

## Supplementary Information

# Enhanced Charge Transport and Thermoelectric Performance of P(NDI2OD-T2) by Epitaxial Crystallization on a Highly Oriented Polyethylene Substrates

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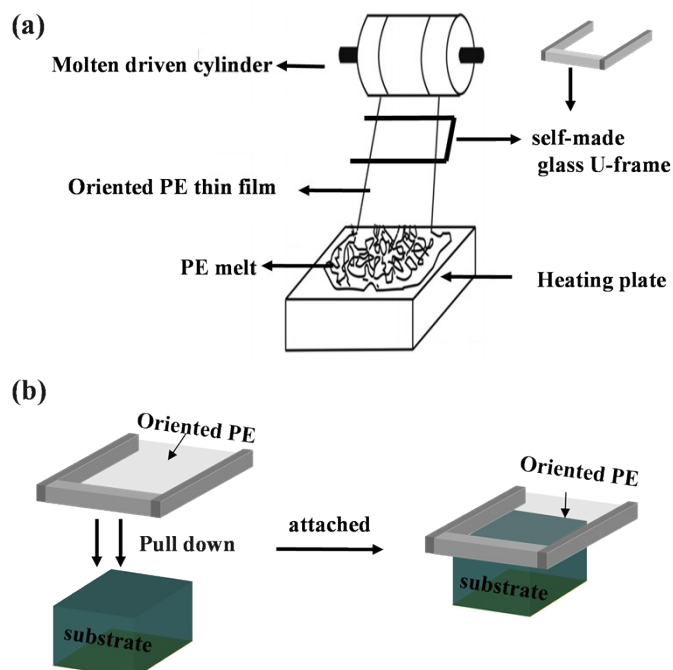
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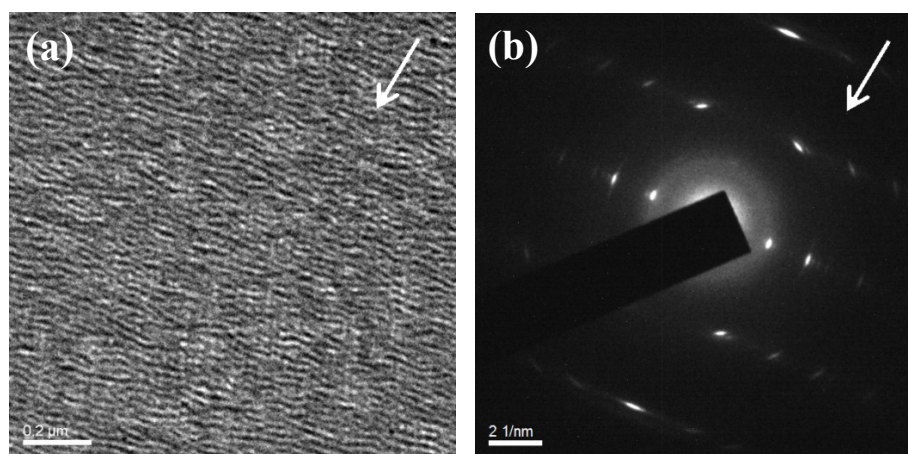
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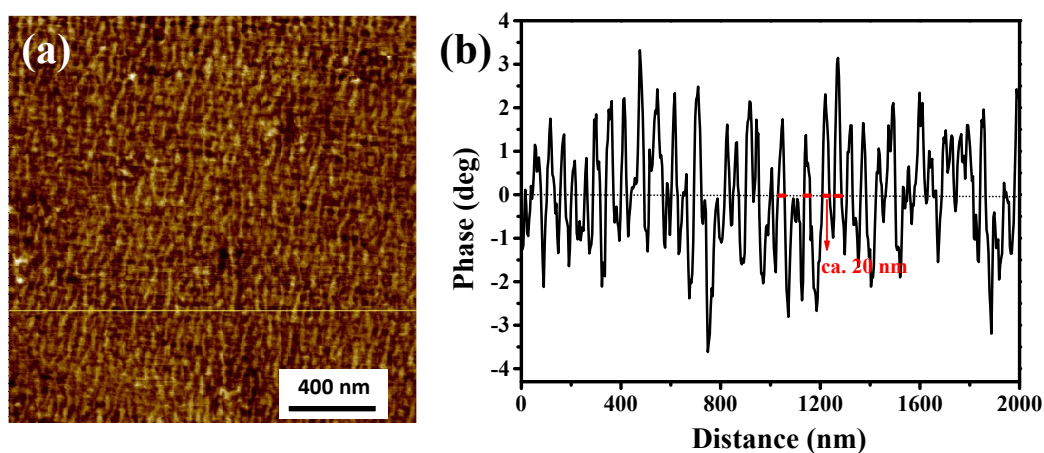
## Supporting Figures



