The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

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2269-3

Workshop on New Materials for Renewable Energy

17 - 21 October 2011

Natural and artificial photosynthesis: Basic concepts

Vincenzo BALZANI

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Natural and artificial photosynthesis: basic concepts

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Workshop on New Materials for Renewable Energies

ICTP Trieste

October 17-21, 2011

If you really wish to understand
a problem, you should first
look at it from
far away

Italo Calvino

Photograph taken by the Cassini Orbiter spacecraft on Sept 15, 2006, at a distance of 1.5 billion km from Earth.


Earthrise
“We came all this way to explore the moon,
and the most important thing is that
we discovered the Earth”

Space-ship Earth

passengers: 7 billions
(8 billions in 2025)

increase:
75 millions per year

new-borns per minute
32 Indians
24 Chinese
....

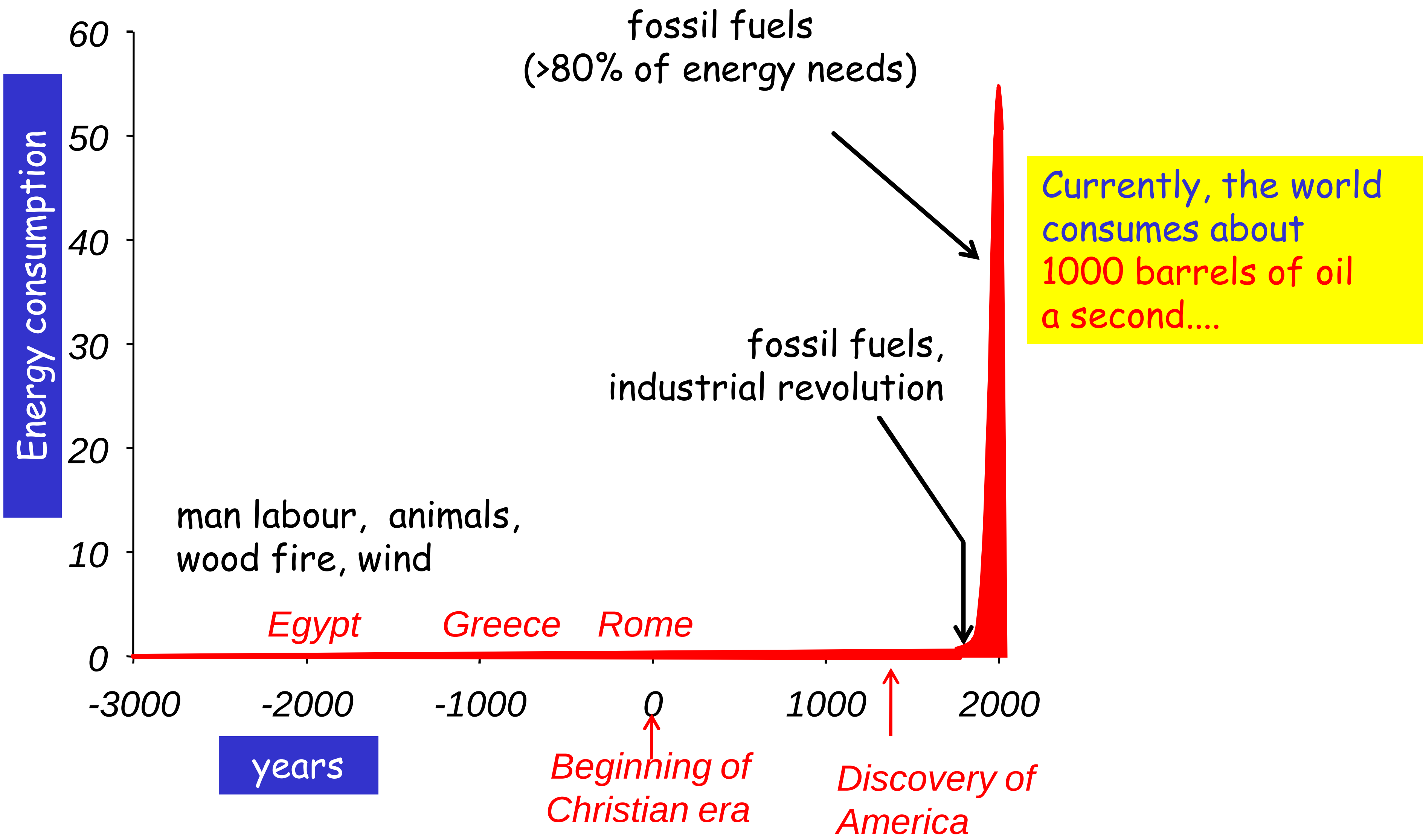
The four most important problems of mankind

food
water
wealth
environment

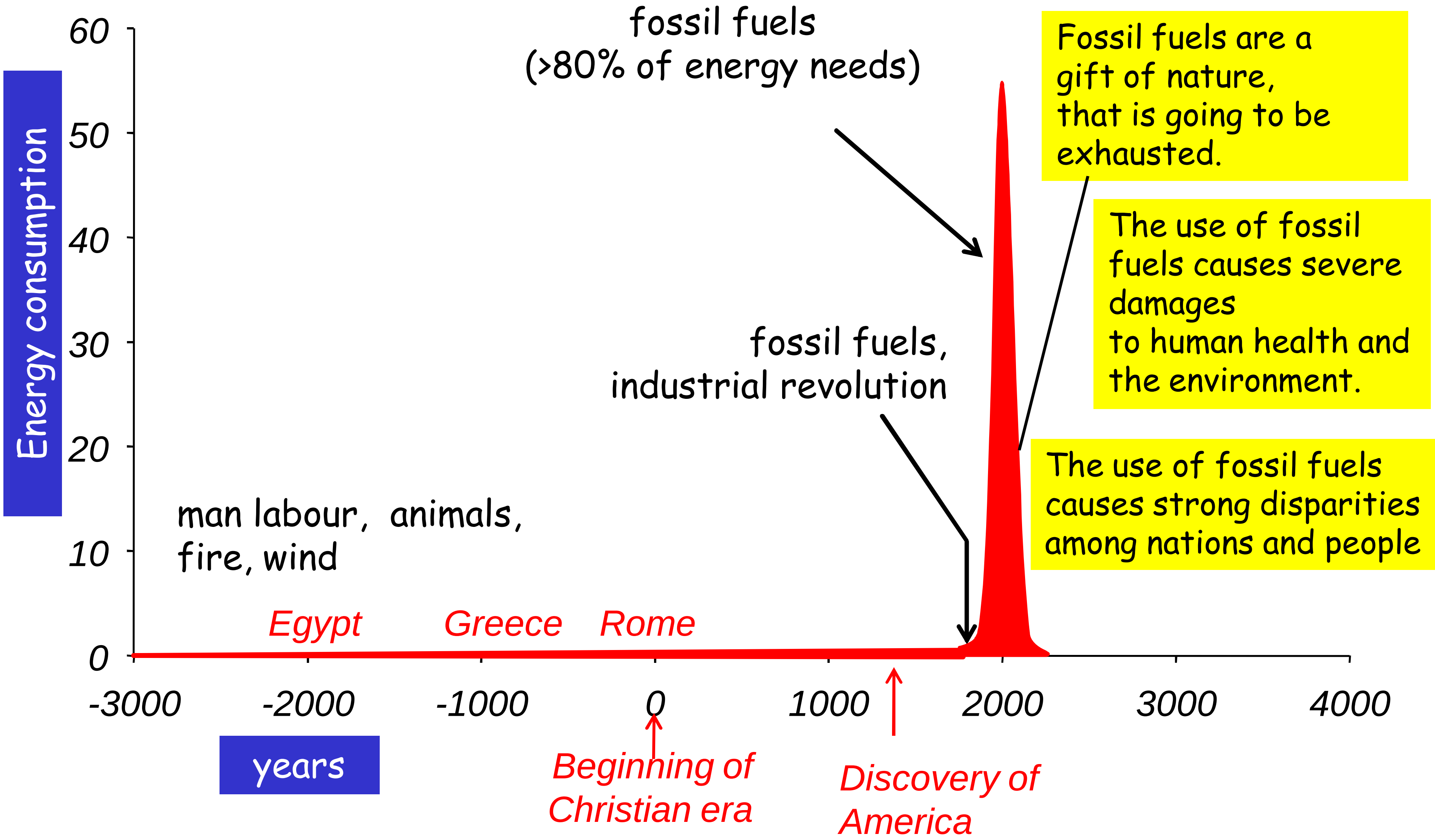
Energy

Everything around us and whatever we do depends on energy

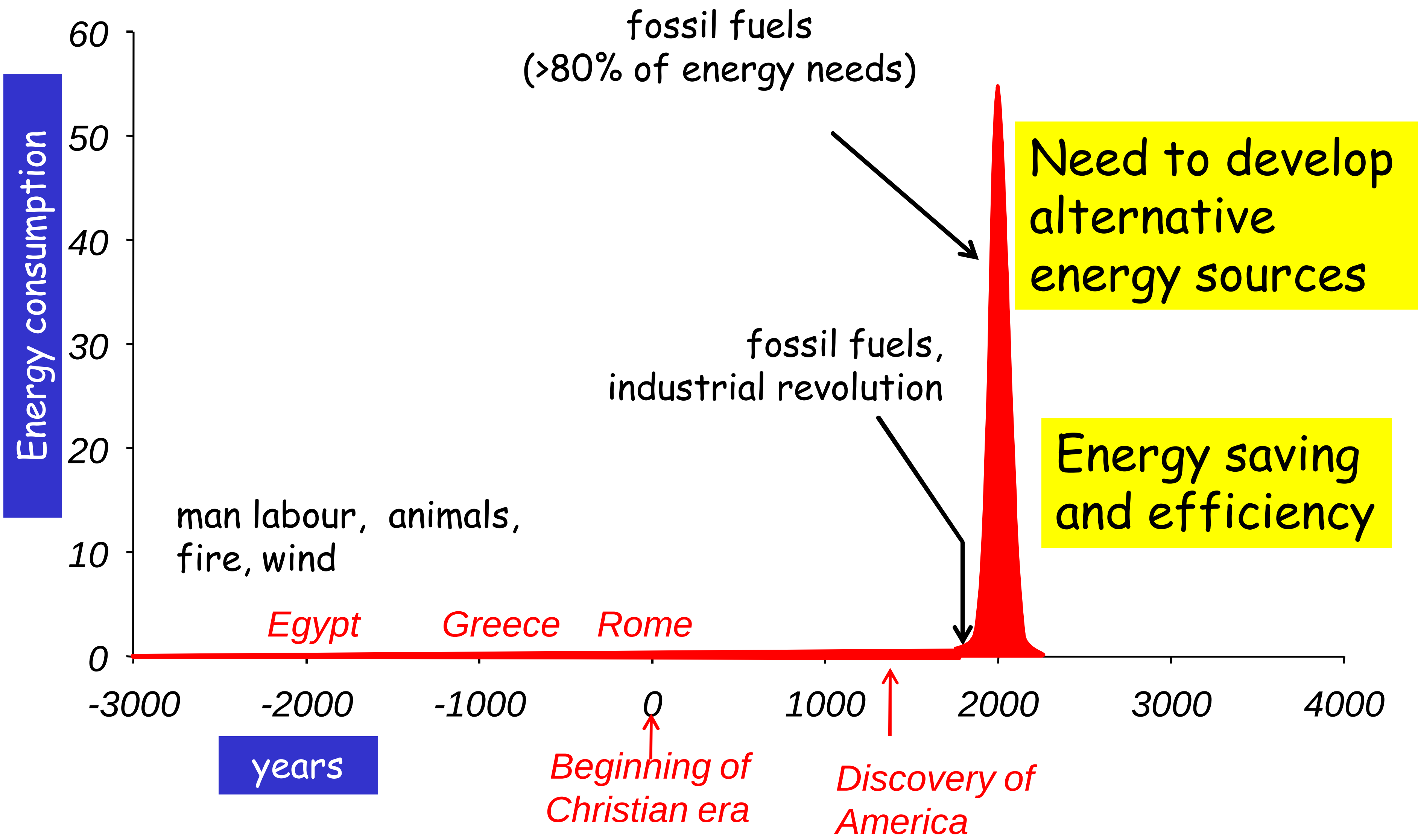
Energy consumption in the history of mankind



Energy consumption in the history of mankind



Energy consumption in the history of mankind



Requirements needed for an ideal energy source capable of taking care of our planet

- abundant

- inexhaustible

- well distributed on the planet

- not dangerous today and in the future

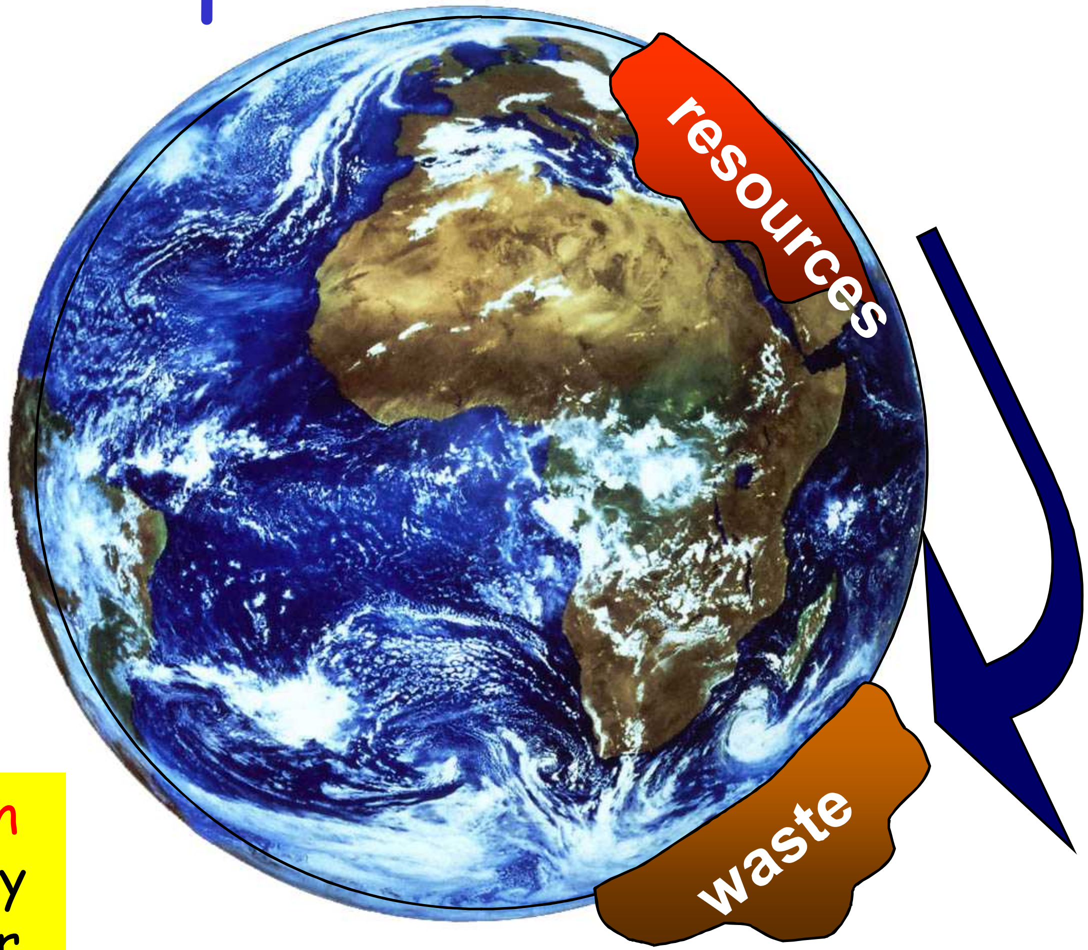
- capable of:
  - supporting the economic development
  - reducing disparities
  - fostering peace

Possible solutions for the energy crisis

-Nuclear energy

- Solar energy (and other renewable energies)

Space-ship Earth

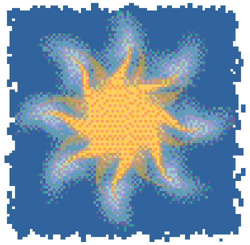


- Earth receives from the Sun in 1 hour the amount of energy consumed by mankind in 1 year.

- Sun will continue to shine for 4,5 billion years.

- Solar energy is fairly well distributed on the Earth.

Solar energy conversion



Natural photosynthesis: food

food and biofuels (in competition)

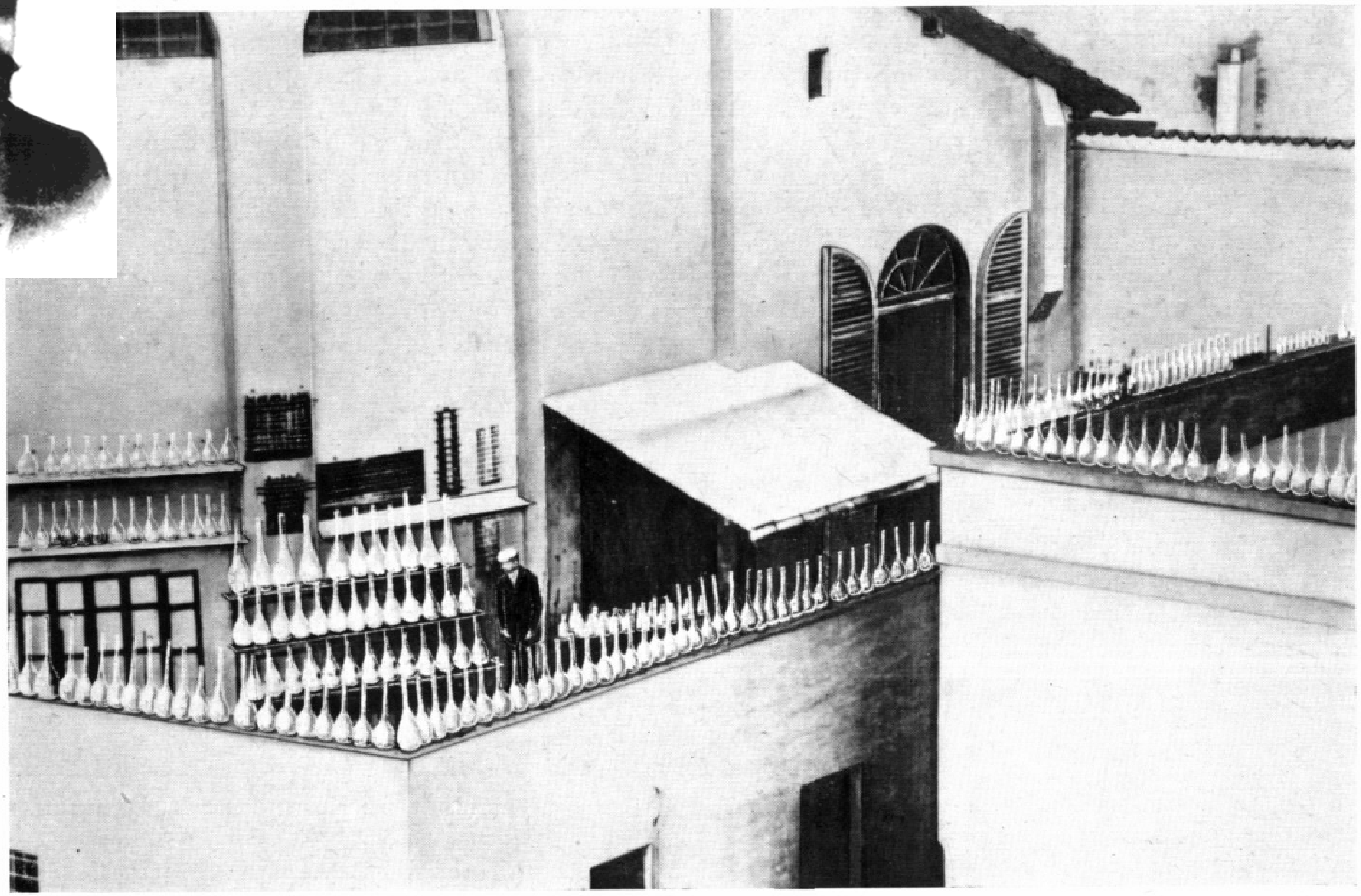
Artifician photosynthesis: fuels

Photovoltaic cells: electricity

Thermal collectors: heat

The chemistry Department in Bologna
is named in honor of Giacomo Ciamician

Giacomo Ciamician (1857-1922)
University of Bologna



Pioneer of photochemistry and prophet of solar energy

REPRINTED FROM

TRANSACTIONS AND ORGANIZATION

EIGHTH INTERNATIONAL

CONGRESS OF APPLIED CHEMISTRY

Washington and New York

September 4 to 13, 1912

THE PHOTOCHEMISTRY OF THE FUTURE

Giacomo Ciamician

Bologna

G. Ciamician: "The Photochemistry of the Future" *Science*, 1912, *36*, 385.

SCIENCE

Friday, September 27, 1912

CONTENTS

MSS. intended for publication and books, etc., intended for review should be sent to the Editor of Science, Garrison-on-Hudson, N. Y.

THE PHOTOCHEMISTRY OF THE FUTURE[1]

Modern civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

The earth still holds enormous quantities of it, but coal is not inexhaustible. The problem of the future begins to interest us, and a proof of this may be seen in the fact that the subject was treated last year almost at the same time by Sir William Ramsay before the British Association for the Advancement of Science at Portsmouth and by Professor Carl Engler before the Versammlung deutscher Naturforscher und Aerzte at Karlsruhe. According to the calculations of Professor Engler Europe possesses to-day about 700 billion tons of coal and America about as much; to this must be added the coal of the unknown parts of Asia. The supply is enormous but, with increasing consumption, the mining of coal becomes more expensive on account of the greater depth to which it is necessary to go. It must therefore be remembered that in some regions the deposits of coal may become practically useless long before their exhaustion.

Is *fossil* solar energy the only one that may be used in modern life and civilization? That is the question.

[1] General lecture before the International Congress of Applied Chemistry, New York, September 11, 1912.

“Where vegetation is rich, photochemistry may be left to the plants and, by rational cultivation, solar radiation may be used for industrial purposes.
In the desert regions, unsuitable to any kind of cultivation, photochemistry will artificially put their solar energy to practical uses”.

Giacomo Ciamician

"The Photochemistry of the Future" *Science*, 1912, *36*, 385

"On the arid lands there will spring up industrial colonies without smoke and without smokestacks; forests of glass tubes will extend over the plants 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

"The Photochemistry of the Future" *Science*, 1912, *36*, 385

And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!".

