Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

P- and N-Dopable Ambipolar Bulk Heterojunction Thermoelectrics Based on Ladder-Type Conjugated Polymers

Qiang He,[†,1,3] Teck Lip Dexter Tam, [†,*,2] Xue Qi Koh,[3] Nguk Neng Tham,[3] Hong Meng,[*,4,5] Wei Huang,[*,1] Jianwei Xu[*,2,3,6]

[1] Frontiers Science Center for Flexible Electronics (FSCFE), Institute of Flexible Electronics (IFE), Northwestern Polytechnical University (NPU), 127 West Youyi Road, Xian 710072, P. R. China.

[2] Institute of Sustainability for Chemical, Engineering and Environment (ISCE[2]), Agency of Science, Technology and Research (A*STAR), 1 Pesek Road, Singapore 627833, Singapore.

[3] Institute of Materials Research and Engineering (IMRE), Agency of Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Innovis, Singapore 138634, Singapore.

[4] School of Electronics and Information, Northwestern Polytechnical University, 127 West Youyi Road, Xi'an, 710072 P. R. China.

[5] School of Advanced Materials, Peking University Shenzhen Graduate School, 2199 Lishui Road, Shenzhen, 518055 P. R. China.

[6] 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. PBBTL and BBL were synthesized according to previous reports.[1, 2] $BV^{\bullet+}$ dopant solution were prepared according to previous report.[1] 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). The AFM-IR imaging and spectra were measured using a NanoIR2 system (Bruker Anasys Instruments) in contact mode, with a gold coated PR-EX-TNIR-A tip, spring constant of 0.07-0.4 N/m and resonant frequency of 9-17 kHz. IR spectra were collected from 900-2000cm^{-1} at an interval of 4cm^{-1} and co-averaging of 128 scans. 5x5um AFM-IR images were scanned at 1700cm^{-1} with 150x150pixels and co-averaging of 16 scans. The molecular packing of was studied by grazing incidence wide angle X-ray diffraction (GIWAXS; Nanoinxider Xenocs).

Preparation of PBBTL:BBL blend films:

Cleaned 1" by 1" microscopic glass was immersed in 30-33 % NH_3 in water for 2 hrs. The glass substrates were immersed in DI water (30 mins) followed by IPA (30 mins). The glass substrates were blow-dried using a N_2 gun and UV/O_3 treated at 100 °C for 10 mins. PBBTL and BBL were separately dissolved in methanesulfonic acid (MSA) at a concentration of 10 mg/mL at 80 °C. The two solutions were mixed at the desired ratio and stirred at 80 °C. The blend solution was spincoated on the glass

substrate at 1000 rpm for 30 s and the wet films were immersed in IPA for about 10 mins before annealing in open-air at 100 °C. The dried films were moved into the glovebox (O_2 and H_2O < 0.1 ppm) and annealed at 200 °C for 1 hr. The thickness of the films obtained this way is in the range of 100-120 nm.

Thermoelectric Device Fabrication:

On the blend films, 100 nm of gold parallel electrodes were thermally evaporated using a shadow mask. 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). P- and n-doping of the films were performed by immersing the device into 5 mM $FeCl_3$ or 5 mM $BV^{\bullet+}$ solution in anhydrous acetonitrile, respectively, for various duration, followed by thermal annealing at 80 °C for 10 mins.

Thermovoltage Measurements

The Seebeck coefficient was measured by using a custom-made setup with a Peltier heater (298 K + Δ*T*) and a Peltier cooler (298 K) which are used to vary the temperature gradient (≈ 1.5 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.

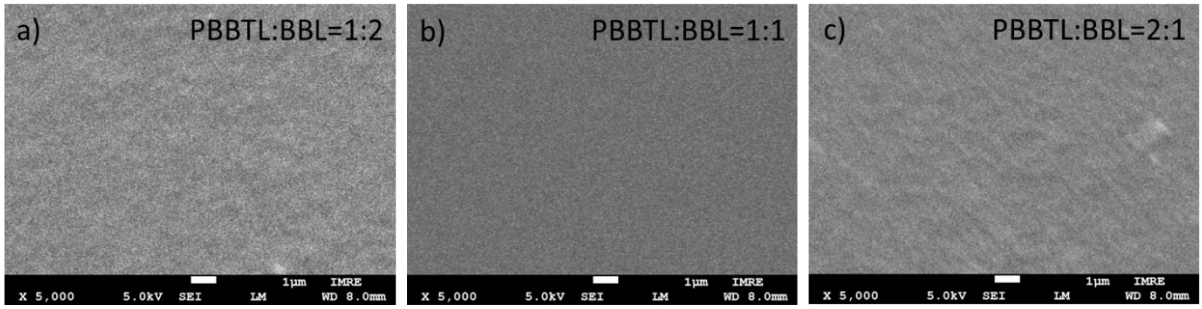

Figure S1. SEM images of the PBBTL:BBL blend films.

