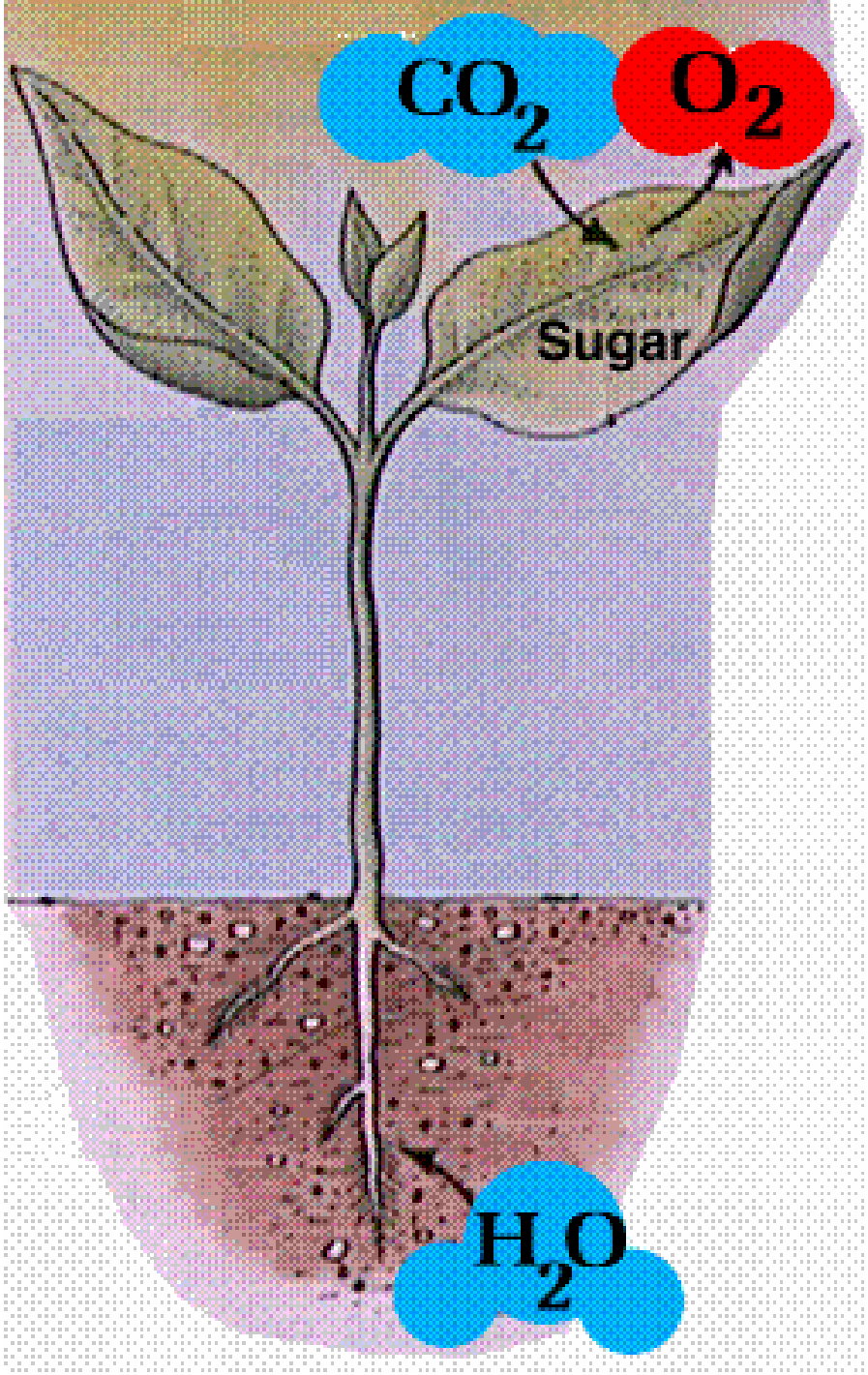
Einige der bahnbrechenden Versuche Priestleys

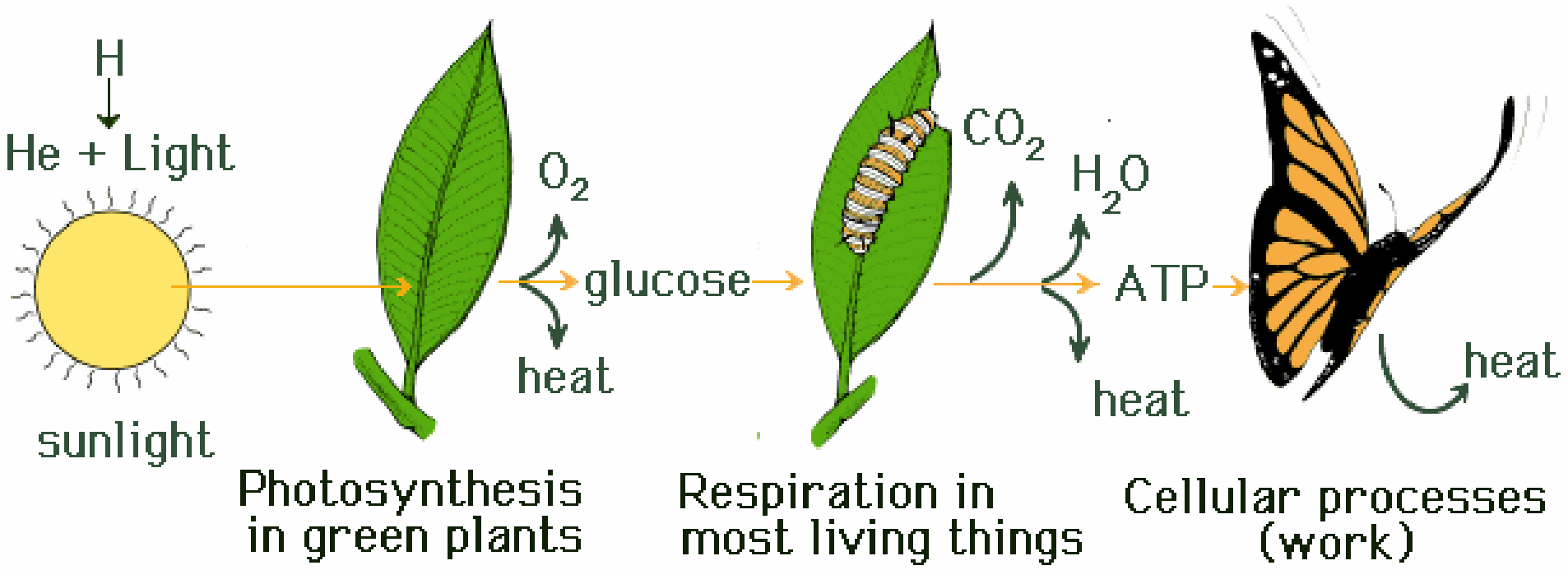


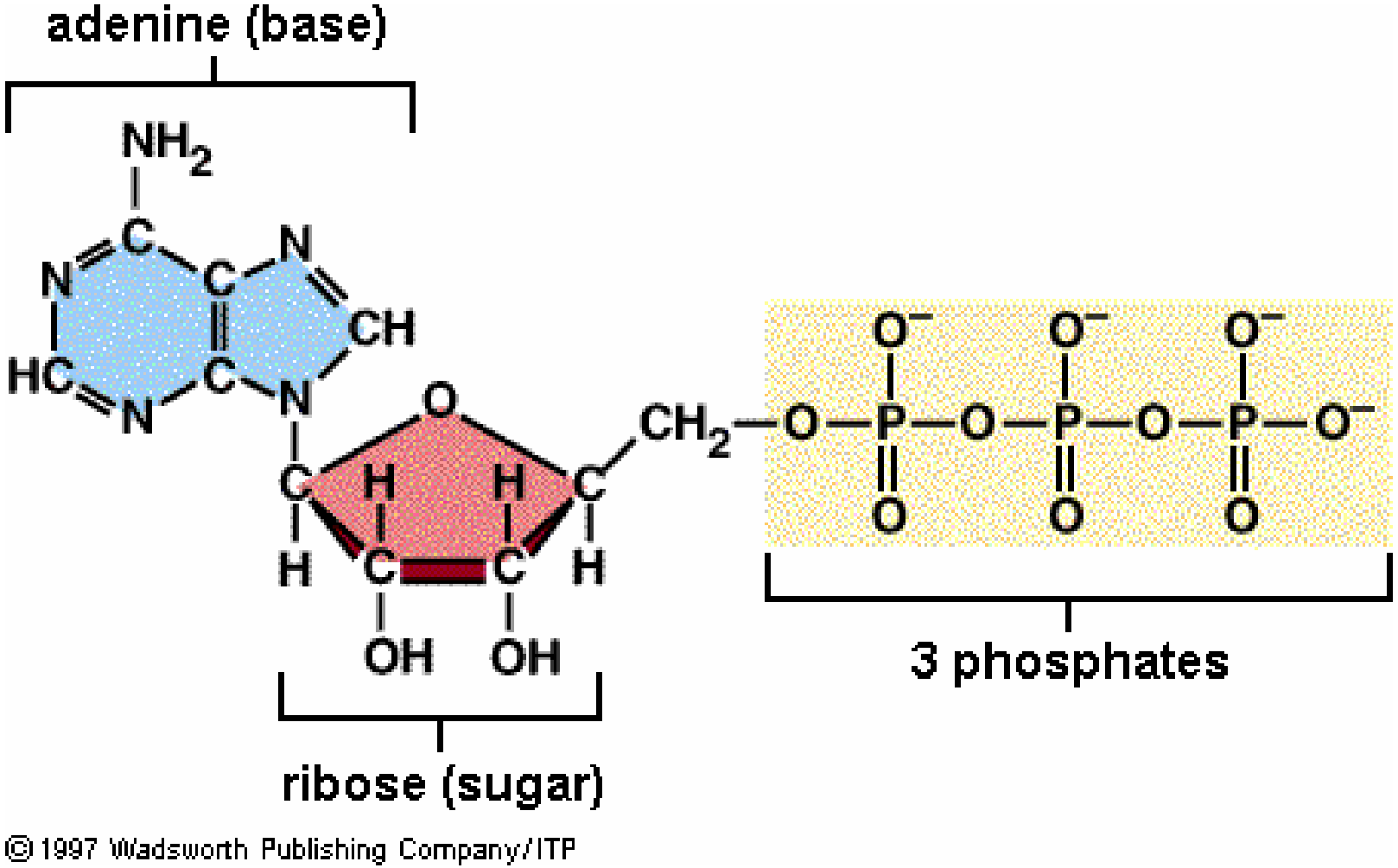
Photosynthese

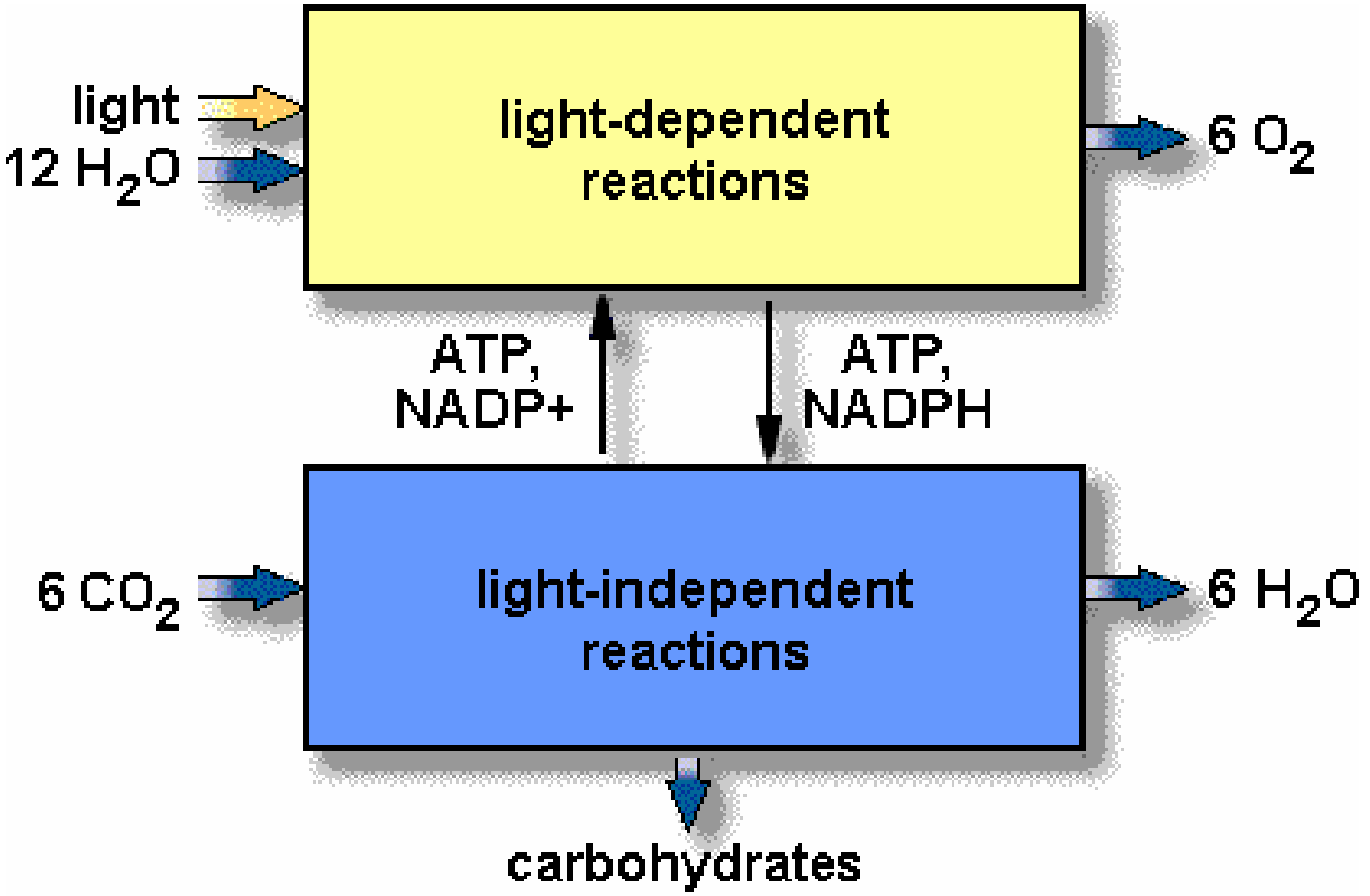
- Pflanzen
- Bakterien

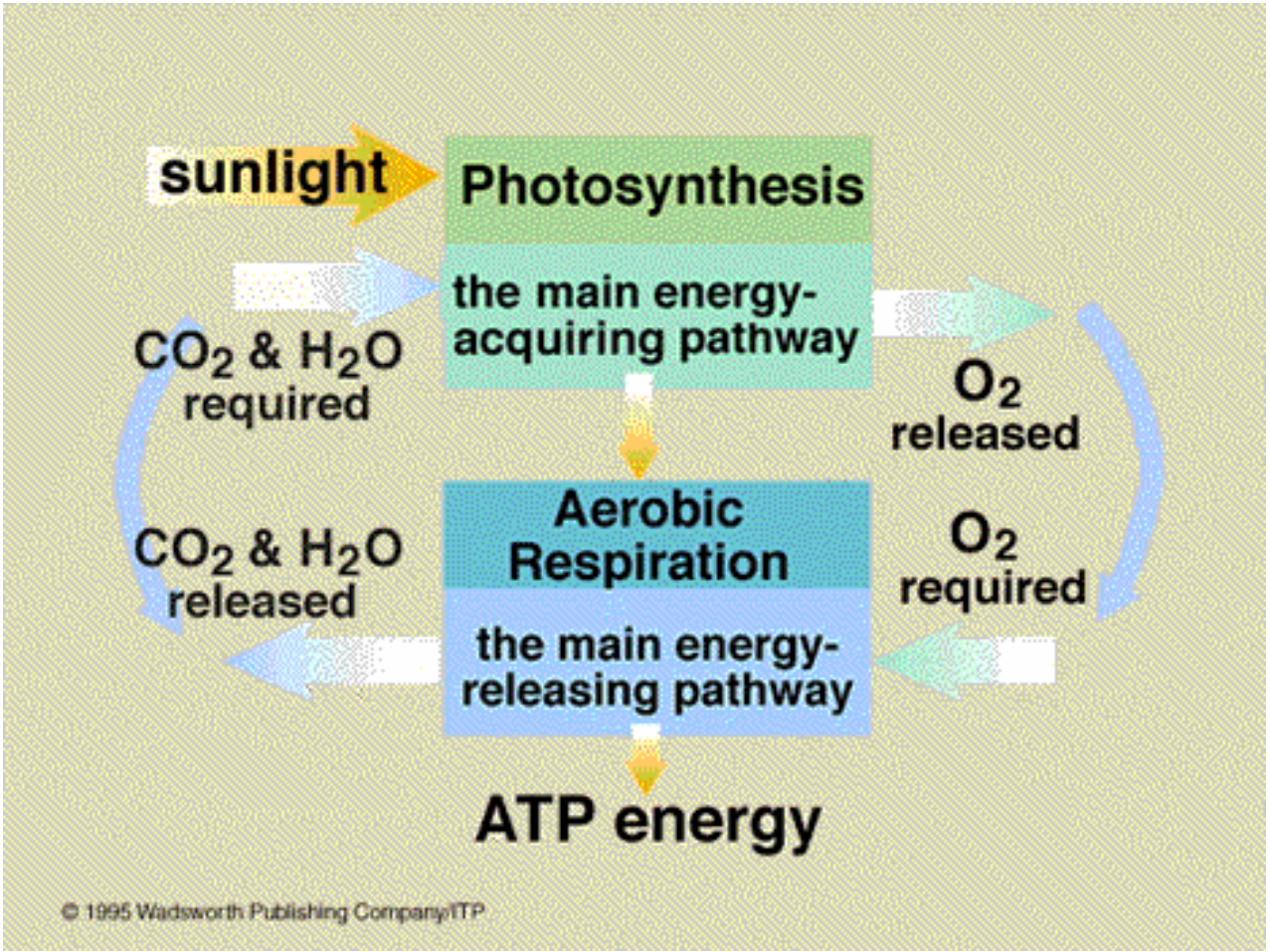
6H2O + 6CO2 =C6H12 + 6O2

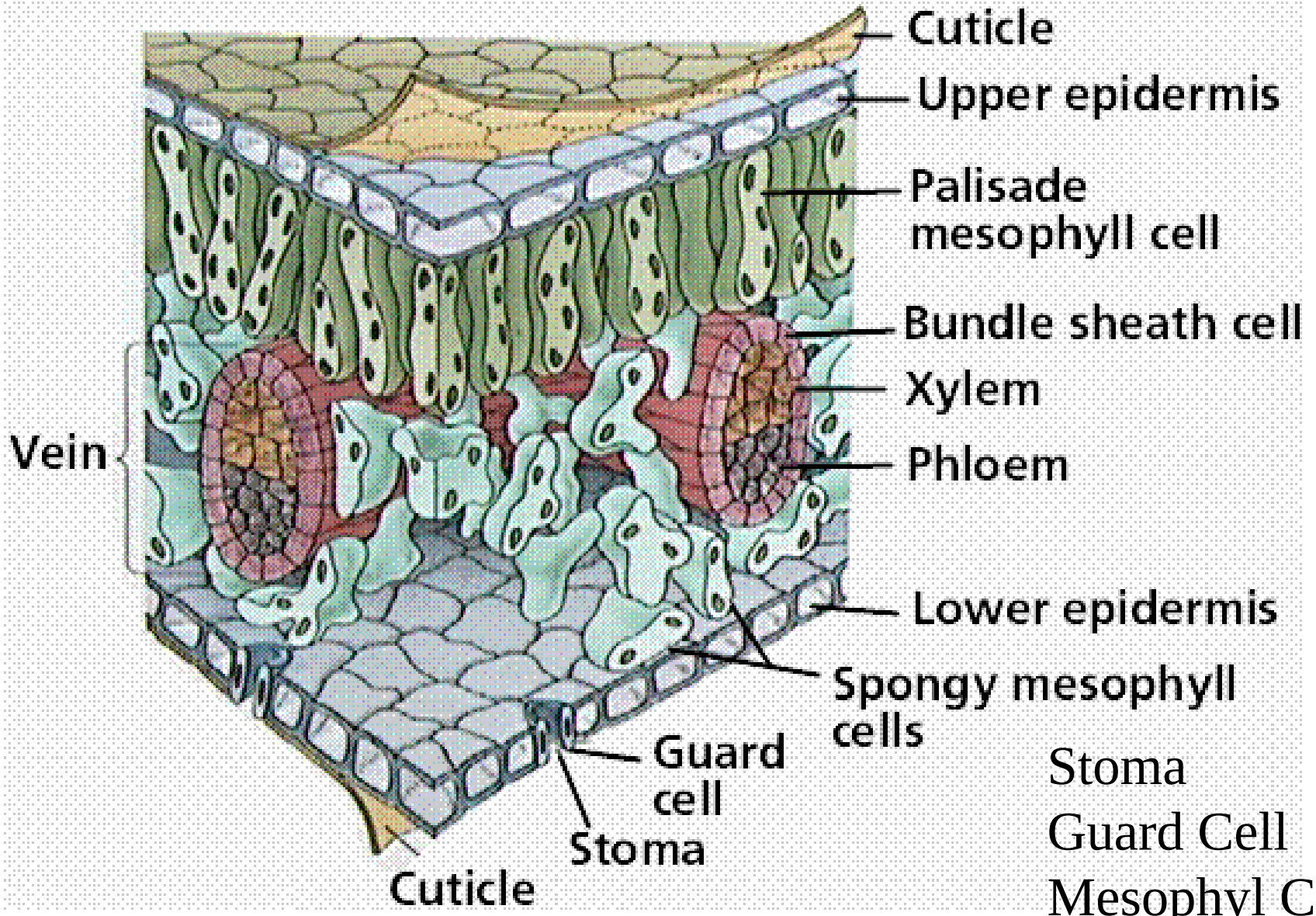
C6H12 ⟶ ATP


H
He + Light
sunlight
O_2
glucose
heat
Photosynthesis
in green plants
CO_2
H_2O
ATP
heat
Respiration in
most living things
heat
Cellular processes
(work)






sunlight
Photosynthesis
the main energy-acquiring pathway
CO_2 & H_2O required
O_2 released
Aerobic Respiration
CO_2 & H_2O released
O_2 required
the main energy-releasing pathway
ATP energy
© 1995 Wadsworth Publishing Company/ITP



