

100 × 10⁹ ton/y di (CH₂O)_n da CO₂

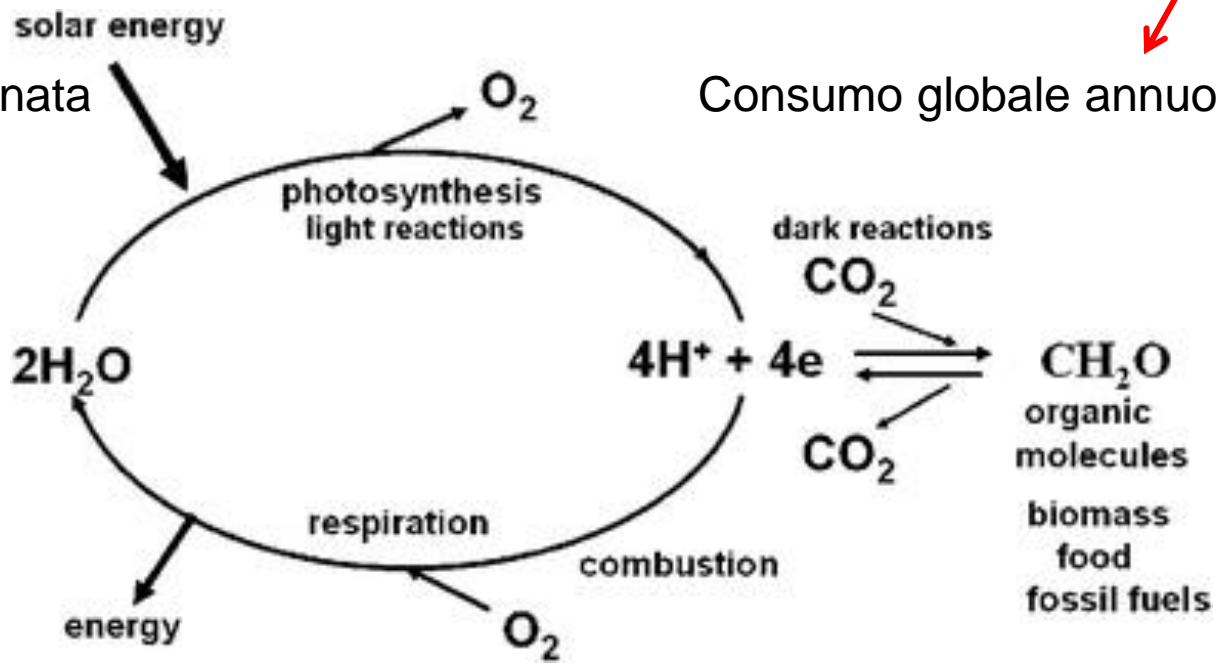
1 g di glucosio per m² di superficie fogliare all'ora

100 TW/y = 0.1% energia solare totale (10⁵ TW)

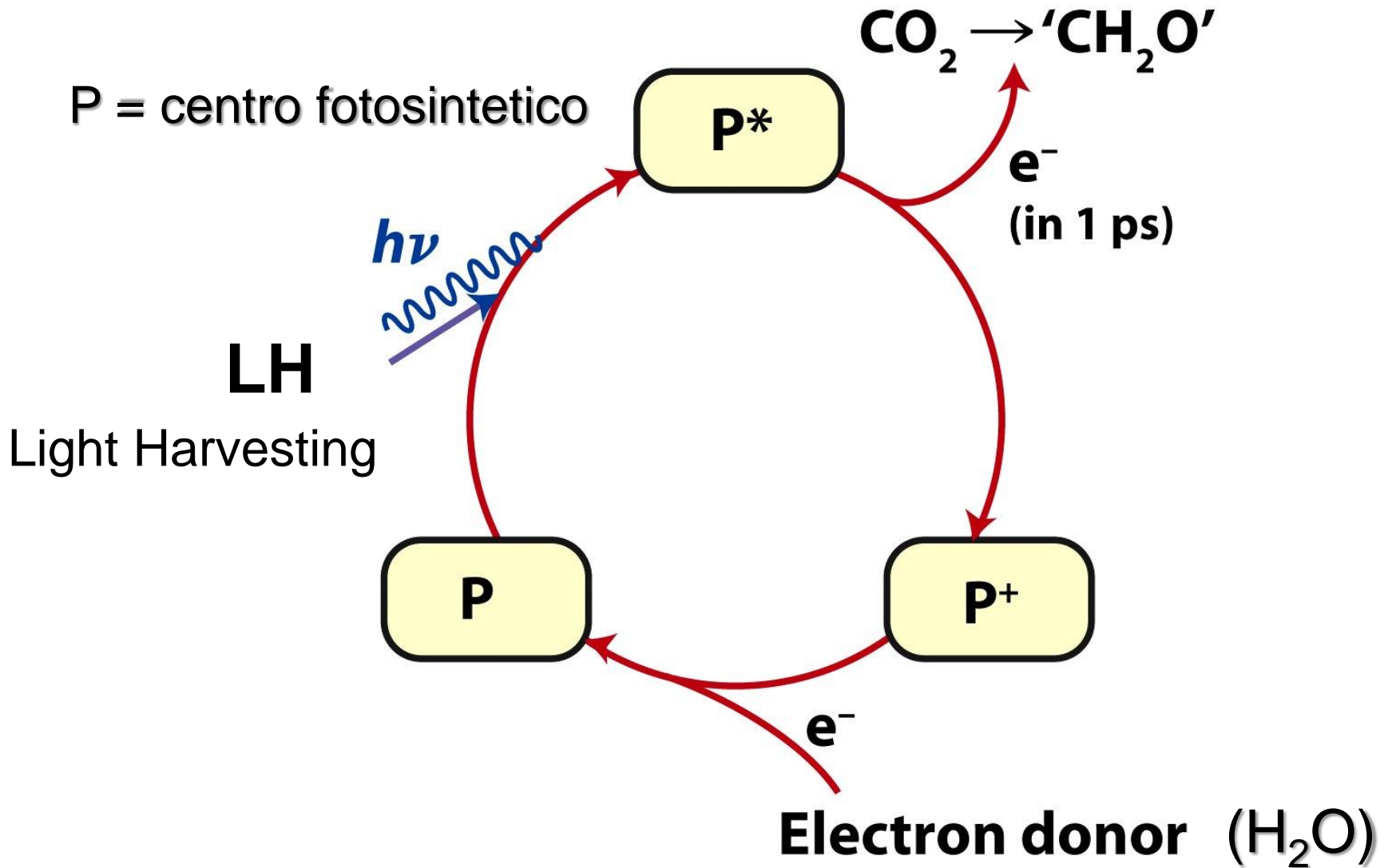


Energia immagazzinata
come biomassa

Consumo globale annuo: 14 TW



Separazione di carica fotoindotta



Processo fotosintetico nelle piante

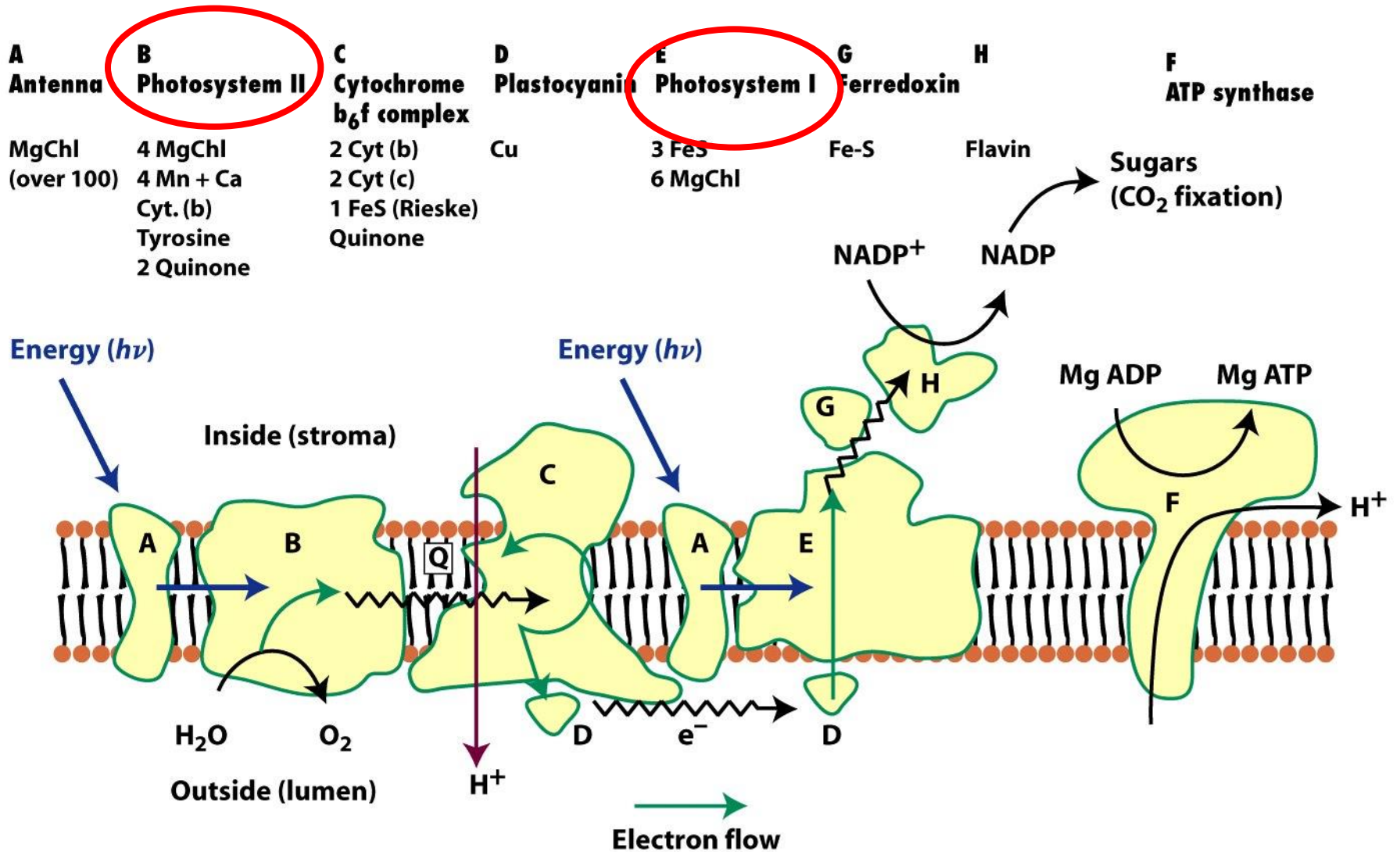
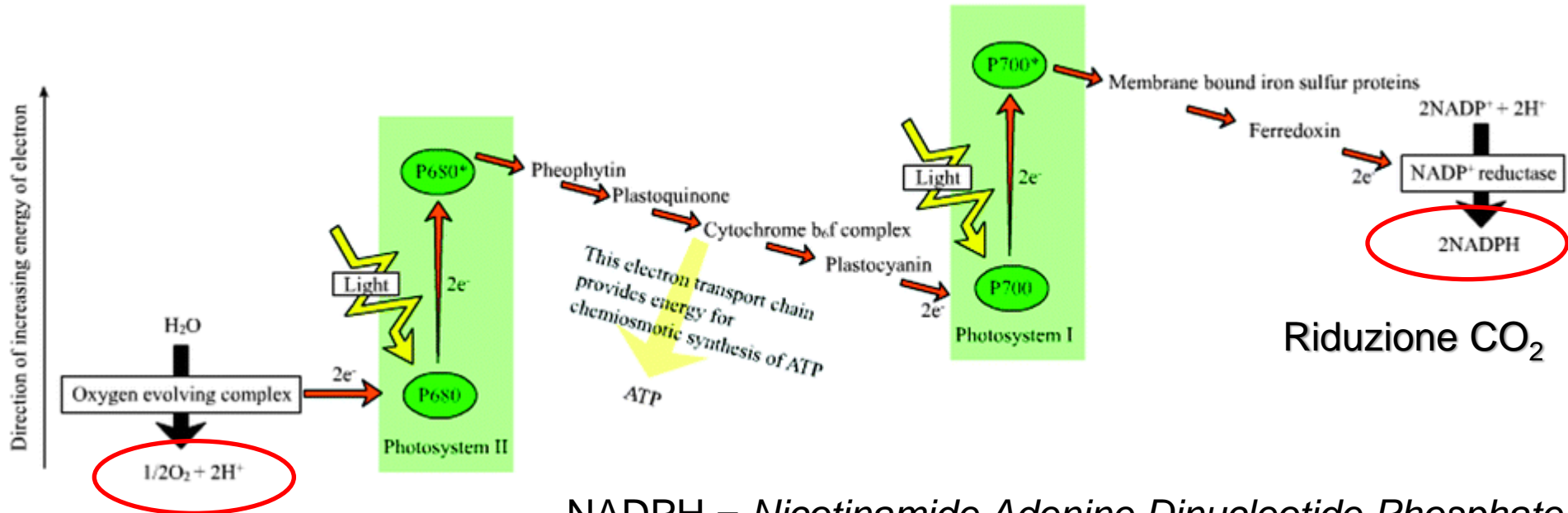
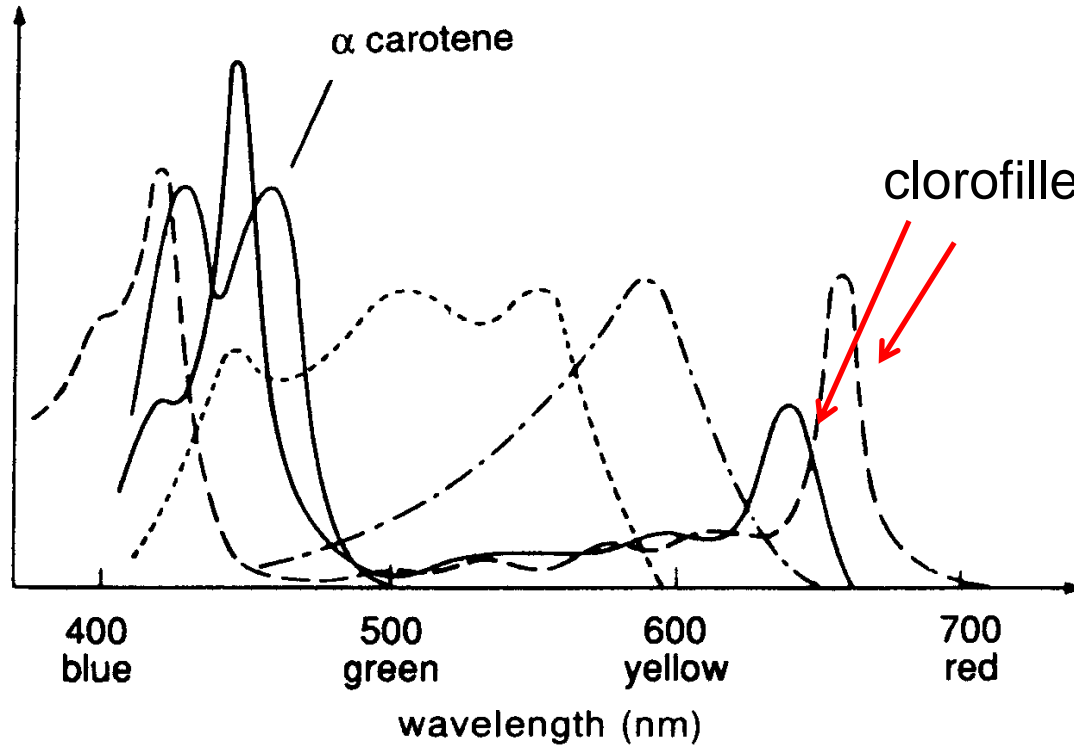
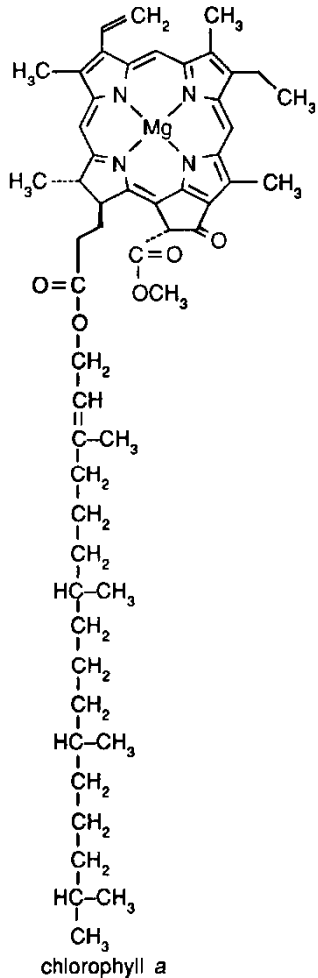


