Supporting information.

Tuning the thermoelectric properties of metalloporphyrin molecular wire sandwiches.

Mohammed Noori[1,2] , Hatef Sadeghi[1*], Qusiy Al-Galiby[1,3], Steven W. D. Bailey[1], and Colin J. Lambert[1*].

[1]Quantum Technology Centre Department of Physics, Lancaster University, Lancaster LA1 4YB, UK

[2]Department of Physics, College of Science, Thi-Qar University, IRAQ

[3]Department of Physics, College of Education, Al Qadisiyah University, IRAQ

**Corresponding author: h.sadeghi@lancaster.ac.uk; c.lambert@lancaster.ac.uk*

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 ΔV and temperature difference ΔT by[38, 39]

$$\begin{pmatrix} I \\ \dot{Q} \end{pmatrix} = \frac{1}{h}\begin{pmatrix} e^2 L_0 & \frac{e}{T}L_1 \\ eL_1 & \frac{1}{T}L_2 \end{pmatrix}\begin{pmatrix} \Delta V \\ \Delta T \end{pmatrix} \qquad (1)$$

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

$$L_n^{\sigma} = \int_{-\infty}^{\infty} (E - E_F)^n T^{\sigma}(E)\left(-\frac{\partial f(E,T)}{\partial E}\right)dE \qquad (2)$$

In this expression, $T^{\sigma}(E)$ is the transmission coefficient for electrons of energy E, spin of σ = [↑,↓]passing through the molecule from one electrode to the other[40] and $f(E,T)$ is Fermi distribution function defined as $f(E,T) = [e^{(E-E_F)/k_BT} + 1]^{-1}$ where k_B is Boltzmann's constant. Equation (1) can be rewritten in terms of the electrical conductance (G), thermopower (S), Peltier coefficient (∏), and the electronic contribution to the thermal conductance (κ_e):

$$\begin{pmatrix} \Delta V \\ \dot{Q} \end{pmatrix} = \begin{pmatrix} 1/G & S \\ \Pi & \kappa_e \end{pmatrix}\begin{pmatrix} I \\ \Delta T \end{pmatrix} \qquad (3)$$

where

$$G = \frac{e^2}{h}L_0 \qquad (4)$$

$$S = -\Delta V/\Delta T = \frac{1}{eTL_0}L_1 \qquad (5)$$

$$\Pi = \frac{1L_1}{eL_0} \qquad (6)$$

$$\kappa_e = \frac{1}{hT}\left(L_2 - \frac{(L_1)^2}{L_0}\right) \qquad (7)$$

$$\kappa_e \approx L_0^{\sigma}TG, \qquad (8)$$

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

$$ZT_e = \frac{(L_1)^2}{L_0L_2 - (L_1)^2} \qquad (9)$$

For E close to EF, if T(E) varies only slowly with E on the scale of k_BT then these formulae take the form[41]:

$$G(T) \approx \left(\frac{2e^2}{h}\right)T(E_F), \qquad (10)$$

$$S(T) \approx -\alpha eT\left(\frac{d\ lnT(E)}{dE}\right)_{E=E_F}, \qquad (11)$$

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

where $\alpha = \left(\frac{k_B}{e}\right)^2\frac{\pi^2}{3}$ 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.

