Light Harvesting in Photosynthesis

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Earth is formed
Life emerges
Photosynthesis
Cyanobacteria
Oxygen-rich atmosphere
Plants
Dinosaurs
Hominids, 3pm
Homo Sapiens, 11:38 pm
US 11:59:58 pm
Age of Earth 4.55 billion yrs
Prevalence of Photosynthesis
Photosynthesis 101

\[
6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2
\]

Efficient:
~90% of energy absorbed is used to initiate photochemistry

Fast:
Turnover rate of photosynthesis: ~ 100-300/sec

Regulated:
~75% of absorbed energy can be dissipated with a 1sec response time
Architecture of Photosynthesis is Optimized to:

- Cover the solar spectrum
- Protect against photochemical damage
- Separate energy and electron transfer
- Transmit excitation to the reaction center with near unit efficiency
- Regulate the efficiency of light harvesting and repair damage (PSII)
Protein Complexes in the Plant

Pigment Protein Complexes

Thylakoid membrane

Chloroplast

Cross-section of the leaf
Overview of photosynthetic supercomplex in plants

Peripheral antennas

Core Complex

Core Complex

Peripheral antennas
Light Harvesting Complex II (LHCII)

- >50% of plant chlorophylls in LHCII
- Functions as antenna complex
- Absorbs light energy and funnels to reaction center
How does Light Harvesting Really Work? Can we find a way to image Functionality?

- Are the excited states localized?
- Are the states optimized in both spatial and energetic landscapes?
- Does the excitation hop?
- Does Quantum Mechanics matter?
- Do only optically allowed transitions matter?
- How is photo-induced damage minimized?
- How do we learn about interactions, pathways and mechanisms when all the molecules are chemically identical?
Spectral Properties of LHCII

- Delocalized excited states allow for energetic jumps
- Chl b localized near Chl a to allow for downhill energy transfer
Two-Dimensional Spectroscopy

- Excitation at one wavelength influences emission at other wavelengths.
- Diagonal peaks are linear absorption.
- Cross peaks are coupling and energy transfer.

Dimer Model (Theory)
Dynamics in 2D Spectroscopy

Dimer Model (Theory)

\[ \omega_t (\text{cm}^{-1}) \]

\[ \omega_{\tau} (\text{cm}^{-1}) \]

T=0 fs  
\[ \begin{array}{c} 13000 \cr 12500 \cr 12000 \cr \end{array} \]

T=500 fs  
\[ \begin{array}{c} 13000 \cr 12500 \cr 12000 \cr \end{array} \]

T=50 ps  
\[ \begin{array}{c} 13000 \cr 12500 \cr 12000 \cr \end{array} \]
Experimental Conditions

• Sample Details
  - Wild type LHCII
  - Extracted from *Arabidopsis Thaliana*

• Sample Conditions
  - 65:35 v/v glycerol to LHCII solution
  - LHCII Solution:
    • 10 mM Hepes/HCl pH 7.6
    • OD$_{670}$=0.18
  - Temperature: 77K
  - 200 um Silanized quartz cell (SigmaCote)

• Laser Conditions
  - 650 nm spectral center, 80 nm FWHM
  - 23 fs pulse (measured by auto-correlation)
  - 99.7 µW incident on sample
LHCII 2D Spectra

$T = 0 \text{ fs}$

$\omega_q (\text{cm}^{-1})$

$\omega_r (\text{cm}^{-1})$

14500 15000 15500 16000 16500 17000

-150 -100 -50 0 50 100 150
LHCII 2D Spectra

\[ T = 10 \text{ fs} \]
LHCII 2D Spectra

$T = 100 \text{ fs}$
LHCII 2D Spectra

$T = 200 \text{ fs}$
LHCII 2D Spectra

$T = 480 \text{ fs}$
LHCII 2D Spectra

$T = 2000 \text{ fs}$
LHCII 2D Spectra

$T = 4000 \text{ fs}$
LHCII 2D Spectra

$T = 12000\, \text{fs}$
LHCII Spectral Dynamics
Energy Transfer in LHCII
Electronic Coupling
Localization of Dynamics
Electronic Coherence
Conclusions & Future Directions

• Coupling creates delocalized excited states over multiple chromophores
• Delocalization means spatial overlap of energetically separate chromophores which allows large energetic jumps

• Chl-b arranged near Chl-a for interband energy transfer

• What specific mechanisms give rise to these energy transfer processes?
• What role does quantum coherence play and how does it change at room temperature?
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References:
Rick Trebino, Georgia Tech
http://www.physics.gatech.edu/gcuo/UltrafastOptics/index.html