

Exciting Photochemistry

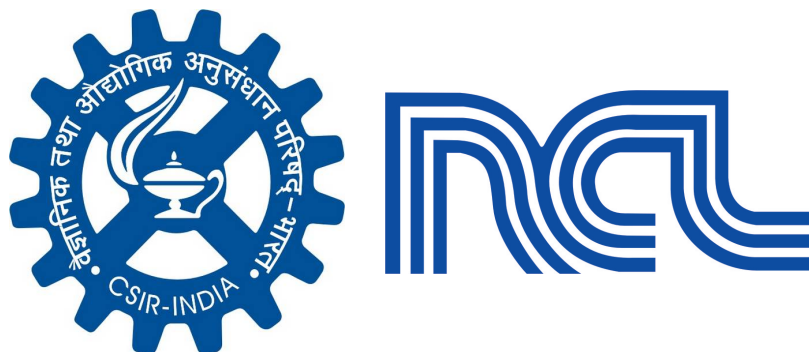
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May 28, 2017



Leonardo da Vinci

(15 Apr 1452 - 2 May 1519)

"Where nature finishes producing its own species, man begins, using natural things and with the help of this nature, to create an infinity of species...".



Jane Marcet
1769 –1858

“I assure you that the most wonderful and the most interesting phenomenon of nature are almost all of them produced by chemical powers”

Conversations on Chemistry, 1817



R. Feynman (1918 – 1988)

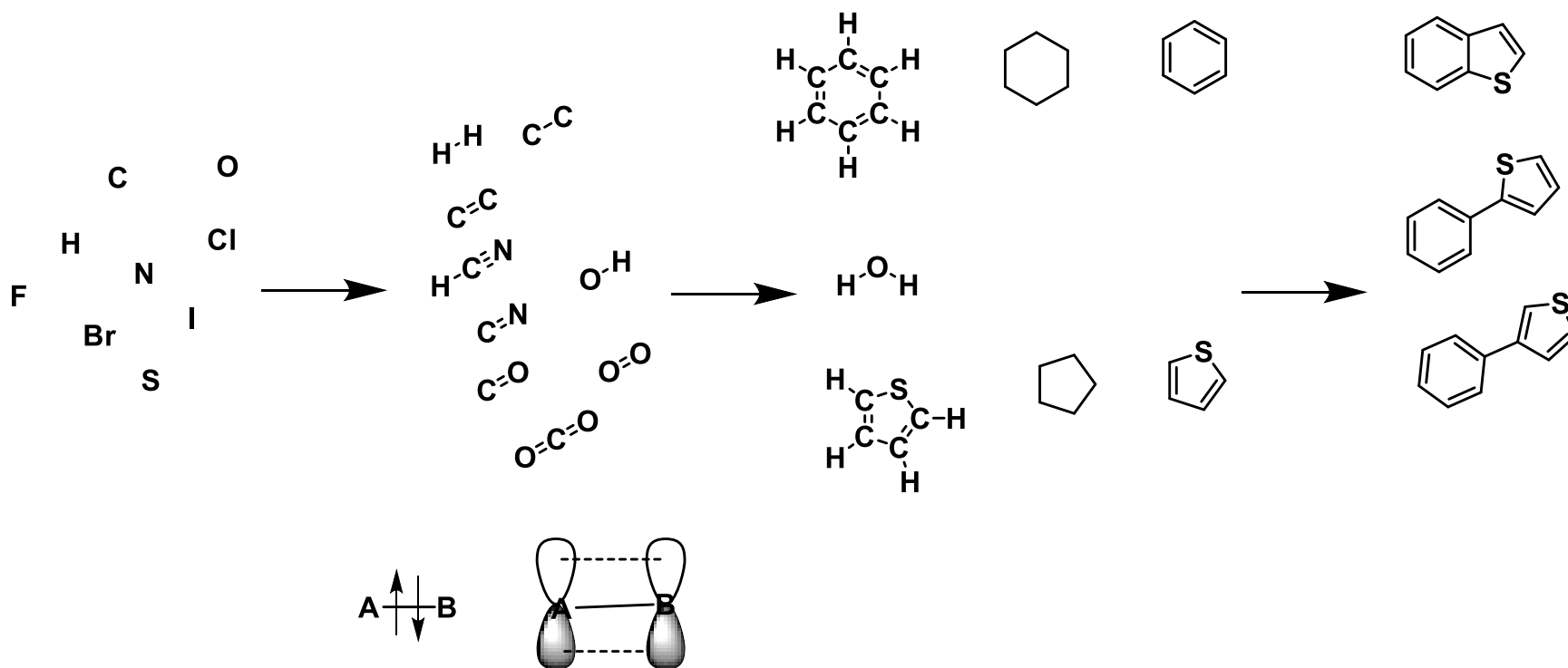
“...everything that is living can be understood in terms of the jiggling and wiggling of atoms.”

1963

Bricks, Walls and Building



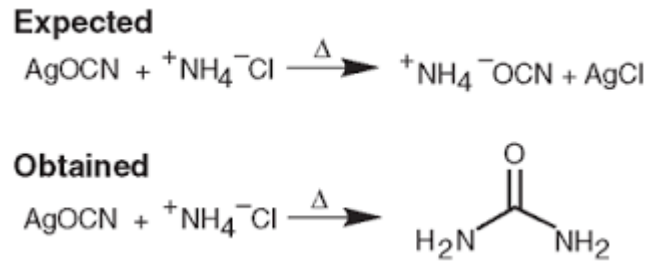
Atom, Bonds, and Molecules



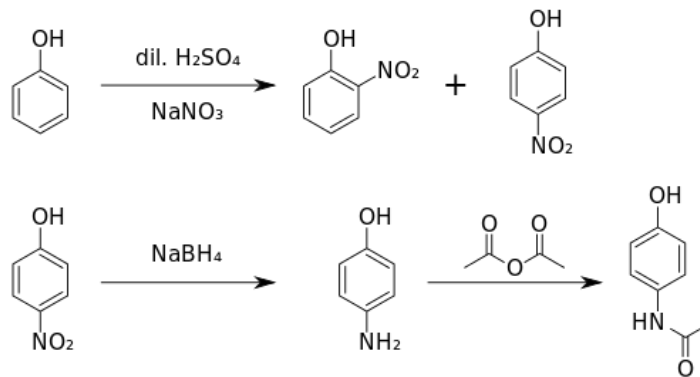
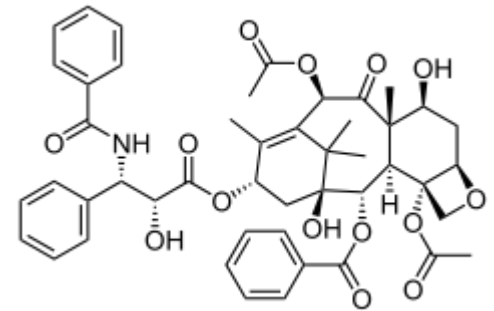
Urea 1828

