Molecular and Supramolecular Photochemistry

Instructor:	V. Ramamurthy (murthy)
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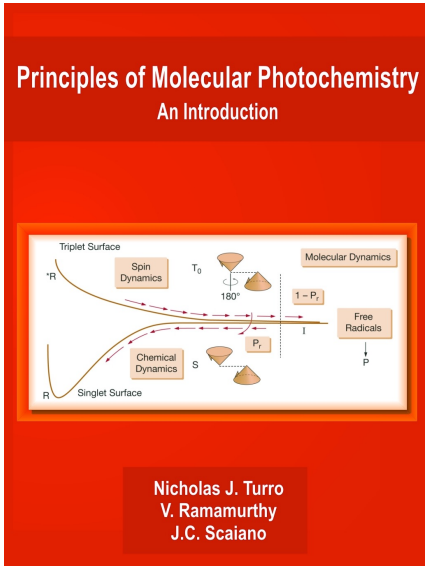
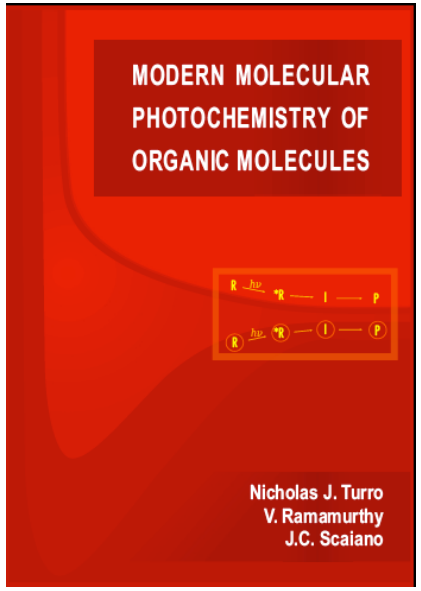
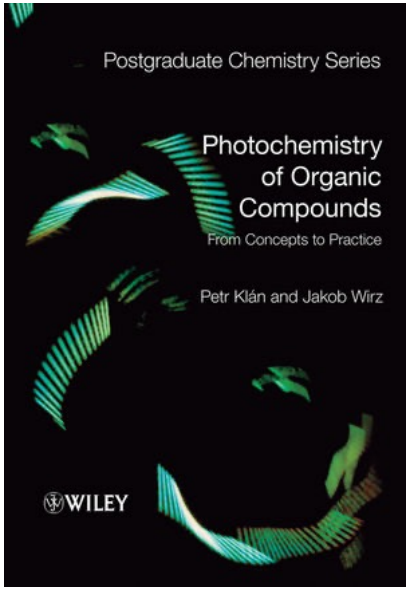
Class timing:	Thursday, 9-11 AM
	Oct 3 to Dec 12

Suggested Textbooks







The first seven chapters of PMP and MMPOM are identical, and this course will cover Ch 1-7

The Approach: "The concepts of photochemistry are described quantitatively and most effectively by the mathematics of quantum mechanics. However, this course (and the text) is directed at students who do not possess the mathematical background necessary for understanding through quantum mechanics. Instead, we will focus on classical representations that are readily visualizable and capture the essence of most of the critical features of quantum mechanics that are needed to understand organic photochemistry."

About this Course

Deals with interaction of Light with Materials, Molecules and in turn Electrons

What is light?

What is a material?

What is a molecule?

What is an electron?

How do light and an electron interact in a molecule?

What are the consequences of such an interaction?

How to control the interaction?

How does Nature utilizes light?

What are the uses of light in our everyday life?

Syllabus

Introduction (Ch. 1)

Why photochemistry?

What is photochemistry?

Molecules: Electronic, Vibrational and Spin States (Ch 2)

Generation of Molecules in electronically excited states (Ch 3 & 4)

Selection rules for spin allowed and spin forbidden transitions, absorption and emission

Deactivation of Molecules: Radiative Transitions, Fluorescence, Phosphorescence, Excimer/exciplex, Delayed fluorescence, TICT emission, Applications of emission

Deactivation of Molecules: Radiationless Transitions (Ch 5)

Mechanism of spin inter-conversion, Spin-orbit coupling, Heavy atom effect; Properties of triplets

Deactivation of Molecules: Energy and Electron Transfer (Ch 7)

Singlet-Singlet ET, Triplet-Triplet ET, Triplet-Triplet annihilation and Singlet fission

Mechanism of electron transfer, Contributions of Weller and Marcus, Long range electron transfer

Role of energy and electron transfer in natural and artificial photosynthesis

Reaction Dynamics (Ch 6)

Grade: Based on a final written examination to be given during the exam period.

Please note 1: I have already scheduled trips to conferences during the semester. Possibly I may miss one or two weeks.

Konark

Suryanar koil

Modhera

Ranakpur

Recognizing the importance of light, SUN- its ultimate source has been worshipped in many ancient cultures.

Only a few have gone beyond to probe its nature.

Light: Prosperity through basic science

Candle lamp
200 BC India

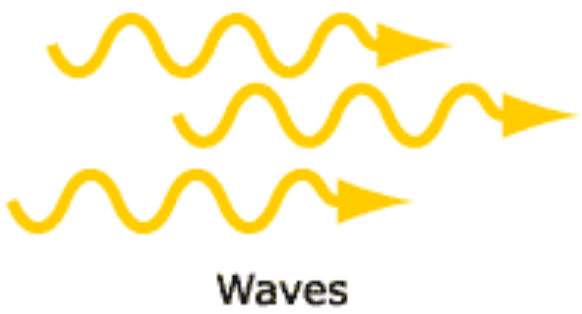
Oil lamp
Humphry Davy

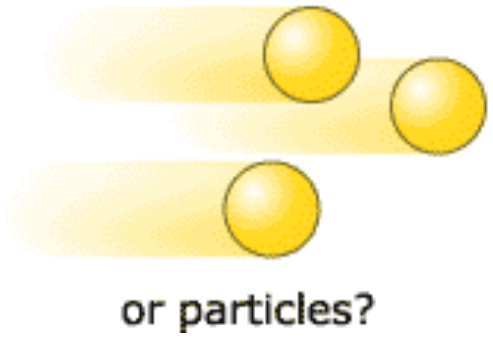
Filament lamp
Thomas Edison

Fluorescent lamp
Edmund Germer1930s

Light emitting diodes (1960s)

Light is both a Wave and a Particle !

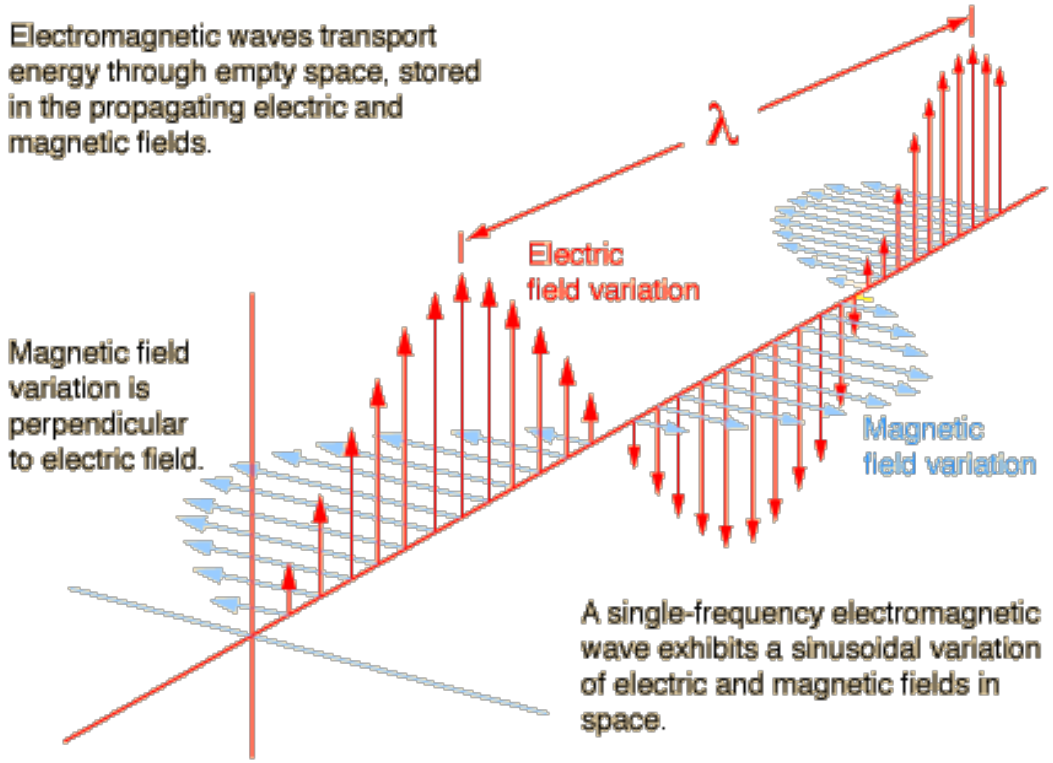




-Light behaves like a wave when it propagates through space

-And as a particle when it interacts with matter

Light is an EM wave



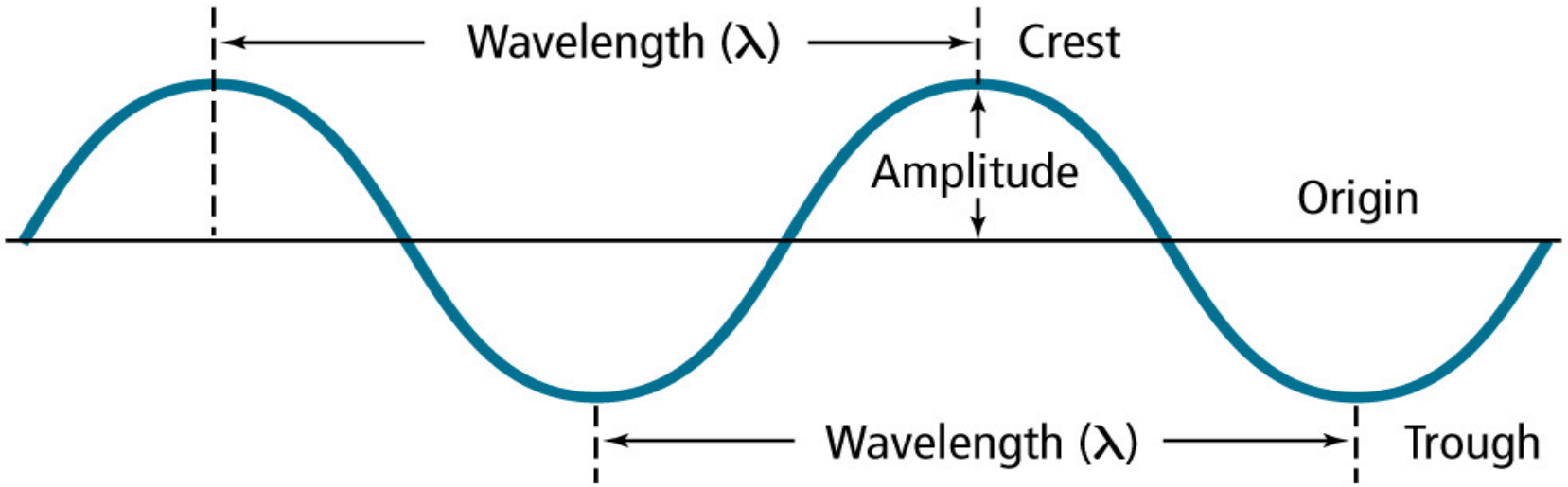
Characterized by:

