MINIREVIEW

Boosting the performance of printed thermoelectric materials by inducing morphological anisotropy

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Thermoelectrics can generate electrical energy from waste heat and work also as active coolers. However, their widespread use is hindered by their poor efficiency, which is aggravated by their costly and hard-to-scale fabrication process. Good thermoelectric performances require materials with high (low) electrical (thermal) conductivity. Inducing morphological anisotropy at the nanoscale holds promise to boost thermoelectric performances, in both inorganic and organic materials, by increasing the ratio electrical/thermal conductivity along a selected direction without strongly affecting the Seebeck coefficient. Recent advances in 2D/3D printed electronics are revealing new simple and inexpensive routes to fabricate thermoelectrics with the necessary morphological control to boost performance by inducing anisotropy.

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Introduction

Thermoelectric (TE) materials are perfect candidates to recuperate part of the heat wasted in industrial/domestic environments, and from organic systems (such as the human skin), because they are capable of a one-step conversion of heat, flowing from a hot to a cold surface, into electrical energy. Thermoelectrics (TEs) are also capable of producing active cooling. The advantages of TEs are linked to their solid-state nature that offer unparalleled compactness, light weight and portability, as well as superior reliability and minimum maintenance due to the absence of any moving part or working fluids. The efficiency, η , of TE materials is a function of the difference in temperature between the hot and the cold surfaces, T_{cold} and T_{hot} , respectively, and the figure of merit zT . For harvesting, η is given by the following expression:¹

$$\eta = \left(1 - \frac{T_{\text{cold}}}{T_{\text{hot}}}\right) \frac{\sqrt{1+zT} - 1}{\sqrt{1+zT} + \frac{T_{\text{cold}}}{T_{\text{hot}}}}, \quad (1)$$

A similar expression exists for active cooling.² The figure of merit zT is defined as:

$$zT = \frac{\sigma S^2 T}{\kappa}, \quad (2)$$

where σ is the electrical conductivity, S is the Seebeck coefficient, κ is the thermal conductivity, and T is the absolute

temperature. $\kappa = \kappa_e + \kappa_{\text{ph}}$ is composed of the contribution to the heat transport from electrons and phonons (lattice contribution). The term σS^2 , known as the power factor (PF), is also often used to compare TE performances when κ cannot be obtained. These three factors, σ , S and κ , are interrelated. The electrical conductivity depends linearly on the charge carrier mobility, μ , and charge carrier concentration, n , as:

$$\sigma = qn\mu, \quad (3)$$

q being the elementary charge. According to Mott's formalism, the Seebeck coefficient depends on the charge carrier concentration and mobility as:^{1,3,4}

$$S = \frac{\pi^2 K_B^2}{3q} T \left[\frac{1}{\mu} \frac{\partial \mu}{\partial E} + \frac{1}{n} \frac{\partial n}{\partial E} \right]_{E_F}, \quad (4)$$

where K_B is the Boltzmann constant, and E_F is the Fermi energy. Therefore, S decreases with charge carrier concentration and mobility although the extent varies from material to material. It has been observed that the power relationship $S \propto \sigma^{-1/4}$ holds for semiconducting polymers upon doping. This relationship leads to a power factor that scales with electrical conductivity as $\text{PF} \propto \sigma^{1/2}$.^{5,6} In some cases, however, S seems to decrease with n but not with μ , as it will be described below.^{3,7–10} Regarding the thermal conductivity, both inorganic and organic materials with low electrical conductivity ($<1 \text{ S cm}^{-1}$) present mostly a contribution from the lattice, thus $\kappa \sim \kappa_{\text{ph}}$. For the rest of materials, the electronic contribution, κ_e , should be also taken into account. Indeed, for material with σ approaching 100 S cm^{-1} , κ_e becomes as impor-

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tant as κ_{ph} .¹¹ κ_e is linearly related to the electrical conductivity σ by the Wiedemann–Franz (W–F) law:

$$\kappa_e = L\sigma T, \quad (5)$$

where L is the Lorenz number, which adopts usually the Sommerfeld value of $\pi^2/3 (K_B/q)^2 = 2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$. Note that the W–F law with the Sommerfeld value does not always hold for conducting polymers because the transport is not only due to electrons or holes, but other particles such as solitons, polarons or bipolarons also play a role.^{12,13}

It has been stated that current TE devices can be attractive for practical applications, and be even competitive with other energy harvesting technologies if their zT is brought up to 1.5–2.^{14,15} Unfortunately, only few works have demonstrated such high figure of merit, and only for lab scale processes.^{16–19} However, those stringent requirements for performance are drawn on the basis of the unfavorable current standards for TE devices fabrication and device form factor. The traditional fabrication of TE devices involves material-wasteful steps like dicing blocks from p- and n-type material pellets,²⁰ as well as cost-inefficient and hard-to-scale steps such as assembling these blocks into modules and interconnecting them.^{21,22} On the other hand, current TE modules present a limiting form factor consisting of small and rigid devices composed of cuboid-shaped TE legs.²³ Thus, developing a more efficient fabrication process that enables broadening the design of TE modules will pave the way to the widespread of TEs even for modest performances.

Printing technologies can answer to the demands of TEs by allowing potentially low-cost, scalable, and large-area deposition and/or patterning of a myriad of materials, and on a wide range of substrates. The term “printing” is used here in its broad sense, as it refers to either 2D and 3D printing (or additive manufacturing). Printing includes ink-based techniques such as inkjet printing, screen printing, dispensing, fused deposition modelling (FDM) or direct ink writing (DIW); as well as light-based techniques such as stereolithography apparatus (SLA), selective laser melting (SLM, also known as laser powder bed fusion) or selective laser sintering (SLS). More details about the use of printing technologies to manufacture TEs can be found in three recent reviews by M. Orrill *et al.*,²¹ Y. Du *et al.*²³ and our group.²⁴

TE materials are often anisotropic, and as such, they display optimal performances in certain preferential directions. These preferential directions correspond to distinct morphologies at the nanoscale (shape, size and orientation of crystallites, phases, molecular aggregates, *etc.*) that are strongly affected by processing.

