Quantum-Interference-Enhanced Thermoelectricity in Single Molecules and Molecular Films

Colin J. Lamberta, Hatef Sadeghiab and Q.H. Al-Galibya,b

aDepartment of Physics, Lancaster University, Lancaster LA1 4YB, UK
bDepartment of Physics, Education of College, Al Qadisiyah University, Iraq
c.lambert@lancaster.ac.uk; h.sadeghi@lancaster.ac.uk; q.agaliby@lancaster.ac.uk

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.

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 \( ZT=GS^2/\kappa \), where \( G \) is the electrical conductance, \( S \) the Seebeck coefficient or thermopower, \( T \) the temperature and \( \kappa \) the thermal conductance. In terms of \( ZT \), the maximum efficiency of a thermoelectric generator is \( \eta_{\text{max}} = \eta_c \frac{(a+1)}{(a-1)} \) where \( \eta_c \) is the Carnot efficiency and \( a = (ZT+1)^{1/2} \), whereas the efficiency at maximum power is \( \eta_p = \eta_{\text{CA}} \frac{(a^2+1)}{(a^2-1)} \), where \( \eta_{\text{CA}} \) is the Curzon-Ahlborn upper bound. In both cases, the efficiency is a maximum when \( ZT \) tends to infinity. In most inorganic materials, the interdependency of transport coefficients constrains the options for materials design and makes optimization 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$_2$Te$_3$ 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 µV/K. Furthermore mechanical gating of Sc$_3$N@C$_{80}$ [34] leads to bi-thermoelectric materials with $S$ ranging from +/- 20 µV/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 µV/K and -285 µV/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 µV/K at 70K, whereas a combination of TTF and Li⁺ yields a maximum thermopower of -600 µV/K at 90K. For diaza-crown-ethers, it was found that TTF doping yields a maximum thermopower of -800 µV/K at 90K, whereas at 50K, the largest thermopower (of -600 µV/K) is obtain by a combination TTF and K⁺ doping. At room temperature, power factors of 73 µW/m.K² are predicted for crown-ether-bridged anthraquinones complexed with TTF and Na and 90 µW/m.K² 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 µW/m.K² and 0.045 µW/m.K² for polyaniline and polypyrrole respectively [36], to 12 µW/m.K² for PEDOT:PSS [46] and 12 µW/m.K² for C₆₀/C₅₇Co₂ 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 energy levels can be tuned relative to the Fermi energy of the electrodes. The resulting single-molecule room-temperature thermopowers vary from almost zero for Co and Cu centres, to +80 µV/K and +230 µV/K for Ni and Zn respectively. In contrast, the thermopowers with Mn(II) or Fe(II) metal centres are negative and lie in the range -280 to -260 µV/K. Complexing these with a counter anion to form Fe(III) and Mn(III) changes both the sign and magnitude of their thermopowers to +218 and +95 µV/K respectively. These Seebeck coefficients are almost independent of temperature at room temperature and are significantly larger than recently-measured values of $S$ at room temperature. For example, measured values include 8.7, 12.9 and 14.2 µV/K for 1,4-benzenedithiol (BDT), 4,4'-dibenzenedithiol, and 4,4''-tribenzenedithiol respectively [38], -1.3 to 8.3 µV/K for the benzene-based series of benzene-dithiol (BDT), 2,5-dimethyl-1,4-benzenedithiol (BDT2Me), 2,3,5,6-tetrachloro-1,4-benzenedithiol (BDT4Cl), 2,3,5,6-tetraflouro-1,4-benzenedithiol (BDT4F) and BDCN [23], [39], 7.7 to 15.9 µV/K for the series BDT, DBDT, TBDT and DMTBDT [40], -12.3 to 13.0 µV/K for a series of amine-Au and pyridine-Au linked molecules [41] and -8.9 to -33.1 µV/K for fullerene-based single-molecule junctions [24], [41].

