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Enhanced Thermoelectric Properties of Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) by Binary Secondary Dopants

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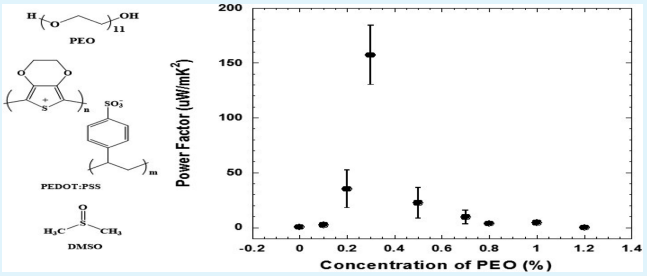
Supporting Information

ABSTRACT: To simultaneously increase the electrical conductivity and Seebeck coefficient of poly(3,4-ethylenedioxythiophene):polystyrenesulfonate (PEDOT:PSS) was a challenge for realizing efficient organic thermoelectrics. In this study, for the first time, we report both increased electrical conductivities and Seebeck coefficients, hence, enhanced thermoelectric properties of PEDOT:PSS thin films by doped with binary secondary dopants, dimethyl sulfoxide (DMSO) and poly(ethylene oxide) (PEO). Without modifying film morphology, the molar ratios of PEDOT to PSS are tuned by PEO, resulting in increased proportions of PEDOT in the bipolaron states. Our study provides a facile route to optimizing thermoelectric properties of PEDOT:PSS thin films.



KEYWORDS: *organic thermoelectrics, PEDOT:PSS, PEO, bipolaron states, power factor*

Thermoelectric properties of materials described by ZT[1] is expressed as $ZT = TS^2\sigma/k$, where T is the absolute temperature, S, σ and k are the Seebeck coefficient, the electrical conductivity, and the thermal conductivity of materials, respectively. Inorganic semiconductors have been applied in thermoelectric devices to convert heat into electricity due to their high electrical conductivity and large Seeback coefficient.[1] In 2001, Venkatasubramanian et al.[2] reported ZT of 2.4 from Bi_2Te_3/Sb_2Te_3 superlattices. Such improvement was attributed to reduced thermal conductivity and unchanged power factor ($S^2\sigma$) of Bi_2Te_3/Sb_2Te_3.[2] In recent years, great efforts have been paid to reduce thermal conductivities by development of new inorganic complex materials to approach high ZT.[3] However, large intrinsic thermal conductivities (>1 W/mK) of inorganic materials highly suppress the improvements in developing inorganic thermoelectrics.[3] Alternately, organic thermoelectrics exhibit great potential due to low thermal conductivities (<0.5 W/mK) of organic materials.[4−7] Among all organic semiconductors being investigated for thermoelectric application, poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) stood out to be one of the most promising organic materials.[8−11] It was reported that the electrical conductivity of PEDOT:PSS thin film can be improved by 3 orders of magnitude via single secondary dopant as compared with pristine PEDOT:PSS thin film.[12−15] For instance, the electrical conductivity of PEDOT:PSS thin film was improved to 289.52 S/cm for PEDOT:PSS doped with 5% (by volume) dimethyl sulfoxide (DMSO).[15] It was found that increased PEDOT in the polaron states, which was due to the strong interactions between DMSO and PSS, was responsible for improved electrical conductivity of these films.[12] Crispin et al. further indicated that larger Seebeck coefficient resulted from PEDOT in the bipolaron states rather than in the polaron states,[16] suggesting that the low Seebeck coefficient of PEDOT:PSS thin film doped with 5% DMSO is limited by the small amount of PEDOT in the bipolaron states.[16,17] Thus, doping another secondary dopant, which possesses a weaker interaction with PSS rather than DMSO, would enlarge the amount of PEDOT in the bipolaron states, consequently, an improved electrical conductivity and an enhanced Seebeek coefficient of PEDOT:PSS thin film would be realized.

