

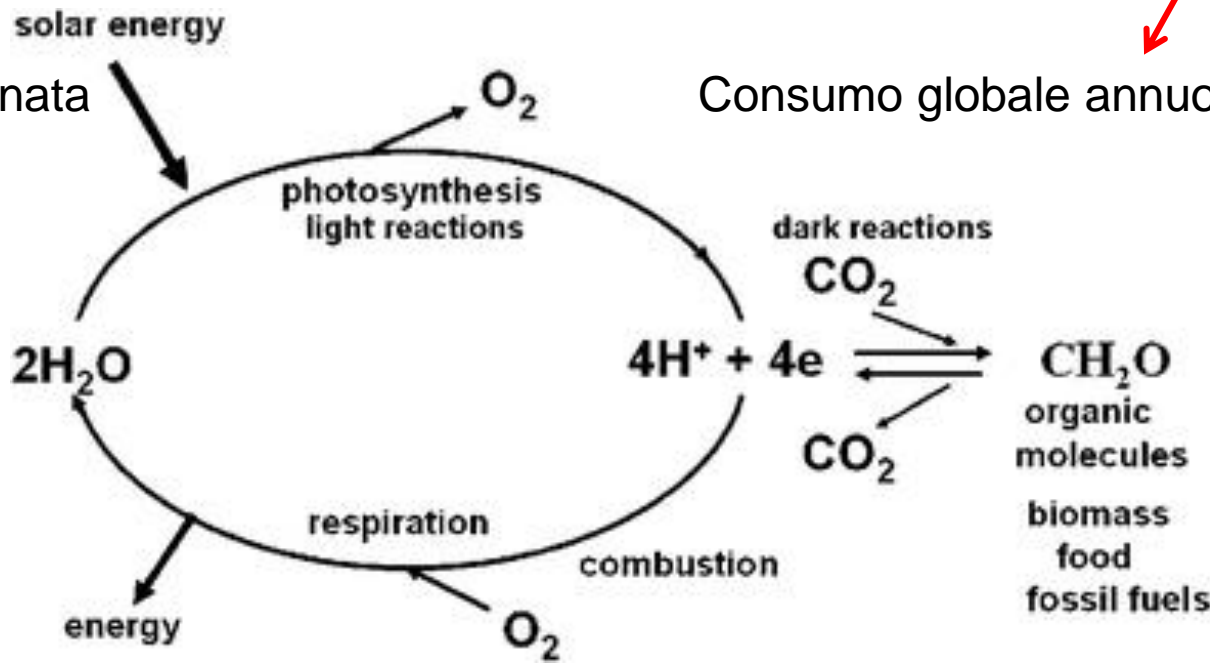
100 × 10<sup>9</sup> ton/y di (CH<sub>2</sub>O)<sub>n</sub> da CO<sub>2</sub>

