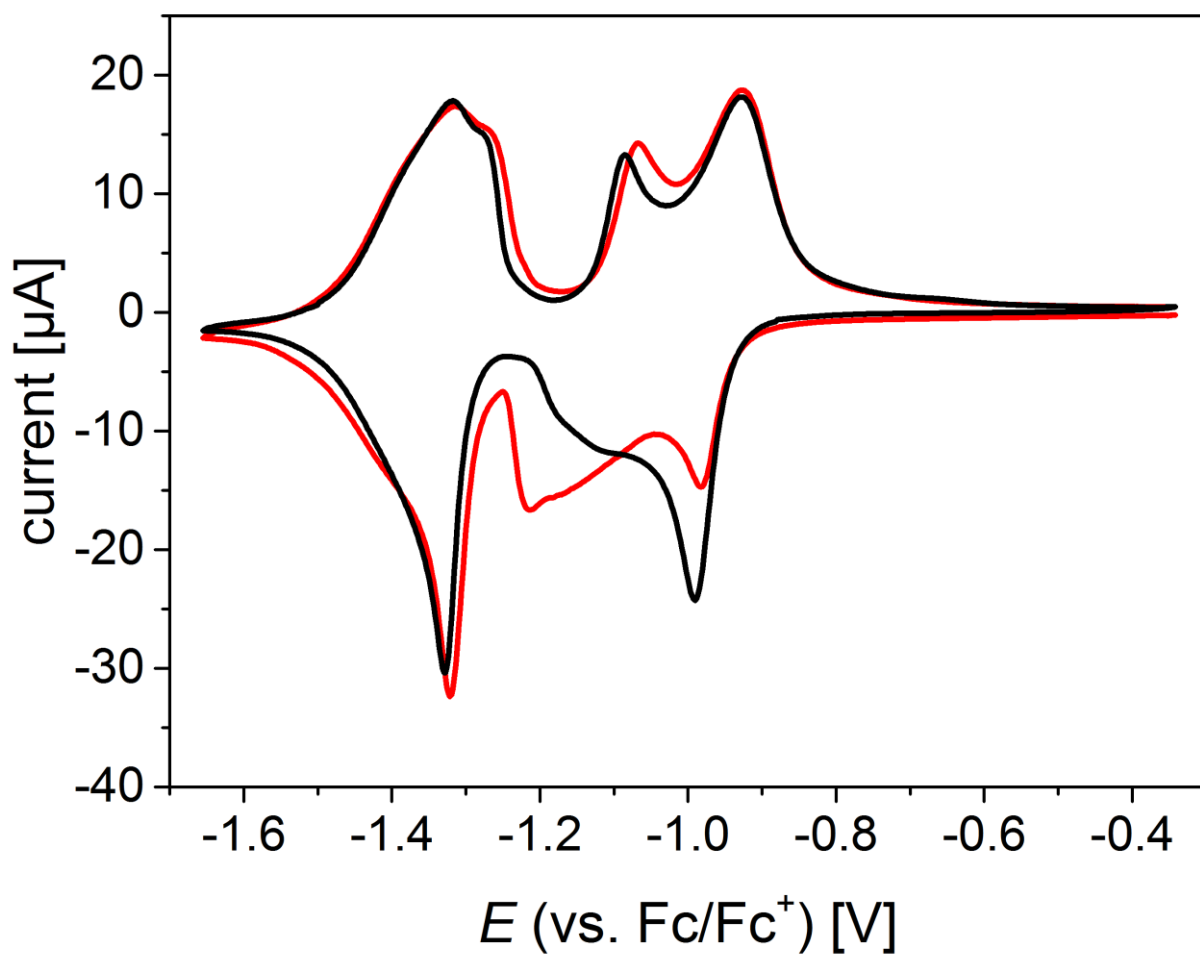


Figure S9: 1st (red) and 2nd (black) cycle of a N2200 (commercial P(NDI2OD-T2)) film spincoated from 3 mg/ml CB solution onto ITO in 0.1 M NBu₄PF₆/MeCN. All cycles were recorded with a scan rate of 20 mV s⁻¹.

