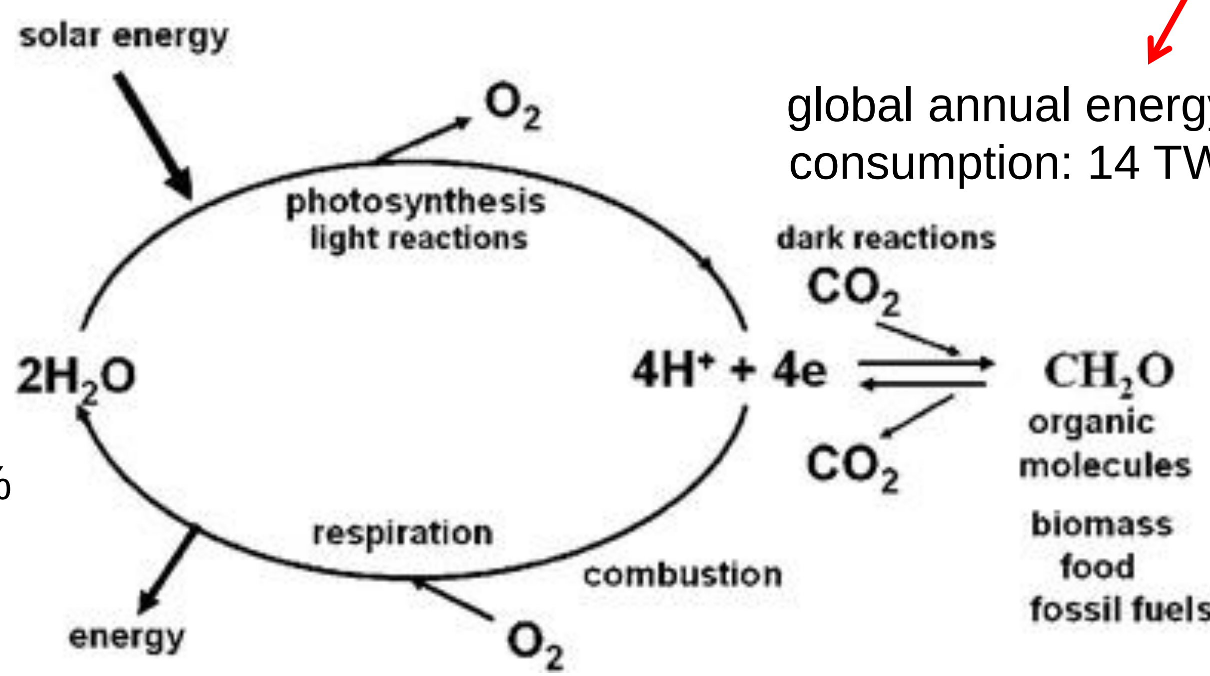
$$H_2O + CO_2 \underset{\textbf{respirazione}\ (\textit{downhill catalysis})}{\overset{\textbf{fotosintesi}\ (\textit{uphill catalysis})}{\rightleftharpoons}} 1/n\ (CH_2O)_n + O_2 \qquad \Delta H = 470\ \text{kJ/mol}$$

100×10^9 ton/y of $(CH_2O)_n$ from CO_2
1 g of glucose per m^2 of leaf surface per hour
100 TW/y = 0.1% of total solar energy (10^5 TW)

Energy stored as biomass

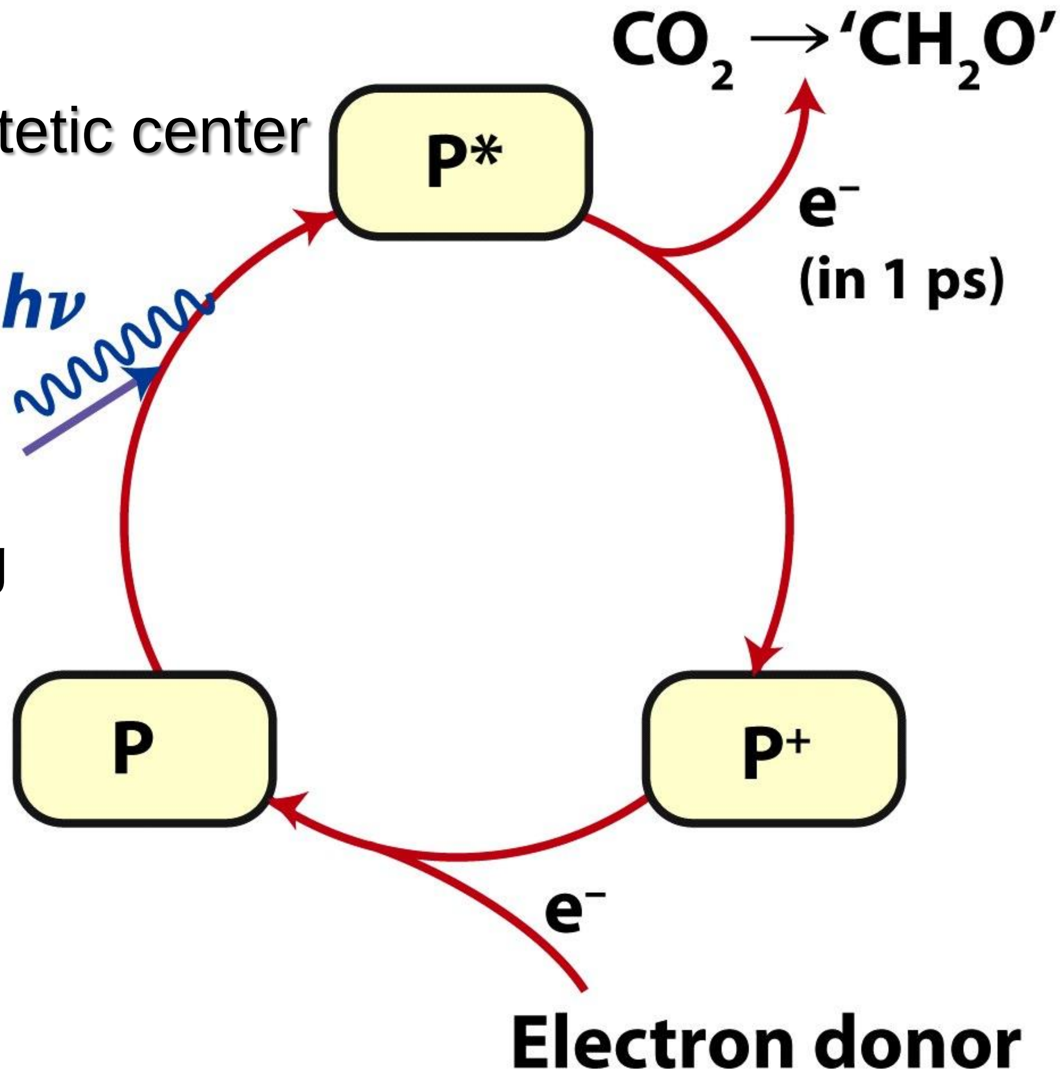
global annual energy consumption: 14 TW



Max efficiency: 4.5%

Photoinduced charge separation

P = photosyntetic center

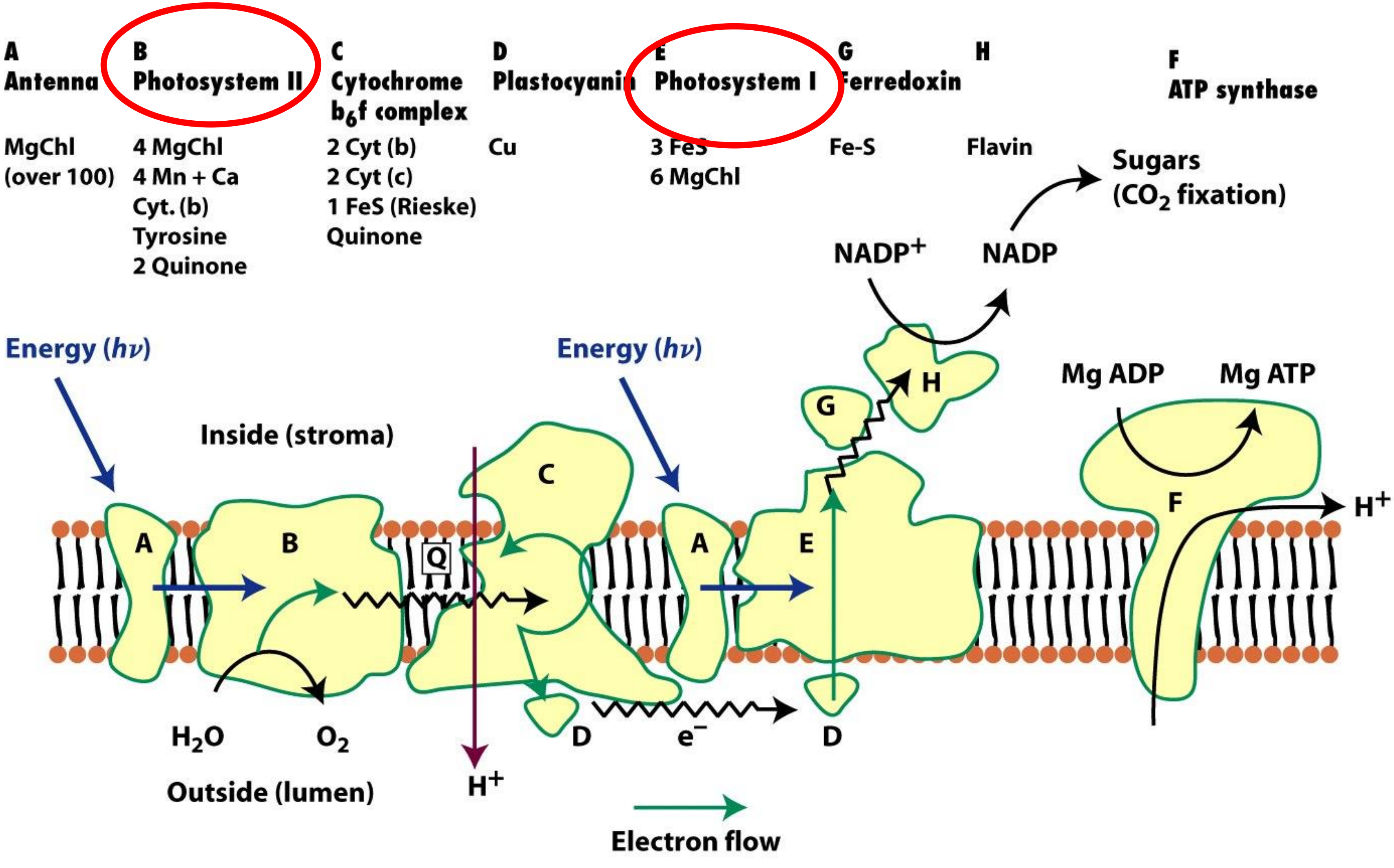


LH

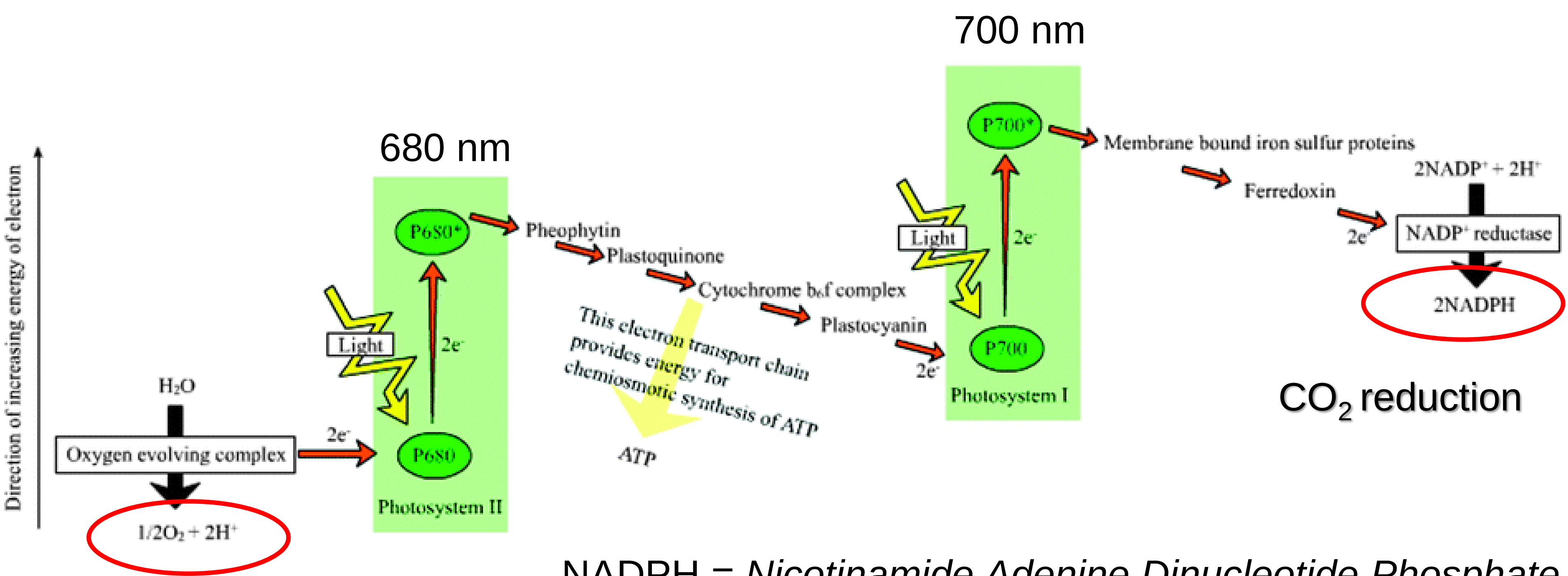
Light Harvesting

(H_2O)

Photosyntetic process in plants



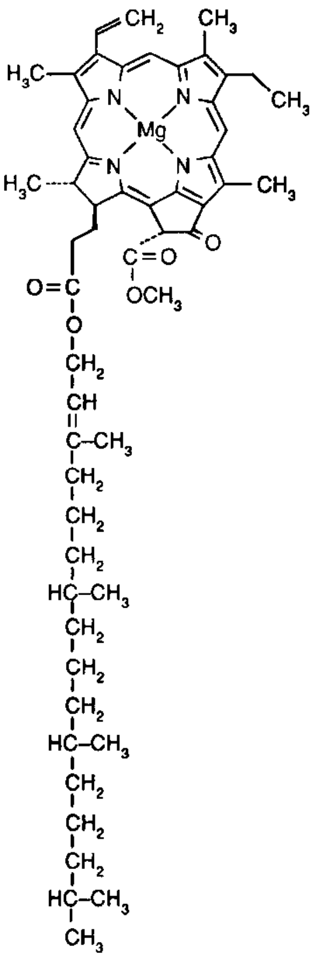
"Z-shaped" diagram for redox potential



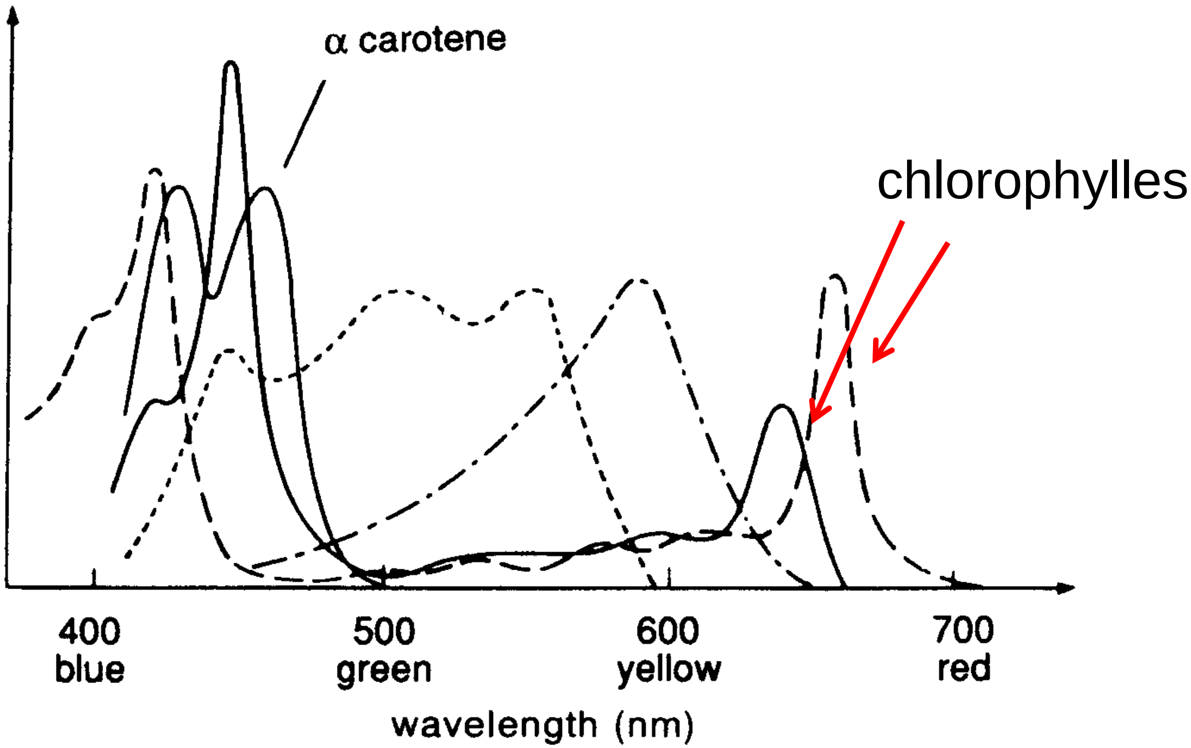
NADPH = *Nicotinamide Adenine Dinucleotide Phosphate*

