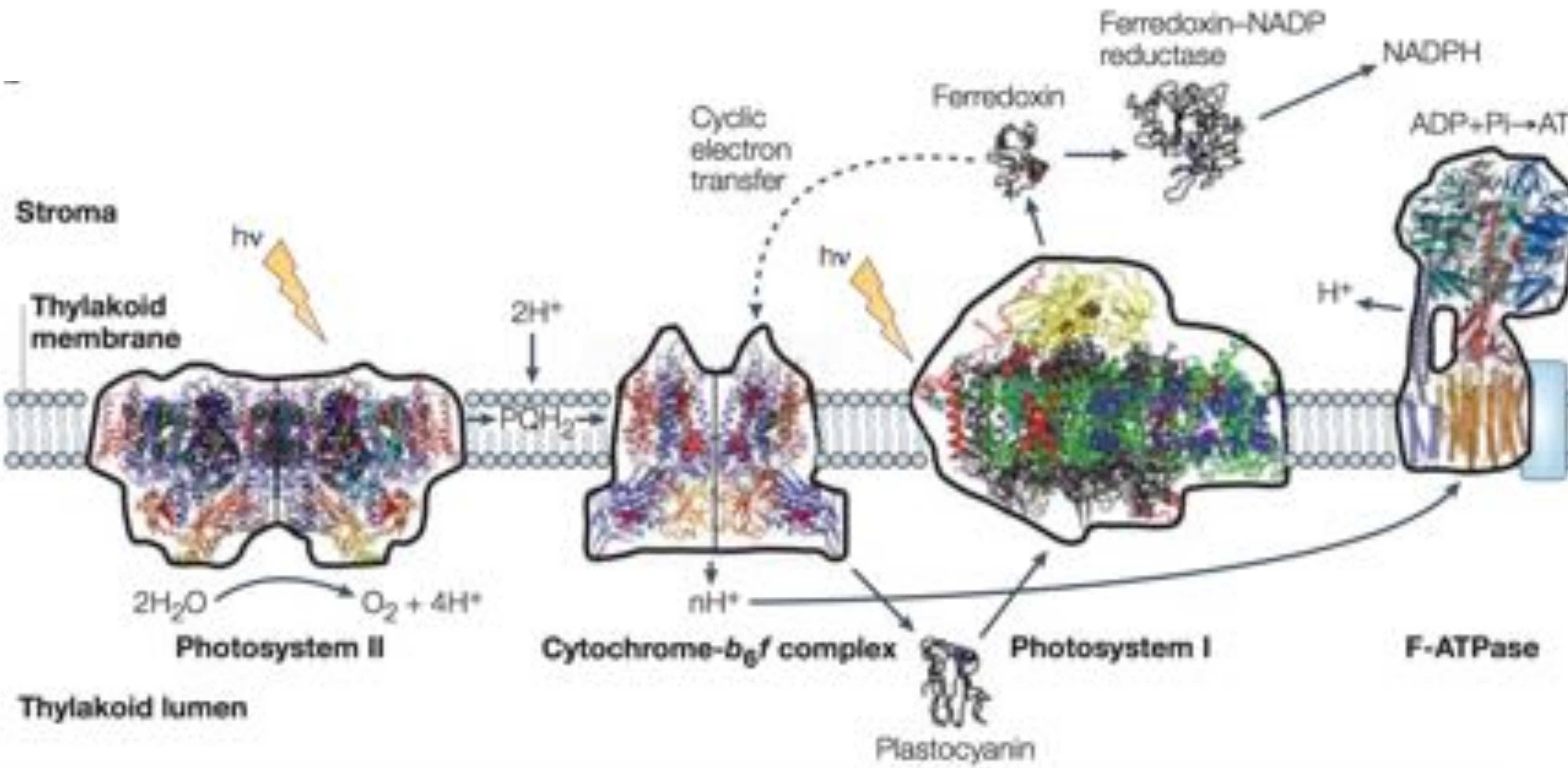
Photosynthesis – An Organic Chemists Guide



Photosynthesis – An Introduction

Photosynthesis

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

- 100 billion tons of CO_2 fixed per year – Humans produce 36 billion tons
- Carbohydrates and oxygen required for survival of all higher life forms
- Photosynthetic organisms first evolved 3.5 billion years ago
- CO_2 reduction is light independent.
- H_2O oxidation is light dependent.

Photosynthesis – An Introduction

Photosynthesis

A bit closer to reality…

Water Splitting

$$H_2O + 2\ \text{Plastoquinone (PQ)} \xrightarrow[h\upsilon]{\text{Photosystem II}} O_2 + 2\ H_2PQ$$

$$2\ \text{Plastocyanin} + 2\ PH_2Q + PQ \xrightarrow{\text{cyctochrome-}b_6f} 2\ \text{Plastocyanin}^{-1} + 2\ PQ + PH_2Q$$

$$2\ \text{Plastocyanin}^{-1} + \text{Ferrodoxin} \xrightarrow[h\upsilon]{\text{Photosystem I}} 2\ \text{Plastocyanin} + \text{Ferrodoxin}^{-2}$$

$$NADP^{+} + \text{Ferrodoxin}^{-2} \xrightarrow[\text{reductase}]{\text{Ferrodoxin NADP}} NADPH + \text{Ferrodoxin}$$

CO2 Reduction

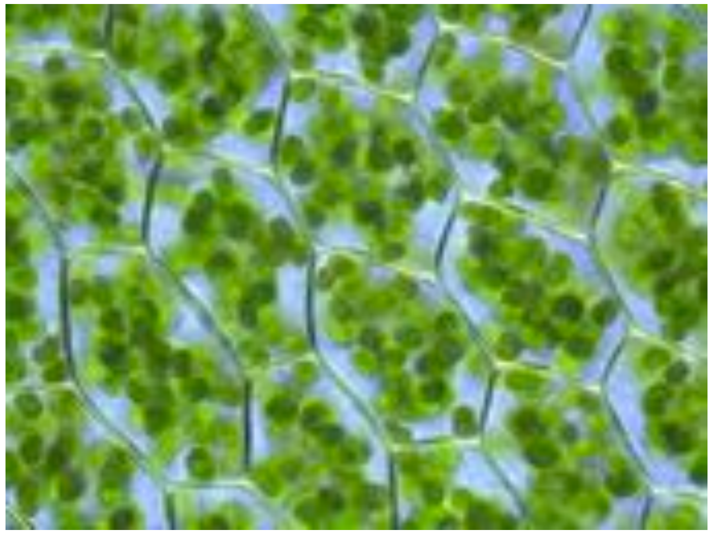
$$12\ NADPH + 6\ CO_2 + 18\ ATP \xrightarrow{\text{Calvin Cycle}} 12\ NADP^{+} + C_6H_{12}O_6 + 18\ ADP + 6\ H_2O$$

Photosynthesis – An Introduction

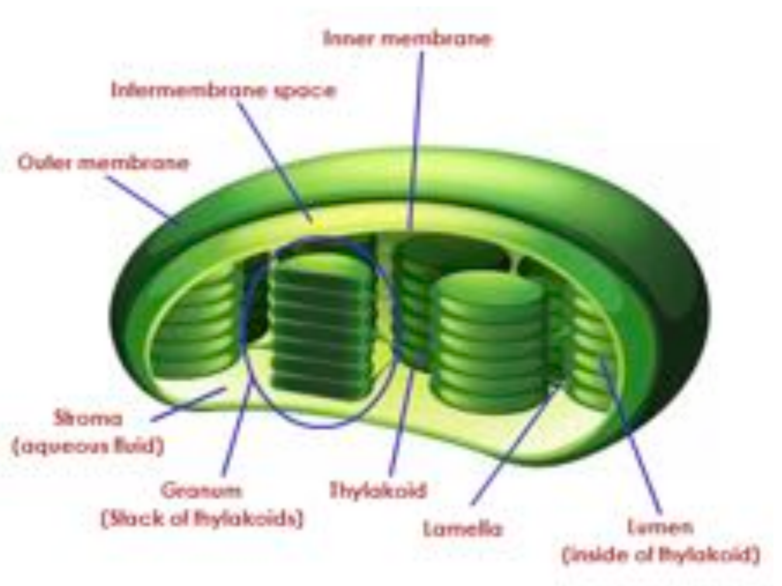
Contents

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Tabita, R. F. *et al. Microbio. Mole. Bio. Revs.,* **2007,** 576–599.

Photosynthesis – Some Cell Biology



The Chloroplast



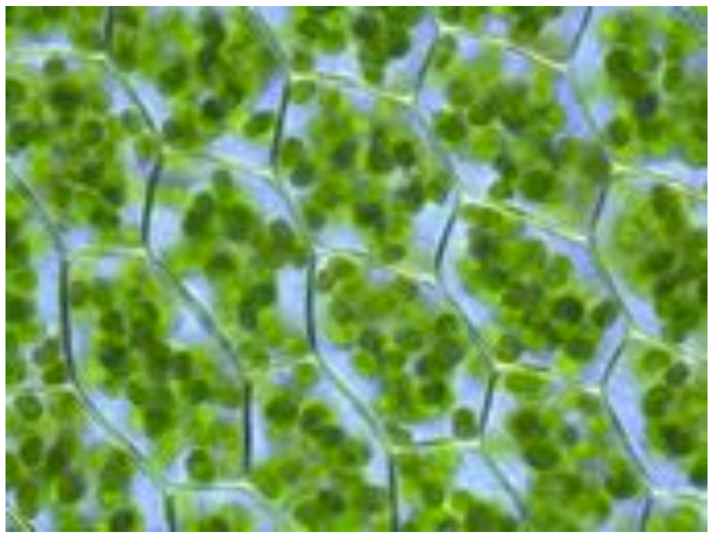
Site of photosynthesis in higher plants

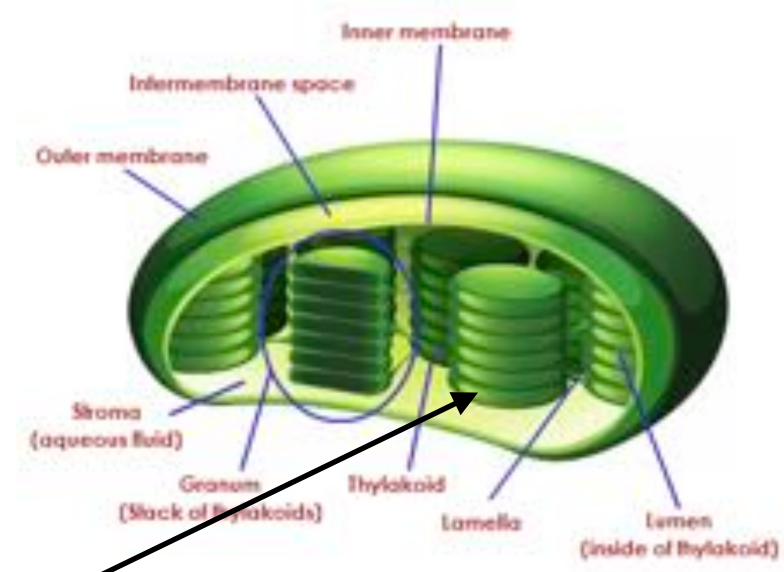
Like Mitochondria they contain their own DNA

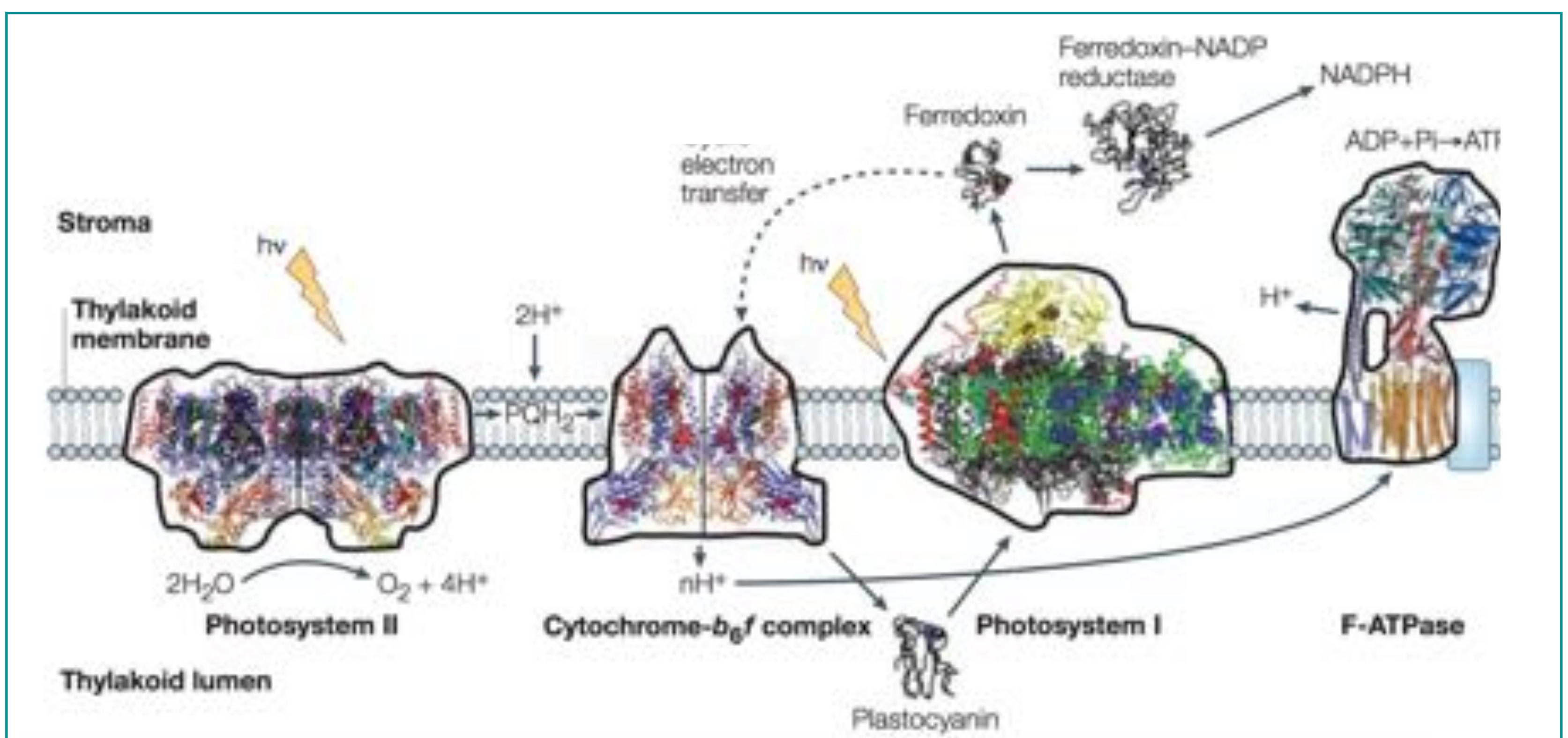
Thought to originate from cyanobacteria which was engulfed by an early eukaryote

Photosynthesis – Some Cell Biology

The Chloroplast







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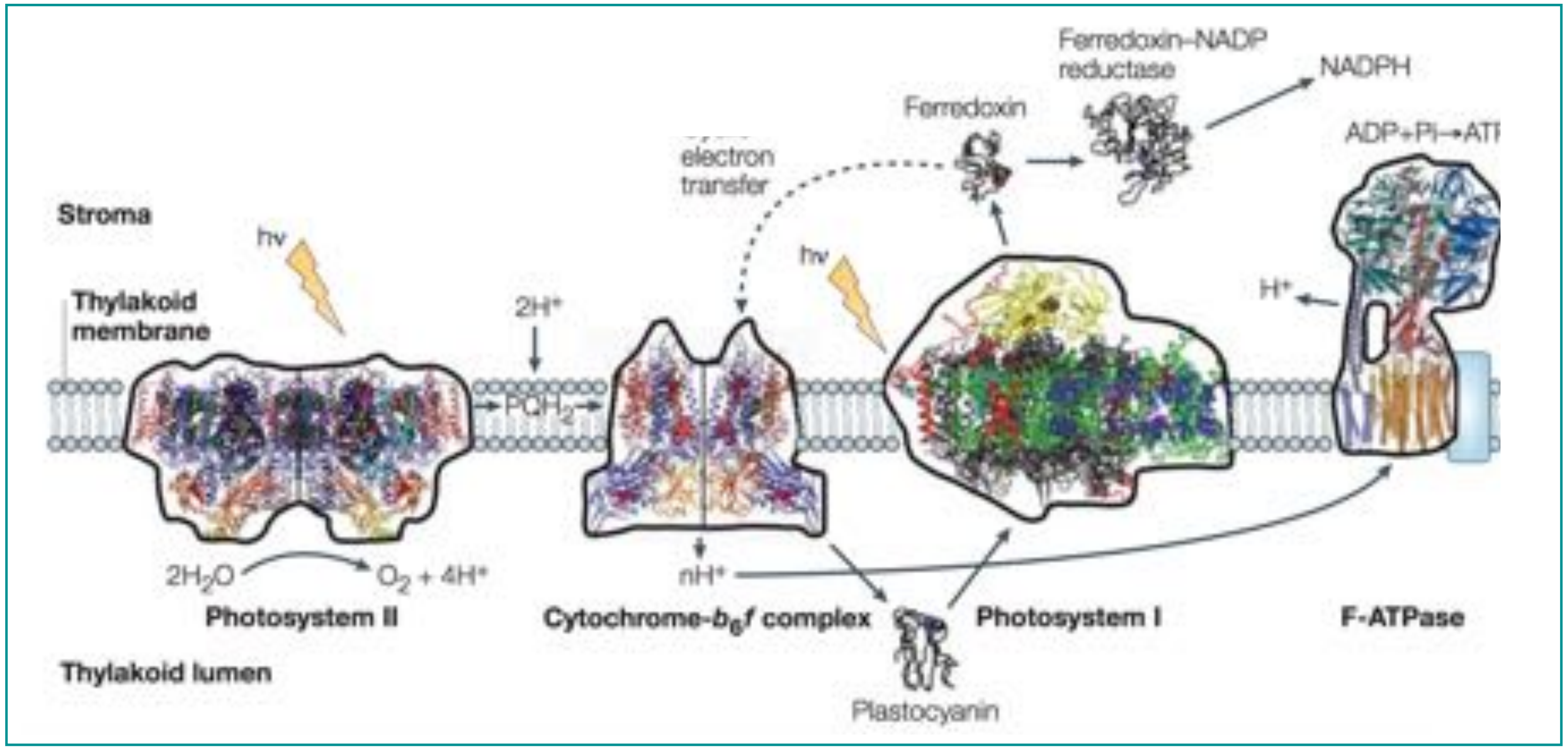


Light Dependent Reaction

Electrochemical gradient ΔpH = 4

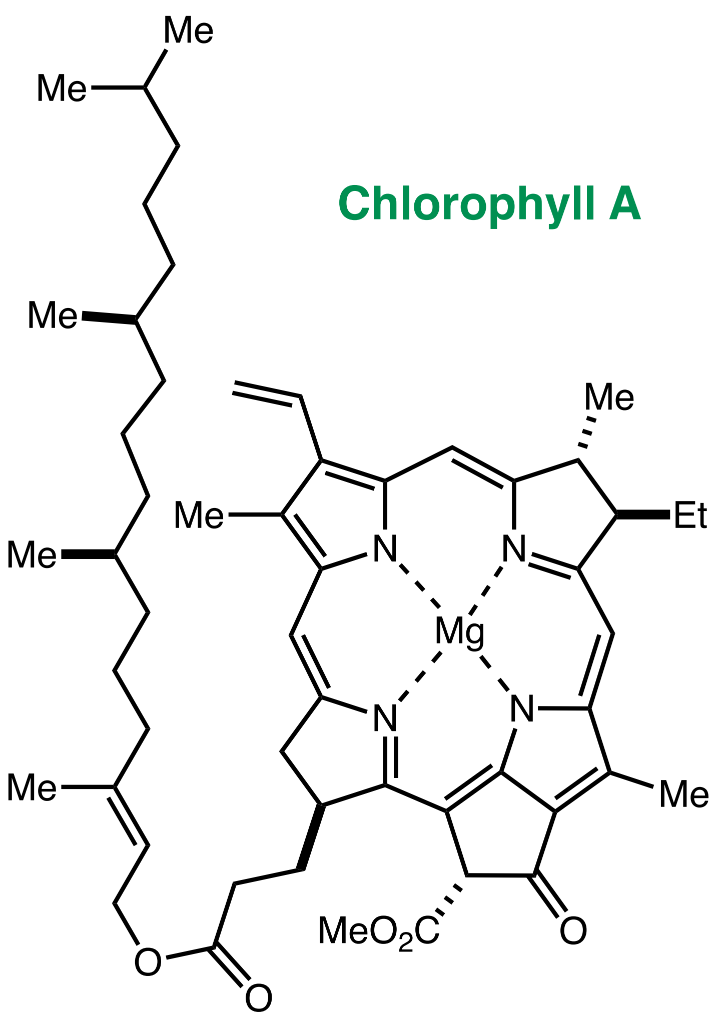
Proton gradient used to drive ATPase

H_2O used to reduce $NADP^+$

Photosystem I and II – Light Harvesting

- **Reaction center – where charge seperation occurs**

Chlorophyll A



Reaction center consists of a special chlorophyll dimer

Photosystem I – P700

Photosystem II – P680

Excitonic coupling exists in this dimer

Spectroscopically behave as a single entity

However reaction center isn't directly responsible for light harvesting

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
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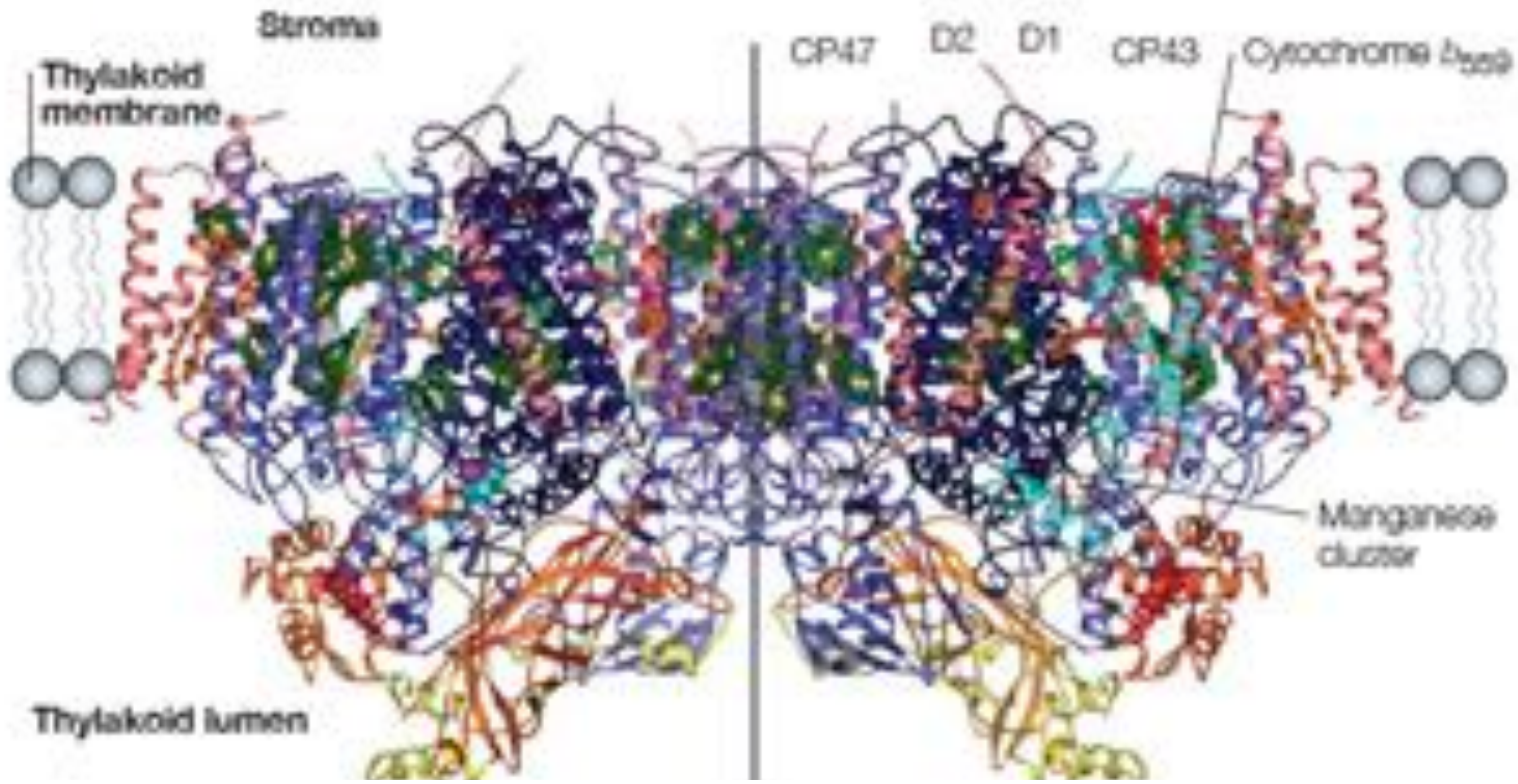
Photosystem I and II – Light Harvesting