- **Wavelength (λ)**
- **Amplitude (A)**
- **Frequency (ν)**

$$\nu = \frac{c}{\lambda}$$

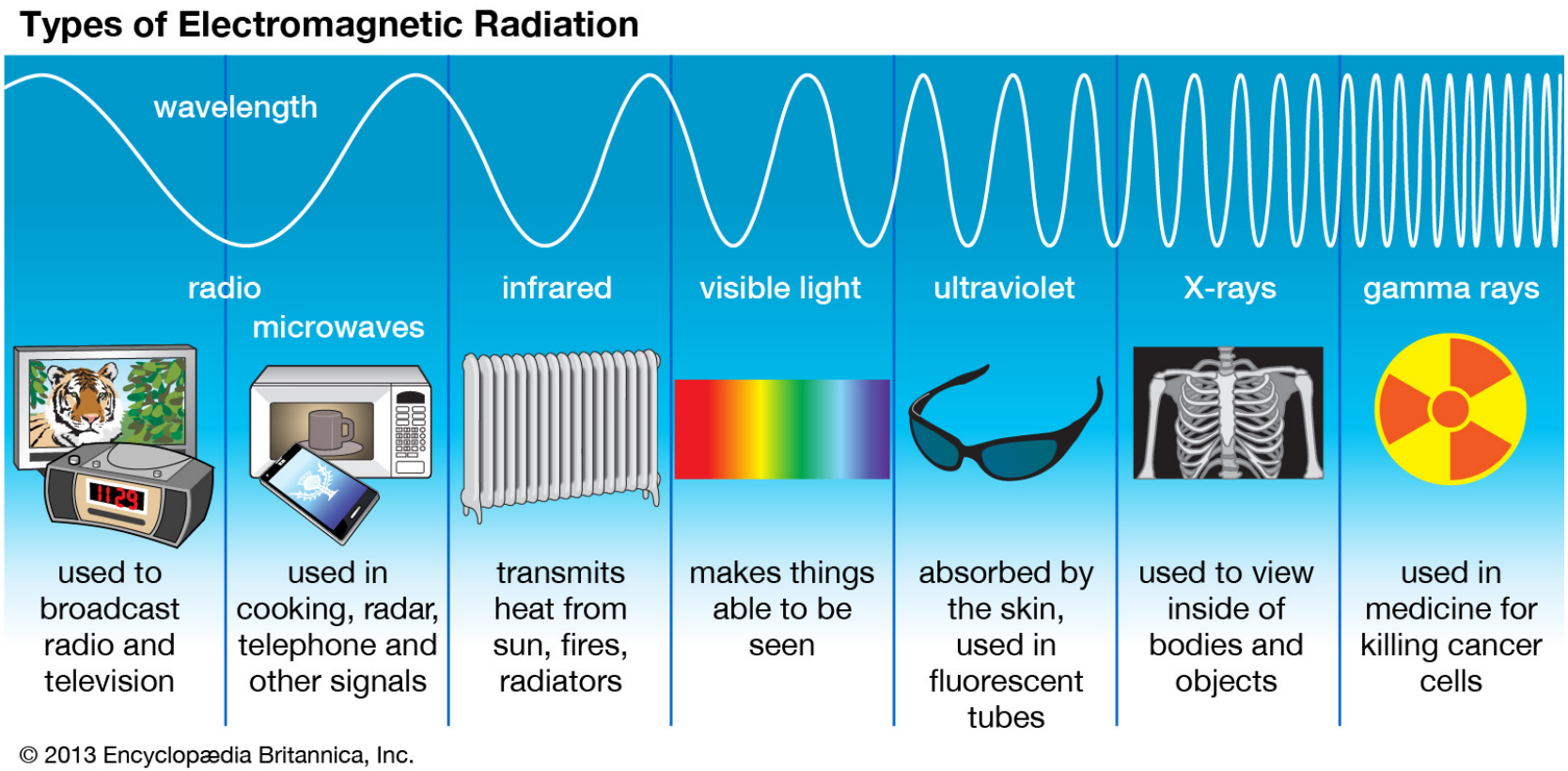
The Wave Nature of Light

– The amplitude is the wave's height from the origin to a crest.



Uses of electromagnetic radiations of different wavelengths

$$\lambda = c/\nu \qquad \nu = c/\lambda$$



Light = Photon

“Light is something like raindrops-each little lump of light is called a photon-and if the light is all one color, all the "raindrops" are the same size.”

Richard P. Feynman
Nobel Prize, 1965

Liquid water is made up of molecules. Amount is measured in terms of mole (M). One mole contains 6.022×10^{23} molecules (Avogadro's number). Weight of one M depends on the weight of the molecule.

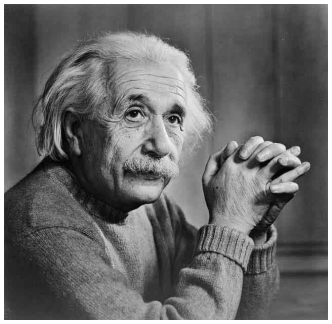
Light is made up of photons. Light is measured in terms of Einstein. One Einstein is the energy in one mole (6.022×10^{23}) of photons. Energy of one E depends on the frequency of photon.

Light in our life

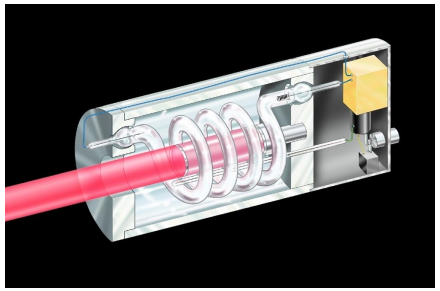
• γ-ray	Medicinal applications (cancer therapy)
• X-ray	Medicinal applications
• Ultraviolet	Lithographic, medical/dental, hygienic/killing bacteria
• Visible light	Fiber optic communications, TV & computer screens, medical, lithographic, photography
• Infrared	Heating devices, night vision goggles, remote controls
• Microwave	Cooking, Cell phones, remote sensing, army
• Radiowave	Radios, TV, mobile phones, computer networks

LASER Invention and Innovation

(Light Amplification by the Stimulated Emission of Radiation)



1917: Albert Einstein derives the theoretical basis for the laser.



1960: The first working (ruby) laser.

Nicolay G. Basov

Charles H. Townes

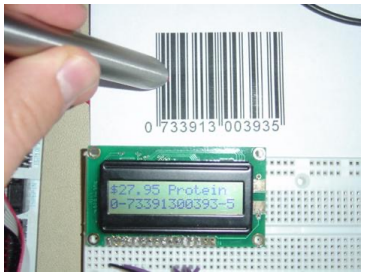
Aleksandr M. Prokhorov

The Nobel Prize in Physics 1964

"for fundamental work in the field of quantum electronics, which has led to the construction of oscillators and amplifiers based on the maser-laser principle."

Laser Applications

1965: The compact laser disc (CD) invented.

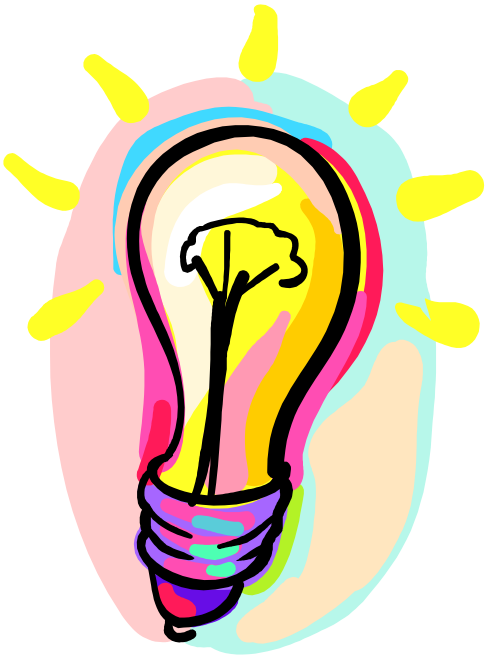


1974: A laser-driven barcode scanner used for the first time.

- **Medical**
- **Metallurgical**
- **Electronic and computer**
- **Military**
- **Communications**
- **Microscopy**
- **Metrological**
- **Entertainment industry**

The world market for laser technology is now over $ 16.7 billion a year (2022)

Light and Life



- Photomedicine
- Lithography
- TiO_2: Environmental Cleanup
- Solar Energy Conversion
- Industrial Synthesis of Chemicals
- Photography, Xeorography and Holography
- Sunscreen, Photochromic Glass
- Photostabilization
- Photocuring

Niels Ryberg Finsen

Finsen Medical Light Institute, Copenhagen, Denmark

The Nobel Prize in Physiology or Medicine, 1903

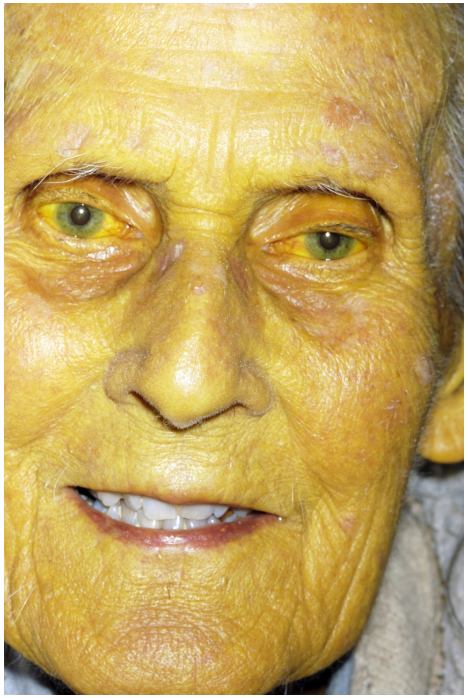
Prize motivation: "in recognition of his contribution to the treatment of diseases, especially lupus vulgaris, with concentrated light radiation, whereby he has opened a new avenue for medical science."

For a time, light therapy was widespread, but eventually it was supplanted by antibiotics.

Photomedicine

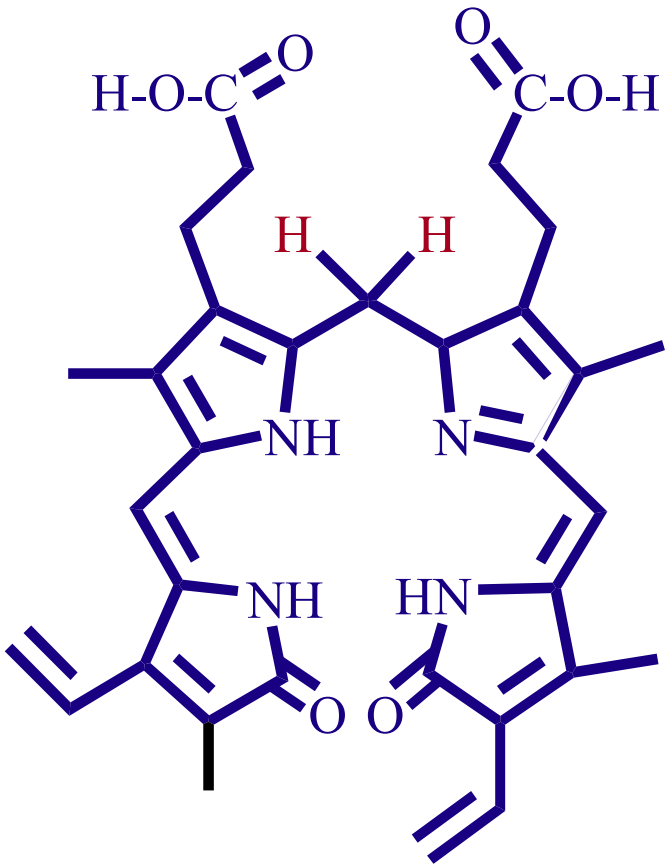
- Phototherapy - Jaundice treatment
- PUVA therapy - Skin disorders, Blood cancer
- Photodynamic therapy - Cancer
- Lasik surgery - Vision correction