As noted in [1], organic thermoelectric materials may be an attractive alternative to inorganics for both thermoelectricity and thermal management, but at present the best organic thermoelectric material with a ZT of 0.6 in room temperature [42-45] is still not competitive with inorganics. Strategies for increasing $ZT = GS^2T/\kappa$ involve either increasing the numerator or decreasing the denominator. For comparison between single molecules and bulk materials, it is convenient to write
\[
ZT = \frac{GS^2T}{\kappa} = \frac{\sigma S^2T}{\gamma T} = \frac{PT}{\gamma T},
\]
where \(\sigma_e\) is the electrical conductivity, \(\gamma T\) the thermal conductivity and \(P = \gamma_e S^2\) the power factor. For a single molecule, the electrical conductivity is not well defined, but for the purpose of comparing with bulk materials, we define \(\gamma_e = GL / A\), where \(L\) is the molecular length and \(A\) the area that the molecule would occupy in a SAM.

Strategies for reducing the denominator (i.e., \(\kappa\)) of \(ZT\) in single-molecule junctions are fundamentally different from inorganic bulk materials. In the latter, phonon transport can be reduced by nanostructuring [48], [49], whereas molecular junctions are naturally nanostructured and additional strategies based on molecular phonon conversion [50] become possible, including the reduction of thermal conductance due to weak overlap between the continuum of vibrational states in the electrodes and discrete vibrational states of the molecules or the weak interaction between different part of the molecules, as in \(\pi-\pi\) stacked structures [51]. In the literature, there are many experiments addressing vibrational properties of single molecules, but far fewer addressing single-molecule phonon transport, because it is extremely difficult to measure the thermal conductance of a single molecule. This difficulty is partly circumvented by scanning thermal microscope measurements of a few thousands of molecules in parallel, such as a recent experimental study of the length-dependent thermal conductance of alkanes by the IBM group [52], which revealed a surprising initial increase in thermal conductance with length for short alkanes, due to interplay between the Debye frequency of the gold and that of the vibrational modes of the molecule [1]. This suggests that alternative metallic electrodes may be attractive [53], [54]. Electroburnt graphene junctions are being developed for contacting single molecules [55]–[57], [14], [58], [59], and form a new class of electrodes, which may be advantageous also in allowing reduction of the effects of defects in the electrodes [60] through the use of extended planar anchor groups [61]–[63]. Other strategies include introducing nanopores into two-dimensional nanoribbons formed from silicene or graphene [64,65], to reduce phonon transport and increase their Seebeck coefficients and figure of merit. As a first step in the development of strategies for maximising \(ZT\), one often focusses on the so-called electronic figure of merit \(ZT_e = \frac{GS^2T}{\kappa_e}\), where \(\kappa_e\) is the contribution from electron transport to the thermal conductance. Clearly, if \(\kappa_e\) vanishes, \(ZT_e\) can be infinite. However for the purpose of maximising the full \(ZT = \frac{GS^2T}{\kappa_e + \kappa_p}\), this is not too useful, because it means that the total thermal conductance \(\kappa = \kappa_e + \kappa_p\) is dominated by the contribution from phonons, \(\kappa_p\) and furthermore, if the Weidemann-Franz law \(\kappa_e \sim TG\) is satisfied, it means that the power factor vanishes. In what follows, we examine alternative strategies for optimising \(ZT\).

2. Towards Enhanced Thermoelectricity in Single Molecules and Molecular Films

To understand how transport resonances and quantum interference lead to high thermoelectric performance, we note that in the linear-response regime, the electric current \(I\) and heat current
\( Q \) passing through a device is related to the voltage difference \( \Delta V \) and temperature difference \( \Delta T \) by [63]

\[
\left( \frac{I}{Q} \right) = \frac{2}{\hbar} \left( \frac{e^2 L_0}{e} T_1 \frac{e L_1}{1} \frac{\Delta V}{\Delta T} \right)
\]

(1)

where \( T \) is the reference temperature and

\[
L_n = \int_{-\infty}^{\infty} (E - E_F)^n T(E) \left( -\frac{\partial f(E, T)}{\partial E} \right) dE
\]

(2)

In this expression \( e=|e| \) is the electronic charge, \( T(E) \) is the transmission coefficient for electrons of energy \( E \), passing through the molecule from one electrode to the other and \( f(E, T) \) is Fermi distribution defined as \( f(E, T) = \left[ e^{(E-E_F)/k_B T} + 1 \right]^{-1} \) where \( k_B \) is Boltzmann’s constant.

