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Photochemical Conversion of Solar Energy

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In memory of Giacomo Ciamician (1857–1922) in the 150th anniversary of his birth

UMASS boston

Artificial Photosynthesis

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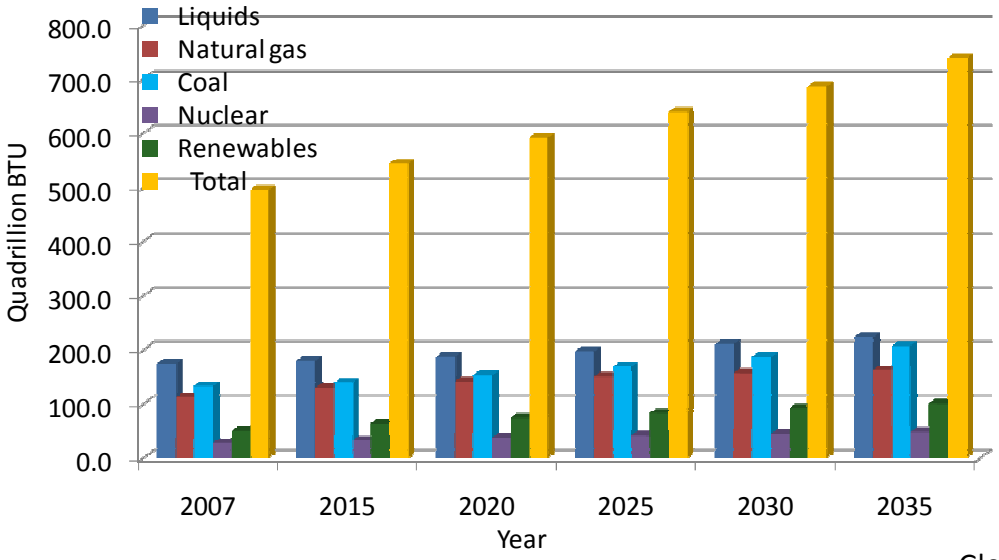
Global Energy Consumption vs. CO_2 Emissions

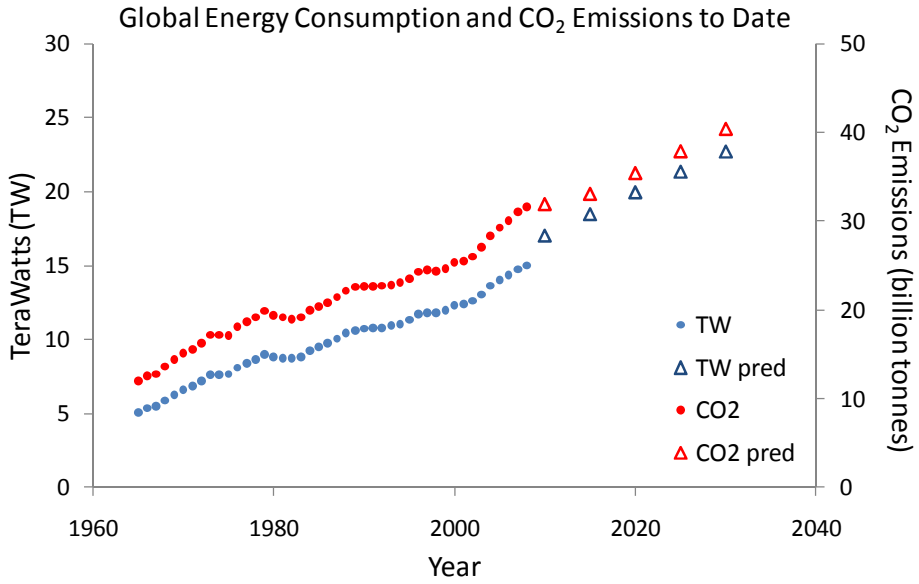


- Today's primary global energy consumption is reported at 15 TW.
- 20% US + 18% China totals almost half of global energy consumption.
- Estimated global energy consumption of 28 TW needed annually by 2050.

International Energy Outlook 2009
(http://www.eia.doe.gov/oiaf/ieo/index.html)

Statistical review of world energy, annual review by BP 2009

(http://www.bp.com/productlanding.do?categoryId=6929&contentId=7044622)



Renewable Energy Resources

Solar 1.2×10^5 TW total
600 TW actual

Wind
2-4 TW
extractable

Tide/Ocean currents
2 TW gross

Geothermal
12 TW gross

Biomass
5-7 TW gross
(all cultivable land not used for food)

Hydroelectric
4.6 TW gross
1.6 TW feasible

Energy gap: + 14 TW by 2050
+ 33 TW by 2100

Photosynthesis – Natures Power Generator

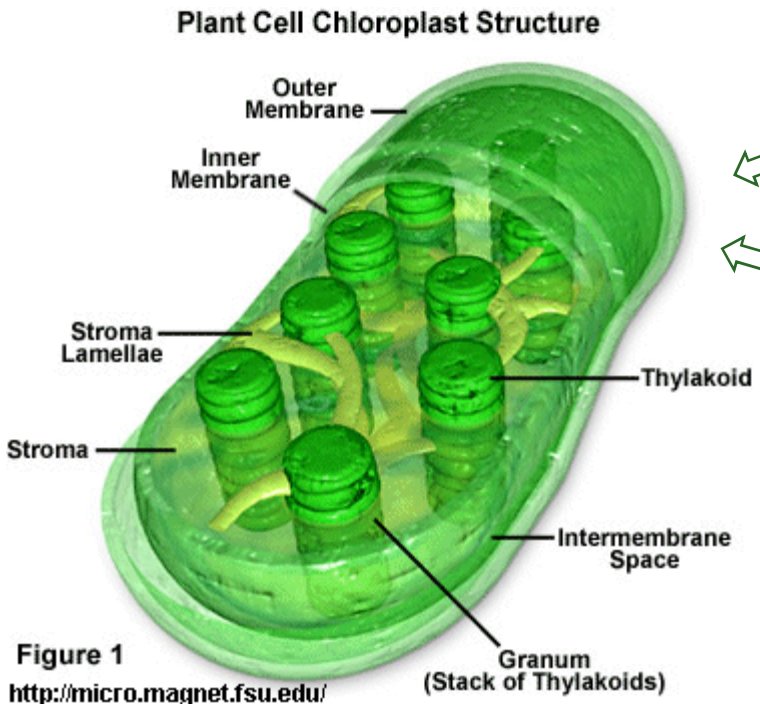
- Can we replicate it ?

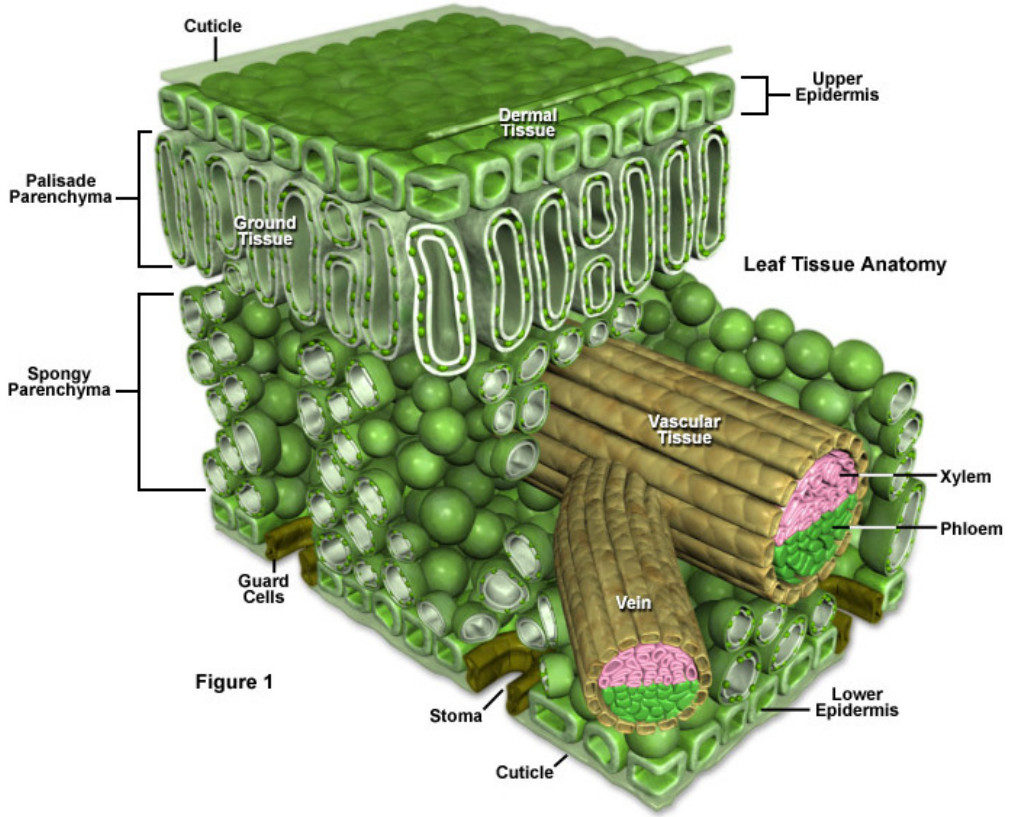
- Photosynthesis can be separated into four fundamental processes:

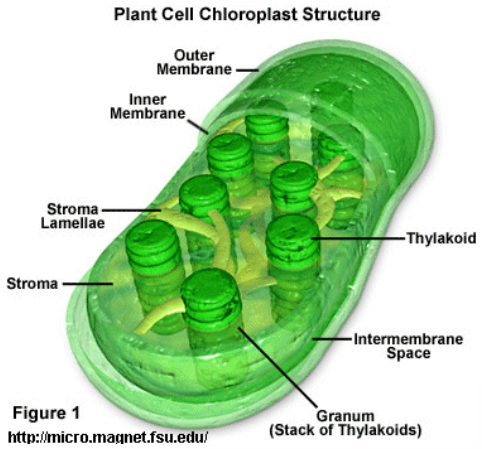
  1. Light harvesting
  2. Photoinduced charge separation.
  3. The oxidation of water to dioxygen (OEC)
  4. The reduction of carbon dioxide (NADPH)

Anatomy of the leaf

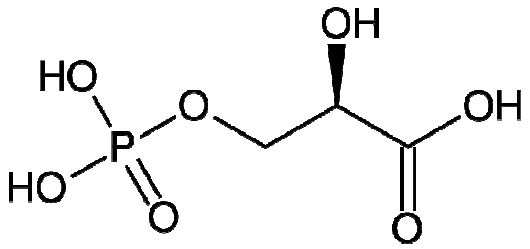
- In plants, the primary photosynthetic events take place in the highly folded, disc-shaped thylakoid membrane vesicles inside chloroplasts.



