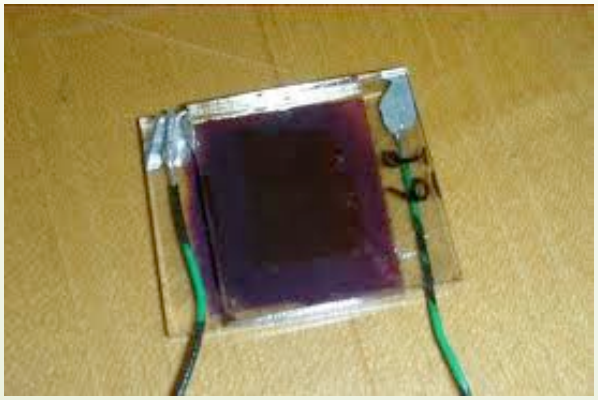
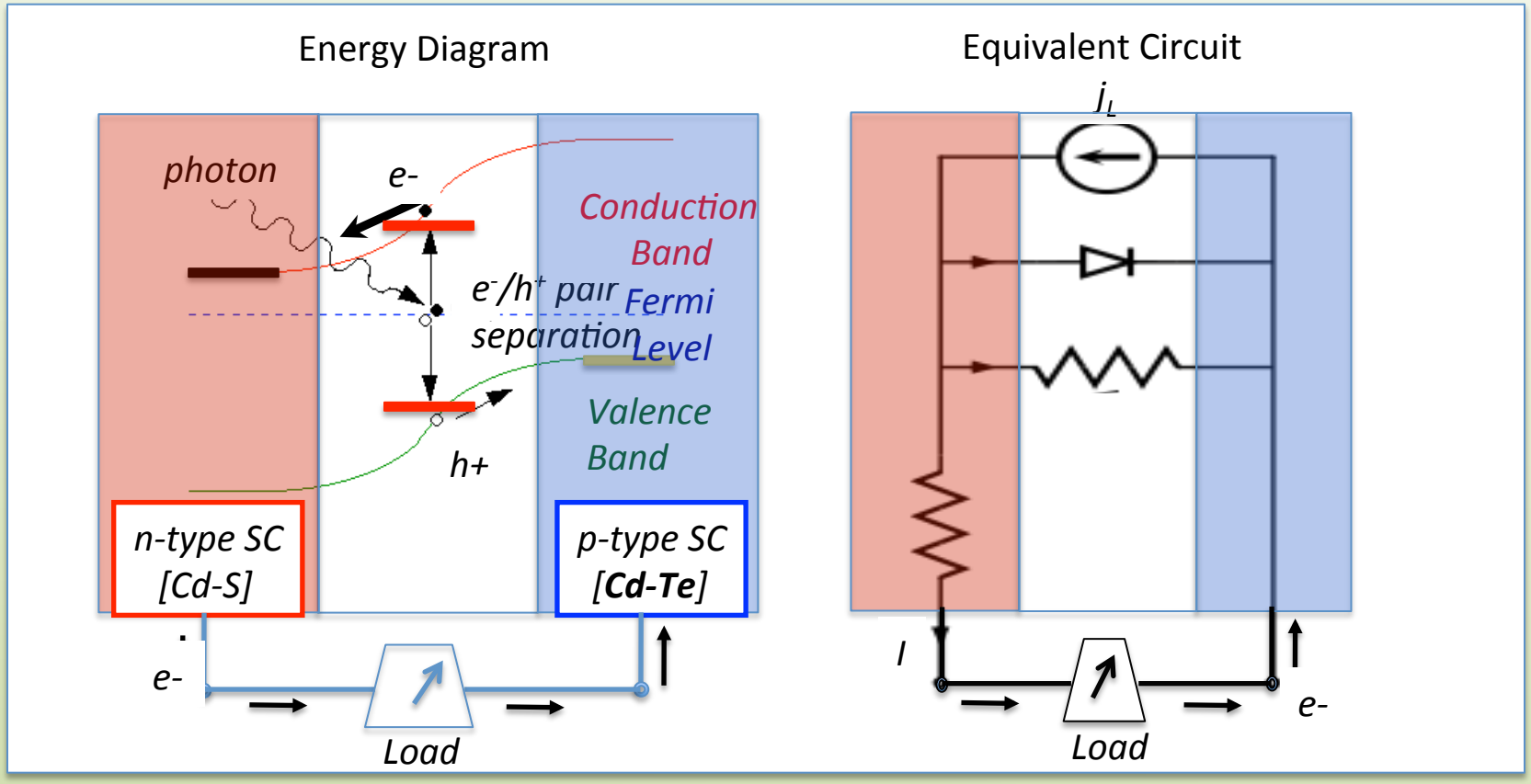


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

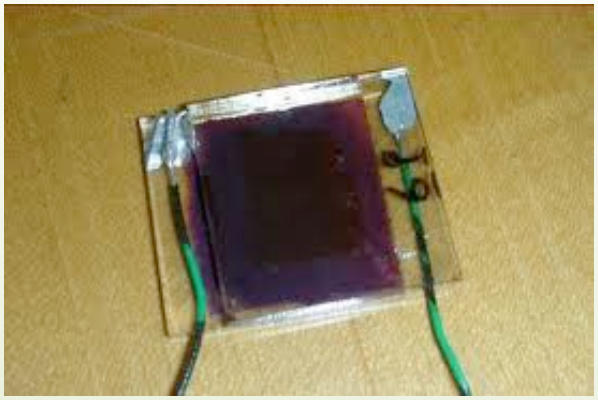
Modeling Photovoltaic Solar Cells

Traditional Photovoltaic Solar Cells

First and Second Generation: p-n junctions



[The Power of the Sun](): Walter Kohn's Description of Photovoltaic Solar Cells



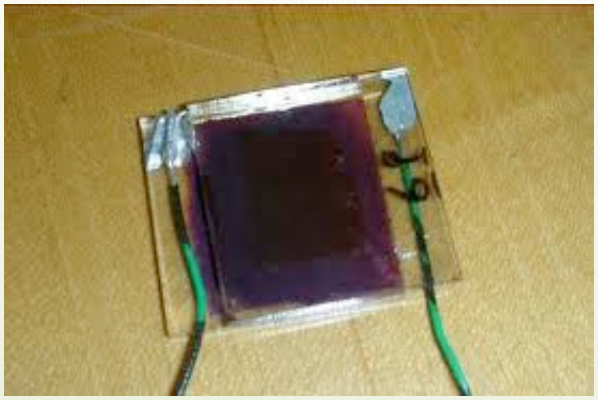
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Section II
Prof. Victor S. Batista

Computational Modeling and Physical Principles

- Computational design and characterization
- Solar cells for electricity
- Photocatalysis, biomimetic water oxidation
- Hydrogen economy

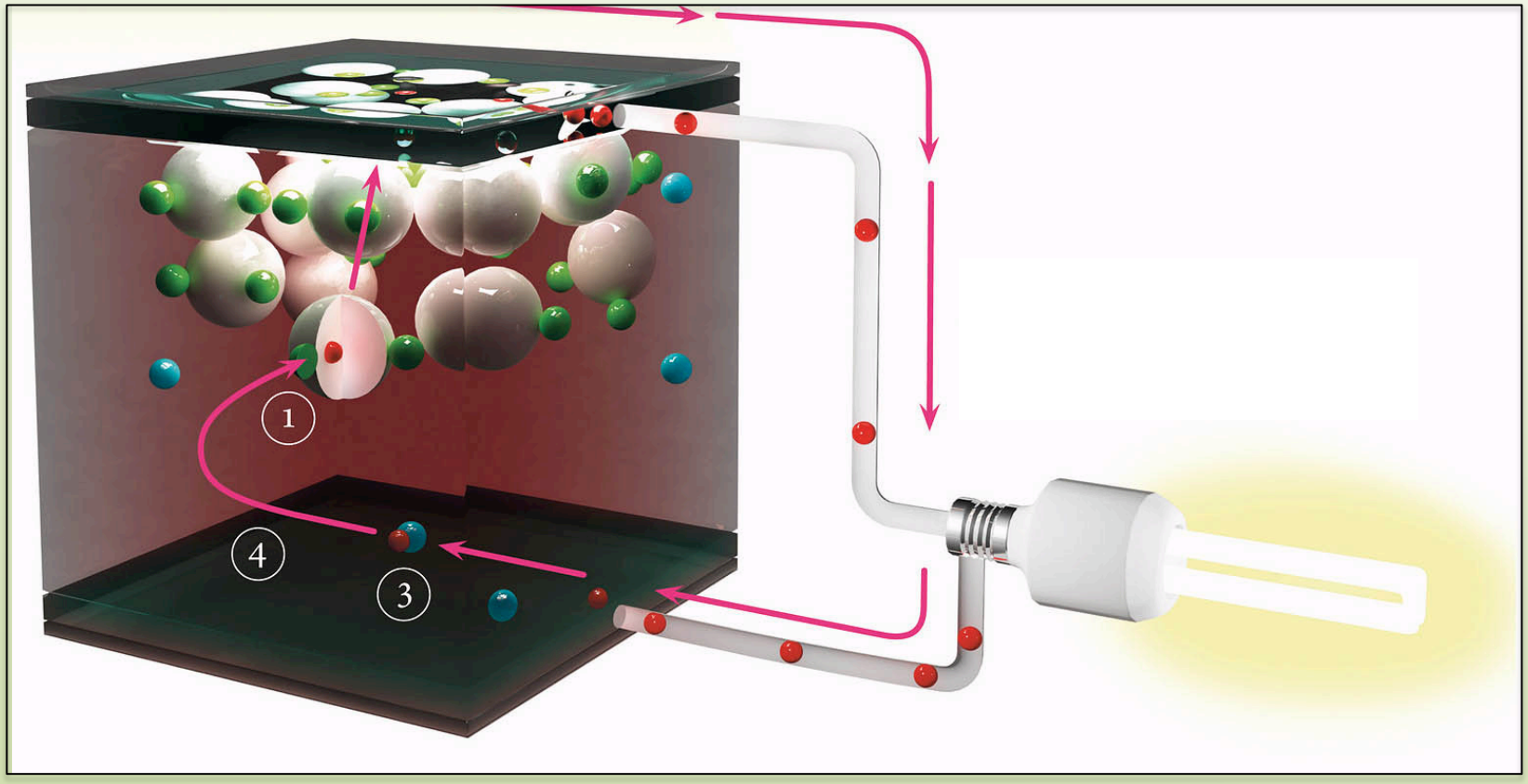


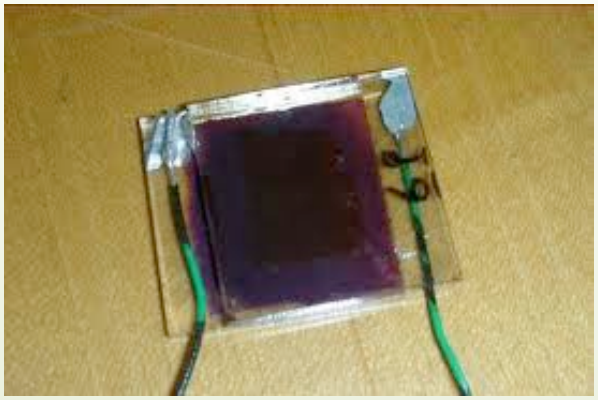
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Dye-Sensitized Solar Cells

Third Generation Photovoltaic Solar Cells

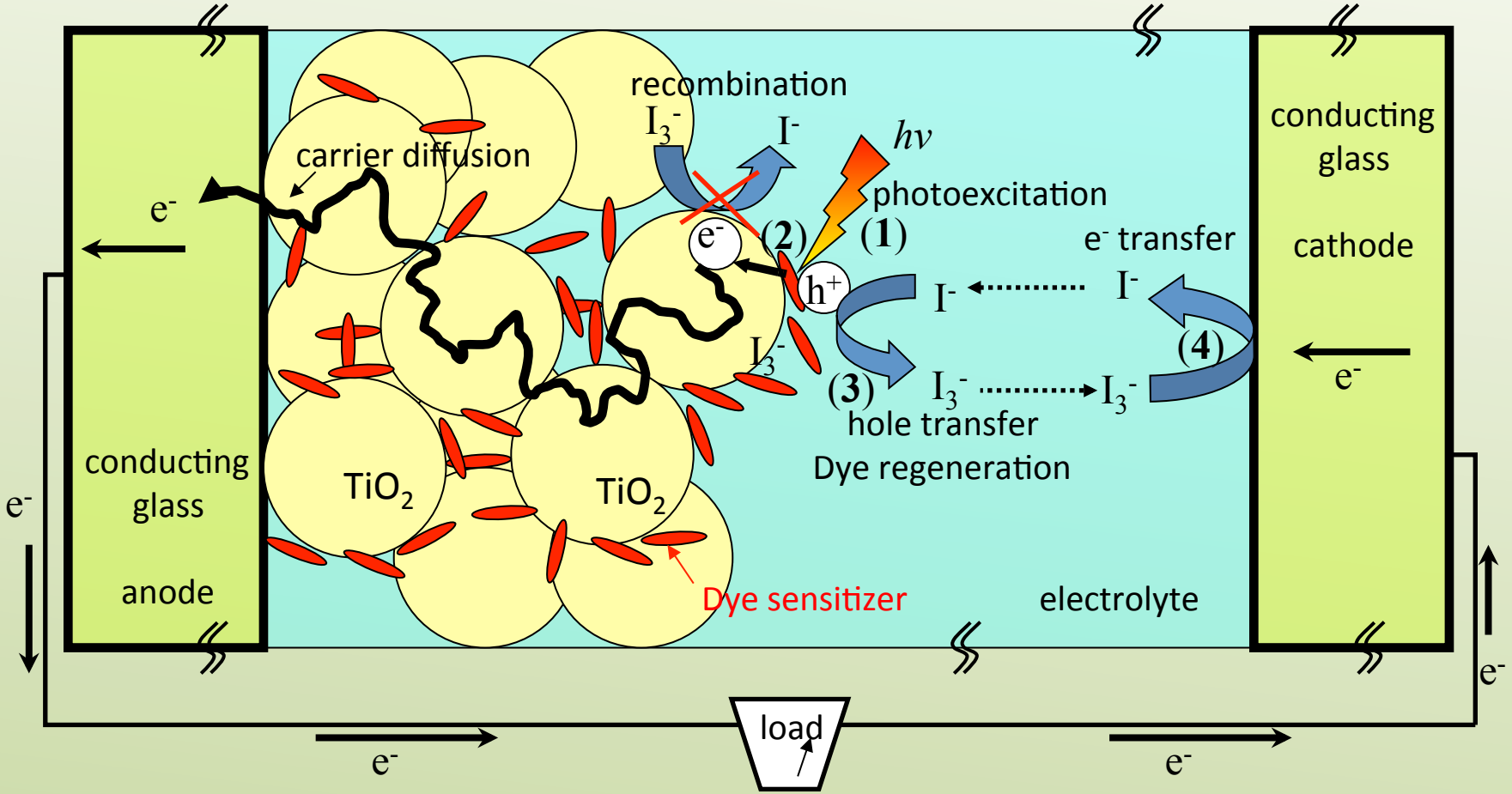


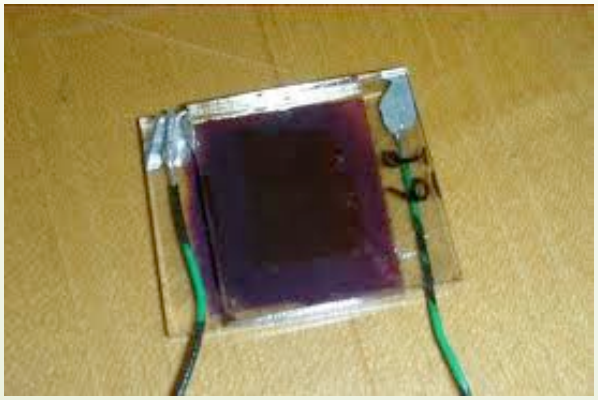


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Photoconversion in 4 steps: (1)-(4)

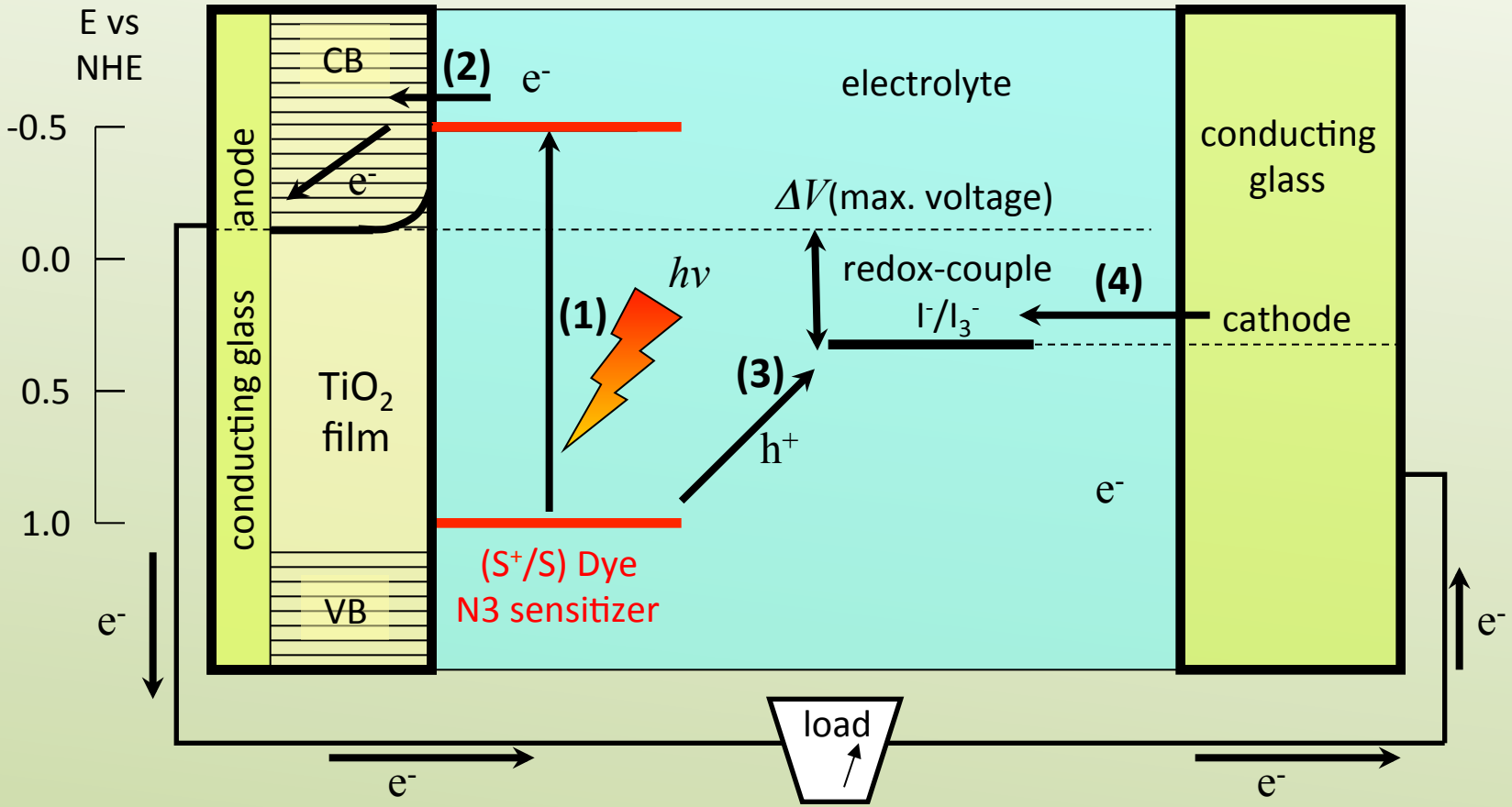


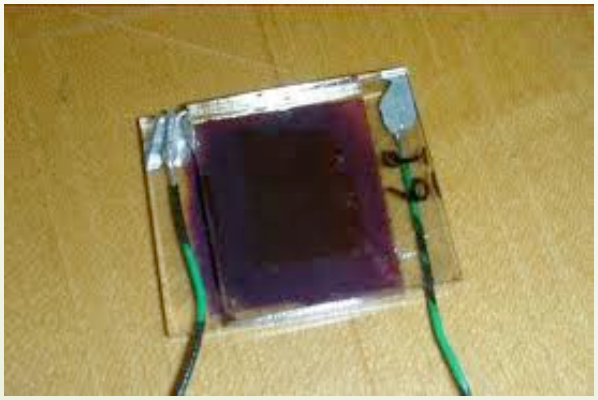


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Photoconversion: Energy Diagram



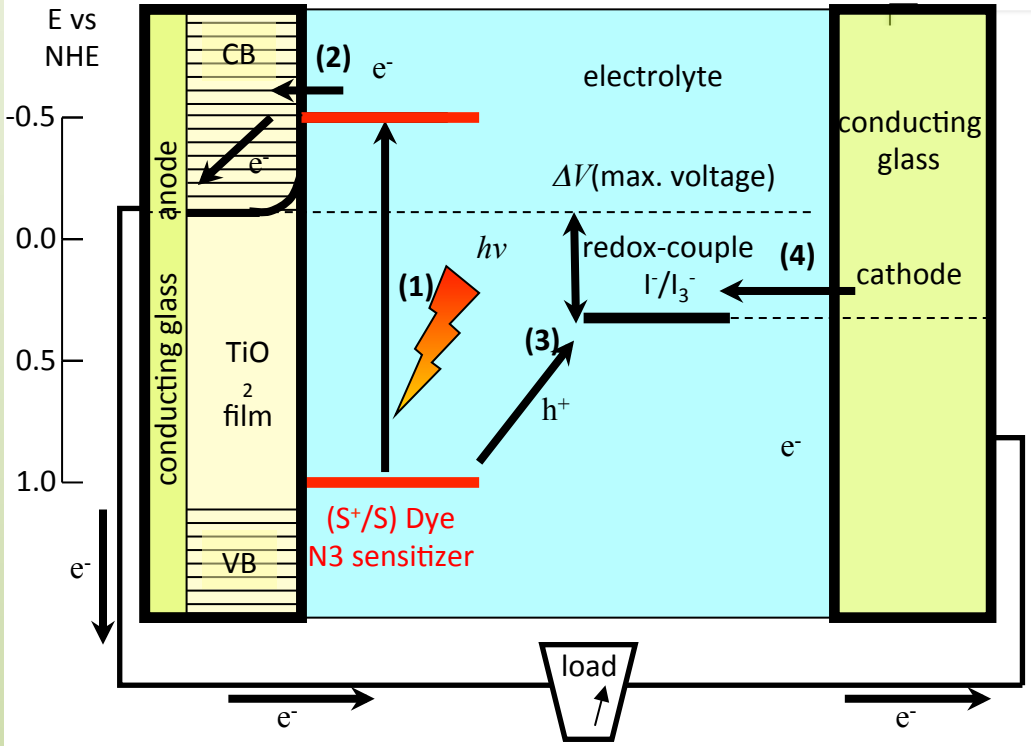


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

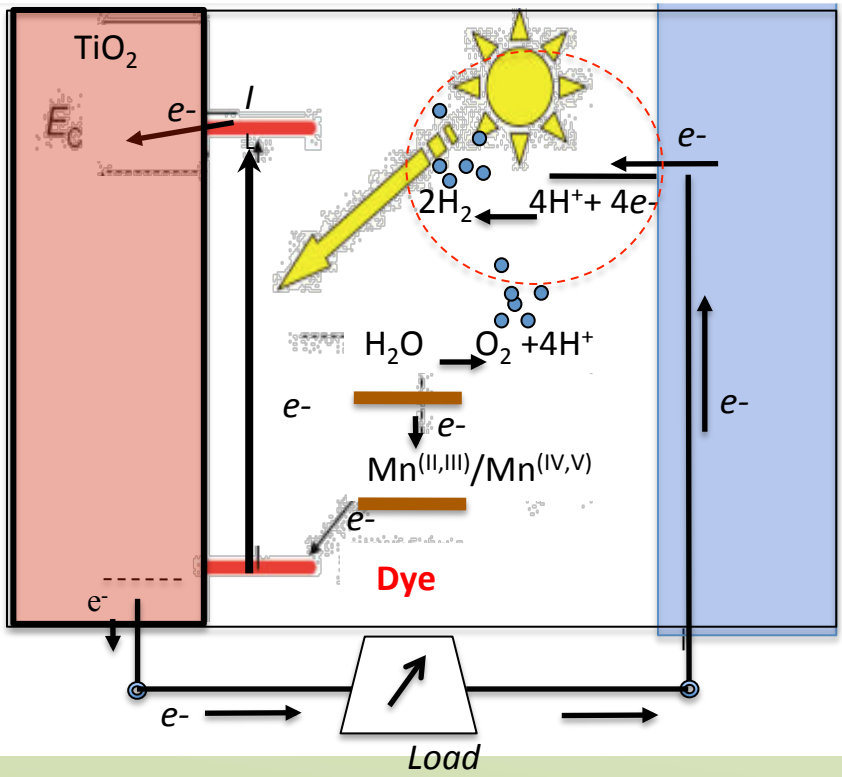
Modeling Dye-Sensitized Solar Cells

Photoconversion into Chemical Bonds: Fuel

Solar-to-Electricity Conversion



Solar-to-Fuel (H_2) Conversion



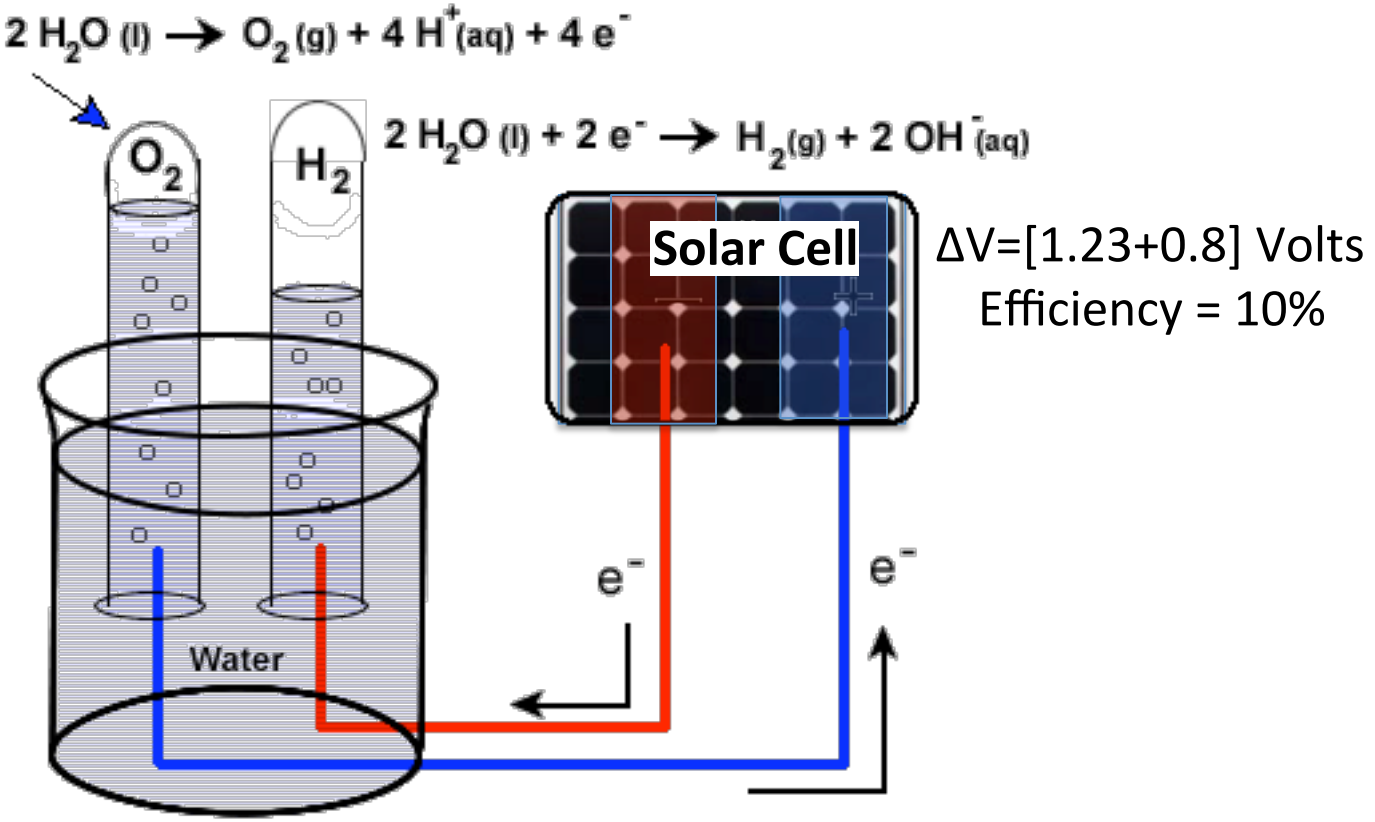
A viable solution to alternative and renewable energy

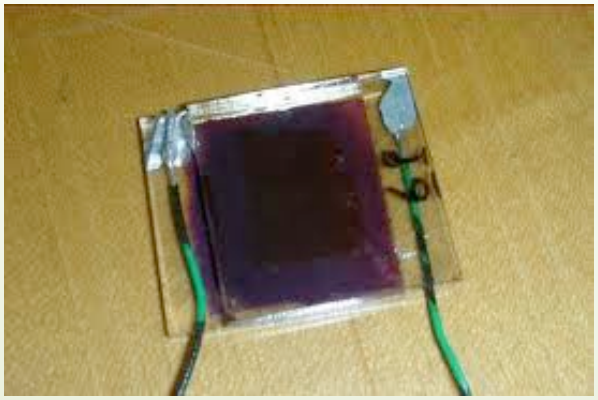
Hydrogen Production by Solar Water-Splitting

$$2H_2O(l) \xrightarrow{\text{sun}} O_2(g) + 4H^+(aq) + 4e^-$$

$$4H^+(aq) + 4e^- \longrightarrow 2H_2(g) \longrightarrow H_2\text{-Storage}$$

SOLAR WATER ELECTROLYSIS

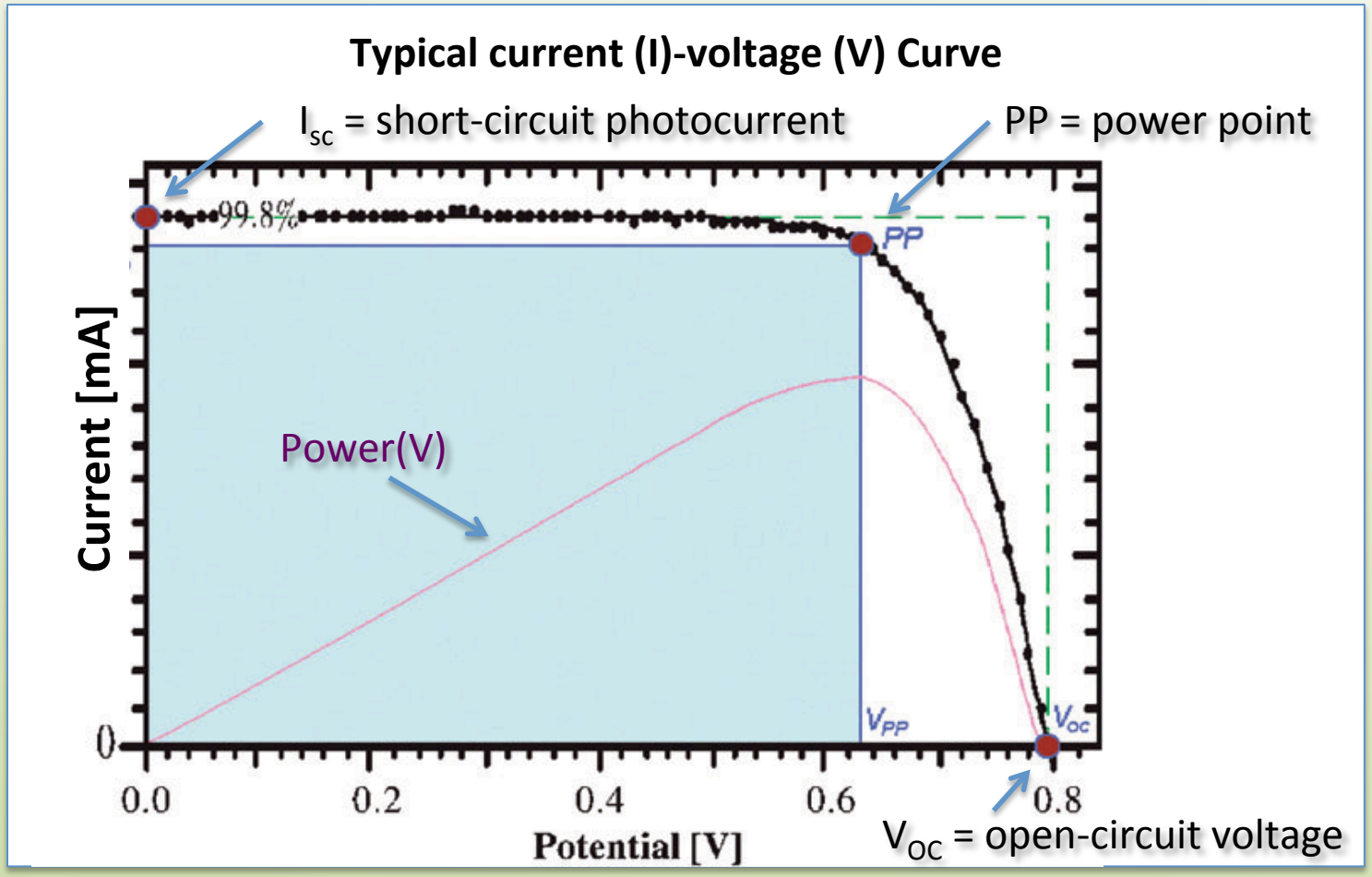


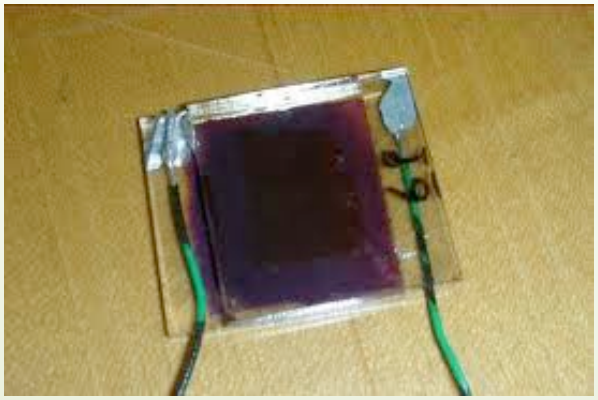


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Characteristic I-V Curve of Photoconversion





CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

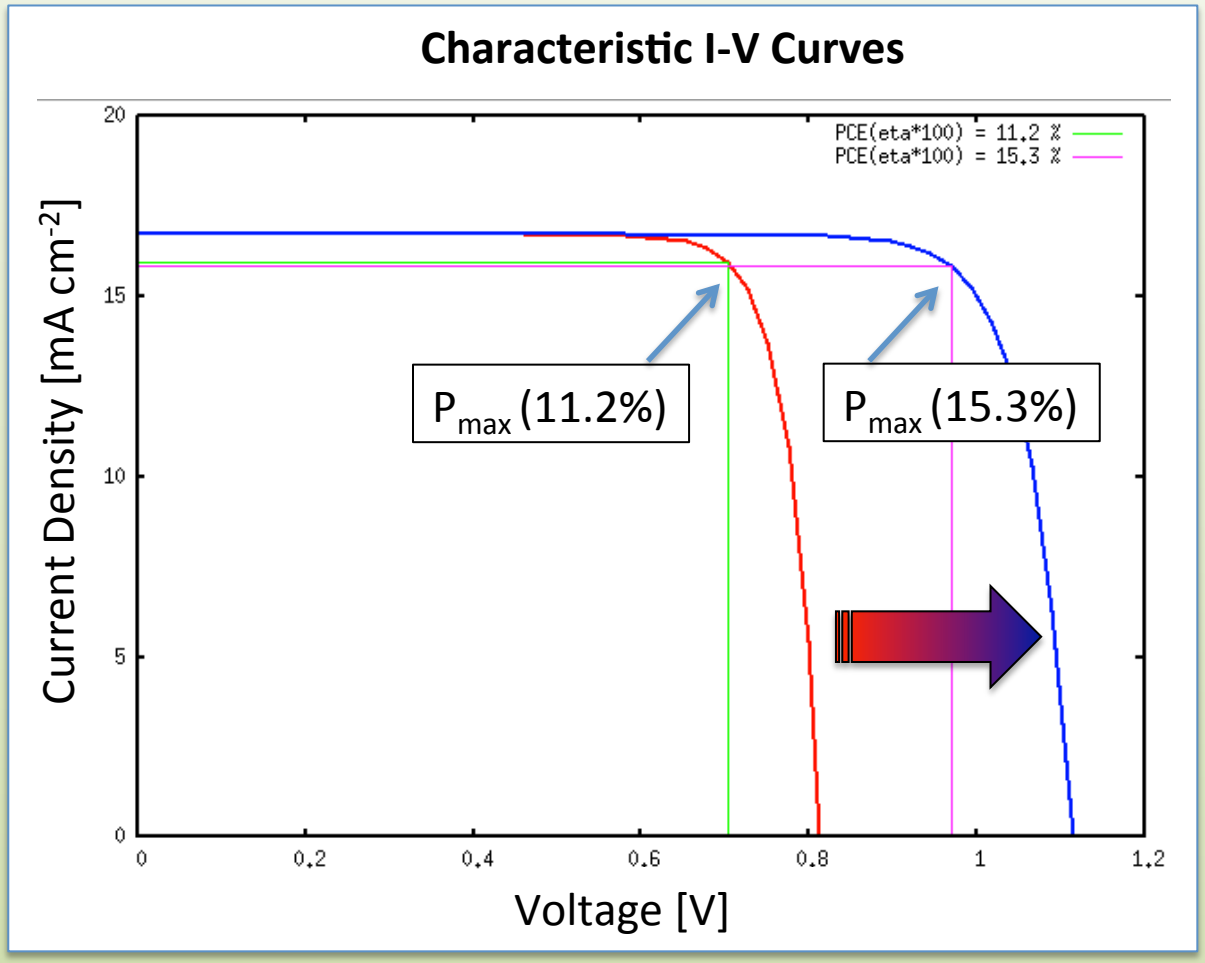
Photoconversion: Efficiency

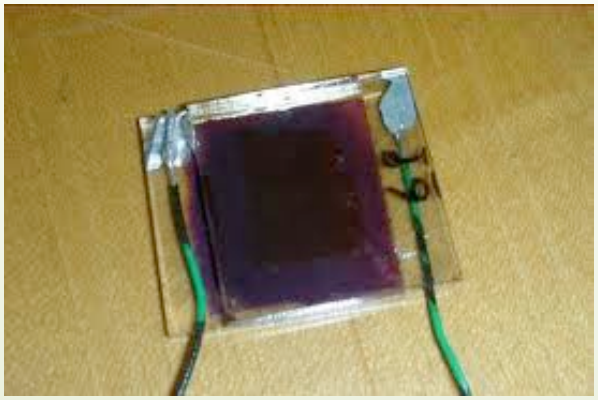
Power output

$P_o = I \times V$

Light-to-electrical power conversion % efficiency

$\eta = 100 \times P_o/P_i$





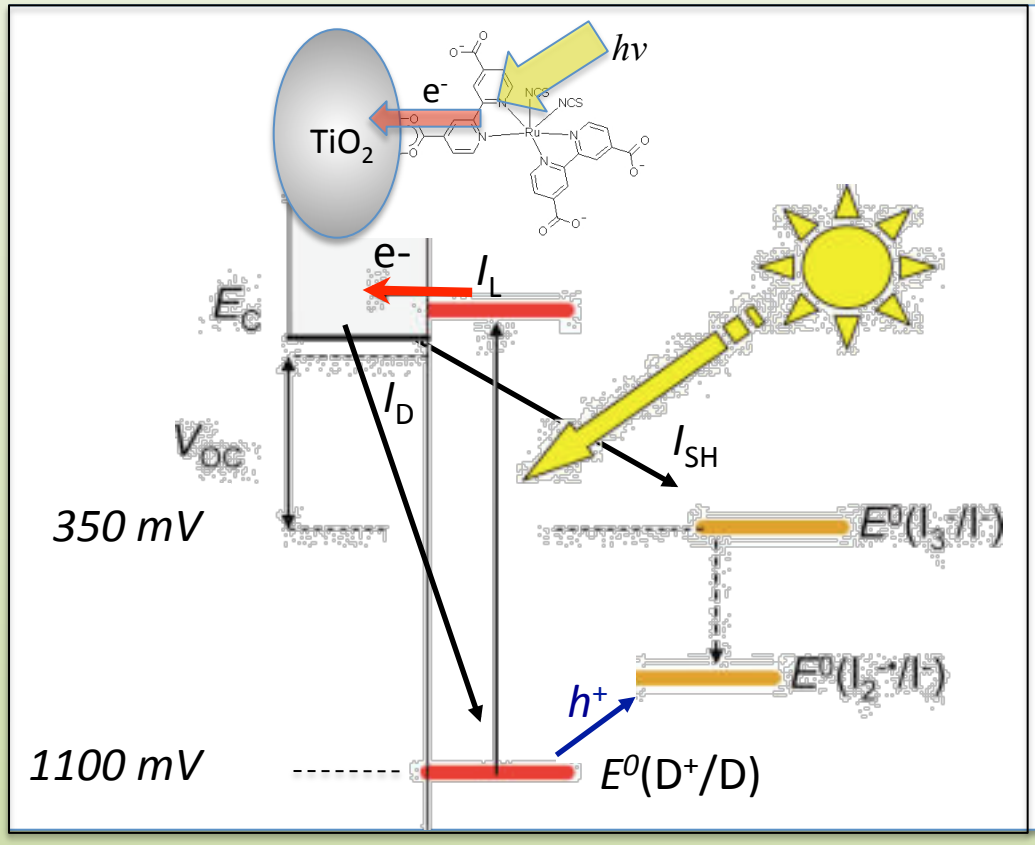
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

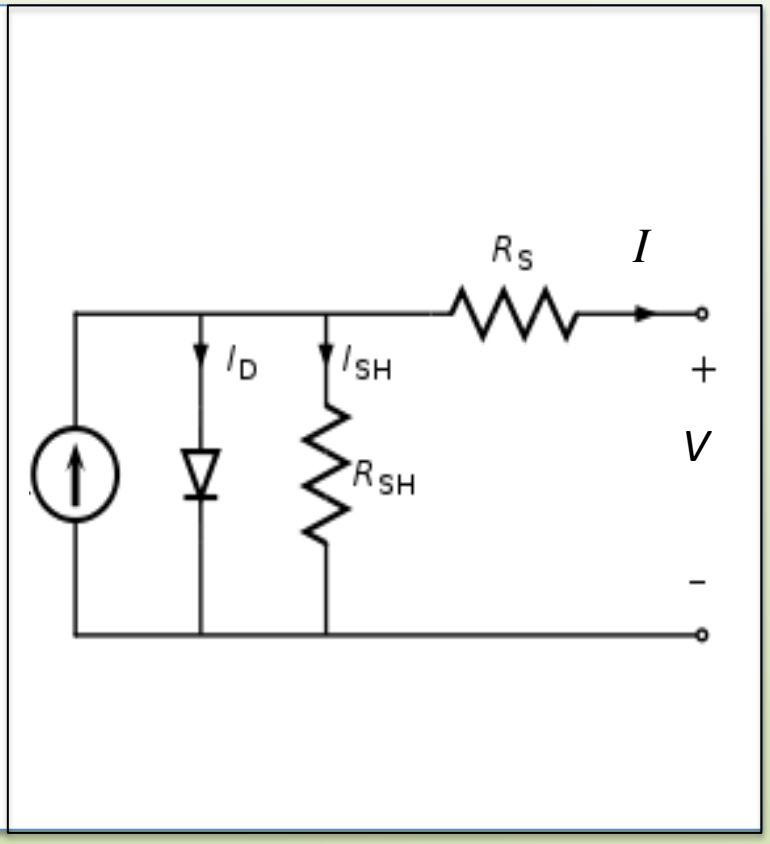
Modeling Dye-Sensitized Solar Cells

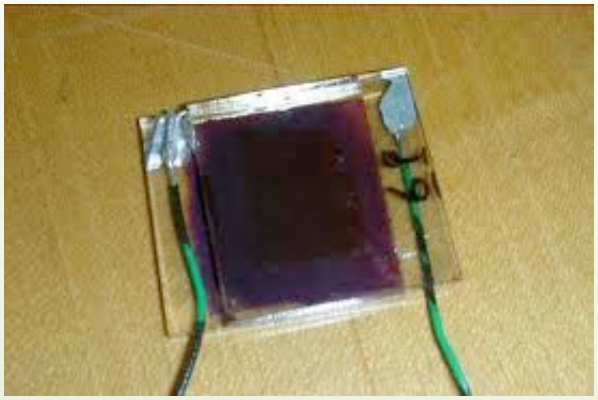
Equivalent Circuit of Photoconversion

Energy Diagram



Equivalent Circuit



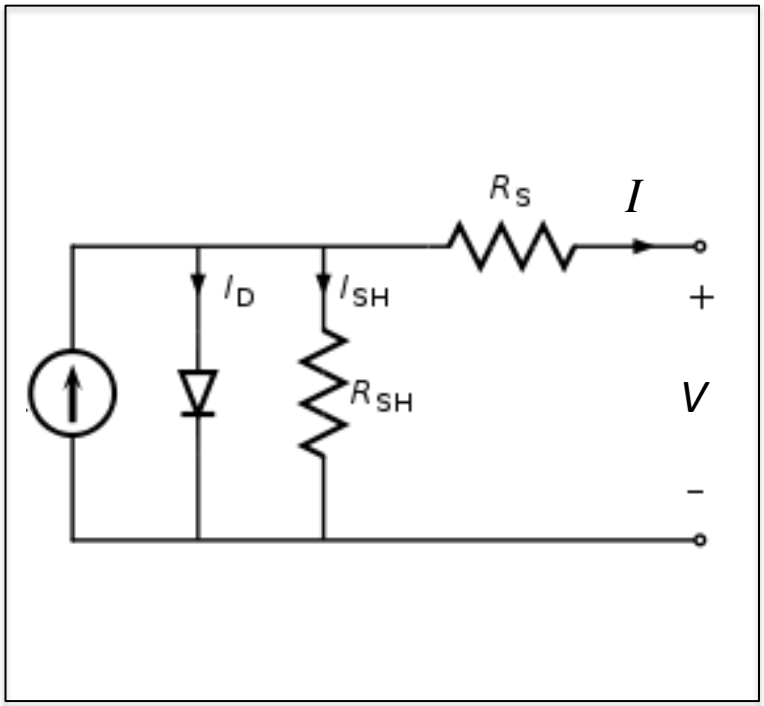


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Photoconversion: Output Current

Equivalent Circuit

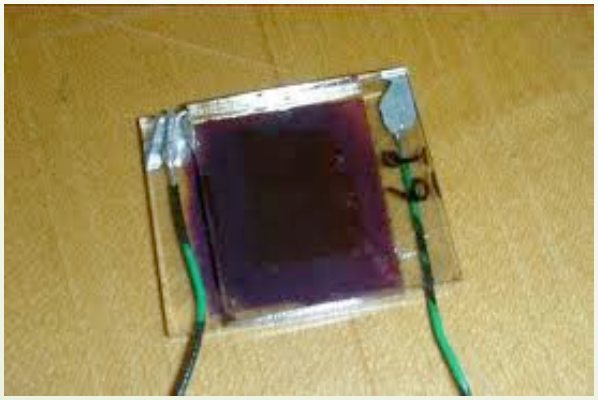


Characteristic I-V Curve

Output Current: $I = I_L - I_D - I_{SH}$

$$I = I_L - I_0 \left\{ \exp\left[\frac{q(V + IR_S)}{nkT} \right] - 1 \right\} - \frac{V + IR_S}{R_{SH}}.$$

Open Circuit Voltage: $$V_{OC} \approx \frac{kT}{q} \ln\left(\frac{I_L}{I_0} + 1 \right).$$



CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Photoconversion Efficiency: Redox Couple

Exercise 1 (due Thursday Sept 25, 2014):

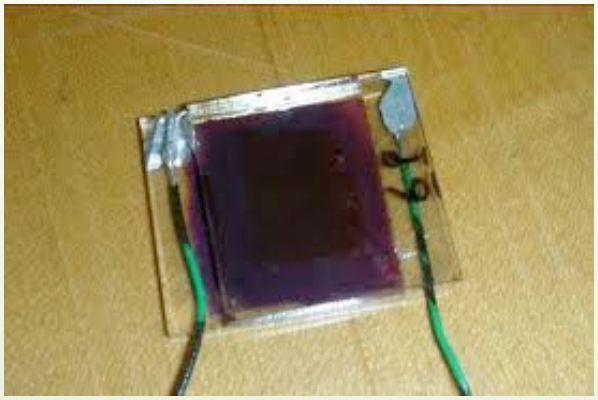
Consider a dye-sensitized solar cell (DSSC) with an equivalent circuit with the following parameters:

- Photogenerated current density: J_L=16.7 mAmperes/cm^2
- Specific series resistance: R_S = 2.0E-4 KΩ*cm^2
- Specific shunt resistance: R_{SH} = 100 KΩ*cm^2
- Open circuit voltage (Volts): $V_{oc} = E^0(I^-/I_3^-) - E_{CB} + \Delta V(pH)$
- Reverse saturation current density: $J_0=J_L\ 10^{-10}$ mAmperes/cm^2
- Diode ideality factor times kT/q= 0.0259 Volts: $nkt=V_{oc}/\log(J_L/J_0+1)$

(a) Compute the I-V characteristic at pH=7.75 assuming $E^0(I^-/I_3^-)$=350mV, and $\Delta V(pH)$=60mV*pH+E_{CB} relative to the hydrogen standard electrode (HSE).

