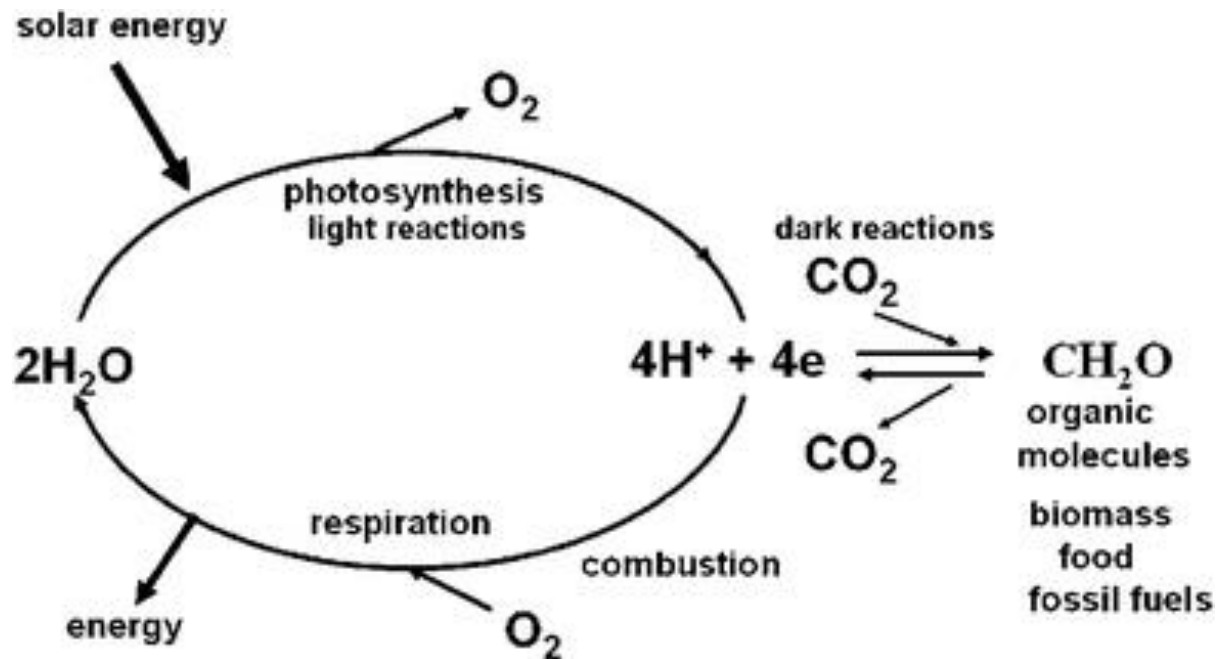
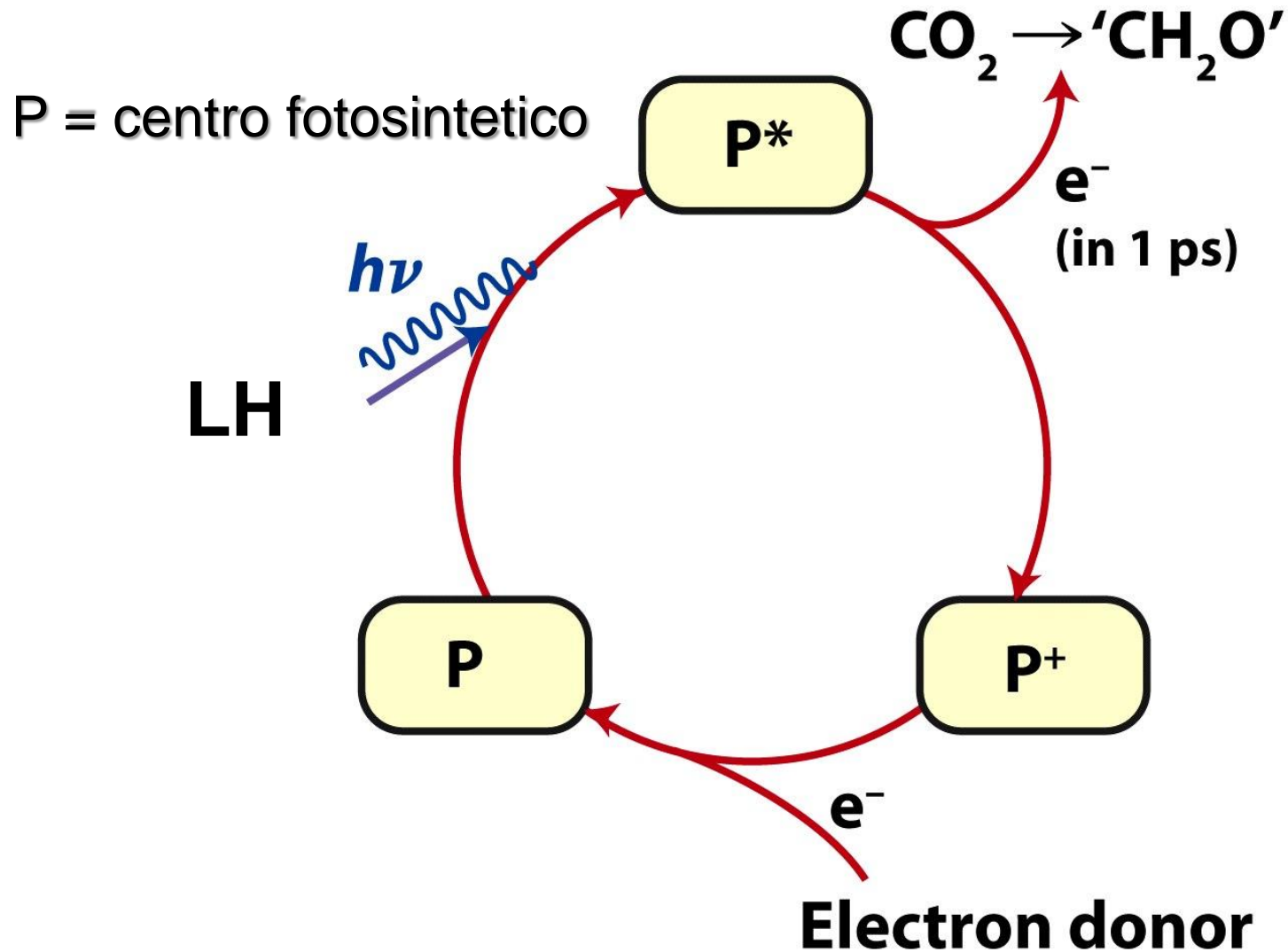


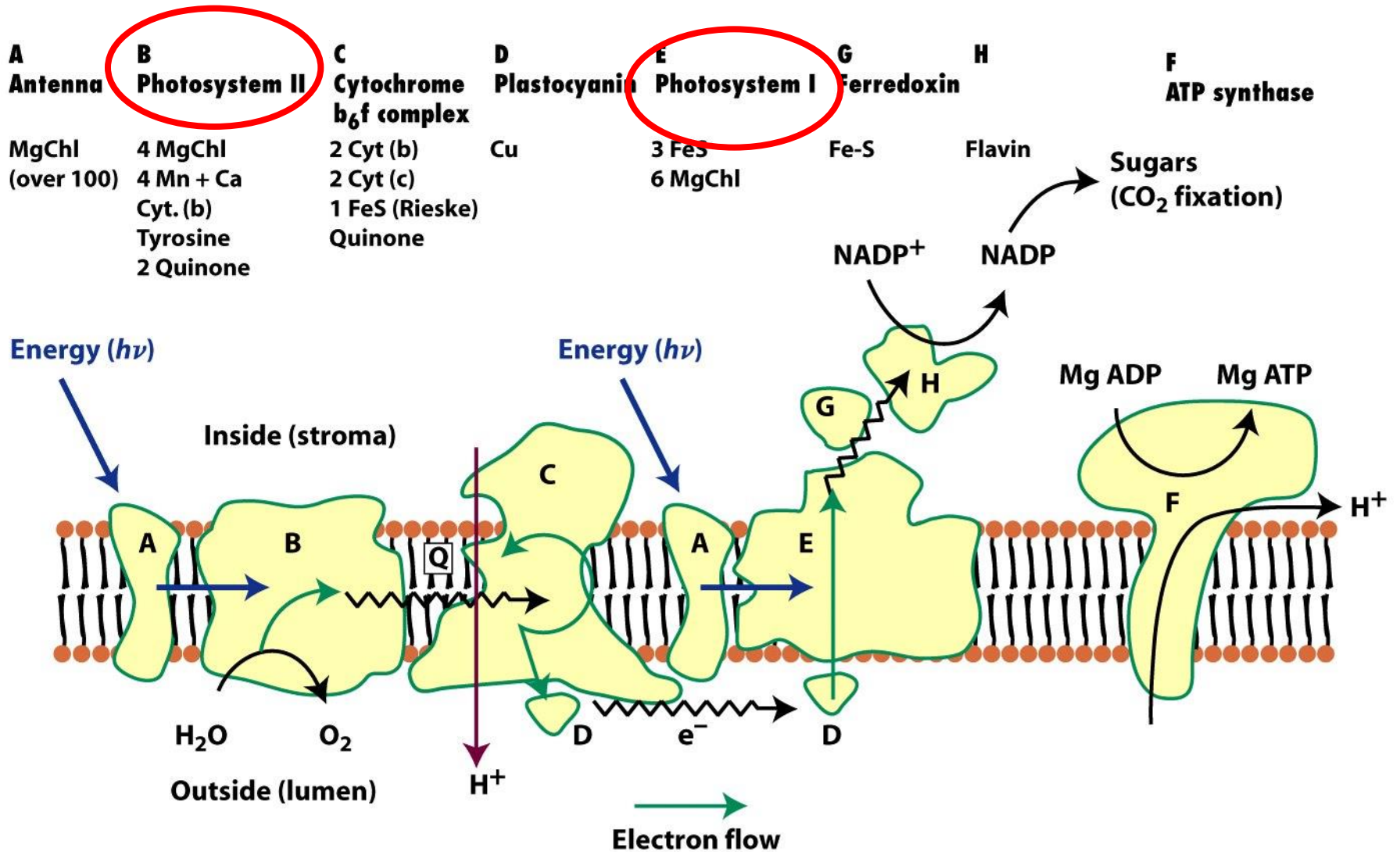
$100 \times 10^9$  ton/y di  $(\text{CH}_2\text{O})_n$  da  $\text{CO}_2$   
 1 g di glucosio per  $\text{m}^2$  di superficie fogliare all'ora  
 $100 \text{ TW/y} = 0.1\%$  energia solare totale ( $10^5 \text{ TW}$ )



