

Supporting Information

## High-Performance & Thermally Stable n-Type Polymer Thermoelectrics Based on Benzyl Viologen Radical Cation-Doped Ladder-Type Conjugated Polymer

Teck Lip Dexter Tam,<sup>\*1</sup> Ming Lin,<sup>1</sup> Albertus Denny Handoko,<sup>1</sup> Ting Ting Lin,<sup>1</sup> 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.

### General Information

All commercially available reagents were purchased from Sigma-Aldrich Chemical Co. Naphthalene-1,4,5,8-tetracarboxylic Dianhydride (97.0 %) was purchased from Tokyo Chemical Industry Co. while tetraaminobenzene tetrahydrobromide (> 96 %) was purchased from Hangzhou Trylead Chemical Technology. UV-Vis-NIR absorption spectra were recorded on a Shimadzu UV-3101PC UV-VIS-NIR Spectrophotometer. Fourier-transform infrared (ATR FT-IR) spectra were obtained via a FT-IR (FT/IR-6000, JASCO). 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). Thermal analysis of the polymer was carried out using TA Q600/2960 from TA Instruments for TGA and DSC 3 from Mettler Toledo for DSC. XPS spectra were measured using VG Thermo Escalab 220i-XL X-ray photoelectron spectroscopy system. XPS data is analyzed using Thermo Avantage v4.12.

### BBL film deposition

BBL was dissolved in methanesulfonic acid at a concentration of 5 mg/mL at 100 °C and spin coated at a 1000 rpm for 1 min. The spin coated films were immersed in DI water, followed by annealing at 100 °C on a hotplate to remove the residual water. The BBL thin films were brought into a N<sub>2</sub> glovebox (O<sub>2</sub> and H<sub>2</sub>O < 1 ppm) and further annealed at 200 °C for 1 hour. The annealed films were then allowed to cool down to room temperature. The thickness of the films is about 50 nm.

### Doping of BBL film with BV<sup>•+</sup>

The BBL thin films were immersed in 5 mM BV<sup>•+</sup> solution in anhydrous acetonitrile for various times in the glovebox (O<sub>2</sub> and H<sub>2</sub>O < 1 ppm), annealed at 100 °C for 30 mins and allowed to cool down to room temperature before any measurements were taken. All electrical measurements were measured in the glovebox.

### Electrical Conductivity Measurements for Thermoelectric Devices

The preparation of the BV<sup>•+</sup>-doped BBL film is the same as above except that the BBL 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. 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).

### Electrochemical Impedance Spectroscopy Measurements

The preparation of the BV<sup>•+</sup>-doped BBL film was the same as above except that the length and width of the electrodes were 2.0 cm by 0.2 cm, and the channel length between the electrodes was 2 mm. Two-probe lateral impedance spectroscopy measurements were conducted using Autolab potentiostat (model PGSTAT30) by Echochimie at a frequency range of 10<sup>5</sup> Hz to 10<sup>2</sup> Hz and at 20 mV RMS. The data was fitted using ZView 2.

### 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.

### Preparation of TEM samples

5 mg/mL BBL dissolved in methanesulfonic acid was spin coated onto pre-cleaned Si wafer. The Si wafer was immersed into DI water and the BBL films was exfoliated from the Si wafer substrate. TEM copper grid coated with lacey carbon membrane was used to scoop the floating BBL film. The BBL films on TEM copper grids were annealed at 100 °C on a hotplate to remove the residual water. The BBL films on TEM copper grids were brought into a N<sub>2</sub> glovebox (O<sub>2</sub> and H<sub>2</sub>O < 1 ppm) and further annealed at 200 °C for 1 hour. The annealed films were then allowed to cool down to room temperature. The TEM study of the as-

obtained films on copper grid was conducted on an FEI Titan 80/300 (S)TEM with an acceleration voltage at 200 KV. The film is stable under electron beams without any visible degradation of crystalline structures.

#### DFT Calculation

All geometries were optimized at a DFT CAM-B3LYP 6-31G\*\* level of theory in the gas phase using NWChem version 6.8.<sup>1</sup> Unrestricted formalism was used for odd-electron negatively charge system. Broken-symmetry approach was used for all unrestricted calculations.

