

Supporting information

Connectivity-driven bi-thermoelectricity in heteroatom-substituted molecular junctions

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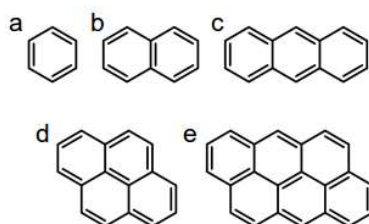


Fig. S1. Examples of polyaromatic hydrocarbon (PAH) molecular cores. (a) benzene, (b) naphthalene, (c) anthracene, (d) pyrene and (e) anthanthrene.

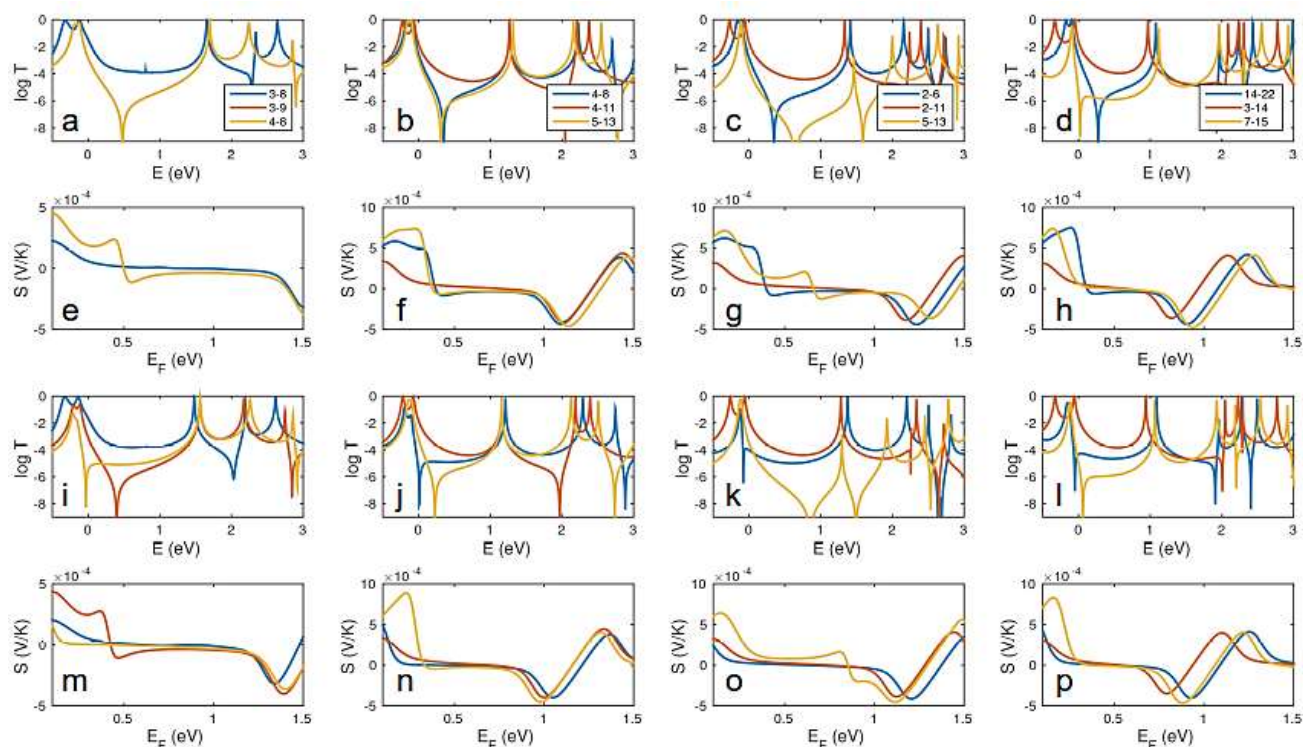


Fig. S2. Full transmission coefficients for connectivities shown in figure 3 and 6 obtained using DFT Hamiltonians and their corresponding Seebeck coefficients. (a-h) for parent molecules without heteroatom and (i-p) with heteroatom substitution.

