Ultrafast Investigations of Transition Metal-Based Complexes

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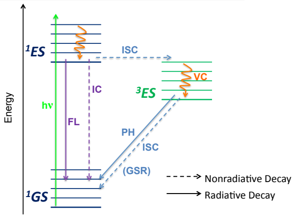
Fundamental Issues

Photophysical Processes

- General processes after photoexcitation (hν):
  - Molecule excited into ^{1}ES from ^{1}GS due to radiative coupling
  - ^{1}ES relaxes back to ^{1}GS via numerous pathways
  - Rates of these pathways are well established for organic systems: $k_{vib} >> k_{IC} >> k_{ISC}$
    - Not entirely clear if transition metal systems follow this order
- Ultrafast measurements track changes from initial excited state (starting point) to longest lived excited state (ending point)
  - Fully characterized before ultrafast measurements
- Questions of interest:
  - How long does it take the longest lived excited state to form?
  - What processes happen inbetween initial excitation and the formation of the longest lived state?
  - Can we identify and correlate geometric changes or electronic properties of molecules to these dynamics?
  - Given these things, can we make synthetic modifications to molecules to control these dynamics?

McCusker, J.K. *Acc. Chem. Res.* **2003**, *36*, 876.

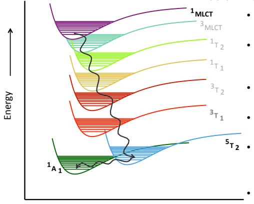


Jablonski Diagram of Photophysical Processes in Cr(III) showing only lower lying excited states.

GS = ground state, ES = Excited state, FL = fluorescence,
PH = phosphorescence, IC = internal conversion,
VC = vibrational cooling, GSR = ground state recovery

Complexes of Interest

Iron(II) Polypyridyls

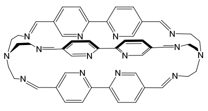


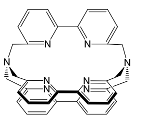
Potential energy surface diagram of excited states in Fe (II) complexes relative to the ground state.

- the ^{1}MLCT -> ^{5}T$_2$ relaxation is <100 fs for many Fe(II) polypyridyls
- ISC (long squiggly arrow), a ΔS = 2, is ultrafast because of strong coupling between excited states
- ^{5}T$_2$ has 0.2 Å increase in in the Fe-N bond length
- Relaxes to ground state (smaller arrow) through a torsional twist
- We found ^{1}MLCT -> ^{5}T$_2$ deactivation faster by blocking torsional twist, <50 fs

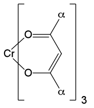
- *New investigation*: rigid cage ligands
- Restrict bond lengthening and twisting motion of excited states
- Possibly extend ^{1}MLCT lifetime?

- Synthesize cage ligands shown here and bind to Fe(II)
- Characterize both steady state and time resolved properties of both systems; especially ultrafast





Chromium(III) Acac Derivatives

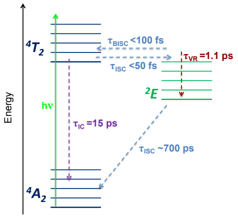


α = H, CH$_3$, CF$_3$, phenyl, cyclohexyl, t-butyl

acac: α = CH$_3$

- Electronically simple systems
- Allows for easy determination of excited state processes

- Previous ultrafast TA measurements on Cr (acac)$_3$ showed only signatures of ^{2}E state
- Experiments using a 50 fs pulse revealed the ISC event
- Oscillation in measurement gave active ligand scissoring motion during ISC (coherence!)



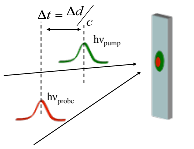
Jablonski diagram summarizing the nonradiative rates in the low-lying ligand field manifold of Cr(acac)$_3$.

- *New investigation*: changing methyl groups which move in scissoring motion
- Initial studies on series shows ISC slows down with bulkier groups in α position
- Further TA studies needed with short pulses for coherence measurements
- Use new longer delays in ultrafast TA to measure GSR

- Deuterated acac derivatives also of synthetic interest

Synthesis, Spectroscopy, and Theory

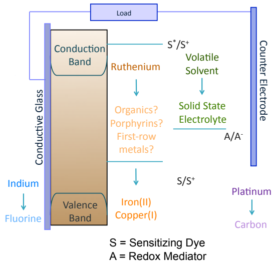
- Steady State Spectroscopies:
  - UV-Vis spectroscopy (absorption out of GS), emission spectroscopy (PH from ^{3}ES), electrochemistry (ox. and red. of GS), spectro-electrochemistry (spectroscopic signatures of ox. and red. species)
- Time-Resolved Spectroscopies:
  - Nanosecond transient absorption (TA) (absorption out of ^{3}ES) and variable temperature emission (time resolved PH out of ^{3}ES)
    - Timescales 13 ns and longer can be recorded
  - Femtosecond TA (absorption out of ^{1}ES and ^{3}ES)
    - Timescales from ~30 fs to 13 ns
      - New 30 fs pulse system; time delays to 1.2 ns
        - Coherence measurements
        - Anisotropy measurements (solvent relaxation)
        - Eventually fluorescence upconversion
      - New delay line on 120 fs system
        - Overlaps with ns system measurements
        - Eventually low temp TA



