Organic-based thermoelectrics

M. Lindorf,†[a] K. A. Mazzio, †*[b] J. Pflaum, [cd] K. Nielsch,[efg] W. Brütting [a]
and M. Albrecht [a]

Thermoelectric materials have the ability to transform thermal energy into electrical energy and *vice versa*. For an extended period of time, only inorganic materials have been considered for thermoelectric research and application, but recent advances in the field of organic semiconductors established the basis for organic thermoelectrics research. Pristine organic semiconductors often face the problem of undesirable suboptimal transport properties and, therefore, recent approaches have focused on combining different materials, where both organic–organic and organic–inorganic hybrid systems have led to improved efficiency in organic thermoelectrics. This review aims to provide a general overview on the recent advances for organic-based thermoelectrics with an emphasis on the most thoroughly investigated material classes and the approaches employed to control their thermoelectric transport properties.

1. Introduction

The first thermoelectric (TE) phenomenon was observed by T. Seebeck in 1821.[1] He observed the generation of a thermal voltage in a material by applying a temperature gradient. In that case, charge carriers will move by thermal diffusion from the hot to the cold side yielding a potential difference that is required to drive an electrical current.[2,3] This phenomenon is nowadays known as the Seebeck effect and the magnitude of the generated thermovoltage is described by the material specific Seebeck coefficient. The Seebeck effect can be applied to convert thermal energy to electric power, which can be used in

[a] *Universität Augsburg, Institut für Physik, 86159 Augsburg, Germany*
[b] *Helmholtz-Zentrum Berlin für Materialien und Energie, GmbH, 12489 Berlin, Germany. E-mail: katherine.mazzio@helmholtz-berlin.de*
[c] *Julius-Maximilians Universität Würzburg, 97074 Würzburg, Germany*
[d] *Bavarian Centre for Applied Energy Research (ZAE Bayern e.V.), 97074 Würzburg, Germany*
[e] *Leibnitz Institute for Solid State and Materials Research Dresden, PO Box 270116, 01171 Dresden, Germany*
[f] *Technical University of Dresden, Institute of Materials Science, Dresden, Germany*
[g] *Technical University of Dresden, Institute of Applied Physics, Dresden, Germany*

† M. Lindorf and K. A. Mazzio contributed equally to this work.

M. Lindorf studied physics at the Technical University of Chemnitz in Germany and finished his diploma thesis in 2012. He joined the group of Manfred Albrecht at the Technical University of Chemnitz as a Ph.D. student and later transferred to the University of Augsburg in Germany. There he received his Ph.D. degree in physics from the University of Augsburg in 2017 studying the process of metal induced crystallization and its influence on the thermoelectric properties of SiGe thin films. His current research topics include the thermoelectric optimization of SiGe thin films and organic hybrid systems.

K. A. Mazzio is a research scientist in the Institute for Nanospectroscopy at Helmholtz-Zentrum Berlin. She received her PhD in Materials Science and Engineering from the University of Washington with Prof. Christine K. Luscombe studying the photophysical properties and new synthetic techniques for hybrid materials based on conducting polymers and inorganic nanostructures for photovoltaics. Since then she has been at Helmholtz–Zentrum Berlin where her research focuses on the design and synthesis of hybrid architectures for energy conversion and storage applications, with a particular emphasis on developing fundamental understandings of the processes occurring at hybrid interfaces through the use of both lab-based and synchrotron-based techniques.

thermoelectric generators (TEGs) to recover waste heat. The field of thermoelectric power generation has become more and more important due to global efforts in finding new energy sources. It has been found that approximately 70% of primary energy consumption is wasted as heat,[4] and therefore great lengths are being taken in an effort to use this energy more efficiently. In particular, remote power generation *via* small, mechanically robust, and stand-alone energy systems is currently of particular research interest and could very well be provided by thermoelectric energy harvesting[5] and even foster the growth of upcoming technologies like the internet-of-things.

For commercial applications, a thermoelectric material should have a large Seebeck coefficient α, a high electrical conductivity σ, and a low thermal conductivity κ, which can be summarized in the dimensionless figure of merit at a given temperature T as

$$ZT = (\alpha^2\sigma/\kappa)T$$

The numerator in the ZT equation, $\alpha^2\sigma$, is referred to as the power factor, and is often taken as a measure of a material performance when there are difficulties in determining κ or if variations in the thermal conductivity are of minor importance for the figure of merit of a given material class. A ZT value of 1 corresponds to an efficiency for the conversion of thermal to electrical energy of 10%, which was the upper limit between 1950 and 1990 for the established bulk materials Bi_2Te_3, SiGe, and PbTe.[6] The main challenge for further enhancement of ZT

J. Pflaum is a solid state physicist working on organic semiconductors at the Julius-Maximilians University in Würzburg. His major research focus addresses electronic and optical excitations in molecular single crystals and thin films and their transport and interrelation with the structural properties on microscopic length scales. By his strong affiliation to the Bavarian Center for Applied Energy Research his fundamental scientific work is also motivated by the implementation of organic and hybrid–organic materials in innovative device applications ranging from thin film photovoltaics and thermoelectric generators to molecular sensors and non-classical light sources based on single molecules.

W. Brütting received his Ph.D. in Physics from the University of Bayreuth in 1995 with a work on charge-density wave systems. Thereafter he moved to the field of organic semiconductors where he could take part in the development of organic light-emitting diodes for display applications. In 2003 he became Professor for Experimental Physics at the University of Augsburg. His current research activities include charge transport and photophysics of organic semiconductors and their device physics. He has published more than 180 journal articles, several book chapters and edited the book Physics of Organic Semiconductors.

K. Nielsch studied physics at the University Duisburg, Germany and performed his master thesis at Lund University, Sweden in 1997. He joined the group of Ulrich Goesele at the Max-Planck-Institute in Halle as a Ph.D. student. As a post-doctoral associate he worked with Caroline Ross at MIT in 2002. From fall 2003 he began leading a BMBF nanotechnology research group on Multifunctional Nanowires and Nanotubes at the Max-Planck-Institute in Halle. In 2006, Hamburg University appointed him as a professor for experimental physics. From 2009 until 2016 he coordinated the German Priority Program DFG-SPP 1386 on Nanostructured Thermoelectrics. Since 2015 he has been director of the Institute of Metallic Materials at IFW Dresden and full professor at TU Dresden.

