

Supporting Information

Thermoelectric Signatures of *d*-orbitals in Tripod-Based Molecular Junctions

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Theoretical Methods

All calculations in this work were carried out by the implementation of DFT in the SIESTA ¹ code. It is used to obtain the optimized geometries of the structures, as shown in Figure S2. SIESTA code is an acronym derived from the Spanish Initiative for Electronic Simulations with Thousands of Atoms. The quantum transport theory (QTT) implemented in GOLLUM ² code which is a program that computes the charge, spin and electronic contribution to the thermal transport properties of multi-terminal junctions has been utilized to calculate the electronic and thermoelectric properties of all molecular junctions. The initial optimization of gas phase molecules and isosurfaces calculations were carried out at the B3LYP level of theory ³ with a LANL2DZ basis set. ^{1,4} All, theories and computational methods and procedures are shown in Figure S1. The optimized geometry, ground state Hamiltonian and overlap matrix elements of

each structure were self-consistently obtained using the SIESTA code. SIESTA employs norm-conserving pseudo-potentials to account for the core electrons and linear combinations of atomic orbitals to construct the valence states. The generalized gradient approximation (GGA) of the exchange and correlation functional is used with a double- ζ polarized (DZP) basis set, a real-space grid defined with an equivalent energy cut-off of 250 Ry. The geometry optimization for each structure is performed to the forces smaller than 20 meV/Å. The mean-field Hamiltonian obtained from the converged DFT calculation was combined with GOLLUM. The transmission coefficient $T(E)$ for electrons of energy E (passing from the source over molecule to the drain) is calculated via the relation:

$$T(E) = T_r \{ \Gamma_R(E) G^R(E) \Gamma_L(E) G^{R\dagger}(E) \} \quad (1)$$

In this expression,

$$\Gamma_{L,R}(E) = i(\Sigma_{L,R}(E) - \Sigma_{L,R}^\dagger(E)) \quad (2)$$

$\Gamma_{L,R}$ describes the level broadening due to the coupling between left (L) and right (R) electrodes and the central scattering region, $\Sigma_{L,R}(E)$ are the retarded self-energies associated with this coupling.

$$G^R = (E\chi - H - \Sigma_L - \Sigma_R)^{-1} \quad (3)$$

G^R is the retarded Green's function, where H is the Hamiltonian and χ is the overlap matrix (both of them are obtained from SIESTA). The transport properties is then calculated using the Landauer formula:

$$G = G_o \int dE T(E) (-\partial f(E,T)/\partial E) \quad (4)$$

where $G_0 = 2e^2/h$ is the conductance quantum, $f(E) = (1 + \exp((E - E_F)/k_B T))^{-1}$ is the Fermi-Dirac distribution function, T is the temperature and $k_B = 8.6 \times 10^{-5}$ eV/K is Boltzmann's constant, E_F is the Fermi energy, e is electron charge and h is the Planck's constant. The thermopower or Seebeck coefficient S is defined as the difference of electrochemical potential per unit temperature difference developing across an electrically isolated sample exposed to a temperature gradient. The Seebeck coefficients and power factor (P) are informative properties. Provided the transmission function, $T(E)$, can be approximated by a straight line on the scale of k_{BT} , the Seebeck coefficient is given by:

$$S \approx -L|e|T \left(\frac{d \ln T(E)}{dE} \right)_{E=E_F} \quad (5)$$

Where L is the Lorenz number $L = \left(\frac{k_B}{e} \right)^2 \frac{\pi^2}{3} = 2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$. In other words, S is proportional to the negative of the slope of $\ln T(E)$, evaluated at the Fermi energy. The power factor is the ratio of the real power absorbed by the load to the apparent power flowing in the circuit. Real power is the average of the instantaneous product of voltage and current and represents the capacity of the electricity for performing work. Based on the Seebeck coefficient, and electrical conductance (G) the power factor was calculated as given in equation (6)

$$P = GS^2 T \quad (6)$$

where T is the temperature $T = 300$ K, G is the electrical conductance and S is the Seebeck coefficient. In conventional devices the maximum efficiency of either heat transfer or current generation is proportional to the dimensionless thermoelectric figure of merit (ZT). The common measure for thermoelectric efficiency is given by ZT, which is given by:⁵

$$ZT = \frac{GS^2}{k_{el} + k_{ph}}T \quad (7)$$

Where G is the electrical conductance, S is the Seebeck coefficient, k_{el} is the electron thermal conductance, k_{ph} is the phonon thermal conductance.

