Molecular and Supramolecular Photochemistry

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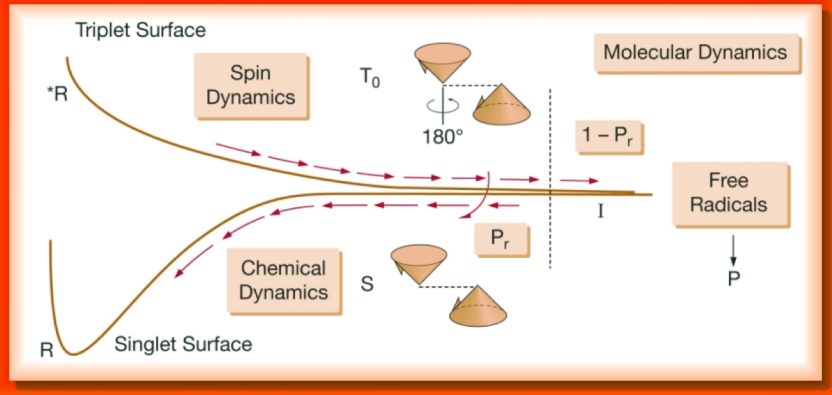
Principles of Molecular Photochemistry

An Introduction



Nicholas J. Turro
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现代分子光化学

（1）原理篇

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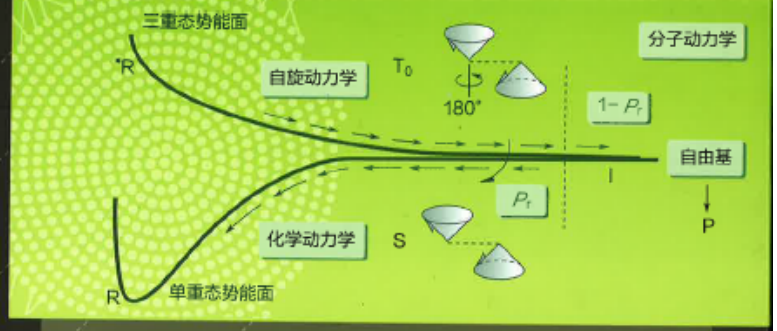

Modern Molecular Photochemistry of Organic Molecules

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分子光化学の原理

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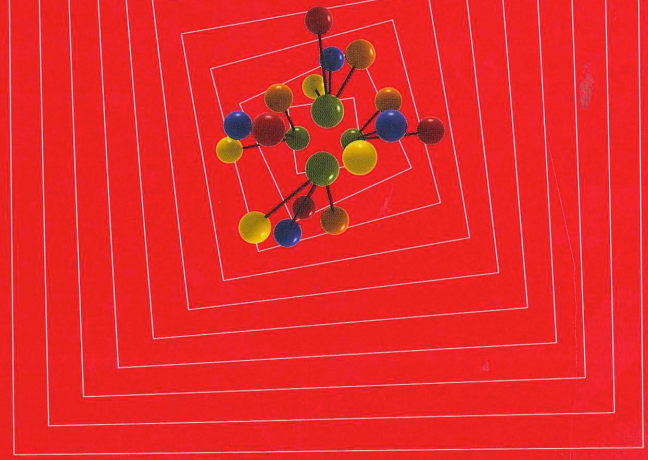

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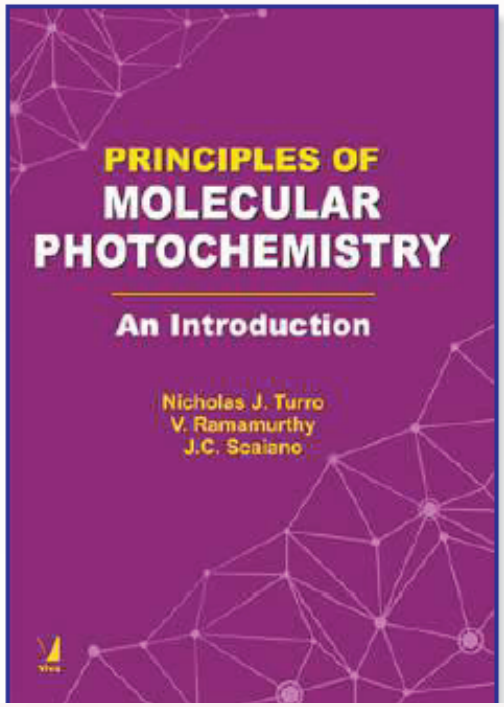

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An Introduction

Nicholas J. Turro, V. Ramamurthy, J C Scaiano

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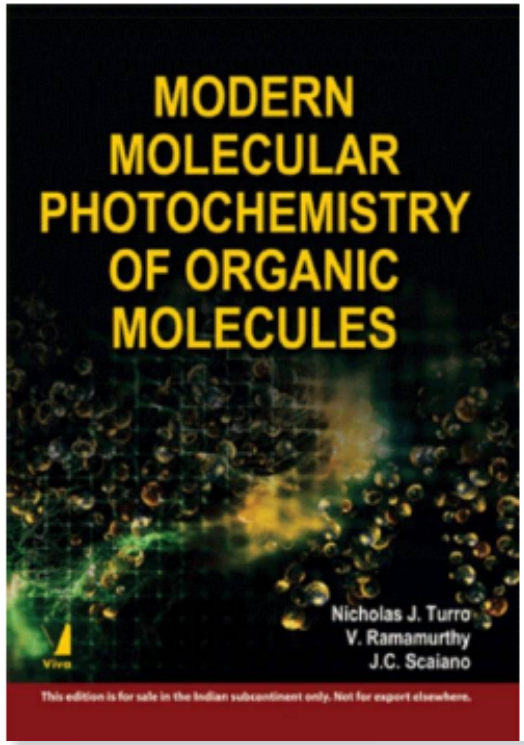

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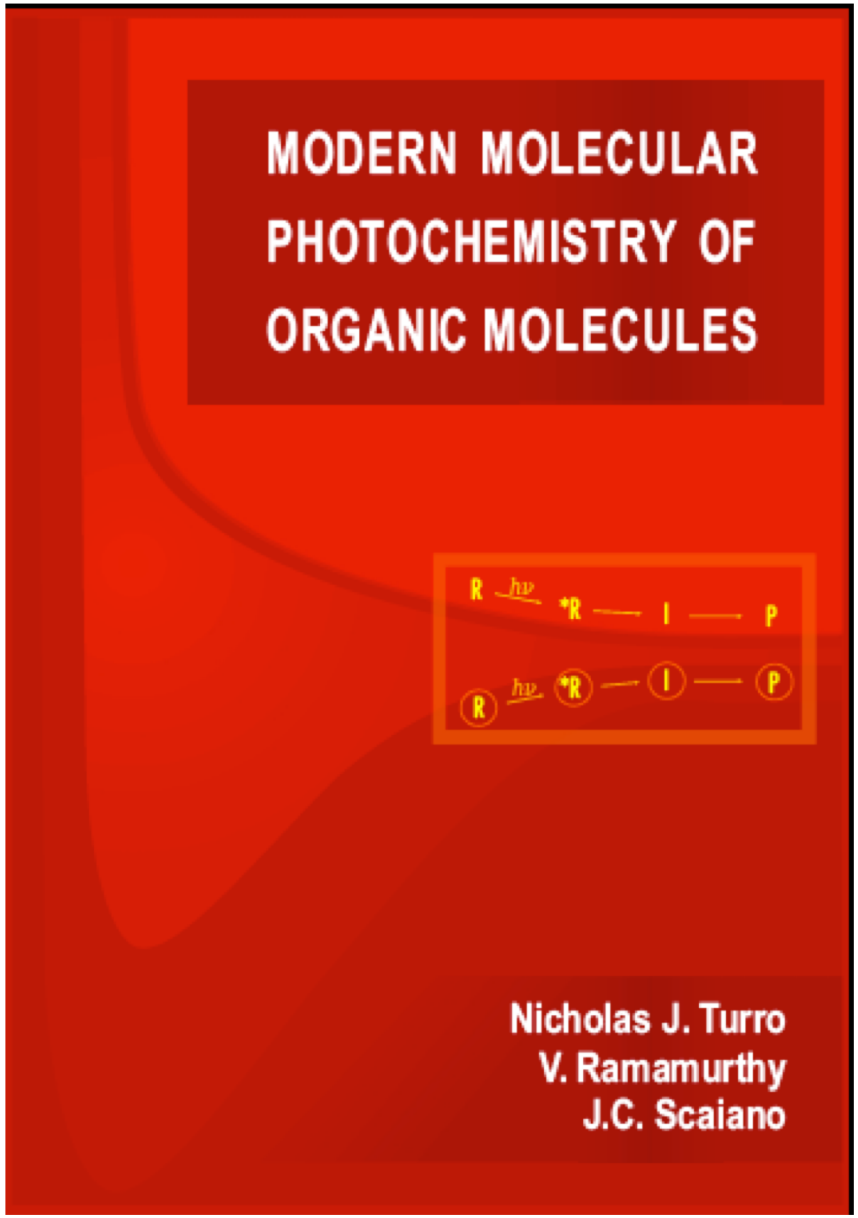
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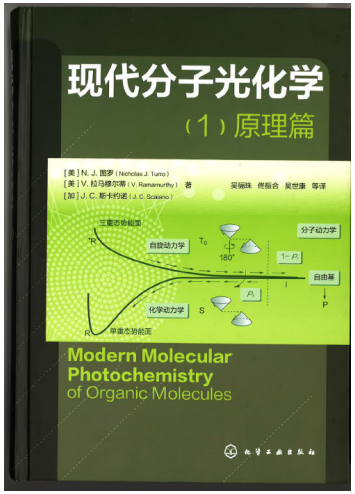
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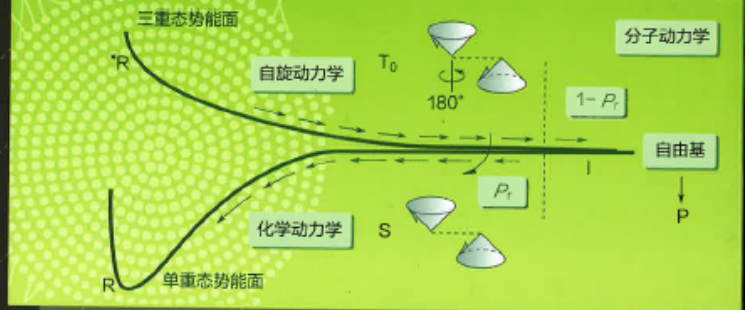

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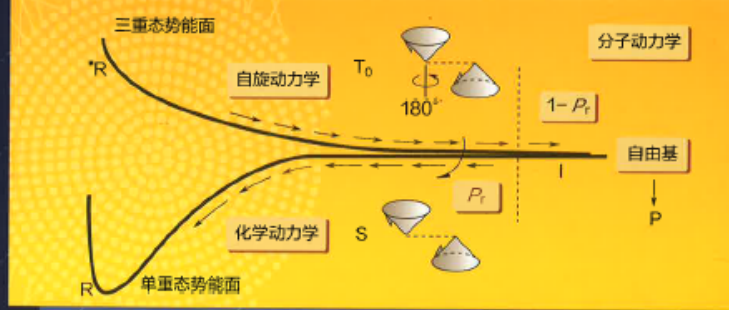

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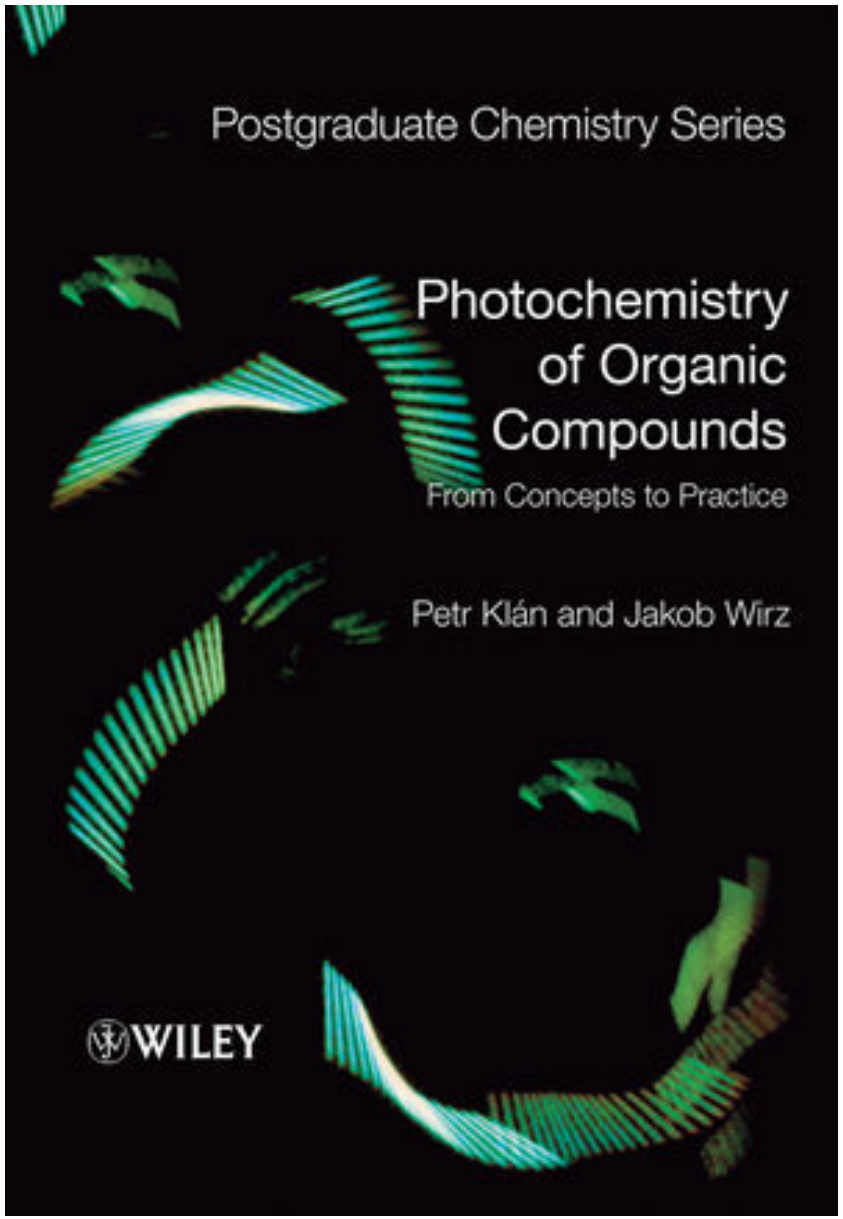
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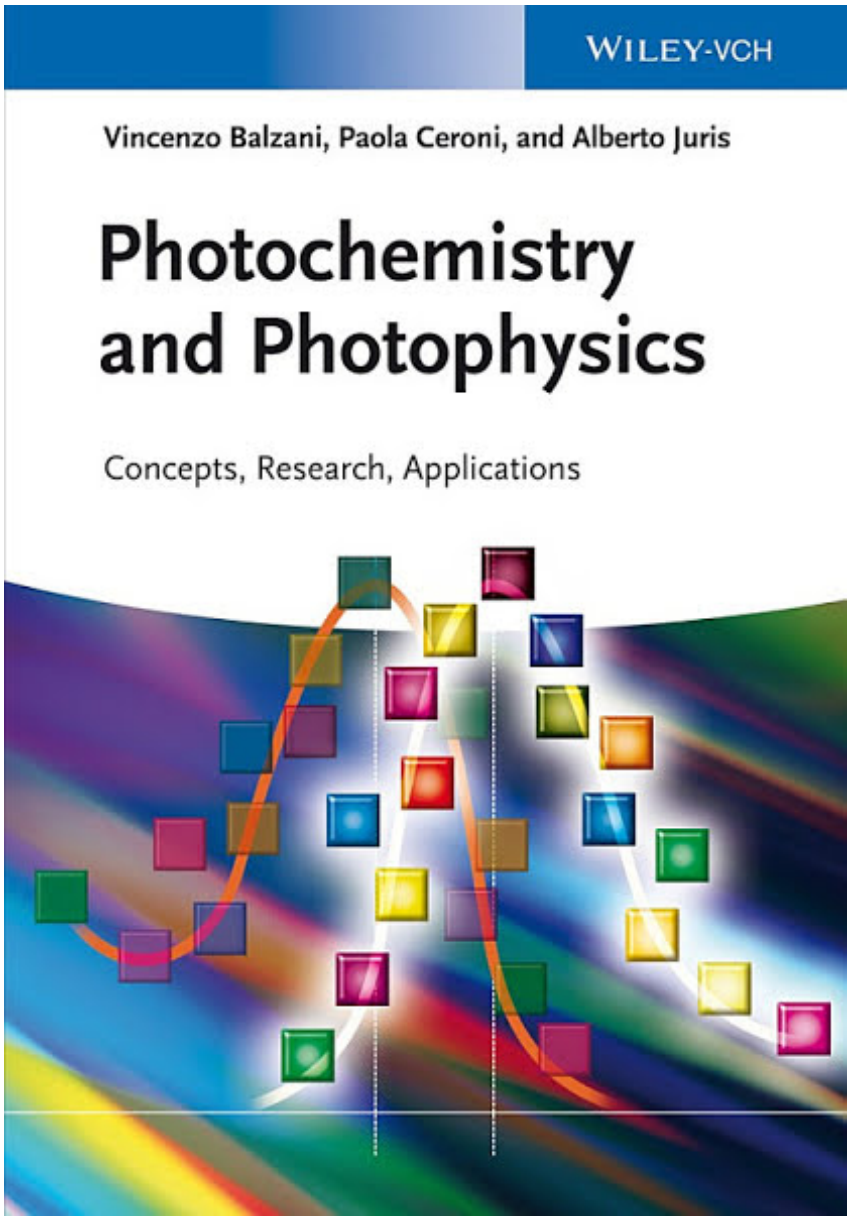
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Vincenzo Balzani, Paola Ceroni, and Alberto Juris
Photochemistry and Photophysics
Concepts, Research, Applications

This Course

Deals with interaction of Light with

Materials, Molecules, Electrons

What is light?

What is a material?

What is a molecule?

What is an electron?

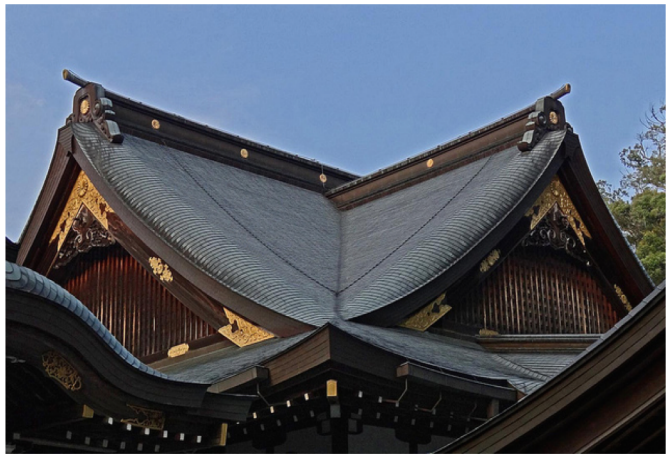
How do light and electron interact?

What are the consequences of interaction?

What are the uses of light in our everyday life?


Light and Life:
Real Life Applications of Photochemistry

Konark



Ise Jingū- the Naikū

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.

What is LIGHT?

Lucretius (50 BC)

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

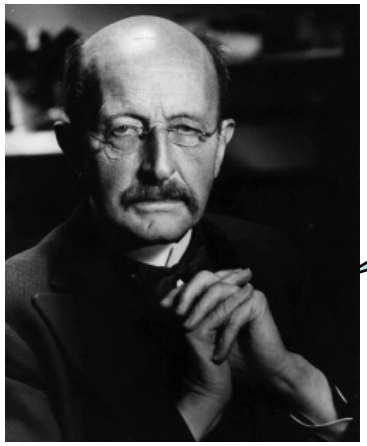
Newton
(1643-1727)

Particles!

Waves!

Maxwell
(1831-1879)

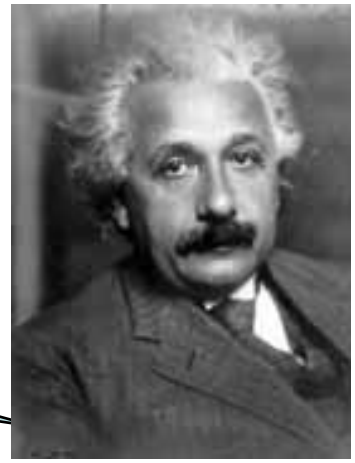
What is LIGHT?



Max Planck (1918)

$E = h\nu$, waves but quantized

$E = h\nu$, particles and photons



Albert Einstein (1921)

Niels Bohr (1922)

$E_2 - E_1 = h\nu$
Energy levels are quantized
Light is absorbed and emitted in quantas

$E = h\nu = mc^2$
particles and waves

De Broglie (1929)

Light: Prosperity through basic science

Candle lamp

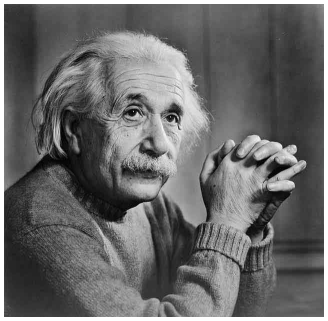
Oil lamp

Filament lamp

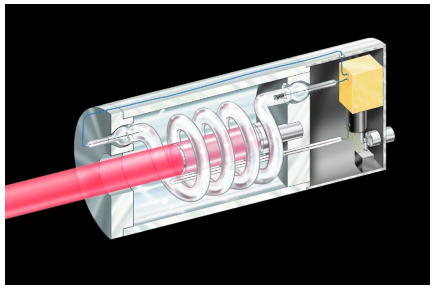
Fluorescent lamp

Light emitting diodes

LASER (Light Amplification by the Stimulated Emission of Radiation) Invention and Innovation

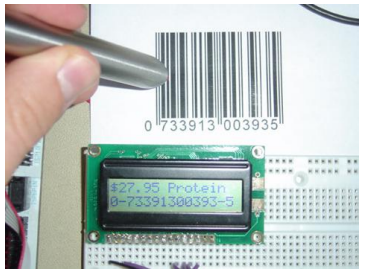


1917: Albert Einstein derives the theoretical basis for the laser.



1960: The first working (ruby) laser.

1965: The compact laser disc (CD) invented.



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

The world market for laser technology is now over $ 5 trillion a year

Light and Life

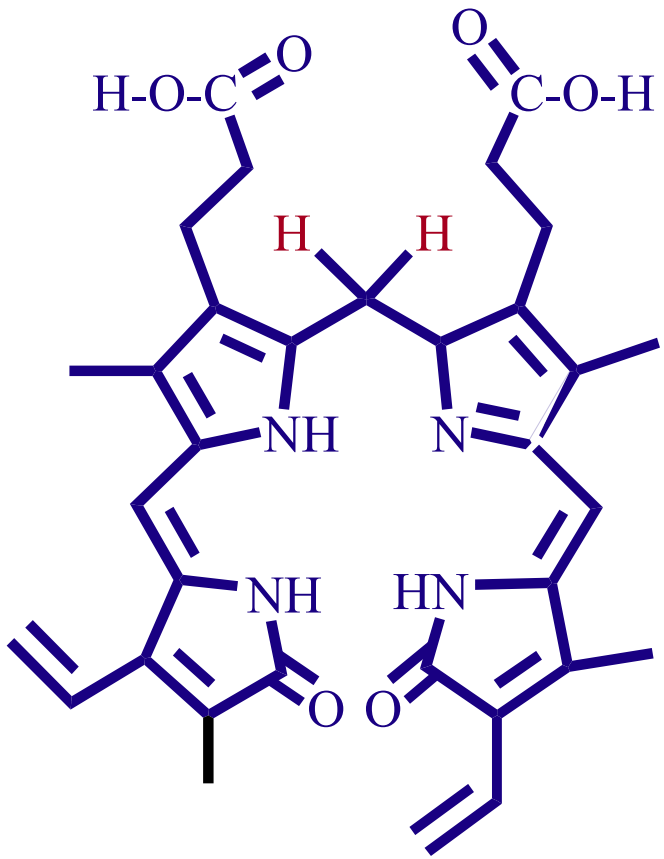
- Photomedicine
- Lithography
- Industrial Synthesis of Chemicals
- Solar Energy Conversion
- TiO_2: Environmental Cleanup
- Photography, Xeorography and Holography
- Sunsscreen, Photochromic Glass
- Photostabilization and Photocuring
- Molecular sensors and machines

Medicinal Applications of Photochemistry

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

Phototherapy for Neonatal Jaundice Treatment

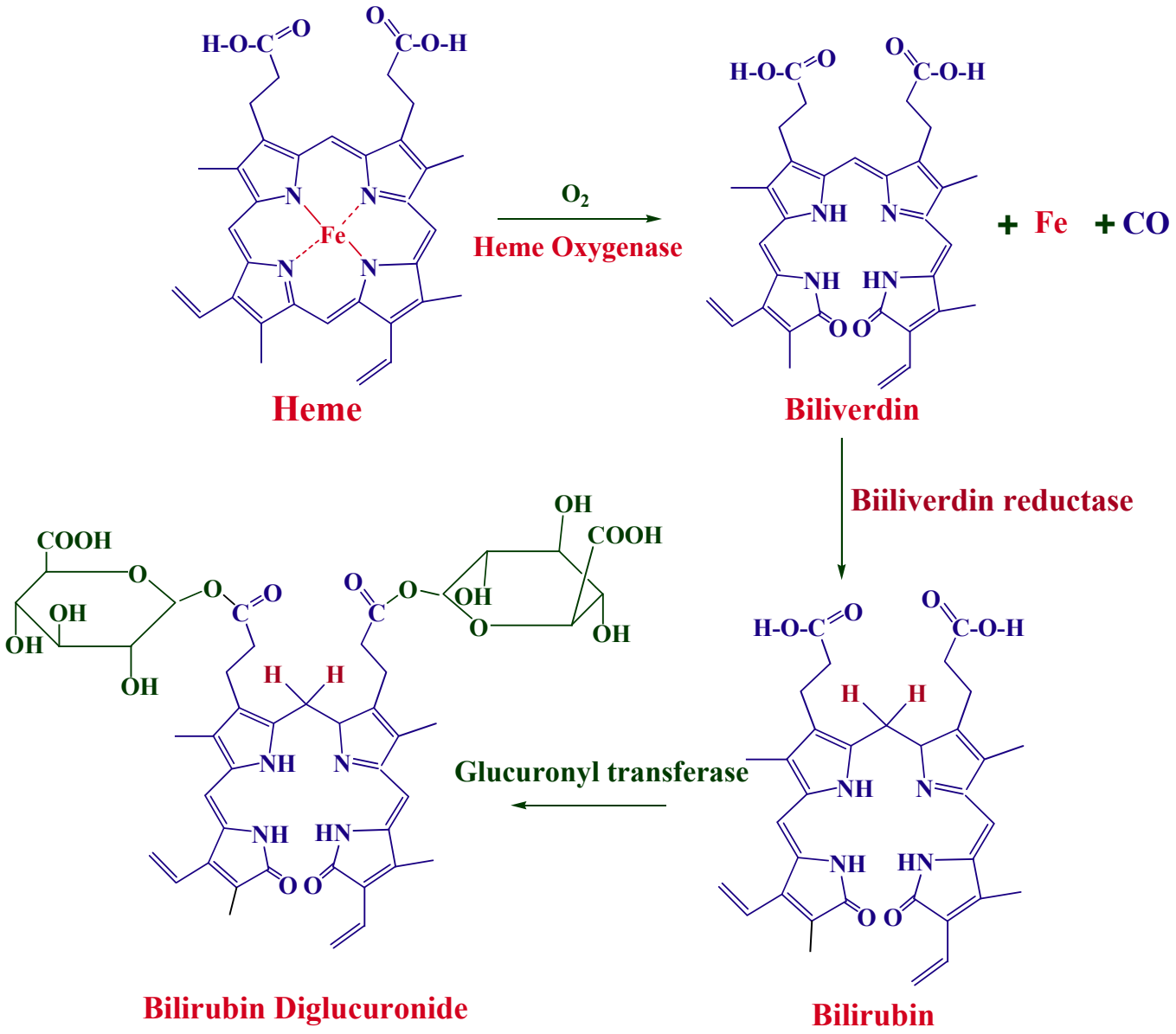
- Accumulation of the potentially toxic yellow liphophilic bilirubin in human serum leads to Jaundice.
- If the percentage of bilirubin increases to 15-25 mg/100 ml, it will lead to hyperbilirubinemia.
- Severe hyperbilirubinemia cases, sufficient pigment may partition into the brain to cause irreversible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