For each electron taken from H_2O and transfered to CO_2 the energy of two photons is necessary, one in PSII and the second in PSI

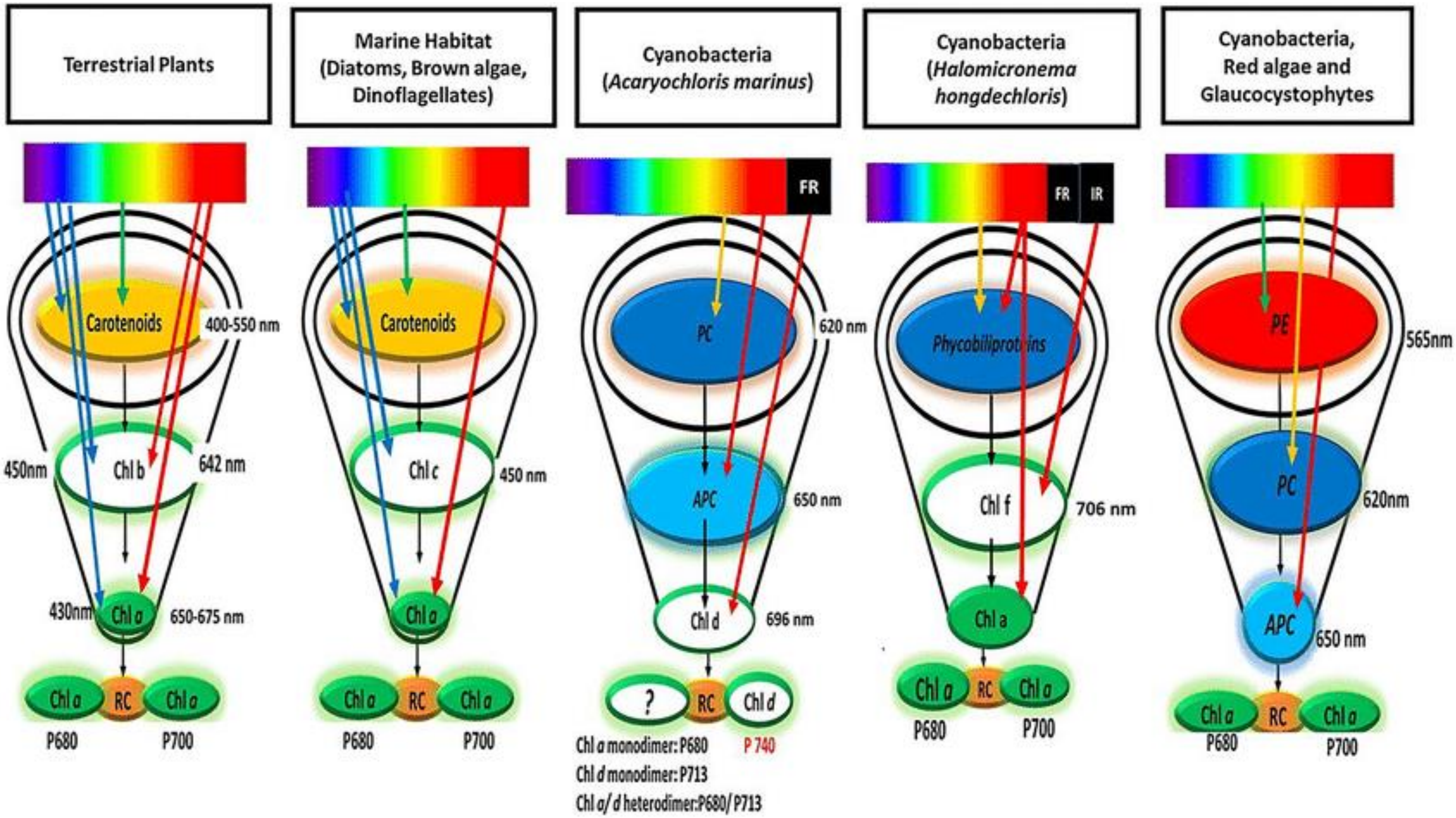
Pigments for *light harvesting*



chlorophyll *a*

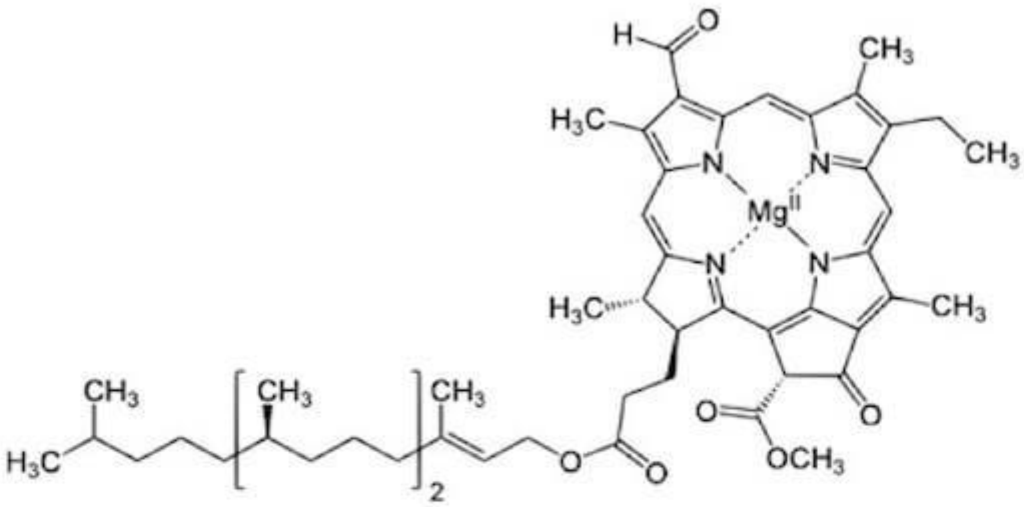


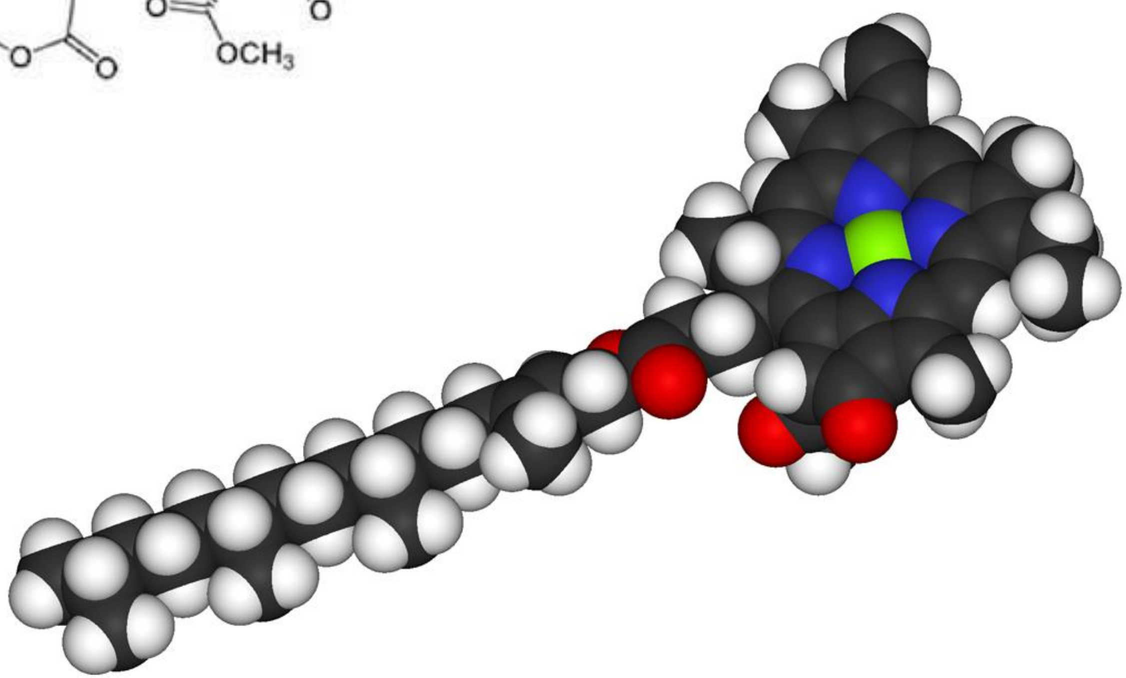
Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (——), phycocyanin (–·–·), phycoerythrin (–––––)



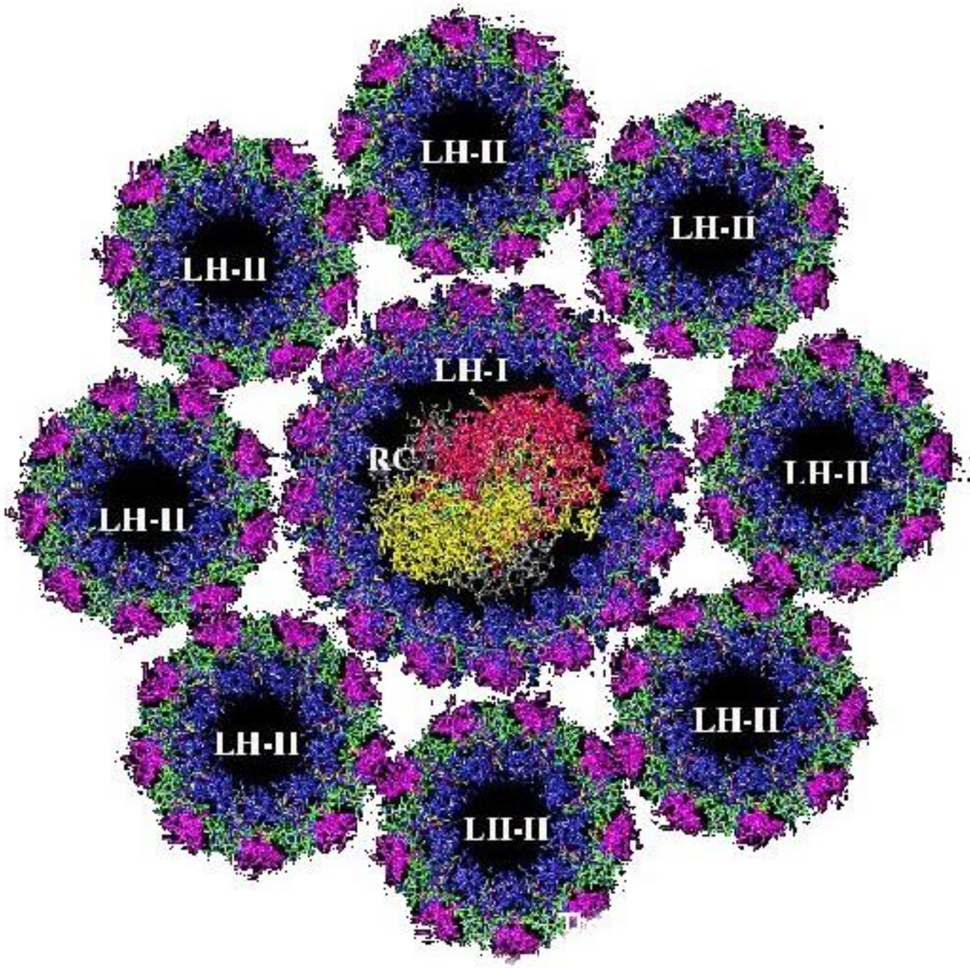
Terrestrial Plants
Marine Habitat (Diatoms, Brown algae, Dinoflagellates)
Cyanobacteria (*Acaryochloris marinus*)
Cyanobacteria (*Halomicronema hongdechloris*)
Cyanobacteria, Red algae and Glaucocystophytes
Carotenoids
400-550 nm
450nm
Chl b
642 nm
430nm
Chl *a*
650-675 nm
Chl *a*
RC
Chl *a*
P680
P700
Carotenoids
Chl c
450 nm
Chl *a*
Chl *a*
RC
Chl *a*
P680
P700
FR
PC
620 nm
APC
650 nm
Chl d
696 nm
?
RC
Chl *d*
Chl *a* monodimer: P680
P 740
Chl *d* monodimer: P713
Chl *a*/ *d* heterodimer:P680/ P713
FR
IR
Phycobiliproteins
Chl f
706 nm
Chl a
Chl *a*
RC
Chl *a*
P680
P700
PE
565nm
PC
620nm
APC
650 nm
Chl *a*
RC
Chl *a*
P680
P700

