High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires.

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12th December 2016

Dear Editor,

It is a pleasure to submit our manuscript "**High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires**" for publication in Nanoscale.

Thermoelectricity in single molecules has attracted increasing interest, following the seminal works [Science **2007**, 315, 1568; Nano Lett. **2008**, 8, 715], in which the Seebeck coefficent S of single molecules was measured for the first time. Since that time, attention has turned to the development of strategies for enhancing thermoelectric properties of organic molecules. For example experimental studies [Nano Lett. **2013**, 13, 2889; J. Am. Chem. Soc. **2011**, 133, 8838] reported systematic changes in the thermopower and electrical conductance of aromatic chains of phenyl rings, upon increasing their length and our own recent collaborations [Nano Letters **2013** 13, 2141; Nature Materials **2016** 15, 289] demonstrated how thermoelectricity in fullerenes could be manipulated in the laboratory.

However these studies ignore the crucial role of phonons in determining the efficiency of a thermoelectric material, which is characterised by the dimensionless thermoelectric figure of merit $ZT=GS^2T/\kappa$, where κ the thermal conductance, G the electrical conductance S the Seebeck coefficient and T is the temperature. For a material to be competitive, ZT must exceed unity. To develop strategies for reducing the denominator (ie κ) of ZT and simultaneously maximising the numerator, fundamental studies of thermal transport due to both electrons and phonons are needed, because both electrons and phonons contribute to κ and the electronic contribution to κ is correlated with S and G.

Here, for the first time, we show that κ, G and S combine optimally in "edge-over-edge" zinc porphyrin to yield a world-record, room-temperature figure of merit of $ZT\approx4$. This high value of ZT is a consequence of the low phonon thermal conductance arising from the stacked nature of the porphyrin rings, which hinders phonon transport through the edge-over-edge molecule and enhances the Seebeck coefficient. This discovery is not by chance; it is based on our experience of recent phonon transport calculations, which were carefully benchmarked against experiments [Nature Communications **2016** 7 11281, Nano. Lett. **2015**, 15(11), 7467; Phys. Rev. Lett. **2014**, 113, 060801] and hinted that the edge-over-edge molecules might be winners.

It is extremely difficult to measure the thermal conductance of a single molecule and therefore *ab initio* theoretical studies such as this are likely to lead the way for the foreseeable future and are needed to identify high-performance materials ahead of their synthesis. We are confident that the fundamental knowledge revealed by our study will be of interest to the wider molecular electronics community and to readers of Nanoscale interested in developing the next generation of thermoelectric materials.

Best regards,

Prof Colin Lambert

Journal Name

ARTICLE

High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires.

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If high efficiency organic thermoelectric materials could be identified, then these would open the way to a range of energy harvesting technologies and Peltier coolers using flexible and transparent thin-film materials. We have compared thermoelectric properties of three zinc porphyrin (ZnP) dimers and a ZnP monomer and find the “edge-over-edge” dimer formed from stacked ZnP rings possesses a high electrical conductance, negligible phonon thermal conductance and a high Seebeck coefficient of order 300 µV/K. These combine to yield a room-temperature figure of merit of $ZT \approx 4$, which is the highest room-temperature *ZT* ever reported for an organic material. This high value of *ZT* is a consequence of the low phonon thermal conductance arising from the stacked nature of the porphyrin rings, which hinders phonon transport through the edge-over-edge molecule and enhances the Seebeck coefficient.

Introduction

Thermoelectric materials, which convert heat to electrical energy, could have enormous impact on global energy consumption, but at present their efficiency is too low and the most efficient materials are toxic and have limited global supply. Recently, in an effort to overcome these limitations, thermoelectric effects in low-dimensional structures and molecular-scale systems have begun to be investigated[1-14]. Nanostructures are promising, because transport takes place through discrete energy levels and in molecular-scale junctions, this leads to room-temperature quantum interference, which opens further avenues for enhancing the conversion of heat into electric energy[15].