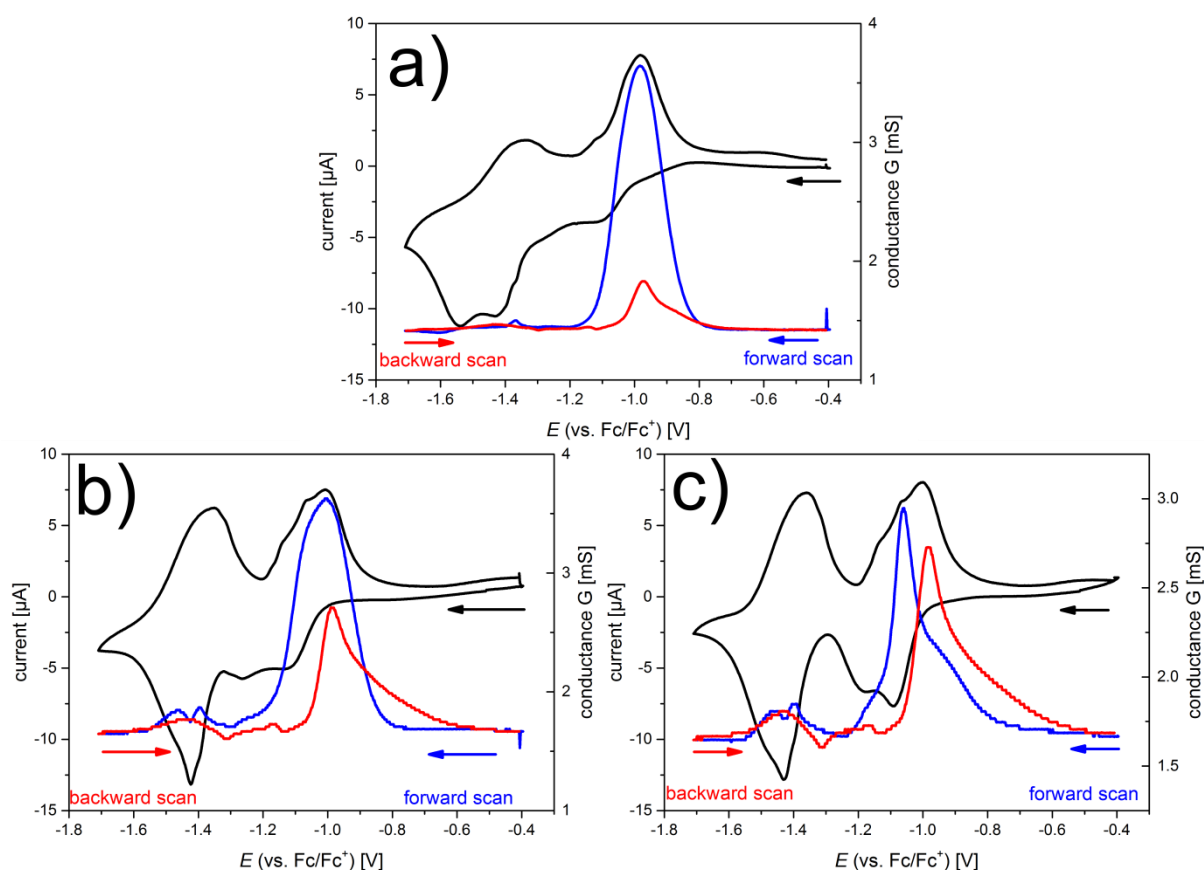


Figure S10: In-situ conductance (blue: forward scan and red: backward scan) and CV measurements (black) of a P(NDI2OD-T2) thin film spincoated from 3 mg/ml CHCl_3 solution onto interdigitating platinum electrodes (channel length = 5 μm , potential difference between working electrode 1 and working electrode 2: 10 mV) in 0.1 M $\text{NBu}_4\text{PF}_6/\text{MeCN}$ with a scan rate of 20 mV/s. Note that, in our electrolyte gated transistor setup the contribution of the background current is rather high ($\neq 0$ mS). Thus, the conductance of 1.4 mS is considered as the background current. a) 1st cycle corresponding to Figure 3 in the main text; b) 1st and c) 2nd cycle of a comparable measurement.