(b) Compute the light-to-electrical power conversion % efficiency (η) of the DSSC, assuming that incident sunpower P_i = 1 kW m^{-2}.

(c) Compute η for an analogous DSSC, where the redox couple I^-/I_3^- has been replaced by a redox pair X^-/X_3^- with $E^0(X^-/X_3^-)$=150mV.



CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

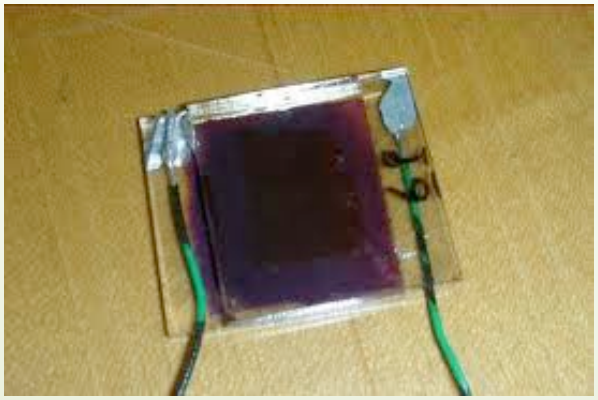
Modeling Dye-Sensitized Solar Cells

Photoconversion Efficiency: Redox Couple

Solution to Exercise 1 (standard fortran):

```
      PROGRAM main
      PARAMETER(npt=100)
      dv=2.4/(npt-1)
      pmax=-1.
      DO i=1,npt
         v=(i-1)*dv
         rv=rj(v,rkt)
         IF(rv.GT.(-10.0)) THEN
            p=v*rv
            PRINT *,p
            IF(p.GT.pmax) THEN
               pmax=p
               vmax=v
               rmax=rv
            END IF
            WRITE(10,22) v,rv
         END IF
      END DO
      PRINT *, "n(ideality factor)", rkt/0.0259
      WRITE(11,22) 0,rmax
      WRITE(11,22) vmax,rmax
      WRITE(11,22) vmax,0.
      PRINT *, "PCE(eta*100)=",pmax
 22   FORMAT(2(e13.6,2x))
      END
```

```
      FUNCTION rj(v,rkt)
c
      rjl=16.7  ! current density
      rs=2.0E-4 ! specific series resistance
      rsha=100. ! specific shunt resistance
      Voc=0.42+0.35+0.045+0.3 ! Voc
      rj0=rjl*1.0E10 ! Rev. sat. curr. Density
C     ideality factor times kT/q= 0.0259 Volts
      rkt=Voc/log(rjl/rj0+1.)
      DO i=1,5
         IF (i.EQ.1) rj=rjl
         rj=rjl-rj0*(exp((v+rj*rs)/rkt)-1.)
     1      -(v+rj*rs)/rsha
      END DO
      RETURN
      END
```



CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Conventional Solar Cells

Cost and Space Requirements

Exercise (Current Scenario) (due Thursday Sept 25, 2014):

Considering that the current US energy consumption is at a rate of 3.5 TWatts:

(1) What percentage of the US energy consumption is supplied by solar panels?

(2) What percentage of the electricity in Germany is supplied by solar panels?

(3) How much would the solar panels cost to supply the US with 3.5 Twatts?

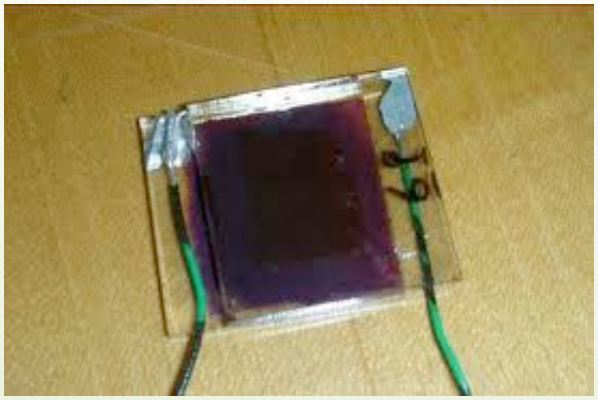
(4) How does that cost compare to the US military budget?

(5) How much area would the solar panels take to supply 3.5 TWatts?

(6) What percentage of the electricity in CT comes from nuclear reactors?

(7) Where are the nuclear power plants?

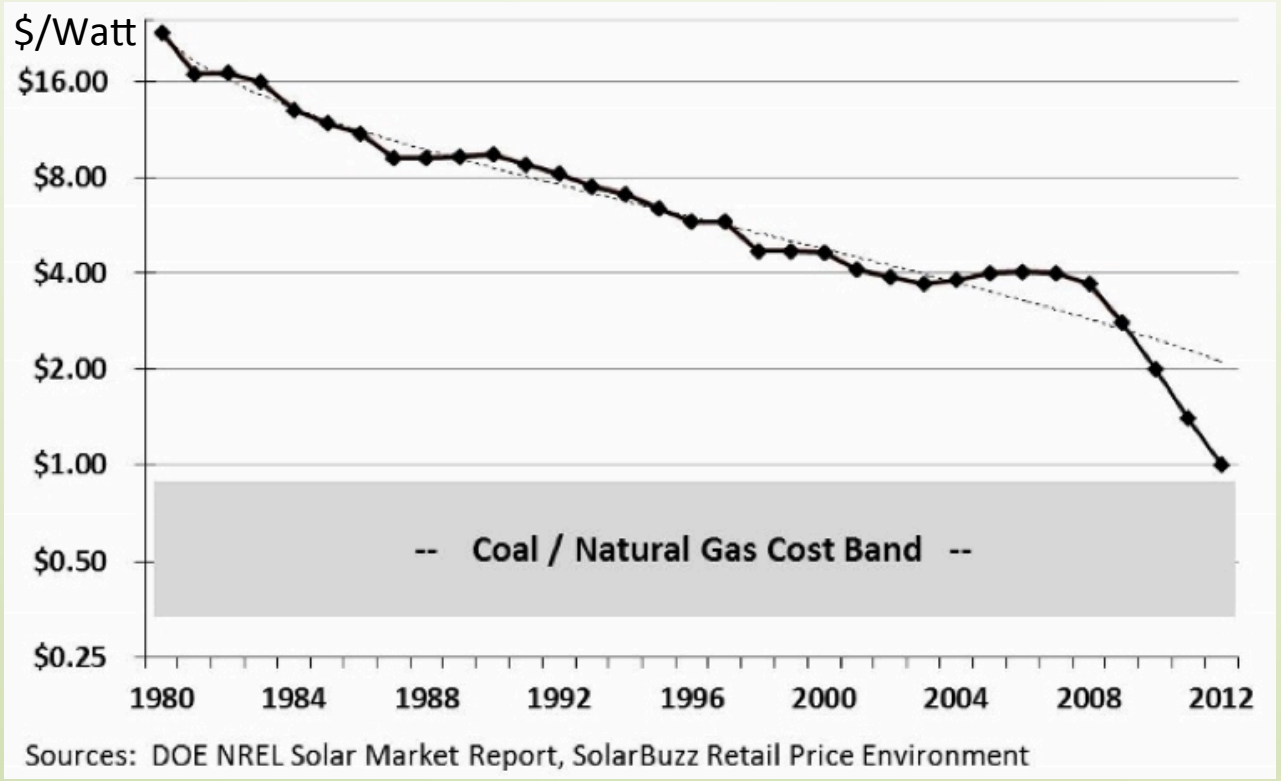
(8) When was the last time a hurricane hit the coast of CT?



CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Plummeting Solar Module Cost

PV Parity?

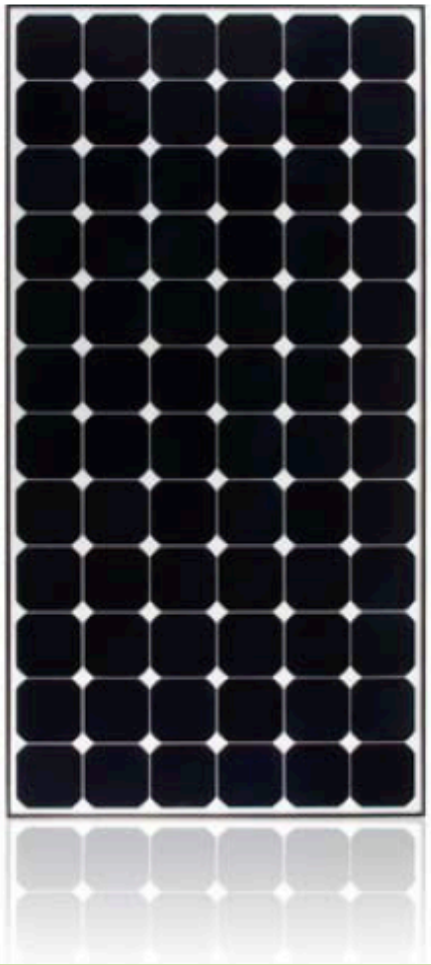


"what is certain is that we're headed for parity with fossil fuels (the gray area in the graph), and then solar will beat them..." **Michael Graham Richard**, May 1, 2013

Considering $1/Watt

230 SOLAR PANEL

EXCEPTIONAL EFFICIENCY AND PERFORMANCE



SUNPOWER

1 KWatt/m^2 18.5/100 = 185 W/m^2

BENEFITS

Highest Efficiency
Panel efficiency of 18.5% is the highest commercially available for residential applications

11.2/0.185 = 60.5 m^2 /person

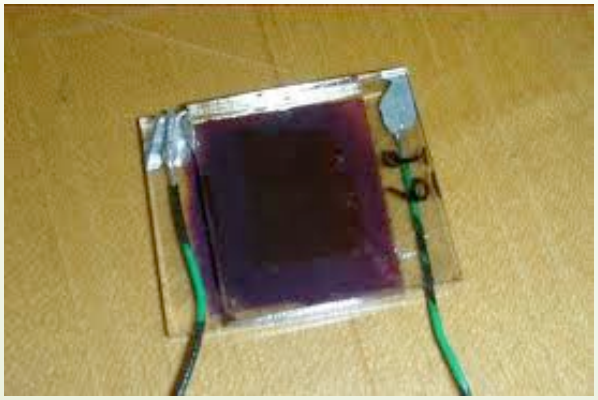
Solar Panel for Current U.S. Energy Consumption Size and Cost

- ✓11.2 KWatts/person = 3.5 10^{12} Watts (3.5 Twatts)
  - ✓Cost of solar panels: $11,200 /person = [$3.5 Trillions]

2012 U.S. military budget = $2,064/person [$0.646 Trillion]

2011 Ivanpah BrightSource Energy = $5.1/person

WASHINGTON (Army News Service, July 8, 2010) --"We view energy security as a critical mission-enabler and an operational imperative, which can provide the Army with an essential tactical advantage," said Jerry Hansen, the Army's senior energy executive, during a bloggers roundtable discussion, July 7, at the Pentagon. "Our Army installations, our tactical operations, Soldier training -- all require secure and uninterrupted access to energy."

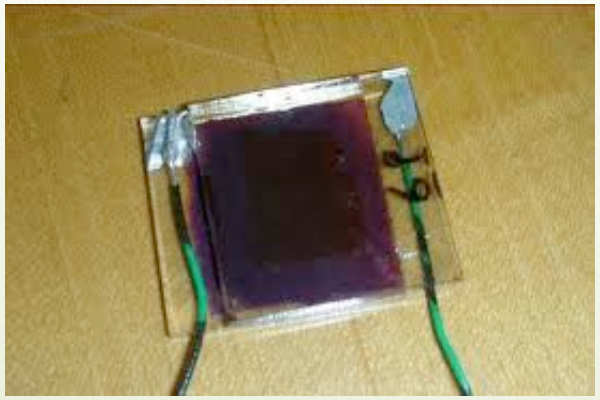


Modeling Photovoltaic Solar Cells
U.S. Energy Consumption

✓11.2 KWatts/person = (3.5 TWatts)

- Each person consumes energy, on average, at a rate comparable to the energy consumption of 11 window air conditioners, or 110 light bulbs (100 Watts each).

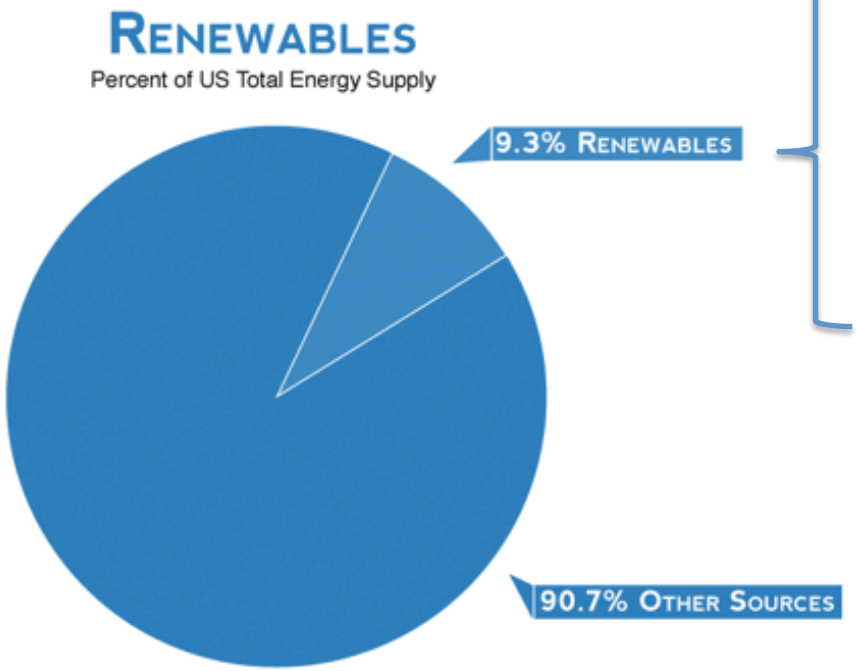
- Sunlight shines on earth at an average flux rate of 1.0 KWatt/m^2. Therefore, the average flux of solar energy shining on 11.2 m^2 (120 ft^2) corresponds to the average energy consumption per capita.



CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

2012 U.S. Renewable Energy Consumption



- Hydropower 2.8%
- Biomass Wood 2.0 %
- Biomass Waste 0.5%
- Biomass Biofuels 2%
- Wind 1.4%
- Geothermal 0.1%
- Solar 0.2%

Source: EIA, MER, April 2013 (6/26/13)

IER

April 11, 2011. DOE Finalizes $1.6 Billion Loan Guarantee for BrightSource Energy

U.S. DEPARTMENT OF ENERGY
LOAN PROGRAMS OFFICE

IVANPAH
Solar Electric Generating System
BrightSource
nrg
Google

IVANPAH: World's Largest Solar Thermal Plant

As World's Largest Solar Thermal Plant Opens, California Looks to End Solar Wars
July 12, 2013. In a few weeks, the largest solar plant of its kind in the world will start producing power in California's Mojave Desert.
The Ivanpah Solar Electric Generating System will supply both Northern and Southern California, inching the state one step closer to its ambitious renewable energy goal.

Summary 9-23-14

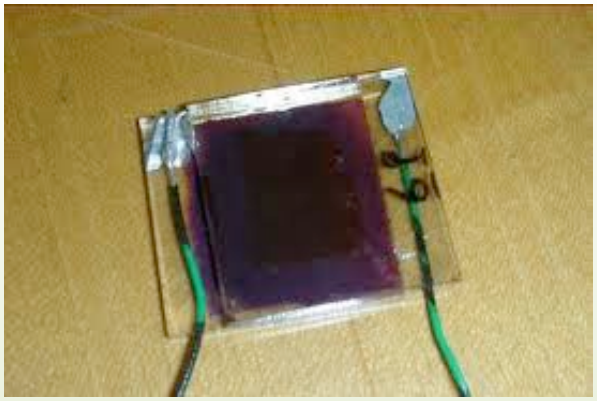
Computational Modeling and Physical Principles

- Solar Photovoltaic (PV)
  - Conventional doped semiconductor (SC) technology
  - SC Band gap matching solar radiance
  - Dye Sensitized Solar Cells (DSSCs)
  - Electricity
  - Fuels (e.g., H_2)
- Conventional Technology
  - Still expensive, close to parity with fossil fuels
  - Based on p-n junction
  - Equivalent circuit: I-V curves

Summary 9-23-14

Computational Modeling and Physical Principles

- Dye Sensitized Solar Cells (DSSCs)
  - Molecular Components
  - Dyes
  - Electrolyte
  - Redox couple
  - Catalyst (DSSCs for fuel production)
- Calculations of I-V curves
  - Iterative approach
  - Power, power point, % efficiency power conversion

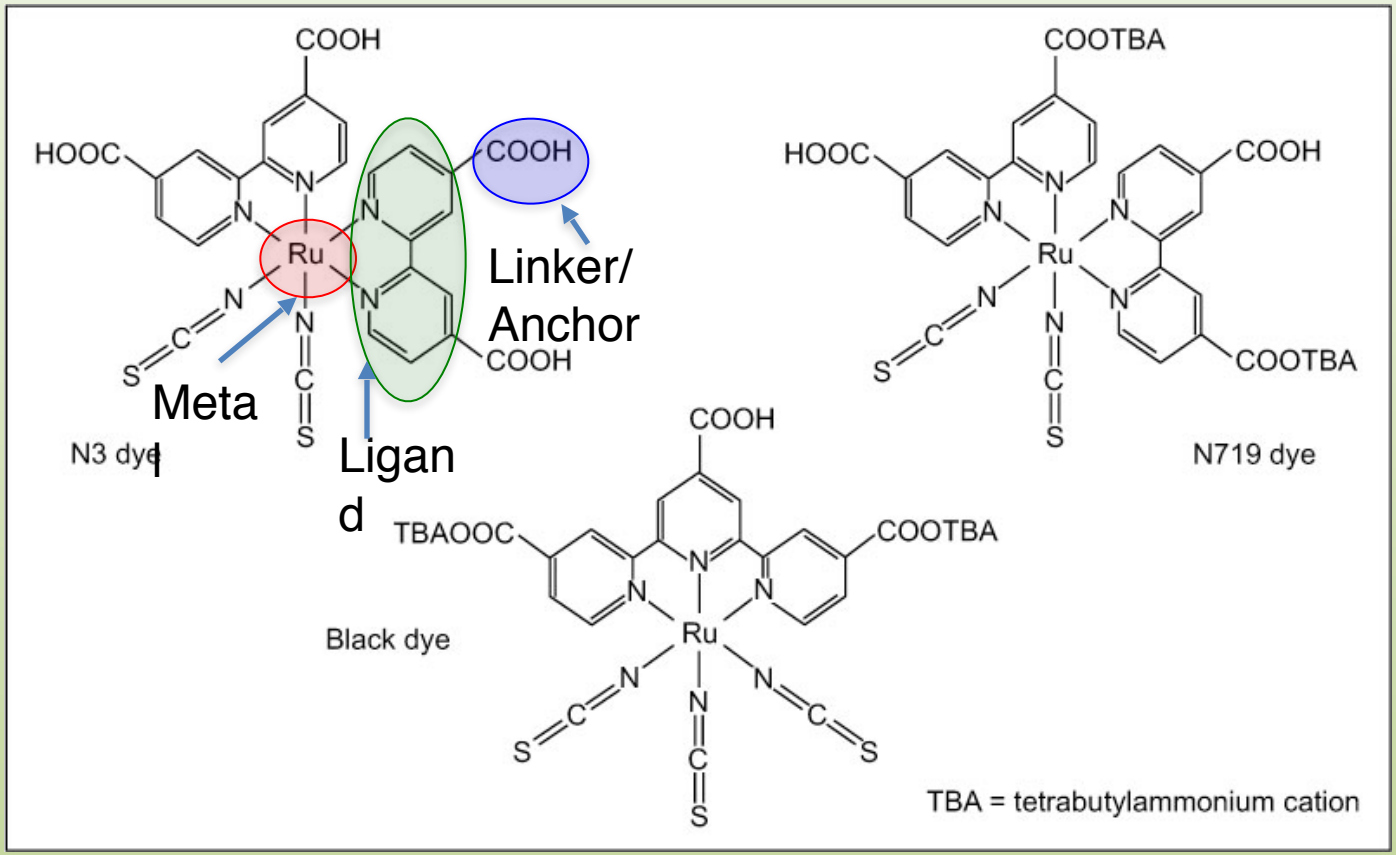


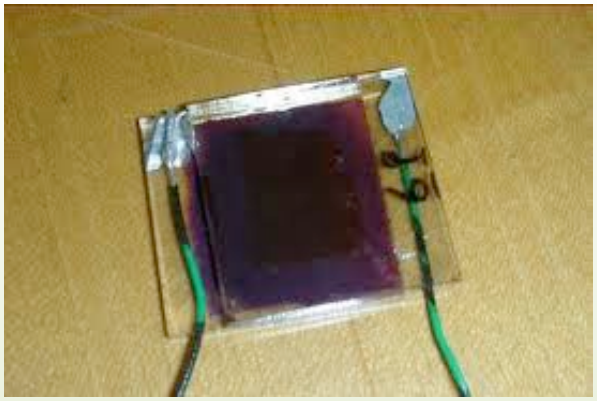
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ru Polypyridyl Dyes: Transition Metal Adsorbates



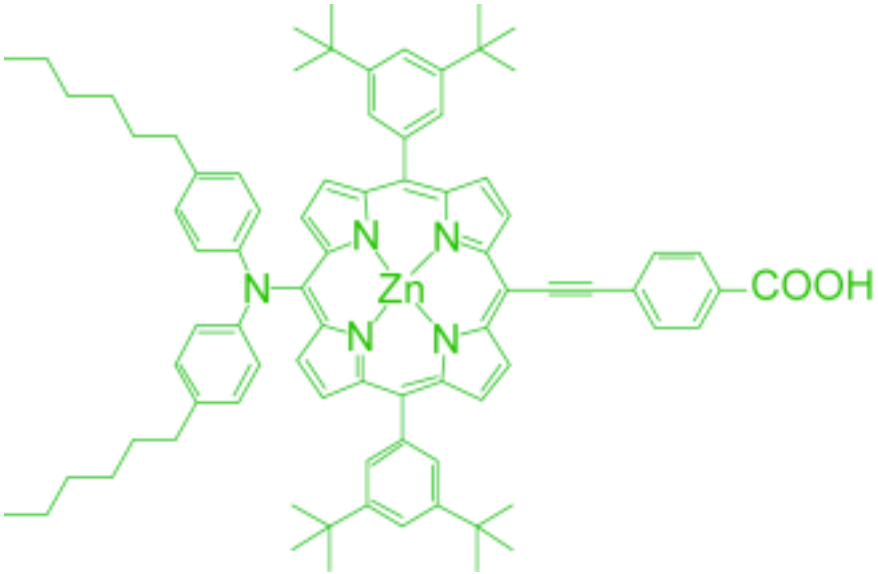


CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

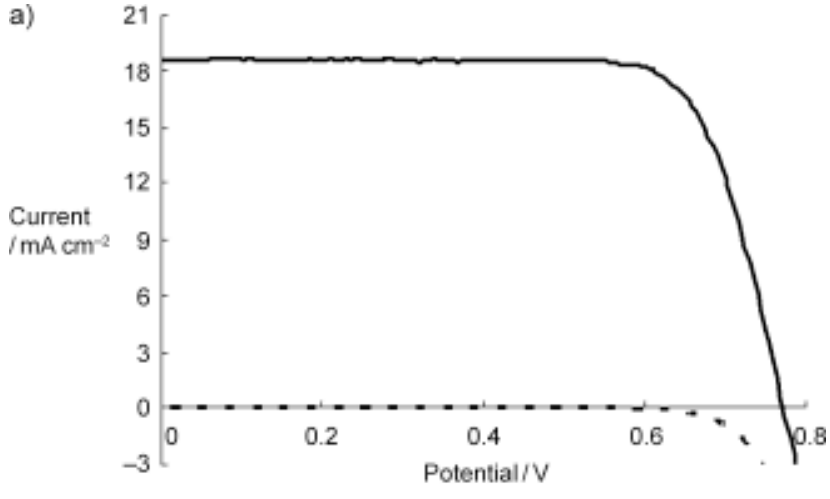
Modeling Dye-Sensitized Solar Cells

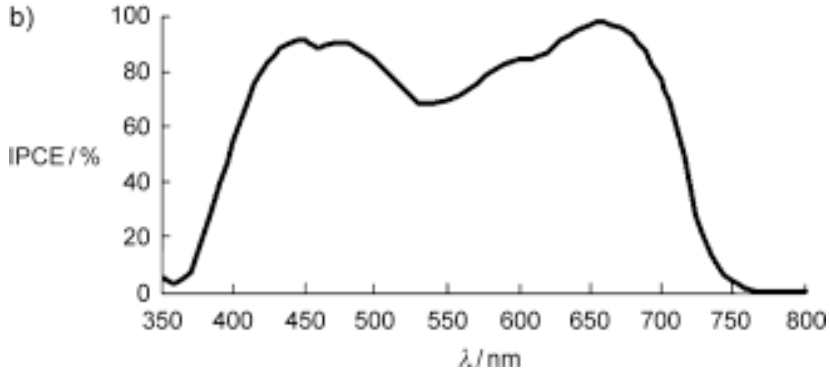
Zn Porphyrin Dyes [August 4, 2010]

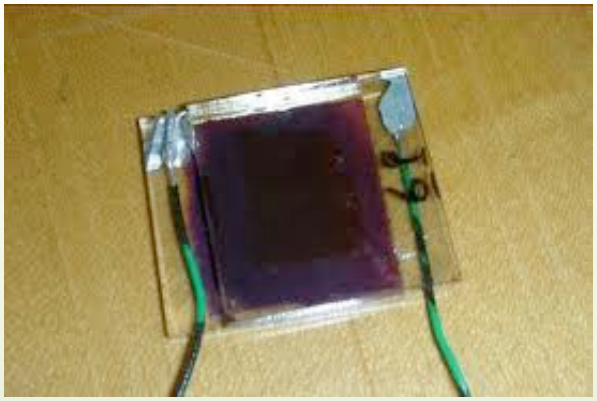


Zn porphyrin chromophore, integrated into a donor–acceptor dye as a π-conjugated bridge, exhibits efficiency of 11 % when used as a photosensitizer in a double-layer TiO2 film.

Angew. Chem. 2010, 122, 6796 –6799



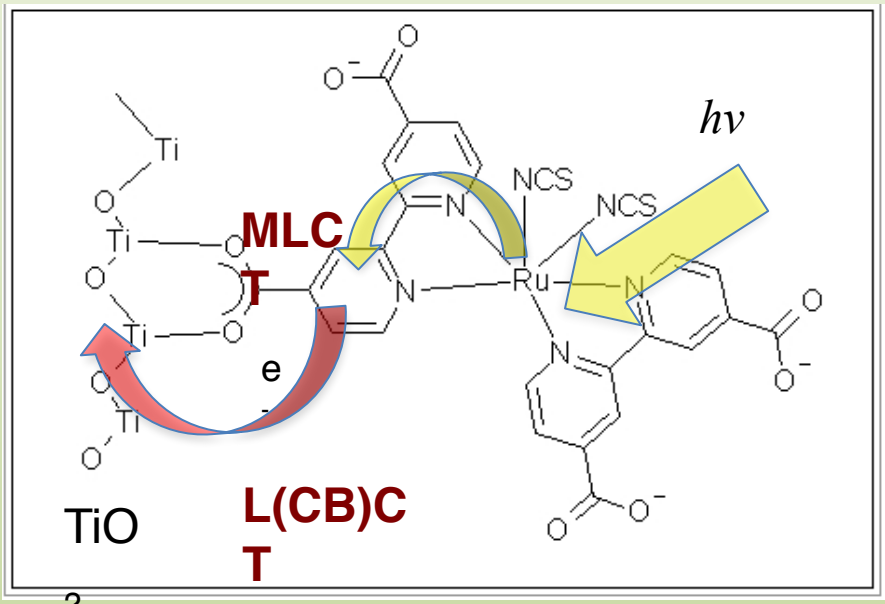


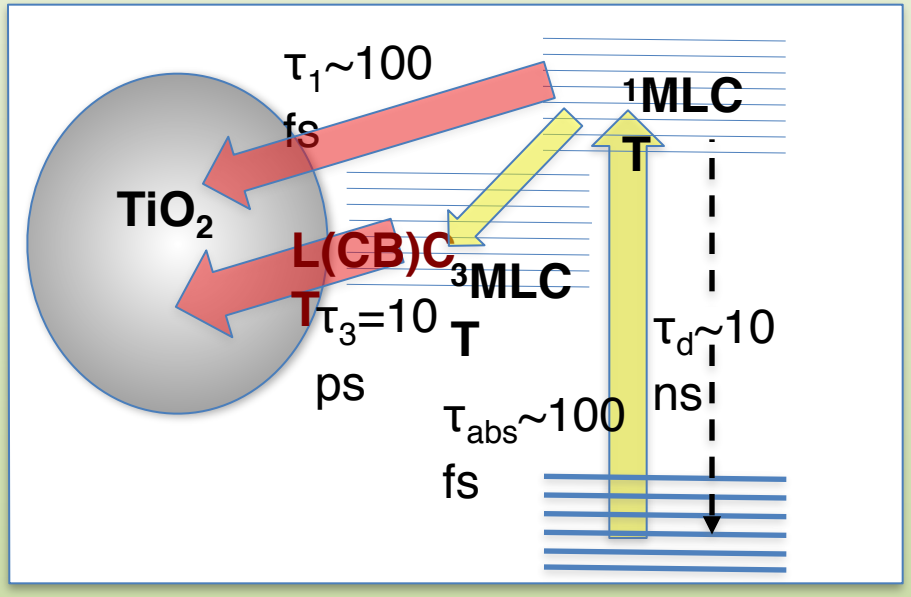


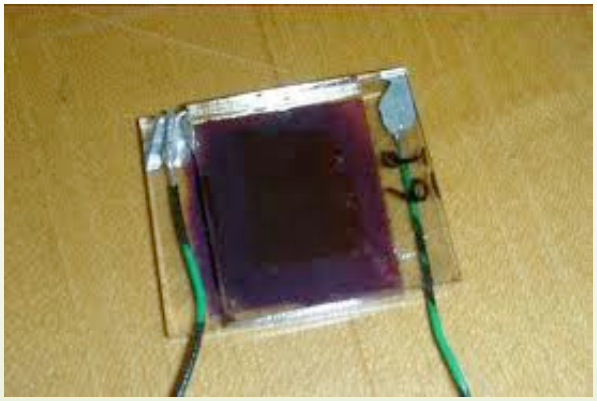
CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

N3-Dye: Ru(II/III) MLCT, Aromatic Linkers





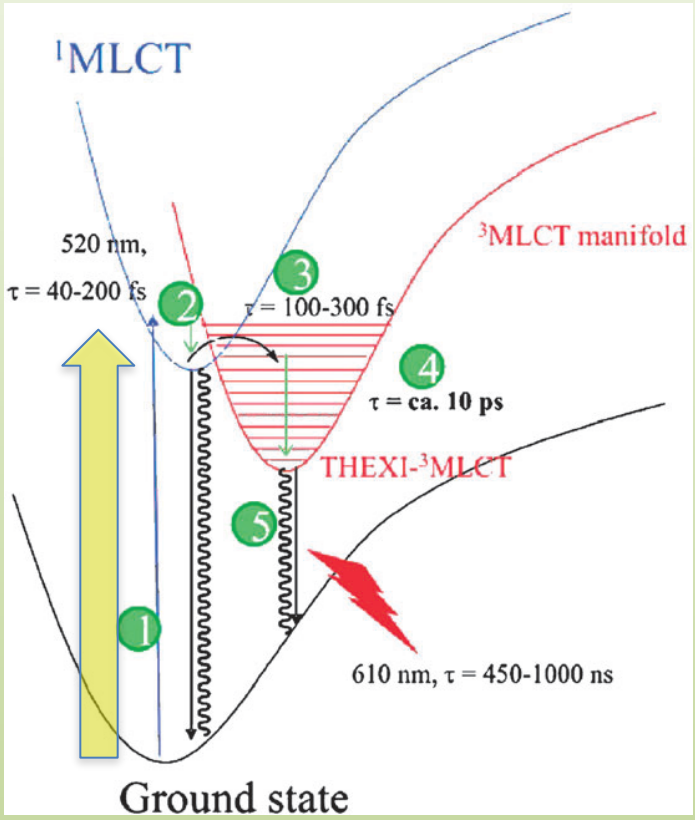


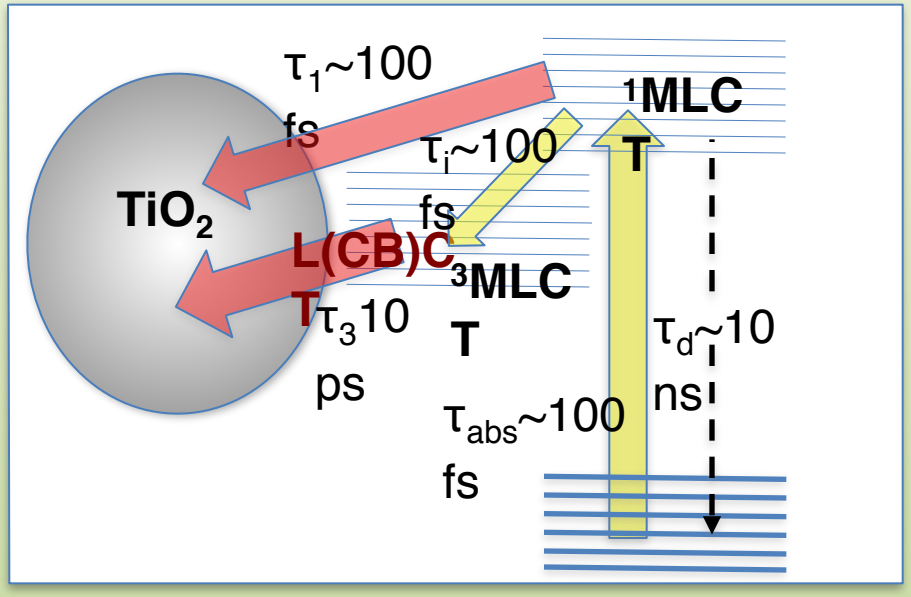
CHEM 505: *Green Chemistry and Alternative Energy*

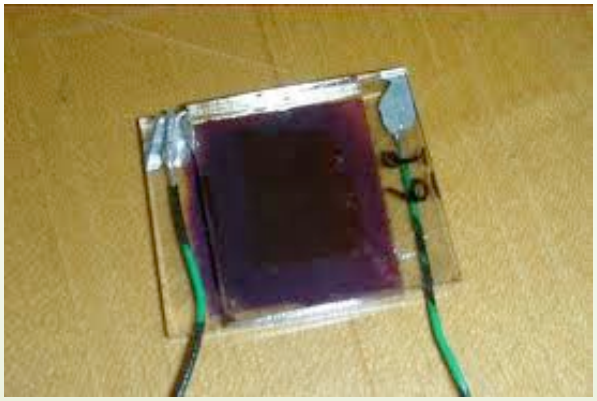
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

N3-Dye: $Ru^{(II/III)}$ MLCT, Aromatic Linkers



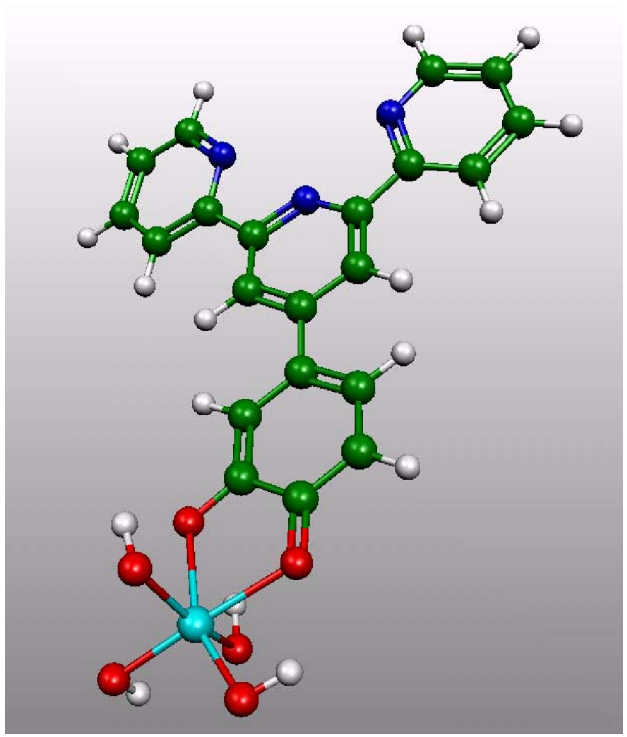




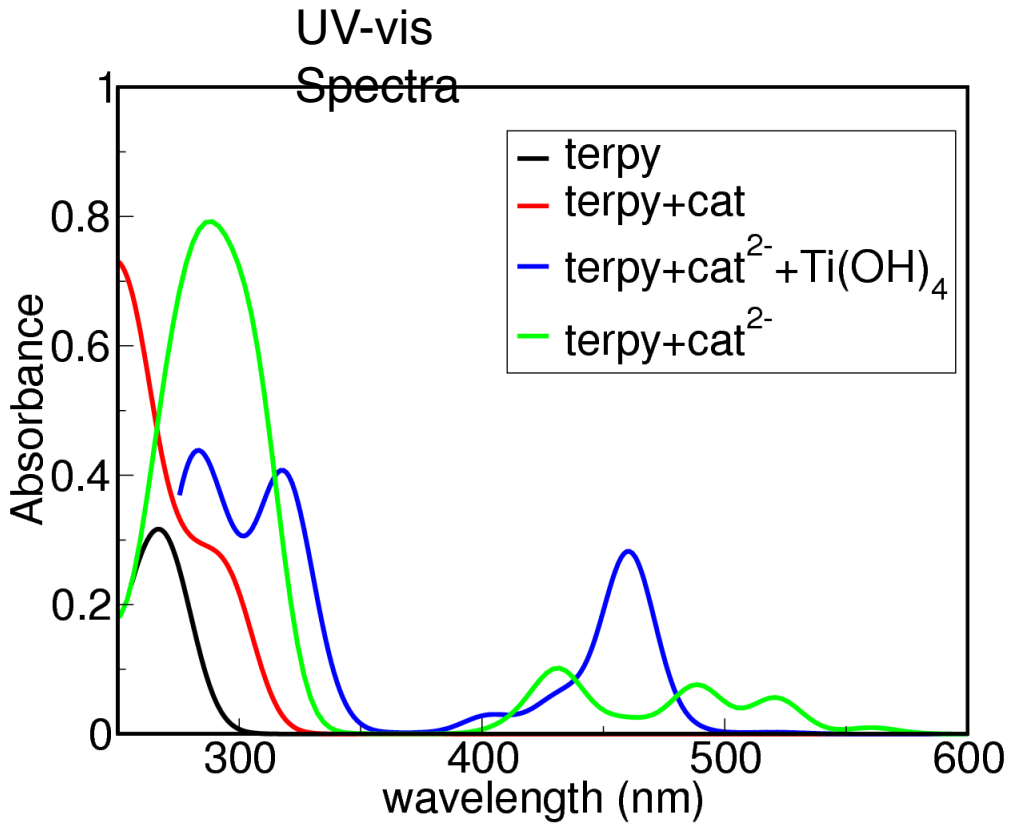
CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

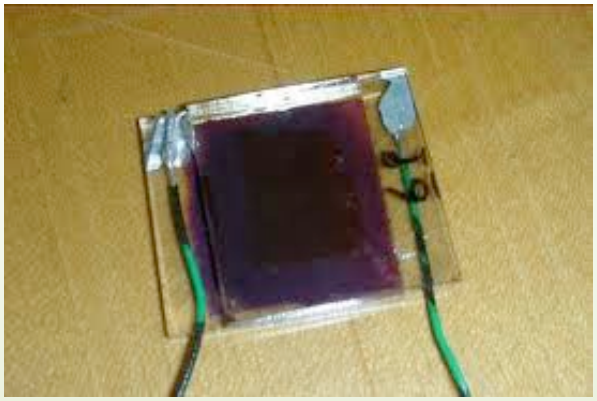
Modeling Dye-Sensitized Solar Cells

Ab Initio Simulations of Photoabsorption Spectra



terpy+cat $^{2-}$ +$Ti(OH)_4$

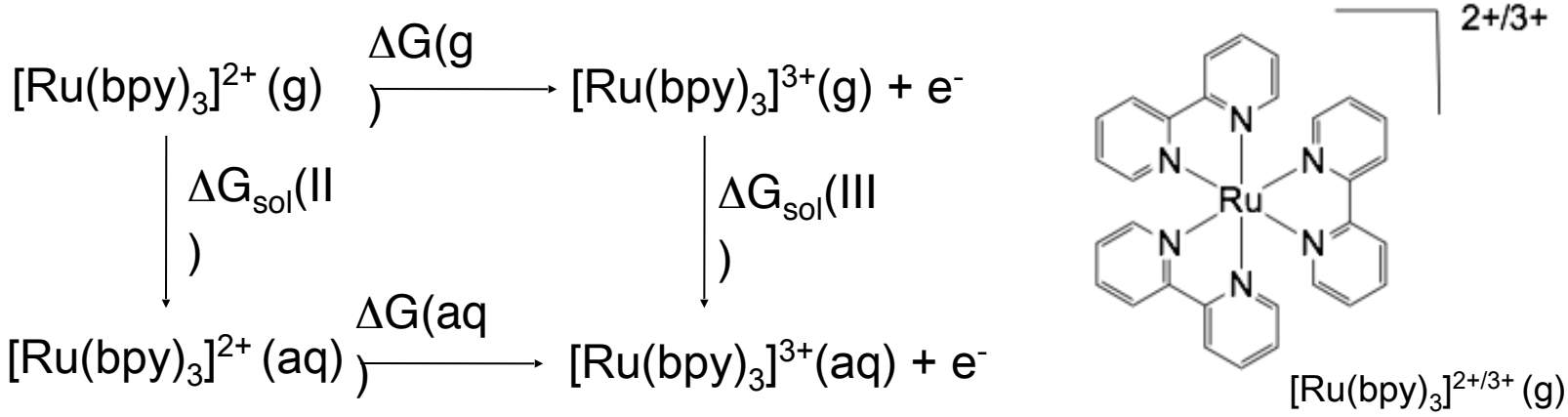




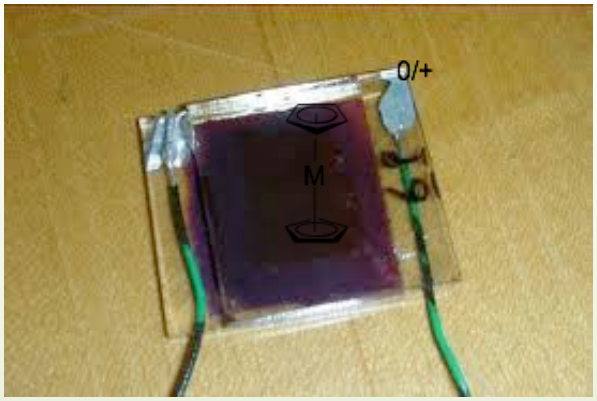
CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ab Initio Redox Potentials: Born-Haber Cycle



The redox potential $E_m^{(2+/3+)}$ is obtained from $\Delta G(aq) = - n F E_m^{(2+/3+)}$, where n = 1 is the # of electrons involved in the redox process. F = 96,500 C and $\Delta G(aq)=\Delta G(g)+\Delta G_{sol}(III)-\Delta G_{sol}(II)$, where $\Delta G(g)=G[Ru(bpy)_3^{3+}(g)] - G[Ru(bpy)_3^{2+}(g)]$, with $G^0 = H^0 - T S^0$, where H^0 is the molecular enthalpy obtained from the minimum energy structure and S^0 is the molecular entropy obtained from a frequency calculation.



CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

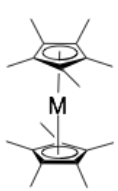
Modeling Dye-Sensitized Solar Cells

Ab Initio Computations of Redox Potentials

Exercise 2:

Consider the redox pairs $[Ru(bpy)_3]^{2+/3+}$, $[CoCp_2]^{0/+}$ and $[FeCp^*_2]^{0/+}$:

$[MCp_2]^{0/+}$ 

and $[MCp^*_2]^{0/+}$ 

with M = Fe, Co.

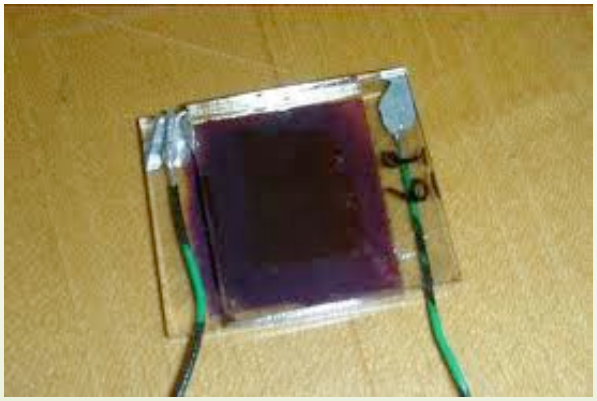
(a) Obtain the minimum energy structures of $[CoCp_2]^{0/+}$ and $[FeCp^*_2]^{0/+}$ and $[FeCp_2]^{0/+}$ at the B3LYP(LACVP/6-311G*) level of theory and compare them to the X-ray crystal structures for $[Ru(bpy)_3]^{2+}$, $[CoCp_2]^0$ and $[FeCp^*_2]^0$.

- Compute the redox potentials of $[CoCp_2]^{0/+}$ and $[FeCp^*_2]^{0/+}$ in DMSO (ε=46.83), versus $[FeCp_2]^{0/+}$ by using a polarizable continuum model (PCM) of solvation, and compare your results to the experimental values the following reference:

Connelly, N.G. & Geiger, W.E., *Chem. Rev.* **1996**, *96*, 877-910.

Solution to Exercise 2:

Download the tutorial notes on calculations of redox potentials and follow the instructions on how to create input files, launch calculations and obtain results from the output files.



CHEM 505: *Green Chemistry and Alternative Energy*

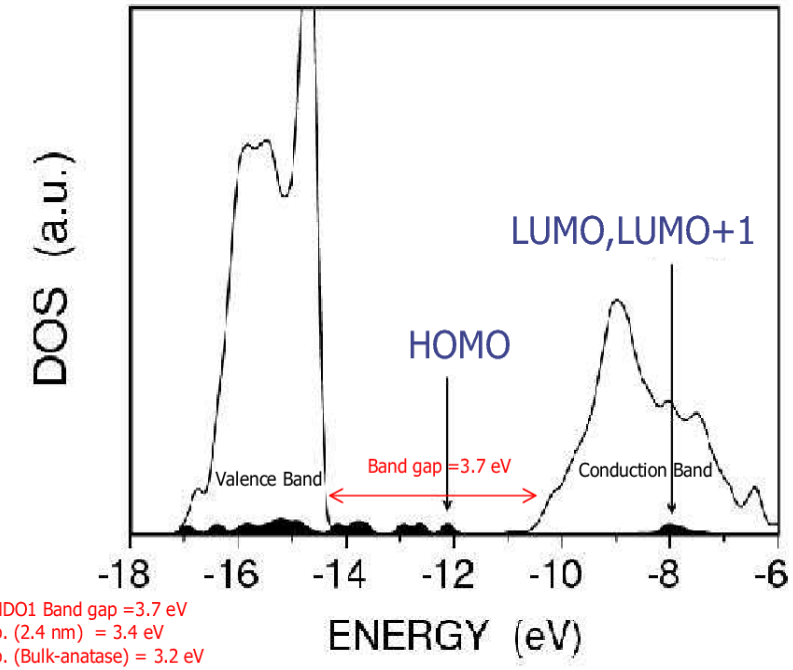
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ultrafast IET: Gerischer Model

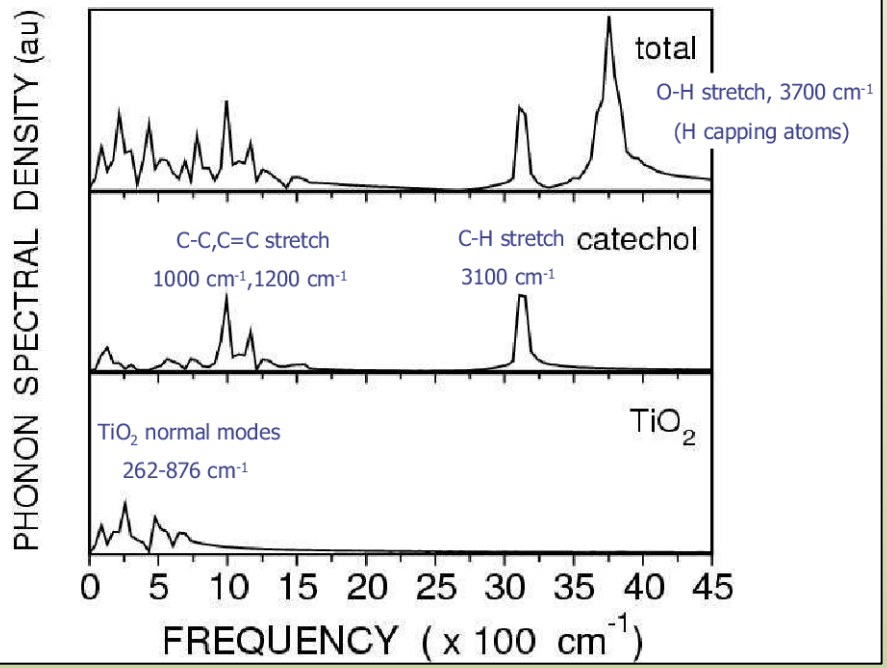
$$k_{inj} \sim \int dE \rho_{CB}(E) * \rho_A(E) * k(E)$$

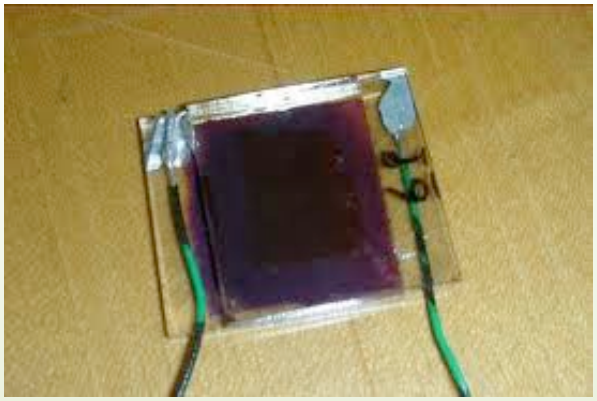
Electronic Density of States (1.2 nm particles)



ZINDO1 Band gap =3.7 eV
Exp. (2.4 nm) = 3.4 eV
Exp. (Bulk-anatase) = 3.2 eV

Phonon Spectral Density



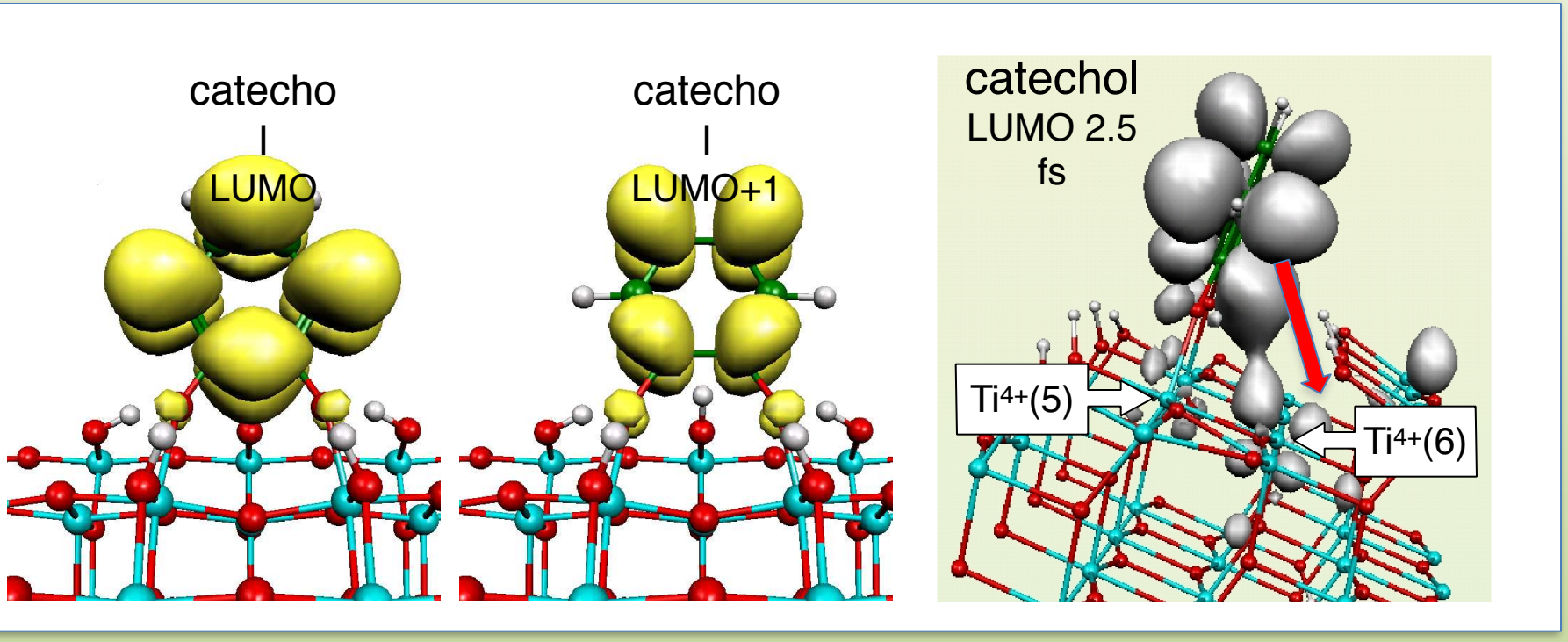


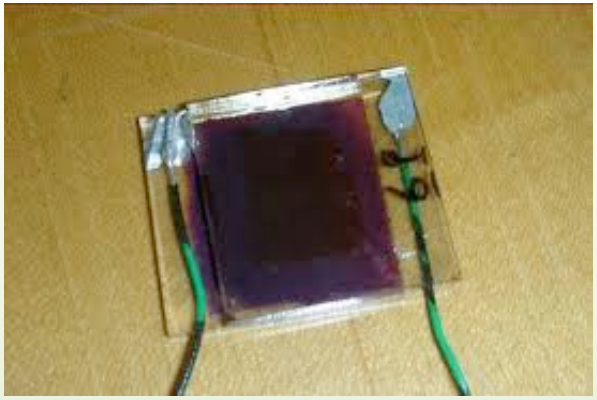
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ligand-to-Conduction Band Electron Transfer



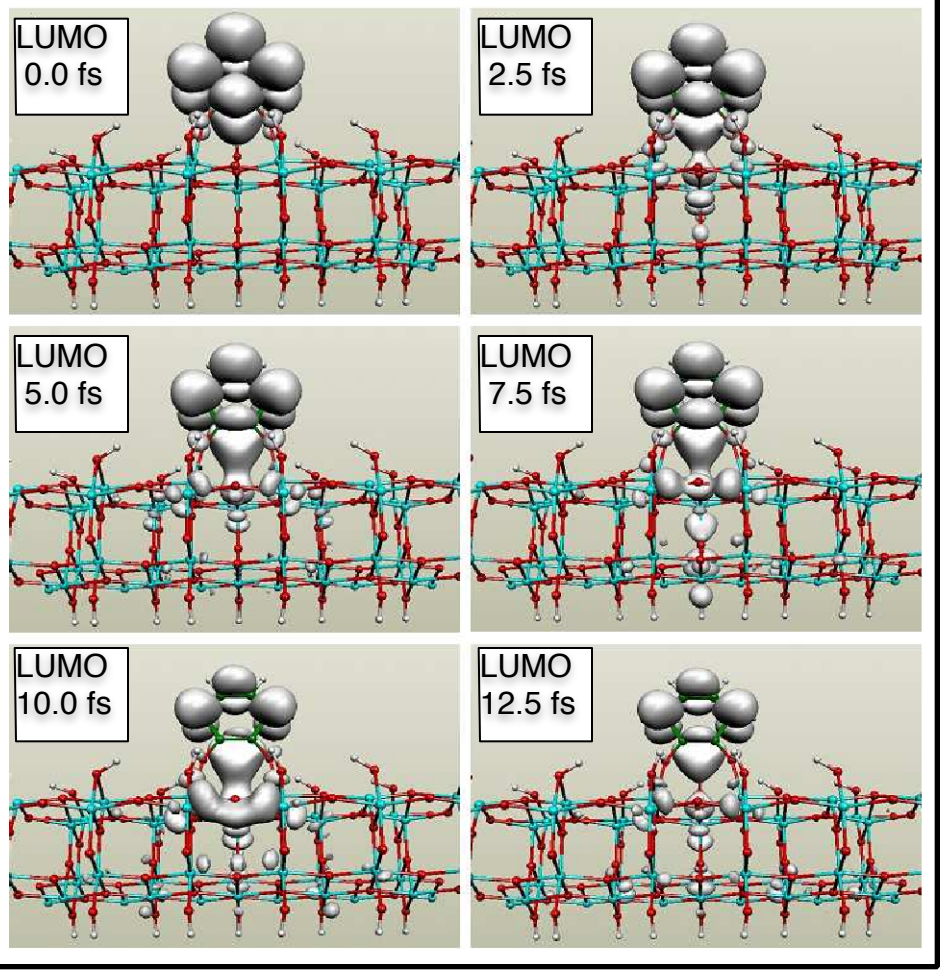


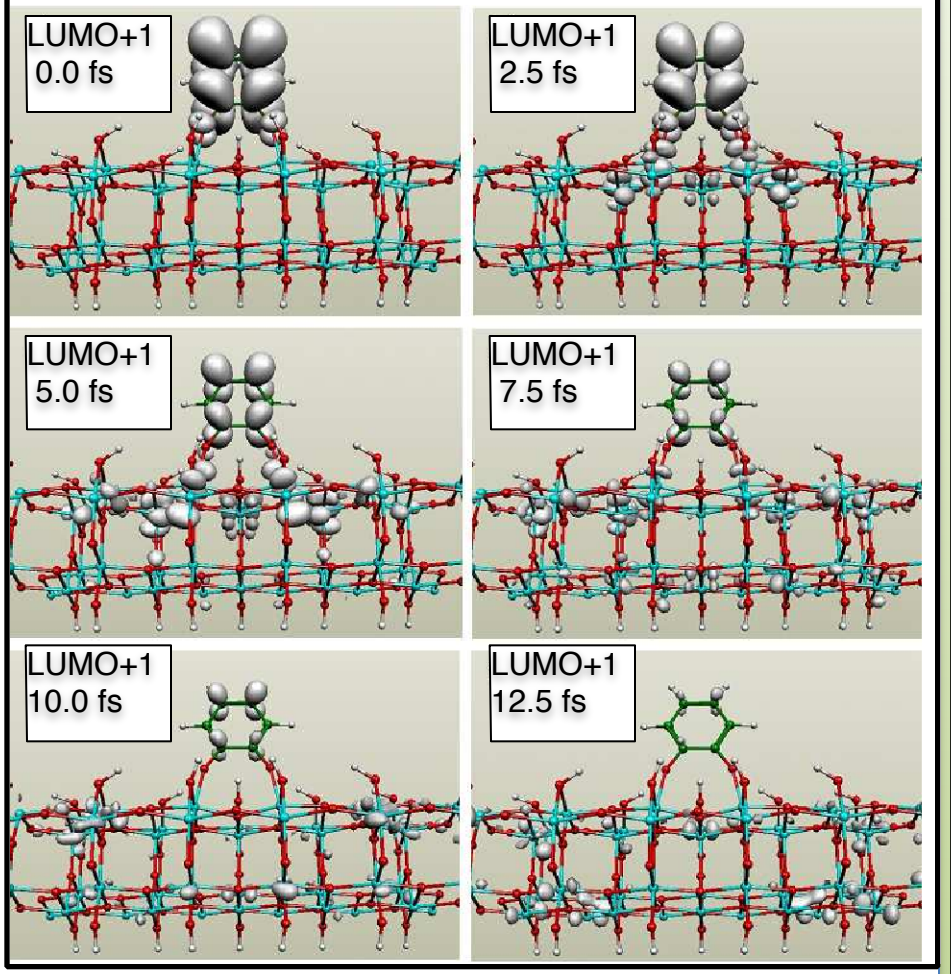
CHEM 505: *Green Chemistry and Alternative Energy*

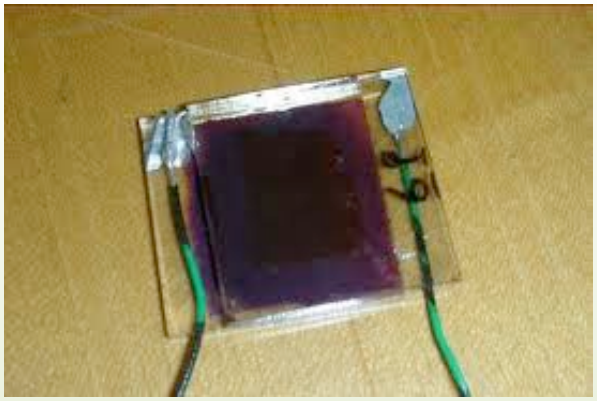
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ligand-to-Conduction Band Electron Transfer







CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Ultrafast IET: Quantum Dynamics Simulations

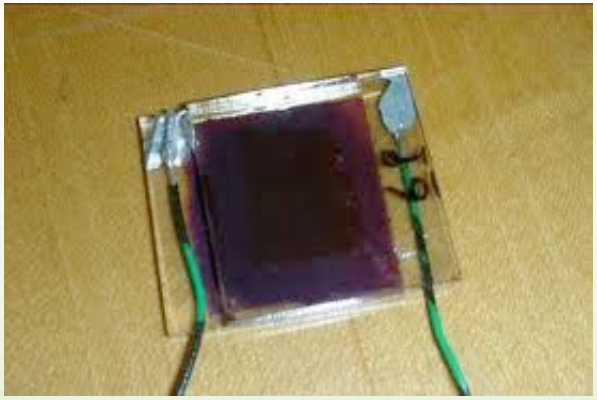
$\left|\Psi(t)\right\rangle = \hat{U}(t)\left|\Psi(0)\right\rangle$, where $\hat{U}(t) = e^{-\frac{i}{\hbar}\int H(t')dt'}$

and where $\left|\Psi(t)\right\rangle = \sum_q B_q(t)\left|\phi_q(t)\right\rangle$, $B_q(t) = \left\langle \phi_q \middle| \Psi(0)\right\rangle e^{-\frac{i}{\hbar}E_q t}$ and the MO's

$\left|\phi_q(t)\right\rangle = \sum_i C_{i,q}(t)\left|K_i(t)\right\rangle$ are obtained in the basis of AO's $\left|K_i(t)\right\rangle$

by solving the extended-Hückel generalized eigenvalue equation:

$$H(t)C(t) = S(t)C(t)E(t)$$



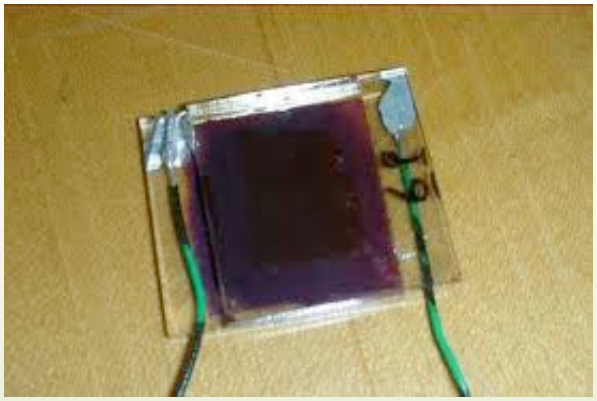
Modeling Dye-Sensitized Solar Cells

Ultrafast IET: Quantum Dynamics Simulations

With this scheme, we can calculate for all $t>0$:

- electronic wavefunction
- electronic density
- Define the **Survival Probability** for electron to be found on initially populated adsorbate molecule

$$P_{MOL}(t) = \left| \sum_{j,\beta}^{SYS} \sum_{i,\alpha}^{MOL} C^{*}_{i,\alpha}(t) C_{j,\beta}(t) S^{i,j}_{\alpha,\beta} \right|$$



CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Dye-Sensitized Solar Cells

Simulations of IET in sensitized TiO_2

Exercise 3: [by Robert C. Snoeberger III]

Consider a TiO_2 slab with atomic coordinates define in file Tio2.com. Download the software package IETsim and compute:

(a) The DOS of TiO_2, as shown in page 7.

(b) The DOS of TiO_2 sensitized with catechol covalently attached to the (101) surface, as shown in page 7.

(c) The time-dependent electronic population of catechol $P_{MOL}(t)$, when the initial state is defined as the LUMO+1 orbital of the isolated catechol on the TiO2-anatase (101) surface. Plot the survival amplitude and estimate the rate. Compare your result with Figure 13 in Reference [1].

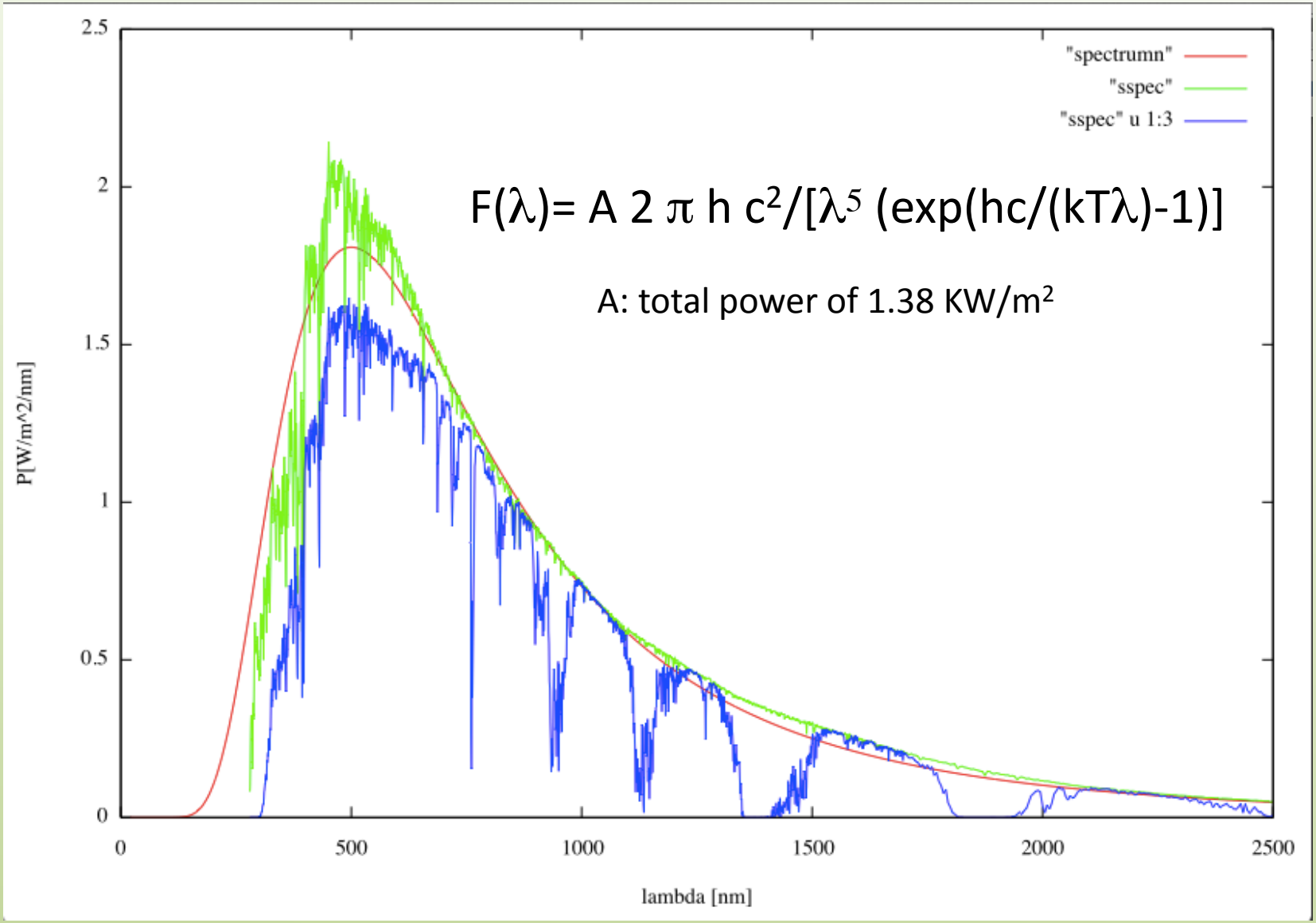
(d) Simulate IET from the HOMO orbital of catechol on the TiO2-anatase (101) surface. Explain why the probability $P_{MOL}(t)$ does not decay to zero.

Solution to Exercise 3:

Follow the instructions in the tutorial notes to install, compile and run IETsim using the input file provided in the directory dynamics/examples. The tutorial also provides guidelines to construct figures of the DOS, the time evolution of the electronic density during IET and the time-dependent electronic population.

Solar Spectrum

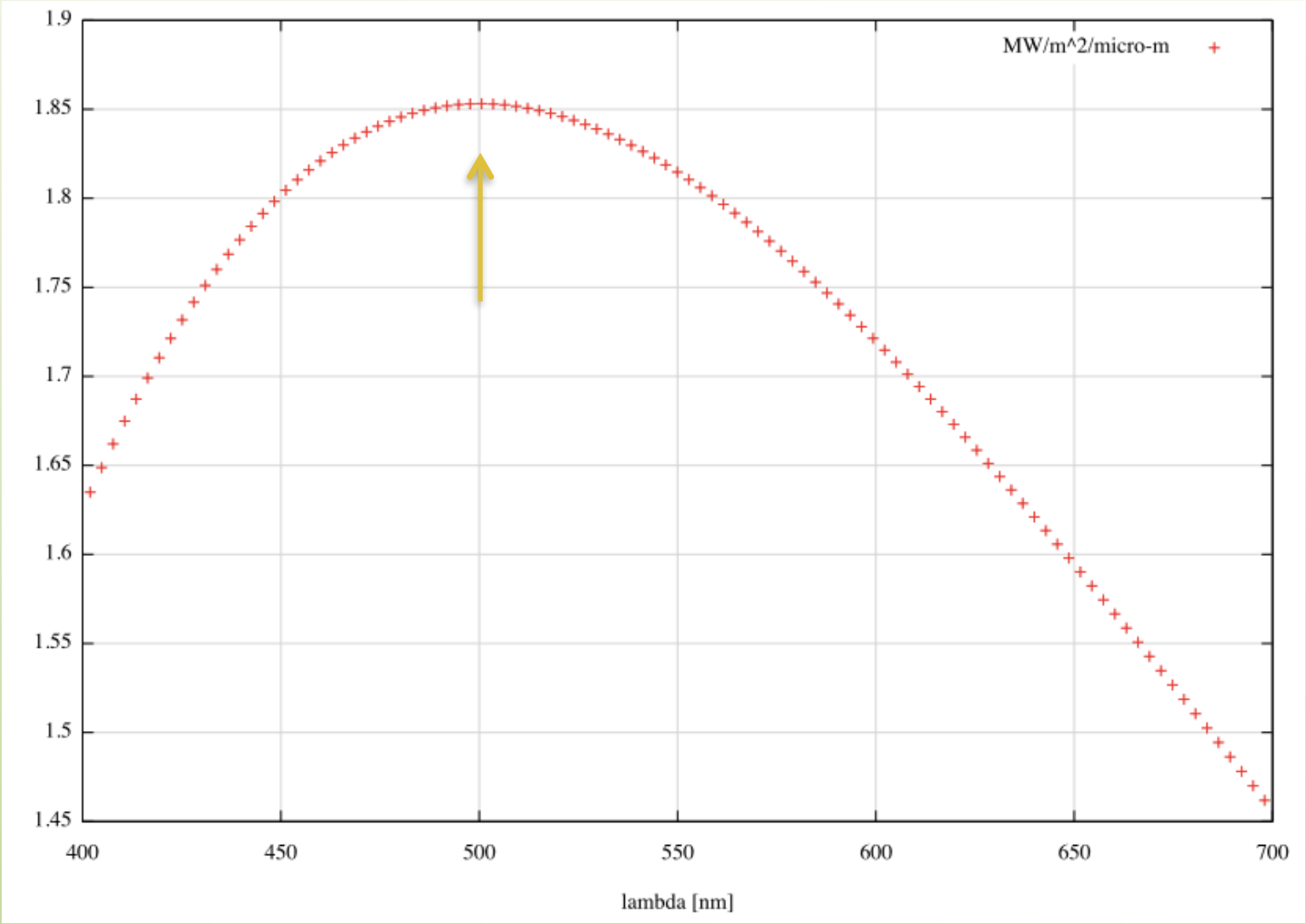
Black body Radiation at 5800 C



$F(\lambda) = A\ 2\ \pi\ h\ c^2/[\lambda^5\ (\exp(hc/(kT\lambda)-1)]$

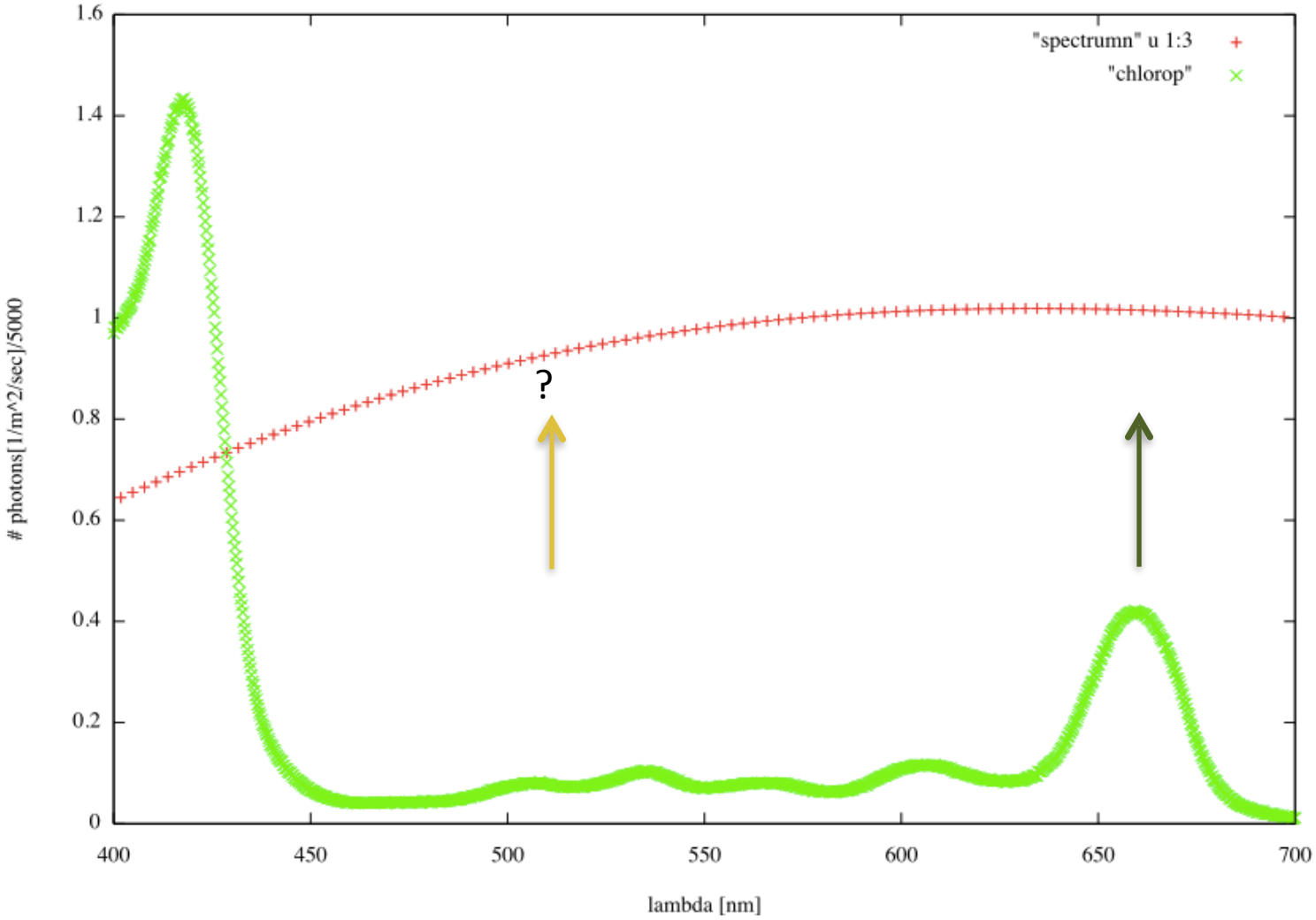
A: total power of 1.38 KW/m^2

Solar Spectrum: Maximum Intensity



Solar Spectrum: Maximum Photon Flux

Comparison to [Spectrum of Chlorophyll a]



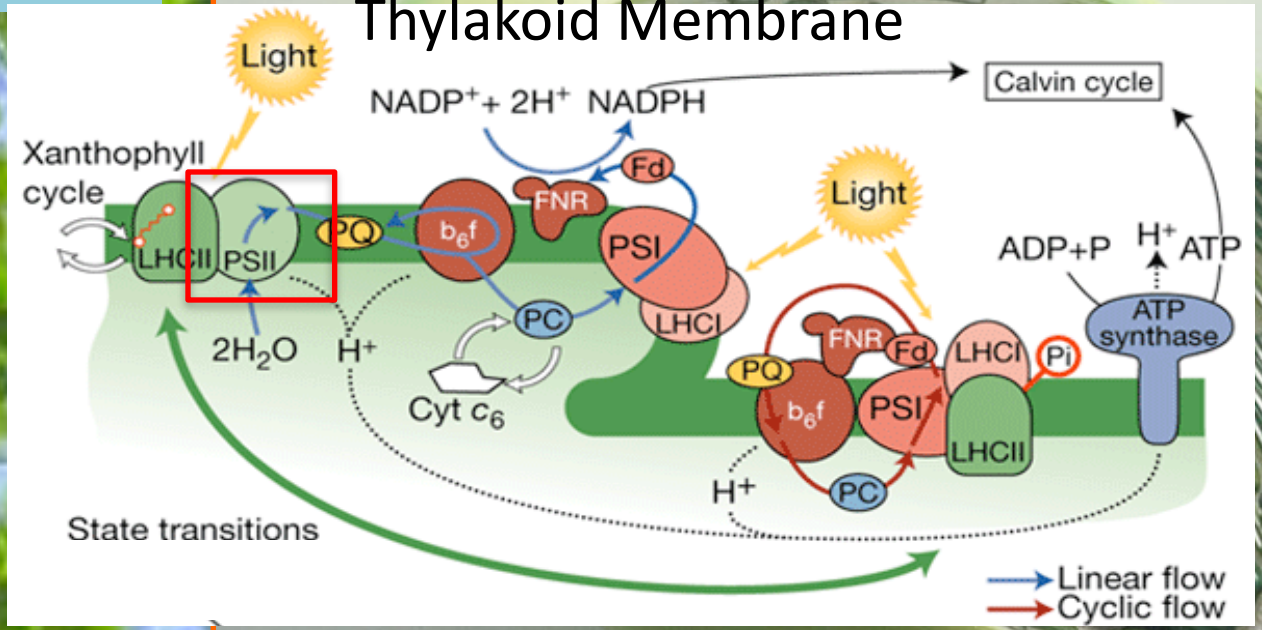
Flux of Solar Photons: Solution

```
      PROGRAM main
      IMPLICIT NONE
      DOUBLE PRECISION rd,rtot,F,rlmax,rlmin,dlambda
      DOUBLE PRECISION R,T,rc,rh,pie,rk,rl,rn,SB
      INTEGER i,J,npt
      npt=1000
      rlmax=3000.0E-9
      rlmin=20.00E-9
      dlambda=(rlmax-rlmin)/(npt-1.)
      rc=3.0E+08                ! Speed of light, m/sec
      rh=6.626E-34              ! Planck's constant, J sec
      pie=acos(-1.0)            ! pi
      rk=1.38E-23               ! Boltzmann constant, J K^{-1}
      T=5800.                   ! Sun Blackbody Temp, K
      SB=5.67E-8                ! Stefan-Boltzmann constant, W/m^2/K^4
      OPEN(1,FILE="spectrumn")
      DO i=1,npt
         rl=rlmin+(i-1)*dlambda
         rd=rl**5*(exp(rh*rc/(rk*rl*T))-1.)
         F=2.0*pie*rh*rc*rc/rd *1380./(SB*T**4) ! W/m^2/m  Blackbody radiation
         rtot=rtot+F*dlambda    ! W/m^2
         WRITE(1,22) rl*(1.0E+9),F*1.0E-9,F*1.0E-24/(rh*rc/rl)/5000. ! KW/m^2/micro-m, #phot/sec/nm^2/nm
      END DO
22    FORMAT(6(e13.6,2x))
      END
```