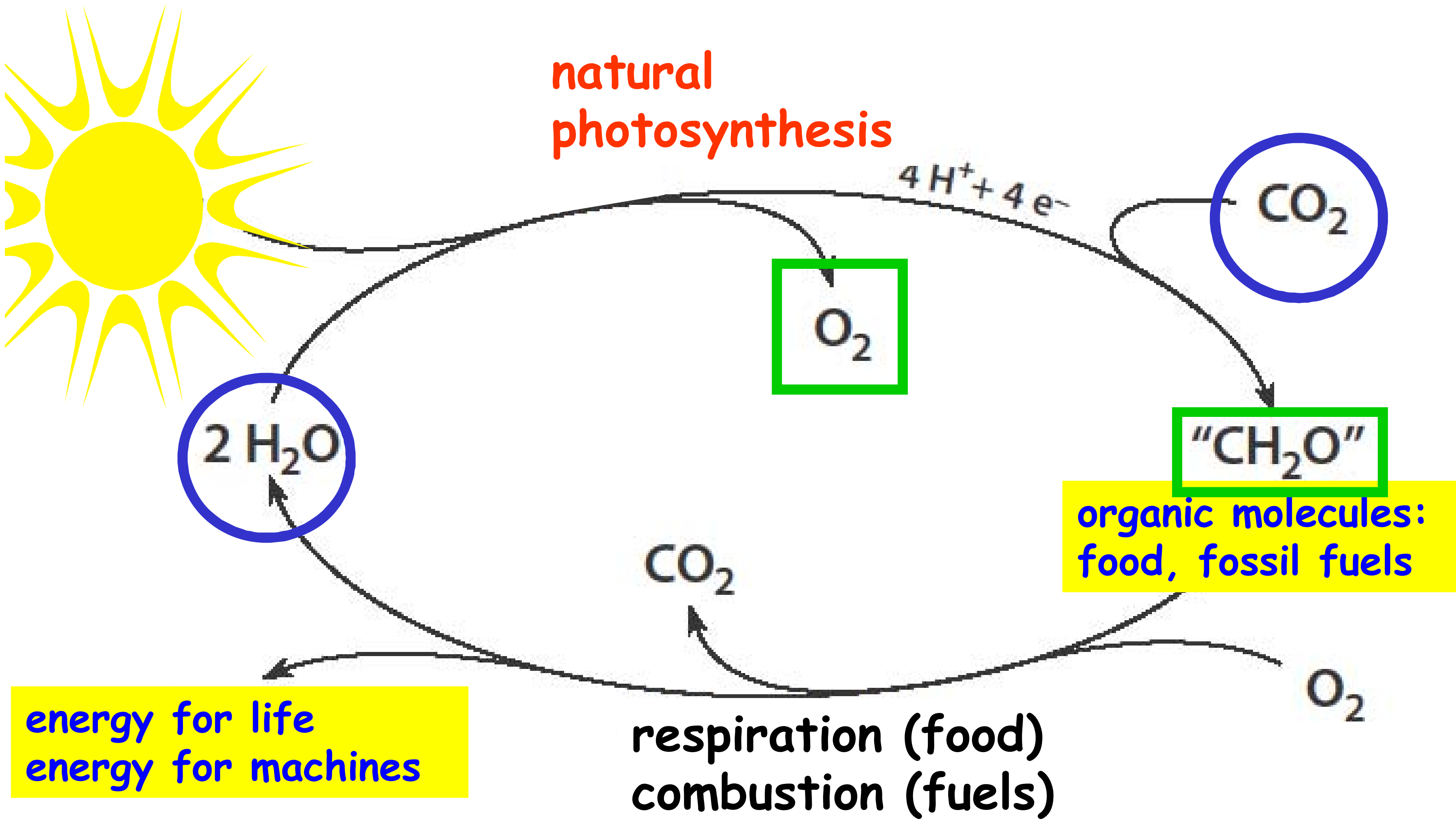
Giacomo Ciamician

"The Photochemistry of the Future" *Science*, 1912, *36*, 385

"... If our black and nervous civilization, based on coal, shall be followed by a quieter civilization based on the utilization of solar energy, that will not be harmful to the progress and to human happiness"

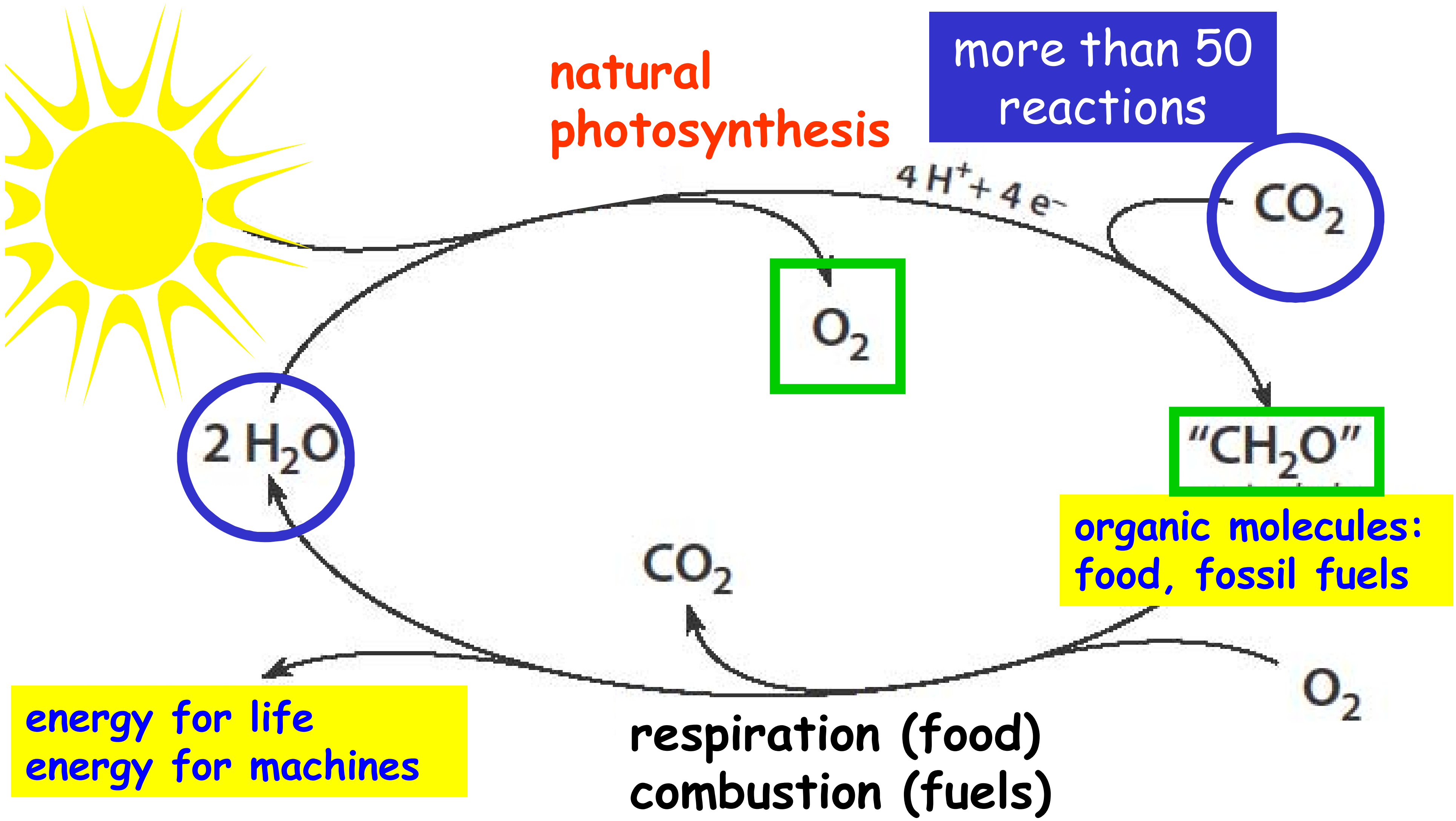
Giacomo Ciamician

"The Photochemistry of the Future" *Science*, 1912, *36*, 385


natural
photosynthesis
4 H⁺ + 4 e⁻
CO_2
O_2
$2 H_2O$
"CH_2O"
organic molecules:
food, fossil fuels
CO_2
O_2
energy for life
energy for machines
respiration (food)
combustion (fuels)

A tree is essentialy
made of
air and sun.
When it is burned,
it goes back to air,
and in the flaming heat
is released
the flaming heat
of the sun
which was bound
to convert
the air into tree.

Richard Feynman



100 billion tons of dry biomass annually

Photochemistry

photon of suitable energy

$$A + h\nu \longrightarrow {}^{*}A$$

ground state molecule

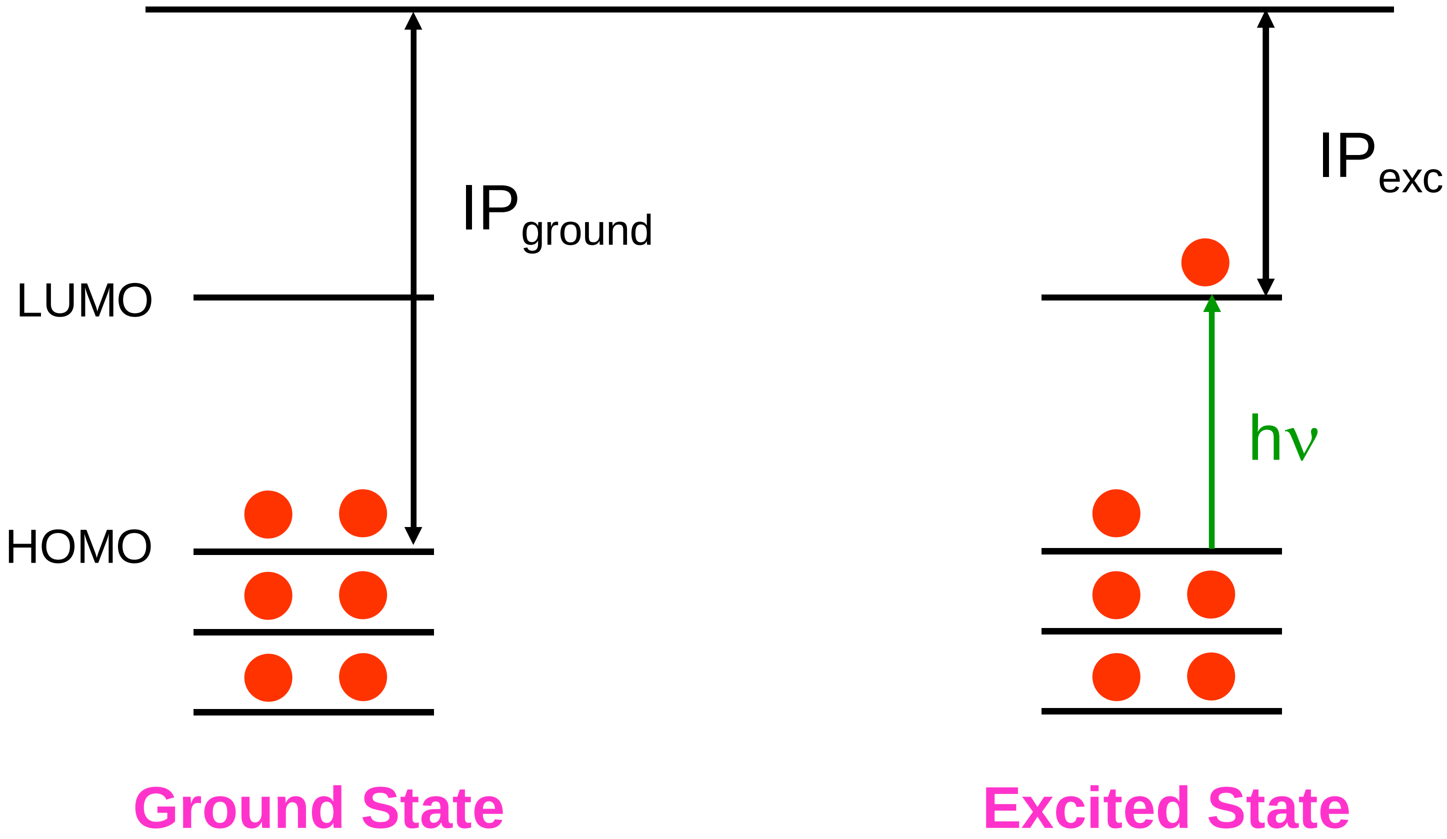
electronically excited state

(an excited state is denoted by an asterisk)

The excited state is a new chemical species with its own chemical and physical properties

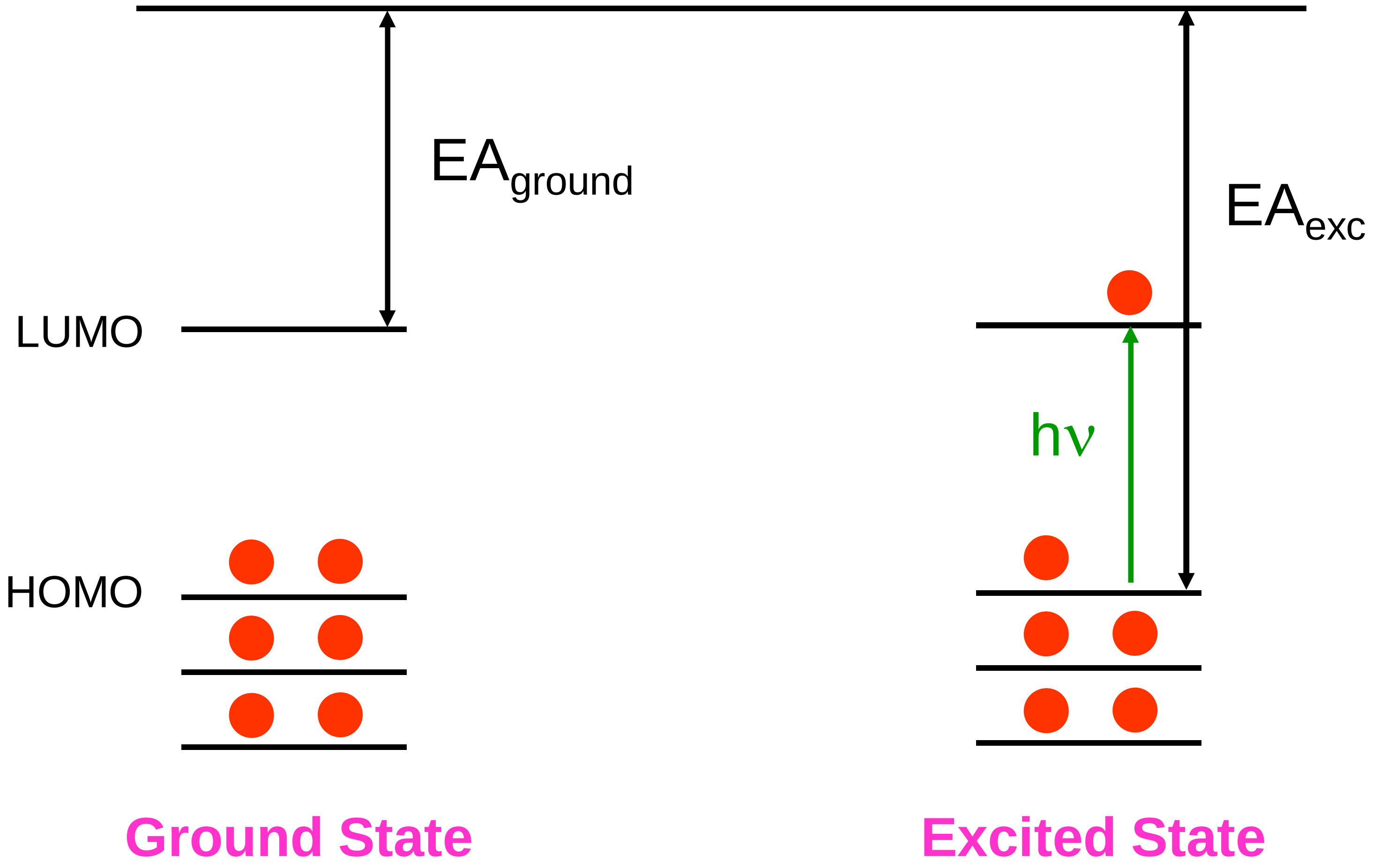
Redox Properties

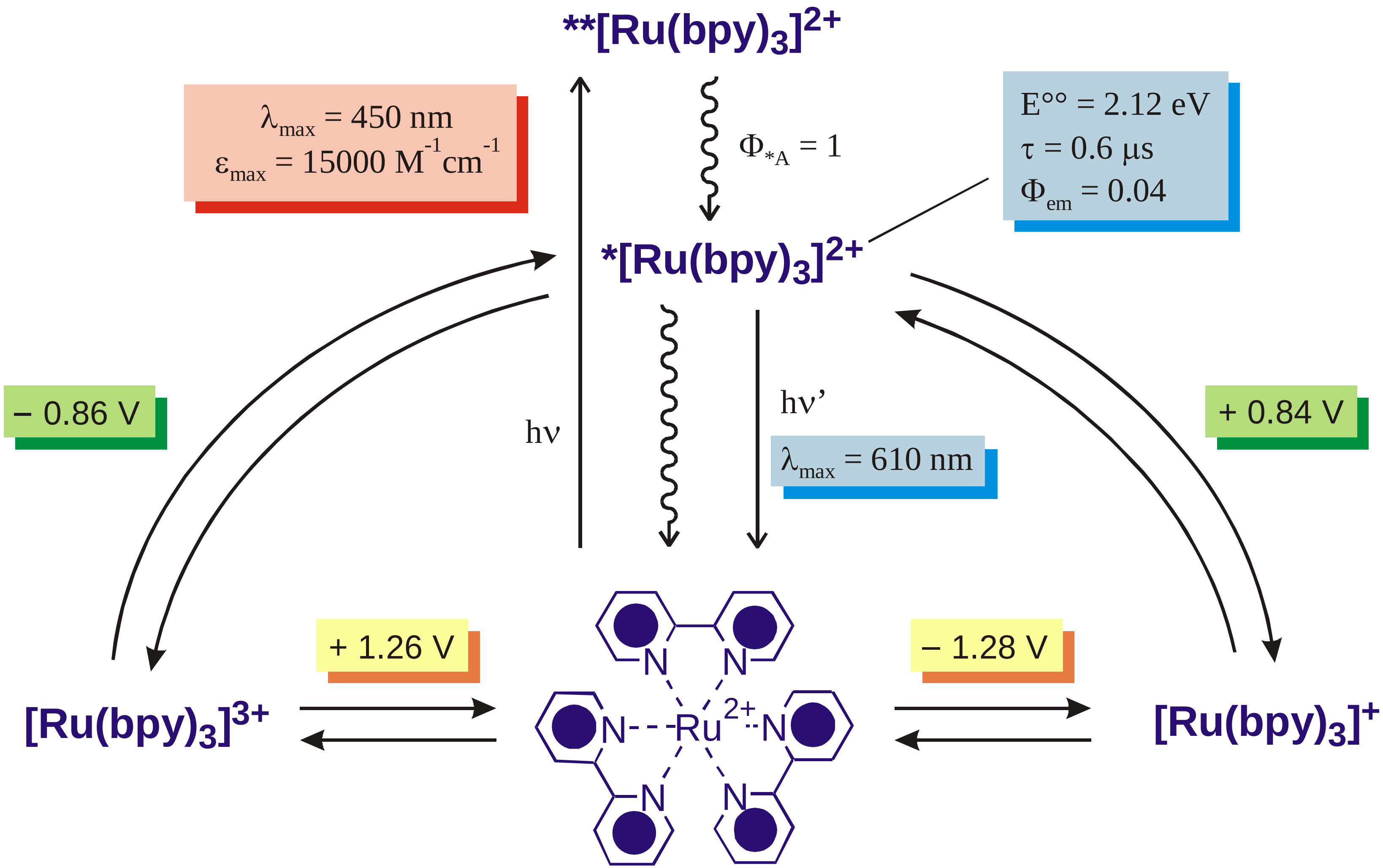
An excited state is always a better reductant than the ground state



Redox Properties

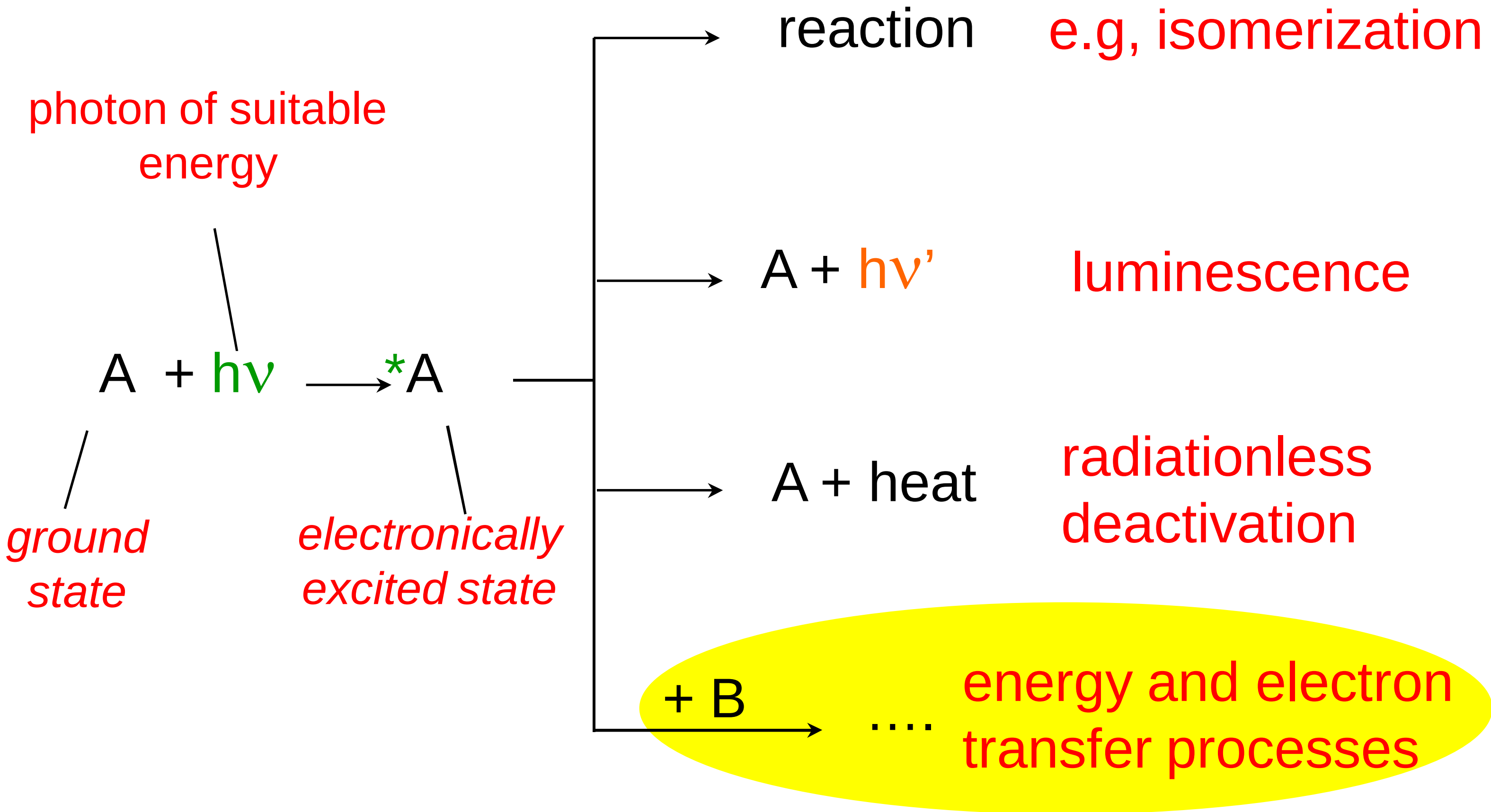
An excited state is always a better oxidant than the ground state





**[Ru(bpy)3]2+
λmax = 450 nm
εmax = 15000 M-1cm-1
Φ*A = 1
E°° = 2.12 eV
τ = 0.6 μs
Φem = 0.04
*[Ru(bpy)3]2+
– 0.86 V
hν
hν'
λmax = 610 nm
+ 0.84 V
+ 1.26 V
– 1.28 V
[Ru(bpy)3]3+
[Ru(bpy)3]+
N
Ru
2+