The efficiency of a thermoelectric (TE) material or device is determined by the dimensionless thermoelectric figure of merit $ZT = GS^2T/\kappa$, where G is the electrical conductance, T is temperature, S is the thermopower (Seebeck coefficient) and $\kappa = \kappa_{el} + \kappa_{ph}$ is thermal conductance due to electrons (κ_{el}) and phonons (κ_{ph}). The Seebeck coefficient characterizes the ability of a thermoelectric material to convert heat to electricity and is defined as $S = -\Delta V/\Delta T$, where ΔV is the voltage difference generated between the two ends of the junction when a temperature difference ΔT is established between them[7, 16-19]. Enhancing the efficiency of TE materials is not easy, because all parameters are correlated. For example at a fundamental level, the electronic properties G, S and κ_{el} are related, because they are all derived from the transmission coefficient $T_{el}(E)$ describing electrons of energy E passing from one electrode to the other through a molecule (see methods). In particular the Seebeck coefficient S is approximately proportional to the slope of the $\ln T_{el}(E)$, evaluated at the Fermi energy E_F, whereas the electrical conductance is proportional to $T_{el}(E_F)$. Therefore, if the Fermi energy lies in a region of high slope, close to a transmission resonance then both G and S are enhanced[20]. On the other hand, to decrease the thermal conductance κ, which appears in the denominator of *ZT,* both electron and phonon transport must be engineered. Therefore, simultaneous consideration of both electron and phonon transport is needed to develop new materials for thermoelectricity.

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* These author contributed equally to this work.

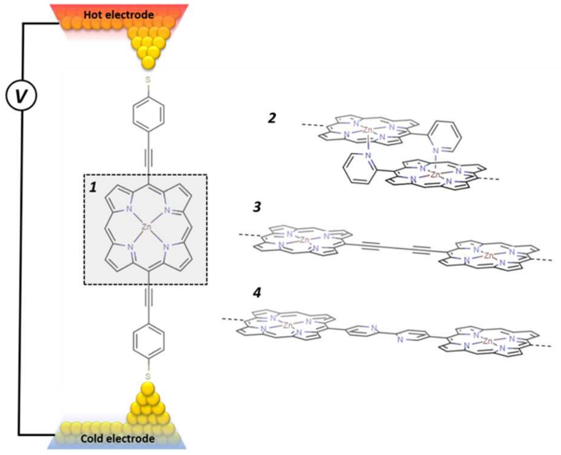

Figure 1. The device structures investigated consist of four different zinc porphyrin (ZnP) monomer structures. (**1**) edge-over-edge ZnP, (**2**) A ZnP-dimer linked by an oligoyne chain, (**3**) A ZnP-dimer linked by two pyridyl rings (**4**).

Since only a few groups worldwide are able to measure the thermal conductance of single molecules, theoretical investigation is needed to identify new strategies to simultaneously suppress phonons and enhance *S* and *G*. Recent proposals to reduce phonon transport in molecular junctions include weakening the overlap between the continuum of vibrational states in the electrodes and discrete vibrational modes of the molecules [21], taking advantage of the weak interaction between different parts of the molecules, as in π–π stacked structures [19] and using the low Debye frequency of electrodes to filter high-frequency phonons[20]. The challenge is to identify new materials and device structures in which such strategies can be realized in the laboratory. In this paper, we present a comparative theoretical study of thermoelectric properties of four different zinc porphyrin structures and elucidate a new strategy for simultaneously increasing their thermopower and reducing their thermal conductance leading to a high value of *ZT*.

Methods

The geometry of each structure consisting of the gold electrodes and a single zinc porphyrin molecule was relaxed to a force tolerance of 20 meV/Å using the SIESTA [28] implementation of density functional theory (DFT), with a double-ζ polarized basis set (DZP) and generalized gradient functional approximation (GGA-PBE) for the exchange and correlation functionals [30, 31], which is applicable to arbitrary geometries. A real-space grid was defined with an equivalent energy cutoff of 150 Ry. From the relaxed *xyz* coordinate of the system, sets of *xyz* coordinates were generated by displacing each atom in positive and negative *x*, *y*, and *z* directions by $\delta q' = 0.01$ Å. The forces in three directions $q_i = (x_i, y_i, z_i)$ on each atom were then calculated by DFT without geometry relaxation. These values of the force is combined with the method described in [20] to calculate dynamical matrix and thermal conductance due to the phonons.