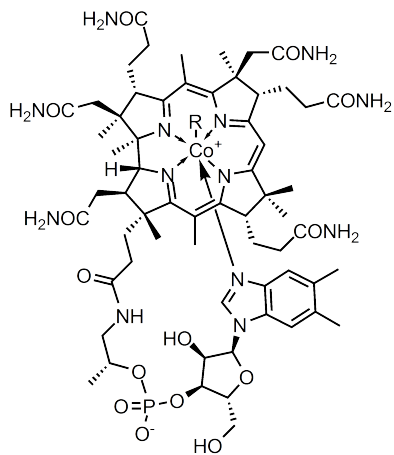


Friedrich Wöhler



Taxol



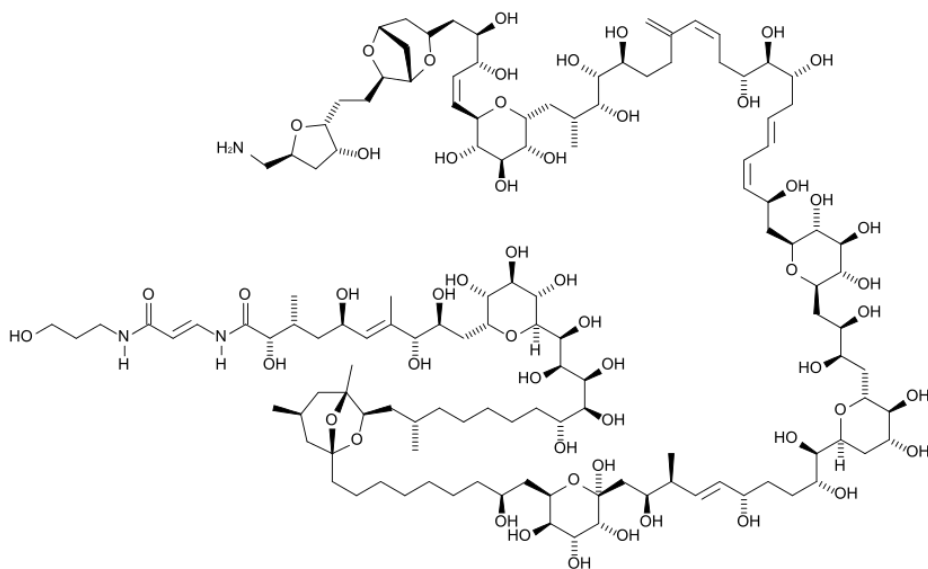


R = 5'-deoxyadenosyl, Me, OH, CN



Elias James Corey

Palytoxin

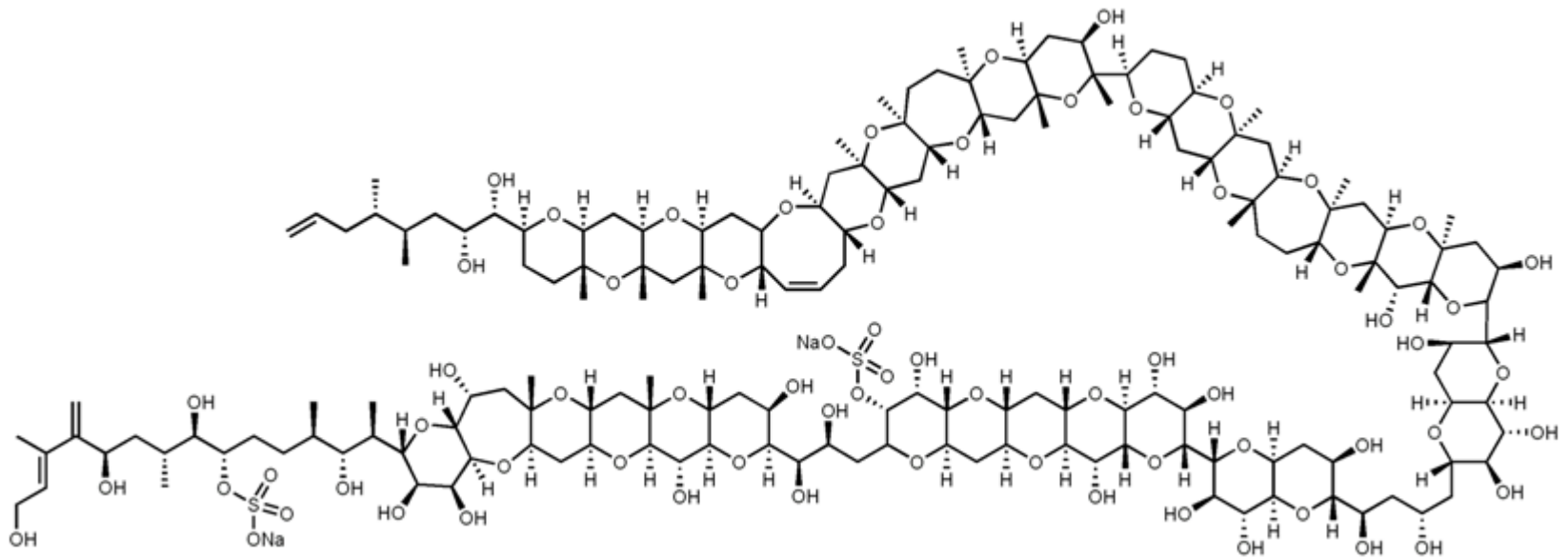


the Mount Everest of organic synthesis

Prof Yoshito Kishi



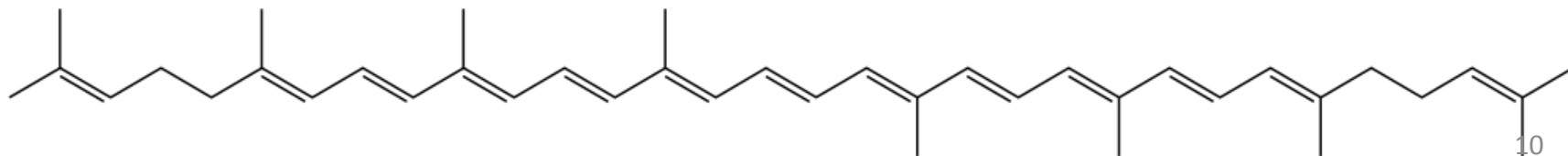
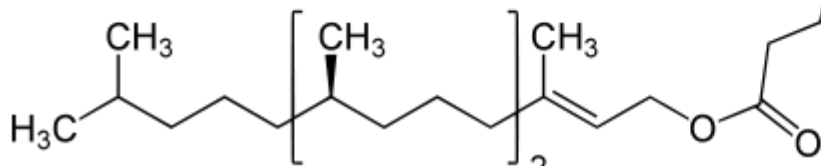
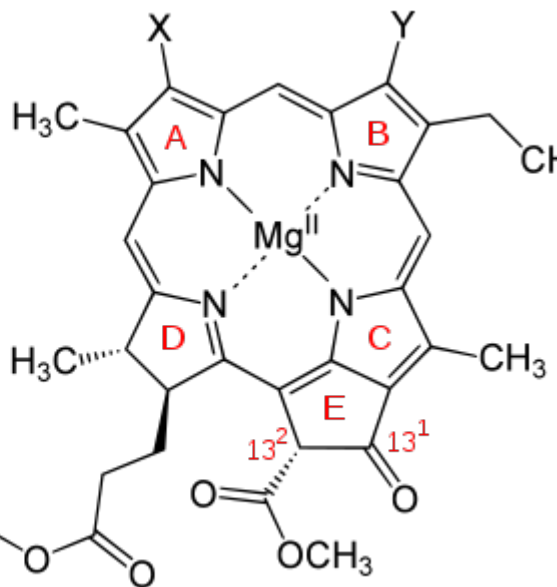
Organic synthesis

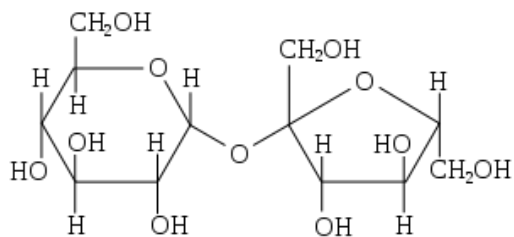
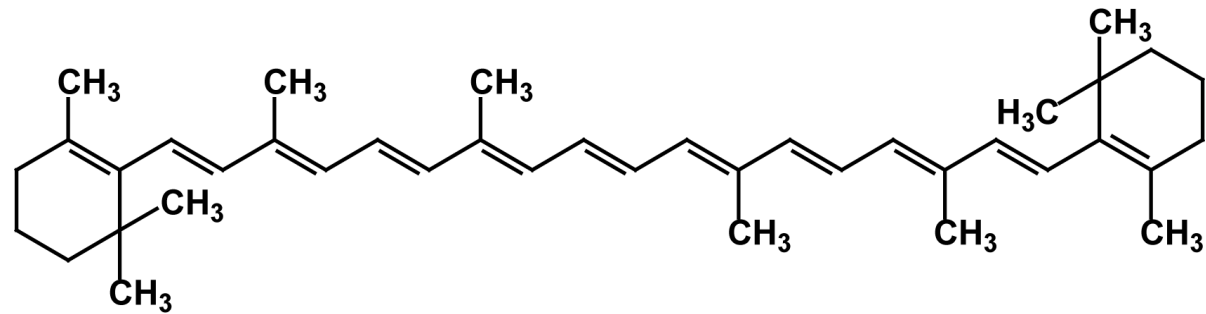
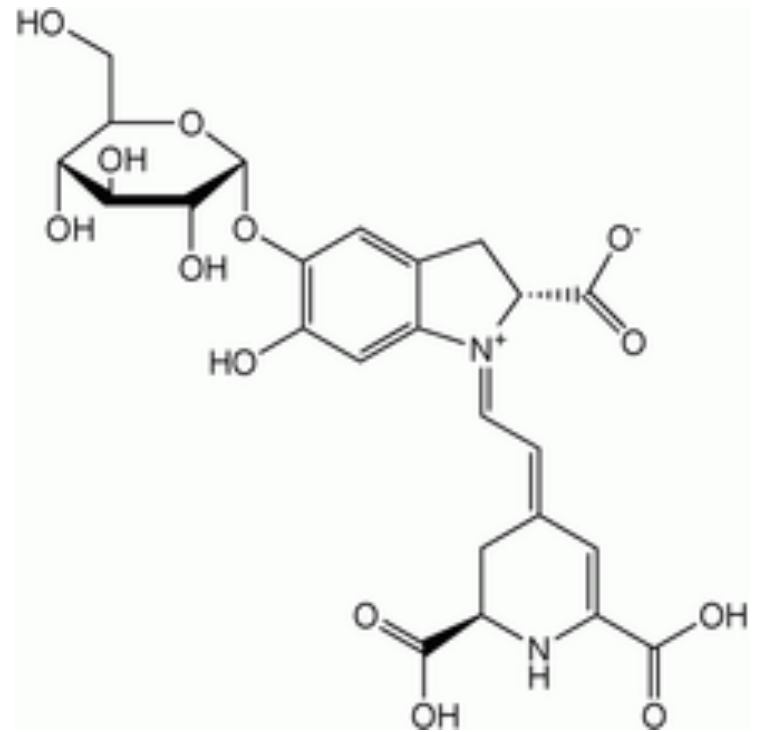


Maitotoxin

Joy of looking at the colors

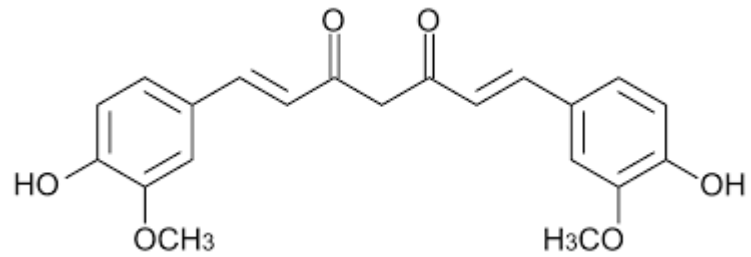
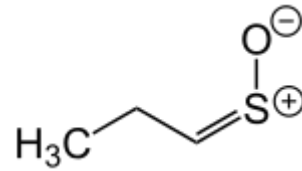
- a** X: CH=CH₂ Y: CH₃
b X: CH=CH₂ Y: CHO
d X: CHO Y: CH₃



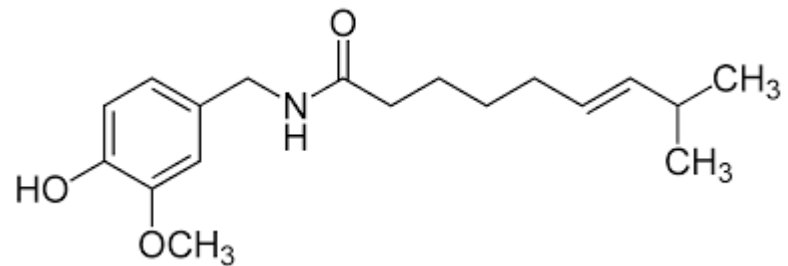


Sucrose: a disaccharide of glucose (left) and fructose(right), important molecules in the body.

syn-Propanethial-S-oxide

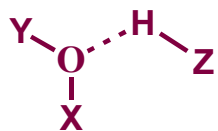


capsaicin

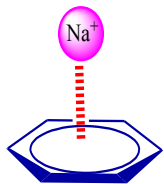


Atom, Bonds, Molecules and Supramolecules

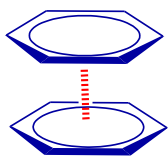
Role of Weak Interactions



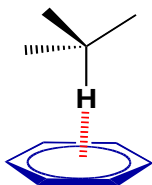
Hydrogen Bond



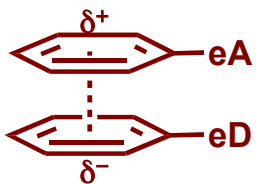
Cation--- π



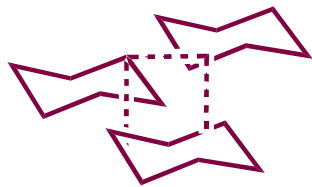
π --- π



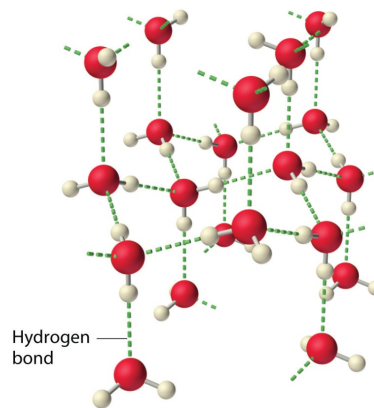
C-H--- π



Charge transfer



Van der Waals

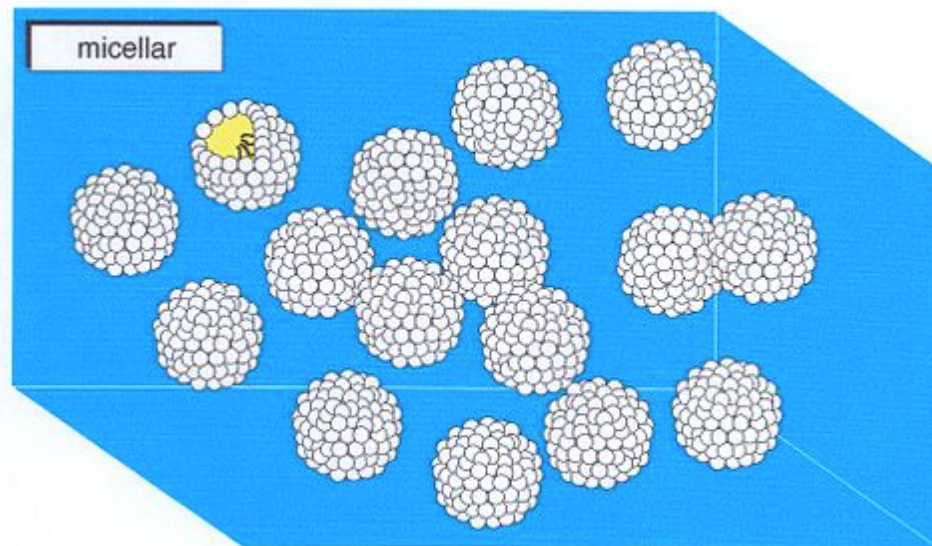
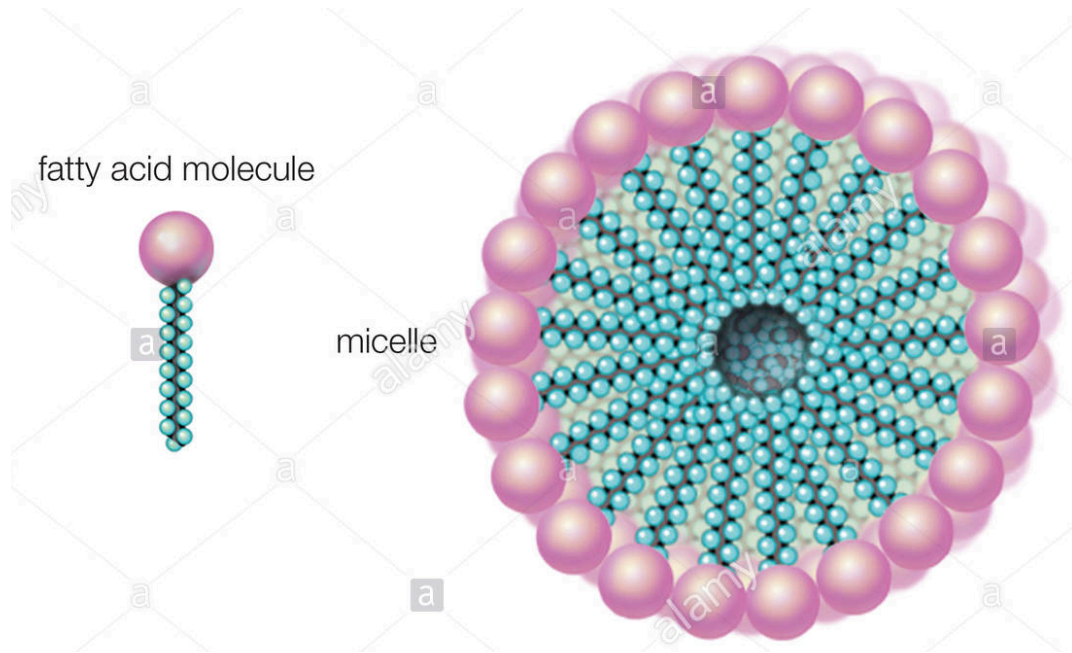


Gulliver vs Lillyputians



Multiple weak forces WIN !

