Thermal Conductivity and Elastic Constants of PEDOT:PSS with High Electrical Conductivity

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ABSTRACT: Mixtures of poly(3,4-ethylenedioxythiophene) and polystyrenesulfonate (PEDOT:PSS) have high electrical conductivity when cast from aqueous suspensions in combination with a high boiling-point cosolvent dimethyl sulfoxide (DMSO). The electronic component of the thermal conductivity of these highly conducting polymers is of interest for evaluating their potential for thermoelectric cooling and power generation. We find, using time-domain thermoreflectance measurements of thermal conductivity along multiple directions of thick (>20 μm) drop-cast PEDOT films, that the thermal conductivity can be highly anisotropic (\(\Lambda_{\perp} \approx 1.0 \text{ W m}^{-1} \text{ K}^{-1}\) and \(\Lambda_{\parallel} \approx 0.3 \text{ W m}^{-1} \text{ K}^{-1}\) for the in-plane and through-plane directions, respectively) when the electrical conductivity in the in-plane direction is large (\(\sigma \approx 500 \text{ S cm}^{-1}\)). We relate the increase in thermal conductivity to the estimated electronic component of the thermal conductivity using the Wiedemann–Franz law, and find that our data are consistent with conventional Sommerfeld value of the Lorenz number. We use measurements of the elastic constants (\(C_{11} \approx 11 \text{ GPa}\) and \(C_{44} \approx 17 \text{ GPa}\)) of spin-cast PEDOT films and through-plane thermal conductivity (\(\Lambda_{\perp} \approx 0.3 \text{ W m}^{-1} \text{ K}^{-1}\)) of drop-cast and spin-cast films to support our assumption that the phonon contribution to the thermal conductivity does not change significantly with DMSO composition.

1. INTRODUCTION

Poly(3,4-ethylenedioxythiophene) (PEDOT) is an extensively studied conducting polymer due to its environmental stability, mechanical flexibility, low cost, tunable electrical conductivity, and solution processability.1,2 Recently, mixtures of PEDOT and polystyrenesulfonate (PSS) have been found to have large electrical conductivity in the in-plane direction when cast from aqueous suspensions in combination with high boiling-point cosolvents such as dimethyl sulfoxide (DMSO), making PEDOT:PSS a promising candidate for applications in thermoelectric energy conversion.3,4

The efficiency of a thermoelectric material is characterized by the dimensionless figure of merit ZT:\n
\[
ZT = \frac{\sigma S^2 T}{\Lambda_e + \Lambda_{ph}} = \frac{S^2}{L} \left( \frac{\Lambda_e}{\Lambda_e + \Lambda_{ph}} \right)
\]

(1)

where \(\sigma\) is the electrical conductivity, \(S\) is the Seebeck coefficient, \(T\) is the absolute temperature, \(\Lambda_e\) is the electronic component of the thermal conductivity, \(\Lambda_{ph}\) is the phonon contribution to the thermal conductivity, and \(L\) is the Lorenz number \(L = \Lambda_e/\sigma T\). All other things being equal, a small value of the Lorenz number enhances ZT.

In metals and highly doped semiconductors, the electronic component of the thermal conductivity is typically proportional to the electrical conductivity following the prediction of the Wiedemann–Franz law (WFL) \(\Lambda_e = L_0 T\). The Lorenz number \(L\) is typically observed to be within 20% of the Sommerfeld value \(L = 2.45 \times 10^{-8} \text{ W} \Omega^{-1} \text{ K}^{-2}\). Theoretical calculations show that the Lorenz number can be more significantly decreased when the bandwidth of the electron or hole dispersion is small.8 Anomalously small values of the Lorenz number have been reported in calculations (e.g., in InGaAs and InGaAlAs superlattices9) and measurements (e.g., in Pt nanowires10,11). However, there have been few studies of conducting polymers to determine if the electronic component of the thermal conductivity is proportional to the electrical conductivity or if the Lorenz number is unusually small or large.

