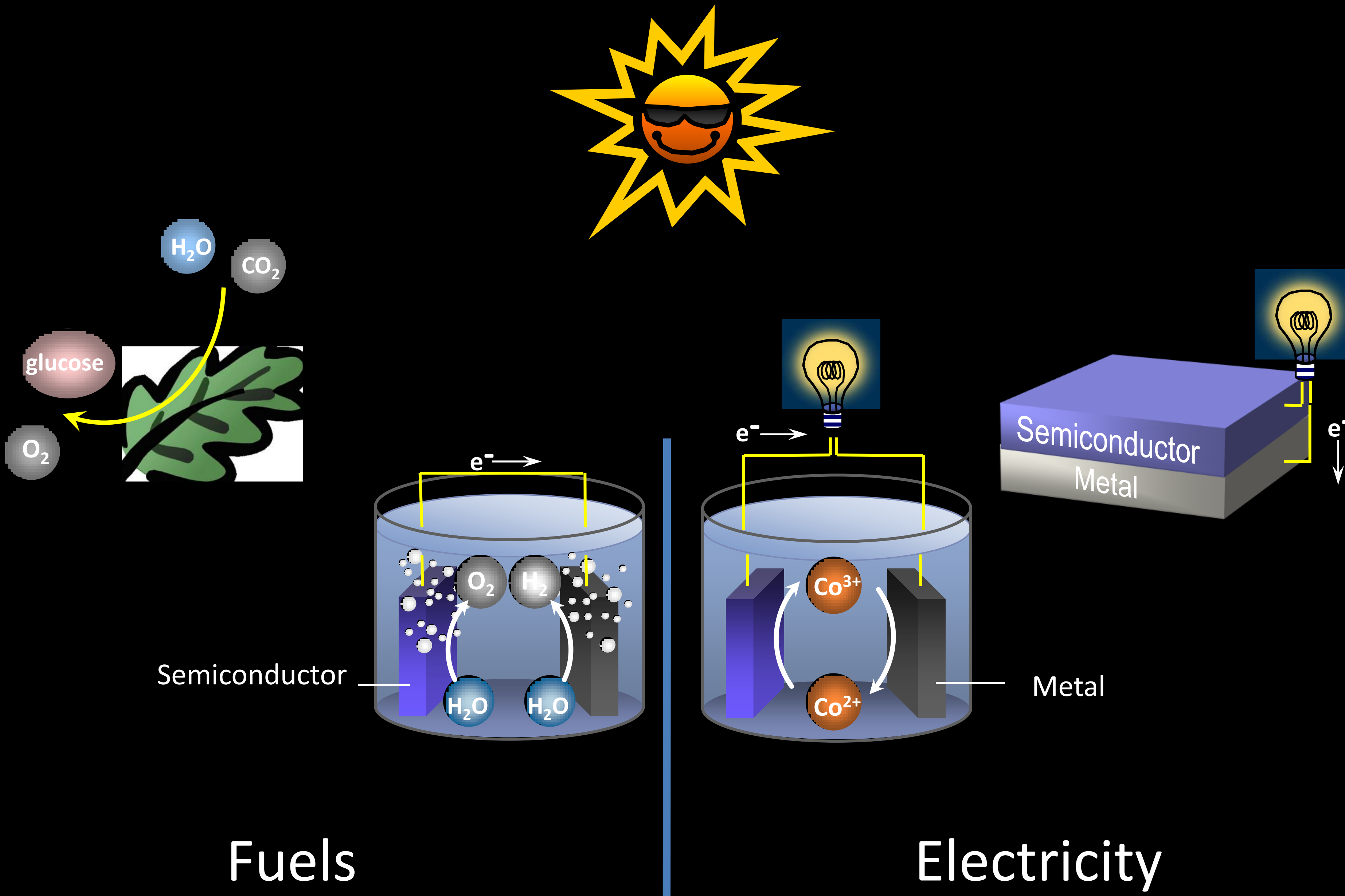
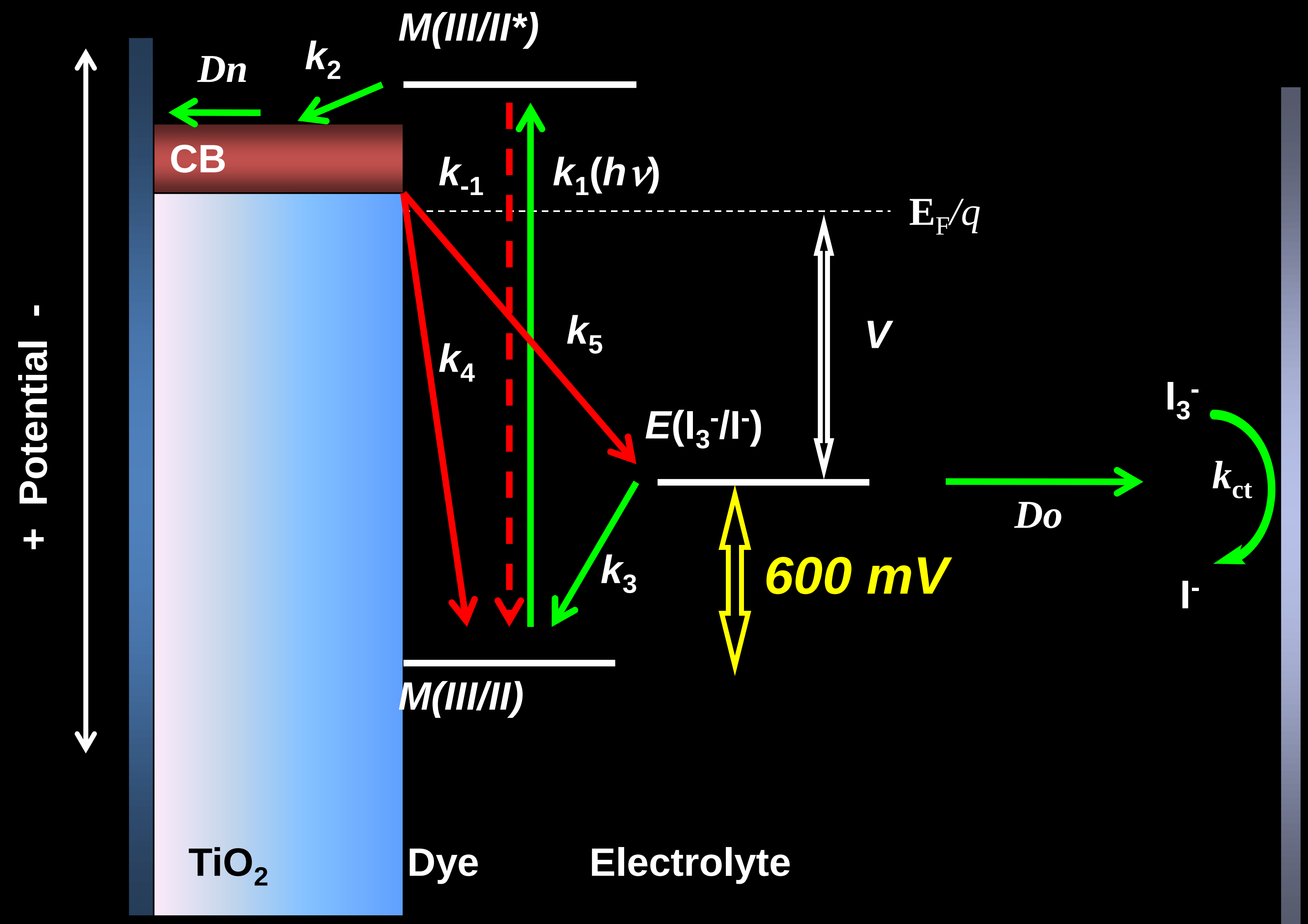
Solar Energy Conversion



Dye-Sensitized Solar Cell (DSSC)

