Supporting Information

Electrochemical Doping for Absorption and Conductivity Tuning of P(NDI2OD-T2) Films

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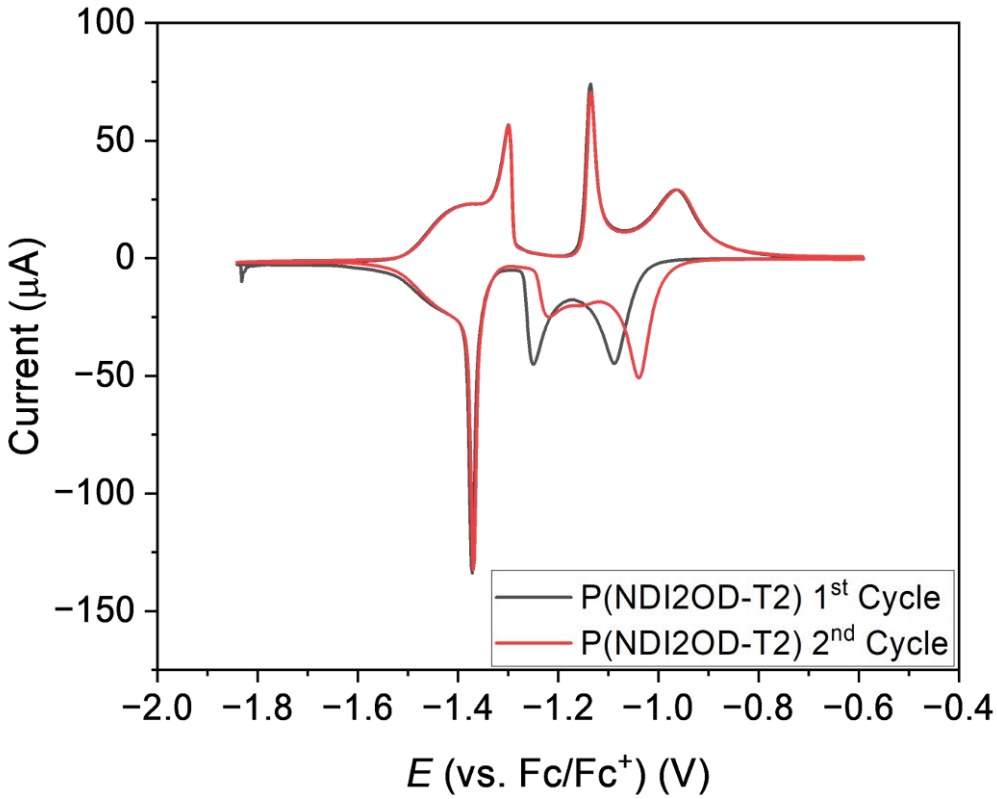

Figure S1. First and second cycle of cyclic voltammetry of P(NDI2OD-T2) film measured in 0.1 M $TBAPF_6$ /MeCN at a scan rate of 20 mV/s. The polymer film was spincoated from 5 mg/mL chloroform solution on an ITO glass substrate.

