fotosintesi (*uphill catalysis*)

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

respirazione (*downhill catalysis*)

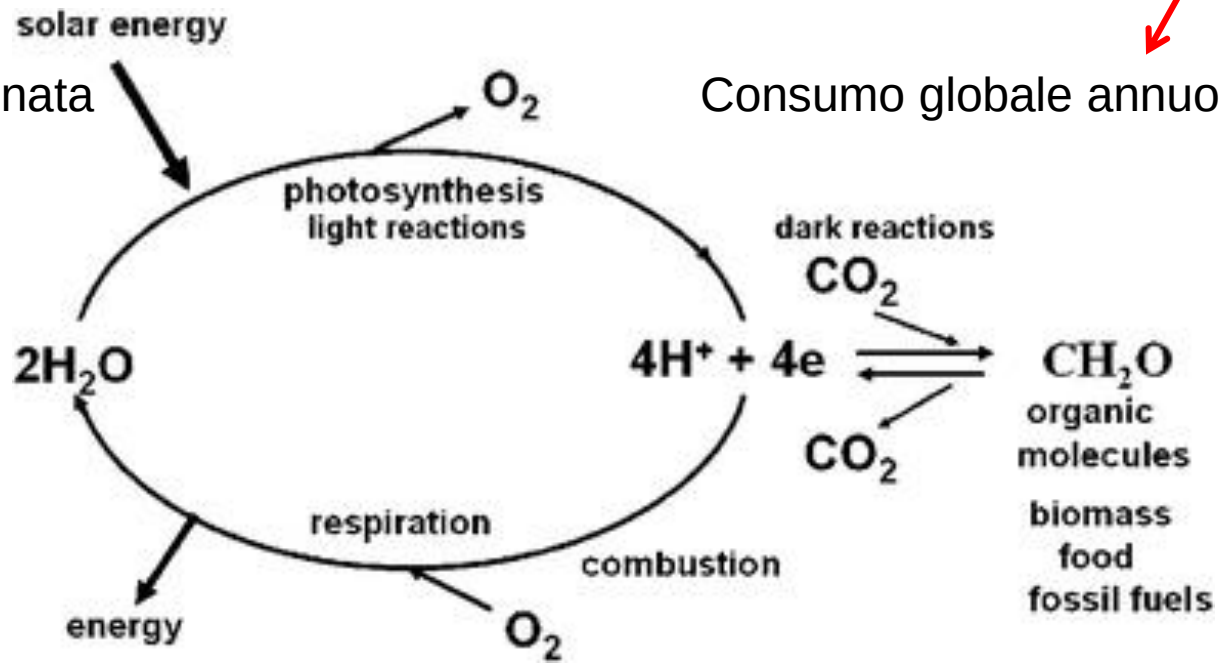
100×10^9 ton/y di $(CH_2O)_n$ da CO_2

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

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

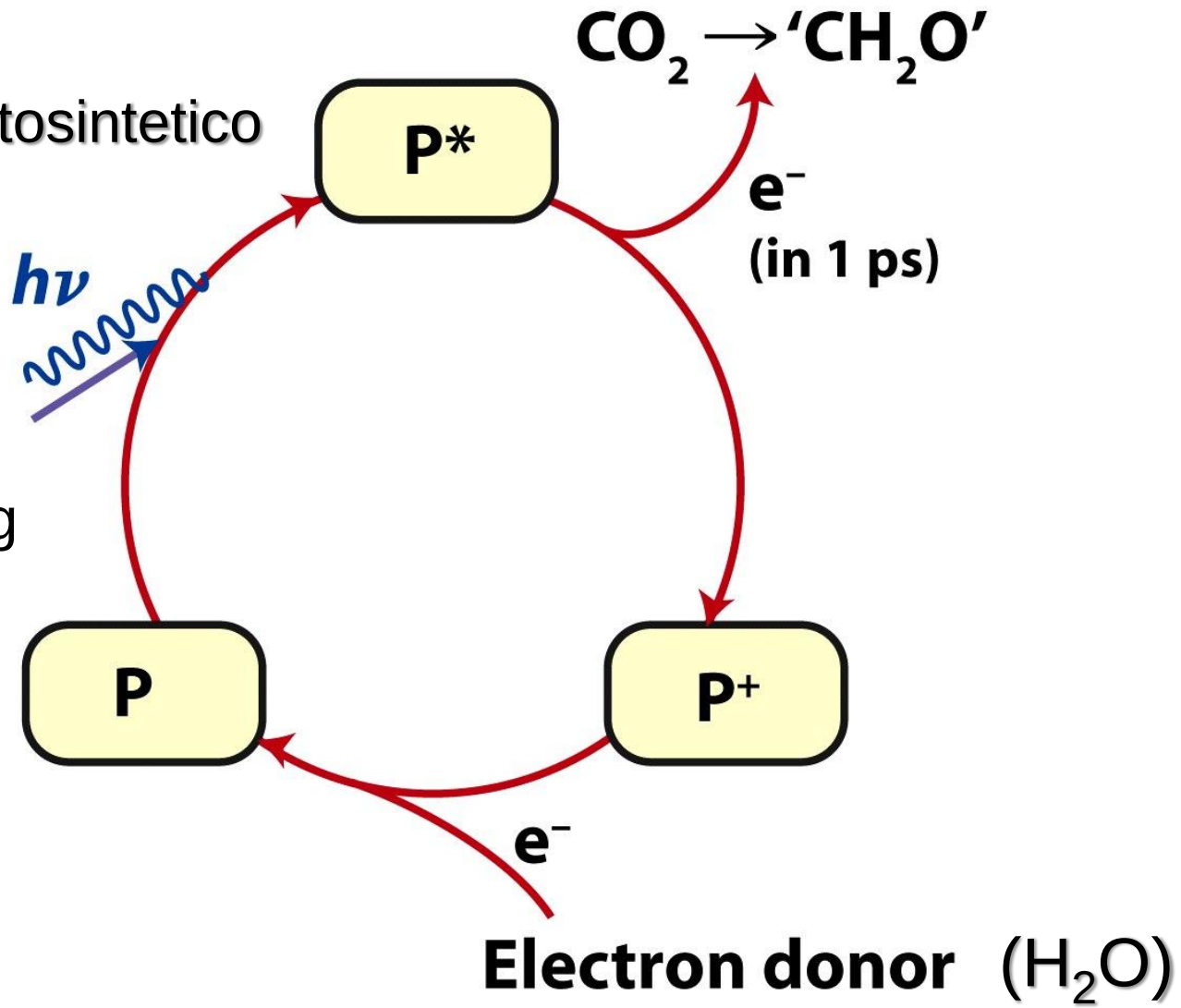
Energia immagazzinata come biomassa

Consumo globale annuo: 14 TW



Separazione di carica fotoindotta

P = centro fotosintetico



Processo fotosintetico nelle piante

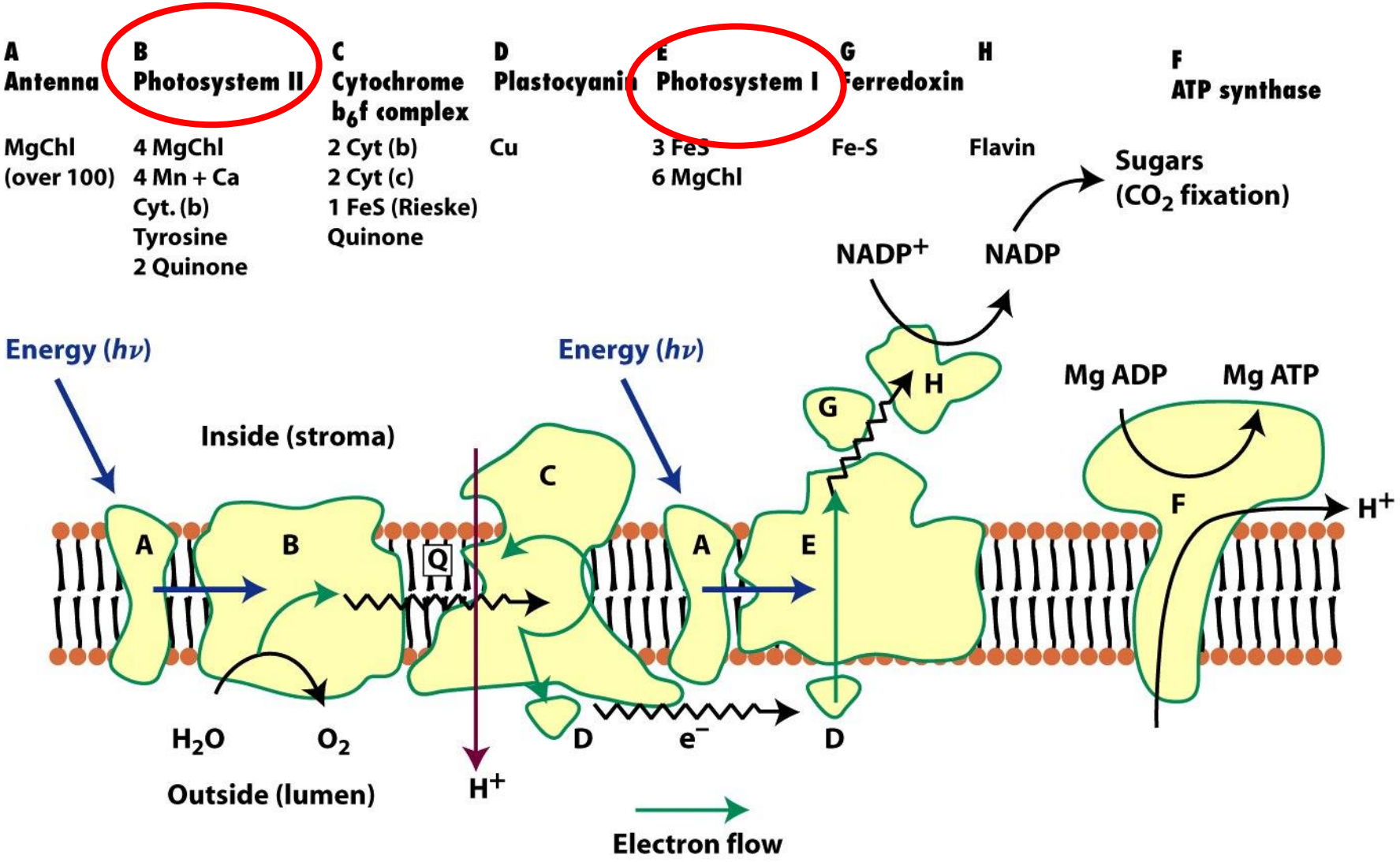
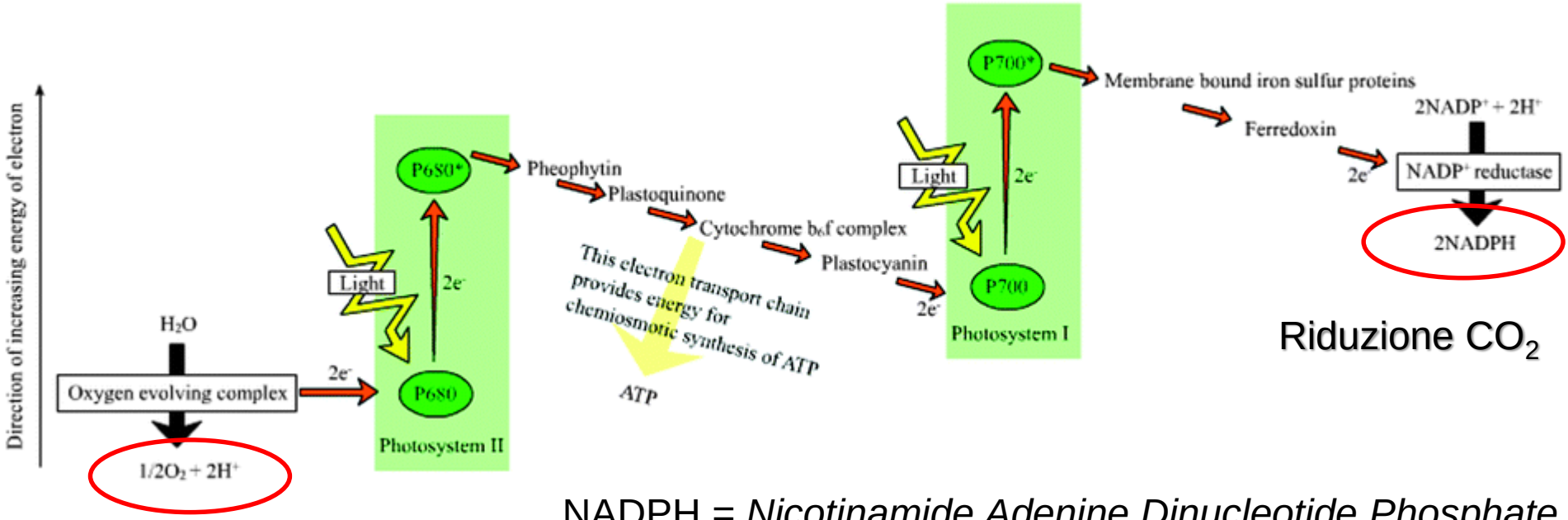


Diagramma di potenziale redox "a Z"

