Tuning the Thermoelectric Properties of a Conducting Polymer through Blending with Open-Shell Molecular Dopants

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S *Supporting Information*

ABSTRACT: Polymer thermoelectric devices are emerging as promising platforms by which to convert thermal gradients into electricity directly, and poly(3,4-ethylene dioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS) is a leading candidate in a number of these thermoelectric modules. Here, we implement the stable radical-bearing small molecule 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO−OH) as an intermolecular dopant in order to tune the electrical conductivity, thermopower, and power factor of PEDOT:PSS thin films. Specifically, we demonstrate that, at moderate loadings (∼2%, by weight) of the open-shell TEMPO−OH molecule, the thermopower of PEDOT:PSS thin films is increased without a marked decline in the electrical conductivity of the material. This effect, in turn, allows for an optimization of the power factor in the composite organic materials, which is a factor of 2 greater than the pristine PEDOT:PSS thin films. Furthermore, because the loading of TEMPO−OH is relatively low, we observe that there is little change in either the crystalline nature or surface topography of the composite films relative to the pristine PEDOT:PSS films. Instead, we determine that the increase in the thermopower is due to the presence of stable radical sites within the PEDOT:PSS that persist despite the highly acidic environment that occurs due to the presence of the poly(styrenesulfonate) moiety. Additionally, the oxidation−reduction-active (redox-active) nature of the TEMPO−OH small molecules provides a means by which to filter charges of different energy values. Therefore, these results demonstrate that a synergistic combination of an open-shell species and a conjugated polymer allows for enhanced thermoelectric properties in macromolecular systems, and as such, it offers the promise of a new design pathway in polymer thermoelectric materials.

KEYWORDS: *polymer thermoelectrics, poly(3,4-ethylene dioxythiophene) doped with poly(styrenesulfonate) (PEDOT:PSS), stable radical species, open-shell molecular doping, nitroxide radicals*
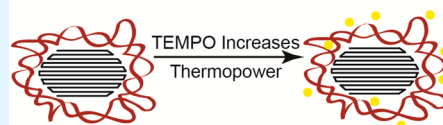
Electrically active macromolecules have been rigorously investigated in recent years because of their potential application in the next generation of environmentally friendly, flexible thermoelectric modules.[1−4] In addition to the direct positive impacts thermoelectric modules could have regarding the global energy landscape, devices fabricated from these organic materials have distinct advantages over many of their inorganic counterparts in that they are often composed of highly abundant materials, and they can be processed from solution using low-temperature, high-throughput (and, thus, potentially low-cost) processing conditions.[3−7] The utility of these thermoelectric materials is often compared through the direct measurement of the parameters contained within the dimensionless figure of merit (zT), as the figure of merit helps to define the upper limit of thermoelectric module performance.[8,9] Specifically, this value can be expressed as the product of three key parameters.

$$zT = \frac{S^2 \sigma}{\kappa} T \qquad (1)$$

Here, S is the thermopower (or Seebeck coefficient) of the material, σ is the electrical conductivity, κ is the thermal conductivity, and T is the average absolute temperature between the hot side and cold side of the device. Polymeric materials offer an attractive starting point for the tuning of these critical parameters because of the inherently low thermal conductivity (including a deviation from the Wiedemann−Franz law normally observed in inorganic materials) typically associated with most macromolecular species.[5] In fact, it is because of this thermally insulating nature that the majority of thermoelectric performance enhancements in electrically active polymers may be attributed to increases in the thermoelectric power factor ($S^2\sigma$).[9,10] While organic materials are capable of competing with the electrical conductivity of several leading inorganic thermoelectric materials, the Seebeck coefficient of many of the highest electrically conductive polymers falls significantly below the corresponding thermopower of their inorganic counterparts.[8] This dearth of thermopower in organic systems results in thermoelectric power factors that are several orders of magnitude below leading inorganic materials. While this has been addressed, in part, through optimizing processing conditions organic thermoelectric systems, most of the previous work has focused almost exclusively on enhancing the power factor through increases in electrical conductivity.[5,10,11]

However, to realize the full potential of macromolecular thermoelectric materials, it is necessary to implement the less-used strategy of thermopower enhancement in order to establish the ability to manipulate the thermoelectric power factor of the conducting polymer. Here, we demonstrate that the addition of small molecules bearing stable radical groups is able to alter the Seebeck coefficient of an oft-used electrically conductive macromolecule, and that this creates a nearly 2-fold enhancement of the power factor of the conducting polymer thin film without needing to invoke an increase in electrical conductivity.