To calculate electronic properties of the molecules in the junction, from the converged DFT calculation, the underlying mean-field Hamiltonian *H* was combined with our quantum transport code, GOLLUM [29] to calculate the transmission coefficient $T_{el}(E)$ for electrons of energy E passing from the source to the drain. The electrical conductance $G_{el}(T) = G_0L_0$, the electronic contribution of the thermal conductance $\kappa_{el}(T) = (L_0L_2 - L_1^2)/hTL_0 =$ and the thermopower $S(T) = -L_1/eTL_0$ of the junction are calculated from the electron transmission coefficient $T_{el}(E)$ where$L_n(T) = \int_{-\infty}^{\infty} dE(E - E_F)^n T_{el}(E)\left(-\frac{\partial f(E,T)}{\partial E}\right)$ and $f(E,T)$ is the Fermi–Dirac probability distribution function $f(E,T) = (e^{(E-E_F)/K_BT} + 1)^{-1}$, T is the temperature, E_F is the Fermi energy, $G_0 = 2e^2/h$ is the conductance quantum, e is electron charge, and h is the Planck's constant.

Results and discussion

Figure 1 shows four different zinc porphyrin (ZnP) structures investigated below. The first **1** is a ZnP monomer[22]. Structure **2** is an edge-over-edge ZnP dimer, in which two ZnPs are locked together by *meso*-position pyridines[23, 24]. Structure **3** comprises two ZnPs connected by an oligoyne linker[22, 25, 26], while **4** comprises two ZnPs connected through *meso*-position pyridines[27]. In what follows, our aim is to demonstrate that of the above structures, the edge-over-edge ZnP dimer **2** is by far the most efficient thermoelectric energy converter. From a structural point of view, this arises because the pyridyl rings of **2** are locked and therefore ring rotation, which would otherwise reduce the electrical conductance, is eliminated. Secondly, the edge-over-edge rigid conformation of **2** increases its rigidity, which pushes the internal vibrational modes to higher frequencies. This reduces room temperature thermal conductance, because modes with frequencies greater than ~25meV do not contribute significantly. Thirdly, longitudinal modes entering one end of the edge-over-edge molecule must convert to flexural modes to pass from one porphyrin to the other, which creates extra phonon scattering and reduces thermal conductance.

For the structures of figure 1, figure 2 shows the transmission coefficients for electrons with energy *E* and phonons of energy $\hbar\omega$, passing through a molecule from the left electrode to the right electrode, calculated using the method described in reference[20]. We first carry out geometry optimization of each molecule placed between two gold electrodes using the SIESTA[28] implementation of density functional theory (DFT) to find the ground state optimized positions of the atoms relative to each other (see methods). From the ground state geometry, we obtain the mean-field Hamiltonian of each system comprising both electrodes and molecule and use our transport code GOLLUM[29] to calculate the transmission coefficients $T_{el}(E)$ (see methods). In each case the optimal angle between the porphyrins is zero, which corresponds to the maximum conductance that could be obtained[22]. The electronic transport properties of **1** and **3** have been studied experimentally in the literature[22], so we used these to benchmark our calculations. As shown in table S1 of the supporting information, our calculated conductances for these molecules are in good agreement with experiment. The electron transmission of **4** is much smaller than both **1**, **2** and **3**, whereas the transmission of **2** is either equal to that of **3** near the HOMO resonance or lower in the vicinity of the middle of the HOMO-LUMO gap. As shown in figure (SI2), this is reflected in the electrical conductance as a function of temperature.

To calculate the vibrational properties of each structure, we use the harmonic approximation to construct the dynamical matrix *D*. Each atom is displaced from its ground-state equilibrium position by $\delta q'$ and $-\delta q'$ in *x*, *y*, and *z* directions and the forces on all atoms calculated in each case. For 3n degrees of freedom (*n* = number of atoms), the $3n \times 3n$ dynamical matrix $D_{ij} = (F_i^q(\delta q_j') - F_j^q(-\delta q_j'))/2M_{ij}\delta q_j'$ is constructed, where *F* and *M* are the force and mass matrices (see reference[20] for more details). For an isolated molecule, the square root of the eigenvalues of *D* determines the frequencies ω associated with the vibrational modes of the molecule in the junction (See SI). For a molecule within a junction, the dynamical matrix describes an open system composed of the molecule and two semi-infinite electrodes and is used to calculate transmission coefficient $T_{ph}(\omega)$ for phonons with energy $\hbar\omega$ passing through the molecule from the right to the left electrodes[20].