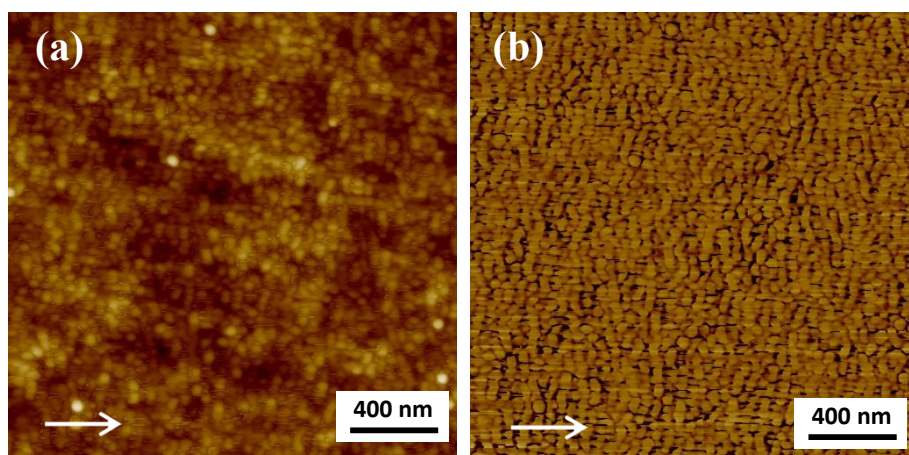
**Figure S1.** The sketch for the preparation and collection of highly oriented PE thin films.  
Schematic illustration of high orientated PE attached to the substrates



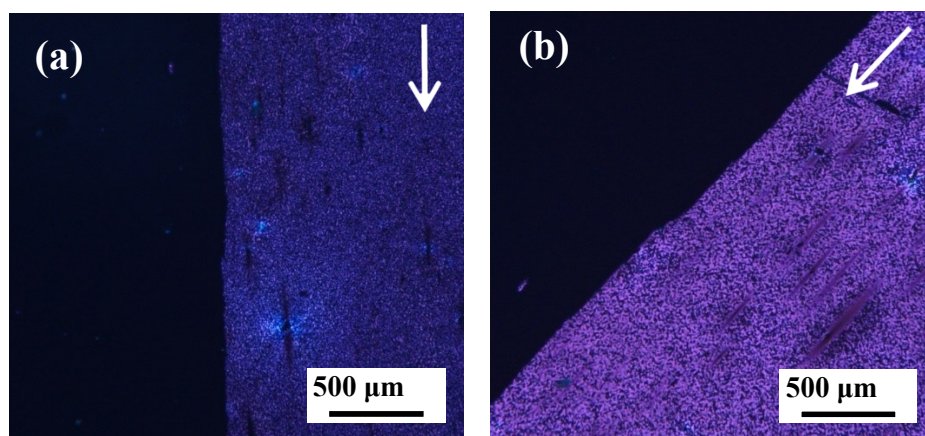
**Figure S2.** Phase-contrast bright field electron micrograph (a) and its corresponding electron diffraction pattern (b) of the highly oriented PE thin films. The arrow in the micrograph indicates the drawing direction during films preparation.