Bilirubin

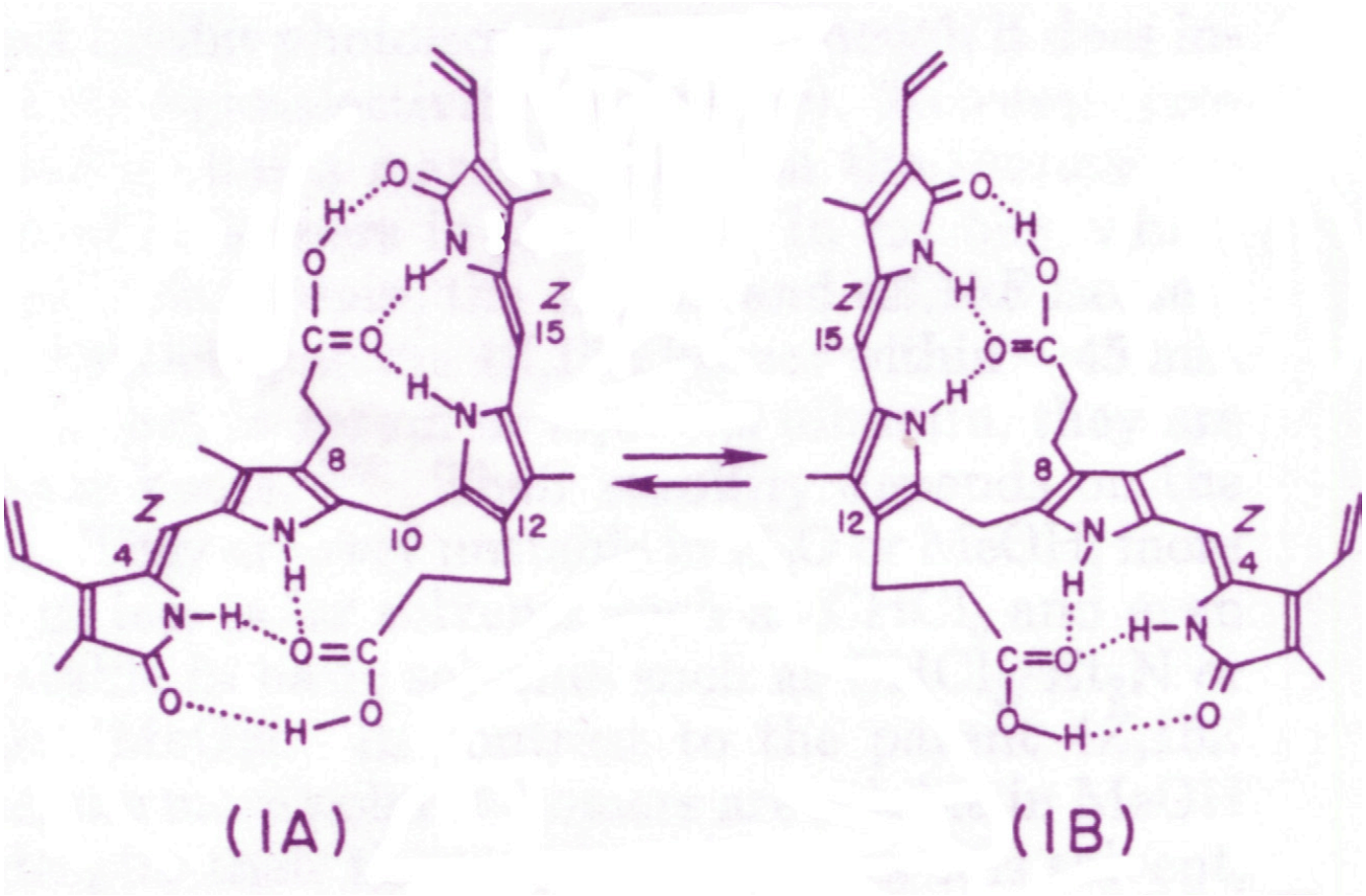
McDonagh etal., *Science*, 208, 1980, 145-151.

Biosynthesis of bilirubin



Glucuronyl transferase activity in fetal and new born liver is very low.

Why bilirubin is lipophilic (hydrophobic) ?



Natural Cure for Jaundice

Different ways to cure jaundice

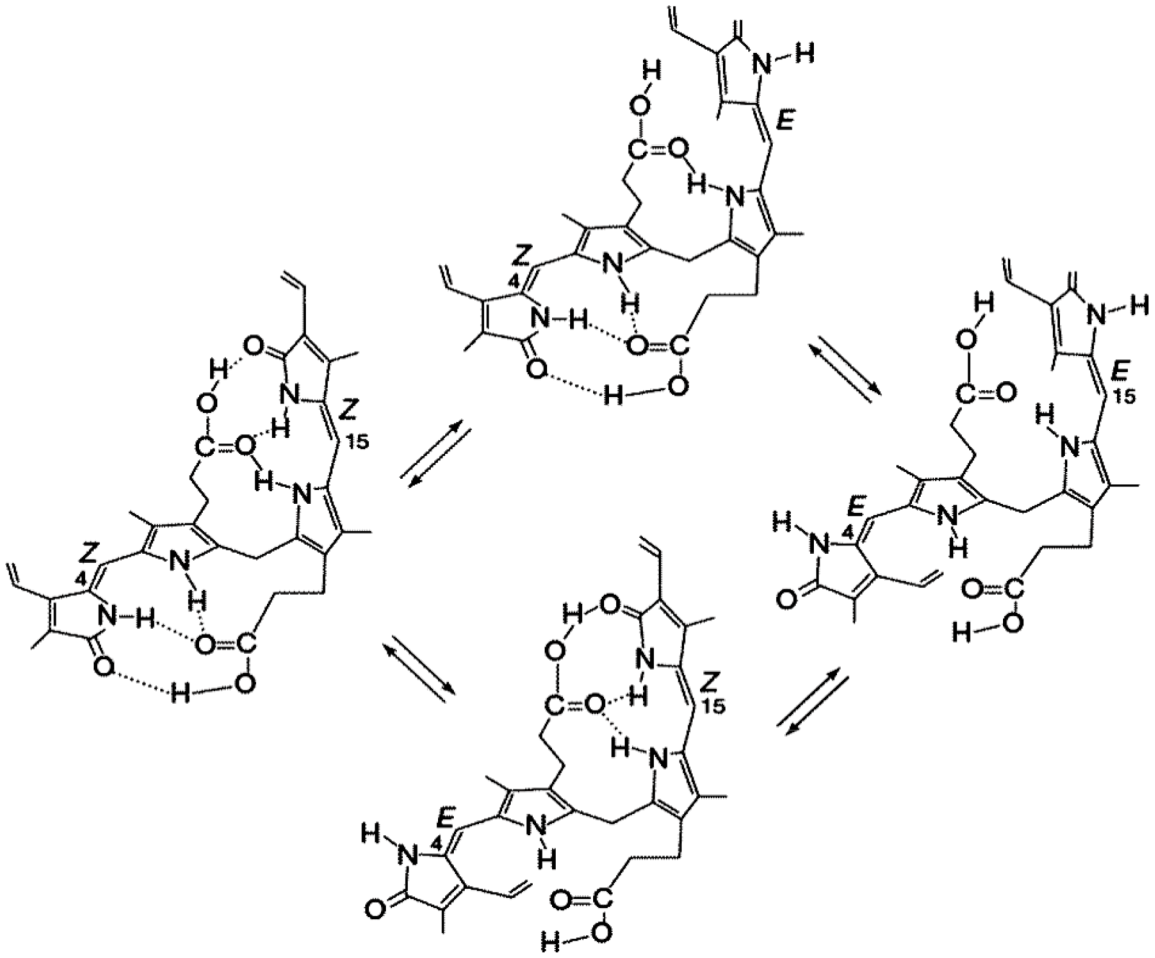
- Wait till liver matures soon enough to clear bilirubin unaided.
- Exchange transfusion: blood along with threatening pigment drained and replaced with clean blood.
- Phototherapy - irradiate the baby with light.

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



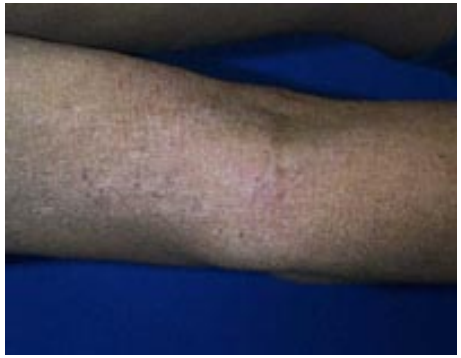
"light converts bilirubin to a less hydrogen bonded (more water soluble) isomer"

Skin Disorders

Psoriasis

Polymorphic light eruption

Vitiligo

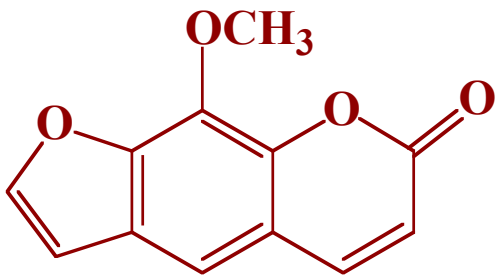


Acute dermatitis

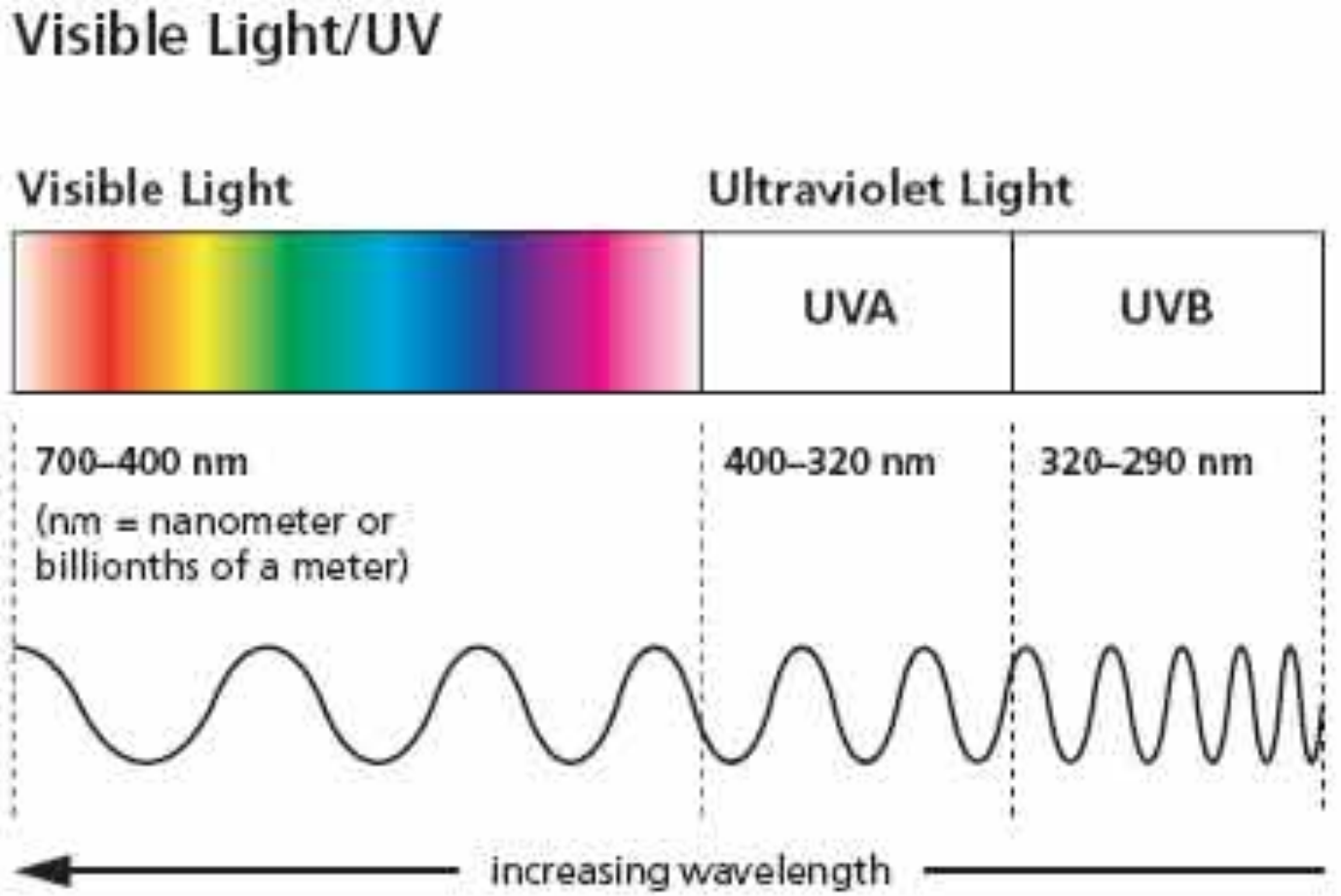
PUVA- therapy

- 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?

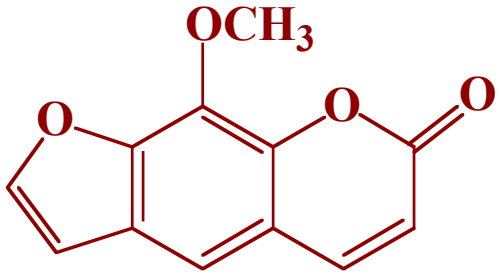


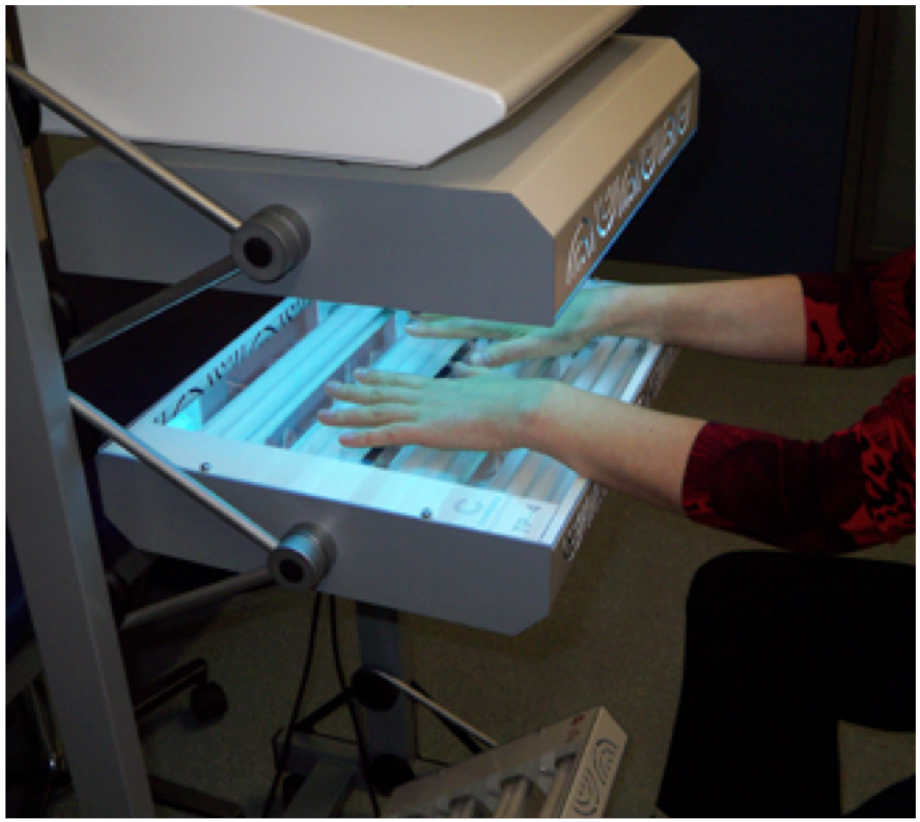
How PUVA therapy is done ?

- 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.

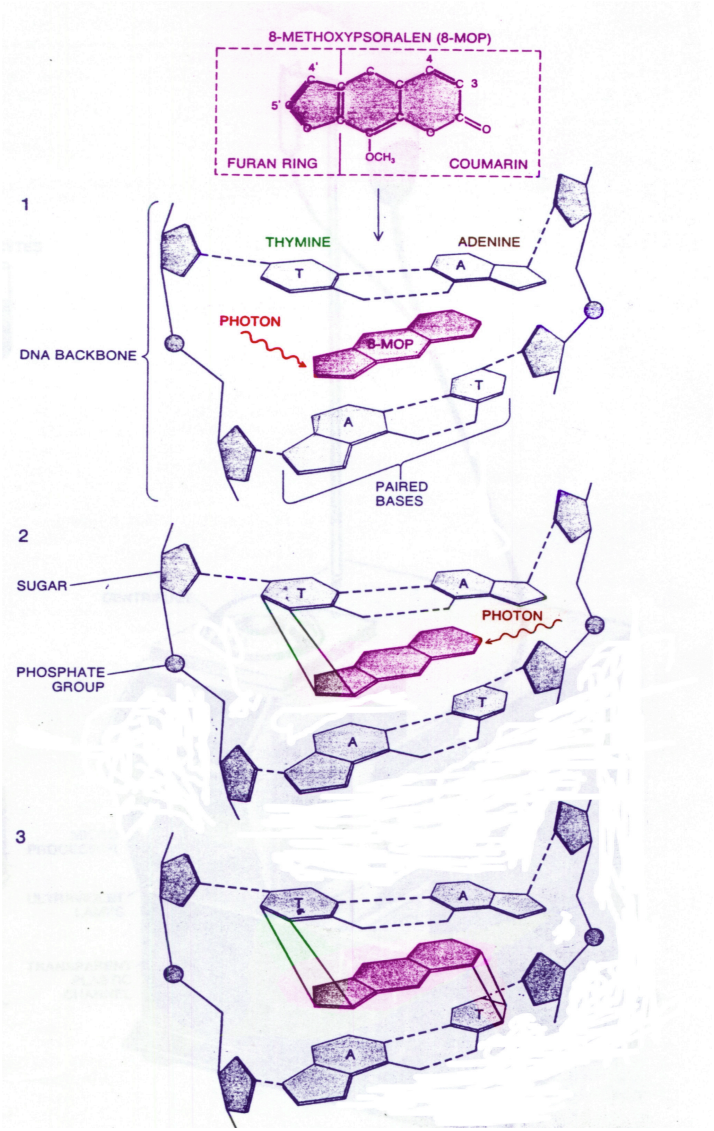
PUVA therapy

Psoralen + Ultraviolet A = PUVA





Photoadduct representation with DNA



- **Intercalation**
- **Monofunctional adduct (3, 4 with pyrimidine base)**
- **Bifunctional crosslinked adduct(3, 4 and 4’, 5’ with pyrimidine bases)**

PUVA -therapy to treat cancer

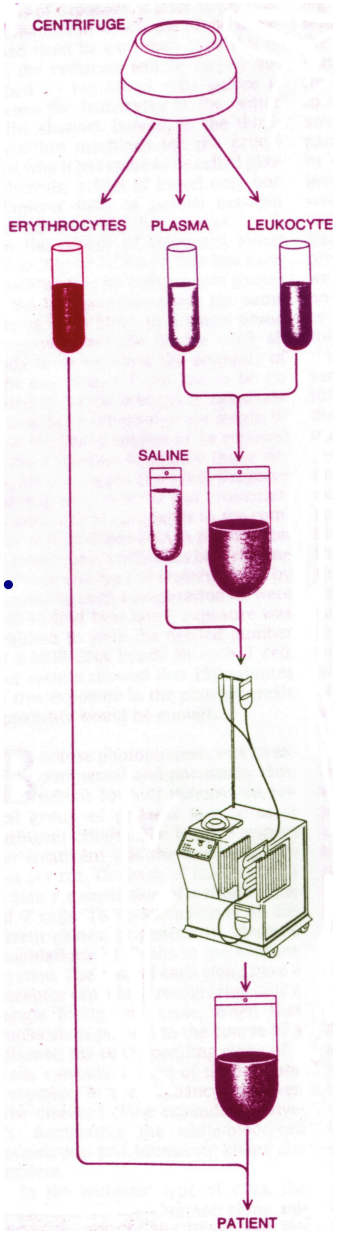
Centrifugation.

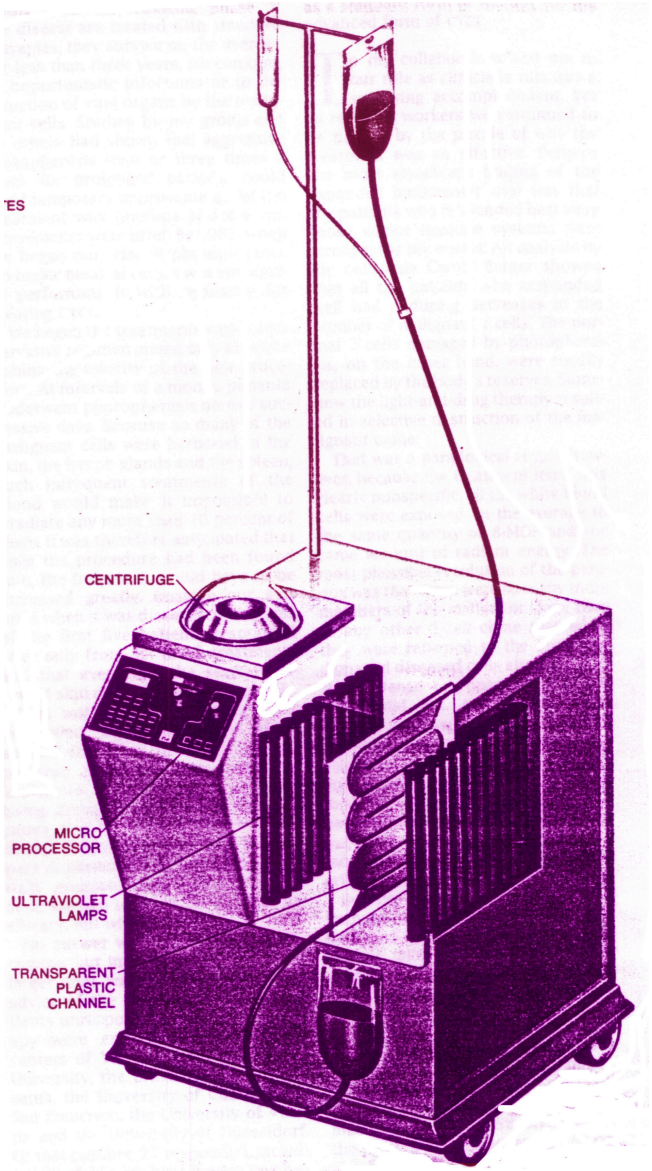
Separate white blood cells.

Drug in saline + Leukocytes.

Irradiate in the machine.

Collect white blood cells.

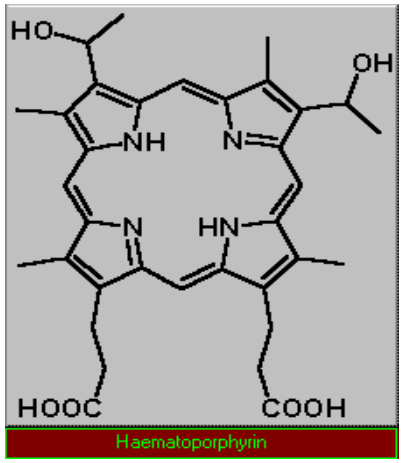




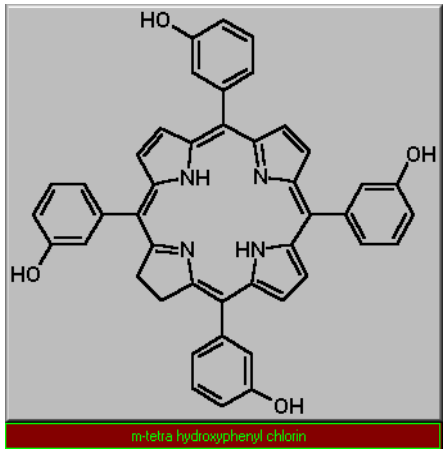
Photodynamic therapy

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

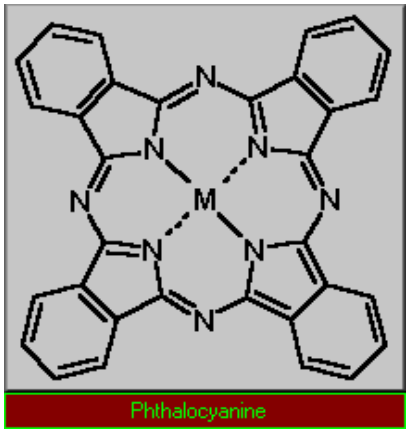
Porphyrins



Chlorins

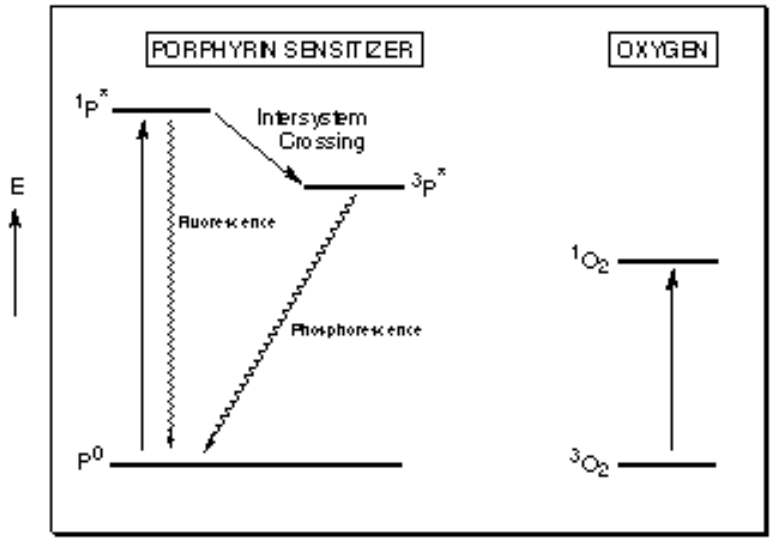


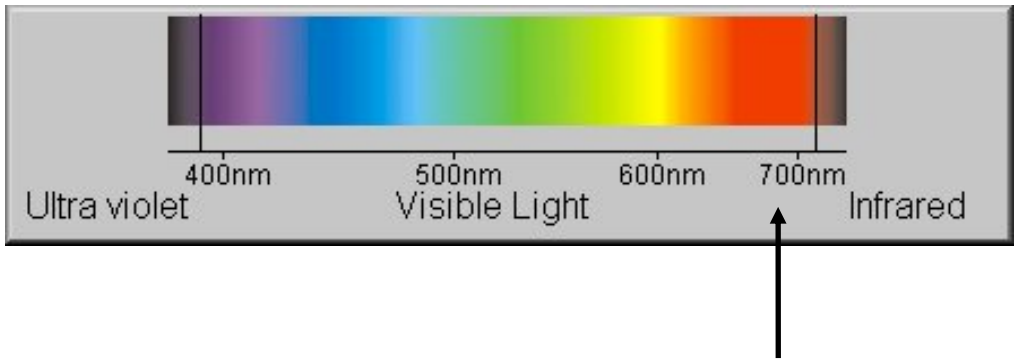
Phthalocyanines



How does photodynamic therapy work?