Jaundice



Phototherapy for Neonatal Jaundice Treatment

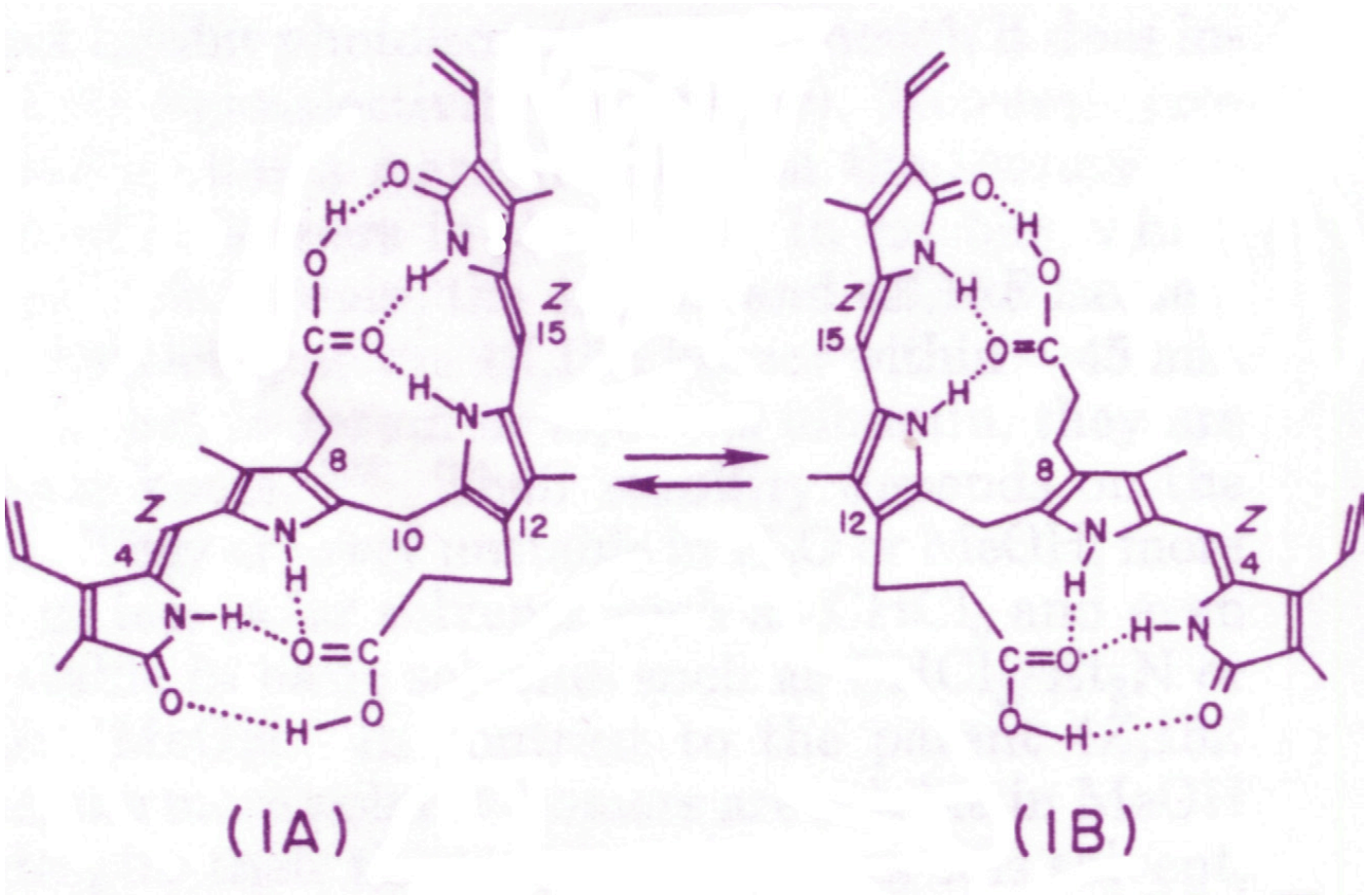
- Accumulation of the potentially toxic yellow liphophilic bilirubin in human serum leads to Jaundice.
- If the percentage of bilirubin increases to 15-25 mg/100 ml, it will lead to hyperbilirubinemia.
- Severe hyperbilirubinemia cases, sufficient pigment may partition into the brain to cause irreversible damage, even death.



Bilirubin

McDonagh etal., *Science*, 208, 1980, 145-151.

Why bilirubin is lipophilic (hydrophobic) ?



Natural Cure for Jaundice

Different ways to cure jaundice

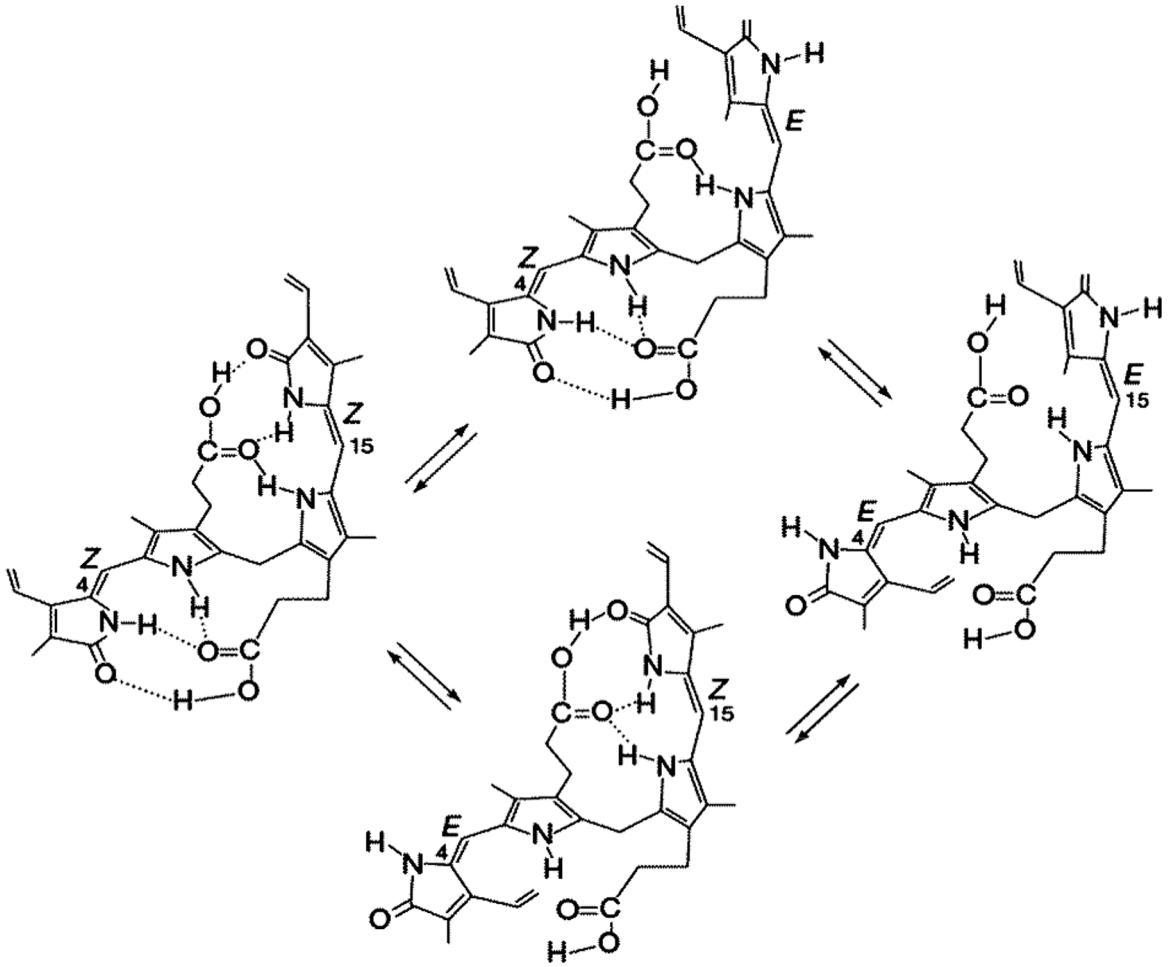
- Wait till liver matures soon enough to clear bilirubin unaided.
- Exchange transfusion: blood along with threatening pigment drained and replaced with clean blood.
- Phototherapy - irradiate the baby with light.

Discovery of phototherapy

The discovery of phototherapy stems from the observations of Sister J. Ward, a nurse in U.K.

Evening walk with hyperbilirubinemia patients - lead to discovery of phototherapy by scientists.

Phototherapy - Jaundice Treatment



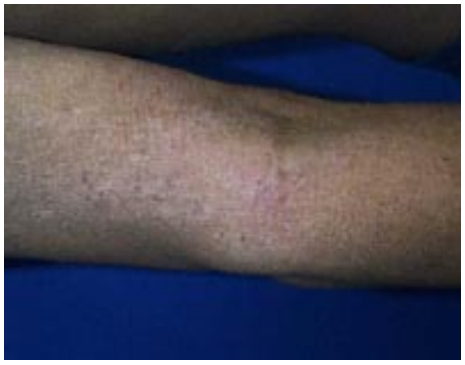
“light converts bilirubin to a less hydrogen bonded (more water soluble) isomer”

Skin Disorders

Psoriasis

Polymorphic light eruption

Vitiligo

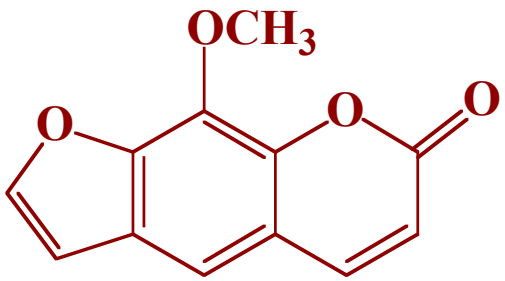


Acute dermatitis

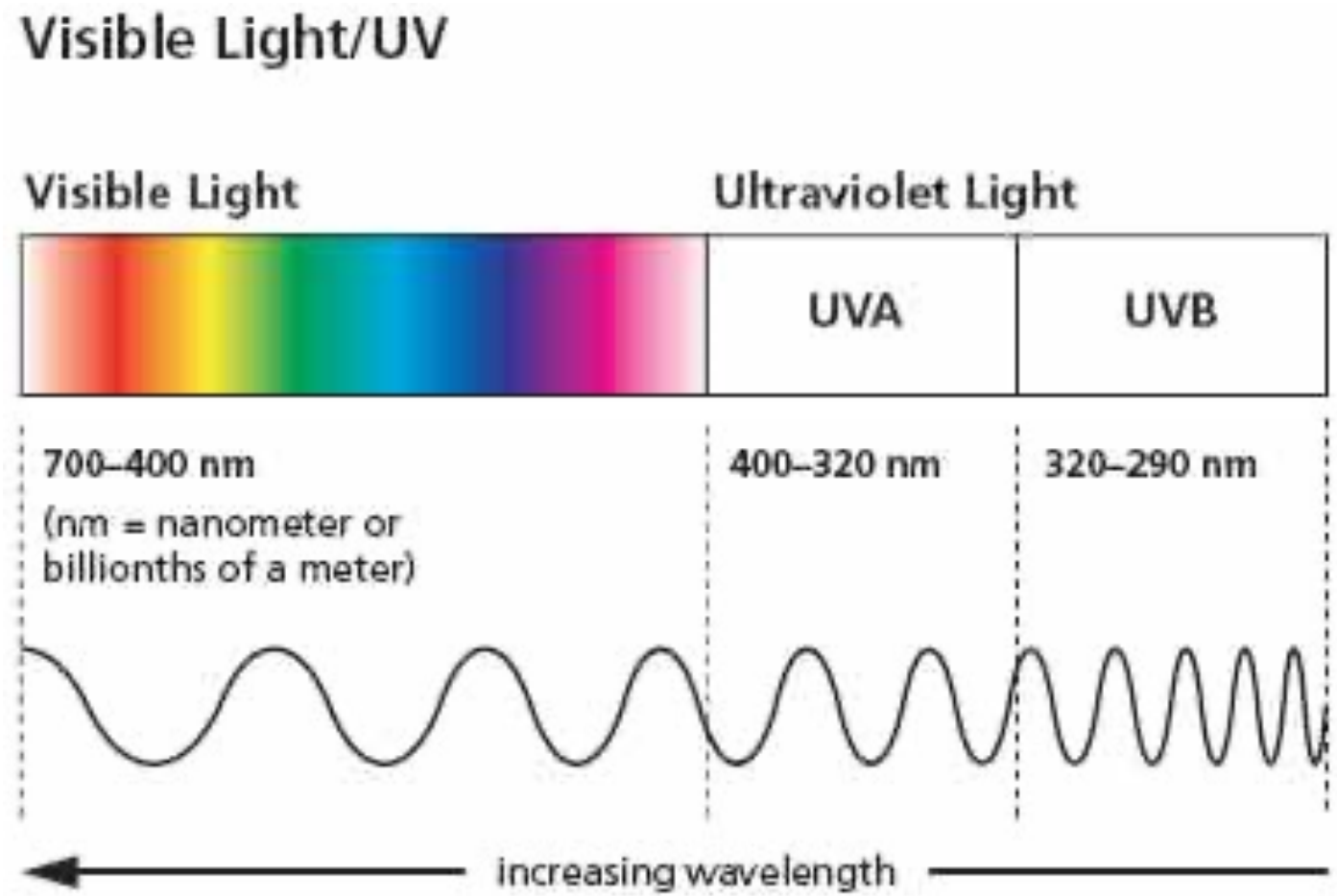
PUVA- therapy

- Egyptians and Asian Indians practiced this therapy centuries ago.
- Boiled extracts of fruits of plants *Ammi majus* in Egypt and *Psoralea Corylifolia* L in India plus sunlight cured vitiligo.
- In 1988, PUVA was the first FDA (Food and Drug Administration) approved selective immunotherapy for skin disorders including cancer.

Psoralen + UVA = PUVA therapy



What is UV-A light?

