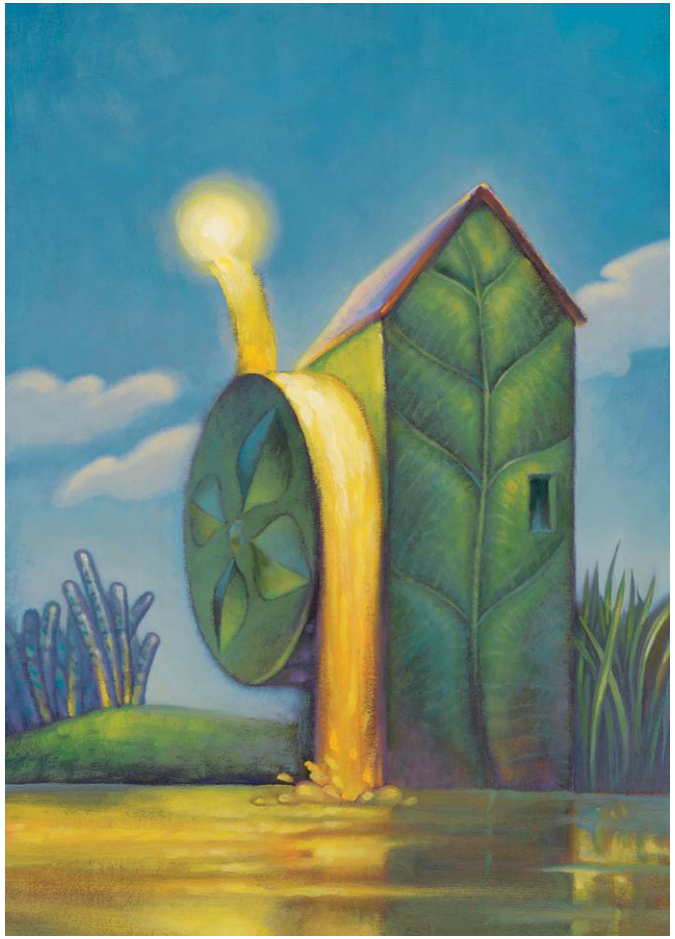

Bio-Inspired Solar Fuel Production

Devens Gust

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Solar Fuels
...inspired by nature

ASU Arizona State University

Requirements for fuel production

- A source of energy — The sun
- A source of electrons — Water oxidation
- A material to reduce to a fuel — H^+ or CO_2

13 Terawatts – Global energy consumption, 1998

Best current "technology" - photosynthesis

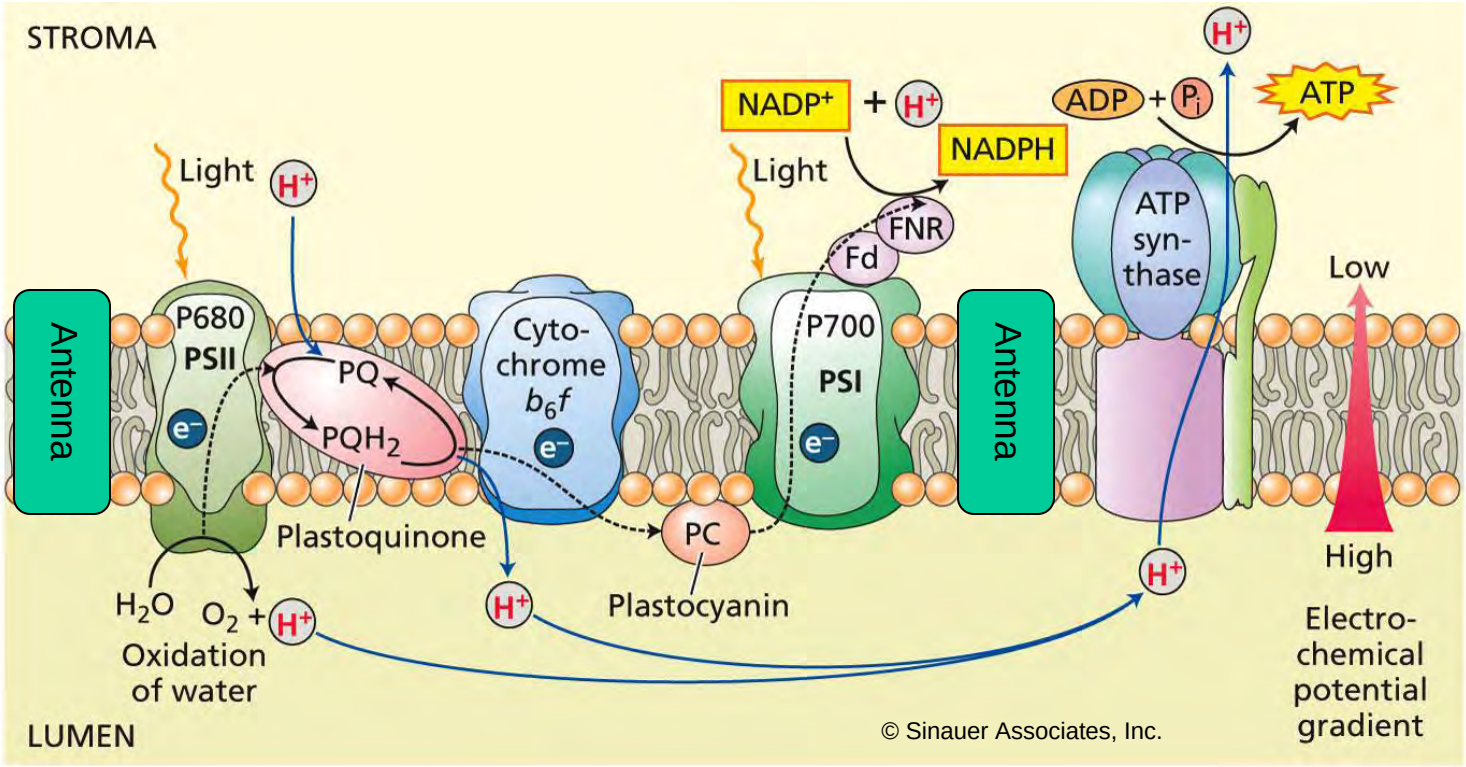
- The source of most of our current energy – fossil fuels
- 10^{14} kg of carbon removed from the atmosphere each year and converted to fuel
- 10^{21} Joules of energy each year

~125 TW

(10 times human needs)

$$CO_2 + H_2O \xrightarrow{\text{light}} (CH_2O) + O_2$$

How does photosynthesis work?



Antennas

Light capture, excitation energy migration, regulation and photoprotection

Reaction centers

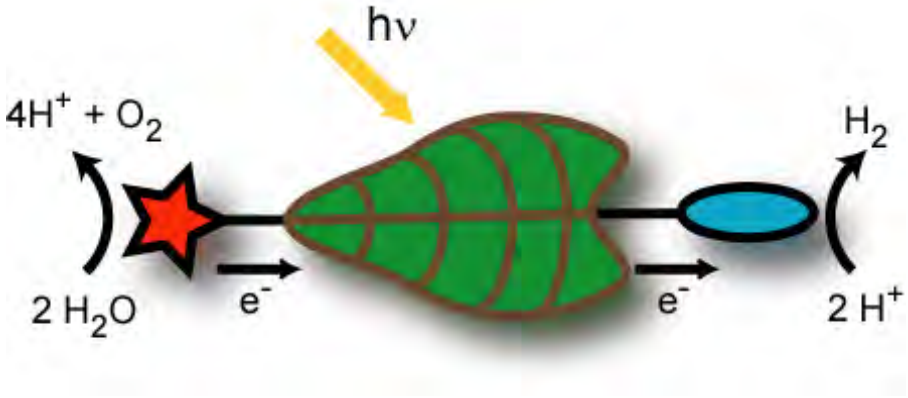
Charge separation, electrochemical energy

Dark chemical reactions

Catalysts for H_2O oxidation, CO_2 reduction and biofuel production, (carbohydrate, biodiesel, hydrogen)

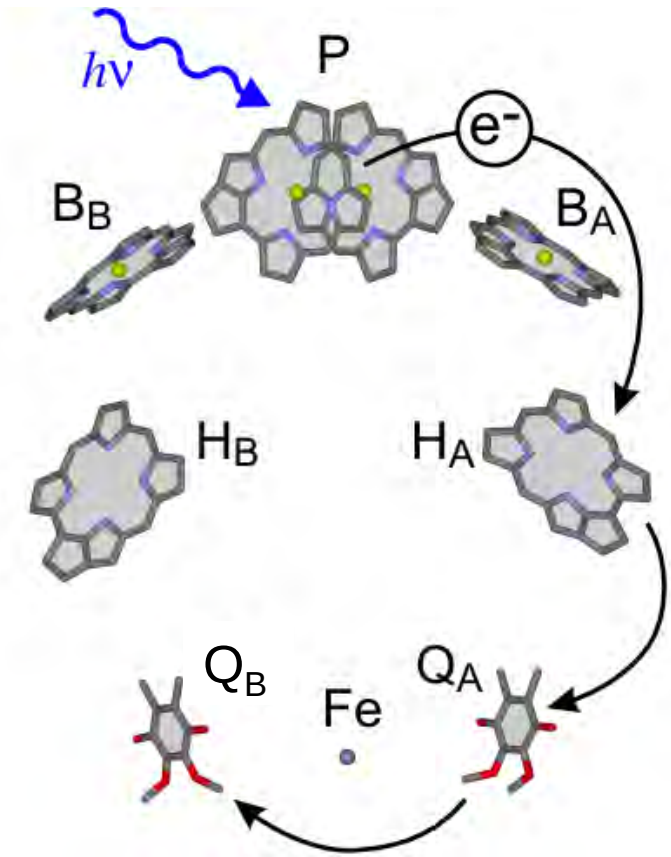
Artificial photosynthesis

- Use the basic scientific principles underlying photosynthesis to design new approaches to solar energy conversion
- Will need:
  - Artificial reaction centers
  - Artificial antennas
  - Water oxidation catalysts
  - Proton or CO_2 reduction catalysts