M. Albrecht is a Professor for Experimental Physics and currently Director of the Institute of Physics at the University of Augsburg in Germany. He received his Ph.D. degree in physics from the University of Konstanz (Germany) in 1999. From 2001 till 2003 he was a Postdoctoral Research Fellow with the IBM Almaden Research Center in San Jose/USA. His current research activities include magnetic thin films and nanostructures for spintronic and THz applications, spin dynamics and magnetic coupling phenomena, as well as thermoelectric materials.

arises from the strong coupling of the transport coefficients α, σ, and κ.

In this regard, the research field was revolutionized by the introduction of nanostructuring approaches and new fabrication technologies, as well as by investigation of new material classes, which have provided the opportunity to partially decouple these coefficients and to optimize them independently.[7] Different approaches have been introduced such as:

- Increasing the electrical conductivity/Seebeck coefficient by quantum confinement in one or more dimensions,[8–11]
- Decreasing the phononic part of the thermal conductivity by scattering at grain boundaries or at interfaces, particles, and defects (while maintaining the electronic properties),[12–14]
- Energy filtering at introduced barriers (*e.g.* interfaces, structural and thereby electronic modulations) and designed energy transitions using band structure engineering,[15,16]
- Violation of the Wiedemann–Franz law which interrelates the electronic contributions to thermal and electric transport by electronic correlations in low dimensional systems,[17] and
- Combining these approaches.[18–20]

In this review, the reader will first be introduced to the different material classes utilized in the field of organic thermoelectrics. A short overview concerning the evolution and driving factors for the research of each material class will be given with the most recent advances and challenges being discussed. Special emphasis will be put on organic-based hybrid systems and the different approaches employed to successfully design the thermoelectric properties in such systems. A comparison of the achieved TE properties for the different materials is given. Afterwards, the advantages and drawbacks of thermoelectric generators based on organic materials will be discussed. In the end, the already achieved goals of organic thermoelectrics will be summarized together with the current challenges lying ahead.

2. Organic thermoelectrics

2.1 Material classes for organic TE

In the past, the broad variety of π-conjugated organic materials sparked interest in basic thermoelectric research since the discovery of low thermal conductivity in electrically conducting polymers in the 1970s.[21] Intrinsically, organic materials exhibit very low thermal conductivities compared to inorganic materials due to their naturally weak van-der-Waals bonding and disordered microstructures in the case of polymers.[20] This is accompanied by rather poor intrinsic electrical conductivities[22] and as such, pristine organic materials have long not been considered for thermoelectric applications. Recent improvements in the electrical conductivity of conjugated organic materials have been achieved through control over the charge carrier concentration *via* doping,[23–27] optimization of the microscopic morphology,[24,28,29] modulation of transport pathways,[30] low dimensional compounds with pronounced spatially anisotropic correlations of their electronic systems,[31] and control over the structural anisotropy in copolymer thin films.[32,33] Even the general model for charge-transport in conducting polymers is currently under discussion with respect to improving electrical transport properties not being able to be described by existing models.[34] This is in large part due to the strong morphological dependence of the electronic properties, which also induces a more complex relationship between the carrier concentration and the Seebeck coefficient or electrical conductivity, and can result in a lower Seebeck coefficient for equivalent electrical conductivity in organic materials relative to their inorganic counterparts. However, the recently explored approaches have also resulted in improvements in the other thermoelectric transport coefficients in the last decades, including the Seebeck coefficient[27,30,35] and the thermal conductivity,[27,36,37] as a better understanding of the basic transport mechanisms has been obtained for organic materials. Most importantly, the empirical finding that the Seebeck coefficient and power factor scale with the electrical conductivity as $\alpha \propto \sigma^{-1/4}$ and $(\alpha^2\sigma) \propto \sigma^{1/2}$, respectively, has allowed developing general strategies for improving the TE performance of organic semiconductors by doping.[38] However, as pointed out recently by Campoy-Quiles,[39] other factors like morphology and texture, depending mainly on the packing at microscopic length scales, or the possibility to tune TE properties by controlling interfaces and mixing in composite materials need to be explored as well.

Most recent thermoelectric research in the field of organic materials has revealed remarkable improvements in hybrid systems where different materials are systematically combined to effectively guide the leading parameters of thermoelectric transport. With this in mind, four main categories of organic based systems have been established in the form of conjugated polymers, coordination polymers, small molecules, and the general class of organic–inorganic hybrids.[21,22,38,40–42]

2.2 Conjugated polymers

Conjugated polymers are prime candidates for organic thermoelectric materials due to their semiconducting character which stems from non-localized π-bonds along the conjugated backbone.[40] Even metal-like behaviour has been achieved *via* doping of conjugated polymers, as was first demonstrated for highly doped polyacetylene (PA) films in the 1970s and awarded the Nobel prize in 2000.[43,44] Despite the superior conductivity along the individual conjugated backbones, the effective conductivity of a polymer layer can be hindered by the poor inter-chain charge carrier transport as well as by the inhomogeneous distribution of amorphous and crystalline regions. The need for control over both the stacking of polymeric chains and the dispersion of molecular weight has led to different synthetic approaches, and an emphasis has been placed on achieving good solubility of the conjugated polymers in common solvents.