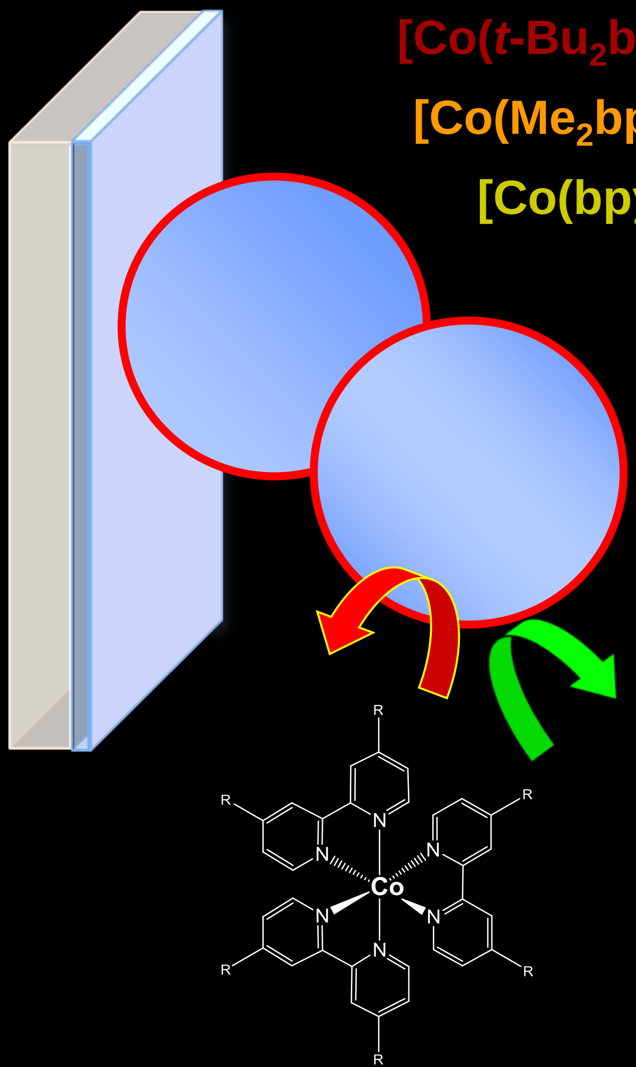


Cobalt Bipyridyl Redox Shuttles

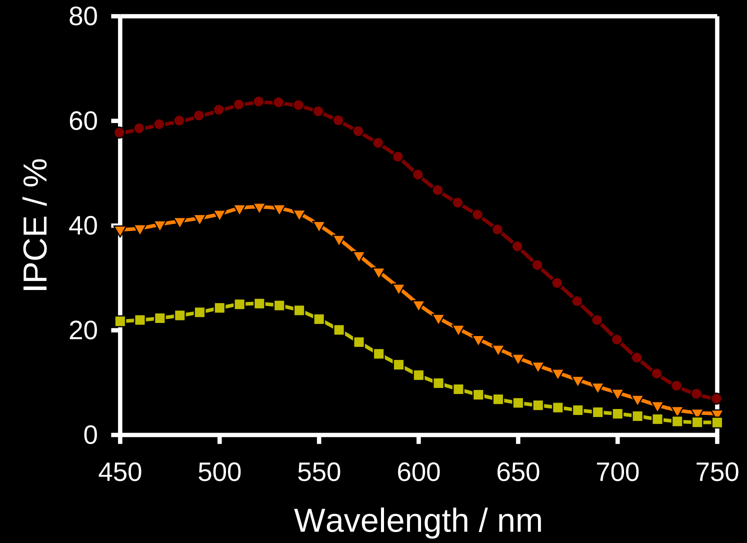
[Co(*t*-Bu$_2$bpy)$_3$]$^{3+/2+}$

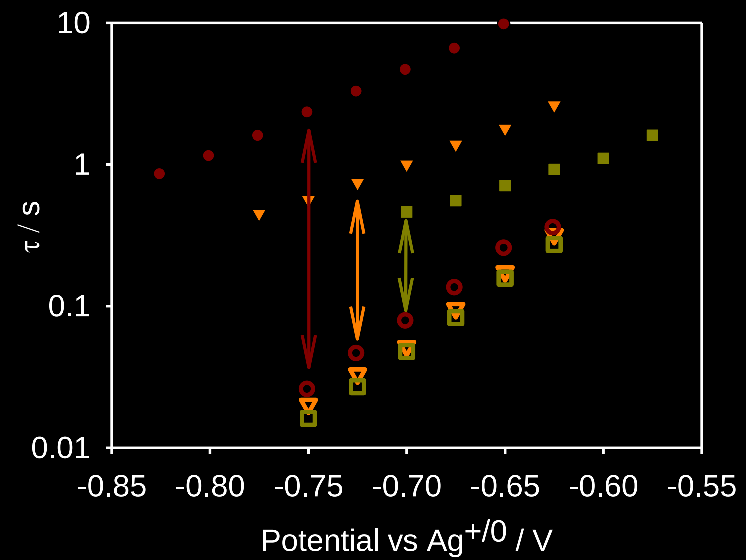
[Co(Me$_2$bpy)$_3$]$^{3+/2+}$

[Co(bpy)$_3$]$^{3+/2+}$



R = H, Me, *t*-Bu

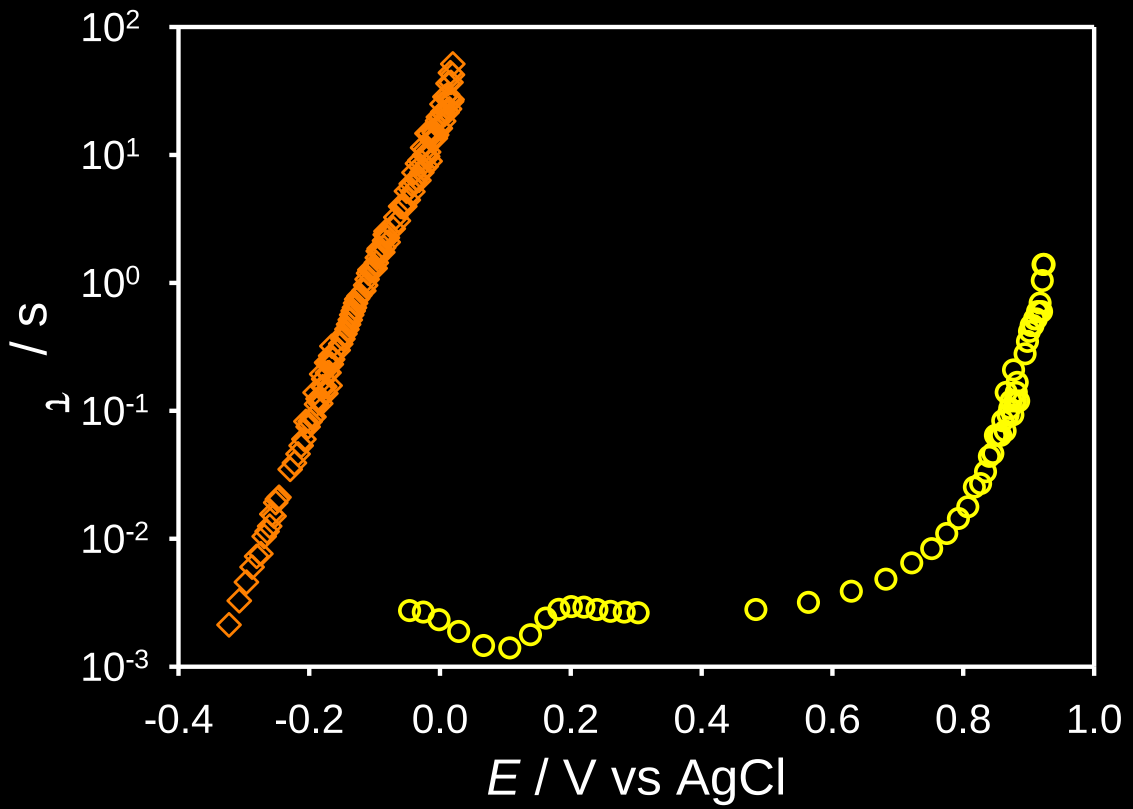


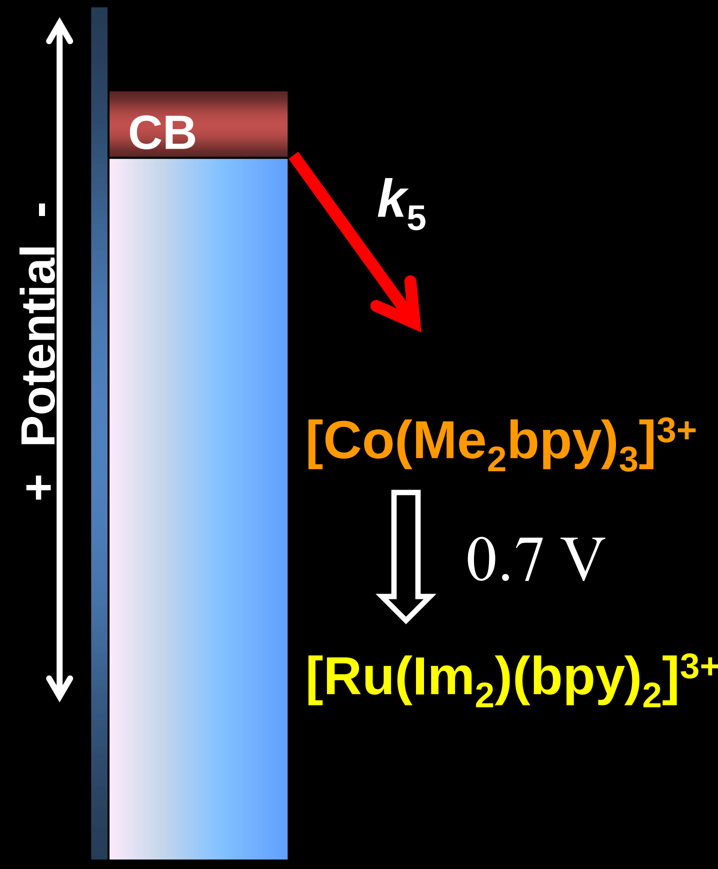


Klahr and Hamann, *J. Phys. Chem. C* **2009**, *113*, 14040-14045
Ondersma and Hamann, *J. Phys. Chem. C* **2010,** 114, (1), 638-645