When \( \Delta T = 0 \), equation (1) yields for the electrical conductance \( G = \frac{I}{\Delta V}\left|_{\Delta T=0} \right. \),

\[
G = \frac{2 e^2}{\hbar} L_0
\]

(3)

Similarly when \( I = 0 \), equation (1) yields for the Seebeck coefficient \( S = -\frac{\Delta V}{\Delta T}\left|_{I=0} \right. ,

\[
S = \frac{-1}{|e| T} \frac{L_1}{L_0}
\]

(4)

Equation (1) can be rewritten in terms of the electrical conductance \( G \), thermopower \( S \), Peltier coefficient \( \Pi \), and the electronic contribution to the thermal conductance \( \kappa_e \):

\[
\left( \frac{\Delta V}{Q} \right) = \left( \frac{1/G}{\Pi} \frac{S}{\kappa_e} \right) \left( \frac{I}{\Delta T} \right)
\]

(5)

where

\[
\Pi = \frac{-1 L_1}{|e| T} \frac{L_0}{L_0}
\]

(6)

\[
\kappa_e = \frac{2}{\hbar T} \left( L_2 - \frac{(L_1)^2}{L_0} \right)
\]

(7)

From the above expressions, the electronic thermoelectric figure \( ZT_e = S^2 GT/\kappa_e \) is given by
\[ ZT_e = \frac{(L_1)^2}{L_0 L_2 - (L_1)^2} \]  

3. Strategies for increasing thermoelectric performance

Based on the above expressions, we now examine three strategies for increasing thermoelectric performance.

**Strategy 1: Utilising a steep slope in \( T(E) \).**

For \( E \) close to \( E_F \), if \( T(E) \) varies approximately linearly with \( E \) on the scale of \( k_B T \) then \( L_0 \approx T(E_F) \), \( L_1 \approx (eT)^2 \alpha \left( \frac{dT(E)}{dE} \right)_{E=E_F} \) and \( L_2 \approx (eT)^2 \alpha T(E_F) \), where \( \alpha \) is the Lorenz number given by

\[
\alpha = \frac{1}{(eT)^2} \int_{-\infty}^{\infty} (E-E_F)^2 \left( -\frac{\partial f(E, T)}{\partial E} \right) dE = \left( \frac{k_B}{e} \right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} \text{ W} \Omega^{-1} \text{K}^{-2}.
\]

Hence in this limit, these formulae take the form [63]:

\[
G \approx \frac{2e^2}{h} T(E_F), \tag{9}
\]

\[
S \approx -\alpha |e| T \left( \frac{d \ln T(E)}{dE} \right)_{E=E_F}, \tag{10}
\]

\[
\kappa_e \approx \alpha T G. \tag{11}
\]

Equation (10) demonstrates that \( S \) is enhanced by increasing the slope of \( \ln T(E) \) and hence quantum-interference-induced resonances or other features in \( T(E) \) with steep slopes close to \( E_F \) are desirable. To estimate what constitutes a “steep slope”, we note that the Wiedemann-Franz Law, (equation 11) yields

\[
ZT_e = \frac{S^2}{\alpha} \tag{12}
\]

Therefore in the low-temperature limit, if \( ZT_e > 1 \), then we require \( S^2 > \alpha \), i.e. \( S > 150 \mu \text{V/K} \)

**Strategy 2: Utilizing resonances in \( T(E) \).**

Insight into alternative strategies for maximising \( ZT_e \) can be obtained by taking a ‘statistical’ view of equation (3, 4, 7 and 8), which demonstrates why the denominator of equation (8) must be positive from a mathematical viewpoint. If the Fermi energy of the reservoirs is \( E_F \), then it is convenient to introduce the non-normalised distribution \( P(E) = -T(E) \frac{\partial f(E)}{\partial E} \) and the corresponding normalized
distribution \( (E) = \frac{P(E)}{L_0} \). Then the mean of \( (E - E_F) \) is \( < E - E_F > = \int dE \rho(E)(E - E_F) \) and the variance is \( \sigma^2 = < (E - E_F)^2 > - < E - E_F >^2 \). This yields for equation (4)

\[
S = \frac{-1}{|e|T} < E - E_F > ,
\]

(13)

Furthermore equation (8) becomes

\[
ZT_e = \frac{< E - E_F >^2}{\sigma^2},
\]

(14)

which is clearly positive.

