# The kinetics of photosynthesis

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# Learning outcomes

- What is photosynthesis?
- Concept of *energy* transfer (FRET)
- Concept of *charge* transfer (Marcus theory)

# Photosynthesis

$$6\ CO_2 + 6\ H_2O + \text{energy} \xrightarrow{\text{(light)}} C_6H_{12}O_6 + 6\ O_2$$

**Challenge**: photons → excitons → **free charges** ($e^-$ + $h^+$)

- chemical reactions driven by net <u>positive charge</u>

  *e.g.* oxidation of water to oxygen

- chemical reactions driven by <u>negative charge</u>

  *e.g.* reduction of quinones to hydroquinones

# Photon absorption in molecules

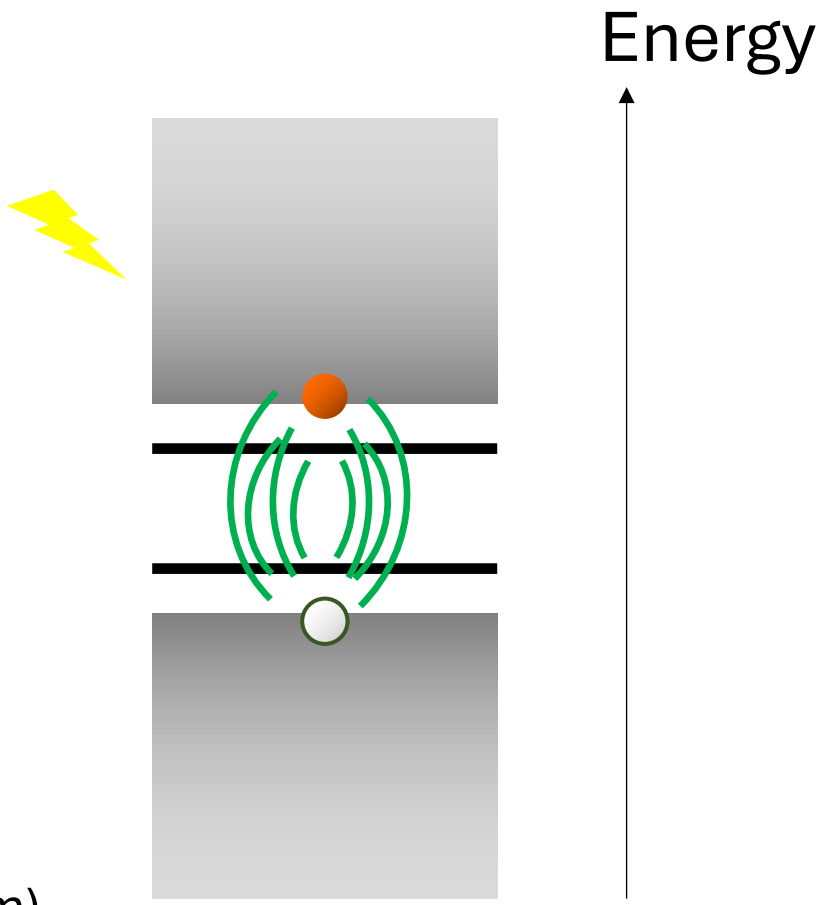
- optical excitation can generate "**excitons**": electron-hole pairs that are bound together through Coulomb interactions

- can be treated in first approximation like a hydrogen atom

$$E_{binding} = \frac{e^4 \mu}{2(4\pi\varepsilon\varepsilon_0\hbar)^2} = \frac{\mu / m}{\varepsilon^2} \times 13.6\,eV$$

m is the reduced mass for the $e^-$ - $h^+$ system:

$$\frac{1}{\mu} = \frac{1}{m_e^*} + \frac{1}{m_h^*}$$



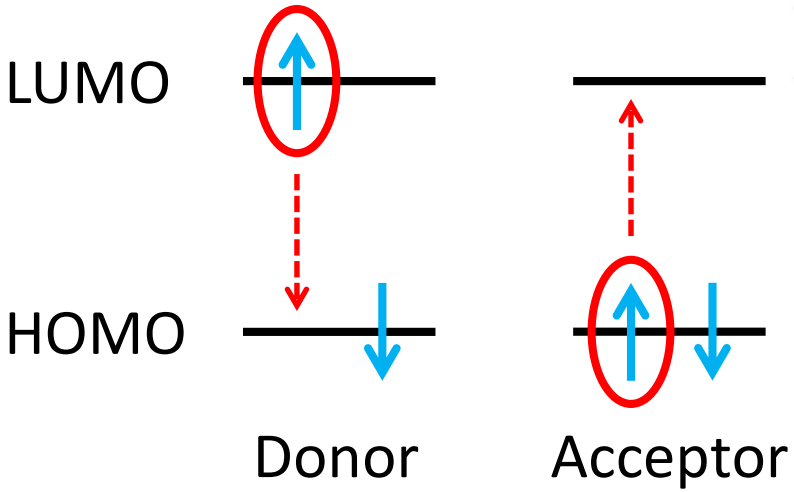

- dielectric constant low: $\varepsilon_r \sim 3-4$
- for $m_e^* = m_h^*$ yields $E_{binding} \sim 0.75$ eV (& Bohr radius $a_r \sim 0.3$ nm)

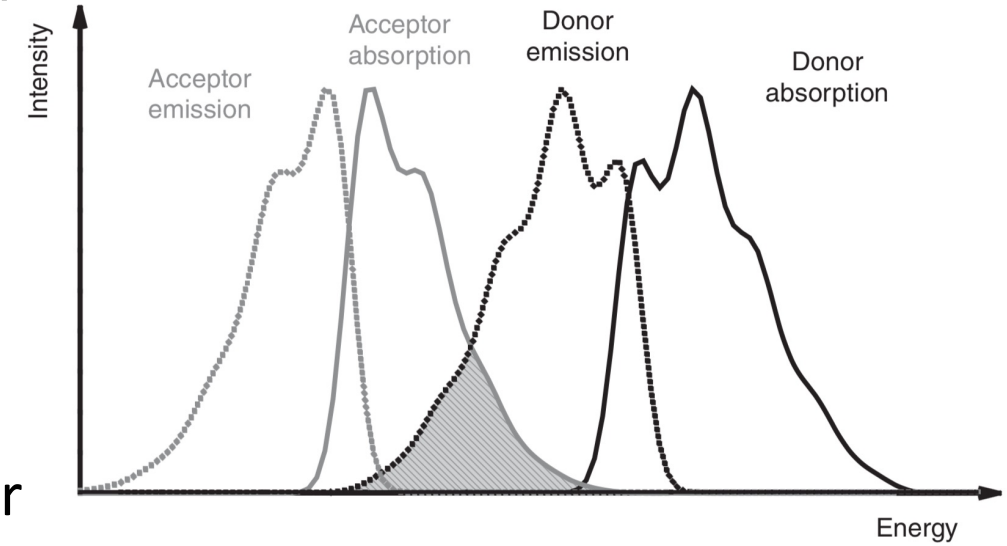
→ **in organic materials: difficult to generate free electrons & holes at room temperature!**
→ **excitons are the dominant species, and we must break them up later for PV**