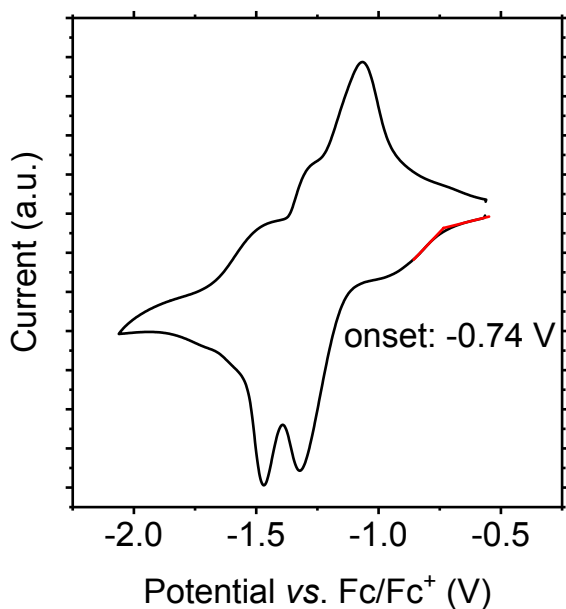


Figure S1. Cyclic voltammogram of pristine BBL film in 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile.

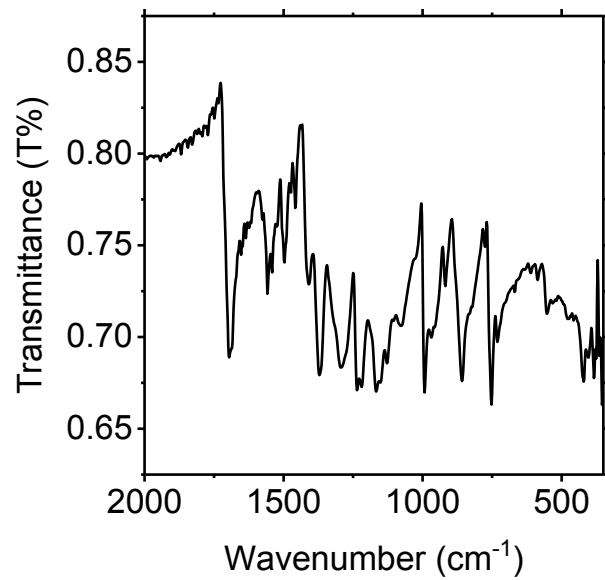


Figure S2. FTIR spectrum of pristine BBL polymer.

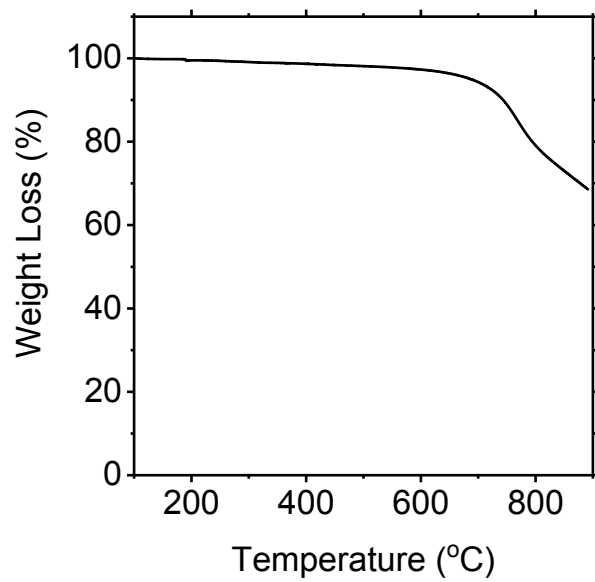


Figure S3. TGA of pristine BBL polymer under N<sub>2</sub>.

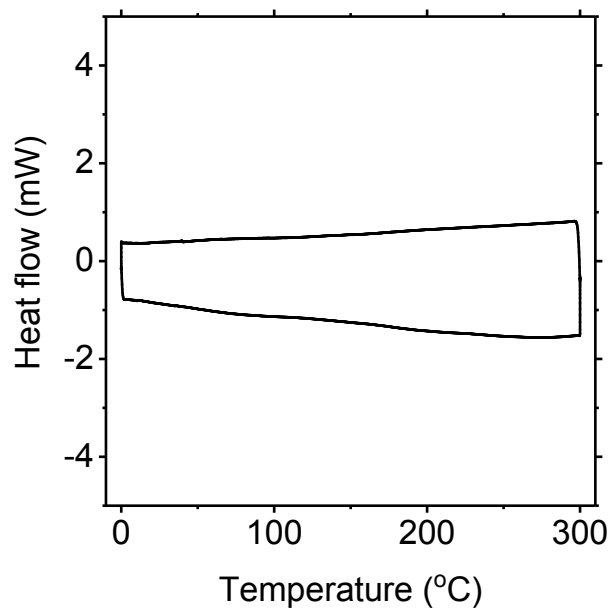


Figure S4. DSC thermograms of pristine BBL polymer under  $N_2$ .