The mean \( < E - E_F > \) and standard deviation \( \sigma \) capture essential features regarding the shape of \( \rho(E) \) and \( P(E) \). Equations (13) and (14) reveal that \( S \) and \( ZT_e \) depend only on these shape parameters and are independent of \( L_0 \). Only the electrical and electronic thermal conductances depend on \( L_0 \). This feature which can be traced to the fact that \( G = \frac{2e^2}{h} L_0 \) and \( k_e = \frac{2L_0 \sigma^2}{hT} \) describe the magnitudes of currents and therefore depend on the normalization \( L_0 \) of \( P(\epsilon) \), whereas \( S \) and \( ZT_e \) involve only ratios. Clearly \( < E - E_F > \) will be non-zero only if \( P(E) = -T(E) \frac{\partial f(E)}{\partial E} \) is an asymmetric function of \( (E - E_F) \) and since \( -\frac{\partial f(E)}{\partial E} \) is a symmetric function of \( (E - E_F) \), \( T(E) \) should be asymmetric with respect to \( E_F \). Examples of two candidate transmission functions are shown in figure 1.

\[\begin{array}{c}
\text{Figure 1.} \quad \text{Two ideal transmission coefficients} \quad T. \quad \text{(a) Delta-function like} \quad T(E) \quad \text{and (b) Step-function like} \quad T(E).
\end{array}\]

Figure 1a is relevant for structures, whose electronic density of states contains narrow resonances, such as single-molecule electrical junctions. Equation (2) reveals that \( ZT_e = \infty \), when \( \sigma = 0 \), which occurs when \( T(E) \) is proportional to a delta function [64] of the form \( T(E) = A\delta(E - E_0) \), in which case, \( \rho(E) = \delta(E - E_0) \), \( S = \frac{-1}{|e|T} (E_0 - E_F) \) and \( ZT_e \) is infinite. Similarly \( G = \frac{2e^2}{h} A(-\frac{\partial f(E_0)}{\partial E_0}) \) and \( k_e = 0 \). Thermal properties of a system with a delta-function-like transmission are shown in figure 2.
Figure 2. Thermal properties of the delta-function like $T(E)$, obtained with $E_F = 0$. (a) conductance, (b) electronic thermal conductance, (c) thermopower and (d) total $ZT$ by assuming a constant phonon thermal conductance. $\gamma$ and $\sigma$ are chosen to be 10.

Figure 3 shows a physical realisation of a structure with delta-function-like transmission. In this case the system consists of a silicene nanoribbon containing a nanopore and the delta function in $T(E)$ arises from the presence of edge states associated with zigzag edges of the ribbon [64].

Figure 3. (a) A silicene nanoribbon containing a nanopore with hydrogen terminated edges. (b) transmission coefficient (c) thermopower and (d) electronic $ZT_e$ versus temperature. For convenience, $E_F = 0$.

**Strategy 3: Utilising steps in $T(E)$.**
As an alternative to using narrow transmission resonances, we now consider the step-like transmission shown in figure 1b, which occurs in periodic structures such as a crystalline lead, where $T(E)$ is equal to the number of open channels and therefore changes in integer steps [65]. As a simple example, we now examine the thermopower and $ZT_e$ of a system with a model step-like transmission coefficient of the form: $T(E) = A$ for $E>E_0$ and $T(E)=0$ for $E<E_0$, where $A$ is an arbitrary constant defining the height of the step and $E_0$ defines the position of the step. In this case, it is convenient to introduce the dimensionless parameter $y = (E - E_F)/(k_BT)$, so the Fermi function takes the form $f(E)=(\exp y + 1)^{-1}$ and write equation (2) in the form

$$L_n = A(k_BT)^n I_n(y_0)$$ (15)

where $y_0 = (E_0 - E_F)/k_BT$,

$$I_n(y_0) = \int_{y_0}^{\infty} dy \left[-\frac{df}{dy}\right] y^n$$ (16)

and $\left[-\frac{df}{dy}\right] = e^y/(e^y + 1)^2$. Clearly all moments depend only on the size of the step (ie the dimensionless parameter $A$) and the dimensionless parameter $y_0$, which defines the location of the step relative to the Fermi energy of the electrodes, in units of $k_BT$. In terms of $I_n$, $\langle E - E_F \rangle = k_BT I_1/I_0$, $\sigma^2 = (k_BT)^2 [I_2/I_0^2 - I_1^2/I_0^2]$. Plots of the dimensionless Fermi integrals $I_n(y_0)$ are shown below.

\[\text{Figure 4. } I_0, I_1 \text{ and } I_2 \text{ for a step-function like transmission coefficient.}\]
Clearly \( I_0(\infty)=0 \) and \( I_0(-\infty)=1 \), because \( I_0(y_0) = \int_{y_0}^{\infty} dy \left[ -\frac{df}{dy} \right] = f(y_0) - f(\infty) = f(y_0) \).