# Energy transfer & exciton motion *via* FRET

- excitons can ‘diffuse’ to lower energy sites *via* Förster resonant energy transfer (FRET)
- dipole-dipole coupling
- can be long-range interaction (few nm)
- very fast (sub-ps)

Förster transfer (singlet)



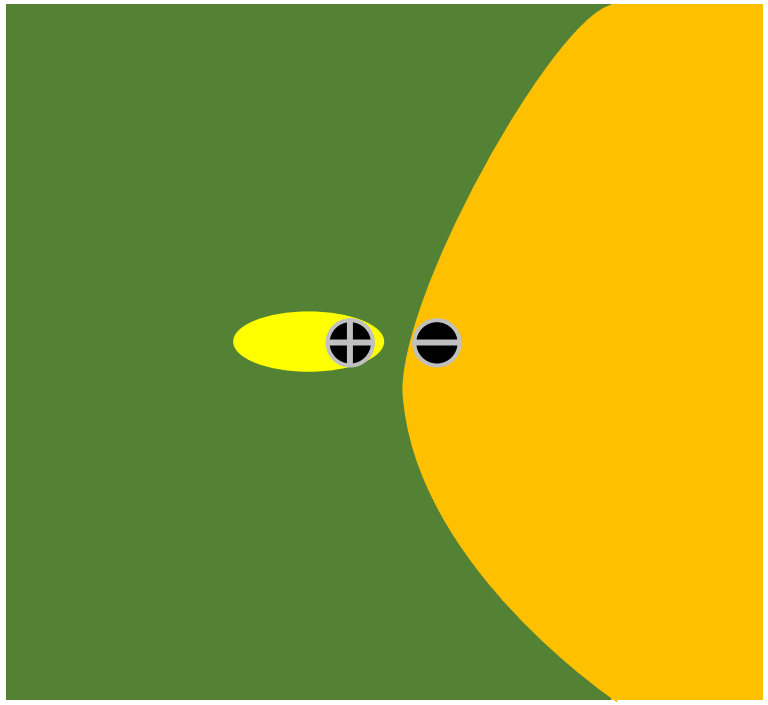

$$I_{DA} \propto \int_0^\infty \frac{F_D(\nu)\varepsilon(\nu)}{\nu^4} d\nu$$

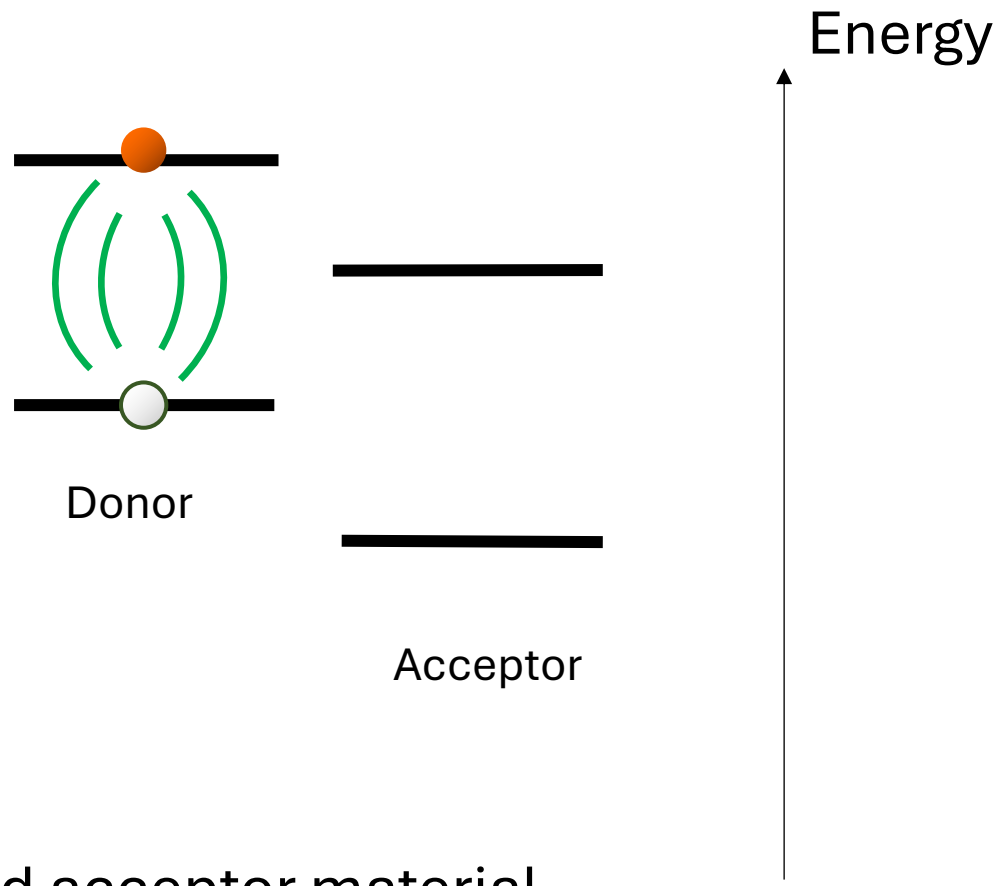
$$k_{DA} = \frac{1}{\tau_D} \frac{9\ln(10)\phi_D}{128\pi^5 N_A n_{solv}^4} c^4 I_{DA} \kappa_{DA} \frac{1}{R_{DA}^6}$$

$$k_{DA}(R) = \frac{1}{\tau}\left(\frac{R_F}{R_{DA}}\right)^6$$

$F_D$ is normalised donor emission rate, $\varepsilon$ is molar absorption coefficient, $f_D$ is the quantum efficiency of luminescence of the donor, and $t_D$ its lifetime, $N_A$ Avogadro’s number, $k_D$ an orientational factor for the dipole, $n_{solv}$ the refractive index in the medium, $R_{DA}$ the donor-acceptor separation