Thus, to leverage the usability of printing TEs, printing techniques must be capable of inducing controlled anisotropic morphology to maximize the performance of TE materials (see Fig. 1). While printed TEs have been usually focused on enabling inexpensive manufacturing routes and flexible devices,^{2,21,23–25} the relationship between printing process, morphology and performance has been largely overlooked in

Fig. 1 Representative examples of induced nanoscale morphology and transport anisotropy in both inorganic and organic TE materials by using printing fabrication techniques: (a) temperature gradient-driven grain orientation along the heat flow direction arises during the re-crystallization of selective laser melted TE materials. The enhancement of electronic and thermal transport along a certain direction is not equivalent, opening the door to zT optimization via controlled grain orientation. The example shown resembles the case of Bi_2Te_3 – based materials near room temperature. (b) Flow shear-induced alignment of organic TE molecules during direct ink writing (inspired by the alignment of high aspect ratio fillers reported in ref. 98). Analogous to the case of inorganic materials, transport is enhanced along a preferential direction, *i.e.* the molecule backbone, but intermolecular electron/hole scattering is less efficient than phonon scattering, resulting in a boost of the figure of merit zT . The example displayed resembles the case of the polymer PEDOT-based materials.

the field. Likewise, the appearance of novel performing materials does not come along with a description of feasible manufacturing techniques. Since anisotropy occurs in both inorganic and organic TE materials, reports gathering both material classes are relevant for the communities of advanced powder materials, organic electronics and engineers interested in the practical implementation of TEs. With the interest in hybrid TEs on the rise,²⁶ it is now more important than ever that those communities, which are usually distant, put their focus on common challenges to facilitate the widespread of TEs.

In this report, the effect of nanoscale morphological anisotropy on the electrical conductivity, thermal conductivity and Seebeck coefficient of both organic and inorganic TE materials will be reviewed. Recent works demonstrating printing of anisotropic TEs will be highlighted. Moreover, different existing strategies to measure TEs parameters along different directions will be mentioned. Finally, the future perspective of the field of printed TEs with controlled morphology will be commented.

Morphological anisotropy in inorganic thermoelectric materials: texture, grain size and porosity

Anisotropy in crystalline thermoelectric materials. Example for bismuth telluride

Although a wide range of inorganic materials displayed TE behaviour,^{27,28} bismuth telluride (Bi_2Te_3) – based materials (or BT materials) are by far the most popular inorganic TE materials due to their stability and reproducible high performance below 350 K. Indeed, most commercial TE devices, such as Peltier elements, are composed of BT materials. The BT single crystal bulk belongs to the $R\bar{3}m$ space group. It consists of groups of five parallel layers (a quintuple) formed by $\text{Te}^{(1)}\text{–Bi–Te}^{(2)}\text{–Bi–Te}^{(1)}$. In the unit cell, the plane containing these layers is the ab plane (associated to the $\langle 110 \rangle$ crystal direction) and the axis perpendicular to the layers is the c axis (coinciding with the $\langle 001 \rangle$ direction, see Fig. 1a). Whereas the bonding within the quintuple is covalent, there is a weak van der Waals bonding between the $\text{Te}^{(1)}$ planes of adjacent quintuples.²⁰ As a result, BT crystals cleave easily in between the $\text{Te}^{(1)}$ planes, giving rise to their platelet shape. It has been demonstrated that near room temperature, BT single crystals present superior electrical and thermal conductivity along the ab plane compared to the c axis (3–6 and ~ 2 times better, respectively), whereas the Seebeck coefficient is roughly isotropic. As a result, the figure of merit zT is 1.5 to 3 times higher along ab than along c .^{29–31} To quantify the degree of texturing, the orientation factor F has been used. F is calculated by integrating the intensity of some X-ray diffraction (XRD) specific peaks obtained along certain direction from textured samples, and comparing to a control isotropic sample of the same material.^{20,32}

Anisotropy in nanostructured inorganic thermoelectric materials

Polycrystalline bismuth telluride and alloys. Compared to single crystals, polycrystalline structures present the potential advantage of reducing the thermal conductivity along the ab plane, to a higher extent than the electrical conductivity (or power factor). This behaviour is a consequence of the fact that the multiple nanograin boundaries in polycrystalline materials scatter phonons more efficiently than electrons,³³ while keeping the Seebeck coefficient unaffected or even enhancing it by the low-energy charge carrier filtering effect.³⁴ As a result, the zT can be further boosted along ab in polycrystalline and textured materials. Within polycrystalline materials, the presence of small but mixed-size grains has been demonstrated beneficial to promote low electrical resistivity channels but effective scattering of phonons with different mean free path, while maintaining a similar S . Such mixed-grain size morphology lead to $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ samples with high zT of 1.4 at 340 K.³⁵ Moreover, compared to single crystals, polycrystalline materials display better mechanical properties.²⁰ Many researchers have focused their effort on different techniques to

obtain polycrystalline and textured BT materials. X. Yan *et al.* demonstrated the fabrication of n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ with average grain size of 1–2 μm . Upon orientation by hot pressing of the ab plane of the grains parallel to the substrate (Fig. 2a), they could achieve a $zT = 1.04$ along that direction (Fig. 2b).³⁶ (001)-Oriented (*i.e.* with the ab plane parallel to the measuring direction) $\text{Bi}_2\text{Te}_3/\text{Te}$ heterostructures have been fabricated by magnetron co-sputtering method. The heterostructure was beneficial to partially decouple S from σ by inducing low-energy carrier filtering and scattering at the interfaces. The authors could improve both parameters simultaneously by tuning the content of Te and achieved a power factor of 25 $\mu\text{W cm}^{-1} \text{K}^{-2}$.³⁷ Very recently, combined hot extrusion and spark plasma sintering (SPS) was used to control the texture of p-type $(\text{Bi}_{0.2}\text{Sb}_{0.8})_2\text{Te}_3$ alloys: hot extrusion produced fibre-like structures where the $\langle 110 \rangle$ direction of the grains aligned with the long axis of the fibres, whereas SPS of the stacked fibres produced (001)-oriented parts (Fig. 2c).³⁸ Being able to access both textures is essential to adapt the material design to the temperature range of the application. Whereas for n-type bismuth tellurium selenides the performance along the $\langle 110 \rangle$ is superior over a wide range of temperature (from room temperature to 500 K), the preferential direction for p-type bismuth antimony tellurides depends on the temperature: $\langle 110 \rangle$ direction is favourable near room temperature; in contrast, $\langle 001 \rangle$ is preferred at high temperature, where minimizing the thermal conductivity is more critical than maximizing electrical conductivity.^{38,39}

Superlattices. An exception to the advantages of the (001)-oriented materials for near room temperature can be found in p-type $\text{Bi}_2\text{Te}_3/\text{Sb}_2\text{Te}_3$ and n-type $\text{Bi}_2\text{Te}_3/\text{Bi}_2\text{Te}_{2.83}\text{Se}_{0.17}$ monolayer-range superlattices, which display enhanced carrier mobility in the through-plane direction. The figure of merit can benefit as well from a reduced through plane phonon contribution, κ_{ph} , leading to high values of $zT \sim 2.4$ and ~ 1.4 at 300 K for p-type and n-type superlattices, respectively.¹⁶ To measure the through-plane conductivity of such thin films, the authors adapted the transmission line model (TLM) technique. The Harman method, extended with variable-thickness approach, was used to measure zT directly. However, these superlattices are difficult to scale up and translate to an applicable device.