The first generation of conjugated polymers was neither soluble nor fusible. Representatives of these polymers include PA, polypyroles (PPy), polythiophenes (PTh), polyanilines (PANi), and poly(3,4-ethylenedioxythiophene) (PEDOT). Initially, only chemical or electrochemical polymerization was available for preparation of these polymers, and large efforts led to the possibility of emulsion polymerization for these materials by employing counterions. Such prepared polymers include the examples of PEDOT:PSS and PANi:CSA, where PSS- and CSA-are poly(styrenesulfonate) and (±)10-camphorsulfonic acid anions, respectively. The most widely investigated conjugated polymer, PEDOT:PSS, is commercially available with a broad variety of transport characteristics showing electrical conductivities for holes between 10^{-4} to 10^{3} S cm^{-1}, making it even comparable to low-doped inorganic semiconductors.[21] By optimizing its composition, *e.g.* by removal of PSS, record values for the power factor of almost 500 μW mK^{-2} and a *ZT* value of 0.42 were achieved.[27]

Other approaches include engineering of the density of states in doped polymer blends, which allows for increasing the entropy of charge carriers by separating their transport and Fermi-level.[45] In that way, large Seebeck coefficients in the range of a few mV K^{-1} could be achieved, although the power factor stayed rather low, as shown in Fig. 1. Nevertheless, one of the major drawbacks besides the inherent disorder impeding the charge carrier transport on macroscopic scales is the lack of long-term stable n-doped hosts, constituting an indispensable necessity for the implementation of polymer based thermoelectric generators.

A recent review compared the thermoelectric properties of several organic semiconductors.[22] Its results and other noteworthy recent organic materials are summarized in Table 1. Here, it becomes obvious that p-type organic semiconductors have been studied more extensively than their n-type counterparts. Both the number of entries and the achieved power factors, $\alpha^2\sigma$, are significantly lower for n-type organic semiconductors, highlighting the need for better developed n-type organic TE materials. In general, one of the great challenges with organic semiconductors is finding stable n-type materials. π-conjugated organic materials typically have energetically shallow lowest-unoccupied molecular orbital (LUMO) levels which results in increased rates of oxidation and sensitivity towards humidity.[46,47] As a result, significant efforts are being pursued to lower the LUMO energy of conducting polymers in an effort to increase their stability.[48] Please note that another recent review by Sun, *et al.* directly highlights the advances for n-type organic TE materials[49] and significant progress could be achieved for organic–inorganic composites consisting of organic semiconductors and carbon nanotubes (CNTs) reaching power factors above 1000 μW mK^{-2}.[49,50]

2.3 Coordination polymers

Coordination polymers (CPs) are complexes whose basic building units are metal ions and organic ligands. In this case, the metal ions act as connectors and the ligands as linkers. Since the 1960s, the main research focus of coordination polymers has revolved around such topics as luminescence, chirality, catalysis, magnetism, and electrical conductivity,[51–59] while only very few studies with respect to thermoelectric properties of CPs were reported in the literature.[60,61] Among the first thermoelectrically promising CPs was a series based on the ligands 4,4′-dihydroxy- 3,3′-diacetyl biphenyl bis-thiosemicarbazone (L-1) and 4,4′-dihydroxy- 3,3′-dipropionyl biphenyl bis-thiosemicarbazone (L-2).[62] The synthesized CPs Cu(L-1) and Cu(L-2) exhibited rather poor thermoelectric properties of nearly insulator-like character with values in the range of 10^{-5} S cm^{-1} and 1.1–1.2 mV K^{-1} for the electrical conductivity and Seebeck coefficient, respectively. A rather recent advance was achieved by Zhu *et al.* in 2012 with the CP poly[A_x(M-ett)].[63] The representative CP poly[K_x(Ni-ett)] exhibited electrical conductivities as high as 63 S cm^{-1} and Seebeck coefficients in the range of −50 to −200 μV K^{-1}. Fig. 2 provides the measured temperature-dependent thermoelectric parameters for different poly[A_x(M-ett)] compositions.

Recently, CPs of the so-called family of metal–organic frameworks (MOFs) have ignited further interest in the field of thermoelectric research as the framework of iron and the 1,2,3-triazolate (tri) ligand in Fe(tri)$_2$ revealed an increase in electrical conductivity by 8 orders of magnitude when oxidized into the state of Fe(tri)$_2$(BF$_4$)$_{0.33}$.[64] This resulted in an electrical conductivity of 0.3 S cm^{-1} and highlights both the potential and need for further research on this class of materials with respect to future applications, not only in the form of thermoelectrics but organic electronics in general. For MOFs, power factors of up to 10 μW mK^{-2} and *ZT* values in the range of 10^{-4} have been achieved.[65]

2.4 Small molecules

Research in the field of small molecules is lagging behind that of conducting polymers, with few notable exceptions, like

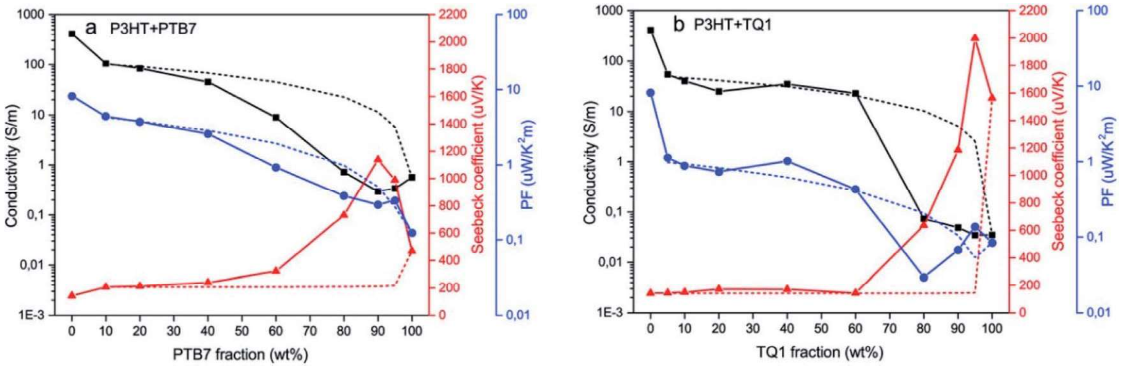


Fig. 1 Thermoelectric properties of P3HT (which has a relatively shallow HOMO level) and its binary mixtures with polymers containing deeper HOMO levels (PTB7 and TQ1). The large increases in Seebeck coefficient are attributed to control over the density of states due to the differences in the ionization potentials of the polymers. Copyright 2017, Wiley. Used with permission from ref. 45, John Wiley and Sons.

