Supporting information

Enhanced Thermoelectric Power Factor of Tensile Drawn Poly(3-hexylthiophene)

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Experimental

Materials. P3HT was obtained from Sungyoung Ltd. (regioregularity ~ 93 %, number-average molecular weight of M_n ~ 91 kg mol^{-1}, polydispersity index ~ 1.8), regio-random P3HT was purchased from Sigma Aldrich (regioregularity ~ 28 %, number-average molecular weight of M_n ~ 16 kg mol^{-1}, polydispersity index ~ 2.8). The regioregularity was determined with a 475 Agilent (Varian) MR 400 MHz spectrometer with $CDCl_3$ as the solvent. The molecular weight was measured with size exclusion chromatography (SEC) on an Agilent PL-GPC 220 integrated high temperature GPC/SEC system in 1,2,4-trichlorobenzene at 150 °C using relative calibration with polystyrene standards. F4TCNQ was purchased from TCI Chemicals and used without further purification. Mo(tfd-$COCF_3$)$_3$ was synthesized according to [28]. Solvents with purity >99% were purchased from Sigma-Aldrich (p-xylene) and Fisher Scientific (acetonitrile).

Sample preparation and sequential doping. P3HT was dissolved at 80 °C at a concentration of 20 g L^{-1} in p-xylene. Films were drop cast from 80 °C hot solutions onto cleaned glass substrates at 90 °C and covered with a petri dish until dry. Substrates were cleaned with soapy water followed by sonication bath; first with acetone (15 min) then with isopropanol (15 min) and finally dried with nitrogen. The dried films were peeled from the substrates and cut before stretching. Tensile drawing was performed using a Q800 DMA (TA Instruments) at 60 °C at a rate of 0.5 mm min^{-1} until a draw ratio of $\lambda \sim 4$ was reached. Sequential doping was performed by immersing the film into a solution of Mo(tfd-$COCF_3$)$_3$ or F4TCNQ in acetonitrile (5 g L^{-1}) for 48 or 72 h; films were then rinsed with acetonitrile and dried under nitrogen flow. The sample weight remained unchanged for at least two weeks after sequential doping, which suggests that no considerable amount of solvent was trapped in the samples.

Energy dispersive X-ray analysis (EDX). EDX was carried out at 5 kV in a Ultra 55 FEG SEM equipped with a Lithium-drifted silicon detector. Samples were freeze-fractured and sputtered with palladium prior to analysis.

Wide angle X-ray scattering (WAXS). WAXS diffractograms were obtained using a Mat:Nordic instrument from SAXLAB equipped with a Rigaku 003+ high brilliance micro focus Cu-radiation source (wavelength = 1.5406 Å) and a Pilatus 300K detector placed at a distance of 88.6 mm from the sample.

Differential scanning calorimetry (DSC). DSC was carried out under nitrogen between 25 to 300 ºC at a scan rate of 10 ºC min^{-1}, using a Mettler Toledo DSC2 calorimeter equipped with a HSS7 sensor and a TC-125MT intracooler. The sample weight was 2 to 3 mg.

Dynamic mechanical analysis (DMA). DMA was performed using a Q800 instrument from TA Instruments in tensile mode. Films (2.5×1cm, gauge length ~1×1cm) were subjected to a dynamic strain of up to 0.1% at a frequency of 1 Hz, while ramping the temperature at 2 °C min^{-1} from -100 °C to +40 °C. T_g was taken as the peak of the loss modulus.

Electrical characterization. The electrical resistance of free-standing films was determined with a Keithley 2400 sourcemeter using a two-point probe configuration by contacting samples with dimensions of 10 mm × 2 mm with silver paste (Agar Scientific); gold electrodes were sputtered on selected samples to rule out a large degree of contact resistance. Seebeck coefficients were measured at 300 K with a SB1000 instrument equipped with a K2000 temperature controller from MMR Technologies using a thermal load of 1 to 2 K and a constantan wire (200 µm diameter) as an internal reference. Samples of about 1×4 mm were mounted on the sample stage using silver paint (Agar Silver Paint, G302); see Figure S0 for a photograph of the sample stage. Samples were first allowed to equilibrate for 60 s, then a heating power of 30 mW was applied, followed by a further 30 s for equilibration before each measurement. Measurements were carried out in ambient atmosphere (instead of vacuum to prevent evaporation of the dopant) but in a closed environment to avoid convection.

