Emerging Organic Thermoelectric Applications from Conducting Metallopolymers

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Thermoelectric (TE) materials are emerging as an attractive and promising candidate for solving the energy crisis in which waste heat is efficiently recycled to generate electricity. In order to realize high thermoelectric energy conversion, an ideal TE material should present high electrical conductivity and Seebeck coefficient, but low thermal conductivity. In recent years, conducting coordination polymers have been recognized as new promising organic materials for TE uses, as they bear the advantages of both inorganic and organic materials: proper integration of metal centers helps to enhance the electrical conductivity, while organic backbones are always heat insulators. Herein, a variety of TE metallopolymers will be

highlighted and their TE properties as well as the related physical factors will be discussed in detail. To the best of our knowledge, the highest *ZT* value of p-type organic polymer up-to-date have reached 0.42, and by comparison, a Ni-based polymer poly(Ni-ett) is the only n-type TE possessing a *ZT* value comparable to those of PEDOT-based p-type counterparts (PEDOT = poly(3,4-ethylenedioxythiophene)). Based on the current achievements, a promising blueprint is displayed to boost up the further development of metallopolymer-based organic TE materials in the near future.

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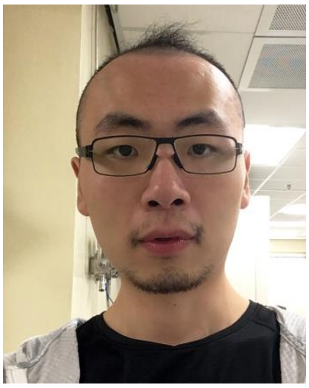

Jiahua Li received his B.Sc. degree in 2012 and M.Sc. degree in 2016 from Shenzhen University. He is now pursuing his Ph.D. degree under the supervision of Prof. Wai-Yeung Wong in the Department of Applied Biology and Chemical Technology at The Hong Kong Polytechnic University. His current research focuses on the design, synthesis and characterization of thermoelectric metallopolymers.

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1. Introduction

With the rapid growth of the world, energy, especially electricity, is playing an increasing crucial role in our daily life, the consumption of which is exhibiting an upward trend.[1] As a consequence, it becomes an urgent problem of how more electric energy could be generated while keeping our environment clean. The traditional approach – thermal power generation, however, plays the leading role still, when compared with other environment-friendly approaches such as solar, hydraulic, geothermal, wind, etc. In this process, more than half of the heat is dissipated with its release to the air,[1] which implies the innovation of technologies that can harvest such wasted heat to regenerated electricity for a second batch is extremely promising. Fortunately, a class of material that realizes this thermoelectric (TE) conversion (and its reversed version) has aroused increasing research interest.[2, 3]

Generally, the conversion efficiency of a given TE material is defined by a dimensionless parameter – figure of merit (ZT) as $ZT = S^2\sigma T/\kappa$, where S is Seebeck coefficient ($V\cdot K^{-1}$), σ ($S\cdot m^{-1}$) is electrical conductivity, κ ($W\cdot m^{-1}\cdot K^{-1}$) is thermal conductivity and T (K) is absolute temperature. Apparently, a high-performance TE material should meet the conditions of high Seebeck coefficient and electrical conductivity, but low thermoelectric conductivity. Actually, optimization of the efficiency is not easy, as these three indexes are inter-related, it is hard to avoid improving one property without affecting the other two negatively.[4, 5] Even so, various inorganic TE materials with high ZT values exceeding 1.0 were prepared during the past decade.[6-11] Nevertheless, the practical application of these materials is restricted due to some disadvantages including the toxicity of heavy metals, higher cost of the rare elements, difficulties in processing and the fact that some inorganics demonstrated superior TE performances only at a relatively high temperature.[4, 12]

For comparison, owing to the features of light weight, flexibility, lower toxicity, the enabled processibility in solution, and the potential to show decent efficiency at around room temperature, organic TE (OTE) candidates will provide a wide variety of applications,[13] especially those in contact with the human body directly.[5, 12, 14] The biological heat given off by human body could be utilized to generate electricity continuously, which implies the possibility to reduce or save the downtime for battery charging or replacement for micropower devices.[5] In light of the above advantages, numerous works on synthesizing new OTE molecules,[15, 16] providing rational strategies for designing robust generators[17-19] or improving OTE properties of available materials[20-24] have begun to flourish. The chemical structures of some representative OTE polymers are illustrated in **Figure 1**. Since the report of the excellent TE performance of poly(metal 1,1,2,2-ethenetetrathiolate)s in 2012,[25] Zhu et al. have successfully expanded the molecular research to the field of OTE metallopolymers. In view of the low thermal conductivity, power factor ($PF = S^2\sigma$) is commonly used to describe and assess the performance of organics and metal-coordinated complexes.

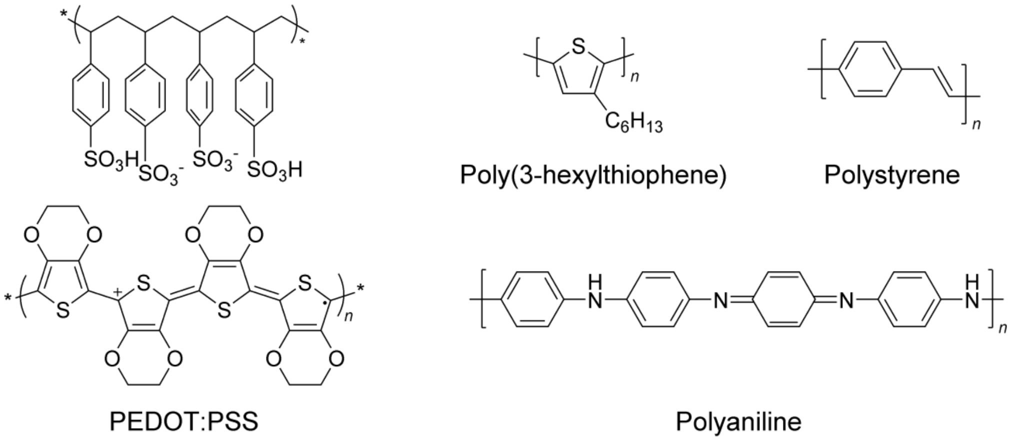


Figure 1. Some examples of OTE materials.

In general, the advantages of metallation includes (1) the ability to generate active species for charge transport through the redox activity of both the metal atom and the organic ligand;[26-28] (2) fine-tuning of the HOMO-LUMO energy gap through the interaction of the d-orbitals of the transition metal with the HOMO and/or LUMO of the ligand;[26, 28-30] (3) diversity of the molecular framework based on the coordination number, geometry, and valence shell of the selected transition metal atom;[29] (4) improving the solubility and tuning the intermolecular π-stacking and/or metallophilicity in the solid state and (5) lowering the thermal conductivity of conjugated organic polymers. The highly coplanar structure of fused aromatic systems not only can facilitate the π-electron delocalization because of the optimal π-orbital overlap but also can promote the π-π intermolecular stacking interaction, which is highly favorable for high charge carrier transport. Thanks to these benefits, it is impressive to investigate metallopolymer-based OTE materials and there is a very bright prospect of research along this line.

In this Trend article, a brief overview of the OTE performance of a series of conducting metallopolymers and their associated physical factors will be put forward, and the development trend of these coordinated TE polymers will be discussed.

2. 1D 1,1,2,2-Ethenetetrathiolate-Based Metallopolymers

The OTE materials of both p-type and n-type 1D metal-coordinated polymers (1D-MCP) containing 1,1,2,2-ethenetetrathiolate (ett) linking bridge (shown in **Figure 2(a)**) began to spring up in recent years after a series of research progress was reported. Poly(metal-ett) polymers were first reported 30 years ago by Poleschner and Cassoux et al., in which the planar ribbon-like polymers exhibited 1D electrical conductivity that could be attributed to the through-bond coupling between the transition metal d-orbitals and ett ligand π-orbitals.[31-33] As 1D poly(metal-ett) (or poly(M-ett)) always exhibited high electrical conductivity (ranging from 10^{-5} S·cm^{-1} to 50 S·cm^{-1}) and low thermal conductivities, they will probably be a promising choice for the future OTE applications.[31-33]

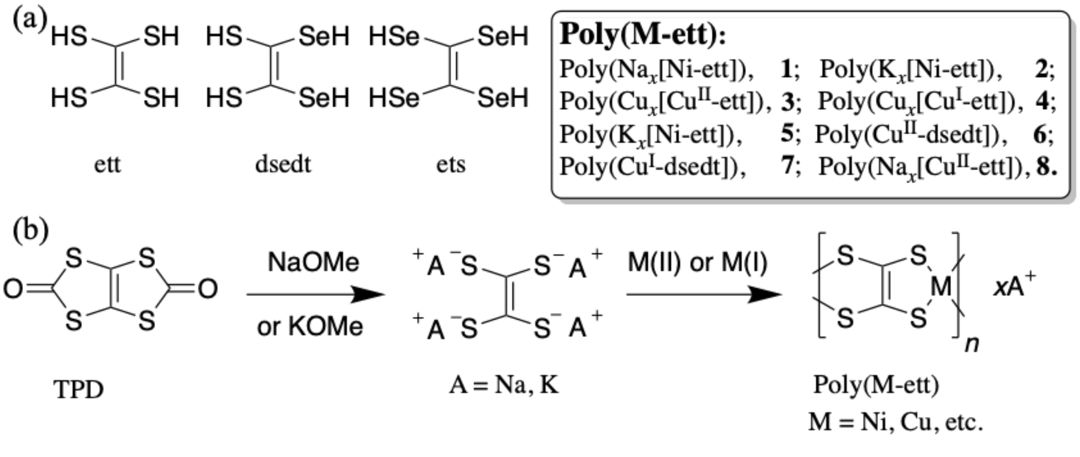


Figure 2. (a) Structures of ett, dsedt, ets, and (b) common synthetic scheme for poly(M-ett).