Currently, the champion polymer thermoelectric material is poly(3,4-ethylene dioxythiophene) doped with poly-(styrenesulfonate) (PEDOT:PSS).[1,5,10,11] In this hole-transporting (p-type) system, charge transport is facilitated through small crystalline domains of the conjugated polymer PEDOT while the PSS simultaneously serves to electrically dope (oxidize) the PEDOT moiety, as well as to disperse the otherwise insoluble PEDOT in an aqueous medium.[12] And, while this PSS-induced oxidation of the PEDOT enhances the electrical conductivity, it is well-established that a large degree of oxidation in the PEDOT species has a deleterious effect on the thermopower of the system.[3] This general trend in the competition between the thermopower and the electrical conductivity of thermoelectric materials is due to the reduced energy difference between the average charge carrier energy and the Fermi energy. That is, as charge carrier density (and, thus, the electrical conductivity) increases, charge carriers exhibit a higher degree of symmetry around the Fermi level, which lowers the thermopower.[8]

The small molecule open-shelled additive utilized in this work, 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO−OH), partially addresses this issue through the use of a stable and molecularly localized nitroxide radical. Previously, both the highly robust nature of this stabilized radical site and its ability to undergo oxidation have been well-characterized.[13,14] In addition to its high potential for one electron chemistry, the highly polar nature of the TEMPO−OH molecule allows for direct incorporation into the water-based PEDOT:PSS suspension. In this way, we are able to tune discrete variations in the PEDOT:PSS-based thermoelectric inks in order to establish the effect of the open-shell molecule on the thermoelectric properties of PEDOT:PSS in a systematic manner. Specifically, we demonstrate that the incorporation of TEMPO−OH to a PEDOT:PSS thin film at low (<30% TEMPO−OH, by weight) loadings enables the composite material to have a better thermoelectric response than pristine films of PEDOT:PSS. Furthermore, the clear and predicable changes induced through the incorporation of TEMPO−OH into the polymer blend are well-explained through a mechanism that mainly involves the selectively scattering of holes after encountering the TEMPO−OH additive. Additionally, there is a slight effect associated with the mild oxidation of the TEMPO−OH species by the PEDOT:PSS blend, which has the potential to impact the thermoelectric properties (to a lesser extent) as well (vide infra). These new physical insights provide a means by which to utilize open-shell dopants to tailor the transport of thermo-electrically active conjugated polymers. In particular, the maximum power factor for the composite system occurs at 2% (by weight) TEMPO−OH loading, and represents significant increase over the pristine PEDOT:PSS thin film. Furthermore, the extent of the reaction of the radical site within

TEMPO−OH is observed through the emergence of a peak associated with reduction of PEDOT, within the casting solution. Additionally, the existence of TEMPO−OH radicals is confirmed through analysis of radical density in the solid film through electron paramagnetic resonance (EPR) spectroscopy. The combined effects of selective hole scattering, and partial dedoping of the PEDOT moiety creates shifts in the characteristic electrical transport temperatures of the composite materials. Finally, atomic force microscopy (AFM) and grazing-incidence X-ray diffraction (GI-XRD) measurements indicate that these phenomena are chemical in nature and are not related to the topographical or crystalline nature of the composite thin films relative to the pristine PEDOT:PSS thin film. As such, we are able to establish that manipulating the chemistry of the thermoelectric polymer thin films allows for marked enhancements in both the thermopower and power factor of a high-performing thermoelectric macromolecule. This key design paradigm will prove useful in the manipulation of the chemical structure of future generations of thermoelectric polymers with both closed and open-shell macromolecular architectures, as it differs significantly from previous attempts to increase the thermopower of PEDOT:PSS thin films through postprocessing treatments.