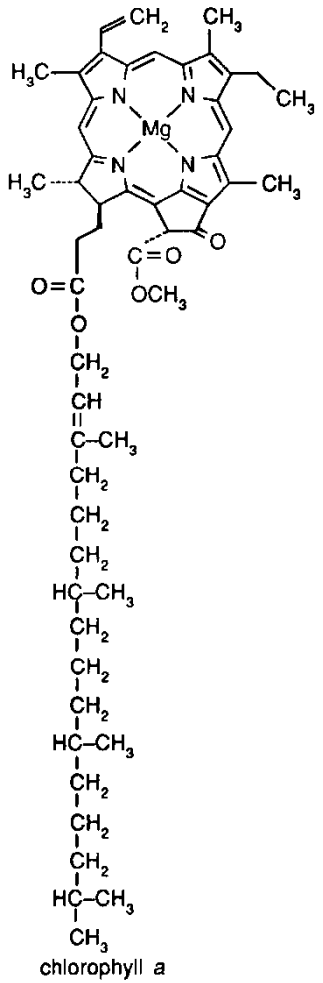


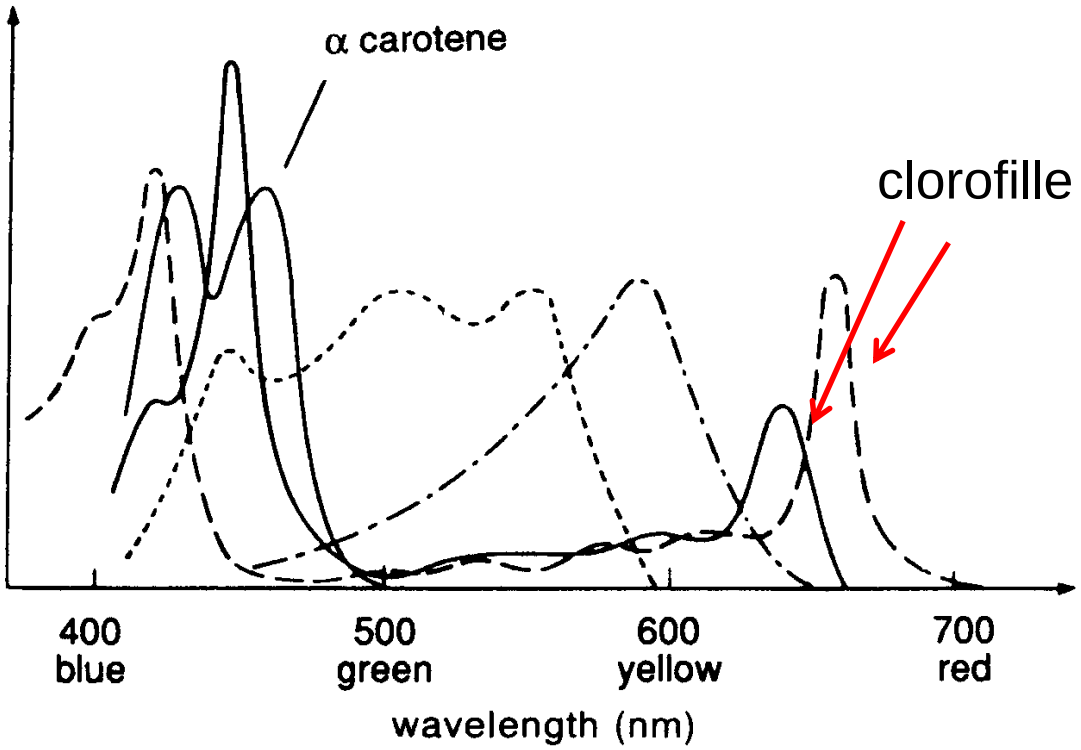
Riduzione CO_2

NADPH = *Nicotinamide Adenine Dinucleotide Phosphate*

Per ogni elettrone estratto dall'acqua e trasferito a CO_2 serve l'energia di due fotoni, uno in PSII e l'altro in PSI

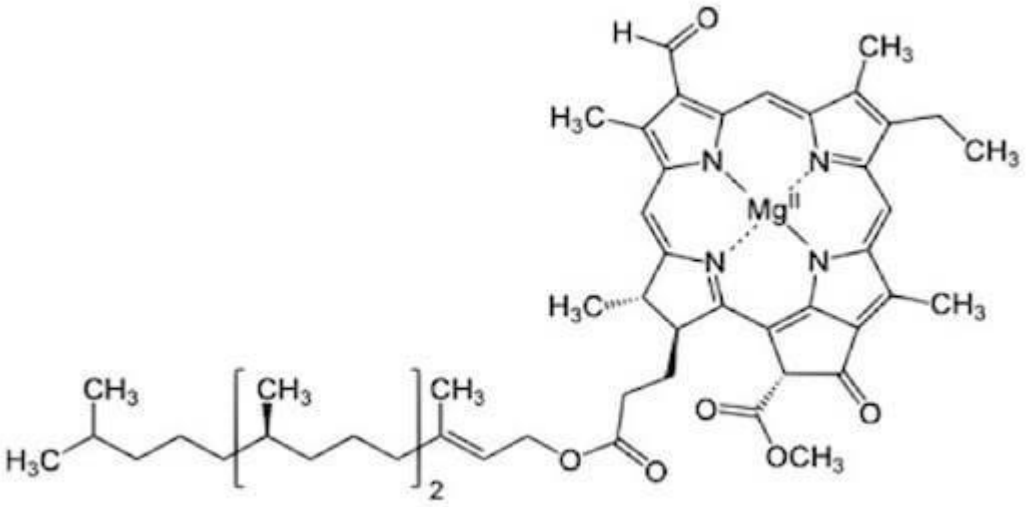
Pigmenti deputati al *light harvesting*

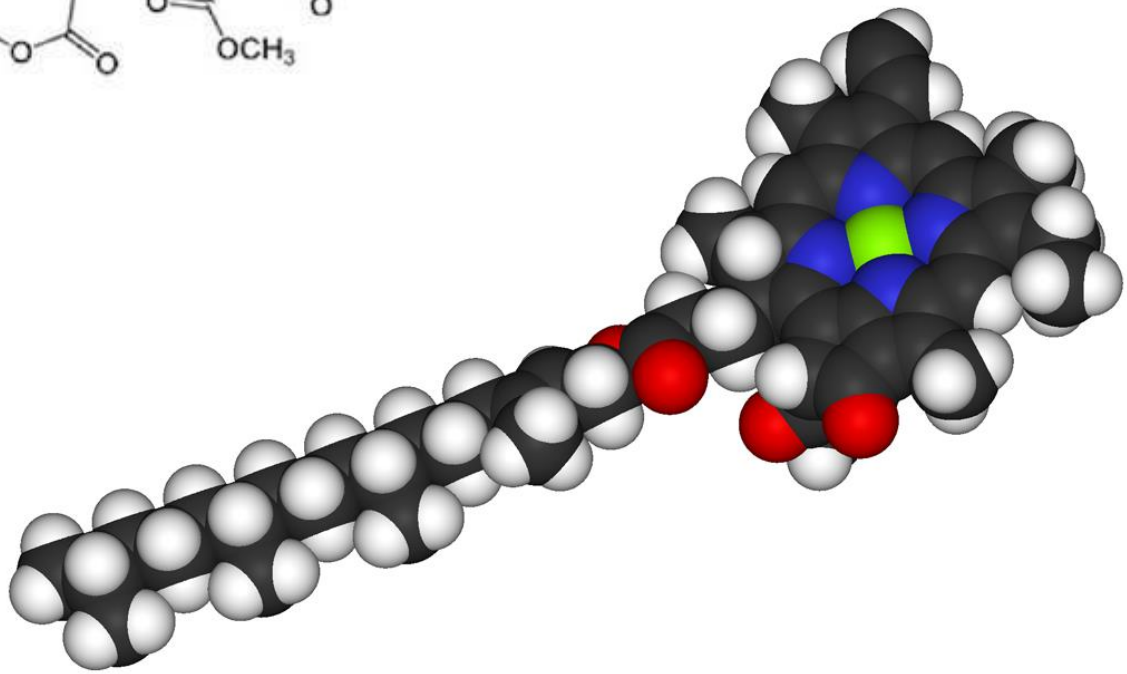




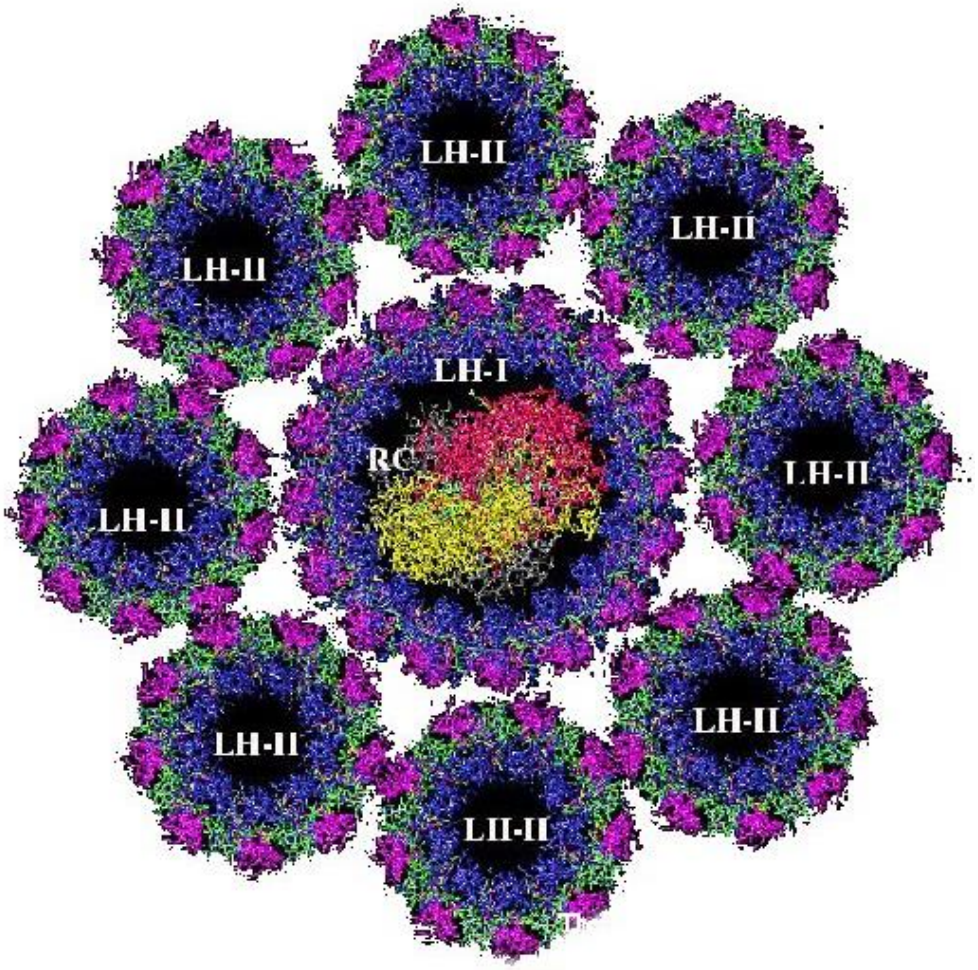
Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (——), phycocyanin (–·–·), phycoerythrin (–––––)