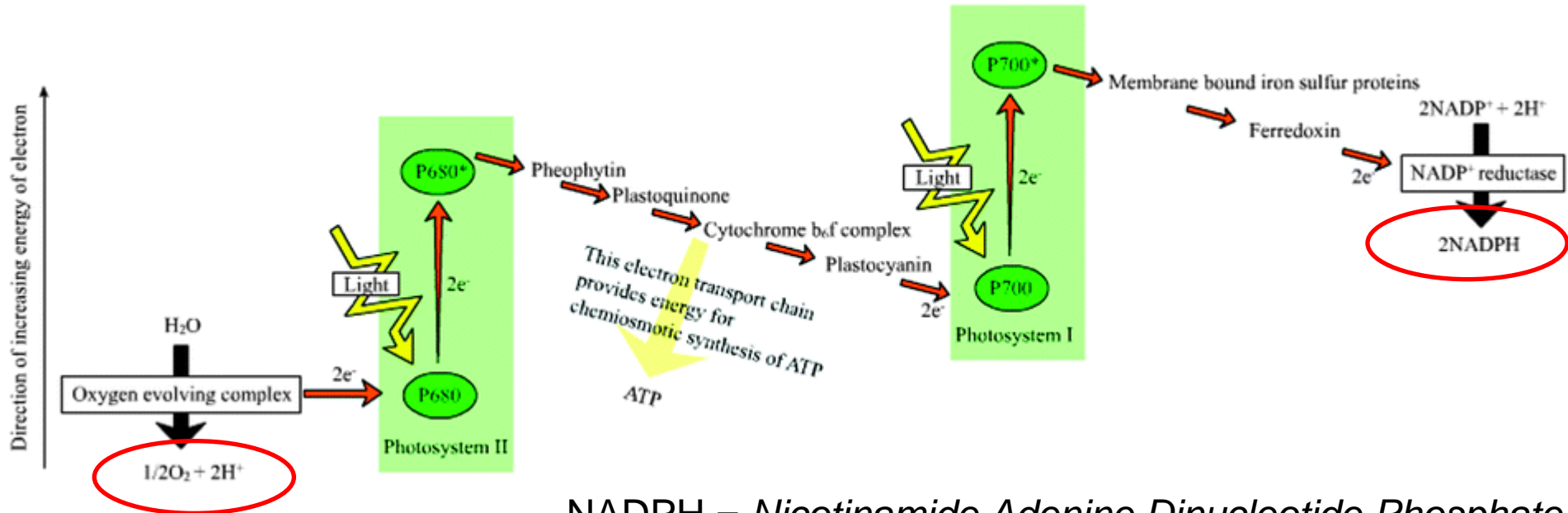
# Separazione di carica fotoindotta



# Processo fotosintetico nelle piante

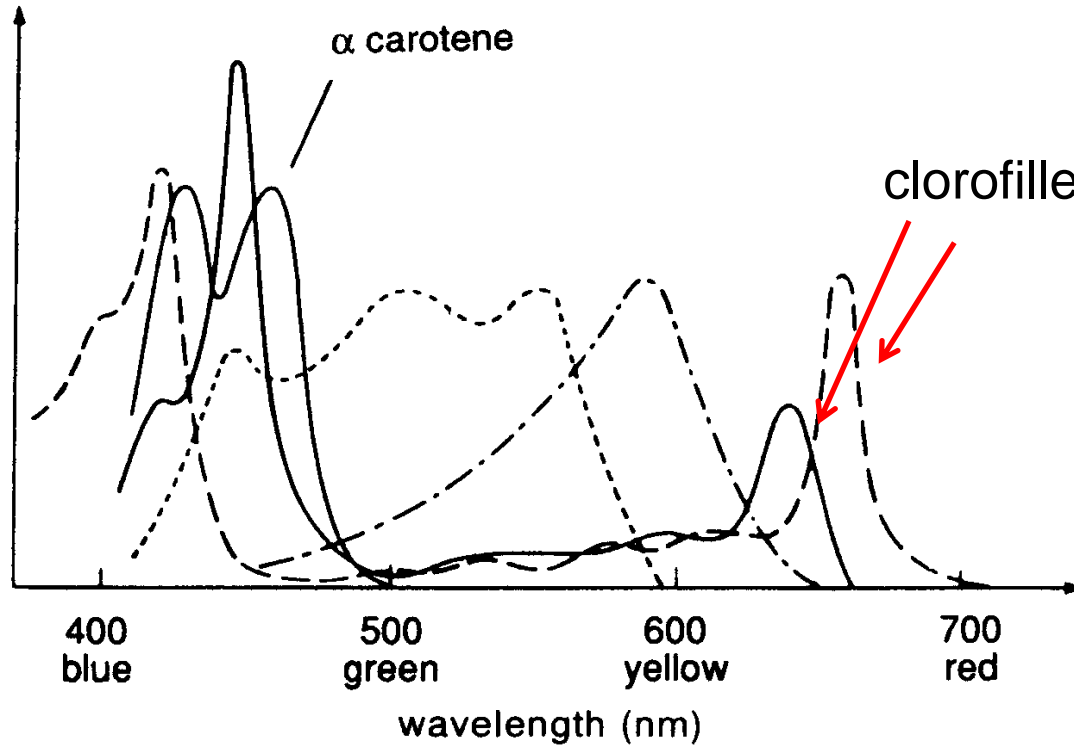
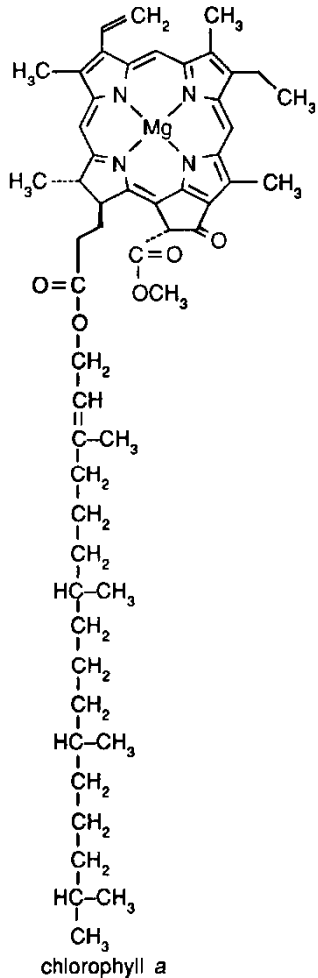


# Diagramma "a Z"



NADPH = *Nicotinamide Adenine Dinucleotide Phosphate*

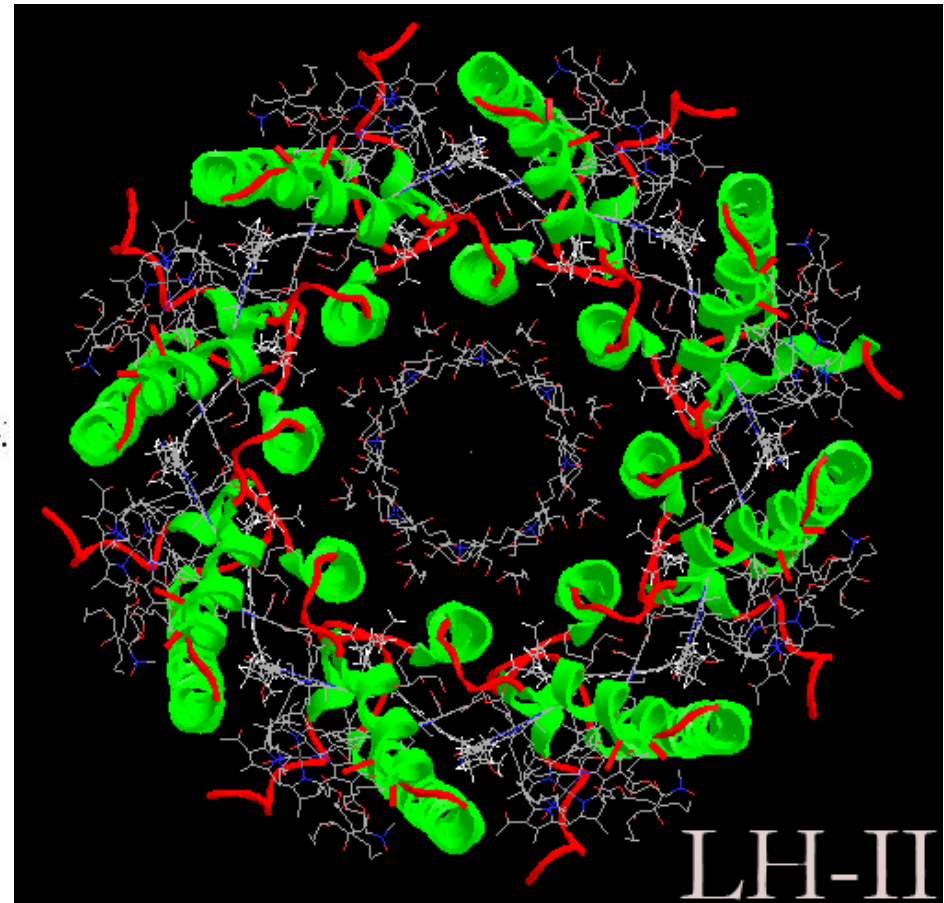
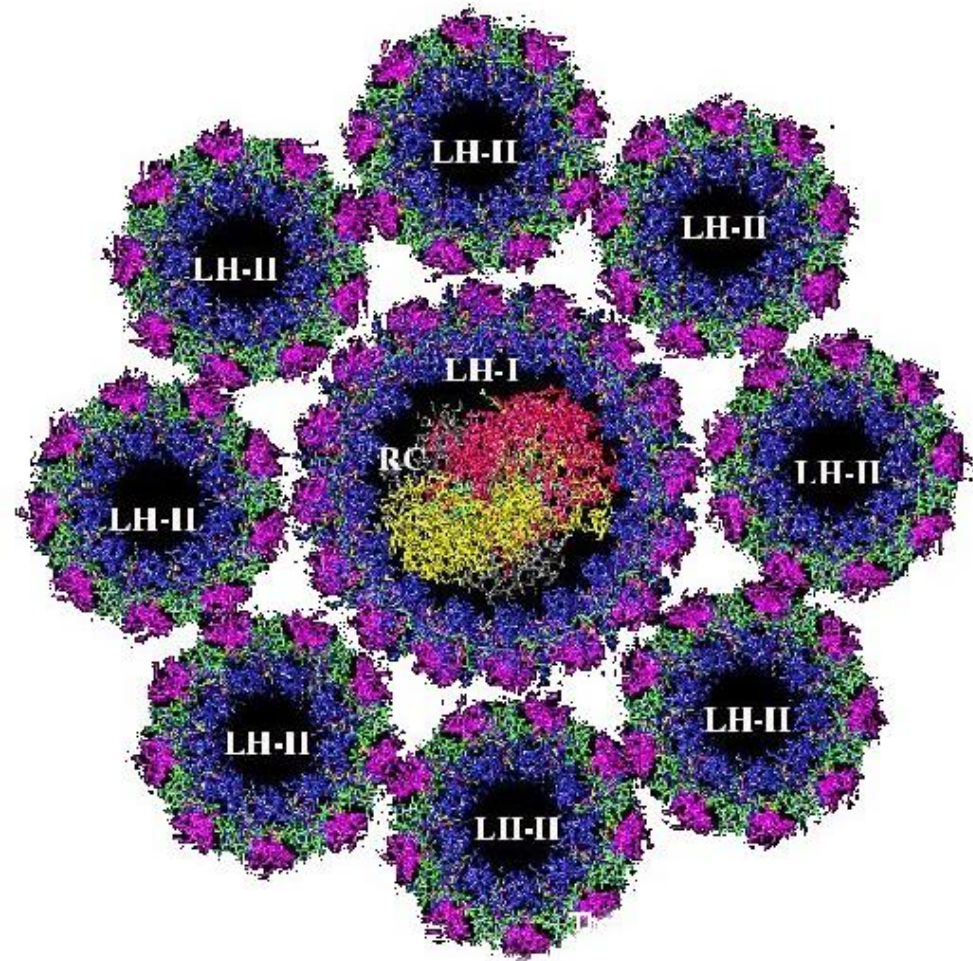
# Pigmenti deputati al *light harvesting*



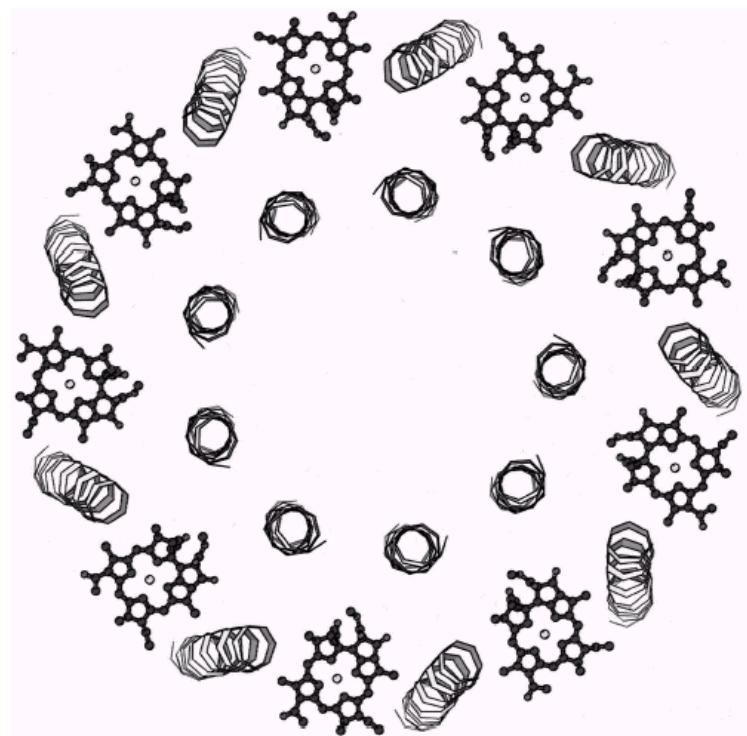
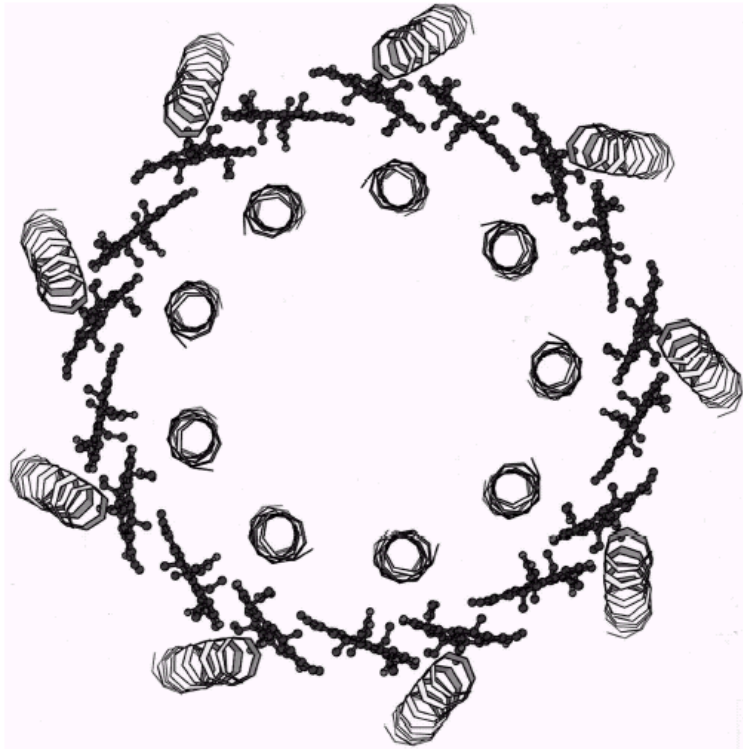
Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——),  $\alpha$ -carotene (——), phycocyanin (-·-·), phycoerythrin (- - - -)



