Artificial Photosynthesis – from Light Absorption to Solar Fuels

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Best current “technology” for solar energy conversion- 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

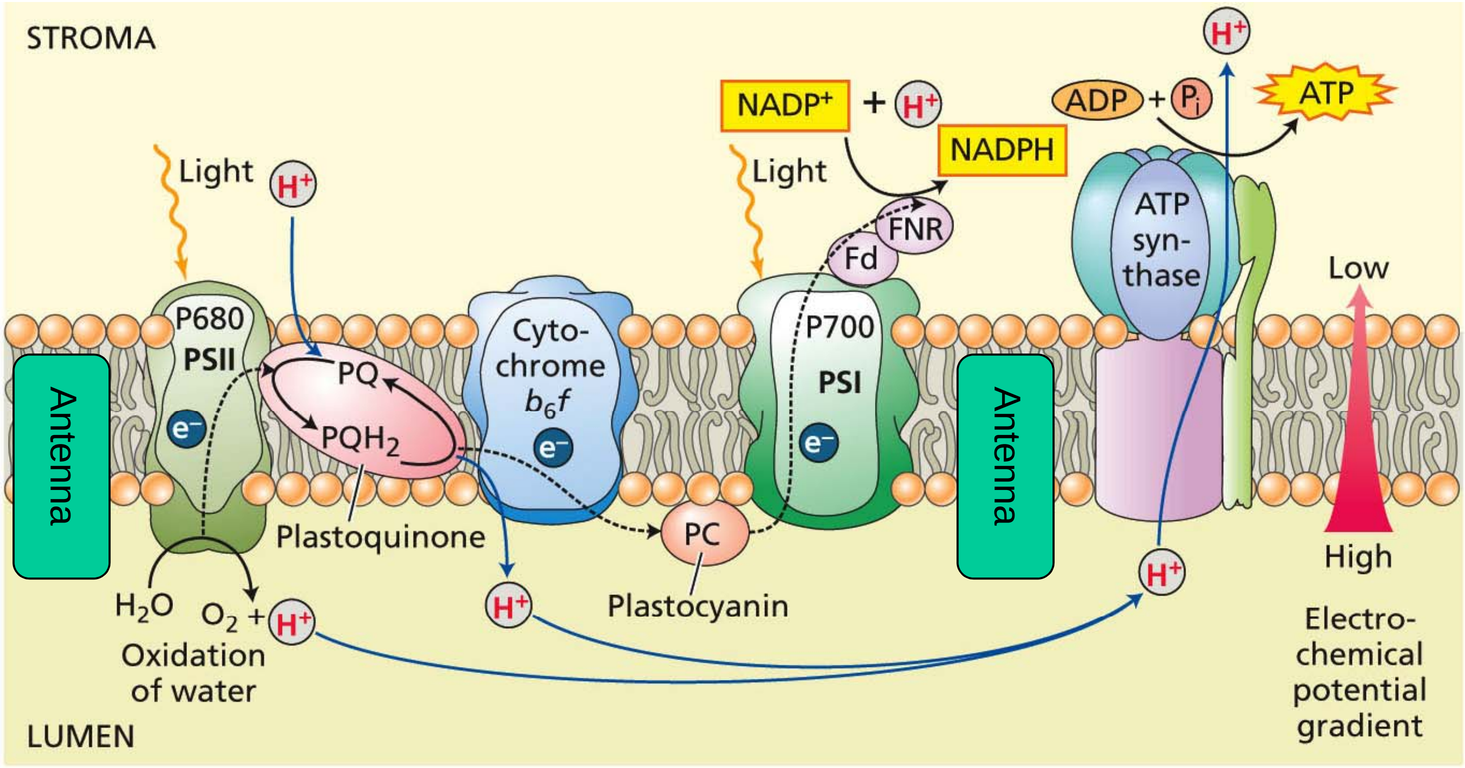
(10 times human needs)

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

Artificial photosynthesis

- Exploiting the physics and chemistry underlying photosynthesis for technological purposes

How does photosynthesis work?



Antennas

Light capture, excitation energy migration, regulation and photoprotection

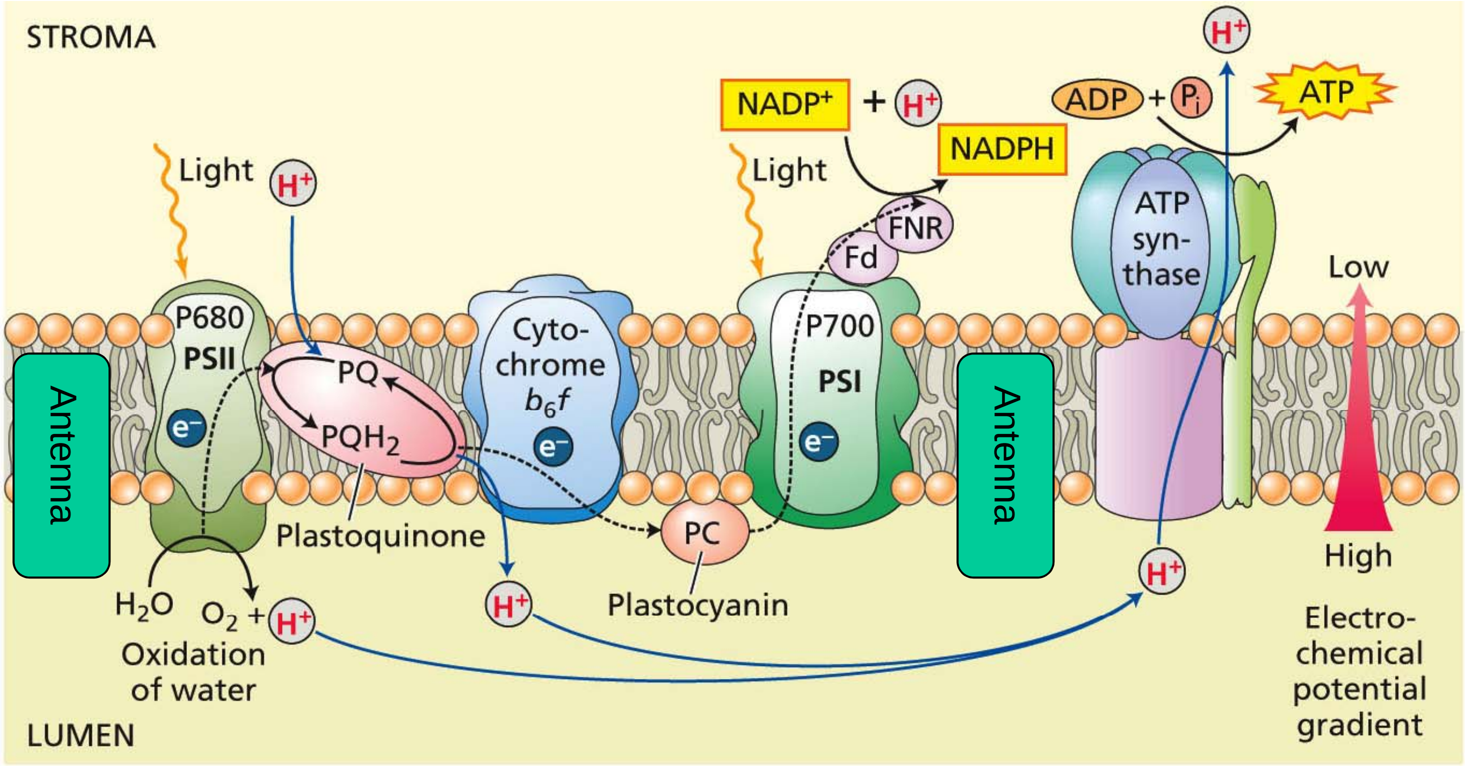
Reaction centers

Charge separation, electrochemical energy

Dark chemical reactions

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

How does photosynthesis work?