Photochemical Processes



Energy and electron transfer processes between molecules in fluid solution

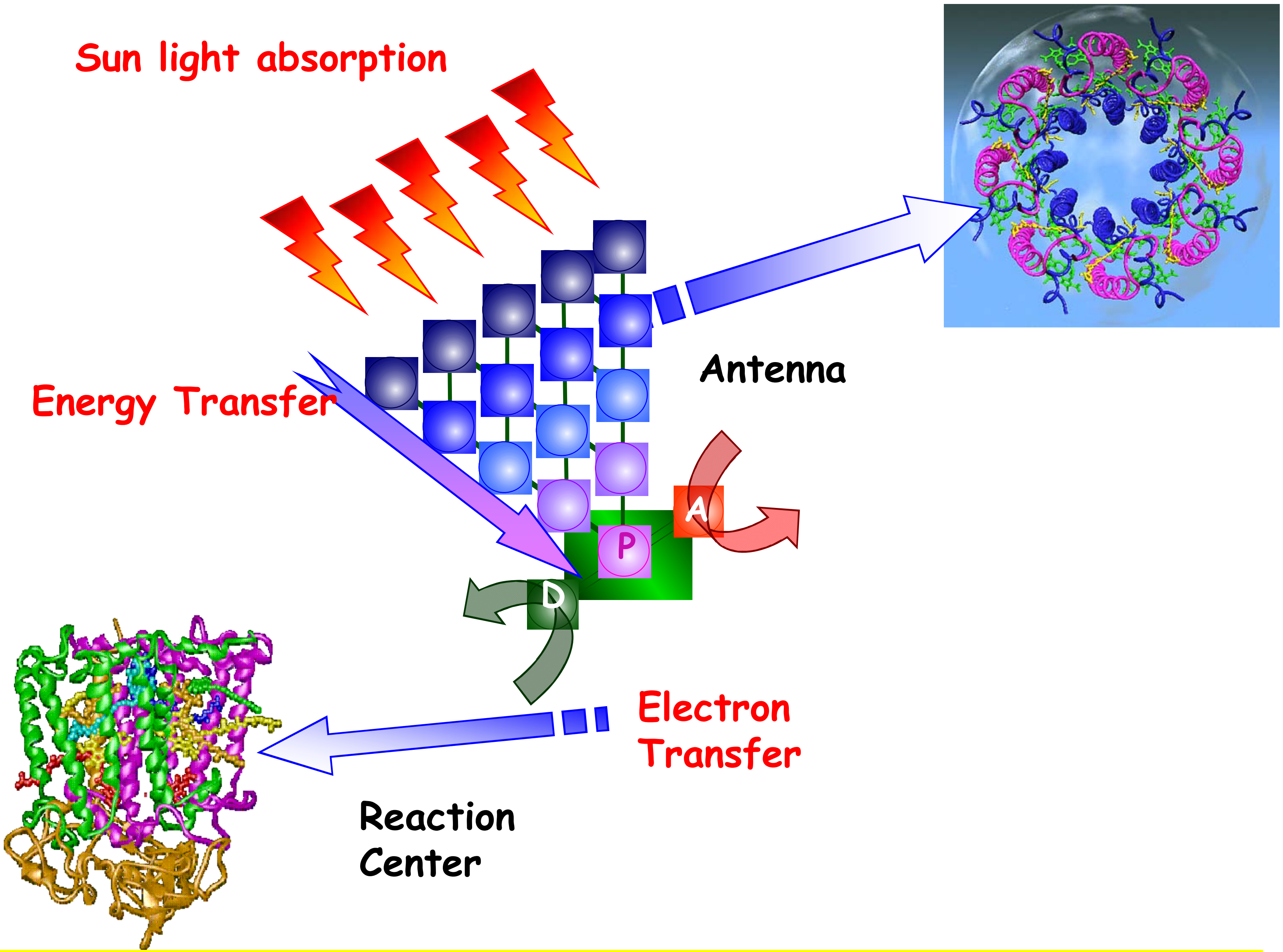
$A + h\nu \rightarrow {}^*A$	**light absorption**
${}^*A + B \rightarrow A + {}^*B$	**energy transfer**
${}^*A + B \rightarrow A^+ + B^-$ (or $A^- + B^+$)	**electron transfer**

Energy and electron transfer processes in organized supramolecular systems

$A \cdots\cdots B + h\nu \rightarrow {}^*A \cdots\cdots B$ **light absorption**

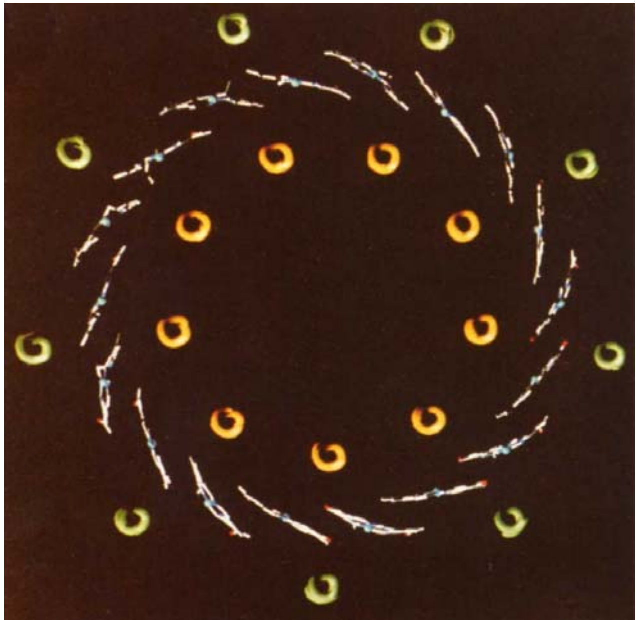
${}^*A \cdots\cdots B \rightarrow A \cdots\cdots {}^*B$ **energy transfer**

${}^*A \cdots\cdots B \rightarrow A^+ \cdots\cdots B^-$ or $(A^- \ldots. B^+)$ **electron transfer**

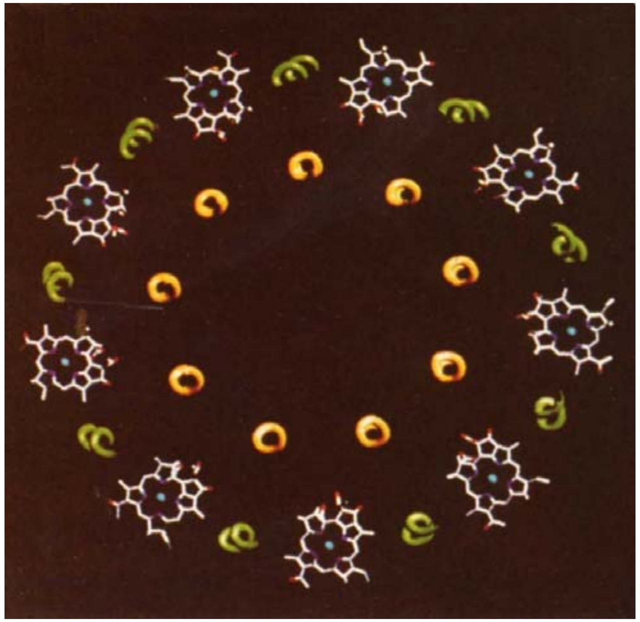


Bacterial photosynthesis

Natural light harvesting antennas



LH1
18 BChl molecules

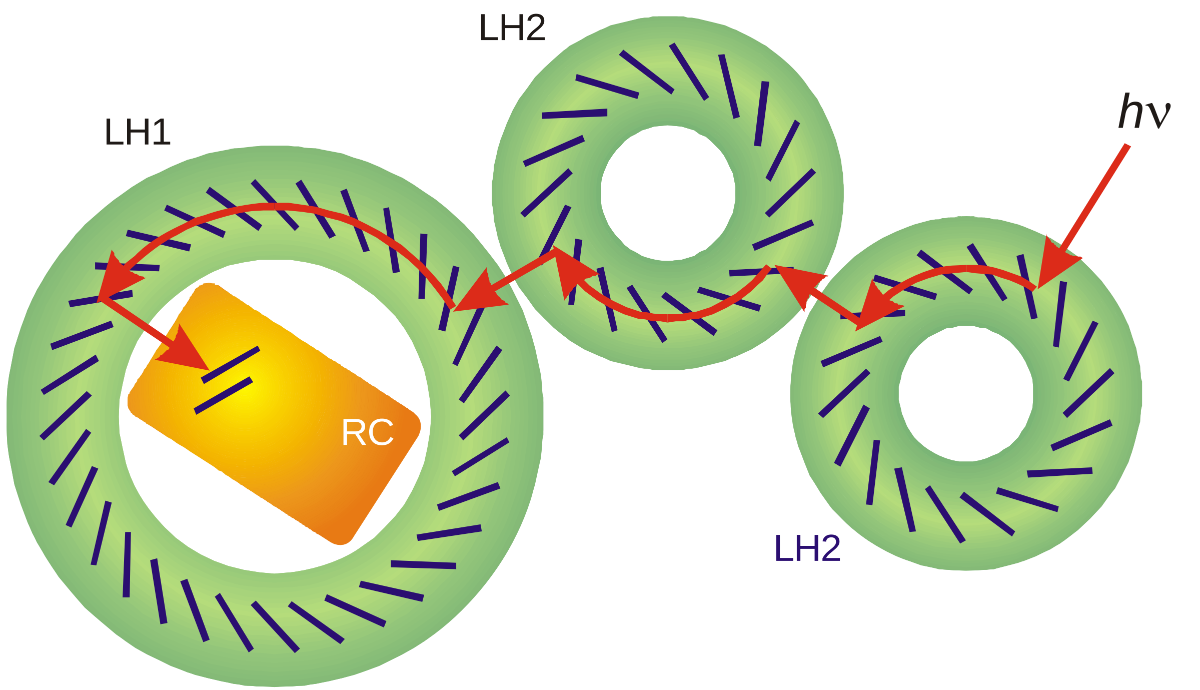


LH2
9 BChl molecules

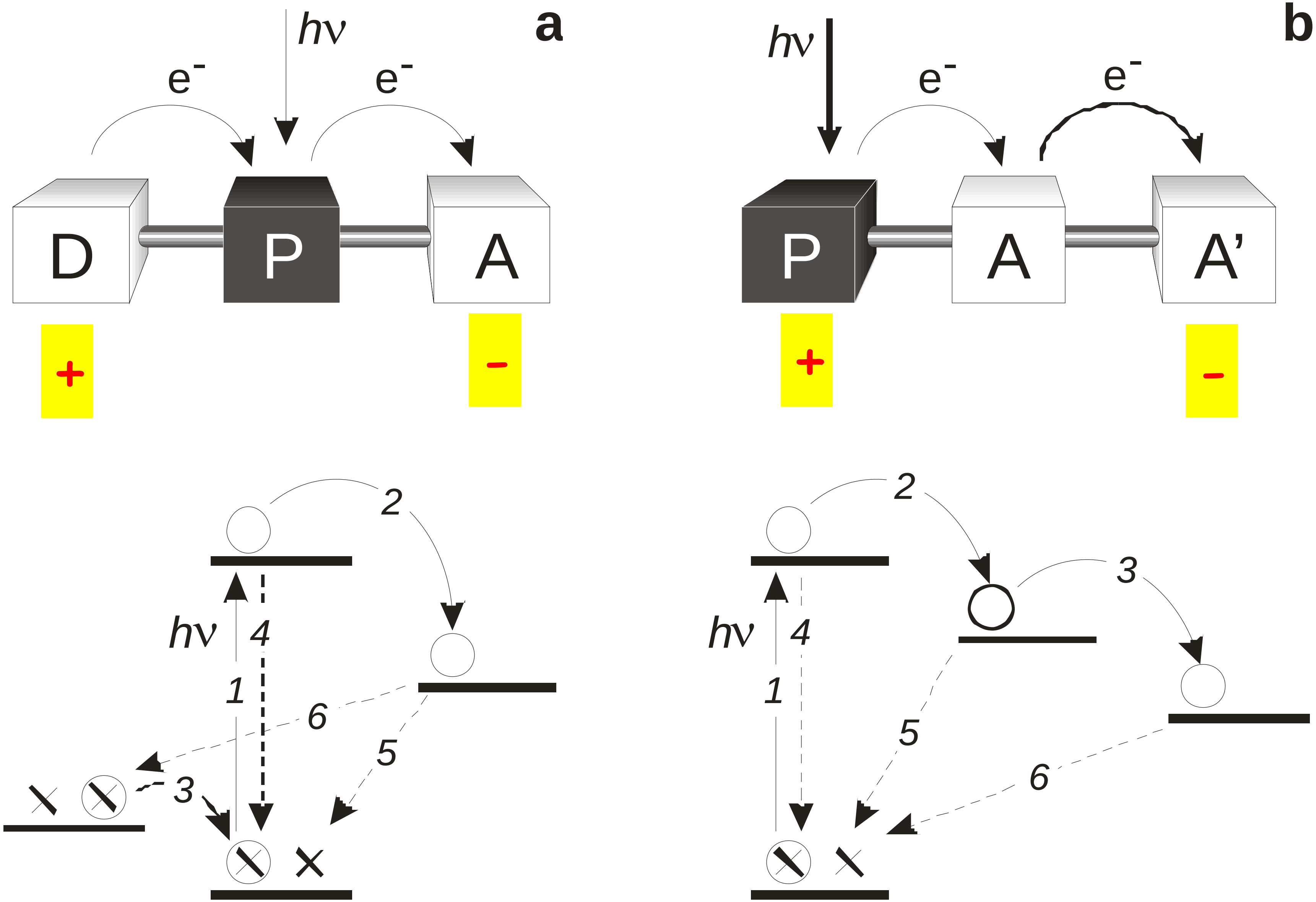
Bacterial photosynthesis

Isaacs, et al., Nature, 1995

Natural light harvesting antennas

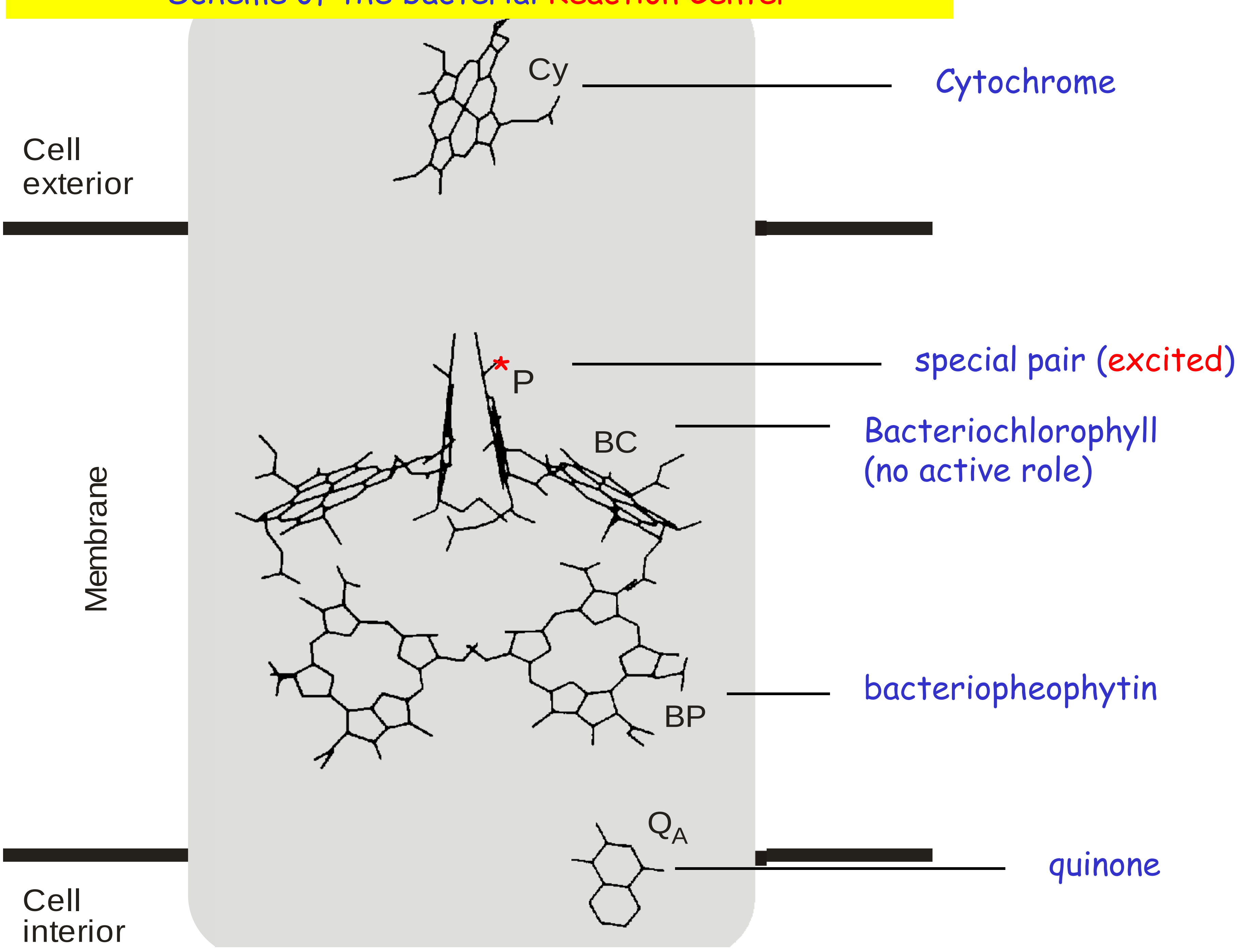


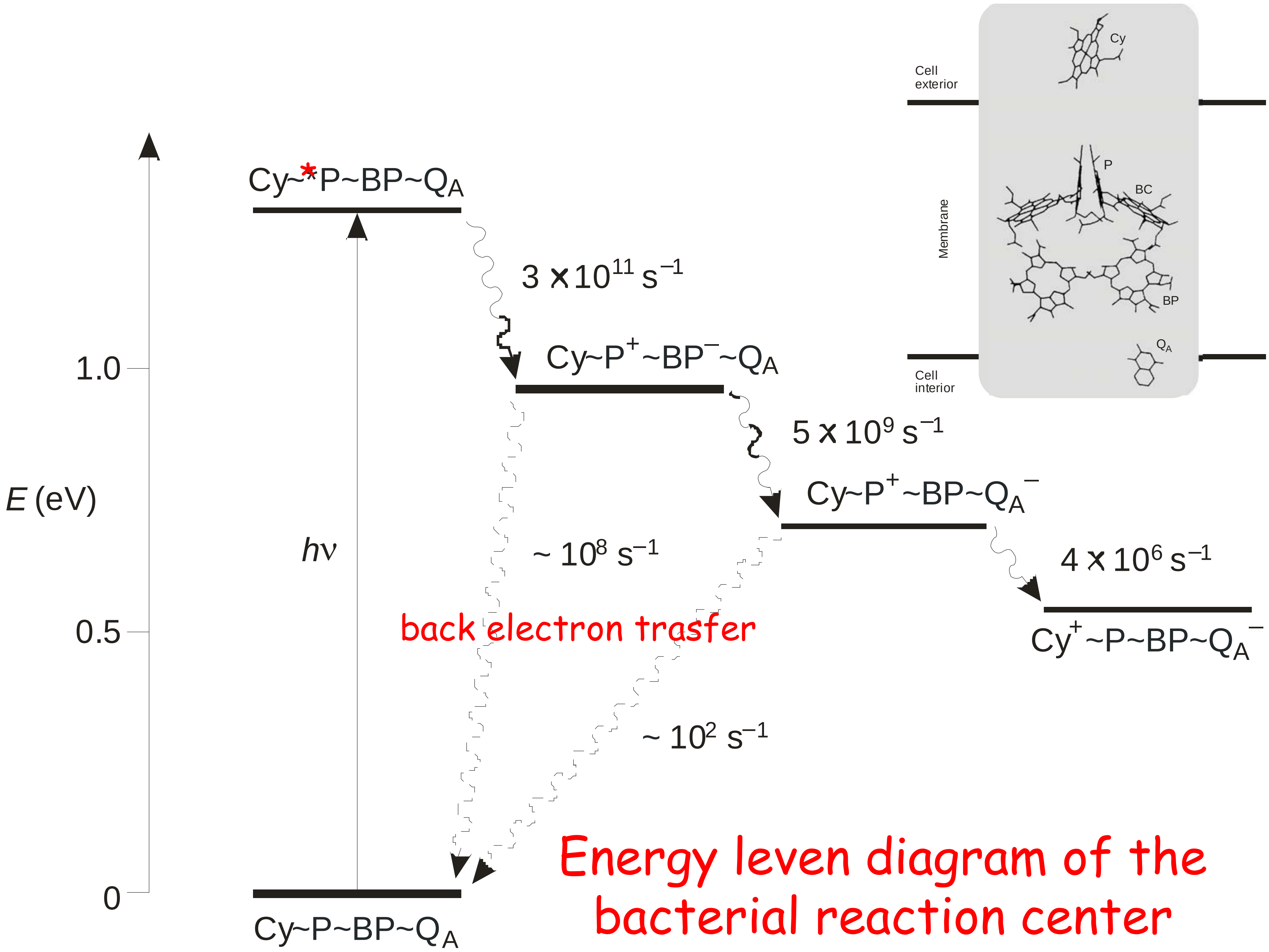
RC is the Reacion Center

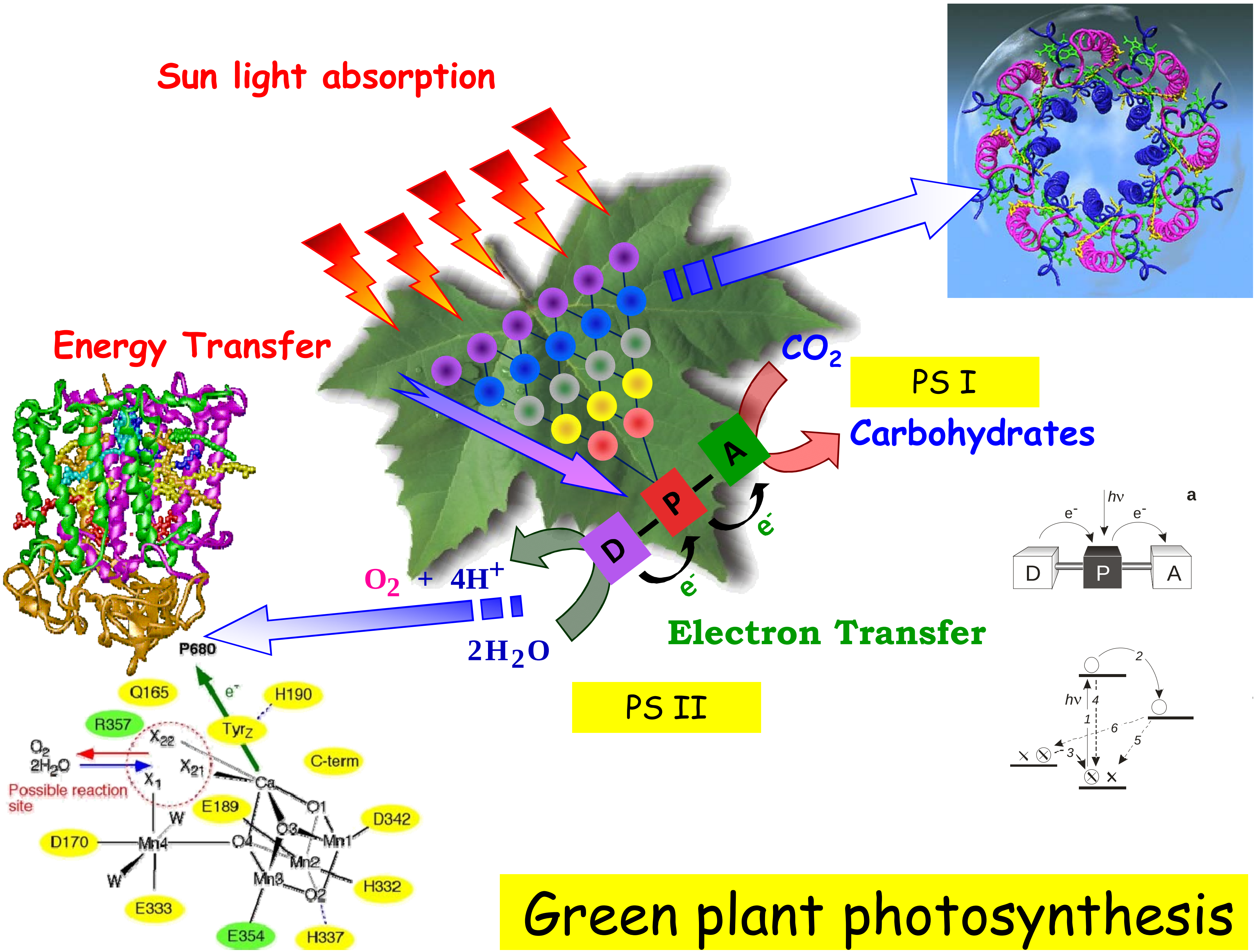


Schematic representation of two possible arrangements for charge separation in a triad

