

## Supporting Information

# Electron *n*-Doping of a Highly Electron-Deficient Chlorinated Benzodifurandione-Based Oligophenylene Vinylene Polymer Using Benzyl Viologen Radical Cation

Teck Lip Dexter Tam<sup>\*1</sup>, Albertus Denny Handoko,<sup>1</sup> Ting Ting Lin<sup>1</sup> and Jianwei Xu<sup>\*1,2</sup>

<sup>1</sup> Institute of Materials Research and Engineering (IMRE), Agency of Science, Technology and Research (A\*STAR), 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore.

<sup>2</sup> Department of Chemistry, National University of Singapore, 3 Science Drive 3, Singapore 117543, Singapore.

## Supporting Information

### General information

UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR Spectrophotometer. Cyclic voltammetry (CV) experiments were performed using Autolab potentiostat (model PGSTAT30) by Echochimie. CV measurements were recorded in dry acetonitrile with 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte (scan rate of 100 mV·s<sup>-1</sup>), glassy carbon disk as working electrode, gold disk as counter electrode and Ag/AgCl as reference electrode. Ferrocene was used as external standard (HOMO = oxidation onset = -4.80 eV). XRD measurements were performed on dropcasted films using Bruker D8 Advance with Cu K $\alpha$  radiation ( $\lambda$  = 1.54060 Å). XPS spectra were measured using VG Thermo Escalab 220i-XL X-ray photoelectron spectroscopy system. XPS data is analyzed using Thermo Avantage v4.12.

### Doping of Cl-BDPPV

All processes and electrical measurements were carried out in the glovebox (H<sub>2</sub>O & O<sub>2</sub> less than 1 ppm) unless otherwise stated. 20 mg of Cl-BDPPV (1-Material, M<sub>w</sub> 85000, PDI 2.5) was dissolved in 1 mL of 1,2-dichlorobenzene at 60 °C. The polymer solution was spin-coated onto pre-clean and UV/O<sub>3</sub> treated (100 °C for 10 mins) glass substrate at 1000 rpm for 90 seconds and annealed at 150 °C for 30 mins. The spincoated films

have a thickness of about 20 nm. The polymer films were allowed to cool down to room temperature after thermal annealing. 20.5 mg of benzyl viologen dichloride (Sigma Aldrich) and 13.1 mg of zinc dust (Sigma Aldrich) were weighed in the glovebox and suspended in 20 mL of anhydrous acetonitrile (Sigma Aldrich) in a 50 mL centrifuge tube. The suspension was sealed carefully with parafilm and taken out of the glovebox. The suspension was sonicated for 100 mins, centrifuged at 3000 rpm for 5 mins and brought back into the glovebox. The resulting blue-colored  $BV^{2+}$  solution was carefully decanted into a staining jar.  $BV^{2+}$  was assumed to be fully converted to  $BV^{\bullet+}$ , with a concentration of 2.5 mM. The polymer films were doped by immersing into the  $BV^{\bullet+}$  solution. After immersed for the designated time, the polymer film was taken out of the  $BV^{\bullet+}$  solution and annealed at 50 °C for 10 mins. The samples were allowed to cool to room temperature before any measurements. For doping using TDAE, we followed the procedures reported by Fabiano and co-workers.<sup>1</sup>

### Electrical Conductivity Measurements

The preparation of the  $BV^{\bullet+}$ -doped CI-BDPPV film is the same as above except that the CI-BDPPV film was spin-coated onto cleaned glass substrates with 120 nm of sputtered parallel electrodes (20 nm Cr followed by 100 nm Au). The length and width of the electrodes were 2 cm by 0.25 cm, and the channel length between the electrodes was 0.25cm. Both two- and four-point resistance measurements resulted in similar resistance values. Electrical conductivity was calculated using the formula  $\sigma = L / (R \times W \times t)$ , where  $R$  is the resistance measured using a Keithley 2400 SourceMeter between two electrodes,  $L$  is the channel length between the electrodes,  $t$  is the thickness of the film and  $W$  is the channel width (length of the electrodes).