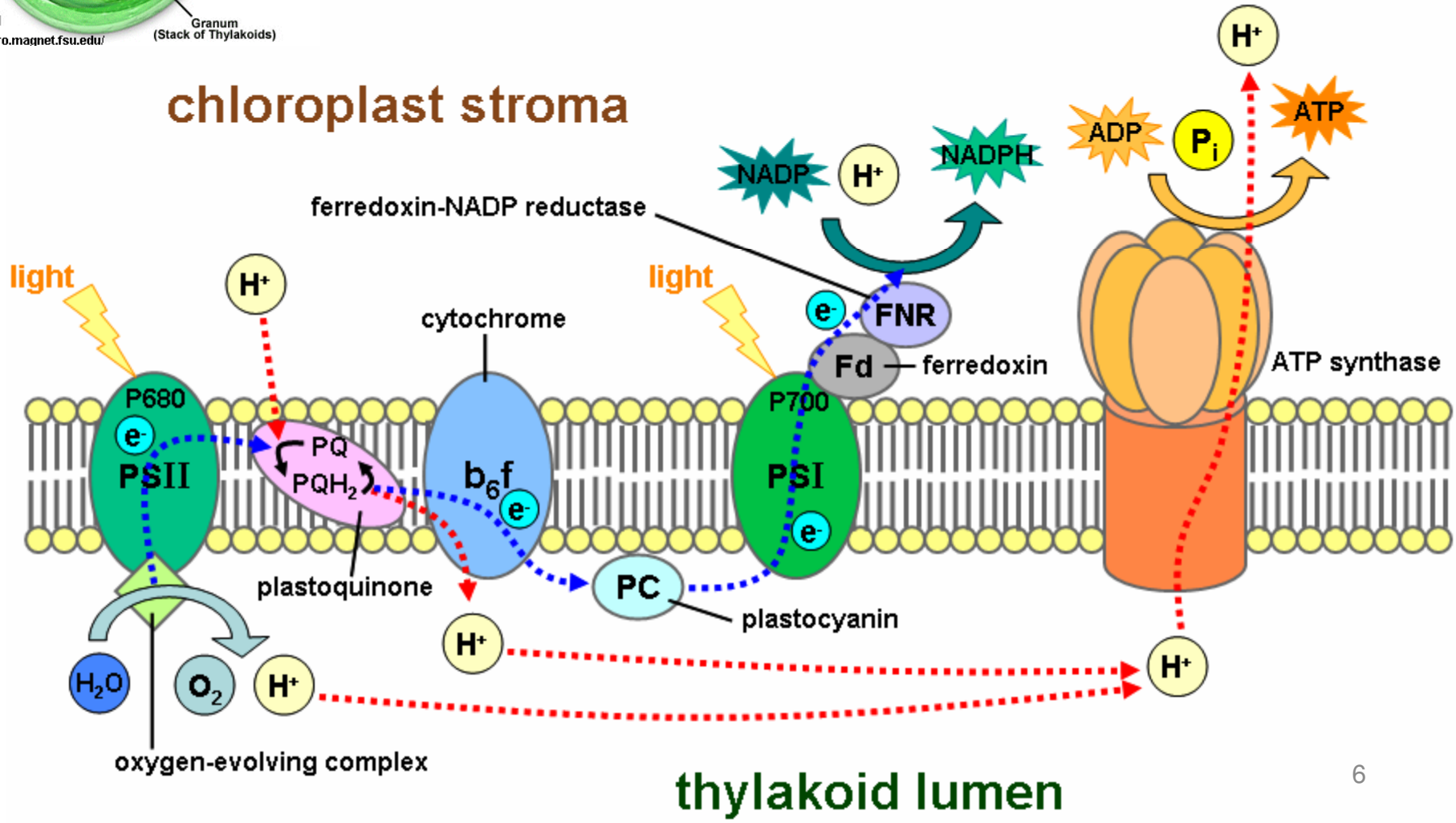




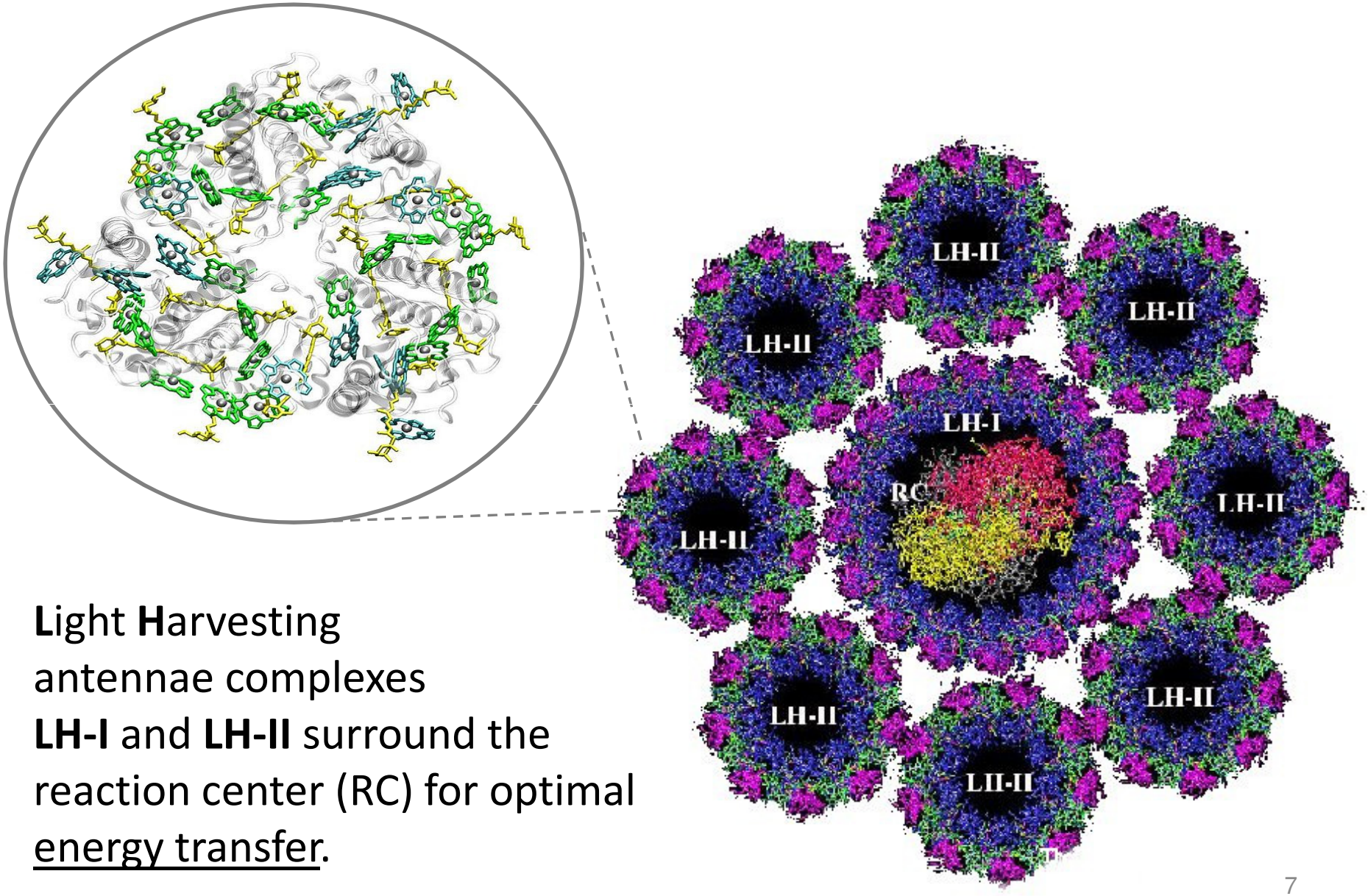
$$3CO_2 + 3H_2O + h\nu \rightarrow$$



$$+ 6\ O_2$$

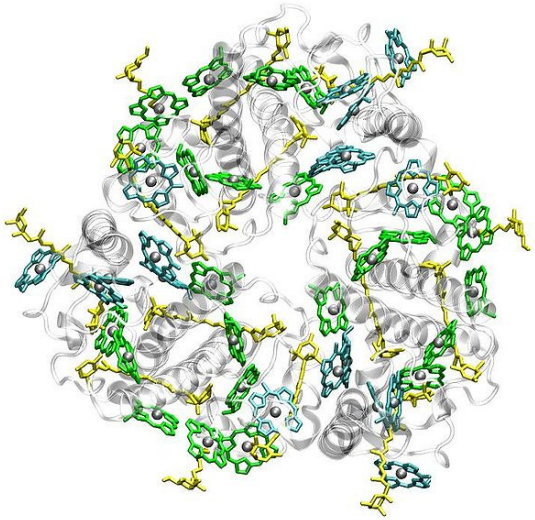


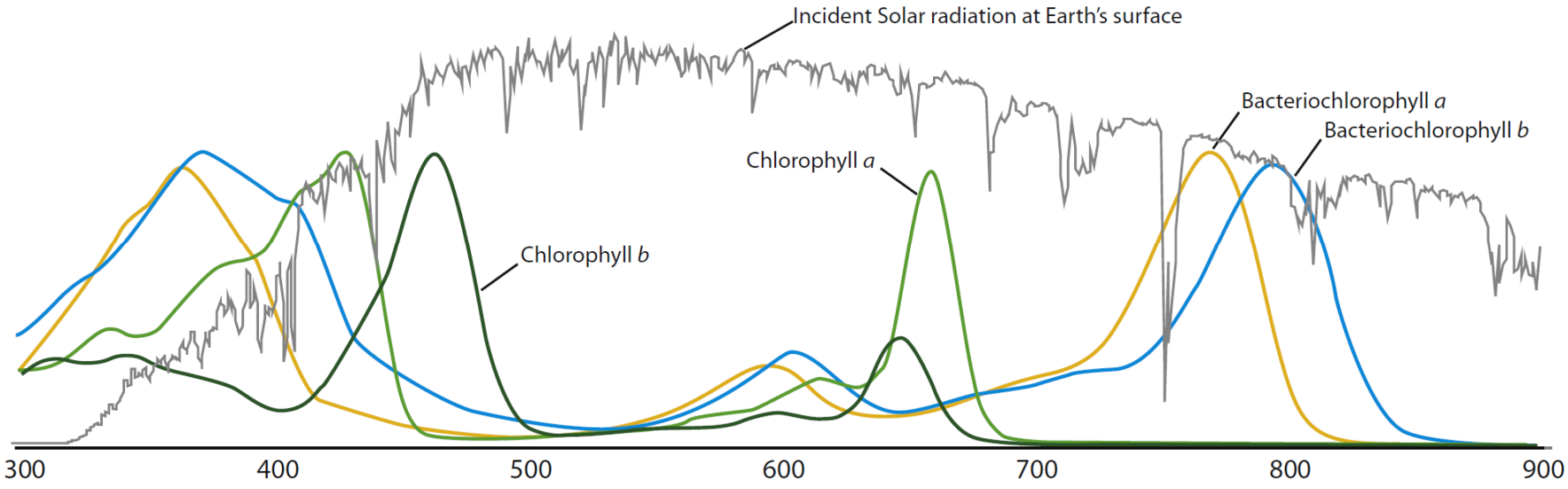
1. Light Harvesting



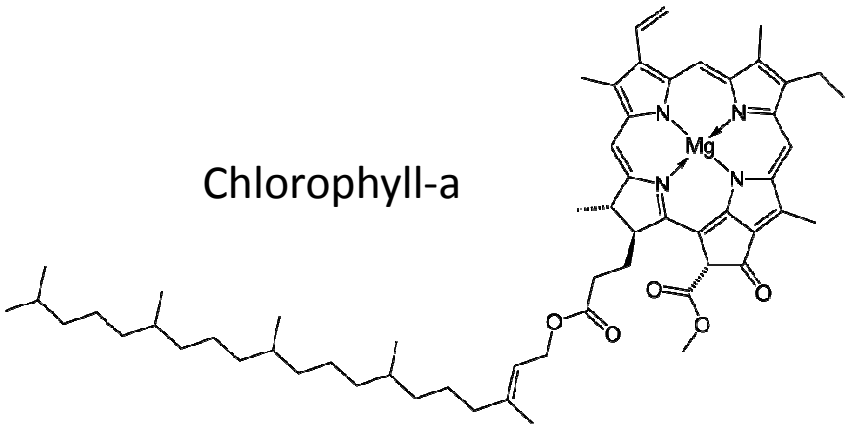
Light **H**arvesting
antennae complexes
LH-I and **LH-II** surround the reaction center (RC) for optimal <u>energy transfer</u>.

A spectrum of incident solar radiation at the Earth's surface featuring superimposed absorption spectra of chlorophyll *a* (—), chlorophyll *b* (—), bacteriochlorophyll *a* (—) and bacteriochlorophyll *b* (—).
[recorded in methanol/ethanol solution].

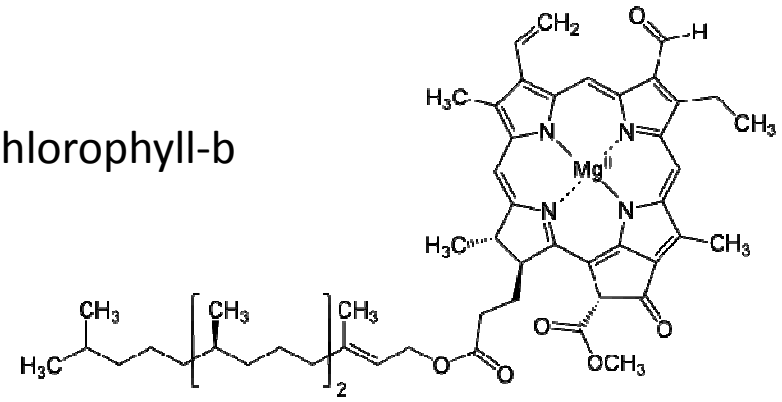


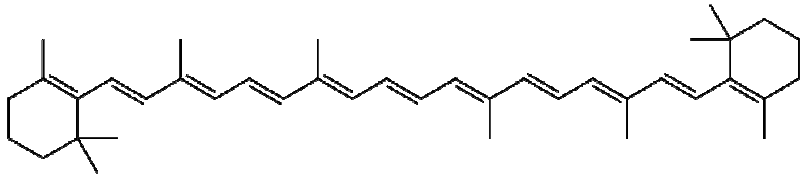


Chlorophyll-a

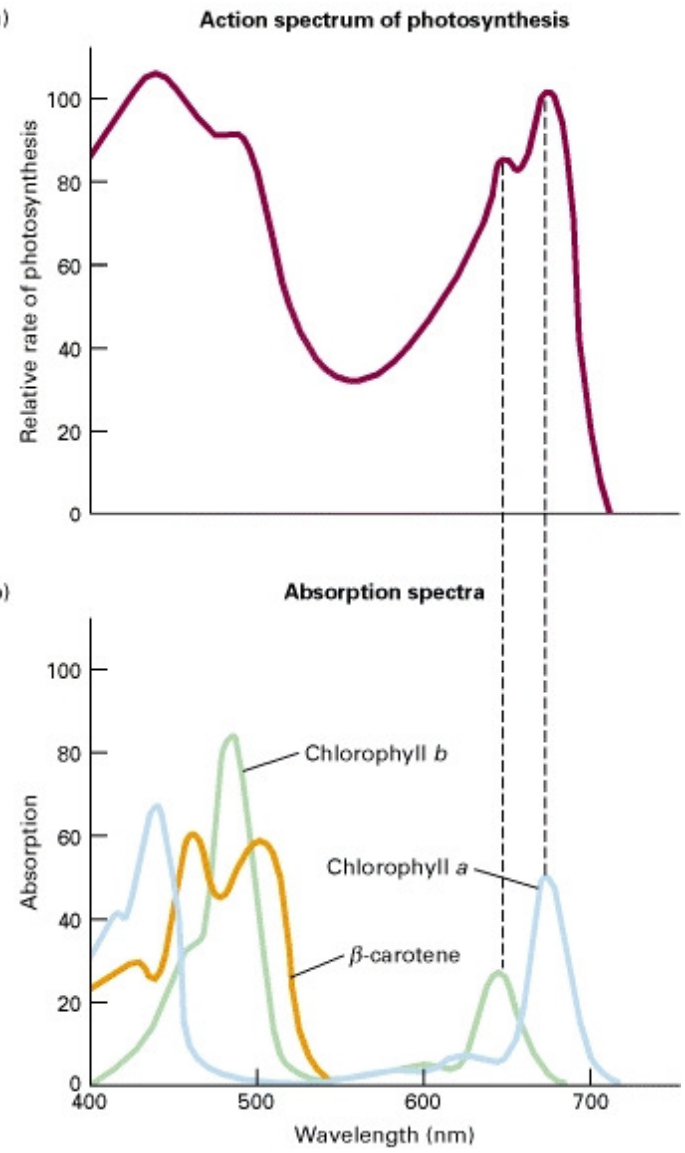


Chlorophyll-b





β-Carotene

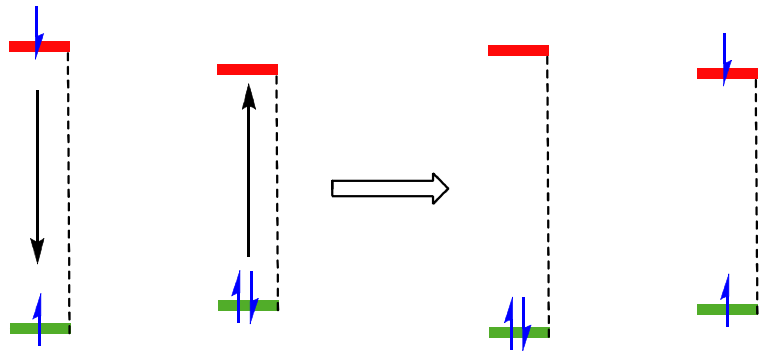


Energy Transfer

- The energy transfer is made possible by a special arrangement of many chlorophyll chromophores in a network of ‘antenna pigments’.
- These chromophores are arranged in spatial proximity and a certain, well-defined orientation; they are able to ‘funnel’ the light energy to the actual reaction centers with about 95 % efficiency within 10-100 ps.
- In physical terms this Forster mechanism of ‘resonance transfer’ proceeds via spectral overlap of emission bands of the exciton source with absorption bands of the exciton acceptor.
- This kind of mechanism also exists for the exciton transfer from other, higher energies absorbing pigments to the reaction centers (energy transfer along an energy gradient) so that the light harvesting complexes of the photosynthetic membrane feature a spatially as well as spectrally optimized cross section for photon capture.