Table 1 Summary of thermoelectric properties of selected organic semiconductors

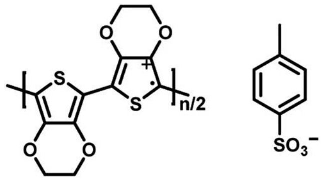
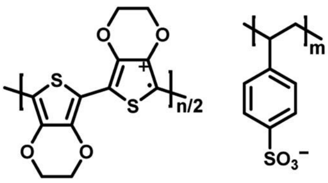
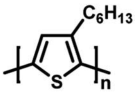
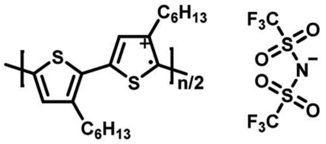
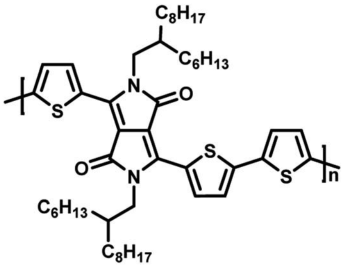
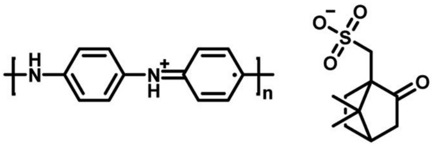
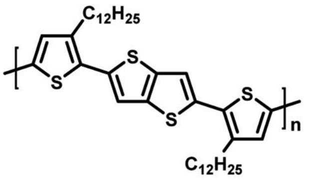
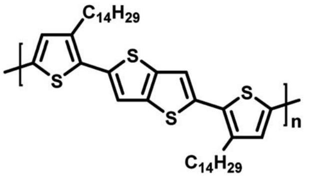
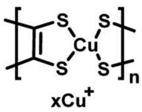
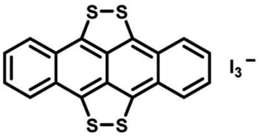
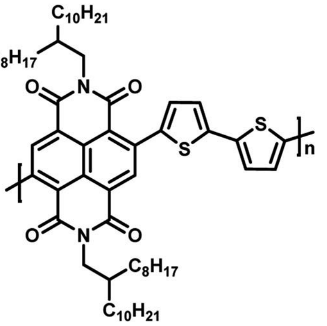
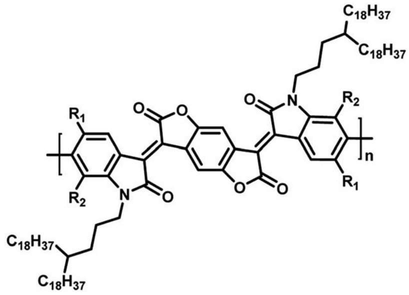
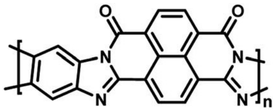
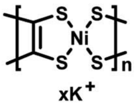
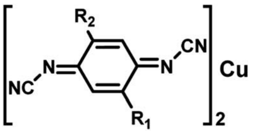
			α (μV K^{-1})	σ (S cm^{-1})	$\sigma\alpha^2$ (μW mK^{-2})	Reference
p-type	PEDOT-tosylate		117	923	1270	24
	PEDOT:PSS		72.6	890	469	27
	P3HT		39.5	2	31	115
	P3HT:TFSI$^-$		51	92	23.9	115
	PDPP3T		70	0.5	25	116
	PANI:CSA		34	169	19	117
	PBTTT-C12		27	1.9	14	116
	PBTTT-C14		32.7	1000	109	118
	Poly[Cu$_x$(Cu-ett)]		83	9.5	6.5	63

Table 1 (*Contd.*)

			α (μV K^{-1})	σ (S cm^{-1})	$\sigma\alpha^2$ (μW mK^{-2})	Reference
	TTT_2I_3		42	2150	387	73
n-type	P(NDI2OD-T2)		−850	0.008	0.6	119
	BDPPV		−141	14	28	120
	BBL		−60	1	0.43	121
	Poly[K_x(Ni-ett)]		−122	44	66	63
	$Cu(DCNQI)_2$		−34	1000	110	73

pentacene, C_{60}, and some thiophene derivatives having Seebeck coefficients in the range of mV K^{-1}.[66] However, thermoelectric interest is on the rise for so called strong charge transfer (CT) complexes.[38] In those binary or even multinary mixtures an integer charge transfer is driven by the strong electron affinity or ionization potential of one of the partners leading to a p- or n-type doping, respectively (Fig. 3). Depending on the specific stoichiometry of the complex and its crystalline packing, the transferred electron or hole can be spread across several molecules, thus behaving like a quasi-free charge carrier. Most of these complexes are based on derivatives of tetrathiafulvalenes (TTFs) which were in the focus of research on organic semiconductors from the early 1970s.[67,68] Emphasis was put on the well-known organic conductor TTF-TCNQ, which forms a one-dimensional columnar CT complex where tetracyanoquinodimethane (TCNQ) and TTF act as the electron acceptor and donor, respectively, *i.e.* the combination of both processes shown in Fig. 3 within the same sample. As the intermolecular electronic couplings along stacked columns of this kind are orders of magnitude larger than between neighbouring columns, quasi one-dimensional metallic transport could be achieved for these CT complex based systems. Even

