

## 512g Ab Initio Based Current-Voltage Characteristics for Stilbene Substituted Octasilsesquioxanes Attached to Au(111) Electrodes

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Molecular junctions performing individual electronic functions such as conduction, switching and storage can be combined to form nanoscale circuits leading to a decrease in the size and an increase in the circuit density as compared to the current semiconductor based microelectronics. This consideration has led to extensive experimental as well as theoretical studies testing new molecules for interesting conductance behavior. Quantum mechanical studies done by Lin, He and Xiao<sup>1</sup> as well as by Lee and Neurock<sup>2</sup> for octasilsesquioxanes report that the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) varies with the functionality as well as the number of the non-hydrogen substituents in the octahydrosilsesquioxane ( $H_8(SiO_{1.5})_8$ ) structure. The HOMO-LUMO energy gap drops from 7.06 eV for octahydrosilsesquioxane ( $H_8Si_8O_{12}$ ) to 4.5 eV for the phenyl substituted species ( $Ph_8Si_8O_{12}$ ). Recent studies done by Laine and coworkers<sup>3</sup> found that stilbene substituents [ $(stilbene)_8Si_8O_{12}$ ] reduce the HOMO-LUMO energy gap to approx. 2.6 eV. This HOMO-LUMO gap value lies in the vicinity of the range reported for conjugated molecular wires such as oligophenylene ethylene ( $\sim 3.0 - 3.8$  eV)<sup>4</sup> which have been widely studied experimentally<sup>5</sup> as well as theoretically<sup>6</sup>.

Herein, we investigate molecular conduction through a monostilbene substituted octasilsesquioxane molecule [ $(stilbene-SH)SH_7Si_8O_{12}$ ] with thiol end groups on the stilbene substituent and on the octasilsesquioxane cage structure. Thiol end groups on opposite ends of the molecule allow adsorption on Au(111) surfaces through the formation of Au-S bonds. The optimum structure for this metal-molecule-metal system is determined by density functional theory and its voltage dependent current characteristics are examined. The current density values found for this system as a function of the bias applied to one of the Au(111) electrodes in the voltage range of [-1,1] V suggests a rectifying behavior. The transmission spectrum for this metal-molecule-metal system along with the projected density of states is examined. These results suggest electron transport through the occupied energy states with higher conduction occurring through the molecular states under higher bias conditions. Adsorption of a distilbene substituted octahydrosilsesquioxane molecule [ $(stilbene-SH)_2H_6Si_8O_{12}$ ] with thiol end groups on the stilbene substituents to Au(111) electrodes alters the molecular structure and electronic configuration. The current-voltage characteristics as well as the underlying electron conduction mechanism are analyzed for this system.

### References:

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