



Mesoscopic thermoelectric phenomena / Phénomènes thermoélectriques mésoscopiques

Quantum-interference-enhanced thermoelectricity in single molecules and molecular films



Effets thermoélectriques amplifiés par interférences quantiques dans les molécules et les films moléculaires

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ABSTRACT

We provide a brief overview of recent measurements and predictions of thermoelectric properties of single-molecules and porous nanoribbons and discuss some principles underpinning strategies for enhancing their thermoelectric performance. The latter include (a) taking advantage of steep slopes in the electron transmission coefficient $T(E)$, (b) creating structures with delta-function-like transmission coefficients and (c) utilising step-like features in $T(E)$. To achieve high performance, we suggest that the latter may be the most fruitful, since it is less susceptible to inhomogeneous broadening. For the purpose of extrapolating thermoelectric properties of single or few molecules to monolayer molecular films, we also discuss the relevance of the conductance-weighted average Seebeck coefficient.

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RÉSUMÉ

Nous procédons à un bref survol des mesures et prédictions récentes concernant les propriétés thermoélectriques de molécules individuelles ou de nanorubans poreux, puis nous discutons quelques-uns des principes sous-jacents aux stratégies visant à augmenter leurs performances thermoélectriques. On relèvera parmi ces dernières (a) l'utilisation de pentes élevées du coefficient de transmission électronique $T(E)$, (b) la création de structures avec des pics de transmission et (c) l'exploitation de ces derniers. Pour atteindre de hautes performances, nous suggérons que cette dernière approche puisse être la plus fructueuse, puisqu'elle est moins susceptible de présenter des élargissements inhomogènes. Afin d'extrapoler les propriétés thermoélectriques d'une ou de quelques molécules à des films moléculaires monocouche, nous discutons aussi la pertinence de l'utilisation d'une moyenne du coefficient Seebeck pondérée par la conductance.

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1. Introduction

Generation of electricity from waste heat via the Seebeck effect is silent, environmentally friendly and requires no moving parts. Waste heat from automobile exhausts, industrial manufacturing processes data farms and the human body could be used to generate electricity economically, provided more efficient thermoelectric materials could be realised. Conversely, Peltier cooling using high-performance thermoelectric materials would have applications ranging from on-chip cooling of CMOS-based devices to home refrigerators. This demand for new thermoelectric materials from the information technologies, aerospace, and automotive industries has led to a world-wide race to develop materials with a high thermoelectric efficiency, characterised by a high-dimensionless thermoelectric figure of merit $ZT = GS^2T/\kappa$, where G is the electrical conductance, S the Seebeck coefficient or thermopower, T the temperature, and κ the thermal conductance. In terms of ZT , the maximum efficiency of a thermoelectric generator is $\eta_{\max} = \eta_c(a - 1)/(a + 1)$, where η_c is the Carnot efficiency and $a = (ZT + 1)^{1/2}$, whereas the efficiency at maximum power is $\eta_p = \eta_{CA} (a^2 - 1)/(a^2 + 1)$, where η_{CA} is the Curzon-Ahlborn upper bound. In both cases, the efficiency is at maximum when ZT tends to infinity. In most inorganic materials, the interdependency of transport coefficients constrains the options for materials design and makes optimisation a difficult task and, despite several decades of development, the best inorganic thermoelectric materials possess a figure of merit ZT slightly above unity only, which is not sufficient to create a viable technology platform for harvesting waste heat from data farms and the ambient environment. Generally, a compromise has been found in nanostructured semiconductors such as Bi_2Te_3 or PbTe-SrTe alloys. However, these materials are toxic and global supplies are limited. As an alternative, organic thermoelectric materials are now being investigated and are beginning to show promising values of both ZT and S . However, fundamental understanding at the molecular level is needed to increase these parameters to values beyond currently-attainable limits. During recent years, several groups have adopted a bottom-up approach to this challenge, by investigating thermoelectric properties of single molecules, which can be regarded as the ultimate nanostructured materials.