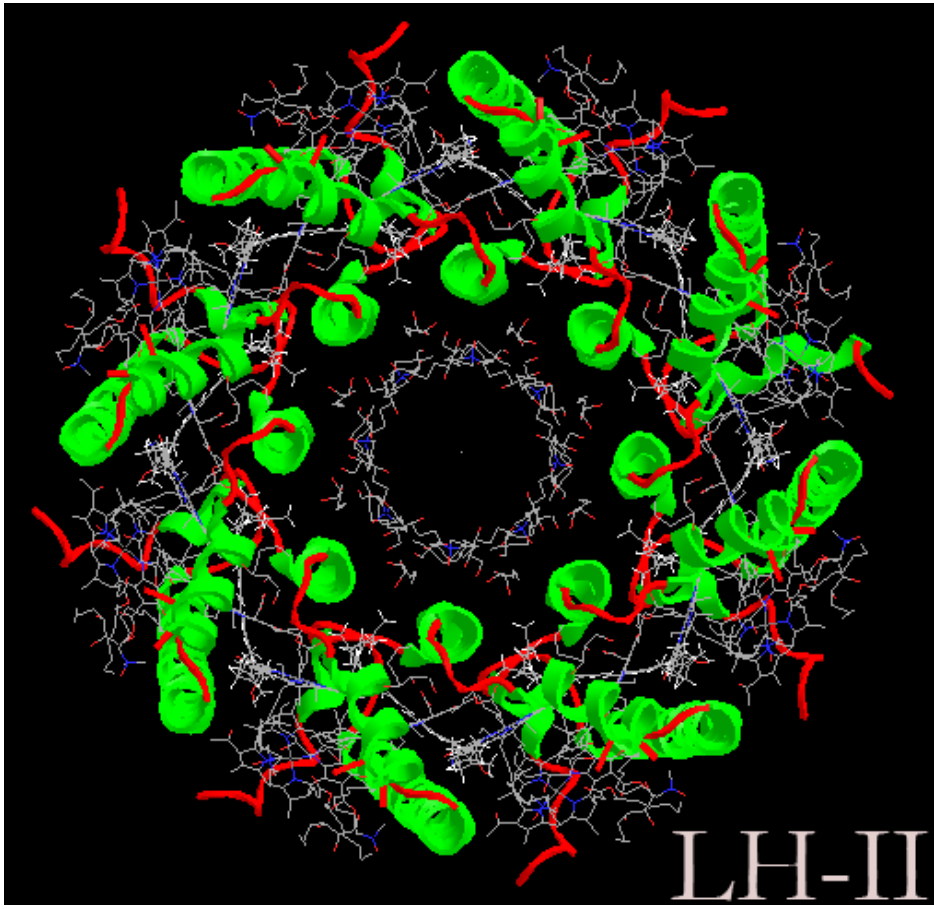
Clorofilla



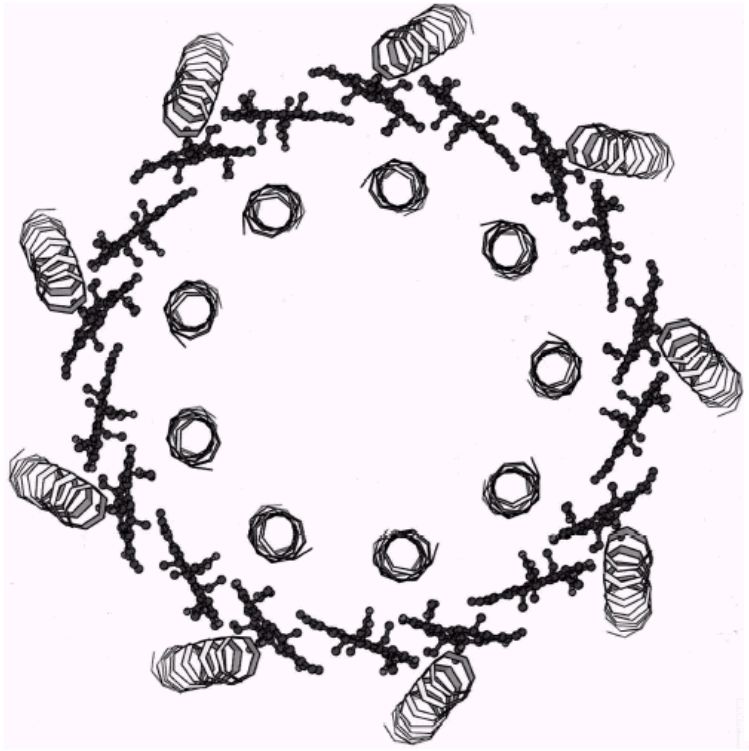


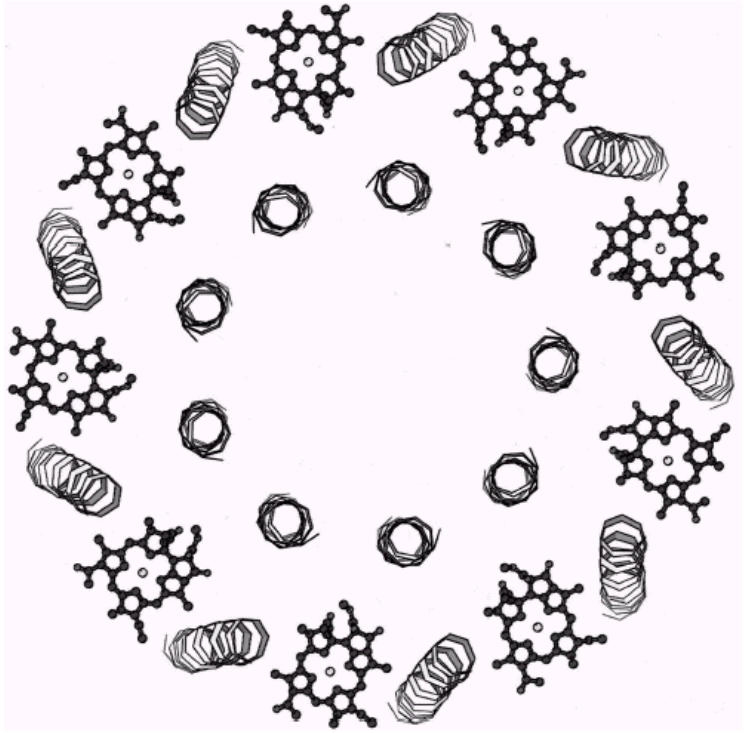
Sistemi antenna per *light-harvesting* e *exciton transfer*



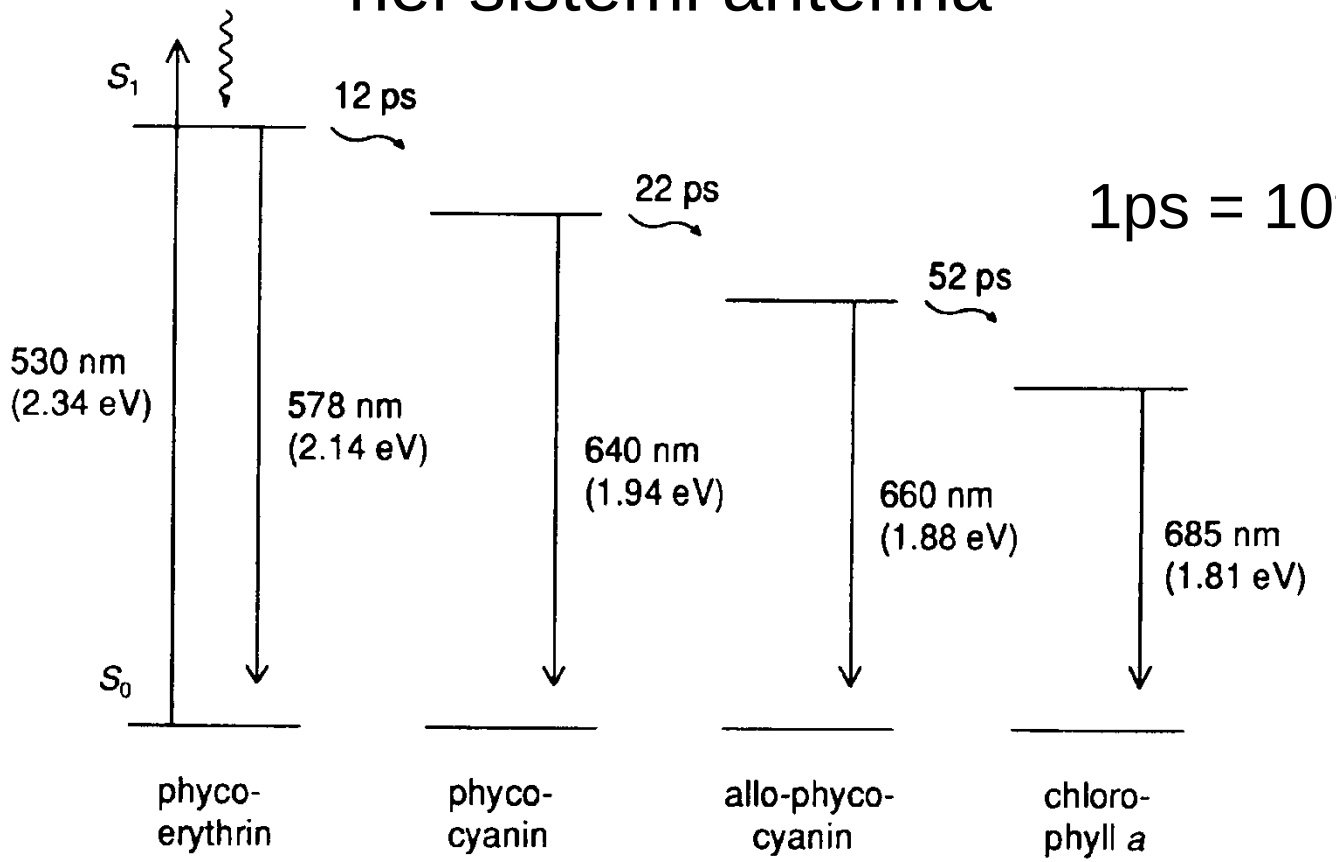


Sistemi antenna per *light-harvesting* e *exciton transfer*





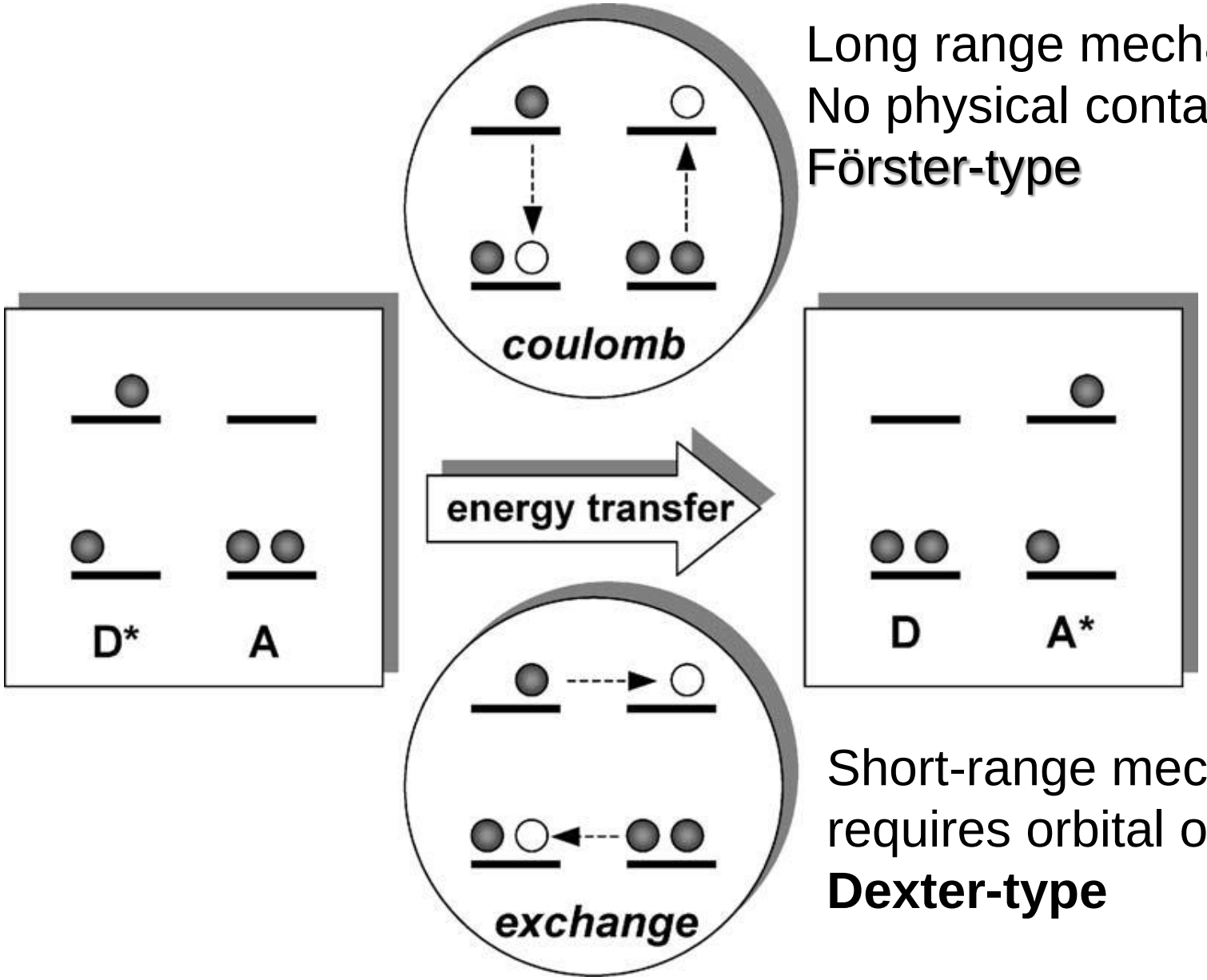
Trasferimento di energia (*exciton transfer*) a cascata nei sistemi antenna



1ps = 10^{-12} s

efficienza del 95%

Meccanismi di *exciton transfer*



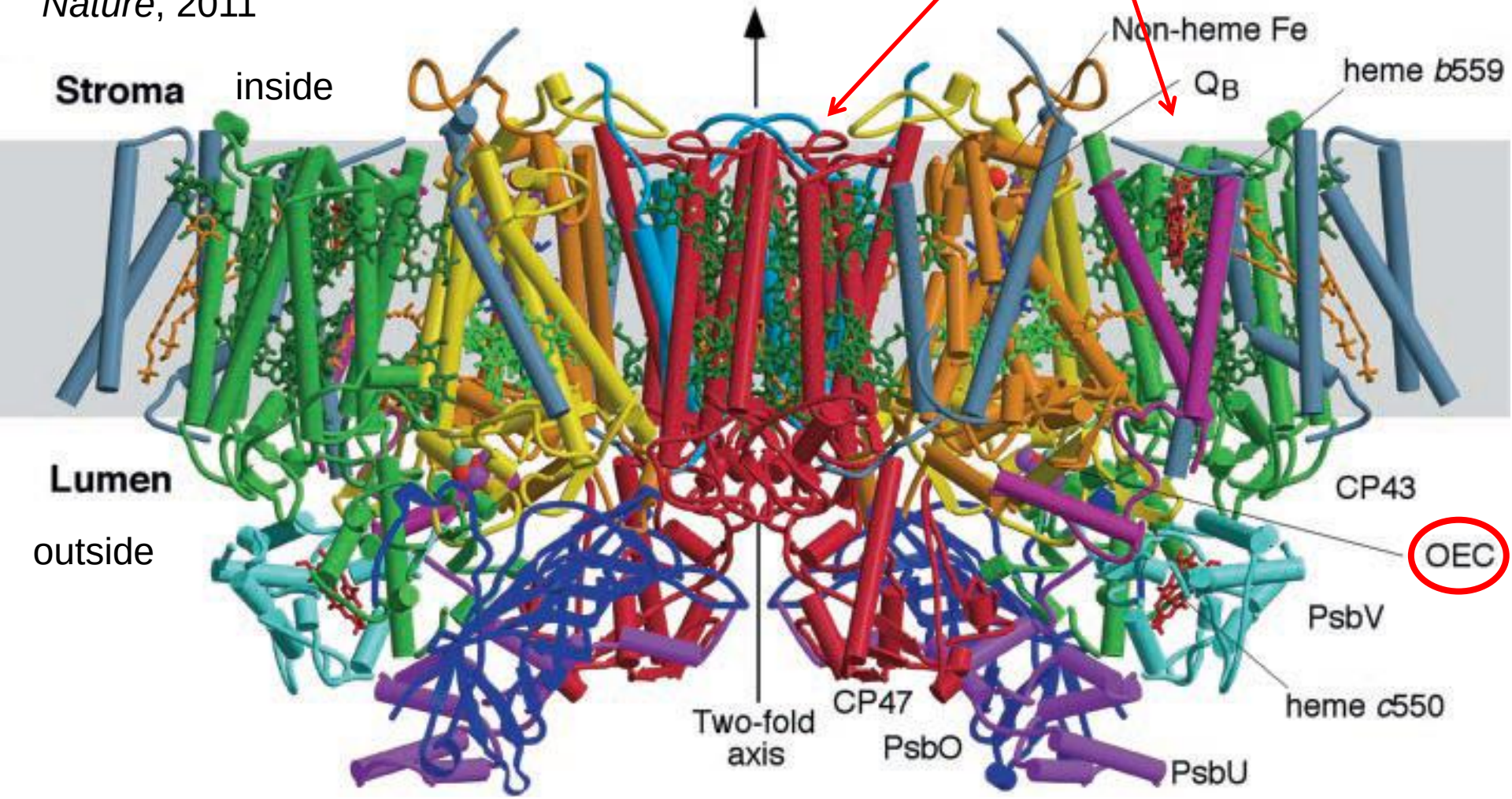
Long range mechanism
No physical contact
Förster-type