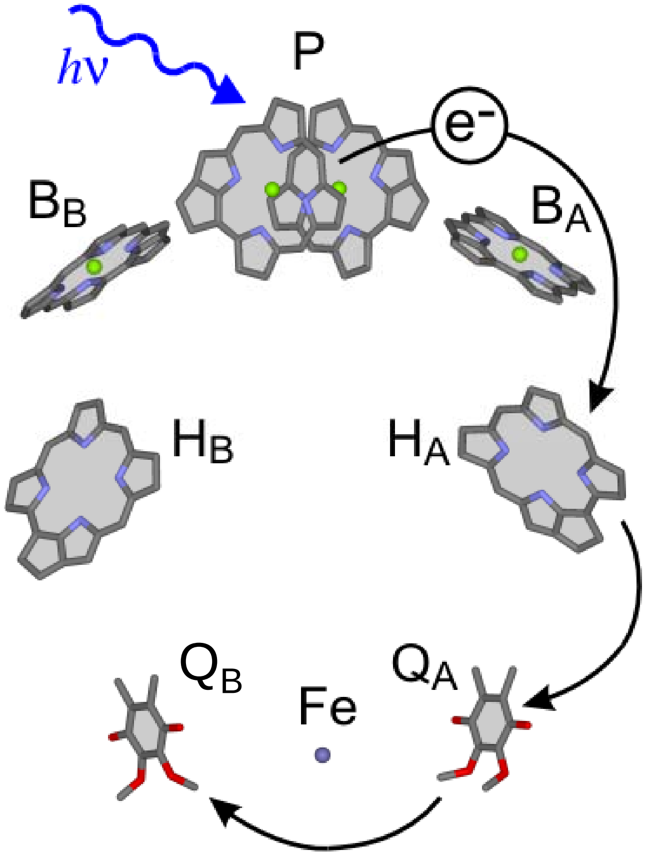


Natural Nanotechnology

Reaction centers

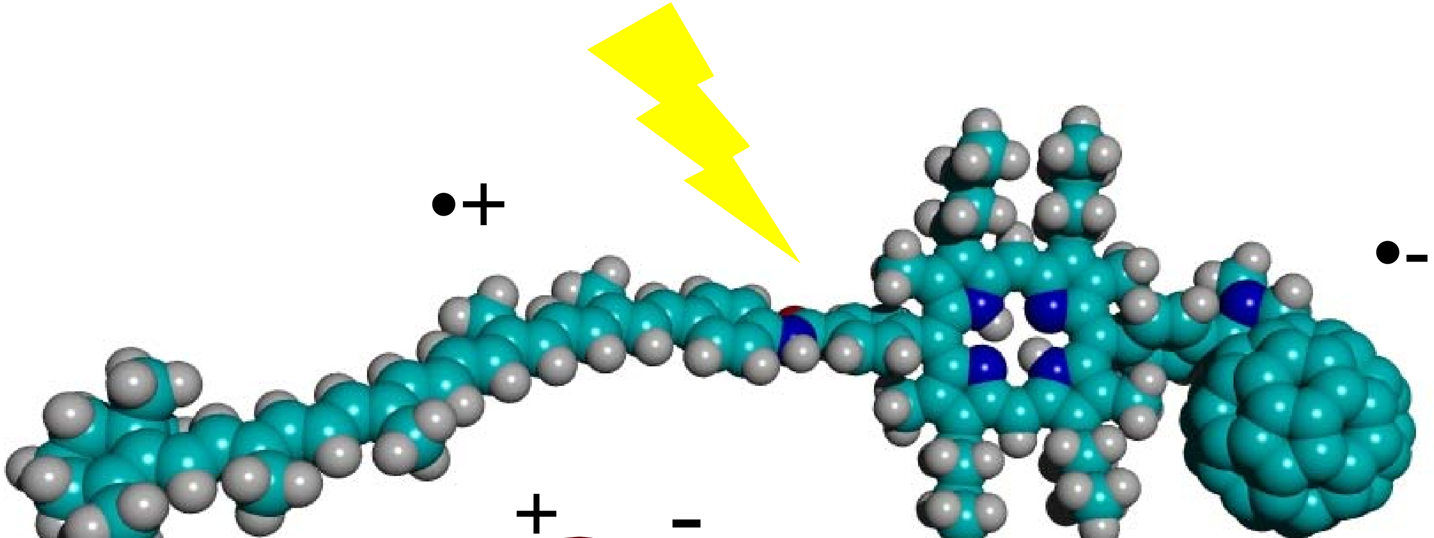
Bacterial reaction center

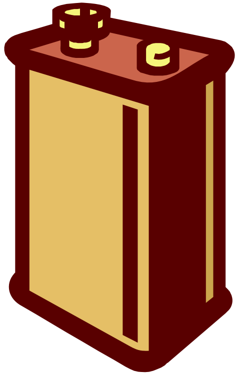
N. Woodbury, Department of Chemistry and Biochemistry,
Arizona State University



http://www.fuchs-research.net

Artificial reaction centers

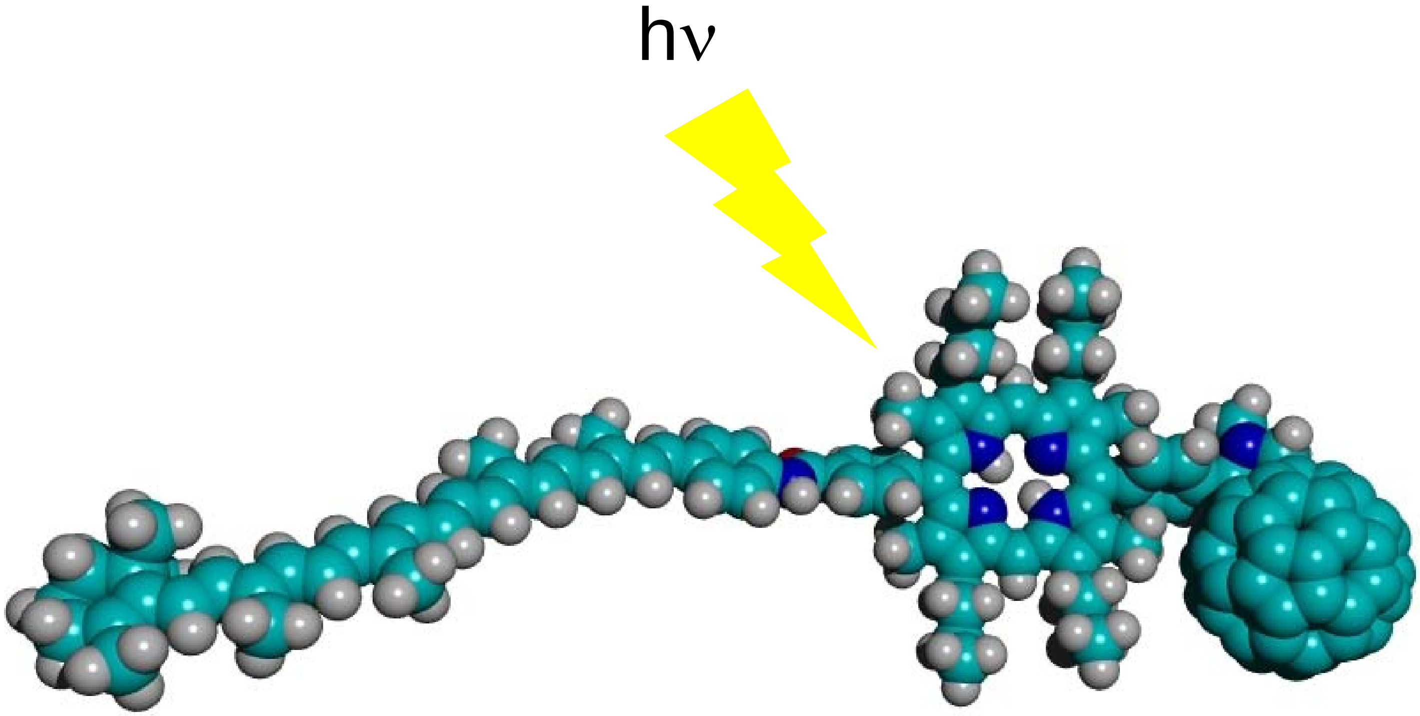




Molecular photovoltaics

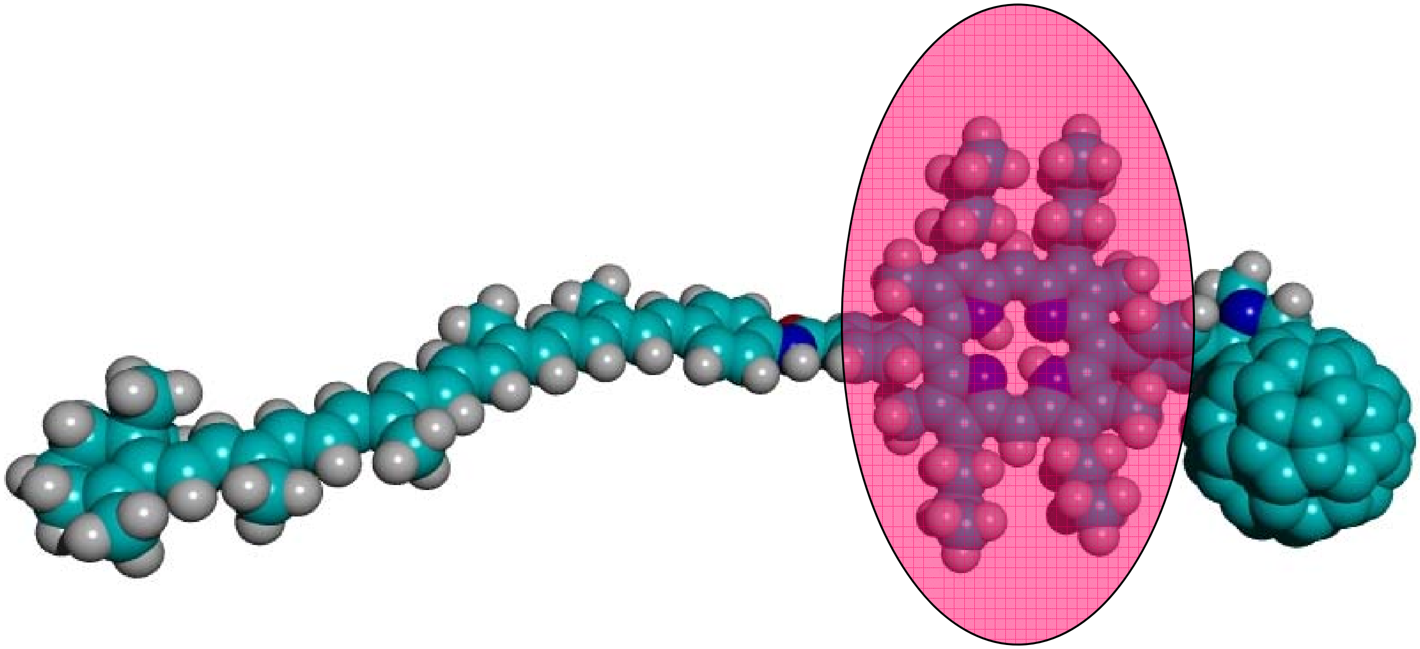
Kuciauskas, D.; Liddell, P. A.; Lin, S.;
Stone, S. G.; Moore, A. L.; Moore, T. A.;
Gust, D. *J. Phys. Chem. B* ***2000***, *104*,
4307