# How do we generate free charges from excitons?

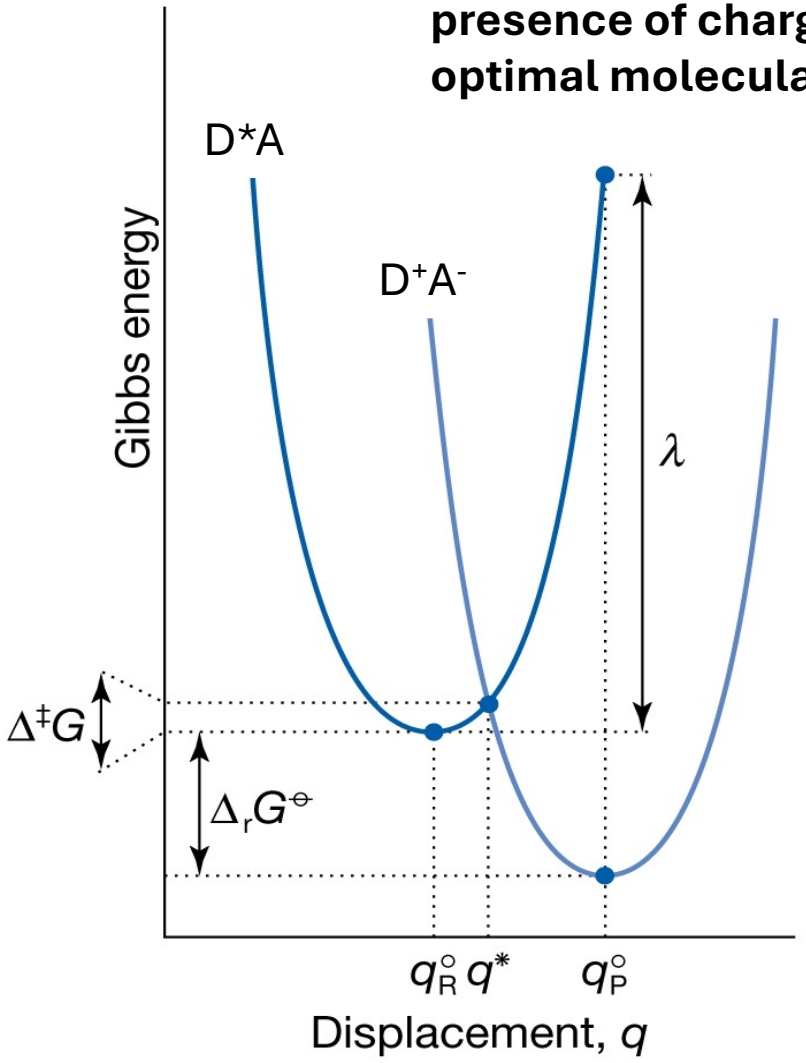





1) Set up a (hetero)junction between a donor and acceptor material

2) Electron (hole) transfer from donor (acceptor) to acceptor (donor) breaks the excitons up and generates charges

# Electron transfer: Marcus theory




- isoenergetic electron transfer requires thermal excitation to crossing point
- activation barrier:

$\Delta G^{\dagger} = (\Delta G^{0} + \lambda)^{2} / 4\lambda$

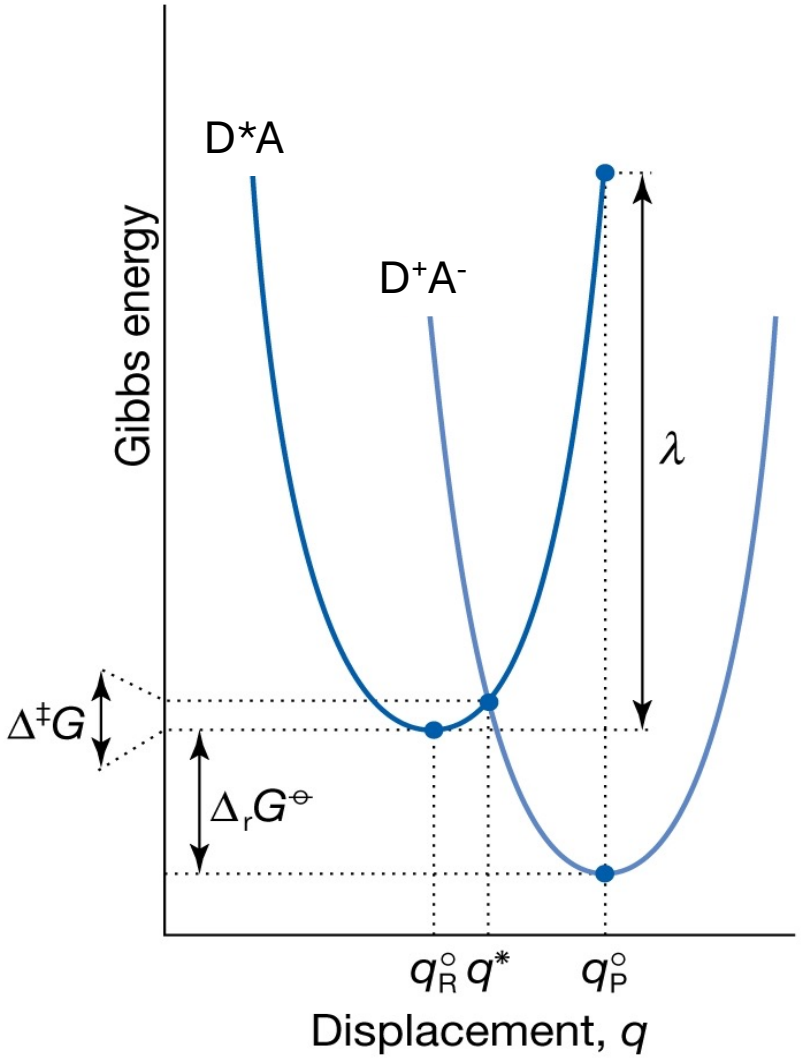
λ is the 'reorganization energy': energy change associated with molecular rearrangements such that $^{1}D^{*}A$ takes up the equilibrium geometry of $D^{+}A^{-}$.

$$k_{transfer\quad rate} \propto V^{2}_{tunnelling} e^{-\left(\frac{(\Delta G^{0}+\lambda)^{2}}{4\lambda k_{B}T}\right)}$$

$$V^{2}_{tunnelling} \propto \langle \psi_{1D^{*}} | \psi_{A} \rangle^{2} \propto \exp\left(\frac{-2r\sqrt{2mV}}{\hbar}\right) = \exp(-\beta r)$$