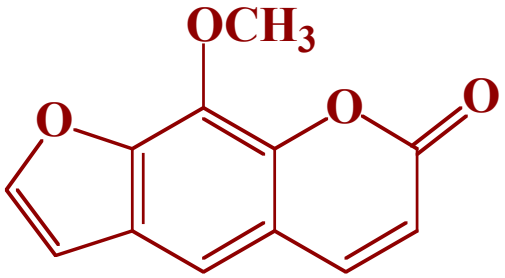


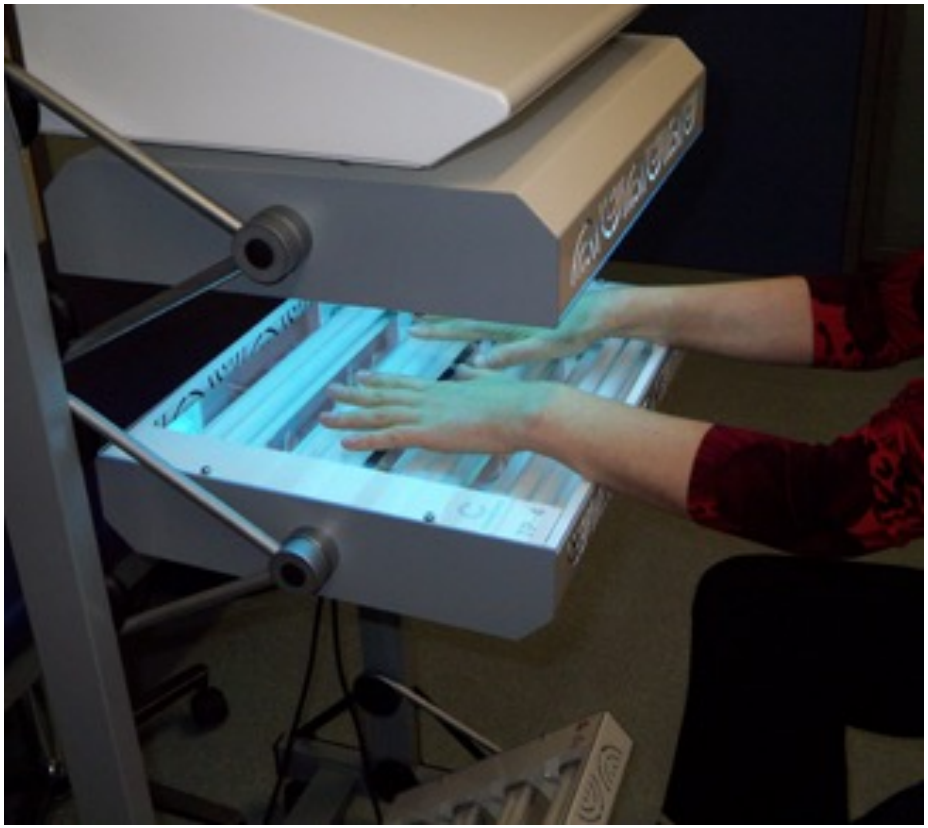
How PUVA therapy is done ?

- Methoxsalen capsules are taken two hours before exposure to UVA.
- Bath PUVA: hands and/or feet are soaked in a dilute solution of methoxsalen for 30 minutes, then exposed to UVA.
- A few patients may be treated with topical tripsor PUVA - a lotion is applied on the affected areas 10 minutes before UVA exposure.

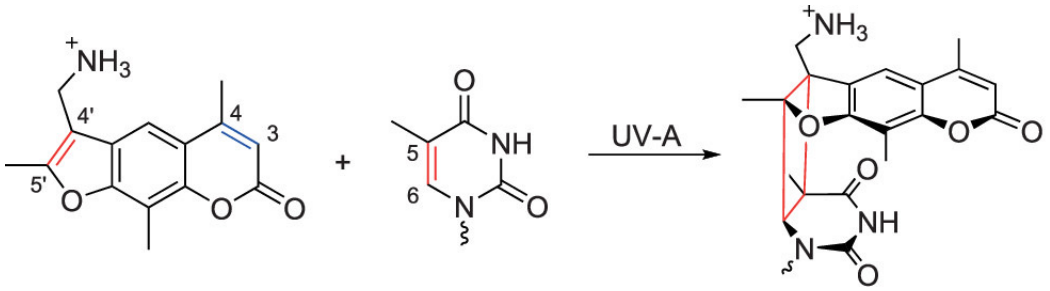
PUVA therapy

Psoralen + Ultraviolet A = PUVA

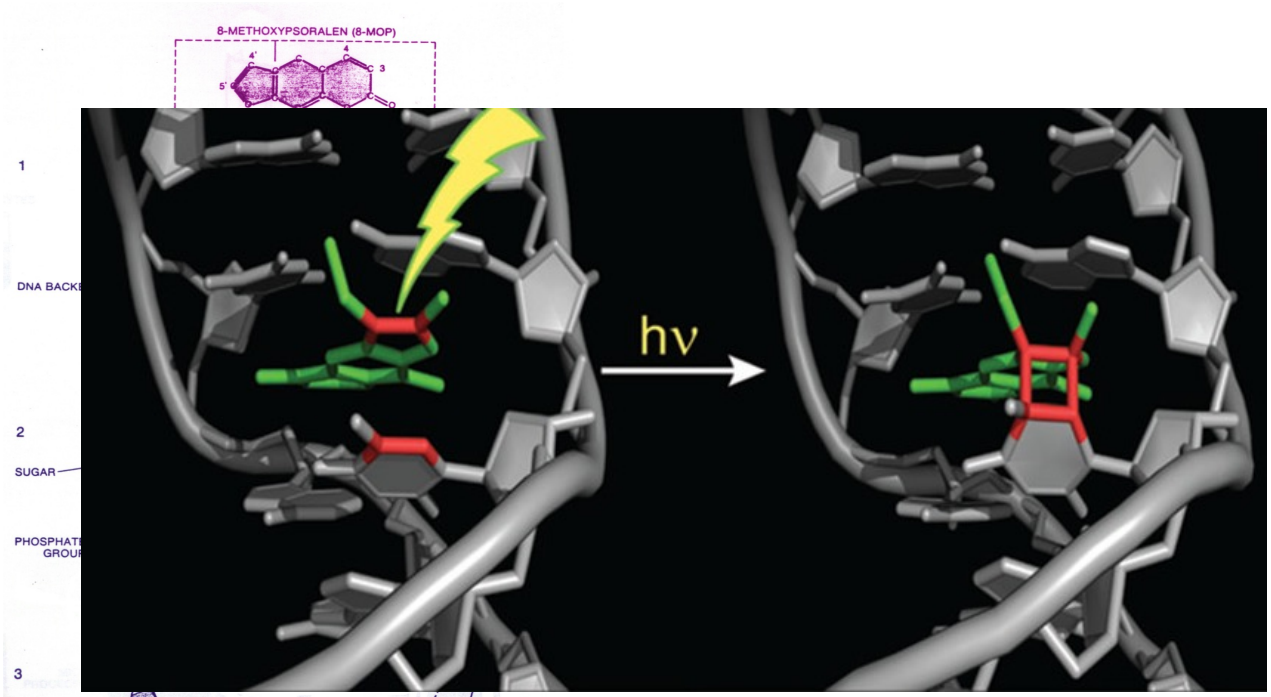




Photoadduct representation with DNA



AMT Thymine base (T) Photo-adduct (AMT=T)

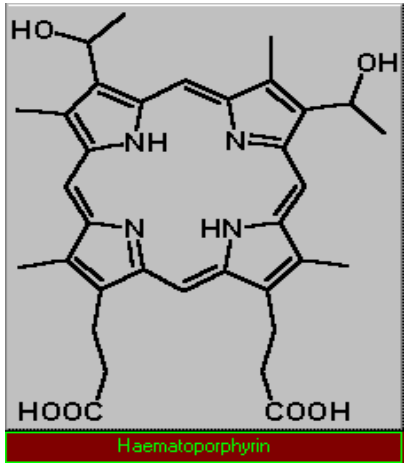


adduct(3, 4 and 4', 5' with pyrimidine bases)

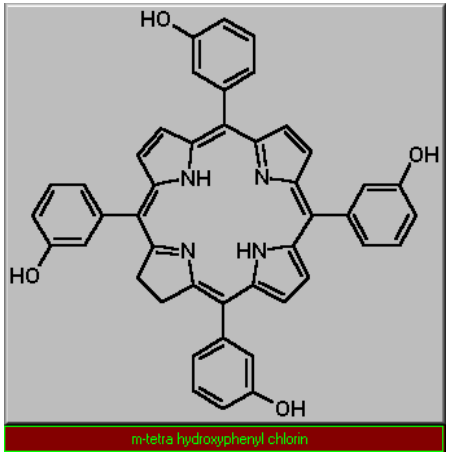
Photodynamic therapy

- Photodynamic therapy first used in 1978.
- Currently several photodynamic drugs are available on the market.
- Approved for the treatment of esophageal and lung cancers.

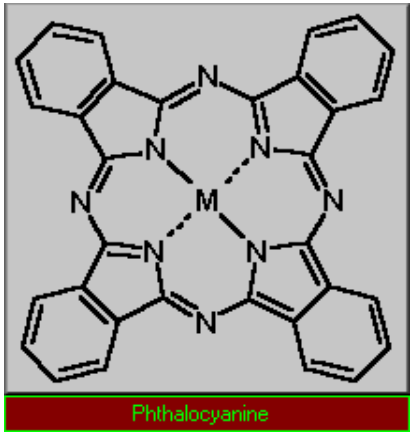
Porphyrins



Chlorins

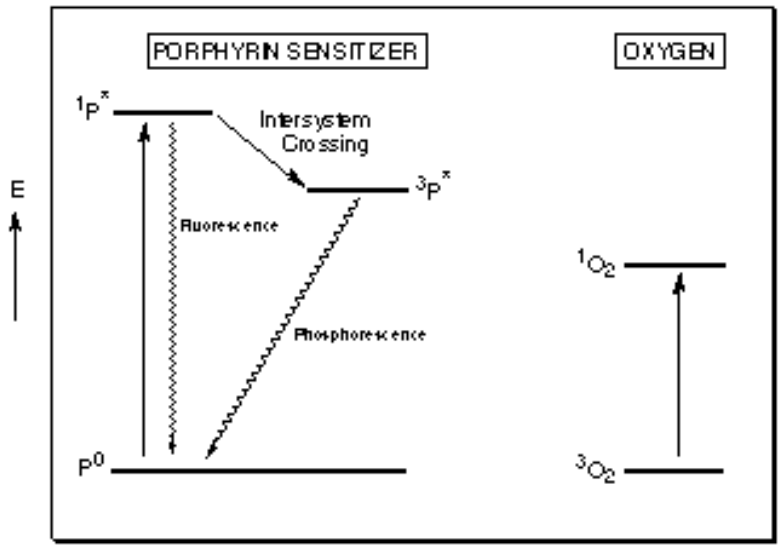


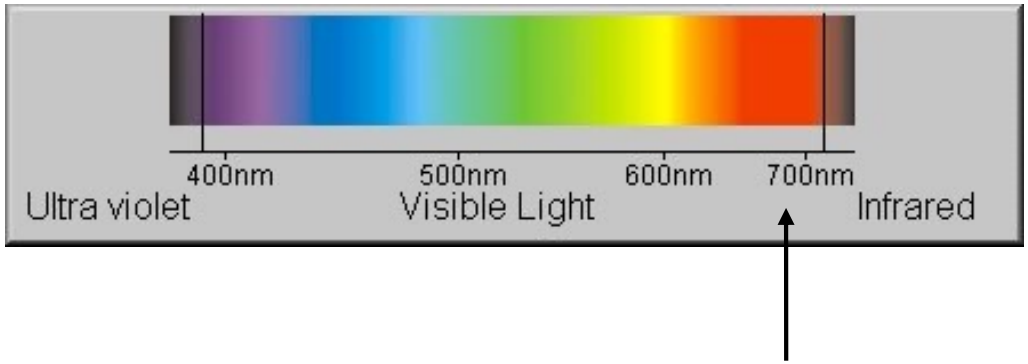
Phthalocyanines



How does photodynamic therapy work?

