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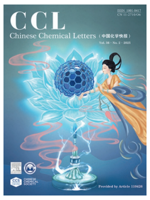

Editorial

“Super-heterojunctioned” thermoelectric polymers

Given the increasing demand for distributed electricity, there is a burning desire to harvest electricity from renewable sources using environmentally friendly methods. Thermoelectric (TE) materials can meet this requirement not only because of their ability to convert heat directly into electricity, enabling energy harvesting from waste heat and natural heat resources, but also because more than 60% of the energy is lost as waste heat [1]. The discovery of the TE effect dates back to the 1820s when T. M. Seebeck observed electricity generation at the junction of two conductors with different temperatures. Additionally, when a voltage is applied to TE materials, they can create a temperature difference to enable solid-state cooling (known as the Peltier effect). Therefore, the TE effect promises both sustainable energy solutions and temperature control technologies. Over the past two decades, the urgent demand for powering ubiquitous Internet of Things devices has sparked significant interest in flexible thermoelectrics (F-TEs), which raises an intriguing question: Is the intrinsically flexible polymer an important candidate for state-of-the-art F-TEs applications?

The efficiency of thermoelectric conversion is characterized by the dimensionless figure of merit, $ZT = S^2\sigma T/\kappa$, where S is the Seebeck coefficient, σ is the electrical conductivity, κ is the thermal conductivity, and T is the absolute temperature. The investigation on organic thermoelectrics began several decades ago, initially using the S to understand the charge transport behavior. By the 2010s, notable progress was made with poly(3,4-ethylenedioxythiophene) (PEDOT)-based p-type and poly[Kx(Ni-ett)]-based n-type thermoelectric materials, achieving ZT values in the range of 0.1 to 0.5 [2–4], while offering good flexibility, lightweight properties, and large-area coating capabilities. Since then, the performance improvement of polymer thermoelectric materials has been limited. Therefore, achieving a ZT greater than 1.0 to match the performance of commercial thermoelectric materials remains a long-sought goal for plastic thermoelectrics.

In order to maximize ZT values, the ideal TE materials should exhibit a high Seebeck coefficient, high electrical conductivity, and low thermal conductivity, conforming to the "phonon-glass, electron-crystal" model. Generally, most polymers exhibit a phonon glass feature, theoretically allowing them to naturally display low thermal conductivity. Therefore, efforts have been made to regulate the Seebeck coefficient, electrical conductivity, and their trade-off relationships through molecular design, assembly, and doping. However, many high-mobility polymer films contain crystalline regions with ordered molecular packing, which significantly differ from the ideal "phonon glass" model. This discrepancy hinders the enhancement of the thermoelectric figure-of-merit for polymers.

In a recent work, Dongyang Wang, Chong-an Di, and their collaborators utilized a "brick-laying" molecular assembly method to create a periodic nanostructure named "Polymeric Multi-Heterojunction (PMHJ)" to boost thermoelectric performance [5]. In the PMHJ, two distinct polymer layers serve as individual bricks, while the mixed interface layer binds the two polymer layers. Notably, the thickness of each polymer layer is precisely controlled to be less than 10 nm, with the interface layer maintained at about 4 nm, which corresponds to approximately two molecular layers. This nanoscale confined structure not only ensures efficient in-plane charge transport but, more importantly, significantly enhances phonon scattering to reduce its in-plane thermal conductivity. Compared to traditional polymer films, this structure better approximates the "phonon glass-electron crystal" and thus might trigger significant enhancement in TE performance.

The research team constructed PMHJ films using two polymers, PDPPSe-12 and PBTTT, combined with molecular cross-linking methods. They revealed the size effect and interfacial diffuse scattering effect on thermal conductivity, finding that when each polymer layer’s thickness approaches the "phonon" mean free path of the conjugated backbone, interfacial scattering significantly enhances, reducing the in-plane lattice thermal conductivity by over 70% to $0.1\ \mathrm{W\ m^{-1}\ K^{-1}}$. Additionally, the doped (6,4,4) PMHJ film exhibits excellent electrical transport properties, with a power factor of up to $628\ \mathrm{\mu W\ m^{-1}\ K^{-2}}$ and a thermoelectric figure-of-merit of 1.28 at 368 K, matching the performance level of commercial materials at room temperature. This breakthrough marks the era of $ZT > 1.0$ for plastic-based thermoelectric materials. Moreover, the PMHJ structure also boasts excellent universality, with processing methods compatible with solution-based preparation techniques, showing significant potential in flexible energy devices (Fig 1).