Stoma

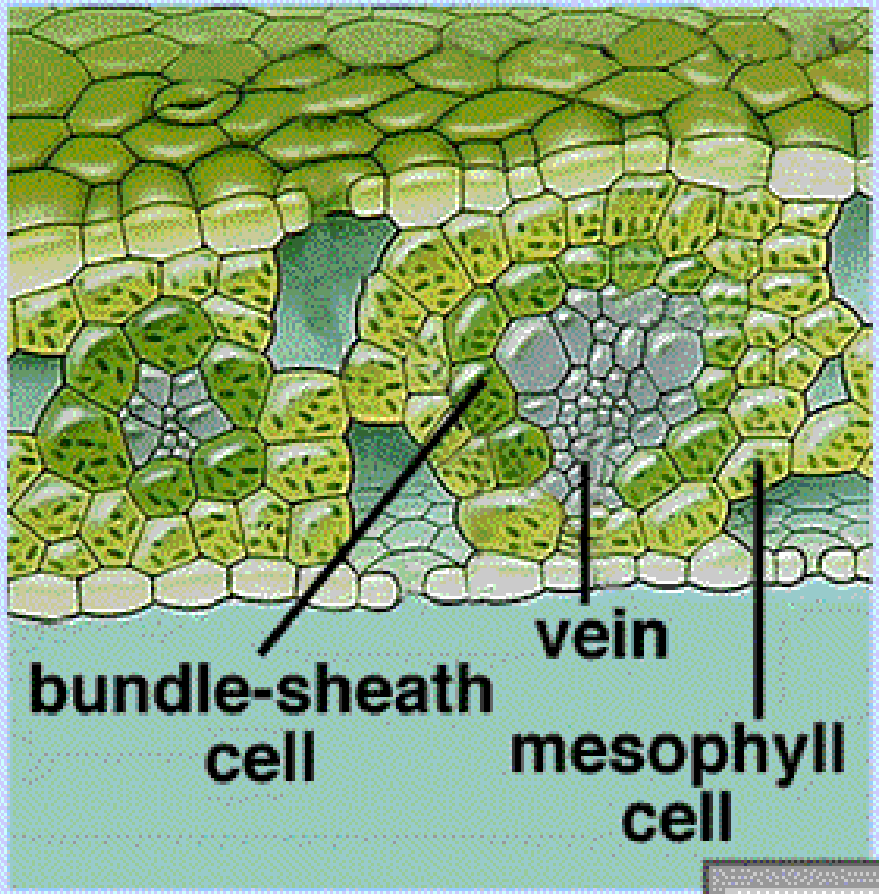
Guard Cell

Mesophyl Cell

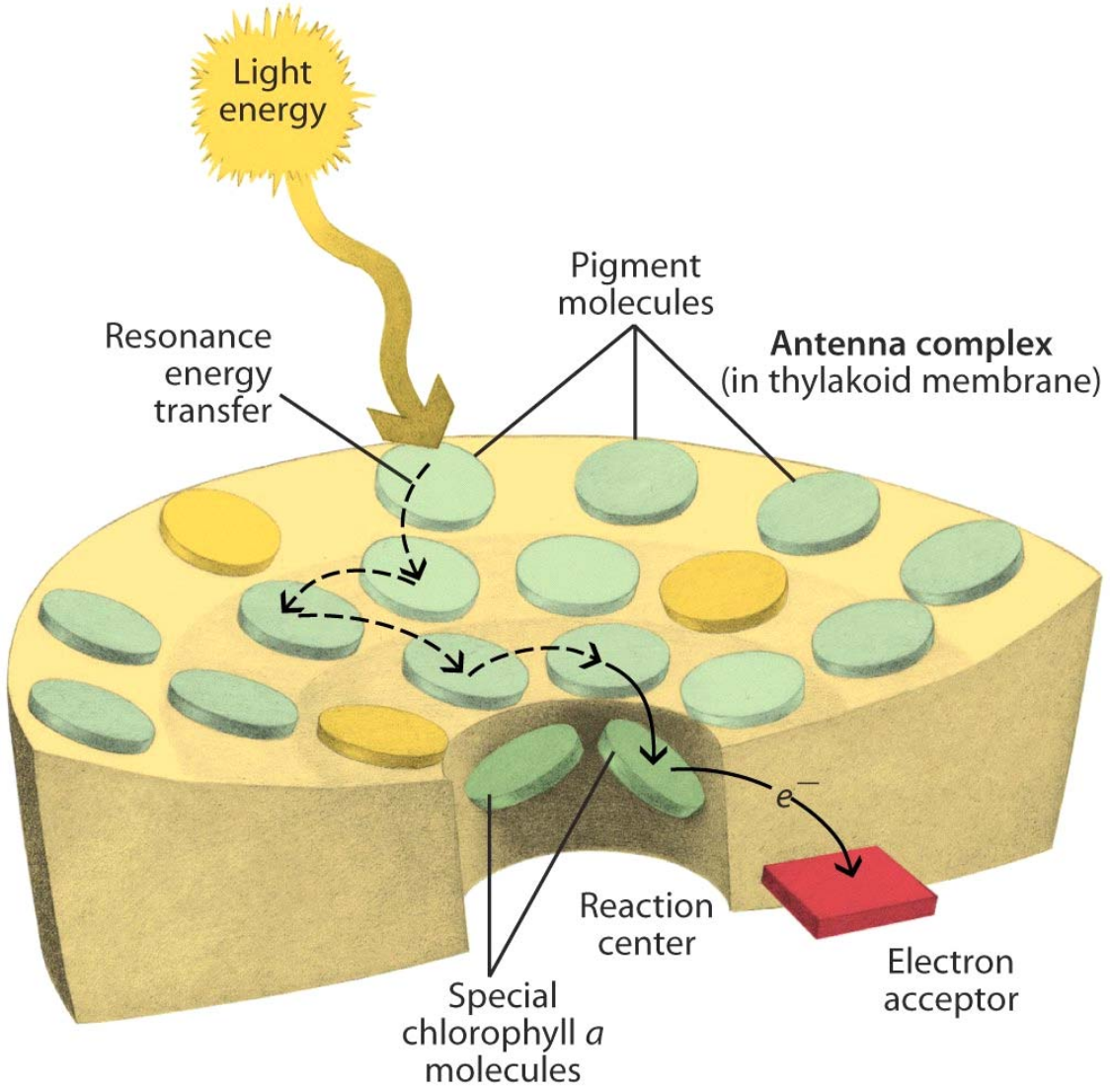
Vein

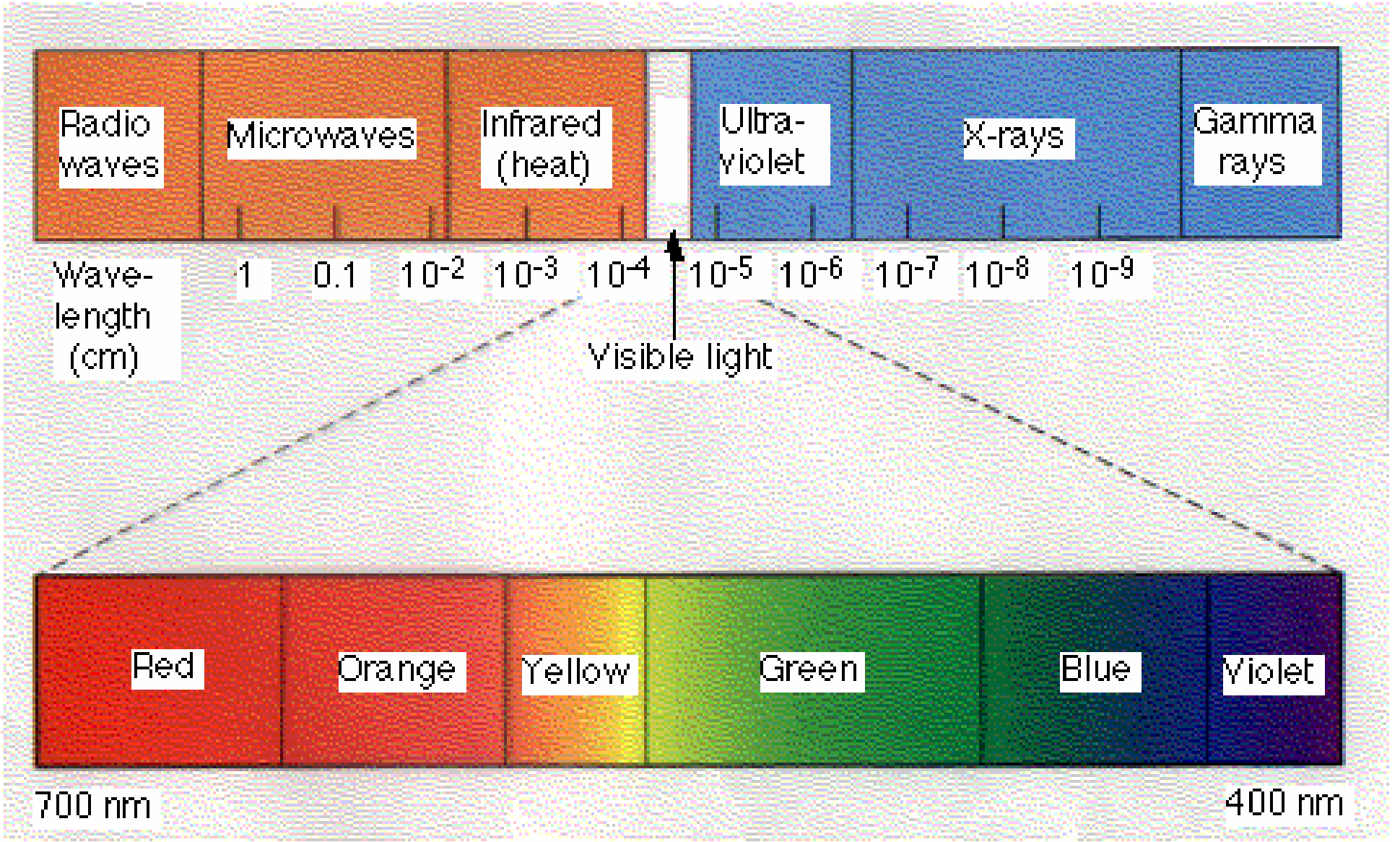
Gas

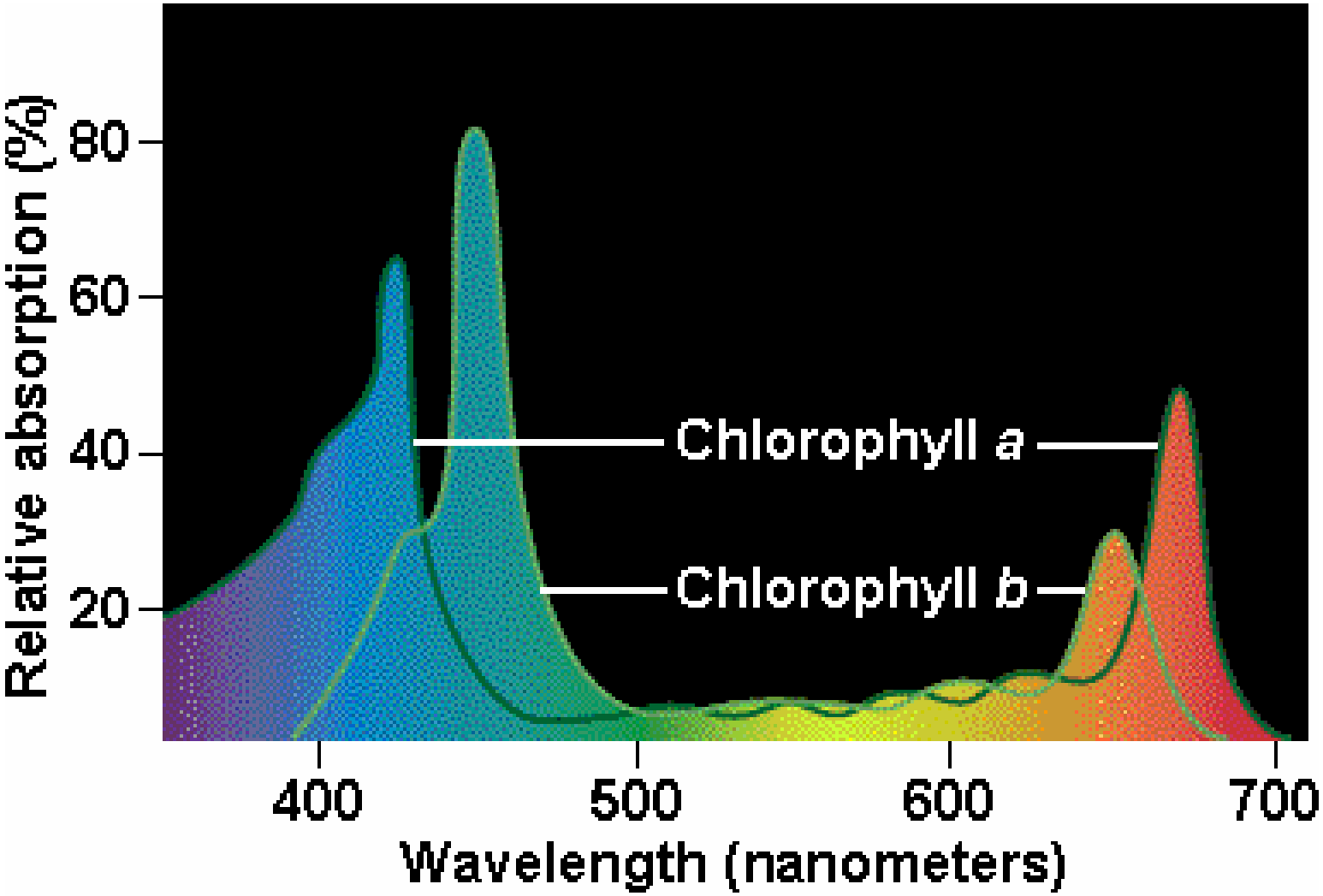
Internal Structure of a Leaf

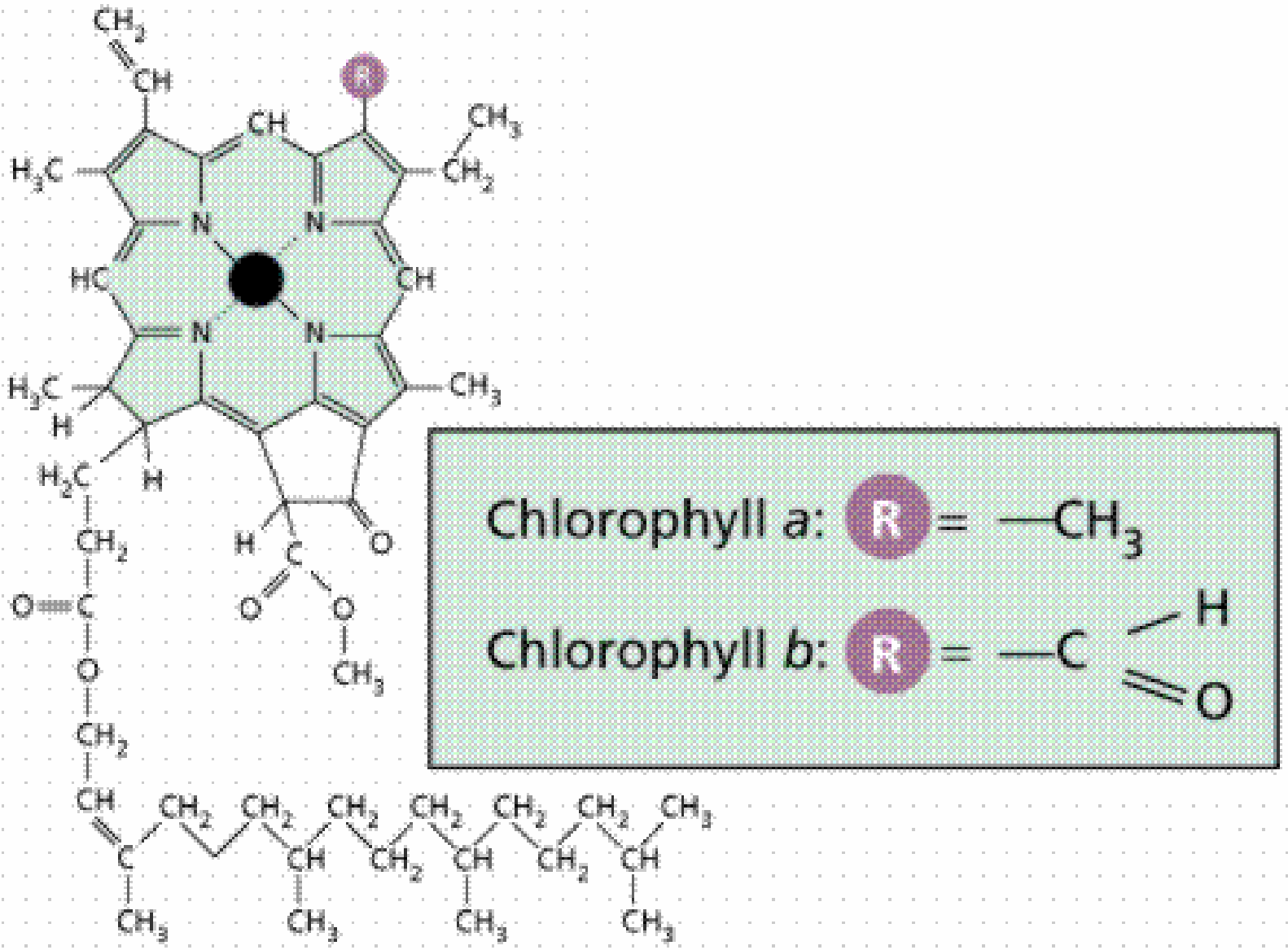


BASIC PRIMARY PHC

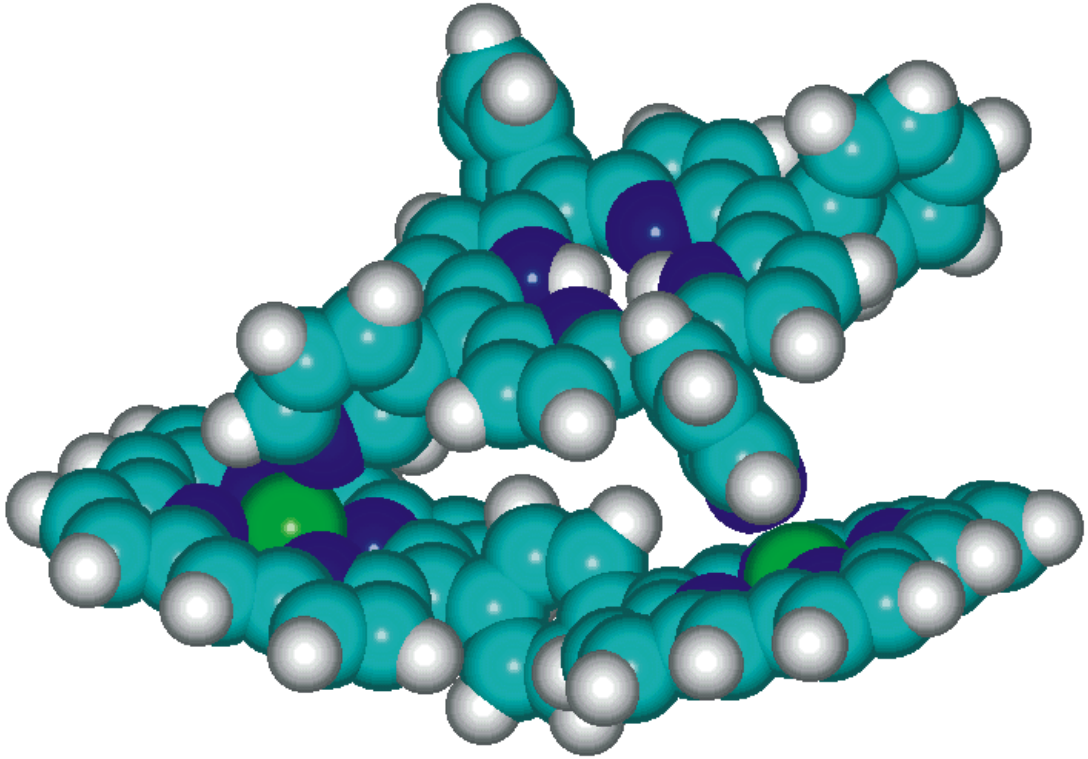


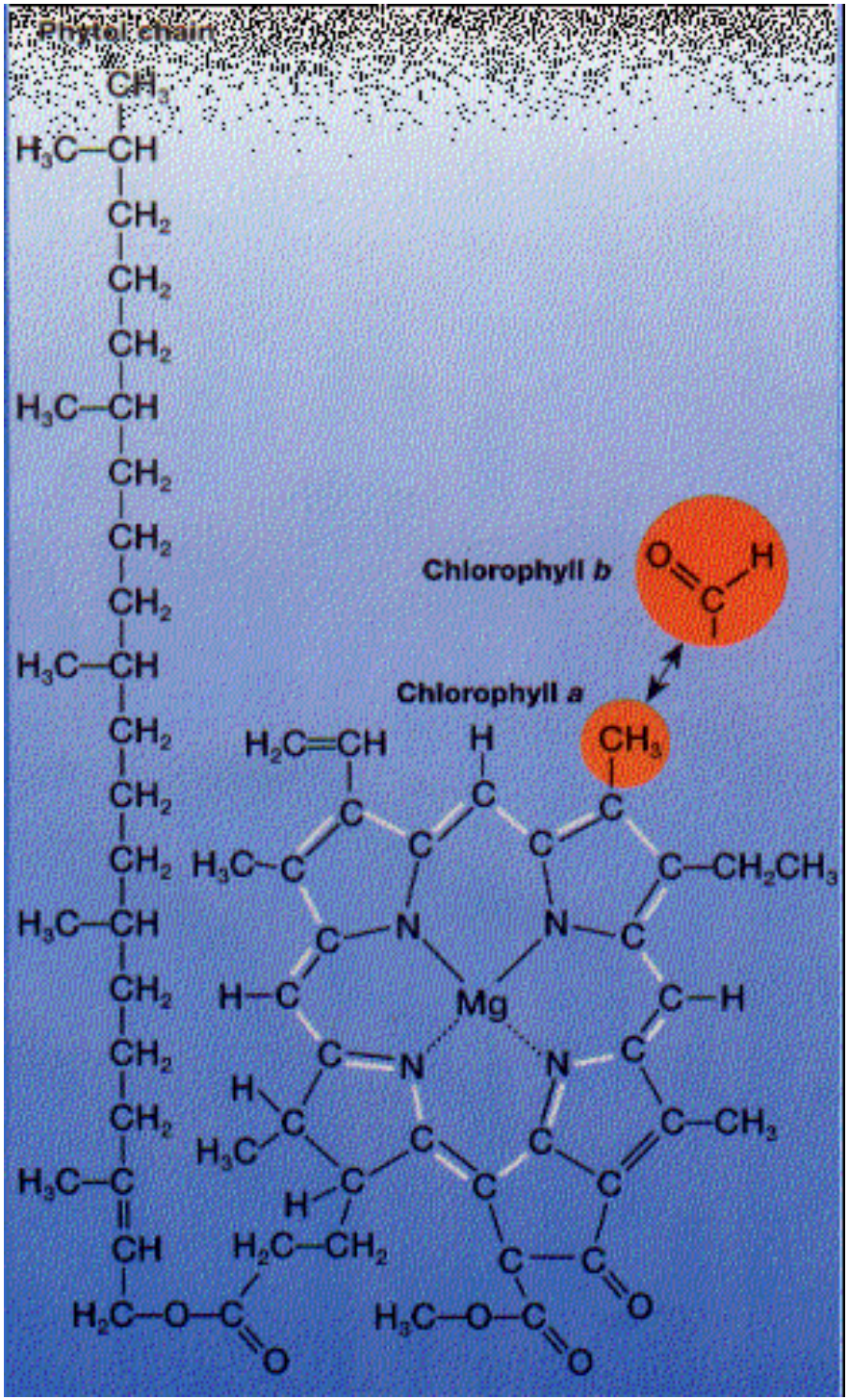

Radio waves
Microwaves
Infrared (heat)
Ultra-violet
X-rays
Gamma rays
Wave-length (cm)
1
0.1
10-2
10-3
10-4
10-5
10-6
10-7
10-8
10-9
Visible light
Red
Orange
Yellow
Green
Blue
Violet
700 nm
400 nm




Chlorophyll a: R = —CH3
Chlorophyll b: R = —C(H)=O

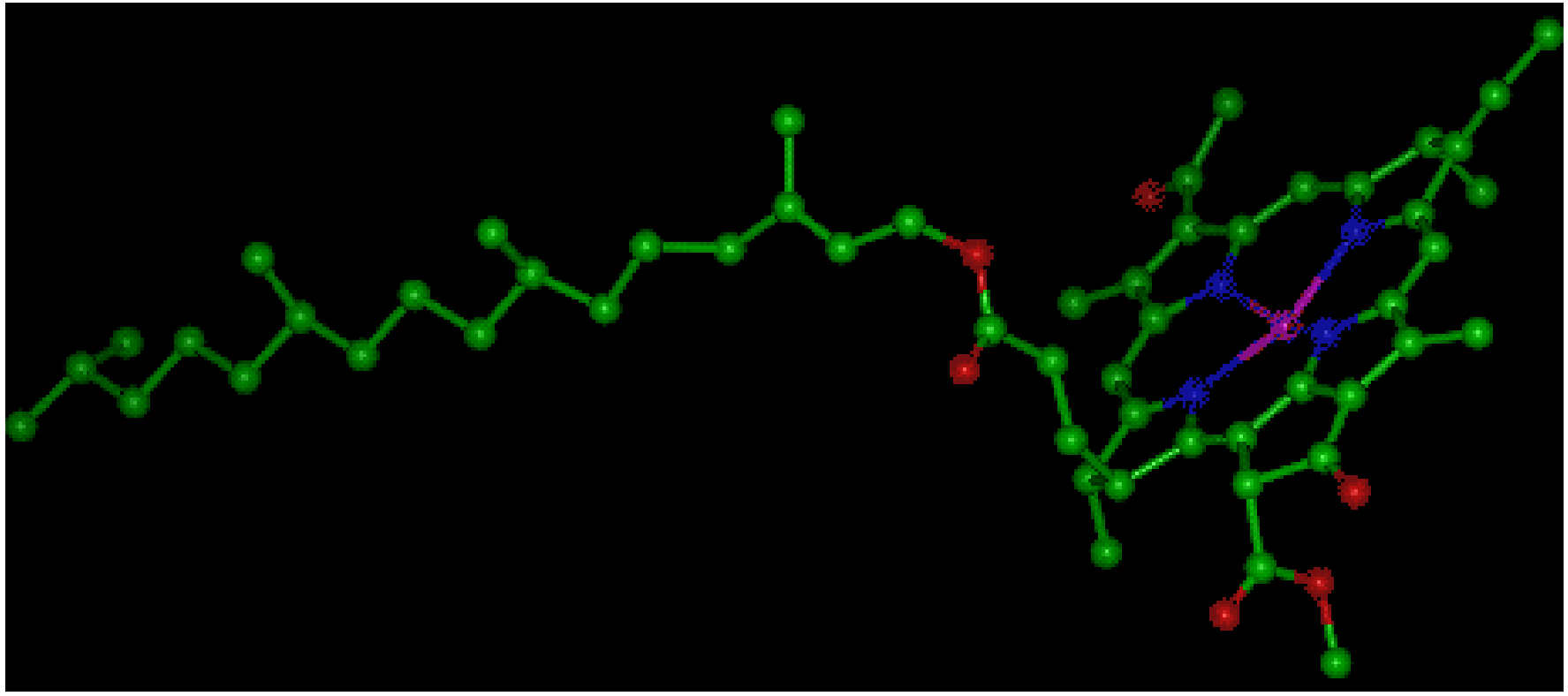
Multiporphyrin Arrays



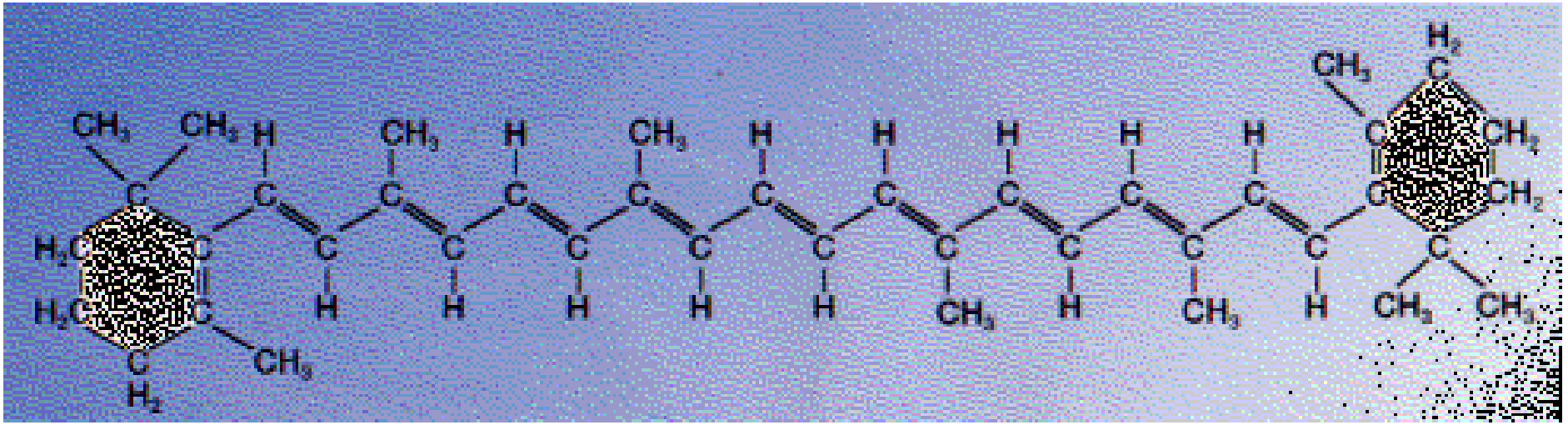


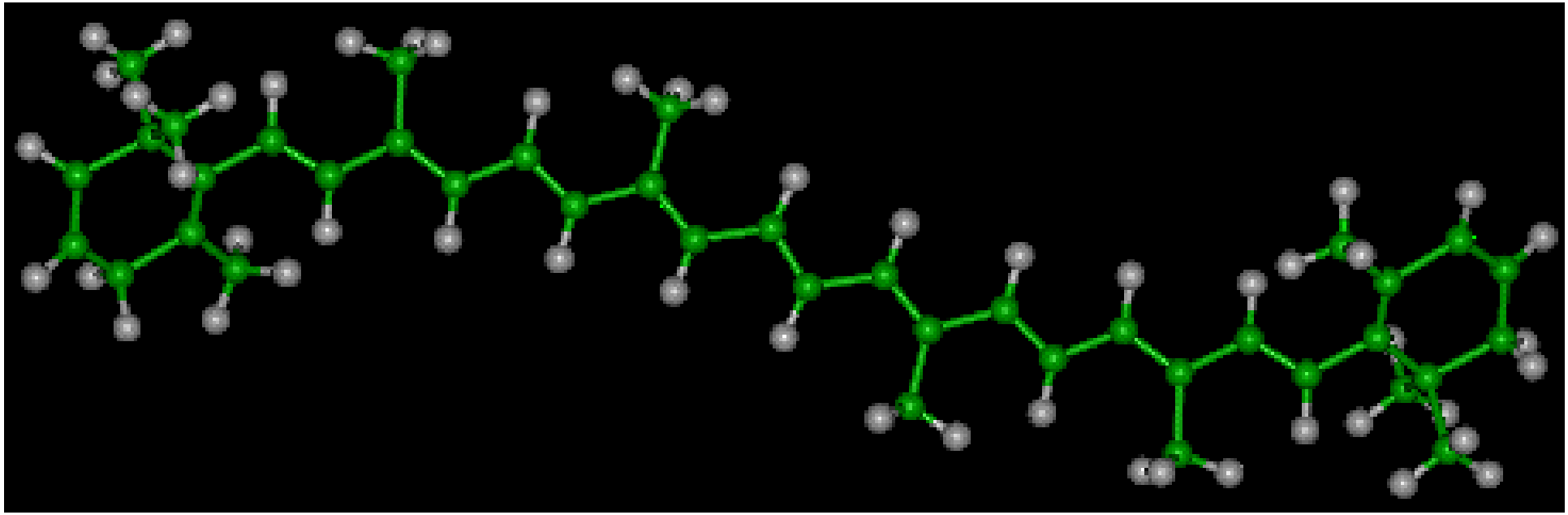
Chlorophyll a
Chlorophyll b

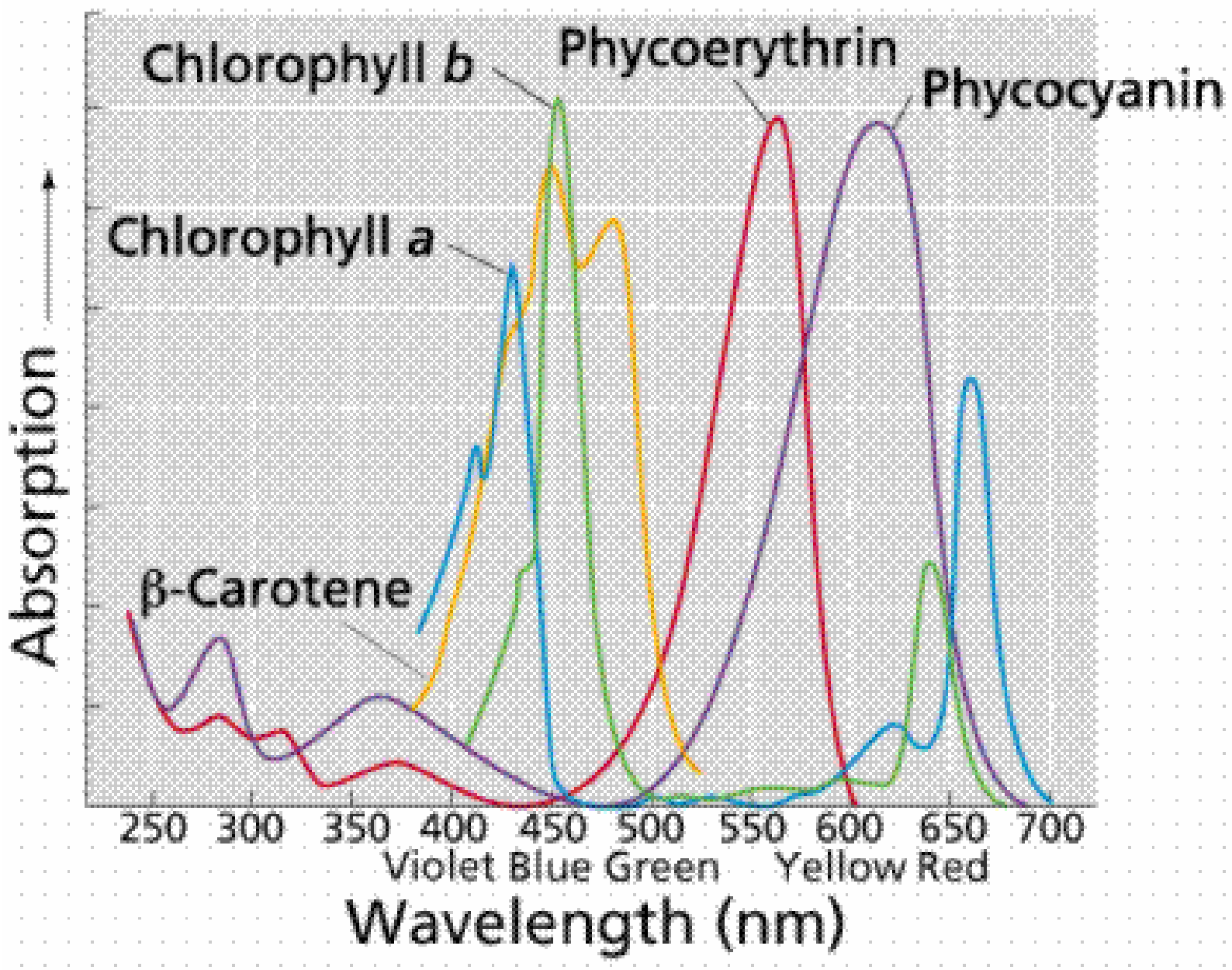
Chlorophyll



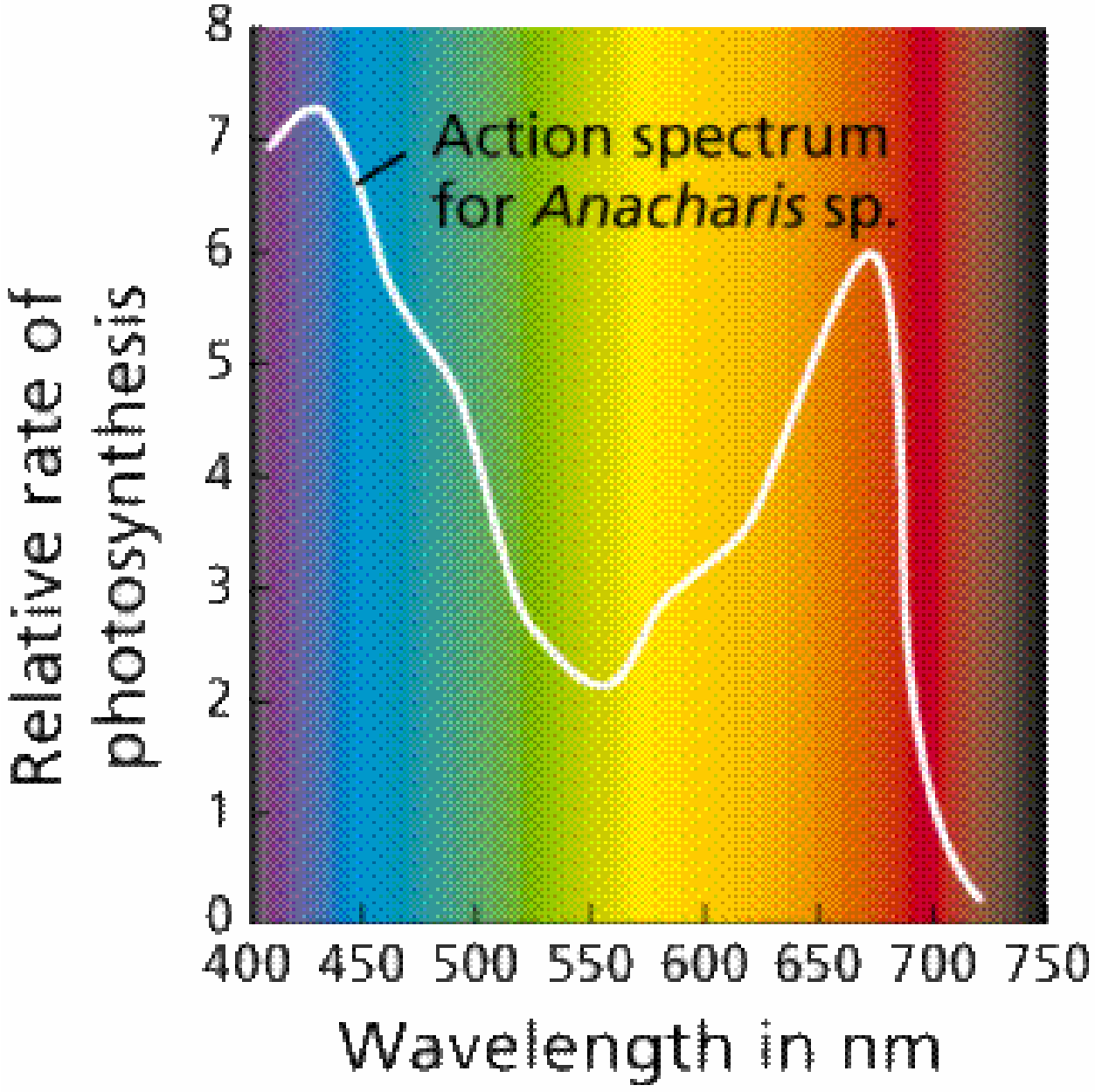
Caratenoid

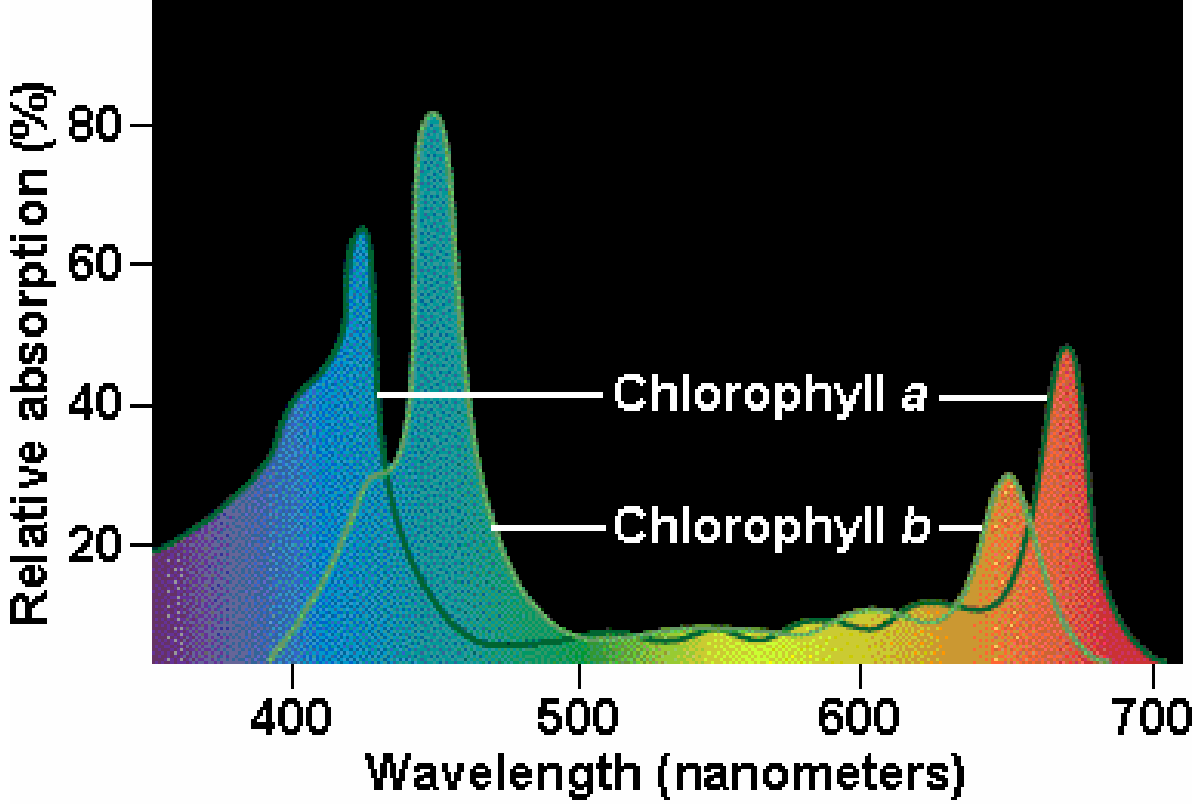


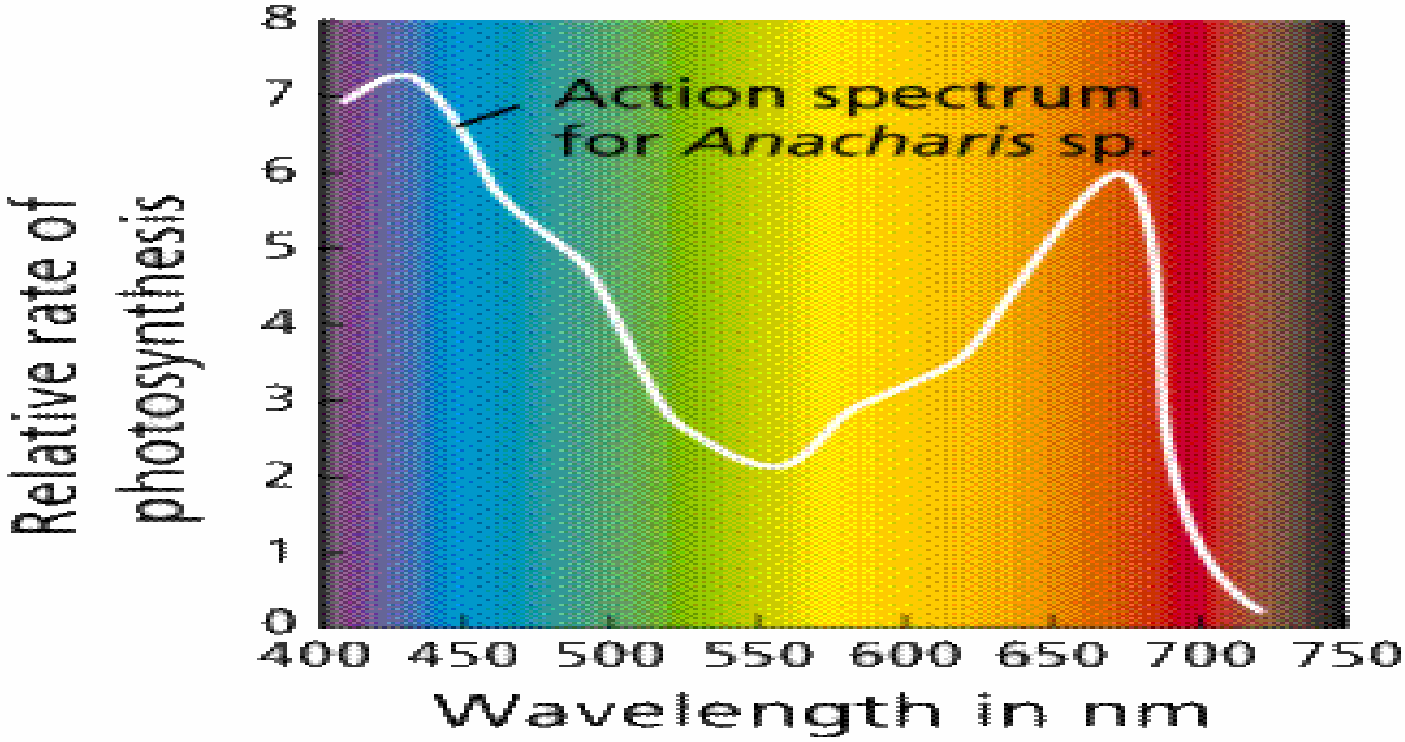



Chlorophyll b
Phycoerythrin
Phycocyanin
Chlorophyll a
β-Carotene
Absorption
250 300 350 400 450 500 550 600 650 700
Violet Blue Green Yellow Red
Wavelength (nm)