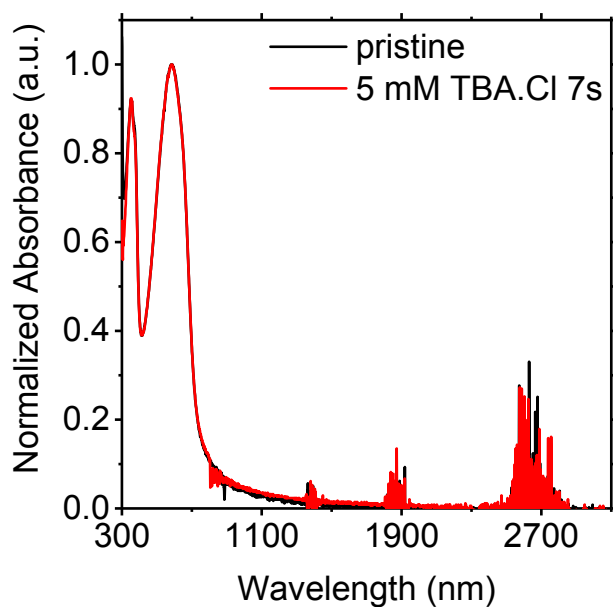


Figure S5. UV-Vis-NIR of pristine BBL film and BBL film immersed in 5 mM tetrabutylammonium chloride solution in anhydrous acetonitrile for 7 s. The absence of observable change in the UV-Vis-NIR spectra suggests that the  $n$ -doping of BBL films is a result of electron transfer from  $BV^{*+}$  to BBL and not due to anion- $\pi$  interaction between  $Cl^-$  and BBL.

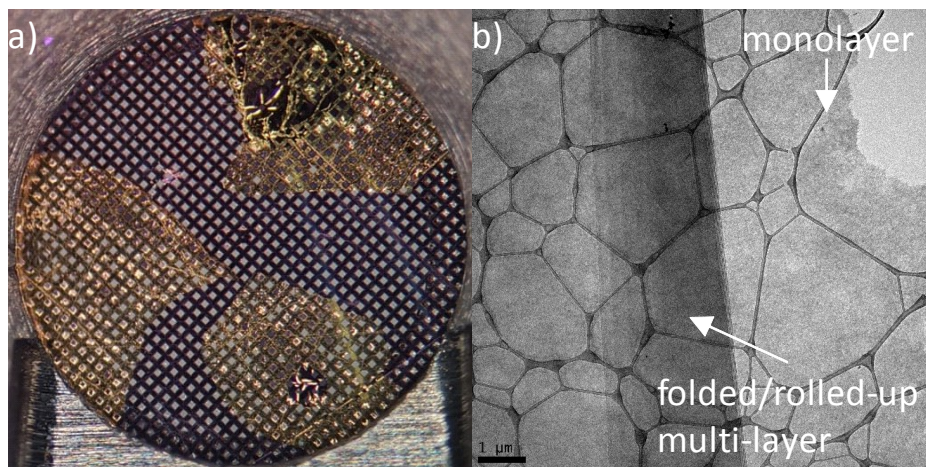


Figure S6. a) Photo of exfoliated BBL films on TEM copper grid and b) Bright-field TEM image of pristine BBL film on the lacey carbon films on copper TEM grid.