The figure of merit is determined from the thermoelectric transport coefficients in equations 5, 8, 9 and 11 in the linear response regime.^{6,7}

$$G = \frac{2e^2}{h}k_0 \quad (8)$$

$$k_{el} = \frac{2}{hT} \left(K_2 - \frac{K_1^2}{K_0} \right) \quad (9)$$

In the expressions $e = |e|$ is the absolute value of the electron charge, h is the Planck constant, and $T = (T_L + T_R)/2$ is the average junction temperature. The coefficients in 8 and 9 are defined as:

$$k_n = \int dE T_{el}(E) \left(-\frac{\partial f(E)}{\partial E} \right) (E - \mu)^n \quad (10)$$

where $T_{el}(E)$ is the electron transmission, and the chemical potential $\mu \approx E_F$ is approximately given by the Fermi energy E_F of the gold electrodes. The corresponding thermal conductance due to the phonons is given in linear response by:

$$k_{ph} = \frac{1}{h} \int_0^\infty dE E T_{ph}(E) \frac{\partial n(E,T)}{\partial T} \quad (11)$$

where $T_{ph}(E)$ is the phonon transmission and $n(E,T) = \{\exp(E/k_B T) - 1\}^{-1}$ is the Bose function, characterizing the phonon reservoirs in the left and right electrodes.

Hence, an upper bound for ZT in the limit of vanishing phonon thermal transport $k_{ph} \rightarrow 0$ is given by the purely electronic contribution⁶ as

$$Z_{el}T = \frac{S^2 G}{k_{el}} T = \frac{S^2}{L} \quad (12)$$

The Lorenz number is $L = k_{el}/GT$. Hence, the figure of merit could be presented in a slightly different form as:

$$ZT = \frac{Z_{el}T}{1 + k_{ph}/k_{el}} \quad (13)$$

Equation 13 was used to calculate the electronic figure of merit ($Z_{el}T$).

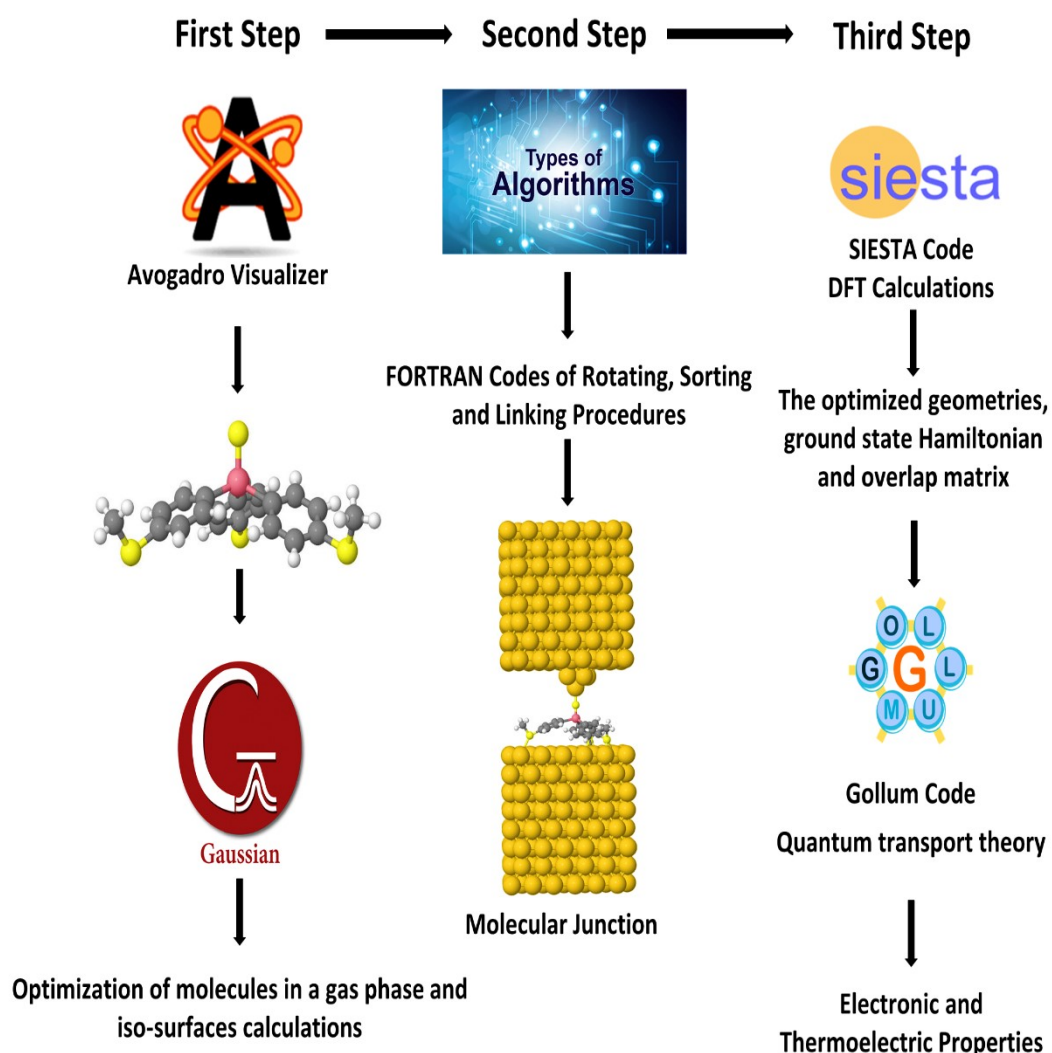


Figure S1. Computational methods and steps.