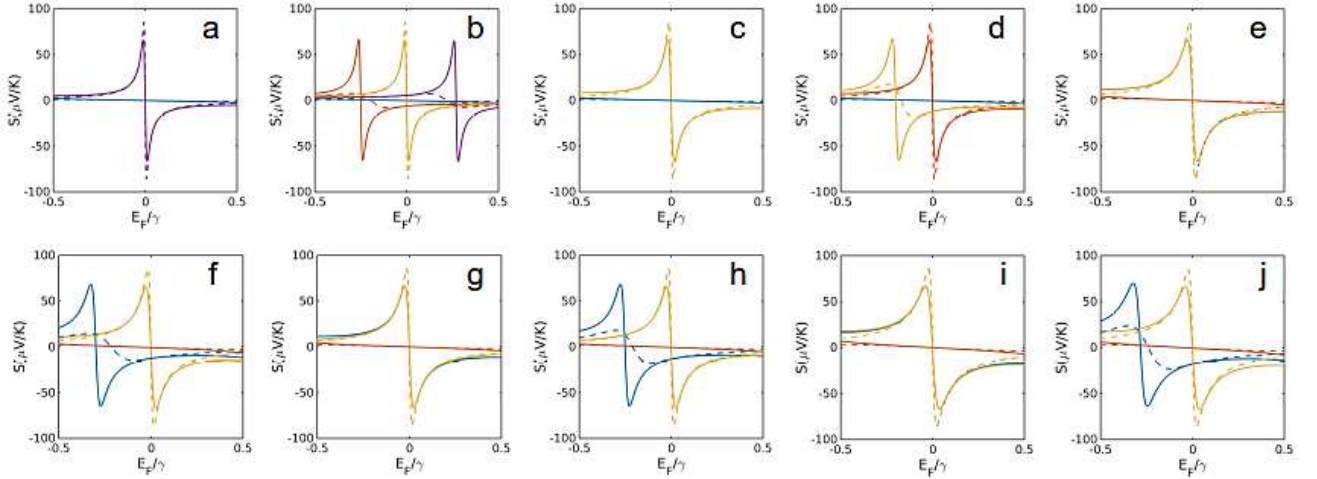


Fig. S3. Seebeck coefficient in (a) benzene, (b) pyridine, (c) naphthalene, (d) quinolone, (e) anthracene, (f) anthracene with heteroatom substitution, (g) pyrene, (h) pyrene with heteroatom substitution, (i) anthanthrene and (j) anthanthrene with heteroatom substitution at $T = 30$ K. Solid lines are obtained using transmission coefficient $T(E) \propto G(E)^2$. Dashed (Solid) lines are obtained using simple description of Seebeck coefficient from equations 4.