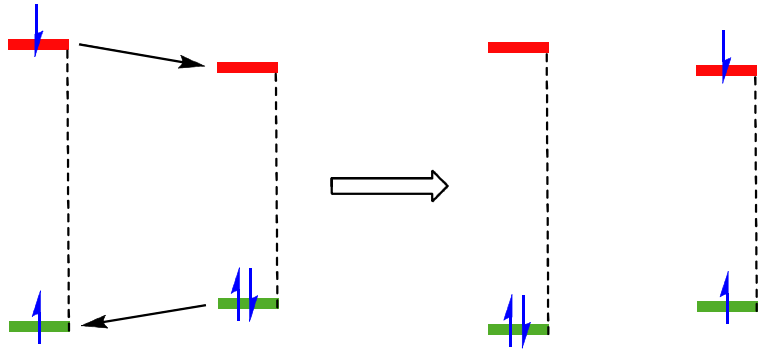
Föster Energy Transfer aka Fluorescence Energy Transfer (FRET)

- A donor chromophore, initially in its electronic excited state, may transfer energy to an acceptor chromophore (in proximity, typically less than 10 nm) through non-radiative dipole–dipole coupling.

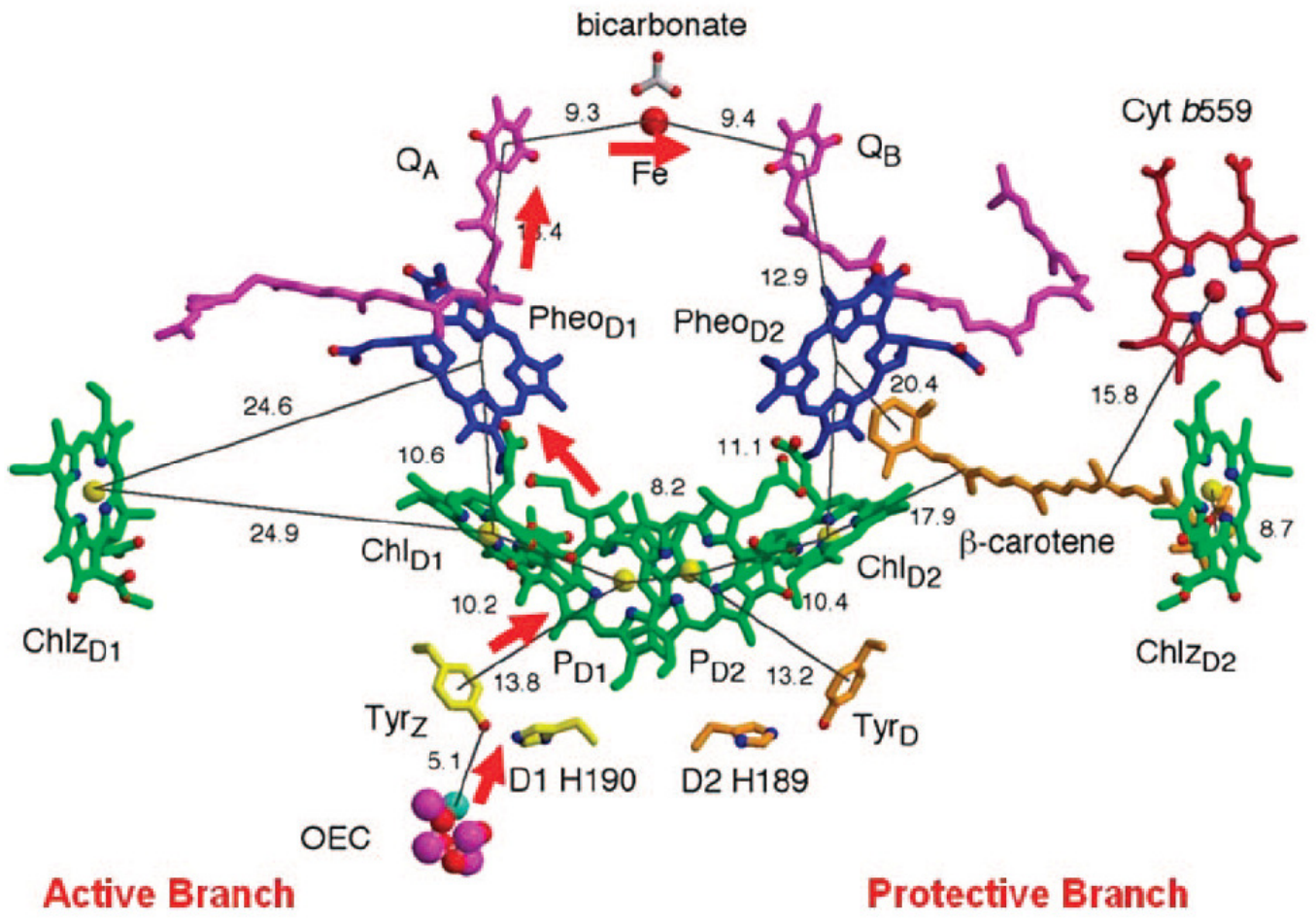


Dexter Energy Transfer

- Requires a wavefunction overlap between the donor and acceptor (i.e. physical communication) and is therefore restricted to short distances; typically of the order 15-20 Å.
- The excited state may be exchanged in a single step, or in two separate charge exchange steps. Sometimes described as electron transfer but overall net-energy transfer occurs.



Electron Transfer - PSII reaction center



- Electronic excitation of the dimer leads to a primary charge separation within a very short time.

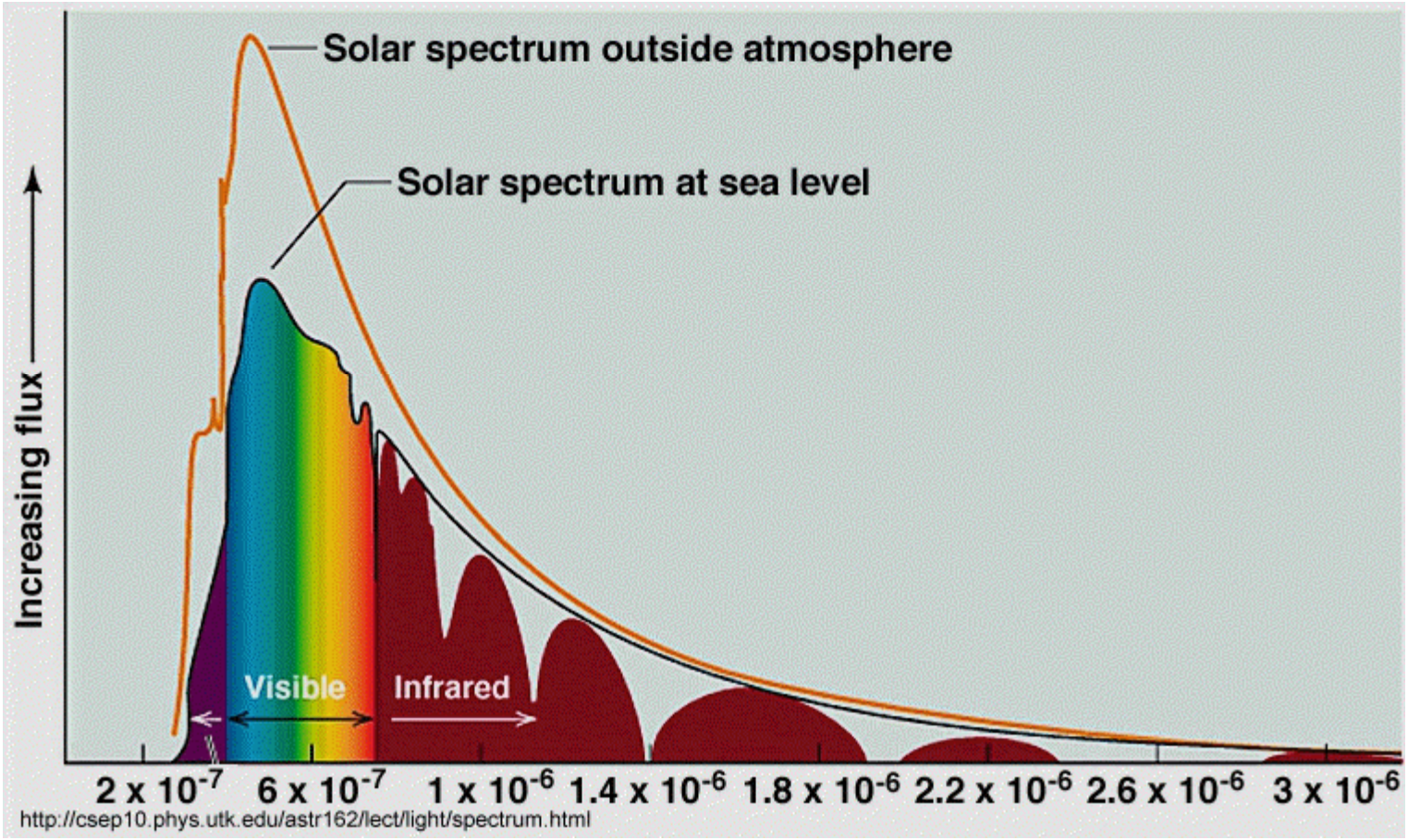
Solar cell efficiencies (2008)