CELLS

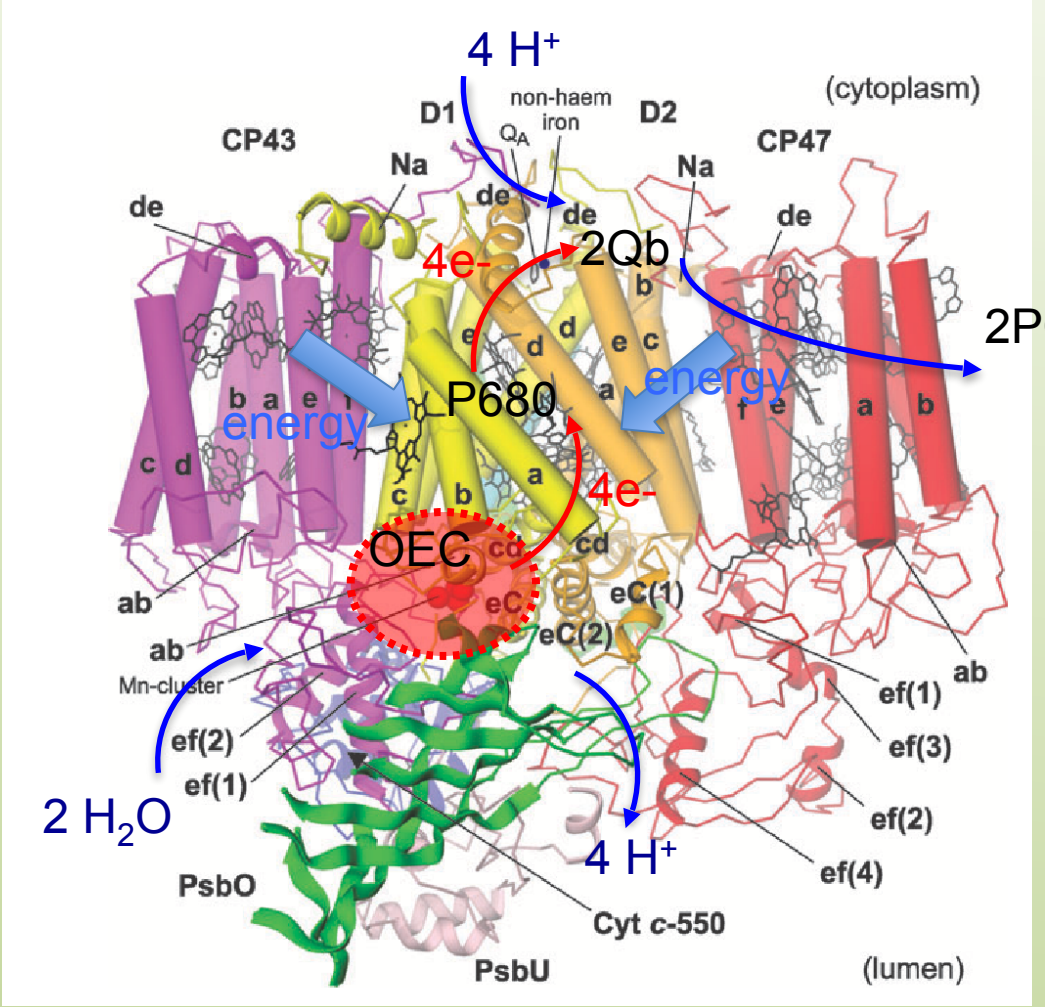
Chloroplast

Thylakoid Membrane

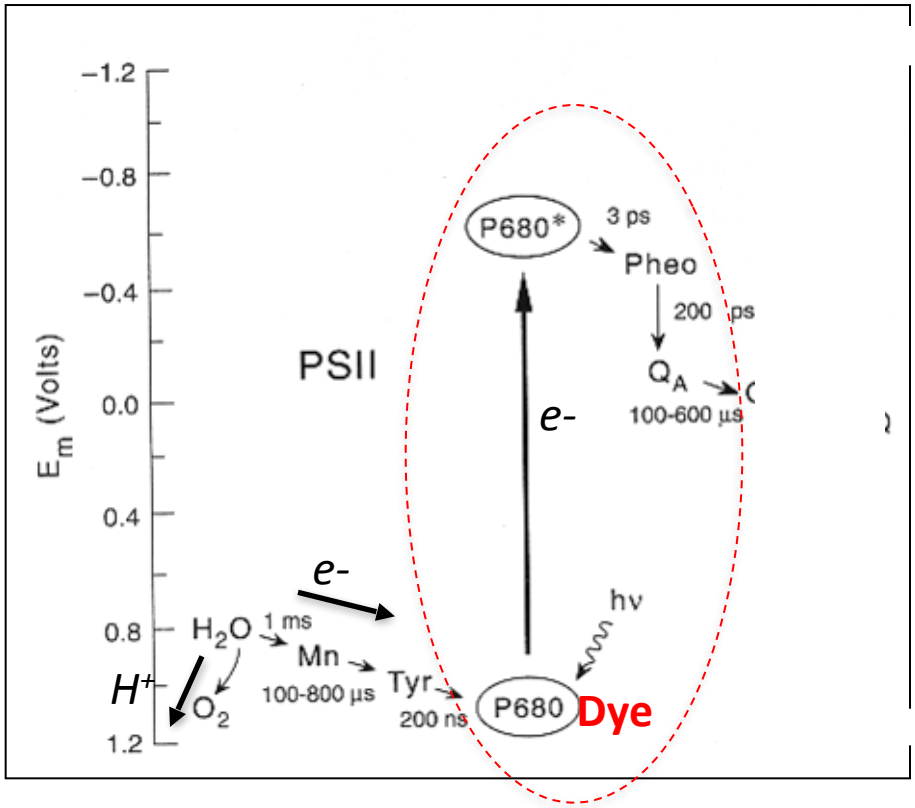


Breakthroughs in X-ray Diffraction Models of Photosystem II

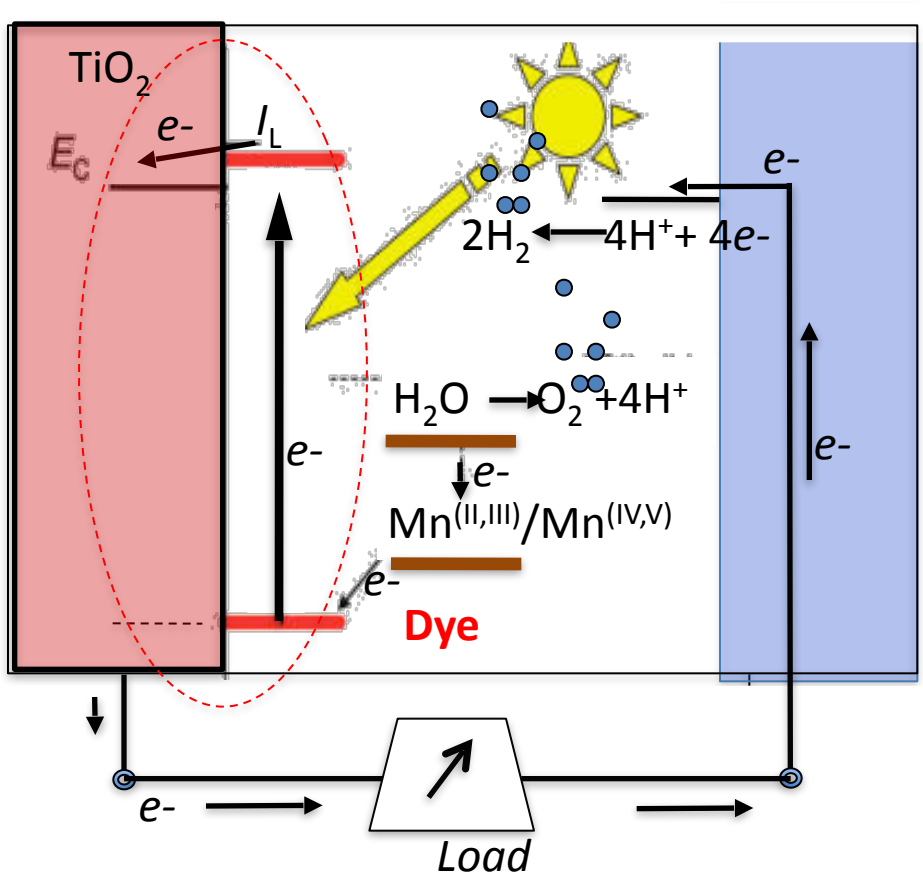
Ferreira, K. N. et al *Science* **2004**, *303*, 1831-1838. [3.5 Å resolution]
Biesiadka, J. et al *Phys. Chem. Chem. Phys.* **2004**, *6*, 4733-4736. [3.2 Å resolution]
Loll, B. et al *Nature* **2005**, *438*, 1040-1044 [3.0 Å resolution]
Guskov A, Kern J, Gabdulkhakov A, et al. *Nature Struct. & Mol. Biol.* **2009**, *16*, 334-342 [2.9 Å resolution]
Umena, Y., Kawakami, K., Shen, J.-R., and Kamiya, N. (2011) *Nature*, 473, 55-60 [1.9 Å resolution]



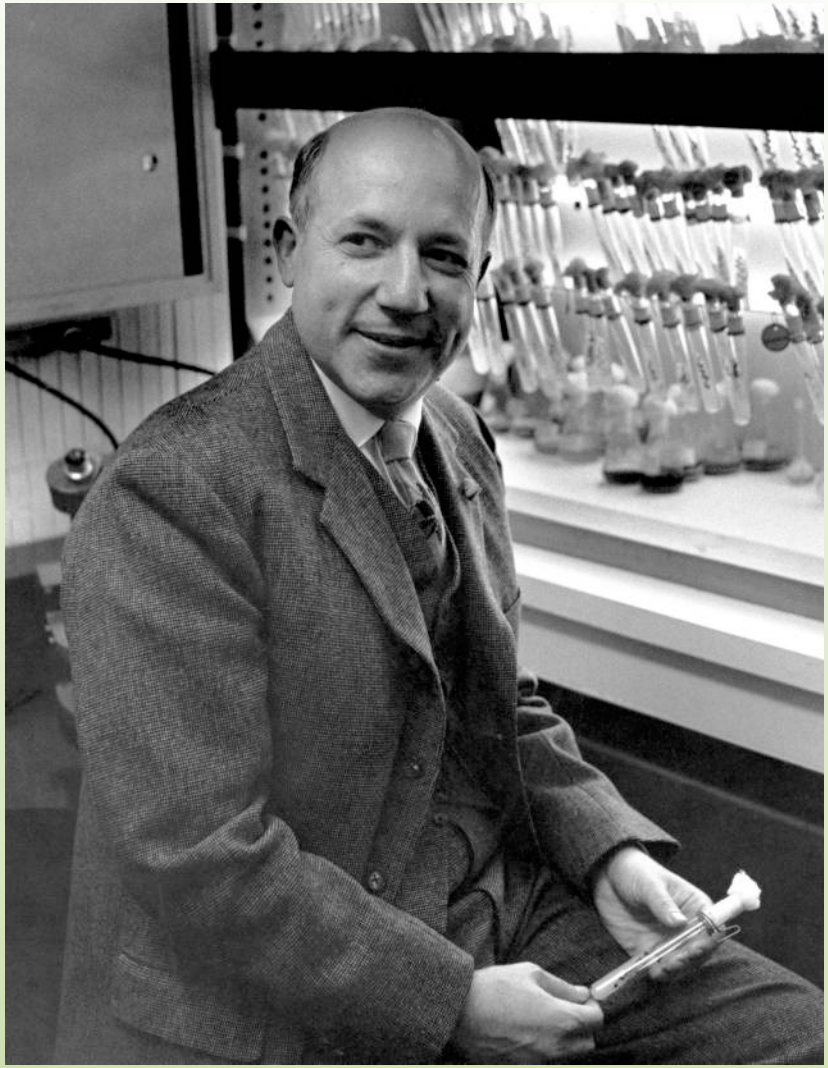
Natural Photosynthesis
PSII Energy Diagram



Artificial Photosynthesis
Dye Sensitized Solar Cell



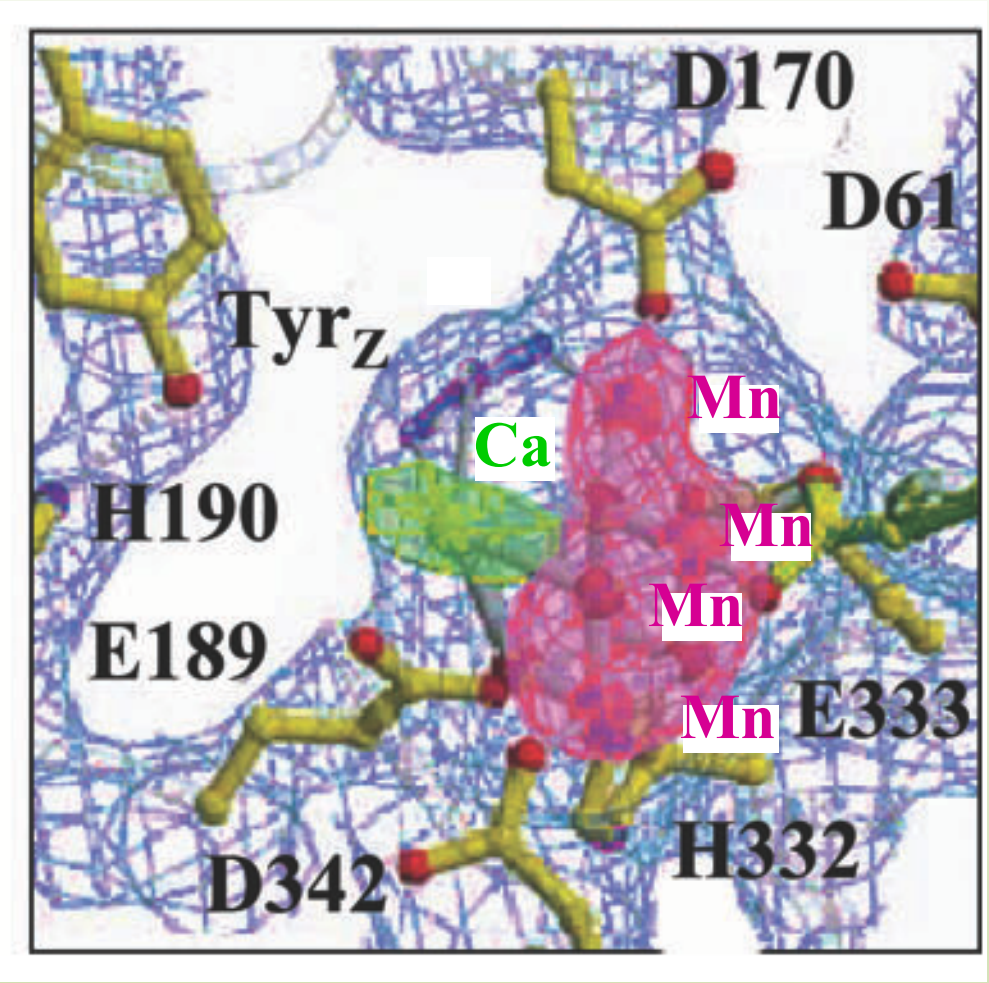
$$2H_2O(l) \xrightarrow{Cat.} O_2(g) + 4H^+(aq) + 4e^-$$



It is time to build an actual *artificial photosynthetic* system, to learn what works and what doesn't work, and thereby set the stage for making it.
Melvin Calvin

Jim Barber's Model

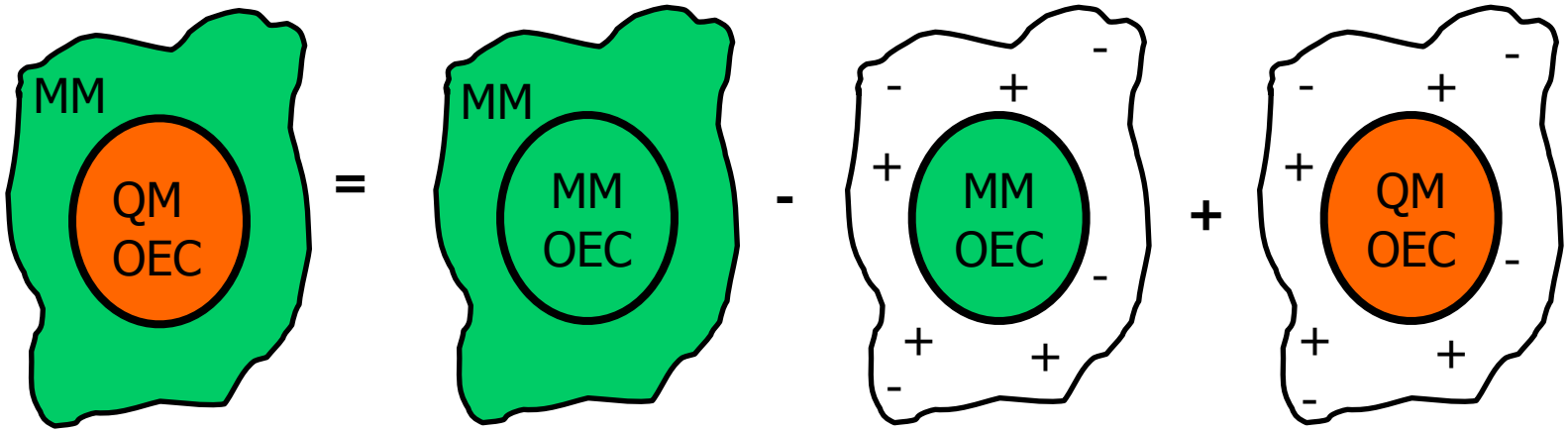
Ferreira et al. *Science* (2004) **303**:1831-1838



The coordinates of the Mn atoms were chosen consistently with the observed dual-lobe electronic density to have Mn-Mn distances of about 2.7 Å and 3.3 Å length as reported by XAS studies [see, e.g., George, G.N.; Prince, R.C. and Cramer, S.P. Science (1989) **243**:789-791] and the cuboidal structure with a dangling Mn suggested by EPR and ENDOR data [Peloquin, J.M.; Campbell, K.A.;Eandall, D.W.;Evanchik, M.A.;Pecoraro, V.L.;Amstrong, W.A.;Britt, R.D. J. Am. Chem. Soc. (2000) **122**:10926-10942].

Quantum Mechanics / Molecular Mechanics (QM/MM) Hybrid Methodology (Warshel, 1976)

Two-layer ONIOM-Electronic Embedding (EE) (Morokuma), G03.



QM = DFT B3LYP/lacvp*
MM = Amber Force Field

UB3LYP ONIOM-EE optimizations

DFT QM/MM:

J.A. Gascon and V.S. Batista, *Biophys. J.* **87**, 2931-2941 (2004)

J.A. Gascon, E.M. Sproviero and V.S. Batista, *J. Chem. Theor. Comput.* **2**, 11-20 (2005)

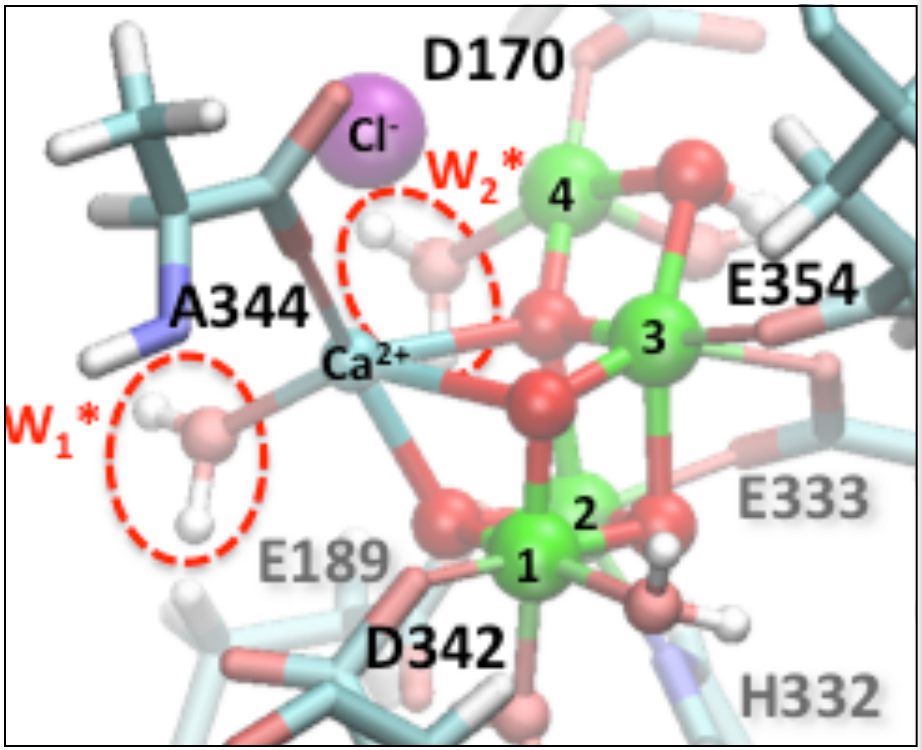
DFT QM/MM Self-Consistent Protein Polarization:

J.A. Gascon, S.S.F. Leung, E.R. Batista and V.S. Batista, *J. Chem. Theor. Comput.* **2**, 175-186 (2006)

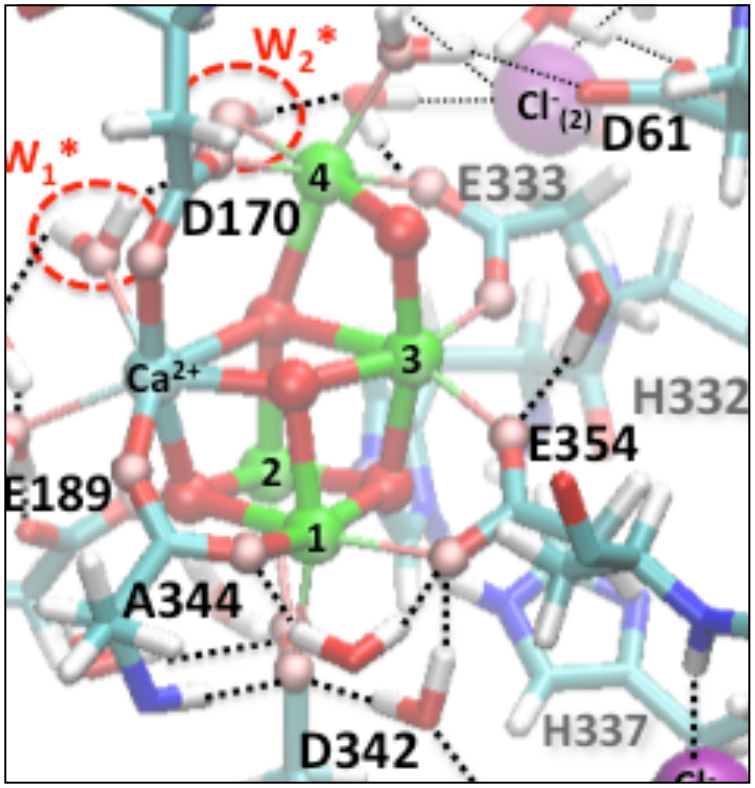
DFT-QM/MM Model

Sproviero, E.M; Gascon, J.A. et. al. *J. Chem. Theor. Comput.*, (2006) **4:**1119-1134; *Curr. Op. Struct. Biol.,* (2007) **17:**173-180; *Phil. Trans. Royal Soc. London B* **363**:1149-1156 (2008); *Coord. Chem. Rev.* **252**:395-415 (2008) ; *J. Am. Chem. Soc.* **130**:3428-3442 (2008); *J. Am. Chem. Soc.* **130**:6427-6430 (2008); *Biochemistry* **50**, 6308-6311 (2011); *Biochemistry* **50**, 6308-6311 (2011); *Biochemistry* **50**, 6312-6315 (2011); *Biochemistry* in press (2013).

2006 DFT QM/MM S_0 model



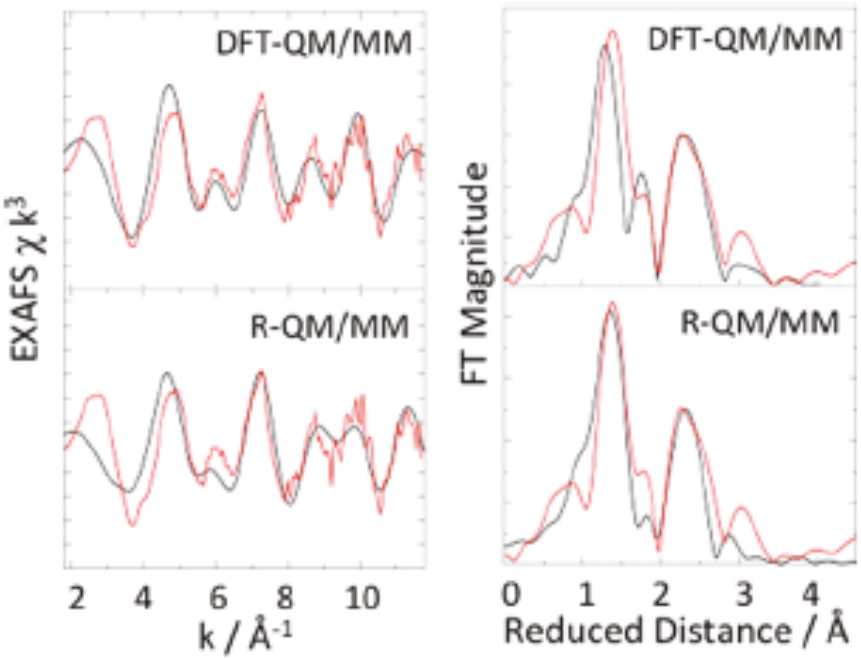
2011 Shen's X-ray model



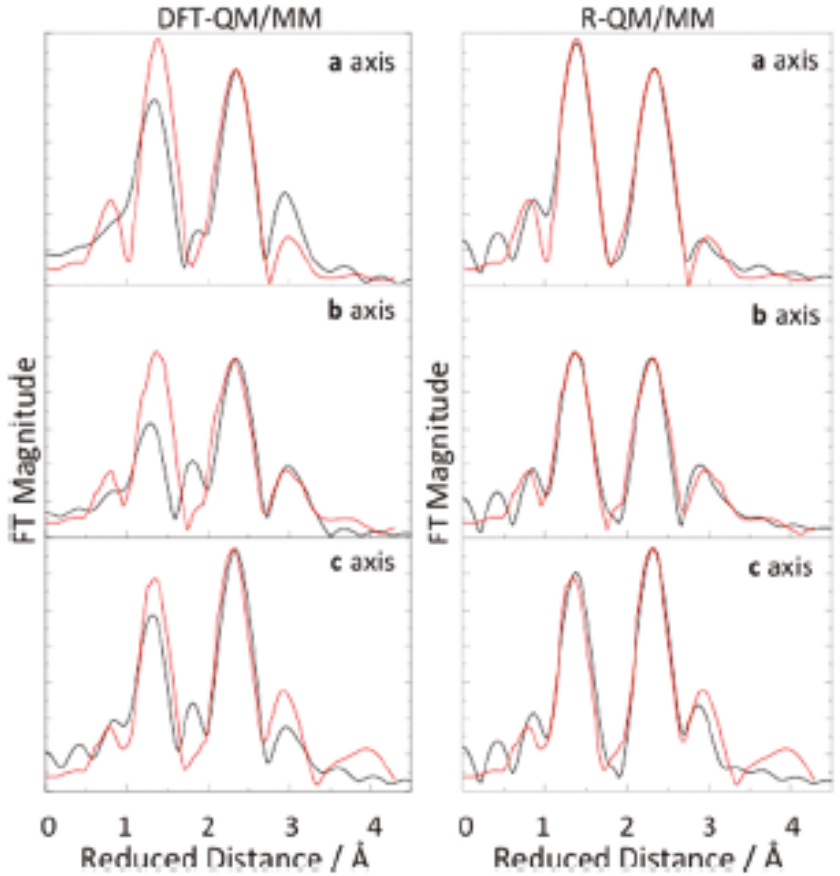
2011 DFT QM/MM Model: Validation by EXAFS Analysis

Biochemistry **50**, 6308-6311 (2011) Sandra Luber, Ivan Rivalta, Y. Umena, K. Kawakami, Jian-R. Shen, N. Kamiya, Gary Brudvig, and Victor S. Batista

Isotropic



Polarized



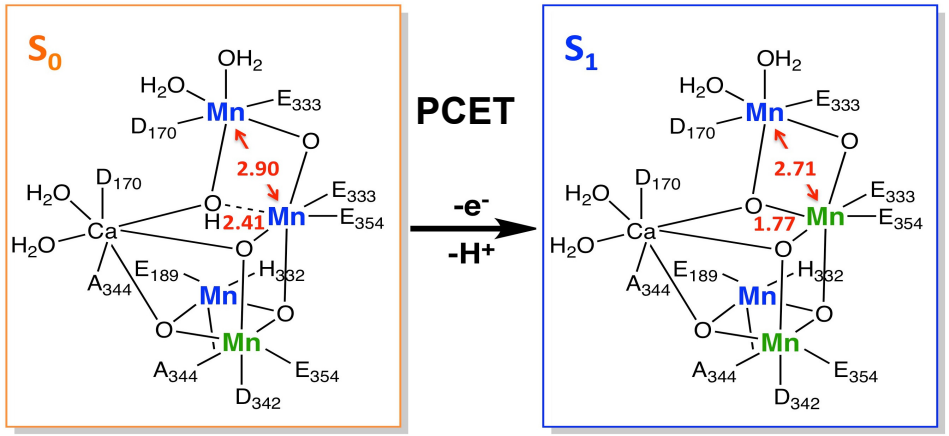
Experimental EXAFS Data:

Haumann, M.; Muller, C.; Liebisch, P.; Iuzzolino, L.; Dittmer, J.; Grabolle, M.; Neisius, T.; Meyer-Klaucke, W.; Dau, H. Biochemistry 2005, 44, 1894–1908.

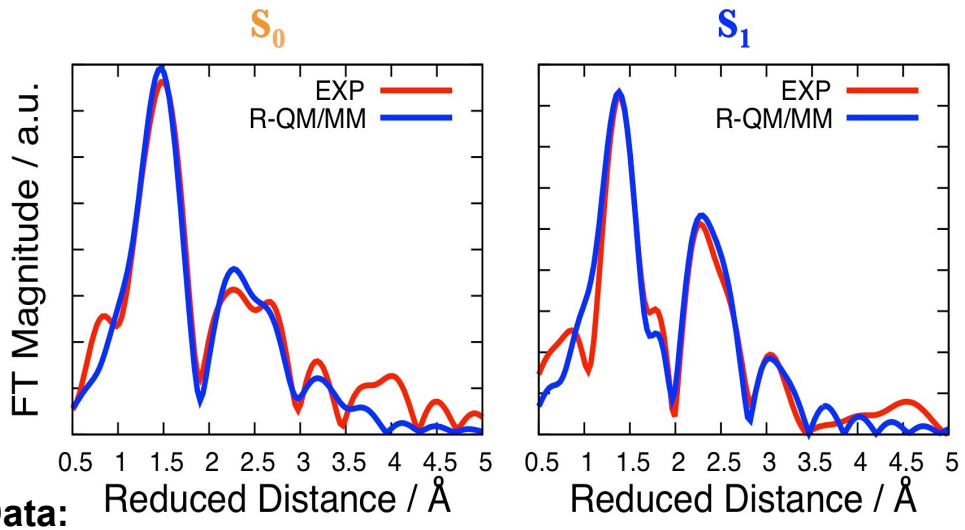
Yano, J.; Kern, J.; Irrgang, K. D.; Latimer, M. J.; Bergmann, U.; Glatzel, P.; Pushkar, Y.; Biesiadka, J.; Loll, B.; Sauer, K.; Messinger, J.; Zouni, A.; Yachandra, V. K. Proc. Natl. Acad. Sci. U.S.A. 2005, 102, 12047–12052.

S_0 -State Model of the OEC of Photosystem II

Biochemistry **52**: 7703-7706 (2013) Rhitankar Pal, Christian F. A. Negre, Leslie Vogt, Ravi Pokhrel, Mehmed Z. Ertem, Gary W. Brudvig, and Victor S. Batista

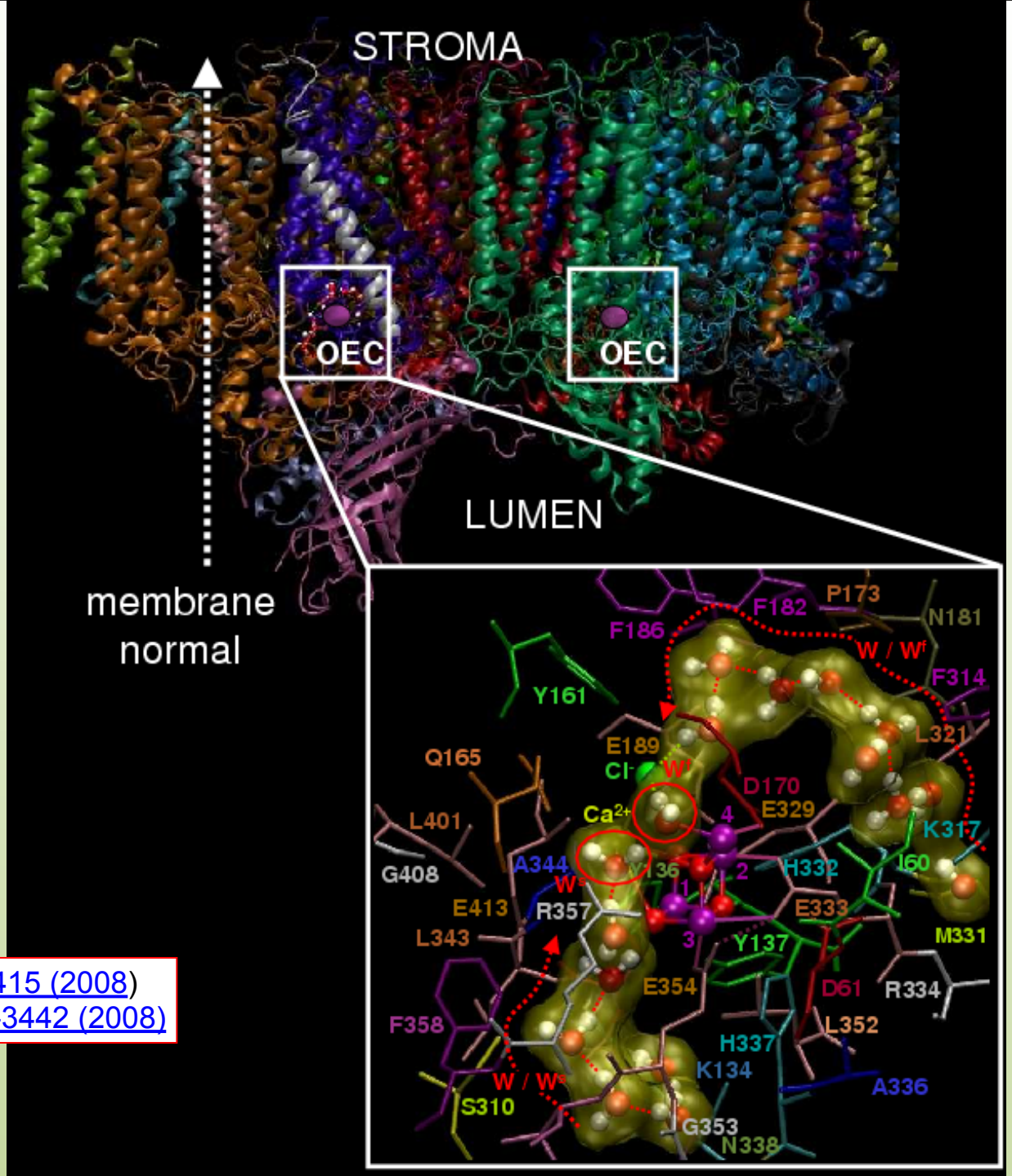


Dr. Rhitankar Pal
Dr. Christian Negre

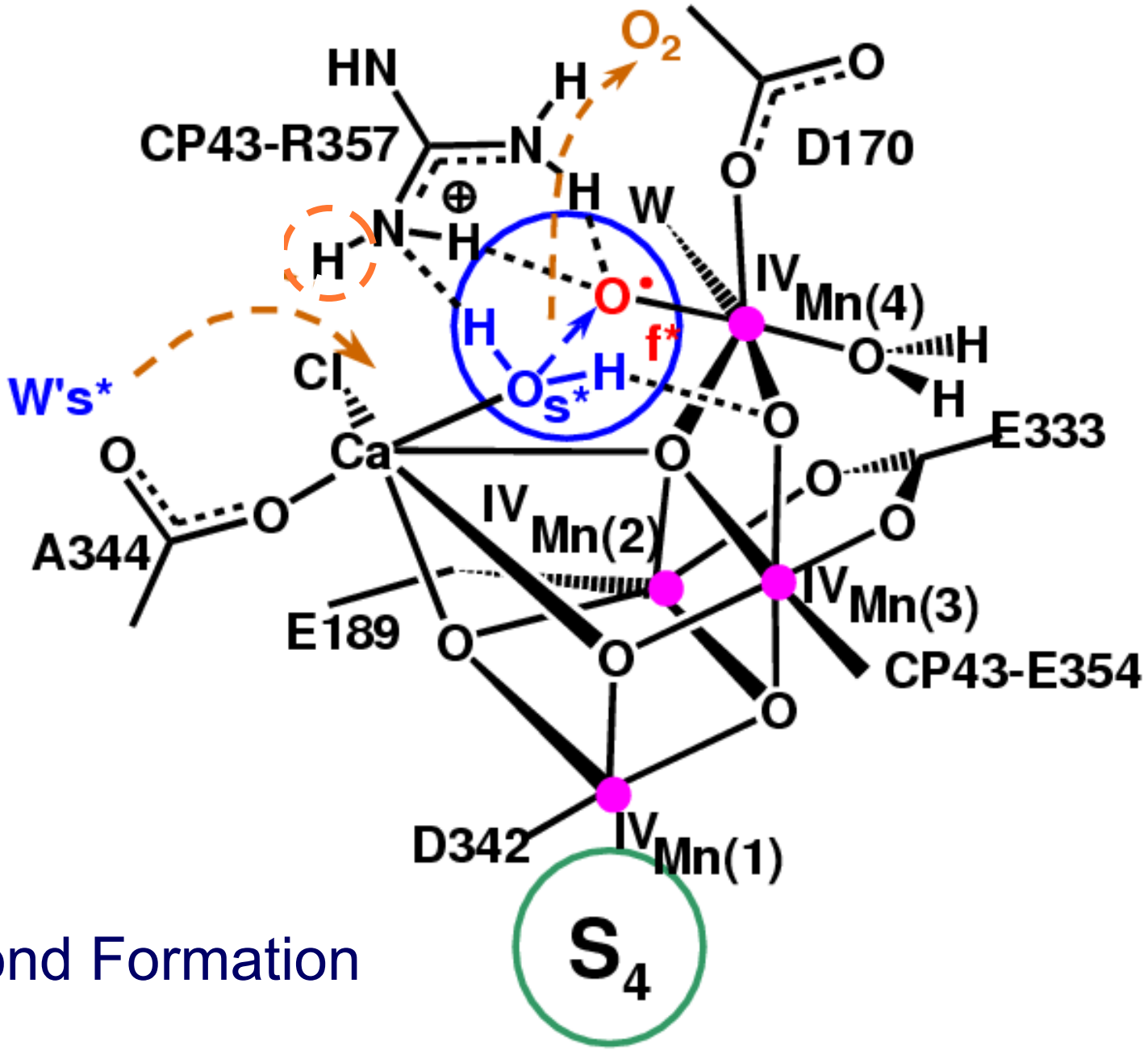


Experimental EXAFS Data:
Haumann, M.; Muller, C.; Liebisch, P.; Iuzzolino, L.; Dittmer, J.; Grabolle, M.; Neisius, T.; Meyer-Klaucke, W.; Dau, H. Biochemistry 2005, 44, 1894–1908.

Water Channels



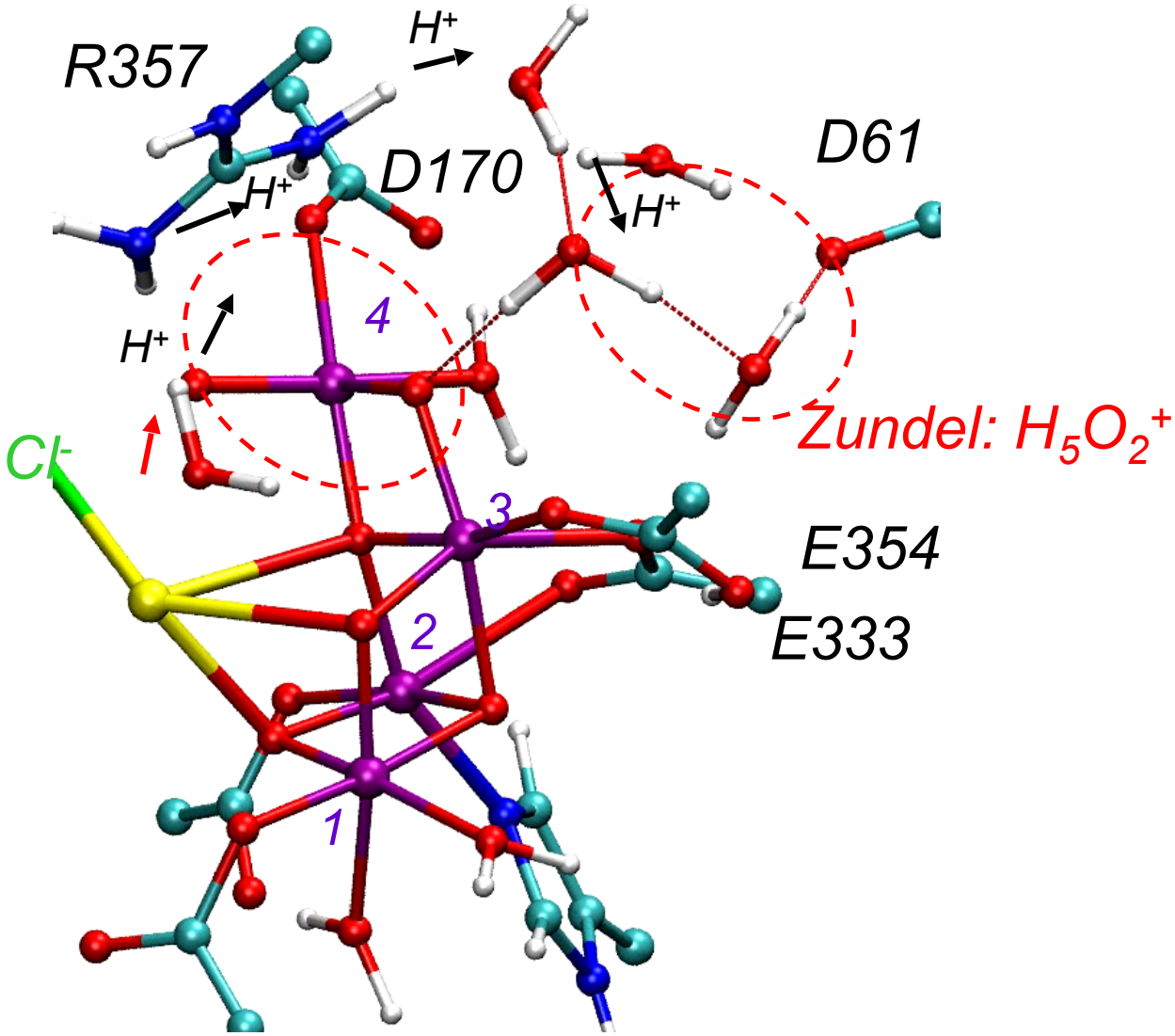
Coord. Chem. Rev. **252**:395-415 (2008)
J. Am. Chem. Soc. **130**:3428-3442 (2008)



O–O Bond Formation

O-O Bond Formation

Zundel/HOO-Mn(4) State Formation



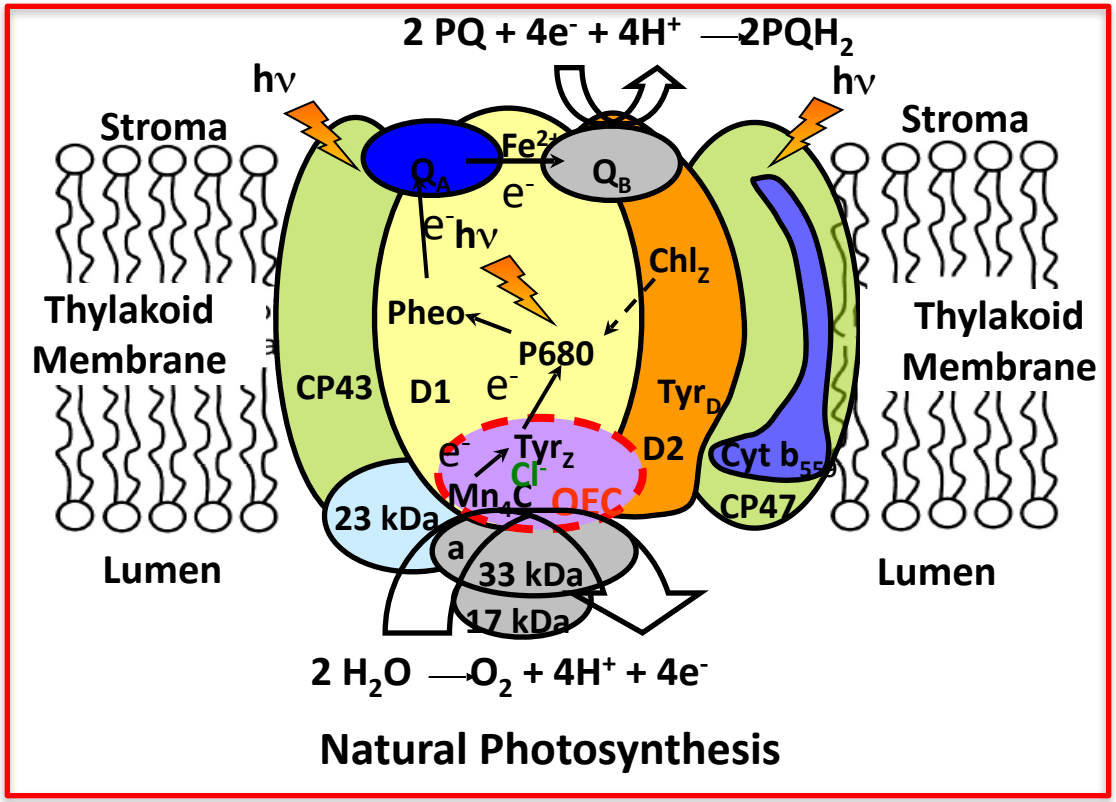
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Water Oxidation

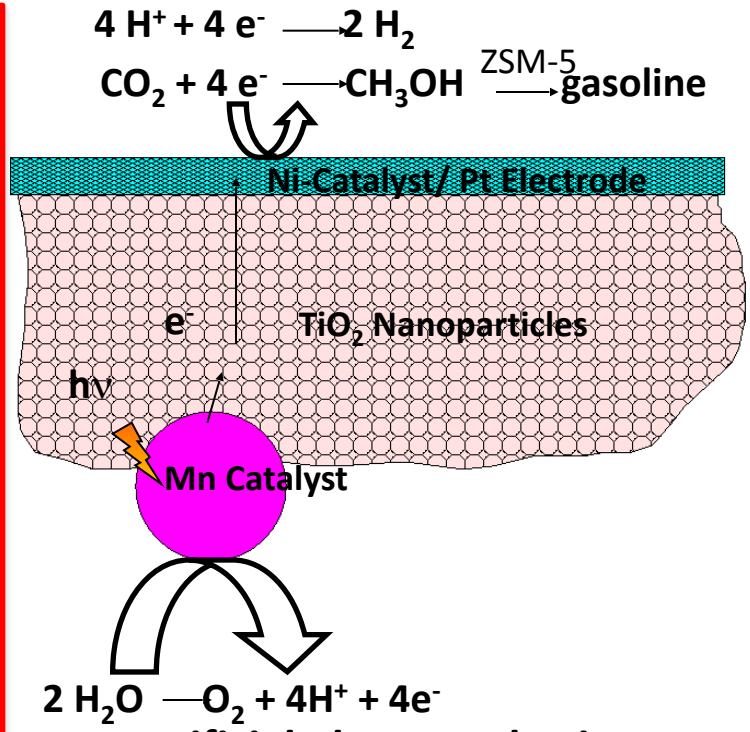
Catalytic Mn Complex Activated by Oxone

Thylakoid Membrane in Chloroplasts



Natural Photosynthesis

Photocatalytic Thin Film



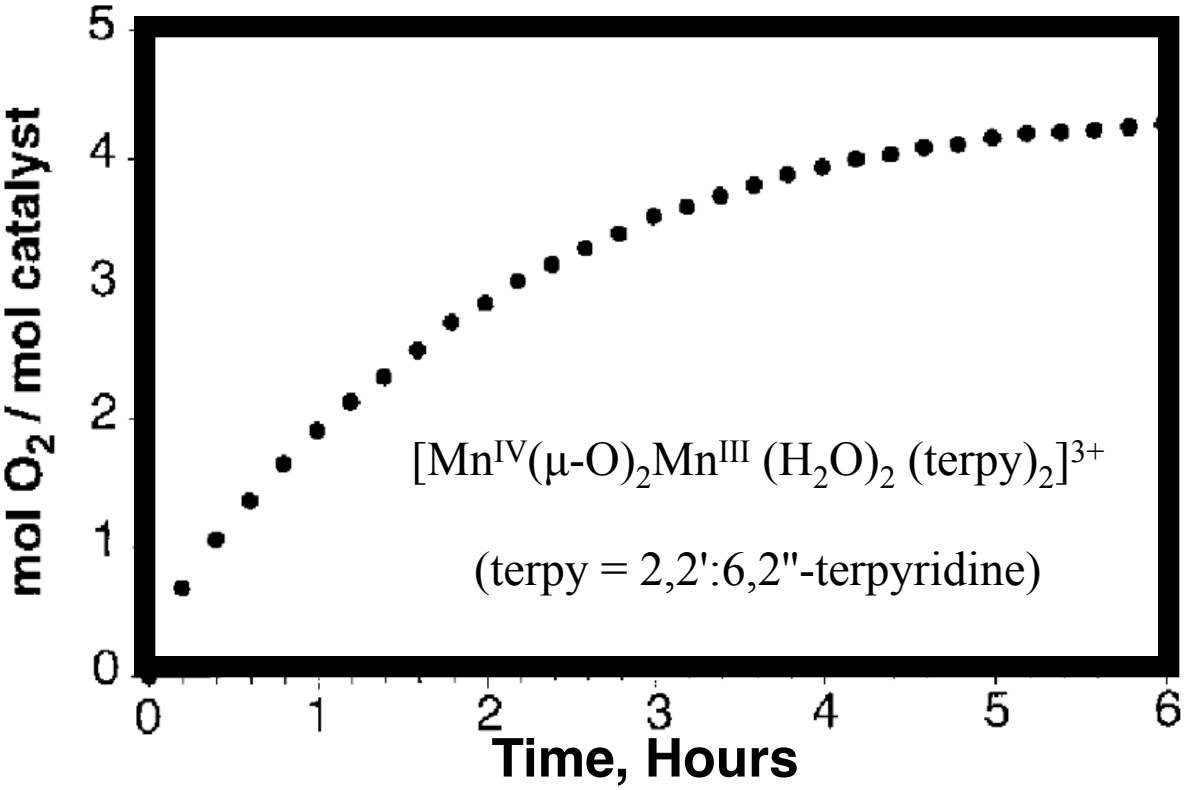
Artificial Photosynthesis

CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Biomimetic Oxygen Evolution

Catalytic Mn Complex Activated by Oxone

Crabtree, Brudvig and co-workers *Science* **283**, 1524-1527 (1999); *J. Chem. Edu.* 791-794 (2005).

