Supporting Information

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Doping Dependent In-Plane and Cross-Plane Thermoelectric Performance of Thin n-Type Polymer P(NDI2OD-T2) Films

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1. Doping Mechanism

According to previous work\textsuperscript{[1,2]}, N-DBPI can react with the host material via a hydride transfer. That means that upon activation of the dopant, which is in our case by stirring the dopant and dopant-polymer mixture at 80 °C temperature, a hydrogen atom is split off at the position marked in red in Figure S1. Subsequently, an unbound electron is left behind that can then be transferred to a reaction partner.

Figure S1. The reaction mechanism of N-DPBI via hydride transfer.
2. UV-Vis Measurements

In the main text, only the highest doping concentration, i.e., 40 wt%, is discussed as it shows the most remarkable changes. For the sake of completeness, the full UV-vis measurements are shown in Figure S2.

**Figure S2.** UV-Vis measurements of a) undoped P(NDI2OD-T2) and b)-e) doped P(NDI2OD-T2) with concentrations of 5 wt%, 10 wt%, 20 wt% and 40 wt%, respectively. Hereby, the top images describe changes upon air exposure with time while the bottom images depict changes at elevated temperatures. In order to distinguish both mechanisms the top images act as a reference as they were recorded in the same time steps as the temperature-dependent measurement.
3. Reciprocal Space Positions of GIWAXS Peaks of Undoped and 40 wt% -Doped P(NDI2OD-T2) on an FTO Substrate

In Table S1 the peak positions in reciprocal space obtained from the evaluation of the GIWAXS data on FTO substrates shown in Figure 4 are given for 0 and 40 wt% dopant.

Table S1. Reciprocal-space positions of the GIWAXS reflexes of pure and 40 wt%-doped P(NDI2OD-T2) extracted from vertical and horizontal sector integrals.

| Concentration (wt%) | Peak Index* | Position q(Å⁻¹) |
|---------------------|-------------|----------------|
| 0                   | (100) subpo | 0.273±0.002    |
| 0                   | (200) subpo | 0.467±0.001    |
| 0                   | (100) supo | 0.394±0.010    |
| 0                   | (200) supo | 0.515±0.052    |
| 0                   | (001) supo | 1.605±0.002    |
| 40                  | (200) supo | 0.587±0.005    |
| 40                  | (001) supo | 1.420±0.017    |
| 40                  | (100) supo | 0.298±0.002    |
| 40                  | (100) subpo| 0.309±0.001    |

* ip: in-plane, op: out-of-plane

4. GIWAXS Study on an FTO/Polymer Thin Film/Aluminum-Stack and on Glass Substrates

In addition to the GIWAXS study performed on FTO reported in Figure 3 of the main text, we performed the same measurements on an FTO bottom electrode-polymer thin film-aluminum top electrode-stack as well as on a glass substrate. The former is employed in the cross-plane geometry samples, the latter in the in-plane geometry samples. The latter has been performed in-house using a Ganesha 300XL instrument (former SAXSLAB; now Xenoxs SAS, Sassenage, France). The X-ray beam of 8.0415 keV impinged the sample in a grazing-incidence geometry at an angle of 0.2°. The sample-detector distance was 108 mm. For sufficient resolution, the measurement time amounted to 4 h. The measurements on the stack were carried out at the DESY as described in the experimental section of the main text.

The trends described in section 2, namely, the re-orientation of the lamellar stacking from in-to out-of-plane as well as the decrease in the out-of-plane π-π stacking, can also be observed
in the measurements given in Figure S3 and S4. Only the intensities in Figure S4 are weakened with respect to Figure 3, which is most likely due to the aluminum top electrode shielding the signal partially.

**Figure S3.** GIWAXS data of the a) FTO substrate, b) pristine P(NDI2OD-T2), and c)-f) doped P(NDI2OD-T2) with dopant concentrations of 5 wt%, 10 wt%, 20 wt% and 40 wt%, respectively. Hereby, the thin film is stacked between an FTO substrate and an aluminum top electrode. The peaks are denoted with (h00) for lamellar and (00l) for π-π stacking.
Figure S4. GIWAXS data of the pristine and doped P(NDI2OD-T2) thin films on glass at different dopant concentrations as indicated.