Short-range mechanism
requires orbital overlap
Dexter-type

PS II

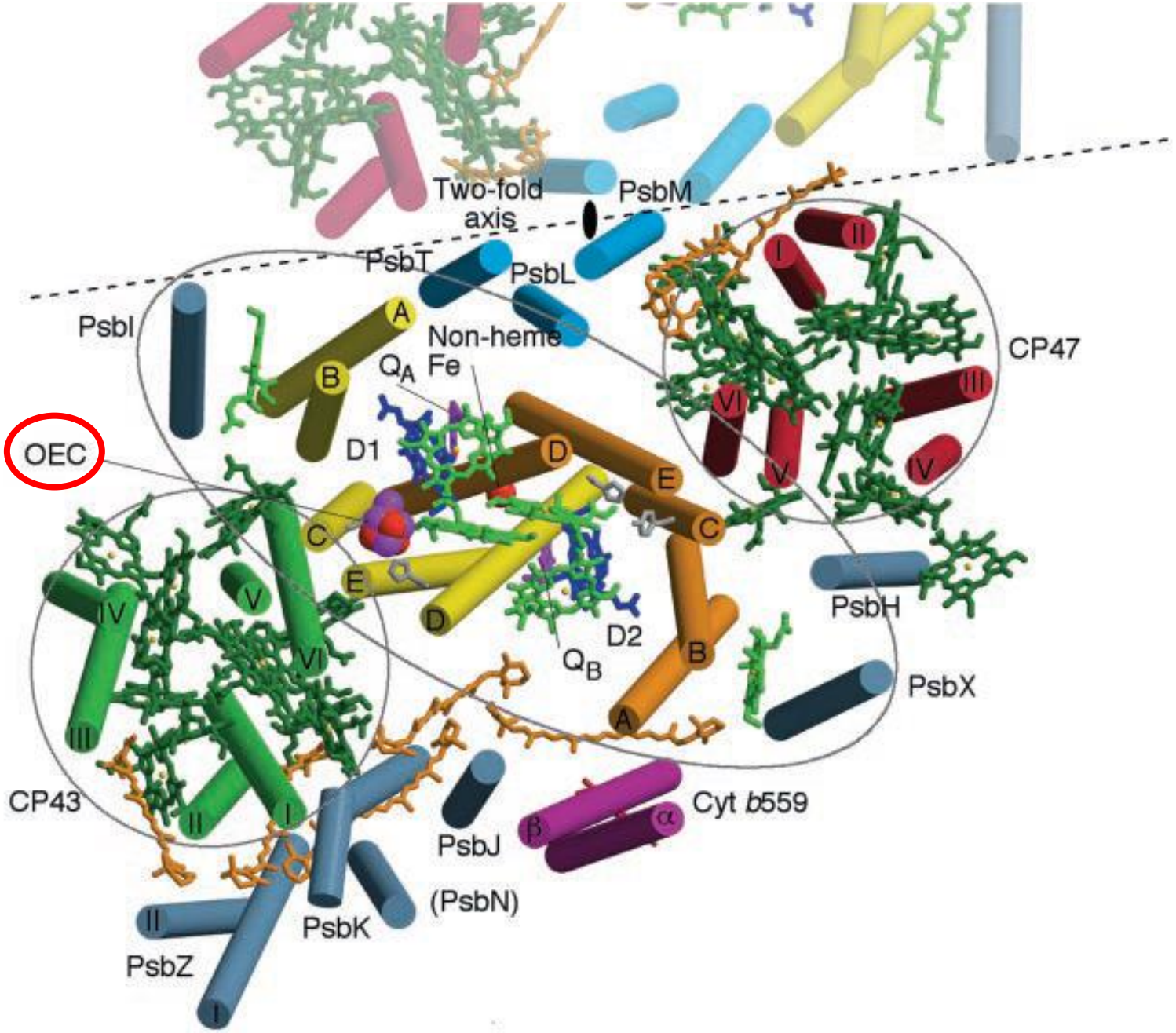
Sistemi antenna

Nature, 2011



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

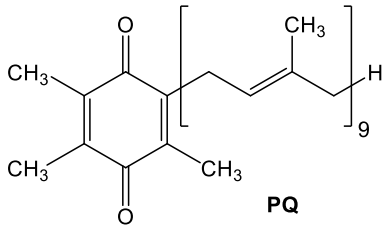
PS II

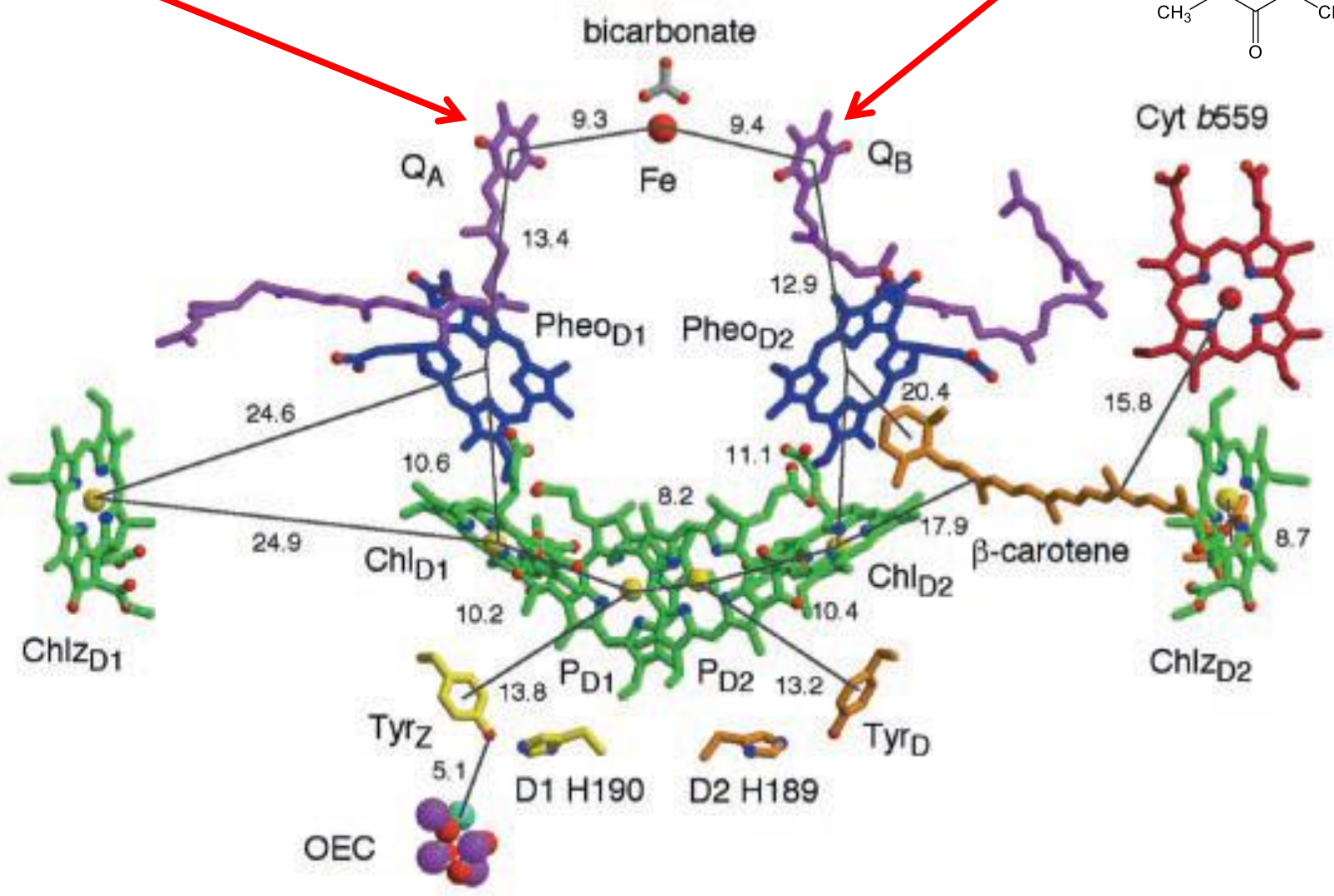

Two-fold axis
PsbM
PsbT
PsbL
PsbI
Non-heme Fe
Q_A
Q_B
D1
D2
CP47
CP43
OEC
PsbH
PsbX
Cyt *b*559
PsbJ
(PsbN)
PsbK
PsbZ