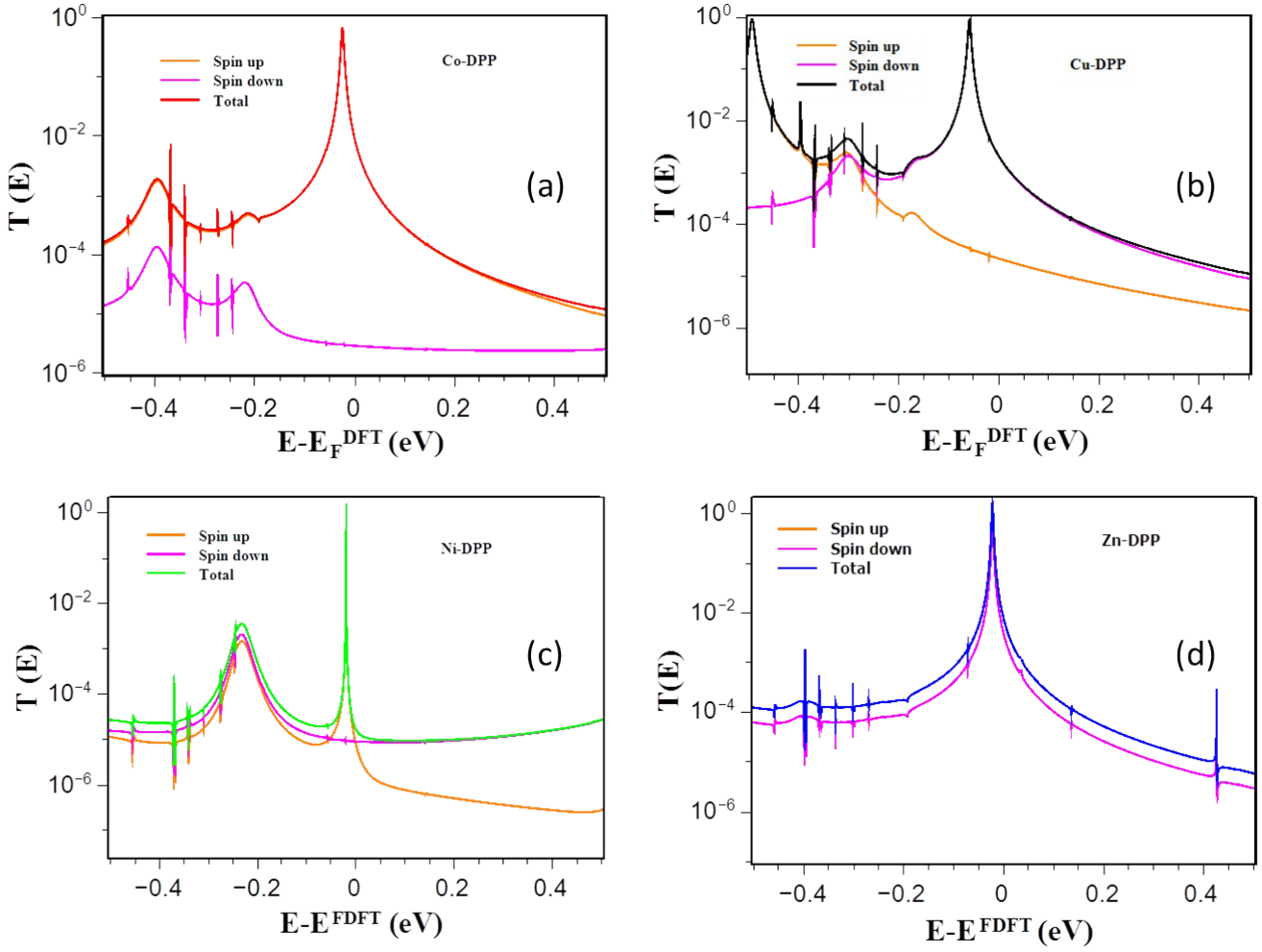

Figure S1 The spin up, spin down and total transmission coefficient as a function of energy for (a) Co-DPP, (b) Cu-DDP, (c) Ni-DPP and (d) Zn-DDP..

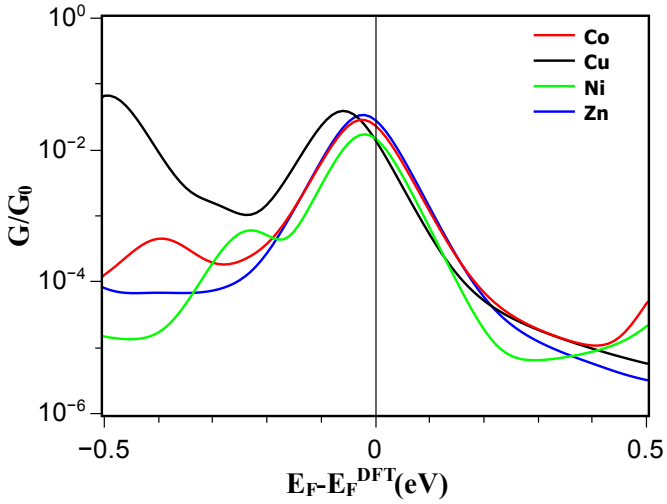

Figure S2 The room-temperature electrical conductances for Co-DPP, Cu-DPP, Ni-DPP and Zn-DPP, over a range of Fermi energies at room temperature for each metallo-porphyrin.