Reaction centers

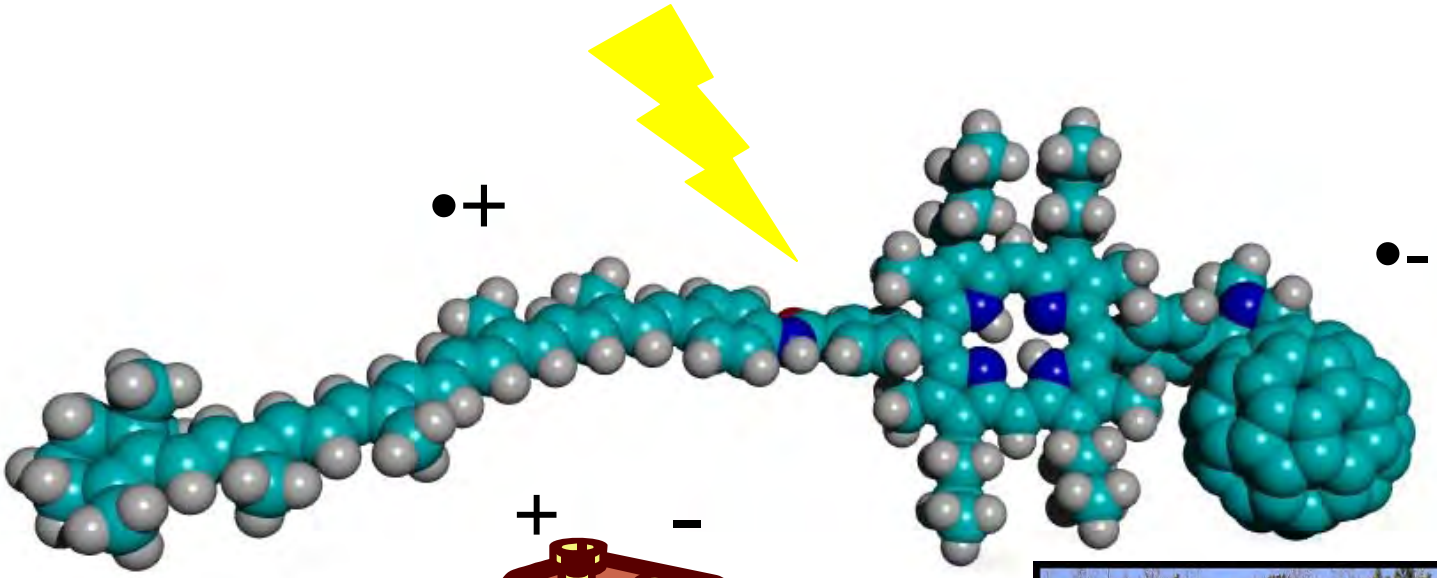
Bacterial reaction center

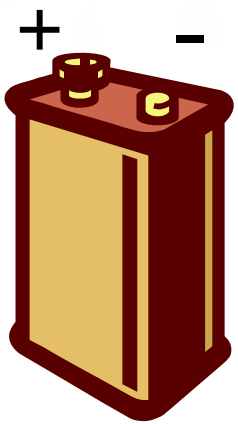


N. Woodbury, Department of Chemistry and Biochemistry,
Arizona State University

http://www.fuchs-research.net

Artificial reaction centers

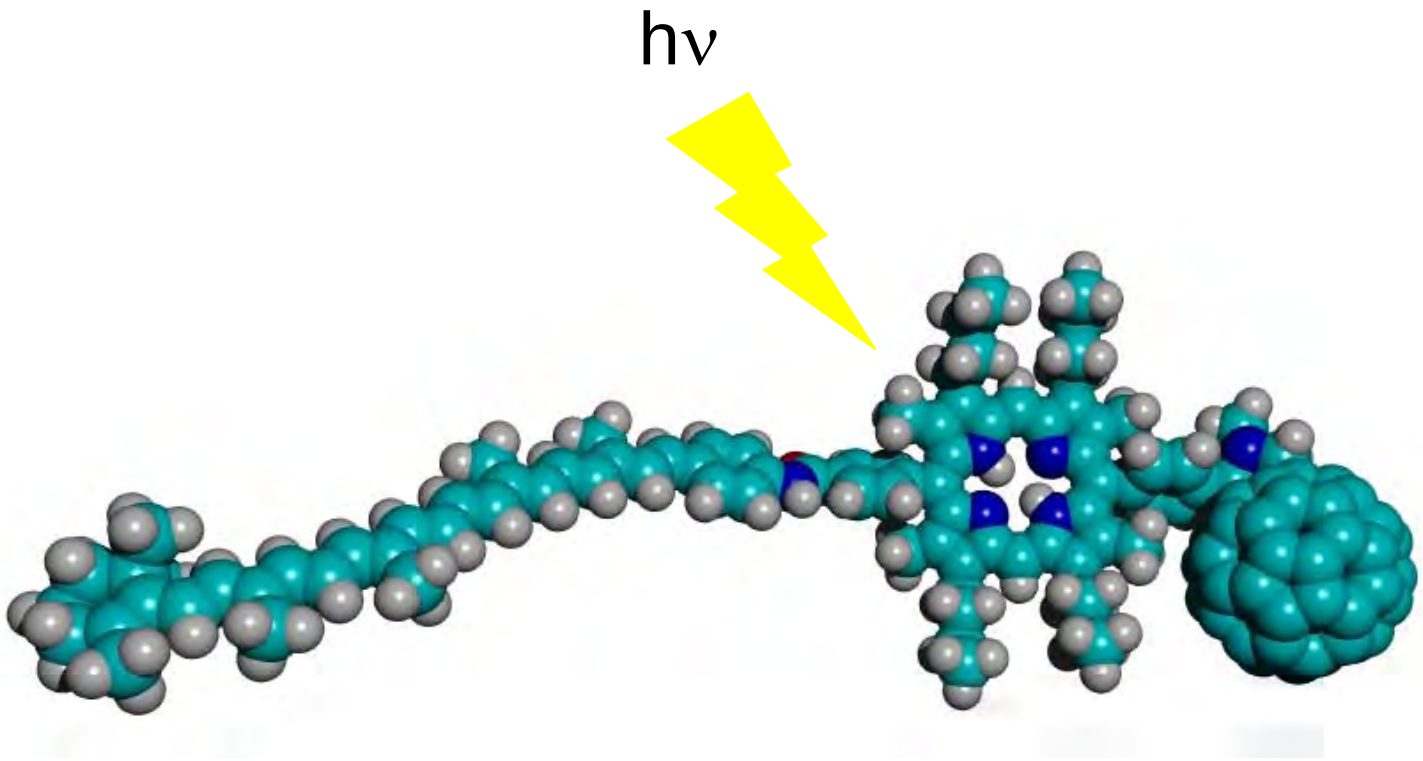




Molecular photovoltaics

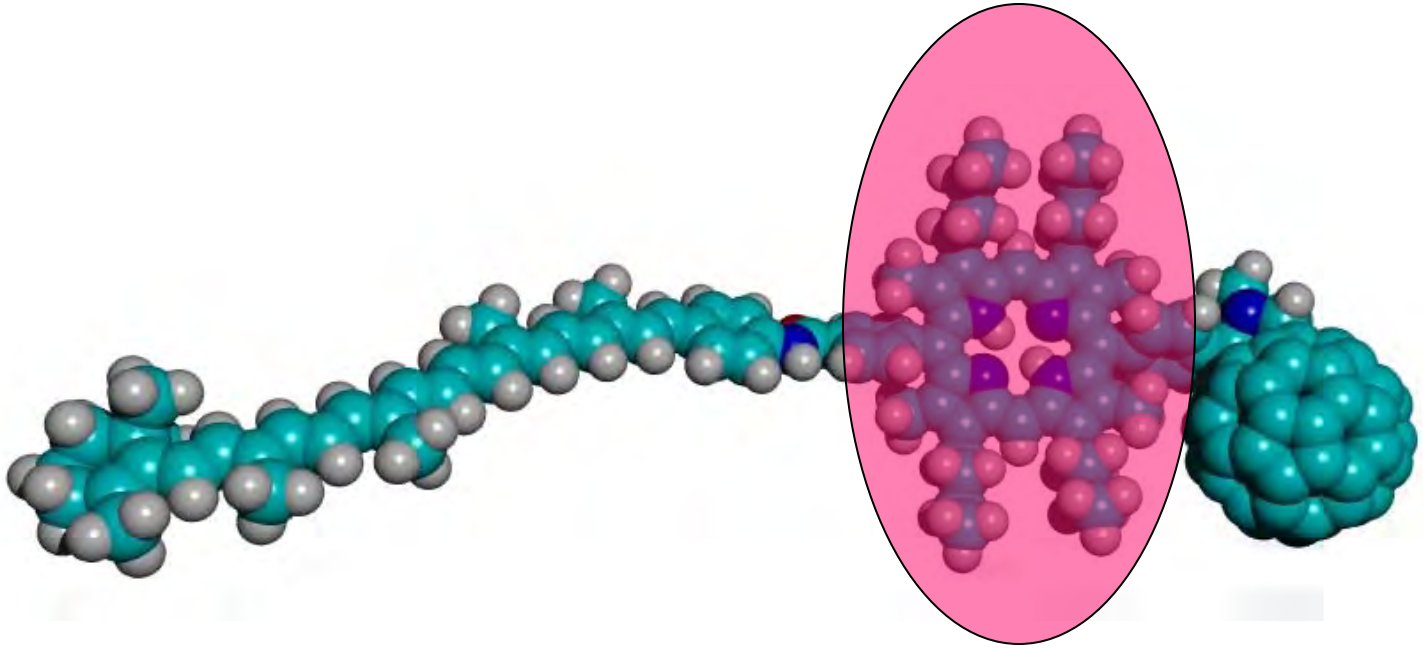
Kuciauskas, D.; Liddell, P. A.; Lin, S.; Stone, S. G.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. B* ***2000***, *104*, 4307