Light absorption



C-P-C_{60}

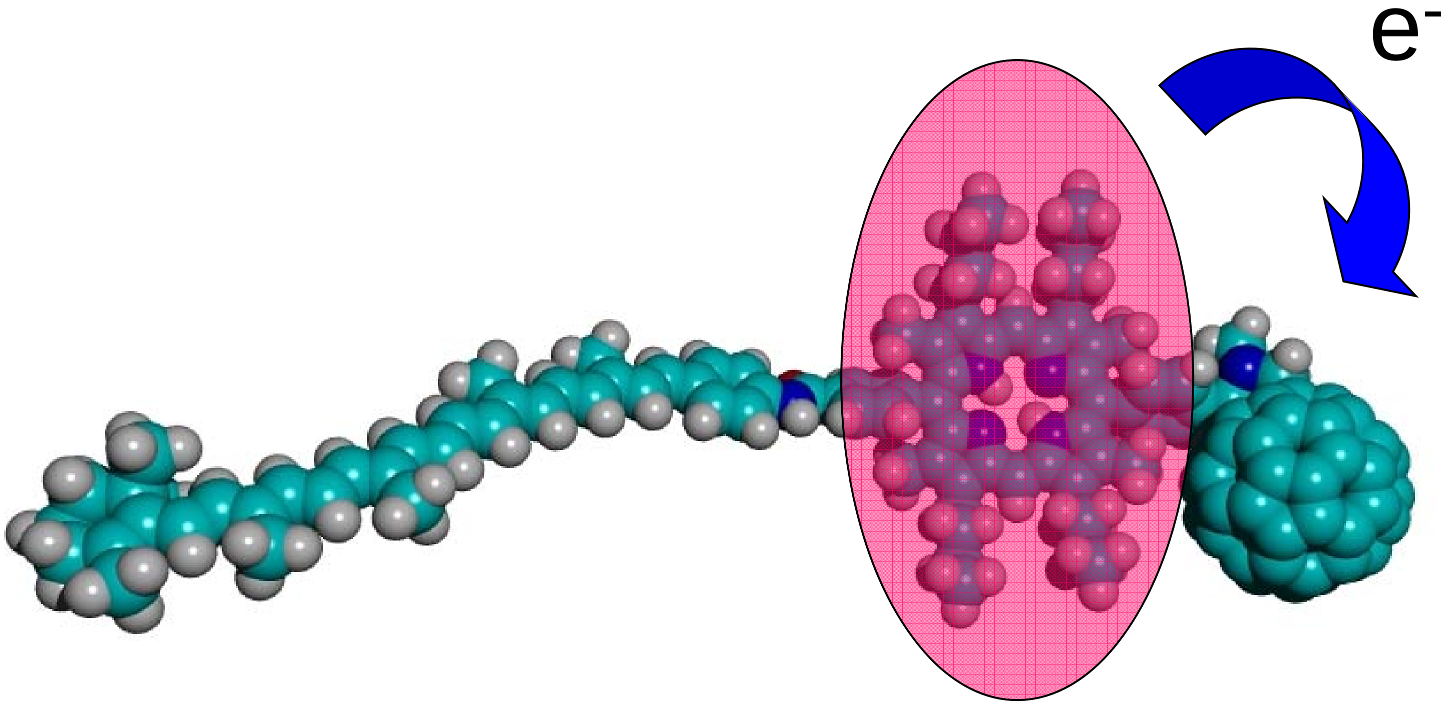
Light absorption



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

Porphyrin first excited singlet state

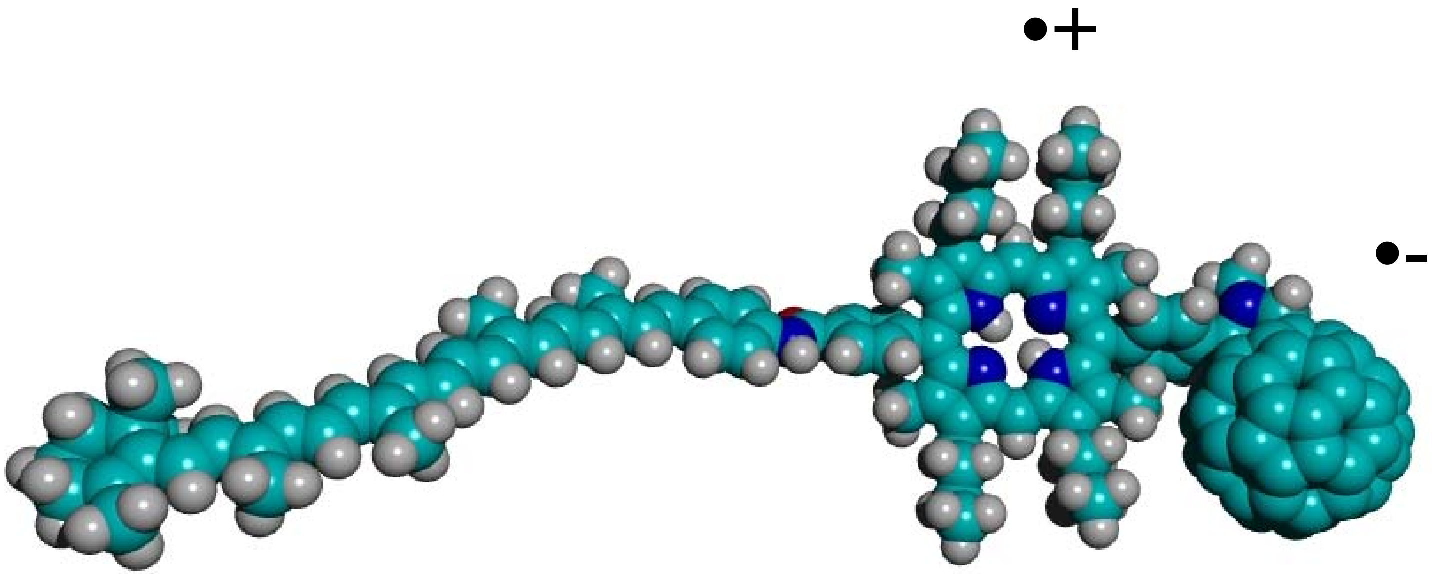
Photoinduced electron transfer



3 picoseconds

(3 x 10^{-12} s)

