Summary 9-23-14

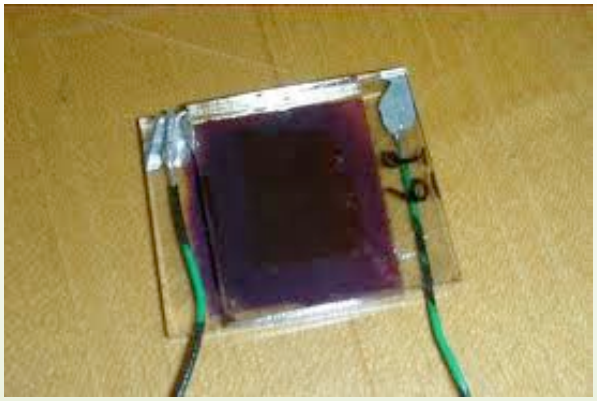
Computational Modeling and Physical Principles

- 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



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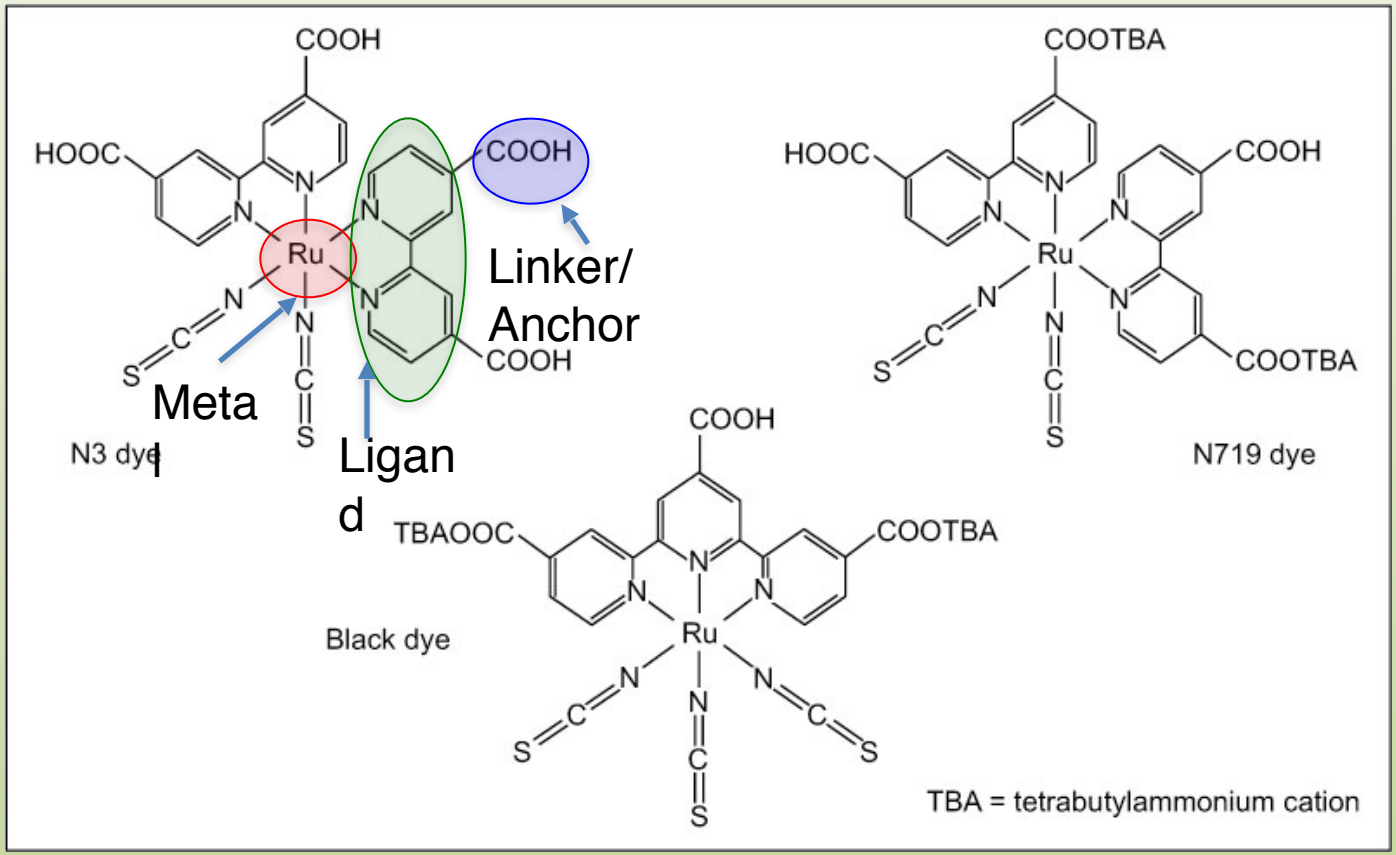
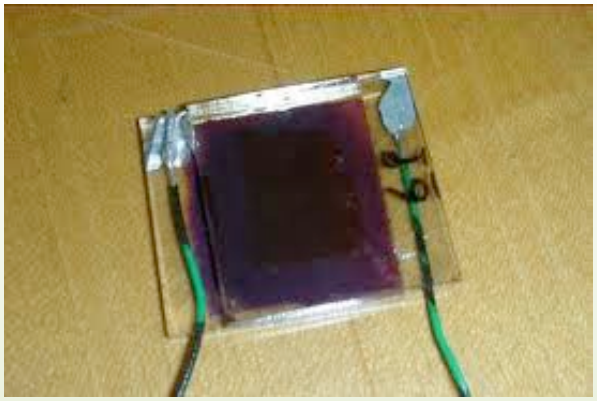
Ru Polypyridyl Dyes: Transition Metal Adsorbates