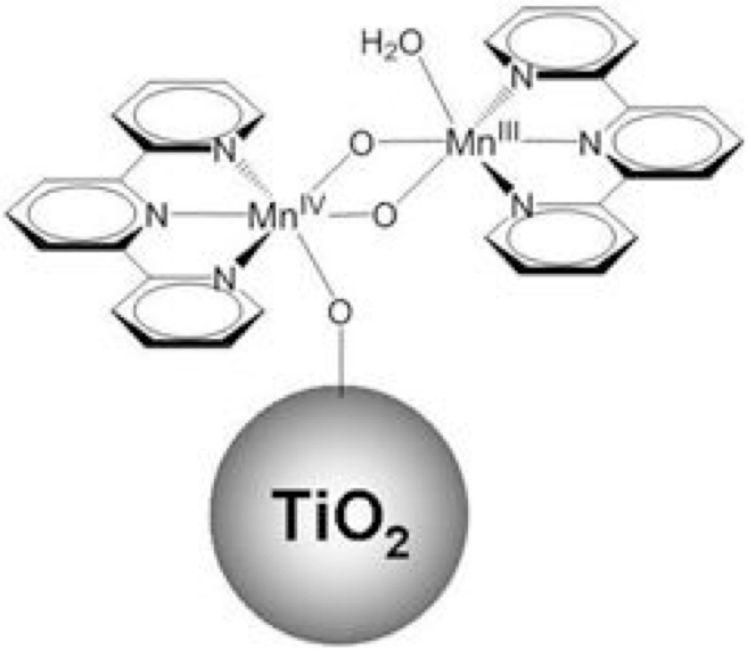


O_2-Evolution by Water Splitting: The Yale Mn-Terpy Dimer in Action

CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

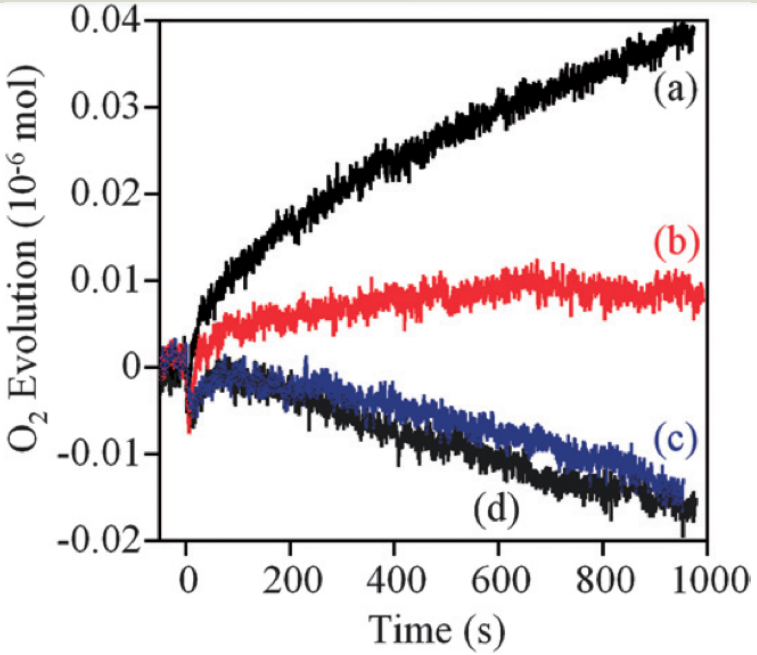
Modeling Biomimetic Oxygen Evolution

Water Oxidation by a Mn-Dimer Adsorbate



Mn Dimer **1** attached to TiO_2

[Li, G. *et al.* Energy Environ. Sci. (2008) 2:230-238]



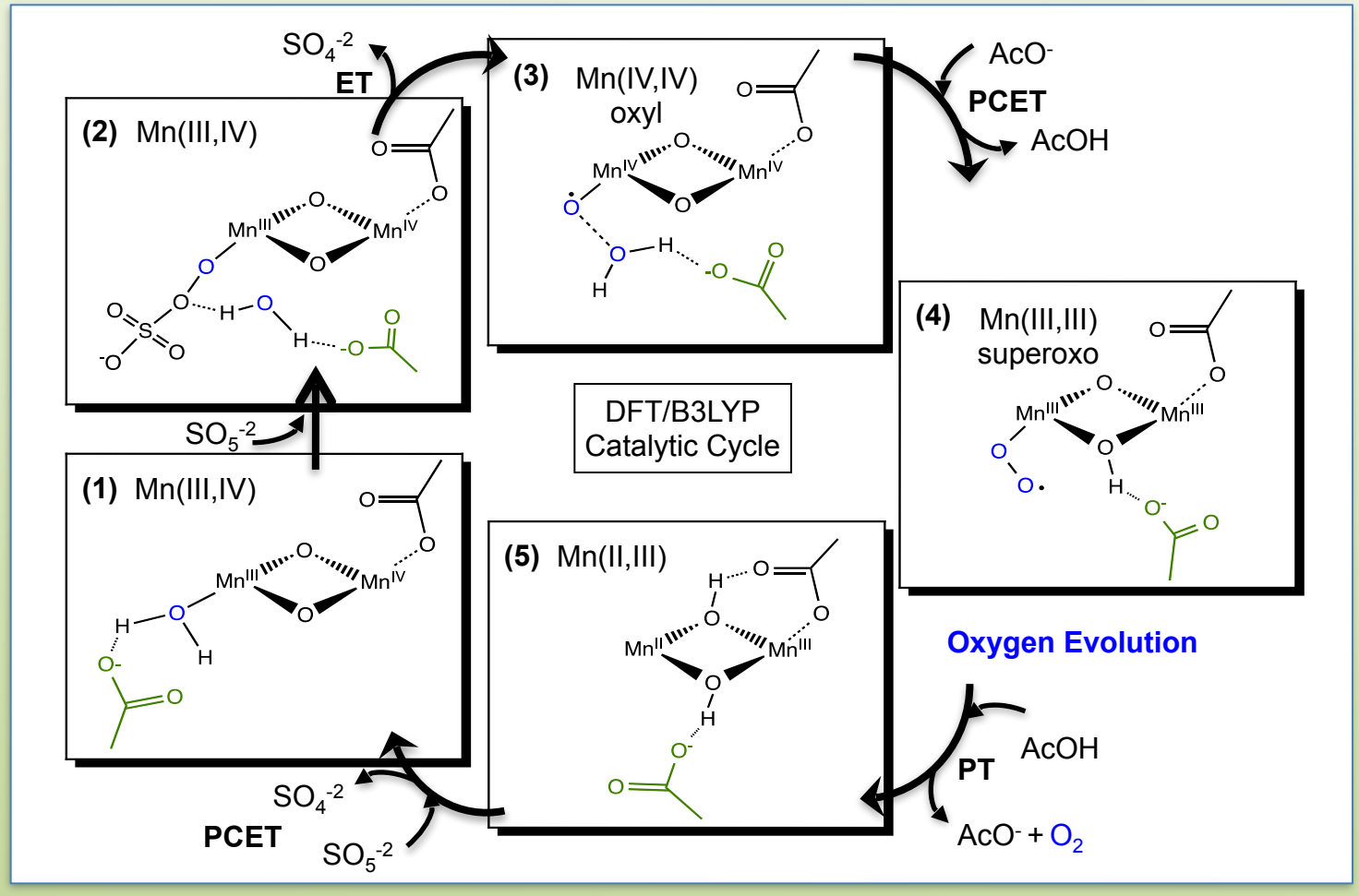
O_2 evolution using Ce^{4+} as a single-electron primary oxidant. **1** was loaded on TiO_2 (50 mg) samples: (a) P25, (b) D450, and (c) D70. A control test was also done using (d) bare P25 NP's as the catalyst.

CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

Water Splitting Catalyzed by a Mn-Dimer

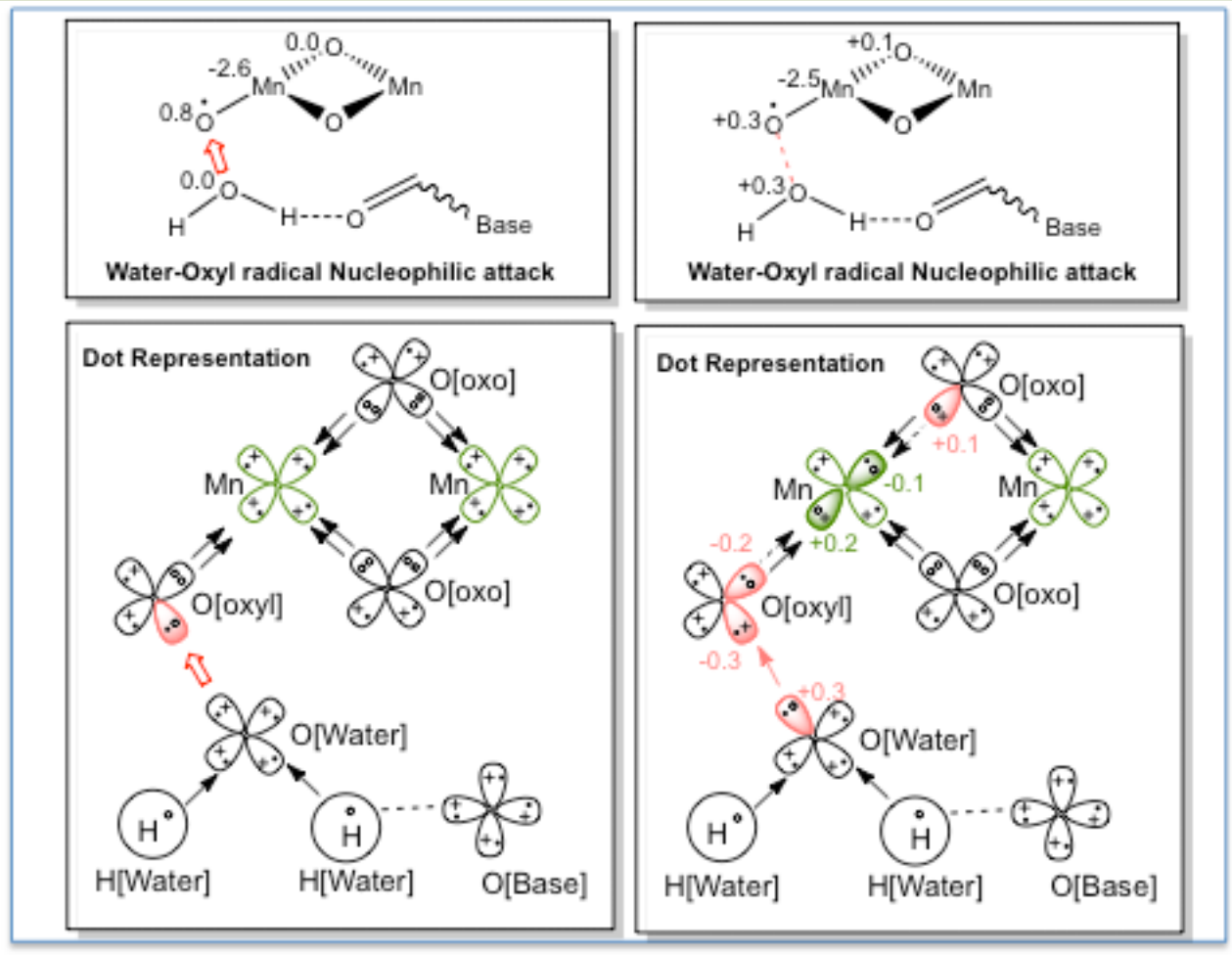


CHEM 505: *Green Chemistry and Alternative Energy*

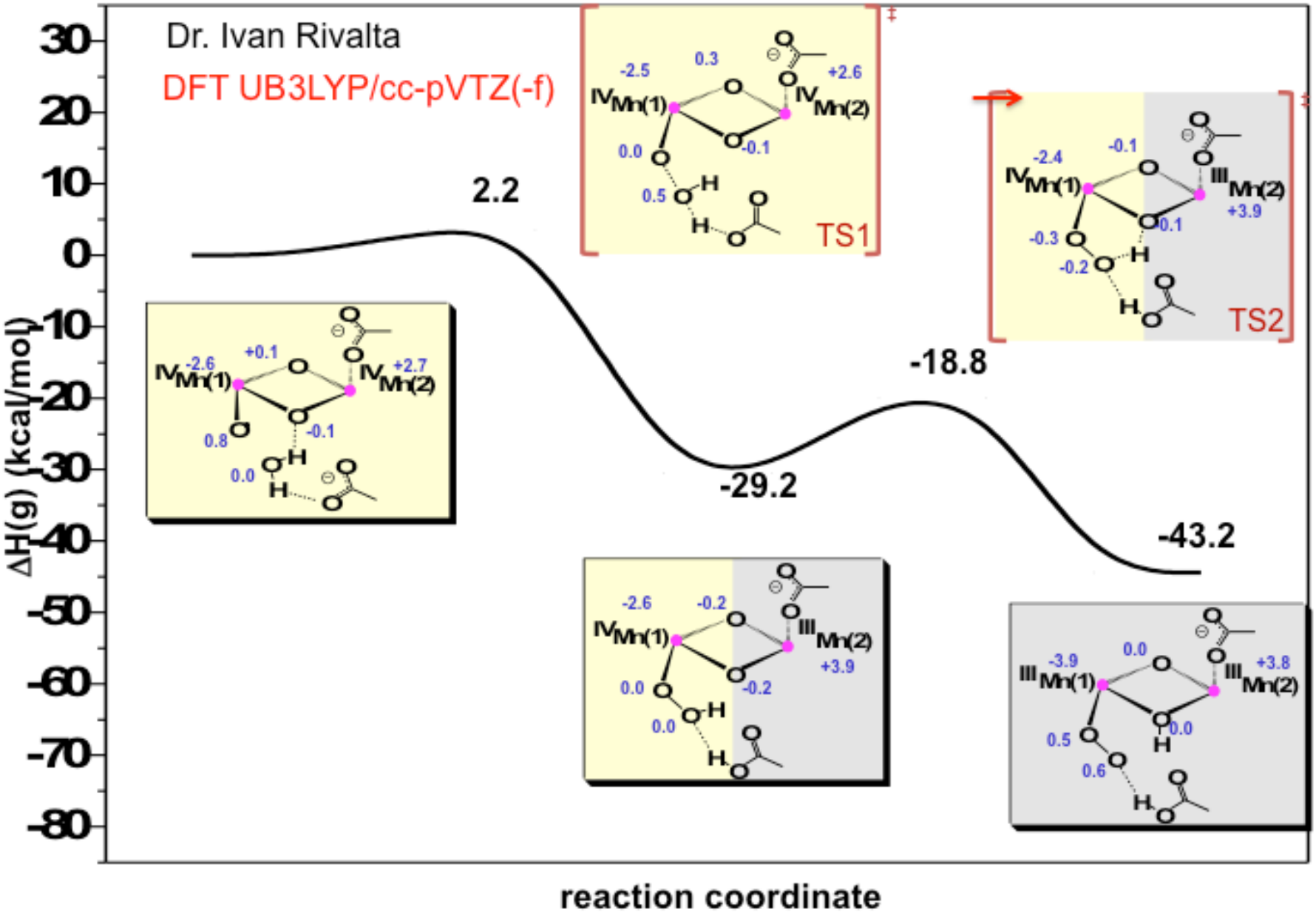
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

O-O Bond Formation: PCET



O-O BOND FORMATION: SUPEROXO INTERMEDIATE

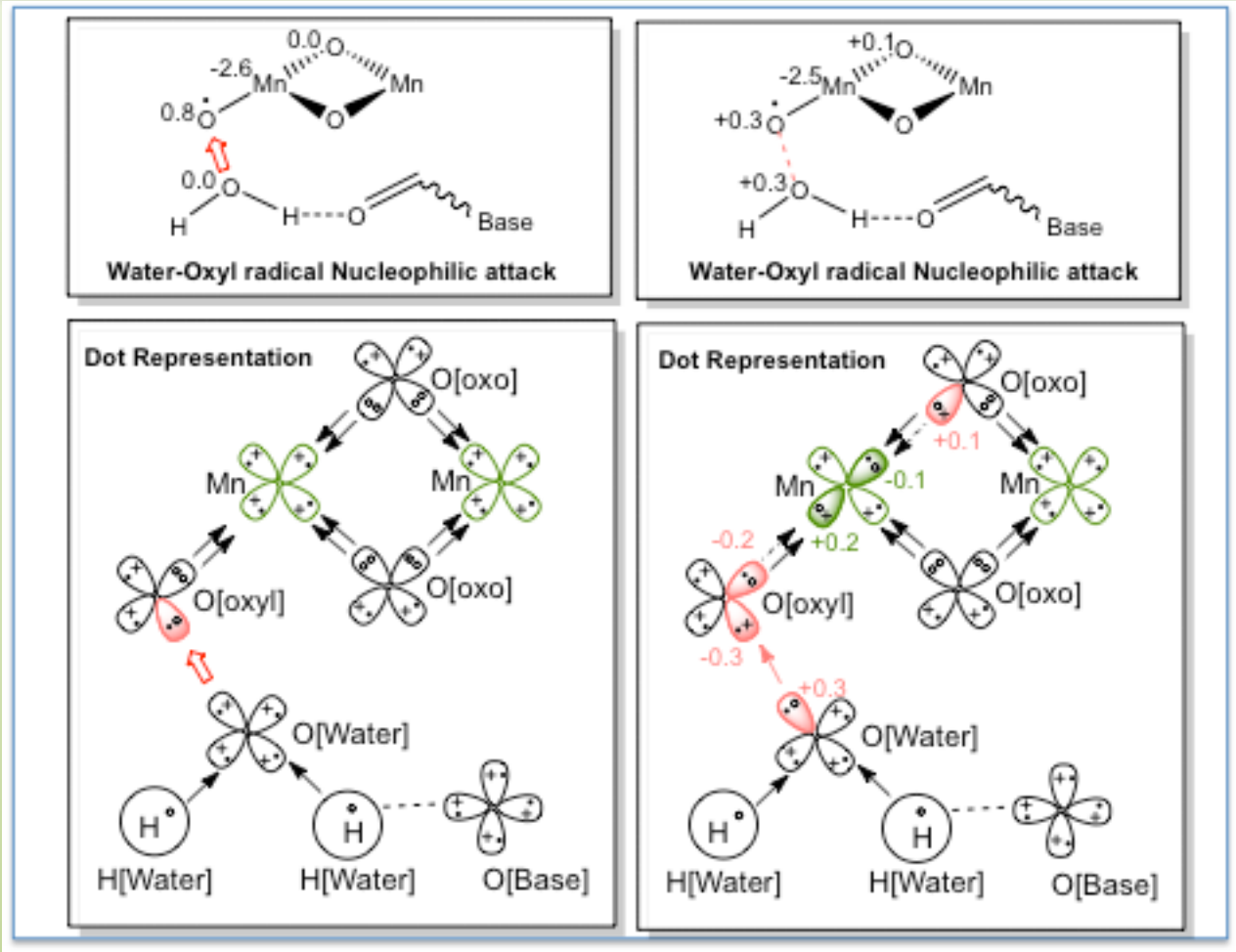


CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Biomimetic water Oxidation

O-O Bond Formation: Spin Injection

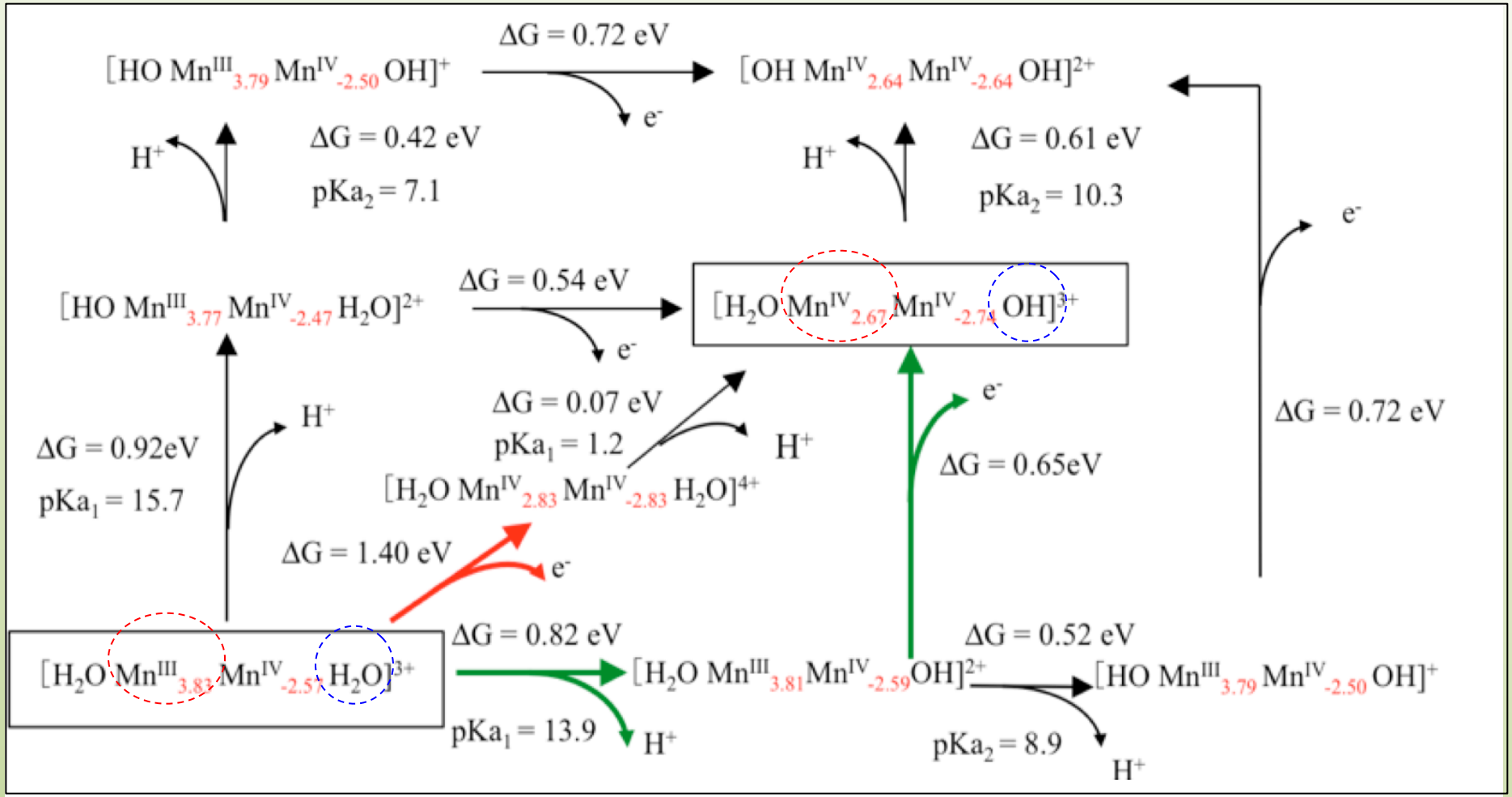


[Wang, T. *et al.* JCTC (2010) 6:755-760]

PCET: Activation Mechanism

Dr. Ting Wang

DFT UB3LYP/cc-pVTZ(-f) Free Energy Calculations: (III,IV) → (IV,IV) Transition



$$[H_2O\ Mn^{III}\ (\mu\text{-}O)_2\ Mn^{IV}\ OH_2]^{3+} \xrightarrow{pH=4.5} [H_2O\ Mn^{IV}\ (\mu\text{-}O)_2\ Mn^{IV}\ OH]^{3+} + H^+ + e^-$$

Pourbaix Diagrams: Theory vs. Experiments

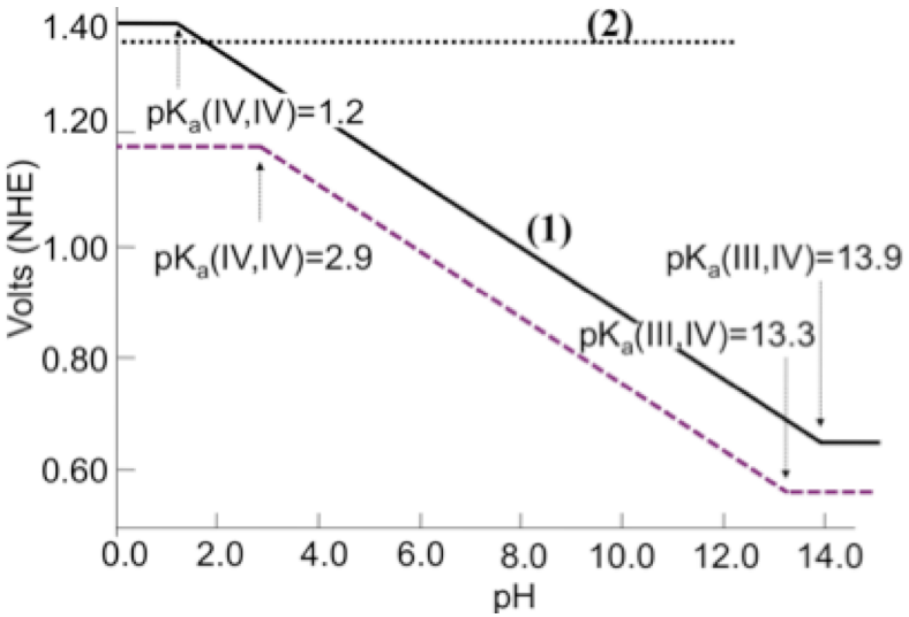
DFT UB3LYP/cc-pVTZ(-f) Free Energy Calculations

Regulation of PCET by Lewis Base (Carboxylate) Binding

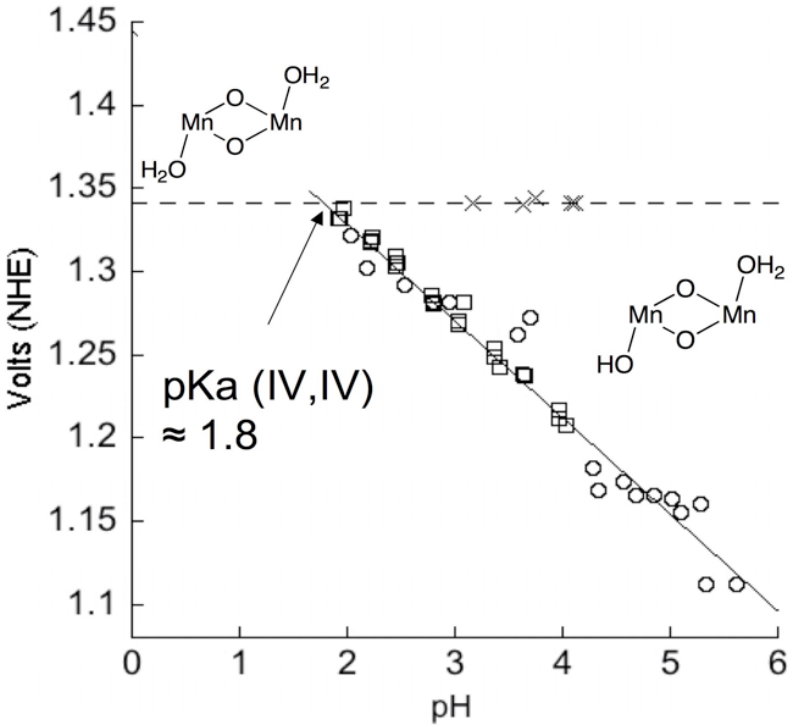
Dr. Ting Wang

[Wang, T. *et al.* JCTC (2010) 6:755-760]

Theory (Batista)



Experiments (Brudvig)



$[H_2O(terpy)Mn^{III}(\mu\text{-}O)_2Mn^{IV}(terpy)CH_3COO]^{2+}$ ⟶

$[HO\ (terpy)\ Mn^{IV}\ (\mu\text{-}O)_2\ Mn^{IV}\ (terpy)\ CH_3COO]^{+}+H^{+}+e^{-}$

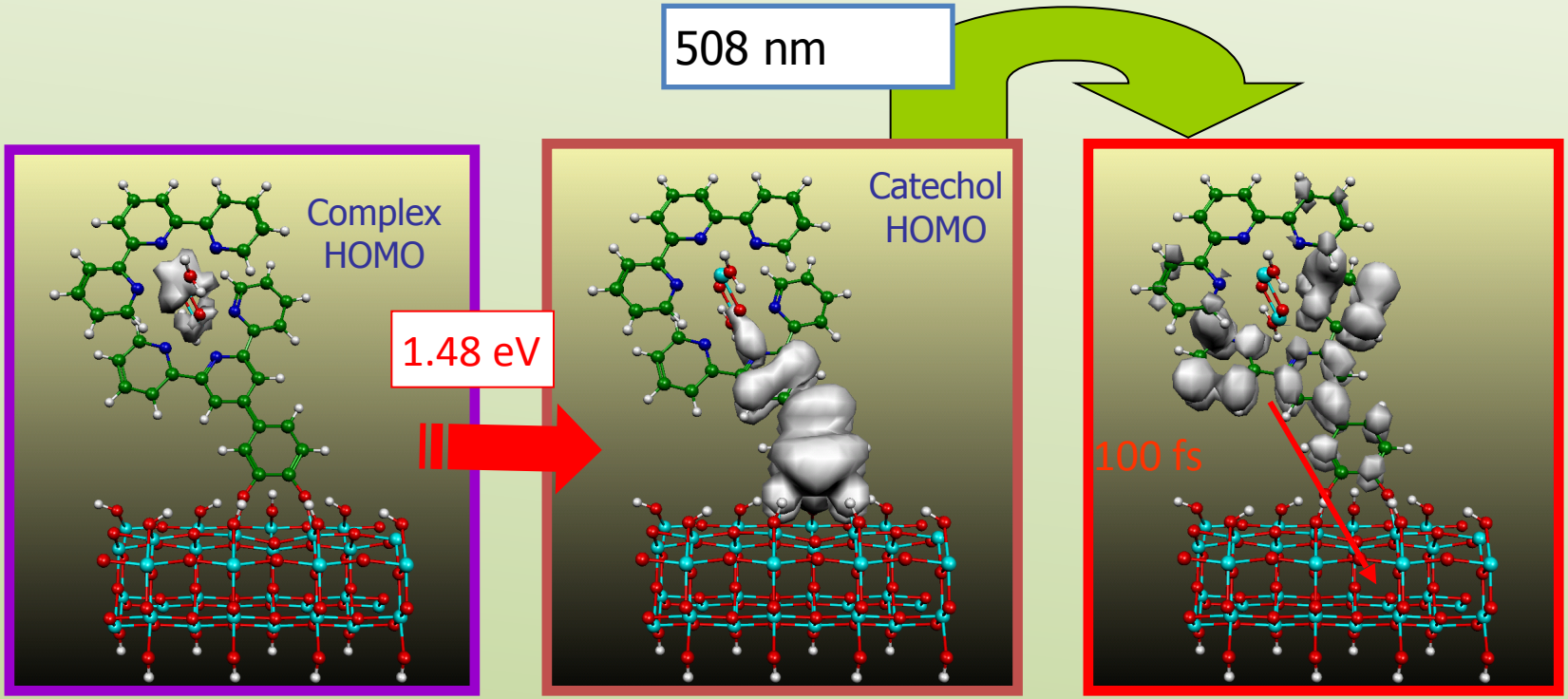
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Visible-Light Photocatalysis

Photoactivation of a Mn-Adsorbate Complex

Sabas G. Abuabara, Clyde W. Cady, Jason B. Baxter, Charles A. Schmuttenmaer, Robert H. Crabtree, Gary W. Brudvig, and Victor S. Batista. J. Phys. Chem. C, 111:11982–11990 (2007).



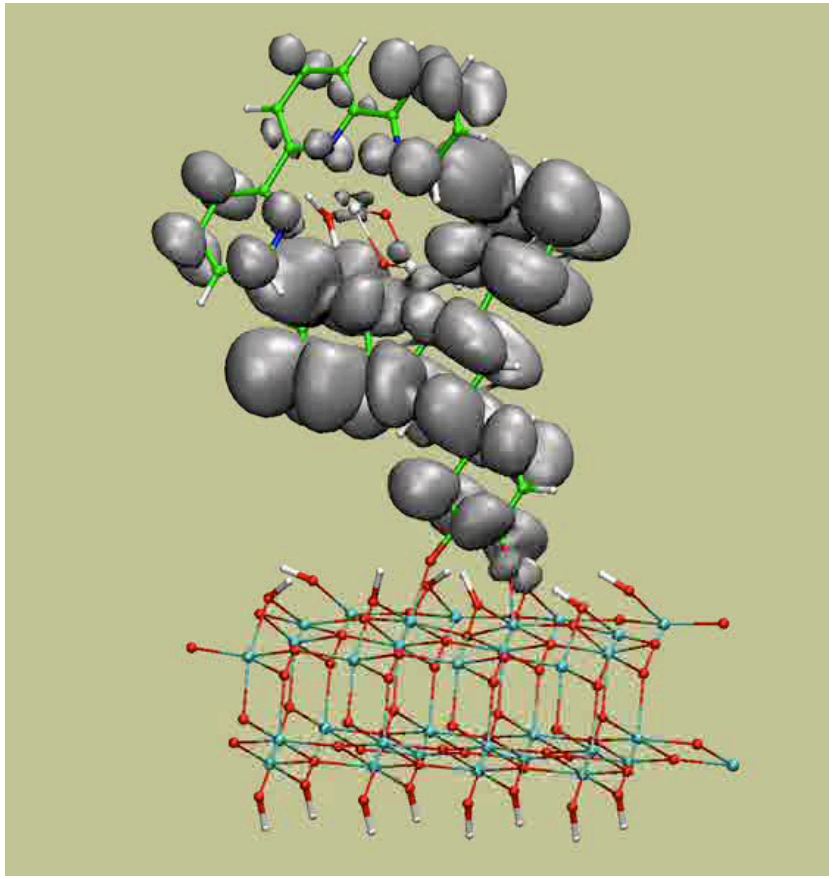
TiO_2 / $[Mn^{IV}(\mu\text{-}O)_2Mn^{III}(H_2O)_2(terpy)_2]^{3+}$

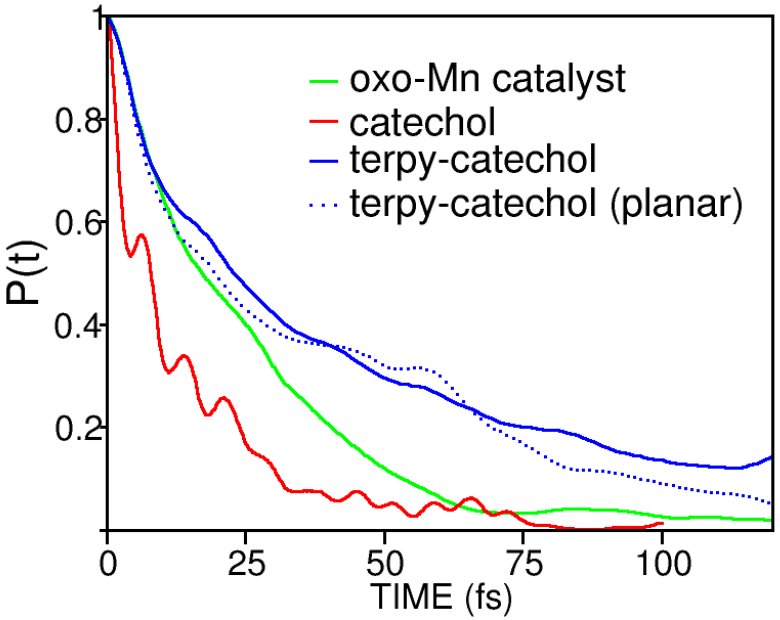
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Biomimetic Oxygen Evolution

Simulations of IET from a Mn Adsorbate



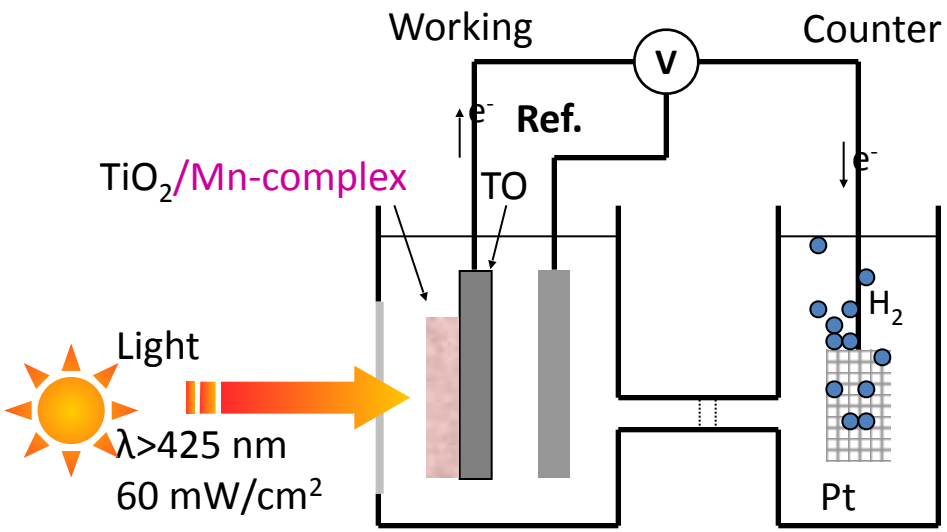


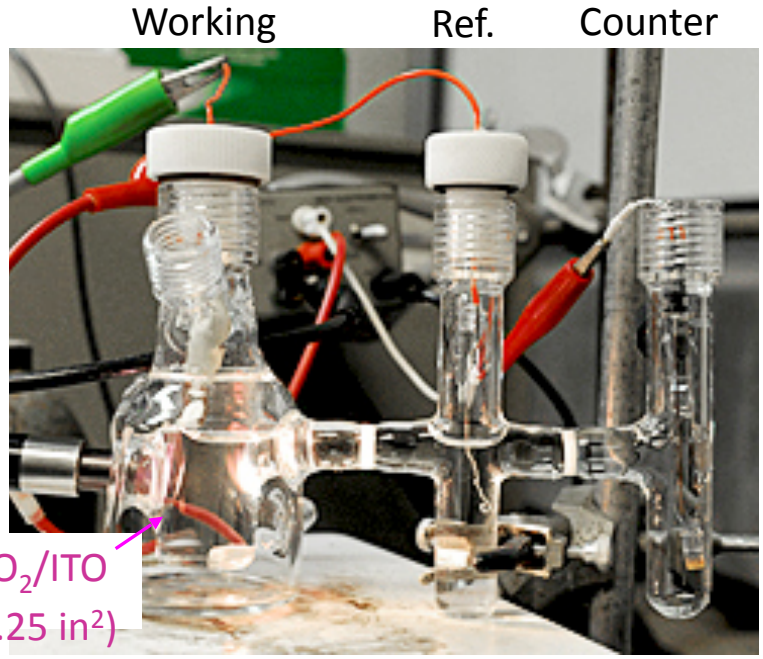
First 100 fs after photoexcitation of the Mn(III,IV) adsorbate

Sabas G. Abuabara

Photocatalysis with Visible Light

J. Catalysis **310**: 37-44 (2014) Photoelectrochemical Oxidation of a Turn-On Fluorescent Probe Mediated by a Surface Mn(II) Catalyst Covalently Attached to Ti_2 Nanoparticles, Alec C. Durrell, Gonghu Li, Matthieu Koepf, Karin J. Young, C.F. A. Negre, L. J. Allen, W. R. McNamara, H. Song, Victor S. Batista, Robert H. Crabtree and Gary W. Brudvig.





