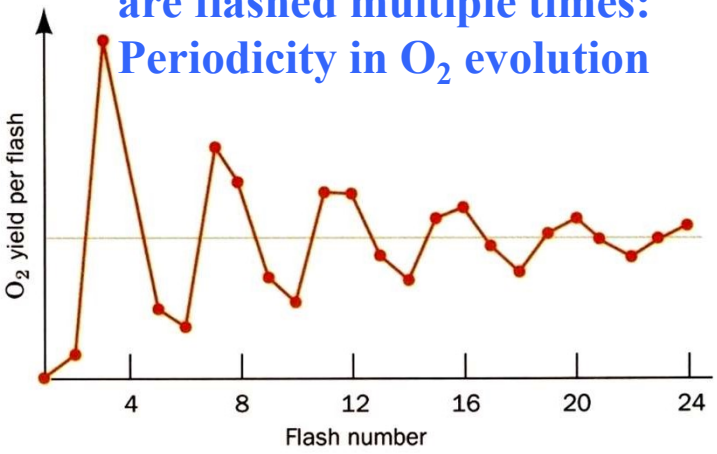
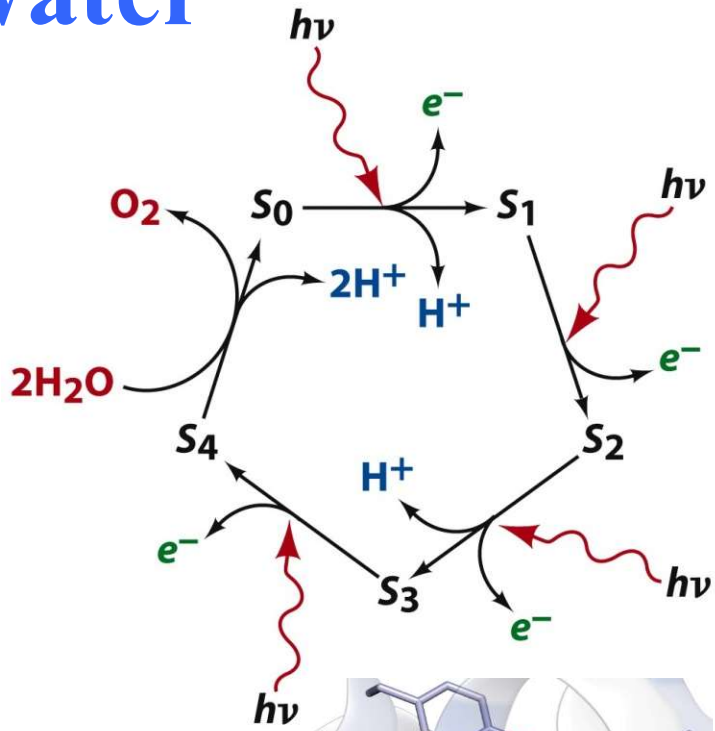
How PS II cracks water

When dark-adapted chloroplasts are flashed multiple times: Periodicity in O_2 evolution