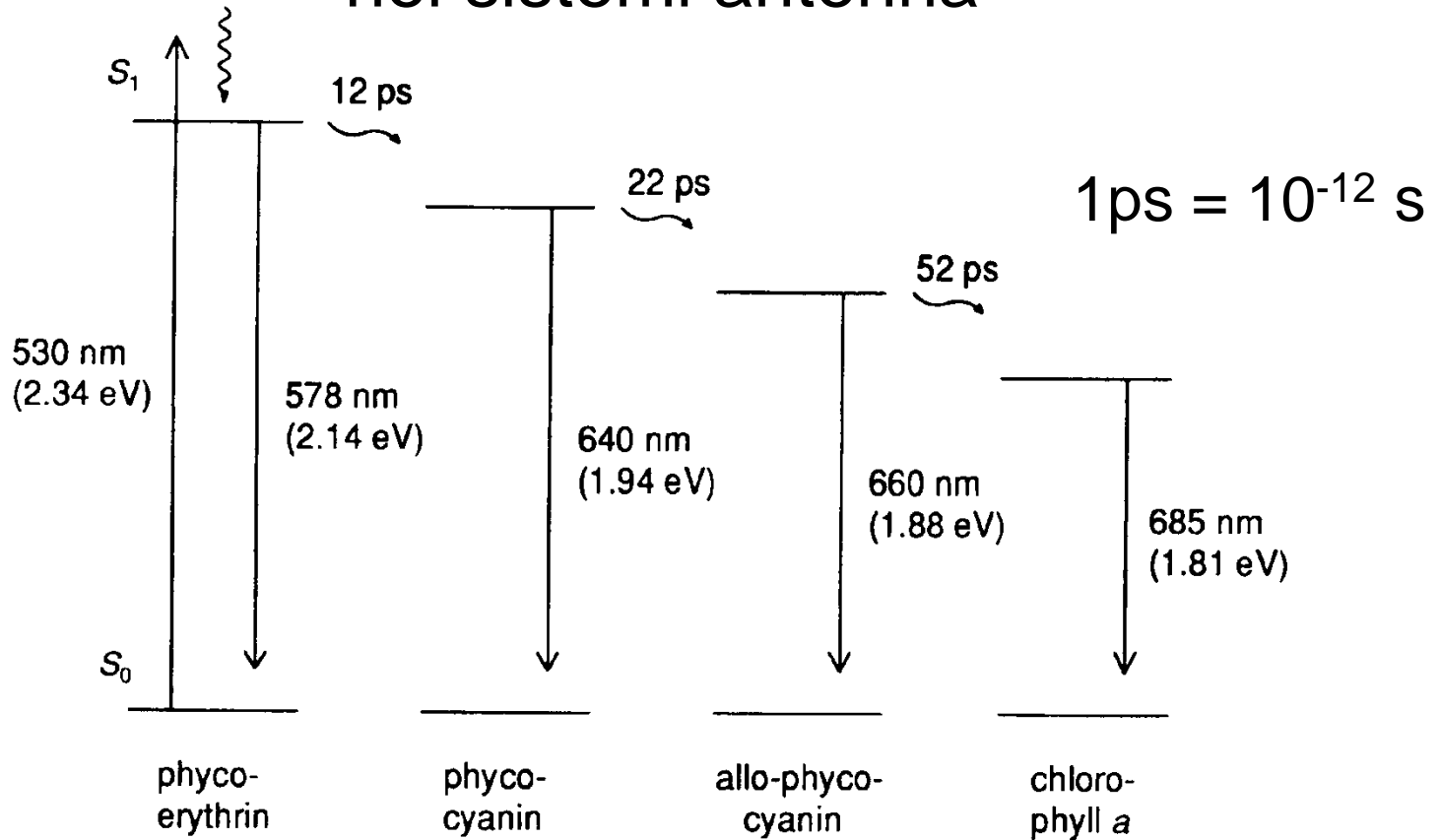
# Sistemi antenna



# Sistemi antenna

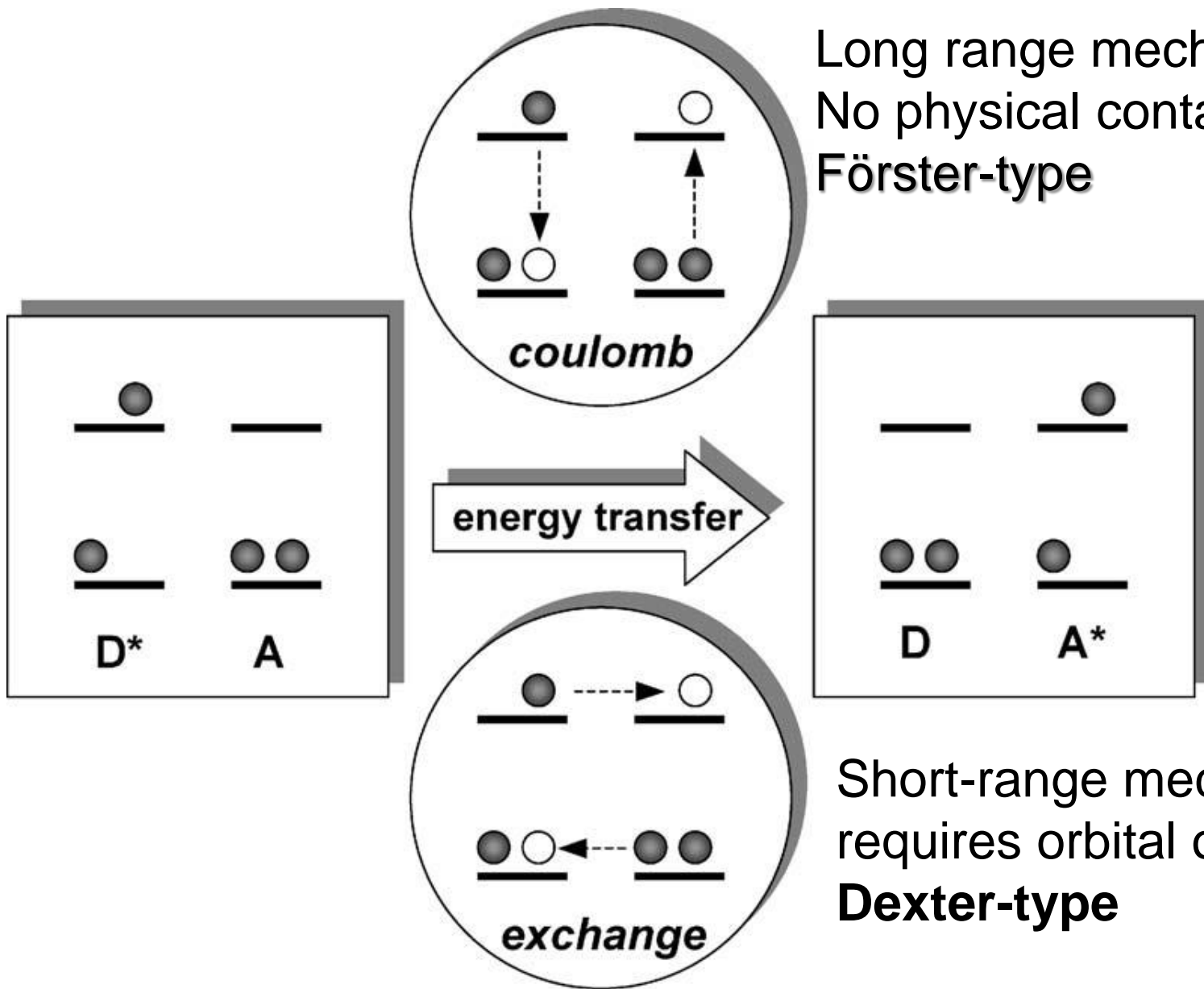


# Trasferimento di energia (*exciton transfer*) a cascata nei sistemi antenna



efficienza del 95%





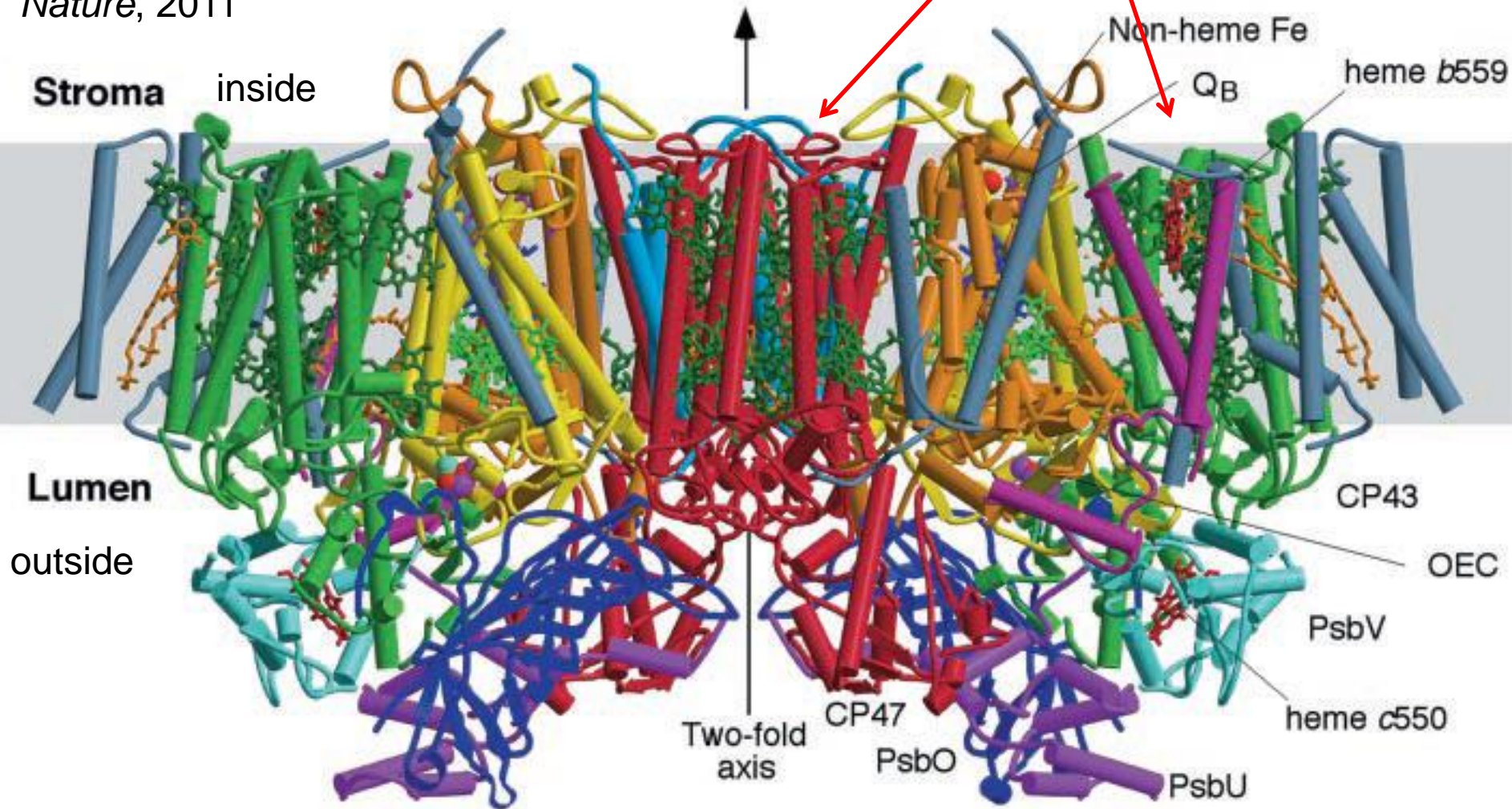
Long range mechanism  
No physical contact  
**Förster-type**