Johann Deisenhofer


Robert Huber


Hartmut Michel

1988 Nobel Prize for
“or the determination of the three-dimensional structure of a photosynthetic reaction centre”

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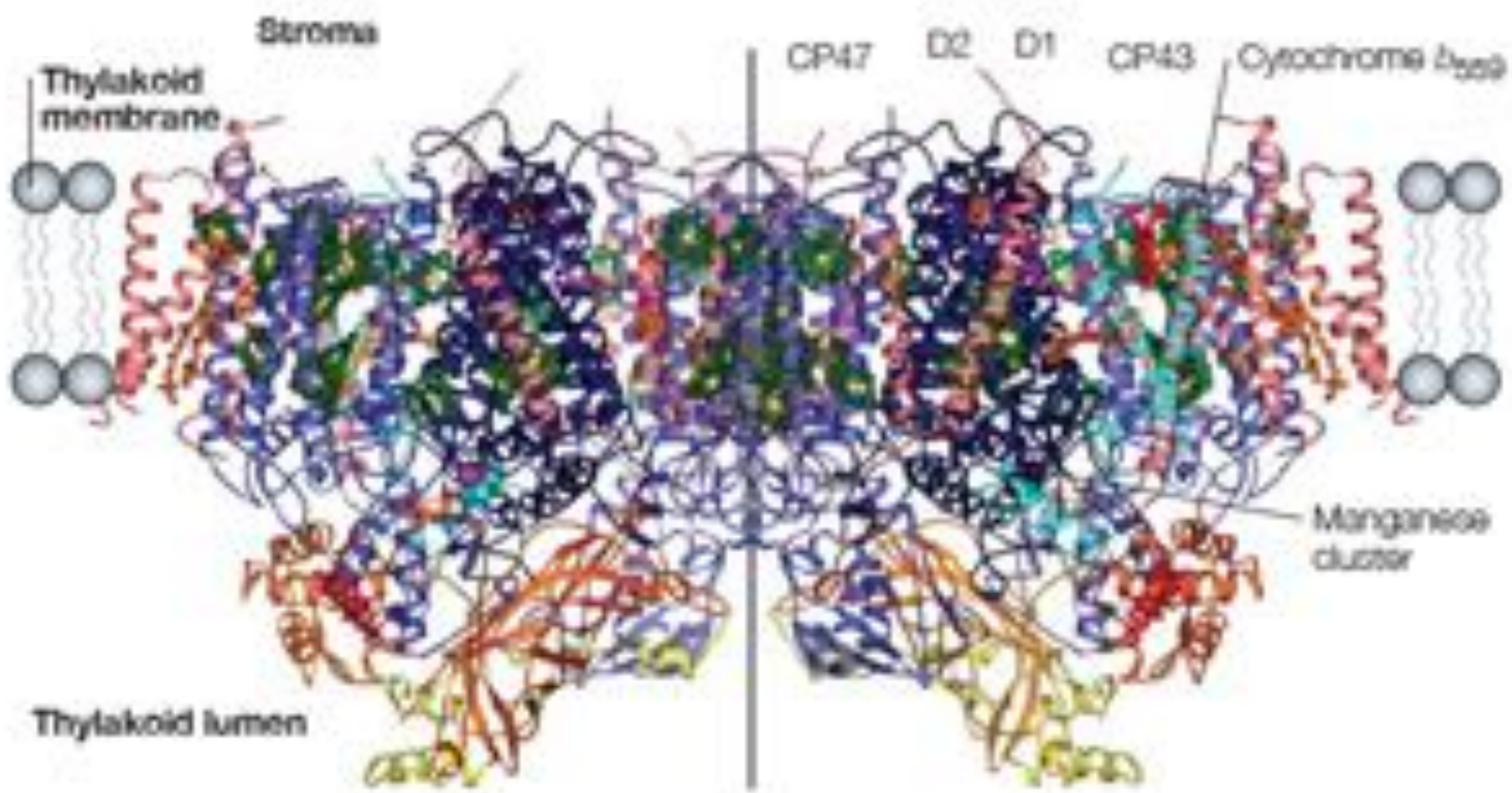

Photosystem II – 2 ~ 40-kDa proteins, 5 transmembrane helices

Vital manganese clusters on the inner side of the membrane – Site of H_2O oxidation

CP43 and CP47 – intrinsic light-harvesting proteins bind 14 and 16 chlorophyll-a molecules

LHCII – extrnsic, peripheral light harvesting complex II. 12–14 chlorophyll-a and -b molecules and up to 4 carotenoids. Degree of co-ordination is controlled homeostatically.

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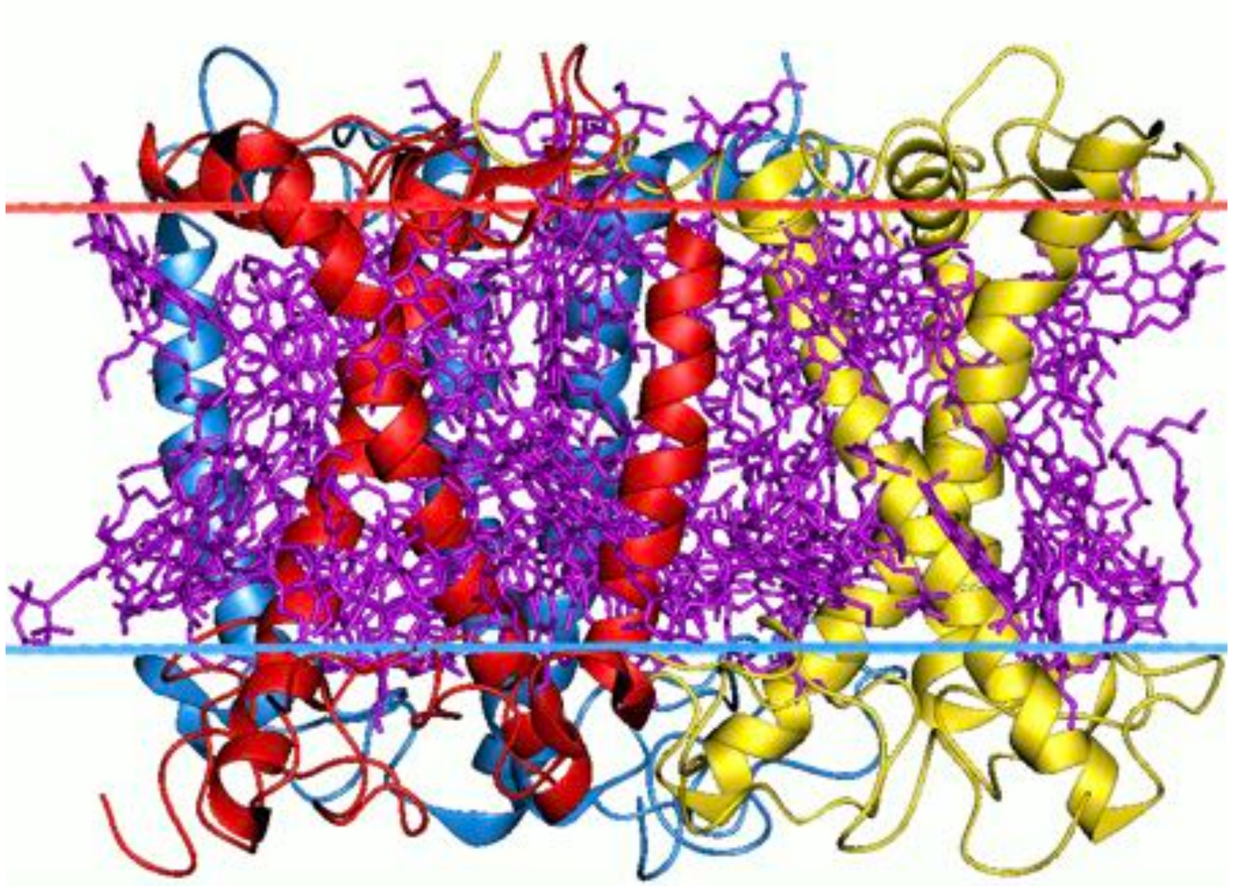
Photosystem I and II – Light Harvesting

Light Harvesting Complex – Many different families



Roughly 2:1 Protein:Pigment

25 kDa of protein
15 kDa of pigment

Chlorophyll A is the primary pigment in higher plants

absorbs light then funnels to the RC via a series of isoenergetic energy transfer events

Can unbind from the photosystem – provides a mechanism of control dependent on light indensity (phosphorylation)

A solution of 0.5M solution of chlorophyll A is strongly quenched, careful arrangement stops this

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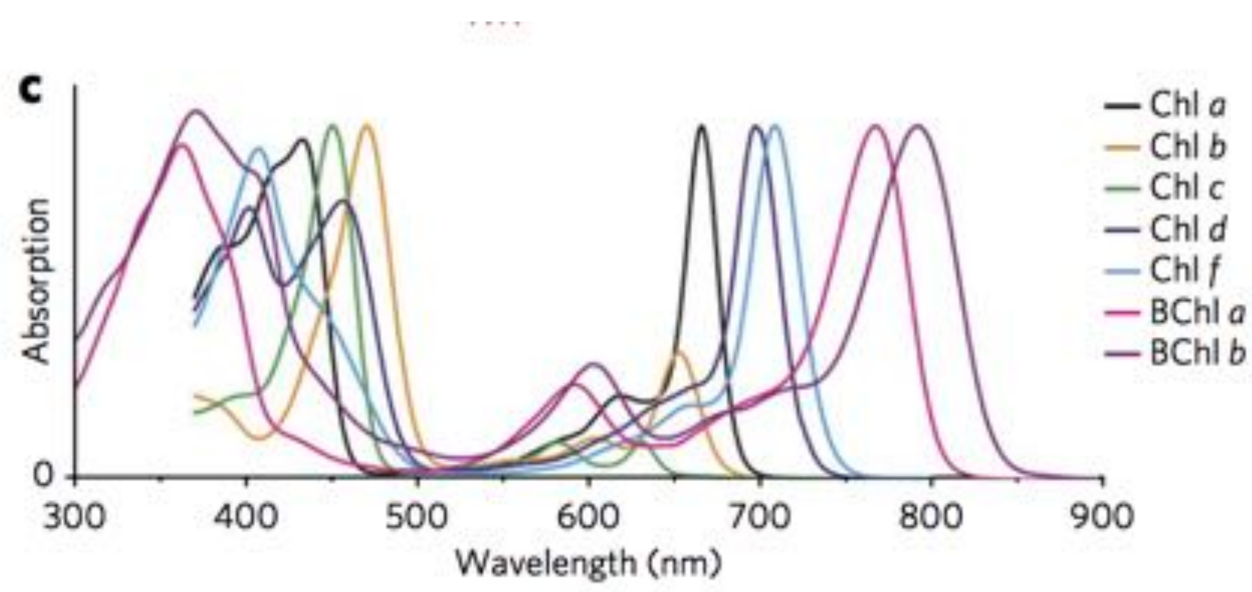
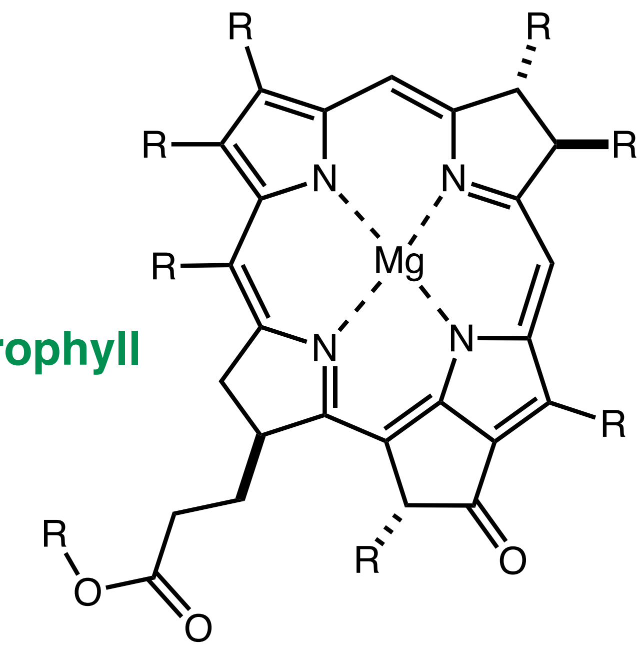
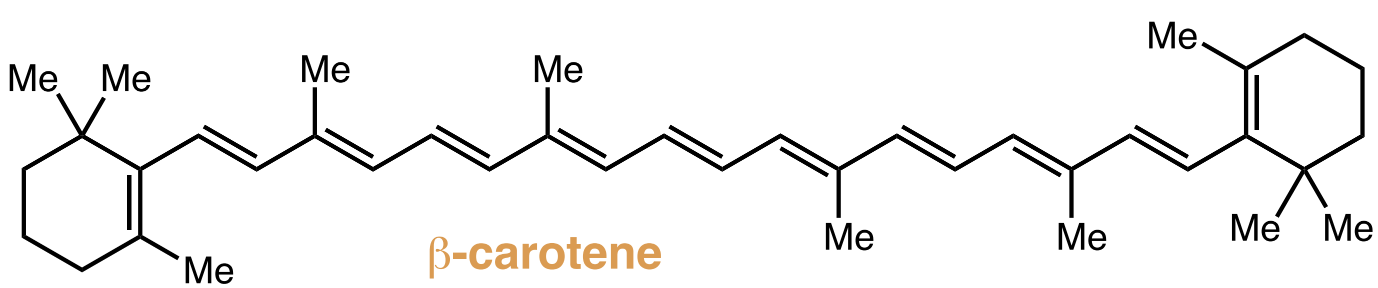
Croce, R.; van Amerongen, H.; *Nature Chemical Biology* **2014**, *10*, 492–501.
Croce, R.; van Amerongen, H.; *J. Photochem. Photobiol. B* **2011**, *104*, **142**–153.
Beddard, G. S.; Porter, G. *Nature*, **1976**, *260*, 366–367.

The Pigments – Light Harvesting

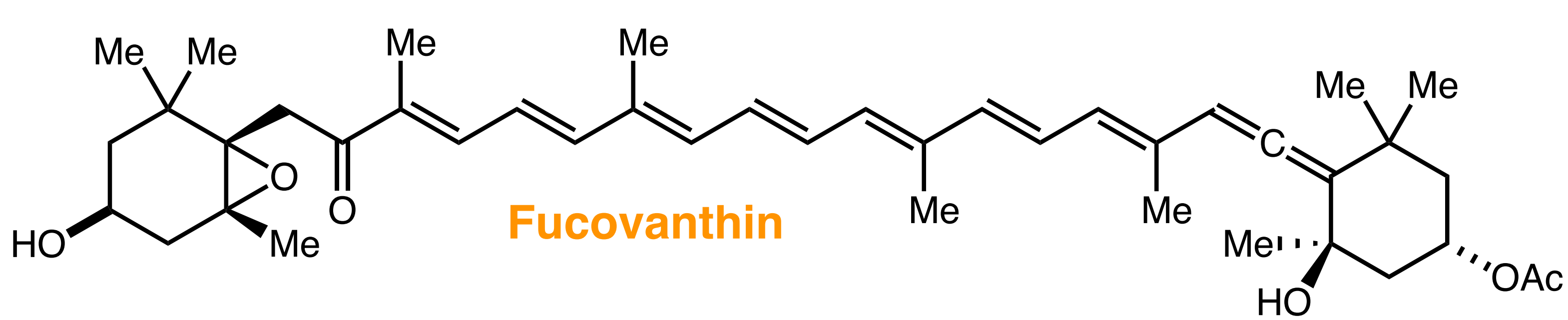




Chlorophyll



β-carotene



Fucovanthin

Croce, R.; van Amerongen, H.; *Nature Chemical Biology* **2014**, *10*, 492–501.

The Pigments – Light Harvesting

Richard Willstatter – 1915
Purification of chlorophyll and early structural work

Hans Fischer – 1930
Structure and synthesis of chlorophyll and haemin (heme)

Paul Karrer – 1937
Structure of carotenoids and flavins

Richard Kuhn – 1938
Structure of carotenoids and vitamins

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
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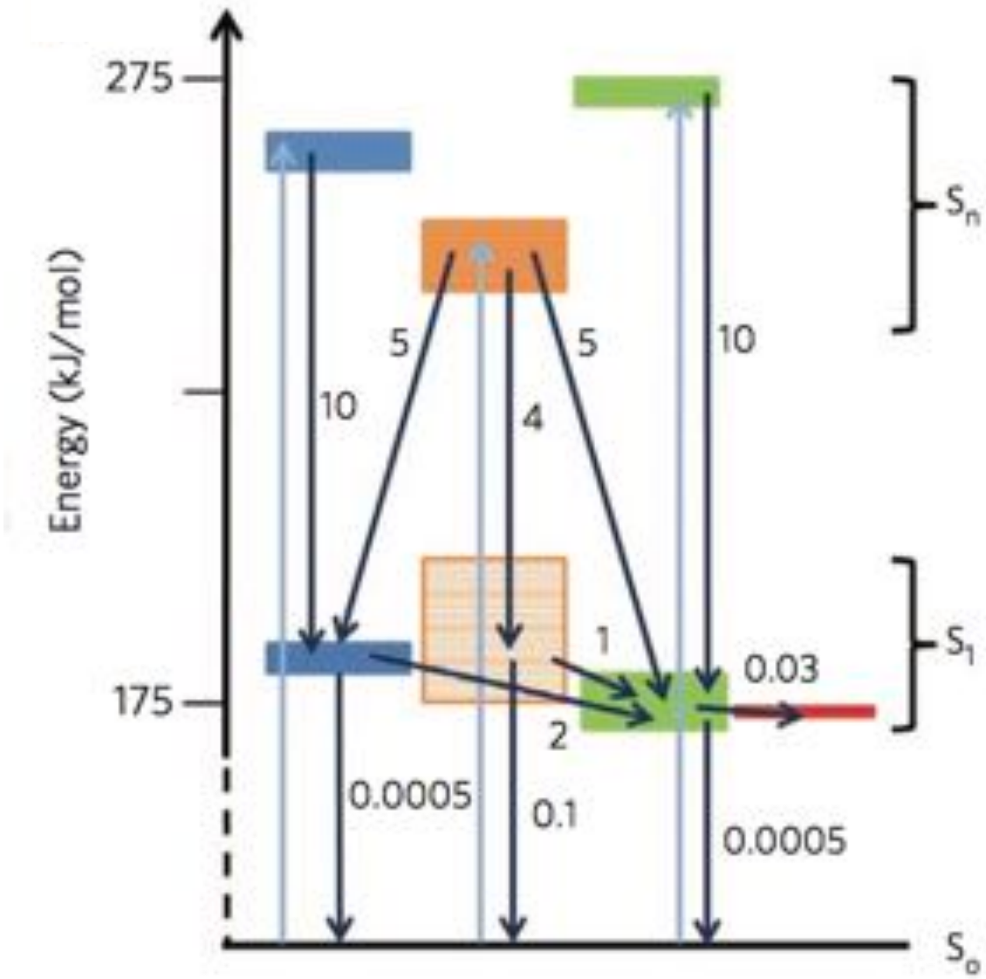
Photosystem I and II – Light Harvesting



Excited states formed on antenna complex.

Energy transfer then funnels excitation to the reaction center.

1.5nm seperation isoenergetic transfer between 2 Chl A molecules – 0.7 ps^{-1}.

Orientation of the pigments matter.

Charge seperation on average occurs 150 ps^{-1} after absorbtion of the photon.

Long range coupling between excited states – they are delocalized over many chromophores. (It's not really FRET).

Ultrafast light harvesting – quantum coherance plays a vital role.

PS I	ψ = **1**
PS II	ψ = 0.85

Solutions of the pigments involved do not harvest light in nearly the same efficiency.