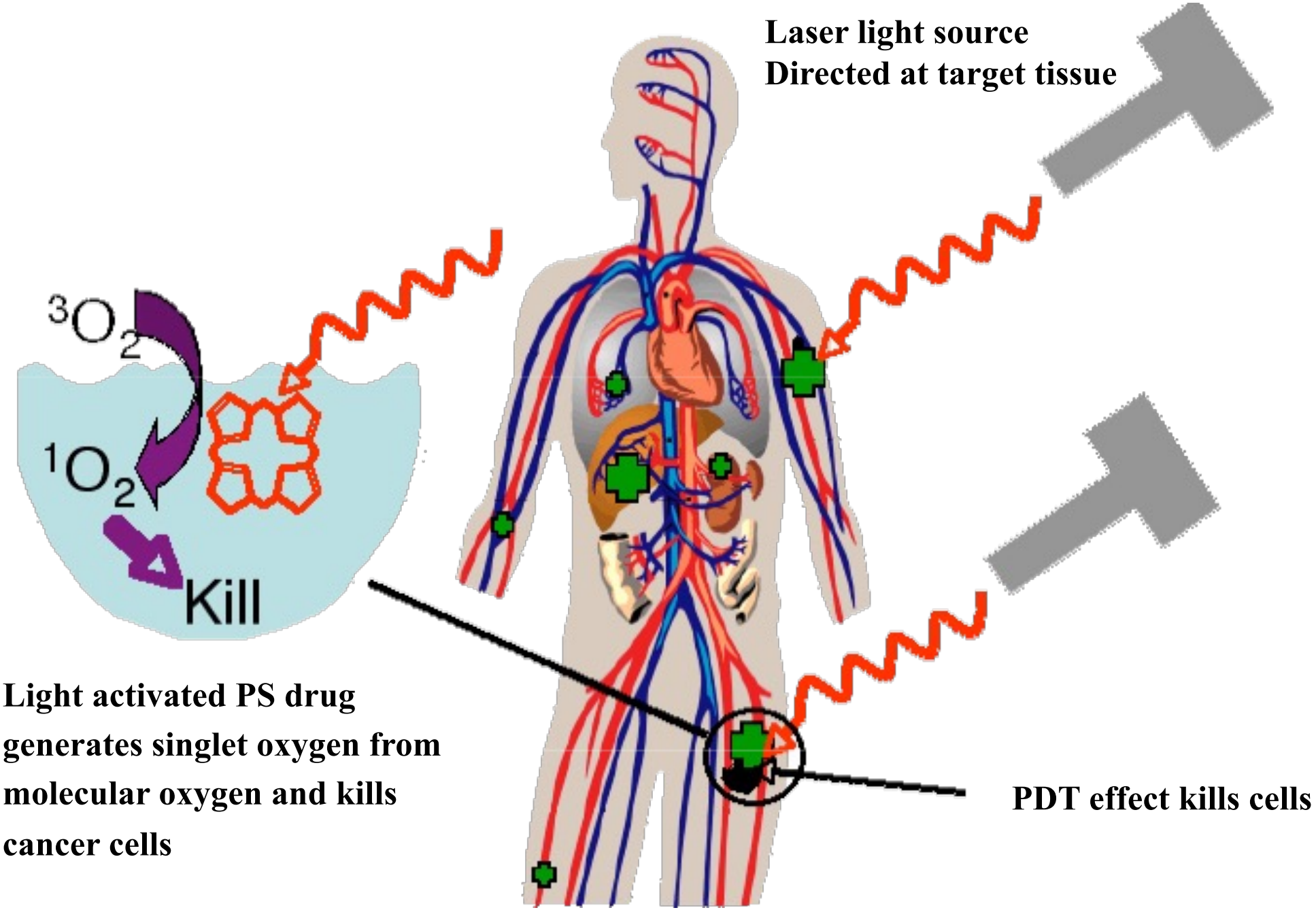
- PDT requires sensitizer, light and oxygen in the target tissue.
- Light generates reactive oxygen species.
- Reactive oxygen species can kill targeted cells either by necrotic mechanisms or by initiating the apoptotic cascade.





Ideal wavelength 650nm

Photodynamic therapy



Lithography to Lasik Surgery

R. Srinivasan

S. Blum

J. Wyne

1981: Discovery of laser ablation technique.

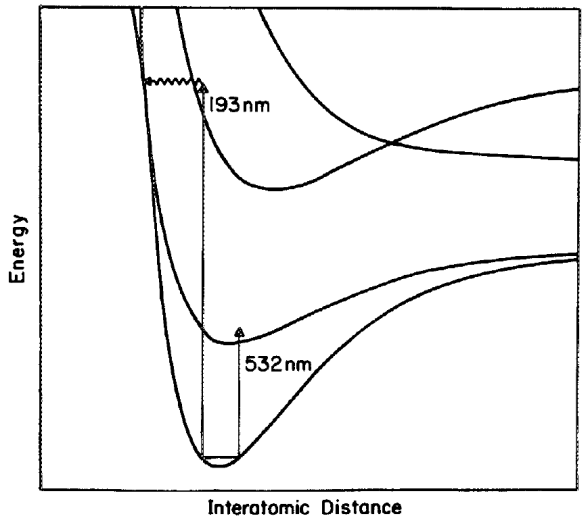
1995: US FDA approval of human Lasik surgery.

2002: Inducted into US Inventors Hall of Fame.

National Medal of Technology and Innovation (2011)

For the pioneering discovery of excimer laser ablative photodecomposition of human and animal tissue, laying the foundation for PRK and LASIK, laser refractive surgical techniques that have revolutionized vision enhancement.

Lithography to Lasik Surgery



R. Srinivasan and W. Leigh, *J. Am. Chem. Soc.*, *104*, 6784, **1982**.

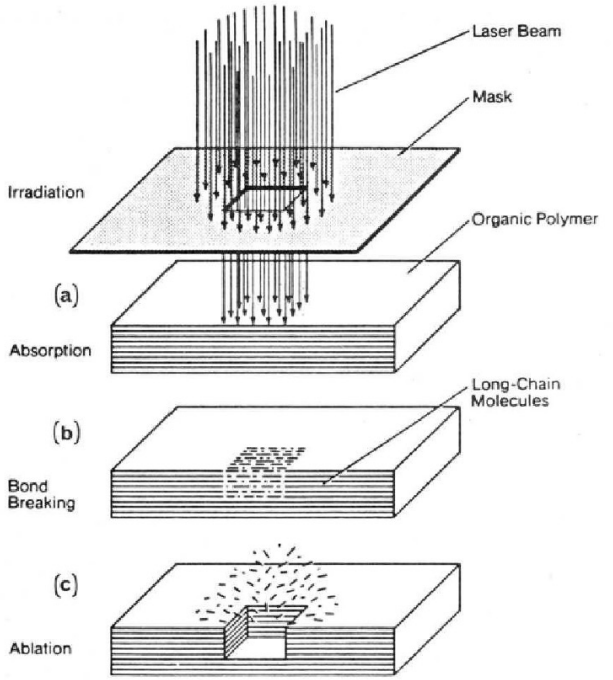
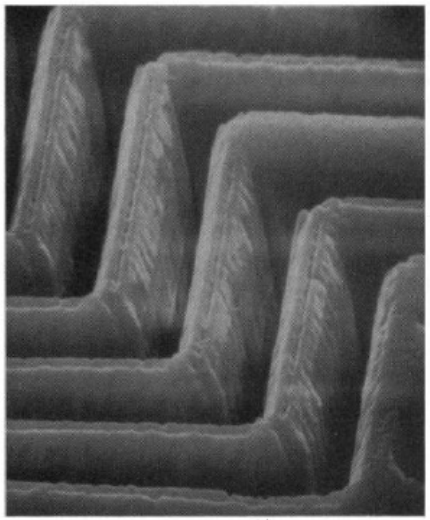
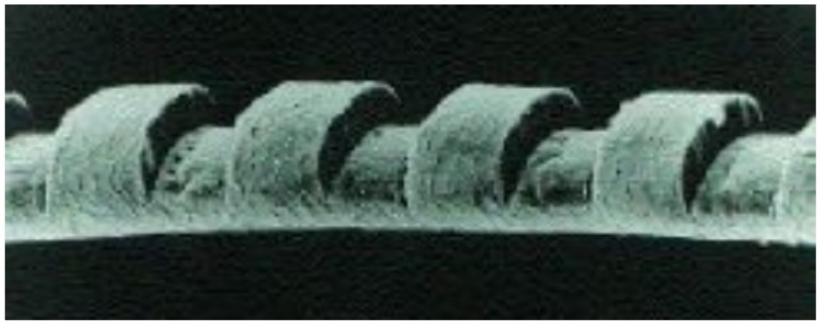


Figure 3. Schematic impact of laser pulse on polymer surface.

Fig. 8. Sample of photoresist film patterned by 193-nm laser pulses. Sample: polyacrylate material (DuPont Riston); lines shown are 5 μm thick. [Scanning electron microphotograph by K. Brown]



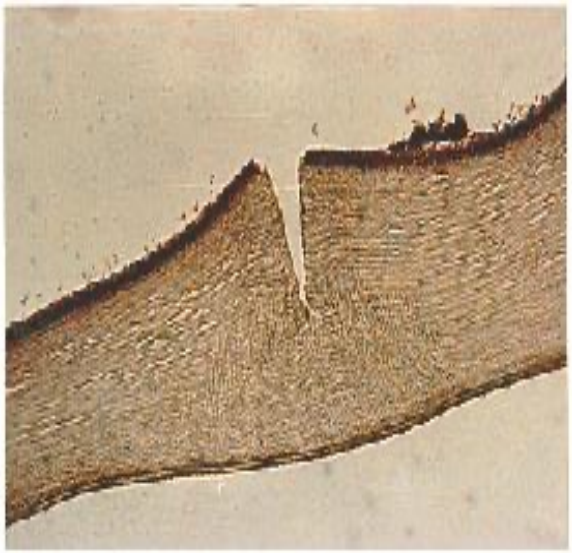


PRECISION A human hair with 50-μm notches etched by an excimer laser.

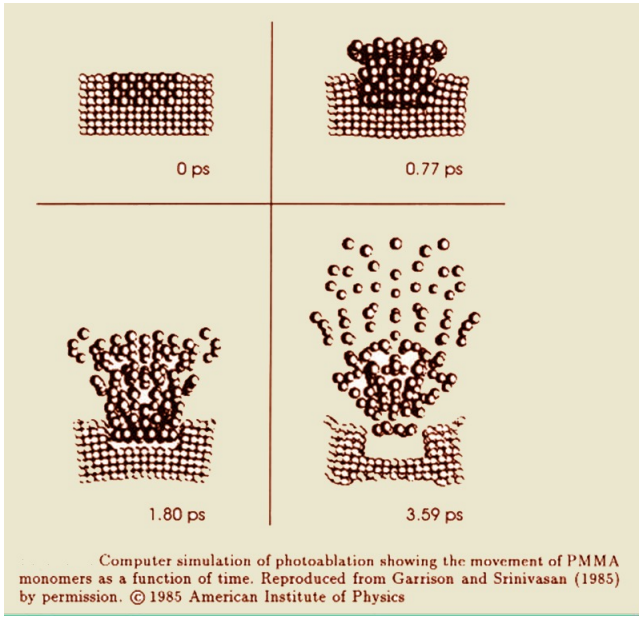
193 nm

532 nm

Fig. 1. Cross section of luminal side of an aortic wall [reproduced from (*5*) with permission of Liss]. (Left) Trench (0.35 mm) produced by laser radiation at 193 nm; pulse duration, 14 nsec; fluence, 0.25 J/cm^2. (Right) Crater (0.4 mm) produced by laser radiation at 532 nm; pulse duration, 5



Histological photo of Rabbit cornea immediately following laser treatment.



Computer simulation of photoablation showing the movement of PMMA monomers as a function of time. Reproduced from Garrison and Srinivasan (1985) by permission. © 1985 American Institute of Physics

B. Garrison and R. Srinivasan, *J. Appl. Physics*, 57, 2909, **1985**

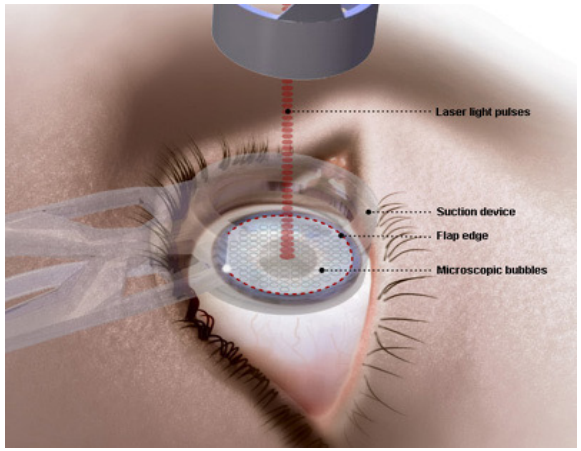
Photoablation with Excimer Lasers

Defined areas of a cornea can be removed by ablating the tissue to a predetermined length.

Far-UV laser irradiation produces a trench with sharp and cleanly defined boundaries by light microscopy. There are no changes in the adjacent tissues due to thermal effects.

Significantly, laser ablation can be used to remove a shaped area of cornea to any depth.

