fotosintesi (*uphill catalysis*)

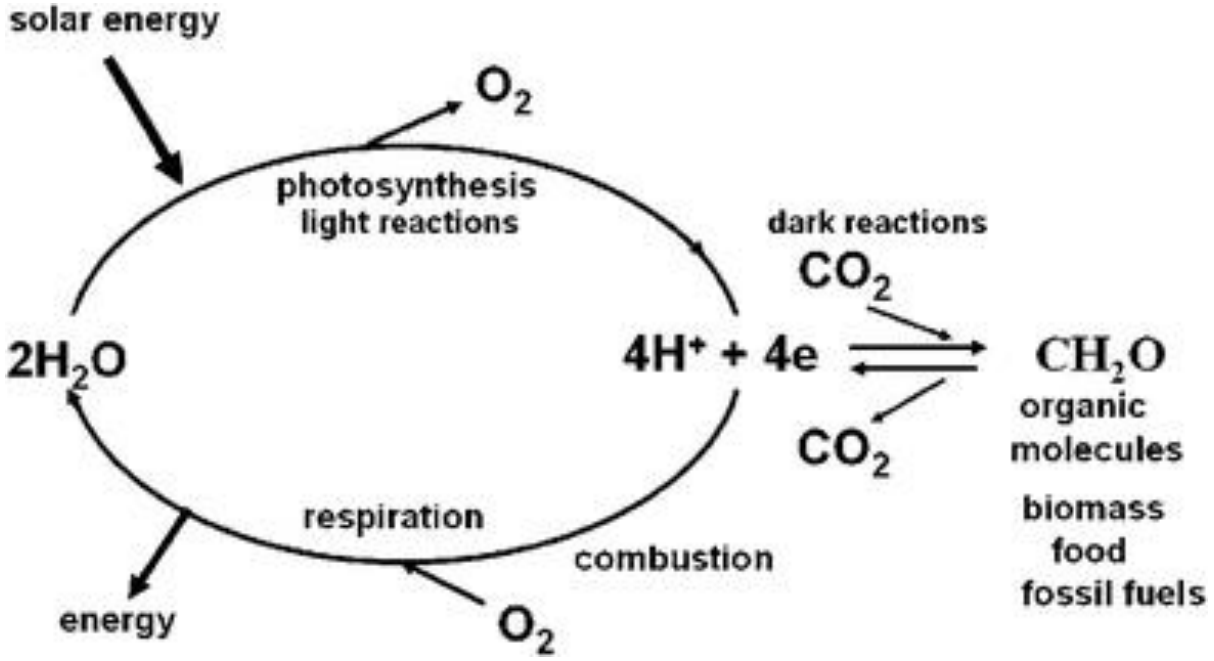
$H_2O + CO_2 \rightleftharpoons 1/n\ (CH_2O)_n + O_2$ $\quad \Delta H = 470$ kJ/mol

respirazione (*downhill catalysis*)

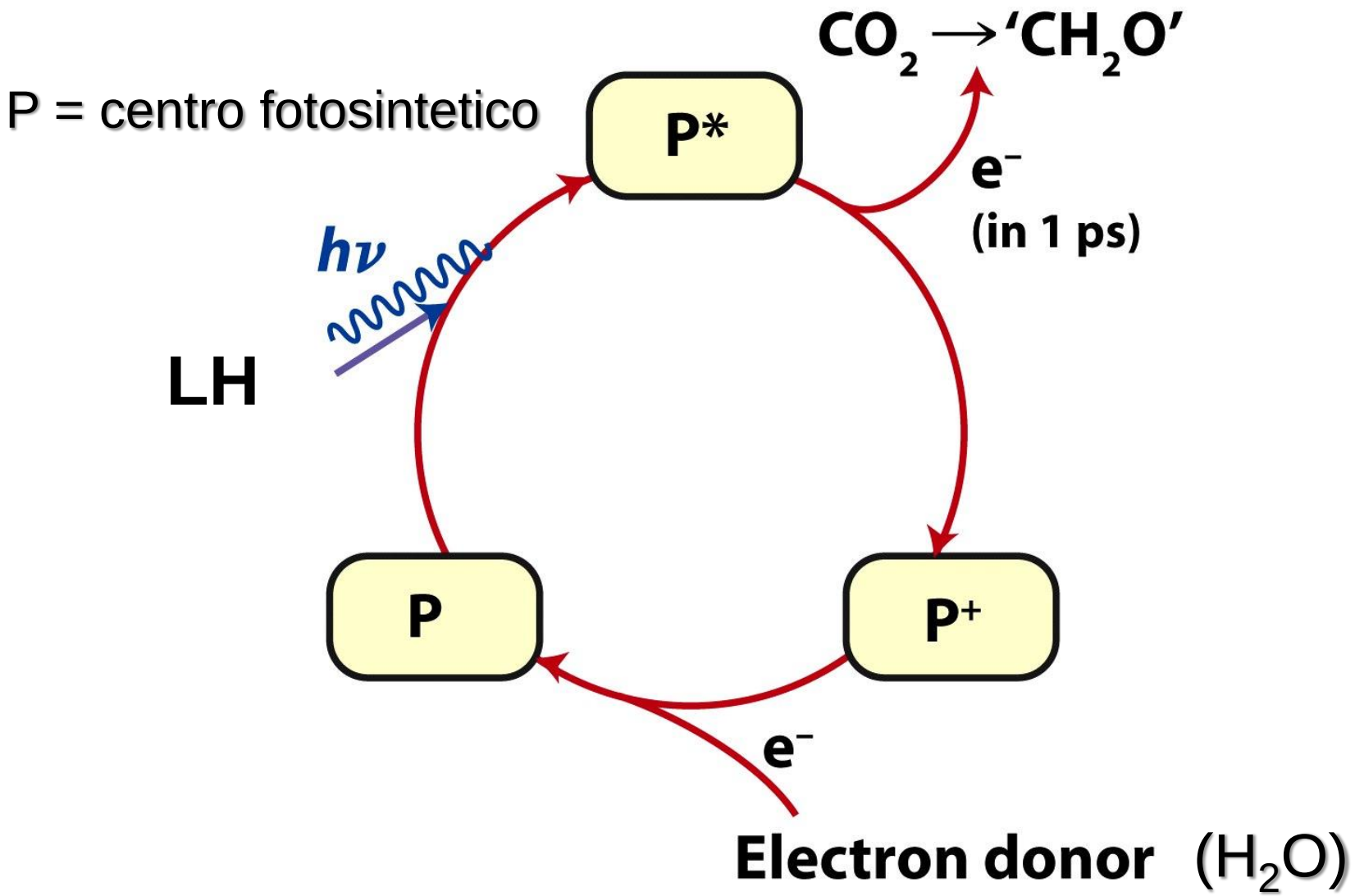
100×10^9 ton/y di $(CH_2O)_n$ da CO_2

1 g di glucosio per m^2 di superficie fogliare all'ora

100 TW/y = 0.1% energia solare totale (10^5 TW)



Separazione di carica fotoindotta



Processo fotosintetico nelle piante

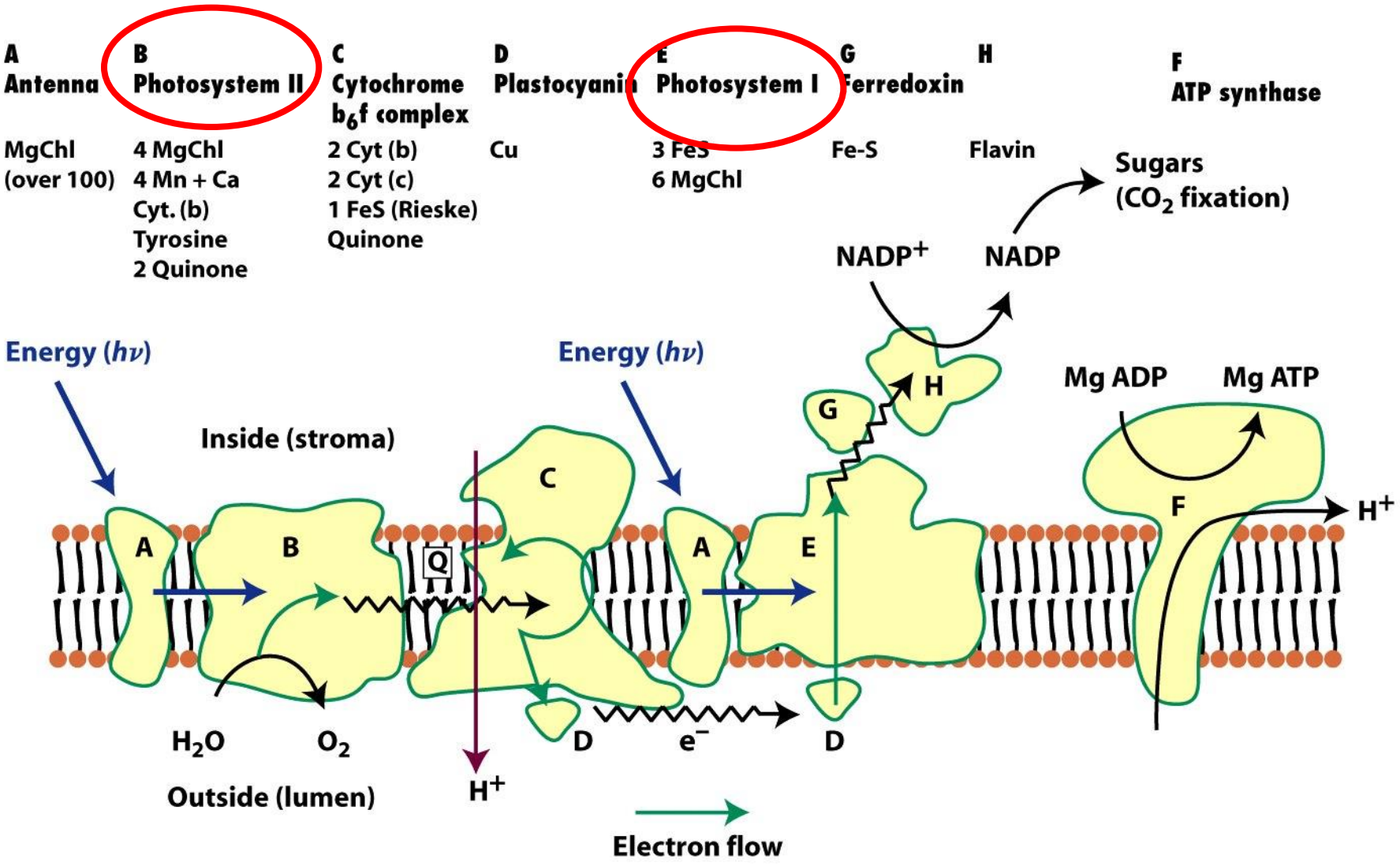
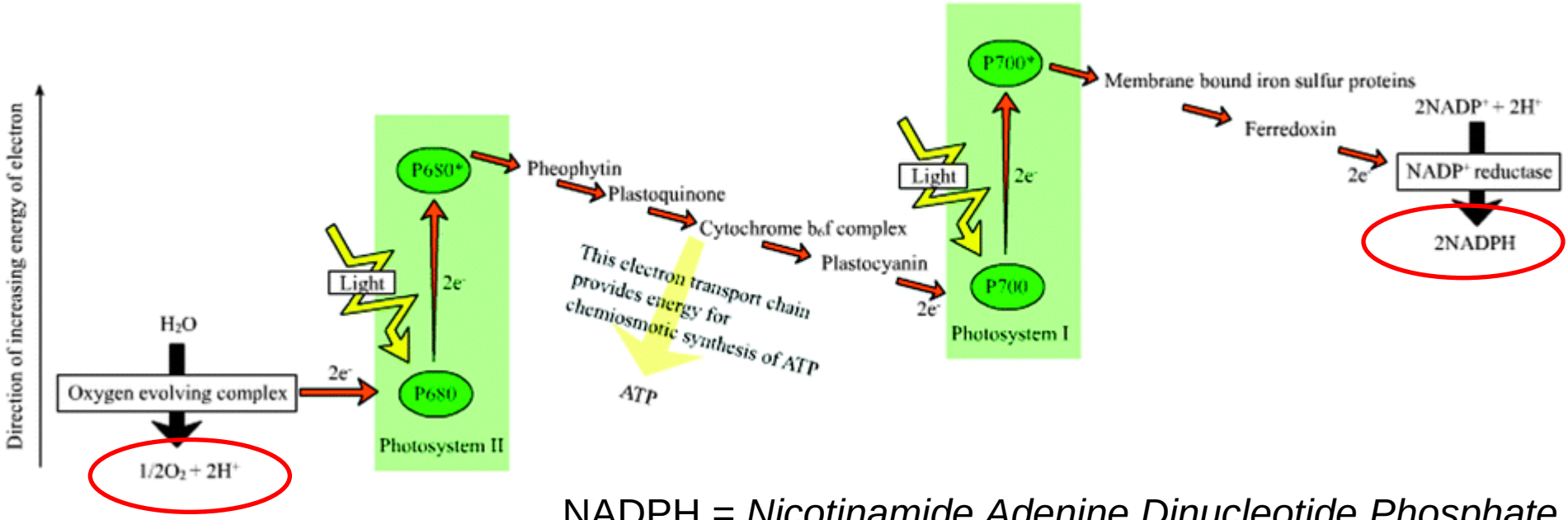
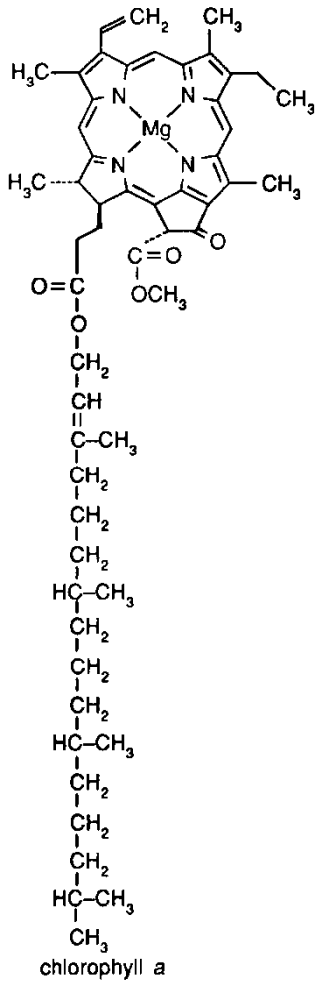