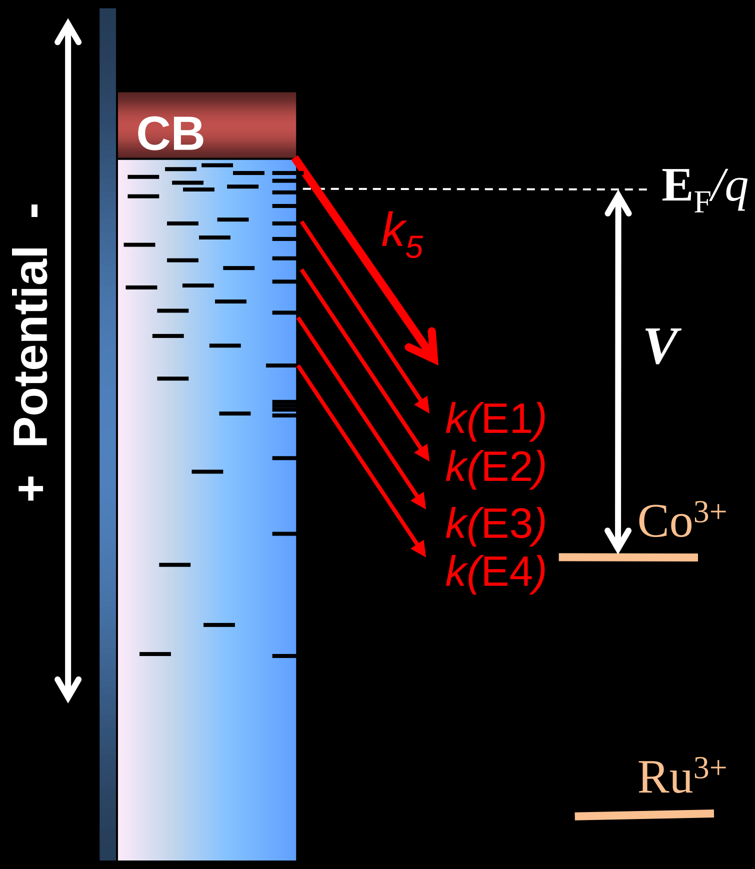
Lifetimes

$$\tau \propto \frac{1}{k_5} \quad ?$$





Recombination From Subbandgap States

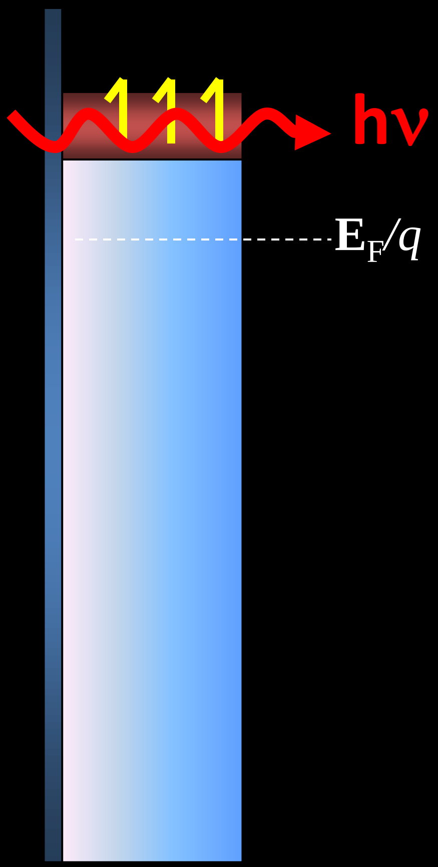


$$-\frac{dn}{dt} = \underbrace{\sum D(E) f(E)}_{n} k_{et}(E)[A]$$

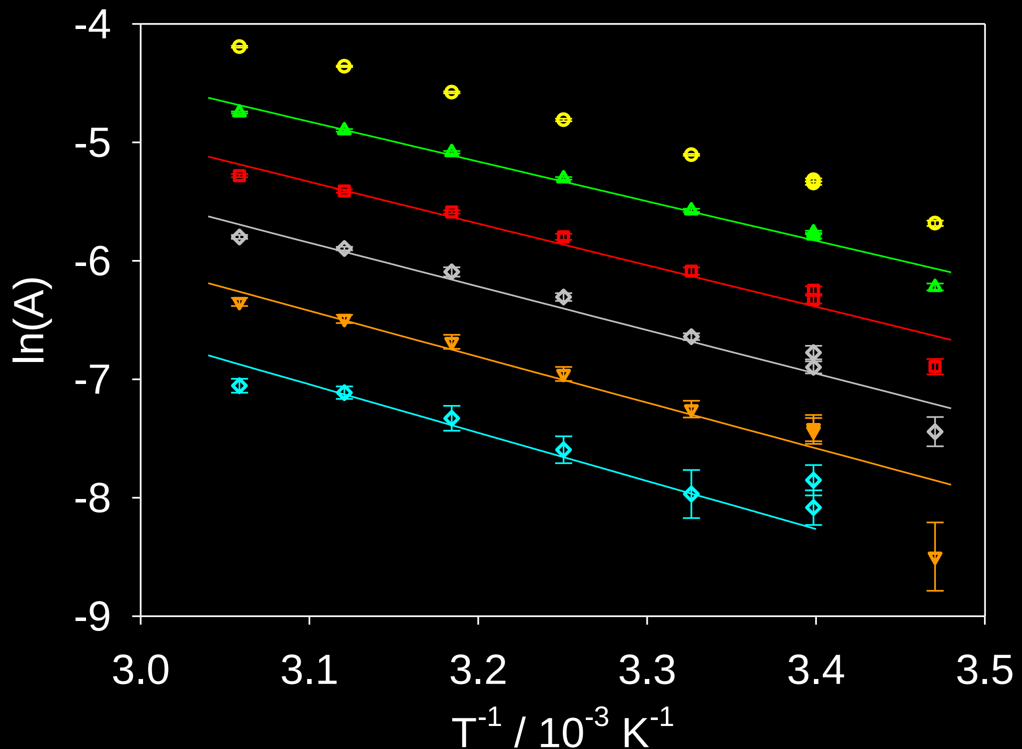
$$\tau_n(\mathbf{E}_\mathrm{F}) = \frac{\partial n(\mathbf{E}_\mathrm{F}) / \partial \mathbf{E}}{\partial U(\mathbf{E}_\mathrm{F}) / \partial \mathbf{E}}$$

Ondersma and Hamann, *J. Am. Chem. Soc.* **2011**, 133 (21), 9264-8271

Variable Temp. Spectroelectrochemistry



$$\ln(A) = \ln(\varepsilon \ell N_C) + \frac{1}{T}\frac{(\mathbf{E}_{CB} - \mathbf{E}_F)}{k_B}$$