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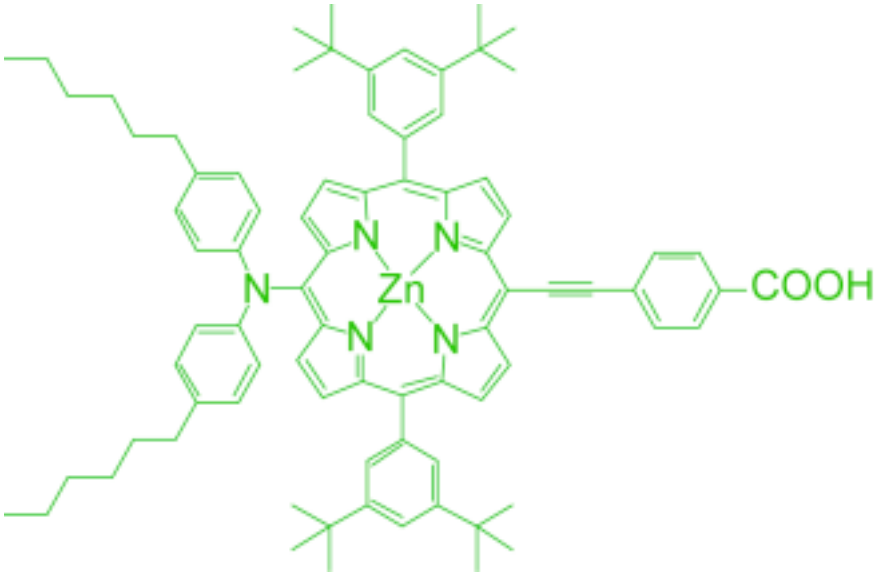
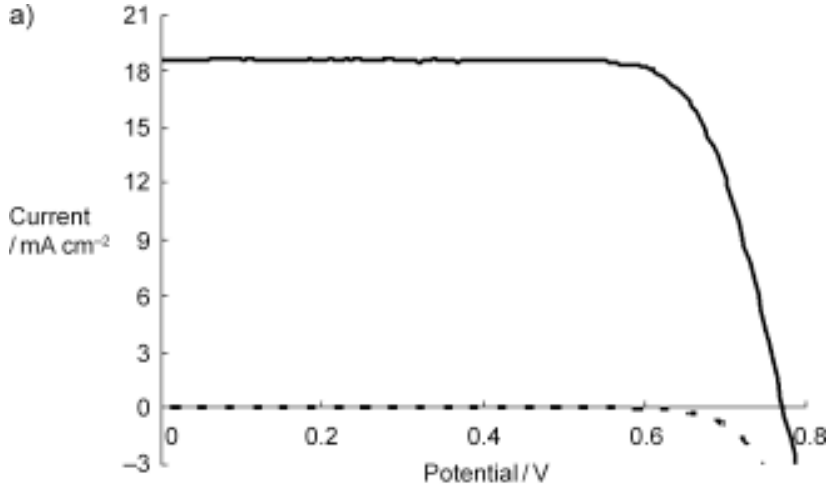
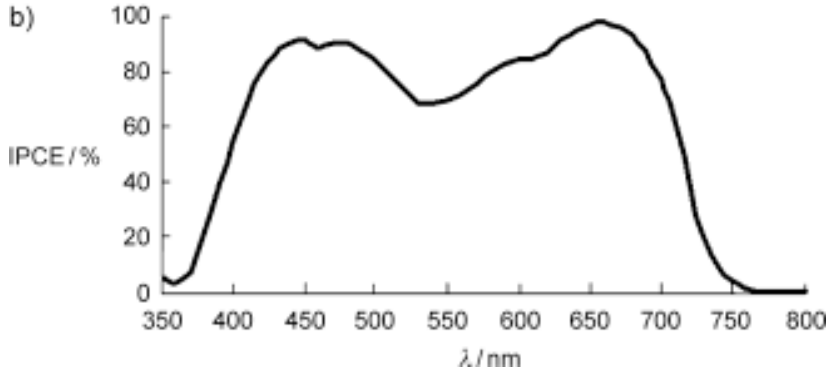
Zn Porphyrin Dyes [August 4, 2010]

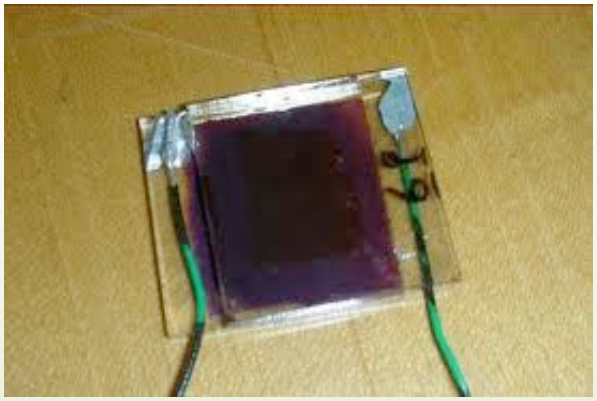


Zn porphyrin chromophore, integrated into a donor–acceptor dye as a π-conjugated bridge, exhibits efficiency of 11 % when used as a photosensitizer in a double-layer TiO2 film.