Mid-gap theory of thermoelectricity

To rationalize the results of figures 1-6, we now present a theory of thermoelectricity for Fermi energies near the mid-gap of PAH molecules. Recently we predicted that for molecules, whose central core is weakly connected to external electrodes, provided the Fermi energy lies within the HOMO-LUMO gap, the ratio of conductances $\sigma_{i,j}$ and $\sigma_{l,m}$ associated with connectivities i and j or l and m is given by the ‘magic ratio rule’ (MRR)^{20,21} $\sigma_{i,j}/\sigma_{l,m} = \tau_{i,j}(E_F)/\tau_{l,m}(E_F) = [M_{i,j}(E_F)/M_{l,m}(E_F)]^2$, where $\tau_{i,j}(E_F)$ and $\tau_{l,m}(E_F)$ are core transmission coefficients and contain no information about the electrodes except via the parameter E_F . If H is a Hamiltonian matrix describing the isolated core, then the core transmissions are given by $\tau_{i,j}(E_F) = |G_{i,j}(E_F)|^2$, where G is the corresponding Green’s function matrix $G = (E_F - H)^{-1}$. $M_{i,j}(E_F)$ is proportional to $G_{i,j}(E_F)$, with a constant of proportionality which does not depend on i, j , but may depend on E_F . The constant of proportionality cancels in the above ratios and is chosen to yield the simplest possible values for the ‘magic numbers’ $M_{i,j}(E_F)$. A simple parameter-free description of electrical conductance through polyaromatic hydrocarbon (PAH) cores is then obtained by assuming $E_F = E_0$, where E_0 is the middle of the HOMO-LUMO gap and identifying the Hamiltonian H of the core with a simple connectivity matrix C , whose entries are either $C_{ij} = -1$ if sites i, j are nearest neighbours or $C_{ij} = 0$ otherwise. This yields $\sigma_{i,j} \propto [M_{i,j}(E_0)]^2$, where $M_{i,j}(E_0) \propto (E_0 - C)^{-1}$. It was shown experimentally that this simple rule can predict the statistically-most-probable experimental conductance ratios measured in for example a break-junction set up^{20,21}. The remarkable agreement between conductance ratios obtained from the quantities $M_{i,j}(E_0)$ and experimental measurements carried out by different groups²⁰, led us to refer to them as ‘magic numbers.’ We now try to generalize the above theory to describe the Seebeck coefficient of molecules whose central core is weakly connected to external electrodes.

The above expressions are valid, because provided the Fermi energy lies within the HOMO-LUMO gap, when electrons of energy E passing from one electrode to another enter the core at orbital i and leave the core from orbital j , the transmission coefficient $T(E)$ is proportional to $\tau_{i,j}(E)$. The low-bias, electrical conductance is given by the Landauer formula $\sigma_{i,j} = G_0 T(E_F)$, where $T(E)$ is transmission coefficient and $G_0 = 2e^2/h$ is the quantum of conductance. This form of the Landauer formula is valid, provided the transmission coefficient does not vary significantly on the scale of $k_B T$, where T is the temperature and $k_B = 8.6 \times 10^{-5}$ eV/K is Boltzmann’s constant. Similarly the Seebeck coefficient is given by

$$S = \frac{-1}{|e|T} \frac{L_1}{L_0} \quad (1)$$

where $L_n = \int_{-\infty}^{\infty} (E - E_F)^n T(E) \left(-\frac{\partial f(E,T)}{\partial E}\right) dE$ is the n -th moment of $T(E) \left(-\frac{\partial f(E,T)}{\partial E}\right)$ and $f(E) = (1 + \exp((E - E_F)/k_B T))^{-1}$ is the Fermi-Dirac distribution function. Hence for a connectivity i, j , the core Seebeck coefficient can be written

$$S_{ij} = \frac{-1}{|e|T} \frac{L_1^{i,j}}{L_0^{i,j}} \quad (2)$$

where $L_n^{i,j} = \int dE [(E - E_F)]^n \tau_{ij}(E) \left(-\frac{df}{dE}\right)$. Provided the transmission coefficient does not vary significantly on the scale of $k_B T$, it is useful to approximate $\tau_{ij}(E)$ by

$$\tau_{ij}(E) = \tau_{ij}^{(0)} + (E - E_F)\tau_{ij}^{(1)} + (E - E_F)^2\tau_{ij}^{(2)} \quad (3)$$

Since $(-df/dE)$ is approximately an even function of $(E - E_F)$, this yields $L_0^{i,j} = \tau_{ij}^{(0)} + b\tau_{ij}^{(2)}$ and $L_1^{i,j} = b\tau_{ij}^{(1)}$ where $b = \int dE [(E - E_F)]^2 \left(-\frac{df}{dE}\right) = (\pi k_B T)^2 / 3$. Dashed lines in the left panel of figure 1-6 show the transmission coefficient obtained using this approximation. It is apparent that this is a good approximation in the vicinity of middle of the HOMO-LUMO gap. From $\tau_{ij}(E)$ and equation 2, we obtain

$$S_{ij} = \frac{-1}{|e|T} \frac{b\tau_{ij}^{(1)}}{\tau_{ij}^{(0)} + b\tau_{ij}^{(2)}} \quad (4)$$