Figures 2b-e shows $T_{ph}(\omega)$ for the four structures of figure 1. It is apparent that the widths of the resonances in the edge-over-edge ZnP-dimer **2** are smaller than those of the other structures and the low energy phonons (in the range 2-5 *meV*) are either suppressed or pushed to the higher frequencies. This can be demonstrated using the participation ratio of the dimer molecular cores **2**, **3** and **4** and comparing the integrated density of states $N(\hbar\omega)$ of **2**, **3** and **4**. As shown in figure S1 of the SI, the participation ratio of the molecule core (ZnPs and linkers) connected to the gold surface is mostly due to the in-plane (PRy) and out of plane (PRx) transverse modes in structures **3** and **4**, whereas out-of plane transverse modes are mainly suppressed or converted to in-plane transverse modes and moved to the higher frequency, reflecting the higher rigidity of the edge-over-edge structure. In addition, the integrated density of states are almost the same for **3** and **4**, whereas for low frequencies, the integrated density of states of **2** is smaller than **3** and **4**. This means the thermal conductance is reduced significantly in **2**, because transmission of the low energy modes is suppressed due to the scattering from in-plane modes to cross-plane transverse modes. In addition, some modes are pushed to higher frequency, although this is smaller effect compared with the suppression of low frequency transmission. Overall, these two effects combine to yield a lower phonon thermal conductance in **2**.

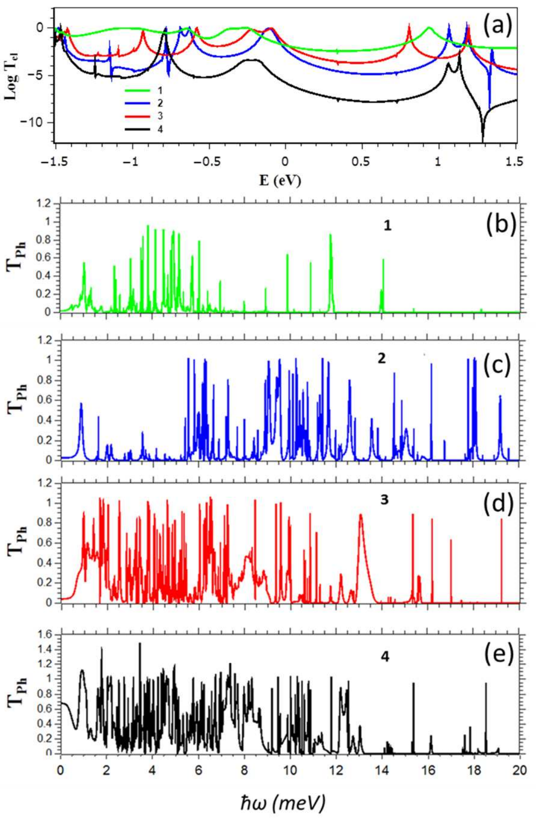

Figure 2. (a) Electron transmission coefficients as a function of energy and (b-e) phonon transmission coefficients as a function of $\hbar\omega$ for the ZnP monomer **1**, the edge-over-edge ZnP **2**, the ZnP dimer connected via an oligoyne chain **3** and ZnP dimer connected through pyridyl rings **4**.

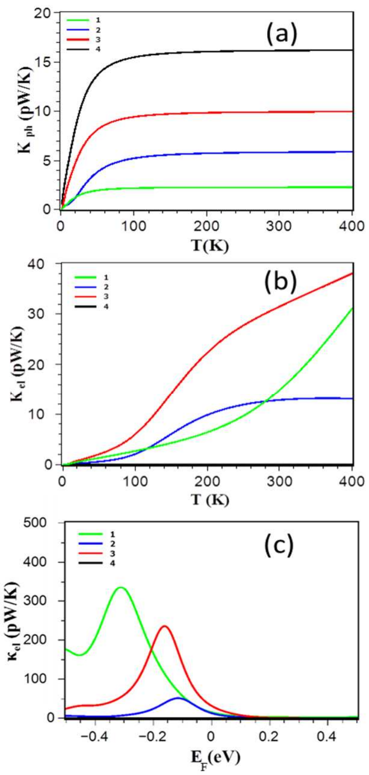

Figure 3. (a) Phonon thermal conductances (b) Electronic thermal conductance as a function of temperature, (c) Room-temperature electronic thermal conductance as a function of Fermi energy E_F calculated using the DFT-predicted Fermi energy. Results are shown for the ZnP monomer **1**, the edge-over-edge ZnP **2**, the ZnP dimer connected through an oligoyne chain **3** and the ZnP-dimer connected through pyridyl rings **4**.