Angew. Chem. 2010, 122, 6796 –6799







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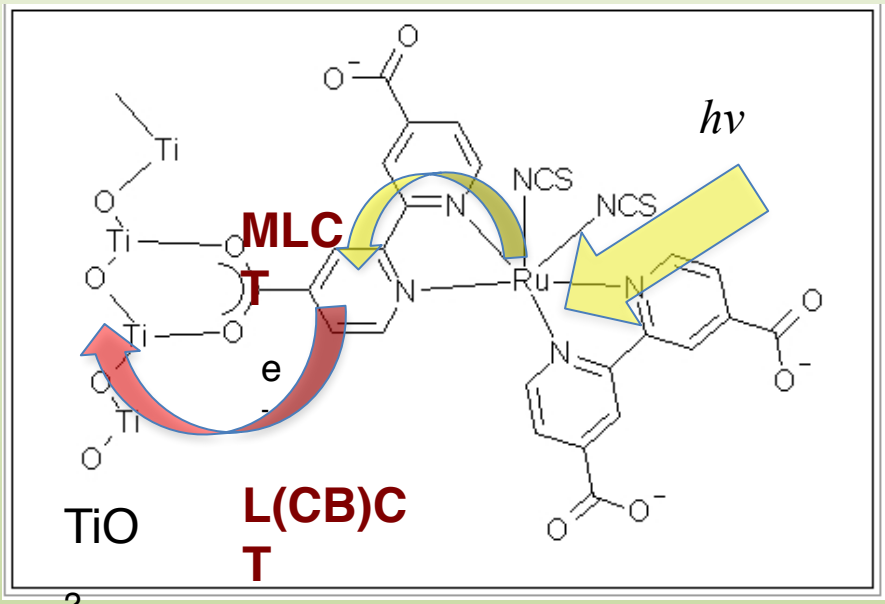
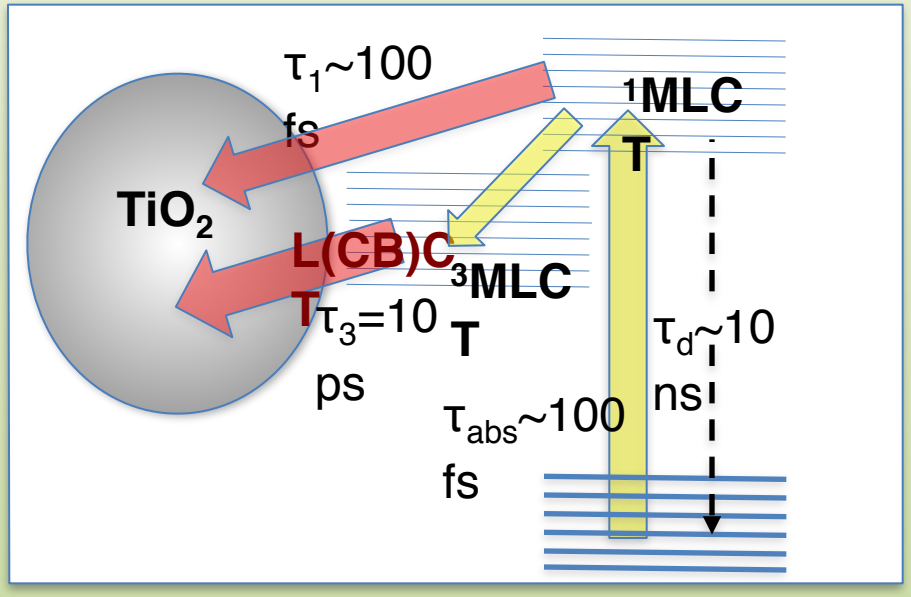
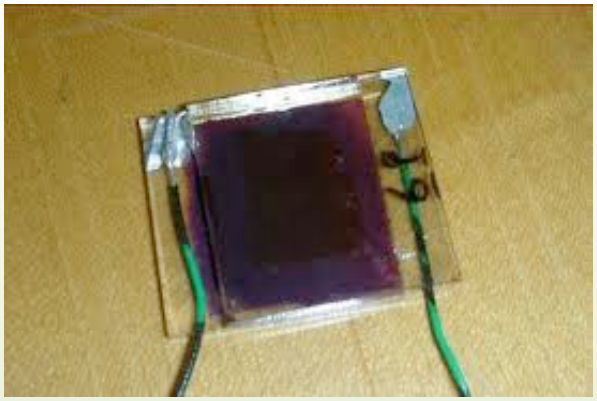
N3-Dye: Ru(II/III) MLCT, Aromatic Linkers







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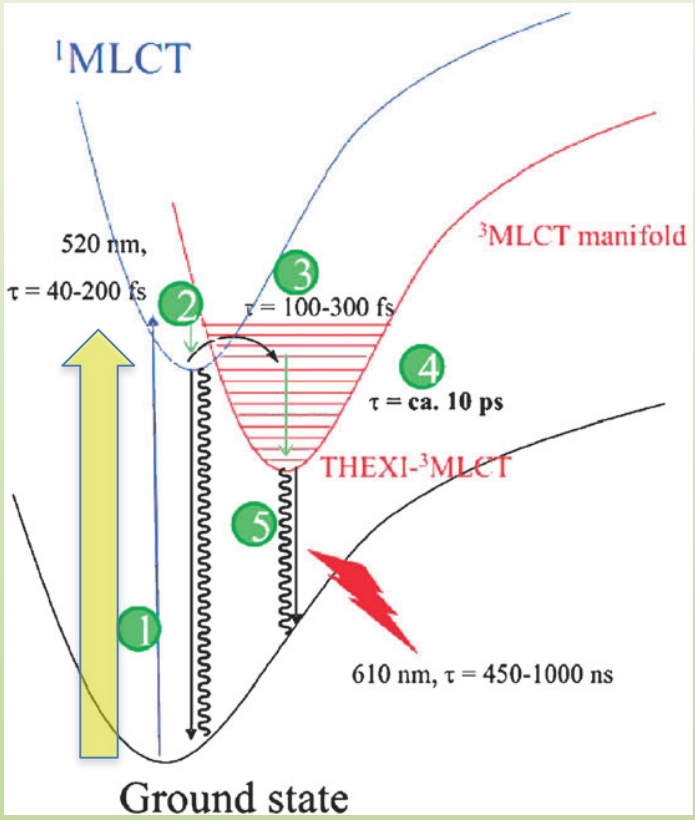
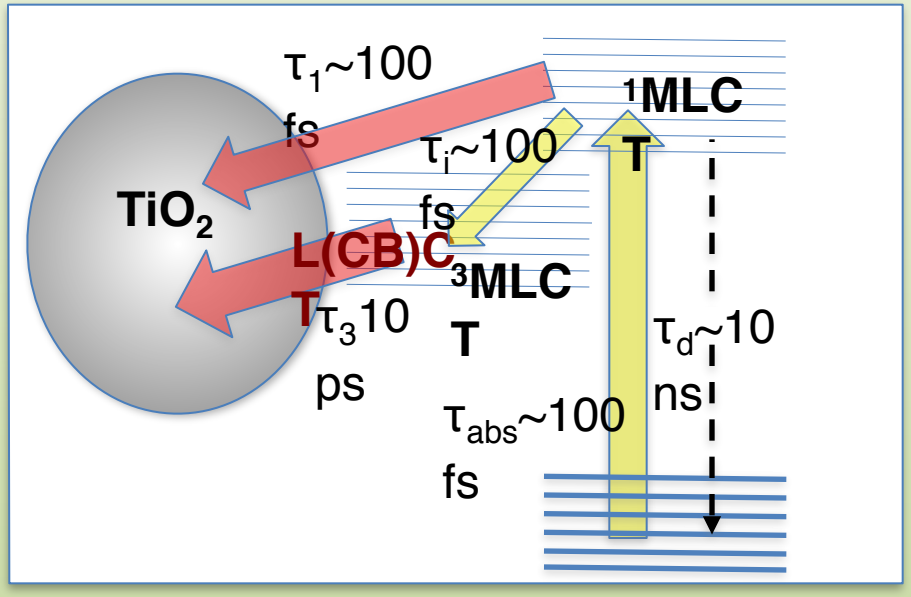
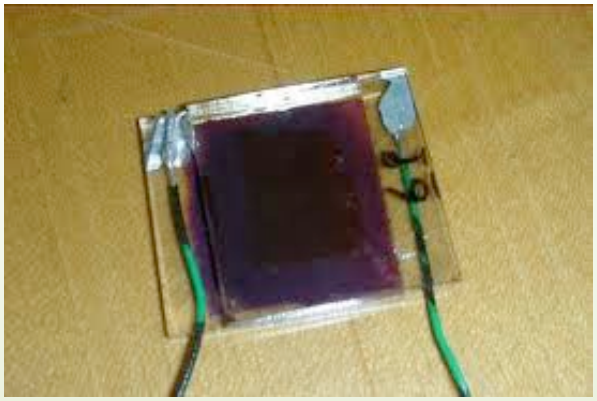
N3-Dye: $Ru^{(II/III)}$ MLCT, Aromatic Linkers