1 g di glucosio per m<sup>2</sup> di superficie fogliare all'ora

100 TW/y = 0.1% energia solare totale (10<sup>5</sup> TW)



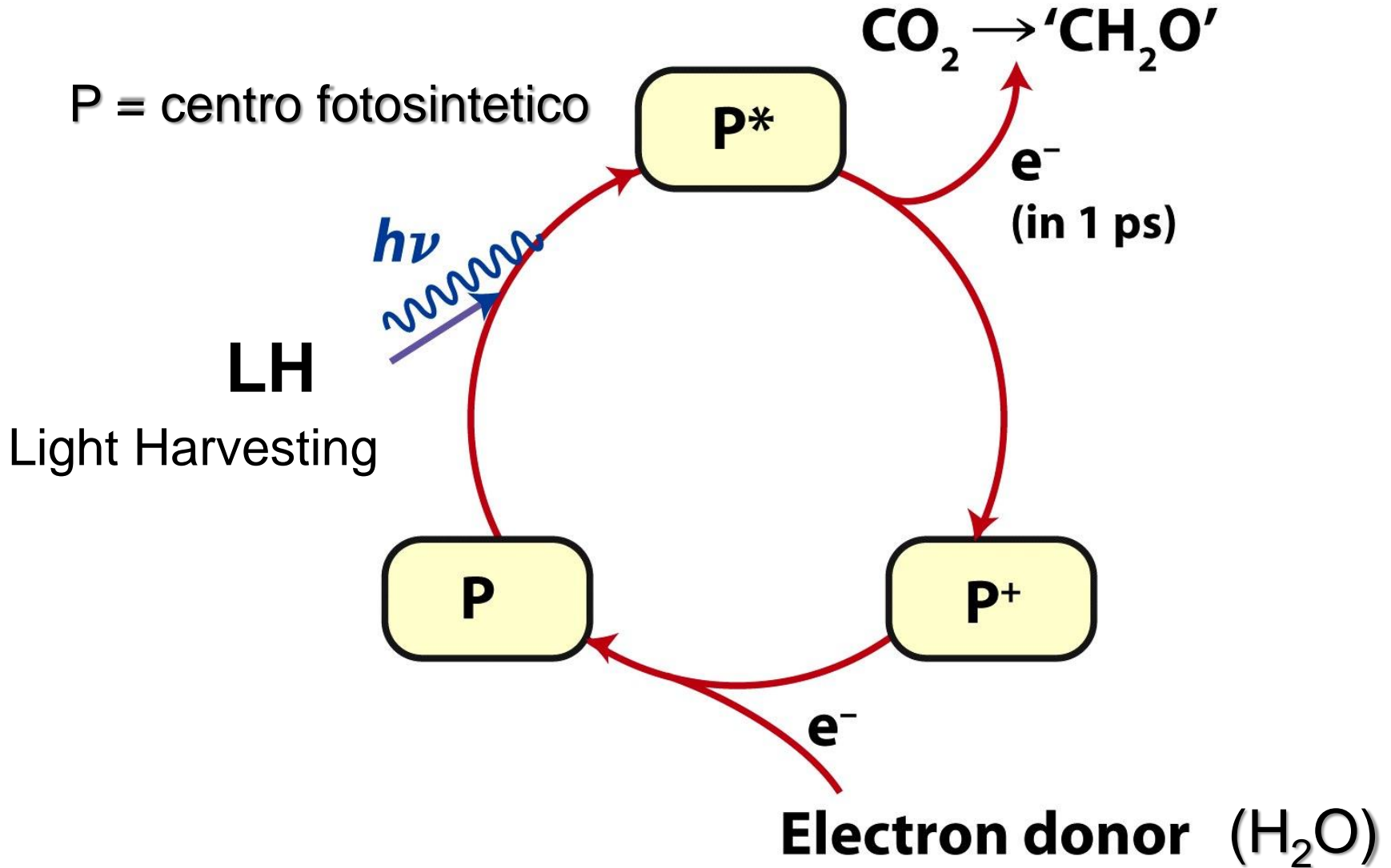
Energia immagazzinata  
come biomassa



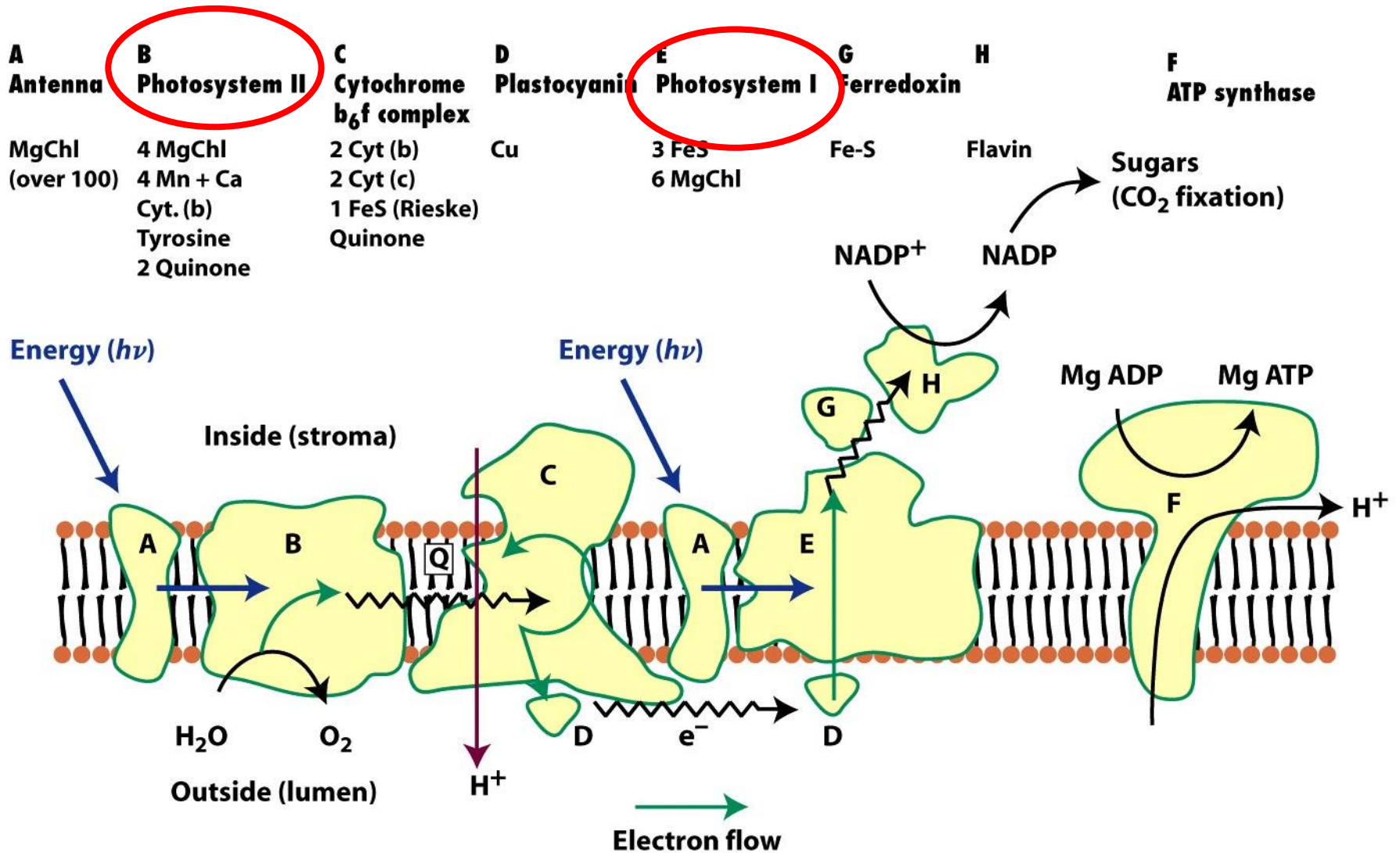
Consumo globale annuo: 14 TW



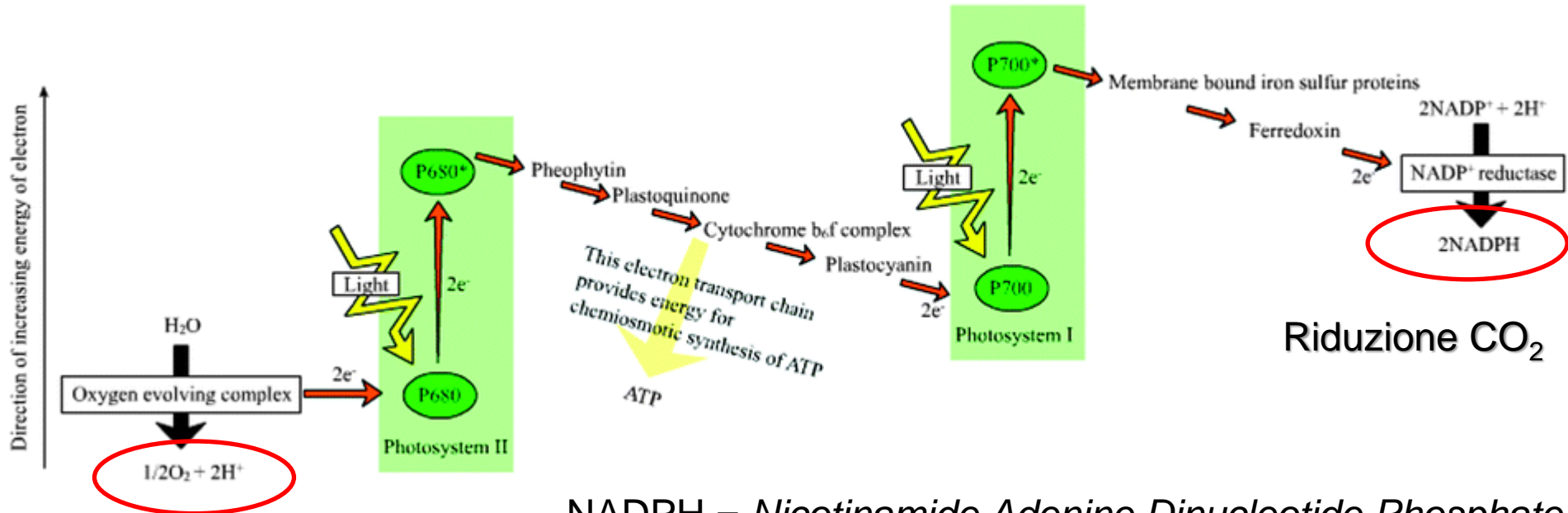
# Separazione di carica fotoindotta



# Processo fotosintetico nelle piante

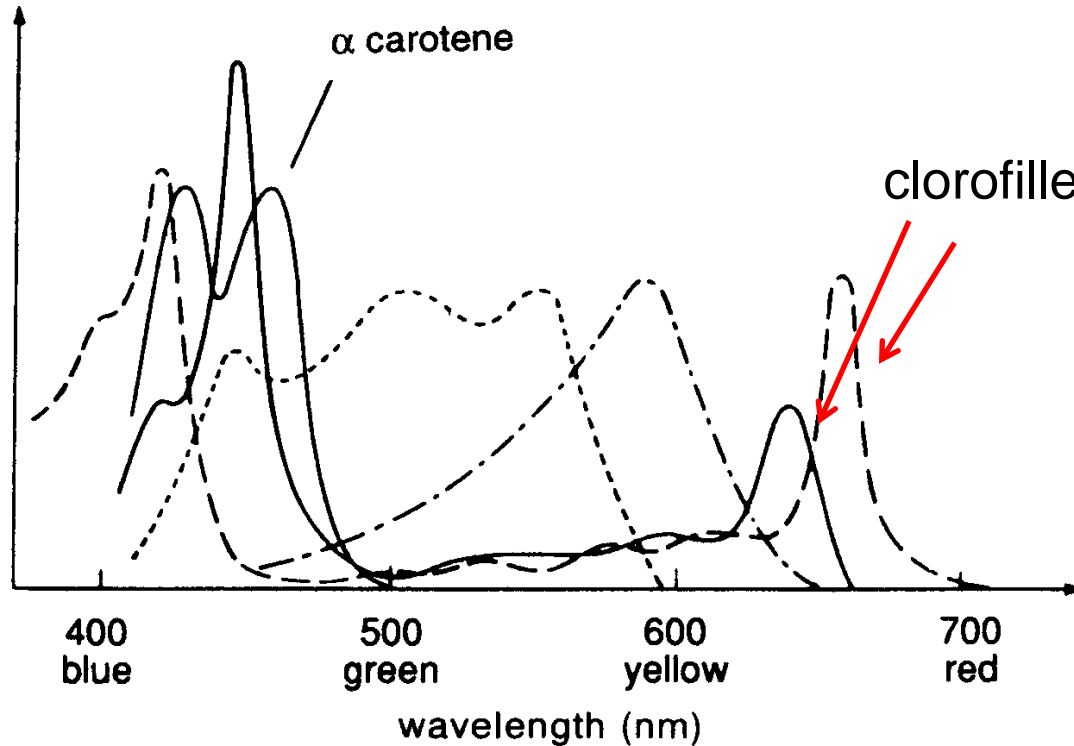
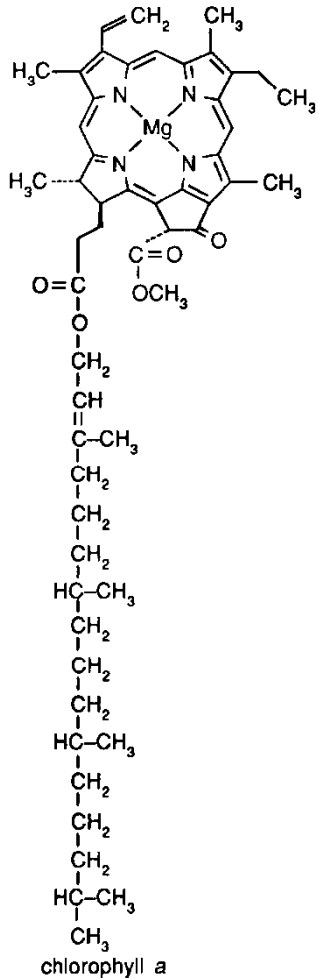