### Thermovoltage Measurements

The Seebeck coefficient was measured by using a custom-made setup with a Peltier heater (298 K +  $\Delta T$ ) and a Peltier cooler (298 K) which are used to vary the temperature gradient ( $\approx 2$  K) across the two ends of the thin film and induce a thermal voltage. Two thermistor temperature sensors, connected to Thermocouple Data Logger GL840 from Graphtec, were placed on the coated thin film alongside two electrical probes which were connected to a Keithley 4200 SCS Semiconductor Characterization System. 3 devices were fabricated and measured for each polymer and immersion time.

### XRD Measurements

Measurements were performed on dropcast pristine and doped (7s immersion) films. X-ray diffraction data was processed using Bruker AXS Topas (v3). Background contribution was fitted to a combination of 3-order Chebychev polynomial function and  $1/x$  bg to

account for possible air scattering contribution at low  $2\theta$  angle. The peak positions, intensity and full width at half maximum (FWHM) of both pristine and doped samples were calculated by manually adding 10 independent peak phases at the apparent peak maxima on the raw diffractogram and then fitting them to a pseudo Voigt function. Three additional peaks at around  $2\theta$  values of  $8^\circ$ ,  $16^\circ$  and  $32^\circ$  were added to both pristine and doped samples for better fitting.

### Density Functional Theory (DFT) Calculation

All geometries were optimized at DFT CAM-B3LYP 6-31G\*\* level of theory in the gas phase using NWChem. For the energy landscape profile calculations, a pair of geometry optimized Cl-BDPPV with 3 repeating units were positioned according to the a-, b- and c-displacements shown in Figure 5f-g. Unrestricted formalism was used for [Cl-BDPPV dimer + BV] $^{\bullet+}$  and [Cl-BDPPV dimer + BV] $^0$  system. Charge transfer integral was estimated using energy-splitting-in-dimer approach. For [Cl-BDPPV dimer + BV] $^{\bullet+}$  and [Cl-BDPPV dimer + BV] $^0$  system, charge transfer integral was calculated from restricted single-point energy calculation (charge = 0) with the BV molecule removed from the geometry optimized structure.

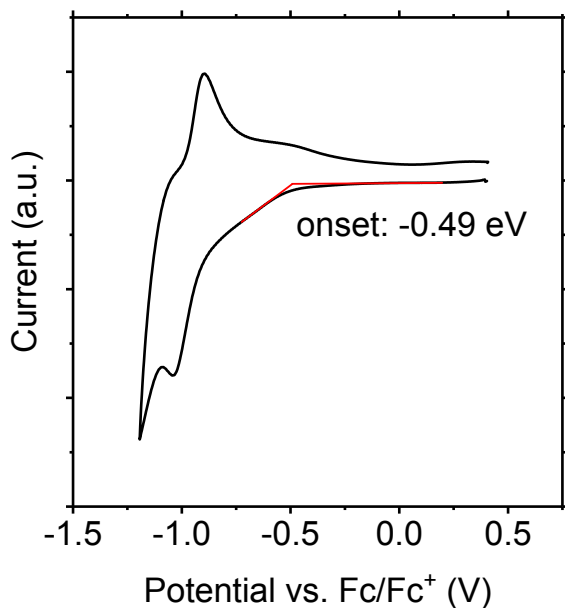


Figure S1. Cyclic voltammogram of Cl-BDPPV thin film.