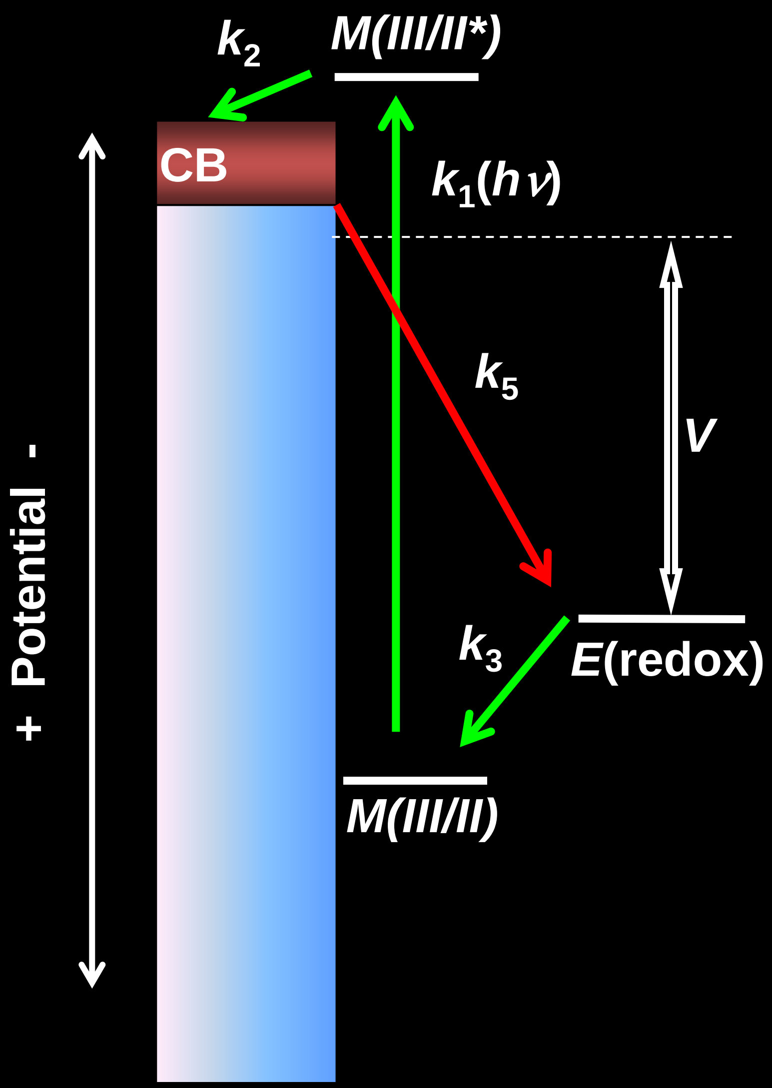


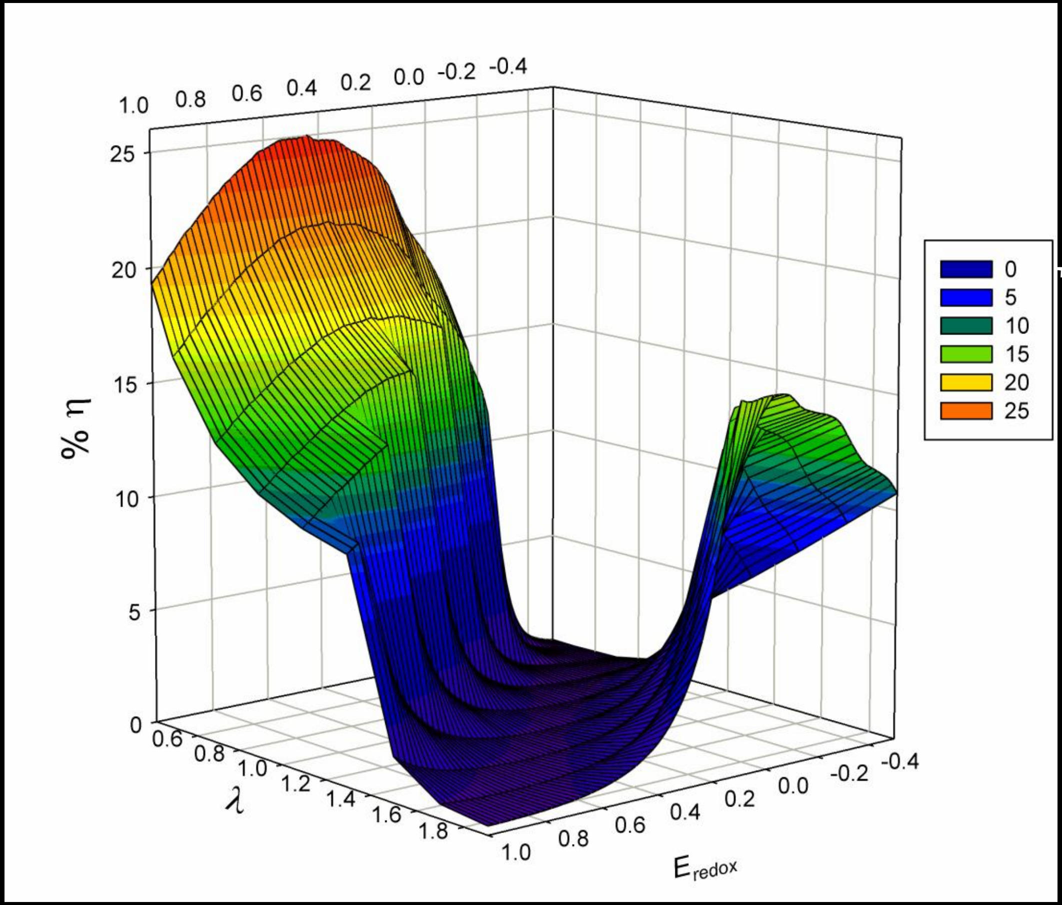
$$\varepsilon = 1 \pm 0.3 \times 10^5\ \mathrm{M^{-1}s^{-1}}$$

$$\mathbf{E}_{CB} \approx -0.8\ \mathrm{V\ vs\ Ag/AgCl}$$

Ondersma and Hamann, *Energy Environ. Sci.* **2012**, **5**, 9476-9480

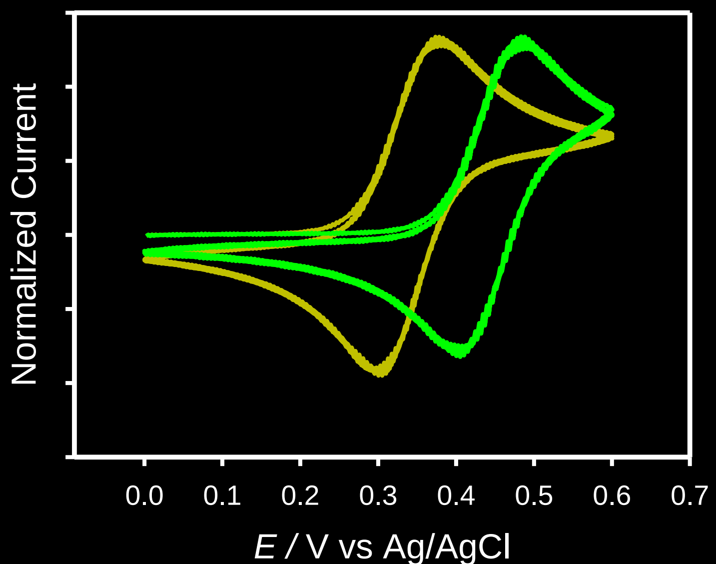
Potential of new redox shuttles

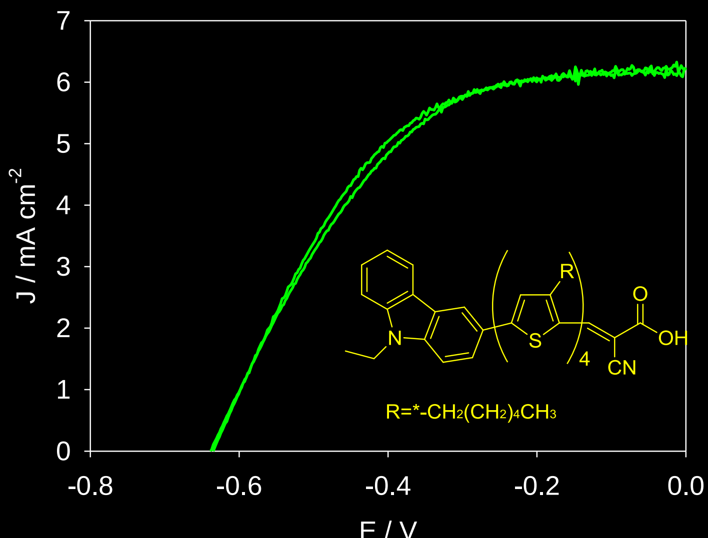




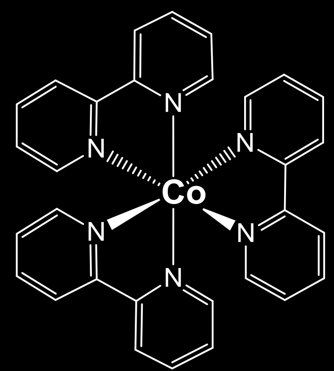
Ondersma and Hamann, *Coord. Chem. Rev.* **2012**, **DOI:** 10.1016/j.ccr.2012.09.010

Designing a Better Dye Regenerator

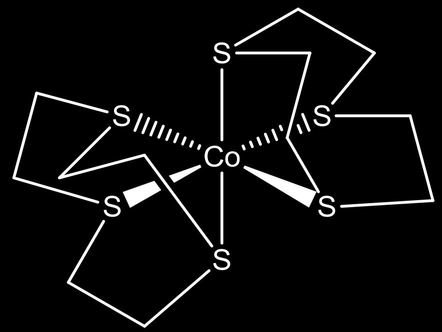




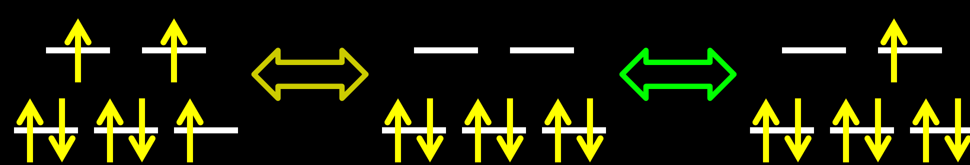
$[Co(bpy)_3]^{3+/2+}$



$[Co(ttcn)_2]^{3+/2+}$



k_{ex} = 20 $M^{-1}s^{-1}$ 1.3 x 10^5 $M^{-1}s^{-1}$



Co(II)-HS Co(III)-LS Co(II)-LS

Xie and Hamann, *J. Phys. Chem. Lett*, **2013**, 4, 328–332

Chandrasekhar and McAuley, *Inorg. Chem.* ***1992, 31, 480-487***

Current Open Questions

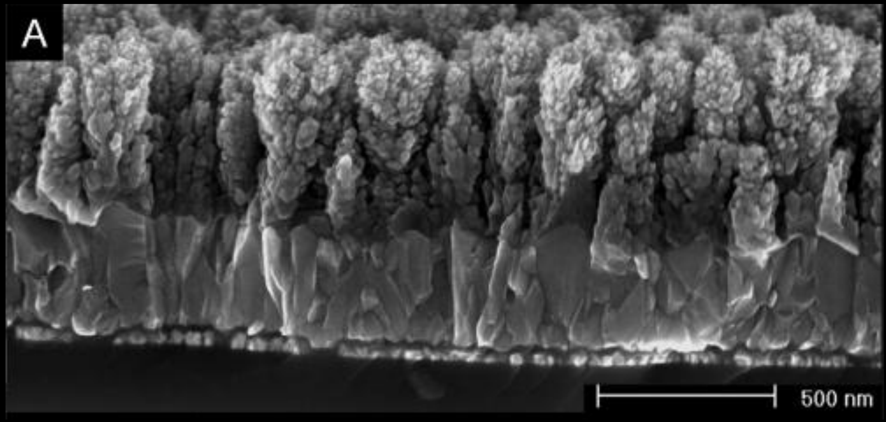
- How do material physical properties affect recombination?

