Supporting Information

Materials

All reactants and solvents were purchased from commercial sources and used without further purification. Anhydrous and deoxygenated solvents were obtained by distillation over sodium benzophenone complex. ITO-coated glass substrates were cleaned in an ultrasonic bath with toluene, acetone, ethanol and deionized water, respectively, and then dried with nitrogen.

Sample preparation

Highly oriented ultrathin i-PP films were prepared according to a melt-draw technique. According to this method, a small amount of a 0.5wt % solution of the i-PP in xylene was poured and uniformly spread on a preheated glass plate where the solvent was allowed to evaporate at the preparation temperature (ca. 135 °C). After evaporation of the solvent, the i-PP thin molten layer (about 1 μm in thickness) was then drawn up by a motor driven cylinder with a drawing speed of about 2 cm/s. The obtained films are 30~50 nm in thickness and show uniaxially fiber orientation.

Electrodeposition of 3-hexylthiophene was performed using a standard one-compartment, three-electrode electrochemical cell attached to a CHI 660E Electrochemical Workstation. The Ag/Ag^+ electrode was used as reference electrode. ITO (1 cm^2) covered with the highly oriented i-PP film was used as the working electrode and titanium metal was used as the counter electrode (1 cm^2).

Characterization

The optical microscopy images were obtained by using an Axioskop 40A Pol optical microscope (Carl Zeiss) under crossed polarizers.

The scanning electron microscopy (SEM) observation was conducted using a JEOL JSM-6701F scanning electron microscope. The fractured surface of sample was obtained by fracturing in liquid nitrogen.

Gel permeation chromatography (GPC) analysis was carried out on a Waters 515-2410 system using polystyrene standards as molecular weight references and tetrahydrofuran (THF) as the eluent.

X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg-Ka radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon. The fitting of the curves was made by Avantage 3.95.

Grazing incidence X-ray diffraction (GIXD) data was were obtained using a Xenocs system equi-PPed with a Cu X-ray source. The grazing-incidence angle was fixed at 0.3°.

Raman spectra were obtained using a 50× objective and a 785 nm laser light source (Renishaw Micro-Raman Spectroscopy System) that has 4 cm^{-1} resolution in the backscattering geometry. For all order parameter measurements of samples, the laser power was 100 mW, and spectra were acquired using exposure times of 6 s with one accumulations.

Polarized photoluminescence measurements (emission mode) were carried out with a

FLS980 spectrofluorometer system (Edinburgh Instruments) having a xenon lamp as the steady-state excitation source. The polarized emission was collected at a perpendicular direction with respect to the excitation light. The plane defined by excitation and emission lights was perpendicular to the drawing direction of i-PP film. For FTIR analysis, a Spectrum 100 FT-IR spectrometer (Perkin-Elmer) was used. The wavenumber of the infrared spectrum starts from 450 to 4000 cm^{-1}, and the polarized infrared was used in order to identify the chain directions of P3HT and i-PP.

Supporting figures:

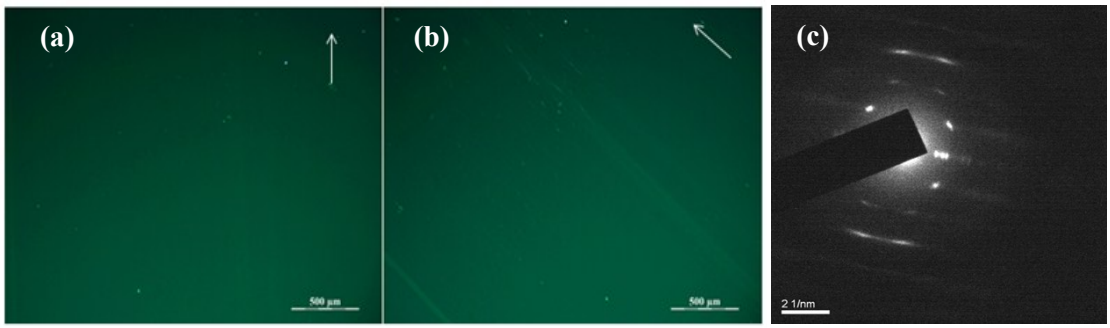

Fig. S1 (a) Optical micrograph of the oriented i-PP. (b) The optical micrograph taken from the same area as shown in part (a) but rotated clockwise for 45° about the light beam. The white arrows indicate the molecular chain directions of i-PP films. (c) Electron diffraction of the oriented i-PP.

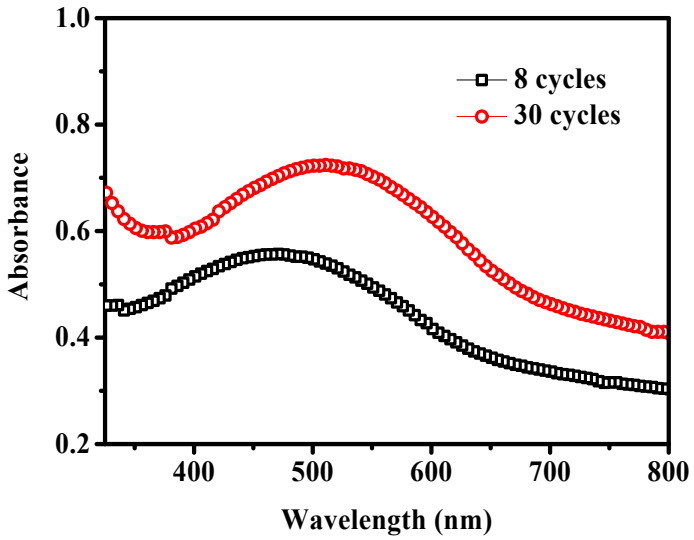

Fig. S2 Uv-vis spectra of the undoped P3HT films with the different cycles.

