

Organic Semiconductors for Thermoelectric Modules: Potential, Limitations and Engineering Perspectives

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Abstract

Thermoelectric (TE) devices enable direct conversion between heat and electricity and offer a solid-state approach to waste-heat recovery and localized cooling. Conventional TE modules are dominated by inorganic semiconductors such as Bi₂Te₃-based alloys, which provide high performance near room temperature but are mechanically brittle and rely on materials with supply and environmental concerns. In recent years, organic semiconductors—particularly conducting polymers, molecular semiconductors, and polymer-carbon nanofiller composites—have emerged as promising candidates for lightweight, mechanically flexible, and potentially more sustainable thermoelectric systems.

This review evaluates the potential of organic TE materials to complement or partially replace traditional inorganic semiconductors in TE modules. Key performance parameters (Seebeck coefficient, electrical conductivity, thermal conductivity, power factor, and figure of merit ZT) are discussed together with engineering constraints such as stability, reproducibility, processing routes, contact resistance, and device integration. The analysis indicates that organic materials are especially attractive for low-grade heat harvesting under small temperature gradients (e.g., body heat and ambient sources), where flexibility, low mass, and scalable manufacturing may outweigh lower ZT relative to state-of-the-art inorganics. Remaining challenges and research directions are identified such as improving of n-type organic performance, long-term thermal and chemical stability, and robust, reproducible fabrication.

Keywords: thermoelectrics, organic semiconductors, conducting polymers, organic thermoelectrics, figure of merit, low-grade waste heat

Introduction

An Interest in thermoelectric devices has grown significantly over the past decades due to the need for energy-efficient technologies that can harvest waste heat and enable compact, maintenance-free cooling. Thermoelectric modules contain p-type and n-type legs connected electrically in series and thermally in parallel [1]. A temperature gradient generates an output voltage (Seebeck effect), while when an electrical current is applied, modules generate cooling capacity (Peltier effect). Commercial room-temperature modules are typically based on Bi₂Te₃-derived alloys because they combine relatively high efficiency with mature manufacturing routes.

Despite of these advantages, conventional inorganic thermoelectrics remain limited by mechanical brittleness, constrained form factors, and concerns related to the environmental footprint and availability of certain elements. These drawbacks motivate the exploration of alternative classes of materials that could enable

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new applications such as conformable energy harvesters integrated with clothing, wearable electronics, or curved surfaces.

Organic semiconductors, including conducting polymers and molecular semiconductors, offer distinctive benefits: low density, mechanical flexibility, solution processability (printing/coating), and potentially reduced environmental impact [2]. However, organic materials typically exhibit lower thermoelectric performance and greater stability challenges compared to crystalline inorganic semiconductors.

1. Objective and scope

The goal of this article is to assess the potential for replacing or complementing conventional inorganic TE materials (e.g., Bi₂Te₃-based alloys) with organic semiconductors in thermoelectric modules. The discussion focuses on fundamental TE parameters and performance metrics, a brief overview of established inorganic TE materials, representative organic TE materials and their performance trends, main engineering barriers for device integration, and application niches where organic materials may provide a net advantage.

2. Thermoelectric effects and performance metrics

2.1. Seebeck, Peltier and Thomson effects

Thermoelectric phenomena are commonly described by three reversible effects: Seebeck effect, Peltier effect and Thomson effect. When two dissimilar conductors or semiconductors A and B form a circuit and their junctions are held at different temperatures, an electromotive force develops (Seebeck effect). The relative Seebeck coefficient is

$$\alpha_{AB} = \frac{\Delta V}{\Delta T} \quad (1)$$

where ΔV is the voltage difference and ΔT is the temperature difference. The relative coefficient can be expressed through absolute coefficients:

$$\alpha_{AB} = \alpha_A - \alpha_B \quad (2)$$

The Peltier effect is the inverse of the Seebeck effect: when a current passes through a junction of two materials, heat is absorbed at one junction and released at the other. The heat rate is

$$\dot{Q}_{\text{Peltier}} = \pi_{AB} I \quad (3)$$

where π_{AB} is the Peltier coefficient and I is the current. The Thomson effect describes reversible heat absorption or release along a single conductor carrying current in the presence of a temperature gradient:

