Improved Anisotropic Thermoelectric Behavior of Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) via Magnetophoresis

Vera A. Zarubin, Tai-De Li, Sunita Humagain, Haojie Ji, Kevin G. Yager, Steven G. Greenbaum, and Luat T. Vuong

ABSTRACT: There is strong demand for achieving morphological control of conducting polymers in its many potential applications, from energy harvesting to spintronics. Here, the static magnetic-field-induced alignment of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) particles is demonstrated. PEDOT:PSS thin films cast under modest mT-level magnetic fields exhibit a fourfold increase in the Seebeck coefficient and doubled electrical conductivity. Atomic force microscopy measurements confirm the presence of conducting islands that exhibit a 10-fold increase in the local charge carrier mobility and threshold behavior that is associated with phase separation. High-resolution scanning electron microscopy identifies a consistent structural coil-to-rod transition, and three-dimensional time-of-flight secondary-ion mass spectrometry imaging shows that the rodlike structures coincide with PEDOT domains that generally align with the magnetic field and cluster on the outer surface. Grazing-incidence small-angle X-ray scattering, Raman spectra, electron paramagnetic resonance, and circular dichroism spectroscopy point to the physical nature of the magnetophoretic alignment, which is expected to occur via magnetic coupling of PEDOT domains with polaron modes. Because casting under mT-level magnetic fields increases the electrical conductivity and Seebeck coefficient of PEDOT:PSS thin films without additional dopants that commonly limit the thermoelectric performance, our research reveals that low-field magnetophoresis significantly influences the structure and corresponding physical properties of PEDOT:PSS. Our results also point to concerns that the presence of small external magnetic fields in laboratory settings may appreciably and inadvertently influence the PEDOT:PSS morphology during settling, drying, or annealing processes.

INTRODUCTION

Conducting polymers (CPs) have attracted extensive attention as thermoelectric materials for low-grade waste heat recovery because of their low intrinsic thermal conductivity, large-area solution processability, and low processing cost for device fabrication. The mechanical toughness, flexibility, and elasticity of CPs point to an exciting range of heat-recovering applications for both soft and lightweight electronic devices. Moreover, CPs offer new routes to optimize thermoelectric efficiency because they are not limited by the Wiedemann–Franz law that dominates for inorganic materials, namely, that correlation between electrical and thermal conductivities are weak. Among CPs, significant attention is focused on poly(3,4-ethylene dioxythiophene) (PEDOT), which shows a relatively high thermoelectric figure of merit. The polymerization of PEDOT using the water-soluble polyelectrolyte
poly(styrene sulfonate) (PSS) facilitates the formation of a stable, aqueous dispersion of colloidal polymer particles, which has further advantages: in the colloid form, CPs may be inexpensively processed with industry-ready large-area methods such as inkjet printing, silkscreening, and spin-coating in ambient air. Moreover, the processing of PEDOT:PSS in aqueous dispersions avoids the environmental issues associated with volatile chemical emissions from organic solvents. Deeper understanding of the aggregation and phase separation of PEDOT:PSS is necessary to improve the control of colloid-to-bulk material properties for future polymer technologies.

Although commercial PEDOT:PSS aqueous dispersions are widely used, challenges remain in optimizing charge transport in solid-state structures. In PEDOT:PSS, electrical charges hop between the PEDOT-rich phases across the insulating PSS phase so that high variability in the processed morphology and physical properties of PEDOT:PSS leads to high variability in the electrical behavior. Solvent additives and film post-treatment with secondary dopants have been shown to improve the electrical conductivity of PEDOT:PSS by aligning PEDOT centers. However, this approach also decreases the effective Seebeck coefficient of the resulting CP. In order to enhance both electrical conductivity and Seebeck coefficient, top-down approaches involving serial processes and advanced microprocessing methods, such as etching and photolithography, have been employed.