The common synthesis of poly(M-ett) polymers was mostly followed by steps shown in **Figure 2(b)**. Tetrathiolate anion was generated *in situ* from the reaction of 1,3,4,6-tetrathiapentalene-2,5-dione (TPD) with methoxide, and the target polymers can be obtained by coordination of thiolate with the corresponding transition metal salts. OTE performance was influenced by varying the methoxide source and the equivalents of metal.[34] However, their poor solubility renders the commonly used structural characterization techniques ineffective, and the amorphous property makes X-ray diffraction impossible to analyze their structures. Nevertheless, their bonding environment and oxidation state could be analyzed *via* X-ray photoelectron spectroscopy (XPS) technique. Elemental analysis (EA) sometimes serves as the only reported characterization for these compounds to a certain extent. Although the insolubility of these materials limited their processability and practicability, they still demonstrated excellent TE properties, as shown in **Table 1**.

Table 1. OTE properties of some typical poly(metal-ett) materials at 300 K.

Sample	**Form**	σ [$S\cdot cm^{-1}$]	S [$\mu V\cdot K^{-1}$]	PF [$\mu W\cdot m^{-1}\cdot K^{-2}$]	**Ref.**
1	Pellet	40	-75	23	25
2	Pellet	44	-122	66	25
3	Pellet	9.5	83	6.5	25
3	Pellet (1 eq. $LiBHEt_3$)	59.4	50.5	15.2	35
4	Pellet (1 eq. $LiBHEt_3$)	186.5	50.5	46.7	36
5/PVDF	Film *via* ball-milling	2.12	-44.9	0.43	34
3/PVDF	Film *via* ball-milling	5.14	41.0	0.86	34
6	Pellet	7.4	90	5.9	37
7	Pellet	35.2	42	6.2	37

1/CNT/PVC a)	Film *via* drop-casting	429.3 ± 7.1	30.2 ± 0.6	39.1 ± 1.6	46
1/CA/CNT a)	Film *via* drop-casting	341.0	33.0	37.0	47

a) Mass ratio: 10/8/3, at 340 K.

As a new type of OTE materials, poly(M-ett) polymers gradually comes to our attention with the investigation of their TE properties by Zhu et al. in 2012.[25] The OTE properties of both p-type conductors (poly(Cu$_x$[Cu$^{\mathrm{II}}$-ett]) (**3**) and poly(Na$_x$[Cu$^{\mathrm{II}}$-ett]) (**8**)) with positive S values and n-type counterparts (poly(Na$_x$[Ni-ett]) (**1**) and poly(K$_x$[Ni-ett]) (**2**)) with negative S values were investigated. Here, the negative (positive) Seebeck coefficient indicates that the major carriers are electrons (holes) in the corresponding materials. Particularly, this is the first example of non-doped n-type OTE material with a ZT value as high as 0.2 at ~400 K. The n-type poly(Na$_x$[Ni-ett]) (**1**) and p-type poly(Cu$_x$[Cu$^{\mathrm{II}}$-ett]) (**3**) were combined as 35 n-p couples to form the OTE module which delivered the power of 2.8 μW·cm^{-2}.

In order to increase the TE performance of p-type bulk OTE materials, the properties of both poly(Cu$_x$[Cu$^{\mathrm{II}}$-ett]) (**3**)[35] and poly(Cu$_x$[Cu$^{\mathrm{I}}$-ett]) (**4**)[36] have been investigated through chemical redox processes, because metal dithiolenes experienced multiple oxidation states (**Table 1**). Another work involves copper (*Z*)-1,2-dihydroselenoethene-1,2-dithiol (dsedt) metallopolymers (**Figure 1(a)**), and the impact of different chalcogen donor atoms on their OTE properties was compared.[37] Specifically, density functional theory calculations were further used to study the effect of S and Se. Results suggested that the intrinsically metallic behavior resulted from the formation of dense intermolecular interaction networks between chalcogen atoms, which endowed poly(Ni-ett), poly(Ni-ethylenetetraselenol) (abbreviated as poly(Ni-ets)), poly(Pd-ett) and poly(Pt-ett) with conspicuous *PF* values (~10^3 $\mu W \cdot m^{-1} \cdot K^{-2}$).[38]

In recent years, scientists have made sustained efforts to improve the processability of this type of OTE materials. Considering the insolubility of these materials, several reports employed ball-milling technique to afford TE composite films consisting of poly(M-ett) and poly(vinylidene fluoride) (PVDF).[34, 39, 40] In a typical process,[40] for example, the powder of the complex was mixed with a solution of poly(vinylidene fluoride) (PVDF) in DMSO and the milling process was maintained for 24 h. After that, the composite slurry was cast on glass substrates, dried *in vacuo* and the resulting films were cut into proper size for TE tests. Further post-treatment of thermal annealing process contributed to the improvement of *PF* value from 0.5 to 12.5 $\mu W \cdot m^{-1} \cdot K^{-2}$ for Ni-ett/PVDF films.[41] Zhu et al. also adopted an innovative method to prepare OTE devices with abundant advantages in terms of flexibility, low cost and solution-processability, which patterned poly[K_x(Ni-ett)] (**2**) on a pre-patterned polyethylene terephthalate (PET) substrate with a printed polydimethylsiloxane (PDMS) layer that served as a mask through the electrochemical process[42], giving the highest power density at 577.8 $\mu W \cdot cm^{-2}$. The insoluble and infusible OTE materials can be inspired by the above-mentioned techniques to fabricate solution-processable TE devices. Other methods such as electrochemical polymerization and potentiostatic deposition were also developed to prepare n-type poly(Ni-ett) thin films.[43, 44] The electrochemical deposition method was employed to improve the OTE performance and processability of poly(M-ett).[43] The highly uniform and flexible film of poly(Ni-ett) can be prepared as continuous large area thin films displaying a degenerate semiconductor character with a narrow bandgap of 0.22 eV. The high quality self-supported films of polycrystalline structure with improved molecular ordering were obtained (**Figure 3**), which could enhance the electrical conductivity and facilitate their processability for further integration into TE generators. The *ZT* value went up to 0.30 ± 0.03 under room temperature, which is the new record for n-type OTE materials, and further improvements will probably make poly(M-ett) more competitive in the future.

