Biomimetic Production of Hydrogen

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Where Do We Get Hydrogen?

- Steam reforming of natural gas – most used
  - $CH_4 + H_2O \rightarrow CO + 3H_2$
  - $CO + H_2O \rightarrow CO_2 + H_2$

  - $CH_4 + 2H_2O \rightarrow CO_2 + 4H_2$

  Electrons and energy from fossil fuels

- Electrolysis of water – most obvious
  - $H_2O \rightarrow H_2 + \frac{1}{2}O_2$

  Energy from fossil fuels

- Other methods

Where Do We Get Hydrogen?

- The energy and some of the materials for today's hydrogen production come from (ancient) photosynthesis.
- Photosynthesis transduces solar energy into more useful forms.
- Thus, the energy content of most of the hydrogen we use today came from sunlight, via photosynthesis.

Biomimetic Hydrogen Production

- For the future, solar energy is the only renewable source abundant enough to fill humanity’s energy needs.
- Why not apply photosynthetic principles to solar production of hydrogen?
- There are two ways to do this:
  - Use living systems to make hydrogen
  - Design artificial systems that mimic the basic chemistry and physics of the biological process

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plains and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but that will have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

Giacomo Ciamician

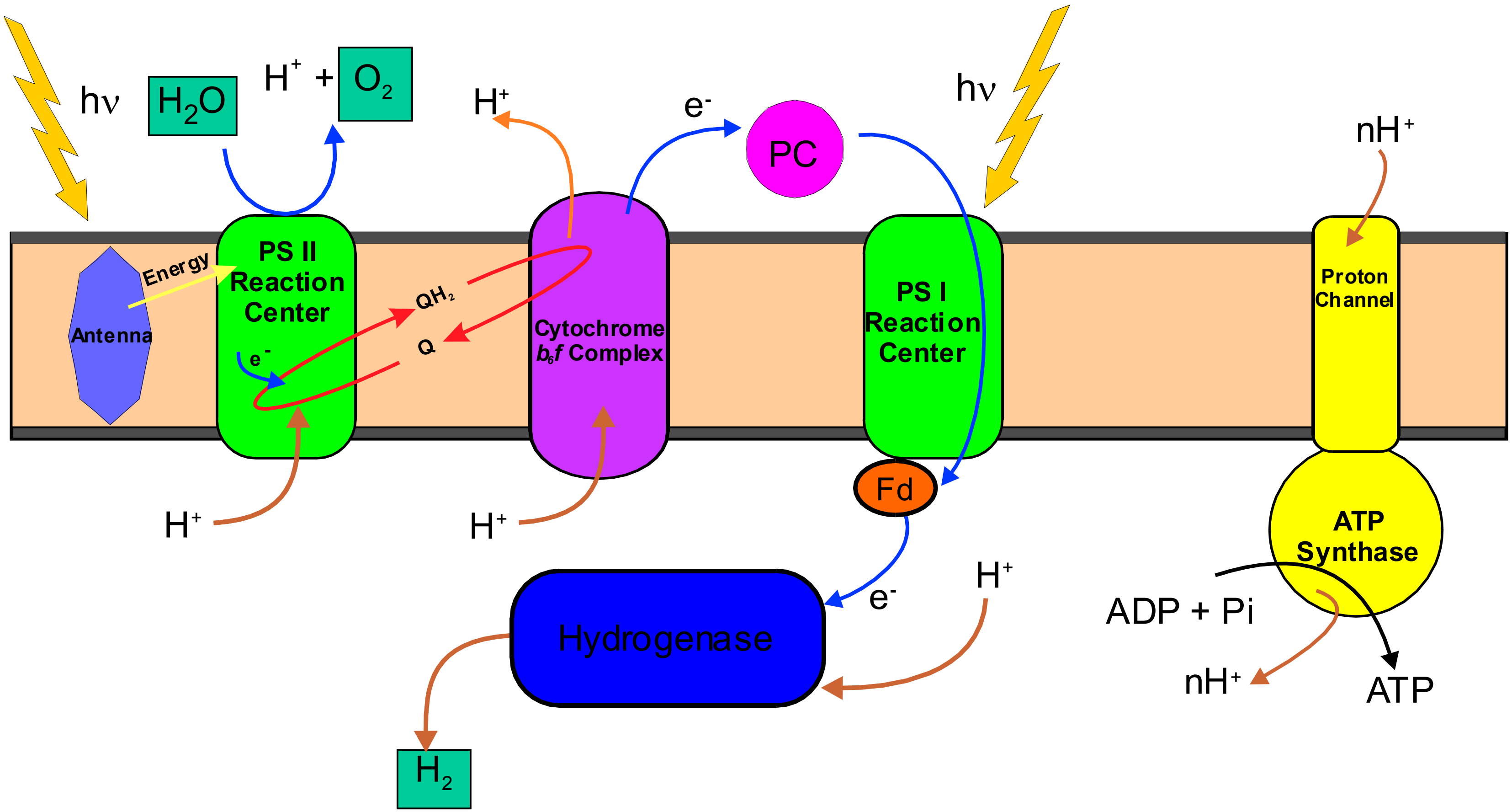
Science **36,** 385 (1912)

Biological Hydrogen Production

- Many different organisms can produce hydrogen. Two classes that draw energy directly from sunlight are:
  - Microalgae and cyanobacteria – “direct biophotolysis” resulting in water splitting
  - Purple bacteria – “photofermentation” using sunlight and oxidizing organic compounds

Microalgae and cyanobacteria

$$H_2O \rightarrow H_2 + ½O_2$$



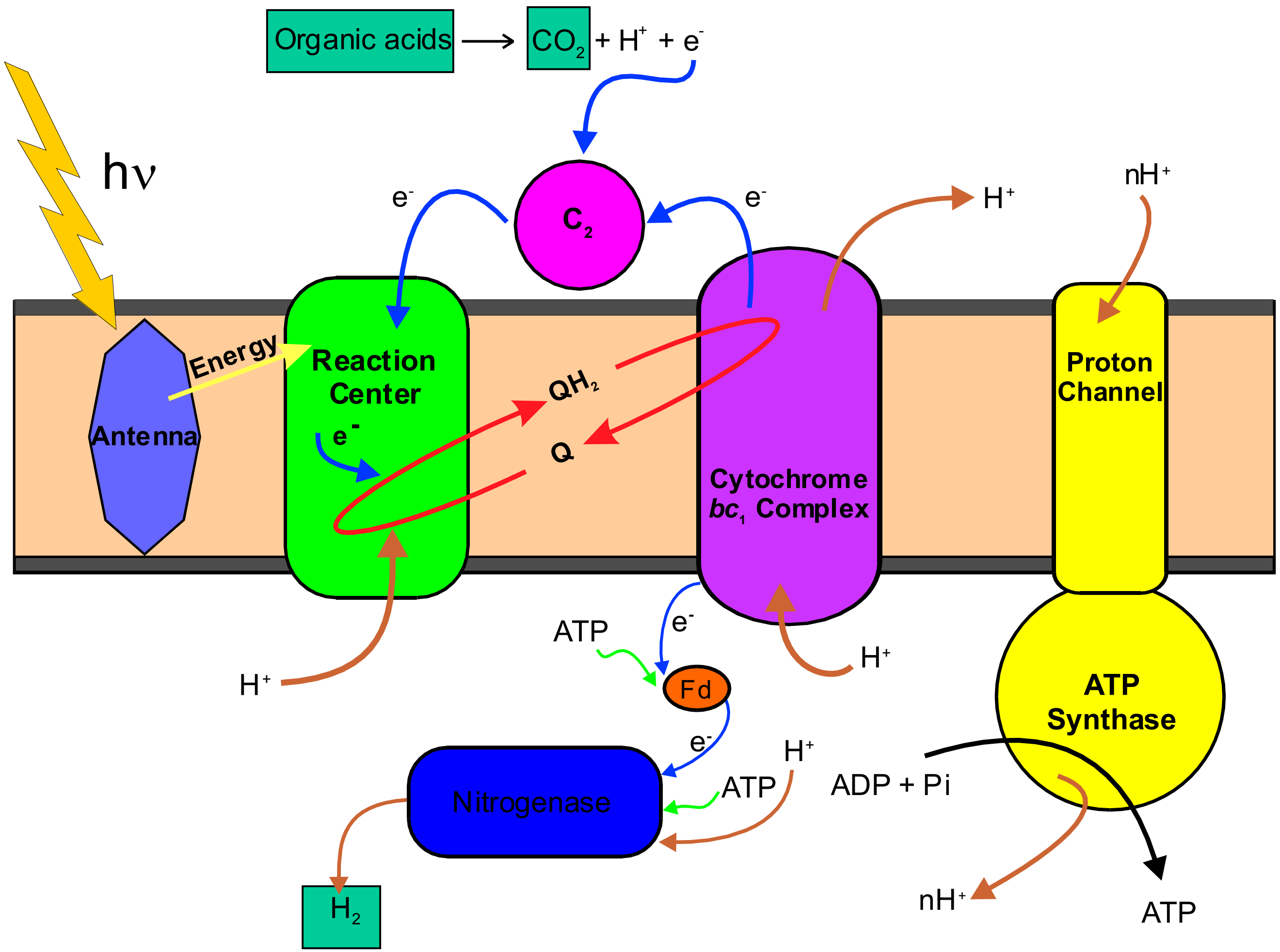
Biological analog of electrolysis

Limitations of Direct Biophotolysis

- Efficiencies are low.
- Oxygen is produced, but hydrogenase does not function in presence of oxygen.
- Possible improvements
  - Separate O_2 and H_2 production temporally.
  - Separate O_2 and H_2 production spatially. (heterocystous cyanobacteria).
  - Use molecular biology to develop hydrogenases that are more oxygen tolerant and more efficient.

Purple Bacteria

$$C_2H_4O_2 + 2H_2O \xrightarrow{h\nu} 2CO_2 + 4H_2$$



Biological analog of steam reforming

Limitations of Photofermentation

- Efficiencies are low.
- Hydrogenase does not function in presence of oxygen (but system is always anaerobic).
  - Produces carbon dioxide, instead of oxygen
  - Inhibited by ammonium ions
  - Requires ATP, thus lowering efficiency
- Possible improvements
  - Find organisms with higher efficiencies.
  - Use molecular biology to develop nitrogenases that are more efficient.