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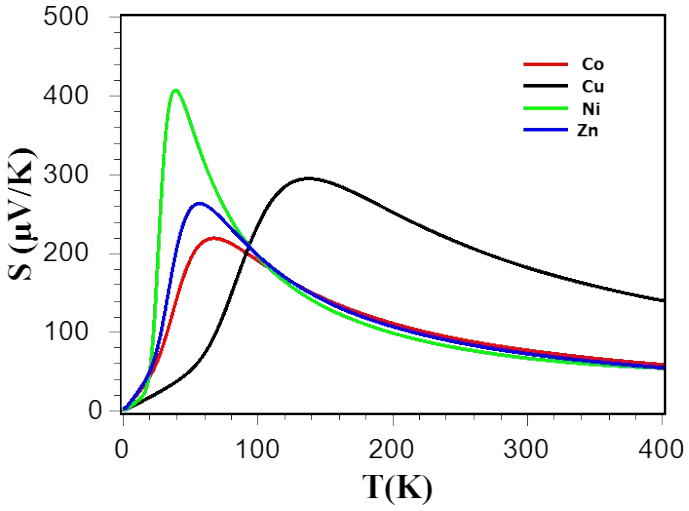

Figure S3 Shows Seebeck coefficient S (thermopower) as a function of temperature, at $E_F = E_F^{DFT}$.

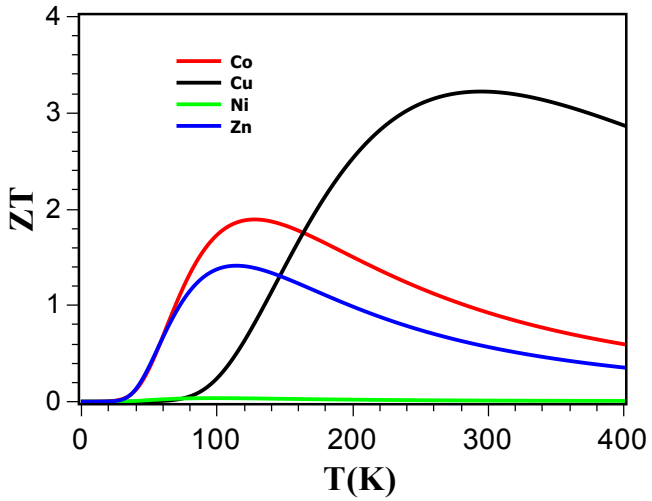

Figure S4 Shows the figure of merit (ZT) as a function of temperature, at $E_F = E_F^{DFT}$

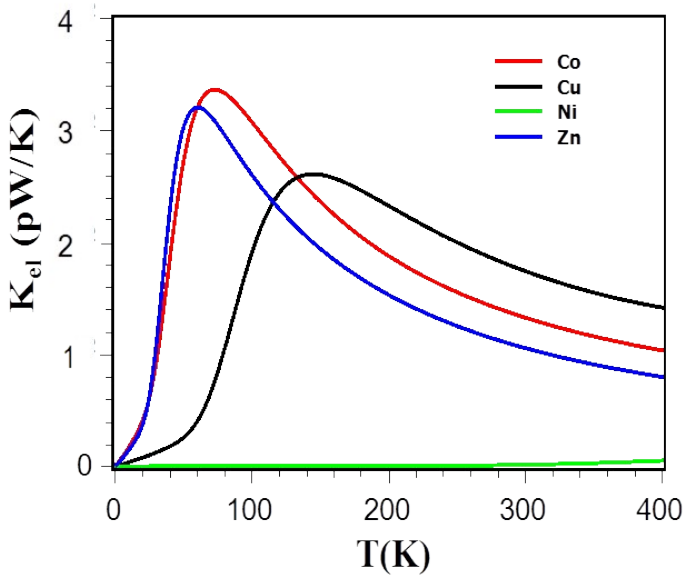

Figure S5 Shows electronic contribution to the thermal conductance as a function of temperature, at $E_F = E_F^{DFT}$