Dashed lines in the right panel of figure 1-6 show that this formula reproduces the main features of the Seebeck coefficient at room temperature. Equation (4) is a good approximation when τ changes linearly in the scale of $k_B T$ for energies close to E_F and therefore the agreement between this formula and the exact value obtained from equation 2 is even better at lower temperatures. For comparison, we have recalculated the Seebeck coefficient shown in figures 1-6 at $T=30K$ in the SI (figure S3). Note that equation (4) is more general than the usual Mott formula. When $\tau_{ij}^{(0)} \gg b|\tau_{ij}^{(2)}|$, equation (4) yields the Mott formula $S_{ij} = \frac{-b}{|e|T} \frac{\tau_{ij}^{(1)}}{\tau_{ij}^{(0)}} = -\alpha |e|T \left(\frac{d \ln \tau_{ij}(E)}{dE}\right)_{E=E_F}$ where $\alpha = \frac{-b}{(eT)^2} = \left(\frac{k_B}{e}\right)^2 \frac{\pi^2}{3} = 2.44 \cdot 10^{-8} \text{ W}\Omega\text{K}^{-2}$ is the Lorentz number. On the other hand, if due to connectivity, $\tau_{ij}^{(0)}$ vanishes, it reduces to

$$S_{ij} = \frac{-1}{|e|T} \frac{\tau_{ij}^{(1)}}{\tau_{ij}^{(2)}} \quad (5)$$

Equation (4) is a key result, because it captures the contribution of connectivity to the Seebeck coefficient. To clarify this point, we note that since $\tau_{ij}(E) = |G_{i,j}(E)|^2$, expanding $|G_{i,j}(E)|^2$ about $E = E_F$ and noting that $\frac{dG(E)}{dE} = -G^2(E)$ yields $G_{ij}(E) = G_{ij}(E_F) - 2[G^2(E_F)]_{ij}(E - E_F) + [G^3(E_F)]_{ij}(E - E_F)^2$. Hence $\tau_{ij}^{(n)} = \tau_{ij}^{(n)}(E_F)$, where

$$\tau_{ij}^{(0)}(E_F) = |G_{ij}(E_F)|^2 \quad (6)$$

$$\tau_{ij}^{(1)}(E_F) = -2\text{Re}\{G_{ij}^*(E_F)[G^2(E_F)]_{ij}\} = -2G_{ij}(E_F)[G^2(E_F)]_{ij} \quad (7)$$

and

$$\tau_{ij}^{(2)}(E_F) = \{|[G^2(E_F)]_{ij}|^2 + 2\text{Re}\{G_{ij}^*(E_F)[G^3(E_F)]_{ij}\}\} = \{|[G^2(E_F)]_{ij}|^2 + 2G_{ij}(E_F)[G^3(E_F)]_{ij}\} \quad (8)$$

where the right hand sides of equation (7) and (8) are valid in the presence of time-reversal symmetry, because G and the Hamiltonian are both real and G describes a closed system. In what follows we use these expressions to investigate the Seebeck coefficient of different PAHs molecules in the absence and presence of a heteroatom substitution.