Nanowires. A different approach to produce TE films with oriented morphology and boosted (anisotropic) performance is nanowire alignment. In 2018, Y. Chen *et al.* described an original technique to manufacture ultrahigh power factor TEs on flexible substrates by uniaxial alignment of Co nanowires (NWs) embedded on a poly(vinylidene fluoride) (PVDF) matrix, using a magnetic field. The NWs/PVDF nanocomposite was deposited from solution and the NW long axis aligned with the direction of the magnetic field lines during the drying process (Fig. 2d). Compared to randomly oriented NWs, the electrical conductivity along the magnetic field direction improved from 5648 to 7141 S cm^{-1} whereas the Seebeck coefficient resulted nearly unchanged. As a result, the best power factor of oriented films reached a high value of 523 $\mu\text{W m}^{-1} \text{K}^{-2}$ at 320 K, among

Fig. 2 Morphological anisotropy in inorganic thermoelectric materials. (a) XRD patterns of hot pressed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ samples collected from the planes perpendicular and parallel to the press direction and the corresponding SEM images of their cross section. Reprinted with permission from ref. 36. Copyright (2010) American Chemical Society. (b) Figure of merit *versus* temperature of the pressed samples measured perpendicular and parallel to the press direction. Reprinted with permission from ref. 36. Copyright (2010) American Chemical Society. (c) Sketch representing the process combining hot extrusion and spark plasma sintering allowing the control of grain orientation. Reprinted with permission from ref. 38, Copyright (2020), with permission from Elsevier. (d) SEM images (top) of Co nanowires/PVDF nanocomposite and schematic illustration (bottom) of the electron transport in the nanowires when they are randomly oriented (left) and magnetically aligned (right). "N" and "S" stands for the north and south poles of the magnet, respectively. Reprinted with permission from ref. 40. Copyright (2018) John Wiley & Sons.

the highest reported values for TE nanocomposites.⁴⁰ Other NW-based TEs such as Te nanorods/PEDOT:PSS⁴¹ nanocomposite or pure BT-based NWs⁴² have been demonstrated by printing techniques (dispensing and inkjet printing, respectively). These materials achieved power factors of $284\ \mu\text{W m}^{-1}\text{K}^{-2}$ and $180\ \mu\text{W m}^{-1}\text{K}^{-2}$, respectively, at room temperature. However, the wires were isotropically oriented in plane. Consequently, the uniaxial anisotropy of the material was not tested.

Porous materials. Similar to grain boundaries in polycrystalline BT materials, porosity holds promise to increase TE performance by hindering thermal transport and sometimes enhancing the Seebeck coefficient. High zT has been reported for porous p-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ parts made by selective laser sintering of powders ($zT = 1.29$ near 325 K),⁴³ and for spark-plasma-sintered hollow n-type $\text{Bi}_2\text{Te}_{2.5}\text{Se}_{0.5}$ structures ($zT = 1.18$ at 463 K).⁴⁴ N-type Bi_2Te_3 nanoplates were prepared by molecular beam epitaxy with orientation of the *ab* plane parallel to the substrate and with controlled formation of nanopores. Although a large $zT > 1.2$ was estimated at 300 K, this value is probably underestimated because the authors could not measure directly the in-plane thermal conductivity.

Instead, they calculated it assuming that the anisotropic factors in these porous structures are the same as in single crystals with similar carrier concentration. This probably leads to an overestimation of the in-plane thermal conductivity.⁴

In summary nanostructuring *via* promoting polycrystallinity, growing superlattices, using nanowires or creating porosity is beneficial to increase the figure of merit zT of inorganic TE by decreasing the thermal conductivity more strongly than the power factor. Moreover, inducing anisotropy by texturing or nanowire alignment contributes further to the enhancement of zT . In particular, bismuth telluride-based materials present generally higher zT along the *ab* plane.

Printed anisotropic inorganic thermoelectric materials

Many studies have reported inorganic TE slurries/powders that can be printed by SLM/SLS,^{43,45,46} DIW^{47–49} or stereolithography⁵⁰ to form ingots. Furthermore, the same materials can be formulated as inks, which can be directly painted onto 3D objects^{51–53} or patterned on flexible substrates by inkjet

printing,^{42,54} aerosol jet printing,^{53,55,56} dispensing,⁵⁷ or screen printing^{52,58–64} to form shape-conformable and flexible devices. However, the combination of those printing techniques with the search of morphological anisotropy to improve the final performance has been largely overlooked. Only recently, some authors are using printing techniques to deposit and/or pattern BT materials while paying attention to the final texture of the printed material. In 2017, K. Wu *et al.* developed a process in which powder of the n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ TE material was dispersed in water with the help of a dispersant and binder agent, to form a slurry that could be nozzle-dispensed into thick films (see Fig. 3a).²² The films were subsequently patterned/sintered by SLM. The process was repeated by staking layers iteratively until 1.5 mm-thick parts were achieved. Contrary to the previous examples, the authors reported a strong ($hk0$) texture when probing with XRD the top of the final parts, which suggested that the SLM technique induced orientation of the ab plane along the building (stacking) direction. Although this orientation of the ab plane perpendicular to the substrate should be, in principle, beneficial for the performance of through-plane devices (at least near room temperature), the calculated value for zT was only 0.3, lower than in samples prepared using traditional techniques, such as zone melting (ZM) or self-propagating high-temperature synthesis (SHS). The reason is that for the calculation of zT , the authors measured both the electrical and thermal con-

ductivity along non-preferential directions: σ was measured in-plane, along the $\langle 001 \rangle$ direction, and κ through plane, across the ab plane. As a result, zT was greatly underestimated.²² SLM-induced (hkl) texture on n-type $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ was confirmed the same year by the same group, which also claimed that the rapid heating and cooling of SLM lead to fine nanostructure beneficial for TE performance (see Fig. 3b). This time, the authors calculated κ along the c axis based on the measured value along ab plane and the orientation factor F . κ along c was almost twice smaller than along ab . As a result, a high $zT = 0.84$ at 400 K was obtained in plane, *i.e.* along the c direction.⁶⁵ Although the performance along ab was not reported, it could be expected to be superior based on the discussion above in which we concluded that for textured polycrystalline materials, zT achieves usually its highest value along the ab direction. A similar work was reported later on, in 2019, by the same group for p-type $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ synthesized by combining for the first time the thermal explosion technique with SLM (Fig. 3c).²⁰ Strong (hkl) texture ($F = 0.9$, close to single crystal) was observed. The authors argued that the rapid heating and cooling of SLM-processed material led to a strong temperature gradient along the building direction, *i.e.* perpendicular to the substrate. The substrate acted as a heat sink, which resulted in a heat flow perpendicular to the substrate that promoted the growth of slender columnar grains with the ab plane oriented along the heat flow direction (see Fig. 1a).