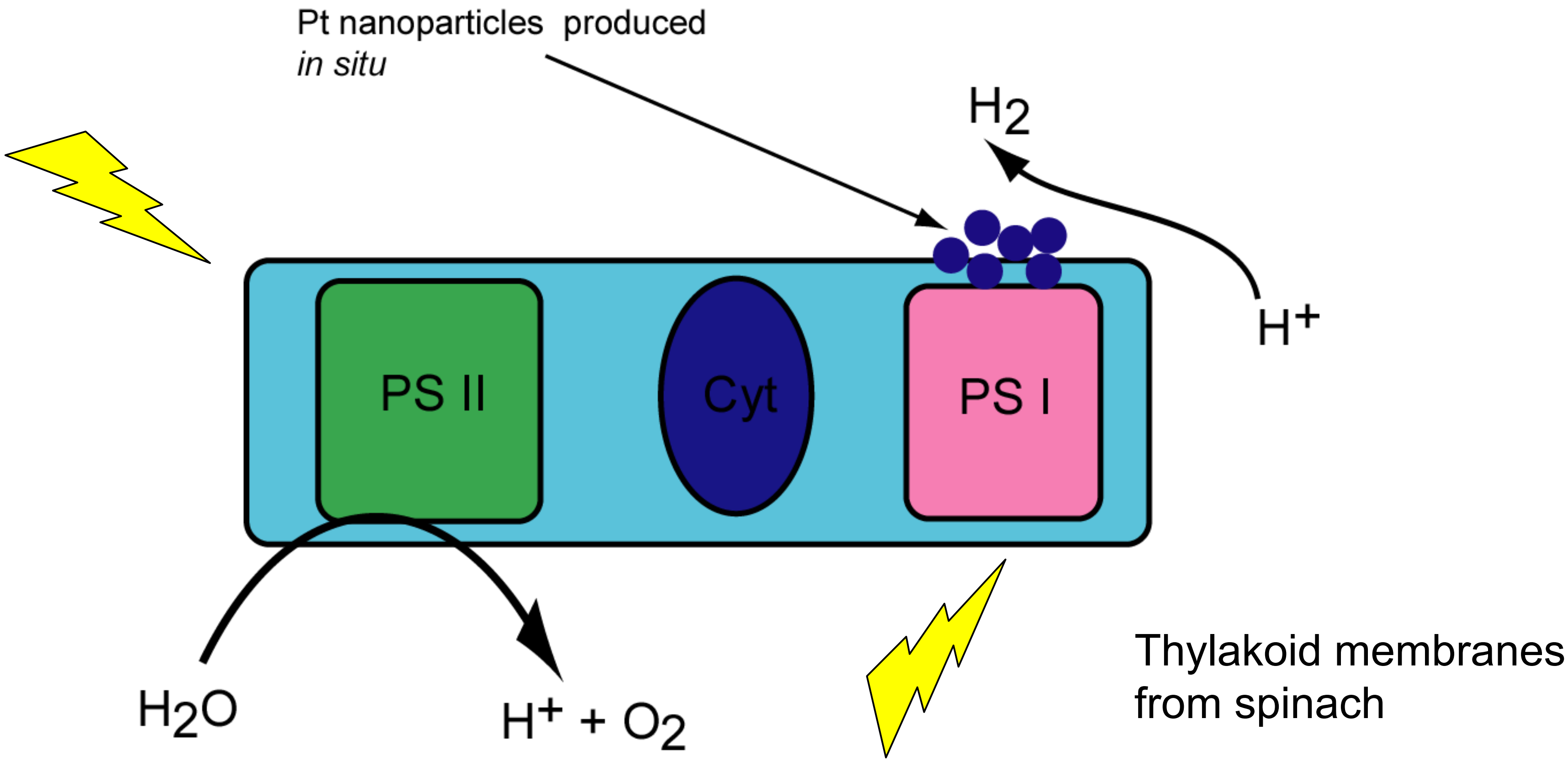
Biomimetic Approach

- Mimic the conversion of light energy into electrochemical redox potential (photosynthetic antenna-reaction center system)
- Use the oxidation potential to oxidize some source of electrons
  - Water
  - Fixed carbon
- Use the reduction potential to make hydrogen from hydrogen ions

Possible Designs

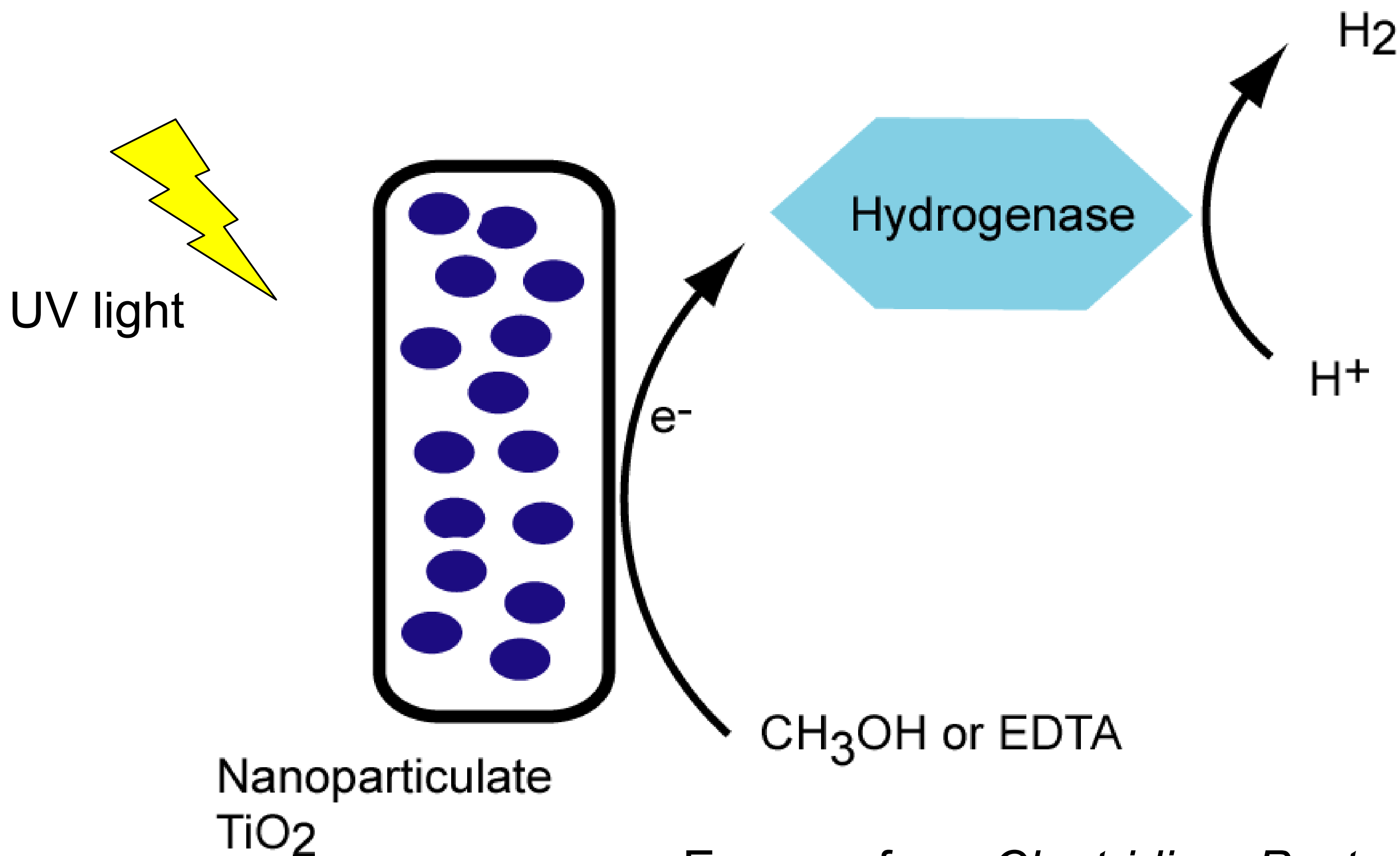
- "Bionic" systems that use a combination of synthetic materials and natural enzymes
- Purely synthetic biomimetics

"Bionic" Hydrogen Production



E. Greenbaum and coworkers, *Science*, **1985**, *230,* 1373; *Energy and Fuels*, **1994,** *8,* 770. See also P. Cuendet and M. Gratzel, *Photobiochem. Photobiophys.* **1981,** *2,* 93.

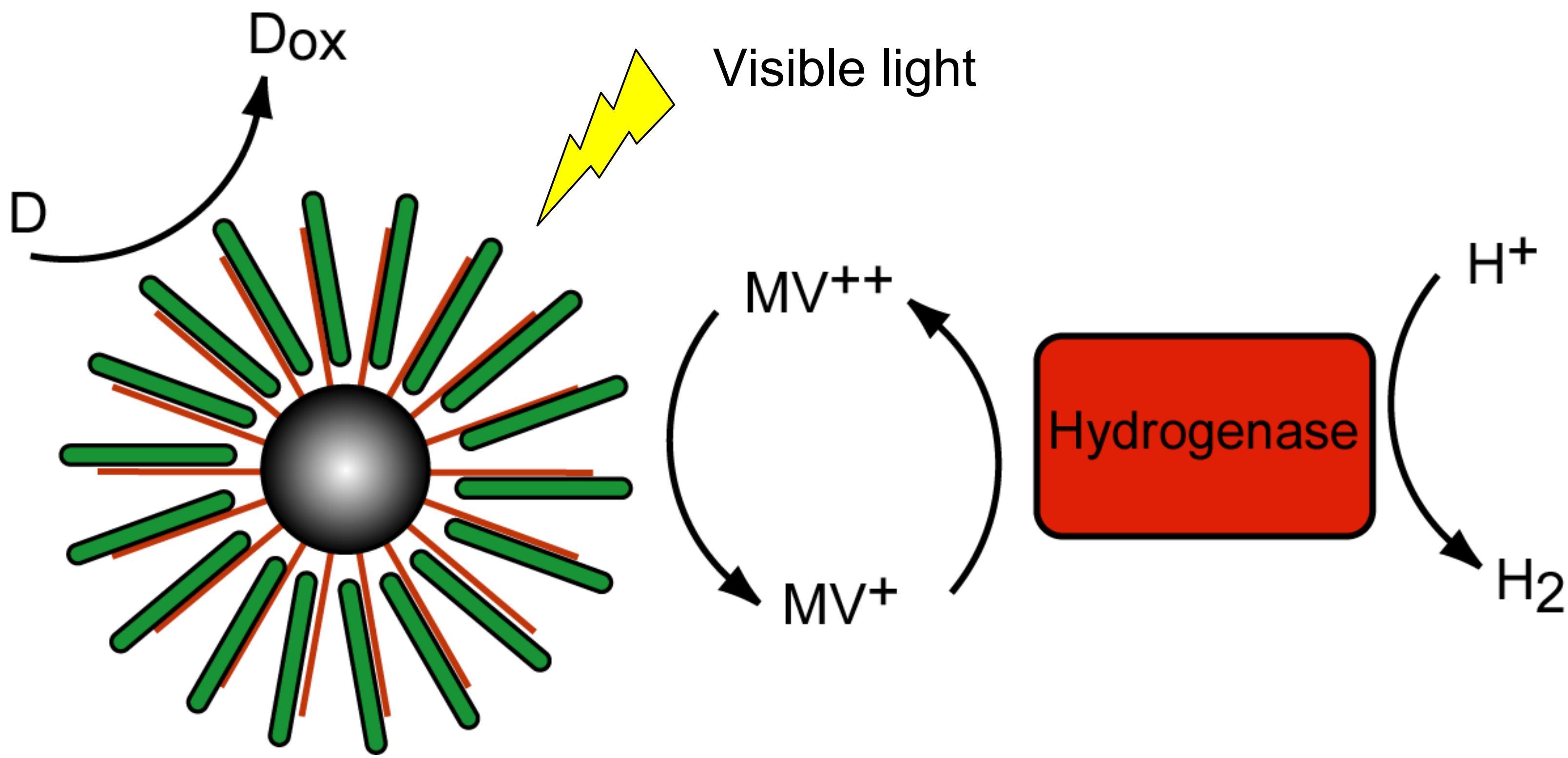
"Bionic" Hydrogen Production



Enzyme from *Clostridium Pasteurianum*

David O. Hall, M. Grätzel and coworkers, *Biochimie*, **1986**, *68*, 217.