The thermal conductance of the junction ($\kappa = \kappa_{ph} + \kappa_{el}$) is obtained by summing the contributions from both electrons (κ_{el}) and phonons (κ_{ph}). The electronic (phonon) thermal conductances are calculated from the electron (phonon) transmission coefficients shown in figure 2a-e. Figure 3a shows that the ZnP monomer **1** has the lowest value of κ_{ph} while **4** has the highest. This is counter-intuitive, because one would expect a higher thermal conductance for shorter molecules. However, due to the more rigid nature of the monomer, its vibrational modes are pushed to the higher frequencies and therefore their contribution to the room temperature conductance is suppressed. In addition, figure 3b,c shows that the thermal conductance due to the electrons κ_{el} of the dimer ZnP **2** is higher than those of the edge-over-edge ZnP and structures **1** and **4** for a wide range of energy in the vicinity of DFT predicted Fermi energy. The crucial point is that almost for all Fermi energies, the electronic contribution to the thermal conductance is higher than the phonon contribution. This is significant, because to achieve a high-ZT material, one needs to only focus on engineering the electronic properties of structure **2**.

To examine the thermoelectric properties of **1**-**4**, we obtained the Seebeck coefficient of all structures from the electron transmission coefficient $T_{el}(E)$, as described in the methods. Figure 4a shows the Seebeck coefficients as a function of Fermi energy E_F (and also as a function of temperature in figure S3 of the SI) and reveals that the edge-over-edge ZnP dimer **2** has a higher Seebeck coefficient than **1**, **2** and **4** due to the higher slope of $\ln T_{el}(E_F)$ over a wide range of Fermi energies between the HOMO and LUMO. Since the electronic contribution to the thermal conductance is higher in **1**, **2** and **3**, the contribution of the phonons is negligible. Furthermore the electrical conductance is proportional to the electronic thermal conductance, so they cancel each other in *ZT*. Consequently as shown in figure 4b, due to the high Seebeck coefficient of the edge-over-edge dimer, a *ZT* as high as ≈4 is obtained when E_F lies in a wide energy window in the vicinity of the DFT-predicted Fermi energy. Figure 4b also shows that the less-rigid structure **4** is not promising for efficient conversion of the heat to electricity. Although all of these structures are made from ZnP, this study shows the importance of the molecular design. The more rigid edge-over-edge ZnP dimer **2** shows very high *ZT*, whereas the less conductive structure **3** is unattractive for thermoelectricity.

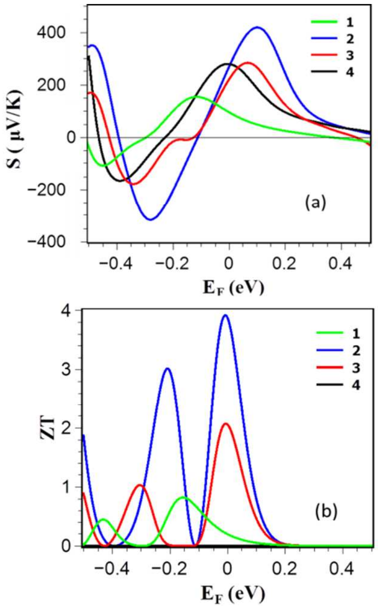

Figure 4. (a) Seebeck coefficient S and (b) full thermoelectric figure of merit ZT as a function of Fermi energy for the ZnP monomer **1**, edge-over-edge ZnP **2**, ZnP connected through an oligoyne chain **3** and ZnP-dimer connected through pyridyl rings **4**.

Conclusions

In summary, we have compared thermoelectric properties of three ZnP dimers and a ZnP monomer and find the edge-over-edge -like dimer possesses a negligible phonon thermal conductance and a high Seebeck coefficient of order 300 μV/K. These transport properties combine to yield a room-temperature figure of merit of ZT≈4, which is the highest room-temperature ZT ever reported for an organic material. This high ZT value is a consequence of low phonon thermal

Acknowledgements

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High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires.