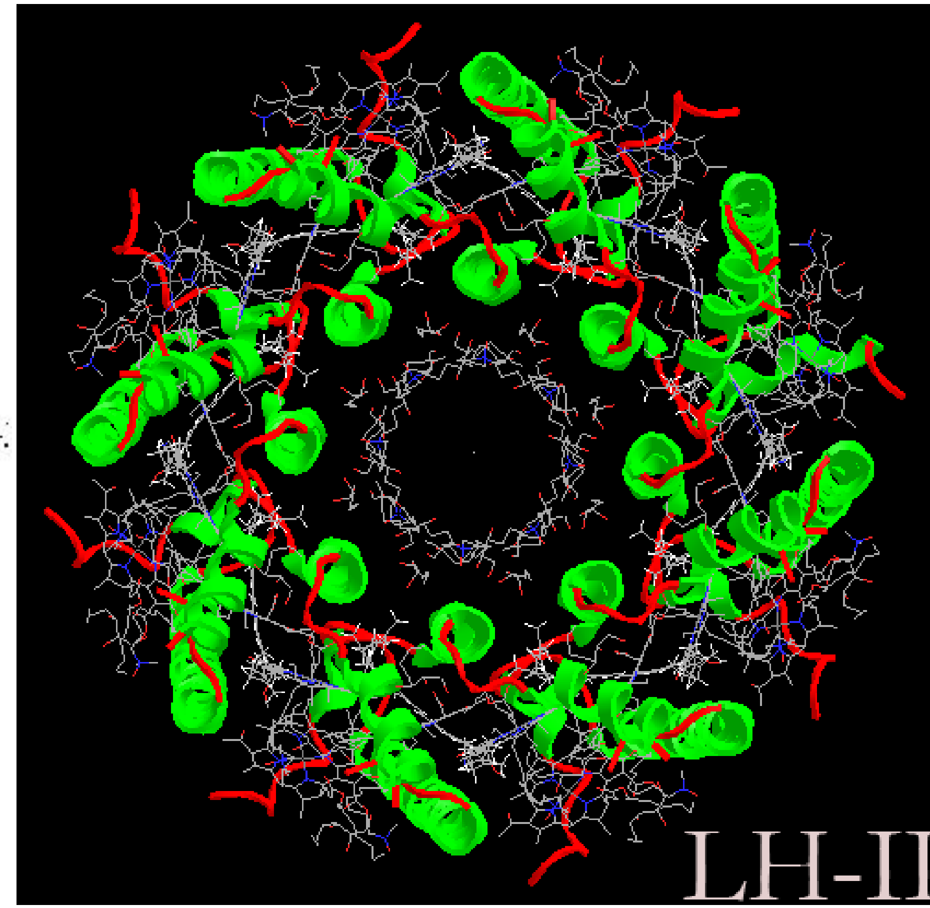
Chlorophyll



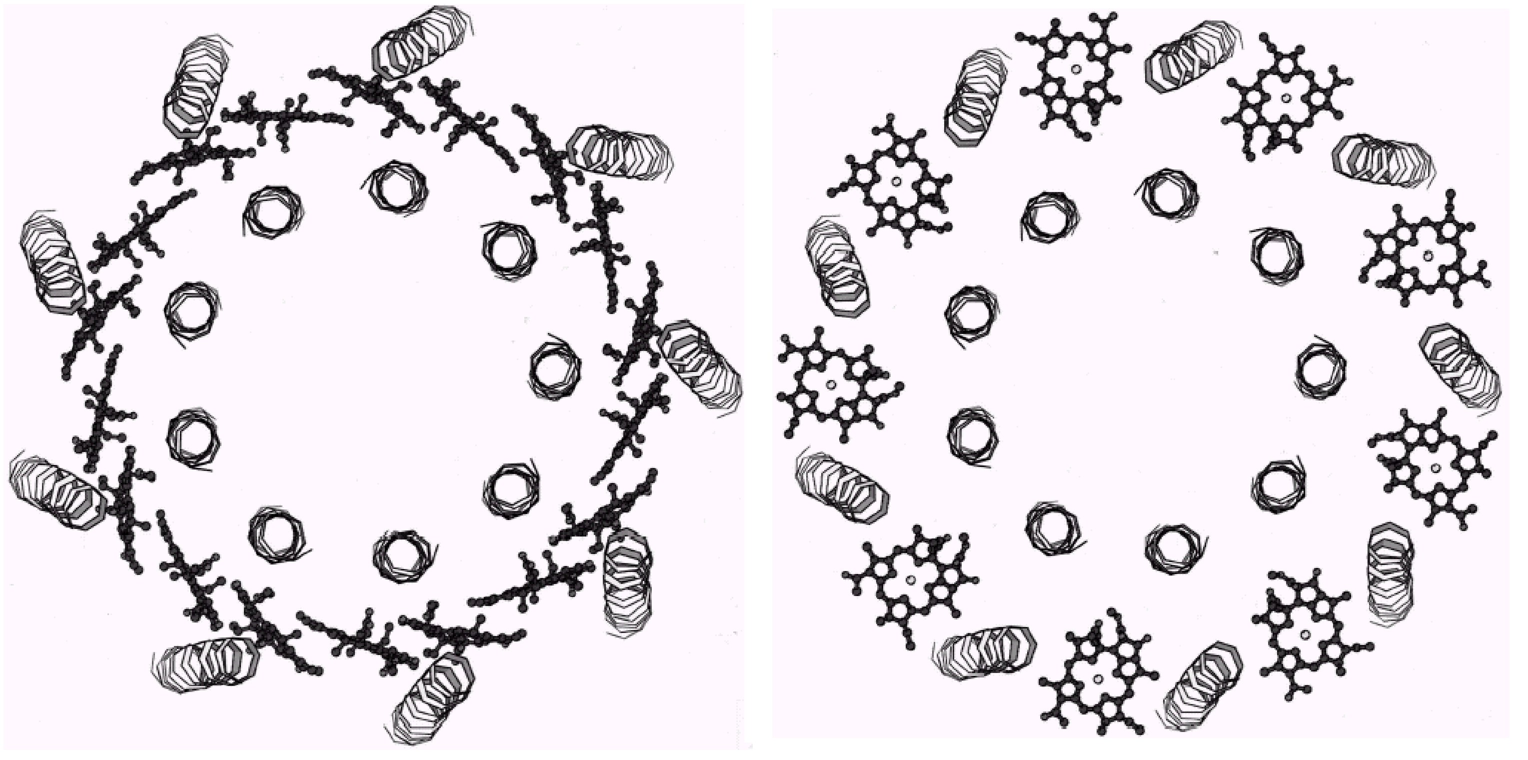


Antenna systems for *light-harvesting* and *exciton transfer*

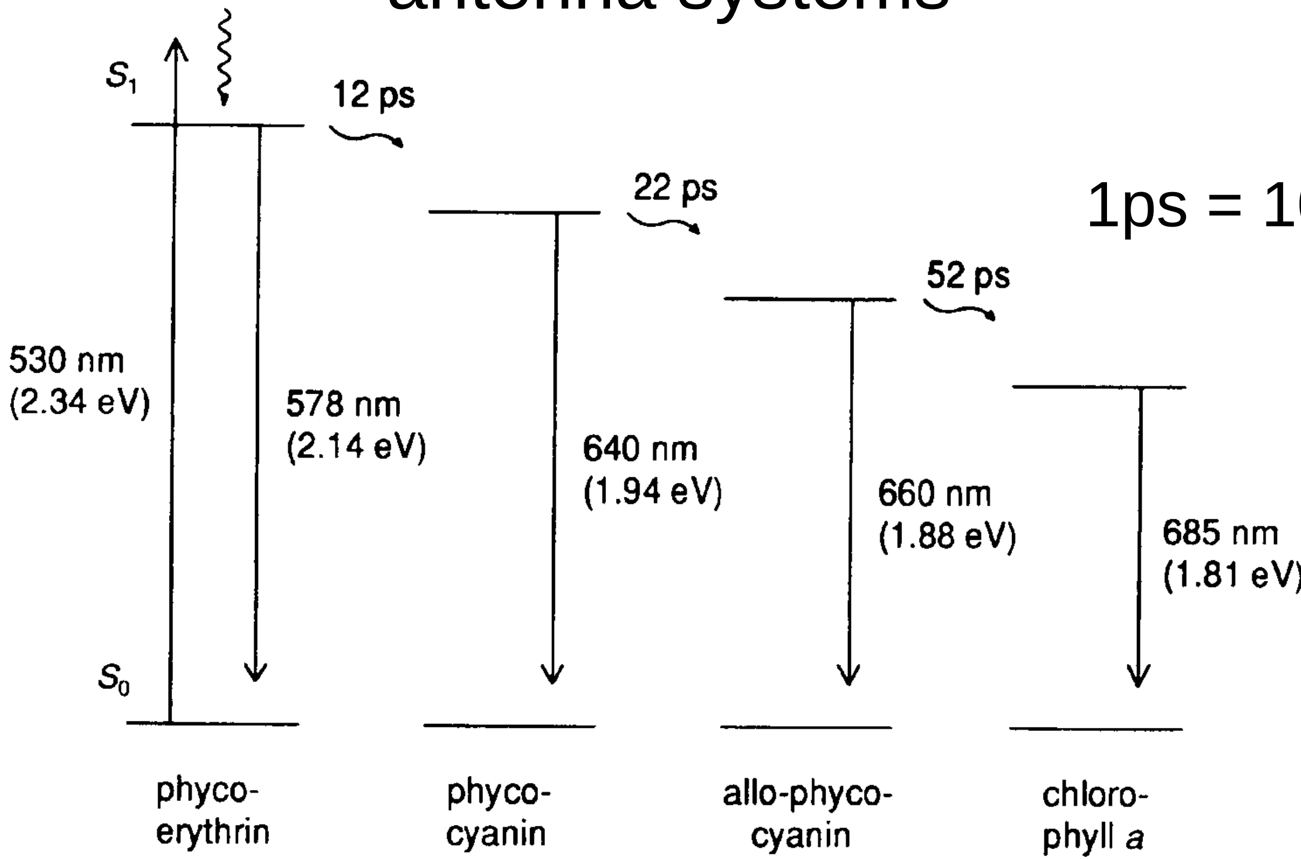




Antenna systems for *light-harvesting* and *exciton transfer*



Cascade energy transfer (*exciton transfer*) in the antenna systems

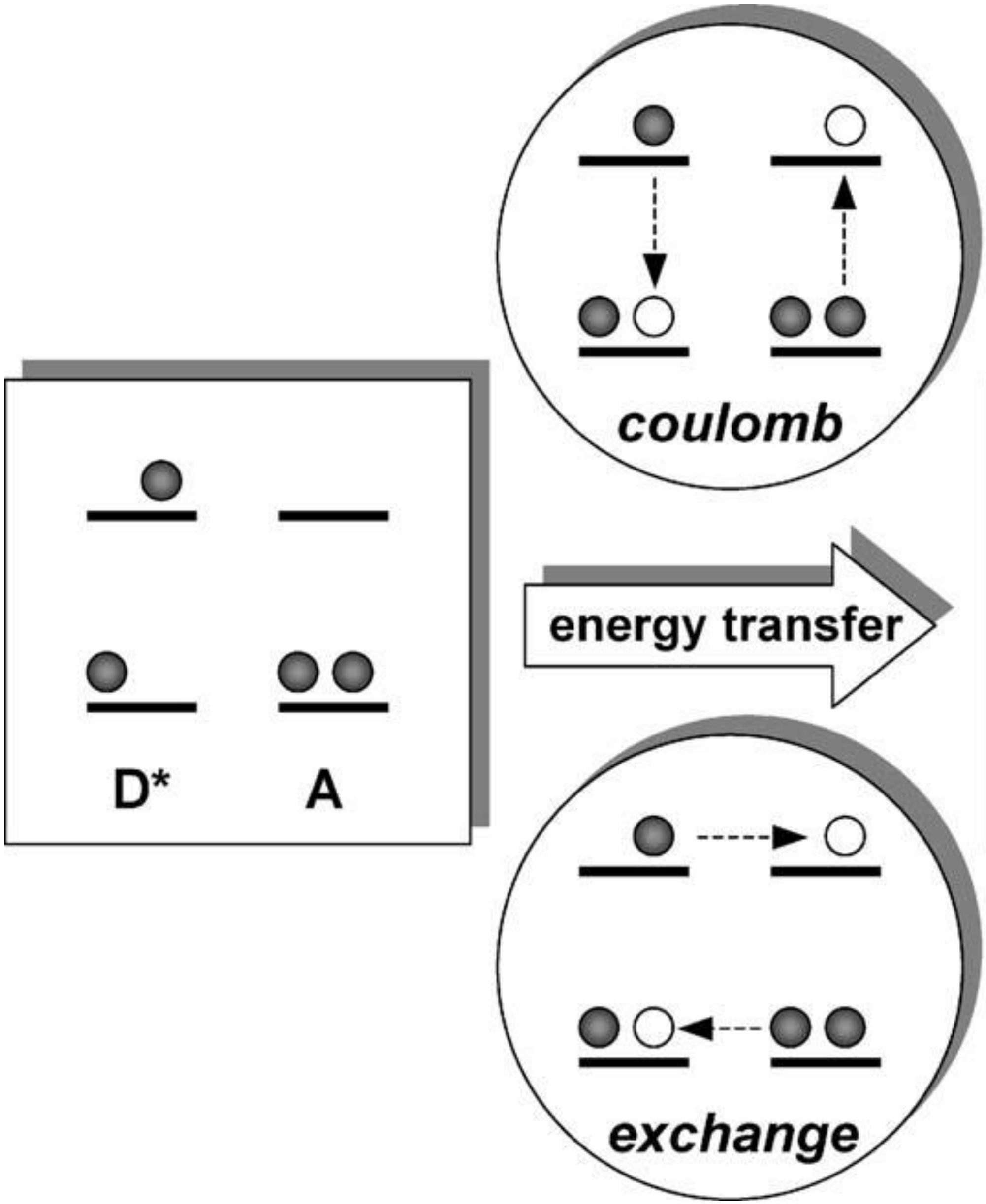


1ps = 10^{-12} s

95% efficiency

Mechanisms for the *exciton transfer*

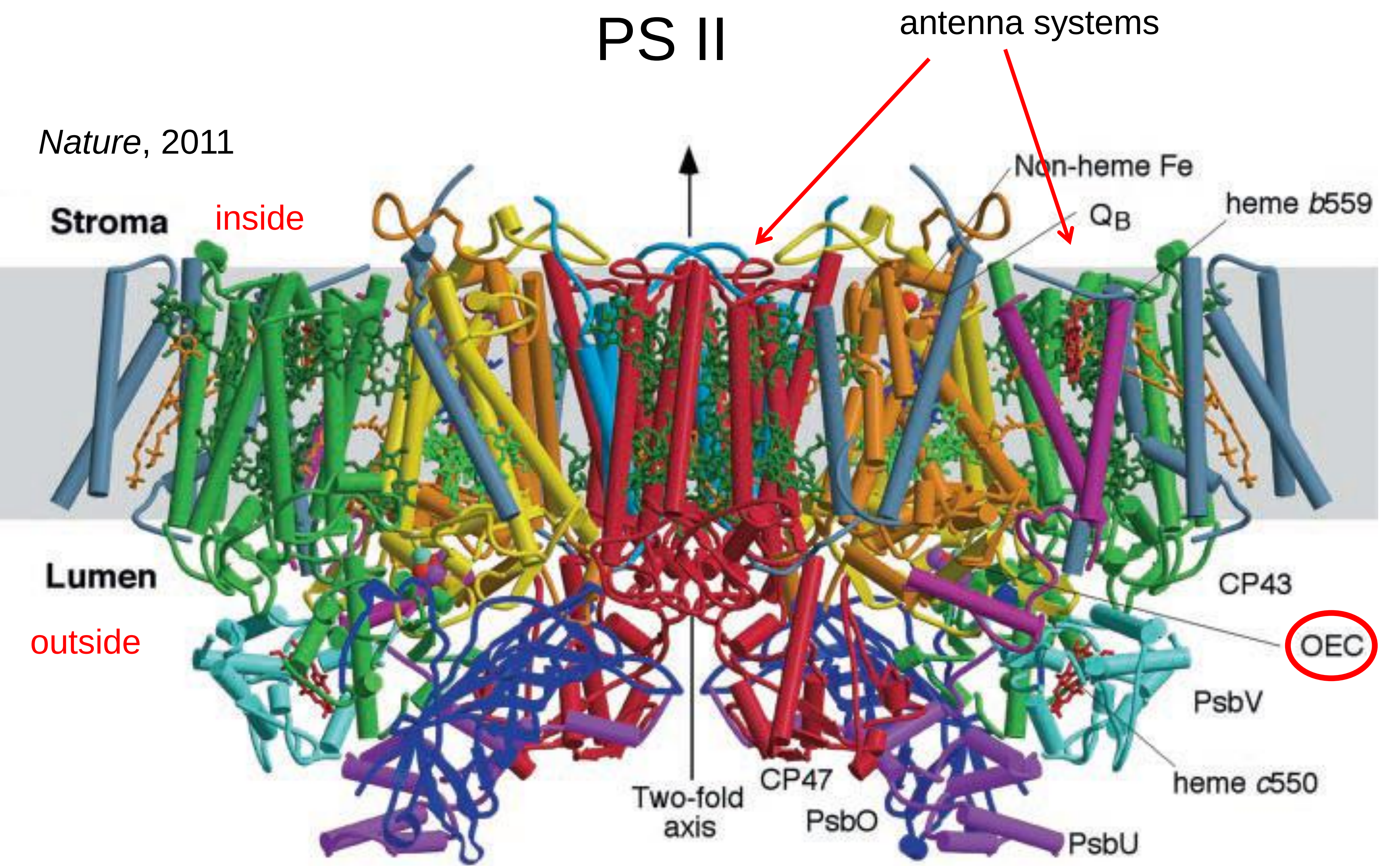
Long range mechanism
No physical contact
Förster-type