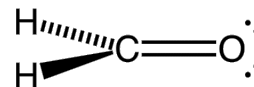
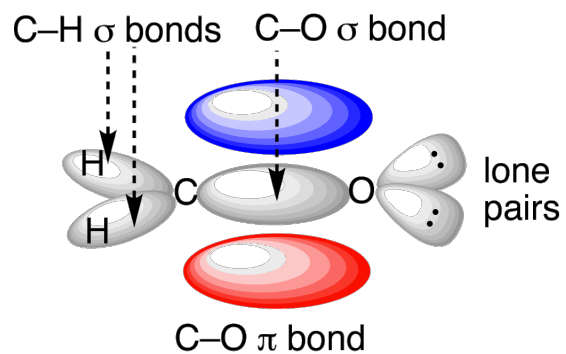
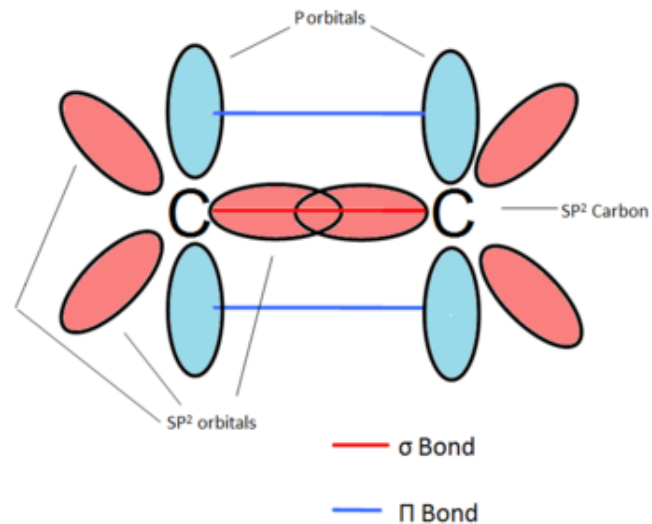
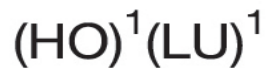
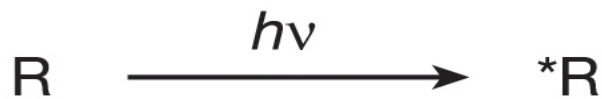
Supramolecules



Duration of Excitement



Photochemistry



What is LIGHT?



Lucretius (50 BC)



The light and heat of the sun is composed of minute particles.



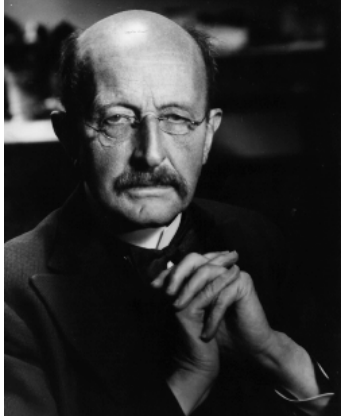
**Newton
(1643-1727)**

Particles!

Waves!



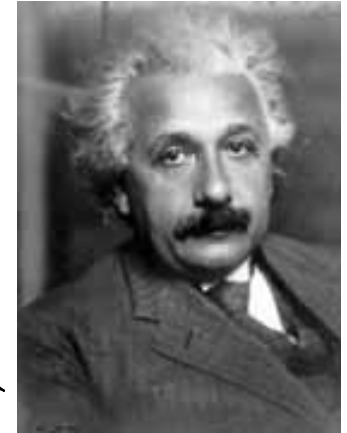
**Maxwell
(1831-1879)**



Max Planck (1918)

$$E = h\nu, \text{ quanta}$$

$$E = h\nu, \text{ photons}$$



Albert Einstein (1921)



Niels Bohr (1922)

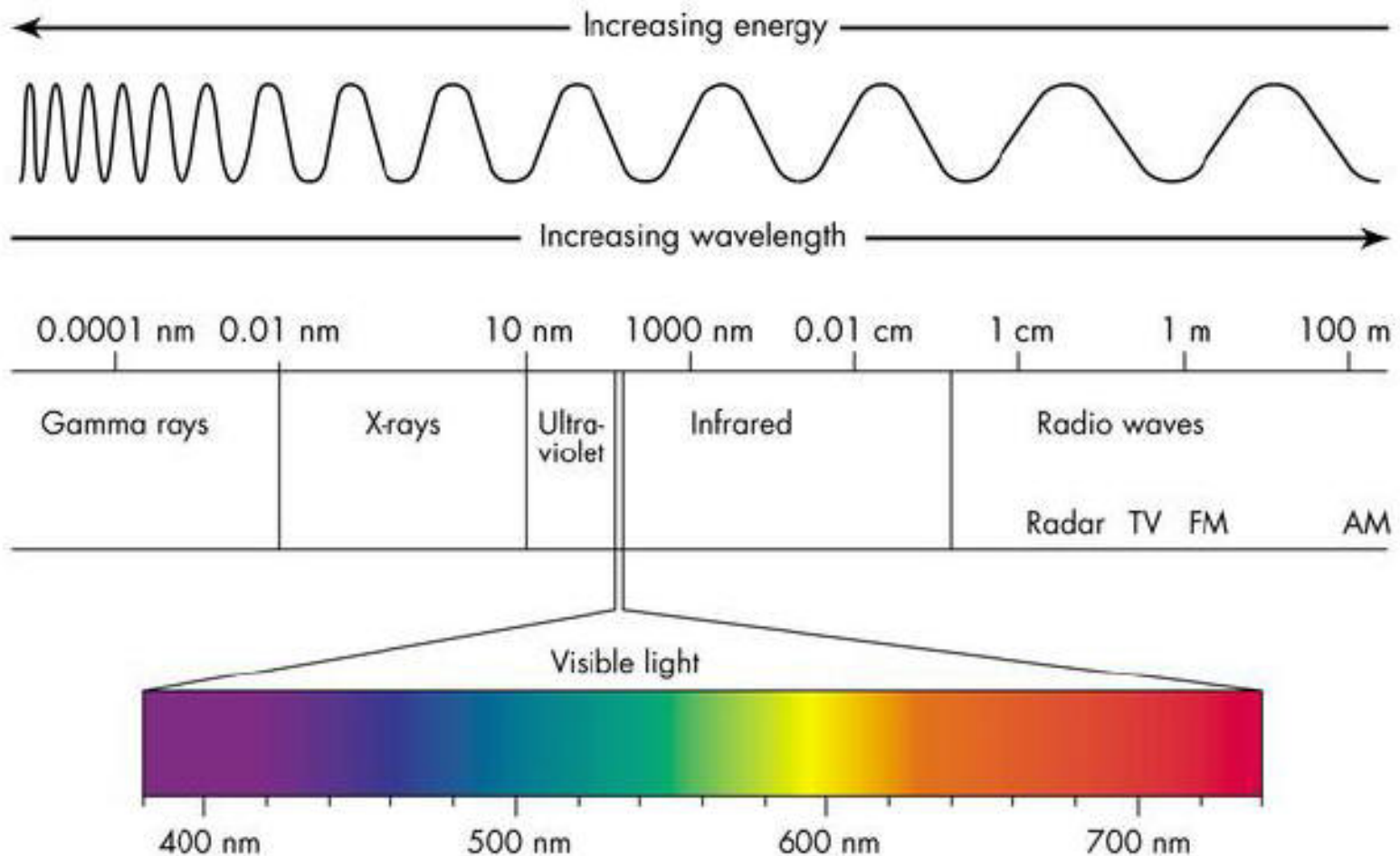
$$E_2 - E_1 = h\nu$$

$$E = h\nu = mc^2$$



De Broglie (1929)

Electro magnetic radiation



$$E = h\nu$$

$$\nu = c / \lambda$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$c = 2.99 \times 10^9 \text{ m/s}$$

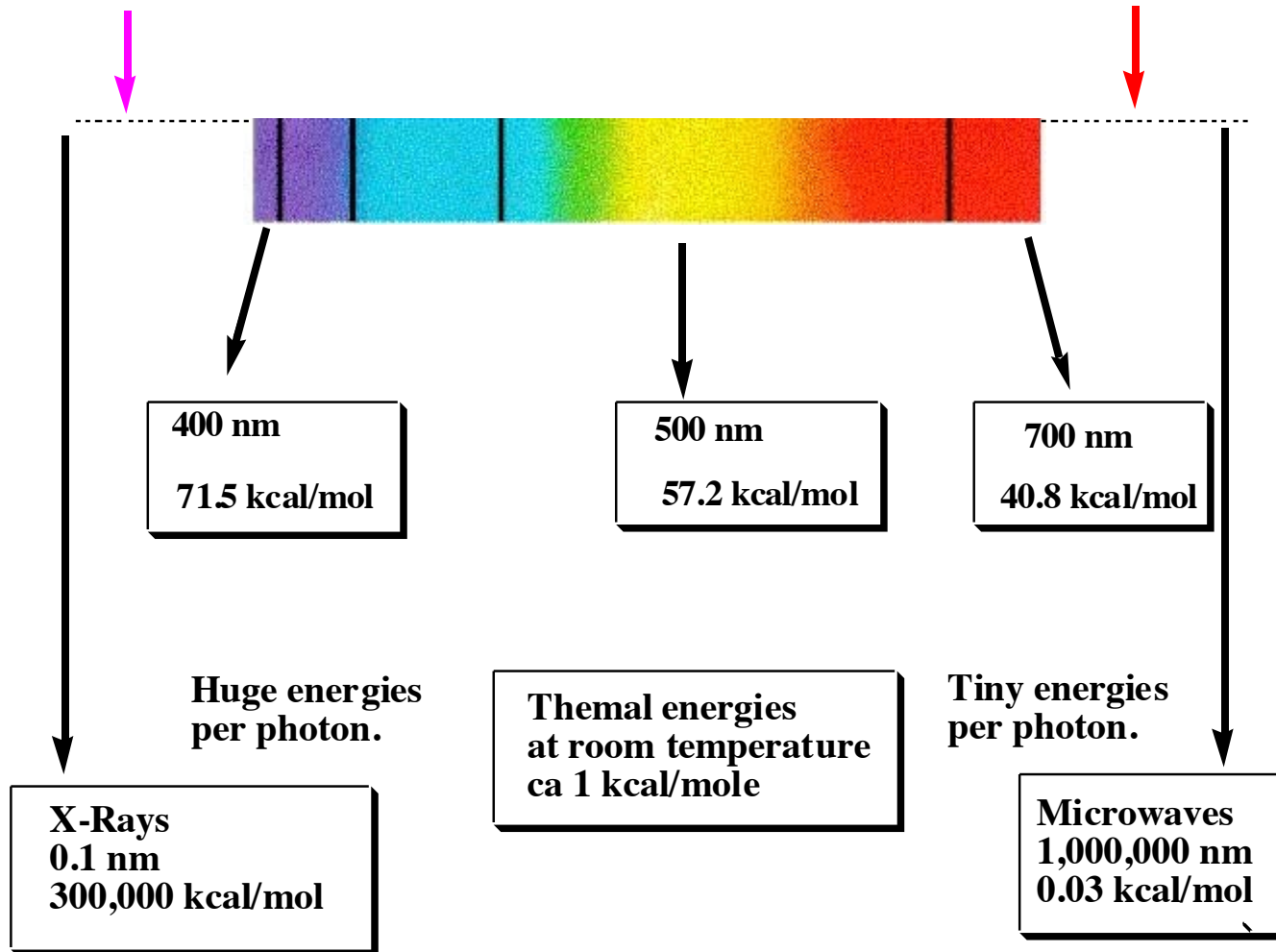
Light and Energy Scales

Ultraviolet Region

Chemical Bonds of
DNA and Proteins
Damaged

Infrared Region

Chemical Bonds Energy
too low to make or break
chemical bonds.



