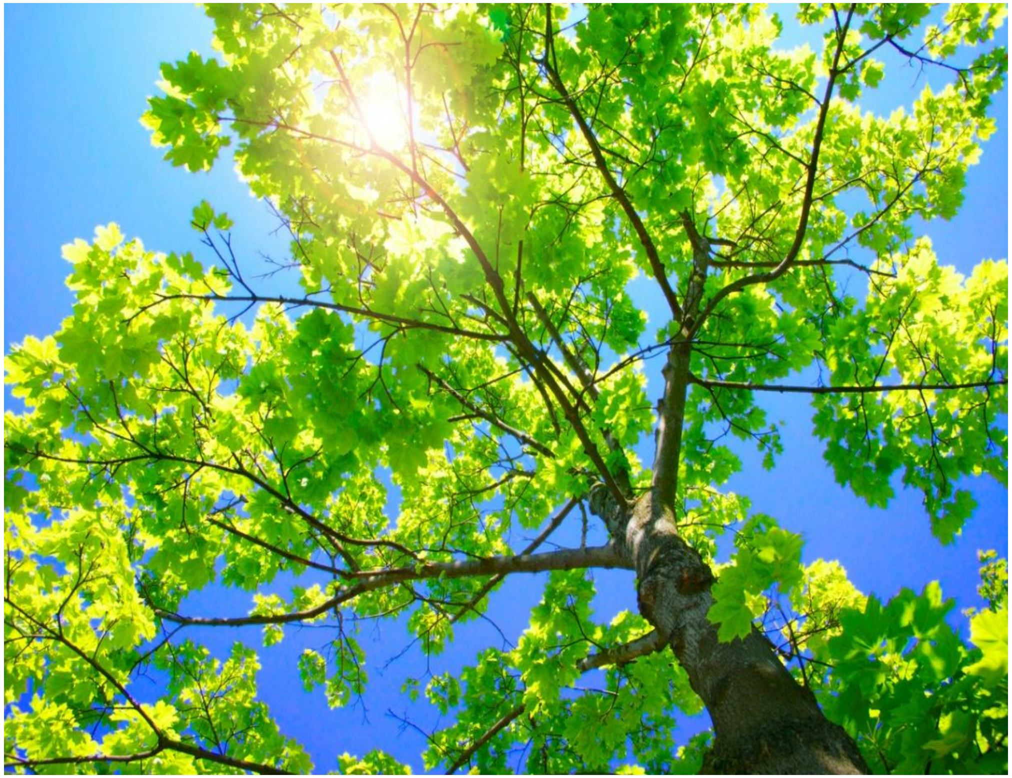
Utilizing Nature's Designs for Solar Energy Conversion

Learn from Nature…



…build with chemistry

ANL Photosynthesis Group

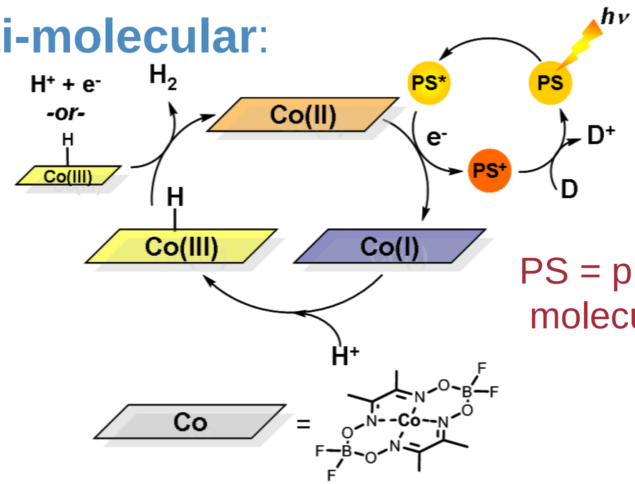
Fundamental Studies

- Solar energy conversion in natural and artificial photosynthesis
  - *Resolve mechanisms, design principles*
- Unique capabilities
  - *Time-resolved, multi-frequency EPR*
  - *Time-resolved synchrotron X-ray*
  - *Ultrafast spectroscopy*

