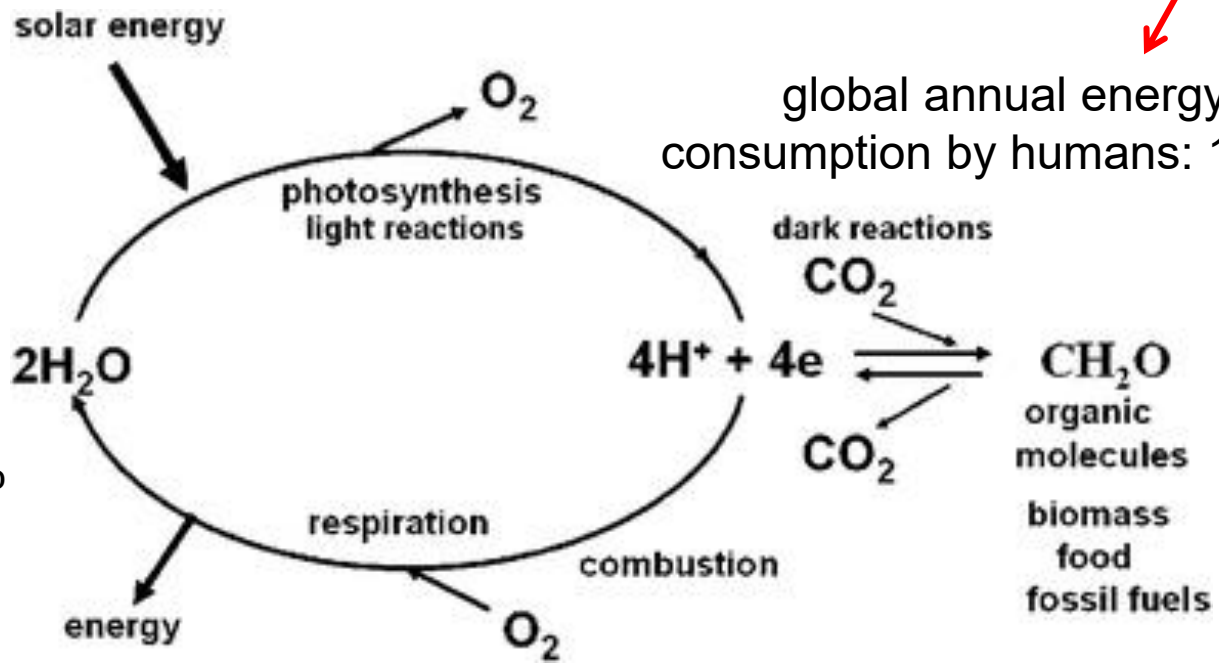


100×10^9 ton/y of dry biomass from CO_2
 1 g of glucose per m^2 of leaf surface per hour
 $100 \text{ TW/y} = 0.1\%$ of total solar energy (10^5 TW)

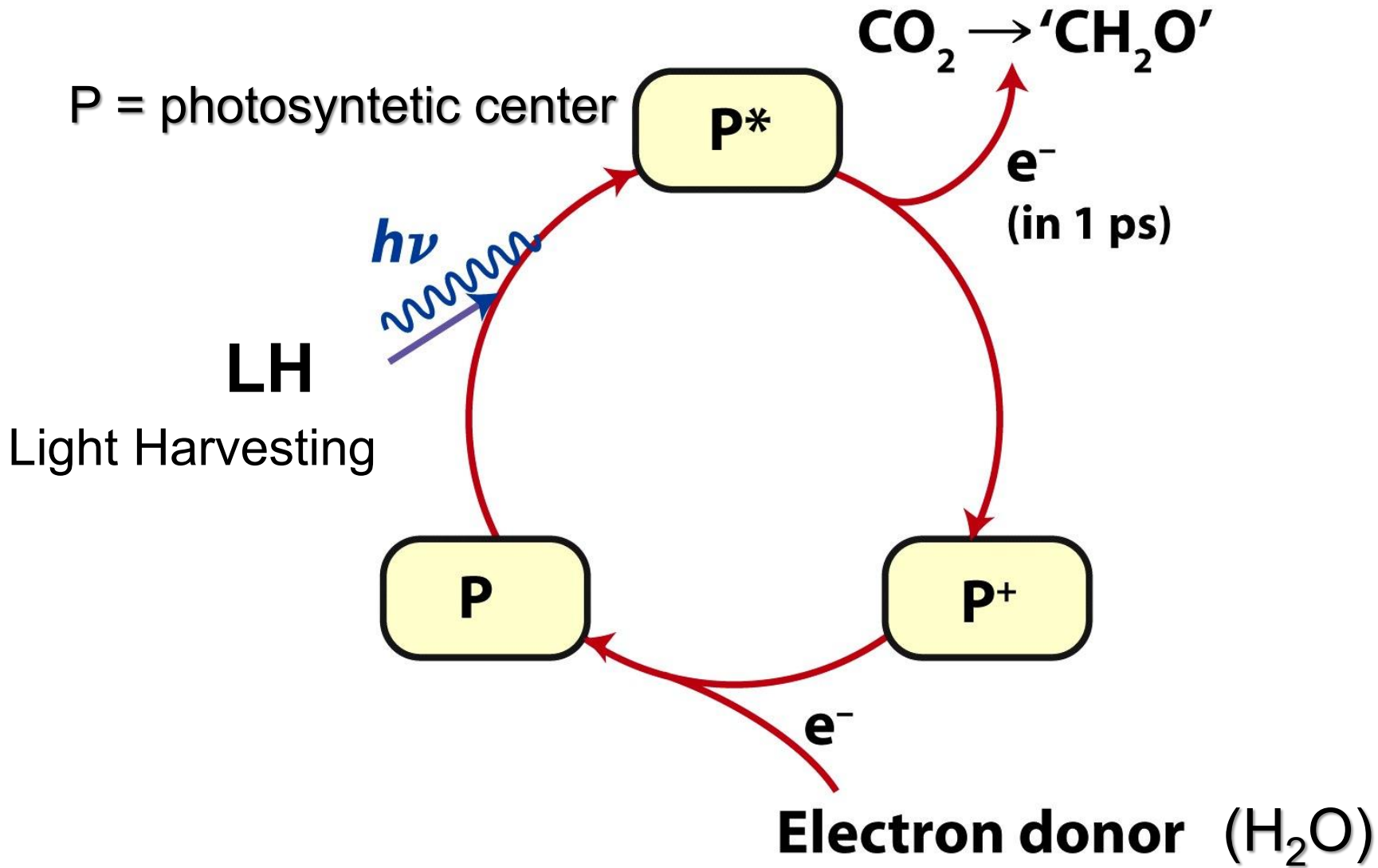
Energy stored as biomass

global annual energy consumption by humans: 14 TW

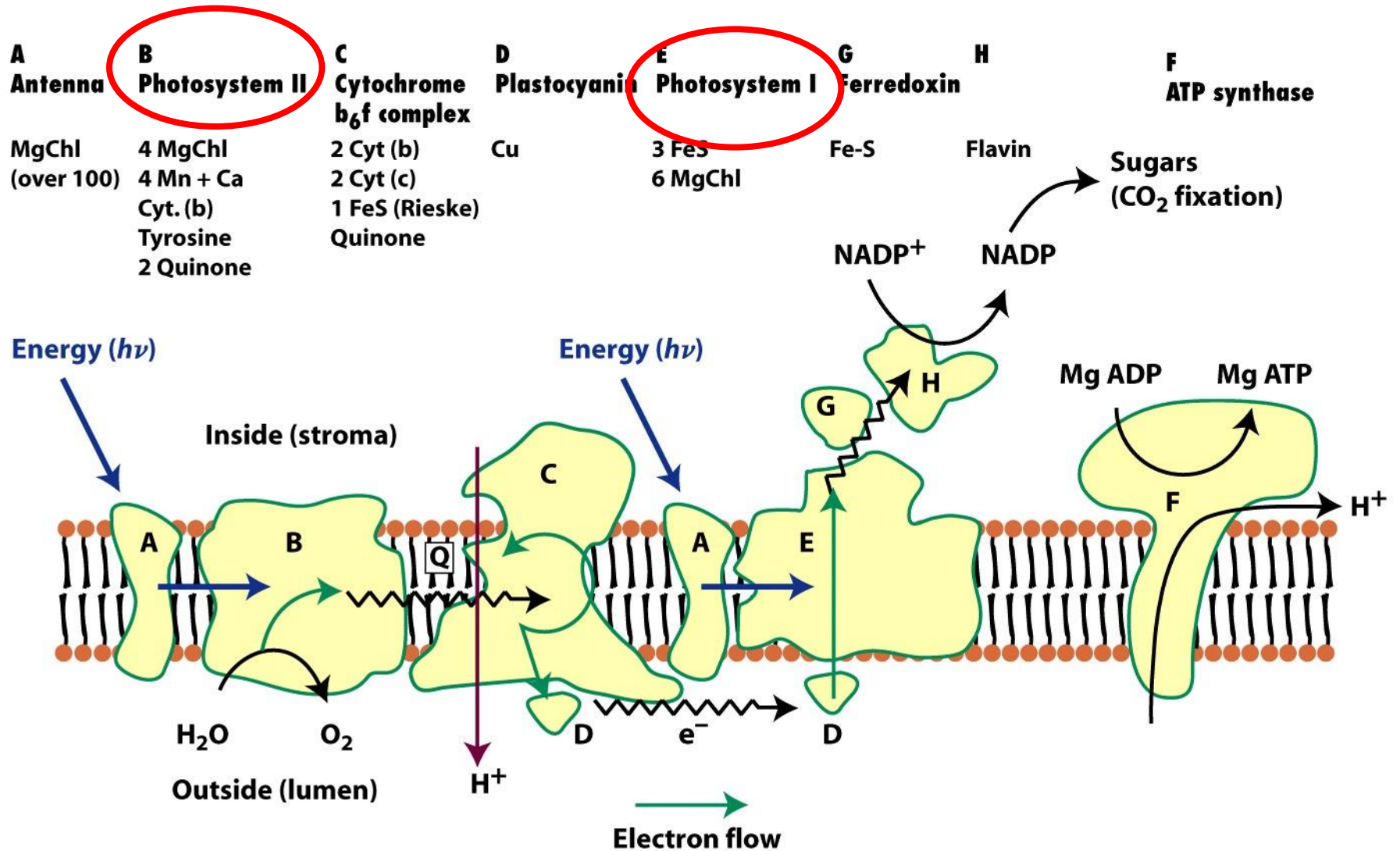
Max efficiency: 4.5%



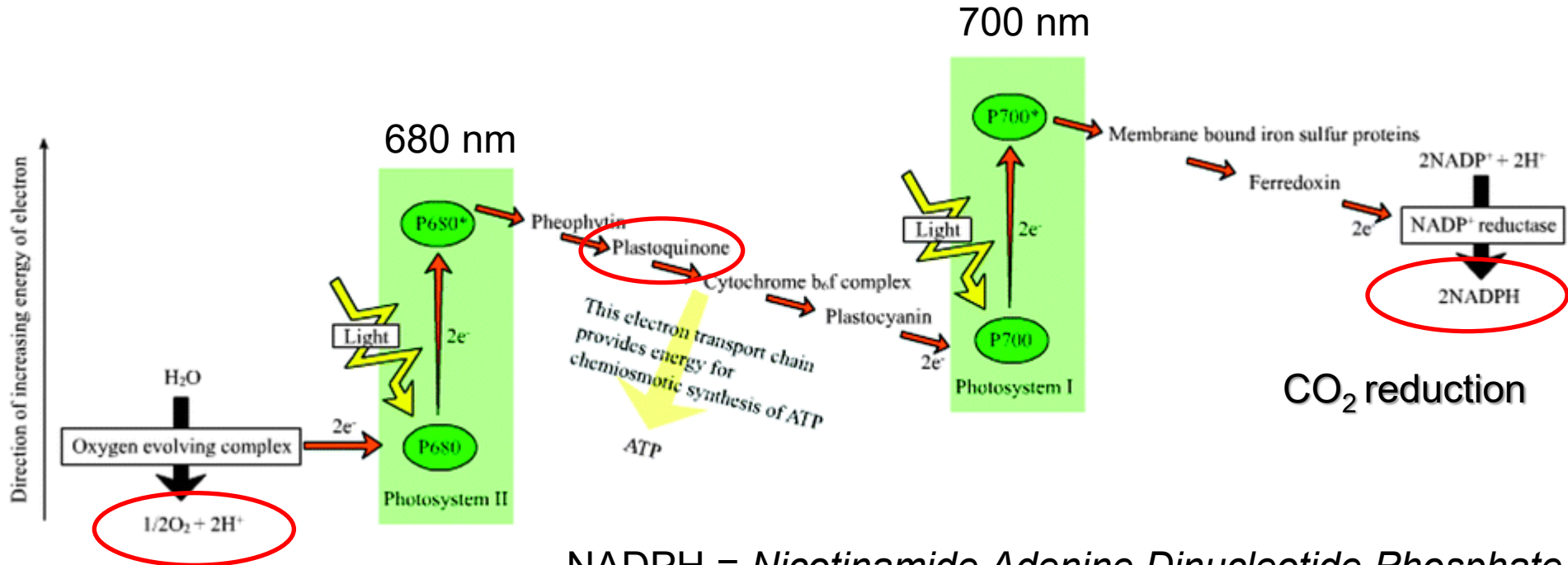
Photoinduced charge separation in photosystems



Photosynthetic process in plants

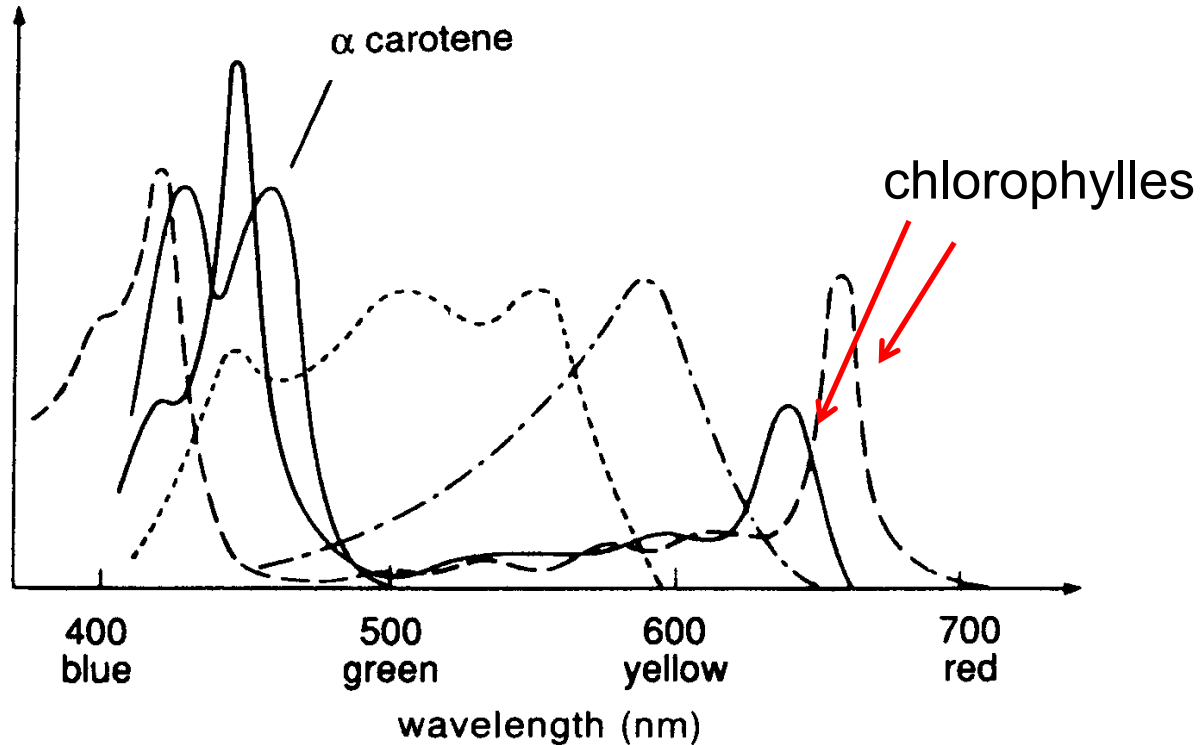
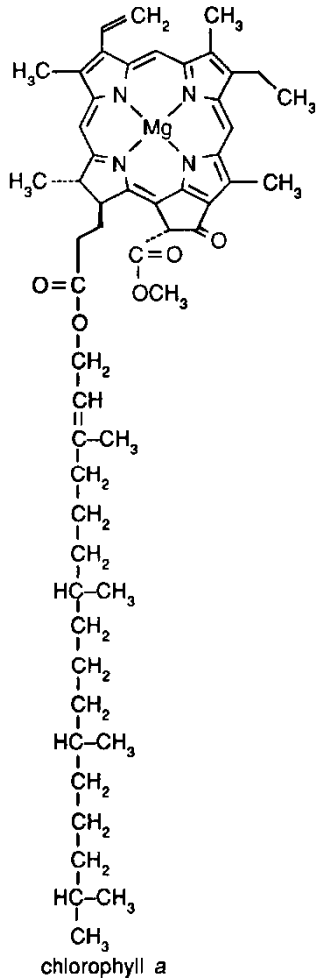