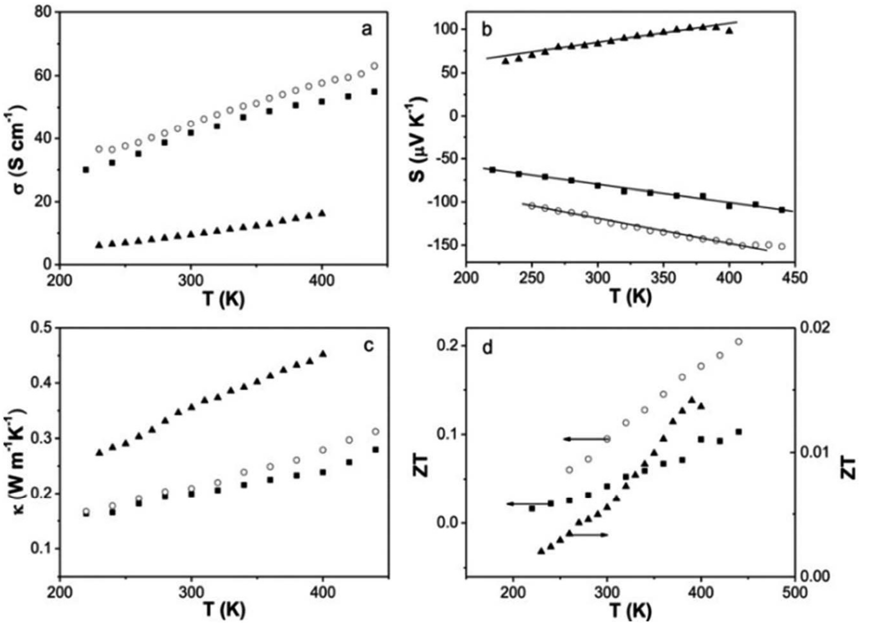


Fig. 2 Temperature dependence of (a) electrical conductivity, (b) Seebeck coefficient, (c) thermal conductivity and (d) figure of merit for poly[Na_x(Ni-ett)] (■), poly[K_x(Ni-ett)] (□) and poly[Cu_x(Cu-ett)] (▲). Copyright 2012, Wiley. Used with permission from ref. 63, John Wiley and Sons.

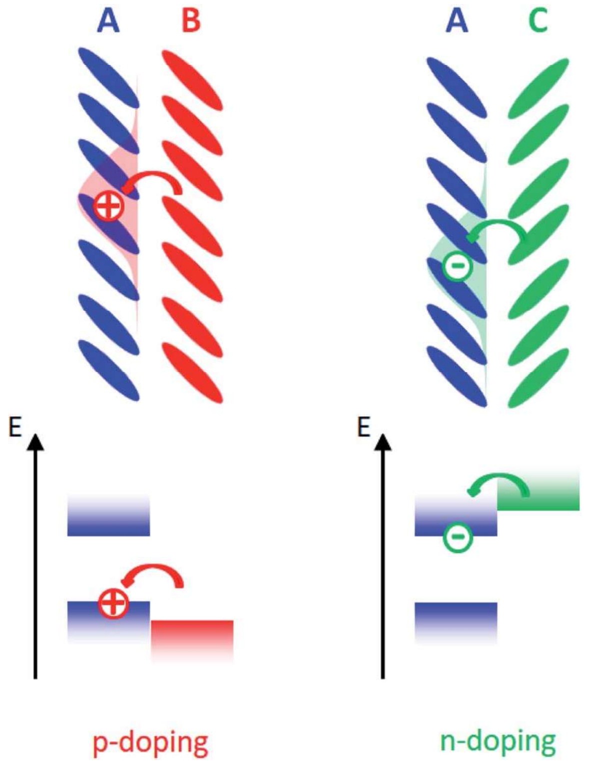


Fig. 3 Schematic illustration of the integer charge transfer (CT) within a CT-complex leading to an effective p-doping (left) or n-doping (right). Shaded areas indicate the possible delocalization of the transferred charge along the crystalline molecular stack.

though high electrical conductivities in the range of 300–500 S cm^{-1} could be achieved for TTF-TCNQ single crystals, the observed Seebeck coefficient was rather low at approximately −28 μV K^{-1}.[69–71] This was attributed to the coexistence of n- and p-type channels, which leads to partial compensation of the thermoelectric power. The thermal conductivity was observed to be dominated by its phononic part at room temperature and the experimentally determined values were as low as 1 W mK^{-1}.[72] Using these reported values, a calculated ZT of 0.7–1.1 × 10^{-2} was determined for TTF-TCNQ crystals. Slightly higher ZT values of 0.03 and 0.2 have been reported for single crystals of iodine doped tetrathiotetracene (TTT_2I_3) and copper-dicyanoquinonediamine ($Cu(DCNQI)_2$) showing p- and n-type conductivity of about 10^3 S cm^{-1} at room temperature, respectively.[73] A two-leg prototypical thermoelectric generator has been demonstrated by the two materials yielding a specific power output of several mW cm^{-2} and, thereby, confirming the potential of this material class. Moreover, by the strong electron phonon coupling in these low dimensional organic metals,[74] phonon drag effects emerge at low temperatures resulting in ZT values of more than 0.15 for $Cu(DCNQI)_2$, which are the highest reported so far for organic n-conductors and even outperform those of established inorganic thermoelectric compounds like $YbAgCu_4$. Fig. 4 presents the thermoelectric properties of TTT_2I_3 and $Cu(DCNQI)_2$.[73] Theoretical studies even predicted the possibility for very high ZT values in the range of $ZT \approx 20$ if the low-dimensional character of these materials as well as their degree of purity could be exploited optimally.[75,76]

Potential applications of these needle-like CT crystals are rather limited right now due to their small diameters in the range of microns and, thus, their weak mechanical strength. To this end, the usage of compressed powders, thin films, or even the combination of CT complexes with polymers into hybrid composites has been proposed for the realization of printable thermoelectric generator (TEG) prototypes. Unfortunately, the