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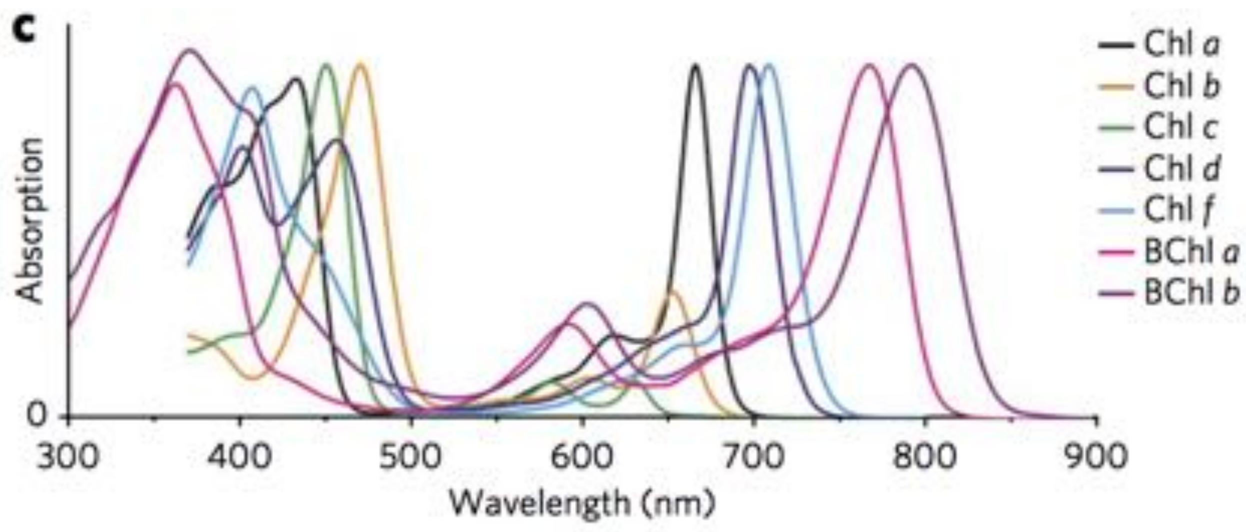
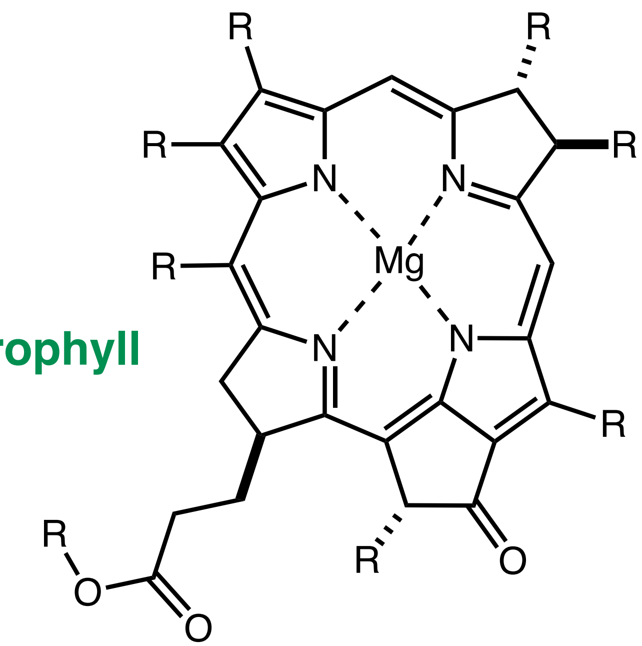
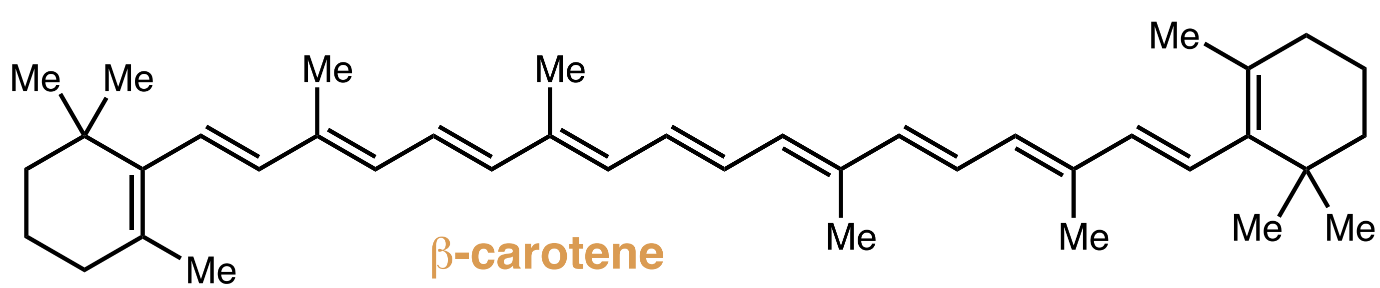
Croce, R.; van Amerongen, H.; *Nature Chemical Biology* **2014**, *10*, 492–501.
Fassioli, F.; Dinshaw, R.; Arpin, P. C.; Scholes, G. D. *Jour. R. Soc. Interface* **2014**, *11*, 20190901.

Photosystem I and II – Light Harvesting

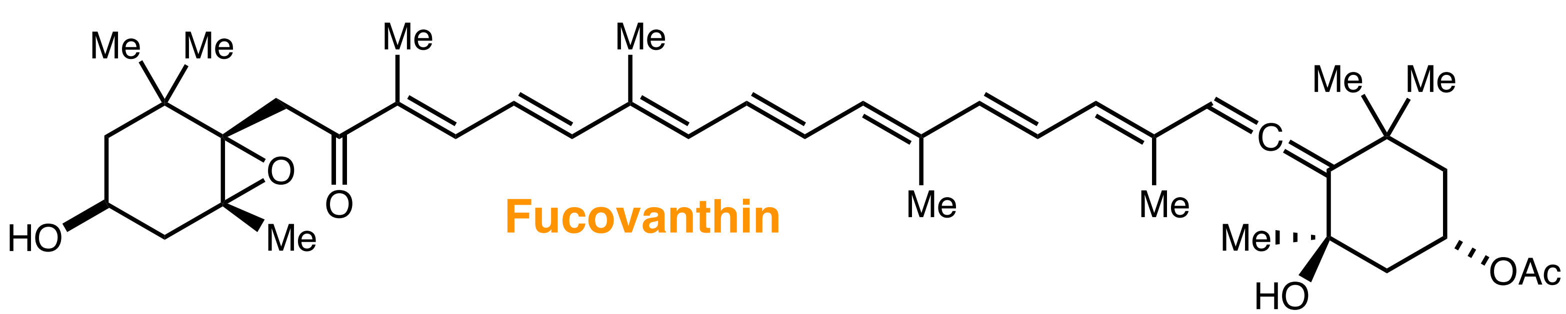


Chlorophyll





β-carotene



Fucovanthin

Higher plants do

not absorb green light

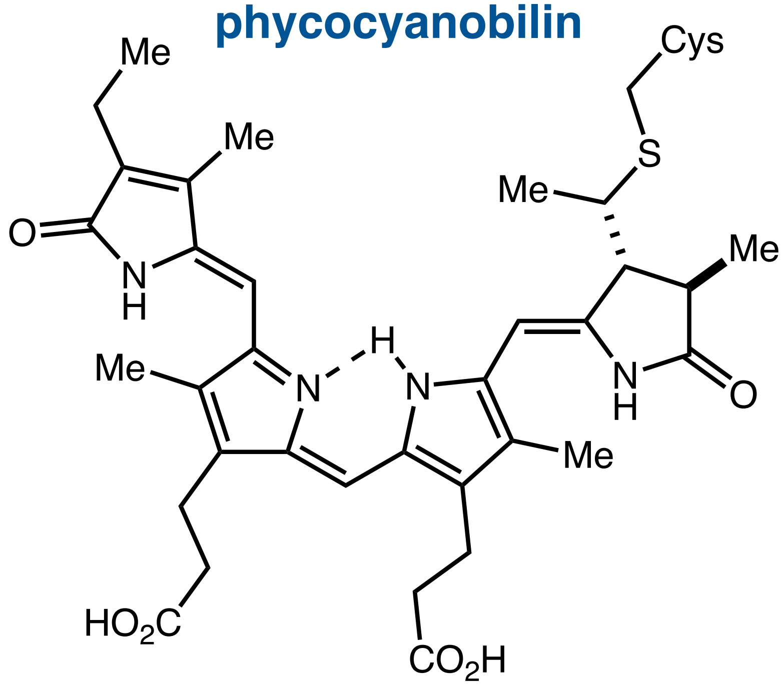
Croce, R.; van Amerongen, H.; *Nature Chemical Biology* **2014**, *10*, 492–501.

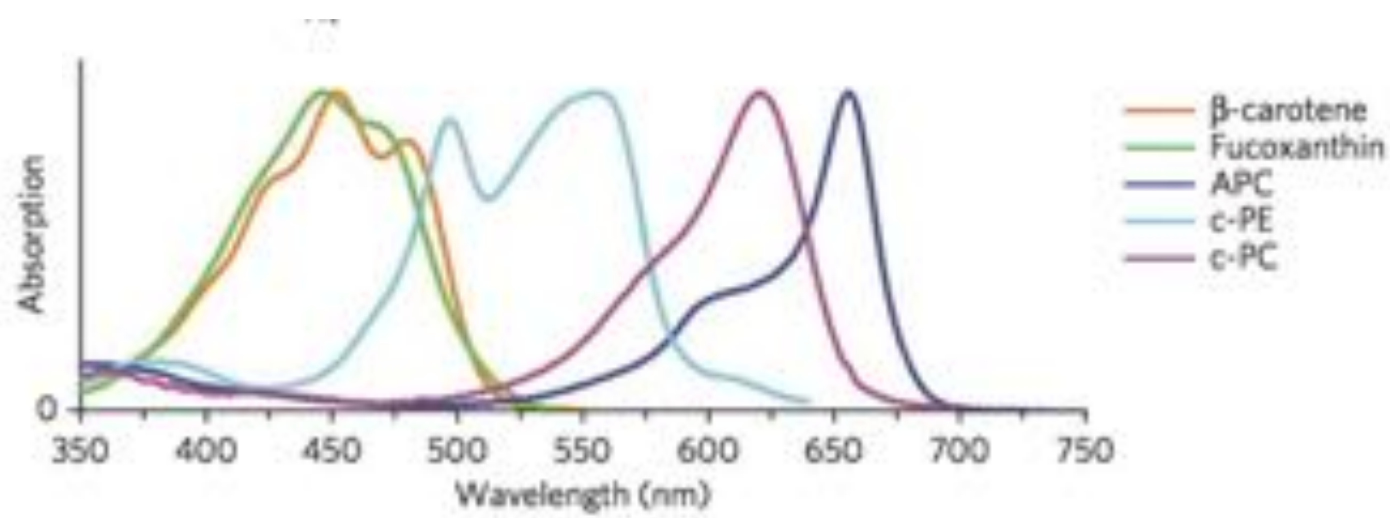
Photosystem I and II – Light Harvesting

Plants have evolved modified pigments for specific low light enviroments

Red Algae
Rhodophyta

phycocyanobilin



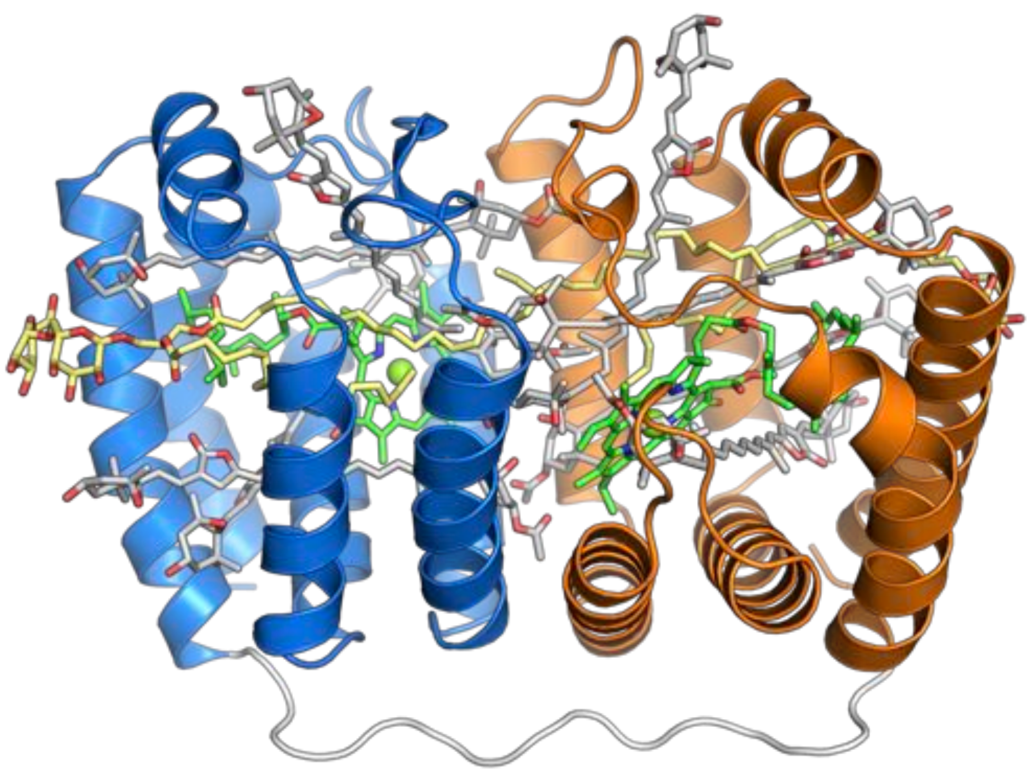


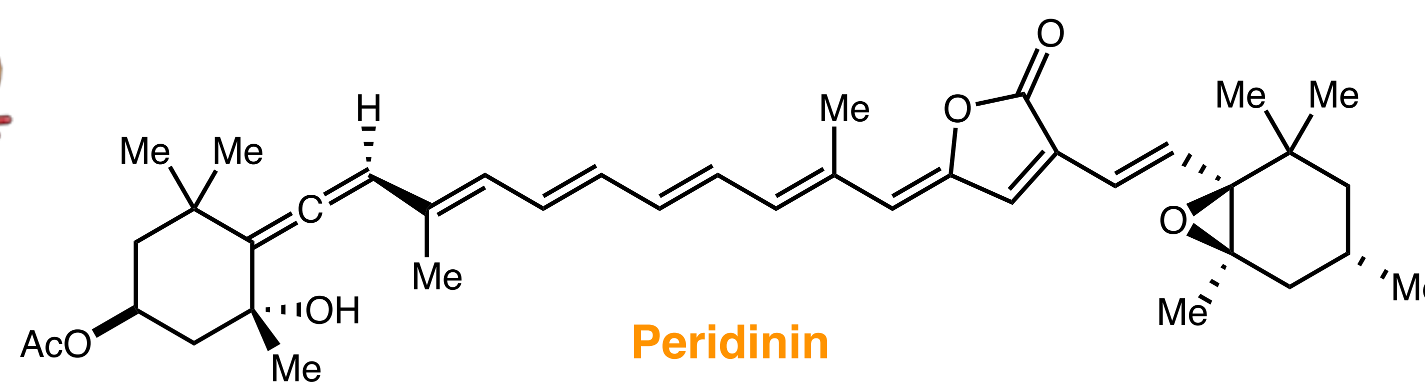
Lepetit, B.; Goss, R.; Jakob, T.; Willhelm, C. *Photosynth. Res.* **2012**, *111*, 245–257.
Croce, R.; van Amerongen, H.; *Nature Chemical Biology* **2014**, *10*, 492–501.
Chen, M. *et. al. Science* **2010**, *329*, 1318–1319.
Stomp, M.; Huisman, J.; Stal, L. J.; Matthijs, H. C. P. *ISME J.* **2007**, *1*, 271–282.

Photosystem I and II – Light Harvesting

Plants have evolved modified pigments for specific low light enviroments

Dinoflagellata

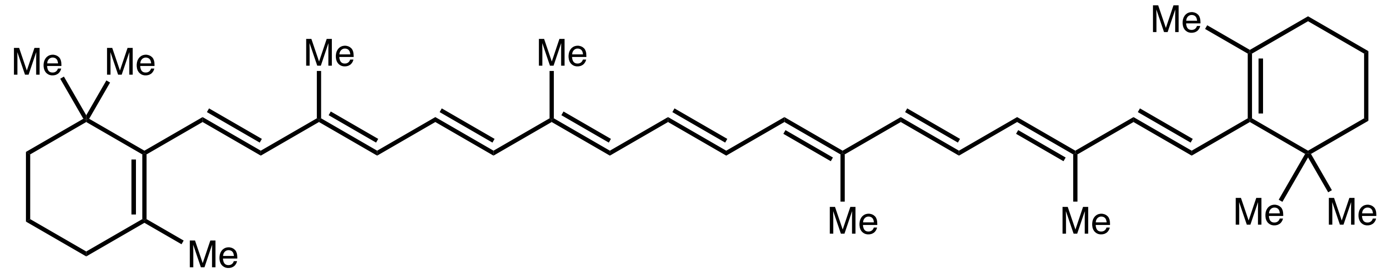




Peridinin

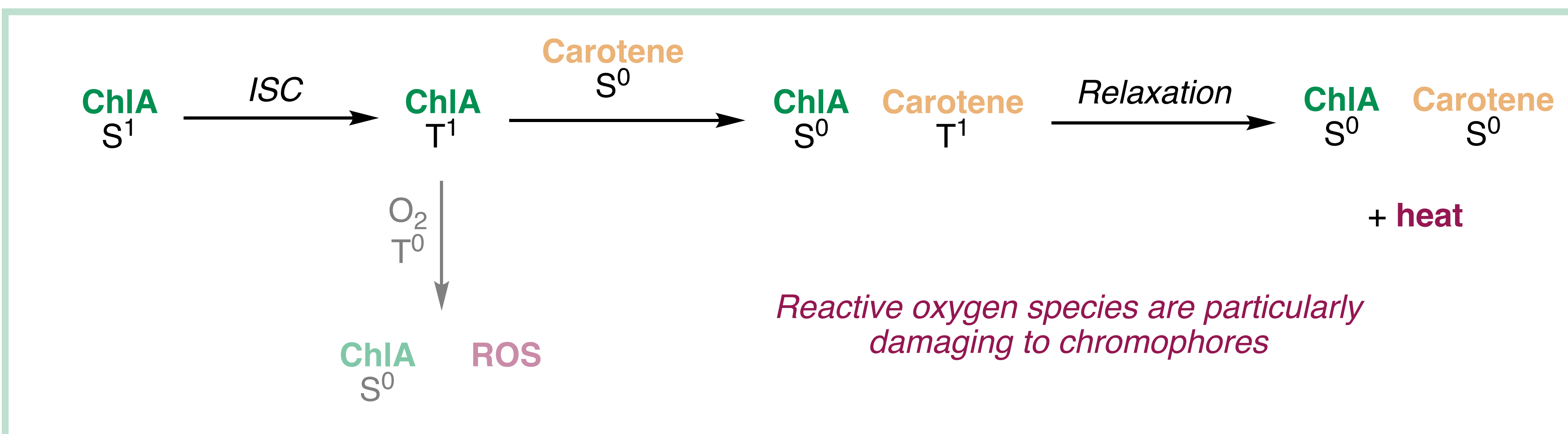
Schute , T. *et al. Proc. Natl. Acad. Sci. USA* **2009**, *106*, 20764–20769.
Krieger-Liszkay, A.; Fufezan, C.; Trebst, A. *Photosynth. Res.* **2008**, *98*, 551–554.

Photosystem I and II – Role of Carotenes



Solution phase excited state lifetime ~ 10ps

Engages in excitation transfer with chlorophyll A (within LHC) ~ 1ps
chlorophyll A has excited state lifetime of several nanoseconds



Carotenes are also important for photoprotection – when light intensity is too high

almost all chlorophyll are in direct electronic contact with a carotenoid

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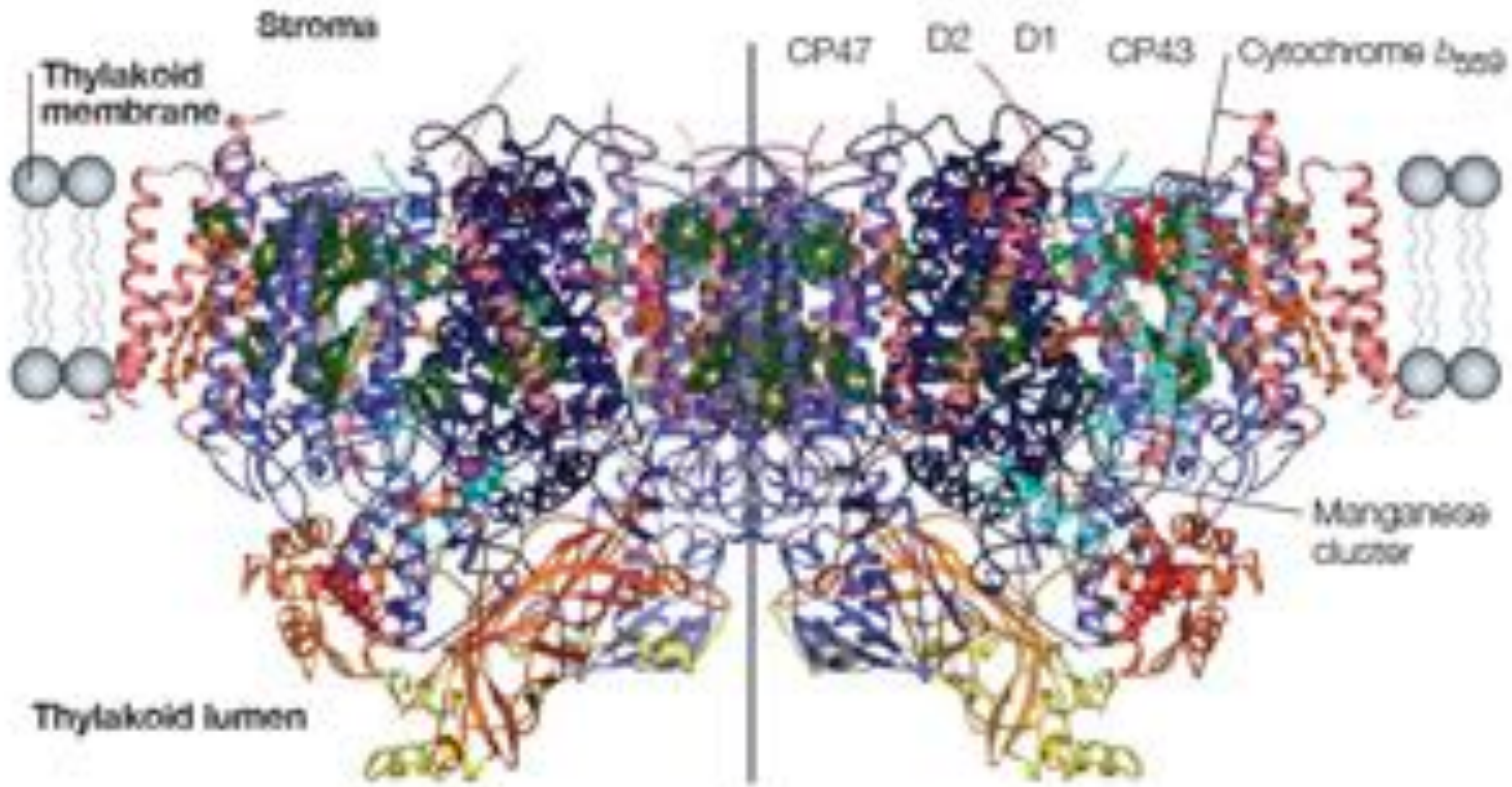
Photosystem I and II – Light Harvesting



Once you've harvested light what can you do with it?