In this study, we report both increased electrical conductivities and Seebeck coefficients, hence, enhanced thermoelectric properties of PEDOT:PSS thin films doped with binary secondary dopants, DMSO and poly(ethylene oxide) (PEO), for the first time. Without significantly modifying thin film morphologies of PEDOT:PSS, introducing PEO into PEDOT:PSS doped with 5% DMSO, the ratios of PEDOT in the bipolaron states are increased, resulting in increased electrical conductivities and Seebeck coefficients. Moreover, the thin film of PEDOT:PSS doped with 5% DMSO

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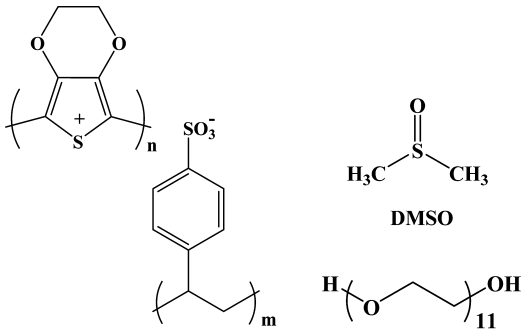
and 0.3% PEO possesses a power factor ($S^2\sigma$) of 157.35 μW/mK^2, which is 10 000 times higher than that of pristine PEDOT:PSS thin film and 100 times higher than that PEDOT:PSS doped with 5% DMSO.

Experimental details are available in the Supporting Information. Note that for Seebeck coefficient measurement, the distance between the two aluminum (Al) electrodes was 0.9 cm, which was significantly larger than the size of an Al contact. Therefore, the effects of device geometry is negligible.[18] For the electrical conductivity and Seebeck coefficient measurements, 10 samples for each conditions were prepared to obtain the statistical results. The molecular structures of PEDOT:PSS, DMSO, and PEO are shown in Scheme 1.

Scheme 1. Molecular Structures of poly(3,4-Ethylenedioxythiophene):poly(styrene sulfonate)(PEDOT:PSS), Dimethyl Sulfoxide (DMSO) and Poly(ethylene oxide) (PEO)



The thicknesses of thin films of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO, another secondary dopant, are shown in Figure 1a. With increasing the concentrations of PEO up to 0.5%, the thickness of the doped films are reduced, which indicates that the packing of the PEDOT molecules probably get more compact in the vertical direction.[19] Further increasing the concentrations of PEO, the thickness of the thin films are increased, which is probably due to the large cohesive energy of the molecules in the films.[19] The electrical conductivities of thin films of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO are shown in Figure 1b. The film of PEDOT:PSS doped with 5% DMSO shows an electrical conductivity of 619 ± 26 S/cm, which is close to the reported value.[8,16] Increasing the concentrations of PEO from 0.1% to 0.2, 0.3, and 0.5%, in PEDOT:PSS doped with 5% DMSO, the electrical conductivities of PEDOT:PSS thin films are increased from 945 ± 18 S/cm to 1016 ± 16, 1061 ± 16, and 1270 ± 13 S/cm, respectively. However, when further increasing the concentrations of PEO to 0.7, 0.8, 1.0, and 1.2%, the electrical conductivities of doped films are reduced to 1176 ± 14, 1054 ± 16, 980 ± 17, and 704 ± 24 S/cm, respectively These results indicate that charge-carrier transport properties of doped PEDOT:PSS are tuned by tuning the concentrations of PEO.