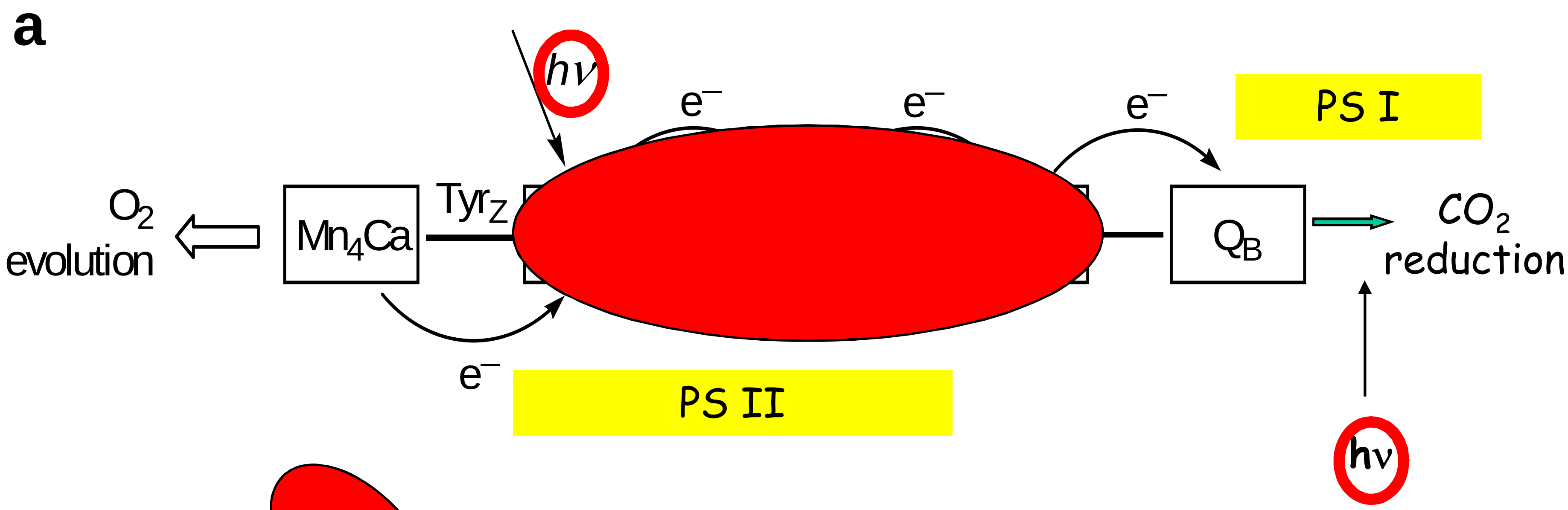
Scheme of the bacterial Reaction Center

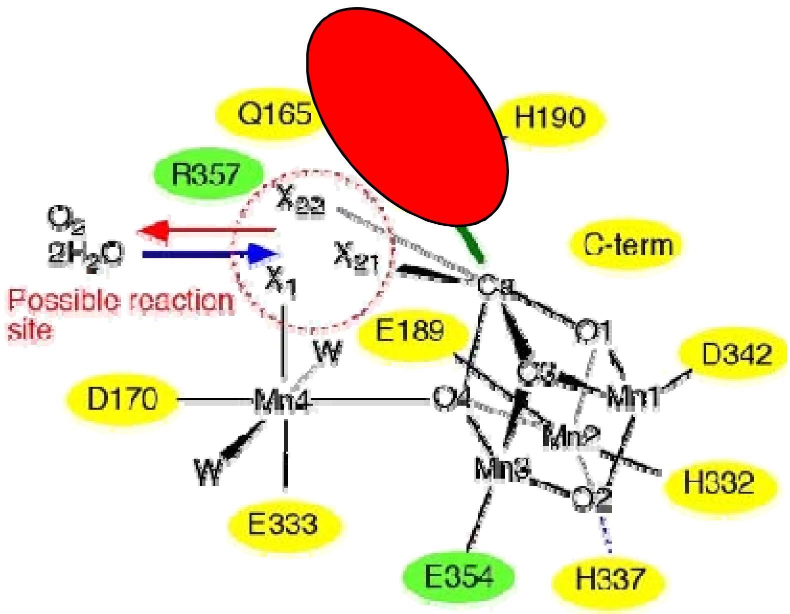



E (eV)
1.0
0.5
0
hν
Cy~*P~BP~QA
Cy~P+~BP−~QA
Cy~P+~BP~QA−
Cy+~P~BP~QA−
Cy~P~BP~QA
3 x 10^11 s−1
5 x 10^9 s−1
4 x 10^6 s−1
~ 10^8 s−1
~ 10^2 s−1
back electron trasfer
Cell exterior
Cell interior
Membrane
Cy
P
BC
BP
QA
Energy leven diagram of the bacterial reaction center



Sun light absorption
Energy Transfer
CO_2
PS I
Carbohydrates
A
P
D
e⁻
e⁻
hν
e⁻
e⁻
a
D
P
A
O_2 + $4H^+$
$2H_2O$
Electron Transfer
P680
PS II
Q165
e⁻
H190
R357
Tyr$_Z$
O_2
$2H_2O$
X_{22}
X_{21}
X_1
C-term
Possible reaction site
Ca
O1
E189
W
O3
D342
D170
Mn4
O4
Mn1
Mn2
W
Mn3
H332
O2
E333
E354
H337
hν
1
2
3
4
5
6
Green plant photosynthesis





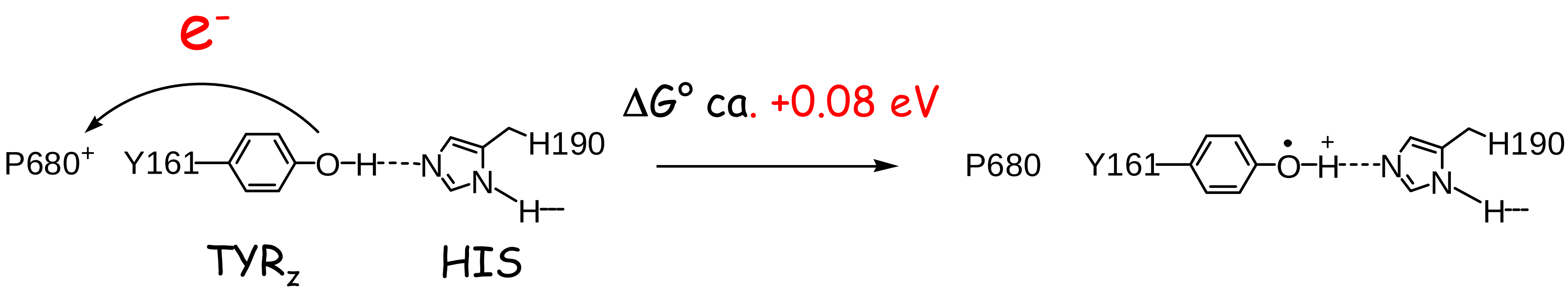
Mn_4Ca

Activation of the Oxygen Evolving Complex

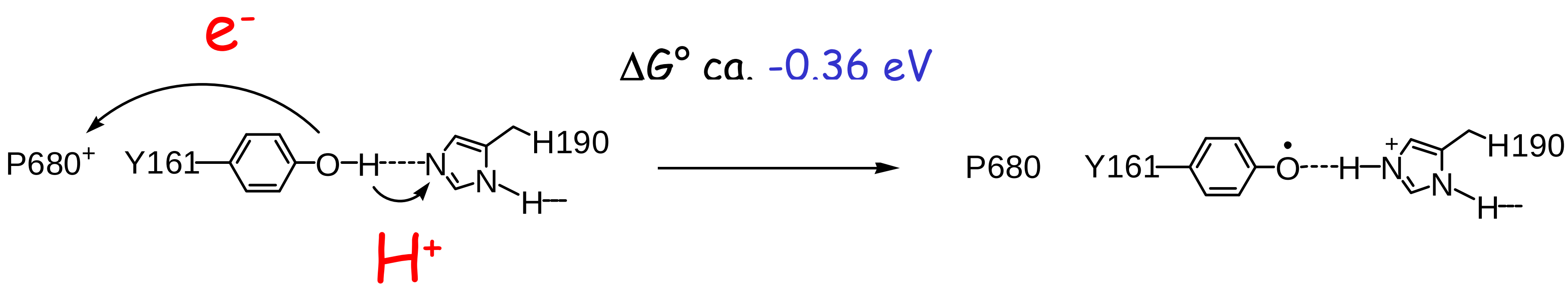
Water oxidation by PSII

Activation of the OEC toward water oxidation

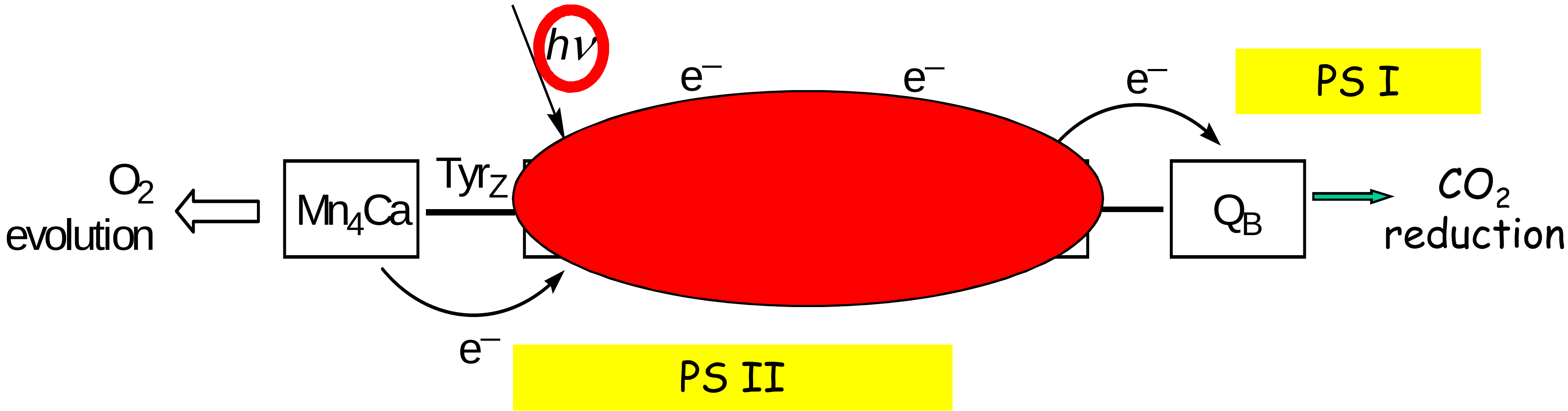
electron transfer (ET)

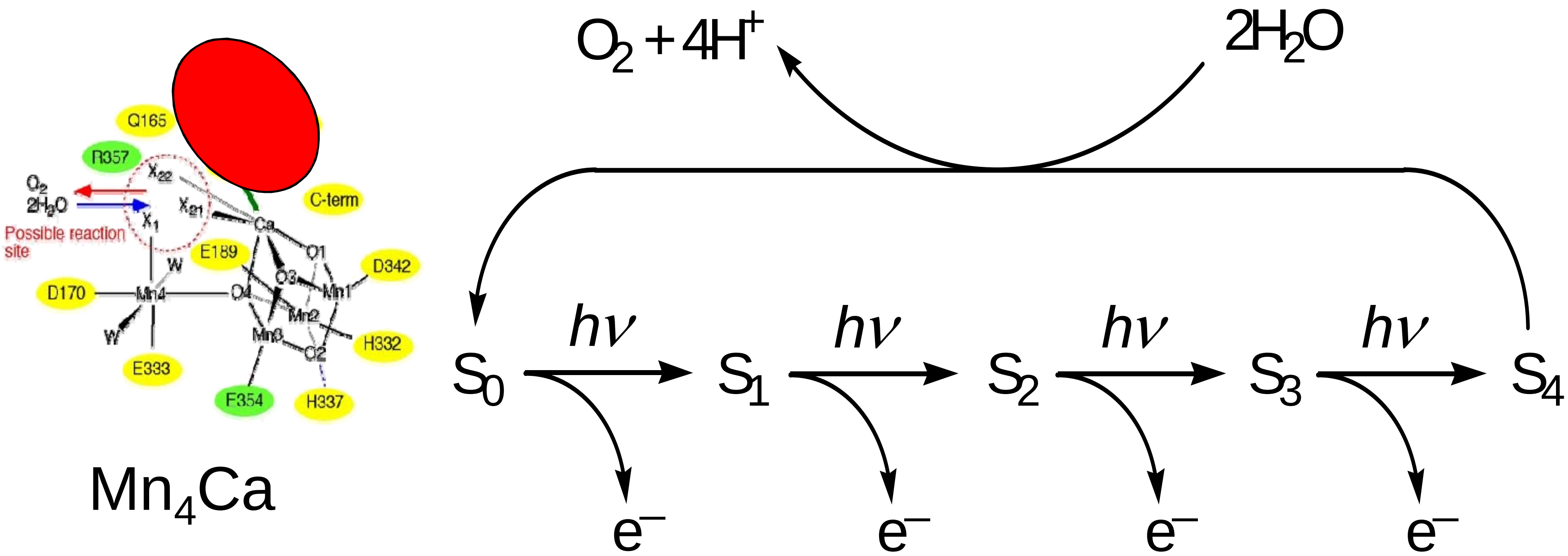


electron-proton transfer (EPT)



T.J. Meyer, et al., Angew.Chem.Int.Ed., 2007





The five redox states (S_0->S_4) of the Mn_4Ca cluster

Efficiency of natural photosynthesis

- Threshold P680: 680 nm, 1.83 eV

- The two photosystems PSII and PSI work in series: therefore two photons are needed to move an electron/proton from H_2O to CO_2.

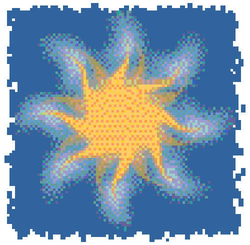
- Formation of O_2 and reduction of CO_2. require 4 electrons

8 photons are needed to generate 1 molecule of O_2 and "fix" 1 molecule of CO_2.

Efficiency of photosynthesis

- 8 photons are needed to generate 1 molecule of O_2 and "fix" 1 molecule of CO_2.
- formation of a molecule of glucose, $C_6H_{12}O_6$, requires at least 48 photons.
- 48 photons with threshold 680 nm (42 kcal/mol), correspond to at least 2016 kcal/mol.
- energy content of glucose: 672 kcal/mol; efficiency of the photosynthetic process: about 30%.
- Threshold and saturation effects reduce the efficiency to 4.5%.
- Maximum real efficiency: about 1
- Normal efficiency: around 0.1

Solar energy conversion



Natural photosynthesis: food

food and biofuels (in competition)

Artifician photosynthesis: fuels

Photovoltaic cells: electricity

Thermal collectors: heat

Towards an artificial photosynthesis

Type of material:

abundant, inexpensive, chemically stable, available everywhere:

nitrogen, water, carbon dioxide

It should also be colored, but if it is not colored we can use a colored sensitizer like Nature does (chlorophyll)

suggested approach to artificial photosynthesis

Reprinted from
12 September 1975, Volume 189, pp. 852-856

SCIENCE

1975, *189*, 856

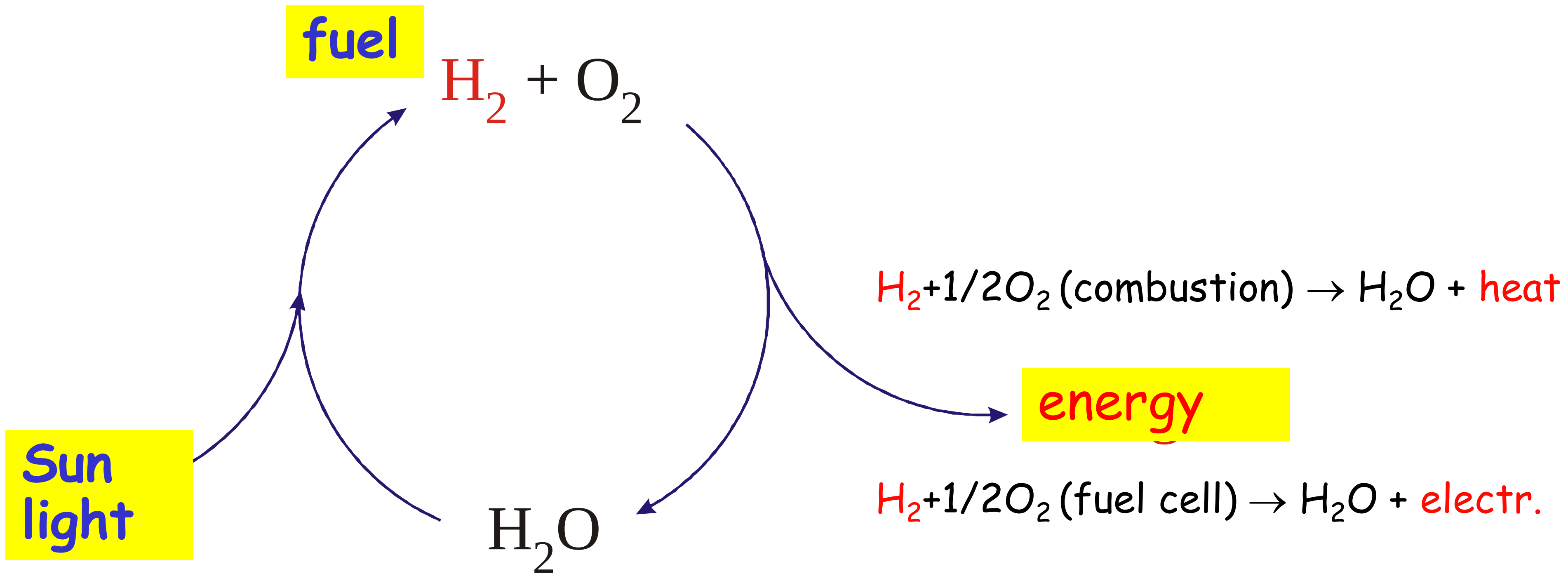
Solar Energy Conversion by Water Photodissociation

V. Balzani, L. Moggi, M. F. Manfrin,
F. Bolletta, M. Gleria

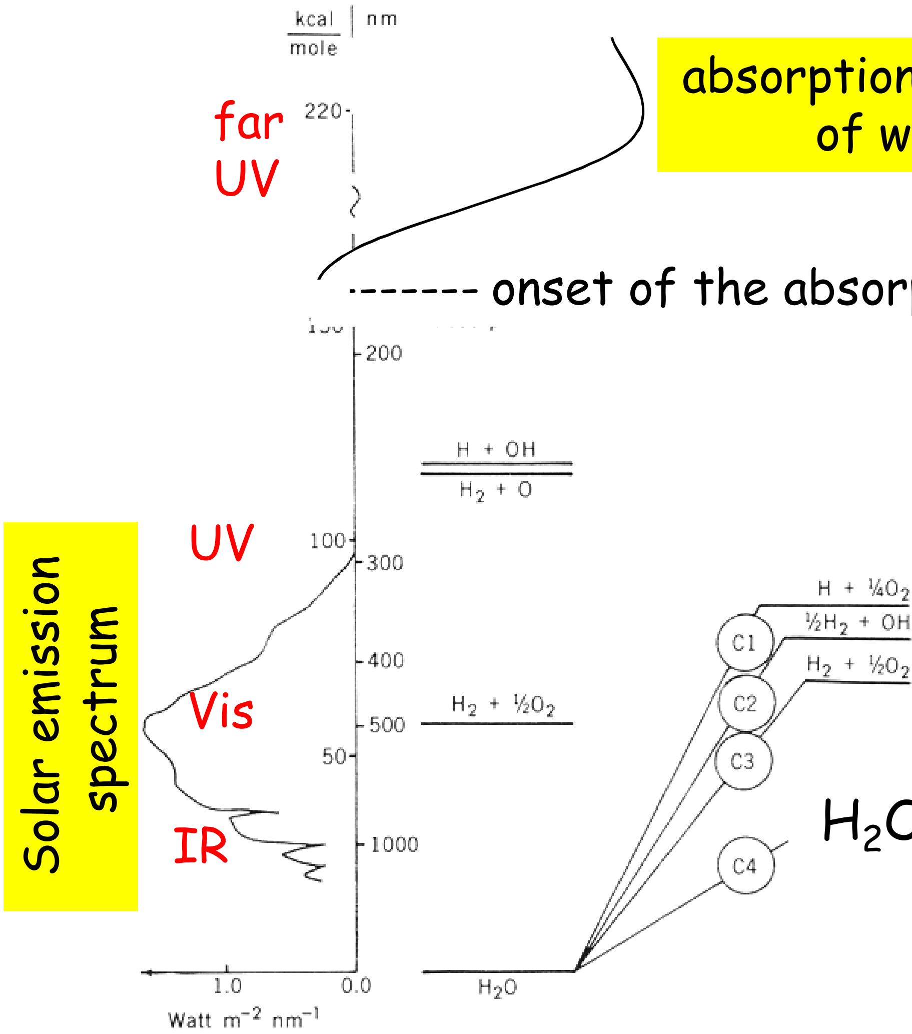
$$H_2O + \text{sunlight} \rightarrow H_2 + 1/2 O_2$$