# Diagramma di potenziale redox "a Z"



*Per ogni elettrone estratto dall'acqua e trasferito a CO<sub>2</sub> serve l'energia di due fotoni, uno in PSII e l'altro in PSI*

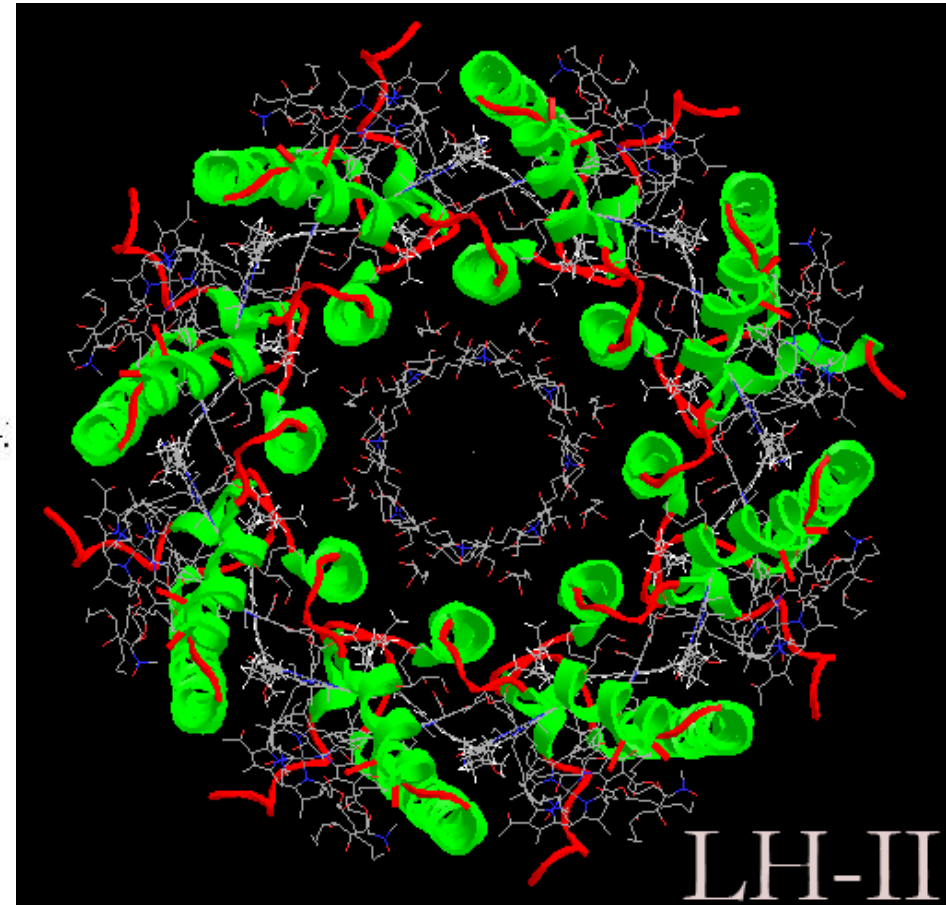
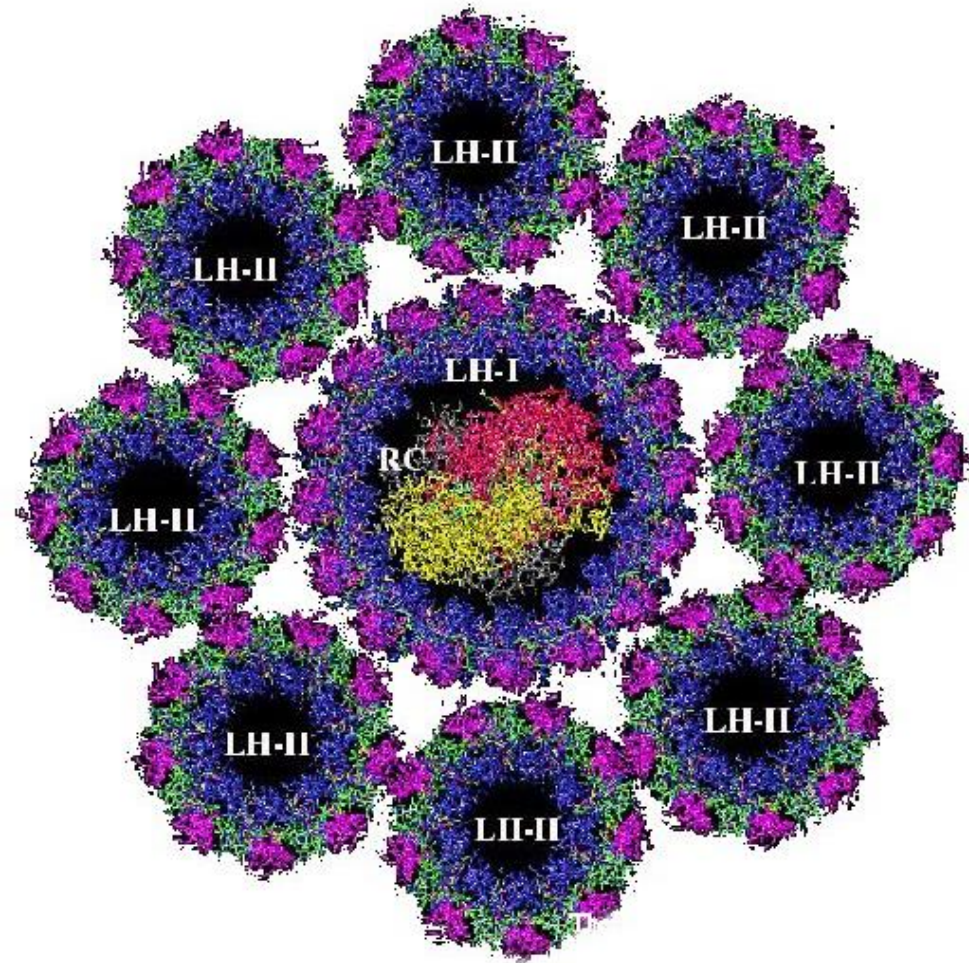
# Pigmenti deputati al *light harvesting*



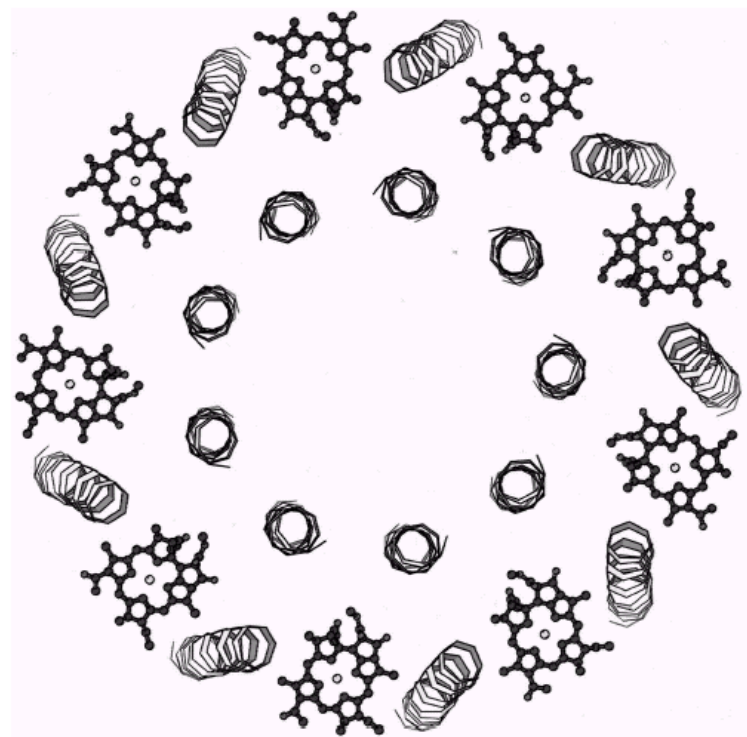
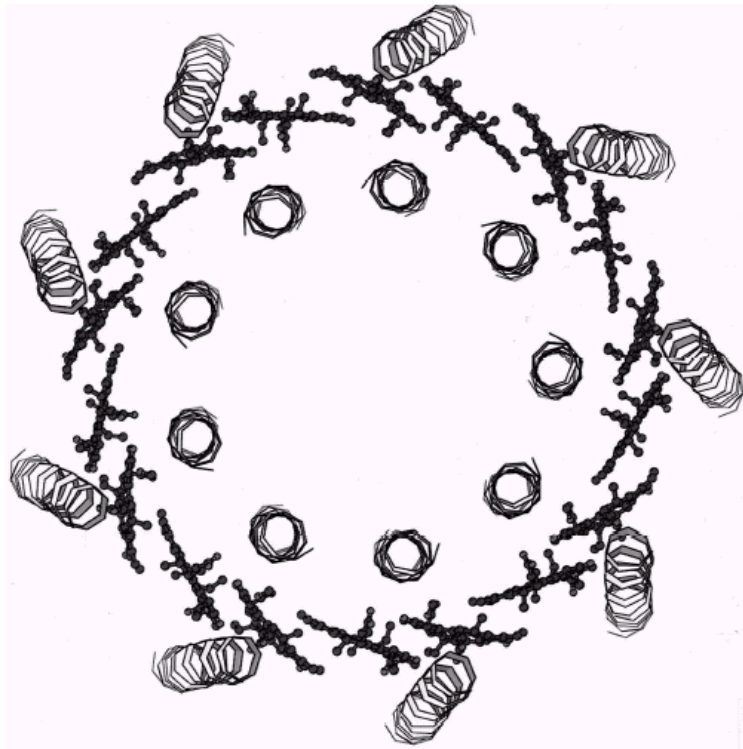
Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (——), phycocyanin (-·-·), phycoerythrin (- - - -)