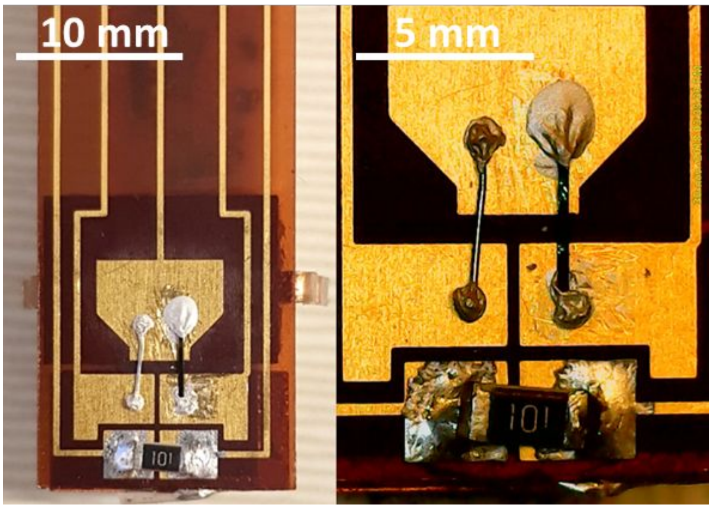


Figure S0. Photograph of the sample stage used to measure Seebeck coefficients; a constantan reference wire (left) and a stretched P3HT film (right) are fixated with silver paste.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) was used to evaluate if the size and amount (peak melting temperature, enthalpy of fusion) of crystallites changed upon solid state drawing at elevated temperature. DSC scans show no change in the peak melting temperature ($T_m \sim 238$ °C) and a small change in the enthalpy of fusion ($\Delta H \sim 17$ and 21 J g^{-1}) between the as-cast and stretched sample (Supporting Information, Figure S1). We conclude that the change during stretching is only affecting the orientation but not the size of crystallites. The crystallinity slightly increases. For both samples, cold crystallization was detected.

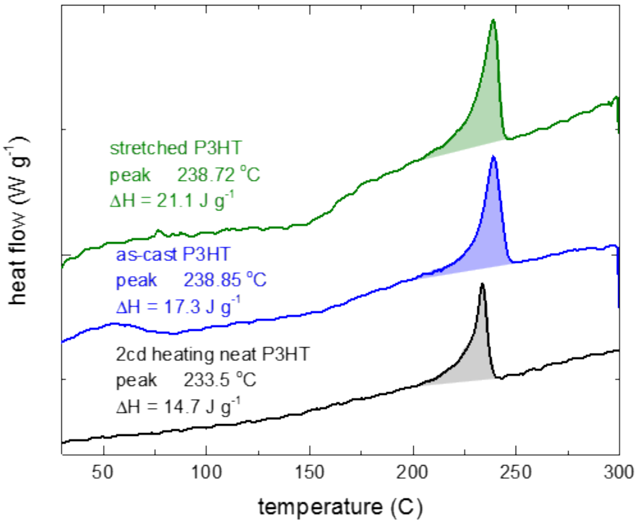


Figure S1. Differential scanning calorimetry (DSC) heating thermograms of neat, as-cast and stretched P3HT, ΔH values obtained by integration (grey area) were 21, 17, and 15 J g^{-1} respectively.

