



Thermoelectric Materials: Current Status and Future Challenges

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INTRODUCTION

Net zero refers to the balance of the amount of greenhouse gas emissions produced and the amount removed from the atmosphere, and many companies and states have committed themselves to net zero targets. In June 2019, the United Kingdom became the first major economy in the world to pass a net zero emissions law. This ambitious target aims to reduce the UK's net emissions of greenhouse gases by 100 per cent relative to 1,990 levels by 2,050 and replaces the UK's previous target to reduce emissions by at least 80%. Sweden, France, Denmark, New Zealand and Hungary have also now succeeded in putting net zero targets into law (Net Zero Emissions Race, 2020).

Progress towards these net zero goals has so far been slow. For example, the United Kingdom is behind on even the original 80% target, and achieving the current aim by 2,050 will be challenging. One thing that is clear to the scientific community is that improvements in technology between now and 2,050 will be key to bring the net zero target within reach. However, this will only happen if we can identify technologies for accelerated development and invest in them now, so we can deliver benefits before the 2,050 deadline. There are multiple areas where new technologies can assist in energy generation and storage, including photovoltaics, wind and water turbines, the hydrogen economy, caloric materials and batteries, as well as energy saving technologies such as low loss electronics. Thermoelectric energy conversion materials were identified by the Henry Royce Institute and the Institute of Physics as a key area of materials research for achieving net zero emissions in the Materials for the Energy Transition (2019) report.

Space heating and cooling (e.g., central heating or air conditioning), is one of the main contributors to emissions and accounts for around 17% of the UK's CO₂ emissions (Department for Business, Energy and industrial Strategy, 2018). In Saudi Arabia, one of the hottest and driest countries in the world, more than 70% of the kingdom's electricity produced per year is consumed purely for air conditioning and cooling purposes, with the demand doubling during the summer (Demirbas et al., 2017). This home water and space heating is typically achieved through burning natural gas in countries with access to natural gas, and through electrically-powered air-source heat pumps elsewhere. More widespread deployment of air-source heat pumps creates increased electricity demand, so solar-integrated heat pumps are also being investigated as another potential alternative to meet current space heating and domestic hot water demands with a reduced draw from the grid. However, these pumps use refrigerants such as HFCs, which are powerful greenhouse gases, so heat pumps that use other types of materials, such as thermoelectric and caloric materials need to be investigated as "greener" options.

Thermoelectric materials use temperature differences to generate electrical energy. They can therefore provide fully electric heating and cooling technology without moving parts or refrigerants. Another advantage of this technology is that it can be used to harvest waste heat from other processes and convert it directly into electricity. As about two thirds of primary energy are wasted as heat (Lawrence Livermore National Laboratory Estimated U.S., 2019) technologies, such as

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thermoelectrics, that can recover this waste will be important for achieving the world's net zero emission goals. This is most readily extracted in high temperature industrial settings, but it is estimated that 49% of the energy input in the residential sector is lost, almost entirely in the form of heat (Forman et al., 2016).

Current thermoelectric devices are robust and the technology has already been applied in niche applications such as within the aerospace sector (Freer and Powell, 2020). However, wider adoption and technology is being held back due to the low efficiency of current thermoelectric devices, as well as the sustainability of state-of-the-art materials (Patyk, 2010). In order for thermoelectric technology to expand into non-niche areas, it needs to be ensured that it can compete on efficiency with incumbent technologies. This will require a concerted effort in developing new sustainable materials with high thermoelectric performance, engineering the nanoscale interfaces in the materials and engineering the devices themselves.

Whilst the challenge is huge, the opportunity for nations and companies in this sector is also huge. There are a large number of new thermoelectric materials being developed, and the market for thermoelectric technology is growing (Harrop and Das, 2020). Therefore, now is an ideal time to capture this momentum and expand the role of thermoelectric technology in society and take us closer to net zero.

The primary way to increase sustainability is to improve the efficiency of devices, and from a materials perspective, this means improving the figure of merit, zT , of the thermoelectric materials deployed. The dimensionless zT is directly proportional to the squared Seebeck coefficient (S) and the electrical conductivity (σ), which together comprise the power factor ($PF = S^2\sigma$), directly proportional to the temperature (T) and inversely proportional to the thermal conductivity (κ). There are now materials with $zT > 1$ from room temperature (Poudel et al., 2008) to 1,000°C (Paik et al., 2011), and $zT \geq 2.5$ has been recorded in PbTe (Tan et al., 2016) and SnSe (Zhao et al., 2014; Chang et al., 2018) alloys. Materials with $zT_{average} \approx 1$ would require a temperature difference across the device of $\Delta T > 250$ K to achieve a 10% conversion efficiency, whereas deployment of materials with $zT_{average} \approx 2$ would only require $\Delta T > 150$ K to achieve the same 10% conversion efficiency. However, to compete on efficiency with other technologies, such as Rankine cycles, a zT of at least four is required (Vining, 2009). This sets a huge materials challenge.

The chalcogenides have perhaps been the most widely explored class of thermoelectric material to date. Bi₂Te₃ and its alloys are the most widely deployed, despite concerns about the long-term availability of tellurium, with zT up to 1.4 in the <200°C regime (Poudel et al., 2008). PbTe alloys have the additional issue of Pb toxicity but have been widely deployed in the space sector (Lalonde et al., 2011) due to a remarkably high zT that can reach 2.5 (Tan et al., 2016). The sulphides have not offered quite the same maximum performance as the other chalcogenides, but elemental abundance is an advantage in materials such as Cu₂S which show $zT \sim 1$ (Ge et al., 2018; Mikula et al., 2020) Half-Heuslers (Joshi et al., 2014; Zhou et al., 2018), clathrates (Deng et al., 2010), and skutterudites (Rogl et al.,

2015; Rogl and Rogl, 2019) have all shown $zT \geq 1$, whilst oxides and SiGe offer good performance at high temperature (Nozariasbmarz et al., 2017).

A programme of materials discovery will likely find significant improvements in zT within these classes of materials, but it is worth considering where else substantial increases in zT may come from. Zintl phases are one such group of materials. Defined by their mixed ionic and covalently bonded structures, and including Yb₁Zn₂Sb₂ ($zT = 0.55$) (Gascoin et al., 2005), Yb₁₄MnSb₁₁ ($zT = 1$) (Brown et al., 2006; Paik et al., 2011), and Mg₃Sb_{1.5}Bi_{0.5}, ($zT = 1.6$) (Zhang et al., 2017) these materials show electron crystal phonon glass behaviour with the low thermal conductivity driven by complex unit cells and strongly anharmonic bonding. Interestingly, they can form crystals with 3D, 2D, 1D, and 0D structure.