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

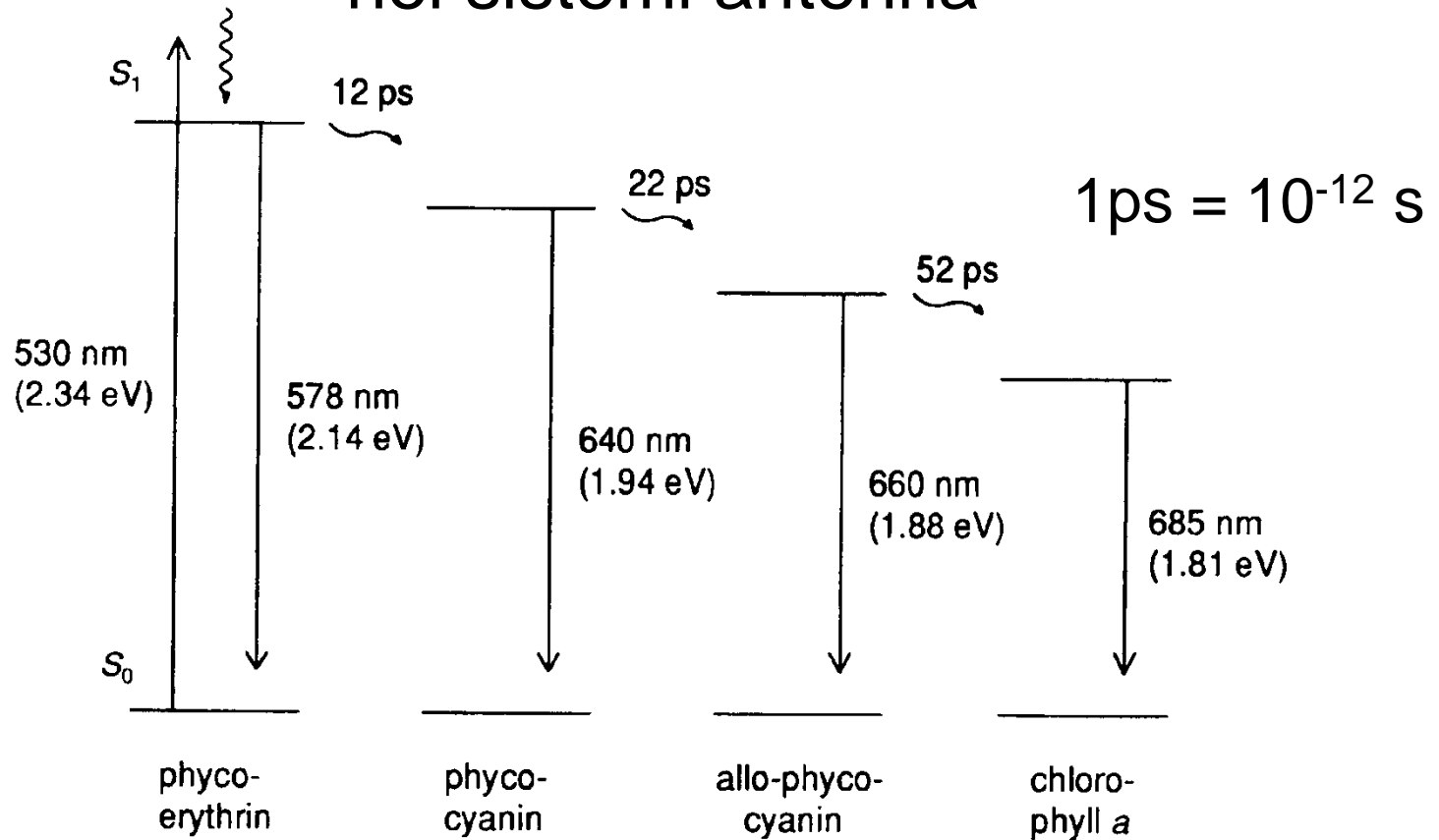


# Sistemi antenna per *light-harvesting* e *exciton transfer*



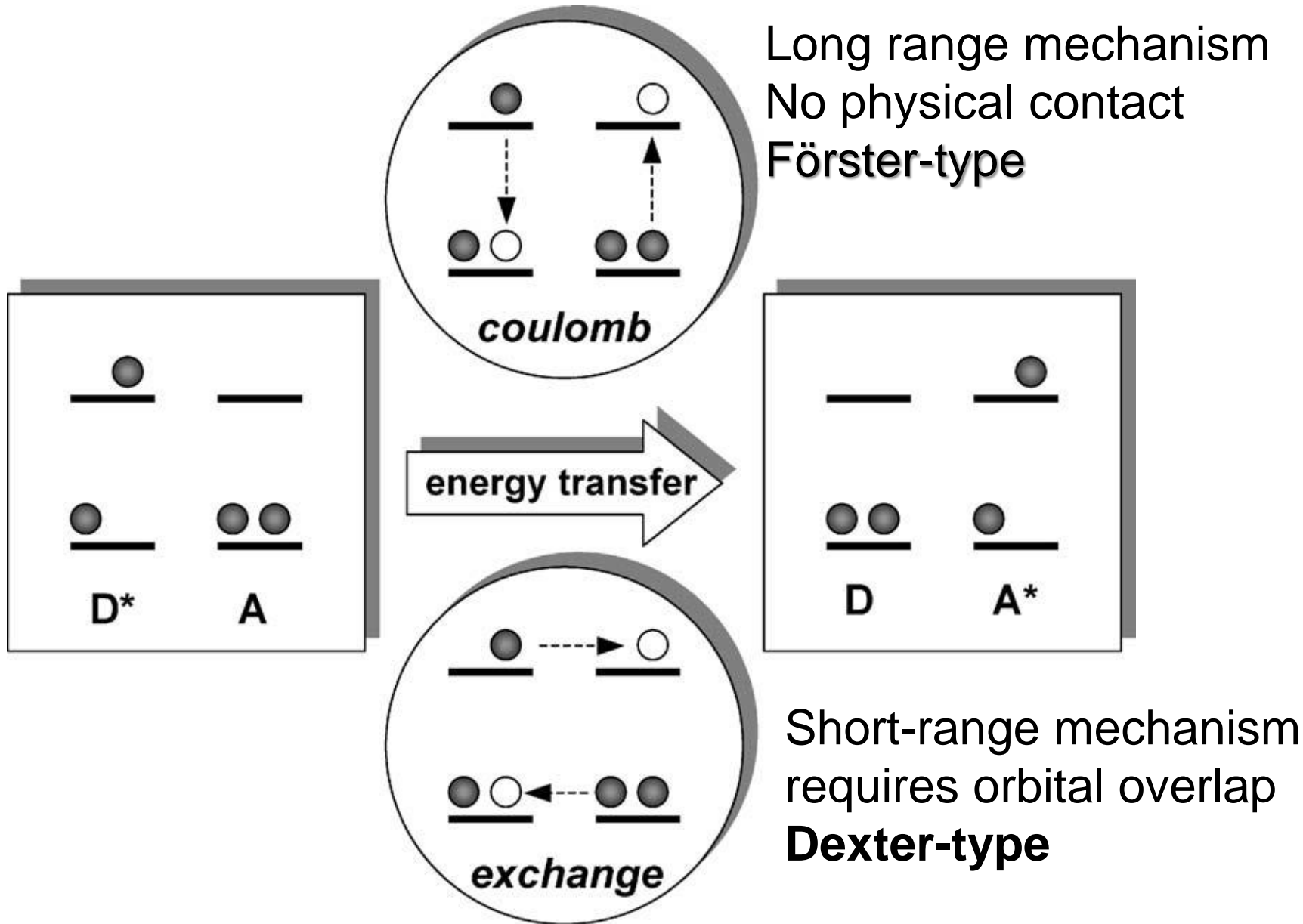


# Trasferimento di energia (*exciton transfer*) a cascata nei sistemi antenna



efficienza del 95%

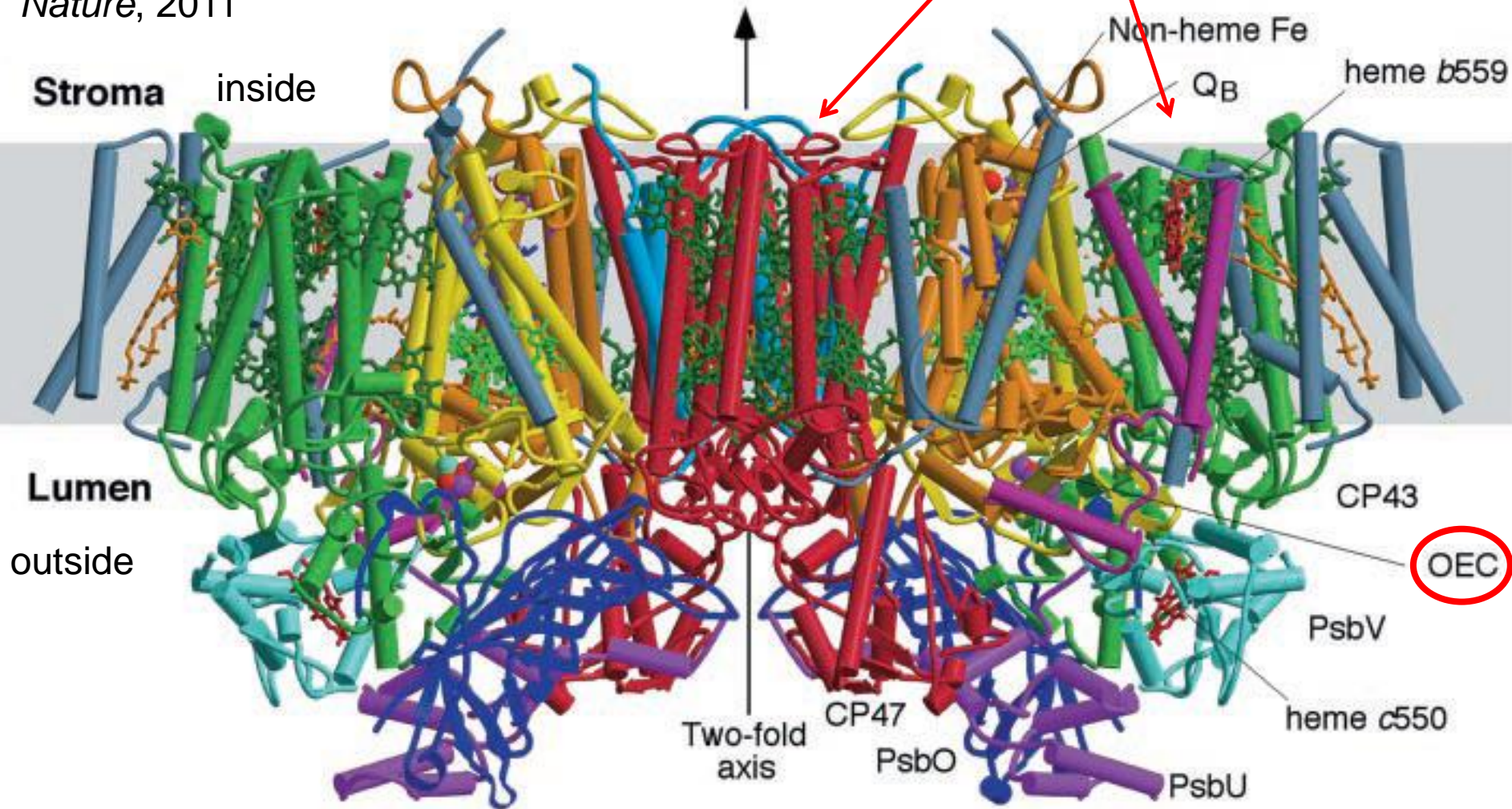
# Meccanismi di *exciton transfer*



# PS II

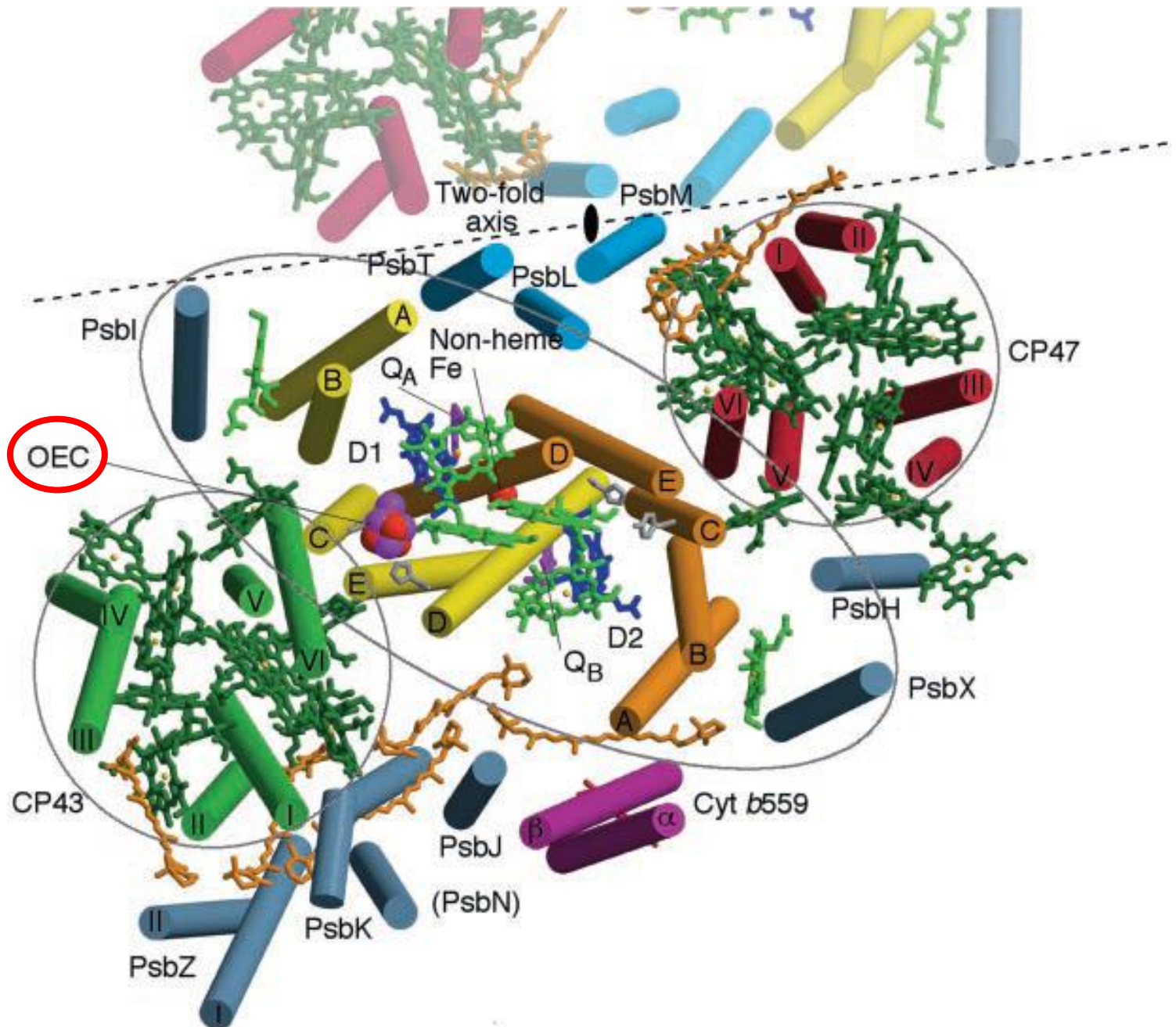
Sistemi antenna

*Nature*, 2011



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

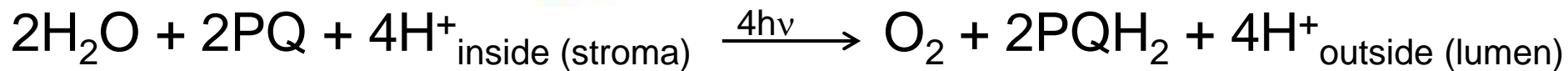
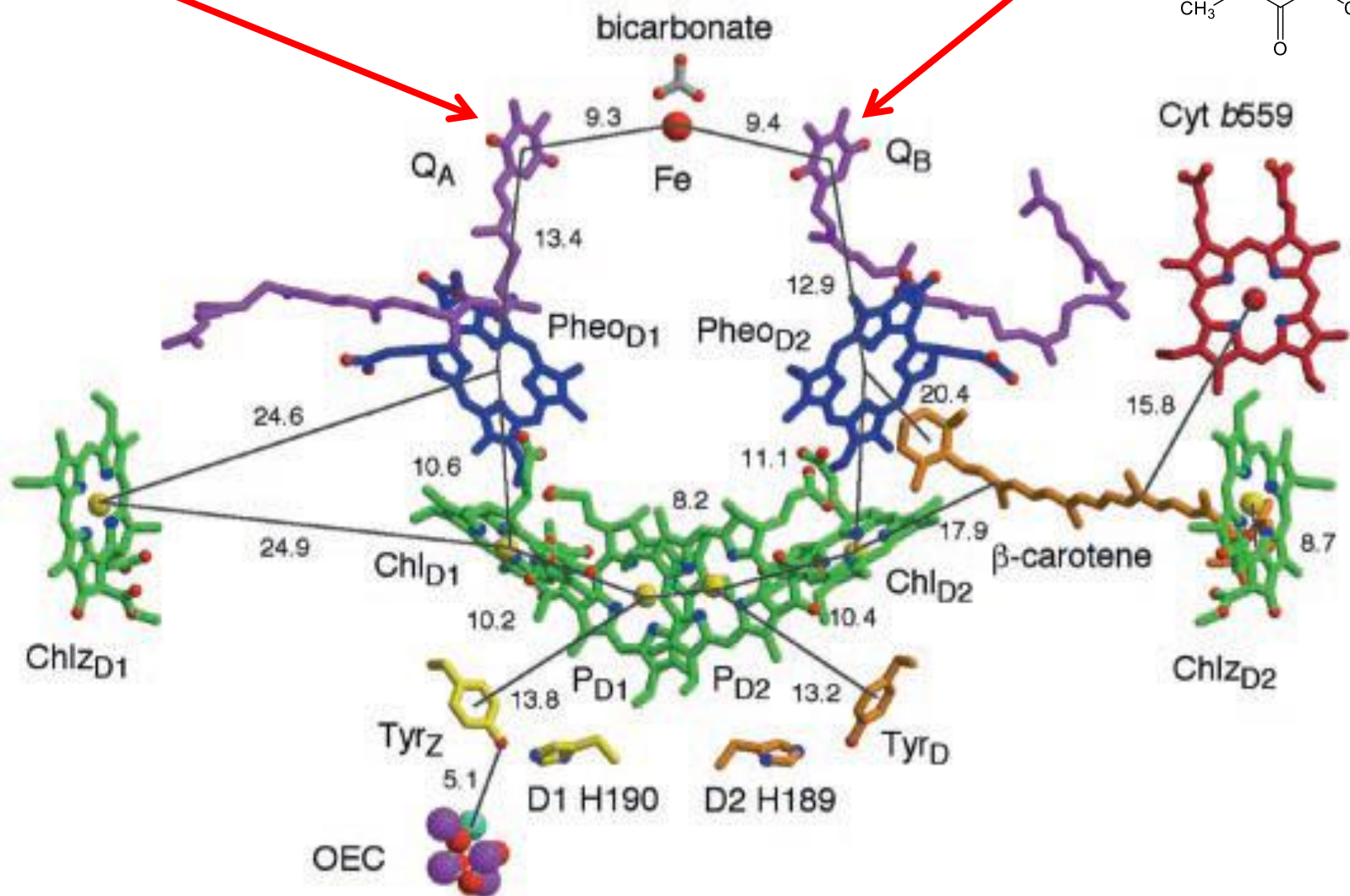
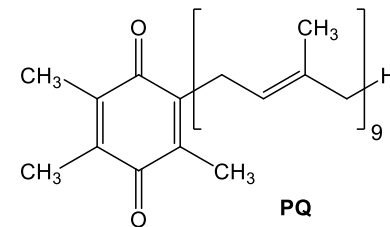
# PS II