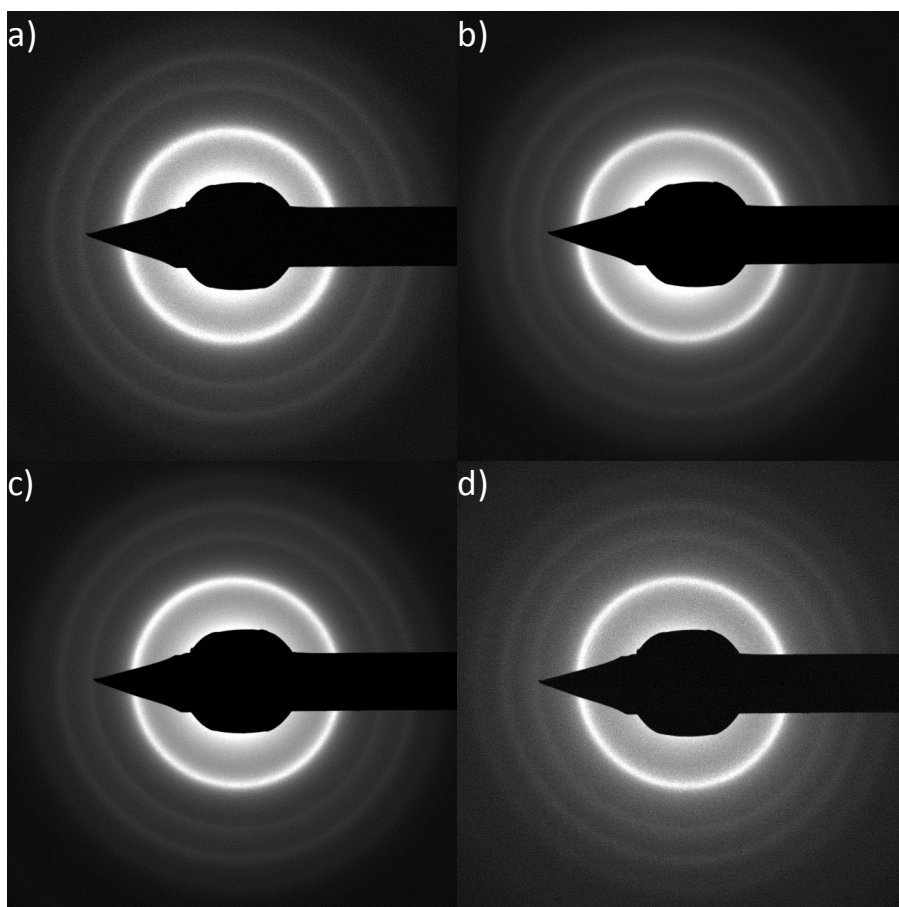


Figure S7. SAED of a) pristine, b) 1s-doped, c) 5s-doped and d) 10s-doped BBL films. The diameter of selected diffraction aperture is  $\sim 550$  nm. Only the crystal planes parallel to the electron beam can give diffraction spots in the patterns.

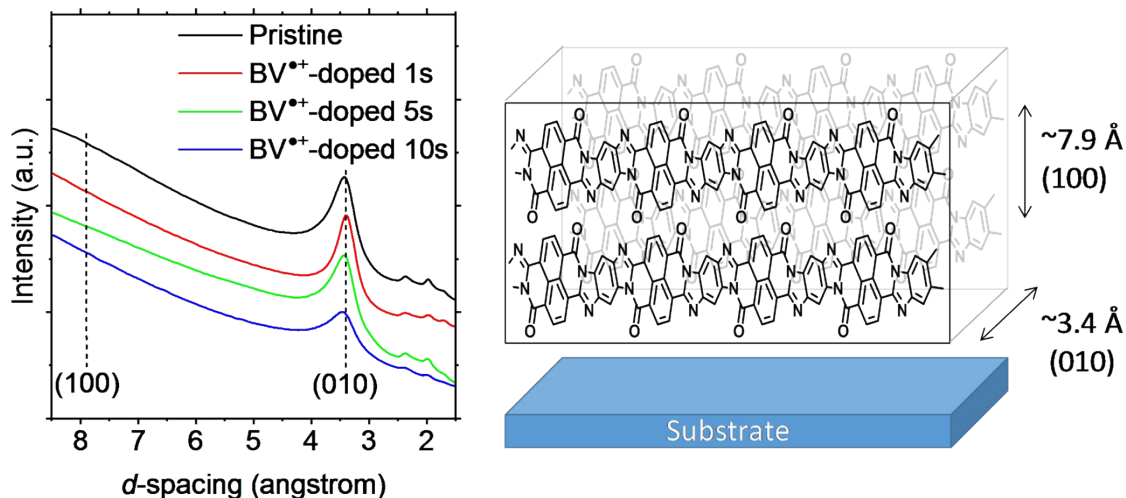


Figure S8. (Left) Line-cuts of the SAED showing the lattice spacing measured in the patterns. The strongest peak measured is around 3.4 Å, corresponding to  $\pi$ - $\pi$  stacking (010) peak. The lamellar stacking (100) peak at around 7.9 Å is missing, indicating (010) planes are mostly oriented normal to the film. This indicates a highly preferred edge-on orientation of BBL. (Right) Schematic showing the  $\pi$ - $\pi$  stacking (010) and lamellar stacking (100) directions.