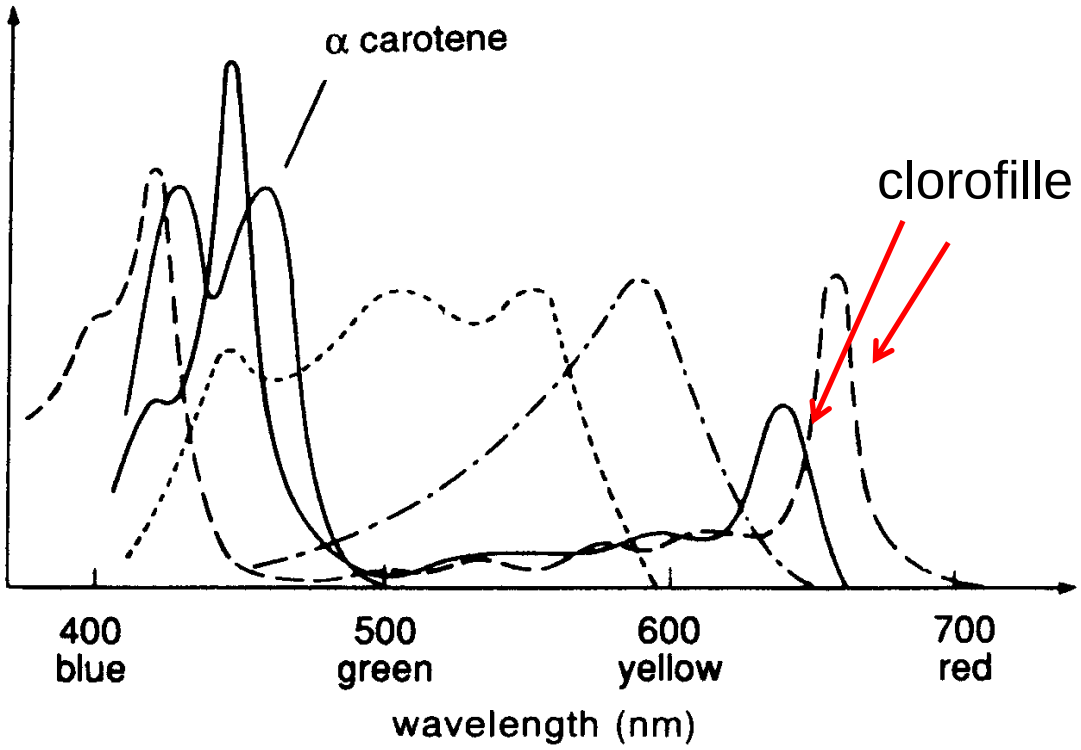
Diagramma "a Z"



NADPH = *Nicotinamide Adenine Dinucleotide Phosphate*

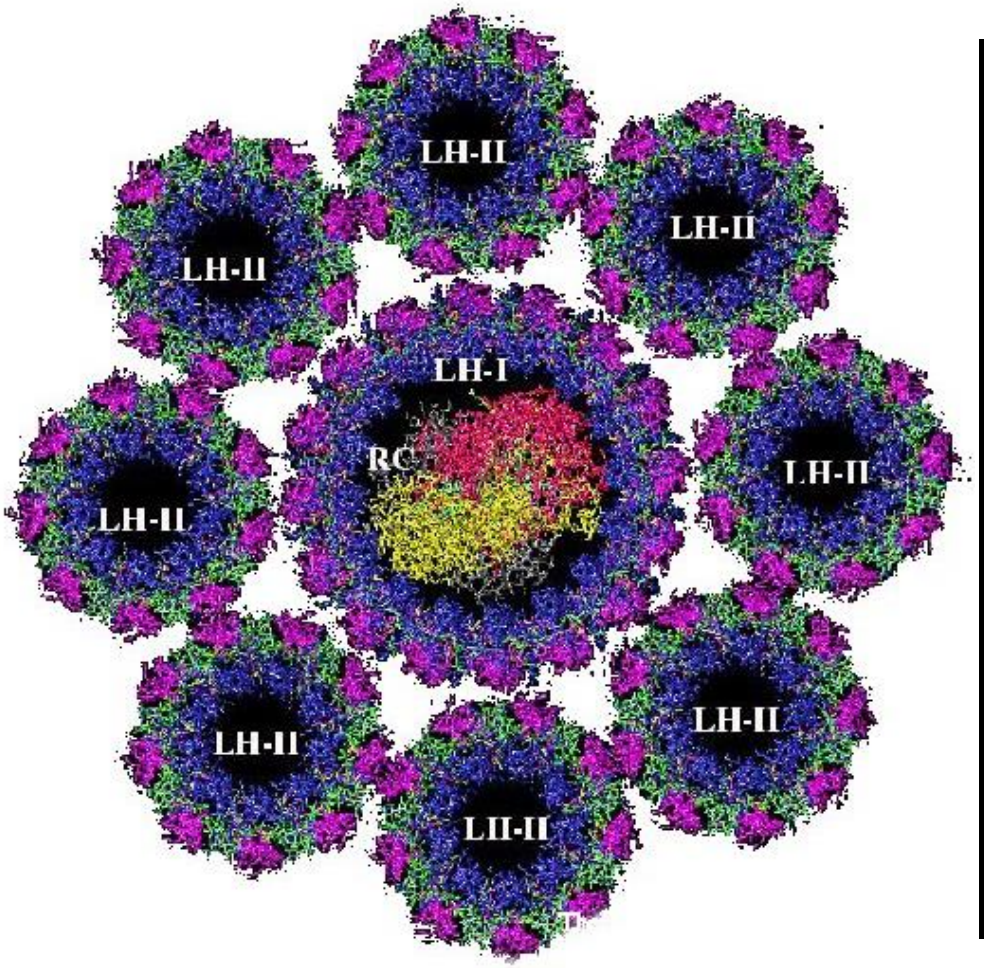
Pigmenti deputati al *light harvesting*

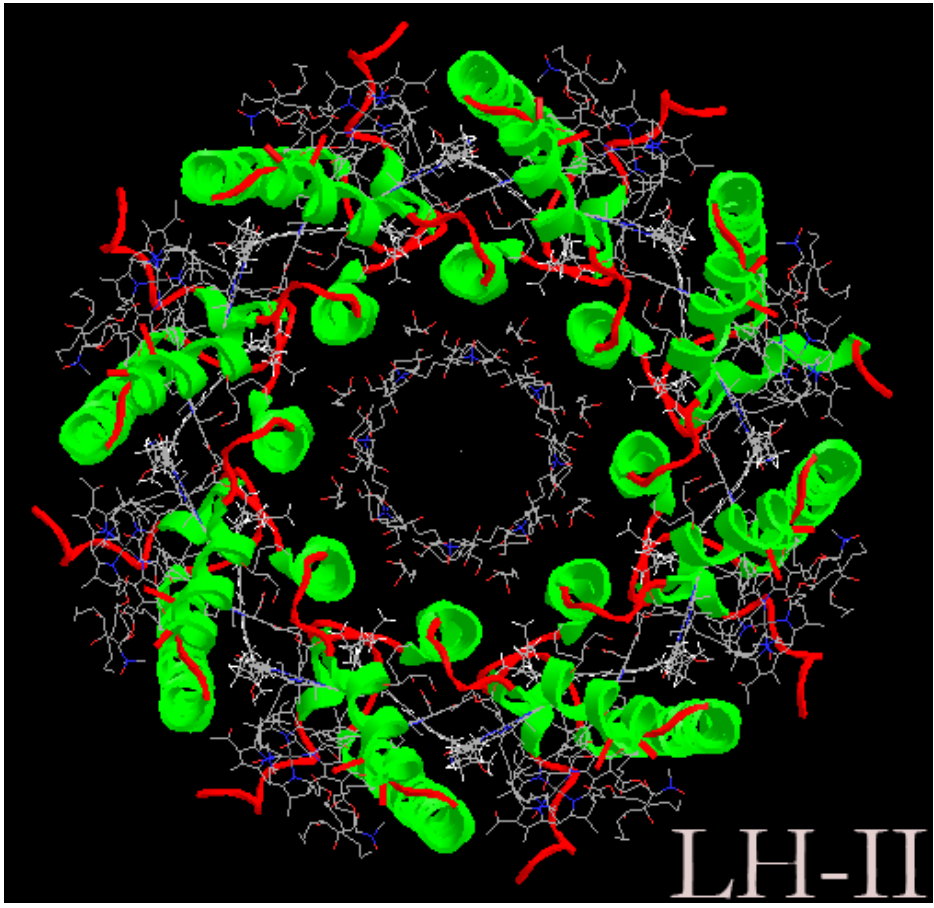




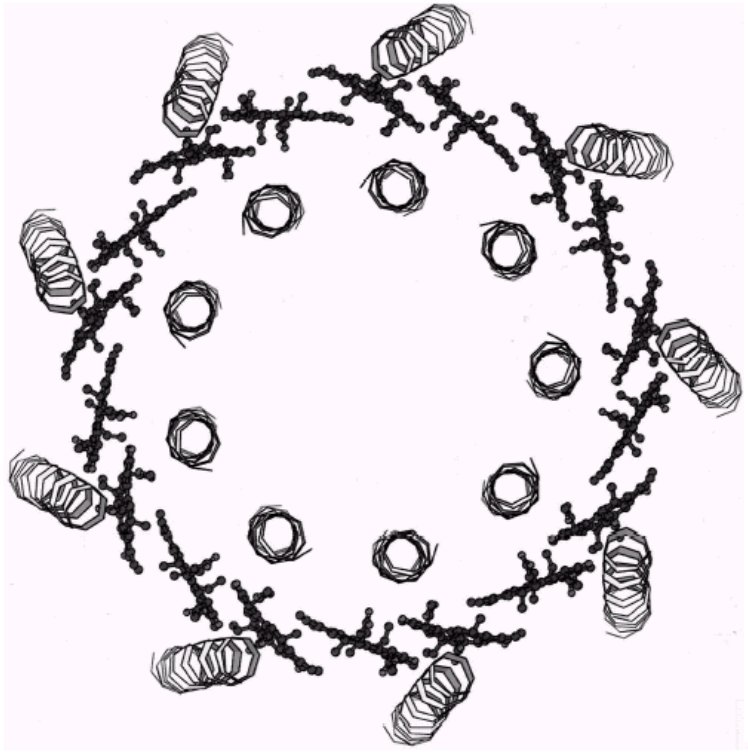
Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (——), phycocyanin (–·–·), phycoerythrin (–––––)