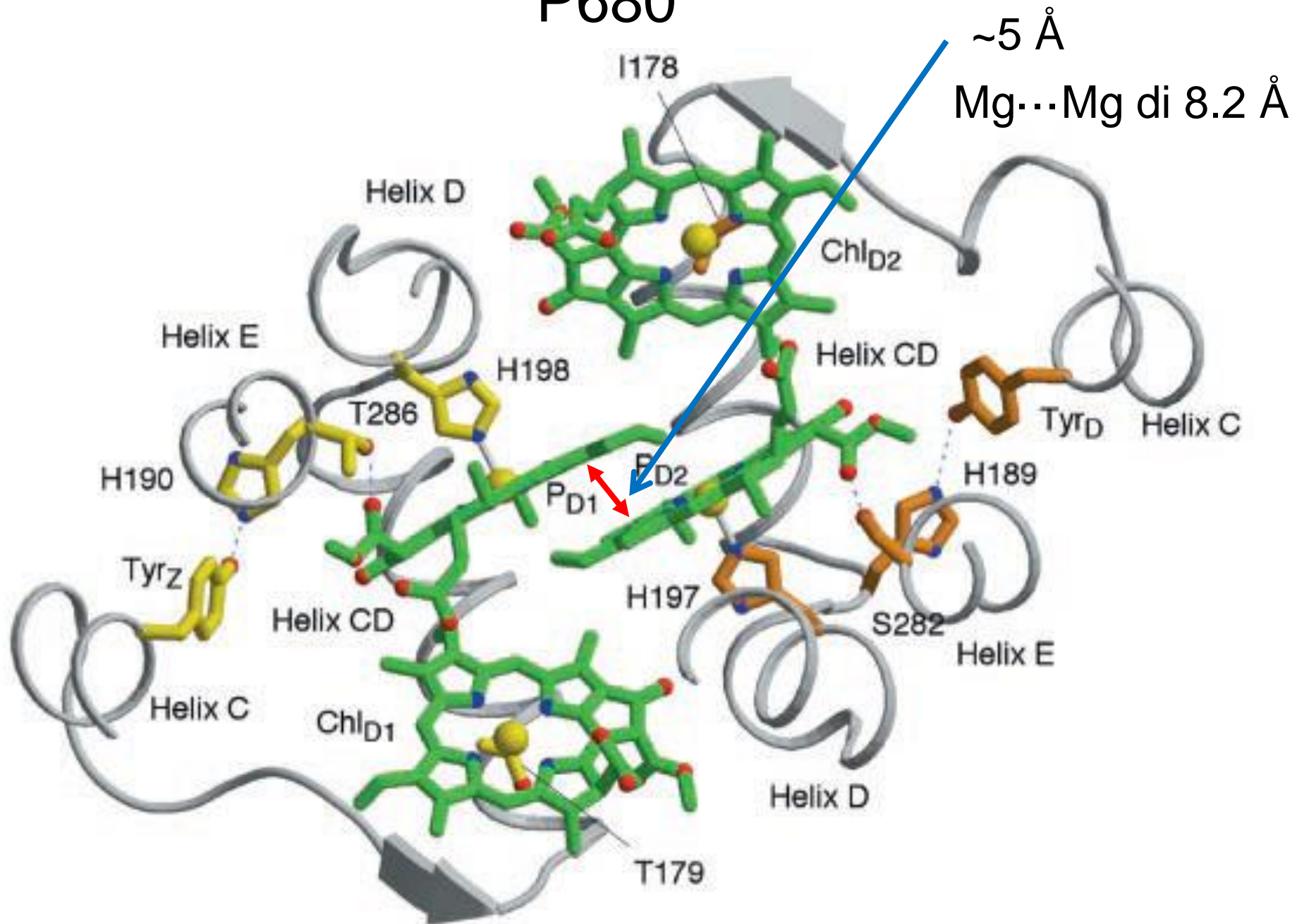
# P680

Plastoquinone fisso

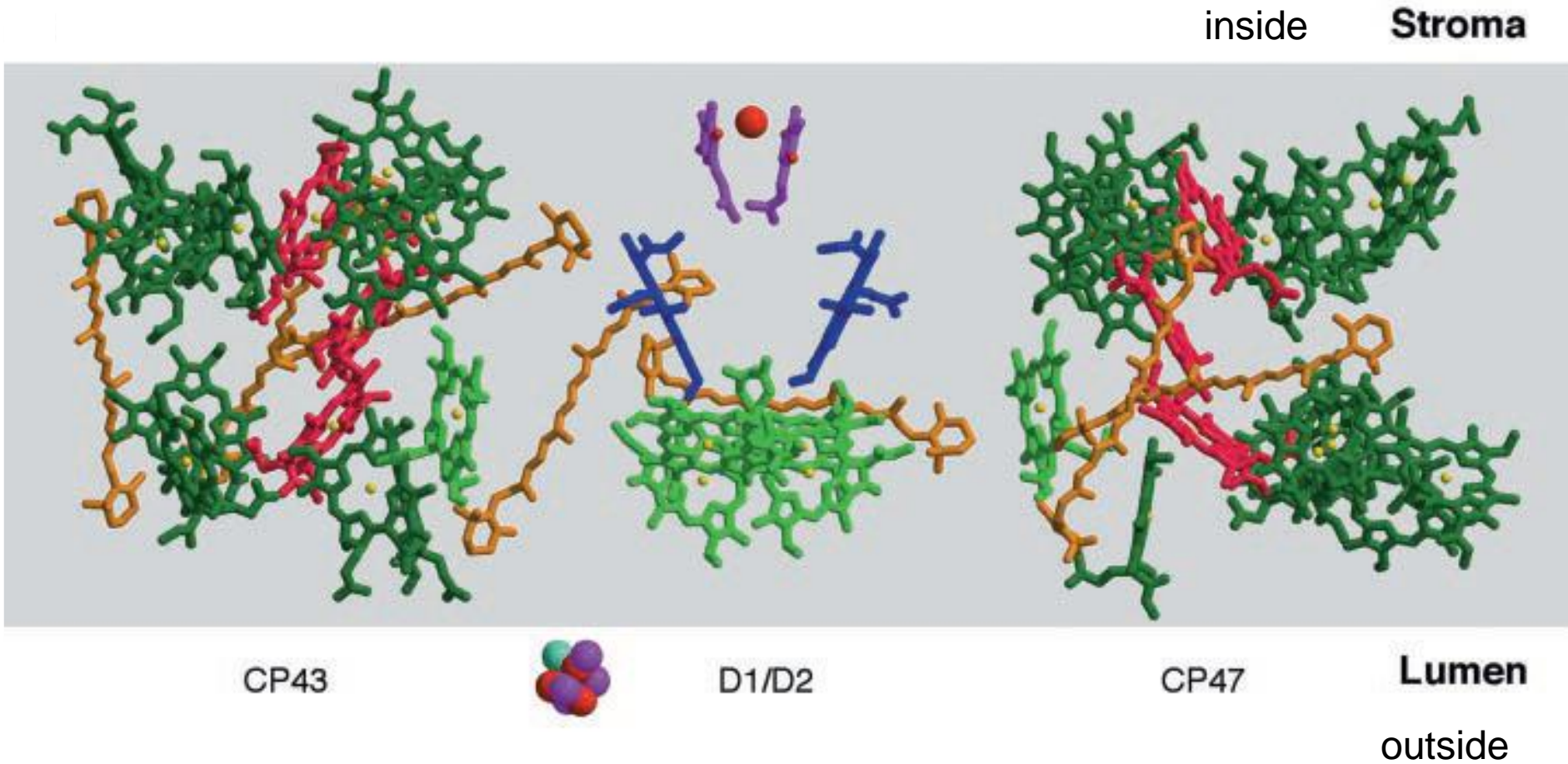
Plastoquinone mobile

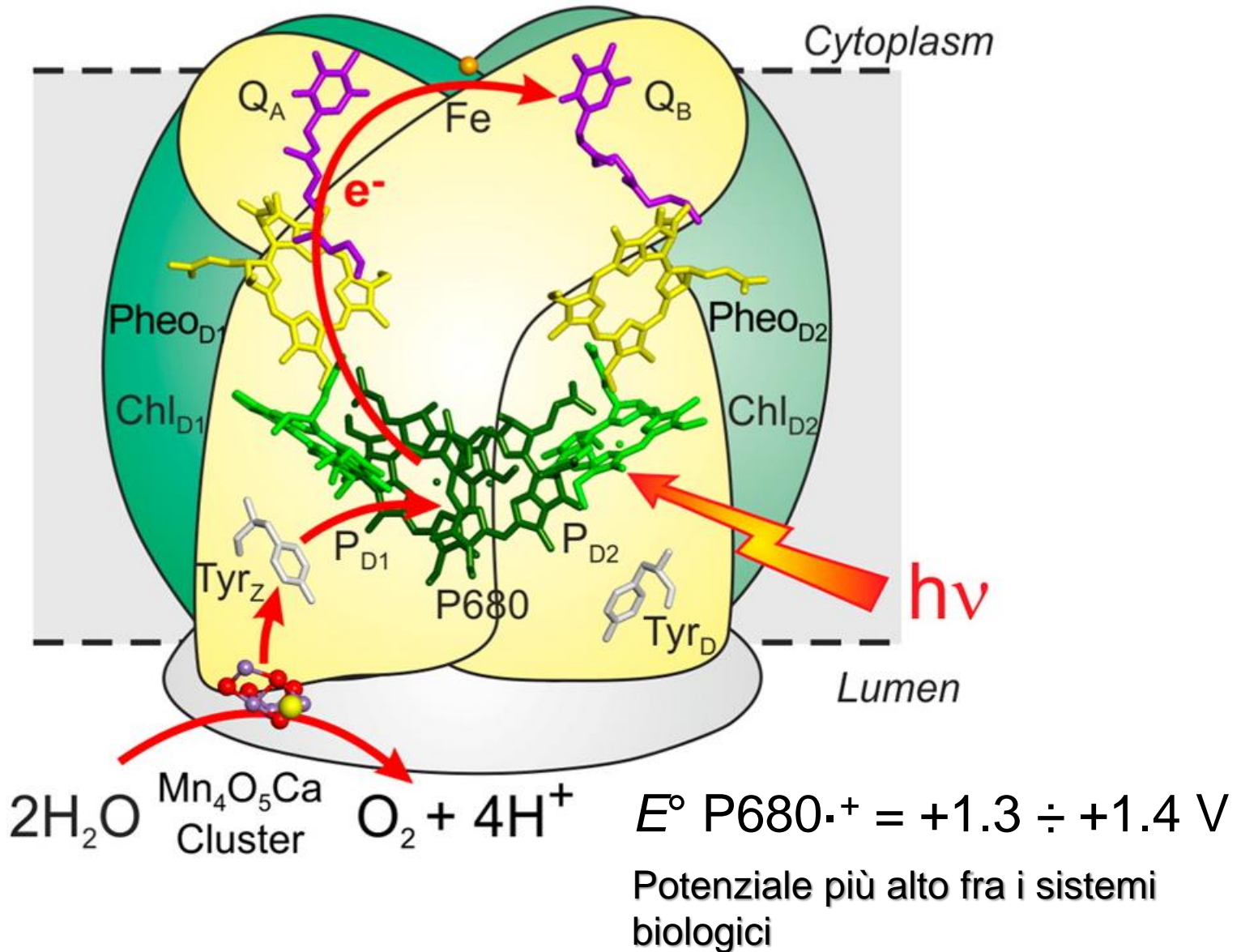


# P680



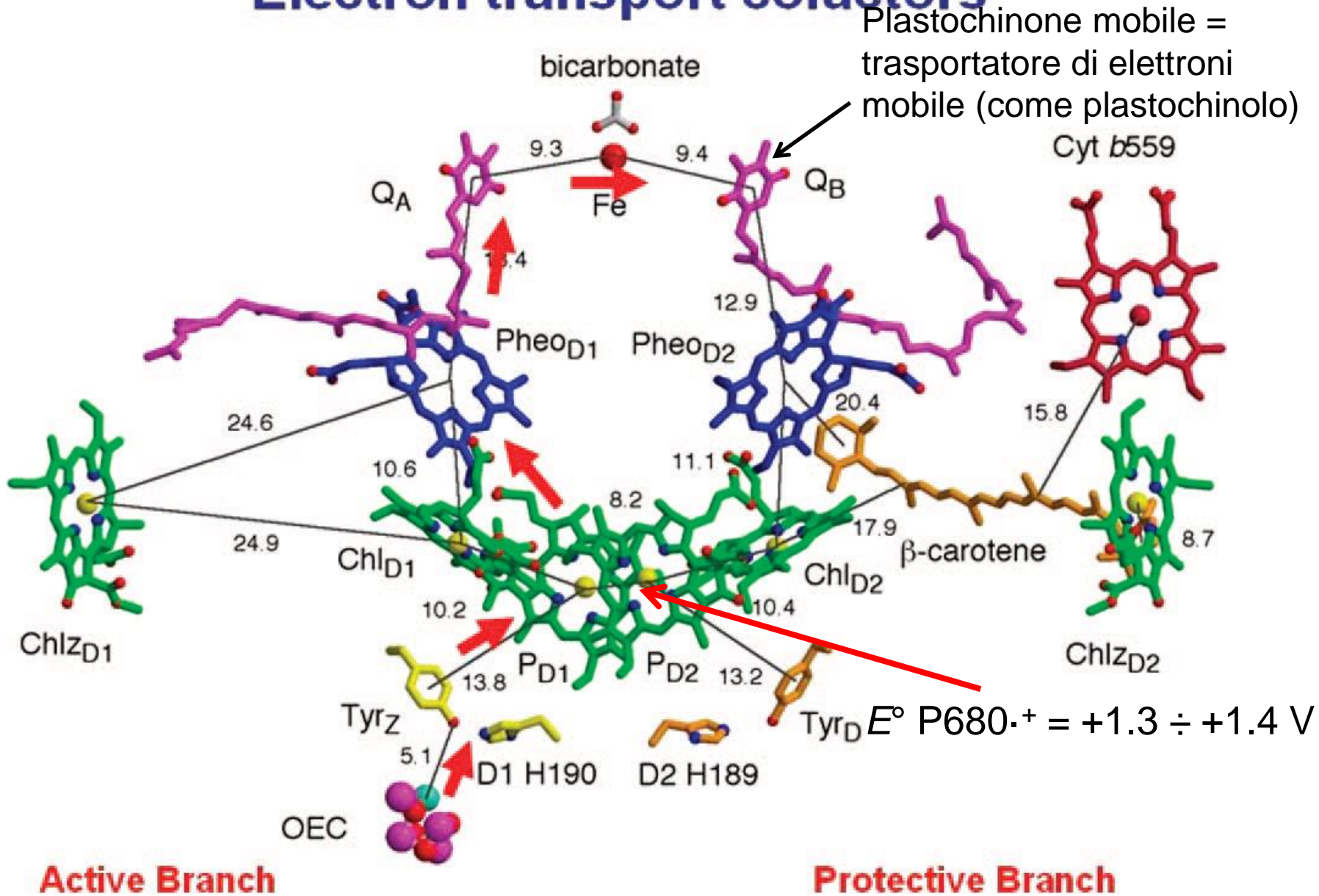
# Centro di foto-reazione e sistemi antenna



