Poly(nickel-ethylenetetrathiolate) and Its Analogs: Theoretical Prediction of High-Performance Doping-Free Thermoelectric Polymers

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Supporting Information

ABSTRACT: It is generally deemed that doping is a must for polymeric materials to achieve their high thermoelectric performance. We herein present the first report that intrinsically metallic behaviors and high-performance thermoelectric power factors can coexist within doping-free linear-backbone conducting polymers, poly(nickel-ethylenetetrathiolate) and its analogs. On the basis of density functional calculations, we have corroborated that four crystalline π-d conjugated transition-metal coordination polymers, including poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4), and poly(Pt-C2S4) exhibit intrinsically metallic behavior arising from the formation of dense intermolecular interaction networks between sulfur/selenium atoms. They show moderate carrier concentrations (10^{19} \text{ cm}^{-3}) and decent conductivities (10^{3} \text{ S cm}^{-1}), among which, poly(Ni-C2S4) possesses high power factors (\sim 10^4 \mu \text{ W m}^{-1} \text{ K}^{-2}).

The cutting-edge solid-state thermoelectric (TE) materials based on Seebeck effect and Peltier effect have enormous potentials in the applications of waste-heat recovery and refrigeration. The efficiency of a TE material is determined by a dimensionless figure of merit, \( zT = (S^2 \sigma T)/\kappa \), where \( S \), \( \sigma \), \( T \), and \( \kappa \) are the Seebeck coefficient, electrical conductivity, thermal conductivity and the average absolute temperature of the hot and cold junctions, respectively. A good TE material must possess a high \( zT \) which requires an excellent conductivity and a high Seebeck coefficient while a poor thermal conductivity. \(^1\)

Promising polymeric TE materials have emerged in recent 20 years.\(^2\)–\(^5\) They exhibit numerous advantages as compared with conventional inorganic TE materials, such as biocompatibility, flexibility, low lattice thermal conductivity, etc. Historically, doping is regarded to be indispensable to achieve acceptable carrier concentrations and thereby decent conductivities for polymeric TE applications.\(^6\) However, dopants inevitably alter the well-ordered microscopic packing structures of conjugated polymers, influence their charge transport properties and consequently degrade the TE performance.\(^7,8\)

On the other hand, owing to the poor chemical doping efficiency in semiconducting polymers, the realization of high carrier concentration is another challenging task.\(^9\) Very recently, intrinsically metallic behaviors defined as no bandgap with the Fermi energy lying inside the band and intrinsically electrically conductive characteristics have been observed in some two-dimensionally (2D) layered metal–organic complex nanosheets, which warrants them as the potential doping-free TE materials. For instance, Cu-BHT (BHT = benzenehexathiol) exhibits intrinsically metallic behavior via ultraviolet photoemission valence band spectrum, and possesses ultrahigh room-temperature conductivity of 2500 S cm\(^{-1}\).\(^10,11\) In addition, crystalline Ni3(HIB)\(_2\) and Cu3(HIB)\(_2\) (HIB = hexaiminobenzene) show intrinsically metallic behavior via ultraviolet-photoelectron spectroscopy, and their room-temperature conductivity can approach up to 1000 S cm\(^{-1}\).\(^12\) However, to our best knowledge, intrinsically metallic behavior has never been reported in linear-backbone conducting polymers.