Small molecules bearing stable radical groups have been of immense utility in a number of organic electronic applications (e.g., magnetic devices,[15] spin-controlled valves[16]); however, the implementation of these functional materials in thermo-electric devices has not been established. This is despite the fact that having a very well-defined, low dispersity transport level has been predicted to yield materials with remarkably high thermopower values in single molecule systems.[17,18] Furthermore, filtering of low energy holes by incorporating another material with a transport level further removed from vacuum (resulting in an average charge carrier energy further from the Fermi level) has been shown to increase thermopower.[19] Because open-shell systems have only a singularly occupied molecular orbital (SOMO) energy level, they present themselves as a means by which to obtain this idealized system (i.e., a system where there are no tails to the transport energy levels, which are present in conjugated electrically active polymers).[13] Here, the TEMPO−OH group was intentionally selected due to the fact that the SOMO level is moderately more removed from vacuum than that of the transport level of PEDOT:PSS (5.1 eV).[20] The energy level of this SOMO was confirmed to be 5.4 eV through cyclic voltammetry measurements and well-established theory (Figure 1a).[21] The combination of these two effects should increase the Seebeck coefficient of the composite films relative to pristine PEDOT:PSS. In fact, it is demonstrated that the inclusion of the open-shell TEMPO−OH species nearly doubles the thermopower of pristine PEDOT:PSS (Figure 1b). In these systems, PEDOT:PSS and TEMPO−OH were codissolved in water to produce a well-dispersed mixture; this mixture was then cast into a thin film readily using a simple blade coating technique. Specifically, the increase in thermopower becomes apparent at very low loadings, as low as 2% TEMPO−OH by weight (resulting in a thermopower of 22 μV K^{-1} compared to 14 μV K^{-1} for pristine PEDOT:PSS at an average temperature of 313 K). The thermopower values of the composite materials peak around 5% TEMPO−OH loading by weight, and the composite materials do not exhibit substantial thermopower increases at higher loadings of TEMPO−OH (Figure 2a). As expected, the carrier type of the composite film does not
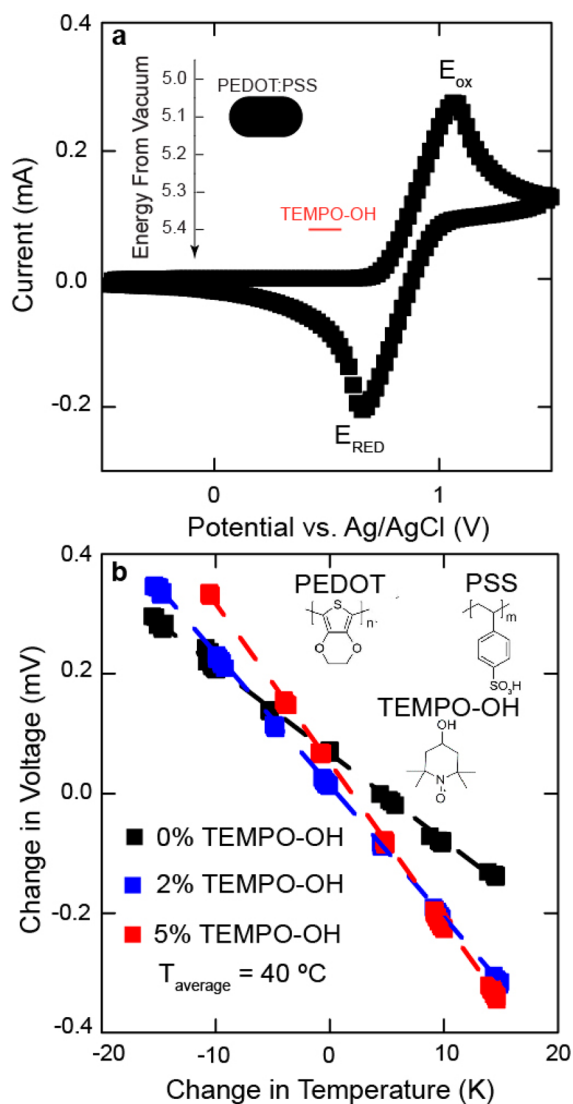
Figure 1. (a) Cyclic voltammogram of 67 mg TEMPO−OH dissolved in 300 mL of dichloromethane with 9 g of tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The voltages are with respect to an Ag/AgCl reference electrode. The SOMO energy level is calculated through the use of a well-known relationship.[21] The inset displays the difference in energy level between the PEDOT:PSS work function and the TEMPO-OH SOMO energy. The line thickness used for the PEDOT:PSS work function is used to represent a wider range in energy levels (i.e., band tails) versus the very narrow transport energy level of TEMPO−OH. (b) Increasing the loading of TEMPO−OH increases the thermopower of PEDOT:PSS thin films. The data in black represent the pristine PEDOT:PSS (0% TEMPO−OH) thin film while the blue and red lines represent blends of PEDOT:PSS and TEMPO−OH containing 2 and 5% TEMPO−OH (by weight), respectively. The squares represent discrete measurements taken at each differential temperature. There are five points of data for each temperature, and the data points overlap, in general. The dashed lines are the linear regressions of the data points. Using these data, the hole-transporting thermopower values calculated for the 3 samples were 14 $\mu V\ K^{-1}$ for the pristine PEDOT:PSS sample, 22 $\mu V\ K^{-1}$ for the 2% TEMPO−OH-loaded sample and 26 $\mu V\ K^{-1}$ for the higher loading of TEMPO−OH sample. The molecular structures of PEDOT:PSS and TEMPO−OH are inset into the figure.