Short-range mechanism  
requires orbital overlap  
**Dexter-type**

# PS II

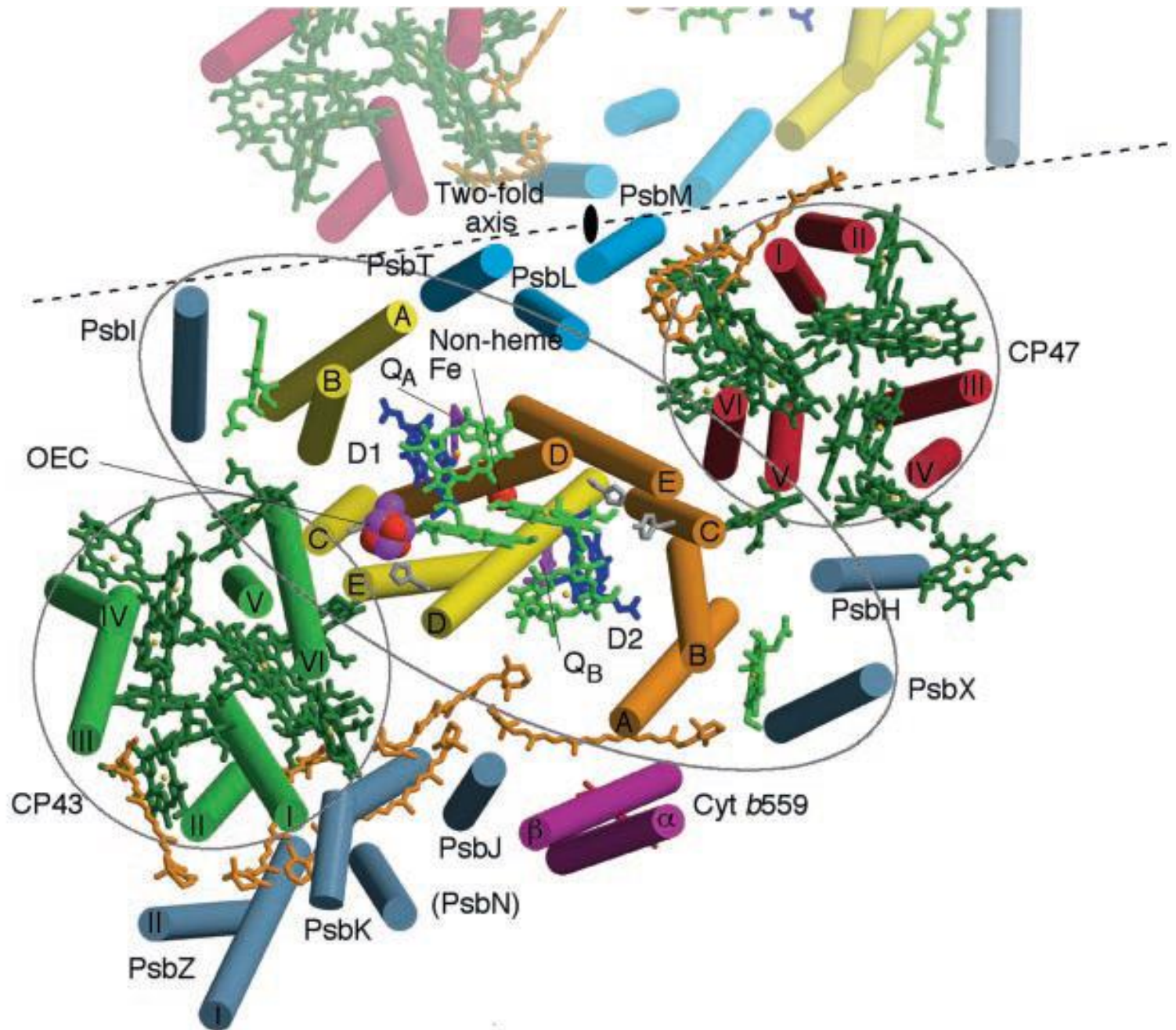
Sistemi antenna

*Nature*, 2011



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

# PS II

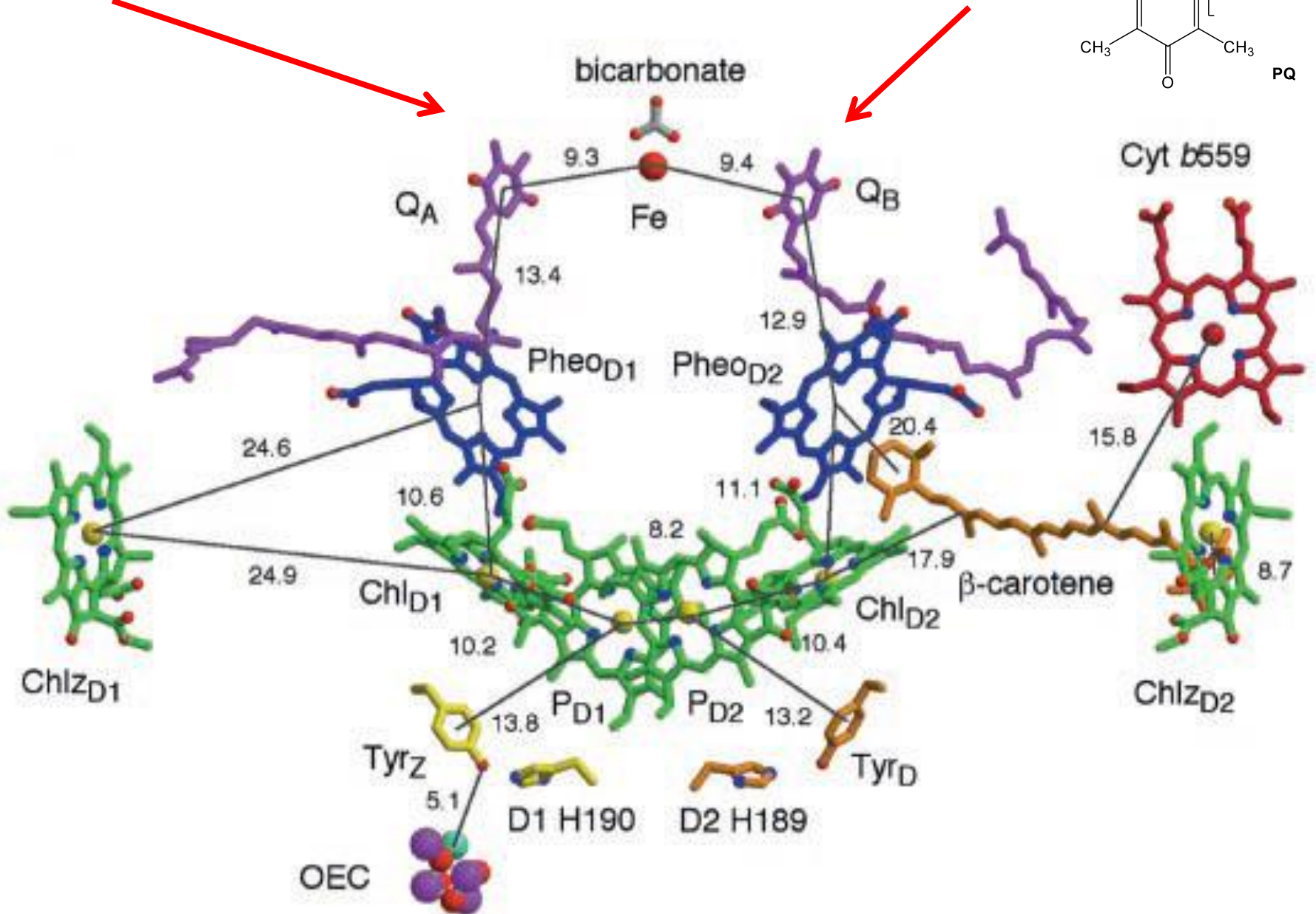
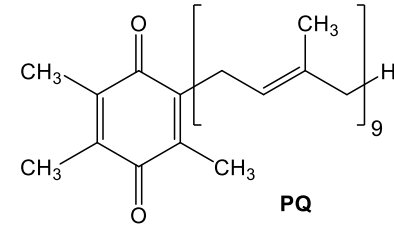