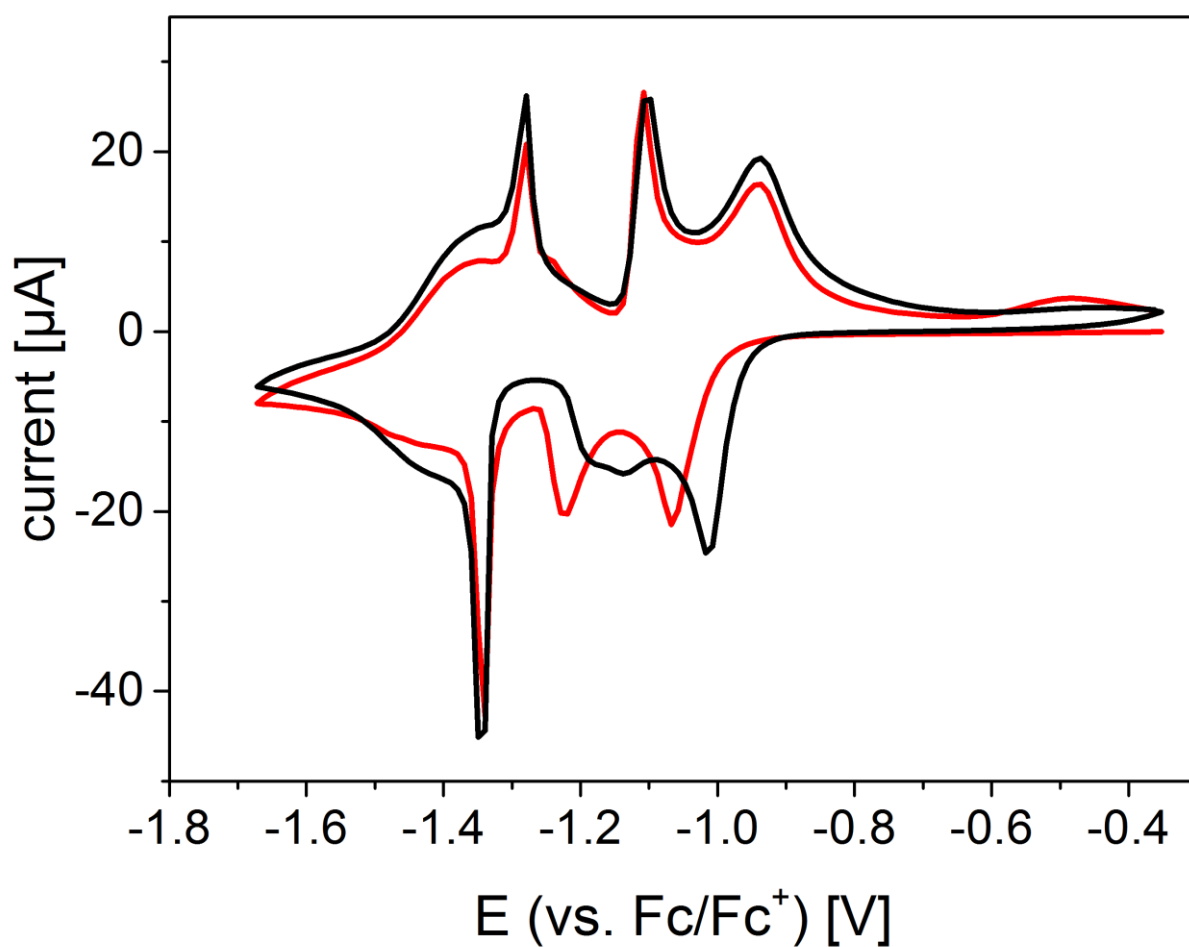


Figure S11: 1st (red) and 2nd (black) cycle of a P(NDI2OD-T2) film spincoated from 3 mg/ml CHCl₃ solution on ITO in 0.1 M NBu₄PF₆/MeCN. All cycles were recorded with a scan rate of 20 mV s⁻¹.