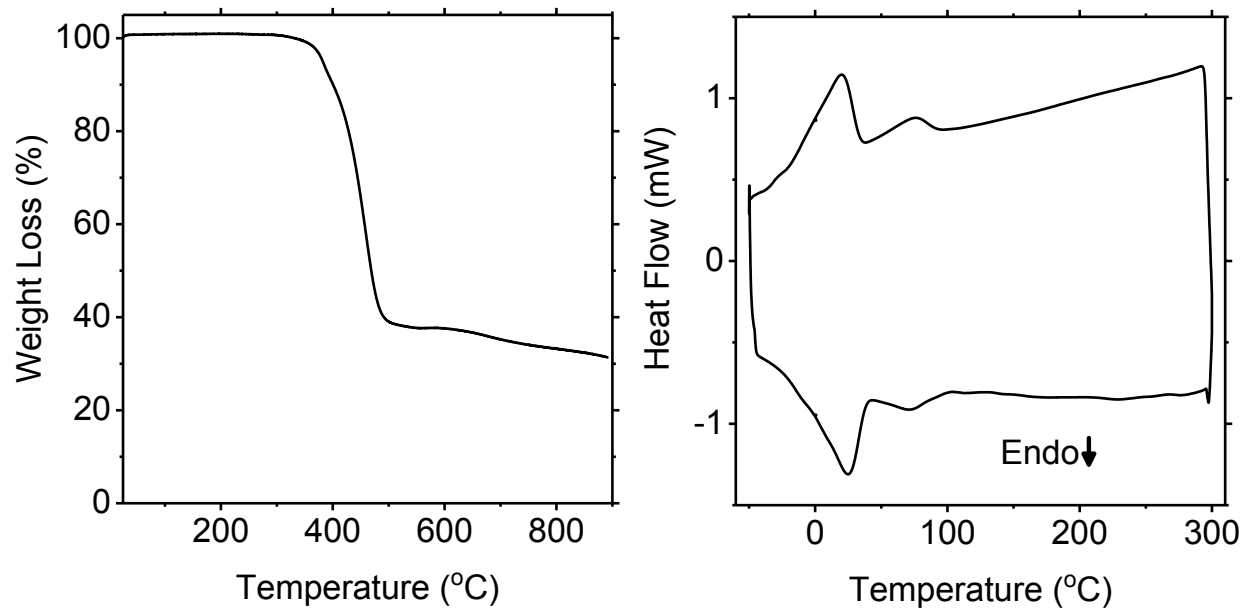


Figure S2. TGA (left) and DSC (right) of Cl-BDPPV.

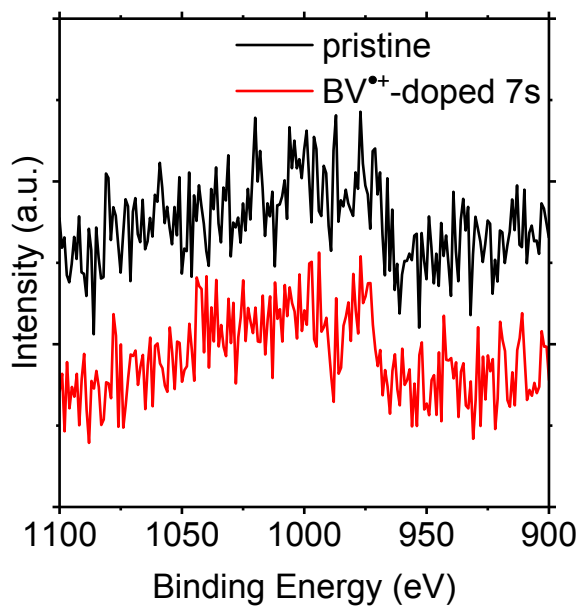


Figure S3. XPS binding energy spectra in the region on 1100-900 eV. No significant zinc species were observed in the doped sample.