"Z-shaped" diagram for redox potential



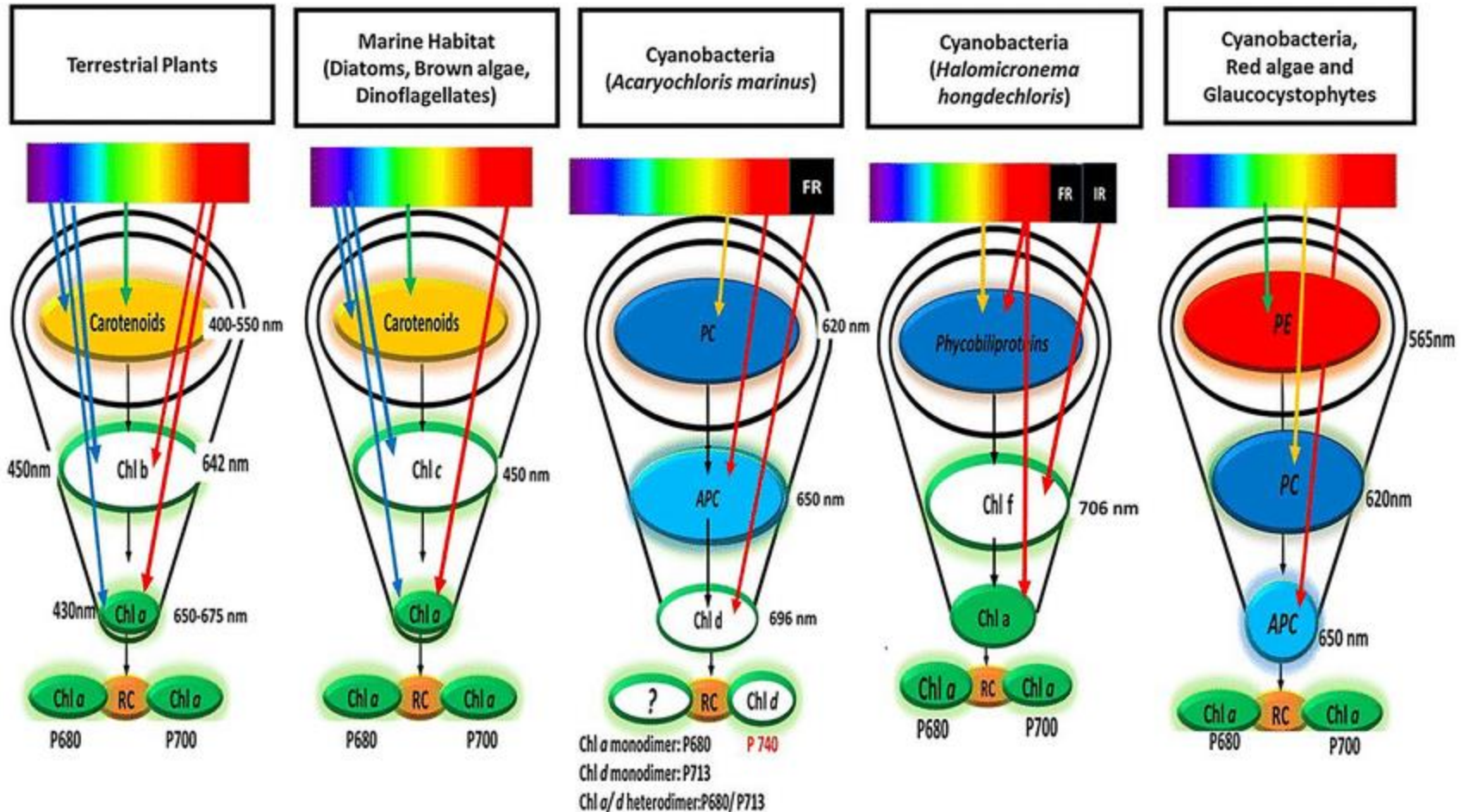
For each electron extracted from H₂O and transferred to CO₂ the energy of two photons is necessary, one in PSII and the second in PSI: in total, 8 photons for each molecule of O₂ produced

Pigments for *light harvesting*

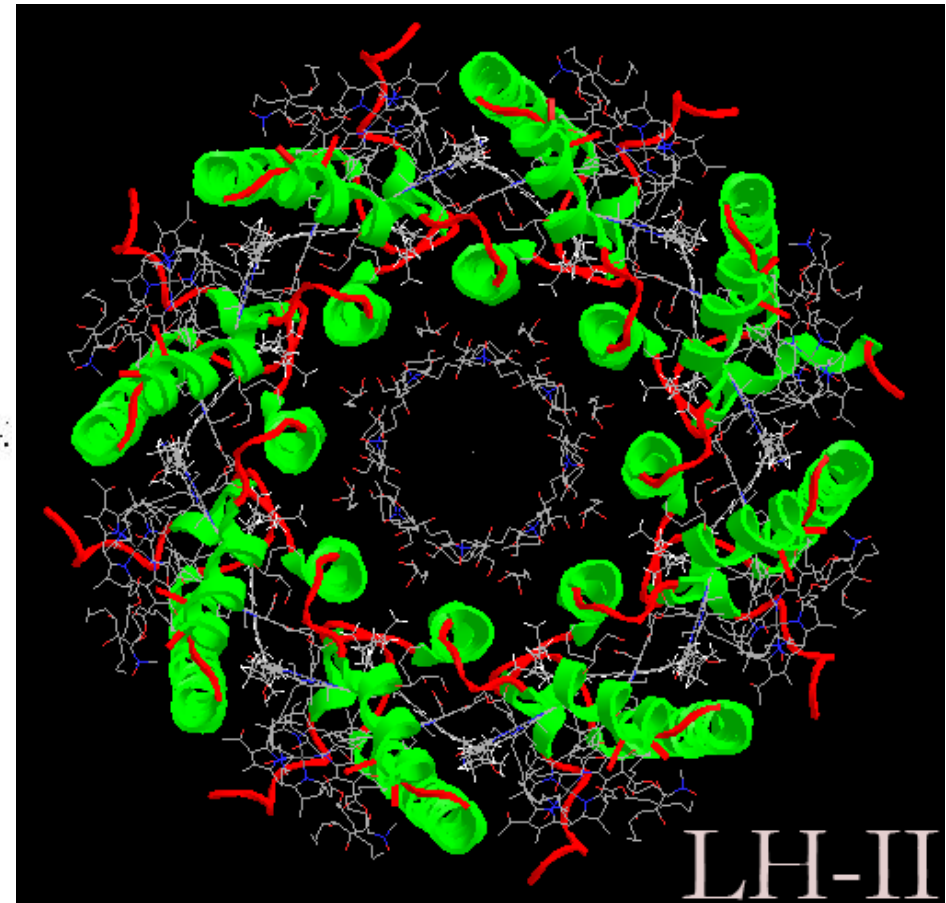
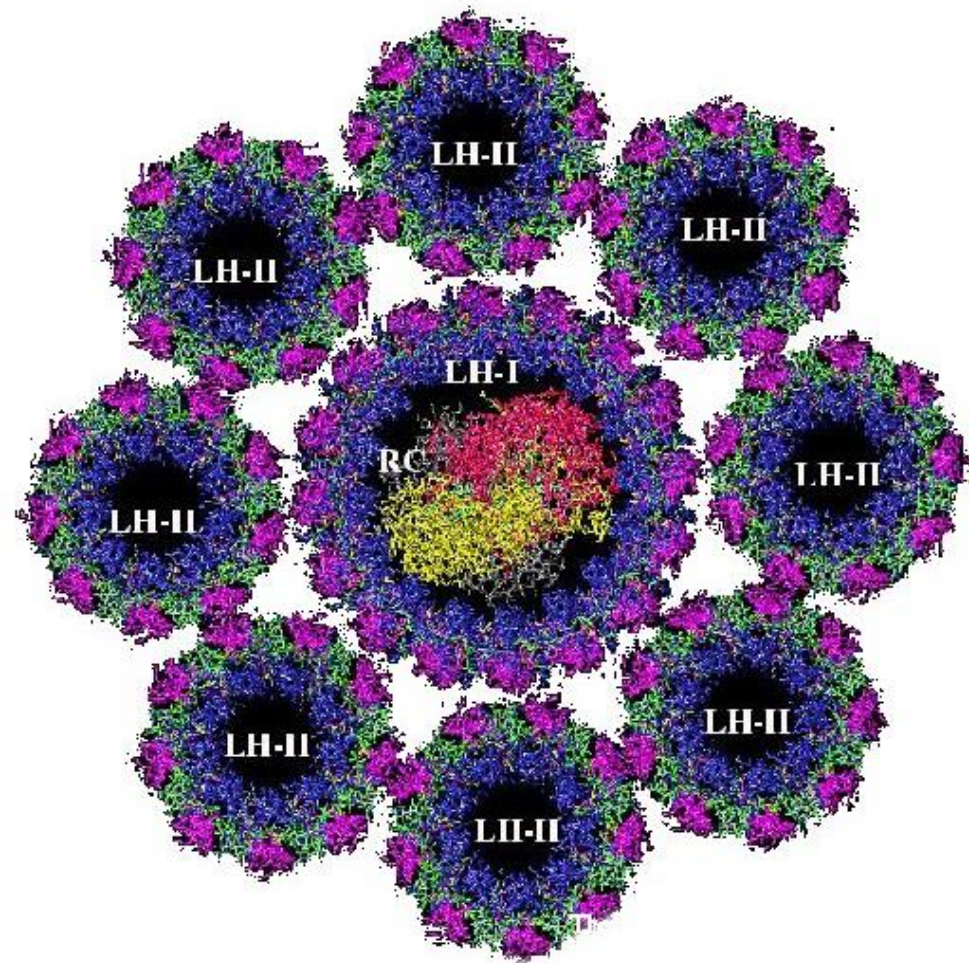


Absorption spectra of various pigments from algae and plants (according to [11]): chlorophyll *a* (— —), chlorophyll *b* (——), α-carotene (—), phycocyanin (-·-·), phycoerythrin (- - - -)

Light harvesting in the antenna systems

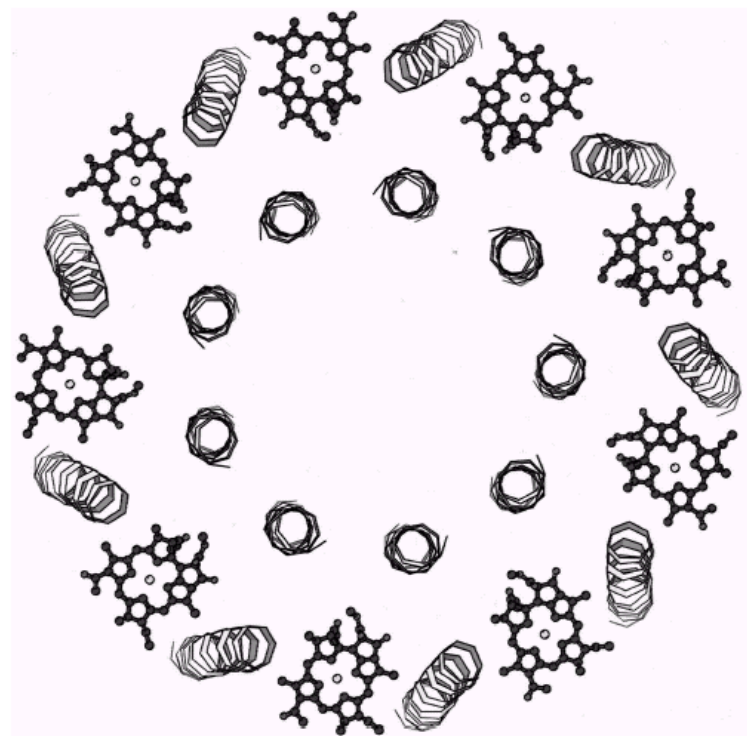
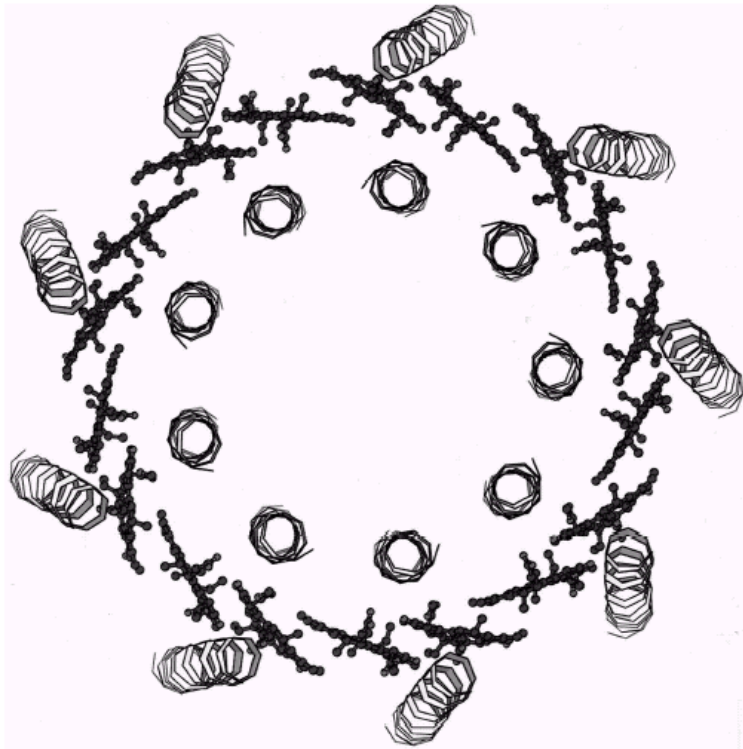