Light: Prosperity through basic science



Oil lamp



Filament lamp



Fluorescent lamp

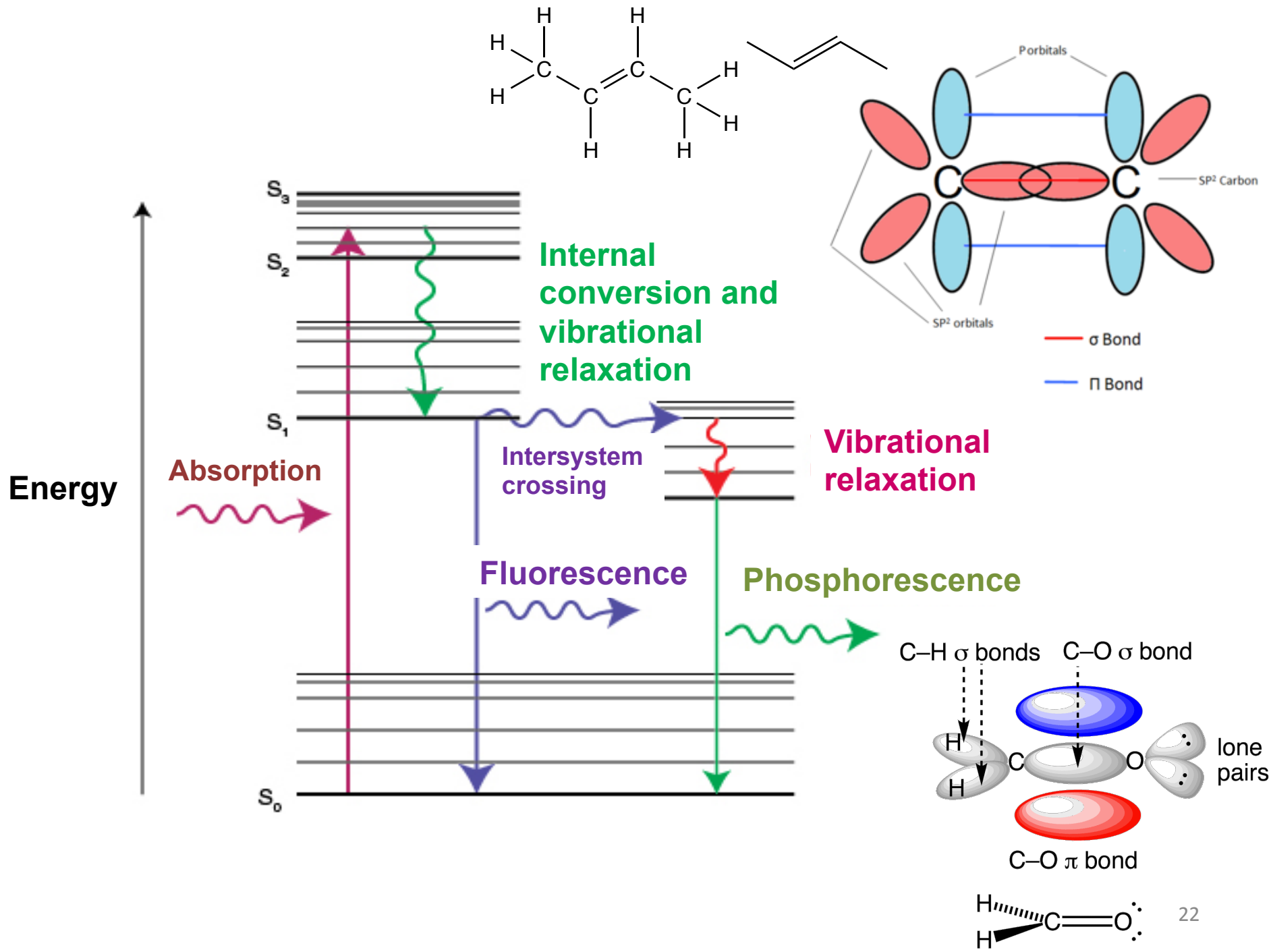


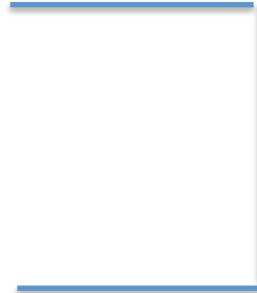
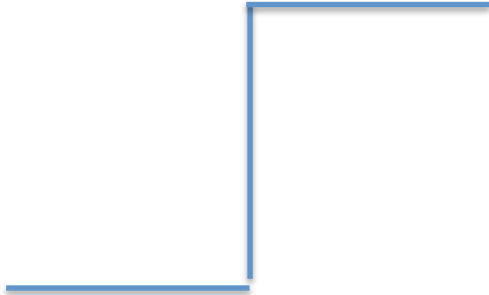
Gas arc lamp



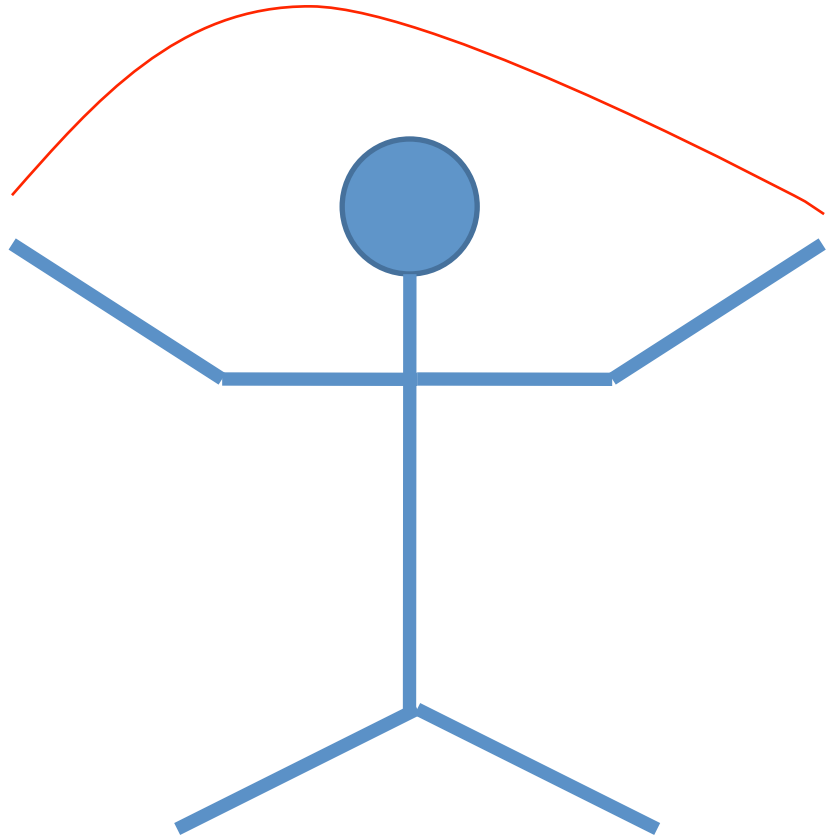
Light emitting diodes



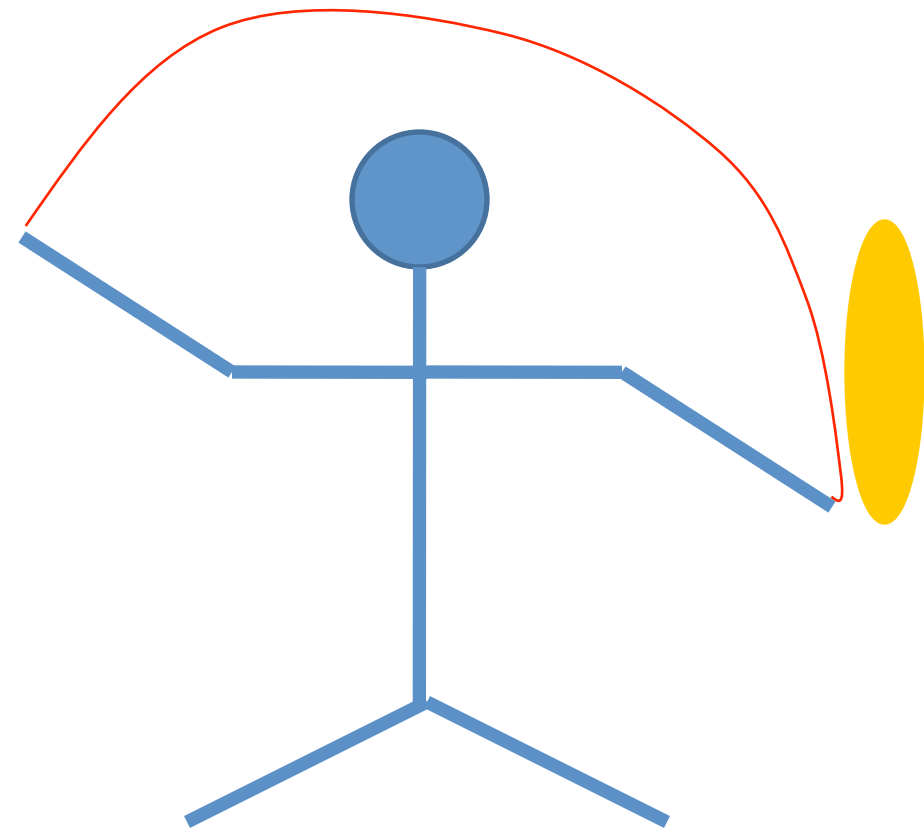




Cis-



Trans-



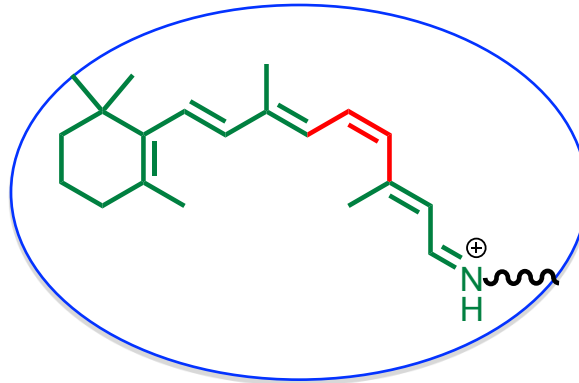
1 m, 0.001 m (mm), 0.000001 m (μm), 0.000000001 m (nm)