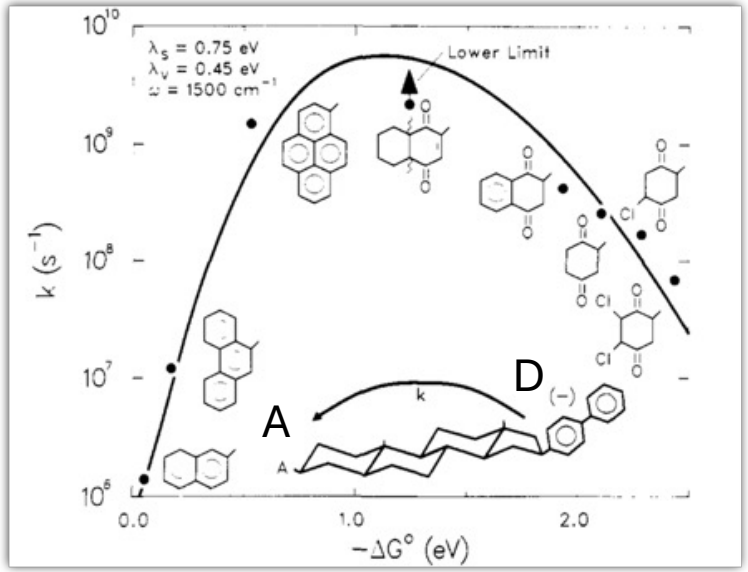
R. Marcus, *J. Chem. Phys*. **24** (5), 966 (1956)

# Transfer rate *vs* free energy Δ*G*




- $\Delta G^0 < 0$ for downhill electron transfer
- as $\Delta G^0$ is reduced, at some point $|\Delta G^0| = \lambda$ and 'Boltzmann factor' = 1

  →'***activationless***' electron transfer!
- as $|\Delta G^0| > \lambda$ , the Boltzmann factor becomes < 1 and rate slows down again: the '***inverted*** Marcus regime'



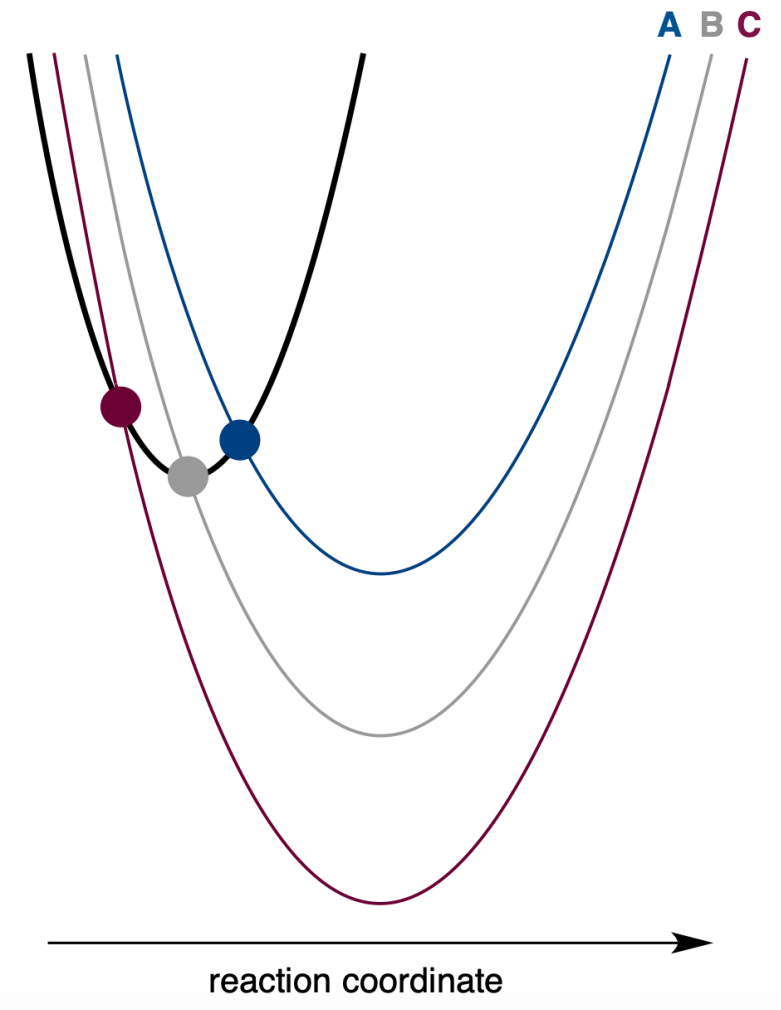

Data for covalently attached D/A pair [1]

$$k_{transfer\quad rate} \propto V^2_{tunnelling}\, e^{-\left(\frac{\left(\Delta G^0+\lambda\right)^2}{4\lambda k_B T}\right)}$$


R. Marcus, *J. Chem. Phys*. **24** (5), 966 (1956)

[1] Miller, Calcaterra & Closs, *JACS* **106**, 3047 (1984)

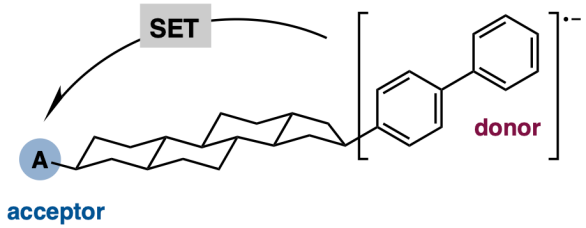
# More about the “Marcus Inverted Region”