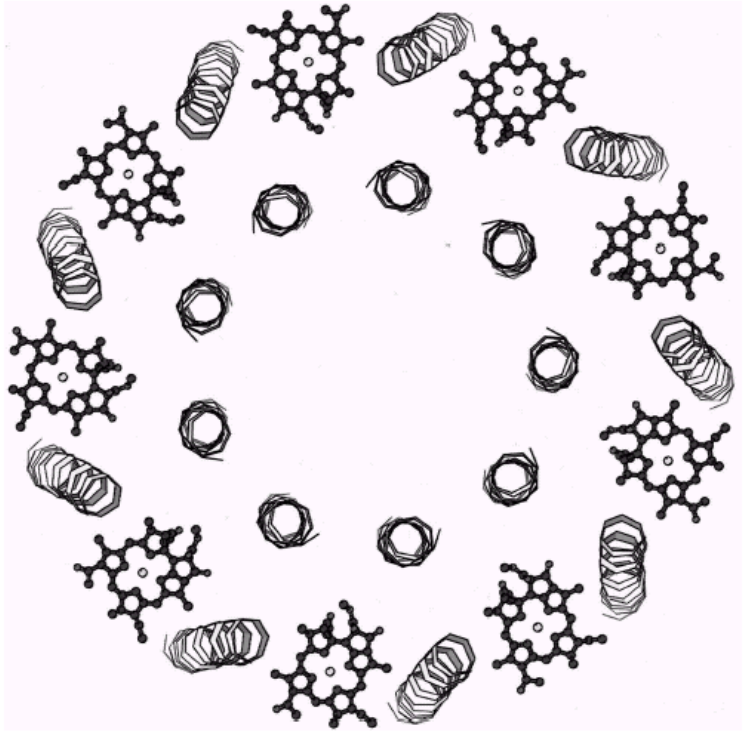
Sistemi antenna



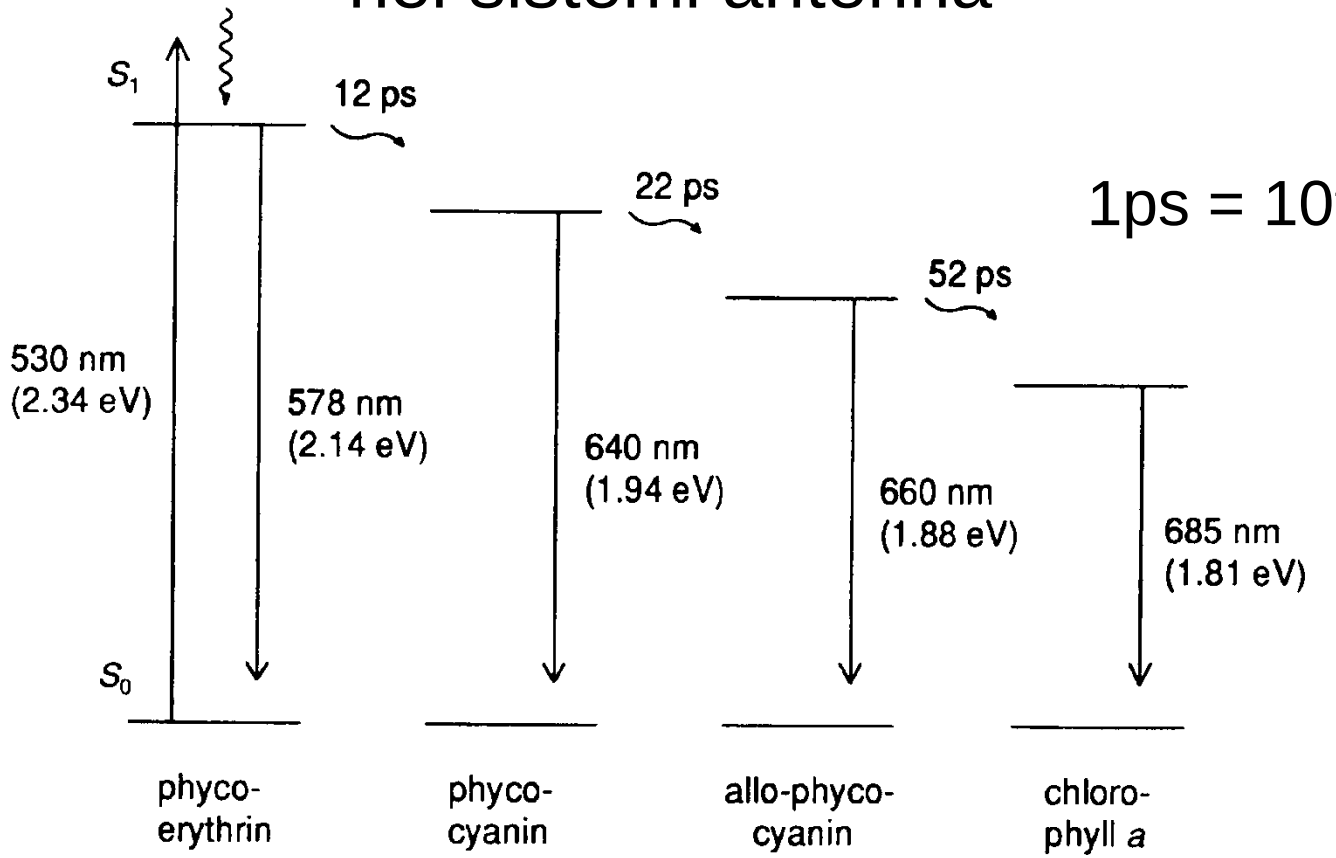


Sistemi antenna



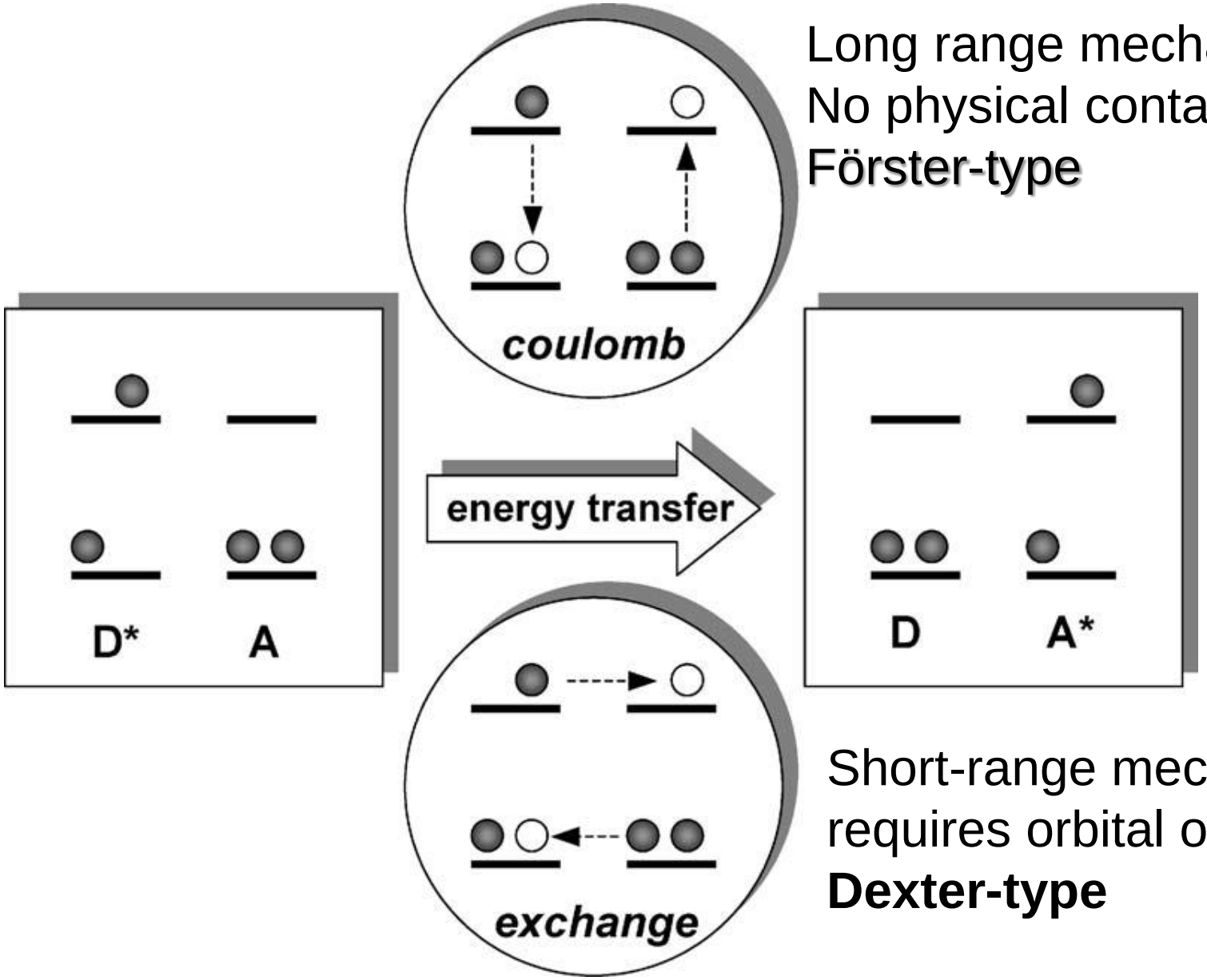


Trasferimento di energia (*exciton transfer*) a cascata nei sistemi antenna



1ps = 10^{-12} s

efficienza del 95%



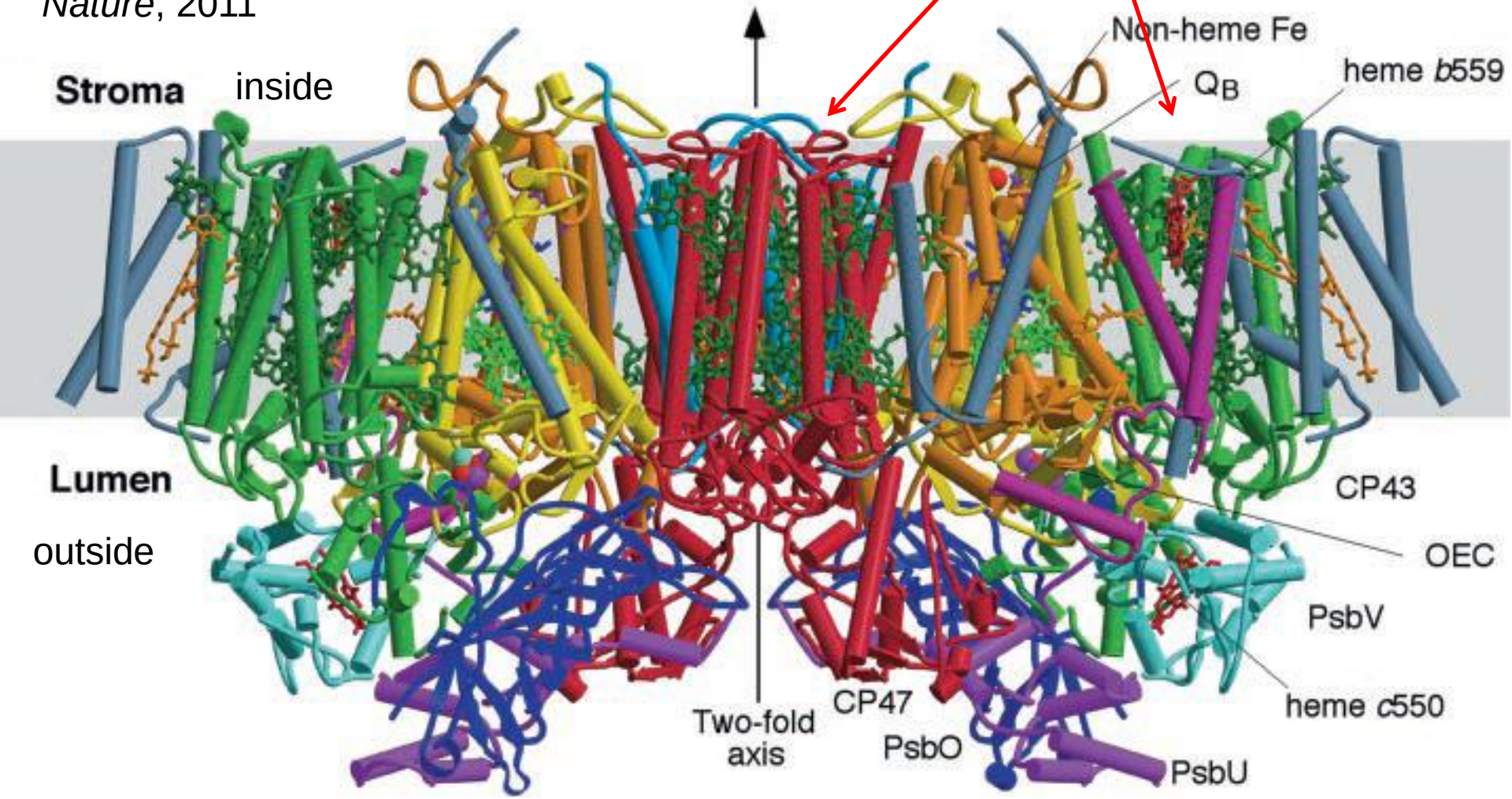
Long range mechanism
No physical contact
Förster-type