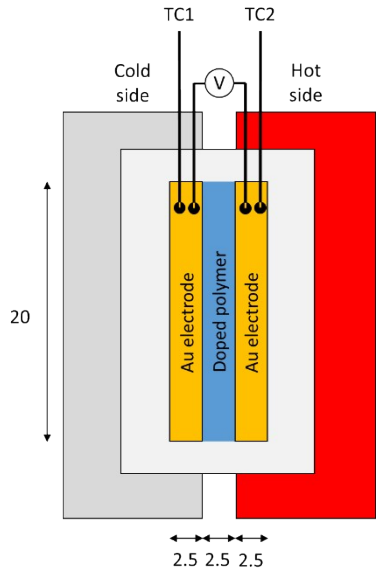

Figure S2. Schematic of the Seebeck coefficient measurement set-up. Dimensions are all in millimeters. TC denotes thermocouple. Electrical resistance of the doped films were measured using the same device setup at room temperature.

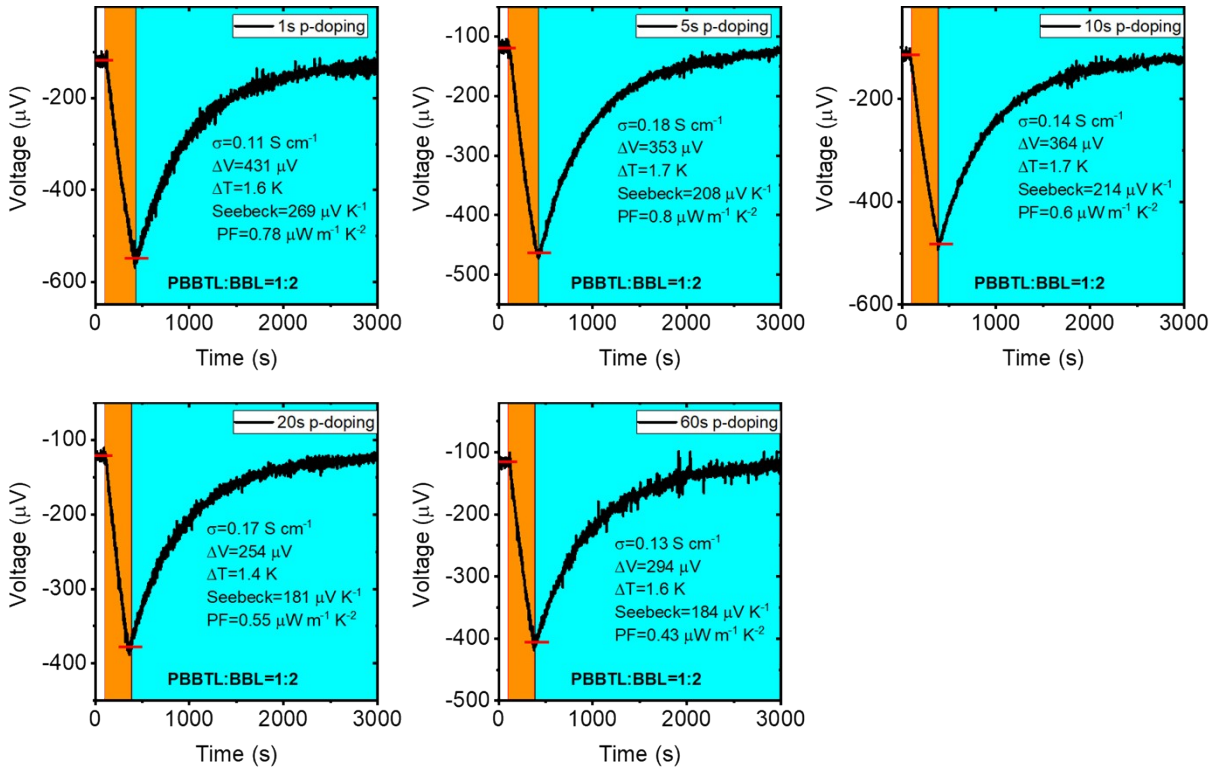

Figure S3. P-doping of PBBTL:BBL 1:2 blend films.