Other interesting routes to explore include the spin Seebeck effect (Sierra et al., 2018) as well as the use of topological states (Xu et al., 2017; Fu et al., 2020), and non-Wiedemann Franz materials (Scheunemann and Kemerink, 2020) that exhibit low electronic thermal conductivity. Compositionally graded materials (Cramer et al., 2018; Ou et al., 2020) can achieve a large $zT_{average}$ by connecting in series, a composition with high-performance at high temperatures with a composition with high-performance at low temperatures.

A second approach to improving the sustainability of thermoelectric devices is to focus on the embedded energy, abundance and toxicity of the thermoelectric materials themselves. There is therefore a parallel search for materials that can be processed at lower temperatures, which are made from abundant elements and in many cases can be printed. This has led to an interest in several new classes of thermoelectric materials: organics (Cowen et al., 2017), 2D materials (including graphene) (Li et al., 2020), carbon nanotubes (Zhou et al., 2017; Ichinose et al., 2019; Statz et al., 2020), polymer-carbon composites (Cho et al., 2016b), halide perovskites (Liu et al., 2019b), and metal organic frameworks (Erickson et al., 2015; Sun et al., 2017) to name a few. This study discusses a few examples of these thermoelectric materials in more detail below.

SEMICONDUCTING POLYMERS

High Performing Materials

While this study focuses on organic semiconducting polymers, significant research also centres on small molecules organic semiconductors. Zhang *et al.* recently explored high mobility organic semiconductors for thermoelectrics (Zhang and Di, 2020). Many different p- and n-type organic materials have been used for thermoelectric studies including, poly (3-hexylthiophene) (P3HT, **Figure 1A**), poly [2,5-bis (3-alkylthiophen-2-yl) thieno [3,2-*b*] thiophene] (PBTTT, **Figure 1A**), diketopyrrolopyrrole (DPP) derivatives, poly (3,4-ethylenedioxythiophene) (PEDOT) and naphthalenediimide (NDI) derivatives. Polythiophenes including, P3HT and PBTTT, are the most widely researched p-type organic polymers for thermoelectric applications due to simple synthetic routes and reasonable air stability (Nielsen and

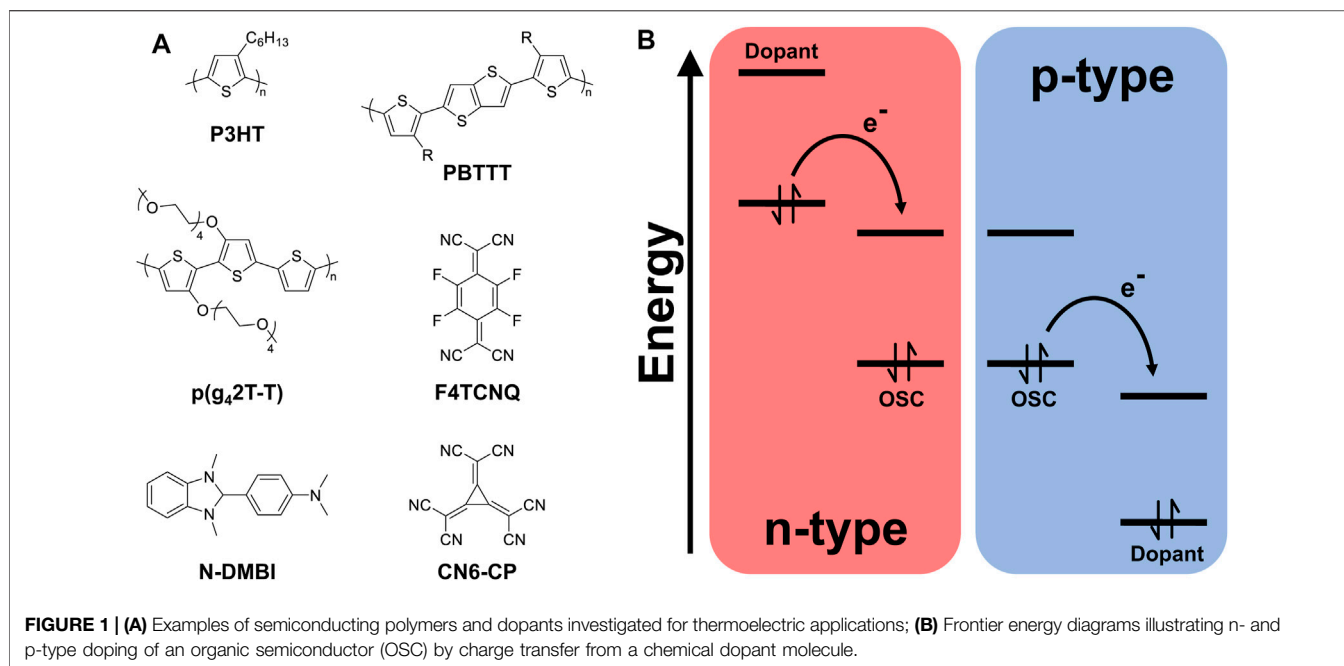


FIGURE 1 | (A) Examples of semiconducting polymers and dopants investigated for thermoelectric applications; **(B)** Frontier energy diagrams illustrating n- and p-type doping of an organic semiconductor (OSC) by charge transfer from a chemical dopant molecule.

McCulloch, 2013). The p-type dopant 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ, **Figure 1A**) is commonly used to improve electrical conductivity. P3HT and F4TCNQ were first blended in solution to increase performance of thin film transistors however, charge transfer in solution leads to aggregation where the newly charged species precipitate out of the processing solvent (Ma et al., 2008). Thermoelectric devices fabricated from these solutions produce inhomogeneous films where the highest power factor (PF) of $0.4 \mu\text{W m}^{-1} \text{K}^{-2}$ has been reported for blended solutions (Lim et al., 2018). Scholes et al. then showed that the solution-sequential processing (SqP) of P3HT films with F4TCNQ in an orthogonal solvent led to much higher conductivities (Scholes et al., 2015). The method requires spin coating of a semi-crystalline polymer film from a chosen solvent, depositing a solution of dopant material for an allotted time and finally spinning off the excess solution. Passivation of the dopant through the semi-crystalline polymer film allows for efficient doping and using an orthogonal solvent, such as acetonitrile, prevents disruption to morphology. Jacobs et al. showed that this method can be used with a variety of electron acceptors in different solvents on P3HT and PBTBT (Jacobs et al., 2016). In addition to SqP, F4TCNQ vapour doping has afforded high thermoelectric properties with PBTBT (Kang et al., 2016, 2019). Patel et al. evaporated F4TCNQ into PBTBT thin films achieving a large PF of $120 \mu\text{W m}^{-1} \text{K}^{-2}$ from a high electrical conductivity of 670 S cm^{-1} (Patel et al., 2017). A new class of isoindoloindole-based p-type polymers have also been used for thermoelectric applications reaching a PF of $35 \mu\text{W m}^{-1} \text{K}^{-2}$ by SqP thin films with F4TCNQ solutions (Yoon et al., 2020a). Poly(2-([2,2'-bithiophen]-5-yl)-3,8-di-fluoro-5,10-bis(5-octylpentadecyl)-5,10-dihydroindolo[3,2-b]indole)) (PIDF-BT) utilises the electron rich isoindoloindole motif for charge transfer to the F4TCNQ electron acceptor and the addition of

