Supporting information.

Tuning the thermoelectric properties of metalloporphyrin molecular wire sandwiches.

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Thermoelectric coefficients

To understand how transport resonances lead to high thermoelectric performance, we note that in the linear-response regime, the electric current \( I \) and heat current \( \dot{Q} \) passing through a device is related to the voltage difference \( \Delta V \) and temperature difference \( \Delta T \) by\textsuperscript{[38, 39]}

\[
\left( \frac{I}{\dot{Q}} \right) = \frac{1}{\hbar} \begin{pmatrix} e^2 L_0 & e L_1 \\ e L_1 & e L_2 \end{pmatrix} \left( \frac{\Delta V}{\Delta T} \right)
\]

(1)

where \( T \) is the reference temperature. Since transport through single molecules is phase-coherent, even at room temperature, the coefficients \( L_n \) are given by \( L_n = L_n^\uparrow + L_n^\downarrow \) \( (n = 0, 1, 2) \), where

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

(2)

In this expression, \( T^\sigma(E) \) is the transmission coefficient for electrons of energy \( E \), spin of \( \sigma = [\uparrow, \downarrow] \) passing through the molecule from one electrode to the other\textsuperscript{[40]} and \( f(E,T) \) is Fermi distribution function defined as \( f(E,T) = [e^{(E - E_F)/k_B T} + 1]^{-1} \) where \( k_B \) is Boltzmann’s constant. 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 (\( \kappa_e \)):

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

(3)
where

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

(4)

\[ S = -\frac{\Delta V}{\Delta T} = \frac{1}{eT} \frac{L_1}{L_0} \]  

(5)

\[ \Pi = \frac{1}{eL_0} \]  

(6)

\[ \kappa_e = \frac{1}{kT} \left( \frac{L_2}{L_0} - \frac{(L_1)^2}{L_0} \right) \]  

(7)

\[ \kappa_e \approx L_0^2 TG, \]  

(8)

From the above expressions, the electronic thermoelectric figure \( ZT_e = S^2 GT / \kappa_e \) is given by

\[ ZT_e = \frac{(L_1)^2}{L_0 L_2 - (L_1)^2} \]  

(9)

For \( E \) close to \( E_F \), if \( T(E) \) varies only slowly with \( E \) on the scale of \( k_B T \) then these formulae take the form \[^{[41]}\):

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

(10)

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

(11)

the power factor is given by \( \sigma_{ec} S^2 \), where \( \sigma_{ec} \) is the electrical conductivity \( \frac{G L}{A} \), \( L \) and \( A \) are the length and sector area of the device respectively.

\[ \alpha = \left( \frac{k_B}{e} \right) \frac{\pi^2}{3} \]  

is the Lorentz number. Equation (11) demonstrates that \( S \) is enhanced by increasing the slope of \( \ln T(E) \) near \( E=E_F \) and hence it is of interest to explore whether or not the ability to vary the metal centre in metallo-porphyrins can be used to move resonances close to \( E_F \).
Figure S1 The spin up, spin down and total transmission coefficient as a function of energy for (a) Co-DPP, (b) Cu-DPP, (c) Ni-DPP and (d) Zn-DPP.

Figure S2 The room-temperature electrical conductances for Co-DPP, Cu-DPP, Ni-DPP and Zn-DPP, over a range of Fermi energies at room temperature for each metallo-porphyrin.
Figure S3 Shows Seebeck coefficient $S$ (thermopower) as a function of temperature, at $E_F = E_{DFT}^F$.

Figure S4 Shows the figure of merit (ZT) as a function of temperature, at $E_F = E_{DFT}^F$. 
Figure S5 Shows electronic contribution to the thermal conductance as a function of temperature, at $E_F = E_F^{DFT}$

Figure S6 Phonon density of state for Cu, Ni, Co and Zn CPP

The wavefunction ($\psi$) corresponding to the vibrational modes are the eigenvectors of the Dynamical Matrix D:

$$D \psi = \omega^2 \psi$$  \hspace{1cm} (S1)
The weight $P_i$ of the wavefunction ($\varphi$) of the degree of freedom ($\theta^i$) on each modes $i$ can be calculated as:

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

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:

$$R = \sqrt{Q^2_x + Q^2_y + Q^2_z} \quad (S3)$$

where

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

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

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**Figure S7.** Participation ratio of the molecular for Cu, Ni, Co and Zn CPP. The number of modes between $\hbar \omega = 0$ and $3\text{meV}$ is 35 for Co, 53 for Zn, 52 for Ni and 53 for Cu. All vibrational modes are calculated in the presence of the axial ligands.
**Figure S8** Electrical and thermal conductance due to the electrons ratios. It is apparent that the ratio is not constant therefore; Wiedemann-franz law is violated.

**Figure S9** Electrical and thermal conductance due to the electrons ratios. It is apparent that the ratio is not constant therefore; Wiedemann-franz law is violated.
**Figure S10** Schematic shows the central and external scattering regions and the principle layers in left and right leads in Gollum code.

All results so far have been obtained using LDA. To demonstrate that results would not change the results significantly using an alternative approximation such as GGA, the following examples show a comparison between results obtained using GGA and LDA. Clearly there are small differences, but the qualitative trends are unchanged.

**Figure S11** The transmission coefficient for (a) Co-DPP and (b) Ni-DPP as a function of Fermi energy, obtained LDA and GGA functionals.
To enable the reader to reproduce our results, we include as an example, the following Gollum input file:

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# type: scalar
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# name: ERange
# type: matrix
# rows: 1
# columns: 3
-3.00 3.00 1501.00

# name: leadp
# type: matrix
# rows: 2
# columns: 3
3 2 0
3 2 0

# name: atom
# type: matrix
# rows: 261
# columns: 4
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2 1 3 0
3 1 3 0
4 1 3 0
5 1 3 0
6 1 3 0
7 1 3 0
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