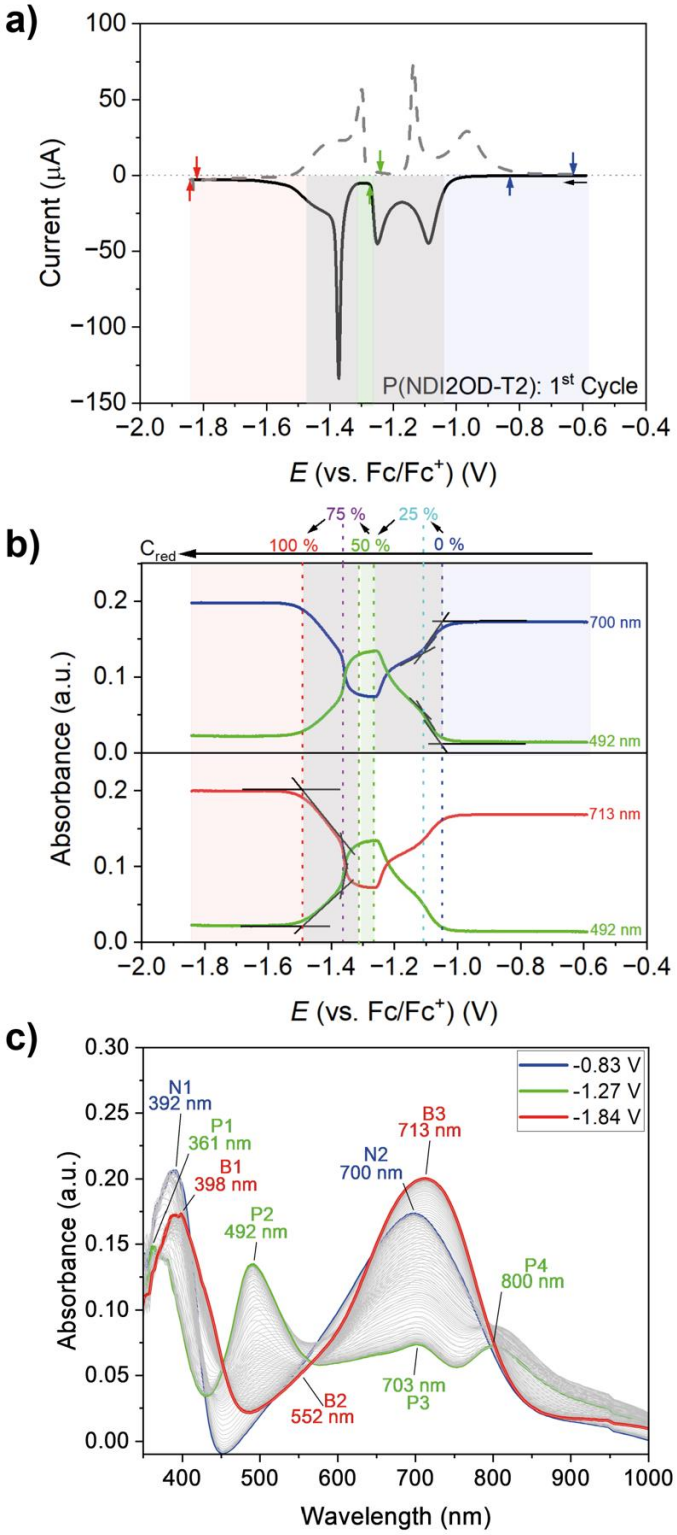

Figure S2. *In situ* spectroelectrochemistry of P(NDI2OD-T2) measured in 0.1 M $TBAPF_6$/MeCN. Spectral evolutions (b) and UV-vis absorption spectra (c) are shown for the forward scan of the first cycle (a) of cyclic voltammetry. The blue, green and red shading indicate the potential ranges of the fully neutral, fully polaron and fully bipolaron states, respectively. The grey shading refers to the potential ranges for the transition mixed valence states. The characteristic spectra for the neutral (N), polaron (P), and bipolaron (B) states of P(NDI2OD-T2) are indicated by blue (N1, N2), green (P1, P2, P3, P4) and red (B1, B2, B3) spectra, respectively.