Light absorption



C-P-C_{60}

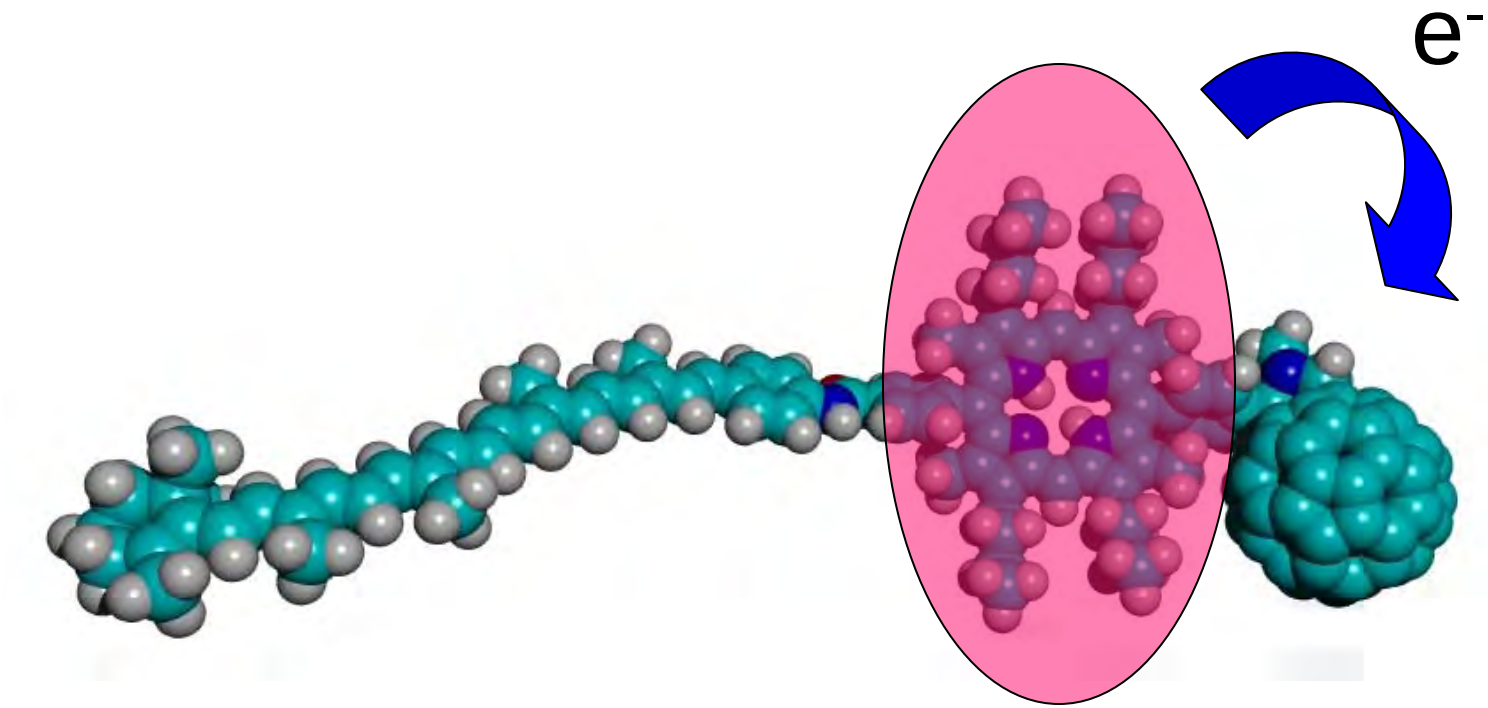
Light absorption



$C\text{-}^{1}P\text{-}C_{60}$

Porphyrin first excited singlet state

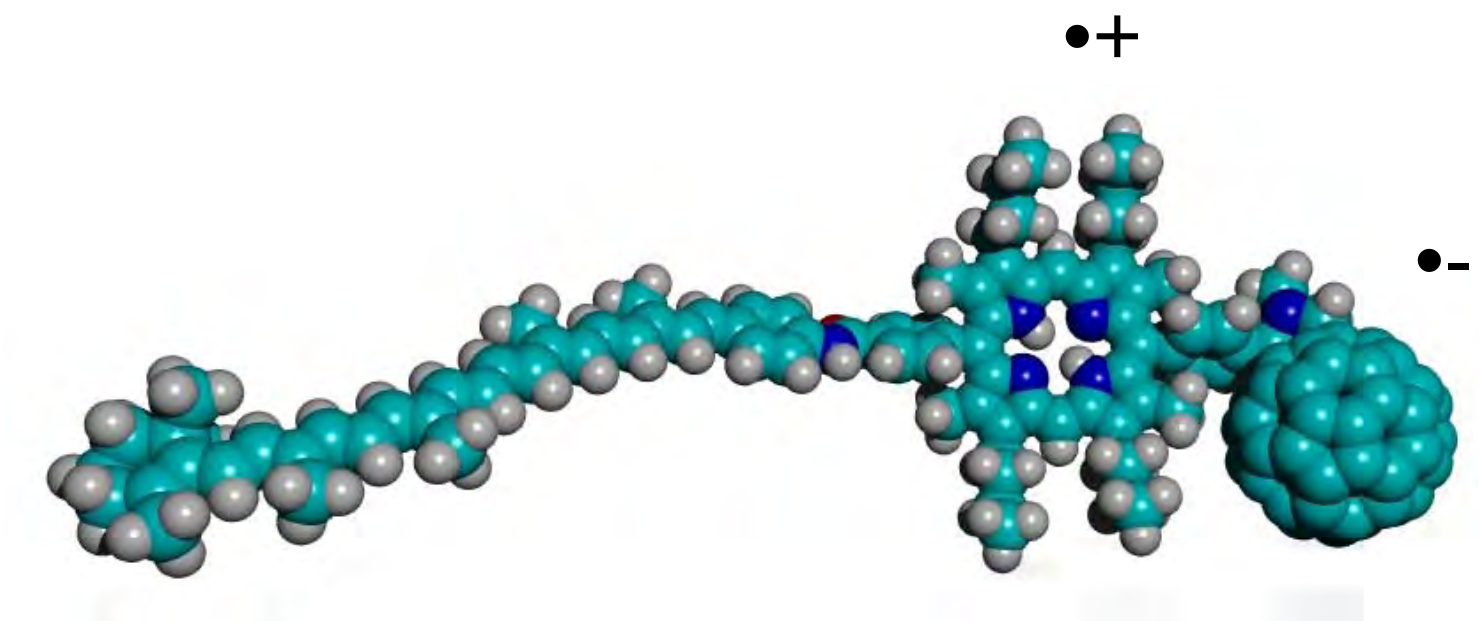
Photoinduced electron transfer



3 picoseconds

(3 x 10^{-12} s)