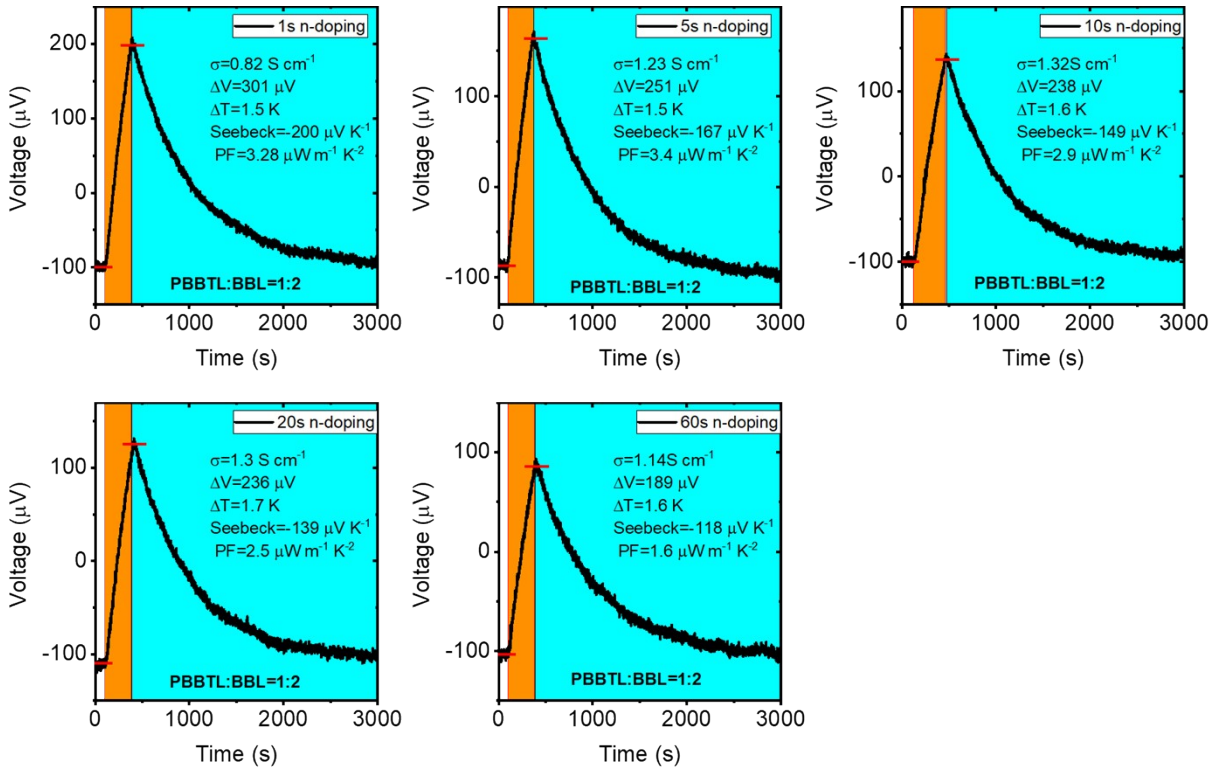

Figure S4. N-doping of PBBTL:BBL 1:2 blend films.