S. Trokel, R. Srinivasan and B. Braren, *American. J. Opthomology*, 96, 710, (1983)



1987: Lasik surgery

R. Srinivasan, *Science 234*, 565, **1986**

S. Trokel, *Refractive and Cosmetic Surgery*, *6*, 357, **1990**

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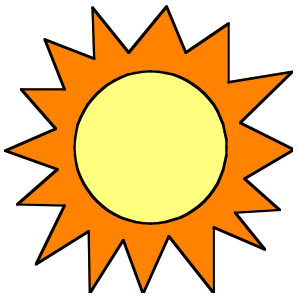
Life without glasses is great! Even so, you may not even imagine it. You wake up in the morning and see everything around you down to the very smallest detail. You will no longer be bothered by dirty glasses, you will never get fossed when you switch from winter to heat. You will experience indescritess of indescritess in sports, travel, trips and everyday life. You do not have to spend on new prescription glasses or contact lenses, just undergo laser vision surgery to solve everything for you - **remove diopter once and for** all.

At present, using laser eye surgery, we can remove both farsightedness and



Photochemistry in Living Systems

Photochemistry in Real Life Systems

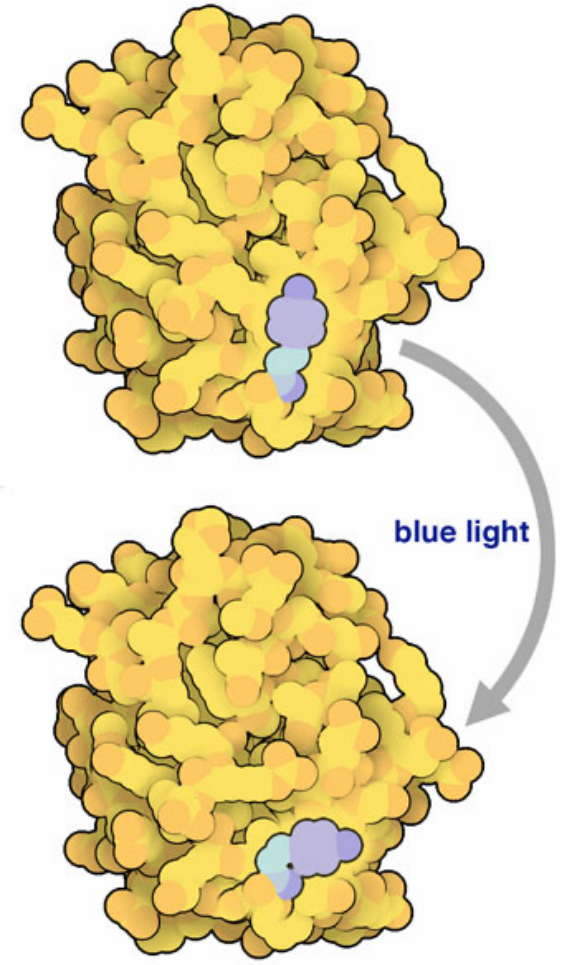
- **PYP and plant growth** ***(cis-trans)***
- **Phytochrome - circadian clock** ***(cis-trans)***
- **Phototropism (e-transfer)**

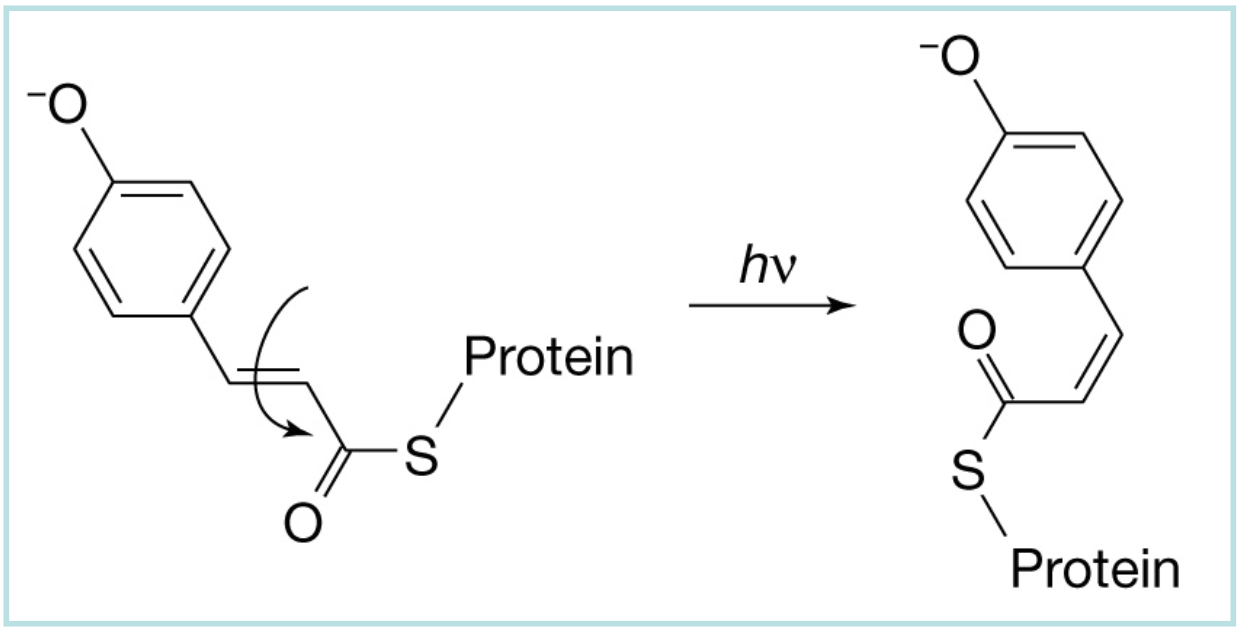
  (bending and growth of plants)
- **Vision** ***(cis-trans)***
- **Photosynthesis (e-transfer)**