$(CH_3)_2CHOH \longrightarrow (CH_3)_2C=O + 2H^+ + 2e^-$ $\qquad 2H^+ + 2e^- \longrightarrow H_2$

Photocatalysis with Visible Light

Dr. Gonghu Li
Dr. Christiaan Richter

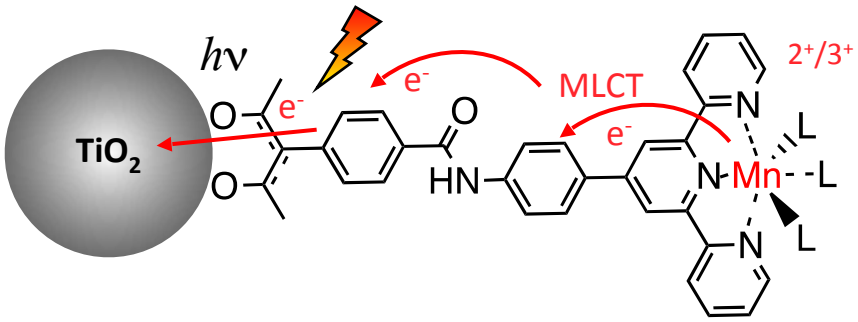
Photooxidation of isopropanol

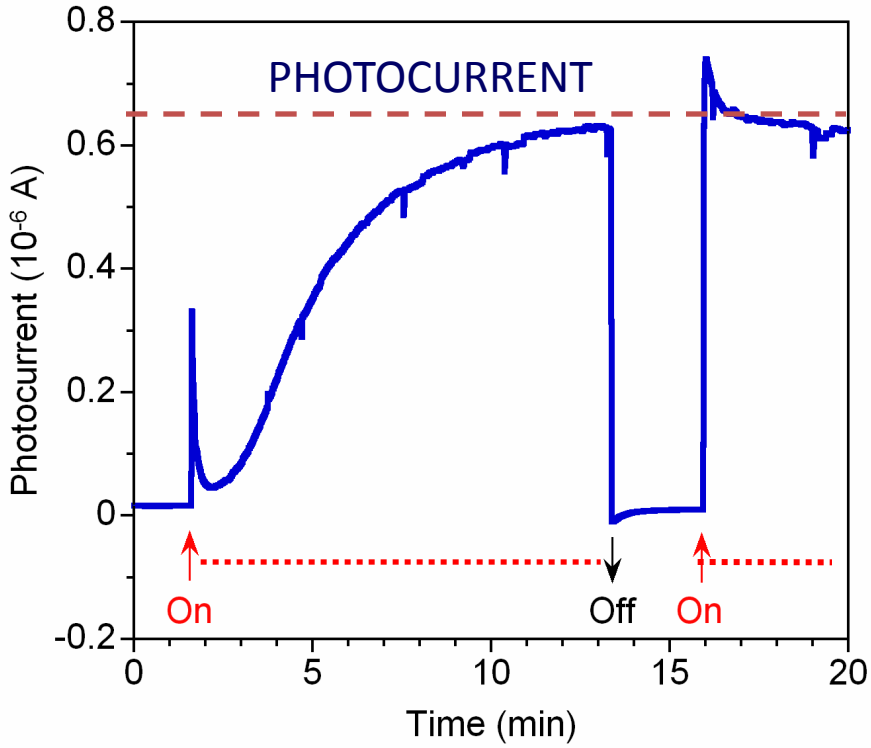
J. Catalysis **310**: 37-44 (2014)

Net redox reaction:

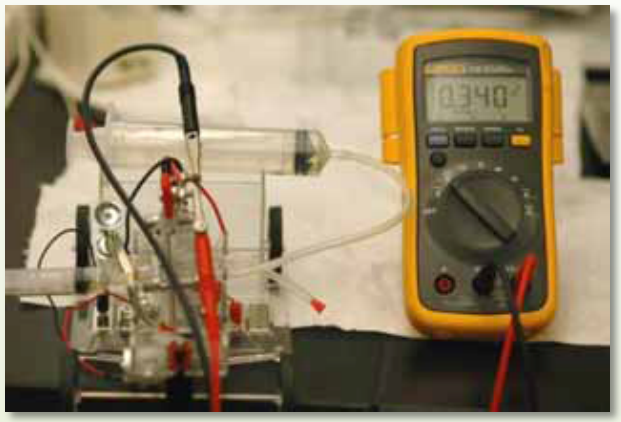
$$(CH_3)_2CHOH \xrightarrow[TiO_2/\text{Mn-cat.}]{h\nu} (CH_3)_2C{=}O + H_2$$

Photoactivation of the catalyst:





Department of Chemistry Yale University



CHEM 505: *Green Chemistry and Alternative Energy*

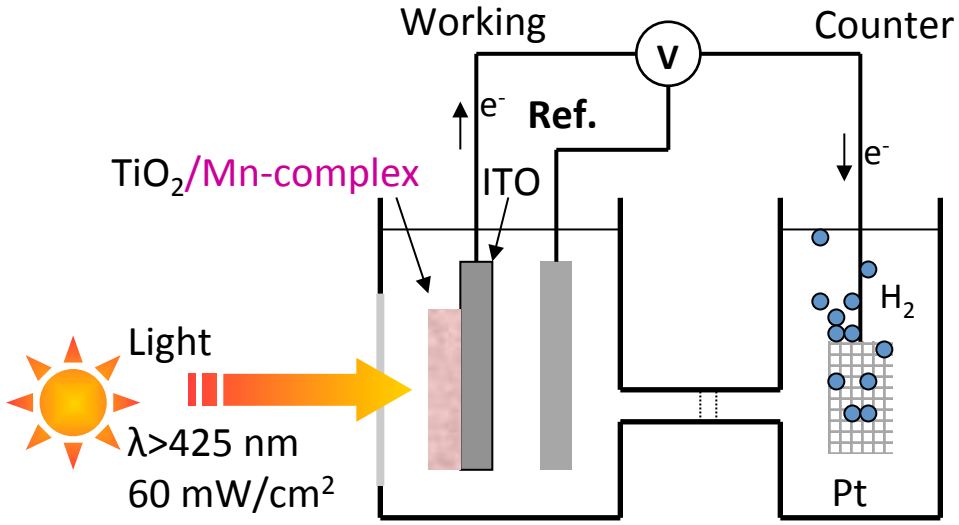
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

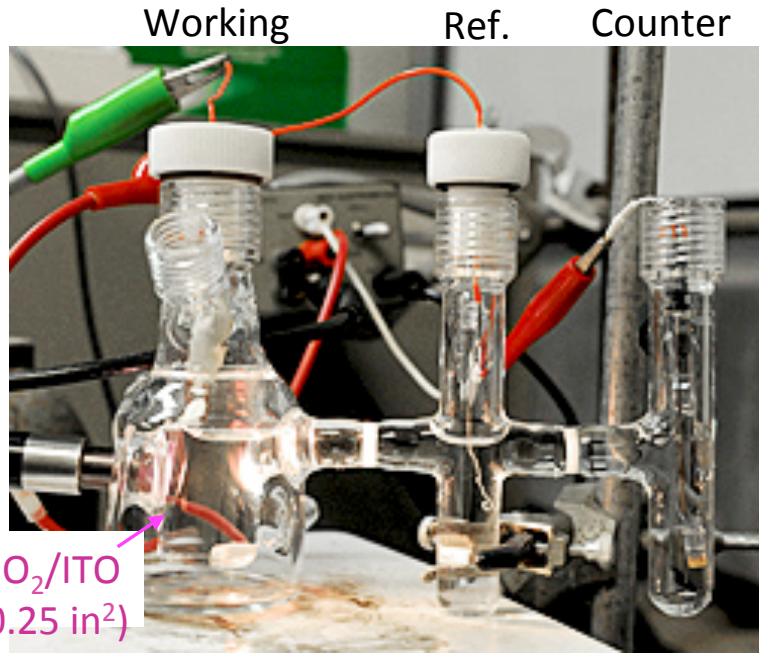
Modeling Systems for a Hydrogen Economy

Photocatalysis with Visible Light

Dr. Gonghu Li
Dr. Christiaan Richter

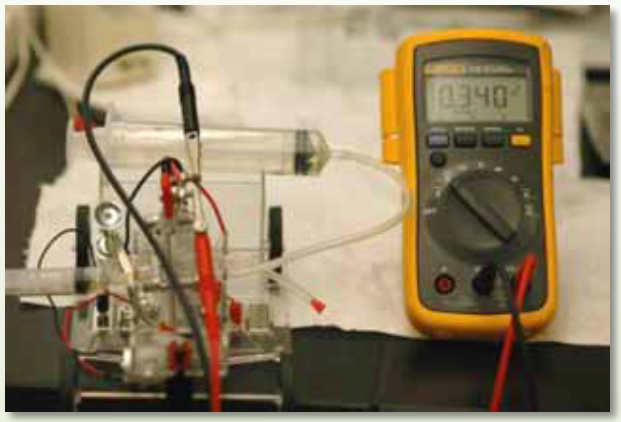
Photooxidation of isopropanol





$(CH_3)_2CHOH \longrightarrow (CH_3)_2C{=}O + 2H^+ + 2e^-$

$2H^+ + 2e^- \longrightarrow H_2$



CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Photocatalysis with Visible Light

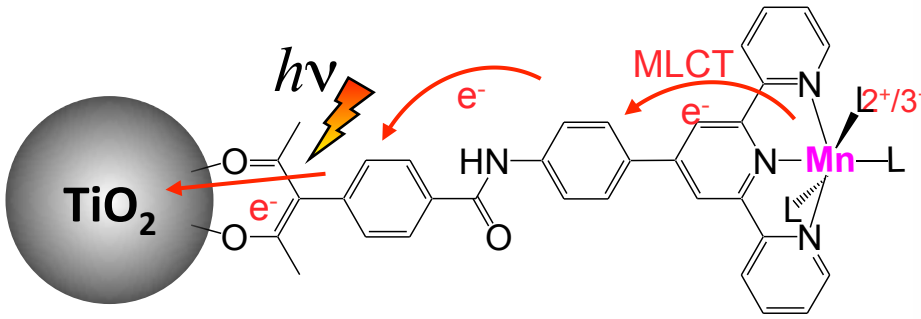
Dr. Gonghu Li
Dr. Christiaan Richter

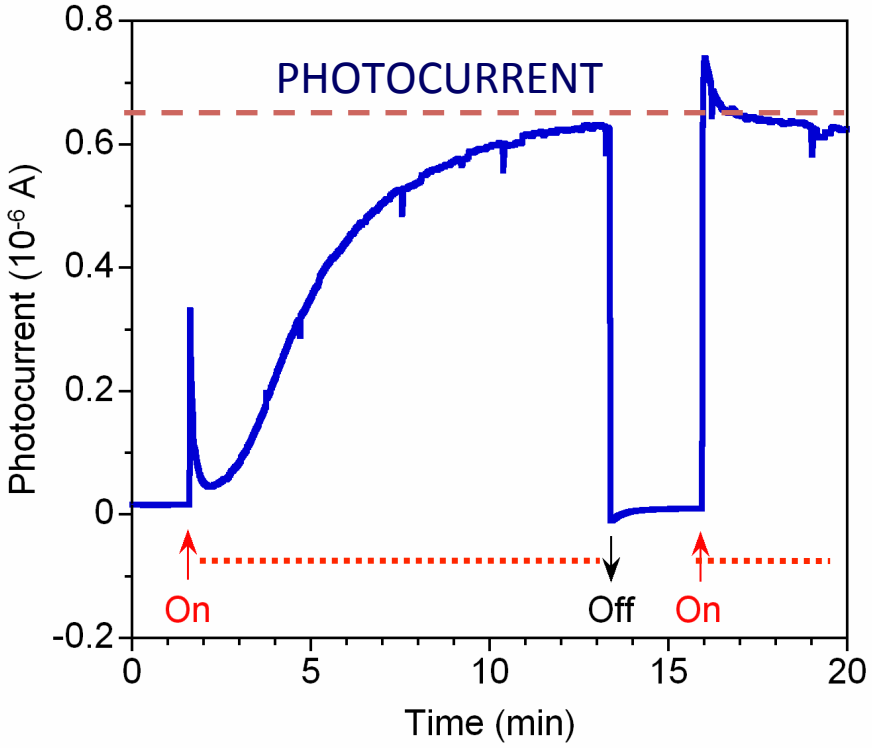
Photooxidation of isopropanol

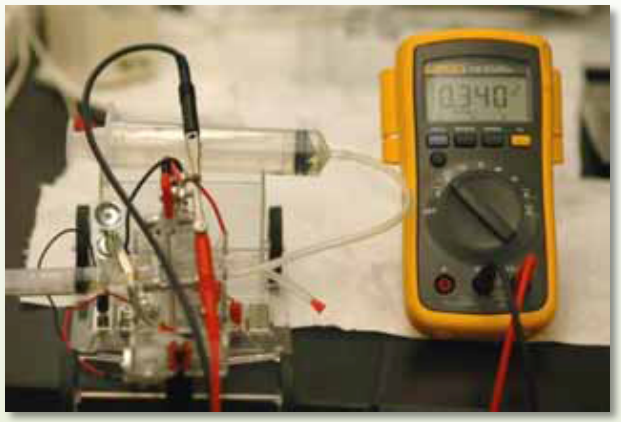
Net redox reaction:

$$(CH_3)_2CHOH \xrightarrow[TiO_2/Mn\text{-}cat.]{h\nu} (CH_3)_2C{=}O + H_2$$

Photoactivation of the catalyst:

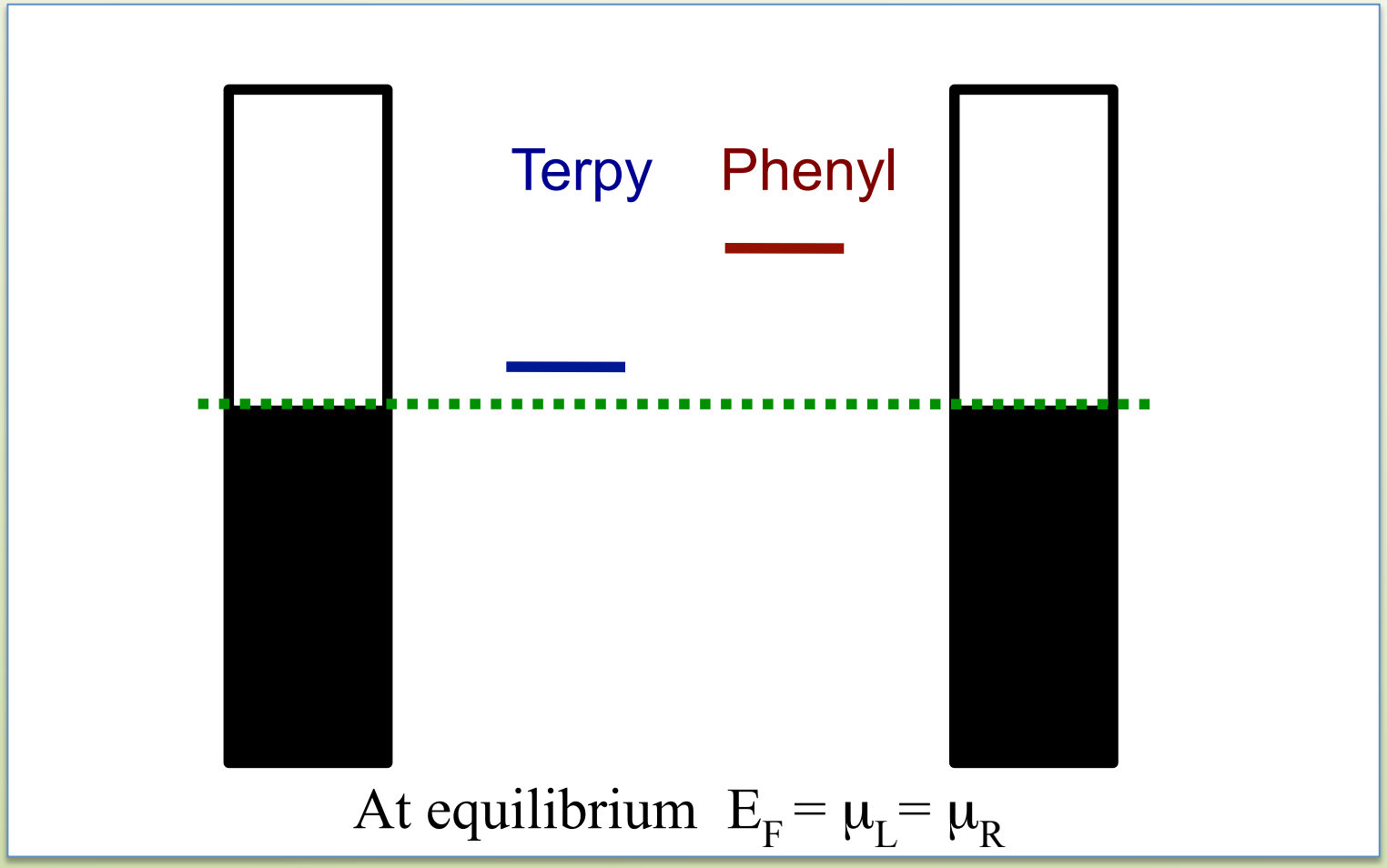


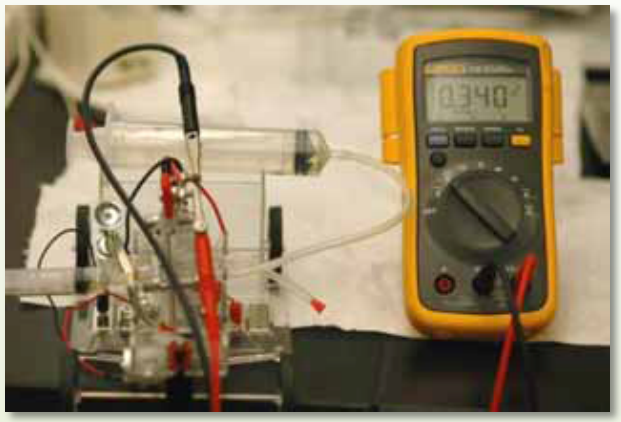




Molecular Rectification: DFT NEGF: I-V Characteristics

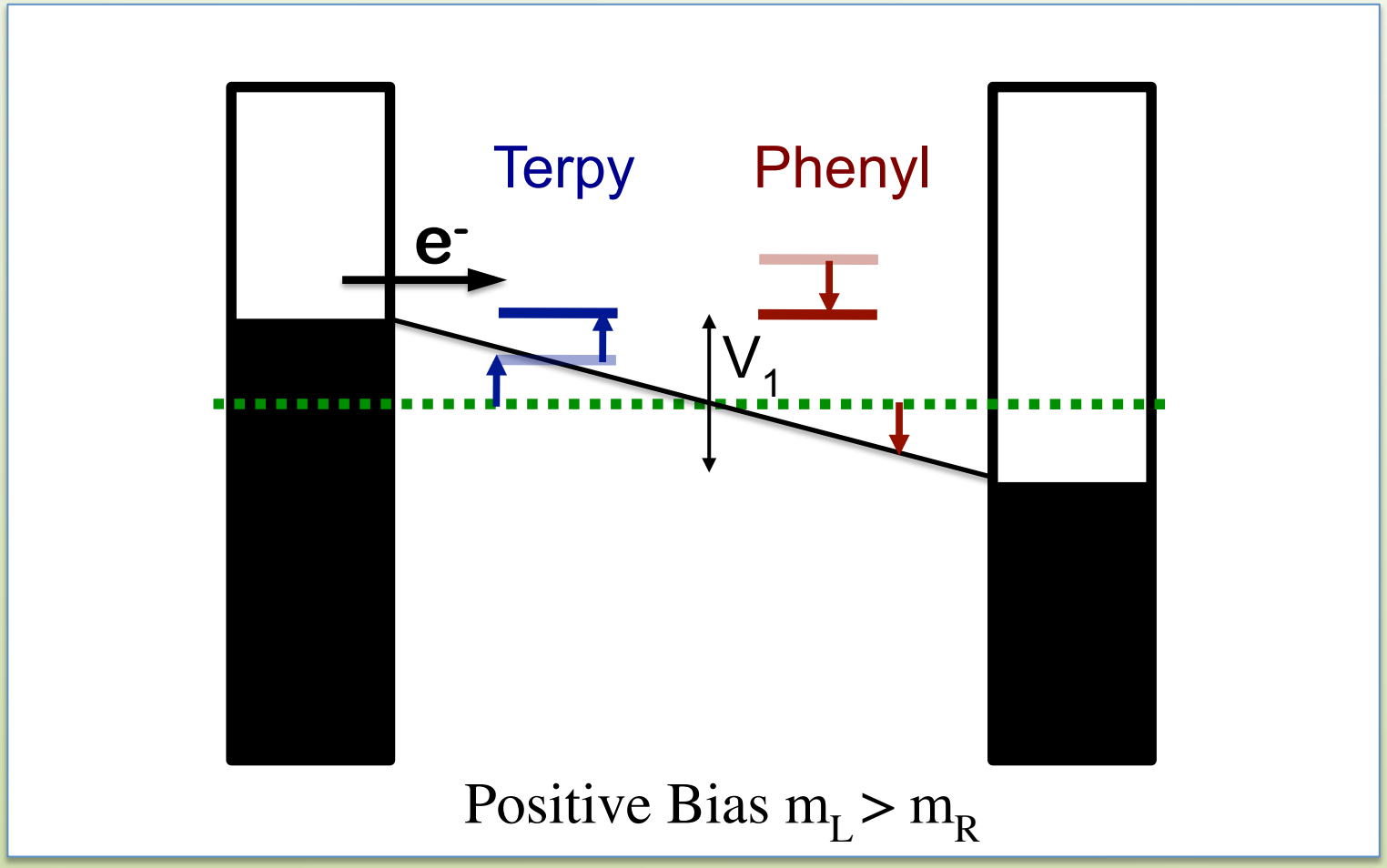
Aviram, M. A. Ratner Chem. *Phys. Lett.* **29**: 277-283 (1974)

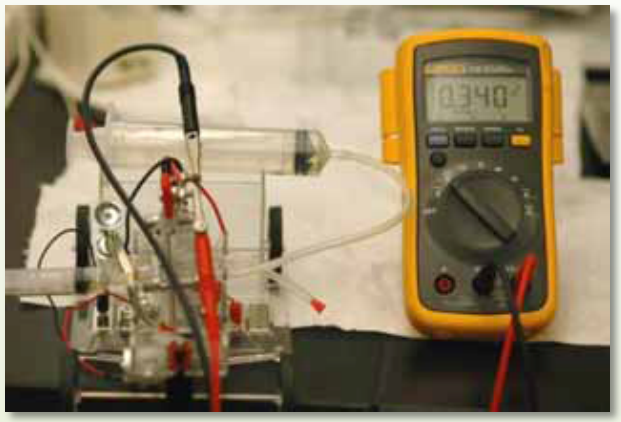




Molecular Rectification: DFT NEGF: I-V Characteristics

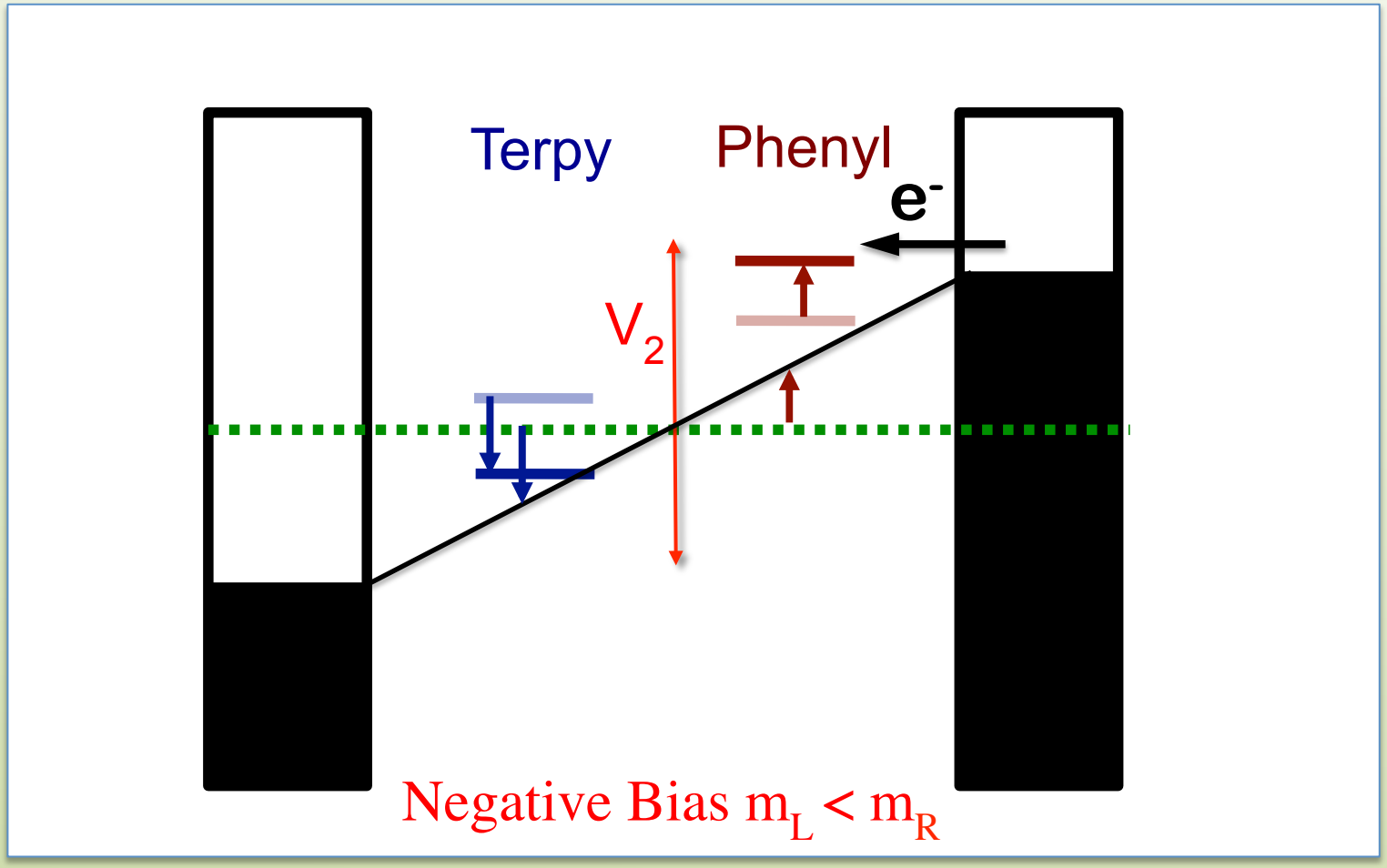
Aviram, M. A. Ratner Chem. *Phys. Lett.* **29**: 277-283 (1974)



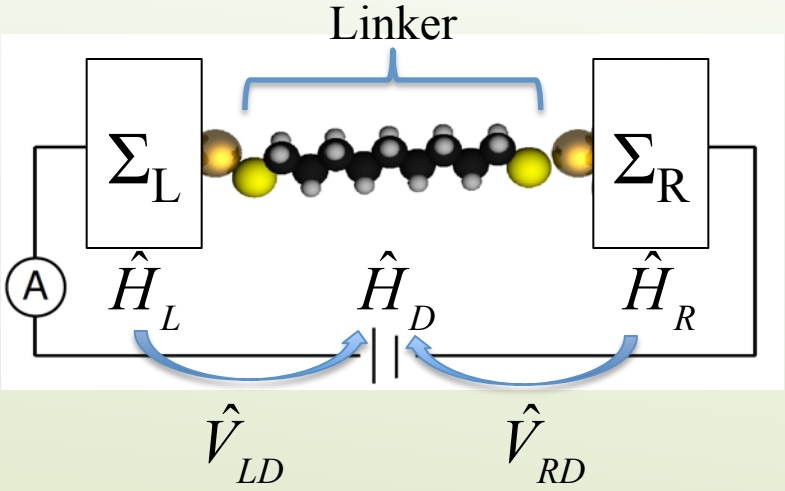


Molecular Rectification: DFT NEGF: I-V Characteristics

Aviram, M. A. Ratner Chem. *Phys. Lett.* **29**: 277-283 (1974)



DFT-NEGF Methodology



$$\hat{H} = \begin{pmatrix} H_L & V_{LD} & 0 \\ V_{LD}^{+} & H_D & V_{RD}^{+} \\ 0 & V_{RD} & H_R \end{pmatrix}$$

$$\Sigma_{L/R} = \left(ES_{LD/RD}^{+} - V_{L/R}^{+}\right) g_{L/R} \left(ES_{LD/RD} - V_{L/R}\right)$$

$$\hat{H} \Rightarrow \hat{G} = \left(E\hat{S} - \hat{H} - \hat{\Sigma}\right)^{-1} \Rightarrow T(E) = Tr\left(\hat{\Gamma}_L \hat{G}_D \hat{\Gamma}_R \hat{G}_D^{+}\right) \Rightarrow \text{Current: } I$$

$$\hat{\Sigma} = \hat{\Sigma}_L + \hat{\Sigma}_R$$

$$G_D = \left(ES_D - H_D - \Sigma_L - \Sigma_R\right)^{-1}$$

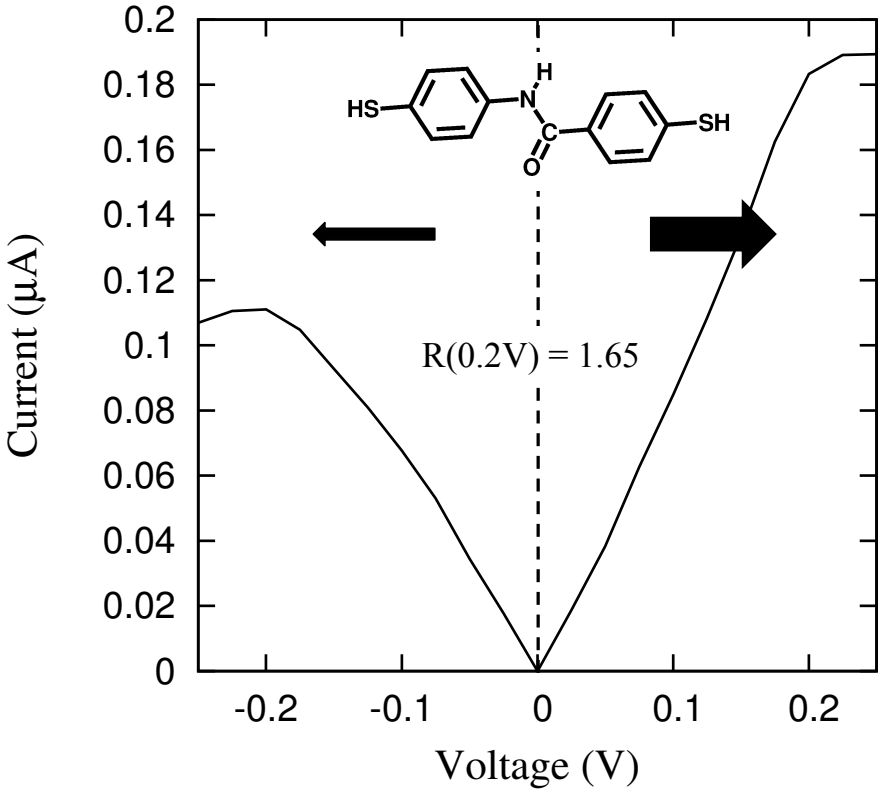
$$\Gamma_{L/R} = i\left(\Sigma_{L/R} - \Sigma_{L/R}^{+}\right)$$

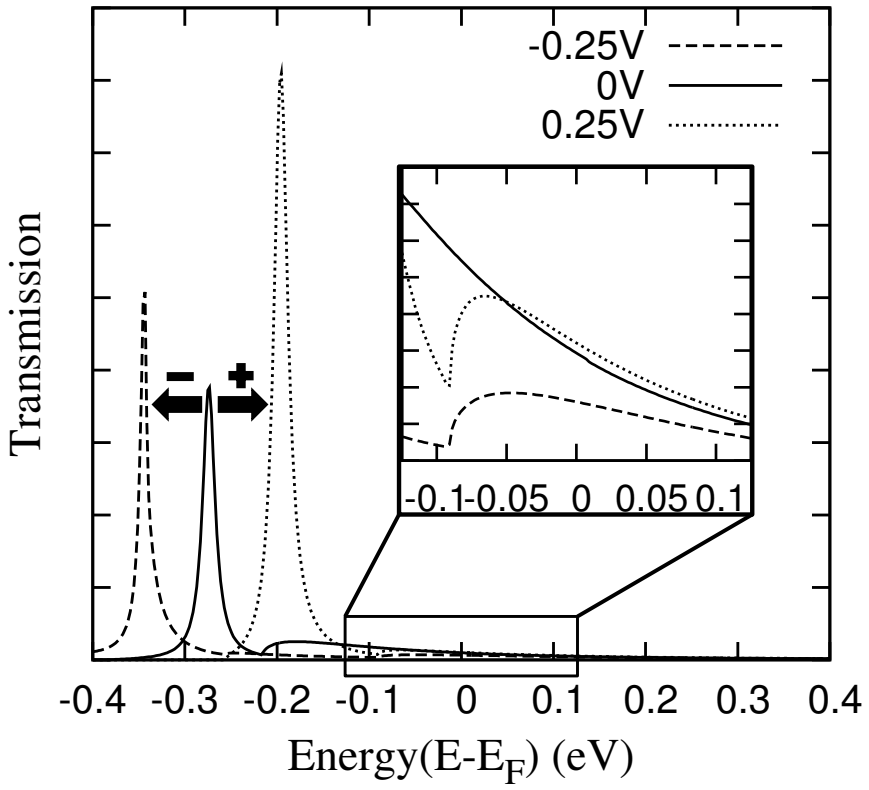
$$I = \frac{2e}{h}\int_{-\infty}^{\infty} dE\ T(E)\left[f_L(E) - f_R(E)\right]$$

$$\approx \frac{2e}{h}\int_{\mu_L}^{\mu_R} dE\ T(E)$$

MOLECULAR RECTIFICATION

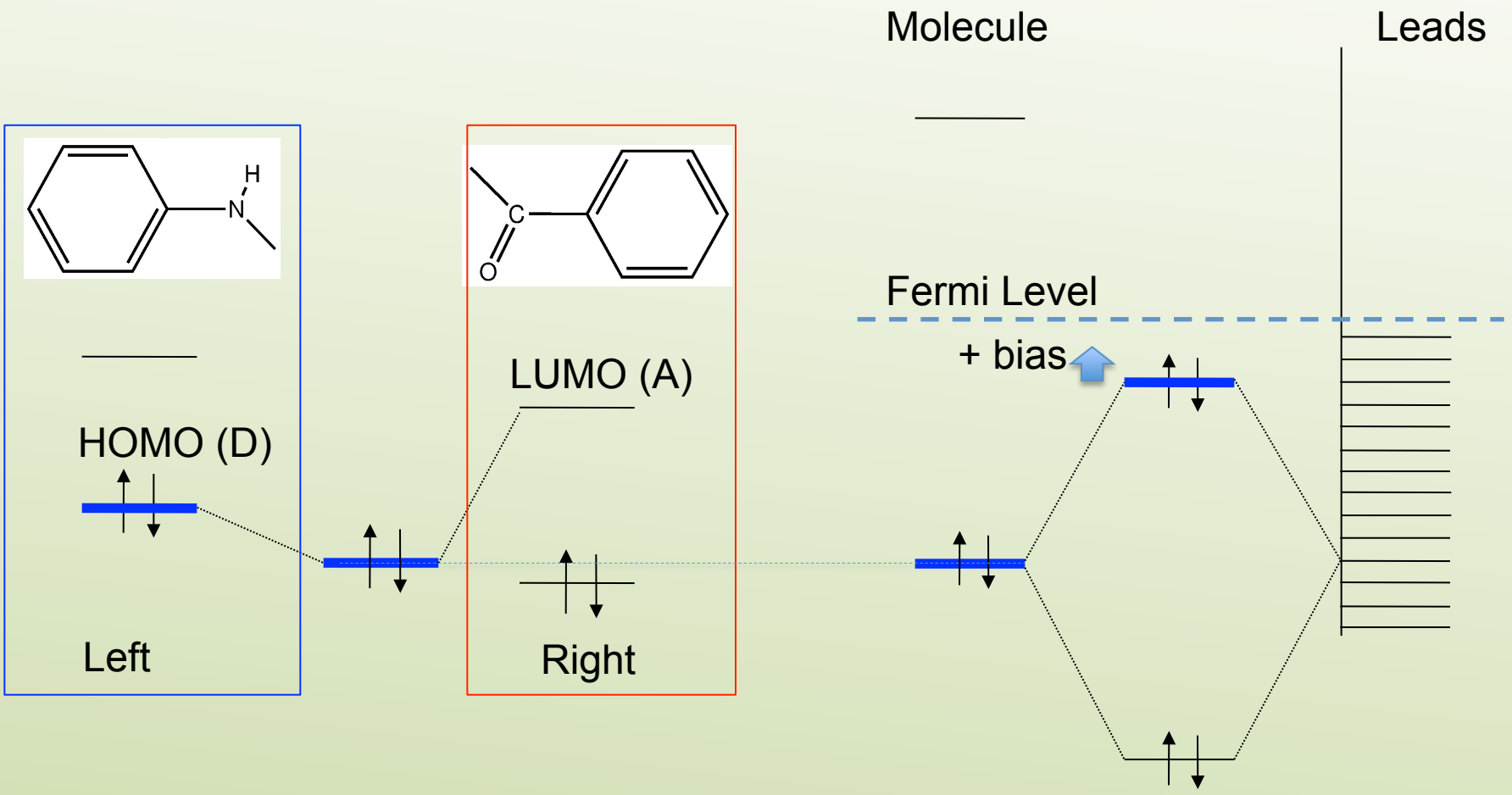
DFT NEGF: I-V Characteristics





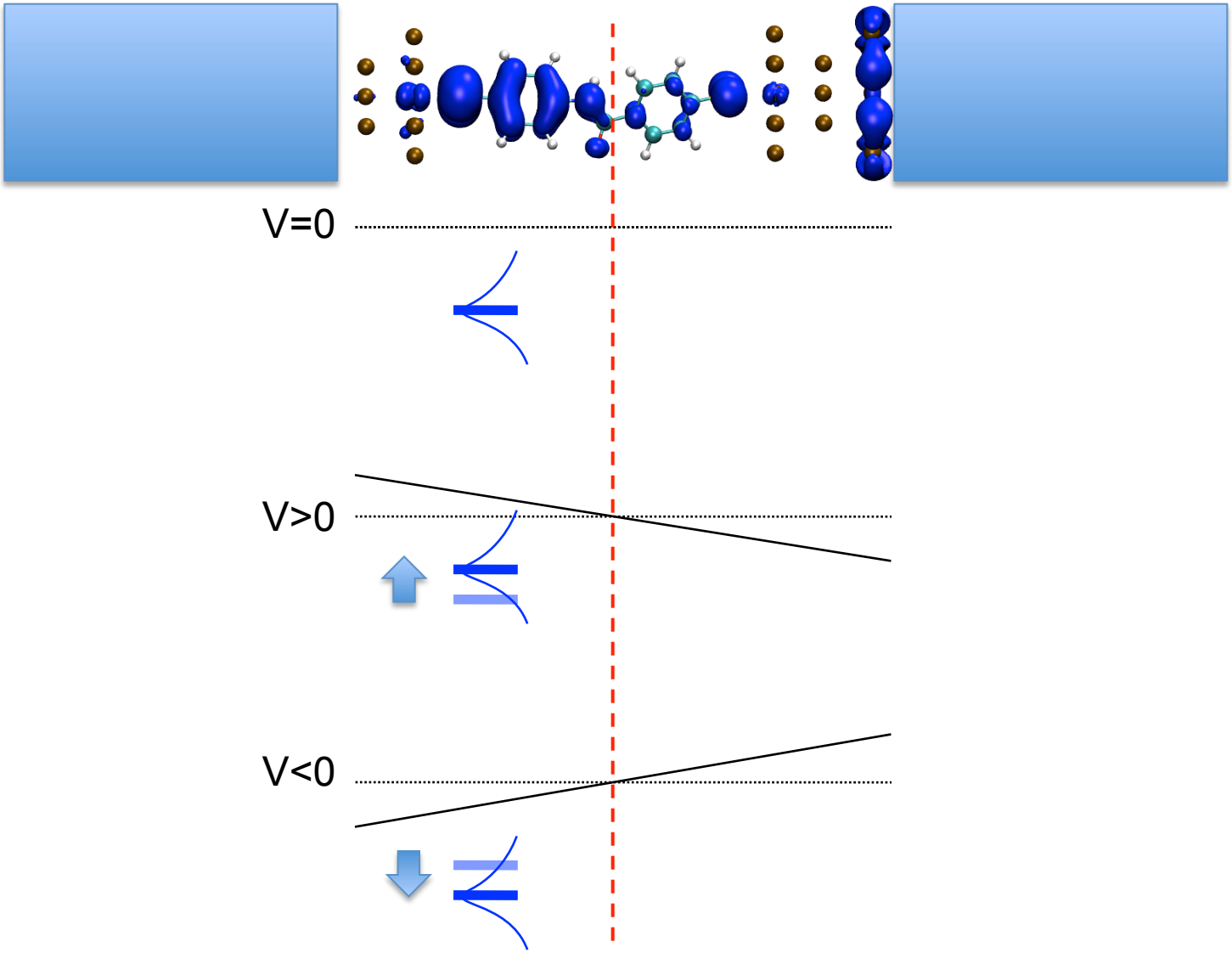
Wendu Ding, Leslie Vogt, Christian F. A. Negre, and Victor S. Batista
[J. Chem. Theory Comput 10: 3393−3400 (2014)]

Molecule-Lead coupling



Wendu Ding, Leslie Vogt, Christian F. A. Negre, and Victor S. Batista
[J. Chem. Theory Comput 10: 3393−3400 (2014)]

Single Frontier Orbital Mechanism

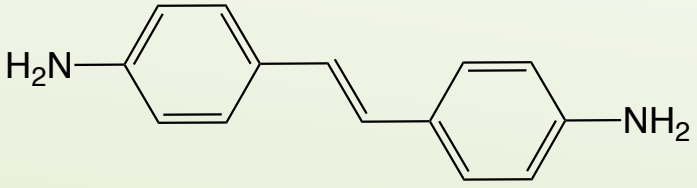


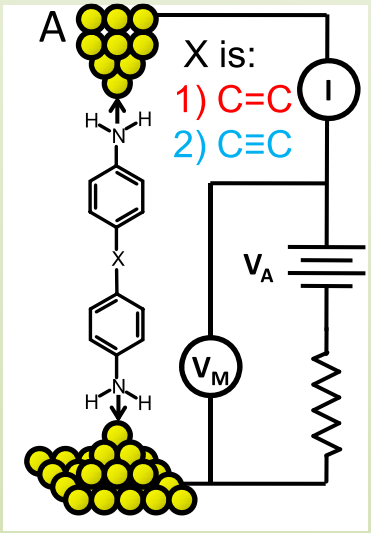
Wendu Ding, Leslie Vogt, Christian F. A. Negre, and Victor S. Batista
[J. Chem. Theory Comput 10: 3393−3400 (2014)]

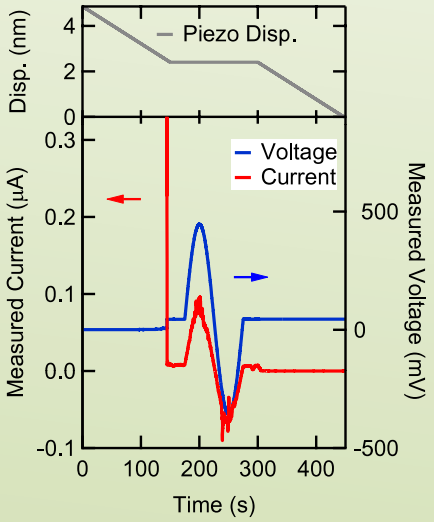
Experimental I-V histograms

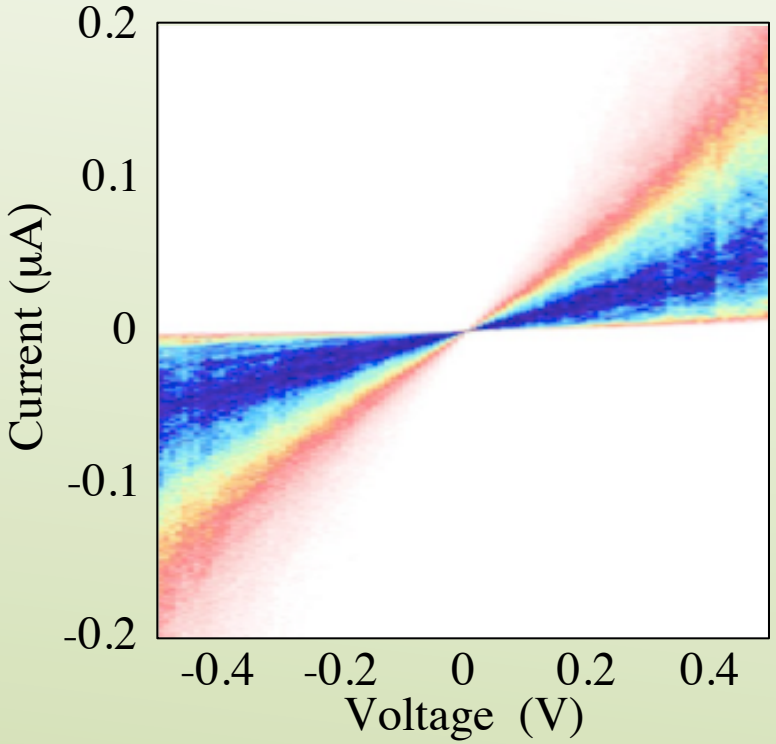
Prof. Latha Venkataraman
Columbia University