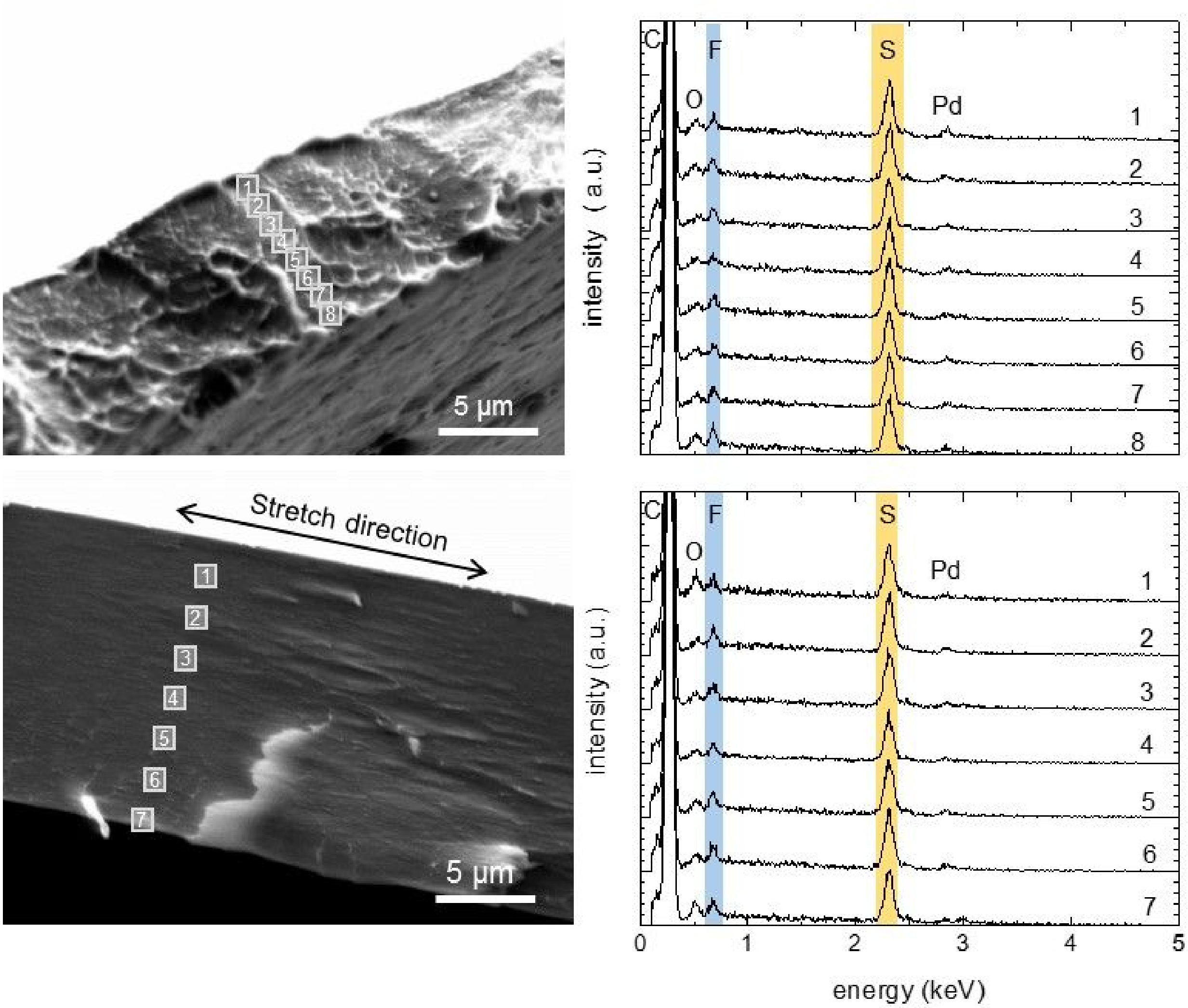


Figure S2. Left, scanning electron microscopy (SEM) images of freeze-fractured Mo(tfd-COCF$_3$)$_3$-doped P3HT films (top: λ = 1 bottom: λ ~ 4). Right, corresponding Energy dispersive X-ray spectroscopy (EDX). Due to overlap in energy between molybdenum with both carbon and sulphur the sulphur and fluorine peaks were used.