Role of Photoactive Yellow Protein (PYP) in plant growth

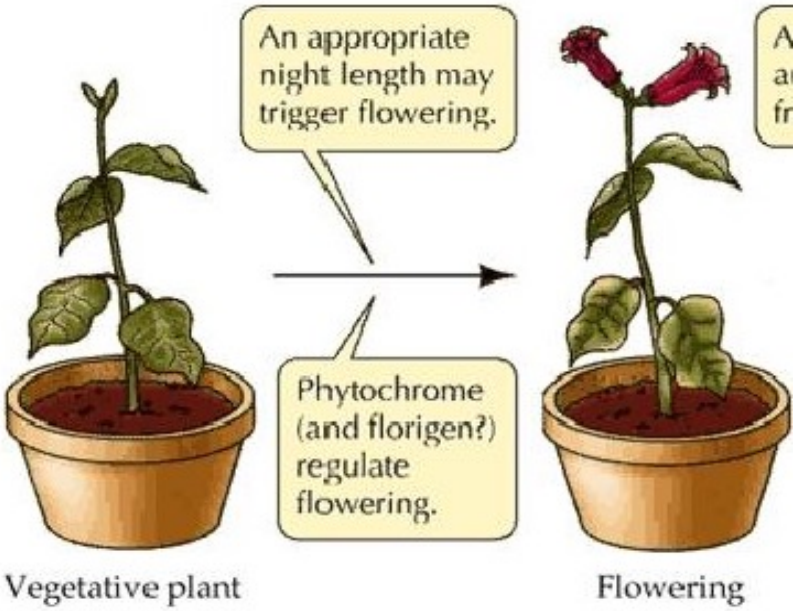
In dark

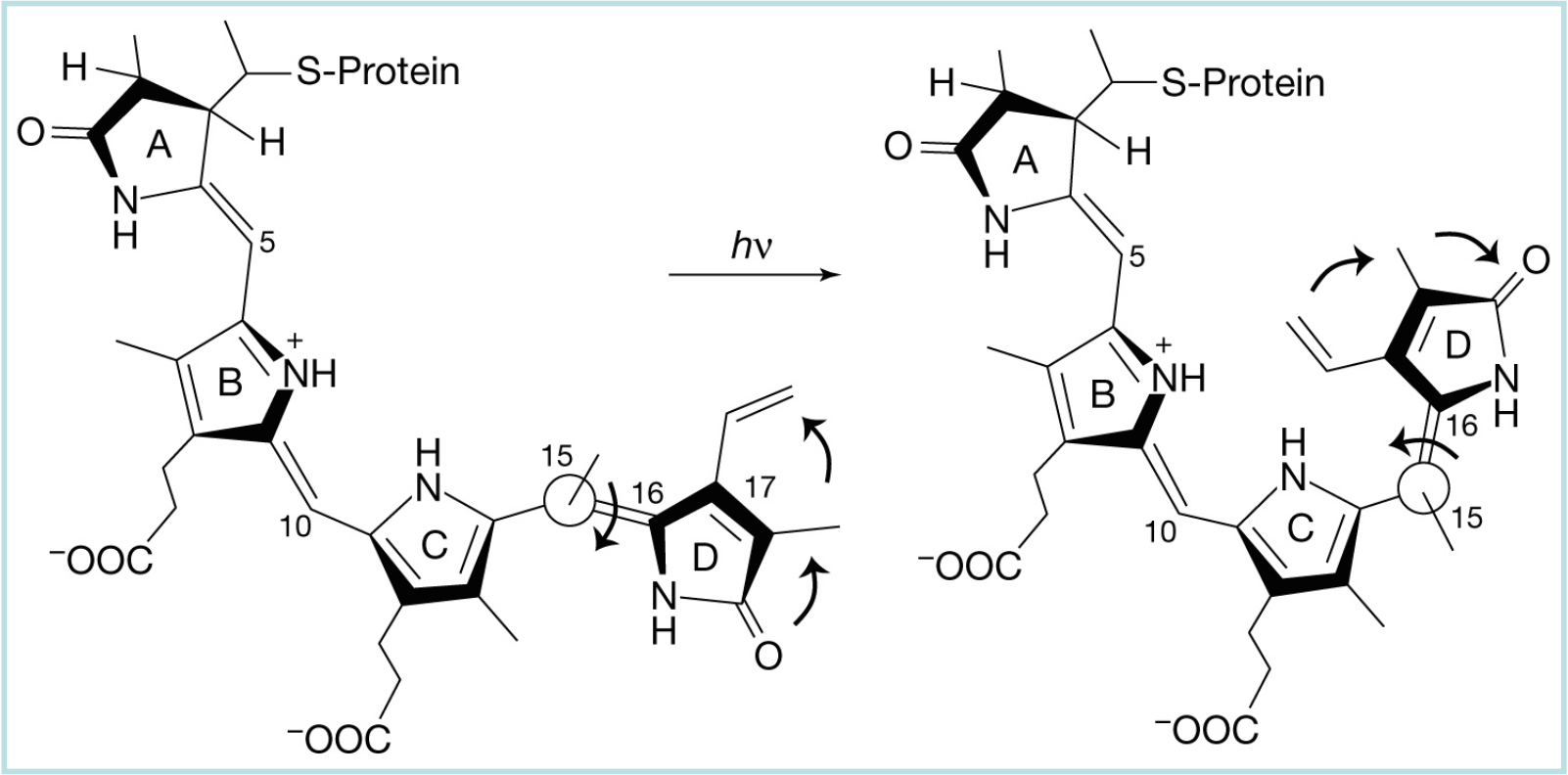
In light



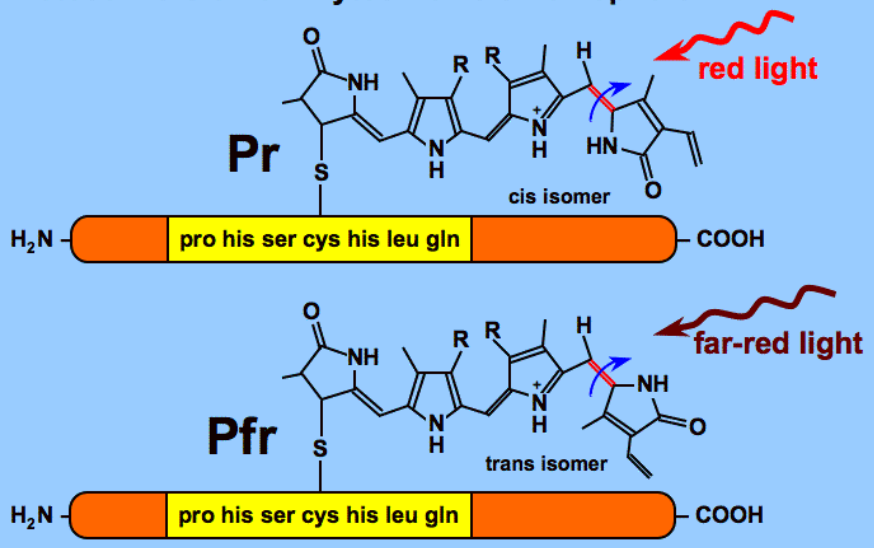


Phytochrome



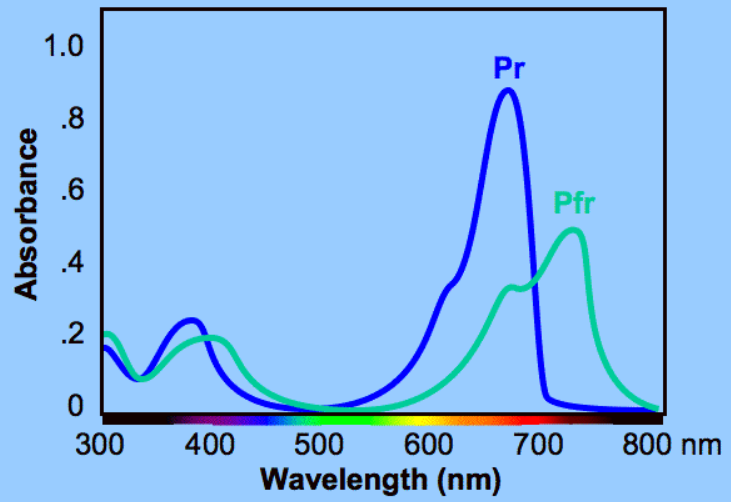


Photoconversion of Phytochrome chromophore

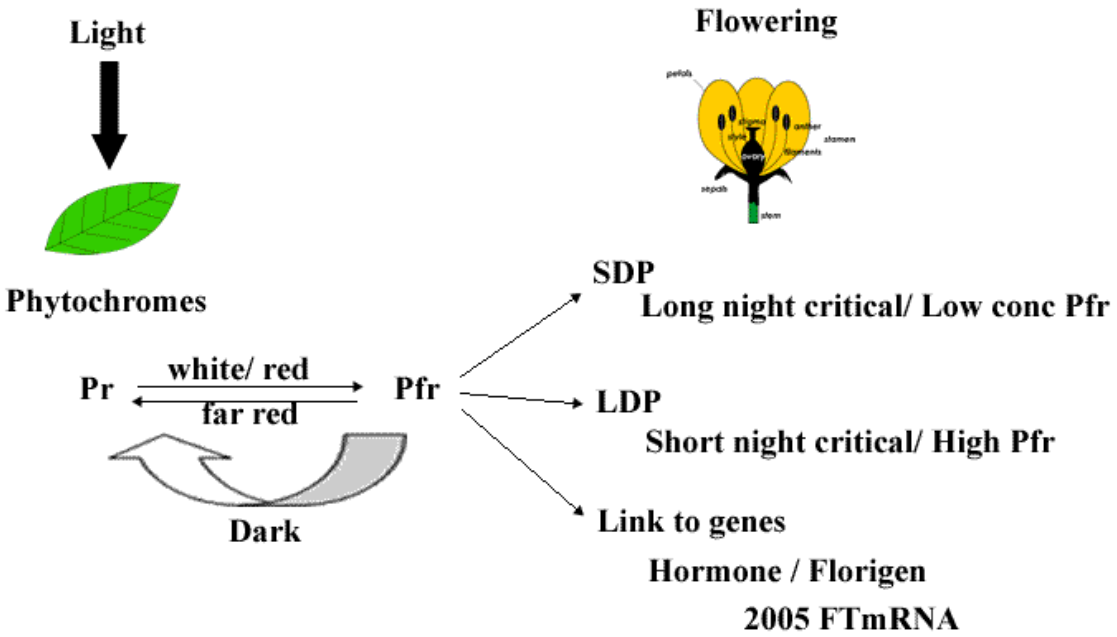


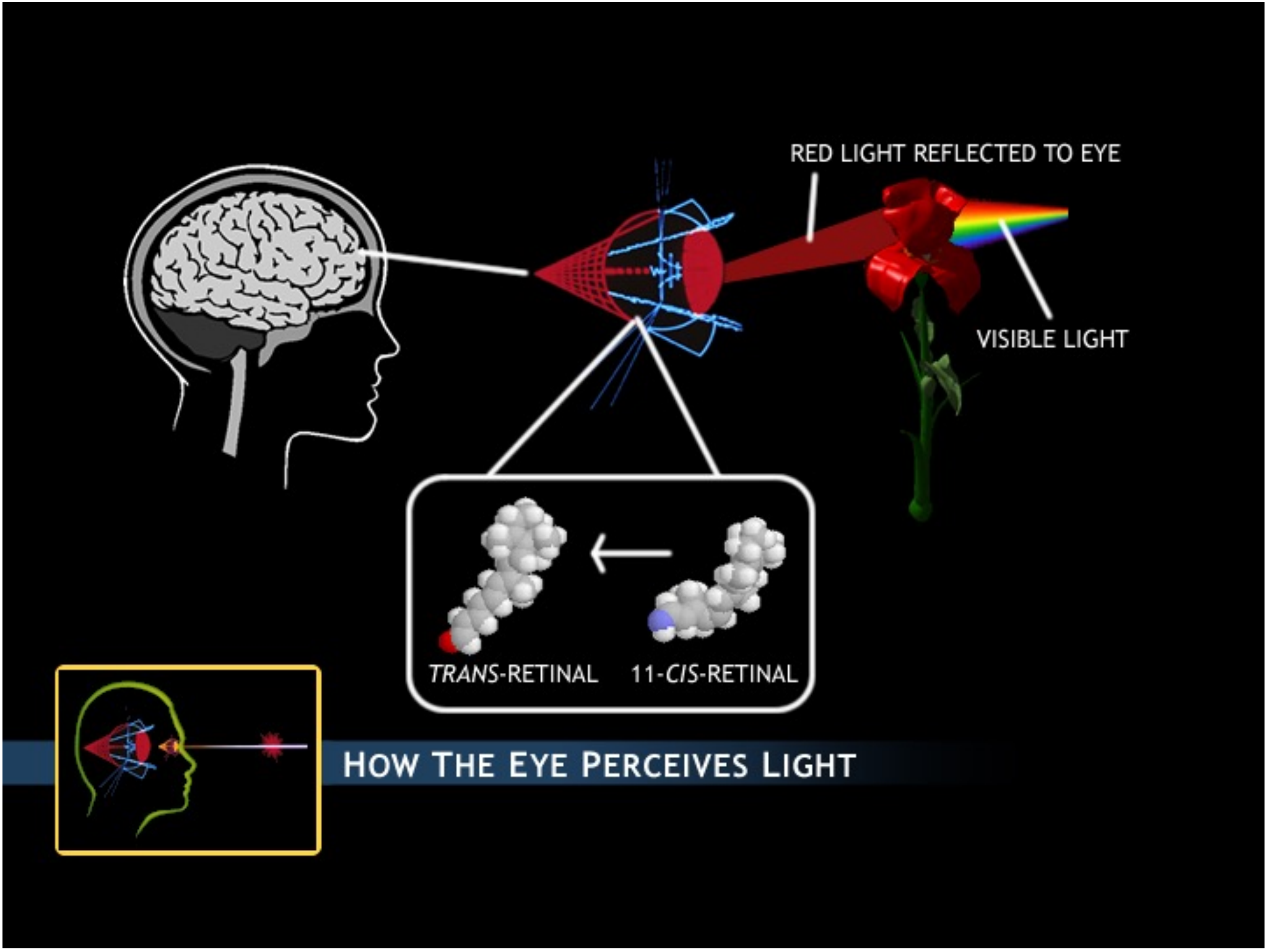
In red light, the phytochrome is in Pfr (trans) form
In far-red light, the phytochrome is in Pr (cis) form

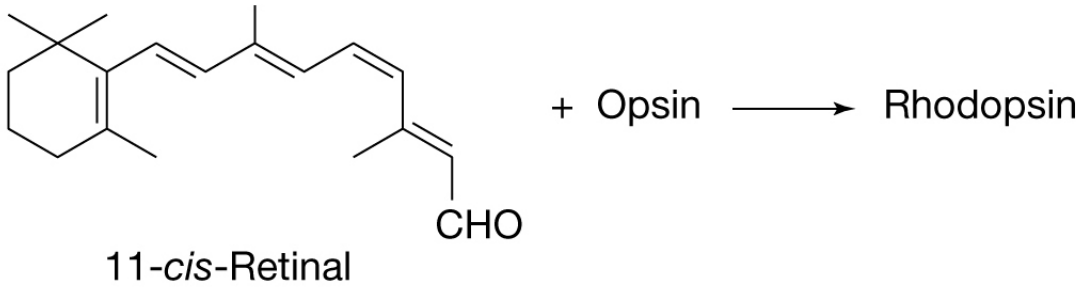
The absorption spectra of the two forms of phytochrome



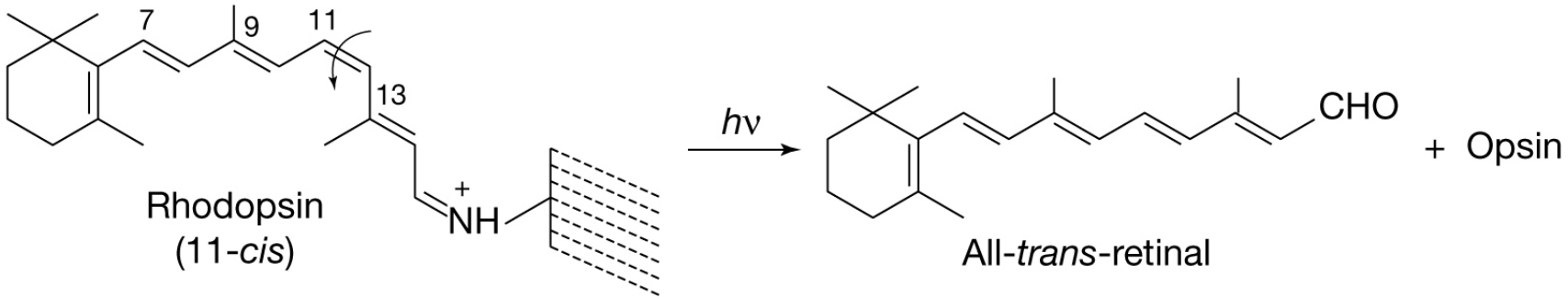
The Pr form of phytochrome absorbs red light
The Pfr form of phytochrome absorbs far-red light




RED LIGHT REFLECTED TO EYE
VISIBLE LIGHT
TRANS-RETINAL
11-CIS-RETINAL
HOW THE EYE PERCEIVES LIGHT

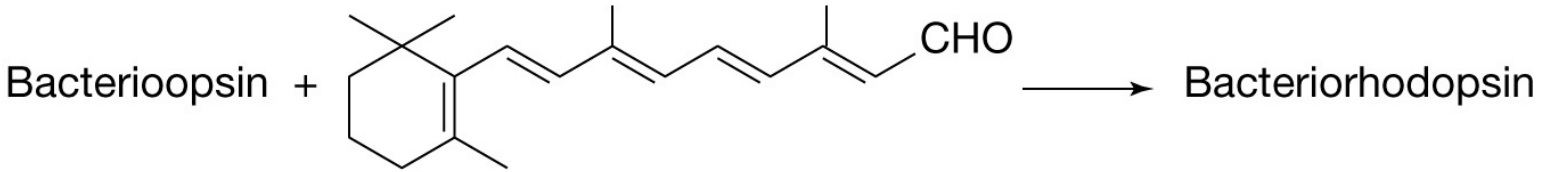


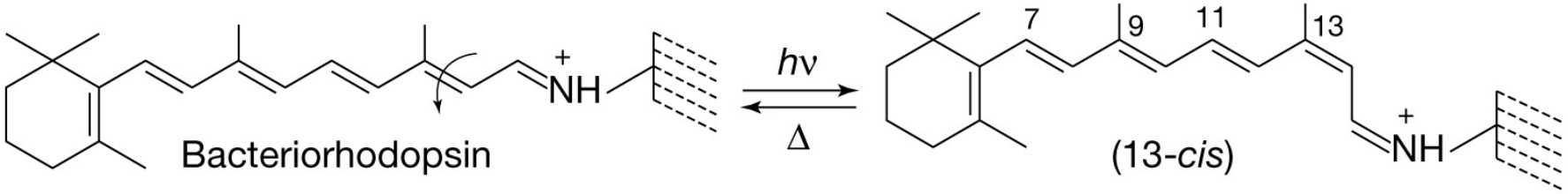
11-*cis*-Retinal



Rhodopsin
(11-*cis*)