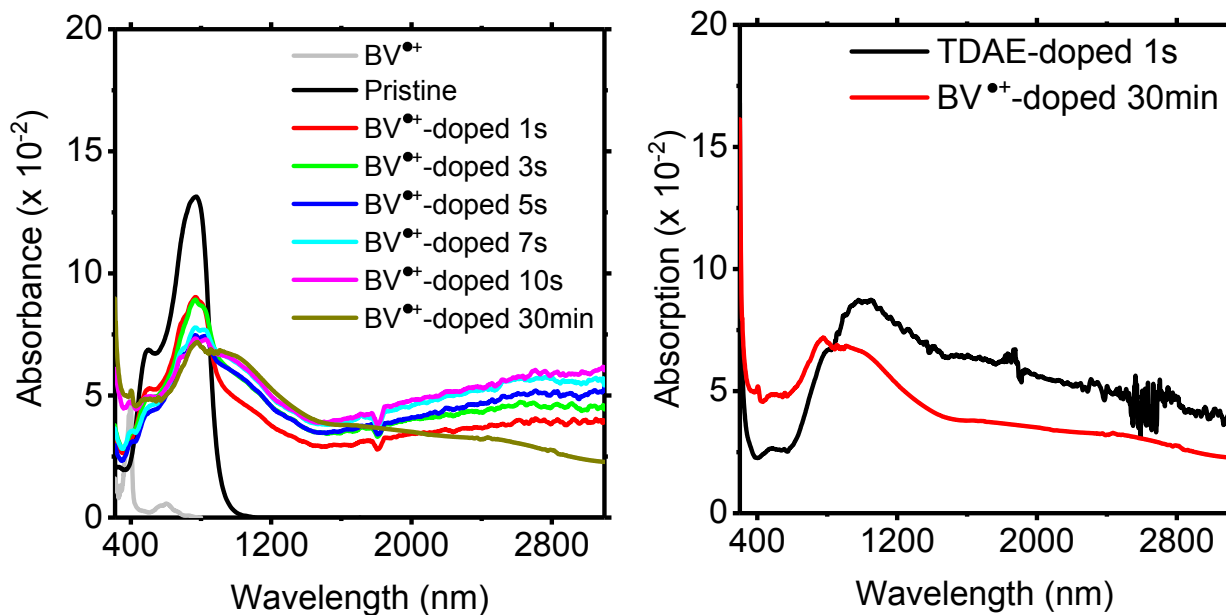


Figure S4. A comparison between the UV-Vis-NIR absorption spectra of BV<sup>•+</sup>, pristine and BV<sup>•+</sup>-doped CI-BDPPV (left) and TDAE-doped 1s and BV<sup>•+</sup>-doped 30min (right) to illustrate the over-doping of CI-BDPPV using BV<sup>•+</sup> with immersion time of 30 min.

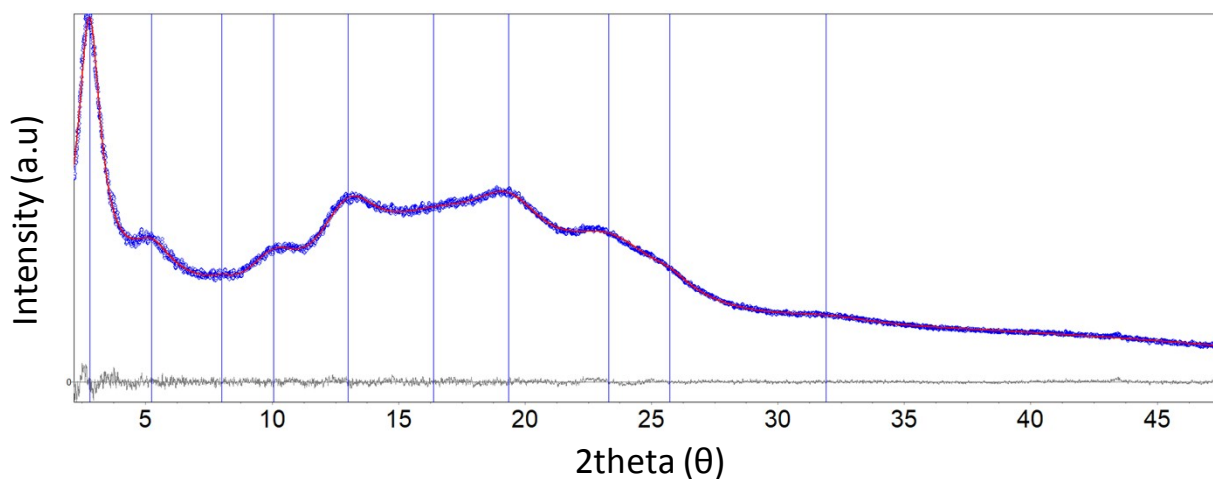


Figure S5. Fitted XRD measurement for pristine dropcast film. Blue circles – experimental data points. Red line – Fitted line.