For bipartite PAH cores with equal numbers of odd ‘o’ sites and even ‘e’ sites, the Hamiltonian has the form $\begin{pmatrix} 0 & H_{oe} \\ H_{eo} & 0 \end{pmatrix}$ and the Greens function satisfies

$$\begin{pmatrix} E & -H_{oe} \\ -H_{eo} & E \end{pmatrix} \begin{pmatrix} G_{oo} & G_{oe} \\ G_{eo} & G_{ee} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (9)$$

which yields

$$G_{oo} = E(E^2 - H_{oe}H_{eo})^{-1}, \quad G_{ee} = E(E^2 - H_{eo}H_{oe})^{-1} \quad (10)$$

and

$$G_{eo} = H_{eo}(E^2 - H_{oe}H_{eo})^{-1} \quad (11)$$

Hence the squares of all Greens function matrix elements are even functions of E and therefore $\frac{d\tau_{ij}(E)}{dE} \sim \frac{dE^2}{dE} \sim 2E$, which vanishes at the mid-HL gap $E = 0$. Consequently for $E_F = 0$, $S_{ij} = 0$ and therefore bipartite PAHs with equal numbers of odd and even atoms are expected to be poor thermoelectric materials. This is also evident from equ. (5), because since $G_{i,j}(0)$ is block off diagonal, $G_{i,j}(0) = 0$ and $[G^3(0)]_{ij} = 0$ if i, j are both odd or both even and they are non-zero otherwise. Similarly $[G^2(0)]_{ij} = 0$ if i is odd and j is even or vice versa and $[G^2(0)]_{ij}$ is non-zero if i, j are both odd or both even. Consequently for $E_F = 0$, $\tau_{ij}^{(1)} = -2G_{ij}(0)[G^2(0)]_{ij} = 0$ for all choices of j and from equ. (5), $S_{ij} = 0$.

On the other hand, if $E_F \neq 0$, the behaviour of $S_{ij}(E_F)$ in the vicinity of $E_F = 0$ is quite different for odd-even compared with even-even and odd-odd connectivities. To explore the Fermi-energy dependence of $S_{ij}(E_F)$, we note that for $E_F \approx E_0$, (where E_0 is an arbitrary reference energy) the dominant behavior is obtained by writing $\tau_{ij}^{(0)}(E_F) \approx \tau_{ij}^{(0)}(E_0) + (E_F - E_0)\tau_{ij}^{(1)}(E_0) + (E_F - E_0)^2\tau_{ij}^{(2)}(E_0)$, $\tau_{ij}^{(1)}(E_F) \approx \tau_{ij}^{(1)}(E_0) + 2(E_F - E_0)\tau_{ij}^{(2)}(E_0)$ and $\tau_{ij}^{(2)}(E_F) \approx \tau_{ij}^{(2)}(E_0)$. Hence

$$S_{ij} = \frac{-b}{|e|T} \frac{\tau_{ij}^{(1)}(E_0) + 2(E_F - E_0)\tau_{ij}^{(2)}(E_0)}{\tau_{ij}^{(0)}(E_0) + (E_F - E_0)\tau_{ij}^{(1)}(E_0) + [b + (E_F - E_0)^2]\tau_{ij}^{(2)}(E_0)} \quad (12)$$

For $E_0 = 0$, since $\tau_{ij}^{(1)}(0) = 0$ for all choices of i, j this yields:

$$S_{ij} = \frac{-b}{|e|T} \frac{2(E_F)\tau_{ij}^{(2)}(0)}{\tau_{ij}^{(0)}(0) + [b + (E_F)^2]\tau_{ij}^{(2)}(0)} \quad (13)$$

From equ. (13) we conclude that

- a. When i is odd and j is even or vice versa, assuming that b and E_F are small compared with $\tau_{ij}^{(0)}(0)/\tau_{ij}^{(2)}(0)$ yields

$$S_{ij} \approx \frac{-2\alpha T |e| (E_F) \tau_{ij}^{(2)}(0)}{\tau_{ij}^{(0)}(0)} \quad (14)$$

In this case, we see that S_{ij} is proportional to E_F and vanishes linearly with E_F at $E_F = 0$.

- b. On the other hand, when i, j are both odd or both even, $\tau_{ij}^{(0)}(0) = 0$. Hence

$$S_{ij} = \frac{-2\alpha T|e|(E_F)\tau_{ij}^{(2)}(0)}{[b + (E_F)^2]\tau_{ij}^{(2)}(0)} \quad (15)$$

In this case, S_{ij} is proportional to $\frac{(E_F)}{[b+(E_F)^2]}$ and therefore exhibits a Fano lineshape as E_F approaches 0.

