Artificial Photosynthesis: lessons from nature

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Plant Photosynthesis

A Tree

• 20,000 leaves
• 1000 billion chloroplasts
• 180 g of chlorophyll

Per Day

• Absorbs 10000 litres of CO₂
• Adds 12 kg biomass
• Creates 10000 litres of O₂
Nature’s blueprint

• The early stages of photosynthesis can operate at high quantum efficiency
• Small reaction volumes: keeps the energy concentrated
• Limited set of components
• Biology engineers the matrix to control the properties of the pigments
Our lab

- From 200nm to 1800nm
- 1.6K to room temperature
- 0-6T
- Absorption and fluorescence
- Non-actinic measurement
- CD and MCD
- CPL and MCPL
- Variety of samples
Photosynthesis

1) Light absorption

2) Charge separation

3) Water splitting (catalytic reaction)

4) Fuel production (catalytic reaction)
Reaction Centre (RC6)

Chlorophyll a

Pheophytin

Plastoquinone
Low temperature absorption of RC6

Low temperature emission of RC6

RC6 from Spinach 2 K

Absorption (OD)

Fluorescence

Wavelength (nm)

Absorption (OD)

Fluorescence
2 K absorption and MCD of RC6

![Graph showing absorption and MCD of RC6 with a MCD deficit highlighted.](graph.png)
MCD ‘deficit’ vs P680 bleach

Transient bleaches
Van Kan et al. 1990

10 ps
1.0 ns
1.7 ms
Low temperature MCPL of RC6

RC6 from Spinach 2 K
What does it all mean??

• Not sure at this stage…
• Clear differences between charge separating and light harvesting pigments
• Differences driven by the protein
• Need an appropriate theoretical model
Conclusions

• Natural systems are an inspiration for next-generation artificial photosynthesis devices
• A combination of optical spectroscopies is a powerful tool for probing photosynthetic protein complexes
• Engineering the matrix offers a whole new toolbox for artificial photosynthesis
• May lead to a whole new class of novel materials
Key challenges in artificial photosynthesis

\[ |r> \quad h\nu_0 \quad \Delta\mu_{st} \quad |p> \]
Absorption/MCD Spectrometer

Photosystem II

CP43 (Antenna)

CP47 (Antenna)

Reaction Centre
1. Light energy is funnelled to ChlD1
2. Charge separation takes place between ChlD1 and PheoD1
3. The positive charge localises on PD1 and the electron is transferred to QA to QB and then further down the electron transport chain
4. The electron is replaced by the oxidation of water at the OEC via the redox-active Tyrz

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]
Low temperature absorption of RC6 from Spinach 2 K

Absorption (OD)

Wavenumbers (nm)

500 550 600 650 700

RC6 from Spinach 2 K

Chla and Pheo $Q_y(0,0)$

Chla $Q_x(0,0)$

Pheo $Q_x(0,0)$

Pheo $Q_x(0,1)$

Chla and Pheo $Q_y(0,1)$

[Diagram of chlorophyll and pheophytin with labels for absorption peaks]
Low temperature CD of RC6

Absorption (OD)

Wavelength (nm)

RC6 from Spinach 2
Low temperature CPL of RC6

RC6 from Spinach 2
K

Absorption (OD)

Fluorescence

Wavelength (nm)
Characteristics of the most-red state

• Absorbs at the red edge of the Qy absorption of chlorophyll (~ 680 nm)
• Is associated with charge separation in the reaction centre
• Has *negative* MCD and MCPL
What could it be??

- Charge transfer state?
- Exceptionally strong vibronic coupling?
Charge transfer state?

• We know that there is at least one CT state from electrochromism measurements.

• But… Charge transfer states do not normally have CD…
  – Multicentre CT??
Vibronic coupling in chlorophyll

- Based on the assignment of Raszewski, Chl$_{D1}$ is the pigment that absorbs most to the red and closest to the MCD deficit.
- A recent analysis in collaboration with our group by Reimers et al showed that when a vibration from the $Q_y$ band is resonant with $Q_x$, then $Q_x$ is split into two components.

Vibronic coupling in RC6

Red-most Qy peak ~ 679 nm

“Normal” Qy peak ~ 672 nm

“Extreme” Qx Origin ~ 623 nm, splitting ~ 2700 cm\(^{-1}\)

“normal” Qx Origin ~ 611 nm, splitting ~ 1000 cm\(^{-1}\)
• If it is a charge-transfer state, what is its nature?
  – Has CD: multi-centre?
• What are the consequences of strong vibronic coupling in Chl$_{D1}$?
  – Is it essential for function?
  – If so, how does it work?
• Future experiments:
  – Spectral “hole burning” in the red edge of the $Q_y$ absorption and then look for the vibrations that are connected to this transition
  – Try to obtain polarisation information about these vibrations.
  – Our hypothesis should be checked by theoretical analysis
If vibronic coupling and/or unusual CT states are critical for function, we need to understand them to a level that we can reproduce them.

Is it connected to quantum coherences that are reported in the literature for many photosynthetic systems?

– Can strong vibronic coupling lead to coherent behaviour, or will it cause the system to rapidly dephase?