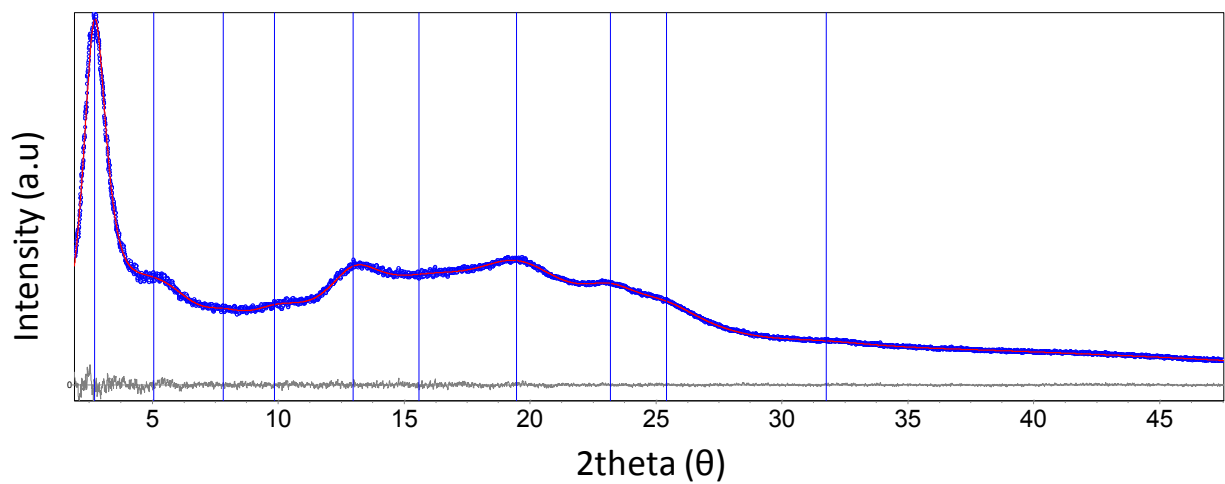


Figure S6. Fitted XRD measurement for doped (7s immersion) dropcast film. Blue circles – experimental data points. Red line – Fitted line.

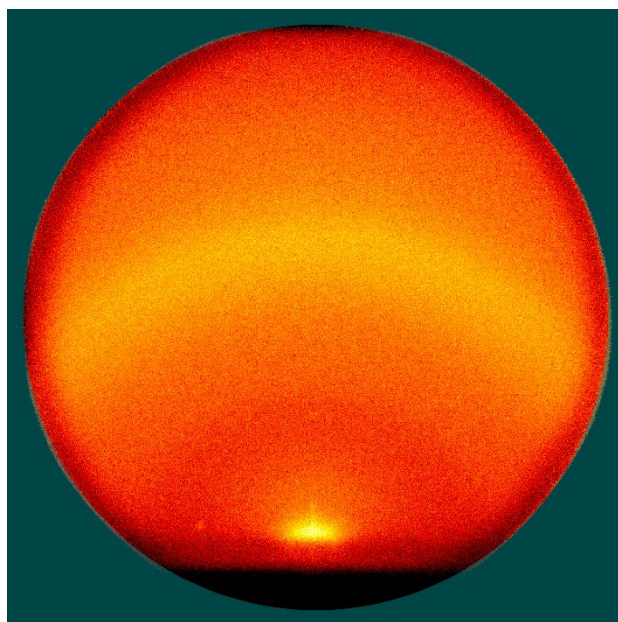


Figure S7. XRD pattern of TDAE-doped CI-BDPPV (7 s).