"Bionic" Hydrogen Production

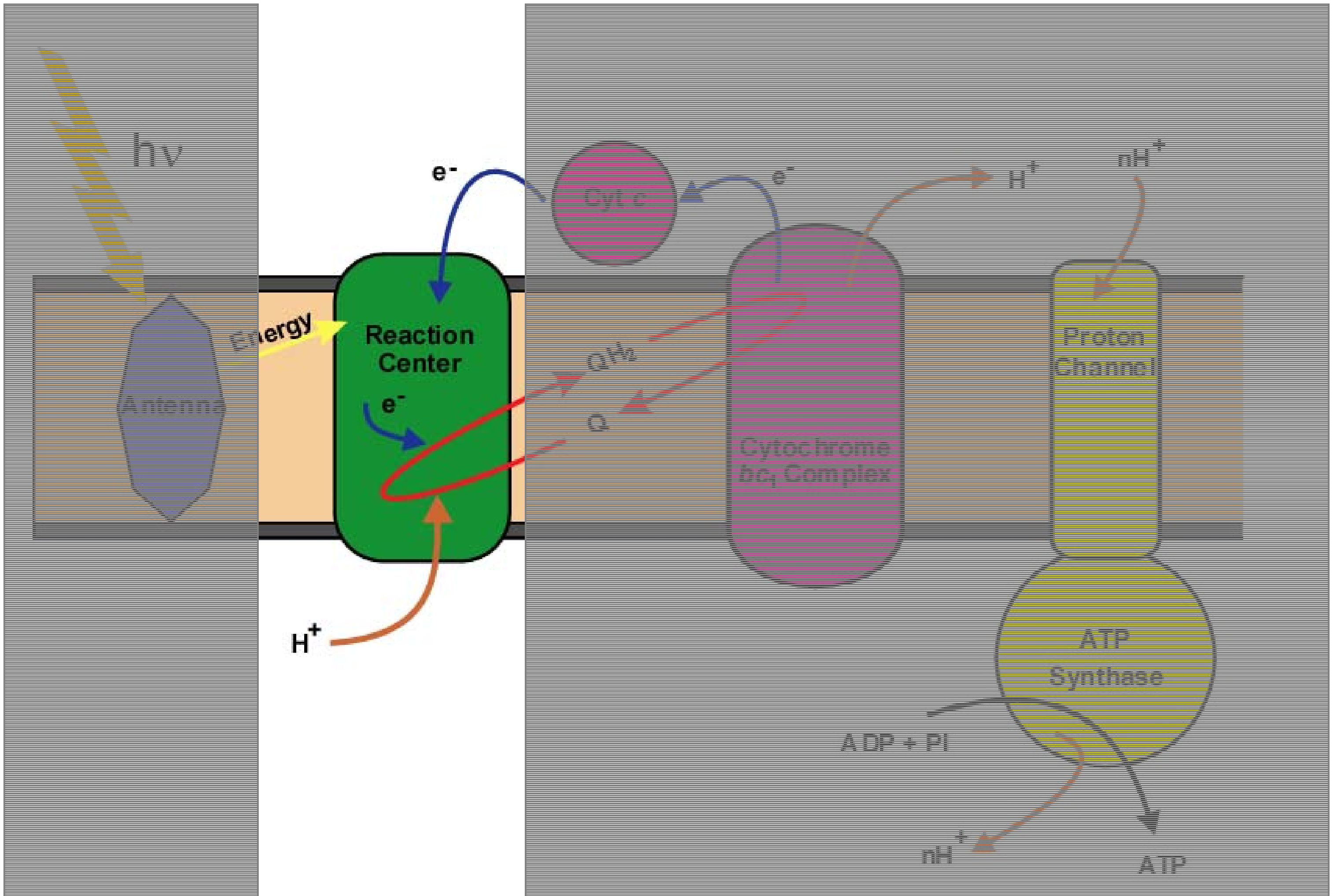


Zinc porphyrin – peptide dendrimer

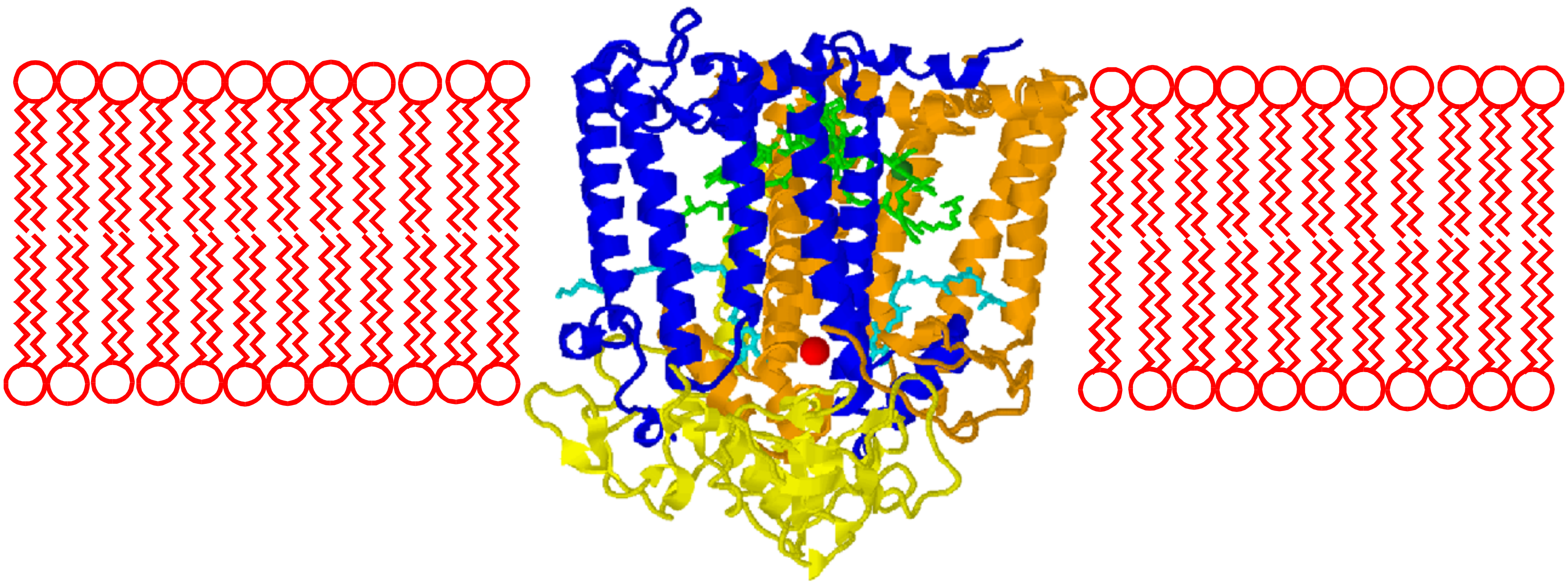
M. Sakamoto, *et al.*, *Biopolymers,* **2001,** *59,* 103.