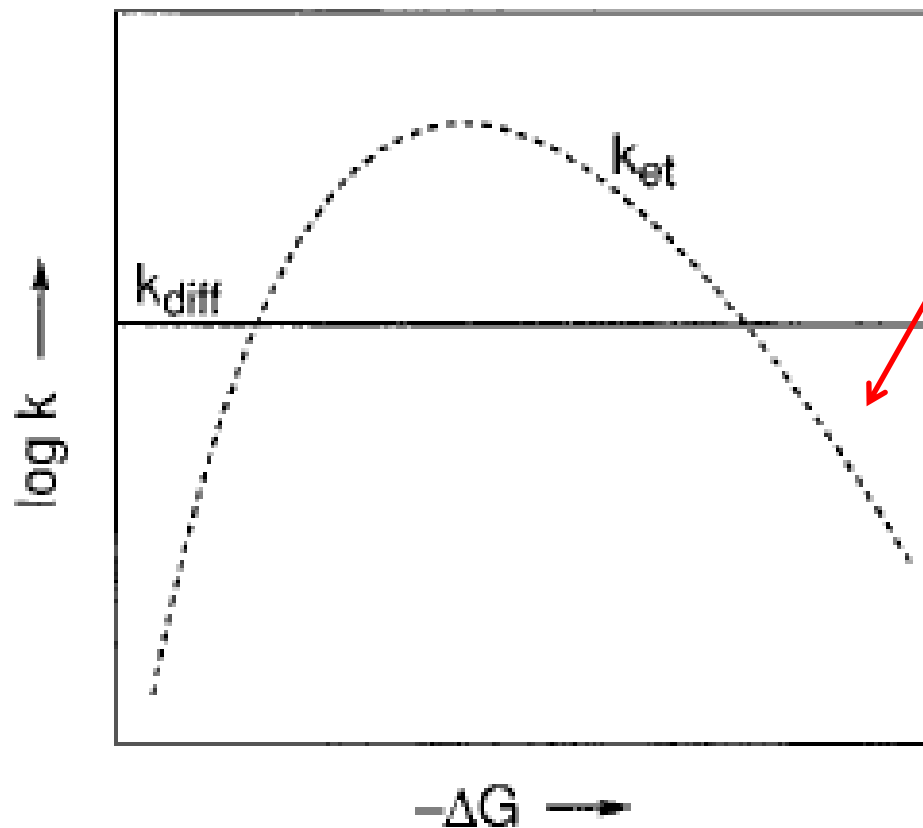




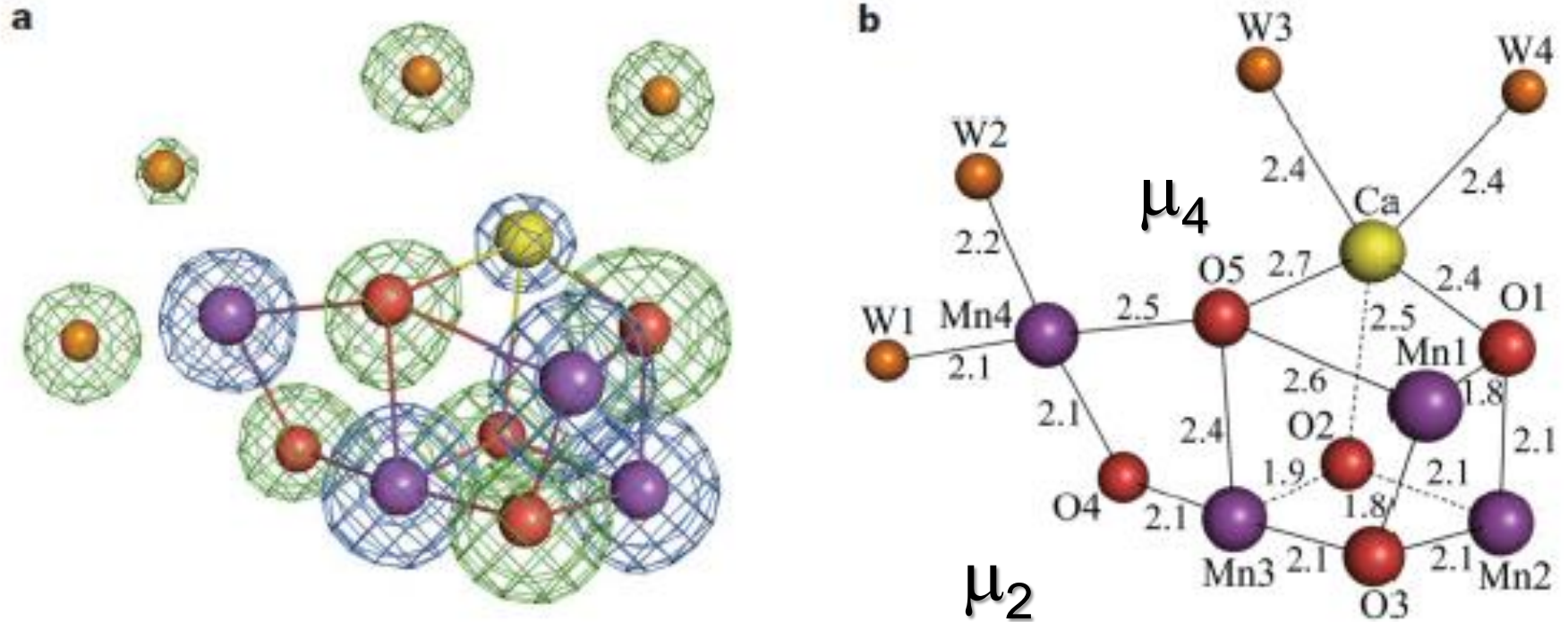
# Electron transport cofactors



# Regione inversa di Marcus

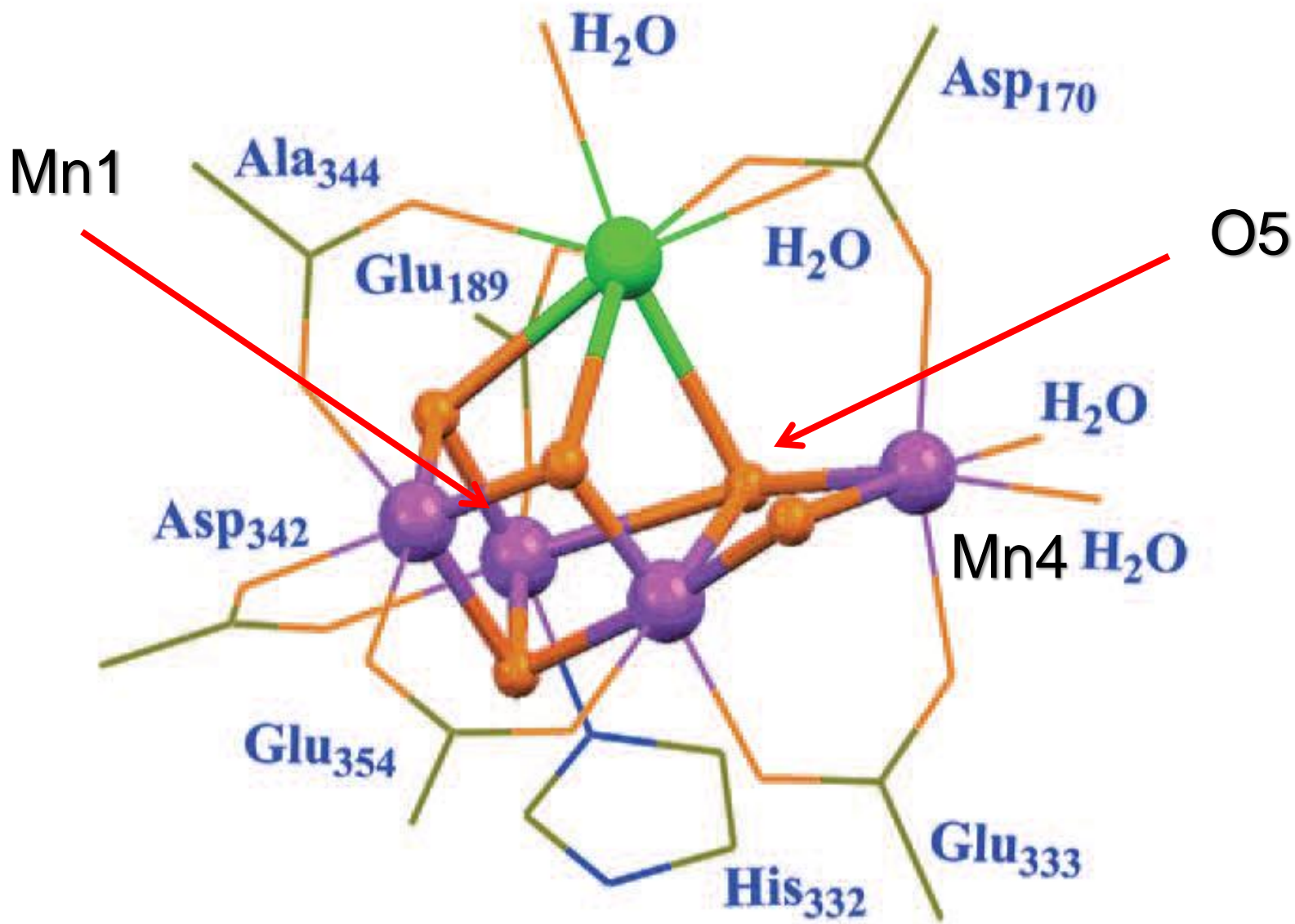


# Oxygen Evolving Complex (OEC)



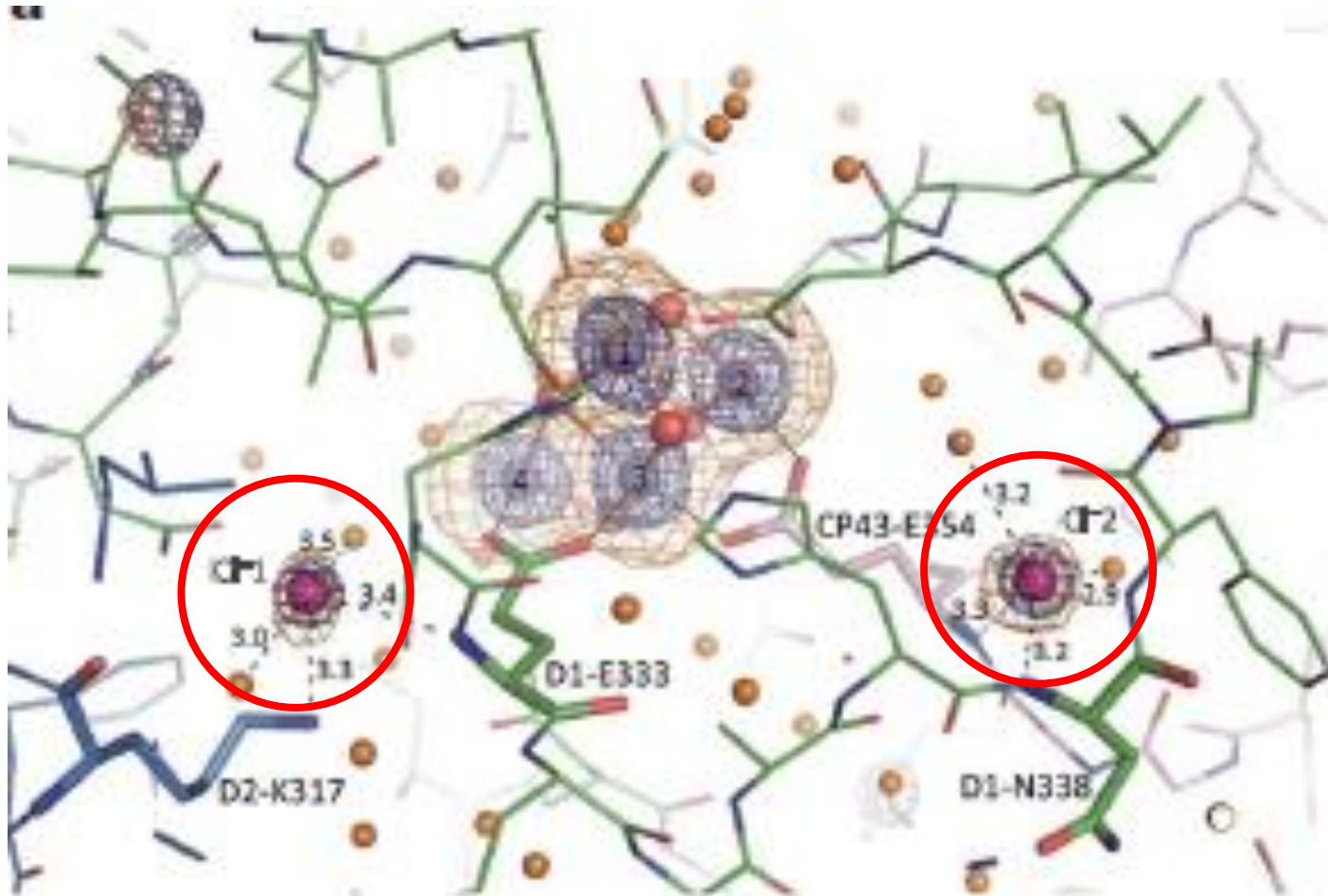
Nature 2011

Ioni Mn sempre ad alto spin

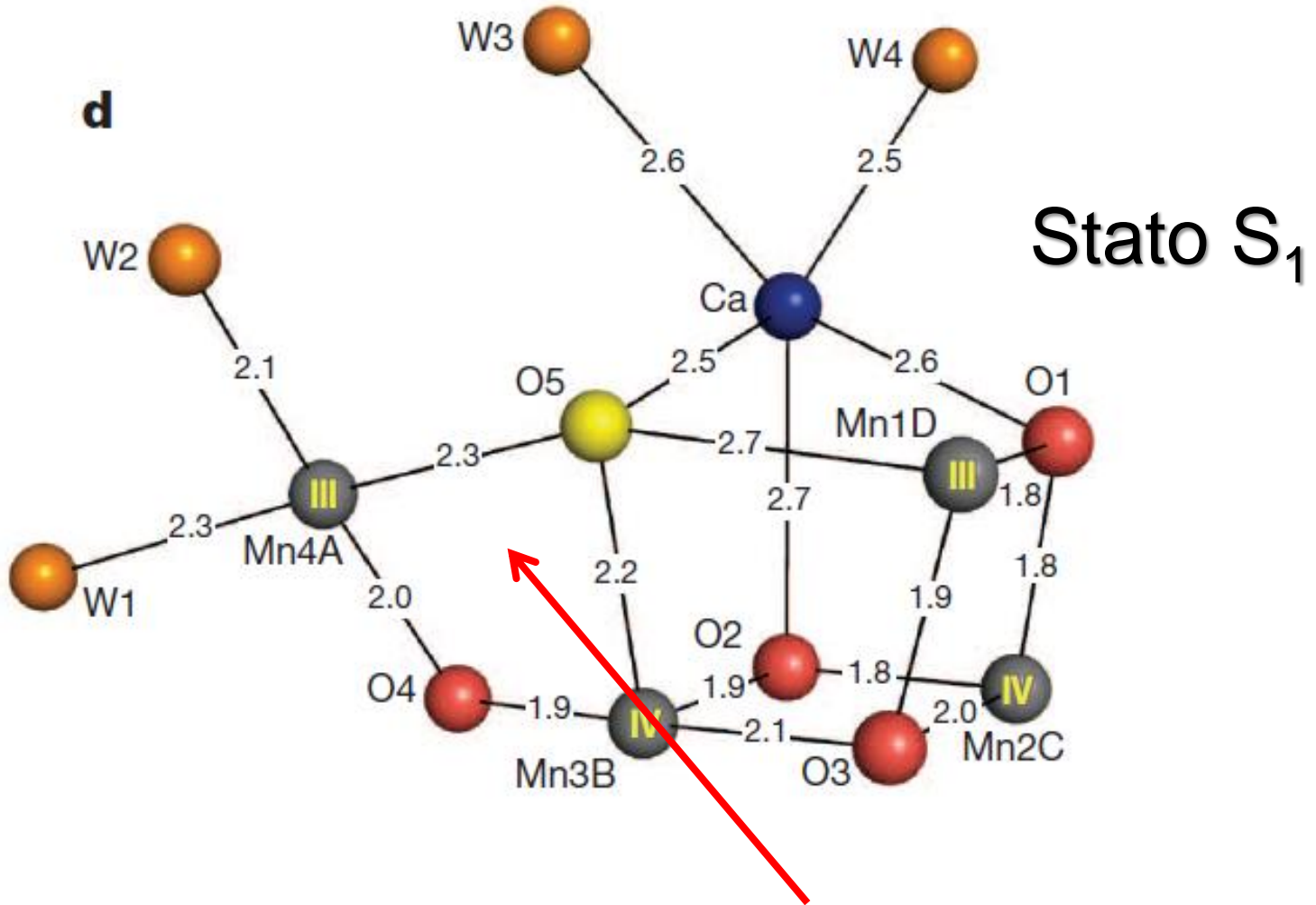


*ogni atomo metallico nell'OEC è coordinativamente saturo*

