Engineered doping of organic semiconductors for enhanced thermoelectric efficiency

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Sample preparation

PEDOT:PSS (PH1000 from H. C. Starck) was mixed with 5 volume % of either EG or DMSO and then filtered by a syringe filter (0.45 μm pore-size PVDF membrane). Solutions were subsequently put into a vacuum chamber for 15 minutes to remove air bubbles. Samples for electrical measurements (S and σ) were prepared by spin-coating at 4000 rpm for 30 seconds on a glass substrate pre-cleaned with detergent, deionized water, acetone, and isopropanol. Samples for thermal measurements (κ) were prepared by spin-coating multiple layers (each layer at 4000 rpm for 30 seconds) to achieve a sample thickness large enough for accurate measurement. A pre-cleaned silicon substrate (capped with a 100 nm SiO₂ layer to yield surface properties similar to glass) was chosen for thermal conductivity measurements to increase the fraction of the temperature drop occurring in the sample versus the substrate and hence increase the measurement signal-to-noise ratio. For doping-dependent cross-plane thermal conductivity (κ⊥) measurements, samples were spin-coated 3 times to yield a film thickness of approximately 180 nm, while for in-plane thermal conductivity (κ∥) measurements, samples were spin-coated 45 times to yield a film thickness of approximately 1.4 μm. Note that individual layer thicknesses were observed to decrease as the
number of layers increased, presumably due to partial removal of the topmost annealed layer during each spin-coating. A thicker sample was required for in-plane measurements in order to resolve the anisotropy in thermal conductivity when using a heater line of 3 μm width. After each spin-coating, all electrical and thermal samples were thermally annealed at 130 °C for 15 minutes. Samples for electrical and cross-plane thermal conductivity measurements were immersed in an EG bath for a certain length of time to induce a desired amount of physical dedoping. All steps for sample preparation including EG treatment were performed in nitrogen gas, while measurements of $S$, $\sigma$, and $\kappa$ were made in ambient (air) conditions. The samples used for cross-plane thermal measurements showed the same trend of decreasing thickness for longer dedoping time (Supplementary Fig. 1) as the samples used for electrical measurements (Fig. 2a), indicating the physical dedoping of PSS.

Supplementary Figure 1 | Measured thicknesses of 3ω samples used for measurements of $\kappa_\perp$ at various EG treatment times. Error bars were defined by the standard deviation of measured thickness at different locations on a given sample.
Determination of $\sigma$

To determine $\sigma$ and $S$ precisely, spacings of various lengths ($L = 60, 80, 100$ and $120$ $\mu$m) between deposited metal contacts (1.2mm wide $\times$ 1.5mm long) were prepared (Supplementary Fig. 2). For $\sigma$ measurements, the electrical resistance for each electrode spacing was determined by the standard four-probe method. As shown in Supplementary Fig. 3a, the slope of electrical resistance versus spacing length defines electrical resistivity (i.e., resistance $= \rho/A \times L$ where $A$ is the cross-sectional area of the sample between the electrodes and $\sigma = 1/\rho$). The cross-sectional area was calculated as the width of the electrode $\times$ the thickness of the PEDOT:PSS film (measured by a Dektak profilometer). The error bars for each $\sigma$ data point in Fig. 3b were calculated as the standard deviation of measured resistances from the fit line (e.g., Supplementary Fig. 3a).

Supplementary Figure 2 | Illustration of methods used to measure $S$ and $\sigma$. The electrical resistance for each electrode spacing ($L$) was determined by the standard four-point method. Temperatures measured by two thermocouples (TCs) were used to find the temperature difference across the spacing ($\Delta T$) which induced the thermal voltage ($\Delta V$) measured by two voltage probes.
**Supplementary Figure 3 | Differential techniques used for measurement of $S$ and $\sigma$.** a–b, Measured (a) electrical resistance and (b) normalized thermal voltage (i.e., thermal voltage across the electrode spacing ($\Delta V$) divided by the temperature difference between the two thermocouples ($\Delta T_{TC}$)) versus the spacing $L$. c, $\Delta V$ across electrode spacings of various lengths as a function of the temperature difference across the spacing ($\Delta T$). The electrical conductivity and Seebeck coefficient were determined by the slope of the linear fitting line, as indicated in a and c.
Determination of $S$