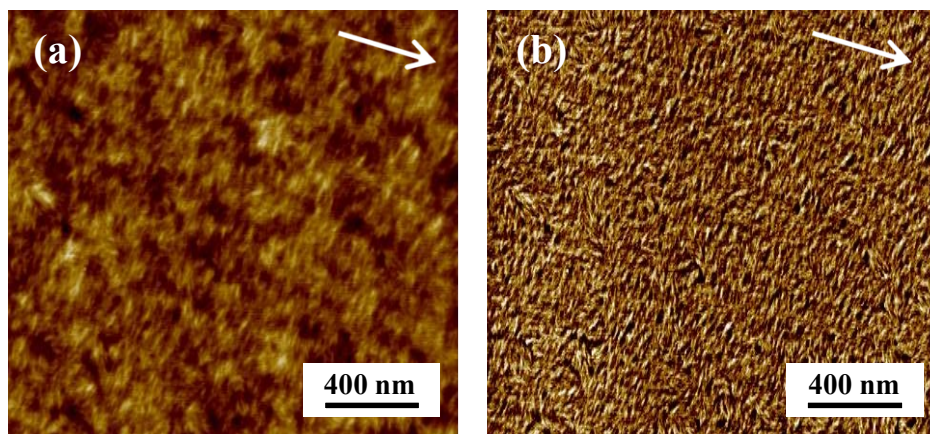
**Figure S3.** (a) The AFM phase image of N2200 and (b) the phase difference in the line marked in phase image.



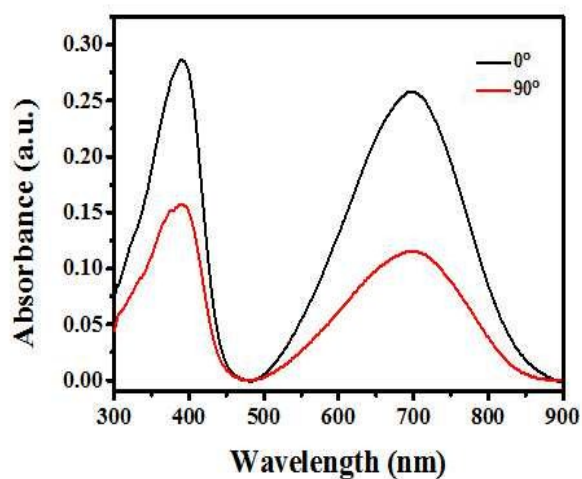
**Figure S4.** AFM height (a) and phase (b) images of the oriented PE films. The arrow shows the drawing direction of PE substrates.



**Figure S5.** POM micrographs of P(NDI2OD-T2) films spin-coated from chloroform solution on the oriented PE films at 0° (a) and 45° (b). The arrow shows the drawing direction of PE substrates.

