Supporting Information

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

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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*+ 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 % NH₃ 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 N₂ gun and UV/O₃ 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 (O₂ and H₂O < 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 \( \sigma = \frac{L}{R \times W \times t} \), 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 FeCl₃ or 5 mM BV** 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 + \( \Delta T \)) 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