Diagramma "a Z"



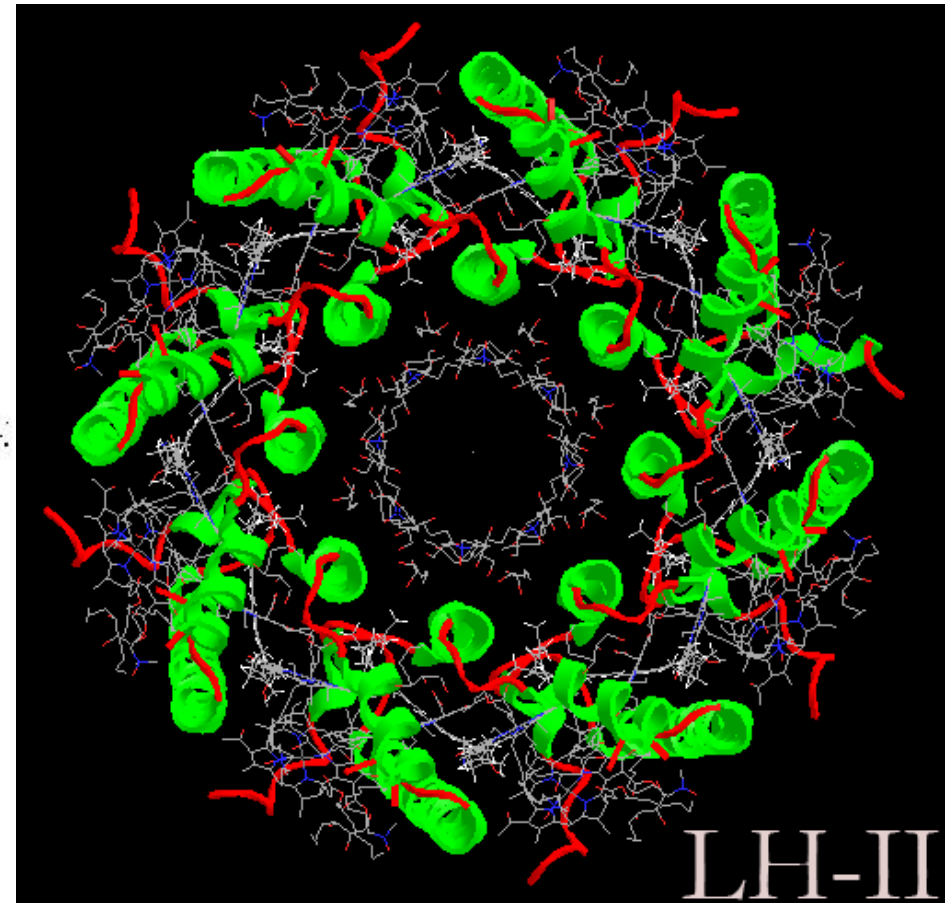
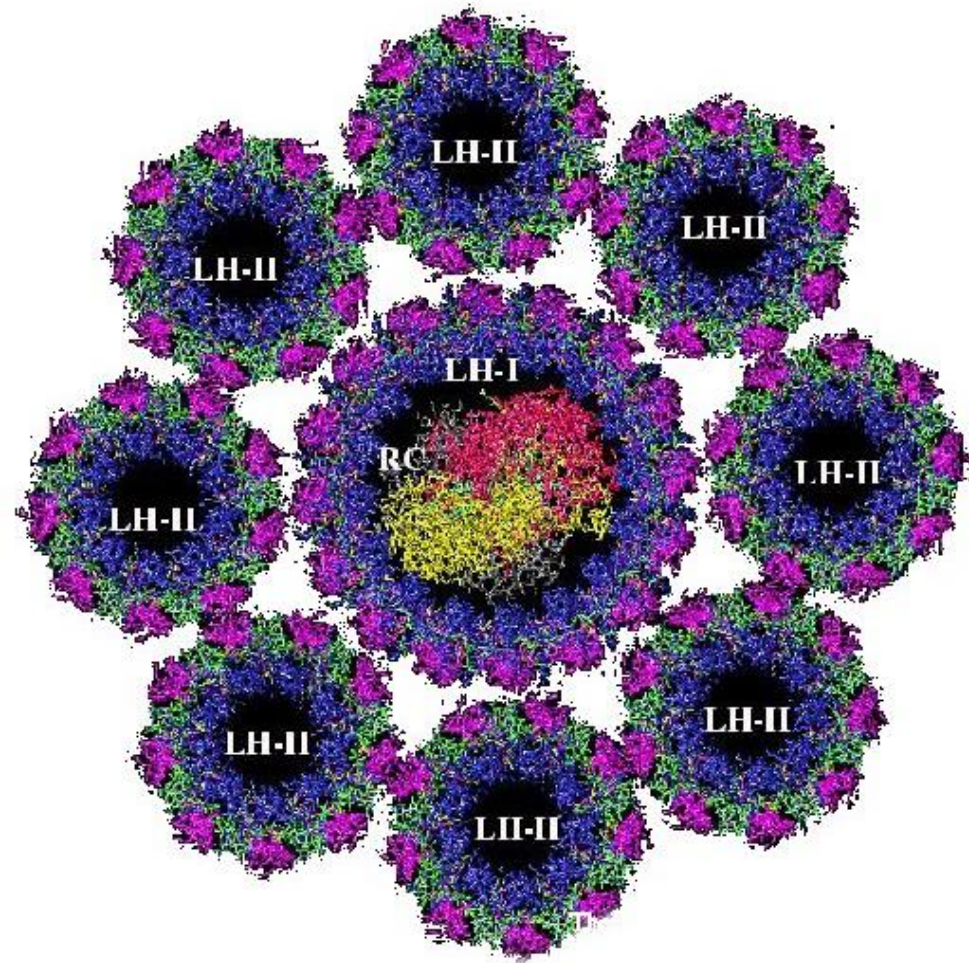
Per ogni elettrone estratto dall'acqua e trasferito a CO₂ serve l'energia di due fotoni, uno in PSII e l'altro in PSI

Pigmenti deputati al *light harvesting*

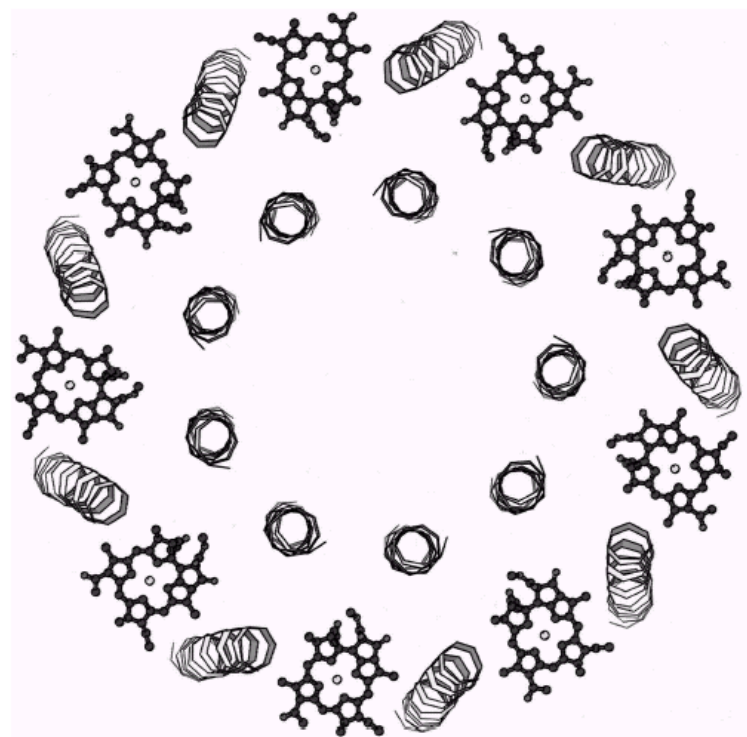
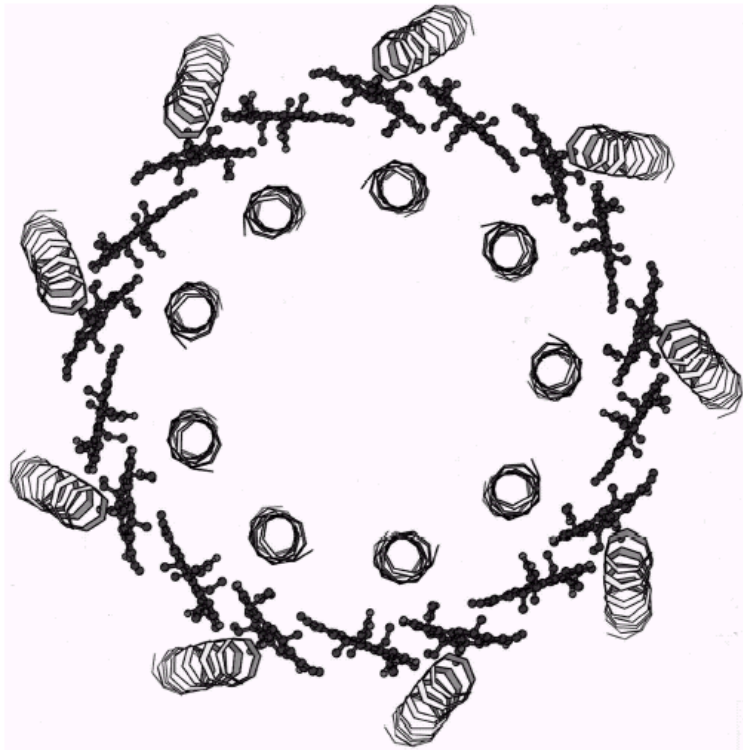


Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (—·—·), phycocyanin (-·-·), phycoerythrin (- - - -)

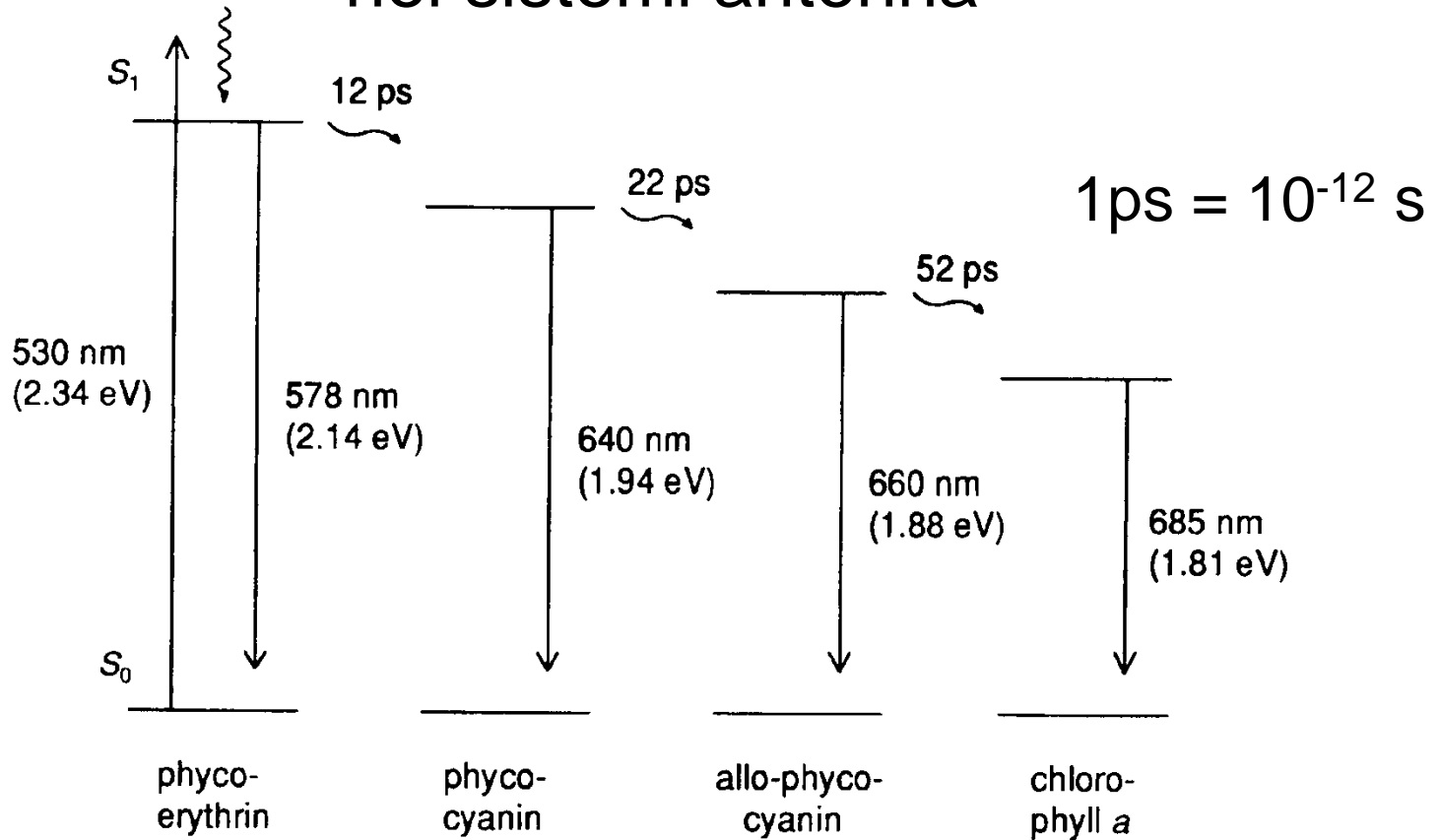
Sistemi antenna per *light-harvesting* e *exciton transfer*



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

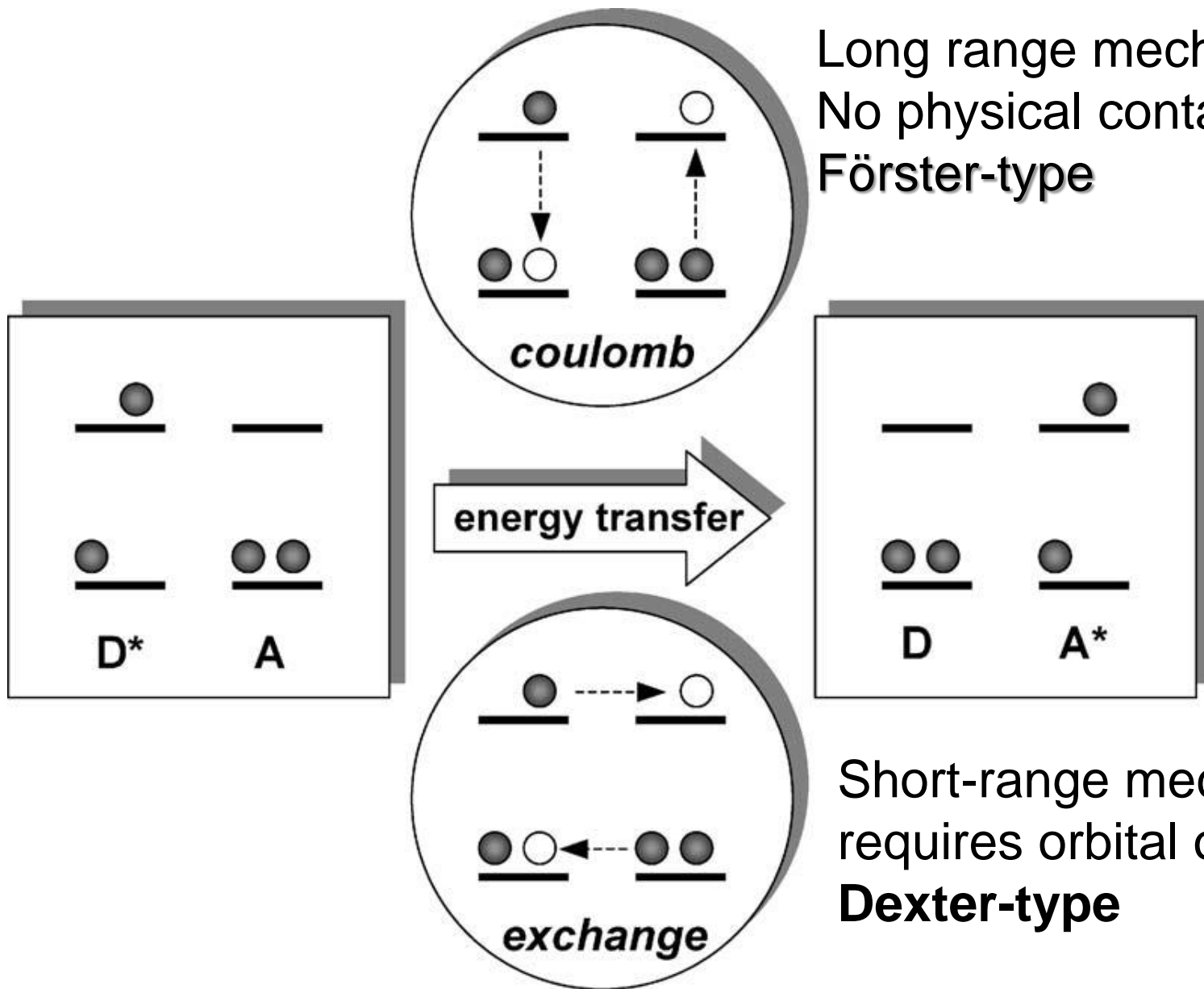


Trasferimento di energia (*exciton transfer*) a cascata nei sistemi antenna



efficienza del 95%

Meccanismi di *exciton transfer*



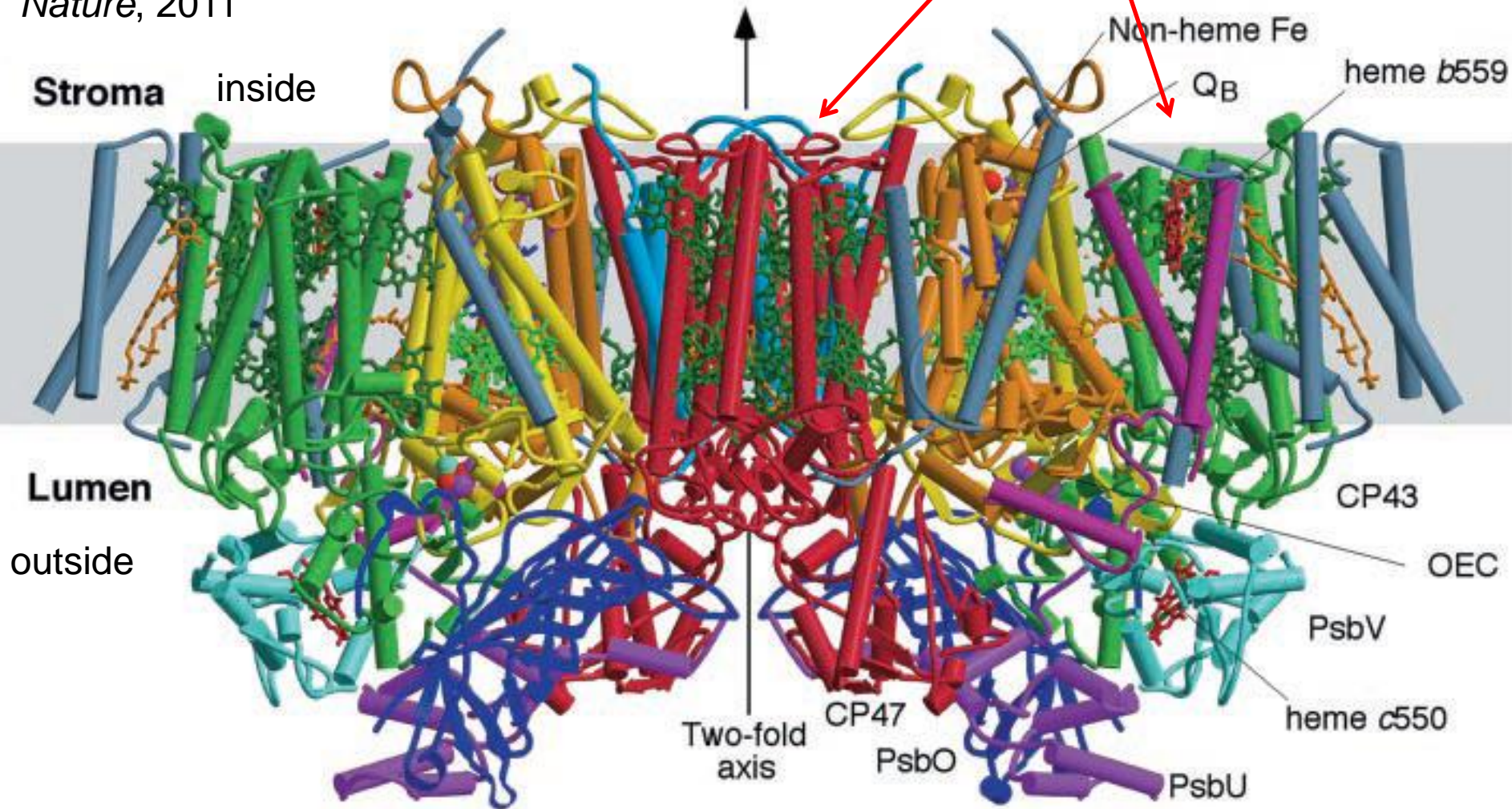
Long range mechanism
No physical contact
Förster-type