If the aromatic core contains heteroatoms, whose site energies differ from that of carbon, then naturally one should add the site-energy difference to the appropriate diagonal element of the Hamiltonian. As an example of the effect of heteroatoms, consider the effect of adding one or more heteroatoms to the odd-numbered sublattice ‘o’ of a bipartite lattice. In this case, equation (9) becomes

$$\begin{pmatrix} E - H_{oo} & -H_{oe} \\ -H_{eo} & E \end{pmatrix} \begin{pmatrix} G_{oo} & G_{oe} \\ G_{eo} & G_{ee} \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (16)$$

which yields

$$G_{oo} = E[E(E - H_{oo}) - H_{oe}H_{eo}]^{-1} \quad (17)$$

and

$$G_{eo} = H_{eo}[E(E - H_{oo}) - H_{oe}H_{eo}]^{-1}, \quad G_{ee} = [E - H_{eo}g_oH_{oe}]^{-1} \quad (18)$$

where $g_o = (E - H_{oo})^{-1}$. Hence at $E=0$, in the presence of heteroatoms on odd-numbered ‘o’ sites, matrix elements (G_{oo}) between ‘o’ and ‘o’ sites remain zero, those of (G_{ee}) between even-numbered ‘e’ and ‘e’ sites become non-zero, while elements of (G_{eo}) between ‘e’ and ‘o’ sites are unchanged.

As an example, consider modelling the effect of a heteroatom by adding a single site energy ε_{l_o} to odd-numbered site l_o . Then if $g_{ij}(E)$ is the Greens function of the lattice without the heteroatom, the new Greens function becomes

$$G_{ij}(E) = g_{ij}(E) + g_{il_o}(E) \frac{\varepsilon_{l_o}}{1 - \varepsilon_{l_o}g_{l_o l_o}(E)} g_{l_o j}(E) \quad (19)$$

To be more precise, since $G(0) = \begin{pmatrix} 0 & G_{oe} \\ G_{eo} & G_{ee} \end{pmatrix}$, we find $G^2(0) = \begin{pmatrix} G_{oe}G_{eo} & G_{oe}G_{ee} \\ G_{ee}G_{eo} & G_{eo}G_{oe} + G_{ee}G_{ee} \end{pmatrix}$ and $G^3(0) = \begin{pmatrix} G_{oe}G_{ee}G_{eo} & G_{oe}(G_{eo}G_{oe} + G_{ee}G_{ee}) \\ G_{eo}G_{oe}G_{eo} + G_{ee}G_{ee}G_{eo} & G_{eo}G_{oe}G_{ee} + G_{ee}(G_{eo}G_{oe} + G_{ee}G_{ee}) \end{pmatrix}$. Combining these with eqs (6) and (7) yields the following table:

Table 1: Greens function G , and transmission τ and their expansion for given connectivity ij when a heteroatom substituted to odd-numbered site l_o .

i	j	$G_{ij}(0)$	$[G^2(0)]_{ij}$	$[G^3(0)]_{ij}$	$\tau_{ij}^{(0)}(0)$	$\tau_{ij}^{(1)}(0)$	$\tau_{ij}^{(2)}(0)$
odd	odd	0	$[G_{oe}G_{eo}]_{ij}$ $= [g(0)g^T(0)]_{ij}$	$[g(0)g^T(0)]_{il_o}\varepsilon_{l_o}[g(0)g^T(0)]_{l_o j}$	0	0	Non-zero
odd	even	$[G_{oe}]_{ij} = g_{ij}(0)$	$[G_{oe}G_{ee}]_{ij}$ $= [g(0)g^T(0)]_{il_o}\varepsilon_{l_o}g_{l_o j}(0)$	$[g(0)g^T(0)g(0)]_{ij} + O(\varepsilon_{l_o}^2)$	$[g_{ij}(0)]^2$	$-2g(0)_{ij}[g(0)g^T(0)]_{il_o}\varepsilon_{l_o}g_{l_o j}(0)$	Non-zero
even	even	$[G_{ee}]_{ij}$ $= g_{il_o}(0)\varepsilon_{l_o}g_{l_o j}(0)$	$[G_{eo}G_{oe} + G_{ee}G_{ee}]_{ij}$ $= [g^T(0)g(0)]_{ij}$ $+ O(\varepsilon_{l_o}^2)$	$O(\varepsilon_{l_o})$	$O(\varepsilon_{l_o})$	$-2g_{il_o}(0)\varepsilon_{l_o}g_{l_o j}(0)[g^T(0)g(0)]_{ij}$	Non-zero