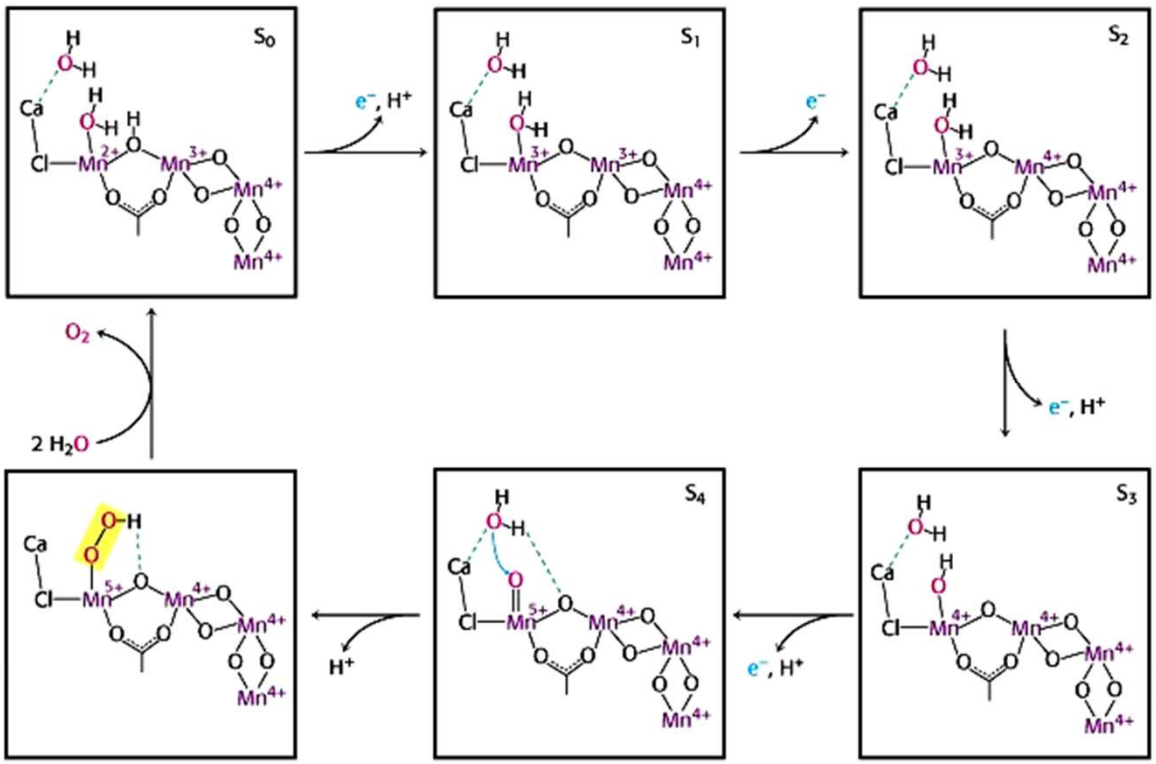


Conclusions:

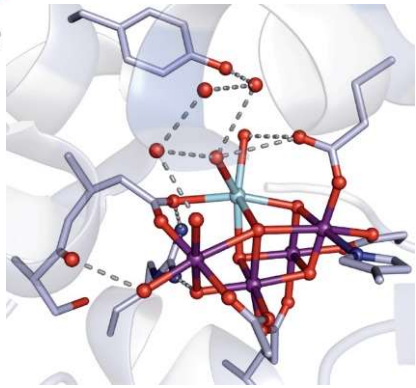
- There must be 4 distinct states that absorb a photon: S_0 to S_3 (= number of e^- removed) ;
- in the fifth state, S_4, O_2 is released;
- each O_2 molecule is produced by a single photosystem



At the heart of the action: A Mn(II/III/IV/V) containing oxygen-evolving complex (OEC):



Refined model:



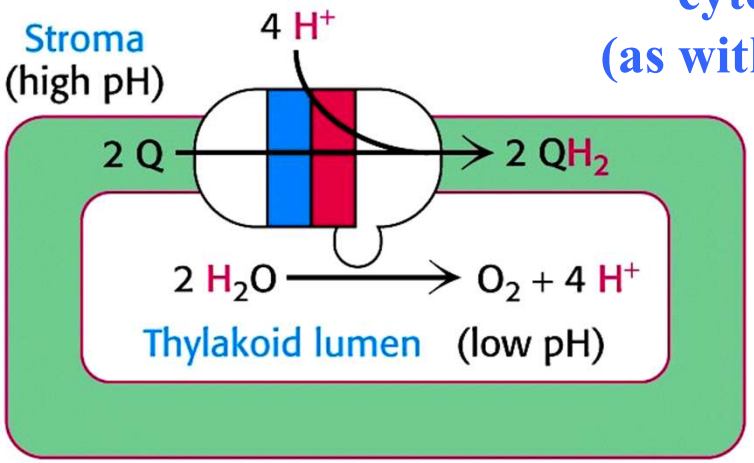
The OEC is oxidized, one electron at a time, until two bound H_2O are linked to form an O_2

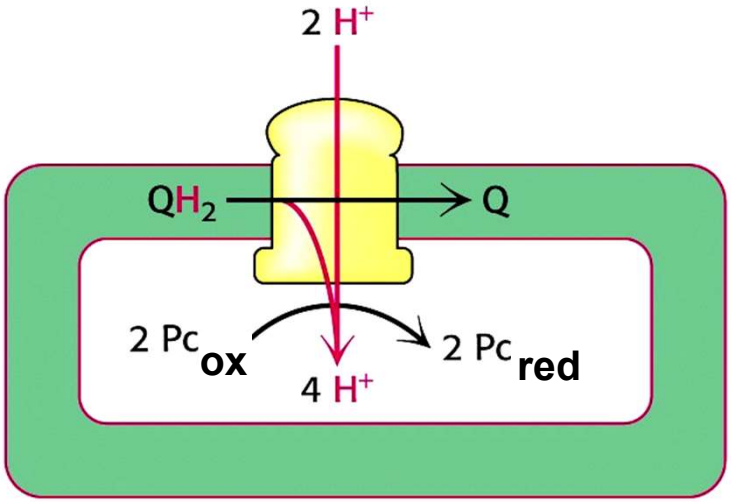
H^+ and Electron Transport in Photosynthesis

1.) PS II in summary:

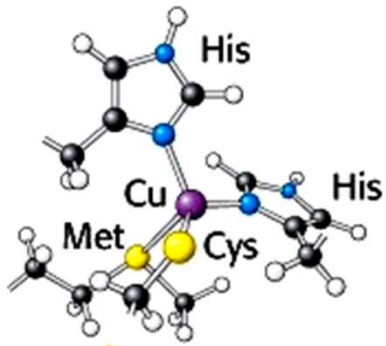
2.) Re-oxidation of plastoquinone by the cytochrome b_6f complex: A Q cycle (as with Complex III of Oxid. Phosphor.)!