Fig. 3 Morphological anisotropy in printed inorganic thermoelectric materials. (a) Sketch representing the dispensing process of a $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ – based slurry (top). SEM image of the optimized printed layer (bottom). Reprinted with permission from ref. 22. Copyright (2017) John Wiley & Sons. (b) XRD pattern of a SLM-printed $\text{Bi}_2\text{Te}_{2.7}\text{Se}_{0.3}$ part for the planes perpendicular and parallel to the stacking direction (left), and SEM images of the sample's cross section (right). Reproduced from ref. 65 with permission from The Royal Society of Chemistry. (c) Sketch of the printed process of $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ parts by SLM. Adapted from ref. 20 with permission from The Royal Society of Chemistry. (d) 3D reconstruction of the texture of the SLM-printed $\text{Bi}_{0.4}\text{Sb}_{1.6}\text{Te}_3$ parts obtained by FESEM. Adapted from ref. 20 with permission from The Royal Society of Chemistry.

This morphology was confirmed by XRD and field emission scanning electronic microscope (FESEM) as shown in Fig. 3d. As a consequence of this texture, the TE properties exhibited strong anisotropy. The electrical conductivity perpendicular to the substrate was more than three times higher than in the other directions, which suggests preferential charge carrier transport in the *ab* plane (without crossing the van der Waals layers of the crystal). Likewise, heat conducting phonons and charge carriers are also less scattered perpendicular to the substrate, leading to a higher thermal conductivity along this direction. However, the degree of anisotropy for thermal conductivity is lower than for electrical conductivity. Hence, the material displayed a higher $max\ zT = 1.1$ at 316 K in the trough-plane direction (compared to $zT = 0.65$ in plane at 326 K). This value is similar to that of single crystals of the same material but the polycrystalline nature of the SLM-printed sample rendered its mechanical properties superior to those of single crystals.²⁰

Printed textured materials integrated on flexible devices

A step forward to enable printed and flexible performing devices is the simultaneous deposition and patterning of oriented BT materials on flexible substrates reported by W. Hou *et al.*³² P-type $\text{Bi}_{0.5}\text{Sb}_{1.5}\text{Te}_3$ /epoxy flexible thick films were printed from slurries on polyimide substrates by brush-printing through a shadow mask. Then, hot-pressing curing (623 K and 4 MPa) processes achieved (001) preferential orientation, *i.e.* the *ab* plane was parallel to the substrate. The mechanism behind the orientation was the applied pressure under heat that caused the BT particles to rearrange along the (001) orientation, which is the plane with the minimum surface energy. Furthermore, fine BT particles were recrystallized and grown along the same plane. This morphology led to a 250% enhancement in the power factor (up to $840\ \mu\text{W m}^{-1}\text{K}^{-2}$ at 300 K) along the preferential direction, compared with non-hot-pressed films. The boost in power factor was due to an enhancement in mobility related to the crystal orientation and better inter-particle contact. Indeed, the electrical conductivity increased accordingly to the mobility but the charge carrier concentration, n , remained mostly constant (see eqn (3)). Despite the change in mobility, S was mostly unchanged upon hot-pressing curing.³²

Morphological anisotropy in organic thermoelectric materials: molecular orientation and crystallinity

The use in thermoelectrics of organic electronic materials is attracting increasing attention because they are abundant and inexpensive.^{66–69} (Semi)conducting polymers are mechanically flexible and normally non-toxic, rendering them perfect candidates for wearable applications such as smart textiles or electronic skin.²⁵ Moreover, organic electronic materials are easy to process from solution, making them potentially printable.

Indeed, most of the examples reviewed below to describe the positive effect of anisotropy on the performance of organic TE materials include solution-processed materials. However, the materials are not patterned or 3D shaped. Hence, those examples should not be included in the field of printed electronics.

Transport in organic electronic materials

Organic electronic materials are based on conjugated molecules (presenting alternating single and multiple bonds) that often include aromatic groups (planar conjugated cyclic molecules). These molecules possess overlapping p orbitals, forming π bonds, where electrons are delocalized. This situation leads to high intramolecular charge carrier mobility. Moreover, the van der Waals interaction between the π orbital of adjacent molecules results in their packing into stacked arrangements (lamellae) conforming crystallites (Fig. 4). This phenomenon is called the π - π stacking and facilitates the electron (or hole) hopping between adjacent molecules. This combination of intramolecular (within the backbone of a single molecule) and intermolecular (along the π - π stacking direction) charge transport is responsible for the long-range charge transport in semicrystalline electronic polymers. In those semicrystalline materials, the charge transport is efficient within crystalline domains, but it is hindered in the disordered regions, where connectivity between crystallites becomes paramount. Long tie chains bridging through the amorphous grain boundary regions are responsible for the connectivity between crystalline aggregates (Fig. 4a). Hence, even a relatively low amount of high molecular weight material providing sufficient connectivity may have a strong positive impact in the final mobility.^{11,70} Indeed, it has been suggested that in order to achieve high mesoscale mobility, it is preferable to promote good connectivity than to increase the overall crystallinity.^{70–72} The reason is that the mean free path of electrons in the π - π stacking direction is in the order of a nanometre.⁷¹ Therefore, seeking higher crystallinity by means of having large crystallites (larger than a nanometre) do not offer extra transport advantages. Moreover, because intramolecular charge trans-

Fig. 4 Sketches representing typical molecular arrangements in electronic polymers. (a) Tie chains connecting crystalline polymer lamellae. Adapted from ref. 11 with permission from The Royal Society of Chemistry. (b) Representation of face-on and edge-on orientation of the polymer conjugated backbone relative to the substrate. Adapted from ref. 11 with permission from The Royal Society of Chemistry.