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Salamon et al.\textsuperscript{12} found that the WFL is valid in tetrathiafulvalene—tetracyanoquinodimethane (TTF—TCNQ) and the Lorenz number is close to the Sommerfeld value. Mermilliod et al.\textsuperscript{13} reported that the increase of thermal conductivity in iodine-doped polycarbonate compared to that of a pristine polycarbonate is larger than what can be explained with an increase of the electronic thermal conductivity based on the Sommerfeld value of the Lorenz number.

In this work, thin ($\approx 65$ nm) spin-coated and thick ($>20$ μm) drop-cast PEDOT:PSS films are prepared with different electrical conductivities by systematically varying the concentration of the DMSO cosolvent. We used time-domain thermoreflectance (TDTR), an ultrashort laser-based pump—probe method,\textsuperscript{14} to measure the thermal conductivity and heat capacity. We use picosecond acoustics and surface acoustic waves to measure the elastic constants. The major contribution of this work is that we find the changes of thermal conductivity as a function of electrical conductivity in PEDOT:PSS films are consistent with the WFL and the Sommerfeld value of the Lorenz number.

2. SAMPLE PREPARATION

The PEDOT:PSS aqueous solution (Clevios PH1000 purchased from Heraeus) containing $\approx 1$ wt % PEDOT: PSS (1:2.5 weight ratio), was mixed with cosolvent DMSO (0−4 wt %). We used dynamic light scattering (DLS) to determine the average particle diameter in the as-received PEDOT: PSS aqueous dispersion, $\approx 19$ nm. Preliminary samples were prepared at the Molecular Foundry; data reported in this paper were acquired on samples prepared at UIUC. Relatively thick films ($>20$ μm) were formed by drop-casting the DMSO-mixed PEDOT:PSS solution onto a polydimethylsiloxane (PDMS) substrate (Sylgard 184, Dow Corning) with a droplet diameter $\approx 2.5$ cm. The droplet was then evaporated at 70 °C for $\approx 3$ h in air. For simplicity, we refer to these DMSO-mixed PEDOT:PSS films as PEDOT films unless the DMSO composition is needed. The drop-cast PEDOT film was then peeled off the PDMS substrate and cut into three pieces: (i) a square piece from the central part ($\approx 0.6$ cm $\times$ 0.6 cm $\times$ 25 μm), where the film thickness is relatively uniform, for electrical conductivity measurement; (ii) a piece ($\approx 0.6$ cm $\times$ 1.0 cm $\times$ 30 μm) for through-thickness thermal conductivity measurement; and (iii) a piece ($\approx 0.2$ cm $\times$ 0.5 cm $\times$ 40 μm) to embed in epoxy matrix for measuring the in-plane thermal conductivity.

We used the same procedure for embedding the PEDOT film in an epoxy matrix as described in our previous work on polymer fibers.\textsuperscript{15} The cross-sectional PEDOT film surface was then prepared by dry-cutting the epoxy matrix parallel to the cross-sectional PEDOT film direction using diamond blade ultramicrotomy (Leica EM UC6). We start the cutting with a large feed (1 μm) and a fast speed (200 mm/s) and then gradually change the conditions to a small feed (30 nm) and a slow speed (30 mm/s). During the dry-cutting, the PEDOT sections are constantly removed by compressed air to keep the blade clean.

Relatively thin PEDOT films ($\approx 65$ nm or $\approx 140$ nm) were spin-coated on a Si substrate with either $\approx 10$ nm or $\approx 315$ nm thermally grown oxides. To improve the uniformity of the spin-coat layers, the DMSO-mixed PEDOT:PSS aqueous solution was sonicated for 20 min and filtered by a syringe filter (0.2 μm pore-size, Nylon membrane) prior to spin-coating at 4000 rpm for 40 s. The sample was annealed on a hot plate at 130 °C for 15 min after each layer was spin-coated. PEDOT thin films with thickness of $\approx 65$ nm and $\approx 140$ nm were obtained by spin-coating once and three times, respectively.