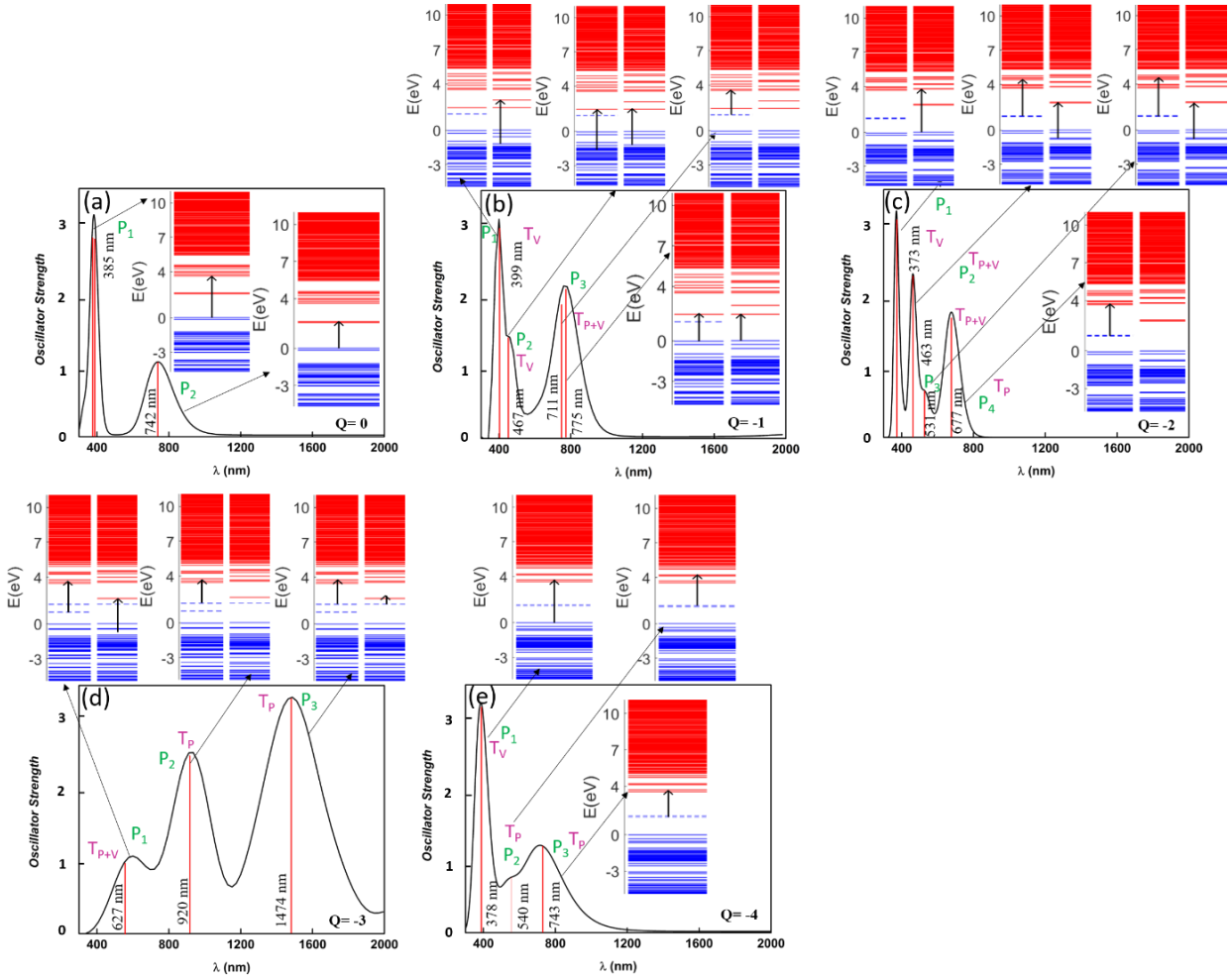

Figure S3. (a) TD-DFT calculated UV vis/NIR absorption spectra of neutral dimer $(NDI\text{-}T2)_2$ with the corresponding electronic transitions, calculated using B3LYP/6-31+G(d). UV vis/NIR absorption spectra of doped dimer $(NDI\text{-}T)_2$ along with its corresponding electronic transition states at various doped states, (b) Q = -1 (C_{red} = 25%), (c) Q = -2 (C_{red} = 50%), (d) Q = -3 (C_{red} = 75%), (e) Q = -4 (C_{red} = 100%).