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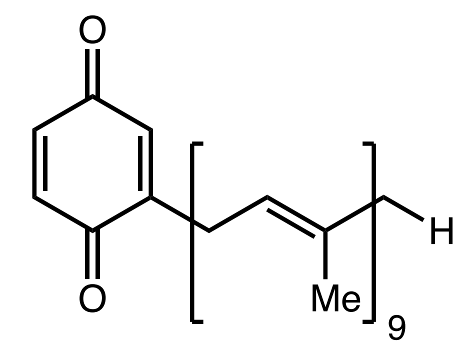
Photosystem II – The Light Dependent Reaction

Reaction Center

2 H_2O 2 plastoquinone ⟶ **O_2** 2 dihydroplastoquinone



Requires 4 quanta of light total which arrive within 1000ps

P680*

Two weakly coupled chlorophylls are the terminus for excitation transfer

Vrettos, J. S.; Limburg, J.; Brugvig, G. W.; *Biochem. Biophys. Acta* **2001**, *1503*, 229–245.
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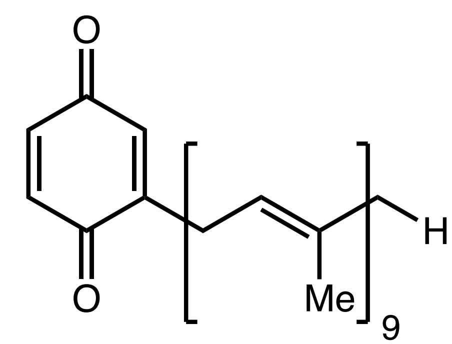

Requires 4 quanta of light total which arrive within 1000ps

P680* ⟶ **$P680^+$ + PQ^{-1}**

Donates an electron via an accessory chlorophyll and a pheophytin molecules to plastoquinone

Oxidized $P680^+$ is the strongest oxidant known in biology

~ 1.3V vs. NHE

oxidative damage of photosystem II is rapid, the D2 subunit is recylced every 20 minutes

Vrettos, J. S.; Limburg, J.; Brugvig, G. W.; *Biochem. Biophys. Acta* **2001**, *1503*, 229–245.
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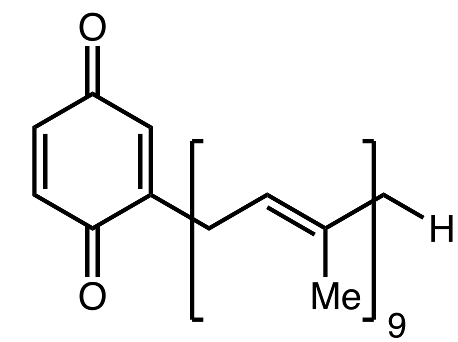

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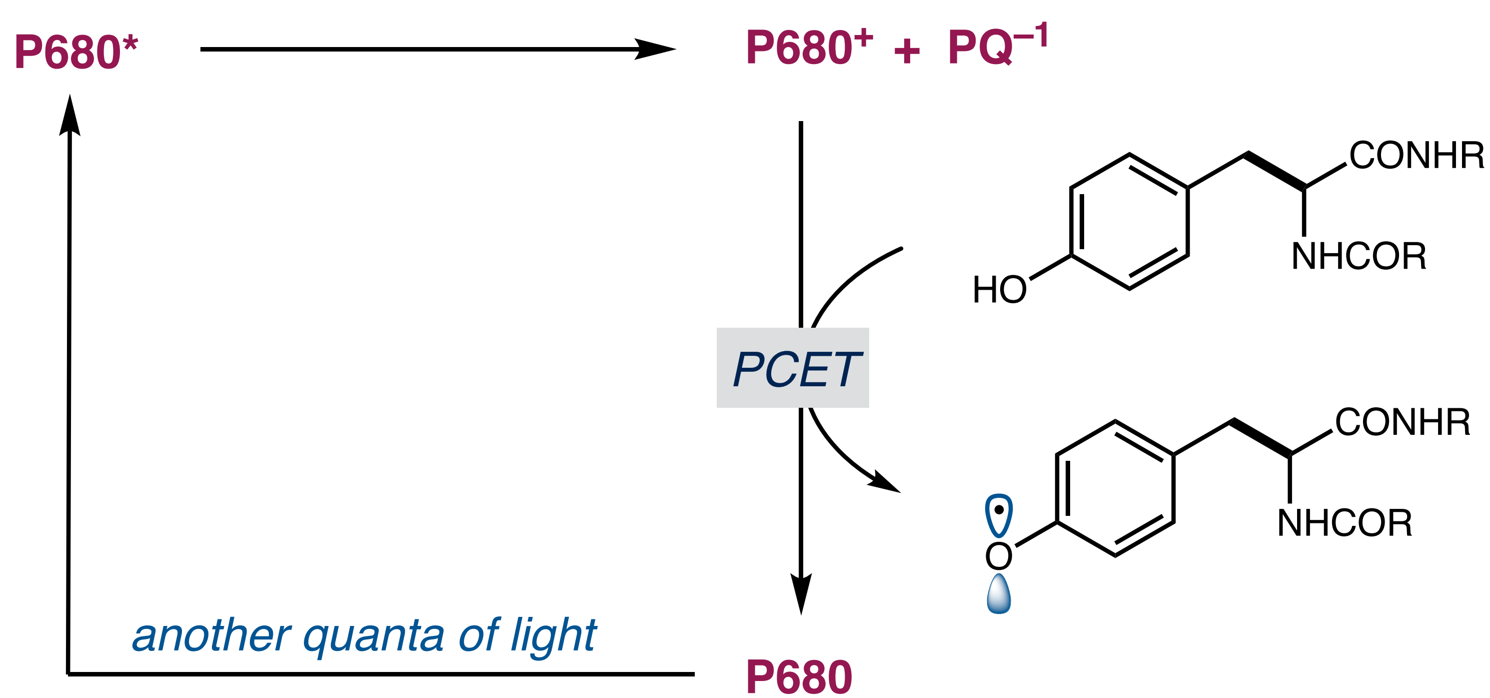

Turns over 4 times for each molecule of O_2 evolved –

generates 2 molecules of reduced quinone

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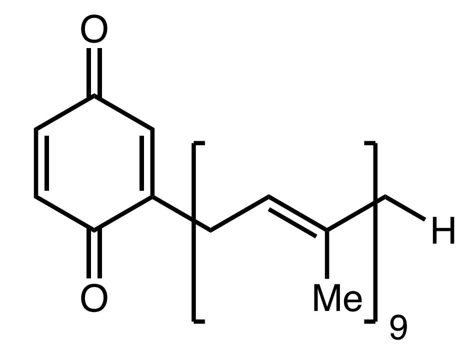

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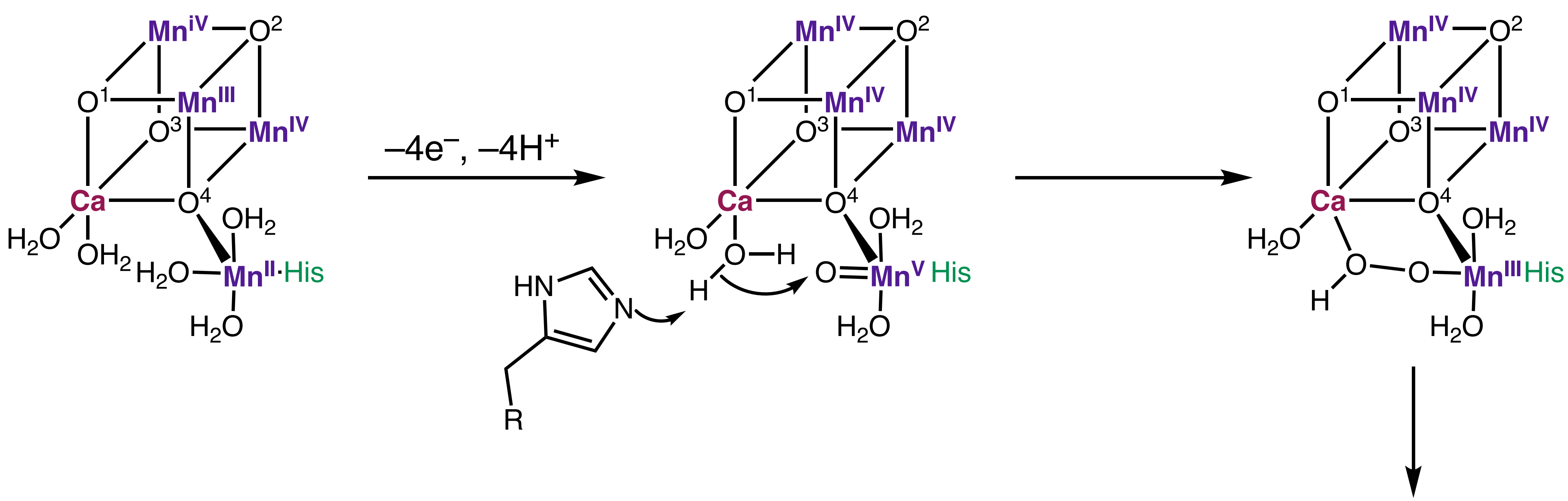

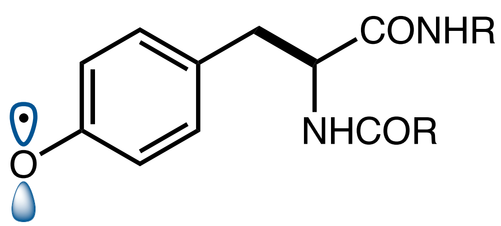

Tyrosyl radical then oxidizes the manganese cluster shown 4 times sequentially

likely *via* HAT

O_2 + Mn_4Ca cluster

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Photosystem II – The Light Dependent Reaction

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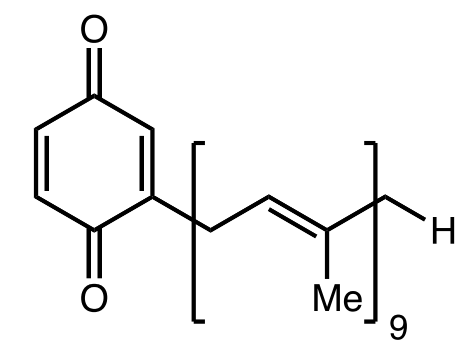
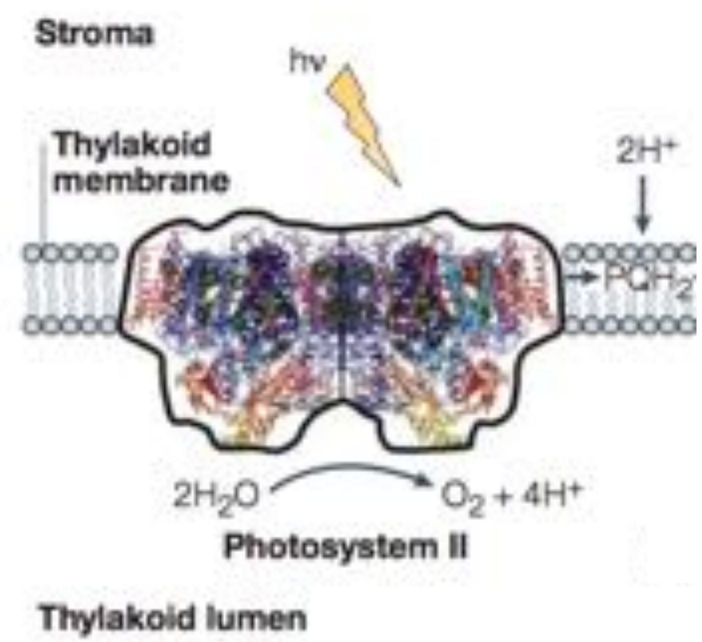


Requires 4 quanta of light total which arrive within 1000ps

Begins to establish the vital proton gradient for ATP synthesis

2 protons picken up in the stroma by plastoquinone

4 protons pumped into the lumen by the H_2O oxidation event



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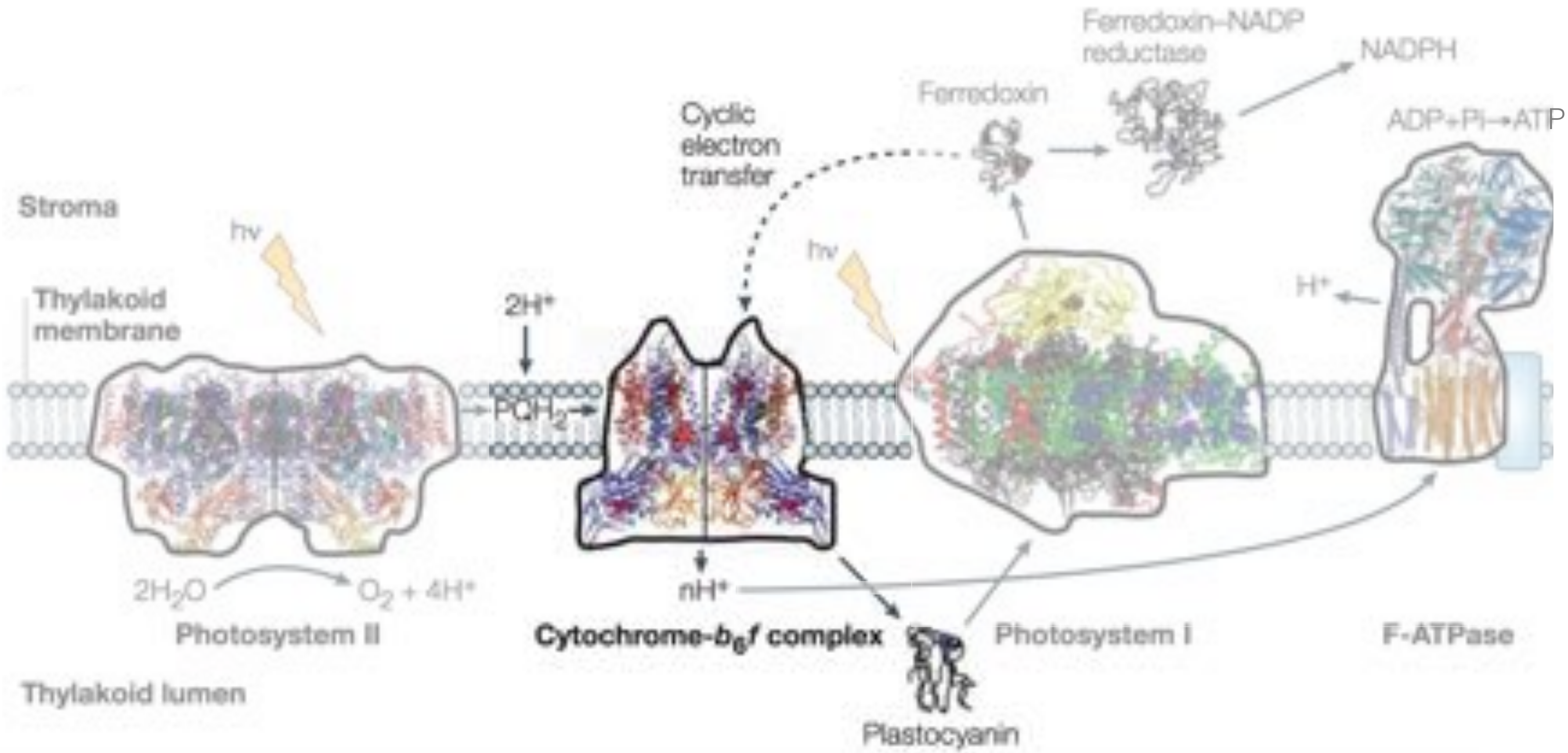
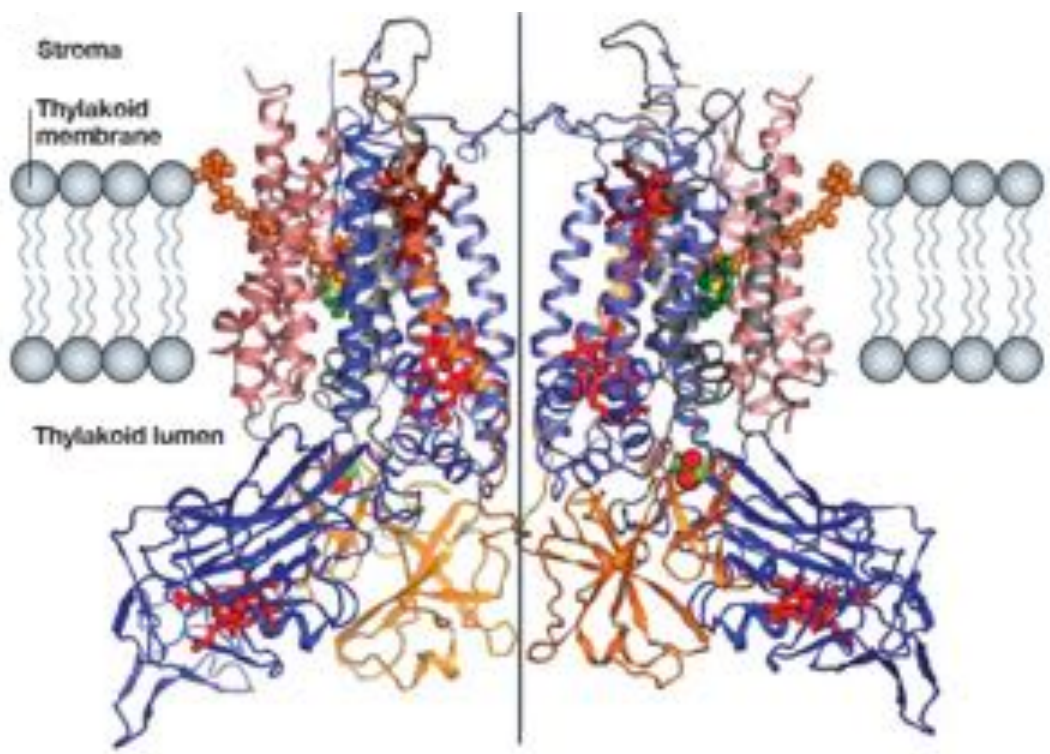
Cytochrome-b_6f Complex – Electron Transfer and More Protons

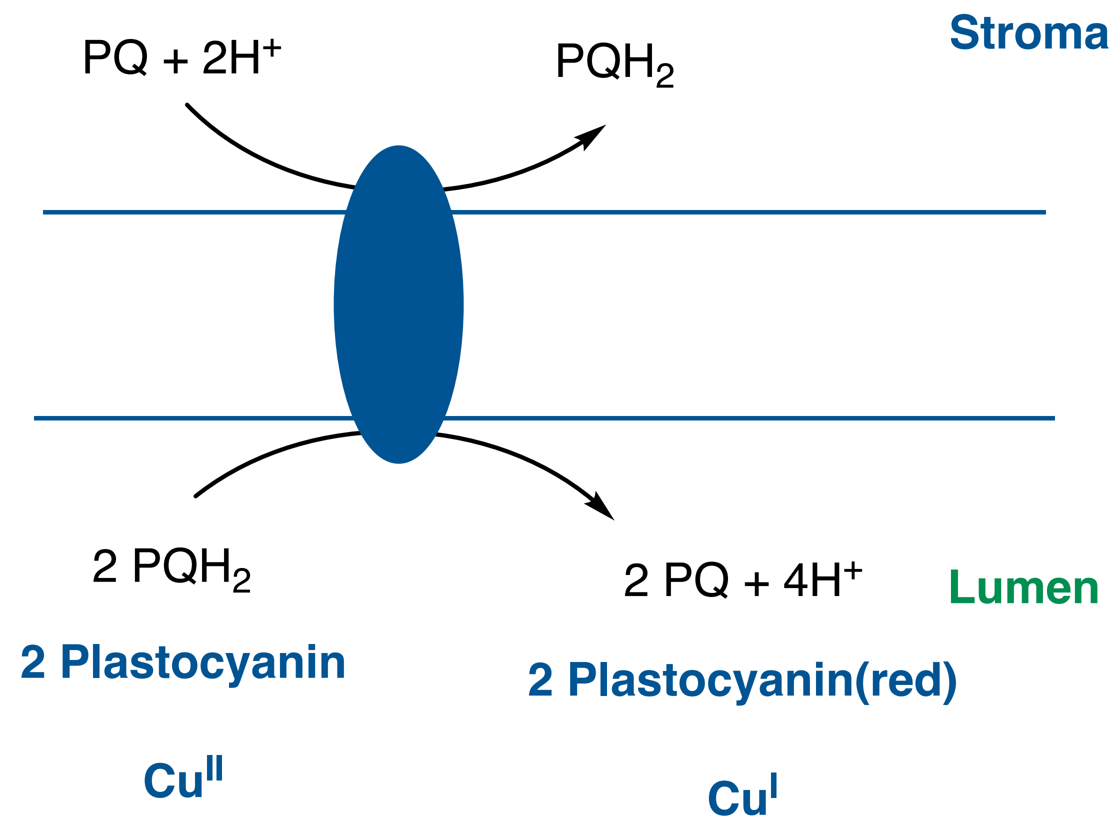


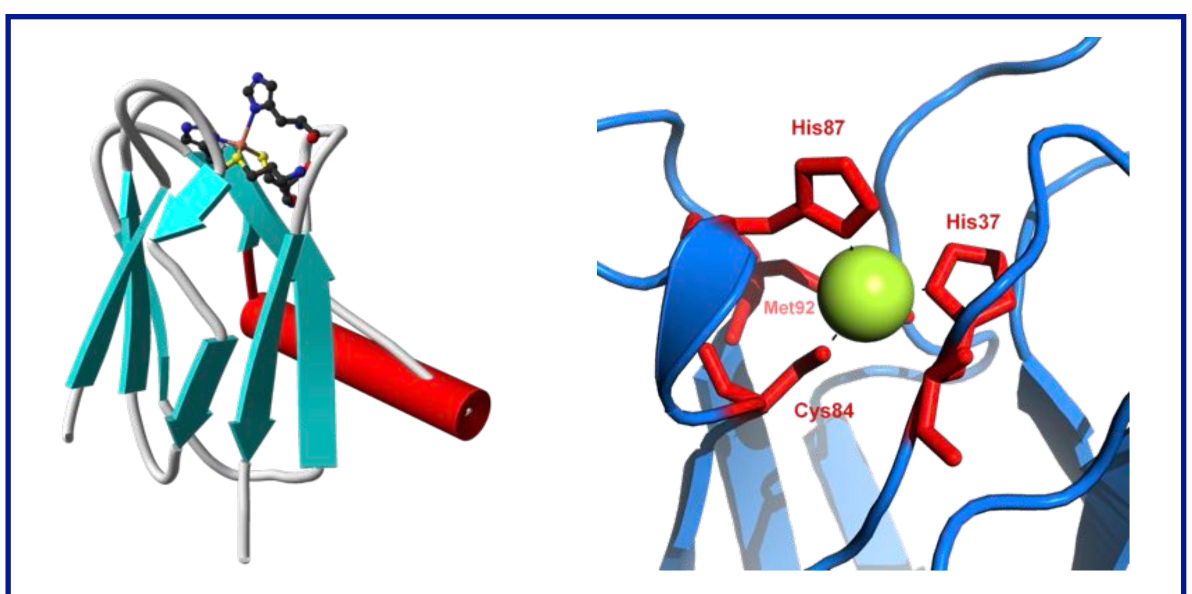
Cytochrome-b_6f Complex – Electron Transfer and More Protons