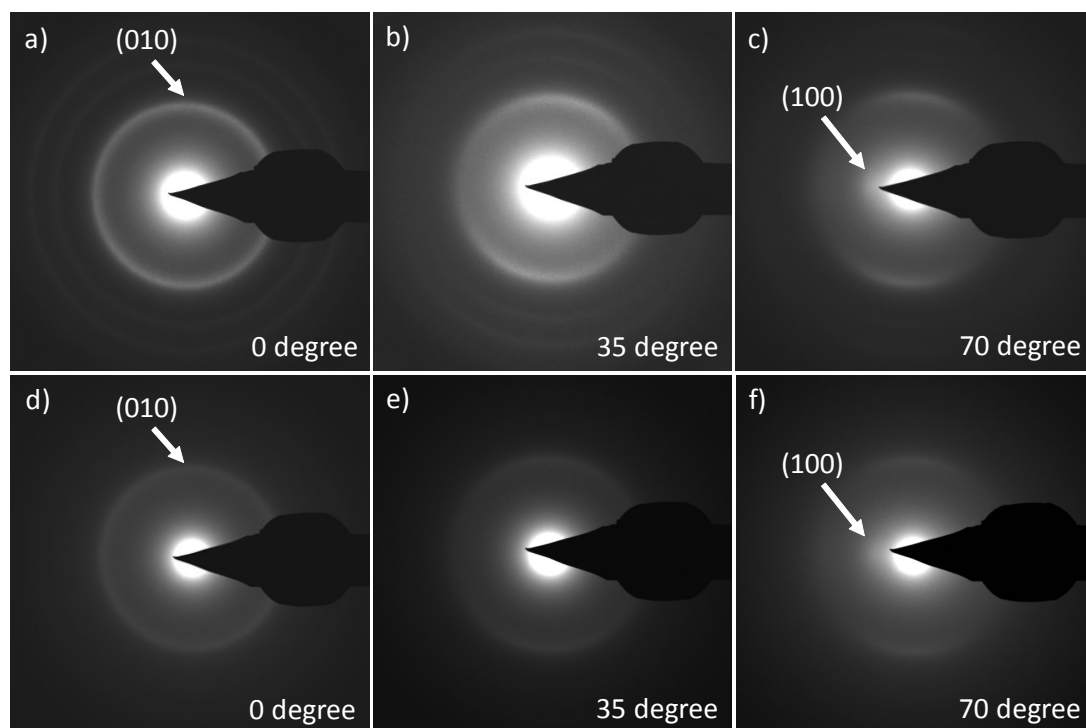


Figure S9. Figure S9. SAED of pristine (a, b, and c) and 10 s BV<sup>•+</sup>-doped BBL films (d, e and f) at various tilting angle. The films were tilted to 35 and 70 ° to illustrate the highly preferential edge-on orientation of the BBL. The absence of any new diffraction features in films after 10 s BV<sup>•+</sup>-doping suggests the BV<sup>•+</sup> molecules deposited into the nanopores of the fibrous BBL films are amorphous in nature.

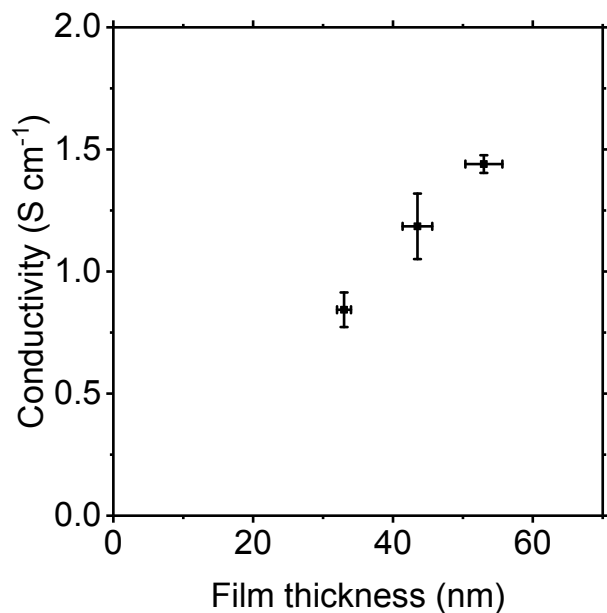


Figure S10. Plot of conductivity versus film thickness. The thicknesses of the films were varied by changing the spincoating speed (1000, 2000 and 3000 rpm) using a 5 mg/mL BBL solution.