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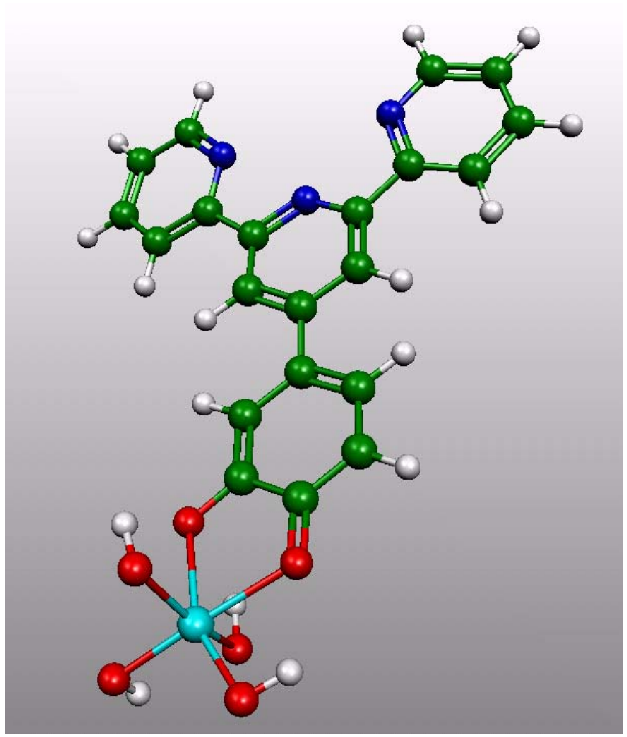
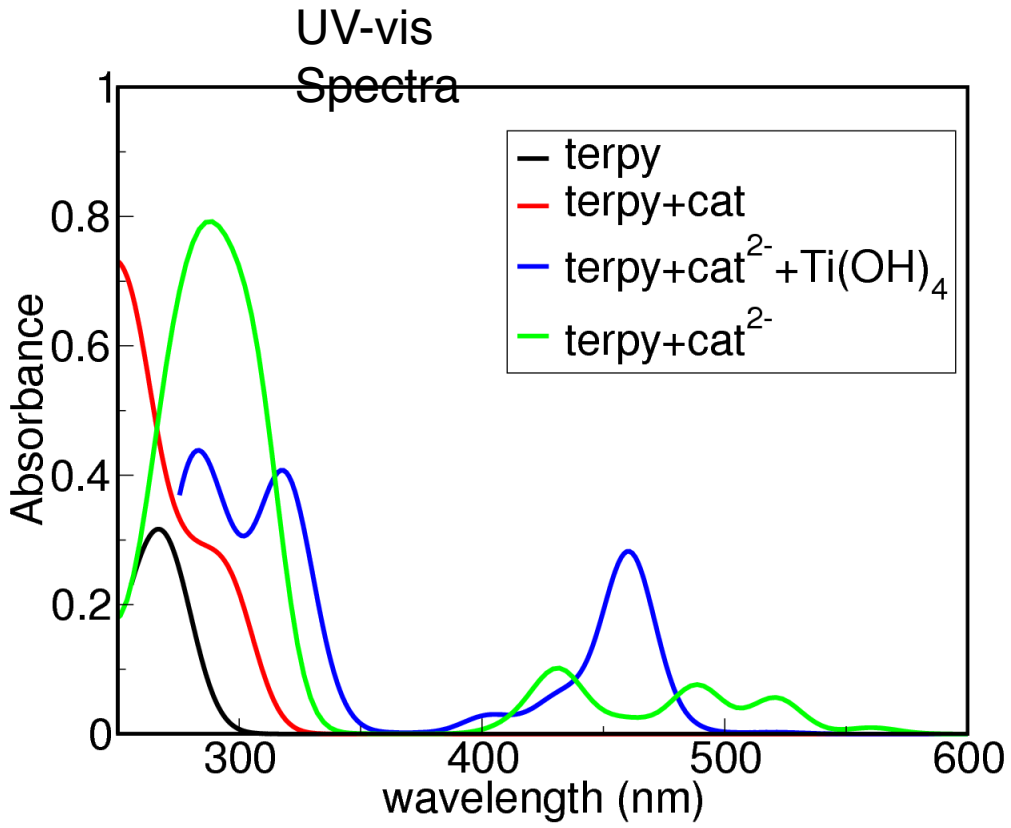
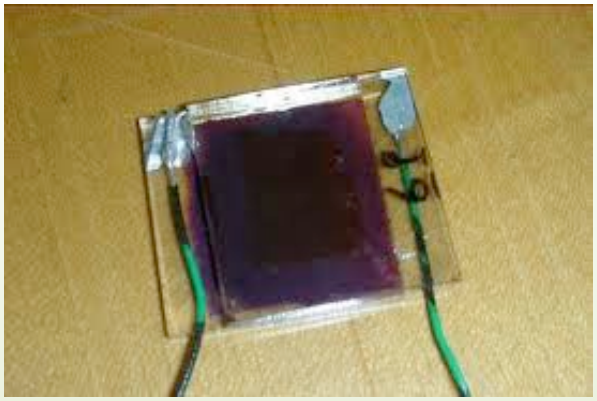
Ab Initio Simulations of Photoabsorption Spectra