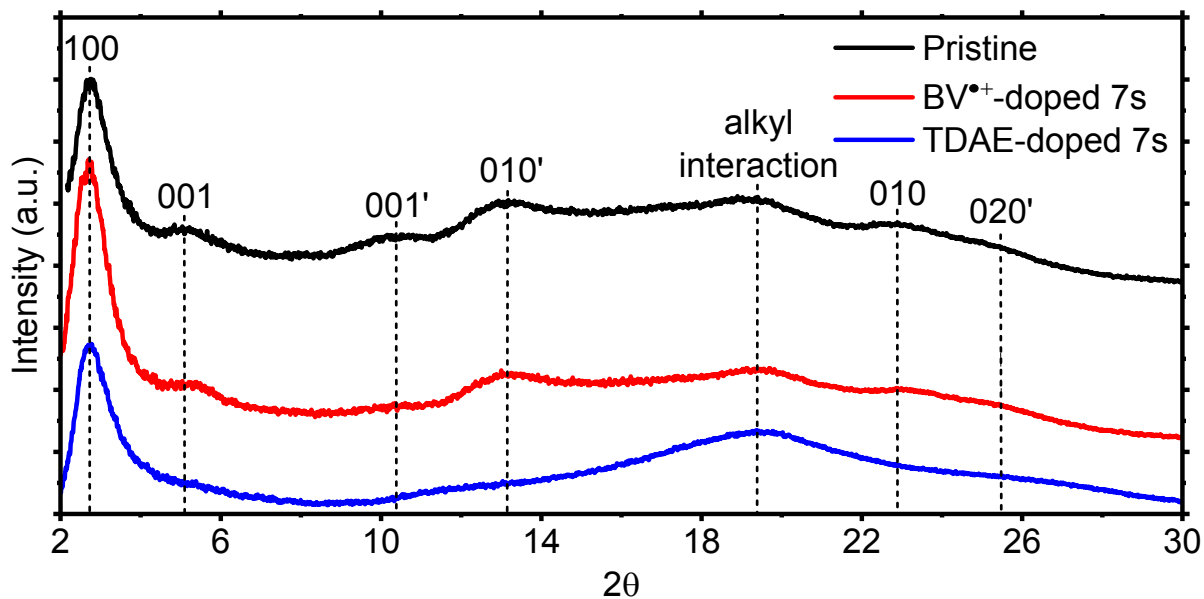


Figure S8. Out-of-plane linecuts for pristine, BV<sup>•+</sup>-doped (7 s) and TDAE-doped (7 s) CI-BDPPV dropcast films.

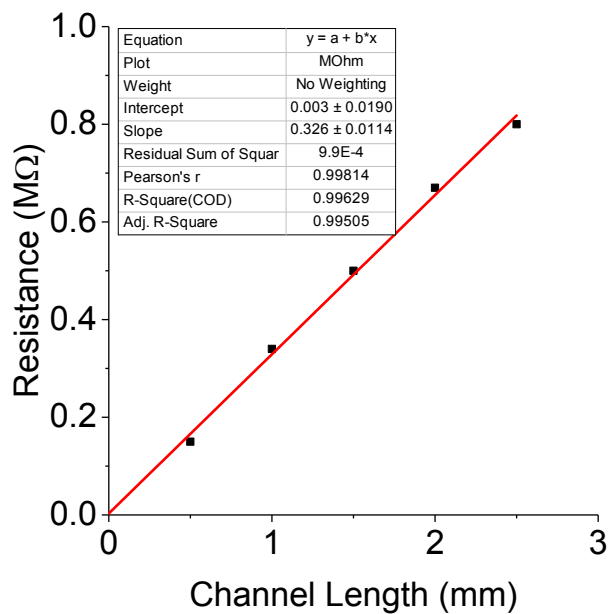


Figure S9. Contact resistance of BV<sup>•+</sup>-doped CI-BDPPV determined using transmission line method.

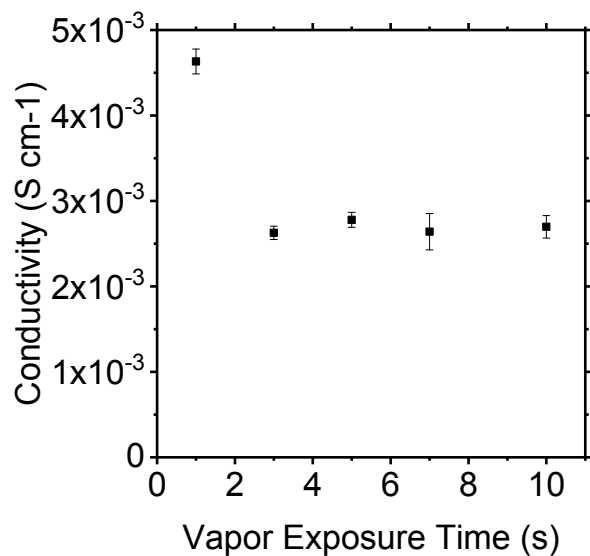


Figure S10. Conductivities of TDAE-doped CI-BDPPV films at different vapor exposure times.

