Measurement and Visualization of Electron Transfer at the Single Molecule Level

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By
Yangjun Xing
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ABSTRACT

Molecular electronics based on bottom-up electronic circuit design is a potential solution to meet the continuous need to miniaturize electronic devices. The development of highly conductive molecular wires, especially for long distance charge transfer, is a major milestone in the molecular electronics roadmap. A challenge presented by single molecule conductance is to define the relative influence of the molecular “core” and the molecular “interconnects” on the observed currents. Much focus has been placed on designing conductive, conjugated molecules. However, the electrode-molecule contacts can dominate the responses of metal-molecule-metal devices. We have experimentally and theoretically probed charge transfer through single phenyleneethynylene molecules terminated with thiol and carbodithioate linkers, using STM break-junction and non-equilibrium Green’s function methods, respectively. The STM break-junction method that utilizes repeatedly formed circuits where one or a few molecules are trapped between two electrodes, at least one of which has nanoscale dimensions. The statistical analysis of thousands of measurements yields the conductance of single molecules. Experimental data demonstrate that the carbodithioate linker not only augments electronic coupling to the metal electrode relative to thiol, but reduces the barrier to charge injection into the phenyleneethynylene bridge. The theoretical analysis shows that the nature of sulfur hybridization provides the genesis for the order-of-magnitude increased conductance in carbodithioate-terminated systems relative to those that feature the thiol linker. Collectively, these data emphasize the promising role for carbodithioate-based
connectivity in molecular electronics applications involving metallic and semi-conducting electrodes.

One of the strategies for building molecular wires that can transfer charge over long distance is to incorporate metal ions into the conductive molecular core. Peptide nucleic acid (PNA) is a great candidate for this purpose. Studying the conductivity of Peptide Nucleic Acids (PNA) can not only contribute to a better understanding of charge transfer through bio molecules, but can also help develop better molecular wires and other building blocks of molecular electronics. We study the charge transfer of PNA molecules using the STM break-junction technique and compared with traditional macroscopic voltammetric measurements. By measuring the resistance of different PNA molecules, we hope to develop a deep understanding of how charge transport though PNA is affected by factors such as the number and type of natural and artificial bases, embedded metal ions, pH, etc.

Self-assembled monolayers (SAMs) of porphyrins are of great interest due to their diverse applications, including molecular devices, nano-templates, electrocatalysis, solar cells, and photosynthesis. We combined a molecular level study of the redox reactions using electrochemical scanning tunneling microscopy (EC-STM) with a macroscopic electrochemical technique, cyclic voltammetry (CV), to study two redox active porphyrin molecule, TPyP \((5,10,15,20\text{-Tetra}(4\text{-Pyridyl})\text{-21H,23H-Porphine})\) and \(5, 10, 15, 20\text{-tetrakis (4-carboxylphenyl)21H, 23H-porphyrin (TCP})\). We showed that the adsorbed oxidized TPyP molecules slowly change to brighter contrast, consistent with the appearance of the reduced form of TPyP, under reduction condition \((0.0V_{\text{SCE}})\). The time scale of the slow reduction is in the order of tens of minutes at \(0.0V_{\text{SCE}}\), but accelerates at
more negative potentials. We propose that protonation and deprotonation processes play an important role in the surface redox reaction due to geometry restriction of the molecules adsorbed on the surface. EC-STM and CV experiments were performed at various pH values to investigate the mechanism of this anomalously slow redox reaction. Our results show that the increased concentration of H$^+$ hinders the reduction of porphyrins, a feature that was never reported. This provides insight into the details of the surface redox reaction.