Short-range mechanism
requires orbital overlap
Dexter-type

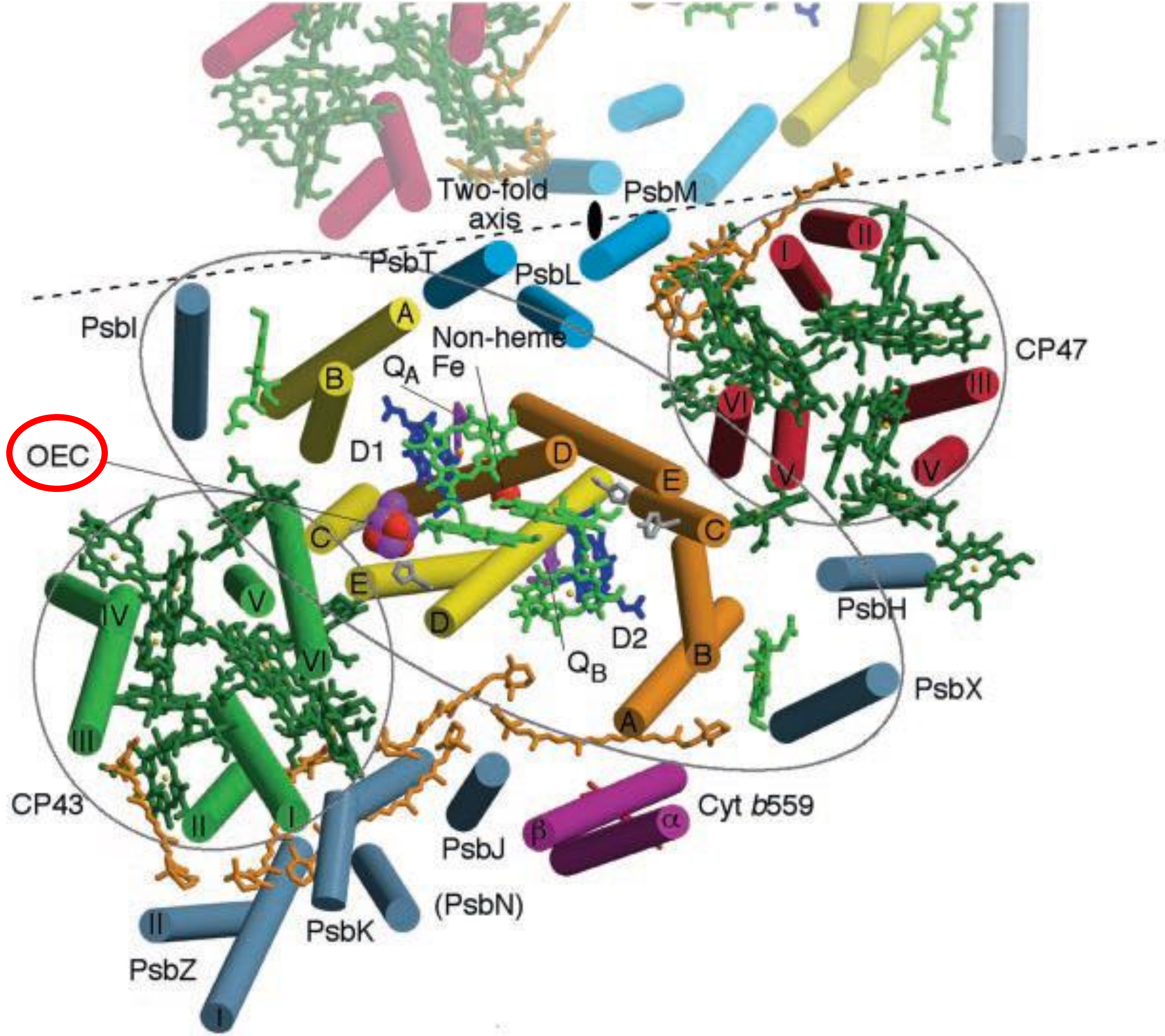
PS II

Nature, 2011

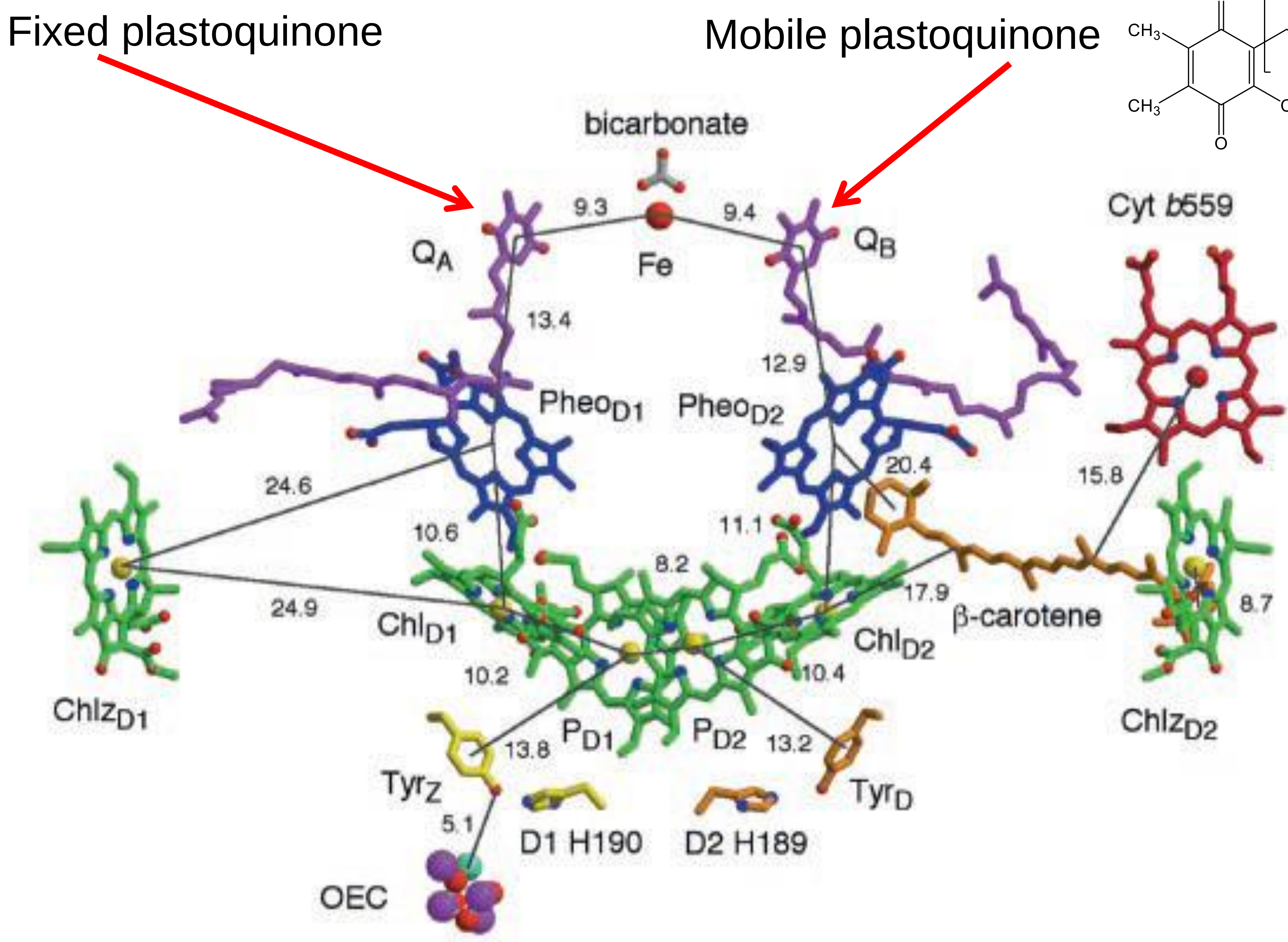


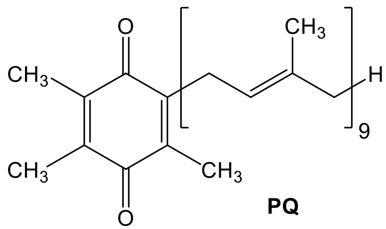
19 proteic subunits, 2 pheophytins, 36 chlorophylles, 11 carotenoids, several cofactors

PS II


Two-fold
axis
PsbM
PsbT
PsbL
PsbI
Non-heme
Fe
Q_A
CP47
D1
OEC
A
B
C
D
E
I
II
III
IV
V
VI
D2
Q_B
PsbH
PsbX
CP43
Cyt *b*559
α
β
PsbJ
(PsbN)
PsbK
PsbZ

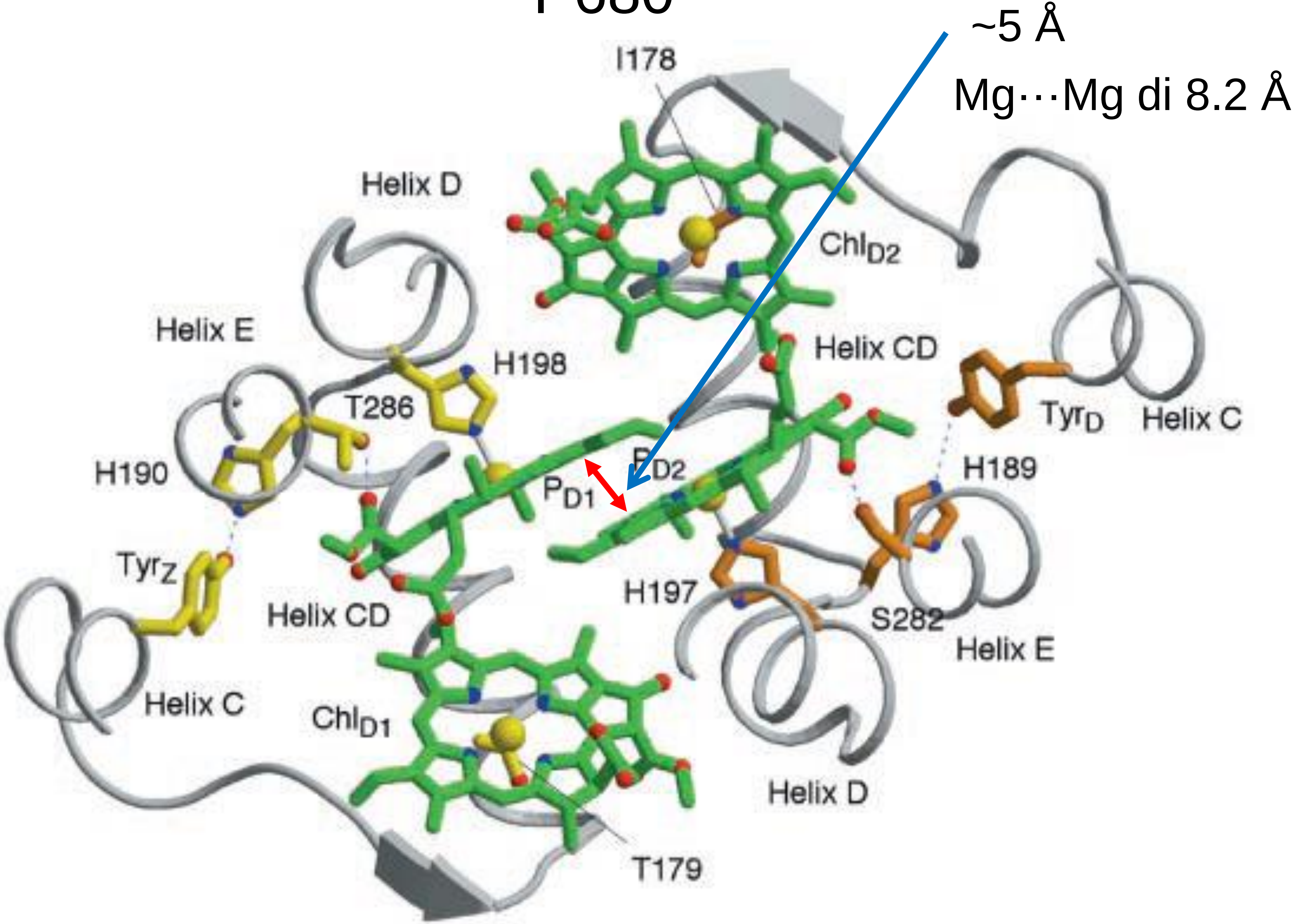
P680



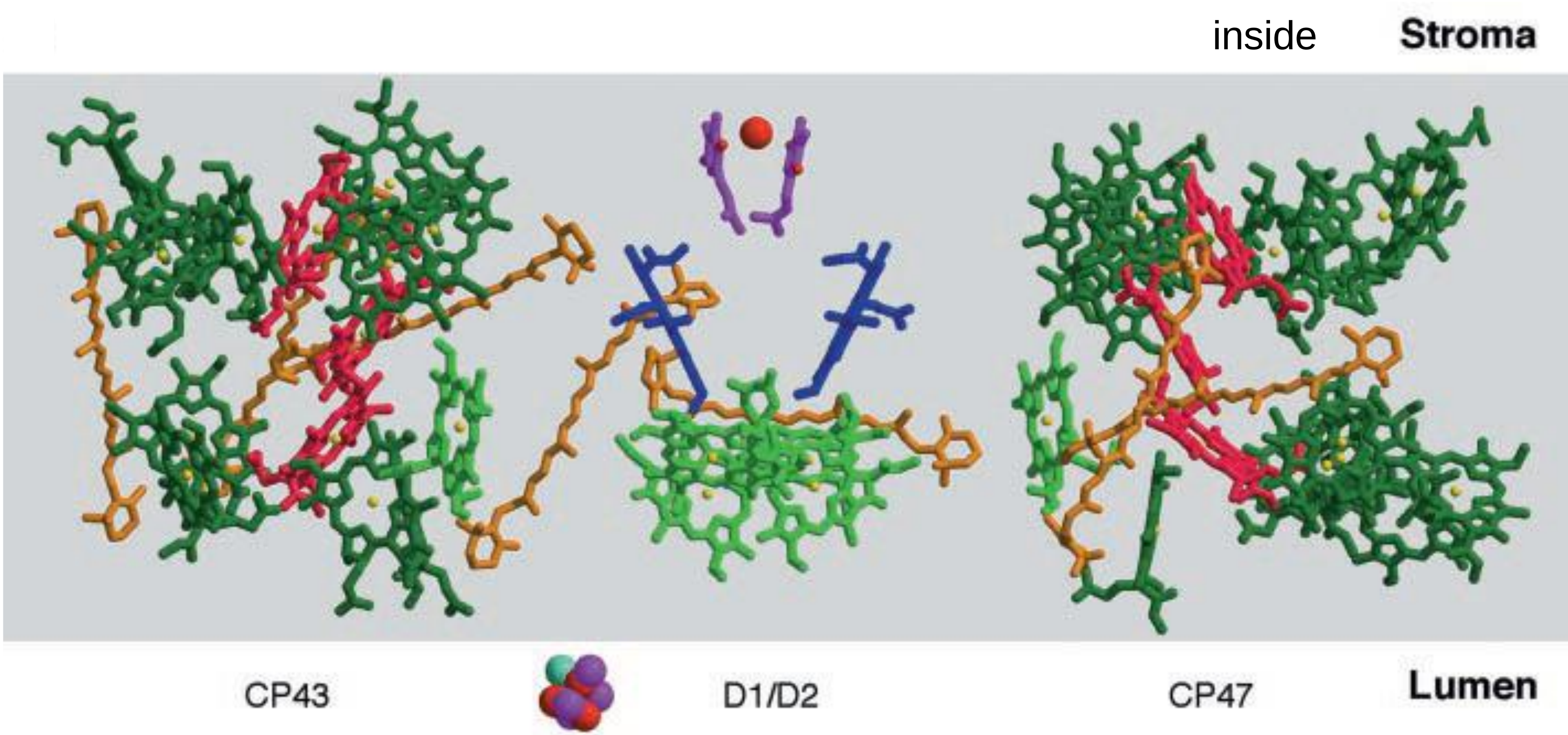


$$2H_2O + 2PQ + 4H^+_{\text{inside (stroma)}} \xrightarrow{4h\nu} O_2 + 2PQH_2 + 4H^+_{\text{outside (lumen)}}$$