A Peltier cooler (300 K - $\Delta T_0$) and Peltier heater (300 K + $\Delta T_0$) were used to apply the temperature gradients used to induce thermal voltage. Two microthermocouples (TCs) of 25 µm diameter were placed on the sample to the left of the left electrode and to the right of the right electrode with a separation of $D$ (which was much larger than the TC diameter, the electrode spacing ($L$), and the error in TC position). The temperature difference between the TCs ($\Delta T_{TC}$) was measured for different values of $D$ (1, 2, 3, 4, and 5 mm) and showed a linear temperature gradient ($\Delta T_{TC}/D =$ constant). Since $\Delta T_{TC}$ and $D$ were much larger than their errors, the error in the derived temperature gradient was small. The temperatures difference across the electrode spacing ($\Delta T$) were derived as $\Delta T = \Delta T_{TC} \times L/D$. To measure thermal voltage, two thin gold wires of 25 µm diameter were brought into contact with the gold electrodes. Thermal voltage ($\Delta V$) was found to increase linearly with the electrode spacing (Supplementary Fig. 3b). The Seebeck coefficient was derived by a linear fit to the measured $\Delta V$ versus $\Delta T$ at different electrode spacings (Supplementary Fig. 3c). The error bars for each data point of $S$ in Fig. 3a were calculated as the standard deviation of measured thermal voltage from the fit line (e.g., Supplementary Fig. 3c).
**Analysis of XPS spectra**

The chemical compositions of PEDOT:PSS at various dedoping levels were analyzed by X-ray photoelectron spectroscopy (XPS) under ultralow vacuum (~$10^{-9}$ Torr) using a Kratos Axis Ultra XPS. Observed XPS spectra were deconvolved using the known intensity ratio (2:1) and energy difference (1.2 eV) of the S(2p) doublet (i.e., $S(2p_{3/2})$ and $S(2p_{1/2})$) for PEDOT:PSS. XPS measurements were performed for samples with various EG treatment times to derive the fraction of PSS ($\chi$) in PEDOT:PSS for a given EG treatment time (Supplementary Fig. 4).

**Supplementary Figure 4 | Ratio of the concentration of dopant (PSS) monomers to the concentration of host (PEDOT) monomers at various EG treatment times.** Relative intensity ratios for PSS and PEDOT monomers were measured by XPS at various EG treatment (dedoping) times and used to derive the dopant-to-host fraction ($\chi$).
Stability of PEDOT:PSS in atmosphere

The stability of PEDOT:PSS in air, which is important to its practical application as a thermoelectric material, was tested by measuring $S$ and $\sigma$ at different times of exposure to air. As shown in Supplementary Fig. 5, $S$ and $\sigma$ remained nearly constant for 5 days. The tested sample was dedoped by the EG treatment for 180 minutes, indicating that PSS dedoping does not detract from the air stability of the PEDOT:PSS thermoelectric performance.

Supplementary Figure 5 | Stability of PEDOT:PSS in atmosphere. Seebeck coefficient (a), electrical conductivity (b), and thermoelectric power factor (c) in an EG-mixed PEDOT:PSS film at different exposure times to air (following 180 minutes of dedoping).
**Determination of doping-dependent cross-plane thermal conductivity $\kappa_{\perp}$**

A differential 3ω method\(^2\) was used to measure the cross-sectional thermal conductivity of the EG-treated PEDOT:PSS films, which had a thickness in the range of 120 to 190nm at various levels of dedoping. As shown in Supplementary Fig. 6, a 50 μm × 2.6 mm gold line heater was patterned on top of a reference substrate without PEDOT:PSS, and a second 50 μm × 2.6 mm gold line heater was patterned on top of the PEDOT:PSS film sample. Since the differential 3ω technique allows measurement of the temperature change across only the PEDOT:PSS layer, it removes uncertainties in the thermal properties of the other layers. A thin insulating layer of Al₂O₃ was deposited on the sample by atomic layer deposition (ALD) to electrically isolate the gold heater lines from the conductive PEDOT:PSS film. The change in temperature across the thin PEDOT:PSS layer ($\Delta T_{i}$) was calculated as\(^2\):

