Biophysics of Photosynthesis
Mechanism of grana stacking

1. LHCII tends to aggregate
2. thylakoids containing a lot of LHCII will stick together, forming grana. PSIIRC nicely fits in because it does not protrude much out of the membrane
3. The more bulky PSIRC and the most bulky ATPase go into stroma regions
Necessary for energy transfer:
stable S1-state

S2

S1

h·ν

S0

Chlorophyll

h·ν

Internal conversion

intersystem crossing

EET

photochemistry

phosphorescence

absorption

Internal conversion

fluorescence

Internal conversion
Necessary for energy transfer:
Overlap of emission/absorption bands
Adjustment of absorption bands by chemical modification

From: Lawlor DW (1990) Thieme, Stuttgart, 377S

Comparison of Energy transfer mechanisms

- For all processes, speed of energy transfer decreases with increasing distance.
- This limits the rate and efficiency of enzymatic and non-enzymatic processes. The longer the transfer time, the higher the risk of energy loss by unwanted processes.
- Light energy transfer is fast and covers large distances, but required re-absorption and thus is not very efficient.
- Electron tunnelling is fast for very short distances, but very slow for longer distances → most relevant <10Å.
- Diffusion speed decreases less with increasing distances, therefore it becomes faster than tunnelling at more than 10-20Å.

Mechanisms of energy transfer between chlorophylls

Short distance, requires overlap of molecular orbitals (→ only Chls in extremely short distance to each other, e.g. special pair): direct transfer of S1 excited state (Dexter-Mechanism)

Larger distance, requires overlap of absorption/emission spectra: Transfer by inductive Resonance ("Förster-Mechanism")

\[
\Gamma_{DA} = k_D \left( \frac{R_0}{R} \right)^6
\]

\[
R_0^6 = 8.8 \times 10^{17} \frac{\kappa^2}{n^4} J
\]
Energy transfer – funnel principle (II): Scheme in higher plants

Energy transfer – funnel principle (II): Scheme in higher plants

Absorb shortest wavelengths → absorb longer wavelengths → absorb longest wavelengths

From: Lawlor DW (1990) Thieme, Stuttgart, 377S
Energy transfer – funnel principle (II): Scheme in cyanobacteria (Trichodesmium)

Transmission of filters for selective excitation

![Graph showing absorption spectra and energy transfer scheme in cyanobacteria.]

- PUB = Phycourobilin
- PE = Phycoerythrin
- PC = Phyco-cyanin
- APC = Allo-Phycocyanin
- Chl = Chlorophyll
- RC = Reaction Center

Absorption

Wavelength / nm

0.2
0.15
0.1
0.05

400 450 500 550 600 650 700
Energy transfer – funnel principle (III):
Transfer times between Chls towards & in PSIIRC

From: vanGrondelle R, Novoderezhkin VI, 2006, PCCP8, 793-807
Regulation of energy transfer (I): the principle of „state transitions“

Higher plants, many algae
The cycle of state transitions

State of adaptation to light 1 (state 1)

PSII-LHCII + PSI

Plastoquinone poised

Plastoquinone reduced

ATP

LHCII kinase

ADP

PSII + LHCII + PSI

Light 1

Plastoquinone oxidized

P_i

Phospho-LHCII phosphatase

PSII + PSI-LHCII-P

Light 2

State of adaptation to light 2 (state 2)

Recent alternative view of the function of state transitions

Regulation of energy transfer (I): „state transitions“ in cyanobacteria and red algae

State 1

State 2

APC core

D

E

PS I CP47 D1/D2 CP43

PS I CP47 D1/D2 CP43
Reversible coupling of individual phycobiliproteins...