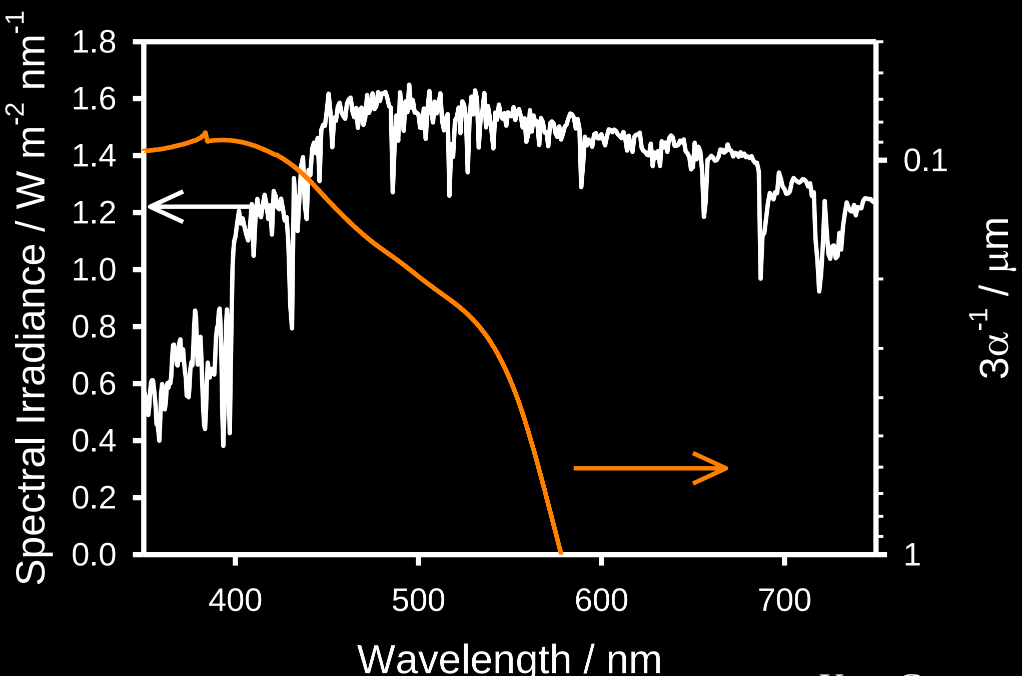
- How do we adapt the Marcus cross relation to understand details affecting regeneration?

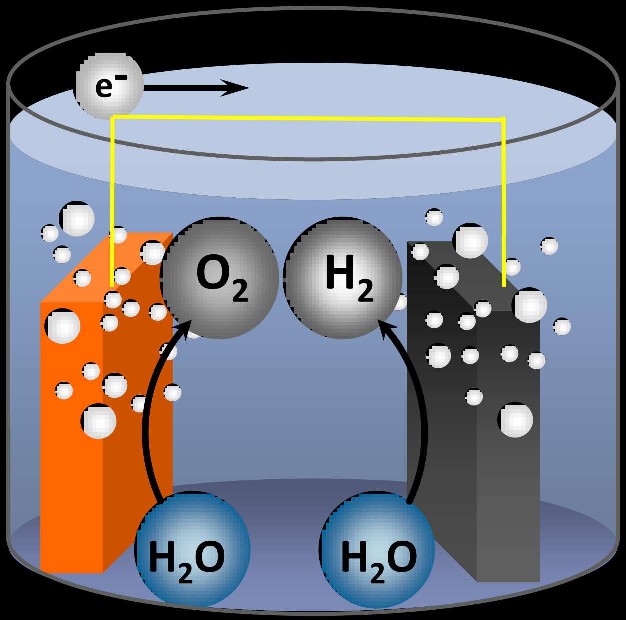
- Can we design better dye regenerators which aren't plauged from recombination losses?

- Ultimate goal is to develop general kinetic model to guide the design of new redox couple / semiconductor / sensitizer combinations which

Hematite (α-Fe_2O_3)