Create new materials that:
capture, convert, store sunlight

Artificial systems for H_2 *photo*catalysis

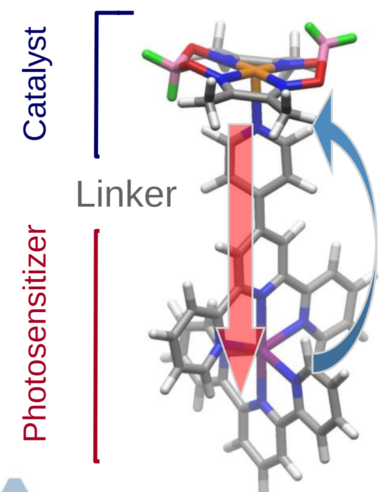
Multi-molecular:



PS = photosensitizer molecule

Supra-molecular:

Linked Molecular Modules



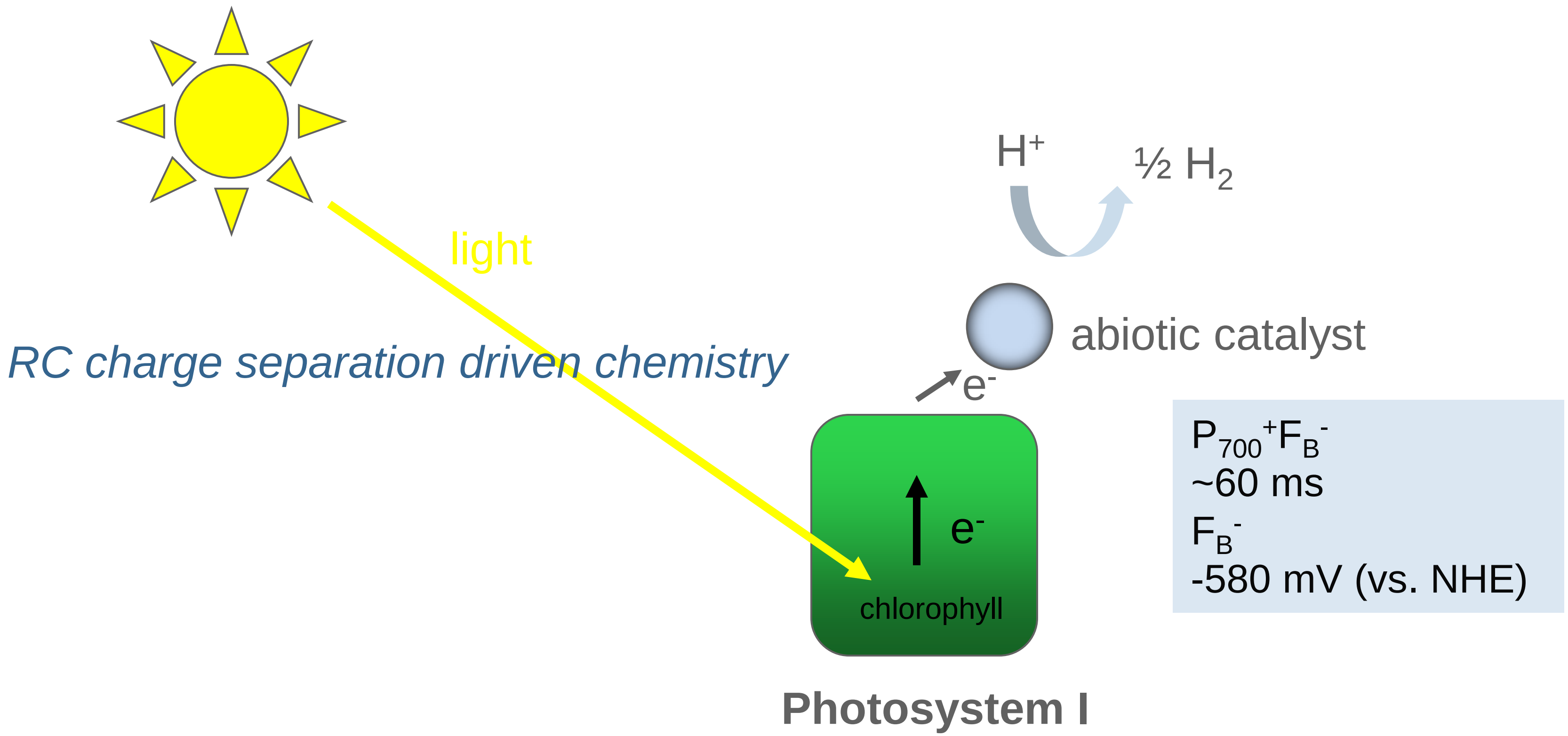
Axial Linkage

- Solution heterogeneity
- Path for fast back ET

- **Limitations:**
  - Large solvent, molecular dependencies
  - Diffusion
  - Lifetimes
  - Uncontrolled back-reactions