Supporting information

High-performance thermoelectricity in edge-over-edge zinc-porphyrin molecular wires.
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The wavefunction (φ) corresponding to the vibrational modes are the eigenvectors of the Dynamical Matrix D:

$$D\varphi = \omega^2\varphi \qquad (S1)$$

The weight P$_i$ of the wavefunction (φ) of the degree of freedom (q') on each modes *i* can be calculated as:

$$P_i = \sum_{j\in q'} |\varphi_{ij}|^2 \qquad (S2)$$

The participation ratio of the modes associated with the center of mass motion on x = [1 0 0], y = [0 1 0] and z = [0 0 1] directions can be calculated as:

$$R = \sqrt{Q_{x'}^2 + Q_{y'}^2\ + Q_{z'}^2} \qquad (S3)$$

where

$$Q_\beta = \langle\varphi|\beta\rangle\ /\sqrt{N} \qquad (S4)$$

$$and \quad \beta = x'\,, y'\ \,, z'$$

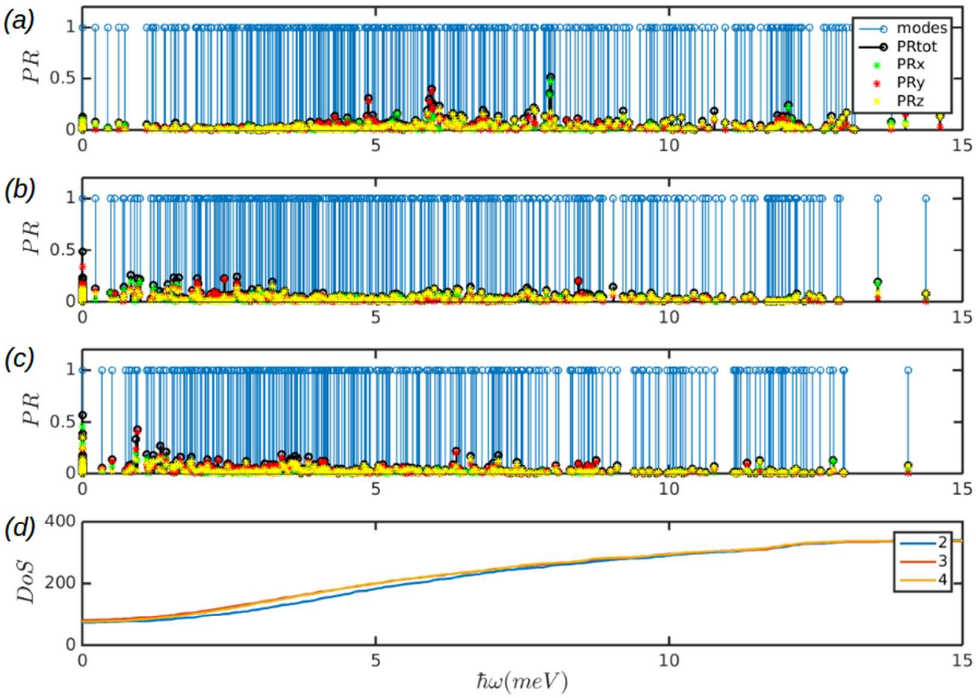


Figure S1. Participation ratio of the molecular cores consisting of the ZnP(s) and linkers on the modes associated with whole of the molecule attached to the surface of the gold electrodes. For the edge-over-edge structre (**2**), the modes has pushed to the higher energies and only in plane transverse modes are transmitted. Out-of plane transverse mode are suppressed due to the more rigid nature of (**2**) compared to (**3**) and (4) in out-of-plane transverse direction. (d) shows the density of modes for (**1-3**).

Structure	**Experimental Conductance**	**Theory Conductance**
Monomer (**1**)	$2.7\text{x}10^{-5}$	$1.09\text{x}10^{-1}$
Dimer (**3**)	$1.55\text{x}10^{-5}$	$6.35\text{x}10^{-2}$
Ratio (monomer/dimer)	1.74	1.72

Table.S1 The experimental and theoretical electrical conductance and their ratio for dimer and monomer.