port within straight molecules is more efficient than inter-molecular transport, promoting molecular alignment is usually a more effective knob to boost mobility than enhancing crystallinity (note that the previous statement is normally true given that a minimum of degree of local aggregation and connectivity by high molecular weight polymer is present in the material^{72–74}). Such particular transport mechanism leads to charge transport anisotropy in conducting polymers with molecular alignment. Since there is a linear relationship between mobility and electrical conductivity (see eqn (3)), the previous discussion for mobility holds also for electrical conductivity. Similar to electrical conductivity, the thermal conductivity of semicrystalline polymers increases usually with both the degree of crystallinity and the molecular orientation. The later promotes also anisotropy.⁷⁵

The directional electrical conductivity of aligned electronic polymers has been studied mostly in the context of organic field effect transistors (OFETs), where molecular alignment led to enhancement of mobility by few folds in the direction of the aligned polymer chains.^{73,76–78} The relevant literature is more scarce for TEs where the three interrelated parameters that affect the figure of merit (σ , κ and S , see eqn (2)) must be taken into account.

PEDOT polymer as case study

Poly(3,4-ethylenedioxythiophene) (PEDOT) is one of the most popular and performing thermoelectric polymer.^{79–81} When blended with poly(styrenesulfonate) (PSS), which acts as an oxidative dopant, PEDOT:PSS displays a high electrical conductivity and becomes soluble in water. A. Mantovani Nardes *et al.* observed that PEDOT:PSS arranges in-plane as pancake-shaped PEDOT-rich domains separated by lamellae of amorphous and electrically insulating PSS. As a consequence of the insulating nature of the PSS, the electrical conductivity through plane was found to be up to three orders of magnitude lower than in plane.⁸² In the previous work, the authors deposited the material by spin coating. As a result, the material was isotropic in plane. The value of in-plane conductivity was low ($\sigma \sim 10^{-4} \text{ S cm}^{-1}$). Much higher conductivities ($500\text{--}2000 \text{ S cm}^{-1}$) can be achieved by adding polar solvents in the PEDOT:PSS solution, or by treating a solid film with those polar solvents, namely methanol, dimethyl sulfoxide (DMSO) or ethylene glycol (EG). These agents, referred to as secondary dopants, can enhance the conductivity by modifying the nanostructure, without increasing the charge carrier concentration. They can also serve to remove the excess of PSS.^{6,11,83}

The anisotropic nature of PEDOT:PSS is also manifested in the thermal conductivity. Higher thermal conductivity has been reported along the in-plane directions compared to the through-plane direction: $0.84 \text{ W m}^{-1} \text{ K}^{-1}$ versus $0.15 \text{ W m}^{-1} \text{ K}^{-1}$, respectively (see Fig. 5a and c).⁸⁴ These values were measured from free-standing samples of thickness $\sim 100 \mu\text{m}$, by the flash analysis method. This method is readily applicable for through-plane measurement of thermal diffusivity. For in-plane measurement, an original sample preparation was

Fig. 5 Anisotropic performance of PEDOT:PSS. (a) Sketch showing the directions of preferential and non-preferential transport in PEDOT:PSS. The blue and yellow lines represent PEDOT chains (oriented in plane) and PSS, respectively. (b) Sketch representing the sample preparation for thermal conductivity measurements in the in-plane direction using the flash analysis method (conceived for through-plane measurements of disks-shaped samples). Freestanding films were cut into ribbons, which were subsequently tightly rolled into a disk. (c) TE parameters vs. temperature measured in plane (||) and through plane (⊥) (note that the thermal diffusivity and the thermal conductivity, κ , are linearly related according to the equation $\kappa = \text{density} \times \text{specific heat capacity} \times \text{diffusivity}$). All the panels are adapted with permission from ref. 84. Copyright 2014 American Chemical Society.

described: it consisted on shredding the free-standing film into ribbons that were subsequently tightly rolled into a disk (Fig. 5b). The reason for a larger in-plane thermal conductivity (diffusivity) was attributed to a larger lattice contribution, κ_{ph} , to the total thermal conductivity from the polymer backbone aligned parallel to the substrate, compared to the numerous PSS amorphous domains existing along the through-plane direction. The electrical conductivity was also higher in plane than through plane (measured with a dedicated 4-wires setup), but the difference was much more remarkable than for the thermal conductivity (around an order of magnitude lower through plane than in plane, $<100 \text{ S cm}^{-1}$ and $\sim 1000 \text{ S cm}^{-1}$, respectively).⁸⁴ Since no difference was observed in the Seebeck coefficient (Fig. 5c), it can be concluded from eqn (2), that the in-plane direction yielded the best performance. This result seems to suggest that aligning the polymer backbone along the thermal gradient would be preferable to maximize the performance of thermoelectric modules.

Conflicting degrees of thermal conductivity anisotropy has been reported for PEDOT-based materials. The ratio between in-plane and through-plane thermal conductivity was 5.6 in the previous example.⁸⁴ However, an earlier anisotropy ratio of 1.1 was reported in 2011 for PEDOT doped with tosylate (PEDOT:Tos). The in-plane thermal conductivity was $0.37 \text{ W m}^{-1} \text{ K}^{-1}$ for a $\sigma \sim 100 \text{ S cm}^{-1}$ and a $S > 200 \mu\text{V K}^{-1}$,

leading to a high $zT = 0.25$.⁷⁹ Later on, in 2013, the anisotropy ratio in thermal conductivity for PEDOT:PSS mixed with DMSO was reported to be 1.4. The in-plane thermal conductivity was $\sim 0.34 \text{ W m}^{-1} \text{ K}^{-1}$ for a $\sigma \sim 900 \text{ S cm}^{-1}$ and a $S > 70 \text{ } \mu\text{V K}^{-1}$, which lead for a record high $zT = 0.42$.⁸⁵ In the previous cases, the samples were prepared from solution by spin coating and the thermal conductivity was measured with the 3-omega technique, adapted for in-plane measurements. This technique introduces certain level of uncertainty because it requires converting the directly measured through-plane thermal conductivity into in-plane conductivity by comparing the heat transport from wide and narrow heaters deposited on the sample, and by applying a model fitting. Other assumptions were made such as the fact that doping (or oxidation state) does not affect thermal conductivity or the anisotropy ratio. Those assumptions justified the use of differently processed samples to measure power factor and thermal conductivity.