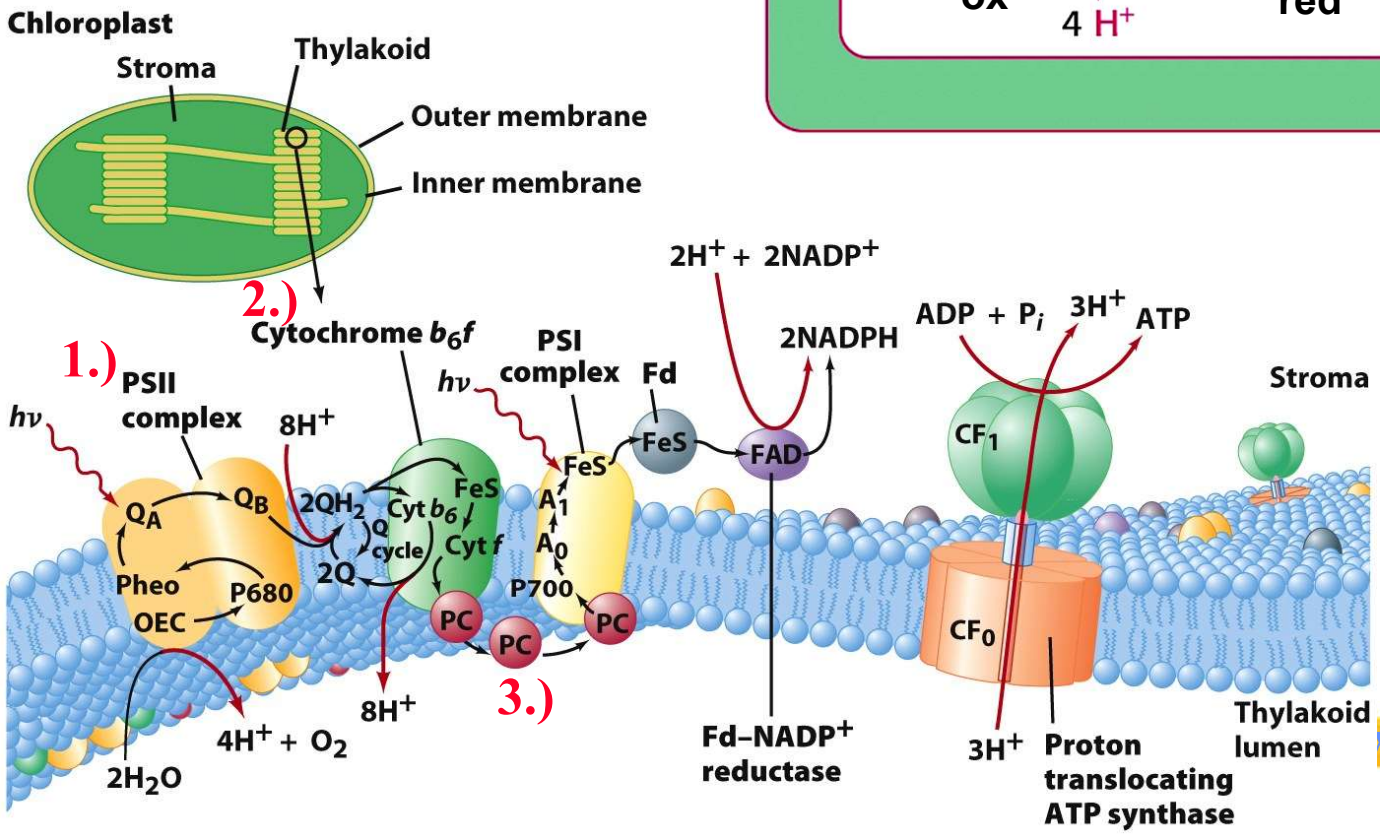
3.) The next e^- carrier: Plastocyanine (PC)

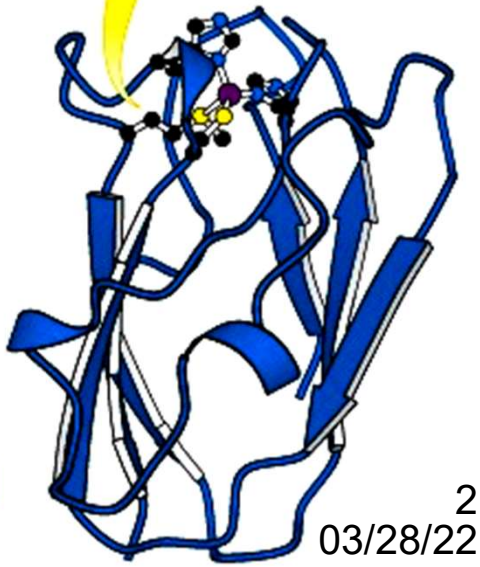




Cu(II) has a high $E^{0'}$ = 0.37V (normal: 0.16V) due to strained tetrahedral (Cu(I)-like!) ligand sphere