change with increased TEMPO−OH. That is, the negative slope observed in the relationship between the observed voltage
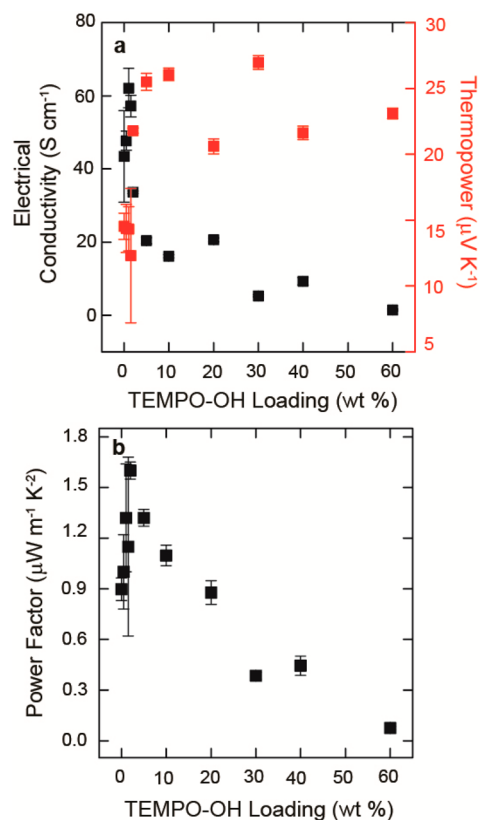
Figure 2. (a) Electrical conductivity and thermopower of the PEDOT:PSS thin films as a function of the TEMPO−OH loading. The conductivity values correspond to the left vertical axis (black points) and the thermopower values correspond to the right vertical axis (red points). Each data point represents the average of measurements collected on three distinct devices, and the error bars represent one standard error from the average. If no error bars are visible, the standard error fell within the size of the square data point shown. (b) The resulting power factor for the TEMPO−OH-doped PEDOT:PSS thin films calculated from the data in part a.

difference and temperature gradient shows that the composite materials are hole-transporting (p-type) materials.

Although energy filtering is beneficial to the materials thermopower, partially removing positive charge from a p-type polymer has a deleterious effect on electrical conductivity. And, despite the fact that the redox-active nature of the TEMPO−OH radical does allow these small molecules to transport charge, these charge transport reactions are not as rapid in the solid state as that associated with the transport of pristine PEDOT:PSS.[20,22,23] Unlike the thermopower values, this change in electrical conductivity (examples of raw data for these calculations are shown in Figure S1) becomes more pronounced with TEMPO−OH loadings beyond 5% loading, by weight (Figure 2a). In turn, this trade-off results in a peak power factor value of ~1.6 $\mu W\ m^{-1}K^{-2}$ (Figure 2b) at a TEMPO−OH loading of 2% TEMPO−OH, by weight. Because the addition of another organic molecule is assumed to not impact the thermal conductivity of the composite system, this increase would more than double the theoretical zT value of a thermoelectric module containing this material. We note that the power factor of the pristine PEDOT:PSS film is significantly lower than those reported for world-record processing conditions;[3,5] however, it is consistent with previous reports that also utilize commercial PEDOT:PSS that has not

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been modified (e.g., through solvent washes or annealing treatments).[10] This lower power factor is mainly the result of a lowered electrical conductivity. The lowered electrical conductivity, in turn, is commonly explained as being due to the presence of excess (i.e., beyond what is needed to dope the PEDOT effectively) poly(styrenesulfonate) (PSS) present in the PEDOT:PSS films. This excess PSS is electrically insulating and lowers the overall conductivity of the composite material. Although these world-record reports have used clever means to increase the electrical conductivity of PEDOT:PSS,[3] the primary focus of this effort is to examine the effect of open-shell dopants in a systematic manner.

Therefore, the relative change in the thermoelectric properties of the organic composites is of greatest concern in these analyses.

Importantly, these changes in thermoelectric properties cannot be correlated to changes in the nanostructure or topology of the composite films. As shown in the grazing-incidence X-ray diffraction (GI-XRD) scattering patterns of Figure S2, the pristine PEDOT:PSS thin film shows the oft-observed broad reflection for the polymer thin film.[24] Similarly, the composite film containing a loading of 50% TEMPO−OH (by weight) demonstrates an identical scattering pattern. This indicates that the TEMPO−OH does not disrupt the crystallinity of the PEDOT phase. Furthermore, this also demonstrates the relatively low loading of TEMPO−OH is well-dispersed through the PEDOT:PSS matrix, and it does not phase separate into distinct TEMPO−OH domains that crystallize in a manner independently of the PEDOT:PSS phase. Again, these effects are reflected by the lack of change in topography between the pristine PEDOT:PSS and TEMPO−OH-loaded PEDOT:PSS thin films (Figure S3), as imaged through atomic force microscopy (AFM). Therefore, the electronic structure of the pristine and composite films must be examined in greater detail.