Here, we show that the alignment and aggregation of PEDOT:PSS particles are influenced by the presence of low-level magnetic fields and that the magnetophoresis coincides with dramatic increases of the electrical conductivity, Seebeck coefficient, and PEDOT:PSS paramagnetic response. The low-level magnetic-field-induced alignment that is demonstrated here improves the physical properties of PEDOT:PSS, with the improvement being greater than that previously reported using secondary dopants. Along with the problems associated with the instability of the doping level, secondary dopants lead to a trade-off relationship between conductivity and Seebeck coefficient because the high doping levels move the Fermi level closer to the conduction band edge, thus reducing transport energy of charge carriers as a result, the population of charged carriers increases, whereas the average mobility decreases, resulting in a net decrease in the Seebeck coefficient. As an alternative to secondary dopants, magnetic assembly has been observed with high-level magnetic fields in PEDOT and block copolymers. The magnetophoresis of CPs remains underexplored; even though there is good understanding of the paramagnetic centers of PEDOT, morphological control with low-level magnetophoresis has not been studied.

Our results show an unusually low threshold for observing the onset of magnetophoresis; mT-strength magnetic fields lead to morphological changes in PEDOT:PSS that are identified by scanning electron microscopy (SEM) and time-of-flight secondary-ion mass spectrometry (TOF-SIMS) imaging, which coincide with a dramatic fourfold increase in the Seebeck coefficient and doubling of the electrical conductivity. We verify that the magnetophoresis arises from a paramagnetic response measured by electron paramagnetic resonance (EPR) and show that the change in morphology coincides with enhanced circular dichroism (CD) in the plane of the substrate or film, which may be useful in monitoring the changes in the nanocrystal morphology. The PEDOT:PSS colloids in films exhibit CD at oblique incidence to a larger degree after the films are prepared in magnetic fields. Our results not only show that applied magnetic field alters the spatial distributions of PEDOT and PSS but also suggest that the magnetophoretic alignment may occur via coupling of the paramagnetic moments of PEDOT centers because of the presence of polarons on PEDOT backbones. This investigation provides initial data, demonstrating critical properties to be further explored. Our work may be relevant to the magnetophoretic crystallization that is observed with organic materials and proteins.

## RESULTS

Thin films prepared under magnetic fields perpendicular to the film surface ("surface-perpendicular") exhibit through-plane agglomeration of PEDOT phases and dispersed rodlike PEDOT phases (Figure 1). The thin films prepared under magnetic fields parallel to the film surface ("surface-parallel") are also composed of rodlike PEDOT phases. However, with surface-parallel samples, the PEDOT rod phases are generally concentrated on the top surface and substrate surface. SEM images of the top surface show that in the absence of a magnetic field, PEDOT:PSS is composed of amorphous grains, which are replaced with rodlike structures when the thin films are exposed to magnetic fields of a few mT (Figure 1). Substrate-parallel samples are composed of rodlike PEDOT phases that are aligned in the direction of the applied magnetic fields under which the samples are dried. Substrate-perpendicular samples also exhibit rod patterns; however, in these samples, as could be expected by symmetry, the PEDOT phases appear dendritic from the top view and randomly dispersed. On the basis of coarse inspection of 100 imaged locations and 20 samples, the rodlike structures are approximately 5–10 μm in length. Moreover, on the outer surface, the presence of the rodlike phases appears to be as prominent in the substrate-perpendicular samples as in the substrate-parallel samples. Figure 1c,e is representative of the surface of the exposed film, though moderate variations in dendritic and random patterns appear across substrate-perpendicular samples.
The surface morphology correlates with experimentally measured changes in the electrical properties of PEDOT:PSS. We analyze the directionality of in-plane charge transport across the thin films by measuring the Seebeck coefficient $S$ and conductivity $\sigma$ as a function of $\theta$ (Figure 2). That is, we compare the direction of the electrical conductivity and thermoelectric effect as it relates to the direction of the applied magnetic field. The $S$ of 10 $\mu$V K$^{-1}$ for control samples is consistent with values reported by previous groups.\cite{21} Higher magnetic fields produce higher measured values in both $S$ and $\sigma$, as indicated by the colormap that distinguishes values measured for samples cast under 10 and 20 mT. Our experiments are limited by the strength of the magnetic field produced by a Helmholtz coil. When a PEDOT:PSS sample is dried adjacent to a permanent magnet with a maximum magnetic field of $B = 1$ T, we subsequently measure values of $S \approx 100$ $\mu$V K$^{-1}$. Unfortunately, because the magnetic field from the permanent magnet is not uniform across the sample, we are not able to correlate the parallel and perpendicular components of the magnetic field with the anisotropy induced in the measured values of the samples.