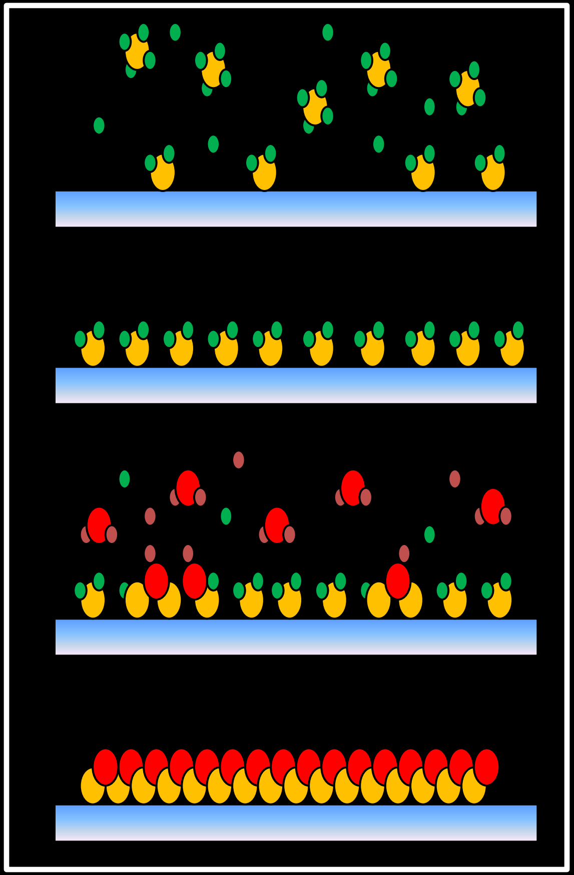


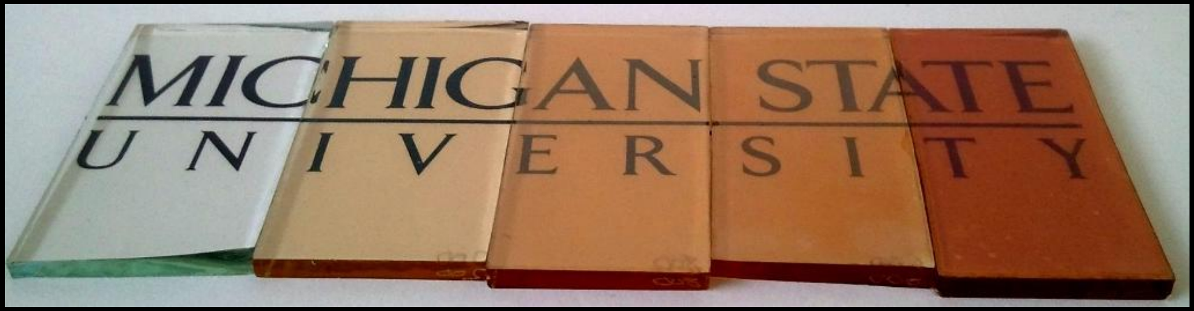


Kay, Cesar and Graetzel *J. Am. Chem. Soc.*, ***2006,*** *128 (49), 15714*

Atomic Layer Deposition

ALD

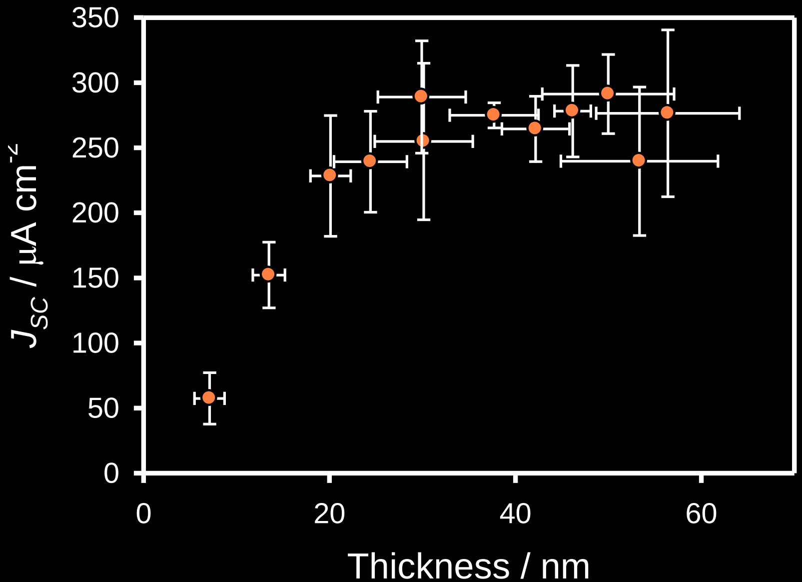


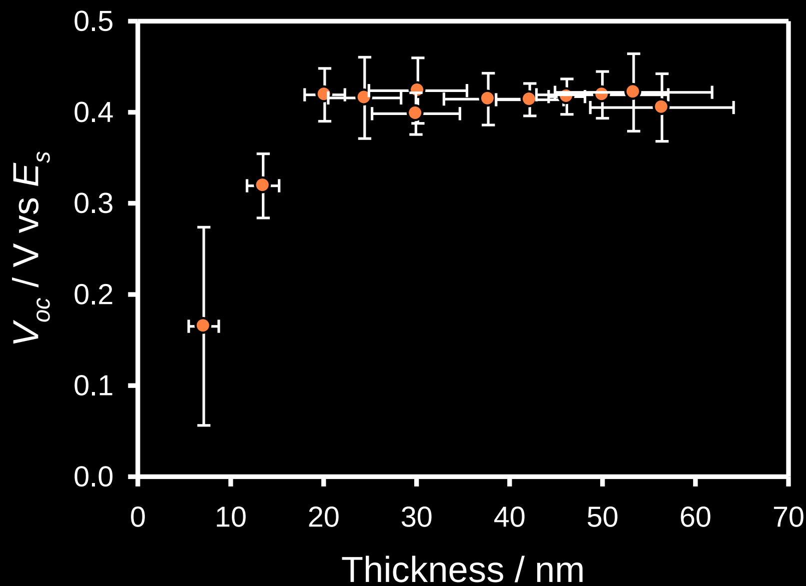


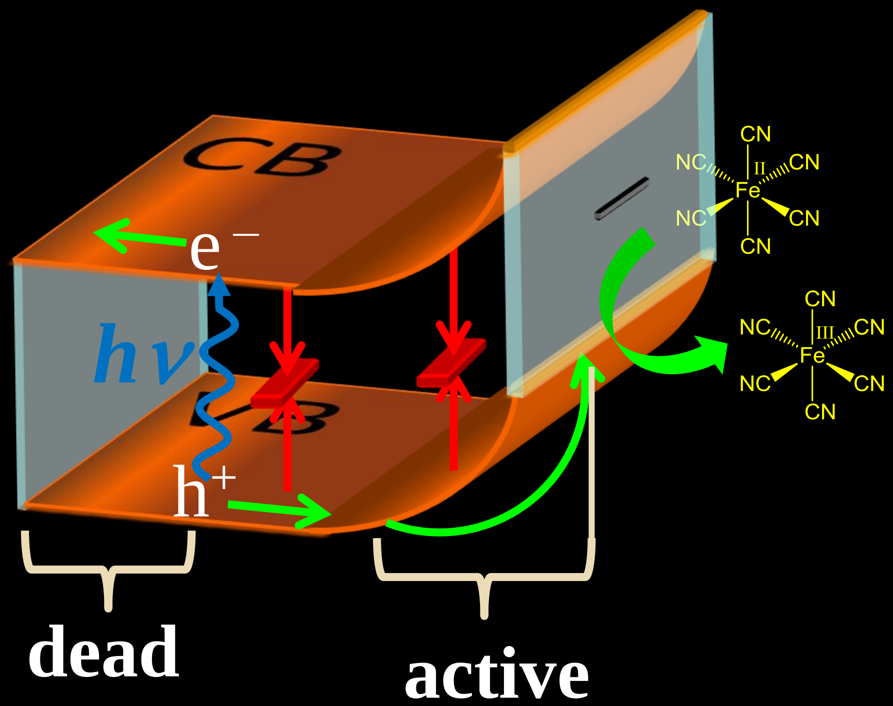
0, 15, 45, 60 and 100 nm Fe_2O_3

Klahr, Martinson, and Hamann, *Langmuir* **2011**, 27, 461

Limiting Thickness





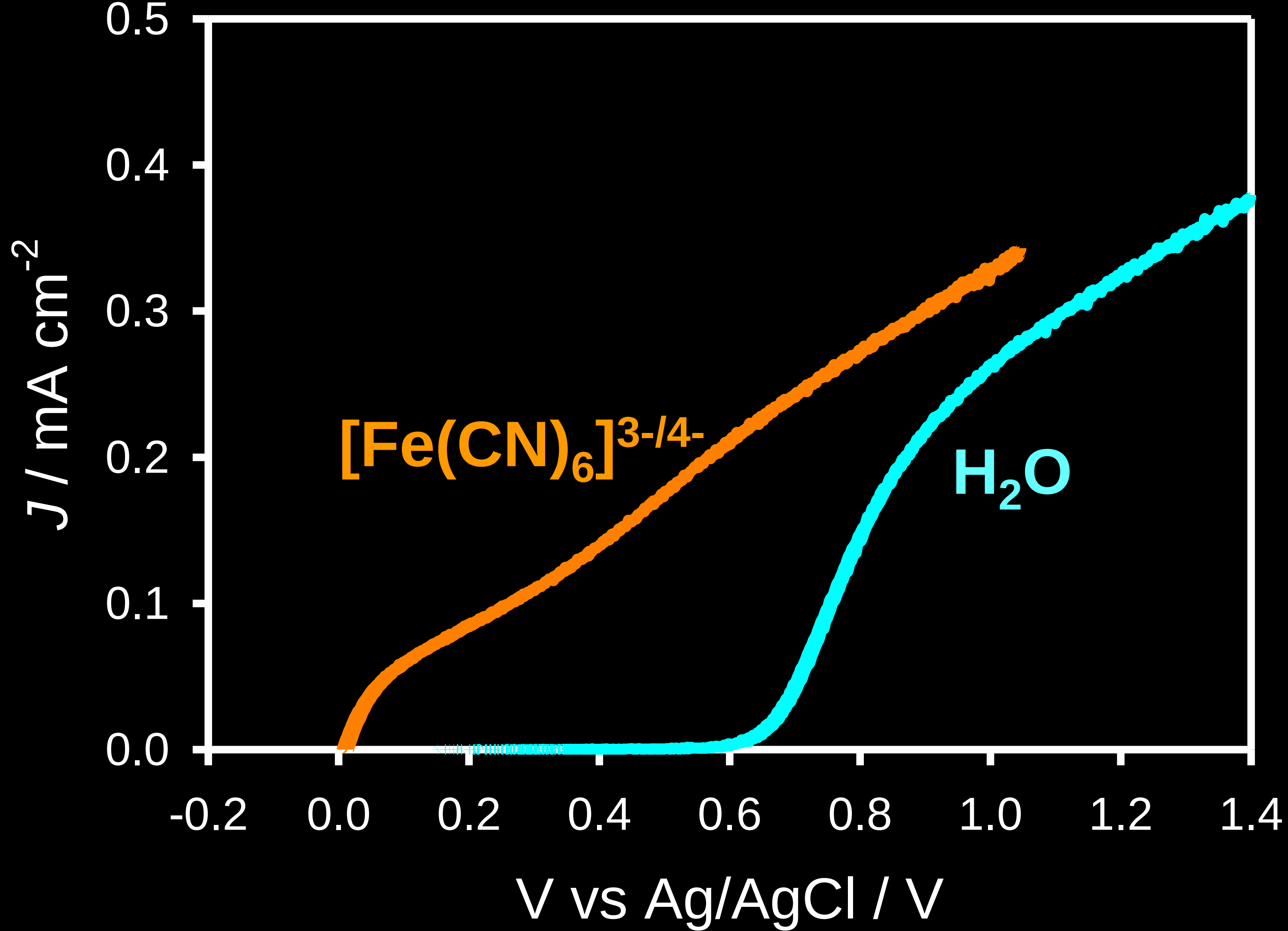


Klahr and Hamann, *J. Phys. Chem. C*, **2011**, 115 (16), 8393-8399

Klahr, Martinson, and Hamann, *Langmuir* **2011**, 27, 461