Specifically, the charge transport model representative of the pristine and TEMPO−OH-loaded thin films was evaluated by measuring the van der Pauw-extracted electrical conductivity as a function of temperature. In particular, because of the disordered nature of conductivity (relative to highly ordered inorganic systems) between PEDOT nanostructures, charge is forced to hop from site to site.[25] Additionally, all of the conductivity measurements were conducted at low temperatures (i.e., in the regime where variable range hopping model is valid).[26] This hypothesis regarding the conductivity mechanism of the films was confirmed by observing a high degree of linearity when plotting the electrical conductivity (on a logarithmic scale) against $T^{[-1/(1+d)]}$ for $d = 1$, 2, or 3; here the d value corresponds to the dimensionality of the charge transport.[25,27] That is, it is observed that the preferred method of transport is one-dimensional in nature when $d = 1$. This model is both physically intuitive and has been used to model pure PEDOT:PSS in the past.[25] Therefore, the electrical conductivity of the composite system (as well as pure PEDOT:PSS) is well-defined by one-dimensional variable range hopping (1-D VRH) model.[25,26] In general, the conductivity of a sample that follows the 1D VRH model can be expressed by the following equation.[25−27]

$$\sigma = \sigma_0 \exp\left[\left(\frac{-T_0}{T}\right)^{(1/1+d)}\right]$$

(2)

Here, T_0 is the characteristic temperature, and σ_0 represents an upper bound for electrical conductivity as a function of temperature. The data closely matched the model of one-dimensional variable range hopping (Figure 3). Furthermore, it
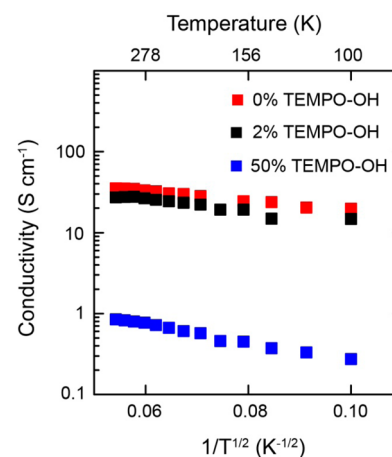
Figure 3. Temperature dependence of the electrical conductivity determined using the van der Pauw method for PEDOT:PSS-based thin films. The electrical conductivity for the pristine and lightly doped samples is relatively high ($\sigma \approx 30$ S cm^{-1}) and in good agreement with a number of previous reports; however, the electrical conductivity does decrease significantly at higher TEMPO−OH loadings (blue symbols). The temperature trends for all of the films are good fits for the Mott variable range hopping model. The calculated high temperature conductivity limits and characteristic temperatures and high temperature bounds of electrical conductivity are $\sigma_0 = 75.8$ S cm^{-1}, $T_0 = 192$ K; $\sigma_0 = 68.0$ S cm^{-1}, $T_0 = 261$ K; $\sigma_0 = 3.56$ S cm^{-1}, $T_0 = 684$ K for the 0, 2, and 50% TEMPO−OH (by weight) samples, respectively.

was clearly observed that the characteristic temperature increases with an increasing TEMPO−OH loading. This increase was attributed to a larger dependence on temperature to provide the energy necessary to hop from one localized region to another. This is to be expected given that the small molecule is both adding less conductive filler, and it also is acting as a reducing agent by removing positive charges from the PEDOT nanocrystals.