Short-range mechanism
requires orbital overlap
Dexter-type

PS II

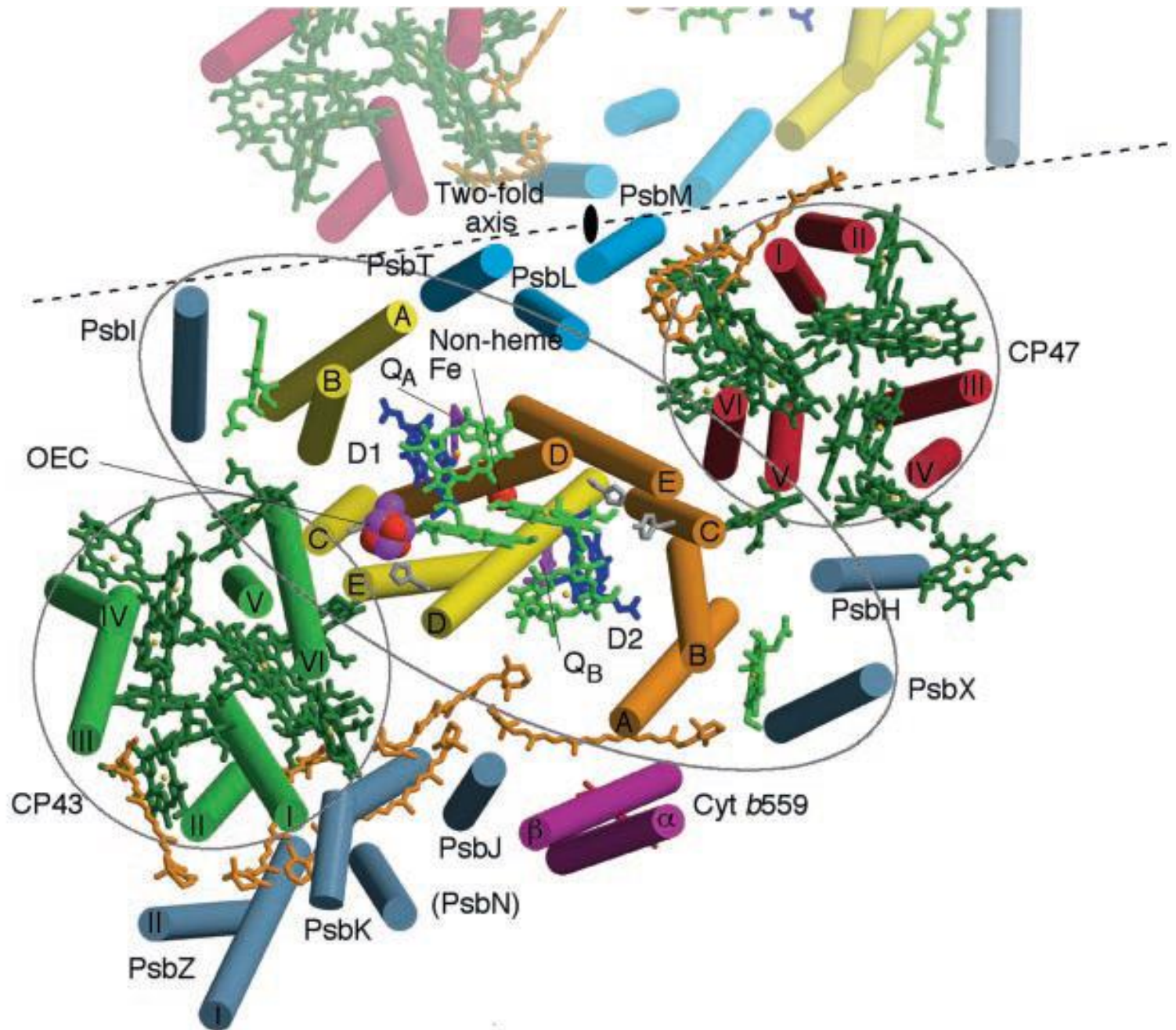
Sistemi antenna

Nature, 2011



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

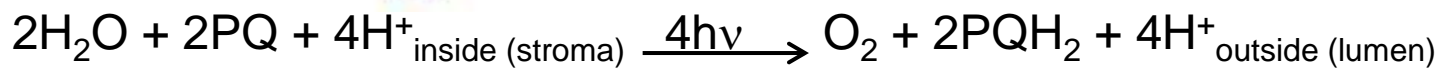
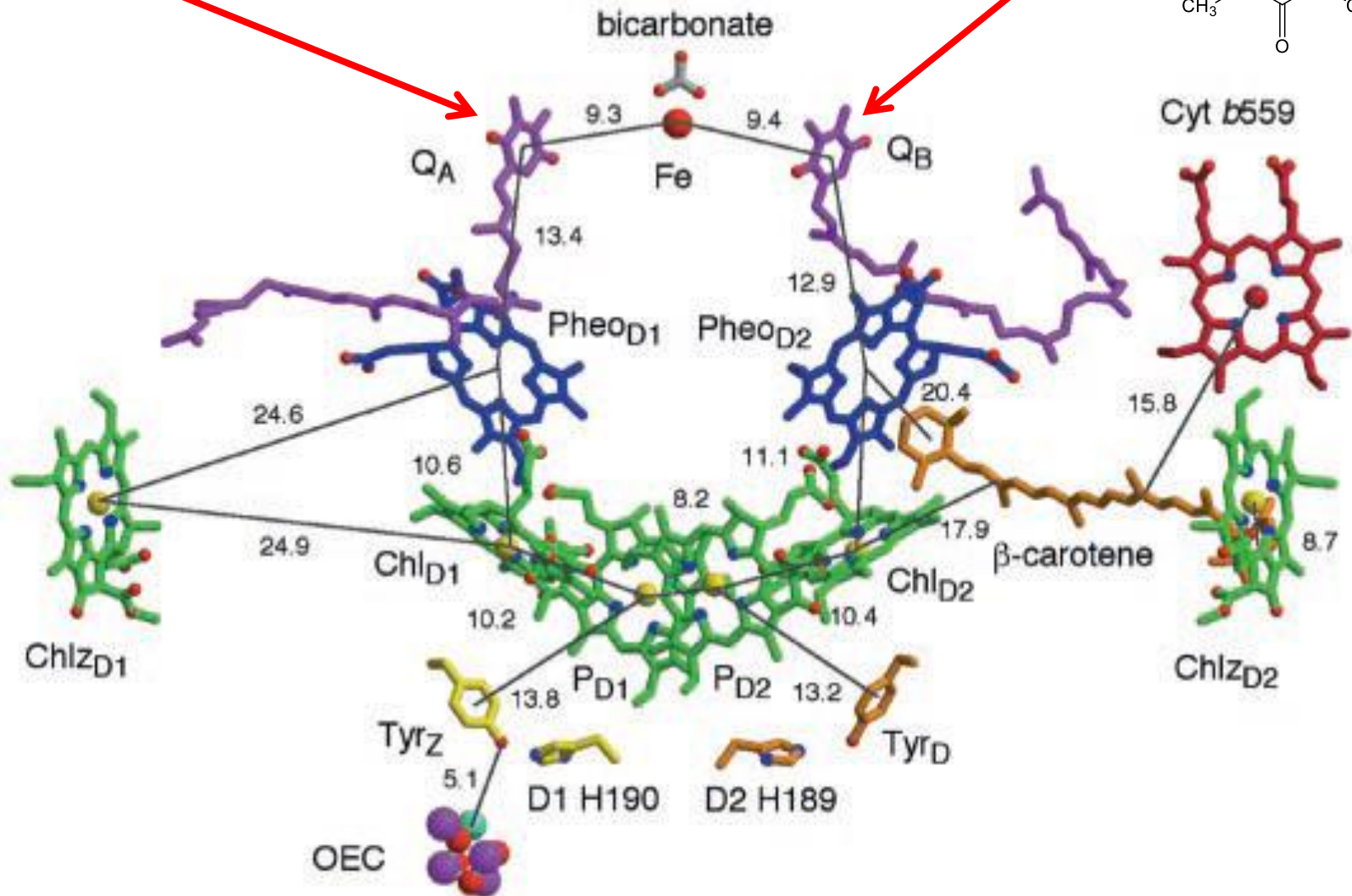
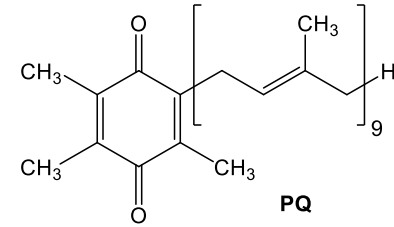
PS II