**A** $\Delta G^\circ < 0$ (somewhat negative)
$\Delta G^\ddagger > 0$, rate $k_A$

**B** $\Delta G^\circ = -\lambda$ (quite negative)
$\Delta G^\ddagger = 0$, rate $k_B > k_A$

**C** $\Delta G^\circ << 0$ (very negative)
$\Delta G^\ddagger > 0$, rate $k_C < k_B$



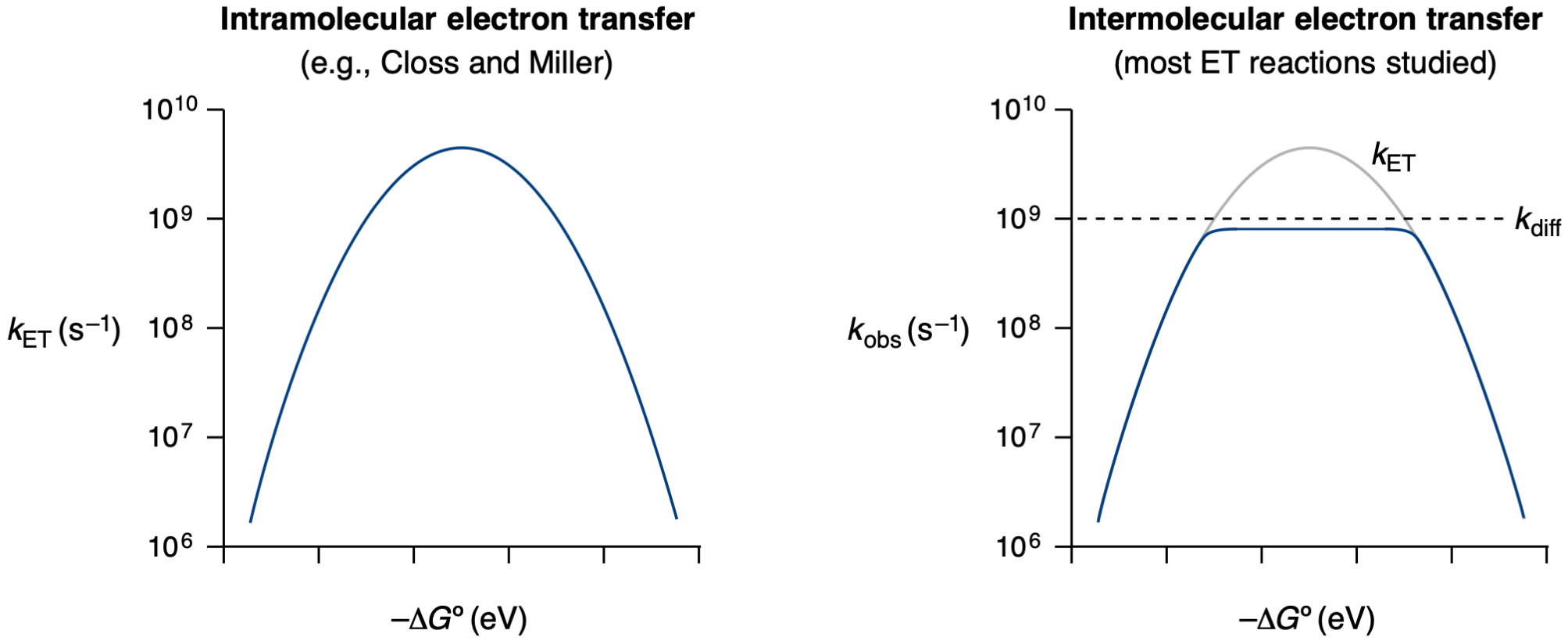

As $\Delta G^\circ$ approaches $-\lambda$, the rate of reaction *increases*

When $\Delta G^\circ = -\lambda$, the reaction becomes barrierless

As $\Delta G^\circ$ becomes even more negative ($\Delta G^\circ < -\lambda$), the rate of reaction *decreases* ($\Delta G^\ddagger > 0$)

***Marcus inverted region***

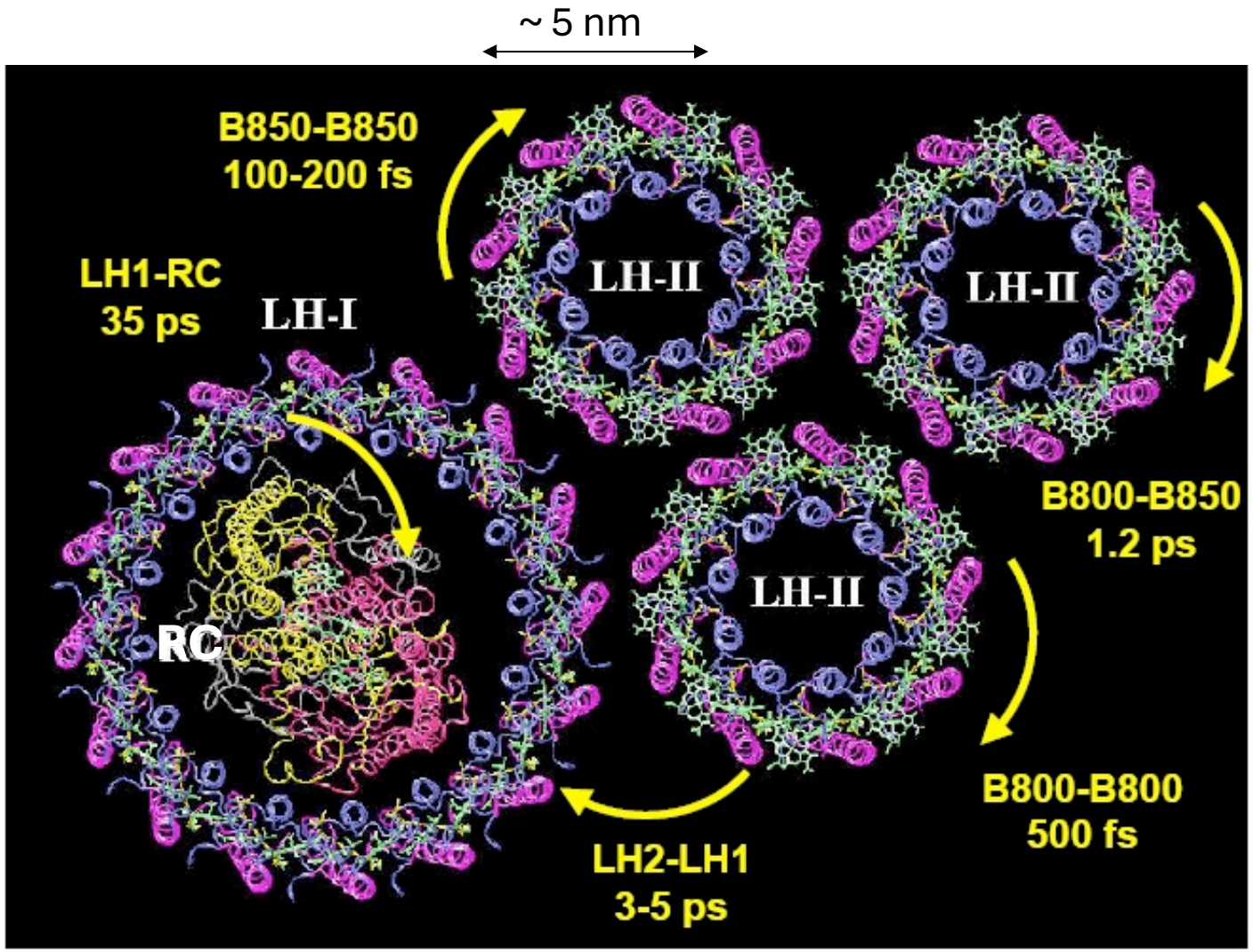
# Why did it take 30 years to verify the existence of the Marcus inverted regime?!