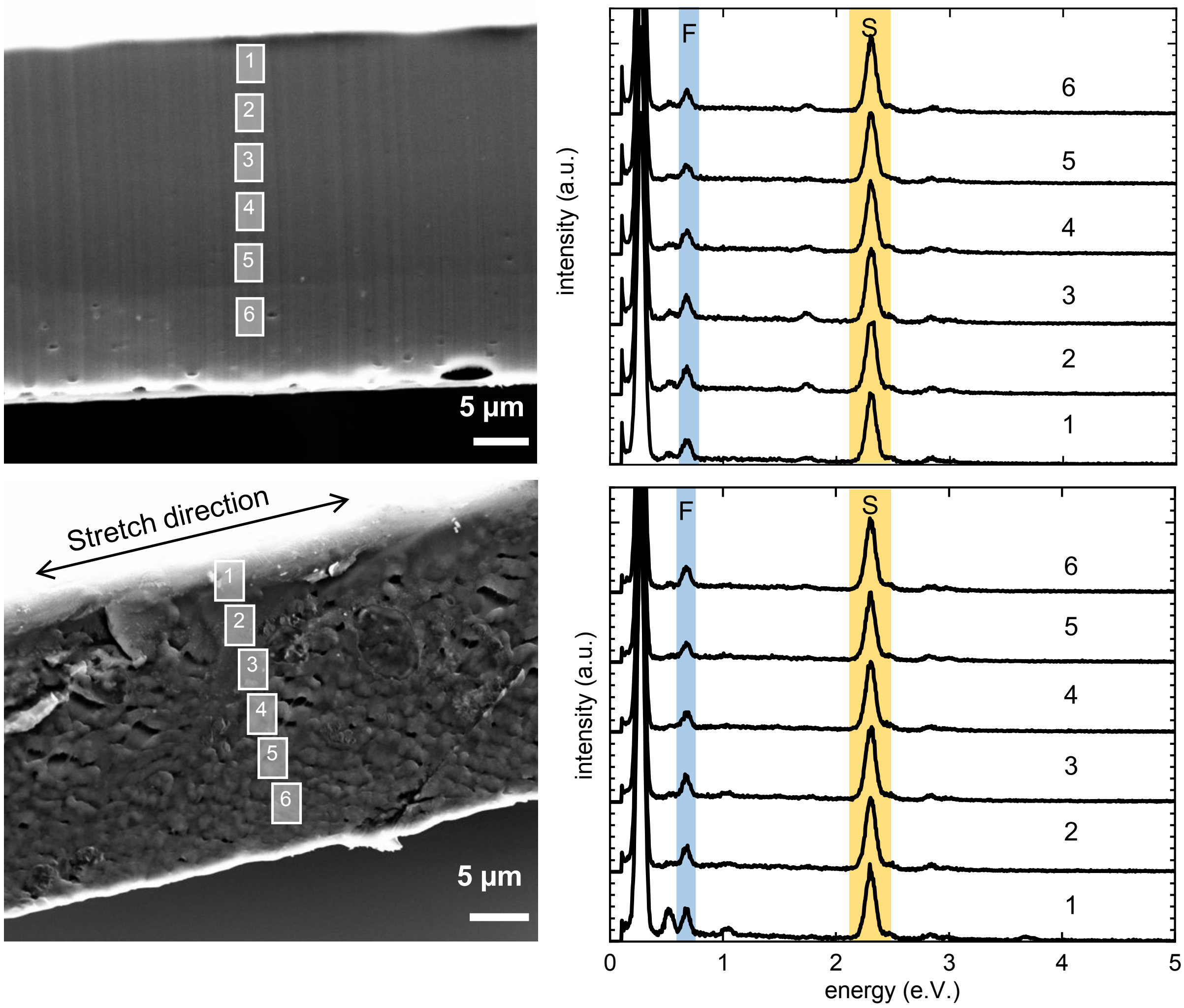


Figure S3. Left, scanning electron microscopy (SEM) images of freeze-fractured F4TCNQ doped P3HT films (top: λ = 1 bottom: λ ~ 4). Right, corresponding Energy dispersive X-ray spectroscopy (EDX). Due to overlap in energy between molybdenum with both carbon and sulphur the sulphur and fluorine peaks were used.