For substrate-parallel samples, we consistently measure peak values in $S$ and $\sigma$ when the thermoelectric and electrical measurements are aligned in the direction of the applied B-field or at $\theta = 90^\circ$ and $\theta = 270^\circ$ (Figure 2). For substrate-perpendicular samples, as expected, the measured values of $S$ and $\sigma$ do not depend significantly on $\theta$. We did not measure the samples at other angles regularly because the thermoelectric measurements appear to be sensitive to sample geometry. At measurement angles of $\theta = 45^\circ$, $135^\circ$, $225^\circ$, and $315^\circ$, or corner-to-corner angles, the measured values of $S$ and $\sigma$ on substrate-perpendicular samples appear slightly higher than the control but the uncertainty in these measurements is considerably larger. We attribute the larger error bars for corner-to-corner measurements to drying dynamics, as colloidal PEDOT:PSS drop-cast on glass tends to form deposits around the edges and corners of a sample.\cite{22}

Positive polarons or bipolarons present in the samples are the sources of the EPR signal.\cite{23,24,25} The narrower part of the control spectrum may be attributed to the presence of spinless bipolarons. The presence of 1/2 spin polarons in magnetic-field-treated PEDOT:PSS causes the broader line shape. These EPR measurements show that substrate-perpendicular samples have the highest radical concentration. The $g$ values of $\sim 2.0038 \pm 0.0001$ obtained for the samples here (Figure 3a) are comparable to those measured in previous studies done on PEDOT:PSS. The line width ($B_{pp}$) of the control sample is found to be 6 Gauss which increases to $\sim 17$ Gauss for magnetically treated samples. The EPR intensity (Figure 3b) is proportional to the corresponding radical concentrations. Through normalization with a standard 4-hydroxy-2,2,6,6-
tetramethylpiperidin-1-oxyl/toluene sample containing a known number of spins, the radical concentrations (spins/g) are computed. The radical concentration of PEDOT:PSS is larger for samples fabricated within the magnetic field (Table 1). We ascribe EPR differences to the changes of the thermoelectric performance of PEDOT:PSS.

Table 1. Radical Concentration and Line Width of Different PEDOT:PSS Samples

| sample                  | radical concentration (spins/g) | $B_{pp}$ (Gauss) |
|-------------------------|---------------------------------|------------------|
| control                 | $2.94 \times 10^{16}$           | 6                |
| substrate-perpendicular | $8.76 \times 10^{16}$           | ~17              |
| substrate-parallel      | $5.64 \times 10^{16}$           | ~17              |

The enhanced paramagnetic response shown in the EPR spectra is consistent with the CD measurements, where magnetically aligned films exhibit enhanced CD associated with polarons on the PEDOT backbone (Figure 3c–e). The control samples exhibit appreciable CD of one handedness when samples are tilted at $45^\circ$ to the incident light. The magnitude of the CD at $45^\circ$ increases by almost 30% with surface-parallel and surface-perpendicular samples. At normal incidence for the control samples, the CD is negligible. In contrast, there is a consistent and non-negligible CD at normal incidence with the magnetically treated samples, which is larger for the surface-perpendicular samples. The CD measurements indicate that PEDOT:PSS exhibits a handedness, which is intrinsic to the PEDOT:PSS polarons, and as such, the CD signal is only subtly enhanced after fabrication under magnetic fields. We expect that the PEDOT backbones disentangle and rearrange to form rods under the magnetic field, undergoing a coil-to-rod transition of PEDOT while preserving the helicity of the PSS moiety. Circularly polarized light does not fully couple into the handedness when light is directed perpendicular to the rods, evidenced by the significantly enhanced CD signal when the sample is tilted from normal incidence. It appears that a small portion of the rods may also be perpendicular to the substrate because there is non-negligible CD in the samples at normal incidence.