fluorine atoms increases planarity through favourable F-H interactions, leading to electrical conductivities over 210 S cm^{-1} (Park et al., 2019). DPP polymers have also been considered as high-performing p- and n-type thermoelectric materials. Donor-acceptor derivatives using thiophene-flanked DPP motifs have shown promise with a PF of $276 \mu\text{W m}^{-1} \text{K}^{-2}$ recorded for PDPP3T SqP-doped with FeCl_3 (Jung et al., 2017) Liu et al. have also shown to increase the PF and electrical conductivity of PDPP5T by replacing one thiophene unit with a more electron rich 3,4-ethylenedioxythiophene (EDOT) to improve unfavourable energetics, increasing the PF markedly from 11 to $298 \mu\text{W m}^{-1} \text{K}^{-2}$ (Liu Z. et al., 2020).

By flanking with the electron-deficient pyrazine and co-polymerising with cyano-functionalised bithiophene monomers, the electron-deficient DPP moiety has also been employed for n-type thermoelectric applications (Yan et al., 2019). Compared to a thiophene-flanked derivative of the same co-polymer, Yan et al. showed that incorporation of pyrazine improves the n-type doping efficiency via increasing the energetic offset leading to a PF of $57.3 \mu\text{W m}^{-1} \text{K}^{-2}$ when doped with 4-(2,3-Dihydro-1,3-dimethyl-1H-benzimidazol-2-yl)-N,N-dimethylbenzenamine (N-DMBI, **Figure 1A**) as a hydride source. However, the highest PF recorded for an n-type organic thermoelectric material utilises the thiophene flanked benzodifurandione oligo (*p*-phenylenevinylene) (BDOPV) motif co-polymerised with thiophene to produce TBDOPV-T, resulting in maximum PF of $106 \mu\text{W m}^{-1} \text{K}^{-2}$ when doped with N-DMBI (Lu et al., 2021). Interestingly, the vinyl derivative of the same polymer (TBDPPV) exhibited a higher maximum electrical conductivity of 90 S cm^{-1} compared to TBDOPV-T, however, the optimal recorded PF is slightly lower with a value of $76 \mu\text{W m}^{-1} \text{K}^{-2}$ but is still among the highest performing n-type organic polymers to date. In terms of

zT , which is less frequently reported for organic materials than the power factor, due to the challenges associated with accurately measuring the thermal conductivity, the current best performing organic thermoelectric materials have zT -values of 0.42 (p-type) (Kim et al., 2013) and 0.34 (n-type) (Liu J. et al., 2020) at room temperature and 120°C, respectively.

Ongoing Materials Development and Future Directions

Although the examples highlighted above show the capabilities of organic semiconductors for thermoelectric applications, important ongoing research into the structure-function relationships of host and dopant to promote dopant stability and efficiency is still crucial for further understanding and improvement in performance. Recently, the engineering of semiconducting polymers to increase the stability of the dopant within the polymer matrix has been a particular focus point (Li et al., 2016; Kroon et al., 2017; Hofmann et al., 2018). A well-explored strategy in this pursuit is to introduce more polar side chains than the archetypical alkyl chains that dominate semiconducting polymer design, hypothesising stronger interactions between charged dopant species and the organic semiconductor. A common motif utilised is ethylene glycol (EG), which has been used by several groups. Kroon et al. showed that polythiophene with tetraethylene glycol side chains, p(g₄2T-T, **Figure 1A**), has enhanced thermal stability compared to P3HT when doped with F4TCNQ (Kroon et al., 2017). By measuring the electrical conductivity as a function of temperature, at ~100°C a decrease is observed for P3HT whereas p(g₄2T-T) displays stable conductivity up to 180°C. They hypothesise that the polar side chain interacts with F4TCNQ anions preventing a reduction in performance at high temperature due to diffusion of dopant species within the film. However, the addition of oligoethylene glycol chains to the polymer backbone must be considered with care as improvement is not always observed. A study by Dong et al. revealed that the introduction of a methylene spacer between the first side chain oxygen and polymer backbone reduces thermal dopant stability observed through the loss in conductivity at 130°C when comparing to the same polymer with the EG motif directly bonded to the backbone (Dong et al., 2020). This has also been observed for another series of EG-functionalised derivatives of P3HT where the thermal stability at 80°C decreased with increasing polar co-monomer content (Finn et al., 2020).

EG motifs have also been added to NDI derivatives to improve the electrical conductivity of n-type polymers. Recently Shin et al. showed the synthesis of a branched oligoethylene glycol NDI derivative that showed thermoelectric properties when doped with the benzimidazole-based n-type dopant N-DiPrBI (Shin et al., 2020). Although lower thermoelectric performance was exhibited when compared to other n-type thermoelectric materials, they showed that the maximum PF was recorded at a low N-DiPrBI concentration of 1-2 wt%, whereas commonly a higher dopant concentration is required, an improvement attributed to the incorporation of EG into the side chain. An interesting case of introducing polarity to NDI derivatives is

utilising amphiphilic side chains to tailor dopant location with respect to the polymer backbone. Liu et al. synthesised two NDI monomers, one with triethylene glycol (TEG) side chains and the other with a C8 alkyl spacer before the TEG motif, labelled NDI2TEG and NDI2C8TEG respectively (Liu et al., 2021). After co-polymerisation with an alkoxy-bithiazole monomer (2Tz) and doping thin films with N-DMBI, both polymers exhibited similar electrical conductivities. However, the alkyl-spacer containing polymer revealed a Seebeck coefficient double that of the NDI2TEG-based polymer and a PF of 16.5 μW m⁻¹ K⁻², the highest reported value for NDI-based materials. Using kinetic Monte Carlo simulations, the authors attribute the higher Seebeck coefficient to reduced coulombic interactions from the larger host-dopant distance.

