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

Wen Shi,† Gang Wu,† Kedar Hippalgaonkar,‡§ Jian-Sheng Wang,# Jianwei Xu,† and Shuo-Wang Yang*†

1Institute of High Performance Computing, Agency for Science, Technology and Research, 1 Fusionopolis Way, #16-16 Connexis, Singapore 138632
2Institute of Materials Research and Engineering, Agency for Science, Technology and Research, 2 Fusionopolis Way, #08-03 Innovis, Singapore 138634
3School of Materials Science & Engineering, Nanyang Technological University, 50 Nanyang Ave, Singapore 639798
4Department of Physics, National University of Singapore, 21 Lower Kent Ridge Rd, Singapore 117551

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. Based on density functional calculations, we have corroborated that four crystalline π-d conjugated transition-metal coordination polymers, including poly(Ni-C$_4$S$_4$), poly(Ni-C$_5$Se$_5$), poly(Pd-C$_4$S$_4$) and poly(Pt-C$_5$S$_5$) exhibit intrinsically metallic behavior arising from the formation of dense inter-molecular interaction networks between sulfur/seelenium atoms. They show moderate carrier concentrations (10$^{19}$-10$^{21}$ cm$^{-3}$) and decent conductivities (10$^5$-10$^6$ S cm$^{-1}$), among which, poly(Ni-C$_4$S$_4$), poly(Ni-C$_5$Se$_5$) and poly(Pd-C$_4$S$_4$) possess high power factors ($\sim 10^7$ µW m$^{-1}$ 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 general 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 twenty years.$^2$ 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 valance band spectrum, and possesses ultrahigh room-temperature conductivity of 2500 S cm$^{-1}$$^{11,12}$ In addition, crystalline Ni$_3$(HIB)$_2$ and Cu$_3$(HIB)$_2$ (HIB = hexaiminobenzene) show intrinsically metallic behavior via ultraviolet-photoelectron spectroscopy, and their room-temperature conductivity can approach up to 1000 S cm$^{-1}$.$^{11,12}$ 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.$^6$ For example, negatively charged poly(nickel-ethylenetetrathiolate) with potassium counter cations, i.e., poly[K(Ni-ett)] powder has a high experimental zT$^{13}$ of 0.2 at 440 K 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$_4$S$_4$), poly(nickel-ethylenetetrathiol) [poly(Ni-C$_4$S$_4$)] and poly[palladium-ethylenetetrathiolate] [poly(Pd-C$_4$S$_4$)] possess narrow band gaps (<1 eV) and large bandwidths (>1 eV).$^{15}$ The inter-molecular S-S/Se-Se interactions widely exist in organic materials, which strengthen the inter-molecular forces and thereby result in metallization.$^{16}$ For these reasons, we hypothesize inter-molecular S-S/Se-Se interaction networks could be formed in the crystalline poly(Ni-C$_4$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-C$_4$S$_4$), poly(Ni-C$_5$Se$_5$), poly(Pd-C$_4$S$_4$), and poly(platinum-ethylenetetrathiolate) [ poly(Pt-C$_5$S$_5$)] using first-principles calculations.
The packing structures of abovementioned 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 Supporting Information (SI). Using extended X-ray absorption fine structure measurement, the bond lengths of Ni-S, C-S, and C-C in poly[Na_{2}(Ni-C_{3}S_{4})] 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 functional with dDsC dispersion correction (PBED) level (see Figure 1b, Figure S3a and Table S1). Besides, our simulated X-ray diffraction pattern for crystalline poly(Ni-C_{3}S_{4}) shows the peaks at 15.0° and 27.1° which are consistent with the experimental observation for poly[Kt(Ni-C_{3}S_{4})] films.

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 relatively positively charged, while the two carbon atoms are relatively negatively charged, which are confirmed by 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 inter-chain 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-C_{3}S_{4}), poly(Pd-C_{3}S_{4}) and poly(Pt-C_{3}S_{4}) to poly(Ni-C_{3}Se_{4}) (Table 1, Figure 1b, S2a, S2d and S2g) due to the increment of coordination bond lengths which are determined by the radii of metallic ions [Ni^{2+} (0.83 Å), Pd^{2+} (1.00 Å) and Pt^{2+} (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-C_{3}S_{4}), poly(Pt-C_{3}S_{4}), poly(Pd-C_{3}S_{4}) to poly(Ni-C_{3}Se_{4}) (Table 1, Figure 1d, S2c, S2f and S2i), because the width of polymer backbones for poly(Ni-C_{3}S_{4}) (3.086 Å) is smaller than those of poly(Pt-C_{3}S_{4}) (3.171 Å), poly(Pd-C_{3}S_{4}) (3.194 Å) and poly(Ni-C_{3}Se_{4}) (3.325 Å) (Table 1, Figure 1b, S2a, S2d and S2g). Among them, poly(Ni-C_{3}Se_{4}) possesses the shortest inter-chain distance (Table 1 and Figure S2c).