4,4'-Diaminostilbene



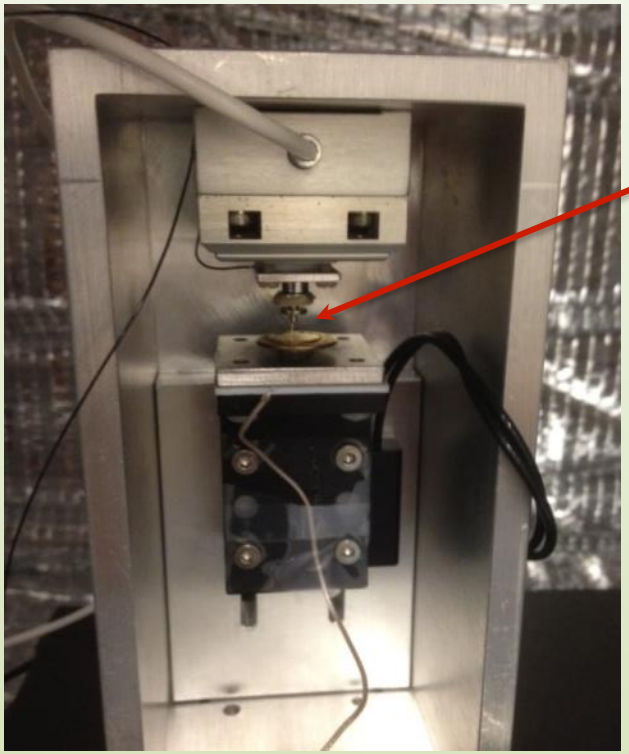


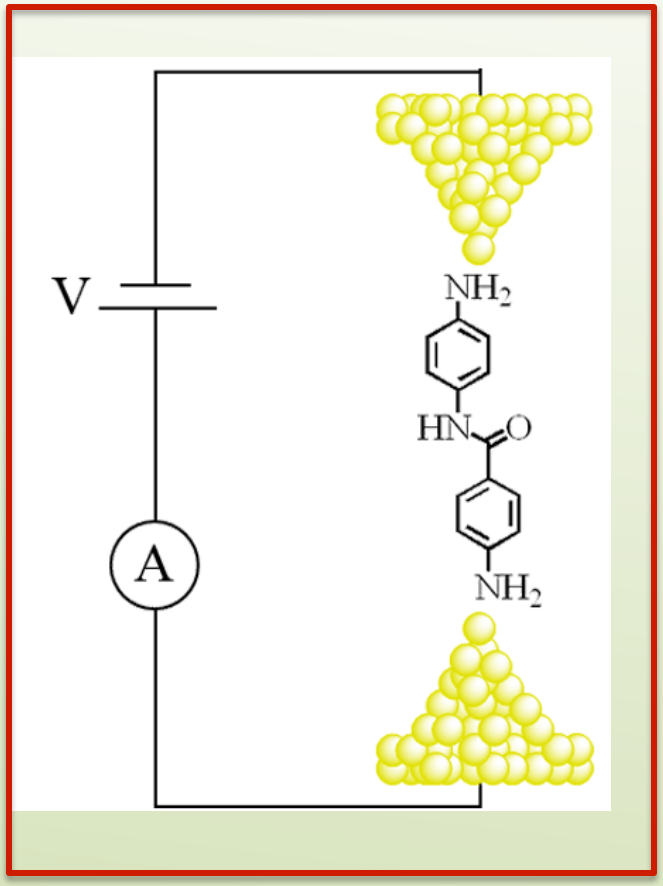




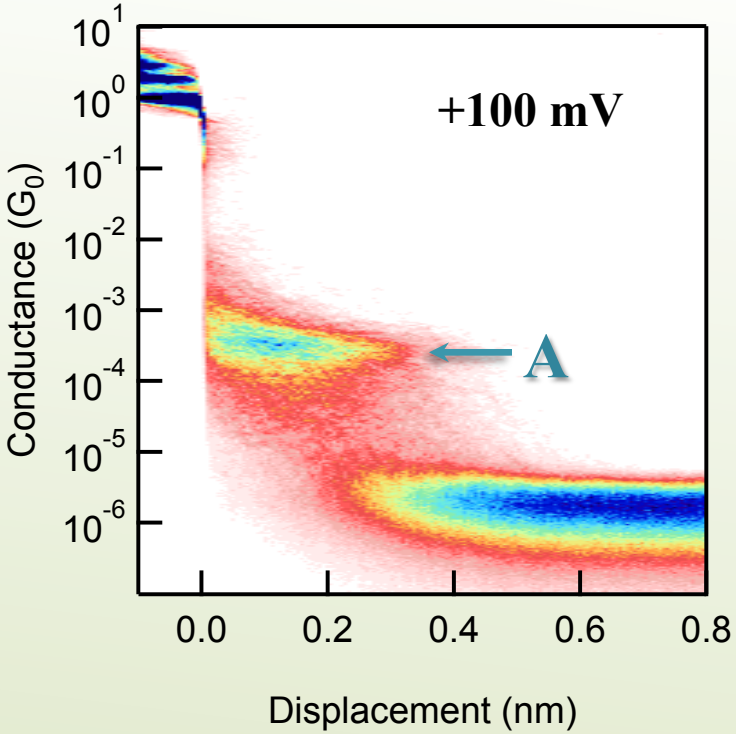
Nanotechnology. **2009**, *20*, 434009

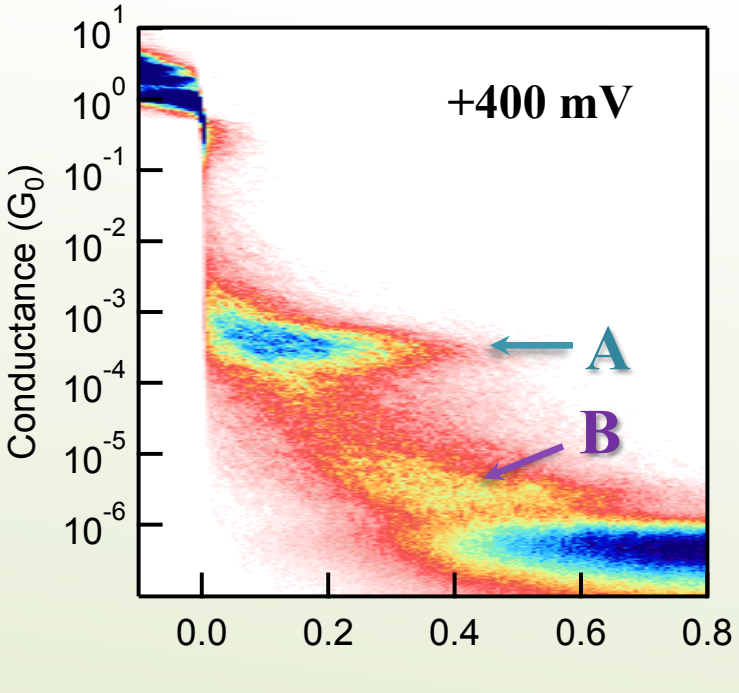
Molecular Rectification:
The Break Junction Technique & Recent Results



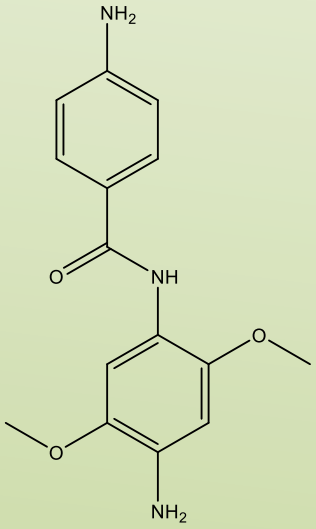


11-1-2013
Chris Koenigsmann

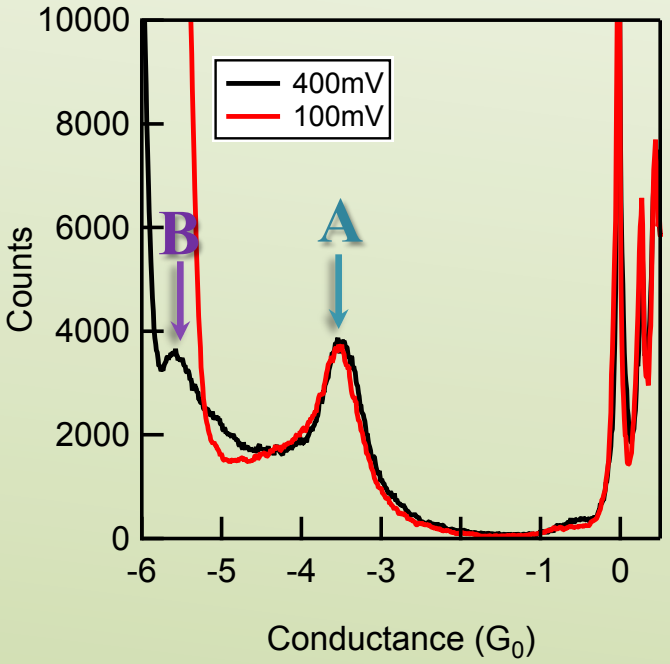




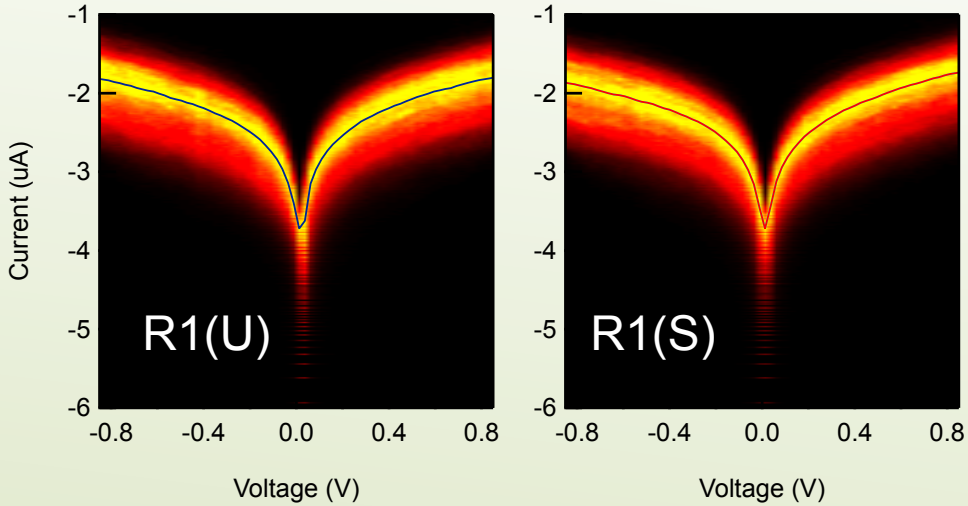
Molecule R5

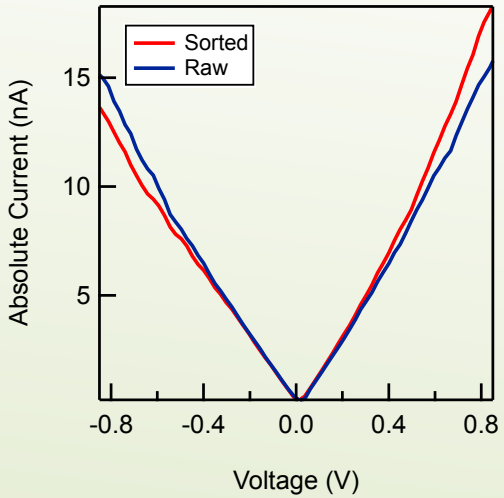


1. Well defined single molecule conductance plateaus (A).
2. Conductance ~2.9 x 10^{-4} G_0
3. Small but measureable increase in conductance as bias increases.
4. A second low-conductance plateau (B) also observed (+400 mV).

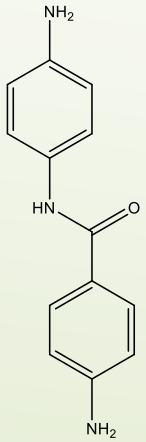


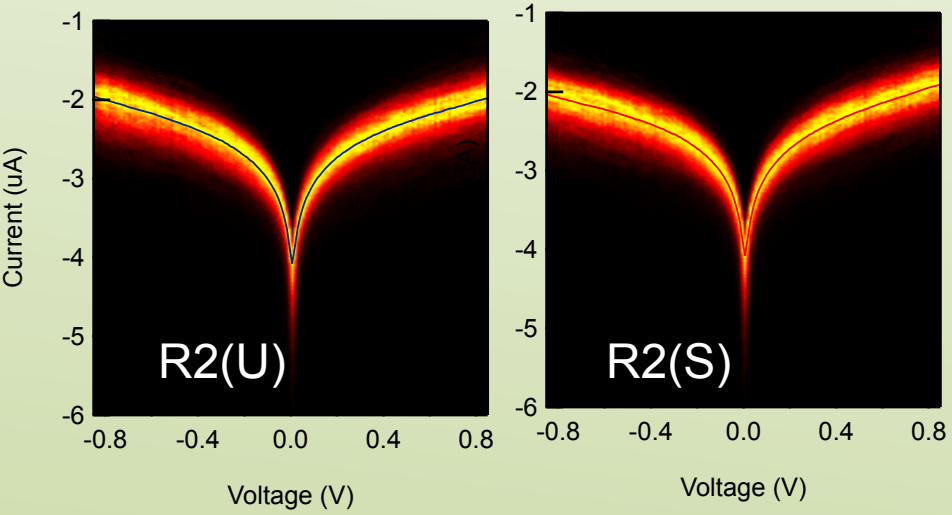
Experimental and Theoretical IV curves

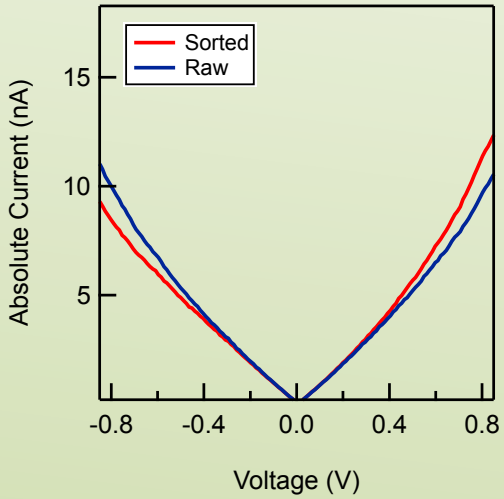




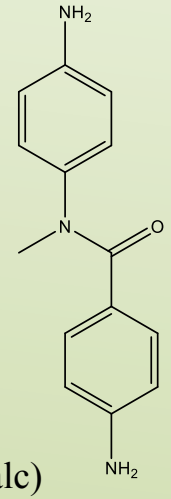
RR@0.85V =1.3







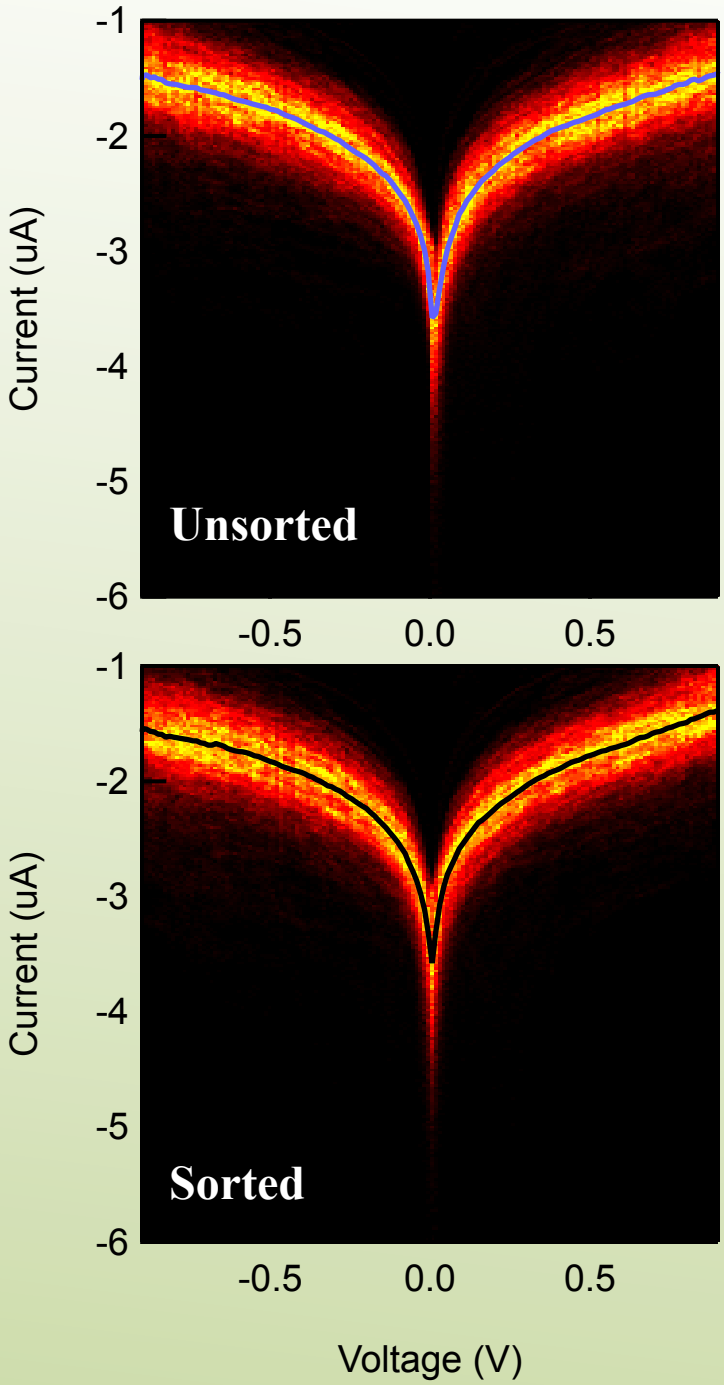
RR@0.85V =1.33

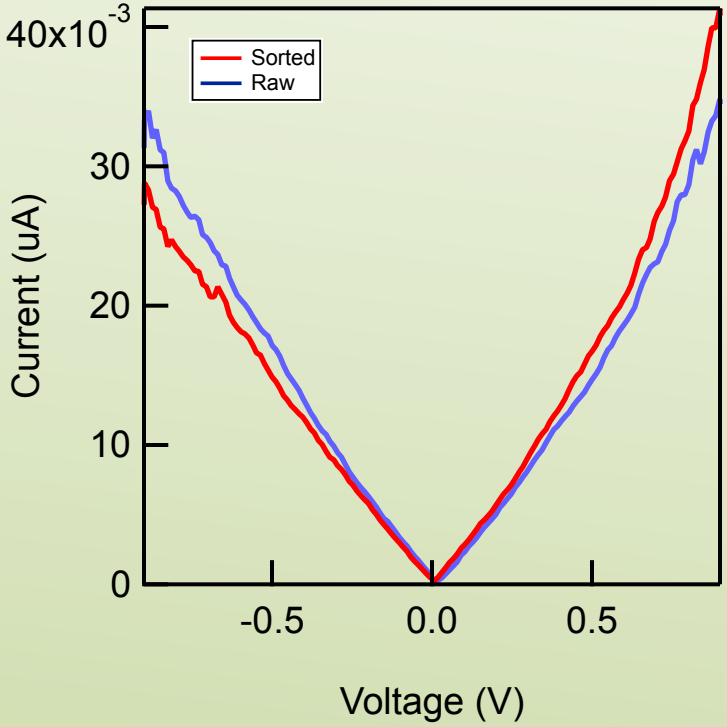


Latha Venkataraman, Chris Koeningsmann (I-V exp), Matthieu Koepf (synthesis), Christian Negre (I-V calc)

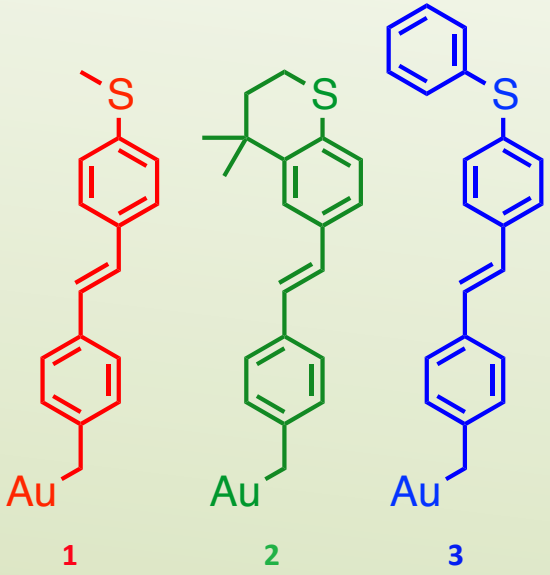
R5, Rectification at 0.85 V = 1.45

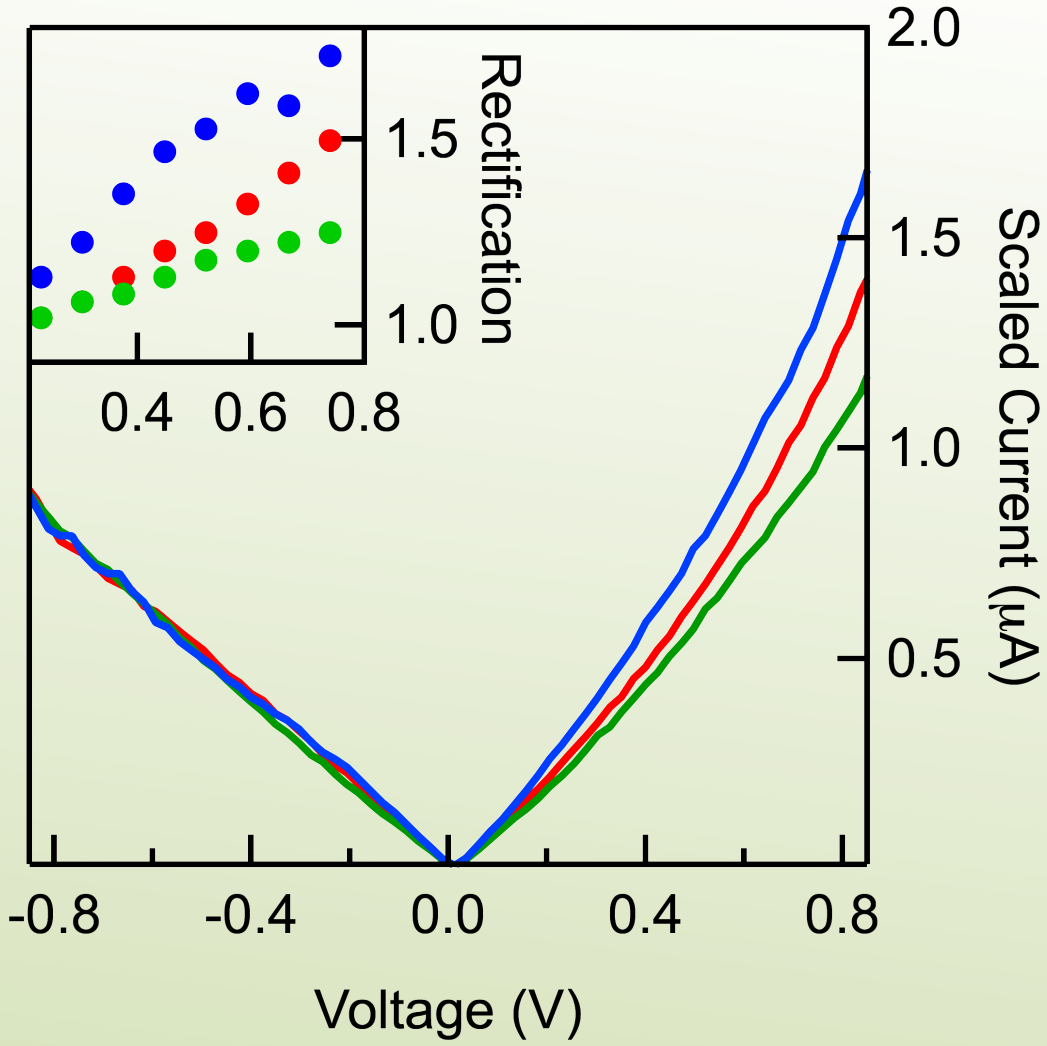
Molecule	Conductance (G_0)	RR
R1	1.7×10^{-4}	1.30
R5	2.9×10^{-4}	1.45



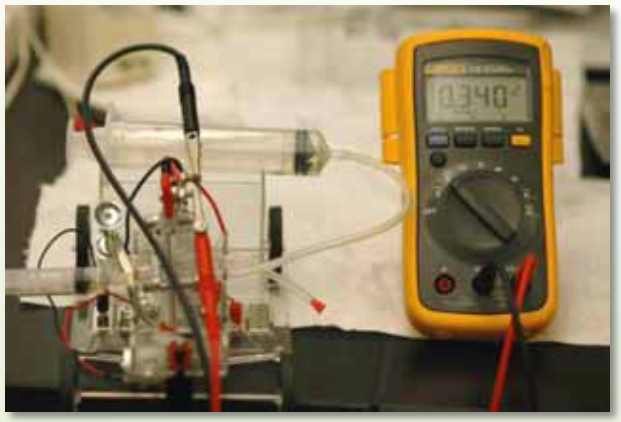


Examples of Rectifying & Poor-Rectifying Molecules





Scaled, statistically most probable IV curves for the three molecules. The curves are calculated from log-binned 2D histograms with bin sizes and histogram ranges kept constant. All curves have been scaled to zero-bias conductance of molecule **3**, with the red curve multiplied by 2 and the blue curve by 4. Inset: Rectification ratio as a function of bias. Molecule **3** rectifies over three times as much as molecule **2**, with rectification at 0.85V approaching 2.



CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Molecular Inverse Design: LCAP Methodology

Dr. Dequan Xiao

Schrödinger equation in EH matrix form is

$$\mathbf{HC} = \mathbf{ESC}$$

Hamiltonian matrix; Eigenvector matrix; Eigenvalue matrix (diagonal matrix); Overlap matrix (AO basis set)

LCAP-EHTB:

Diagonal terms

$$H_{ii}^{(\mathrm{var})} = \sum_{A=1}^{N_{type}^{i}} b_A^i h_{ii}^{(A)}$$

Off-diagonal terms

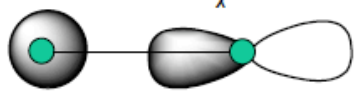
$$H_{ij} = \sum_{A=1}^{N_{type}^{i}} \sum_{A'=1}^{N_{type}^{j}} b_A^i b_{A'}^j h_{ij}^{(A,A')}$$

constraints

$$0 \le b_A^i \le 1$$

$$\sum_{A=1}^{N_{type}^{i}} b_A^i = 1$$

Example:



1 2

O C, O

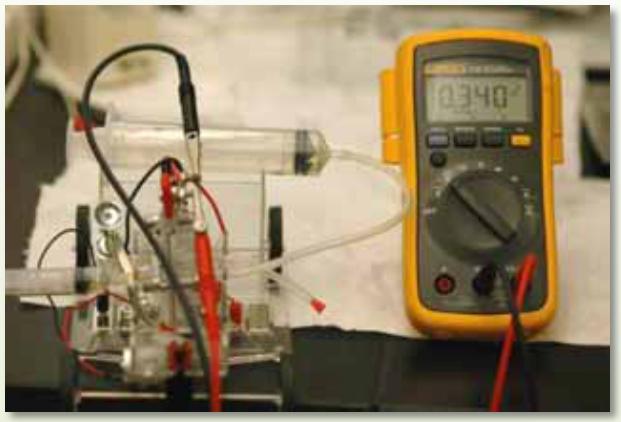
b_C^2 b_O^2

Diagonal term

$$H_{22}^{P_x} = b_C^2 \cdot h_{22}^{(C_{P_x})} + b_O^2 \cdot h_{22}^{(O_{P_x})}$$

Off-diagonal term

$$H_{12}^{SP_x} = b_O^1 \cdot b_C^2 \cdot h_{12}^{(O_S, C_{P_x})} + b_O^1 \cdot b_O^2 \cdot h_{22}^{(O_S, O_{P_x})}$$



CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Inverse Design: Molecular Sensitizers

Target molecular property: the total visible absorbance

Dr. Dequan Xiao

$$f = \sum_{p,q} f_{pq} \quad \text{+ constraint: } 400nm \le \lambda_{qp} \le 800nm$$

f_{pq} is the oscillator strength of the p to q electronic transition, and λ_{pq} is the wavelength of the electronic transition.

$$f_{pq} = \frac{8\pi^2 \nu_{pq} m_e}{3he^2} \left|\mu_{pq}\right|^2$$

$\mu_{pq} = \langle \psi_q | r | \psi_p \rangle$: transition dipole moment,

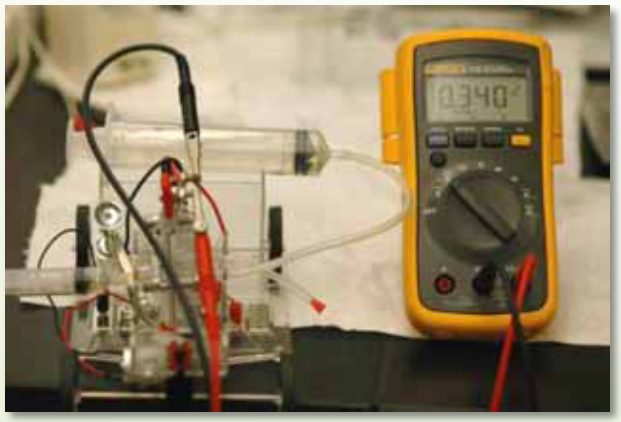
ν_{pq} : wavenumber of the electronic transition,

m_e : electron mass.

Gradients of molecular property:

$$\frac{\partial f}{\partial b_A^i} = \frac{f(+\delta b_A^i) - f(-\delta b_A^i)}{2\delta b_A^i}$$

Finally, the **continuous optimization** of *f* by varying $\{b_A^i\}$ is performed based on a quasi-Newton (BFGS algorithm) method.

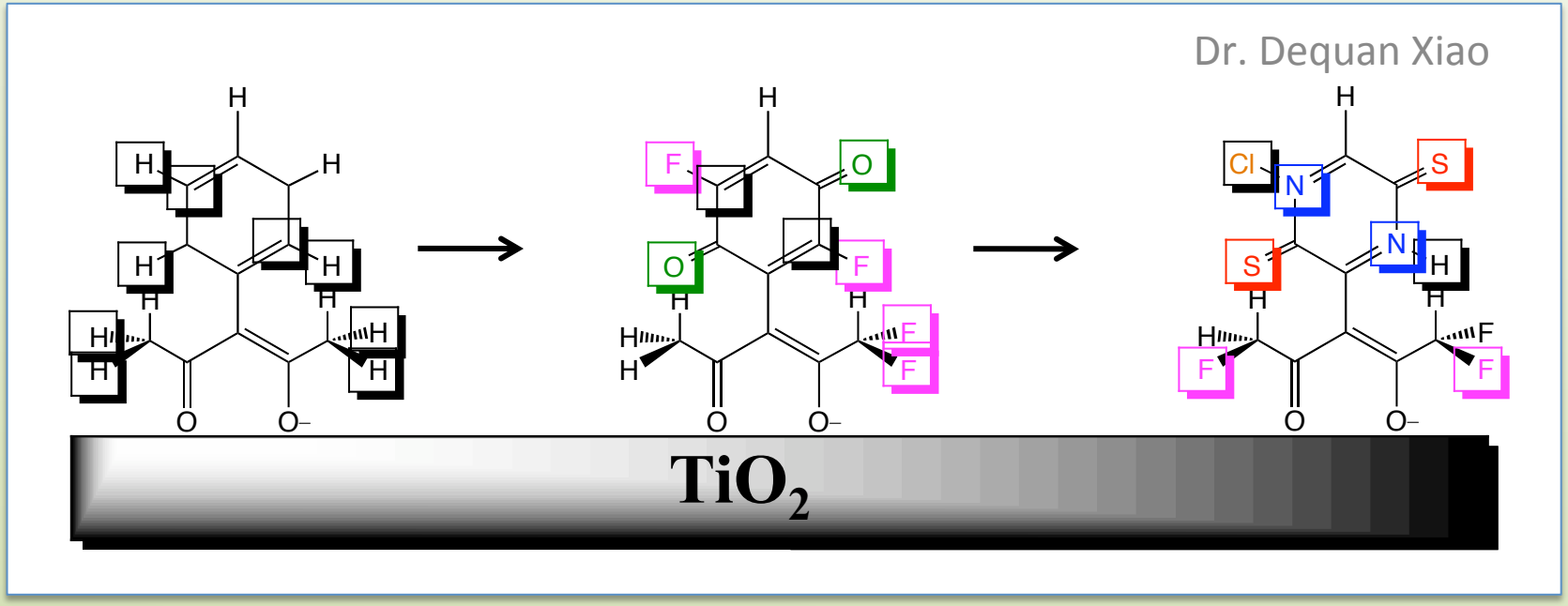


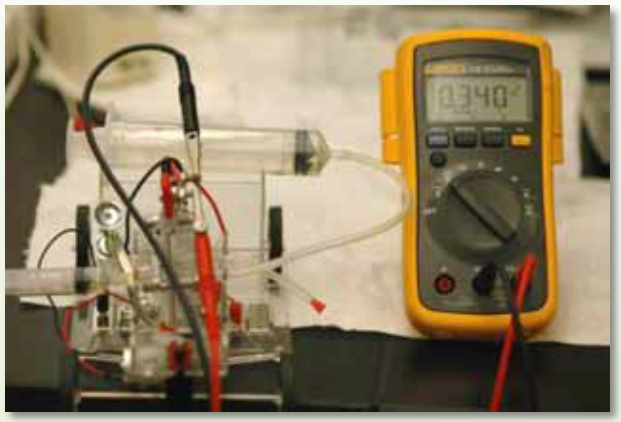
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Inverse Design: Molecular Sensitizers





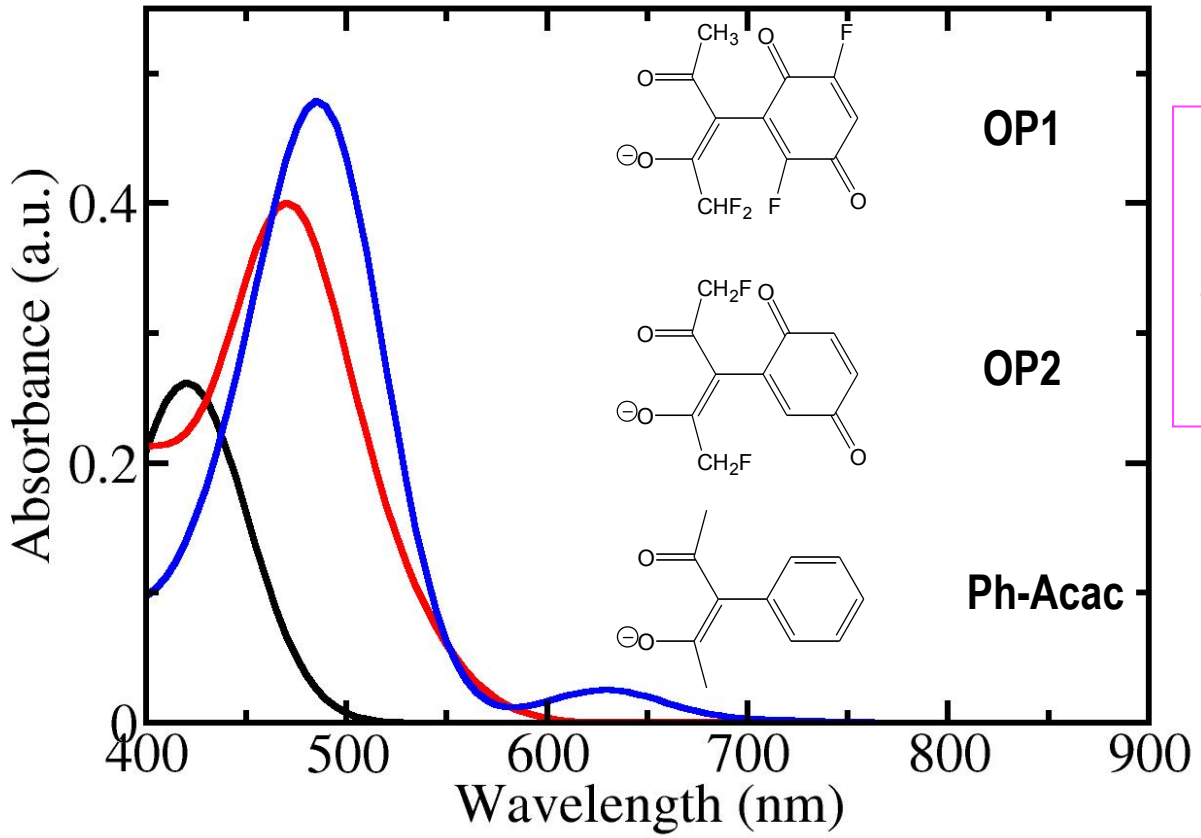
CHEM 505: *Green Chemistry and Alternative Energy*

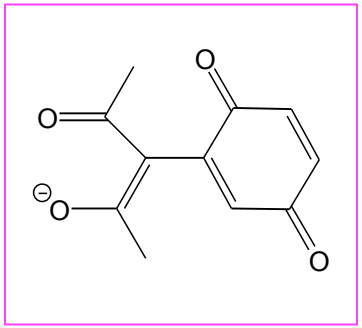
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

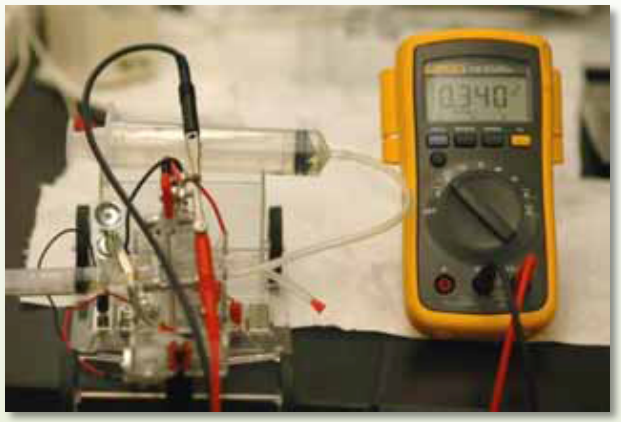
Inverse Design: Molecular Sensitizers

Dr. Dequan Xiao





OP

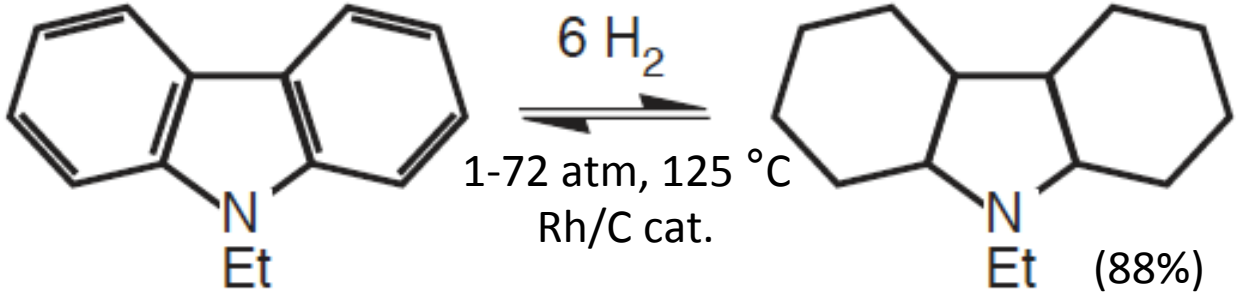


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

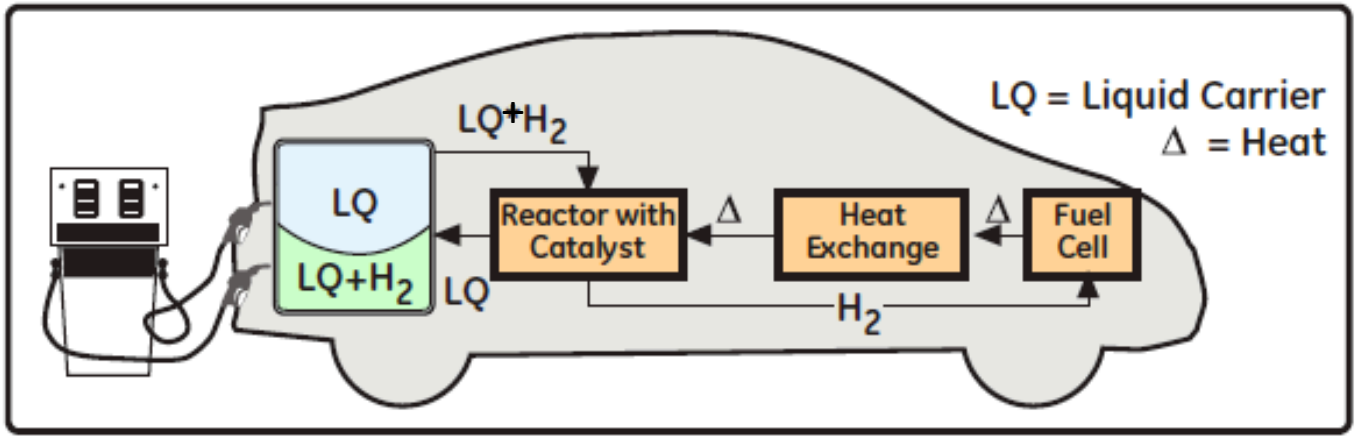
Modeling Systems for a Hydrogen Economy

Liquid H-Carriers: Fuel Cell/Flow Battery Concept

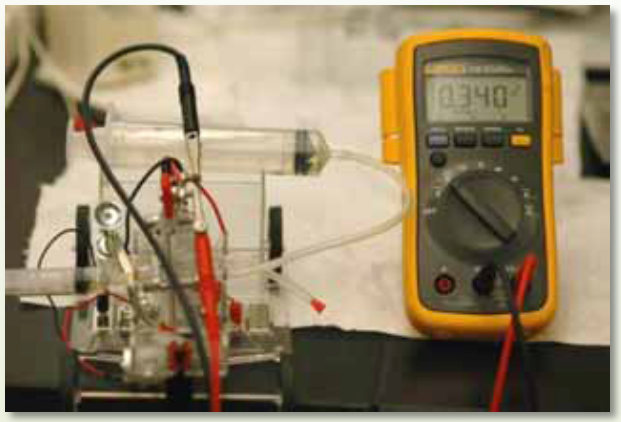
Thermal (de)hydrogenation



G. P. Pez, A. R. Scott, A. C. Cooper and H. Cheng, *US patent*, 7101530 (2006)



Courtesy AIR PRODUCTS



CHEM 505: *Green Chemistry and Alternative Energy*

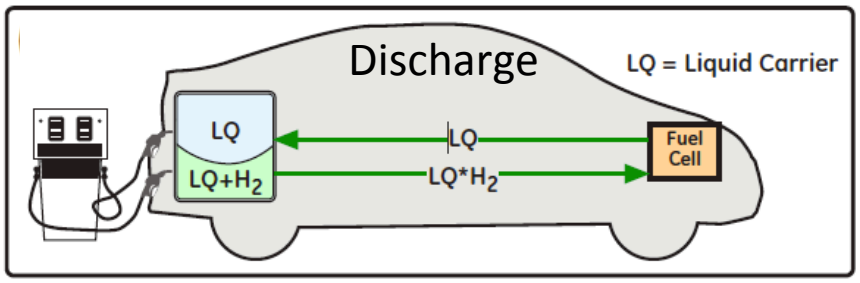
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

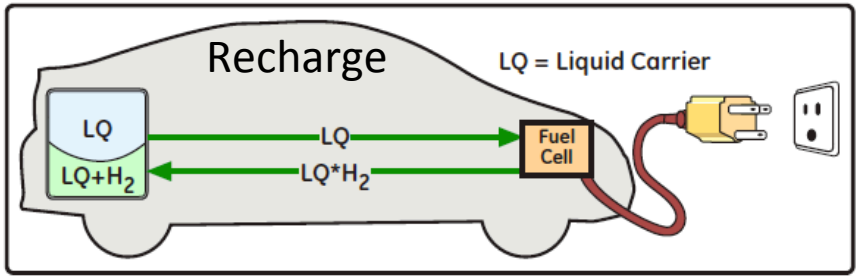
Modeling Systems for a Hydrogen Economy

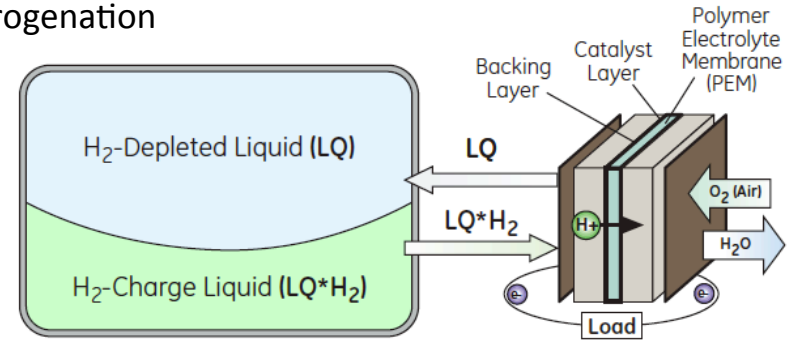
Organic Fuel Cell/Flow Battery Concept

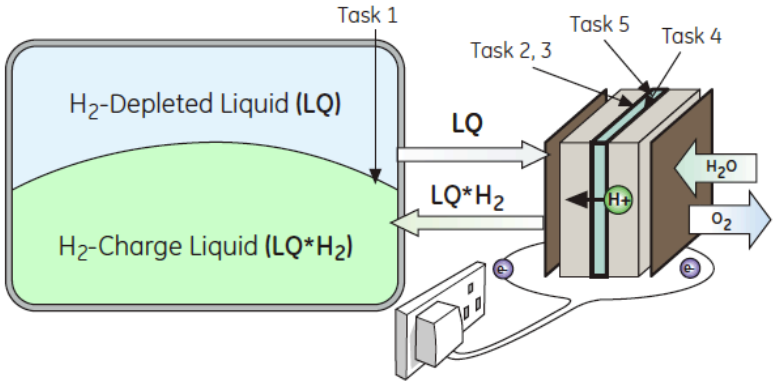
"Feed the hydrogenated organic liquid carrier directly into the fuel cell where it is electrochemically dehydrogenated without ever generating H_2"

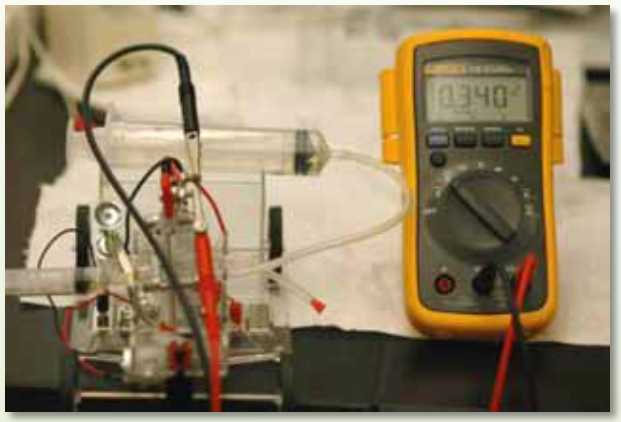
Electrochemical (de)hydrogenation









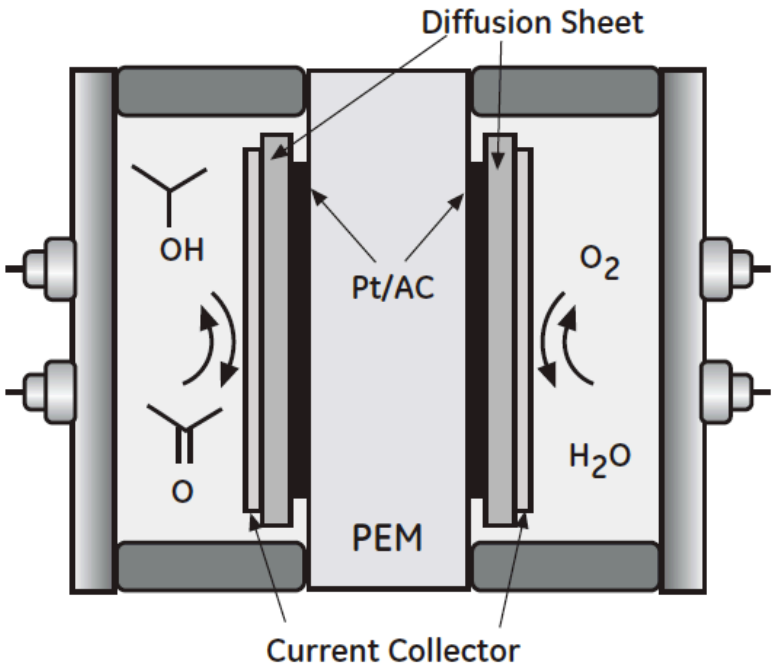


CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Organic Fuel Cell/Flow Battery Concept

"Electrochemical dehydrogenation can be done at lower temperatures and high rates"



$$LQ^*H_n \rightarrow LQ + n\,H^+ + n\,e^- \quad (1)$$

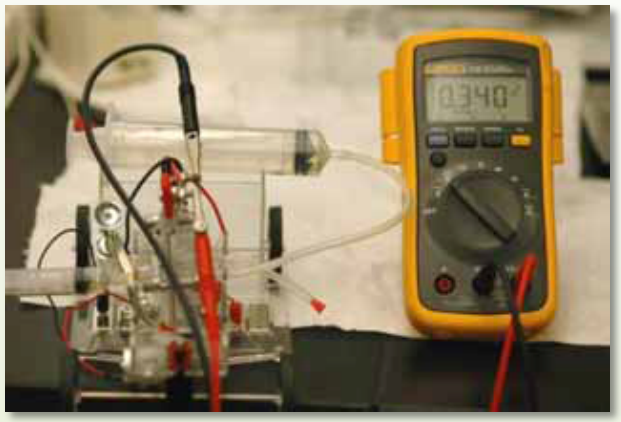
$$n/2\,O_2 + n\,H^+ \rightarrow n/2\,H_2O - n\,e^- \quad (2)$$

$$LQ^*H_n + n/2\,O_2 \rightarrow n/2\,H_2O + LQ \quad (3)$$

*where LQ stands for an organic carrier molecule

Electrochemical dehydrogenation of saturated cyclic hydrocarbons (e.g., cyclohexane and decaline) is possible in alkaline electrolyte using Pd and Rh catalysts.