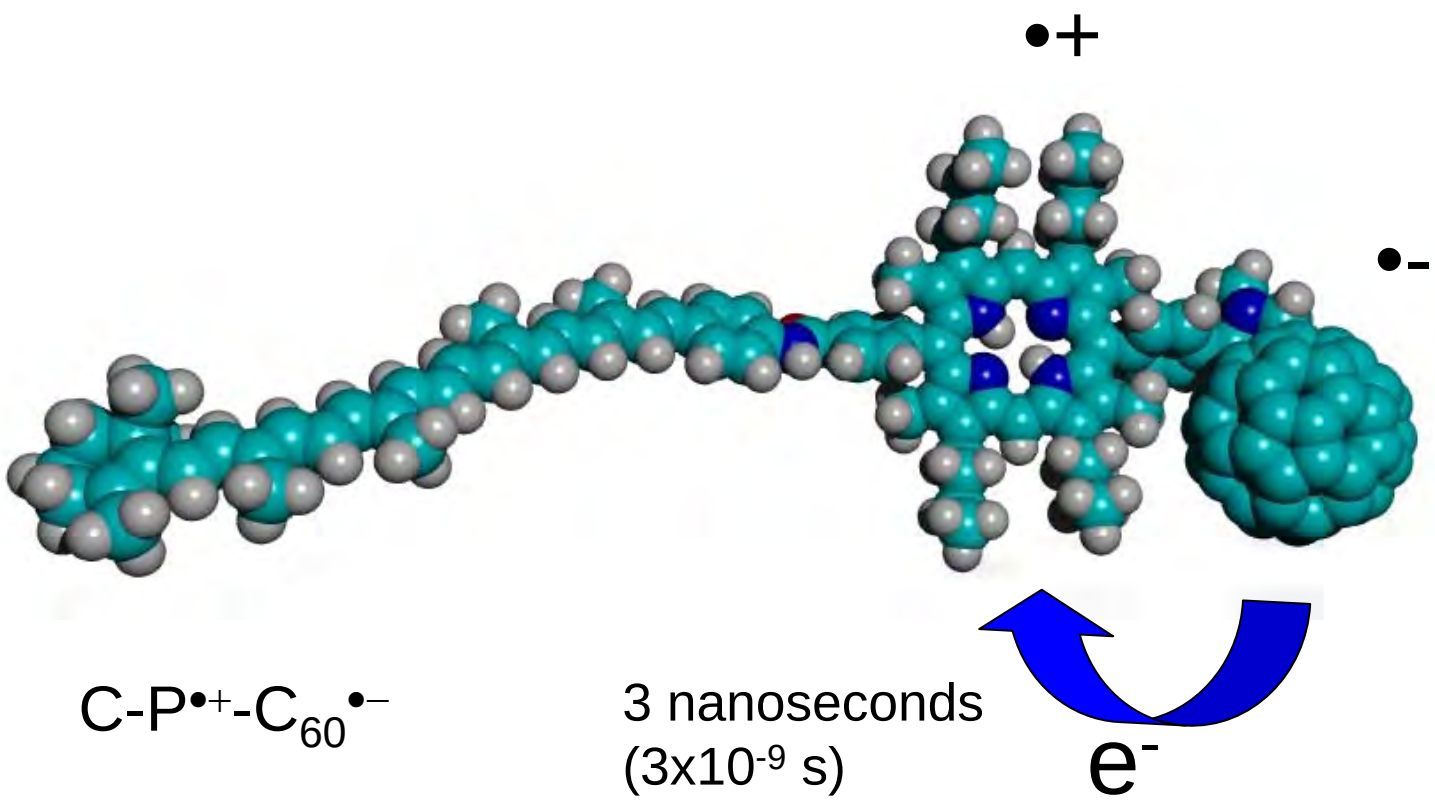
Photoinduced electron transfer



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

Charge-separated state

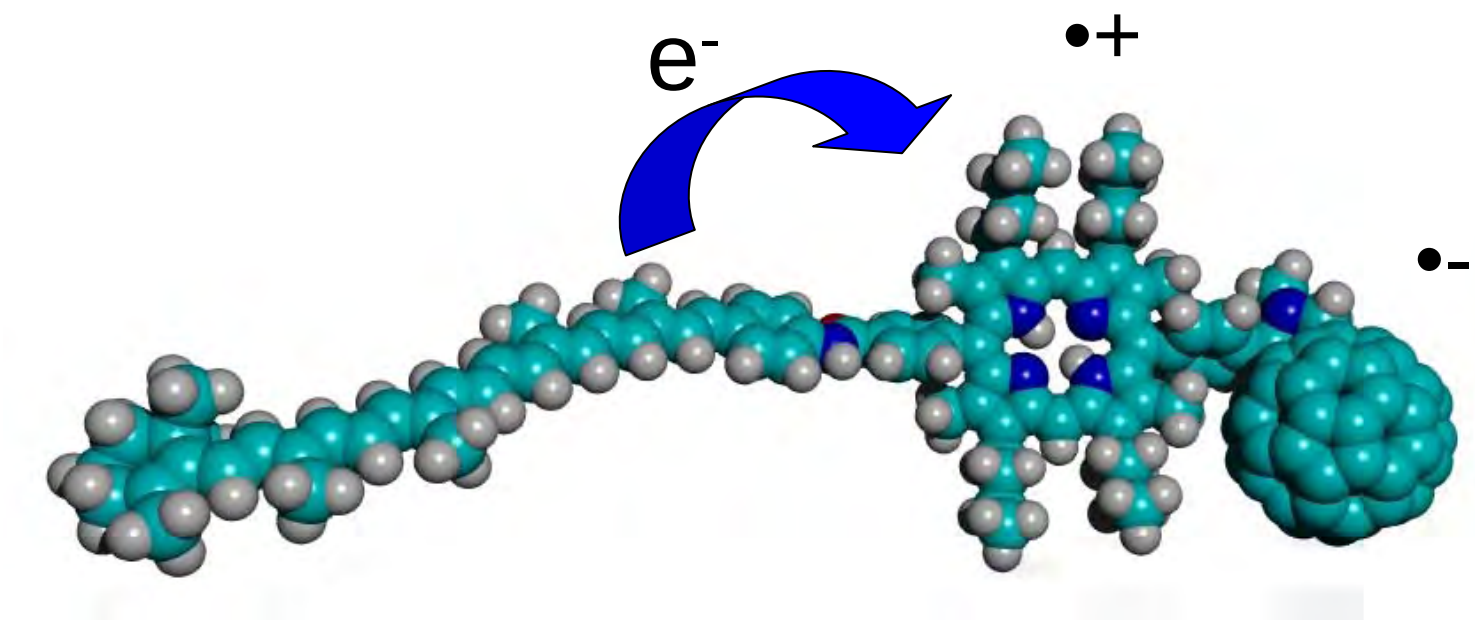
Charge recombination



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

3 nanoseconds
(3×10^{-9} s)

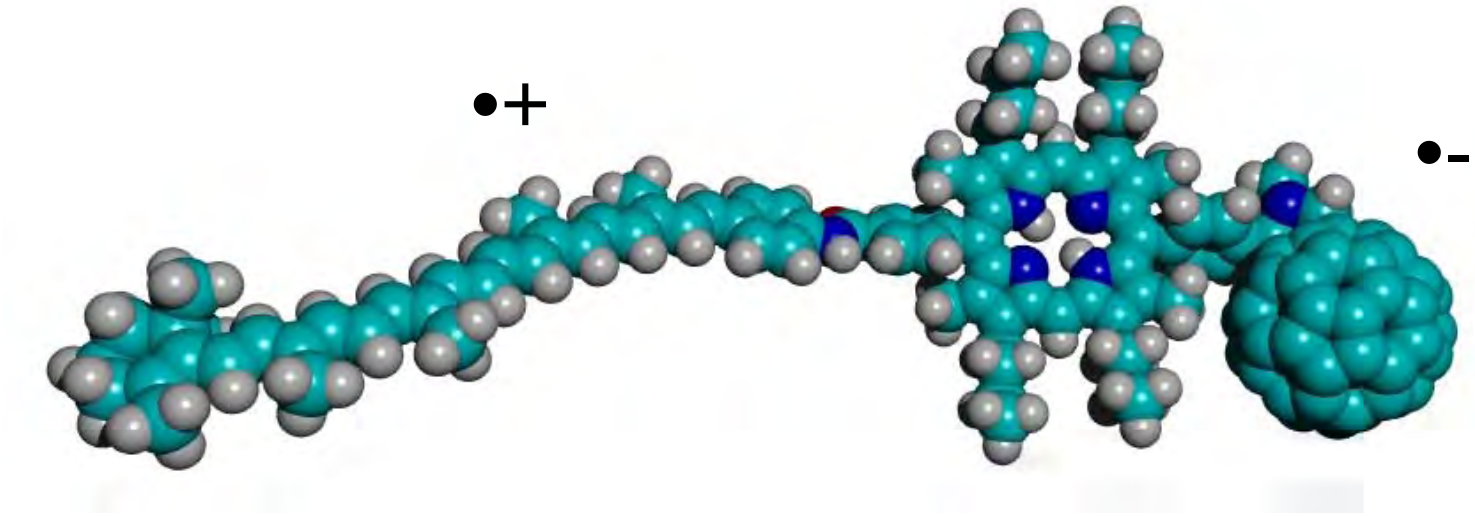
Charge shift reaction



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

67 picoseconds

Light energy stored as electrochemical energy



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

Final charge-separated state

Light energy stored as electrochemical energy

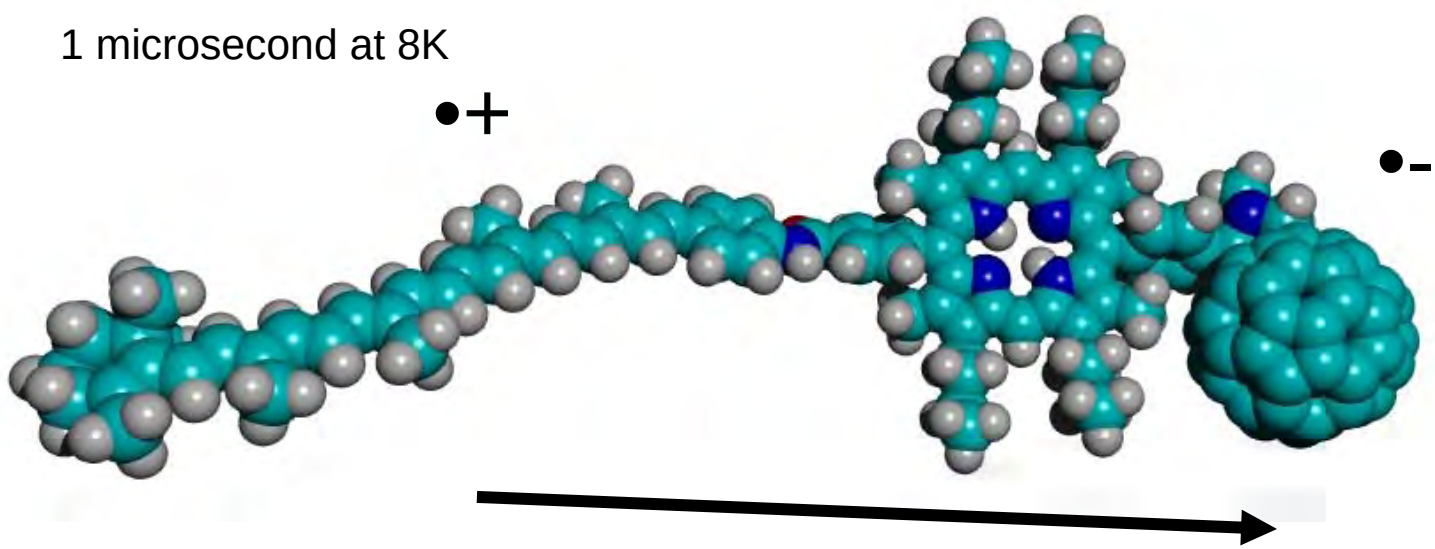
Yield of charge separated state ~ 100%

Stored energy ~1.0 electron volt

Lifetime = hundreds of ns at room temp.