Antenna systems for *light-harvesting* and *exciton transfer*

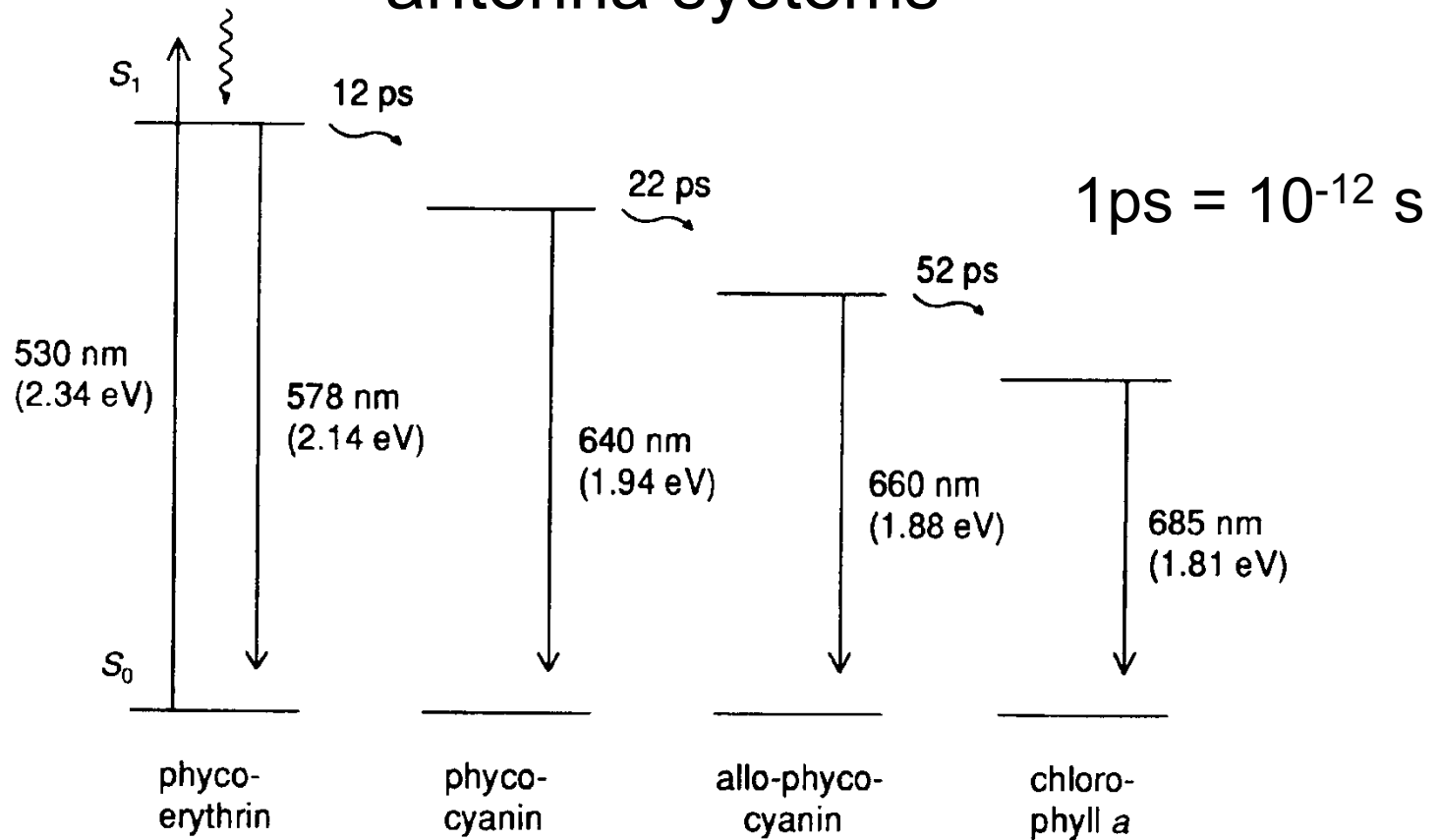


More than 98% of chlorophyll molecules are in the LH systems

Antenna systems for *light-harvesting* and *exciton transfer*

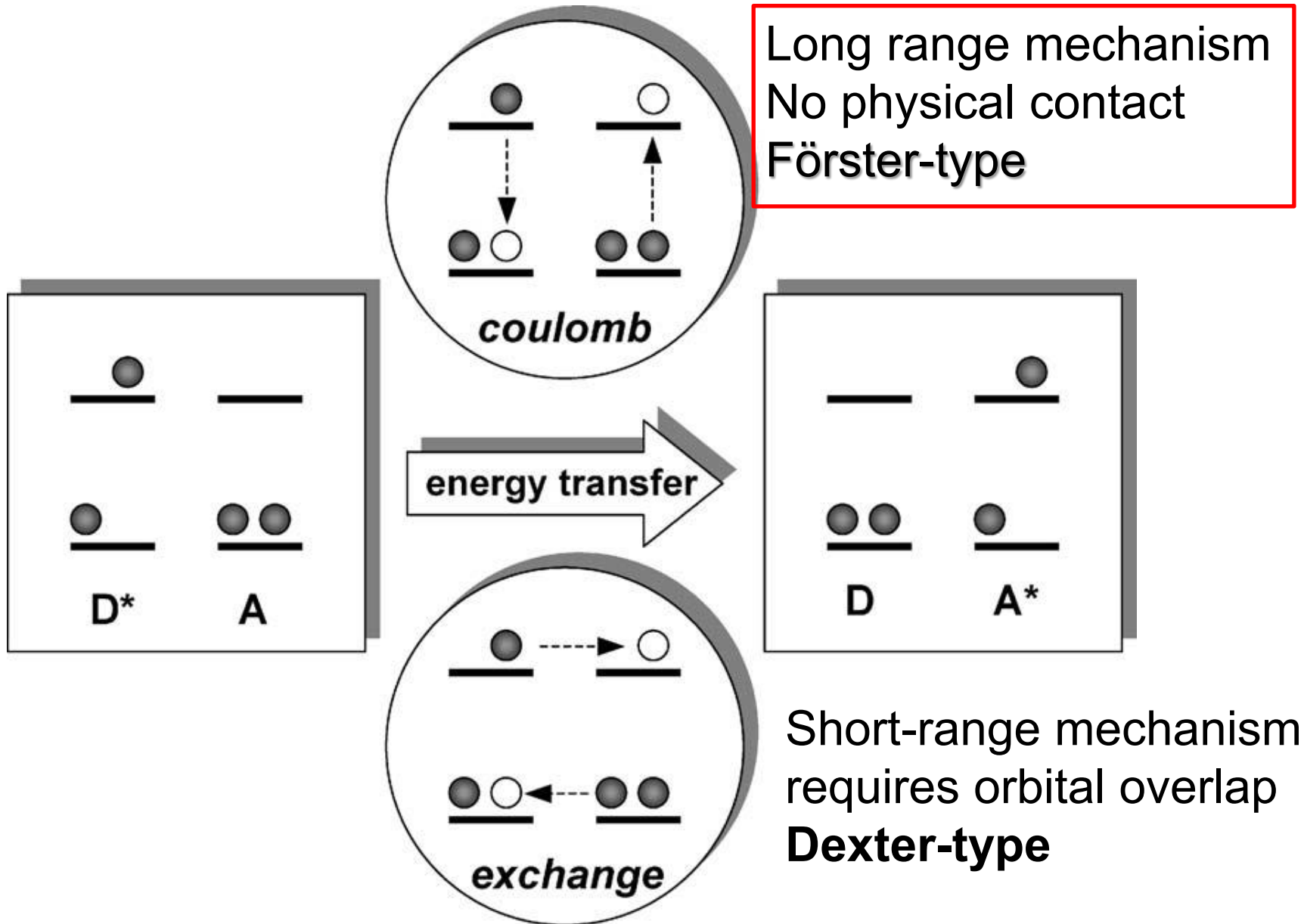


Cascade energy transfer (*exciton transfer*) in the antenna systems

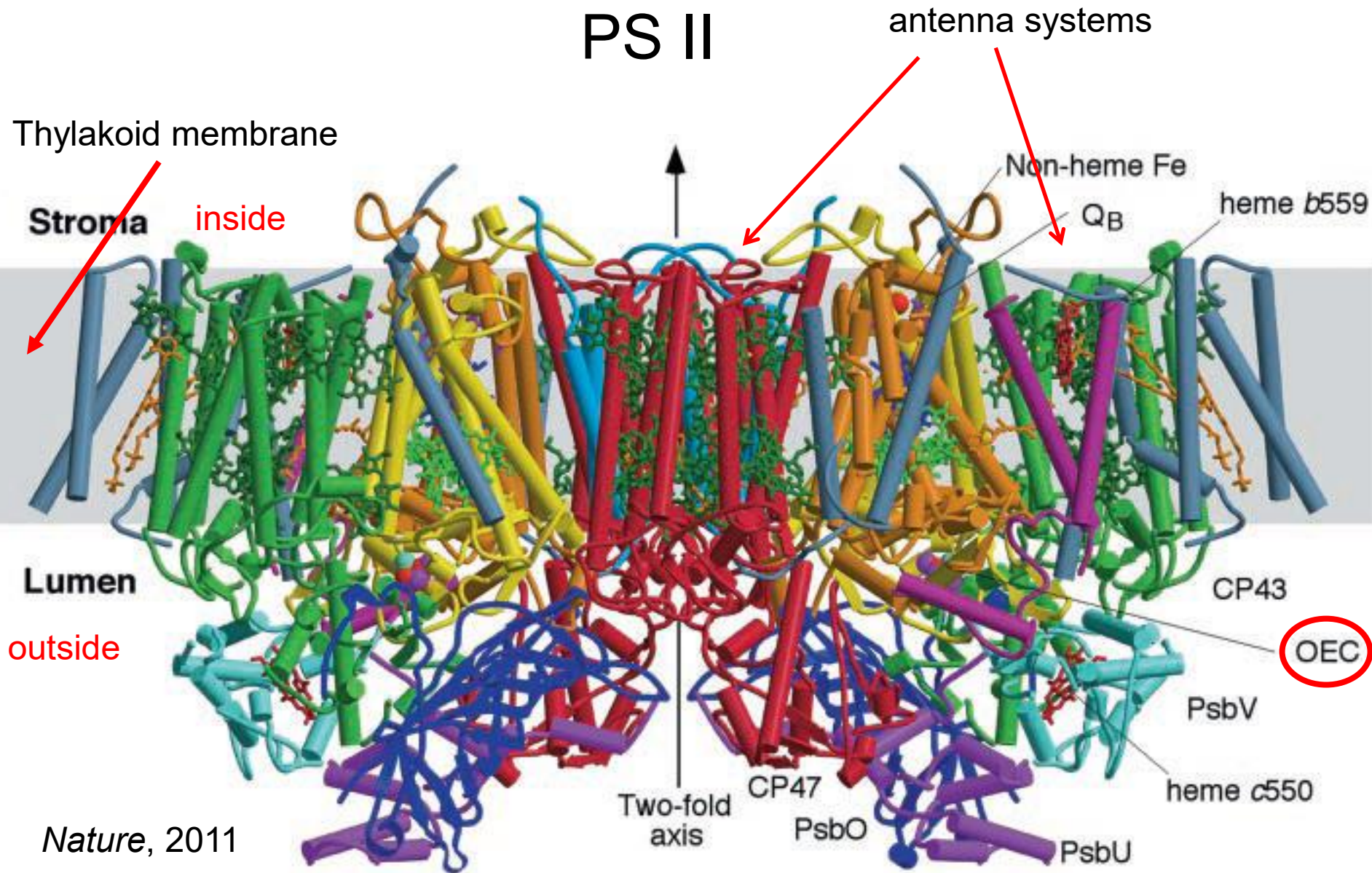


95% efficiency

Mechanisms for the *exciton transfer*

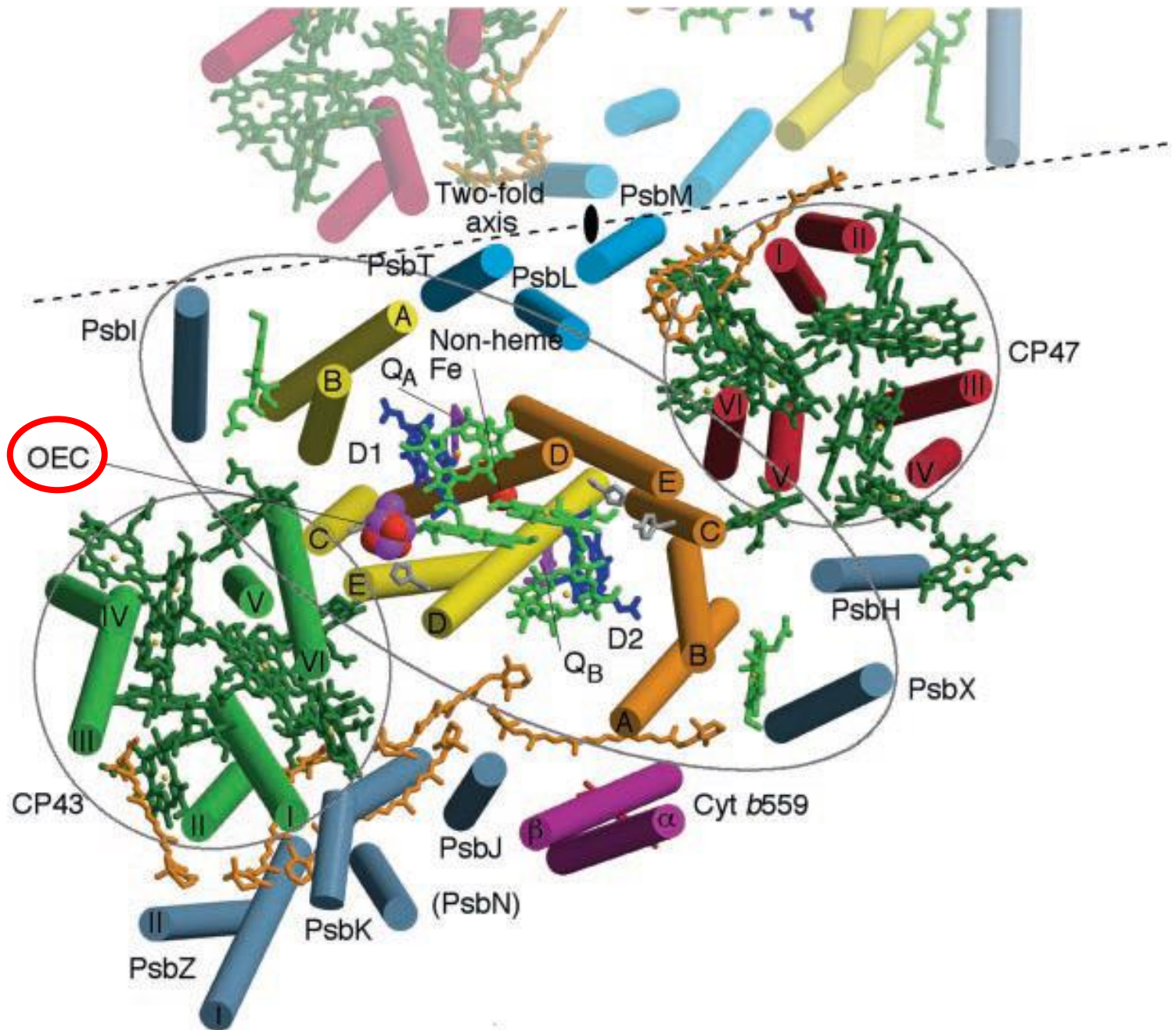


PS II



19 proteic subunits, 2 pheophytins, 36 chlorophylls, 11 carotenoids, several cofactors