The mechanisms pinpointed by EPR and CD are physical in nature, as the Raman peaks do not shift for magnetically treated samples (Figure 4a). Rather, the magnetic fields affect the orientation and arrangement of the molecules, but not their chemical bonds or molecular structures. Grazing-incidence small-angle X-ray scattering (GIWAXS) is used to measure the structural order averaged over wide film areas. The GIWAXS scattering patterns exhibit several scattering features characteristic for PEDOT:PSS (Figure 4b–d), including a diffuse isotropic rings at $q \approx 1.8$ Å$^{-1}$, that are ascribed to the chain packing distance (aromatic ring stacking of PSS at $q \approx 1.3$ Å$^{-1}$, and PEDOT at $q \approx 1.7$ Å$^{-1}$), and broad peaks oriented out-of-plane ($q_\perp \approx 0.3$ Å$^{-1}$) arising from lamellar ordering. The scattering patterns for control and magnetically ordered materials are broadly similar, with minor intensity variations that are roughly similar to the intensity variation that was measured on nominally identical samples. The variation in overall scattering intensity likely arises from small differences in sample preparation (e.g., film thickness) or sample measurement (e.g., the grazing-incidence alignment). The features within scattering patterns, including peak positions and angular distributions, are nearly identical for control and magnetically ordered samples, suggesting broadly similar structural ordering in these different samples. We note that GIWAXS measures the overall/average molecular structural order, and the signal is thus dominated by the preponderant structural motif. In combination with the results presented above, this suggests that the role of the magnetic field is to reorder the microscale morphology of the material (as imaged by TOF-SIMS) without significantly altering the local molecular packing motifs (as probed by GIWAXS).

Although chemical and morphological differences between control and magnetically treated samples appear subtle, the electrical mobility of the conducting agglomerations is dramatically elevated in the magnetically treated samples (Figure 5). Atomic force microscopy (AFM) current maps indicate that the maximum current for a fixed bias voltage is 10 times greater for the magnetically treated samples (Figure 5). The AFM-measured enhanced conductivities, measured perpendicular to the PEDOT:PSS film, are consistent with the enhanced two-point probe measurements made along the film surface (Figure 2). AFM measurements also point to nonlinear electrical behavior of the PEDOT:PSS samples, which warrant further study (Figure 5). The local through-plane charge carrier behavior of the PEDOT-rich phases is shown. The $I$–$V$ curves are dependent on the direction of the swept voltage bias, and the behavior is also distinctly different for magnetically treated PEDOT:PSS. The magnetically treated samples exhibit breakdown behavior characteristic to p–n junctions, whereas the control samples exhibit linear $I$–$V$ characteristics that are resilient to breakdown. For the magnetically treated samples, the breakdown voltage is different depending on the direction swept. We expect that the strong threshold behavior in the magnetically treated samples is associated with phase separation of conducting PEDOT and insulating PSS domains. The electrical current is expected to simultaneously produce and be influenced by the paramagnetic response.

### DISCUSSION AND SUMMARY

We anticipate that the imaged rodlike microscale PEDOT domains correspond to the conformal coil-to-rod transition, phase separation, and aggregation of PEDOT:PSS via...
magnetoresistance. The PEDOT microstructures coincide with increased values of $S$ and $\sigma$ on the outer surface, particularly when the rodlike formations are aligned in the direction of measurement. However, our results may not be surprising because other groups have observed a magnetophoretic effect coinciding with enhancements of the electrical conductivity, only at higher field strengths (>0.5 T). Magnetic assembly has also been demonstrated by the template approach with iron oxide nanoparticles.

We anticipate that there are two stages of the magnetic field on the assemblies of polymer particles. In one stage, which is more established and more easily understood, polymer complexes respond to the applied magnetic field because of their paramagnetic susceptibilities derived from polarons. The PEDOT:PSS phases align and migrate in order to minimize their energy $E = -\mu B$, where $\mu$ is the magnetic moment of the dipole and $B$ is the magnetic flux density. Indeed, the molar paramagnetic susceptibility of PEDOT:PSS is small but significant and has been estimated with EPR to be $6.0 \times 10^{-5}$ emu mol$^{-1}$. By symmetry, we expect that if thin films would carry the same composition of anisotropic rodlike PEDOT domains whose conductivity was solely determined by the rod alignment, then substrate-parallel samples and substrate perpendicular samples should exhibit the same average values of $S$ and $\sigma$ across all angles. However, this is not the case: values of $S$ and $\sigma$ in the surface-perpendicular samples are lower than expected, suggesting that the dendritic assemblies of PEDOT rods suppress in-plane hopping mechanisms and charge transport. It is not only the direction of the rodlike domains that determine macroscopic electrical properties but also their relative clustering and network across the top surface.