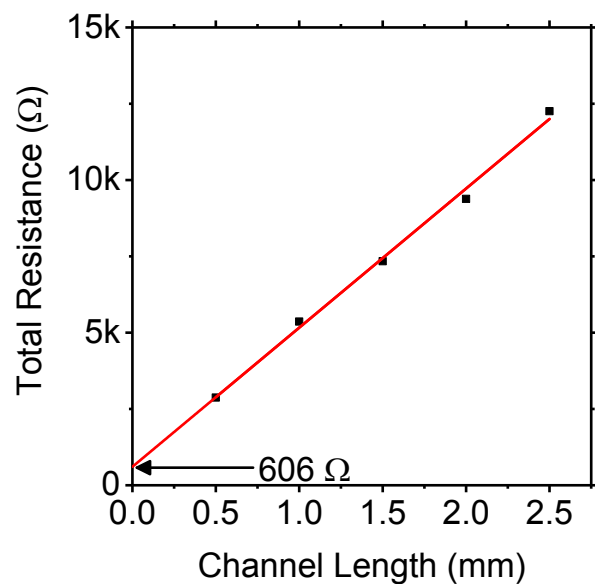


Figure S11. Contact resistance of BV<sup>•+</sup>-doped BBL thin film device (7 s immersion) determined using the transmission line method.



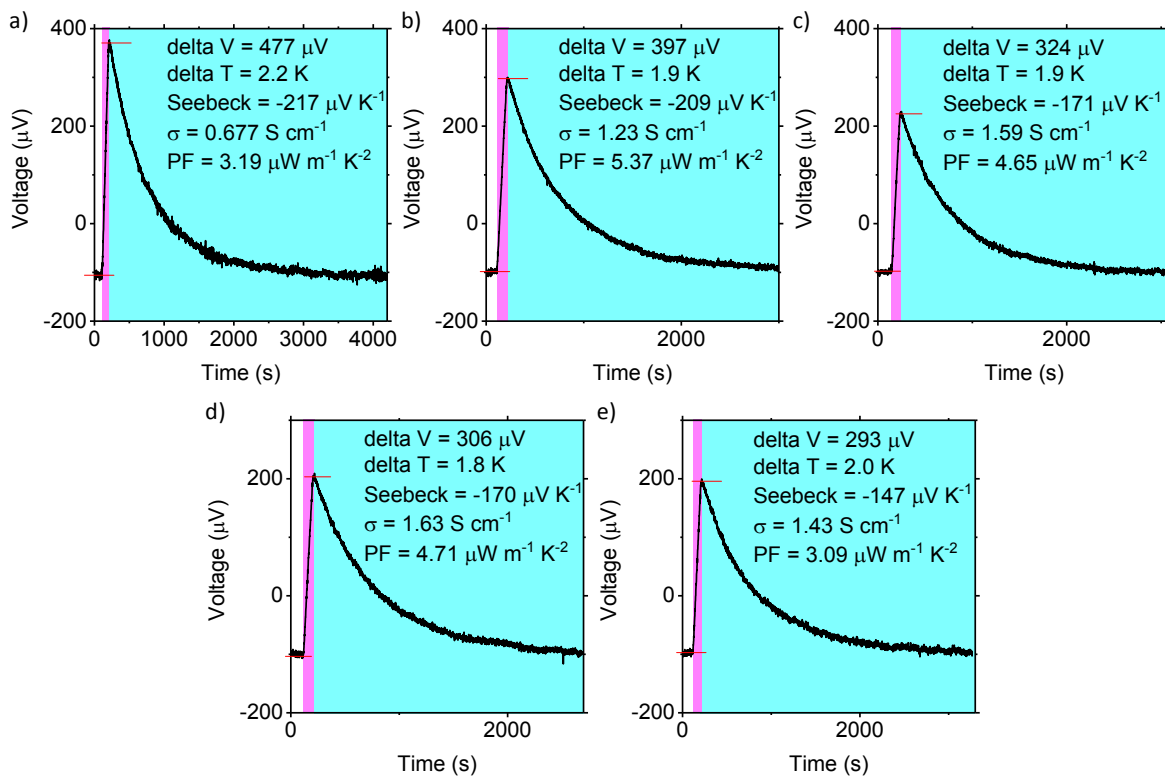


Figure S12. Representative thermovoltage measurements against time. a) 1s, b) 3s, c) 5s, d) 7s and e) 10s immersion in  $\text{BV}^{\bullet+}$  solution. All samples were held at RT for about 100 s before heating. White region: holding at RT. Pink region: heating. Blue region: natural cooling.