Short-range mechanism
requires orbital overlap
Dexter-type

PS II

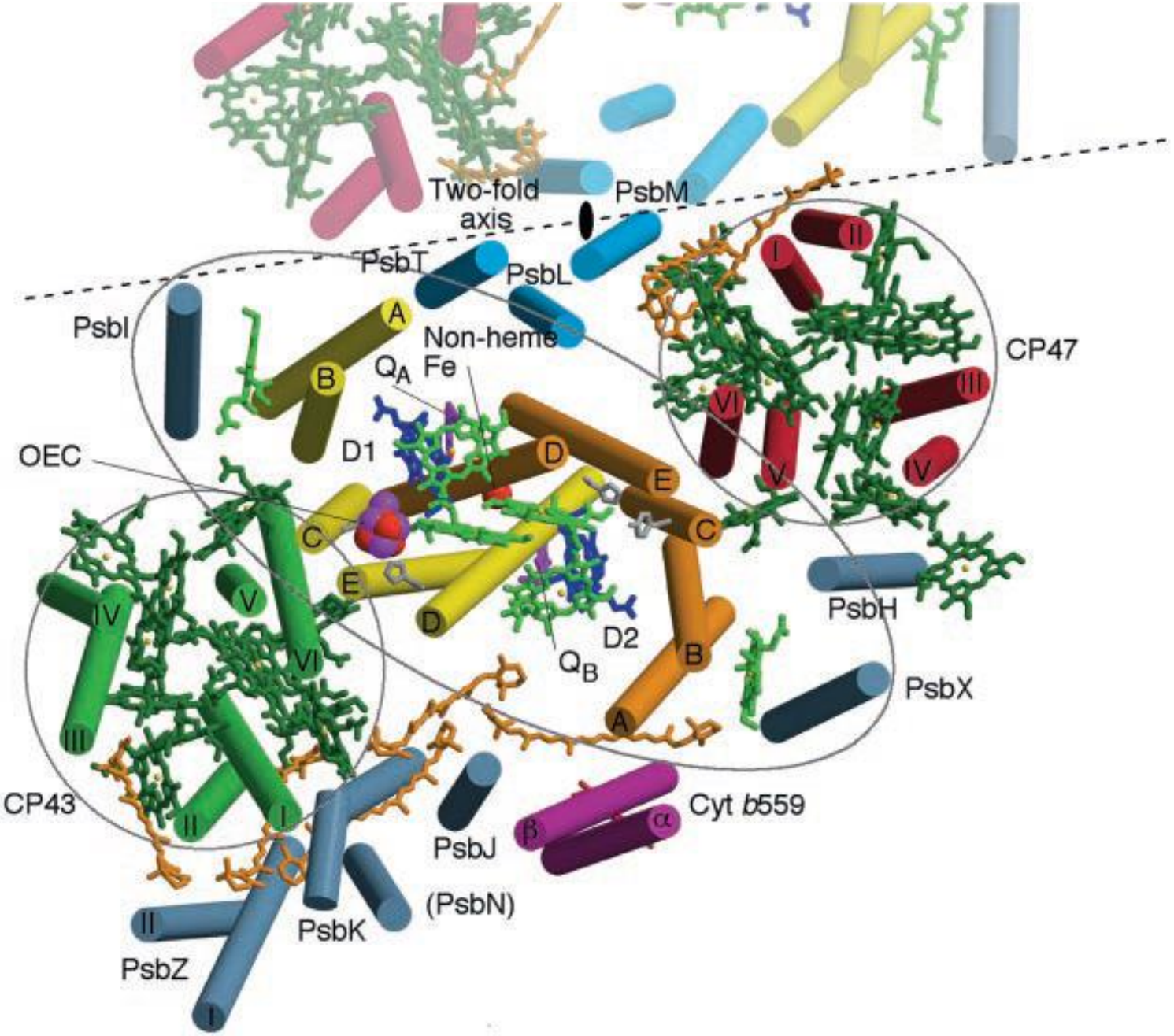
Sistemi antenna

Nature, 2011



19 subunità proteiche, 2 feofitine, 36 clorofille, 11 carotenoidi, vari cofattori

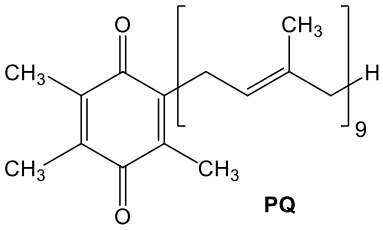
PS II

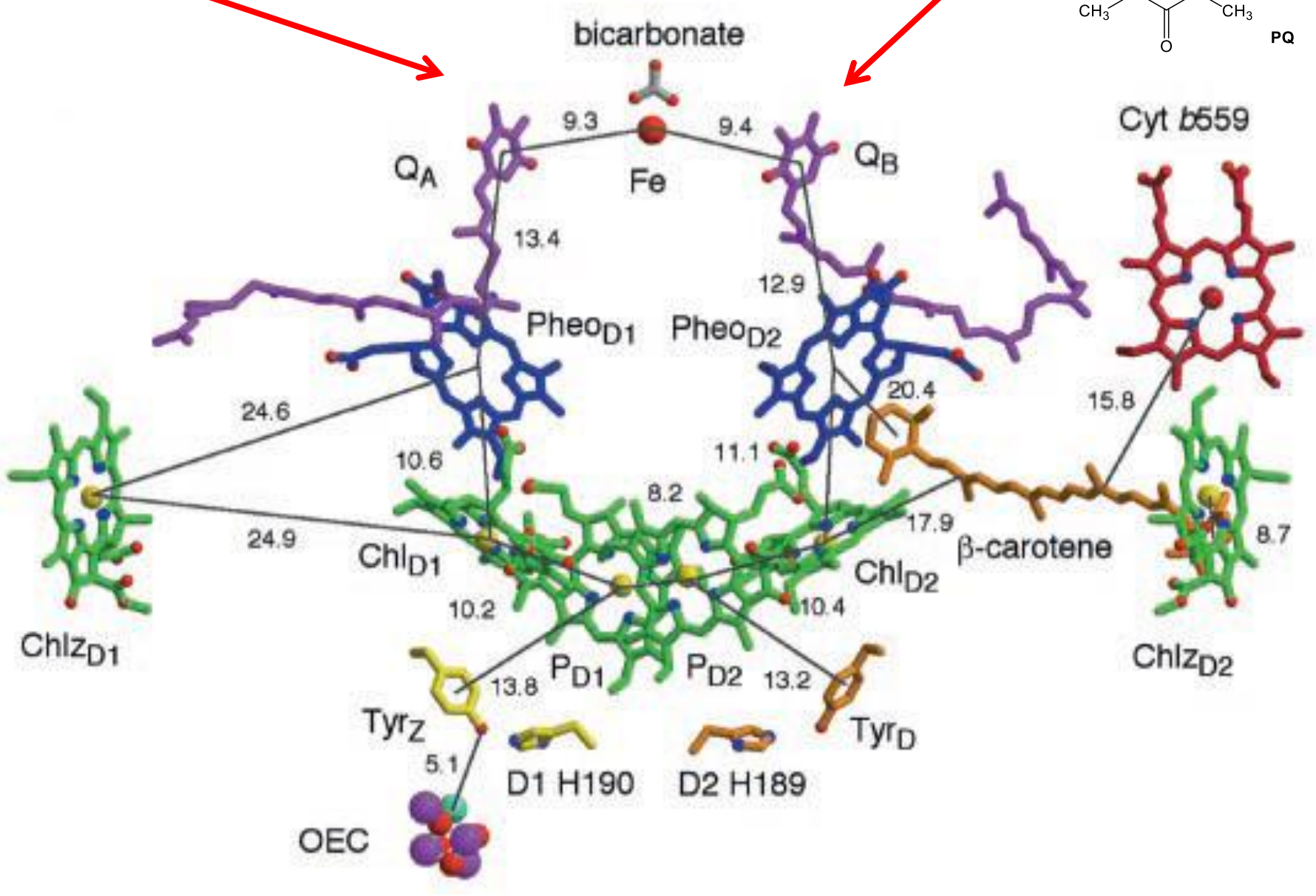

Two-fold axis
PsbM
PsbT
PsbL
PsbI
A
B
Non-heme Fe
Q_A
D1
D
E
C
CP47
I
II
III
IV
V
VI
OEC
CP43
D2
Q_B
PsbH
PsbX
Cyt *b*559
β
α
PsbJ
(PsbN)
PsbK
PsbZ