The high anisotropy of the Seebeck coefficient due to domain orientation does not contradict findings of previous groups. Although the Mott equation suggests that the Seebeck coefficient is independent of grain orientation, the Seebeck coefficient shows substantial spatial dependence in anisotropic systems of gold nanowires, bismuth telluride, and tin selenide. For conjugated polymers, charge mobility is highest along the chain direction and the $\pi$-stacking direction and negligible along the alkyl side chains. When the semi-conducting backbone aligns with the magnetic field, mobility is suppressed perpendicular to the backbone in the direction of the insulating alkyl side chains. Furthermore, for substrate-parallel samples, the rodlike PEDOT domains in the in-plane direction may lead to a carrier localization length larger than the molecular spacing, which would result in a high in-plane conductivity.

Evidence of the conformational changes in shape/morphology is supported by the increased spin concentration and excitation and shown in EPR, CD, and AFM measurements. Our experimental PEDOT:PSS samples exhibit broadly negative CD at non-normal incidence, which is derived from the polaron band and the partially coiled or helical structure of PEDOT:PSS. We expect that the CD is only visible at non-normal angles of incidence because the polymer rods are aligned largely parallel to the plane of the substrate; therefore,
in order to excite the polarons and tune into the handedness of the PSS moiety, light needs to illuminate the sample at an oblique angle. With magnetically treated samples, we observe a stronger CD measurement, indicating that strong paramagnetic polarons on the PEDOT chains are excited. AFM $I−V$ measurements point to nonlinear electrical behavior of the PEDOT:PSS samples associated with the mobility-coupled paramagnetic response and PEDOT:PSS phase separation, which warrant further study.

SEM, TOF-SIMS, and GIWAXS data indicate that the low-level magnetic fields induce the strongest morphological changes at the surface of the polymer thin film. The structural ordering of conducting PEDOT domains observed under SEM appears to be concentrated on the top surface from the 3D TOF-SIMS images. The complementary GIWAXS measurements average over the entire film thickness. The strong similarity of GIWAXS data for control and magnetically ordered samples suggests that the changes in molecular packing induced by a magnetic field are small compared to the bulk ordering. The results indicate that the magnetophoresis takes effect from the outside and propagates inward. Magnetophoresis with CPs may occur more readily in the absence of surface pinning effects, when viscosity is lower, or when the colloidal diffusion is higher. Further research into the magnetophoretic spatiotemporal dynamics may provide new approaches for large-area nanostructuring and microstructuring of PEDOT:PSS.

It is important for us to mention that we conducted experiments at a variety of temperatures with different homemade Helmholtz coils and comparable-temperature control samples. Given that similar morphological effects are observed when PEDOT:PSS samples are dried on a permanent magnet, for example, we confirm that the coil-to-rod transition is not a thermal effect. The magnetophoretic behavior of CPs remains largely overlooked and underexplored; however, several connections between prior efforts and our preliminary measurements are made. The helicity of PEDOT:PSS is associated with the broadly negative CD and paramagnetic response that we measure, which depends on and is controlled by processing techniques. The connection to and relation between these properties and low-level magnetophoresis deserve further study.

The PEDOT aggregation induced via magnetophoresis appears distinctly different from the morphological changes that are induced via chemical additives. Those chemically induced changes in PEDOT:PSS, which have led to improvements in the thermoelectric response comparable to what we measure, have been successfully correlated with Raman scattering and GIWAXS data. However, Raman scattering measurements pumped at 532 nm currently do not discern distinct chemical changes, and GIWAXS does not indicate new crystal structures that are not previously present in the control samples. Because TOF-SIMS data show that the alignment of PEDOT-rich domains are dramatic with magnetically treated samples, we infer that the effect of the magnetic field is to rearrange and separate PEDOT and PSS phases in randomly dispersed aggregations at the nanoscale.