Aktionsspektrum der Photosynthese

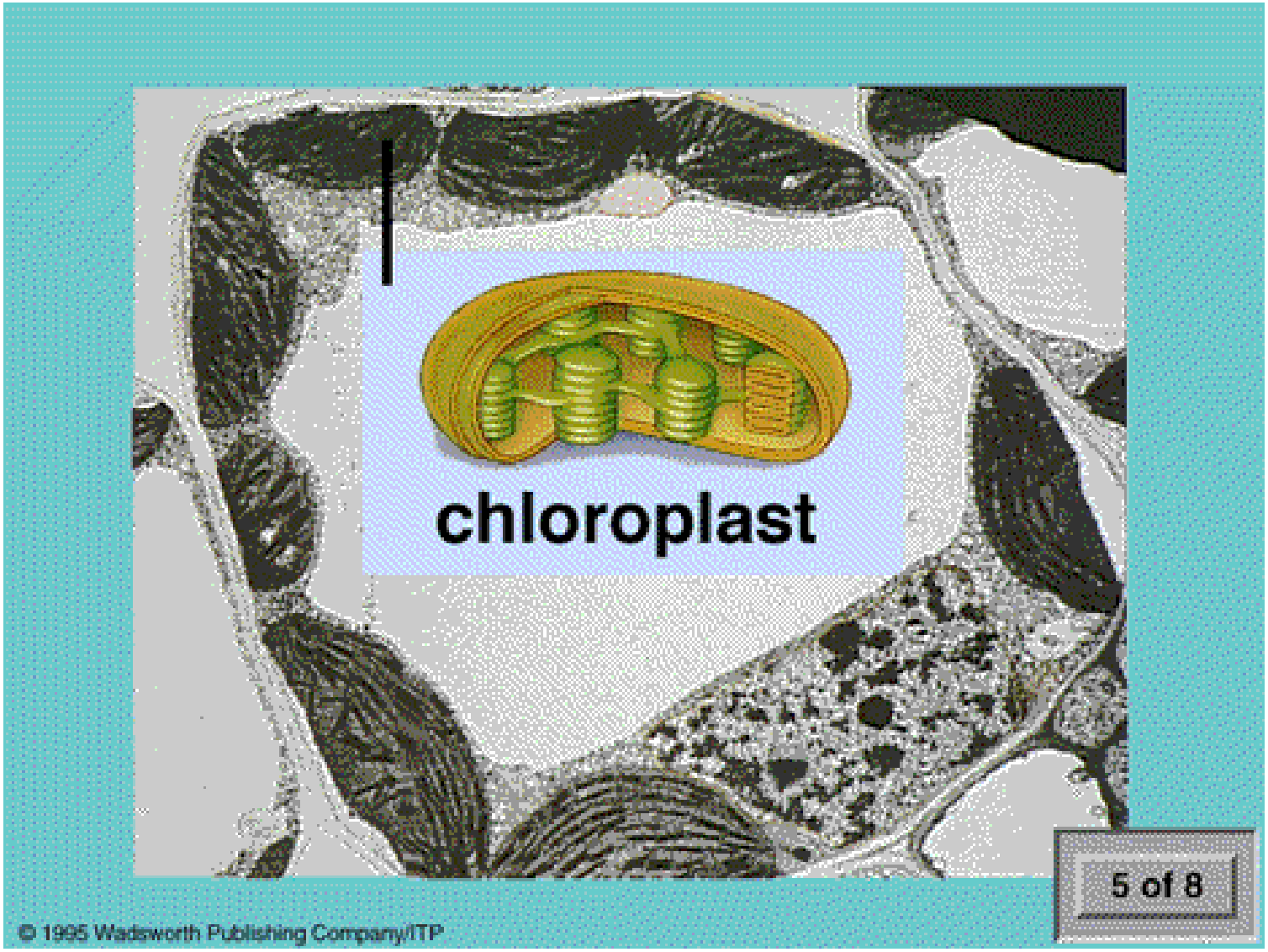




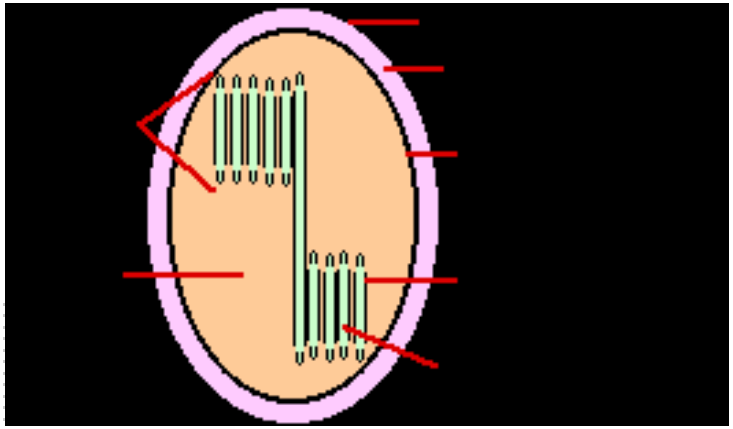


Zelle einer Alge

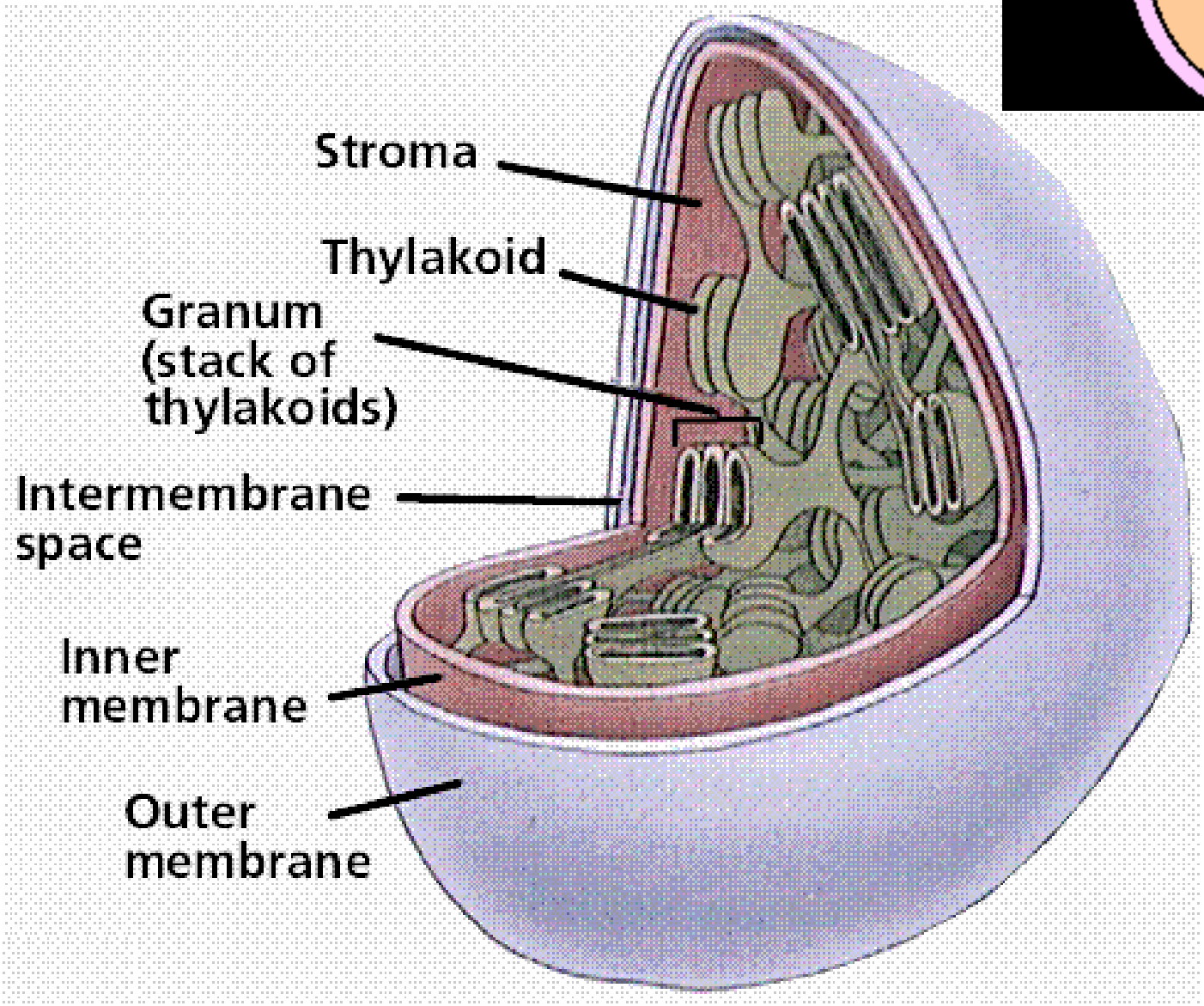
Chloroplast

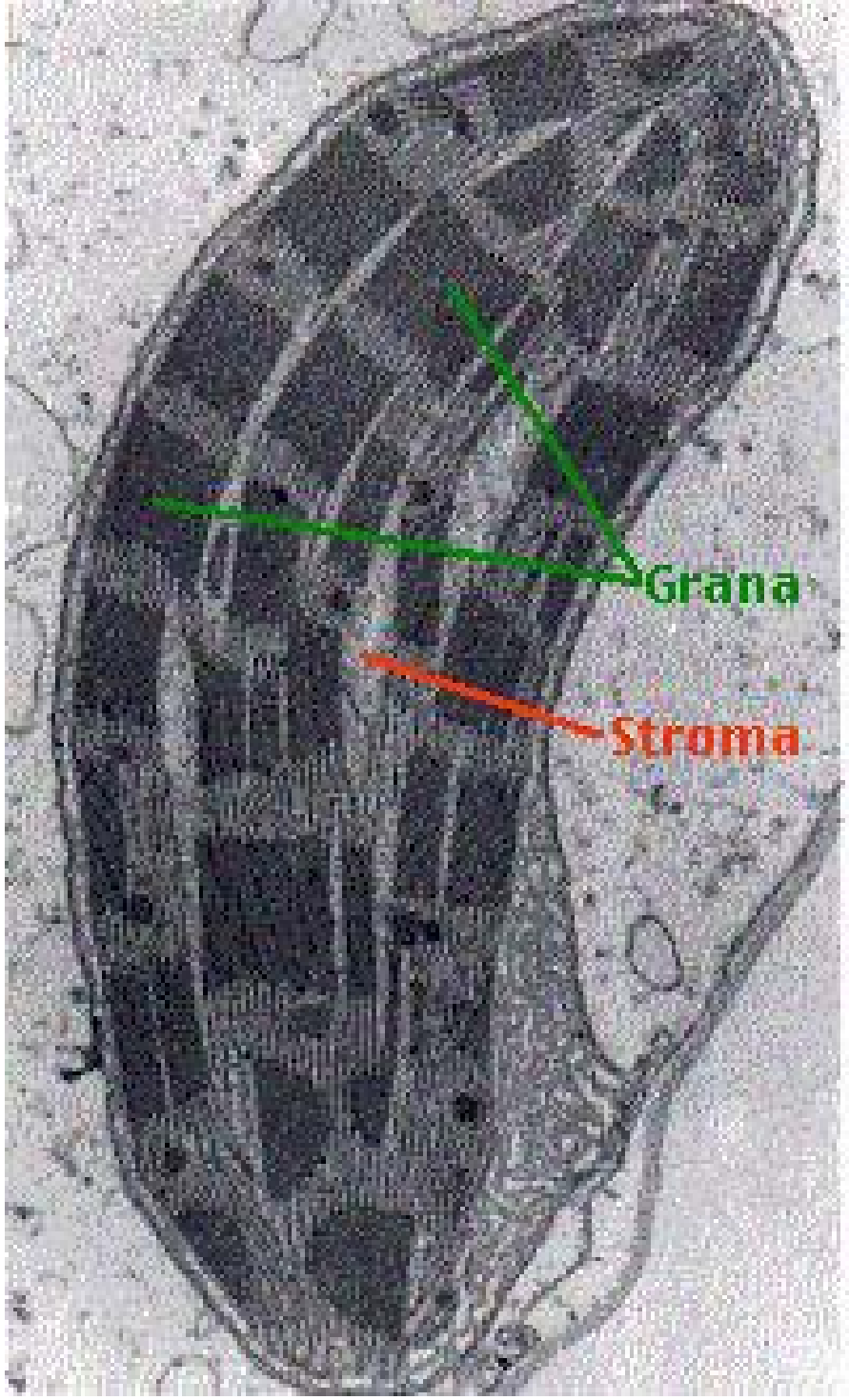


Chloroplast



Thalakoid = Funktionseinheit der Photosynthese



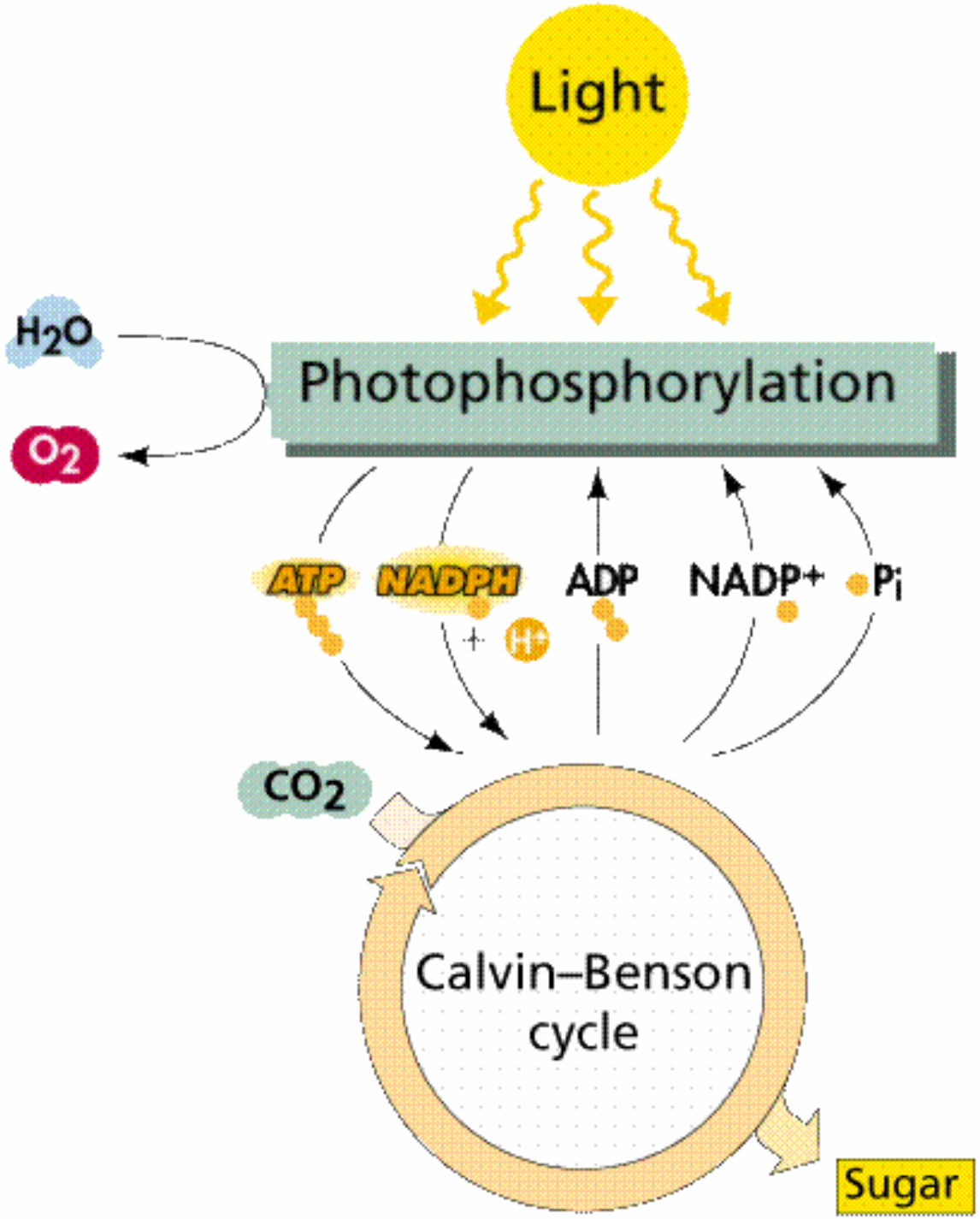


Chloroplast

Gestapelte Thylakoids = Grana

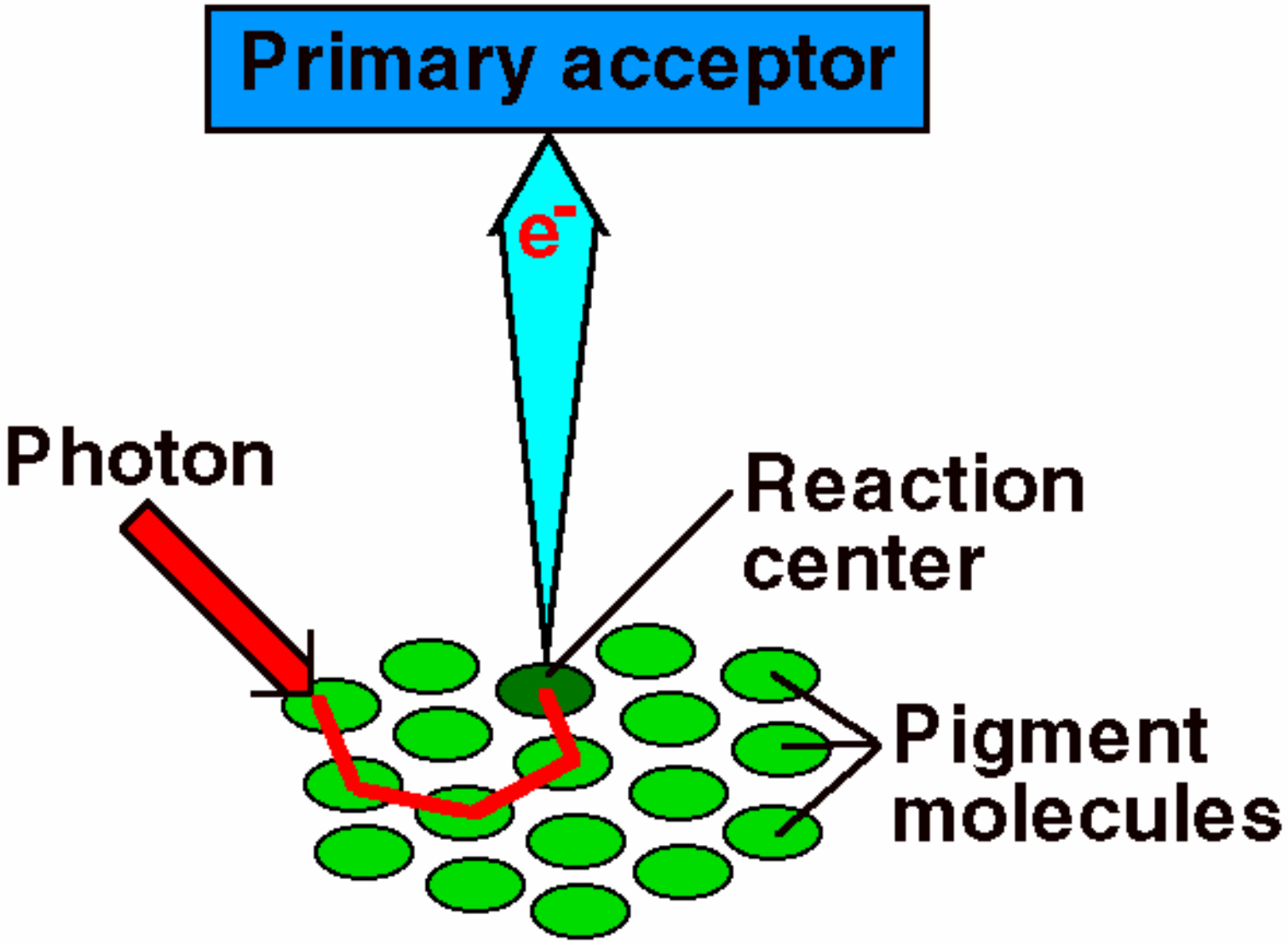
Zelle einer Cyanobakterie

Thylakoide

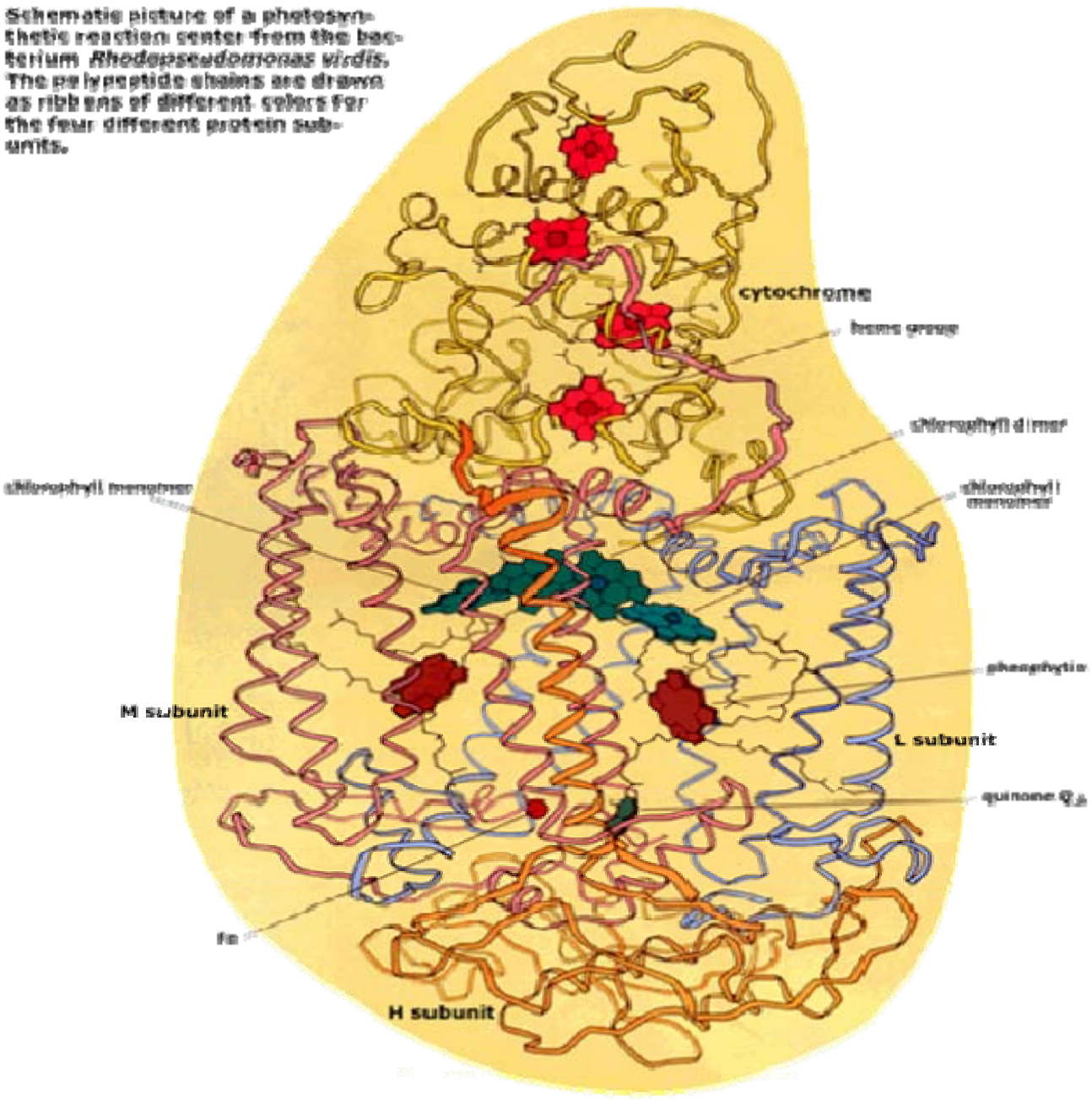


Grana

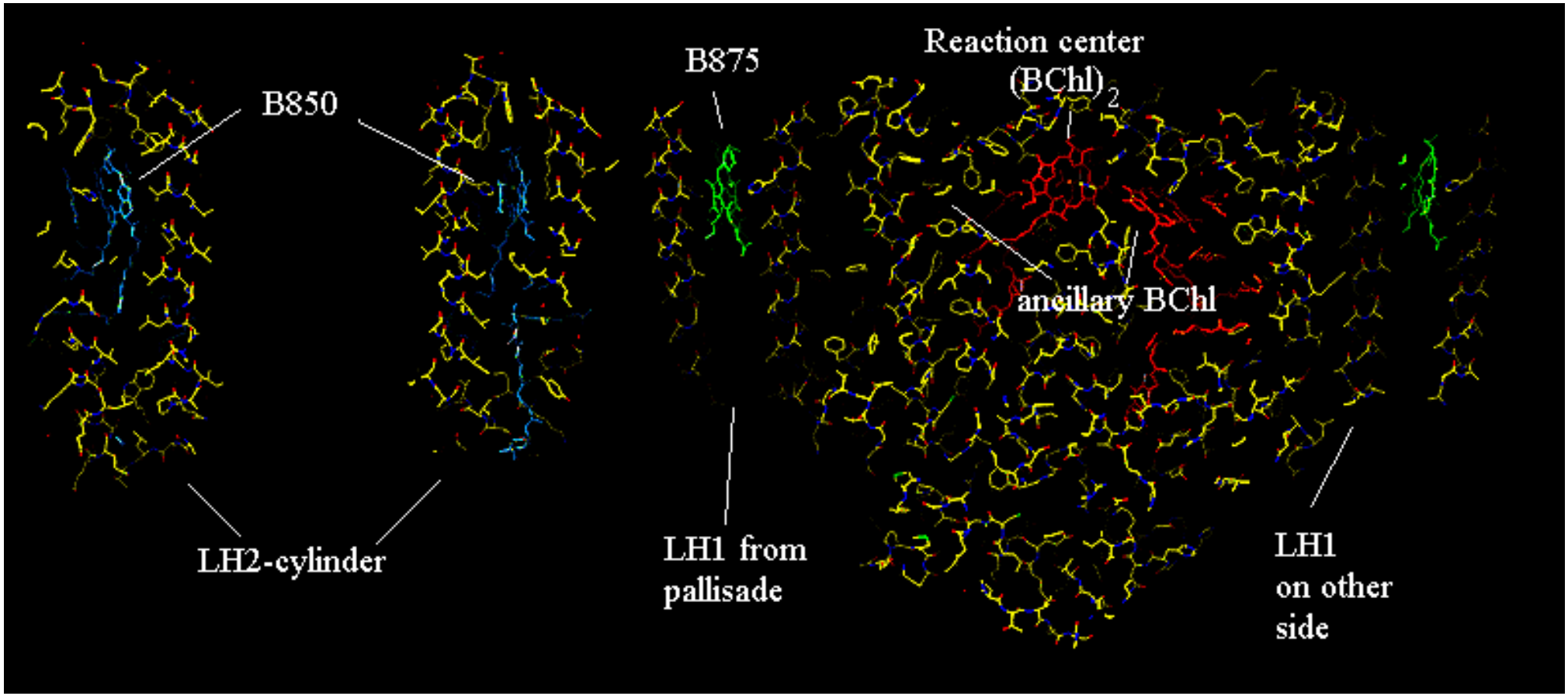
Stroma

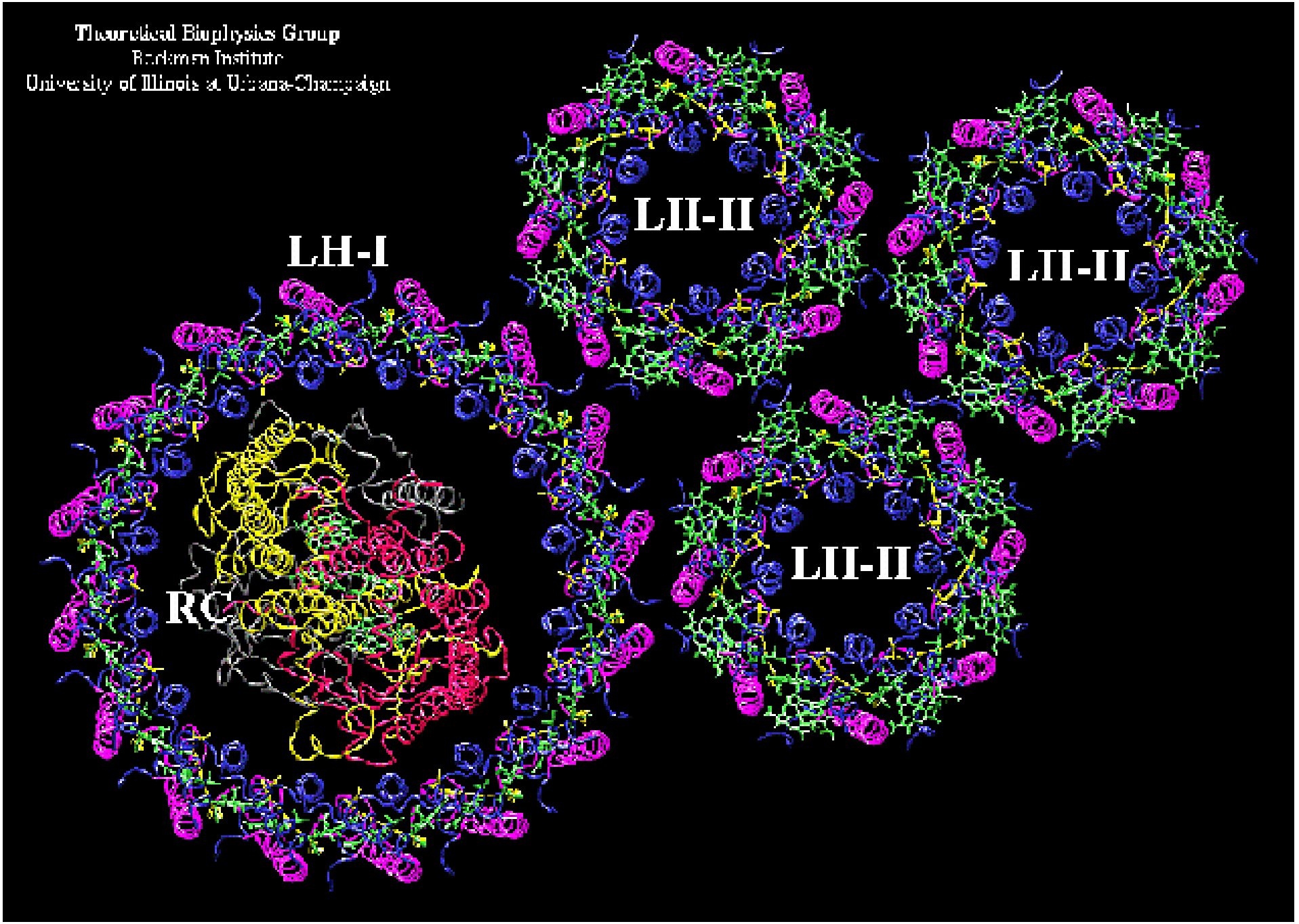

Primary acceptor
e-
Photon
Reaction center
Pigment molecules

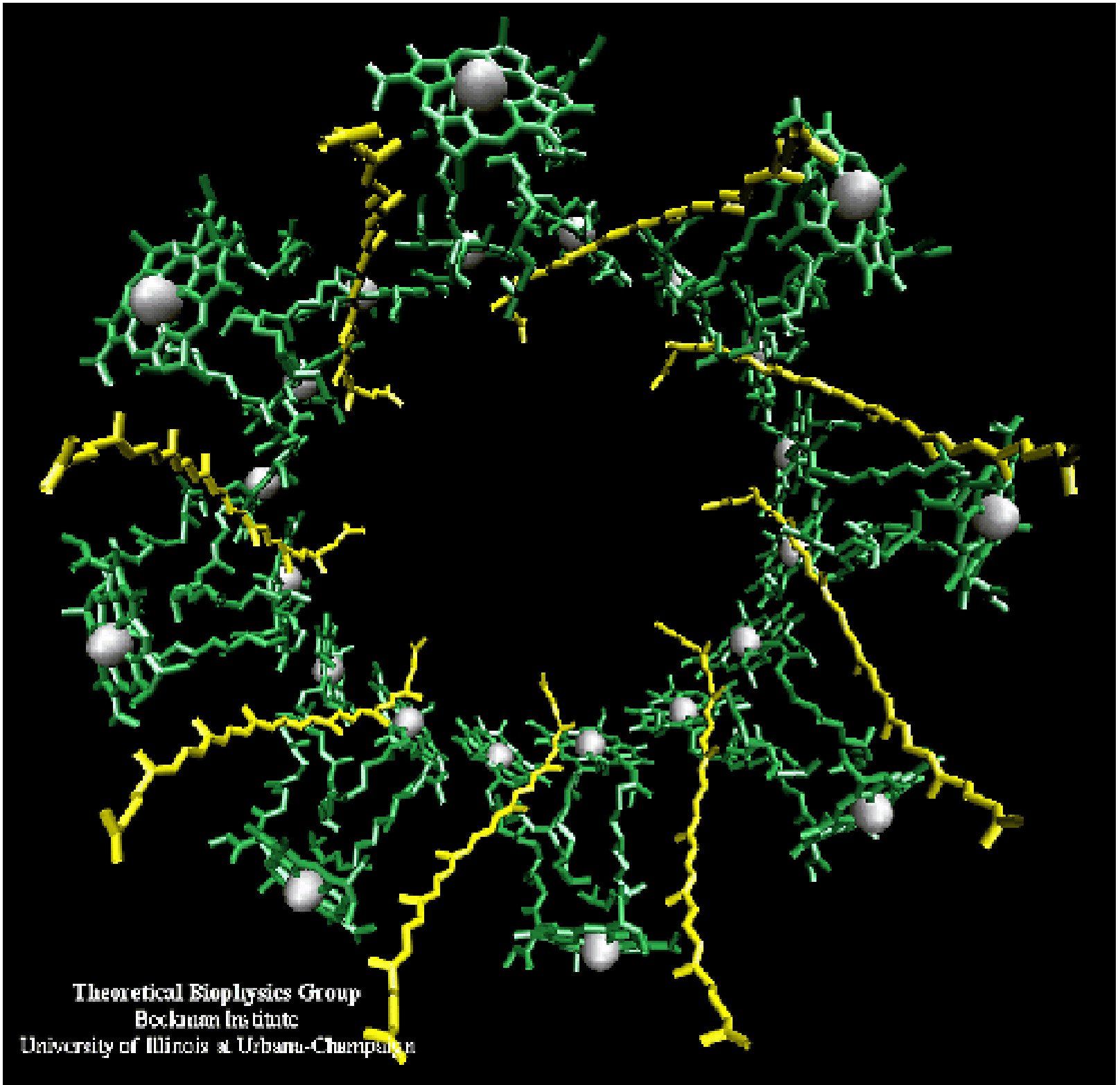
BACTERIAL REACTION CENTER

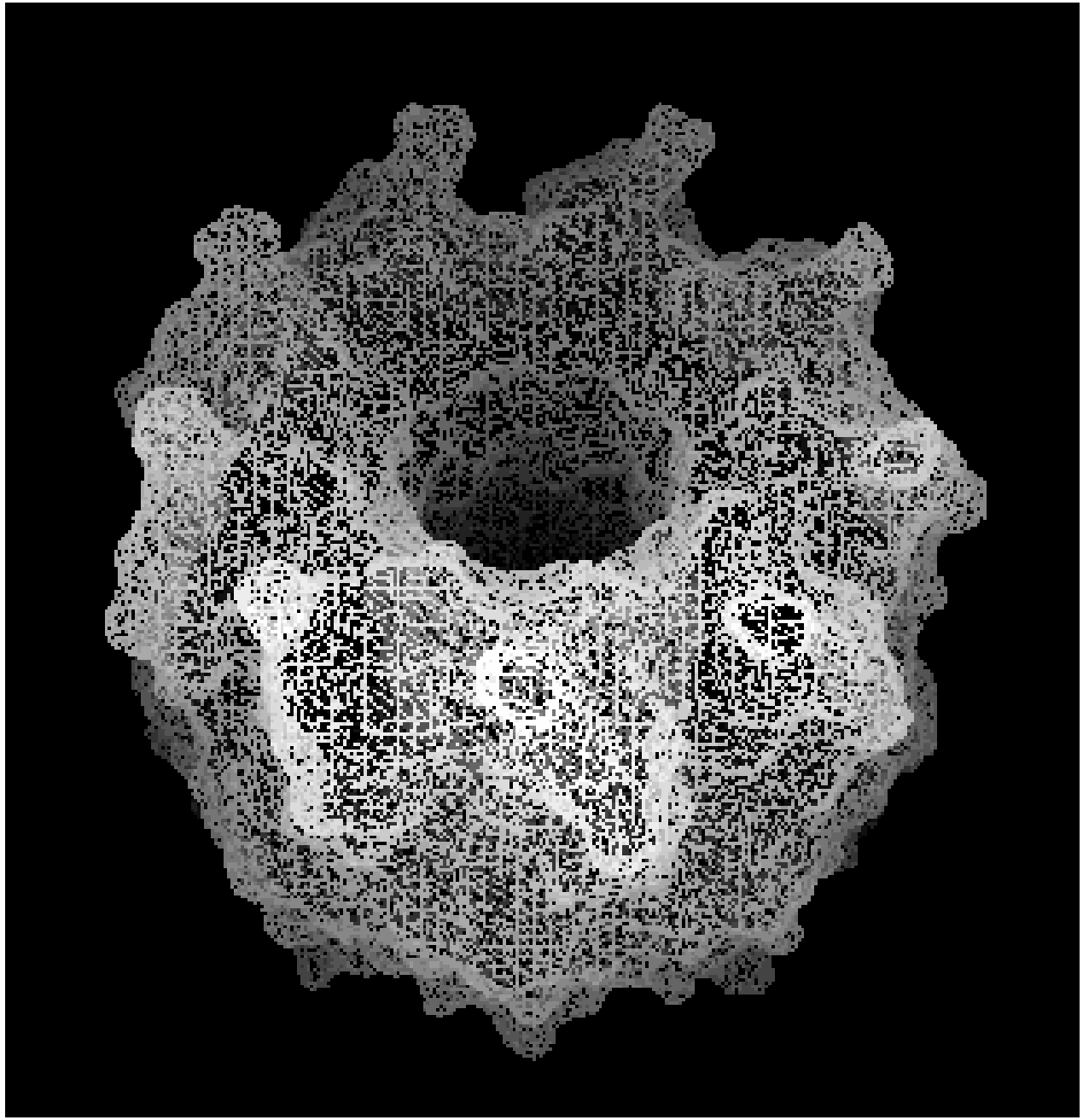


Struktur der Light-Harvestingkomplexe und des Primären Reaktionszentrums



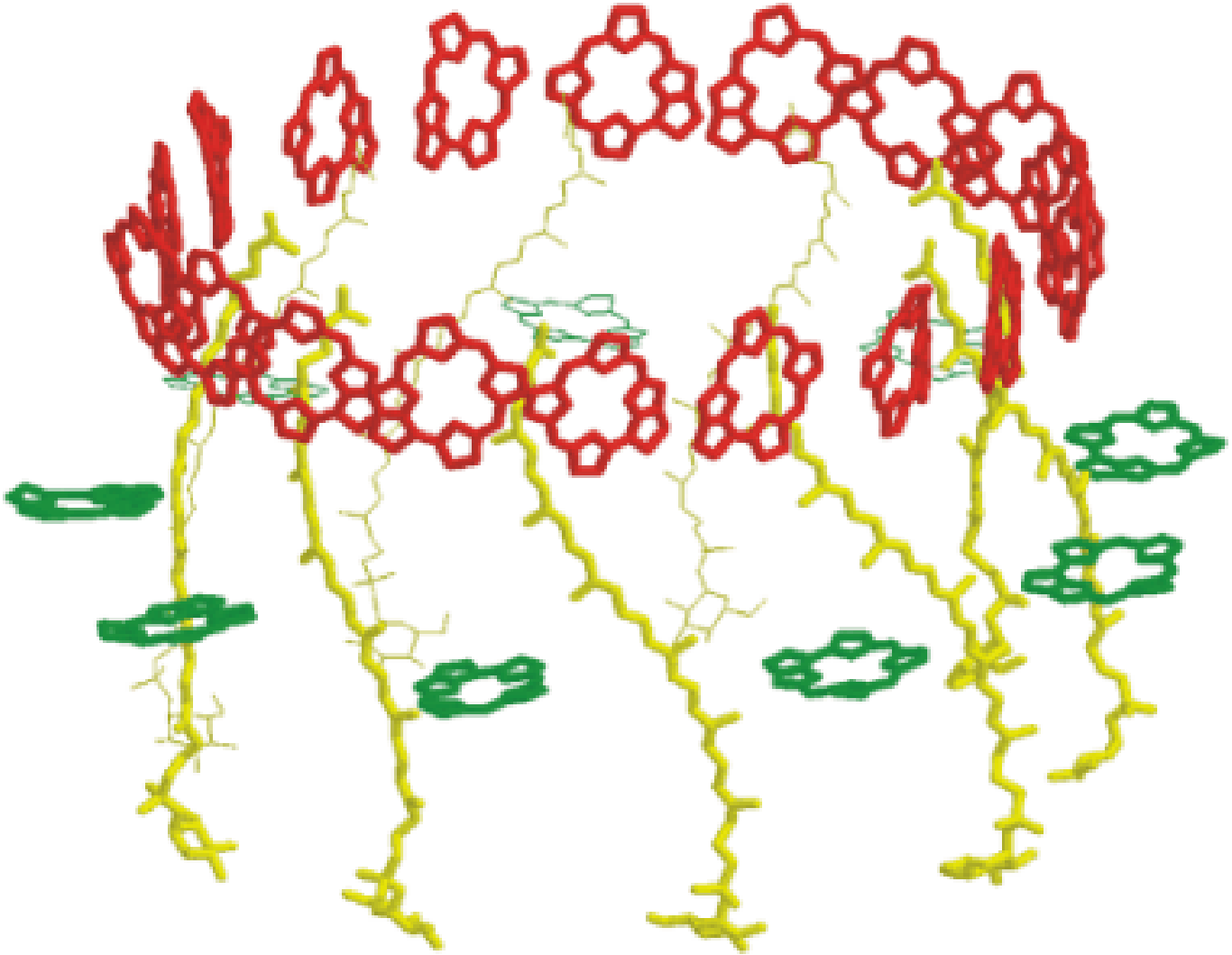

Theoretical Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign