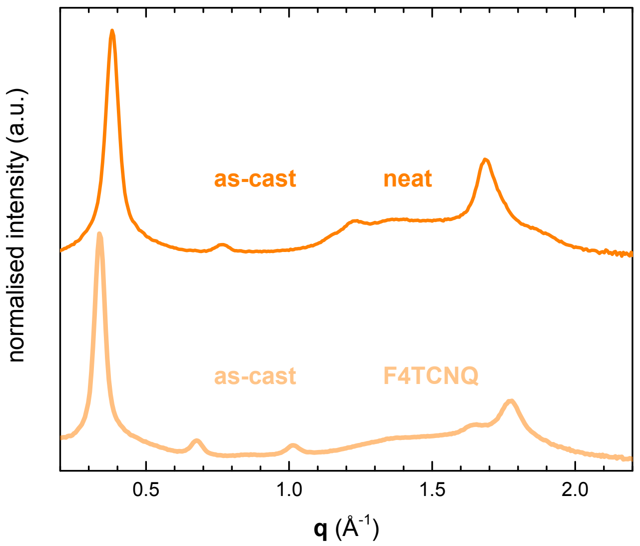
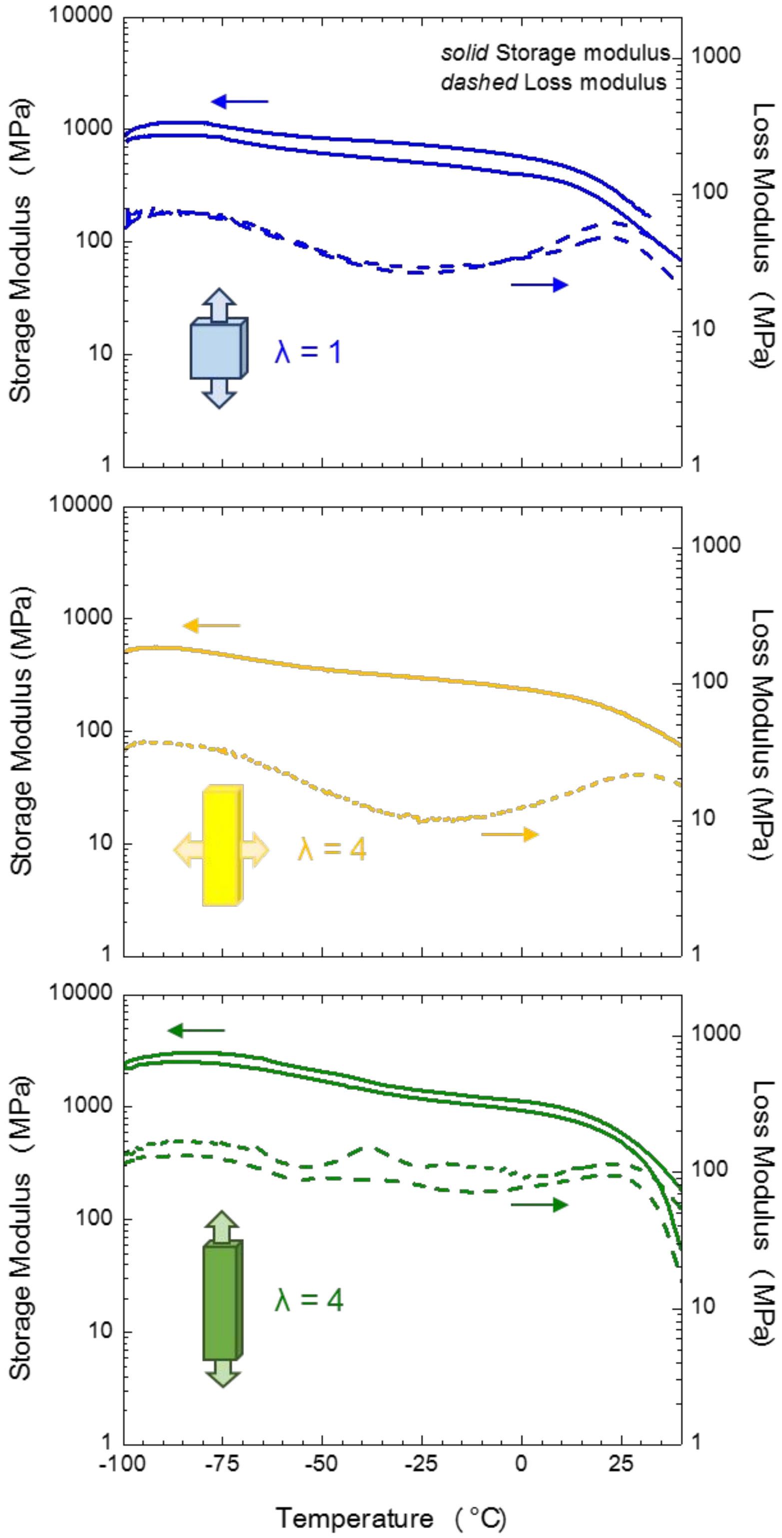