***1. For intermolecular ET, observed rate is limited by diffusion ($k_{obs} = k_{diff}$ when $k_{ET} >> k_{diff}$)***

***2. To escape the diffusion "leveling effect," $\Delta G°$ must be very, very negative (difficult to achieve)***

# The photosystem

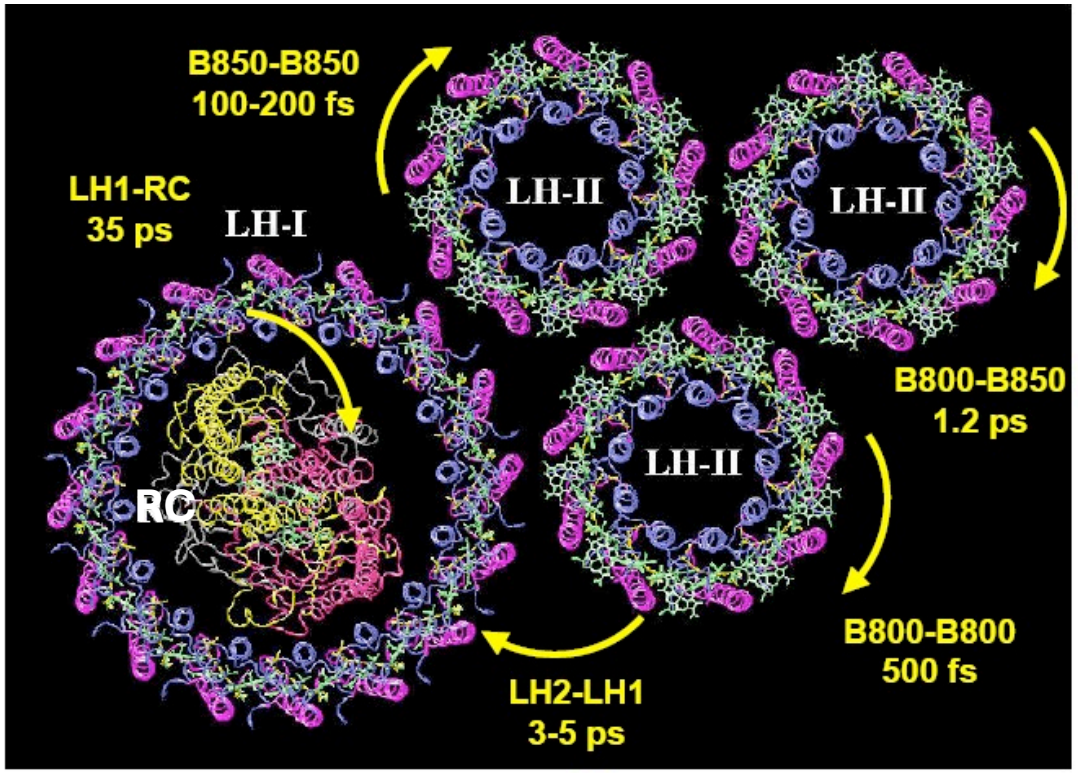



Top view of bacterial photosynthetic membrane
green = chlorophylls

- Photosystem consists of 2 different light-harvesting complexes: **LH-I** and **LH-II**
- Ultimately charge separation at the **Reaction Center (RC)**

- electronic energy transfer cascade to RC
- up to 200 chromophores per RC
- concept common to all photosynthetic organisms; detailed structure varies

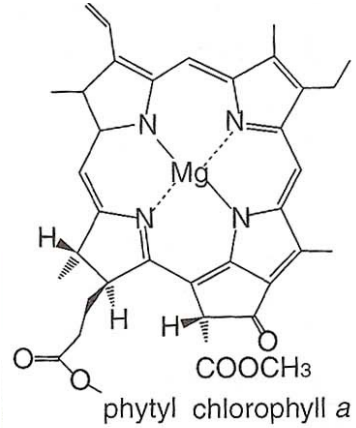
# Step 1: Energy transfer




- antennae molecules
  - absorb incident photons (creating excitons)
  - transfer energy quickly towards reaction center (RC), avoiding non-radiative decay channels
- transfer from B800 to B850 in LH-2, from LH-2 to LH-1, and from LH-1 to the RC is by Förster Transfer
  - “downhill” energy transfer to give overlap of absorption and emission spectra
  - distances carefully controlled by protein structure to control rates
  - avoids very close contact – wavefunction tunnelling would lead to non-radiative states

# More about the light-harvesting antennae

- Typically a few *hundred* light-absorbing molecules per RC
- Various types, incl. chlorophylls and carotenes