P680

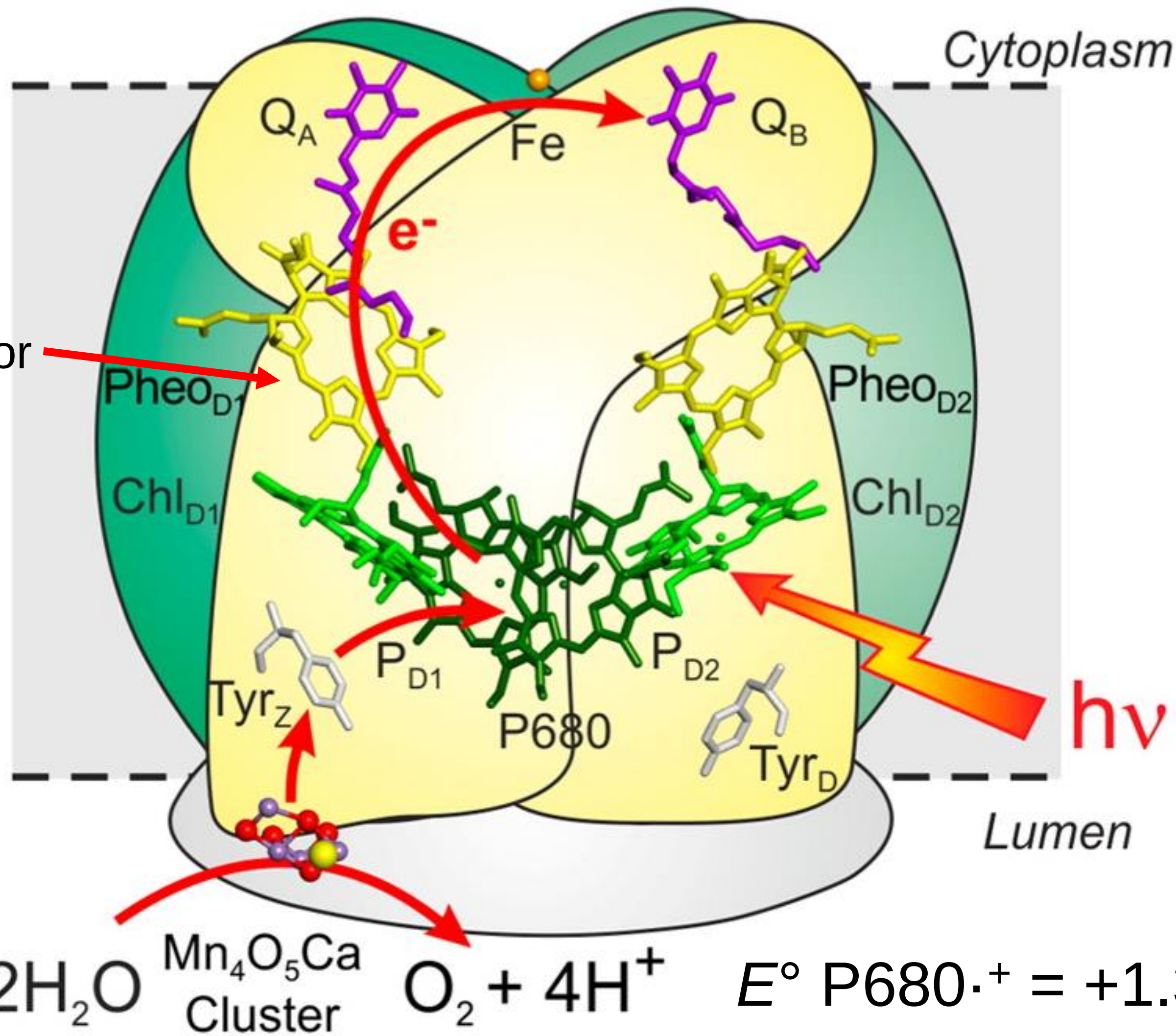

~5 Å
Mg···Mg di 8.2 Å
I178
Helix D
ChlD2
Helix E
H198
Helix CD
T286
TyrD
Helix C
H190
PD2
PD1
H189
TyrZ
H197
Helix CD
S282
Helix E
Helix C
ChlD1
Helix D
T179

Photoreaction center and antenna systems



The photoreaction center of photosystem II, P680

Primary acceptor



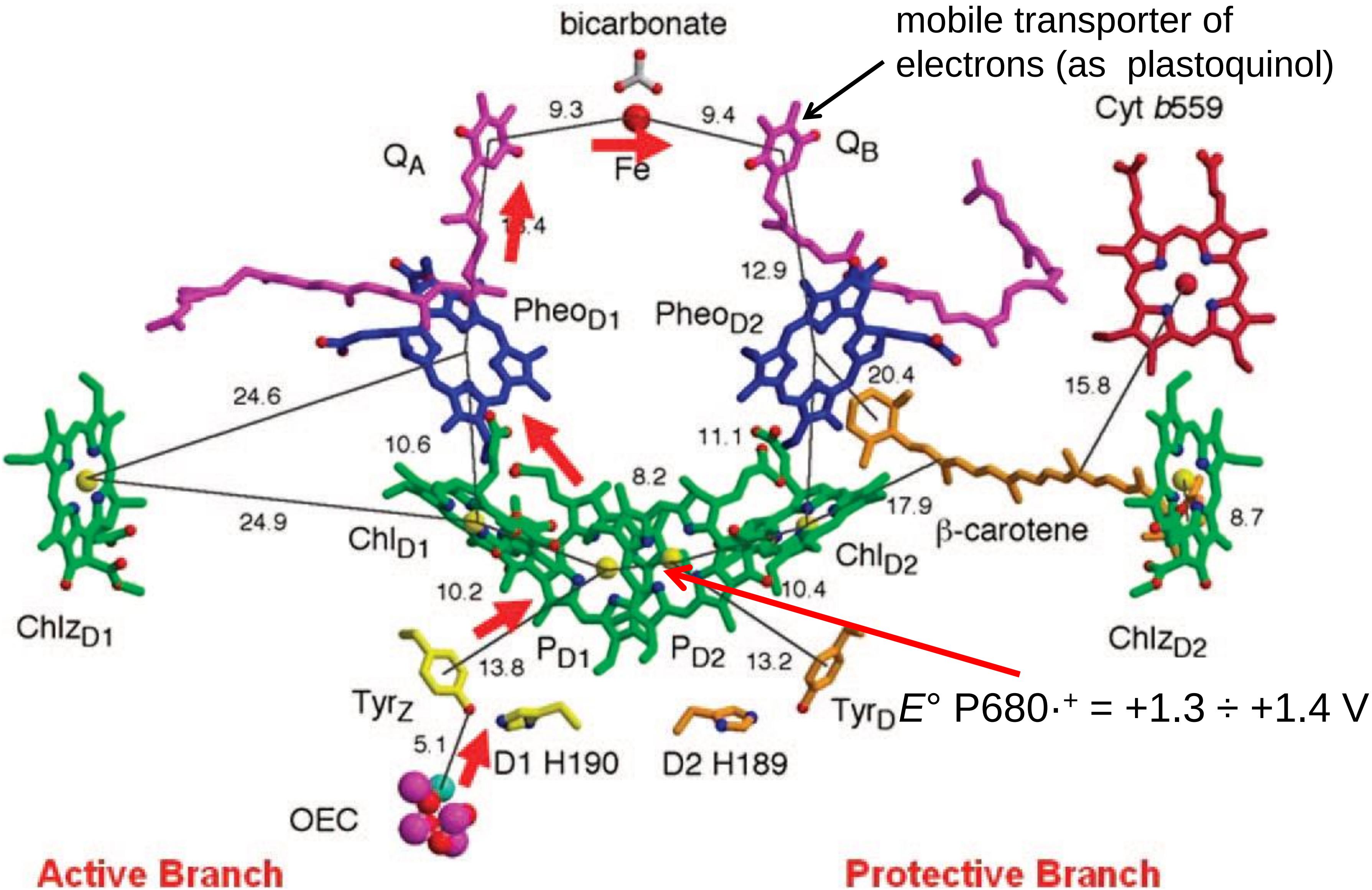
inside

outside

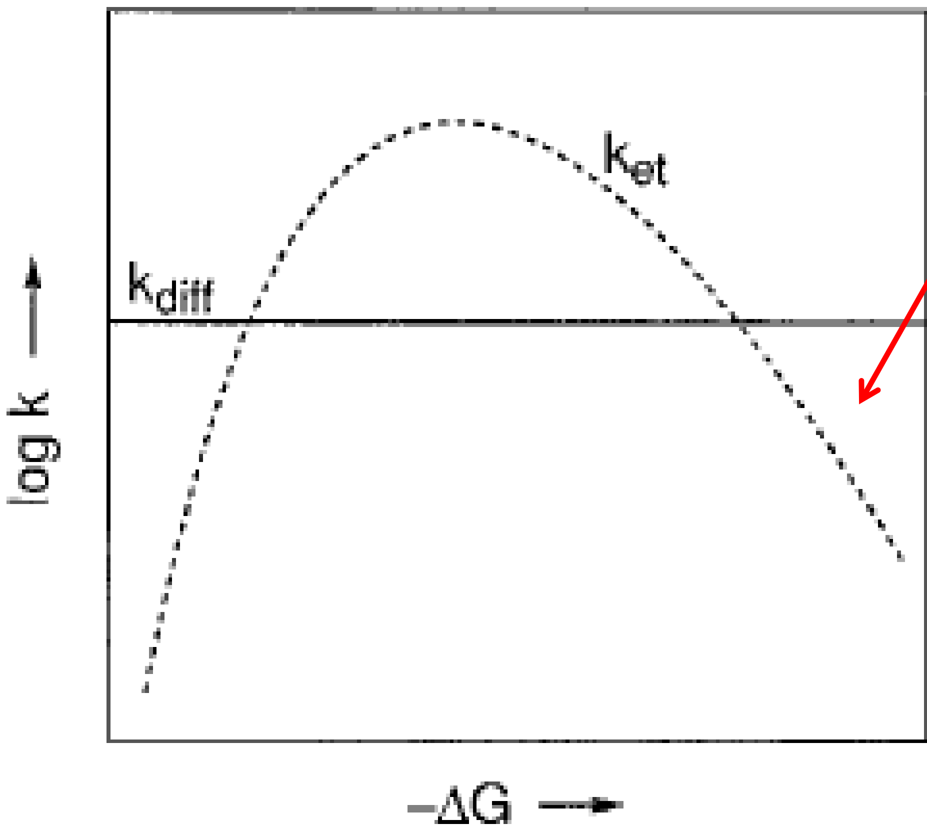
$E°$ P680$\cdot^+$ = +1.3 ÷ +1.4 V

The highest potential in biological systems

Electron transport cofactors

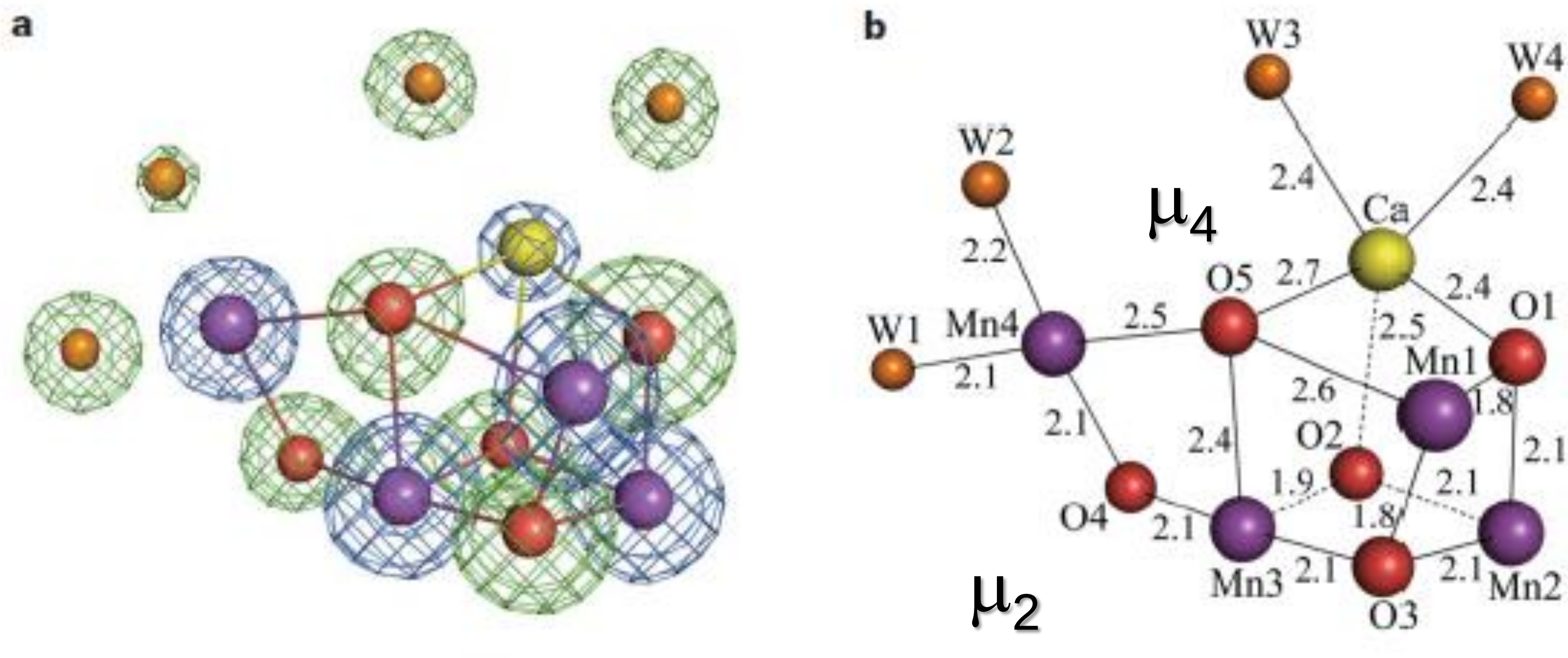


Marcus inverted region



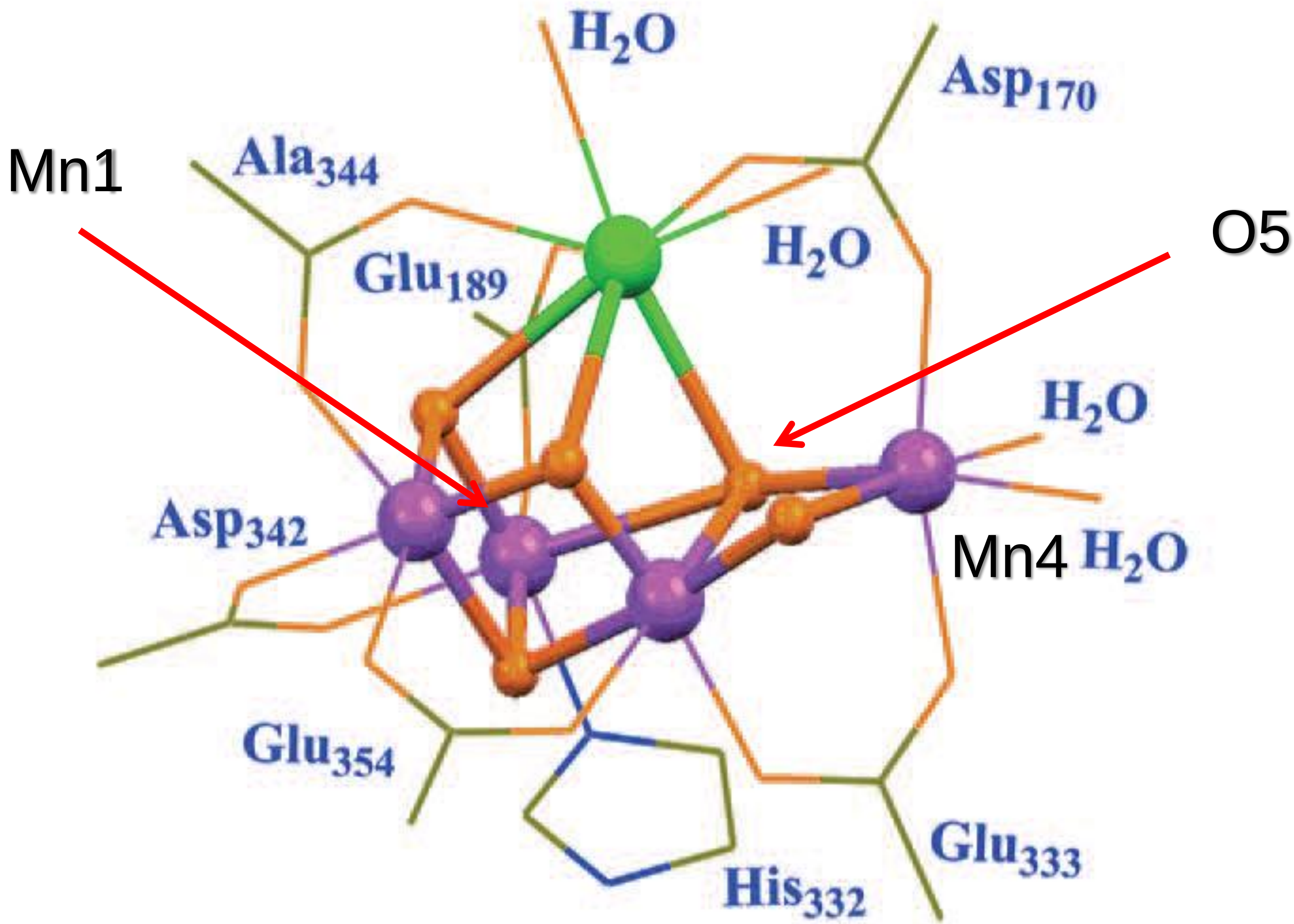
Oxygen Evolving Complex (OEC)