$$\dot{Q}_{\text{Thomson}} = \tau I \Delta T \quad (4)$$

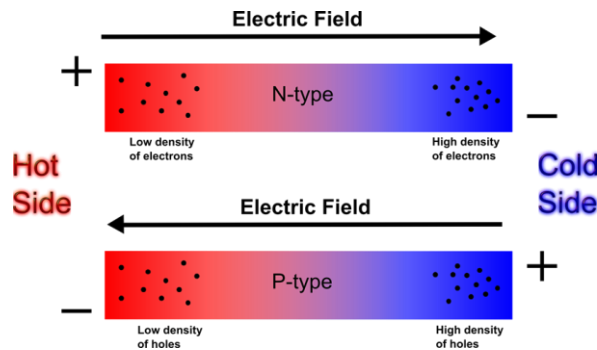


Figure 1. Thermocouple model [3]

Kelvin relations connect these coefficients:

$$\pi = \alpha T \quad (5)$$

$$\tau_B - \tau_A = T \frac{d\alpha}{dT} \quad (6)$$

2.2. Figure of merit and power factor

A high-performance TE material should exhibit high electrical conductivity σ (low resistive/Joule losses), high Seebeck coefficient S (also denoted α), and low thermal conductivity κ (to maintain temperature gradients).

These requirements are combined in the thermoelectric figure of merit:

$$Z = \frac{S^2 \sigma}{\kappa} \quad (7)$$

and the dimensionless figure of merit:

$$ZT = \frac{S^2 \sigma T}{\kappa} \quad (8)$$

A commonly used intermediate metric is the **power factor**:

$$PF = S^2 \sigma \quad (9)$$

For organic thermoelectrics, much of the literature focuses on strategies that increase PF via doping, microstructural control, and composite design, while maintaining low κ .

3. Conventional inorganic thermoelectric materials

3.1. Bi₂Te₃-based alloys (near room temperature)

Bi₂Te₃ and related alloys (e.g., Bi₂Te₃-Sb₂Te₃ and Bi₂Te₃-Se₂Te₃) are the most established materials for near-room-temperature thermoelectric modules. Their performance can reach ZT values of approximately one near room temperature. These materials can be engineered for both p-type and n-type legs, but their layered structure and weak interlayer bonding may lead to cleavage planes and reduced mechanical robustness, motivating alloying and microstructural optimization.



Figure 2. Single crystal of bismuth telluride [4]

3.2. PbTe (mid-temperature range)

PbTe (Lead Telluride) is the thermoelectric material for intermediate temperatures (approximately 600–800 K). Performance can be enhanced via doping and band-structure engineering; for example, Tl doping has been reported to increase ZT to around 1.5 at 773 K. The fabrication of large, high-quality single crystals can be challenging; therefore, polycrystalline routes and doping strategies are widely used.



Figure 3. Model of PbTe [5]

3.3. Si–Ge alloys (high-temperature range)

Si–Ge alloys are well known for high-temperature thermoelectric power generation (above ~ 750 K up to >1000 K). Typical ZT values can approach ~ 1 at elevated temperatures, and nanocomposites or multiphase designs may further reduce thermal conductivity.

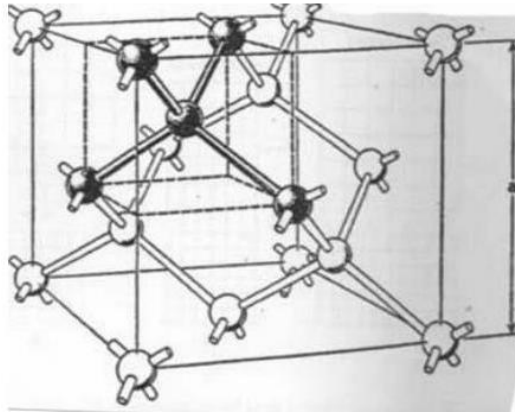


Figure 4. Unit cell of Si-Ge [6]

3.4. Other families: skutterudites and oxides

Skutterudites (e.g., CoSb_3) and selected oxide semiconductors are considered for specific temperature ranges and operating environments. Inorganic systems benefit from high thermal and chemical stability and mature module architectures but are often limited in mechanical flexibility and form factors.