P680

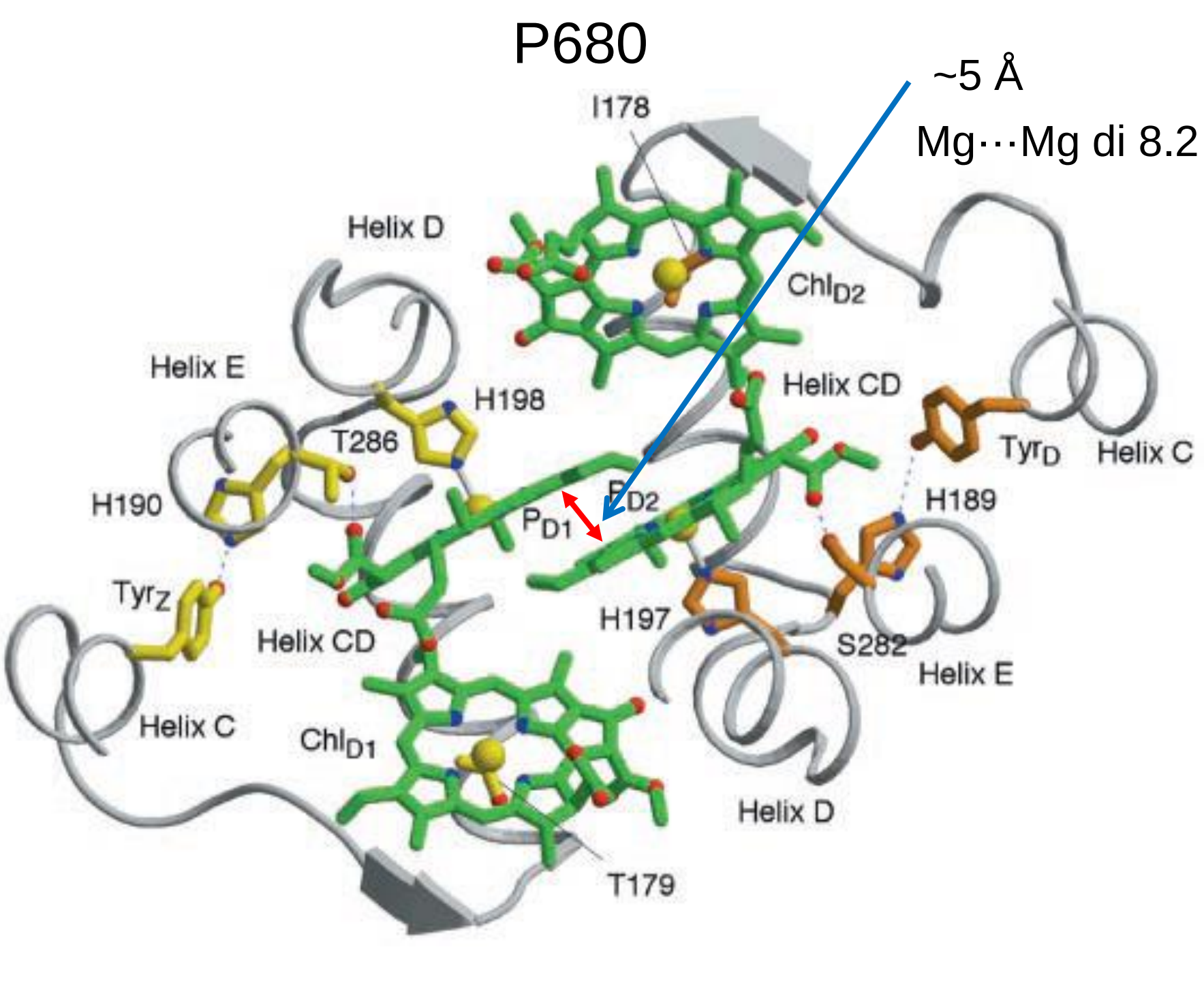
Plastochinone fisso

Plastochinone mobile

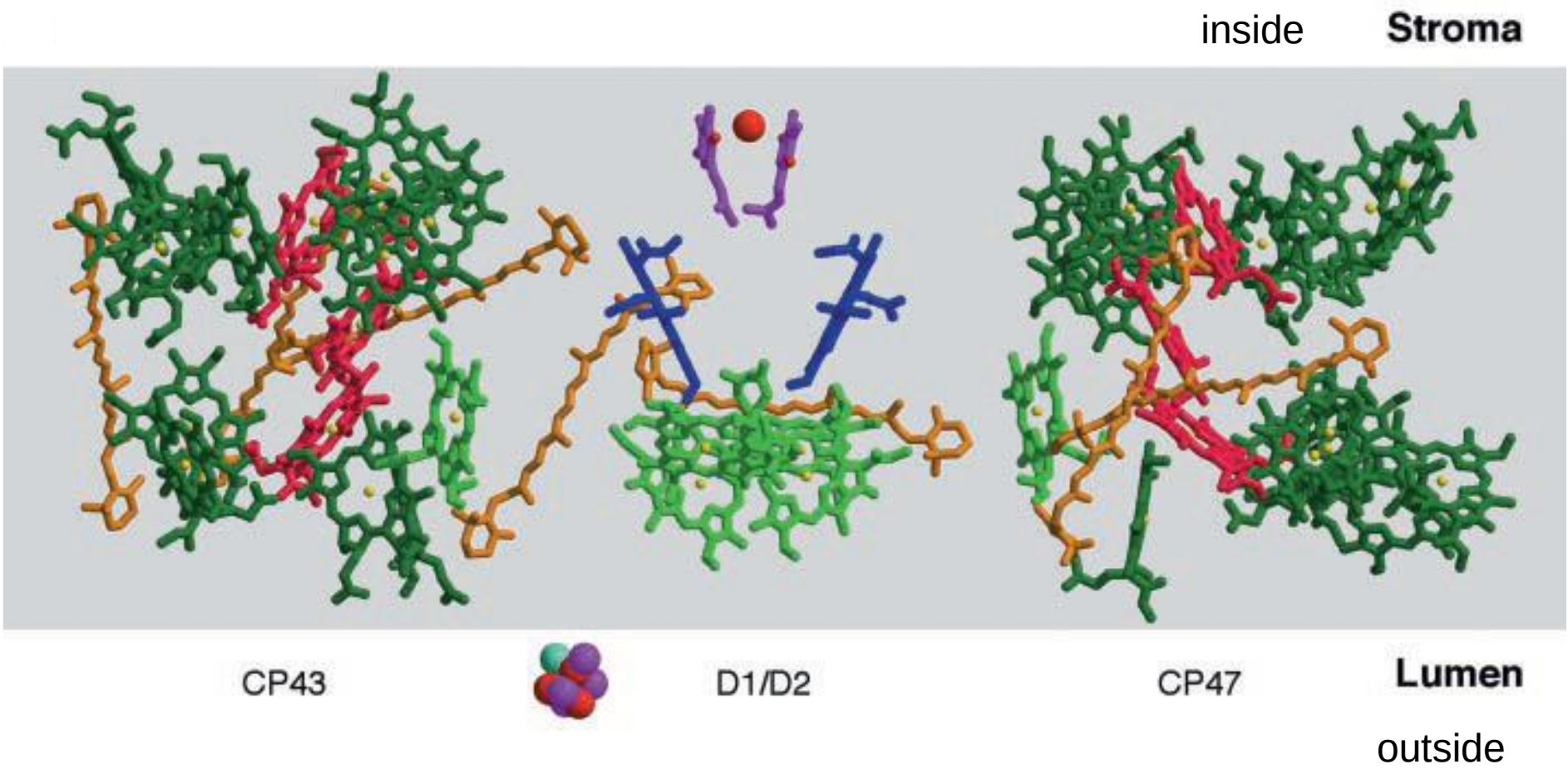


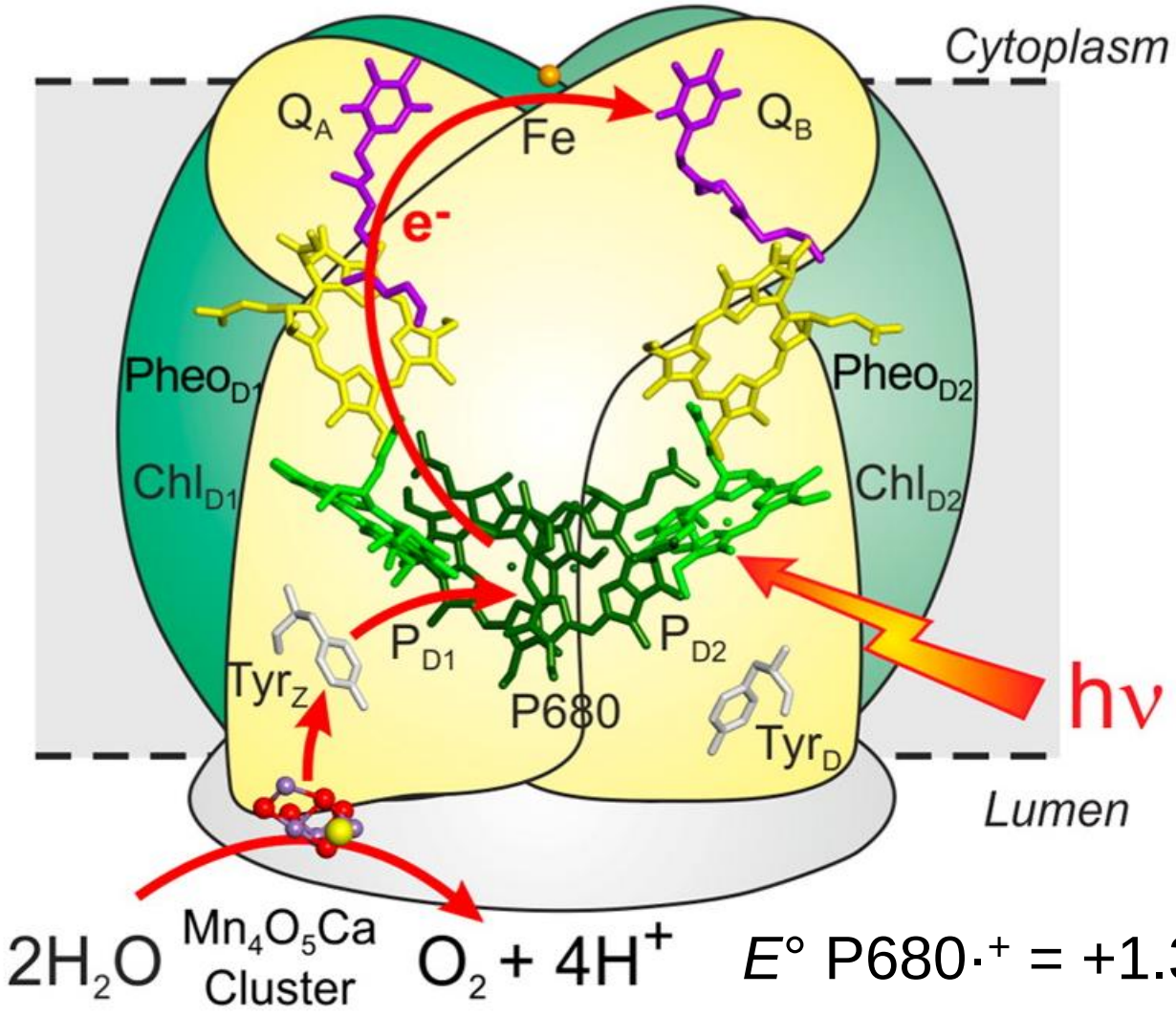


$$2H_2O + 2PQ + 4H^+_{\text{inside (stroma)}} \xrightarrow{4h\nu} O_2 + 2PQH_2 + 4H^+_{\text{outside (lumen)}}$$


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

Centro di foto-reazione e sistemi antenna

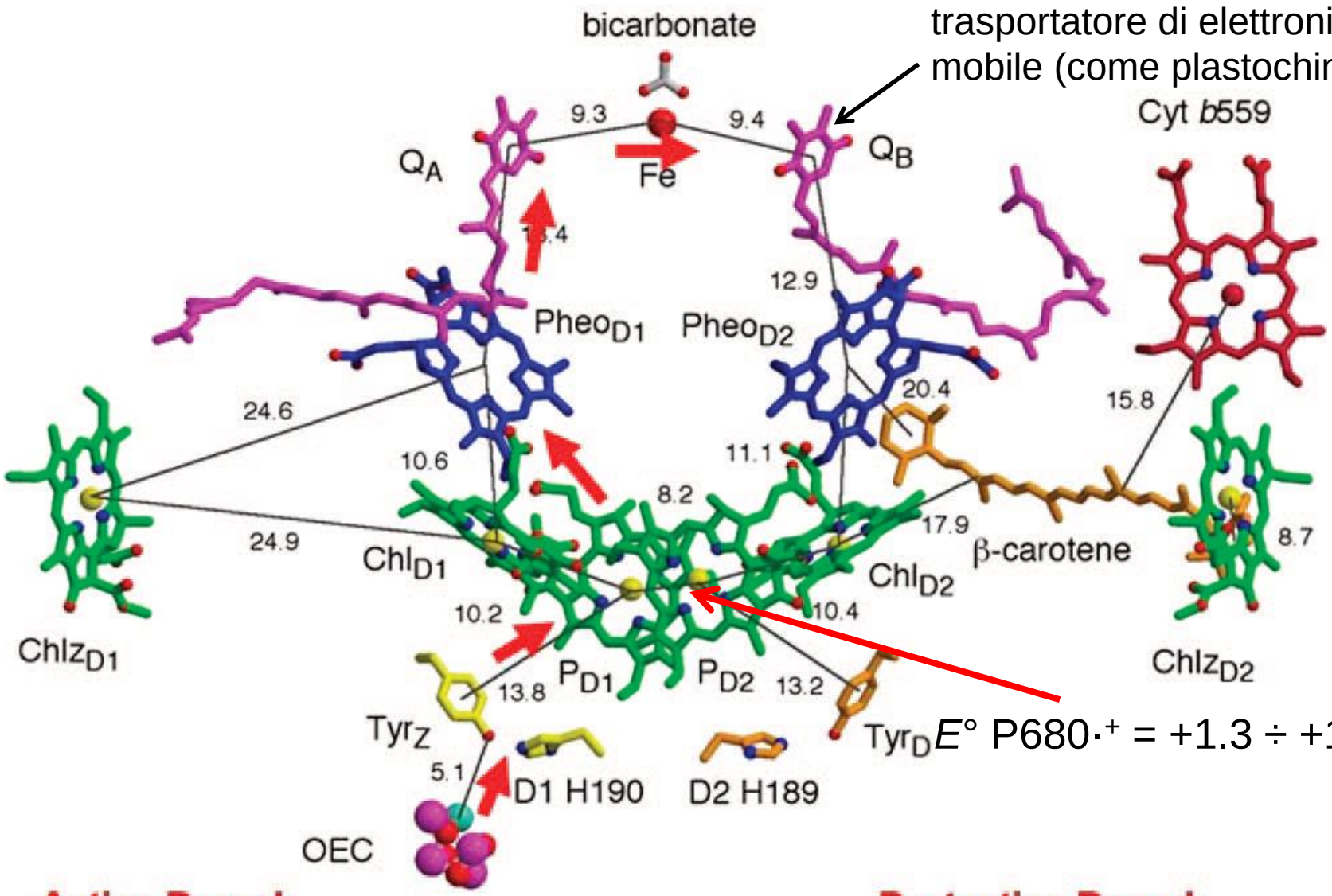




$E°$ P680$^{\cdot+}$ = +1.3 ÷ +1.4 V

Potenziale più alto fra i sistemi biologici

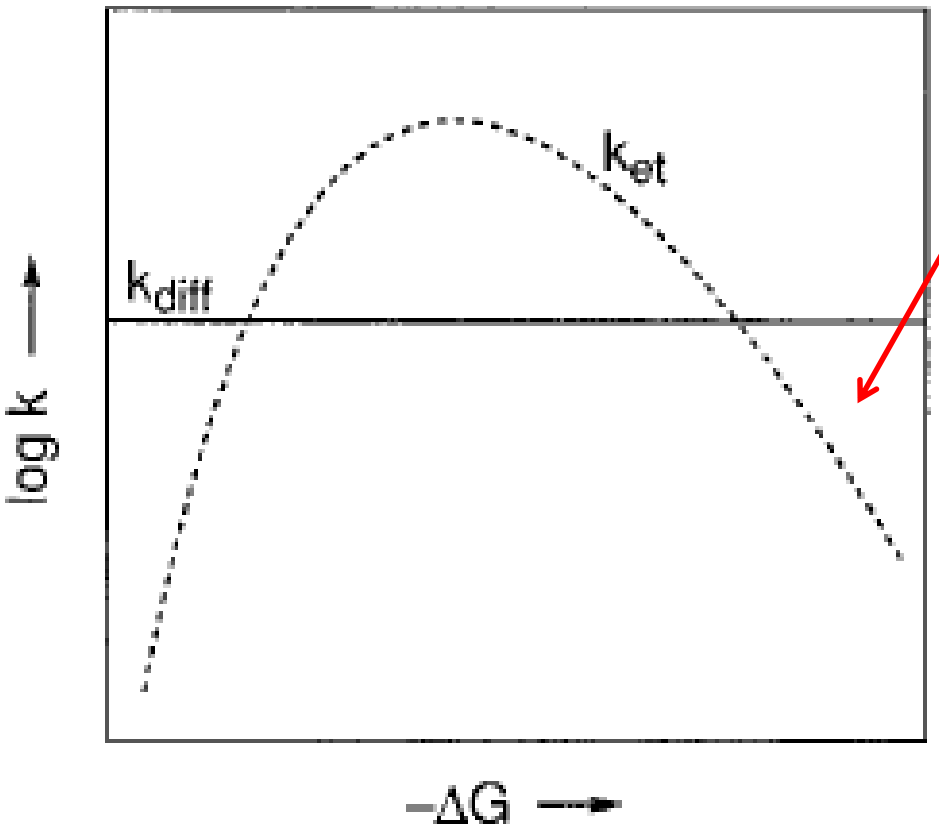
Electron transport cofactors



Plastochinone mobile = trasportatore di elettroni mobile (come plastochinolo)