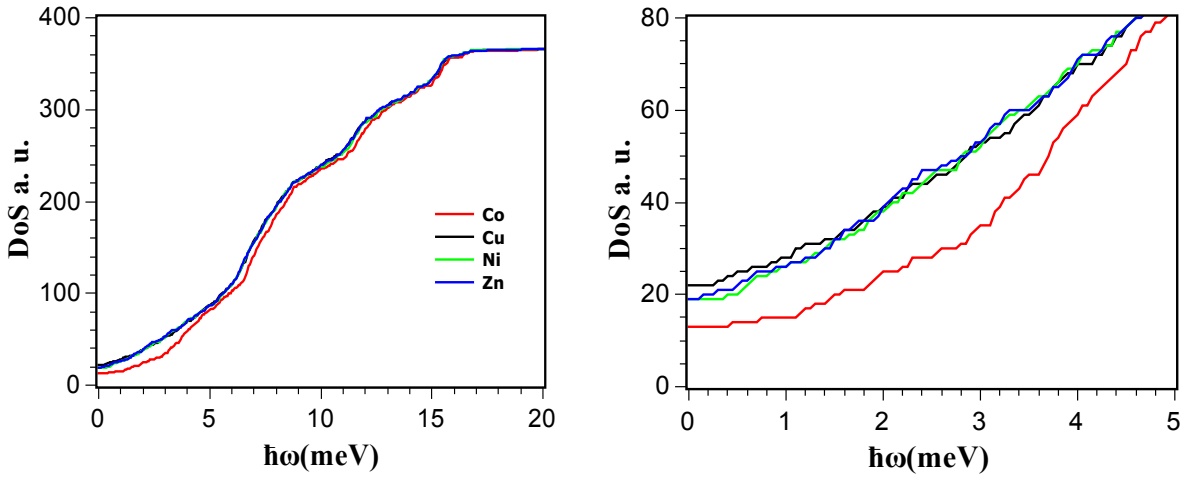

Figure S6 Phonon density of state for Cu, Ni, Co and Zn CPP

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

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

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

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

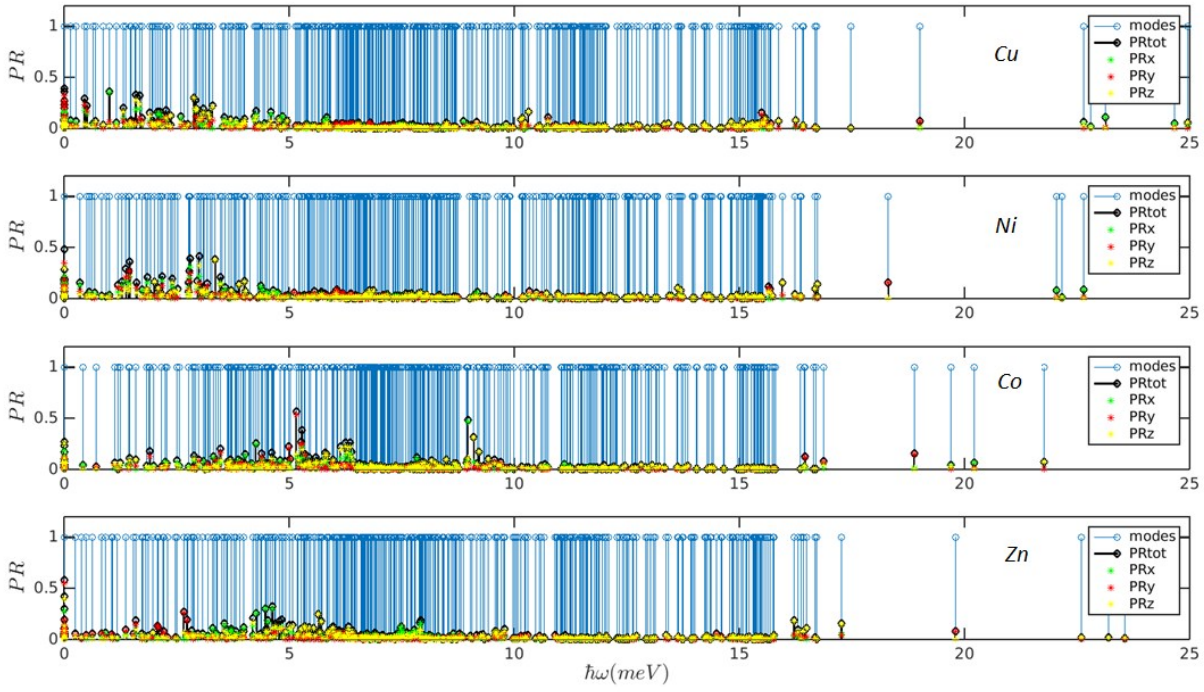

Figure S7. Participation ratio of the molecular for Cu, Ni, Co and Zn CPP. The number of modes between $\hbar\omega$ =0 and 3meV is 35 for Co, 53 for Zn, 52 for Ni and 53 for Cu. All vibrational modes are calculated in the presence of the axial ligands