In the above table, the non-zero values of $\tau_{ij}^{(2)}(0)$ are given by $\tau_{ij}^{(2)}(0) = \{[g^2(0)]_{ij}\}^2 + 2g_{ij}(0)[g^3(0)]_{ij} + O(\varepsilon_{l_o})$. Since $\tau_{ij}^{(1)}(0)$ is proportional to ε_{l_o} it is convenient to write $\tau_{ij}^{(1)}(0) = \varepsilon_{l_o} \bar{\tau}_{ij}^{(1)}(0)$. Then from equ. (12), setting $E_F = E_0 = 0$ yields

$$S_{ij} = \varepsilon_{l_o} \bar{S}_{ij} \quad (20)$$

where

$$\bar{S}_{ij} = \frac{-b}{|e|T} \frac{\bar{\tau}_{ij}^{(1)}(0)}{\tau_{ij}^{(0)}(0) + b\tau_{ij}^{(2)}(0)} \quad (21)$$

Equation (20) is a key result, because it shows that the mid-gap Seebeck coefficient is a product of two parameters. The first is ε_{i_0} which depends on the nature of the heteroatom (electron donating or accepting) and the second is \bar{S}_{ij} which depends on connectivity, but not on the nature of the heteroatom. Since the sign of the mid-gap Seebeck coefficient depends on connectivity, heteroatom substituted PAHs are bi-thermoelectric.

From equation (7), the mid-gap Seebeck coefficient between even and even or odd and even sites is no longer zero, because $\tau_{ij}^{(1)}(0)$ no longer vanishes. On the other hand the mid-gap Seebeck coefficient between odd and odd sites remains at zero. These features are clearly present in the right-hand columns of figures 2-6.