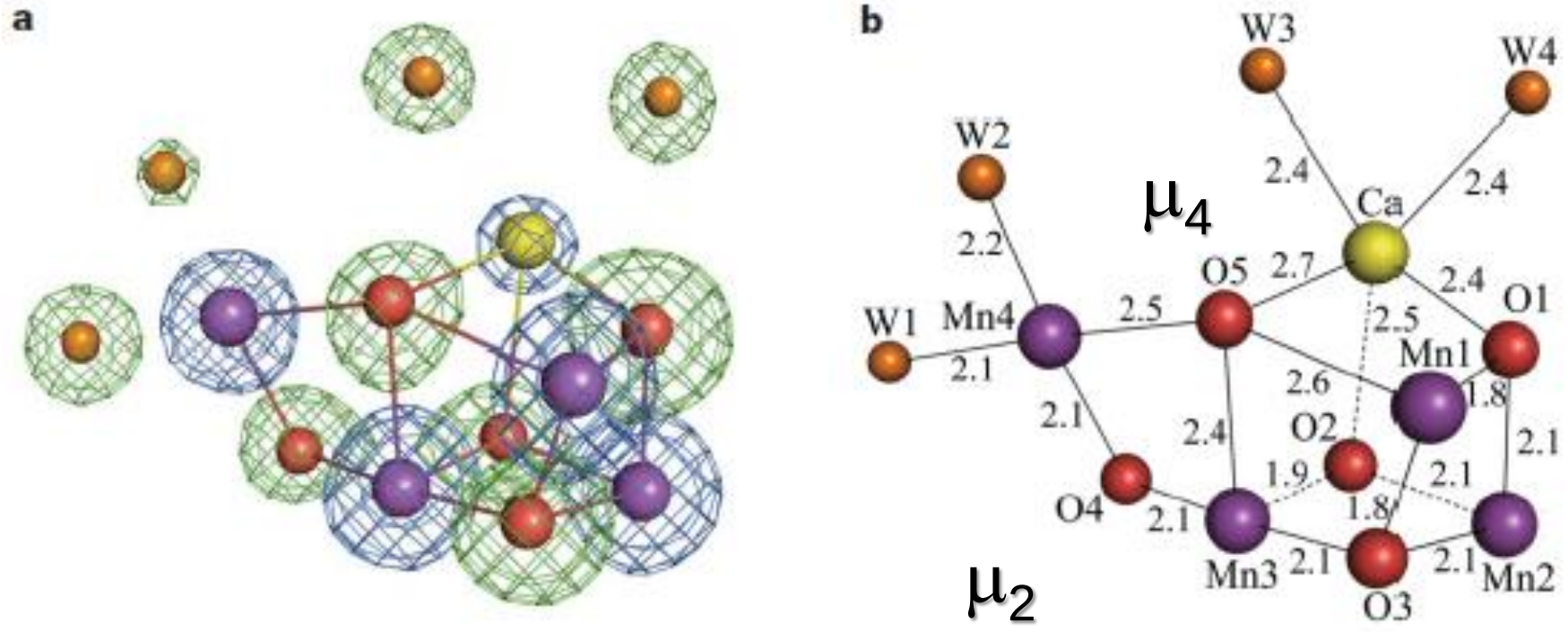
$E°$ $P680^{\cdot+}$ = +1.3 ÷ +1.4 V

Regione inversa di Marcus

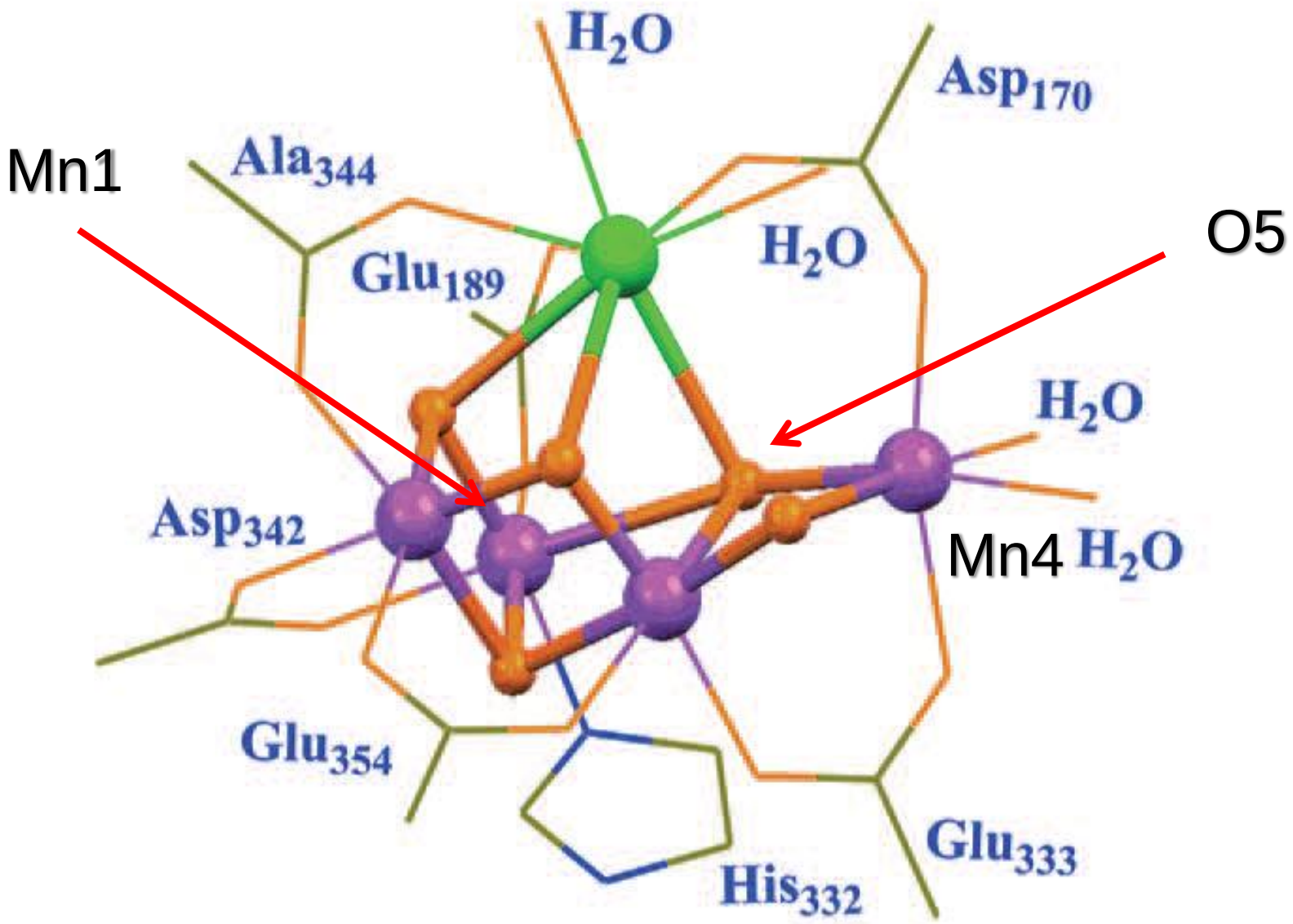


Oxygen Evolving Complex (OEC)