Purely Synthetic Approach

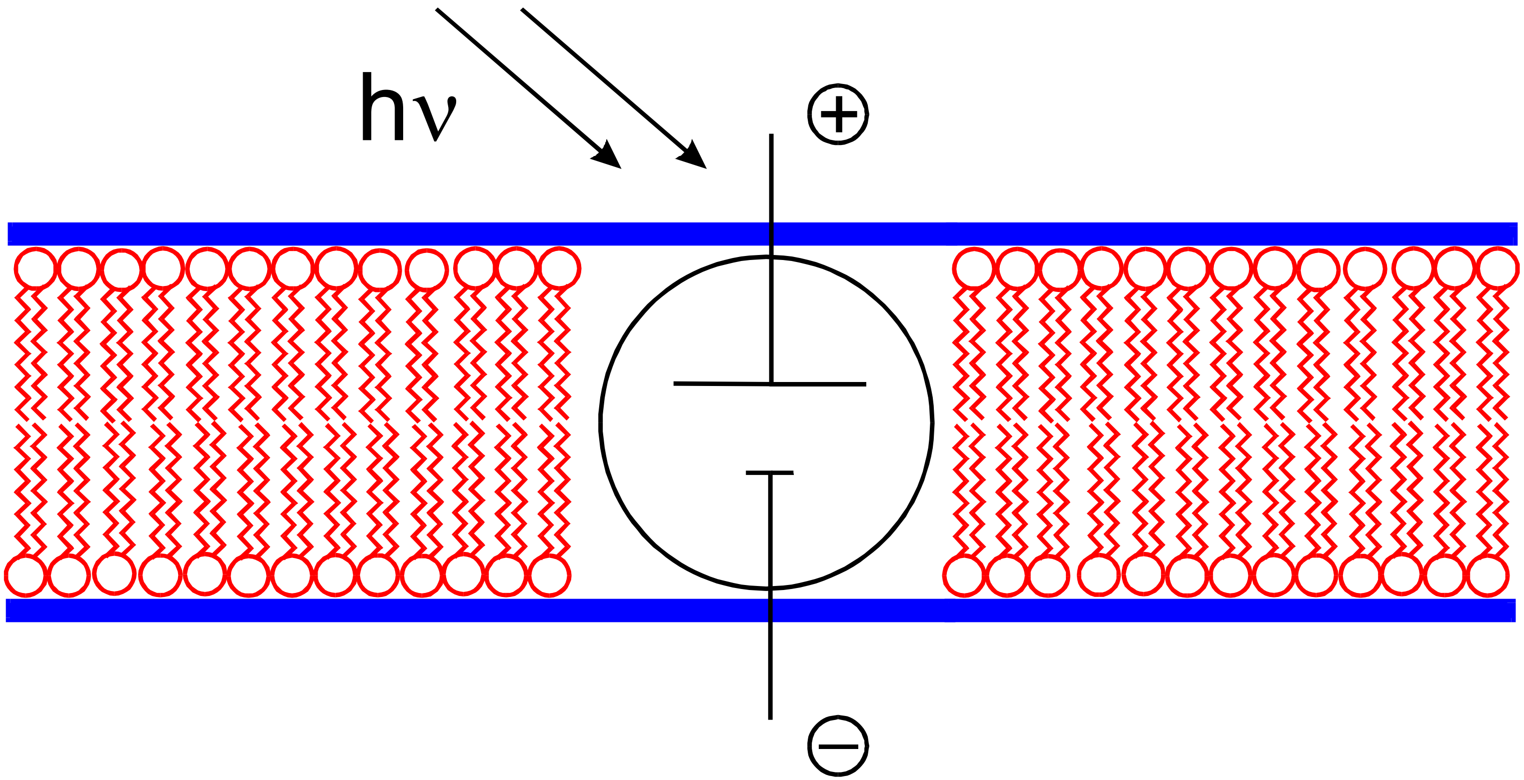
Mimicking the Reaction Center



Bacterial Photosynthetic Reaction Center



A Molecular Photovoltaic



Artificial Reaction Centers

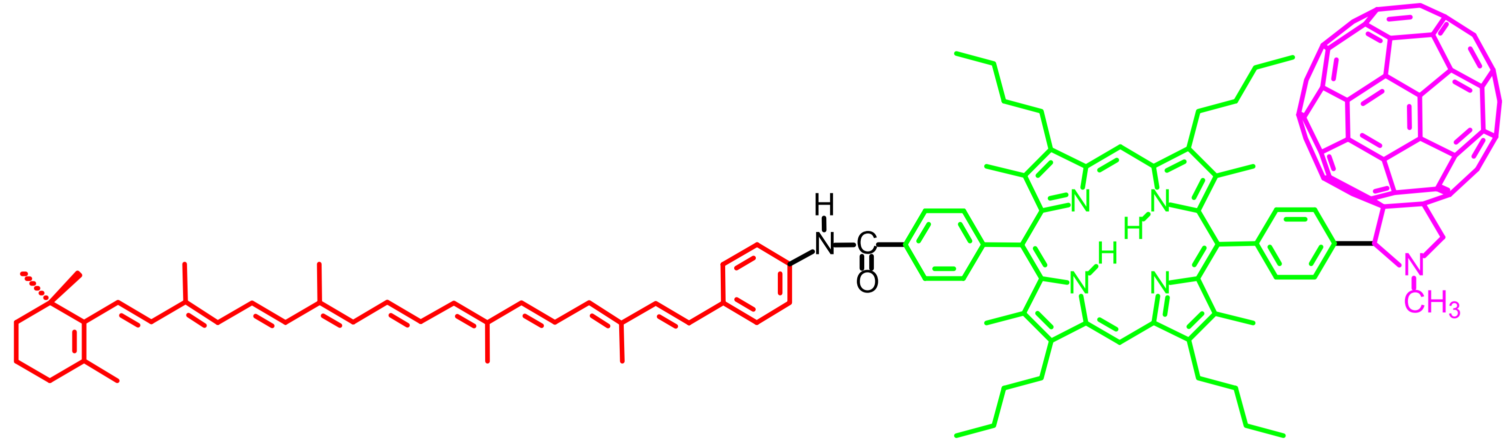
- Basis is photoinduced electron transfer

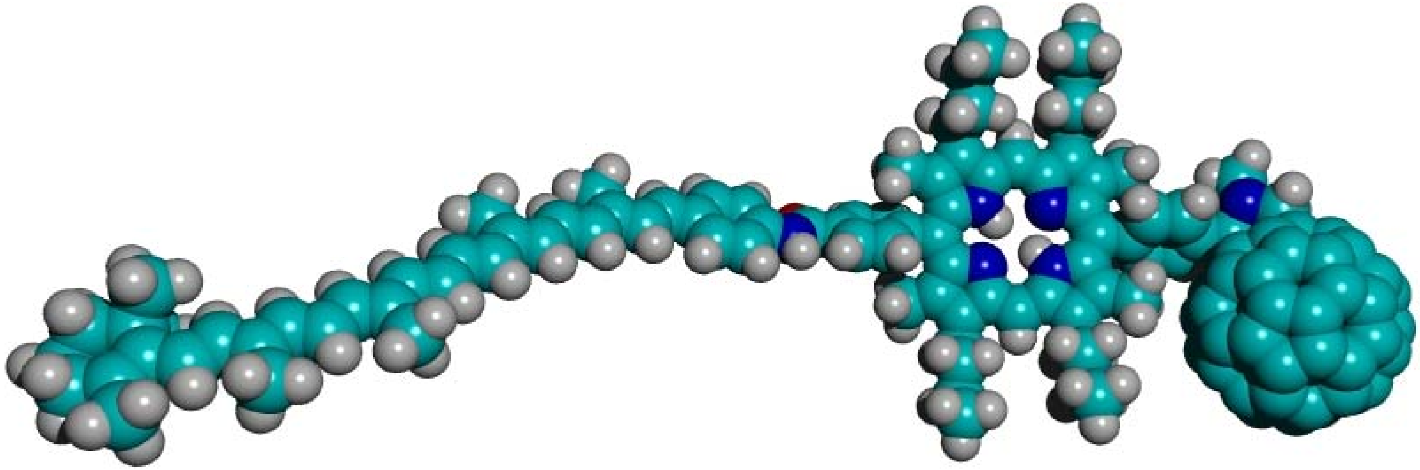
$$\text{D-A} \xrightarrow{h\nu} {}^{1}\text{D-A}$$

$${}^{1}\text{D-A} \rightarrow \text{D}^{\bullet+}\text{-A}^{\bullet-}$$

- Minimum requirements
  - Donor chromophore
  - Suitable electron acceptor
  - Electronic coupling
- Useful systems require more complexity

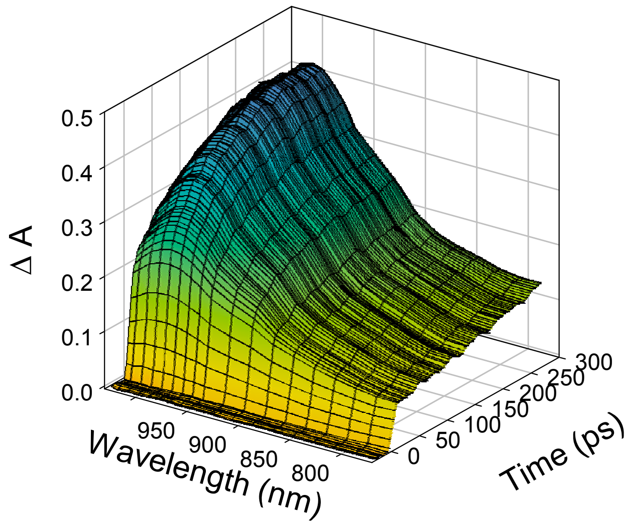
A Carotenoporphyrin-Fullerene Triad



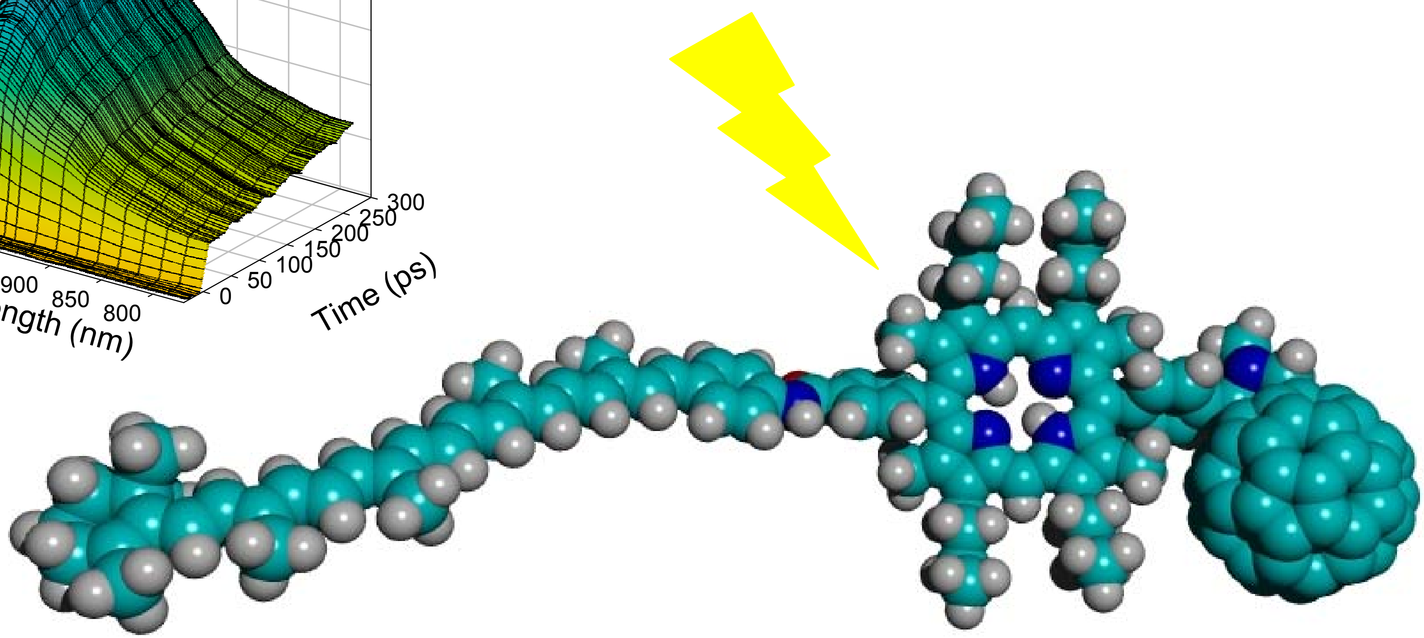


Liddell, P. A.; Kuciauskas, D.; Sumida, J. P.; Nash, B.; Nguyen, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1997**, *119*, 1400-1405

