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Authors: Colin John Lambert, Marjan Famili, Iain Grace, and Hafez Sadeghi

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Suppression of phonon transport in molecular Christmas trees

Marjan Famili^[a], Iain Grace^[b], Hatf Sadeghi^[b] and Colin J. Lambert^[a]

Abstract:

Minimising the phonon thermal conductance of self-assembled molecular films, whilst preserving their electrical properties, is highly desirable, both for thermal management at the nanoscale and for the design of high-efficiency thermoelectric materials. Here we highlight a new strategy for minimising the phonon thermal conductance of Christmas-tree-like molecules composed of a long trunk, along which phonons can propagate, attached to pendant molecular branches. We demonstrate that phonon transport along the trunk is suppressed by Fano resonances associated with internal vibrational modes of the branches and that thermal conductance is suppressed most-effectively in molecules with pendant branches of different lengths. As examples, we use density functional theory to demonstrate the reduction in phonon transport in tree-like molecules formed from alkane or acene trunks with various pendant branches.

The combined electricity consumption of IT systems (communication networks, personal computers, data centres, etc.) was 900 TWh in 2012, or 4.6% of global electricity use, and this figure is set to double by 2025 [1]. To meet this challenge, research laboratories around the world are competing to create high-performance materials for thermal management and thermoelectricity, starting from single molecules [2-27] and scaling up to self-assembled molecular films (SAMs) [28-38]. For example, following the seminal works of [6,21], in which the Seebeck coefficient S of single molecules was measured for the first time, experimental studies [10,12] reported systematic changes in S and electrical conductance G of aromatic chains of phenyl rings, upon increasing their length. Our own recent work [14,17] reported a similar trend for fullerenes and identified new strategies for controlling the sign and magnitude of S . However, these studies provide only part of the fundamental knowledge needed to understand and optimise such materials at the molecular scale, because they ignore the crucial role of phonons. A key parameter for thermoelectric power generation is the dimensionless thermoelectric figure of merit $ZT = GS^2T/\kappa$, where T is the temperature and the thermal conductance is $\kappa = \kappa_e + \kappa_{ph}$ where, κ_e is the electronic contribution to thermal conductance, while κ_{ph} is the contribution from phonons. ZT is a measure of the efficiency of energy conversion from heat to electricity and unless ZT exceeds unity, a material is not competitive. Since phonons play no useful role in the conversion of heat into electricity, strategies for minimizing κ_p are highly desirable. In inorganic materials, nanostructuring has been utilized to reduce κ_{ph} . [39-44] Recently some theoretical studies have probed this issue by introducing specific single molecules which have low phonon conductance. [45-47] Here, we take a significant step forward by introducing a general strategy to design molecules which reduce phonon transport.

In what follows, our aim is to develop a new strategy for reducing molecular-scale phonon transport by attaching pendant 'branches' to the backbones or 'trunks' of molecules. Figure 1a shows an example of a SAM formed from molecules with alkane trunks (oriented vertically), and figure 1b shows examples of molecules to which various pendant branches are attached to the trunks (in this case the trunks are oriented horizontally). In what follows we demonstrate that these branches can be designed to suppress phonon transport over a range of frequencies, leading to a significant reduction in κ_p .

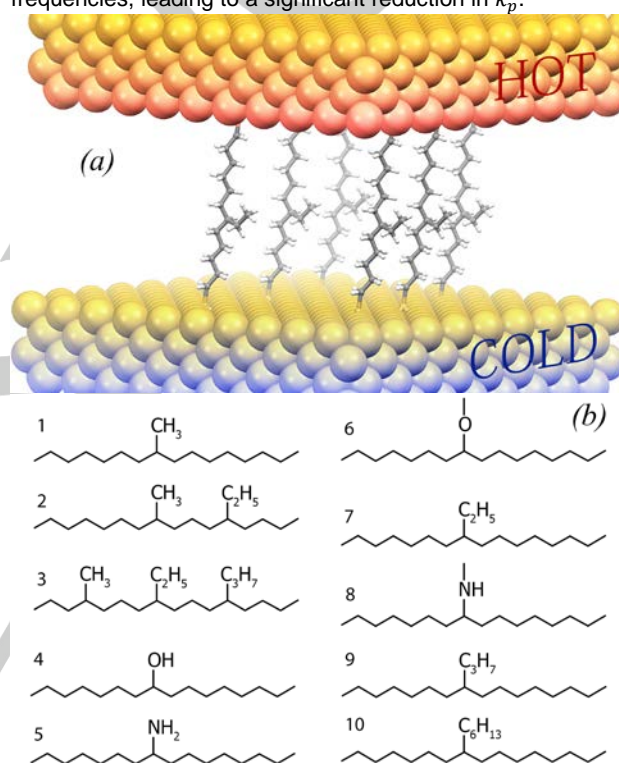


Figure 1. (a) A SAM connected between hot and cold electrodes. (b) Examples of molecules possessing pendant groups (oriented vertically) connected to molecular trunks (oriented horizontally) formed from alkyl chains.