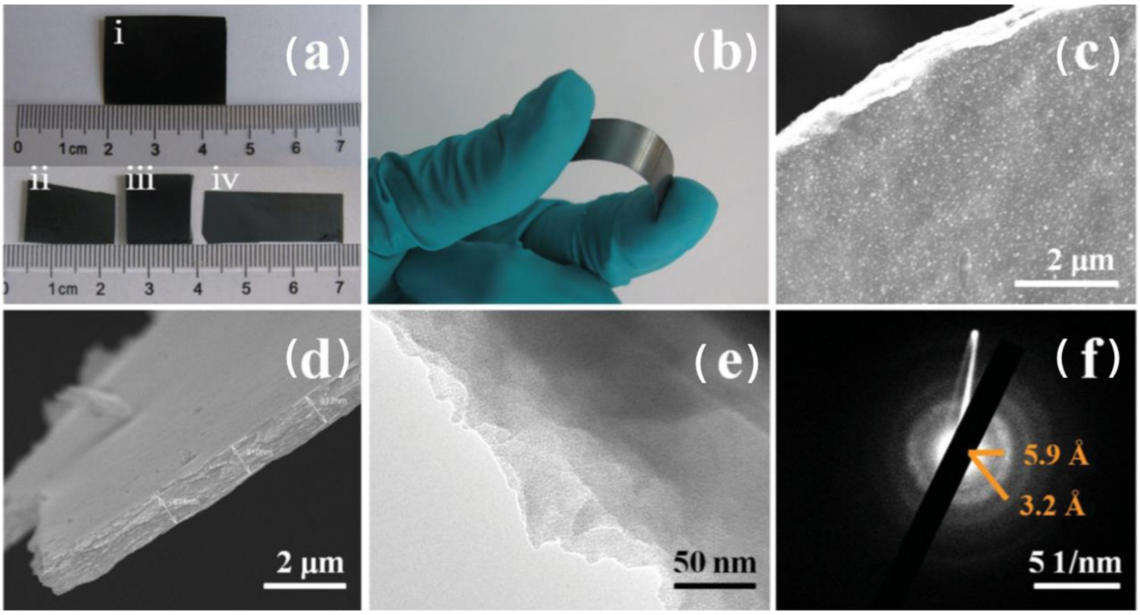


Figure 3. Morphologies of poly(Ni-ett) films. (a) The images of poly(Ni-ett) films deposited on polyimide (PI) (i), poly(tetrafluoroethylene) (Teflon) (ii), quartz (iii), and poly(ethylene terephthalate) (PET) (iv) substrates. (b) The flexibility of the thin film deposited on PET. (c,d) Top-view c) and cross-section view d) of scanning electron microscopy (SEM) images of poly(Ni-ett) film. (e) Transmission electron microscopy (TEM) image of poly(Ni-ett) film. The edge of the film clearly shows a multilayer feature. (f) Selected-area electron diffraction (SAED) pattern of poly(Ni-ett) film. The ring pattern indicates the polycrystalline

characteristics of the film. Reproduced with permission from Ref. [43], copyright 2016 John Wiley and Sons.

In 2018, the first example to explore the Peltier effect in OTE films using suspended poly(Ni-ett) films has been reported by Zhu's group[45], which indicated that organic materials hold the ultimate potential to enable flexible solid-cooling applications.

Toshima et al. explored the TE properties of three-component hybrid materials that were formed from nanodispersed poly(metal-ett), carbon nanotubes (CNTs), and insulating poly(vinyl chloride) (PVC) or cellulose acetate (CA).[46, 47] PVC or CA act as a blocker in the heat transfer process, while CNTs offer the main tunnels of charge transfer and poly(metal-ett) can work as a promoter not only for carrier transfer between CNTs, but also for the dispersion of CNTs. Therefore, the hybrid material is able to enhance the electrical conductivity and reduce the thermal conductivity.

3. 2D Metallopolymers

In recent years, metallopolymers with 2D structures are becoming more and more popular in the field of TE molecular design. Metal-organic framework (MOF) and covalent organic framework (COF) materials, in particular, have drawn much research attention, owing to their unique features including regular ordering of the building blocks, paralleled and unidirectional alignment of 2D sheets[48], which are in favor of establishing highly efficient transporting channels for charge carriers, and are essential conditions to realize TE materials with excellent performance.

3.1 M$_3$(2,3,6,7,10,11-hexaiminotriphenylene)$_2$

A well-studied example in this category is the HITP-based metallopolymer Ni$_3$(HITP)$_2$ (HITP = 2,3,6,7,10,11-hexaiminotriphenylene) which was first synthesized by Sheberla et al. in 2014, as shown in **Figure 4**.[49] Electrical tests suggested an extremely high conductivity of 2 and 40 S·cm^{-1} for the pellet and film, respectively, rendering this material as a top-class MOF conductor. By employing pressed pellets from a hydraulic machine, further targeted work[50] indicated the n-type TE behavior of this complex, with a constant Seebeck coefficient near -12 μV·K^{-1} within the temperature range between 25 °C and 45 °C. More importantly, the periodically repeated, porous structure endowed this material with an ultralow, invariable thermal conductivity, κ = 0.21 W·m^{-1}·K^{-1} over the same temperature range. As a result, a maximum ZT of 1.34 × 10^{-3} was obtained at 45 °C. Besides, Nonoguchi's work proved that the TE properties of this coordination polymer were influenced by the employed nickel source and a larger crystal grain size was in favor of elevating the electrical conductivity.[51]

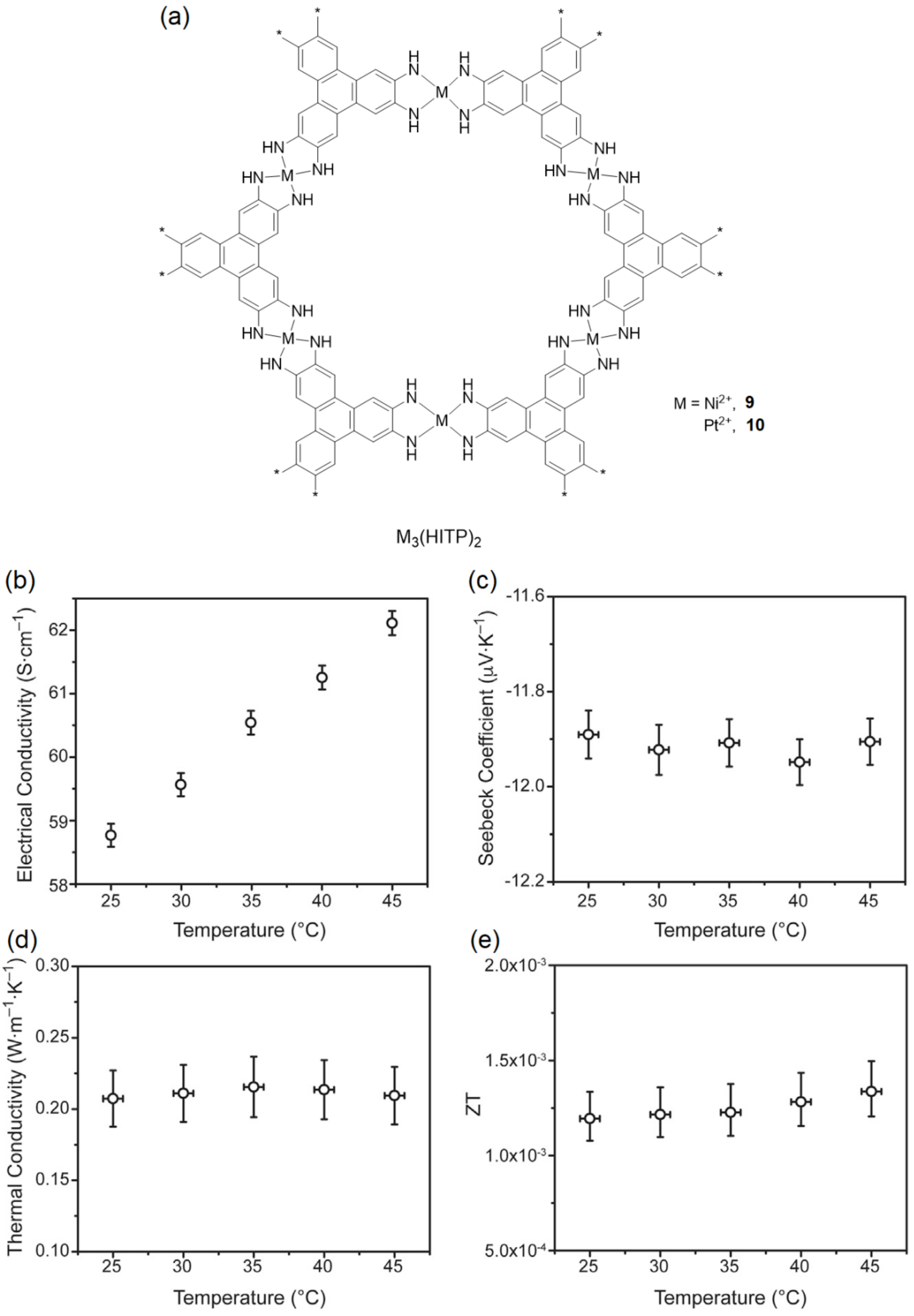


Figure 4. (a) Schematic representation of $M_3(HITP)_2$ (compounds **9** and **10**). Temperature-dependent tests of (b) electrical conductivity, (c) Seebeck coefficient, (d) thermal conductivity and (e) *ZT* of pressed pellets of **9**. (Figures 4b-4e reproduced with permission from Ref. [50], copyright 2017 Elsevier.)

Theoretical study[52] by He and co-workers further expanded the coordinated metal to the whole Group 10 elements (Ni, Pd and Pt). Positive feedback was given in which all these analogues may show high TE performance and an enhanced charge carrier transmission could be realized by employing heavier metal ions.