Mn_4CaO_5



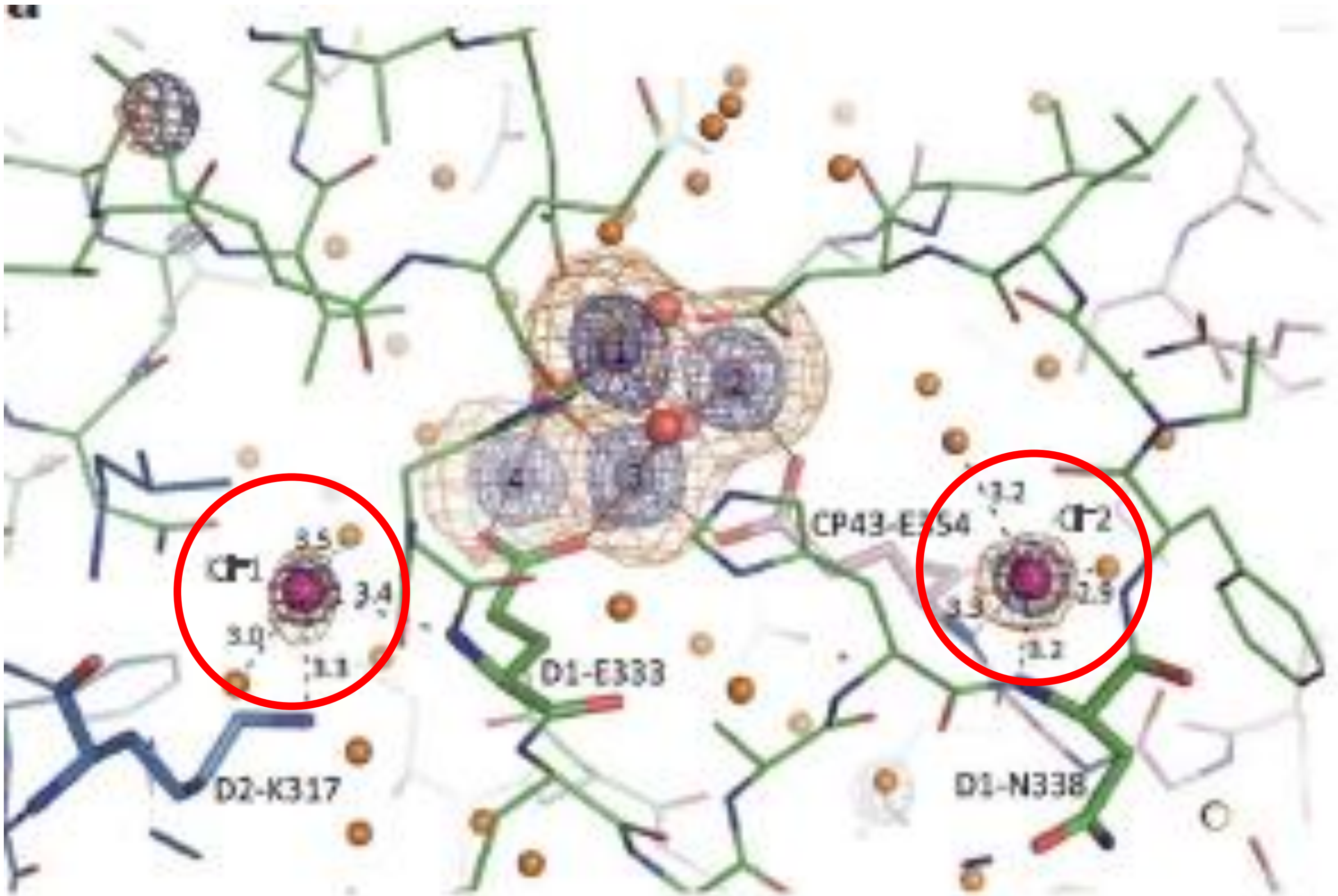
Nature 2011

Mn ions are always high spin

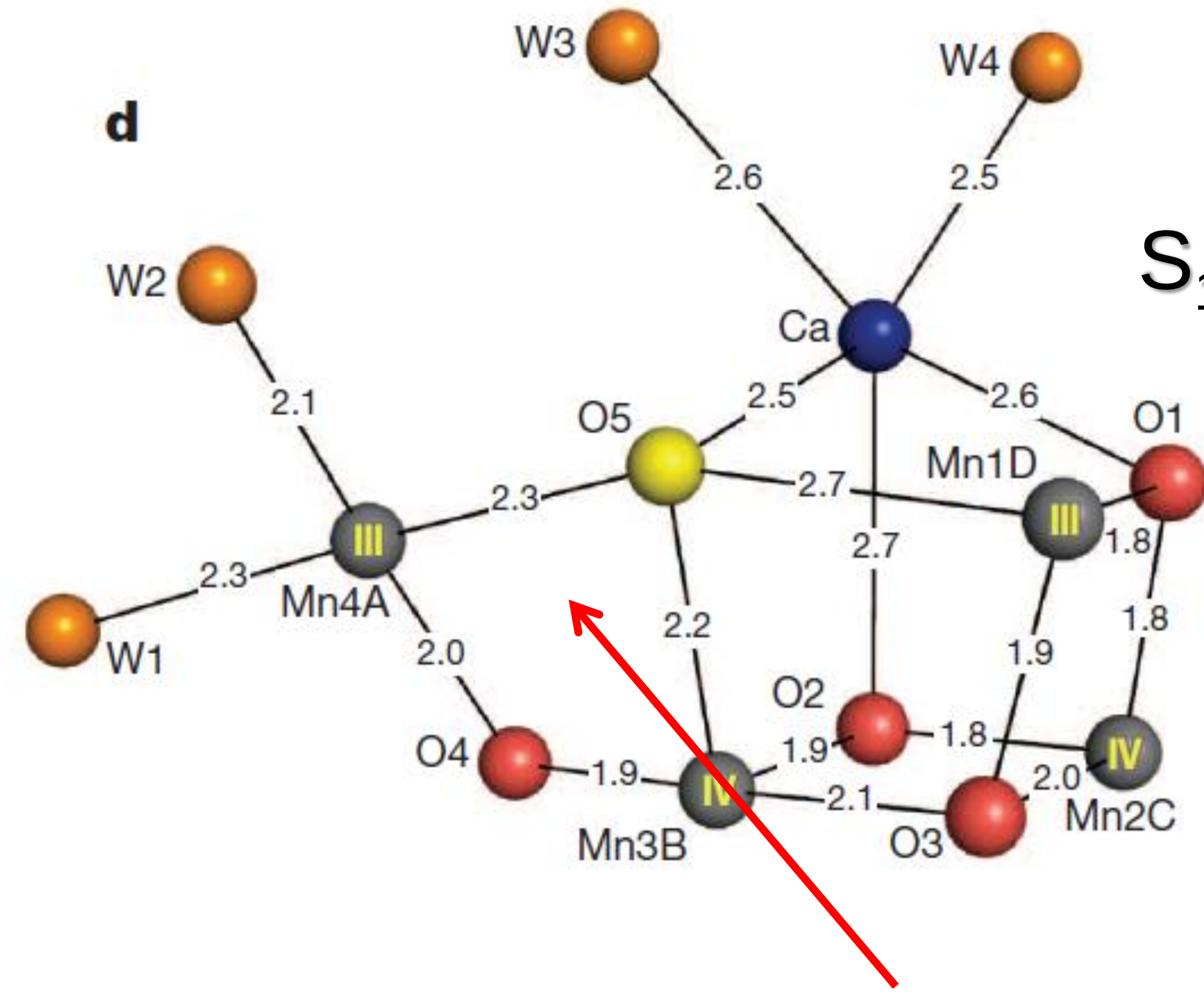


Each metal atom in OEC is coordinatively saturated (6 for Mn, 7 for Ca)

2 Chlorides



Mn(III), d^4, high spin → Jahn-Teller effect



S$_1$ state

Nature 2015

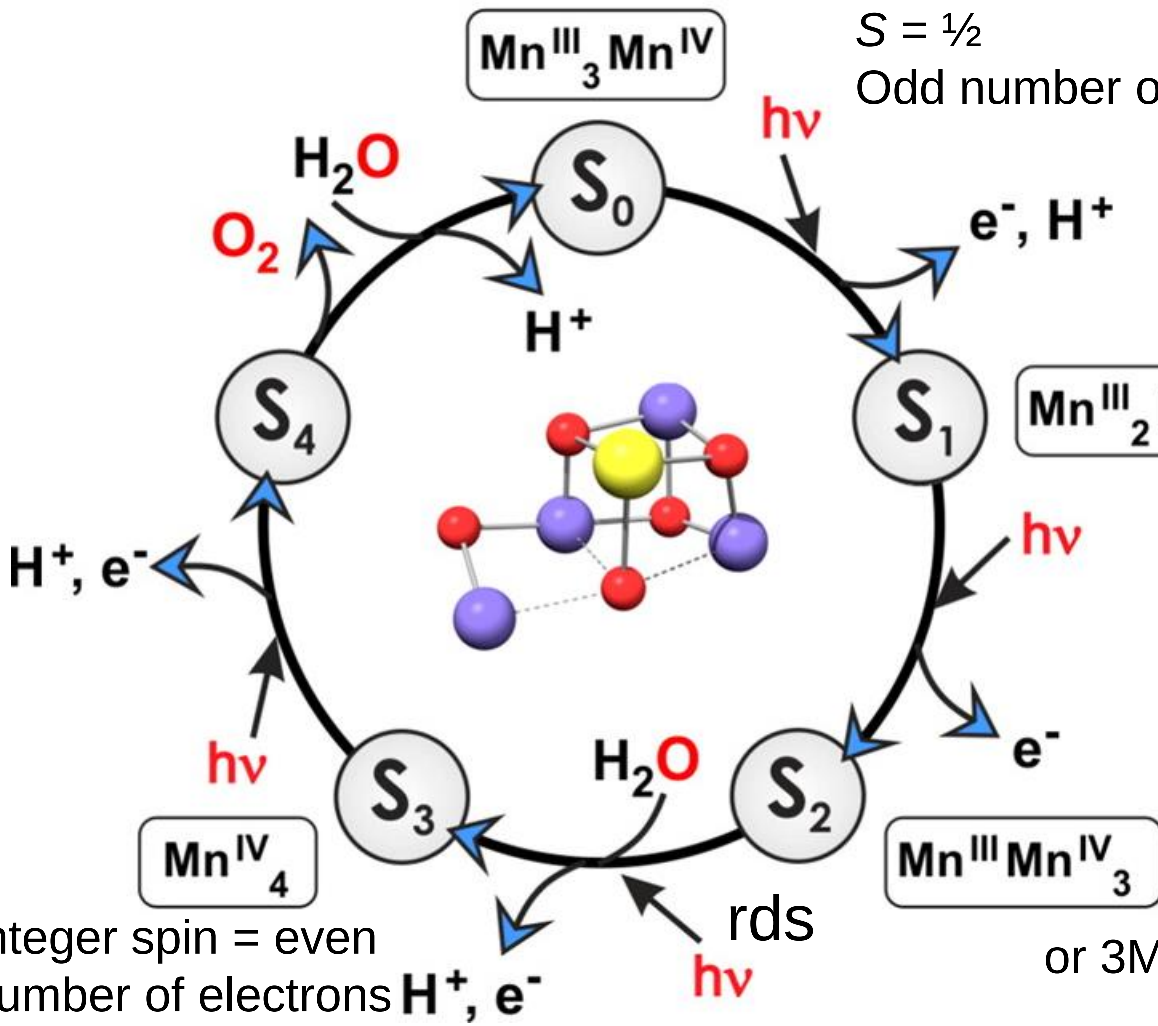
X-ray free-electron laser (XFEL)

Mn4–O5 is shorter by 0.2 Å

(meaning that most likely Mn4 had been reduced to Mn(II) in previous structure)

Kok cycle or *S clock*

Mn always h.s.



$S = ½$
Odd number of electrons

Integer spin = even number of electrons

Mn(III), d^4
Mn(IV), d^3

$S = ½$
Odd number of electrons

or $3Mn^{III}Mn^{IV}$ (*Low Valent* hypothesis)?