LH-I
LII-II
LII-II
LII-II
RC

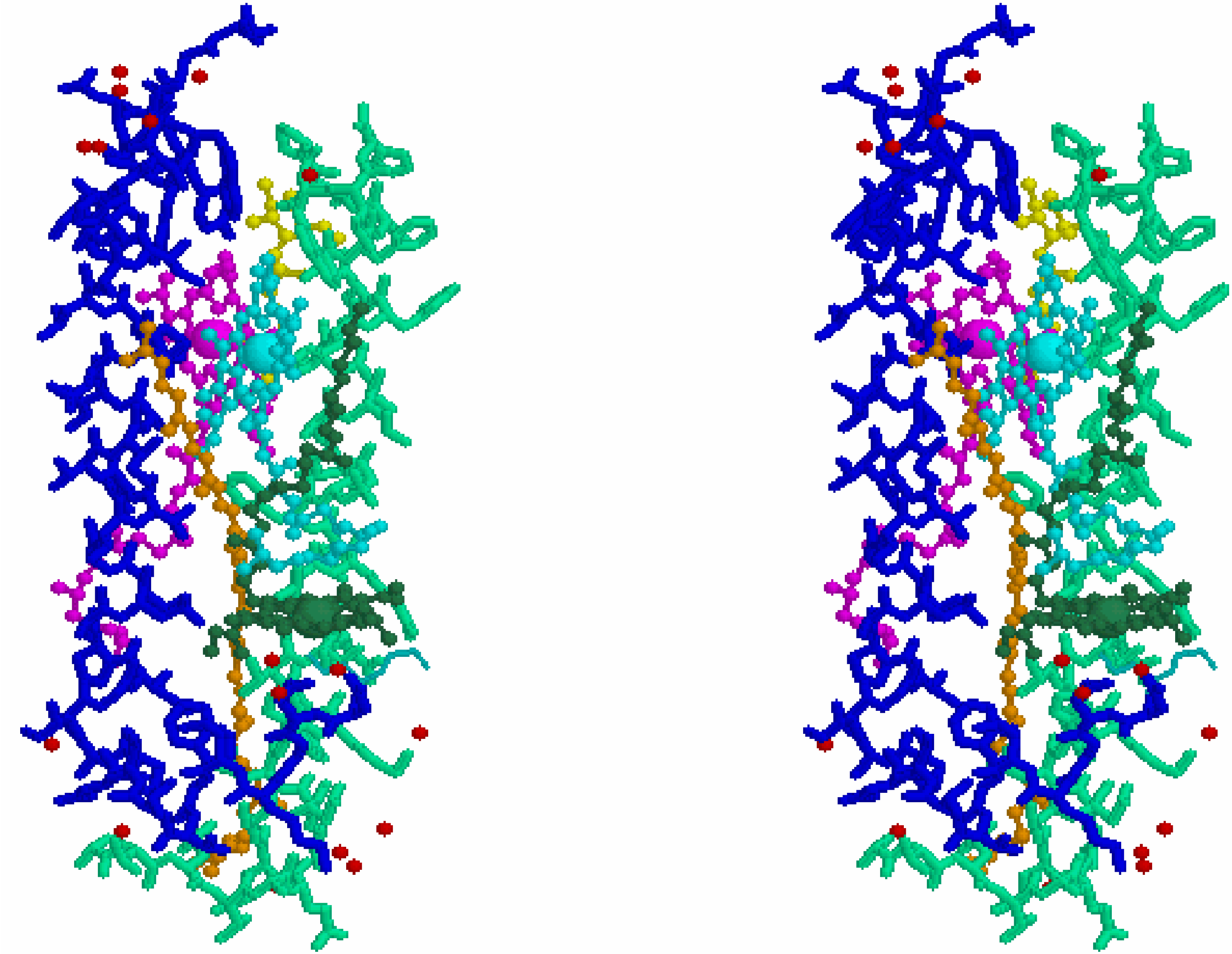

Theoretical Biophysics Group
Beckman Institute
University of Illinois at Urbana-Champaign



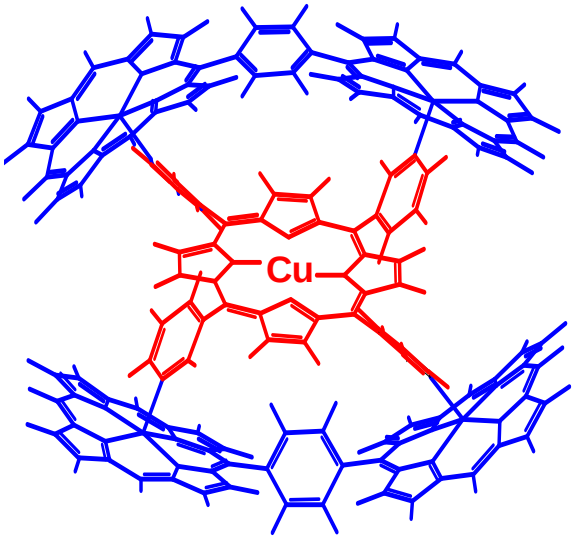
LIGHT-HARVESTING ANTENNA COMPLEX BChl

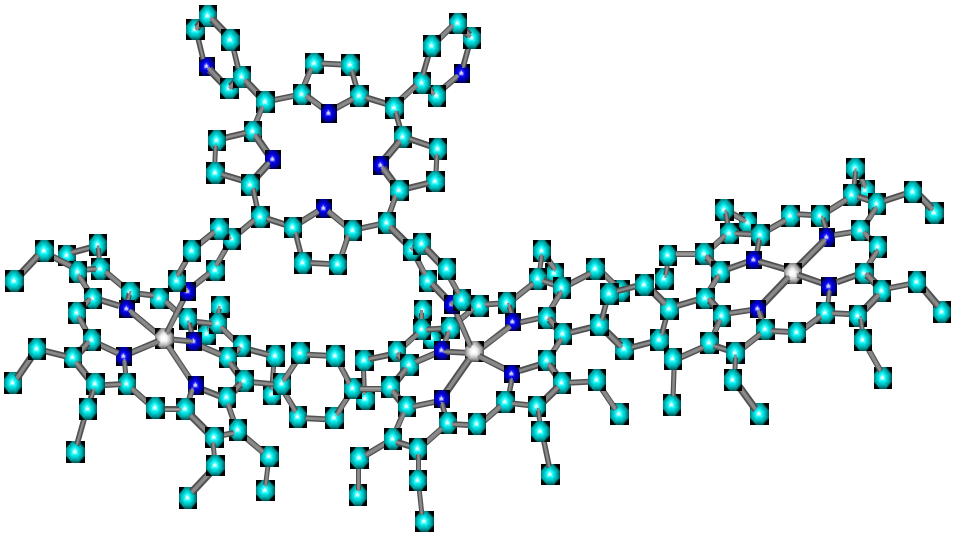
LH2

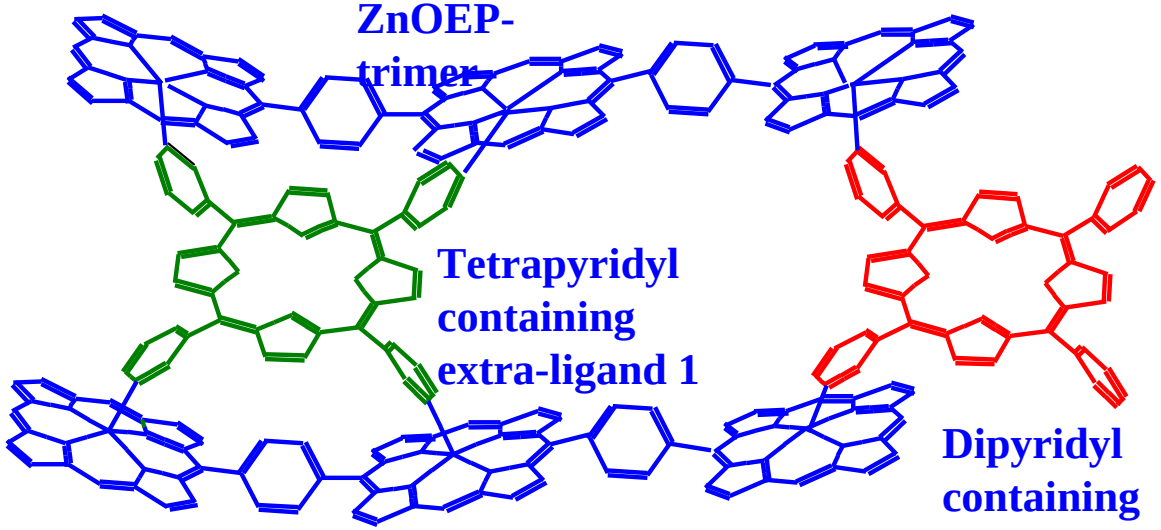


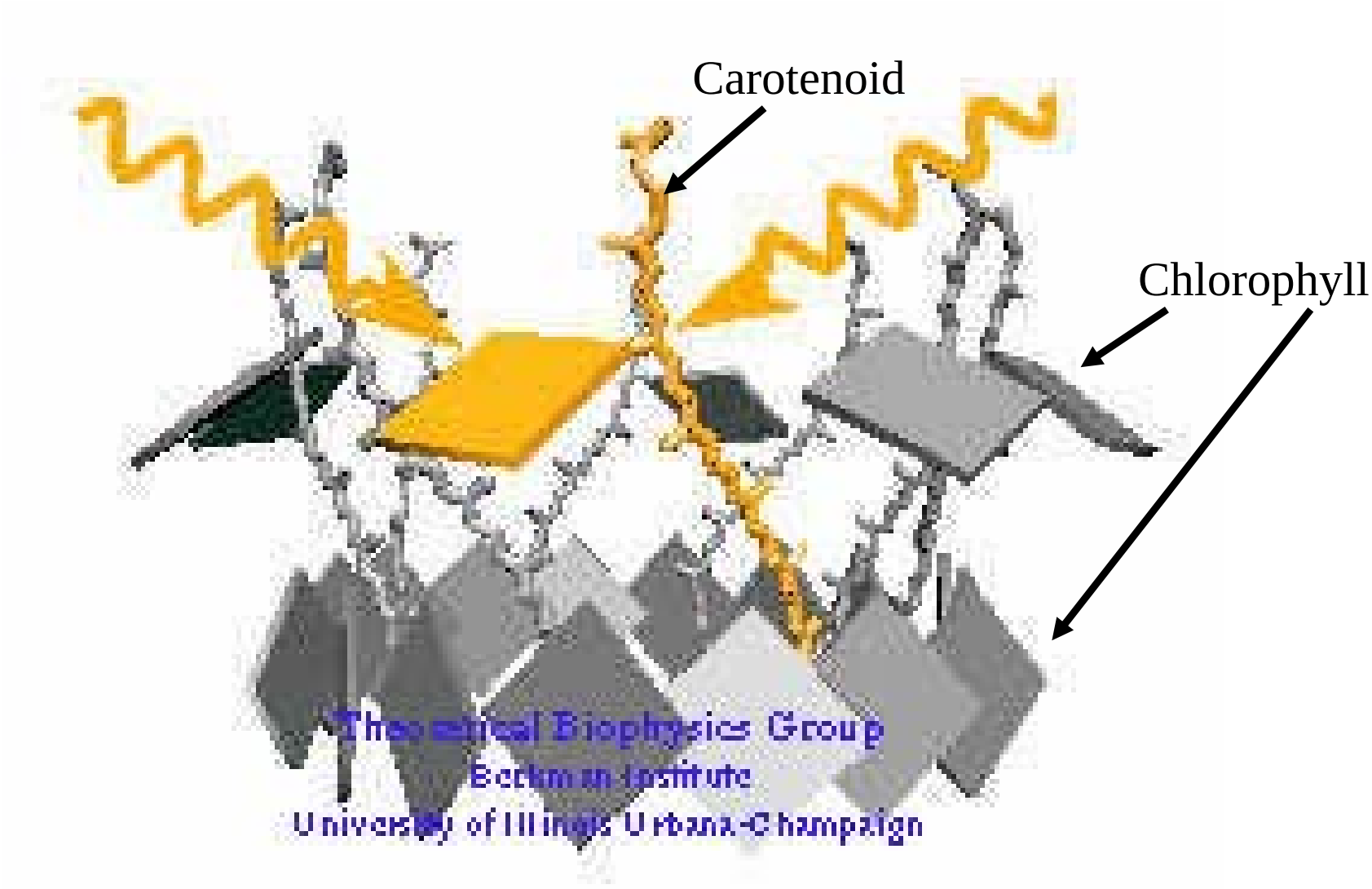


Multiporphyrin Arrays

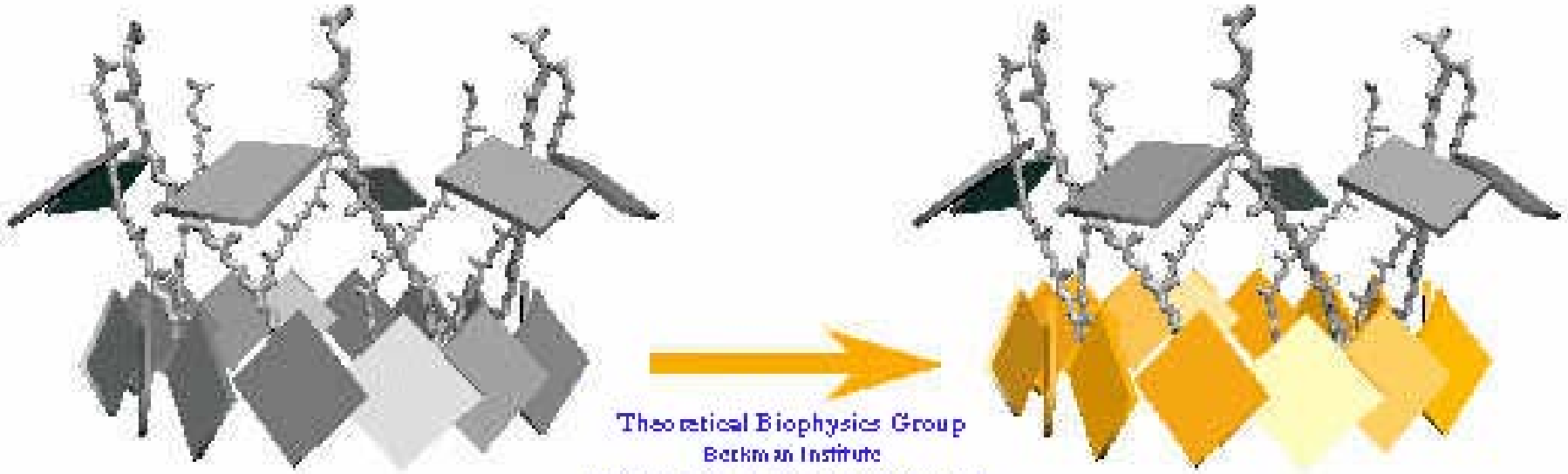







Carotenoid
Chlorophyll
Theoretical Biophysics Group
Beckman Institute
University of Illinois Urbana-Champaign


Theoretical Biophysics Group
Beckman Institute
University of Illinois Urbana-Champaign


Theoretical Biophysics Group
Beckman Institute
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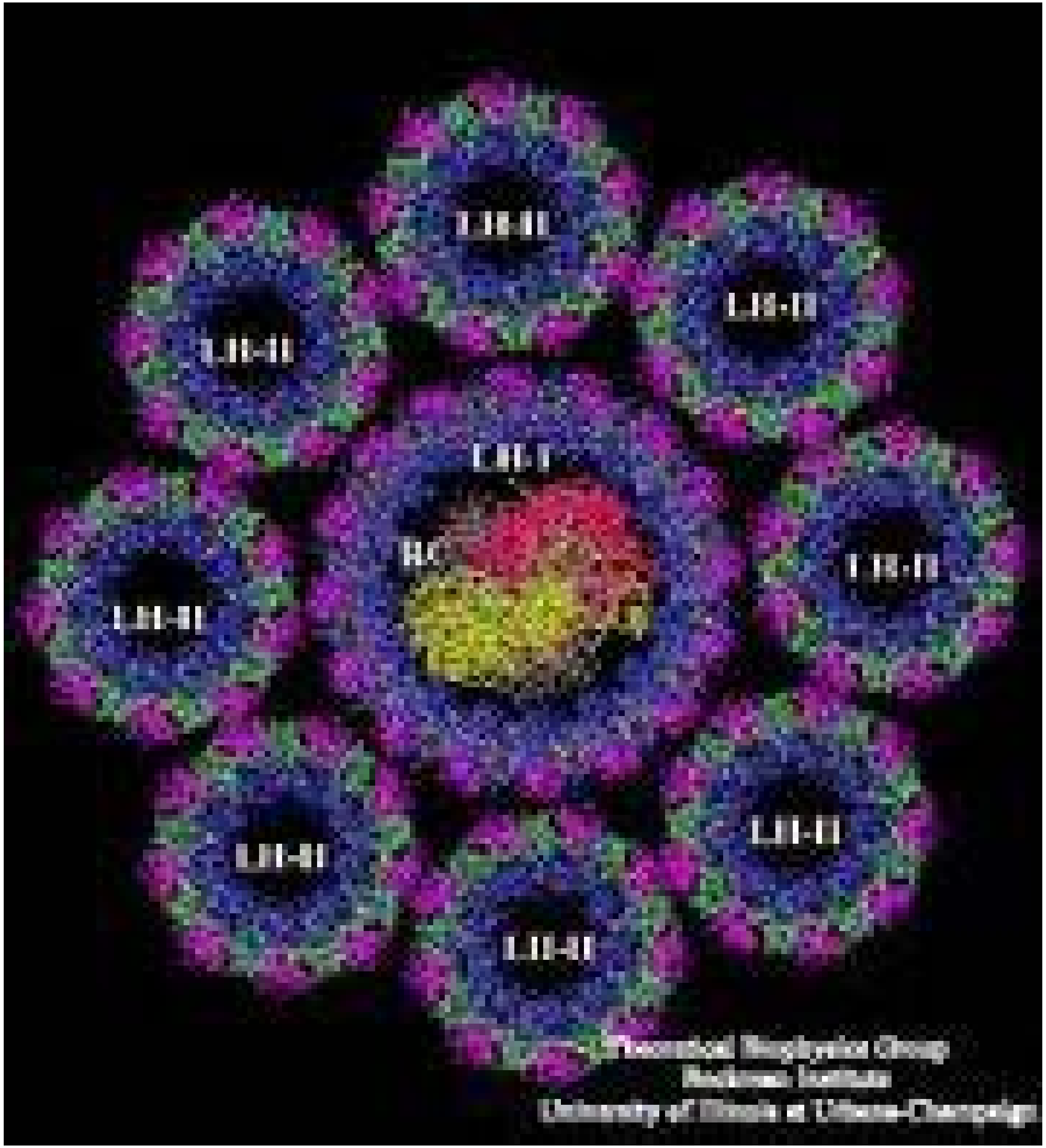
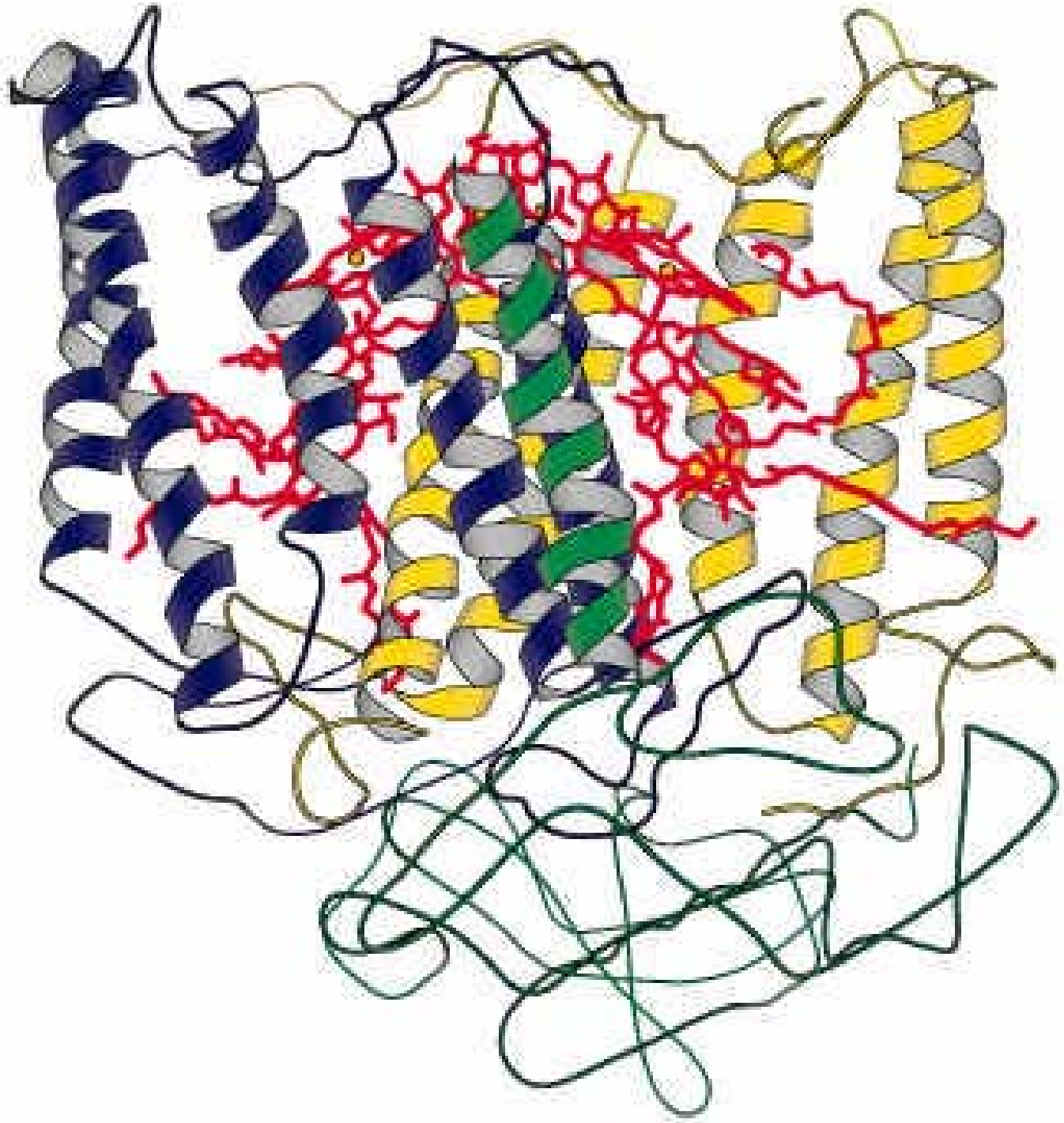
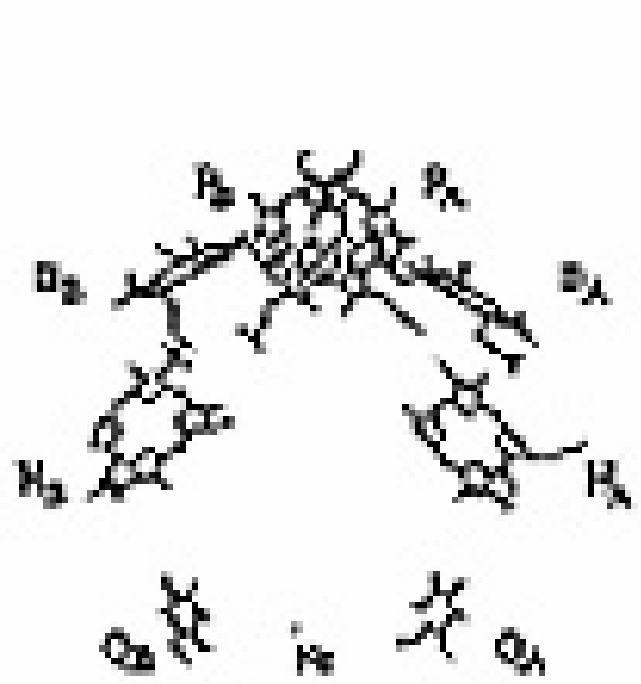
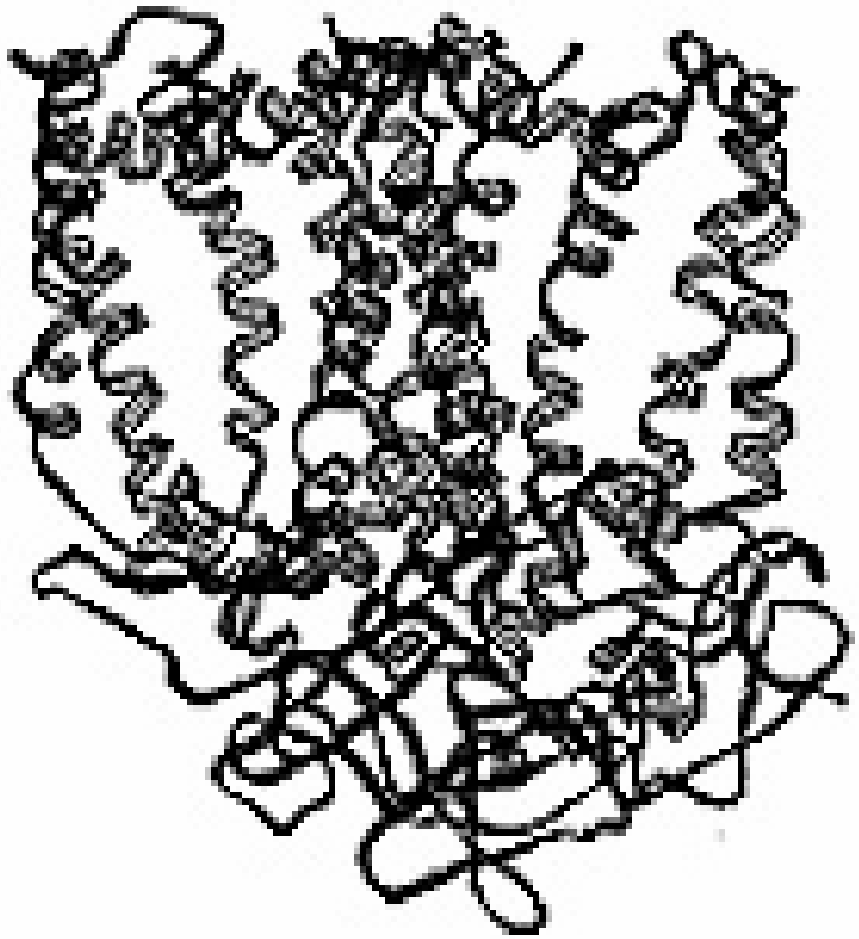
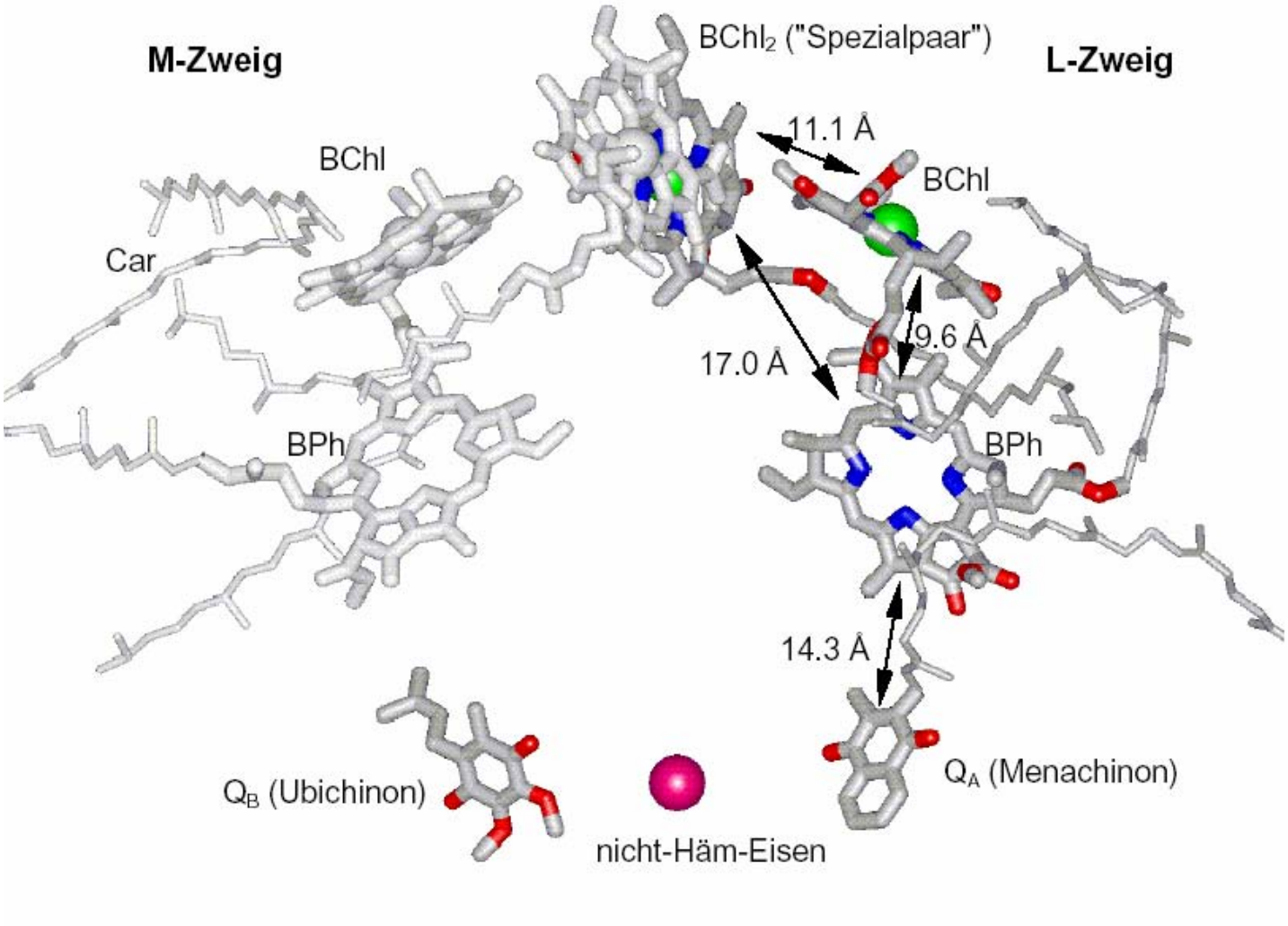