Also since \( \left[ -\frac{df}{dy} \right] y \) is odd, \( I_1(\mp\infty)=0 \) and \( I_1(y_0) \) is a maximum at \( y_0 = 0 \). Furthermore, \( I_2(-\infty) = \frac{\pi^2}{3} \) and since \( \left[ -\frac{df}{dy} \right] y^2 = 0 \) at \( y = 0 \), the slope of \( I_2(y_0) \) vanishes at \( y_0 = 0 \).

In terms of \( I_n(y_0) \) the thermoelectric parameters become

\[
G = \frac{2e^2}{h} A I_0, \quad \text{(17)}
\]

\[
S = \frac{k_B I_1}{I_0}, \quad \text{(18)}
\]

\[
k_e = \frac{2A(k_B)^2 T}{h} (I_2 - \frac{I_1^2}{I_0}), \quad \text{(19)}
\]

\[
ZT_e = \frac{[\frac{I_1^2}{I_0^2}]}{[\frac{I_2^2}{I_0^2} -\frac{I_1^2}{I_0^2}]}, \quad \text{(20)}
\]

These equations show that the natural unit of \( G \) is \( \frac{2e^2}{h} = 77 \mu S \), of \( S \) is \( \frac{k_B}{e} = 86 \mu V/K \) and of \( k_e \) is \( \frac{2(k_B)^2 T}{h} = 173 \, pW/K \) at room temperature (ie 300K). Clearly \( G \) and \( k_e \) are both proportional to step size \( A \), whereas \( S \) and \( ZT_e \) are independent of \( A \). Plots of the dimensionless thermopower \( \bar{S} = \frac{I_1}{I_0} \) and dimensionless electronic thermal conductance \( \bar{k}_e = (I_2 - \frac{I_1^2}{I_0}) \) are shown in figure 5.

![Figure 5](image)

**Figure 5.** Dimensionless thermopower \( \bar{S}(y_0) = \frac{I_1}{I_0} \) and dimensionless electronic thermal conductance \( \bar{k}_e = (I_2 - \frac{I_1^2}{I_0}) \) and the electronic thermoelectric figure of merit \( ZT_e \).

Obviously, since the moments \( L_n \) in equation (2) are linear in \( T(E) \), the above analysis can be applied to various combinations of steps. For example for the step-like transmission coefficient of the form:

\( T(E) = B \) for \( E<E_0 \) and \( T(E)=0 \) for \( E>E_0 \), the relevant integrals are \( J_n(y_0) = \int_{y_0}^{\infty} dy \left[ -\frac{df}{dy} \right] y^n \) and equation (15) is replaced by \( L_n = B(k_B T)^n J_n(y_0) \).
Similarly for a two-step transmission of the form $T(E) = B$ for $E < E_0$ and $T(E) = 0$ for $E_1 > E > E_0$ and $T(E) = B$ for $E > E_1$, $L_n = (k_B T)^n [B_j(y_1) + A j_n(y_0)]$, etc.

So far we have ignored phonons, whose contribution to the thermal conductance is

$$\kappa_{\text{ph}}(T) = \frac{1}{2\pi} \int_0^\infty \hbar \omega T_{\text{ph}}(\omega) \frac{\partial f_{BE}(\omega,T)}{\partial T} d\omega$$  \hfill (21)

where $f_{BE}(\omega,T) = (e^{\hbar \omega/k_B T} - 1)^{-1}$ is the Bose–Einstein distribution function and $T_{\text{ph}}(\omega)$ is the transmission coefficient for phonons of energy $\hbar \omega$ [1]. Since

$$\frac{\partial f_{BE}(\omega,T)}{\partial T} = \left[\frac{\hbar \omega}{k_B T} e^{\hbar \omega/k_B T} (e^{\hbar \omega/k_B T} - 1)^{-2}\right]$$  \hfill (22)

$$\kappa_{\text{ph}}(T) = \frac{k_B}{2\pi} \int_0^\infty T_{\text{ph}}(\omega)[\hbar \omega/k_B T]^2 e^{\hbar \omega/k_B T} (e^{\hbar \omega/k_B T} - 1)^{-2} d\omega$$  \hfill (23)

$$\kappa_{\text{ph}}(T) = \frac{3g_0}{\pi^2} \int_0^\infty T_{\text{ph}}(y) y^2 e^y (e^y - 1)^{-2} dy$$  \hfill (24)