Chemistry within Confined Space



Rhodopsin

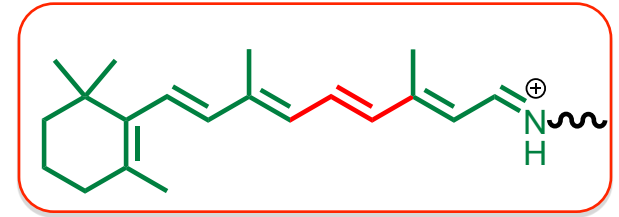
cis – same side



11-*cis*-retinal
protonated Schiff base

$h\nu$

trans – opposite side



11-*trans*-retinal
protonated Schiff base

Quantum yield for photochemical *cis* - *trans* isomerization 0.67

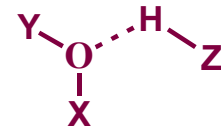
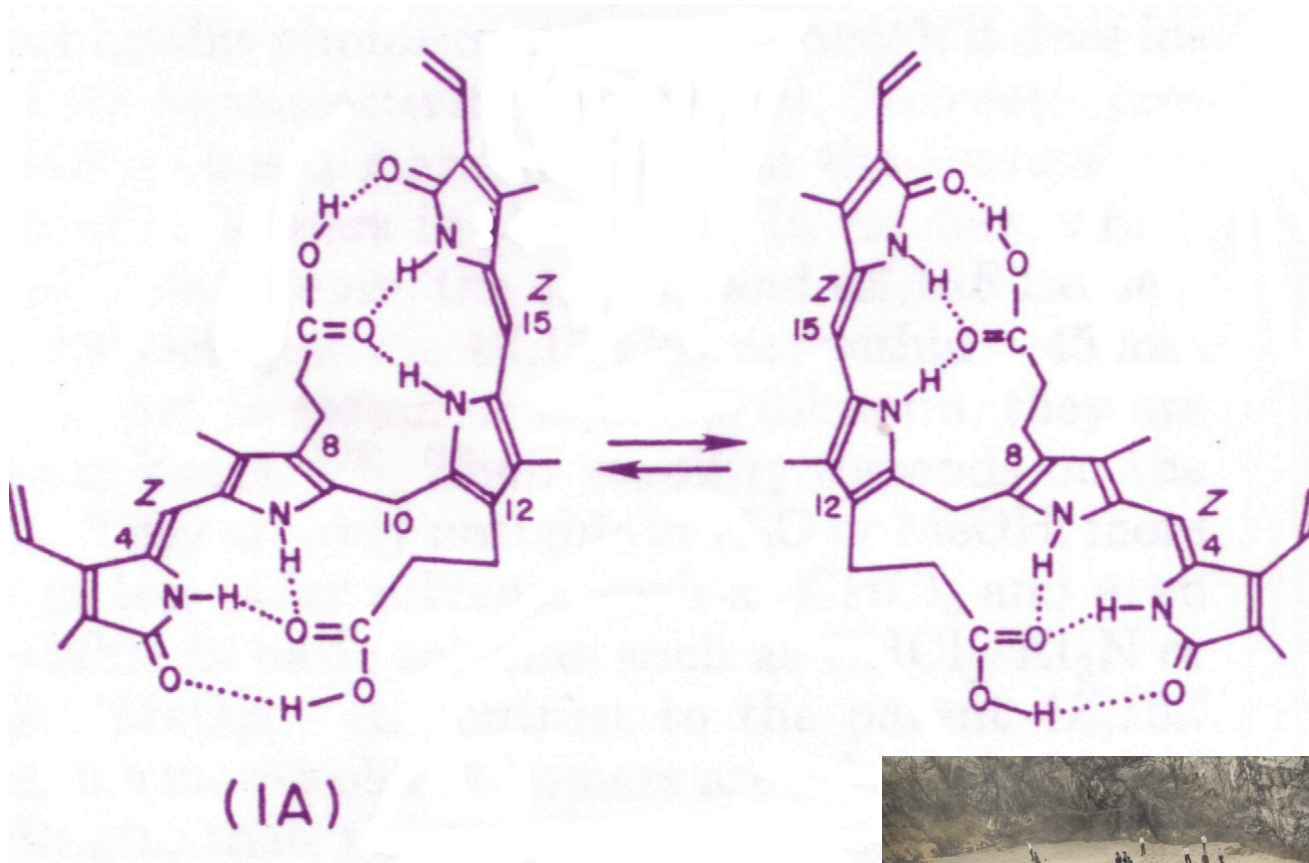
Selectivity 100 %

Rhodopsin function in signal transduction requires conformational changes.

The Nobel Prize in Physiology or Medicine 1967

Ragner Granit, Haldan Hartline and George Wald

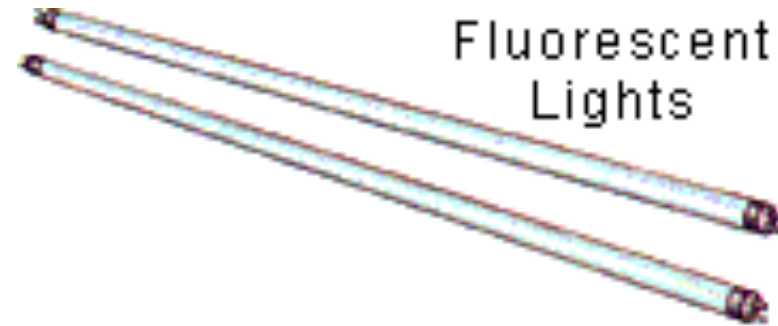
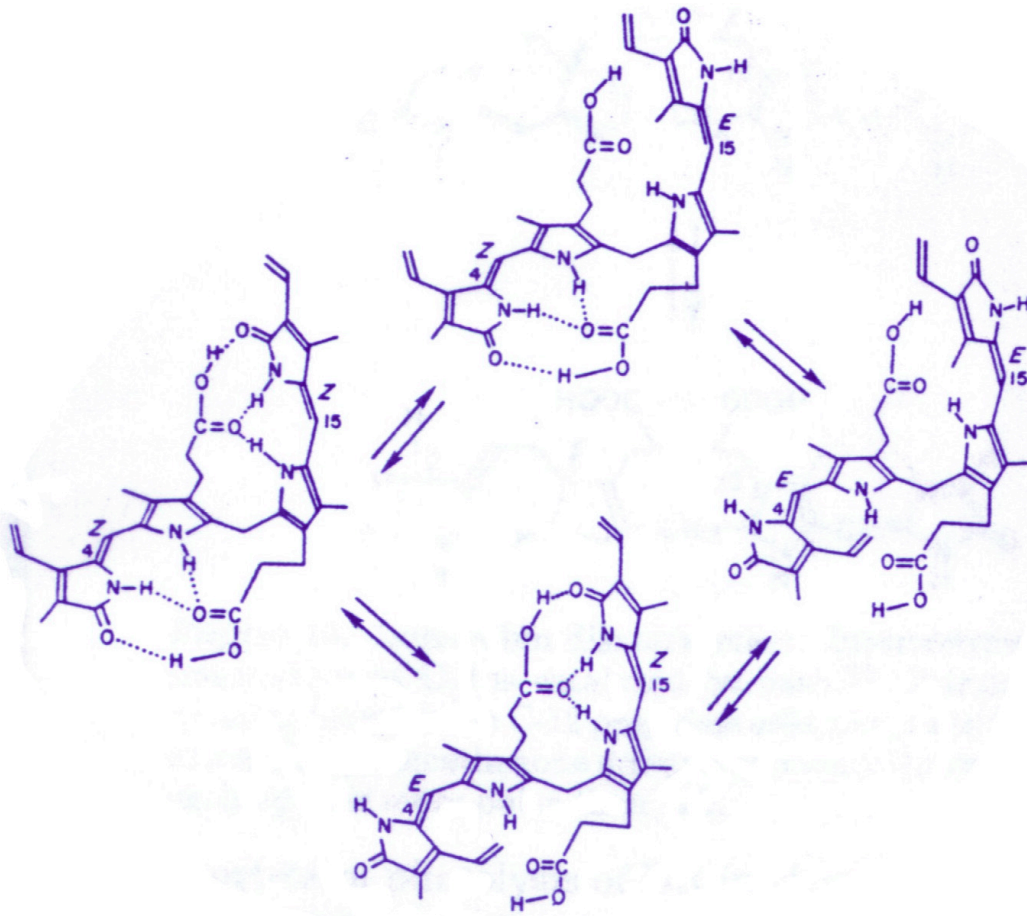
Why bilirubin is lipophilic (hydrophobic) ?



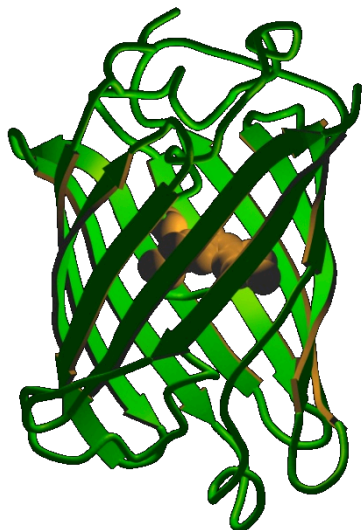
Hydrogen Bond



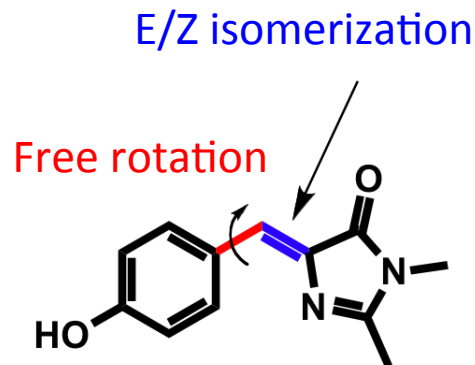
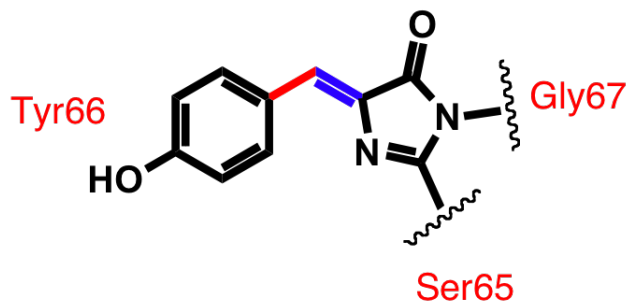
“ light converts bilirubin to a less hydrogen bonded (more water soluble) isomer”



Chemistry within Confined Space



Green Fluorescent Protein (GFP)

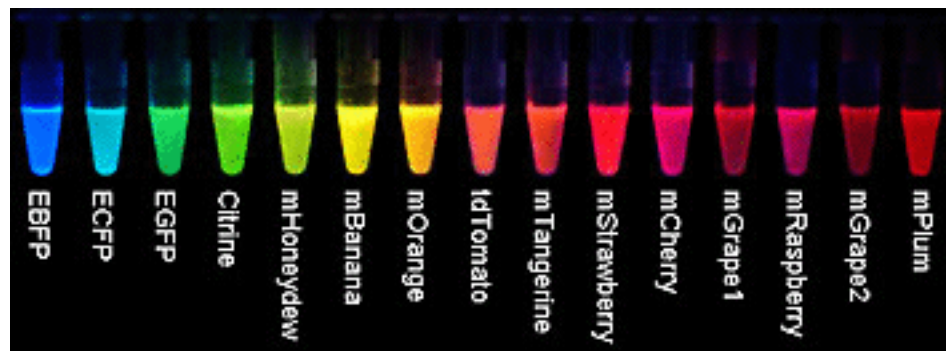


Fluorescence quantum yield 0.70

Tightly packed nature of the barrel structure excludes solvent molecules, protecting the chromophore fluorescence from quenching by water.

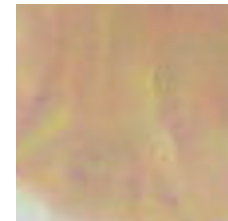
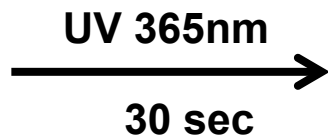
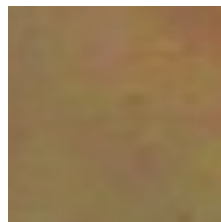
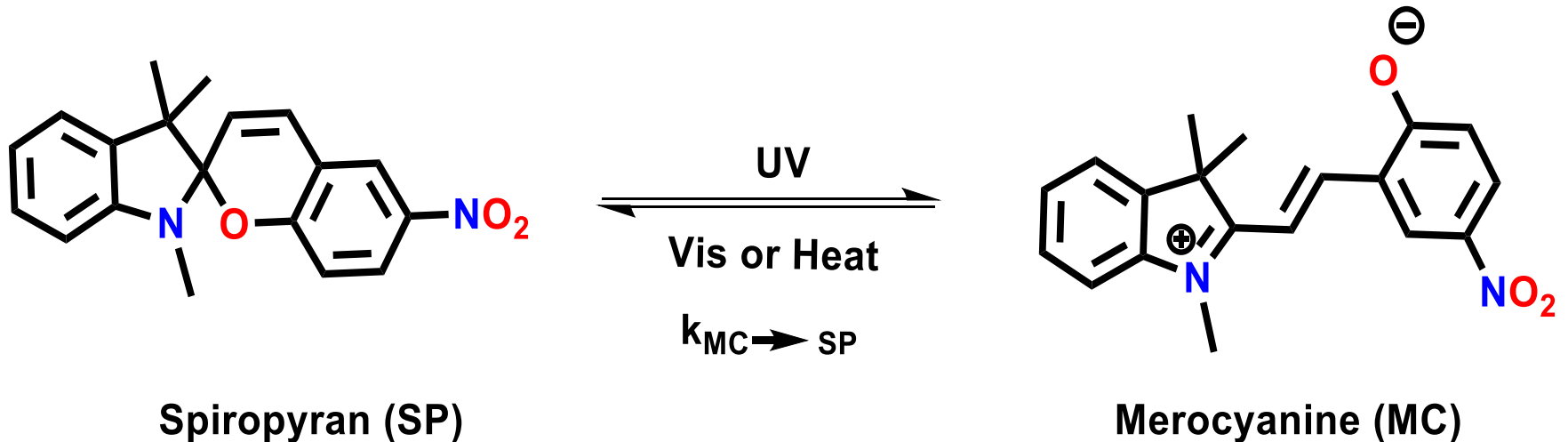
The Nobel Prize in Chemistry 2008

Osamu Shimomura, Martin Chalfie and Roger Tsien

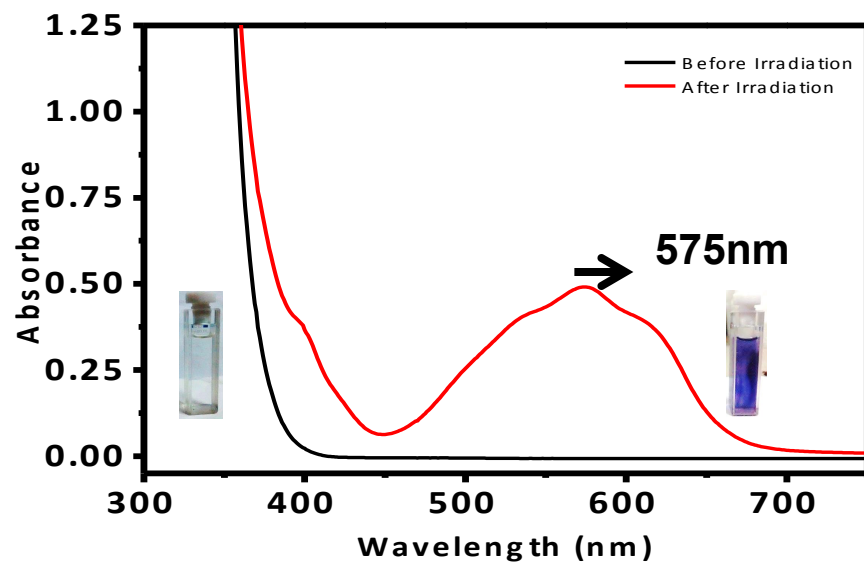


Photochromic molecules

Photochromism is a phenomenon, when molecules change reversibly their structure and absorption spectrum, induced by photochemical radiation.