LH-II
LH-II
LH-II
LH-I
RC
LH-II
LH-II
LH-II
LH-II
LH-II



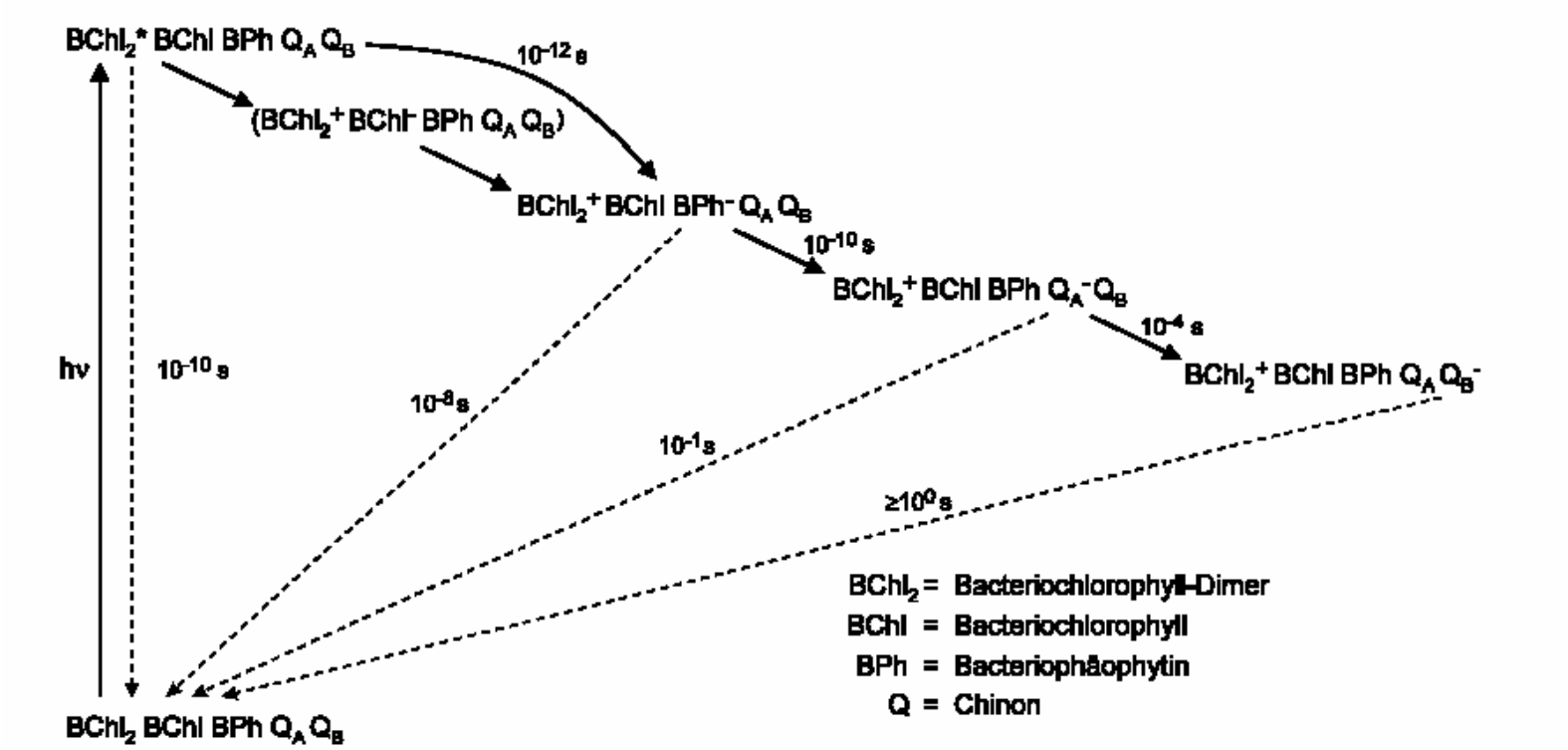


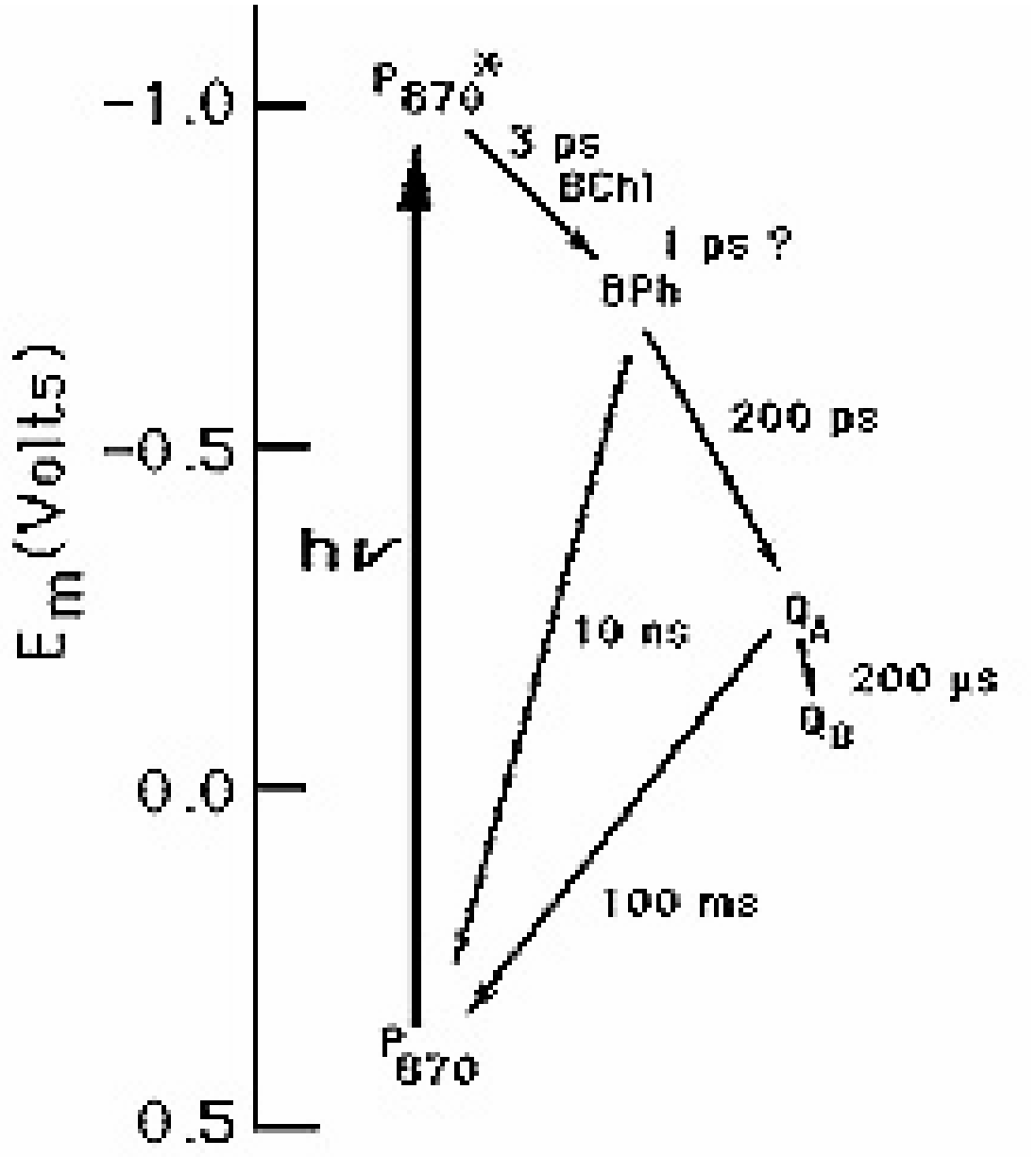


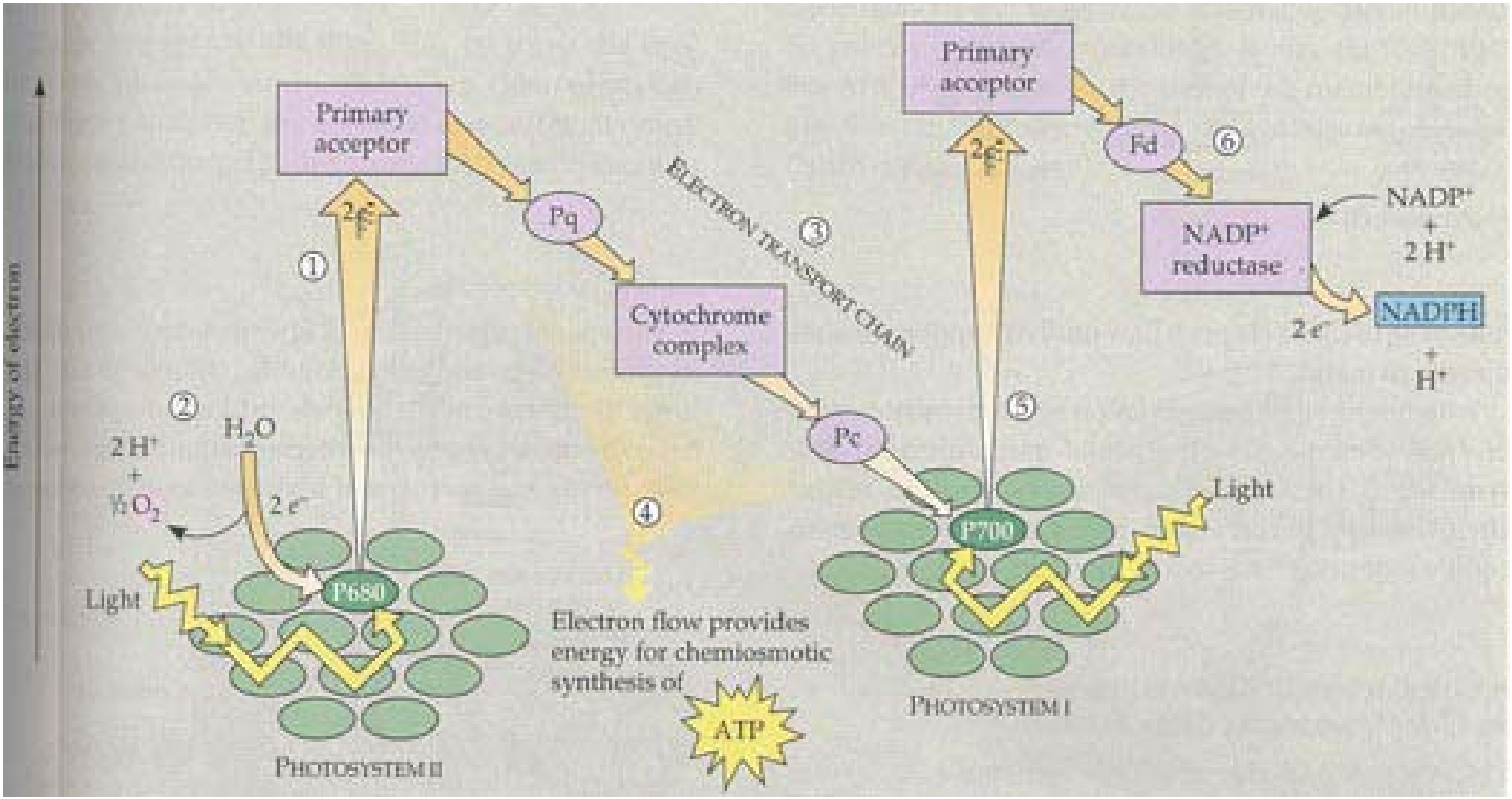
Primäres Reaktionszentrum

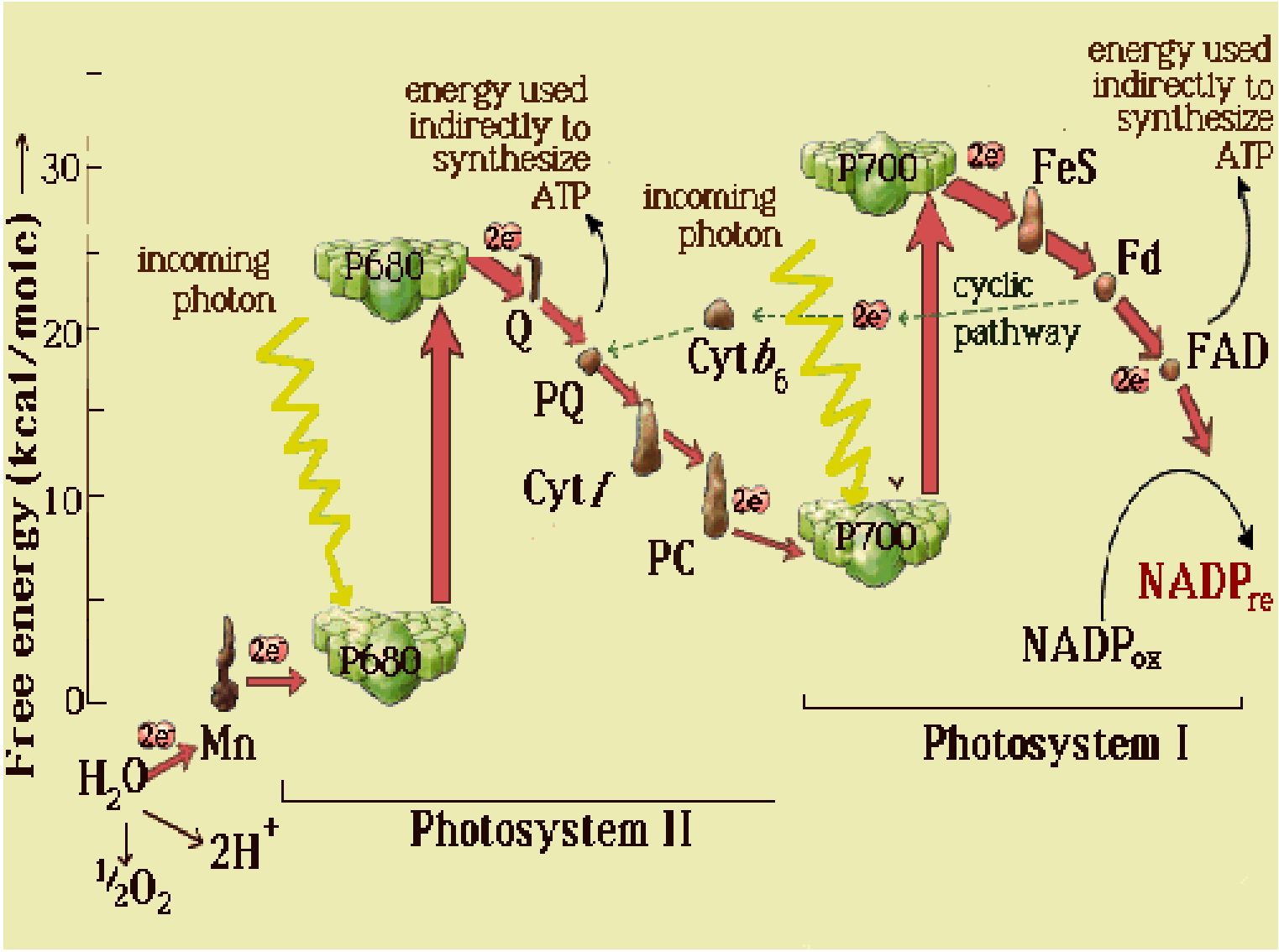


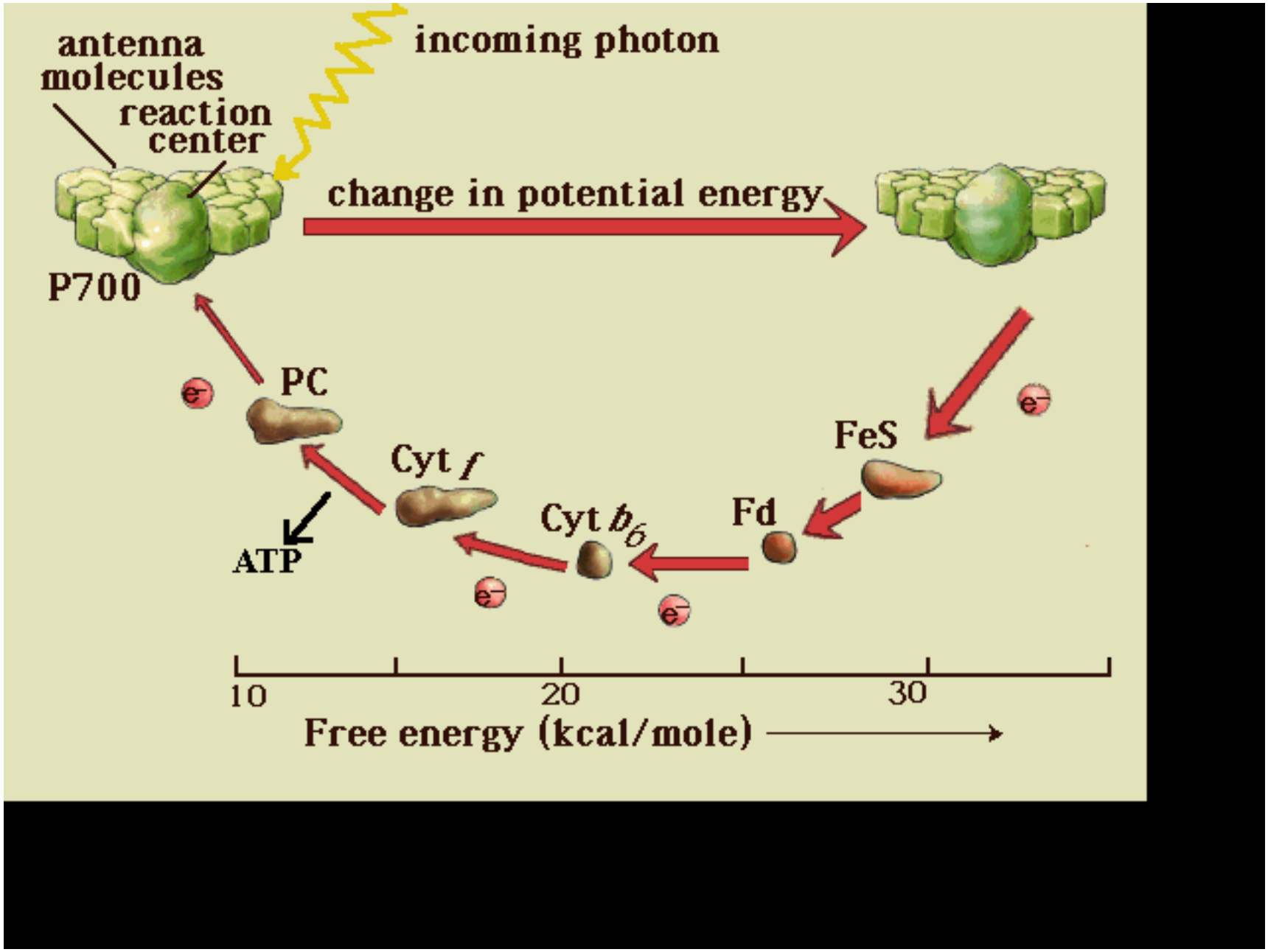
Electron Transfer - Schritte im Primären Reaktionszentrum




−1.0
−0.5
0.0
0.5
E_m (Volts)
P_{870}^*
3 ps
BChl
1 ps ?
BPh
200 ps
hν
10 ns
Q_A
200 μs
Q_B
100 ms
P_{870}


Energy of electron
Primary acceptor
Pq
Cytochrome complex
Pc
Primary acceptor
Fd
NADP+ reductase
NADP+ + 2 H+
NADPH + H+
2 e−
2 e−
2 e−
ELECTRON TRANSPORT CHAIN
1
2
3
4
5
6
2 H+ + ½ O2
H2O
2 e−
Light
P680
PHOTOSYSTEM II
Electron flow provides energy for chemiosmotic synthesis of
ATP
P700
Light
PHOTOSYSTEM I


Free energy (kcal/mole)
30
20
10
0
energy used indirectly to synthesize ATP
incoming photon
P680
2e⁻
Q
PQ
Cyt f
PC
Cyt b6
P700
FeS
Fd
FAD
cyclic pathway
NADPre
NADPox
Mn
H2O
2H+
½O2
Photosystem II
Photosystem I


antenna molecules
reaction center
incoming photon
change in potential energy
P700
PC
Cyt f
Cyt b_6
FeS
Fd
ATP
e⁻
10
20
30
Free energy (kcal/mole)

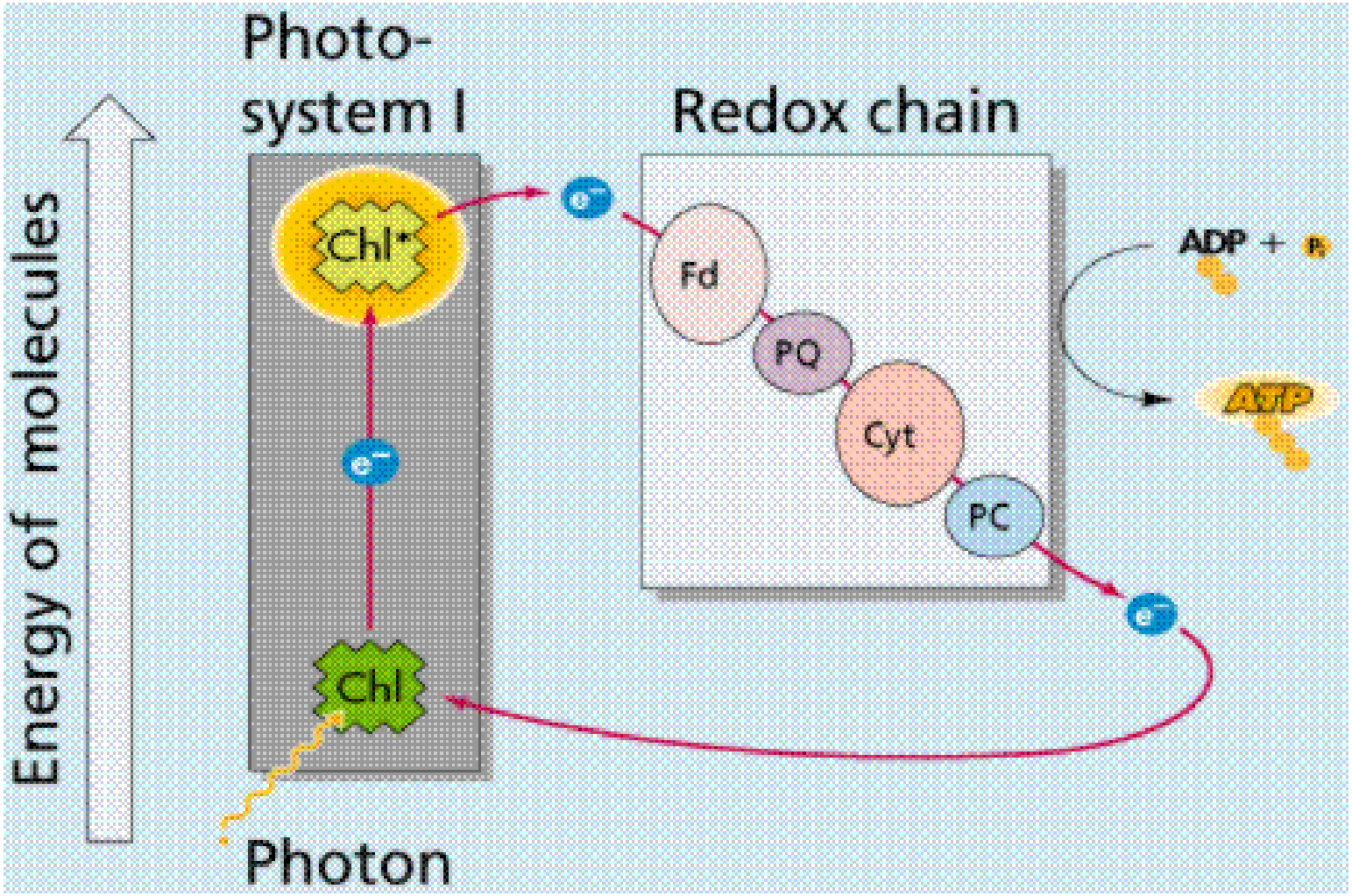
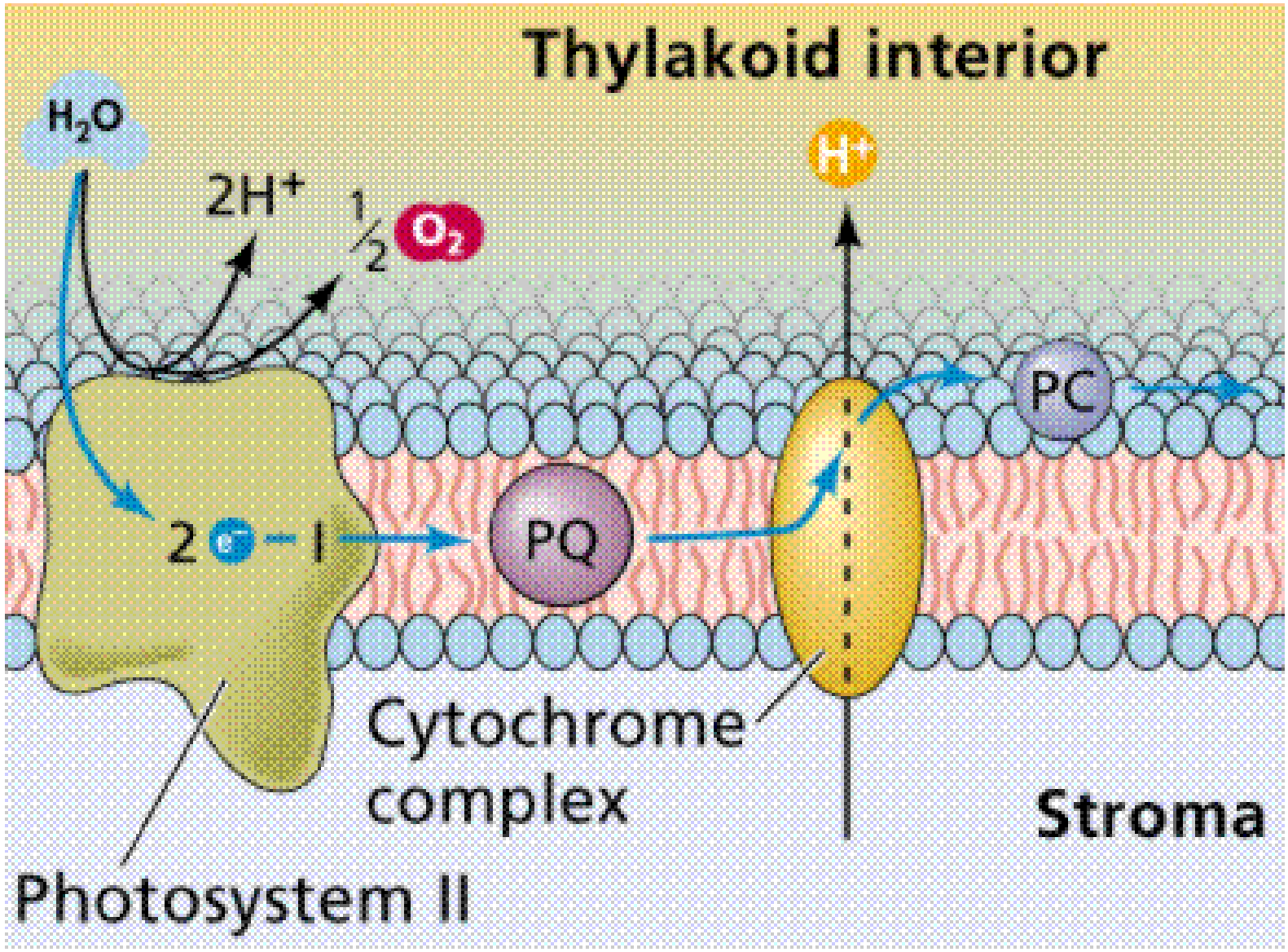
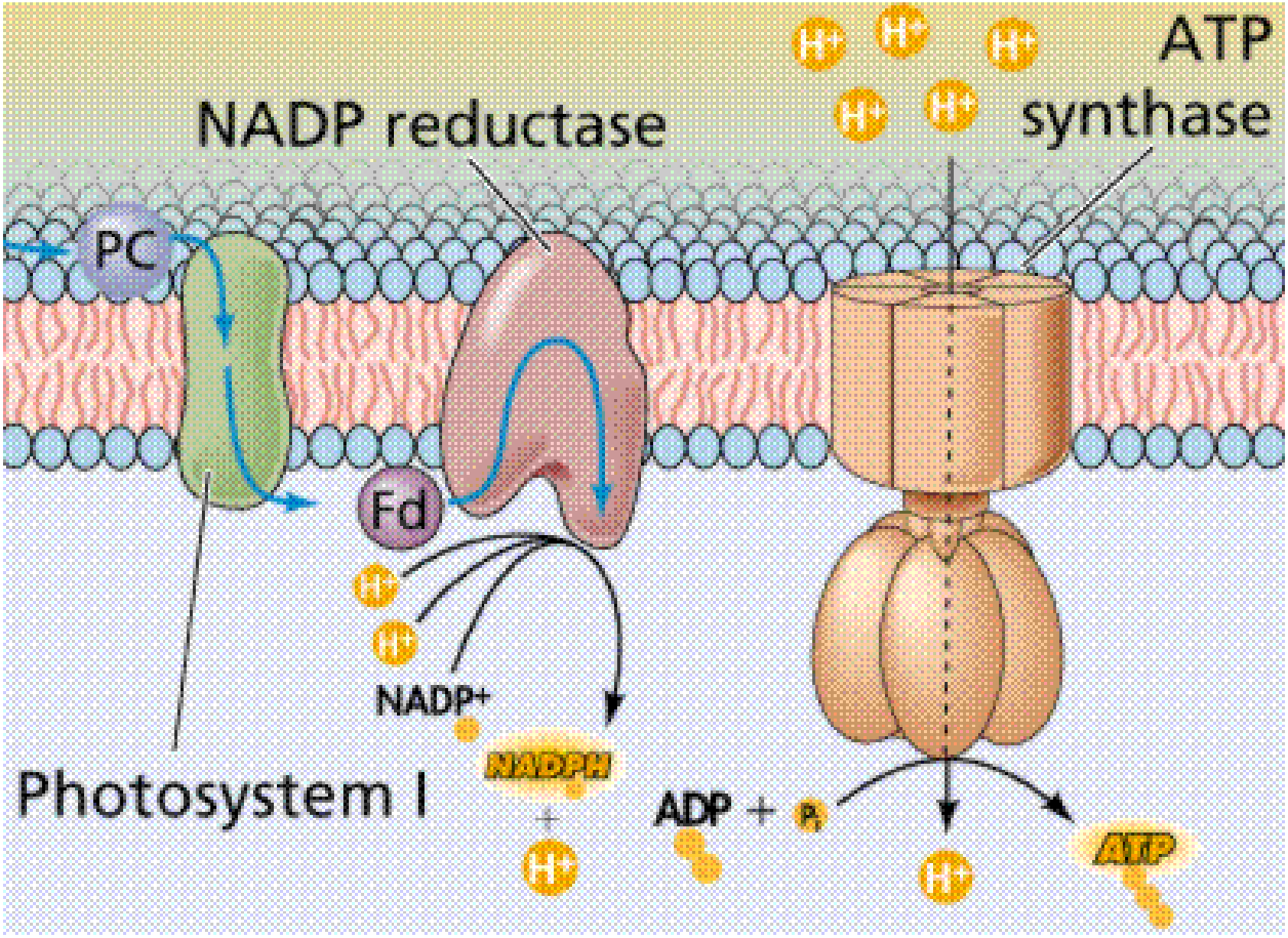
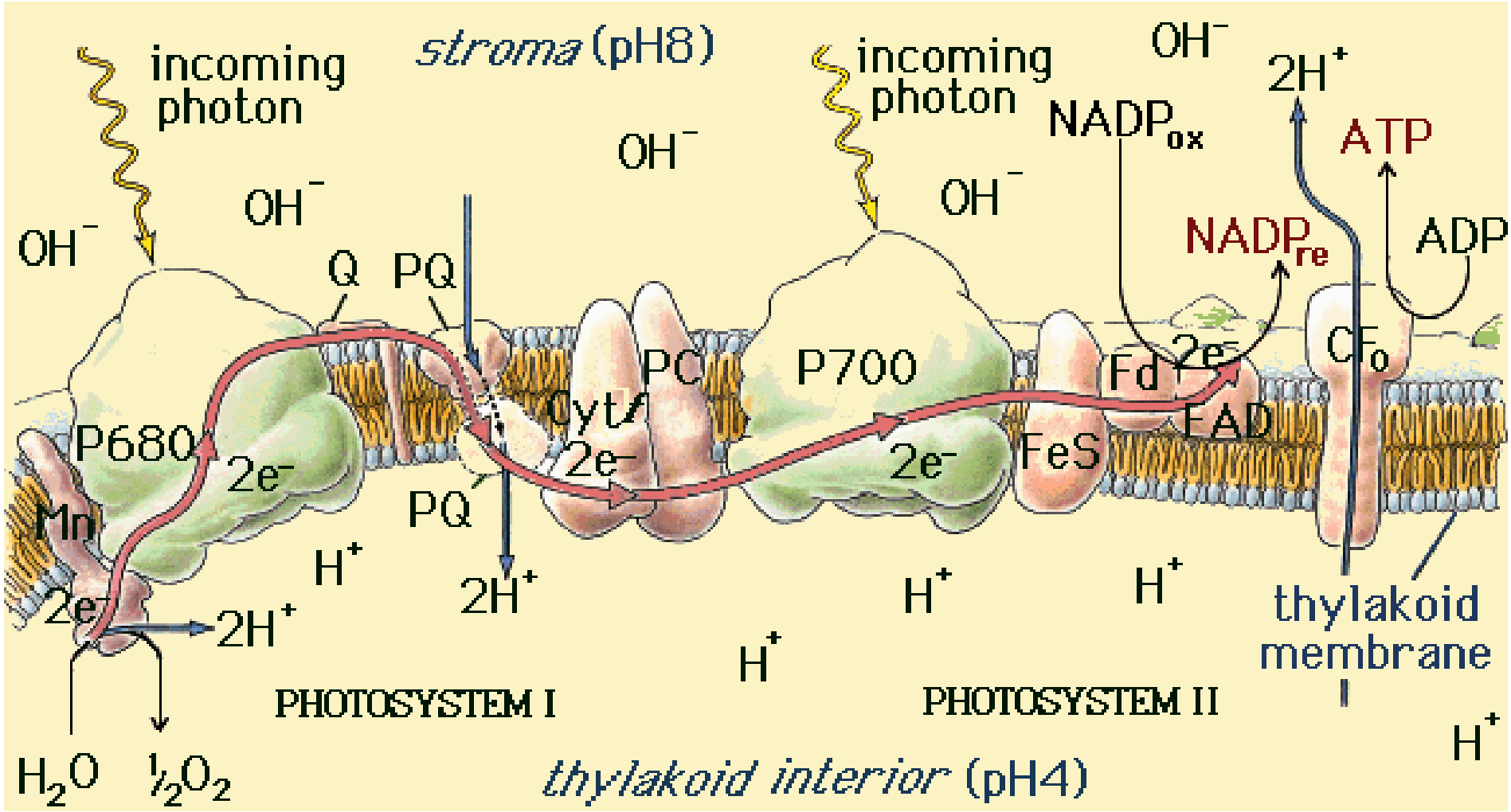
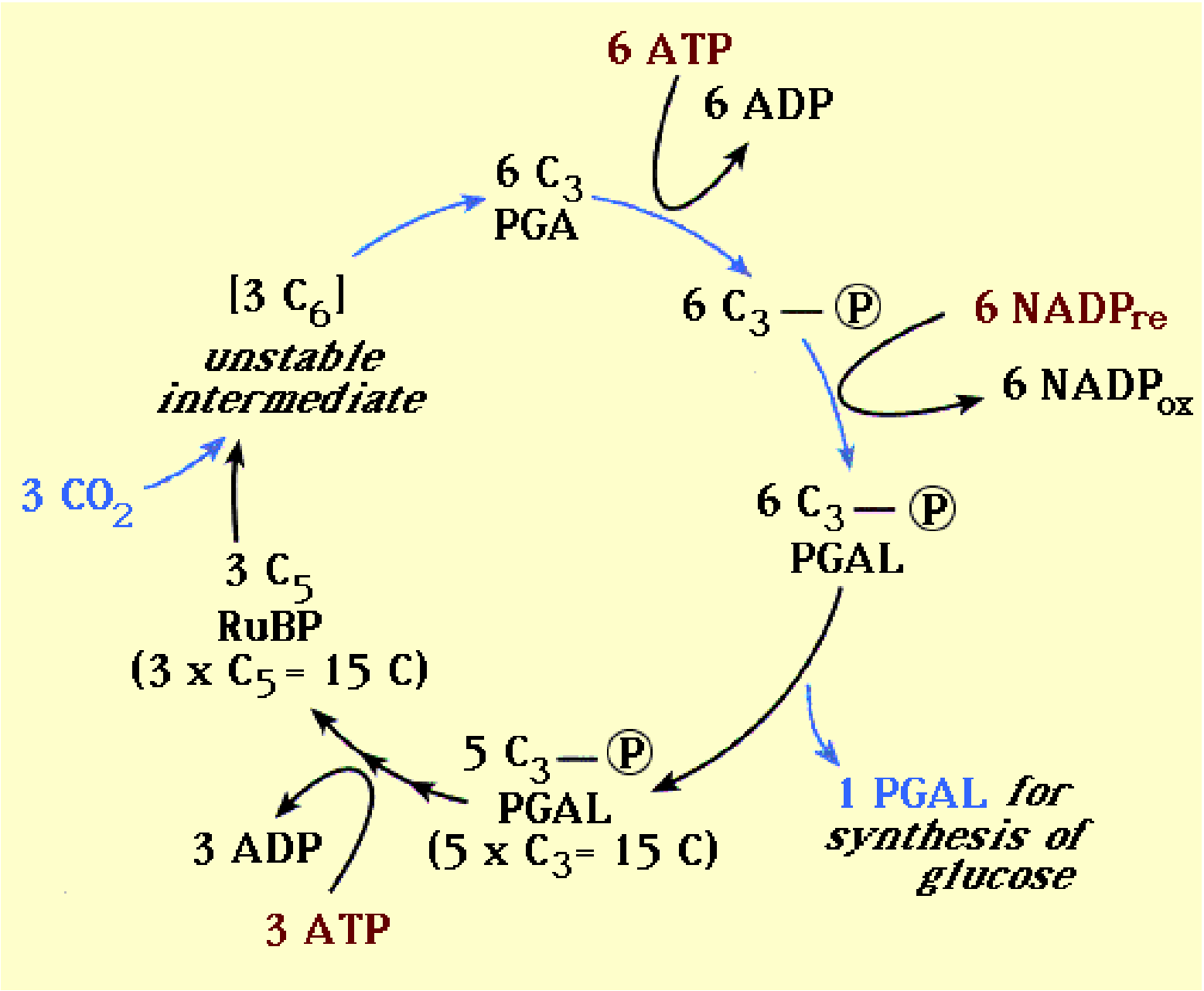