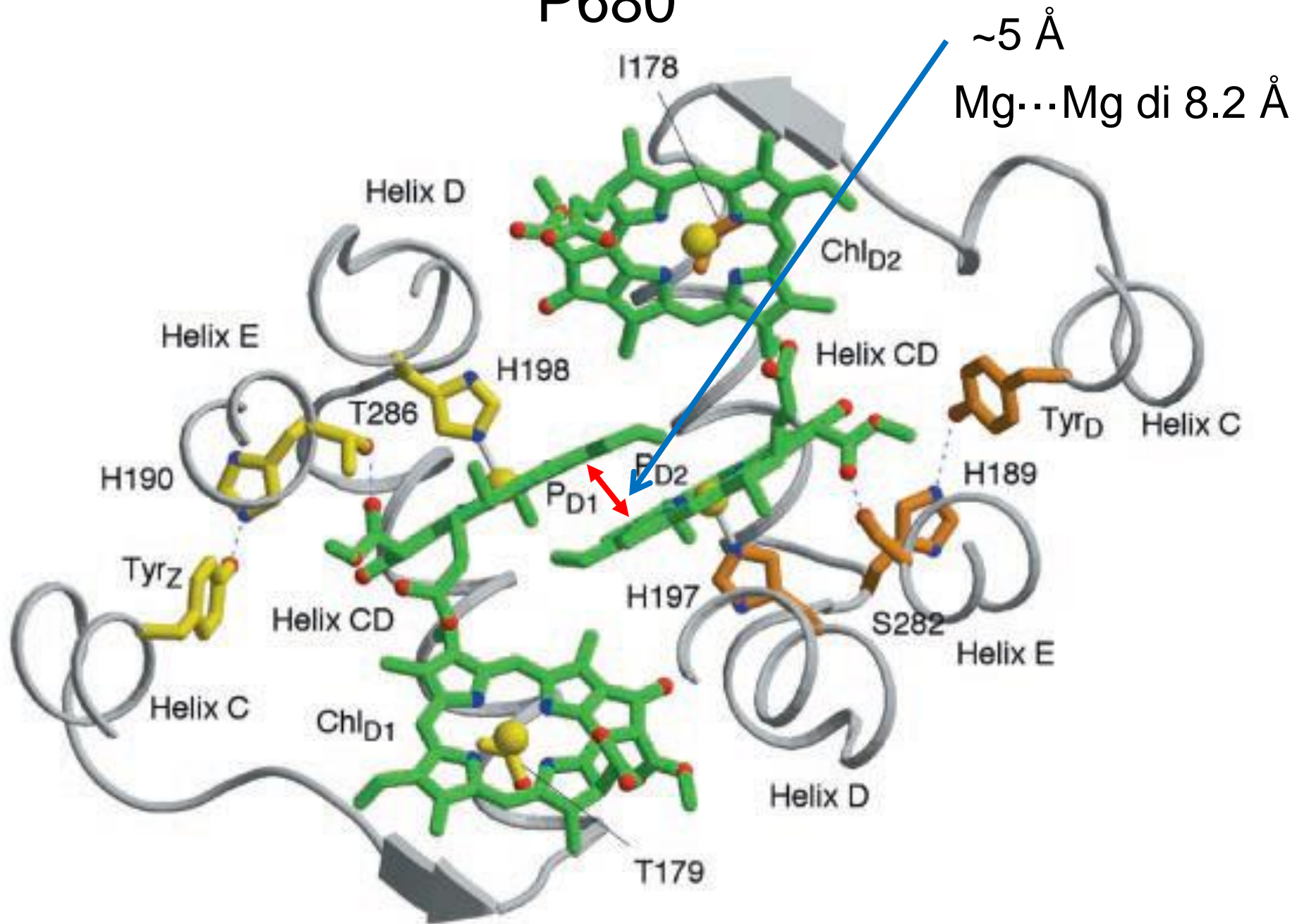
P680

Plastoquinone fisso

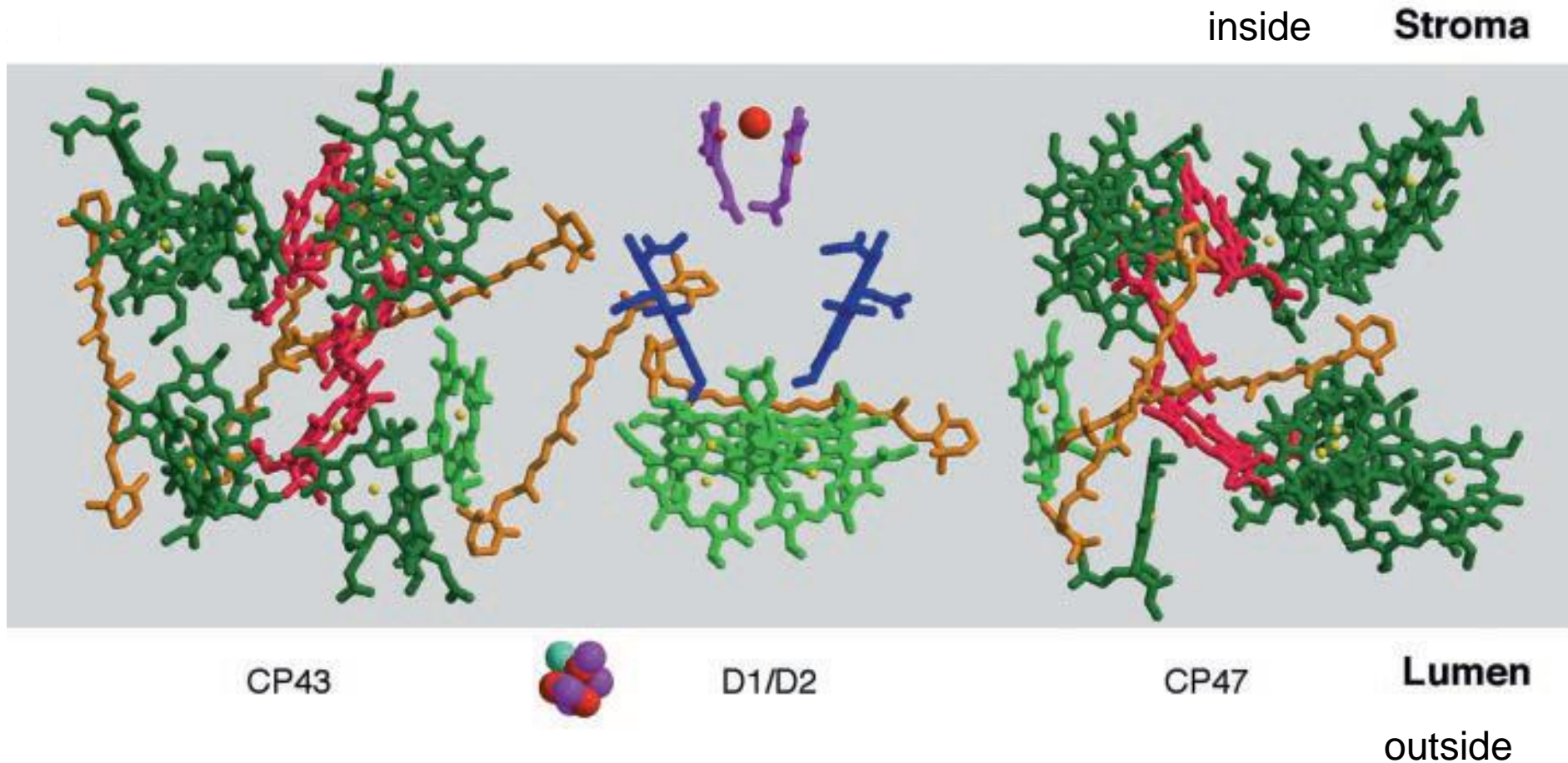
Plastoquinone mobile

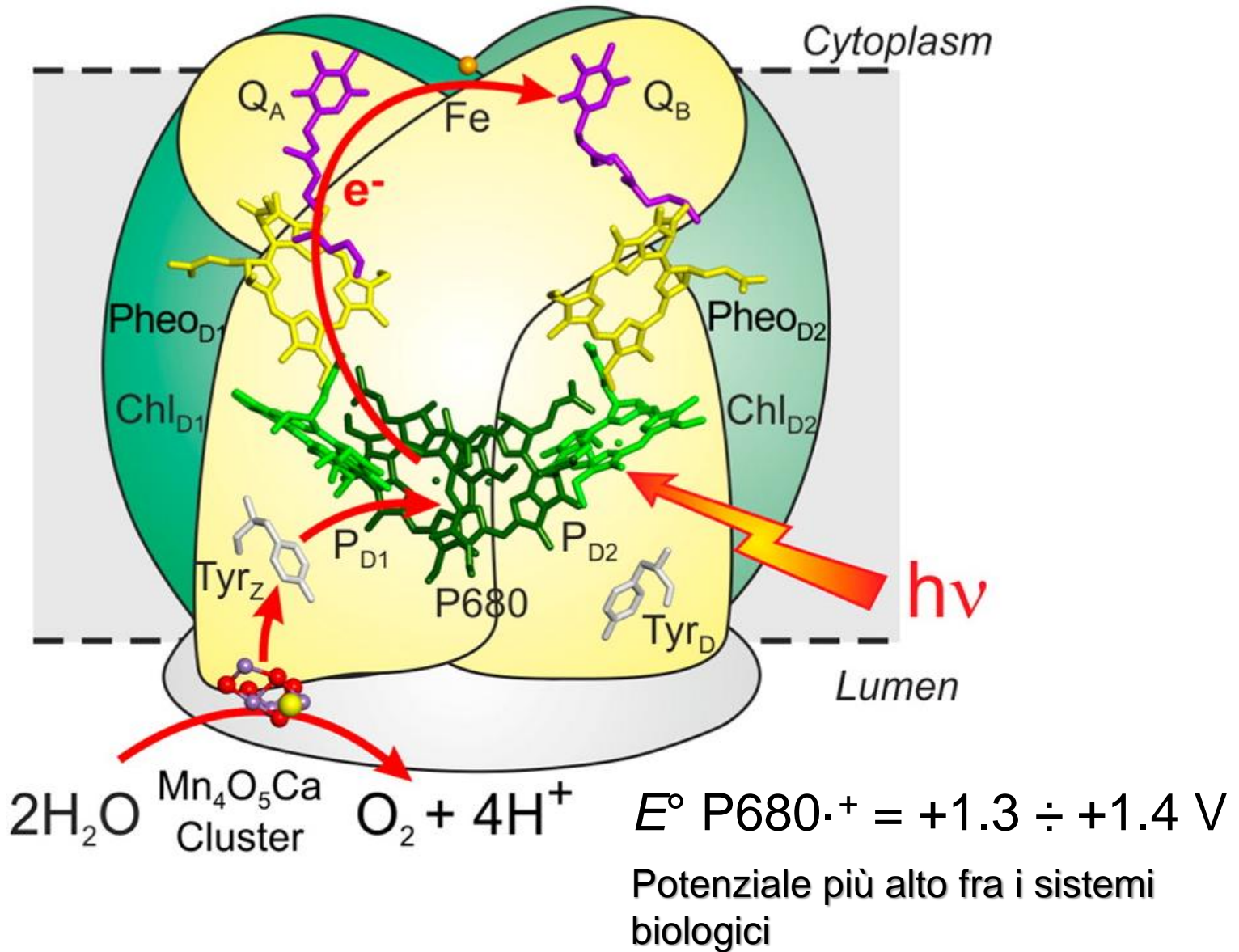


P680



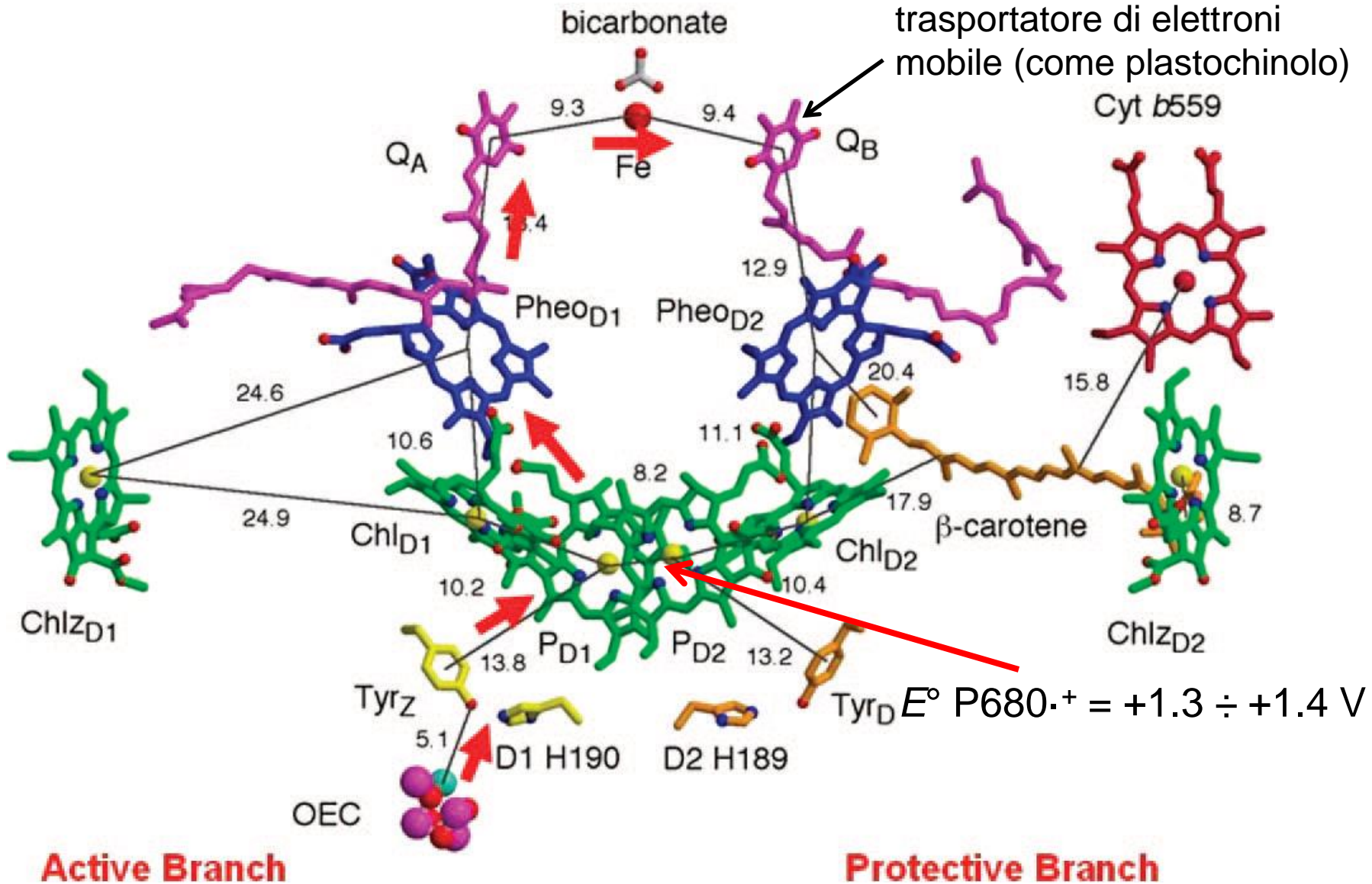
Centro di foto-reazione e sistemi antenna