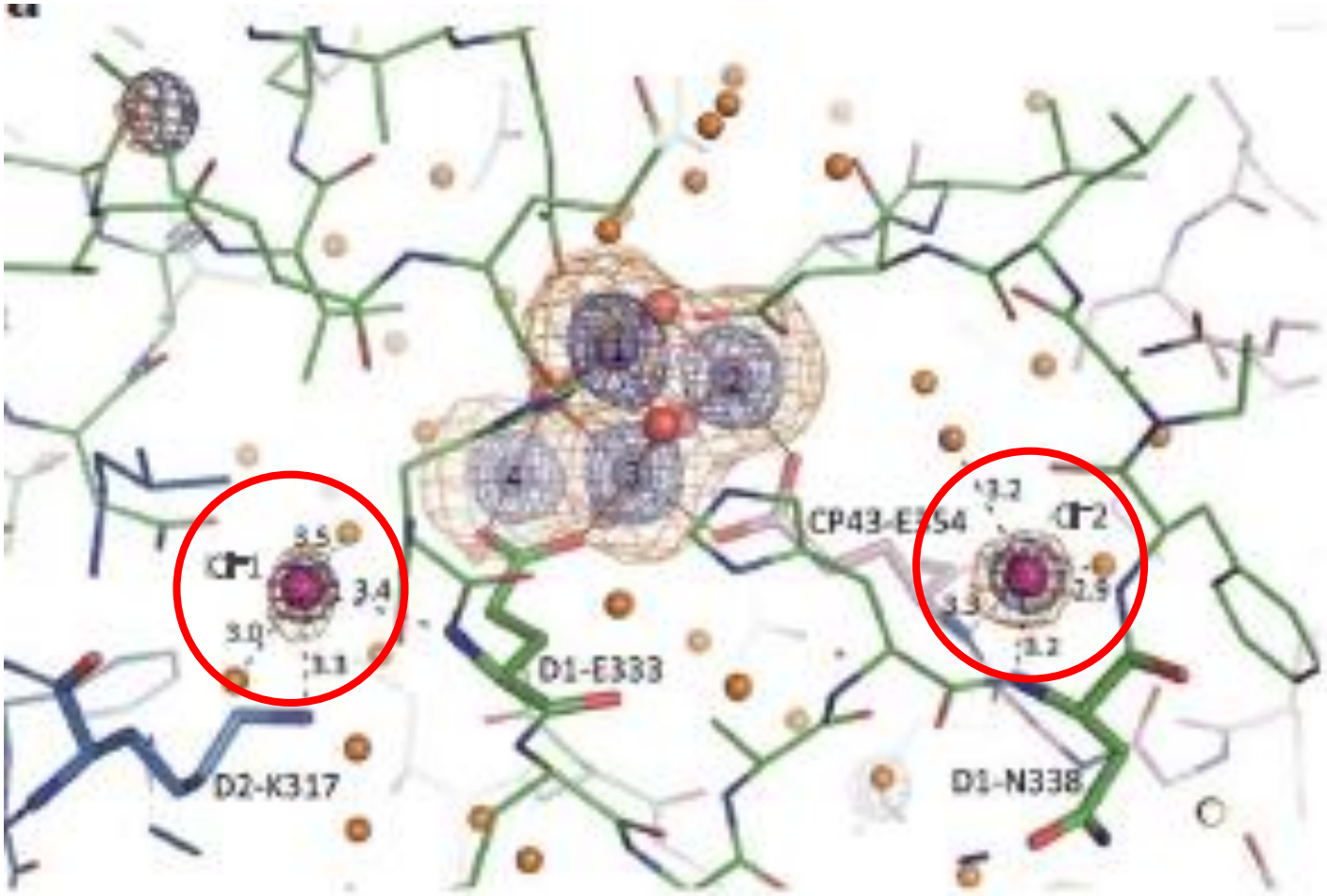
Mn_4CaO_5



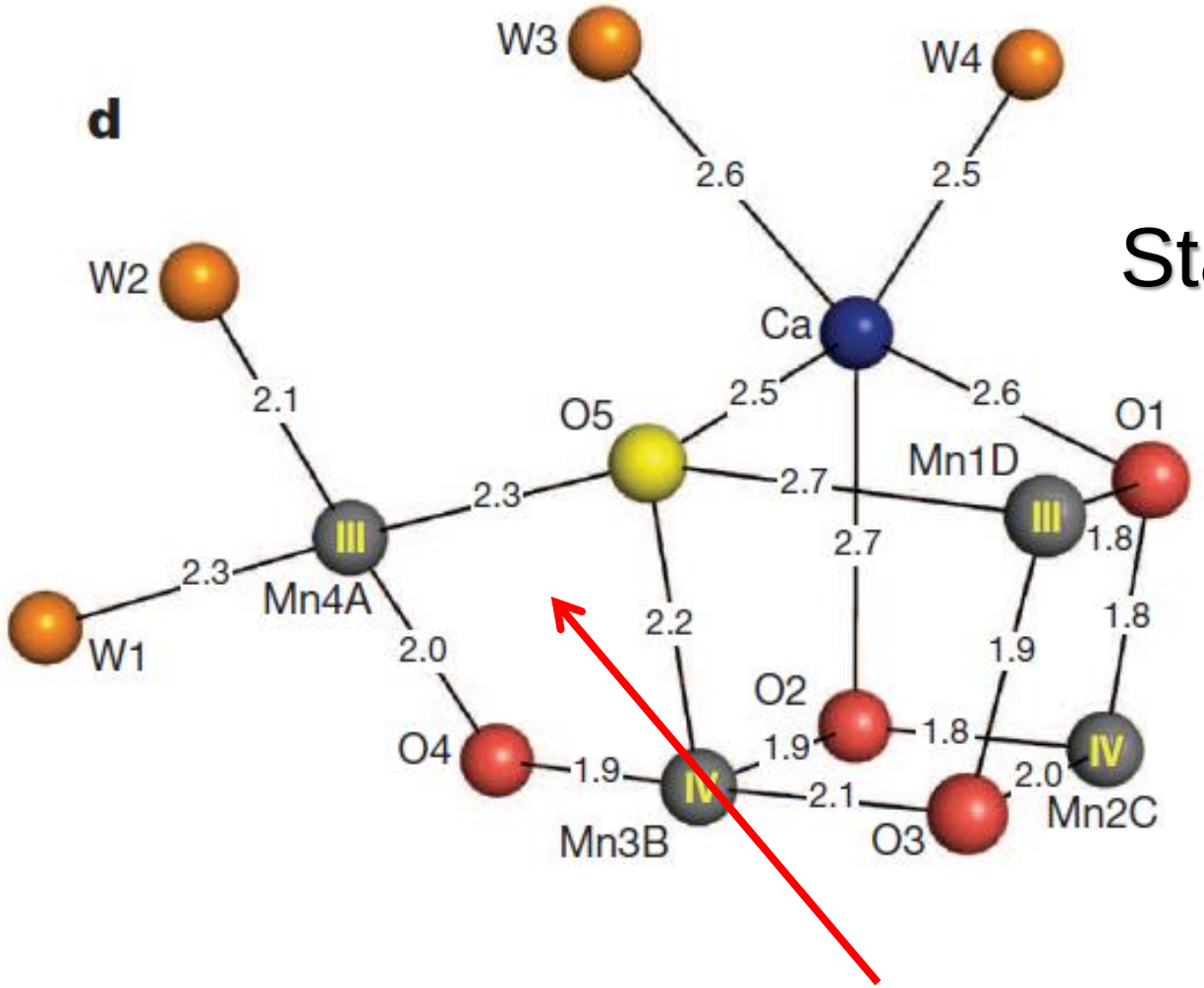
Nature 2011


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

2 Cloruri



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



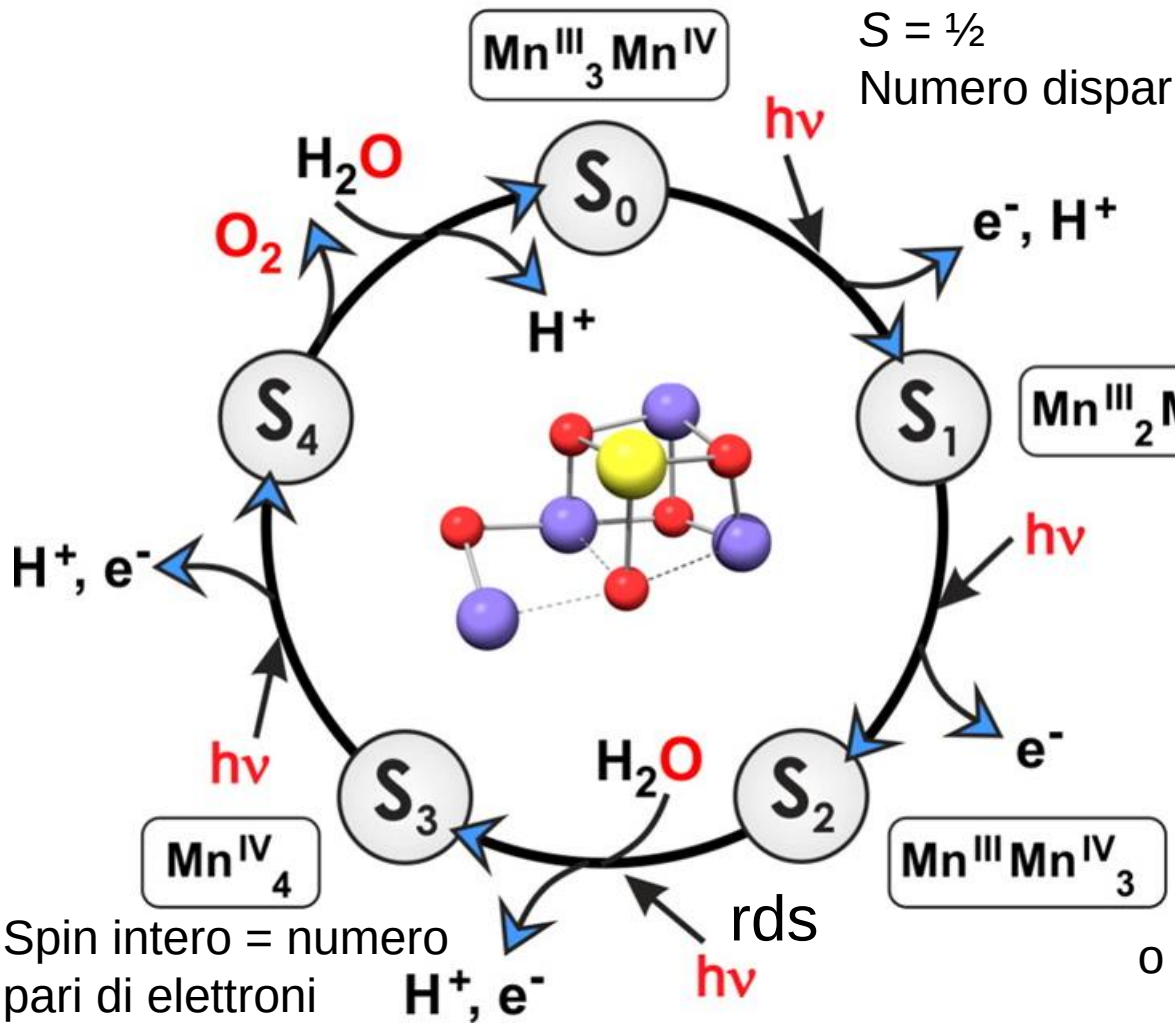
Stato S_1

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

Mn4–O5 più corta di 0.2 Å

Ciclo di Kok o *S clock*

Mn sempre h.s.



S = ½
Numero dispari di elettroni

Spin intero = numero pari di elettroni

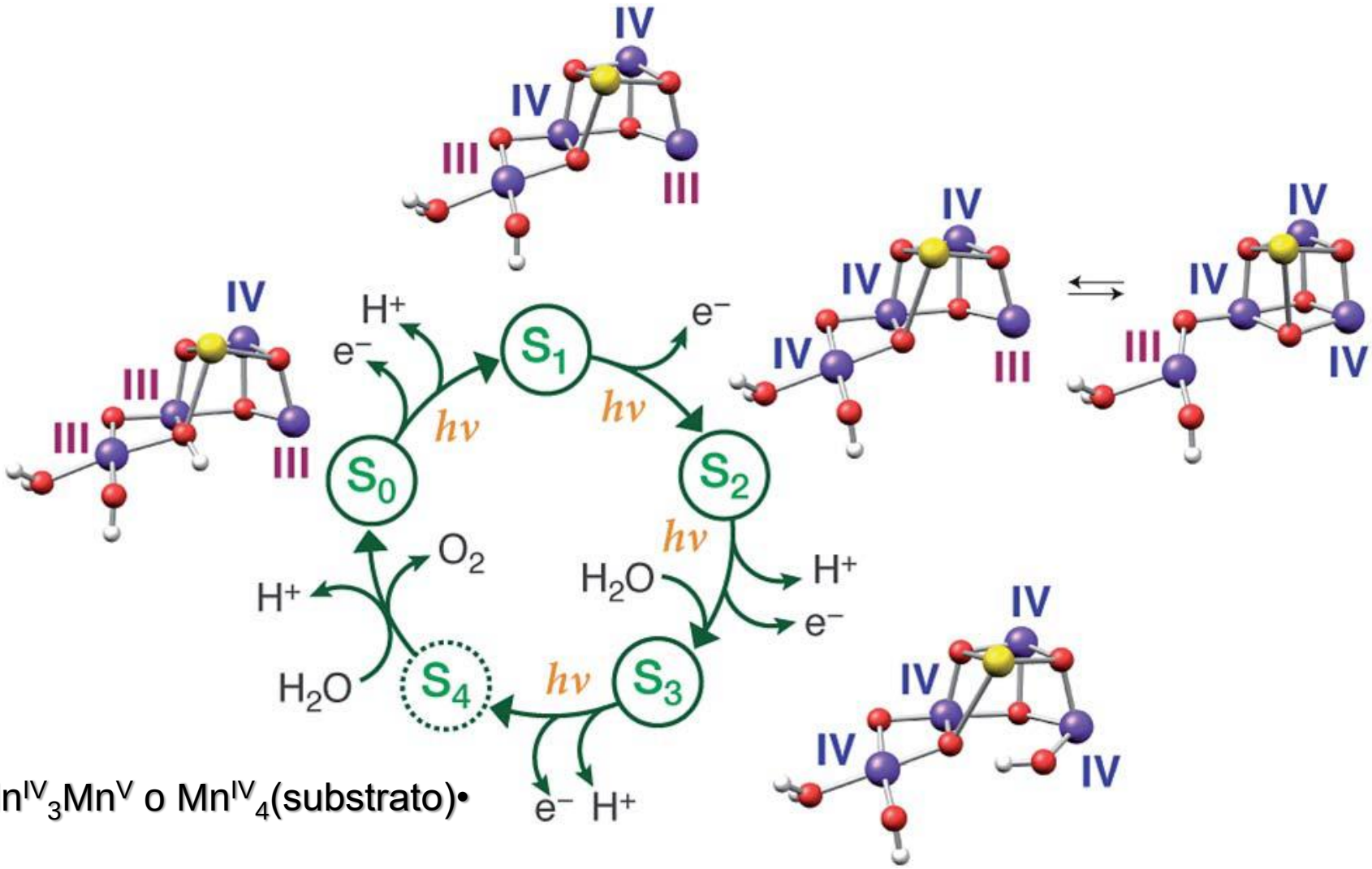
S = ½
Numero dispari di elettroni

Spin intero = numero pari di elettroni

o $3Mn^{III}Mn^{IV}$ (ipotesi *Low Valent*)?

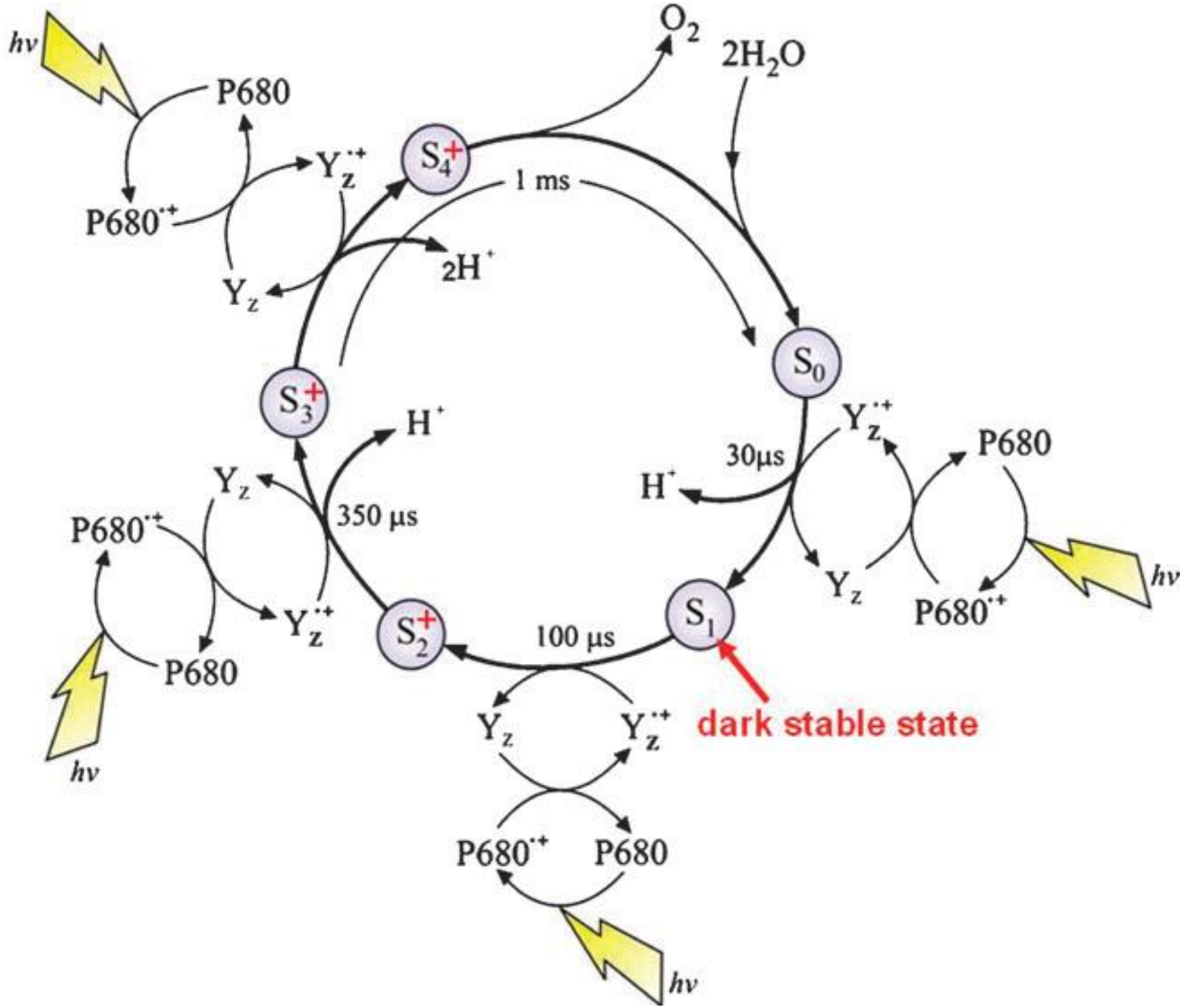
OEC ossida fino a 1000 molecole di H_2O (500 cicli) per secondo!