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





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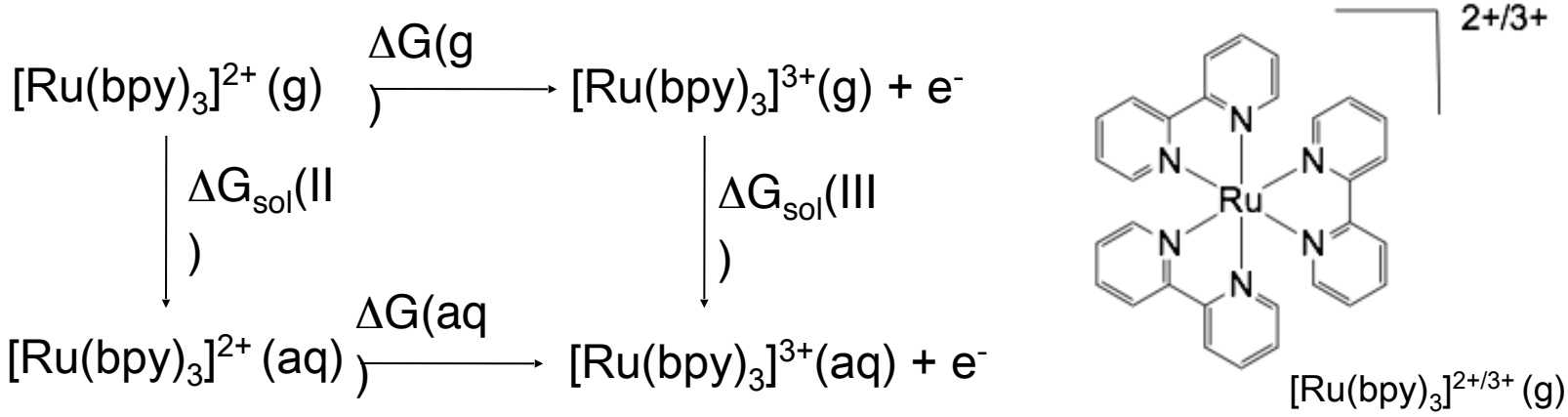
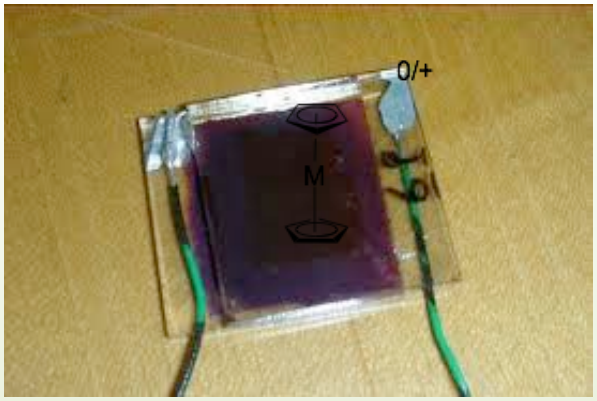
Ab Initio Redox Potentials: Born-Haber Cycle



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.



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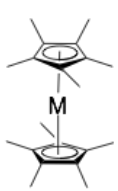
Ab Initio Computations of Redox Potentials

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.

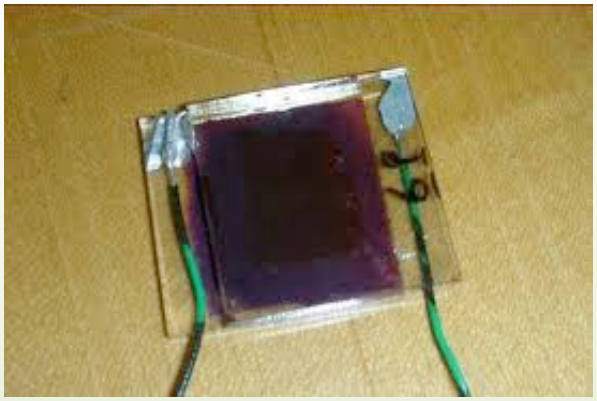
(a) Obtain the minimum energy structures of $[CoCp_2]^{0/+}$ and $[FeCp^*_2]^{0/+}$ and $[FeCp_2]^{0/+}$ at the B3LYP(LACVP/6-311G*) level of theory and compare them to the X-ray crystal structures for $[Ru(bpy)_3]^{2+}$, $[CoCp_2]^0$ and $[FeCp^*_2]^0$.