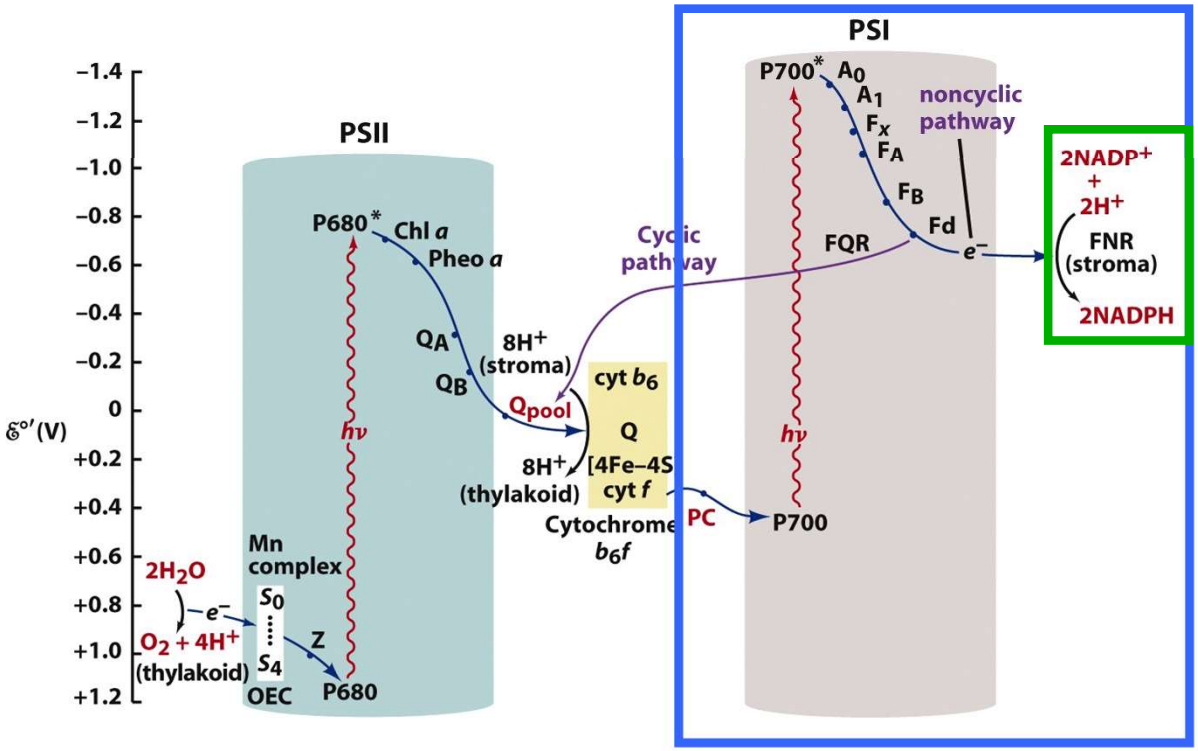




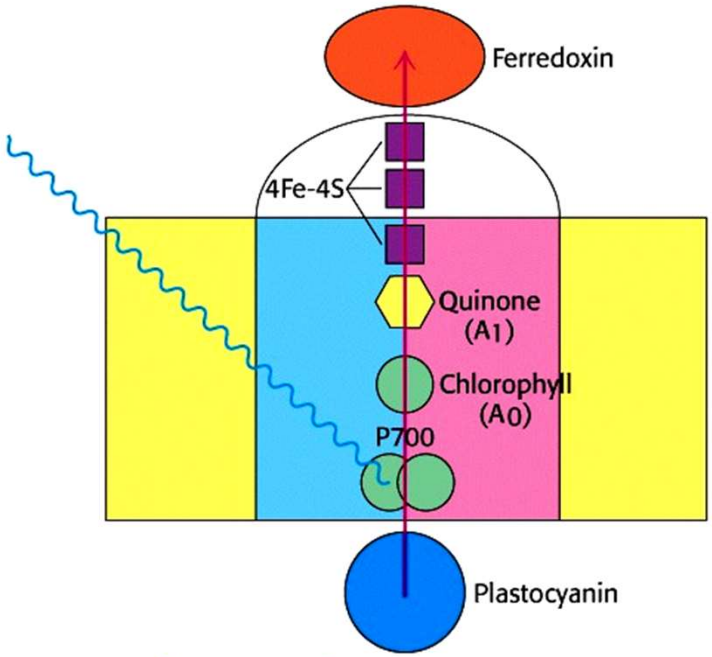


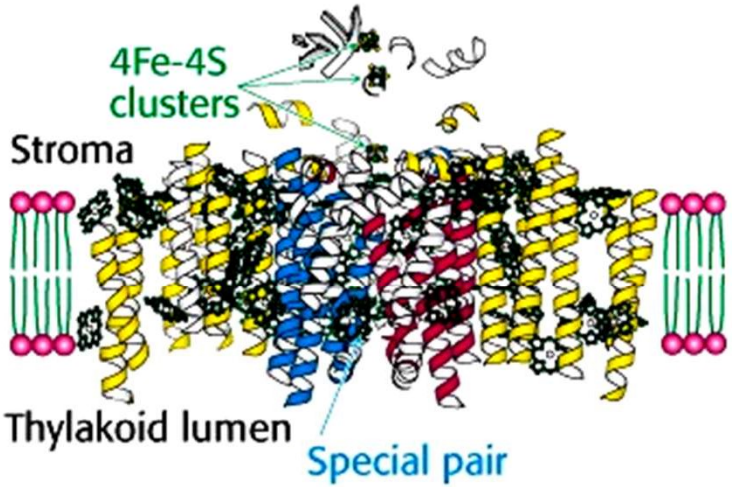
Valter:

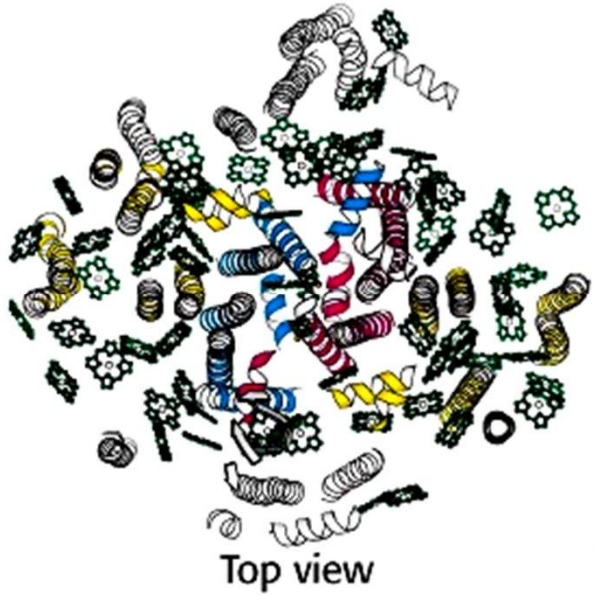
Photosystem I of Plants



PS I uses light to elevate e⁻ further to reduce ferredoxin (Fe-S cluster protein)