As a brief summary, the OTE performances of these HITP-based metallopolymers are extracted and listed in **Table 2**.

Table 2. OTE properties of some reported $M_3(HITP)_2$ materials.

Sample	**Form**	σ **[S·cm^{-1}]**	S **[μV·K^{-1}]**	PF **[μW·cm^{-1}·K^{-2}]**	**Other parameters**	**Ref.**
9	Pellet	2	-	-	-	49
	Film	40	-	-	-	
9	Pellet	58.8	-11.9	8.31×10^{-3}	at 25 °C $\kappa = 0.21$ W·m^{-1}·K^{-1} $ZT = 1.19 \times 10^{-3}$	50
		62.1	-11.9	8.80×10^{-3}	at 45 °C $\kappa = 0.21$ W·m^{-1}·K^{-1} $ZT = 1.34 \times 10^{-3}$	
9	Pellet	~ 0.7	~ -20	1.5×10^{-10}	$NiCl_2$ as the nickel source	51
10	Calculated result	-	600	-	at a charge carrier concentration of 1×10^{10} cm^{-2}	52

3.2 Metal Bis(dithiolene) Compounds

With its compelling OTE performances, metal bis(dithiolene)-fashioned (abbreviated as $M(dt)_2$) frameworks (**Figure 5**) have been a research hotspot for years. A representative case involves the development of layered structure of **11**. Prepared through interfacial polymerization, the formed thin film at the aqueous-organic interface was cast on a SiO_2 substrate and this ambipolar conductor presented exceptionally high conductivity near 1600 $S\cdot cm^{-1}$.[53]

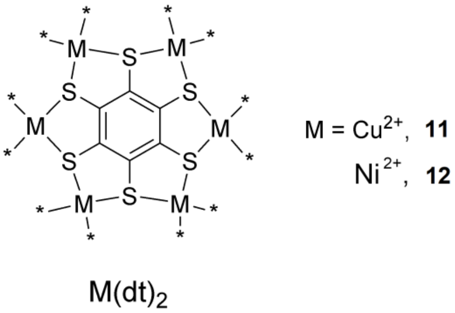


Figure 5. Molecular structures of $M(dt)_2$ (compounds **11** and **12**).

Additionally, Kambe et al. measured the conductivity of a single microflake of **12** by the van der Pauw method under SEM control.[54] Electrical studies showed that the redox process showed an impact on the conductivity, and the maximum conductivity of 1.6×10^2 $S\cdot cm^{-1}$ was monitored with a chemically oxidized flake. Further experiments proved that such a high conductivity stemmed from the low activation energy, prominent Fermi edge[54] and intense S-S interactions within the neighboring sheets.[55] Although there is no additional OTE-related parameter available yet, these metallopolymers are of promising application prospect in OTE devices.

3.3 Metalloporphyrin and Its Analogues

Metalloporphyrins are widely applied to diverse aspects, such as sensors[56, 57], water purification[58, 59], catalysis[60, 61] and even biological or medical uses[62-64]. For the past few years, a growing number of papers have demonstrated that metallopophyrin may also be a promising choice for developing OTE materials.[65-69] In 2012, Feng et al. looked into the conductive properties of two metalloporphyrin COFs (MP-COFs, **Figure 6a**).[48] X-ray diffraction, together with the simulation studies, indicated that both frameworks adopted a face-to-face, AA stacking alignment rather than the AB stacking mode. This arrangement enabled two carrier transporting channels (**Figure 6b**): holes were hopped through adjacent organic backbones in an interlayered fashion, while electrons were transmitted through the aligned metal arrays. Interestingly, these materials showed totally different conducting behavior due to different metal centers. Owing to the pronounced ligand-to-metal charge transfer effect induced by Cu^{2+}, metal-to-metal electron transmission was predominant in **13**; while for framework **14**, holes and electrons were transferred evenly through both channels, due to the lack of ligand-to-metal charge transfer.

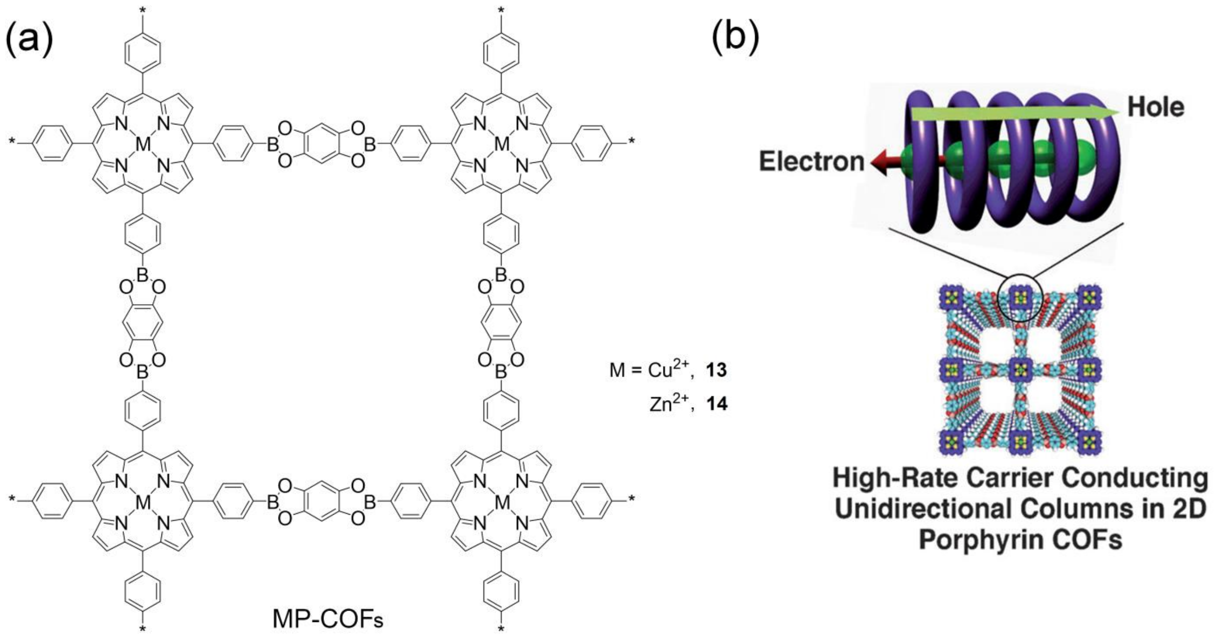


Figure 6. (a) Molecular structure of metal-coordinated MP-COFs and (b) their electrical conducting behavior. (Figure 6b reproduced with permission from Ref. [48], copyright 2012 John Wiley and Sons).

The first theoretical study aiming at the TE properties of 2D COFs took a page from first principles to simulate two nickel-containing COF materials: phthalocyanine based framework NiPc and its benzothiadiazole-modified counterpart NiPc-BTDA.[70] Results showed that the OTE properties of the high-performance NiPc frameworks were direction-dependent: an n-type nature was revealed in the in-plane directions, displaying the highest *ZT* above 0.8 at 700 K and a thermal conductivity at 0.021 $W \cdot m^{-1} \cdot K^{-1}$; along *c* axis, a hole-transport motion played a leading role.

Although the OTE research on metalloporphyrin-based polymers is not yet abundant currently, related studies on porphyrin-containing small molecules are blooming. For example, some reports have provided clear suggestions, from the perspective of molecular structure, on the guidelines how porphyrin-based OTE materials with excellent properties should be designed. In 2019, by introducing diverse heteroatoms, electron withdrawing or donating groups to 5,10,15,20-tetraphenylporphyrin molecule (**Figure 7a**), Zhou et al. found that the improved hydrophobicity of porphyrins (**15-19**) and the well-dispersed morphologies of the resulting composite (with single-walled carbon nanotubes, SWCNTs) together render the materials superior TE properties.[71] As a consequence, **15**-containing composite gave the highest room-temperature *PF* at 279.3 $\mu W \cdot m^{-1} \cdot K^{-2}$ (**Figure 7d**). Inspired by the encouraging results, further efforts have been made to explore the important role that the metal centers play in tuning the properties of OTE materials. In Zhou's another work,[69] by coordinating ligand **17** with metal ions Fe^{3+}, Cu^{2+} and Zn^{2+}, metalloporphyrins **20-22** were synthesized (**Figure 8**). After doping with SWCNTs, **22** yielded the highest *PF* of around 200 $\mu W \cdot m^{-1} \cdot K^{-2}$ at room temperature (**Figure 8d**). In addition to the advantages brought by a more uniform morphology, higher performances of the composites were also benefited from the stronger interactions through metal centers and SWCNTs.