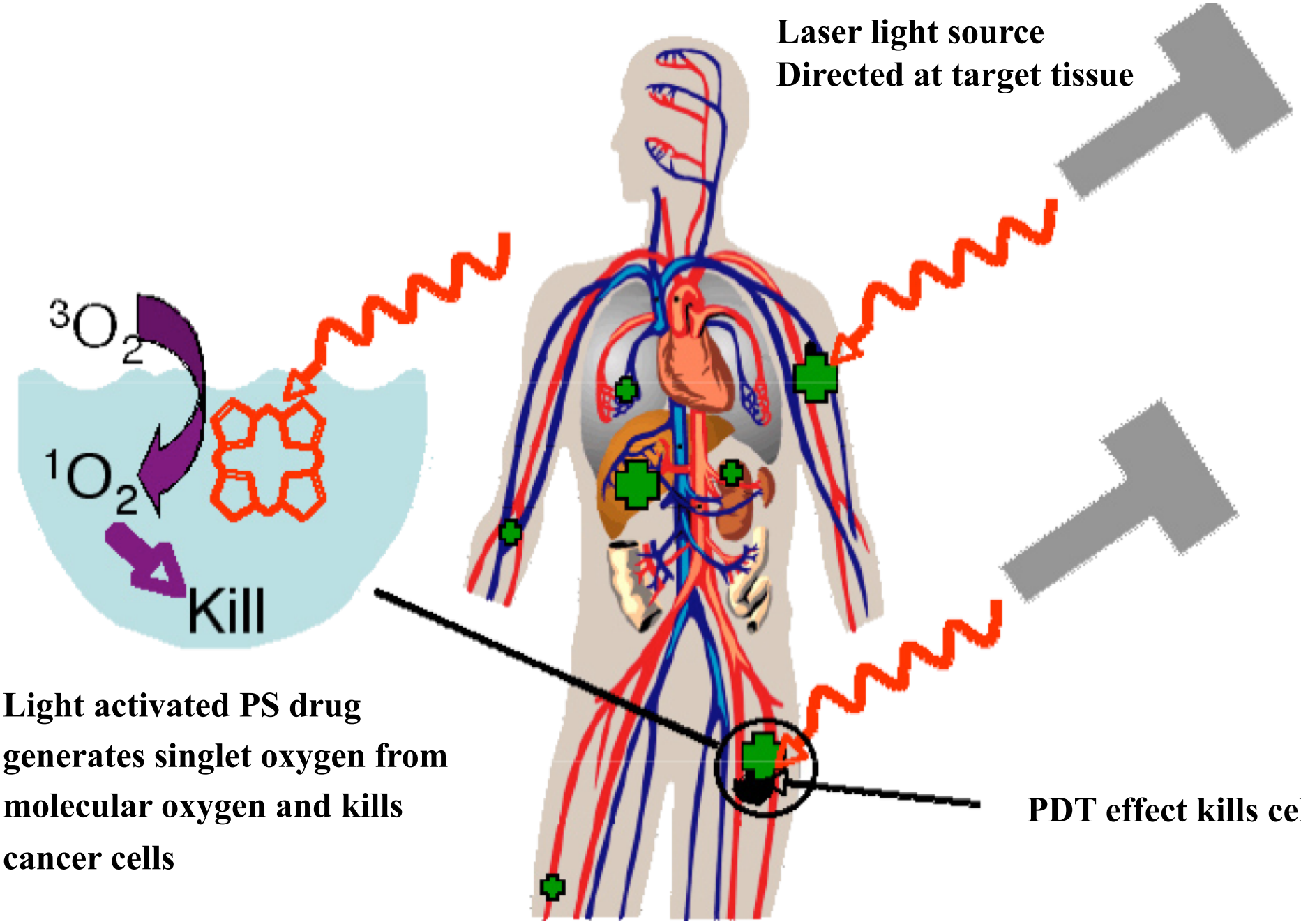
- PDT requires sensitizer, light and oxygen in the target tissue.
- Light generates reactive oxygen species.
- Reactive oxygen species can kill targeted cells either by necrotic mechanisms or by initiating the apoptotic cascade.





Ideal wavelength 650nm

Photodynamic therapy



Lithography to Lasik Surgery

R. Srinivasan

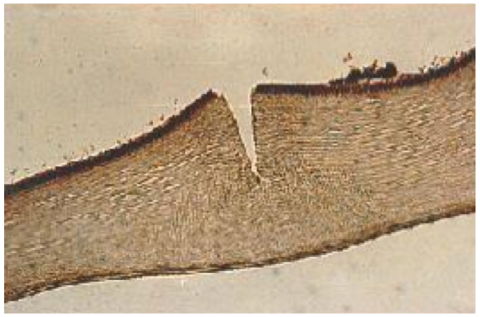
S. Blum

J. Wyne

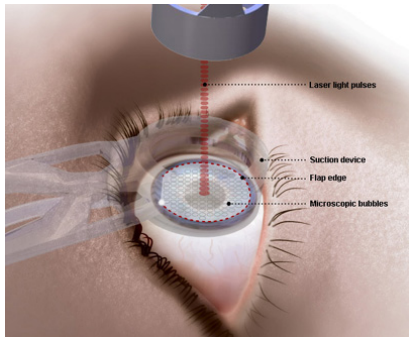
1981: Discovery of laser ablation technique.

1995: US FDA approval of human Lasik surgery.

2002: Inducted into US Inventors Hall of Fame.



1981: Discovery of laser ablation

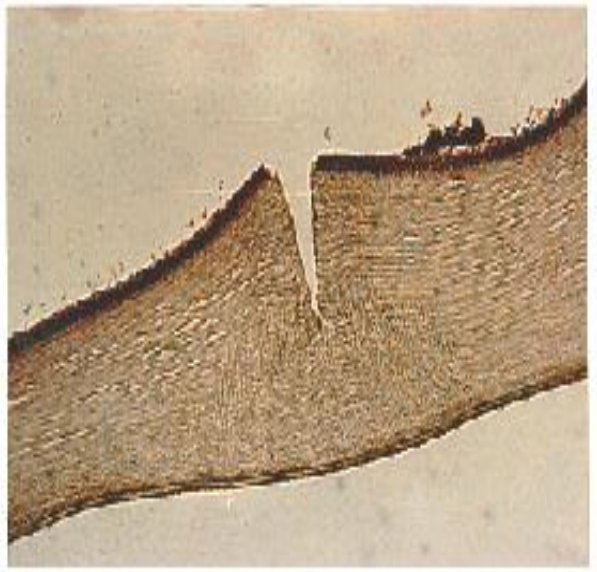


1987: Lasik surgery

Photoablation with Excimer Lasers

Short wavelengths of light (190 to 300 nm) breaks molecular bonds (ablation)

Photablation with eximer laser (eg: ArF, KrF) can be done with a micron accuracy.

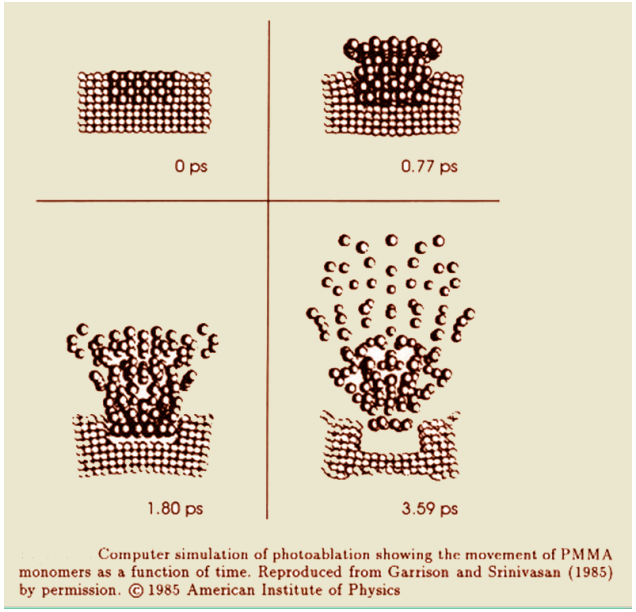


Histological photo of Rabbit cornea immediately following laser treatment.

Refractive surgeries

PRK – Photorefractive keratotomy

LASIK – Laser assisted insitu keratomileusis

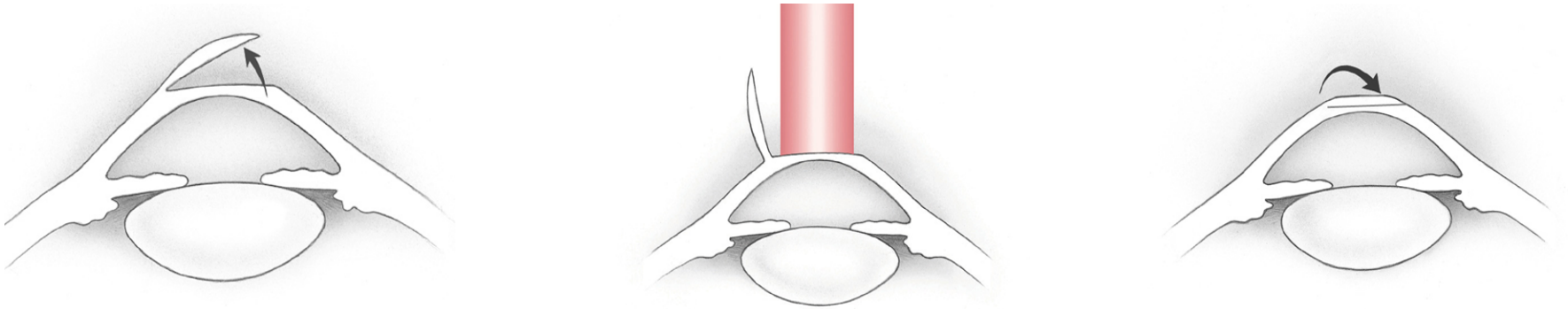


Computer simulation of photoablation showing the movement of PMMA monomers as a function of time. Reproduced from Garrison and Srinivasan (1985) by permission. © 1985 American Institute of Physics

R. Srinivasan, *Science* 1986, 234, 559-565

How LASIK differs from PRK?

- LASER In-situ keratomilieusis (LASIK)
  - First step is the lifting of corneal flap and then ablation
  - Treatment is given beneath the flap



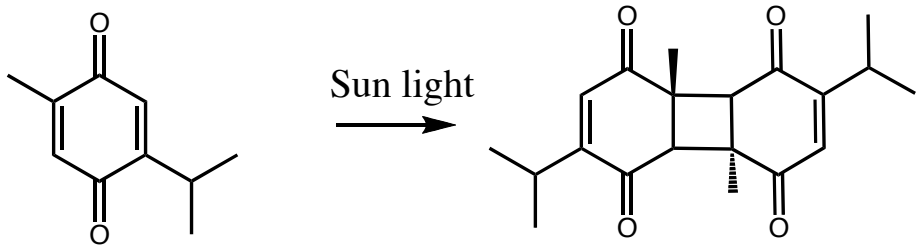
  - Brief recovery time
  - Very low infection risk and low enhancement rate
  - Very low risk of scarring and minimal discomfort

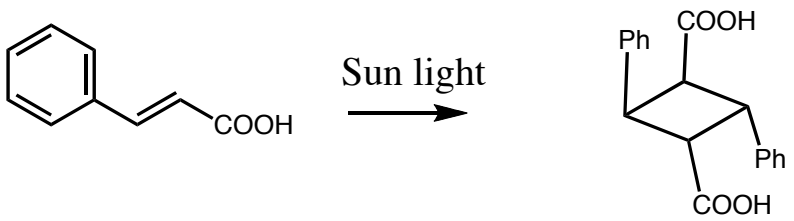
Photolithography

A reaction discovered in 19th century revolutionized the lithographic industry

C. T. Libermann

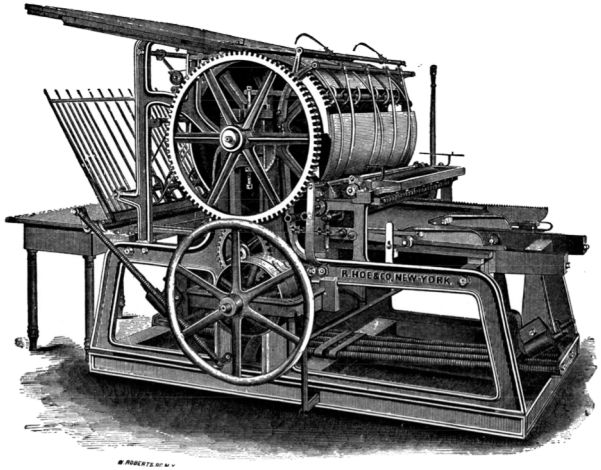
1842–1914





Ann. Chem. Pharm. 158, 300, **1871**

Pre-Lithographic Time



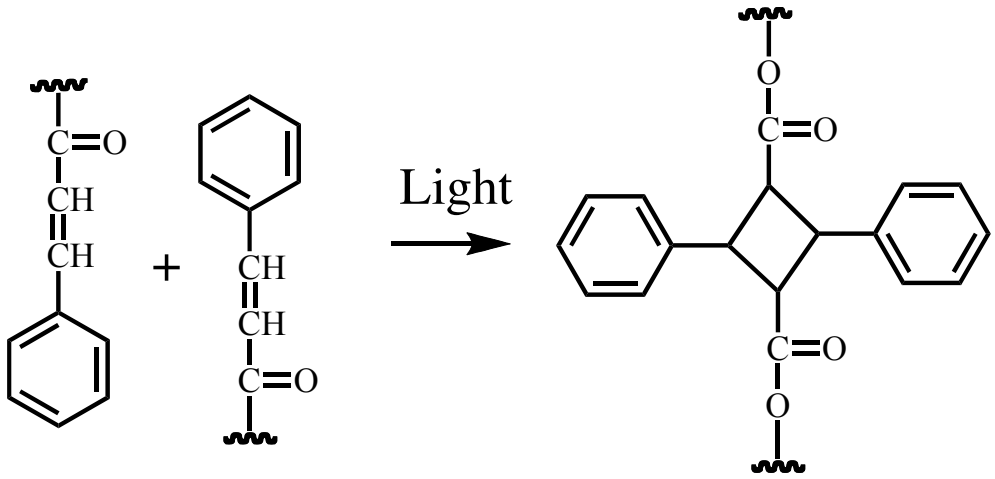
Photolithography: Invention 1949-50

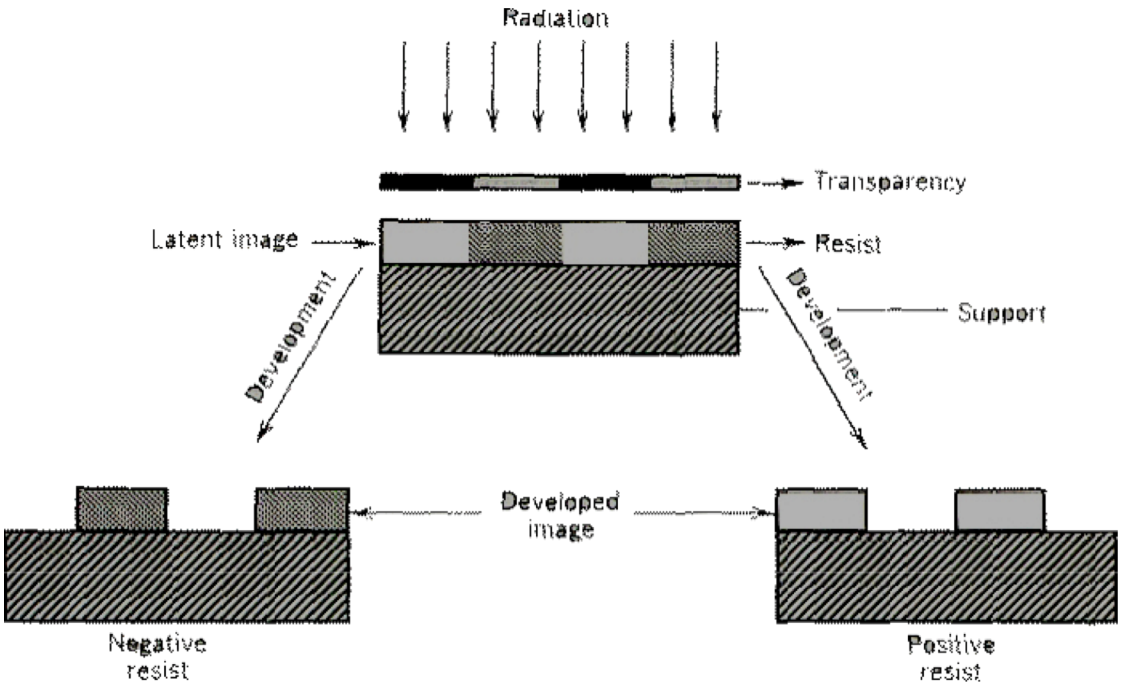
Louis Minsk (Kodak)
Polyvinylcinnamate-Based
Photoressist

Otto Suess (Kalley's)
Diazoquinone-Based
Positive Photoressist

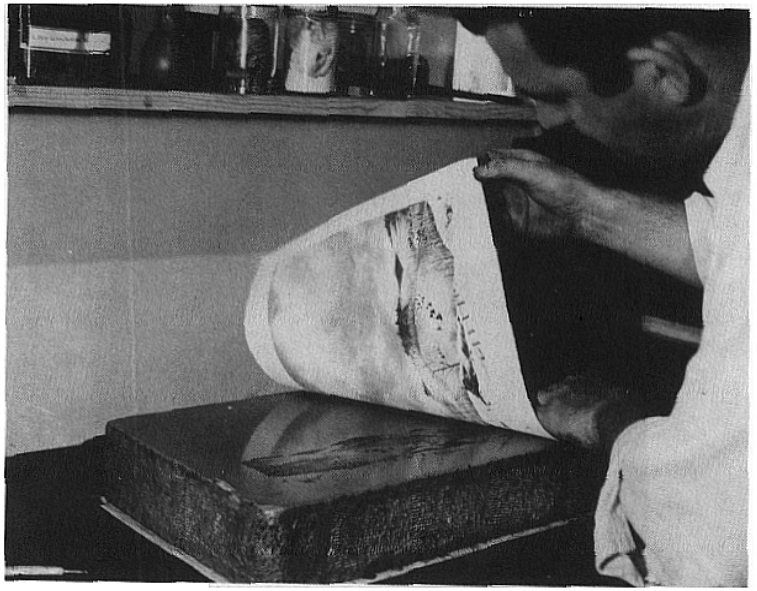
Louis C. Plambeck (DuPont)
Acrylate-Based
Photopolymer Imaging

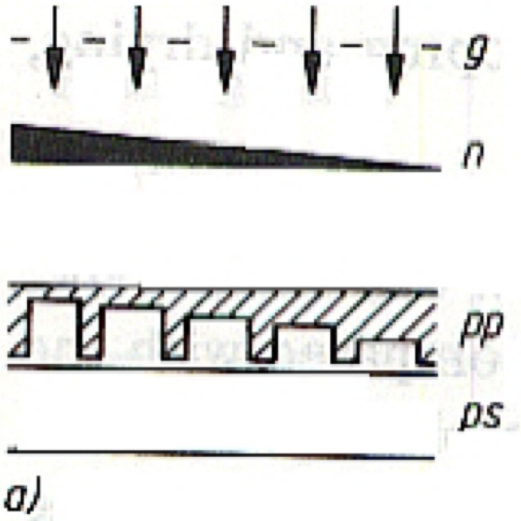
Photoresist

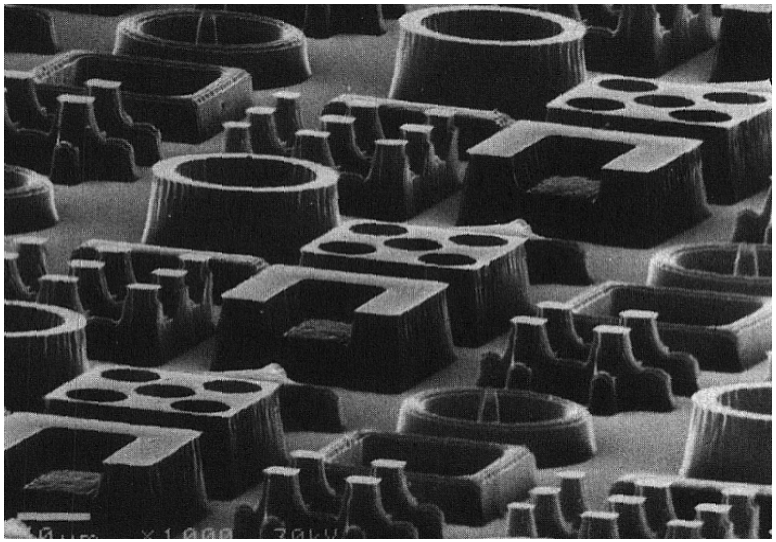


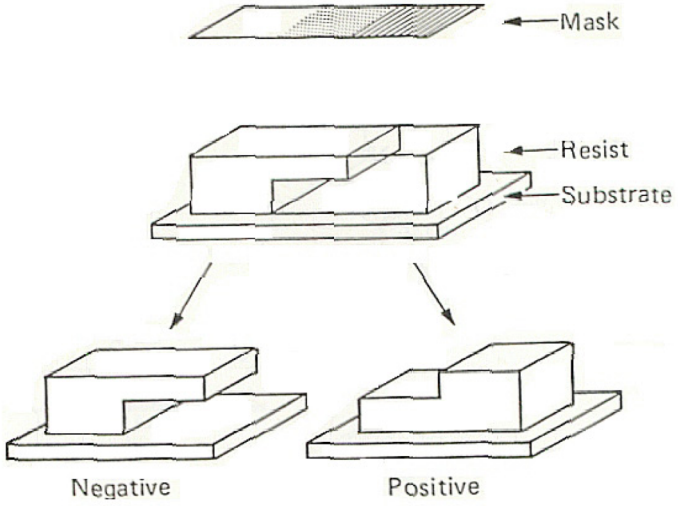


Gray Shading









Applications of the Principles of Photoresists and Lithography

The Workhorses of Electronics and Printing

- **Printing, Litho, Package, Billboards**
- **Color Printing**
- **Printed Circuit Boards (PC)**
- **Integrated Circuit Chips (IC)**
- **Photopatterning-DNA and Biochips**
- **Micromachines**

Lithographic Printing Is the Backbone of Modern Printing Industry

DU PONT PROGRESS REPORT

Better Things for Better Living . . . through Chemistry

WILMINGTON, DEL. MARCH 13, 1958 No. 2a Mid-Atlantic Edition

DU PONT DISPLAYS PLATE AT NEWSPAPER CONFERENCE

Photorelief plates for rotary and flat bed use.

Plans Three Types of Photopolymer Plates

PITTSBURGH, Pa., Mar. 13 — The Photo Products Department of E. I. du Pont de Nemours & Co., Inc., exhibited samples of experimental photopolymer printing plates today to the newspaper production men attending the Mid-Atlantic Newspaper Mechanical Conference.

These plates are composed of a layer of photosensitive plastic (termed photopolymer) bonded to a metal support. As described in a progress report in October, 1957, ultra-violet light exposure of the plate through a high contrast negative (right reading from the emulsion side) causes the plastic to harden throughout its entire depth. Subsequent "wash out" with a dilute alkaline water solution removes the unexposed and unhardened photopolymer leaving the text and art at proper printing height. The exposure and wash out steps can be completed in about 15 minutes.

A Du Pont Photo Products spokesman, W. H. Vinton, Manager, New Products Development, stated that current plans are to market three types of plates — a steel-supported plate about .086 inch thick with .030 inch relief; a steel-supported plate about .060 inch

expected to be available in about two years, the time required to construct production facilities. Sizes up to 20 by 24 inches are contemplated initially.

Present indications are that early use of photopolymer printing plates in newspaper production may be most attractive in direct printing of R.O.P. color, photocomposed advertising and similar areas where quality considerations and the availability of a photographic negative offer many distinct advantages.

This entire page was printed direct from a photorelief plate on a rotary press as an example of present status of the project, but Du Pont personnel stress that final product characteristics have not been firmly established and that considerable developmental work still remains to be done prior to commercialization.

Printing Development Laboratory Established

WILMINGTON, Del.,

Three Color Printing

- Color Printing Requires Color Separation
- Color Printing is Done Through Four Color Processing