Cytochrome-b_6*f* complex reduces plastocyanin and pumps protons across the membrane

Q-cycle







The Cu-S^{met} distance in 282pm (v. long) which destablizes the Cu^{II} state

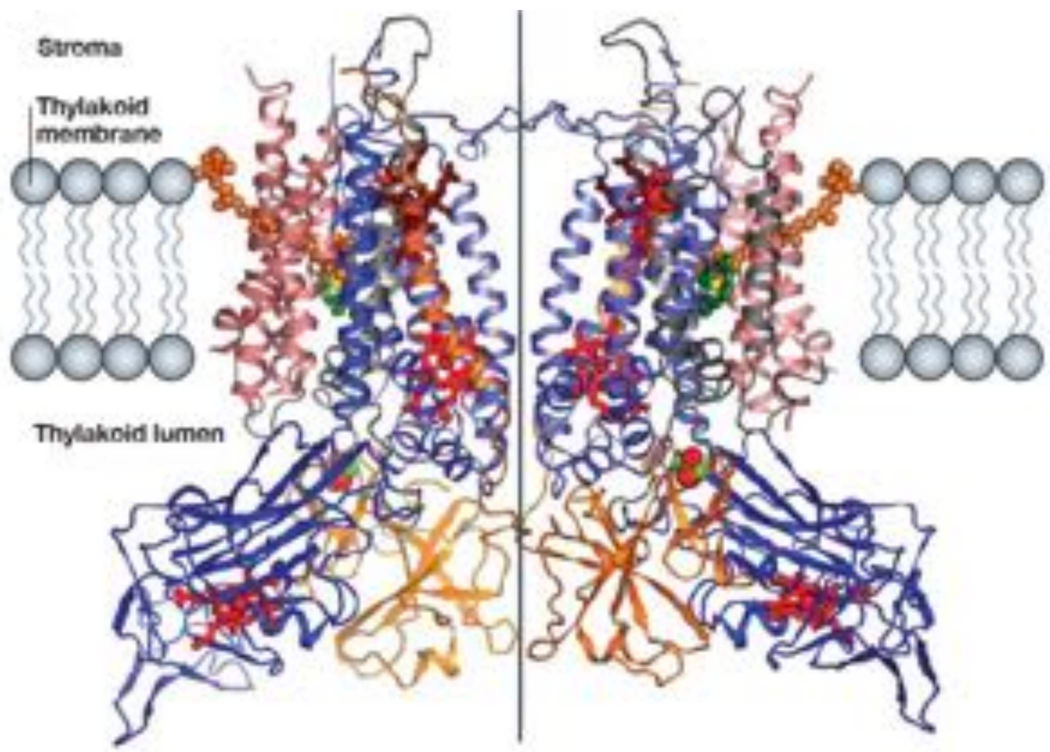
In the Cu^I state His87 becomes protonated and the copper center planarizes stablizing the Cu^I

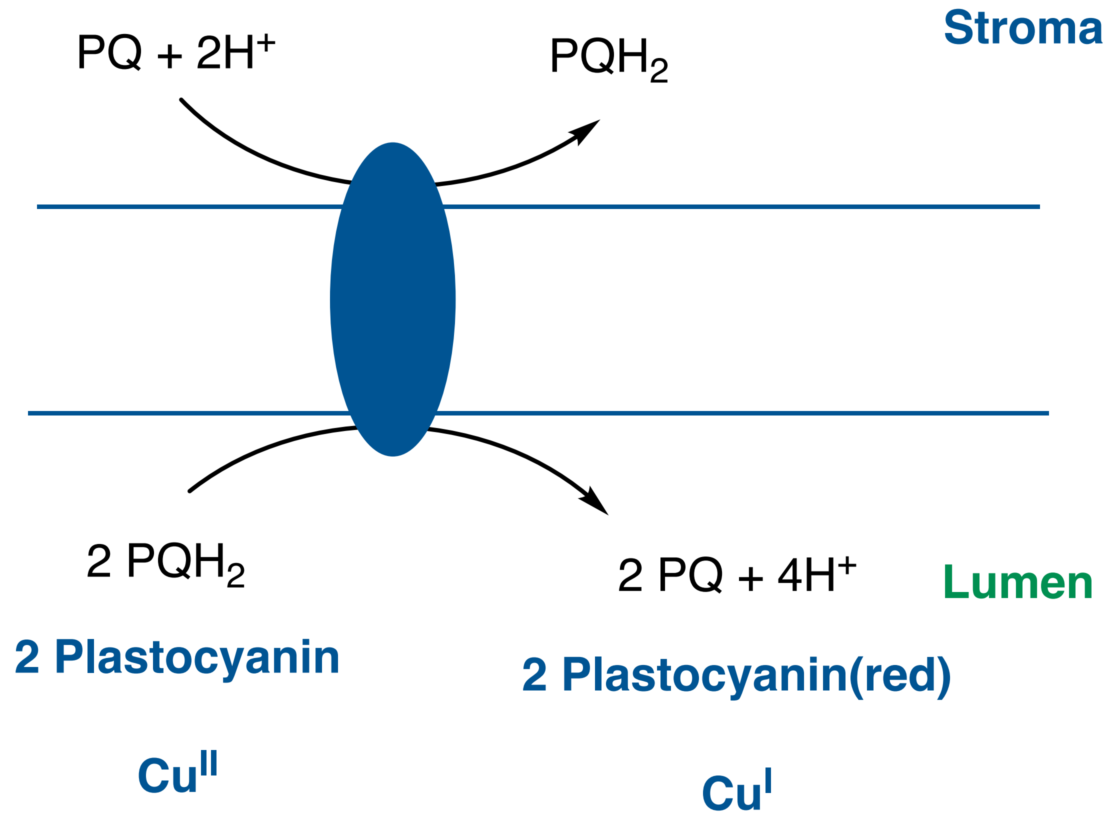
Hurt, E.; Hauska, G. A. *Eur. J. Biochem.* **1981**, *117*, 592–595.
Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Mitchell, P. *J. Theor. Biol.* **1976**, *62*, 327–367.
Trumpower, B. L. *J. Biol. Chem.* **1990**, *265*, 11409–11412.

Cytochrome-b_6f Complex – Electron Transfer and More Protons

Cytochrome-*b_6f* complex reduces plastocyanin and pumps protons across the membrane

Q-cycle



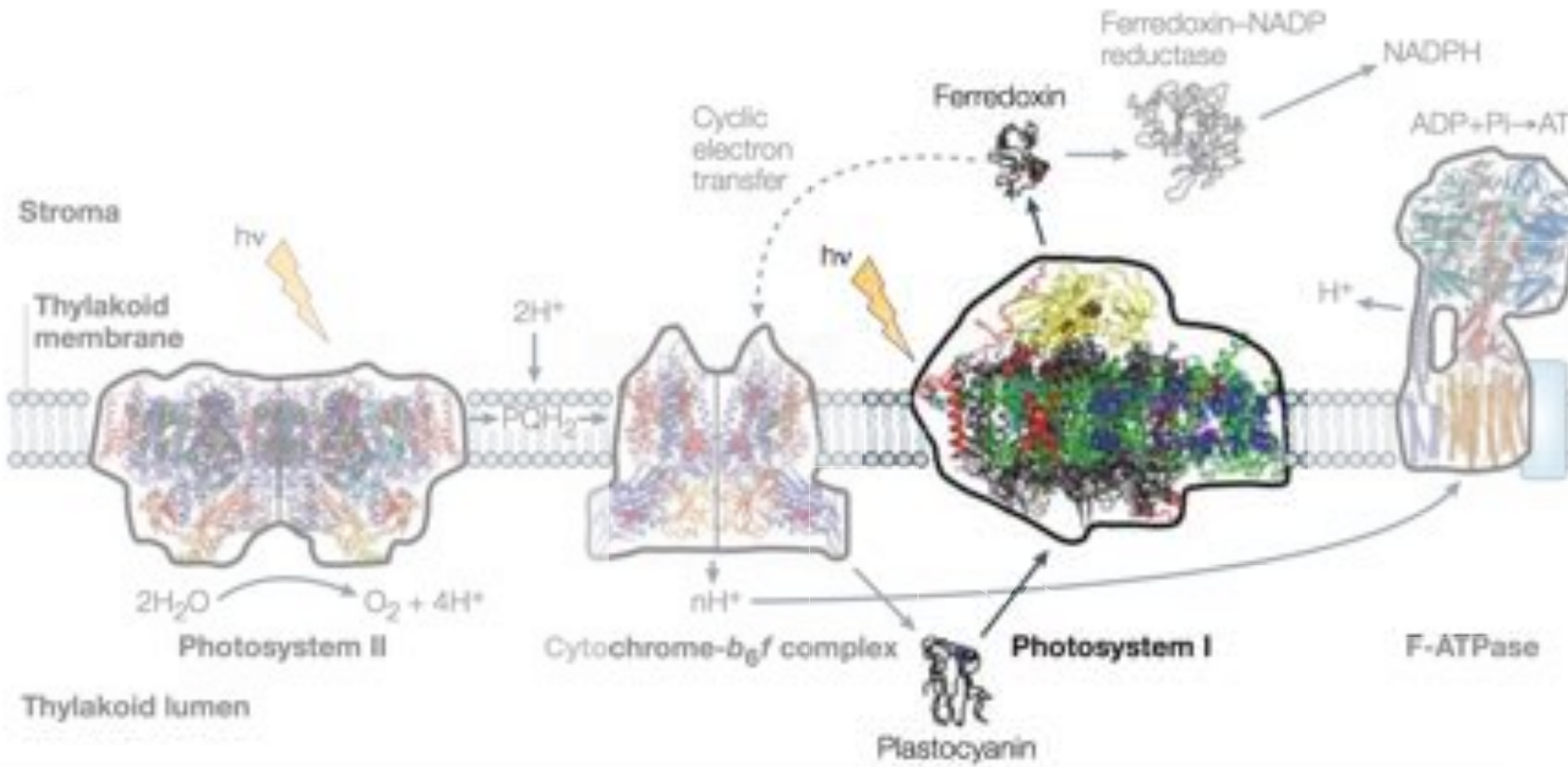


Electrons are transferred through the membrane via a series of haem groups and a iron sulphur cluster protein (Riesk)

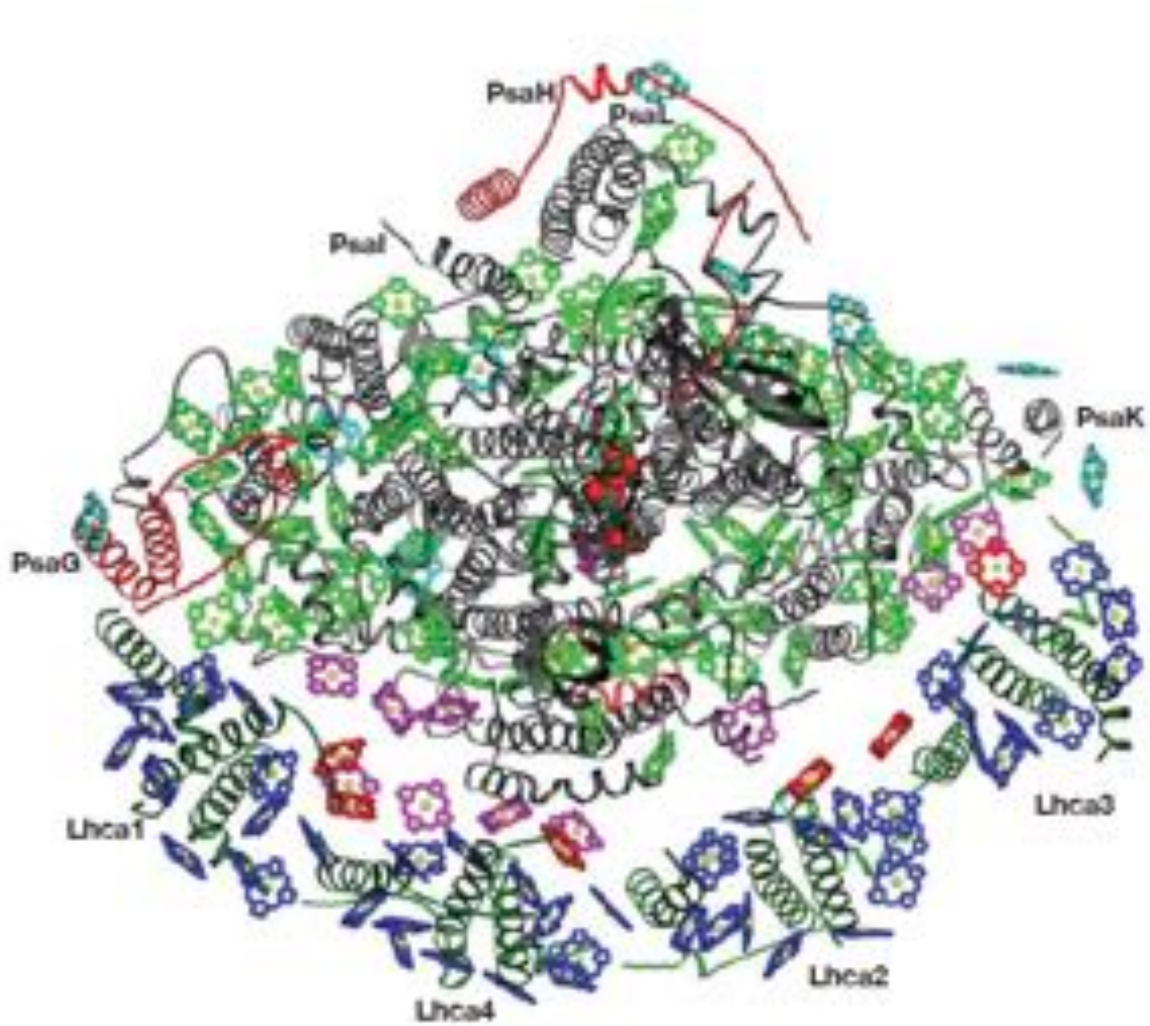
Also contains chlorophyll A and β-carotene co-factors and a haem site the functions of which have yet to be elucidated

Thought to plat some role in a cyclic photophosphorylation pathway which may regulate communication between PSI and PSII

Photosystem I – The Light Dependent Reaction



Photosystem I – Ferrodoxin Reduction



The second “photocatalytic” protein complex

12-14 protein subunits (organism dependent)

P700 chlorophyll pair make up the reaction center

~80 chlorophyll molecules function as light harvesting component

3 Fe-S clusters to facillitate electron transfer

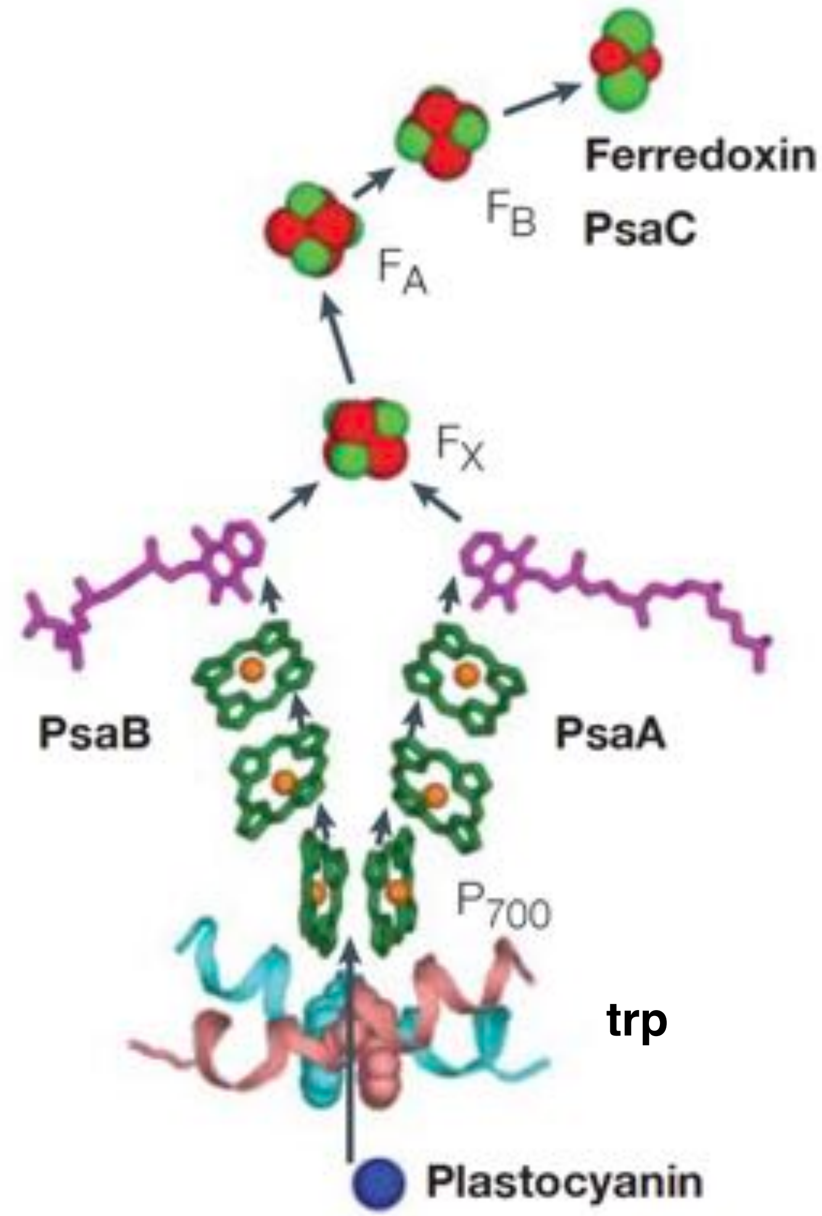
The substrates of photosystem I are two proteins

- Reduced Plastocyanin – Cu^{I}
- Ferrodoxin – Iron Sulfur containing

Morphologically very similar to PS II, however different co-factors – PS I is very reducing

Nelson, N.; Ben-Shem, A.; *Photosyth. Res.* **2002**, *73*, 193–206.
Jordan, P. *et. al.* *Nature*, **2001**, *411*, 909–917.
Ben-Shem, A.; Frolow, F.; Nelson, N. *Nature*, **2003**, *426*, 630–635.