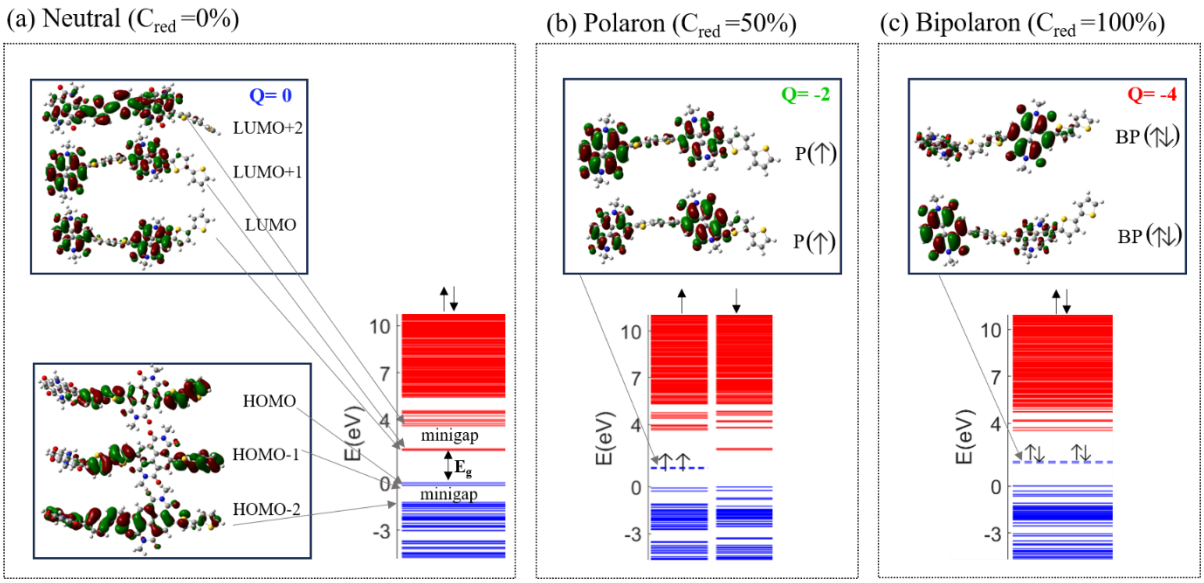

Figure S4. Energy band diagram of NDI-T2 dimer for different reduction levels (a) C_{red} = 0%, (b) C_{red} = 50%, and (c) C_{red} = 100%. The occupied states within the valence band and the unoccupied states in the conduction band are depicted via blue and red lines, respectively; the occupied polaron and bipolaron states are depicted by dashed blue lines. Inset shows representative electron density distribution of (a) the highest occupied molecular orbital (HOMO) and lower-lying occupied molecular orbitals, HOMO-1, HOMO-2 and the lowest unoccupied molecular orbital (LUMO) and higher-lying unoccupied orbitals, LUMO+1, LUMO+2; (b) polaron states; (c) bipolaron states. Up and down arrows signify different spin states.