The thickness of drop-cast PEDOT films $d$ was measured by profilometry; the thickness of spin-cast PEDOT films $d$ was measured by tapping-mode atomic force microscopy (AFM). The rms surface roughness derived from AFM measurements over a $15 \times 15$ μm$^2$ area are $3−6$ nm for drop-cast cross-sectional microtomed PEDOT films, $\approx 7$ nm for the surface of drop-cast PEDOT films, and $\approx 5$ nm for spin-cast PEDOT films. This satisfies the requirements of TDTR measurements, where typically an rms roughness of $<15$ nm is sufficient to avoid artifacts created by thermoelastic effects that modulate the intensity of diffuse light scattering.\textsuperscript{16}

3. MEASUREMENTS

3.1. Electrical Conductivity. The in-plane electrical sheet resistance of drop-cast and spin-cast PEDOT films was measured by a four-point probe station specially designed for measuring soft materials. The homemade circuit box places the sample film in series with a reference resistor. The voltage drops across the sample film and series resistor were measured using a high-impedance multimeter. The probe tip radius is 25 μm and the force on each tip is $\approx 0.4$ N. Since the PEDOT films have a finite area ($\approx 6 \times 6$ mm$^2$) for drop-cast films and $\approx 10 \times 10$ mm$^2$ for spin-cast films) compared to the tip spacing ($\approx 1$ mm), a correction factor is applied to the measured resistance.\textsuperscript{17} At least five measurements were done on the electrical resistance of each sample. The error bars are calculated by taking into account the uncertainty in the film thickness and the uncertainty in the multiple measurements of electrical resistance.

3.2. Thermal Conductivity. Prior to the TDTR measurements, Al thin films were deposited on the samples by magnetron sputtering. In TDTR, a mode-locked Ti:sapphire laser produces a train of pulses at a repetition rate of 80 MHz. A mechanical delay stage is used to change the optical path difference between the pump and probe before they are focused through an objective lens onto the sample surface. The pump beam is modulated at frequency $f$ so that the thermoreflectance change at the sample surface can be detected by the probe beam through lock-in detection. Further details on TDTR can be found elsewhere.\textsuperscript{14,16,18}

We used frequency-dependent TDTR\textsuperscript{18−20} to measure both the thermal conductivity $\Lambda$ and heat capacity $C$ of spin-cast films. This approach is based on the fact that the sensitivities of the measurement signal to $\Lambda$ and $C$ vary differently with $f$. At relatively high $f$, the film thickness $d$ is usually much larger than the thermal penetration depth in the sample $L = (\Lambda/\pi C)^{1/2}$ (\& $L$); in this case, the thermal effusivity of the film $(\Lambda C)^{1/2}$ governs the heat flow in the sample. At sufficiently low $f$, $d \ll L$, the thermal resistance $d/\Lambda$ governs the heat flow in the sample and the signal is more sensitive to $\Lambda$ and less sensitive to $C$. For intermediate modulation frequencies, the sensitivity of the measurement signal to $C$ crosses through zero.

We measured thin DMSO-mixed PEDOT spin-cast films ($\approx 65$ nm) with different DMSO compositions on a Si substrate with $\approx 10$ nm thermal oxide at three modulation frequencies, 2.0, 3.4, 9.8 MHz, with a $1/e^2$ radius of the focused laser beams of $w_0 = 11.7$ μm. For each sample, we simultaneously fit the TDTR ratio data at the three modulation frequencies to extract $\Lambda$ and $C$ of the PEDOT thin films. In the fitting, the heat capacities of Al and Si are adopted from literature values.\textsuperscript{1,22} The thickness of Al thin film was obtained from picosecond
acoustics using a longitudinal speed of sound 6.42 nm/ps. The thermal conductivity of the Al thin film was calculated using the WFL and the electrical resistance of the same transducer layer deposited on a ≈315 nm SiO$_2$ on Si reference sample.