Light Absorption

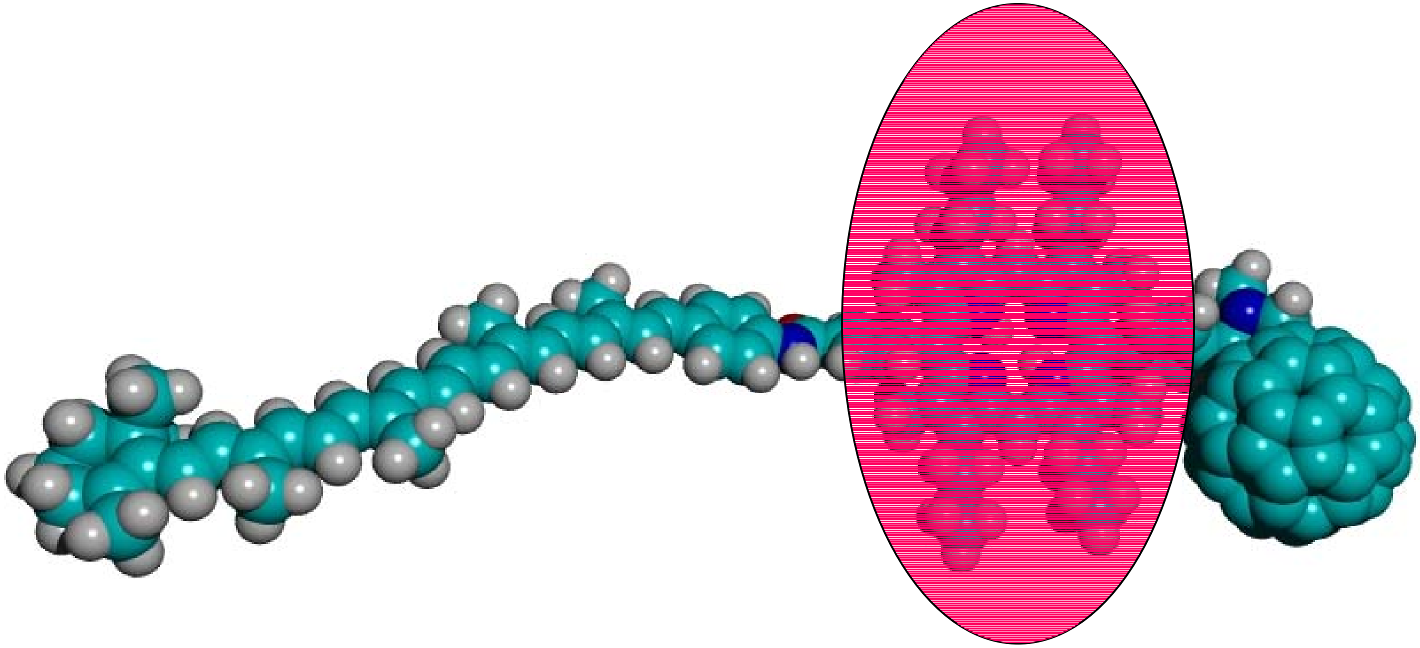


hν



$C\text{-}P\text{-}C_{60}$

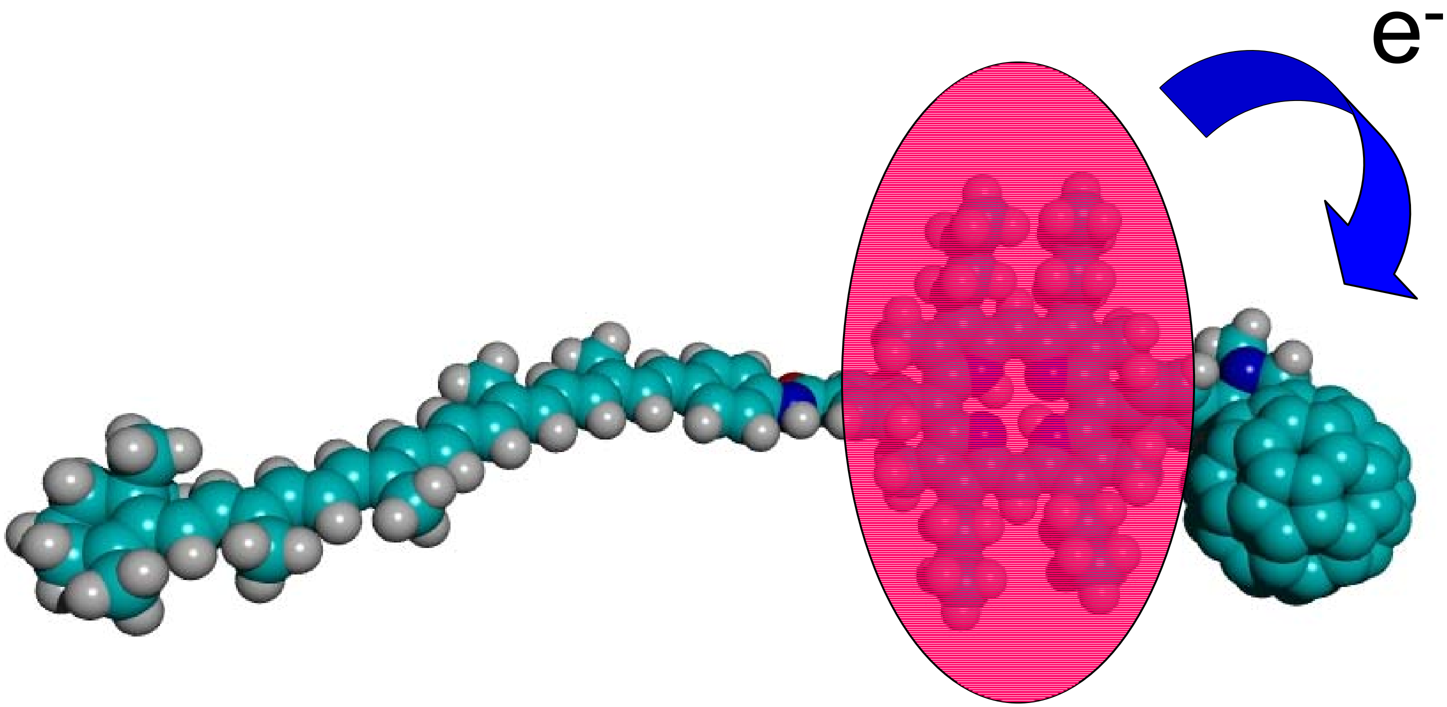
Light Absorption



C-^{1}P-C_{60}

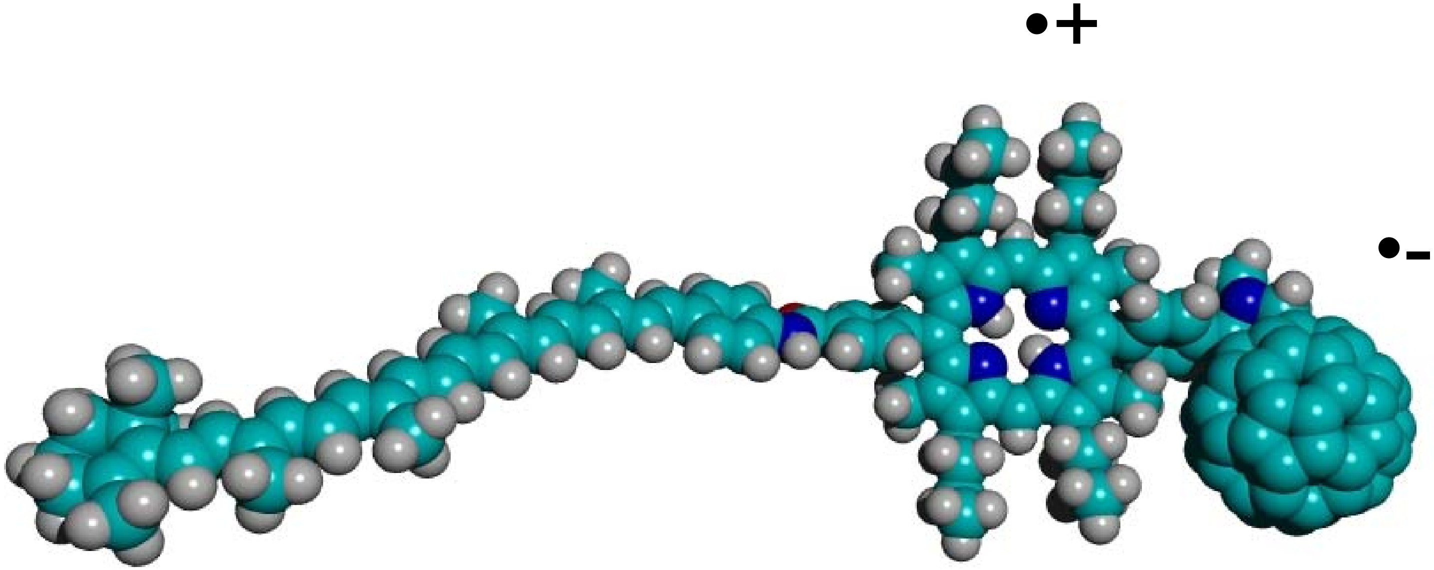
Porphyrin first excited singlet state

Photoinduced Electron Transfer



3 picoseconds

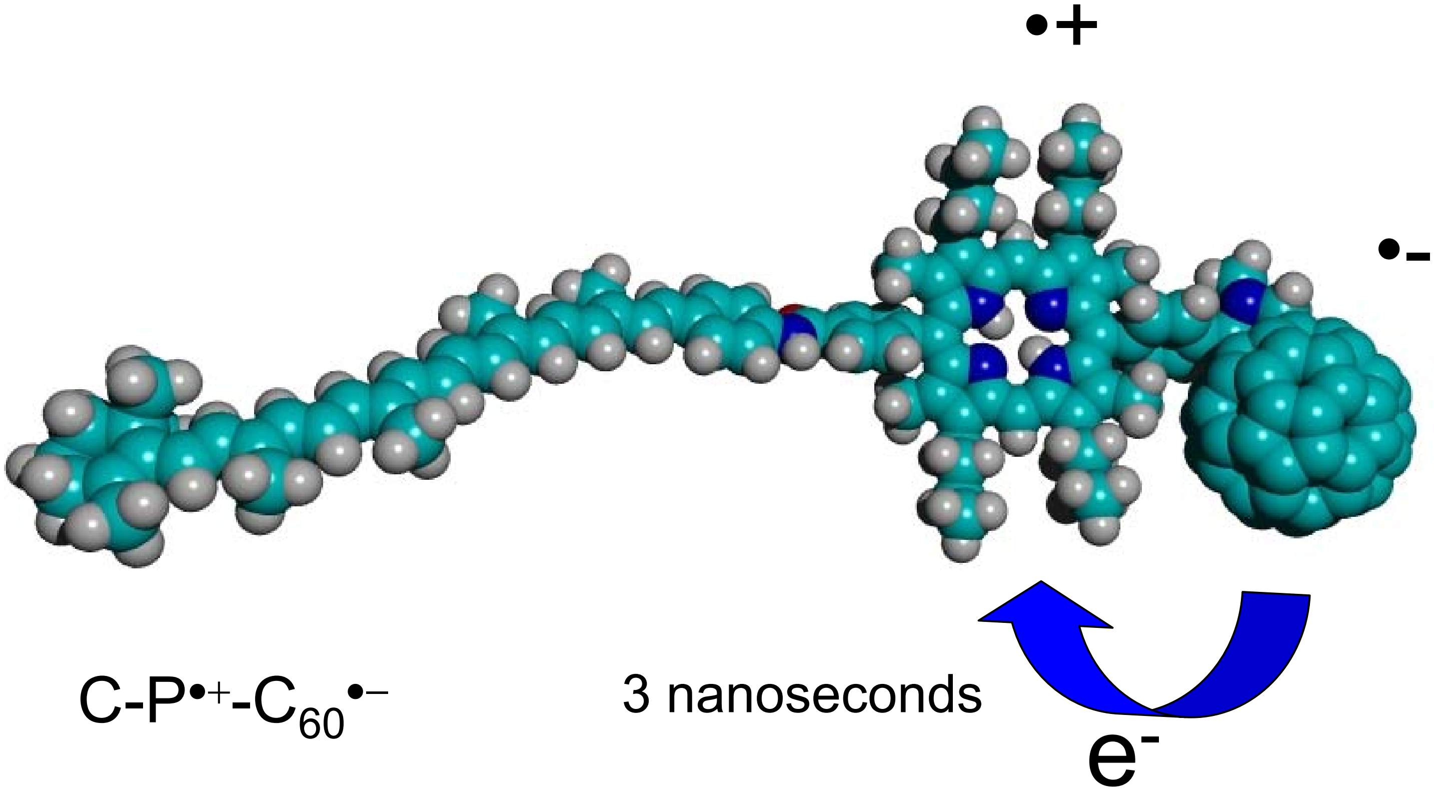
Photoinduced Electron Transfer



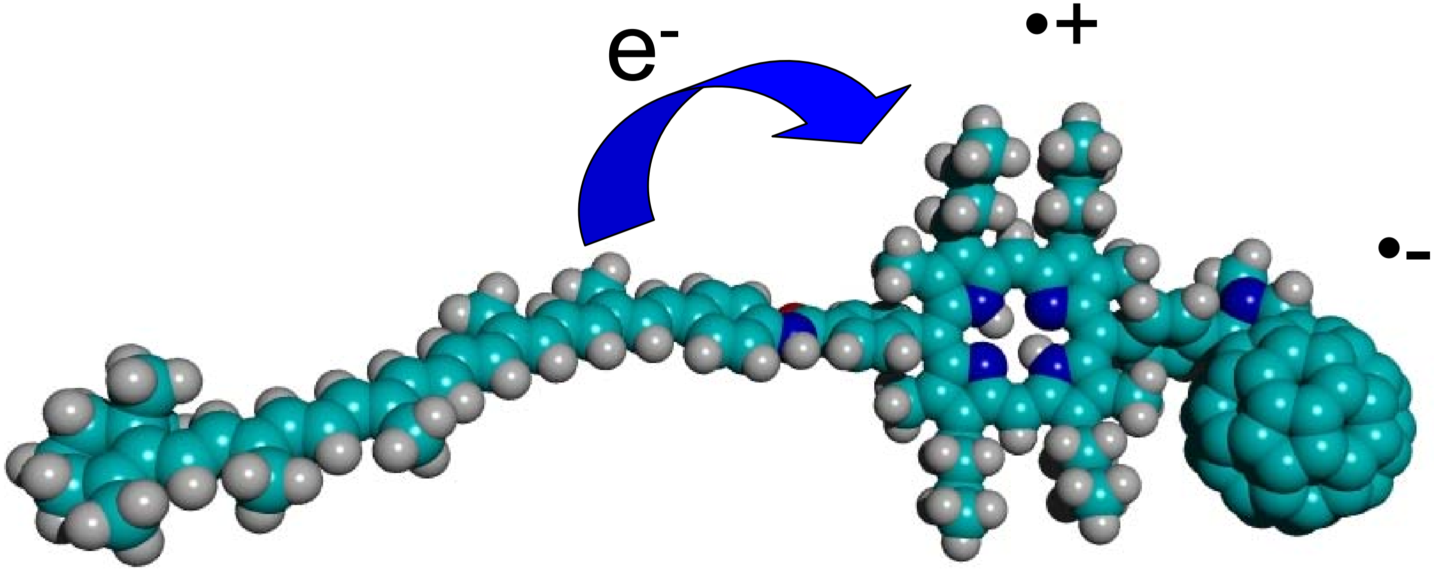
$C\text{-}P^{\bullet+}\text{-}C_{60}^{\bullet-}$