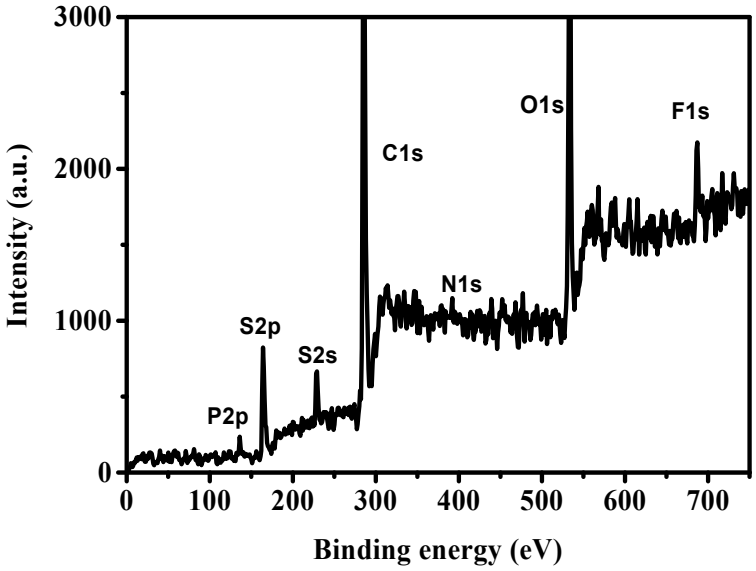

Fig. S3 XPS spectrum of the doped P3HT on i-PP film.

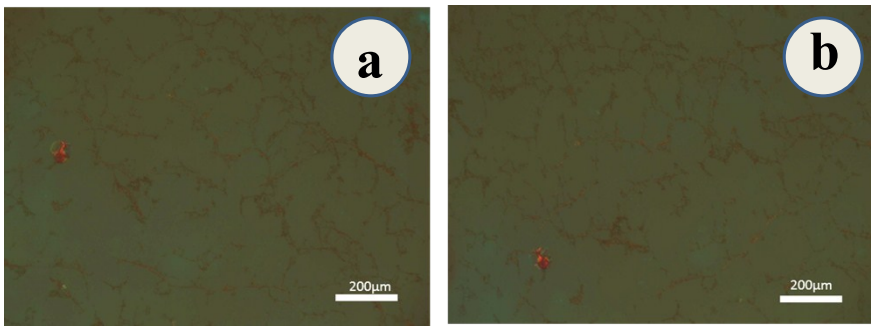

Fig. S4 (a) Polarized optical micrograph of a P3HT film directly electrodeposited onto bare ITO glass and then dedoped. (b) The same sample shown in frame (a) but rotated by 45^0 about the light beam axis.

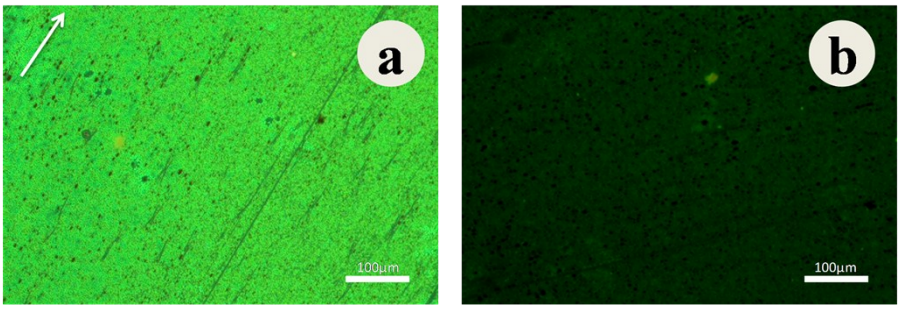

Fig. S5 (a) Polarized optical micrograph of a doped P3HT film electrodeposited onto i-PP coated ITO glass. (b) The same sample shown in frame (a) but rotated by 45^0 about the light beam axis. The white arrows indicate the molecular chain directions of i-PP films.

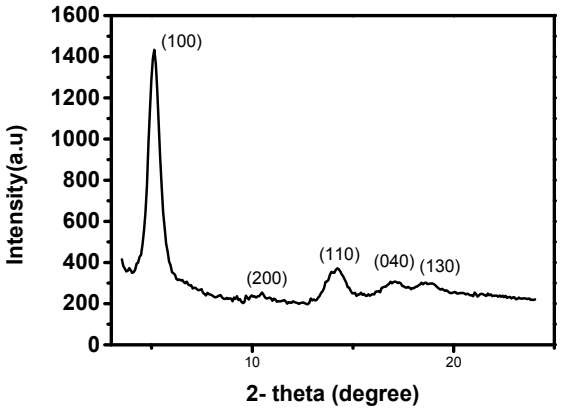

Fig. S6 One-dimensional integral curve corresponding to the 2D GIXD is portrayed in Fig. 3a.

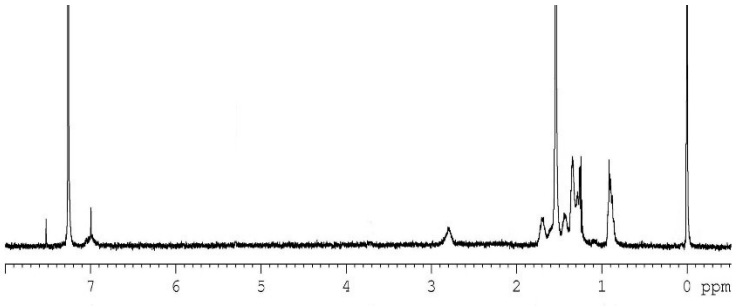

Fig. S7 ^{1}HNMR spectrum of the dedoped P3HT in the $CDCl_3$.