Introduction to Biophysics of Photosynthesis
**Photosynthesis**

- **O₂**
- **photosystem II**
- **electron transport system**
- **photosystem I**
- **electron transport system**
- **NADPH + H⁺**
- **ATP**
- **CO₂**
- **H₂O**
- **PPRC**
- **sugar phosphate**

**Components:**
- **granalum**
- **stroma**
- **THYLAKOID COMPARTMENT**
- **(H⁺ reservoir)**
- **ATP formation at separate membrane site**
- **STROMA**
- **sugar phosphate**
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

Chlorophyll

EET

photochemistry

phosphorescence

Internal conversion

fluorescence

intersystem crossing

absorption

absorption

internal conversion

internal conversion
Necessary for energy transfer:
Overlap of emission/absorption bands

From: bio.libretexts.org
Adjustment of absorption bands by chemical modification

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

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“)

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

\[
R_0^6 = 8.8 \times 10^{17} \frac{\kappa^2}{n^4} J
\]
Comparison of other 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.

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

Energy transfer – funnel principle (II): debated modern view

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
Energy transfer – funnel principle (II): Scheme in purple bacteria


From: Jaime-Perez N et al. (2019) unpublished data H330
Energy transfer – funnel principle (III):
Transfer times between Chls towards & in PSIIRC

From: vanGrondelle R, Novoderezhkin VI, 2006, PCCP8, 793-807
Photosynthesis related Proteins with metal centres

1. Excitation transfer times between light harvesting complexes

Regulation of energy transfer (I): the principle of „state transitions“

Higher plants, many algae
Regulation of energy transfer: The cycle of state transitions

Regulation of energy transfer: another view of „state transitions“

Alternative view of the function of state transitions

State I

CO₂ → Calvin cycle

O₂ + 4H⁺ → 2 H₂O

LHCCI  PSII  Cyt b₆f  PSI

Linear electron flow

State II

PSII membrane domains (grana)  |  PSI membrane domains (stroma lamellae)

PSII  Cyt b₆f  PSI  LHCCI

Cyclic electron flow

ATPsynthase

Regulation of energy transfer (I): „state transitions“ in cyanobacteria and red algae
Reversible coupling of individual phycobiliproteins... as a basis for diazotrophic photosynthesis

normal non-diazotrophic (large phycobiliprotein antenna coupled to PSI)

bright I → diazotrophic (large PUB antenna coupled to PSII)

low fluorescence (quenching) (unknown quenching arrangement, probably phycobiliprotein aggregation)

Excitation energy transfer
between chlorophyll derivatives and singlet oxygen

S2

intersystem crossing

S1

h·ν

intersystem crossing EET

h·ν

intersystem crossing

S0

chlorophyll

photochemistry

absorption

intersystem crossing

fluorescence

intersystem crossing

phosphorescence

EET

intersystem crossing

intersystem crossing

S1

phosphorescence

intersystem crossing

T1

oxygen
Photosynthesis related Proteins with metal centres
1. LHCII & PSIIRC: generation & quenching of $^1\text{O}_2$

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**:
  - Violaxanthin
  - Chlorophyll a
  - Light harvesting, shorter conjugation length

- **Much light**:
  - Zeaxanthin
  - Chlorophyll a
  - Quenching, longer conjugation length

- **Little light**:
  - Zeaxanthin
  - Violaxanthin de-epoxidase
  - High light only

- **Much light**:
  - Antheraxanthin
  - Zeaxanthin epoxidase
  - High light only
  - Violaxanthin de-epoxidase
  - Violaxanthin
Fast adaptation to irradance 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 PSIIRC

- 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“
Mechanism of charge separation

1. Special pair chlorophylls (=P680) accept excitons from antenna
2. Chl_{D1} transfers an electron to Pheo (“initial charge separation”)
3. Within a few ps, the electron hole in Chl_{D1} is filled from P680 (→ P680^+ / Phe^-) “primary charge separation”
4. (according to other authors, the initial charge separation is in P680, and ChlD1 transfers the electron to Pheo, see next scheme...)

From: Barber J, 2003, QuartRevBiophys36, 71-89
Biophysical aspects of photosynthetic electron transport
A) Photosystem II reaction centre: speeds of electron transfer
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
Functional characteristics
- Transfers e- from PQ to plastocyanin (PC),
- It uses the difference in potential between QB 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 (Cu^{2+}) plastocyanin accepts electron from Cyt_{b6f} complex,
- Reduced (\(\rightarrow\) Cu\(^{+}\)) plastocyanin diffuses to the PSIRC
- Plastocyanin releases the electron (Cu\(^{+}\) \(\rightarrow\) 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⁻ to A₀ via A (both Chl a)
- e⁻ transport via A₁ (phylloquinone) and the [4Fe4S]-clusters Fₓ, Fₐ and Fₐ to the [4Fe4S]-cluster of ferredoxin
- P700 is re-reduced by plastocyanin

All slides of my lectures can be downloaded from my workgroup homepage

Biology Centre CAS → Institute of Plant Molecular Biology → Departments → Department of Plant Biophysics and Biochemistry,

*or directly*

http://webserver.umbr.cas.cz/~kupper/AG_Kuepper_Homepage.html