All molecules in a gas phase has been designed using Avogadro ⁸ visualizer, then the ground-state energy optimization of molecules and iso-surfaces calculations achieved using Gaussian ⁹ program. The second step involves the rotation, sorting and linking the molecules to the gold electrodes to obtain the theoretical models of molecular junctions (see Figure S2), using a set of FORTRAN algorithms. After that the molecular junctions (source|molecule|drain) have been optimized using SIESTA. ¹ The data (Hamiltonian and overlap matrix) was then fed to Gollum code, which calculating the electronic and thermoelectric properties of all molecular junctions.

Theoretical Models of Molecular Junctions

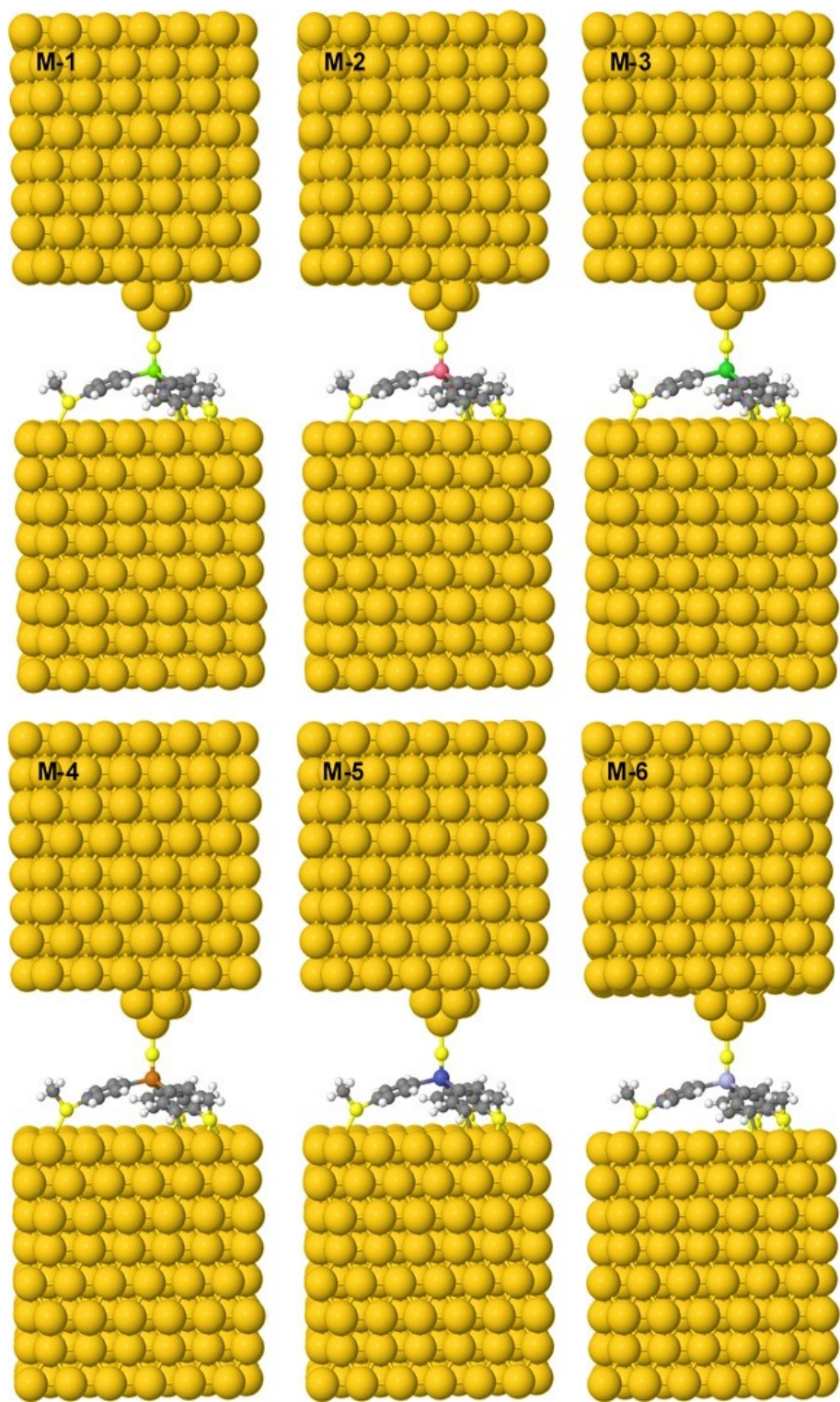


Figure S2. Theoretical models of molecular junctions.

Theoretical model of molecular junctions was constructed using eight layers of (111)-oriented bulk gold with each layer consisting of 6×6 atoms and a layer spacing of 0.235 nm were used to create the molecular junctions. These layers were then further repeated to yield infinitely

long current carrying gold electrodes. Each molecule was attached to two (111)-directed gold electrodes; one of these electrodes was pyramidal, representing the tip of scanning tunnelling microscopy (STM), while the other was a planar slab representing the electrode formed by the idealized Au(111) substrate in the I(s)-based molecular junction. The molecules and first layers of gold atoms within each electrode were then allowed to relax again, to yield the optimal junction geometries. From these model junctions the transmission coefficient, $T(E)$, was calculated using the GOLLUM code.¹⁰⁻¹²

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