

# Enhancing Thermoelectric Efficiency of Organometallic Molecular Junctions by Quantum Interference

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Due to their size where quantum effects dominate the carriers transport, Molecular Junctions (MJ) offers a rich field for both experimental and basic science exploration. Since the proposal of Aviram and Ratner for constructing molecular rectifiers<sup>1</sup>, the number of investigations in MJ is growing, as long as the fine-tuning capability of chemical structure and electronic configuration enables the design of different applications such as conducting wire<sup>2</sup>. Among their possible functions, MJ can present interesting thermal and thermoelectric properties, that could be used to fabricate energy nano-converters and nano-coolers<sup>3</sup>. The presence of metals in molecular systems can promote the frontier orbitals closer to the Fermi level and induce quantum interference, leading to highly conductive molecular wires with increased thermoelectric properties<sup>4</sup>. Quantum interference (QI) effects influence the transmission probability of charge carriers across molecular junctions, Fano resonance and anti-resonance being the manifestations of this phenomenon. In this work, by molecular design, we explore QI for electronic transport in linear response regime to increase significantly the Seebeck coefficient. QuantumATK<sup>5</sup> simulations were performed to tackle this question using non-equilibrium Green functions associated with density function theory (DFT) calculations (GGA rev-PBE/DZP and SZP for Au). The electronic and transport properties of different organometallic systems will be presented, which includes charged and spin polarized molecular junctions. A comparison with experimental results will also be provided.

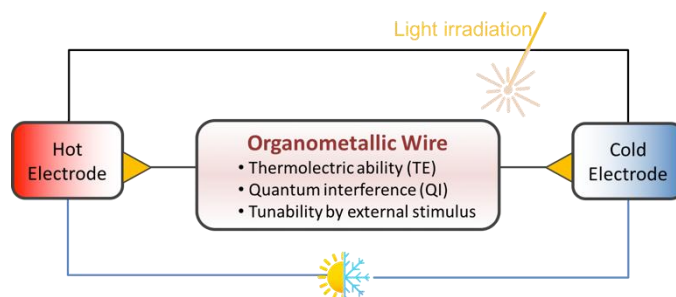


Figure 1. Thermoelectric ability can be improved by Quantum Interference and external stimulus.

**Keywords:** charge transport, energy conversion, thermoelectricity, molecular junctions, Fano resonance.

<sup>1</sup> Arieh Aviram and Mark A. Ratner, "Molecular Rectifiers," *Chemical Physics Letters* 29, no. 2 (November 1974): 277–83, [https://doi.org/10.1016/0009-2614\(74\)85031-1](https://doi.org/10.1016/0009-2614(74)85031-1).

<sup>2</sup> Florian Schwarz et al., "High-Conductive Organometallic Molecular Wires with Delocalized Electron Systems Strongly Coupled to Metal Electrodes," *Nano Letters* 14, no. 10 (October 8, 2014): 5932–40, <https://doi.org/10.1021/nl5029045>.

<sup>3</sup> Kun Wang, Edgar Meyhofer, and Pramod Reddy, "Thermal and Thermoelectric Properties of Molecular Junctions," *Advanced Functional Materials*, October 3, 2019, 1904534, <https://doi.org/10.1002/adfm.201904534>.

<sup>4</sup> Sohyun Park et al., "High Seebeck Coefficient Achieved by Multinuclear Organometallic Molecular Junctions," *Nano Letters* 22, no. 23 (December 14, 2022): 9693–99, <https://doi.org/10.1021/acs.nanolett.2c03974>.

<sup>5</sup> Søren Smidstrup et al., "QuantumATK: An Integrated Platform of Electronic and Atomic-Scale Modelling Tools," *Journal of Physics: Condensed Matter* 32, no. 1 (January 1, 2020): 015901, <https://doi.org/10.1088/1361-648X/ab4007>.