UV-Vis spectra for Spiropyran in Hexane



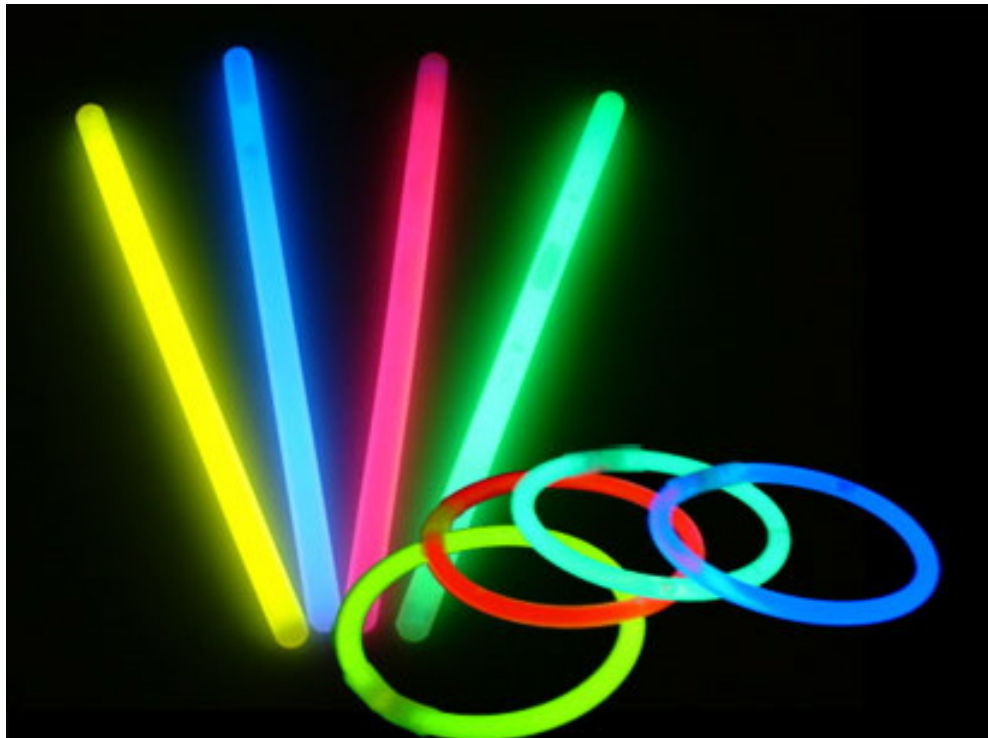


Firefly luciferin

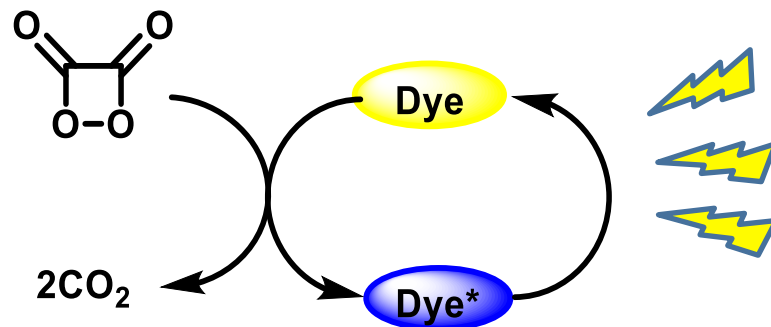
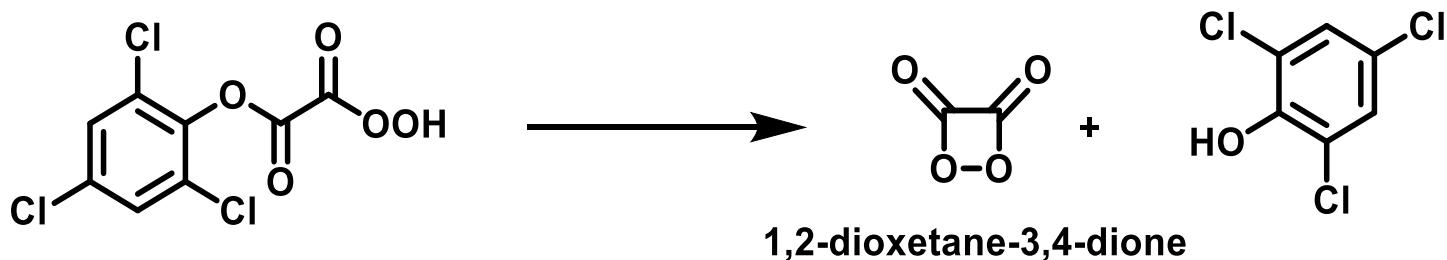
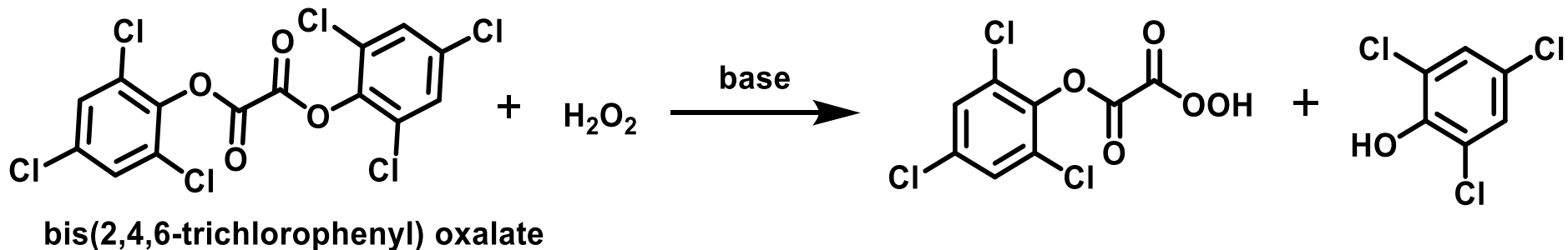


Green Fluorescent Protein (GFP)

Natural chemiluminescence (Bioluminescence)

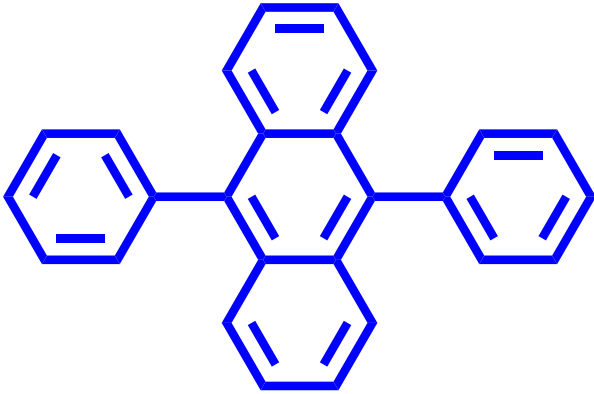


Chemiluminescence

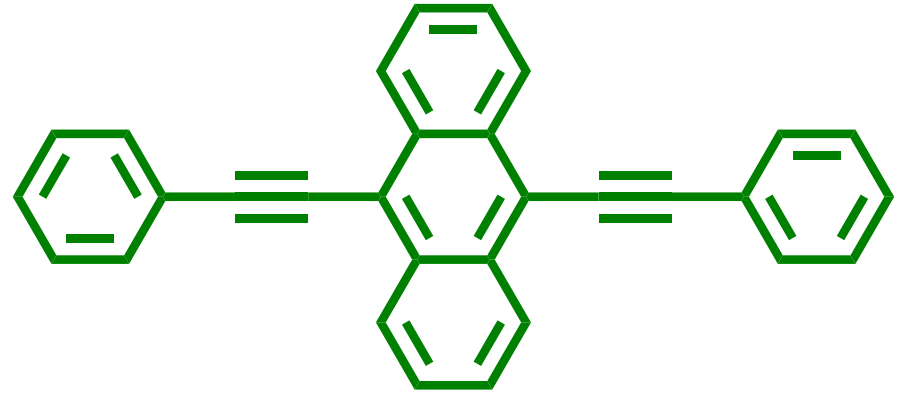


Mechanism inside a glow stick

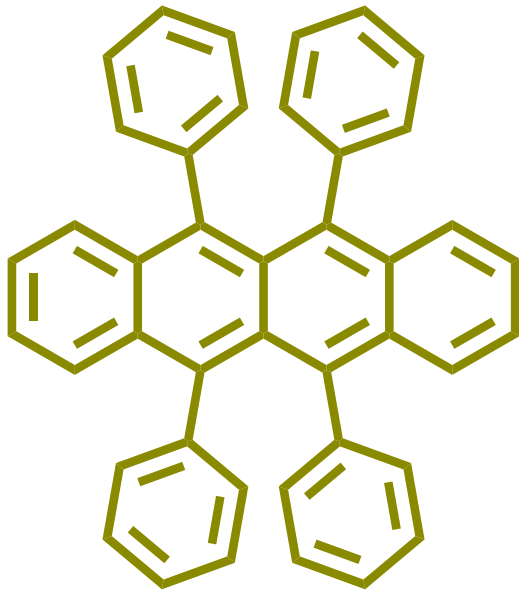
Different dyes emit different color



9,10-Diphenylanthracene (blue)



9,10-bis(phenylethynyl)anthracene (green)



Rubrene (yellow)



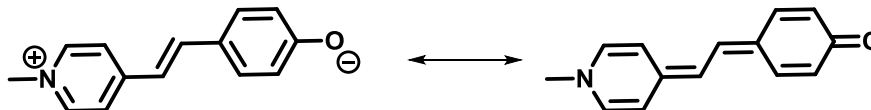
Perylene (Sky blue)

Solvatochromism

- Solvatochromism is the ability of a chemical substance to change color due to a change in **solvent polarity**
- Negative solvatochromism corresponds to hypsochromic shift (or blue shift) with increasing solvent polarity.