Dynamics of model Christmas trees

To illustrate why pendant branches suppress phonon transport, consider an infinite linear harmonic trunk of single-degree-of-freedom masses m , (depicted by the brown masses in figure 2), connected by nearest neighbour springs of force constant γ , whose dispersion relation is given by the textbook expression $m\omega^2 = 4\gamma\sin^2(\frac{ka}{2})$, where a is the spacing between the masses, ω is the phonon frequency and k is their wavenumber (See SI). For such an ideal crystalline trunk with one degree of freedom and no pendant branches, the transmission coefficient $T(\omega)$ describing phonons of frequency ω entering the trunk from the top and exiting from the bottom (ie travelling from $-\infty$ to $+\infty$) is unity, provided the phonon frequency ω lies between zero and the Debye frequency Ω_D of the trunk, where $\Omega_D^2 = 4\gamma/m$. Now consider a pendant mass M attached by a spring of force

[a] M Famili, Prof. C.J Lambert
Physics Department
Lancaster University
Lancaster, United Kingdom, LA1 4YB
E-mail: m.famili@lancaster.ac.uk, C.lambert@lancaster.ac.uk

[b] Dr. I. Grace, Dr. H. Sadeghi
Physics Department
Lancaster University
Lancaster, United Kingdom, LA1 4YB

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constant α , to one of the atoms of such a chain, as shown by the green mass in figure 2a. In this case we find (see SI)

$$T(\omega) = 1/[1+x] \quad (1)$$

where x is a positive number and therefore unsurprisingly, the presence of the pendant mass reduces $T(\omega)$ to below the ideal value of unity. However perhaps more surprisingly, at a certain frequency Ω_M , the presence of the pendant group causes x to diverge and $T(\omega)$ to vanish. To quantify this effect, (known as a Fano resonance [2]) we note that if the brown masses in the trunk of figure 2a are of infinite mass, then the green pendant mass would behave as a harmonic oscillator with a single vibrational normal mode of frequency Ω_M given by $\Omega_M^2 = \frac{\alpha}{M}$. For the structure of figure 2a, when the brown masses are finite, one finds (see SI)

$$x = \frac{\Omega_M^4 \omega^2}{(\Omega_M^2 - \omega^2)^2 (\Omega_D^2 - \omega^2)} \quad (2),$$

where $\Omega_M^2 = \alpha/m$. Equation (2) shows that when $\omega = \Omega_M$, $x = \infty$ and therefore $T(\omega) = 0$.

This suppression of transmission along a chain, which occurs when the frequency ω of a phonon travelling along the trunk resonates with a normal mode Ω_M of a pendant branch, is a generic feature (see SI, equation S1), which we aim to exploit in the design of molecules with low phonon thermal conductance. Figure 2b shows an example of a vertical trunk (coloured brown) with two pendant branches (coloured green) of different lengths, which would cause $T(\omega)$ to vanish at their respective normal-mode frequencies.

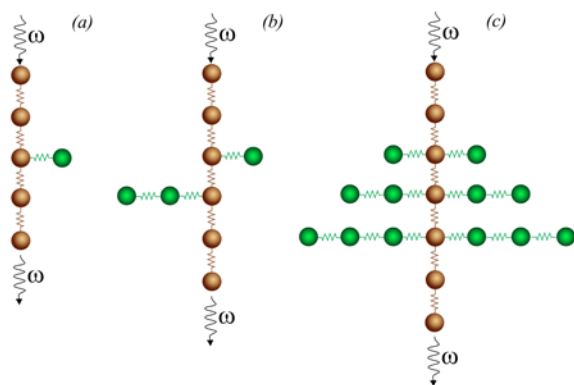


Figure 2. Idealised examples of vertical molecular backbones, with pendant side branches. The mass of the brown “atoms” is m and the mass of the green “atoms” is M . The brown spring constants are γ and the green spring constants are α .