$$\frac{\Delta T_{i}}{P_{s}} = \frac{\Delta T_{s}}{P_{s}} - \frac{\Delta T_{r}}{P_{r}}, \quad (S1)$$

where $\Delta T_{s}$ and $\Delta T_{r}$ are the 2ω temperature signals for the line heaters on the sample and reference respectively, and $P_{s}$ and $P_{r}$ are the corresponding power dissipations. Subscripts f, s, and r denote the PEDOT:PSS layer, the sample (including all layers), and the reference, respectively. $\Delta T_{s}$ and $\Delta T_{r}$ were determined by\(^3\):

$$\Delta T_{s,r} = 2R \frac{dT}{dR} \frac{V_{3\omega}}{V_{1\omega}}, \quad (S2)$$

where $R$ and $dR/dT$ are the electrical resistance and temperature coefficient of electrical resistance for the line heater and $V_{1\omega}$ and $V_{3\omega}$ are the 1\(^{st}\) and 3\(^{rd}\) harmonic voltages. Typical experimental data is shown in Supplementary Fig. 7a. The 2ω temperature oscillation ($\Delta T_{s}$ and $\Delta T_{r}$) is a linear function of
logarithm frequency\(^3\); the presence of the PEDOT:PSS layer produces a frequency-independent increase in the 2\(\pi\) temperature oscillation (denoted by \(\Delta T_f\))\(^4\). The temperature drop across the PEDOT:PSS layer is large relative to the other temperature drops in the sample (\(\Delta T_f \sim 0.2\, \text{K} \geq \Delta T_s - \Delta T_f\)), indicating that the thermal conductivity of PEDOT:PSS is much lower than that of the other layers, improving the reliability of the measurement.

Since the width of the heating line is much larger than the film thickness, heat transfer across the PEDOT:PSS layer is 1-dimensional, and the cross-sectional thermal conductivity of the PEDOT:PSS is given by\(^4\):

\[
\kappa_\perp = P \cdot d_f / \left( w_h \cdot l_h \cdot \Delta T_f \right),
\]

(S3)

where \(d_f\) is the film thickness (measured by a Dektak profilometer) and \(w_h\) and \(l_h\) are the width and length of the heater line, respectively.

Supplementary Figure 6 | Cross-section of the sample geometry used for differential measurements of doping-dependent \(\kappa_\perp\). One region included a PEDOT:PSS film and another region (which acted as a reference) did not. 50 \(\mu\)m \(\times\) 2.6 mm gold lines (which each acted as both a heater and a thermometer) were patterned on top of a 40 nm thick electrical barrier layer of \(\text{Al}_2\text{O}_3\).
Supplementary Figure 7 | Measured temperature drop across the PEDOT:PSS layer. a–b. Temperature oscillation amplitudes of 50 μm heater on thin PEDOT:PSS film used for measurements of doping-dependent $\kappa_1$ (a), and thick PEDOT:PSS film used for measurements of pristine $\kappa_0$ (b). Temperature oscillations of the heater on the sample with PEDOT:PSS layer (circles) and the heater on the reference substrate (squares) are plotted. $\Delta T_i$ denotes the $2\omega$ temperature drop across the PEDOT:PSS layer.
Determination of in-plane thermal conductivity $\kappa_{\parallel}$

The centrifugal force applied during spin-coating has been shown to produce a microscale pancake-like morphology in PEDOT:PSS$^{5,6}$, which is expected to result in an anisotropic thermal conductivity. Since measuring $\kappa_{\parallel}$ in a very thin polymer film has numerous practical difficulties, relatively thick films were prepared by multiple spin-coatings that used the same conditions as those used for the thin films. Supplementary Fig. 8 shows schematic sample geometries for the in-plane thermal conductivity measurement. Anisotropy in heat transfer along the in-plane and cross-plane directions was measured by comparing $\Delta T_f$ between wide (50 $\mu$m) and narrow (2.1 $\mu$m for DMSO-mixed and 3.0 $\mu$m for EG-mixed) heating lines, the widths of which were measured by scanning electron microscopy. For the wide heater line, the assumption of 1D heat conduction across the PEDOT:PSS layer holds, and $\kappa_{\perp}$ was determined by the same process used in the previous section (see Supplementary Fig. 7b). For the narrow line, the heater width is comparable to the PEDOT:PSS film thickness, and considerable lateral heat spreading occurs, causing heat transfer to no longer be one-dimensional and $\Delta T_f$ (determined differentially by Eq. S1) to depend on both $\kappa_{\parallel}$ and $\kappa_{\perp}$.

