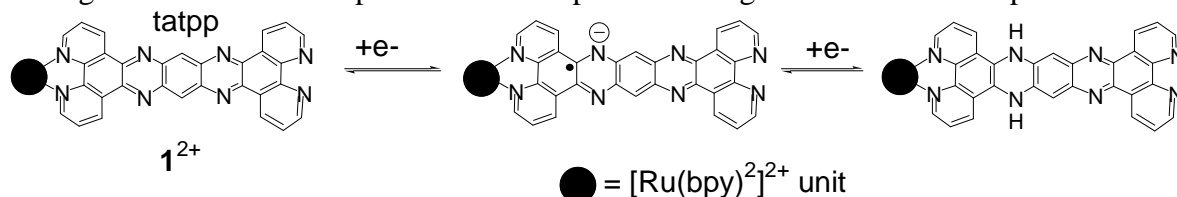


# INSIGHTS INTO THE MECHANISM OF MULTI-ELECTRON PHOTOREDUCTION IN RUTHENIUM COMPLEXES OF THE TETRAAZATETRAPYRIDOPENTACENE LIGAND

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Interest in molecular photocatalysts designed to utilize solar energy for the production of fuels, such as hydrogen, has increased considerably in the past few years.<sup>1-3</sup> While the development of true water-splitting photocatalysts still faces a number of technical challenges, one central issue is matching the one-photon/one-electron nature of most molecular photoexcitations with the multi-electron and multi-proton requirements of important fuel making reactions, such as hydrogen and oxygen evolution reactions. The mononuclear and dinuclear ruthenium complexes,  $[(bpy)_2Ru(tatpp)]^{2+}$  ( $1^{2+}$ ), and  $[(bpy)_2Ru(tatpp)Ru(bpy)_2]^{2+}$  ( $2^{4+}$ ) both undergo a net two electron photoreduction upon visible light irradiation in the presence of



sacrificial donors,<sup>4</sup> making these complexes potentially useful hydrogen-generation photocatalysts. Both electrons in this process are stored on the tatpp ligand and the negatively charged tatpp ligand is protonated to varying degrees depending on the solution pH. The mechanism of photoreduction is strongly dependent on the solution pH and switches from a sequential two one-electron reductive quenching process at basic pH to a one electron reduction, protonation and then disproportionation mechanism at neutral and acidic pH. Importantly, we have demonstrated that the singly reduced intermediates  $[(bpy)_2Ru(tatpp^{\cdot-})]^{+}$  and  $[(bpy)_2Ru(tatpp^{\cdot-})Ru(bpy)_2]^{3+}$ , containing the tatpp radical anion, are photochemically competent for reductive quenching, thus both the acidic and basic mechanism ultimately store two electrons via a net two-photon mechanism. Details in how the mechanism was determined using a combination of photochemistry, cyclic voltammetry, differential pulse voltammetry and spectroelectrochemistry will be presented.

## References

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