These transport data can be correlated to energy filtering, and, to a smaller extent, the electrochemical oxidation state of the PEDOT:PSS species and the presence of lone electron spins present due to the TEMPO−OH loading. That is, in addition to filtering of low energy holes, the reaction of the PSS moiety with the alternative oxidation site provided by the TEMPO−OH prevents the acidic PSS polymer from oxidizing PEDOT as much as would occur in the pristine thin films. In turn, this oxidation of the radical sites results in a termination of the stabilized nitroxide radical moiety in TEMPO−OH, and this reduces the amount of spin sites present in the composite thin films. This effect may be observed through the emergence of absorbance peaks that correspond to neutral PEDOT species ($\lambda \approx 370$ nm) as well as the emergence of a polaron peak ($\lambda \approx 900$ nm). As shown in Figure 4a, these peaks increase in intensity when PEDOT:PSS and TEMPO−OH are codissolved in water.[28,29] The time-dependent increase in the absorbance of the sample near the characteristic TEMPO−OH peak ($\lambda \approx 450$ nm) is likely caused by the emergence of the cation form of TEMPO−OH. The characteristic absorption spectra of both the radical and cation form of TEMPO−OH are provided as Figure S4.
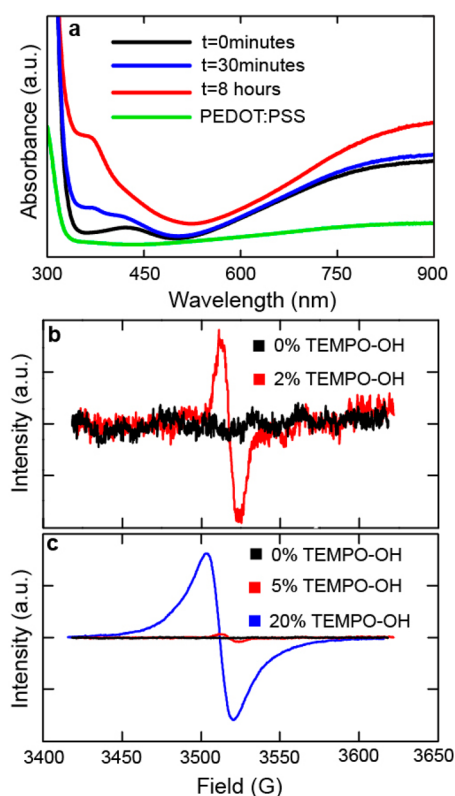
Figure 4. (a) Ultraviolet−visible (UV−vis) light absorption spectra of a PEDOT:PSS in water solution and a blend of TEMPO−OH and PEDOT:PSS in water as a function of time (i.e., immediately after making the solution (0 m), 30 m after mixing, and 8 h after mixing). Note the time-dependent absorption increases at both lower ($\lambda < 400$ nm) and higher wavelengths ($\lambda > 700$ nm), which are likely due to the reduction of PEDOT upon incorporation of TEMPO−OH. It is important to note that both the cation and radical form of TEMPO−OH are redox-active. (b, c) First derivatives of the EPR absorbance spectra for a neat PEDOT:PSS powder and for PEDOT:PSS powders containing various loadings of TEMPO−OH. The two plots are shown to highlight the difference in scale with respect to the radical signal upon larger TEMPO−OH loadings.

While clearly altering the total amount of lone electron sites present, as is observed through a shift in the TEMPO−OH absorbance spectra, the PSS moiety does not completely eliminate the stabilized radical throughout the composite thin films. In fact, the presence of unpaired electrons associated with the TEMPO−OH species within composite thin films has been confirmed through electron paramagnetic resonance (EPR) spectroscopy. Figure 4b, c demonstrates that, as the loading of TEMPO−OH is increased in casting solution, the signal associated with the presence of the nitroxide radical increases in the solid-state EPR spectra. As expected, no unpaired spins are observed for the pristine PEDOT:PSS thin film in the field range reported. Importantly, the TEMPO−OH EPR signal occurs at a field strength greater than the strength normally associated with PEDOT polarons (3310 G), and no EPR signal was observed at this 3310 G field value.[30] Critically, this demonstrates the potential possibility of charge transport (and, therefore, energy filtering) through TEMPO−OH domains. This, in turn, allows for enhanced asymmetry of charge carriers around the Fermi energy level.

PEDOT:PSS is a leading polymer thermoelectric material, and it affords itself as an amazingly useful test bed for

elucidating mechanisms by which to enhance the thermo-electric performance of polymeric conductors. Here, we demonstrate a simple, one-step process capable of nearly doubling the thermopower of pristine PEDOT:PSS thin films, and, as such, this leads to doubling the power factor of the organic thermoelectric composites. Note also that, unlike many other methods, this process results in a solution that could be directly printed without any further postprocessing conditions (e.g., soaking in specific solvents for a given period of time) required after film deposition. Furthermore, the mechanism for this increase in the thermoelectric properties of PEDOT:PSS is understood through a combination of two effects that do not rely on the introduction of structural changes to the thin films.