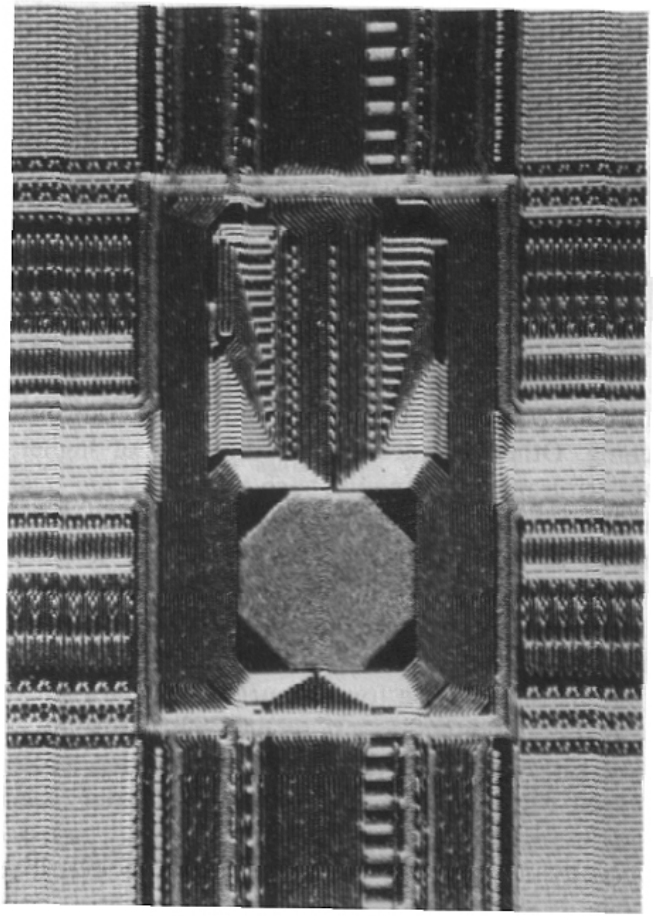
Yellow

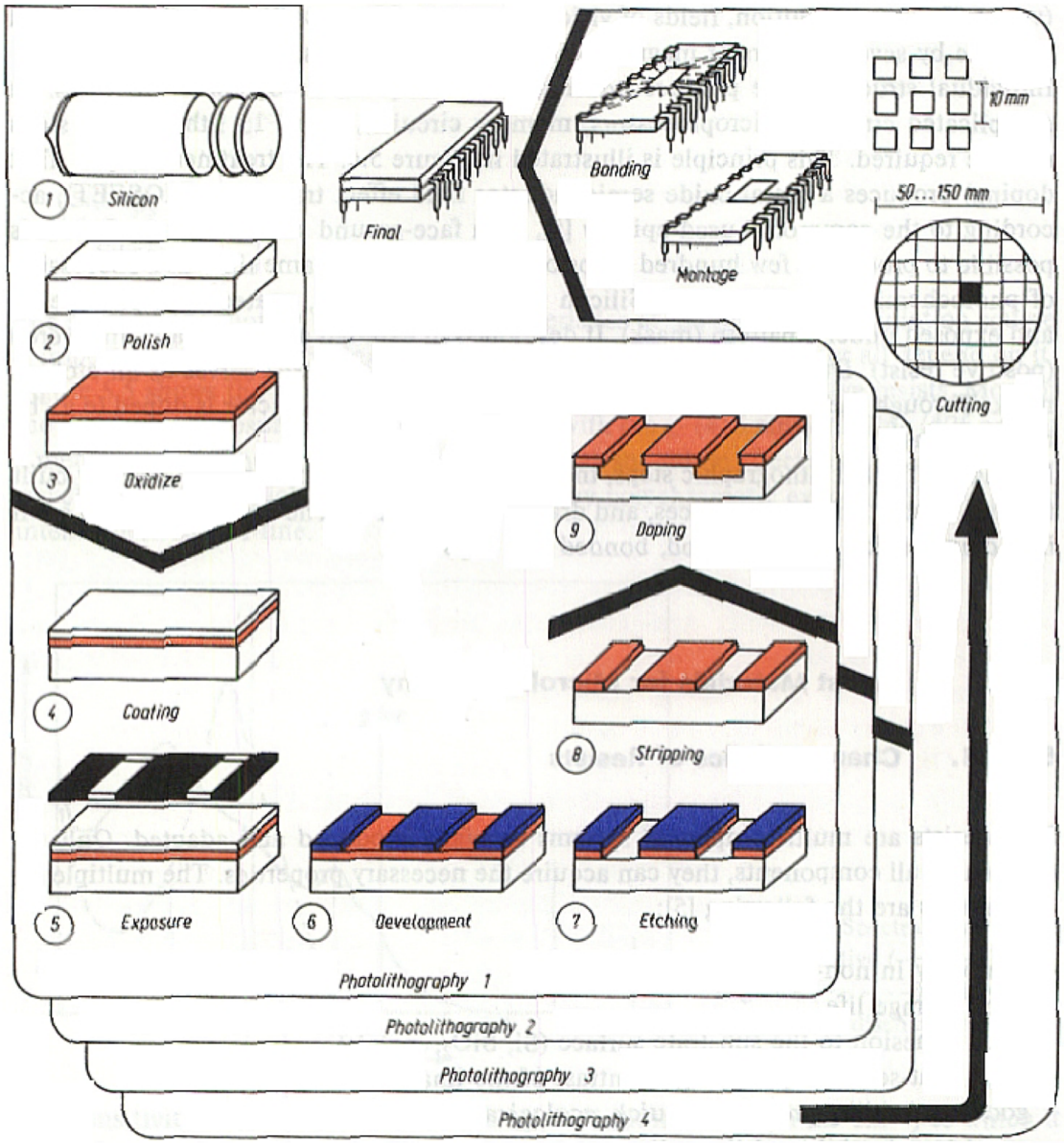
Magenta

Cyan

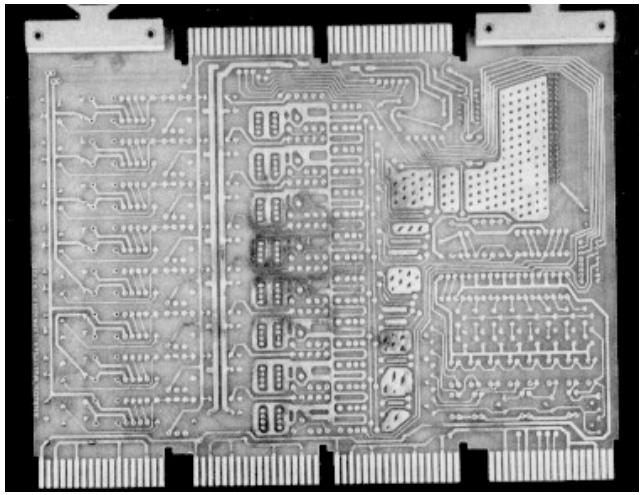
Overlay of the three

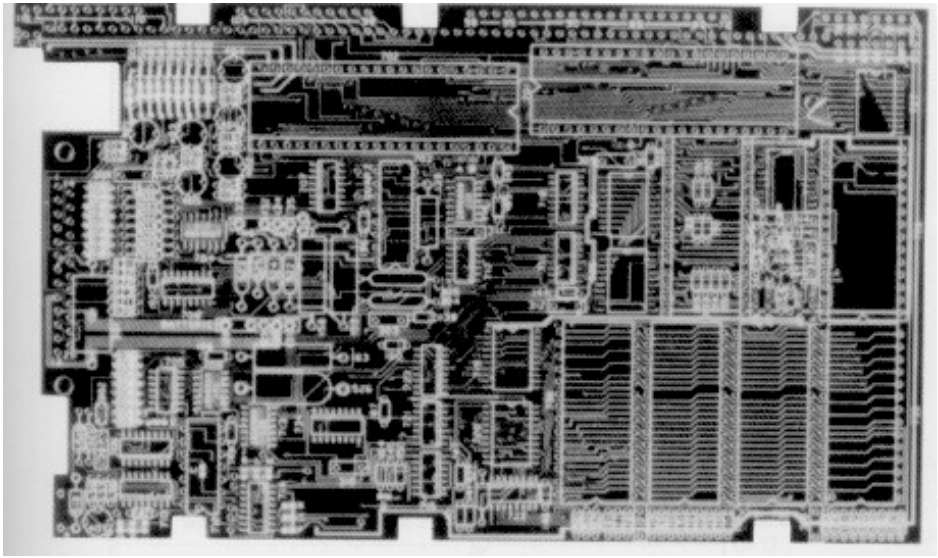
From Sand to Computer Chips

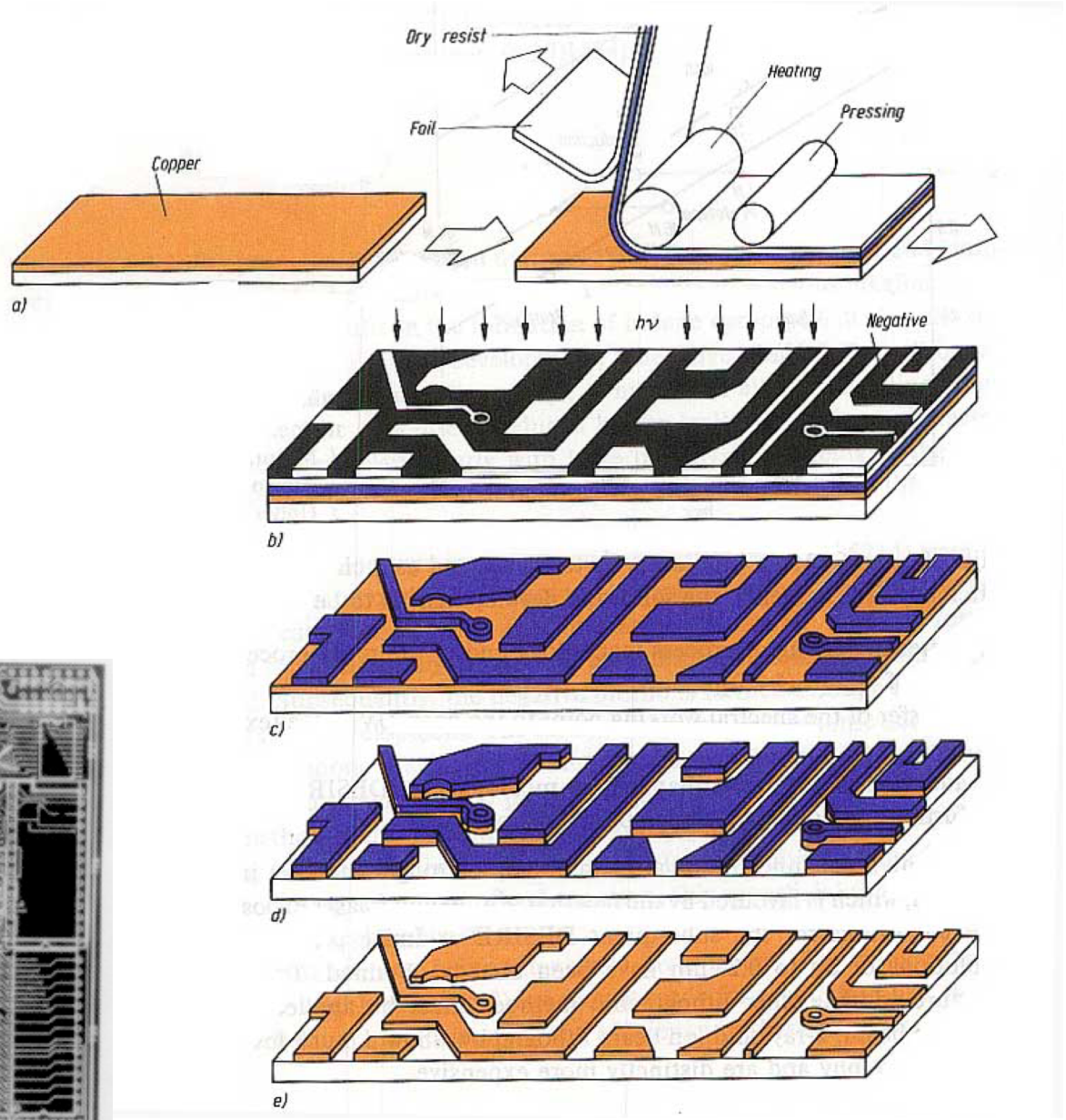




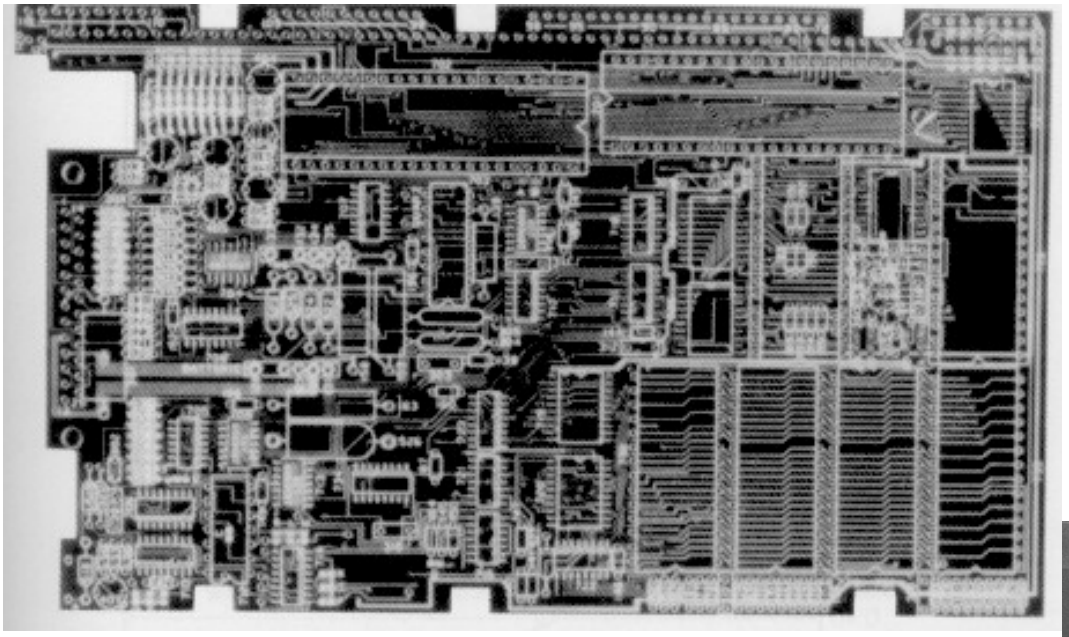
Printed Circuit Board Making



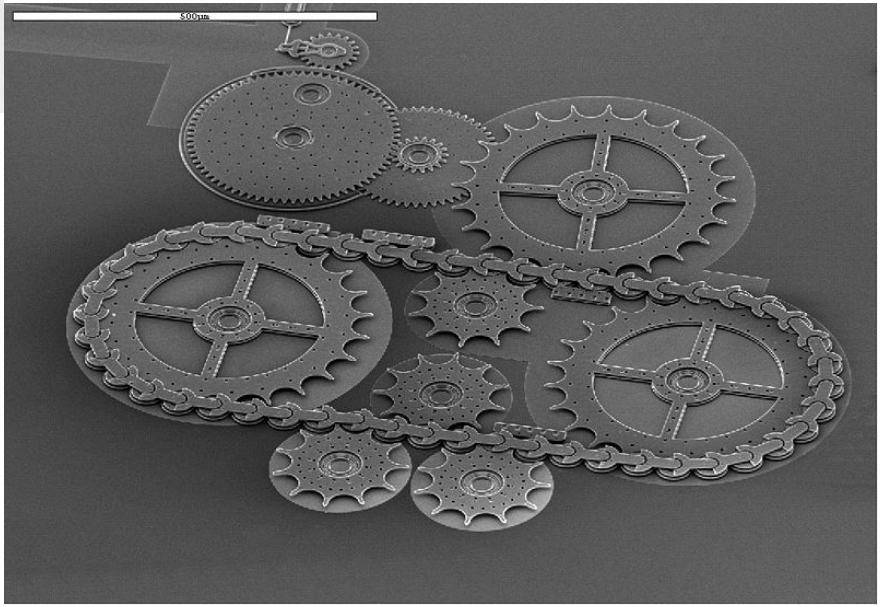




Photolithography Applications in Electronic Industry

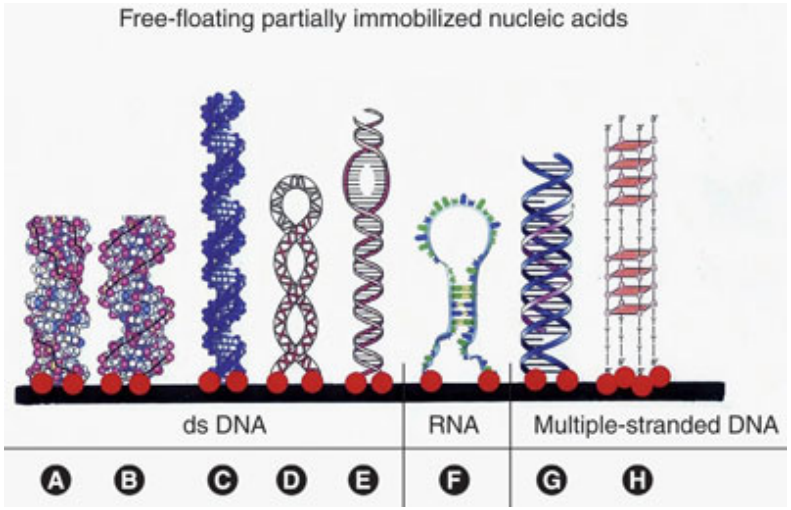


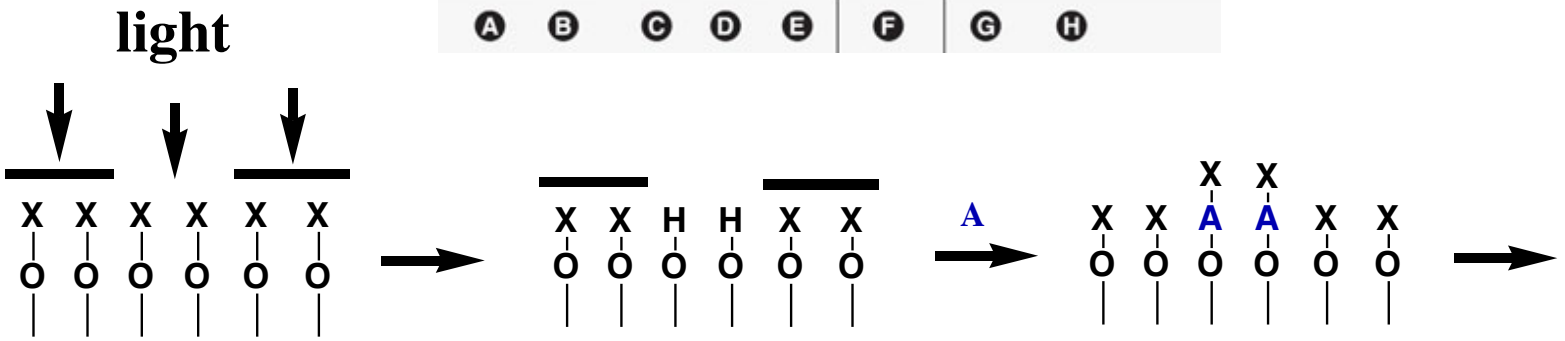
Printed Circuit Boards

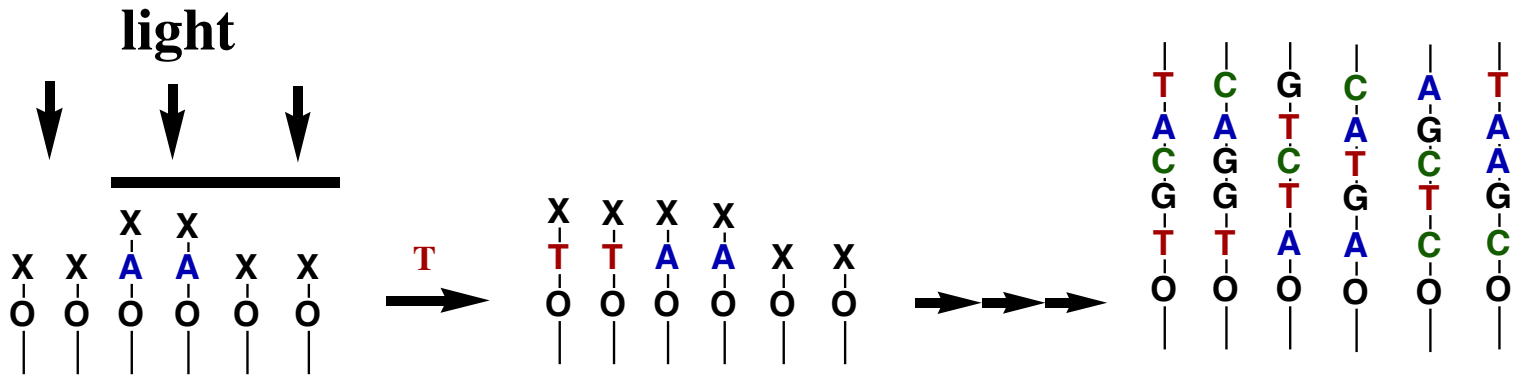


Micro-Electro Mechanical Systems (MEMS)

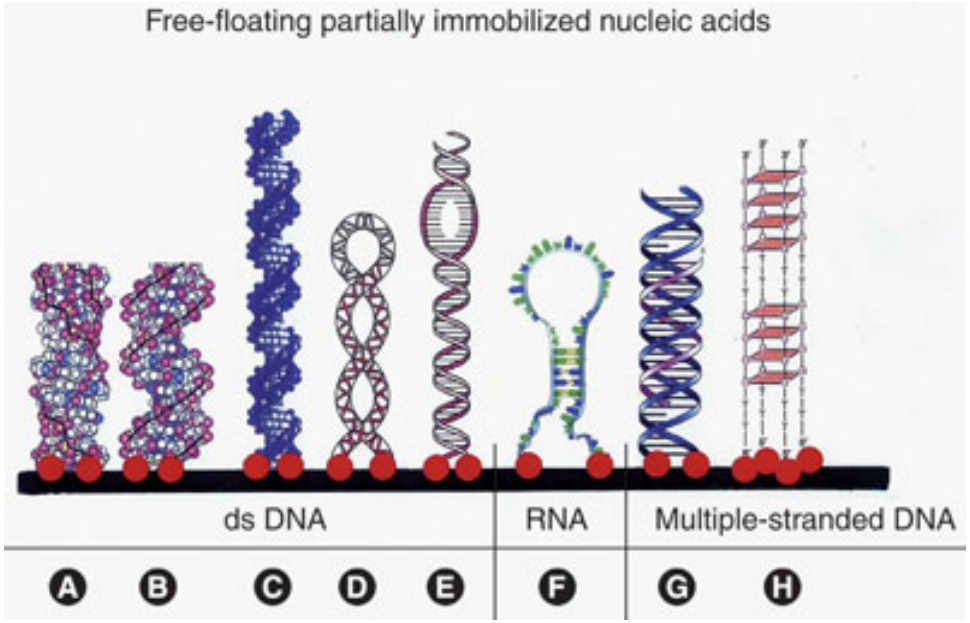
Photo Patterning-DNA Chips

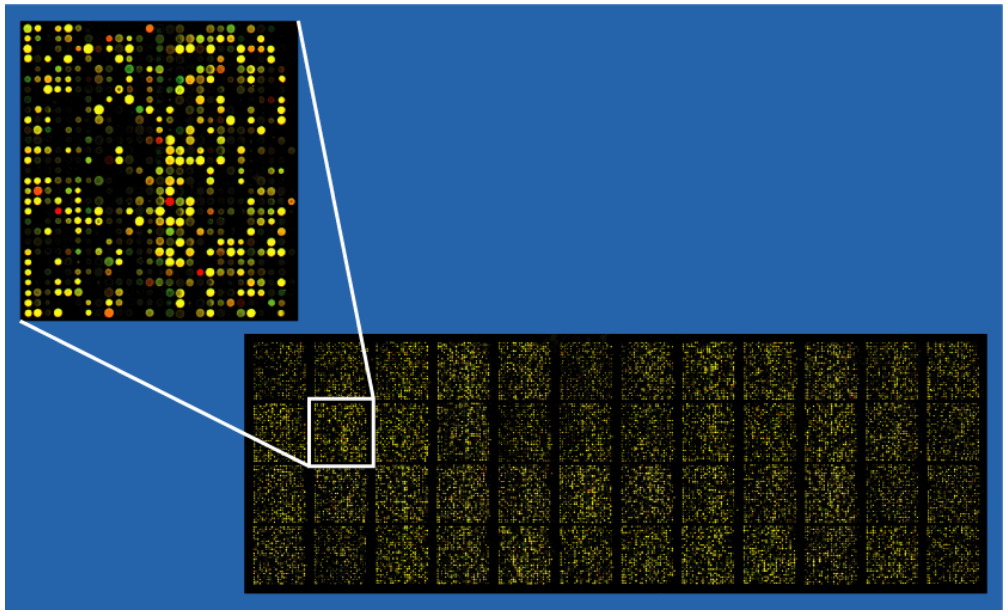






Biosensors Based on Photopatterning





Applications

- blood glucose measurements for diabetes management
- testing food for the presence of pathogenic microorganisms (*Salmonella* and *E. coli)*
- sensing chemical and biological warfare agents

Light in Chemical Industry

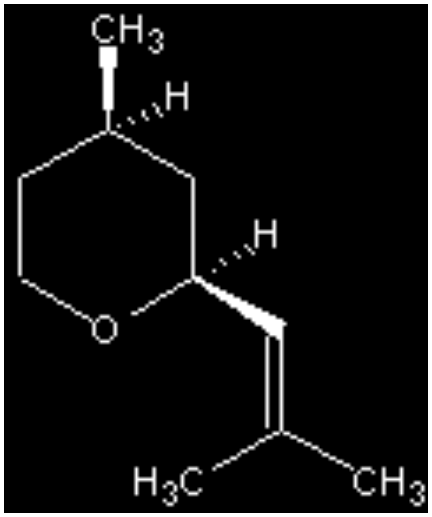
Photochemical synthesis of Rose oxide

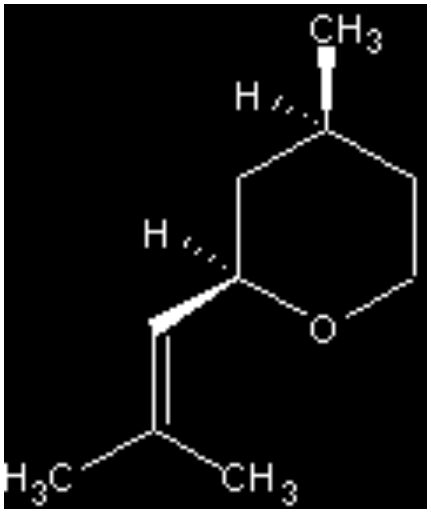
Photochemical synthesis of Vitamin – D

Photooximation - Synthesis of caprolactam

Photochlorination

Rose oxide





(4r,2s)-(-)-cis-roseoxide

floral green with clean sharp, light, rose green note, diffusive, strong (Matsuda); also has been described as powerful fruity.

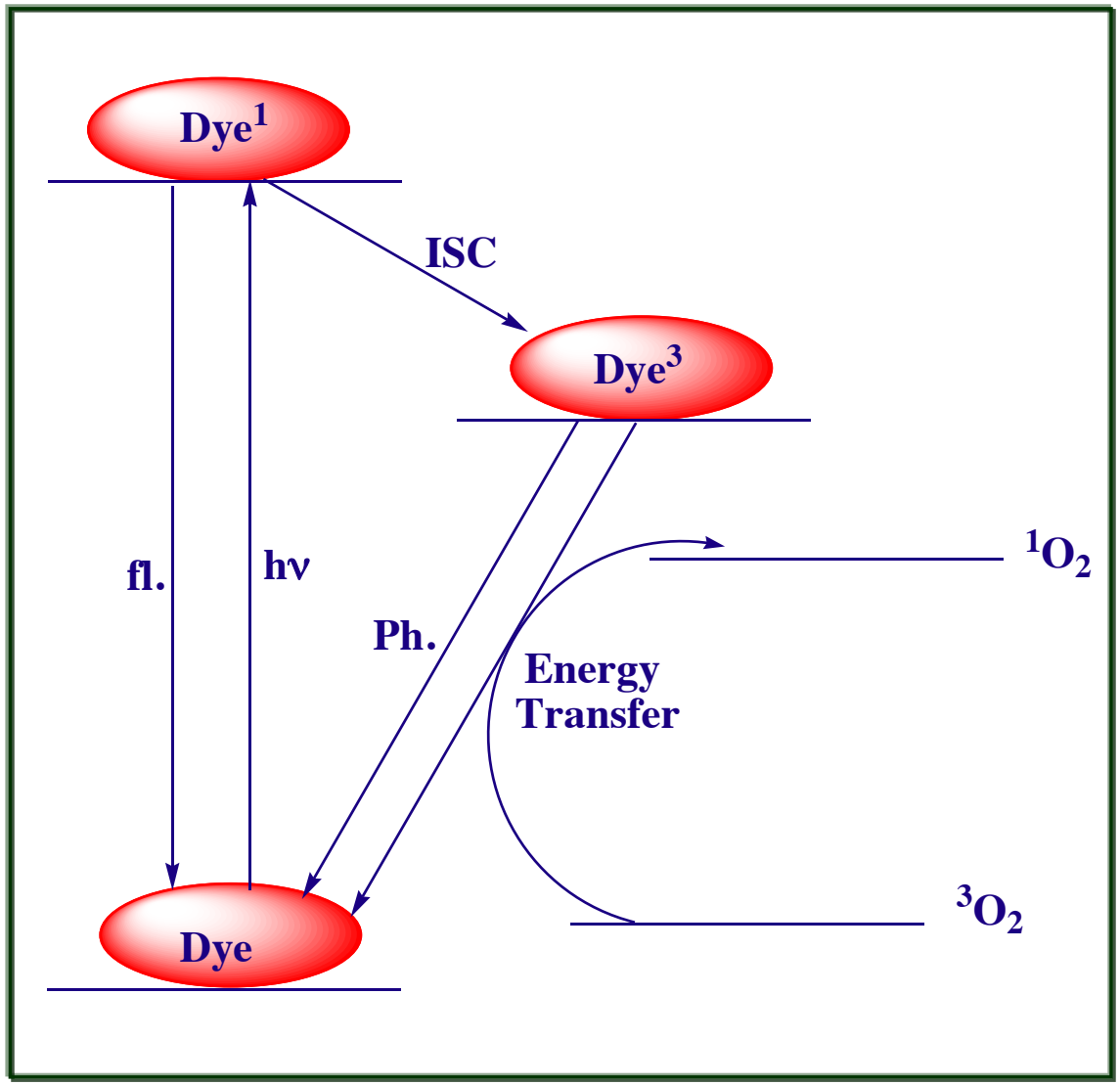
Odor Threshold = 0.5 ppb

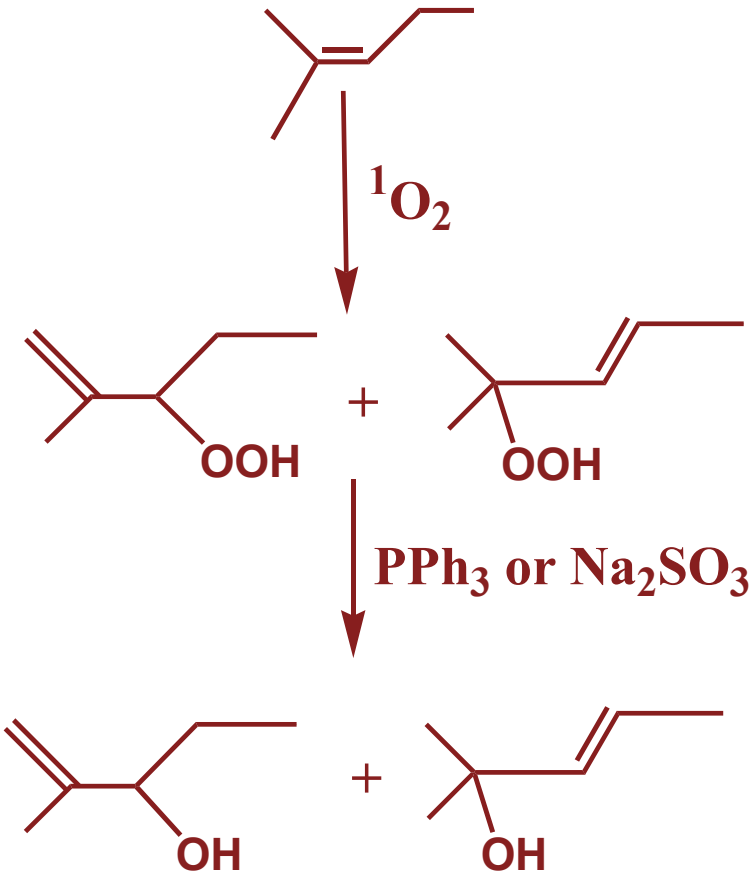
(4s,2r)-(+)-cis-roseoxide

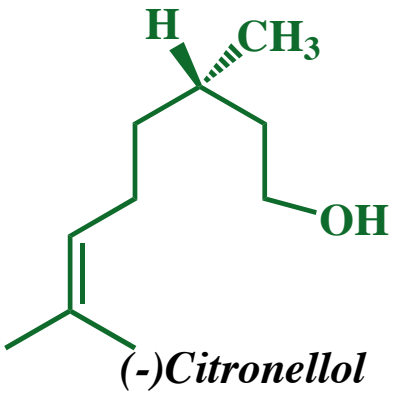
herbal, green floral, hay green, earthy, heavy (Matsuda); also has been described as sweet, floral