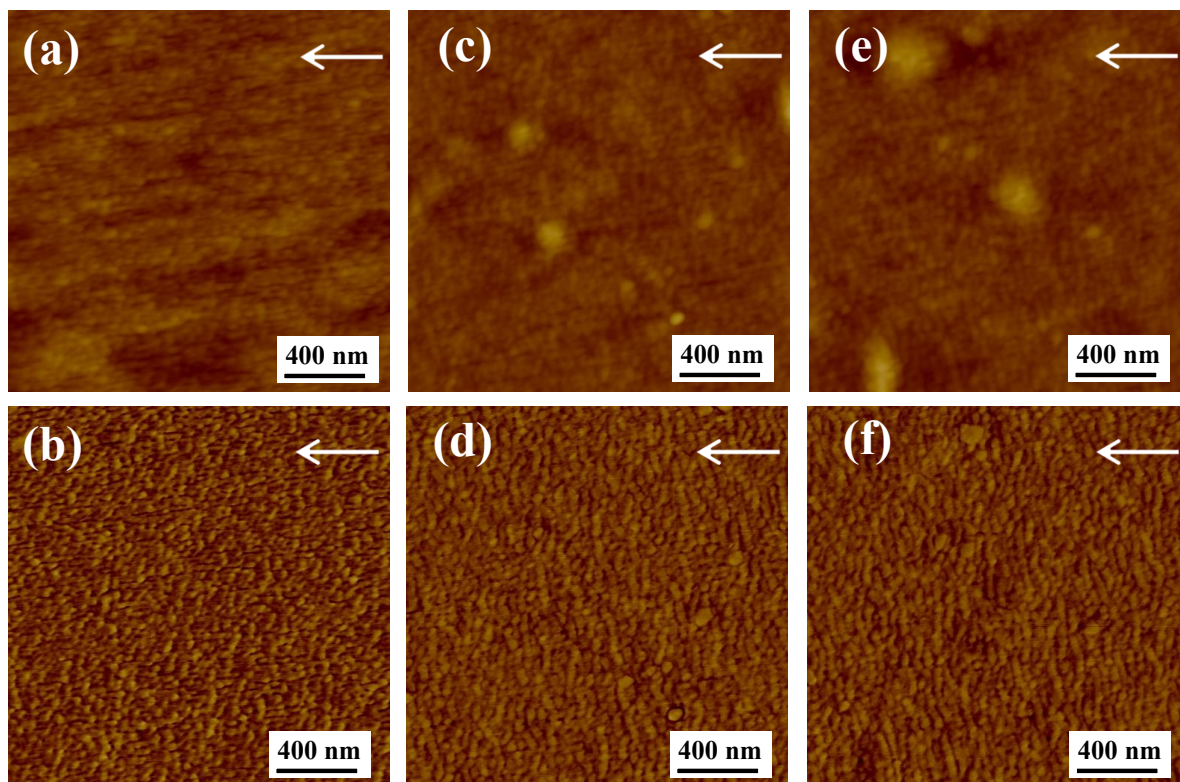


**Figure S6.** AFM height image (a) and phase image (b) of P(NDI2OD-T2) films spin-coated from chloroform solution on the oriented PE substrates. The arrow shows the drawing direction of PE substrates.