To minimise the phonon thermal conductance $\kappa_{ph}(T)$ at temperature T , it will be necessary to eliminate phonon transmission along a molecular trunk over a range of frequencies between zero and $k_B T$ and for this purpose, it is desirable to attach multiple pendant groups with a variety of different normal mode frequencies. Figure 2c shows an example of a ‘Christmas tree’ with $N=3$ pendant branches of sequentially-increasing lengths from 1 to N masses, connected to a vertical molecular trunk. In this case the variety of normal-mode frequencies associated with different-length branches suppresses phonon transmission over a wide range of frequencies. This Christmas-tree strategy is illustrated in Figure 3, which shows the transmission coefficient $T_{ph}(\omega)$ for model Christmas trees containing $N=1, 3$ and 10 branches of sequentially-increasing lengths from 1 to N and demonstrates that the number of zeros in $T_{ph}(\omega)$ increases with the number of pendant branches.

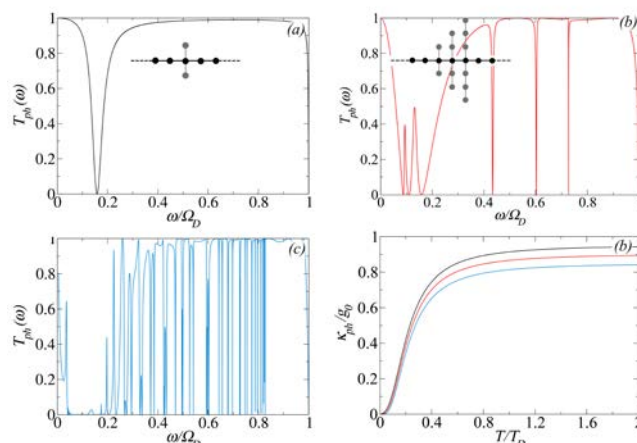


Figure 3. For model Christmas trees formed from single-degree-of-freedom masses, such those shown in figure 2, (a), (b) and (c) show the transmission coefficient for $N=1, 3$ and 10 side branches respectively. In each case, the lengths of the branches increase sequentially from 1 to N . (d) The phonon thermal conductances of structures 3a (black), 3b (red) and 3c (blue) obtained by combing the transmission coefficients 3(a-c) with equation (3). Results are shown on the scale of Debye temperature $T_D = \hbar\Omega_D/k_B$. See SI for more details of the dynamical model used for these structures.

Figure 3d shows the effect of these zeros on the phonon thermal conductance $\kappa_{ph}(T)$, obtained by evaluating the formula

$$\kappa_{ph}(T) = \frac{1}{2\pi} \int_0^\infty \hbar\omega T_{ph}(\omega) \frac{\partial f_{BE}(\omega, T)}{\partial T} d\omega \quad (3)$$

where $f_{BE}(\omega, T) = (e^{\hbar\omega/k_B T} - 1)^{-1}$ is the Bose–Einstein distribution function and $T_{ph}(\omega)$ is the transmission coefficient for phonons of energy $\hbar\omega$ [38] travelling along a backbone. (5)

When $T_{ph}(\omega) = 1$, this expression reduces to, the quantum of thermal conductance $g_0 = \frac{(\pi/k_B)^2}{h} T = 9.456 \times 10^{-13} \left(\frac{W}{K^2}\right) T$. As an example, at room temperature, the quantum of thermal conductance g_0 is 284 pW/K, which is the maximum room-temperature phonon thermal conductance per channel and occurs only if the upper cut off ($\hbar\Omega_D$) of the phonon channel is greater than approximately $5k_B T$. Figure 3d shows the thermal conductance versus temperature for each of the structures in figures 3 a-c and demonstrates that thermal conductance is suppressed by the presence of pendant branches.

To suppress phonon transmission further, it is desirable to increase the width of the Fano resonances by increasing the strength of the coupling α between the side branches and the trunk. For a system with 5 side branches, figures 4(a-c) shows $T_{ph}(\omega)$ when $\alpha = 0.2, 0.4$ and 0.7 respectively and demonstrates that the width of a Fano resonances increases with increasing α . Figure 4d shows that increasing the coupling of the branches to the trunk leads to a corresponding suppression of the thermal conductance.