  - Most PS contain noble metals
  - Organic solvent/high proton requirements.

Fihri, et. al. *Angew. Chem. Int. Ed.* **2008**, 47, 564
Mulfort, Tiede. *J. Phys. Chem. B*, **2010**, *114,* 14572.

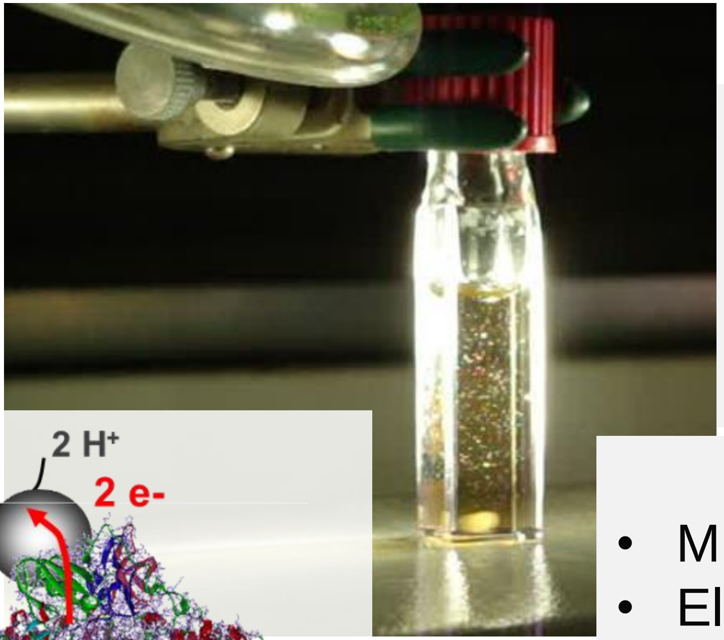
Biohybrids for Solar Hydrogen Production

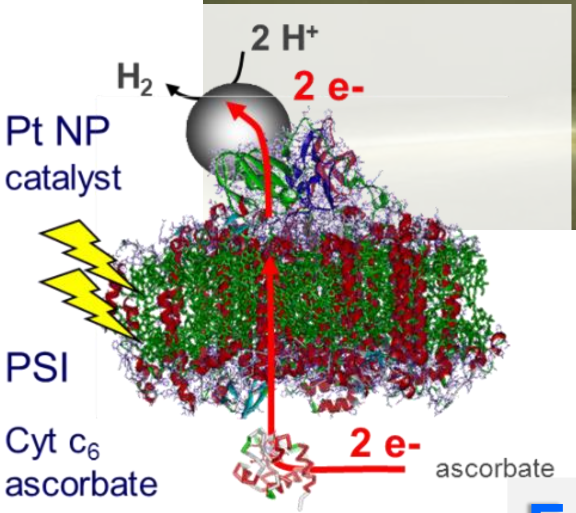


Fundamental Scientific Challenges:

- Efficient coupling of photons to fuels
- Sustainable
- Cheap processing, scalable