<table>
<thead>
<tr>
<th>Polymer</th>
<th>d_{MM} (Å)</th>
<th>W_{S} (Å)</th>
<th>d_{inter-chain} (Å)</th>
<th>d_{parallel-chain} (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>poly(Ni-C_{3}S_{4})</td>
<td>5.982</td>
<td>3.086</td>
<td>3.175</td>
<td>5.695</td>
</tr>
<tr>
<td>poly(Ni-C_{3}Se_{4})</td>
<td>6.420</td>
<td>3.325</td>
<td>3.028</td>
<td>6.484</td>
</tr>
<tr>
<td>poly(Pd-C_{3}S_{4})</td>
<td>6.209</td>
<td>3.194</td>
<td>3.345</td>
<td>6.152</td>
</tr>
<tr>
<td>poly(Pt-C_{3}S_{4})</td>
<td>6.214</td>
<td>3.171</td>
<td>3.459</td>
<td>5.645</td>
</tr>
</tbody>
</table>

These four polymers all show intrinsically metallic band structures with zero bandgap (Figure 2c and S6), which is the first observation of metallic behavior in doping-free linear-backbone conducting polymers. Our previously theoretical work has verified that 2D multilayered nickel bis(dithiolene) sheets show intrinsically metallic behavior due to the interlayer interaction between the sulfur atoms in adjacent layers.20 Interestingly, the inter-molecular 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-C_{3}S_{4}), poly(Ni-C_{3}Se_{4}), poly(Pd-C_{3}S_{4}) and poly(Pt-C_{3}S_{4}), respectively (Figure 1e and S7). Such distances are shorter than or comparable with the sum of van der Waals radii of S (3.60 Å) or Se (3.80 Å) atoms. Accordingly, we can confirm nonbonding S-S/Se-Se attractive interaction networks form, which greatly strengthen the inter-molecular forces and stabilize the polymeric stacking structures. So, the inter-molecular S-S/Se-Se attractive interaction networks are 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-C$_2$S$_4$) (2.56×10$^{19}$ cm$^{-3}$) is much lower than those of rest polymers [poly(Pd-C$_2$S$_4$) (7.34×10$^{20}$ cm$^{-3}$), poly(Pt-C$_2$S$_4$) (1.16×10$^{21}$ cm$^{-3}$) and poly(Ni-C$_2$Se$_4$) (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-C$_2$Se$_4$), poly(Pd-C$_2$S$_4$), poly(Pt-C$_2$S$_4$) to poly(Ni-C$_2$S$_4$) (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$^{-3}$, and the carrier concentration for bismuth interfacial doped thiophene-diketopyrrolopyrrole-based quinoidal films can reach to 1.6×10$^{20}$ cm$^{-3}$. Compared with these two experimental examples, the same carrier concentration level can be easily achieved for these four doping-free polymers.