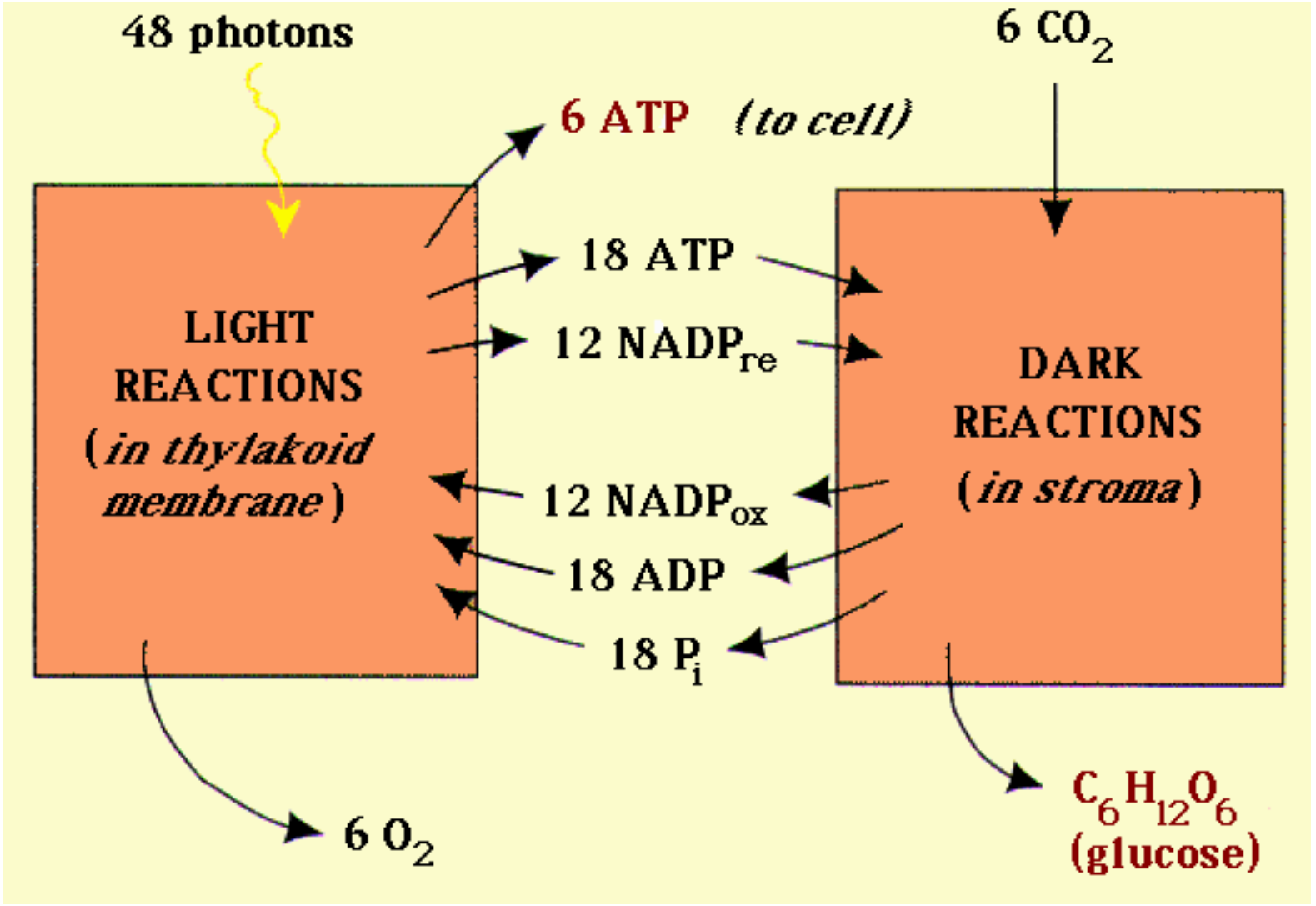
Photo-
system I
Redox chain
Energy of molecules
Chl*
Chl
e⁻
e⁻
e⁻
Fd
PQ
Cyt
PC
ADP + Pi
ATP
Photon

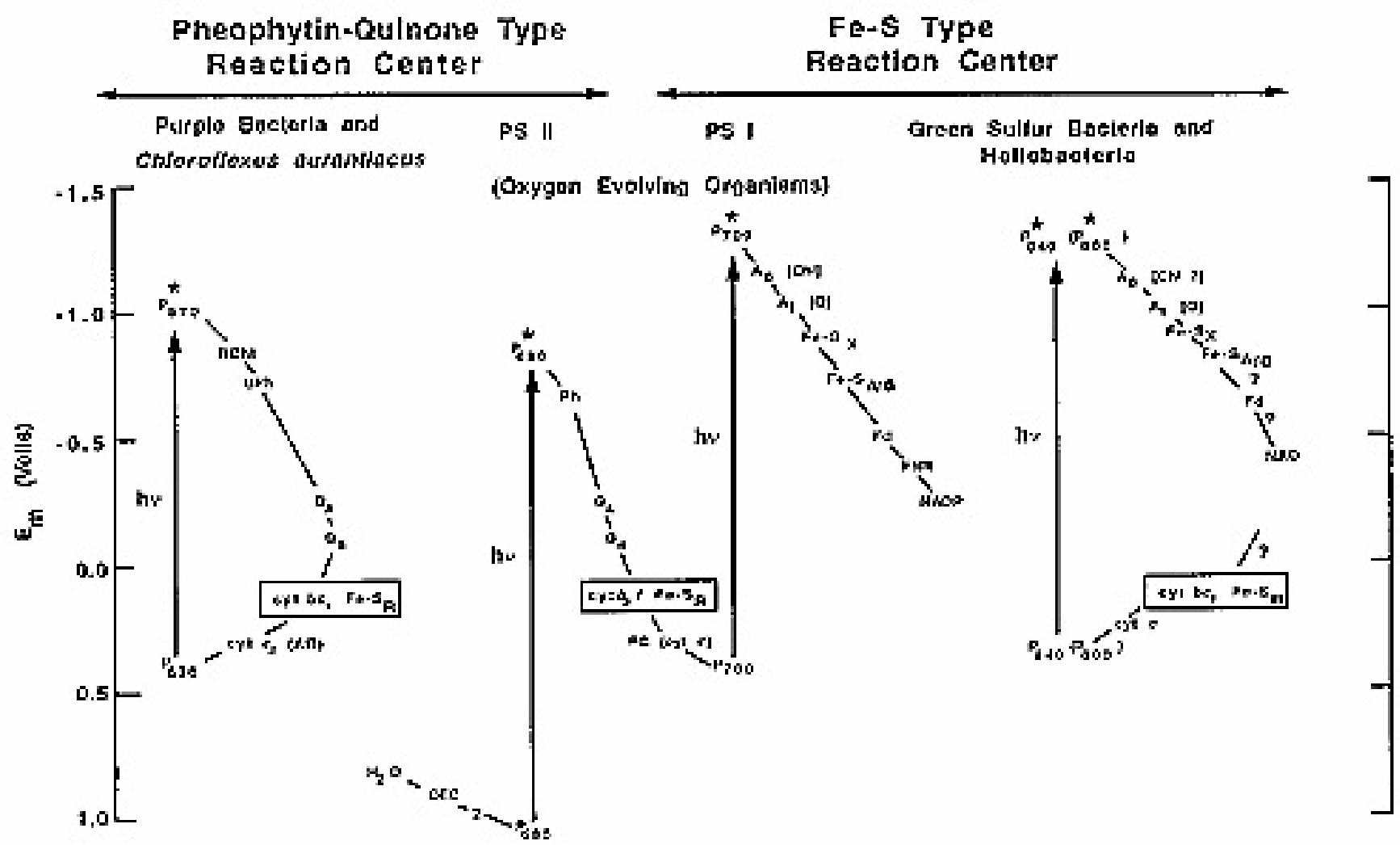

Thylakoid interior
H_2O
$2H^+$
$\frac{1}{2}$ O_2
H^+
PC
$2e^-$
PQ
Cytochrome complex
Stroma
Photosystem II

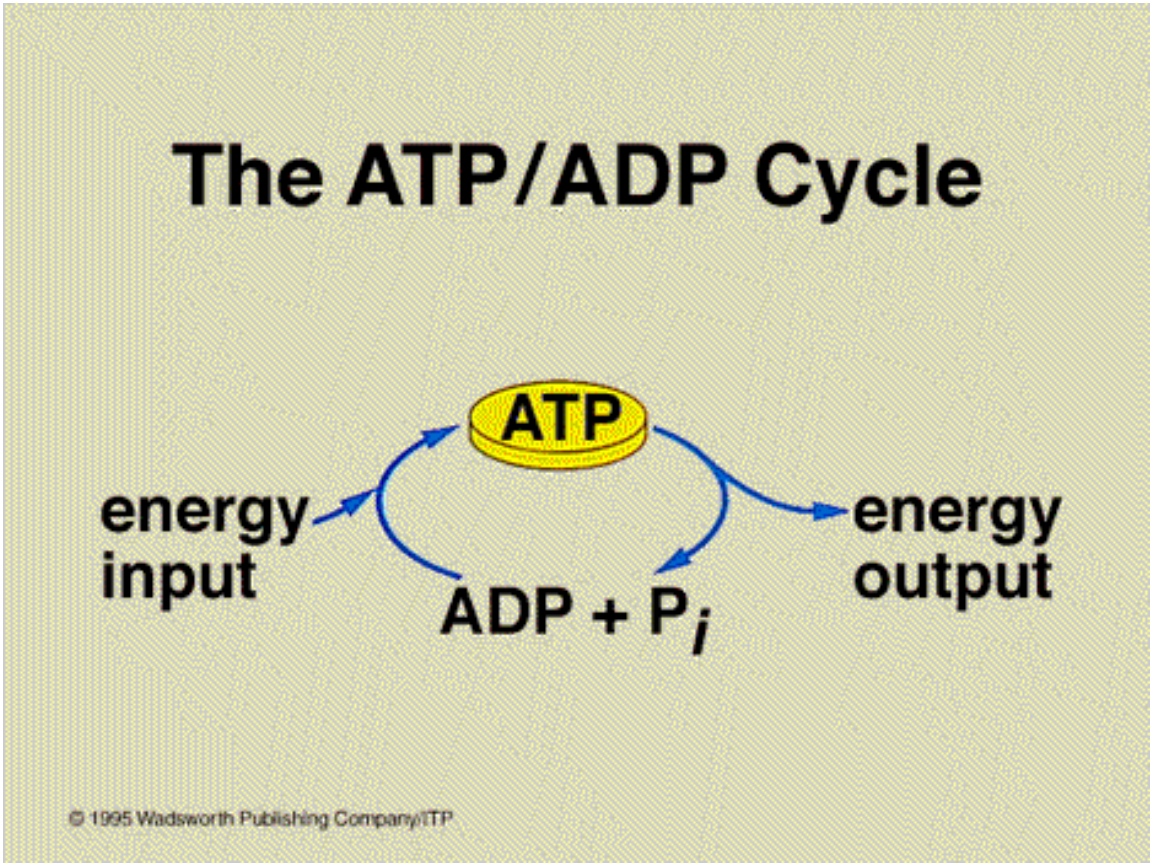

ATP
synthase
NADP reductase
PC
Fd
NADP+
NADPH
Photosystem I
ADP + Pi
ATP


incoming photon
stroma (pH8)
OH⁻
OH⁻
OH⁻
Q
PQ
PC
cyt f
P680
2e⁻
Mn
2e⁻
2H⁺
H⁺
PQ
2H⁺
2e⁻
H₂O
½O₂
PHOTOSYSTEM I
incoming photon
OH⁻
OH⁻
P700
FeS
H⁺
H⁺
H⁺
NADPox
OH⁻
2H⁺
ATP
NADPre
ADP
Fd
2e⁻
FAD
CFo
thylakoid membrane
PHOTOSYSTEM II
H⁺
thylakoid interior (pH4)


6 ATP
6 ADP
6 C_3
PGA
6 C_3 — Ⓟ
6 $NADP_{re}$
6 $NADP_{ox}$
6 C_3 — Ⓟ
PGAL
1 PGAL *for synthesis of glucose*
5 C_3 — Ⓟ
PGAL
(5 x C_3 = 15 C)
3 ADP
3 ATP
3 C_5
RuBP
(3 x C_5 = 15 C)
3 CO_2
[3 C_6]
unstable intermediate


48 photons
6 CO_2
6 ATP (to cell)
18 ATP
12 $NADP_{re}$
LIGHT REACTIONS (in thylakoid membrane)
DARK REACTIONS (in stroma)
12 $NADP_{ox}$
18 ADP
18 P_i
6 O_2
$C_6H_{12}O_6$ (glucose)


Pheophytin-Quinone Type
Reaction Center
Fe-S Type
Reaction Center
Purple Bacteria and
Chloroflexus aurantiacus
PS II
(Oxygen Evolving Organisms)
PS I
Green Sulfur Bacteria and
Hellobacteria
-1.5
-1.0
-0.5
0.0
0.5
1.0
hν
hν
hν
hν


The ATP/ADP Cycle
ATP
energy input
energy output
ADP + P$_i$
© 1995 Wadsworth Publishing Company/ITP

Nobel Prize Winners in Photosynthesis Research

(For more info on all the nobel laureates, click here).

- Paul D. Boyer and John E. Walker (1997, Chemistry): Elucidation of enzymatic mechanism underlying the synthesis of adenosine triphosphate (ATP).

- Rudolph Marcus (1992, Chemistry): Electron transfer theory: included application to photosynthesis. [He was at UIUC, Urbana; had attended my course in "Bioenergetics in Photosynthesis"; is currently at Cal Tech in Pasadena, CA.]

- Hartmut Michel; Robert Huber; and Johannes Deisenhofer (1988, Chemistry): X-ray structure of bacterial reaction center. [Michel has visited Urbana several times and I have had many conversations with him before and after his prize; I have casually met Deisenhofer, but never Huber. The work was done at Munich, Germany.]

- Peter Mitchell (1978, Chemistry ..to check): Oxidative and photosynthetic phosphorylation: chemi-osmotic theory.[The work was done in England, UK]

- Robert Burns Woodward (1965, Chemistry): Total synthesis of chlorophyll, vitamin B12, and other natural products.[He was at Harvard University]

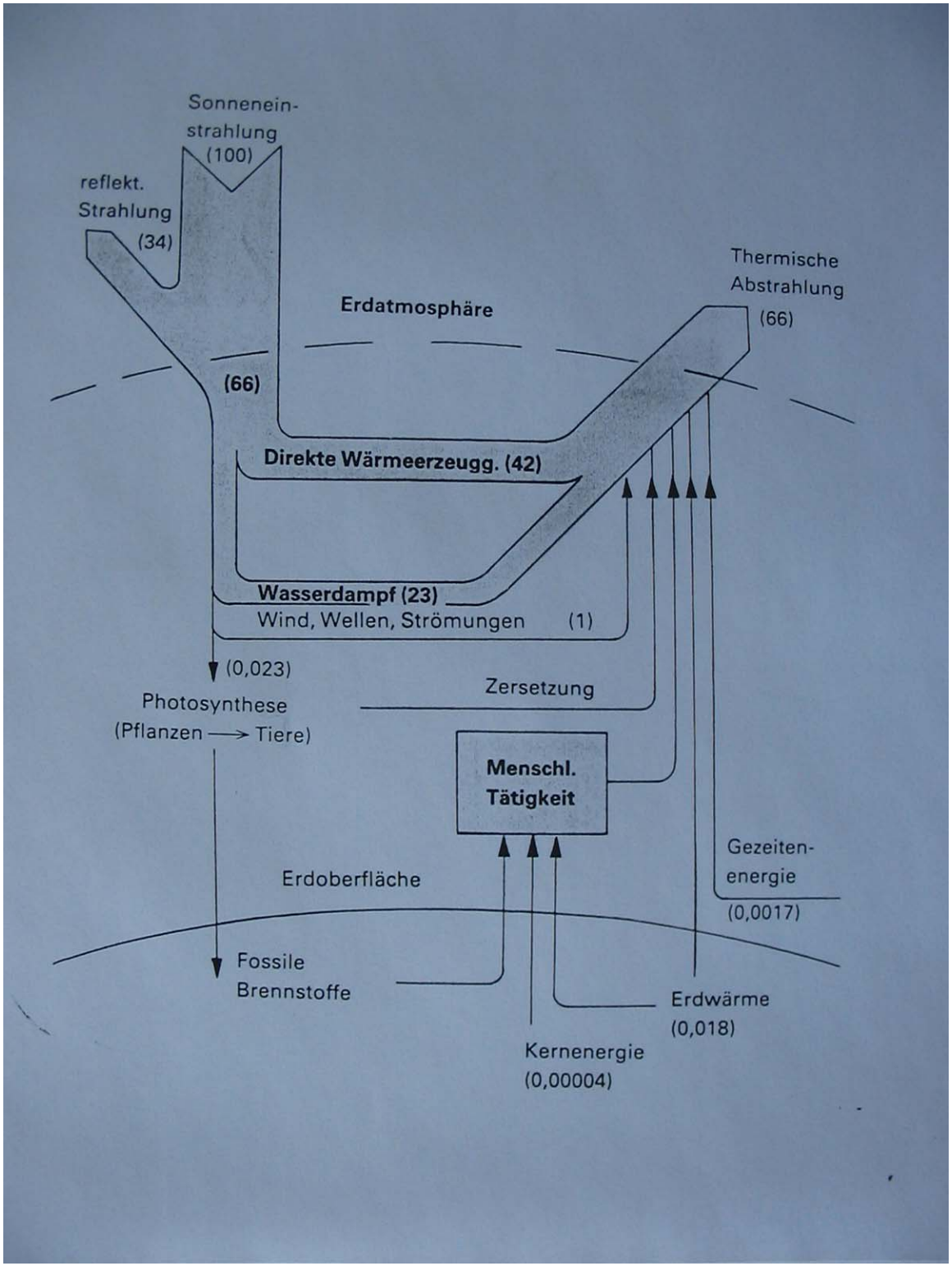
- Melvin Calvin (1961, Chemistry): Carbon-di oxide assimilation in photosynthesis.[The work was done at Berkeley; Professor Calvin is known to me as he has visited UIUC, and, he is one of the two professors I had applied to do PhD with; the person who discovered 14C (Martin Kamen),that was crucial for Calvin's experiments, is known to me personally.]

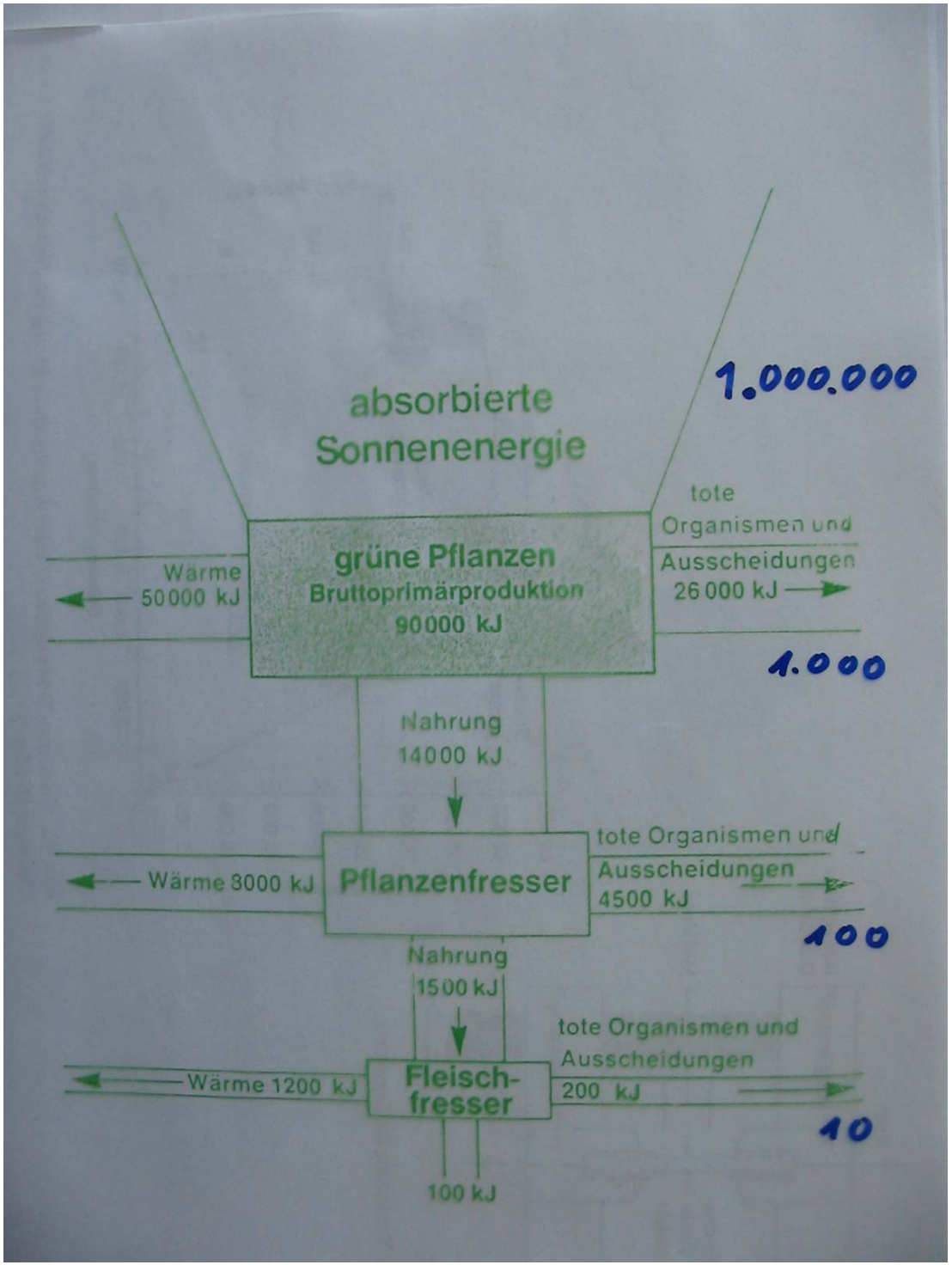
- Richard Kuhn (1938, Chemistry): carotenoids; vitamins [Germany]

- Paul Karrer (1937, Chemistry): Carotenoid structure; flavins; vitamin B2[Germany]

- Hans Fischer (1930, Chemistry): Chlorophyll chemistry; hemin synthesis[Germany]

- Richard Martin Wilstatter (1915, Chemistry): Chlorophyll purification and structure, carotenoids, etc.[Germany]


Sonneneinstrahlung
(100)
reflekt.
Strahlung
(34)
Thermische
Abstrahlung
(66)
Erdatmosphäre
(66)
Direkte Wärmeerzeugg. (42)
Wasserdampf (23)
Wind, Wellen, Strömungen (1)
(0,023)
Photosynthese
(Pflanzen → Tiere)
Zersetzung
Menschl.
Tätigkeit
Gezeitenenergie
(0,0017)
Erdoberfläche
Fossile
Brennstoffe
Erdwärme
(0,018)
Kernenergie
(0,00004)