The Seebeck coefficients of thin films of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO are shown in Figure 1c. The Seebeck coefficient of thin film of PEDOT:PSS doped with 5% DMSO is 2.2 ± 0.7 μV/K, which is slightly lower than the results after geometry correction.[18] This difference is due to the energy barrier at the contact between the electrode and the prepared films.[20] However, the Seebeck coefficient is increased to 38.4 ± 7.1 μV/K when PEDOT:PSS doped with 5% DMSO and 0.3% PEO. Further increasing the concentrations of PEO, from 0.5% to 0.7, 0.8, 1.0, and 1.2%, the Seebeck coefficients are decreased to 13.3 ± 5.2, 9.0 ± 3.7, 5.8 ± 1.1, 6.7 ± 0.9, and 1.5 ± 0.3 μV/K, respectively. These results confirm that charge-carrier transport properties in doped PEDOT:PSS films are modified.[12,13,15]

The thermoelectric properties of thin films are characterized by the power factor, PF. The PF is described as PF = $S^2\sigma$.[8,10,21−24] The PF values of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO are shown in Figure 1d. Because all of thin films possess the same order of magnitude of electrical conductivities, σ, the PF is solely dependent on the Seebeck coefficient, S. As shown in Figure 1d, the PF is increased and then decreased along with increasing doping concentrations of PEO. The highest PF of 157.35 ± 27.01 μW/mK^2 is observed from PEDOT:PSS doped with 5% DMSO and 0.3% PEO. This PF value is 10,000 times higher than that from pristine PEDOT:PSS thin film,[20] and 100 times higher than that from PEDOT:PSS doped with 5% DMSO (0.29 ± 0.05 μW/mK^2). These results demonstrate that binary secondary dopants have a great influence on the thermoelectric properties of doped PEDOT:PSS thin films.

To understand the improved thermoelectric properties of PEDOT:PSS doped with DMSO and PEO, atomic force microscopy (AFM) is carried out to investigate the thin film morphologies of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO. Figure 2 presents the AFM phase images of thin film morphologies of doped PEDOT:PSS. Fiber-like PEDOT domains are observed from the thin film of PEDOT:PSS doped with 5% DMSO. However, with increasing PEO concentrations, the size and shape of PEDOT domains remain unchanged. These fibers show a geometry with 38 ± 4 nm in length and 10 ± 2 nm in width. These fibers also forms continuous network for electron transporting. The root-mean-square (RMS) roughness of PEDOT:PSS doped with 5% DMSO is ∼1.0 nm, which indicates the prepared film has a smooth surface. After increasing the concentrations of PEO in the binary secondary dopants, the surface roughness is almost unchanged, with a RMS roughness of ∼1.1 nm when 1.2% PEO is added. These results demonstrate that thin film morphologies of PEDOT:PSS are not affected by additional PEO. However, this observation is different from that observed from the thin film of PEDOT:PSS doped with DMSO, where the increased thermoelectric properties are attributed to modified thin film morphologies of PEDOT:PSS by DMSO.[13,15,19,25]

To further understand the increased thermoelectric properties of PEDOT:PSS doped with DMSO and PEO, we carried out Raman spectroscopy to investigate the proportions of PEDOT in the polaron and bipolaron states of PEDOT:PSS thin films because both PEDOT in the polaron and the bipolaron states are responsible for the thermoelectric properties of doped PEDOT:PSS.[26,27] Figure 3 shows Raman spectra of thin films of doped PEDOT:PSS. The peaks at 1420 and 1560 cm^{-1} are attributed to $C_\alpha = C_\beta$ symmetric stretching and C_α=C_β asymmetric stretching of PEDOT in the polaron states and the bipolaron states, respectively.[26,27] Compared with thin film of PEDOT:PSS doped with 5% DMSO, more intense and broader peak at 1560 cm^{-1} from the thin films with 0.1% PEO and 0.3% PEO indicate that the proportions of PEDOT in the bipolaron states are increased and the electrons are more delocalized on the conjugated backbone of PEDOT.[27] Blue