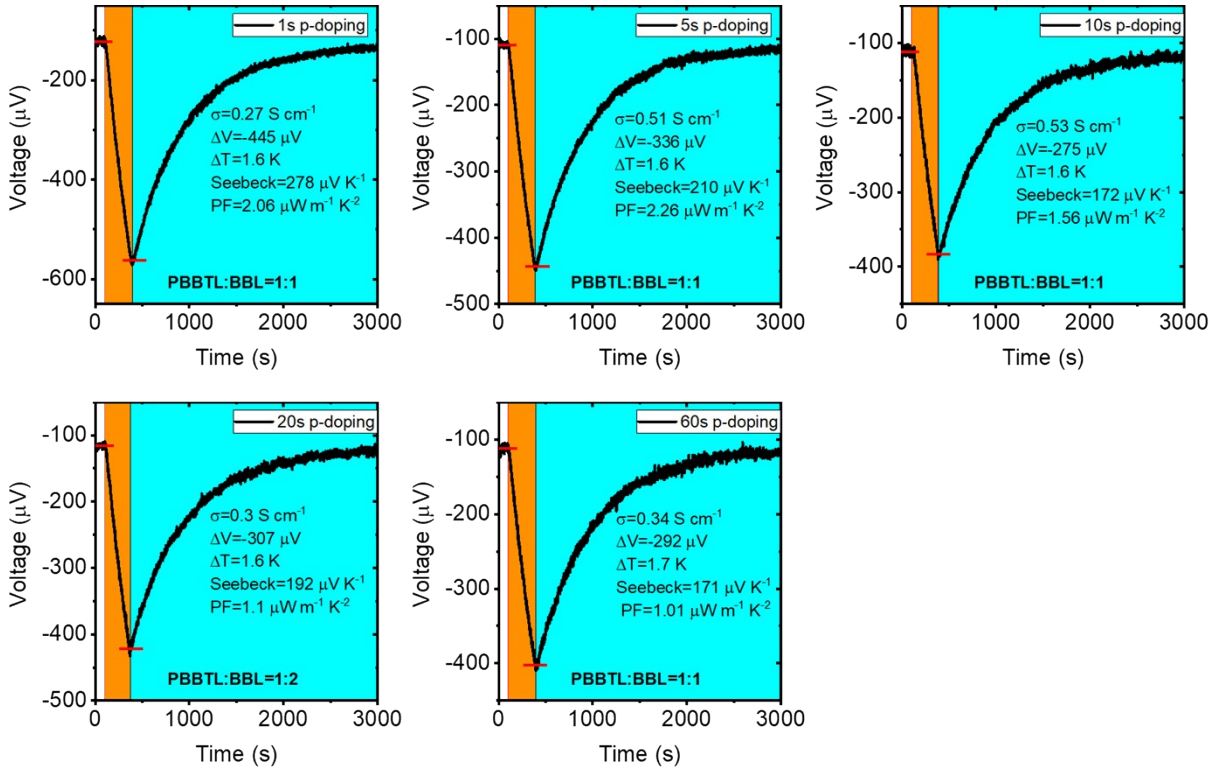

Figure S5. P-doping of PBBTL:BBL 1:1 blend films.