## 2 Cloruri



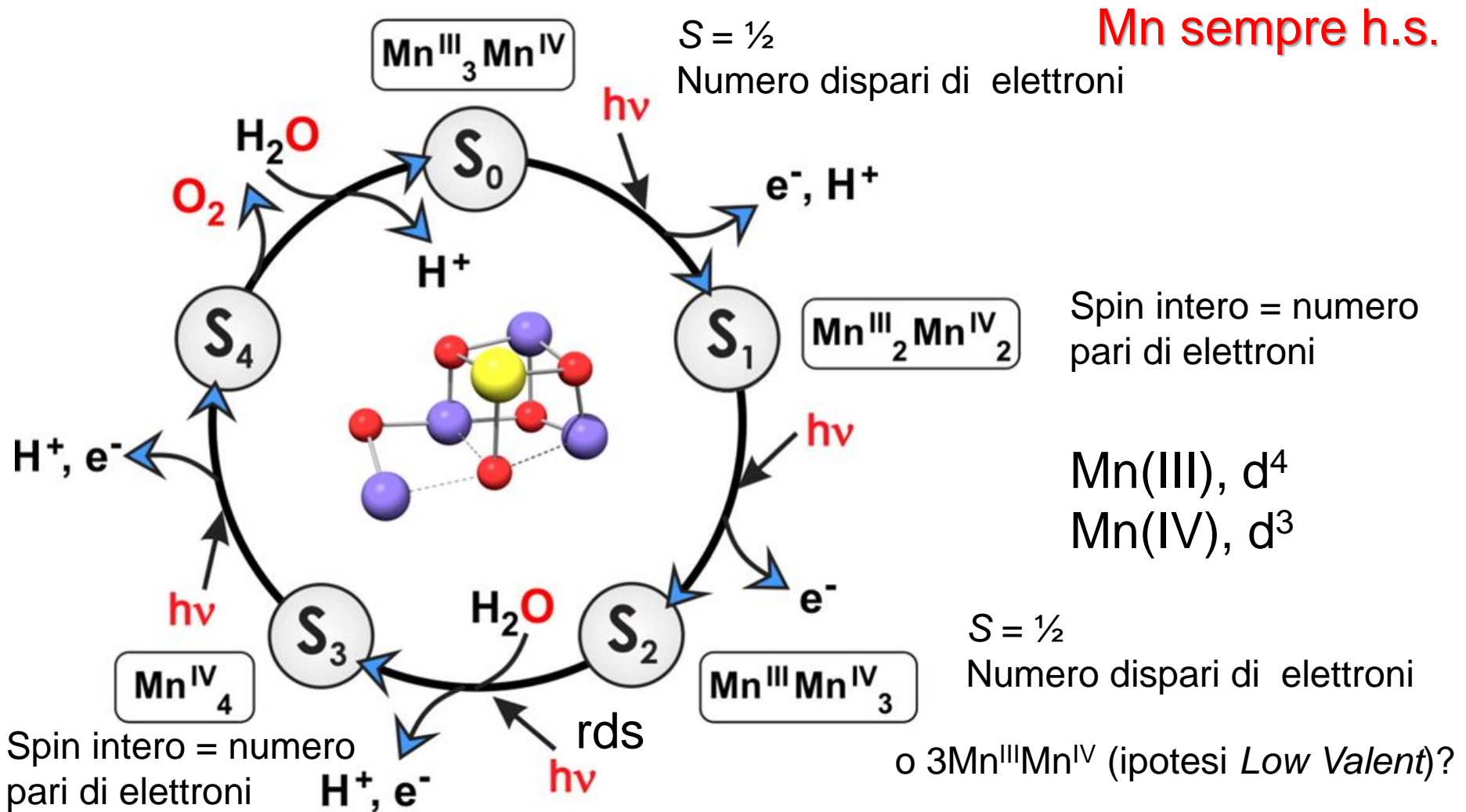
Mn(III),  $d^4$ , alto spin  $\rightarrow$  effetto Jahn-Teller



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

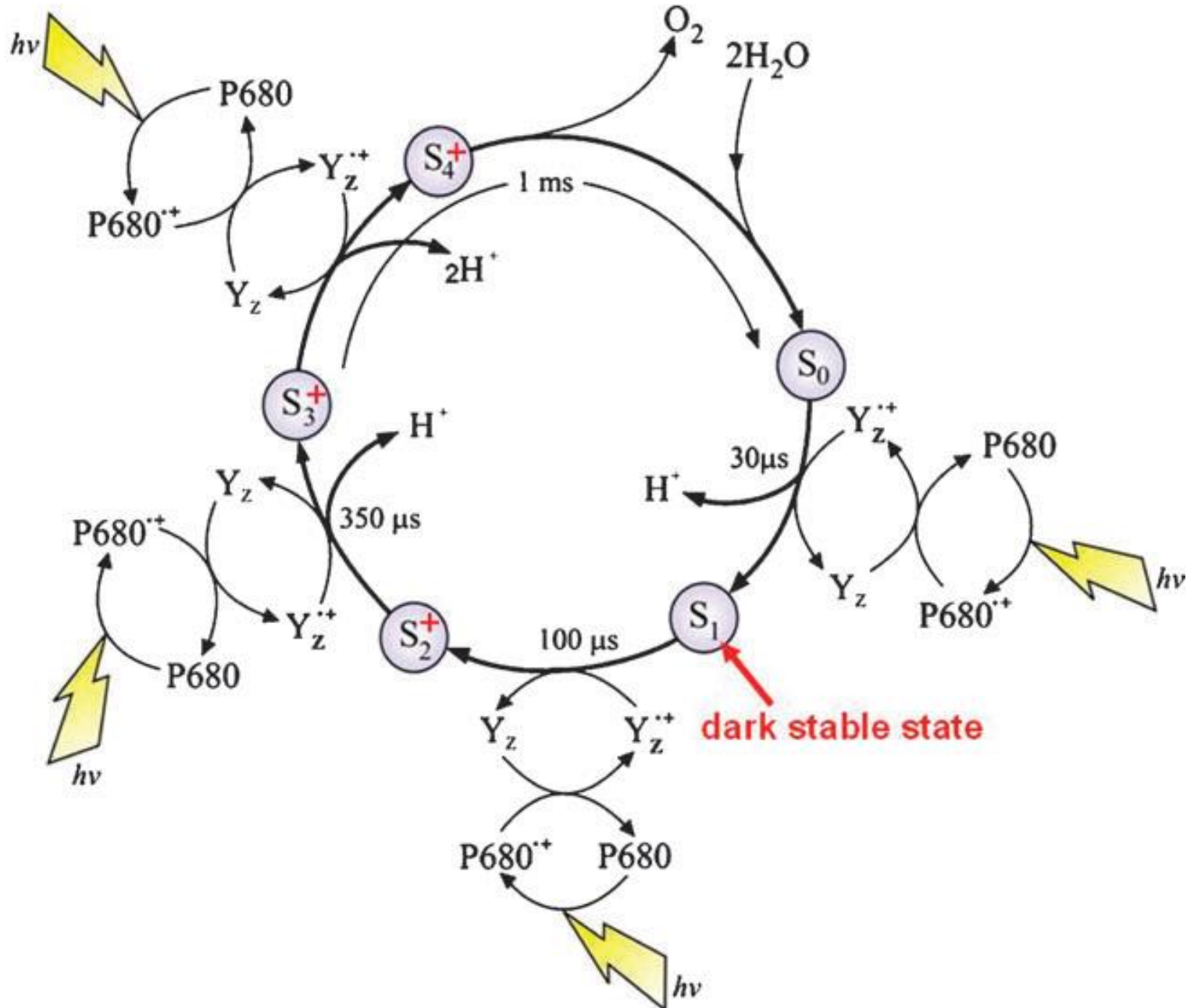
Mn4–O5 più corta di 0.2 Å

# Ciclo di Kok o *S clock*



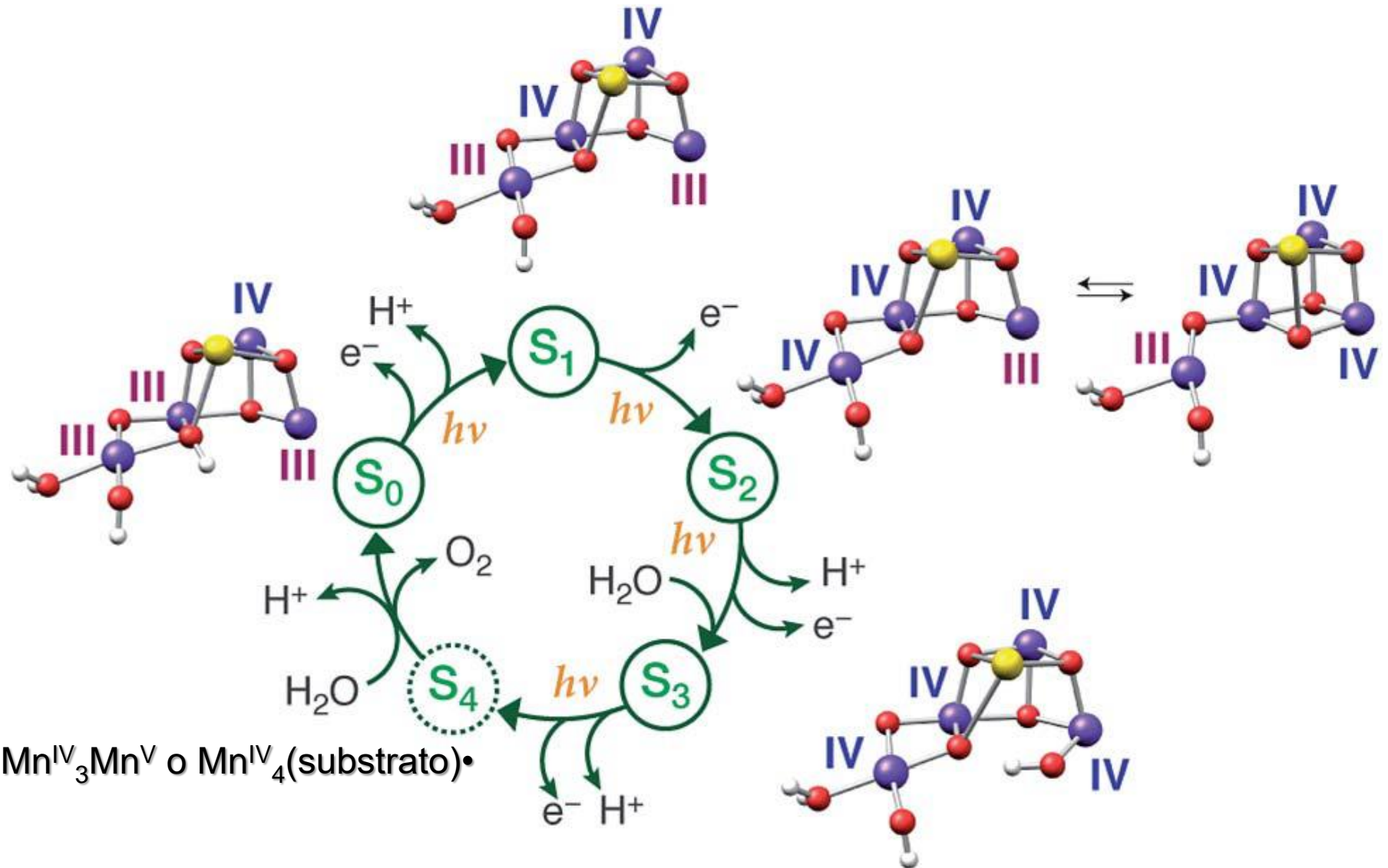
OEC ossida fino a 1000 molecole di  $\text{H}_2\text{O}$  (500 cicli) per secondo!  
 TON  $\approx$  ca.  $10^6$