4. Organic thermoelectric materials

Organic semiconductors are typically composed of conjugated molecules or polymers with π -electron systems, sometimes incorporating heteroatoms (N, S, O). They can form molecular crystals or amorphous/semicrystalline thin films [7, 8]. In TE applications, organic materials are most often processed as films or composites using solution-based routes, enabling lightweight and flexible devices.

4.1. p-type organic thermoelectrics: PEDOT:PSS and related polymers

Among p-type organic TE materials, PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate)) is one of the most studied due to its chemical stability, processability, and relatively high electrical conductivity after post-treatment. Reported ZT values for PEDOT:PSS-based systems can reach approximately 0.25, with improvements achieved via:

- secondary doping or solvent treatments (e.g., ethylene glycol, DMSO) that increase σ by reorganizing morphology and enhancing charge transport,
- optimization of doping level to balance S and σ ,
- interface and heterostructure approaches (e.g., ionic-liquid-related strategies) that can enhance S and therefore PF.

The general trade-off is that increased doping tends to enhance σ while reducing S , so maximum performance occurs at an optimum doping/morphology point.

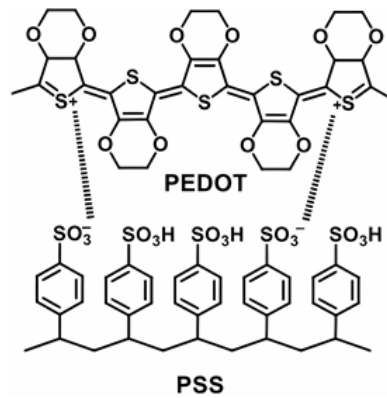


Figure 5. Chemical structure of PEDOT:PSS [9]

4.2. n-type organic thermoelectrics: performance gap and candidate systems

A major limitation in organic TE module development is the performance and stability gap between p-type and n-type organic materials. Achieving stable n-type behavior in air is challenging because many n-doped organics are sensitive to oxygen and moisture, leading to dedoping and performance loss.

Representative approaches include:

- molecular semiconductors and fullerene derivatives (e.g., C₆₀-based systems) doped to achieve n-type transport,
- conjugated polymers designed for electron transport (e.g., systems based on electron-deficient building blocks),
- coordination polymers such as poly(nickel-ethylenetetrathiolate), poly(Ni-ett), reported as an air-stable n-type material with ZT values around 0.2, and improved film-based implementations reaching ~0.3 due to enhanced electrical conductivity and better molecular ordering.

Although progress is significant, n-type organic systems remain a key bottleneck for practical all-organic TE modules.

4.3. Carbon nanofiller composites: CNT/polymer systems

Carbon nanotubes (CNTs) and related nanocarbons provide high electrical conductivity and can form percolating networks in polymer matrices. However, CNTs also exhibit high thermal conductivity, which can increase κ and reduce ZT if not controlled. Composite strategies aim to increase σ through conductive networks, maintain or limit κ via interface engineering and filler dispersion, and tune TE polarity (p-type vs n-type) through selection of polymer electrolytes and dopants.

These composites are attractive for flexible devices and often show improved air stability compared to strongly doped neat polymers.

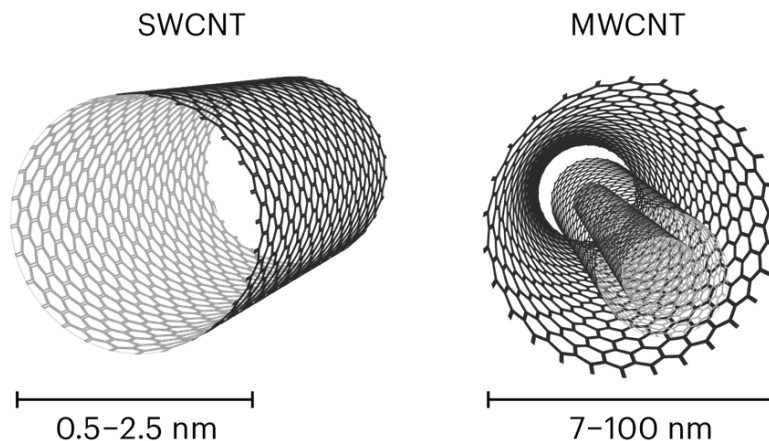


Figure 6. Different structures of CNT [10]