Table I. Confirmed terrestrial cell and submodule efficiencies measured under the global AM1.5 spectrum (1000 W/m^2) at 25°C (IEC 60904-3: 2008, ASTM G-173-03 global)

Classification[a]	Effic.[b] (%)	Area[c] (cm^2)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF[d] (%)	Test centre[e] (and date)	Description
Silicon							
Si (crystalline)	**25.0 ± 0.5**	4.00 (da)	0.705	**42.7**	82.8	Sandia (3/99)[f]	UNSW PERL[12]
Si (multicrystalline)	**20.4 ± 0.5**	1.002 (ap)	0.664	**38.0**	80.9	NREL (5/04)[f]	FhG-ISE[13]
Si (thin film transfer)	**16.7 ± 0.4**	4.017 (ap)	0.645	**33.0**	78.2	FhG-ISE (7/01)[f]	U. Stuttgart (45 μm thick)[14]
Si (thin film submodule)	**10.5 ± 0.3**	94.0 (ap)	0.492[g]	**29.7**[g]	72.1	FhG-ISE (8/07)[f]	CSG Solar (1-2 μm on glass; 20 cells)[15]
III-V cells							
GaAs (crystalline)	**26.1 ± 0.8**	0.998 (ap)	1.038	**29.7**	84.7	FhG-ISE (12/07)[f]	Radboud U. Nijmegen[6]
GaAs (thin film)	**26.1 ± 0.8**	**1.001 (ap)**	**1.045**	**29.5**	**84.6**	**FhG-ISE (07/08)[f]**	**Radboud U. Nijmegen[6]**
GaAs (multicrystalline)	**18.4 ± 0.5**	4.011 (t)	0.994	**23.2**	79.7	NREL (11/95)[f]	RTI, Ge substrate[16]
InP (crystalline)	**22.1 ± 0.7**	4.02 (t)	0.878	**29.5**	85.4	NREL (4/90)[f]	Spire, epitaxial[17]
Thin film chalcogenide							
CIGS (cell)	**19.4 ± 0.6**[h]	0.994 (ap)	0.716	**33.7**	80.3	NREL (1/08)[f]	NREL, CIGS on glass[18]
CIGS (submodule)	**16.7 ± 0.4**	16.0 (ap)	0.661[g]	**33.6**[g]	75.1	FhG-ISE (3/00)[f]	U. Uppsala, 4 serial cells[19]
CdTe (cell)	**16.7 ± 0.5**[h]	1.032 (ap)	0.845	**26.1**	75.5	NREL (9/01)[f]	NREL, mesa on glass[20]
Amorphous/nanocrystalline Si							
Si (amorphous)	9.5 ± 0.3[i]	1.070 (ap)	0.859	17.5	63.0	NREL (4/03)[f]	U. Neuchatel[21]
Si (nanocrystalline)	10.1 ± 0.2[j]	1.199 (ap)	0.539	24.4	76.6	JQA (12/97)	Kaneka (2 μm on glass)[22]
Photochemical							
Dye sensitised	10.4 ± 0.3[k]	1.004 (ap)	0.729	**22.0**	65.2	AIST (8/05)[f]	Sharp[23]
Dye sensitised (submodule)	8.2 ± 0.3[k]	25.45 (ap)	**0.705**[g]	**19.1**[g]	61.1	AIST (12/07)[f]	Sharp, 9 serial cells[24]
Dye sensitised (submodule)	8.2 ± 0.3[k]	18.50	0.659[g]	**19.9**[g]	62.9	AIST (6/08)[f]	Sony, 8 serial cells[25]
Organic							
Organic polymer	5.15 ± 0.3[k]	1.021 (ap)	0.876	**9.39**	62.5	NREL (12/06)[f]	Konarka[26]
Organic (submodule)	1.1 ± 0.3[k]	232.8 (ap)	29.3	0.072	51.2	NREL (3/08)[f]	Plextronics (P3HT/PCBM)[27]
Multijunction devices							
GaInP/GaAs/Ge	32.0 ± 1.5[j]	3.989 (t)	2.622	14.37	85.0	NREL (1/03)	Spectrolab (monolithic)
GaInP/GaAs	30.3[j]	4.0 (t)	2.488	14.22	85.6	JQA (4/96)	Japan Energy (monolithic)[28]
GaAs/CIS (thin film)	25.8 ± 1.3[j]	4.00 (t)	—	—	—	NREL (11/89)	Kopin/Boeing (4 terminal)[29]
a-Si/μc-Si (thin submodule)[j,l]	11.7 ± 0.4[j,l]	14.23 (ap)	5.462	2.99	71.3	AIST (9/04)	Kaneka (thin film)[30]

[a]CIGS = CuInGaSe2; a-Si = amorphous silicon/hydrogen alloy.
[b]Effic. = efficiency.
[c](ap) = aperture area; (t) = total area; (da) = designated illumination area.
[d]FF = fill factor.
[e]FhG-ISE = Fraunhofer Institut für Solare Energiesysteme; JQA = Japan Quality Assurance; AIST = Japanese National Institute of Advanced Industrial Science and Technology.
[f]Recalibrated from original measurement.
[g]Reported on a 'per cell' basis.
[h]Not measured at an external laboratory.
[i]Stabilised by 800 h, 1 sun AM1.5 illumination at a cell temperature of 508°C.
[j]Measured under IEC 60904-3 Ed. 1: 1989 reference spectrum.
[k]Stability not investigated.
[l]Stabilised by 174 h, 1 sun illumination after 20 h, 5 sun illumination at a sample temperature of 508°C.

The Solar Spectrum

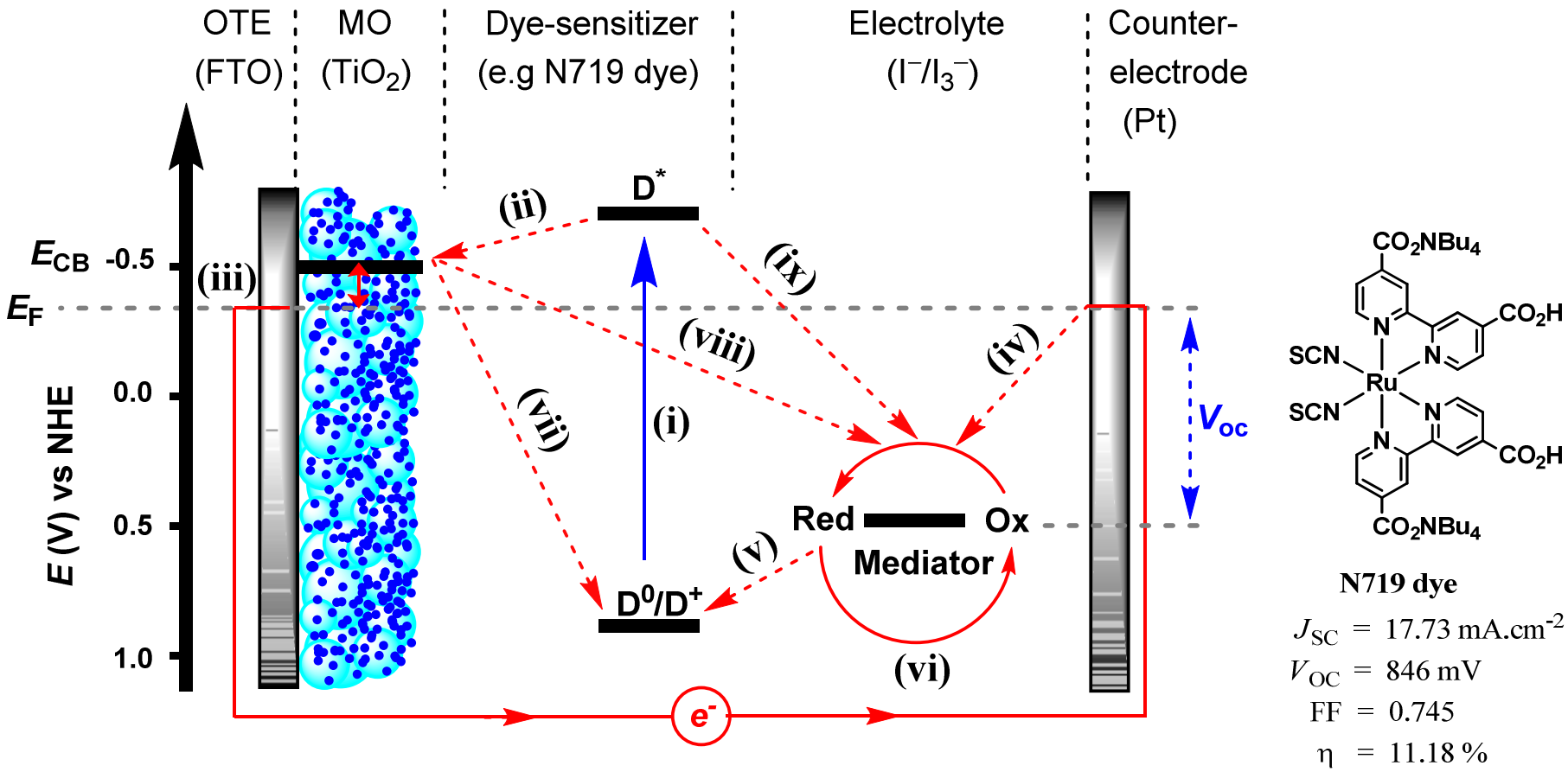


Dye-sensitized solar cells (Grätzel cells)

- Dye-sensitized solar cells (DSSCs) are one of the most promising molecular photovoltaics and have been attracting considerable attention since the pioneering study of Grätzel et al. because of the potential of low-cost production.
- In order to improve the **solar-to-electric power conversion efficiency (*η*),** both metal complexes and metal-free organic dyes, as sensitizers of nanocrystalline TiO_2 electrode, have been extensively investigated and developed in terms of optical absorption extension to the red or infrared region through molecular design.
- The highest *η* for DSCs has so far reached 11 % obtained from Ru polypyridine complexes.

$$\eta = \textbf{maximum power output } (P_{max}) \textbf{/ power input } (P_{light})$$

Operation of Dye Sensitized Solar Cells



N719 dye

J_{SC} = 17.73 mA.cm^{-2}
V_{OC} = 846 mV
FF = 0.745
η = 11.18 %

- Charge separation and charge recombination are competitive!