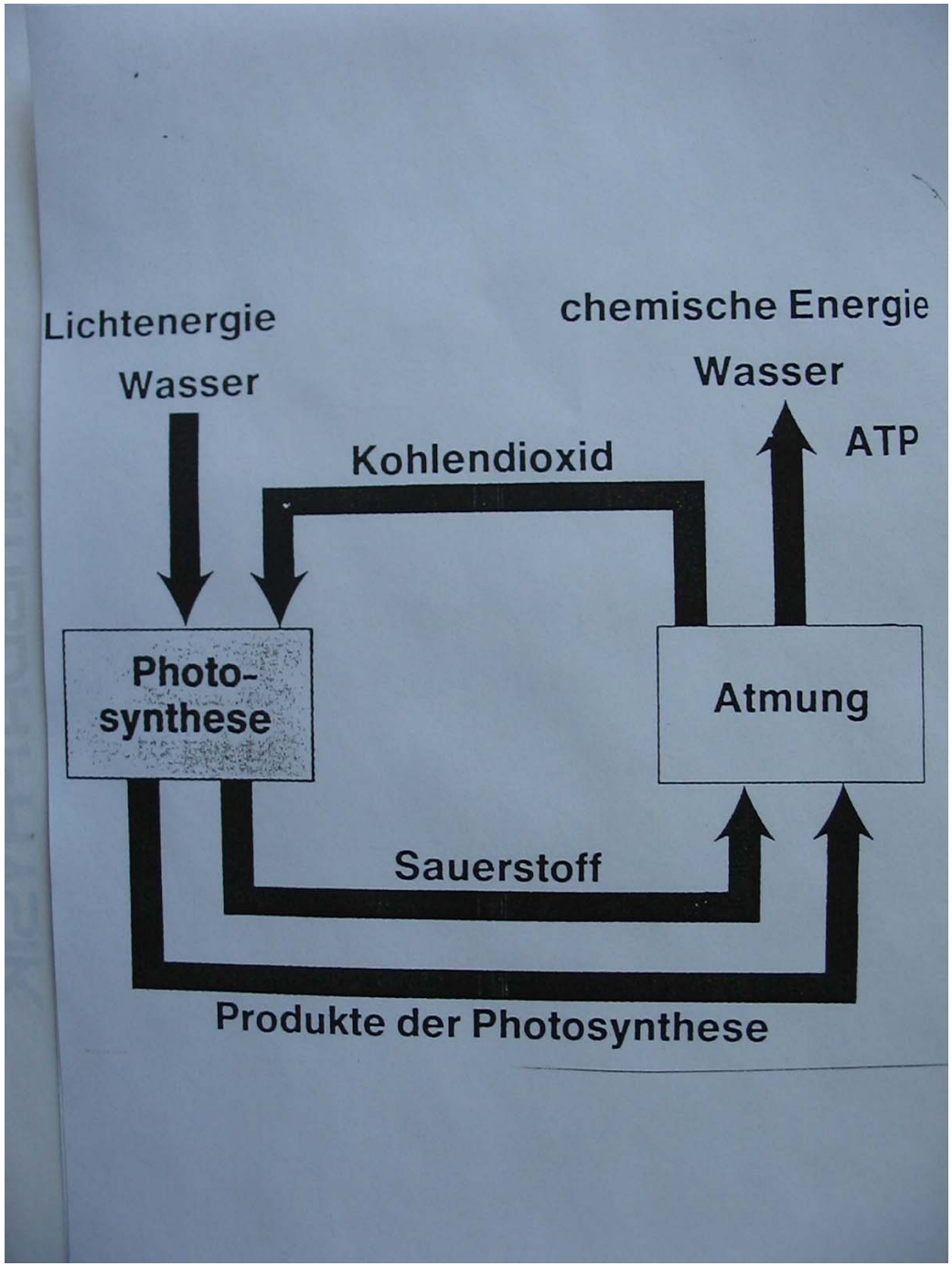

absorbierte
Sonnenenergie
1.000.000
grüne Pflanzen
Bruttoprimärproduktion
90000 kJ
Wärme
50000 kJ
tote
Organismen und
Ausscheidungen
26000 kJ
1.000
Nahrung
14000 kJ
Pflanzenfresser
Wärme 8000 kJ
tote Organismen und
Ausscheidungen
4500 kJ
100
Nahrung
1500 kJ
Fleisch-
fresser
Wärme 1200 kJ
tote Organismen und
Ausscheidungen
200 kJ
10
100 kJ

Globale tägliche Sonnenenergiezufuhr	**$6.7 \cdot 10^{18}$ kJ**
Chemische Energie durch Photosynthese	**0.12 %**

Globale tägliche Pflanzenproduktion (netto Trockensubstanz)	**$4.5 \cdot 10^{8}$ t**
Pflanzliche Nahrungsmittel	**1 %**

Täglicher Energieverbrauch eines Menschen

— **Nahrung**	**$1 \cdot 10^{4}$ kJ**
— **Energie**	**$1{,}4 \cdot 10^{5}$ kJ**


Lichtenergie
Wasser
chemische Energie
Wasser
ATP
Kohlendioxid
Photo-
synthese
Atmung
Sauerstoff
Produkte der Photosynthese

Photosynthese im Web

http.//photosience.la.asu.edu/photosyn/photoweb/default.html

MOTIVATION

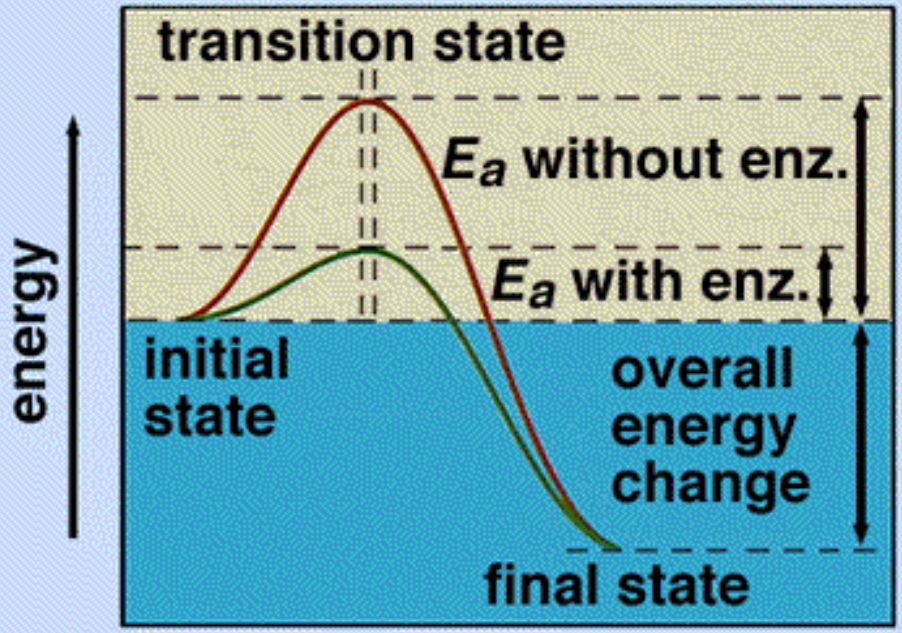
- **Formation of well-defined artificial supramolecular systems of nanoscale size with controllable number and photophysical properties of porphyrinic subunits** ***using the combination of two fundamentally different approaches: 1) chemical synthesis of covalently linked Zn-porphyrin dimers and trimers with or without additional electron acceptors; 2) self-assembly non-covalent interactions with pyridyl substituted tetrapyrrole extra-ligands (two-fold extra-ligation effect with "key-hole" principle)***

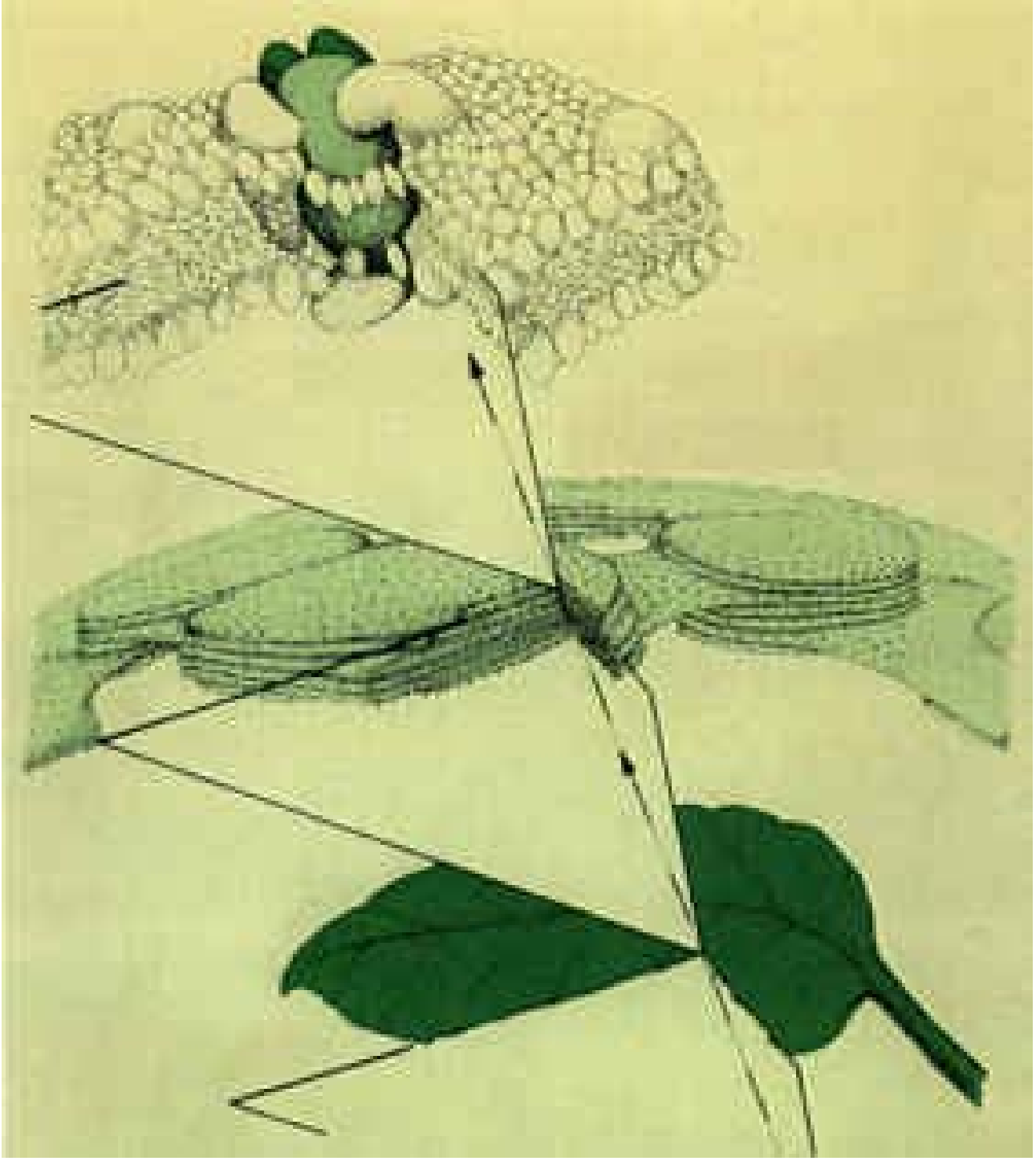
- **Experimental verification of the non-radiative energy migration and photoinduced charge separation processes** ***for the systems of interest upon variation of the solvent polarity and temperature (77-350 K)***

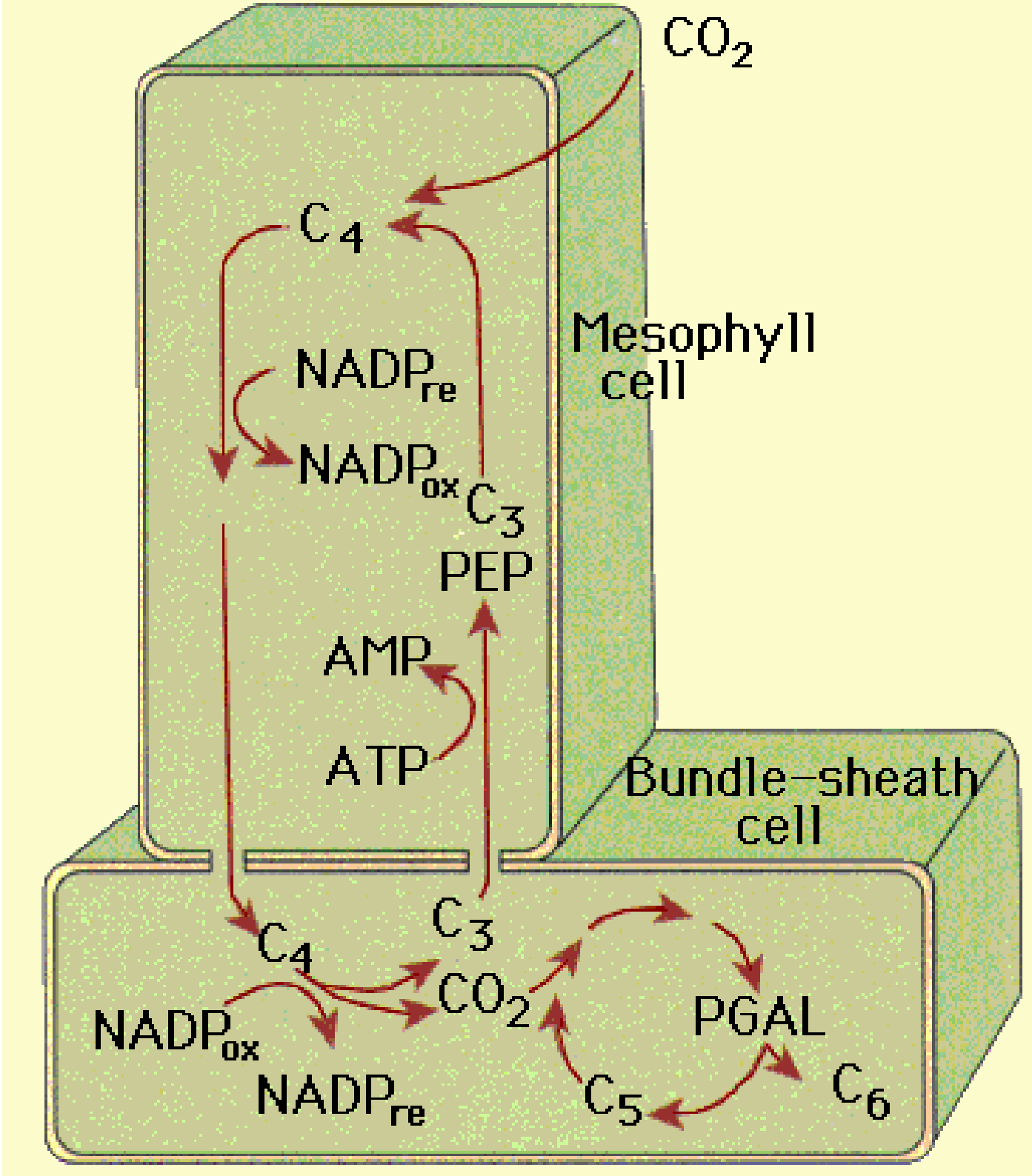
- **Specificity of self-assembly interactions between CdSe/ZnS nanocrystals and tetrapyrrolic compounds** ***using the tunability of the nanoparticle band gap via size variation and chemical engineering of functionalized organic molecules***

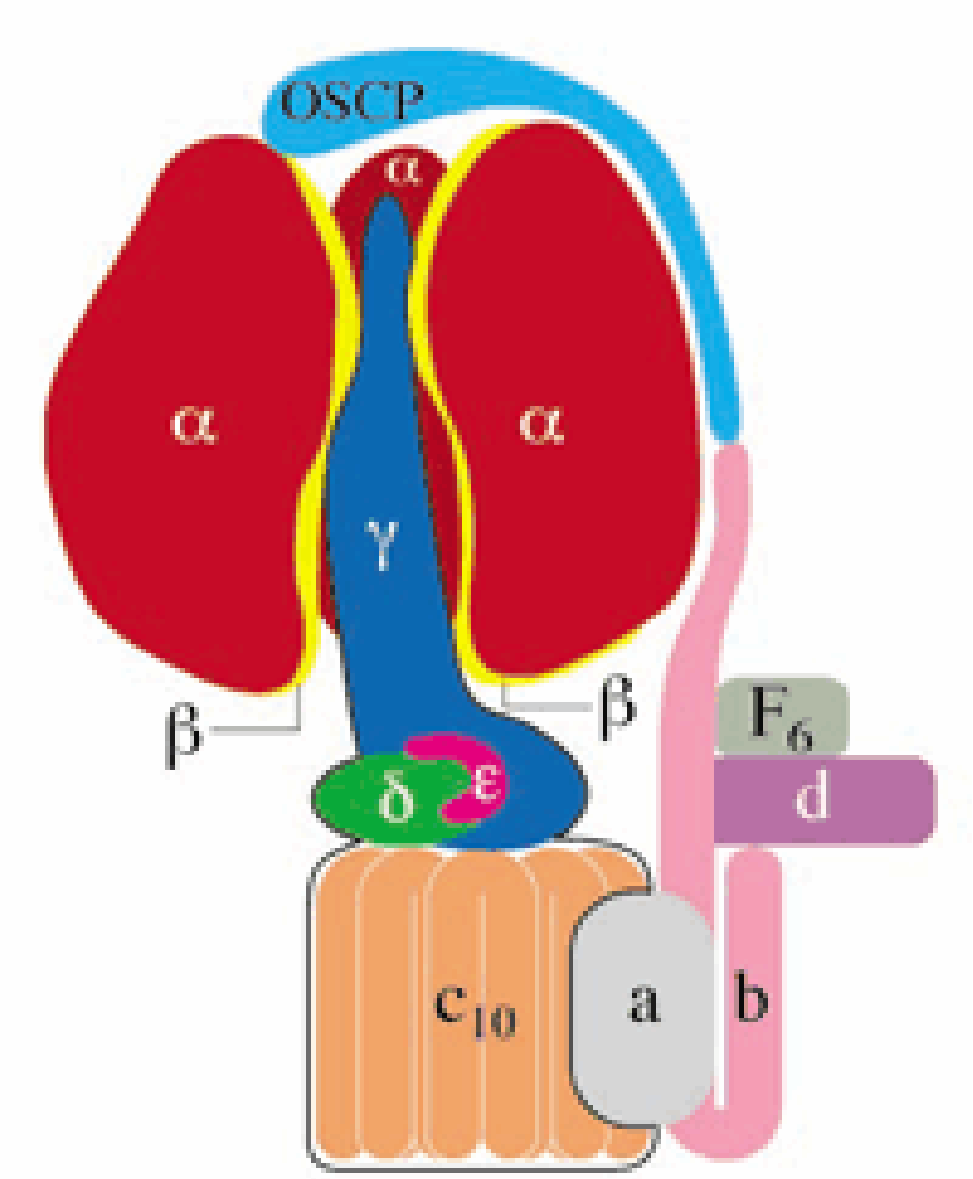
- **Elucidation of the energetic pathways and possible mechanisms of the electronic energy deactivation in supramolecular arrays** ***based on experimental data and theoretical considerations***

Energy Hill Diagram

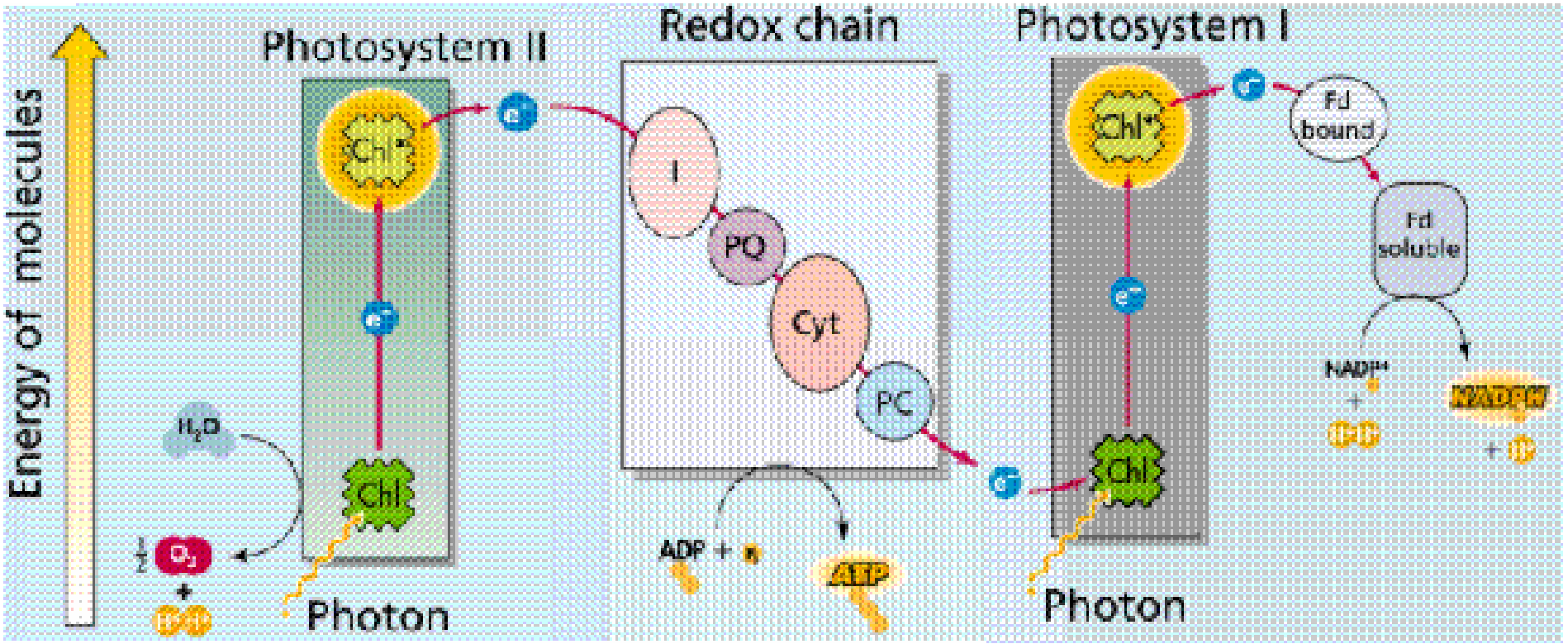


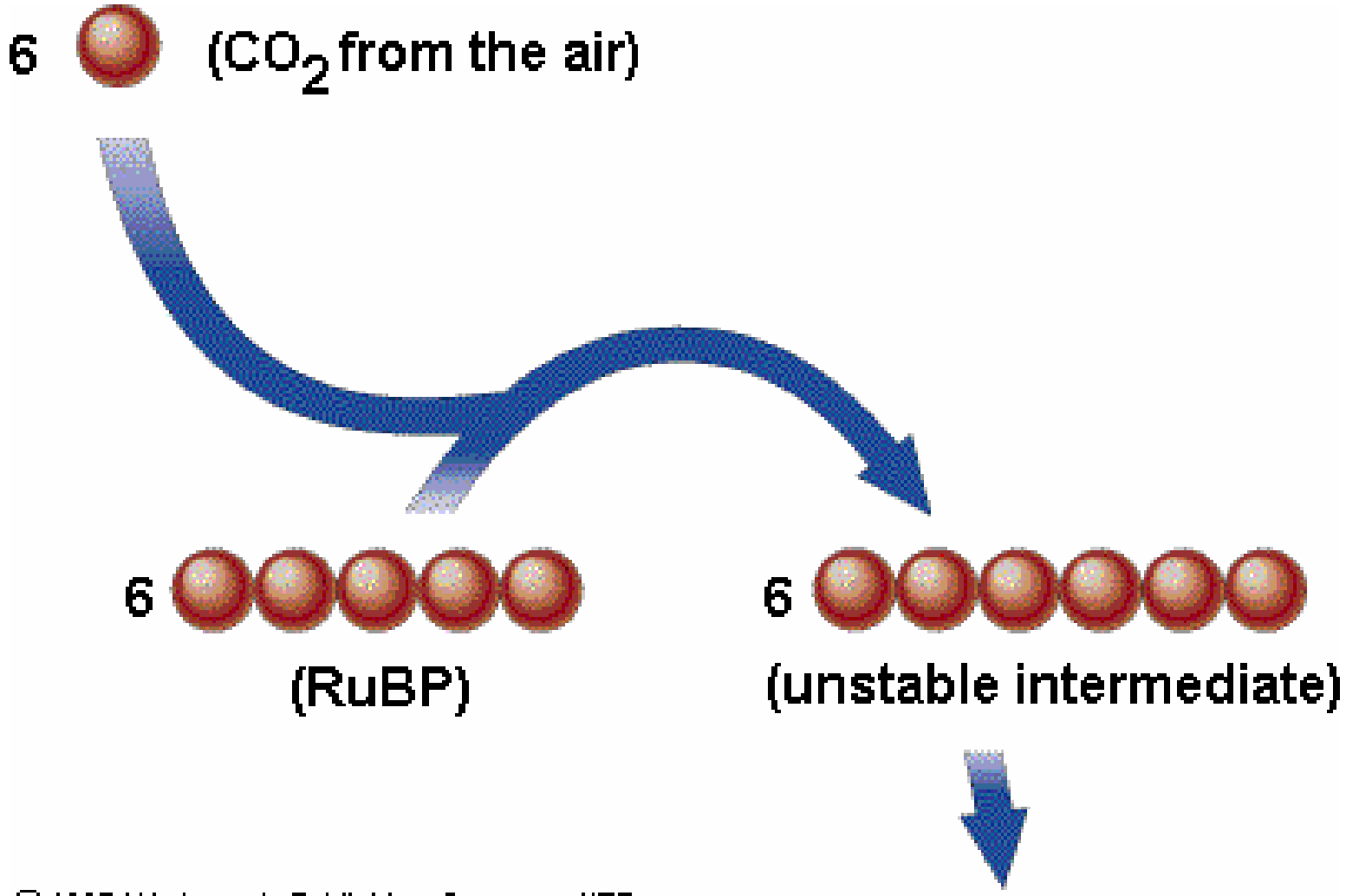


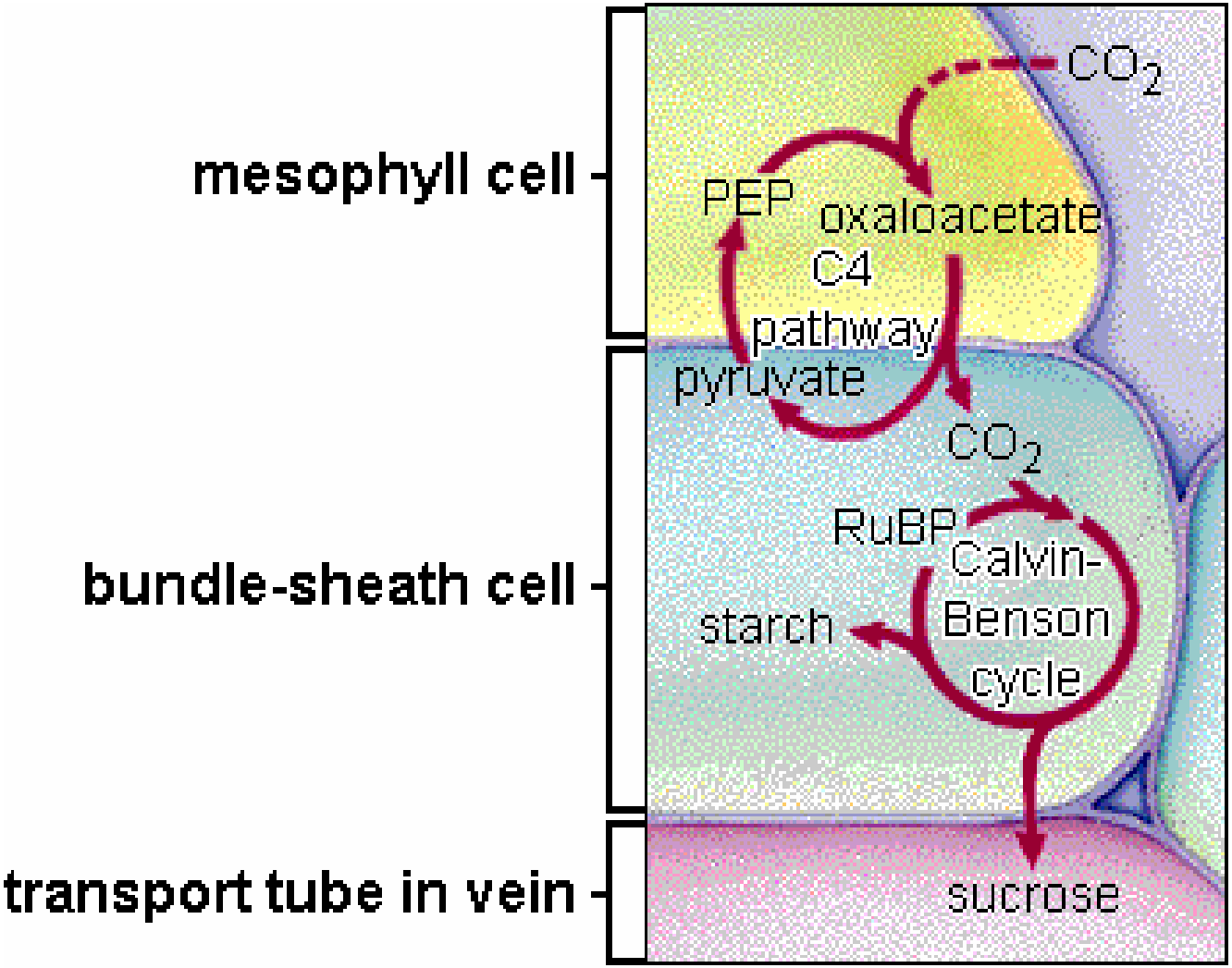

CO_2
C_4
Mesophyll cell
$NADP_{re}$
$NADP_{ox}$
C_3
PEP
AMP
ATP
Bundle-sheath cell
C_4
C_3
CO_2
$NADP_{ox}$
$NADP_{re}$
PGAL
C_5
C_6

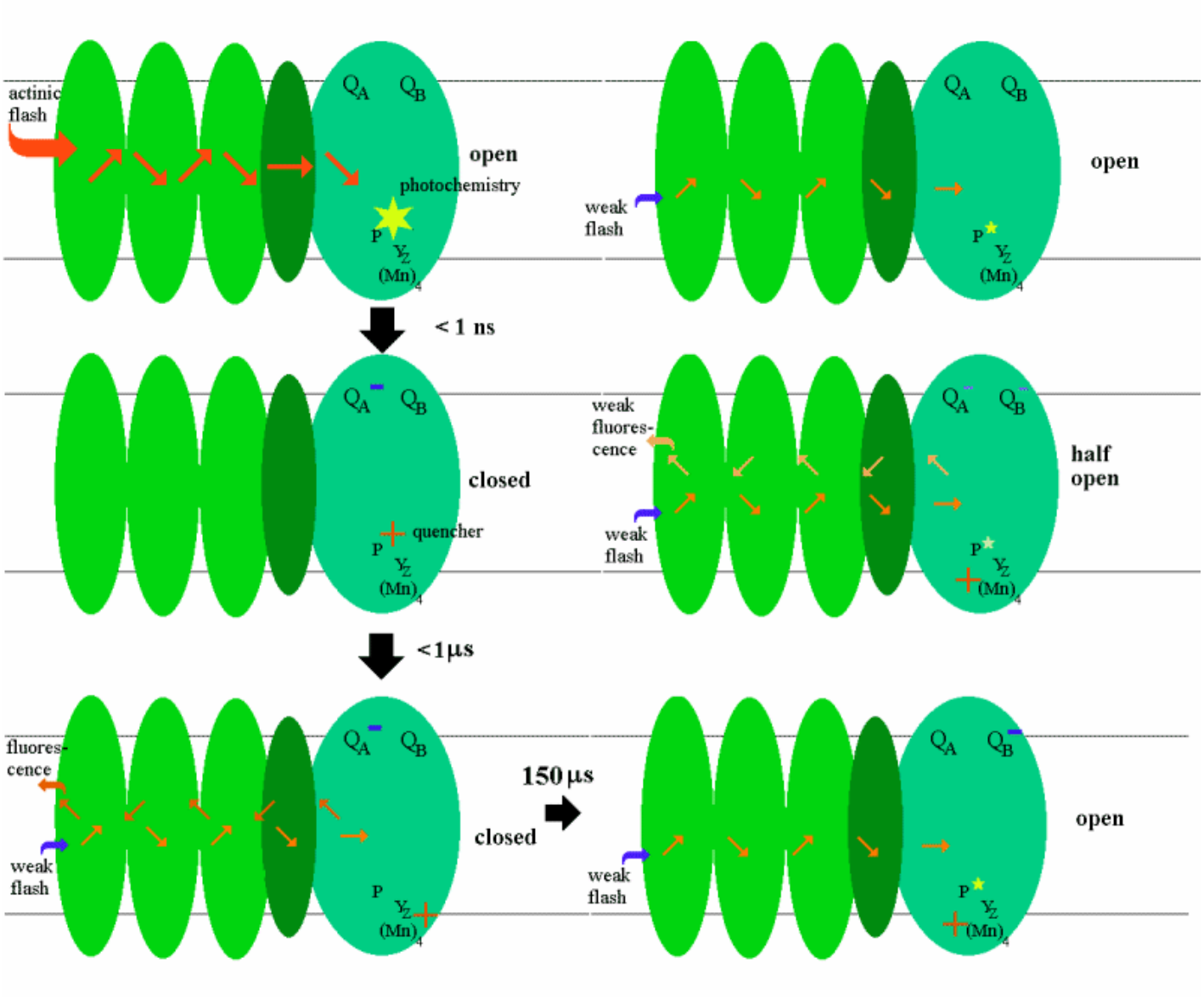


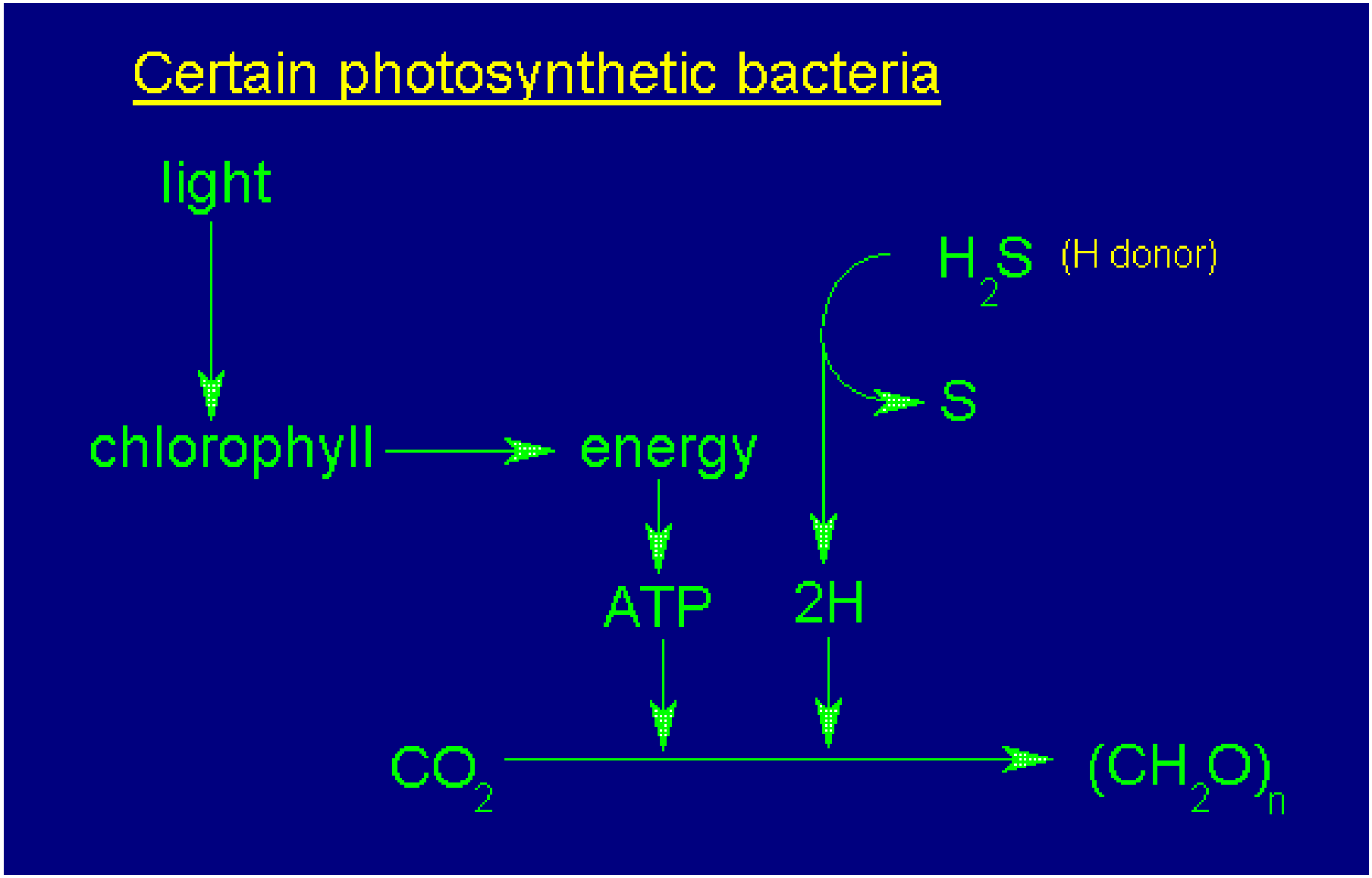
(a)