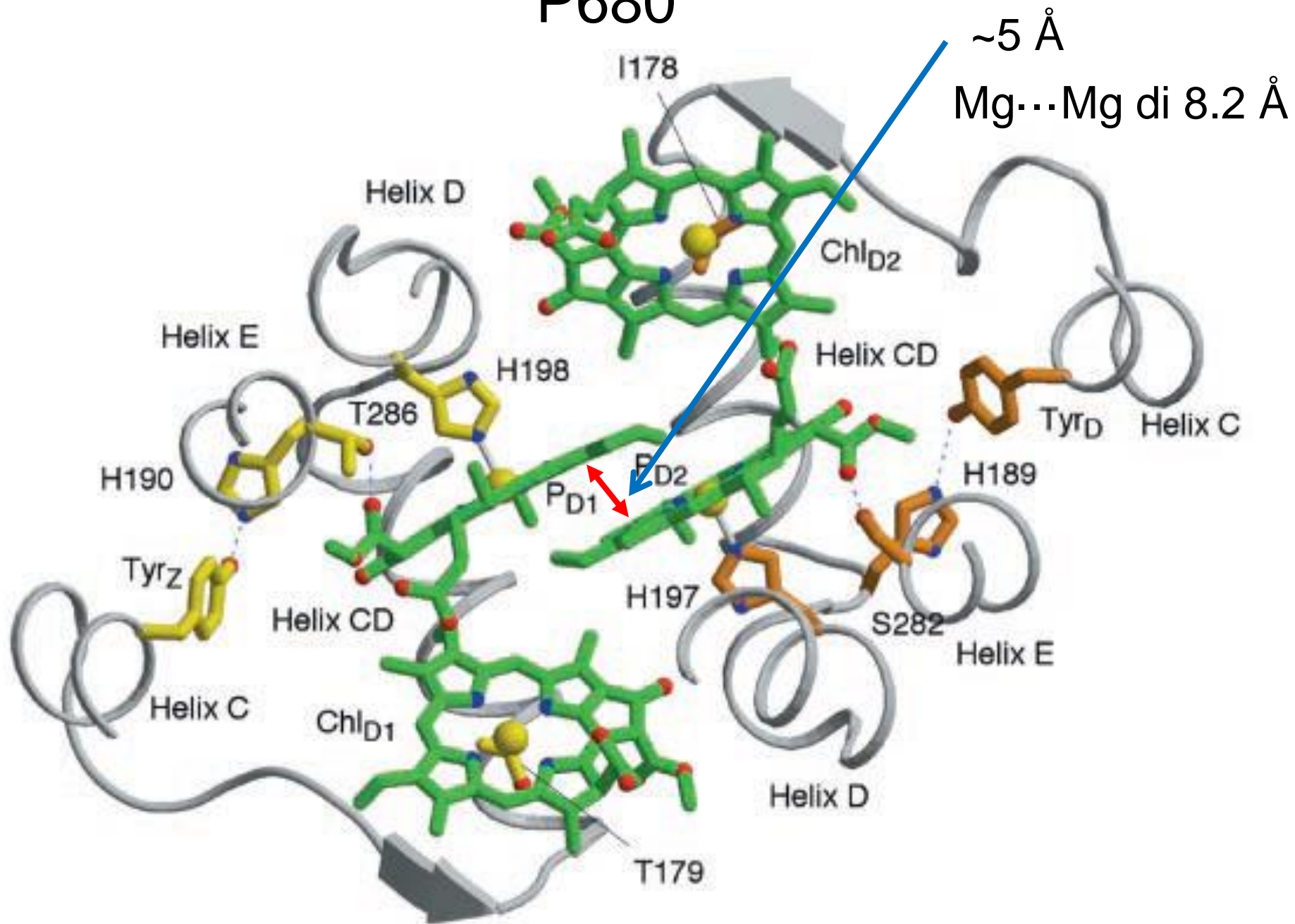
# P680

Plastochinone fisso

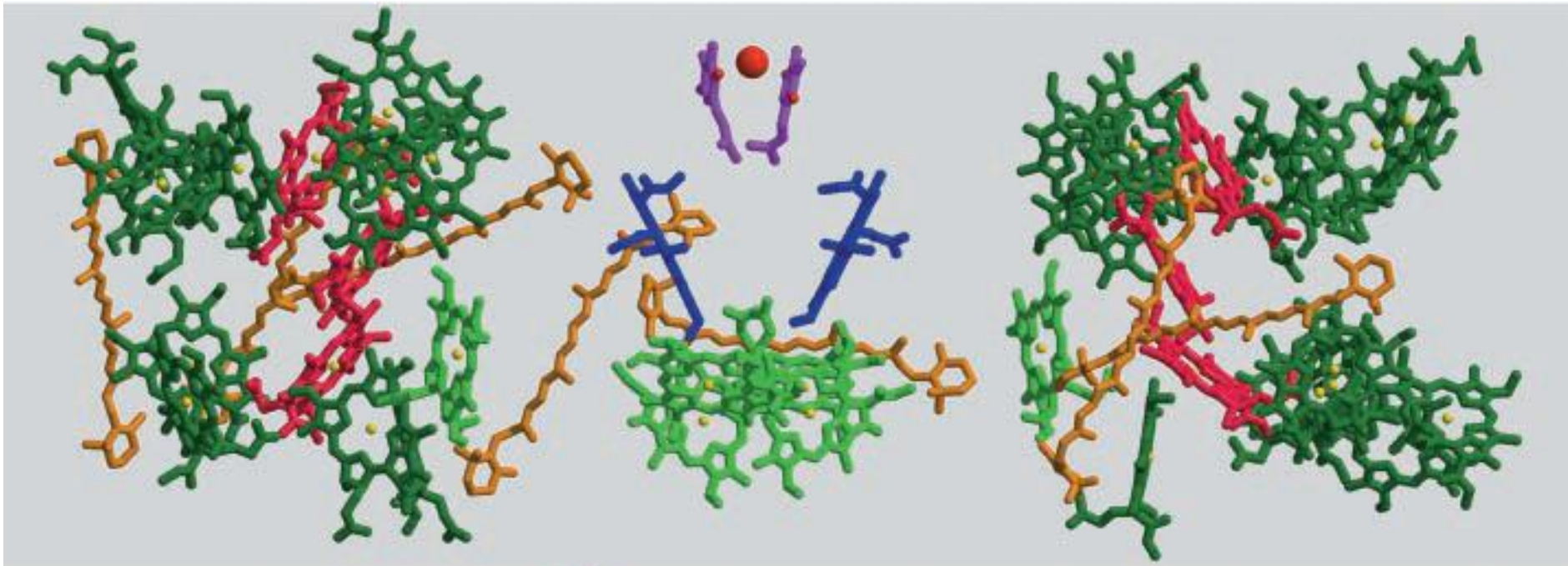
Plastochinone mobile



# P680



inside **Stroma**



CP43

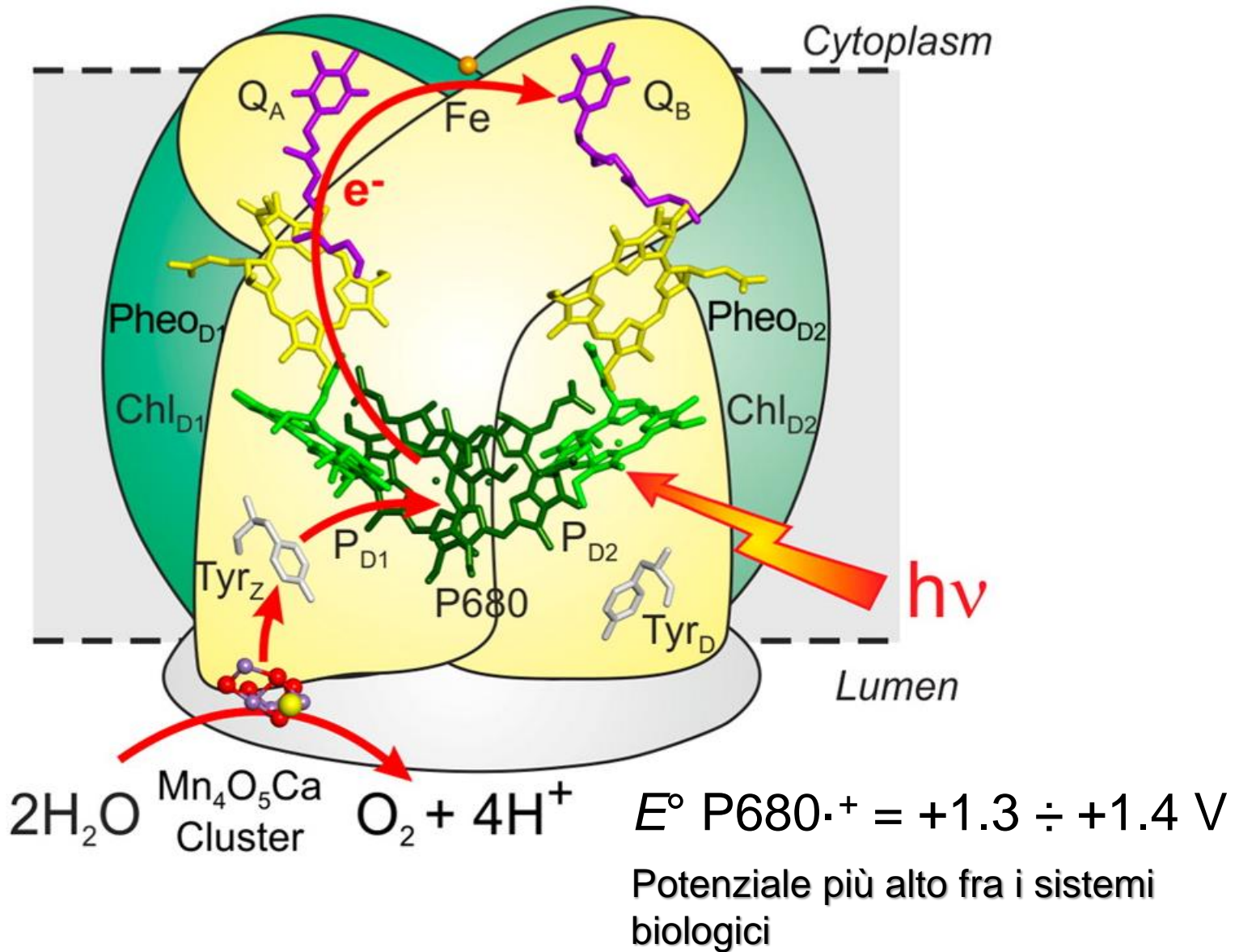


D1/D2