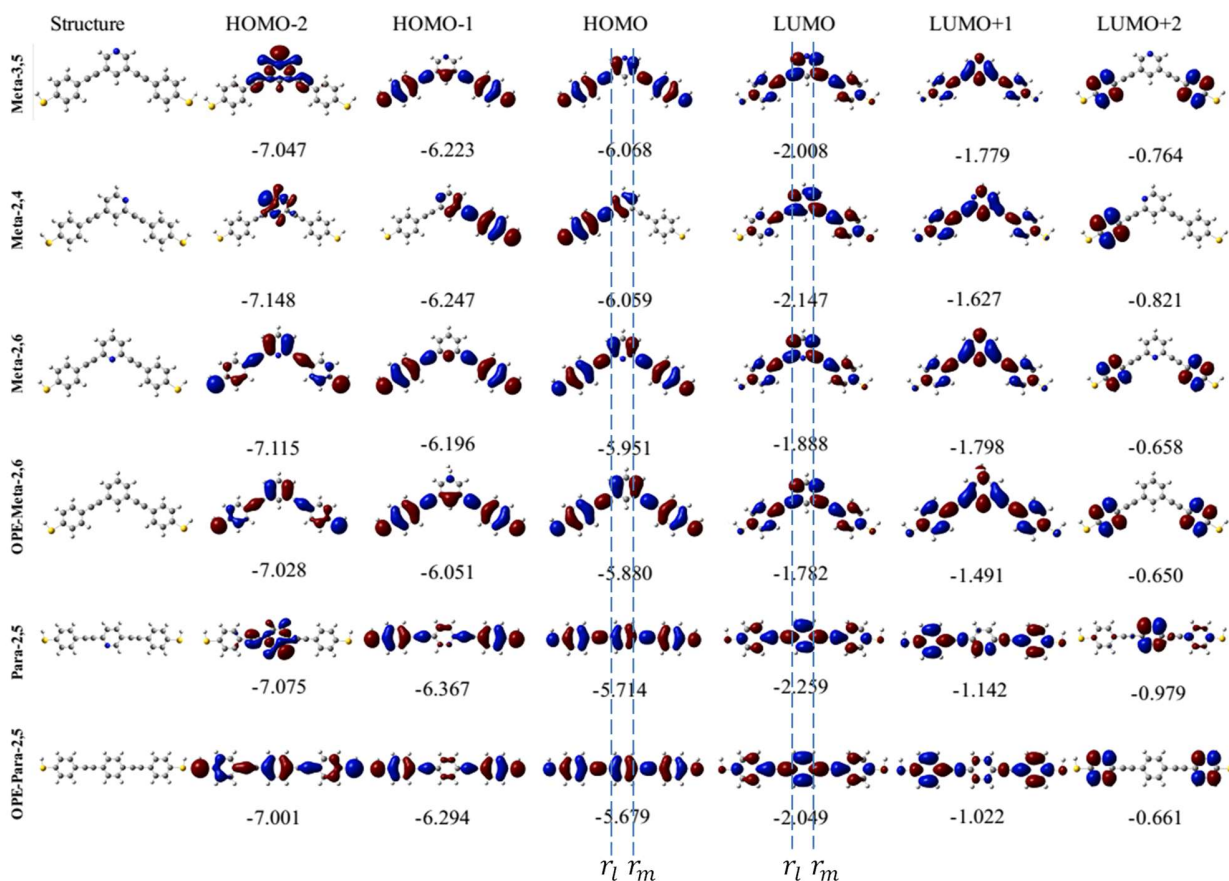


Fig S4. Frontier molecular orbitals of the molecules shown in figures 1 and 2. The intercepts between the vertical lines and the connections between the acetylene linkers and the central 6-fold ring show the points at which molecular orbitals $\psi^H(r_l)$, $\psi^L(r_l)$, $\psi^H(r_m)$ and $\psi^L(r_m)$ are to be evaluated. Red = positive and blue = negative.

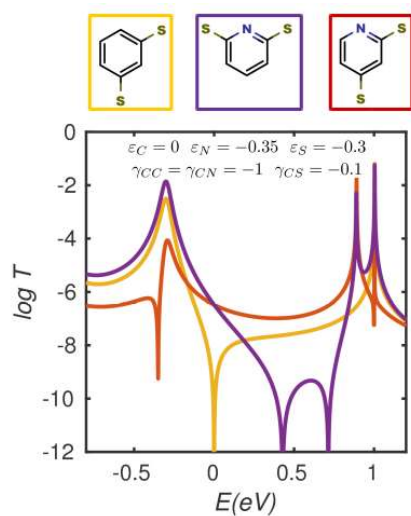


Fig. S5. Results for the tight binding transmission, obtained by weakly coupling two pendant pi orbitals (labelled S) to the central core. These are a simple extension of the tight binding model of the main text, used to obtain figure 2a and 2b. As for the former, the site energies of the carbons are $\epsilon_C = 0$, the site energy of the nitrogen is $\epsilon_N = -0.35$ and the C-C and C-N couplings are -1. The site energies of the pendant sites are $\epsilon_S = -0.3$ and the weak couplings to the pendant sites are $\gamma_{CS} = -0.1$. This shows that the anti-resonance of the 2-4 connectivity is shifted towards the HOMO, in agreement with figure 2c.