# Ciclo di Kok o *S clock*





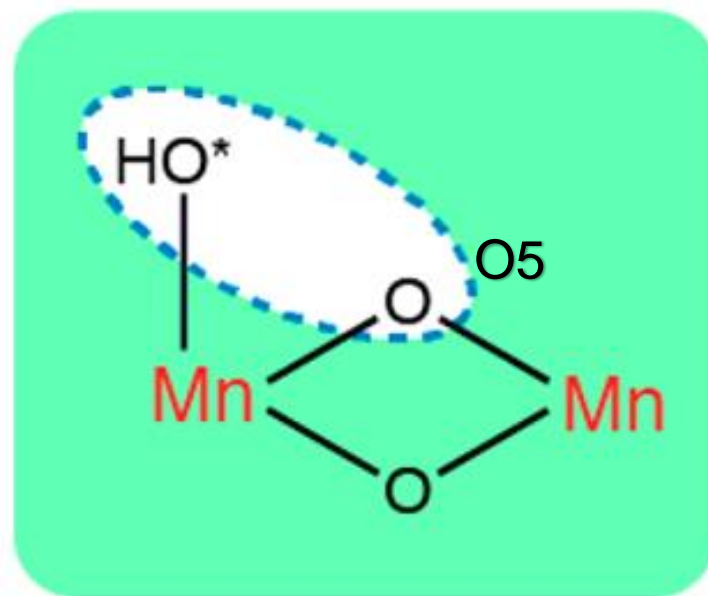
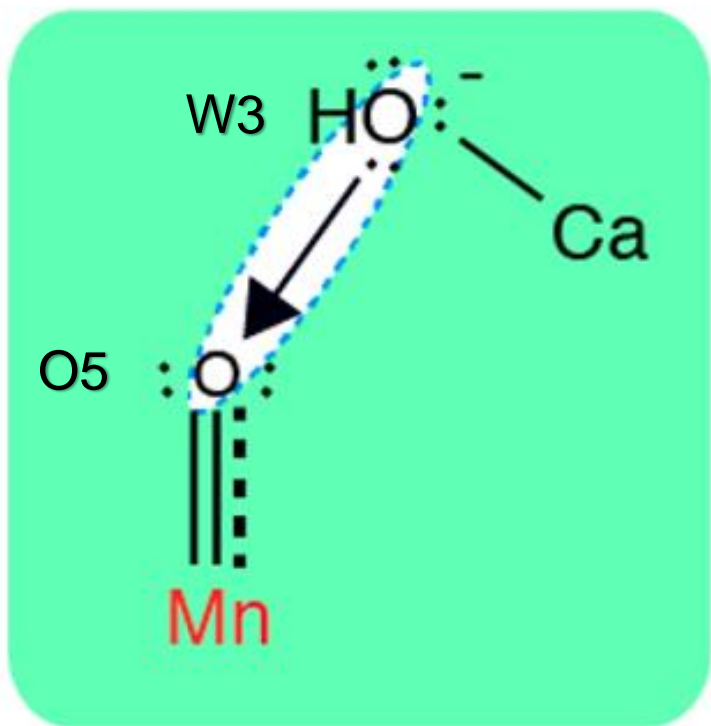
# Ipotesi più accettata



# 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*

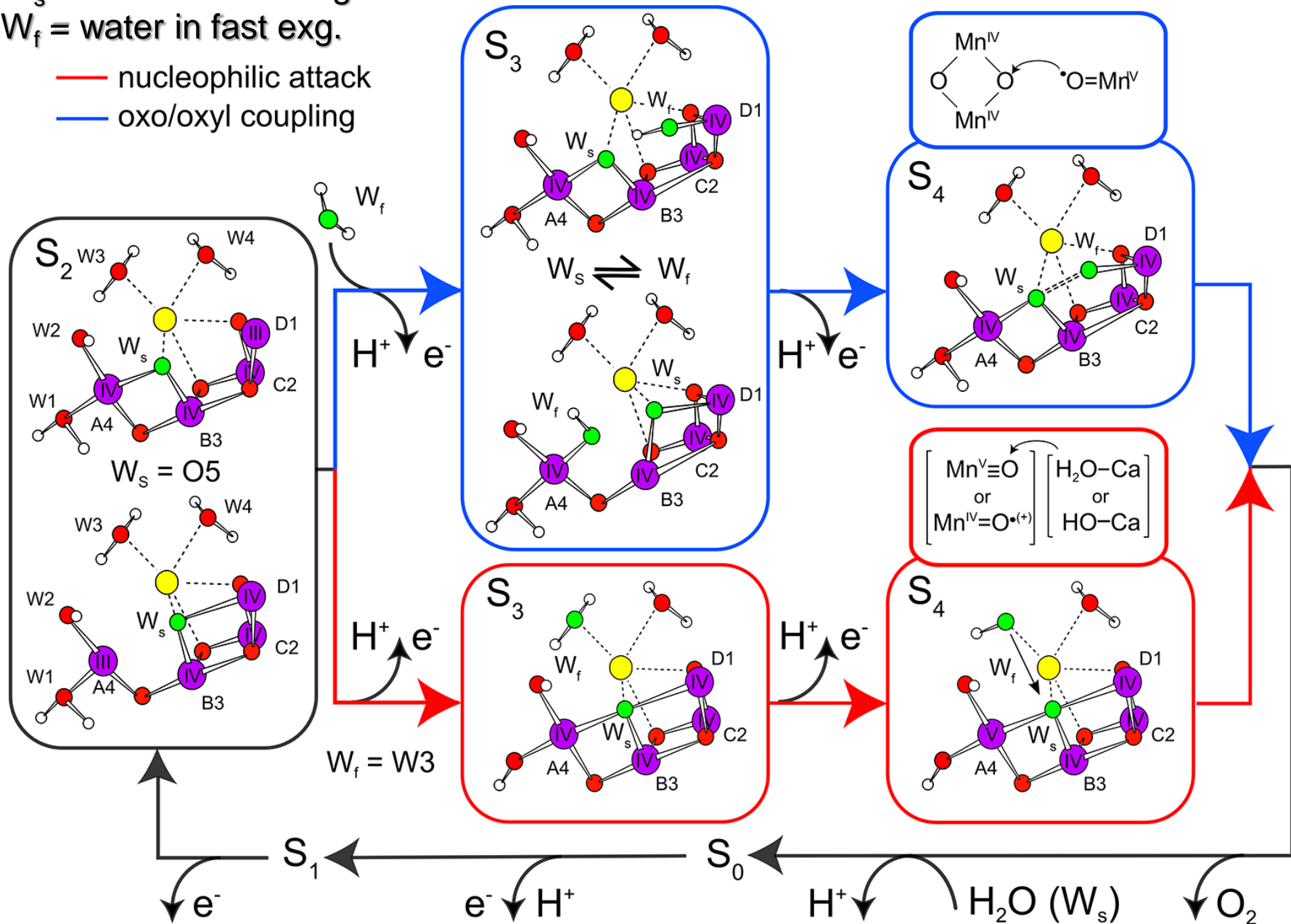
In questo meccanismo l'ultimo elettrone viene estratto da O, non da Mn

$W_s$  = water in slow exg.

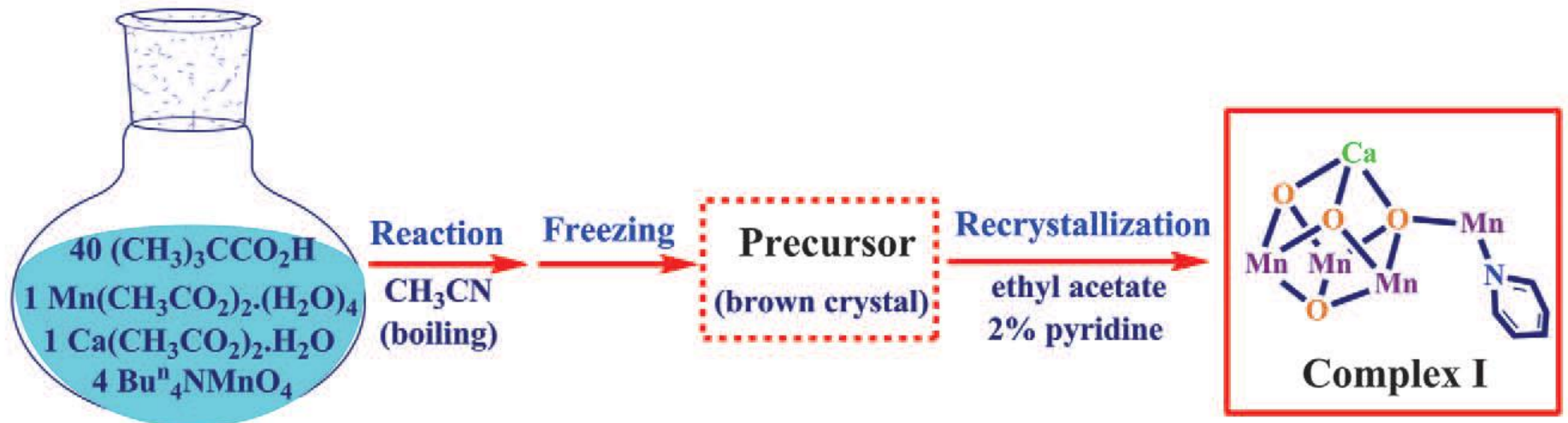
$W_f$  = water in fast exg.

— nucleophilic attack

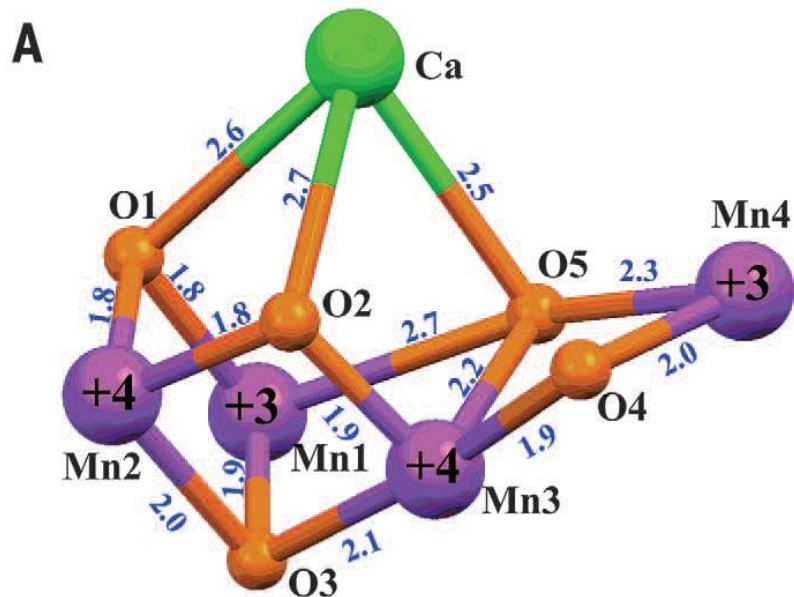
— oxo/oxyl coupling



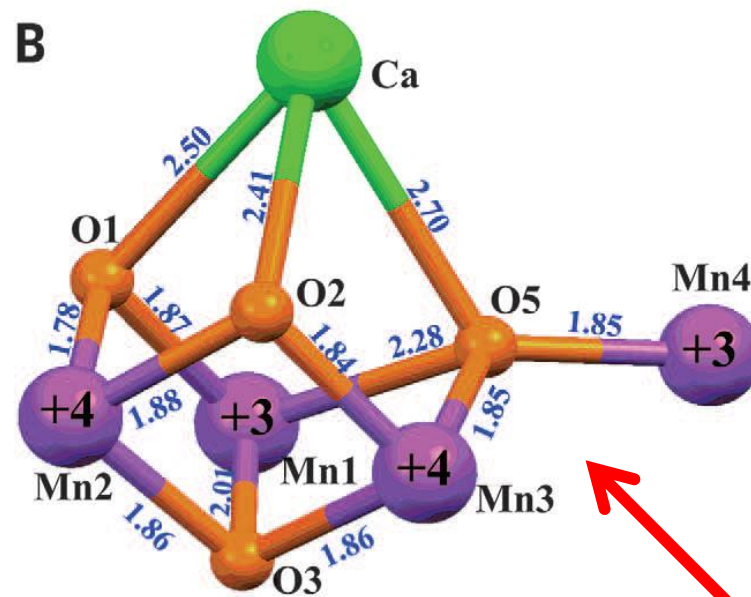
# Sistemi modello



Natural catalyst



Artificial complex



sono accessibili  
cinque stati redox