In this expression, the quantum of thermal conductance is $g_0 = \frac{(\frac{T}{k_B})^2 T}{\hbar} = (9.456 \times 10^{-13} \text{ W/K}^2)T$. As an example, the quantum of thermal conductance $g_0$ is $284 \text{ pW/K}$, at room temperature, which is the maximum room-temperature phonon thermal conductance per channel and occurs only if the upper cut off of the phonon channel is greater than approximately $5k_B T$. In contrast, for electrons, the quantum of phonon thermal conductance is $\frac{2(k_B T)^2}{\hbar} = \frac{(k_B T)^2}{\pi \hbar} = 173 \text{ pW/K}$ at room temperature.
For the above step-like model of electron transmission, where \( T(E) = A \) for \( E>E_0 \) and \( T(E)=0 \) for \( E<E_0 \), two-dimensional plots of thermoelectric coefficients are shown below, where when computing the full \( ZT \), we have assumed a phonon thermal conductance of \( \kappa_p = 300 \text{pW/K} \).

**Figure 7.** Thermal properties of the step-function like \( T(E) \). (a) conductance, (b) electronic thermal conductance, (c) thermopower and (d) total \( ZT \) by assuming a constant phonon thermal conductance \( 300 \text{pW/K} \). \( \gamma \) and \( \sigma \) are chosen to be 10.

Figure 8 shows an example of a graphene nanoribbon with step-function-like electron transmission coefficient around the Fermi energy \( E_F = 0 \) [65]. The structure is formed by two overlapping monolayer ribbons with hydrogen edge terminations, with the overlapping bilayer region containing a nanopore, whose edges are terminated by oxygen. Electrons flow from a left electrode connected to the top ribbon, to an electrode connected to the bottom ribbon, through the overlap region. Over the energy interval shown, there is one open scattering channel in the crystalline nanoribbons. In this case the oxygen-terminated pore blocks electron transmission over the energy interval 0 to 0.2 eV and an asymmetric step in \( T(E) \) arises from the asymmetry created by the presence of the oxygens.
Figure 8. (a) Bilayer graphene nanoribbon with hydrogen terminated edges and containing a nanopore whose inner edge is oxygen terminated. (a) molecular structure, (b) transmission coefficient, (c) thermopower and (d) electronic $ZT_e$ at $E_F = 0$ and versus temperature.

**Strategy 4: Minimizing the effect of inhomogeneous broadening**

In a thin film, such as that shown in figure 9, the properties of many molecules in parallel will depend on intermolecular interactions, quantum interference between nearby molecules mediated by the contacts, defects in the electrodes, impurities, pinholes and fluctuations in dopant concentrations.

Figure 9. A SAM formed on a gold bottom electrode, in contact with a graphene top electrode.

As a first step towards understanding the role of such inhomogeneous broadening, if intermolecular interactions are ignored in a SAM of $N$ molecules in parallel, then if molecule $j$ has a transmission coefficient $T_j(E)$, the moments $L_n$ appearing in equations (1) and all subsequent equations should be replaced by $\bar{L}_n = \sum_{j=1}^N L_{nj}$, where
\[ L_n^j = \int_{-\infty}^{\infty} (E - E_F)^n T_j(E) \left( -\frac{\partial f(E,T)}{\partial E} \right) dE \]  

(25)

This means that equation (4) is replaced by

\[ S = \frac{-1}{|e|T_L} \frac{L_1}{L_0} = \frac{\tilde{S}G}{\tilde{G}} \]  