Photosystem I – Ferrodoxin Reduction

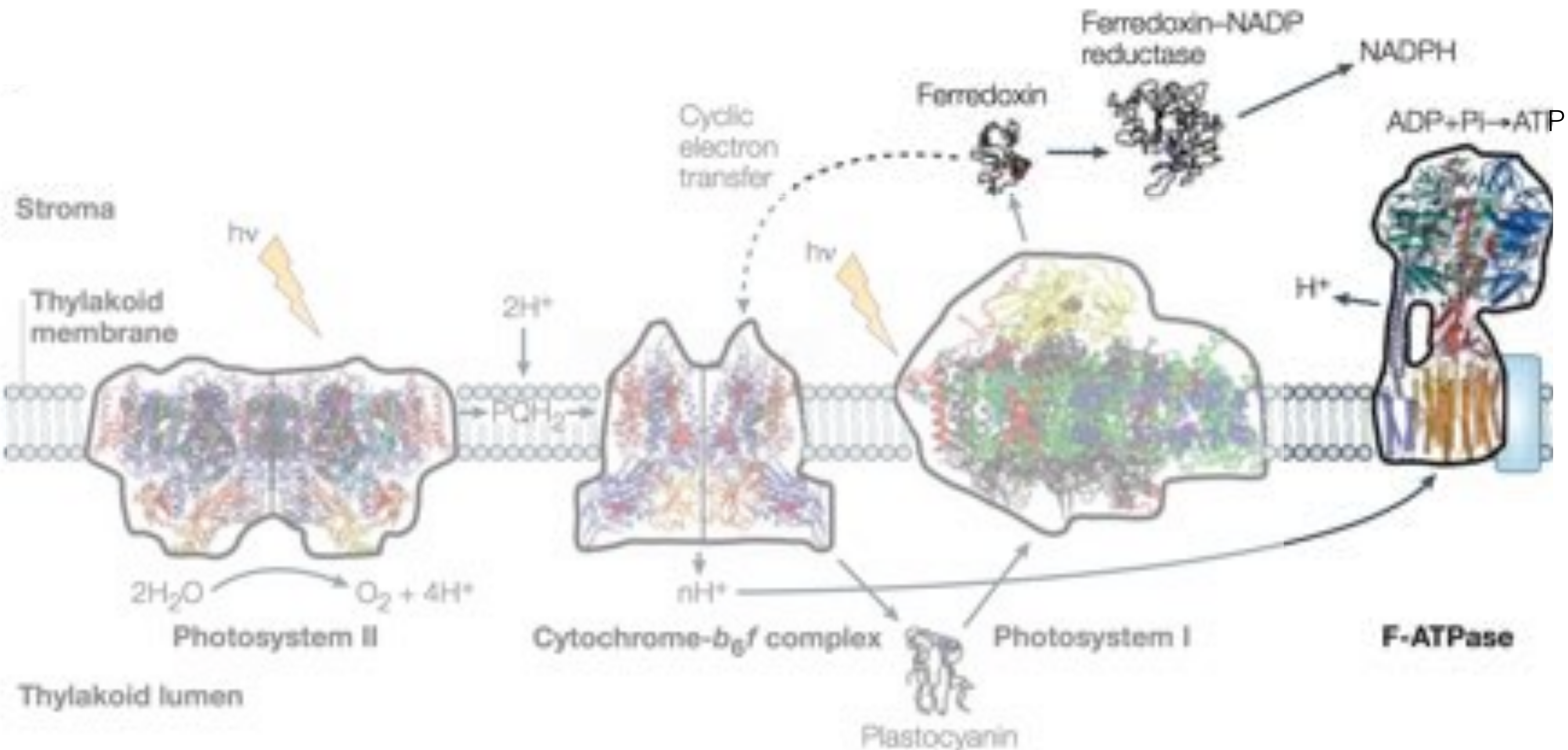


Electrons are pumped across the membrane – Plastocyanin releases one proton as Cu^{I} is oxidized to Cu^{II}

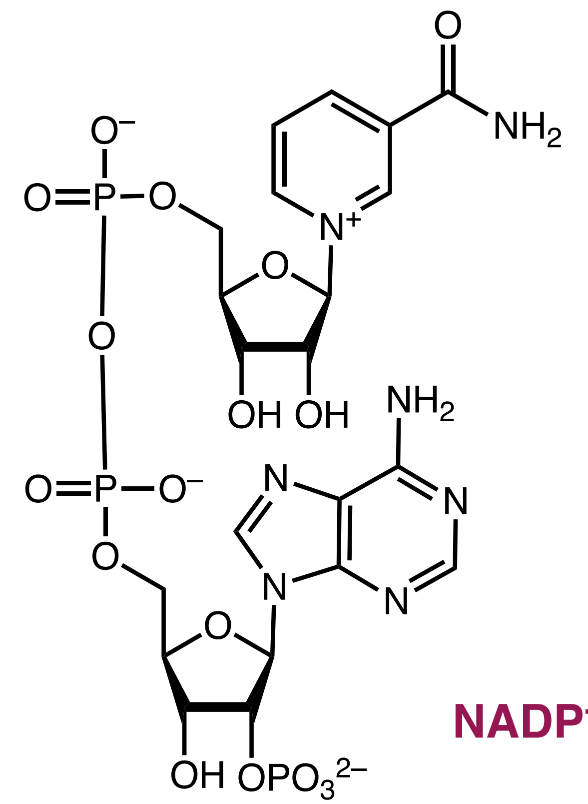
Reduced Ferredoxin is then used to reduce NADP to NADPH

Nelson, N.; Ben-Shem, A.; *Photosyth. Res.* **2002**, *73*, 193–206.
Jordan, P. *et. al.* *Nature*, **2001**, *411*, 909–917.
Ben-Shem, A.; Frolow, F.; Nelson, N. *Nature*, **2003**, *426*, 630–635.

ATPase and NADP reductase



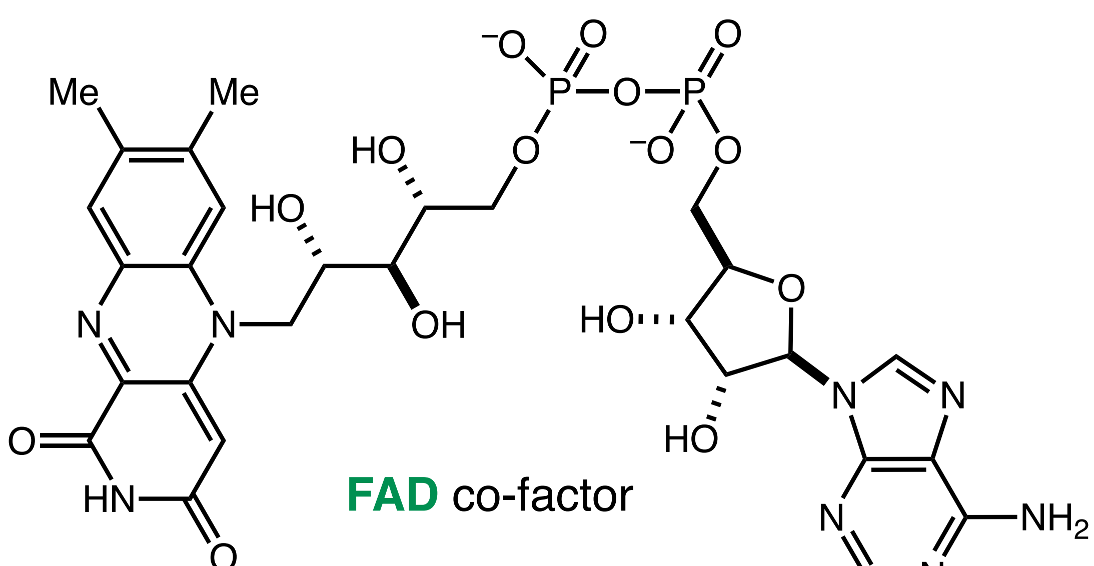
NADP reductase



NADP⁺

$$2\ Fd\ (Fe^{II}) \quad H^+ \quad NADP \longrightarrow NADPH \quad 2\ Fd\ (Fe^{III})$$

Converts 1 electron carrier to two electron carrier – allowing 2 electron chemistry

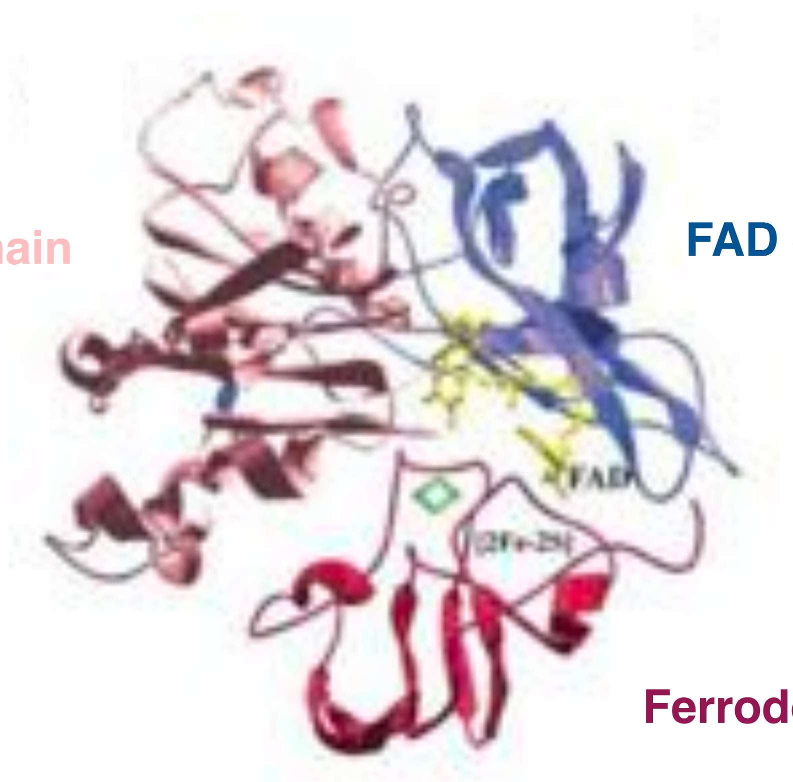


FAD co-factor

Carrillo, N.; Ceccarelli, E. A. *Eur. J. Biochem.* **2003**, *270*, 1900–1915.
Karplus, P. A.; Daniels, M.J.; Herriott, J. R.; *Science*, **1991**, *251*, 60–66.

NADP reductase

NADP domain



FAD domain

Ferrodoxin

NADP$^+$ binds first

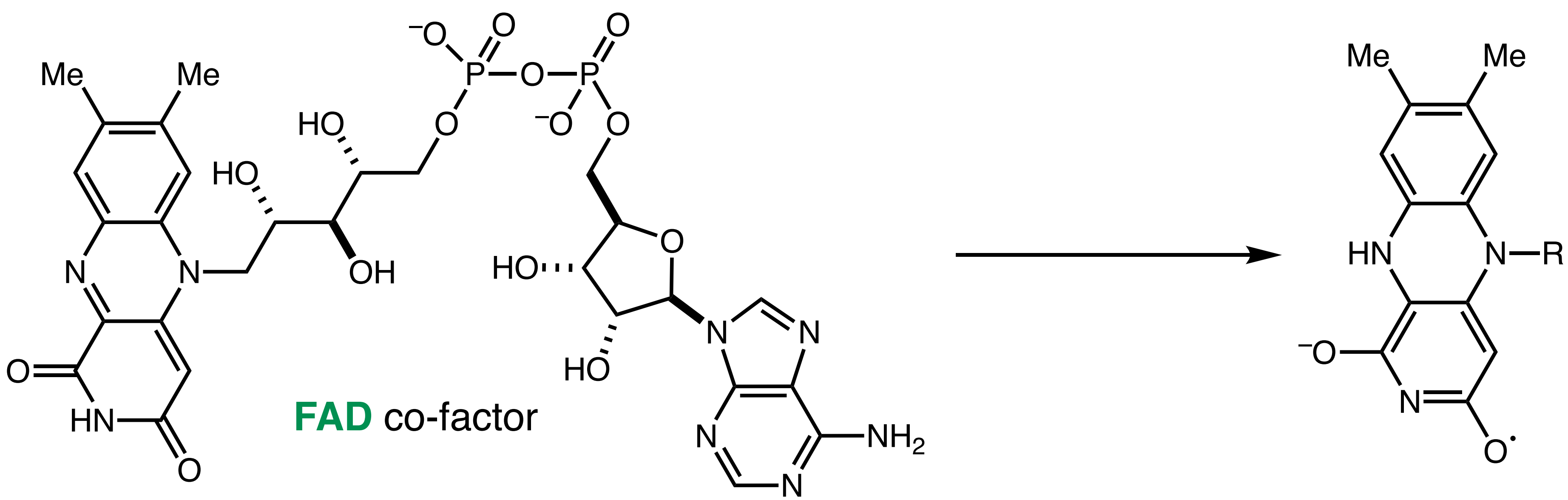
2nd step is binding of ferridoxin – protein-protein interaction

$K_d = 1.7\ \mu m$

60 pm seperation between the 2Fe-2S cluster and FAD

rate of precomplex formation and electron transfer

$6 \times 10^4\ s^{-1}$ – v. fast



FAD co-factor

Semiquinonyl Radical

Unstable in solution

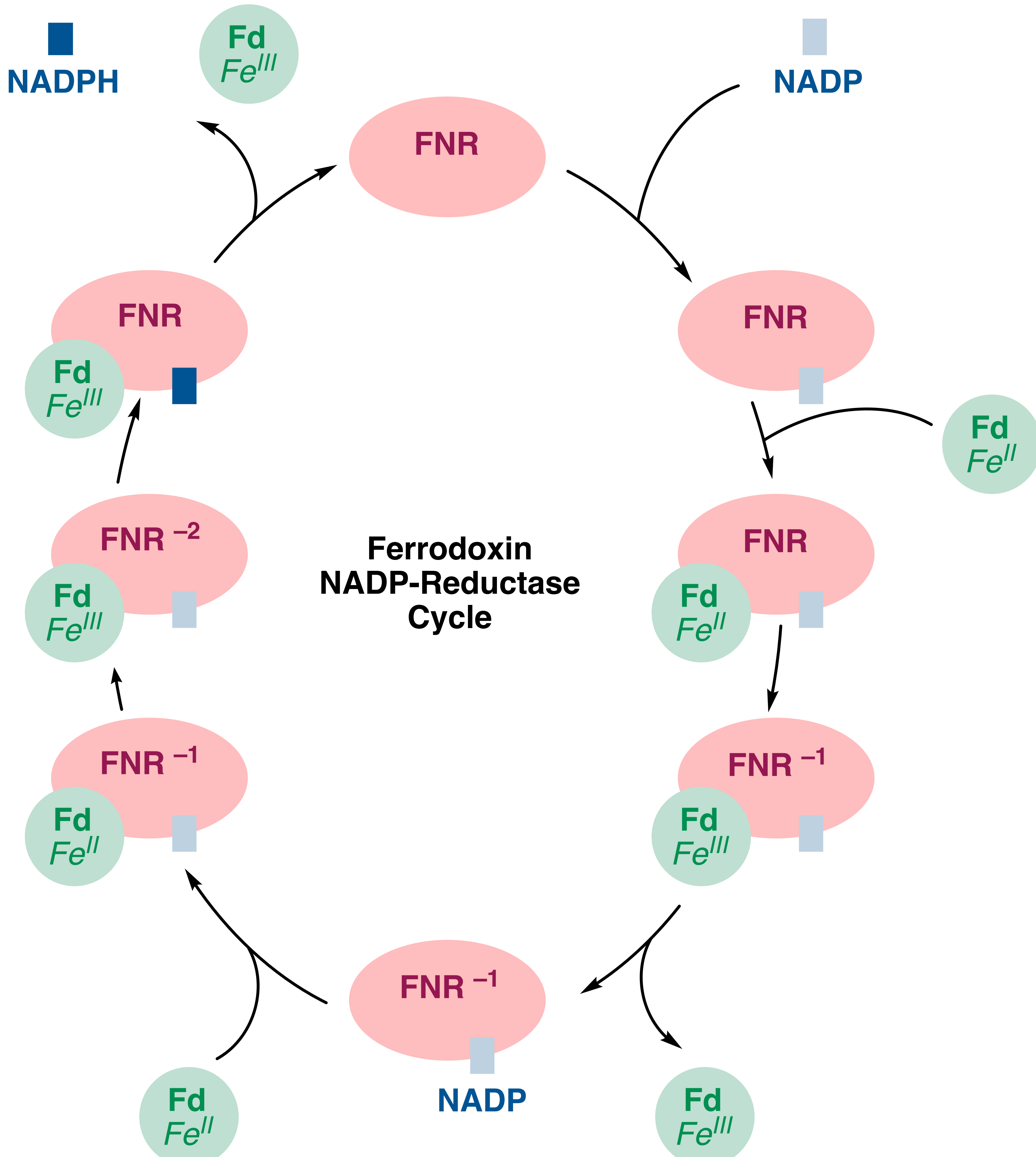
Stable in active site

Carrillo, N.; Ceccarelli, E. A. *Eur. J. Biochem.* **2003**, *270*, 1900-1915.

Karplus, P. A.; Daniels, M.J.; Herriott, J. R.; *Science*, **1991**, *251*, 60–66.

Hurley, J. K.; Morales, R.; Martinez-Julvez, M.; Brodie, T. M. ; Medina, M.; Gomez-Moreno, C.; Tollin, G.; *Biochim. Biophys. Acta.* **2002**, *1554*, 5–21.

NADP reductase



NADPH is the final reduced product of the thylakoid apparatus

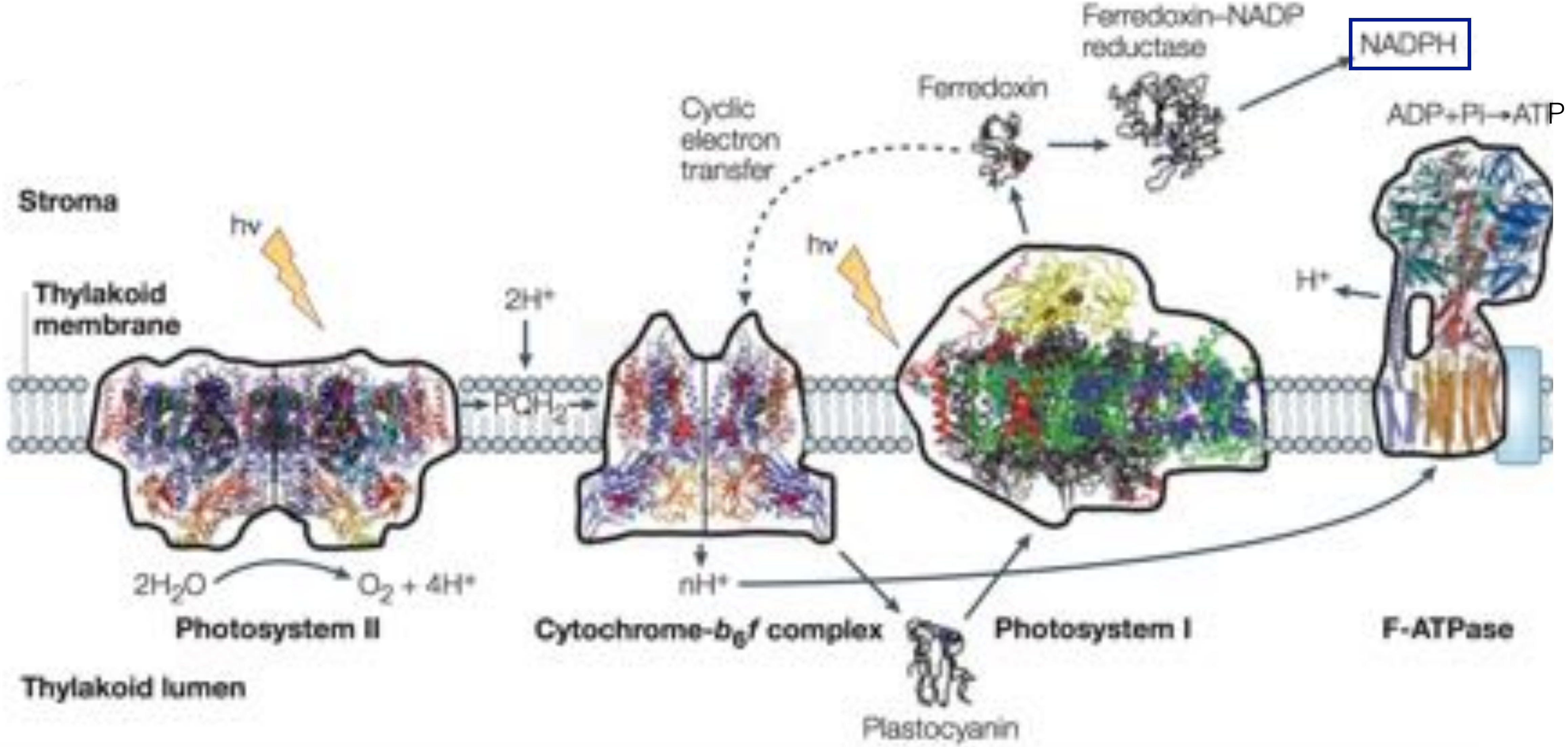
Rate determining step is binding of the second ferrodoxin – kinetics and mechanism of subsequent steps hard to verify

Reaction is inhibted by Fe^{III} and NADPH, the reverse reaction is actually important in metabolism

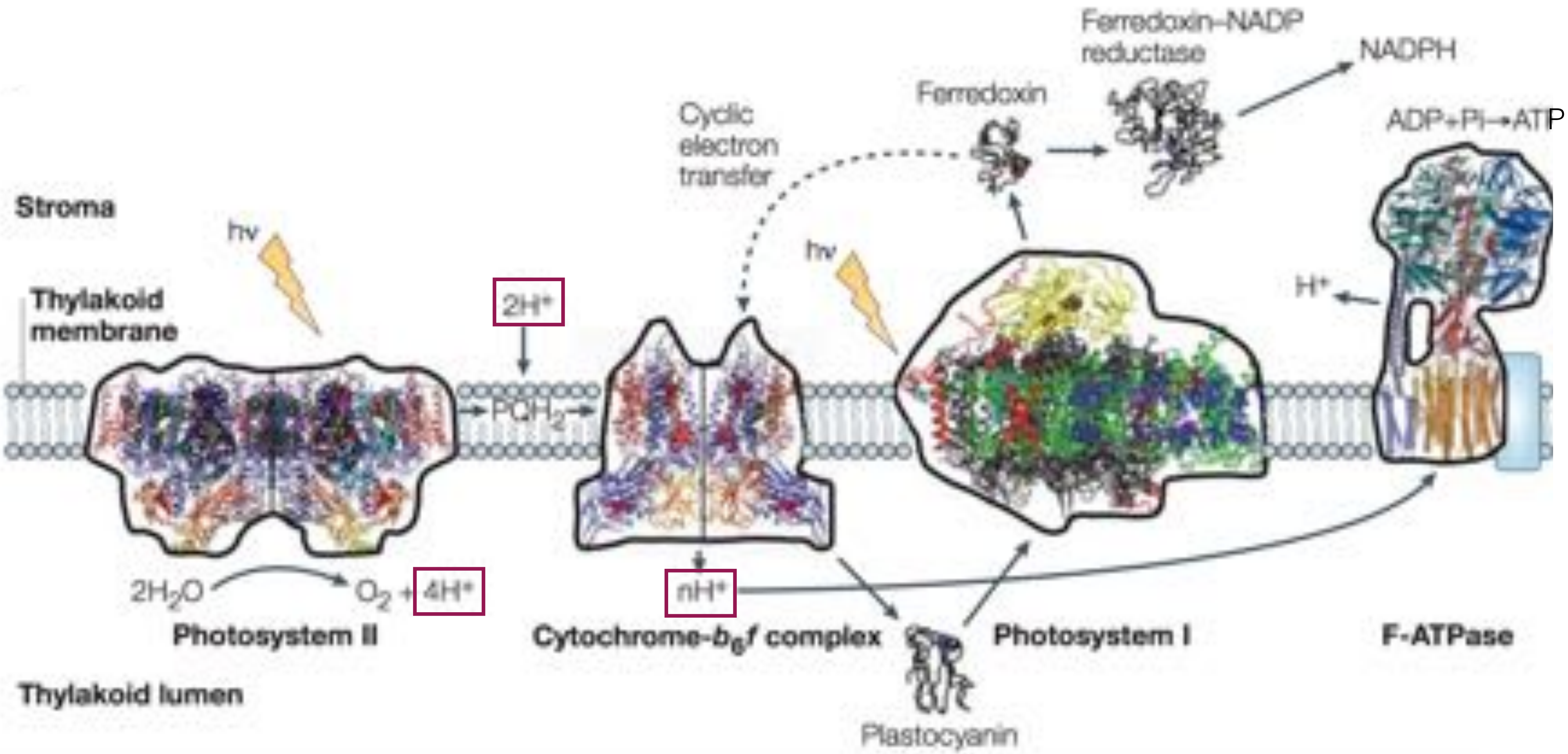
Based on studies of the reverse reaction NADP reduction is likely stepwise – charge transfer then H atom transfer

Carrillo, N.; Ceccarelli, E. A. *Eur. J. Biochem.* **2003**, *270*, 1900–1915.
Karplus, P. A.; Daniels, M.J.; Herriott, J. R.; *Science*, **1991**, *251*, 60–66.
Hurley, J. K.; Morales, R.; Martinez-Julvez, M.; Brodie, T. M. ; Medina, M.; Gomez-Moreno, C.; Tollin, G.; *Biochim. Biophys. Acta.* **2002**, *1554*, 5–21.