- 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.



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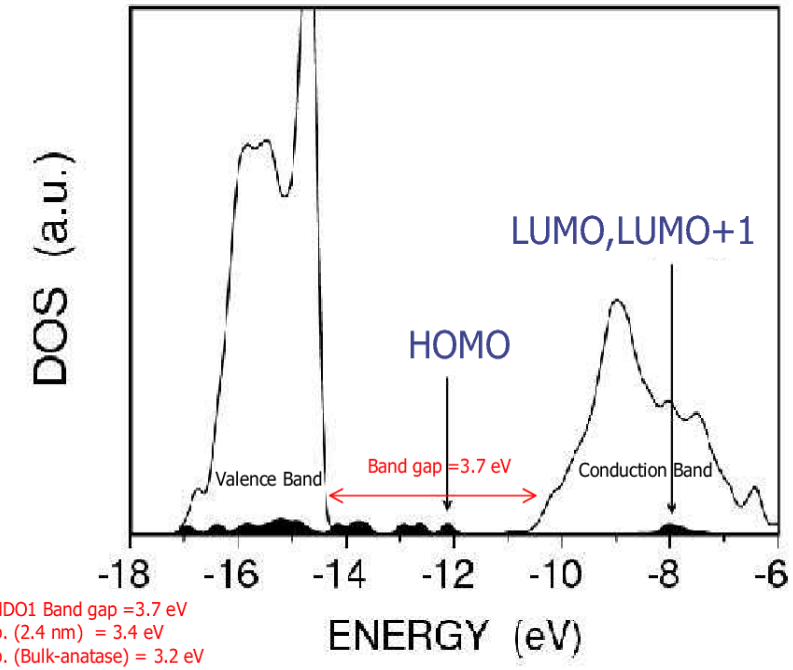
Modeling Dye-Sensitized Solar Cells

Ultrafast IET: Gerischer Model

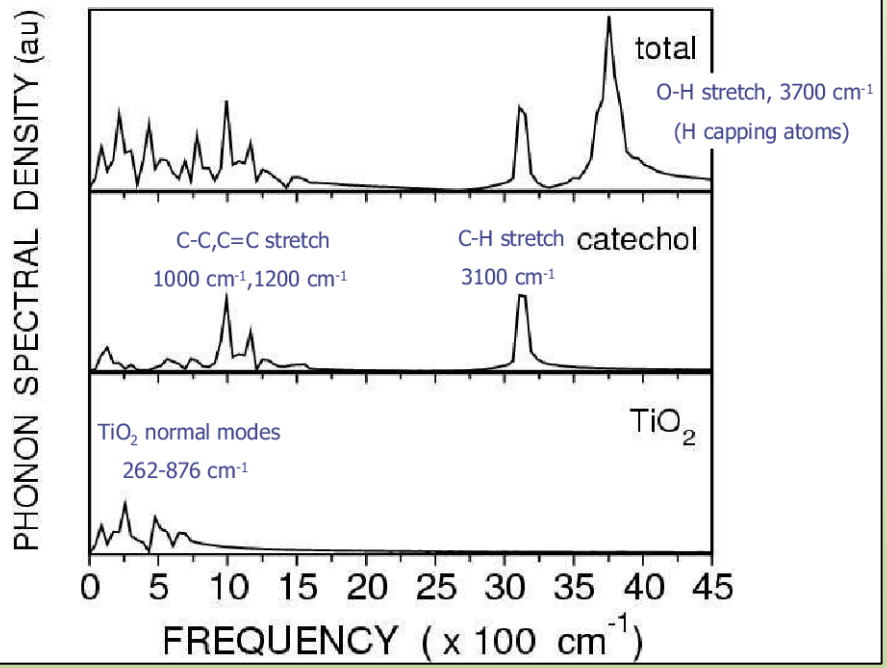
$$k_{inj} \sim \int dE \rho_{CB}(E) * \rho_A(E) * k(E)$$

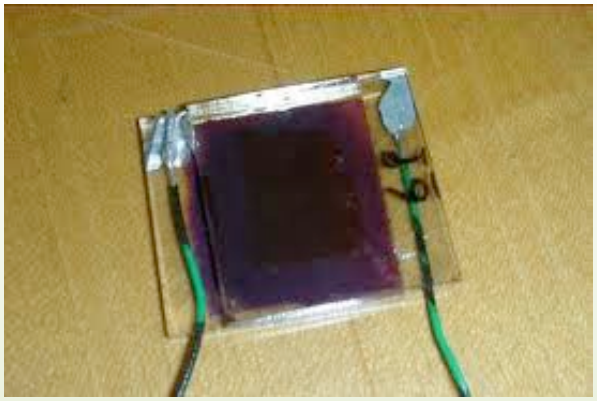
Electronic Density of States (1.2 nm particles)