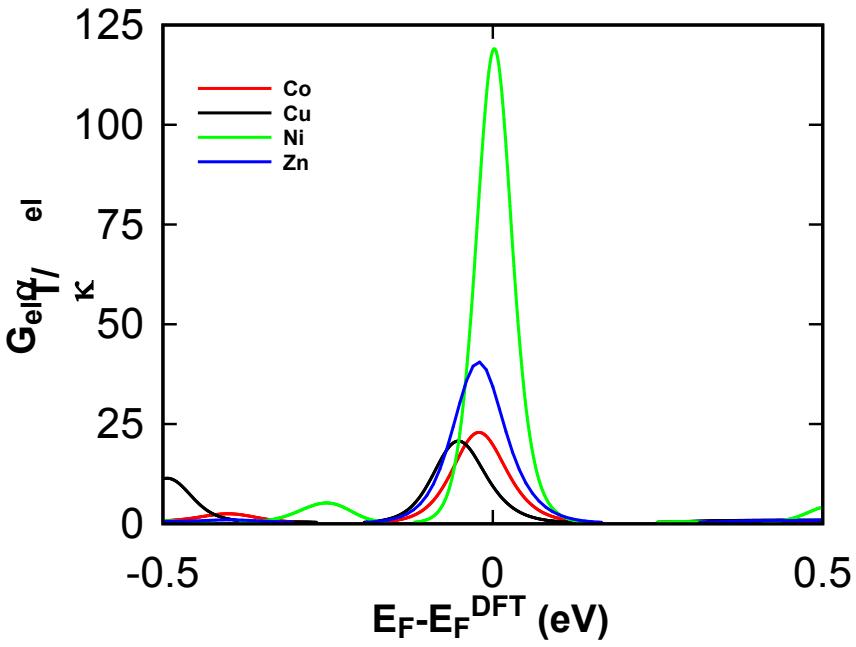

Figure S8 Electrical and thermal conductance due to the electrons ratios. It is apparent that the ratio is not constant therefore; Wiedemann-franz law is violated.

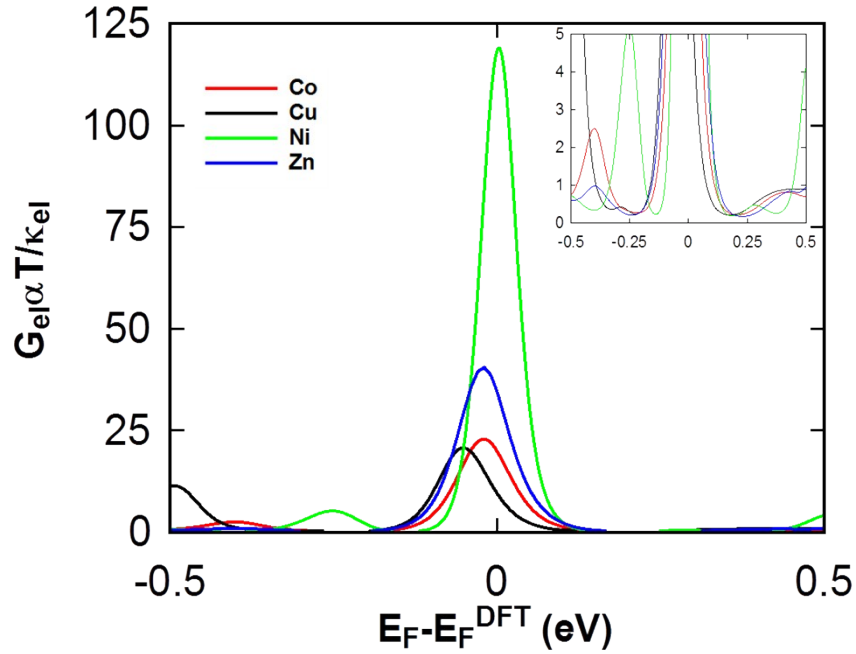

Figure S9 Electrical and thermal conductance due to the electrons ratios. It is apparent that the ratio is not constant therefore; Wiedemann-franz law is violated.