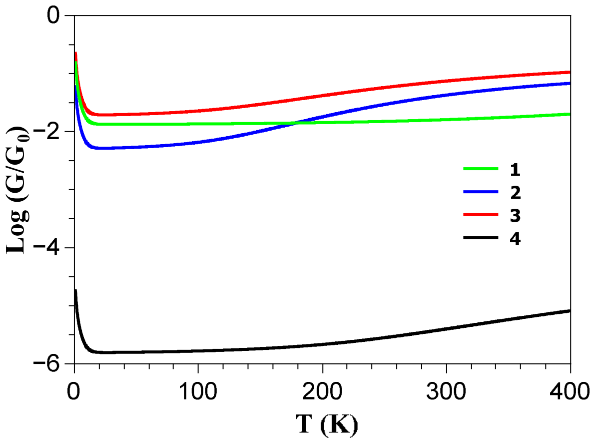


Figure S2. The electrical conductance as a function of temperature for ZnP monomer (**1**), edge-over-edge ZnP (**2**), ZnP connected through an oligoyne chain (**3**) and ZnP-dimer connected through pyridyl rings (**4**).

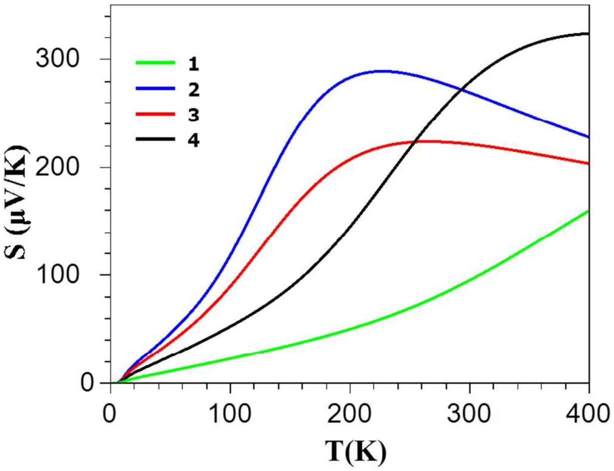
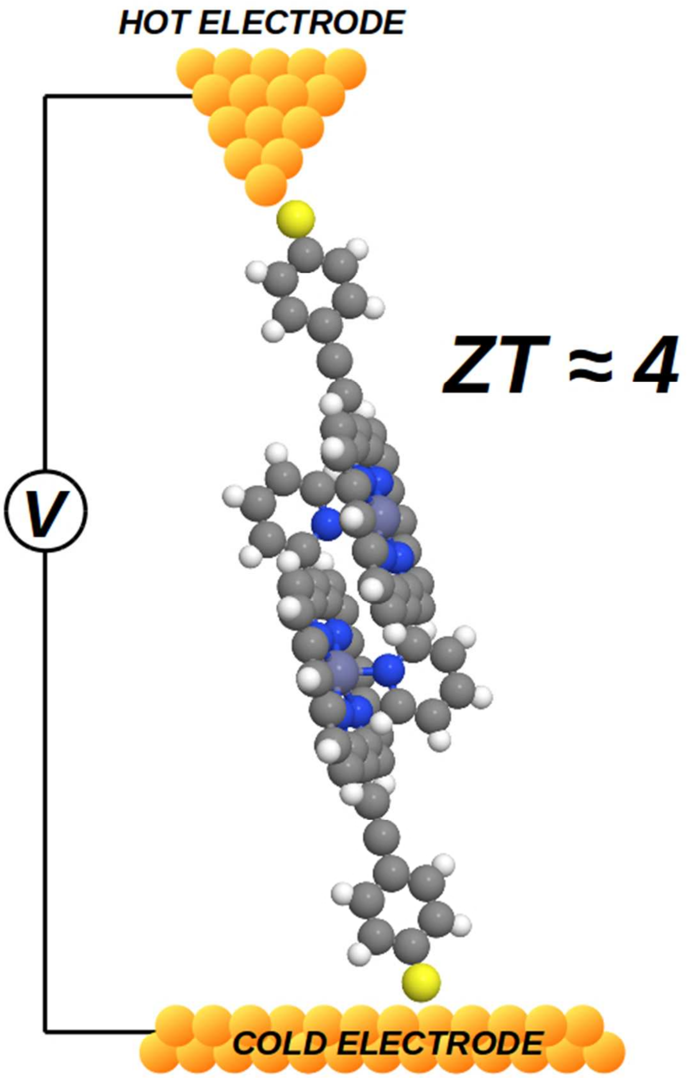


Figure S3. The Seebeck coefficient S as a function of temperature for ZnP monomer (**1**), edge-over-edge ZnP (**2**), ZnP connected through an oligoyne chain (**3**) and ZnP-dimer connected through pyridyl rings (**4**).


HOT ELECTRODE
ZT ≈ 4
V
COLD ELECTRODE