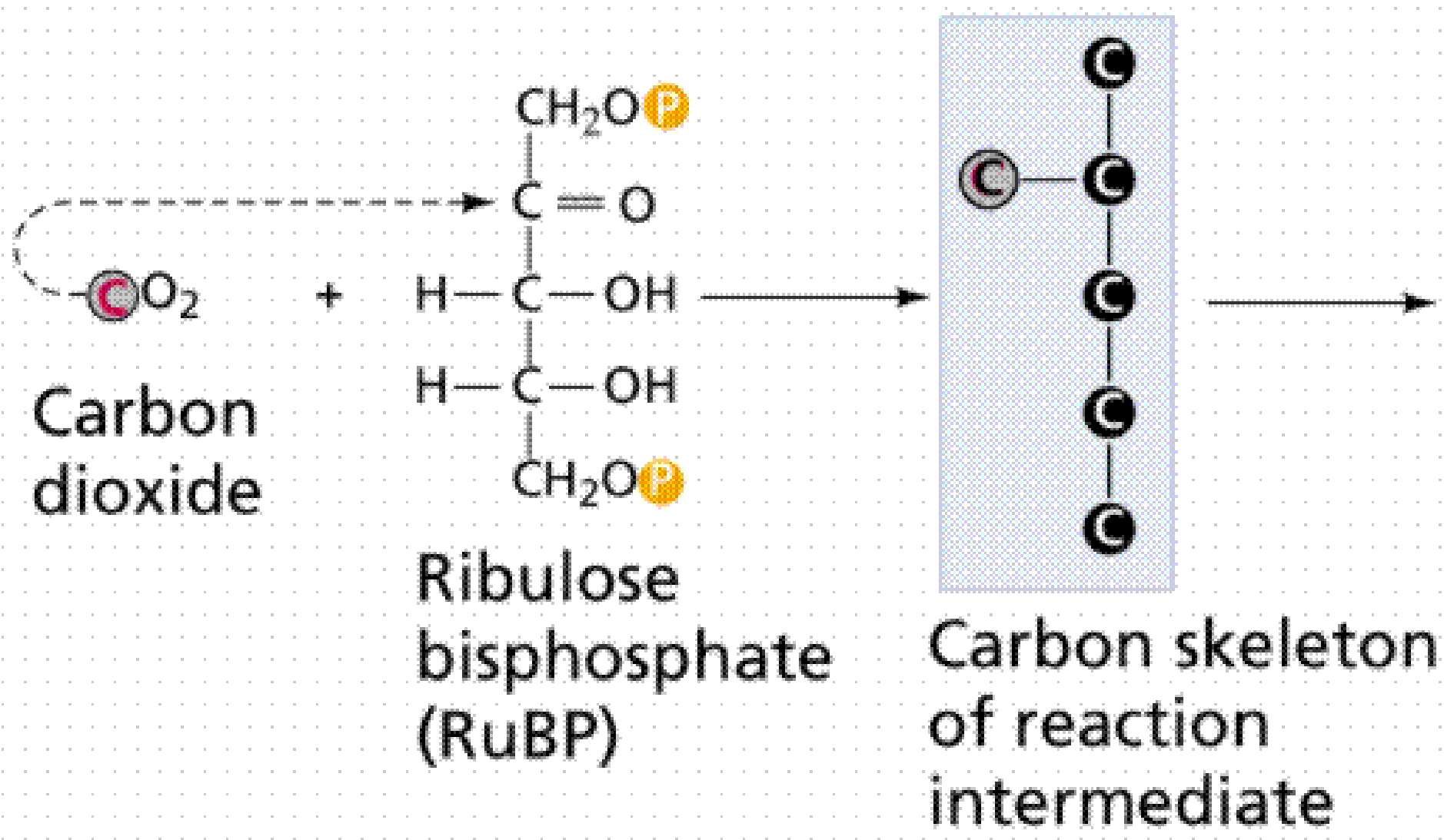

Energy of molecules
Photosystem II
Chl*
Chl
Photon
Redox chain
I
PQ
Cyt
PC
ADP + P
ATP
Photosystem I
Chl*
Chl
Photon
Fd bound
Fd soluble
NADP+ + H
NADPH + H

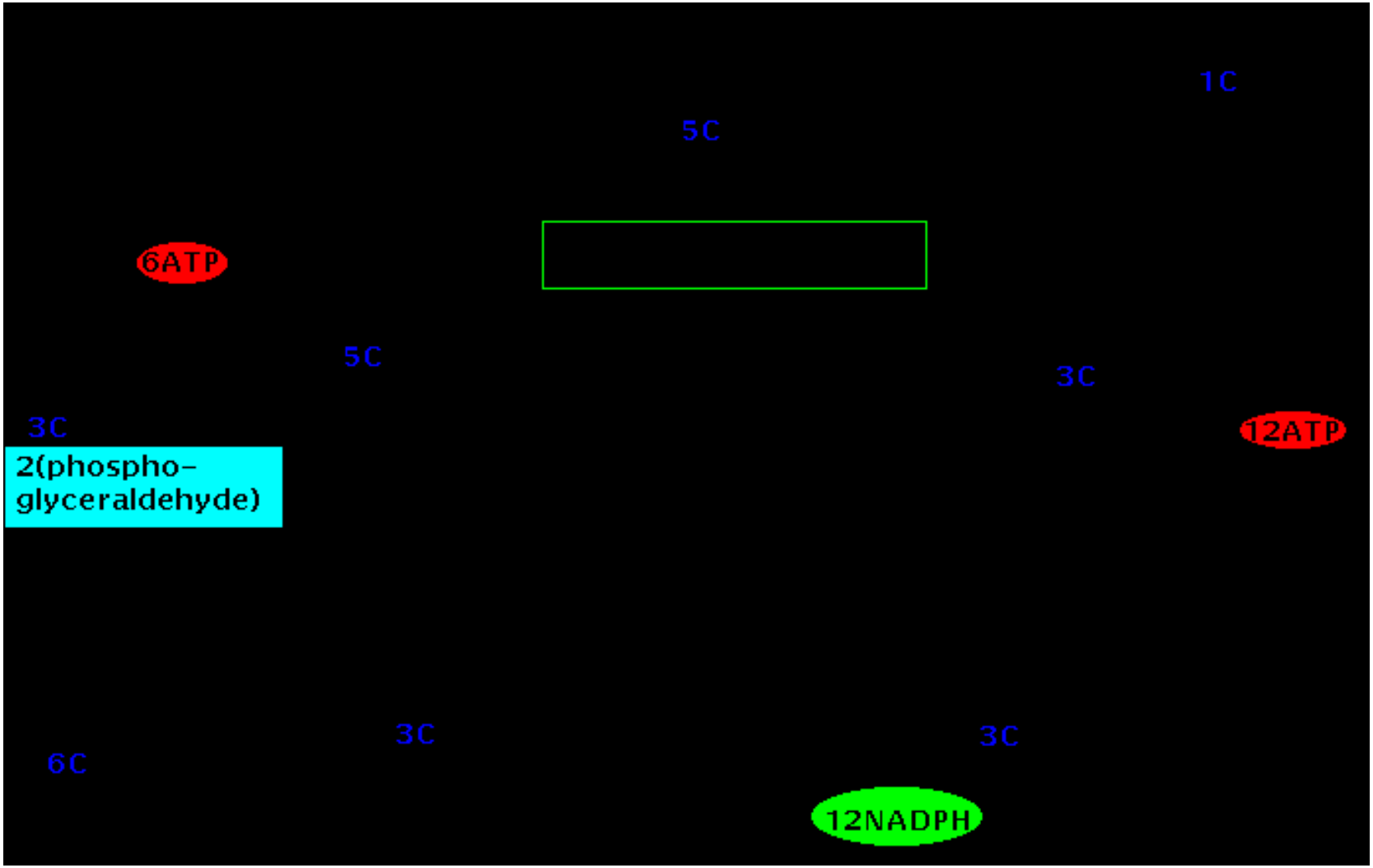


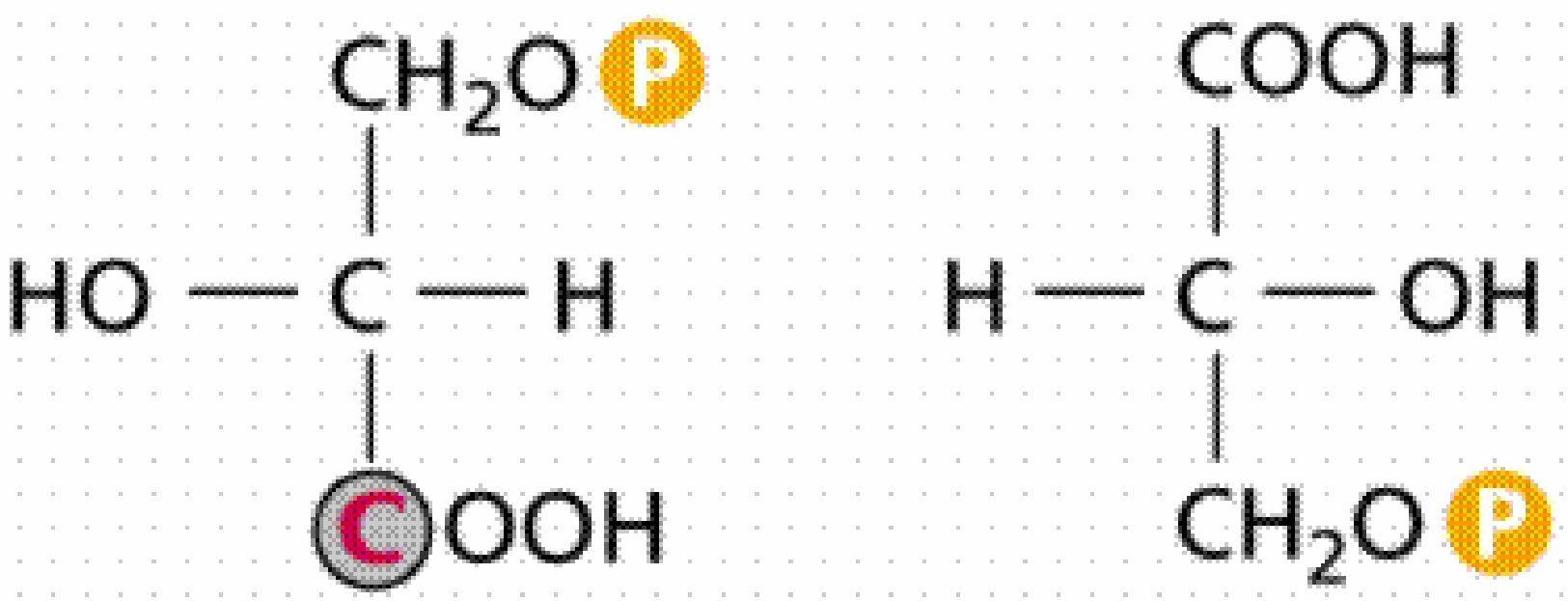



actinic flash
Q_A Q_B
open
photochemistry
P
Y_Z
$(Mn)_4$
weak flash
open
< 1 ns
Q_A^- Q_B
closed
quencher
weak fluores-cence
half open
<1µs
fluores-cence
Q_A^- Q_B^-
150 µs
closed
open

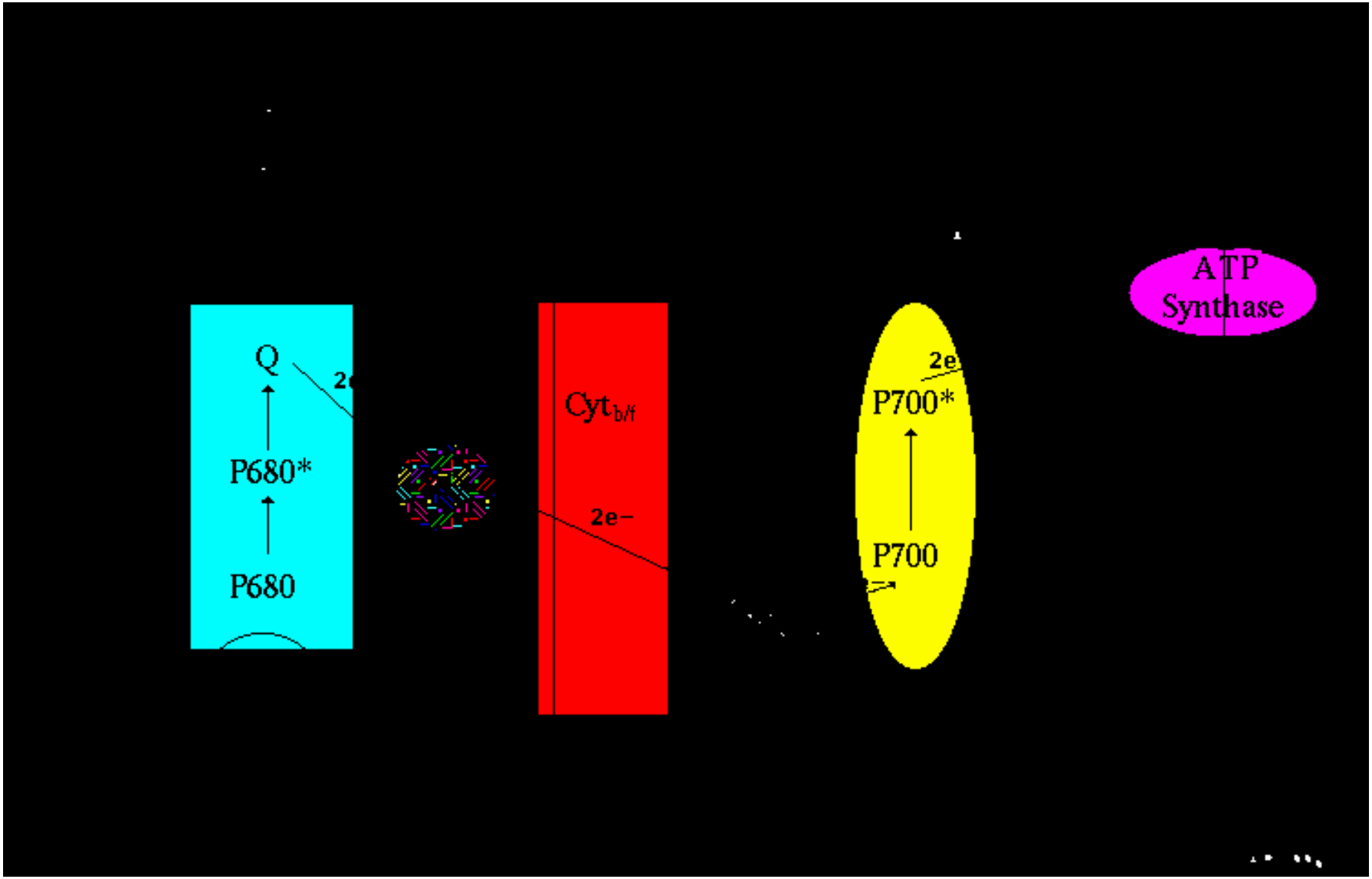

Certain photosynthetic bacteria
light
chlorophyll
energy
ATP
2H
H2S (H donor)
S
CO2
(CH2O)n

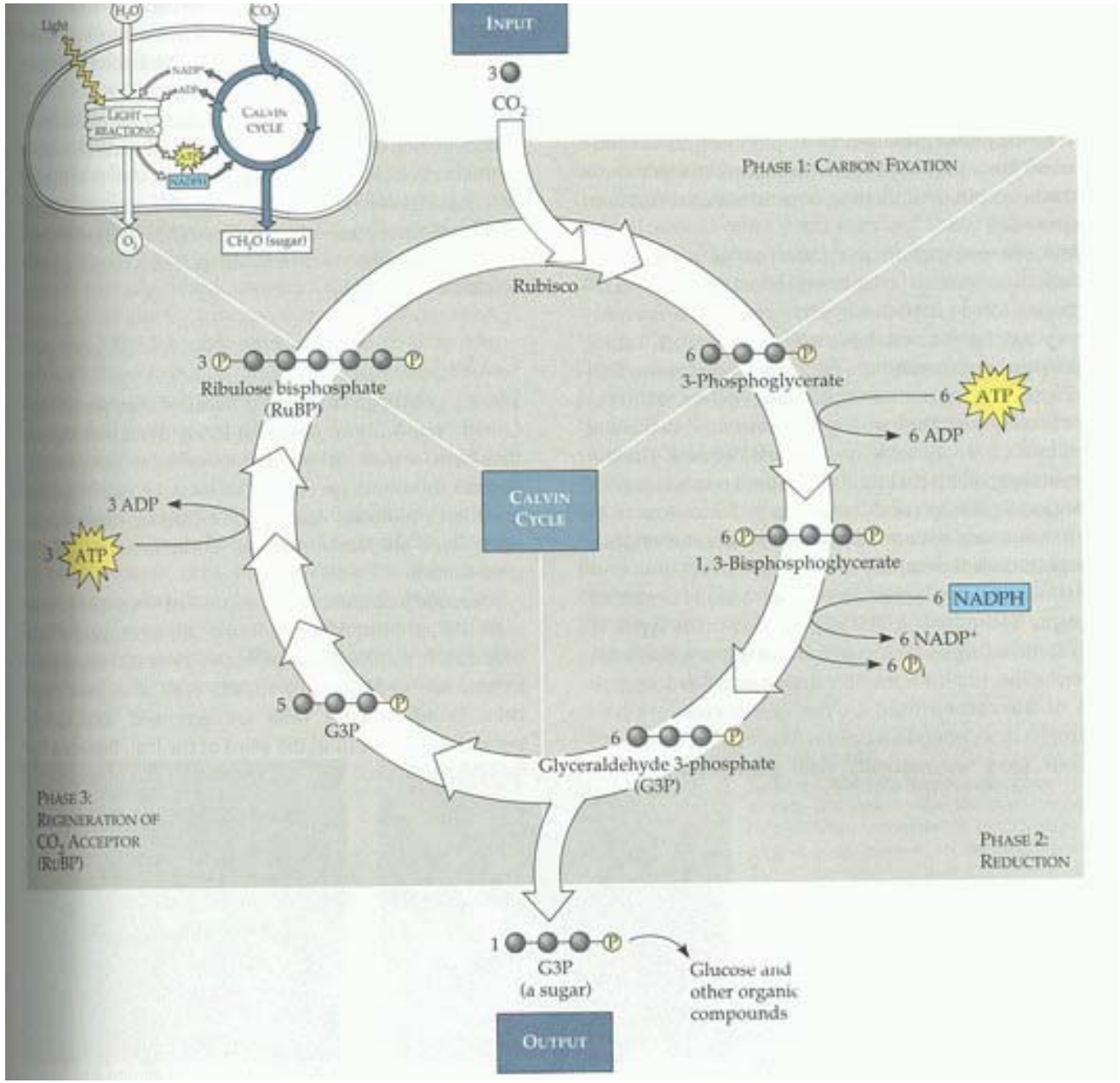

CO_2
+
CH_2O P
C = O
H — C — OH
H — C — OH
CH_2O P
Carbon dioxide
Ribulose bisphosphate (RuBP)
Carbon skeleton of reaction intermediate

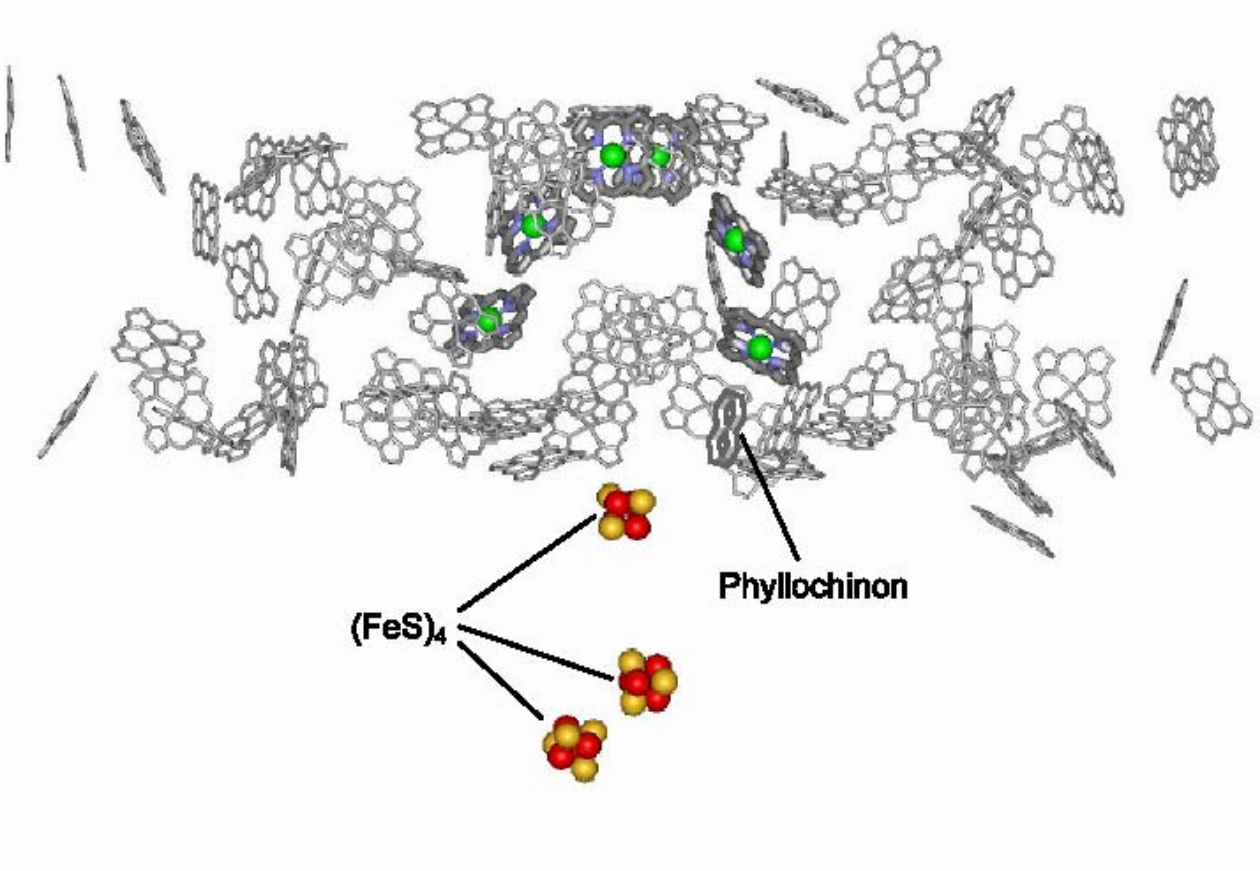

1C
5C
6ATP
5C
3C
3C
12ATP
2(phospho-
glyceraldehyde)
3C
3C
6C
12NADPH

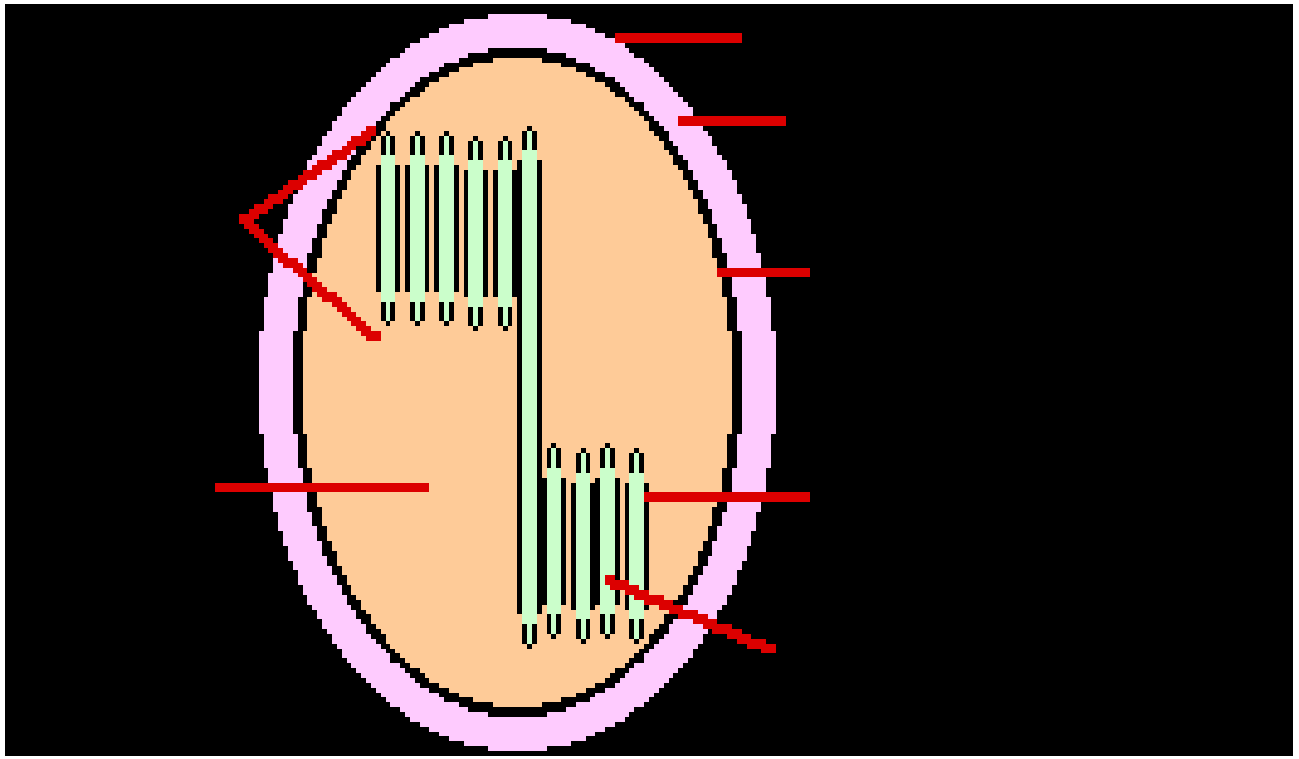


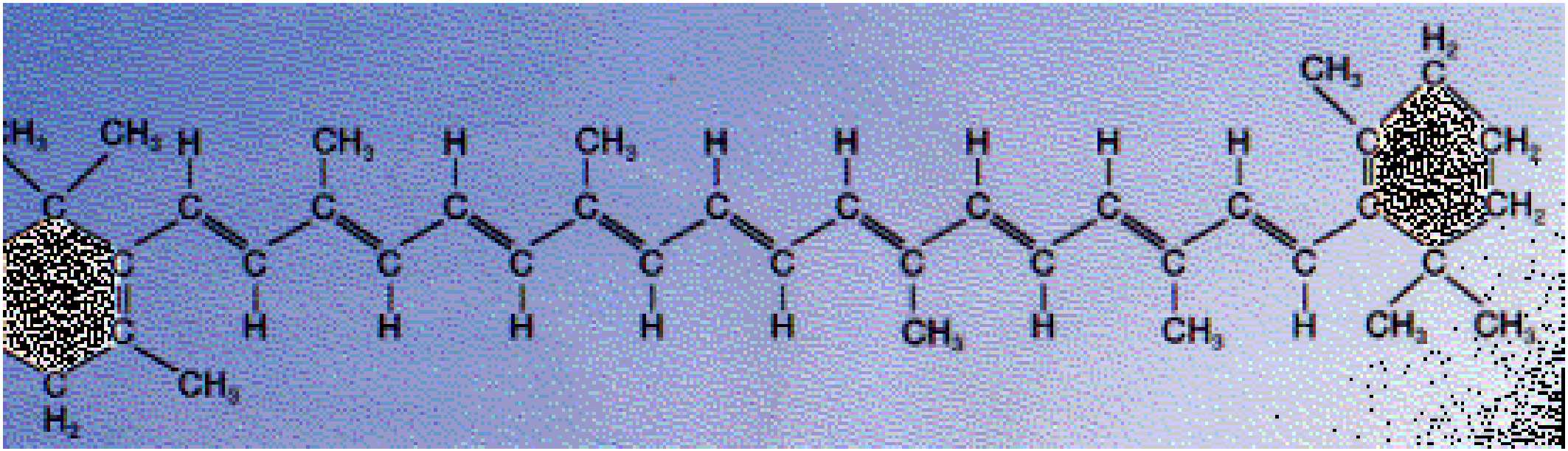
Two molecules of
3-phosphoglyceric acid
(3PG)

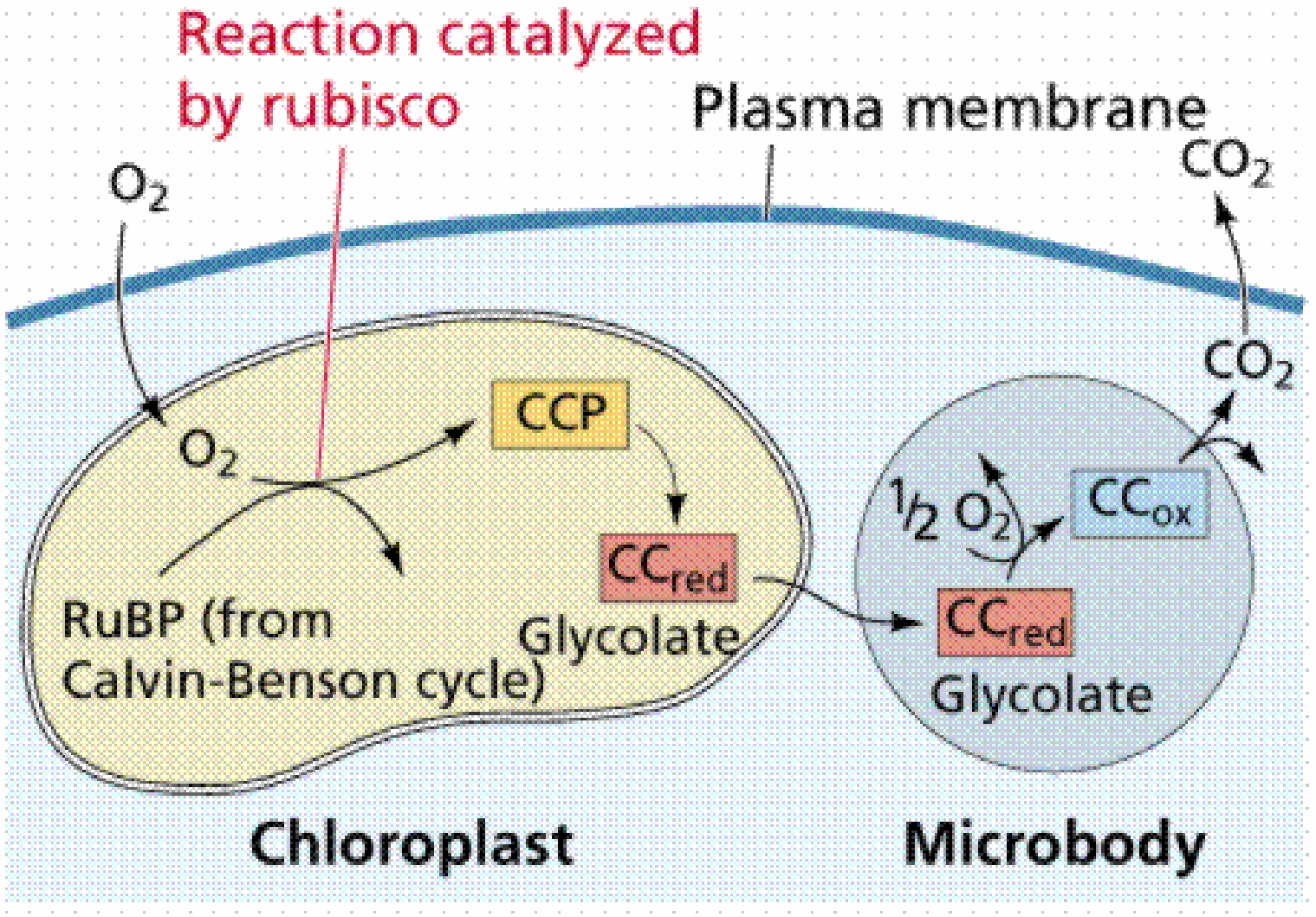

Q
P680*
P680
Cyt$_{b/f}$
2e−
2e
P700*
P700
ATP
Synthase


Light
H_2O
CO_2
NADP+
ADP
Light Reactions
Calvin Cycle
ATP
NADPH
O_2
CH_2O (sugar)
Input
3
CO_2
Phase 1: Carbon Fixation
Rubisco
3 P P P P P
Ribulose bisphosphate (RuBP)
6 P P P
3-Phosphoglycerate
6 ATP
6 ADP
Calvin Cycle
3 ADP
3 ATP
6 P P P P
1, 3-Bisphosphoglycerate
6 NADPH
6 NADP+
6 P_i
5 P P P
G3P
6 P P P
Glyceraldehyde 3-phosphate (G3P)
Phase 3: Regeneration of CO_2 Acceptor (RuBP)
Phase 2: Reduction
1 P P P
G3P (a sugar)
Glucose and other organic compounds
Output


(FeS)4
Phyllochinon






Reaction catalyzed
by rubisco
Plasma membrane
O_2
CO_2
O_2
CCP
CC_{red}
RuBP (from
Calvin-Benson cycle)
Glycolate
CO_2
½ O_2
CC_{ox}
CC_{red}
Glycolate
Chloroplast
Microbody