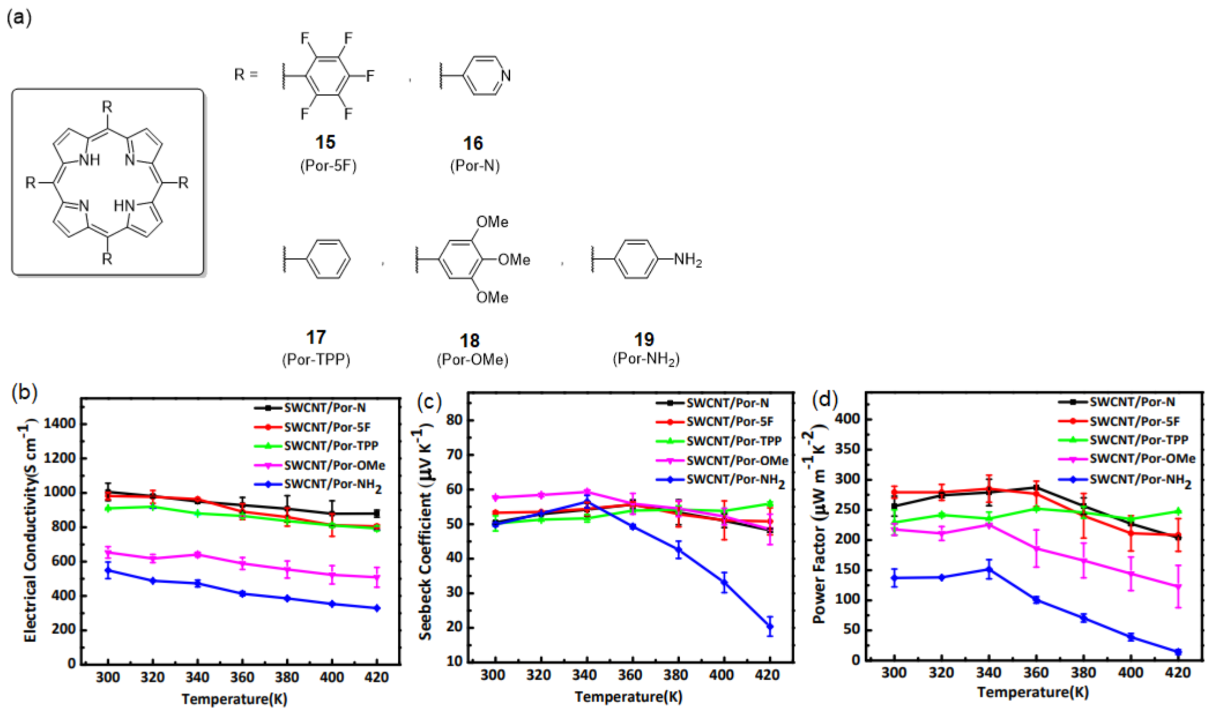


Figure 7. (a) Molecular structures of porphyrins **15-19**. (b) The electrical conductivity, (c) Seebeck coefficient and (d) *PF* of the composite film with single-walled carbon nanotubes at different temperatures with a composite ratio of 1:2. (Figures 7b-7d reproduced with permission from Ref. [71], copyright 2019 American Chemical Society).

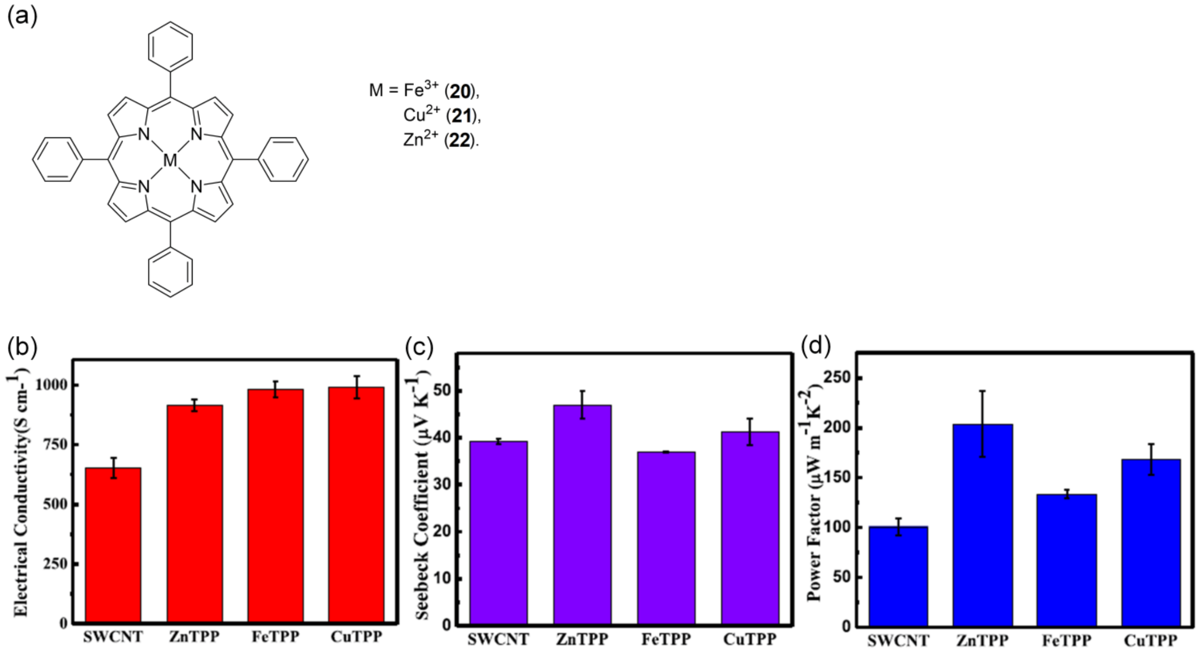


Figure 8. (a) Molecular structures of porphyrins **20-22**; (b) The electrical conductivity, (c) Seebeck coefficient and (d) *PF* of the composite film with single-walled carbon nanotubes at different temperatures with a mass ratio of SWCNTs : porphyrins = 1 : 2 at room temperature. (Figures 8b-8d reproduced with permission from Ref. [69], copyright 2019 Elsevier).

Moreover, some studies have focused on the single-molecule behavior of conducting metalloporphyrins. Zinc porphyrin was found to exhibit two conductance states in the conducting process by using scanning tunneling microscopy (STM) technology.[72] Al-Galiby et al. tuned the energy levels and the OTE properties of a single metalloporphyrin molecule by selecting and inserting a range of transition metal ions (Mn^{2+}, Mn^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}) to a porphyrin ligand (**Figure 9a**).[66] After geometry optimization of every single metalloporphyrin (**23-30**), the molecule was then subjected between two gold electrodes (**Figure 9b**) and the OTE properties were simulated. Calculation results indicated that metal centers determined the conducting type of the coordination compounds. Molecules

30 and **23** acted as a p-type and an n-type conductor respectively, and produced the highest Seebeck coefficients of +230 and -280 mV·K^{-1}. Prediction of the room-temperature *PF* showed that compound **26** presented the highest value of 9.5 × 10^{-4} W·m^{-1}·K^{-2}, which uncovers its potential to be a competitive molecular-scale OTE device.

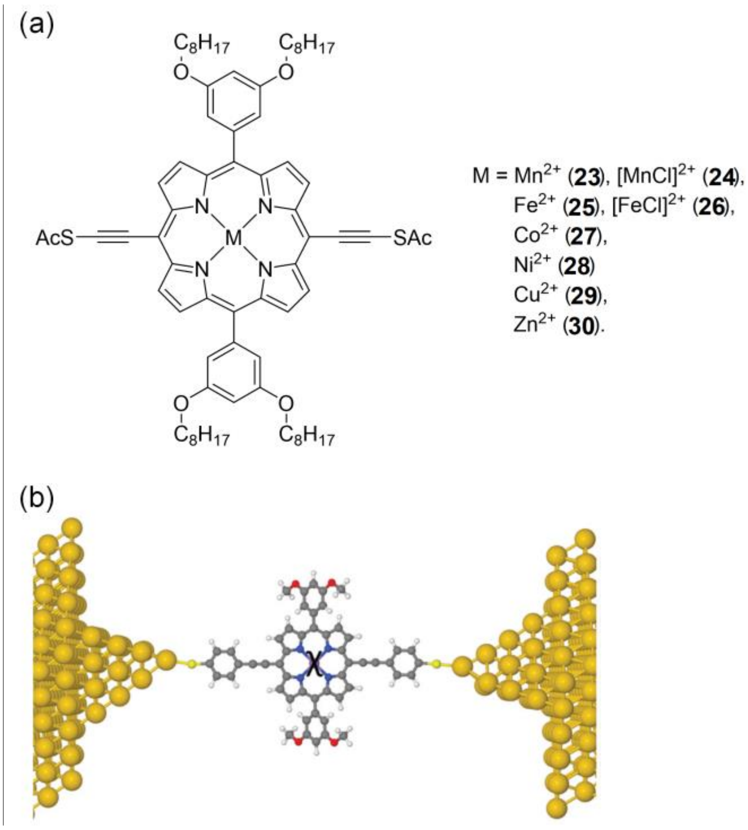


Figure 9. (a) Molecular structures of porphyrins **23-30**; (b) An optimized junction that a single porphyrin molecule was attached to two gold electrodes. The long alkyl chains were replaced by the methyl groups to simplify the computational work. (Figures 9b reproduced with permission from Ref. [66], copyright 2016, Royal Society of Chemistry).