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

Phonon Spectral Density





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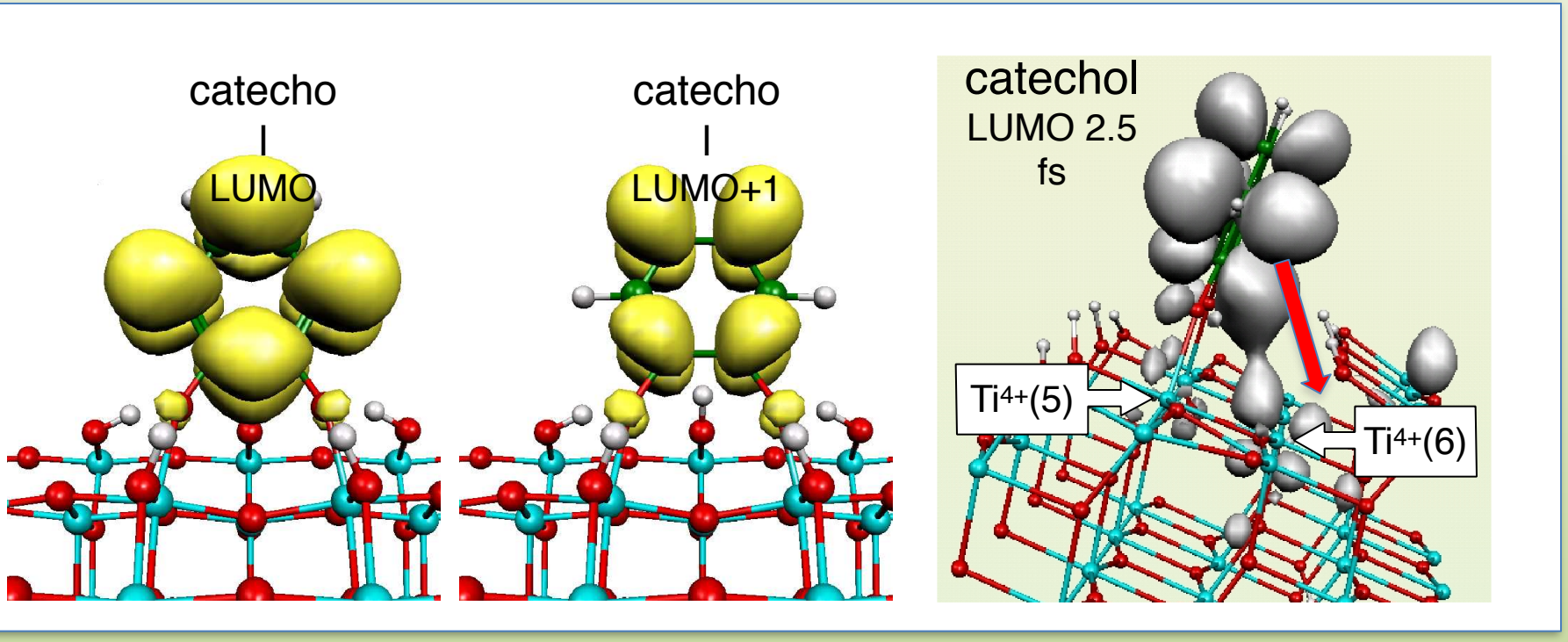
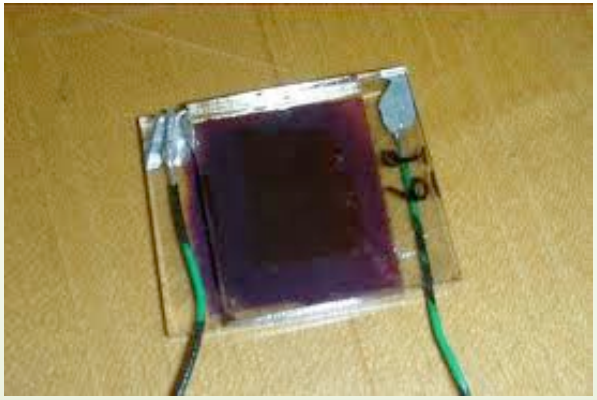
Ligand-to-Conduction Band Electron Transfer