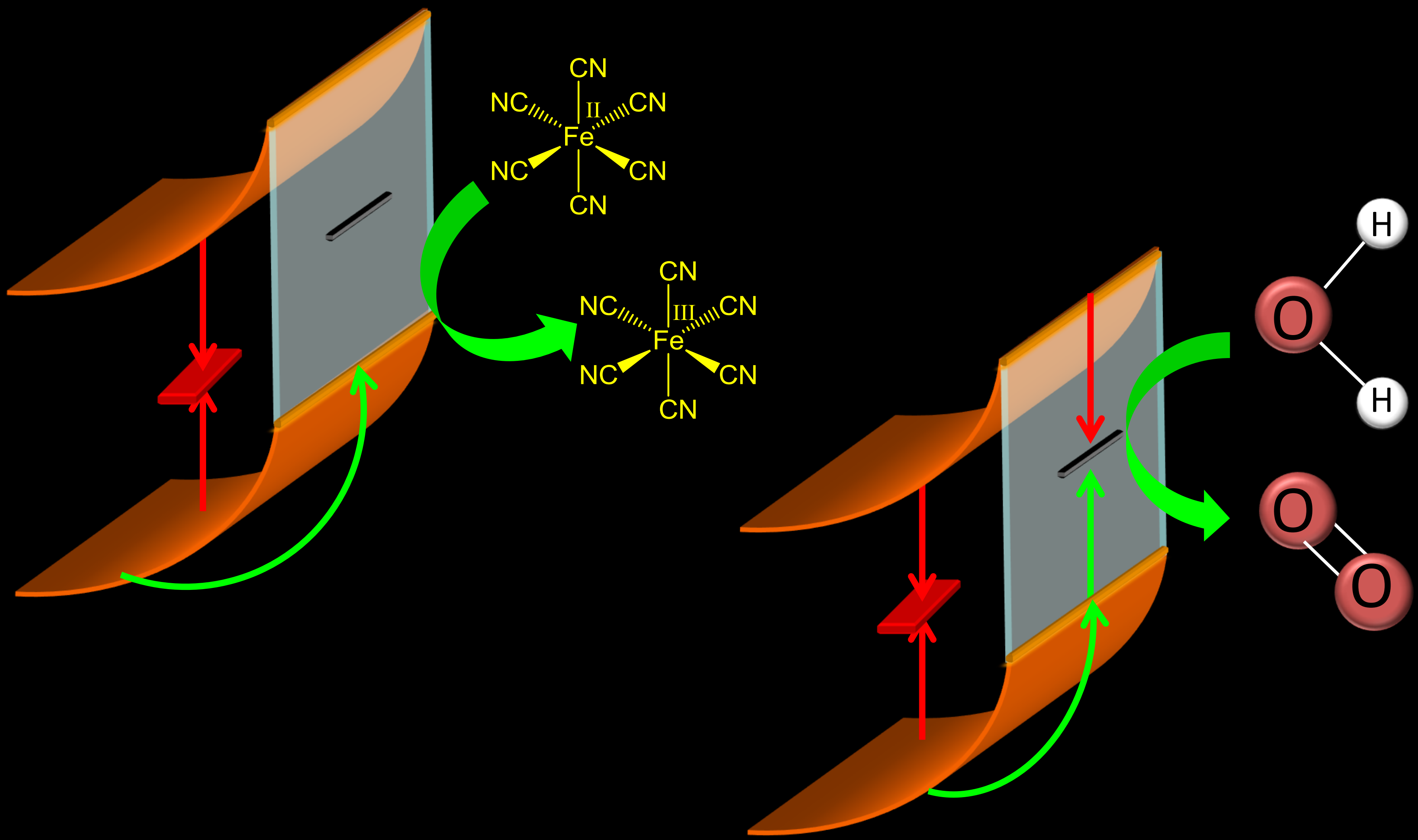
Dotan, Sivula, Gratzel, Rothschild, Warren *Energy Environ. Sci.*, **2011**, **4**, 958-964

H_2O vs. $[Fe(CN)_6]^{3-/4-}$



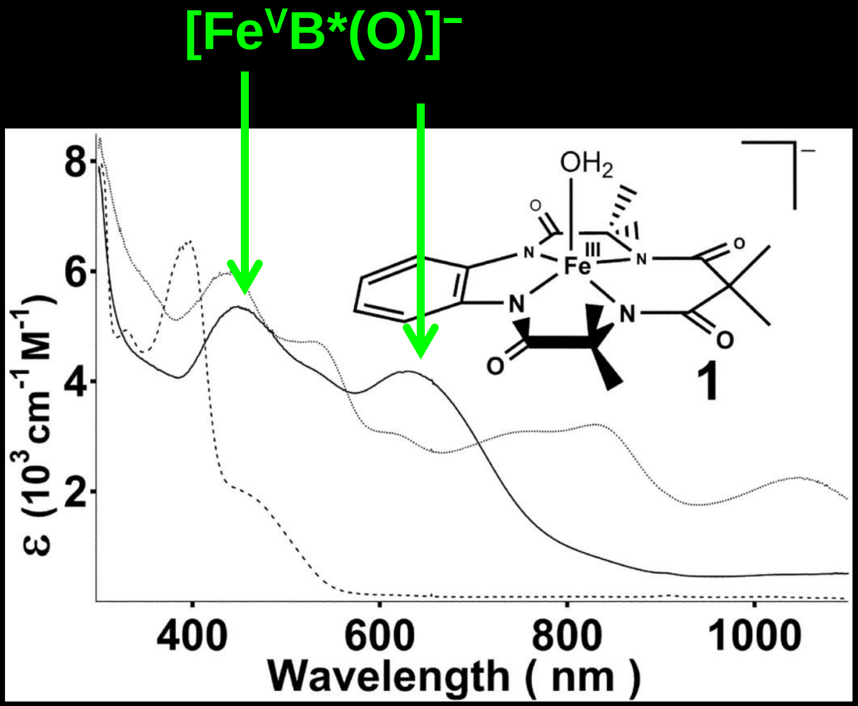
Klahr, Gimenez, Fabregat-Santiago, Bisquert, and Hamann, *Energy Environ. Sci.*, **2012,** *5 (6)*, 7626-1636

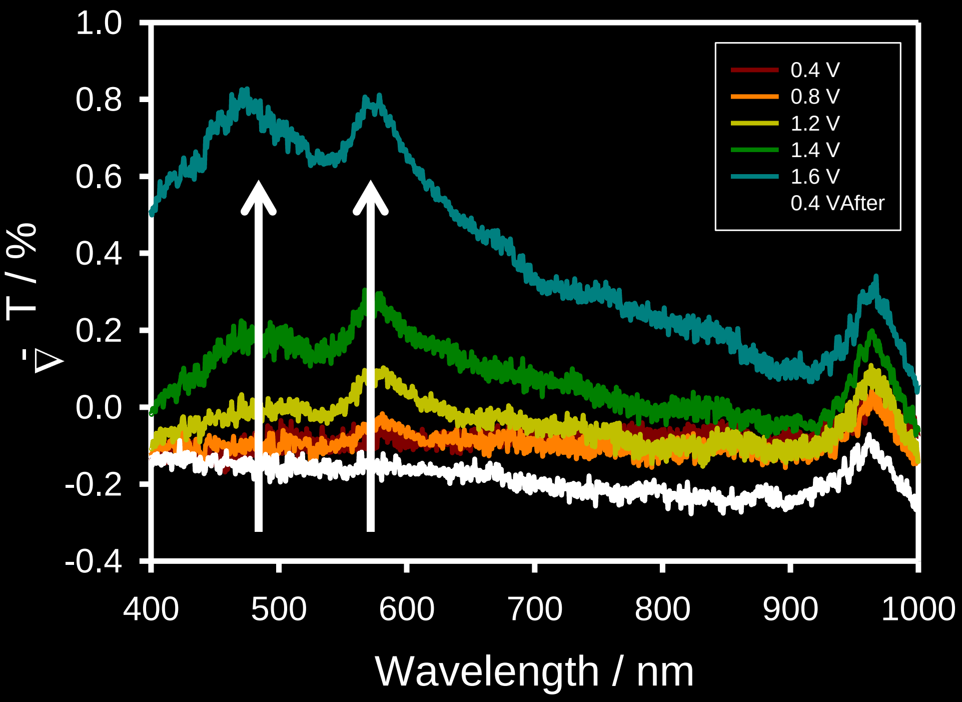
Conclusions



Klahr, Gimenez, Fabregat-Santiago, Bisquert, and Hamann, *Energy Environ. Sci.*, **2012,** *5 (6)*, 7626-1636
Klahr, Gimenez, Fabregat-Santiago, Hamann, and Bisquert, *J. Am. Chem. Soc.* **2012**, *134* (9), 4294–4302