To sum up, with elaborate molecular design, it is conceived that metalloporphyrin polymers will probably be a type of powerful materials for practical OTE uses in the future.

4. Other Promising Metallopolymers

4.1 Metallated Poly-Schiff Bases

In addition to the above-mentioned structures, Schiff base is another building block for OTE molecular design. In the early years, D’Sa et al. synthesized a series of thiosemicarbazone-based metallopolymers (**Figure 10a**) and investigated their electrical properties.[73] Although the electrical conductivity of the most conductive polymer **31** fell below 10^{-5} S·cm^{-1}, the authors conceived that charge carriers were localized and a weaker interaction between a metal center and its donor ligand resulted in a higher conductivity. The reported Seebeck coefficient of this compound is 1.15 mV·K^{-1}, suggesting a p-type semiconductor. After that, several salen-like structures (**Figure 10b**) were studied.[74] Experiments indicated positive Seebeck coefficients and low electrical conductivity with the highest record of around 8.55×10^{-7} S·cm^{-1} for metallopolymer **32**.

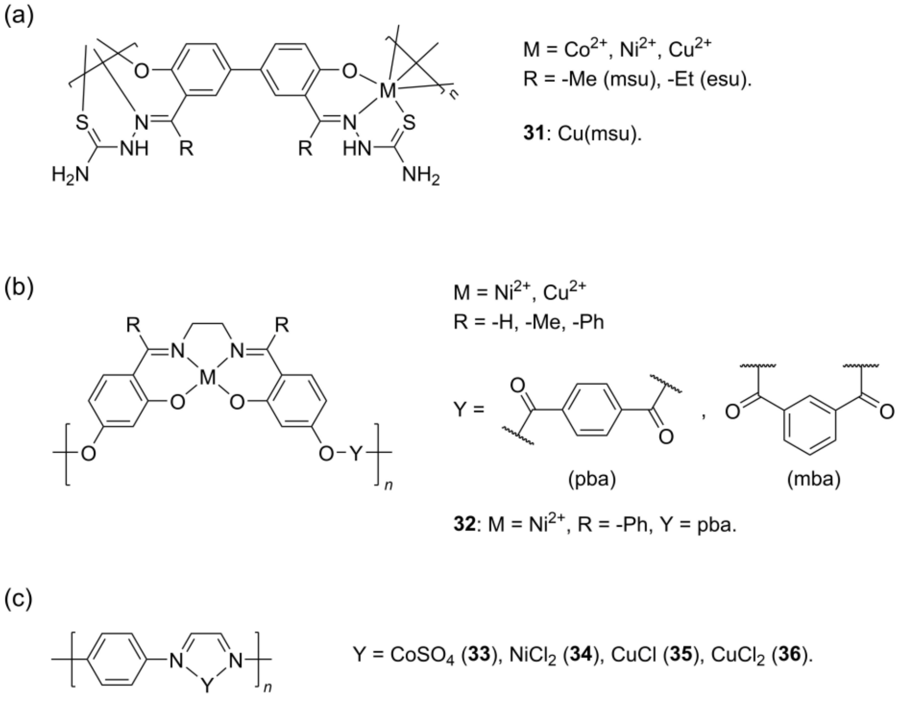
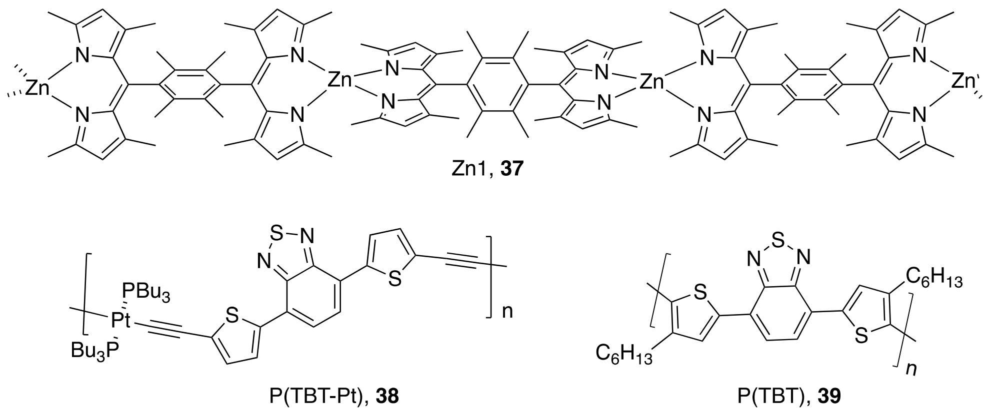


Figure 10. Molecular structures of reported metallated imine-based OTE materials **31-36**.

In 2014, Gao et al. developed a mixed system where metallo-Schiff bases **33-36** (**Figure 10c**) were blended with single-walled carbon nanotubes (SWCNTs) in various mass ratios.[75] The TE properties were studied at a doping ratio of 10/1 (poly-Schiff base / SWCNTs). Electrical conductivities of all materials were above 35 $S \cdot cm^{-1}$, higher than the non-chelated analogue, inferring that the involvement of the metal centers changed the conductive pathway. Besides, all of these materials exhibited their Seebeck coefficient at around 30 $\mu V \cdot m^{-1} \cdot K^{-1}$.

4.2 Other OTE materials from MCPs

In addition to 1D ett OTE materials, other MCPs also showed signs of a budding stage on the TE property. Sakamoto and Nishihara et al. synthesized a series of MCPs (**37-39**) based on the dipyrrin-metal framework, of which **37** (**Figure 11**) retained its chain structure when dispersed in an organic solvent.[76] By taking advantage of the processability of **37**, the authors attempted to fabricate a conjugate with SWCNTs (**Zn1-SWCNT**), which afforded better TE property over the pristine SWCNTs.



Zn1, **37**

P(TBT-Pt), **38**

P(TBT), **39**

Figure 11. Molecular structures of other reported OTE materials.

In 2019, a novel platinum(II) acetylide polymer of **38** and a homologue structure of **39** without platinum acetylide moiety, were synthesized and investigated (**Figure 11**).[77] The reported highest *PF* of P(TBT)-Pt/SWCNT reached 130.7±3.8 $\mu W \cdot m^{-1} \cdot K^{-2}$ at ambient temperature that is much higher than those without platinum acetylides (59 $\mu W \cdot m^{-1} \cdot K^{-2}$). It was shown that the planar moiety of platinum acetylide could enhance the intermolecular interaction with the SWCNTs *via* π-π and d-π interaction, thus resulting in higher OTE performance. All these descriptions suggest that MCPs with different structures have broad research prospects in TE research.

5. Outlook

In this Trend article, we have summarized the recent research progress of some conducting metallopolymer-based OTE materials (both 1D and 2D). These polymers possess a variety of molecular skeletons such as ett-, porphyrin- and polyamine-based chromophores which can exhibit diverse OTE performance. Metalated conjugated materials are attractive class of OTE materials due to their low thermal conductivities. Although the field is still in its infancy, merging metallic elements and organic polymers in metallopolymers can achieve the best of both worlds in the development of new OTE materials as converters for thermal/electrical energies. While researchers have only used a limited number of metal elements in these polymers, the research can also be extended to other unexplored metals. In some cases, the hybridization of metallopolymers with inorganic components appeared to be an effective protocol to enhance the OTE properties. The dynamic field of OTE is gaining momentum through continued breakthroughs in materials and device performance enhancements.

Recent years have witnessed the rapid development of the research works on metallopolymer-based OTE materials, and a promising application vista is anticipated, despite a number of challenges in this field. For example, the introduction of metal centers has been demonstrated to be an effective and flexible way to improve the OTE properties of conjugated polymers, but deeper investigations concerning the optimization work at the molecular level are still worth exploring, since a general platform for designing high-performance OTE metallopolymers is still not quite clear yet. Currently, theoretical models of studying the relationship among molecular structure, energy level, the density of states, and OTE property can provide guidance to allow a better understanding of the structure-property relationship which is conducive to the advancement of high-performance OTE materials. In a related context, fine-tuning of the energy gap through the interaction of the d-orbitals of the transition metal with the HOMO and/or LUMO of the ligand typically results in tunable electrical conductivity, and the larger band gap usually leads to relatively small electrical conductivity compared with those of state-of-the-art materials. Therefore, an extension of the work to some efficient metallopolymers with better OTE performance is worthy of investigation for very low-bandgap conducting metallopolymers that can be synthesized through rational molecular design.