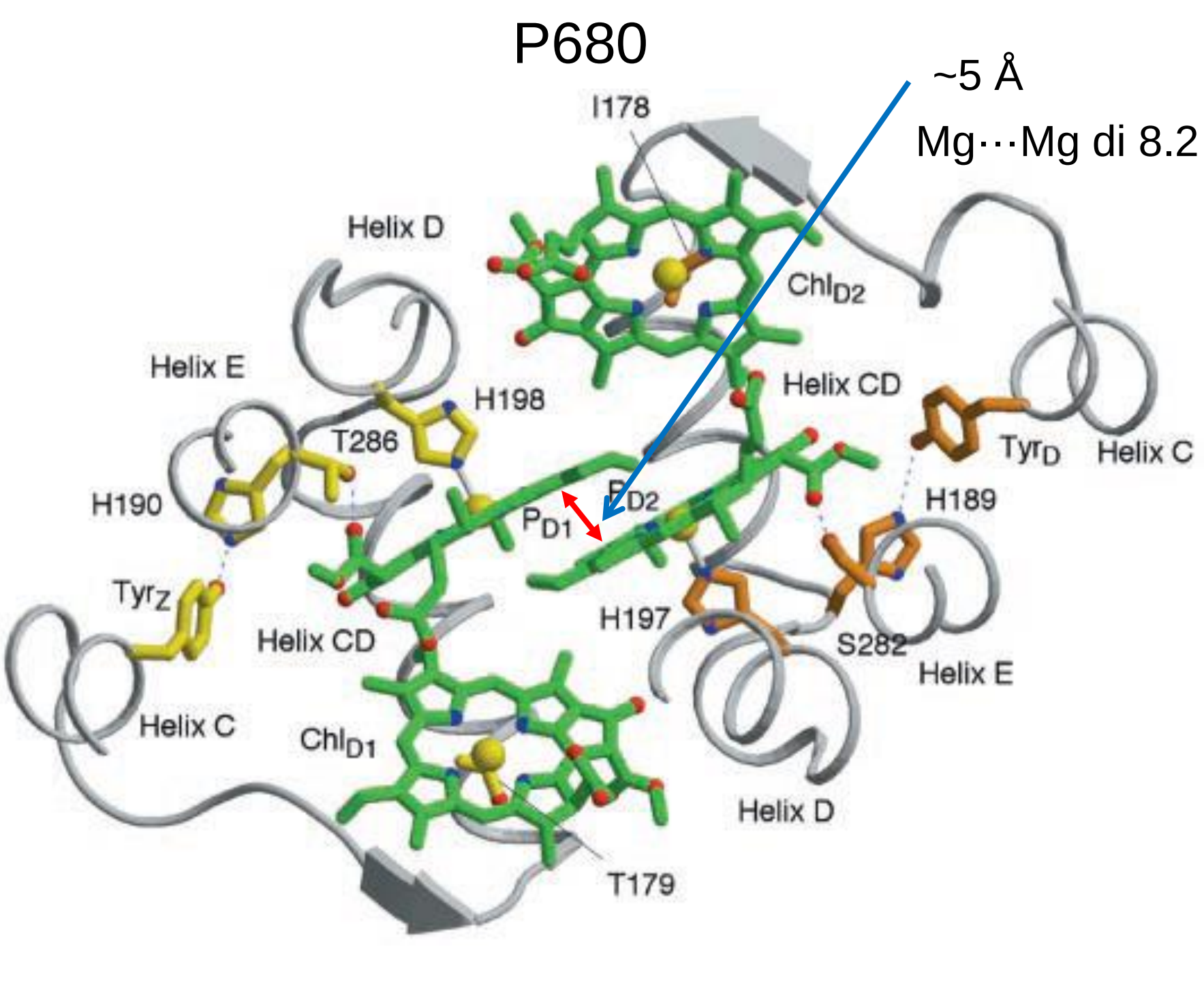
P680

Plastochinone fisso

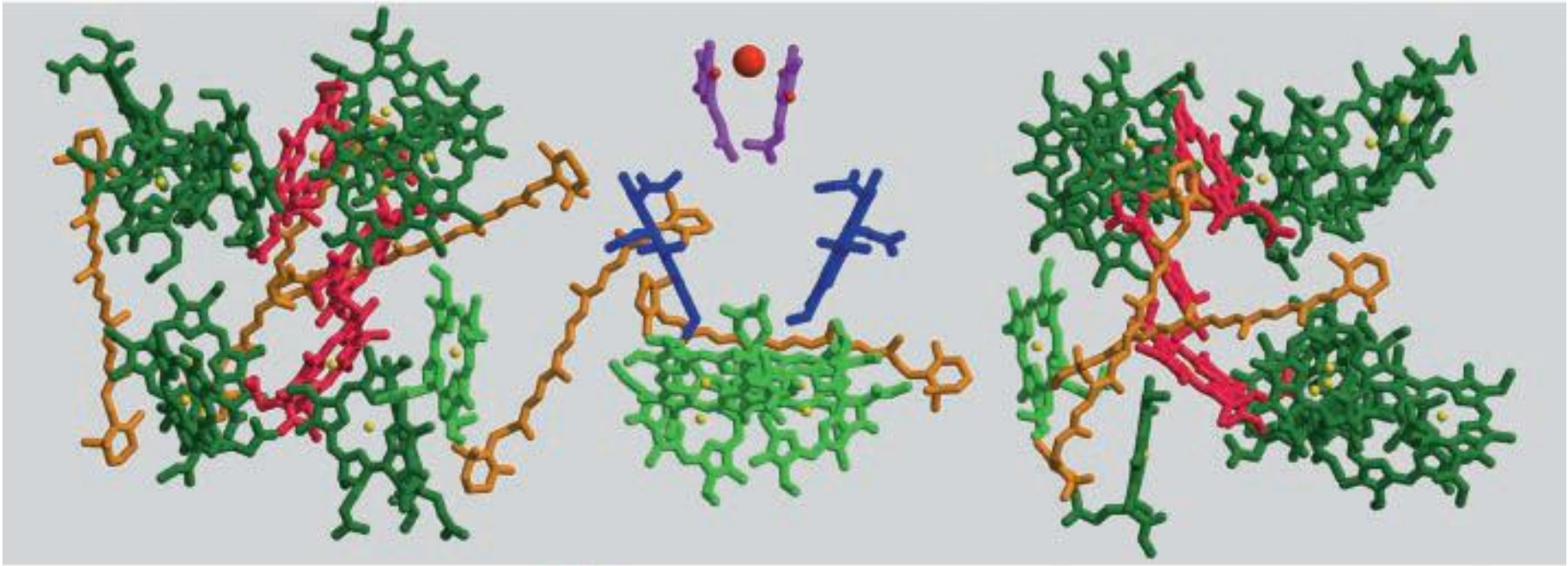
Plastochinone mobile





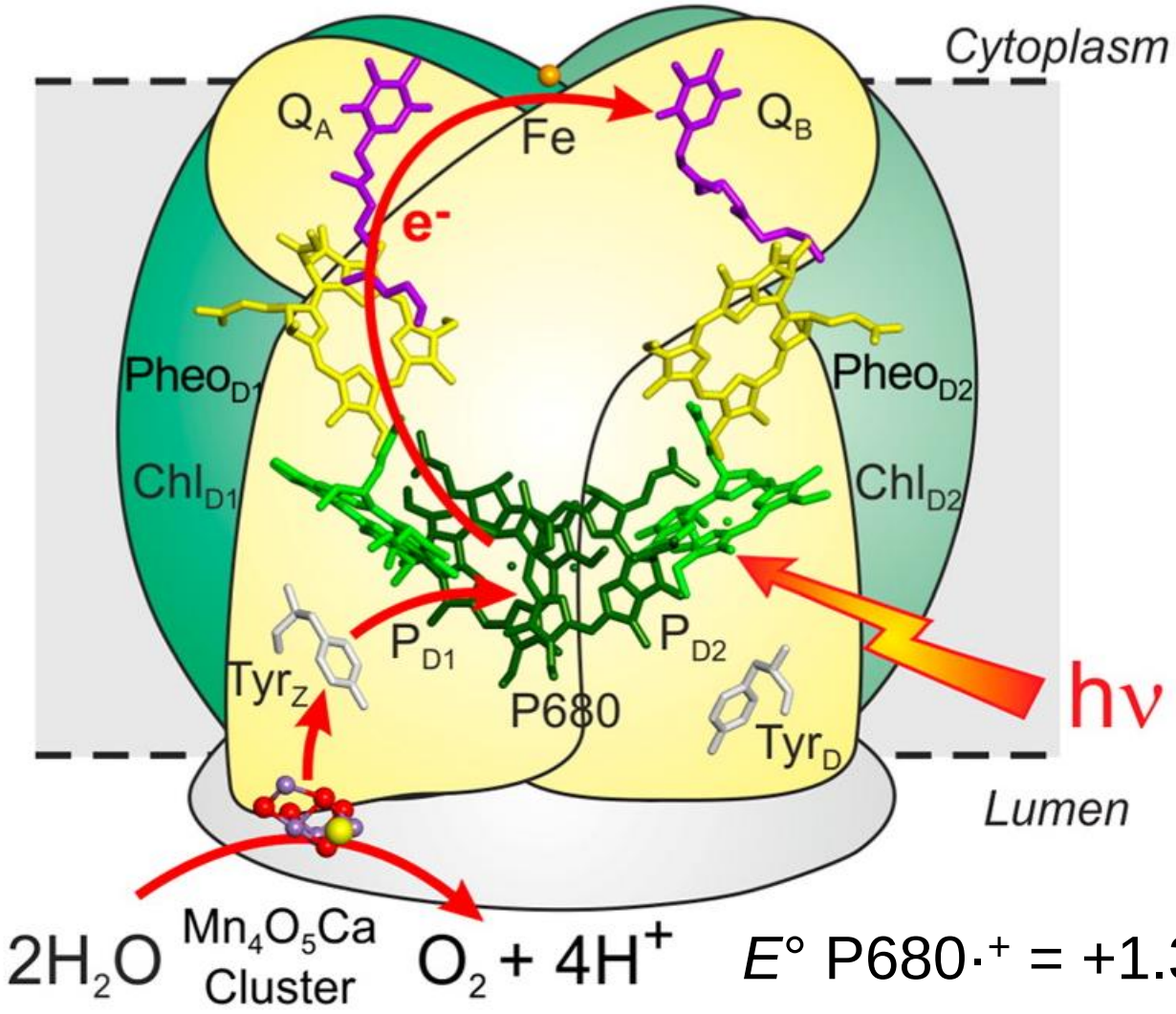

P680
~5 Å
Mg···Mg di 8.2 Å
I178
Helix D
Chl$_{D2}$
Helix E
H198
Helix CD
T286
Tyr$_D$
Helix C
H190
P$_{D2}$
P$_{D1}$
H189
Tyr$_Z$
H197
S282
Helix CD
Helix E
Helix C
Chl$_{D1}$
Helix D
T179

inside Stroma



CP43 D1/D2 CP47 Lumen

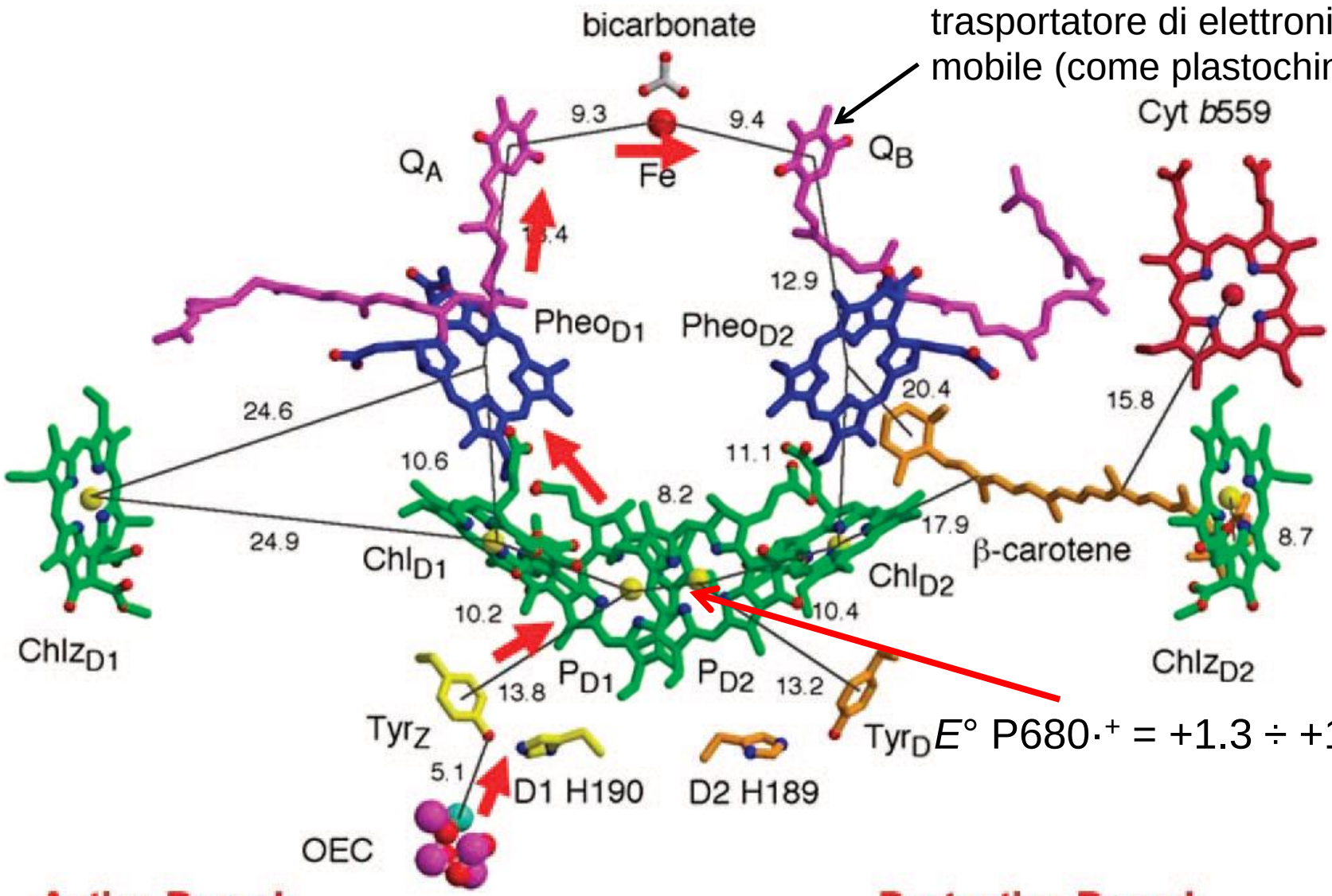
outside



$E°$ P680$^{\cdot+}$ = +1.3 ÷ +1.4 V

Potenziale più alto fra i sistemi biologici

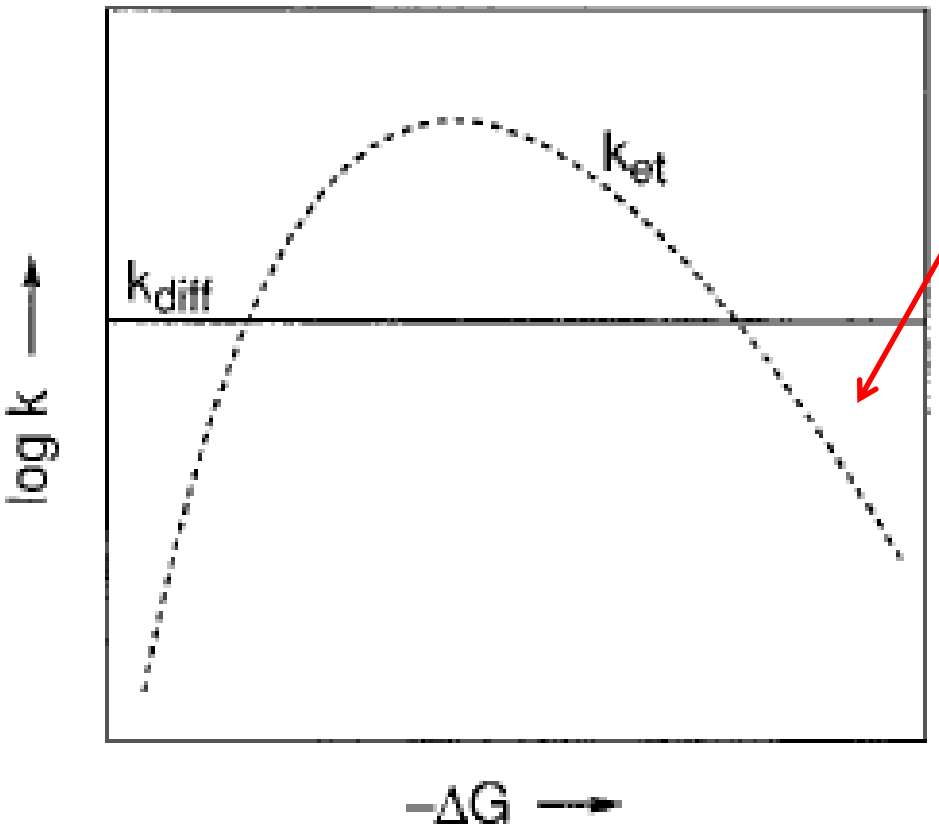
Electron transport cofactors



Plastochinone mobile = trasportatore di elettroni mobile (come plastochinolo)