TON ≈ ca. 10^6



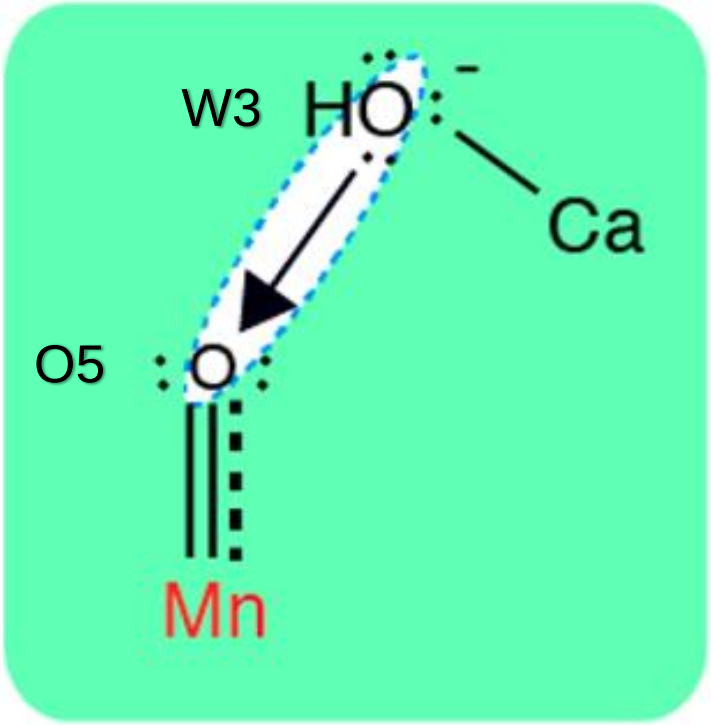
$Mn^{IV}_3Mn^{V}$ o Mn^{IV}_4(substrato)•

Ciclo di Kok o *S clock*

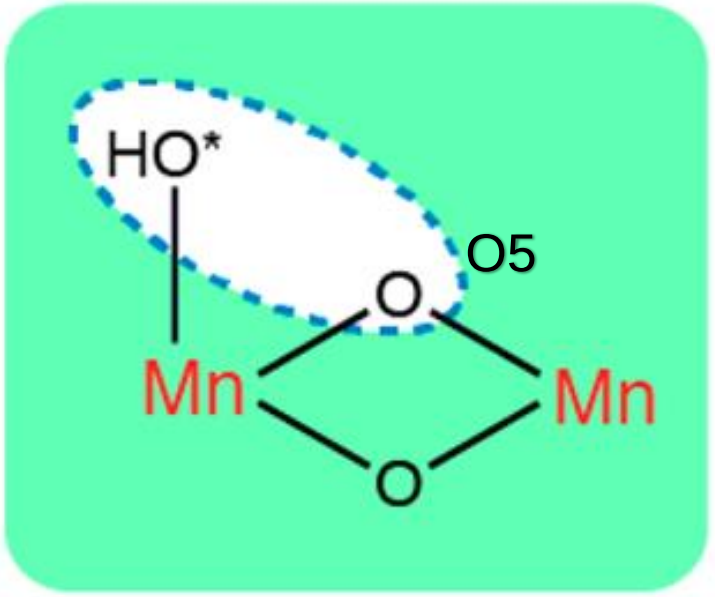


Ipotesi di formazione del legame O–O

nucleophilic attack



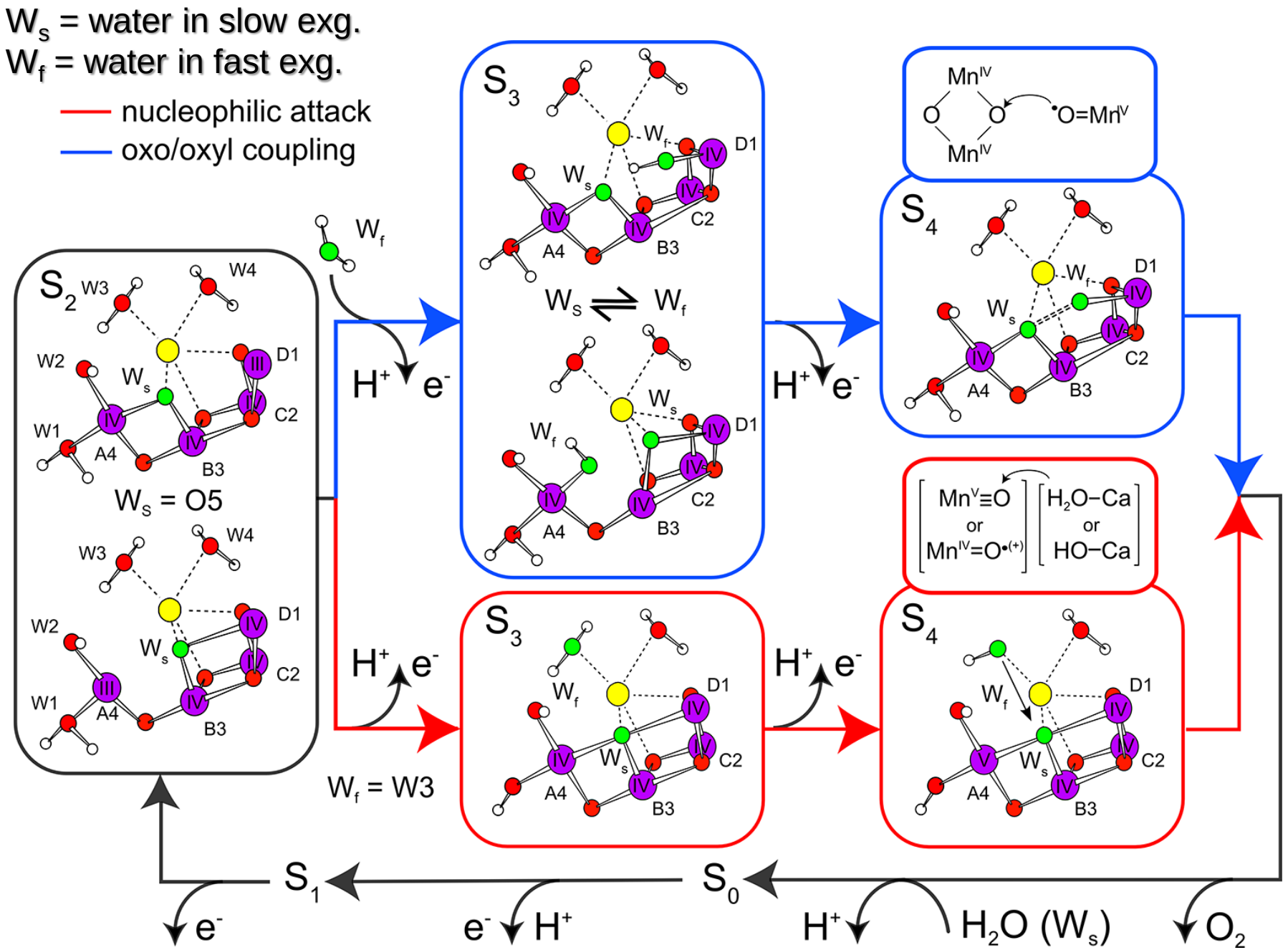
terminal oxyl radical with bridging oxo



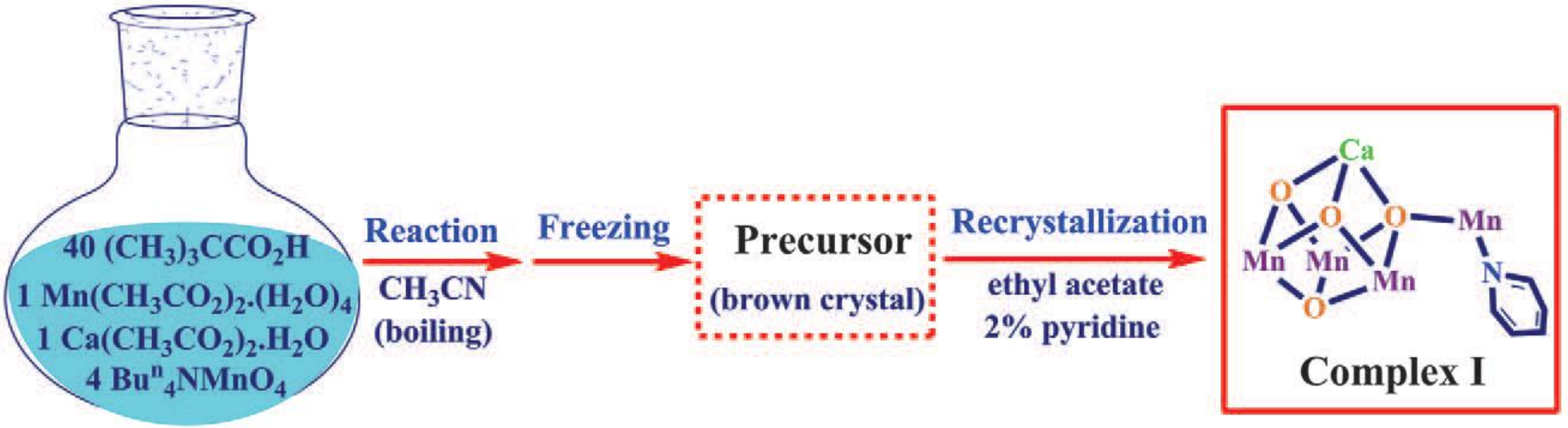
Mn(V)≡O o Mn(IV)=O•

oxo/oxyl radical coupling mechanism

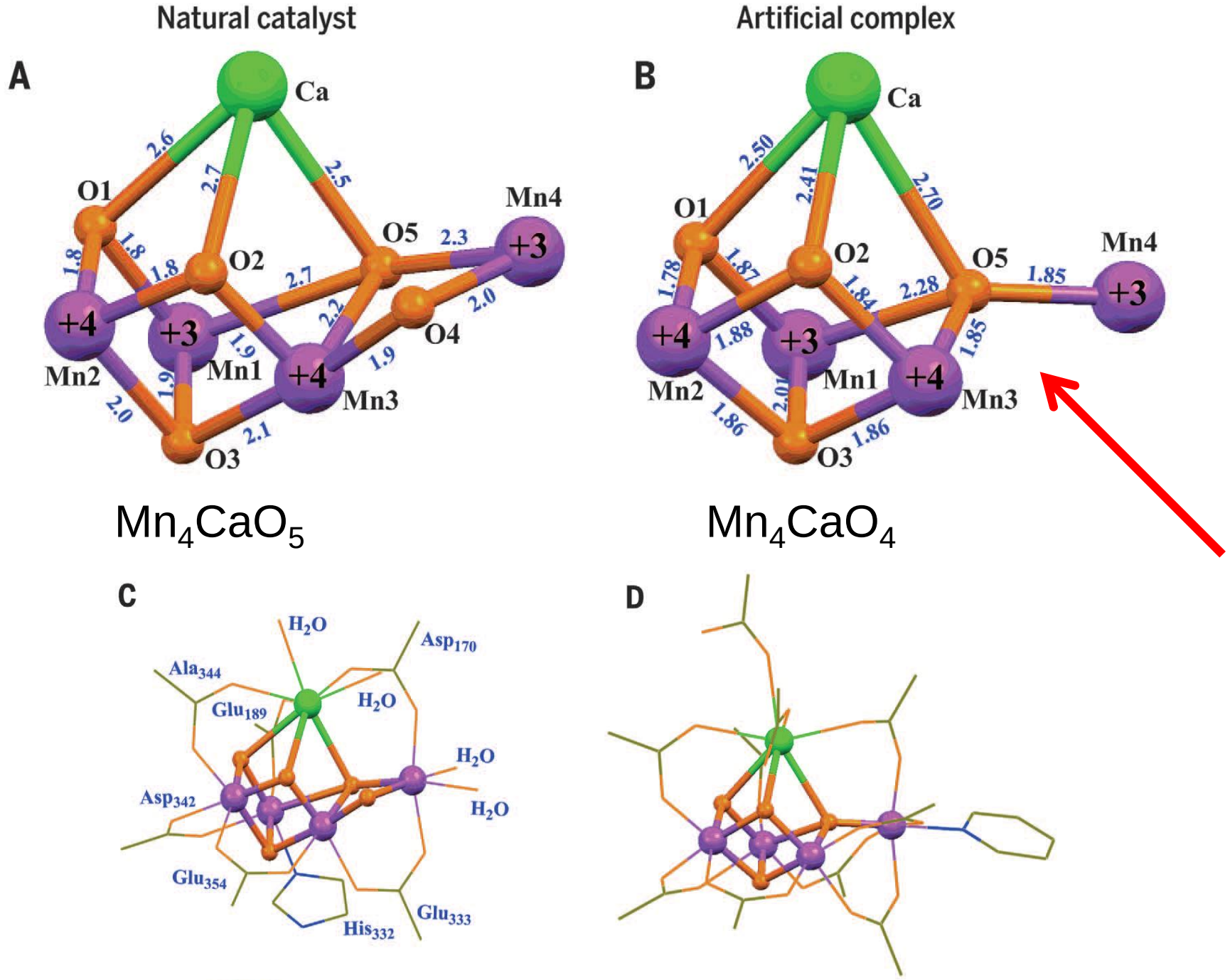
In questo meccanismo l'ultimo elettrone viene estratto da O, non da Mn


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

Sistemi modello



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
2.0
2.1
2.50
2.41
2.70
1.78
1.87
1.84
2.28
1.85
1.88
2.01
1.85
1.86
1.86
Mn4CaO5
Mn4CaO4
C
D
H2O
Asp170
Ala344
Glu189
H2O
H2O
H2O
Asp342
Glu354
His332
Glu333