Low band gap polymers containing heavier chalcogens have proven to be interesting for TE applications. Heeney et al. synthesised the regioregular analogue of P3HT, poly(3-hexylselenophene) (P3HS), replacing sulphur with selenium (Heeney et al., 2007). Thin film UV-Vis absorption spectra reveal a large red-shift indicating a smaller band gap energy, which is attributed to increased backbone planarity as modelled using DFT by Wijsboom et al. (2009). Selenium is less electronegative than sulphur, which also leads to a decrease in ionisation potential that is preferable for donating electrons to an electron acceptor (Patra and Bendikov, 2010). Scholes et al. studied the effect of increasing selenophene content in the copolymer P37S-*stat*-P3HT and found the ionisation potential to decrease with increasing 3-heptylselenophene content (Scholes et al., 2019). When doped with F4TCNQ *via* SqP, charge carrier concentration only increases a small amount across the series whereas conductivity increases dramatically with increasing selenophene content. Using Hall Effect measurements, they found that the conductivity increase arises from increased Hall mobility due to increased crystallinity. Gregory et al. and Panchuk et al. took a different approach by synthesising a series of poly(3-alkylchalcogenophenes) with sulphur, selenium and tellurium and 3,7-dimethyloctyl as the side chain (Gregory et al., 2018; Panchuk et al., 2019). Dip-doping in low concentrations of FeCl₃ and Fe (Tos)₃ revealed moderate doping efficiencies and electrical conductivities when moving down group 16, showing that using the heavier chalcogens is a promising strategy to increase electrical conductivity. However, the most impressive use of sulphur replacement for thermoelectric applications is the DPP derivative PDPPSe-12 (Ashraf et al., 2015; Ding et al., 2019). PDPPSe-12 doped with FeCl₃ exhibits a conductivity and power factor of 997 S cm⁻¹ and 348 μW m⁻¹ K⁻² respectively, due to excellent charge carrier mobilities. Using the combination of heavy atom substitution and side chain engineering, field-effect hole mobilities of 9.4 cm² V⁻¹ s⁻¹ have been reported for PDPPSe-12 demonstrating the importance of investigating and optimising chemical and morphological structure in organic thermoelectric materials (Wang et al., 2018).

Designing molecular dopants with improved doping efficiency and stability is as important as enhancing the properties of the organic semiconductor for thermoelectric applications, and the two main types of molecular doping are acid/base and

reduction/oxidation reactions. P-type acid (n-type basic) doping requires proton (hydride) transfer from an acid (base) to an organic semiconductor, a process that has been shown to work through both co-processing and SqP techniques. The polar side chain functionalised p(g₄2T-T), co-processed with various sulphuric acids, exhibits conductivities up to 120 S cm⁻¹ facilitated by proton transfer, as explored in a study by Hofmann et al. (2018). This study also found that 1,3-propanedisulfonic acid doped p(g₄2T-T) thin films retain conductivity at 120°C for 20 h, indicating the high thermal stability of acid doping in combination with the polar side chains. The most employed n-type doping system employs organic semiconductors with large electron affinities, sequentially doping them with n-type dopants such as N-DMBI and N-DPBI exploiting hydride transfer between the dopant and semiconductor (Naab et al., 2013). The other approach for molecular doping utilises redox reactions between electron donor and acceptor molecules for n- and p-type doping, as illustrated in **Figure 1B** (Jacobs and Moulé, 2017). For n-type doping, designing electron rich molecules to create an energetic route for charge transfer from the highest occupied molecular orbital (HOMO) of the dopant to the lowest unoccupied molecular orbital (LUMO) of the semiconductor is usually accomplished by introducing highly electron-donating groups onto the dopant. On the other hand, p-type dopants have deep-lying LUMO energy levels, allowing charge transfer to occur from the semiconductor's higher lying HOMO, and are typically designed by introducing highly electron-withdrawing groups. Two examples of this are tetrakis (dimethylamino) ethylene (TDAE), a reducing agent (n-type dopant), and F4TCNQ, an oxidising agent (p-type dopant). TDAE has four electron-donating dimethylamino moieties increasing electron density on the C = C double bond, which in turn raises the frontier orbitals. On the other hand, F4TCNQ has two malononitrile groups in the 1- and 4-positions and four fluorine atoms in the other positions of the benzoquinone ring. These groups are strongly electron-withdrawing, which results in a highly electron-deficient molecule. Chemical design can be used to control the frontier energy levels of both the organic semiconductor and the dopant (Bronstein et al., 2020). A remarkable example was given by Kiefer et al. (2019), who showed that increasing the electron density on a polythiophene led to energetics so favourable with a strong p-type dopant that two electron transfers occur, effectively double-doping the polymer.

$$E(\delta) = (IP - EA)\delta - k\frac{e^2}{r}\delta^2 \quad (1)$$

The formation of an ion pair after charge transfer can be described by the ion pair energy $E(\delta)$ shown in **Equation 1**, where δ is the degree of charge transfer, r is the separation between electron and hole, k is the Coulomb's constant, e is the electric charge and IP and EA are the ionisation potential and electron affinity, respectively (Torrance et al., 1981; Jacobs and Moulé, 2017). The equation describes the energy to form an ion pair and arises from the free energy of ionisation between the

donor and acceptor (IP-EA) and Coulombic interaction between the electron and hole, quantified by the electrostatic energy (Madelung energy) (ke^2/r). The degree of charge transfer also plays a role in ion pair formation. With $\delta = 1$ denoting complete transfer of charge, referred to as integer charge transfer, while $\delta < 1$ indicate that charge transfer complexes can form. Charge transfer complexes form when the HOMO of the donor and the LUMO of the acceptor hybridise forming new local "bonding" and "antibonding" states and the charge is shared by the dopant and the semiconductor. Méndez et al. compared doping of quaterthiophene (4T) and P3HT with F4TCNQ and found that 4T:F4TCNQ forms charge transfer complexes whereas integer charge transfer occurs for P3HT:F4TCNQ. (Méndez et al., 2015) UV-Vis absorption spectroscopy revealed optical transitions between the bonding and antibonding orbitals of the charge transfer complex, while no F4TCNQ radical anion peaks were observed ruling out ion pair formation. Comparing the C≡N stretches of doped films to F4TCNQ radical anions using infra-red (IR) spectroscopy, they revealed a resonance frequency shift depending on the degree of charge transfer. This useful tool for analysing semiconductor: F4TCNQ systems have also been used in the assignment of integer charge transfer and charge transfer complex states in F4TCNQ doped PBTTT films by Zapata-Arteaga et al., who investigated how the degree of charge transfer affected thermal stability (Zapata-Arteaga et al., 2020). Upon controlling the substrate temperature during the vapour doping of PBTTT thin films with F4TCNQ, they were able to control the degree of charge transfer complex states and thus explore the electrical and thermal conductivities along with the Seebeck coefficients. They found that films rich in charge transfer complex states are more thermally stable when exposed to 100 °C for 10 h as compared to high integer charge transfer fractions and utilising a moderate degree of charge transfer complex states also led to good thermoelectric performance.

