THE USE OF RUTHENIUM (II) DIIMINE COMPLEXES
IN SOLAR ENERGY CONVERSION

By

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ABSTRACT

In this thesis the evidence for electron transfer quenching by different Ru-diimine photosensitizers have been studied by the photogalvanic effect, luminescence quenching, quantum yield of quenching, and the laser flash photolysis study of MV⁺⁺, which is an important precursor to water reduction to H₂.

Photogalvanic experiments were done for the complexes [Ru(bpy)(pyq)₂]²⁺, [Ru(bpy)(dmbpy)₂]²⁺, [Ru(bpy)(dpp)₂]²⁺, [Ru(bpz)₂(dpq)]²⁺, [Ru(bpy)₂(bpd)]²⁺, and [Ru(bpy)(dbpq)₂]²⁺ using Fe³⁺ as a quencher. The [Ru(bpy)(dmbpy)₂]²⁺-Fe³⁺ system exhibits a large photogalvanic effect (190 mv in 1N H₂SO₄), which is better than Ru(bpy)³⁺ under the same conditions. The [Ru(bpy)(pyq)₂]²⁺-Fe³⁺ system gives (100 mv in 1N H₂SO₄), but there is a photochemical reaction occurring while light is on, which gives a photoproduct that has a reversible photogalvanic effect with medium photopotential. Other studied complexes show poor results due to a photochemical change via the d-d state. In the presence of SDS, the photopotential is reduced for [Ru(bpy)(dmbpy)₂]²⁺, and [Ru(bpy)(pyq)₂]²⁺, while the other complexes show an enhancement of photopotential due to a photoelectrochemical reaction. So to understand the effect of micellization, photochemistry-luminescence, photogalvanic luminescence, emission intensity ratio (I₀/I) vs SDS concentration, and cyclic voltammetry experiments were carried out.
Quenching studies of [Ru(bpy)(pyq)\(_2\)]\(^{2+}\), [Ru(bpy)(dmbpy)\(_2\)]\(^{2+}\), [Ru(bpy)(dpp)\(_2\)]\(^{2+}\), and [Ru(bpz)\(_2\)(dpq)]\(^{2+}\) by EDTA and MV\(^{2+}\) were done at pH 4 and 11. A dynamic and static quenching are occurring during the quenching of our studied complexes. Most complexes are quenched at less than diffusion controlled rates.

Irradiation of Ru(II)/MV\(^{2+}\)/EDTA system (where Ru(II) = [Ru(bpy)(pyq)\(_2\)]\(^{2+}\), [Ru(bpy)(dmbpy)\(_2\)]\(^{2+}\), [Ru(bpy)(dpp)\(_2\)]\(^{2+}\) and [Ru(bpz)\(_2\)(dpq)]\(^{2+}\)) produces MV\(^{-}\). The quantum yield of MV\(^{-}\) (\(\phi(MV^{-})\)), at pH 11 are greater than those at pH 4. Non-linear plots of [MV\(^{-}\)] vs irradiation time at pH 4, an increment in absorbance, and blue shift for [Ru(bpy)(dmbpy)\(_2\)]\(^{2+}\)/MV\(^{2+}\)/EDTA system as a function of irradiation time are discussed. The best photosensitizer for photodecomposition of water relative to studied complexes is the [Ru(bpz)\(_2\)(dpq)]\(^{2+}\), which has the highest quantum yield until now (\(\phi(MV^{-})\)=1.9).

Laser flash photolysis techniques were used to study the photodynamics of the [Ru(bpz)\(_2\)(dpq)]\(^{2+}\)/MV\(^{2+}\)/EDTA system at pH 11. By using this technique we observed that the quenching of [*Ru(bpz)\(_2\)(dpq)]\(^{2+}\) by EDTA in alkaline solution generates [Ru(bpz)\(_2\)(dpq)]\(^{+}\) which reacts with MV\(^{2+}\) to yield MV\(^{-}\), the reducing EDTA radical, reacts with MV\(^{2+}\) to yield a second equivalent to MV\(^{-}\).