

Investigation of Trinuclear Ruthenium Clusters as Probes of Weak Interactions of Ligand-Receptor Binding

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Weak interactions between small molecules and proteins, such as van der Waals forces and hydrogen bonding, are important in living systems but are difficult to measure directly. Marcus theory of electron transfer relates these weak interactions to reorganization energy and electron transfer rate. Therefore, information on weak interactions can be obtained through electrochemical experiments to measure the rate of electron transfer and reorganization energy. Initial studies were performed using the biotin/avidin system. Utilizing two different avidin binding ligands, 4-DMP and 4-BMP, monovalent and bivalent trinuclear ruthenium clusters were synthesized. Experiments were performed to investigate the strength of binding of these clusters to avidin. The clusters were incorporated into self-assembled monolayers to facilitate electrochemical experiments. Cyclic voltammetry (CV) and alternating current voltammetry (ACV) were performed on these monolayer systems before and after protein binding. The redox potential, current, and amount of charge transferred upon oxidation and reduction of the clusters were measured. The data before avidin binding and after avidin binding were compared. In the 4-DMP and monovalent 4-BMP systems, changes in CV and ACV data were negligible. This means there is no measureable change in electron transfer rate and reorganization energy upon protein binding for these systems. For the bivalent 4-BMP system, a shift in redox potential of -43 mV was observed upon avidin binding. In the future, trinuclear ruthenium clusters with different binding ligands will be synthesized to maximize electrochemical changes upon protein binding. This research has potential applications in the development of protein biosensors.