1 microsecond at 8K

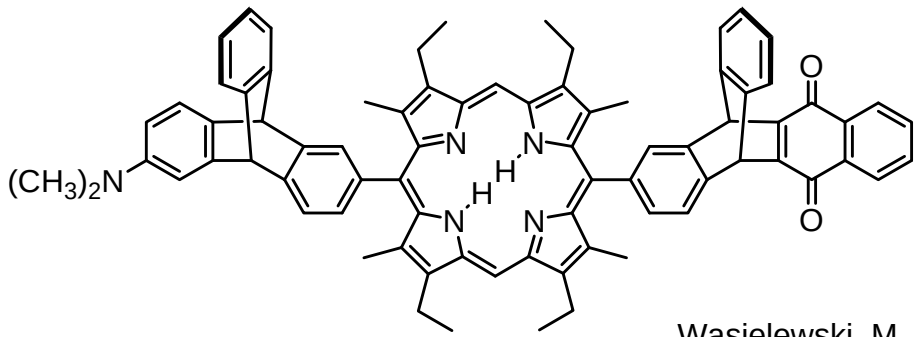
$C^{\bullet+}$-P-$C_{60}^{\bullet-}$



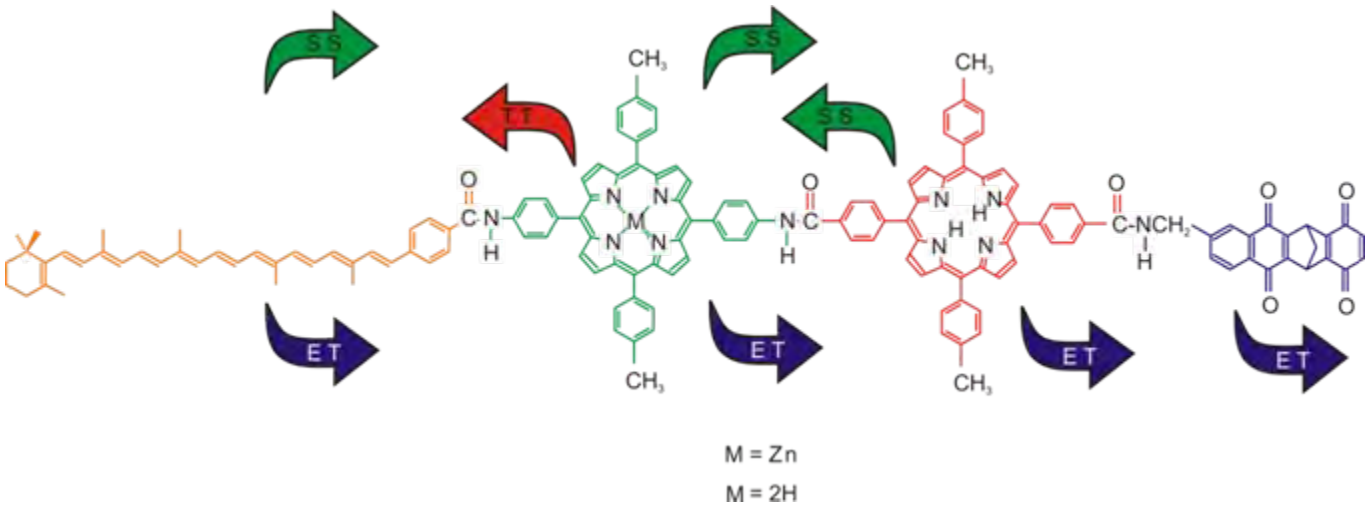
Dipole moment ~160 D

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

Many approaches to artificial reaction centers

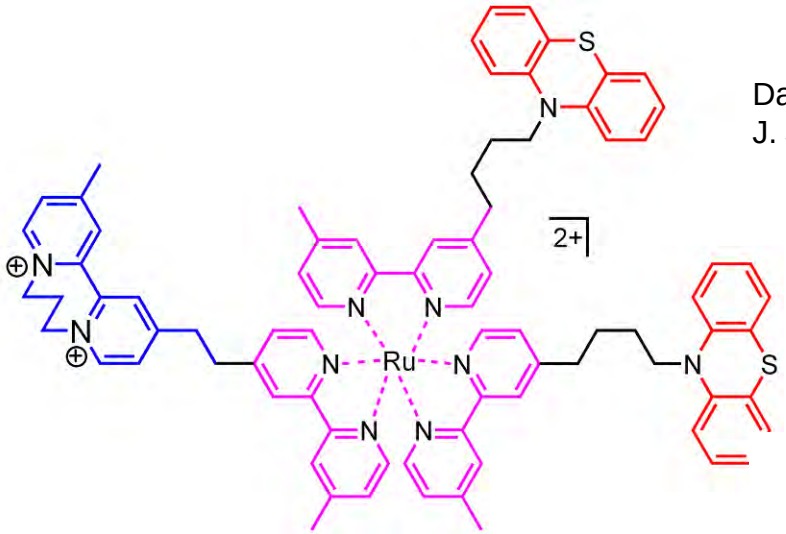


Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 5562

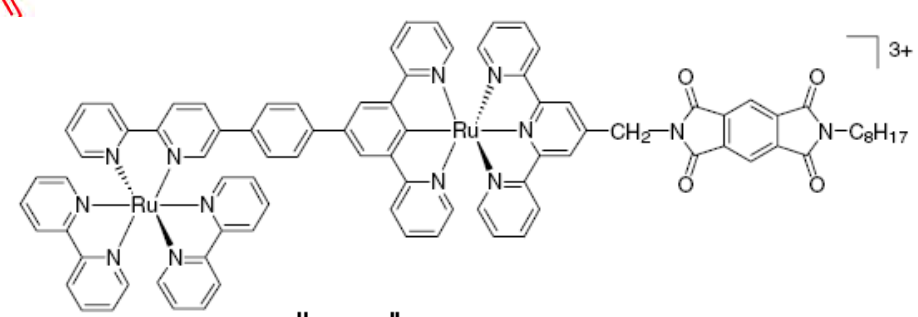


Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res*. **1993**, *26*, 198

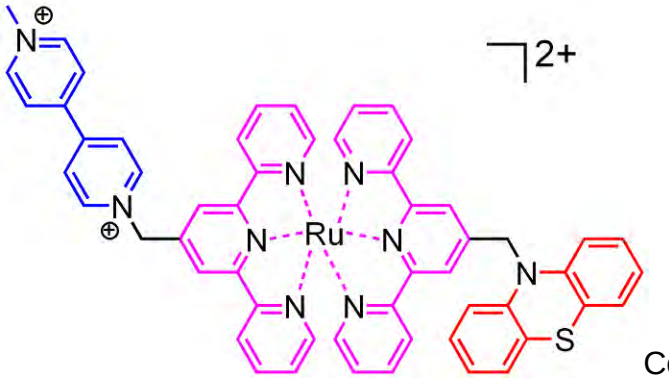
Ruthenium-based triads



Danielson, E.; Elliott, C. M.; Merkert, J. W.; Meyer, T. J. *J. Am. Chem. Soc.* **1987,** *109*, 2519-2520.



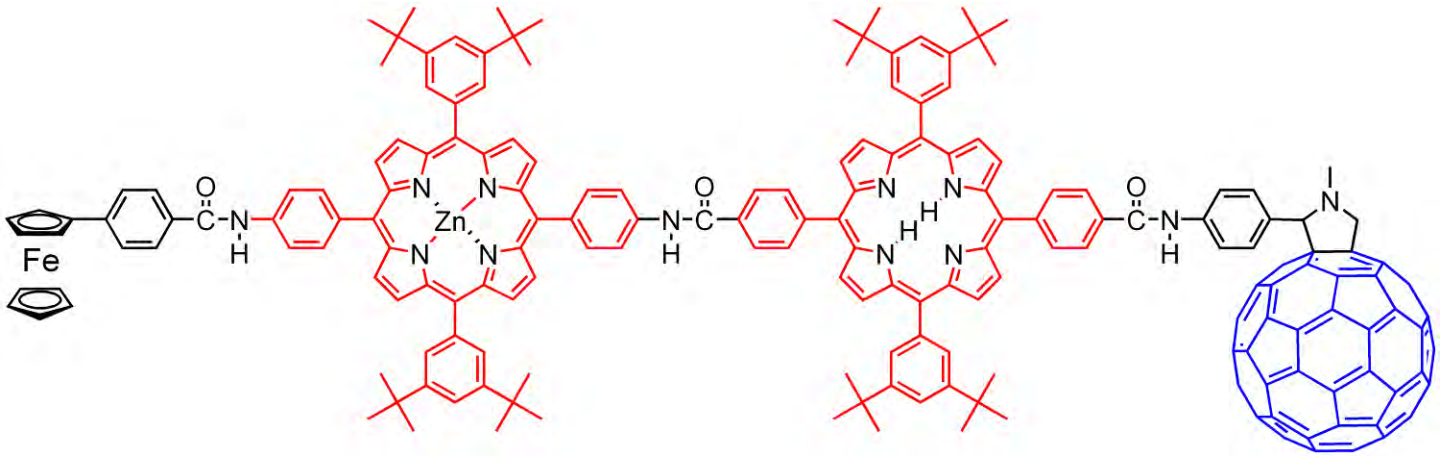
Ru^{II}-φ-Ru_C^{II}-PI



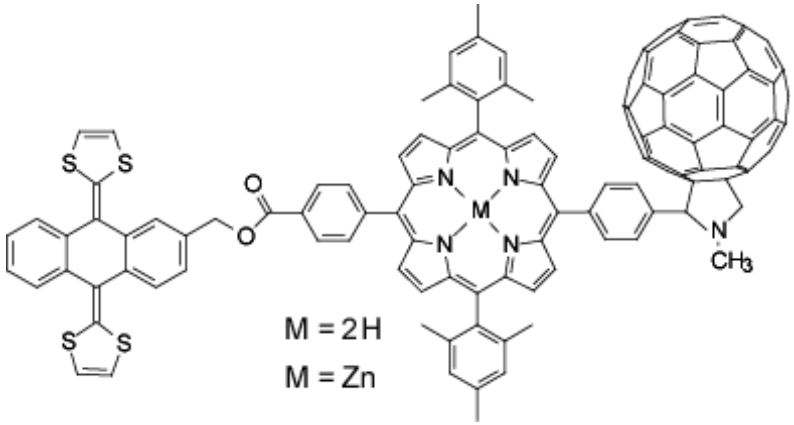
Falkenström, M.; Johansson, O.; Hammarström, L. *Inorg. Chim. Acta* **2007** *360*, 741

Collin, J.-P.; Guillerez, S.; Sauvage, J.-P.; Barigelletti, F.; DeCola, L.; Flamigni, L.; Balzani, V. *Inorg. Chem.* **1991**, *30*, 4230

Additional fullerene-based systems



Imahori, H.; Guldi, D. M.; Tamaki, K.; Yoshida, Y.; Luo, C.; Sakata, Y.; Fukuzumi, S. *J. Am. Chem. Soc*. **2001**, *123*, 6617

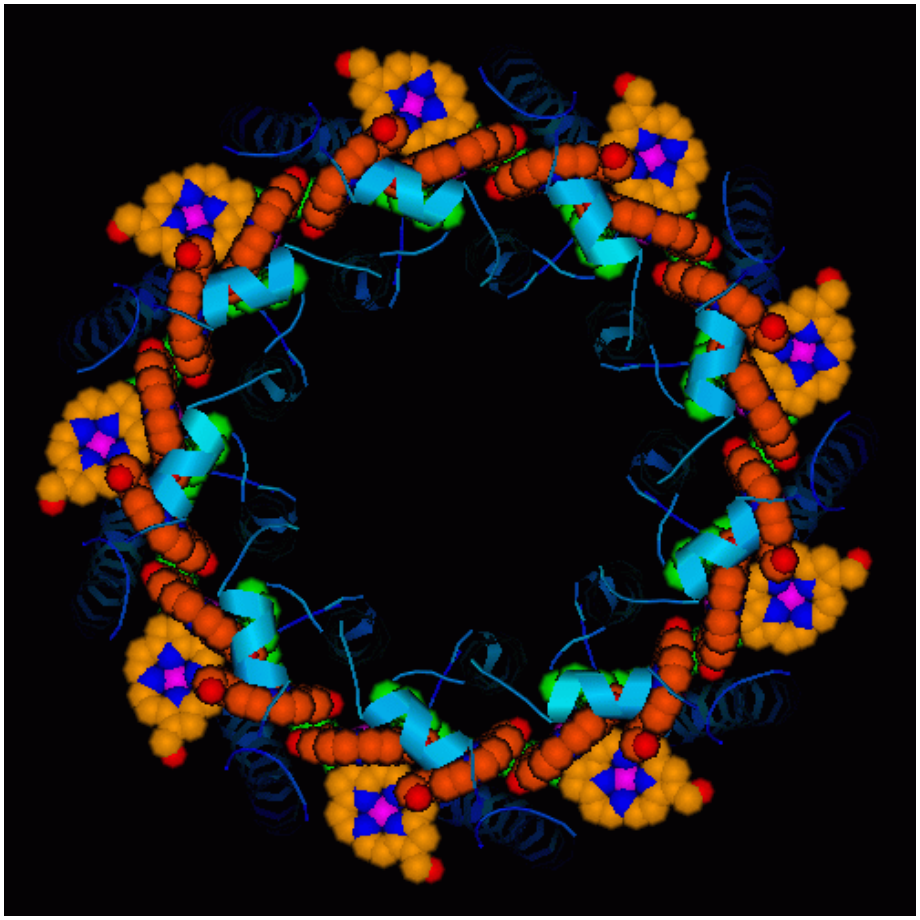


Kodis, G.; Liddell, P. A.; de la Garza, L.; Moore, A. L.; Moore, T. A.; Gust, D. *Journal of Materials Chemistry*, **2002**, *12*, 2100