Odor Threshold = 50 ppb

Schenk ‘ene’ - Reaction

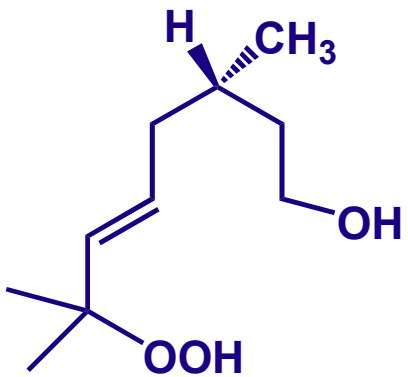




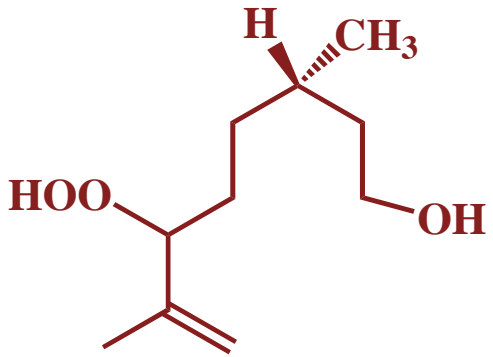


(-)Citronellol

1) hν, Rose bengal, O_2



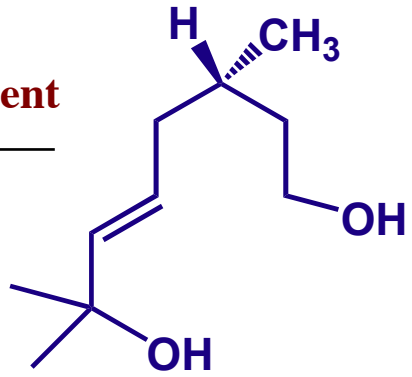
+



Na_2SO_3

Citronellol is separated from citronella oil by fractional distillation

H^+ / Rearrangement



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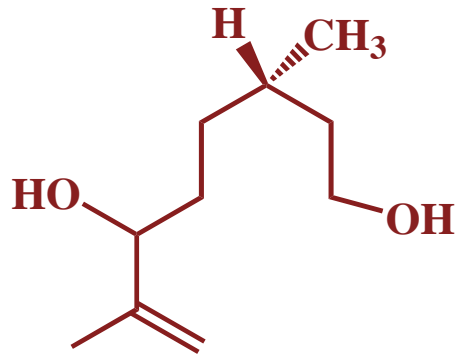
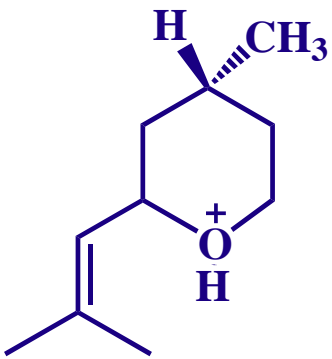
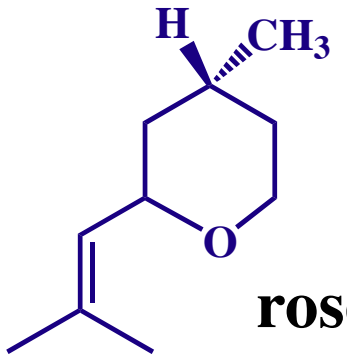




$-H^+$

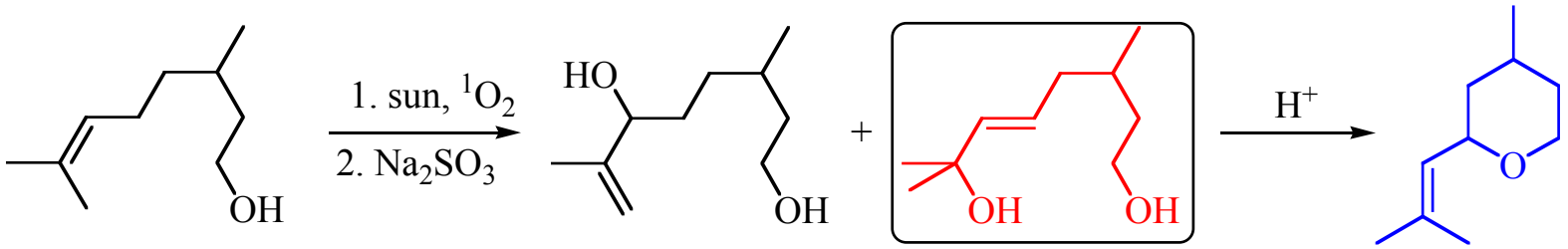


rose oxide

Photograph of the cylindrical immersion type reactors used by Dragoco for the production of (-)-rose oxide

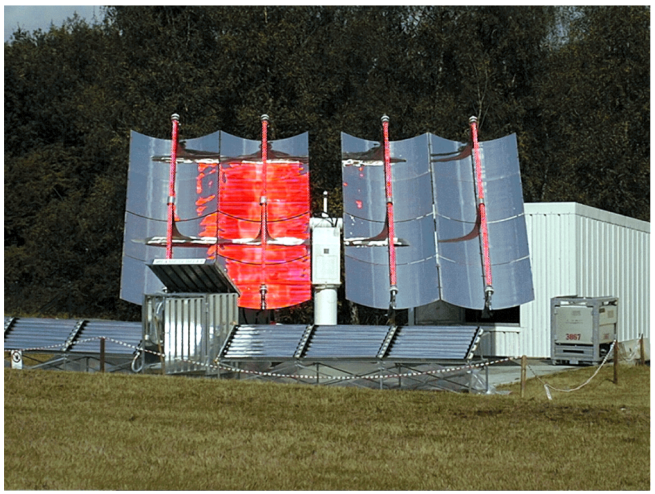
The reactor is about 3 m tall, and is equipped with a 5 k W light source.

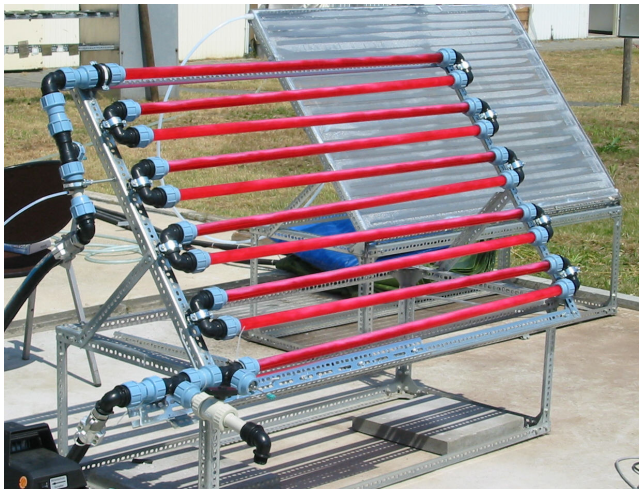
Scanned from *Photochemical technology,* Braun, A. M., Maurette, M-. T., Oliveros, E.



citronellol

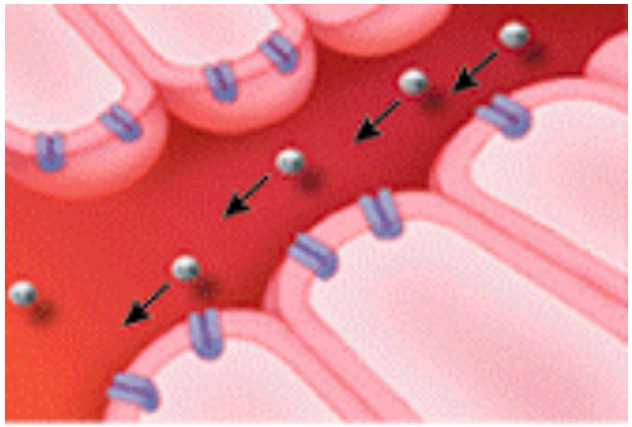
rose oxide



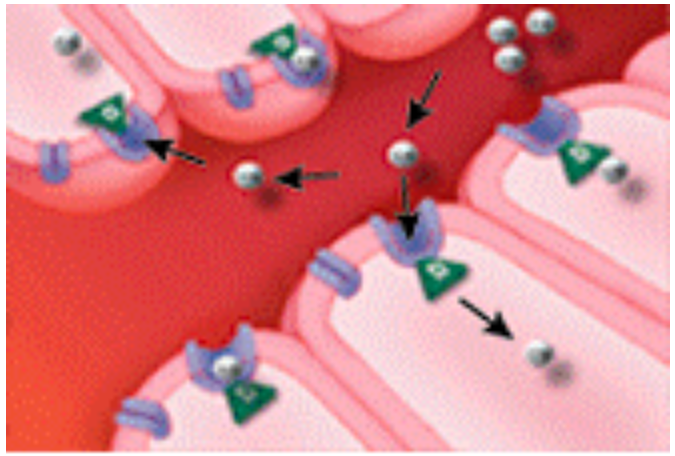


Courtesy of Prof. M. Oelgemöller

Vitamin D is absolutely necessary for the efficient absorption of calcium and phosphate from our diet



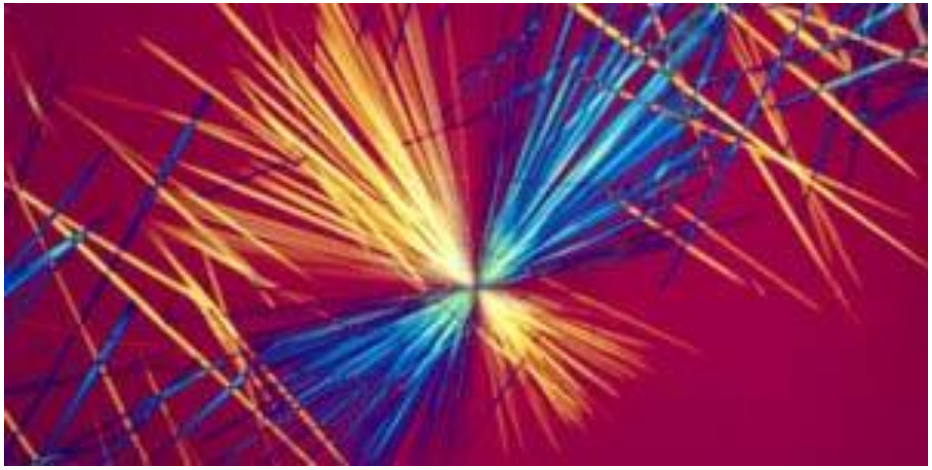
Without vitamin D, the calcium passes through the digestive system unused.



Vitamin D is essential for the body's absorption of calcium.

Child with rickets

At the present time almost all milk sold commercially in the United States has 400 IU of chemically synthesized vitamin D_3 added per quart.



vitamin D_2 (ergocalciferol: plant origin)

vitamin D_3 (cholecalciferol: animal origin).

Vitamin D crystals

Commercially synthesized by Roche-Vitamins

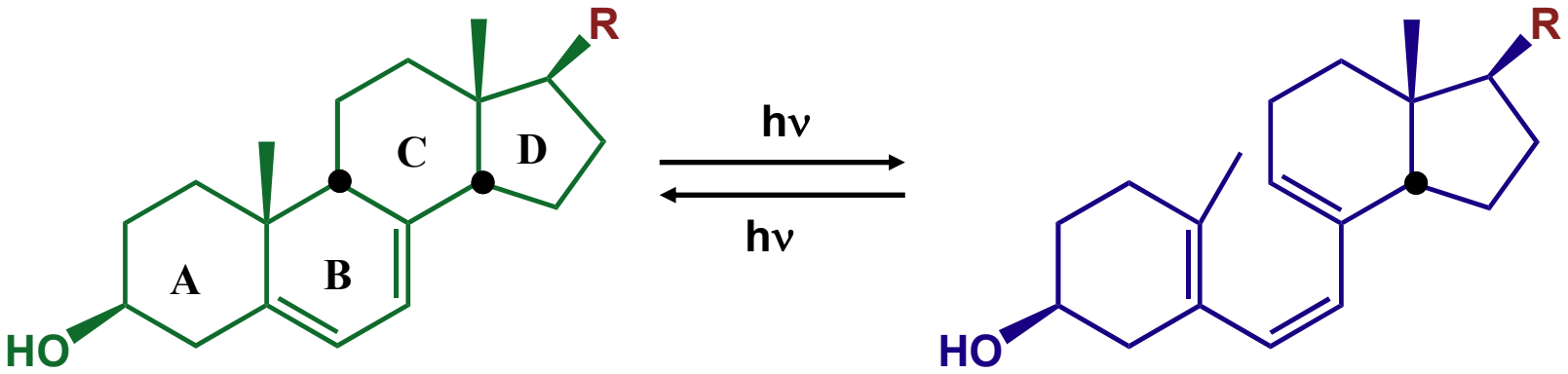
Commercial production of vitamin D_3 :

a) 7-dehydrocholesterol

Extracted from animal skins (cow, pig or sheep) followed by an extensive purification.

b) cholesterol.

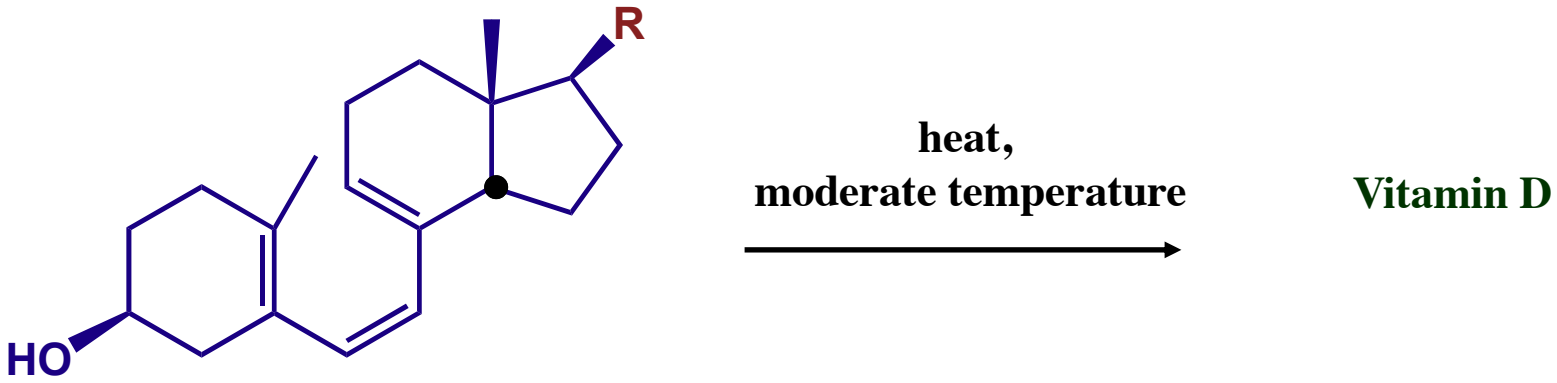
Extracted from the lanolin of sheep wool and can be converted to 7-dehydrocholesterol.



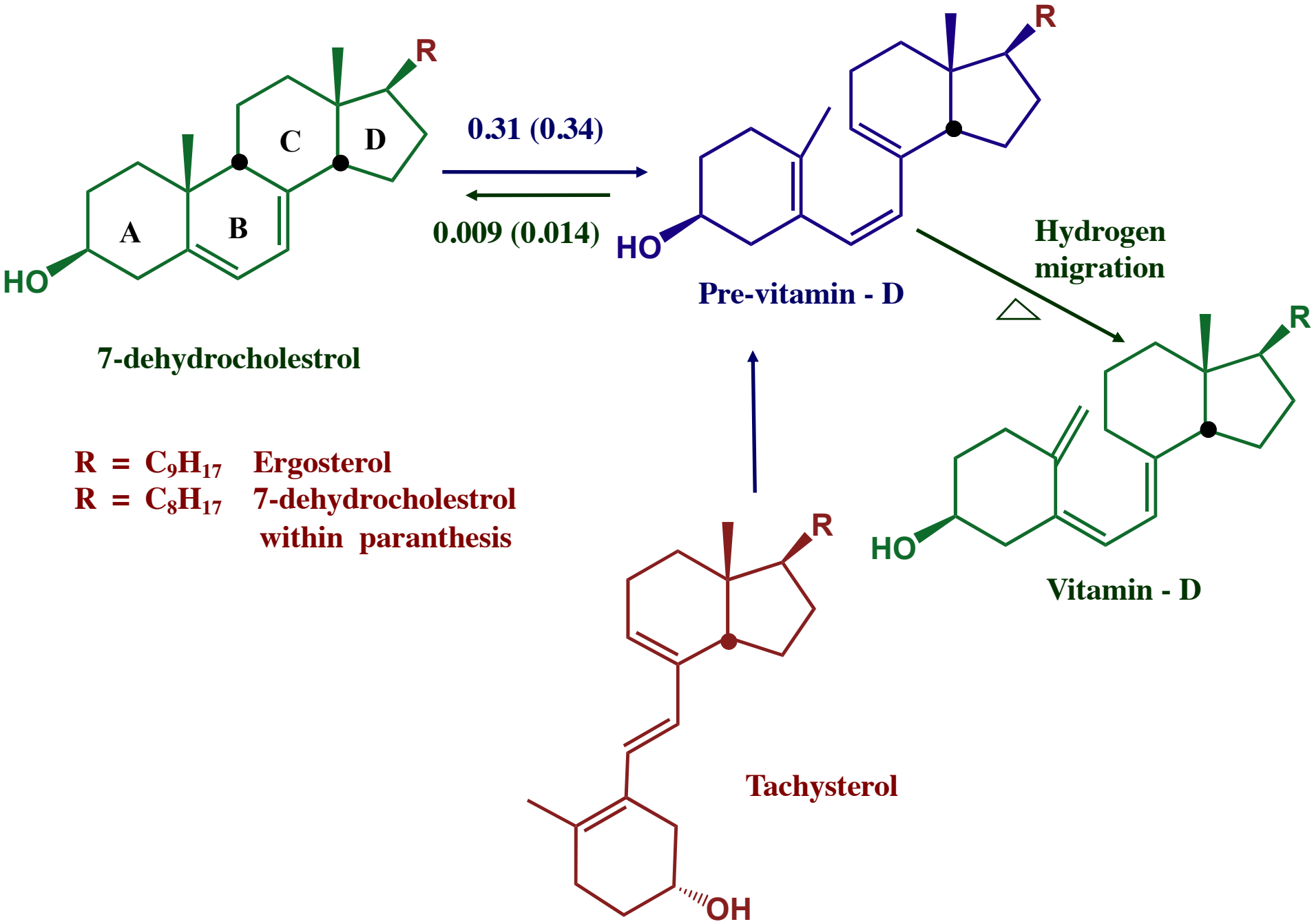
R = C_9H_{17} ergosterol
R = C_8H_{17} 7-dehydrocholestrol

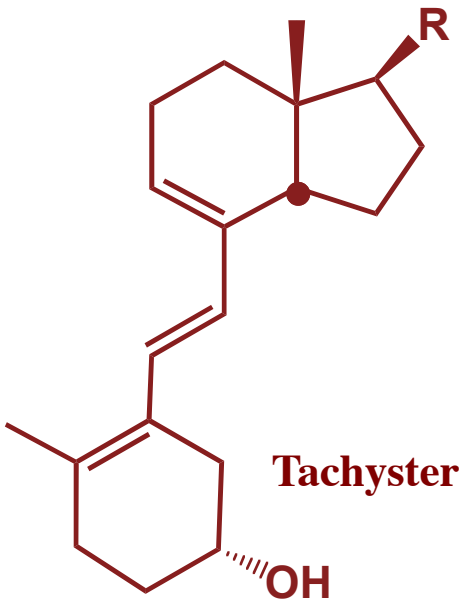
ergosterol ⟶ Pre-vitamin-D_2
7-dehydrocholestrol ⟶ Pre-vitamin-D_3

The ring opening take place from the first excited singlet state



Vitamin D

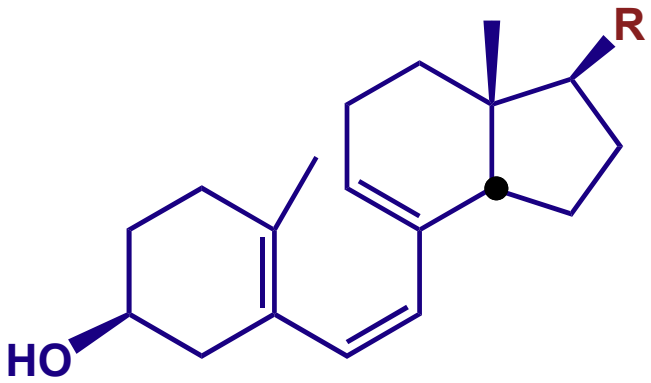

R
C
D
A
B
HO
0.31 (0.34)
0.009 (0.014)
HO
R
Pre-vitamin - D
Hydrogen
migration
7-dehydrocholestrol
R = C9H17 Ergosterol
R = C8H17 7-dehydrocholestrol
within paranthesis
R
HO
Vitamin - D
R
Tachysterol
OH



Tachysterol (Tch)

(Sens. 0.15)

(Sens. 0.58)

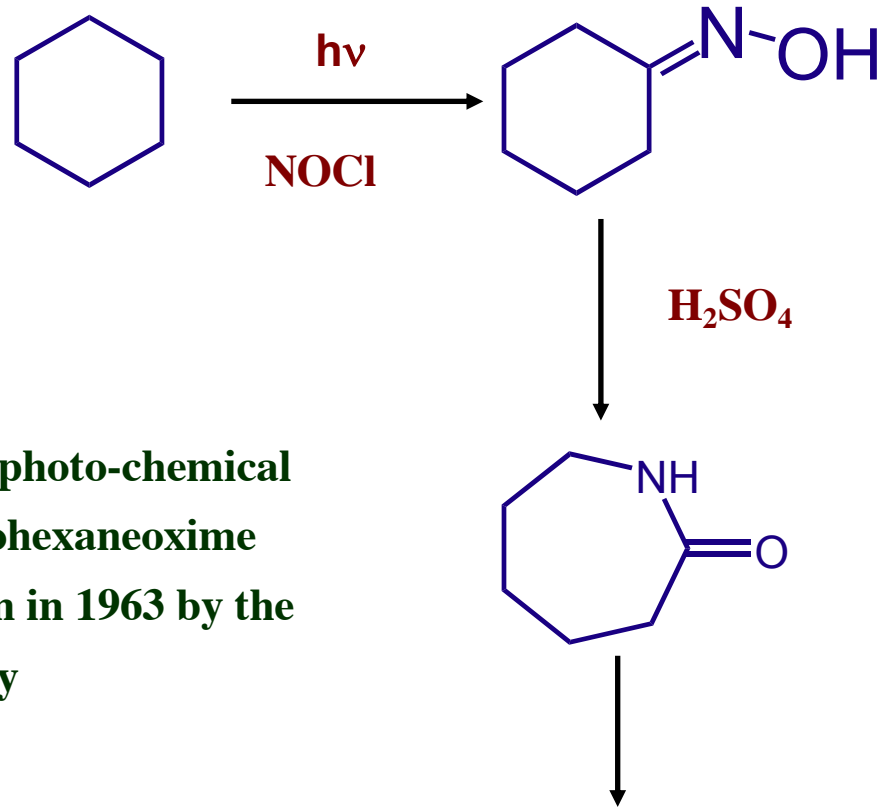


Pre-vitamin - D (P-D)

Sensitizer	E_T KJ Mol^{-1}	(P-D/Tch)
Benzopheonone	286.3	2.6
Anthraquinone	260.8	2.1
2-Naphthylphenylketone	247.8	1.5
Benzil	225.0	1.8
9-Fluorenone	222.8	4.4
Benzanthrone	196.5	5.6
7,12-Dimethylbenzanhracene	185.2	16.3

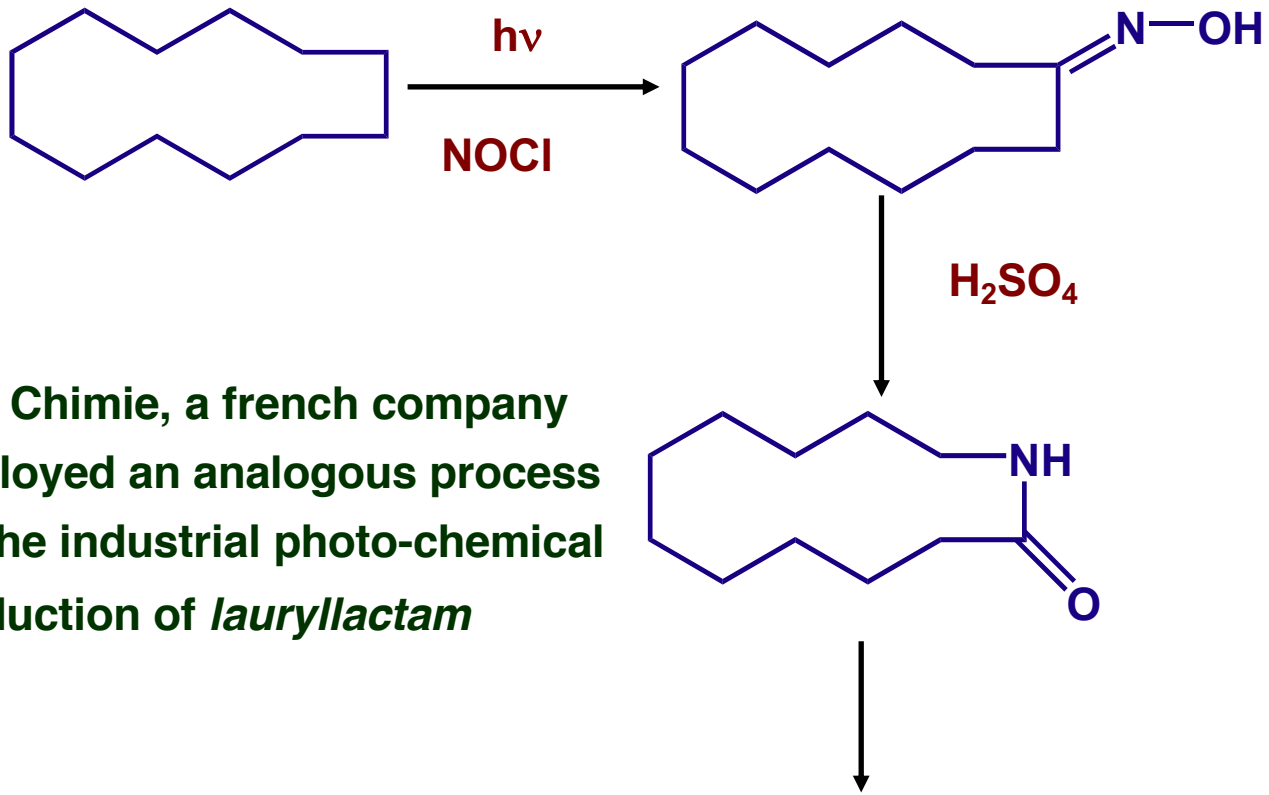
Initial ratio (P-D/Tch)= 0.5; solvent=ethyl ether.