Charge-separated state

Charge Recombination

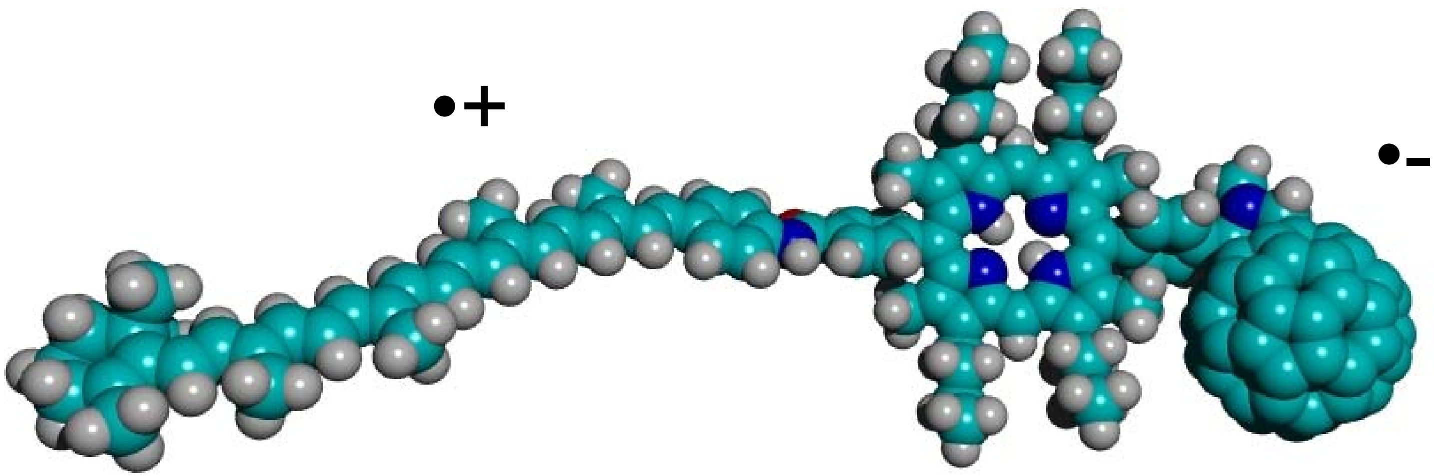


Charge Shift Reaction



$C\text{-}P^{\bullet +}\text{-}C_{60}^{\bullet -}$ 67 picoseconds

Light Energy Stored as Electrochemical Energy



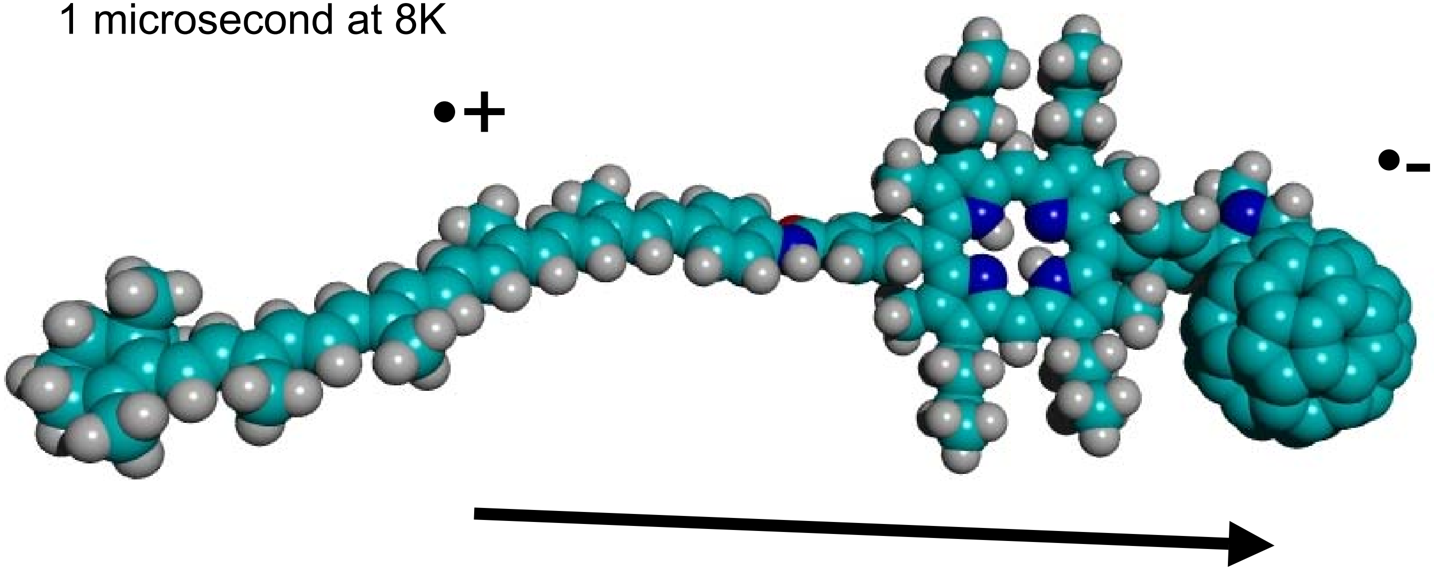
C $^{\bullet+}$ -P-$C_{60}^{\bullet-}$

Final charge-separated state

Light Energy Stored as Electrochemical Energy

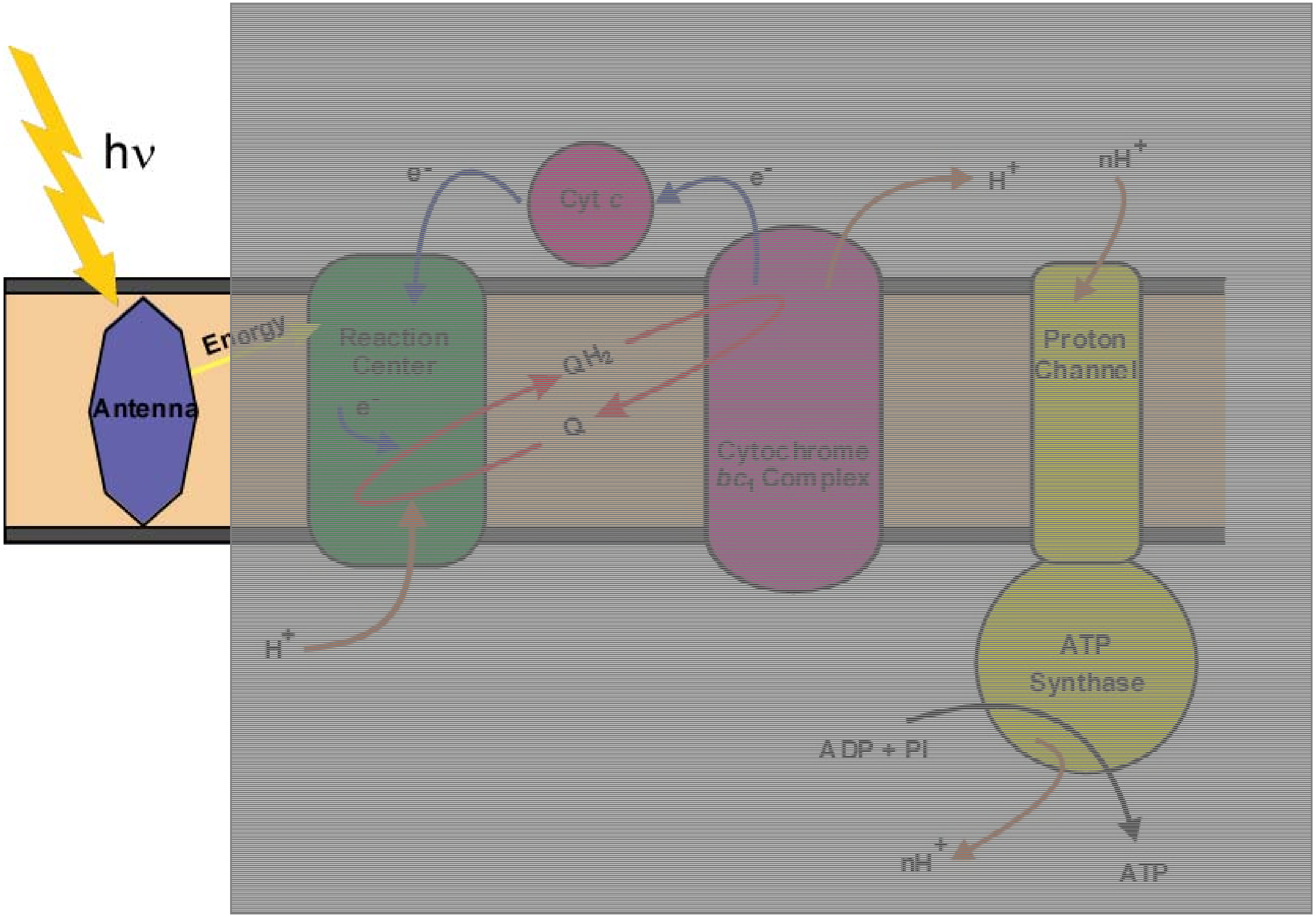
The best C-P-C_{60} triads:
Yield of charge separated state ~ 100%