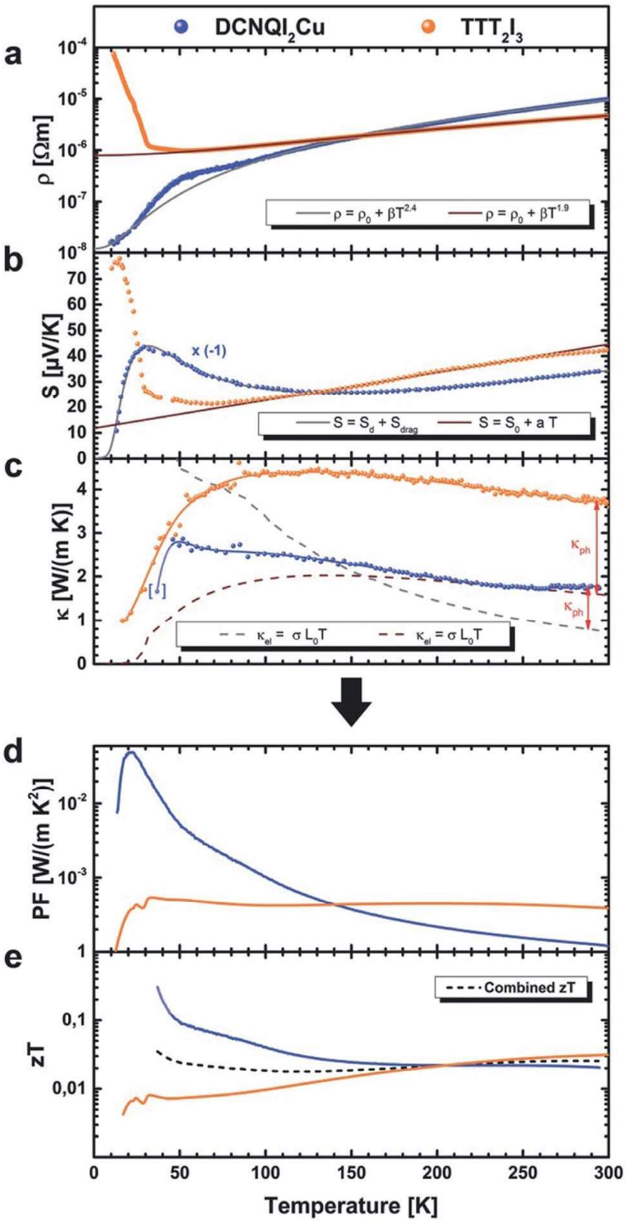


Fig. 4 Temperature dependence of (a) resistivity, (b) Seebeck coefficient, (c) thermal conductivity, (d) power factor, and (e) *ZT* for DCNQI$_2$Cu and TTT$_2$I$_3$. Copyright 2017, Wiley. Used with permission from ref. 73, John Wiley and Sons.

electrical transport properties of such samples deteriorated significantly down to values of 1–7 S cm^{-1} and 20–75 μV K^{-1} for the electrical conductivity and Seebeck coefficient, respectively.[77,78] This was attributed to interparticle and intergrain hopping processes rather than the desired one-dimensional transport, and highlights the need for further research with respect to the application of CT complexes.

2.5 Organic/nanoparticle hybrids

Another recent approach to advance TE research is to combine organic materials with nanoparticles into nanocomposite hybrid systems. In these cases, the organic material can be insulating or conducting, and the nanoparticles can be inorganic or nanostructured organics, such as CNTs. Even though modern inorganic TE materials often consist of expensive, non-abundant, rather brittle, and frequently even toxic materials based on elements like Bi, Te, Sb, Pb, and Ge, such materials are far better understood due to extensive prior research and can often be engineered on the nanoscale to directly guide important TE parameters like band structure and charge carrier concentration.[79] However, organic TE materials are cheap, non-toxic, abundant, light-weight, flexible, and solution-processable, but unfortunately also less explored in comparison to inorganic TE materials. The combination of these material classes affords the opportunity to take advantage of the good characteristics of each, and there is currently a tremendous amount of interest in this area in the field of thermoelectrics. In particular, the goal is to improve upon the typically low thermopower of the organic material with the introduction of the nanoparticles, in conjunction with maintaining high conductivities and allowing for solution processing and low thermal conductivities through the organic component.

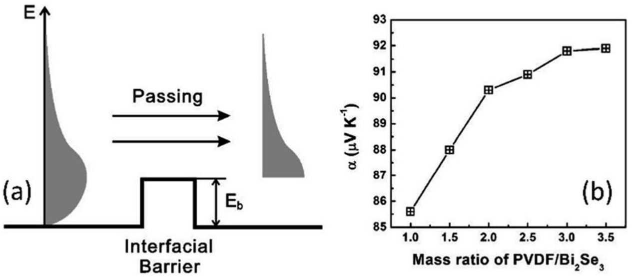


Fig. 5 (a) Schematic of energy distribution of charge carriers before and after passing through an energy barrier of height E_b, and (b) change in Seebeck coefficient with changing mass ratio of PVDF/Bi$_2$Se. Copyright 2015, Elsevier. Used with permission from ref. 92, Elsevier.

There are two primary methods for obtaining organic-nanoparticle hybrids, which include physical mixing and *in situ* wet chemical synthetic methods.[80] During physical mixing, the organic and inorganic materials are synthesized separately, followed by mixing in either solution or the solid state. Physical mixing has been applied *via* both solution and solid state methods, and many examples can be found in the literature, in particular for blends of conducting polymers with chalcogenide-based nanostructures[81–83] or metal nanoparticles.[84,85] There are also reports of a combination of these mixing and *in situ* processes. One example of the combined process was reported by Wang, *et al.* for a hybrid thermoelectric material synthesis whereby PbTe nanoparticles are first synthesized, followed by a second step involving the *in situ* polymerization of PEDOT.[80] By controlling the concentration of PbTe nanoparticles added during the polymerization process, they were able to vary the composite thermoelectric properties, and reported obtaining a maximum power factor of 1.44 μW mK^{-2} at 28.7 wt% PbTe.

While physical mixing can allow for control over the individual component properties, this process offers limited ability to direct interface formation or produce reproducible composite morphologies. *In situ* approaches, on the other hand, allow for greater control over the hybrid interface. In addition, they often eliminate the need for insulating ligands during inorganic nanoparticle growth, and allow for better mixing of the components in the solid state.