Artificial photosynthesis

photochemical water splitting



a closed, pollution free energy cycle



absorption spectrum of water

------- onset of the absorption spectrum of water ----------------

direct

H_2O + sunlight ----/ /------→

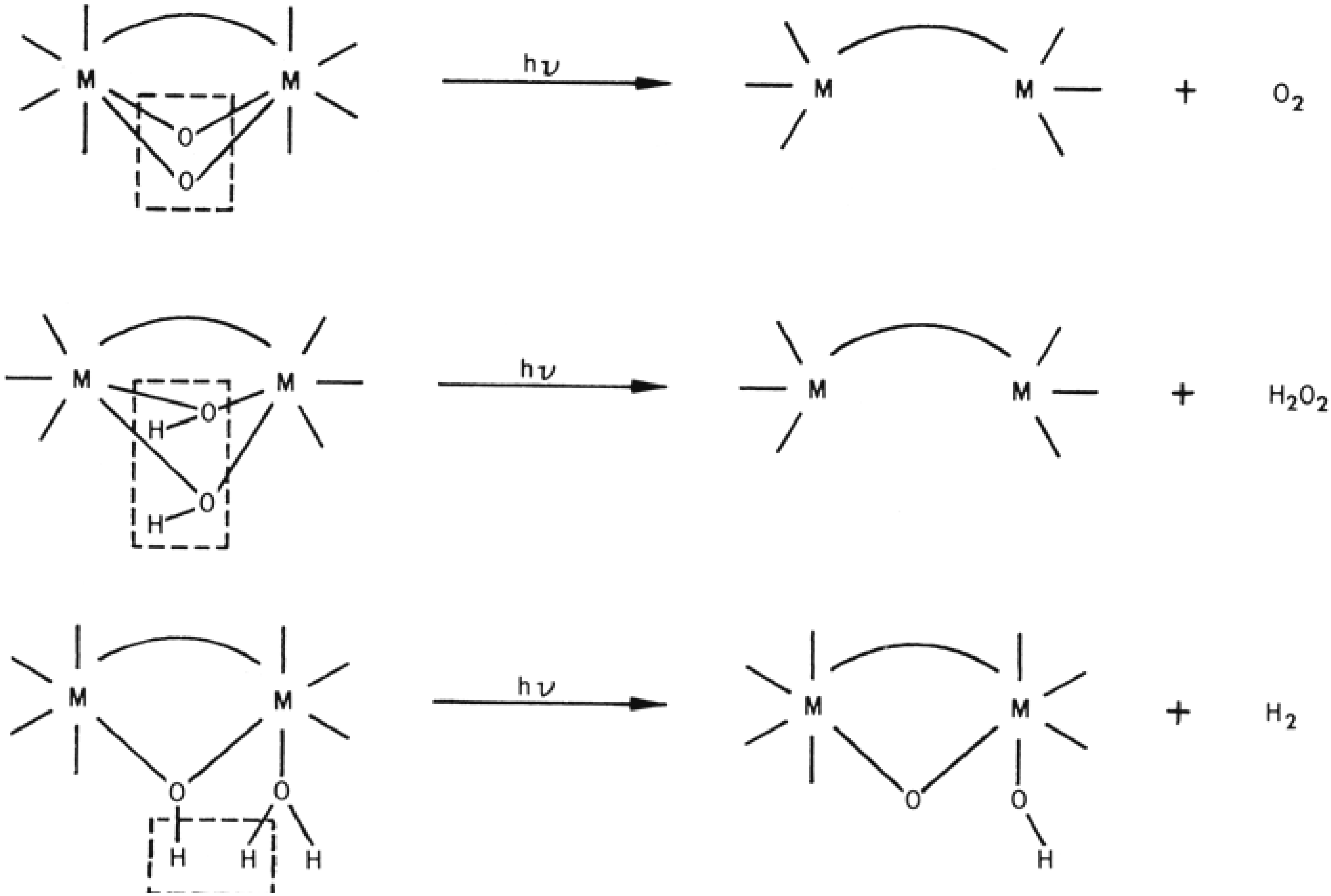
photosensitizer P

$$H_2O + \text{sunlight} \xrightarrow{P} 1/2\ H_2 + 1/4 O_2$$

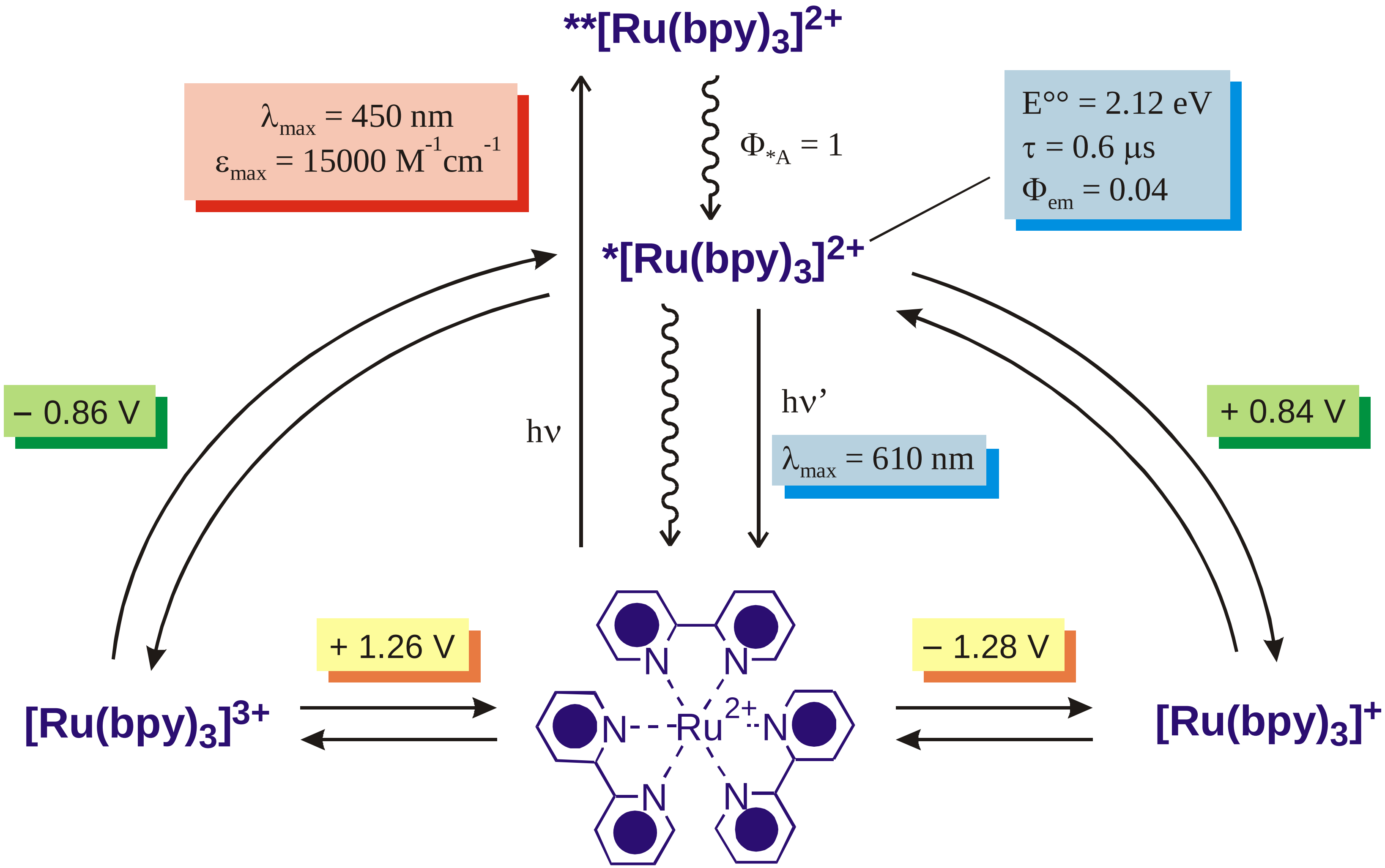
$$H_2O + 1.23\ \text{eV}\ (1010\ \text{nm}) \longrightarrow 1/2 H_2 + 1/4 O_2$$

V. Balzani, et al. *Science*, 1975, *189*, 852

Proposed photosensitizers



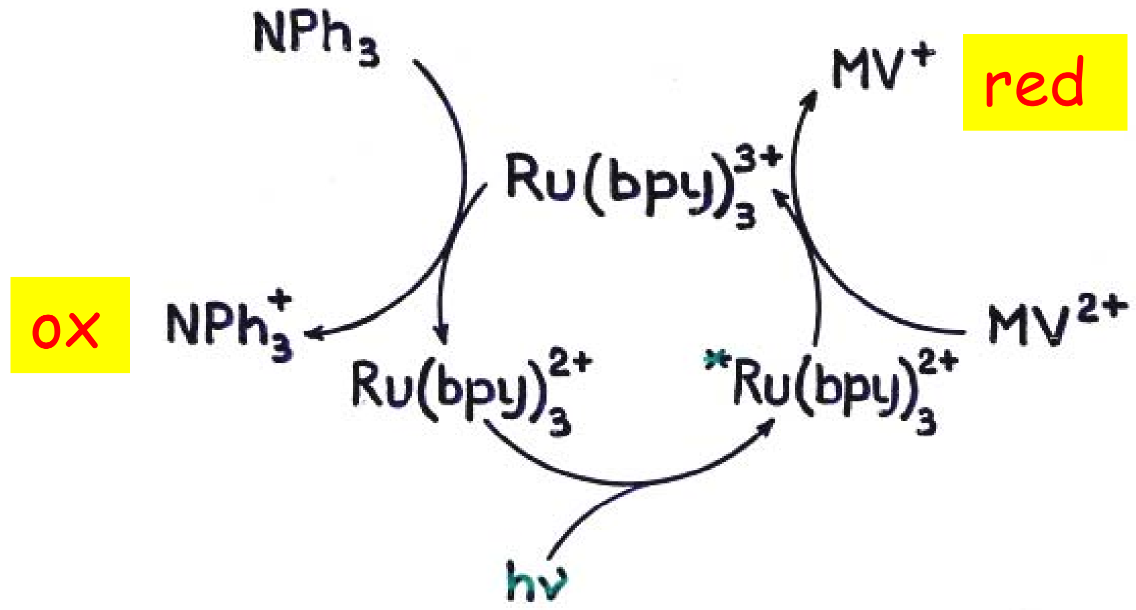
V. Balzani, et al. *Science*, 1975, *189*, 852



*$Ru[(bpy)_3]^{2+}$ has an energy content of 2.12 eV

$$H_2O + 1.23\ eV \longrightarrow 1/2H_2 + 1/4O_2$$

Conversion of light energy into chemical energy mediated by an electron transfer photosensitizer



$$MV^{2+} + NPh_3 \not\longrightarrow MV^{+} + NPh_3^{+} \qquad \Delta G = +1.45\ eV$$

$$MV^{2+} + NPh_3 + h\nu(\text{visible}) \xrightarrow{Ru(bpy)_3^{2+}} MV^{+} + NPh_3^{+}$$

T.J. Meyer et al. 1975

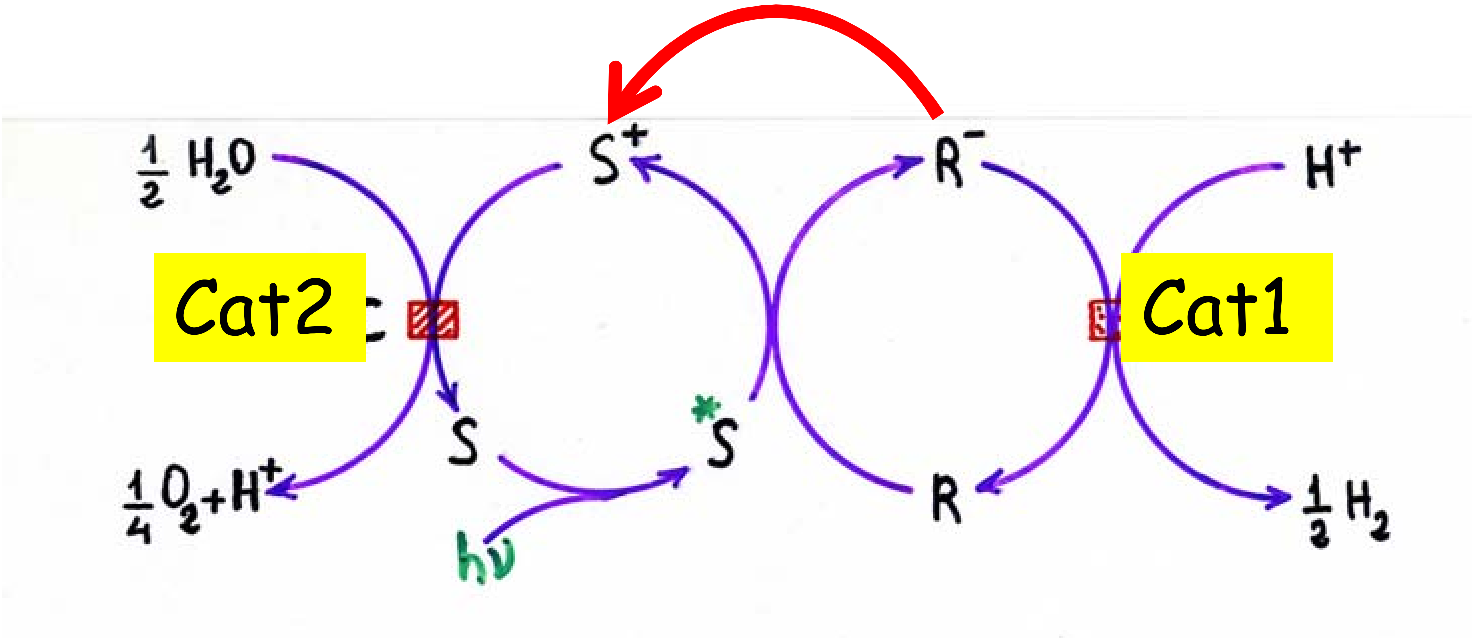
Artificial photosynthesis

$$h\nu \text{ (sunlight)} \xrightarrow{P} e^- + h^+$$

photoinduced charge separation

$$2H_2O + 2e^- \xrightarrow{\text{Cat1}} H_2 + 2OH^-$$

$$2H_2O + 4h^+ \xrightarrow{\text{Cat2}} O_2 + 4H^+$$



S: $Ru[(bpy)_3]^{2+}$ photosensitizer

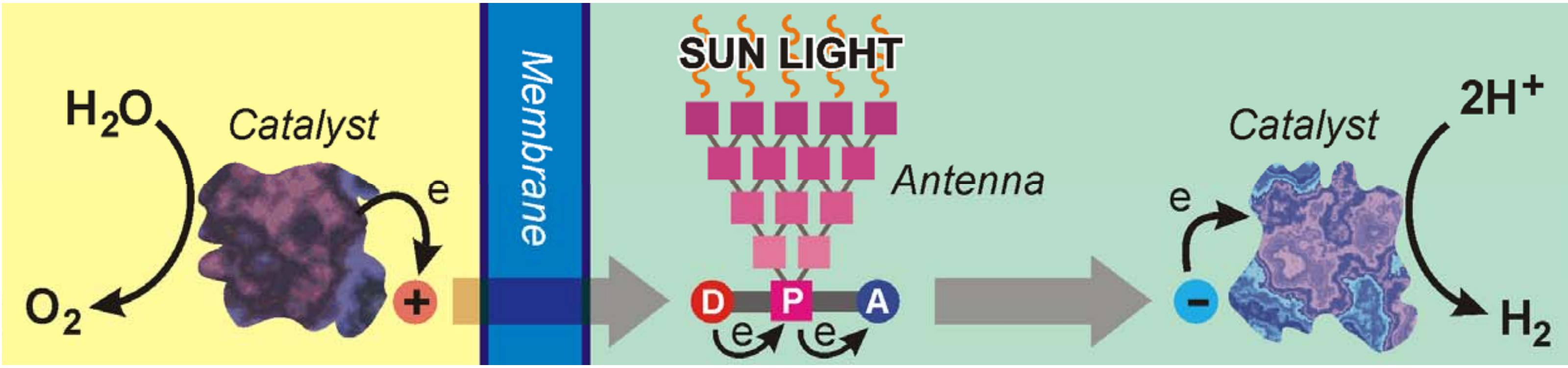
R: methyl viologen electron relay

Cat1 colloidal Pt reduction catalyst

Cat2 ruthenium oxide oxidation catalyst

Artificial photosynthesis

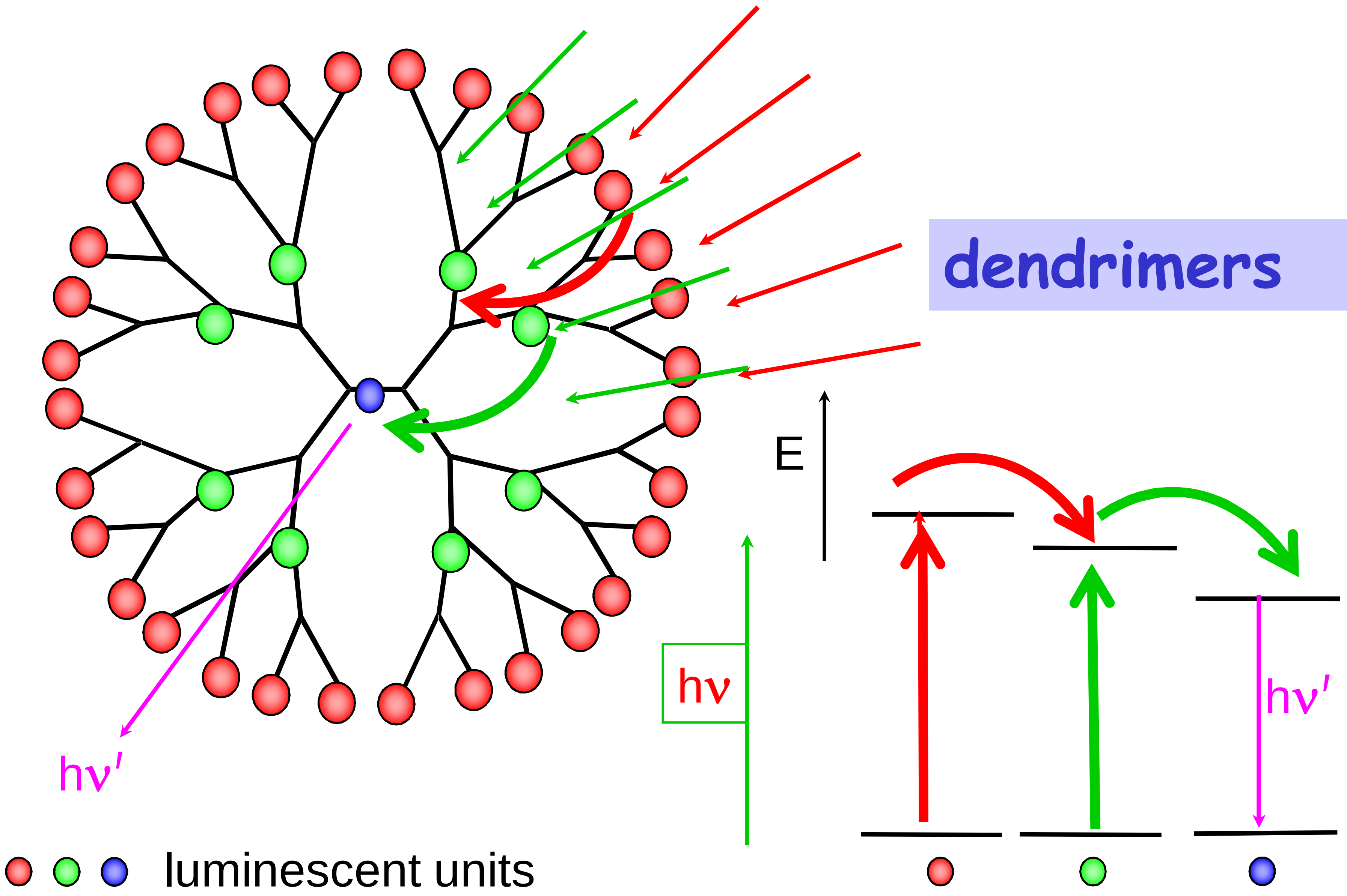
$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$



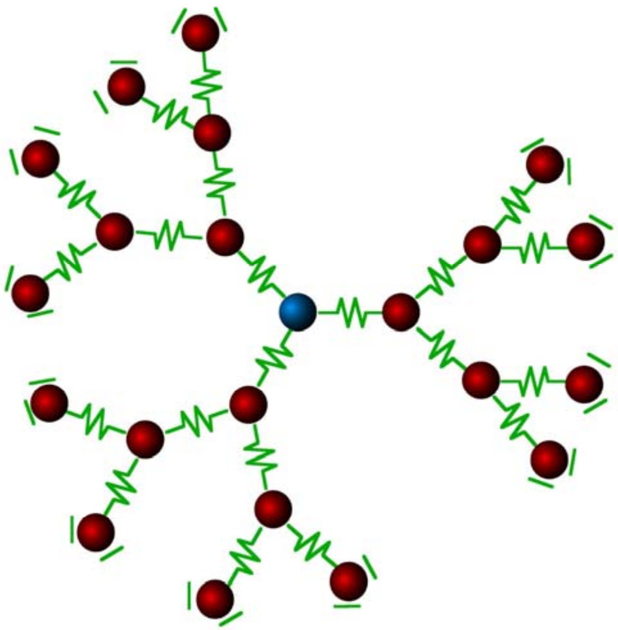
Reaction center

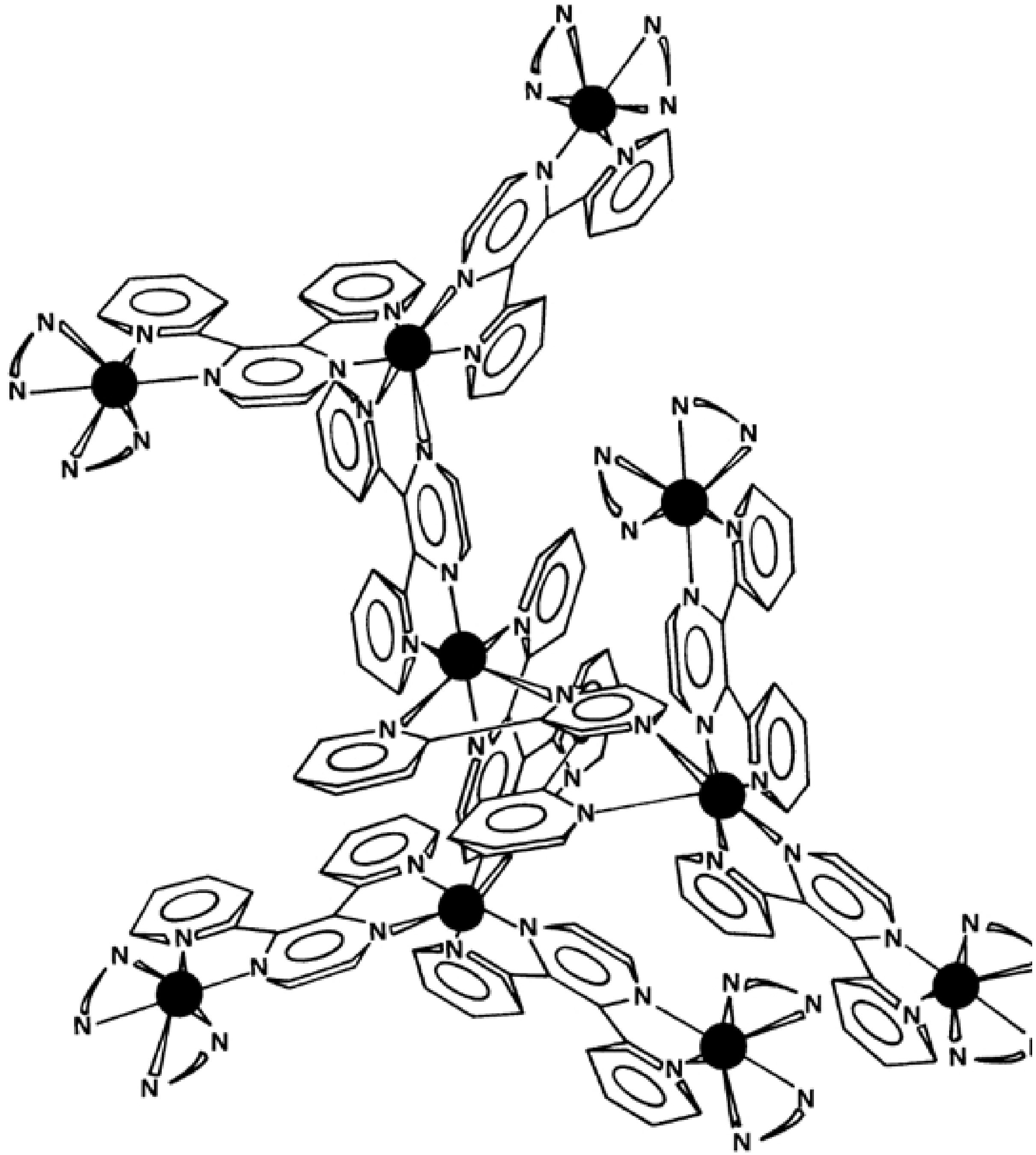
- Artificial antenna systems
- Artificial reaction centers
- Artificial membrane
- Artificial catalyst for H_2 evolution (2 el. process)
- Artificial catalyst for O_2 evolution: (4 el. process)