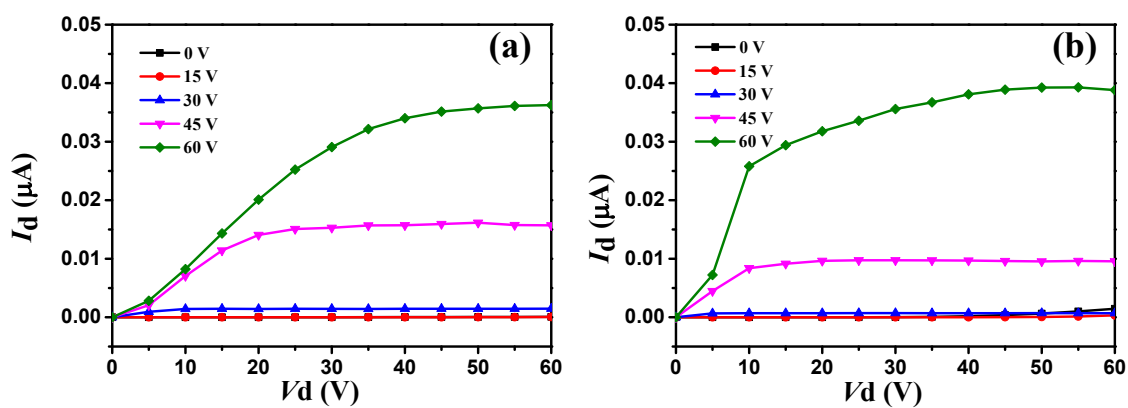


**Figure S7.** Polarized UV-vis absorption spectra of oriented P(NDI2OD-T2) films spin-coated from chloroform solution.

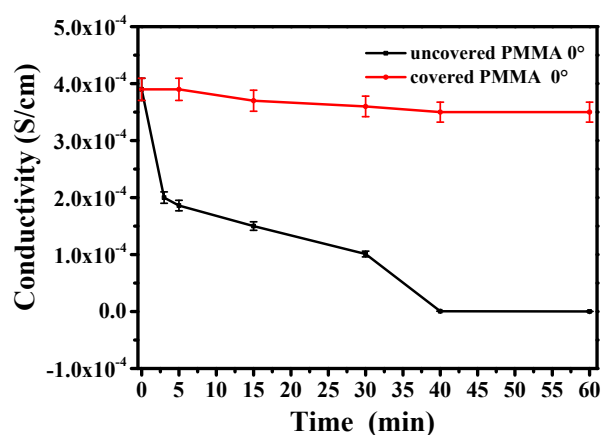




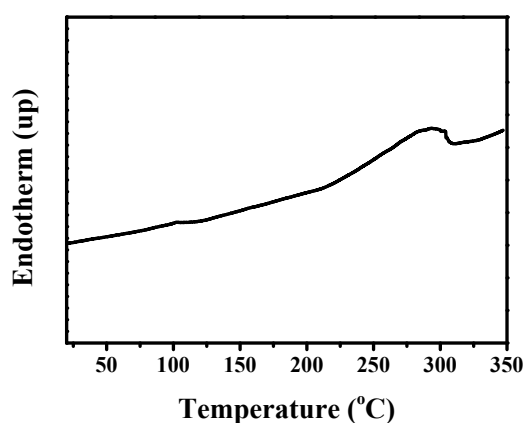
**Figure S8.** AFM height (a, c, e) and phase (b, d, f) images of P(NDI2OD-T2) thin film crystallized epitaxially on an oriented PE substrates prepared at different spin-coating temperatures from o-xylene solution (a, b) 100 °C; (c, d) 70 °C; (e, f) 50 °C. The arrow shows the drawing direction of PE substrates.



**Figure S9.** Output characteristics of transistors for the oriented P(NDI2OD-T2) perpendicular to the direction of chains (a) and the unoriented P(NDI2OD-T2) (b).



**Figure S10.** The conductivity of the doped P(NDI2OD-T2) films in the parallel direction of PE chains in air.



**Figure S11.** DSC curve of P(NDI2OD-T2) determined at 10 °C/min under nitrogen.

## Supplementary Methods

*Characterization:* Highly oriented PE thin films were prepared according to a melt-drawing technique frequently described in Figure S1. The polyethylene/xylene solution with a concentration of 0.5% (mass fraction) was poured onto the neat glass plate at the preheating temperature of 130 °C and evenly spread out. After the solvent evaporated completely, the polymer supercooled melt film on the glass plate was pulled up by a mechanical drum at a speed of about 20 cm/s. The transparent, non-porous and flat PE ultra-thin film was collected on the self-made glass frame (Figure S1a) and then the highly oriented PE film was attached to the substrate (Figure S1b). Different tests only used different substrates, but the process of

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film attachment is the same as shown in the Figure S13. The polarized optical microscopy (POM) images of P(NDI2OD-T2)/PE thin films on neat glass substrate were obtained by using the Axioskop 40A Pol optical microscope (Carl Zeiss). The surface morphology of P(NDI2OD-T2) films on the PE substrates was studied by using an Agilent Technologies 5500 atomic force microscope (AFM) (Agilent Technologies Co. Ltd., U.S.) at room temperature in air. The images were obtained by means of tapping mode (height and phase) with Silicon tips (Al-coating, resonance frequency of 303 kHz, and a spring constant of about 50 N/m, and the scanning rates varied from 2 to 5  $\mu\text{m/s}$ . For fourier transform infrared (FTIR) analysis, a Spectrum 100 FTIR spectrometer (Perkin-Elmer) was used. Absorption spectra were recorded using a UV-vis spectrophotometer (UV-2550, Shimadzu). For the polarized absorption characterization, a prism polarizer accessory was placed between the light source and the samples to provide the polarized incident light. For transmission electron microscopy (TEM) examination, the P(NDI2OD-T2)/PE thin films were detached from the substrate glass slide with the help of poly(acrylic acid) (PAA) and mounted onto 400 mesh TEM copper grids without any further thermal treatment. TEM observations were performed using a JEOL JEM-2100 with an accelerating voltage of 200 kV. To minimize radiation damage by the electron beam, focusing was carried out on an area; then the specimen film was translated to an adjacent undamaged area for recording the images immediately. Doping Process: N-DMBI with different mole percentages were added to the P(NDI2OD-T2) solutions. After being fully mixed, the solutions were utilized to fabricate films on PE substrates by spin-coating in nitrogen atmosphere.