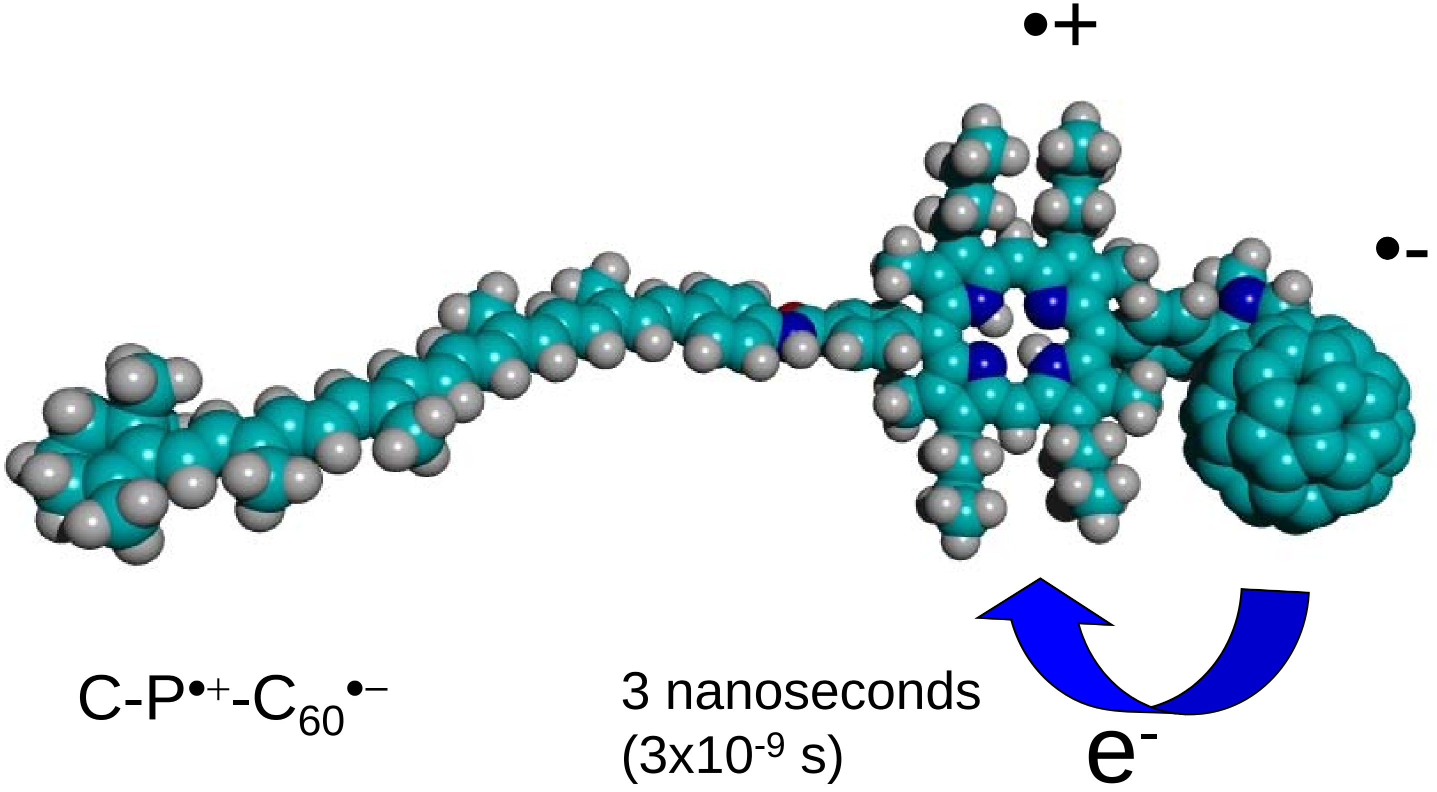
Photoinduced electron transfer



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

Charge-separated state

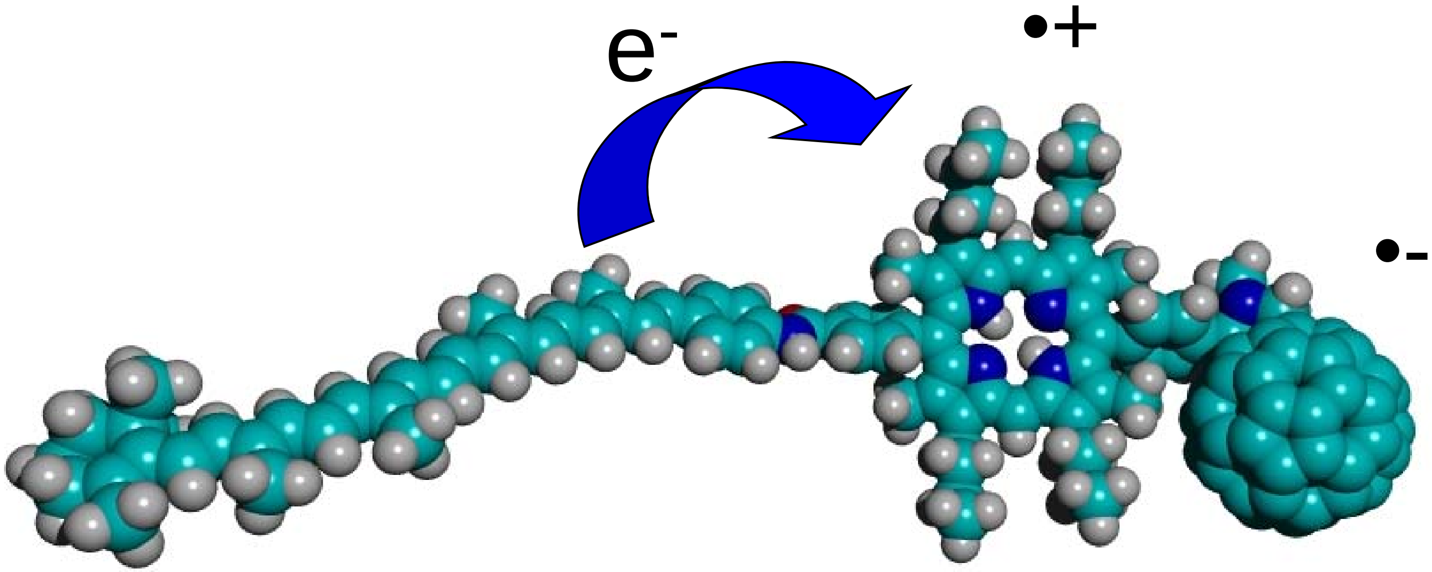
Charge recombination



C-P•+-C_{60}•–

3 nanoseconds
($3x10^{-9}$ s)

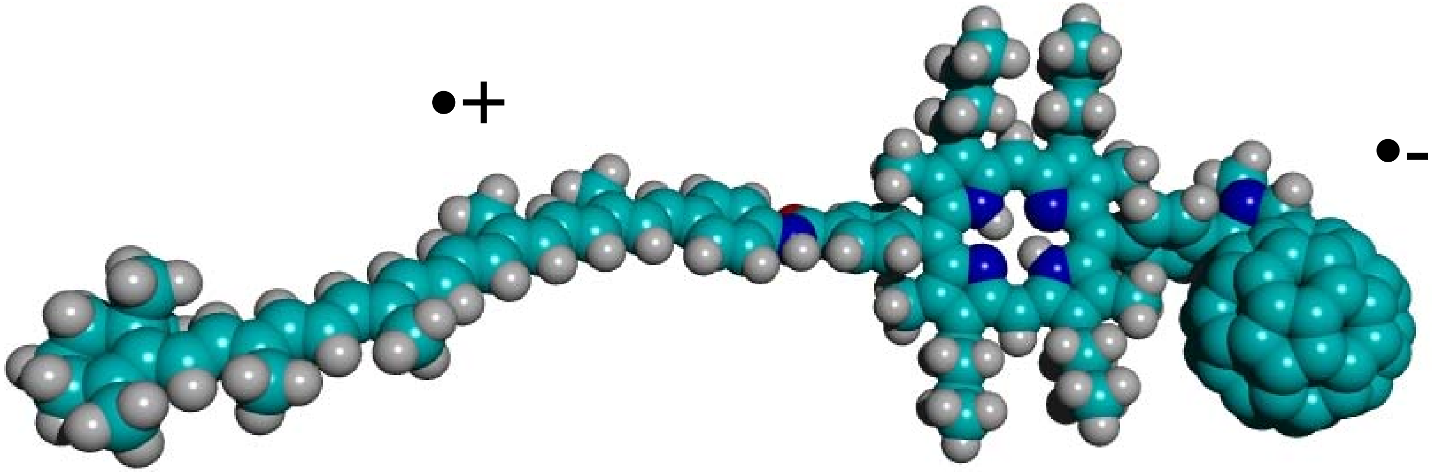
Charge shift reaction



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

67 picoseconds

Light energy stored as electrochemical energy



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

Final charge-separated state

Light energy stored as electrochemical energy

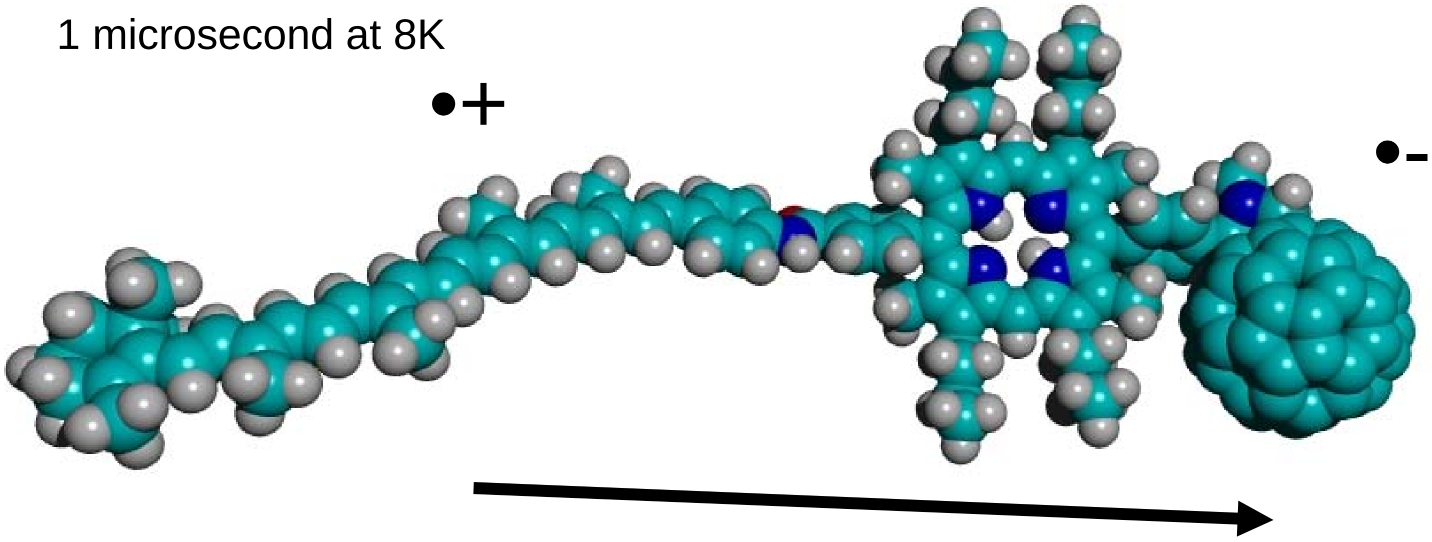
Yield of charge separated state ~ 100%

Stored energy ~1.0 electron volt

Lifetime = hundreds of ns at room temp.