ANL Photosystem I-Pt Nanoparticle hybrid





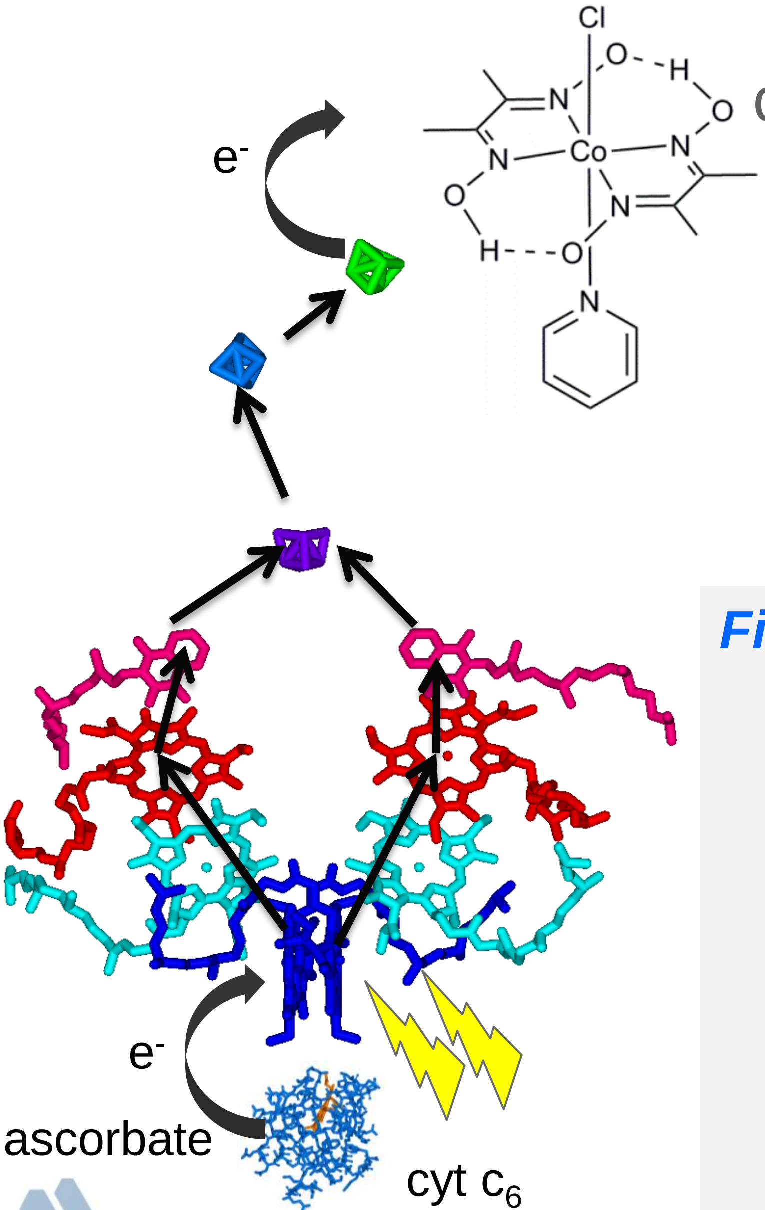
- Noncovalent, Self-Assembly
- Native Photosystem I
- Best PSI-Pt photo H_2 evolution to date
- Out performs currently reported rates for photosensitizer-catalyst systems

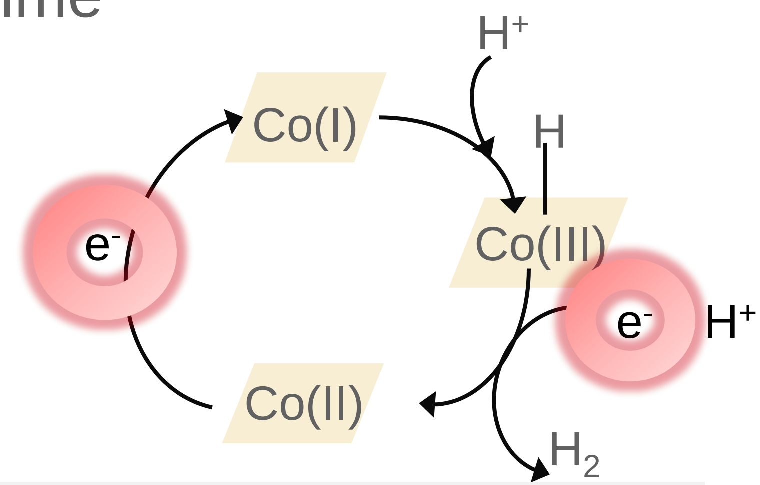
- Mimic acceptor protein
- Eliminate paths for fast charge recombination?
- Direct wire to cofactor not necessary