Antenna systems

LH2 Photosynthetic antenna

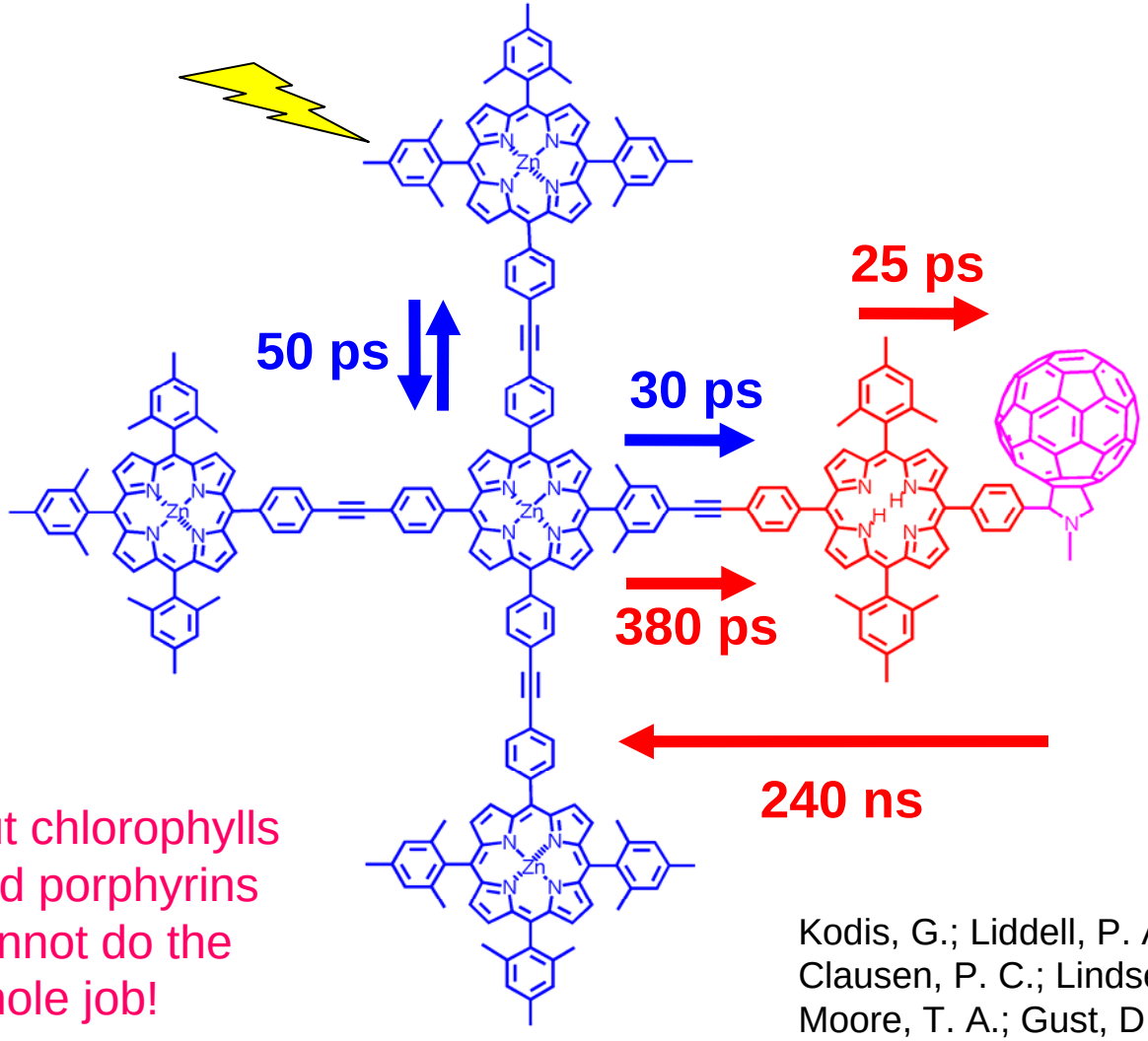
Rhodopseudomonas acidophila



R. Cogdell,

N. Isaacs

Artificial antenna-reaction center complex

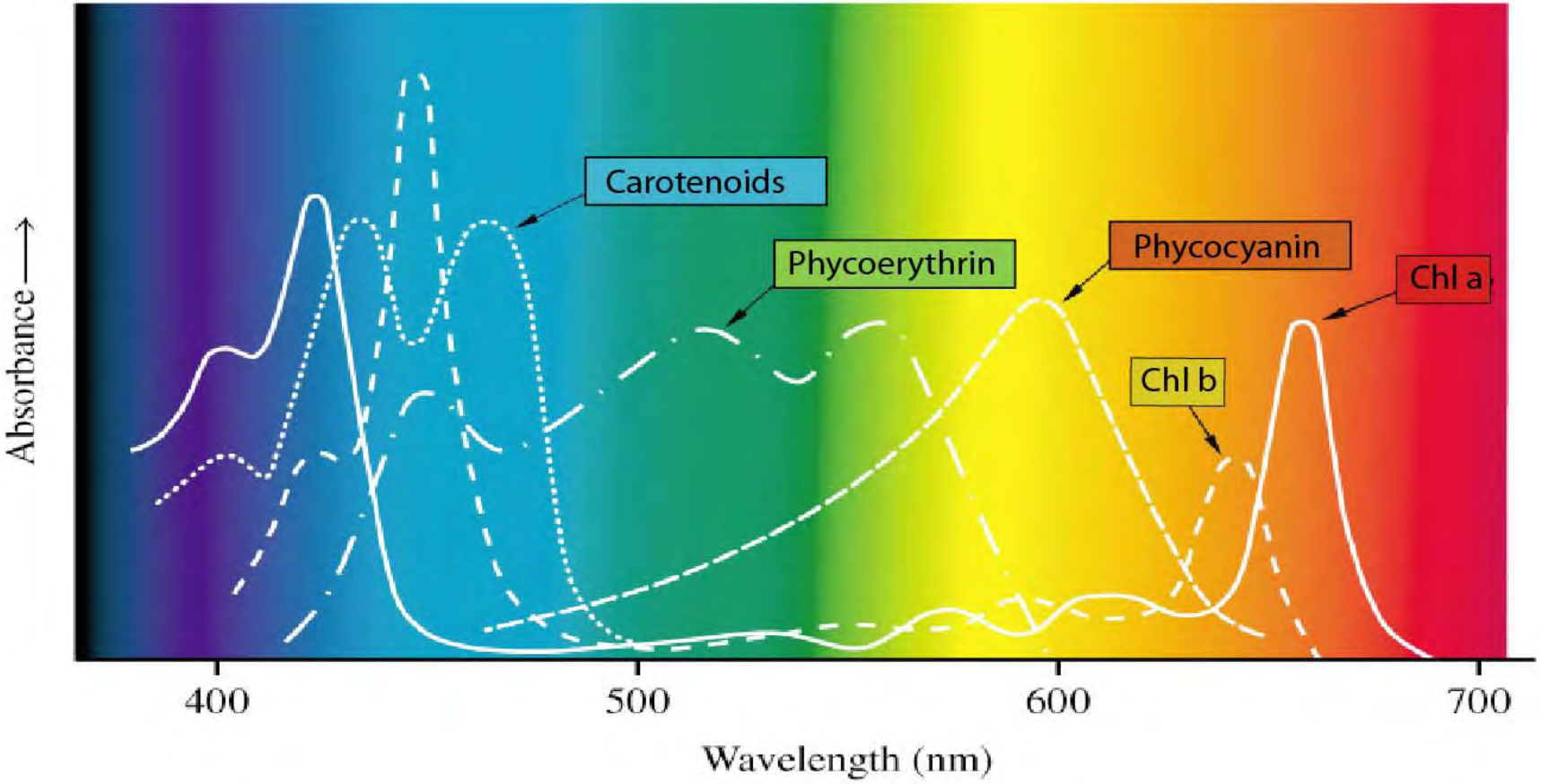


$\Phi \sim 90\%$

But chlorophylls and porphyrins cannot do the whole job!