To validate our measurement approach, a ≈100 nm-thick poly(methyl methacrylate) (PMMA) film was spin-cast on a silicon substrate and measured using a similar approach. The best-fit values are $\Lambda = 0.18 \pm 0.02$ W m$^{-1}$ K$^{-1}$ and $C = 1.7 \pm 0.2$ J cm$^{-3}$ K$^{-1}$, and the difference is within 5% as compared with the reported values of PMMA.

Figure 1 shows the geometry of TDTR measurements of through-plane and in-plane thermal conductivity of drop-cast PEDOT films. Through-plane thermal conductivity of drop-cast PEDOT films $\Lambda_\parallel$ was measured using TDTR at $f = 9.8$ MHz using a 5x objective lens ($w_0 \approx 11.7 \mu$m) and a sample configuration as shown in Figure 1a. The drop-cast PEDOT films are “thermally thick” under this measurement condition since $d \gg L$ ($d \approx 40 \mu$m and $L \approx 0.07 \mu$m). We assume the heat capacity of the drop-cast PEDOT films is the same as the spin-cast PEDOT films since these PEDOT samples were cast from the same DMSO-mixed PEDOT:PSS aqueous solution and should have similar spectra of vibrational modes.

To measure the in-plane thermal conductivity of the drop-cast PEDOT film $\Lambda_\parallel$, the film was embedded in an epoxy matrix as prepared by diamond blade microtomy as described above. This sample was then oriented so that the direction of the incident laser beam is parallel to the original plane of the drop-cast film. Heat propagates along the laser beam direction to create a heat flow in the original in-plane direction of the drop-cast film. We measured $\Lambda_\parallel$ at 9.1 MHz using both 10x ($w_0 = 6.7 \mu$m) and 20x objective lenses ($w_0 = 3.4 \mu$m). Because of the small laser spot size and substrate with low thermal conductivity used in this TDTR measurement, steady-state heating $\Delta T_{\lambda}$ of the probed region of PEDOT film limits the laser power that can be used in the measurement. $\Delta T_{\lambda}$ can be calculated by setting the modulation frequency to zero in the thermal modeling. We set the power of the pump and probe beam accordingly to maintain $\Delta T_{\lambda} < 30$ K. The largest $\Delta T_{\lambda}$ appears when measuring in-plane thermal conductivity of thick PEDOT films using 20x objective lens. The laser powers are reduced so that the pump and probe power absorbed in the transducer is ≈0.4 mW and ≈0.2 mW, respectively. The corresponding $\Delta T_{\lambda} \approx 27$ K when the thermal conductivity of PEDOT thick film is ≈0.3 W m$^{-1}$ K$^{-1}$. Lateral heat spreading in the Al film helps to reduce $\Delta T_{\lambda}$. Different laser powers were used in the measurements of in-plane thermal conductivity of PEDOT:PSS samples with different DMSO concentrations to maintain the similar $\Delta T_{\lambda}$. In comparison, the total laser power absorbed in the transducer when measuring spin-cast thin PEDOT films was ≈5 mW, which results in $\Delta T_{\lambda} \approx 3$ K.

The sensitivity of the data analysis to the interfacial thermal conductance $G$ of the Al-transducer/sample interface is small when the thermal conductivity $\Lambda$ is low. As shown in Figure 20 of ref 16, the ratio data are much less sensitive to $G$ in comparison to $\Lambda$ over the range of thermal conductivities (0.2 < $\Lambda < 1$ W m$^{-1}$ K$^{-1}$). This low sensitivity makes any attempt to fit the interface conductance highly susceptible to systematic errors but also reduces the propagation of errors from uncertainties in $G$ into uncertainties in $\Lambda$. The key parameter for determining this error propagation is the ratio of the sensitivities to the two parameters $S_G/S_\Lambda$. With decreasing $\Lambda$ and increasing $G$, the sensitivity ratio $S_G/S_\Lambda$ decreases, which reduces the error propagation from the uncertainty in $G$.