ATP Synthesis

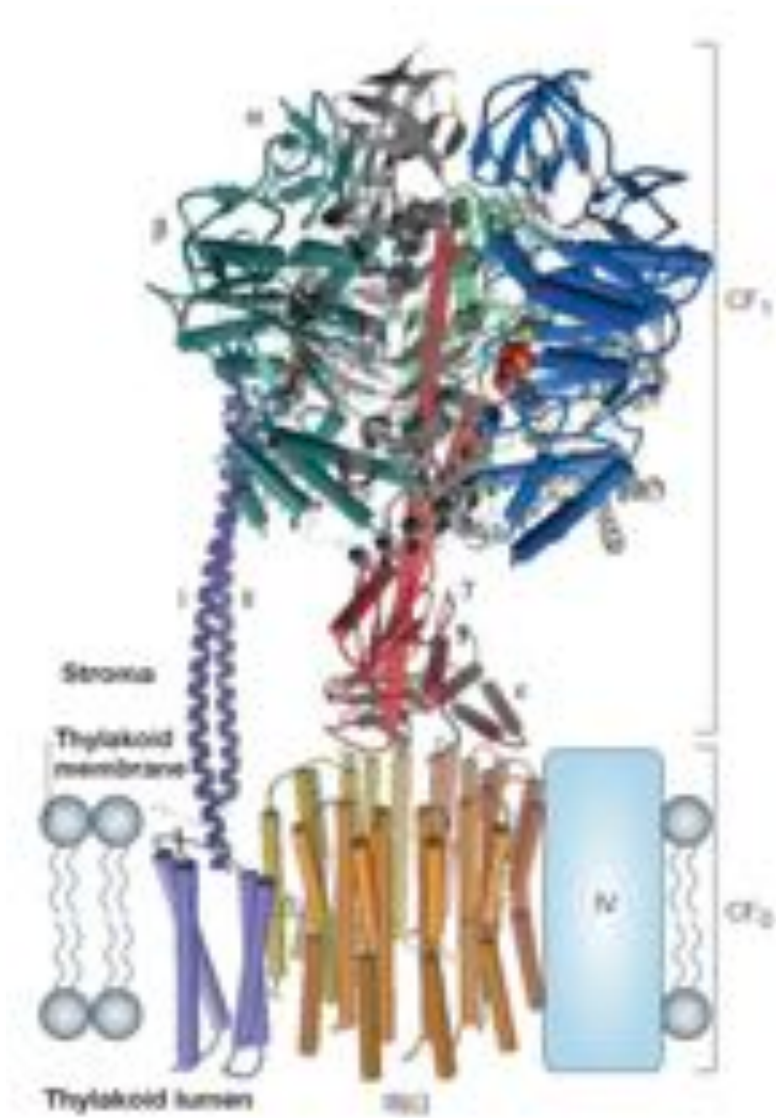


ATP Synthesis



ΔpH = 4

ATP Synthesis



Family of enzymes ubiquitous to energy-transducing membranes

In chloroplasts - uses the protomotive force generated by the pH gradient to synthesis ATP.

Converts energy stored in the proton gradient to chemical energy

The CF_0 subunits rotate as protons are transfered to them through an entry channel from the lumen

After almost complete rotation of the rotor the protons exit through a channel into the stroma

Rotational energy is transfered through the shaft to the β unit of the CF_1 component

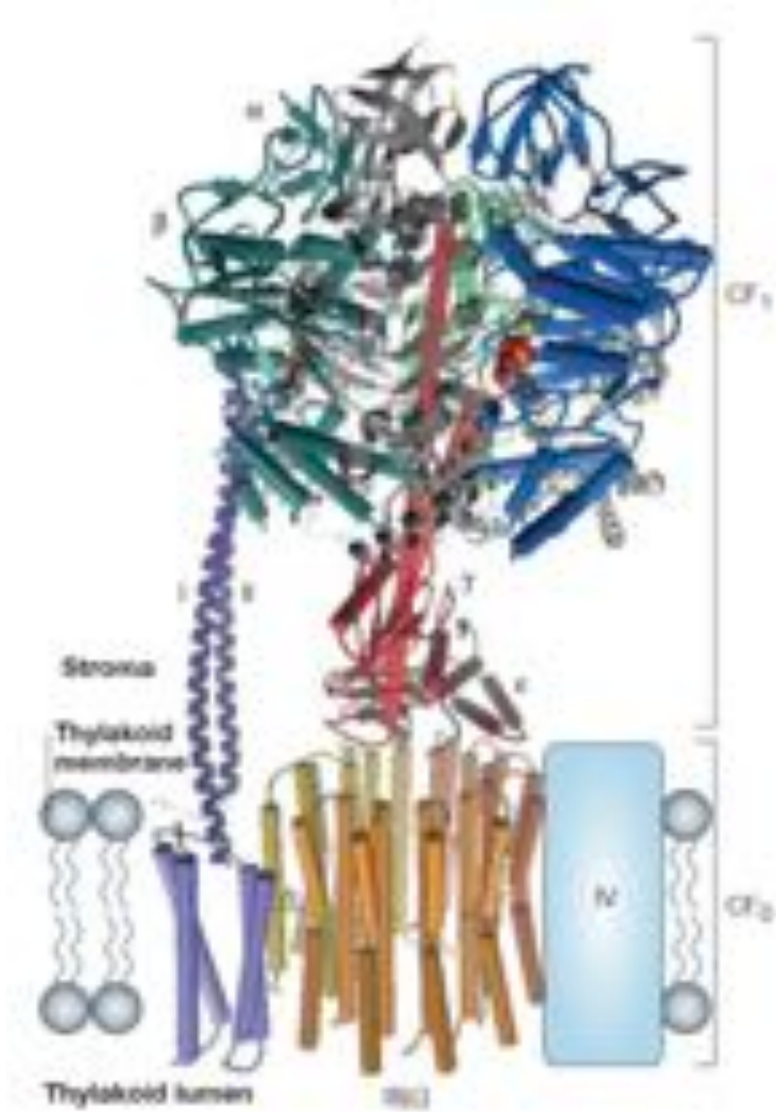
Conformation changes in the CF_1 unit drive ATP synthesis

Electrochemical energy → **Mechanical energy** → **Chemical energy**

pH gradient → rotation of membrane subunit → ATP

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Abrahams, J. P.; Leslie, A. G. W.; Lutter, R.; Walker, J. E. *Nature*, **1994**, *370*, 621–628.
Boyer, P. D. *Annu. Rev. Biochem.* **1997**, *66*, 717–749.
Gibbons, C.; Montgomery, M. G.; Leslie, A. G. W.; Walker, J. E. *Nature. Struc. Biol.* **2000**, *7*, 1055–1061.
Stock, D.; Leslie, A. G. W.; Walker, J. E. *Science*, **1999**, *286*, 1770–1705.

ATP Synthesis



In higher plant chloroplasts 14 protons are required to complete a turn of the rotor

14 indivdual proteins in subunit 3, each takes one proton during the rotation

Each rotation produces 3 molecules of ATP

ATPase can run in reverse if the inverse proton gradient builds up

The CF_1 subunits are held stationary by subunits I and II (stator)

It really is built like a motor

Electrochemical energy	→	**Mechanical energy**	→	**Chemical energy**
pH gradient		rotation of membrane subunit		ATP

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Abrahams, J. P.; Leslie, A. G. W.; Lutter, R.; Walker, J. E. *Nature*, **1994**, *370*, 621–628.
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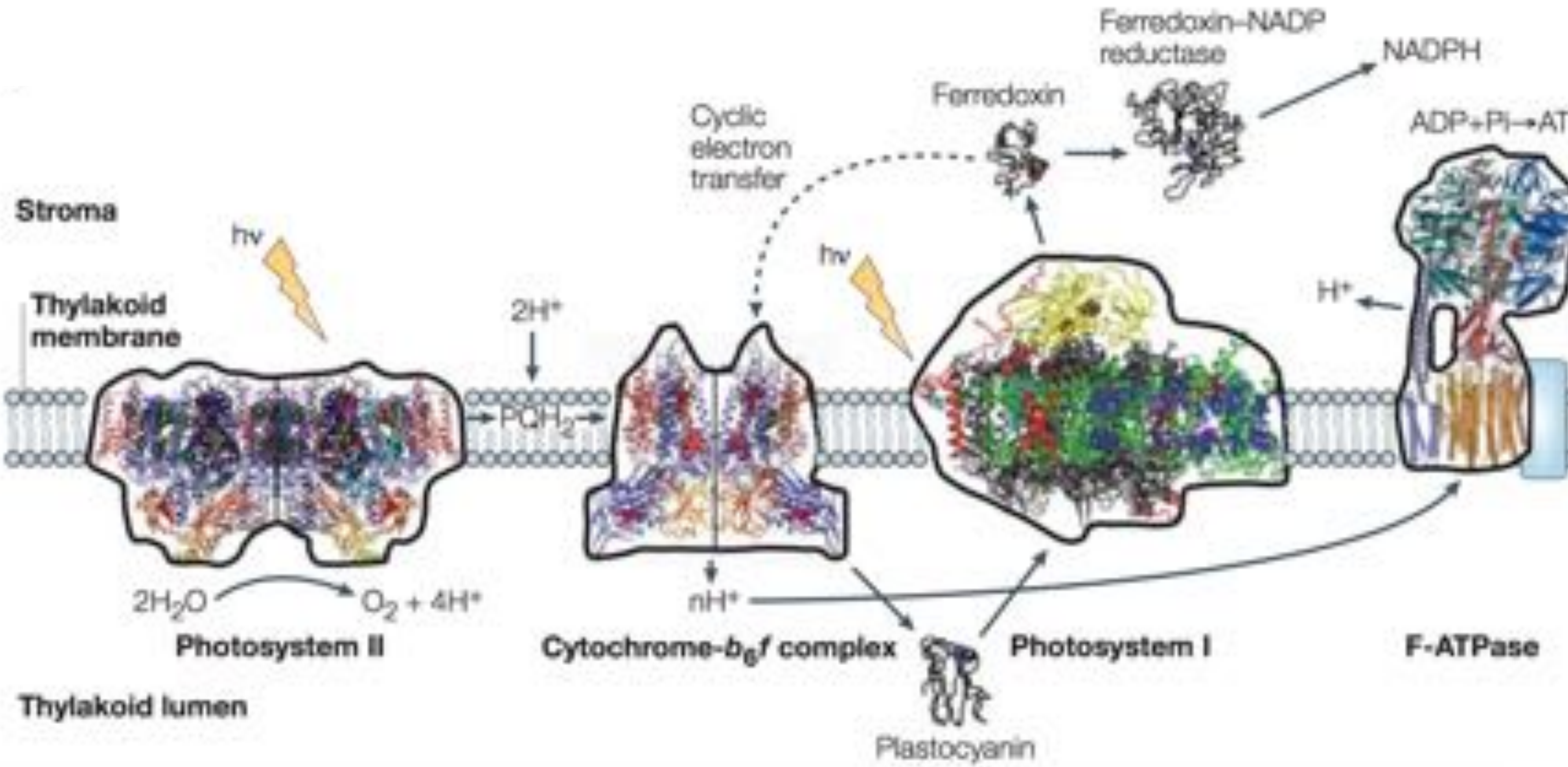
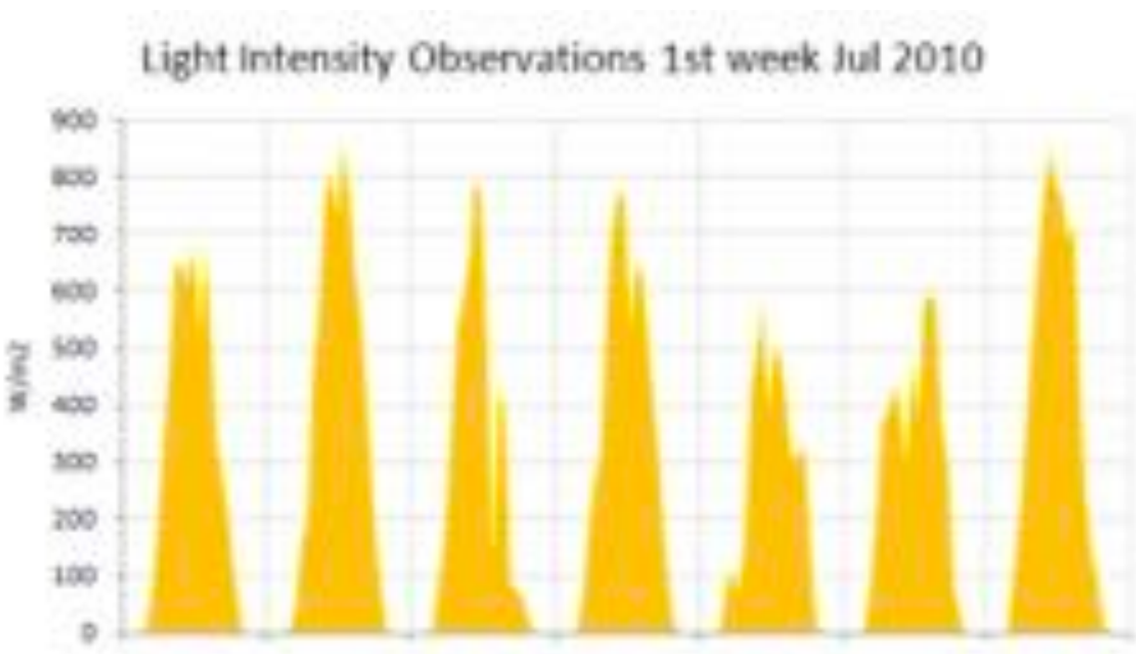
ATP Synthesis



Photoprotection



Plants must be able to cope with variable light intensity and composition

Carotenoids offer some photoprotections

Long term changes in light intensity leads to modulation of antenna complex size – less LCHII binds

–low light enviroments leads to production of more LCHII

In some bacteria changes in light composition also changes the pigments produced

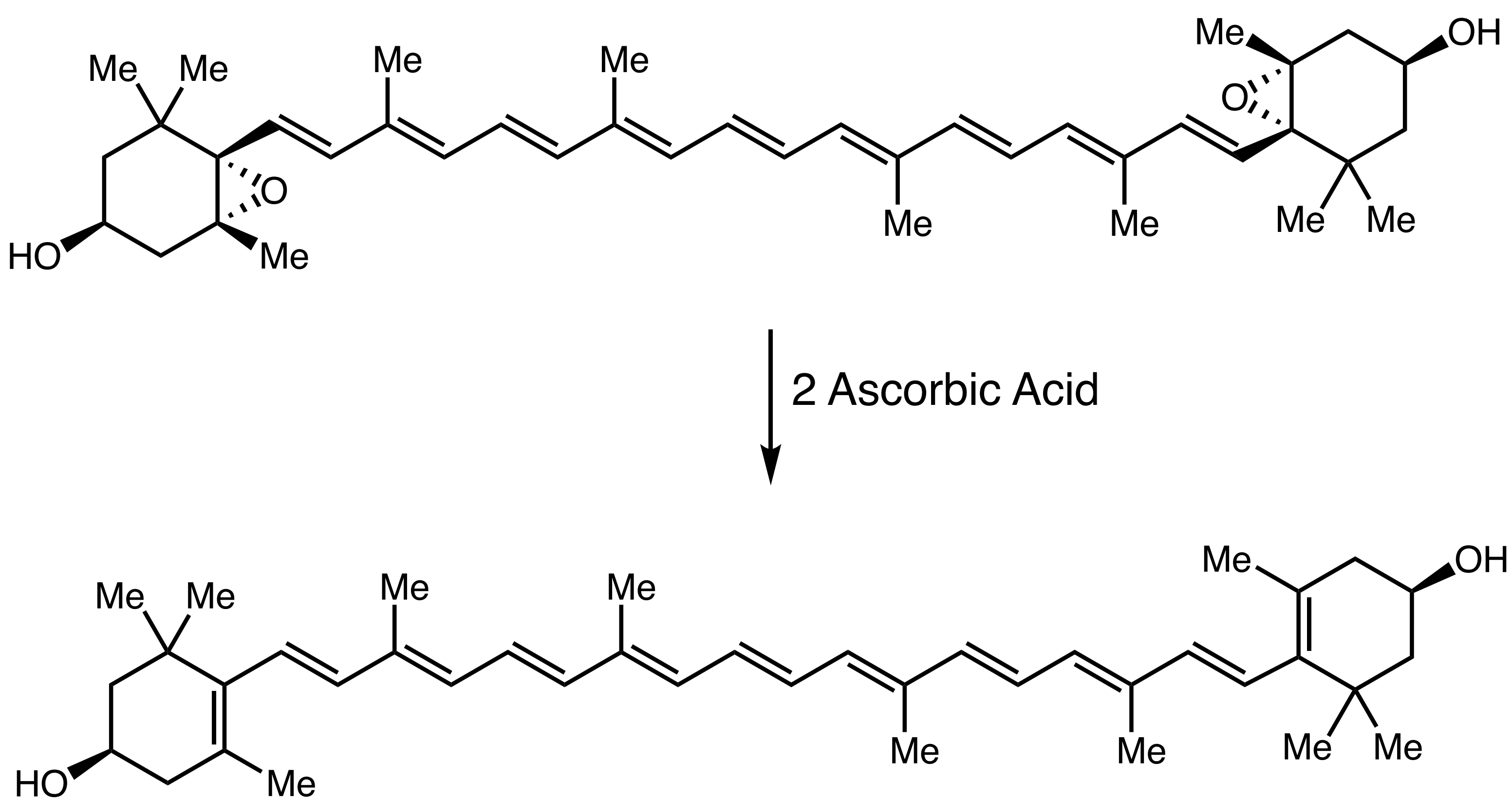
What about short term changes?

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Demmig-Adams, B.; Adams, W. W. III *New Phytol.* **2006**,_ *172*, 11–21.
Gutu, A.; Kehow, D. M. *Mol. Plant.* **2012**, *5*, 1–13.
Kruger, T. P.; Wientjes, E.; Croce, R.; van Grondelle, R. *Proc. Natl. Acad. Sci.* **2011**, *108*, 13516–13521.
Peers, G. *et al. Nature* **2009**, *462*, 518–521.
Kruger, T. P. *et al. Biophys. J.* **2012**, *102*, 2669–2676.
Holt, N. E. *et al. Science* **2005**, *307*, 433–436.
Ruban, A. V. *et al. Nature*, **2007**, *450*, 575–578.

Photoprotection

Photosystem II is highly oxidizing – need someway to slow it down in high light enviroments to stop excessive oxidative damage

Some pigments undergo pH dependent strutural changes which can lead to increased quenching



Violaxanthin

Zeaxanthin

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
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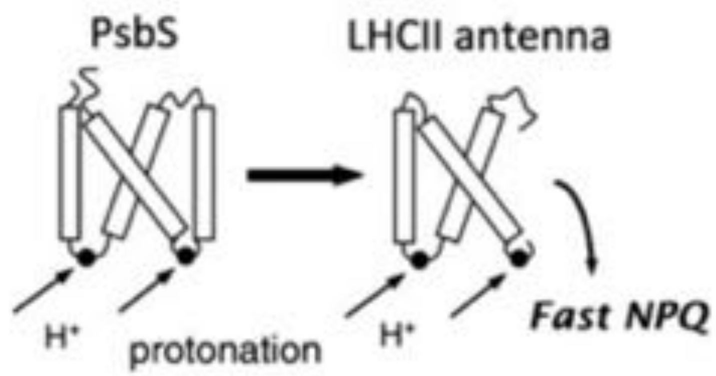
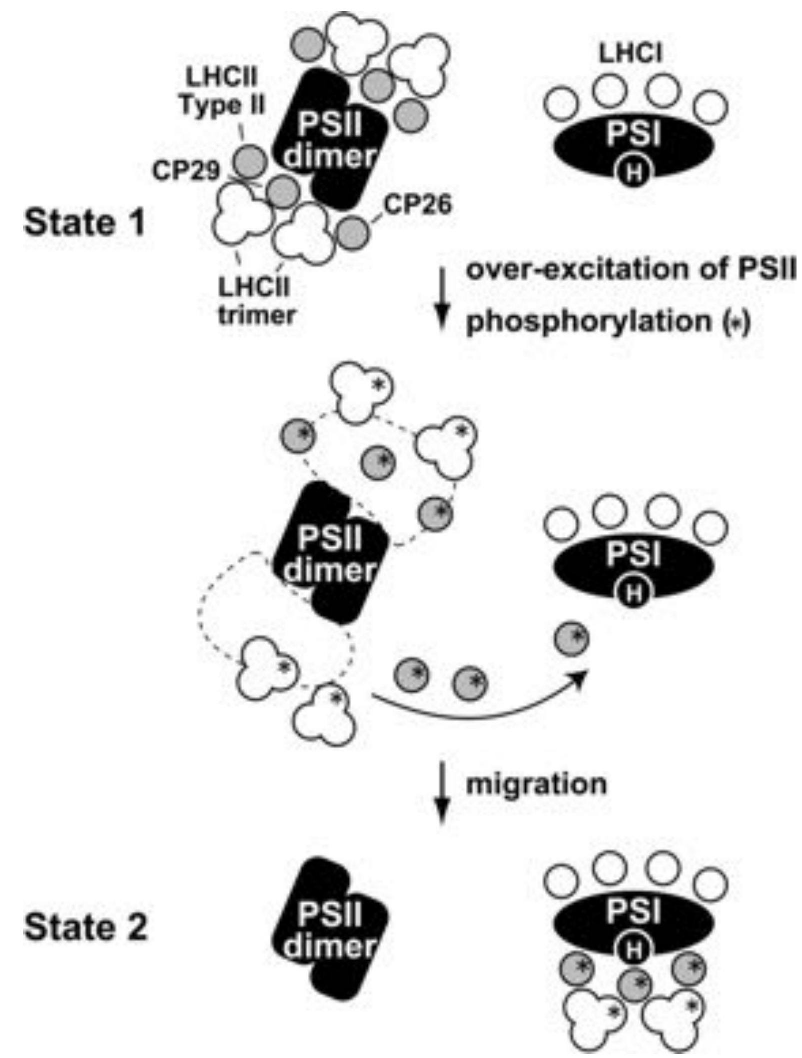
Ruban, A. V. *et al. Nature*, **2007**, *450*, 575–578.