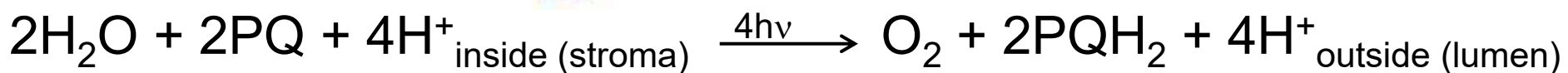
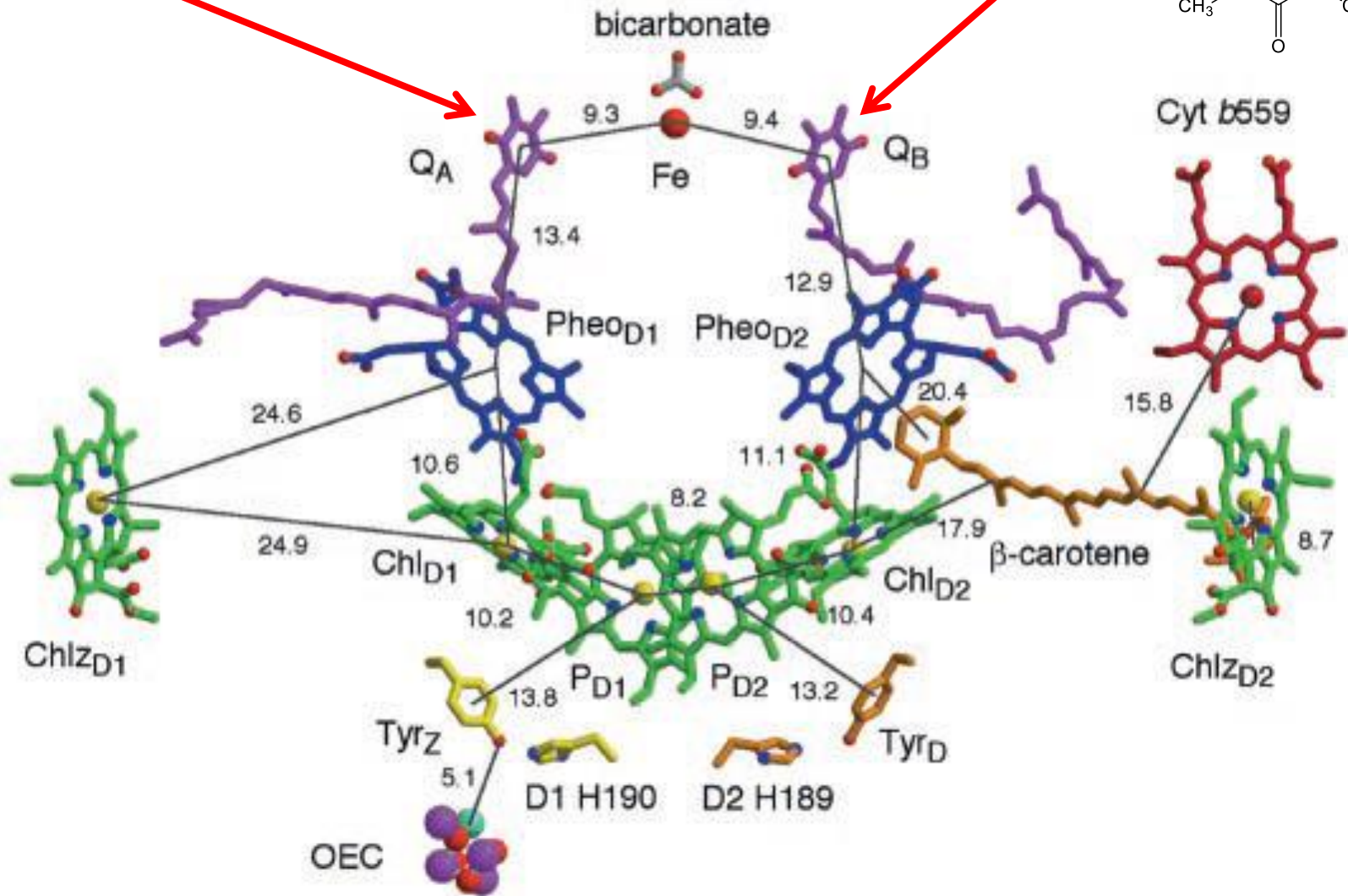
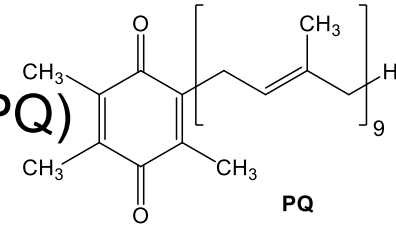
PS II



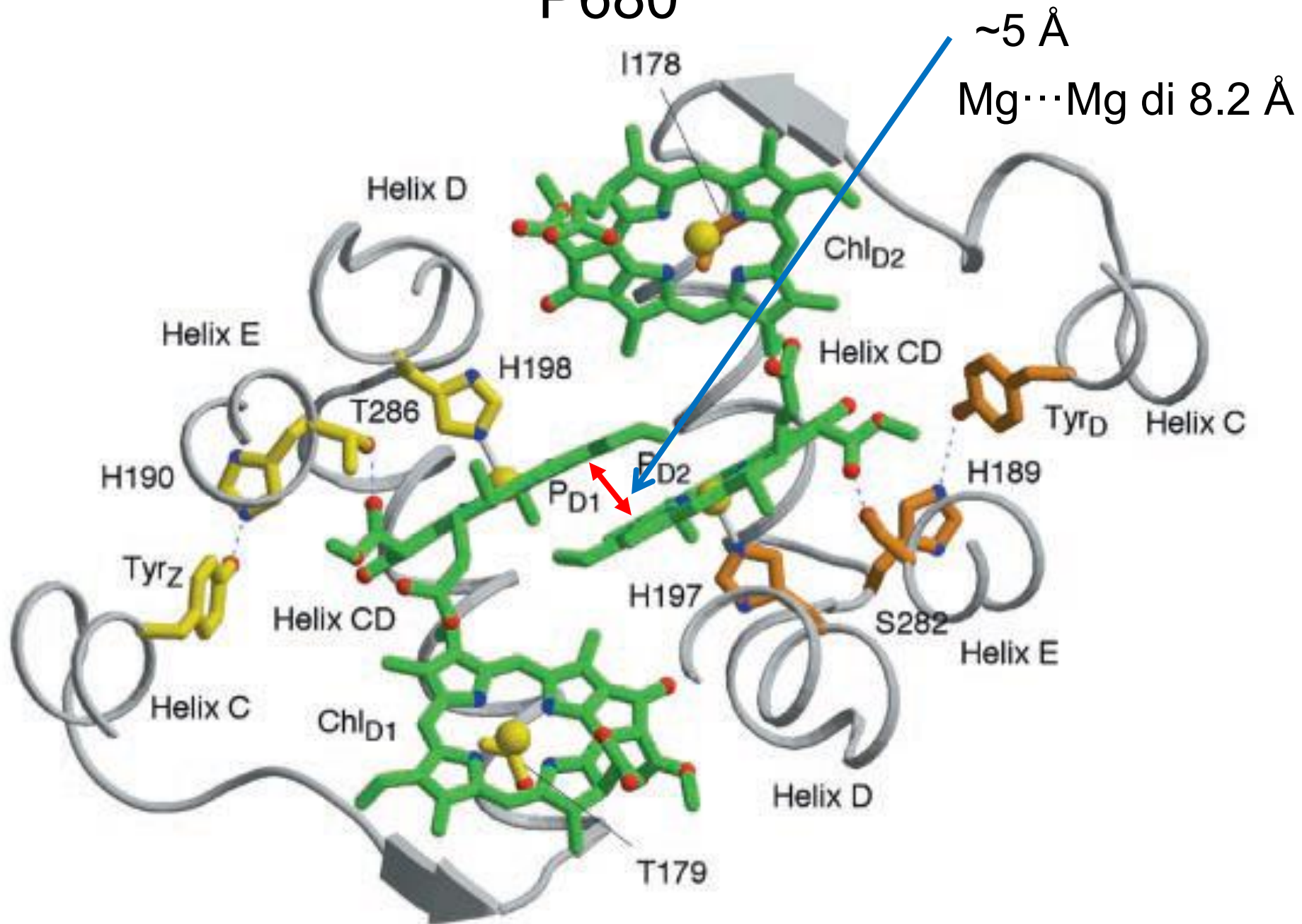
P680

Fixed plastoquinone

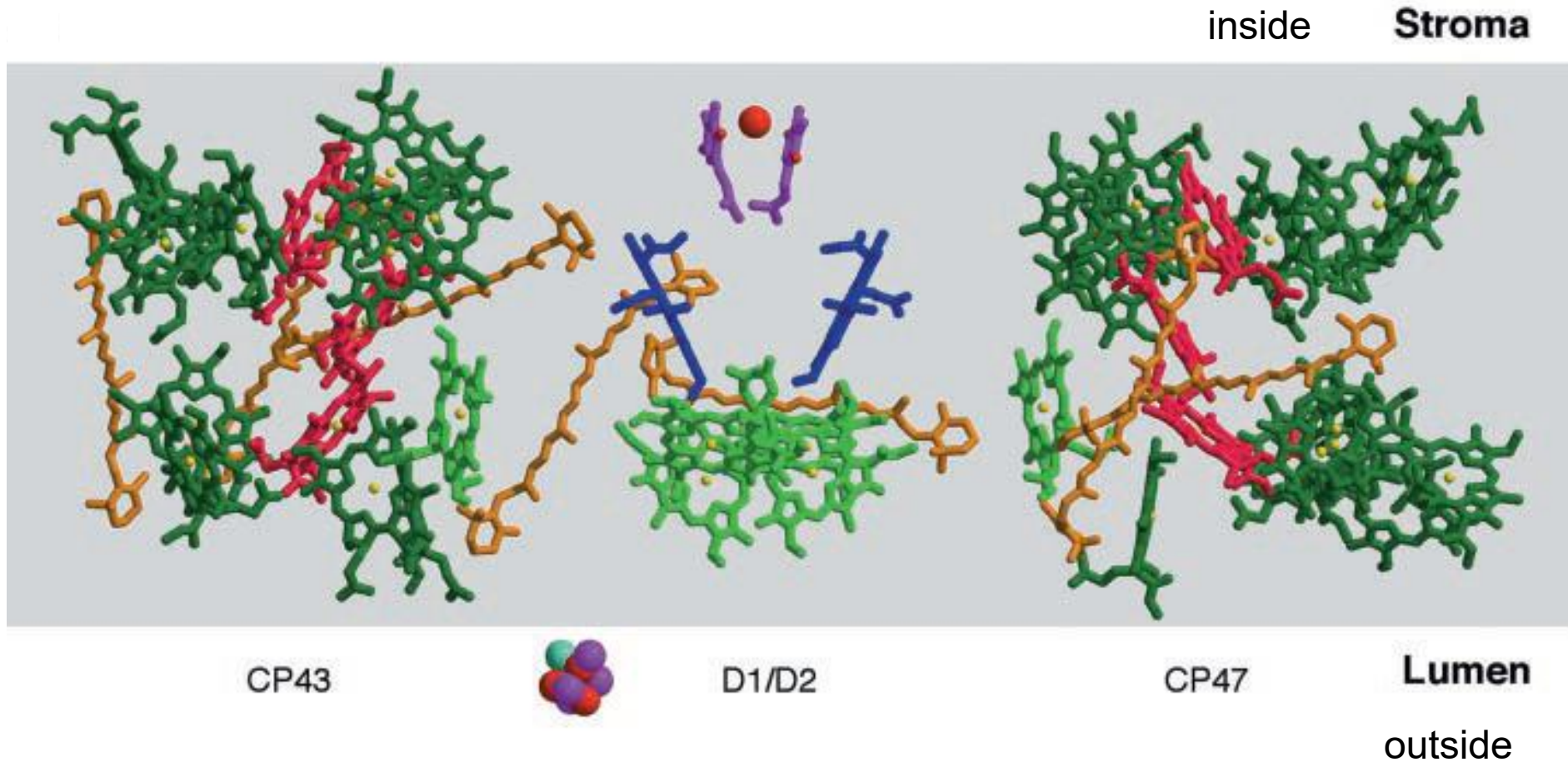
Mobile plastoquinone (PQ)



