

Non-Nernstian Two-Electron Transfer Photocatalysis at Metalloporphyrin–TiO₂ Interfaces

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Introduction

A long standing question in the photochemical sciences concerns how to integrate single electron transfers to catalytic multi-electron transfer reactions that produce useful chemical fuels. Here we provide a strategy for the two-electron formation of C-C bonds with molecular catalysts anchored to semiconductor nanocrystallites. The blue portion of the solar spectrum provides band gap excitation of the semiconductor while longer wavelengths of light initiate homolytic cleavage of metal-carbon bonds that, after interfacial charge transfer, restore the catalyst. (1)

Experimental

The semiconductor utilized was the anatase polymorph of TiO₂ present as a nanocrystalline mesoporous thin film. The catalyst was cobalt *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin chloride, Co(TCPP)Cl or heme.

Results and Discussion

The catalyst cobalt *meso*-5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin chloride, Co(TCPP)Cl and iron protoporphyrin IX chloride, Fe(PPIX)Cl, displayed two distinct and sequential metal-based M^{III/II} and M^{II/I} reductions were observed under band gap illumination. Spectroelectrochemical characterization indicated that both reductions were non-Nernstian, behavior attributed to an environmentally dependent potential drop across the molecular-semiconductor interface. Reaction of Co^I(TCPP)/TiO₂ with organobromides (RBr = 1-Br-hexane or benzyl bromide) resulted in the formation of Co^{III}-R(TCPP)/TiO₂. Visible light excitation induced homolytic cleavage of the Co-C bond and the formation of C-C bonded products. The reactions were catalytic when band gap excitation or an electrochemical bias provided TiO₂ electrons to the oxidized catalyst. Sustained photocurrents were quantified in photoelectrosynthetic solar cells under forward bias.

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References

- (1) Ardo, S.; Achey, D.; Morris, A.J.; Abrahamsson, M.; Meyer, G.J., *J. Am. Chem. Soc.* **2011**, *133*, 16572-16580.