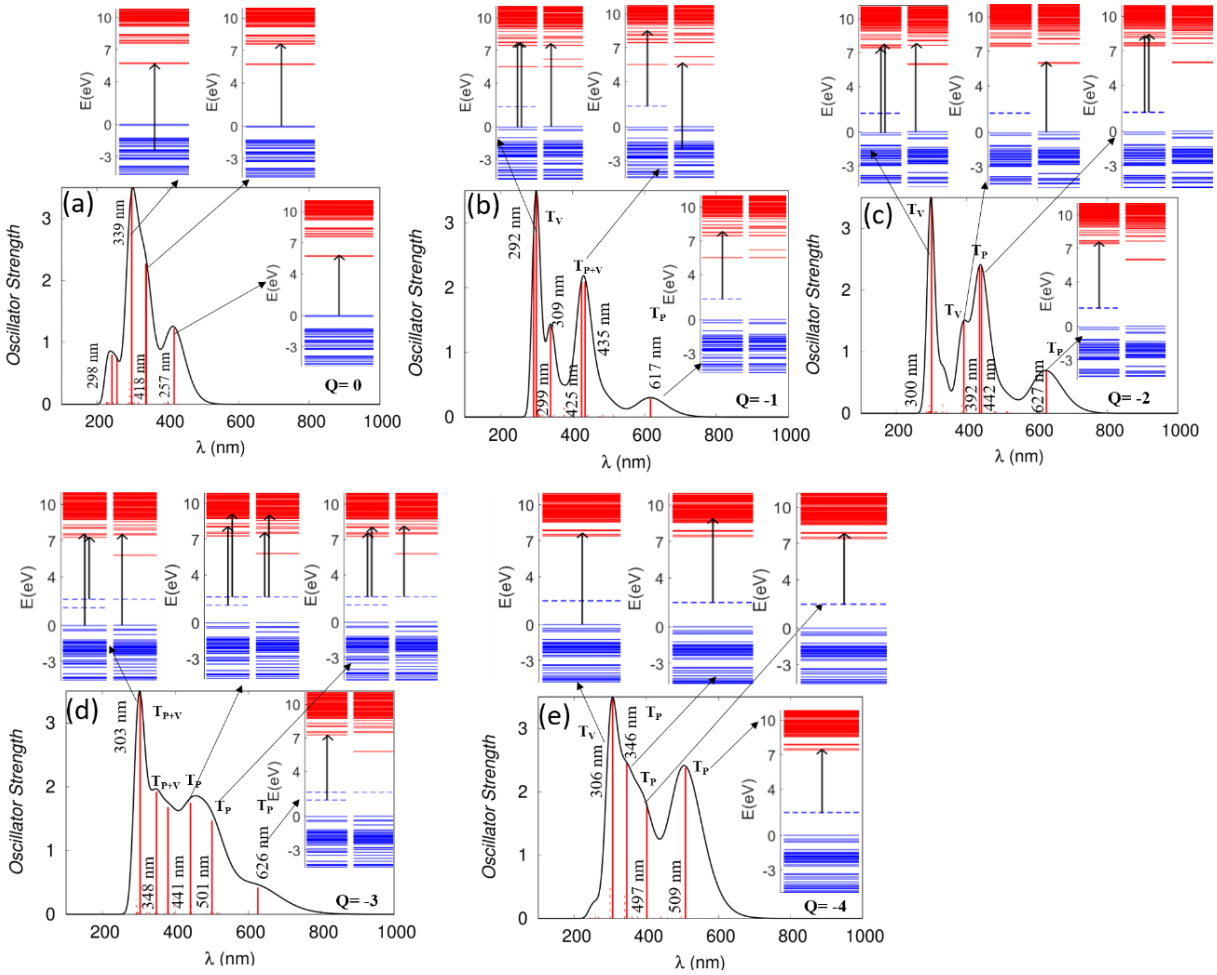

Figure S5. UV vis/NIR absorption spectra NDI-T2 dimer along with its corresponding electronic transitions at various reduction levels, (a) Q = 0 (C_{red} = 0%) (b) Q = -1 (C_{red} = 25%), (c) Q = -2 (C_{red} = 50%), (d) Q = -3 (C_{red} = 75%), (e) Q = -4 (C_{red} = 100%). Calculations are performed with the long-range corrected hybrid functional ωB97XD.