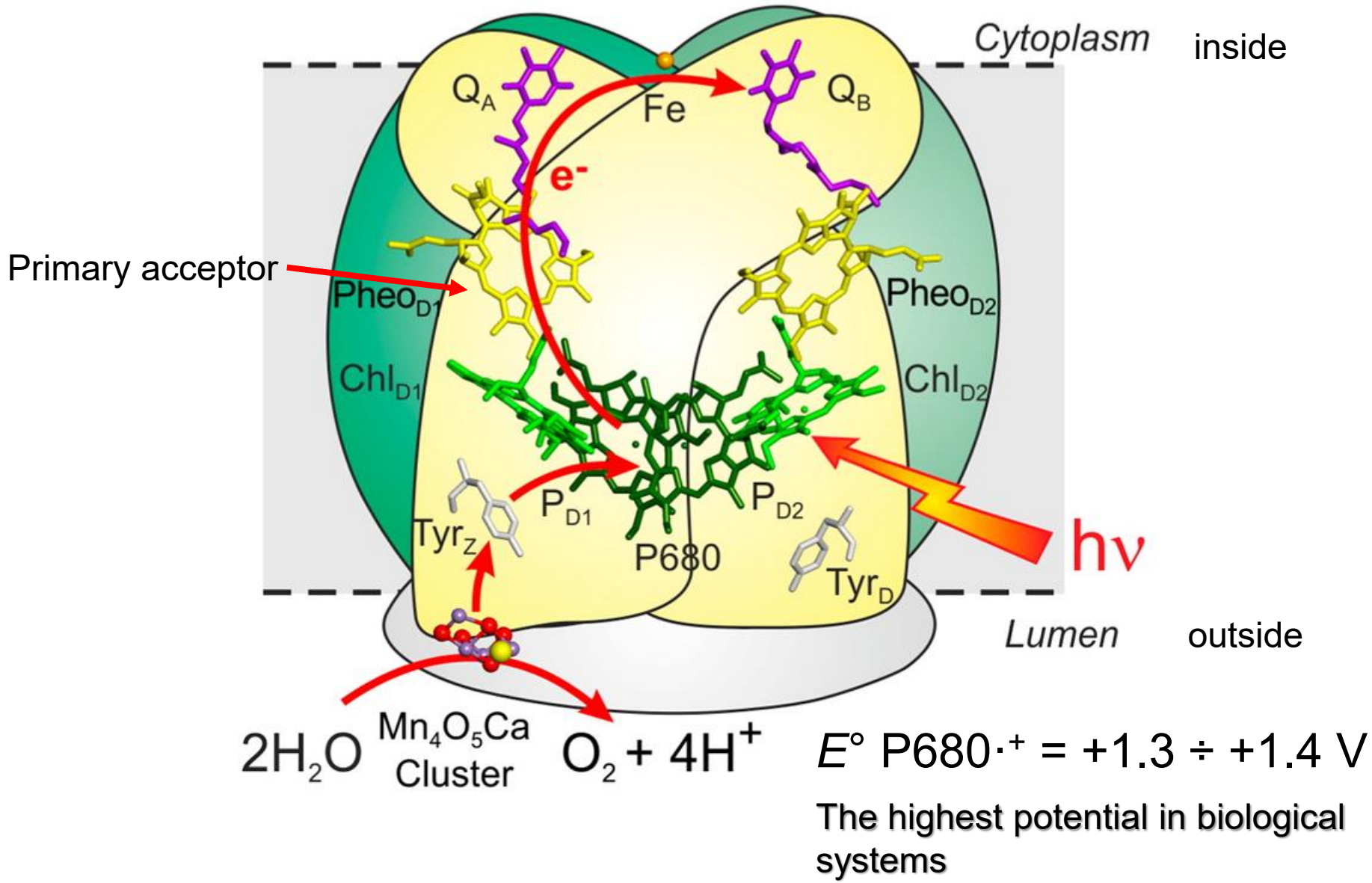
P680



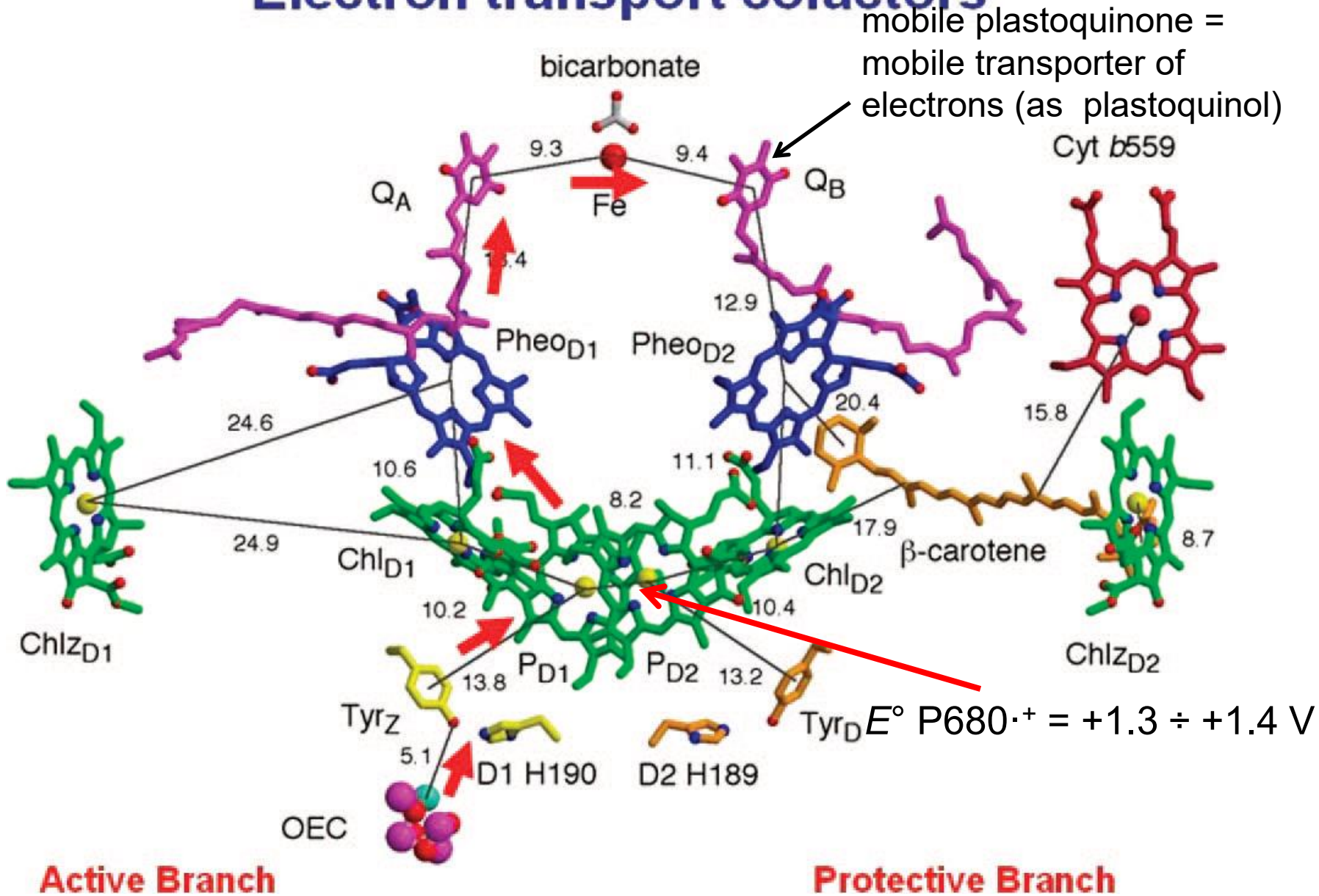
Photoreaction center and antenna systems



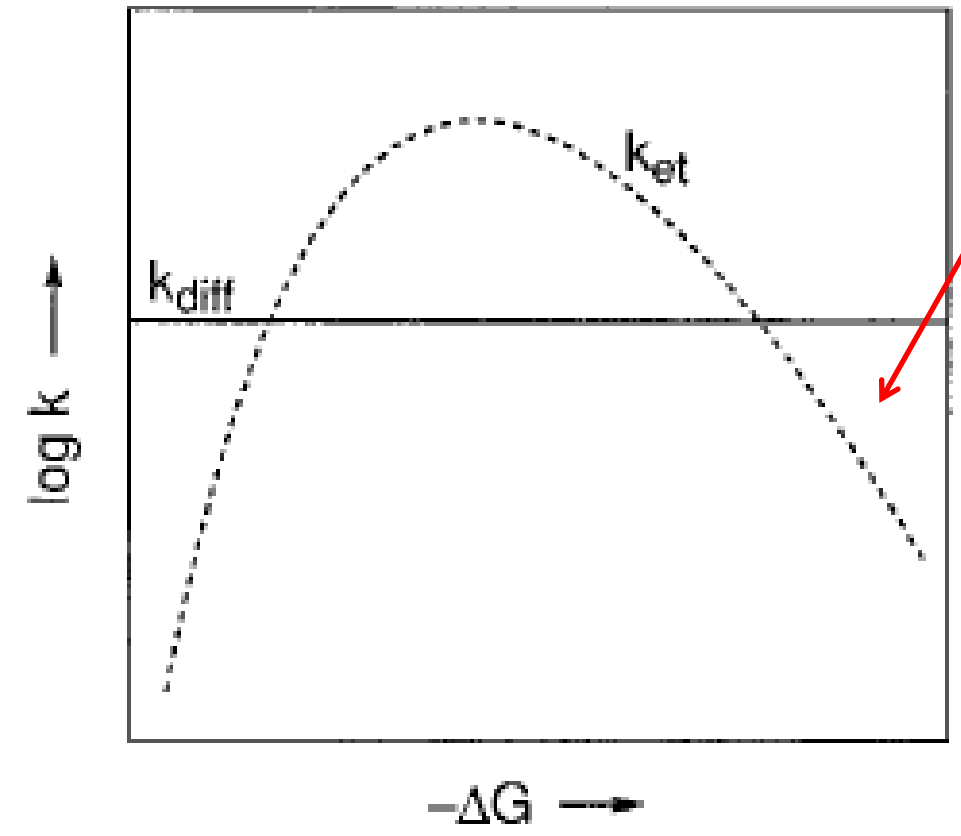
The photoreaction center of photosystem II, P680



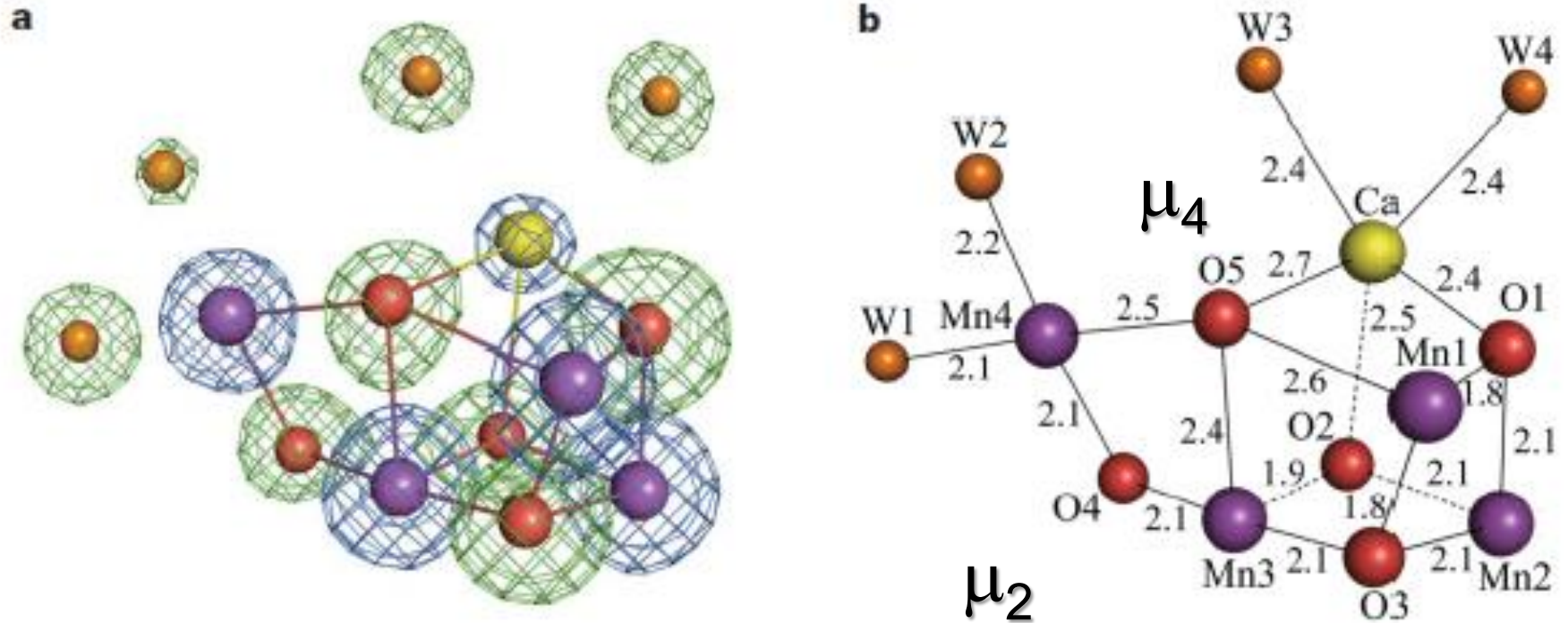
Electron transport cofactors



Marcus inverted region

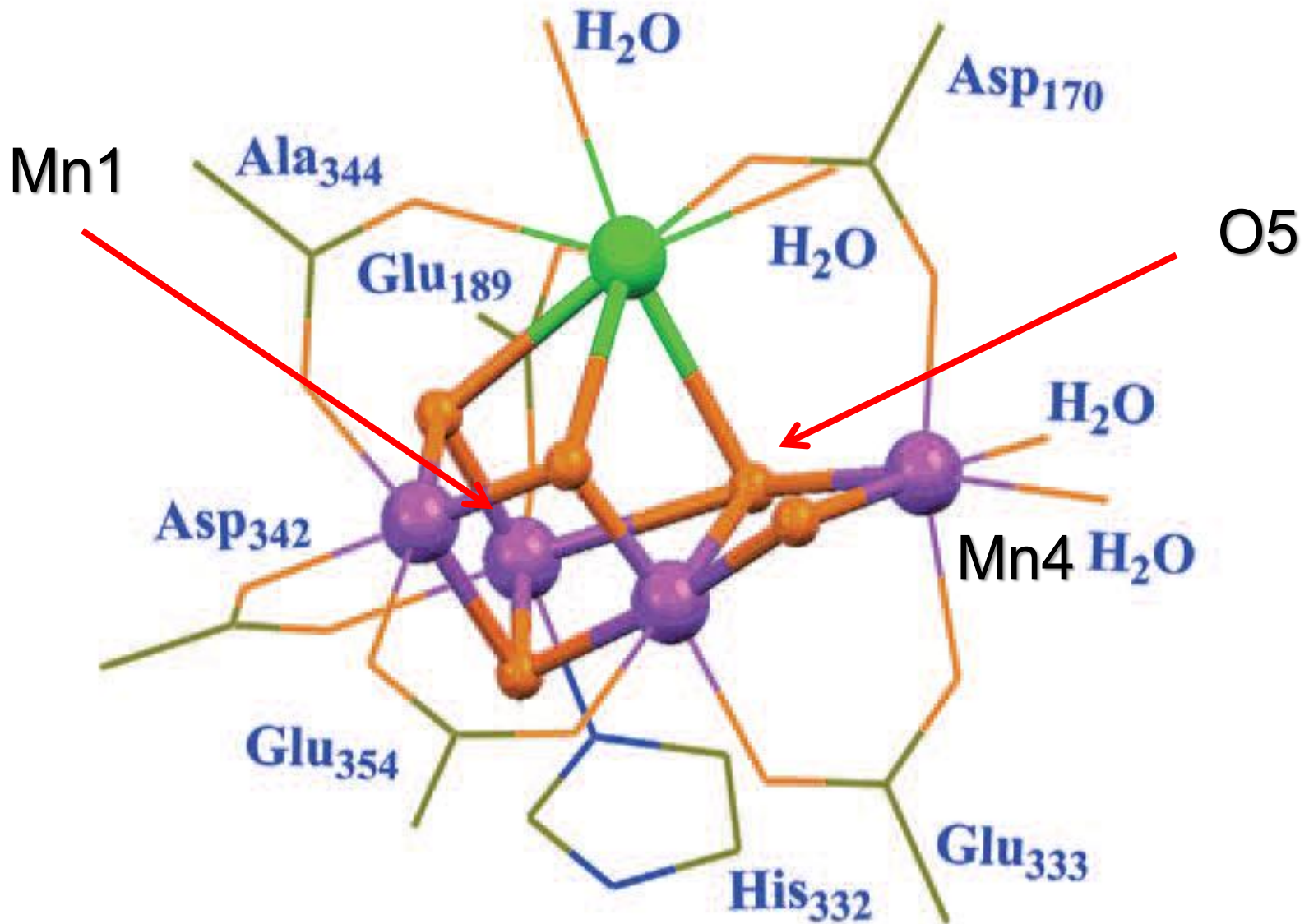


Oxygen Evolving Complex (OEC)