(26),

The conductance-weighted averaged Seebeck coefficient \( \tilde{S} = \frac{S G}{\tilde{G}} \) is quite different from the average \( \tilde{S} = \frac{1}{N} \sum_{j=1}^{N} S_j \), where \( S_j = \frac{-1}{|e| T_L} \frac{L_1^j}{L_0^j} \) is the Seebeck coefficient of molecule \( j \). Indeed \( \tilde{S} \) is dominated by large individual values of \( S_j \) (ie molecules with small values of electrical conductance \( L_0^j \)), whereas small values of \( G \) do not contribute significantly to \( \tilde{S}G \). Since \( \bar{L}_n = \int_{-\infty}^{\infty} (E - E_F)^n \bar{T}(E) \left( -\frac{\partial f(E,T)}{\partial E} \right) dE \), where \( \bar{T}(E) = \sum_{j=1}^{N} T_j(E) \), then the advantages of steep slopes or sharp delta-function-like resonances in \( T_j(E) \) will be lost if such features appear at different random energies for different molecules. This suggests that as a strategy for optimizing thermoelectric performance, the delta-function-like transmission of figure 1a has drawbacks, because the sign of the thermopower and the coefficients \( L_1^j \) depend on the location of the resonance \( E_0 \). This means that due to inhomogeneous broadening, the thermopower of a self-assembled monolayer of such molecules may be very low, even though the thermopower of each individual molecule is high. Furthermore, since the electronic thermal conductance vanishes, the denominator of the full figure of merit is dominated by phonons, so the fact that \( ZT_e = \infty \), when the width of the resonance vanishes is irrelevant. On the other hand, as shown in figures 4c and 5a, fluctuations in the positions of step-like features in \( T(E) \) do not change the sign of the Seebeck coefficient and therefore molecules or nanoribbons exhibiting step-like transmission coefficients may be more resilient to inhomogeneous broadening.

The above classical behaviour occurs when the spacing between molecules is greater than the inelastic scattering length (sometimes called the dephasing length) \( l_\phi \), beyond which a classical Boltzmann-based description can be used [66]. In a more dense SAM, the role of intermolecular interactions would have to be included up to length scales of order \( l_\phi \). In this case, one should divide the SAM into \( M \) plaquettes of area \( l_\phi^2 \) and compute the coefficients \( L_0^{(A)} \) and \( L_1^{(A)} \) for each plaquette (labelled \( A \)), whose values will depend on the arrangement of the \( \frac{N}{M} \) molecules within each plaquette and on defects in the electrodes contacting the plaquette. The quantities \( \bar{L}_n \) would then be averages over all such plaquettes; ie \( \bar{L}_n = \frac{1}{M} \sum_{A} L_n^{(A)} \). In this expression, \( L_n^{(A)} \) is not simply an average over single-molecule values \( L_n^{(a)} \), but instead should be computed by solving for the transmission coefficient of a
whole plaquette or measured in for example an STM break junction using a tip of cross sectional area greater than or equal to $l^2 \phi$. Nevertheless, with this redefinition of $\Gamma_n$, equations (25) and (26) remain unchanged.

4. Conclusion
In conclusion, we have provided a brief overview of recent measurements and predictions of thermoelectric properties of single-molecule and nanoribbons and discussed some principles underpinning strategies for enhancing their thermoelectric performance. The latter include (a) taking advantage of steep slopes in $T(E)$, (b) creating structures with delta-function-like transmission coefficients and (c) utilising step-like features in $T(E)$. To achieve high performance, these strategies should be combined with methods for reducing inhomogeneous broadening and minimising the phonon thermal conductance. Of the above three strategies, the third appears to be the most resilient. It is not yet known if these strategies will be successful in achieving values of $ZT$ in excess of unity in organic thin films. However for structures obeying the Weidemann-Franz law, this is possible, provided the Seebeck coefficient exceeds $S = 150 \, \mu V/K$. Diaza-crown-ethers and metalloporphyrins are predicted to possess Seebeck coefficients exceeding this value and therefore there are grounds for optimism.

Author Information
Corresponding Authors

\textit{c.lambert@lancaster.ac.uk}
\textit{h.sadeghi@lancaster.ac.uk}
\textit{q.agaliby@lancaster.ac.uk}

Acknowledgments
This work was supported by the European Commission (EC) FP7 ITN “MOLESCO” (project no. 606728) and UK EPSRC (grant nos. EP/M014452/1 and EP/N017188/1).

References