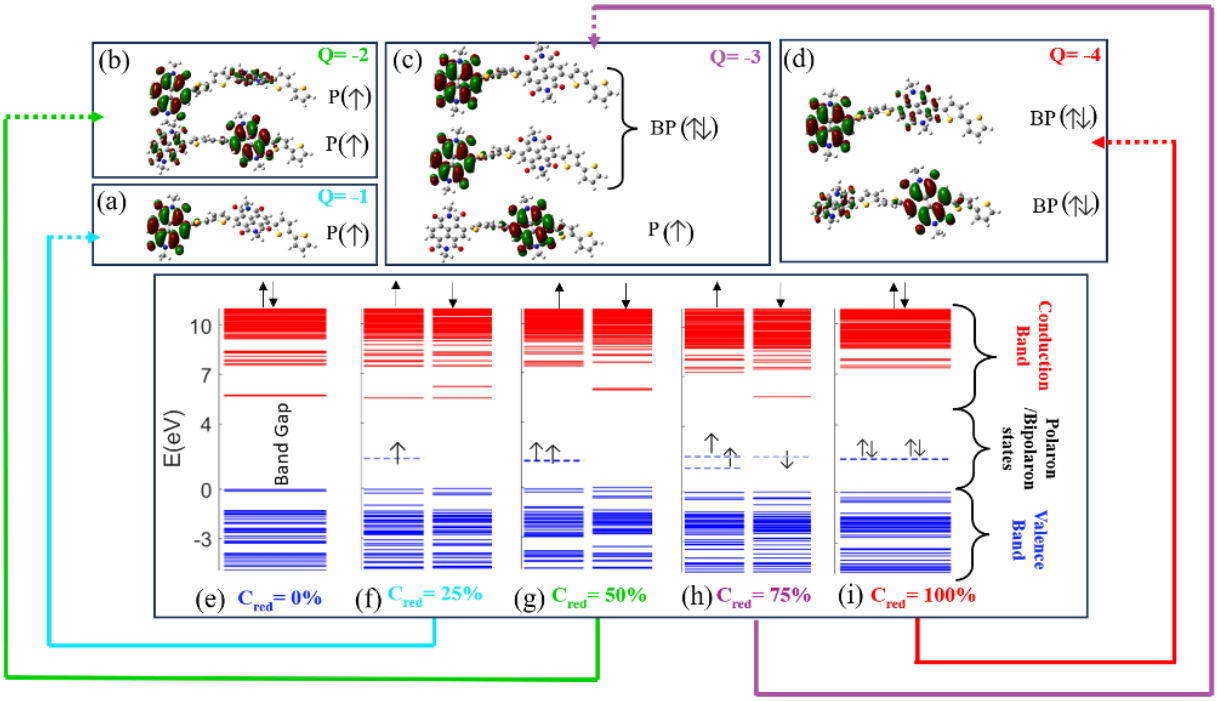

Figure S6. Energy band diagram of NDI-T2 dimer for different reduction levels (e) C_{red} = 0%, (f) C_{red} = 25%, (g) C_{red} = 50%, (h) C_{red} = 75% and (i) C_{red} = 100%. The occupied states within the valence band and the unoccupied states in the conduction band are depicted via blue and red lines, respectively; the occupied polaron and bipolaron states are depicted by dashed blue lines. Inset shows representative electron density distribution of polaron and bipolaron states. Calculations are performed with the long-range corrected hybrid functional ωB97XD.

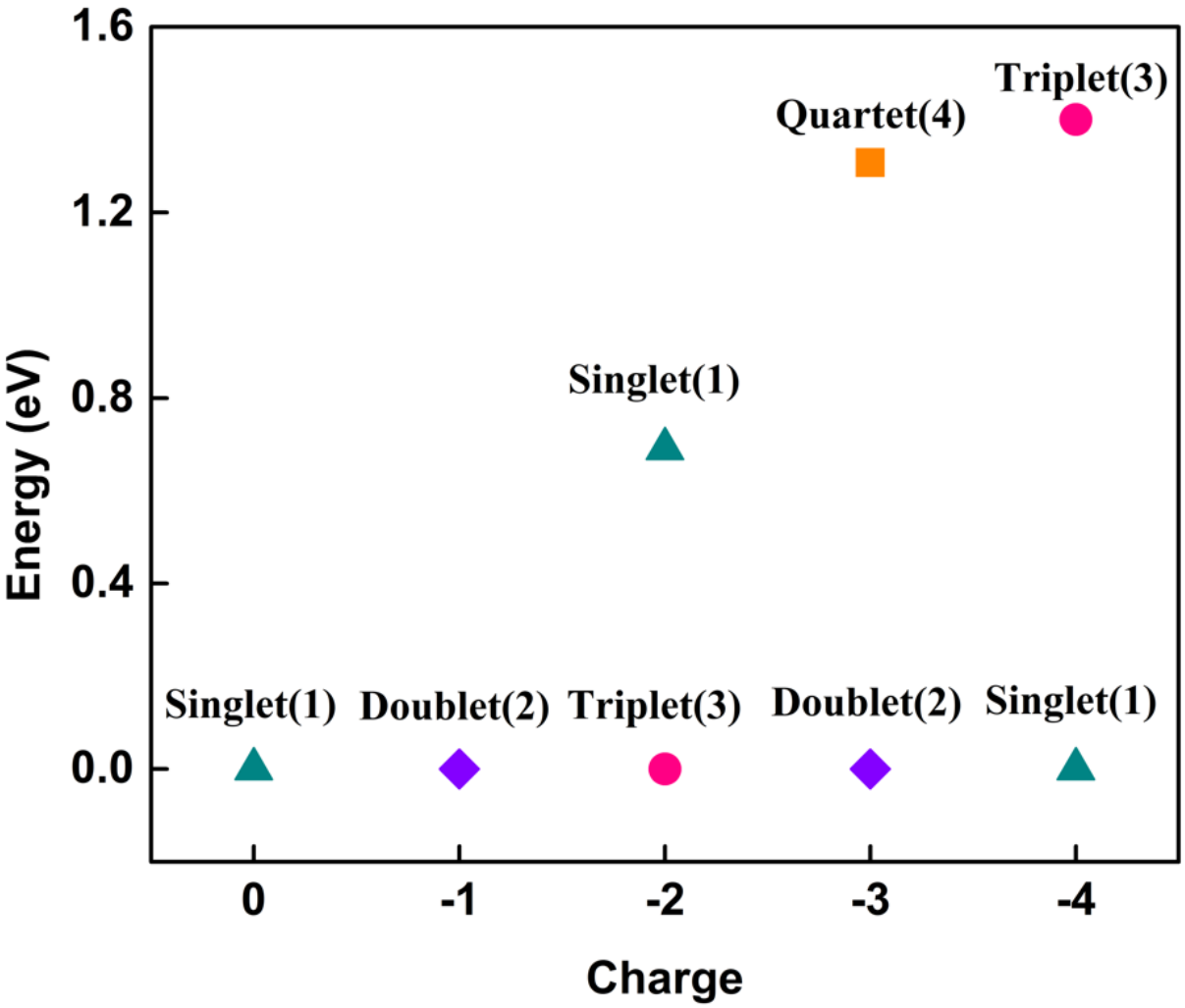

Figure S7. The total energy of the NDI-T2 polymer chain at different spin states of neutral and reduced at different charged states from 0 to -4 in solvent phase, where all the ground-state energies are set to zero for convenience.

