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# Roles of self-exchange electron transfer between anchored metal-polypyridyl dyes to mesoporous metal-oxide thin films

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## Abstract

Solar water splitting can supply our future energy demands in a clean and sustainable fashion, but it requires that a challenging redox reaction be driven efficiently with sunlight, i.e. the four electron and four proton oxidation of water to $O_2$. A major challenge in realizing a molecular system for solar water splitting is the ability to deliver multiple photogenerated charges to multiple-electron-transfer catalysts. Our approach to accomplish this is to utilize self-exchange electron-transfer reactions between molecular sensitizers anchored to mesoporous thin films of $TiO_2$ in order to accumulate multiple charges at catalysts, a prerequisite for water splitting chemistry. Herein, we report on the influence that ions have on the rates of these self-exchange processes. Spectroelectrochemistry was used to characterize self-exchange electron transfer between *cis*-Os(dcb)2(NCS)2 (dcb is 4,4'-(COOH)2,2'-bipyridine) and Ru(bpy)2(dcb)(PF6)2 (bpy is 2,2'-bipyridine) dyes when anchored to mesoporous $TiO_2$ thin films and immersed in Ar-sparged electrolyte solutions containing salt of one anion (hexafluorophosphate, tetrafluoroborate, perchlorate, or chloride ions) and one cation (lithium, sodium, or *n*-tetrabutylammonium ions). A fixed potential step was applied to the working electrode to initiate dye oxidation and the resulting rate of oxidation was quantified using electronic absorption spectroscopy by monitoring the change in the absorbance of the metal-to-ligand charge-transfer band of the dye over time. The self-exchange electron transfer rate constant was determined by fitting the absorbance versus time data to a modified Anson equation. From studies using the osmium dye, when small cations were present the slowest self-exchange electron transfer rates were observed, and the rate was largest when the dye was in the presence of n-tetrabutylammonium cations and perchlorate anions. This results will be compared with ruthenium counterparts and the combine results will be presented. These exciting results show that the local electrostatic environment around dyes greatly affects its reorganization energies and the resulting rates of electron transfer. Results from this study will provide theoretical and experimental bases for further research into the fundamentals of ion-coupled electron transfer, and notably as it pertains to solar fuels devices.

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