...as a basis for diazotrophic photosynthesis

Excitation energy transfer between chlorophyll derivatives and singlet oxygen
Photosynthesis related Proteins with metal centres

1. LHCII & PSIIRC: generation & quenching of $^1$O$_2$

From: Pospisil P (2012) Biochimica et Biophysica Acta 1817, 218-31
Regulation of energy transfer (II):
Mechanisms of protection by carotenoids against singlet oxygen

From: Lawlor DW (1990) Thieme, Stuttgart, 377S
Regulation of energy transfer: xanthophyll cycle

little light

much light

light harvesting shorter conjugation length

Quenching longer conjugation length

Zeaxanthin

Violaxanthin de-epoxidase

High light only

Zeaxanthin epoxidase

High light only

Violaxanthin de-epoxidase
Fast adaptation to irradiance changes: combination of LHCII-aggregation with xanthophyll cycle


NPQ = non-photochemical quenching

Fast adaptation to irradiance changes: combination of LHCII-aggregation with xanthophyll cycle

From: http://photosynthesis.peterhorton.eu/research/lightharvesting.aspx (Horton lab web page)
Model depicting the differential roles of PSII-LHCII protein phosphorylation in the regulation of excitation energy distribution between PSII and PSI. Such regulation mostly occurs in grana margins where PSII and PSI are in close proximity.

PsbS modulation of the structure and function of the PSII antenna

- At relatively high but not inhibitory light, relatively many unstacked grana exist, where LHCII is not efficiently coupled to PSIIIRC.

- At low (limiting) light, enhanced grana stacking occurs, regulated via an increase of Mg2+.

- At inhibitory high light, grana unstack again, and in addition protonation of PsbS leads to strong non-photochemical quenching of excitons.

Overview of photosynthetic light reactions the „Z-scheme“

From: accessscience.com
Biophysical aspects of photosynthetic electron transport
A) Photosystem II reaction centre:
special pair chlorophyll and pheophytins

Mechanism of charge separation

1. Special pair chlorophylls (=P680) accept excitons from antenna
2. P680 transfers an electron to Chl$_{D1}$ (“initial charge separation”)
3. Within a few ps, the electron is further transferred to Phe (→ P680$^+$ / Phe$^-$) “primary charge separation”
Biophysical aspects of photosynthetic electron transport
A) Photosystem II reaction centre: speeds of electron transfer
Water splitting complex of the photosystem II reaction centre proposed mechanism

- 2 of the 4 Mn ions are redox-active (\(3^+/4^+\)), accepting electrons from water and transferring them to P680
- Ca\(^{2+}\) helps in binding the water

Biophysical aspects of photosynthetic electron transport
B) Cytochrome b₆f complex: mechanism

Functional characteristics

- Transfers e- from PQ to plastocyanin (PC).
- It uses the difference in potential between Qₐ and PC for translocating a proton via 2x2 heme b groups and 2x1 heme x group.
- Electrons are transferred from the heme b groups to PC via a “Rieske” [2Fe2S]-cluster and a heme f group.
- Cyclic electron transport occurs via coupling of ferredoxin to heme x.

**Biophysical aspects of photosynthetic electron transport**

C) **Plastocyanin**

**Functional characteristics**

- Oxidised \((\text{Cu}^{2+})\) plastocyanin accepts electron from \(\text{Cyt}_{\text{b6f}}\) complex,
- Reduced \((\rightarrow \text{Cu}^{+})\) plastocyanin diffuses to the PSIRC
- Plastocyanin releases the electron \((\text{Cu}^{+} \rightarrow \text{Cu}^{2+})\)
- Rigid protein structure facilitates fast red/ox-changes, but recent data show that copper binding still causes changes in structure ("induced rack" rather than "entatic state")

Biophysical aspects of photosynthetic electron transport
D) Photosystem I reaction centre

Functional characteristics:

- primary charge separation:
  special pair (=P700, Chl a / Chl a’ heterodimer), releases e\textsuperscript{-} to A\textsubscript{0} via A (both Chl a)
- e\textsuperscript{-} transport via A1 (phylloquinone) and the [4Fe4S]-clusters F\textsubscript{x}, F\textsubscript{A} and F\textsubscript{B} to the [4Fe4S]-cluster of ferredoxin
- P700 is re-reduced by plastocyanin

All slides of my lectures can be downloaded

from my workgroup homepage
www.uni-konstanz.de → Department of Biology → Workgroups → Küpper lab,

or directly
http://www.uni-konstanz.de/FuF/Bio/kuepper/Homepage/AG_Kuepper_Homepage.html

and

on the ILIAS website