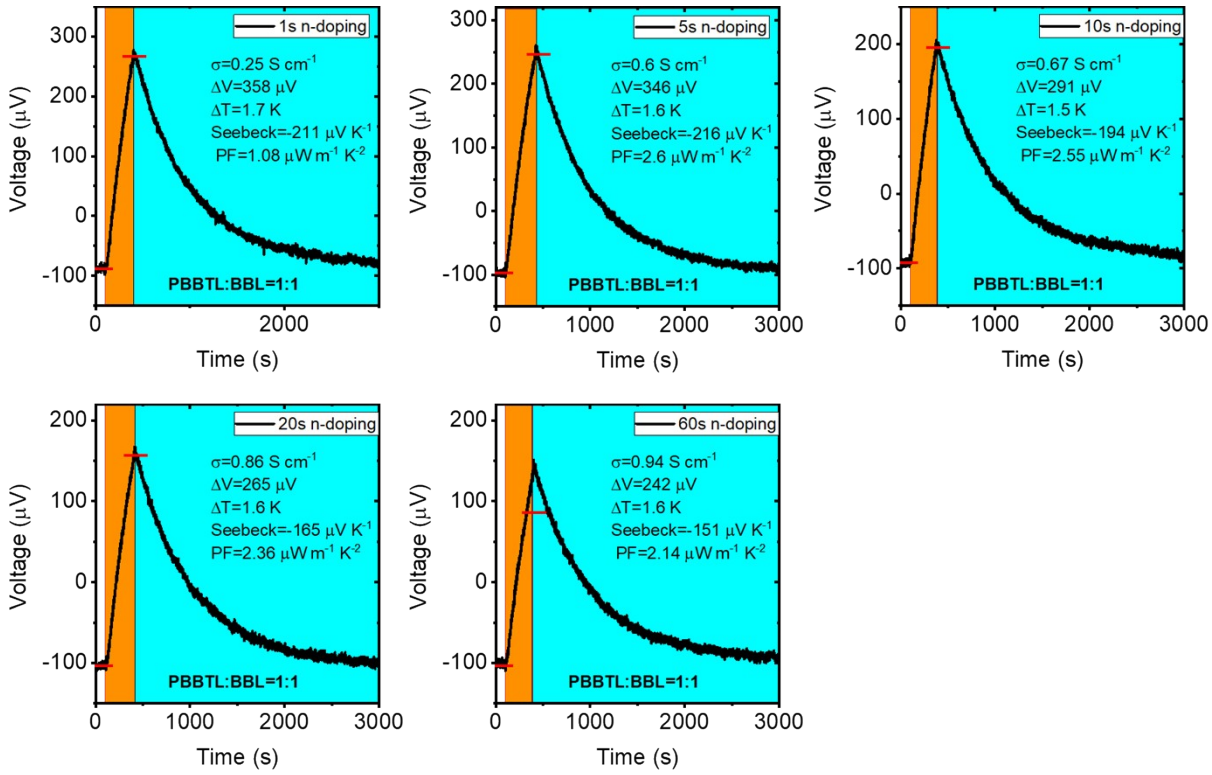

Figure S6. N-doping of PBBTL:BBL 1:1 blend films.

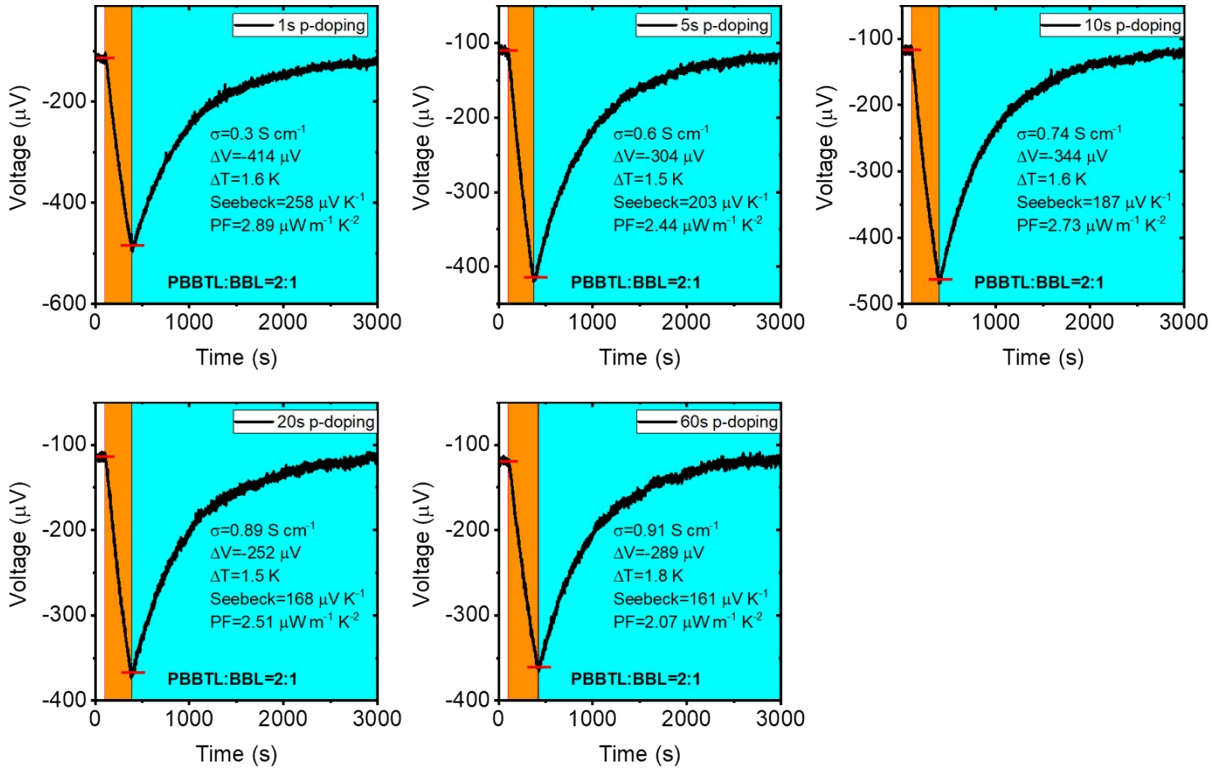

Figure S7. P-doping of PBBTL:BBL 2:1 blend films.