4.4. Polyaniline (PANI) and tunable doping chemistry

Polyaniline (PANI) is notable for its multiple oxidation states and tunable conductivity via acid/base doping. Its electrical conductivity can vary widely depending on doping and morphology. Reports also suggest that Seebeck sign and magnitude can be tuned through chemical environment and dopants, enabling p- to n-type transitions under certain conditions [11, 12, 13]. Some nanostructured PANI systems have shown high ZT at cryogenic temperatures (e.g., values around 0.77 at ~45 K), which is scientifically interesting but must be interpreted cautiously for room-temperature applications.

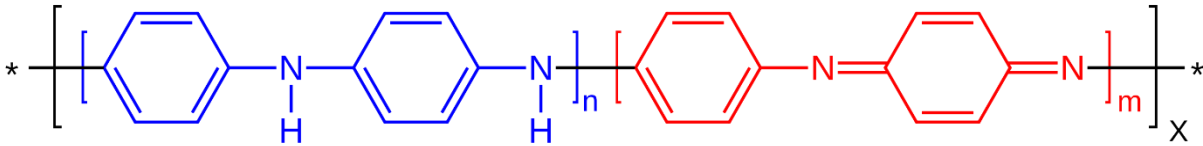


Figure 7. PANI – Polyaniline chemical structure

5. Engineering challenges for implementing organic materials in TE modules

5.1. Thermal and chemical stability

Many conducting polymers remain stable only up to approximately 150 °C, and performance can degrade due to thermal decomposition, dopant diffusion, or chemical reactions with air or moisture. In practical modules, stability under thermal cycling and long-term operation is critical.

5.2. Processing routes, scalability and reproducibility

Conventional inorganic TE processing (ball milling, hot pressing, high-temperature sintering) is typically incompatible with solution-processed organics. Organic films are commonly fabricated by spin coating or drop casting, while scalable approaches (screen printing, inkjet, roll-to-roll coating) are still being optimized for repeatability. Batch-to-batch variations in polymer molecular weight, dopant level, or microstructure can lead to significant performance scatter.

5.3. Measurement reliability and substrate effects

Accurate electrical measurements often require four-probe methods to reduce contact contributions. For thin organic films on substrates, it is crucial that the film resistance is much lower than substrate resistance to avoid parasitic current paths. Measuring thermal conductivity is particularly challenging in thin films; different methods and assumptions can yield different κ , directly affecting computed ZT.

5.4. Film adhesion, mechanical durability and brittleness after doping

Flexible devices require strong adhesion to substrates or mechanically robust free-standing films. Many organic films exhibit limited adhesion due to their amorphous or semicrystalline nature, and heavy doping can increase brittleness. Approaches include binders, surface treatments, and interfacial polymerization to form free-standing films, but an engineering balance is needed between TE performance and mechanical reliability.

5.5. Contact resistance and module-level losses

Even if a material shows high PF or ZT in laboratory measurements, module performance can be limited by electrical and thermal contact resistances, interconnect reliability, and packaging. For organics, interfaces between soft films and metallic interconnects require careful design to prevent delamination and minimize parasitic resistance.

6. Comparison of organic vs inorganic thermoelectrics and application niches

6.1. Performance comparison: basic trends

Table 1 summarizes qualitative differences and engineering trade-offs between conventional inorganic materials and organic systems.

Table 1. Qualitative comparison of inorganic and organic thermoelectric materials for modules

Aspect	Inorganic TE (e.g., Bi ₂ Te ₃ , PbTe, SiGe)	Organic TE (polymers, composites, molecular)
Typical ZT	High; near unity (RT) and above in optimized systems	Lower; improving, but often below inorganics at RT
Mechanical properties	Brittle, rigid	Flexible, lightweight
Processing	Sintering, hot pressing, high-T routes	Solution processing; printing/coating feasible
Thermal stability	Generally high	Often limited; dopant/structure sensitive
Environmental/supply concerns	Possible critical elements; high processing energy	Potentially lower footprint, but depends on dopants/solvents
Module integration maturity	High, industrial	Emerging; interface/contact challenges

Organic TE materials may be advantageous where temperature gradients are small (low-grade heat sources), where there are conformability and low mass matter (wearables, textiles, curved surfaces), where manufacturing via printing or coating enables low-cost, large-area devices, and where required power is modest (sensor nodes, low-power electronics).