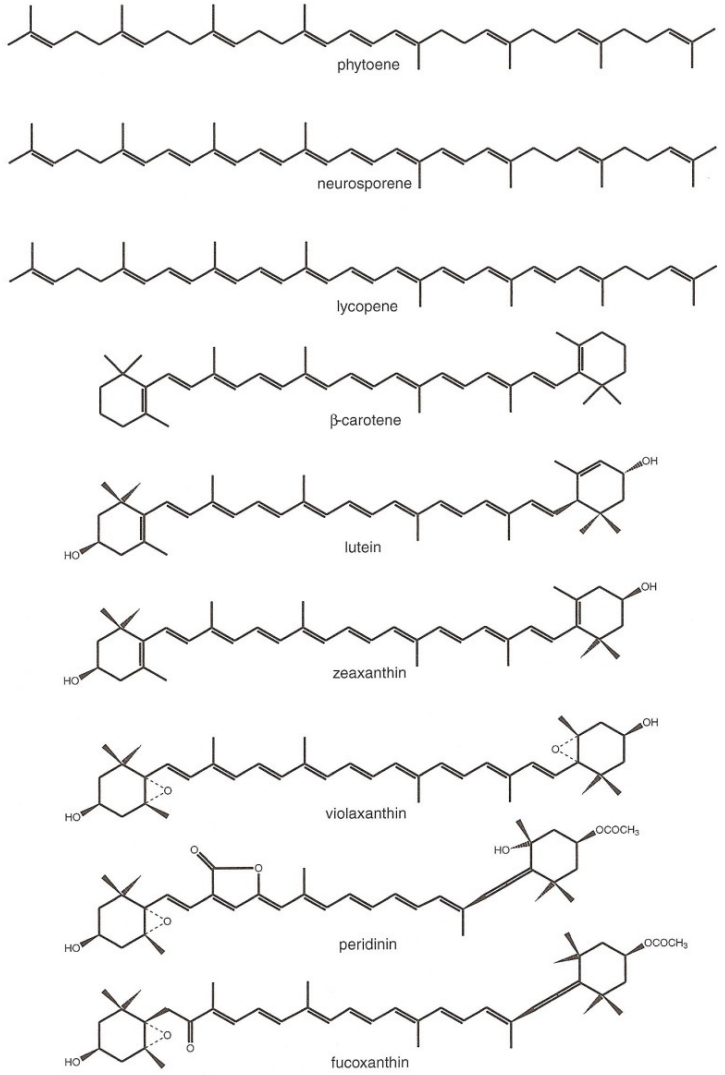


phytyl chlorophyll *a*

**Why even bother with antennae?**

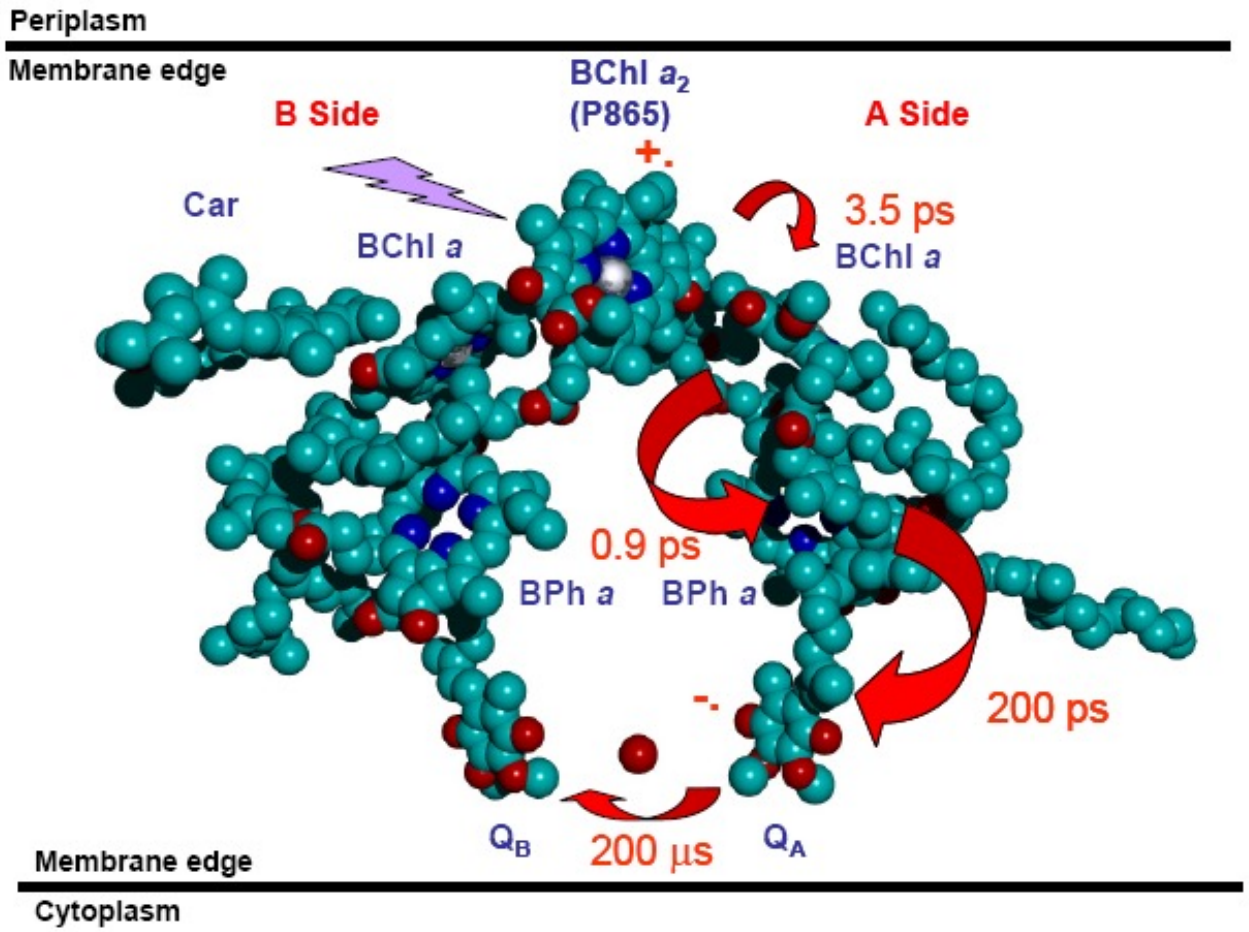
1) about 10 photons/s absorbed under full sunlight in one chlorophyll – much slower than rate at which the RC can operate!

2) RC much more expensive to build!



various carotenoid molecules used in photosynthesis

# Step 2: Charge transfer




side view of bacterial reaction centre, with protein not shown

Exciton transfers from antennae to pair of chlorophylls which are arranged to have correct exciton energy to collect from the antennae – the ***special pair***

– usually labelled by this energy (in nm) in its name

– electron transfer 'across the heterojunction' – in green plants to a pheophytin; subsequent transfer to lower-energy sites

$$k_{transfer\quad rate} \propto V^2_{tunnelling} e^{-\left(\frac{\left(\Delta G^0+\lambda\right)^2}{4\lambda k_B T}\right)}$$