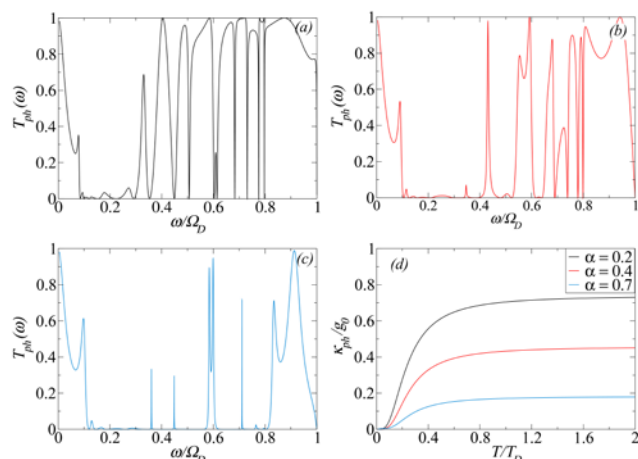


Figure 4. (a-c) Transmission coefficients of a Christmas-tree with 5 side branches of successively-increasing length, when $\alpha = 0.2, 0.4$ and 0.7 . (d) The corresponding thermal conductances versus temperature.

It is interesting to note that when a trunk is attached to more than one branch, as in figures 2b and 2c, then in addition to suppression due to Fano resonances, phonons also undergo multiple scattering from the points of attachment of the branches to the trunk. To distinguish between these two effects and to highlight the importance of Fano resonances, the black curve of figure 5a shows the transmission coefficient of a six-branch Christmas tree shown in the inset of figure 5a. For comparison, the red curve of figure 5a shows the transmission coefficient obtained when the masses of the branches are set to infinity, so that their normal mode frequencies vanish. In this case, Fano resonances are absent and only multiple scattering from the attachment points remains. Clearly the latter contributes to a reduction in phonon transmission, but as shown by Figure 5b, the lowest thermal conductance (black curve) is obtained when both Fano resonances and multiple scattering are present.

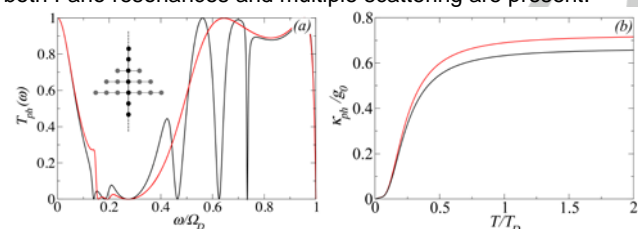


Figure 5. Red and black curves show the $T_{ph}(\omega)$ (on the left) and κ_{ph} (on the right) for a trunk attached to three side branches, when the masses of the atoms within the side branches are infinite (red) and finite (black).

Dynamics of molecular Christmas trees

So far we have considered only an ideal model of vibrations, using artificial single-degree-of-freedom masses. To examine whether or not the 'Christmas-tree' phonon-reduction strategy applies to more realistic molecules, we now use density-functional theory (DFT) to analyse phonon transmission along the alkane chains shown in figure 1b, containing various pendant branches using the method of ref [37], in which the dynamical matrix is constructed from the forces calculated using DFT [48] and the Gollum transport code [49] is used to calculate the phonon transmission coefficient (See SI for details). Figure 6 shows the transmission coefficients and thermal conductances of molecules **1**, **2** and **3** of figure 1b, with side branches of CH_3 for molecule **1**, CH_3 and C_2H_5 for molecule **2** and CH_3 , C_2H_5 and C_3H_7 for molecule **3**. This demonstrates that the Christmas tree strategy successfully suppresses phonon transport in realistic molecules.

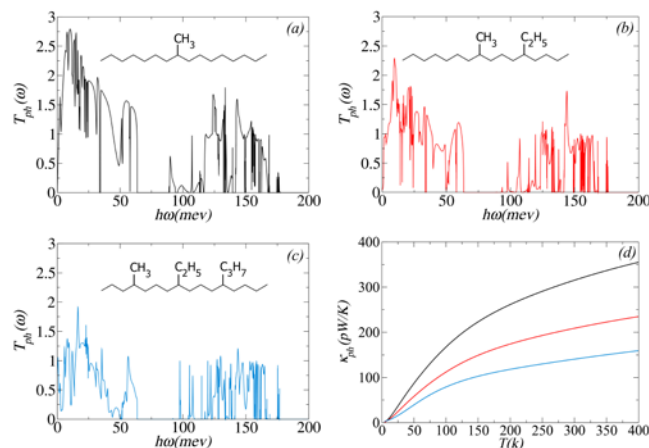


Figure 6. DFT results for the transmission coefficients and thermal conductances of molecules **1** (black), **2** (red) and **3** (blue) of figure 1b, where the trunks are formed from infinitely-long alkyl chains.