Photo-oximation of cyclohexane - industrial synthesis of *caprolactam*



The first unit for the photo-chemical manufacture of cyclohexaneoxime was installed in Japan in 1963 by the Toyo Rayon Company

Photo-oximation of cyclododecane – industrial synthesis of *lauryllactam*



ATO Chimie, a french company employed an analogous process for the industrial photo-chemical production of *lauryllactam*

Photochemical technology, **Braun, A. M., Maurette, M-. T., Oliveros, E.**

Tessenderlo's chemicals platform in Limburg, Belgium.

Photochlorination

The photochlorination plant produce

a)15,000 tonnes of benzyl chloride and benzylidene chloride.

b) 7,000 tonnes of benzaldehyde.

These are some new addition to its range of synthetic organic products.

Investment, totals ~ FRF 170 million

New chlorinated toluene derivatives production unit, Capacity > 60,000 tonnes a year

Photo-oximation

- **Photo-oximation is a special case of photo-nitrosylation.**
- **Accidentally discovered by Lynn in 1919.**
- **Important use in industrial application.**

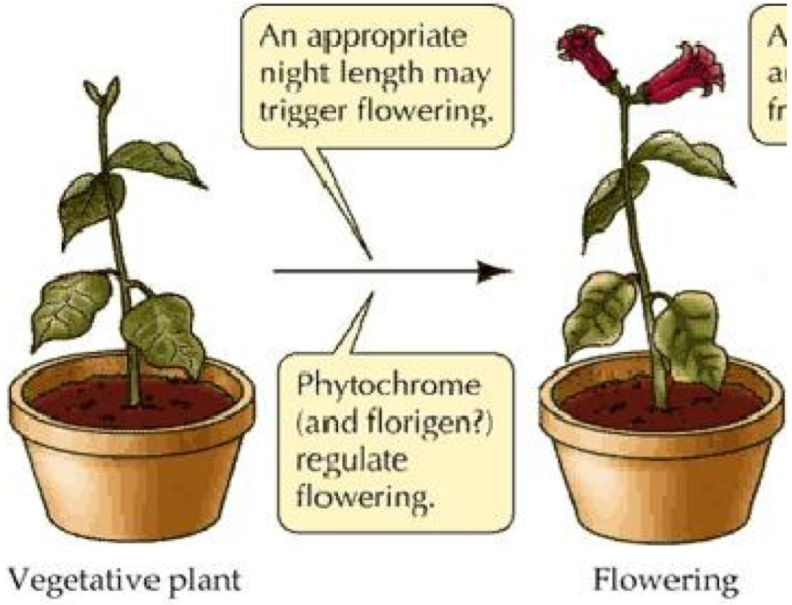
Light and Life

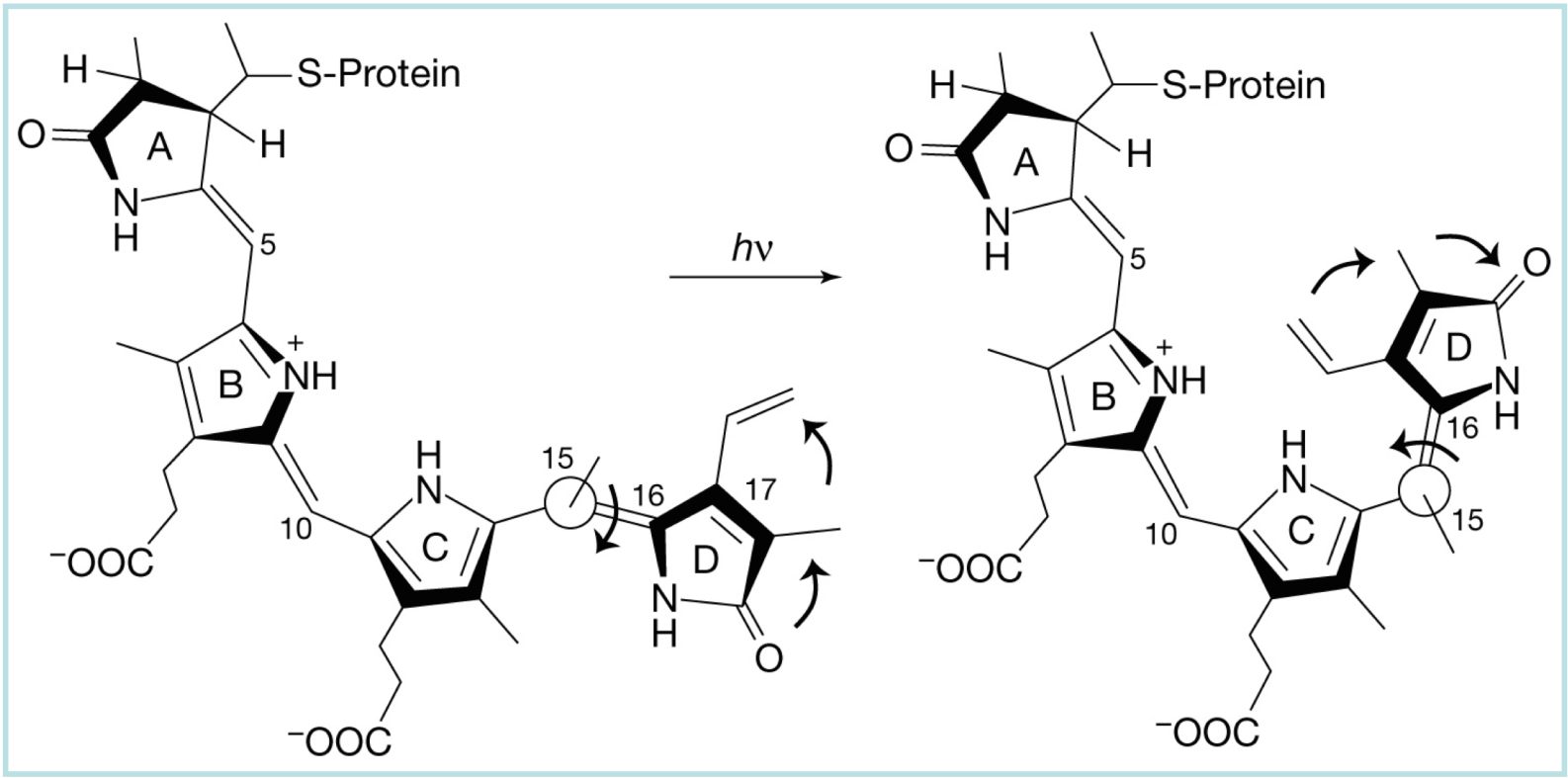
- Photomedicine
- Lithography
- Industrial Synthesis of Chemicals
- Solar Energy Conversion
- TiO_2: Environmental Cleanup
- Photography, Xeorography and Holography
- Sunsscreen, Photochromic Glass
- Photostabilization and Photocuring
- Molecular sensors and machines

Photochemistry in Real Life Systems

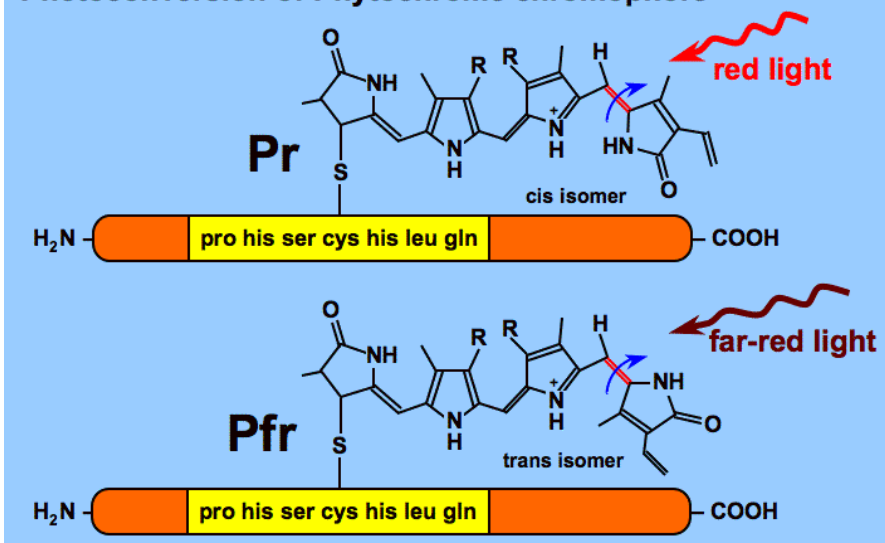
- **Phytochrome - circadian clock** *(cis-trans)*
- **PYP and plant growth** *(cis-trans)*
- **Vision** *(cis-trans)*
- **Phototropism** (e-transfer)
  (bending and growth of plants)
- **Photosynthesis** (e-transfer)

Phytochrome
Circadian clock



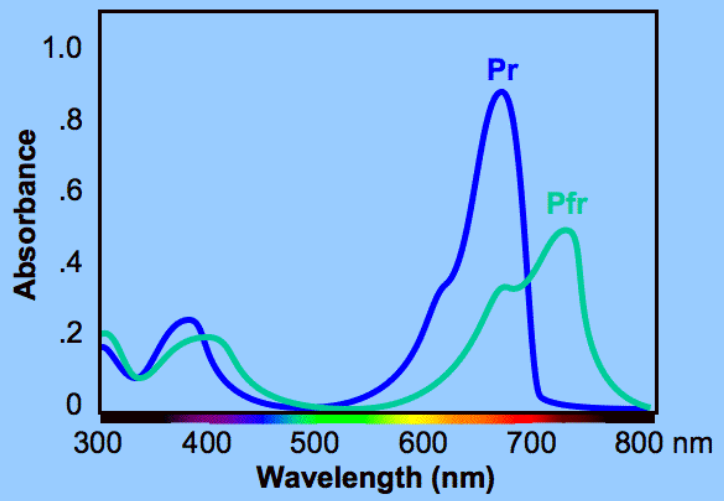


Photoconversion of Phytochrome chromophore

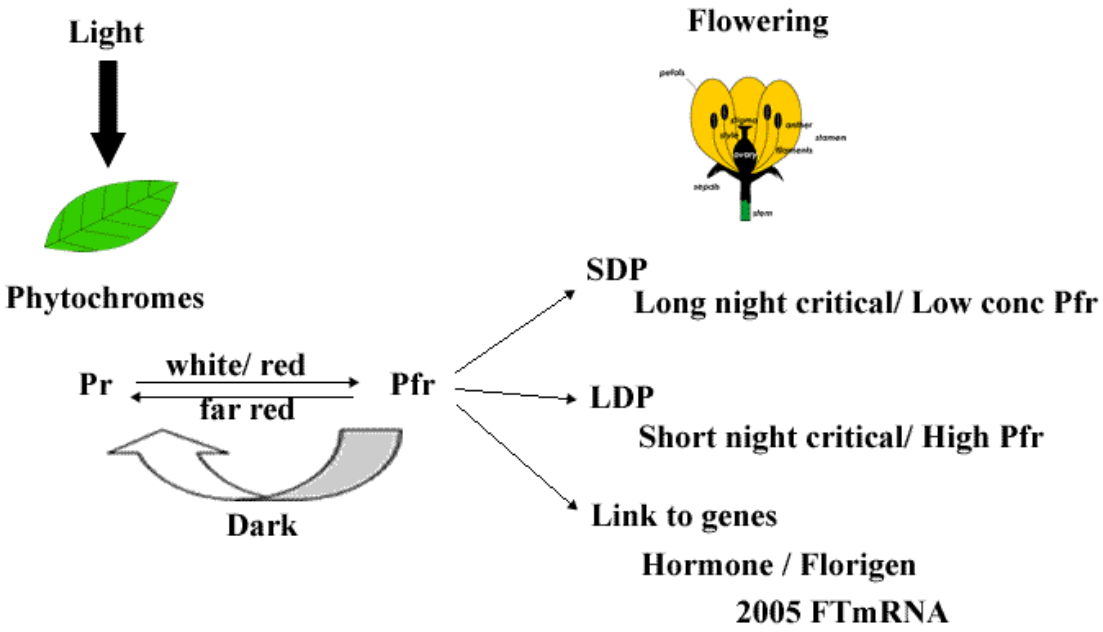


In red light, the phytochrome is in Pfr (trans) form
In far-red light, the phytochrome is in Pr (cis) form

The absorption spectra of the two forms of phytochrome

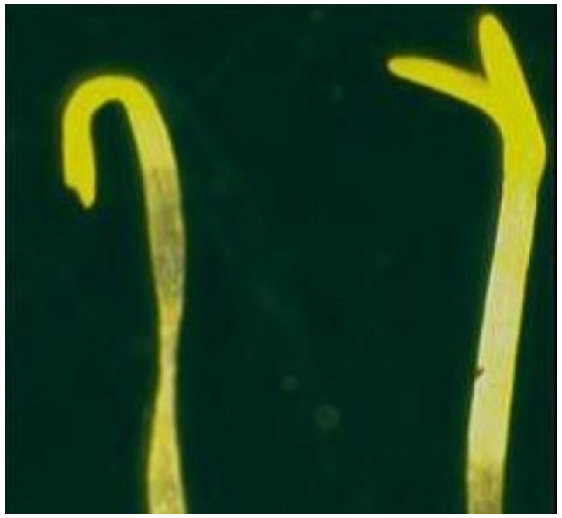


The Pr form of phytochrome absorbs red light
The Pfr form of phytochrome absorbs far-red light

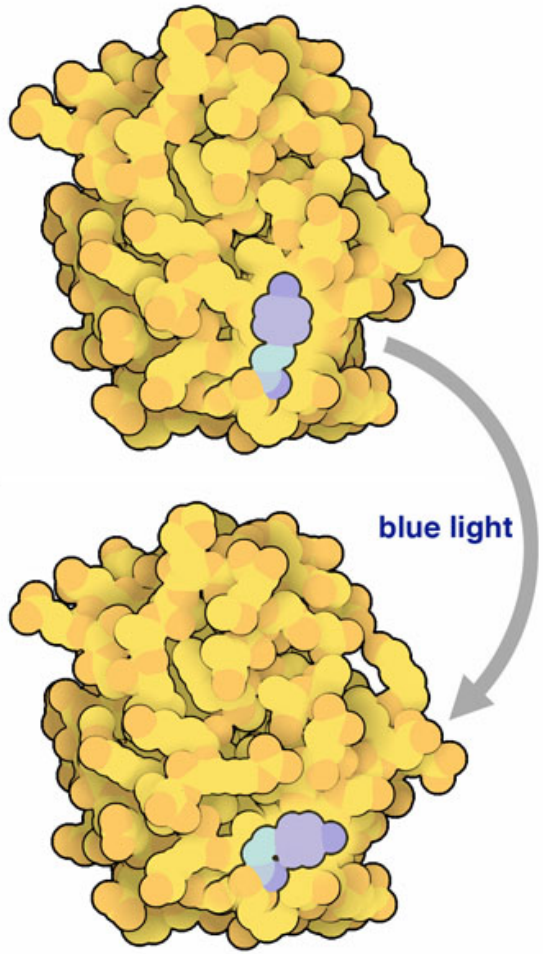


Role of Photoactive Yellow Protein (PYP) in plant growth

In dark



In light



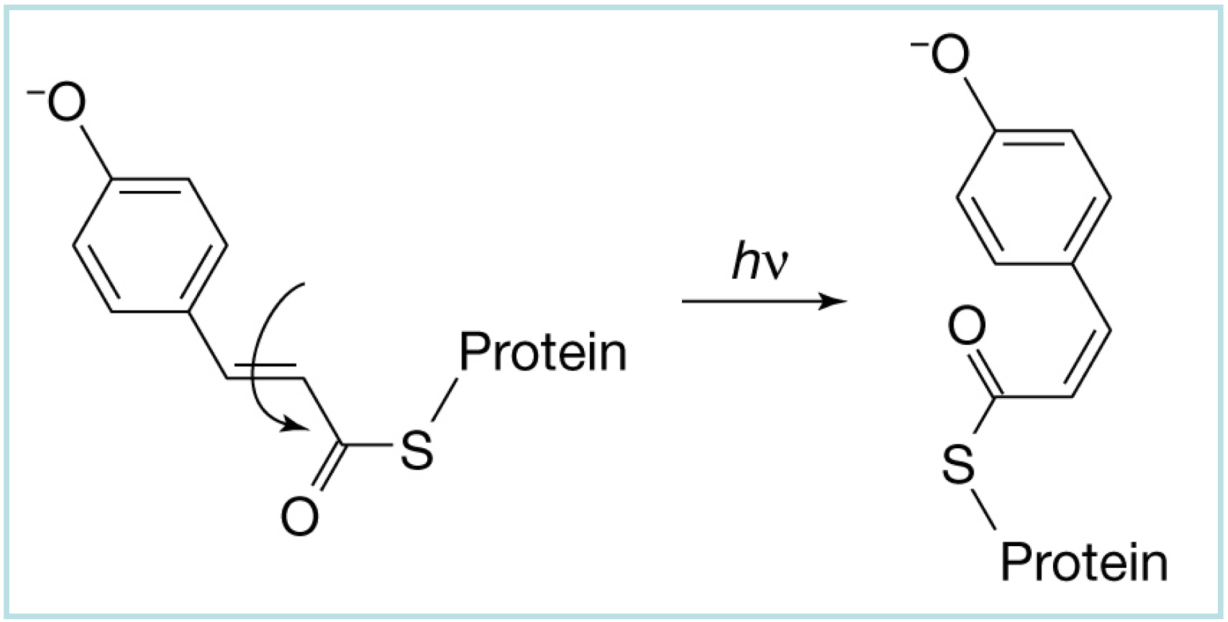
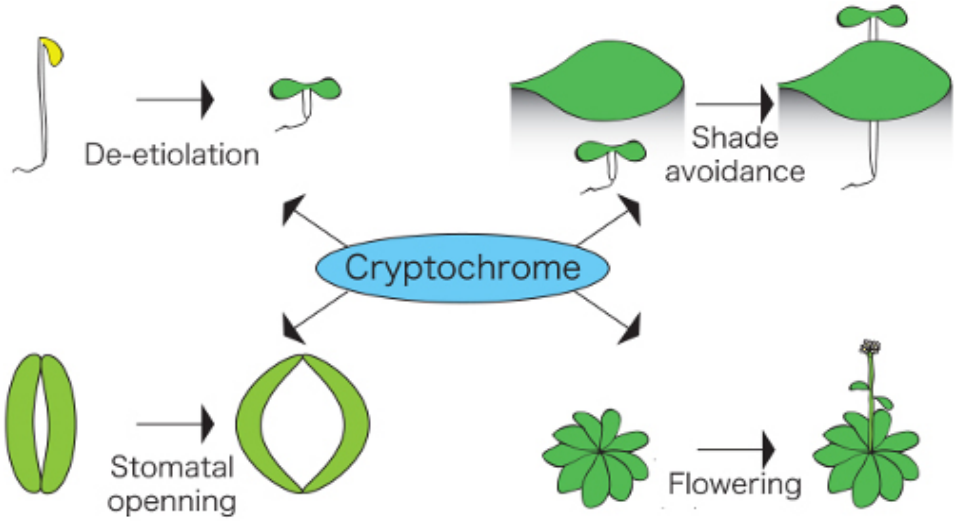
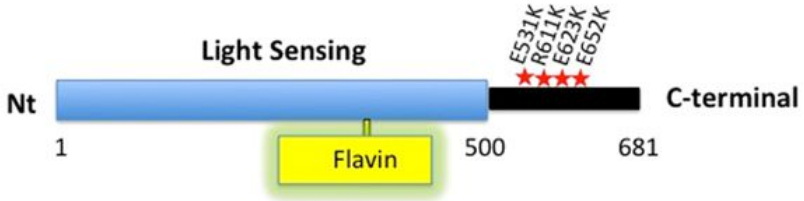


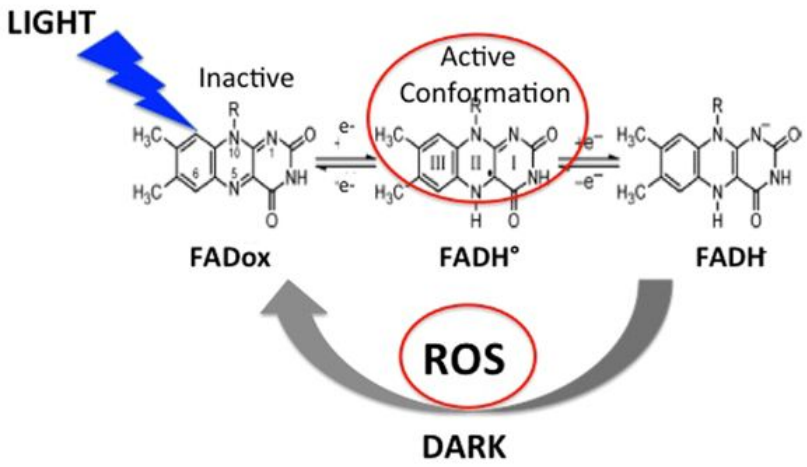
Photo-taxi in plants

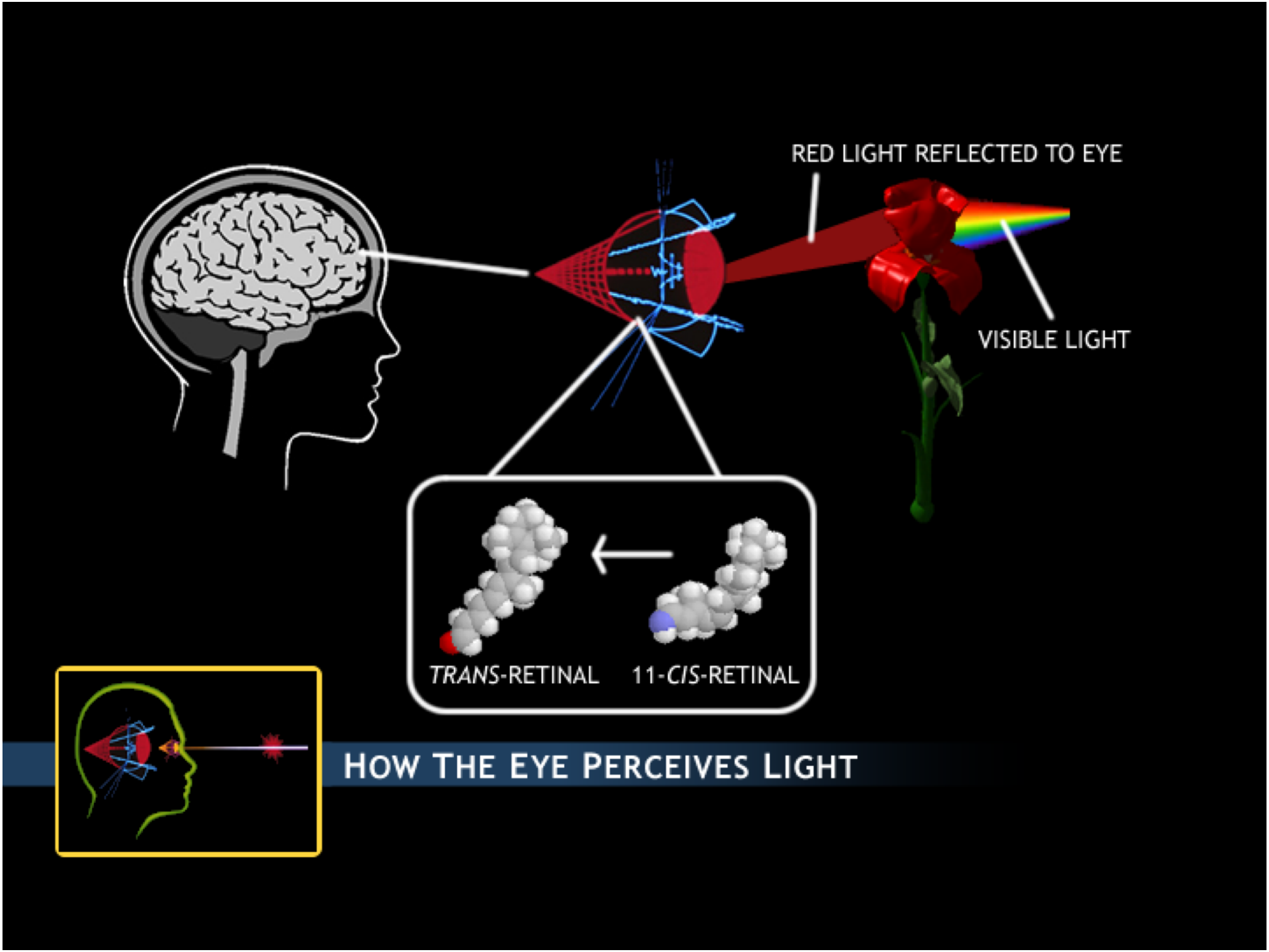


a.

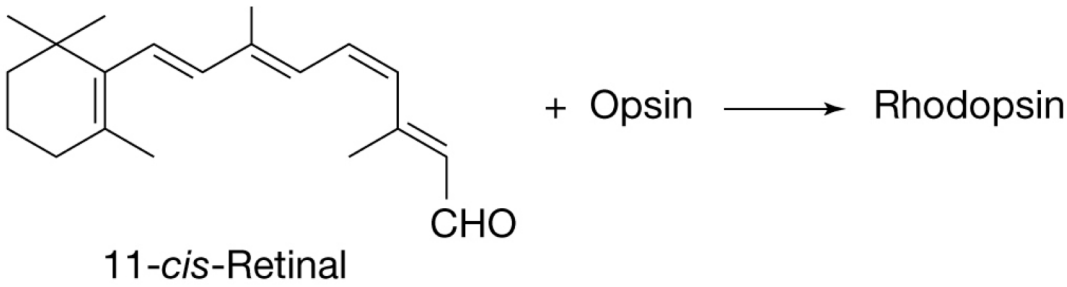


b.