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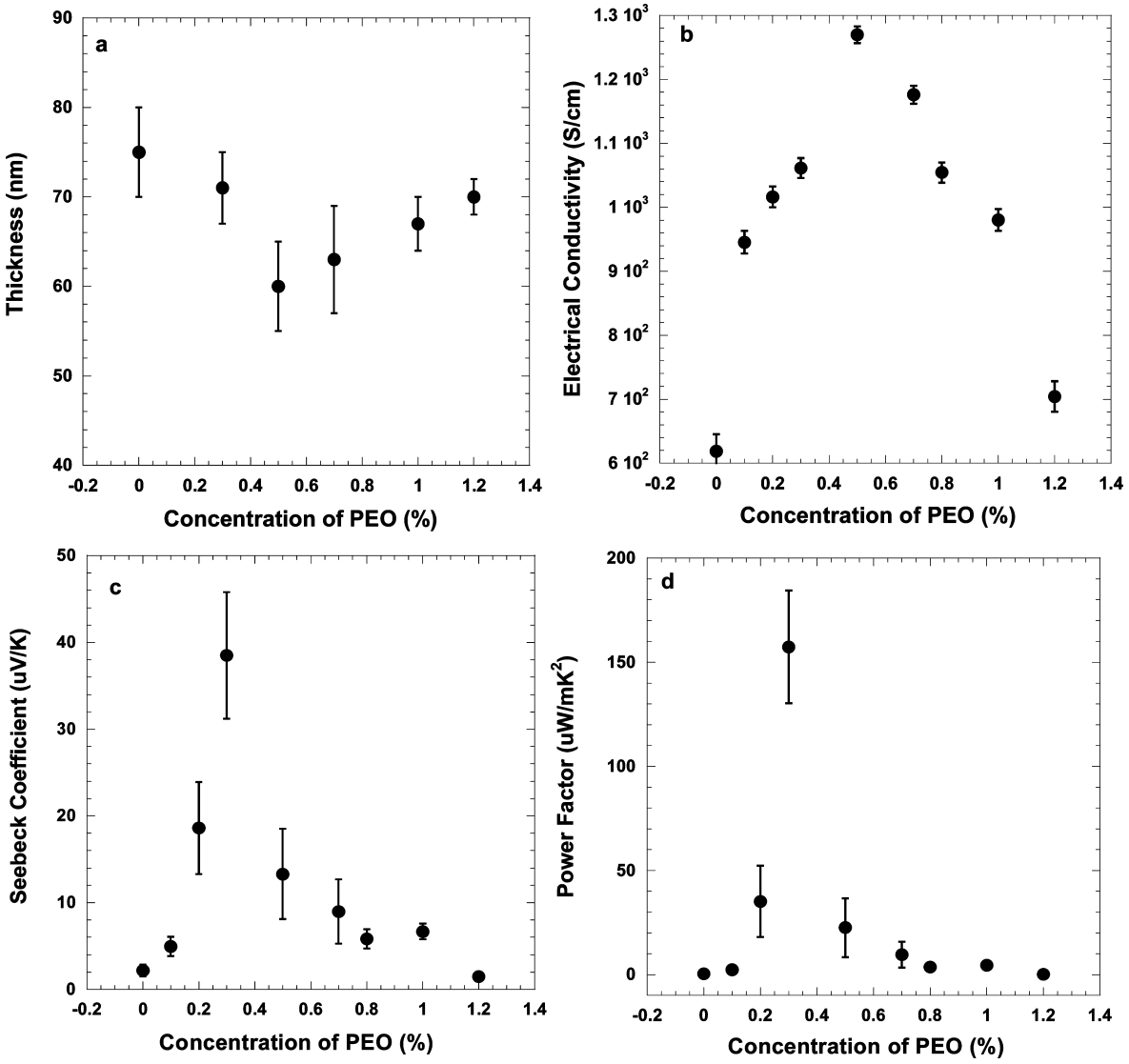

Figure 1. (a) Thickness, (b) electrical conductivities, (c) Seebeck coefficients, and (d) power factors of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO.

shifts of this peak position were also observed, which is also to the fact that electrons are more delocalized on PEDOT, the larger the proportions of PEDOT in the bipolaron states, the larger the blue shifts. As a result, high electrical conductivity is observed from these thin films. With further increasing the concentrations of PEO, suppressed intensities of the peak at 1560 cm^{-1} and red shifts of this peak are observed. These results indicates that the proportion of PEDOT in the bipolaron states are decreased; consequently, the electrical conductivity of PEDOT:PSS are reduced.