η = **maximum power output (P_{max})/ power input (P_{light})**

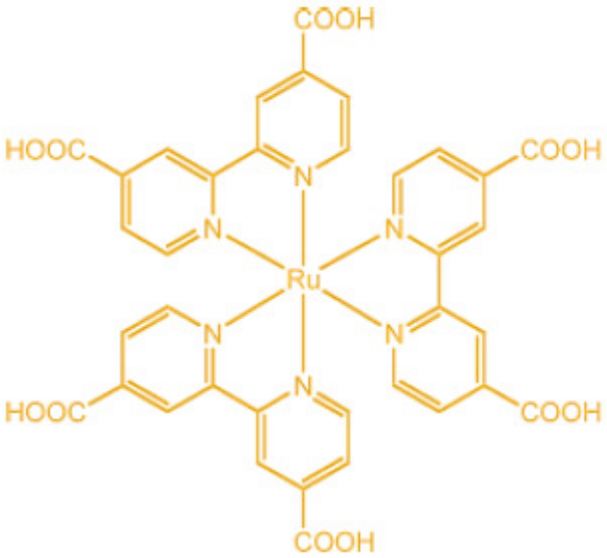
Molecular Engineering for DSSCs

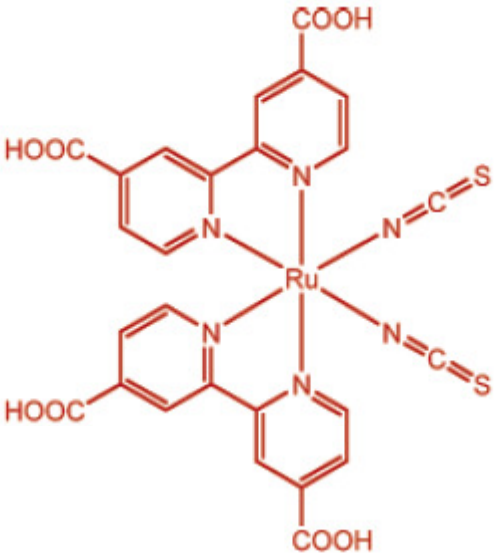
- **Energy matching** of the HOMO and LUMO of the dye with the redox mediator and E_{CB} of the TiO_2 electrode, respectively.

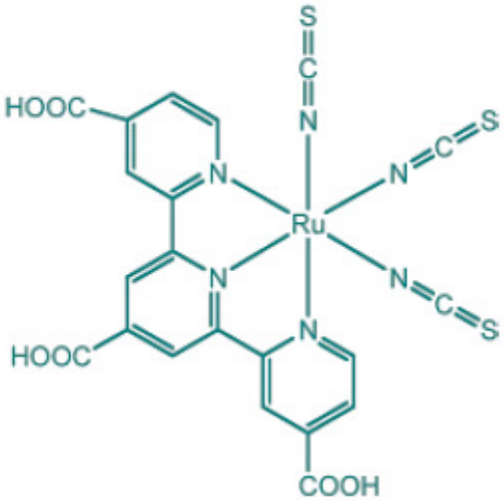
- **Donor-π-conjugation-linkage-acceptor (D-π-A) structure** required for a wide range absorption extending across the UV-vis-NIR spectrum.

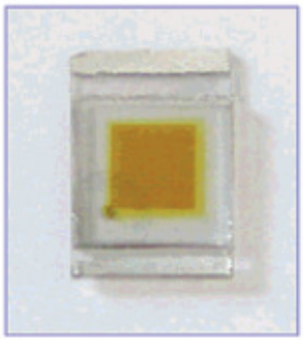
- **Anchoring groups** such as carboxylic acid or phosphonic acid groups are required for a strong adsorption onto the surface of TiO_2.

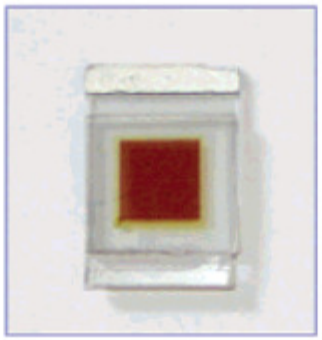
Light harvesting in DSSCs

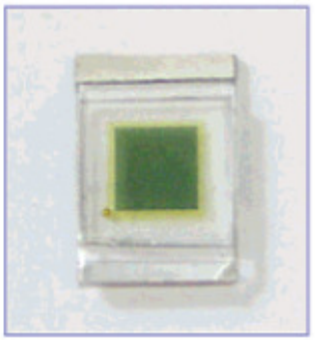




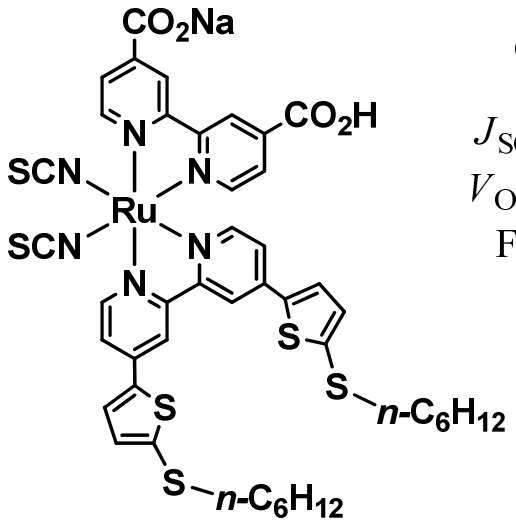






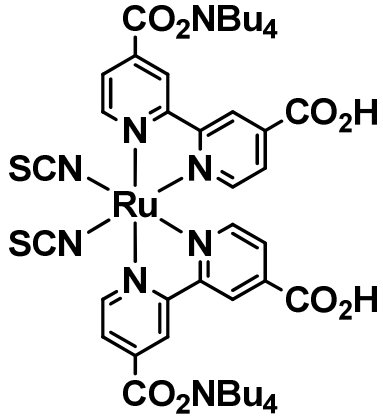


Champion DSSC Dyes



C106 dye

J_{SC} = 19.78 mA.cm^{-2}
V_{OC} = 758 mV
FF = 0.779
η = 12.10 %

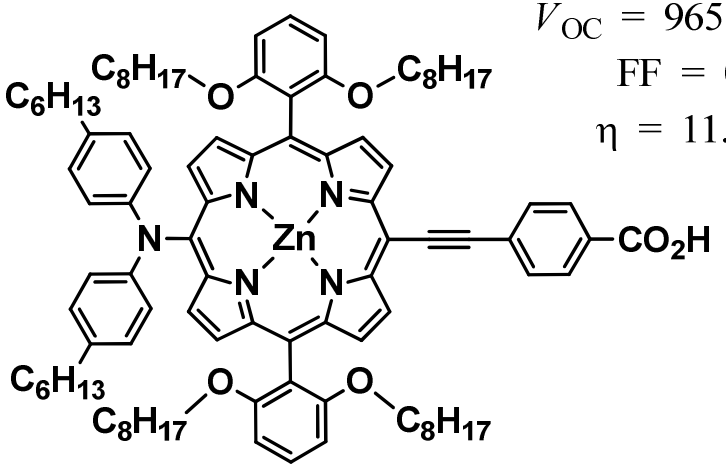


N719 dye

J_{SC} = 17.73 mA.cm^{-2}
V_{OC} = 846 mV
FF = 0.745
η = 11.18 %

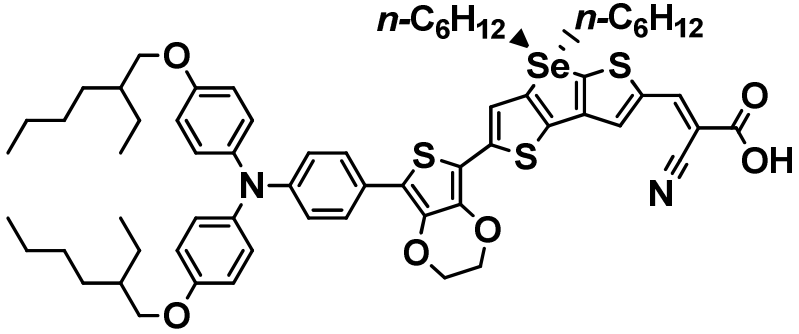
YD2-*o*-C8 dye

J_{SC} = 17.30 mA.cm^{-2}
V_{OC} = 965 mV
FF = 0.71
η = 11.9 %



J_{SC} = 17.94 mA.cm^{-2}
V_{OC} = 770 mV
FF = 0.730
η = 10.3 %

C219 dye



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Yella et al. *Science* **2011,** *334*, 629-634.