The interfacial thermal conductance can be determined reliably only when the thermal conductivity is high. Wang et al. reported that the interfacial thermal conductance between Al and a polymer fiber with the microtomed interface is $G = 52$ MW m$^{-2}$ K$^{-1}$. In the data analysis below, we therefore fix the interfacial thermal conductance between PEDOT and the Al transducer at $G = 50$ MW m$^{-2}$ K$^{-1}$. The error bars on the data points include the error propagation created by a wide range of values for the interfacial thermal conductance $G = 30 < G < 200$ MW m$^{-2}$ K$^{-1}$. Losego et al. reported $G > 200$ MW m$^{-2}$ K$^{-1}$ for interfaces between Al and extremely thin polymer films. Hsieh et al. also found a negligible effect of interfaces on the effective thermal conductivity of thin PMMA films. (We set the thermal conductance of the PEDOT/substrate interface to $G = 50$ MW m$^{-2}$ K$^{-1}$ but the sensitivity of the data to the PEDOT/Si interface is negligible except for measurements of the thinnest layers at low modulation frequency.)

The error bars of the TDTR measurements can be obtained by taking into account the individual uncertainties and sensitivities of the parameters in the thermal model. When measuring $\Lambda_\parallel$ of drop-cast PEDOT films, higher magnification objective lens (10x and 20x) were used, which results in larger error propagation compared with using 5x objective lens. For example, assuming a 5% uncertainty in beam spot size, errors in measuring thermal conductivity propagated from the uncertainty in the beam spot size are 0.6% using 5x, 2% using 10x, and 10% using 20x, respectively. In addition, the error bars of in-plane thermal conductivity also include the variations from the measurements done by different objective lenses and at different locations (at least three locations) on the sample surface, which is why the error bars are larger for in-plane thermal conductivity.

3.3. Elastic Constants. The elastic constants of spin-cast PEDOT films ($C_{11}$ and $C_{12}$) were measured using pump–probe techniques. $C_{11}$ is calculated from $p_0^2 f$, where the longitudinal speed of sound $v_L = 2d/t$, where $t$ was measured using the longitudinal acoustic echoes in a TDTR measurement on a ≈60 nm-thick spin-cast PEDOT film; The film density $\rho$ is calculated by determining the film composition and areal density of atoms (atoms per area) in the spin-cast PEDOT thin films using Rutherford backscattering spectrometry (RBS). For
example, in the 149 ± 5 nm spin-cast PEDOT film (the film thickness is measured by AFM), the areal density of C, S, O, and H atoms is 0.45 × 10^{18} \text{atoms/cm}^2, 0.06 × 10^{18} \text{atoms/cm}^2, 0.16 × 10^{18} \text{atoms/cm}^2, and 0.41 × 10^{18} \text{atoms/cm}^2, respectively, so the film density is 1.2 ± 0.1 g/cm^3.

C_{44} is determined from the velocity of surface acoustic wave (SAW) \( v_{\text{SAW}} \) measured for a Al(160 nm)/PEDOT(140 nm)/SiO2(315 nm)/Si layered structure. SAW are generated and detected in the pump–probe experiment using an elastomeric phase-shift mask made of PDMS. Conventional PDMS (Sylgard 184, Dow Corning) was cast and cured on a silicon substrate (700 nm periodicity, 50% duty cycle, and 350 nm groove depth) to make the mask. The mask spatially modulates the incident light intensity of the pump beam, thereby creating a periodic temperature profile and generating SAW. The mask also spatially modulates the sensitivity of the reflected intensity to surface displacements and enables detection of SAW.