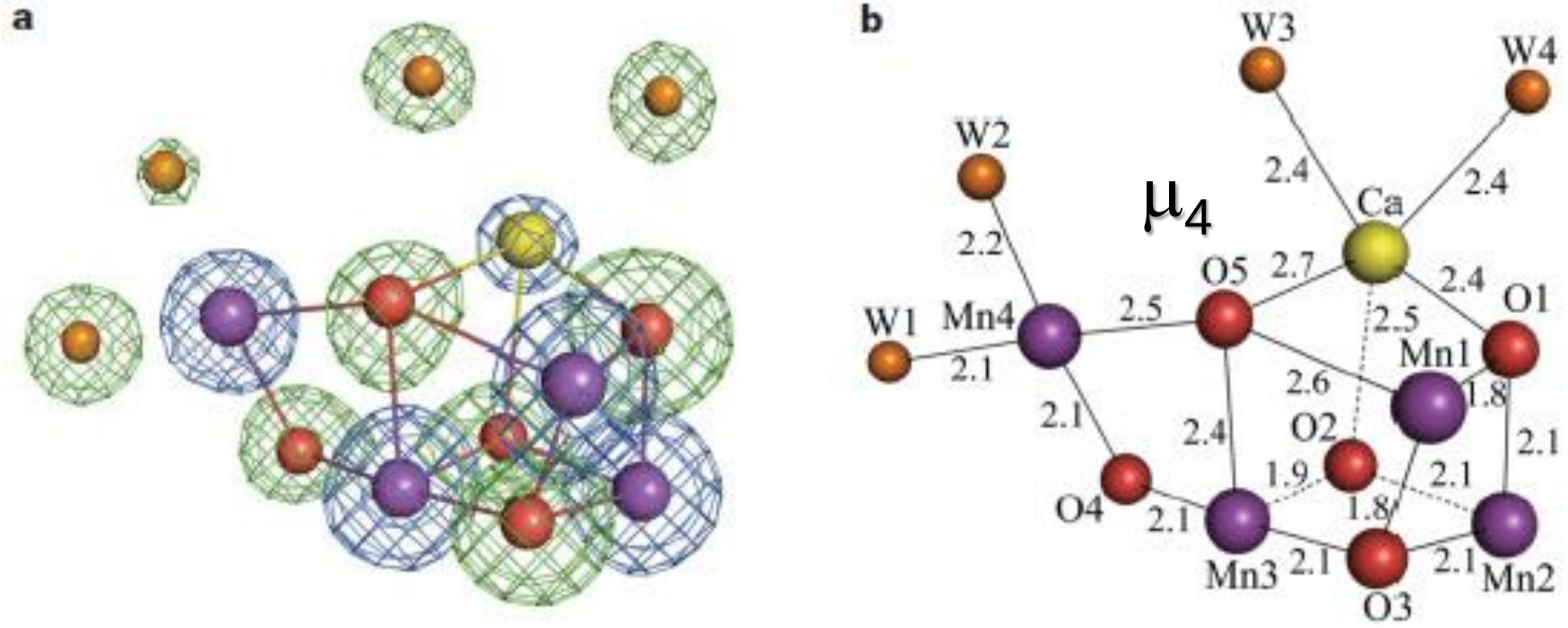
$E°$ $P680^{\cdot+}$ = +1.3 ÷ +1.4 V

Regione inversa di Marcus

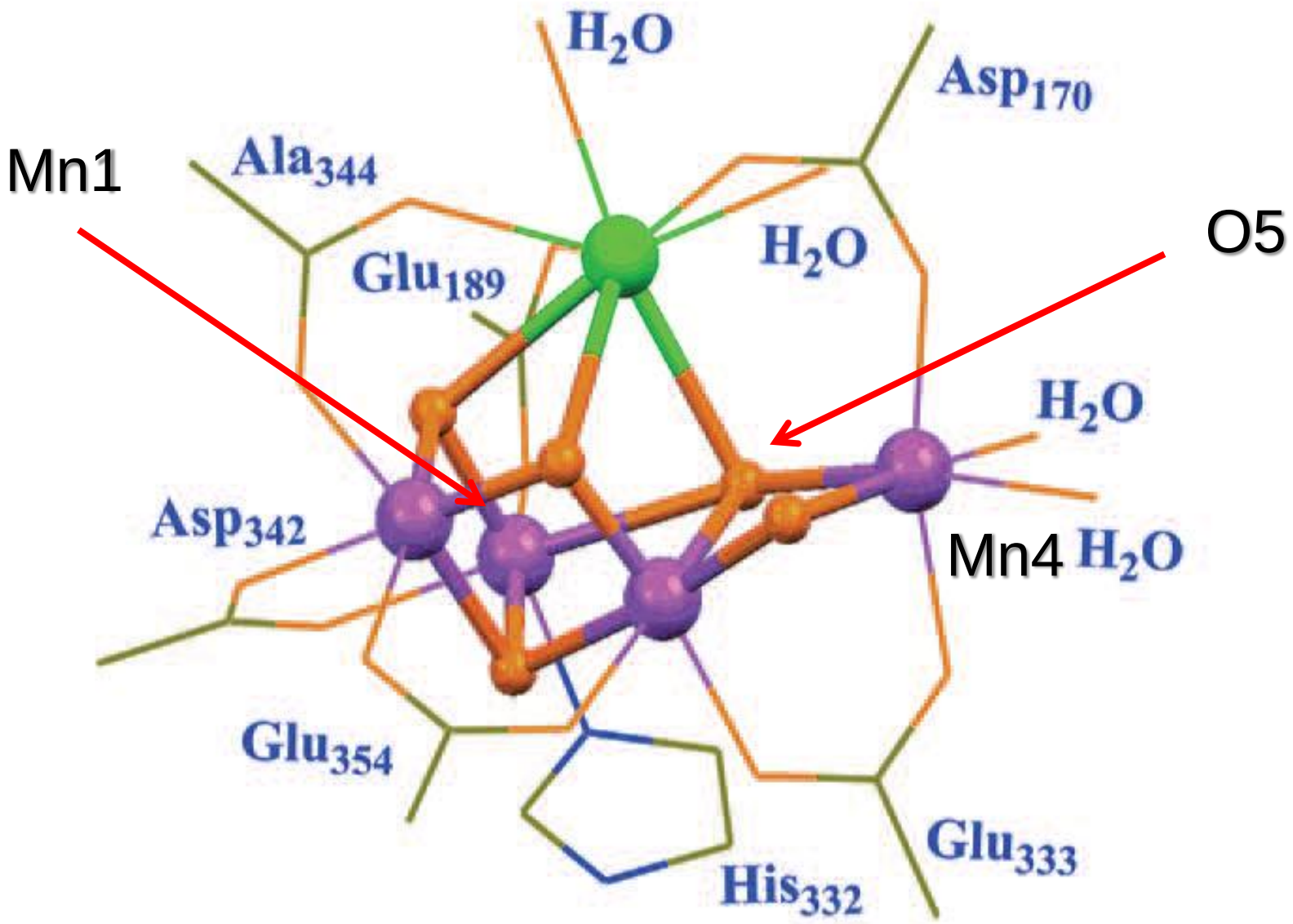


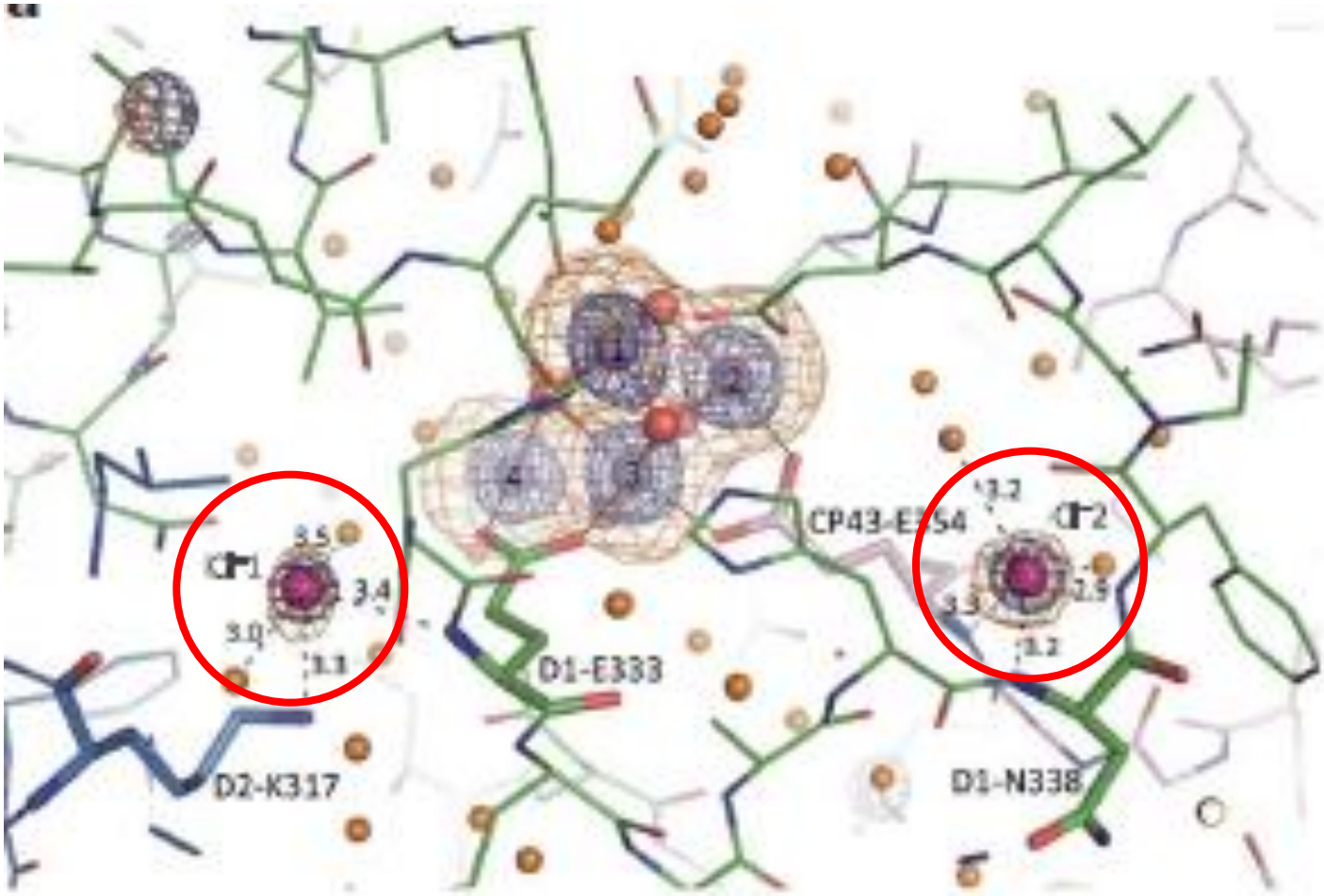
Oxygen Evolving Complex (OEC)

Mn_4CaO_5

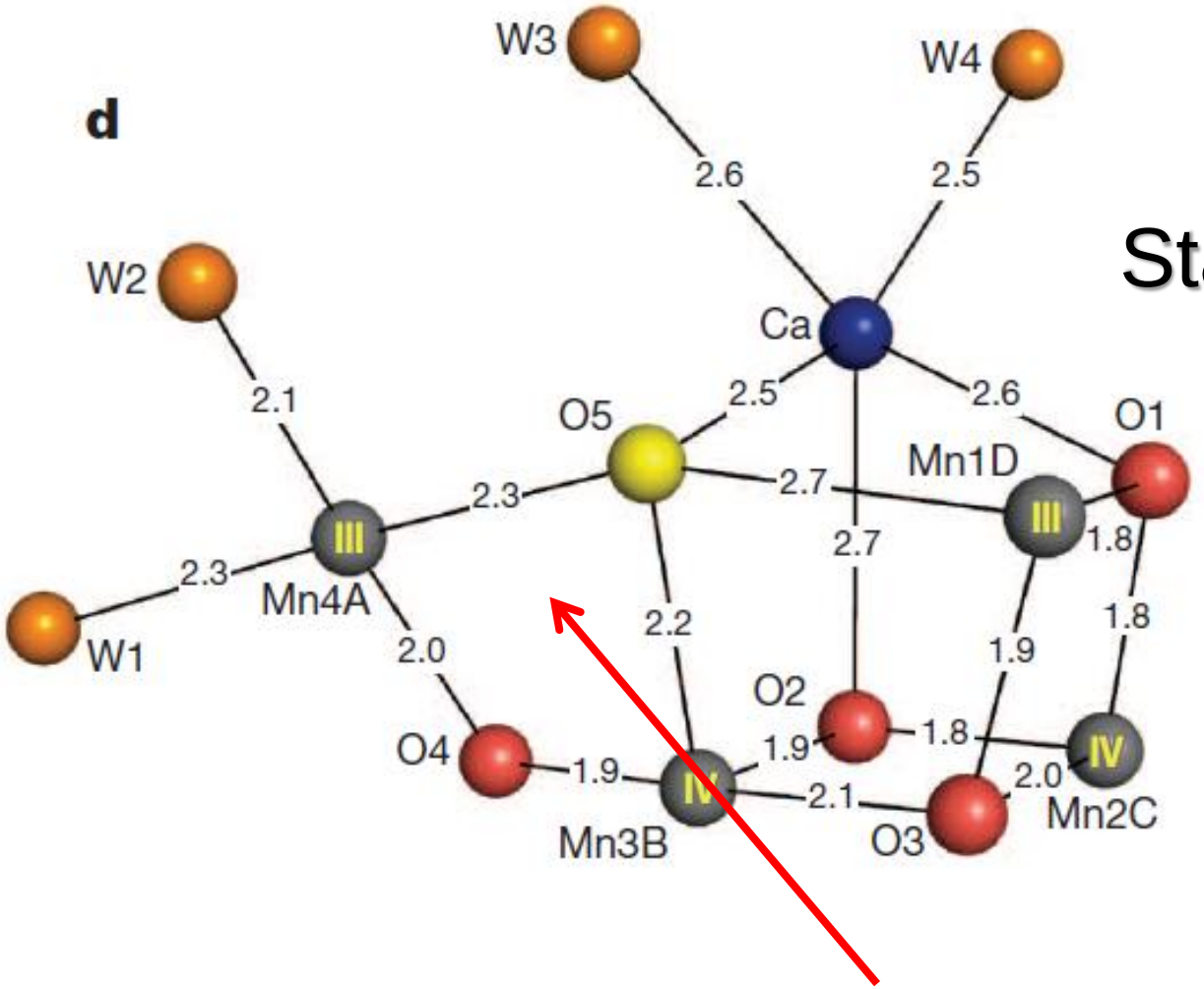


Nature 2011


Mn1
O5
H_2O
Asp_{170}
Ala_{344}
Glu_{189}
H_2O
H_2O
Asp_{342}
Mn4 H_2O
Glu_{354}
Glu_{333}
His_{332}