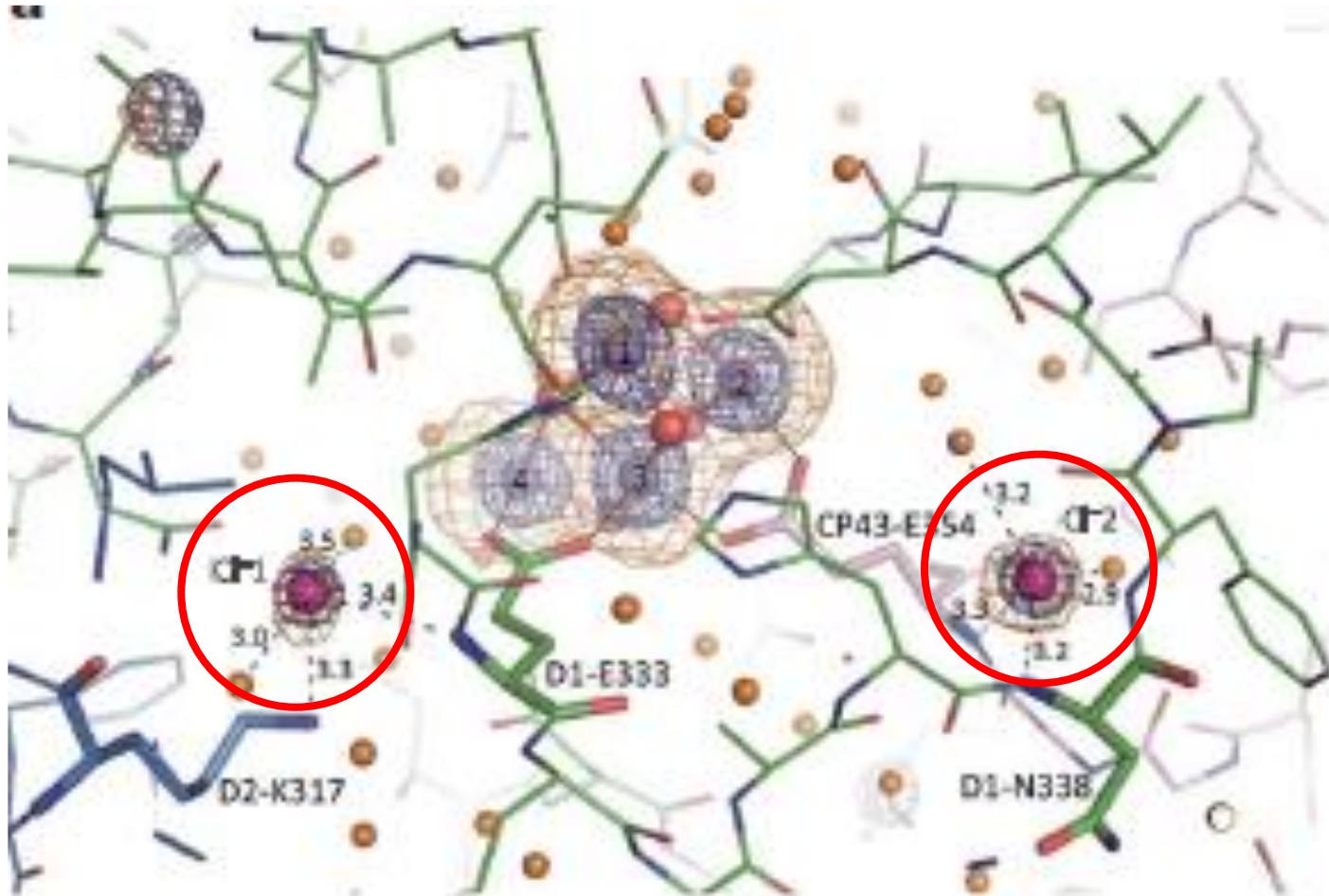
Nature 2011

Mn ions are always high spin

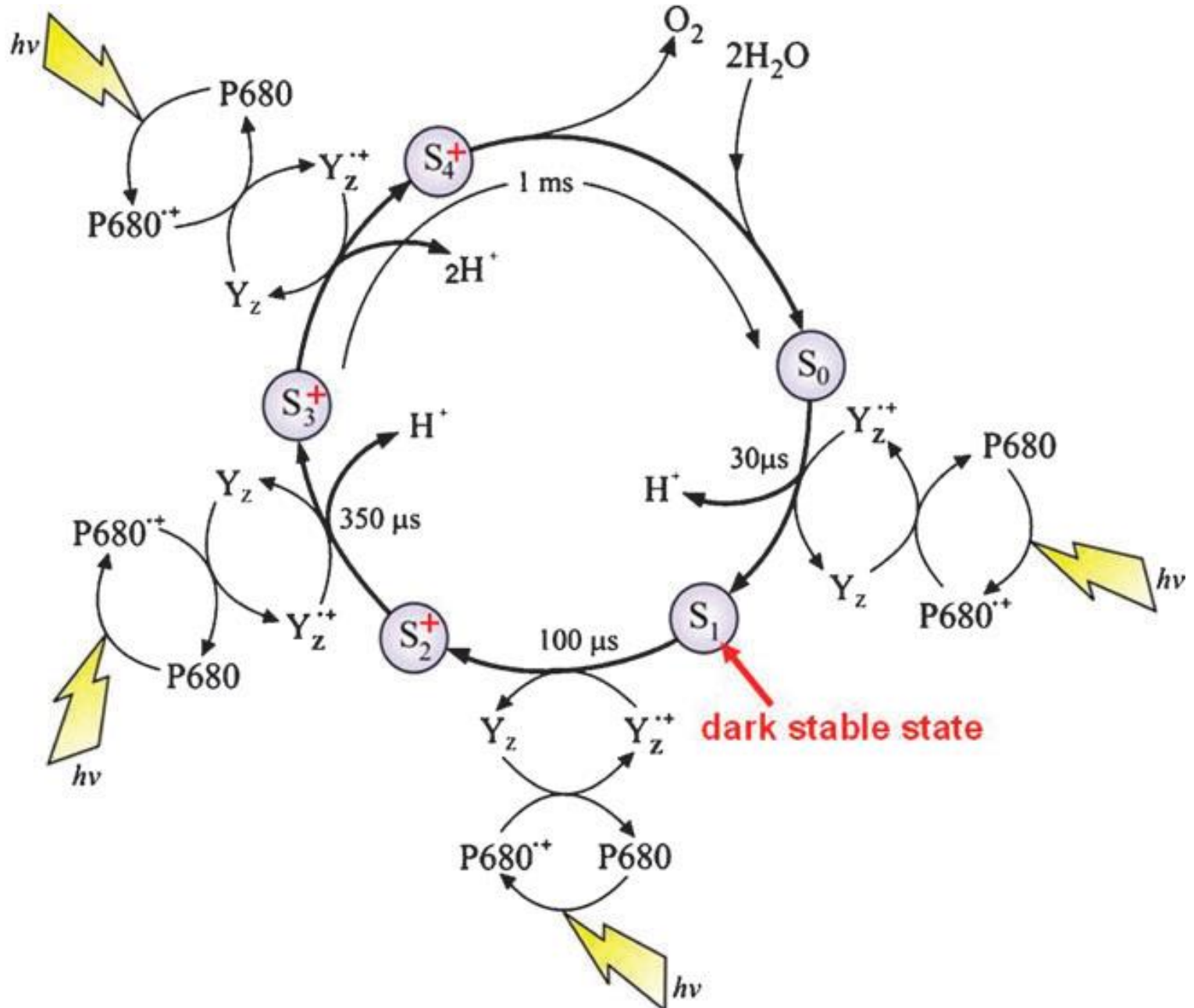


Each metal atom in OEC is coordinatively saturated (6 for Mn, 7 for Ca)

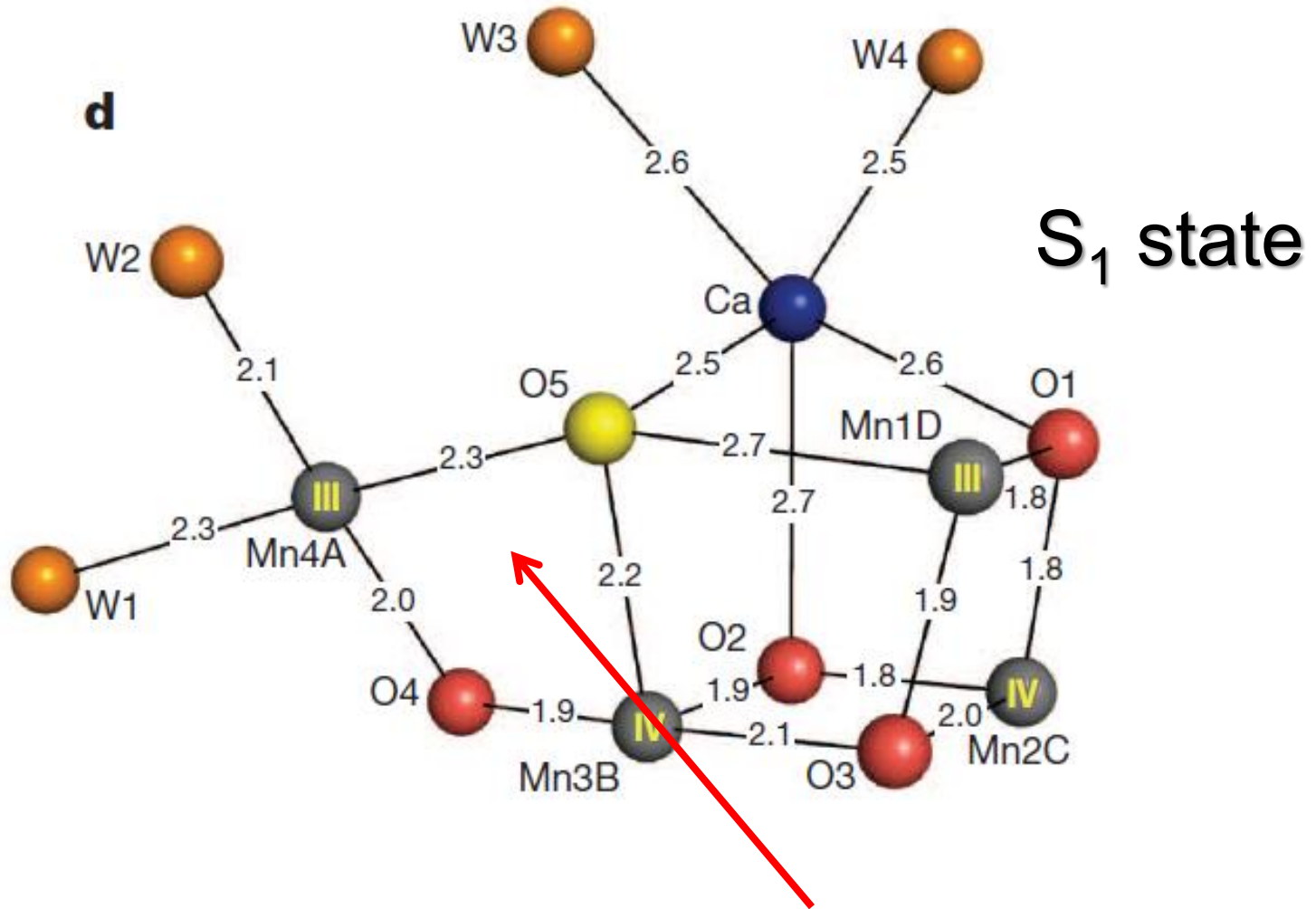
2 Chlorides



Kok cycle or *S* clock



Mn(III), d^4 , high spin \rightarrow Jahn-Teller effect

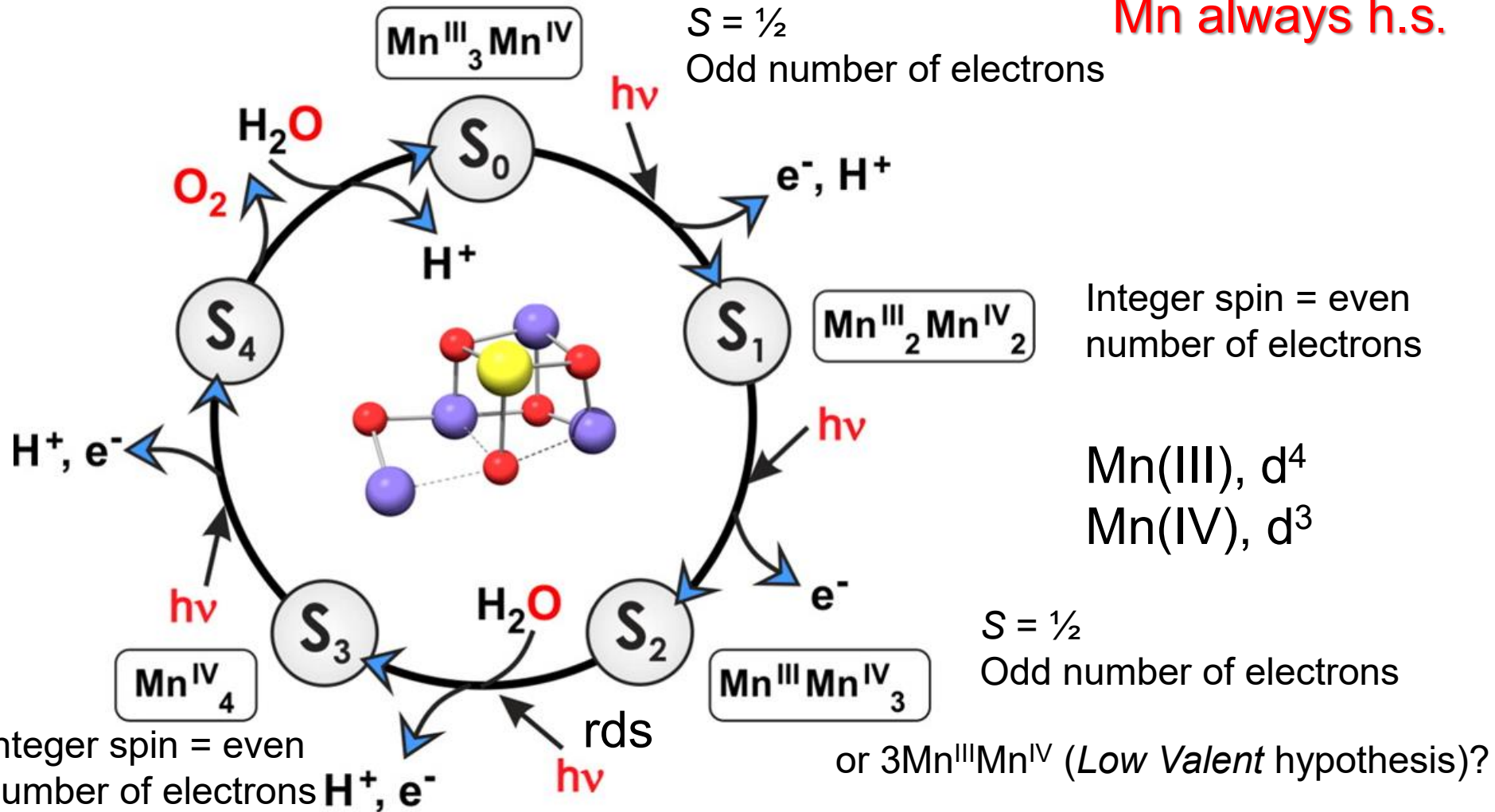


Nature 2015
X-ray free-electron laser (XFEL)

Mn4–O5 is shorter by 0.2 Å
(meaning that most likely Mn4 had been reduced to Mn(II) in previous structure)