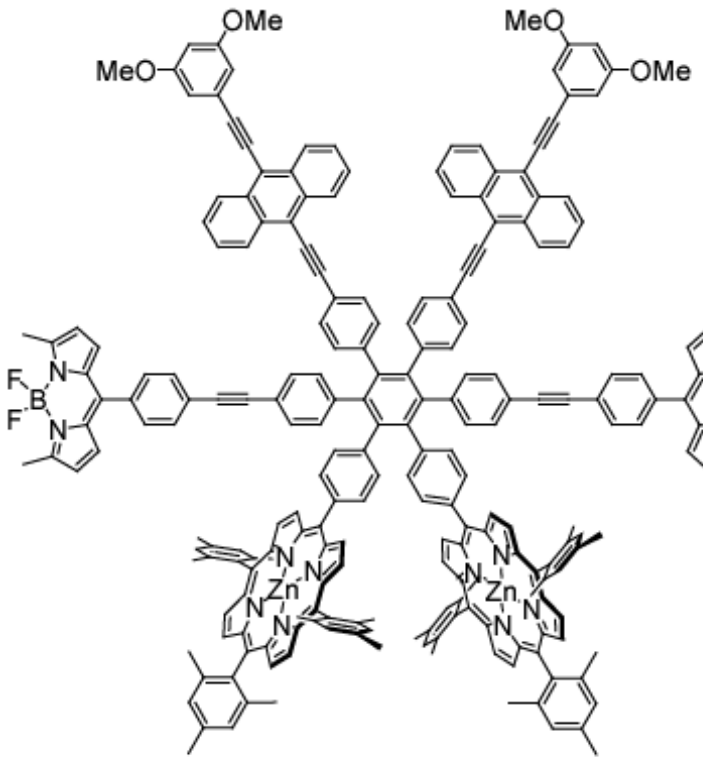
Kodis, G.; Liddell, P. A.; de la Garza, L.; Clausen, P. C.; Lindsey, J. S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Phys. Chem. A.* **2002**, *106*, 2036-2048

Other photosynthetic antenna chromophores



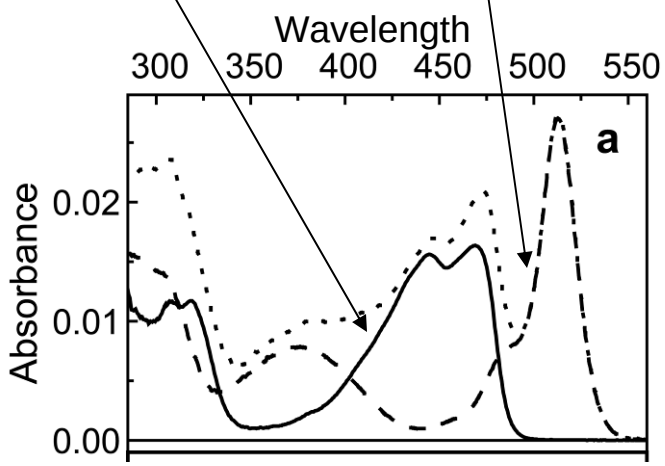
Based on Govindjee and Govindjee, R. (1974), Sci. Am. 231(6):68-82

A funnel-like antenna – RC complex

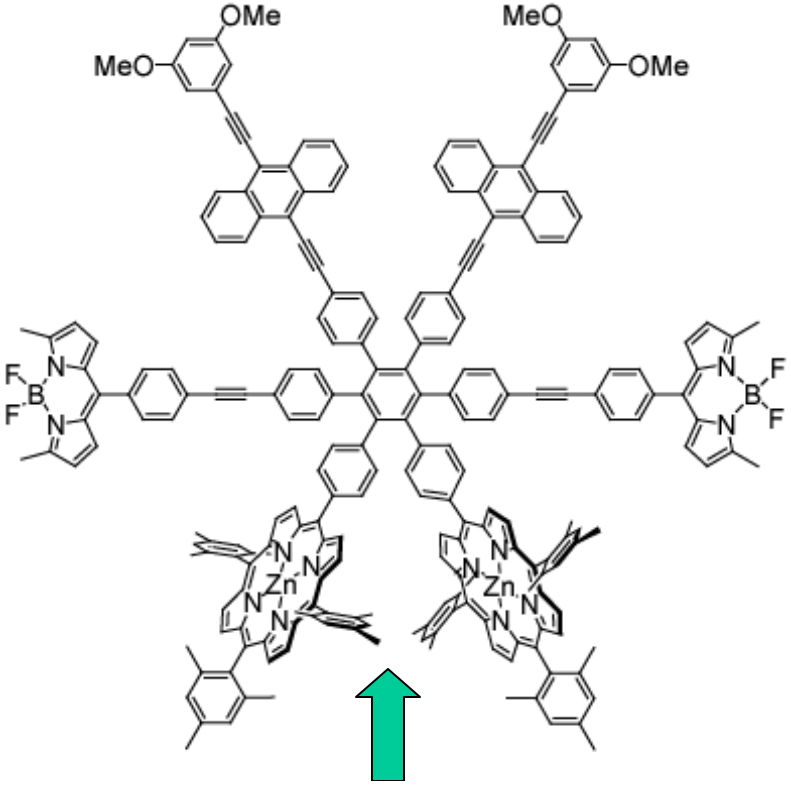


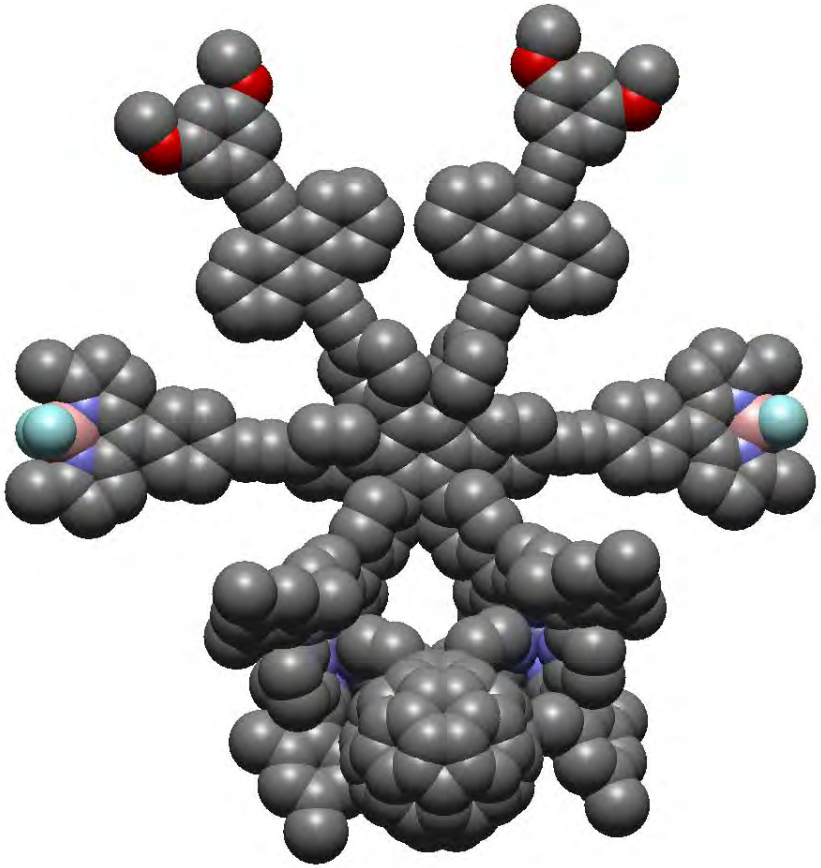
BPEA
Absorbs in blue region

BDPY
Absorbs in green region



A funnel-like antenna – RC complex

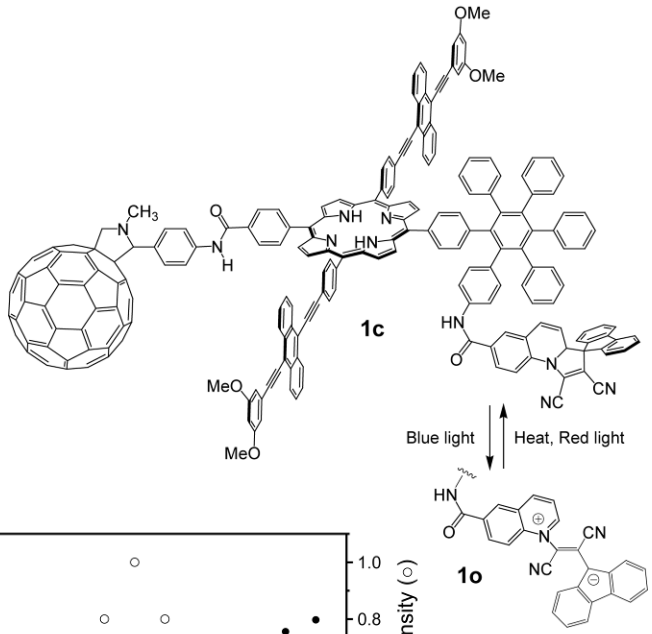


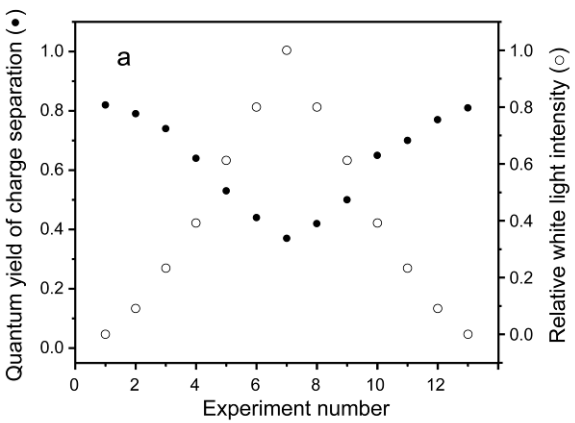


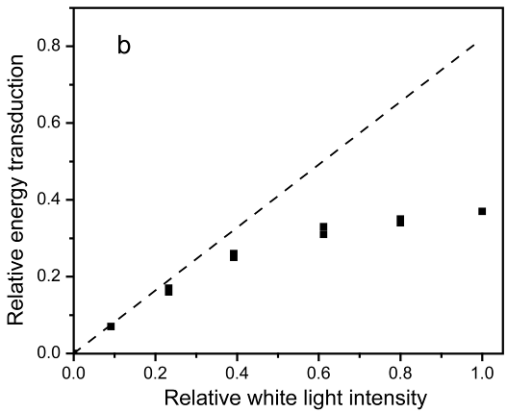
Photoprotection

- Photosynthetic organisms prevent photodamage by:
  - Protecting themselves from light-generated reactive species
  - Regulating photosynthesis to prevent formation of reactive species
  - Repairing photodamage