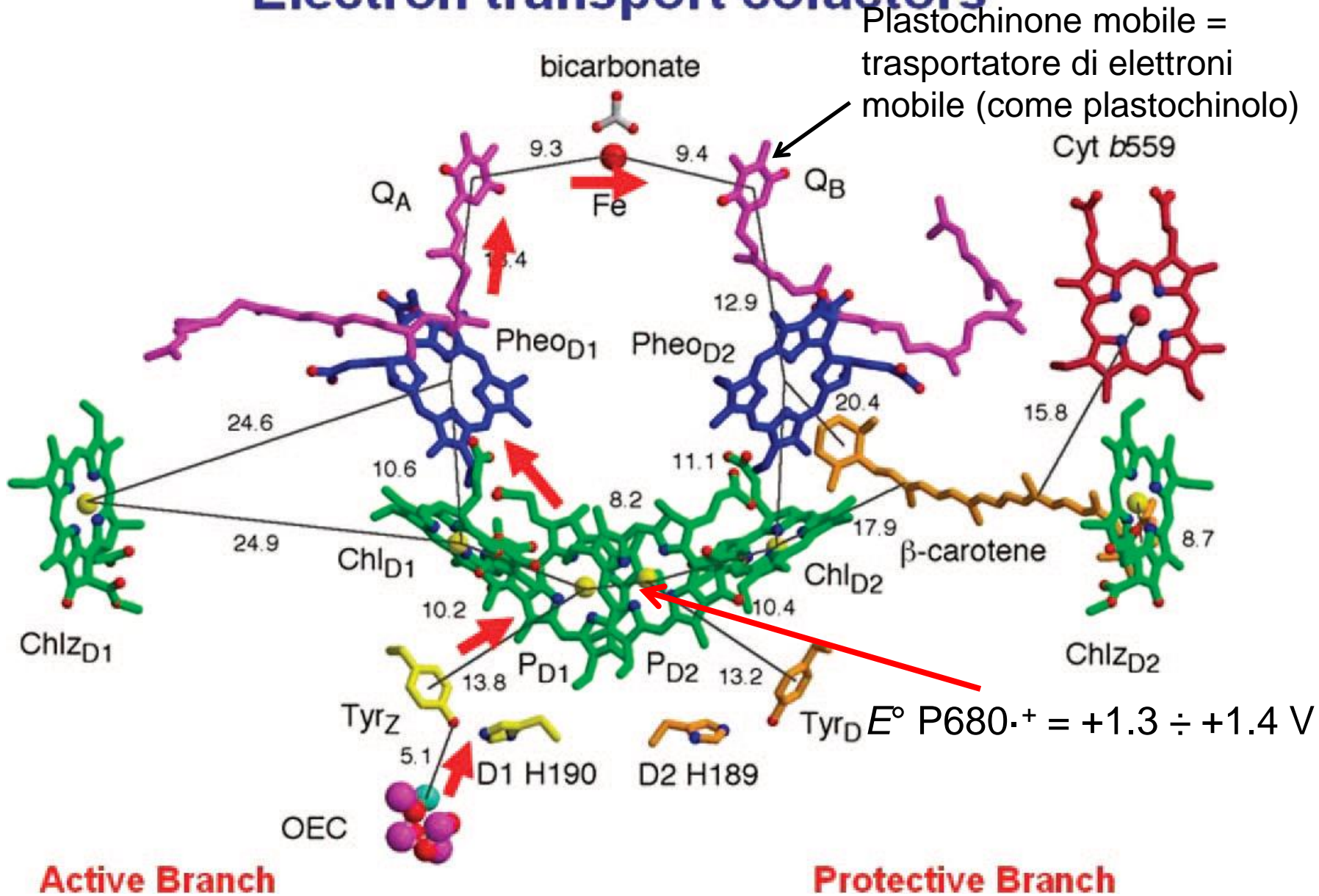
CP47

**Lumen**  
outside

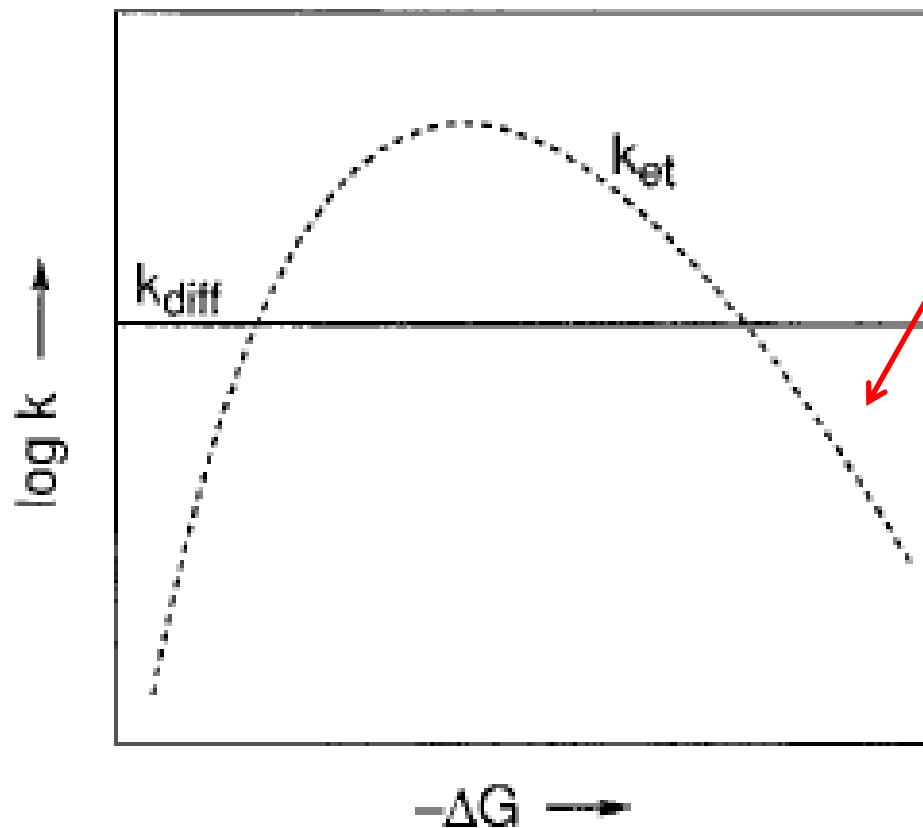




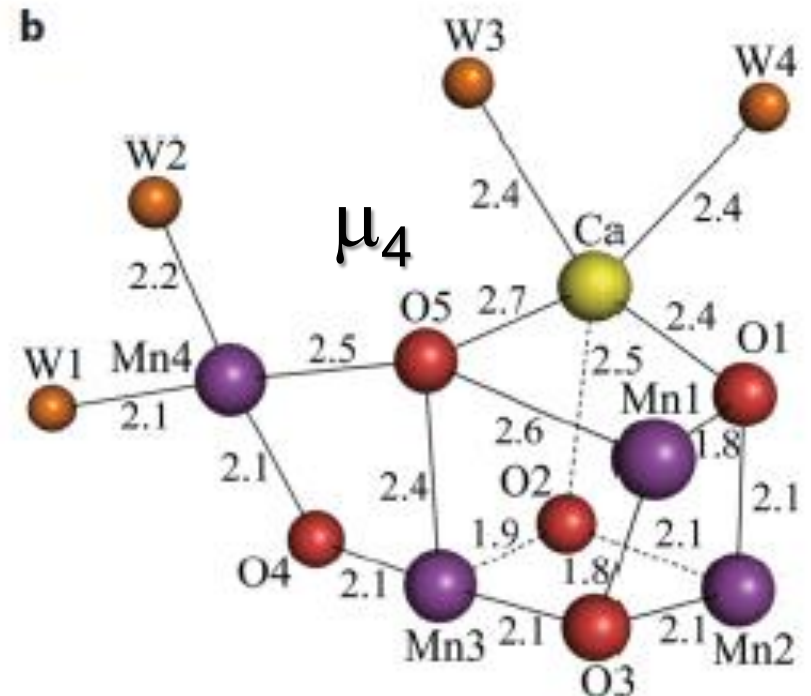
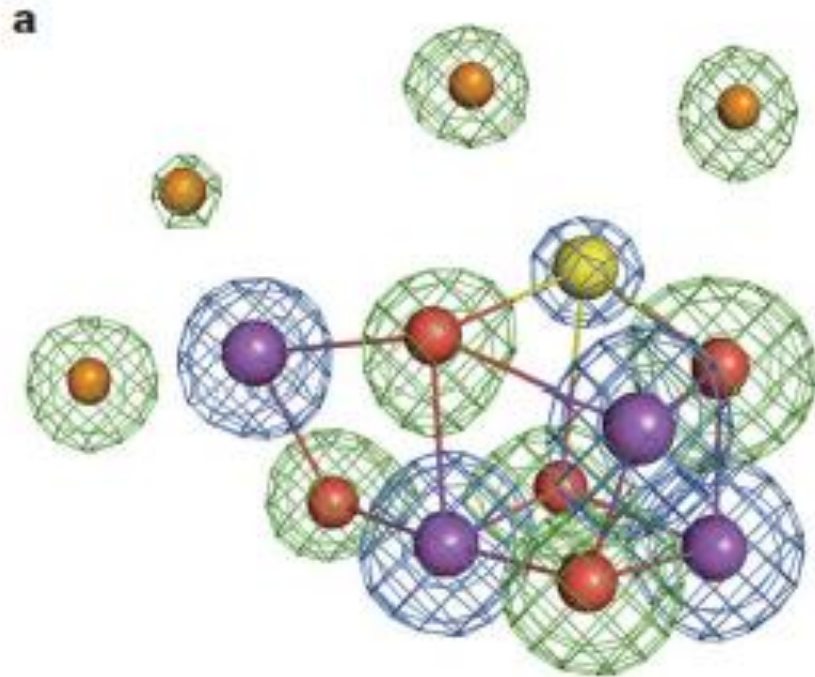
# Electron transport cofactors