Photoprotection

Photosystem II is highly oxidizing – need someway to slow it down in high light enviroments to stop excessive oxidative damage

When the lumenal pH becomes too low, proteins in the light harvesting cluster become protonated and undergo conformation changes





Phosphorylate LHC II has reduced affinity for PC II.
More phosphorylated PC II less excitation reaches the reaction center

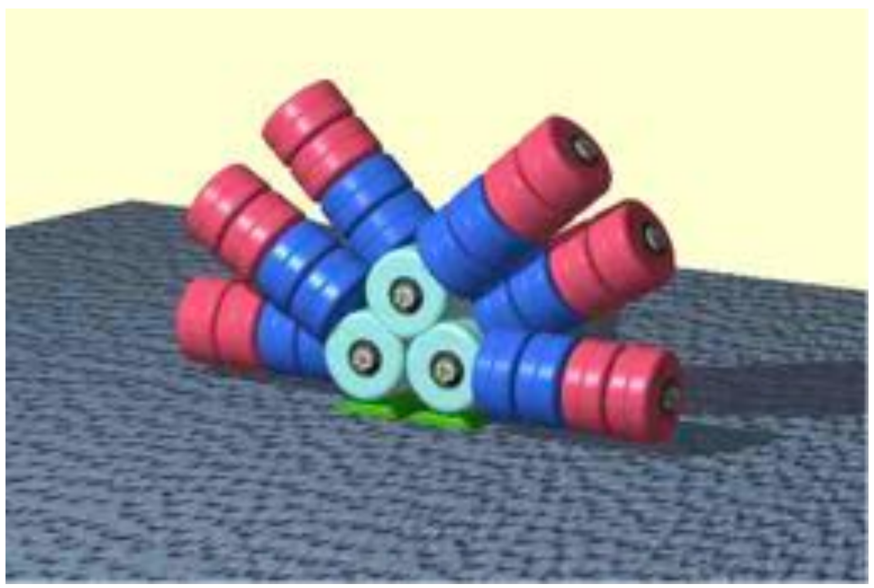
Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Ruban, A. V. *et al. Nature*, **2007**, *450*, 575-578.
Rochaix, J. D. *et. al. Phil. Trans. R. Soc. Lond. B* **2012**, *367*, 3466–3474.
Unlu, C.; Drop, B.; Croce, R.; van Amerongen, H. *Proc. Natl. Acad. Sci. USA.* **2014**, *111*, 2337–2342.

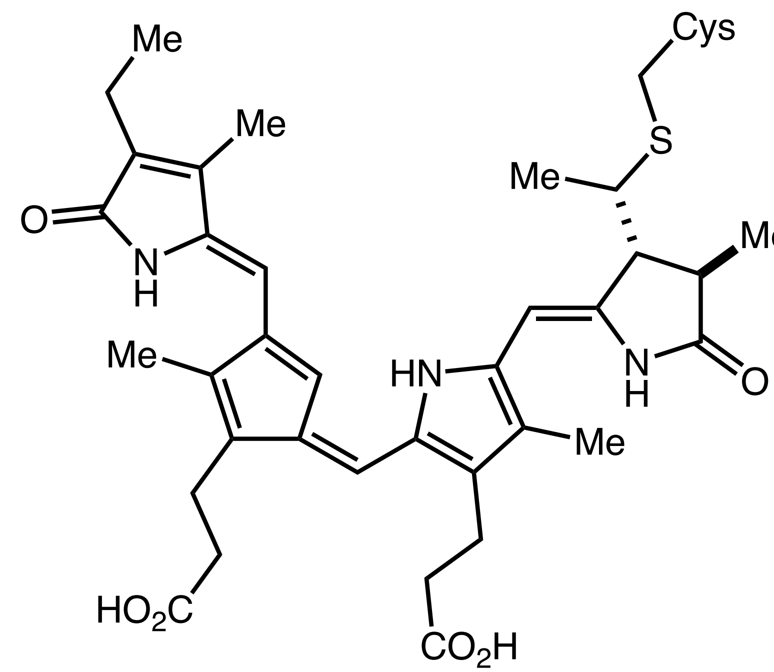
Photoprotection

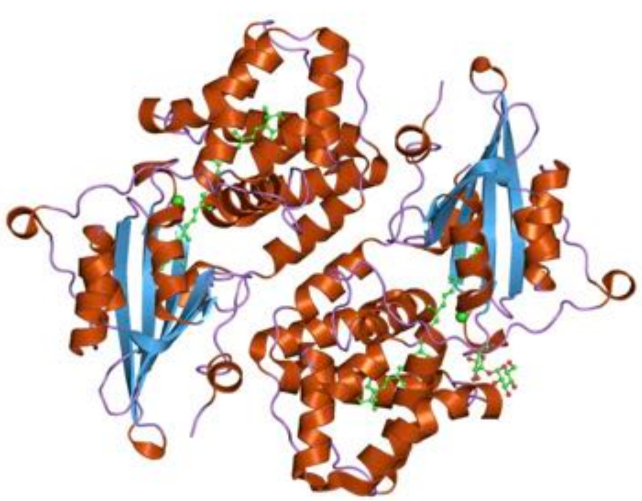
Photosystem II is highly oxidizing – need someway to slow it down in high light enviroments to stop excessive oxidative damage

Cyanobacteria have a unique mechanism to protect aginst oxadative stress

Phycobilisome – light harvesting complex in blue green algae







Orange caretenoid protein

everytime it absorbs a photon – finite chance it changes conformation to a red form which binds to the phycobilisome and dissapates **80%** of the excitation formed as heat

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.
Ruban, A. V. *et al. Nature*, **2007**, *450*, 575–578.
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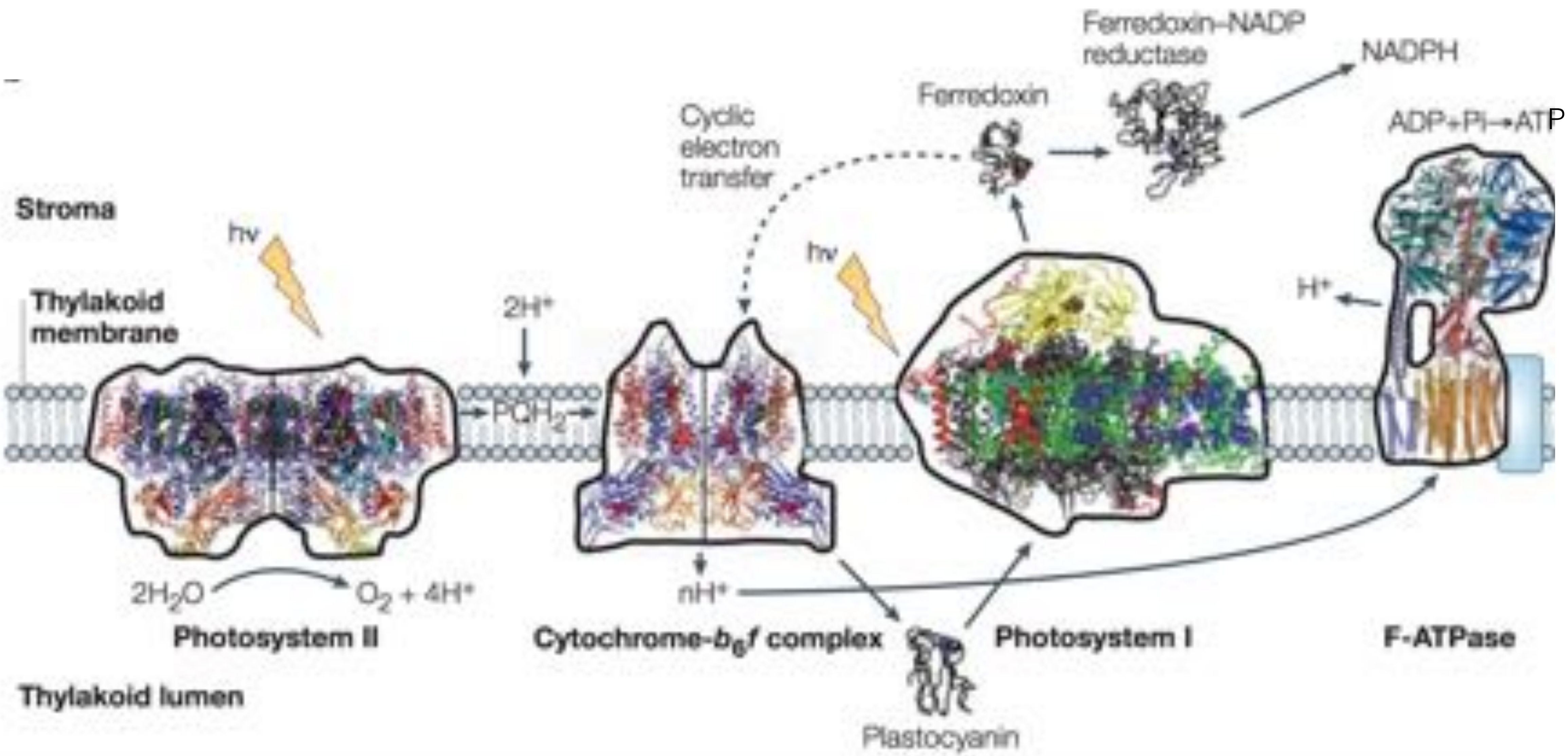
Unlu, C.; Drop, B.; Croce, R.; van Amerongen, H. *Proc. Natl. Acad. Sci. USA.* **2014**, *111*, 2337–2342.

Light Dependent Reaction



Electrochemical gradient ΔpH = 4

Proton gradient used to drive ATPase

H_2O used to reduce $NADP^+$

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.

Light Independent Reaction

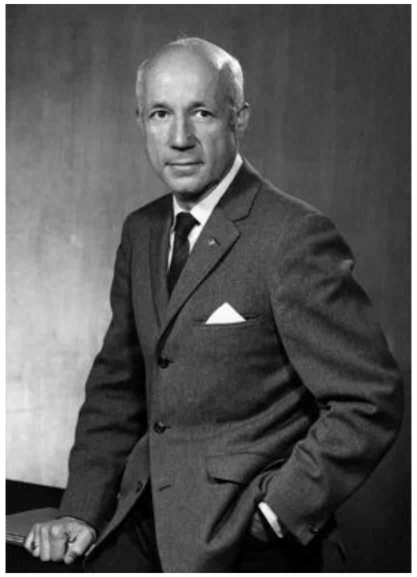
Photosynthesis

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

- NADPH and ATP are low density forms of energy
- Carbohydrates are much denser in energy
- Readily oligermized for convient storage
- CO_2 reduction is light independent.

Nelson, N.; Ben-Shem, A. *Nature Revs. Mol. Cell. Bio.* **2004**, *5*, 971–982.

Light Independent Reaction – Calvin Benson Cycle



Melvin Calvin

UC Berkley

Andrew Benson

Calvin's postdoc

Scripps

to Calvin

1961

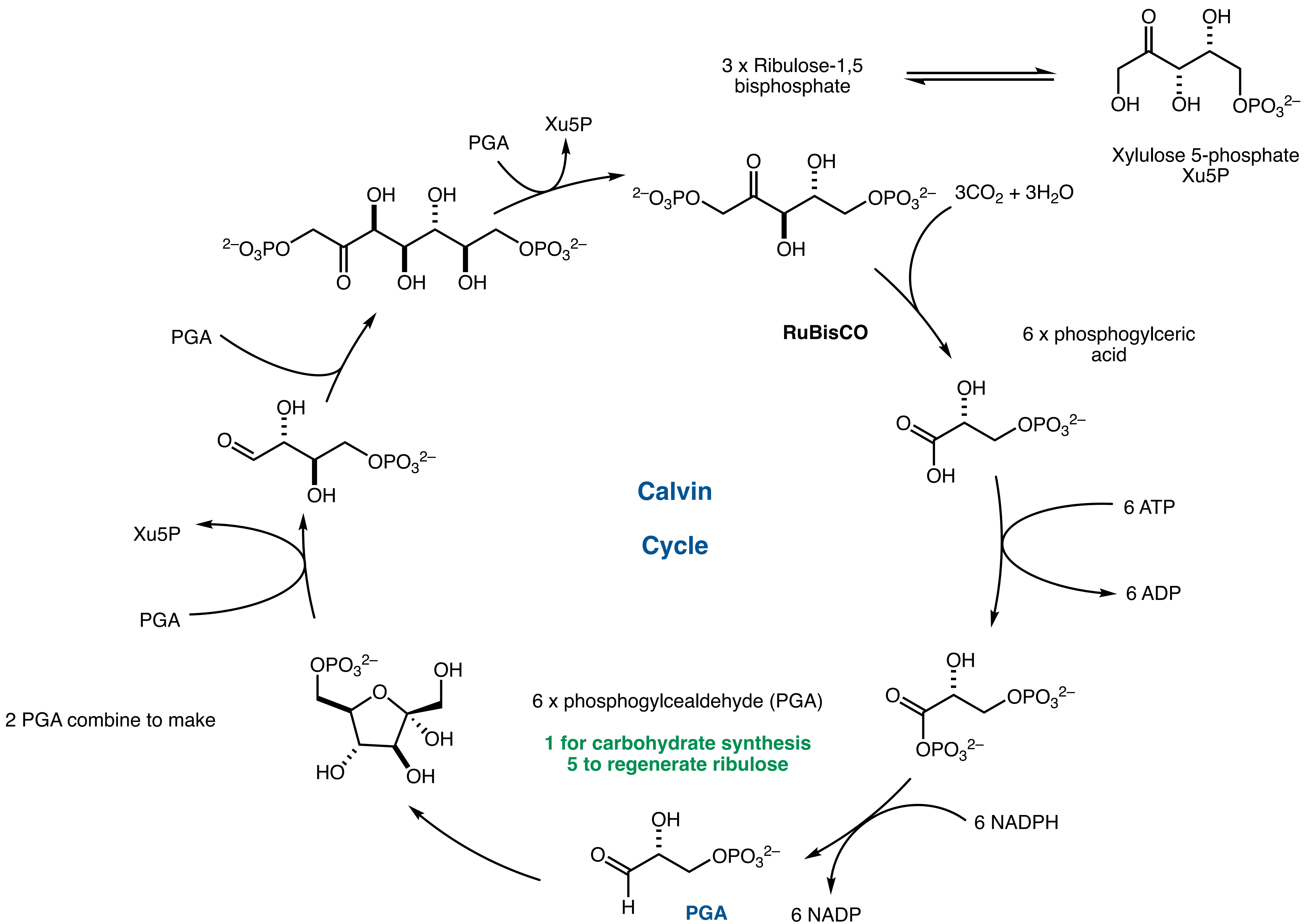
"for his research on the carbon dioxide assimilation in plants"

tracked the fate of ^{14}C following short exposure of photosynthetic organisms to $^{14}CO_2$

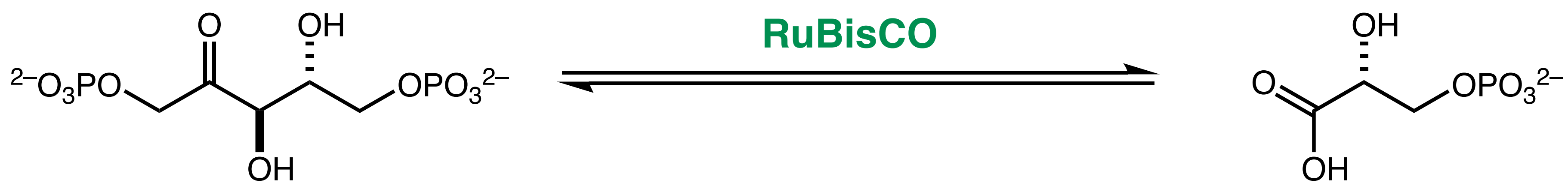
mechanism of CO_2 known as the Calvin (Calvin-Benson) cycle

Bassham, J. A.; Benson, A. A.; Kay, L. D.; Harris, A. Z.; Wilson, A. T.; Calvin, M. *J. Am. Chem. Soc.* **1954**, *76*, 1760–1770.
Mayaugon, J.; Benson. A. A.; Calvin, M. *Biochim. Biophys. Acta* **1957**, *23*, 342–351.
Benson, A.; *Annual Review Plant Biol.* **2002**, *53*, 1–25.
Wildman SG. **1998**. *Discovery of Rubisco. In Discoveries in Plant Biology,* ed. S-D Kung, S-F Yang, 163–73. Singapore: World Sci. Publ.
Professor Andrew Benson Interview – https://www.youtube.com/watch?v=GfQQJ2vR_xE&feature=youtu.be

Light Independent Reaction – Calvin Benson Cycle



Carbon Fixation – RuBisCO



Carbon Fixation – RuBisCO

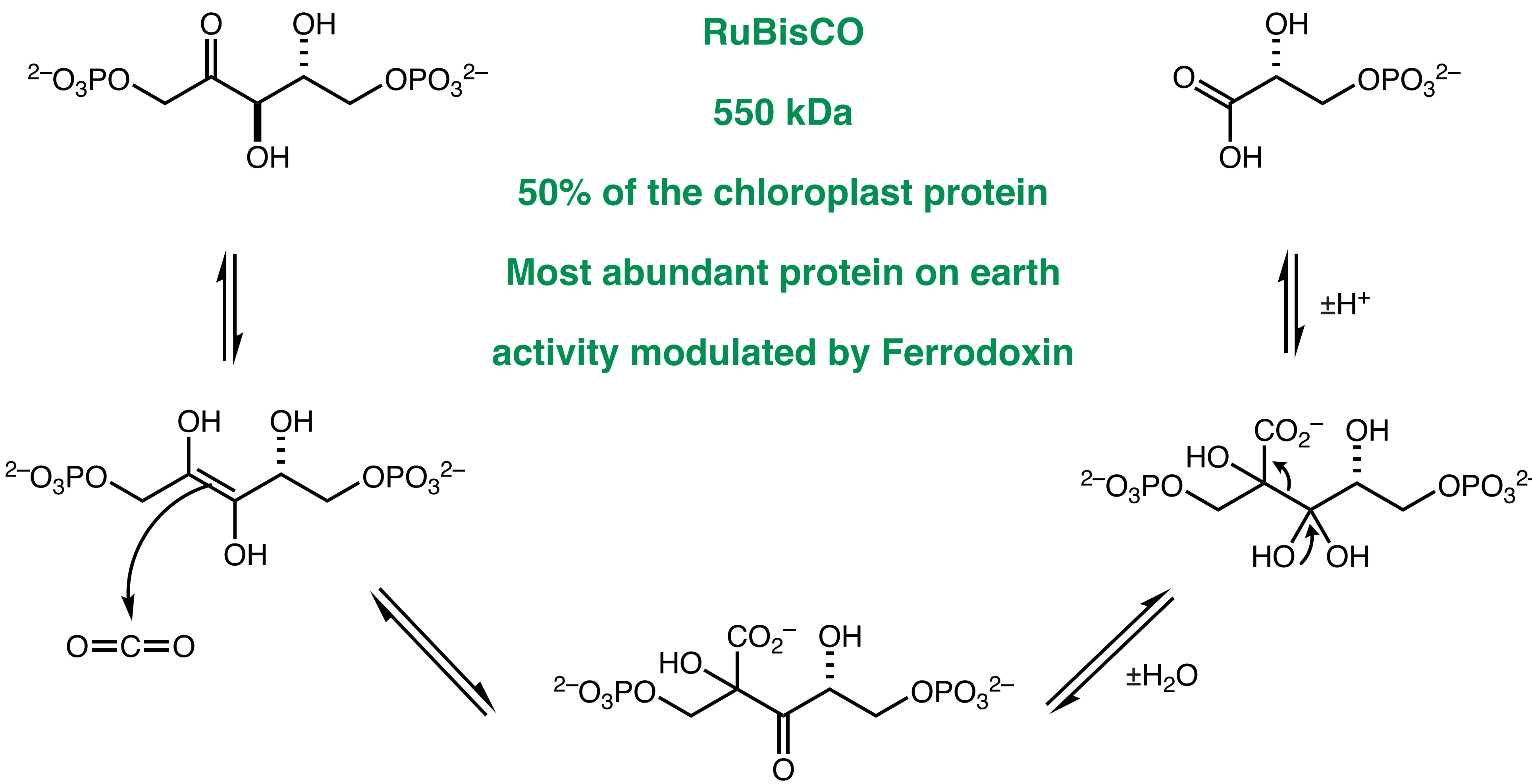
RuBisCO

550 kDa

50% of the chloroplast protein

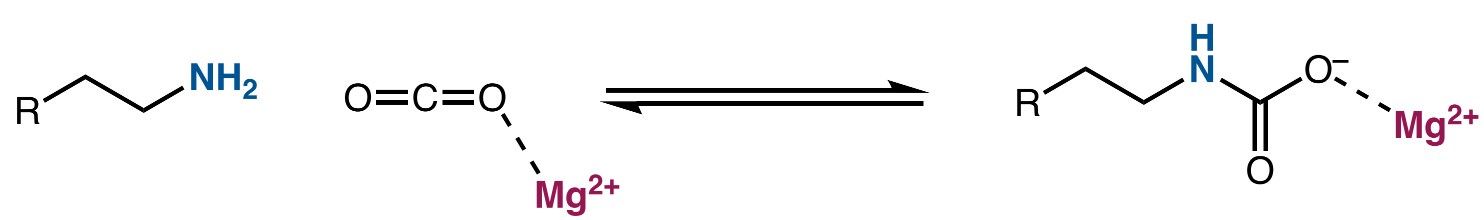
Most abundant protein on earth

activity modulated by Ferrodoxin



Enol trapping of CO_2 is thermodynamically highly unfavourably, second step is highly favourable

CO_2 is also not particularly polar, CO_2 binding mechanism is unique. Vital lysine residue and Mg^{2+} cofactor



Photosynthesis