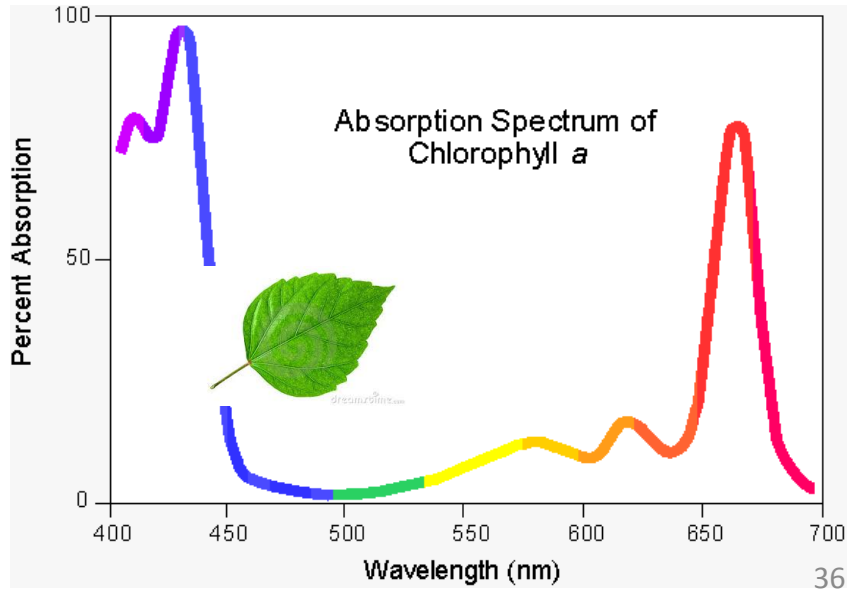
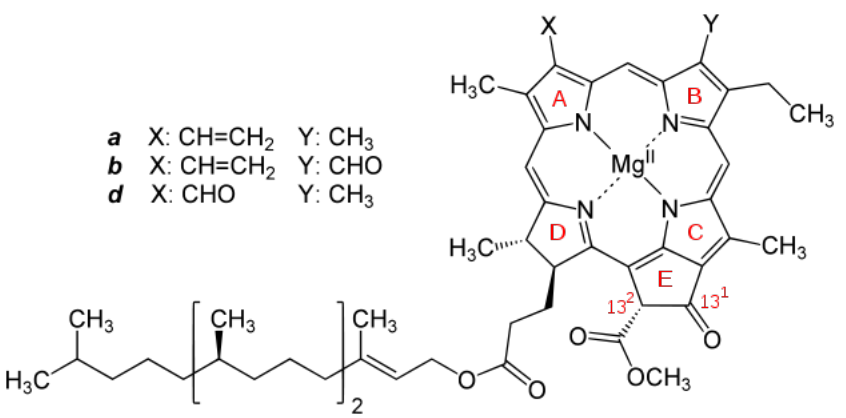
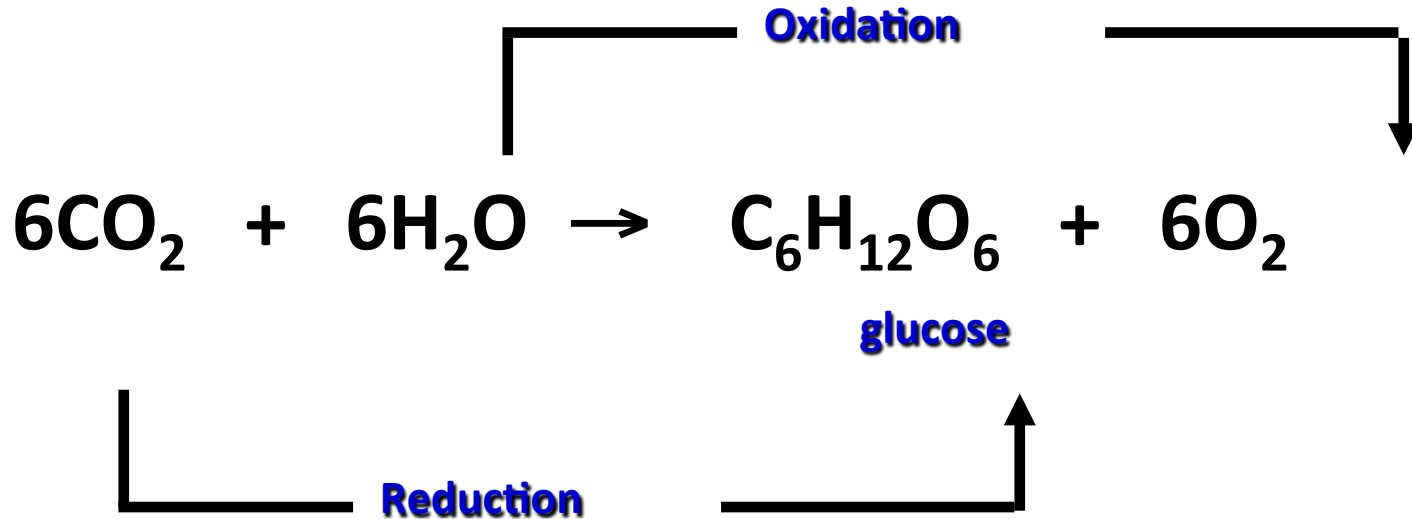
Brooker's merocyanine



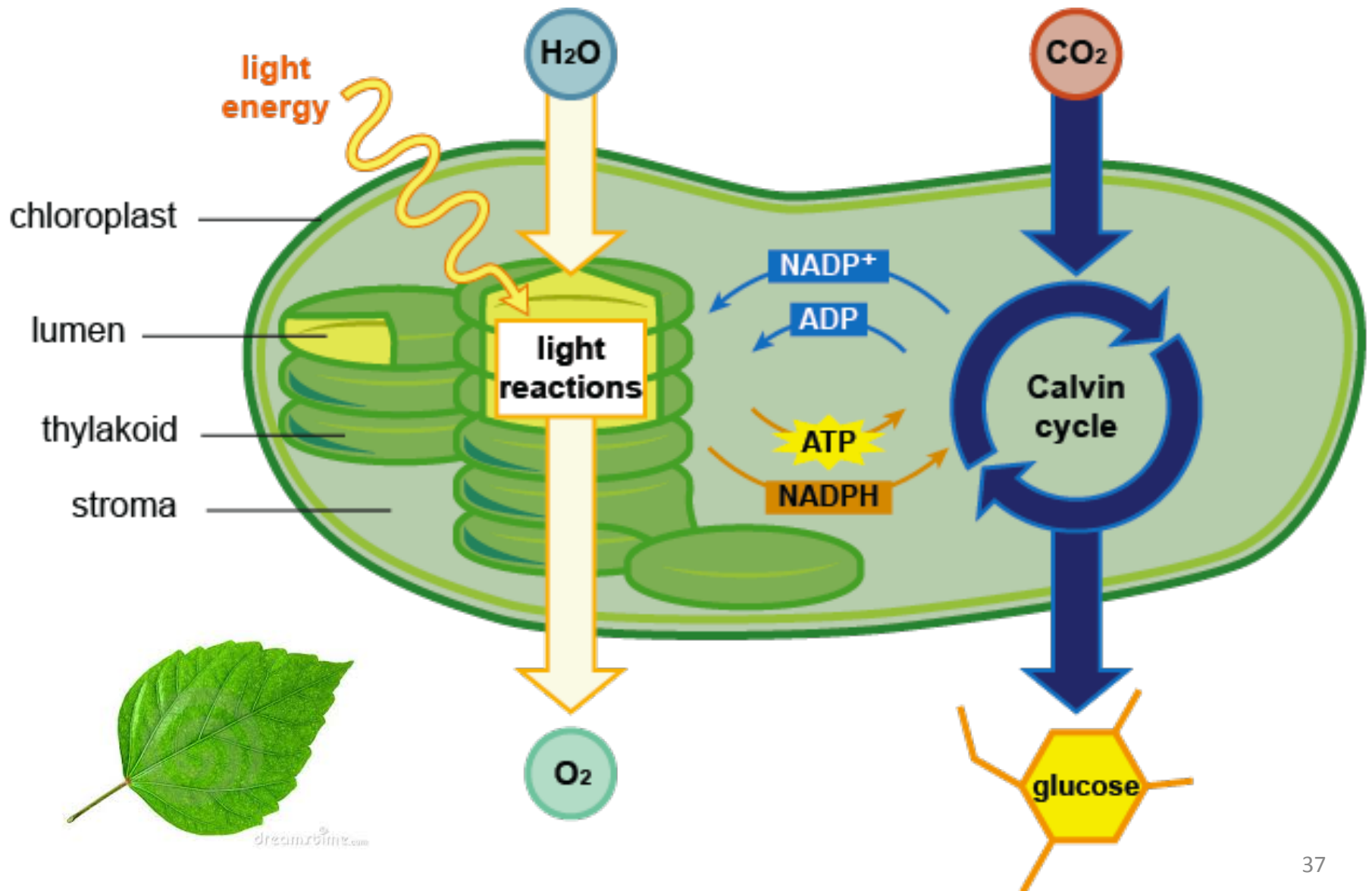
DMSO
 THF
 Methanol
 2-propanol
 Acetonitrile
 DMF
 Water
 Acetic acid
 Ethanol
 Acetone

S.No	Solvent	Dielectric constant
1	Water	80.1
2	Acetonitrile	37.5
3	Ethanol	24.5
4	Acetone	20.7
5	Dichloromethane	8.93

