ABSTRACT

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Title: Tuning the Thermoelectric Performance of Conjugated Polymers with Open-Shell Dopants
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In recent years, organic thermoelectric (TE) materials have received significant interest given their ability to convert waste heat to electricity using earth abundant resources. However, the widespread implementation of organic thermoelectric technology requires a higher theoretical efficiency than is commonly achieved in the current state of the art. From a materials standpoint, the performance is enhanced when electrical conductivity (σ) and thermopower (S) are maximized, while thermal conductivity (κ) is minimized. Fortunately, macromolecular materials are thermally insulating (with κ values around 0.1 W $m^{-1}K^{-1}$). Due to the already favorable lack of thermal conductivity, enhancement of organic thermoelectric materials occurs through improvement of the power factor (σS^2) of the materials. Unfortunately, optimization of this value is a nontrivial endeavor given the traditionally inverse relationship between charge carrier density and thermopower. It is important to establish and evaluate alternative thermoelectric enhancement pathways.

Here, we elucidate the effect of the incorporation of open shell species as molecular dopants for π-conjugated polymer TE materials, and propose a mechanism for the enhanced thermoelectric performance of the resulting composite material. Specifically, we incorporate 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO) into the high-performing polymer blend poly(3,4ethylene dioxythiophene) doped with poly(styrene

sulfonate) (PEDOT:PSS), resulting in a near 100% increase in material thermopower with radical species loadings as low as 2% by weight. The low loading of TEMPO-OH does not have an impact on the crystallinity or surface topology of the radical containing composites relative to the neat PEDOT:PSS thin films. While the gains in thermopower are offset, in part, by a decrease in electrical conductivity, the material power factor is observed to undergo a 77% increase in comparison to neat PEDOT:PSS. As such, this work represents the first example of enhancing the thermoelectric performance of an organic material through the incorporation of a radical containing molecular dopant.

Further, the effect of different radical materials is evaluated on the semiconducting (as opposed to conducting) polymer system, regioregular poly(3-hexylthiophene) (P3HT). Specifically, we incorporate both TEMPO-OH, and 2,6-Di-tert-butyl-α-(3,5-di-tert-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-p-tolyloxy (GAV) as molecular dopants for P3HT. To that end, an 8,000% and 5,000% improvement in the P3HT power factor for the P3HT-TEMPO and P3HT-GAV composite systems, respectively, is demonstrated. The lack of oxidation behavior is confirmed via optical spectroscopy and x-ray diffraction. Becasue this gain is obtained without changing the materials oxidation state (and therefore leaving the material's thermopower intact), the classic inverse relationship between thermopower and electrical conductivity is broken, and the potential for new thermoelectric enhancement pathways for macromolecular materials is elucidated.

This synergistic combination of open-shell species and π-conjugated macromolecules may serve as the basis for the future design of polymeric semiconductors. As such, early attempts are made toward the design and synthesis of π-conjugated materials with radical pendent groups, which are referred to as conjugated radical polymers (CRPs).

Specifically, the viability of a pendent TEMPO group on both PEDOT and thiophene is evaluated. While initial electrical conductivities are low (10^{-6} S cm^{-1}), important insights are gained into future design considerations of new CRPs. These insights may provide a pathway toward the creation of the next generation of polymer thermoelectric materials.