Artificial antenna

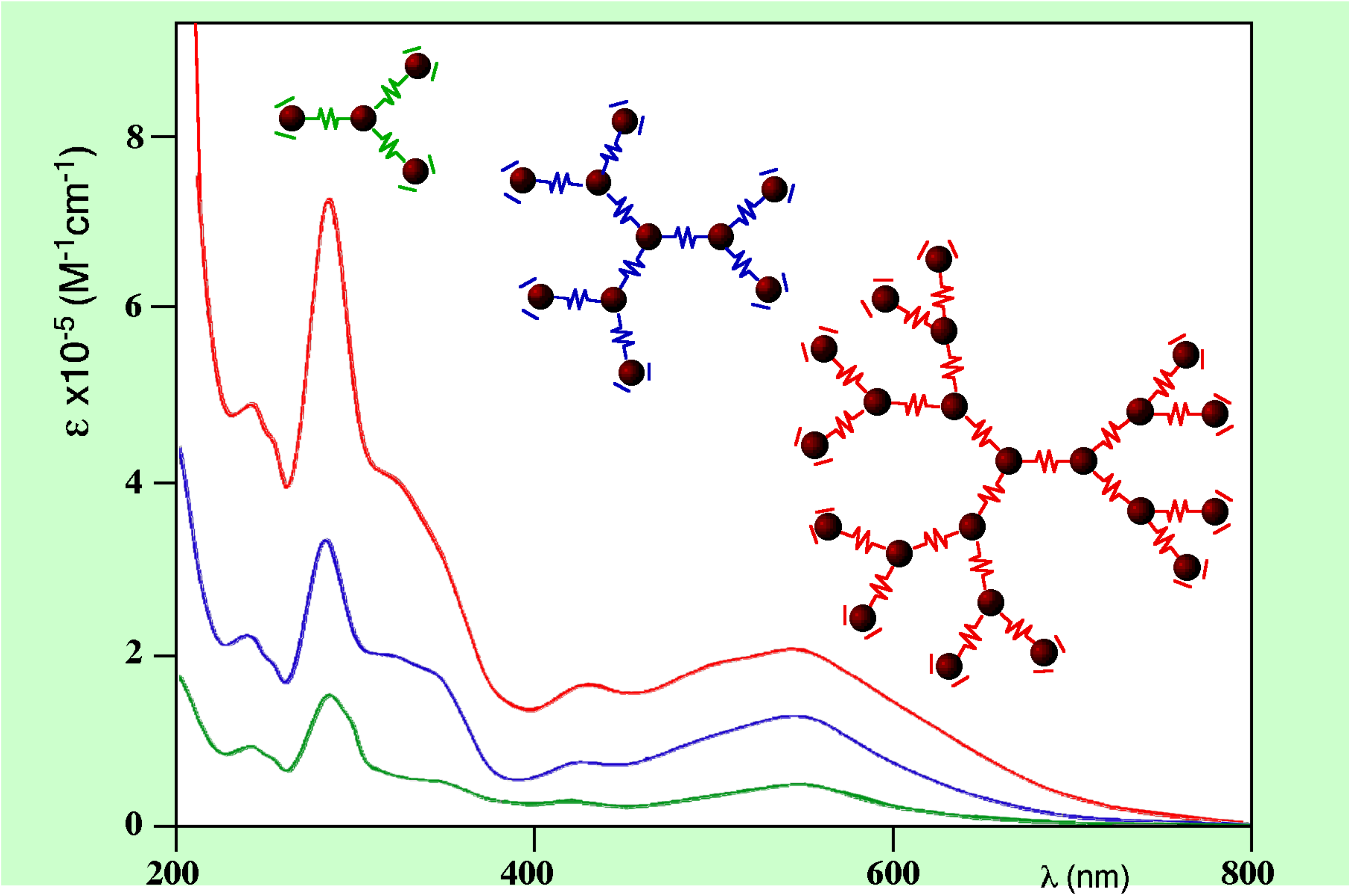


dendritic
deca nuclear
Ru metal complex





First, Second and Third generations of Ru(II) dendrimers



Balzani, Denti, Campagna, et al. *Acc. Chem. Res.* 1998

DEPARTMENT OF THE ARMY
ARMY RESEARCH OFFICE
P.O. BOX 12211
RESEARCH TRIANGLE PARK, NC 27709-2211

REPLY TO
ATTENTION OF

November 21, 1994

Chemical & Biological Sciences
Division

Dear Prof. (Dr.): Balzani,

You have been recognized as an active researcher working directly in the area of dendrimer technology or a closely aligned field. As such, it is our pleasure to invite you to a two-day workshop sponsored by the Army Research Office which will be focused on "dendrimer technology and its potential military applications to the U.S. Army." As you may know, the U.S. Army Research Office supports basic research in academia, at private research organizations and at government laboratories. The Polymer Chemistry Branch of ARO is investigating new research areas to enhance U.S. Army capabilities and has elected to assess the dendrimer area for these possibilities.

In order to appraise and exploit the unique features of "dendrimer science", representatives from academia, government laboratories and industry will be invited to present and share their perspectives at this conference. Because of the importance of your role in forming a workplan from this meeting, attendance for both days is requested. The workshop will take place at the Best Western Crown Park Hotel at Miami Blvd. and Interstate 40, Research Triangle Park, North Carolina next spring on March 15-16, 1995. Expenses for academia/non-profit organizations will be covered with details to follow later. We hope your schedule will allow you to attend this workshop. With this letter we are attempting to define commitment for attendance; therefore, we must receive a response by December/2, 1994.

DENDRIMER TECHNOLOGY WORKSHOP
(Abstract and Plan)

This workshop will identify specific areas of dendrimer research to solve U.S. Army problems. Unique dendrimer properties which include the ability to precisely control critical molecular design parameters (CMDP's) such as size, shape, surface chemistry, flexibility and topology suggest numerous applications of interest to DoD and the civilian sector. We believe dendrimers will be useful (1) for the detection and detoxification/destruction of chemical weapons

US Army and MIT go nano

The Institute for Soldier Nanotechnologies was launched recently as a research collaboration between Massachusetts Institute of Technology (MIT), US, and the US Army.

Occupying a 2600m² site, the institute will combine basic and applied research into defence-related nanotechnology concentrating on three areas: protection, improving performance, and injury intervention and cure.

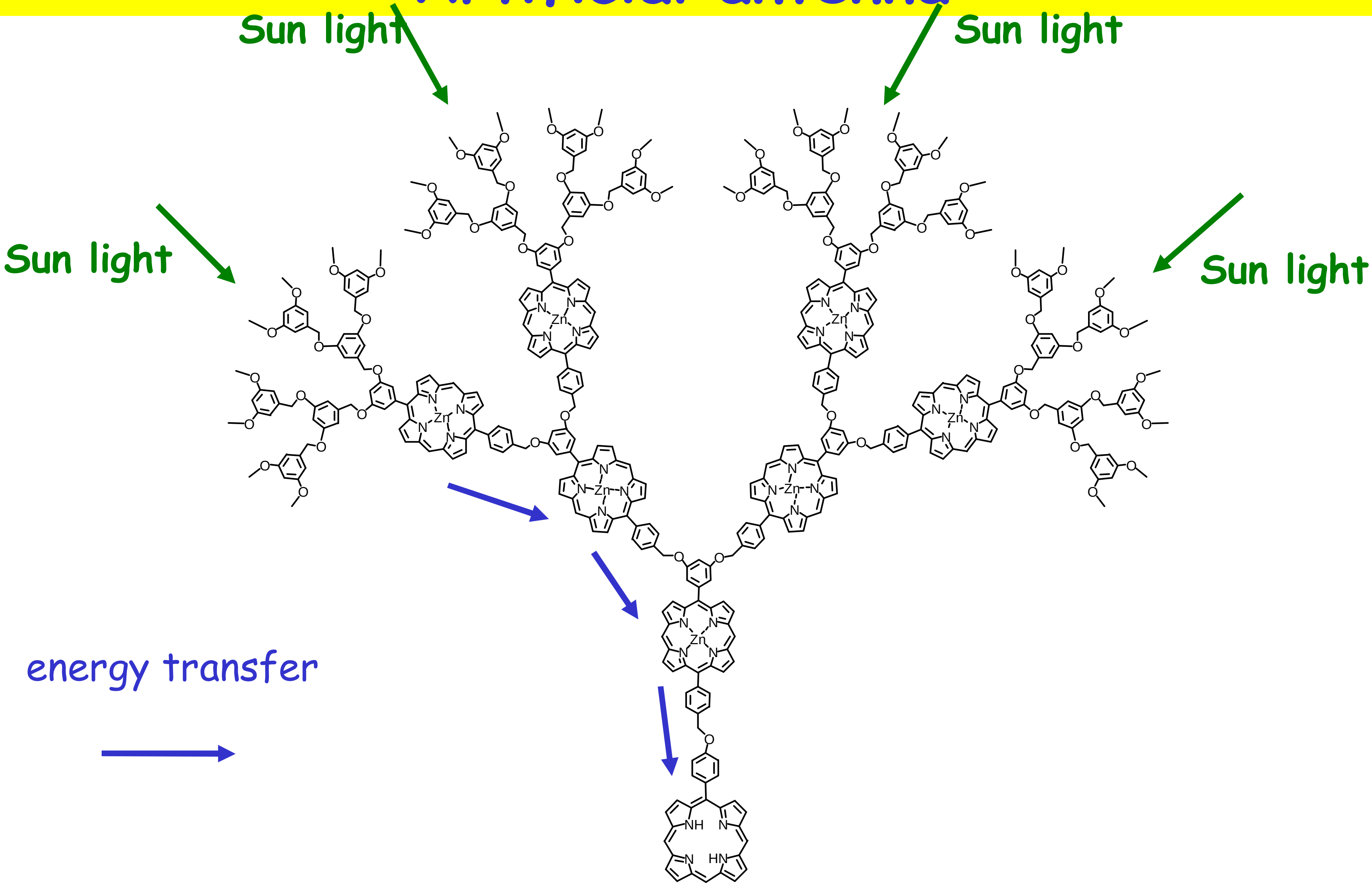
The institute will work with various industrial partners including DuPont, Dow Corning, Carbon Nanotechnologies, Triton Systems and Dendritic Nanotechnologies. The institute will also work with the US Army's research laboratory on 'field-ready' products.

Michael Andrews, deputy assistant secretary for research and technology in the US Army, said: 'The Institute for Soldier Nanotechnologies is an exciting innovation in government–academic–industry teamwork, promising breakthrough nanotechnologies and that will lighten our soldiers' loads, treat wounds and protect them from injuries'.

Current research projects underway at the institute include protection from conventional, chemical and biological weapons. Products could include sensors and fabric coatings that would be built into the soldiers' battlesuits.

Other projects are investigating ways of using nanotechnology for novel methods of healing wounds as well as the potential for treating injured soldiers while they are still in combat. □

Artificial antenna



Aida, et al., 2001

Molecular antennas

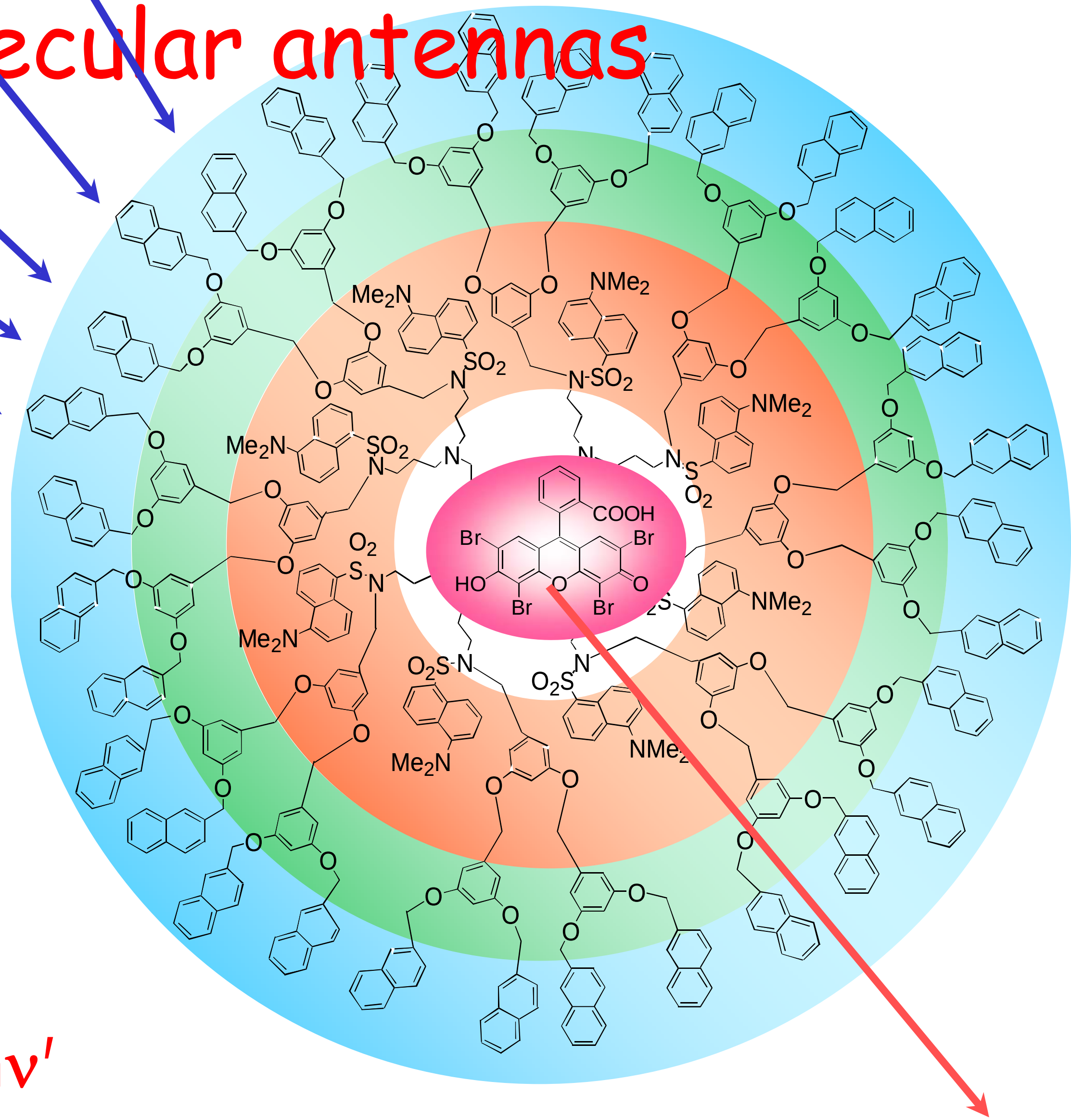
Light harvesting dendrimers

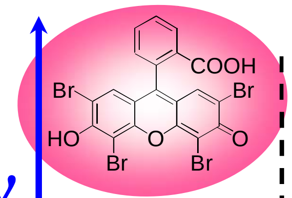
64 chromophoric units:

32 naphthyl **UV abs**

24 dimethoxibenzene

8 dansyl





hν

Eosin

extracted from water

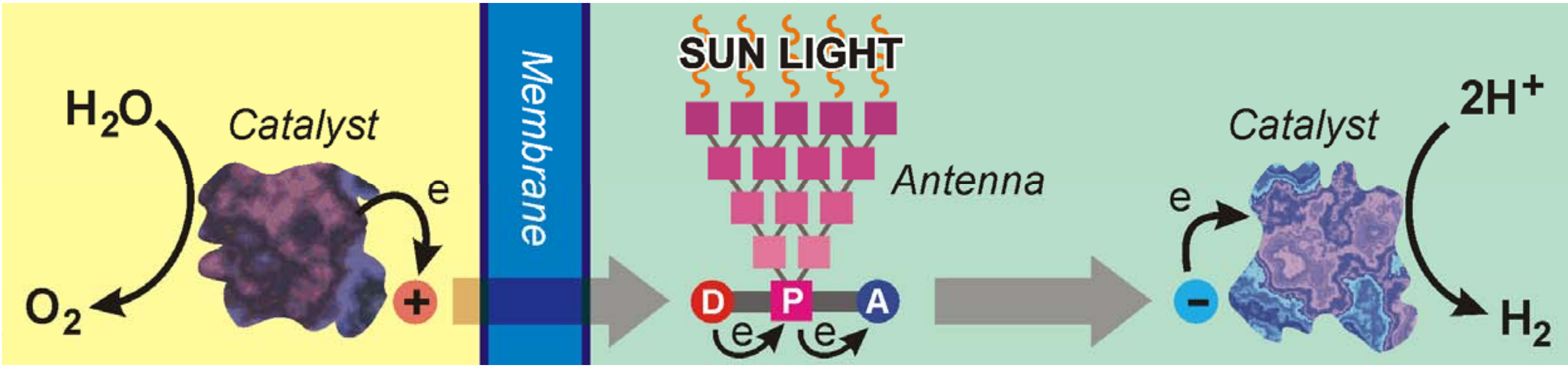
hν′

emission 500 nm

Ceroni, et al., 2002

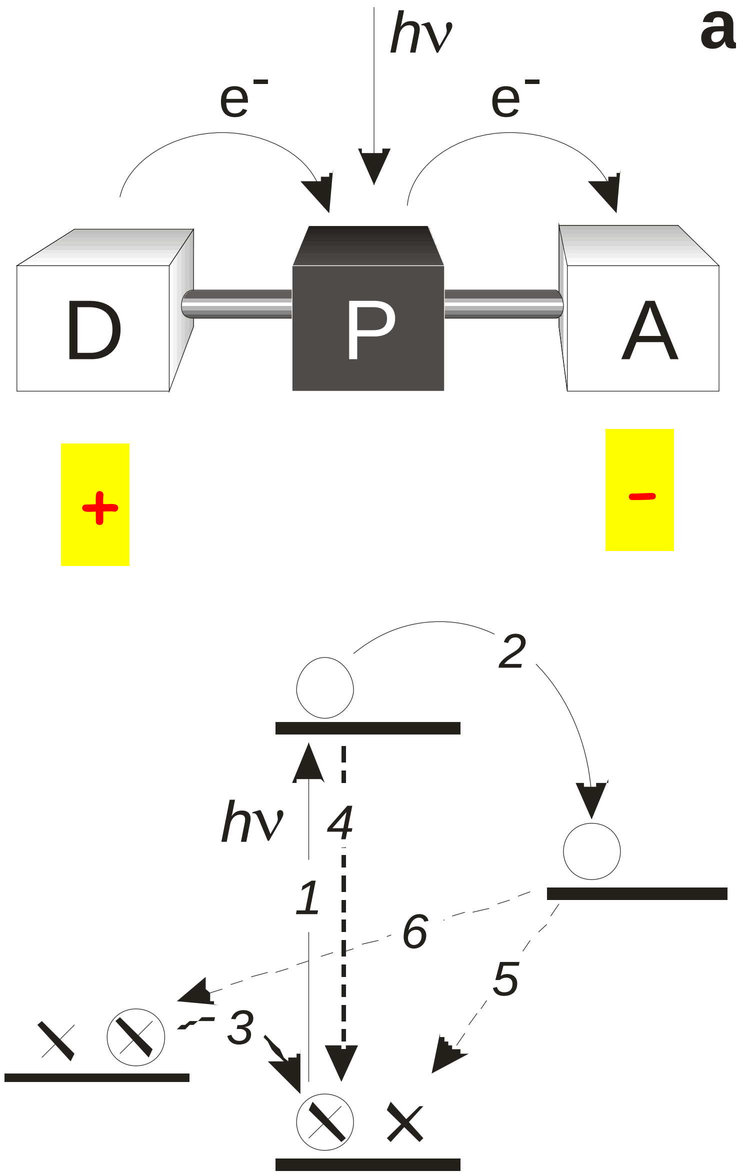
Artificial photosynthesis

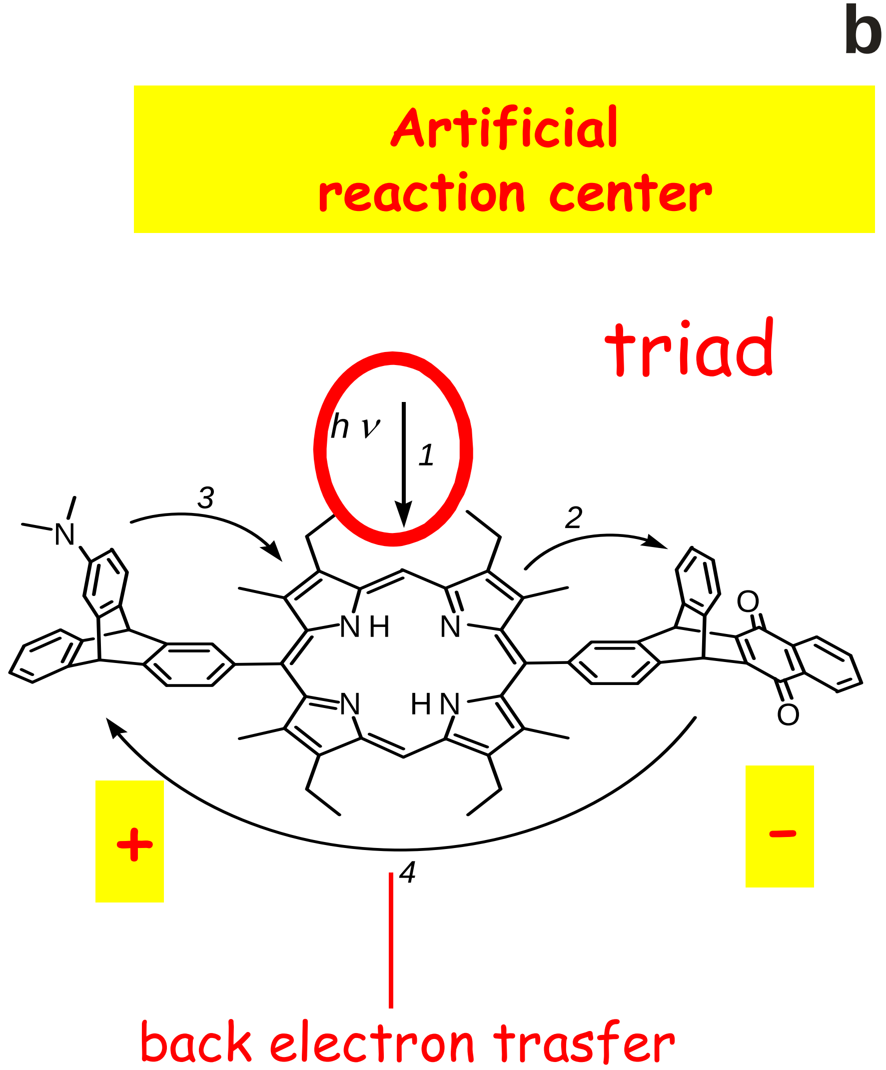
$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$