In conclusion, low-level magnetophoresis is demonstrated as a viable bottom-up approach to assemble PEDOT:PSS thin films. Overall, a fourfold increase in the thermoelectric Seebeck coefficient and doubled measurements of the electrical conductivity is achieved. It appears from the TOF-SIMS images that the PEDOT phase may separate more distinctly from the PSS phase when the CP settles in the presence of the applied magnetic field. We furthermore attribute coil-to-rod alignment and aggregation into channels because of the CP paramagnetic centers. The alignment and aggregation of PEDOT into channels result in an anisotropic enhancement of the electrical conductivity. The conductivity increases in the direction of the applied magnetic field. Because the Raman and GIWAXS measurements do not identify the presence of new spatial or spectral features, we expect that the effect of the applied magnetic field is to rearrange intermolecular bonds that are already present in a manner that improves charge transport. The transport appears to be nonlinear and influenced by the magnetophoretic alignment because AFM measurements indicate that the current depends on the direction of the electrical bias. We speculate that higher magnetic fields will lead to deeper morphological changes that others have observed. The enhancement of electrical transport properties in the direction of the previously applied fields points to magnetic-field-induced alignment, phase separation, and aggregation within PEDOT:PSS, which are strongest at the thin-film surface.

## EXPERIMENTAL SECTION

**Fabrication of Thin Films.** The aequous dispersion of PEDOT:PSS (Sigma-Aldrich electronic grade in water, 0.5% PEDOT, 0.8% PSS wt) is placed in a glass vial, sealed with a parafilm, and sonicated for 10 min. Plastic substrates (Pella 2225, 22 × 22 × 0.18 mm, polyvinyl chloride) are rinsed with deionized water, blown dry with nitrogen, and plasma-cleaned in a vacuum chamber (Harrick PDC-362) for 5 min. The substrate is placed in the center of a Helmholtz coil with field lines oriented perpendicular or parallel (Figure 1) to the substrate and a strength of 10 or 20 mT. A glass volumetric pipette is used to deposit 400 μL of PEDOT:PSS on the center of the substrate. Because of resistive heating of the Helmholtz coil, the air temperature 1–2 mm above the sample surface is approximately 25–27 °C (time-averaged), measured with two thermocouples (Omega HH309a Datalogger Thermometer). Control samples are produced at ambient air conditions with heated Peltier tiles to provide equivalent conditions of 25–27 °C 1–2 mm above the sample surface (Figure 1). All samples are thermally annealed at 50 °C for 1 h in an oven to remove residual water (Hotpack Vacuum Oven).

**TOF-SIMS Measurement.** 3D chemical distribution maps of PEDOT:PSS films are obtained by TOF-SIMS imaging (nanoTOF II, Physical Electronics). The MW of PEDOT is estimated to be 41 g/mol. The primary analysis ion is 20 kV Ga+, and the depth profile sputtering gun is a giant cluster ion beam (Ar+ 2500, 20 kV). During SIMS measurement, the surface charge is neutralized with low-energy electron gun and gas gun (Ar+). The analysis area is 300 × 300 μm², and the sputtering area is 500 × 500 μm² to ensure that the analyzed area is uniformly sputtered. The measuring pressure is under ultrahigh vacuum (~10⁻⁶ Pa). The thickness of the film is measured by a stylus profilometer (Bruker Dektak-XT) to be 4 μm, and the sputter rate is back-calculated with the thickness. The ITO coating is grounded to the metal sample holder with silver paste.

**Electrical Conductivity and Seebeck Coefficient Measurement.** The electrical sheet resistance $R$ of the PEDOT:PSS films is determined using gold point probes as electrodes and a Keithley 2611A SourceMeter. The electrical conductivity ($\sigma$) is given
\[ \sigma = \frac{L}{R t W} \]

where the sample has a resistance \( R \), thickness \( t \), length \( L \), and width \( W \). The average \( t \) of the samples is determined from cross-sectional views under SEM to be 200 ± 5 μm. The Seebeck coefficient \( (S) \) of the PEDOT:PSS film is obtained from the slope of the graph of \( \Delta V \) as a function of \( \Delta T \)

\[ S = \frac{\Delta V}{\Delta T} \]

The temperature difference \( \Delta T \) is produced across the sample by two Peltier modules and measured by two thermocouples (Omega HH309a Datalogger Thermometer). The induced voltage difference \( \Delta V \) is measured by two probes of a fixed distance (Keithley 2182A Nanovoltmeter).