Doping efficiency also needs to be considered as the formation of an ion pair and does not directly lead to high electrical conductivities. After charge transfer from the organic semiconductor to the dopant (p-type), the newly formed polaron must escape the Coulombic trap of the ion pair to become a free charge carrier. Aubry et al. showed that large dodecaborane-based dopants (~2 nm in size) can electrostatically shield counter anions from polarons formed upon doping P3HT (Aubry et al., 2019). They also tune the doping strength of the dodecaborane-based dopants achieving an estimated 96% doping efficiency by optimising the free energy of ionisation and coulombic interaction (Aubry et al., 2020).

Improving dopant miscibility within the polymer matrix has also shown positive results in the literature where the addition of polar groups and side chains has led to increased conductivity. Li et al. showed that monoester substituted F4TCNQ derivatives have greater doping effectiveness due to miscibility with P3HT, although the energetics are less favourable than for the parent F4TCNQ (Li et al., 2015). Saska et al. took the same approach via the substitution of three cyano-groups with methyl esters on the strong oxidant hexacyano-[3]-radialene (CN6-CP, **Figure 1A**). The ester-functionalised derivative shows solubility and stability

in halogenated solvents (Saska et al., 2019). Karpov *et al.* also showed that the radical anion salt of CN6-CP with a tetrabutylammonium counter cation can be solution co-processed with P3HT in organic solvents (Karpov et al., 2018, 2019, 2020). Co-processing through the blending of semiconductor and dopant usually leads to insoluble materials thus producing inhomogeneous films. However, the addition of alkyl chains to the counter cation leads to enhanced processability and miscibility. Altering molecular dopant size has been shown to influence the electrical performance upon doping due to the position of the dopant within the polymer microstructure. This can be shown by the comparison between two hydride n-type dopants, N-DMBI and a trisaminomethane derivative (Yang et al., 2020). Lu *et al.* reported a record high n-type power factor of $80 \mu\text{W m}^{-1} \text{K}^{-2}$ upon doping a BDOPV-based polymer with the trisaminomethane dopant (Lu et al., 2020). They ascribed the high power factor to improved conductivity owing to decreased disorder upon doping. Among other improved characteristics, the dopant cation resides in the side chain whereas N-DMBI sits within the polymer backbone perturbing conjugation and reducing charge transport. Similarly, using a BDOPV-based polymer, Pei and co-workers recently developed an efficient N-heterocyclic carbene based n-type dopant generated by thermal decarboxylation of a stable precursor affording an electrical conductivity of 8.4 S cm^{-1} (Ding et al., 2020).

Doping efficiency has also been improved using two new similar methods reported in the literature, anion exchange and cascade doping. Similar to sequential processing techniques, anion exchange doping utilises molecular dopants in concentrated solutions of electrolytes. (Yamashita et al., 2019; Murrey et al., 2021). Deposition of the anionic exchange solution onto a polymer film allows for the reduced p-type dopant to substitute with the anion from the electrolyte, leading to higher doping levels. Yamashita *et al.* showed that PBTTT doped using anion exchange solutions containing F4TCNQ and LiTFSI as the dopant and electrolyte, respectively, led to conductivities of 620 S cm^{-1} compared to 260 S cm^{-1} for just F4TCNQ. A similar approach has recently afforded conductivities up to 1200 S cm^{-1} again using PBTTT as the semiconductor (Jacobs et al., 2021). Alternatively, Yoon *et al.* demonstrated the scope of cascade doping whereby SqP firstly with F4TCNQ solutions then secondly with NOBF_4 solutions onto thin films of the p-type polymer PIDF-BT (Yoon et al., 2020b). Similar to the anion exchange method, BF_4 anions exchange with F4TCNQ anions; increased doping levels ascribed to the low activation energy of the PIDF-BT-F4TCNQ- BF_4 transition state explain the increased electrical conductivity.

Orientation of semiconducting polymer thin films has also been considered for thermoelectrics, whereby alignment of the polymer crystallites within the film reveals directional thermoelectric characteristics. Brinkmann *et al.* have carried out extensive work using high-temperature rubbing, whereby heating the polymer film and mechanically rubbing using a micro-fibre cloth attached to a rotating cylinder produces highly oriented polymer films (Hamidi-Sakr et al., 2016). Polarised UV-Vis absorption spectroscopy reveals anisotropic

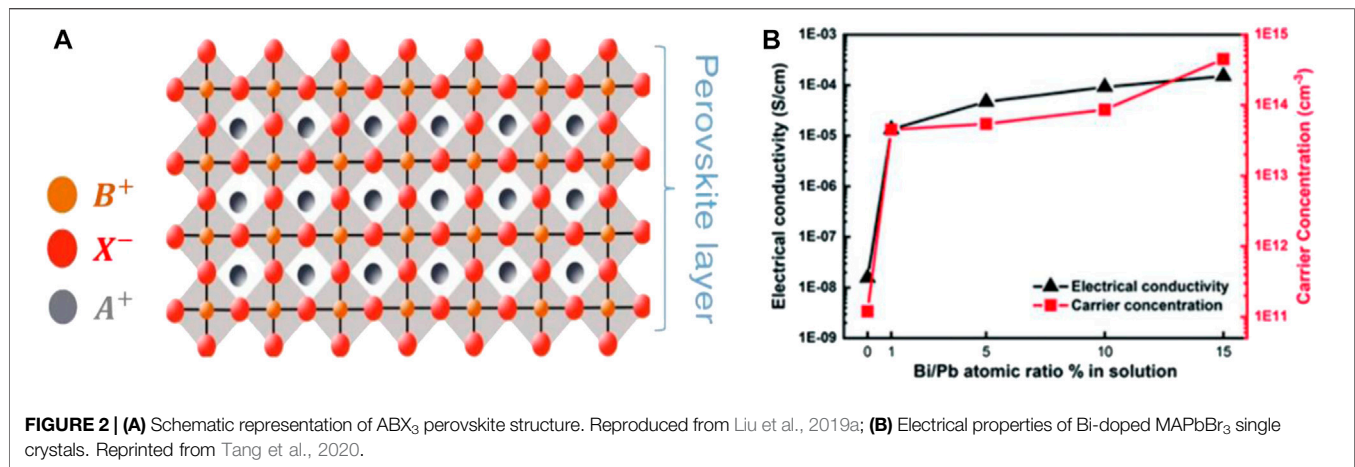
absorption of the π - π^* transition in the parallel direction of rubbing indicative of alignment of crystalline regions. Electron diffraction patterns also show temperature dependent orientation of P3HT relative to the substrate, where high rubbing temperatures primarily induce face-on orientation. Early work using SqP of aligned P3HT thin films with F4TCNQ in acetonitrile solutions produced a conductivity and power factor of 22 S cm^{-1} and $8.5 \mu\text{W m}^{-1} \text{K}^{-2}$, respectively, in the parallel direction. Polarised UV-Vis absorption spectra reveal absorption of F4TCNQ anions in the perpendicular direction and the doped polymer in the parallel direction. Supported by electron diffraction data, they conclude from this observation that F4TCNQ sits between the alkyl side chains, perpendicular to the P3HT backbone (Hamidi-Sakr et al., 2017). High-temperature rubbing on PBTTT also shows anisotropic power factor and electrical conductivity of $100 \mu\text{W m}^{-1} \text{K}^{-2}$ and 193 S cm^{-1} when doped sequentially with F4TCNQ (Vijayakumar et al., 2019a). They even reported outstanding conductivities of 10^5 S cm^{-1} and power factors $>2 \text{ mW m}^{-1} \text{K}^{-2}$ from highly oriented PBTTT films, using immersive doping in a solution of FeCl_3 in nitromethane (Vijayakumar et al., 2019b). However, recently Vijayakumar *et al.* have shown that the simple change in the SqP technique using incremental concentration doping can improve the electrical conductivity and PF of a thermoelectric material (Vijayakumar et al., 2020). When compared to the 920 S cm^{-1} measured *via* direct doping of aligned PBTTT films with F4TCNQ as the dopant measured in the direction parallel to rubbing, the incremental concentration doped films exhibit an improved conductivity of $1,380 \text{ S cm}^{-1}$ highlighting that simple changes in processing methods can lead to vast improvements.