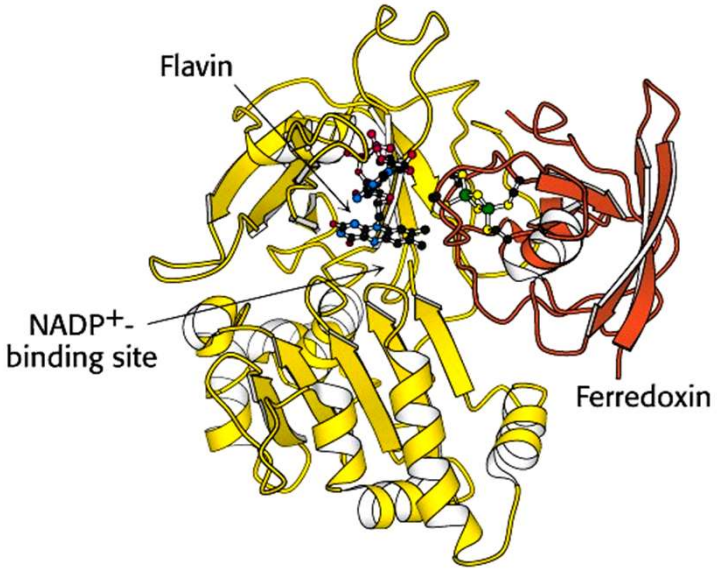


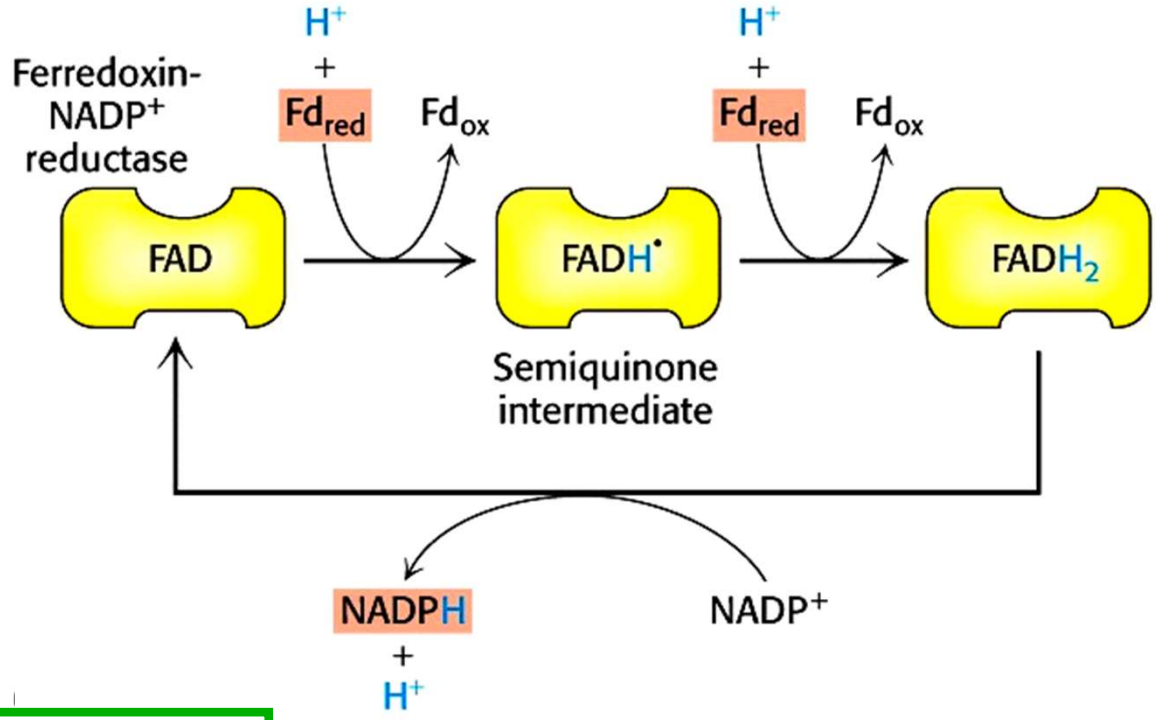


- forms trimers;
- one trimer of the plant photosystem I contains ~200 chlorophyll a (Chl a) molecules;
- also contains "special pair" of Chl a = P700;