Figure S4. Representative graph of intensity as a function of q obtained by integration of scattering spectra for as-cast neat and F4TCNQ doped P3HT.

Table S1: Herman's orientation factor obtained by angular integration of the (100) diffraction peak

sample	**Herman's orientation factor (100)**
neat λ ~ 1	- 0.01
neat λ ~ 4	- 0.35
Mo(tfd-COCF$_3$)$_3$ λ ~ 1	- 0.01
Mo(tfd-COCF$_3$)$_3$ λ ~ 4	- 0.30


10000
1000
100
10
1
Storage Modulus (MPa)
Loss Modulus (MPa)
solid Storage modulus
dashed Loss modulus
λ = 1
λ = 4
λ = 4
-100
-75
-50
-25
0
25
Temperature (°C)

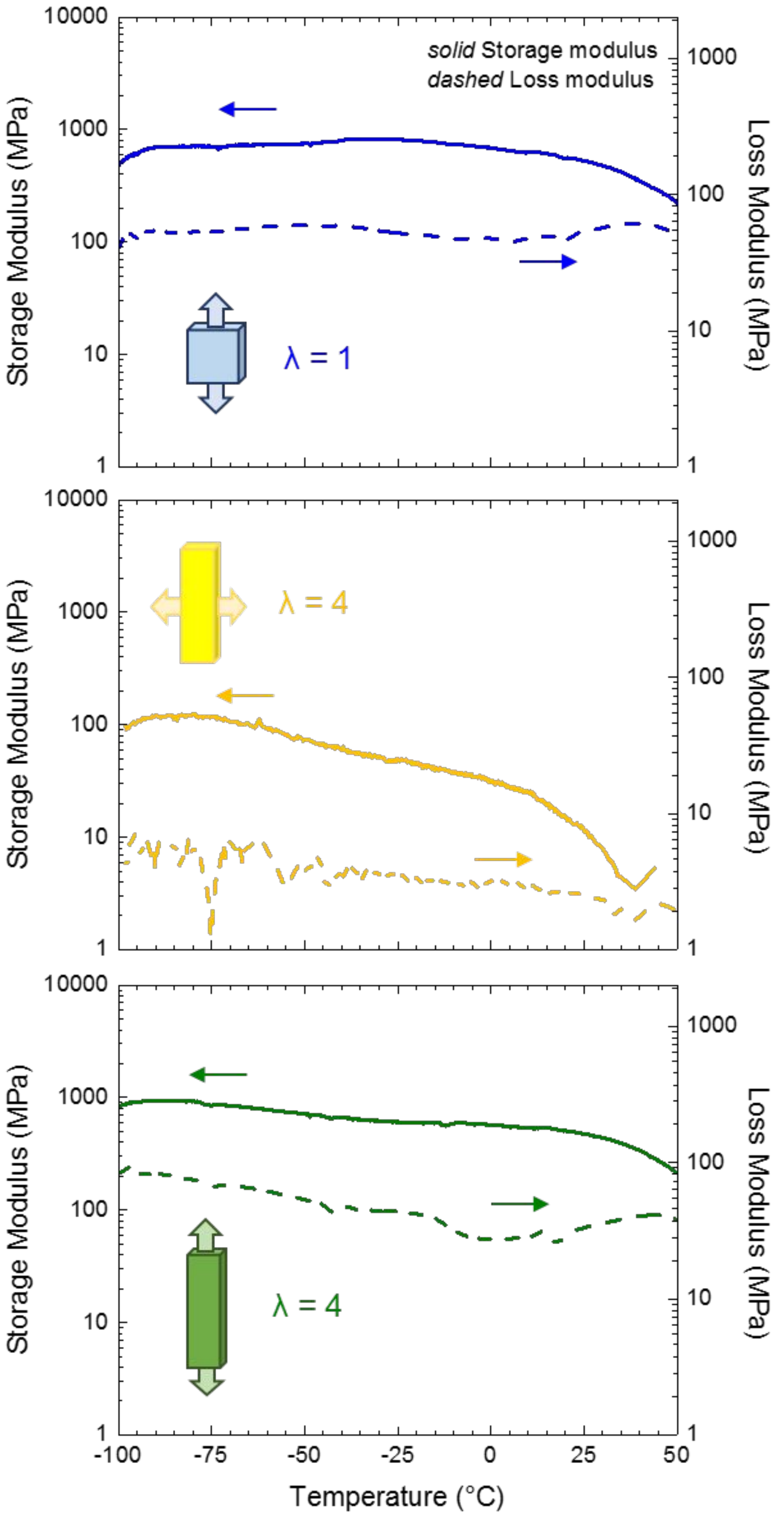


Figure S5. Representative DMA curves for neat P3HT; λ = 1 (blue), λ = 4 transverse (yellow), λ = 4 parallel to the stretching direction (green). Storage modulus (solid line); Loss modulus (dashed line).

Figure S6. Representative DMA curves for F4TCNQ doped P3HT; λ = 1 (blue), λ = 4 transverse (yellow), λ = 4 parallel to the stretching direction (green). Storage modulus (solid line); Loss modulus (dashed line); doping with F4TCNQ results in a slight increase in the glass transition temperature to $T_g \sim 40$ °C for $\lambda = 1$ and $\lambda = 4$ parallel.