We model \( v_{\text{SAW}} \) of the trilayer structure (Al/PEDOT/SiO2) numerically using a Green’s function method. The inputs to the model are elastic constants, density and thickness of each layer. The Al layer (\( C_{11} = 108 \text{ GPa}, C_{12} = 63 \text{ GPa}, C_{44} = 28.3 \text{ GPa}, \rho = 2.7 \text{ g/cm}^3 \)) is (111) textured film. The PEDOT film is modeled using two elastic constants, \( C_{11} \) and \( C_{44} \). \( C_{11} \) of PEDOT film is taken from the measured value on a ≈60 nm-thick film; \( C_{44} \) of PEDOT film is the adjustable parameter in the model. The substrate is treated as an semi-infinite amorphous SiO2 layer (\( C_{11} = 78 \text{ GPa}, C_{44} = 31.6 \text{ GPa}, \rho = 2.2 \text{ g/cm}^3 \)).

\( v_{\text{SAW}} \) of the PEDOT film is determined by adjusting \( C_{44} \) in the model to make the measurement of \( v_{\text{SAW}} \) match with the model prediction. The thicknesses of Al and PEDOT layers in the structure are optimized for the measurement of \( C_{44} \). If the PEDOT film is too thick (\( d \gg \lambda \), where \( \lambda \) is the wavelength of SAW), the PDMS mask can drastically affect the wave modes because PDMS and PEDOT have similar elastic constants. If the PEDOT film is too thin, the sensitivity of \( v_{\text{SAW}} \) to \( C_{44} \) is small. A relatively thick Al film (≈160 nm) is needed in the SAW measurement of a thin layer to optimize the sensitivity of \( v_{\text{SAW}} \) to \( C_{44} \). This is because the SAW velocity is relatively insensitive to elastic constants near the surface and more sensitive to the elastic constants at a depth on the order of \( \approx\lambda/\pi \). For a typical optimized geometry in our measurements (Al(160 nm)/PEDOT(140 nm)/SiO2(315 nm)/Si), the sensitivity of \( v_{\text{SAW}} \) to \( C_{44} \) of PEDOT film is ≈0.12.

We validated our approach using an Al/PMMA/Si stack and varied the thickness of the PMMA film between 50 to 450 nm. When the PMMA film is thinner than 200 nm, the measured \( v_{\text{SAW}} \) agrees with the predicted \( v_{\text{SAW}} \). When the PMMA film is thicker than 200 nm, multiple high frequency modes, which are clearly not the SAW of the sample, dominate the signal, indicating the failure of this approach when the polymer layer is thicker than 200 nm.

4. RESULTS AND DISCUSSION

Figure 2 shows the dependence of \( \sigma \) on the DMSO concentration in aqueous solution for drop-cast and spin-cast PEDOT films. Adding cosolvent DMSO significantly increases \( \sigma \), which is believed to act as a structural dopant for changes in the film morphology. In the PEDOT:PSS aqueous solution, the PEDOT molecules are bound to the PSS chains by ionic interactions and form core–shell micelles with a PEDOT-rich core and a PSS-rich shell. The addition of a high boiling-point polar solvent is thought to enable the reorganization of the conducting PEDOT molecules and the insulating PSS chains, leading to an interconnected network of elongated, densely packed, reoriented PEDOT molecules.

However, the increase of \( \sigma \) with DMSO concentration in drop-cast and spin-cast PEDOT films has different trends. In the drop-cast films, \( \sigma \) increases rapidly from \( \approx 0 \) to \( \approx 500 \text{ S cm}^{-1} \) when adding 0–1.2 wt % DMSO in the PEDOT:PSS solution and reaches a plateau with additional DMSO. The maximum electrical conductivity we obtained is lower than 945 S cm^{-1} on 3–10 μm-thick DMSO-mixed PEDOT:PSS films from ref 38: (open squares) \( \sigma \) reported in ref 39 for 5–8 μm-thick films prepared using 5 wt % DMSO (open squares); \( \sigma \) for spin-cast 120 nm-thick films from ref 40 (open circles); and \( \sigma \) for a spin-cast 130 nm-thick film from ref 41 (open circles).