[K.V. Kordesch, J.F. Yeager, J.S. Dereska, *US Patent* 3280014 (1966); M. Okimoto, Y. Takahashi, K. Numata, G. Sasaki, *Heterocycles*, **65** (2005) 371]



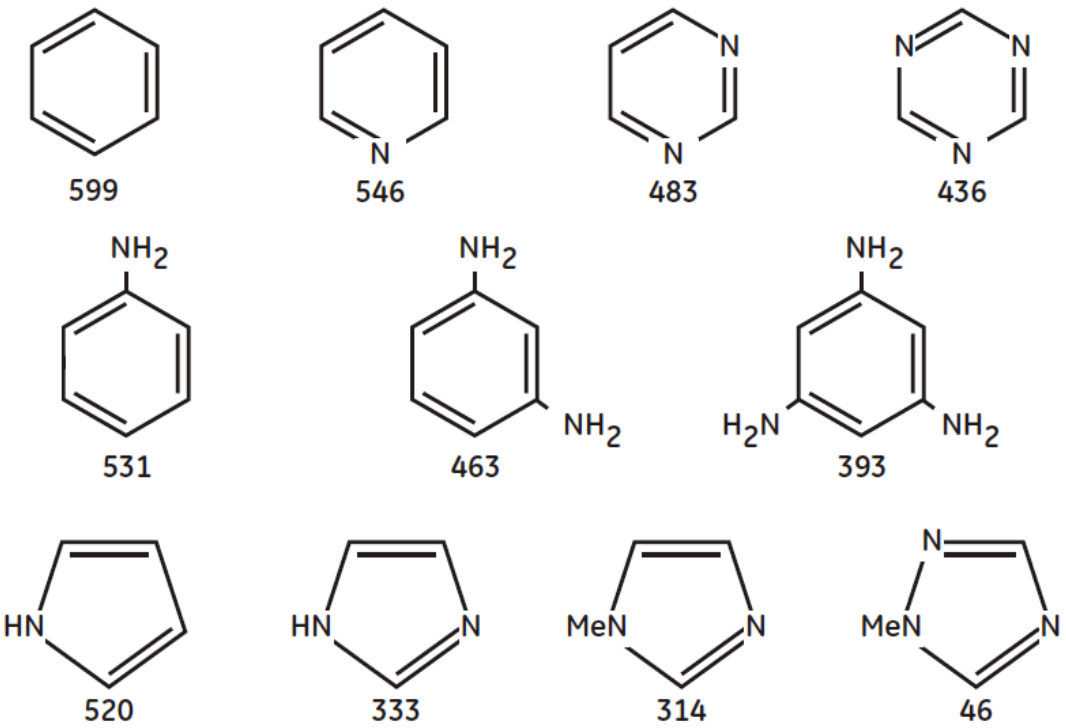
CHEM 505: *Green Chemistry and Alternative Energy*

Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

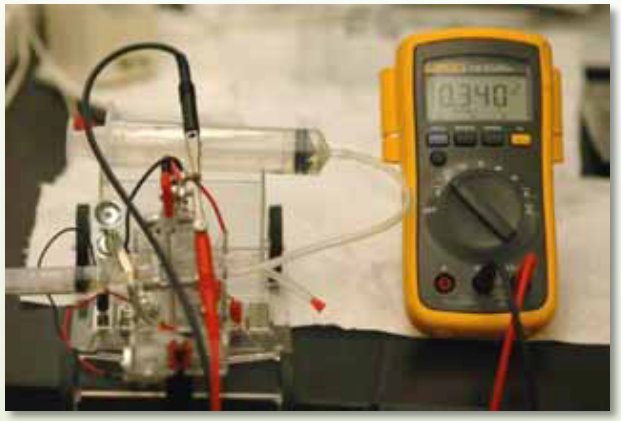
Modeling Systems for a Hydrogen Economy

Organic Liquid H-Carriers

Temperature (K) for spontaneous (de)hydrogenation ΔG = 0 (DFT B3PW91)



E. Clot, O. Eisenstein, R.H. Crabtree, *Chem. Commun*. 22:2231-2233 (2007).



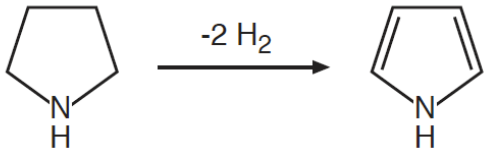
CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for a Hydrogen Economy

Organic Liquid H-Carriers

Exercise 4:

Nitrogen atoms introduced into heterocycles tune the thermodynamic tendency to absorb or release H_2, or to absorb or release 2(H+ and e-). A particularly favorable condition is when aromatic stabilization can be achieved after cleavage of only four C-H bonds as in the following reaction:



This can be analyzed by computing the temperature $T = T_d$ that makes the dehydrogenation free energy $\Delta G = \Delta H - T\,\Delta S$ equal to zero. At this point ($T = T_d$) the unfavorable enthalpy due to the endothermicity of the reaction is exactly compensated by the favorable entropy of H_2 release.

(a) Find the minimum energy configurations of reactants and products for the dehydrogenation reaction shown above in the gas-phase at the DFT B3PW91 level of theory.

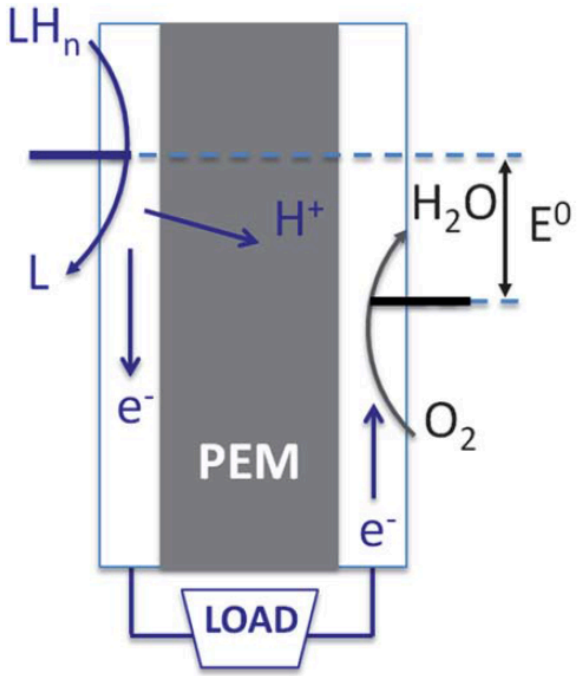
(b) Perform a frequency calculation for reactants and products and compute the temperature T_d at which the dehydrogenation becomes spontaneous.

(c) Compare your results with the analogous calculation of dehydrogenation T_d for cyclopentane.

Solution Exercise 4: See tutorial notes on ab initio free energy calculations.

Organic fuel cell/flow battery: Fuel selection from thermodynamic considerations Energy Env Sci 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim ,
Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista



$$LH_n \leftrightarrow L + nH^+ + ne^-$$

$$+\ n/4\ O_2 + nH^+ \leftrightarrow n/2\ H_2O - ne^-$$

$$LH_n + n/4\ O_2 \leftrightarrow L + n/2\ H_2O$$

$$E^0 = -\Delta G_r/nF$$

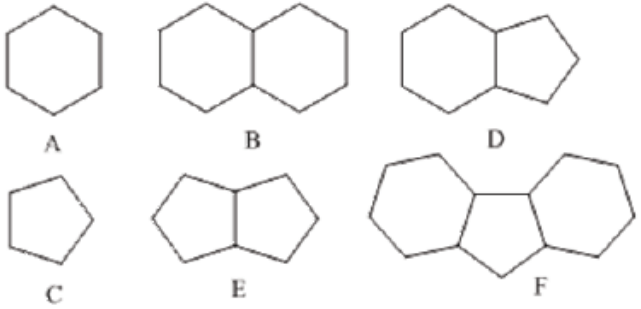
$$\Delta G_r = G_L + n/2\ G_{H_2O} - G_{LH_n} - n/4\ G_{O_2}$$

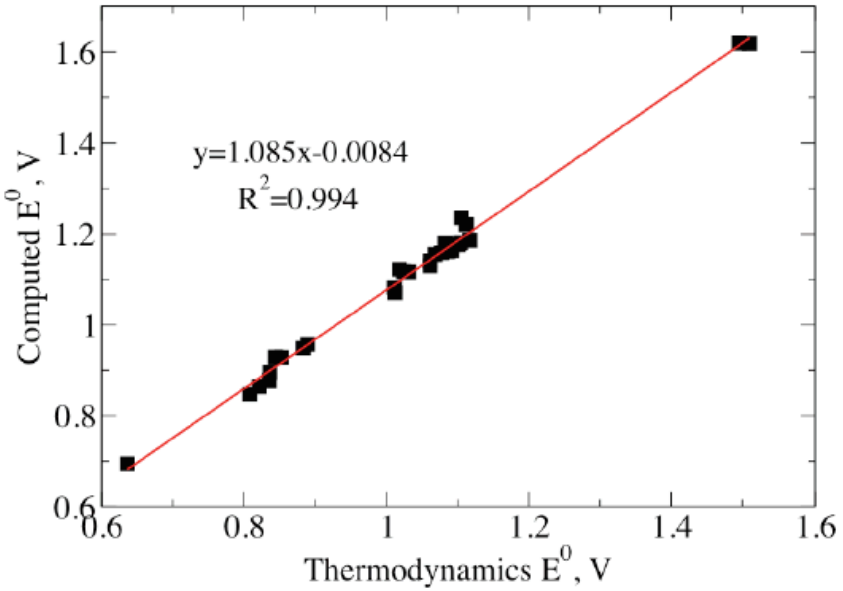
$$H = E_{elect} + U_{vib} + U_{trans} + U_{rot} + PV \qquad G = H - T(S_{vib} + S_{rot} + S_{trans})$$

$$H = H^0 + C_p(T - 298.15\ K) \qquad S = S^0 + C_p \ln(T/298.15\ K)$$

Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim , Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista





Correlation between OCP's obtained from the calculated free energies at B3LYP/cc-PVTZ theory level and from the experimental thermodynamic data (NIST database).

Calculated open circuit potentials and hydrogen gravimetric densities for six- (type A) and five-member (type C) ring fuels.

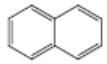
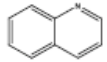
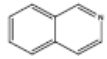
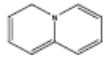
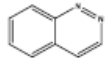
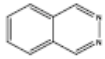
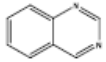
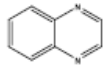
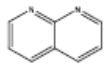
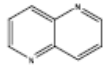
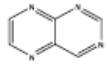
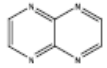
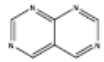
LOHC (in dehydrogenated state)		H, wt. %	E^0, V
Name	**Structure**		
Benzene		7.19	1.049
Pyridine		7.10	1.081
Pyrimidine		7.02	1.116
Pyridazine		7.02	1.085
1,3,5-triazine		6.94	1.198
Cyclopentadiene		5.75	0.854
Furan		5.59	1.004
1H-pyrrole		5.67	1.092
1H-imidazole		5.59	1.203
1H-pyrazole		5.59	1.269
1H-1,2,3-triazole		5.52	1.351
1H-1,2,4-triazole		5.52	1.328

Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim ,
Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista

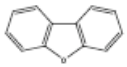
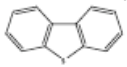
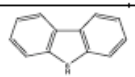
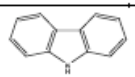
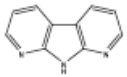
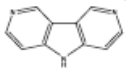
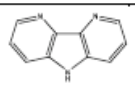
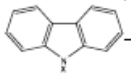
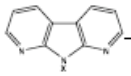
Calculated open circuit potentials and hydrogen gravimetric densities for fused six- (type D) and five-member (type E) ring fuels.

Organic carrier (in dehydrogenated state)		*H, wt. %*	*E^0, V*
Name	**Structure**		
1H-indene		6.49	1.041
benzofuran		6.39	1.084
benzo[b]thiophene		5.67	1.080
1H-indole		6.54	1.128
2H-isoindole		6.54	1.092
indolizine		6.54	1.064
1H-benzo [d]imidazole		6.49	1.187
1H-indazole		6.49	1.206
1H-pyrrolo [2,3-b]pyridine		6.39	1.167
imidazo[1,2-a] pyrazine		6.34	1.145
7H-purine		6.29	1.228
1,4-dihydropentalene		5.49	0.901
1H-pyrrolizine		5.44	1.017
1,4-dihydropyrrolo [3,2-b]pyrrole		5.39	1.159
1,4-dihydroimidazo [4,5-d]imidazole		5.30	1.313

Organic carrier (in dehydrogenated state)		*H, wt %*	*E^0, V*
Name	**Structure**		
naphthalene		7.29	1.078
quinoline		7.24	1.097
isoquinoline		**7.24**	1.098
4H-quinolizine		**5.79**	0.946
cinnoline		**7.19**	1.087
phthalazine		7.19	1.098
quinazoline		7.19	1.119
quinoxaline		7.19	1.108
1,8-naphthyridine		7.19	1.112
1,5-naphthyridine		7.19	1.115
pteridine		7.09	1.128
pyrazino[2,3-b] pyrazine		7.09	1.122
pyrimido[4,5-d] pyrimidine		7.09	1.160

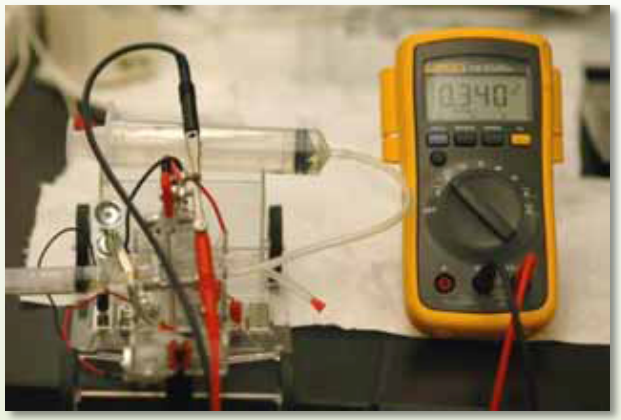
Fuel selection for regenerative organic fuel cell/flow battery: thermodynamic consideration, EES 5: 9534-9542 (2012)

C. Moyses Araujo, Davide L. Simone, Steven J. Konezny, Aaron Shim , Robert H. Crabtree, Grigorii L. Soloveichik, and Victor S. Batista

Organic carrier (in dehydrogenated state)		*H, wt %*	*E^0, V*
Name	**Structure**		
9H-fluorene		6.78	1.109
dibenzo[b,d]furan		6.71	1.125
dibenzo[b,d] thiophene		6.16	1.117
5H-dibenzo [b,d]borole		6.81	1.108
9H-carbazole		6.75	1.152
9H-pyrrolo [2,3-b:5,4-b'] dipyridine		6.67	1.206
5H-pyrrolo [3,2-c:4,5-c'] dipyridine		6.67	1.191
5H-pyrrolo [3,2-b:4,5-b'] dipyridine		6.67	1.181
9X-carbazole		H 6.75	1.152
		Et	1.167
9X-1,8-diazacarbazole		H 6.67	1.206
		Me	1.222
		Et	1.230

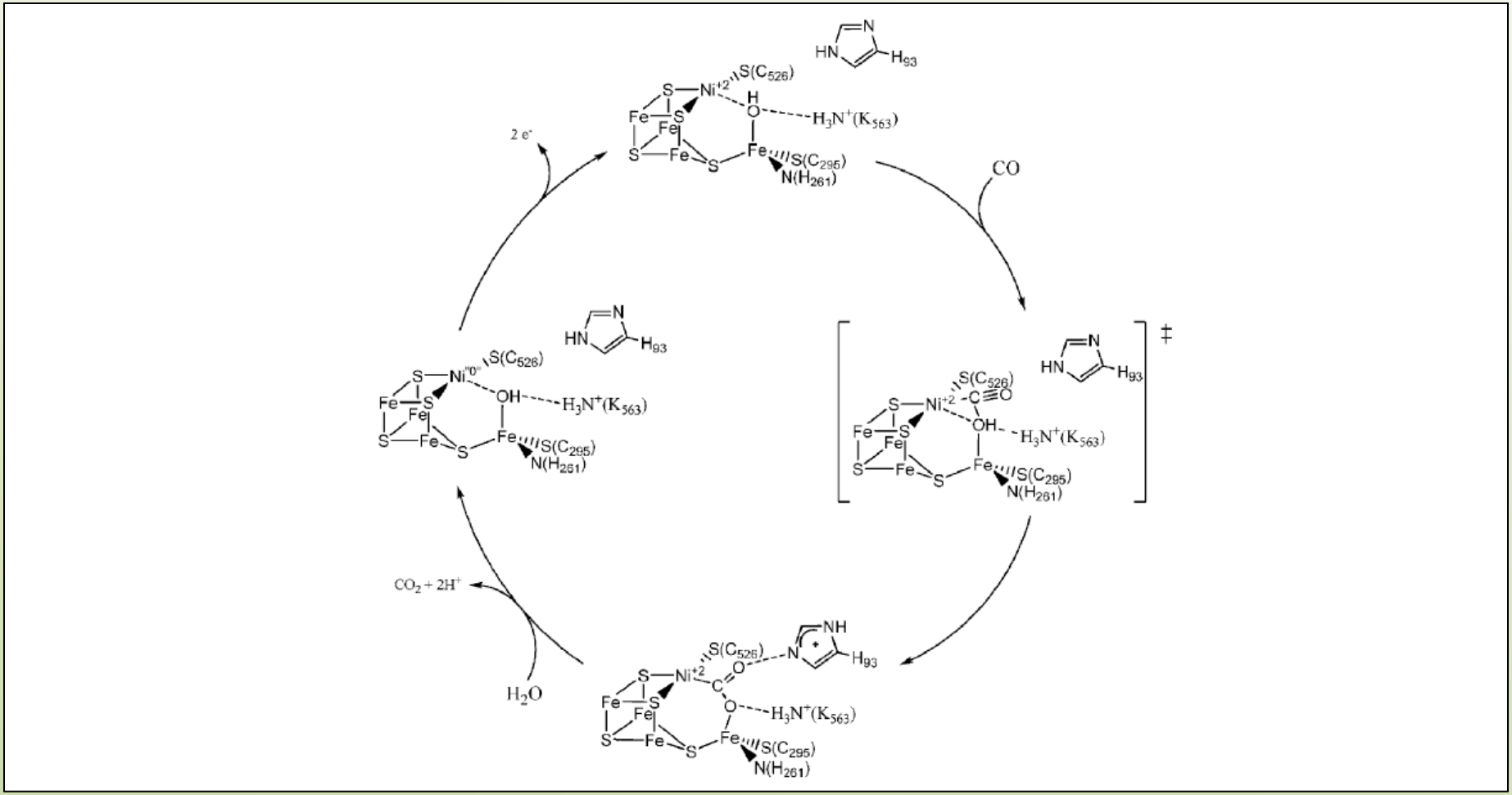
Boiling point, specific energy and energy density of selected organic fuels, and theoretical efficiency of fuel cells based on dehydrogenation.

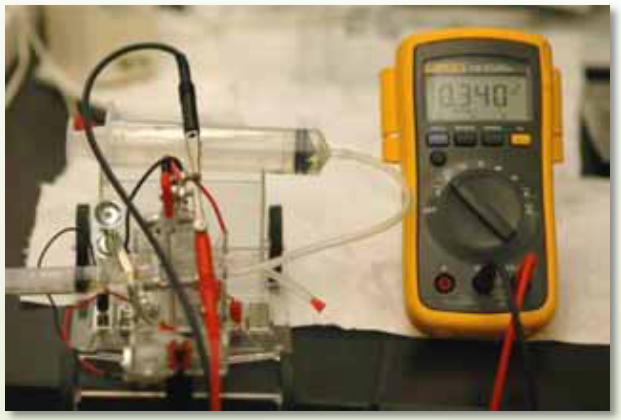
Organic carrier (in hydrogenated state)	Boiling point, °C	Specific energy, Wh/kg	Energy density, Wh/L	Efficiency, %
Liquid hydrogen	-252.9	-	2539	83.0
Pyrrolidine	87	1660	1438	92.8
Tetrahydrofurane	66	1500	1334	93.4
Tetrahydrothiophene	119	1196	1195	93.5
Cyclohexane	80.7	2025	1578	94.1
Methylcyclohexane	101	1747	1345	94.3
Cyclohexylamine	134.5	1772	1532	95.2
Chlorocyclohexane	66	1403	1403	93.4
Cyclohexanol	160.8	1686	1622	93.0
Cyclohexanethiol	158	1292	1227	94.0
Piperidine	106	2046	1764	94.2
2-methylpiperidine	118	1776	1499	94.5
Piperazine	146	2055	2260	95.7
trans-Decalin	187	2095	1877	93.1



Modeling Systems for CO_2/CO Conversion

Lesson From CO Dehydrogenases

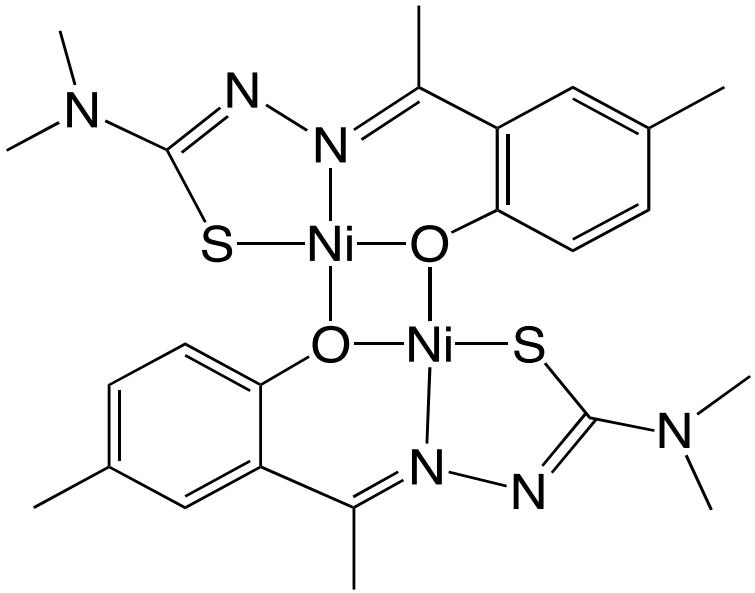




CHEM 505: *Green Chemistry and Alternative Energy*
Crabtree – Brudvig – Schmuttenmaer – Batista
Department of Chemistry – Yale University

Modeling Systems for CO/CO_2 Conversion

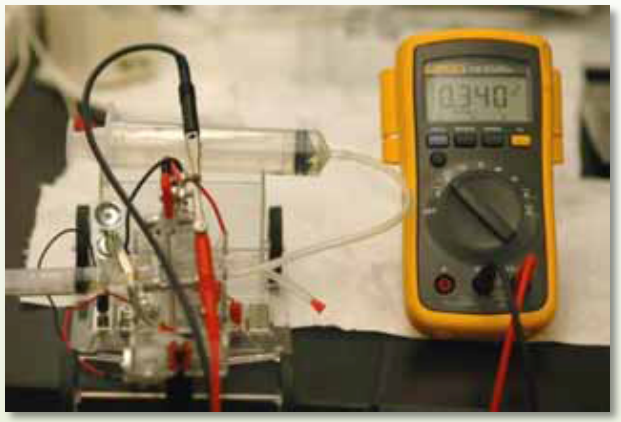
Crabtree's Biomimetic Ni Catalyst



1

$$CO + H_2O + 2AcO^- + 2mv^{2+} \rightleftharpoons CO_2 + 2AcOH + 2mv^+$$

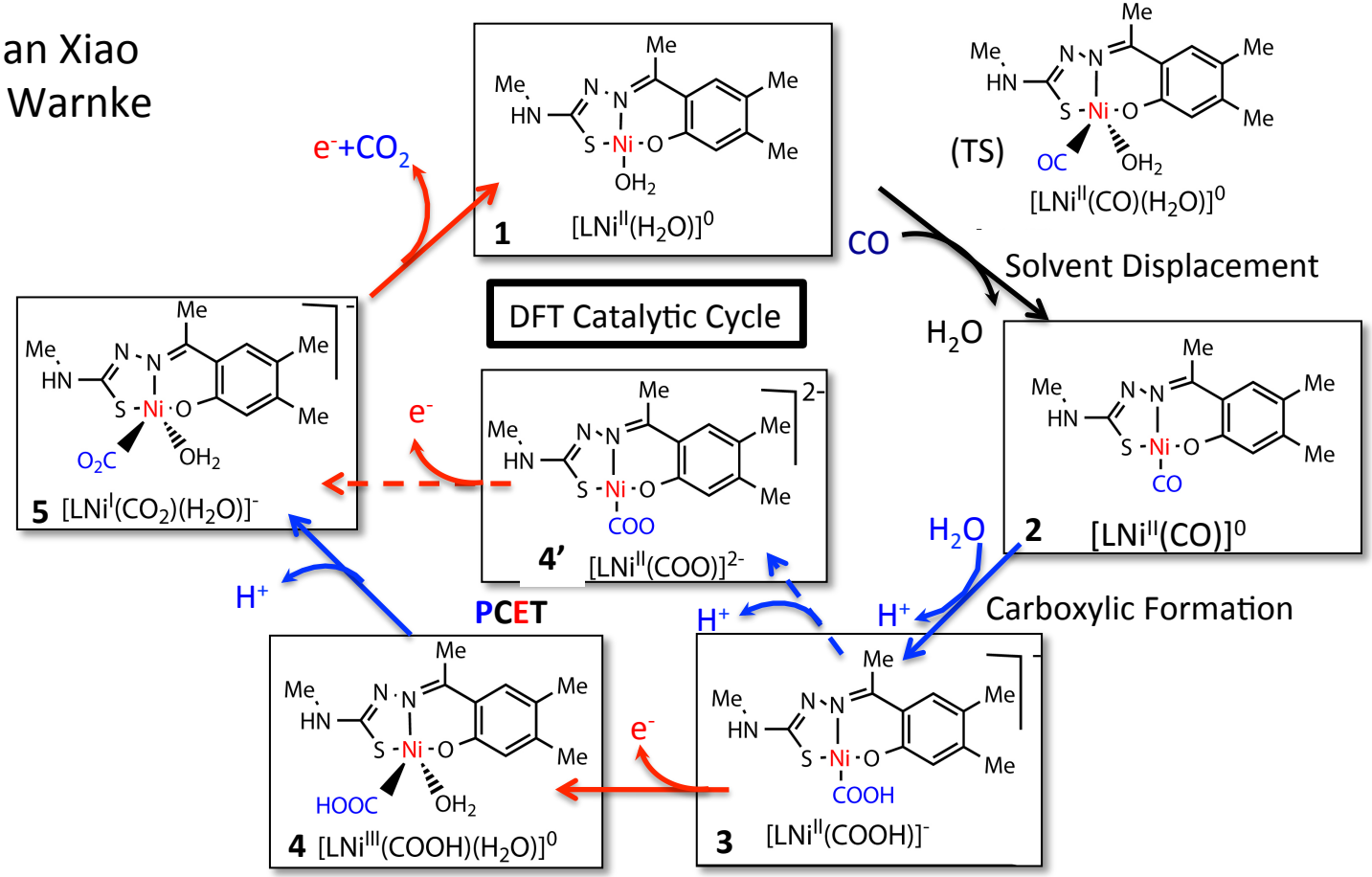
Lu, Z.; Crabtree, R. H. *J. Am. Chem. Soc.* **1995**, *117*, 3994

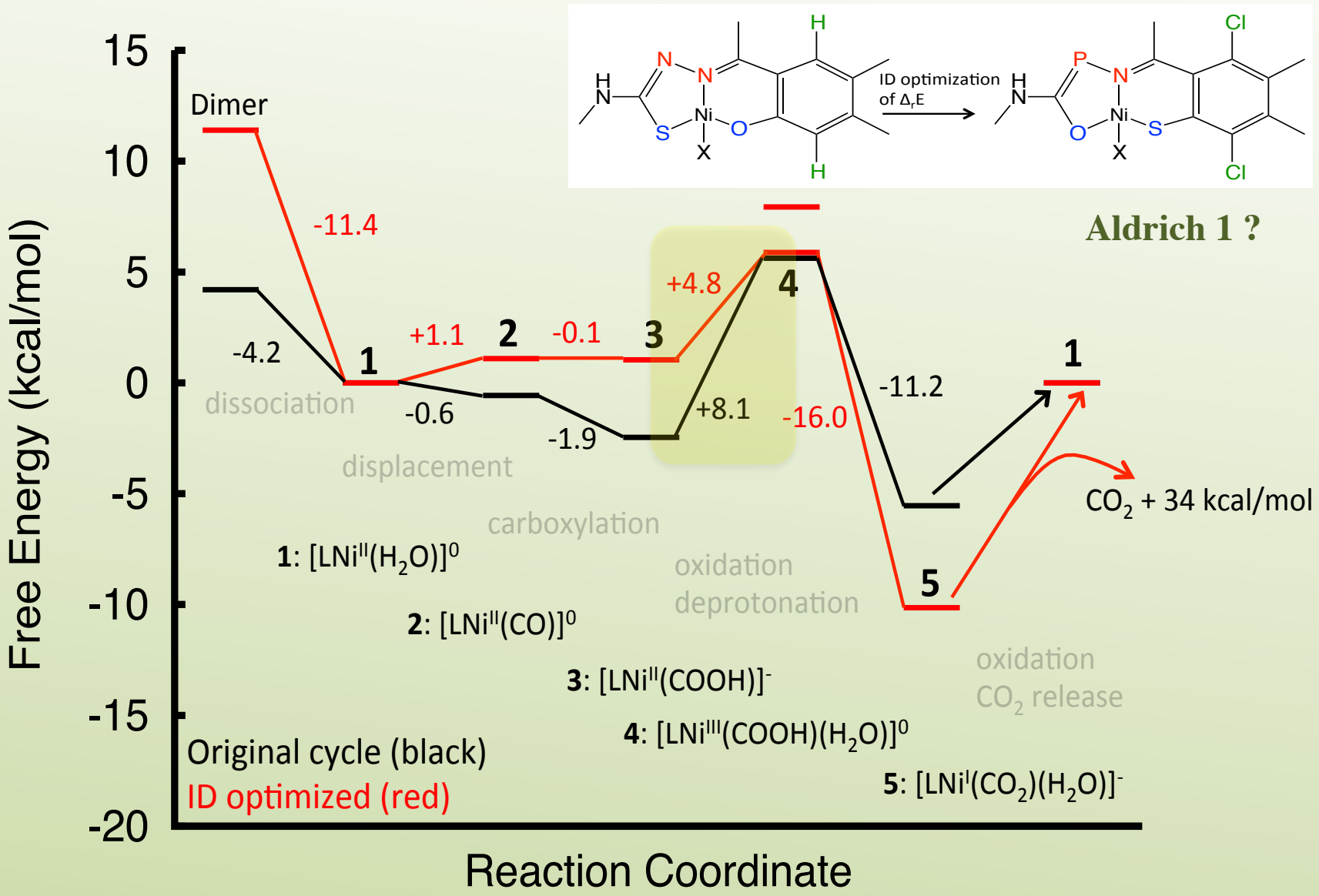


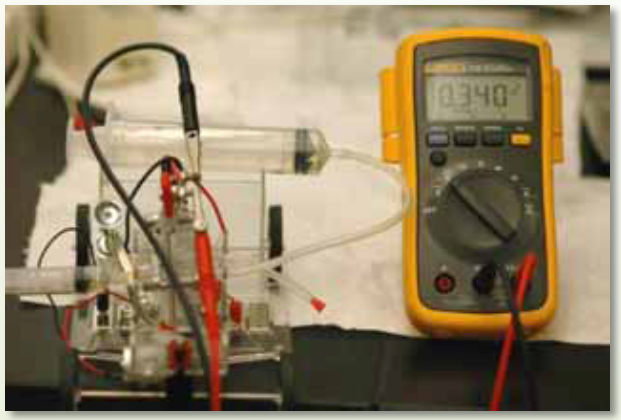
Inverse Design of Electrocatlysts: CO/CO_2 Conversion

Crabtree's Biomimetic Ni Catalyst

Dr. Dequan Xiao
Dr. Ingolf Warnke




15
10
5
0
-5
-10
-15
-20
Free Energy (kcal/mol)
Reaction Coordinate
Dimer
-11.4
-4.2
1
dissociation
+1.1
2
-0.1
3
displacement
-0.6
-1.9
+4.8
4
+8.1
-16.0
-11.2
1
carboxylation
oxidation
deprotonation
5
oxidation
CO2 release
CO2 + 34 kcal/mol
1: [LNiII(H2O)]0
2: [LNiII(CO)]0
3: [LNiII(COOH)]-
4: [LNiIII(COOH)(H2O)]0
5: [LNiI(CO2)(H2O)]-
Original cycle (black)
ID optimized (red)
ID optimization of ΔrE
Aldrich 1 ?



Modeling Systems for a Hydrogen Economy

CO Conversion into Liquid Fuel

The Fischer-Tropsch Process

1) Synthesis Gas Formation

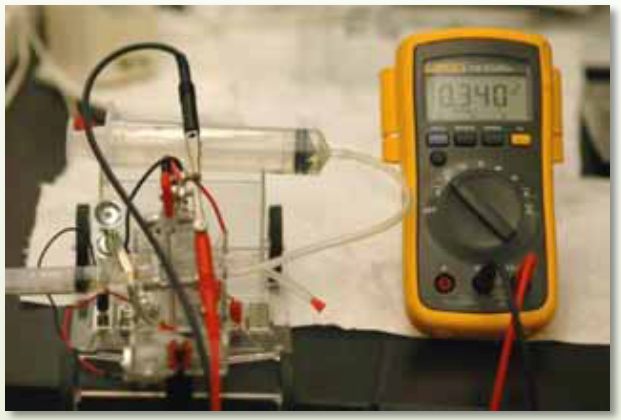
$$CH_n + O_2 \xrightarrow{\text{(Catalyst)}} \tfrac{1}{2}\, n\, H_2 + CO$$

2) Fischer-Tropsch Reaction

$$2n\, H_2 + CO \xrightarrow{\text{Catalyst}} -(CH_2-)_n- + H_2O$$

3) Refining

$$-(CH_2-)_n- \xrightarrow{\text{(Catalyst)}} \text{Fuels, lubricants, etc.}$$



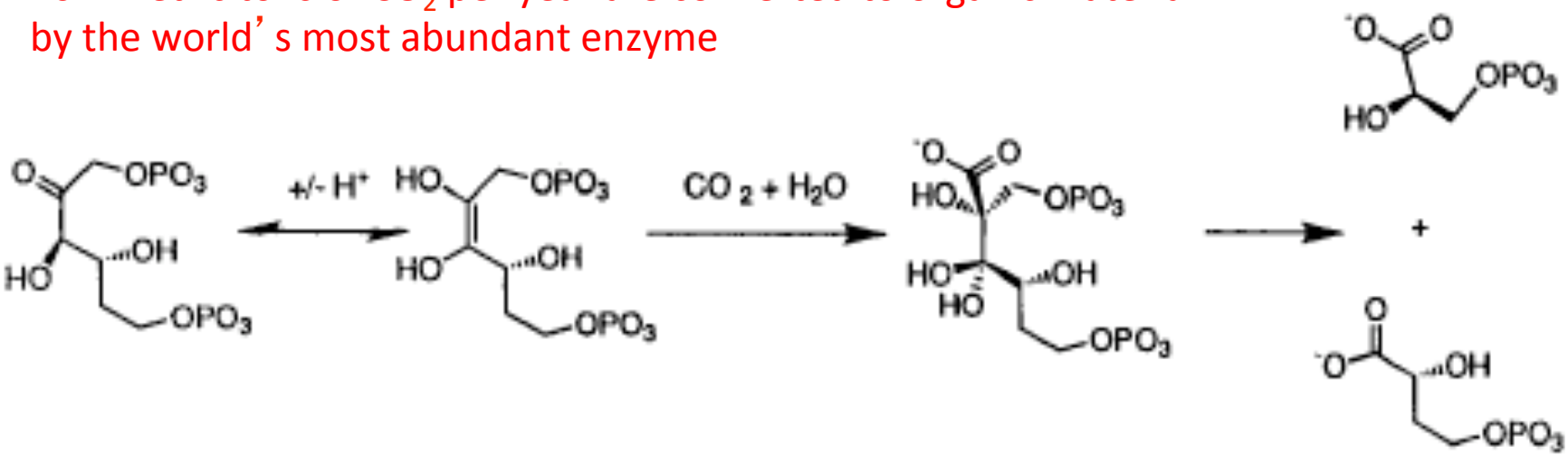
Modeling Systems for CO_2 Conversion

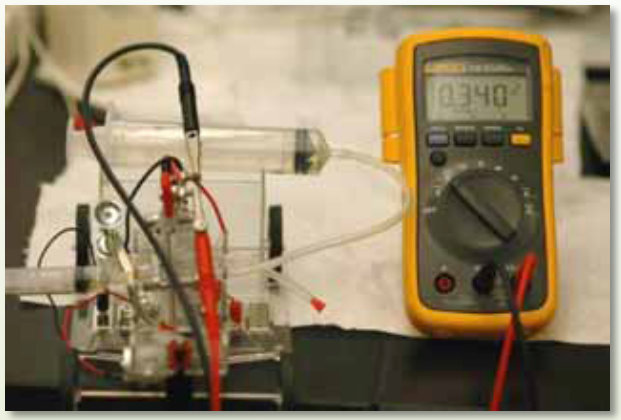
Lesson From Rubisco: CC Bond Formation

Natural CO_2 Fixation based on Mg Catalysts?

Carboxylation in Ribulose 1,5-BisPhosphate carboxylase (Rubisco)

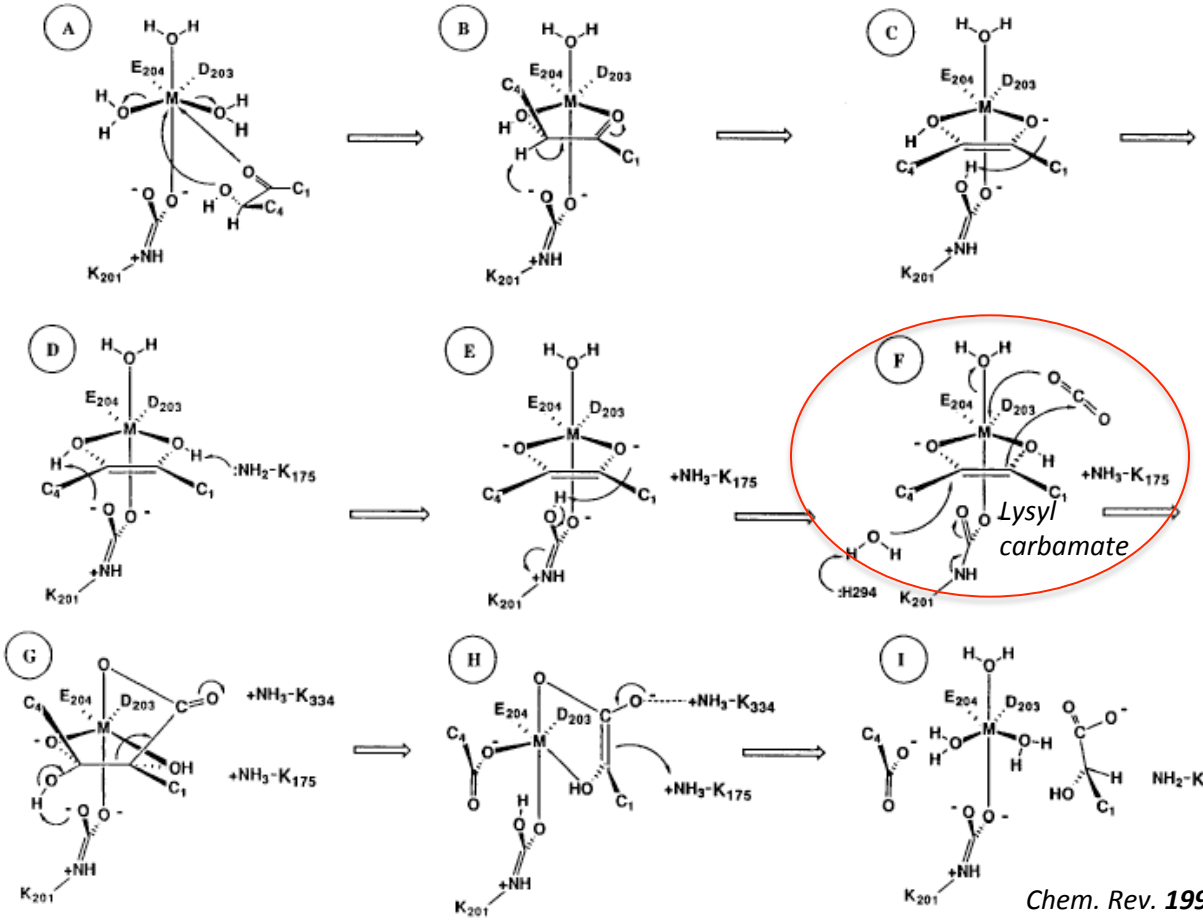
10^{11} metric tons of CO_2 per year are converted to organic material by the world's most abundant enzyme





Modeling Systems for CO_2 Conversion

Lesson From Rubisco: CC Bond Formation



Chem. Rev. ***1998, 98, 549-561***