The low electrical conductivity of pristine organic semiconductors is overcome by increasing the charge carrier concentration through chemical doping, although a balance must be struck as the Seebeck coefficient decreases with increasing charge carrier concentration. The chemical doping process is further complicated by the fact that it can compromise the charge carrier mobility due to the structural changes upon doping and that untethered dopants tend to diffuse within and out of the film at elevated temperatures required for energy harvesting.

The above discussion has outlined some of the current challenges in organic thermoelectrics. Much effort is being devoted to addressing these shortcomings from several different angles - including semiconductor optimisation, dopant modifications, new processing and doping strategies, and judicious control of the complicated polymer:dopant microstructure. While great strides are being taken, further progress is still needed in all these aspects in order to realise competitive organic thermoelectric devices.

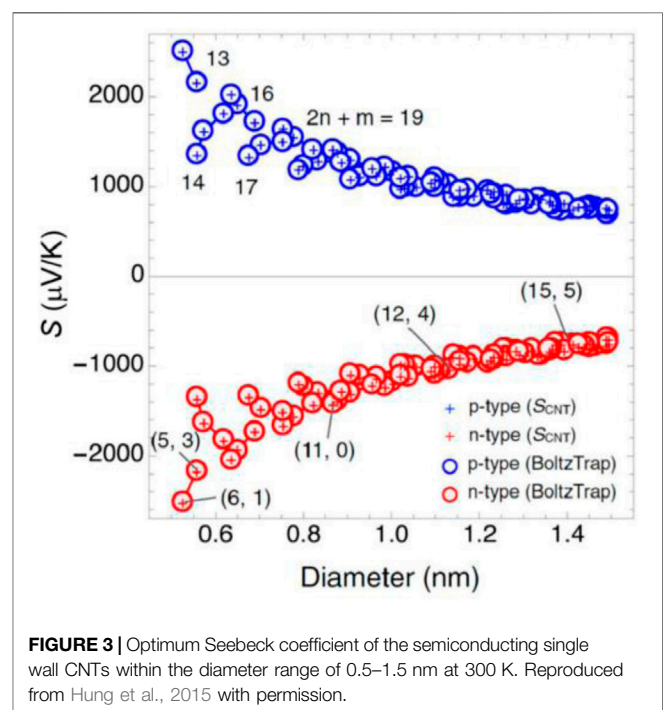
HALIDE PEROVSKITES

Halide perovskites have increasingly been the focus of thermoelectric investigation due to their ultralow thermal conductivity, high charge carrier mobility, and high Seebeck coefficient as well as their low cost and ease of fabrication by solution processes (Stoumpos et al., 2013; He and Galli, 2014;



Dong et al., 2015; Hata et al., 2016; Yue et al., 2016; Haque et al., 2020). They have the general chemical formula of ABX_3 where A is an organic or inorganic cation (e.g., Cs^+ , $CH_3NH_3^+$, $NH_2CHNH_2^+$), B a metal cation (e.g., Pb^{2+} , Sn^{2+}), and X a halide anion (e.g., Cl^- , Br^- or I^-) as illustrated in **Figure 2A**, and the manipulation of A, B and X sites leads to diverse material properties and unique opportunities (Haque et al., 2020). Inorganic halide perovskites, $CsPbX_3$, Cs_4PbX_6 , and $CsPb_2X_5$ (X: Br or Cl) were first reported in the 1890s (Wells, 1893), whilst hybrid organic-inorganic halide perovskites were first synthesized in the late 1970s (Weber, 1978). In recent years they have been developed rapidly for photovoltaic devices with single junction efficiency of up to 25.5% (Best Research-Cell Efficiency Chart, 2021). Additionally, they have been identified as “phonon glass electron crystals” due to the observations of ballistic charge transport and diffusive phonon transports (Miyata et al., 2017). The origin of the phonon glass electron crystal behaviour is the cation on the A-site, which is relatively weakly bonded to the lattice and can rattle and rotate in the perovskite cage structure. Electron and phonon transport is entirely on the metal halide lattice in the halide perovskites, but the anharmonicity caused by motion [in particular rotation (Liu et al., 2019a)] of the A-site cation can scatter the propagating phonons and reduce thermal conductivity into the ultralow regime ($<0.5 \text{ W m}^{-1} \text{ K}^{-1}$). Recent computational studies have indicated promising thermoelectric applications (Filippetti et al., 2016; Shukla et al., 2020), with predictions of zT up to 2 when the charge carrier density is $\sim 10^{18-19} \text{ cm}^{-3}$ (Lee et al., 2015; Filippetti et al., 2016; Guo and Wang, 2016; Zhao et al., 2017).

Realising this performance with halide perovskites is challenging but some early studies in this area have already achieved promising zT values of up to 0.14 (Lee et al., 2017; Liu et al., 2017; Liu et al., 2019b; Saini et al., 2020). One of the principal challenges is in finding doping strategies to increase carrier concentrations to $\sim 10^{18-20} \text{ cm}^{-3}$. Experimentally, chemically-induced doping of $CH_3NH_3PbI_3$ and the photo-induced doping of $MASnI_3$ improved zT by more than two orders of magnitude (Mettan et al., 2015). Substitutional doping of $CH_3NH_3PbBr_3$ with Bi has been shown to increase the electrical conductivity by more than three orders of



magnitude as shown in **Figure 2B** (Tang et al., 2020) and modulation of the stoichiometry has also been shown to increase electrical conductivity (Haque et al., 2019). However, in these cases, zT remained low. On the other hand, adjustment of the stoichiometry in the copper based perovskite $C_6H_4NH_2CuBr_2I$ enabled carrier concentrations of $\sim 10^{20} \text{ cm}^{-3}$ and power factors up to $1.9 \text{ mV m}^{-2} \text{ K}^{-1}$ (Liu et al., 2017). Tin and germanium perovskites open up the possibility of using self-doping processes of Sn^{2+} and Ge^{2+} to Sn^{4+} and Ge^{4+} to achieve electrical conductivities $>100 \text{ S cm}^{-1}$ (Takahashi et al., 2013). The electrical conductivity of Cs_3SnI_3 thin films has been enhanced through the self-doping mechanism to achieve the highest zT values of this class of material of 0.14 (Lee et al., 2017; Liu et al., 2019b; Saini et al., 2019). Many challenges remain in realising the

full thermoelectric potential of halide perovskite, but there are promising candidates for low temperature applications.