The primary means of alteration is the presence of lone electrons and the corresponding SOMO energy levels of the open-shell TEMPO−OH moiety. In a secondary effect, the TEMPO−OH tweaks the oxidation state of the PEDOT moiety as it is more readily oxidized by the PSS species relative to the PEDOT. As such, the presence of the TEMPO−OH increases the thermopower of the PEDOT moiety by decreasing the amount of free charge carriers present in the polymer conductor. Importantly, this enhancement may be achieved by the simple addition of a small molecule in solution during the easily tuned and scalable ink formulation step. Therefore, this work demonstrates a clear and easily implemented method to manipulate and optimize the thermo-electric performance of scalable conducting polymers through the introduction of open-shell organic small molecules.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

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> Materials and thin film preparation and detailed experimental procedures, example electrical conductivity and thermopower measurements, AFM micrographs, and GI-XRD data (PDF)

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Author Contributions
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Notes
The authors declare no competing financial interest.

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■ REFERENCES

(1) Yue, R. R.; Xu, J. K. Poly(3,4-ethylenedioxythiophene) as Promising Organic Thermoelectric Materials: A Mini-review. *Synth. Met.* **2012**, *162*, 912−917.

(2) Boudouris, B. W. Engineering Optoelectronically Active Macromolecules for Polymer-Based Photovoltaic and Thermoelectric Devices. *Curr. Opin. Chem. Eng.* **2014**, *2*, 294−301.

(3) Bubnova, O.; Khan, Z. U.; Malti, A.; Braun, S.; Fahlman, M.; Berggren, M.; Crispin, X. Optimization of the Thermoelectric Figure of Merit in the Conducting Polymer Poly(3,4-ethylenedioxythiophene). *Nat. Mater.* **2011**, *10*, 429−433.

(4) Kim, G. H.; Hwang, D. H.; Woo, S. I. Thermoelectric Properties of Nanocomposite Thin Films Prepared with Poly(3,4-ethylenedioxythiophene) Poly(styrenesulfonate) and Graphene. *Phys. Chem. Chem. Phys.* **2012**, *14*, 3530−3536.

(5) Kim, G. H.; Shao, L.; Zhang, K.; Pipe, K. P. Engineered Doping of Organic Semiconductors for Enhanced Thermoelectric Efficiency. *Nat. Mater.* **2013**, *12*, 719−723.

(6) Zhang, K.; Zhang, Y.; Wang, S. Enhancing Thermoelectric Properties of Organic Composites Through Hierarchical Nanostructures. *Sci. Rep.* **2013**, *3*, 1−7.

(7) Scholdt, M.; Do, H.; Lang, J.; Gall, A.; Colsmann, A.; Lemmer, U.; Koenig, J. D.; Winkler, M.; Boettner, H. Organic Semiconductors for Thermoelectric Applications. *J. Electron. Mater.* **2010**, *39*, 1589−1592.

(8) Shakouri, A. Recent Developments in Semiconductor Thermoelectric Physics and Materials. *Annu. Rev. Mater. Res.* **2011**, *41*, 399−431.

(9) He, M.; Qiu, F.; Lin, Z. Q. Towards High-Performance Polymer-Based Thermoelectric Materials. *Energy Environ. Sci.* **2013**, *6*, 1352−1361.

(10) Yee, S. K.; Coates, N. E.; Majumdar, A.; Urban, J. J.; Segalman, R. A. Thermoelectric Power Factor Optimization in PEDOT:PSS Tellurium Nanowire Hybrid Composites. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4024−4032.

(11) Luo, J. J.; Billep, D.; Blaudeck, T.; Sheremet, E.; Rodriguez, R. D.; Zahn, D. R. T.; Toader, M.; Hietschold, M.; Otto, T.; Gessner, T. Chemical Post-Treatment and Thermoelectric Properties of Poly(3,4-ethylenedioxylthiophene):Poly(styrenesulfonate) Thin Films. *J. Appl. Phys.* **2014**, *115*, 0549081−0549085.

(12) Takano, T.; Masunaga, H.; Fujiwara, A.; Okuzaki, H.; Sasaki, T. PEDOT Nanocrystal in Highly Conductive PEDOT:PSS Polymer Films. *Macromolecules* **2012**, *45*, 3859−3865.

(13) Tomlinson, E. P.; Hay, M. E.; Boudouris, B. W. Radical Polymers and Their Application to Organic Electronic Devices. *Macromolecules* **2014**, *47*, 6145−6158.

(14) Rostro, L.; Baradwaj, A. G.; Boudouris, B. W. Controlled Radical Polymerization and Quantification of Solid State Electrical Conductivities of Macromolecules Bearing Pendant Stable Radical Groups. *ACS Appl. Mater. Interfaces* **2013**, *5*, 9896−9901.

(15) Mas-Torrent, M.; Crivillers, N.; Rovira, C.; Veciana, J. Attaching Persistent Organic Free Radicals to Surfaces: How and Why. *Chem. Rev.* **2012**, *112*, 2506−2527.