1 microsecond at 8K

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



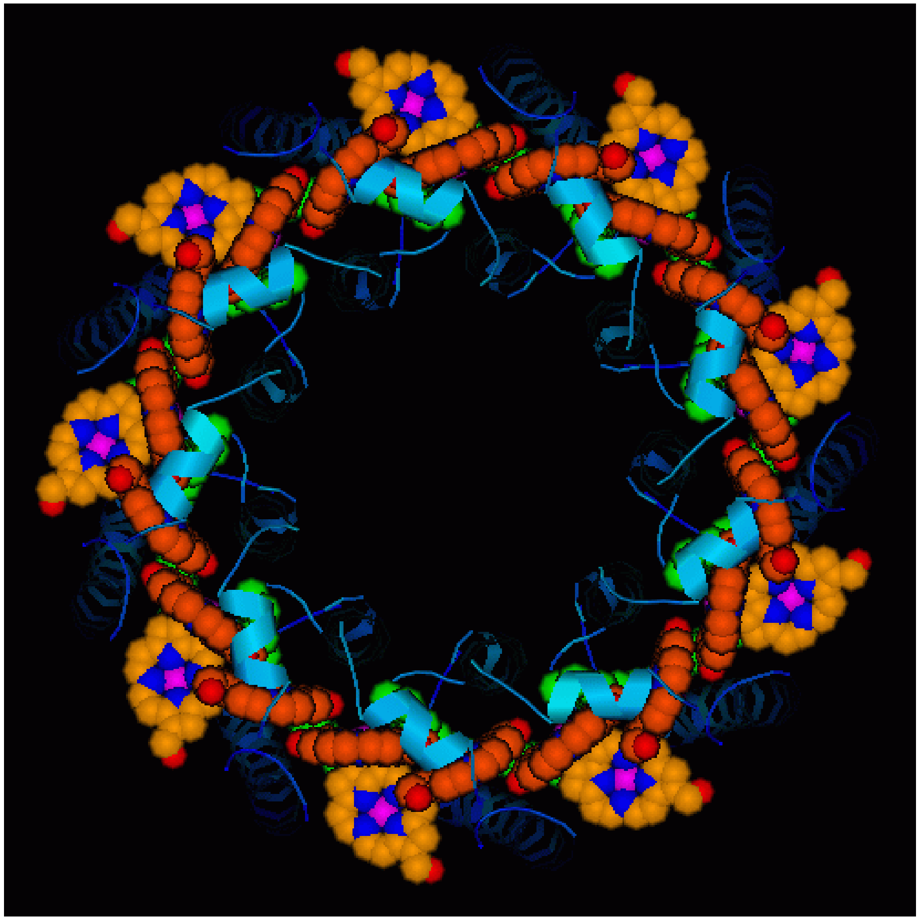
Dipole moment ~160 D

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

Artificial antenna systems

LH2 Photosynthetic antenna

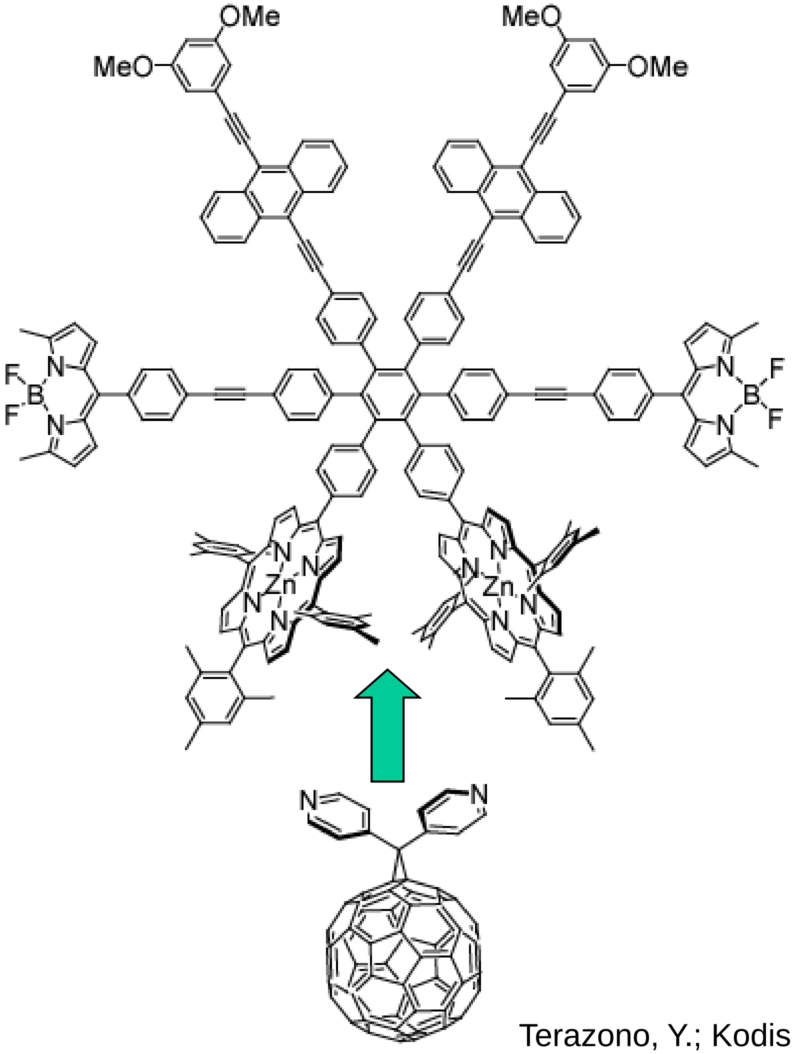
Rhodopseudomonas acidophila

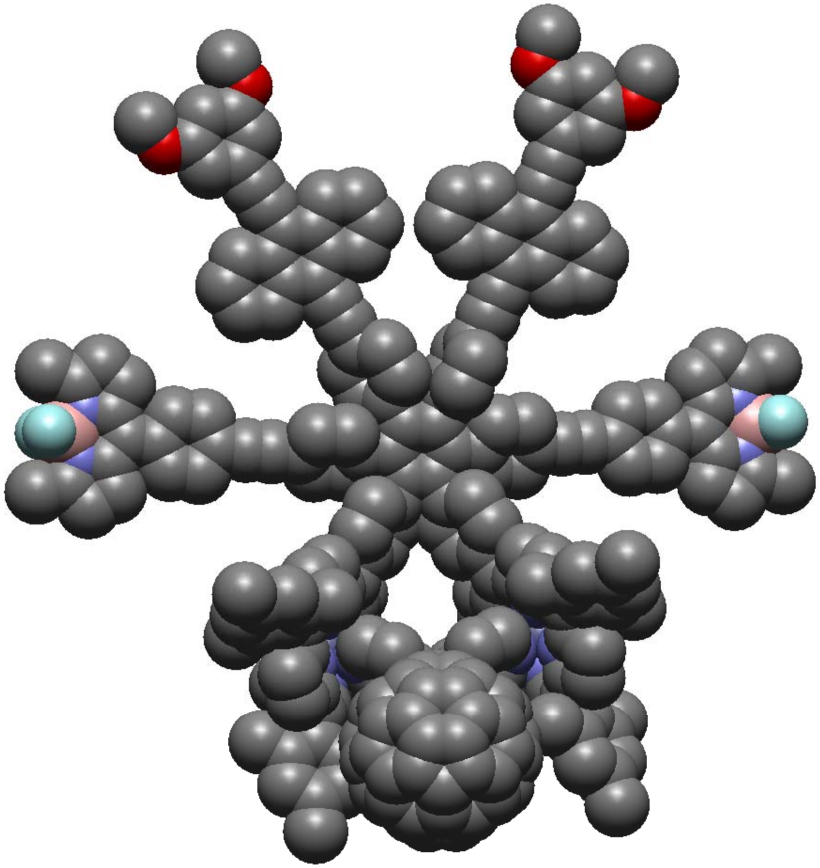


R. Cogdell,

N. Isaacs

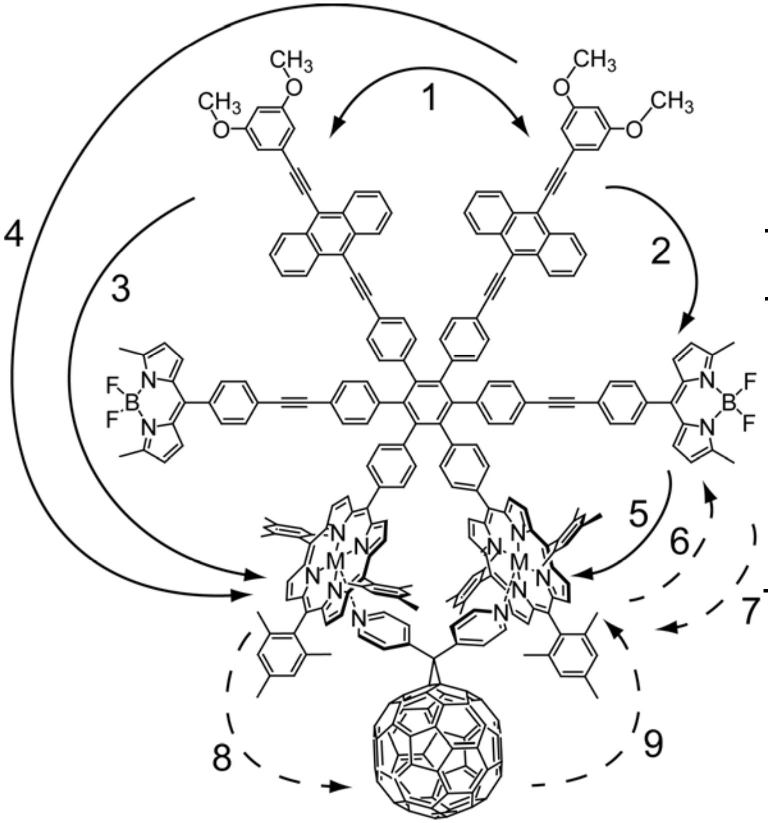
A funnel-like antenna – RC complex





Terazono, Y.; Kodis, G.; Liddell, P. A.; Garg, V.; Moore, T. A.; Moore, A. L.; Gust, D. *J. Phys. Chem. B* **2009**, *113*, 7147-7155

Energy and electron transfer



Time constants for photochemical processes (ps)

	porphyrin hexad	zinc		porphyrin fullerene
process	free base	hexad		heptad
	2-meTHF	2-meTHF	1,2-DFB	1,2-DFB
step 1	0.4	0.4	0.4[d]	0.4
step 2	5 - 14	5 - 14	5 - 13	5 - 13
step 3	8	7	7[d]	7
step 4	4	6	6	6
step 5	5 - 26	4 - 21	2 - 15	2 - 15
step 6		570	230	230
step 7		4800	1500	1500
step 8				3
step 9				230

Both energy transfer to the porphyrins and photoinduced electron transfer are highly efficient.