Current research in organic thermoelectrics aims to deliver high performance by exploiting room-temperature quantum interference (QI) at the single molecule level [1] and then translating this enhanced functionality to technologically-relevant thin-film materials and devices. Since thermopower is an intrinsic property, it should be possible to design molecules with built-in QI functionality and demonstrate that fundamental manifestations of QI can be manipulated and exploited in many-molecule ultra-thin films. Whereas single-molecules on gold or other metals can be electrically contacted using a STM tip, mono- or few-layer assemblies of molecules will require a planar top contact, which does not affect the integrity of the assembly [2]. For many years, this requirement has been a roadblock to the development of molecular-scale devices, because deposition of a top contact can easily degrade a molecular film. The use of graphene top contacts may overcome this roadblock [3–6] and allow the creation of a proper understanding of the integrity of the QI performance at the many-molecule level.

Although the dream of utilising quantum interference (QI) effects [6] in single molecules has been discussed for many years [7–14], experimental indications of room-temperature QI in single molecules were obtained only recently [15–22]. Building on these measurements, we anticipate the next breakthrough to be the active and continuous control of QI-based functionality in single-molecular junctions by external triggers, including electrostatic and mechanical gating. Indeed it has been demonstrated both experimentally and theoretically that at a molecular scale, thermopower S can be controlled by varying the chemical composition [23], tuning the position of intra-molecular energy levels relative to the work function of metallic electrodes [24,25], systematically increasing the single-molecule lengths and varying the binding groups within a family of molecules [26–30], by tuning the interaction between two neighbouring molecules [31], and by controlling the transport properties with an electrostatic [32] or electrochemical gate [33]. These single-molecule experiments yielded room-temperature values of S ranging in magnitude from ca. 1 to 50 $\mu\text{V}/\text{K}$. Furthermore mechanical gating of $\text{Sc}_3\text{N@C}_{80}$ [34] leads to bi-thermoelectric materials with S ranging from $\pm 20 \mu\text{V}/\text{K}$, depending on pressure and orientation.

Other approaches include developing strategies for increasing the thermopower of crown-ether-bridged anthraquinones [35]. The novel design feature of these molecules is the presence of either crown-ether or diaza-crown-ether bridges attached to the side of the current-carrying anthraquinone wire. The crown-ether side groups selectively bind alkali-metal cations, and when combined with TCNE or TTF dopants, provide a large phase-space for optimising thermoelectric properties. Recently, it was found [35] that the optimal combination of cations and dopants depends on the temperature range of interest. The thermopowers of both crown-ethers and diaza-crown-ethers are negative and at room temperature are optimised by binding with TTF alone, achieving thermopowers of $-600 \mu\text{V}/\text{K}$ and $-285 \mu\text{V}/\text{K}$, respectively. At much lower temperatures, which are relevant to cascade coolers, crown ethers complexed with TTF and Na^+ are predicted to achieve a maximum thermopower of $-710 \mu\text{V}/\text{K}$ at 70 K, whereas a combination of TTF and Li^+ yields a maximum thermopower of $-600 \mu\text{V}/\text{K}$ at 90 K. For diaza-crown-ethers, it was found that TTF doping yields a maximum thermopower of $-800 \mu\text{V}/\text{K}$ at 90 K, whereas at 50 K, the largest thermopower (of $-600 \mu\text{V}/\text{K}$) is obtained by a combination of TTF and K^+ doping. At room temperature, power factors of $73 \mu\text{W}/\text{m}\cdot\text{K}^2$ are predicted for crown-ether-bridged anthraquinones complexed with TTF and Na and $90 \mu\text{W}/\text{m}\cdot\text{K}^2$ for diaza crown-ether-bridged anthraquinones complexed with TTF. These compare favourably with power factors of other organic materials, whose reported values range from $0.016 \mu\text{W}/\text{m}\cdot\text{K}^2$ and $0.045 \mu\text{W}/\text{m}\cdot\text{K}^2$ for polyaniline and polypyrrole respectively [36], to $12 \mu\text{W}/\text{m}\cdot\text{K}^2$ for PEDOT:PSS [46] and $12 \mu\text{W}/\text{m}\cdot\text{K}^2$ for $\text{C}_{60}/\text{Cs}_2\text{Co}_3$ Dph-BDT [47].

Recently [37], the thermoelectric properties of metalloporphyrins connected by thiol anchor groups to gold electrodes were investigated. By varying the transition-metal centre over the range Mn, Co, Ni, Cu, Fe, and Zn, their molecular en-

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