X-ray photoemission spectroscopy (XPS) is further used to identify the molar ratio between PEDOT and PSS. Figure 4 presents XPS spectra of PEDOT:PSS thin films doped with 5% DMSO and different concentrations of PEO. The spin-split core level of the sulfur in PSS has a peak with maximum at 169 eV, whereas the spin-split core level feature originating from the PEDOT sulfur has peaks with maximum located at 164 eV. By fitting the signal of sulfur from PSS with peak with two spin-split doublets and fitting the signal of sulfur from PEDOT with an asymmetric distribution doublets, the relative intensities from sulfur atoms in PEDOT and PSS could be obtained. Comparing the relative intensities of the main core level features of these two sulfur atoms adjusted by the lens transfer function and atomic sensitivity factors, the ratios between PEDOT and PSS in different PEDOT:PSS thin film are estimated.[8,28,29] The results are summarized in Table 1. The ratio for PEDOT to PSS is 1:2.18 for the film of PEDOT:PSS doped with 5% DMSO. However, the ratio becomes to 1:2.59 for the film of PEDOT:PSS doped with 5% DMSO and 0.3% PEO. With further increasing the concentrations of PEO, the ratios are decreased to 1:2.43 and 1:2.42 for the films of PEDOT:PSS doped with 5% DMSO, and 0.5% and 0.7% PEO, respectively. For the film of PEDOT:PSS doped with 5% DMSO and 1.2% of PEO, the ratio of PEDOT to PSS goes down to 1:2.18, which is the same value to the film of PEDOT:PSS doped with 5% DMSO. These results demonstrate that the molar ratios of PEDOT to PSS are modified by PEO. Therefore, the proportions of PEDOT in the bipolaron state are tuned by the concentration of PEO in the binary secondary dopants.[8]

It was reported that the Fermi level located in the middle of the polaron states for PEDOT in the polaron states, and the

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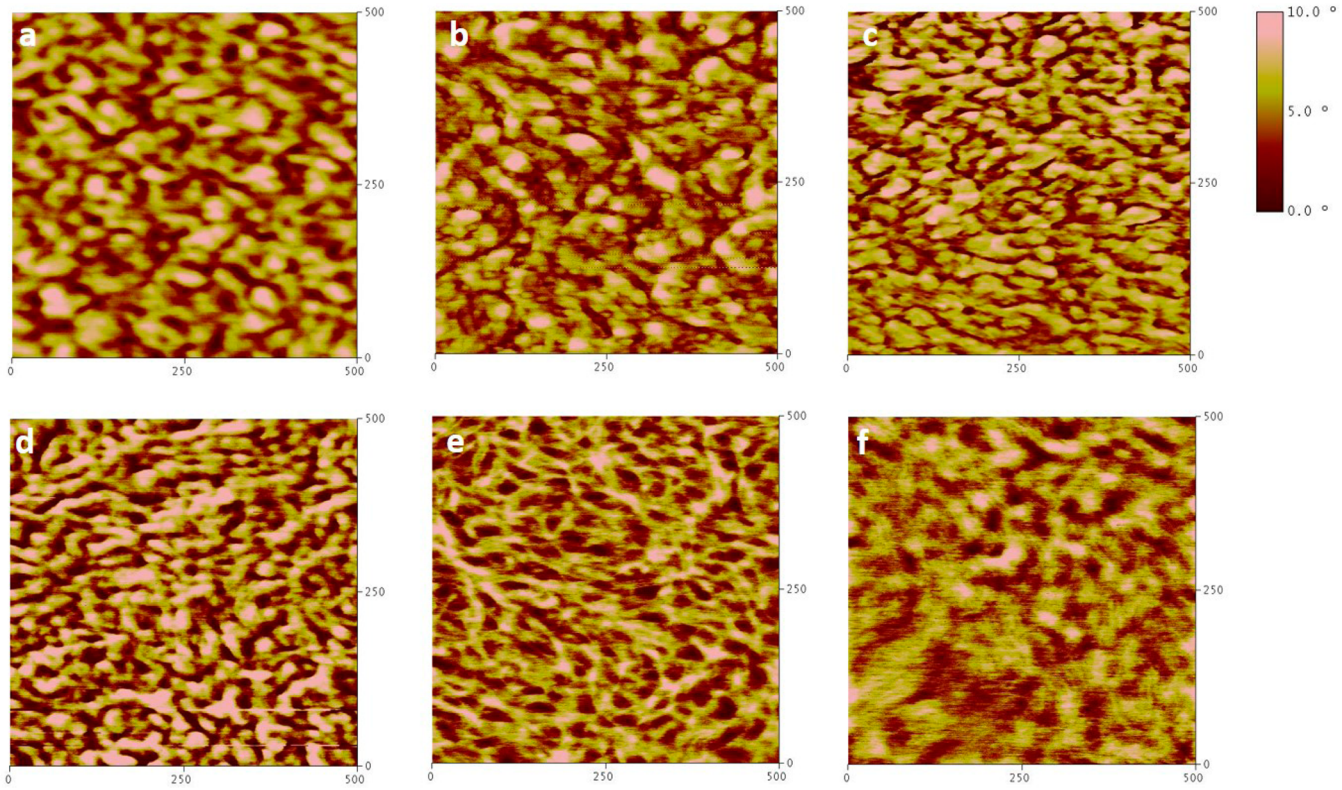