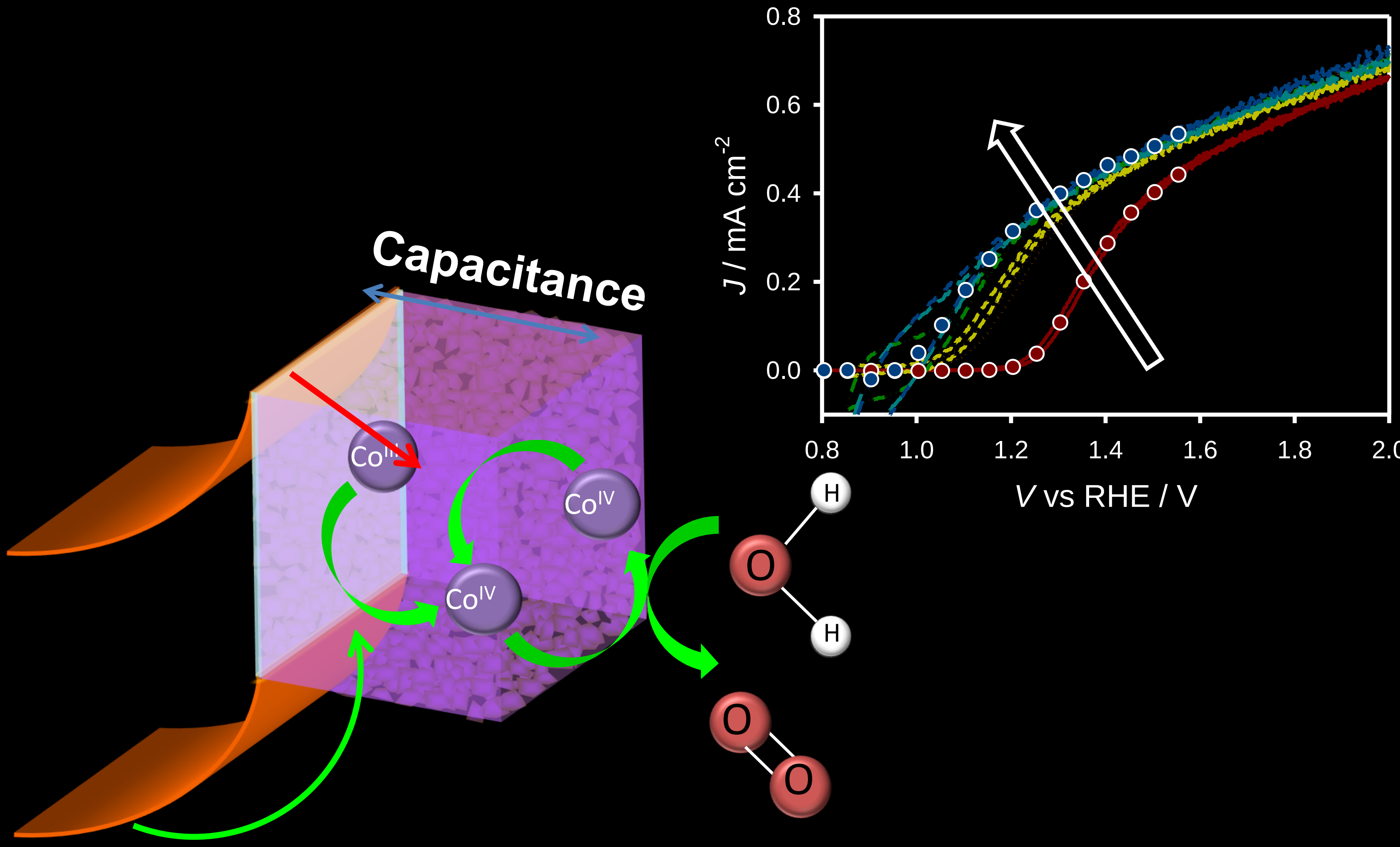
Potential Modulated Absorbance





de Oliveira, F. T., et. al. *Science* ***2007, 315, 835.***

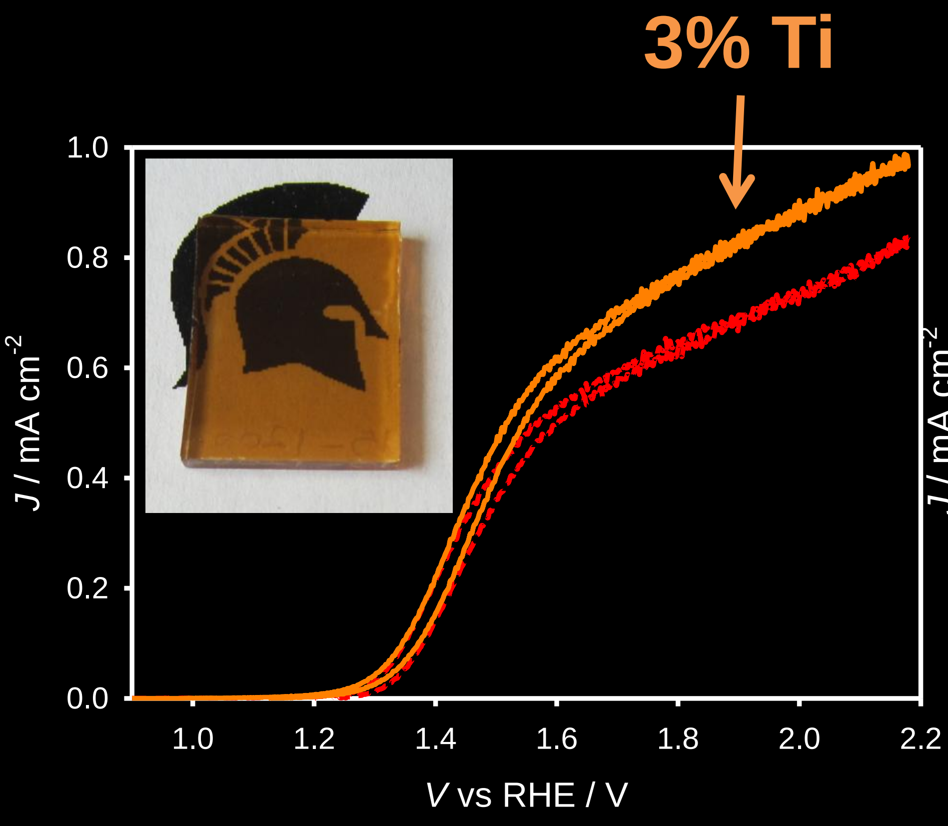
JV Curves



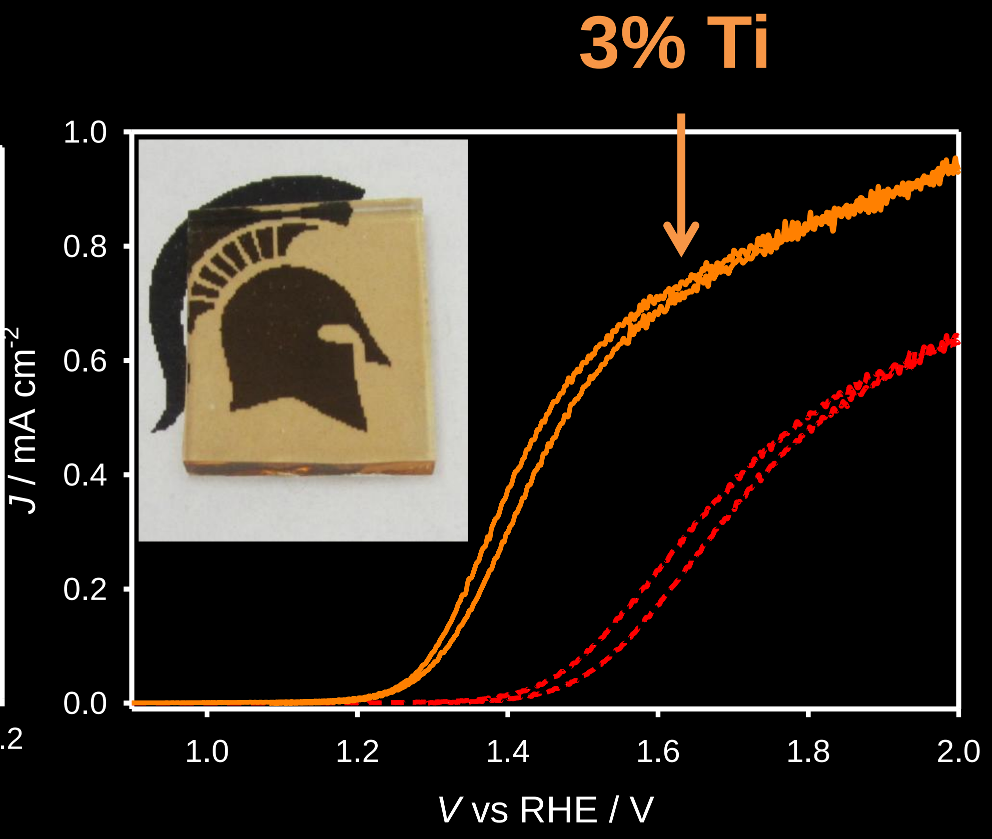
Klahr, Gimenez, Fabregat-Santiago, Bisquert, and Hamann, *J. Am. Chem. Soc.* **2012**, 134 (40), 16693–16700

The Effect of Ti “Dopants”

72 nm Fe_2O_3



18 nm Fe_2O_3



Zandi, Klahr, and Hamann, *Energy Environ. Sci.*, accepted

Current Open Questions

- What (chemically) are the surface states involved in water oxidation?

- How does the water oxidation mechanism / performance depend on metal oxide surface?

- Can we make a heterojunction to more efficiently separate charge at the surface?

- How do these “dopants” affect the structure of hematite? How do we understand effect of “doping” in general ?

Thank You!

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Mandal Dhritabrata

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ANL

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Stephanie Castle
Yuan Gao
Dan Little

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