To date, alkali metal doped π-d conjugated nickel coordination polymers are one of the best polymeric TE materials.\(^5\) For example, negatively charged poly(nickel-ethylenetetrathiolate) with potassium counter cations, i.e., poly[K\(_n\)(Ni-ett)] powder has a high experimental \( zT \) of 0.2 at 440 K\(^{13}\) and its \( zT \) can even reach up to 0.32 in films at 400 K.\(^14\) We have elucidated theoretically that the isolated polymer chains for poly(Ni-C\(_2\)S\(_4\)), poly(nickel-ethylenetetrathiolate), poly(Ni-C\(_2\)Se\(_4\)) and poly(Pd-C\(_2\)S\(_4\)) possess narrow band gaps (<1 eV) and large bandwidths (>1 eV).\(^15\) The intermolecular S–S/Se–Se interactions widely exist in organic materials, which strengthen the intermolecular forces and thereby result in metallization.\(^16\) For these reasons, we hypothesize intermolecular S–S/Se–Se interaction networks could be formed in the crystalline poly(Ni-C\(_2\)S\(_4\)) and its analogs, which may narrow down the band gaps and even facilitate the intrinsically metallic behavior. To verify our hypotheses, we
systematically investigate the stacking structures, electronic features and TE performance of crystalline poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(platinum-ethylenedithiolate) [poly(Pt-C2S4)] using first-principles calculations. The packing structures of above-mentioned four crystalline polymers (Figure 1 and S2) are predicted through first-principles molecular dynamics (MD) simulations combined with simulated annealing, and the details are shown in Section 1 of the Supporting Information (SI). Using extended X-ray absorption fine structure measurement, the bond lengths of Ni–S, C–S and C–C in poly[Na₄(Ni-C₂S₄)] are measured to be 2.169, 1.75, and 1.35 Å correspondingly; and the bond angles of S–Ni–S and Ni–S–C are 95° and 103°, respectively, which are well reproduced by our prediction at Perdew–Burke–Ernzerhof functional¹⁸ with dDsC dispersion correction (PBED) level (Figure 1b, Figure S3a and Table S1). Besides, our simulated X-ray diffraction pattern for crystalline poly(Ni-C₂S₄) shows the peaks at 15.0° and 27.1° correspond to the parallel-chain distance (5.695 Å) and interchain distance (3.175 Å) (Figure S4a), which is consistent with the experimental observation for poly[K₅(Ni-C₂S₄)] films.¹⁸

These four polymers adopt a face-to-face packing with a shift of one five-membered ring distance along the backbone direction, so that the metal centers face the carbon–carbon bonds in the adjacent polymeric chain along the π–π stacking direction (top views of Figure 1c, S2b, S2e and S2h). This is because the metal centers are positively charged, while the two carbon atoms are negatively charged, which are confirmed via electron localization function maps (Figure 2a and S8) and Bader charge analysis (Figure 2b and S8). Meanwhile, the packing structures show slip-stacked conformation from the side views, and the polymer planes shift half interchain distance along the π–π stacking direction (Figure 1d, S2c, S2f and S2i).

The distance of two adjacent polymeric backbone metal centers increases from poly(Ni-C₂S₄), poly(Pd-C₂S₄), poly(Pt-C₂S₄) to poly(Ni-C₂Se₄) (Table 1, Figure 1c, S2b,e,h) due to the increment of coordination bond lengths which are determined by the radii of metallic ions [Ni²⁺ (0.83 Å), Pd²⁺ (1.00 Å) and Pt²⁺ (0.94 Å)] and the van der Waals radii of coordination atoms [Se (1.90 Å) and S (1.80 Å)]. At the same time, the parallel-chain distances increases from poly(Ni-C₂S₄), poly(Pt-C₂S₄), poly(Pd-C₂S₄) to poly(Ni-C₂Se₄) (Table 1, Figure 1d, S2c,f,i), because the width of polymer backbone for poly(Ni-C₂S₄) (3.086 Å) is smaller than those of poly(Pt-C₂S₄) (3.171 Å), poly(Pd-C₂S₄) (3.194 Å) and poly(Ni-C₂Se₄) (3.325 Å) (Table 1, Figure 1b, S2a,d,g). Among them, poly(Ni-C₂Se₄) possesses the shortest interchain distance (Table 1 and Figure S2c).

These four polymers all show intrinsically metallic band structures with zero bandgap (Figures 2c and S6), which is the first observation of metallic behavior in doping-free linear-backbone conducting polymers. Our previously theoretical work has