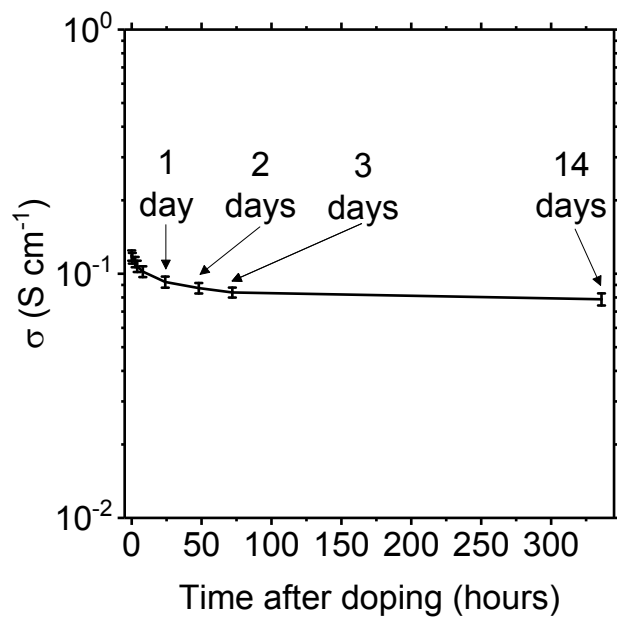


Figure S11. Stability of the conductivity of BV<sup>•+</sup>-doped CI-BDPPV films (immersion time 7 s).



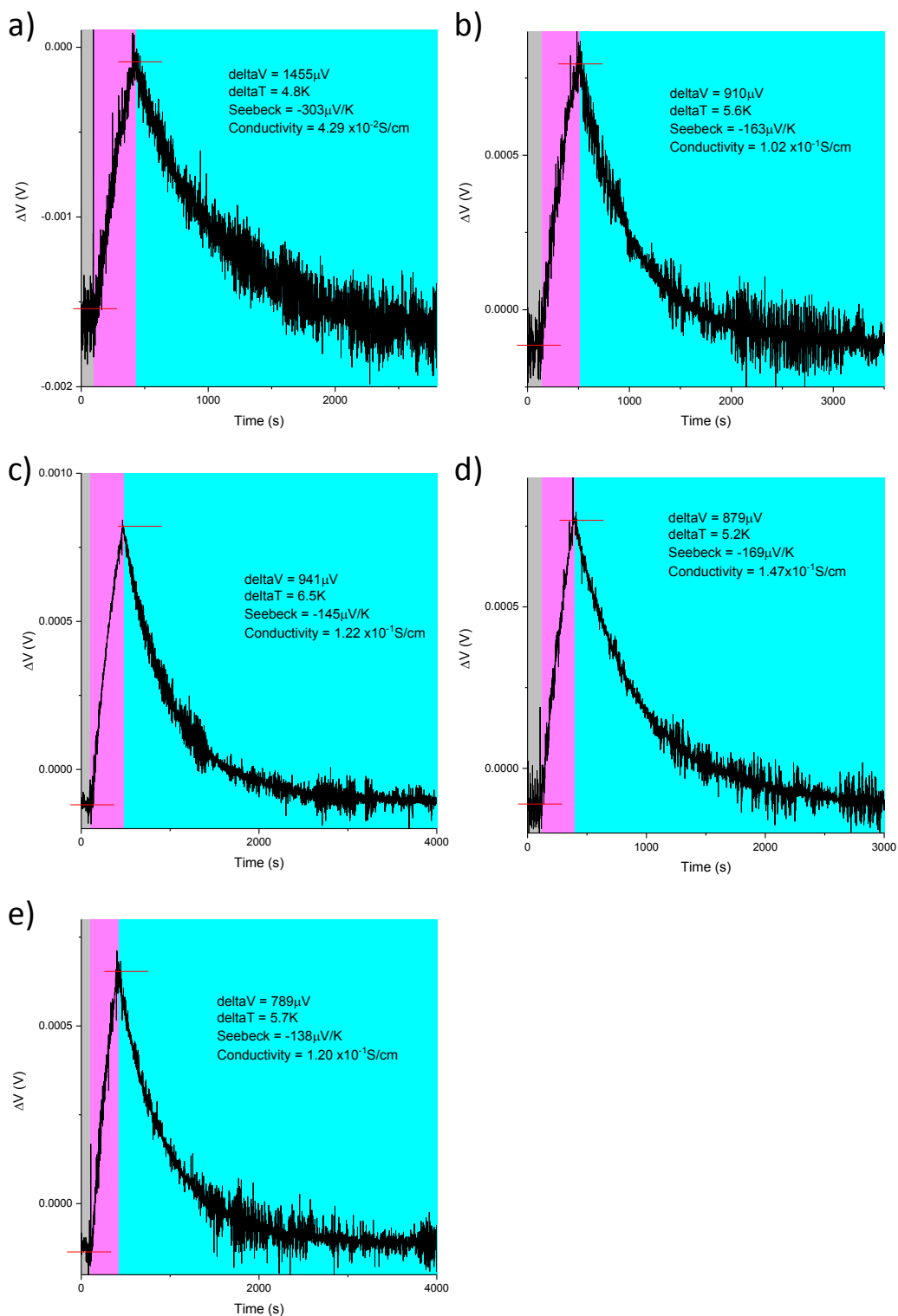
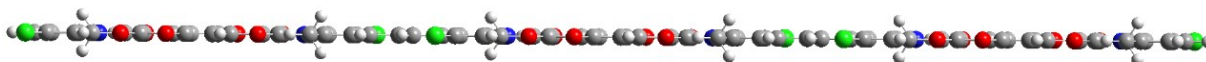
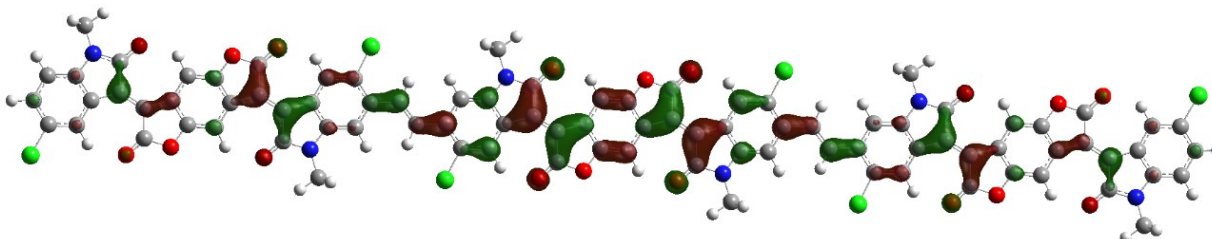