To allow us to focus on phonon scattering due to pendant branches only, the side branches in the molecules of figure 6 are attached to an infinitely-long alkane trunk, which also acts as a waveguide for phonons entering and leaving the scattering region. This idealisation avoids interface scattering at electrode molecule interfaces that would be present in a real device and would further reduce phonon transport. In the absence of pendant branches, the transmission coefficient is simply equal to the number of open scattering channels, which is plotted as a function of frequency in figure S2 and vanishes in the approximate frequency ranges 63-87 meV. Since the number of open channels is also an upper bound to $T_{ph}(\omega)$, this leads to gaps in $T_{ph}(\omega)$ over these frequency ranges, which are visible in figures 6a-c.

As discussed earlier, stronger coupling to the trunk can further suppress phonon transmission. In real molecules, this can be achieved by changing the chemical character and the stiffness of the bond connecting the branch to the trunk. This effect is demonstrated in figure 7, which shows the transmission coefficients of molecule **6**, **7** and **8** (OCH_3 , C_2H_5 and NCH_3) of figure 1b, which each contain a single side branch, but with terminal branch atoms C, N and O connected to the trunk. Our DFT calculations show that the minimum-energy bond lengths of terminal branch atoms C, N, and O connected to the alkyl trunk are 1.51, 1.44 and 1.41 Å respectively. As expected, Figure 7d shows that phonon thermal conductance is smaller in the presence of the shorter (and therefore stiffer) bond lengths between the N- and O- terminated side branches and the trunk. Similarly, thermal conductance is higher in the presence of the longer bond length between the C-terminated branch and the trunk. As shown in the SI, (fig SI4) this correlation is also present for molecules **1**, **4** and **5** of figure 1b.

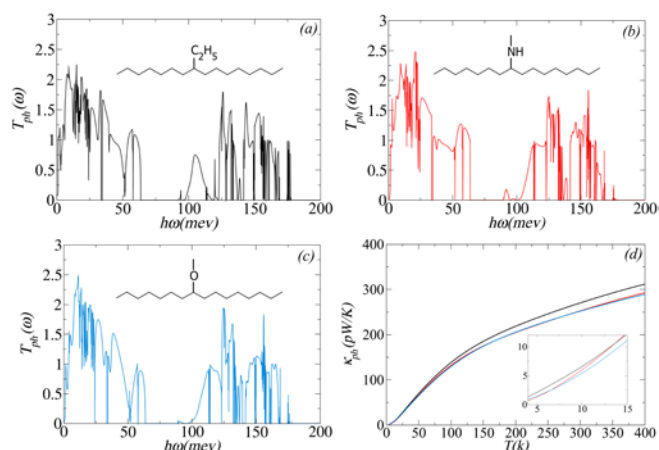


Figure 7. Phonon transmission through alkane trunks with (a) CH_3 , (b) NCH_4 and (c) OCH_3 side branches. Figure (d) shows the phonon thermal conductances of alkyl trunks with OCH_3 (blue), C_2H_5 (black) and NCH_4 (red) branches.

To demonstrate that the Christmas-tree strategy is generic and applies to different molecular trunks, we have also examined phonon transport along molecules with an acene trunk, which is more rigid than an alkane chain (See SI for more details.). As expected, phonon transmission is suppressed by the presence of pendant branches. For such conjugated trunks, electronic transmission in the pi cloud would be increased, which is highly desirable, because the electronic transmission appears in the numerator of the thermoelectric figure of merit ZT.