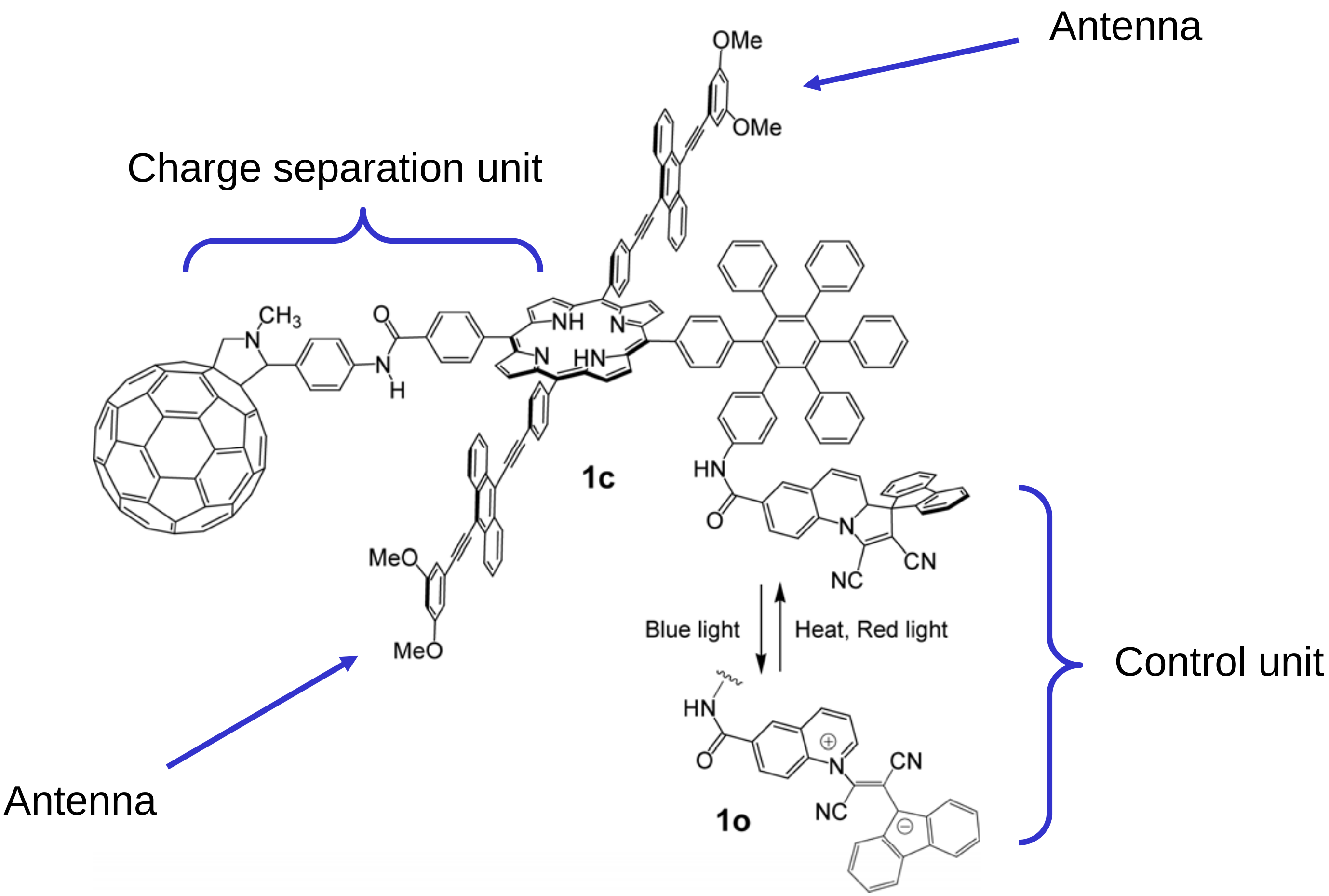
Regulation and photoprotection

- Sunlight is diffuse, so photosynthesis uses antennas to maximize delivery of excitation energy to reaction centers.
- If the sunlight intensity suddenly increases, photosynthesis is overdriven. Singlet oxygen, reactive radicals, redox intermediates, and other destructive species are produced.
- Photosynthetic organisms have evolved regulatory mechanisms to down-regulate delivery of excitation energy to reaction centers under such conditions. (e.g., “non-photochemical quenching, NPQ”)

Regulation in nanotechnology

- Functional nanoscale systems, including artificial photosynthesis, will need self-regulation and control circuits.
- How can we design photocatalysts or other molecular components that are not only functional, but also adaptive, responding to changes in their environment?

Self-regulation of photoinduced electron transfer by a molecular nonlinear transducer



Antenna

Charge separation unit

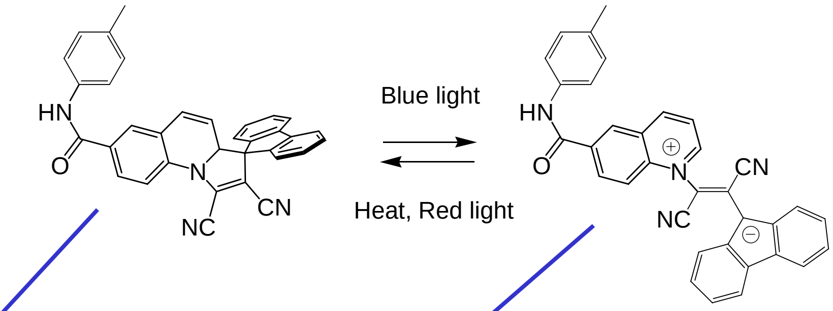
Control unit

Antenna

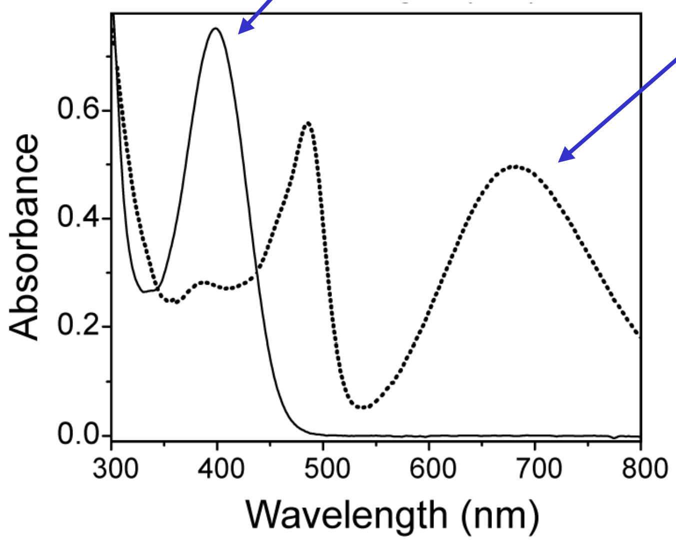
Straight, S. D.; Kodis, G.; Terazono, Y.;
Hambourger, M.; Moore, T. A.; Moore, A. L.;
Gust, D. *Nature Nanotechnology* **2008**, *3*, 280