- evolutionarily distinct from PS II and bacterial photoreaction center of purple photosynthetic bacteria

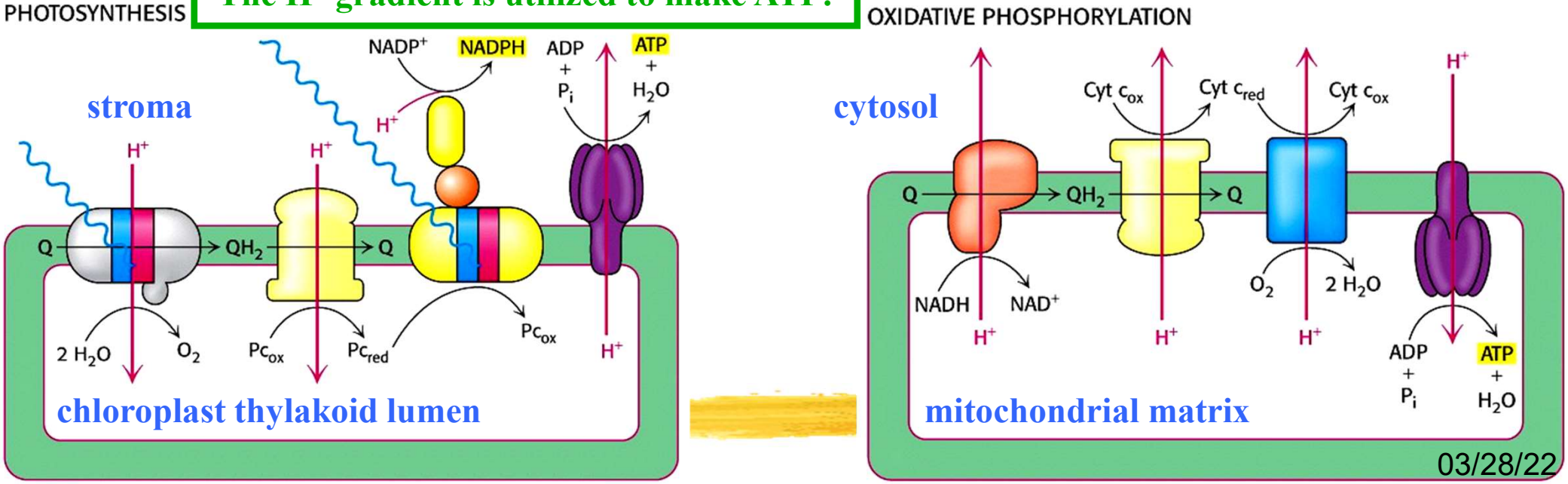
The Final Steps: Making NADPH and ATP

Ferredoxin-NADP$^+$ reductase:

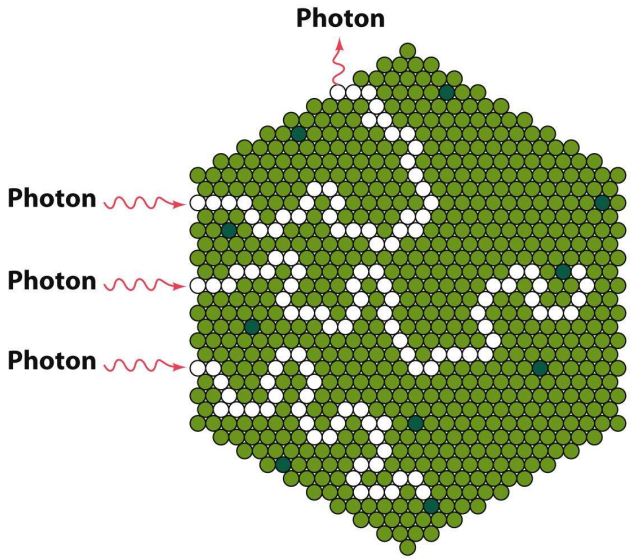




The H$^+$ gradient is utilized to make ATP:



Light Harvesting, Segregation, Regulation



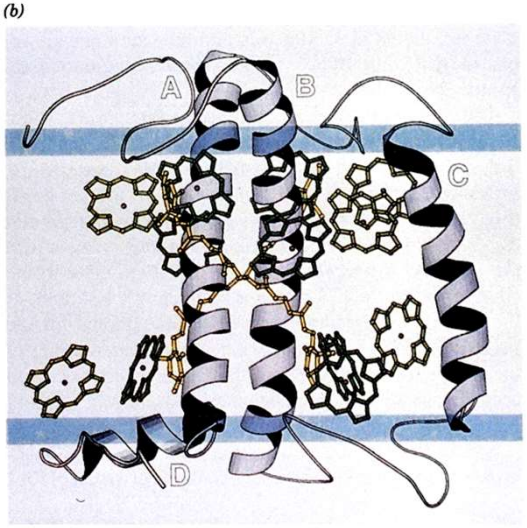
➢ **LHC-II:**

♣ most abundant protein in chloroplast membranes;

♣ 26kD subunit, forms trimers;

♣ binds 7 Chl a + 6 Chl b (= half the chlorophyll in the biosphere), 2 carotenoids;

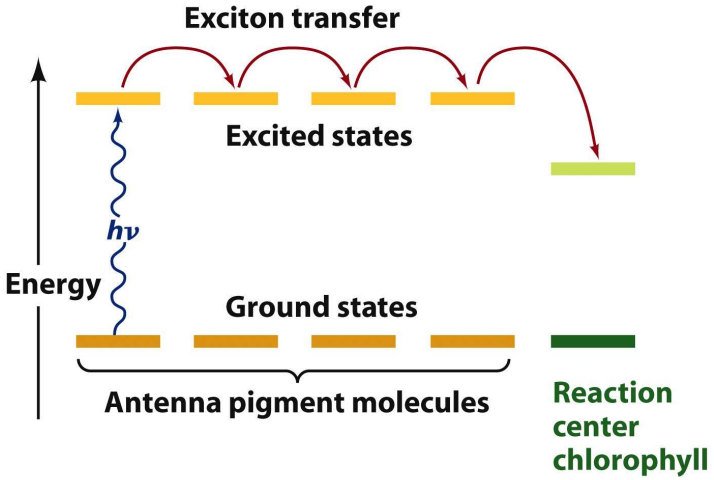
♣ also prevents e^- transfer to O_2



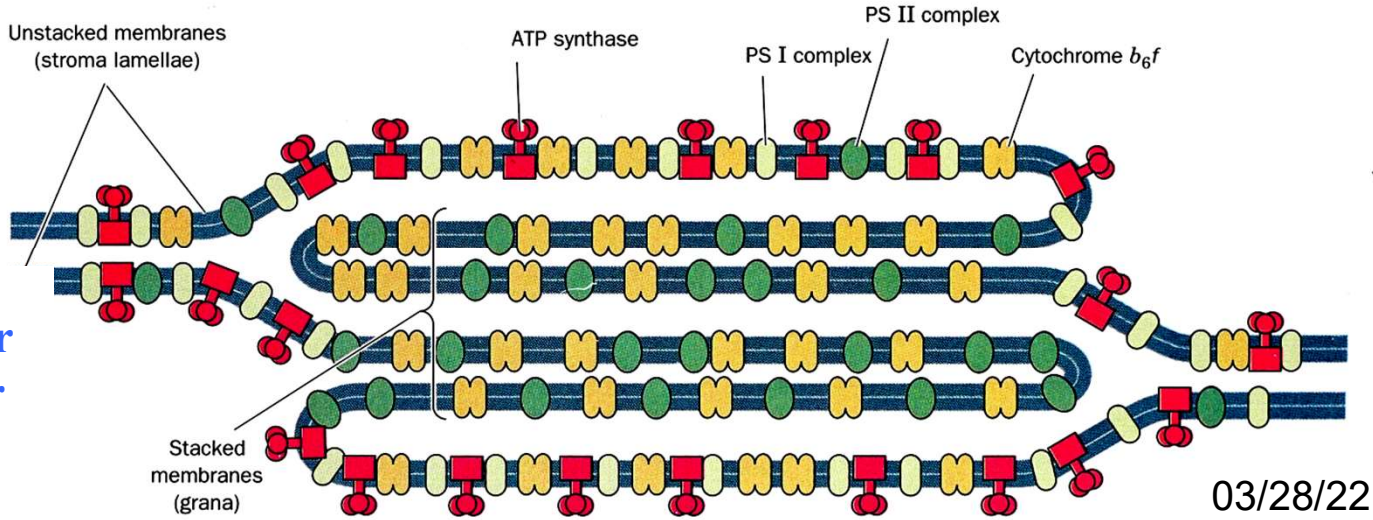
➢ **PS II and PS I are physically separated between stacked grana and unstacked lamellae, respectively:**