Reaction center

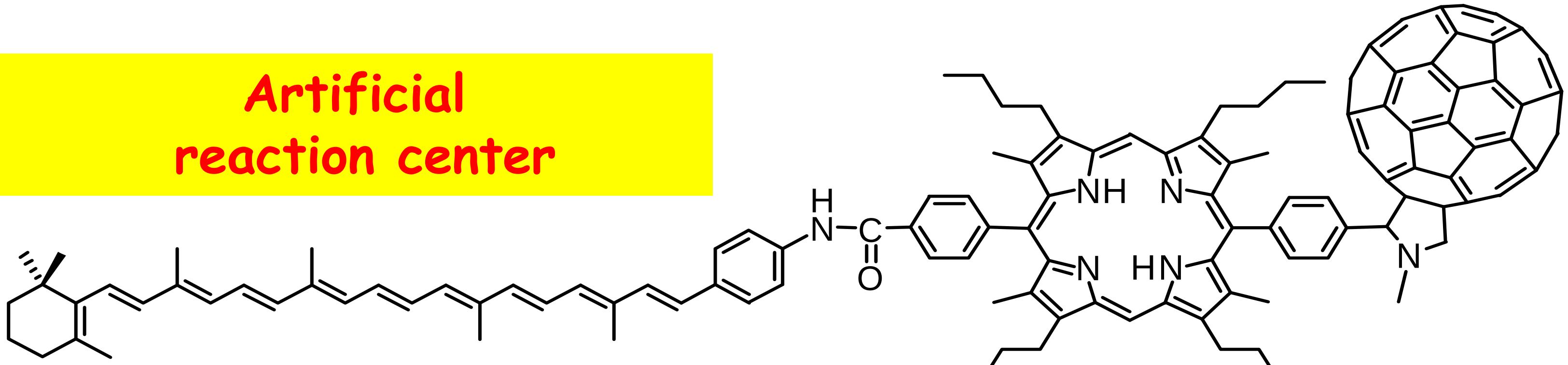
- Artificial antenna systems
- Artificial reaction centers
- Artificial membrane
- Artificial catalyst for H_2 evolution (2 el. process)
- Artificial catalyst for O_2 evolution (4 el. process)





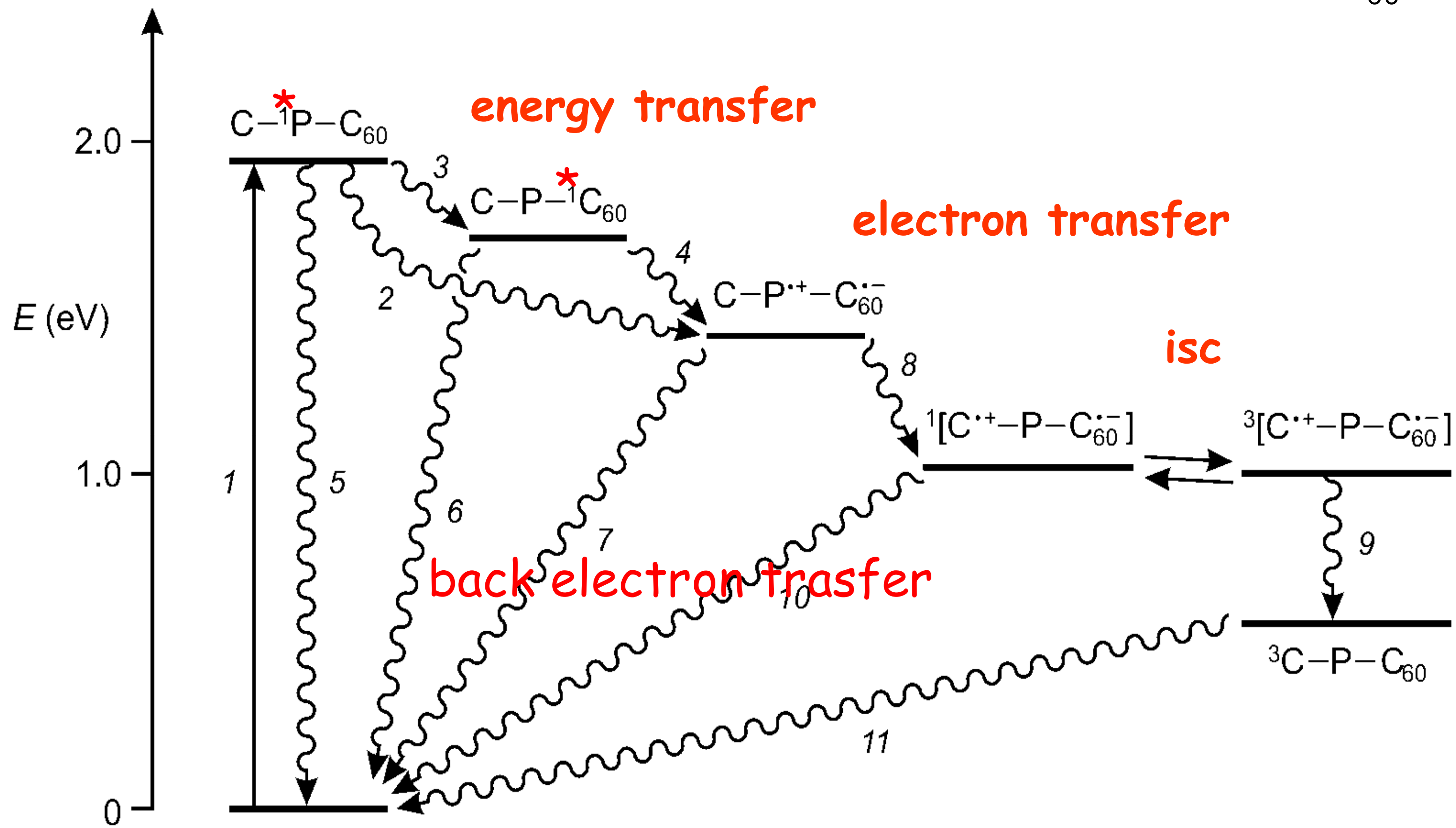
Wasielewski, et al.

Artificial reaction center



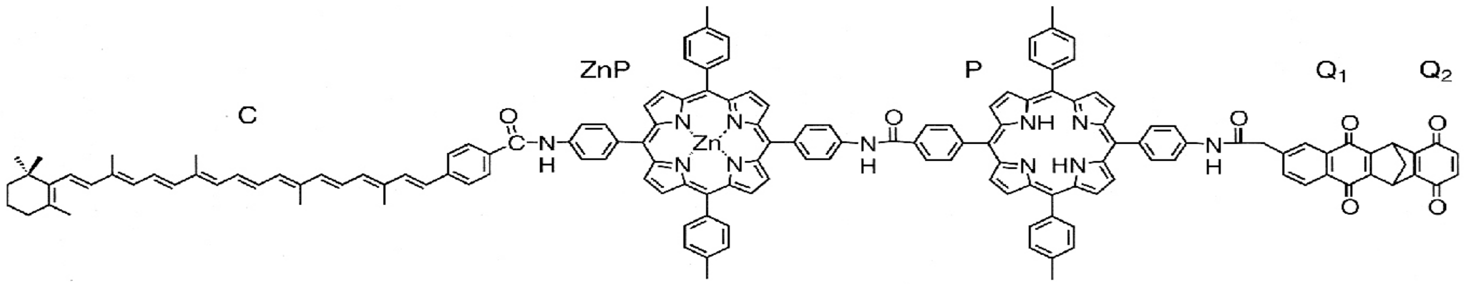
triad

C P C_{60}



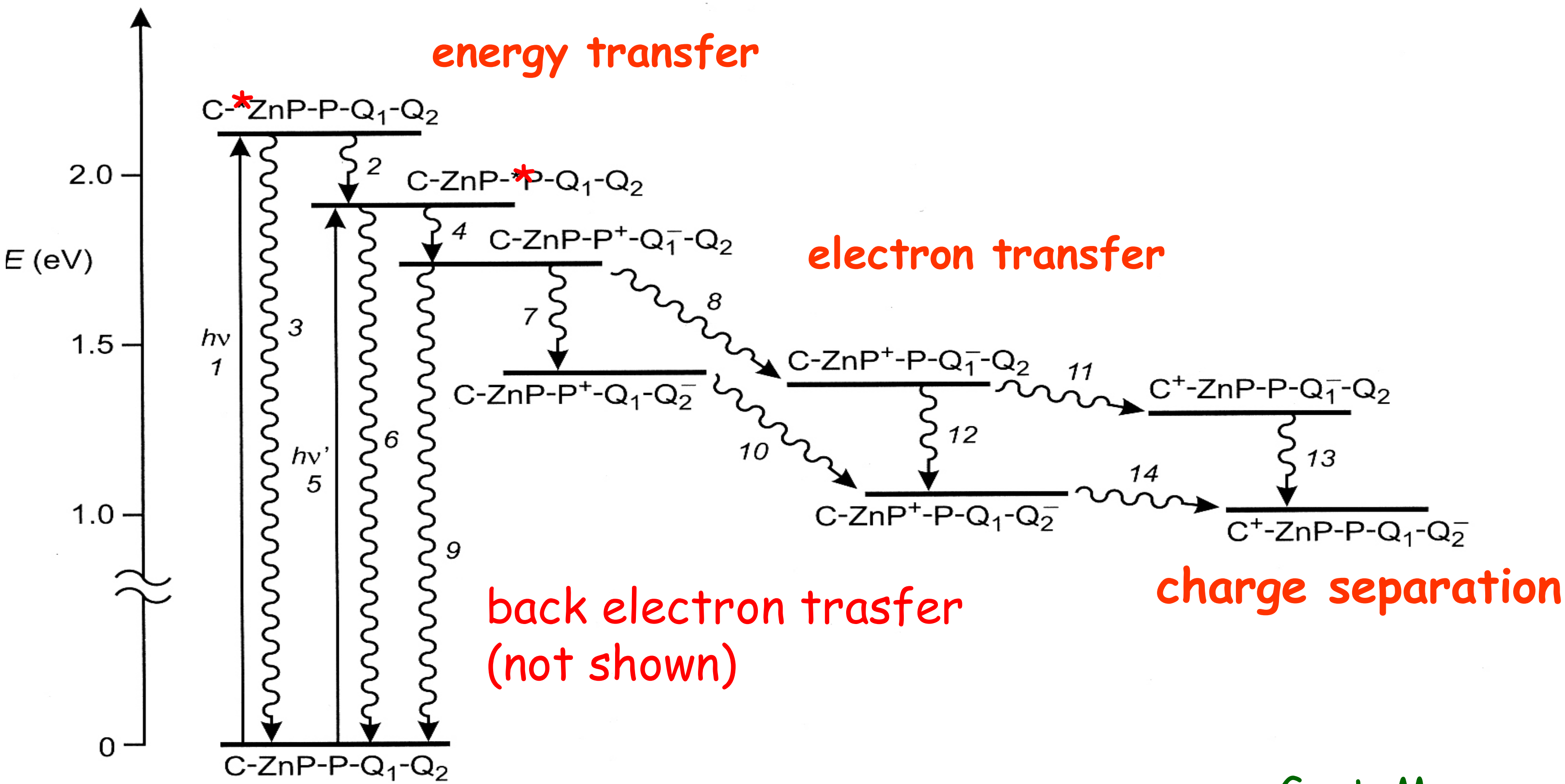
Φ = 0.04; τ = 300 ns; η = 0.02

Gust, Moore, et al.



Artificial reaction center

pentad

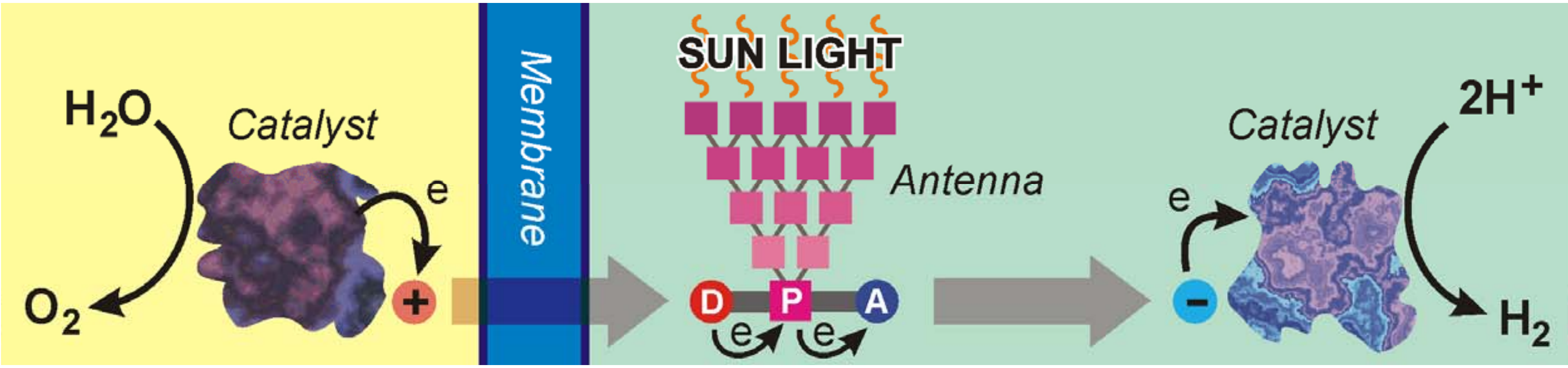


Φ = 0.83; τ = 55 μs; $\eta = 0.5$

Gust, Moore, et al.

Artificial photosynthesis

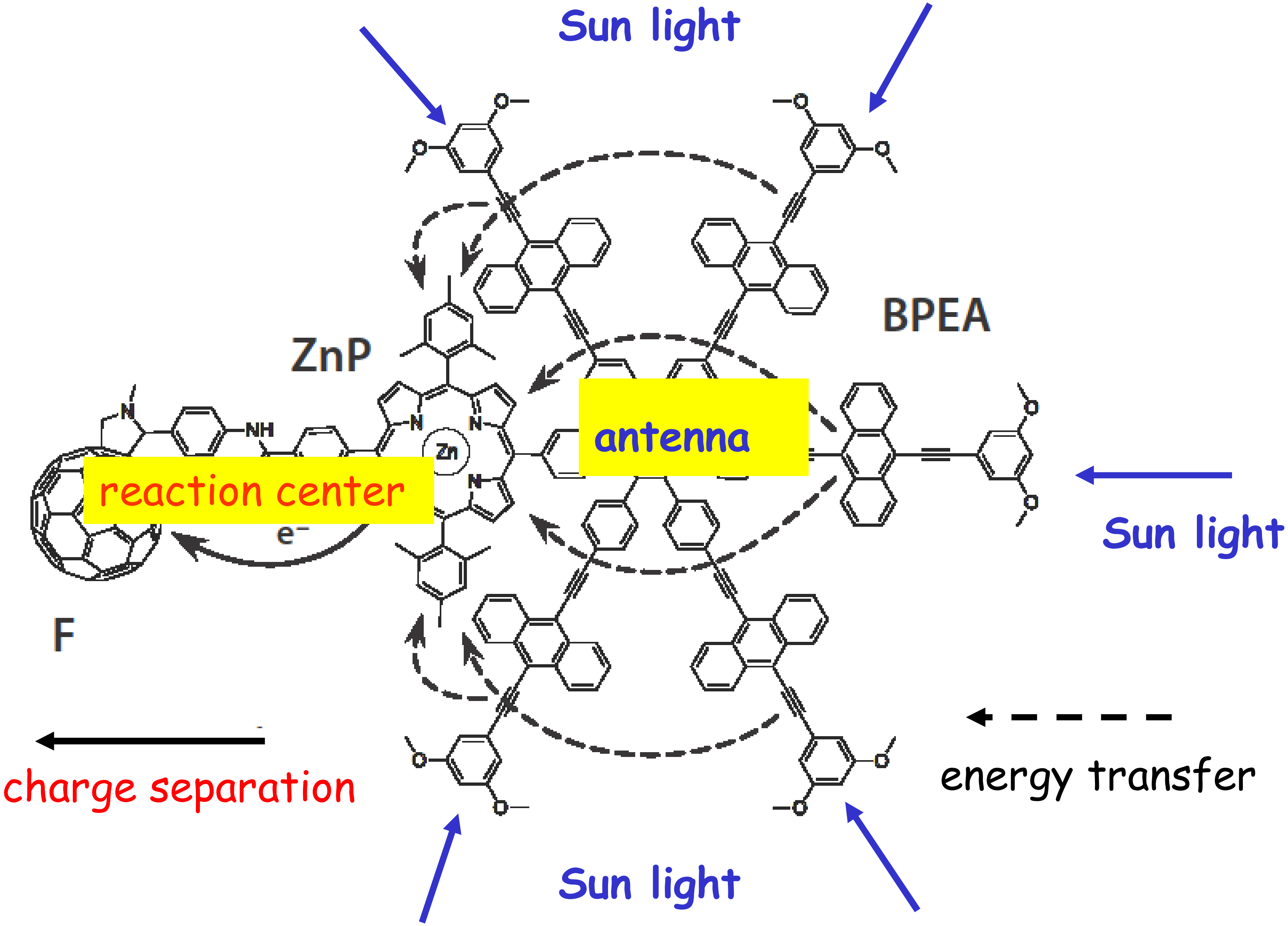
$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$



Reaction center

- -Artificial antenna systems
- -Artificial reaction centers] connection
- -Artificial membrane
- -Artificial catalyst for H_2 evolution (2 el. process)
- -Artificial catalyst for O_2 evolution (4 el. process)

Combined antenna-reaction center system

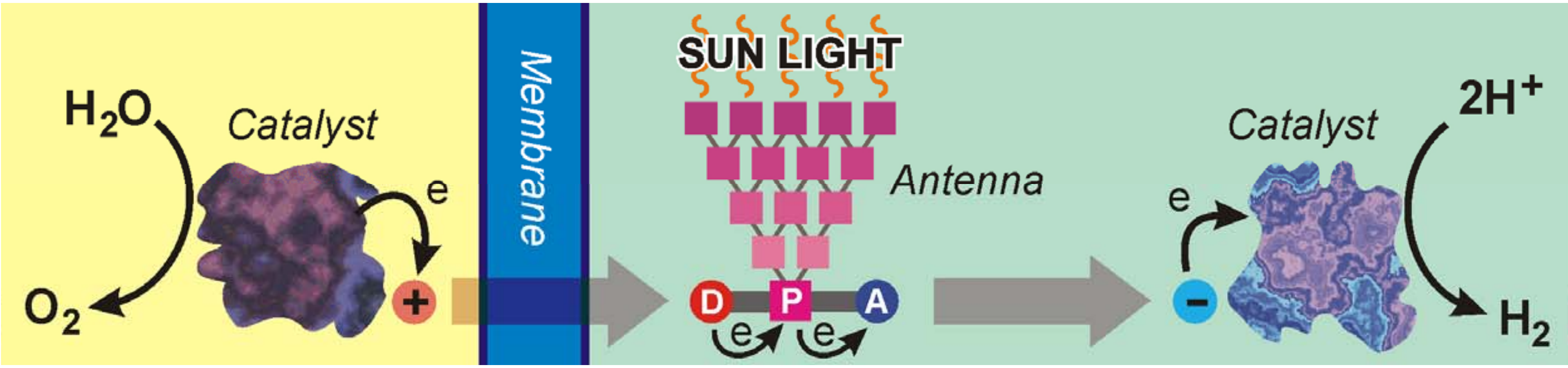


Φ = 1 τ = 10 ns

Kodis, et al. 2006

Artificial photosynthesis

$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$

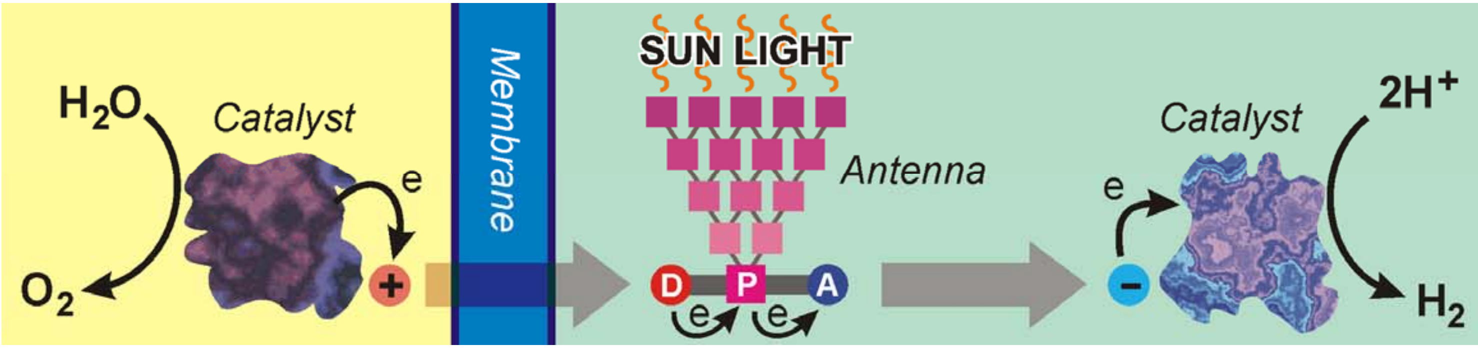


Reaction center

- -Artificial antenna systems
- -Artificial reaction centers
- -Artificial membrane
- -Artificial catalyst for H_2 evolution (2 el. process)
- -Artificial catalyst for O_2 evolution (4 el. process)

Artificial photosynthesis

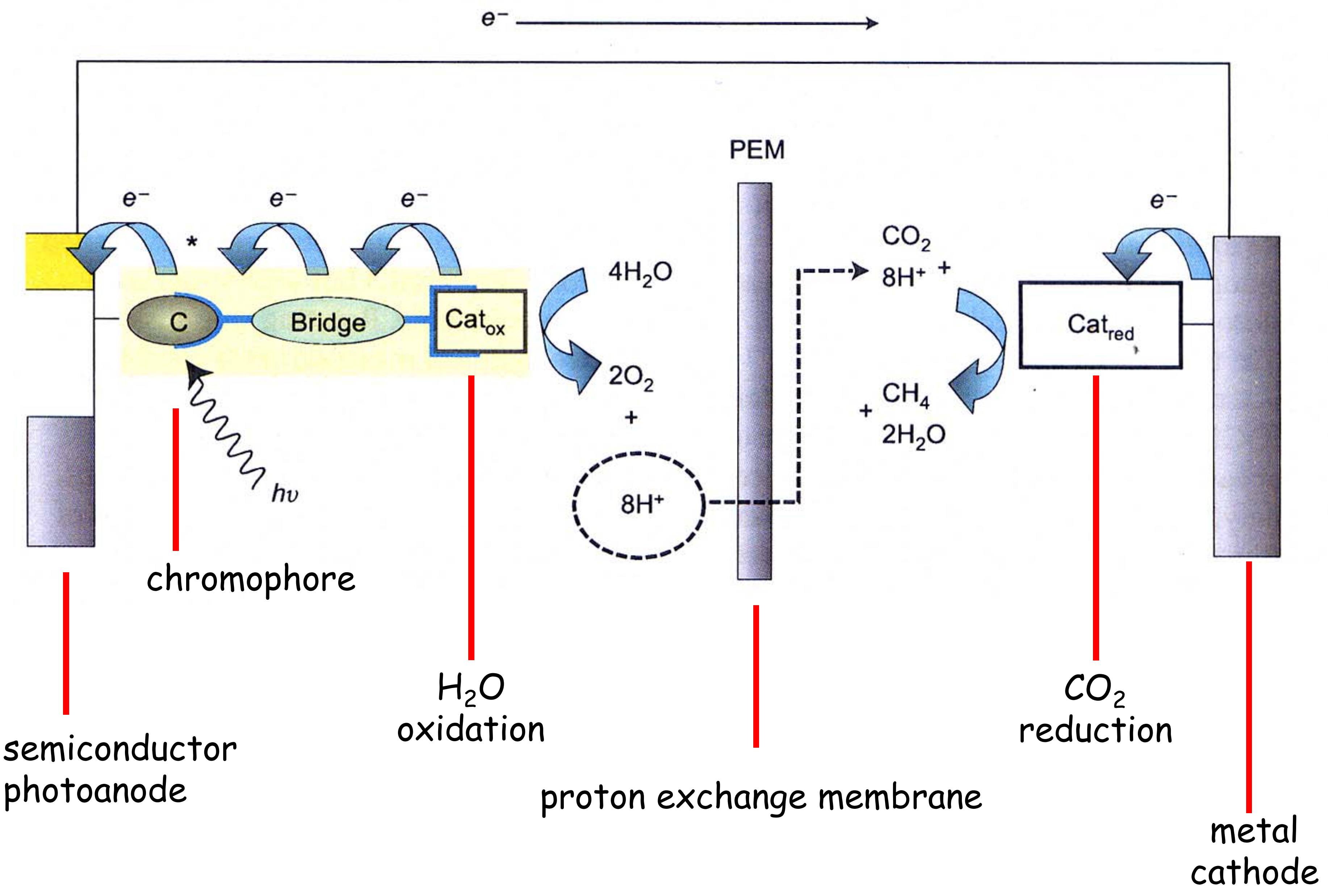
$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$



- Light excitation and charge separation:
molecular components in solution or solid state (semiconductor) materials?

