Molecular Conductance Switching Processes through Single Ruthenium Complex Molecules in Self-Assembled Monolayers

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For the design of real applicable molecular devices, current-voltage properties through molecular nanostructures such as metal-molecule-metal junctions (molecular junctions) have been studied extensively. In thiolate monolayers on the gold electrode, the chemical bonding of sulfur to gold and the van der Waals interactions between the alkyl chains of neighboring molecules are important factors in the formation of well-defined monolayers and in the control of the electron transport rate. Charge transport through the molecular junctions depends significantly on the energy levels of molecules relative to the Fermi levels of the contacts and the electronic structure of the molecule. It is important to understand the interfacial electron transport in accordance with the increased film thickness of alkyl chains that are known as an insulating layer, but are required for molecular device fabrication.

Thiol-tethered RuII terpyridine complexes were synthesized for a voltage-driven molecular switch and used to understand the switch-on mechanism of the molecular switches of single metal complexes in the solid-state molecular junction in a vacuum. Electrochemical voltammetry and current-voltage (I-V) characteristics are measured to elucidate electron transport processes in the bistable conducting states of single molecular junctions of a molecular switch, Ru(II) terpyridine complexes. (1) On the basis of the Ru-centered electrochemical reaction data, the electron transport rate increases in the mixed self-assembled monolayer (SAM) of Ru(II) terpyridine complexes, indicating strong electronic coupling between the redox center and the substrate, along the molecules. (2) In a low-conducting state before switch-on, I-V characteristics are fitted to a direct tunneling model, and the estimated tunneling decay constant across the Ru(II) terpyridine complex is found to be smaller than that of alkanethiol. (3) The threshold voltages for the switch-on from low- to high-conducting states are identical, corresponding to the electron affinity of the molecules. (4) A high-conducting state after switch-on remains in the reverse voltage sweep, and a linear relationship of the current to the voltage is obtained. These results reveal electron transport paths via the redox centers of the Ru(II) terpyridine complexes, a molecular switch.

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