- Synthetic techniques commonly used:
  - Pfitzner-Moffat Oxidation, Riley Oxidation, TEMPO Oxidation
  - Khronke Ring Cyclization for pyridyl systems
  - Transition metal catalyzed reactions
  - Schlenk line techniques
  - Inert atmosphere dry box syntheses
- Characterization via:
  - ^{1}H and ^{13}C Nuclear magnetic resonance spectroscopy
  - Infrared spectroscopy
  - Electrospray mass spectrometry
  - Elemental analysis
  - X-ray crystallography
- Calculations via:
  - *Gaussian 03*
  - *Solid-G* (Developed at the University of Wisconsin-Madison)
  - *SolidAngleGL8*

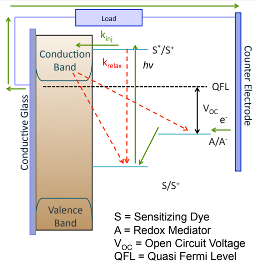
Applications

Alternative Materials in Dye-Sensitized Solar Cells



S = Sensitizing Dye
A = Redox Mediator

- Dye-Sensitized Solar Cells (DSSCs) have shown great promise and improvements since their introduction.
- The most efficient and most widely studied cells and materials have included rare and expensive elements.
- Further development of DSSCs is based on strategies that employ earth-abundant materials.



S = Sensitizing Dye
A = Redox Mediator
V_{OC} = Open Circuit Voltage
QFL = Quasi Fermi Level

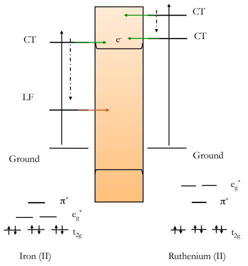
- Photon absorption results in a metal-to-ligand charge transfer (MLCT) excited state.
- Electron injection initializes current through the cell to the counter electrode.
- A redox mediator in solution shuttles electrons from the counter electrode to the oxidized sensitizer.
- Efficiency improving processes are shown in green, efficiency decreasing processes in red.
- k_{inj} must compete effectively with k_{relax}.

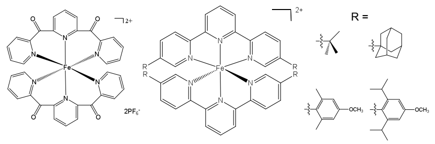
Designing Sensitizers

Desirable characteristics: Absorb well in sun's spectral region, MLCT excited state that is long lived and above the CB in energy, good electronic coupling to the semiconductor.

Iron(II)-based Sensitizers

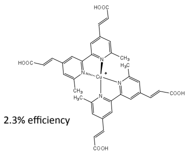
- Ultrafast deactivation of the injecting charge transfer states to low lying ligand field (LF) states result in low injection yields.
- 'Hot injection' is required in iron(II) dyes since LF states are too low in energy for injection to occur.
- Extension of the electron injecting state lifetime is the objective.
- It has been shown that the rate of ultrafast deactivation can be modulated with ligand variations.
- Work is currently underway to introduce anchoring groups to select structures to determine applicability for use in DSSCs.



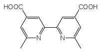


Copper(I)-based Sensitizers

- Cu(I) molecules have MLCT excited states which would be capable of injecting into a semiconductor.
- A handful of Cu(I) bpy-based sensitizers have been incorporated into full DSSCs with modest success. The highest efficiency to date is 2.3% in fully optimized cells.
- Our group will study the individual properties of the sensitizer in solution as well as its injection dynamics on thin films.

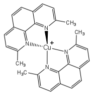


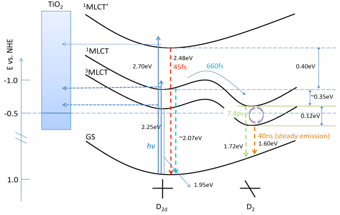
2.3% efficiency



1.9% efficiency

Bessho, T., *et al.* **Chem. Commun.**, 2008, 3717-3719.

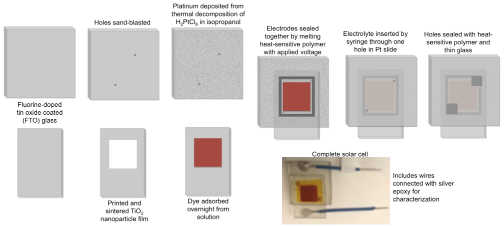




Solar Cell Fabrication and Characterization

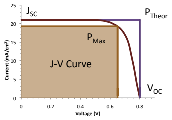
Thermodynamics and conversion efficiencies will be measured in order to forge a link between the steady-state and time-resolved spectroscopic properties of the cells with their performance metrics as a means of identifying which aspects of cell performance require the greatest attention in order to improve overall efficiency.

Fabrication Method



Characterization Techniques

- Energy Conversion Efficiency
  - J-V curve
  - Incident Photon-to-Current Efficiency measurements
- Investigation of Films
  - Transmission Electron Microscopy
  - Scanning Electron Microscopy
  - Ellipsometry
  - Electrochemical Impedance Spectroscopy



$$\eta = \frac{V_{OC} \times J_{SC} \times FF}{P_{in}}$$

J_{SC} = Short Circuit Current Density
V_{OC} = Open Circuit Voltage
P_{Max} = Maximum Power Out
P_{Theor} = Theoretical Power Out
P_{in} = Incident Power
FF = Fill Factor = P_{Max}/P_{Theor}