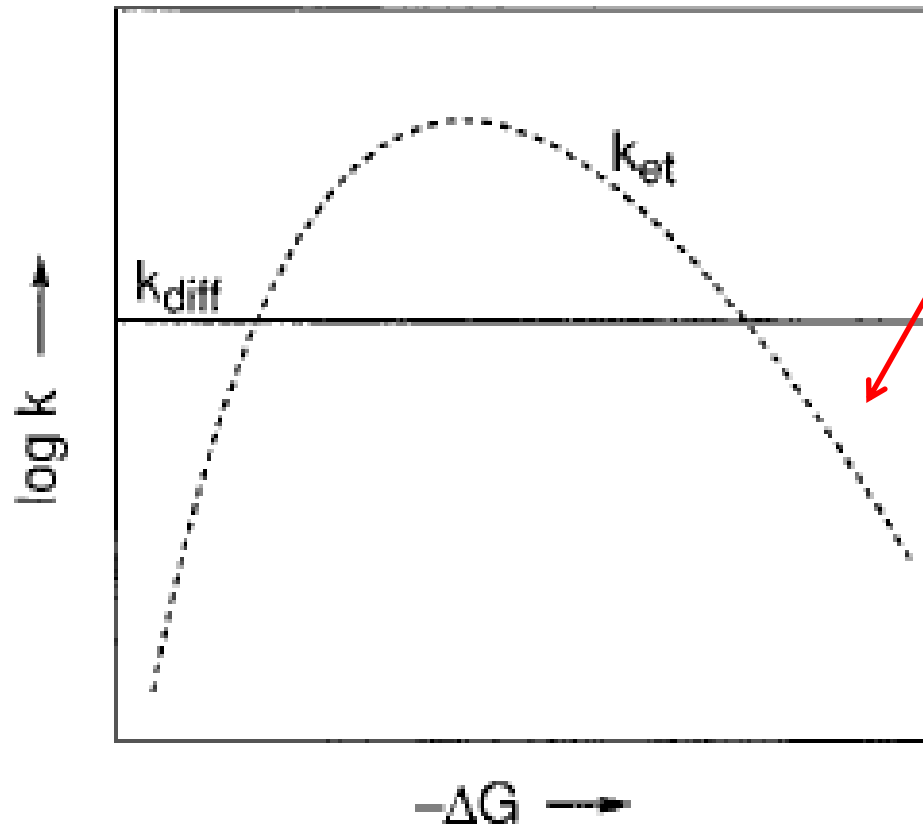


Electron transport cofactors

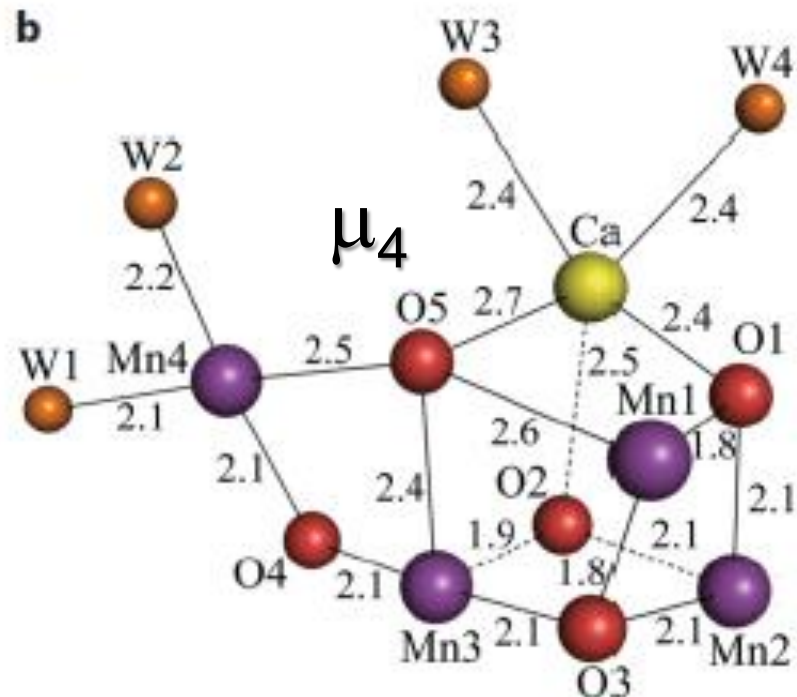
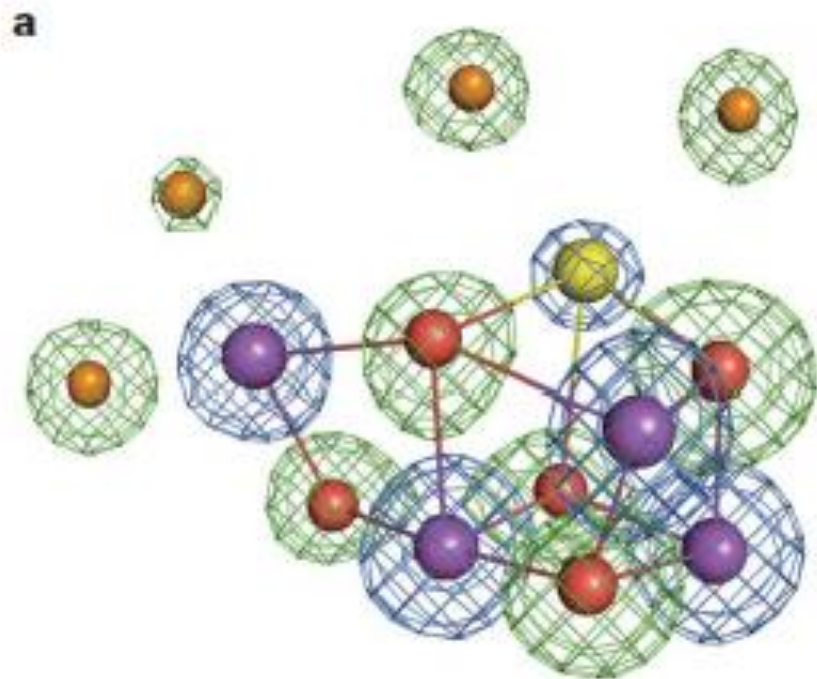
Plastoquinone mobile =
trasportatore di elettroni
mobile (come plastoquinolo)

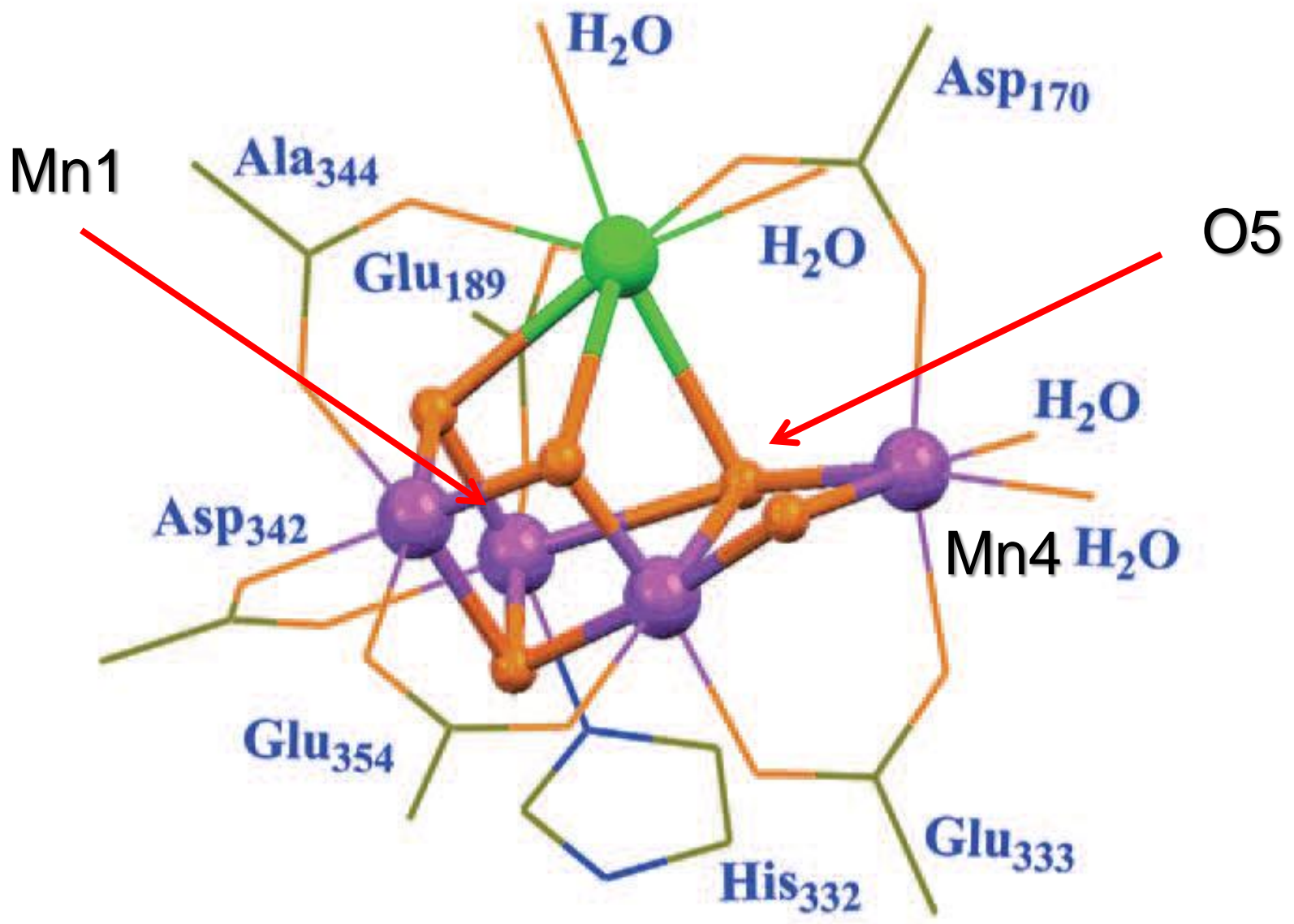


Regione inversa di Marcus

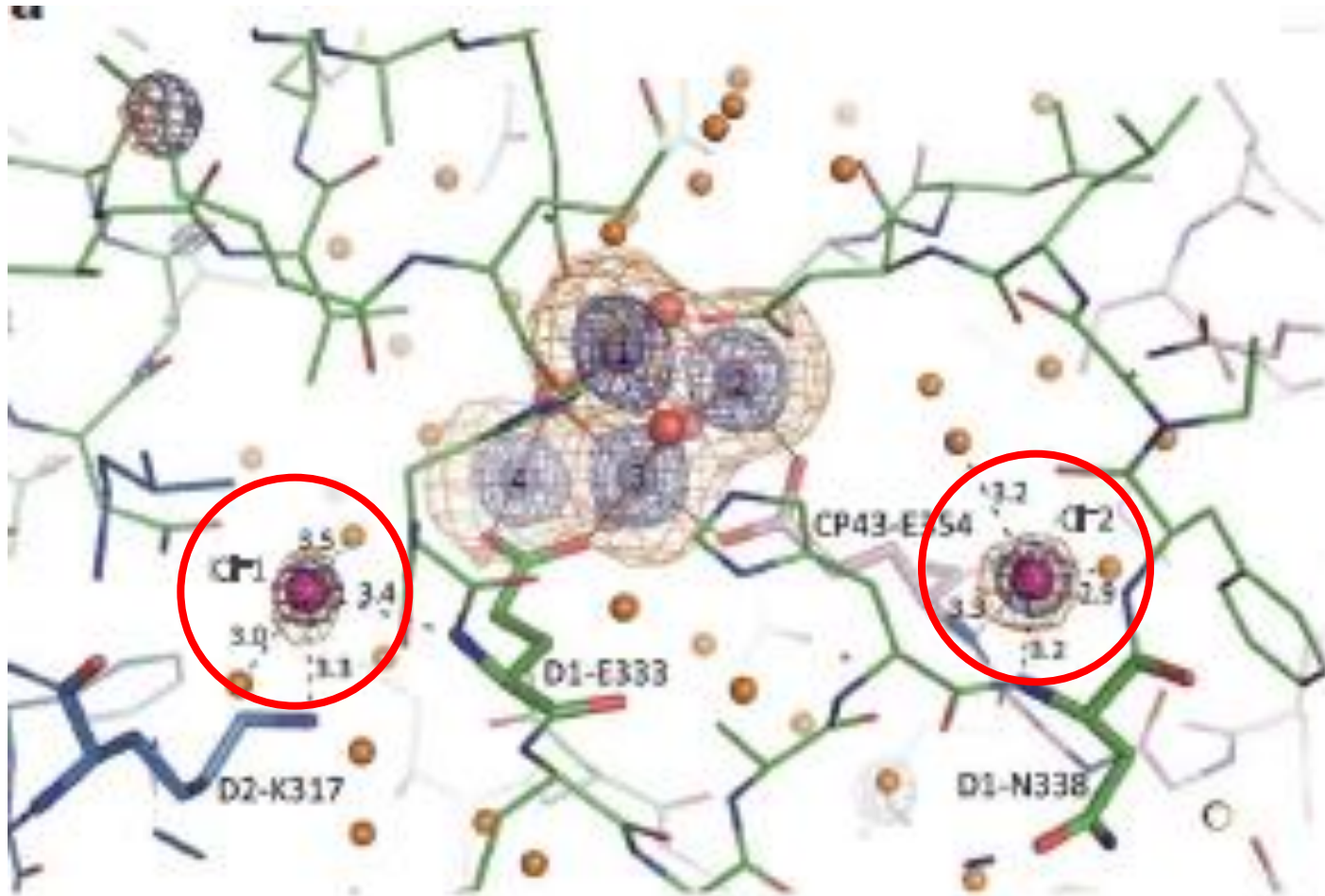


Oxygen Evolving Complex (OEC)