Figure 6d clearly demonstrates that the suppression of thermal conductance increases with the number of branches. It is interesting to note that in contrast with studies of energy transfer in conjugated dendrimers, the reflection of phonons due to Fano resonances is energy conserving and involves no energy transfer into the branches. A subtle question (addressed in the SI) is whether or not it is more favourable to incorporate a larger number of small though different side branches or a smaller number of more complex branches. As demonstrated in the SI, at least for alkane branches the former is the more effective. For example a structure with one methyl and one ethyl side branch has a lower thermal conductance than a structure with a single propyl side branch. Similarly a structure with single methyl, ethyl and propyl side branches has a lower thermal conductance than a structure with a single hexyl branch. This occurs because each side branch contributes a number of low frequency modes controlled by the relatively-weak coupling between the branches and the backbone and therefore the number of such modes increases with the number of branches. In contrast, although a longer branch has more low frequency modes than a short branch, these are controlled by the intra-molecular couplings, which are generally stronger than intermolecular couplings. Consequently, many shorter branches of different lengths with a collective total of N alkyl units, lead to more low-frequency modes than a single large branch, with the same number of N alkyl units. Molecular Christmas trees formed from branches of different lengths are typically asymmetric and therefore it is of interest to ask if asymmetry is important. As shown in figure S15 of the SI, symmetry can be restored by adding further branches. However, such additions barely change the thermal conductance; therefore we conclude that presence of asymmetry or otherwise is not central to the Christmas tree strategy.

Clearly thermal conductance below a temperature T can only be affected by Fano resonances of frequency ω lower than $k_B T/\hbar$ and therefore to reduce the low-temperature thermal

conductance high-mass pendant branches with low-frequency normal modes of vibration are of interest. To illustrate this feature, figure 8 compares the phonon transmission and thermal conductance of molecule 3 of figure 1b, with the same molecule where all carbons on side branches are replaced by ^{13}C .

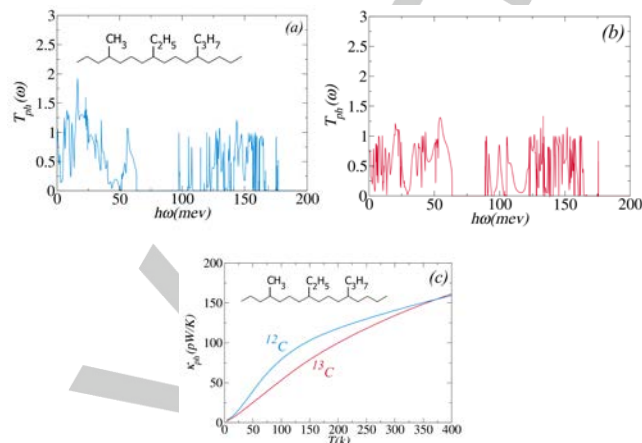


Figure 8. (a) Phonon transmission through molecule 3 in figure 1b (b) Phonon transmission for molecule 3 where all the carbons in the side branches are replaced by ^{13}C . (c) Comparison between the phonon thermal conductance of both systems.

Figure 8c clearly demonstrate that heavier side branches move the Fano-resonances to lower frequencies and suppress the phonon conductance further, in the temperature range of desire.

Finally, to demonstrate that molecular Christmas tree strategy is effective in the presence of metallic electrodes, figure 9 shows the phonon conductance of molecules 2 and 7 when attached to gold leads by S-Me anchor groups. This shows that increasing the number of pendant branches from one to two causes a 18%

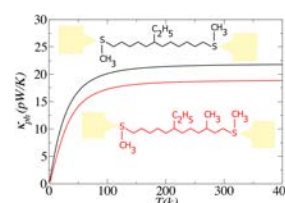


Figure 9. Phonon conductance through molecule 2 and 7 when placed between two gold leads.

decrease in phonon conductance and demonstrates that the Christmas tree strategy remains effective.

In summary, we have outlined a new strategy for controlling phonon transport in Christmas-tree-like molecules and demonstrated its effectiveness in a range of molecules. Pendant groups such as alkane chains are often attached to organic molecules to increase their solubility and processability [50, 51], without affecting electrical properties or to control their conformation [52]. Here we have shown that such groups can be further utilised to minimise the phonon thermal conductance of such organic materials, thereby increasing their attractiveness for thermal management and thermoelectricity. Most theories of thermoelectricity in single molecules assume that electrons remain phase coherent as they pass through the molecule. There is a large body of evidence showing that even at room temperature, electron transport through conjugated molecules containing

pendant groups remains phase coherent, provided the molecules are not too long. For example, figure 4 in ref [53] shows that electron transport through oligo(aryleneethynylene) (OAE) derivatives remains phase coherent up to lengths of order 3nm. These molecules contain hexane pendant groups, which suggests that the presence of pendant groups does not significantly affect the phase coherent nature of electron transport along the trunks of molecules.

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