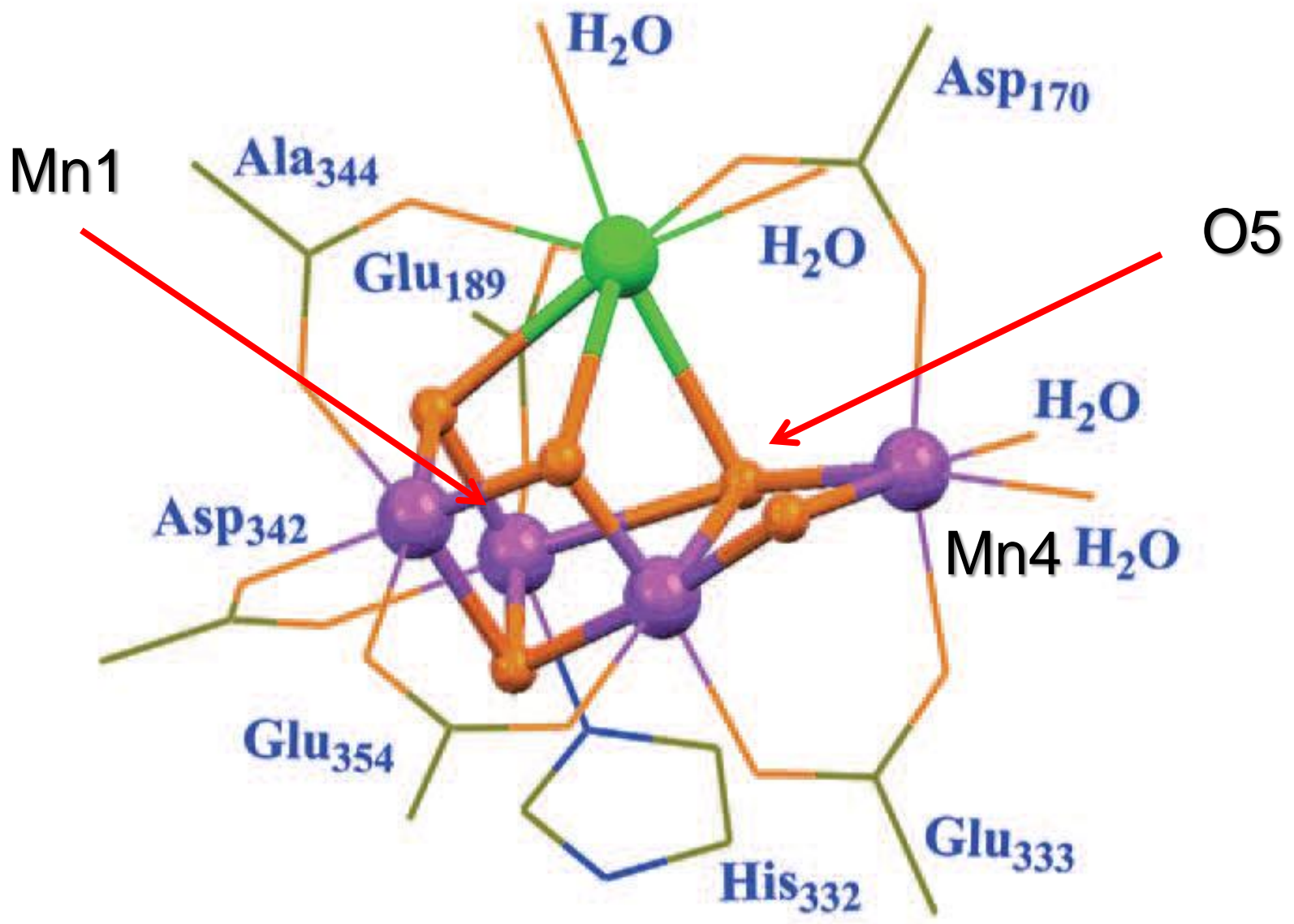


# Regione inversa di Marcus

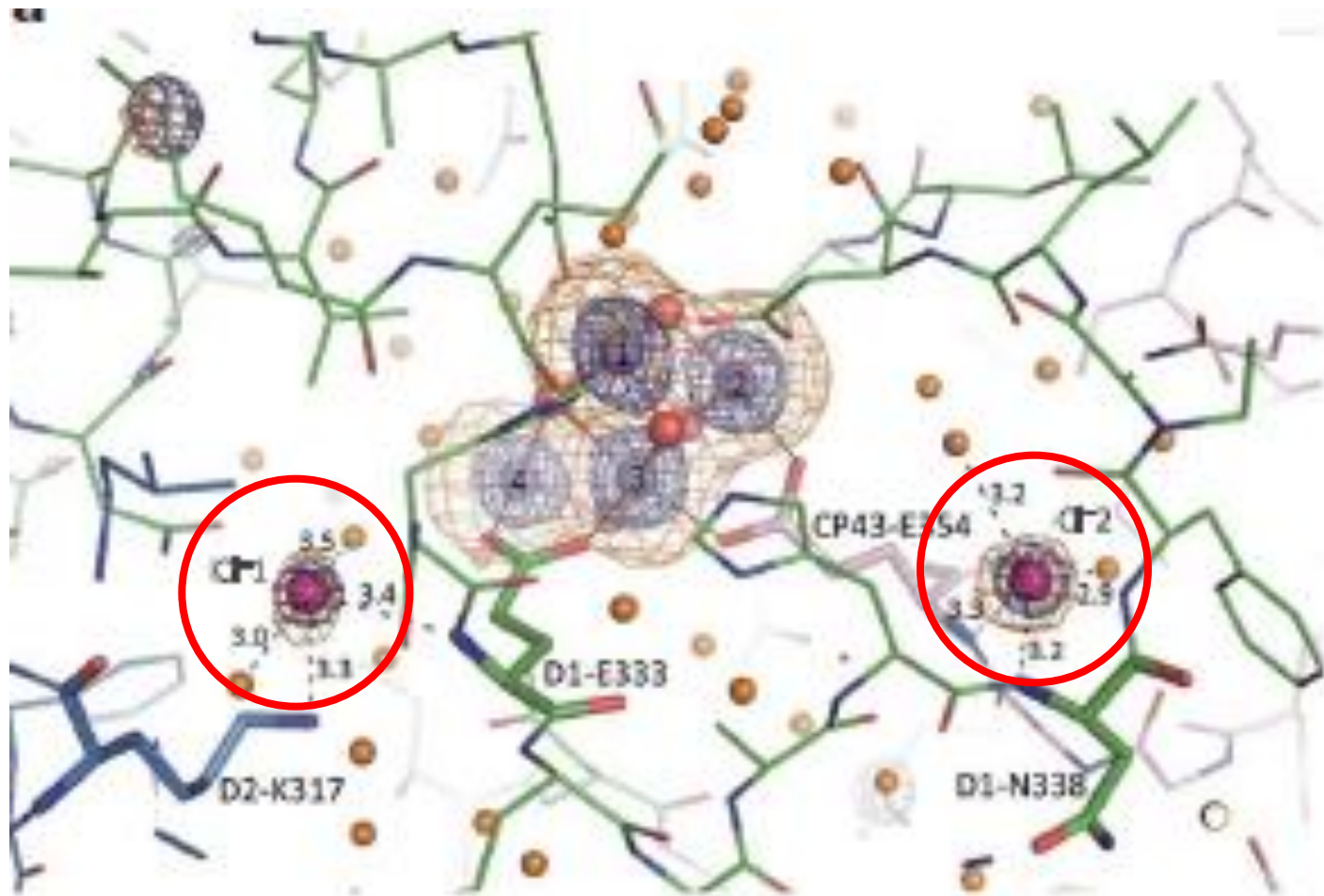


# Oxygen Evolving Complex (OEC)



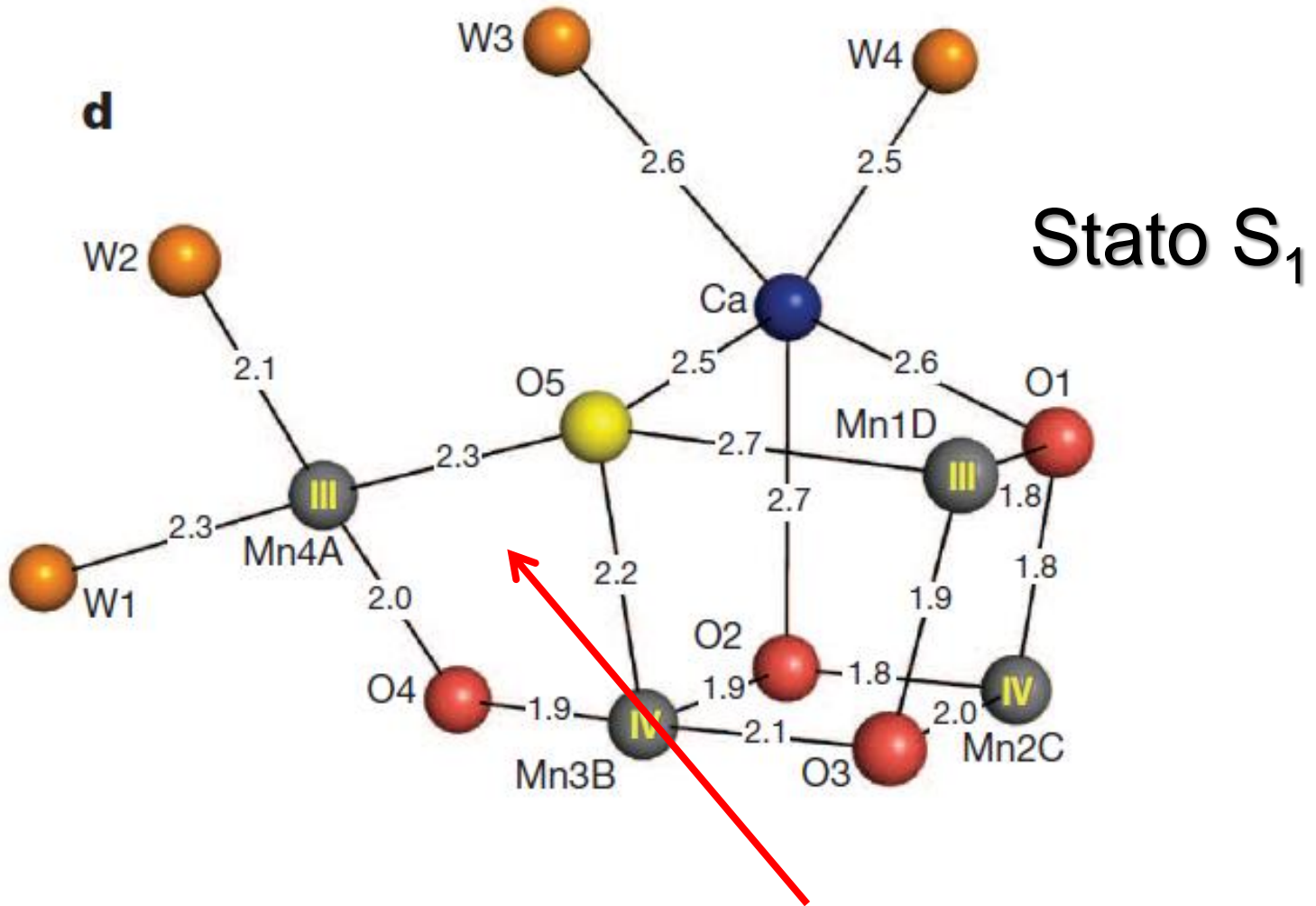








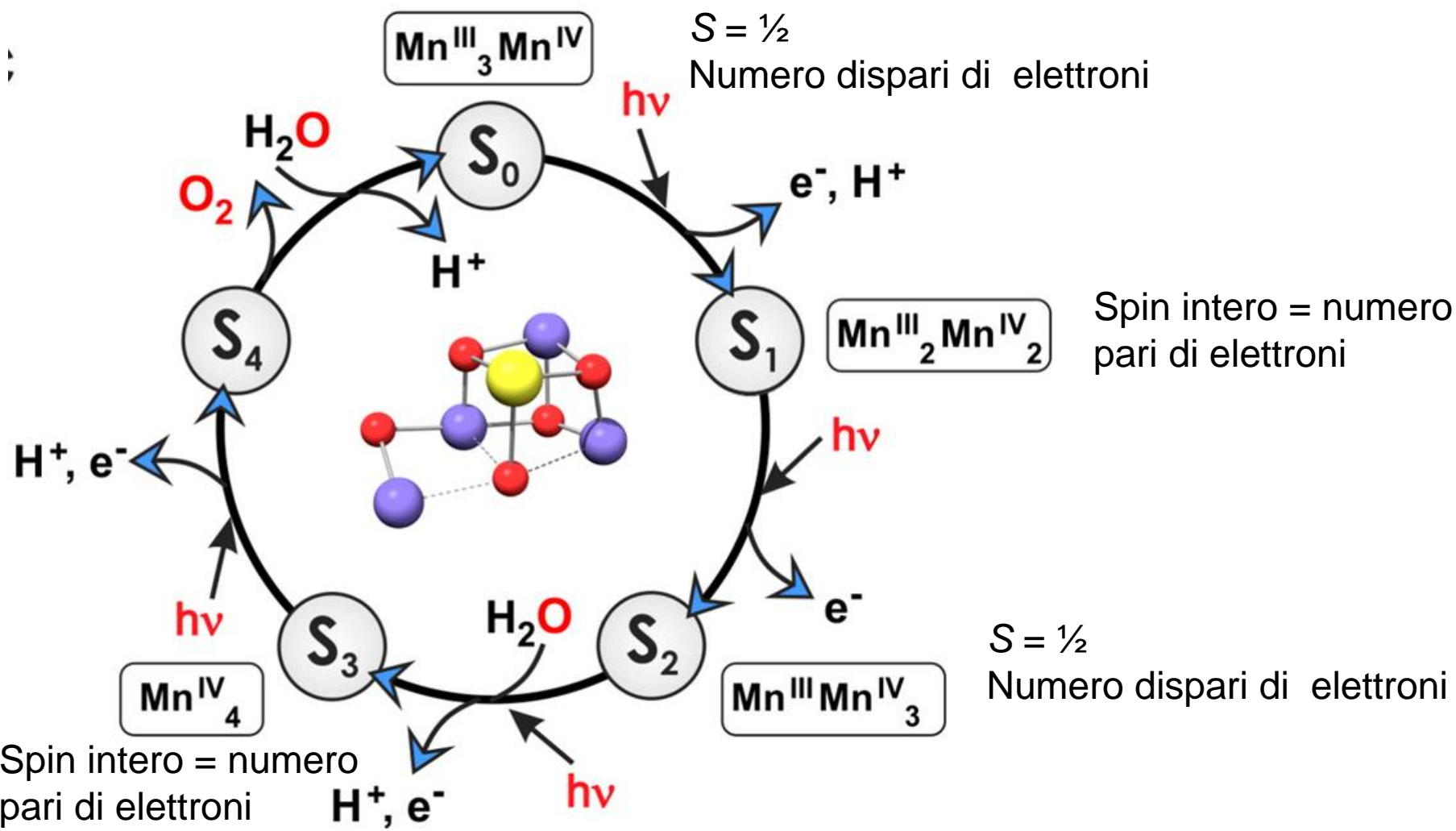
Mn(III),  $d^4$ , alto spin  $\rightarrow$  effetto Jahn-Teller



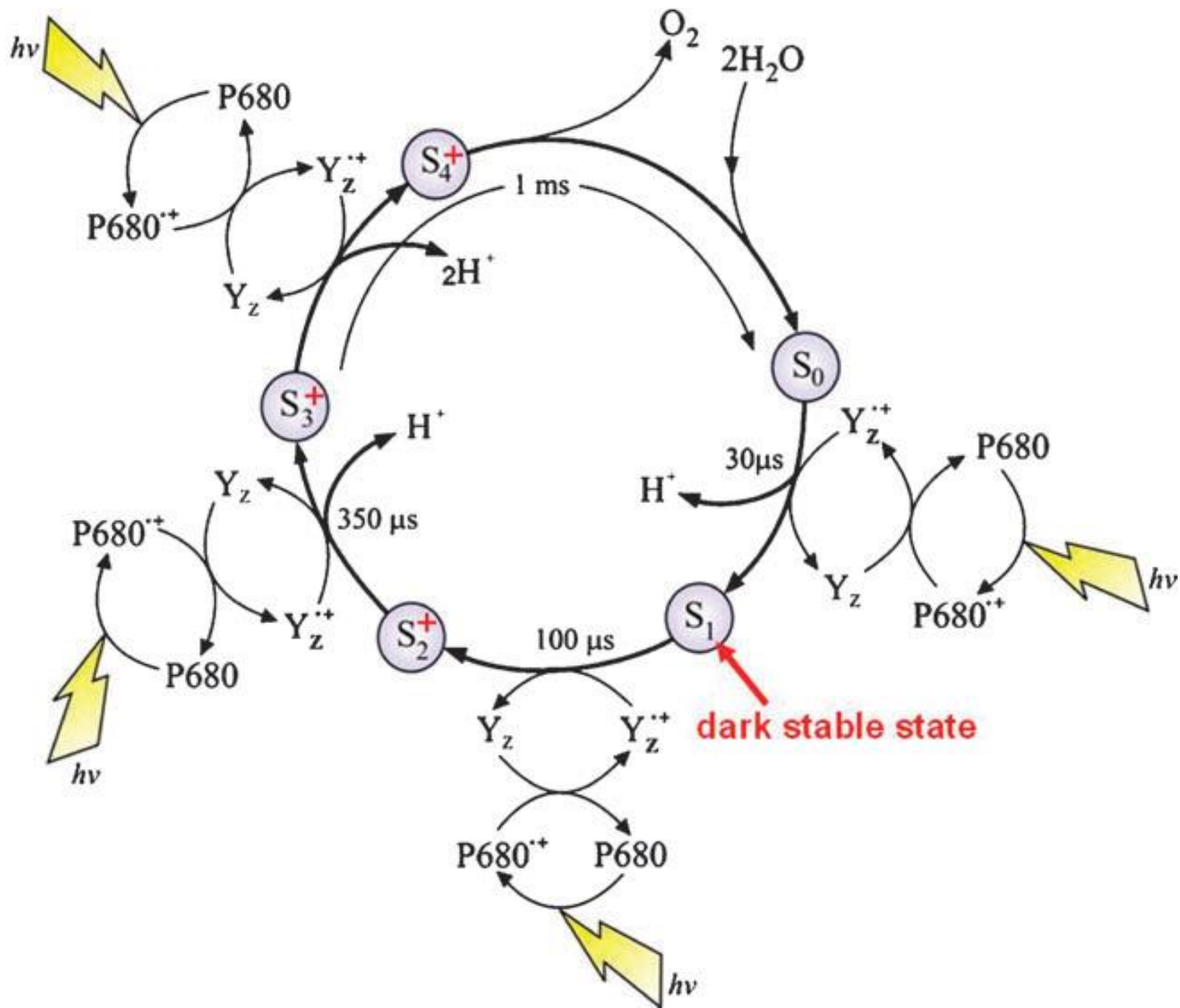
*Nature* 2015  
X-ray free-electron laser (XFEL)