Figure S12. Representative Seebeck coefficient measurements of BV<sup>•+</sup>-doped Cl-BDPPV films for each immersion time. a) 1s, b) 3s, c) 5s, d) 7s, e) 10s. Grey box: no heating. Pink box: heating. Blue box: natural cooling.

a)



b)



c)

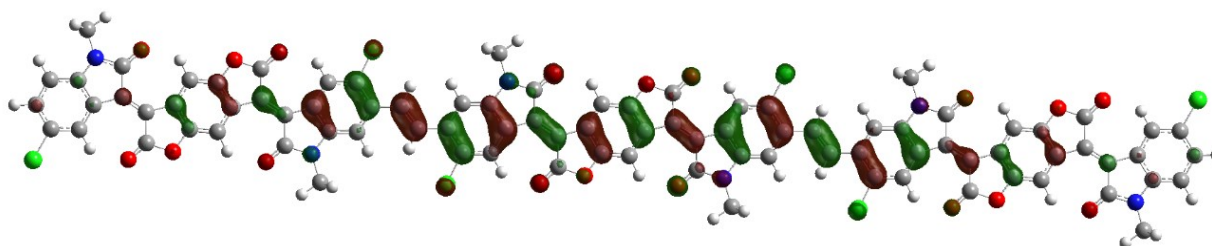


Figure S13. DFT optimized geometry of a trimer of CI-BDPPV. a) Side-view, b) LUMO and d) HOMO.

#### References:

1. S. Wang, H. Sun, U. Ail, M. Vagin, P. O. Å. Persson, J. W. Andreasen, W. Thiel, M. Berggren, X. Crispin, D. Fazzi and S. Fabiano, *Adv. Mater.*, 2016, **28**, 10764-10771.