Preparation of TiO_2 nanoparticle films

$Ti(i\text{-}PrO)_4$

dil. HNO_3 | hydrolysis

↓

TiO_2 colloid

Δ 8 hr. | peptidization

↓

TiO_2 Sol-gel

↓

Autoclave 12 hrs. @ 400 ^{0}C

↓

PEG addition

↓

Film Deposition

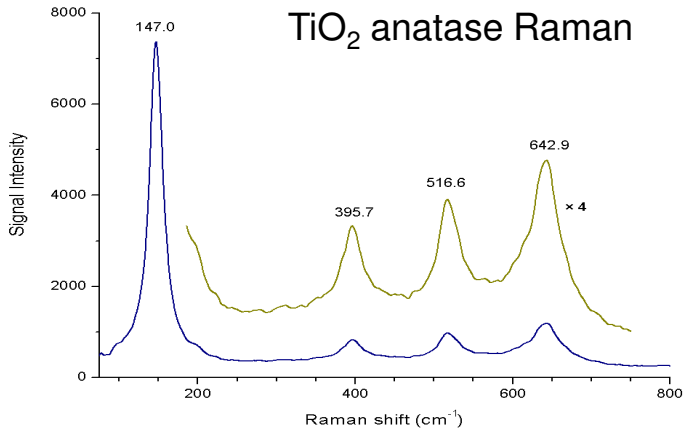
↓

Sintering 30 min. 450 ^{0}C

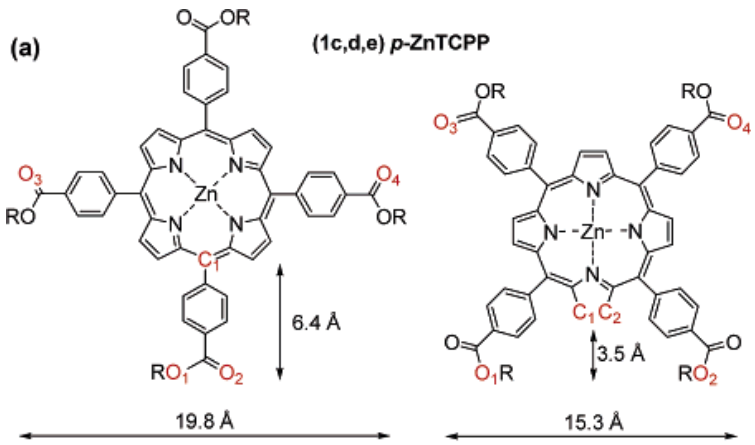
↓

TiO_2 mesoporous film

- TiO_2 anatase
  - nanoparticles size ~ 20 nm
  - thin film thickness ~10 mm

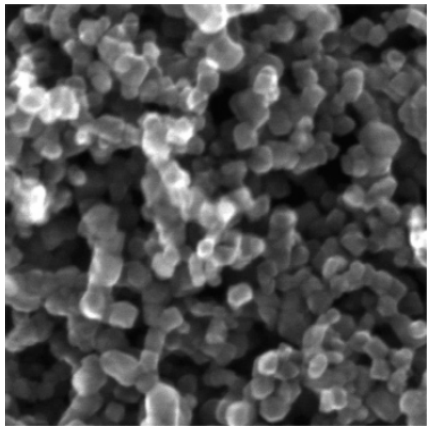


blank & sensitized
TiO_2 films with ZnTCPP

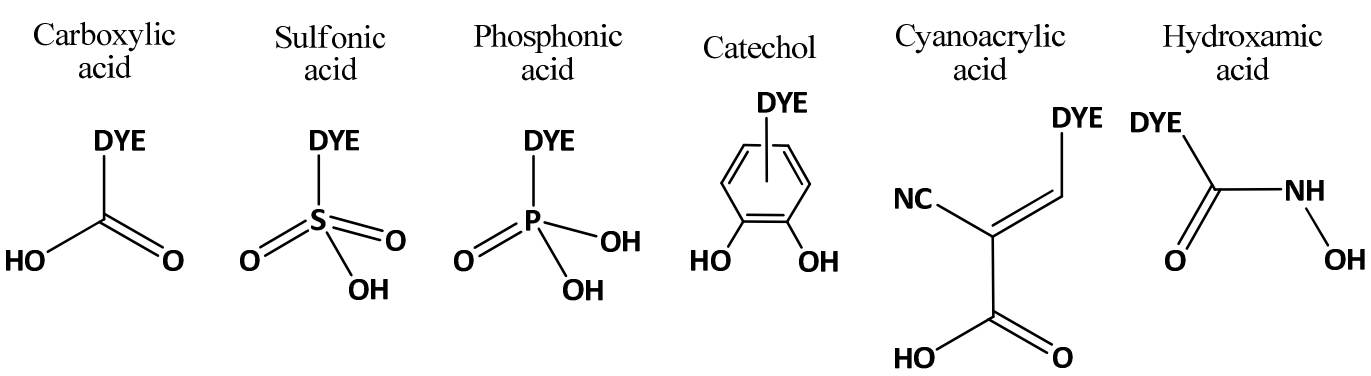


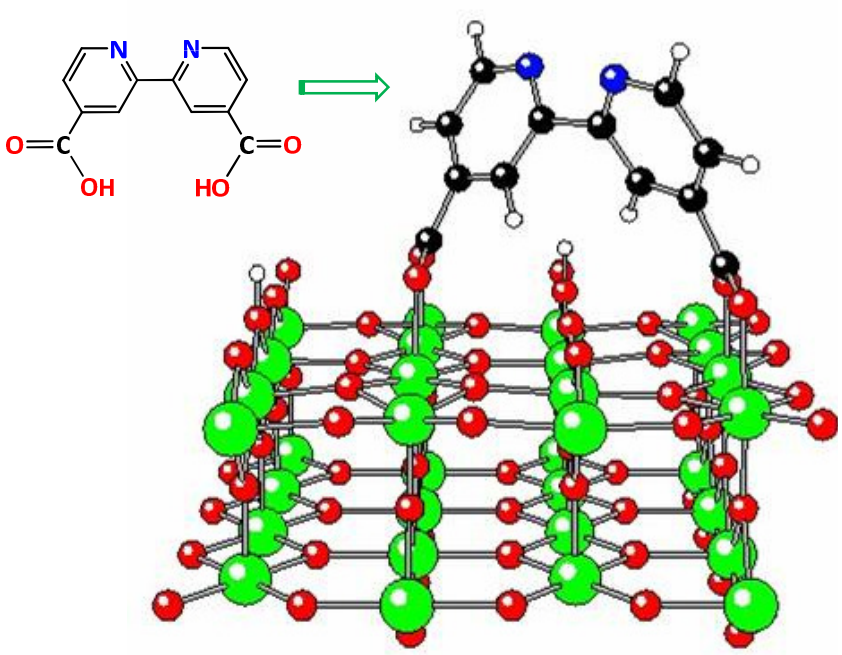
Rochford J.; Chu D.; Hagfeldt A.; Galoppini E. *J. Am. Chem. Soc.* , 2007, 129, 4655.

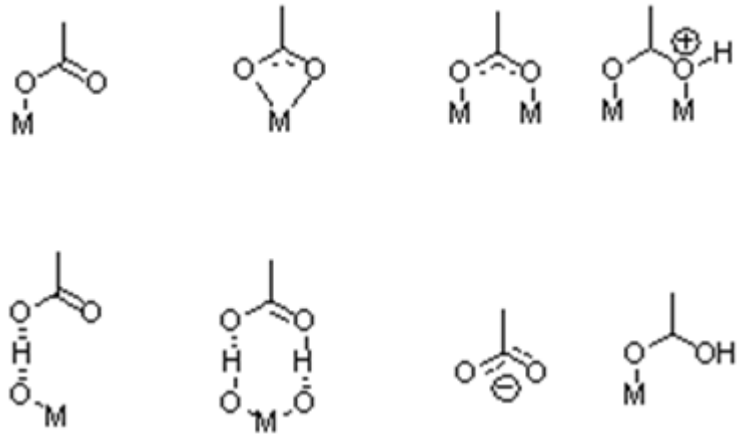
TiO_2 & anchoring groups



Scanning electron micrograph of a sintered mesoscopic TiO_2 (anatase) film supported on an FTO glass. The average particle size is 20 nm.

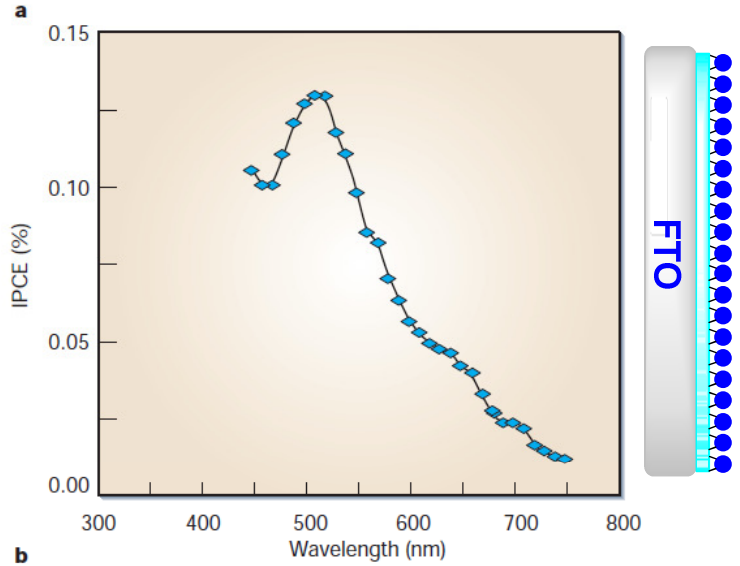


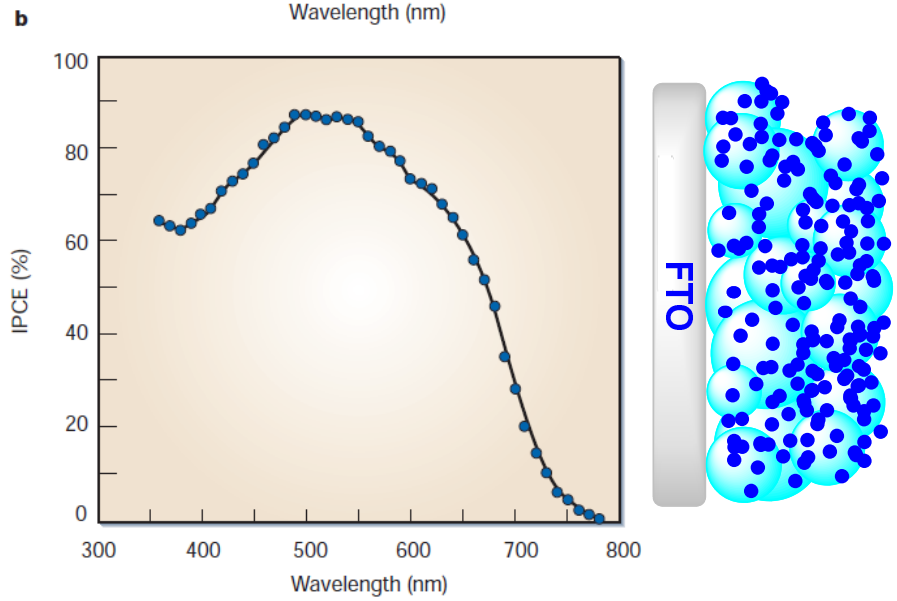




Possible binding modes for a carboxylic acid anchoring group at TiO_2 (M = Ti)