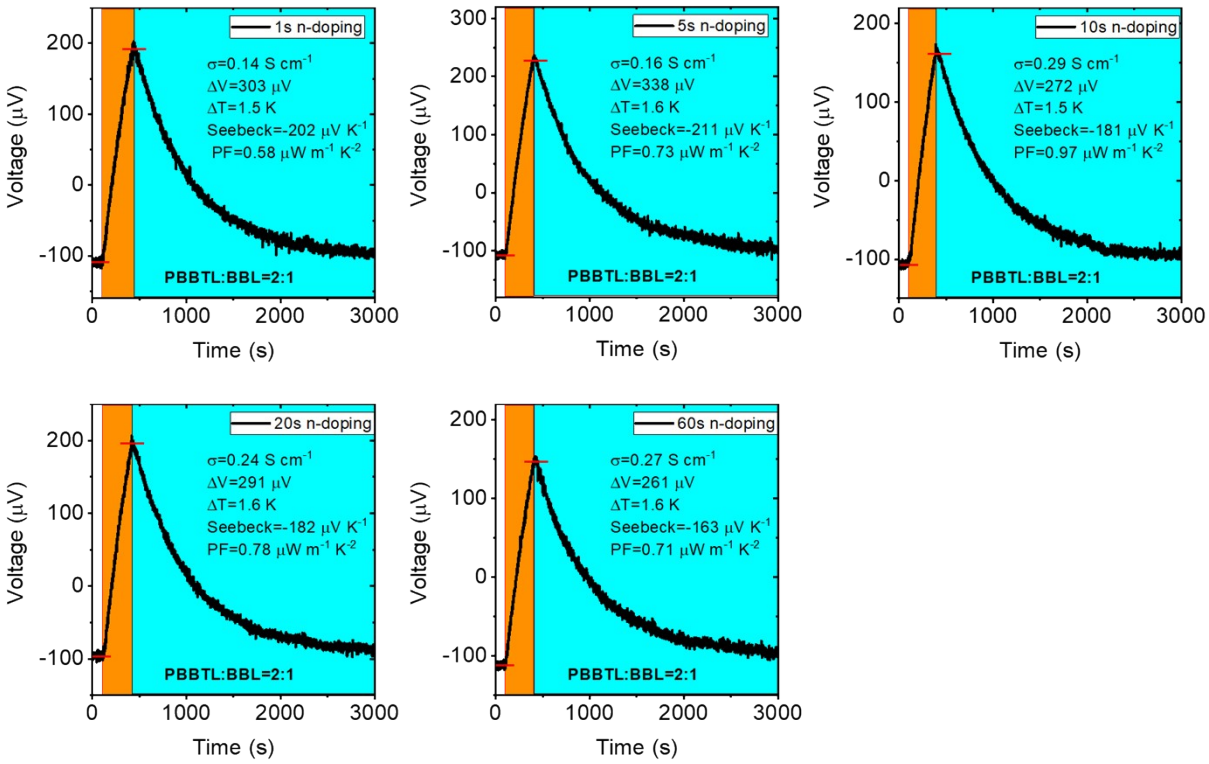

Figure S8. N-doping of PBBTL:BBL 2:1 blend films.

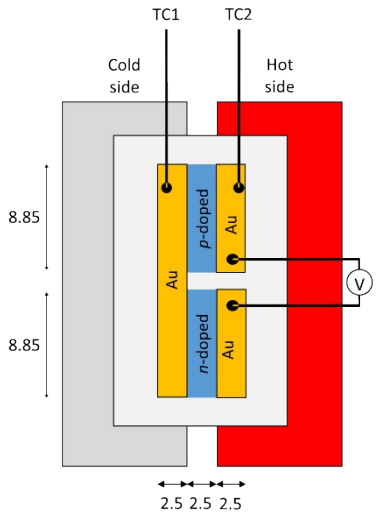

Figure S9. Schematic of the I-V curve measurement set-up for the full device. Dimensions are all in millimeters. TC denotes thermocouple.

References

(1) Tam, T. L. D.; Lin, M.; Handoko, A. D.; Lin, T. T.; Xu, J. High-Performance & Thermally Stable Polymer Thermoelectrics Based on n-Doped Ladder-Type Conjugated Polymer and Benzyl Viologen Radical Cation. *J. Mater. Chem. A* **2021**, *9*, 11787-11793.
(2) Tam, T. L. D.; Lin, M.; Chien, S. W.; Xu, J. Facile Synthesis of Solubilizing a Group-Free, Solution-Processable p-Type Ladder Conjugated Polymer and Its Thermoelectric Properties. *ACS Macro Lett.* **2022**, *11*, 110-115.