**EPR Measurement.** The samples are cut in small rectangular pieces (\( \sim 100 \times 30 \text{ mm}^2 \)) and packed in 4 mm quartz tubes to perform EPR measurements. Spectra are measured at room temperature with a Bruker EMX EPR spectrometer operating at X-band frequency (9.74 GHz), modulation frequency of 100 MHz with an amplitude of 3 G, 81.92 ms conversion time, and 20.48 ms time constant. The background effect of the glass substrate has been removed in the given spectra. The modulated and phase-sensitive-detected output signal is the first derivative of the absorption spectrum. Spin concentrations are therefore computed as the double integral of the output signal.

**CD Measurement.** CD measurements of the PEDOT:PSS films are performed with white light from a Newport xenon solar simulator. The circularly polarized light is generated with an achromatic linear polarizer and a broadband quarter-wave plate (\( \lambda/60 \) retardance accuracy) that is connected to a Thorlabs motorized rotation stage (PRM1Z8). The samples are also connected to a motorized rotation stage to control the motion within 10⁻³ degrees. The transmitted light is captured via a CCD, fiber-coupled spectrometer (Filmetrics F20-UV).

**Raman Spectra Measurement.** A Renishaw InVia micro-Raman system is used to measure the Raman spectra of the PEDOT samples. The laser excitation is at 532 nm, and the laser is linearly polarized. The focused laser spot size is 1 μm in diameter after a 50x objective and has a laser intensity less than 8000 W/cm² in order to avoid sample damage. Raman spectra are centered at 1300 cm⁻¹ and are measured with 1 s integration time, averaging every minute.

Samples are placed perpendicular to the laser pump and angled 45° with respect to the input laser. Samples are tested with different orientations with respect to the laser pump polarization. Substrate-parallel samples are rotated so that the laser polarization is characterized both parallel and perpendicular to the direction of the applied magnetic field used to cast samples.

**GIWAXS Measurement.** GIWAXS experiments are performed at the complex material scattering (11-BM) beamline at the National Synchrotron Light Source II. An X-ray energy of 13.5 keV (X-ray wavelength 0.9184 Å) is selected using a multilayer monochromator; a beam size of 200 μm (horizontal) by 50 μm (vertical) is obtained using a two-slit system. Two-dimensional X-ray scattering data are collected on a fiber-coupled CCD area detector positioned 230 mm downstream of the sample. Conversion of data into reciprocal space is accomplished by measuring a silver behenate powder as a calibration standard. In the presented data, the \( q_x \) direction is defined to be the film normal direction, whereas \( q_y \) is the orthogonal direction within the film plane. Data presented here are collected at an incidence angle of 0.2°, which is above the critical angle of the PEDOT:PSS materials and thus probes the entire thickness of the polymer films.

**AFM Measurement.** Surface topography and conductivity (current) maps of the PEDOT:PSS films are measured using AFM (Multimode 8, Bruker) in the conductive (C-AFM) mode. In brief, a conductive AFM probe (SCM-PTSI, Bruker) is scanning and in contact with the sample surface at a constant force, whereas a constant voltage bias is applied to the sample. The height and current signals are recorded by the conductive probe simultaneously. The local \( I-V \) curves are measured with the same conductive AFM probe under the same constant-force contact at single individual positions on aggregations and uniform flat surface.

**AUTHOR INFORMATION**

**Corresponding Author**

*E-mail: luatv@ucr.edu (L.T.V.).

**ORCID**

Vera A. Zarubin: 0000-0003-4708-2253

Kevin G. Yager: 0000-0001-7745-2513

Luat T. Vuong: 0000-0002-0652-4214

**Notes**

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V.A.Z. made samples and completed SEM, electrical, and CD measurements. L.T.V. and V.A.Z. analyzed data and wrote the paper. T.-D.L. completed AFM and TOF-SIMS measurements. H.J. completed Raman scattering studies. S.H. and S.G.G. completed EPR studies. K.G.Y. completed GIWAXS studies. This research used resources of the Center for Functional Nanomaterials and the National Synchrotron Light Source II, which are U.S. DOE Office of Science Facilities, at Brookhaven National Laboratory under Contract no. DE-SC0012704. Authors gratefully acknowledge funding via NSF DMR 115-1783 and 1709446 and CBET 1604504.

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