A self-regulating artificial photosynthetic molecule







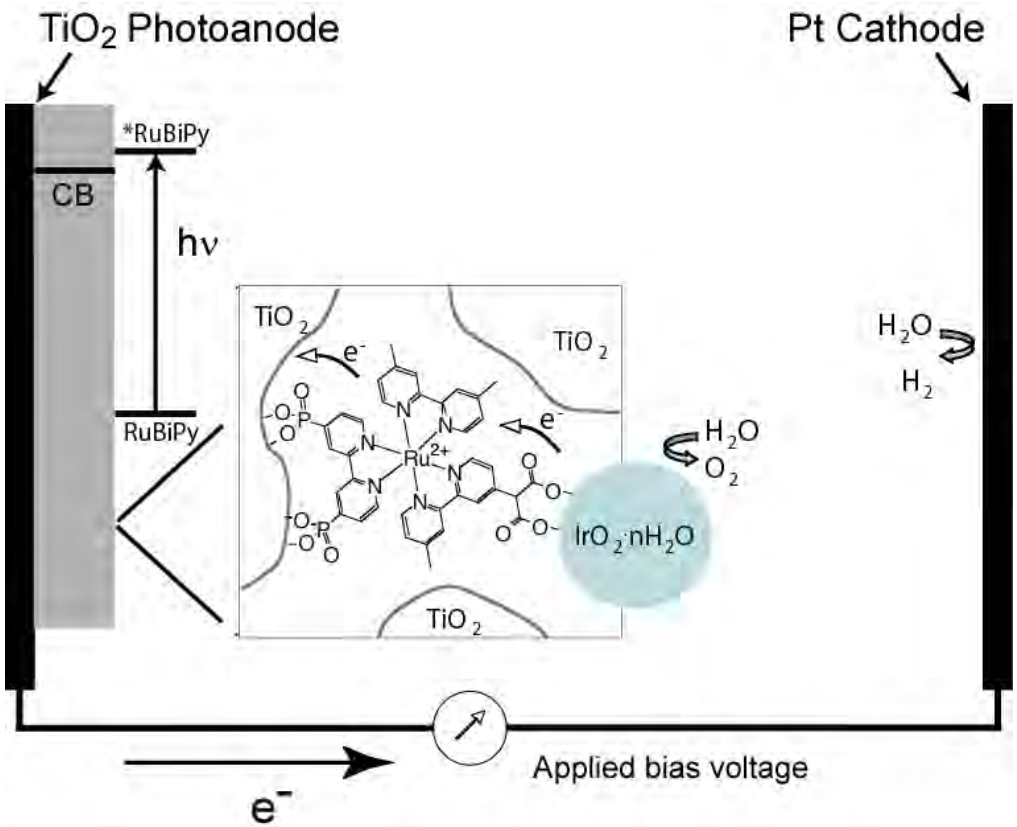
This molecule converts light energy to electrochemical potential, and responds nonlinearly to the light intensity, down-regulating energy conversion at high light levels. This adaptive behavior functionally mimics a mechanism that plants use to prevent photodamage at high levels of sunlight.

Straight, S. D.; Kodis, G.; Terazono, Y.; Hambourger, M.; Moore, T. A.; Moore, A. L.; Gust, D. *Nature Nanotechnology* **2008**, *3*, 280-283.

Solar fuel production

- How can artificial antenna-reaction center complexes be interfaced to catalysts for water oxidation and fuel production?
- What catalysts will be useful?
  - High turnover number
  - Low overpotential (activation energy)
  - Use earth-abundant elements

Photocatalytic water splitting

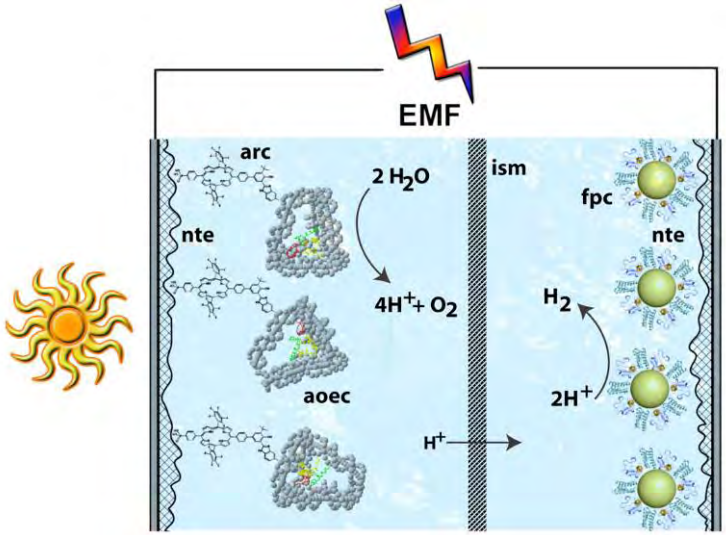


W. J. Youngblood, S.-H. A. Lee, Y. Kobayashi, E. A. Hernandez-Pagan, P. G. Hoertz, T. A. Moore, A. L. Moore, D. Gust, T. E. Mallouk, *J. Am. Chem. Soc.*, **2009**, *131*, 926-927

Φ ~ 0.9 %, additional potential needed, uses rare element, not particularly stable

Energy Frontier Research Center for Bio-Inspired Solar Fuel Production

The goal of the Center is to construct a complete system for solar-powered production of fuels such as hydrogen via water splitting. Design principles will be drawn from the fundamental concepts that underlie photosynthetic energy conversion.



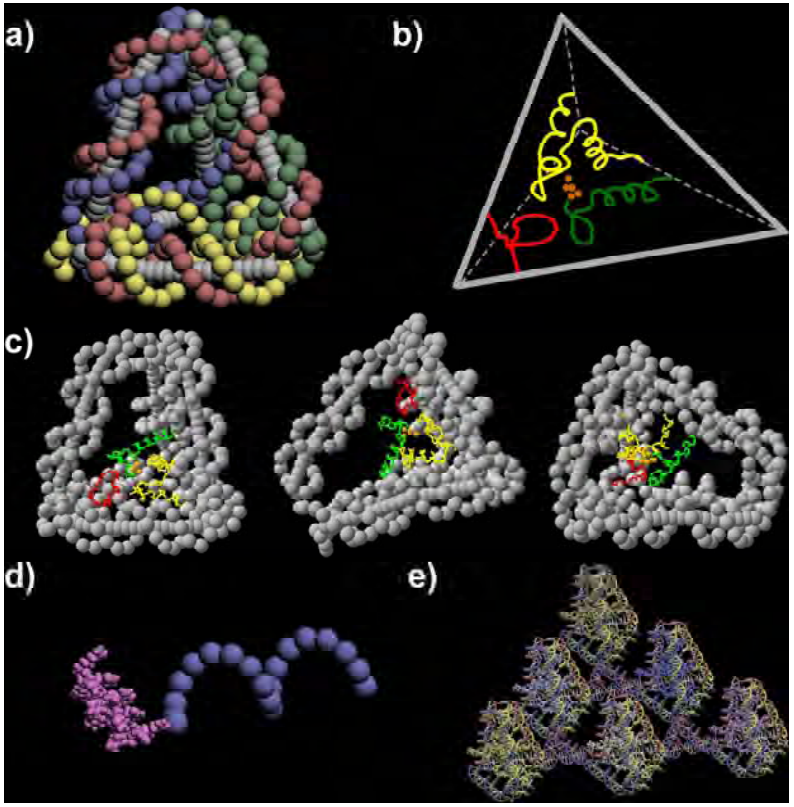
RESEARCH PLAN AND DIRECTIONS

The chemistry of photosynthetic reaction centers, water oxidation proteins, and hydrogen-producing enzymes will be incorporated into nanoscale artificial constructs that make hydrogen using sunlight. Success requires advances in electron transfer chemistry, synthetic enzymes, DNA as a structural material, and functional nanostructured metal oxides. Success will lead to new technologies for solar fuels.

ARIZONA STATE UNIVERSITY

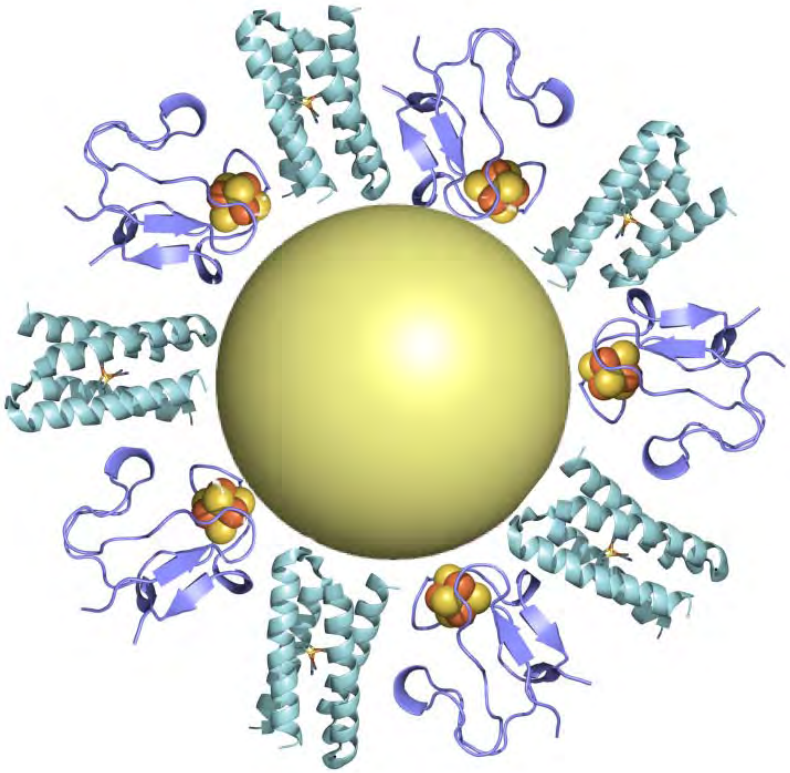
http://solarfuel.asu.edu/EFRC/

Water oxidation complex



- Based on the natural photosynthetic oxygen evolving complex of PSII
- Short peptides will assemble an inorganic complex for water oxidation.
- The peptides will be organized by a self-assembled DNA framework.
- The assembled complex will donate electrons to the oxidized artificial reaction center complex.

Fuel production complex



- Based on hydrogenase enzymes and natural redox proteins
- Short peptides will organize inorganic complexes for accumulation of reduction potential and proton reduction.
- Metal nanoparticles will accept electrons from the artificial reaction center and deliver them to the hydrogen production site.

Conclusions

- Photosynthetic principles can guide the design of artificial systems that convert sunlight into useful forms of energy
  - Antenna function
  - Photoinduced charge separation
  - Regulation and photoprotection
  - Production of useful fuels
- Such systems are in general not yet practical for technological applications – more research is needed