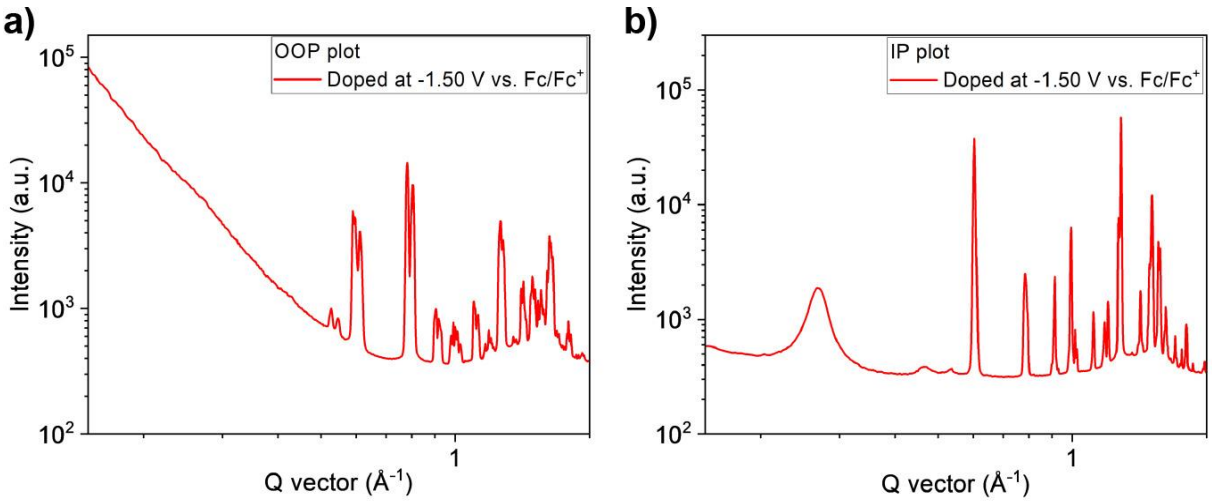

Figure S8. *Ex situ* measured GIWAXS data of an aligned film of P(NDI2OD-T2) on gold substrates. The film is doped at -1.50 V vs. Fc/Fc^+ in 0.1 M $TBAPF_6$/acetonitrile electrolyte. The sample is dried and transferred to the beam line under inert conditions. Line cuts OOP and IP are presented in (a) and (b).

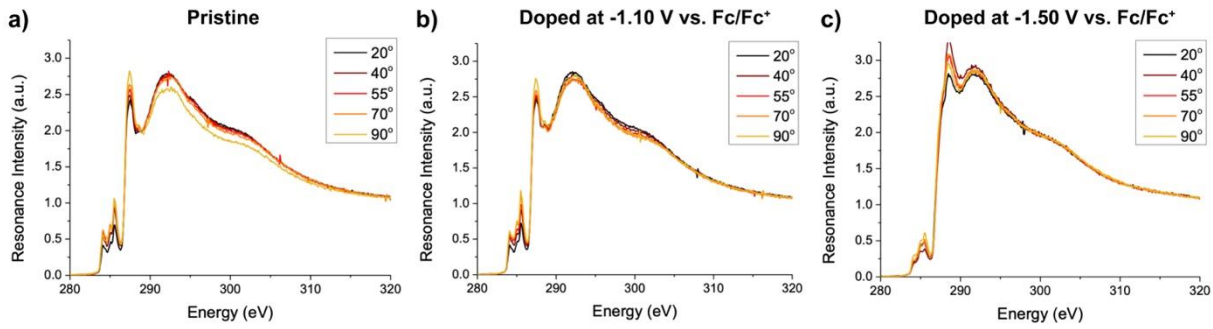

Figure S9. Surface-sensitive NEXAFS data of samples in: (a) pristine, (b) doped at -1.10 V vs. Fc/Fc^+, and (c) doped at -1.50 V vs. Fc/Fc^+.