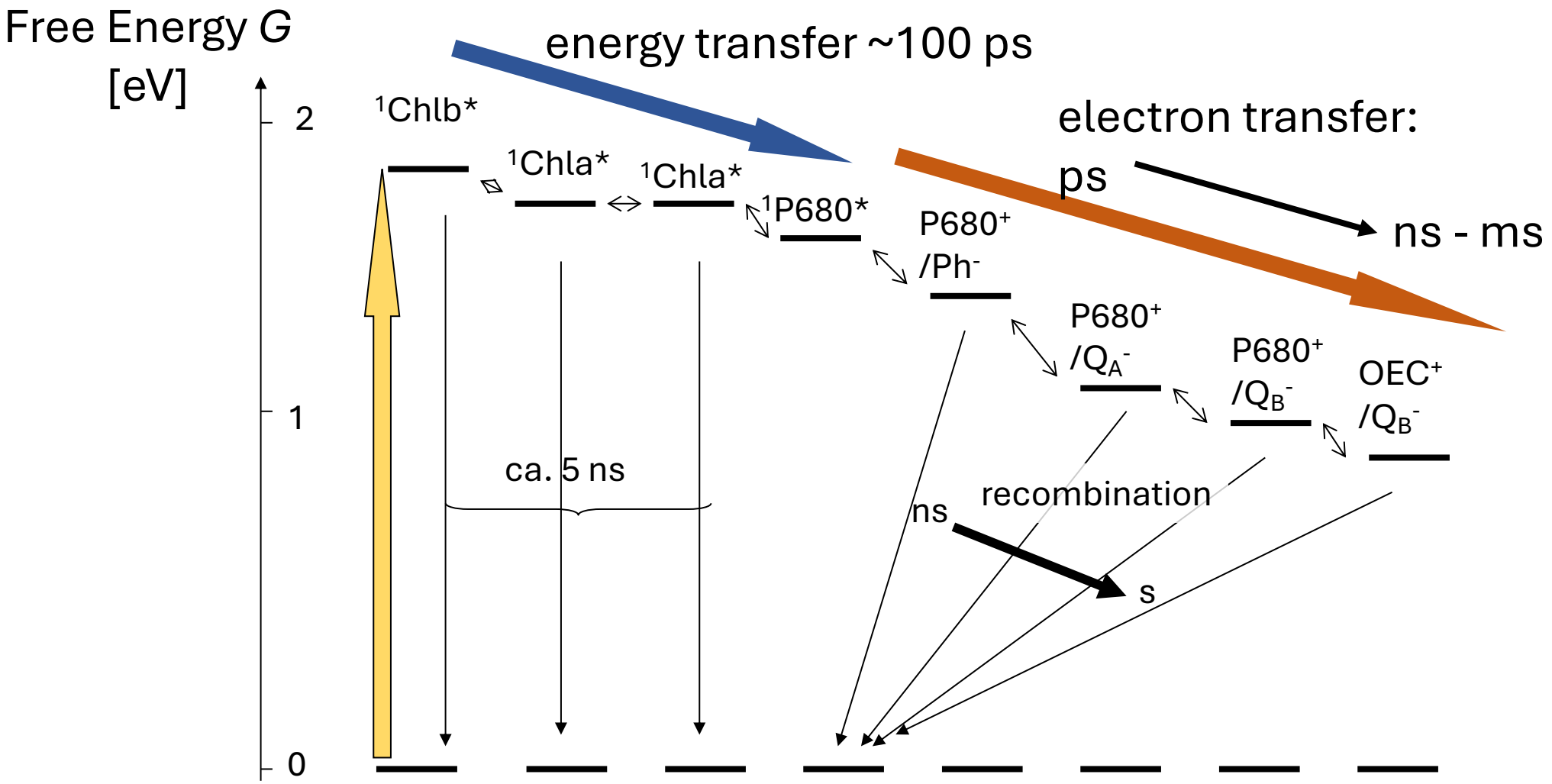
**Photosynthetic reaction centers evolved such that:**

✓**non-polar interior (l ≤ 1 eV)**

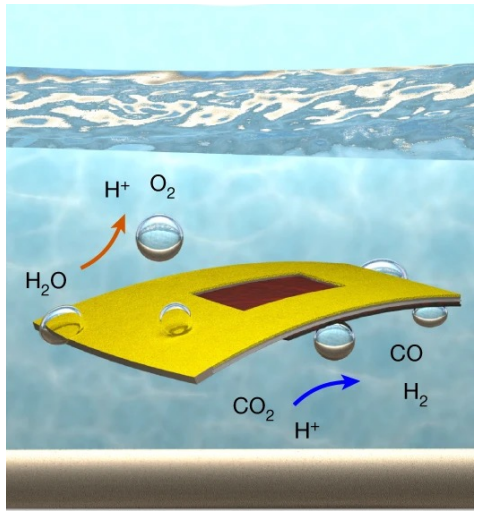
✓**forward reactions activationless: |D*G*⁰| = l: <u>fast</u>**

✓**reverse reactions in inverted region: |D*G*⁰| > l: <u>slow</u>**

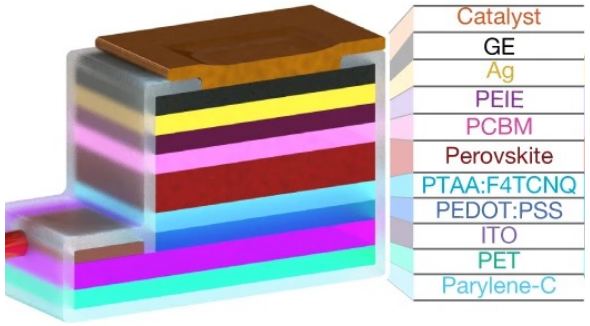
# Energetics & kinetics in green plants

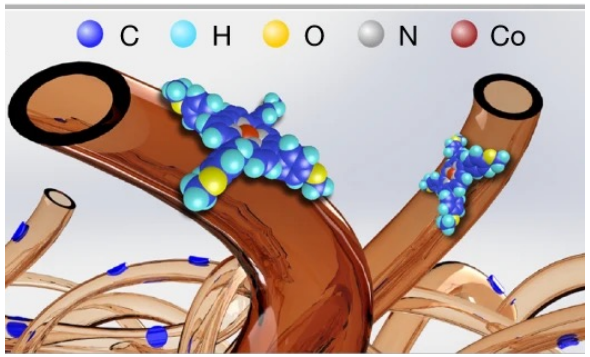


# Outlook: Artificial leaves to save the planet?




0.58% efficiency of $H_2$ production




...and quite expensive to make

*Nature* **608**, 518–522 (2022)

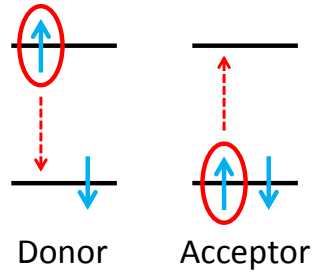
# Summary

- **What is photosynthesis?**

Cleverly engineered system of dyes to turn light energy into chemical energy, by generating and transferring excitons, before breaking them up into free charges for redox reactions

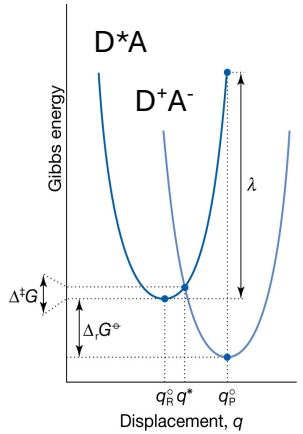
- **Concept of *energy* transfer (FRET)**

Excitons ‘diffuse’ *via* Förster transfer to sites of lower energy, dependent on spectral overlap and distance ($\sim R^{-6}$)




- **Concept of *charge* transfer (Marcus theory)**

Rates governed by trade-off between free energy ($\Delta G$) and reorganization energy ($\lambda$)



# Further reading

If you are interested in learning more on…

**… Electronic structure and processes in molecular systems:**
*Electronic Processes in Organic Semiconductors and processes: An Introduction*
by A. Köhler and H. Bässler, Chapter 1

**… Photosynthesis:**
*Molecular Mechanisms of Photosynthesis*
by R. E. Blankenship, Chapters 5-7

**… Marcus theory:**
*Recent lecture (Feb. 2022) by Rudolph Marcus (N.P. 1992)*
youtube.com/watch?v=CR2gPgpUWxk