For the TDTR measurement of thermal conductivity and heat capacity of spin-cast PEDOT films, we define a parameter \( \xi \), as in our previous work in measuring organic thin films, to quantify the goodness-of-fit. \( \xi \) is the sum of the standard deviation between the model prediction and measurement data at all three frequencies and delay times from 0.1 to 4 ns. Figure 3a shows the contour of constant \( \xi = 2\sigma_{\text{max}} \) (i.e., a 95%
thickness. Both \( C_{11} \) and \( C_{44} \) of spin-cast PEDOT films are independent of DMSO compositions within the uncertainty of our measurements. We find \( C_{11} \approx 11 \) GPa and \( C_{44} \approx 1.7 \) GPa.

These measurements of the elastic constants and through-plane thermal conductivity of spin-cast PEDOT films support our assumption that the phonon contribution to thermal conductivity in PEDOT films does not change significantly with DMSO composition.

Figure 5 shows \( \Lambda_{\parallel} \) and \( \Lambda_{\perp} \) of drop-cast PEDOT films as a function of \( \sigma \). \( \Lambda_{\perp} \) of the drop-cast layers does not change with \( \sigma \) and is consistent with \( \Lambda_{\perp} \) measured on spin-cast films. Thermal conductivity of the drop-cast PEDOT film is anisotropic with \( \Lambda_{\perp} \approx 2 \Lambda_{\parallel} \) when the PEDOT film is not electrically conductive. This result suggests that even in the absence of DMSO, the molecular alignment created during the evaporation process has a preferred direction parallel to the film surface. The anisotropy

Figure 4. Elastic constants \( C_{11} \) (dots) and \( C_{44} \) (squares) as a function of in-plane electrical conductivity \( \sigma \) of spin-cast DMSO-mixed PEDOT:PSS films. \( C_{11} \) is measured by picosecond acoustics; \( C_{44} \) is measured by velocity of surface acoustic waves. The dashed lines are the average values \( C_{11} \approx 11 \) GPa and \( C_{44} \approx 1.7 \) GPa. The uncertainties of \( \sigma \) are smaller than the size of the data symbols.

Figure 5. Through-plane (\( \Lambda_{\perp} \), fill circles) and in-plane (\( \Lambda_{\parallel} \), filled squares) thermal conductivity of drop-cast DMSO-mixed PEDOT:PSS films measured by TDTR as a function of in-plane electrical conductivity \( \sigma \) measured at \( T = \pm 325 \) K. \( \Lambda_{\parallel} \) of the drop-cast DMSO-mixed PEDOT:PSS films does not change with \( \sigma \) (dot line is the average value \( \Lambda_{\parallel} \approx 0.3 \) W m\(^{-1}\) K\(^{-1}\) ). \( \Lambda_{\parallel} \) of drop-cast DMSO-mixed PEDOT:PSS film increases from \( \Lambda_{\parallel} \approx 2 \Lambda_{\perp} \) for the pristine film to \( \Lambda_{\parallel} \approx 3 \Lambda_{\perp} \) for the DMSO-mixed film with the highest electrical conductivity. The Wiedemann–Franz law and Sommerfeld value of Lorenz number \( L_{o} \) plotted as a dashed line (\( \Lambda_{\parallel} = L_{o} T \)), is consistent with the variation of \( \Lambda_{\parallel} \) on \( \sigma \) assuming the phonon contribution to thermal conductivity \( \Lambda_{\parallel} \) is constant.

Figure 3. (a) Contour map derived from the goodness-of-fit for frequency-dependent TDTR data as a function of thermal conductivity \( \Lambda \) and heat capacity \( C \) for \( \approx 65 \) nm-thick spin-cast DMSO-mixed PEDOT:PSS films with different DMSO compositions (0–4 wt % DMSO; 0%, green; 1%, blue; 2%, red; and 4%, black), measured at \( T = 300 \) K. The contour for a validation measurement of a \( \approx 100 \) nm-thick PMMA sample is also shown. The contour lines represent 95% confidence level that the true values of \( \Lambda \) and \( C \) fall within the contour. (b) \( \Lambda \) as a function of in-plane electrical conductivity \( \sigma \) of spin-cast DMSO-mixed PEDOT:PSS films. The dashed lines are the average values \( \Lambda \approx 0.29 \) W m\(^{-1}\) K\(^{-1}\). The uncertainties of \( \sigma \) are smaller than the size of the data symbols.