Further considerations regarding thermal conductivity: lack of agreement in the W-F law. In the previous works,^{79,85} the relationship between σ and κ_e given by the W-F law (for the Lorenz number taking the Sommerfeld value, see eqn (5)), was underemphasized. That means that the electronic contribution to the thermal conductivity seemed to be lower than for inorganic electronic materials. Other later work published in 2015 reported the opposite behaviour for a similar PEDOT-based system, *i.e.* an increase of κ_e with σ stronger than the predicted by the W-F law in eqn (5).¹² While the authors admitted that the doping (responsible for the increase in σ) could affect also κ_{ph} , they put the emphasis in the hypothetical contribution of phonon-assisted hopping and bipolarons to κ_e . Those contributions would result in a Lorenz number above the Sommerfeld value, and explain the abnormal fast rise of κ with σ . The total thermal conductivity κ achieved displayed a high value of $1.8 \text{ W m}^{-1} \text{ K}^{-1}$ for a moderate $\sigma \approx 500 \text{ S cm}^{-1}$. Finally, the same year J. Liu *et al.* found a good match between the behaviour of drop-casted PEDOT:PSS mixed with DMSO and the W-F law with the Sommerfeld value.⁸⁶ The in-plane to through-plane thermal conductivity ratio was larger than 3 ($\kappa_{\text{in-plane}} \approx 1.0 \text{ W m}^{-1} \text{ K}^{-1}$ and $\kappa_{\text{through-plane}} \approx 0.3 \text{ W m}^{-1} \text{ K}^{-1}$) when the in-plane electrical conductivity was high ($\sigma \approx 500 \text{ S cm}^{-1}$).

In summary, in-plane molecular alignment is beneficial to enhance the figure of merit zT (in plane) of PEDOT (and probably other organic TE materials) because σ increases with alignment more significantly than κ , while S is barely affected. This is because the increase in σ occurs *via* an alignment-induced increase in mobility instead of an increase in charge carrier density, which is more detrimental for S . Moreover, the lack of agreement in the relationship between σ and κ reflects the strong influence that morphology has in the electronic transport of organic electronic materials, as well as the existing gaps in our current understanding of such transport. Developing further our insight into these relationships will open the door to boosting the performance organic TE materials.

The empirical relationship between S and σ and the role of crystallinity

The power relationship $S \propto \sigma^{-1/4}$ (or $\text{PF} \propto \sigma^{1/2}$) usually holds for doped organic semiconductors.⁵ However, this relationship can be challenged when the electrical conductivity is enhanced through molecular organization (instead of doping) as demonstrated by O. Bubnova *et al.* for PEDOT:Tos.⁹ Upon crystallinity increase, the material transitioned from a Fermi glass to a semi-metal based on a bipolaron network, and both σ and S increased. This approach opened the door to achieving a PF that scales with σ faster than $\text{PF} \propto \sigma^{1/2}$, presenting an enormous opportunity in the advancement of organic thermoelectrics. I. Petsagkourakis *et al.* demonstrated that by increasing the molecular weight of PEDOT, and by using additives such as EG, dimethylformamide (DMF) and DMSO, the crystallinity of spin-coated PEDOT:Tos increased. Consequently, the density of states (DoS) was modified in such a way that it benefited both μ and S . A transition from a quasi-1D to a 2D hopping transport was observed for long chains, but the charge carrier concentration was not affected.^{3,10} As a result of a higher S and σ (related to μ by eqn (3)), the authors reported an enhancement of the power factor from 25 to $78.5 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$.¹⁰ Later on, the same group derived the following power law relationship between S and charge carrier mobility, μ : $S \propto \mu^{0.2}$.³ In 2019, D. Ju *et al.* reported a high $\text{PF} = 700.2 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ and $zT = 0.25$ in spin-coated PEDOT:PSS.⁶ That was achieved *via* doping with the small-molecule anionic dopants, sodium alkyl sulfonates (C(N)^-). The optimization of dopants size lead to an effective reduction of the electrostatic interaction between PEDOT and PSS, which modified the material film morphology: the PEDOT-rich domains evolved from the typical pancake-shapes to nanofibers that provided improved connectivity of the carrier pathways (Fig. 6a). The crystallinity of the material increased by planarization of the PEDOT chains, which promoted π - π intrachain transfer. Similar to the previous examples, where a deviation from the typical trade-off relationship between S and σ was observed, the increase in σ was associated to an increase in mobility; in this case, possibly by releasing tightly bound states between holes in PEDOT and PSS anions when weakening the electrostatic interaction between both materials. Indeed, the oxidation level of PEDOT was decreased with this alternative dopant compared to the initial PEDOT:PSS system, *i.e.* the material was less doped. This was reflected positively in the value of S , which is negatively correlated to the charge carrier concentration, n (see eqn (4)). This reduction of the carrier concentration had also a positive impact in the in-plane thermal conductivity, which decreased from $1.46 \text{ W m}^{-1} \text{ K}^{-1}$ for the standard PEDOT:PSS to $0.85 \text{ W m}^{-1} \text{ K}^{-1}$ for the doped version, presumably due to a reduction of the electronic component κ_e .

Besides PEDOT-based materials, performances exceeding the empirical power relationship $S \propto \sigma^{-1/4}$ (or $\text{PF} \propto \sigma^{1/2}$) have been reported for solution-casted poly(3-hexylthiophene) (P3HT) films, vapor doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetra-

Fig. 6 Implications of morphology in the TE performance of PEDOT-based materials. (a) Sketch representing the change in morphology in PEDOT:PSS upon decreasing the electrostatic interaction between PEDOT and PSS by introducing C(N)⁻ dopants. Reprinted with permission from ref. 6. Copyright (2019) John Wiley & Sons. (b) Simulated figure of merit, zT , versus crystallinity, X_c , for uniaxial-aligned PEDOT fibres with two different values of molecular weight. (c) Graphical representation of the effect of uniaxial alignment and crystallinity in the transport. (d) Sketch representing the typical scattering events for phonons and charge carriers in a crystallite. Panels (b)–(d) reprinted with permission from ref. 88. Copyright (2017) John Wiley & Sons.

cyanquinodimethane (F4TCNQ) molecules. The doping promoted crystallinity and long-range molecular connectivity which markedly increased σ (dominated by an enhanced mobility) without strongly degrading S . As a result, a power factor $\sim 11 \mu W m^{-1} K^{-2}$ was achieved.⁸⁷