Figure 2. AFM phase images of PEDOT:PSS doped with 5% DMSO and different concentrations of PEO (a) 0% PEO, (b) 0.1% PEO, (c) 0.3% PEO, (d) 0.5% PEO, (e) 0.7% PEO, and (f) 1.2% PEO.

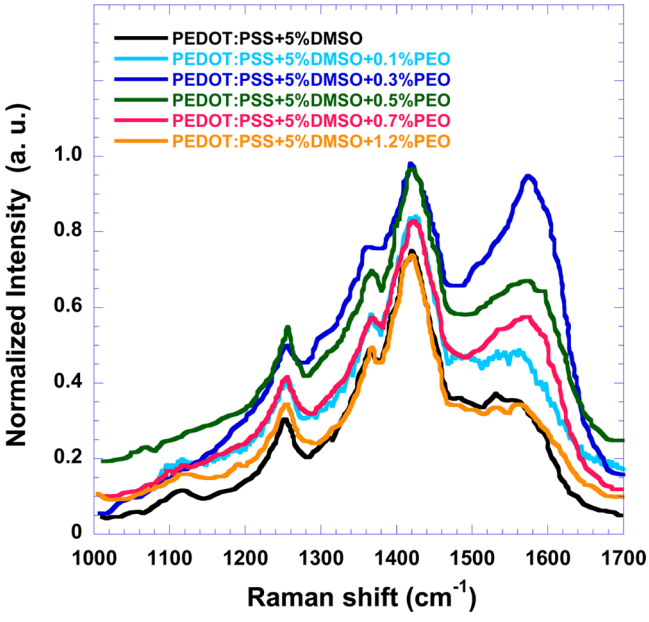

Figure 3. Raman spectra of PEDOT:PSS films doped with 5% DMSO and different concentrations of PEO with an excitation wavelength of 532 nm.