Cl1
3.5
3.4
3.0
3.1
Cl2
3.2
3.3
2.9
3.2
CP43-E354
D1-E333
D2-K317
D1-N338

Mn(III), d^4, alto spin → effetto Jahn-Teller

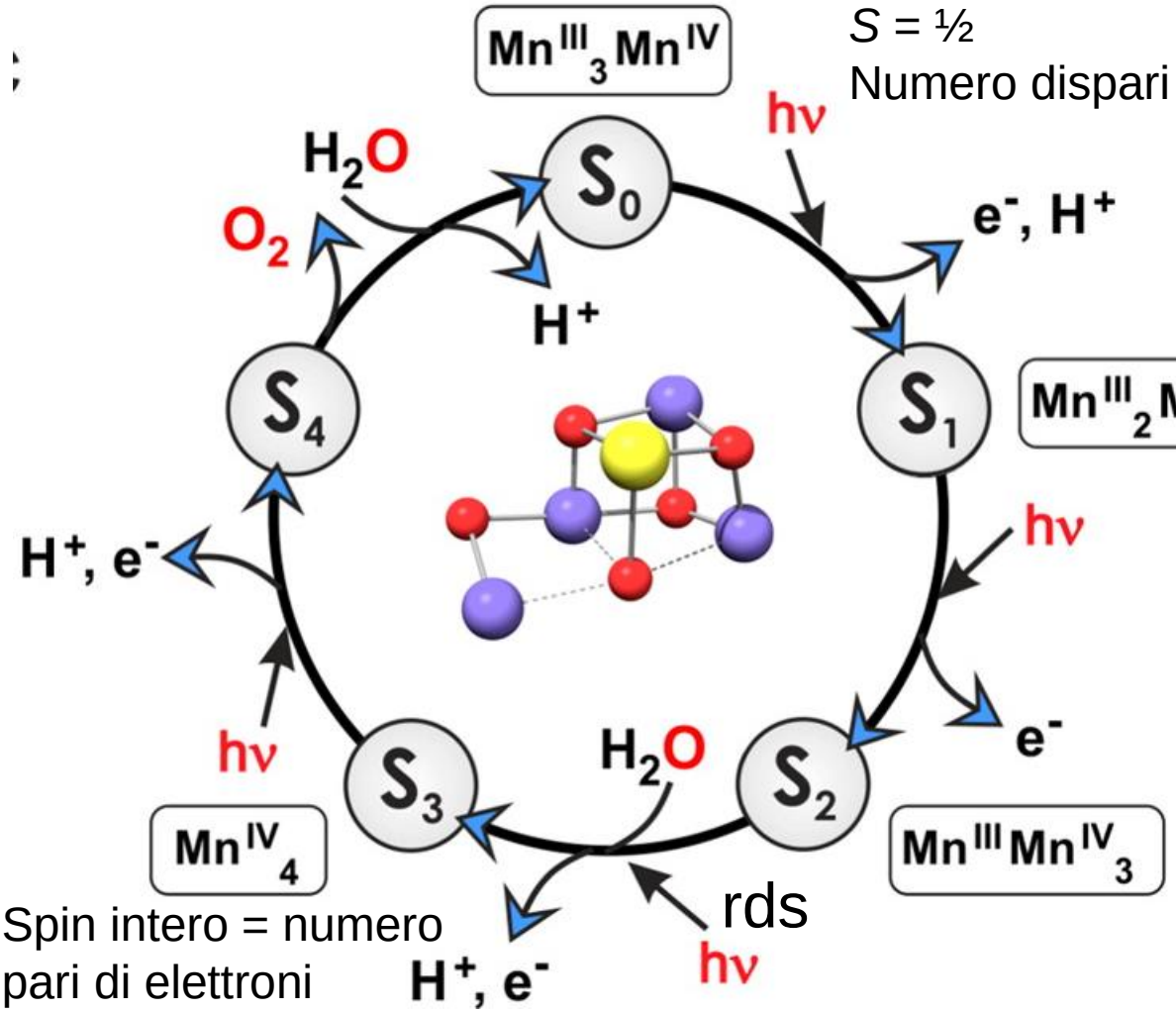


Stato S_1

Nature 2015
X-ray free-electron laser (XFEL)

Mn4–O5 più corta di 0.2 Å

Ciclo di Kok o *S clock*



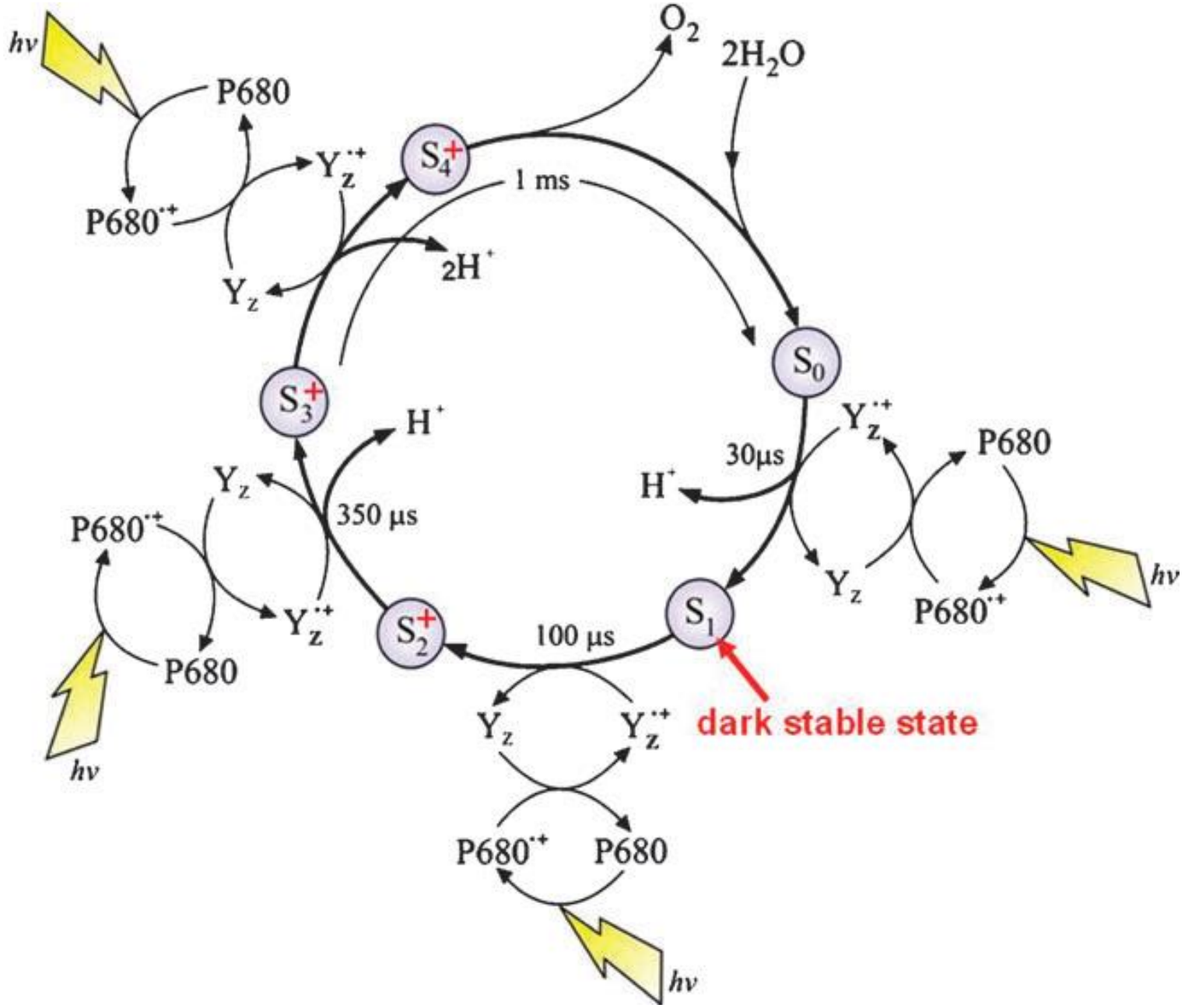
S = ½
Numero dispari di elettroni

Spin intero = numero pari di elettroni

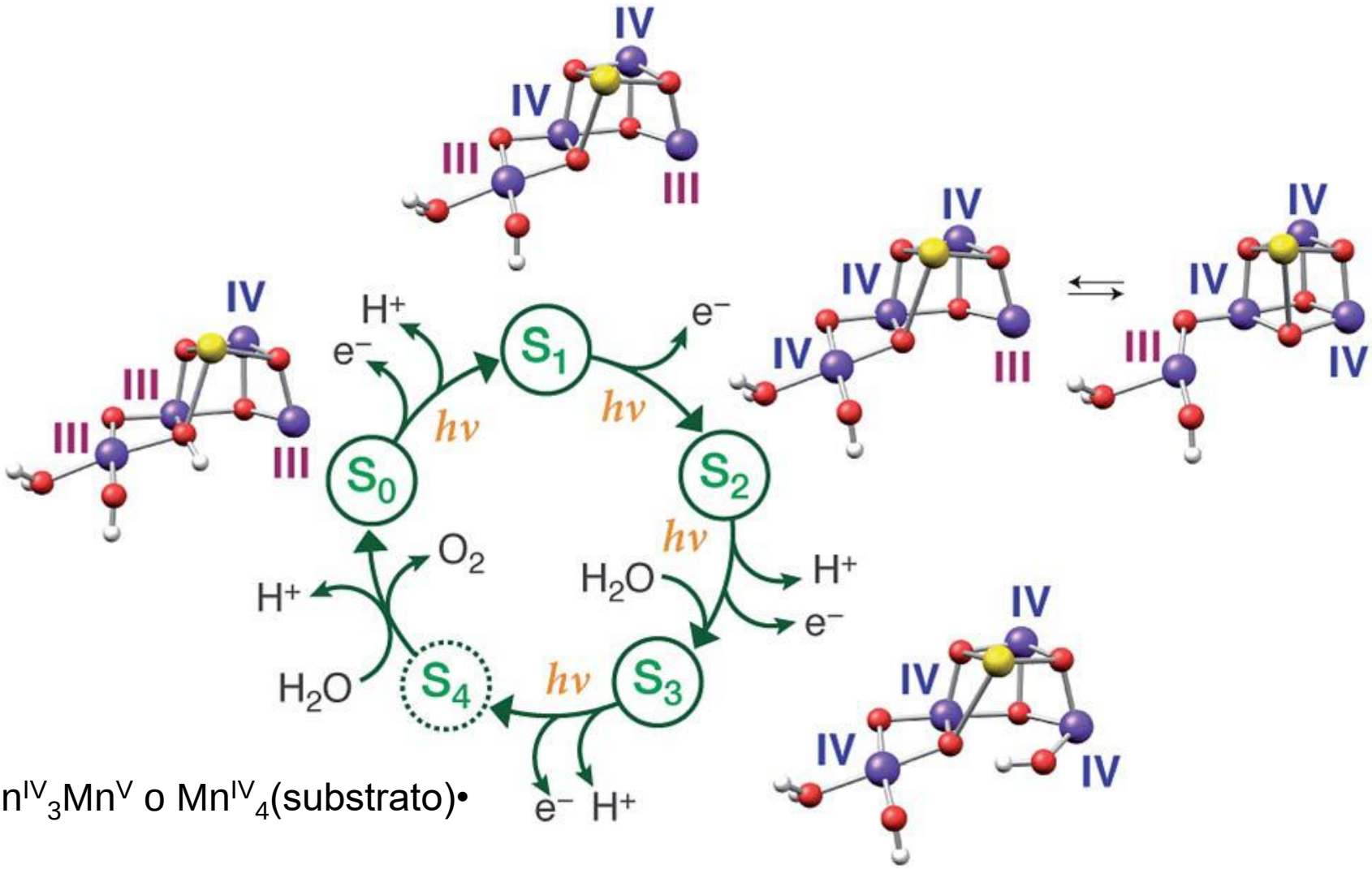
S = ½
Numero dispari di elettroni

Spin intero = numero pari di elettroni

OEC ossida fino a 1000 molecole di H_2O per secondo!
TON ≈ ca. 10^6



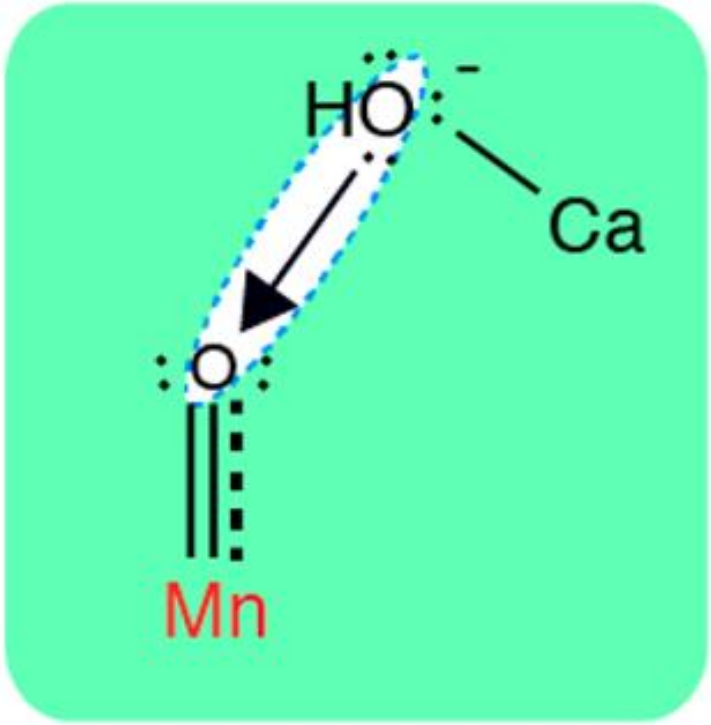
hν
P680
P680•+
Yz•+
Yz
S4+
O2
2H2O
1 ms
2H+
S0
S3+
H+
Yz•+
P680
30μs
H+
Yz
350 μs
P680•+
Yz•+
P680
hν
S2+
100 μs
S1
Yz
P680•+
hν
Yz
Yz•+
dark stable state
P680•+
P680
hν