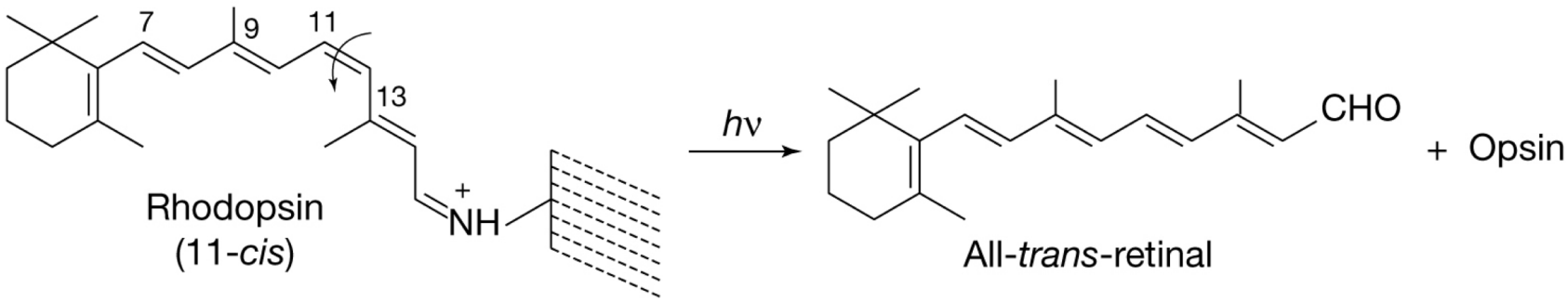




How The Eye Perceives Light

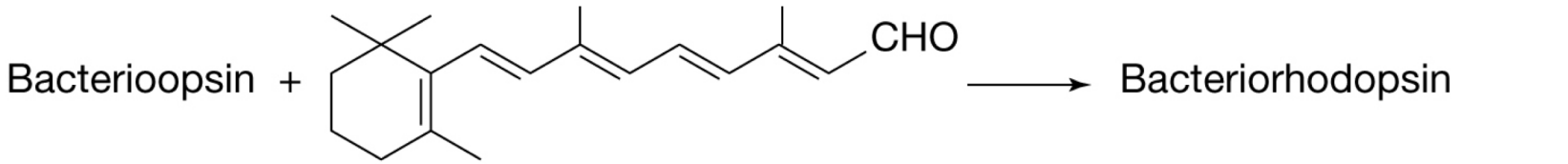


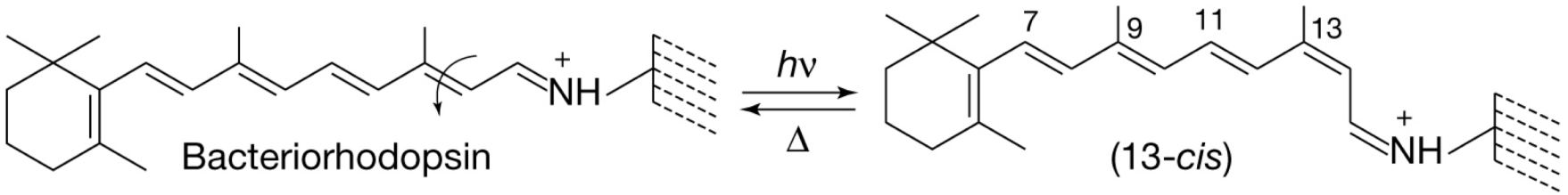
11-*cis*-Retinal



Rhodopsin (11-*cis*)

All-*trans*-retinal

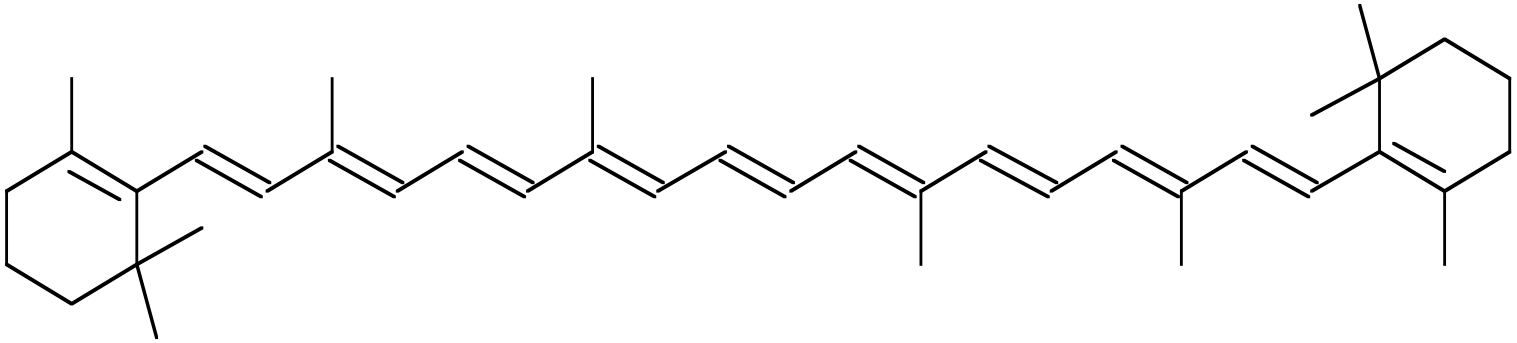




Bacteriorhodopsin

(13-*cis*)

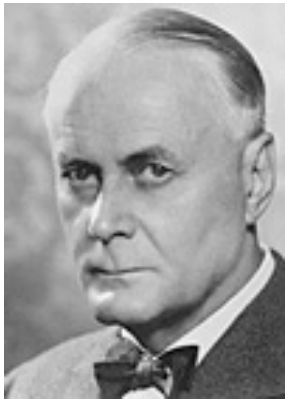
β-Carotene



11 double bonds

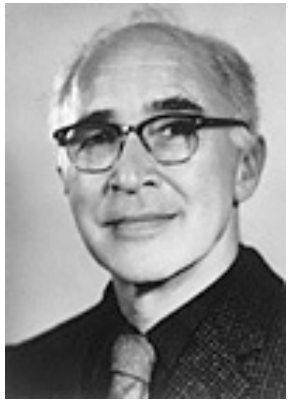
λ_{max} 460 nm (ε 139,000)

The Nobel Prize in Physiology or Medicine 1967



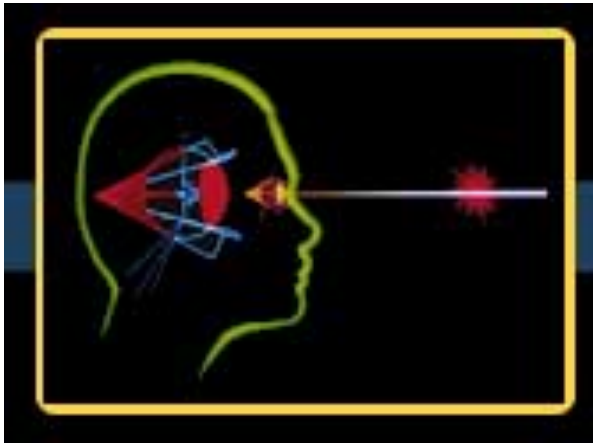
Ragnar Granit

Haldan Keffer Hartline

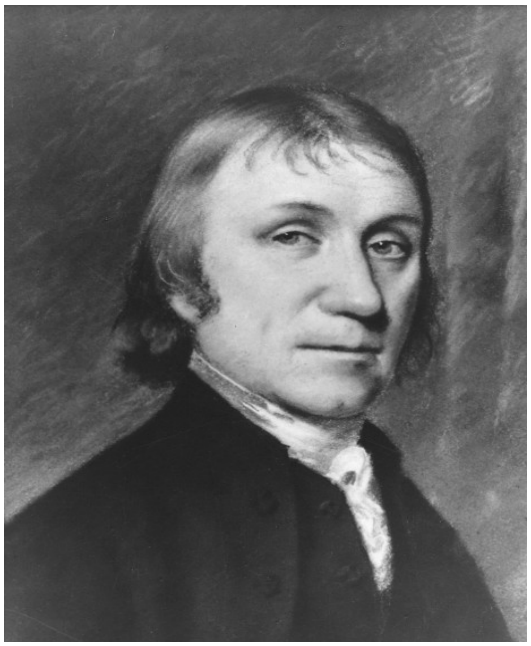


George Wald

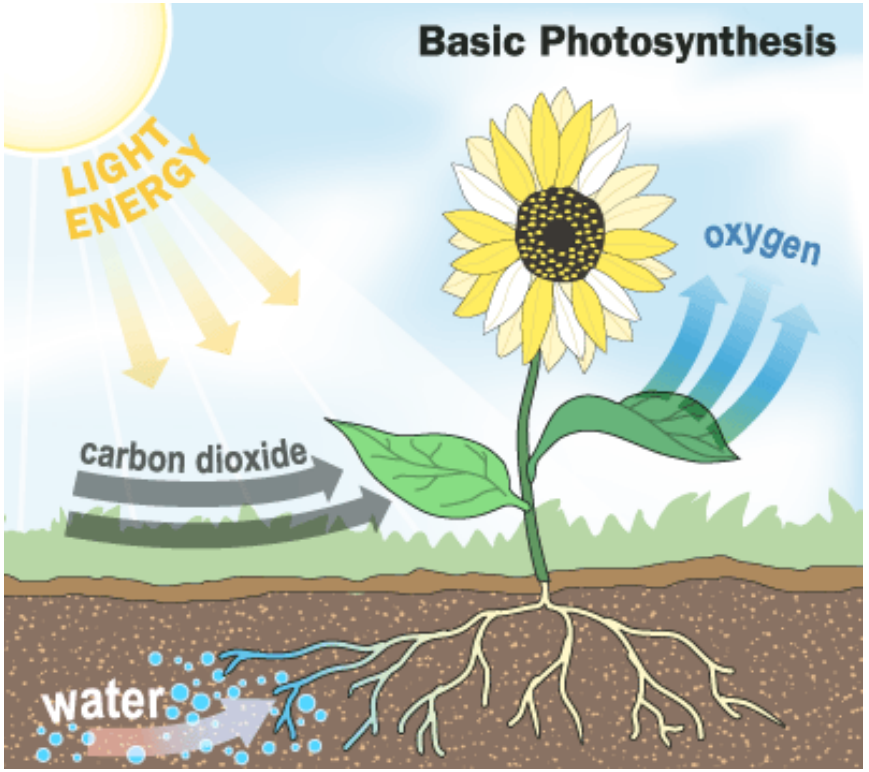
"for their discoveries concerning the primary physiological and chemical visual processes in the eye"



Survival Strategy: Photosynthesis

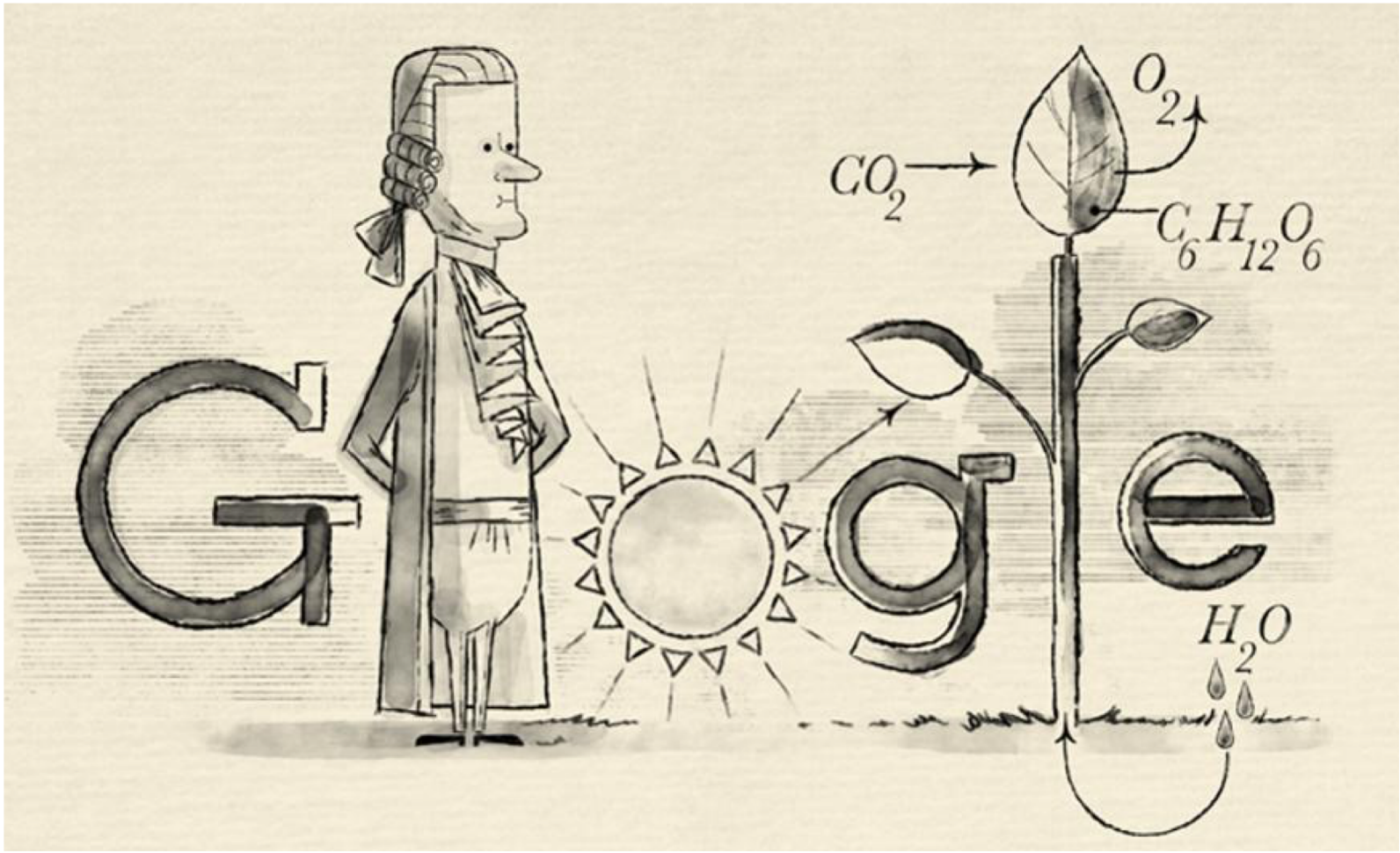


Joseph Priestley
1733–1804



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

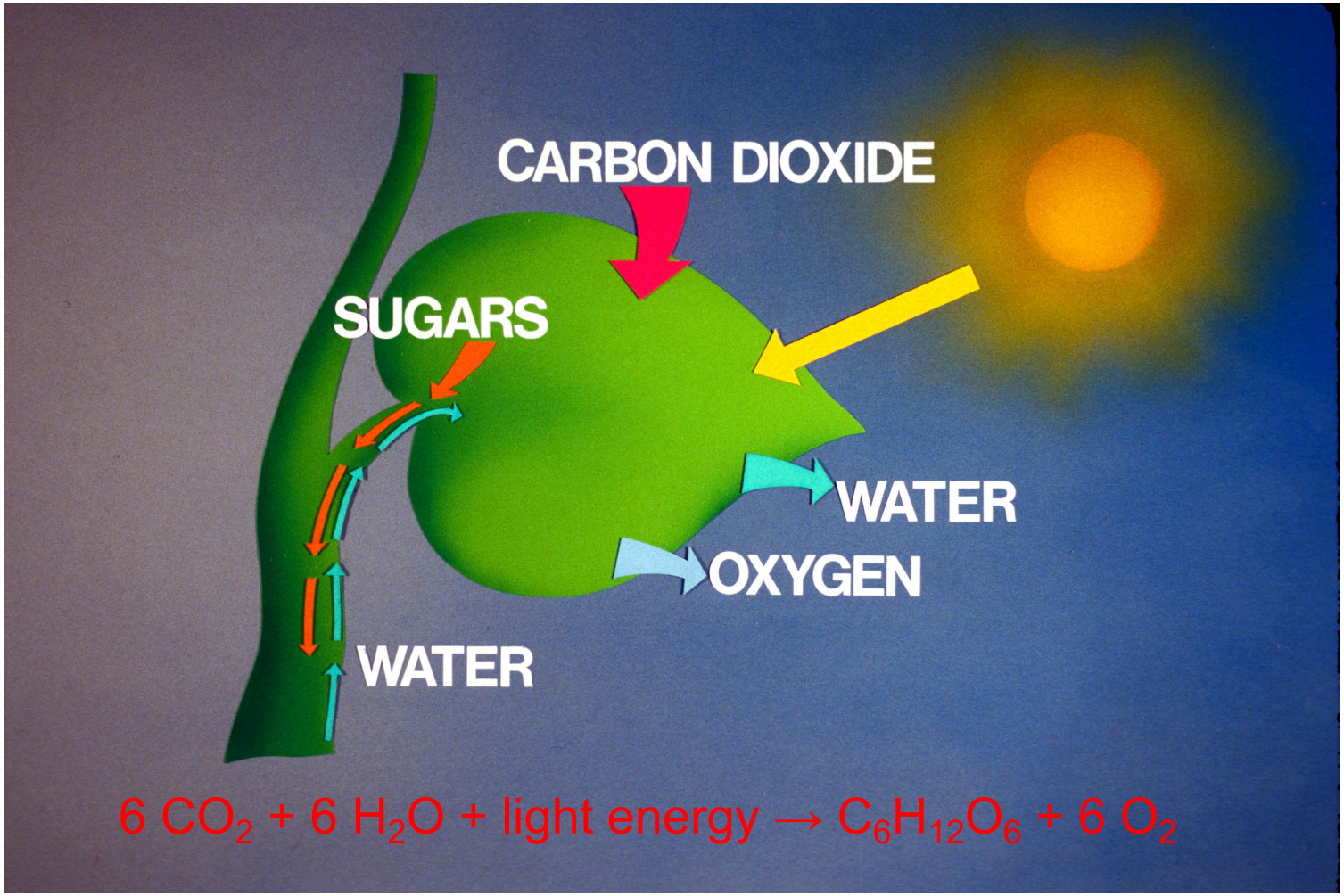
Light Energy Harvested by Plants



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

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: photosynthesis.

Light Energy Harvested by Plants



Importance of Photosynthesis

Provides energy for plants

Provides energy for animals that eat plants

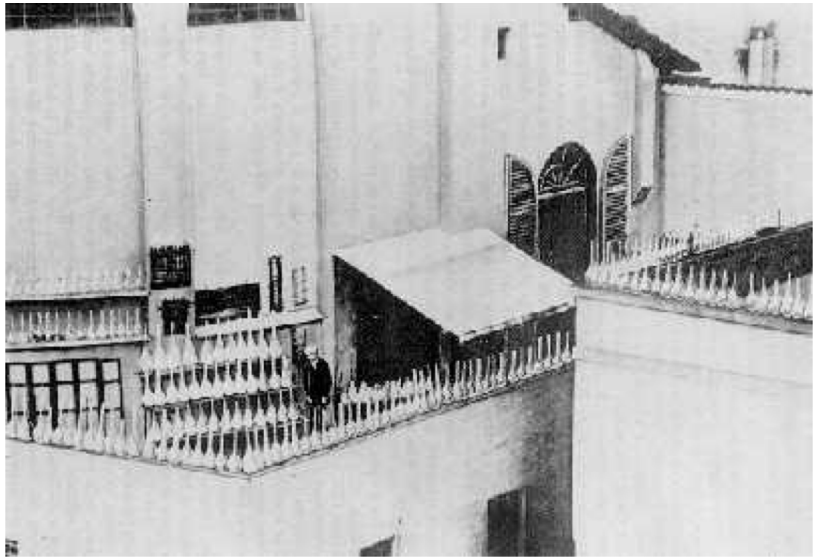
Provides energy for animals that eat animals that ate plants

Provides energy for organisms that break down all of the above

Provides the energy for most ecosystems on earth

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."

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

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LABORATORY OF CHEMICAL BIODYNAMICS

BERKELEY, CALIFORNIA 94720

October 30, 1979

Professor Anthony M. Trozzolo
Department of Chemistry
University of Notre Dame
Notre Dame, Indiana

Dear Professor Trozzolo:

I read with interest your letter on "Solar Photochemistry" in the October 8, 1979 issue of C&EN. I sent my secretary to the library and was able to get a Xerox copy of the article "The Photochemistry of the Future" by G. Ciamician. I found it absolutely fascinating, and certainly appropriate. It expressed very well some of our own feelings concerning the dependence on fossil fuel.

For the past five years we have had underway here at the University of California several projects with the aim of lessening our dependence on exhaustible resources and focussing on renewable energy sources. Some of the ideas expressed in Professor Ciamician's timely article are germane even today.

I am enclosing a selection of reprints from our laboratory which have two main thrusts--one to use the green plant itself as a source of renewable resources and the other to create in the laboratory synthetic chloroplasts which could accomplish the same end.

Thank you for bringing our attention to this most interesting and, as you say, prophetic work.

Very truly yours,

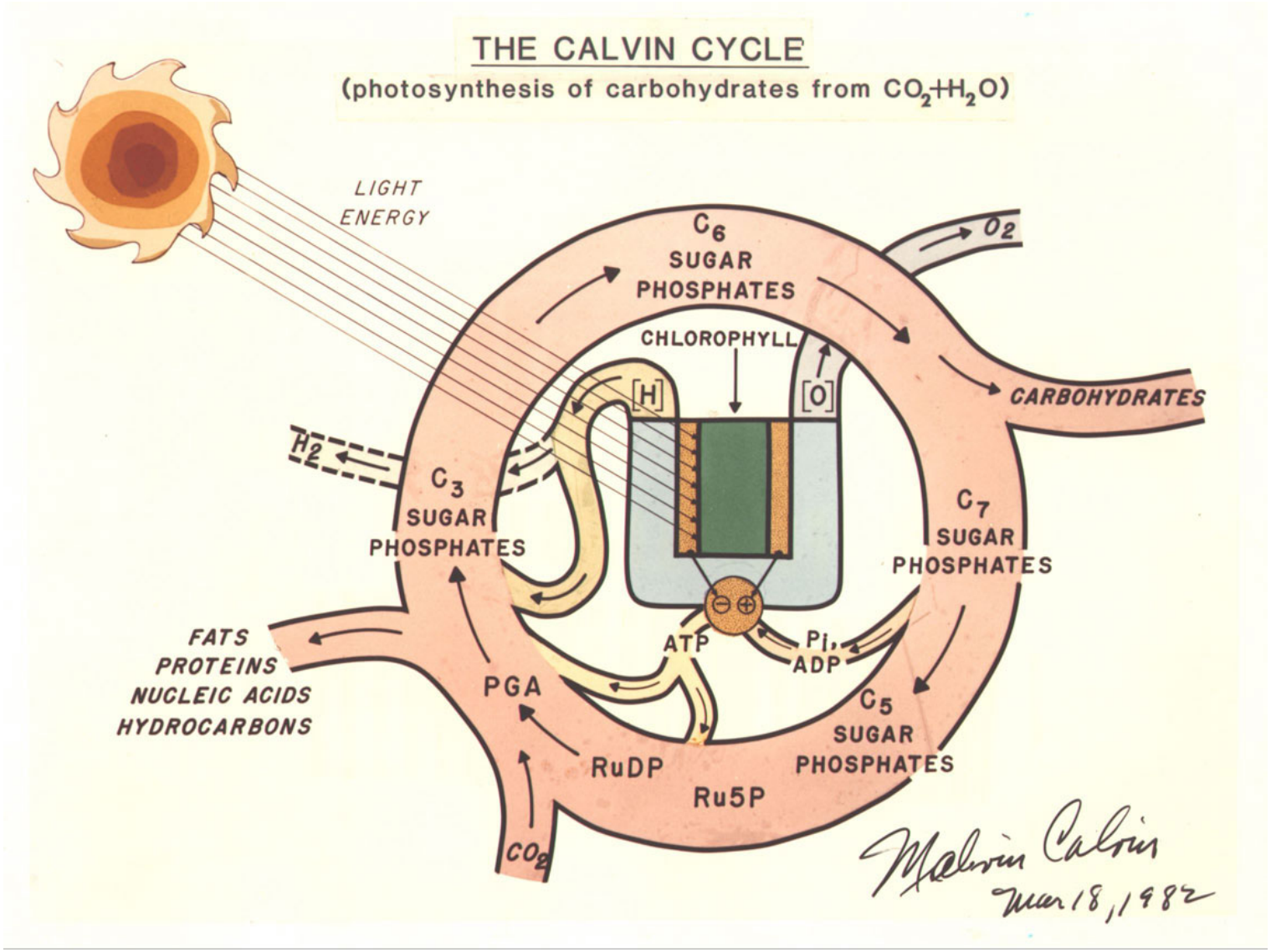
Melvin Calvin

Melvin Calvin

Photosynthesis

(1961 Nobel Prize)

M. Calvin
1911-1997



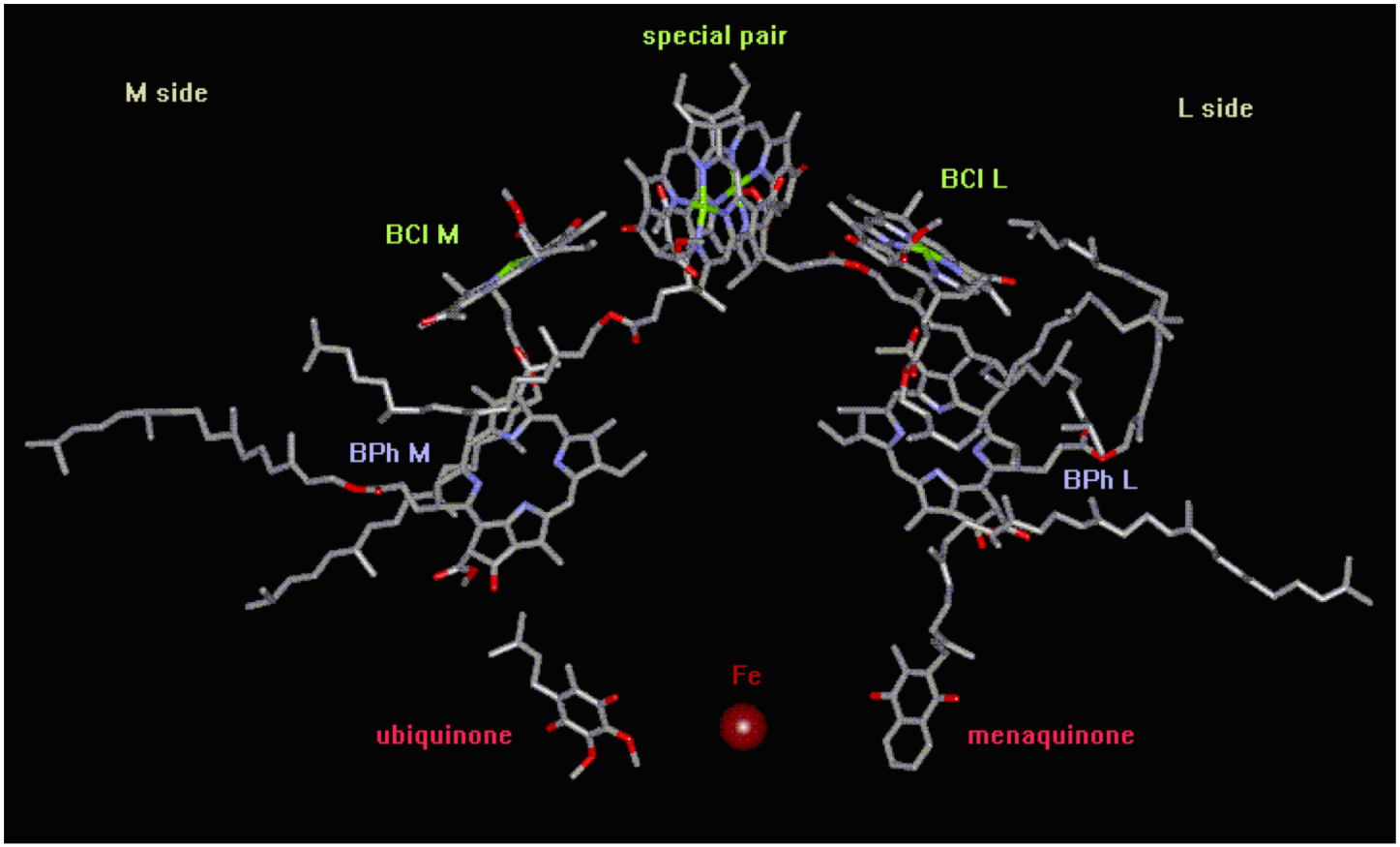
Photosynthetic Reaction Center

(1988 Nobel Prize)

J. Deisenhofer

R. Huber

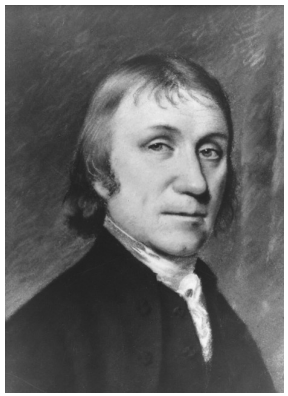
H. Michel



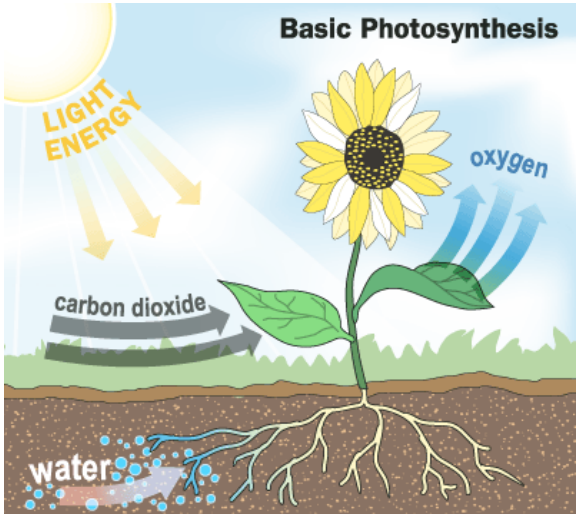
http://www.mpibp-frankfurt.mpg.de/~michael.hutter/rcenter.html