We herein used Boltzmann transport theory$^{23}$ and deformation potential theory$^{24}$ to model the TE transport properties, and the details are shown in Section 1 of SI. Figure 4a shows the intrinsically excellent conductivities of these four polymers. Poly(Ni-C$_2$S$_4$) exhibit a high conductivity of 3.2×10$^{4}$ S cm$^{-1}$ owning 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 polycrystalline films after doping with iodine (2×10$^{2}$ S cm$^{-1}$).$^{25}$ Recently, a high conductivity of 2.5×10$^{4}$ S cm$^{-1}$ was detected for copper benzenehexathiocarbocyanine coordination polymer films.$^{19}$ Our predicted conductivities for poly(Ni-C$_2$Se$_4$) (4.1×10$^{4}$ S cm$^{-1}$) and poly(Pt-C$_2$S$_4$) (1.4×10$^{4}$ S cm$^{-1}$) are of the same order of magnitude. In addition, both poly(Ni-C$_2$Se$_4$) (-74 μV K$^{-1}$) and poly(Pd-C$_2$S$_4$) (-106 μV K$^{-1}$) show decent negative Seebeck coefficients, while poly(Ni-C$_2$S$_4$) (20 μV K$^{-1}$) and poly(Pt-C$_2$S$_4$) (4 μV K$^{-1}$) show small positive Seebeck coefficients, because Fermi energy levels for poly(Ni-C$_2$S$_4$) and poly(Pt-C$_2$S$_4$) are mainly located in the valence bands (Figure 2 and S6c). The Seebeck coefficients for poly(Ni-C$_2$Se$_4$) (-74 μV K$^{-1}$) and poly(Pd-C$_2$S$_4$) (-106 μV K$^{-1}$) are comparable with that of poly[K$_3$(Ni-eti)] films (-125 μV K$^{-1}$) (Figure 4a).$^{14}$ The trend of absolute Seebeck coefficients, [S], can be understood from Mott’s formula.$^{26}$ As Figure S1I shows, [S] increases along the product of the differential DOS at Fermi energy and the reciprocal intrinsic carrier concentration. The doping-free poly(Ni-C$_2$S$_4$), poly(Ni-C$_2$Se$_4$) and poly(Pd-C$_2$S$_4$) with intrinsically metallic behavior possess not only ultra-high 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 poly[K$_3$(Ni-C$_2$S$_4$)],$^{14}$ p-type poly(styrenesulphonate) doped poly(3,4-ethylenedioxythiophene) (PEDOT)$^3$ etc. (Figure 4a).

Poly(Ni-C$_2$S$_4$) (2234 μW m$^{-1}$ K$^{-2}$), poly(Ni-C$_2$Se$_4$) (1240 μW m$^{-1}$ K$^{-2}$) and poly(Pd-C$_2$S$_4$) (1034 μW m$^{-1}$ K$^{-2}$) have decent power factors. (Figure 4b and Table S5). The n-type power factor of hydrides of carbon nanotubes and PEDOT treated by tetrakis(dimethylamino)ethylene was measured to be 1050 μW m$^{-1}$ K$^{-2}$.$^{28}$ Compared with this report, our calculated n-type power factor for poly(Pd-C$_2$S$_4$) (1034 μW m$^{-1}$ K$^{-2}$) is comparable. Besides, an ultra-high p-type power factor of 1270 μW m$^{-1}$ K$^{-2}$ has been achieved in tosylate doped PEDOT films,$^4$ which is quite close to our predicted p-type power factor for poly(Ni-C$_2$Se$_4$) (1240 μW m$^{-1}$ K$^{-2}$).

In addition, these four polymers show decent mobilities (Figure 4b). Poly(Pd-C$_2$S$_4$) (7.764 cm$^2$ V$^{-1}$ s$^{-1}$) and poly(Pt-C$_2$S$_4$) (7.367 cm$^2$ V$^{-1}$ s$^{-1}$) exhibit nearly the same mobilities (Figure 4b and Table S3). Poly(Ni-C$_2$Se$_4$) has a high mobility of 989.6 cm$^2$ V$^{-1}$ s$^{-1}$ mainly due to its dispersed bands near Fermi energy. The intra-chain hole mobility of isolated ladder-type poly(p-phenylene) chains was detected to be around 600 cm$^2$ V$^{-1}$ s$^{-1}$ through time-resolved microwave conductivity measurement,$^{29}$ the same order of magnitude of poly(Ni-C$_2$Se$_4$). Meanwhile, poly(Ni-C$_2$Se$_4$) show a good mobility of 66.65 cm$^2$ V$^{-1}$ s$^{-1}$. Recently, a high field-effect electron/hole mobility of 116/99 cm$^2$ V$^{-1}$ s$^{-1}$ were reported for Cu-BHT films composed 2D nanosheets.$^{10}$ Compared with this experimental result, the mobility of poly(Ni-C$_2$Se$_4$) 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-C$_2$S$_4$), poly(Ni-C$_2$Se$_4$), poly(Pd-C$_2$S$_4$),
and poly(PT-C3S). The reason behind is the formation of dense inter-molecular S-Si/Se-Se attractive interaction networks, which strengthen the inter-molecular forces. Moreover, we found these four polymers possess moderate carrier concentrations and decent conductivities. Poly(Ni-C3S), poly(Ni-C3Se) and poly(Pd-C3S) exhibit intrinsically prominent power factors (~ 10^4 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.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website. Supporting computational details, discussions, figures, tables, and supporting references (PDF)

AUTHOR INFORMATION

Corresponding Author

E-mail: yangsw@ihpc.a-star.edu.sg

Notes

The authors declare no competing financial interests.

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