<table>
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<th>d(Parallel-chain) (Å)</th>
<th>d(Inter-chain) (Å)</th>
<th>d(Parallel-chain) (Å)</th>
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<tr>
<td>poly(Ni-C₂S₄)</td>
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<td>3.194</td>
<td>3.345</td>
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<td>6.214</td>
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<td>3.459</td>
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verified that 2D multilayered nickel bis(dithiolene) sheets show intrinsically metallic behavior due to the interlayer interaction between the sulfur atoms in adjacent layers. Interestingly, the intermolecular S–S/Se–Se distances in these polymers are in the range of 3.0–4.0 Å; and the shortest ones are along the π–π stacking direction, namely, 3.3, 3.0, 3.3 and 3.5 Å for crystalline poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(Pt-C2S4), respectively (Figure 3a). Through two experimental examples, the same carrier concentration leaves the origin of the metallization of these four polymers. This finding indicates the intrinsically metallic characteristic can be realized not only in 2D layered transition-metal coordination nanosheets but also in linear-backbone π-d conjugated transition-metal coordination polymers. Moreover, the p orbitals of coordination atoms (S and Se), d orbitals of metallic centers (Ni, Pd and Pt) and p orbitals of carbon atoms all contribute to the states near Fermi energy (Figure 2c and S6), indicating the high degree of π-d conjugation along the polymeric backbones. The room-temperature carrier concentration of poly(Ni-C2Se4) (2.56 × 10\(^21\) cm\(^-3\)) is much lower than those of rest polymers [poly(Pd-C2S4) (7.34 × 10\(^20\) cm\(^-3\)), poly(Pt-C2S4) (1.16 × 10\(^21\) cm\(^-3\)) and poly(Ni-C2S4) (3.01 × 10\(^21\) cm\(^-3\))] (Figure 3a). This can be understood from their DOS near Fermi energy, where the intrinsic carrier concentration increases linearly along the increment of integral DOS in the order of poly(Ni-C2Se4), poly(Pd-C2S4), poly(Pt-C2S4) to poly(Ni-C2S4) (Figure 3b). Through field-effect-modulated doping, the carrier concentration for conducting polymers, indacenodithiophene-co-benzothiadiazole films can be realized around 4.0 × 10\(^19\) cm\(^-3\),\(^1\) and the carrier concentration for bismuth interfacial doped thiophene-diketoarylopyrrole-based quinoidal films can reach to 1.6 × 10\(^19\) cm\(^-3\).\(^2\) Compared with these two experimental examples, the same carrier concentration leaf can be easily achieved for these four doping-free polymers. We herein used Boltzmann transport theory\(^3\) and deformation potential theory\(^4\) to model the TE transport properties, and the details are shown in Section 1 of the SI. Figure 4a shows the intrinsically excellent conductivities of these four polymers. Poly(Ni-C2S4) exhibits a high conductivity of 3.2 × 10\(^4\) S cm\(^-1\) owing to its intrinsically high carrier concentration of 3.01 × 10\(^21\) cm\(^-3\) and moderate mobility of 66.65 cm\(^2\) V\(^-1\) s\(^-1\) (Figure 4b). Its conductivity is of the same order of magnitude as that for the high-quality polyacetylene films after doping with iodine (2 × 10\(^8\) S cm\(^-1\)).\(^5\) Recently, a high conductivity of 2.5 × 10\(^3\) S cm\(^-1\) was detected for copper benzenedithiolate coordination polymer films.\(^6\) Our predicted conductivities for poly(Ni-C2Se4) (4.1 × 10\(^3\) S cm\(^-1\)) and poly(Pt-C2S4) (1.4 × 10\(^3\) S cm\(^-1\)) are of the same order of magnitude. In addition, both poly(Ni-C2S4) (−74 μV K\(^-1\)) and poly(Pd-C2S4) (−106 μV K\(^-1\)) show decent negative Seebeck coefficients, while poly(Ni-C2S4) (20 μV K\(^-1\)) and poly(Pt-C2S4) (4 μV K\(^-1\)) show small positive Seebeck coefficients, because Fermi energy levels for poly(Ni-C2S4) and poly(Pt-C2S4) are mainly located in the valence bands (Figure 2 and S6c). The Seebeck coefficients for poly(Ni-C2S4) (−74 μV K\(^-1\)) and poly(Pd-C2S4) (−106 μV K\(^-1\)) are comparable with that of poly[K(Ni-ett)] films (−125 μV K\(^-1\)) (Figure 4a).\(^7\) The trend of absolute Seebeck coefficients, LSI can be understood from Mott’s formula.\(^8\) As Figure S11 shows, LSI increases along the product of the differential DOS at Fermi energy and the reciprocal intrinsic carrier concentration. The doping-free poly(Ni-C2S4), poly(Ni-C2Se4) and poly(Pd-C2S4) with intrinsically metallic behavior possess not only ultrahigh conductivities (>10\(^3\) S cm\(^-1\)), but also decent Seebeck coefficients, which makes them competitive to the currently state-of-the-art doped organic TE materials, such as n-type.

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**Figure 3.** (a) Intrinsic carrier concentration, N for poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(Pt-C2S4) at room temperature, respectively. (b) Carrier concentration, N vs integral DOS for poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(Pt-C2S4), respectively.