Functional ↔ Spectroscopy ↔ Mechanism

L. M. Utschig, et. al. *J. Phys. Chem. Lett.* **2011**, *2*, 236-241

Photosystem I- transition metal catalyst hybrids





First-of-a-kind hybrid that combines:

Synthetic molecular catalyst:

- first-row transition metal
- inexpensive, earth abundant
- O_2 tolerant
- enables tunability

Nature’s Reaction Center Proteins:

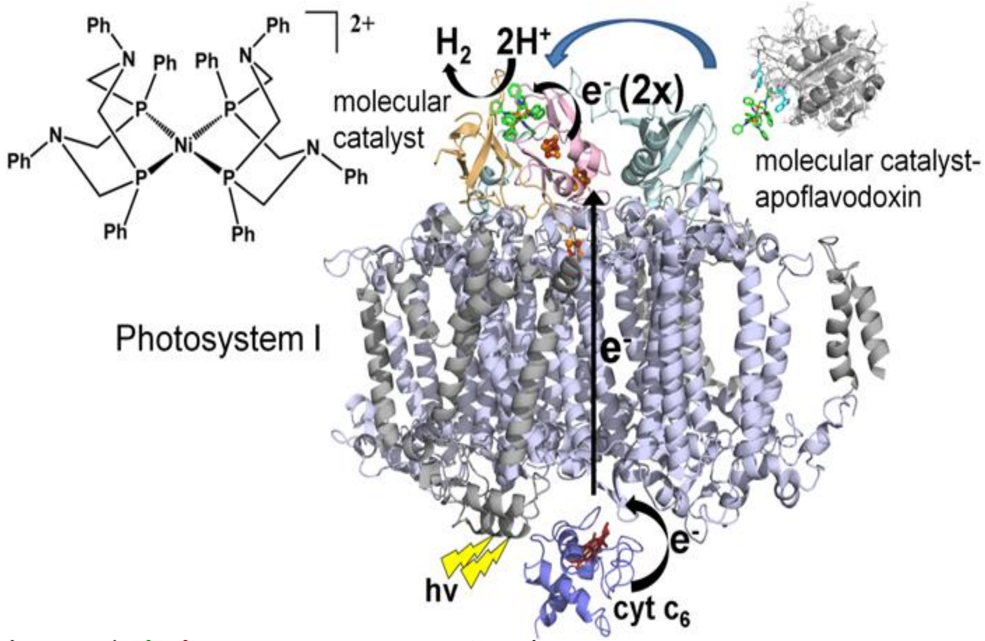
- optimized solar capture and conversion

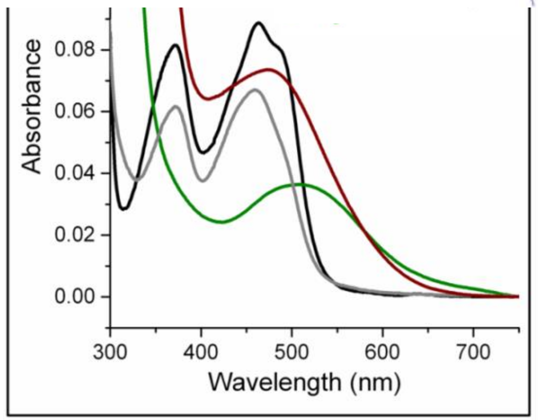
Rapid, light-induced* H_2 *Production

- out-performs artificial systems
- completely aqueous

L. M. Utschig, S. C. Silver, K. L. Mulfort, D. M. Tiede *J. Amer. Chem. Soc.* **2011,** *133*, 16334-16337

Protein directed delivery of catalyst to PSI





Issues: catalyst stability
where & how bind to PSI

Ni-PSI and Ni-apoFld + PSI:

- 10^2 x H_2 evolution rate vs. reported photosensitizer system
- Unprecedented chemistry for Ni diphosphine catalyst
- Protein stabilization of catalyst
- Strategy for self-repair
- EPR spectra of Ni(I)/protein

S. C. Silver, J. Niklas, P. Du, O. G. Poluektov, D. M. Tiede, L. M. Utschig *J. Amer. Chem. Soc.*, **2013**, *135, 13246-13249*

Solar Energy Conversion Group

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Lin Chen/Ultrafast optical & XAFS

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