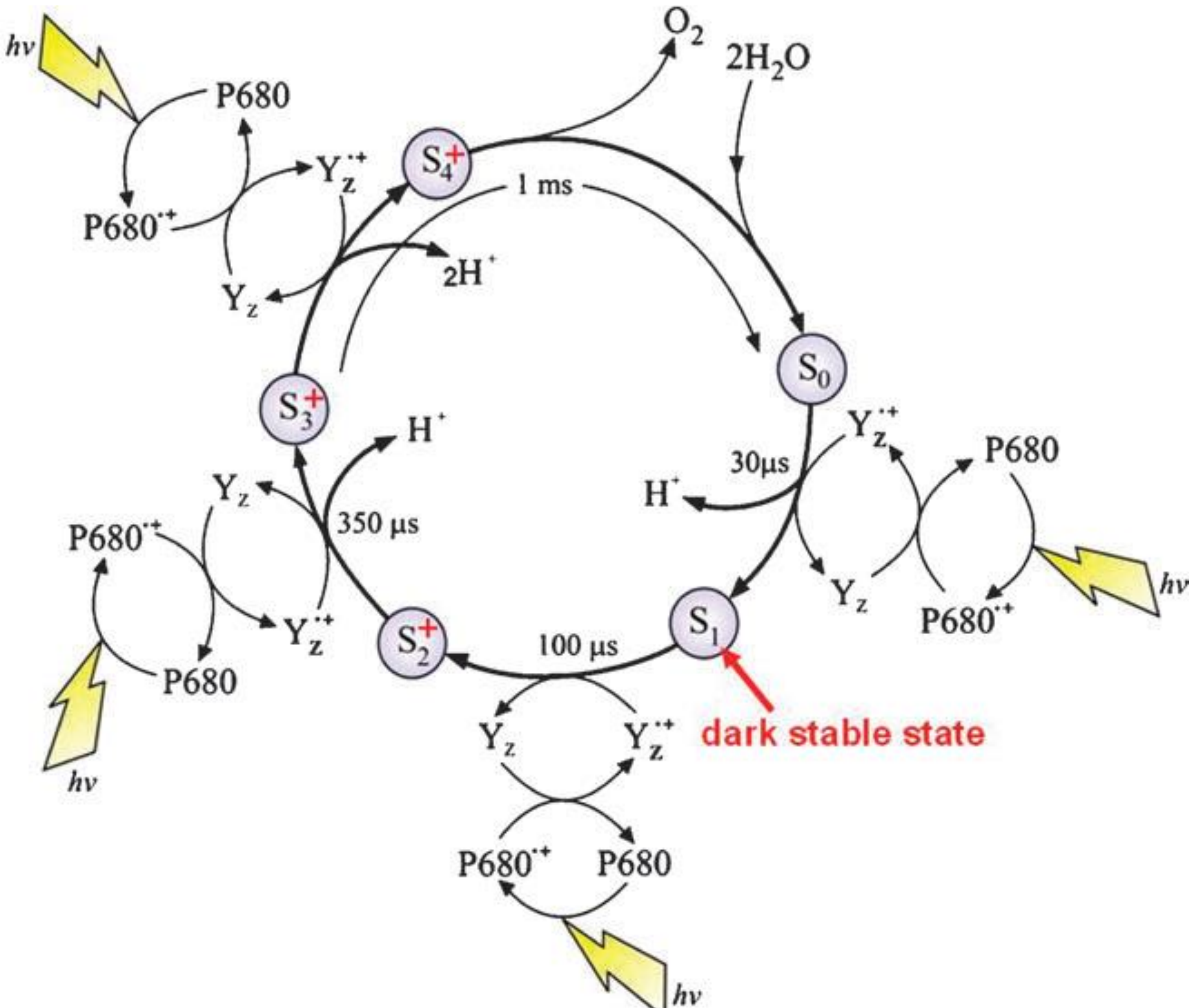
rds

Integer spin = even number of electrons

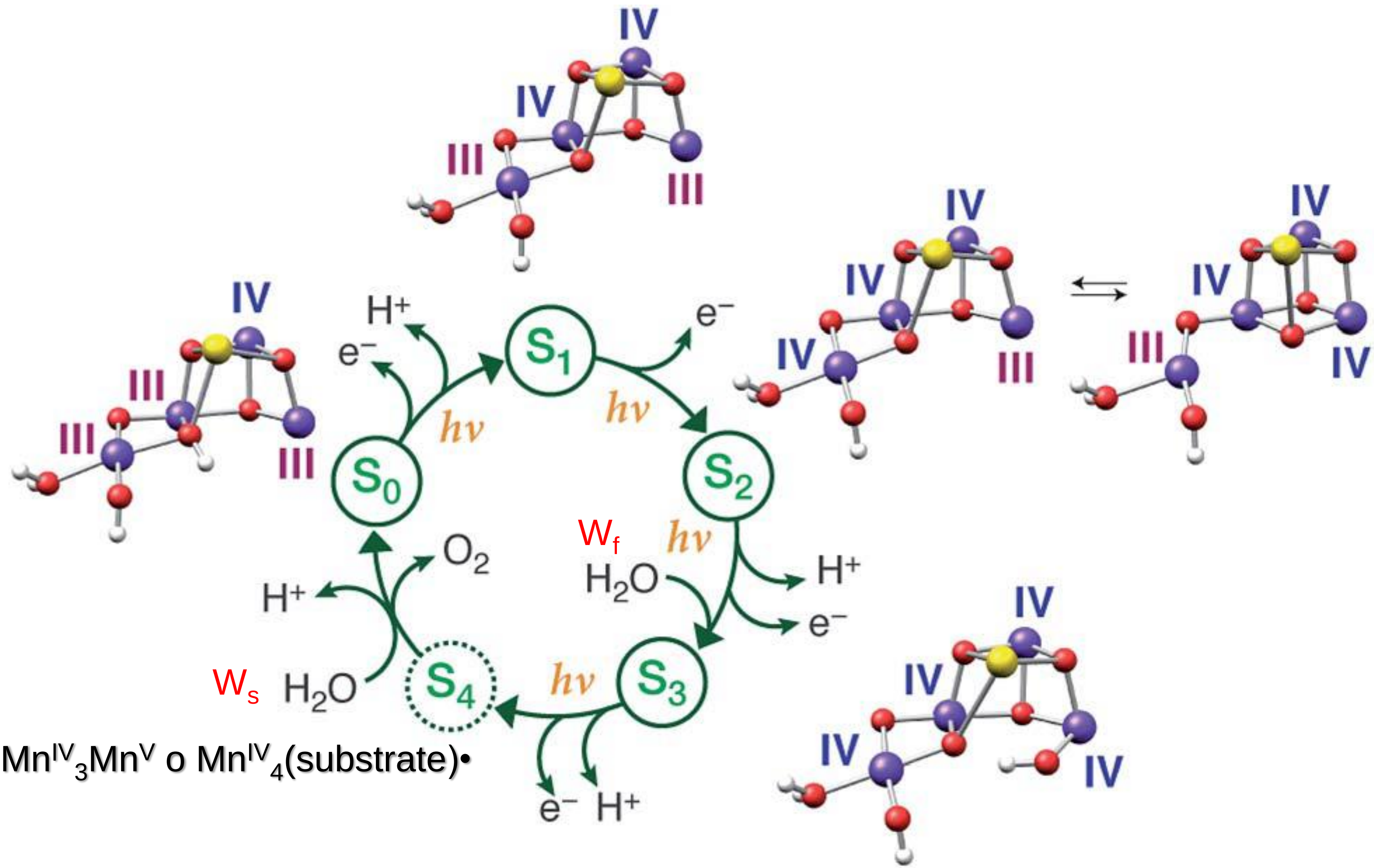
OEC oxidizes up to 1000 molecules of H_2O (500 cycles) per second!