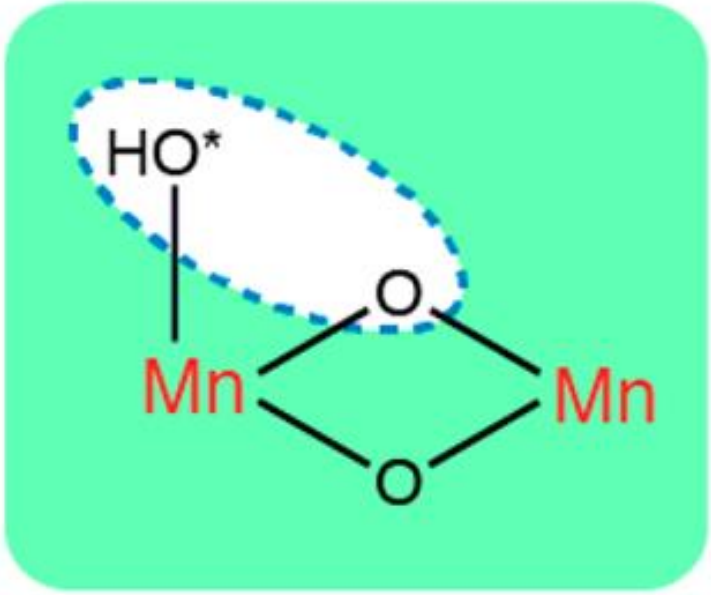
$Mn^{IV}_3Mn^{V}$ o Mn^{IV}_4(substrato)•

Ipotesi di formazione del legame O–O

nucleophilic attack



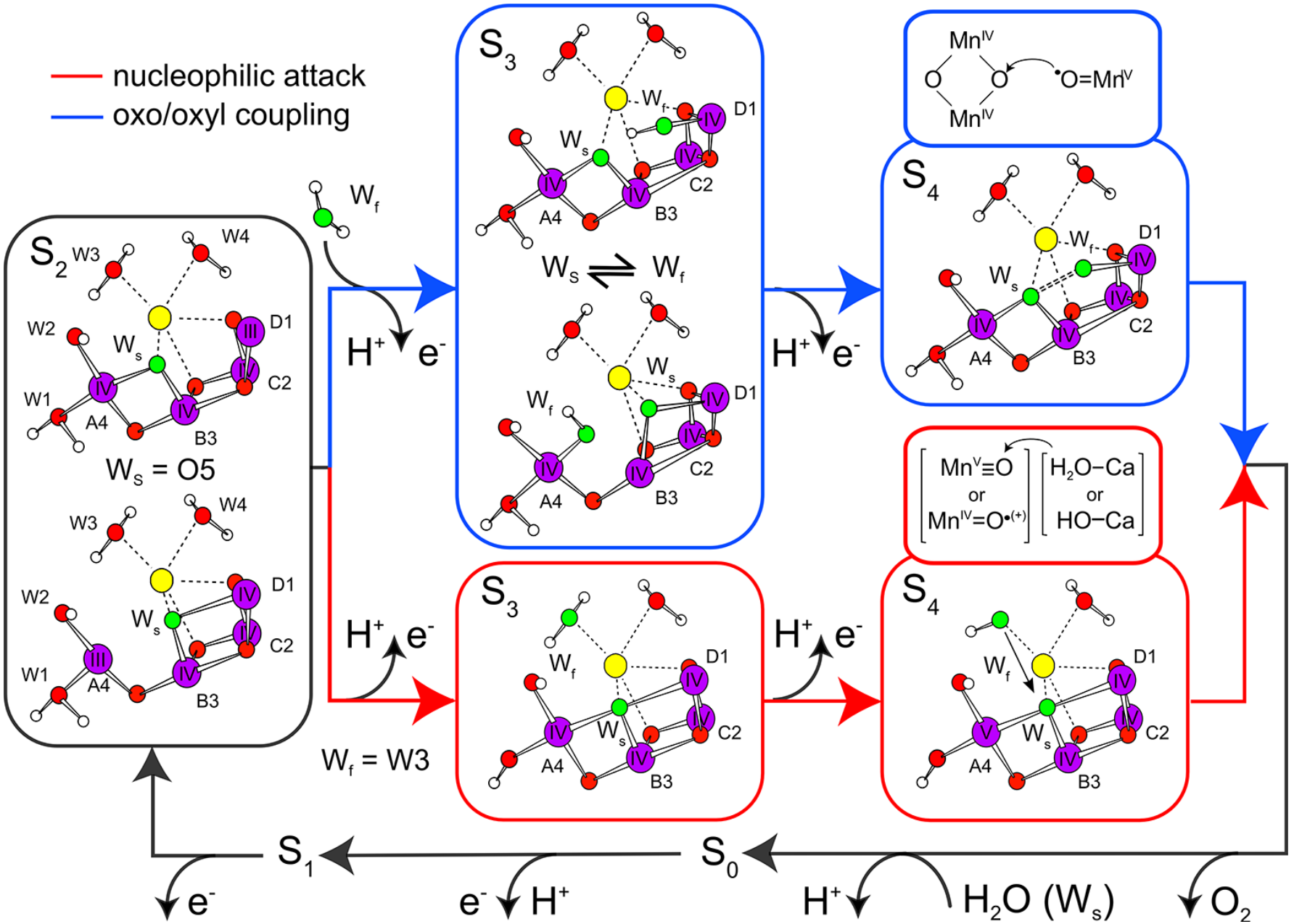
terminal oxyl radical with bridging oxo



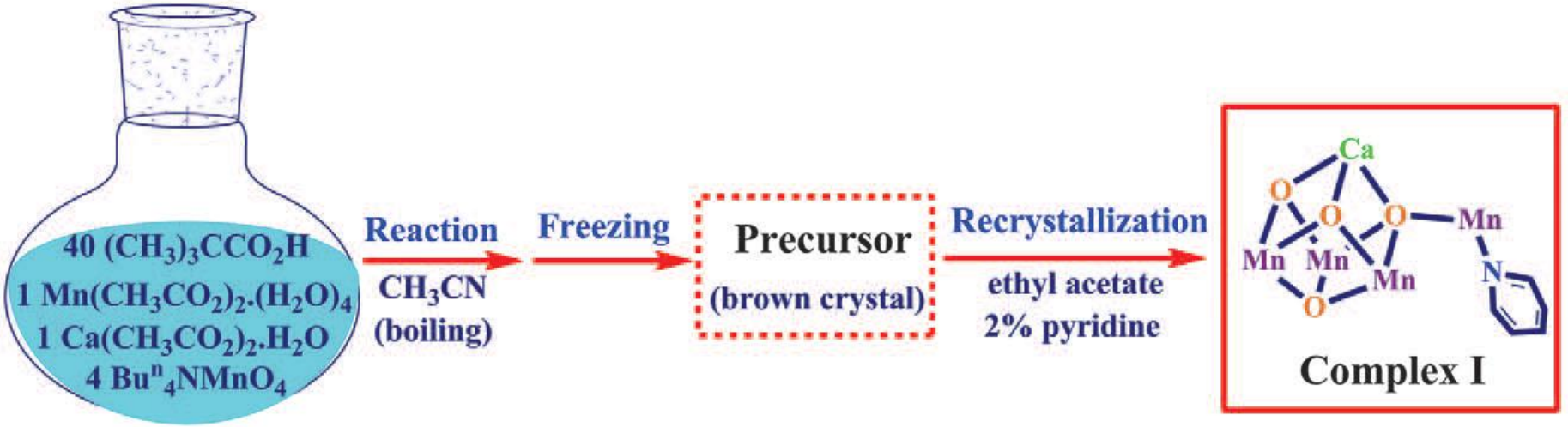
Mn(V)≡O o Mn(IV)=O•

oxo/oxyl radical coupling mechanism

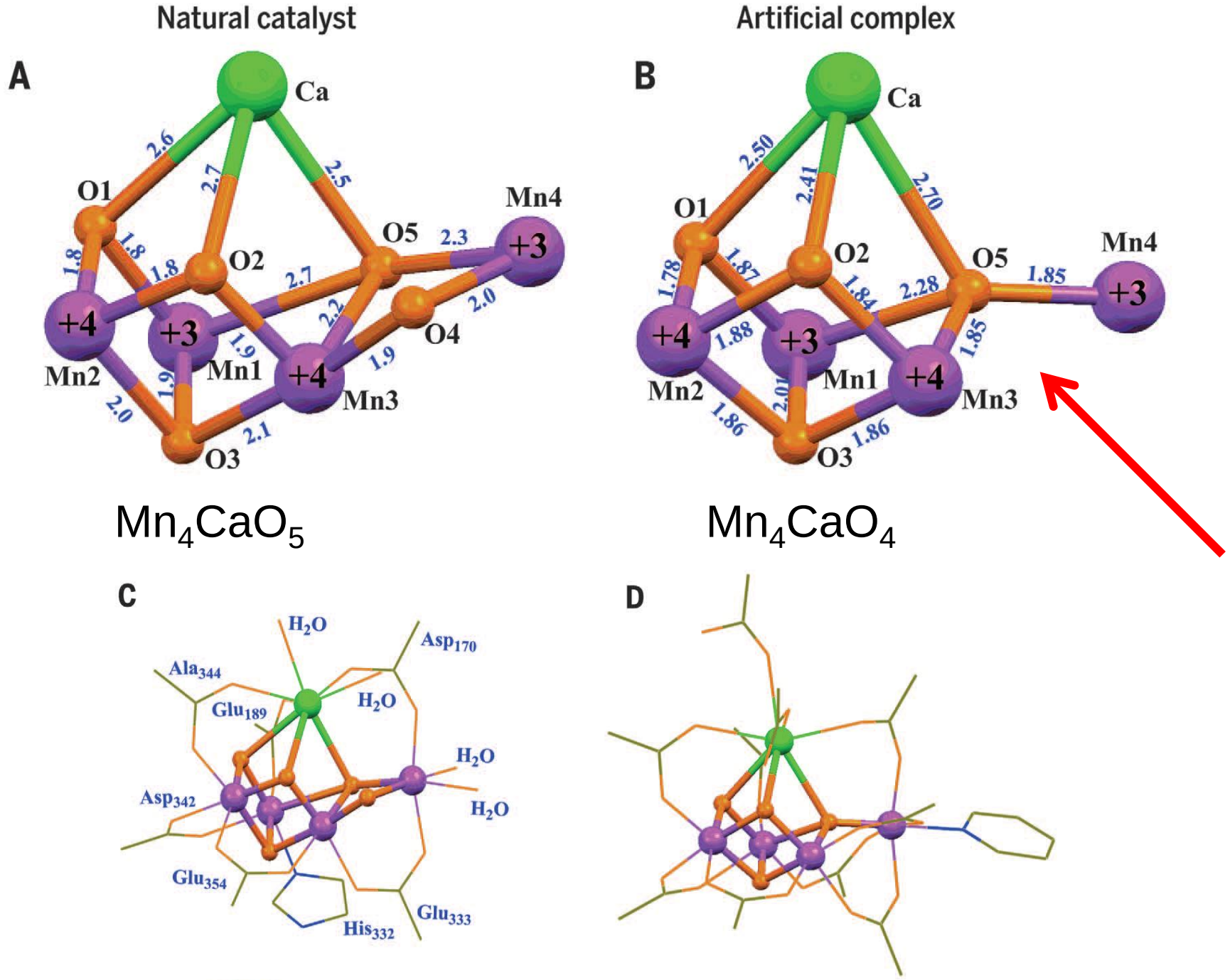
In questo meccanismo l'ultimo elettrone viene estratto da O, non da Mn


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

Sistemi modello



Science 2015


Natural catalyst
Artificial complex
A
B
Ca
O1
O2
O3
O4
O5
Mn1
Mn2
Mn3
Mn4
+3
+4
2.6
2.7
2.5
2.3
1.8
1.8
1.8
2.7
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
C
D
H2O
Asp170
Ala344
Glu189
H2O
H2O
Asp342
H2O
Glu354
Glu333
His332