♣ otherwise energy transfer from PS II (P680) to PS I (P700);

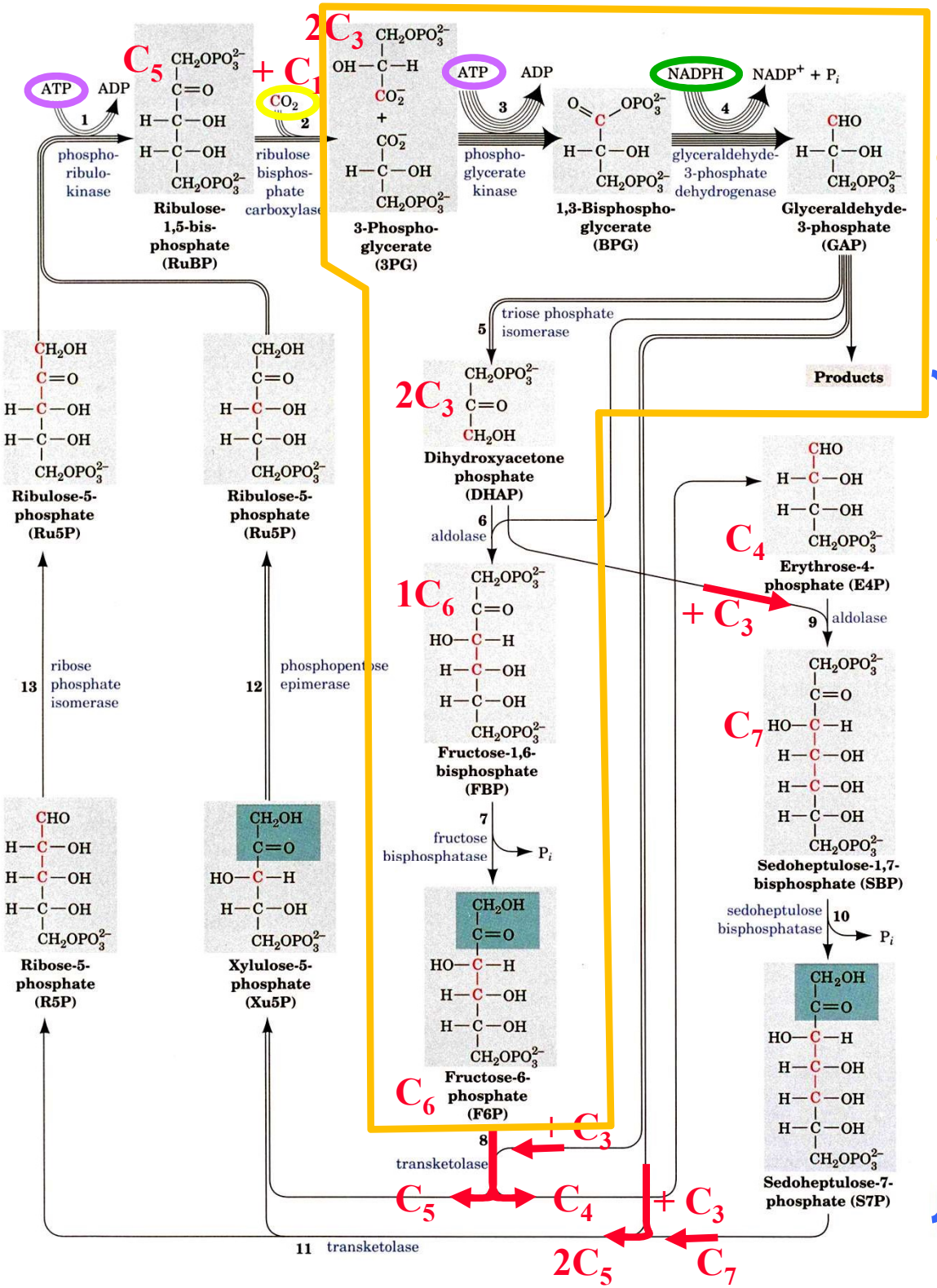
♣ allows regulation:
under high illumination, PS II absorbs more light than PS I ⇒ QH_2 dominates ⇒ activates kinase to phosphorylate LHC, which moves to unstacked region to bind to PS I, sensitizing it;
under low illumination, the opposite happens



➢ <u>Light-harvesting complexes</u> (LHCs) act as antennae to transfer photon energy to a reaction center in 10^{-10} s with 90% efficiency



The Dark Reactions: The Calvin Cycle



Overall stoichiometry: $5C_3 \rightarrow 3C_5$