CARBON NANOTUBE BASED COMPOSITES

Polymer (nano) composites offer a new route to decouple the interrelated thermoelectric parameters. Therefore, conductive polymer nanocomposites have recently been largely explored as thermoelectric materials. The main strategies have been the combination of (conductive) polymers with inorganic thermoelectric (nano)particles (e.g., p- and n-type Bi_2Te_3) (Zhang et al., 2010) as well as polymer composites based on carbon nanomaterials (Kim et al., 2010; Wang et al., 2015). Among carbon nanomaterials, carbon nanotubes (CNTs) have attracted the most attention, being a “one-dimensional material” (Hicks and Dresselhaus, 1993). Specifically, the power factor of CNTs can be dramatically increased by enhancing the mobility along the tube direction. Theoretically, the Seebeck coefficient of semiconducting single-wall CNTs (SWCNTs) can reach a value larger than $2000 \mu\text{V K}^{-1}$ at room temperature as the tube diameter decreases to 0.6 nm (see **Figure 3**) (Hung et al., 2015). When combined with a polymer matrix, the intrinsically high electrical conductivity can be retained while reducing the high thermal conductivity due to the presence of the polymer.

The most direct benefit of the presence of the polymer matrix is the reduction in thermal conductivity. For example, Chuizhou et al. reported an *in-situ* chemically polymerised polyaniline (PANI) layer, uniformly coated on a freestanding CNT network containing randomly entangled individual CNTs and CNT bundles (Meng et al., 2010). The thermal conductivity of the 20 wt% PANI/CNT composites dropped to $\sim 0.5 \text{ W m}^{-1} \text{ K}^{-1}$ close to that of PANI ($\sim 0.45 \text{ W m}^{-1} \text{ K}^{-1}$) with the electrical conductivity of 60 S cm^{-1} and the Seebeck coefficient of $28 \mu\text{V K}^{-1}$. Kim et al. reported a segregated network composites of CNTs/PEDOT:PSS with vinyl acetate ethylene copolymer (Kim et al., 2010). The dissimilar bonding and vibrational spectra between CNT and PEDOT:PSS along with the segregation by vinyl acetate ethylene copolymer, reduced the thermal conductivity of the composites to $0.3 \text{ W m}^{-1} \text{ K}^{-1}$. The interconnected network morphology (colloidal PEDOT:PSS particles bridging CNT-CNT junctions) guaranteed an electrical conductivity as high as 400 S cm^{-1} with 35 wt% SWCNTs.

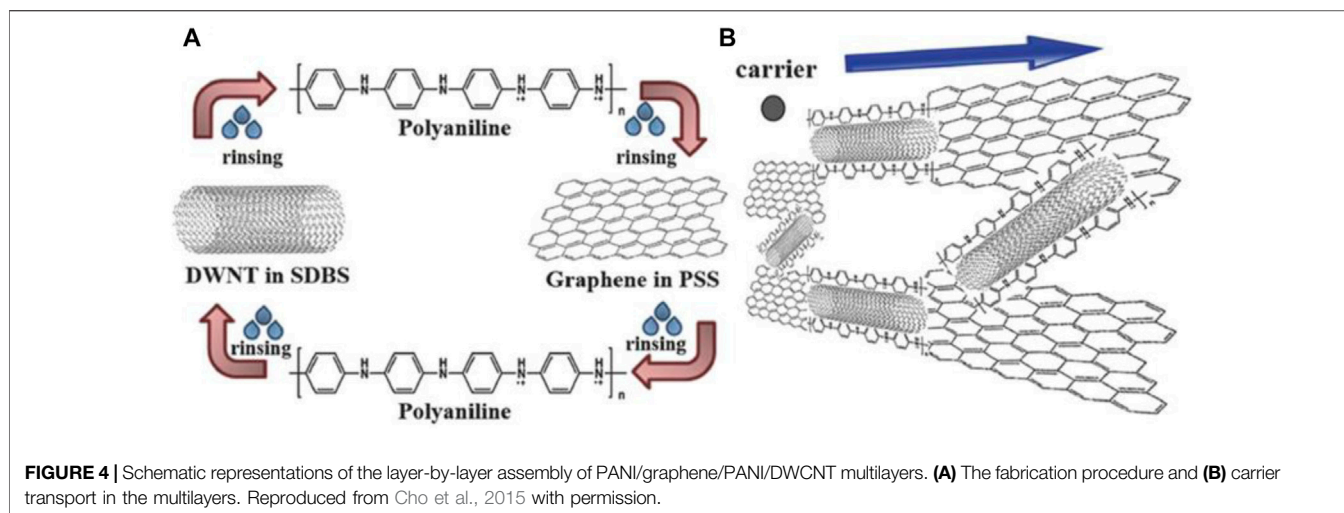
An effective decoupling of electrical conductivity and Seebeck coefficient has also been demonstrated in the carbon-based thermoelectric nanocomposites. For example, in SWCNT/PEDOT:PSS nanocomposites (Moriarty et al., 2013b), barriers at the SWCNTs/PEDOT:PSS interface preferentially hindered the transport of low-energy charge carriers and only allowed high-energy carriers to pass across the tube junctions, so to increase the mean carrier energy. This SWCNT/PEDOT:PSS showed an increase in electrical conductivity from 500 S cm^{-1} – 4000 S cm^{-1} , with the SWCNTs content increasing from 20 to 95 wt%, while the Seebeck coefficient remained relatively unaltered at around

$20 \mu\text{V K}^{-1}$, resulting in a power factor as high as $140 \mu\text{W m}^{-1} \text{ K}^{-2}$. Similar works that used multi-wall carbon nanotube (MWCNT) and double wall carbon nanotube (DWNT) (Moriarty et al., 2013a), PEDOT:PSS, and additional meso-tetra(4-carboxyphenyl)porphine also observed a decoupling between the Seebeck coefficient, electrical conductivity and thermal conductivity. The electrical conductivity of these organic composites increased to approximately 95 S cm^{-1} , in the case of MWCNTs and 960 S cm^{-1} , in the case of DWNTs, as the concentrations of both the CNTs and PEDOT:PSS were increased. The Seebeck coefficient ($\sim 40 \mu\text{V K}^{-1}$ for MWCNTs and $70 \mu\text{V K}^{-1}$ for DWNTs) and thermal conductivity ($\sim 0.12 \text{ W m}^{-1} \text{ K}^{-1}$), however, remained relatively unaffected by the increase in concentration.