The effect of uniaxial molecular alignment and crystallinity on TE performance

Examples for PEDOT. Uniaxial molecular alignment can be a powerful tool to enhance further the figure of merit of organic thermoelectrics. Although not intended for TE applications, an electrical conductivity value as high as $4600 S cm^{-1}$ was measured for PEDOT:PSS along the preferential direction for uniaxial-aligned thin films produced by solution shearing.⁸³ Related to TEs, W. Shi *et al.* simulated the thermal behaviour of uniaxially chain-oriented PEDOT fibres and found an interesting relationship between thermal conductivity, crystallinity and chain length.⁸⁸ They concluded that as long as uniaxial alignment is maintained, reducing the crystallinity from $X_c \sim 0.9$ to 0.5, and the relative molecular weight from 14 000 to 5600, resulted in a reduction of the axial lattice thermal conductivity, κ_{ph} , from 6.66 to $0.97 W m^{-1} K^{-1}$. Meanwhile, the charge transport properties were not degraded. Because of this situation, an enhanced simulated value of zT up to 0.48 at

298 K was reported (Fig. 6b). The authors argued that the mean free path (MFP) of phonons is longer than that of charge carriers. Therefore, by tailoring the length of the oriented molecules (or the size of the crystallites) to be longer than the charge carriers MFP but shorter than the phonons MFP, higher boundary scattering will occur for phonons. Thus, thermal transport will be suppressed more efficiently than charge carrier transport (Fig. 6c and d). A suitable chain length to achieve that goal would be between 13.2 Å and 479 Å. Crystallinity affects this balance.

Examples for P3HT. P3HT has also displayed anisotropic thermoelectric properties. In particular, M. Muñoz Rojo *et al.* reported that the thermal conductivity across the long axis of P3HT nanowires (NWs) decreased from $2.29 W K^{-1} m^{-1}$ to $0.5 W K^{-1} m^{-1}$, as the wire diameter shrank from 350 nm to 120 nm. This behaviour was attributed to the change in crystal orientation, which was observed with wide-angle X-ray scattering (WAXS, see Fig. 7a). In particular, as the wire diameter decreased, the P3HT molecules arrangement transitioned from having the π - π stacking direction, $\langle 010 \rangle$, oriented along the NW long axis, to having it perpendicular to the long axis. The molecules backbone was always oriented perpendicular to the NW long axis. The thermal transport is efficient along the covalent bonds in the backbone direction and along the

Fig. 7 Uniaxial alignment of P3HT. (a) WAXS diffractograms of P3HT NWs with different diameter (in decreasing order from top to bottom) probed on the planes parallel and perpendicular to the nanowire long axis. Adapted from ref. 75 with permission from The Royal Society of Chemistry. (b) Representation of the possible change in molecular arrangement as the NW diameter shrinks (from left to right). Adapted from ref. 75 with permission from The Royal Society of Chemistry. (c) Sketch of the 2-steps fabrication method of uniaxial-aligned P3HT crystalline films. (d) Cross-polarized optical microscope images of a film indicating molecular alignment and crystallinity (the orientations of the polarizer and analyser are represented by the double arrows). (e) Polarized UV-vis-IR and FTIR spectra of a film indicating molecular alignment. Panels (c)–(e) reprinted with permission from ref. 7. Copyright (2017) John Wiley & Sons.

compact π - π stacking direction. Since both directions were perpendicular to the long axis as the wire diameter shrank (Fig. 7b), the thermal conductivity was the lowest in the smallest nanowires.⁷⁵ Uniaxial alignment in spin-coated films of doped P3HT was also achieved by high-temperature rubbing (Fig. 7c). The films were doped afterwards with F₄TCNQ⁻ anions, which arranged with their long molecular axis perpendicular to the polymer backbone.⁷ According to the study performed using transmission electron microscopy (TEM) and UV-vis-NIR spectroscopy, the films displayed the typical lamellae structure alternating crystalline domains and amorphous domains. The dopant did not alter this structure but increased the periodic distance along the side chain from 16.6 Å to 18.0 Å and the π - π distance from 3.75 Å to 3.55 Å. As expected from the rubbing-induced uniaxial molecular alignment (Fig. 7d and e), in-plane anisotropy was found in the thermoelectric properties. The highest values for electrical conductivity, σ , and Seebeck coefficient, S , were found in the rubbing direction: $\sigma = 22 \text{ S cm}^{-1}$ and $S \sim 60 \text{ } \mu\text{V K}^{-1}$, respectively. Compared to non-oriented films, σ and S increased up to 4 and 2-fold, respectively. Furthermore, whereas σ depended strongly on the dopant concentration, S was almost insensitive, which suggests that the dopants improved σ mostly *via* modifying the morphology, which in turns boosted the mobility, rather than *via* modifying the charge carrier concentration (see eqn (3)). Those improvements led to a high power factor $\text{PF} =$

$8.5 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$ along the rubbing direction. Uniaxial alignment of P3HT has been also demonstrated by tensile drawing of self-standing thick films.⁸ Upon doping the aligned films with a molybdenum tris(dithiolene) complex, the power factor was boosted by 5-fold, reaching a value of $\text{PF} = 16 \text{ } \mu\text{W m}^{-1} \text{ K}^{-2}$. This improvement resulted from a boost in the value (and anisotropy) of electrical conductivity, which reached a high value of $\sigma = 13 \text{ S cm}^{-1}$ parallel to the alignment direction (drawing direction), with an anisotropy of $\sigma_{\text{parallel}}/\sigma_{\text{perpendicular}} \sim 8$. On the contrary, the Seebeck coefficient was barely impacted by the tensile drawing. Interestingly, the authors related the changes in morphology with the mechanical properties of the films too. They hypothesized that the dopants contributed to stiffening the polymer chains, increasing the glass transition temperature and leading to a more brittle material.

Uniaxial alignment involves an extra degree of order (and anisotropy) compared to in-plane alignment. As such it is not surprising that it can surpass the advantages of in-plane alignment in terms of enhancing TE performance. When dealing with well-oriented organic materials, crystallinity becomes an important factor due to the facilitated transport occurring through the π - π stacking direction, which can become comparable with the transport along the backbone direction. From the articles reviewed in here, it can be extracted that low crystallinity and uniaxial alignment seems to be the best configuration to maximize zT due to an optimized balance between σ

and κ . Moreover, the length of the polymer molecules or the size of the oriented crystallites must be adjusted to lie in between the mean free path of electrons and phonons, in order to promote the scattering of the latter more efficiently than the former.