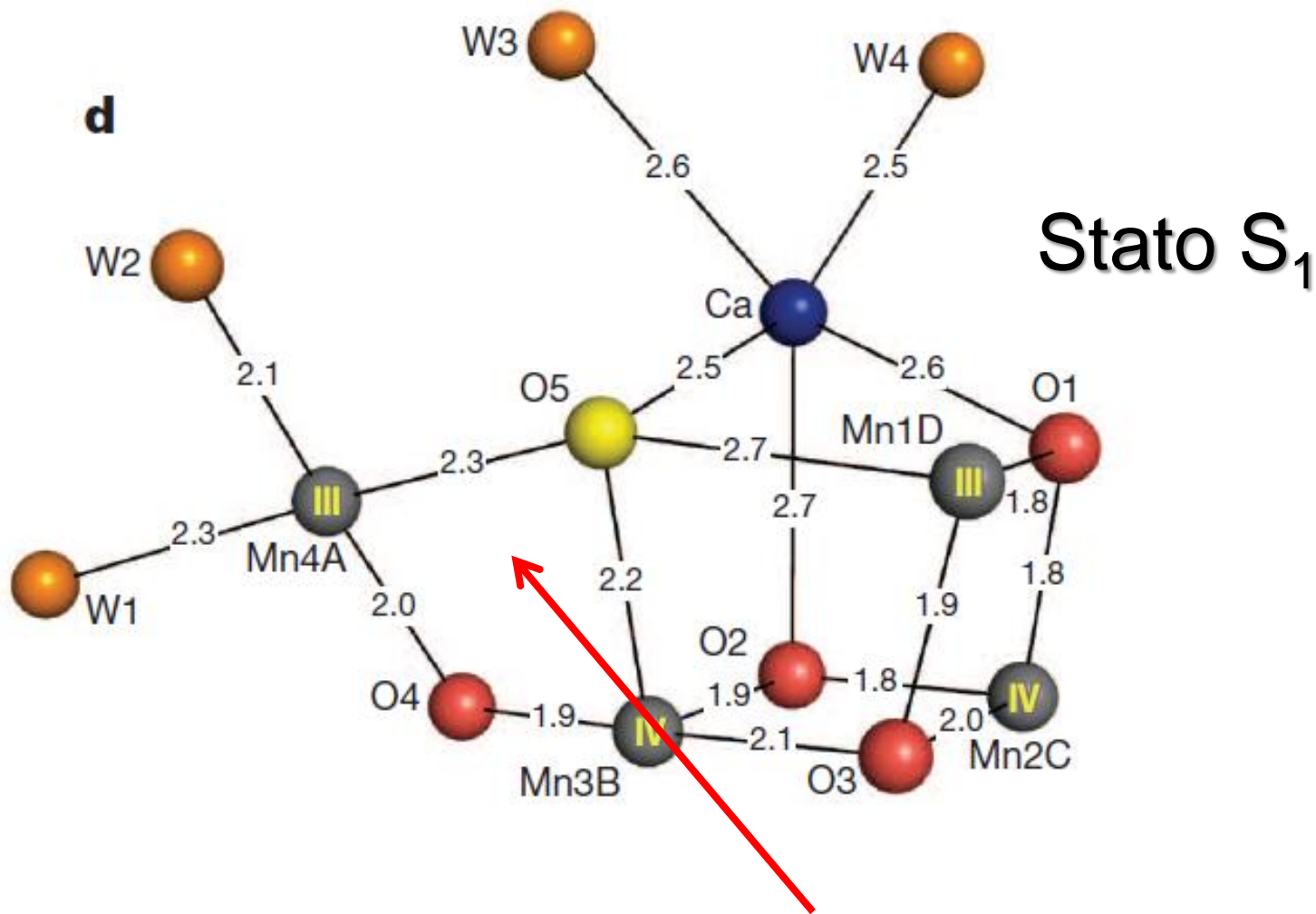




2 Cloruri



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

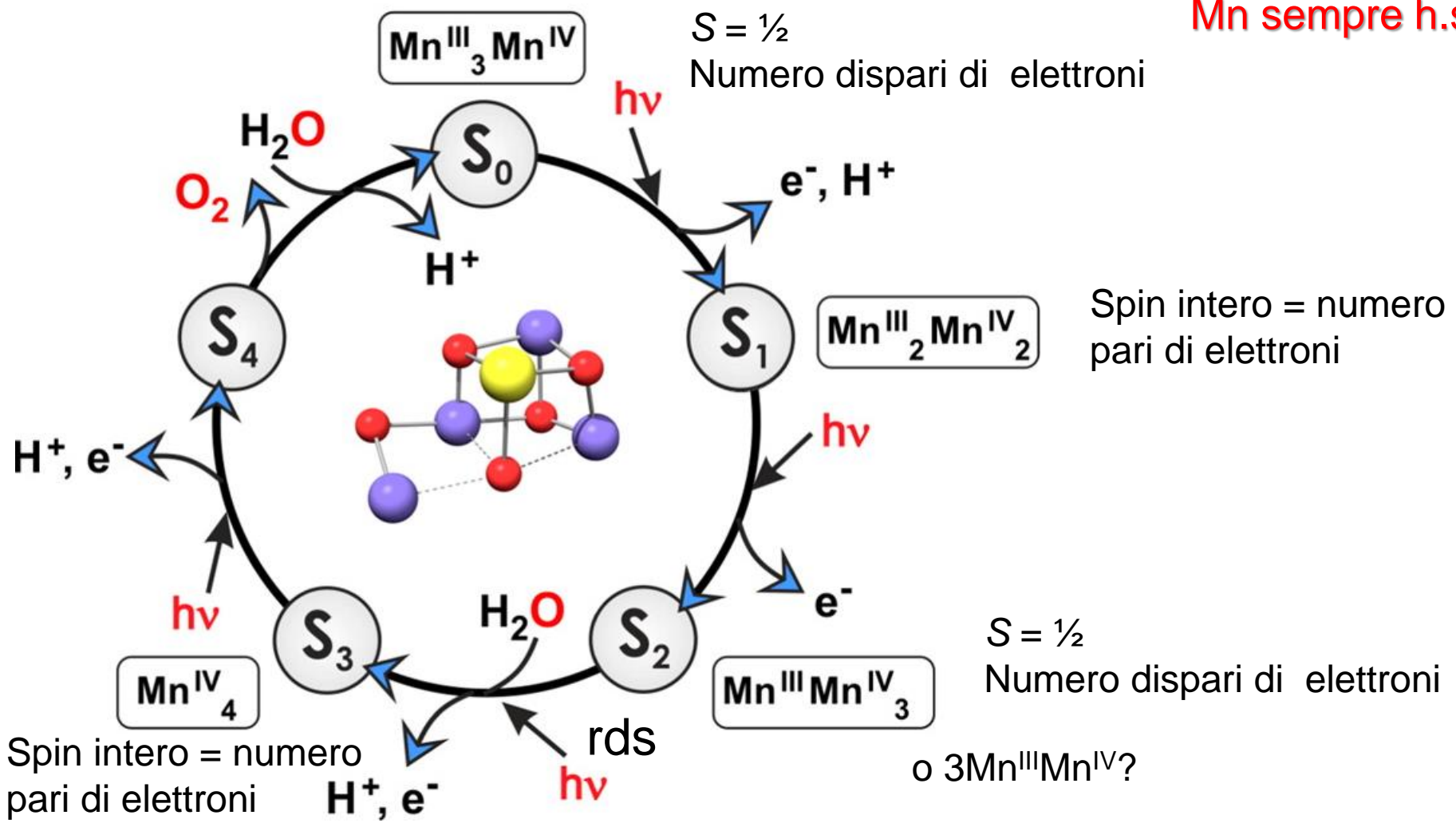


Nature 2015
X-ray free-electron laser (XFEL)

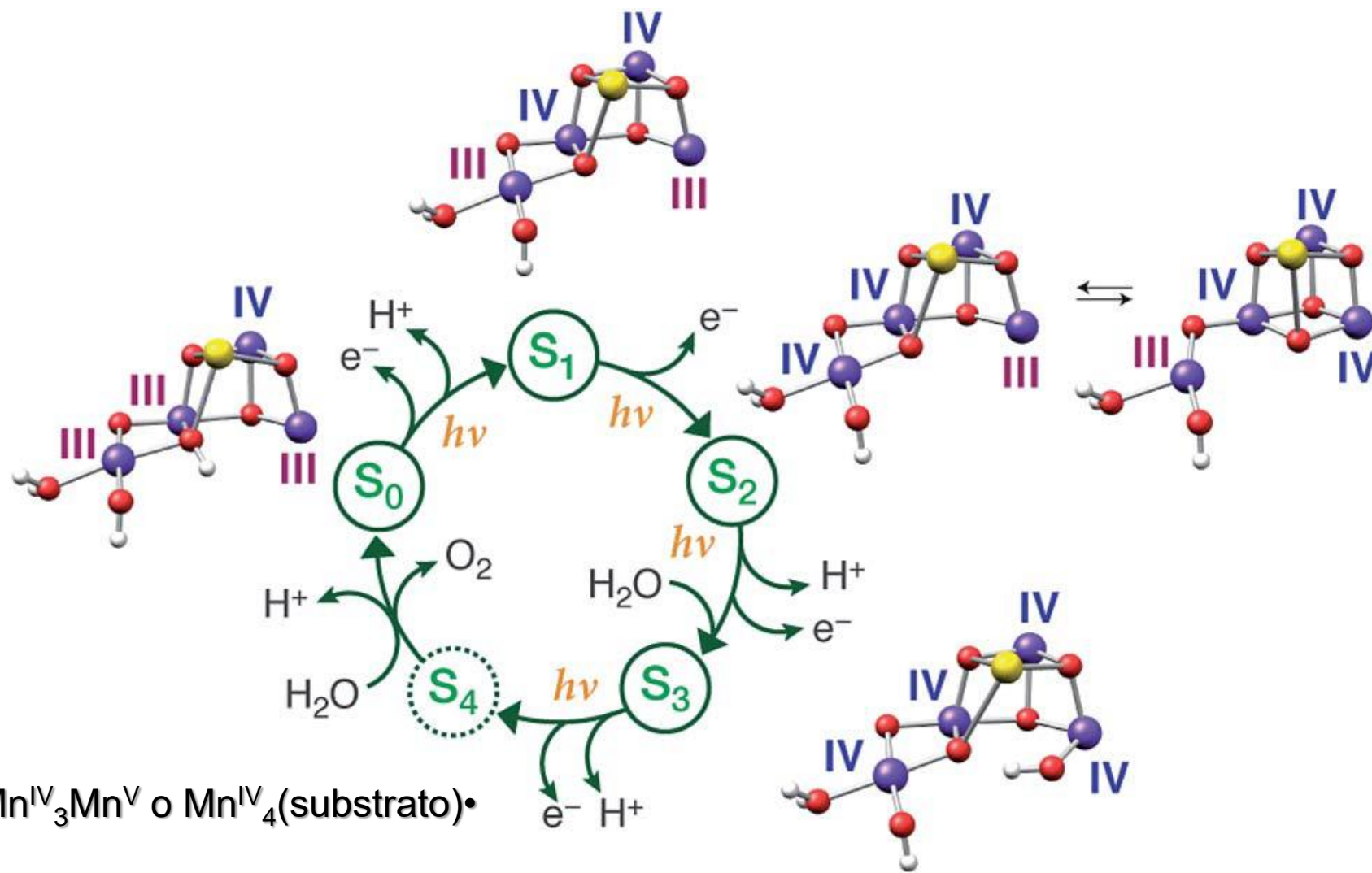
Mn4–O5 più corta di 0.2 Å

Ciclo di Kok o *S clock*

Mn sempre h.s.

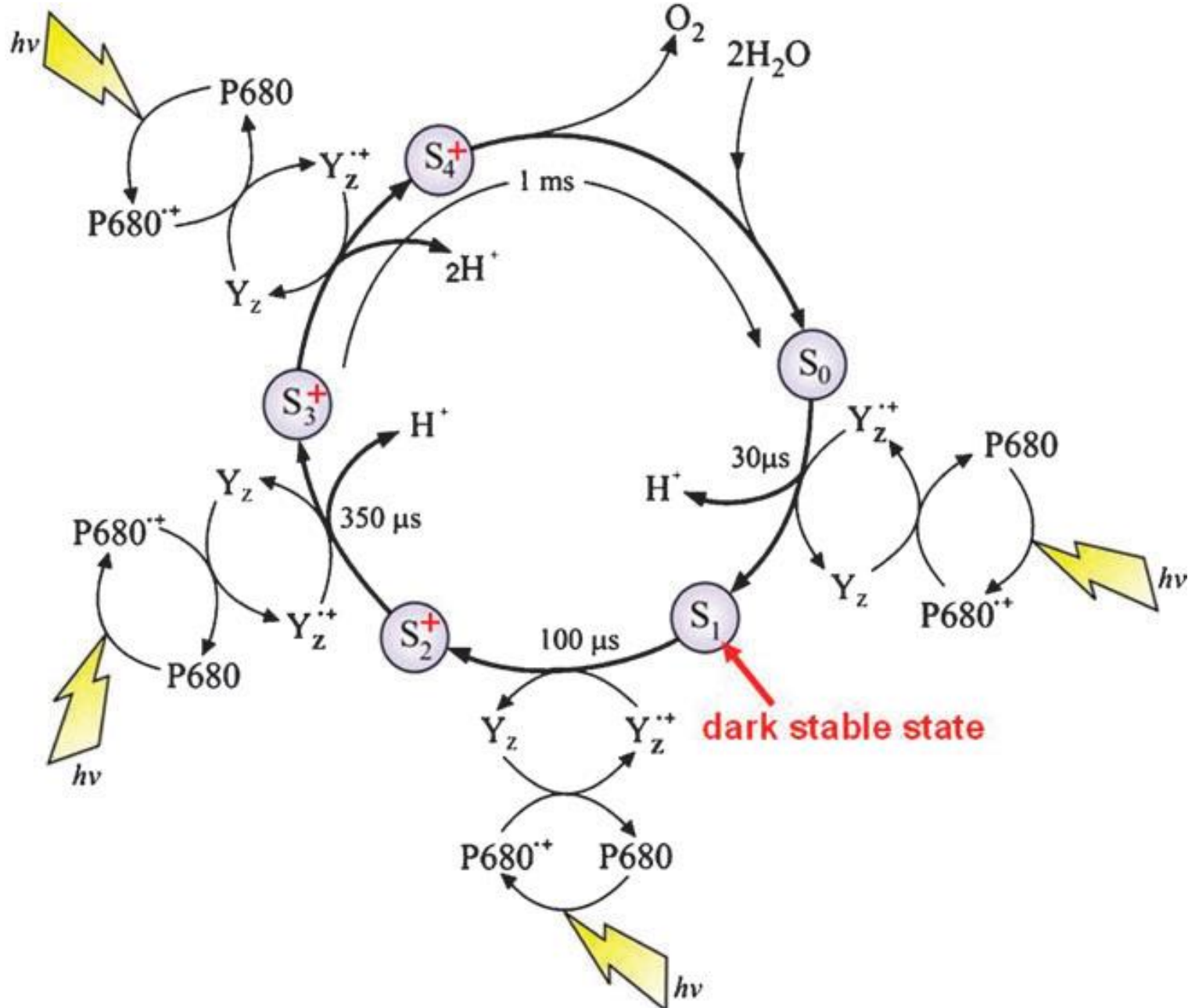


OEC ossida fino a 1000 molecole di H_2O (500 cicli) per secondo!
 TON \approx ca. 10^6