TON ≈ ca. 10^6

Kok cycle or *S clock*

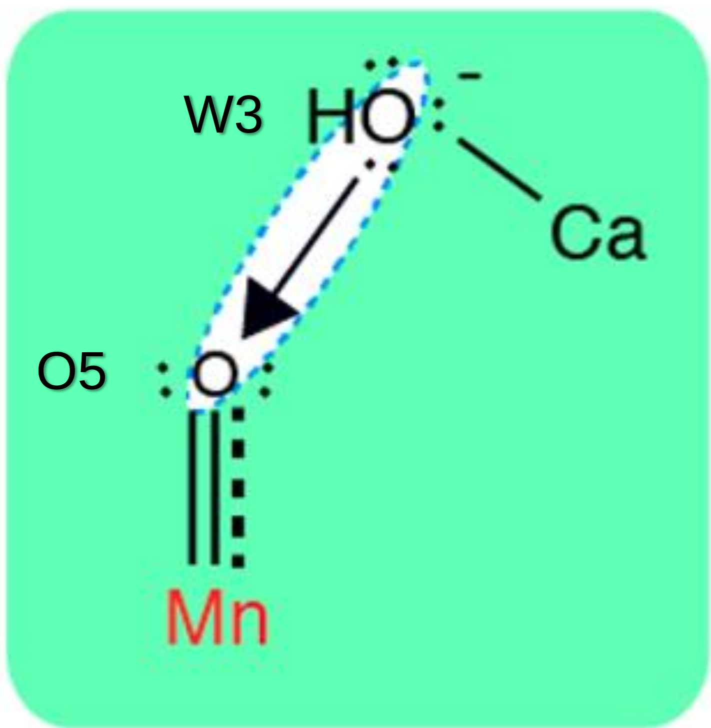


Most accepted hypothesis

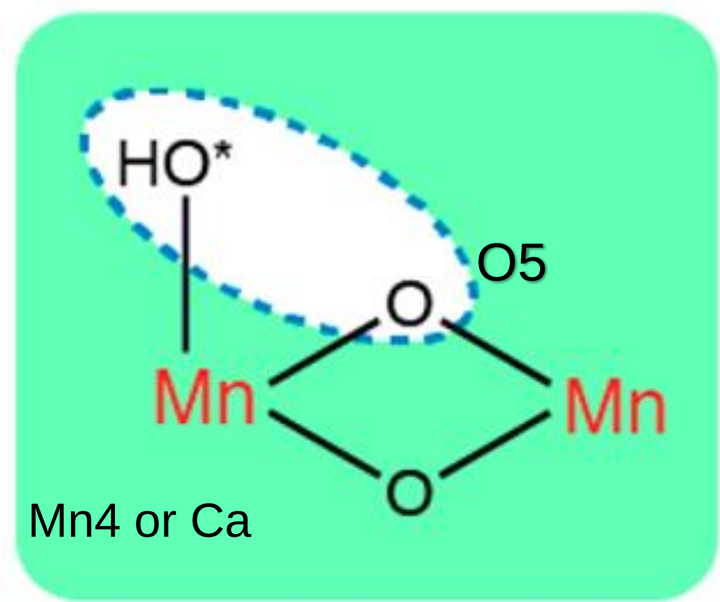


Hypotesis for the O–O bond formation

nucleophilic attack



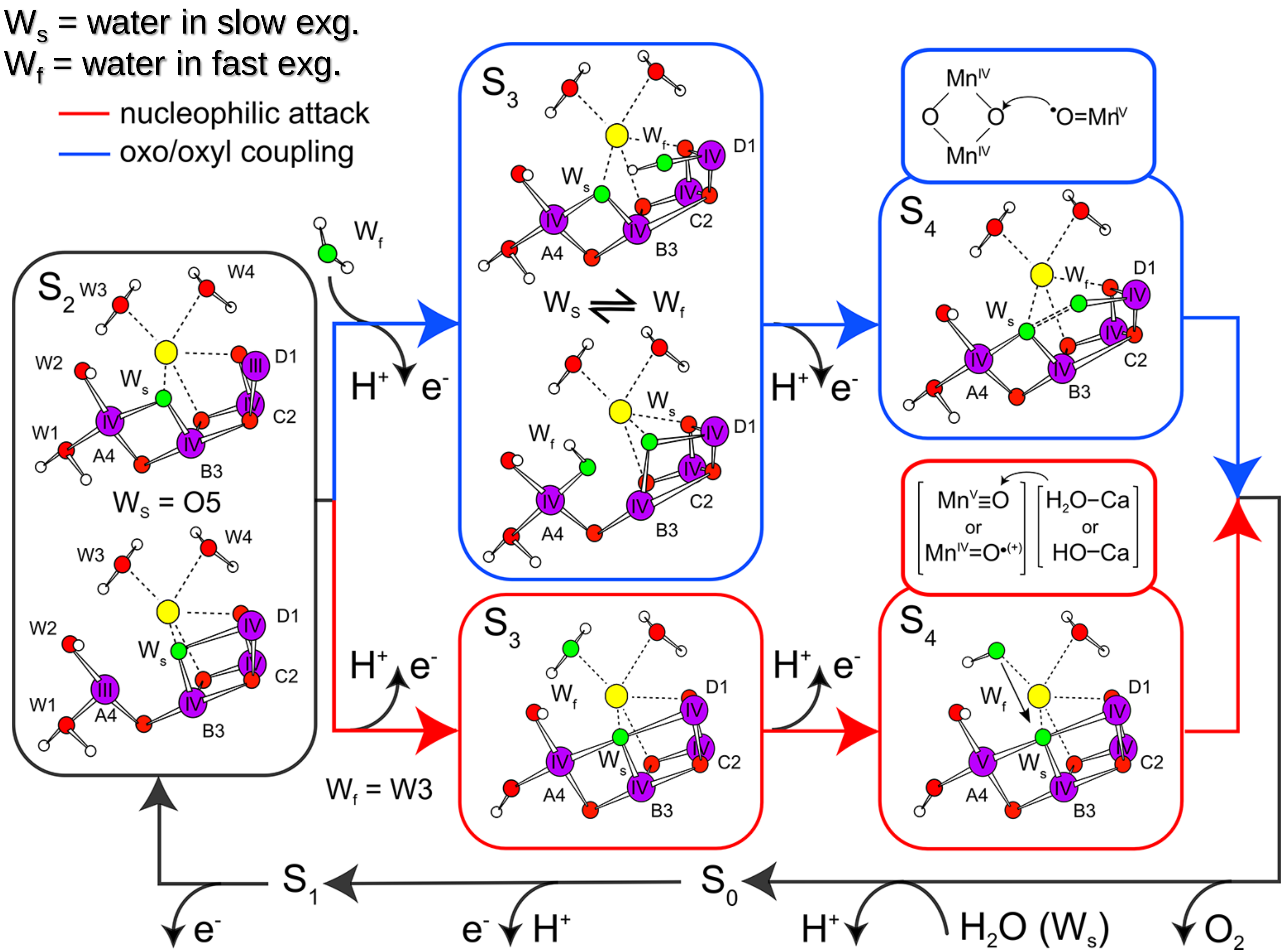
terminal oxyl radical with bridging oxo



Mn(V)≡O or Mn(IV)=O•

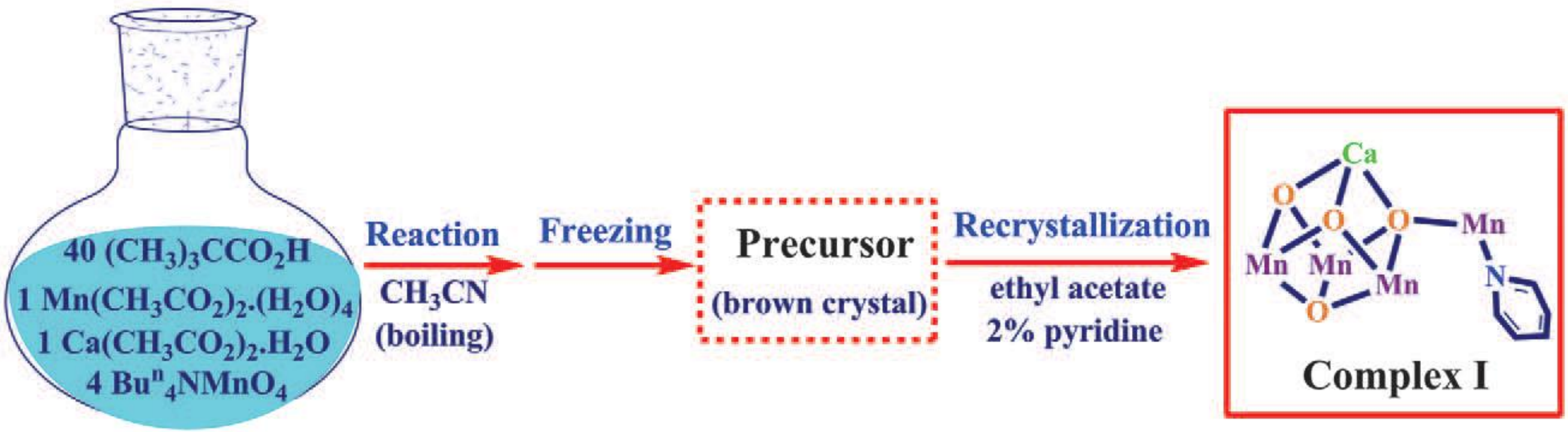
oxo/oxyl radical coupling mechanism

In this mechanism the last electron comes from an O atom, not from Mn

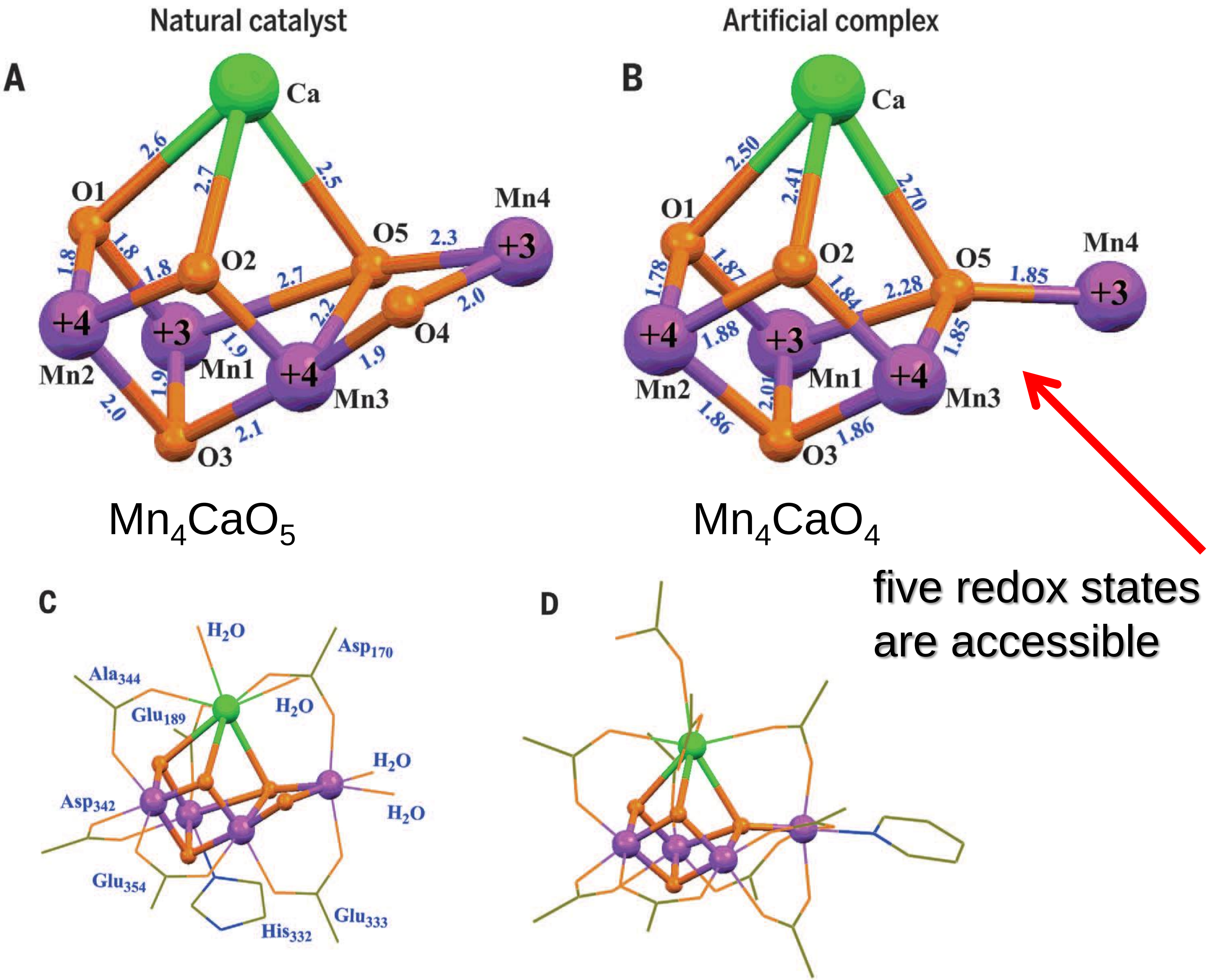


Ws = water in slow exg.
Wf = water in fast exg.
nucleophilic attack
oxo/oxyl coupling
S2
W3
W4
W2
Ws
D1
III
IV
C2
W1
A4
B3
Ws = O5
III
Wf
H+ e-
Wf = W3
S3
Ws ⇌ Wf
D1
C2
B3
A4
S4
Mn^IV
O
O
•O=Mn^IV
Mn^V≡O
or
Mn^IV=O•(+)
H2O−Ca
or
HO−Ca
V
S1
S0
e-
H+
H2O (Ws)
O2

Model systems



Science 2015


Natural catalyst
Artificial complex
A
B
Ca
O1
O2
O3
O4
O5
Mn1
Mn2
Mn3
Mn4
+4
+3
+4
+3
2.6
2.7
2.5
1.8
1.8
1.8
2.7
2.3
2.2
2.0
1.9
1.9
1.9
2.0
2.1
2.50
2.41
2.70
1.78
1.87
1.84
2.28
1.85
1.88
1.85
2.01
1.86
1.86
Mn4CaO5
Mn4CaO4
five redox states
are accessible
C
D
H2O
Asp170
Ala344
Glu189
H2O
H2O
H2O
Asp342
Glu354
His332
Glu333

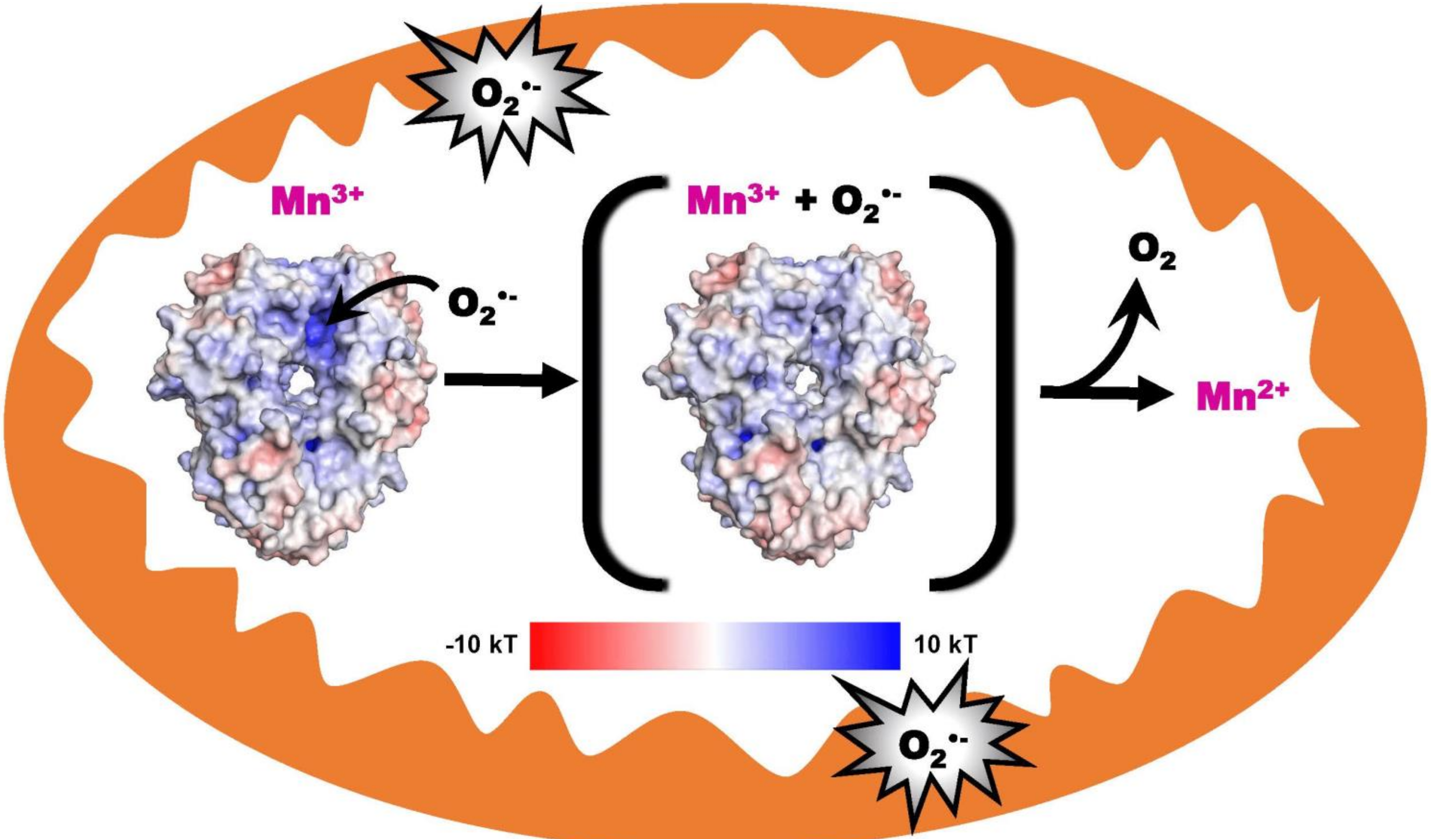
What Mn has to do with the oxidative stress?

Pure Green Tea

Il tè verde *Pure Green Tea* Twinings è un pregiato **tè verde orientale** dal sapore rinfrescante e delicato, adatto per una deliziosa pausa in ogni momento della giornata.

Fonte naturale di Manganese – 0,31 mg per 100 ml di tè preparato (15% VNR) –, che contribuisce alla **protezione delle cellule dallo stress ossidativo**. Ti consigliamo di berne almeno una tazza (200 ml) al giorno, consumata nell'ambito di una dieta varia ed equilibrata e di uno stile di vita sano, di cui ti ricordiamo l'importanza.

Mn SOD



MnSOD is a homotetramer localized exclusively in the mitochondrial matrix.

MnSOD has one of the fastest and most efficient reaction rates of all enzymes, with a k_{cat} of 40.000 s^{-1}

The mitochondrial matrix is an organelle compartment with a high rate of endogenous superoxide generation.

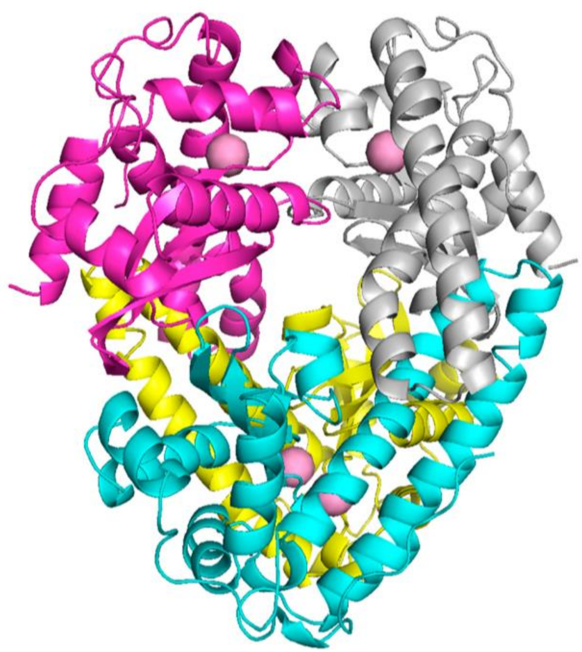
Electrons leak from the electron-transport chain and perform a one-electron reduction of diatomic oxygen to form superoxide.

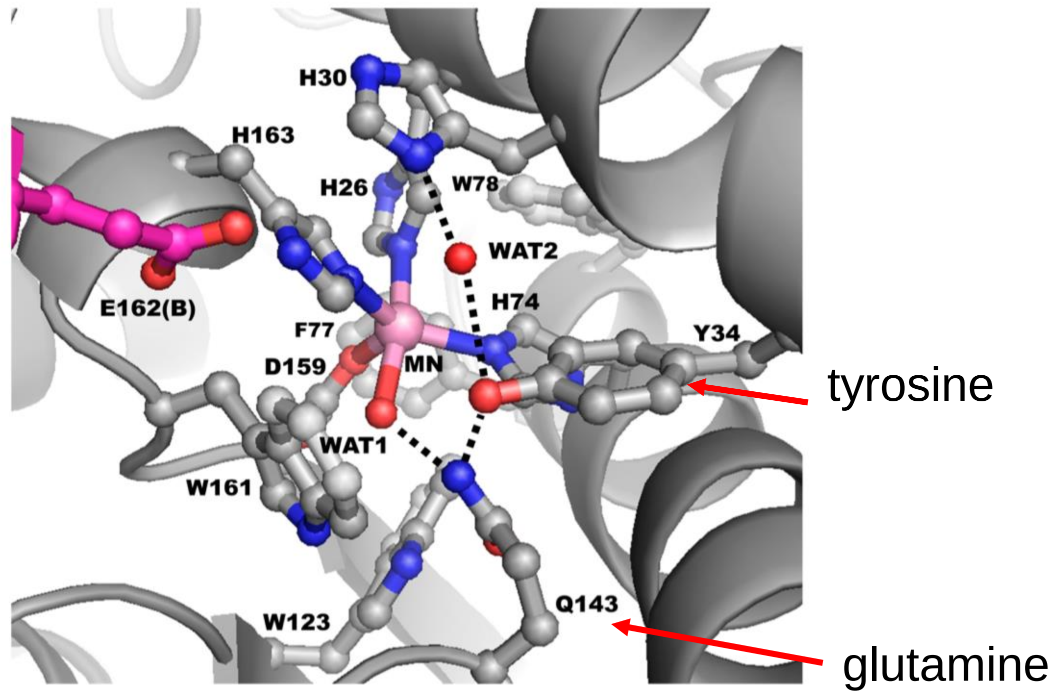
The ability of MnSOD to decrease superoxide levels in the mitochondria is associated with longevity of eukaryotic organisms.

$$Mn^{3+} + O_2^{\bullet -} \leftrightarrow Mn^{2+} + O_2$$

$$Mn^{2+} + O_2^{\bullet -} + 2H^{+} \leftrightarrow Mn^{3+} + H_2O_2$$

Human MnSOD functions as a homotetramer, with each subunit containing an active site surrounding a manganese ion. The metal is coordinated by His26, His74, His163, Asp159, and a single oxygen-containing molecule (denoted WAT1), thought to be either H_2O or OH^-

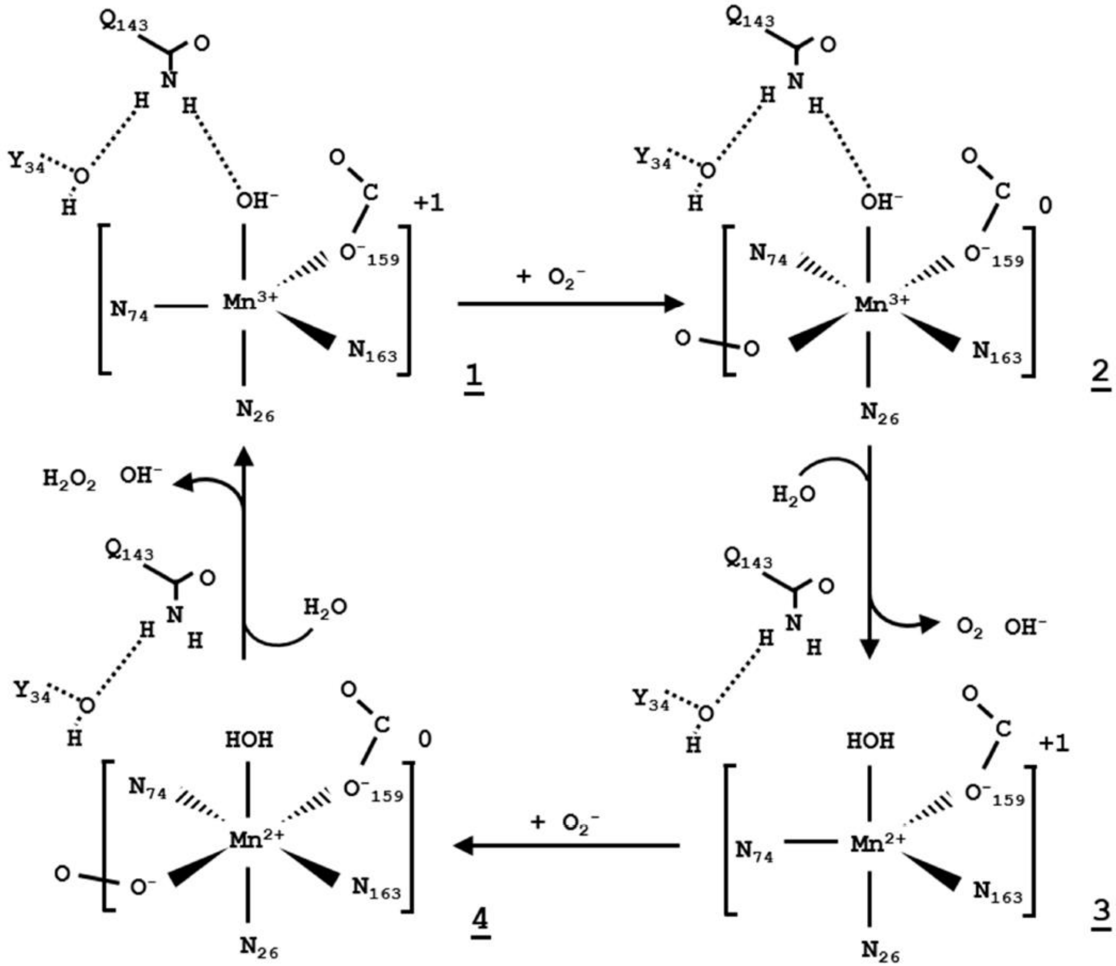




The active site of human MnSOD is within a cavity formed by two adjacent subunits.

The substrate most likely binds to the manganese ion in the position opposite Asp159.

The proposed 5-6-5 mechanism



For MnSOD to perform its enzymatic function efficiently it must shuttle protons to the active site for proton-assisted electron transfer (PCET) in a systematic manner.