The effect of edge-on vs. face-on structure on TE performance

The disposition of conjugated molecules relative to the substrate (face-on or edge-on, Fig. 4b) plays an important role in TE performances. A significant enhancement in electrical conductivity (from 0.2 to 1200 S cm⁻¹) for slot-die-printed PEDOT:PSS coincided with an increase of the edge-on orientation and larger crystallites upon post-treatment with EG.⁸⁹ Another approach to induce edge-on orientation is molecular engineering. In 2018, J. Liu *et al.* reported that the power factor of n-type donor-acceptor copolymers was enhanced by a factor of >1000, up to a PF = 4.5 $\mu\text{W m}^{-1} \text{K}^{-2}$, by tailoring the density of states through molecular design. This strategy led to higher molecular planarity along with a transition from a face-on-dominated morphology to a preferential edge-on one.⁹⁰ More recently, an improvement in power factor from PF ~ 10 to 19 $\mu\text{W m}^{-1} \text{K}^{-2}$ was obtained by modifying the side chain of doped regioregular spin-coated P3HT. The boost in PF was correlated with a change in the polymer backbone orientation, from a face-on to a dominant edge-on orientation, along with a higher crystallinity and a closer π - π staking distance.

All the previous examples suggest the existence of a correlation between edge-on orientation, enhanced crystallinity and a boosting of the power factor. Nevertheless, the implications of face-on vs. edge-on in the thermal transport were not reported. Furthermore, a deeper understanding of that relationship is still needed.

Conclusions and perspectives

As discussed in this minireview, the performance of TE materials is closely related to their morphology, which in turns depends on their processing method. Given that most TE applications involved the presence of a unidirectional thermal gradient, it seems reasonable to seek TE materials with an optimized uniaxial preferential direction. Such implication of morphology in performance must be taken into account in the design of TE modules too. Indeed, the performance of typical π -type thermoelectric devices is determined by the through-plane TE properties of the used material, whereas that of planar modules is determined by the in-plane thermoelectric properties (Fig. 8a). It seems thus obvious the importance of closing the existing gap between research on material design and device engineering: the former unveils record-performing materials, but does not provide guidance for their integration in working devices; whereas the latter demonstrates original implementations that even exploits printing techniques on flexible substrates²⁴ and alternative suitable sintering methods (such as photonic or electrical),^{64,91} but neglects largely the relationship morphology-performance. This mismatch

Fig. 8 (a) Sketch of the two main configurations of TE modules: the vertical π -type design for through-plane operation (top) and the planar design for in-plane operation (bottom). Adapted from ref. 11 with permission from The Royal Society of Chemistry. (b) Graphical description of the ERC-2020-STG project 3DALIGN, which aims at 3D printing of organic TE materials with enhanced performance via uniaxial molecular alignment. The alignment results from the combination of shear stress pre-alignment during printing and electric field assisted molecular alignment.

arises from the discipline distance between both research communities.

It is also worth mentioning that only few TE materials have been studied in detail with respect to the relationship anisotropy-performance: BT-based materials are predominant for inorganics, and PEDOT and P3HT for organics. This fact indicates that the field is still in its infancy and plenty of opportunities lie ahead. On top of that, most of the materials described to date were processed using techniques that are hard to scale up and do not allow neither selective deposition nor patterning, which is of paramount importance to the subsequent development of functional TE modules. These techniques are spin-coating, drop-coating or solution casting for organic materials; and spark plasma sintering, zone melting or hot pressing for inorganic materials. Hence, we are lacking holistic approaches that bridge material morphological control with a viable industrial device fabrication route, such as printing. Indeed, the field of inorganic TE has barely started to demonstrate examples of printed uniaxial aligned materials. Few recent examples reviewed here reported laser-printed of textured BT materials (see Fig. 3).^{20,22,65} Those examples could be just considered as “the tip of the iceberg” since they use printing only to form bulk parts that must be then diced and assembled into a TE module using the traditional techniques. Only one reviewed work reported on an innovative technique for printing directly textured inorganic materials into a flexible planar device.³² No printed vertical π -type devices have been demonstrated yet. Regarding organic materials, plenty of work has been done on printed devices by screen printing,⁹² inkjet printing,^{79,93–95} aerosol jet printing⁵⁶ or dispensing⁹⁶ but none of them considered molecular alignment as a tool to improve the TE performance.

Tightening up the relationship morphology-device design will open the door to a new class of TEs where the material and device must be designed in unison to adapt to specific applications. As an example, by creating TE legs with controlled graded-phase materials, one could select at each space

point of the leg the most favourable material for the foreseen operating temperature. This has been done for material composition,^{47,56} but not for texture: for instance, for a p-type BT material, it would be advantageous to orient the $\langle 110 \rangle$ crystal direction along the thermal gradient for the sections of the leg closer to the cold side of the module. This is because $\langle 110 \rangle$ shows the best performance around room temperature. On the contrary, the texture should gradually shift to $\langle 001 \rangle$ parallel to the thermal gradient as we get closer to the hot side, since $\langle 001 \rangle$ is preferable above 450 K.^{38,39}

The examples reviewed earlier suggest the goodness of inducing morphological anisotropy in organic thermoelectric. In the cases of uniaxial alignment mentioned above for P3HT,^{7,8} S did not degrade with the increase of σ , as usually predicted by the power law relationship $S \propto \sigma^{-1/4}$. This behavior suggests that the combination of uniaxial alignment with the right dopant contributes to improve the electrical conductivity along the alignment direction not by increasing charge carrier density, but by boosting the mobility *via* molecular alignment (see eqn (3)). This situation resembles the examples mentioned for PEDOT:Tos where S and σ also increased simultaneously,^{3,9,10} suggesting a certain material agnosticism for the benefits of uniaxial alignment in the performance of organic TEs.

Despite these evidences, the number of printed organic TE materials with molecular alignment are scarce. This scenario is surprising when considering that one of the strong claims of organic TE materials is its superior solution processability (compared to their inorganic counterparts) and higher potential for inexpensive fabrication routes of flexible and large-area devices.²¹ This lack of the field motivated the funding of the project 3DALIGN: enhancing the performance of 3D-printed organic thermoelectrics by electric field-assisted molecular alignment (European Research Council, Horizon 2020, starting grant, agreement no. 948922), which has been granted this year to my research group. 3DALIGN aims at developing performing organic TE materials by inducing uniaxial molecular alignment while defining a clear line of sight for feasible production of TE modules *via* printing (see Fig. 8b). The alignment will be achieved by using shear stress and externally applied electric fields^{77,97} in solution-processed polymers. The use of 3D-printing will enable a versatile fabrication route for vertical π -type TE structures that will lead to novel applications.

Conflicts of interest

There are no conflicts to declare.

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