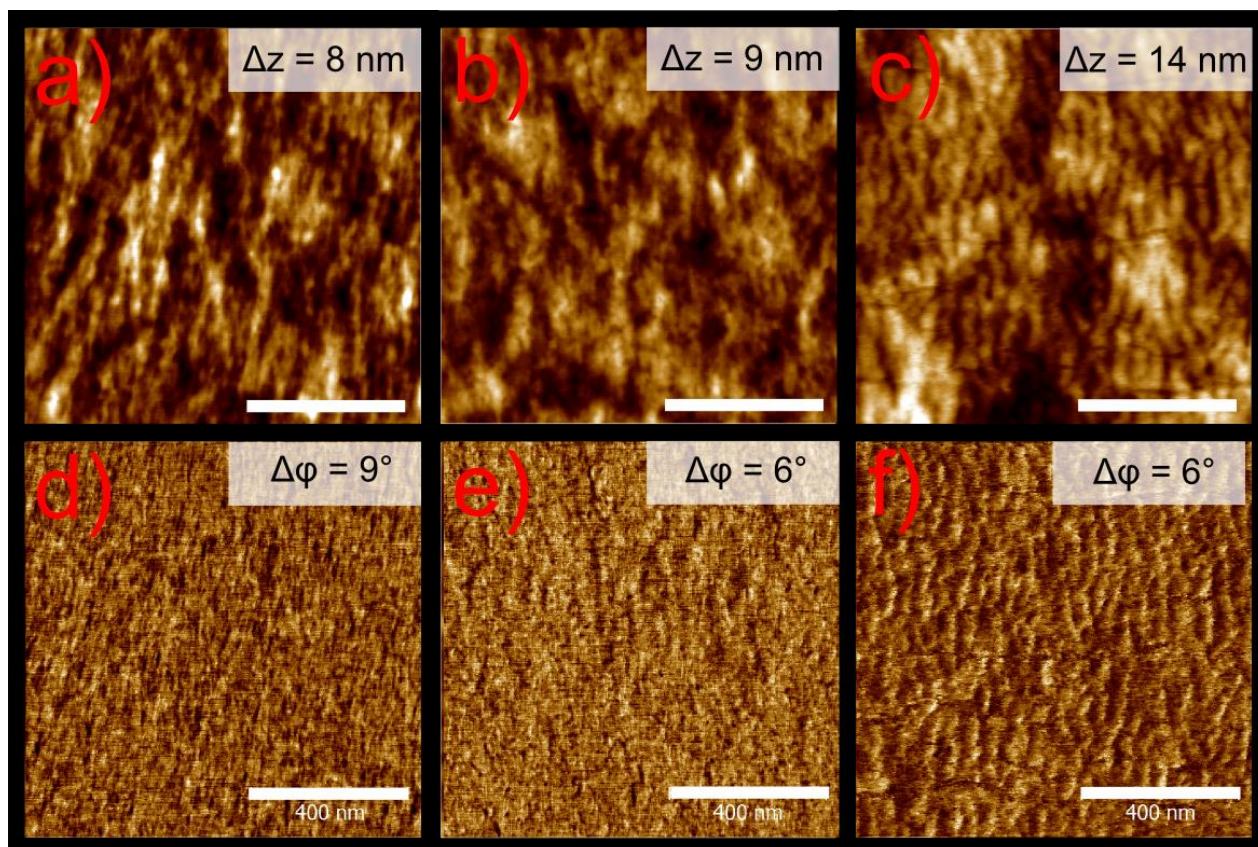


Figure S12: AFM images of P(NDI2OD-T2) films on ITO. AFM height a) and phase d) image of a film spincoated from CB. AFM height b) and phase e) image of a film spincoated from CB and afterwards annealed at 220°C. AFM height c) and phase f) image of a film spincoated from CB and afterwards annealed at 300°C.