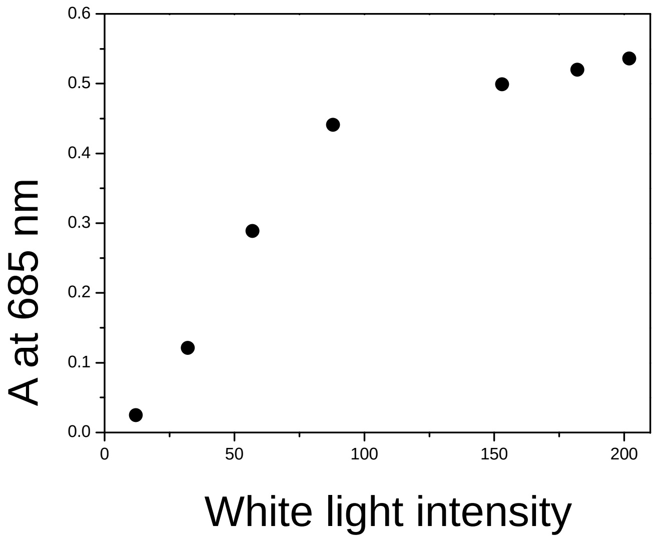
Photochromic control unit

DHI
dihydroindolizine



BT
betaine





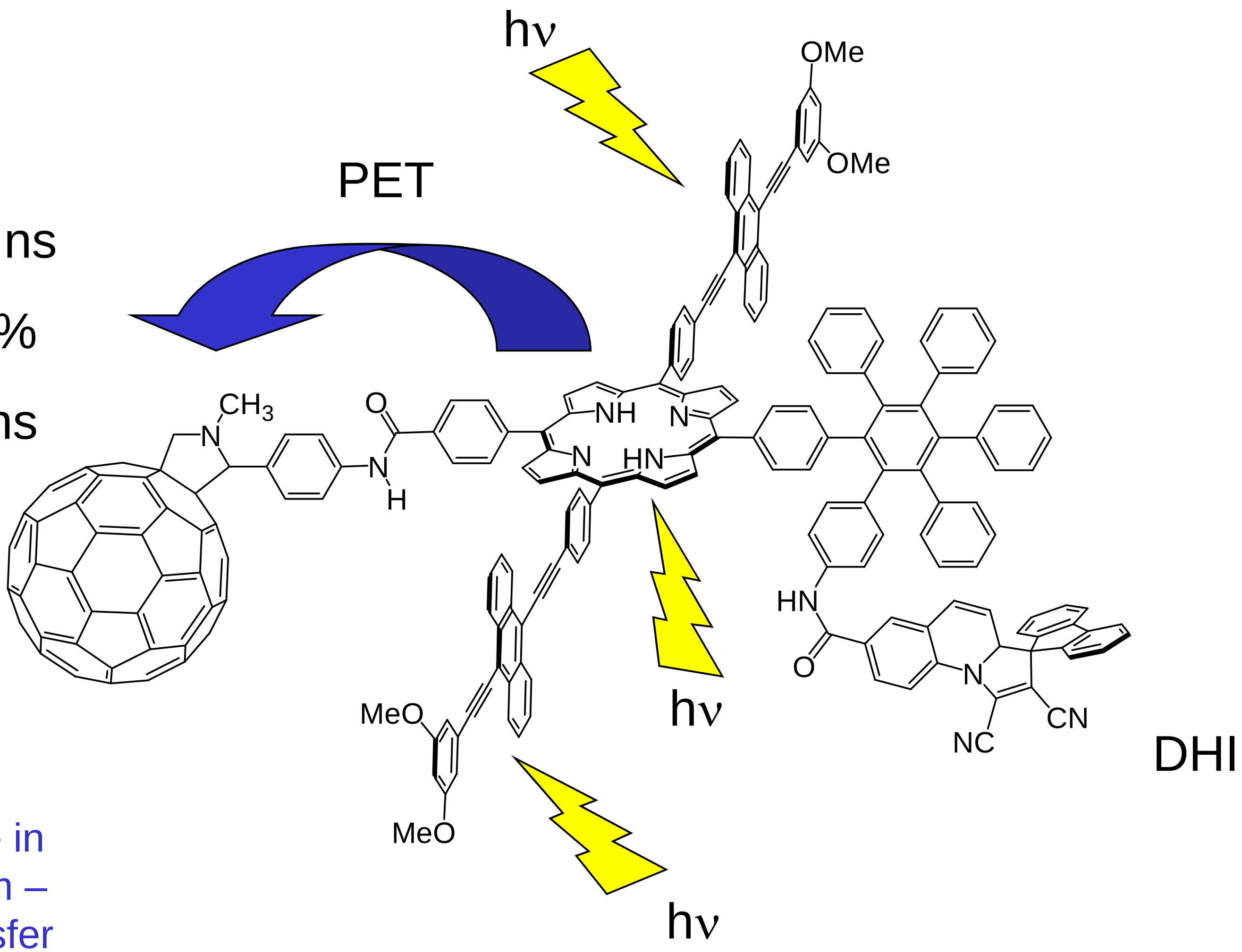
Photostationary
distribution

Principle of operation

τ_{cs} = 2.2 ns

Φ_{cs} = 82%

τ_{cr} = 14 ns

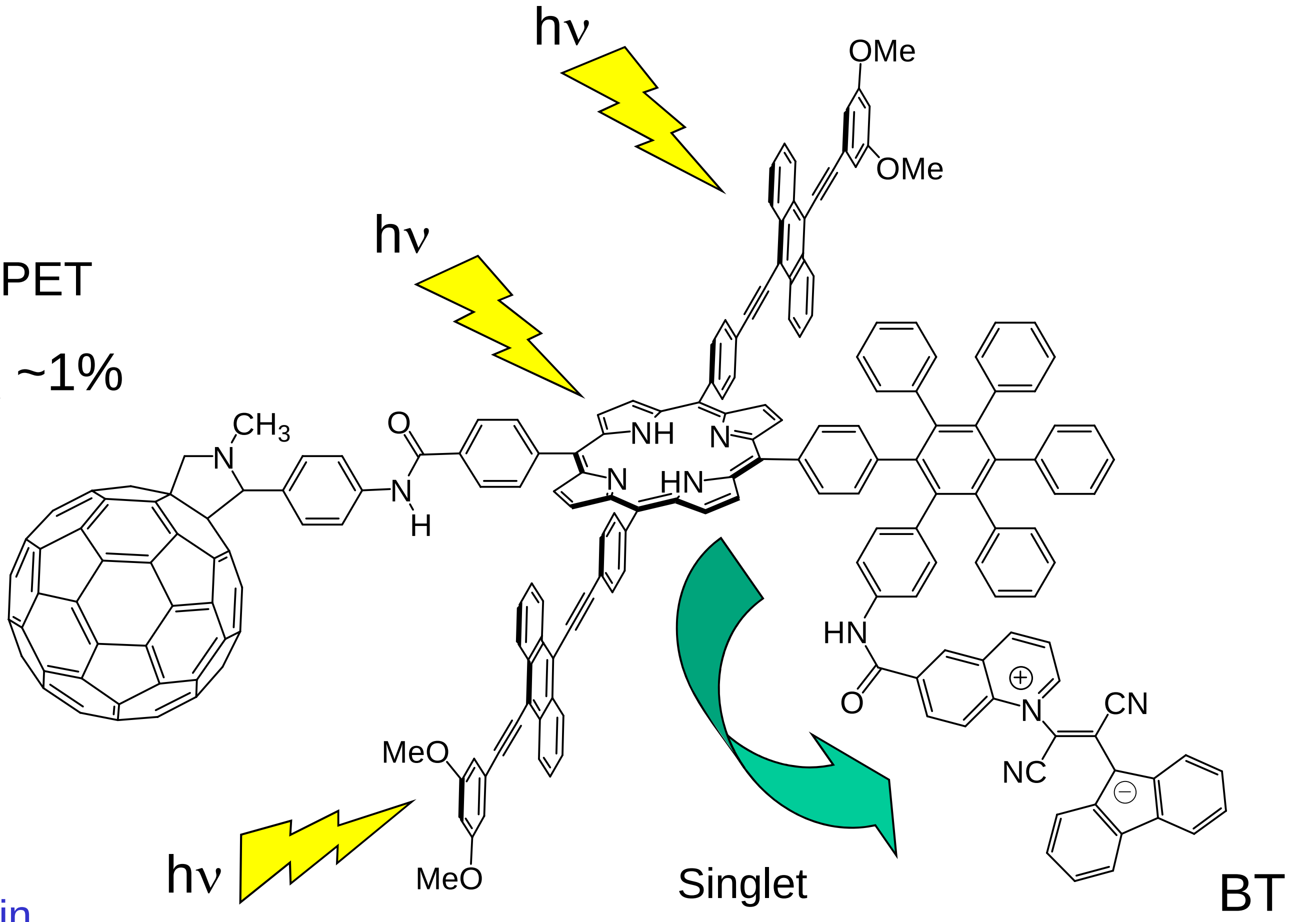


Photochrome in colorless form – electron transfer

Principle of operation

No PET

Φ_{cs} ~1%

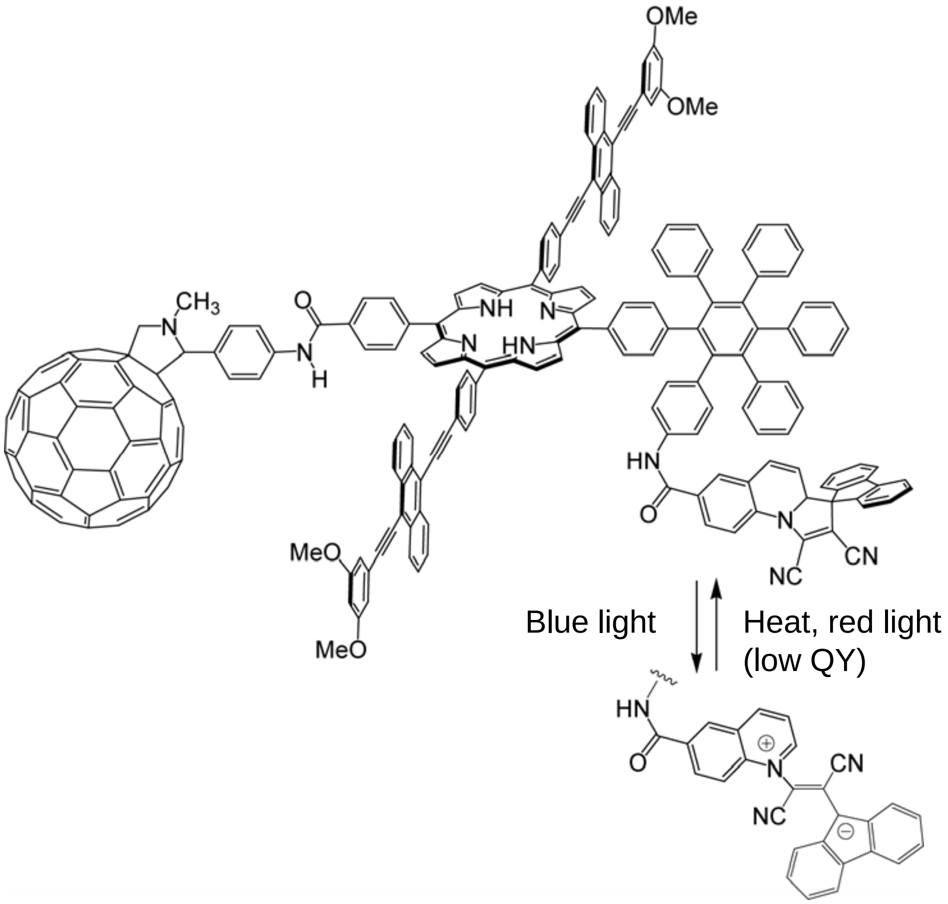


Singlet energy transfer quenching

τ_{ent} = 33 ps

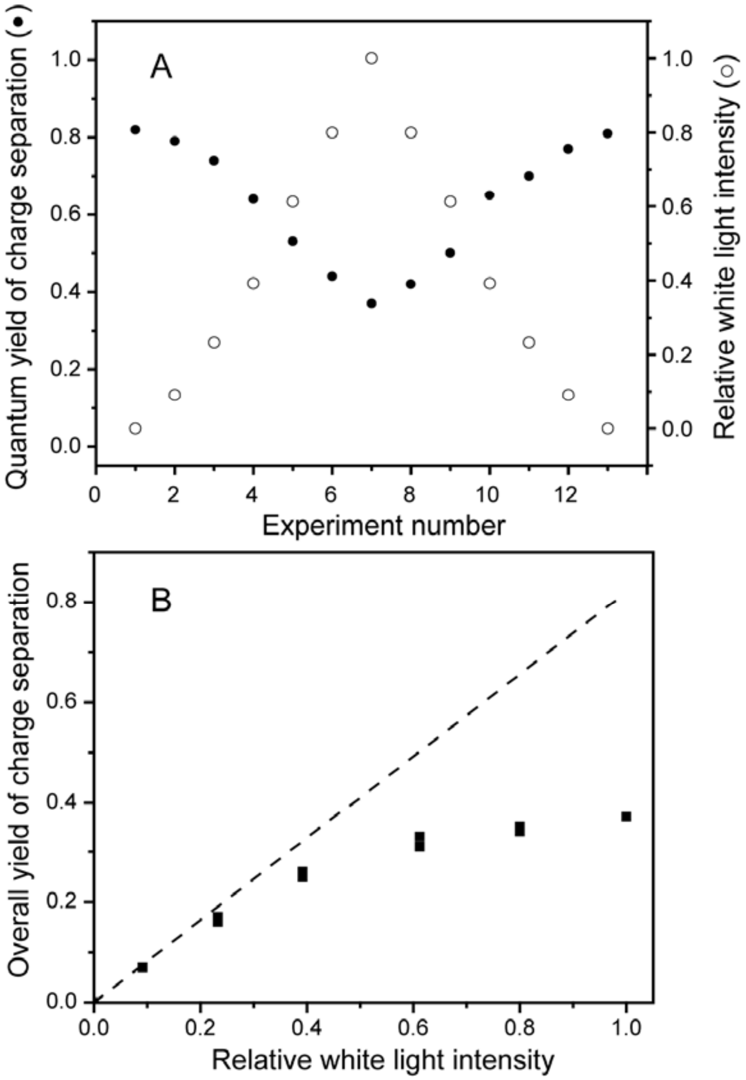
Photochrome in colored form – no electron transfer

Principle of operation



Isomer ratio, and therefore the amount of quenching, is determined by white light intensity and temperature

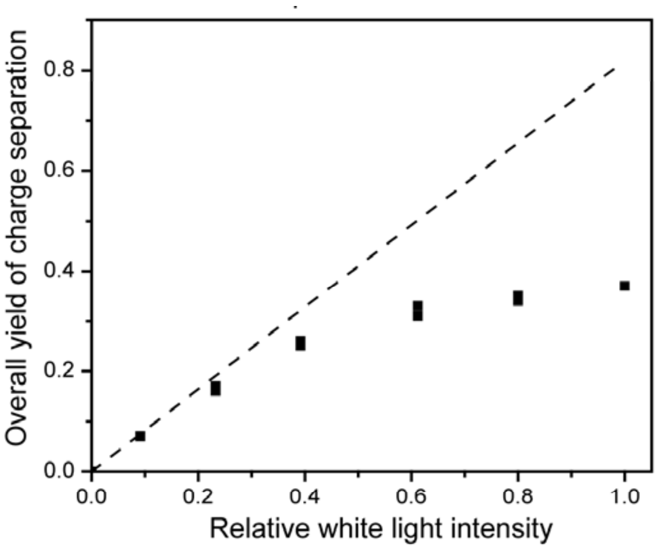
Operation



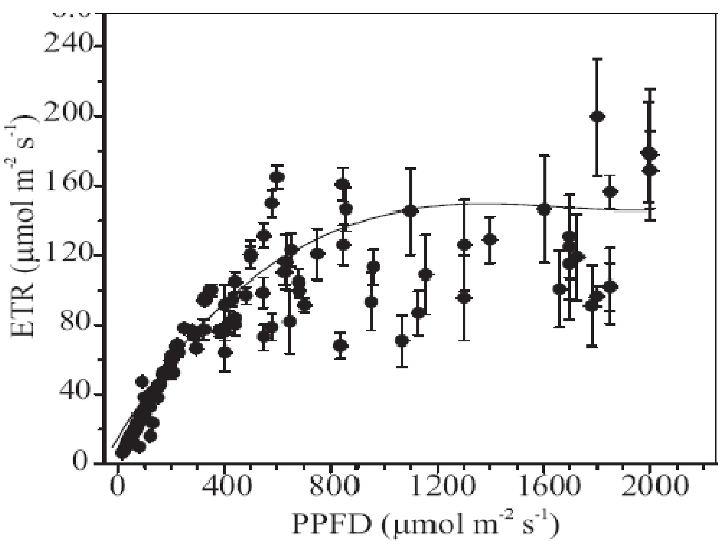
Quantum yield of charge separation is reduced from 82% at low light to as low as 27% under bright white light.