The seminal work of See, *et al.* revolved around the *in situ* synthesis of Te nanorods with the water soluble polymer PEDOT:PSS.[86] Here, the PEDOT:PSS covers the Te nanorods conformally and a two-component film consisting of a continuous electrical network of nanoscale organic/inorganic interfaces is formed. Both p-type materials on their own have rather poor ZT values in the range of 10^{-4} to 10^{-6}. The Te nanorods have very poor electrical conductivity of 0.08 S cm^{-1} but a high Seebeck coefficient of 408 $\mu\mathrm{V\ K}^{-1}$, while the opposite is observed for the PEDOT:PSS with 1.32 S cm^{-1} and 18.9 $\mu\mathrm{V\ K}^{-1}$ for the electrical conductivity and Seebeck coefficient, respectively. The hybrid material exhibits an intermediate Seebeck coefficient of 163 $\mu\mathrm{V\ K}^{-1}$ due to doping effects, but surprisingly the electrical conductivity of the compound film exceeds the values of both basic materials with 19.3 S cm^{-1}. This great increase in electrical conductivity for the hybrid material has been largely attributed to the development of highly conducting interfacial polymer species.[87,88] As the intrinsically low thermal conductivity of the PEDOT:PSS remained unchanged at roughly 0.25 W mK^{-1}, this resulted in an increase of more than 4 orders of magnitude for ZT to 0.1. This highlights the enormous potential of organic–inorganic hybrid thermoelectrics caused by functionalization and interface effects.[87]

One interesting application of organic–inorganic hybrid systems is the combination of inorganic nanoparticles, *e.g.* a highly conductive 3D topological insulator with insulating polymers, such as poly(vinylidene fluoride) (PVDF). In this case, the organic properties of interest primarily revolve around the film forming properties, plasticity, and thermal stability.[89] It is possible to take advantage of these properties if the insulating polymer is employed in tandem with conductive nanostructures that are able to form electronic percolation pathways throughout the active area.[90,91] Dun, *et al.* reported the fabrication of n-type Cu-doped Bi_2Se_3/PVDF hybrid systems.[92] They controlled the Cu concentration during solution synthesis, and reported an optimized power factor and ZT of 103 $\mu\mathrm{W\ m}^{-1}\ \mathrm{K}^{-2}$ and 0.10, respectively, for a composition of $Cu_{0.1}Bi_2Se_3$. The PVDF introduced an interfacial energy barrier that promoted energy filtering effects, and they observed a dramatic improvement in mobility *via* Cu doping when concentrations were low enough to not form $Cu_{2-x}Se$ subphases which act as impurities. A schematic of the energy barrier and its effect on the carrier energy distribution in the hybrid Bi_2Se_3/PVDF system is provided in Fig. 5a along with the change in Seebeck coefficient with changing PVDF concentration in Fig. 5b. Overall this work is important for demonstrating the ability to decouple the Seebeck coefficient from the electrical conductivity in these hybrid systems.

Another broadly investigated type of hybrid system are those involving CNTs. As these can be directly doped by organic materials,[93,94] infiltrated by them,[94,95] or simply used for functionalization with polymer chains,[96–98] CNTs have been thoroughly explored not only by the TE community.[99–102] Both p-type and n-type CNTs have been successfully synthesized and the

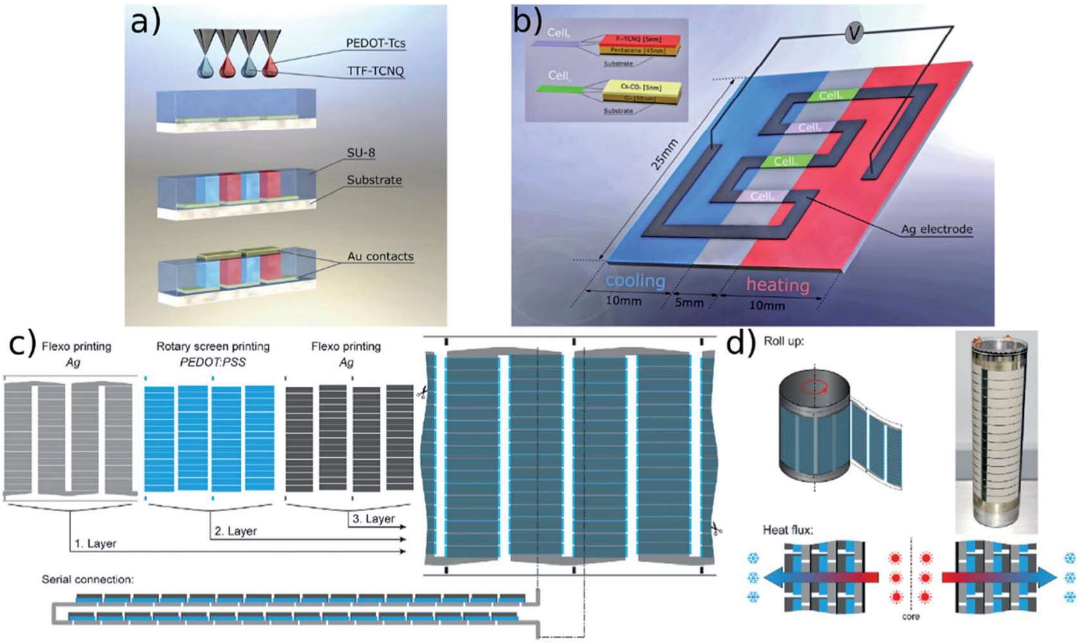


Fig. 6 (a) Fabrication of an all-organic TEG through photolithography patterning and ink-jet printing.[23] (b) Four-terminal prototype TEG fabricated by thermal deposition of pentacene and C_{60}.[106] (c) Film-based TEG employing only one type of thermoelectric material processed by roll-to-roll printing. Reproduced with permission.[107] (d) Final rolled-up device and heat-flow direction therein. Reproduced with permission.[107]

resulting electrical conductivities were in the range of 10^2 S cm^{-1} to 10^4 S cm^{-1} while the absolute Seebeck coefficient reached values of up to 100 μV K^{-1}.[22] As the thermoelectric research on CNTs is a vast field, the reader is hereby referred to a very comprehensive review by Blackburn, *et al.*[103]

3. Thermoelectric generators

The construction of organic TEGs is an integral step towards the application of organic TE materials. Many considerations for organic TEG design originate from those of inorganic TEGs, but the solution processability of many organic materials allows for attaining unique thin film and conformal geometries over non-planar surfaces. Typical inorganic thermoelectric generators consist of many alternating p-type and n-type legs that are connected electrically in series and thermally in parallel through metallic interconnects. In commercial devices, significant engineering has gone into creating efficient heat exchangers in an effort to promote heat transfer from the heat source to the hot side of the TE materials, and similarly to facilitate removal from the cold side. The use of both p-type and n-type legs in tandem is used to help boost the output voltage across the full device. However, for efficient operation, this necessitates the use of n-type and p-type materials with similar properties. There are many open questions and challenges related to organic TEGs beyond the development of materials with good properties.