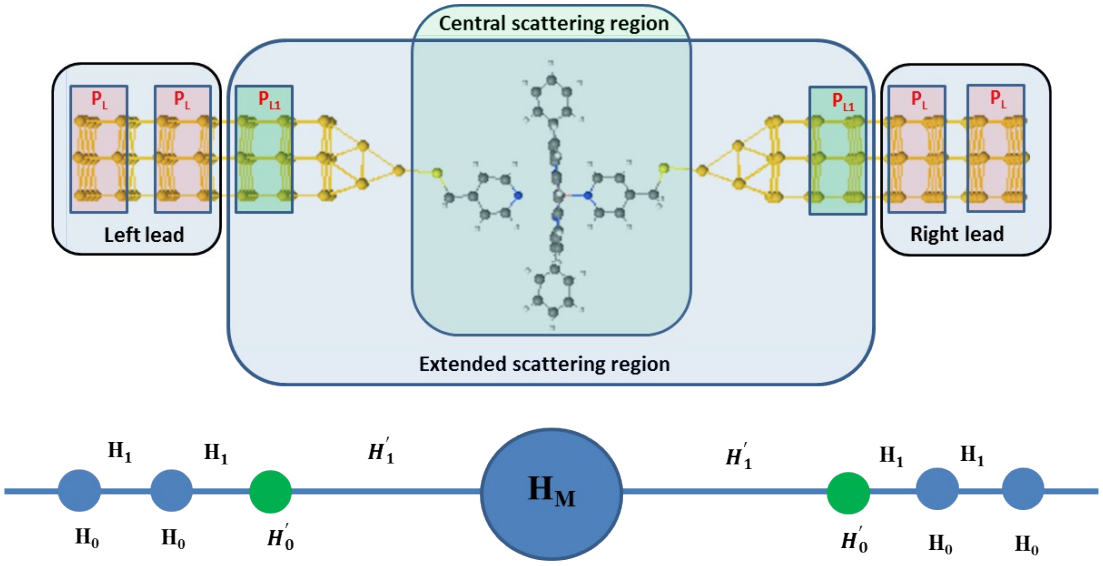

Figure S10 Schematic shows the central and external scattering regions and the principle layers in left and right leads in Gollum code

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.

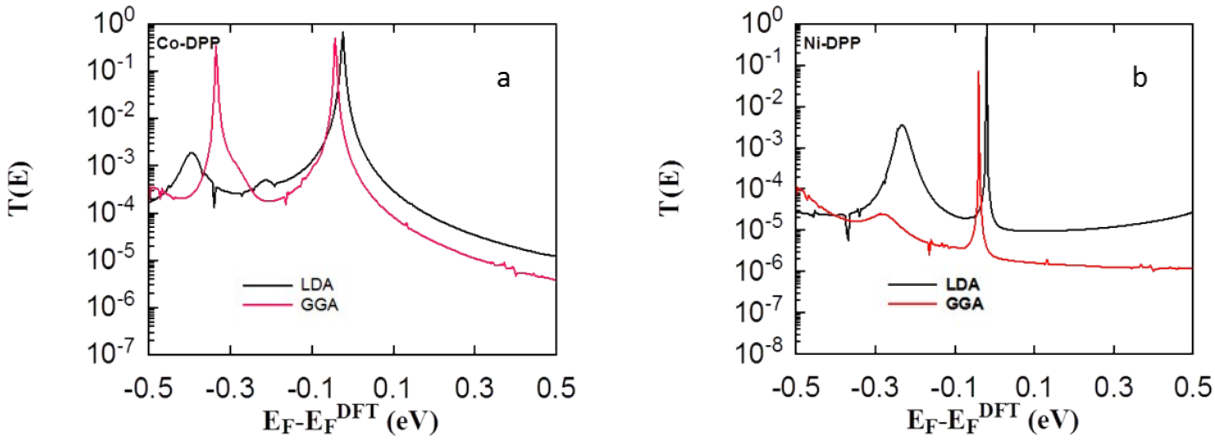

Figure S11 The transmission coefficient for (a) Co-DPP and (b) Ni-DPP as a function of Fermi energy, obtained LDA and GGA functionals.

To enable the reader to reproduce our results, we include as an example, the following Gollum input file:

```
# name: Mode
# type: scalar
1
# 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
1        1        3        0
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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