Stored energy ~1.0 electron volt
Lifetime = hundreds of ns at room temp.
1 microsecond at 8K

$C^{\bullet +}$-P-$C_{60}^{\bullet -}$

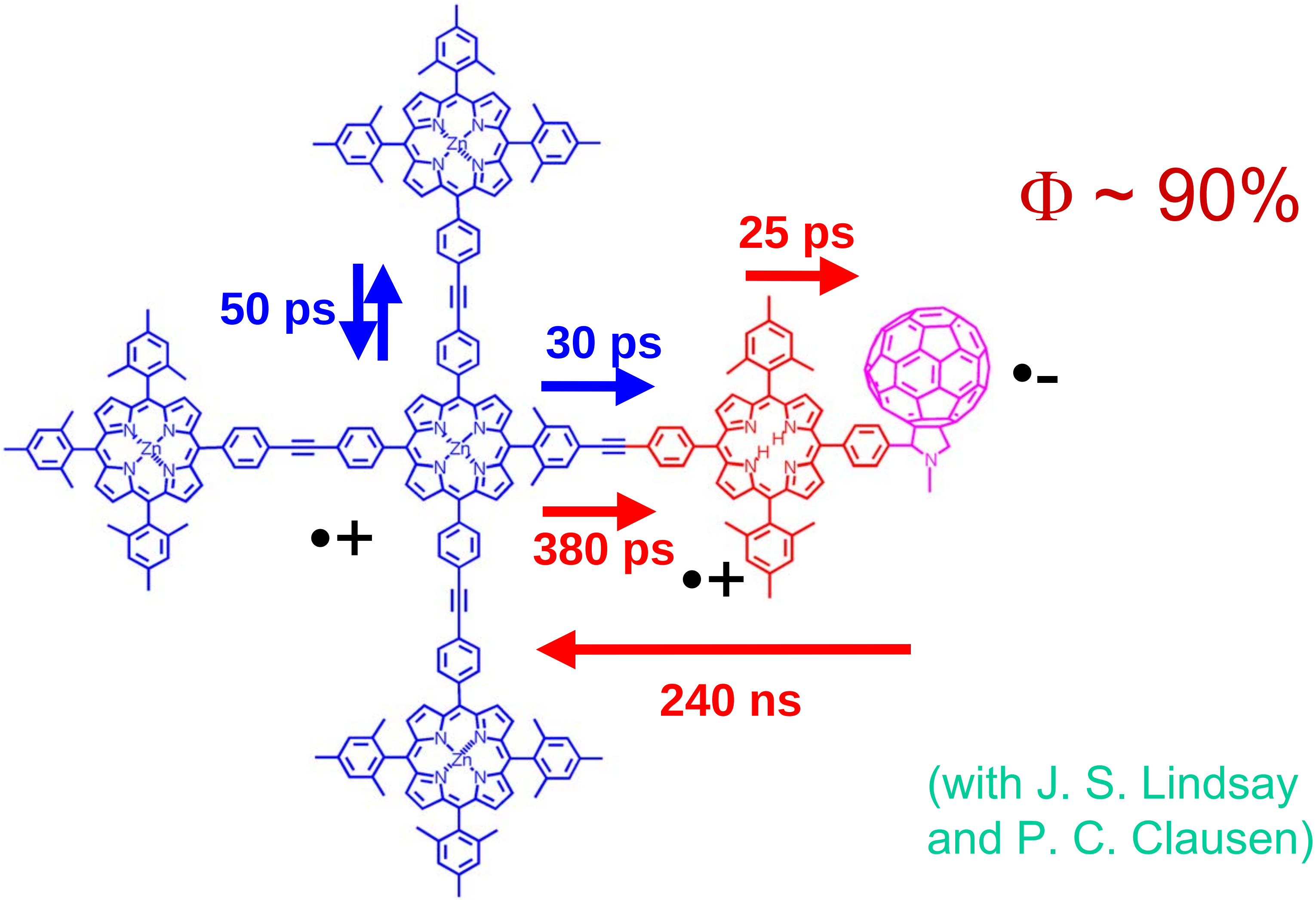


Smirnov, S. N.; Liddell, P. A.; Vlassiouk, I. V.; Teslja, A.; Kuciauskas,D.; Braun,C. L.; Moore, A. L.; Moore, T. A.; and Gust, D. *J. Phys. Chem. A*, **2003**, *107*, 7567-7573

Mimicking Antenna Function



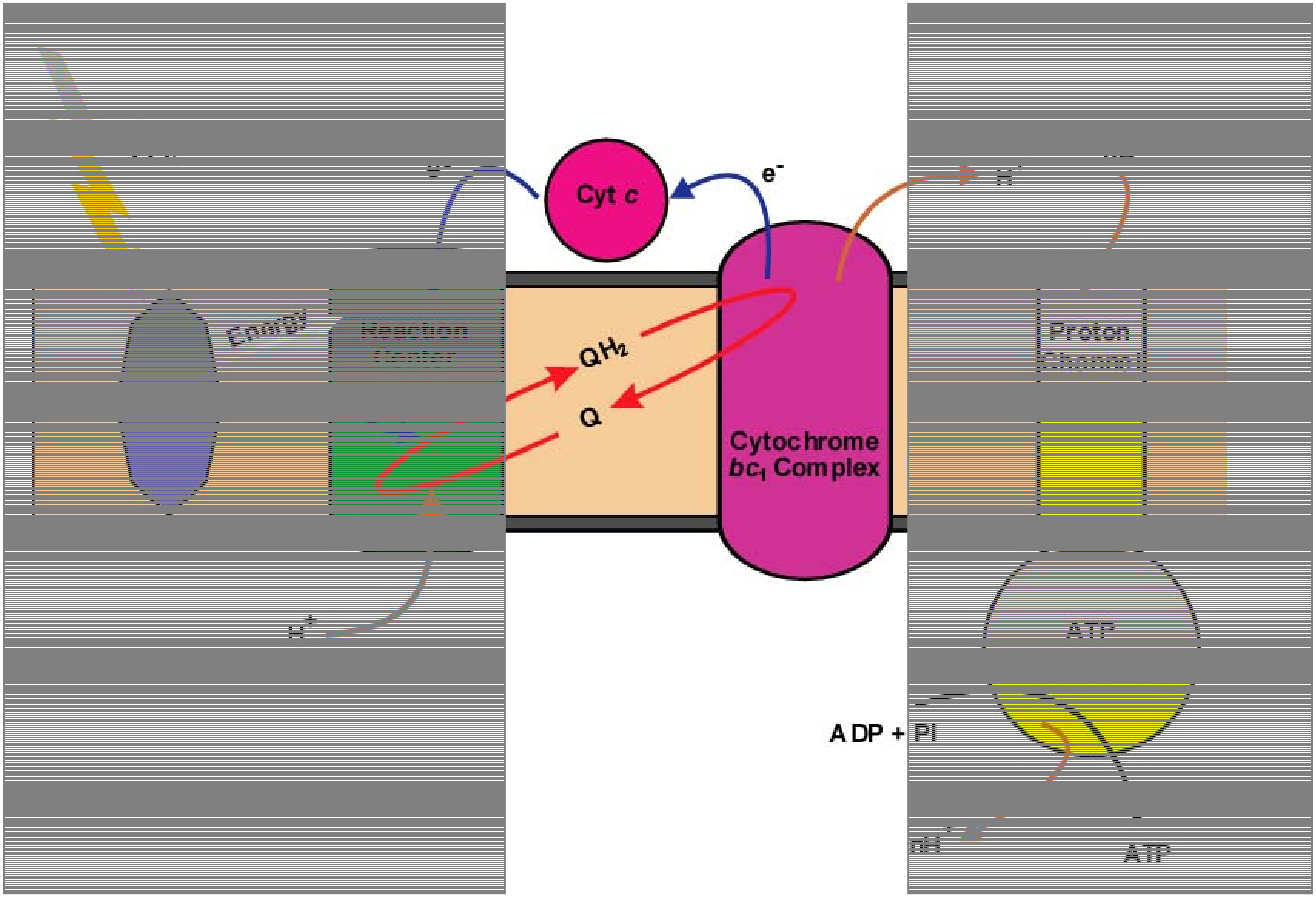
Artificial Antenna-Reaction Center Complex