(16) Li, B.; Kao, C. Y.; Yoo, J. W.; Prigodin, V. N.; Epstein, A. J. Magnetoresistance in an All-Organic-Based Spin Valve. *Adv. Mater.* **2011**, *23*, 3382−3386.

(17) Reddy, P.; Jang, S. Y.; Segalman, R. A.; Majumdar, A. Thermoelectricity in Molecular Junctions. *Science* **2007**, *315*, 1568−1571.

(18) Yee, S. K.; Malen, J. A.; Majumdar, A.; Segalman, R. A. Thermoelectricity in Fullerene−Metal Heterojunctions. *Nano Lett.* **2011**, *11*, 4089−4094.

(19) Ko, D.-K.; Kang, Y.; Murray, C. B. Enhanced Thermopower Via Carrier Energy Filtering in Solution-Processable Pt−Sb$_2$Te$_3$ Nanocomposites. *Nano Lett.* **2011**, *11*, 2841−2844.

(20) Nardes, A. M.; Kemerink, M.; de Kok, M. M.; Vinken, E.; Maturova, K.; Janssen, R. A. J. Conductivity, Work Function, and Environmental Stability of PEDOT:PSS Thin Films Treated with Sorbitol. *Org. Electron.* **2008**, *9*, 727−734.

(21) D'Andrade, B. W.; Datta, S.; Forrest, S. R.; Djurovich, P.; Polikarpov, E.; Thompson, M. E. Relationship Between the Ionization and Oxidation Potentials of Molecular Organic Semiconductors. *Org. Electron.* **2005**, *6*, 11−20.

(22) Baradwaj, A. G.; Rostro, L.; Alam, M. A.; Boudouris, B. W. Quantification of the Solid-State Charge Mobility in a Model Radical Polymer. *Appl. Phys. Lett.* **2014**, *104*, 2133061.

(23) Bubnova, O.; Khan, Z. U.; Wang, H.; Braun, S.; Evans, D. R.; Fabretto, M.; Hojati-Talemi, P.; Dagnelund, D.; Arlin, J. B.; Geerts, Y. H.; Desbief, S.; Breiby, D. W.; Andreasen, J. W.; Lazzaroni, R.; Chen, W. M. M.; Zozoulenko, I.; Fahlman, M.; Murphy, P. J.; Berggren, M.; Crispin, X. Semi-Metallic Polymers. *Nat. Mater.* **2014**, *13*, 190−194.

(24) Zhang, X.; Chang, D.; Liu, J.; Luo, Y. Conducting Polymer Aerogels from Supercritical CO$_2$ Drying PEDOT-PSS Hydrogels. *J. Mater. Chem.* **2010**, *20*, 5080−5085.

(25) Aleshin, A. N.; Williams, S. R.; Heeger, A. J. Transport Properties of Poly(3,4-ethylenedioxythiophene)/Poly-(styrenesulfonate). *Synth. Met.* **1998**, *94*, 173−177.

(26) Nardes, A. M.; Janssen, R. A. J.; Kemerink, M. A Morphological Model for the Solvent-Enhanced Conductivity of PEDOT: PSS Thin Films. *Adv. Funct. Mater.* **2008**, *18*, 865−871.

(27) Yu, D.; Wang, C. J.; Wehrenberg, B. L.; Guyot-Sionnest, P. Variable Range Hopping Conduction in Semiconductor Nanocrystal Solids. *Phys. Rev. Lett.* **2004**, *92*, 2168021.

(28) Jeuris, K.; Groenendaal, L.; Verheyen, H.; Louwet, F.; De Schryver, F. C. Light Stability of 3,4-Ethylenedioxythiophene-Based Derivatives. *Synth. Met.* **2003**, *132*, 289−295.

(29) Fabiano, S.; Braun, S.; Liu, X.; Weverberghs, E.; Gerbaux, P.; Fahlman, M.; Berggren, M.; Crispin, X. Poly(ethylene imine) Impurities Induce n-Doping Reaction in Organic (Semi)Conductors. *Adv. Mater.* **2014**, *26*, 6000−6006.

(30) Zykwinska, A.; Domagala, W.; Czardybon, A.; Pilawa, B.; Lapkowski, M. In Situ EPR Spectroelectrochemical Studies of Paramagnetic Centres in Poly(3,4-ethylenedioxythiophene) (PEDOT) and Poly(3,4-butylenedioxythiophene) (PBuDOT) Films. *Chem. Phys.* **2003**, *292*, 31−45.