- catalysis:
homogeneous or heterogeneous catalysts?

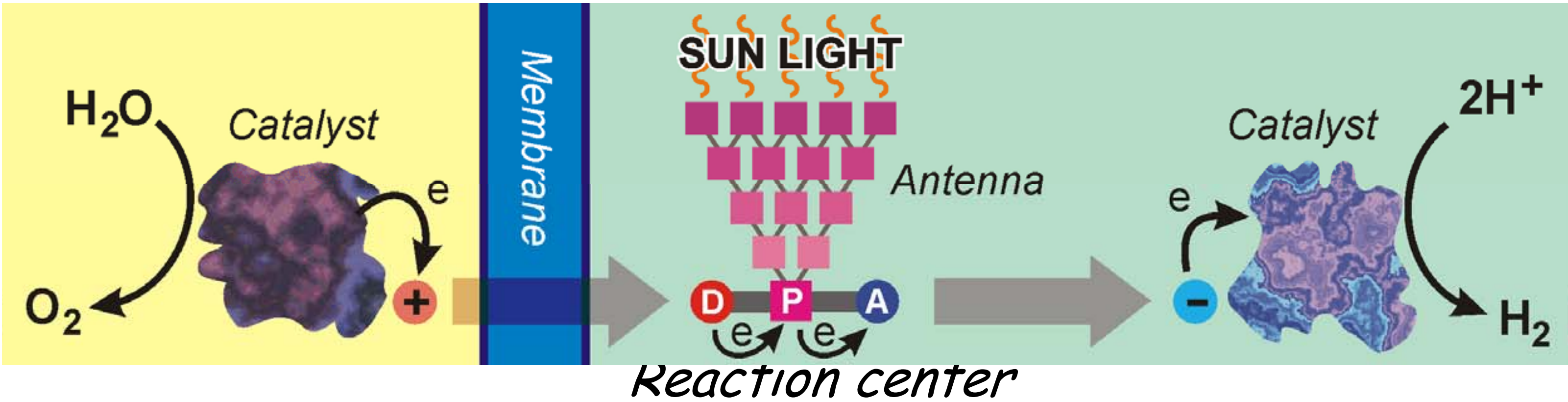
A dye-sensitized photoelectrosynthesis cell



W. Song et al., Pure Appl. Chem. 2011, 83, 749

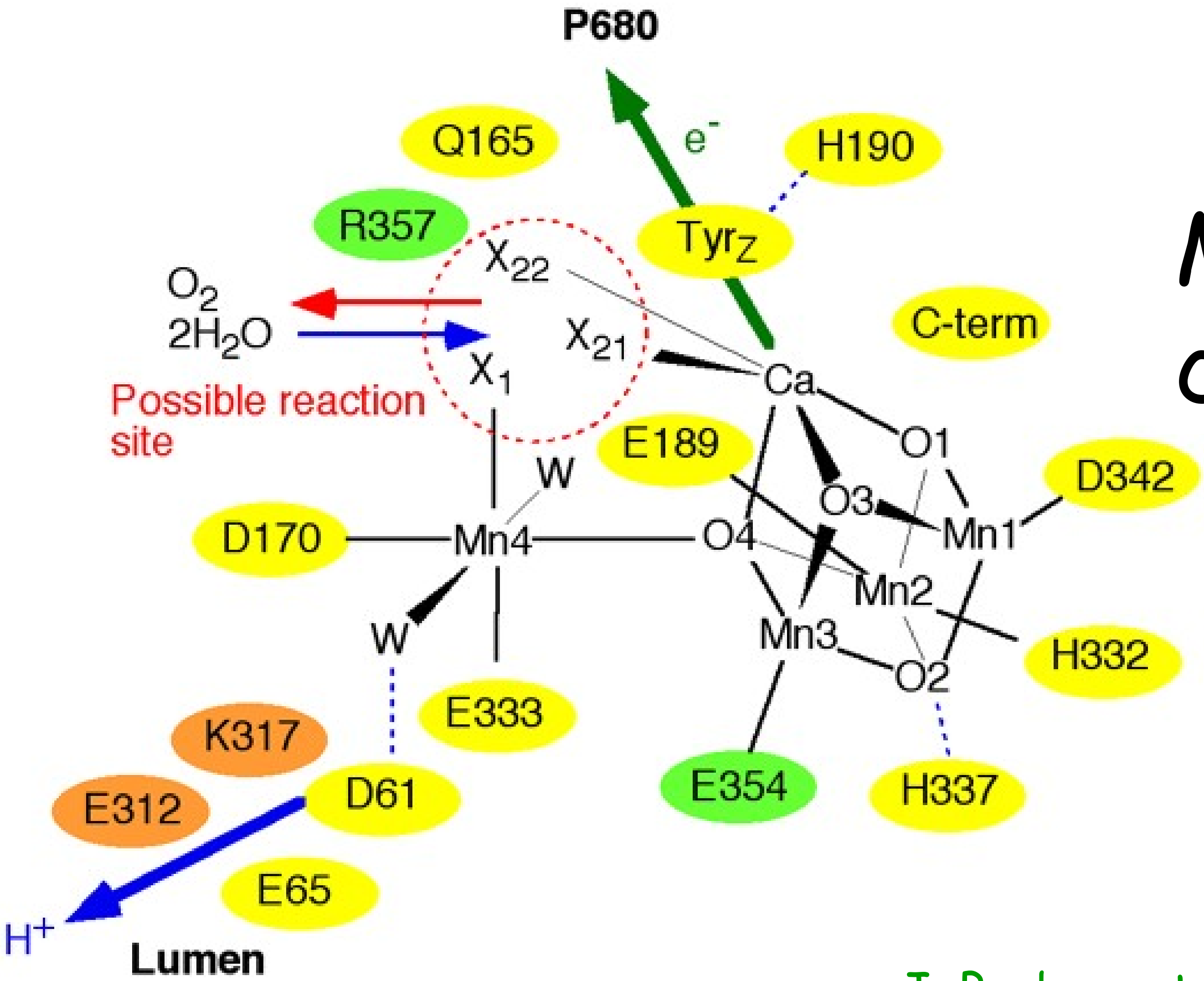
Artificial photosynthesis

$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$



- Artificial antenna systems
- Artificial reaction centers
- Artificial membrane
- Artificial catalyst for H_2 evolution (2 el. process)
- Artificial catalyst for O_2 evolution (4 el. process)

The oxygen evolving complex (OEC)



Mn_4Ca cluster

J. Barber, et al. *Science* 2004

J. Yano, et al., *Science*, 2006

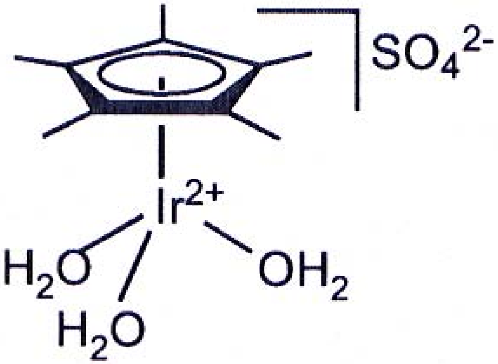
Attempts to design artificial

- homogeneous catalysts
- heterogeneous (film) catalysts

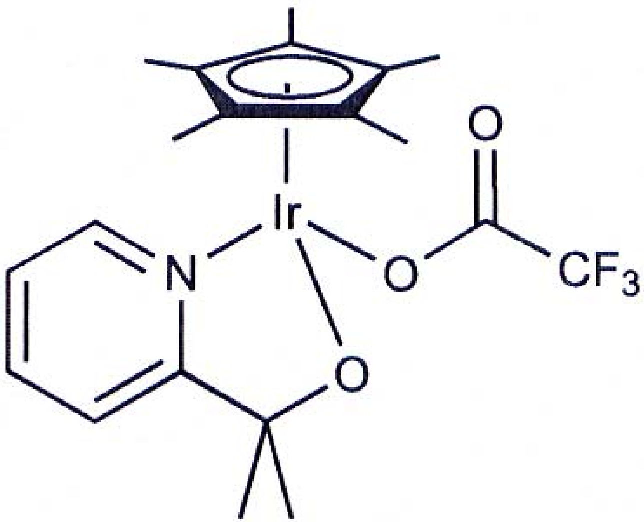
Attempts to evaluate their performance by

- chemical or electrochemical catalysis
- sacrificial photocatalytic processes

Iridium complexes



Precursor to a heterogeneous catalyst



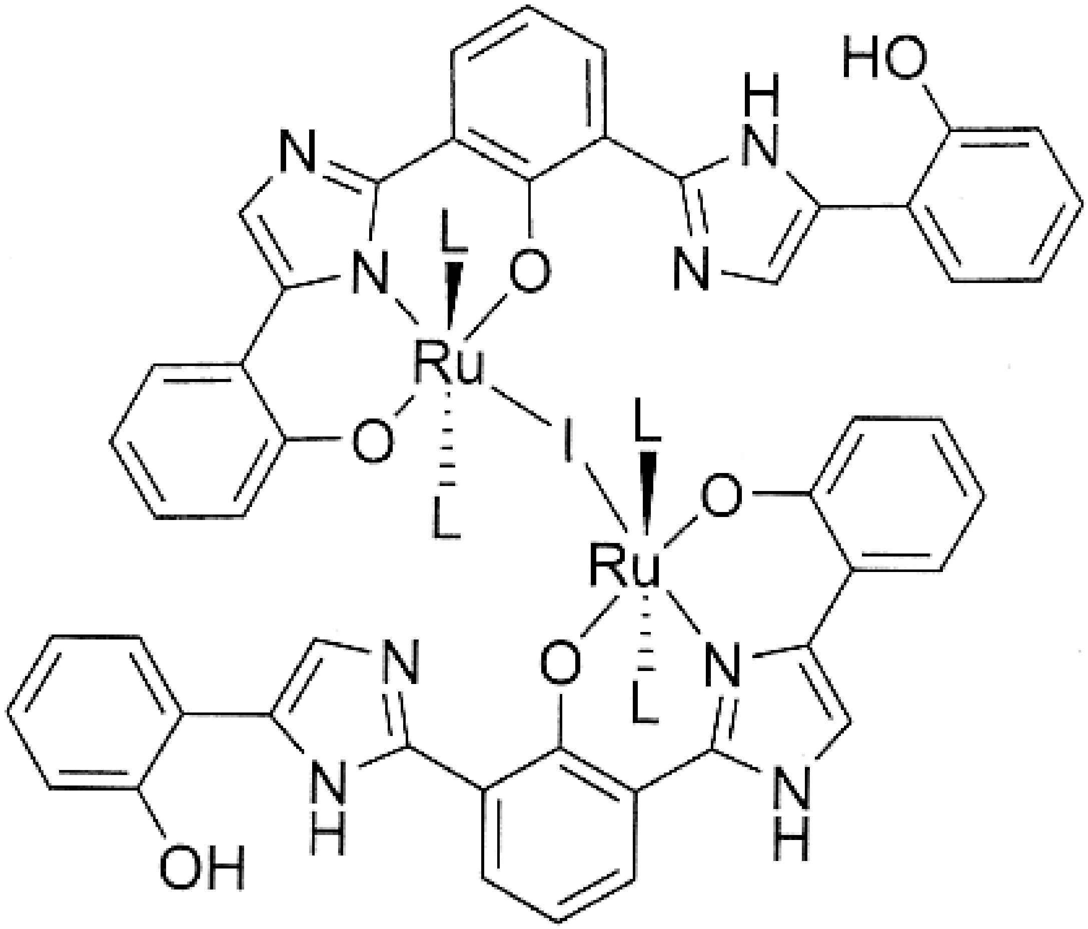
Homogeneous catalyst

Depending on the composition, they can behave has heterogeneous or homogeneus catalysts

N.D. Schely, et a, *J. Am.Chem. Soc.*, 2011
T.J. Meyer, *Nature Chemistry*, 2011

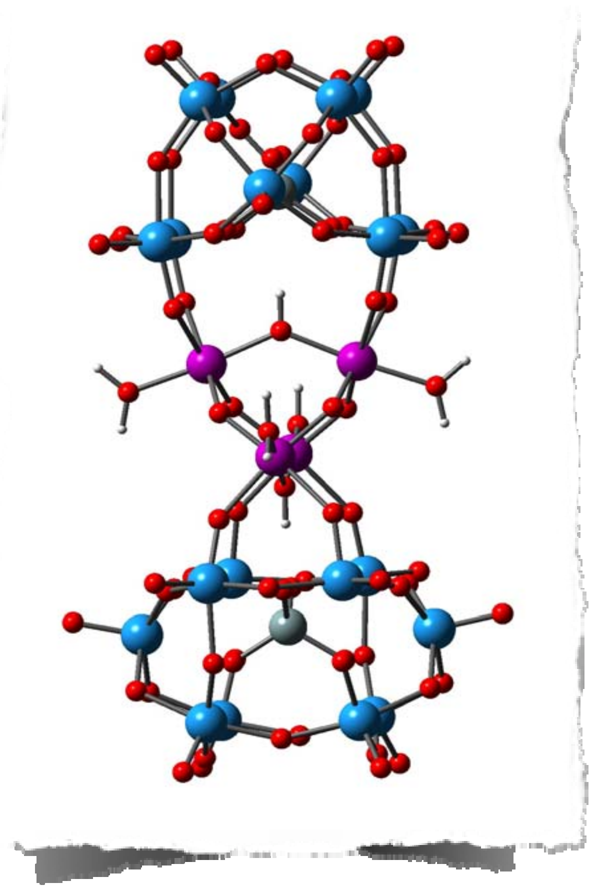
A homogeneus binuclear Ru catalyst (water oxidation by Ce^{4+} and $Ru[(byp)_3]^{3+}$)

L = pyridine

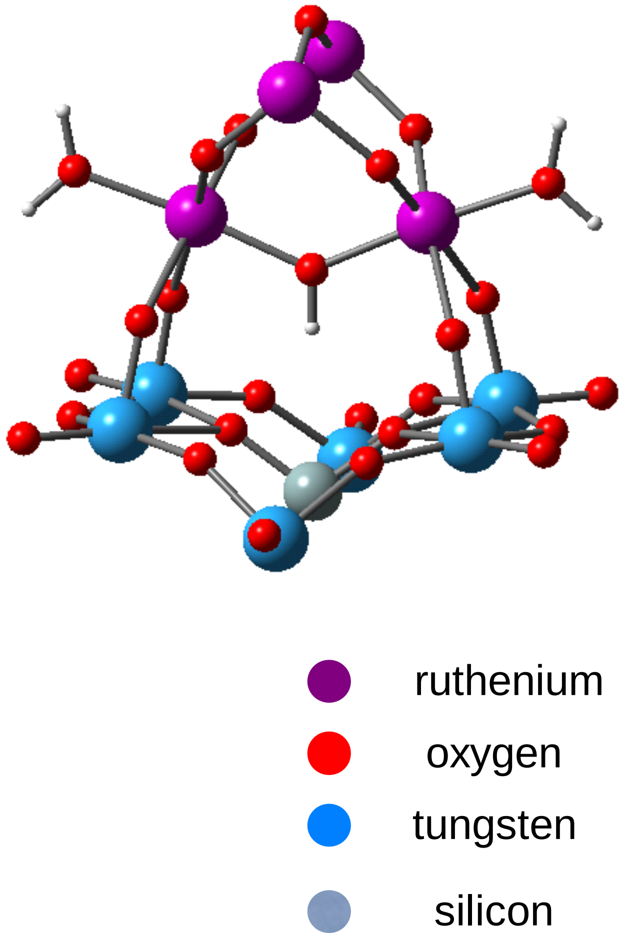


B. Akermark et al., Chem.Eur.J., **2011**, *17*, 7953

A homogeneus tetranuclear Ru catalyst (water oxidation by: electrochenistry; photochemistry with Ru[(byp)$_3$]$^{2+}$ and persulphate)



$Ru_4(\mu{-}O)_4(\mu{-}OH)_2(H_2O)_4(\gamma{-}SiW_{10}O_{36})_2]^{10-}$



Bonchio et al., J. Am. Chem. Soc. **2008**,
Scandola et al.,Chem. Comm. **2010**,

Splitting water with cobalt

V. Artero, et al.,

Angew. Chem. Int. Ed., 2011, 50, 7238

Cobalt compounds, either as molecular species or materials, can be used as catalysts for reductive ($Co^{II/I}$) or oxidative ($Co^{III/II}$) electrochemical reactions of water.

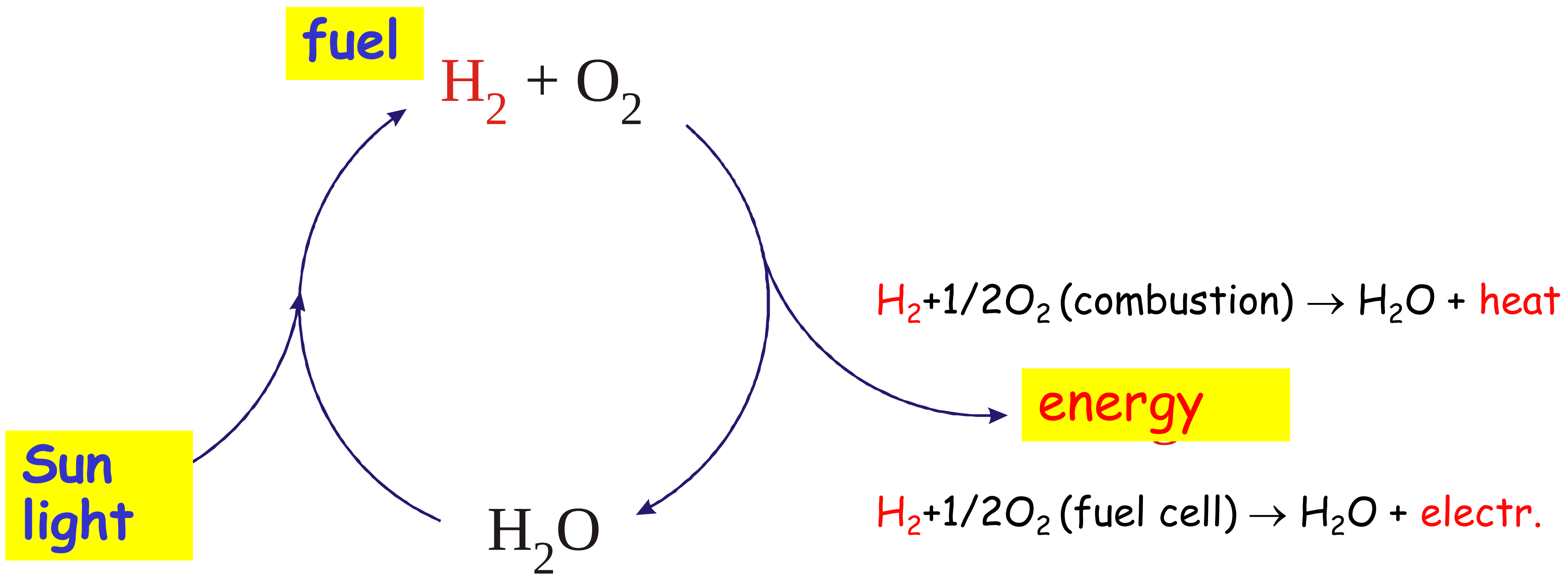
Efficient water oxidation catalysts based on readily available iron complexes

J.L. Fillol, et al.,

Nature Chemistry, 2011, 3, 807

Iron coordination complexes catalyze homogeneous water oxidation by Cerium(IV)

Artificial photosynthesis



The grand challenges of chemistry:
the artificial production of a solar fuel that can be stored and transported and that, when used, is reversibly converted into the starting material.

Artificial photosynthesis

$$2H_2O + 4\,h\nu \rightarrow 2\,H_2 + O_2$$

Education has produced

many people

who are able to read,

but unable to distinguish

what's worth reading

G.M. Trevelyan

Scientific education

has produced many people

who are able to make science,

but unable to distinguish

what's worth making with science

As scientists and citizens, we have a great social responsibility.

We must carefully control that science and technology are used

For peace, not for war

For alleviating poverty, not for maintaining privileges

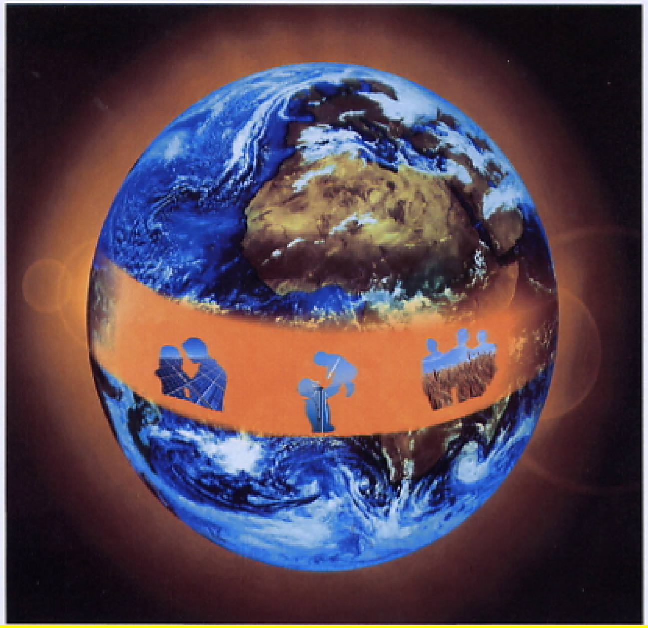
For reducing, not for increasing the gap between developed and underdeveloped countries

WILEY-VCH

Nicola Armaroli, Vincenzo Balzani

Energy for a Sustainable World

From the Oil Age to a Sun-Powered Future



2011