Supplementary Figure 8 | Cross-section of the sample geometry used for differential measurements of $\kappa_{\parallel}$. Heaters of two different widths were employed to measure the ratio between lateral (in-plane) and vertical (cross-plane) thermal conductivities. A differential technique (similar to Supplementary Fig. 6) was used to isolate the temperature profile in the PEDOT:PSS layer.
Defining reduced temperature as the temperature drop across the film (ΔT₁) divided by the line heater heat flux, the ratio of the reduced temperatures associated with the wide (ΔT₁D) and narrow (ΔT₂D) heater lines can be expressed as:

\[
\frac{\Delta T_{2D}}{\Delta T_{1D}} = \left(\frac{\kappa_{\perp}}{\kappa_{\parallel}}\right)^{1/2} \frac{w_n}{d_f} \frac{K}{2K'},
\]

where \(w_n\) is the width of the narrow heater line and \(K(\lambda)\) and \(K'(\lambda)\) are the complete and complementary complete elliptical integrals of the first kind. The argument \(\lambda\) is given by:

\[
\frac{1}{\lambda} = \cosh \left[ \frac{\pi w_n}{4 d_f} \left( \frac{\kappa_{\perp}}{\kappa_{\parallel}} \right)^{1/2} \right].
\]

The reduced temperatures of the wide (ΔT₁D) and narrow (ΔT₂D) heater lines measured at different frequencies are shown in Figs. S8A and S8B. Their ratio (ΔT₂D/ΔT₁D) and measured value of \(w_n/d_f\) (2.427 for EG-mixed and 1.423 for DMSO-mixed) were fit to Eq. S4 in order to derive \(\kappa_{\parallel}/\kappa_{\perp}\) (Supplementary Fig. 9c). The error in \(\kappa_{\parallel}/\kappa_{\perp}\) is defined as its standard deviation over the given range of frequencies. For pristine EG-mixed PEDOT:PSS, the anisotropy ratio \(\kappa_{\parallel}/\kappa_{\perp}\) was found to be 2.30±0.47, which yields \(\kappa_{\parallel} = 0.52±0.11\) W/mK based on the measured value of \(\kappa_{\perp}\) (0.227±0.002 W/mK). For pristine DMSO-mixed PEDOT:PSS, the ratio \(\kappa_{\parallel}/\kappa_{\perp}\) was found to be 1.73±0.27, which yields \(\kappa_{\parallel} = 0.42±0.07\) W/mK based on the measured value of \(\kappa_{\perp}\) (0.242±0.002 W/mK). Note that the
cross-plane thermal conductivities for these thick films were found to be smaller than those of the thin films, which is expected as their decreasing layer thicknesses lead to an increase in interface density and hence a greater contribution from thermal boundary resistances.

Having thus measured the in-plane thermal conductivity of pristine PEDOT:PSS and the doping-dependent cross-plane thermal conductivity of 3-layer PEDOT:PSS, we calculate the thermal anisotropy factor ($\kappa_\parallel/\kappa_\perp$) of pristine 3-layer DMSO-mixed PEDOT:PSS as $1.40\pm0.22$ and that of pristine 3-layer EG-mixed PEDOT:PSS as $1.62\pm0.35$. Based on the expectation that dopants have an isotropic effect on thermal transport, we assume the thermal anisotropy factor to be constant with dedoping and use it to calculate doping-dependent $\kappa_\parallel$, which was then used to derive doping-dependent $ZT$.

Supplementary Figure 9 | Determination of the anisotropy in thermal conductivity. Reduced temperature associated with the wide line heater ($\Delta T_{1D}$) (squares) and narrow line heater ($\Delta T_{2D}$) (circles) in (A) EG-mixed and (B) DMSO-mixed PEDOT:PSS layers. (C) Ratio of the two reduced temperatures ($\Delta T_{2D}/\Delta T_{1D}$) (triangles) used to derive the anisotropy in thermal conductivity ($\kappa_\parallel/\kappa_\perp$).
Supplementary references