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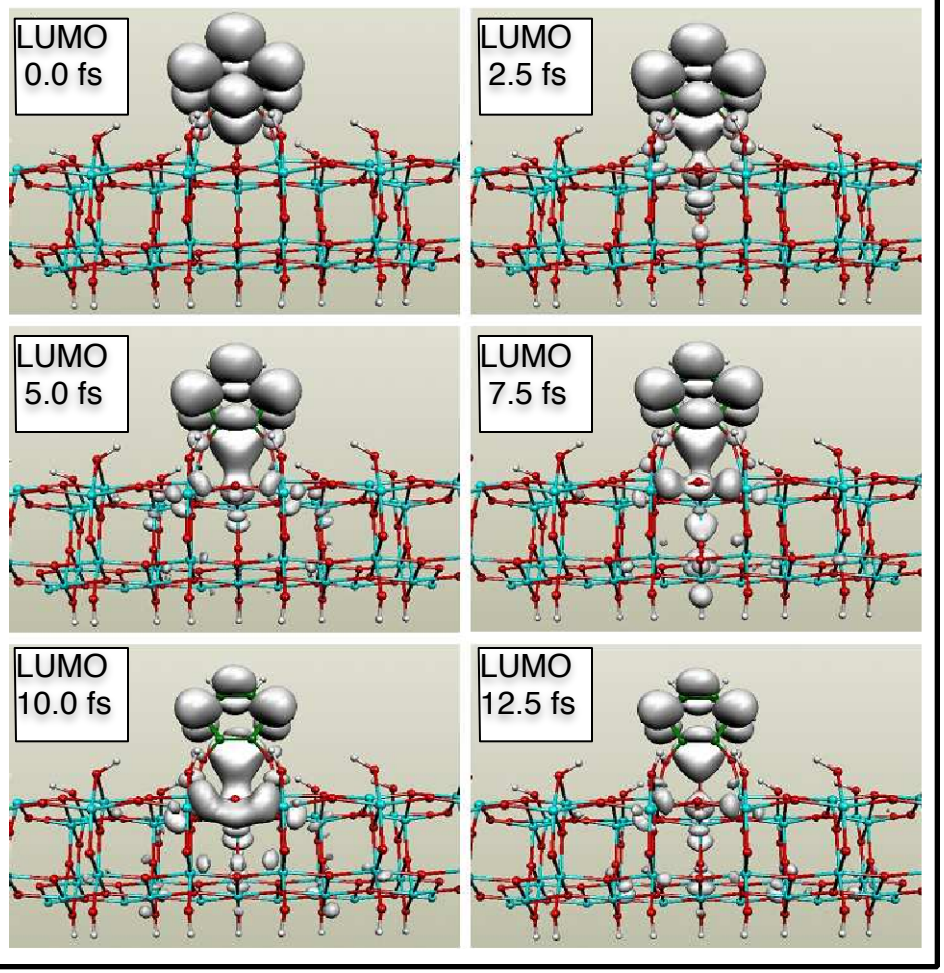
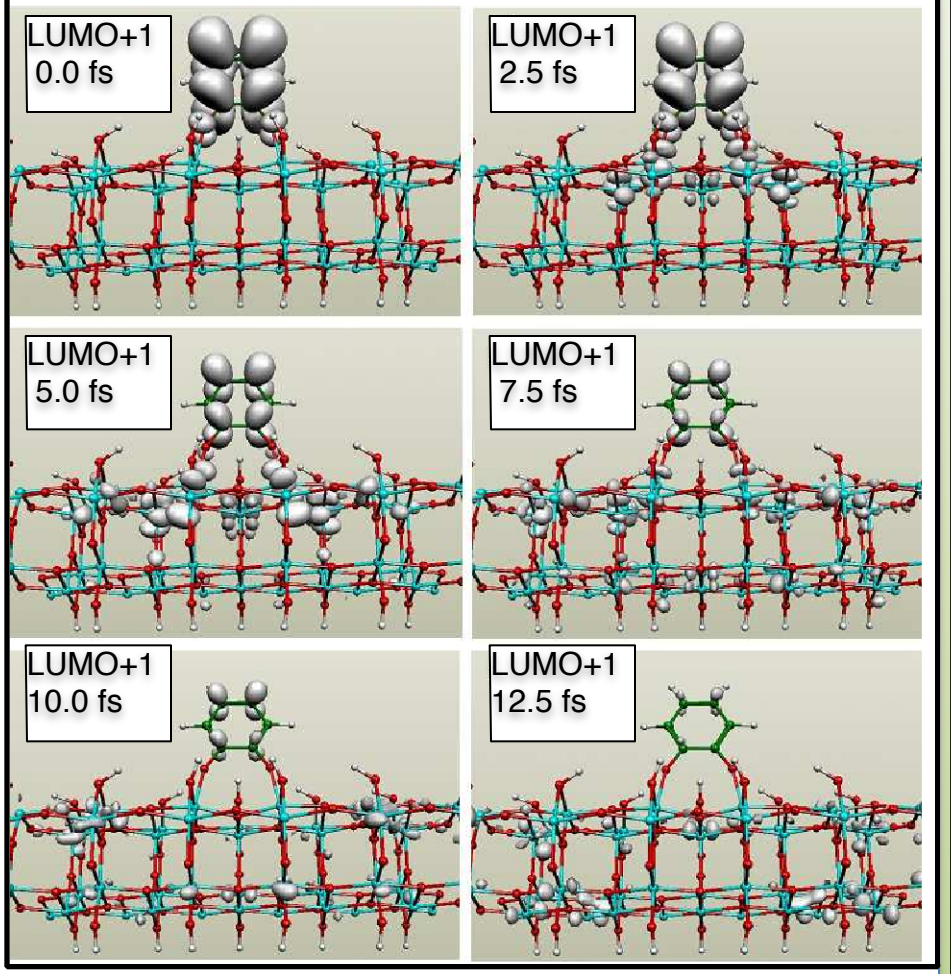
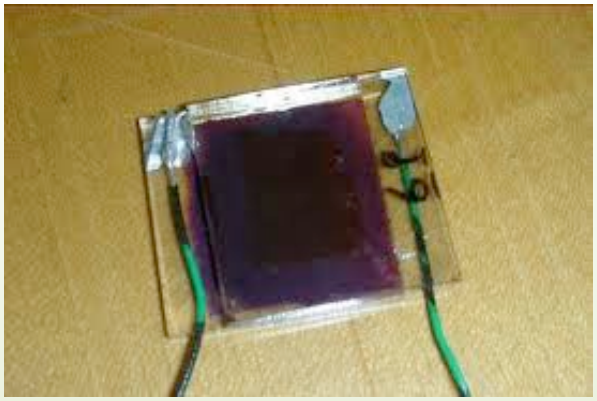
Ligand-to-Conduction Band Electron Transfer







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Ultrafast IET: Quantum Dynamics Simulations

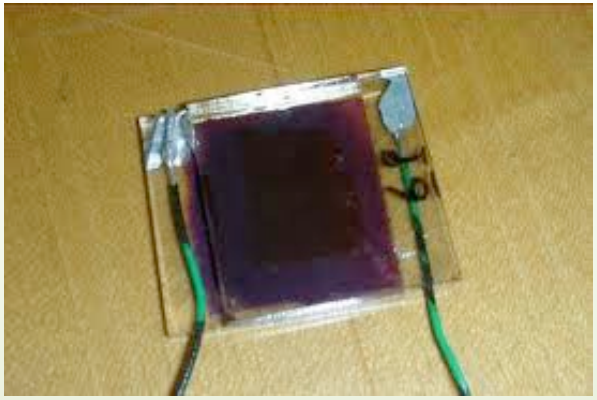
$\left|\Psi(t)\right\rangle = \hat{U}(t)\left|\Psi(0)\right\rangle$, where $\hat{U}(t) = e^{-\frac{i}{\hbar}\int H(t')dt'}$

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:

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



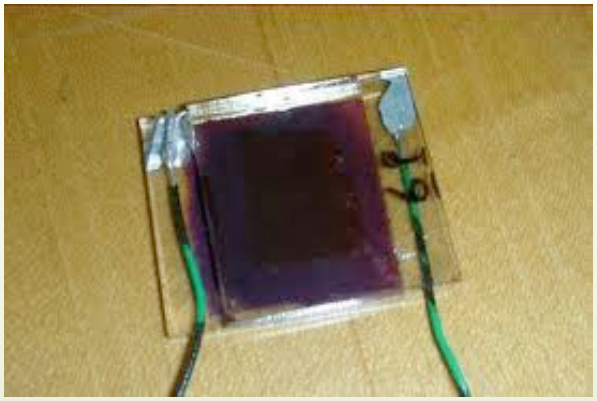
Modeling Dye-Sensitized Solar Cells

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

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



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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.