Practical engineering difficulties like making efficient electrical contacts still need to be overcome and pose challenges on a fundamental basis where the structure–property relationships have to be tackled, but also could lead to improvement in the performance of organic TE materials by engineering their interfaces.[74,104] For organic semiconductors, the engineering of contact materials for the efficient transfer of charge carriers without potential barriers has always been a technical challenge. Nevertheless, many optimised contact materials have been found in recent years, which can be adopted for thermoelectric devices based on organic TE materials. For instance, conducting paste based on metal particles such as silver are often being used for prototypical device screening, but might lead to pronounced contact resistances, thereby diminishing the voltage across a TEG and thus its output performance. As an alternative approach, charge carrier injection can be improved by colloidal carbon based paints yielding contact resistances in the range of a few Ohms only and being of technological relevance for printing techniques.[74] Alternative strategies rely on controlled surface doping by spatially restricted ion diffusion and might lower the charge carrier injection barriers and thus the macroscopic contact resistance.[105] Overall, optimization of metal/organic interfaces towards ohmic behaviour relates to the multifarious efforts on organic thin film electronics and will benefit by the achievements obtained in this field.

The biggest advantage of organic TEG design is their flexibility paired with the possibility of directly printing TE materials, as most of them are solution processable. These benefits have been directly translated into the development of TEGs with an emphasis on rolling or folding the materials once they have been solution processed onto flexible substrates. However, it is critical to note that the thermal and electronic properties of organic materials are intricately linked with their morphology, and the morphology is highly dependent on the substrate and processing conditions. Several proof-of-concept organic TEGs have been explored in the literature and will be presented in this section.

An ink-jet printing approach has been showcased by using a p-type ink consisting of the monomer EDOT with an oxidant solution containing a polymerization inhibitor and an n-type ink of crystalline TTF-TCNQ powder blended with poly(vinyl chloride) in toluene.[23] The principal fabrication process for this TEG is shown in Fig. 6a. A small molecule-based organic TEG was fabricated *via* thermal deposition of F_4TCNQ-covered pentacene (p-type) and Cs_2CO_3-covered C_{60} (n-type).[106] The thin film design for this TEG approach is shown in Fig. 6b. Another recent proof of principle for design of an organic TEG was achieved by large-area roll-to-roll printing of p-type PEDOT:PSS. Silver was applied as the n-type leg for this TEG and a total of 18 000 serially connected silver/PEDOT:PSS(1.2 μm)/silver junctions were stacked on a 60 μm PET foil.[107] Afterwards this structure was rolled up on an aluminium cylinder and demonstrated a different working principle for this TEG, as shown in Fig. 6c and d.

Many different design approaches for organic TEGs have been demonstrated for applications that emphasize the flexibility of organic TE materials. However, the variety of design strategies results in difficulties making comparisons between the different geometries. Standardization of the number of legs, the measurement temperature, and the applied thermal gradient across the different module designs would assist researchers in identifying what works well and where improvements can be made in TEG design. In addition, some metrics will become increasingly important as organic TEGs come closer to commercialization, such as reporting the power density per unit mass or the power density per unit area of the device.[108] Due to the emerging nature of organic TEGs, direct comparisons can be difficult. Nevertheless, organic TE materials with higher *ZT* values are needed to warrant the future broad scale application of organic TEGs. Furthermore, the change in TE properties of the materials prepared as inks proves further challenges but offers possibilities to further enhance the efficiency of such systems.

4. Conclusions and perspectives

Research on organic TE materials has made significant progress in the last decade and revealed remarkable *ZT* values of 0.42 at room temperature (p-type) and 0.20 at 440 K (n-type) for PEDOT:PSS[27] and the coordination polymer poly[K_x(Ni-ett)],[63,109] respectively. Such values are directly comparable to inorganic nanomaterials currently employed in window glasses for power generation *via* thermoelectricity.[110] Several families of organic materials such as conjugated polymers, coordination polymers, and small molecules hold high interest not only for thermoelectric research but also on a fundamental basis relating the electronic and structural properties, and thereby enabling additional strategies to further improve their performance. In addition, the interaction of organic and inorganic materials in hybrid compounds holds a high potential for the TE community both on a fundamental and application driven basis. Nevertheless, future applications require the development of more efficient organic materials and, especially, better suited n-type candidates have to be developed. One current and future trend is the combination of thermoelectric energy harvesting and battery technology, leading to the development of so-called electrochemical thermocells.[111,112] In many demonstrations semiconducting polymers and CNT/polymer composites play a very important role. For temperature gradients of 50 °C, power densities of larger than 10 W m^{-2} and efficiencies of 4% of the Carnot efficiency have been demonstrated.[111,113,114] Different approaches for the design of all-organic TEGs have been successfully prototyped and such devices were fabricated by printing technologies like screen-printing, ink-jet printing, and roll-to-roll printing. Besides obvious engineering challenges for implementation of those devices, research also has to focus on how the TE properties of organic materials change when prepared in the form of printable inks or regarding their environmental stability. With this, organic TE materials are to be considered as an emerging and promising field in need of cooperation by scientists from all backgrounds to enable their advance into future broad scale applications.

Conflicts of interest

There are no conflicts to declare.

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