Besides, additional efforts can be made to enrich the applications of OTE materials. For example, the concept of using body heat to generate electricity endows wearable and biointegrated OTE devices with great research value and application prospect, which is worthy of further explorations. In addition, to the best of our knowledge, most OTE materials have been mainly used as mini-power generators that recycle waste heat, but we should not neglect their pronounced potential as Peltier coolers in the refrigeration processes.[45] Moreover, inspired by the fact that the TE principles have been utilized to design gas sensors by detecting heat signals produced during gas-phase reactions[78], the OTE materials have good promise to be applied to the thermoelectric sensors. In addition, given the fact that practical TE devices are often built on the p-n junctions, high TE performances are essential for both p- and n-type conductors. Compared with p-type OTE materials, the current development of n-type counterparts still lags behind, even though a few excellent examples which possess *ZT* values comparable to those of p-type OTE generators were reported.

Efficient TE materials bearing solution-processible capabilities also show great development prospects, due to their advantages of possible large-area applications and lower cost. For this purpose, OTE materials are required to possess good solubility in water or organic solvents. Additionally, OTE and doped OTE thin films can make the materials anisotropic, therefore, an appropriate instrumental configuration for these materials is desired. This issue has been noticed by some scientists and some feasible methods have been provided. As a consequence, further research on the design strategy is worth exploring, which will greatly promote the research in this area and thus improve the relevant application. In the next stage of developments, it is also necessary to ensure that the materials can withstand wear and tear. Despite all these recent results, many aspects of the field are still yet to be explored and vast opportunities remain and many challenges still need to be tackled. We are looking forward to these exciting advances with much optimism.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

thermoelectric material, conducting polymer, metallopolymer, energy conversion, transition metal

[1] A. Shakouri, *Ann. Rev. Mater. Res.* **2011**, *41*, 399.

[2] T. M. Tritt, *Ann. Rev. Mater. Res.* **2011**, *41*, 433.

[3] X. Zhang, L.-D. Zhao, *J. Materiomics* **2015**, *1*, 92.

[4] G. Chen, W. Xu, D. Zhu, *J. Mater. Chem. C* **2017**, *5*, 4350.

[5] B. Russ, A. Glaudell, J. J. Urban, M. L. Chabinyc, R. A. Segalman, *Nat. Rev. Mater.* **2016**, *1*, 16050.

[6] Y. Pei, A. LaLonde, S. Iwanaga, G. J. Snyder, *Energy Environ. Sci.* **2011**, *4*, 2085.

[7] Q. Zhang, H. Wang, W. Liu, H. Wang, B. Yu, Q. Zhang, Z. Tian, G. Ni, S. Lee, K. Esfarjani, G. Chen, Z. Ren, *Energy Environ. Sci.* **2012**, *5*, 5246.

[8] K. Biswas, J. He, I. D. Blum, C. I. Wu, T. P. Hogan, D. N. Seidman, V. P. Dravid, M. G. Kanatzidis, *Nature* **2012**, *489*, 414.

[9] M. Tan, W. D. Liu, X. L. Shi, H. Gao, H. Li, C. Li, X. B. Liu, Y. Deng, Z. G. Chen, *Small Methods* **2019**, *3*, 1900582.

[10] B. Jabar, X. Qin, D. Li, J. Zhang, A. Mansoor, H. Xin, C. Song, L. Huang, *J. Mater. Chem. A* **2019**, *7*, 19120.

[11] D. Souchay, S. Schwarzmüller, H. Becker, S. Kante, G. J. Snyder, A. Leineweber, O. Oeckler, *J. Mater. Chem. C* **2019**, *7*, 11419.

[12] H. Wang, C. Yu, *Joule* **2019**, *3*, 53.

[13] S. N. Patel, M. L. Chabinyc, *J. Appl. Polym. Sci.* **2017**, *134*, 44403.

[14] Y. Sun, W. Xu, C.-a. Di, D. Zhu, *Synth. Met.* **2017**, *225*, 22.

[15] J. Lee, J. Kim, T. L. Nguyen, M. Kim, J. Park, Y. Lee, S. Hwang, Y.-W. Kwon, J. Kwak, H. Y. Woo, *Macromolecules* **2018**, *51*, 3360.

[16] J. Ding, Z. Liu, W. Zhao, W. Jin, L. Xiang, Z. Wang, Y. Zeng, Y. Zou, F. Zhang, Y. Yi, Y. Diao, C. R. McNeill, C. A. Di, D. Zhang, D. Zhu, *Angew. Chem. Int. Ed.* **2019**, *58*, 18994.

[17] K. Shi, F. Zhang, C. A. Di, T. W. Yan, Y. Zou, X. Zhou, D. Zhu, J. Y. Wang, J. Pei, *J. Am. Chem. Soc.* **2015**, *137*, 6979.

[18] D. Huang, H. Yao, Y. Cui, Y. Zou, F. Zhang, C. Wang, H. Shen, W. Jin, J. Zhu, Y. Diao, W. Xu, C. A. Di, D. Zhu, *J. Am. Chem. Soc.* **2017**, *139*, 13013.

[19] Y. Lu, J.-Y. Wang, J. Pei, *Chem. Mater.* **2019**, *31*, 6412.

[20] C. Meng, C. Liu, S. Fan, *Adv. Mater.* **2010**, *22*, 535.

[21] O. Bubnova, Z. U. Khan, A. Malti, S. Braun, M. Fahlman, M. Berggren, X. Crispin, *Nat. Mater.* **2011**, *10*, 429.

[22] Q. Zhang, Y. Sun, W. Xu, D. Zhu, *Energy Environ. Sci.* **2012**, *5*, 9639.

[23] M. Culebras, C. M. Gómez, A. Cantarero, *J. Mater. Chem. A* **2014**, *2*, 10109.

[24] A. M. Glaudell, J. E. Cochran, S. N. Patel, M. L. Chabinyc, *Adv. Energy Mater.* **2015**, *5*, 1401072.

[25] Y. Sun, P. Sheng, C. Di, F. Jiao, W. Xu, D. Qiu, D. Zhu, *Adv. Mater.* **2012**, *24*, 932.

[26] M. T. Nguyen, R. A. Jones, B. J. Holliday, *Macromolecules* **2017**, *50*, 872.

[27] W. Liu, W. Huang, C.-H. Chen, M. Pink, D. Lee, *Chem. Mater.* **2012**, *24*, 3650.

[28] B. J. Holliday, T. M. Swager, *Chem. Commun.* **2005**, 23.

[29] R. P. Kingsborough, T. M. Swager, *Adv. Mater.* **1998**, *10*, 1100.

[30] X. Yong, W. Shi, G. Wu, S. S. Goh, S. Bai, J.-W. Xu, J.-S. Wang, S.-W. Yang, *J. Mater. Chem. A* **2018**, *6*, 19757.

[31] H. Poleschner, W. John, F. Hoppe, E. Fanghänel, S. Roth, *J. für Praktische Chem.* **1983**, *325*, 957.

[32] G. E. Holdcroft, A. E. Underhill, *Synth. Met.* **1985**, *10*, 427.

[33] R. Vicente, J. Ribas, P. Cassoux, L. Valade, *Synth. Met.* **1986**, *13*, 265.

[34] A. K. Menon, R. M. W. Wolfe, S. R. Marder, J. R. Reynolds, S. K. Yee, *Adv. Funct. Mater.* **2018**, *28*, 1801620.

[35] P. Sheng, Y. Sun, F. Jiao, C. Liu, W. Xu, D. Zhu, *Synth. Met.* **2014**, *188*, 111.

[36] P. Sheng, Y. Sun, F. Jiao, C. Di, W. Xu, D. Zhu, *Synth. Met.* **2014**, *193*, 1.

[37] Y. Cui, J. Yan, Y. Sun, Y. Zou, Y. Sun, W. Xu, D. Zhu, *Sci. Bull.* **2018**, *63*, 814.

[38] W. Shi, G. Wu, K. Hippalgaonkar, J.-S. Wang, J. Xu, S.-W. Yang, *J. Am. Chem. Soc.* **2018**, *140*, 13200.

[39] H. M. Elmoughni, A. K. Menon, R. M. W. Wolfe, S. K. Yee, *Adv. Mater. Technol.* **2019**, *4*, 1800708.