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in the thermal conductivity increases with increasing in-plane electrical conductivity, reaching \( \Lambda_\parallel \approx 3\Lambda_\perp \) for the samples with the highest in-plane electrical conductivity.

We relate the increase in \( \Lambda_\parallel \) of drop-cast PEDOT films as a function of electrical conductivity to the estimated electronic component of the thermal conductivity using the WFL and the Sommerfeld value of the Lorenz number, \( \Lambda_\parallel = \Lambda_{ph} + \text{Le}T^2 \); we assume that the phonon component of the thermal conductivity \( \Lambda_{ph} \) is constant. This relationship is plotted in Figure 5 as dashed line. Our data are consistent with these assumptions. If we further assume that the Sommerfeld value of the Lorenz number also applies in the through-thickness direction, then we conclude that the through thickness electrical conductivity is much smaller than the in-plane electrical conductivity.

Kim et al.\(^4\) measured the anisotropic thermal conductivity of \( \approx 1.4 \) \( \mu \text{m} \)-thick spin-cast DMSO-mixed PEDOT:PSS film and found \( \Lambda_\parallel = 0.42 \pm 0.07 \text{ W m}^{-1} \text{K}^{-1} \) and \( \Lambda_\perp = 0.30 \pm 0.02 \text{ W m}^{-1} \text{K}^{-1} \) when \( \sigma \approx 620 \text{ S cm}^{-1} \), which suggests an anomalously small value of \( L \). Our data for drop-cast layers extrapolates to \( \Lambda_\parallel \approx 1.1 \text{ W m}^{-1} \text{K}^{-1} \) at this electrical conductivity, a factor of 2.5 higher than reported by Kim et al.\(^4\). If we use our measurements of thermal conductivity and the power factors \( \sigma^2 \) reported in ref 4, we estimate that the maximum \( ZT \) at room temperature of highly conducting PEDOT:PSS is \( ZT \approx 0.11 \) at a conductivity of \( \sigma \approx 900 \text{ S cm}^{-1} \).

Note: while our paper was under review, a closely related paper by Wei et al.\(^24\) was published. They demonstrated the anisotropic electrical conductivity and thermal conductivity of PEDOT: PSS films treated with 3 wt % ethylene glycol (\( \sigma_\parallel \approx 36 \text{ S cm}^{-1} \), \( \sigma_\perp \approx 820 \text{ S cm}^{-1} \)), \( \Lambda_\parallel = 0.15 \pm 0.04 \text{ W m}^{-1} \text{K}^{-1} \) and \( \Lambda_\perp = 0.84 \pm 0.33 \text{ W m}^{-1} \text{K}^{-1} \), which was measured on 100 \( \mu \text{m} \) and 3.5 mm-thick PEDOT: PSS films, respectively. They attribute the observed anisotropic thermal conductivity to the lattice contribution from PSS due to a more parallel-to-substrate chain orientation.

5. SUMMARY
We find that thermal conductivity of drop-cast DMSO-mixed PEDOT:PSS films is highly anisotropic when the electrical conductivity is large, in part due to a significant electronic contribution to the in-plane thermal conductivity. The changes of thermal conductivity as a function of electrical conductivity data are consistent with the Wiedemann–Franz law and the Sommerfeld value of the Lorenz number. Measurements of the elastic constants and through-plane thermal conductivity of spin-cast DMSO-mixed PEDOT:PSS films support the assumption that the phonon contribution to thermal conductivity does not change significantly with DMSO composition.

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