$Mn^{IV}_3Mn^V$ o $Mn^{IV}_4(\text{substrato})\bullet$

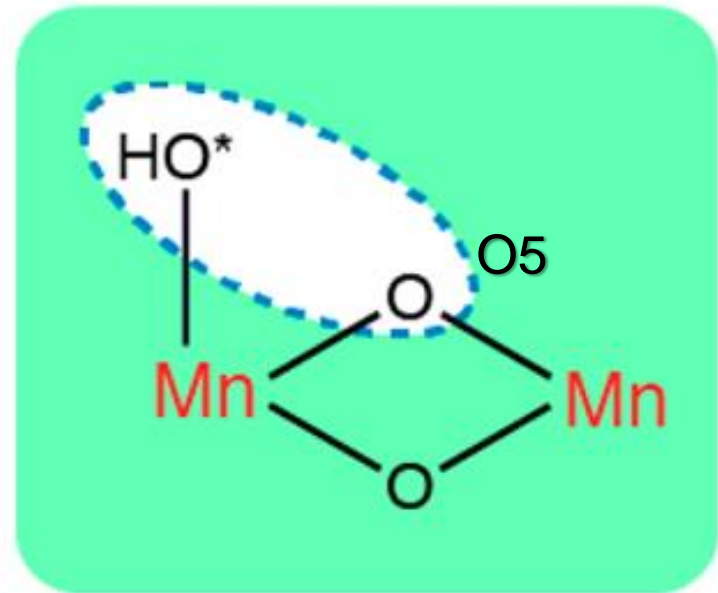
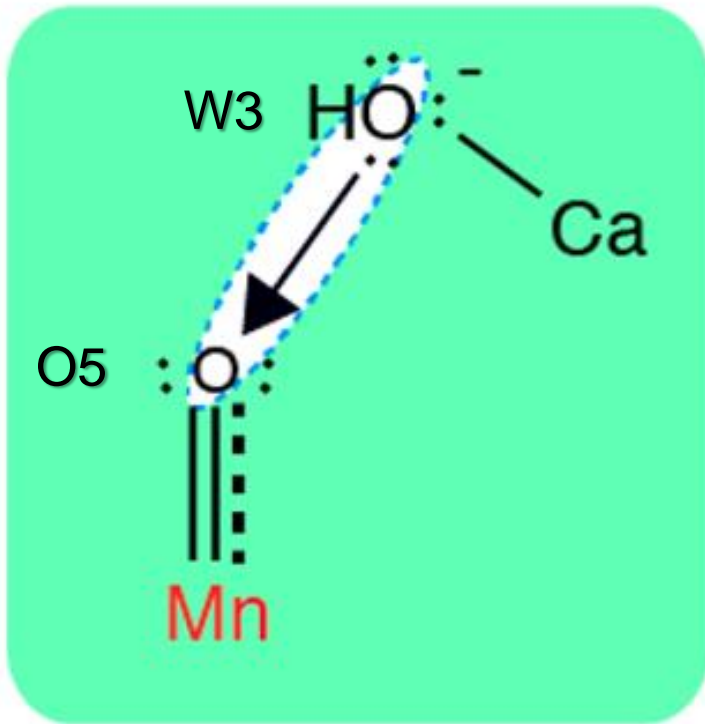
Ciclo di Kok o *S clock*



Ipotesi di formazione del legame O–O

nucleophilic attack

terminal oxyl radical
with bridging oxo



$\text{Mn(V)}\equiv\text{O}$ o $\text{Mn(IV)}=\text{O}\cdot$ *oxo/oxyl radical coupling mechanism*

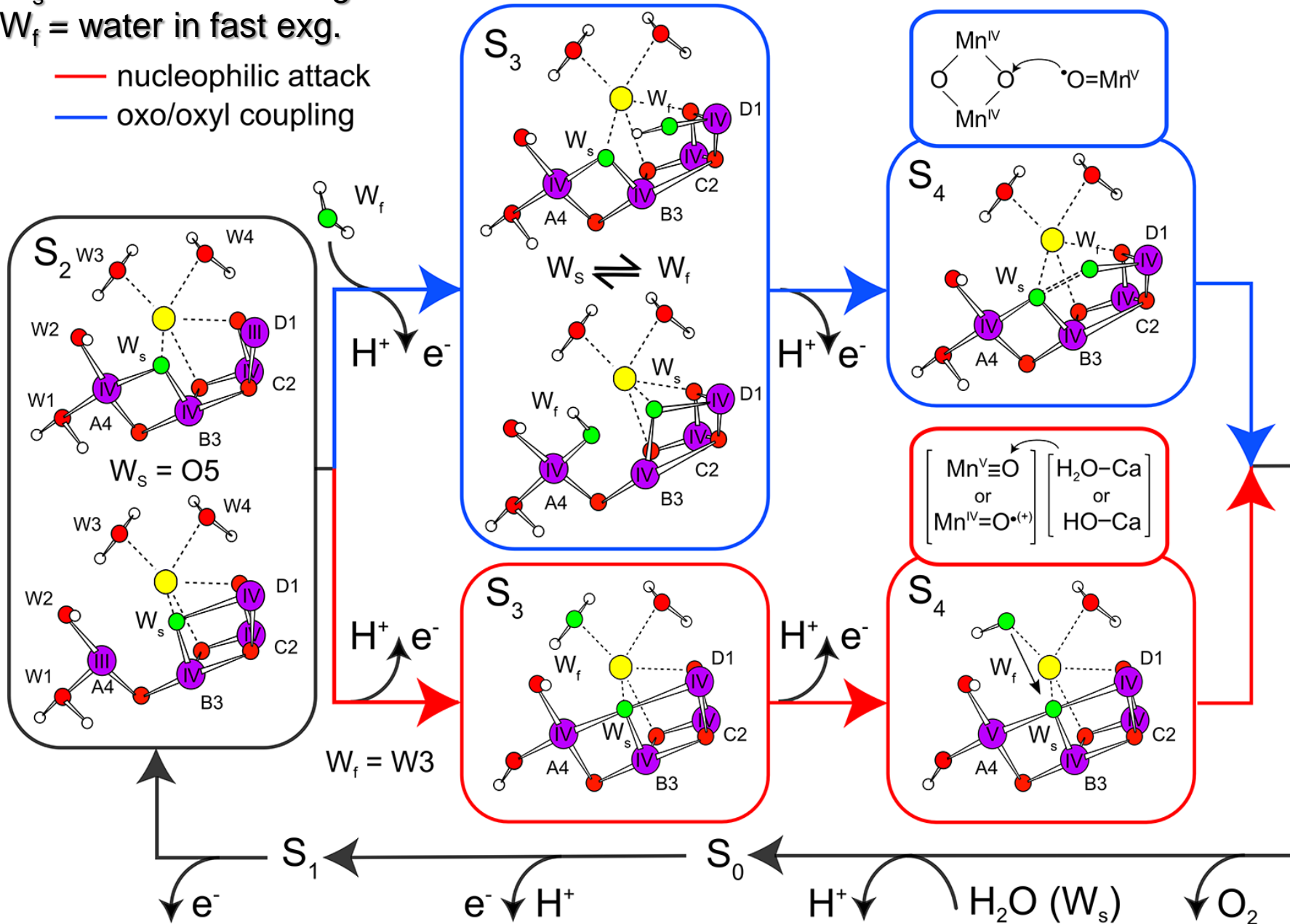
In questo meccanismo l'ultimo elettrone viene estratto da O, non da Mn

W_s = water in slow exg.

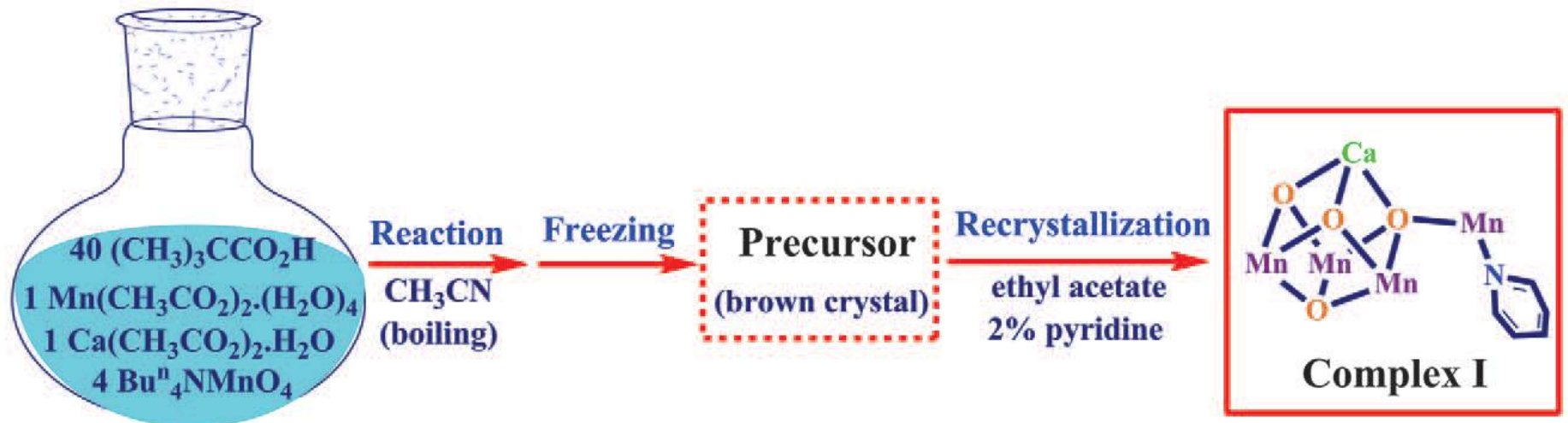
W_f = water in fast exg.

— nucleophilic attack

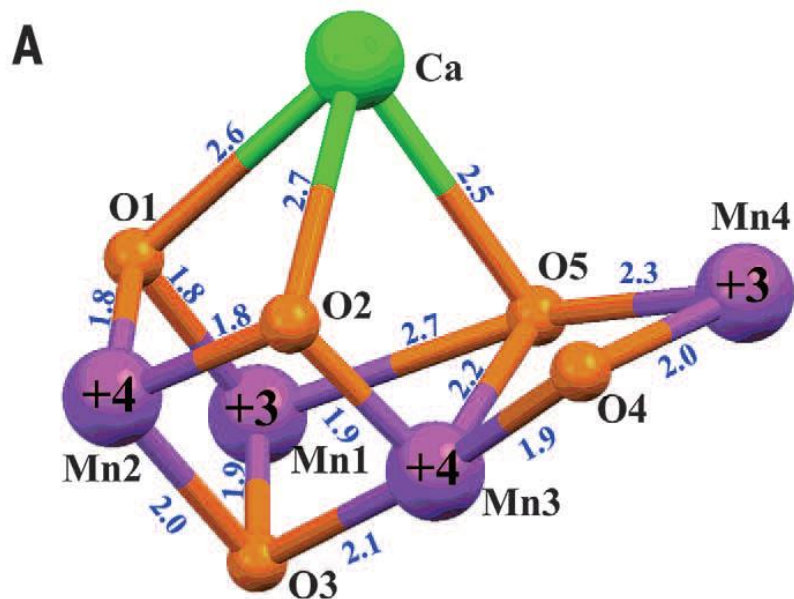
— oxo/oxyl coupling



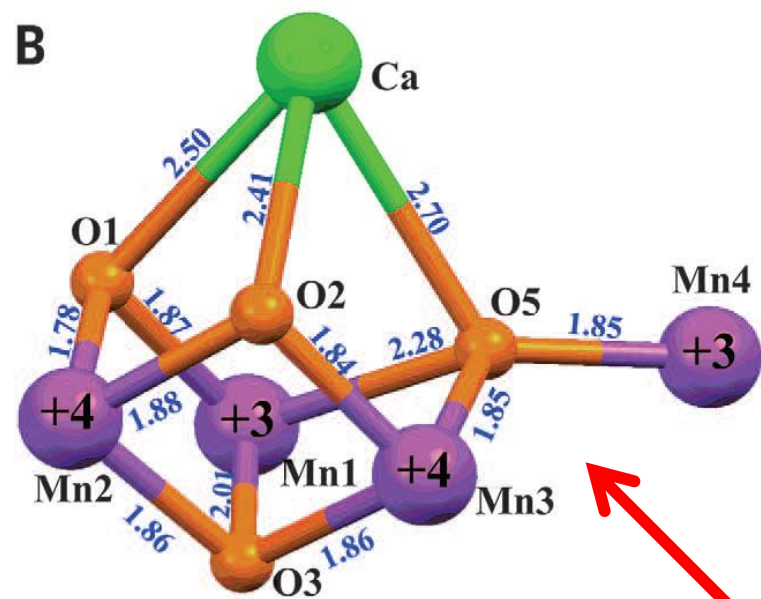
Sistemi modello



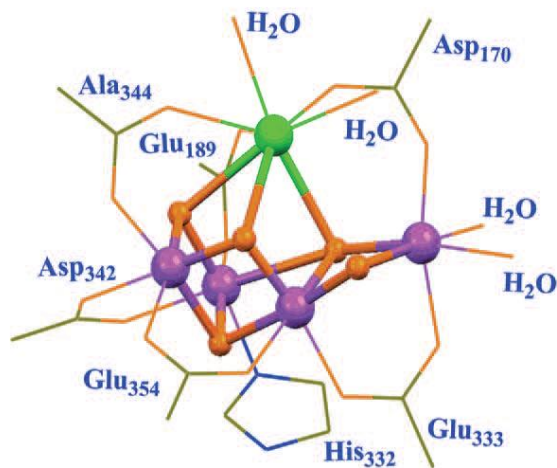
Natural catalyst



Artificial complex



C



D