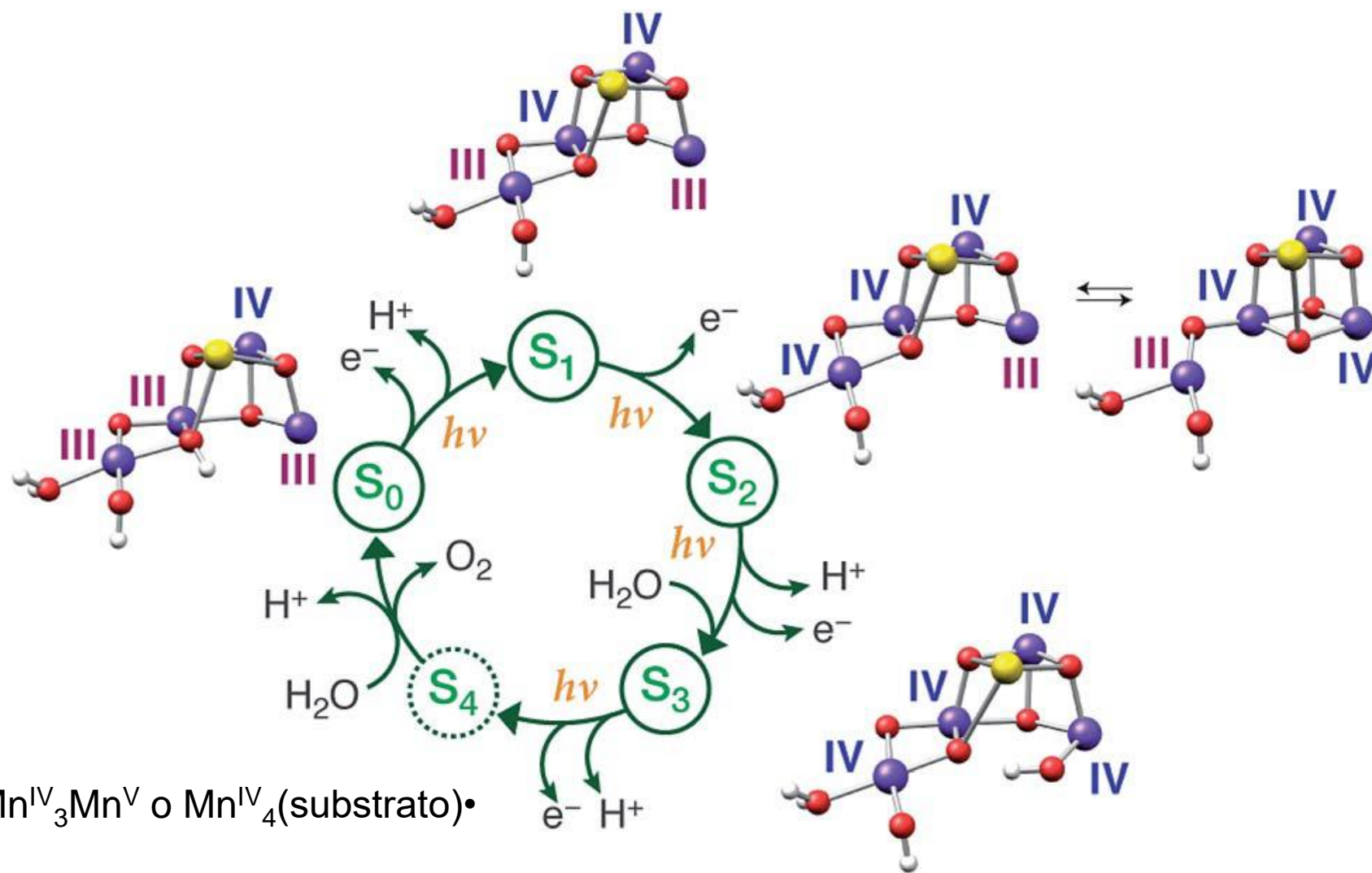
Mn4–O5 più corta di 0.2 Å

# Ciclo di Kok o *S clock*



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

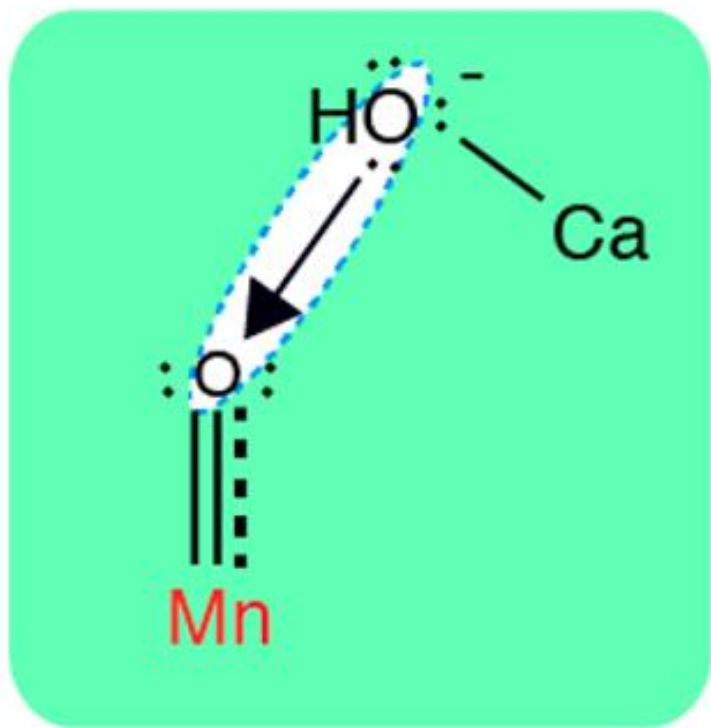




$Mn^{IV}_3Mn^V$  o  $Mn^{IV}_4(\text{substrato})\bullet$

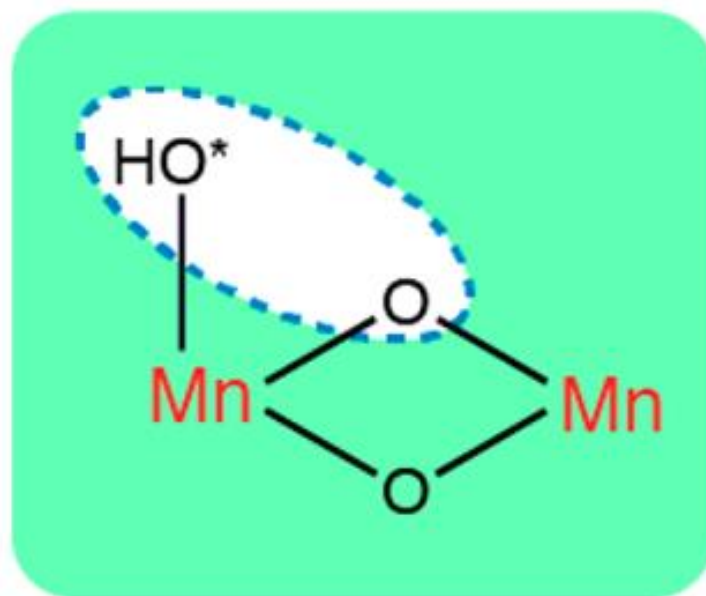
# Ipotesi di formazione del legame O–O

nucleophilic attack

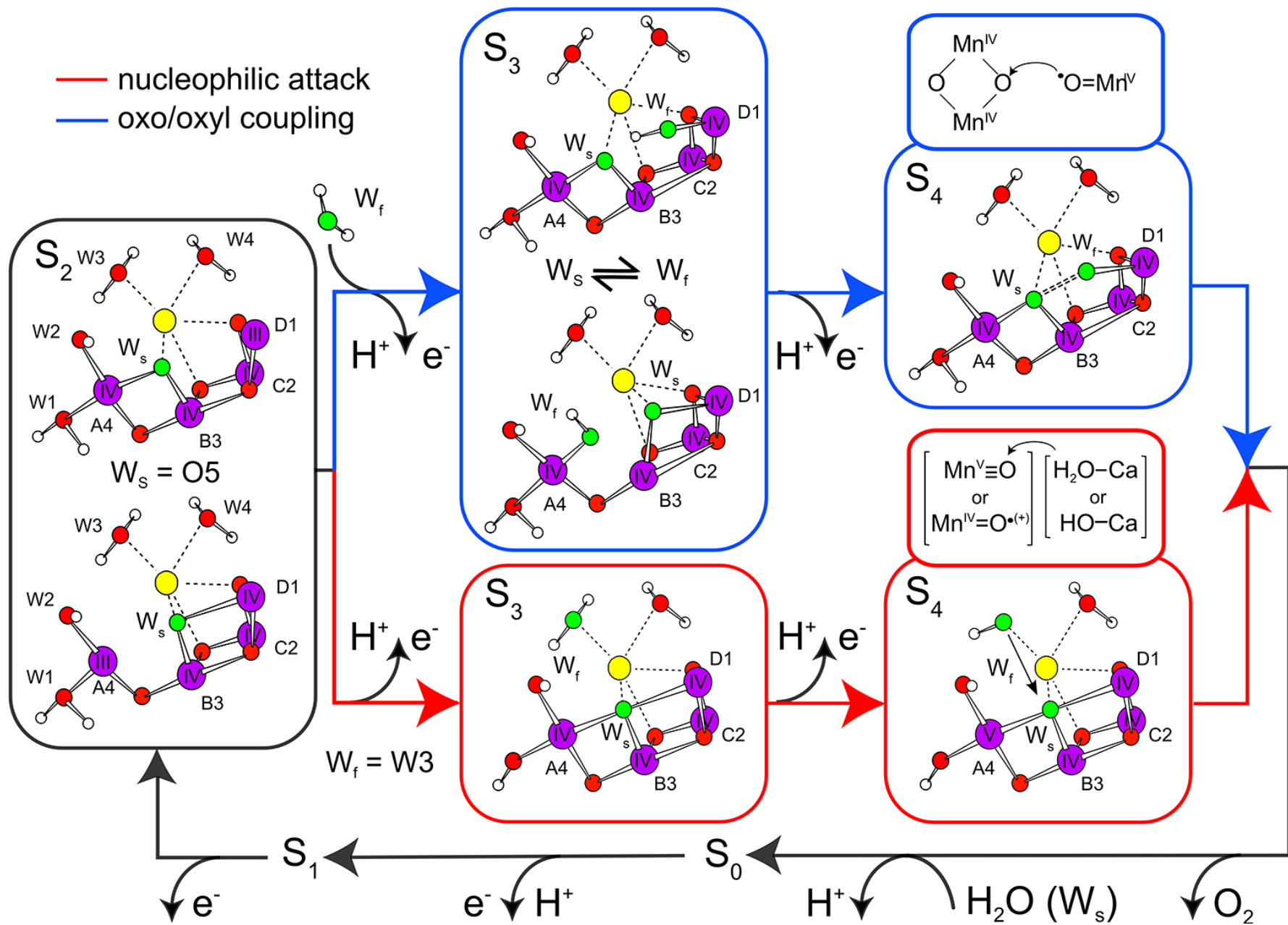


$\text{Mn(V)}\equiv\text{O}$  o  $\text{Mn(IV)}=\text{O}\cdot$

terminal oxyl radical  
with bridging oxo

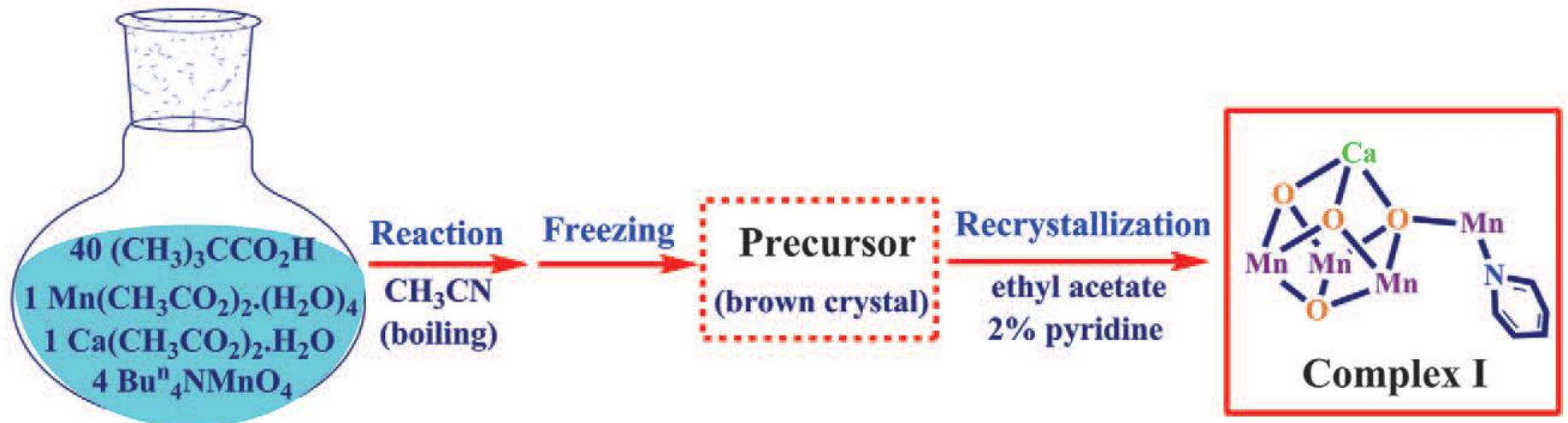


*oxo/oxyl radical coupling mechanism*

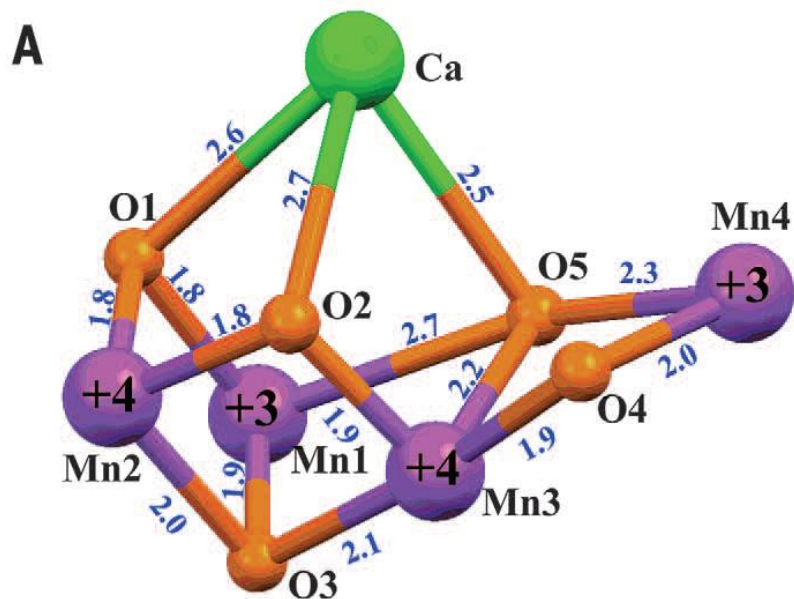




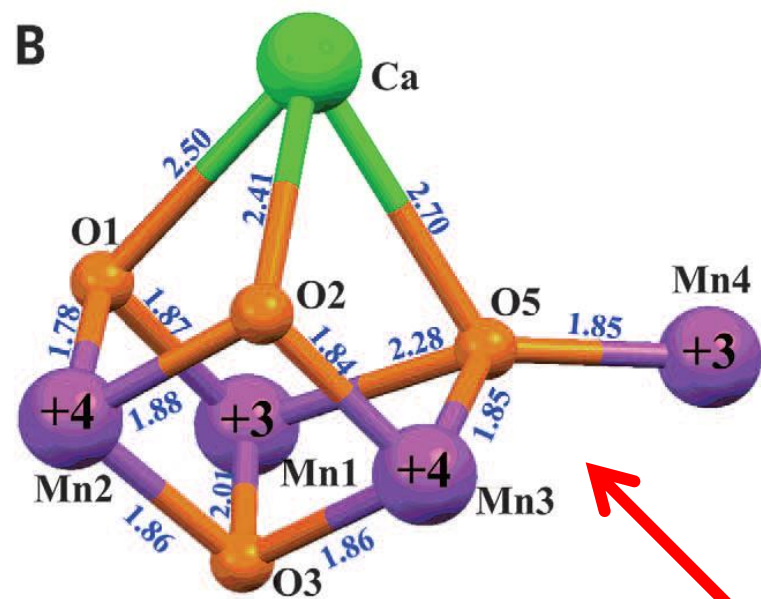
# Sistemi modello



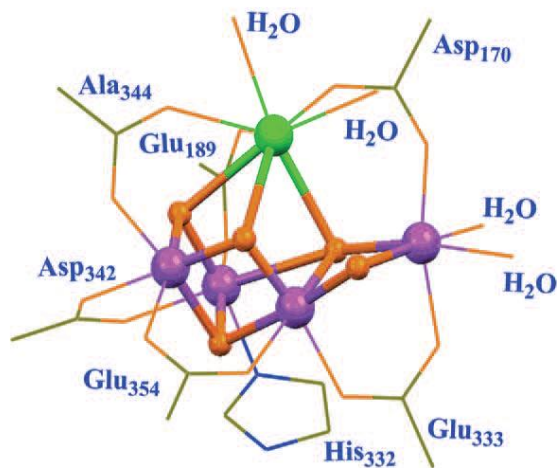
Natural catalyst



Artificial complex



**C**



**D**