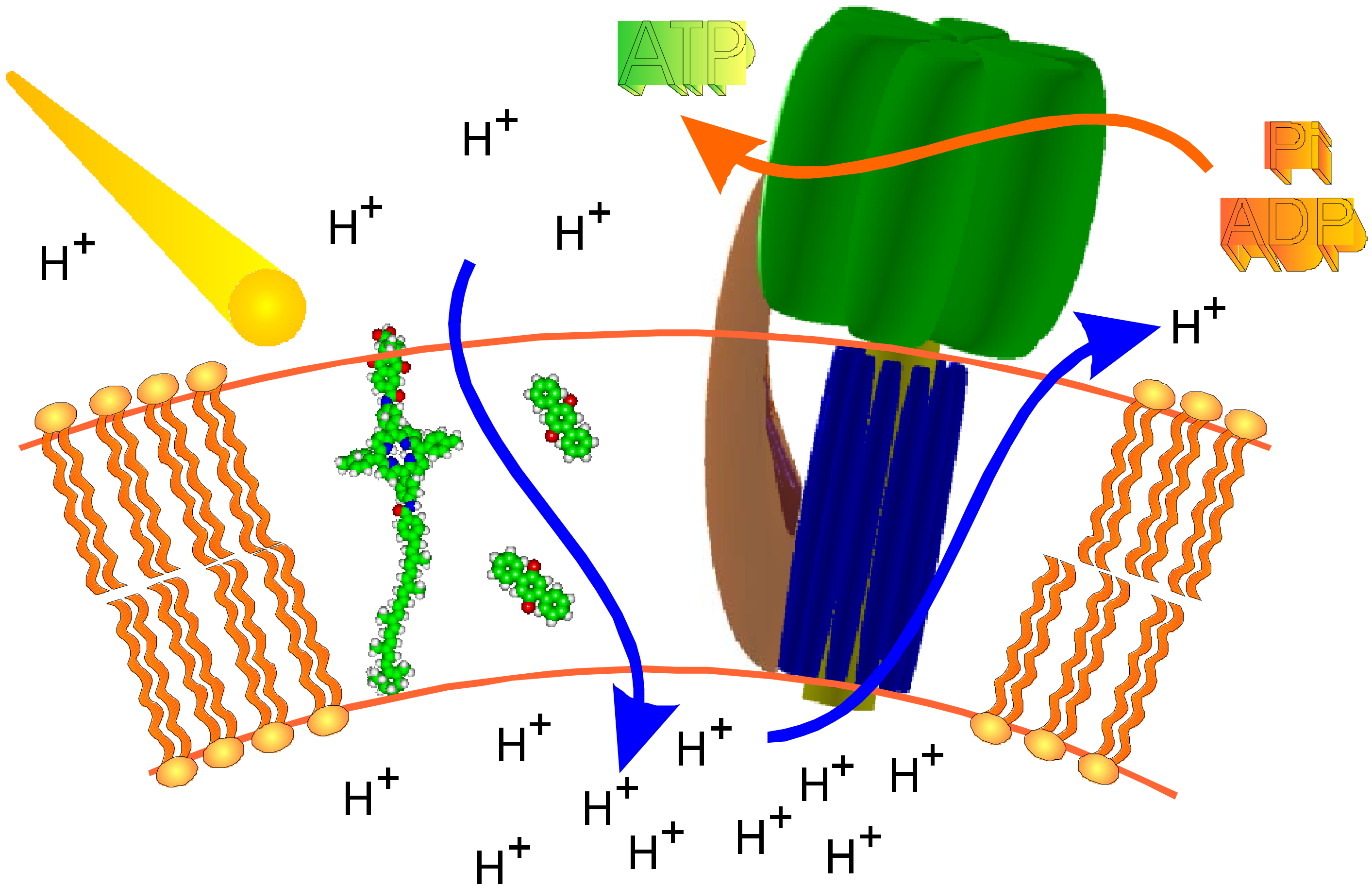
(with J. S. Lindsay and P. C. Clausen)

Kodis, G.; Liddell, P. A.; de la Garza, L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; and Gust, D. *J. Phys. Chem. A.* **2002**, *106*, 2036-2048

Mimicking the Proton Pump

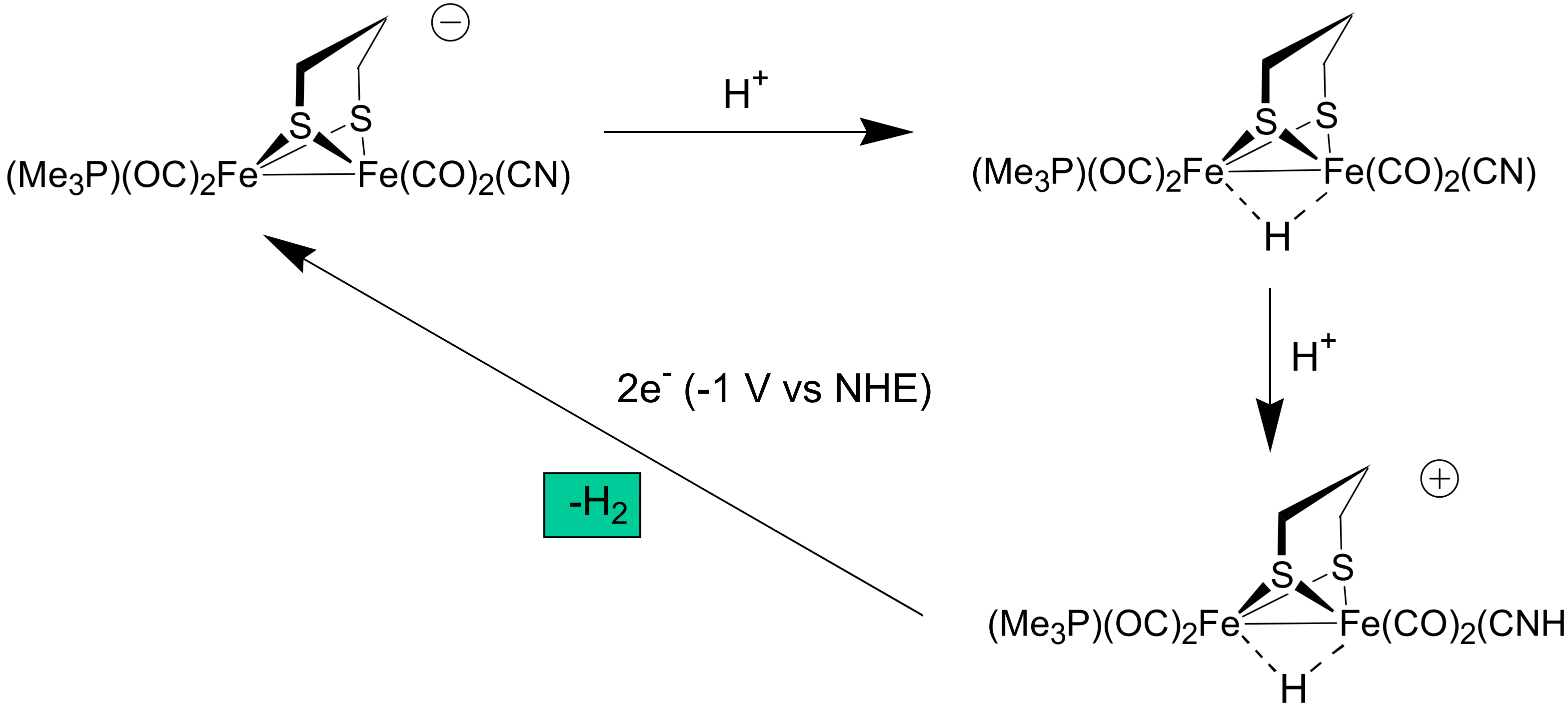


Artificial Biological Power Plant



Steinberg-Yfrach, G.; Rigaud, J. L.; Durantini, E. N.; Moore, A. L.; Gust, D.; Moore, T. A. *Nature (London)* **1998**, *392*, 479-482

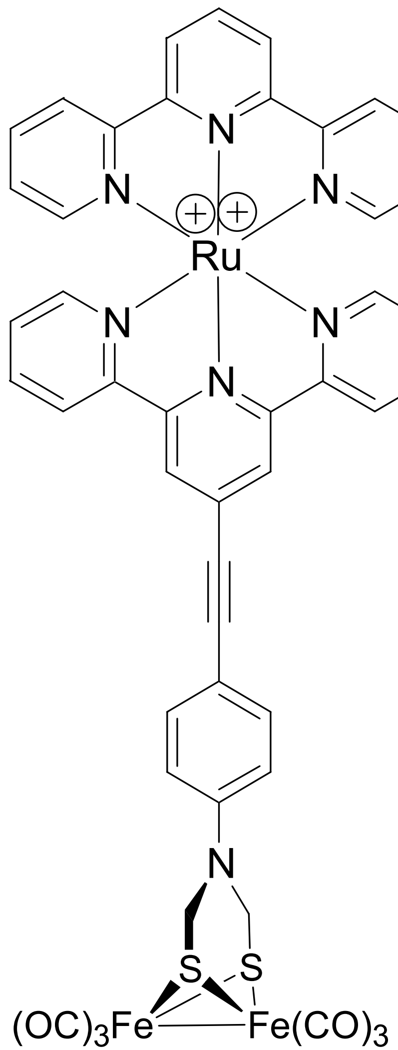
Mimicking Hydrogenase

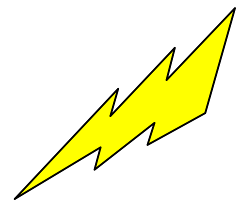


Synthetic model of active site of an Fe-only hydrogenase

Thomas B. Rauchfuss, *et al*., *J. Am. Chem. Soc.*, **2001,** *123,* 9476

Artificial Hydrogenase





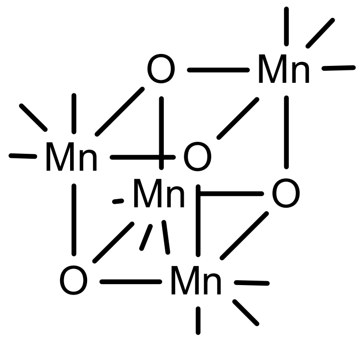
Licheng Sun, Björn Åkermark and coworkers,
Angew. Chem. Int. Ed., **2003,** *42,* 3285

$$2\,H^+ \xrightarrow{?} H_2$$

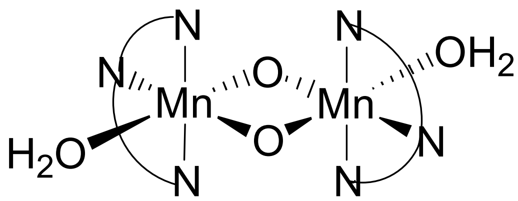
Artificial Water Oxidation

- The structure of the manganese-containing water oxidation enzyme from photosynthesis is not yet completely known.
- Several research groups are attempting to build model systems.

Approaches to Mn Complex



M. Maneiro, G. L. McLendon, G. C. Dismukes and coworkers, *Proc. Natl. Acad. Sci.*, **2003,** *100,* 3707



R. H. Crabtree, G. W. Brudvig and coworkers, *Science,* **1999,** *283,* 1524