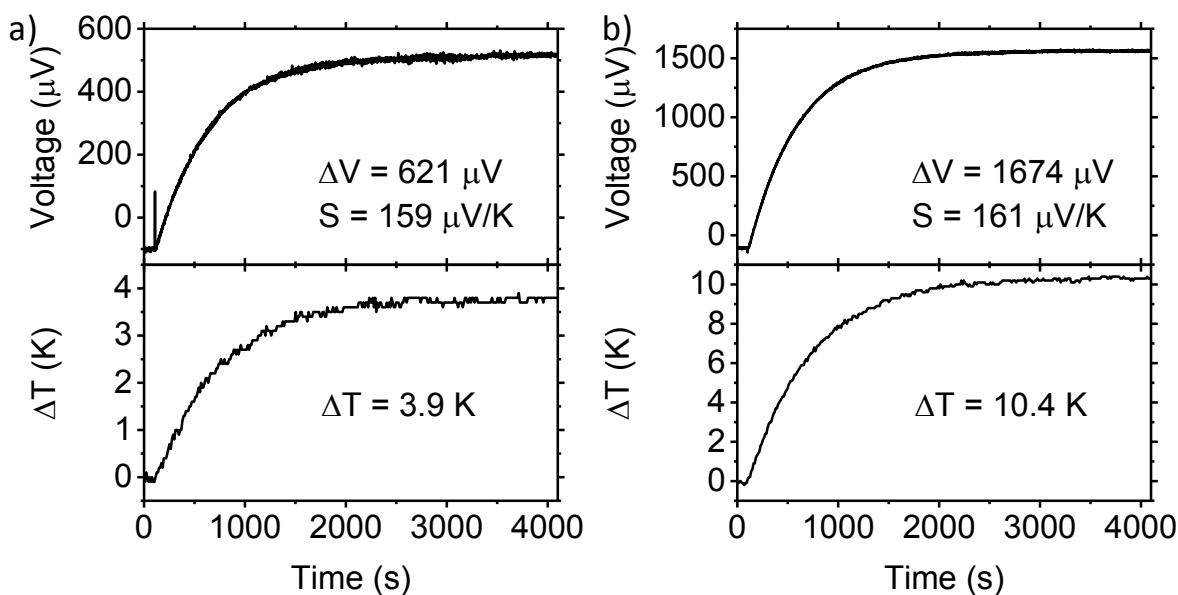


Figure S13. Thermovoltage measurements of a  $\text{BV}^{\bullet+}$ -doped BBL thin film device (10 s immersion time) with stabilized temperature difference of approximately a) 4 K and b) 10 K.

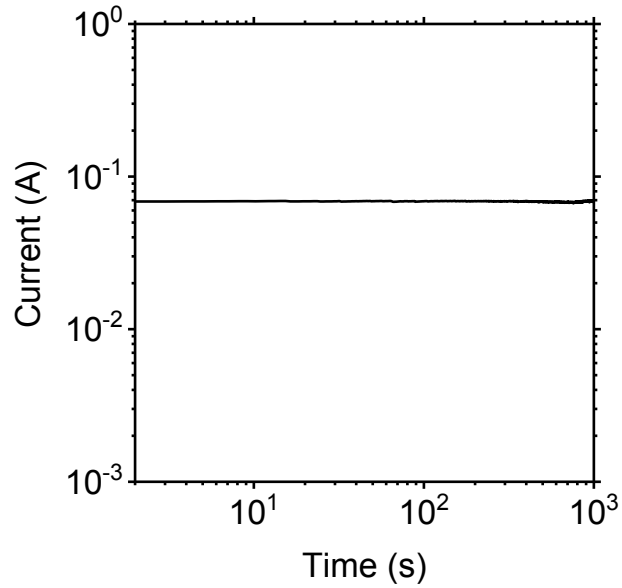


Figure S14. Measured current versus time at constant bias (0.1 V).

