Quasi-Ohmic Single Molecule Charge Transport through Highly Conjugated meso-to-meso Ethyne-Bridged Porphyrin Wires

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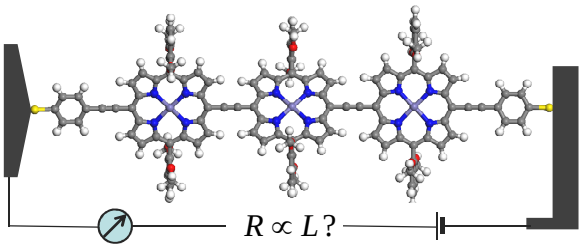

Understanding and controlling electron transport through functional molecules is of primary importance to the development of molecular scale devices. We report the single molecule resistances of meso-to-meso ethyne-bridged (porphinato)zinc(II) structures, $(PZn)_X$ compounds where x=1-3, connected to gold electrodes via (4´-thiophenyl)ethynyl termini, determined using STM-based break junction methods.[1] These experiments show that each α,ω-di[(4´-thiophenyl)ethynyl]-terminated $(PZn)_x$ compound, dithiol-$(PZn)_x$, manifests a dual molecular conductance. In both the high and low conductance regimes, the measured resistance across these metal–dithiol-$(PZn)_x$–metal junctions increases in a near linear fashion with molecule length. These results signal that meso-to-meso ethyne-bridged porphyrin wires afford the lowest β value (β = 0.034 $Å^{-1}$) yet determined for thiol-terminated single molecules that manifest a quasi-ohmic resistance dependence across metal–dithiol-$(PZn)_x$–metal junctions.

To probe the effect of anchoring groups on metal–molecule–metal junctions, STM break junction experiments were used to investigate the molecular conductances of two [5,15-bis((4'-X-phenyl)ethynyl)-porphinato]zinc(II) (X = S^-, $^-$**S-PZn-S**$^-$; CS_2^-, $^-$**S$_2$C-PZn-CS$_2^-$**) complexes.[2] The data highlight a single molecule conductance for carbodithioate-anchored junctions that is an order of magnitude greater than that determined for $^-$**S-PZn-S**$^-$ molecules that exploit thiolate Au-surface linkers. Interestingly, current histogram analyses and detailed examination of hundreds of current-distance traces reveal that **Au-S$_2$C-PZn-CS$_2$-Au** junctions display additional, infrequent single molecule conductances that deviate substantially from the most commonly observed value. These lower conductance values derive respectively from **Au-S$_2$-PZn-S$_2$-Au** junctions in which one or both of the carbodithioate anchors interacts with the Au surface in a monodentate fashion. This work thus reveals hapticity-dependent single molecule conductances; furthermore, because the magnitude of the tunneling barrier depends upon carbodithioate linker hapticity, these experiments provide new insights into the origin of molecule-to-molecule conductance heterogeneity in molecular charge transport measurements, and the factors that optimize electrode-molecule-electrode electronic coupling and reduce the effective barrier for charge transport.

References

1. Quasi-Ohmic Single Molecule Charge Transport through Highly Conjugated Meso-to-Meso Ethyne-Bridged Porphyrin Wires, Zhihai Li, Tae-Hong Park, Jeff Rawson, Michael J. Therien, and Eric Borguet Nano Letters, 12 (6), 2722–2727 (2012)

2. Hapticity-Dependent Single Molecule Conductance of Carbodithioate-Terminated [5,15-Bis(phenylethynyl)porphinato]-zinc(II) Complexes in Metal-Molecule-Metal Junctions, Zhihai Li, Tae-Hong Park, Jeff Rawson, Michael J. Therien, and Eric Borguet (submitted)