Kok cycle or *S* clock

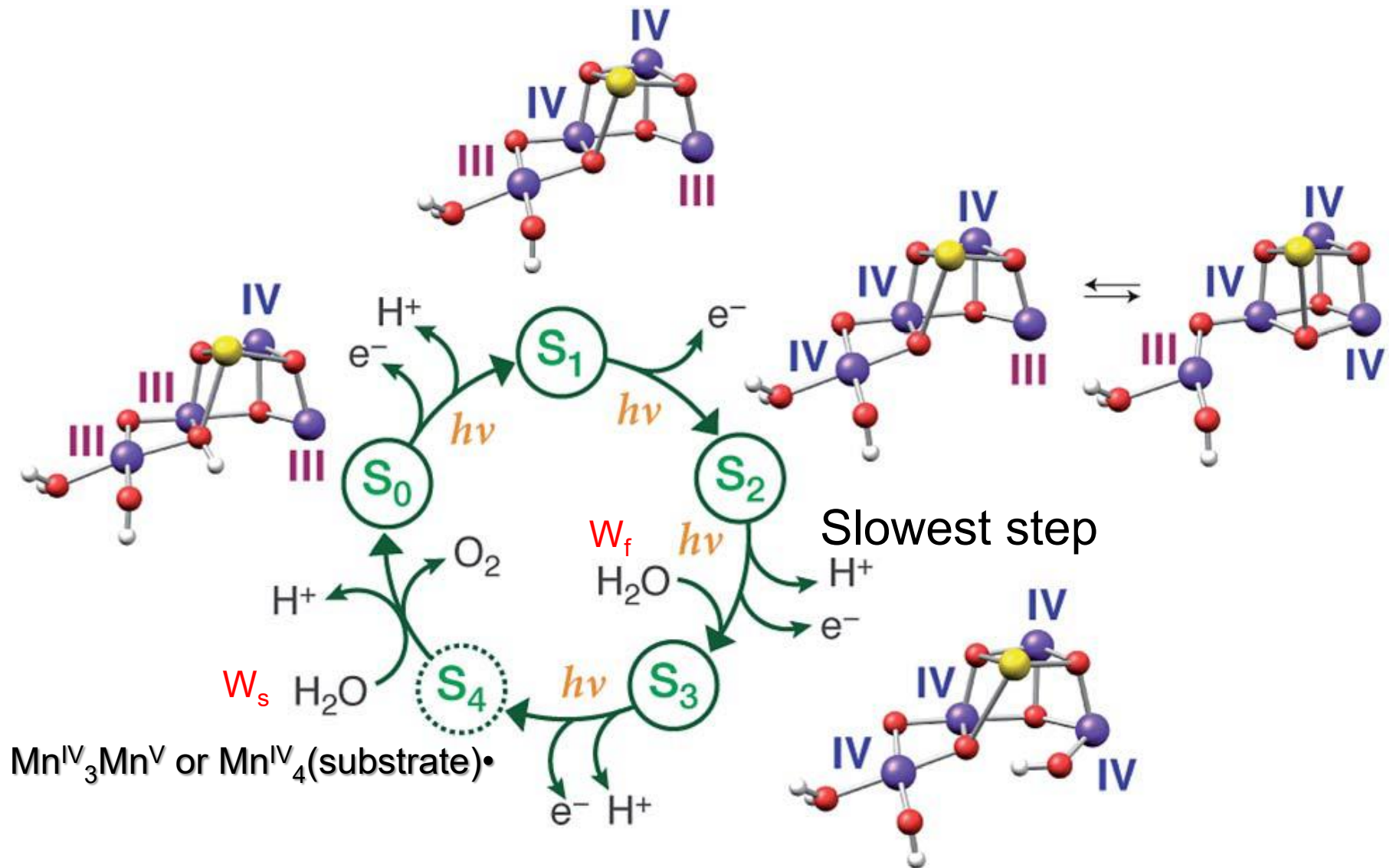
Mn always h.s.



OEC oxidizes up to 1000 molecules of H₂O (500 cycles) per second!

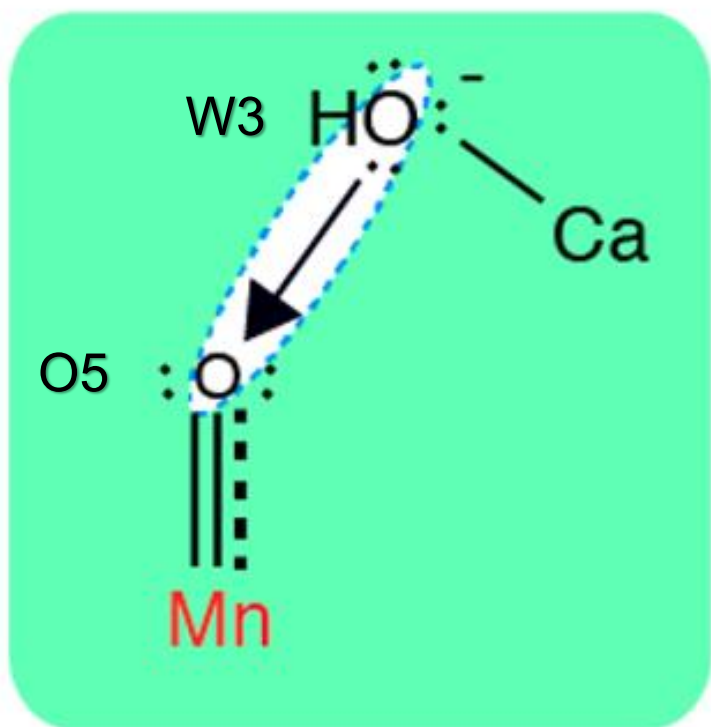
TON \approx ca. 10^6

Most accepted hypothesis

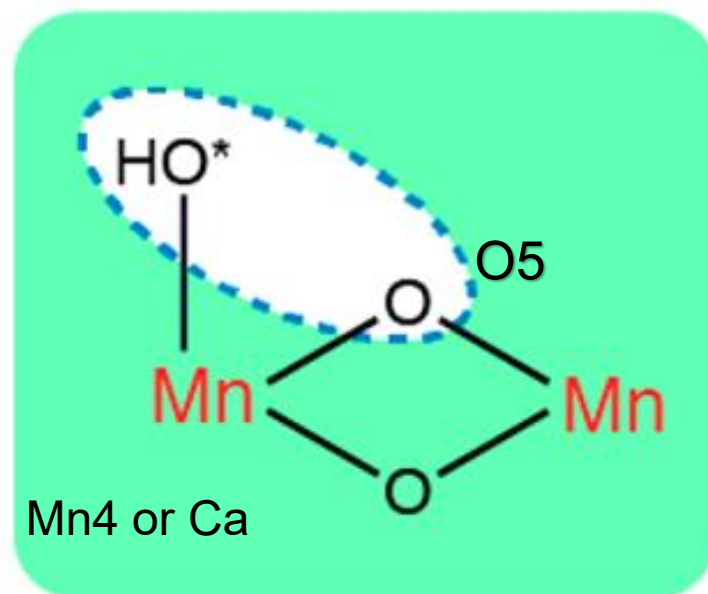


Hypotesis for the O–O bond formation

nucleophilic attack



terminal oxyl radical
with bridging oxo



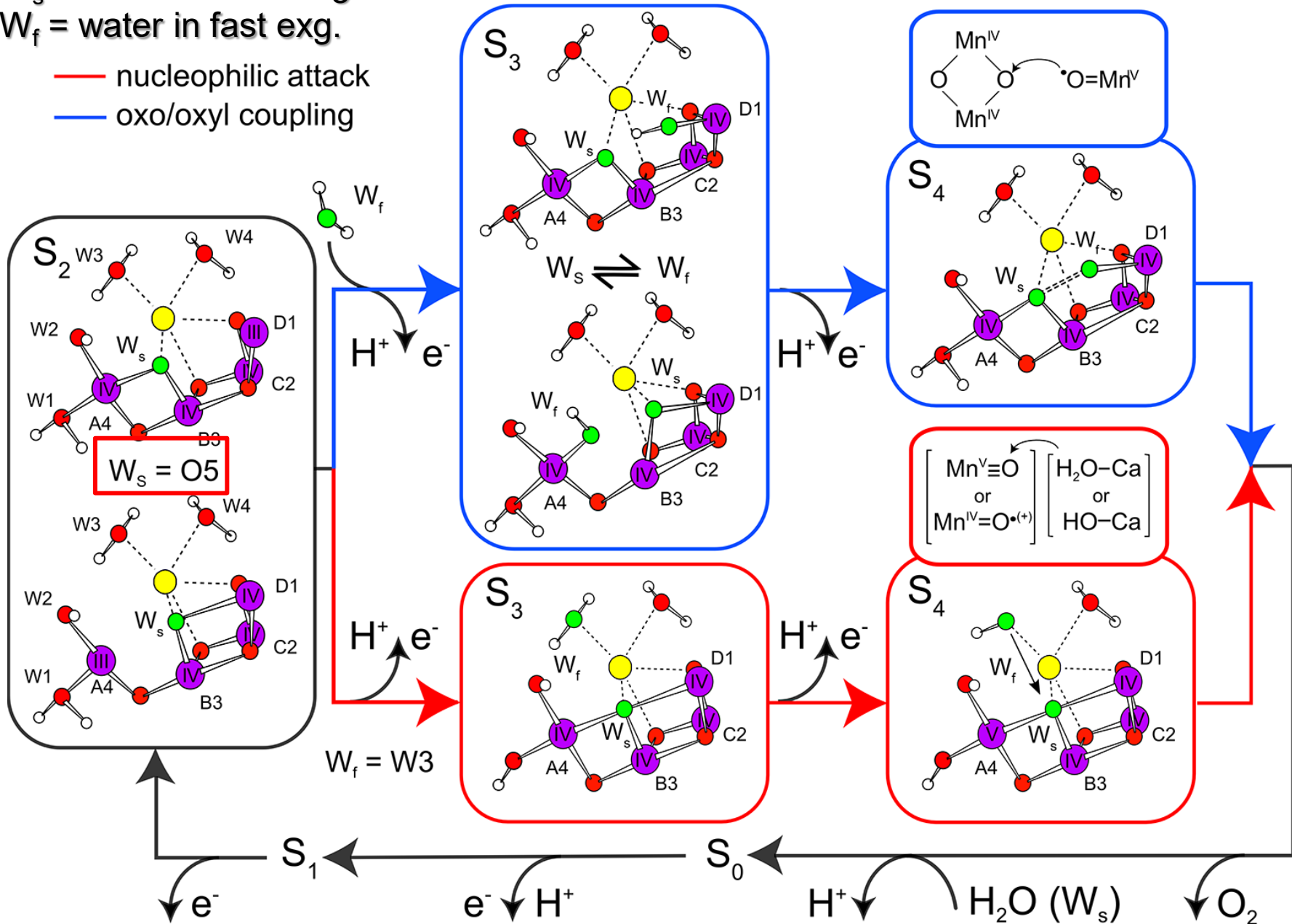
$\text{Mn(V)}\equiv\text{O}$ or $\text{Mn(IV)}=\text{O}\cdot$ *oxo/oxyl radical coupling mechanism*
In this mechanism the last electron comes from an O atom, not from Mn

W_s = water in slow exg.

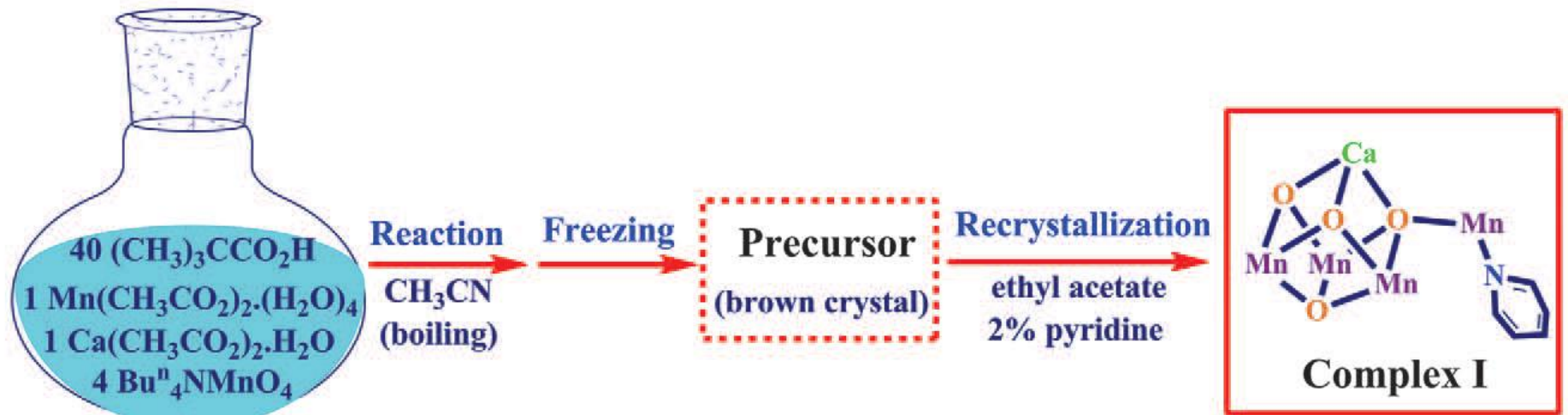
W_f = water in fast exg.

— nucleophilic attack

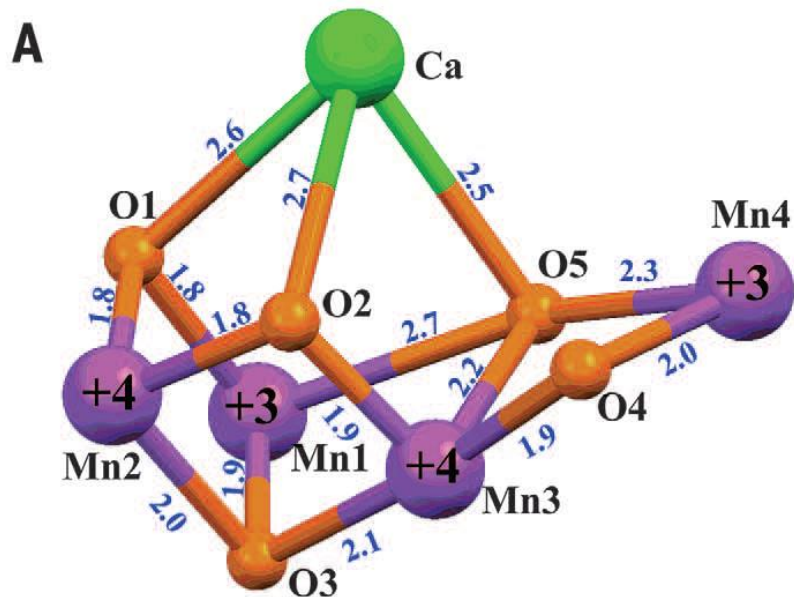
— oxo/oxyl coupling



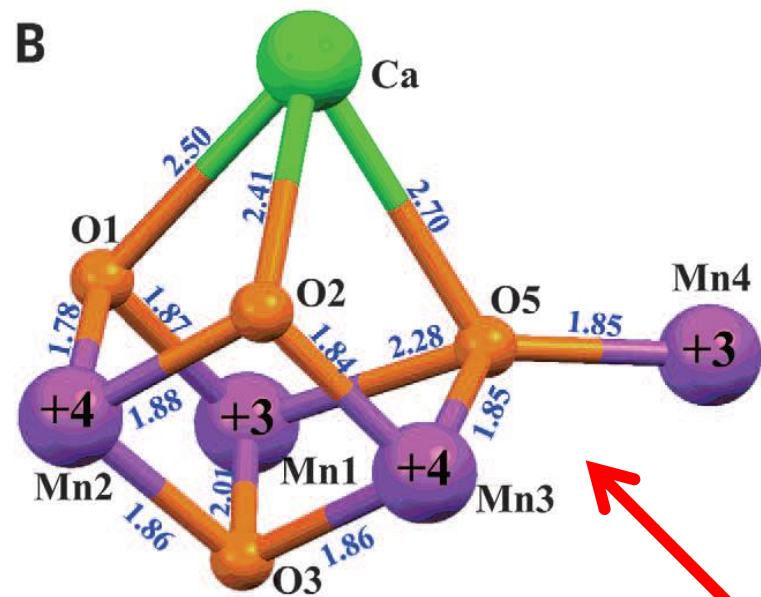
Model systems



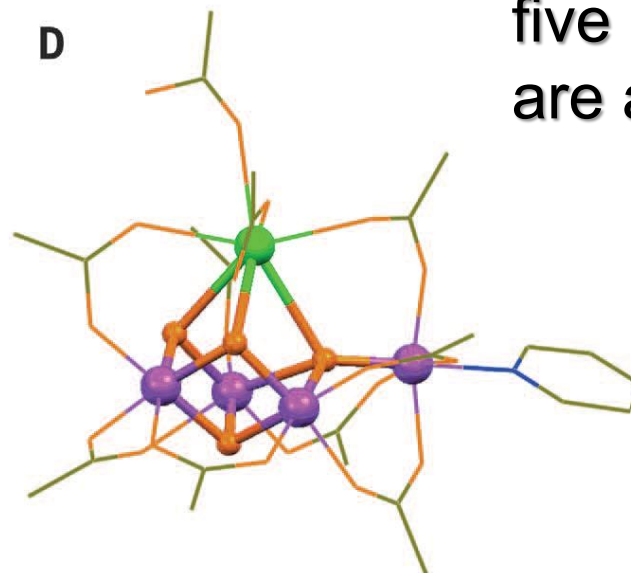
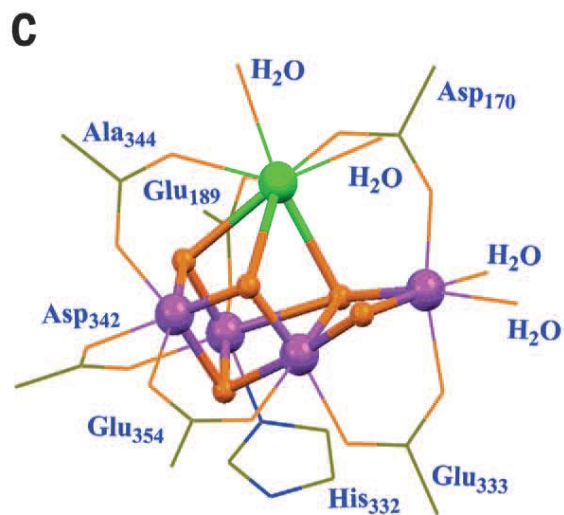
Natural catalyst



Artificial complex



five redox states
are accessible



What Mn has to do with the oxidative stress?