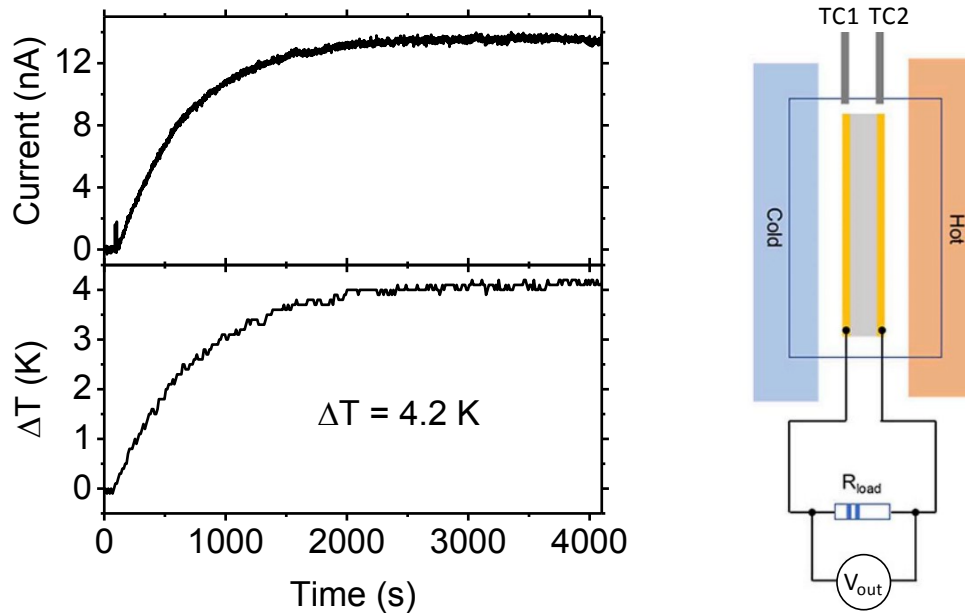


Figure S15. (Left) Current measurement of a  $BV^{*+}$ -doped BBL thin film device (10 s immersion time) with stabilized temperature difference of approximately 4 K. (Right) Schematic for the measurement. The resistance of the device is 25 kOhm, and is connected in parallel with an external load (25 kOhm resistor).

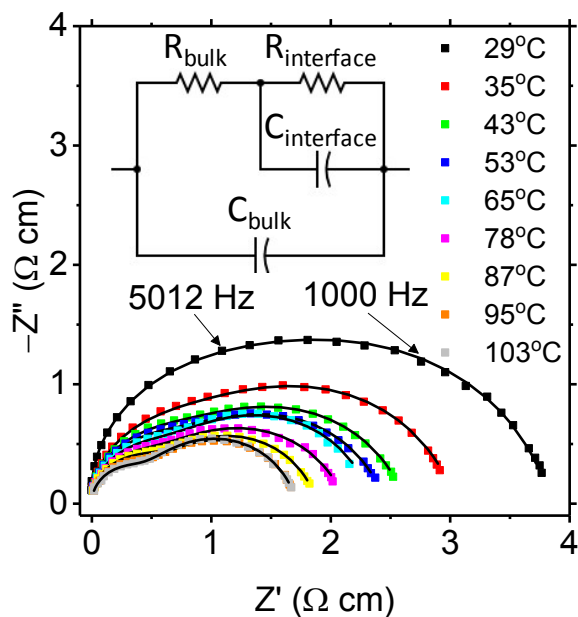


Figure S16. Temperature-dependent impedance measurement of BV<sup>•+</sup>-doped BBL thin film device (1 s immersion). Inset: Equivalent circuit used for fitting.

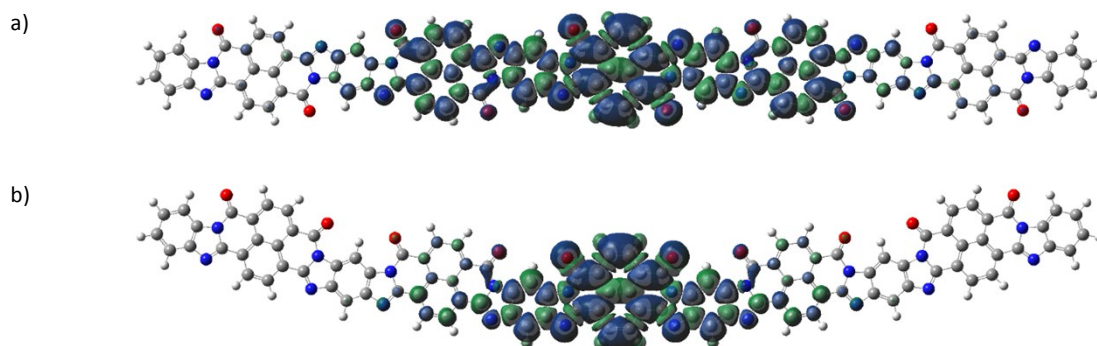


Figure S17. Spin density (isovalue 0.00005) for a negatively charged five repeating units of a) trans- and b) cis-BBL.

#### References:

1. M. Valiev, E.J. Bylaska, N. Govind, K. Kowalski, T.P. Straatsma, H.J.J. van Dam, D. Wang, J. Nieplocha, E. Apra, T.L. Windus, W.A. de Jong, *Comput. Phys. Commun.* 2010, 181, 1477.