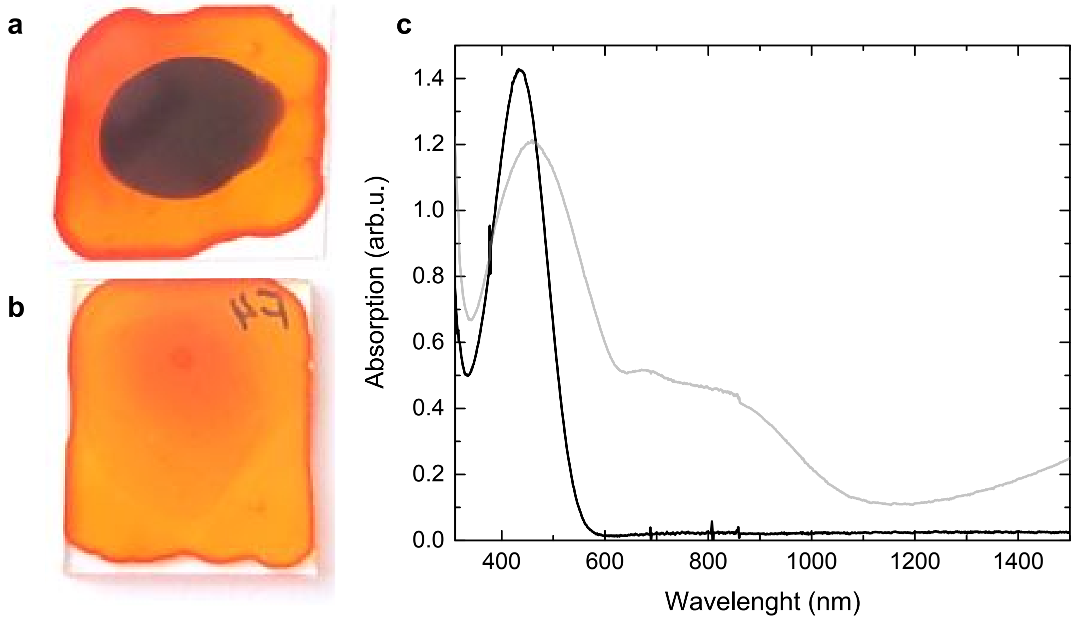


Figure S7. Dropcast film of (a) region-random P3HT doped with Mo(tfd-$COCF_3$)$_3$ (σ = 0.09 ± 0.02 S cm^{-1}); (b) Regio-random P3HT “doped” with F4TCNQ (σ was too small and could not be measured); (c) optical absorption spectra of regio-random P3HT neat (black) and doped with Mo(tfd-$COCF_3$)$_3$ (grey).

Calculation of anisotropy

The anisotropy in conductivity is calculated via $\sigma_{\parallel}/\sigma_{\perp} = I_{\parallel}/I_{\perp}$, where the currents $I_{\parallel/\perp}$ are obtained as the total current in the direction of an applied (small) voltage in the indicated direction ($\parallel$ or $\perp$ to the drawing direction) by solving Kirchhoff's laws. From the resulting answer, the Seebeck coefficient $\alpha_{\parallel/\perp}$ and the corresponding anisotropy ratio $\alpha_{\parallel}/\alpha_{\perp}$ is calculated as[1]

$$\alpha_{\parallel/\perp} = \frac{E_F - E_{t,\parallel/\perp}}{qT} \qquad \text{(S1)}$$

where q is the positive elementary charge and $E_{t,\parallel/\perp}$ the transport energy that is defined as

$$E_{t,\parallel/\perp} = \int \frac{E\sigma_{\parallel/\perp}(E)}{\sigma_{\parallel/\perp}} dE \qquad \text{(S2)}$$

where $\sigma_{\parallel/\perp}(E)$ is the conductivity distribution function, such that $\sigma_{\parallel/\perp} = \int \sigma_{\parallel/\perp}(E)dE$. Since all currents I_{ij} through all resistors R_{ij} are known, E_t is obtained as

$$E_{t,\parallel/\perp} \approx \frac{\sum E_{ij} I_{ij,\parallel/\perp}}{\sum I_{ij,\parallel/\perp}} \qquad \text{(S3)}$$

with $E_{ij} = (E_i + E_j)/2$. This expression follows directly by applying Equation S2 to the individual resistances in the network and averaging over the entire grid. Note that contributions perpendicular to the applied voltage, i.e. perpendicular to the direction of entropy transport, are averaged out due to the absence of a net current in that direction.

The Fermi energy E_F is calculated from the condition

$$c = \frac{n}{N_0} = \int f(E - E_F) g(E) dE \qquad \text{(S4)}$$

where f and g are the Fermi-Dirac and the (normalized) density of states distribution functions, respectively, and c the charge carrier concentration relative to the total site density

N_0 that was set to $c = 0.1$. All simulations where averaged over 25 random configurations of a 50×50 grid.

References

(1) Fritzsche, H., A General Expression for the Thermoelectric Power. *Solid State Commun.* **1971,** *9*, 1813-1815.