

# DIODE LINKERS FOR COVALENT ATTACHMENT OF TRANSITION METAL CATALYSTS TO METAL OXIDE SURFACES

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## Introduction

The development of photo-optic devices based on robust and inexpensive semiconductor materials would impact a wide range of technological developments, including effective phototransduction mechanisms for solar energy conversion and artificial photosynthesis. In fact, semiconductor nanoparticles functionalized with molecular adsorbates have already attracted significant interest for technological developments since they are robust, both chemically and photochemical, and inexpensive. However, molecular design principles for efficient optical manipulation of electron-hole pair separation and recombination dynamics remain unclear. We focus on transition metal complexes covalently attached to metal oxide surfaces  $\text{TiO}_2$ ,  $\text{SnO}_2$  and  $\text{ZnO}$  surfaces that are central for solar photovoltaic and photocatalytic cells.

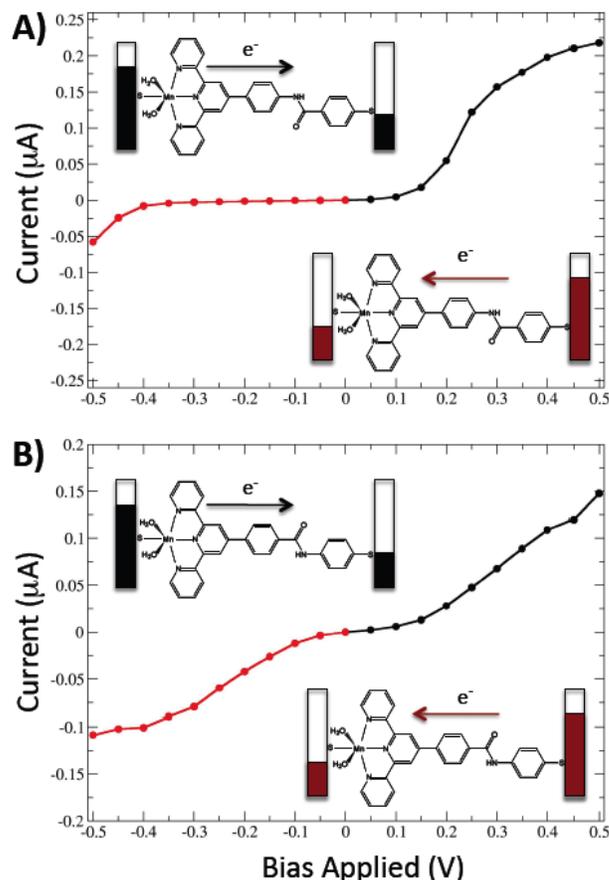
## NEGF DFT Methods

Ab initio computational methods for electronic transport in nanoscaled systems are extremely valuable tools for the design and characterization of quantum devices. Our studies of molecular rectifiers aim to assist the development and characterization of molecular adsorbates that would induce directionality of interfacial electron transfer in functionalized semiconductor surfaces, suppressing detrimental recombination processes responsible for reducing performance of photovoltaic devices. We evaluate I-V characteristics of atomic junctions with the software package SMEAGOL integrating the nonequilibrium Green's function (NEGF) method with density functional theory (DFT) as implemented in the SIESTA package for electronic structure calculations. The systems are modeled in the usual three-subsystem segmentation, including the left and right electrodes and the central part between the electrodes where the electron scattering process takes place. We construct the surface Green's functions, describing the current-voltage probes, as a direct summation of both open and closed scattering channels together with a regularization procedure of the Hamiltonian that provides great improvement over standard recursive methods. This approach allows us to tackle material systems with complicated electronic structures, including molecular adsorbates and functionalized semiconductor materials with transition metals.

## Results and Discussion

Figure 1 shows the calculated I-V characteristics for two molecular adsorbates Mn-L1 and Mn-L2 that differ only on the orientation of an amide functional group conjugated with the phenylterpyridine ligand. We find remarkable differences between the electron transport properties of the two systems, suggesting molecular design principles for rectification. The I-V characteristics show high degree of asymmetry for Mn-L1 (Figure 1A), with the current steadily increasing with positive bias voltages. In contrast, the current is suppressed with the bias potential is reversed. For Mn-L2 (Figure 1B) the electron transport properties show a low degree of rectification as shown

by the symmetry of the I-V curve. These results are consistent with the experimental characterization of interfacial electron transfer based on THz spectroscopy and recombination dynamics probed by EPR spectroscopy.



**Figure 1.** Calculated I-V characteristic curves for A) Mn-L1 and B) Mn-L2. Current under negative (red) and positive (black) bias voltages are represented in the -500–500 mV range.

## Conclusions

We have characterized the electronic rectification properties of molecular linkers that covalently bind transition metal catalysts to  $\text{TiO}_2$  surfaces. We focused on Mn complexes with phenylterpyridine ligands attached to 3-phenylacetylacetonate anchors via amide bonds. We found that a suitable choice of the amide linkage yields directionality of interfacial electron transfer, essential to suppress recombination. Our findings are supported by calculations of current-voltage (I-V) characteristics at metallic atomic junctions, based on first-principles methods that combine non-equilibrium Green's function techniques with density functional theory. Our computational results are consistent with EPR measurements, confirming an asymmetry of electron transfer rates for linkers with significant rectification. The reported studies are particularly relevant for the development of photovoltaic, or photocatalytic, devices based on functionalized metal oxide thin-films where the overall performance is affected by recombination processes competing with interfacial electron injection.

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