The mesoporous nanocrystalline effect

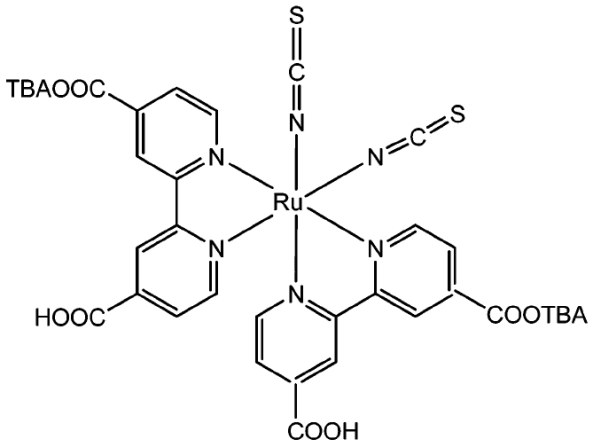




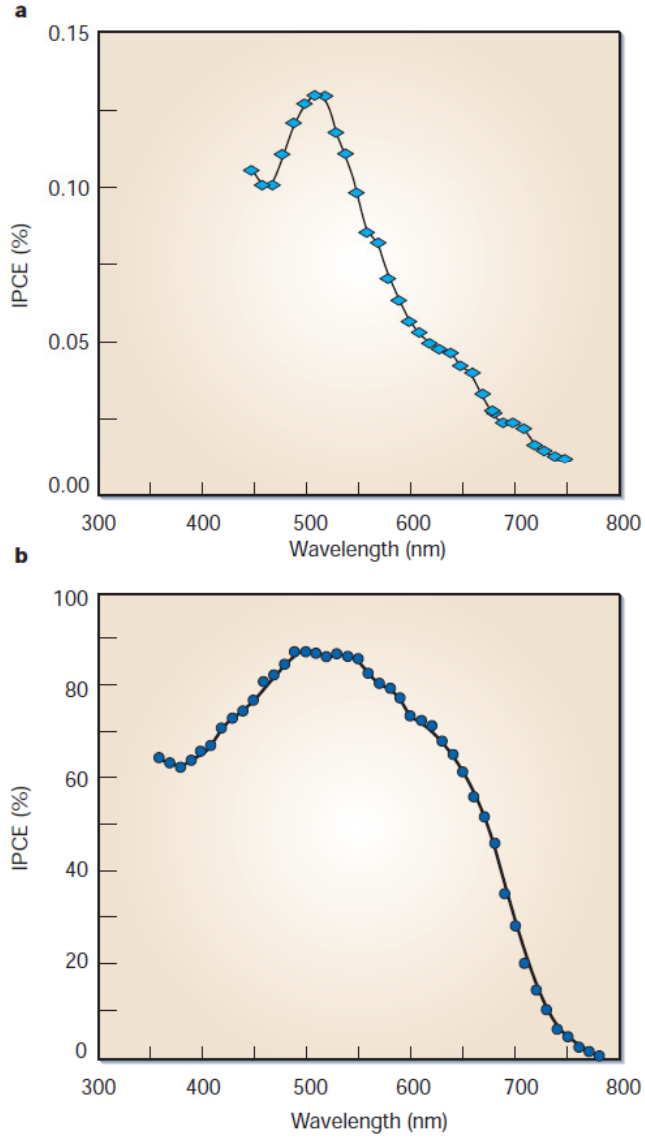
The incident-photon-to-current conversion efficiency **(IPCE)** is plotted as a function of the excitation wavelength.

a) Single-crystal anatase TiO_2.

b) Nanocrystalline TiO_2 anatase film.



Incident photon-to-current conversion efficiency



The (IPCE), sometimes referred to also as "external quantum efficiency" (EQE), corresponds to the number of electrons measured as photocurrent in the external circuit divided by the ***monochromatic photon flux*** that strikes the cell.

$$\mathbf{IPCE = LHE_{\lambda} \cdot \phi_{inj} \cdot \eta_{coll}}$$

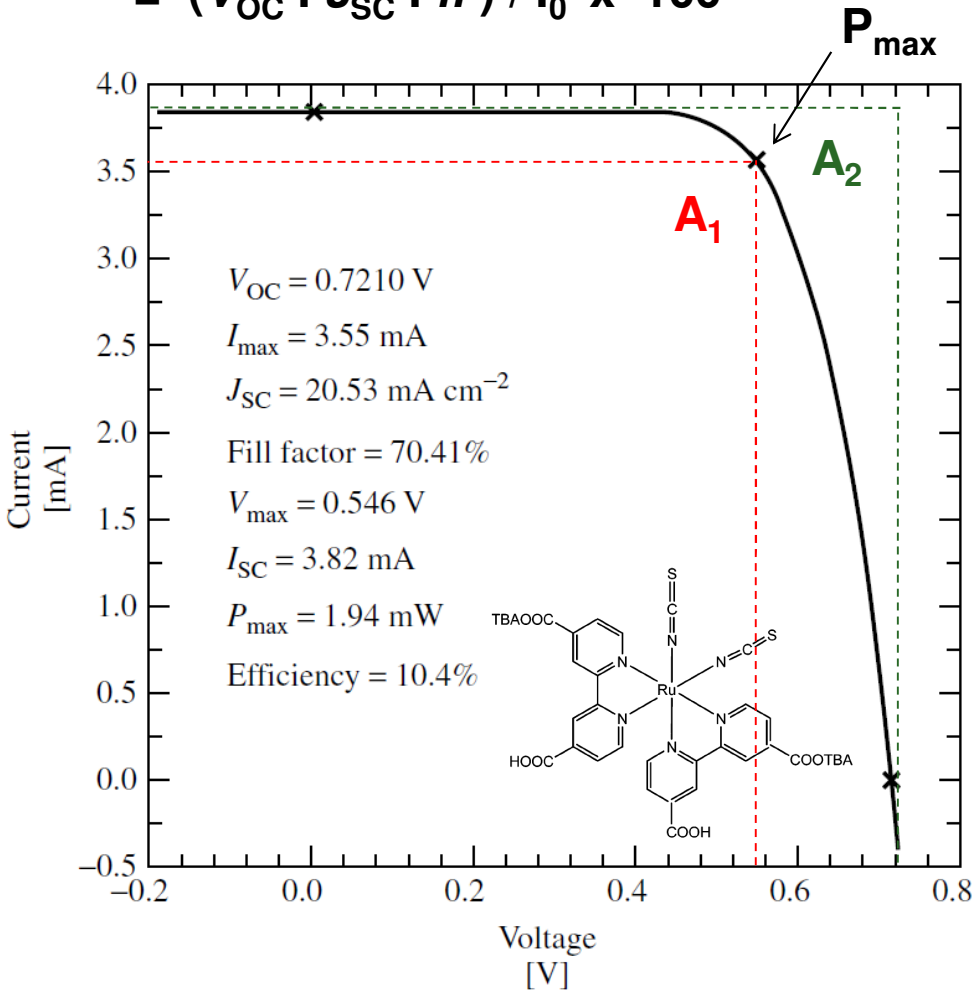
LHE_{λ} = light harvesting efficiency
ϕ_{inj} = *quantum yield for charge injection*
η_{coll} = charge collection efficiency at FTO electrode

IPCE = monochromatic efficiency

APCE = monochromatic efficiency corrected for transmitted photons

DSSC efficiency

$$\eta = P_{max} / P_{light}$$
$$= (V_{OC} \cdot I_{SC} \cdot ff) / (I_0 \cdot A) \times 100$$
$$= (V_{OC} \cdot J_{SC} \cdot ff) / I_0 \times 100$$



By increasing the resistive load on an irradiated cell continuously from zero (***short circuit***) to a very high value (***open circuit***) one can determine the **maximum-power point**, the point that maximizes V×I; i.e. the load for which the cell can deliver maximum electrical power at that level of irradiation.

(The output power is zero in both the short circuit and open circuit extremes)

V_{OC} = open circuit voltage

I_{SC} = short circuit current

A = area

J_{SC} = short circuit current density = I_{SC} / A

ff = *fill factor* = A_1 / A_2

I_0 = incident light flux (e.g. AM 1.5)

Determining Fill Factor

$$FF = P_{max\ obtainable} / P_{max\ theoretical}$$
$$= P_{max} / (V_{OC} \cdot J_{SC})$$