**Figure 4.** (a) Absolute Seebeck coefficients, LSI and conductivities, \(\sigma\) for poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(Pt-C2S4), respectively (red dots). Some experimental values are displayed (blue X-type). The materials for 1–8 are n-type 4-(1,3-dimethyl-2,3-dihydro-1H-benzoimidazol-2-yl)phenyl dimethylamine doped dihydropyrrolo[3,4-c]pyrrole-1,4-diylidenethiophene (thieno[3,2-b]thiophene),\(^9\) n-type bismuth doped thiophene-diketoarylopyrrole-based quinoidal,\(^10\) p-type PEDOT:Tos,\(^11\) n-type poly[K(Ni-C2S4)] power,\(^12\) n-type poly[K(Ni-C2Se4)] films,\(^13\) p-type PEDOT:Tos, p-type PEDOT:PSS, and p-type bis(trifluoromethylsulfonyl)imide (BTFMSI) doped PEDOT,\(^14\) respectively. (b) Power factors, \(S\sigma\) and mobilities, \(\mu\) for poly(Ni-C2S4), poly(Ni-C2Se4), poly(Pd-C2S4) and poly(Pt-C2S4), respectively.
intrinsically metallic behavior can be realized in doping-free PEDOT etc. (Figure 4a).

Poly(Ni-C₅S₅) (2234 μW m⁻¹ K⁻²), poly(Ni-C₅S₆) (1240 μW m⁻¹ K⁻²) and poly(Pd-C₅S₄) (1034 μW m⁻¹ K⁻²) have decent power factors (Figure 4b and Table S5). The n-type power factor of hybrids of carbon nanotubes and PEDOT treated by tetakis(dimethylamino)ethylene was measured to be 1050 μW m⁻¹ K⁻². Compared with this report, our calculated n-type power factor for poly(Pd-C₅S₄) (1034 μW m⁻¹ K⁻²) is comparable. Besides, an ultrahigh p-type power factor of 1270 μW m⁻¹ K⁻² has been achieved in tosylate doped PEDOT films, which is quite close to our predicted p-type power factor for poly(Ni-C₅Se₅) (1240 μW m⁻¹ K⁻²).

In addition, these four polymers show decent mobilities (Figure 4b). Poly(Pd-C₅S₄) (7.764 cm² V⁻¹ s⁻¹) and poly(Pt-C₅S₄) (7.367 cm² V⁻¹ s⁻¹) exhibit nearly the same mobilities (Figure 4b and Table S3). Poly(Ni-C₅Se₅) has a high mobility of 989.6 cm² V⁻¹ s⁻¹ mainly due to its dispersed bands near Fermi energy. The intrachain hole mobility of isolated ladder-type poly(p-phenylenes) chains was detected to be around 600 cm² V⁻¹ s⁻¹ through time-resolved microwave conductivity measurement,²⁹ the same order of magnitude of poly(Ni-C₅Se₅). Meanwhile, poly(Ni-C₅Se₅) shows a good mobility of 66.65 cm² V⁻¹ s⁻¹. Recently, a high field-effect electron/hole mobility of 116/99 cm² V⁻¹ s⁻¹ were reported for Cu-BHT films composed 2D nanosheets.¹⁰ Compared with this experimental result, the mobility of poly(Ni-C₅Se₅) is of the same order of magnitude.

In conclusion, we have demonstrated for the first time the intrinsically metallic behavior can be realized in doping-free linear-backbone poly(Ni-C₅S₅), poly(Ni-C₅S₆), poly(Pd-C₅S₄) and poly(Pt-C₅S₄). The reason behind is the formation of dense intermolecular S/Se−S−Se attractive interaction networks, which strengthen the intermolecular forces. Moreover, we found these four polymers possess moderate carrier concentrations and decent conductivities. Poly(Ni-C₅S₅), poly(Ni-C₅Se₅) and poly(Pd-C₅S₄) exhibit intrinsically prominent power factors (∼10⁻⁵ μW m⁻¹ K⁻²), which are comparable with those of the currently state-of-the-art doped TE polymers. We anticipate this work would spark new routes to design intrinsically electrically conducting polymers for TE applications.

**REFERENCES**

(1) He, J.; Tritt, T. M. Science 2017, 357, eaak9997.
(24) Bardeen, J.; Shockley, W. Phys. Rev. 1950, 80, 72−80.