[40] F. Jiao, C. A. Di, Y. Sun, P. Sheng, W. Xu, D. Zhu, *Philos. Trans. A Math. Phys. Eng. Sci.* **2014**, *372*, 20130008.

[41] R. M. W. Wolfe, A. K. Menon, T. R. Fletcher, S. R. Marder, J. R. Reynolds, S. K. Yee, *Adv. Funct. Mater.* **2018**, *28*, 1803275.

[42] L. Liu, Y. Sun, W. Li, J. Zhang, X. Huang, Z. Chen, Y. Sun, C. Di, W. Xu, D. Zhu, *Mater. Chem. Front.* **2017**, *1*, 2111.

[43] Y. Sun, L. Qiu, L. Tang, H. Geng, H. Wang, F. Zhang, D. Huang, W. Xu, P. Yue, Y. S. Guan, F. Jiao, Y. Sun, D. Tang, C. A. Di, Y. Yi, D. Zhu, *Adv. Mater.* **2016**, *28*, 3351.

[44] Y. Sun, J. Zhang, L. Liu, Y. Qin, Y. Sun, W. Xu, D. Zhu, *Sci. China Chem.* **2016**, *59*, 1323.

[45] W. Jin, L. Liu, T. Yang, H. Shen, J. Zhu, W. Xu, S. Li, Q. Li, L. Chi, C. A. Di, D. Zhu, *Nat. Commun.* **2018**, *9*, 3586.

[46] N. Toshima, K. Oshima, H. Anno, T. Nishinaka, S. Ichikawa, A. Iwata, Y. Shiraishi, *Adv. Mater.* **2015**, *27*, 2246.

[47] K. Oshima, H. Asano, Y. Shiraishi, N. Toshima, *Jpn. J. Appl. Phys.* **2016**, *55*, 02bb07.

[48] X. Feng, L. Liu, Y. Honsho, A. Saeki, S. Seki, S. Irle, Y. Dong, A. Nagai, D. Jiang, *Angew. Chem. Int. Ed.* **2012**, *51*, 2618.

[49] D. Sheberla, L. Sun, M. A. Blood-Forsythe, S. Er, C. R. Wade, C. K. Brozek, A. Aspuru-Guzik, M. Dincă, *J. Am. Chem. Soc.* **2014**, *136*, 8859.

[50] L. Sun, B. Liao, D. Sheberla, D. Kraemer, J. Zhou, E. A. Stach, D. Zakharov, V. Stavila, A. A. Talin, Y. Ge, M. D. Allendorf, G. Chen, F. Léonard, M. Dincă, *Joule* **2017**, *1*, 168.

[51] Y. Nonoguchi, D. Sato, T. Kawai, *Polymers* **2018**, *10*, 962.

[52] Y. He, C. D. Spataru, F. Leonard, R. E. Jones, M. E. Foster, M. D. Allendorf, A. Alec Talin, *Phys. Chem. Chem. Phys.* **2017**, *19*, 19461.

[53] X. Huang, P. Sheng, Z. Tu, F. Zhang, J. Wang, H. Geng, Y. Zou, C. A. Di, Y. Yi, Y. Sun, W. Xu, D. Zhu, *Nat. Commun.* **2015**, *6*, 7408.

[54] T. Kambe, R. Sakamoto, T. Kusamoto, T. Pal, N. Fukui, K. Hoshiko, T. Shimojima, Z. Wang, T. Hirahara, K. Ishizaka, S. Hasegawa, F. Liu, H. Nishihara, *J. Am. Chem. Soc.* **2014**, *136*, 14357.

[55] S. Li, T.-Y. Lü, J.-C. Zheng, S.-W. Yang, J.-S. Wang, G. Wu, *2D Mater.* **2018**, *5*, 1900582.

[56] K. Koren, S. M. Borisov, I. Klimant, *Sensor Actuat. B - Chem.* **2012**, *169*, 173.

[57] B. Zelelow, G. E. Khalil, G. Phelan, B. Carlson, M. Gouterman, J. B. Callis, L. R. Dalton, *Sensor Actuat. B - Chem.* **2003**, *96*, 304.

[58] M. Thandu, C. Comuzzi, D. Goi, *Int. J. Photoenergy* **2015**, *2015*, 1.

[59] D. La, R. Hangarge, S. V. Bhosale, H. Ninh, L. Jones, S. Bhosale, *Appl. Sci.* **2017**, *7*, 643.

[60] Z. Li, C.-G. Xia, *Tetrahedron Lett.* **2003**, *44*, 2069.

[61] P. Kaur, J. T. Hupp, S. T. Nguyen, *ACS Catal.* **2011**, *1*, 819.

[62] R. Bonnett, *Chem. Soc. Rev.* **1995**, *24*, 19.

[63] E. D. Sternberg, D. Dolphin, C. Brückner, *Tetrahedron* **1998**, *54*, 4151.

[64] S. C. Rozinek, R. J. Thomas, L. Brancaleon, *Biochem. Biophys. Rep.* **2016**, *7*, 295.

[65] M. Dongol, A. El-Denglawey, A. F. Elhady, A. A. Abuelwafa, *Appl. Phys. A* **2014**, *118*, 345.

[66] Q. H. Al-Galiby, H. Sadeghi, L. A. Algharagholy, I. Grace, C. Lambert, *Nanoscale* **2016**, *8*, 2428.

[67] M. Noori, H. Sadeghi, Q. Al-Galiby, S. W. D. Bailey, C. J. Lambert, *Phys. Chem. Chem. Phys.* **2017**, *19*, 17356.

[68] M. Noori, H. Sadeghi, C. J. Lambert, *Nanoscale* **2017**, *9*, 5299.

[69] Y. Zhou, Y. Liu, X. Zhou, Y. Gao, C. Gao, L. Wang, *J. Power Sources* **2019**, *423*, 152.

[70] Y. Chumakov, F. Aksakal, A. Dimoglo, A. Ata, S. A. Palomares-Sánchez, *J. Electron. Mater.* **2016**, *45*, 3445.

[71] Y. Zhou, X. Yin, Y. Liu, X. Zhou, T. Wan, S. Wang, C. Gao, L. Wang, *ACS Sustainable Chem. Eng.* **2019**, *7*, 11832.

[72] G. Qian, S. Saha, K. M. Lewis, *Appl. Phys. Lett.* **2010**, *96*, 243107.

[73] J. T. D'Sa, V. J. Rao, K. C. Patel, R. D. Patel, *Angew. Makromol. Chem.* **1979**, *79*, 133.

[74] M. Spiratos, G. I. Rusu, A. Airinei, A. Ciobanu, *Angew. Makromol. Chem.* **1982**, *107*, 33.

[75] C. Gao, G. Chen, *J. Mater. Chem. A* **2016**, *4*, 11299.

[76] R. Matsuoka, R. Toyoda, R. Sakamoto, M. Tsuchiya, K. Hoshiko, T. Nagayama, Y. Nonoguchi, K. Sugimoto, E. Nishibori, T. Kawai, H. Nishihara, *Chem. Sci.* **2015**, *6*, 2853.

[77] T. Wan, X. Yin, C. Pan, D. Liu, X. Zhou, C. Gao, W. Y. Wong, L. Wang, *Polymers* **2019**, *11*, 593.

[78] H. Jin, J. Li, J. Iocozzia, X. Zeng, P. C. Wei, C. Yang, N. Li, Z. Liu, J. H. He, T. Zhu, J. Wang, Z. Lin, S. Wang, *Angew. Chem. Int. Ed.* **2019**, *58*, 15206.

Emerging Organic Thermoelectric Applications from Conducting Metallopolymers

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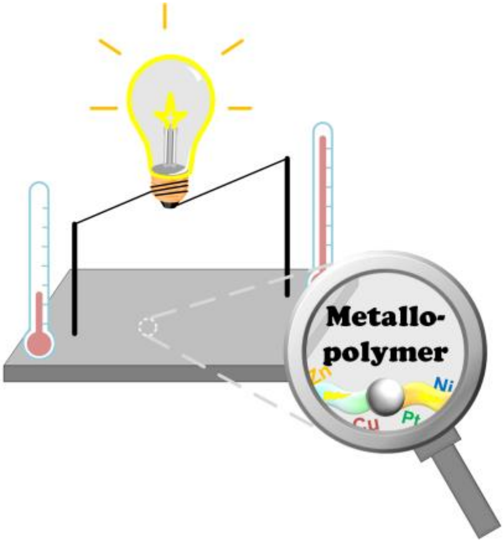
FIGURE FOR ToC_ABSTRACT



This Trend article highlights the recent developments of organic thermoelectric metallopolymers with various structural features. Based on the current achievements, metallopolymers are demonstrated to be a type of promising organic thermoelectric materials and this field is certainly worthy of future exploration.