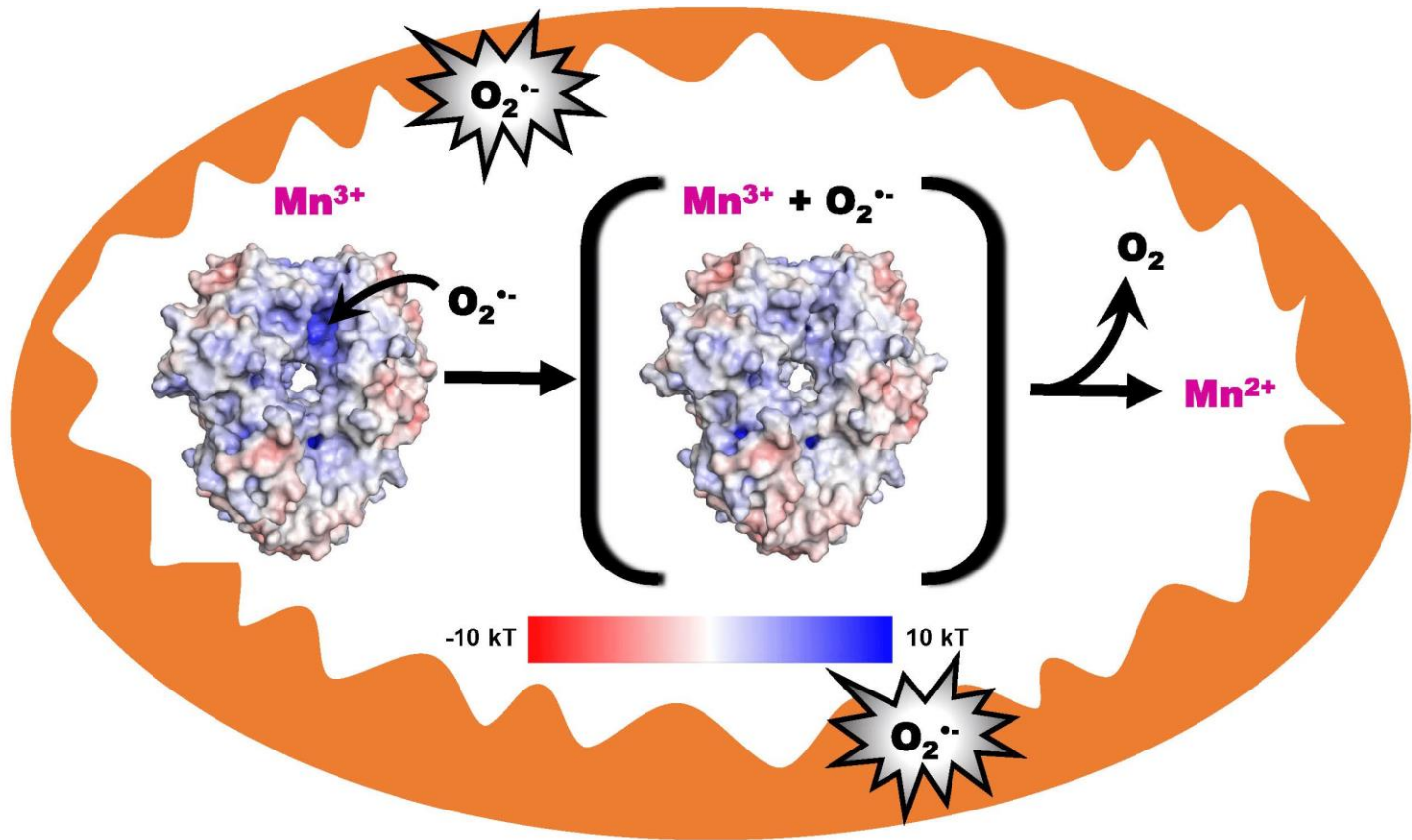


Pure Green Tea

Il tè verde *Pure Green Tea* Twinings è un pregiato **tè verde orientale** dal sapore rinfrescante e delicato, adatto per una deliziosa pausa in ogni momento della giornata.

Fonte naturale di Manganese - 0,31 mg per 100 ml di tè preparato (15% VNR) -, che contribuisce alla **protezione delle cellule dallo stress ossidativo**. Ti consigliamo di berne almeno una tazza (200 ml) al giorno, consumata nell'ambito di una dieta varia ed equilibrata e di uno stile di vita sano, di cui ti ricordiamo l'importanza.

Mn SOD



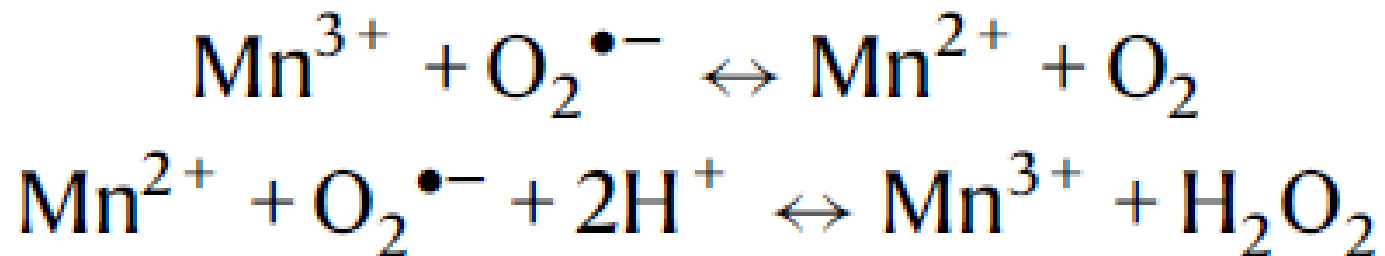
MnSOD is a homotetramer localized exclusively in the mitochondrial matrix.

MnSOD has one of the fastest and most efficient reaction rates of all enzymes, with a k_{cat} of 40.000 s^{-1}

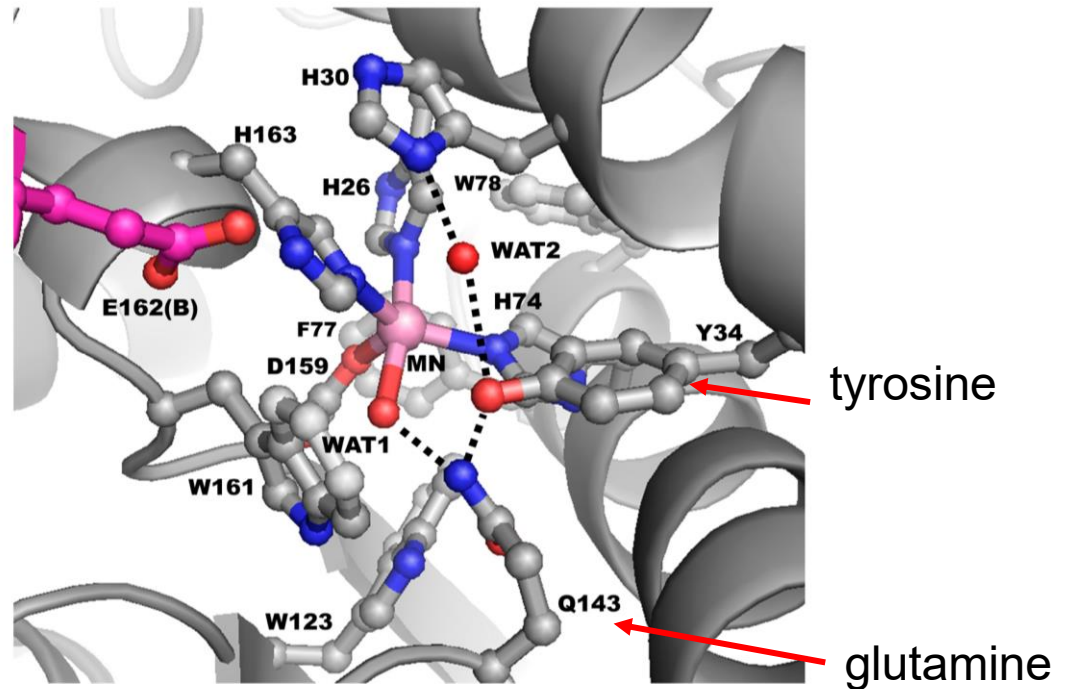
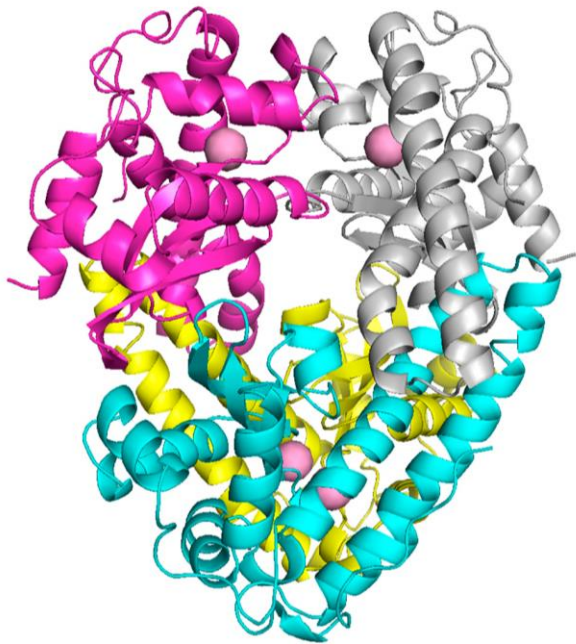
The mitochondrial matrix is an organelle compartment with a high rate of endogenous superoxide generation.

Electrons leak from the electron-transport chain and perform a one-electron reduction of diatomic oxygen to form superoxide.

The ability of MnSOD to decrease superoxide levels in the mitochondria is associated with longevity of eukaryotic organisms.



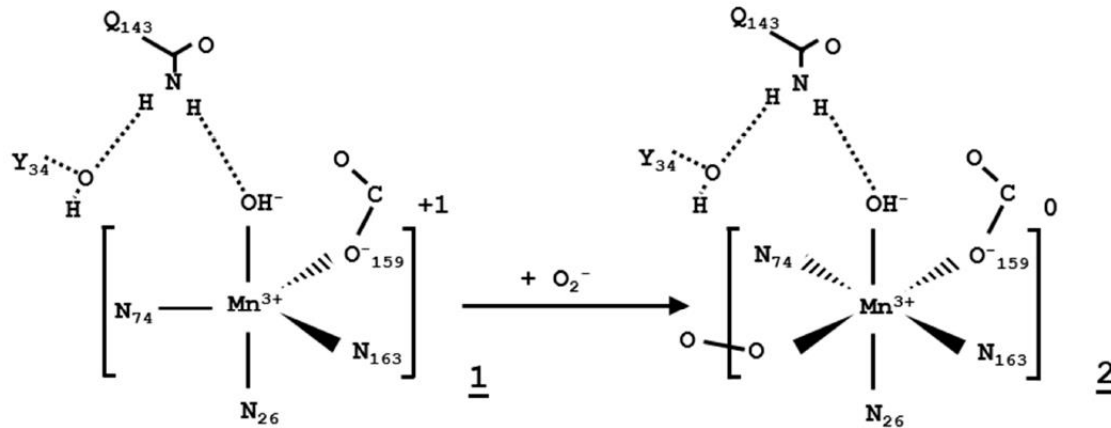
Human MnSOD functions as a homotetramer, with each subunit containing an active site surrounding a manganese ion. The metal is coordinated by His26, His74, His163, Asp159, and a single oxygen-containing molecule (denoted WAT1), thought to be either H_2O or OH^-



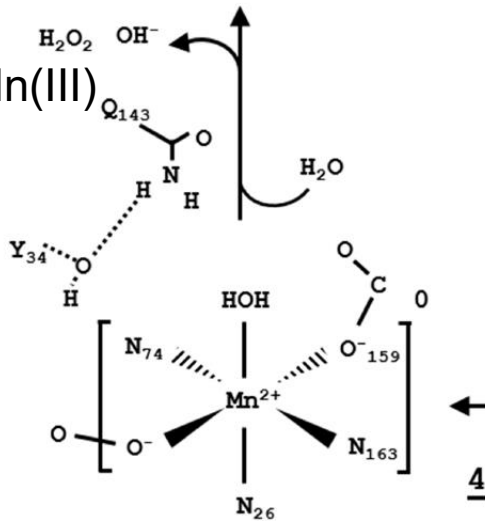
The active site of human MnSOD is within a cavity formed by two adjacent subunits.

The substrate most likely binds to the manganese ion in the position opposite Asp159.

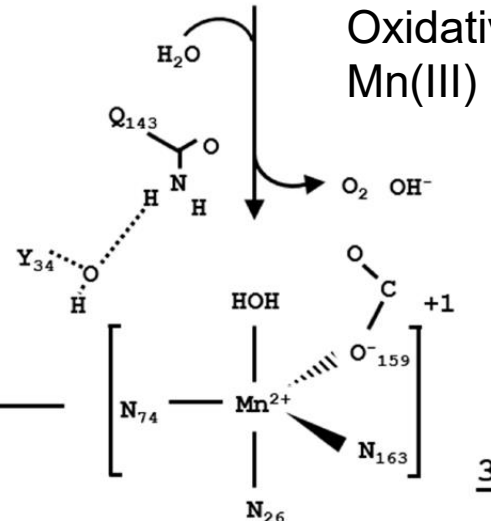
The proposed 5-6-5 mechanism



Reductive step
Mn(III) oxidized to Mn(II)



Oxidative step
Mn(III) reduced to Mn(II)



For MnSOD to perform its enzymatic function efficiently it must shuttle protons to the active site for proton-assisted electron transfer (PCET) in a systematic manner.