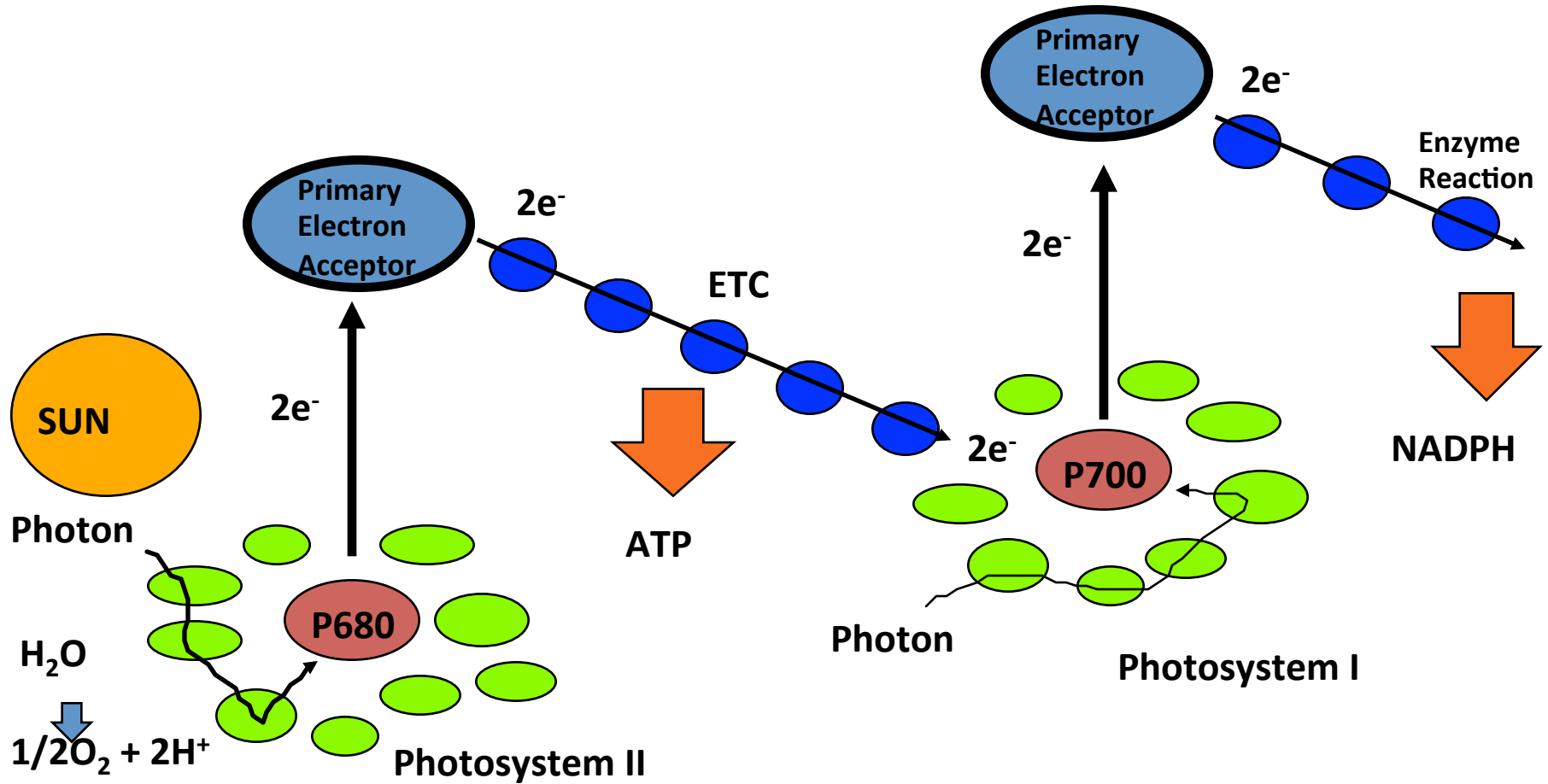
Photosynthesis



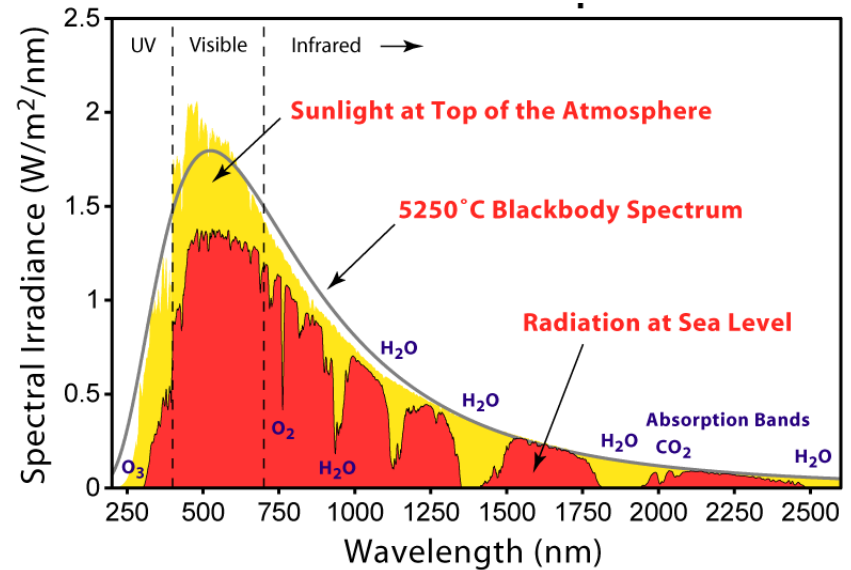
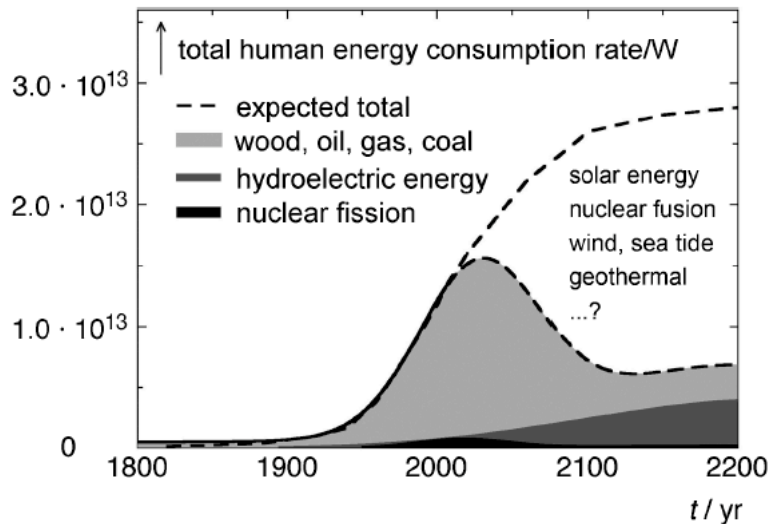
Photosynthesis



Photosynthesis

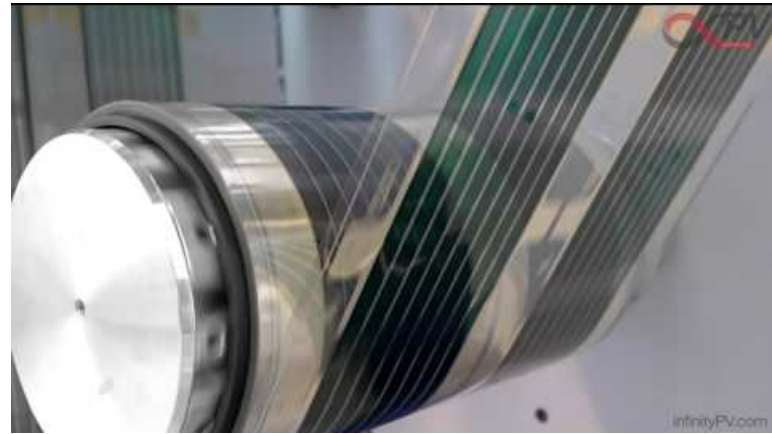
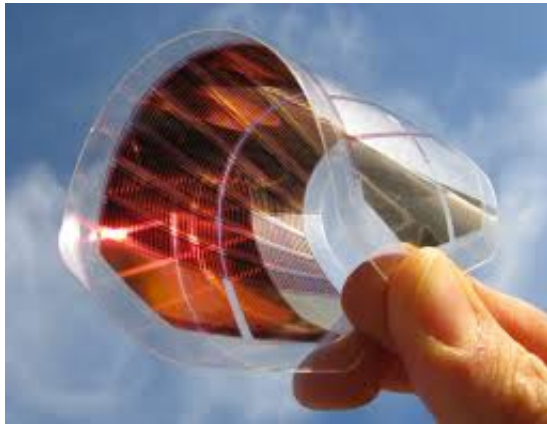


Energy for the Future: Solar Energy

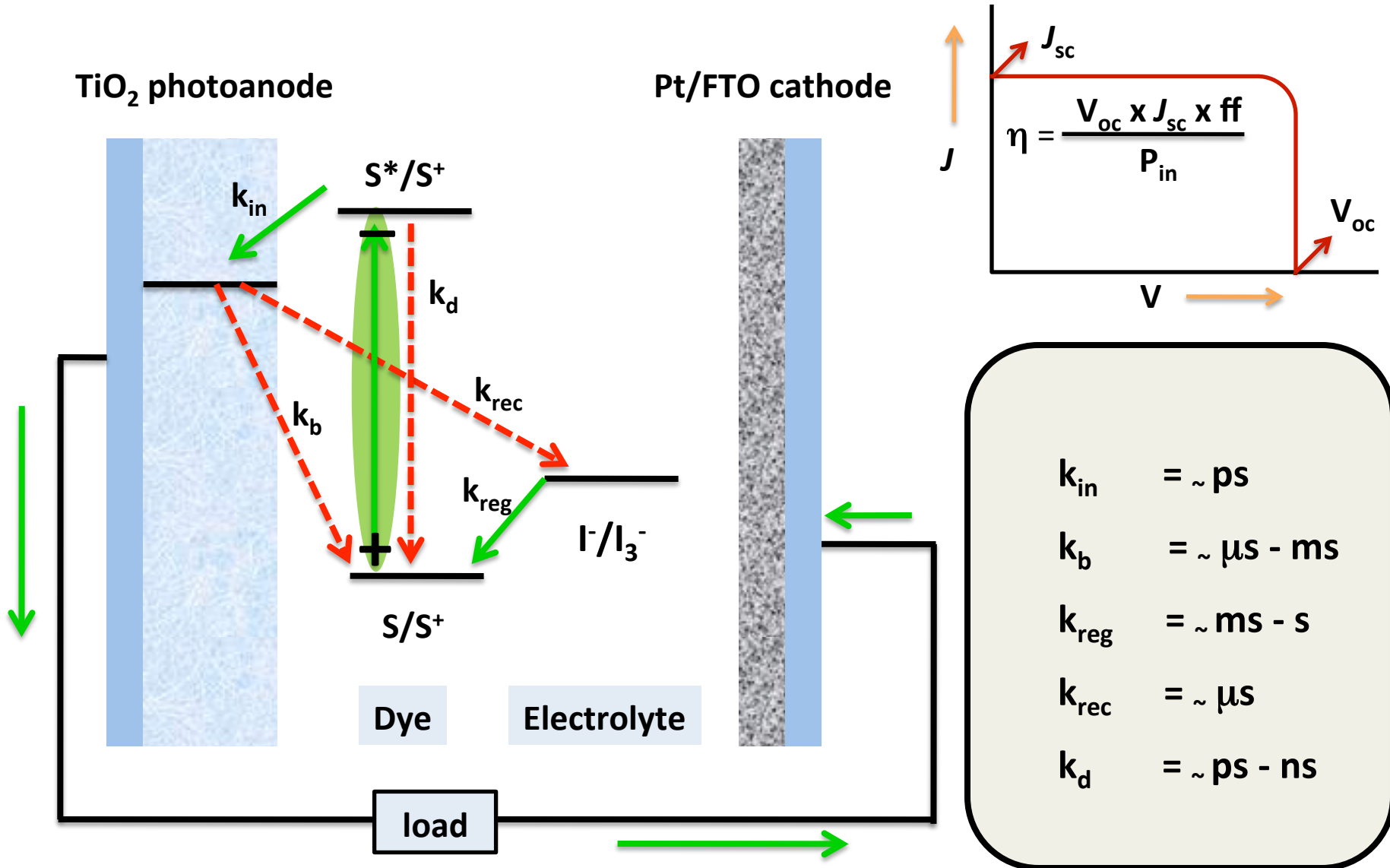


- Solar energy has the largest potential to satisfy the future global need for renewable energy.

- One hour of sunshine (3.8×10^{23} kW) has more than enough to satisfy human demand for energy for an entire year (1.6×10^{10} kW in 2005).



Dye-Sensitized Solar Cells



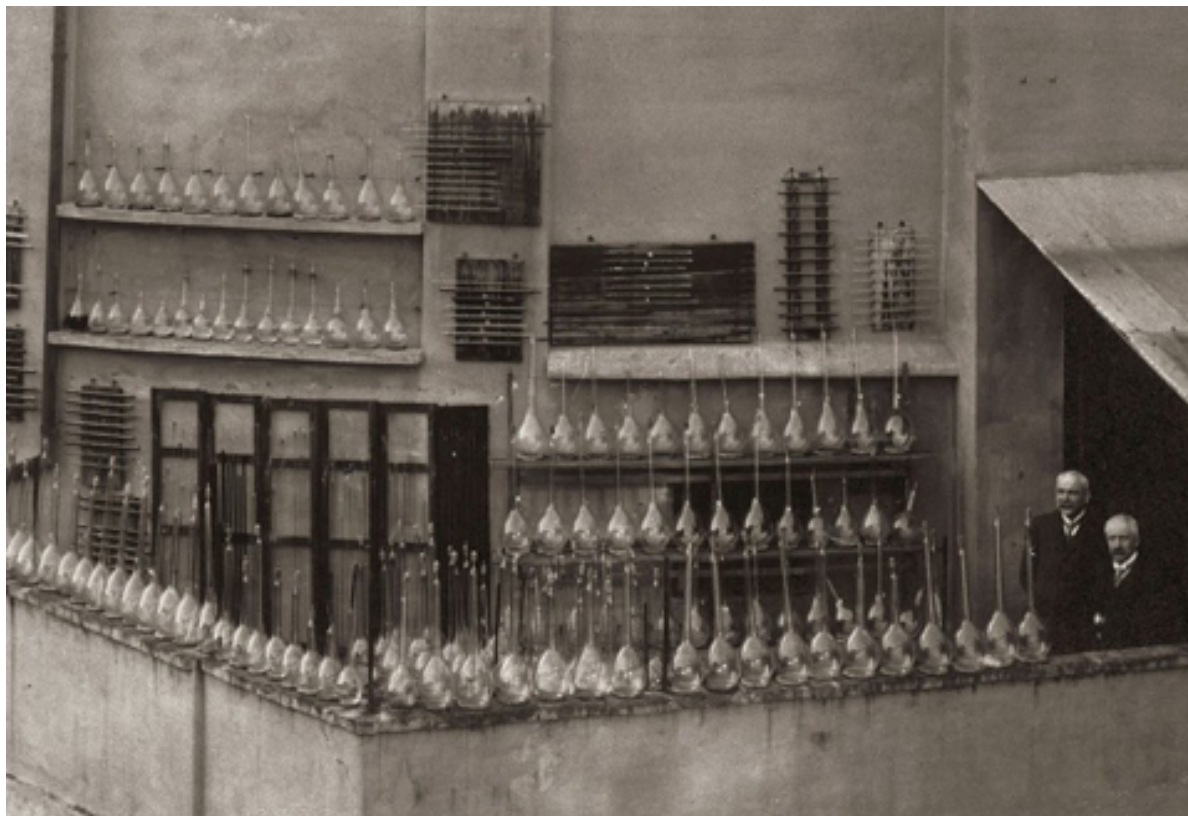
Application of Photochemistry

Photolithography

Photography, Xerography, Photoconductivity

Synthesis of Vitamin D3

Artificial Photosynthesis



G. Ciamician

Giacomo Luigi Ciamician

University of Bologna

...And if in a distant future the supply of coal becomes completely exhausted, civilization will not be checked by that, for life and civilization will continue as long as the sun shines!"

SCIENCE

FRIDAY, SEPTEMBER 27, 1912

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THE PHOTOCHEMISTRY OF THE FUTURE¹

MODERN civilization is the daughter of coal, for this offers to mankind the solar energy in its most concentrated form; that is, in a form in which it has been accumulated in a long series of centuries. Modern man uses it with increasing eagerness and thoughtless prodigality for the conquest of the world and, like the mythical gold of the Rhine, coal is to-day the greatest source of energy and wealth.

Thank you

Mr. Munavvar Fairoos

Mr. Ambarish Kumar Singh

Mr. Rajesh Bisht

Mr. Manik Chandra Sil

Ms. Neeta Karjule

Mr. V. Punitharasu

E-mail: j.nithyanandhan@ncl.res.in