Human body heat and near-ambient gradients are particularly relevant: while available ΔT is limited, flexible devices can be worn comfortably and integrated unobtrusively, enabling continuous energy harvesting for low-power electronics.

In opposite inorganic thermoelectrics remain preferred where high power density is required, operating temperatures are moderate to high for long durations, long-term stability and proven reliability dominate over flexibility, and module integration and supply chains require established standards [15, 16].

7. Conclusions and outlook

Organic semiconductors provide a compelling pathway toward flexible, lightweight thermoelectric systems, particularly for low-grade heat harvesting and wearable or portable applications. Conducting polymers such as PEDOT:PSS demonstrate the most mature p-type performance among organics, while n-type organic materials remain the primary bottleneck due to lower performance and limited air stability. Beyond intrinsic material properties, engineering issues—particularly reproducible processing, reliable thermal and electrical measurements, adhesion and mechanical durability, and contact resistance—strongly influence real device efficiency.

Future progress is expected from stable, high-performance n-type organic systems, better control of doping and morphology to optimize both S and σ . Then scalable manufacturing routes with consistent quality, and interface engineering for low-loss module integration are very important. In the near term, hybrid module concepts that combine inorganic and organic elements may offer a practical bridge between high efficiency and mechanical flexibility.

References

- [1] K. V. Selvan, M. N. Hasan, and M. S. M. Ali, "State-of-the-Art Reviews and Analyses of Emerging Research Findings and Achievements of Thermoelectric Materials over the Past Years," *Journal of Electronic Materials*, vol. 48, no. 2, 2019.

- [2] H. Naarmann, "Polymers, Electrically Conducting," in *Ullmann's Encyclopedia of Industrial Chemistry*. Wiley-VCH, 2002.
- [3] <https://www.mn.uio.no/fysikk/english/research/projects/bate/thermoelectricity/> (access: 13.09.2025)
- [4] <https://facts.net/science/chemistry/40-facts-about-bismuth-telluride/> (access: 13.09.2025)
- [5] https://en.wikipedia.org/wiki/Lead_telluride#HeroSection (access: 13.09.2025)
- [6] https://slidetodoc.com/semiconductor-fundamentals-outline-general-material-properties-crystal-structure/#google_vignette (access: 13.09.2025)
- [7] D. Jérôme, A. Mazaud, M. Ribault, and K. Bechgaard, "Superconductivity in a synthetic organic conductor (TMTSF)₂PF₆," *J. Physique Lettres*, 1980.
- [8] H. Shirakawa, E. J. Louis, A. G. MacDiarmid, C. K. Chiang, and A. J. Heeger, "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)_x," *J. Chem. Soc., Chem. Commun.*, 1977.
- [9] <https://www.hanspub.org/journal/PaperInformation?paperID=80638> (access: 13.09.2025)
- [10] https://www.researchgate.net/figure/Structure-of-CNT-SWCNT-and-MWCNT-carbon-based-nanomaterials_fig6_339534300 (access: 13.09.2025)
- [11] B. Abad et al., "Improved power factor of polyaniline nanocomposites with exfoliated graphene nanoplatelets," *J. Mater. Chem. A*, vol. 1, pp. 10450–10457, 2013.
- [12] Y. W. Park et al., "Thermopower and conductivity of metallic polyaniline," *Solid State Communications*, vol. 63, pp. 1063–1066, 1987.
- [13] M. Khalid et al., "Electrical conductivity studies of polyaniline nanotubes doped with different sulfonic acids," *Indian Journal of Materials Science*, 2013.
- [14] https://www.researchgate.net/figure/Two-dimensional-chemical-structure-of-polyaniline-PANI-57-Copyright-C-2011-Elsevier_fig3_369198741 (access: 13.09.2025)
- [15] M. A. Kamarudin et al., "A review on the fabrication of polymer-based thermoelectric materials and fabrication methods," *The Scientific World Journal*, 2013.
- [16] O. Bubnova, *Thermoelectric properties of conducting polymers*, PhD Thesis, Linköping University, 2013.