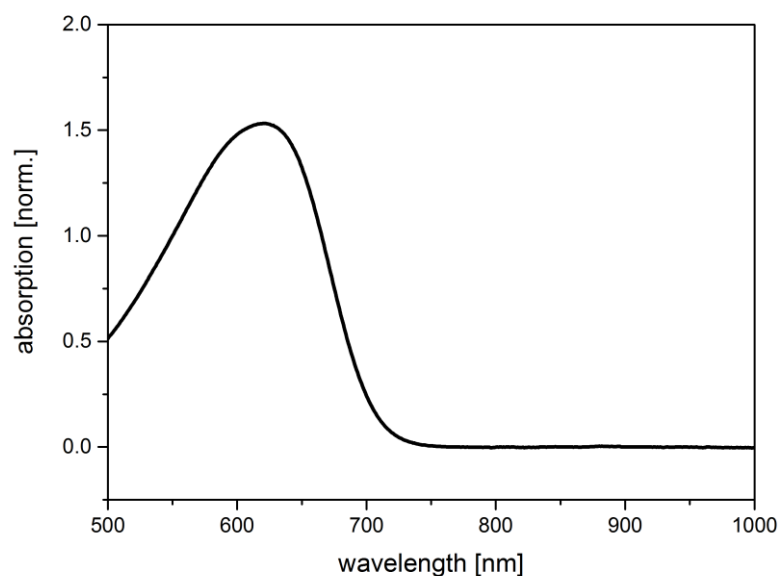


Figure S13: UV-vis absorption spectrum of a 0.01 mg/ml P(NDI2OD-T2) solution in 1-chloronaphthalene. The spectrum is normalized to its intensity at 550 nm.

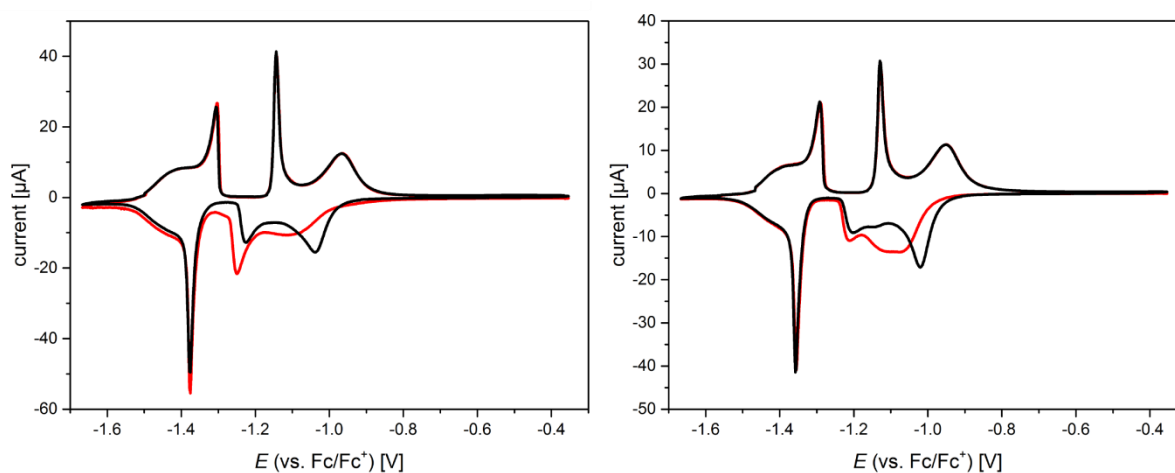


Figure S14: 1st (red) and 2nd (black) cycle of a P(NDI2OD-T2) film spincoated from 3 mg/ml CB solution on ITO in 0.1 M NBu₄PF₆/MeCN. Left: Original CVs after spincoating of the polymer film; right: CV of the same film after washing of the film with MeCN and drying at 100°C for 30 min. All cycles were recorded with a scan rate of 20 mV s⁻¹.