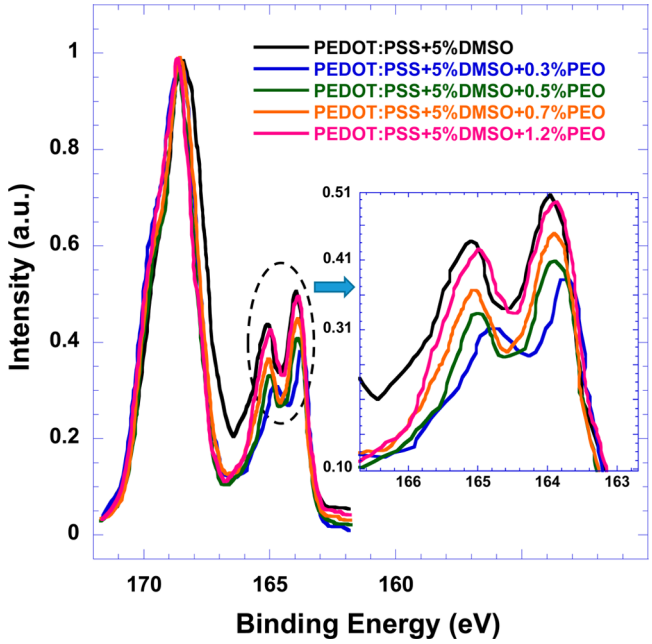

Figure 4. XPS spectra of PEDOT:PSS films doped with 5% DMSO and different concentrations of PEO, inset: high-resolution spectra in low binding energy.

Fermi level located in between the bipolaron states and the highest occupied molecular orbital (HOMO) level for PEDOT in the bipolaron states.[4] The distribution of the logarithm of density of states is symmetric at Fermi level (E_F) for PEDOT in the polaron states. However, it is highly asymmetric at E_F for PEDOT in the bipolaron states.[16] On the basis of Mott's formula, $S \approx (dN(E)/dE)D(E)\ |E_F$,[16] where $N(E)$, $D(E)$, and E_F are the density of states of charge carriers, diffusion coefficient of charge carriers and Fermi level, respectively, Seebeck coefficient is proportional to the derivative of the density of states at Fermi level. For PEDOT:PSS doped with binary secondary dopants, the increased proportions of PSS are activated to contribute to increased ratios of PEDOT in the

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Table 1. Component Ratios between PEDOT to PSS in Thin Films Prepared from Solutions with Different Concentrations of PEO

films from different solutions	PEDOT to PSS ratio
PEDOT:PSS+5% DMSO	1:2.18
PEDOT:PSS+5% DMSO +0.3% PEO	1:2.59
PEDOT:PSS+5% DMSO +0.5% PEO	1:2.43
PEDOT:PSS+5% DMSO +0.7% PEO	1:2.42
PEDOT:PSS+5% DMSO +1.2% PEO	1:2.18

bipolaron states.[30] Therefore, increased Seebeck coefficients are obtained from doped PEDOT:PSS films with enhanced ratios of PEDOT in the bipolaron states. As indicated by Raman spectra (Figure 3) and XPS spectra (inset of Figure 4), a high ratio of PEDOT in the bipolaron states is observed from PEDOT:PSS doped with 5% DMSO and 0.3% PEO. Hence, the thin film of PEDOT:PSS doped with 5% DMSO and 0.3% of PEO possesses high electrical conductivity and large Seebeck coefficient, consequently, efficient thermoelectric performance.

In this study, we reported both increased electrical conductivities and Seebeck coefficients, hence, enhanced thermoelectric properties of PEDOT:PSS thin films doped with binary secondary dopants, DMSO and PEO, for the first time. AFM images of PEDOT:PSS thin films doped with binary secondary dopants indicated that addition of PEO did not change the film morphologies, but the ratio of PEDOT to PSS was tuned, which was evidently demonstrated by Raman spectra and X-ray photoelectron spectra. The increased ratio of PEDOT in the bipolaron states resulted in increased electrical conductivities and Seebeck coefficients, hence, enhanced thermoelectric properties of doped PEDOT:PSS thin films. Moreover, the thin film of PEDOT:PSS doped with 5% DMSO and 0.3% PEO possesses a power factor ($S^2\sigma$) of 157.35 μW/mK^2, which is 10 000 times higher than that of PEDOT:PSS thin film and 100 times higher than that of PEDOT:PSS doped with 5% DMSO. Our study provides a facile route to approach high thermoelectric properties of PEDOT:PSS thin films.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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