The π - π interactions between CNT and polymer can positively influence the alignment of polymers, affect the polymer structural morphology and further increase its power factor (Bounioux et al., 2013; Wang et al., 2014). Typically, *in-situ* polymerization of polymers on CNT templates can grow polymers in an ordered manner on the surface of the CNTs. This hybrid structure can increase the effective carrier delocalisation and thus enhance the carrier mobility in conjugated polymers (Yao et al., 2010; Liu et al., 2011). For example, Qin et al. found that CNTs tune the molecular chain arrangement of PANI from a compacted coil to an expanded coil, by using *m*-cresol (Yao et al., 2014b; 2014a). The electrical conductivity of PANI/SWCNTs has been highly increased to 769 S cm^{-1} thus obtaining a maximum power factor of $176 \mu\text{W m}^{-1} \text{ K}^{-2}$. Combining both *in-situ* polymerization with the *m*-cresol solvent processing, the SWCNTs/PANI composite films reached a power factor of $217 \mu\text{W m}^{-1} \text{ K}^{-2}$ at room temperature (Wang et al., 2016).

Research on layer-by-layer deposition polymer on CNTs has recently shown the ability to easily adjust nanotube distance, density, and film thickness, which alters the Seebeck coefficient (Rivadulla et al., 2010). The layered structure seemed to improve carrier mobility, increasing both electrical conductivity and the Seebeck coefficient. Cho et al. reported a 40 PANI/graphene/PANI/DWNT quad-layered composite film prepared by the layer-by-layer assembly, as illustrated in **Figure 4** (Cho et al., 2015), exhibiting an electrical conductivity of 1080 S cm^{-1} and a Seebeck coefficient of $130 \mu\text{V K}^{-1}$, resulting in a remarkable power factor of $1825 \mu\text{W m}^{-1} \text{ K}^{-2}$. The authors pointed to the continuous 3D PANI-wrapped DWNTs and connected graphene network as the reason for the exceptional performance. By alternately layer-by-layer depositing DWCNTs, stabilized by polyethylenimine (PEI), and graphene stabilized by polyvinylpyrrolidone (PVP), they also reported a high power factor n-type 80-bilayer DWNT-PEI/graphene-PVP composites film (Cho et al., 2016a). In addition to its remarkable power factor of $-190 \mu\text{W m}^{-1} \text{ K}^{-2}$ at room temperature, the highly ordered graphene layers also offered a barrier to gas diffusion, resulting in a relatively air-stable n-type composite film.

The mixture of CNTs with polymers can bring other advantages, such as increased mechanical flexibility and even stretchability to the as-fabricated composites. For example, Cho and Son fabricated a stretchable thermoelectric multilayer film by



alternately depositing 0.1 wt% polyethylene oxide (PEO) and 0.03 wt% DWNT, dispersed with 0.1 wt% polyacrylic acid (PAA) (Cho and Son, 2019). Because of the weak bond strength and high chain mobility between PEO and PAA layers, the PEO/DWNT-PAA multi-layered composite exhibits a crack-free surface of up to 30% strain and retains thermoelectric performance of 90% of the unstretched sample. The resultant 25 bi-layered composite films (~500 nm thick) displayed an electrical conductivity of 19.6 S cm^{-1} , a Seebeck coefficient of $60 \mu\text{V K}^{-1}$, and attributed to the three-dimensional conjugated network of DWNT.

PERSPECTIVE ON NEXT GENERATION THERMOELECTRIC MATERIALS

The herein highlighted classes of emerging thermoelectric materials, covering organic polymers, CNT-based thermoelectric composites, inorganic and hybrid organic-inorganic perovskites, have all undergone remarkable progress with many high-performing systems being developed in recent years. While these thermoelectric materials are still in the initial development stage and face a number of challenges, the wide variety of materials and approaches offer many avenues for new material combinations and fine-tuning and optimisation of thermoelectric properties.

Organic and hybrid organic-inorganic materials still suffer from the scarcity of high-performing thermoelectric materials. For the development of next generation state-of-the-art thermoelectric materials, further understanding of the fundamental mechanisms of doping, thermal and electrical transport are required, which is a significant challenge considering the often complex systems with several components and a mixture of ordered and disordered phases. For organic semiconductors, the molecular structure and the morphology of their pristine phases or composites e.g., with CNTs, are also highly important and in many cases difficult to control and understand in detail. For example, a systematic investigation of the critical roles of a conjugated backbone, side chains, and polymer molecular weight relationship with the

thermoelectric performance can guide future materials selection. Processing, with its multitude of variable parameters, is likewise an area that will benefit from a better understanding of detailed structure-property relations for the semiconducting polymer as well as for the possible composite components viewed together. With the ongoing development of tailor-made organic semiconductors for thermoelectric applications, a promising future direction for composite thermoelectrics could be the tailored design of semiconducting polymers with specific interactions with CNTs.

From a technical side, precise measurements of key thermoelectric parameters for organic thermoelectric materials, often prepared as thin polymer films, are different from inorganic bulk materials. Seebeck coefficients and in-plane thermal conductivities reported by different groups are measured by different home-made systems, some of which are affected by environmental conditions, sample size, shape and substrate. Thus, the resulting accuracy and comparability need to be considered. A standard for measuring organic thermoelectric device performance does not exist, due to the various types and structures. More work in this area will undoubtedly be helpful for the continued progress and further development of high-performing thermoelectric systems.

Apart from growing interest in improving the power factor of thermoelectric materials, the mechanical properties of the new generation of emerging thermoelectric materials and composites are attracting particular attention. Efforts should also be dedicated towards new designs for flexible thermoelectric devices and exploring potential applications, taking advantage of positive features like mechanical flexibility while offsetting drawbacks like low efficiency. Finding the right application for new thermoelectric devices using emerging materials classes will ultimately make better use of the unique properties of these promising materials. While not mentioned specifically in this perspective, there are a number of other materials that are also entering the field of thermoelectrics. Here it is worth mentioning crystalline framework materials including metal-organic frameworks and covalent organic frameworks as well as other classes of porous materials such as conjugated microporous

polymers, gels, and foams. There are still many promising directions for the exploration of materials that are still wide open, making the prospects of thermoelectric materials and devices hugely exciting.

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AUTHOR CONTRIBUTIONS

All authors listed have made a substantial, direct, and intellectual contribution to the work and approved it for publication.

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