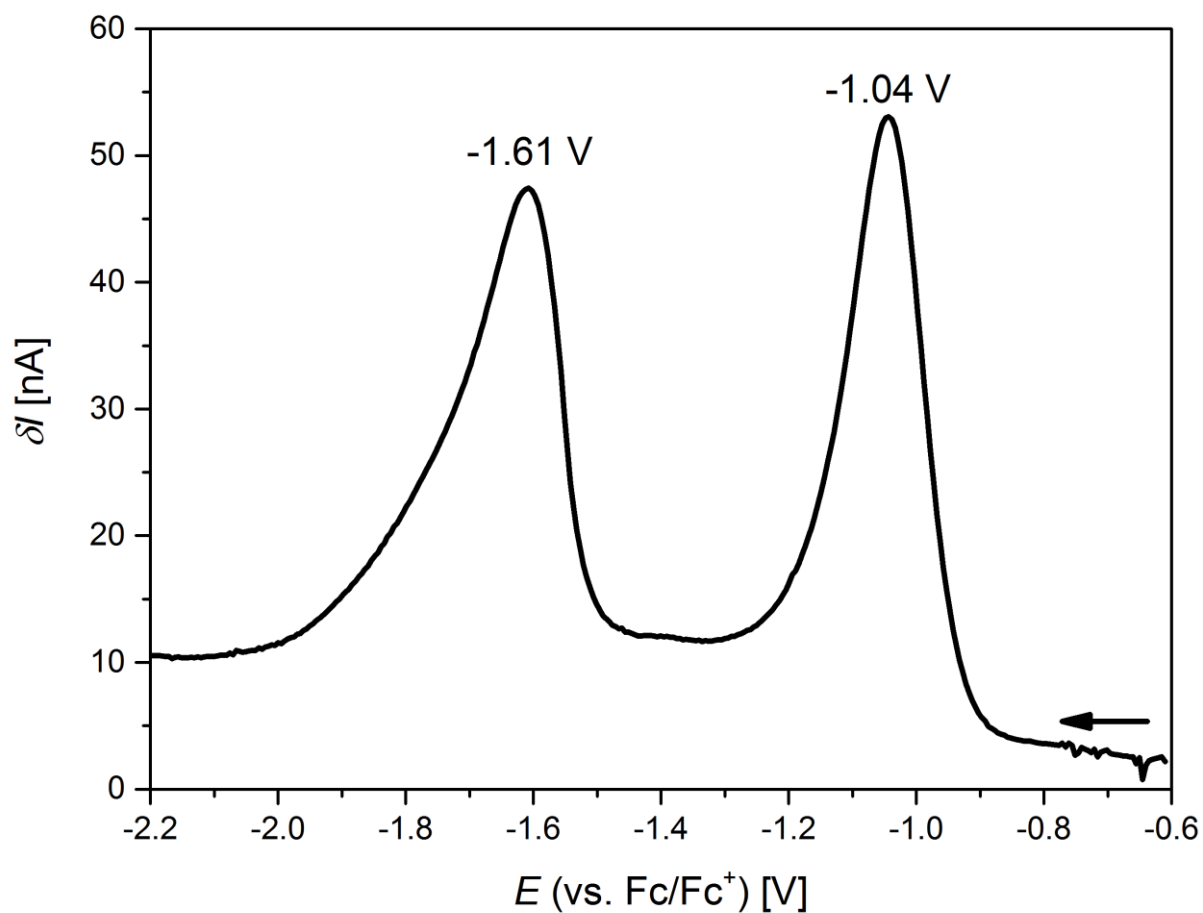


Figure S15: Differential pulse voltammogram (modulation amplitude: 0.025 V) of Br-NDI2OD-T2-Br in THF (1.00 mg/ml, supporting electrolyte: NBu_4PF_6 ; First reduction: $E_{\text{max}} = -1.04 \text{ V}$, $E_{1/2} = -1.05 \text{ V}$; second reduction: $E_{\text{max}} = -1.61 \text{ V}$, $E_{1/2} = -1.62 \text{ V}$; pulse amplitude = 25 mV, pulse duration = 0.05 s, step potential = 5 mV, interval time = 0.5 s).

References

- (1) Smie, A.; Synowczyk, A.; Heinze, J.; Alle, R.; Tschuncky, P.; Götz, G.; Bäuerle, P. B, β -Disubstituted Oligothiophenes, a New Oligomeric Approach towards the Synthesis of Conducting Polymers. *J. Electroanal. Chem.* **1998**, 452 (1), 87–95.