The overall yield of charge separation is a non-linear function of white light intensity

Comparison with natural NPQ



Photosynthetic electron transport



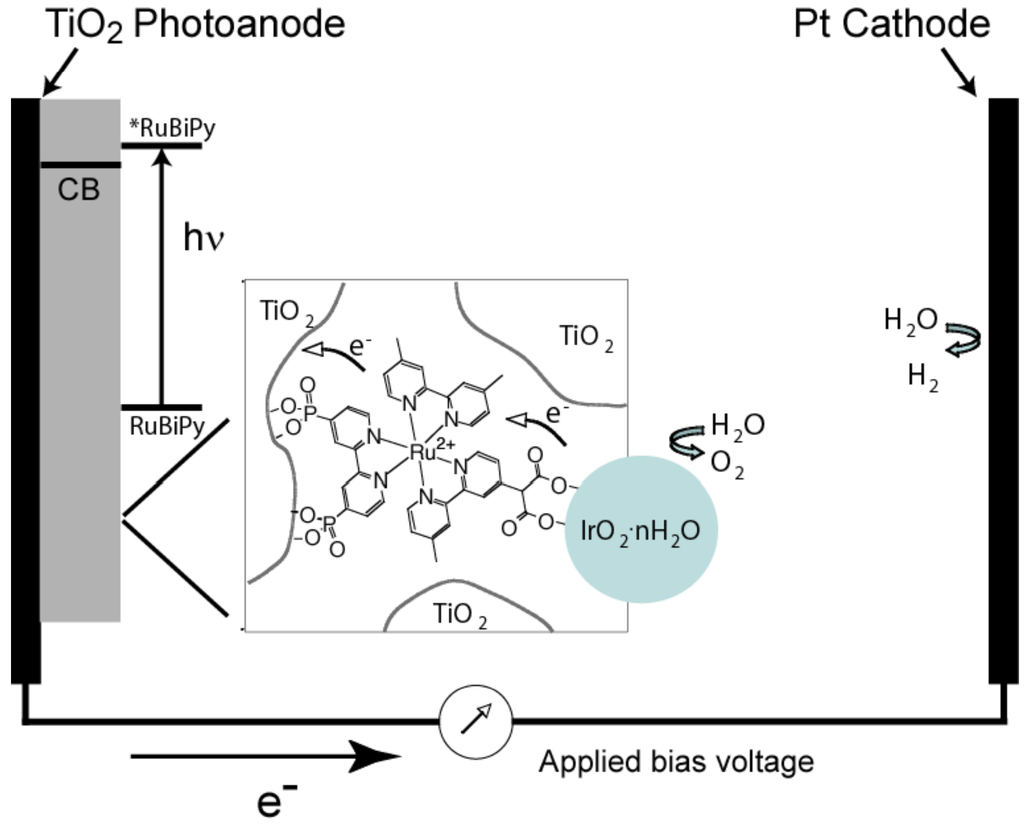
Photon flux density

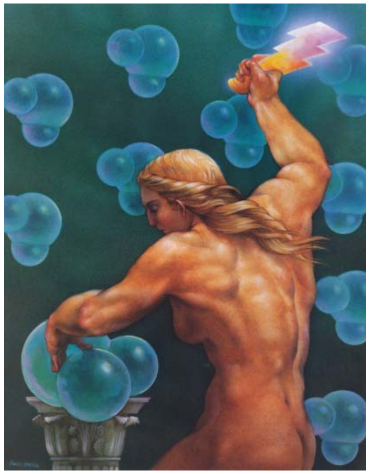
Self-regulation in molecular system

Natural regulation in orange trees

Ribeiro, R. V.; Machado, E. C. *Braz. J. Plant Physiol.* ***2007,*** *19*, 393-411.

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

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 or electricity

- Such systems are in general not yet practical for technological applications – more research is needed

Many thanks to

- Tom Moore, Ana Moore, Tom Mallouk, Sergei Smirnov, Chuck Braun
- Many students and postdocs – listed on the slides
- The Department of Energy and National Science Foundation for funding