All-*trans*-retinal

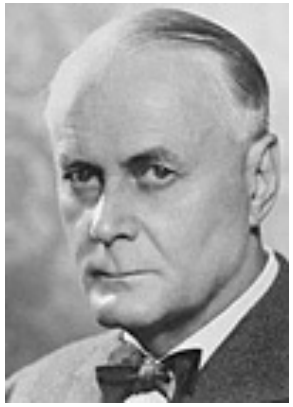




Bacteriorhodopsin

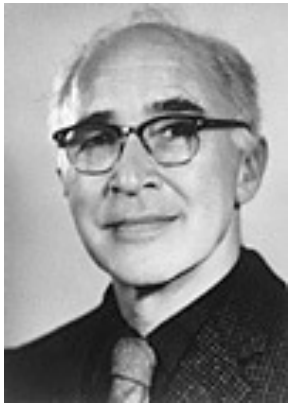
(13-*cis*)

The Nobel Prize in Physiology or Medicine 1967



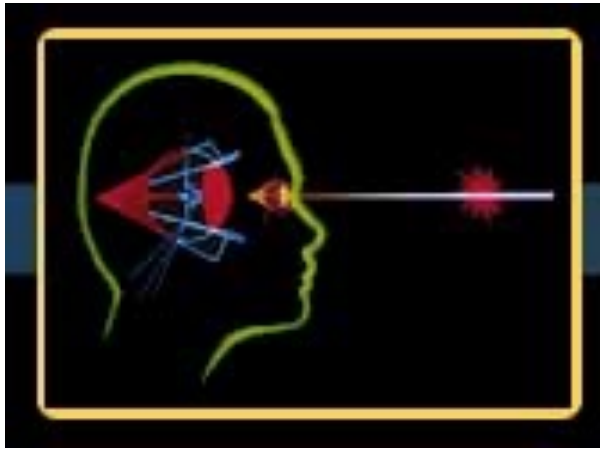
Ragnar Granit

Haldan Keffer Hartline



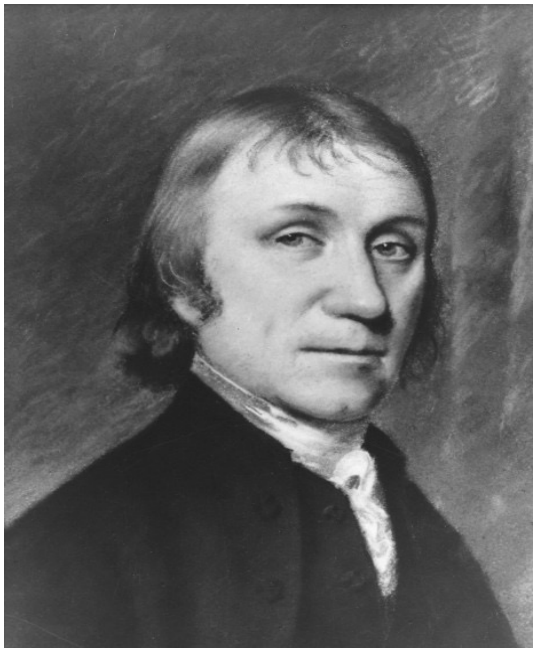
George Wald

"for their discoveries concerning the primary physiological and chemical visual processes in the eye"

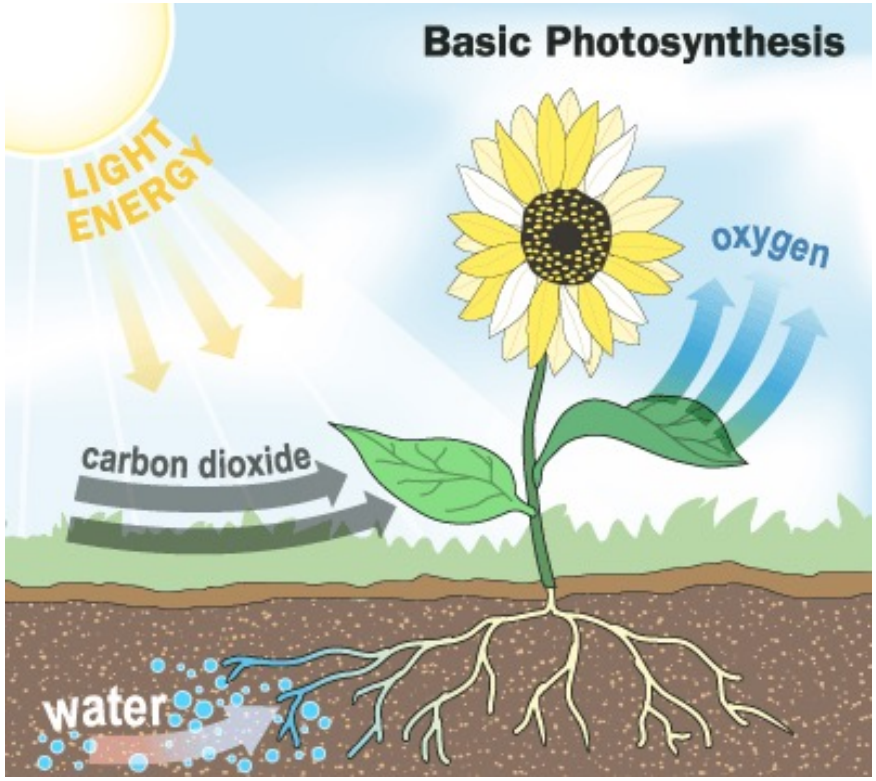


Survival Strategy: Photosynthesis

Plants that commonly grow in the shade benefit from having a variety of light-absorbing pigments. Each pigment can absorb different wavelengths of light, which allows the plant to absorb any light that passes through the taller trees.

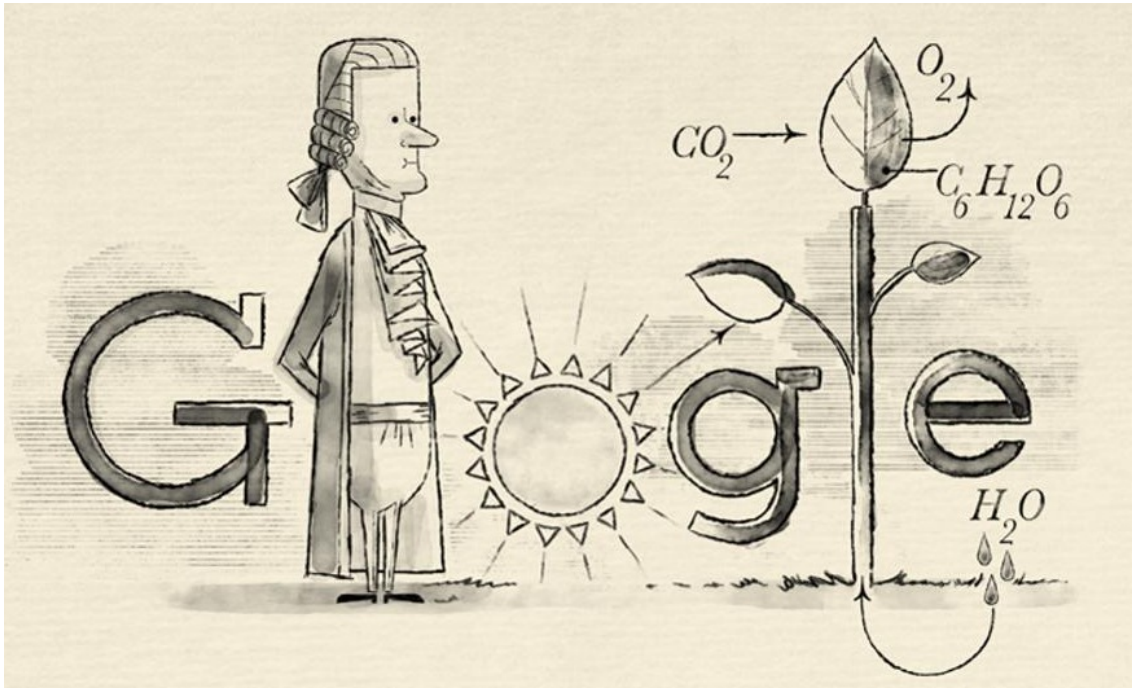


Joseph Priestley
1733–1804



Joseph Priestley published in 1774: "Green plants absorb carbon dioxide from the atmosphere and give of oxygen".

Light Energy Harvested by Plants



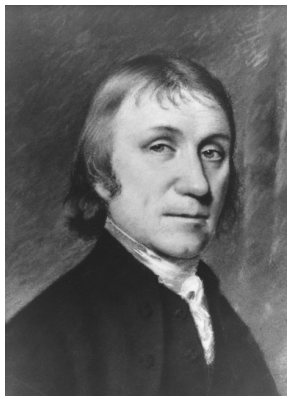
1730 – 1799

$$6\ CO_2 + 6\ H_2O + \text{light energy} \rightarrow C_6H_{12}O_6 + 6\ O_2$$

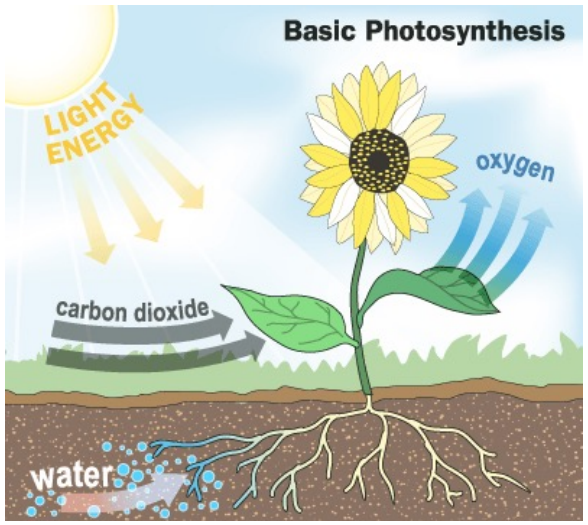
Ingenhousz, along with **Benjamin Franklin** and a few other traveling companions paid a visit to scientist **Joseph Priestly**, who had recently discovered that plant leaves absorb and emit gases. That exchange led Ingenhousz to eventually discover the chemistry that forms the foundation of nearly every food chain on Earth is light: photosynthesis.

Photosynthesis and Solar Energy

The Nobel Prize in Chemistry 1961



Joseph Priestley
1733–1804



M. Calvin
1911-1997

The Nobel Prize in Chemistry 1988

J. Deisenhofer

R. Huber

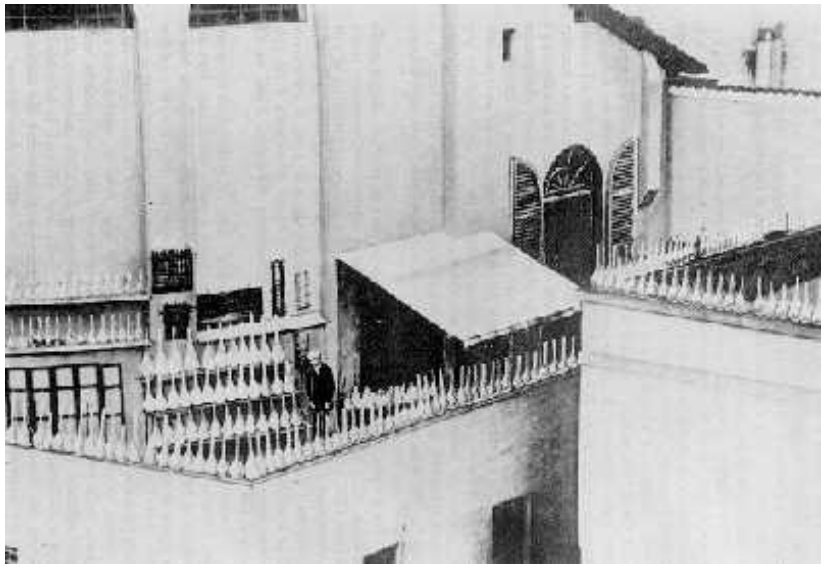
H. Michel

The Nobel Prize in Chemistry 1992

R. Marcus

Giacomo Ciamician

1857-1922



"On the arid lands there will spring up industrial colonies without smoke and without smokestacks, forests of glass tubes will extend over the plains, and glass buildings will rise everywhere; inside of these will take place the photochemical processes that hitherto have been the guarded secret of the plants, but have been mastered by human industry which will know how to make them bear even more abundant fruit than nature, for nature is not in a hurry and mankind is."

(G. Ciamician, *Science* **1912**, *36*, 385.)