Although different from the ideal superlattice, the PMHJ still allows charges to pass unhindered while preventing heat transfer, effectively functioning as a “super-heterojunction” plastic. This research presents a breakthrough for flexible thermoelectrics and opens up a new direction for developing state-of-the-art thermo-

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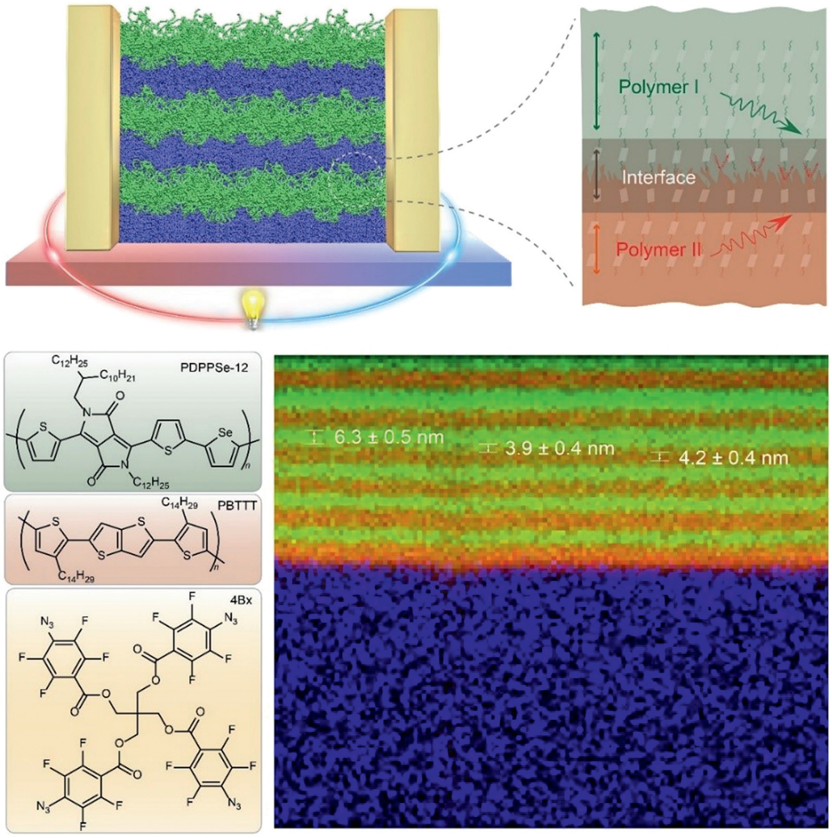

Fig. 1. Illustration of the concept and TOF-SIMS result of PDPPSe-12:PBTTT PMHJ film. The PDPPSe-12 and PBTTT layers are depicted in blue and green, respectively. The colon in PDPPSe-12:PBTTT stands for a sequentially processed periodic film. PDPPSe-12 and PBTTT were photocrosslinked by a four-armed azide-based crosslinker. The TOF-SIMS cross-sectional images along y–z axis of a single PDPPSe-12:PBTTT PMHJ (six period) film. Reproduced with permission [5], Springer Nature Ltd.

electric plastics, potentially unlocking their full solid-state power generation and cooling capabilities.

Declaration of competing interest

The authors declare no conflict of interest.

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References

[1] C. Di, W. Xu, D. Zhu, Natl. Sci. Rev. 3 (2016) 269–271.
[2] O. Bubnova, Z.U. Khan, A. Malti, et al., Nat. Mater. 10 (2011) 429–433.
[3] G. Kim, L. Shao, K. Zhang, et al., Nat. Mater. 12 (2013) 719–723.
[4] Y. Sun, L. Qiu, L. Tang, et al., Adv. Mater. 28 (2016) 3351–3358.
[5] D. Wang, J. Ding, Y. Ma, et al., Nature 632 (2024) 528–535.