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

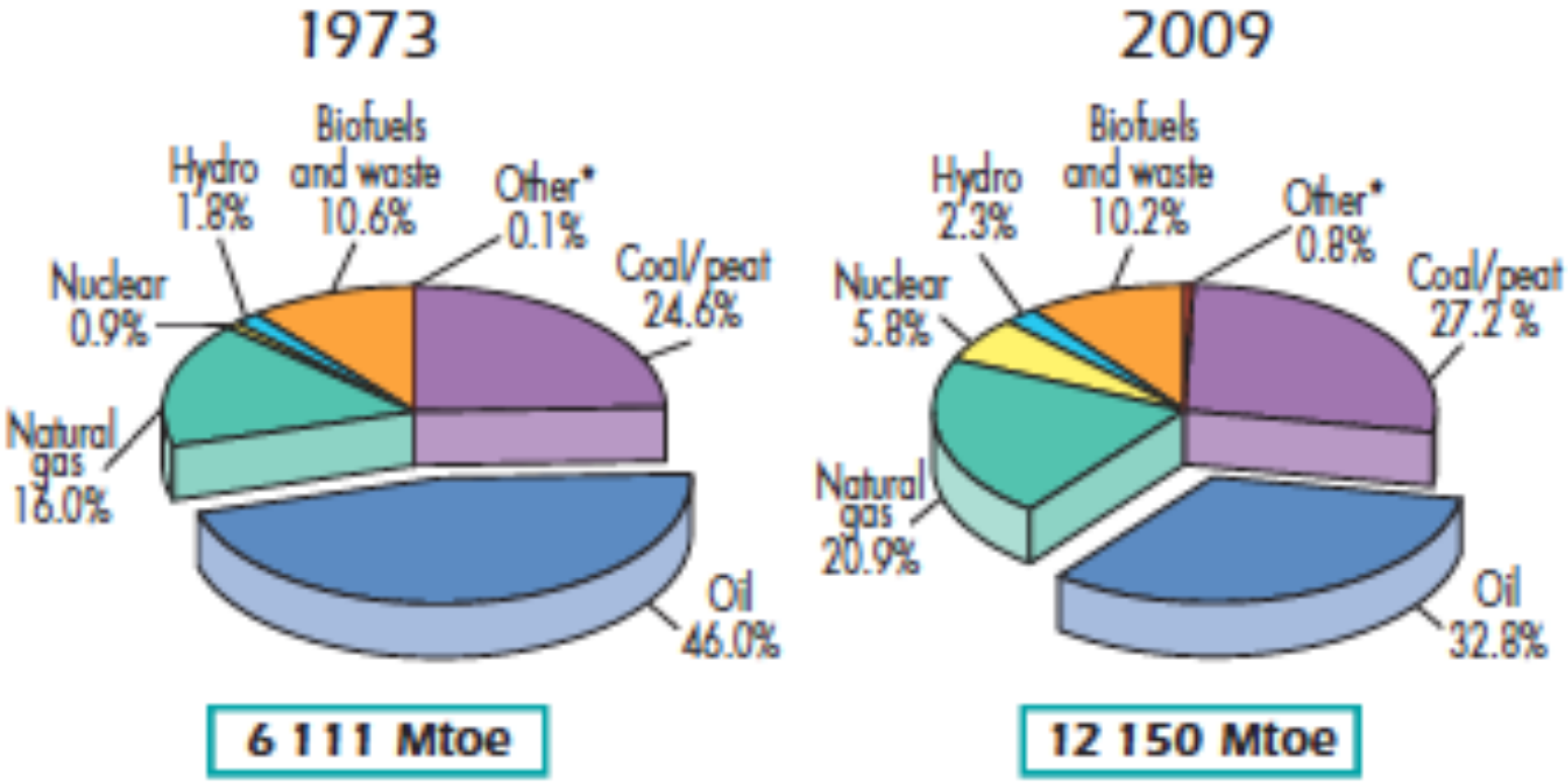
H. Michel

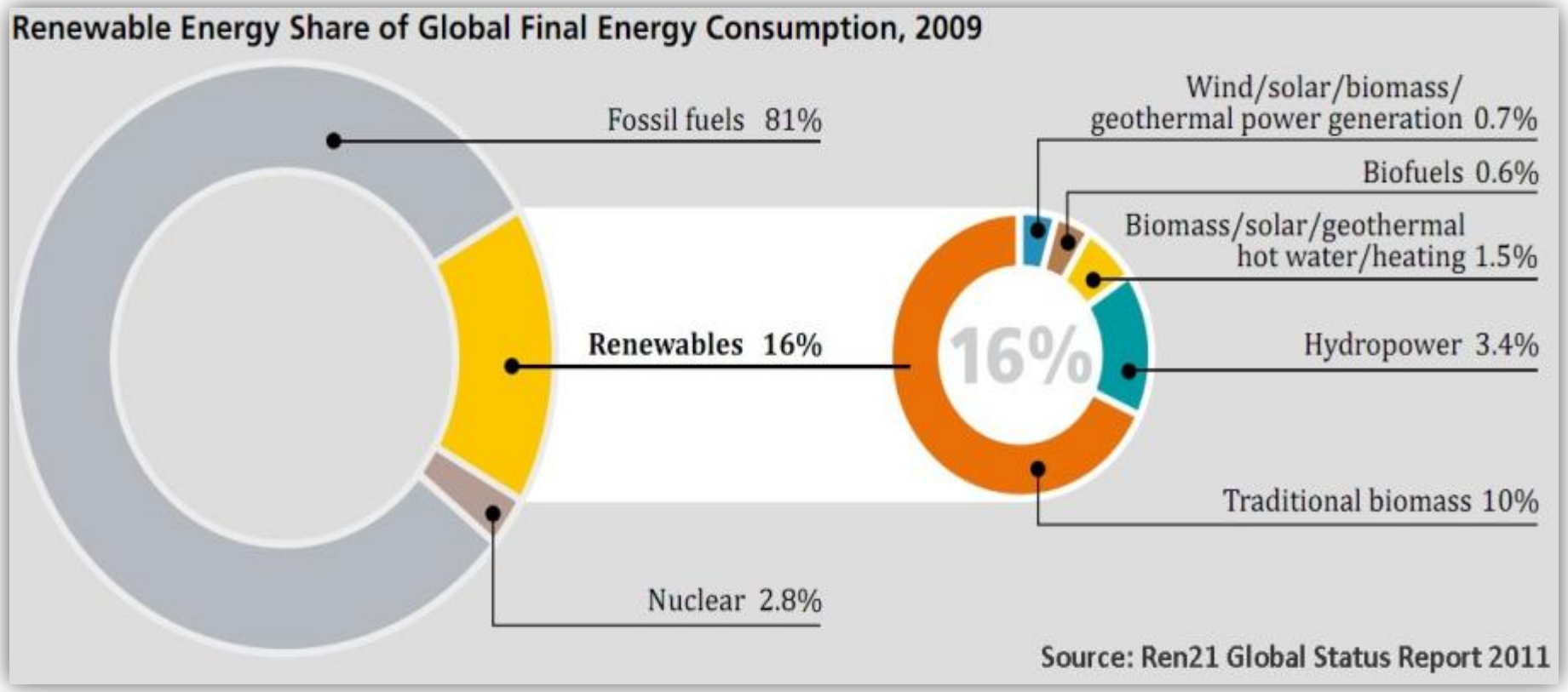
The Nobel Prize in Chemistry 1992

R. Marcus

TOTAL PRIMARY ENERGY SUPPLY

1973 and 2009 fuel shares of TPES




Renewable Energy Share of Global Final Energy Consumption, 2009
Fossil fuels 81%
Renewables 16%
Nuclear 2.8%
16%
Wind/solar/biomass/
geothermal power generation 0.7%
Biofuels 0.6%
Biomass/solar/geothermal
hot water/heating 1.5%
Hydropower 3.4%
Traditional biomass 10%
Source: Ren21 Global Status Report 2011

We started using fossil fuels ambitiously around 1800.

If we have a 500 year supply remaining....

And it took at least 70 million years to produce the fossil fuels we use today....

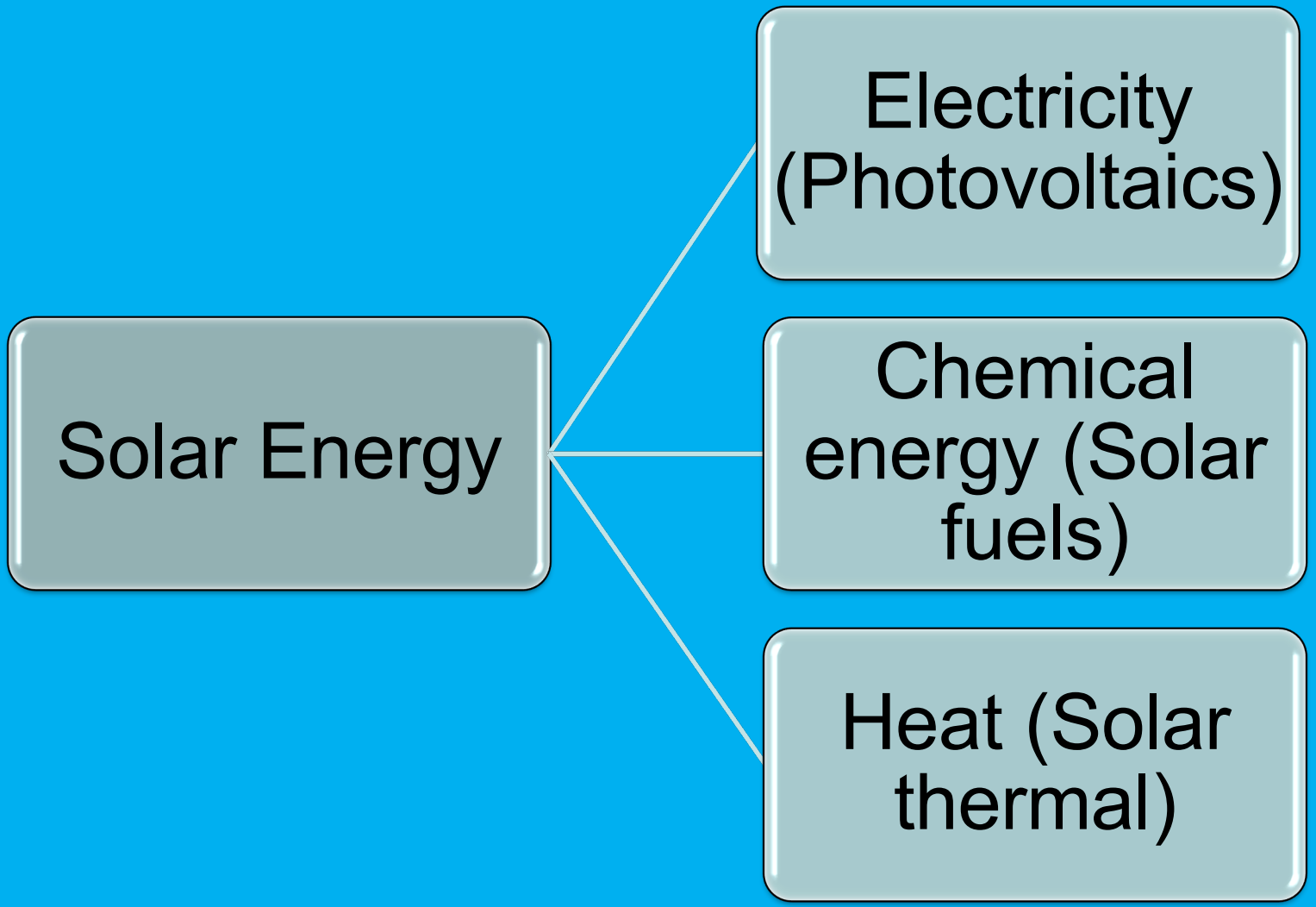
Once we use our 500 year supply, all we have to do is ...

WAIT ANOTHER 70 MILLION YEARS !!

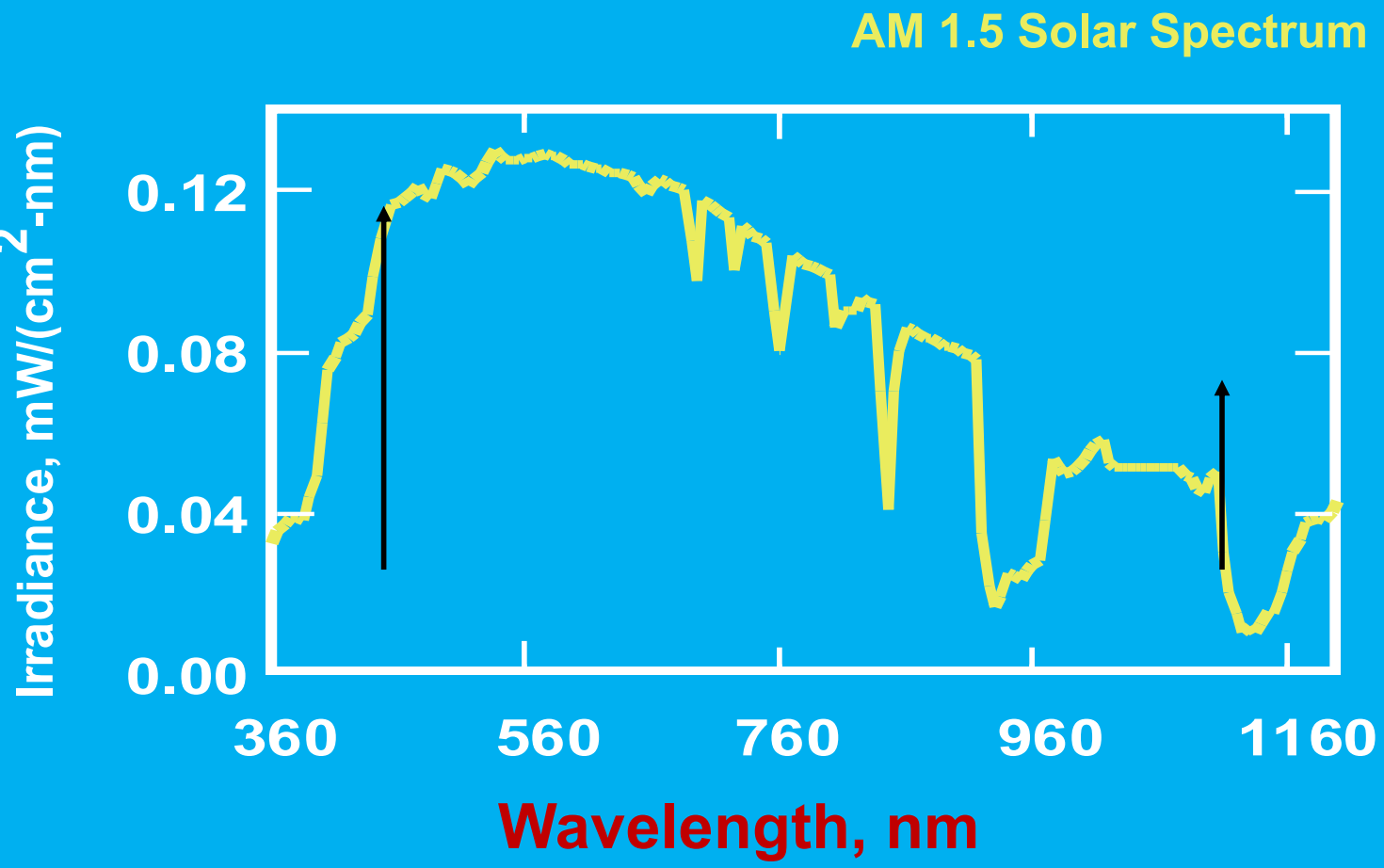
tick, tick, tick ....

Learn Photochemistry

Conversion of Solar Energy



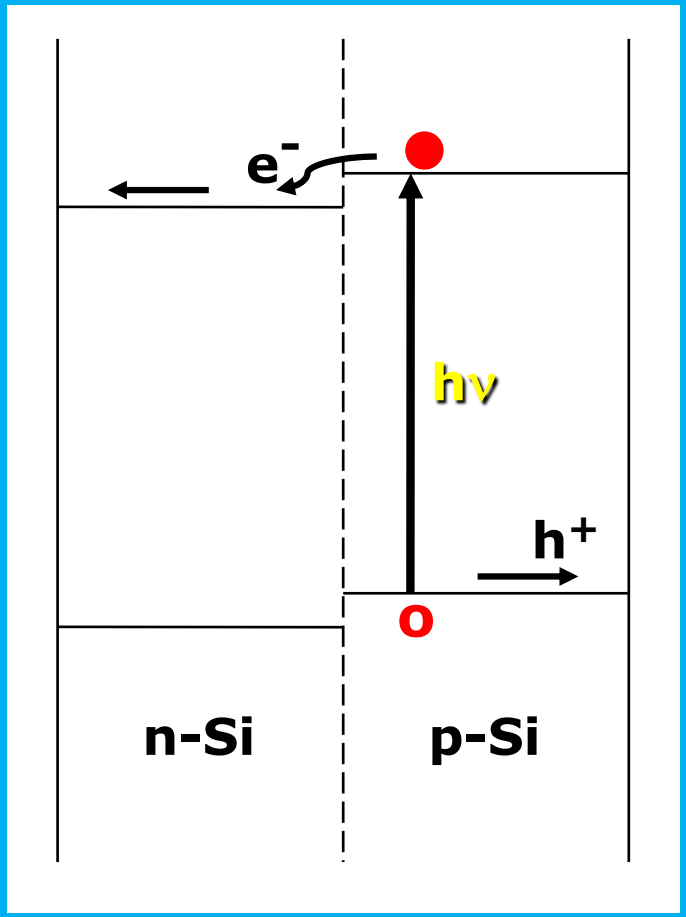
Solar Spectrum



Standard reference solar spectrum, the solar spectral irradiance distribution(diffuse and direct) incident at sea level on sun-facing 37-degree tilted surface.

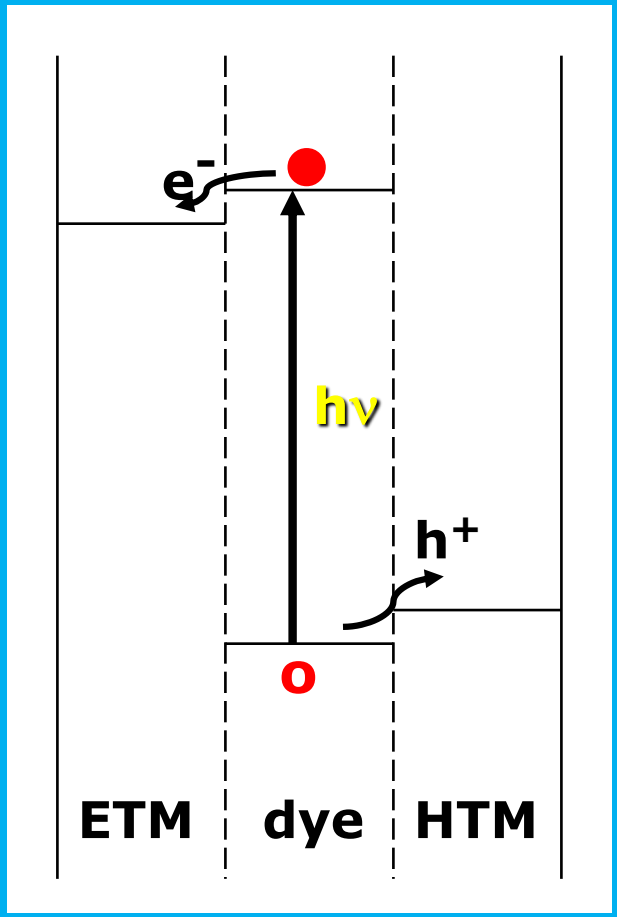
Solar Cells

Silicon p/n Junction



- light absorption
- charge separation (holes and electrons)

Dye-Sensitized (Grätzel) Cell



What is Solar Cell ?

Solar cell is a basic device which can convert solar energy directly into electricity, either directly *via* the photovoltaic (PV) effect , or indirectly by first converting the solar energy to heat or chemical energy.

The most common form of solar cells are based on the PV effect in which light falling on a two layer semi-conductor device produces a photovoltage or potential difference between the layers. This voltage is capable of driving a current through an external circuit and thereby producing useful work.

The History of PV Solar Cells

In 1839 Edmund Becquerel, the French experimental physicist discovered the photovoltaic effect – that light falling on certain materials can produce electricity .

In 1921 Albert Einstein won the Noble Prize for his theories(1904 paper) explaining the photoelectric effect

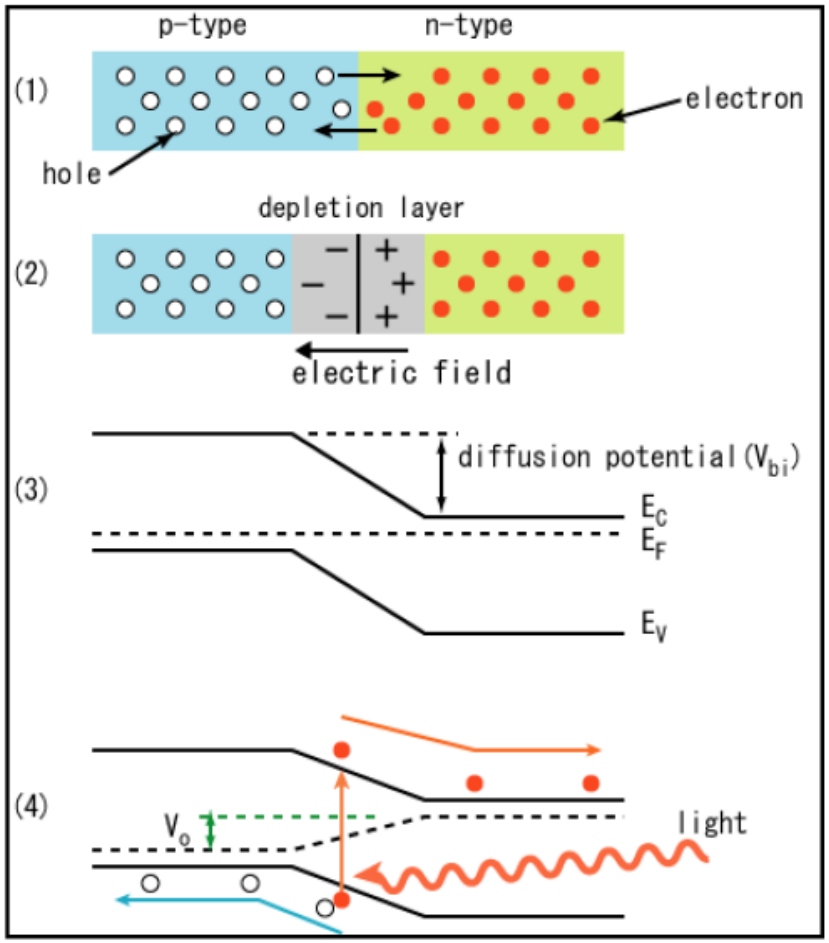
In 1930s, Scientists discovered "semi-conductors." Primitive photovoltaic cells were developed using selenium, but they were very expensive, only less than 1% efficiency.

Early in 1954, a small team of scientists, Chapin, Fuller and Pearson at Bell Lab. Using crystalline silicon semi-conductors, 6% of the sunlight energy can be converted into electricity.

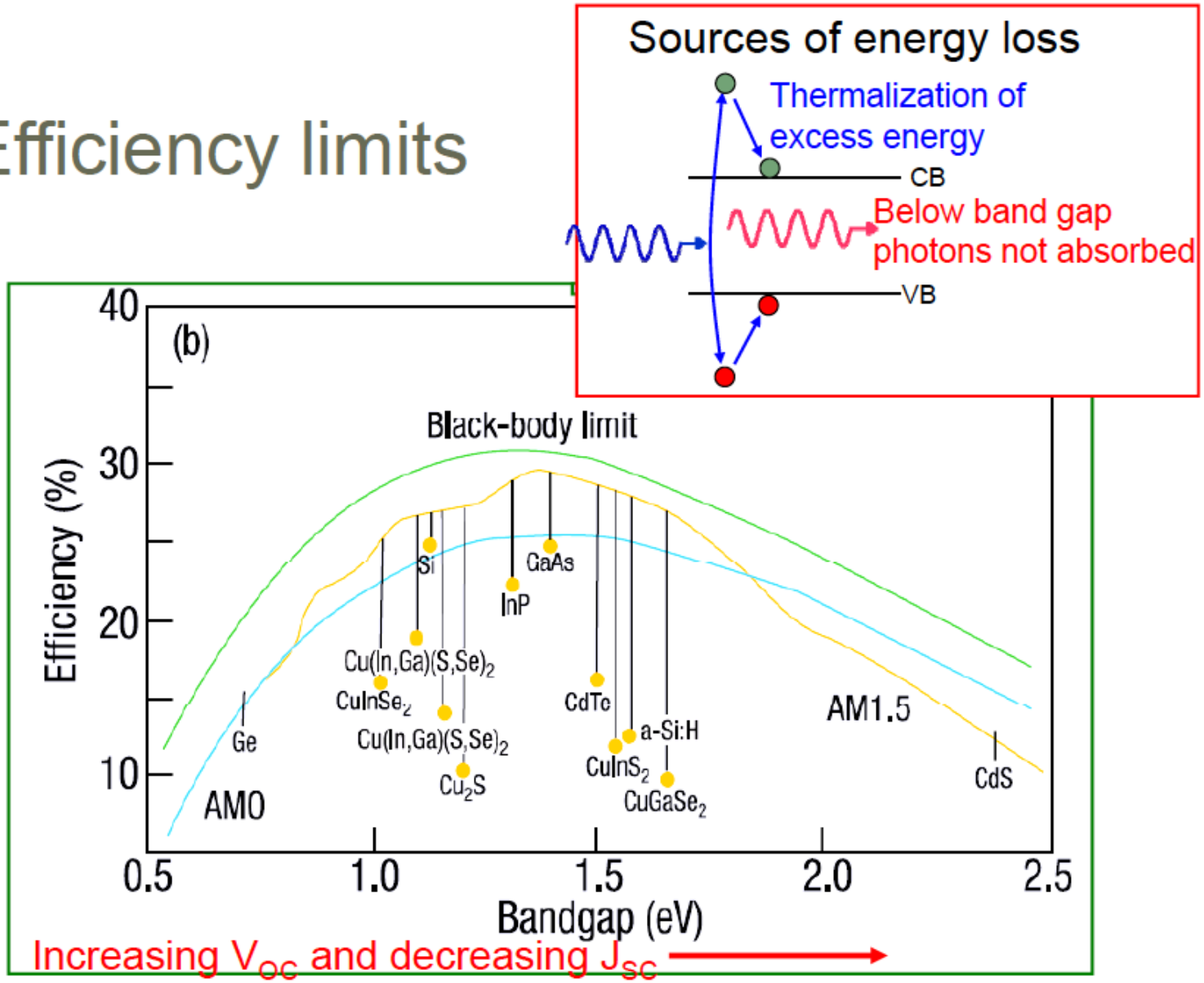
In 1958 silicon solar cells were boosted into orbit aboard Vanguard I, the second U.S. Satellite. And throughout the 1960s, solar cells were principally used to power all satellites.

In the 1980s, the overall market for photovoltaics has increased more than ten-fold, due to the cost of PV modules has dropped from about $50 per watt to $5 or $6 per watt , resulting from continuous enhancement of PV cell efficiencies, about 18% (commercially), more than 30% at laboratories. PV power is becoming a more popular power source from individual consumer to industrial utility networks.

Conventional p-n junction photovoltaic (solar) cell

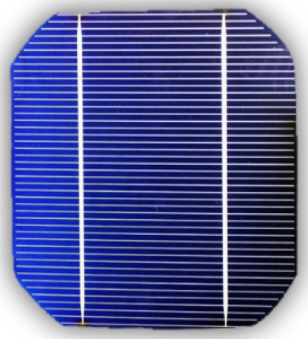


Efficiency limits



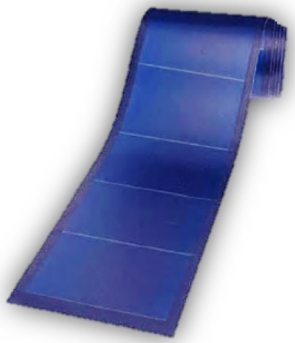
Advantages of Silicon Solar Cells

- Non-toxic
- Abundant
- Relatively cheap
- Mature infrastructure from computer industry



c-Si Cell

p-Si Cell



a-Si Cell

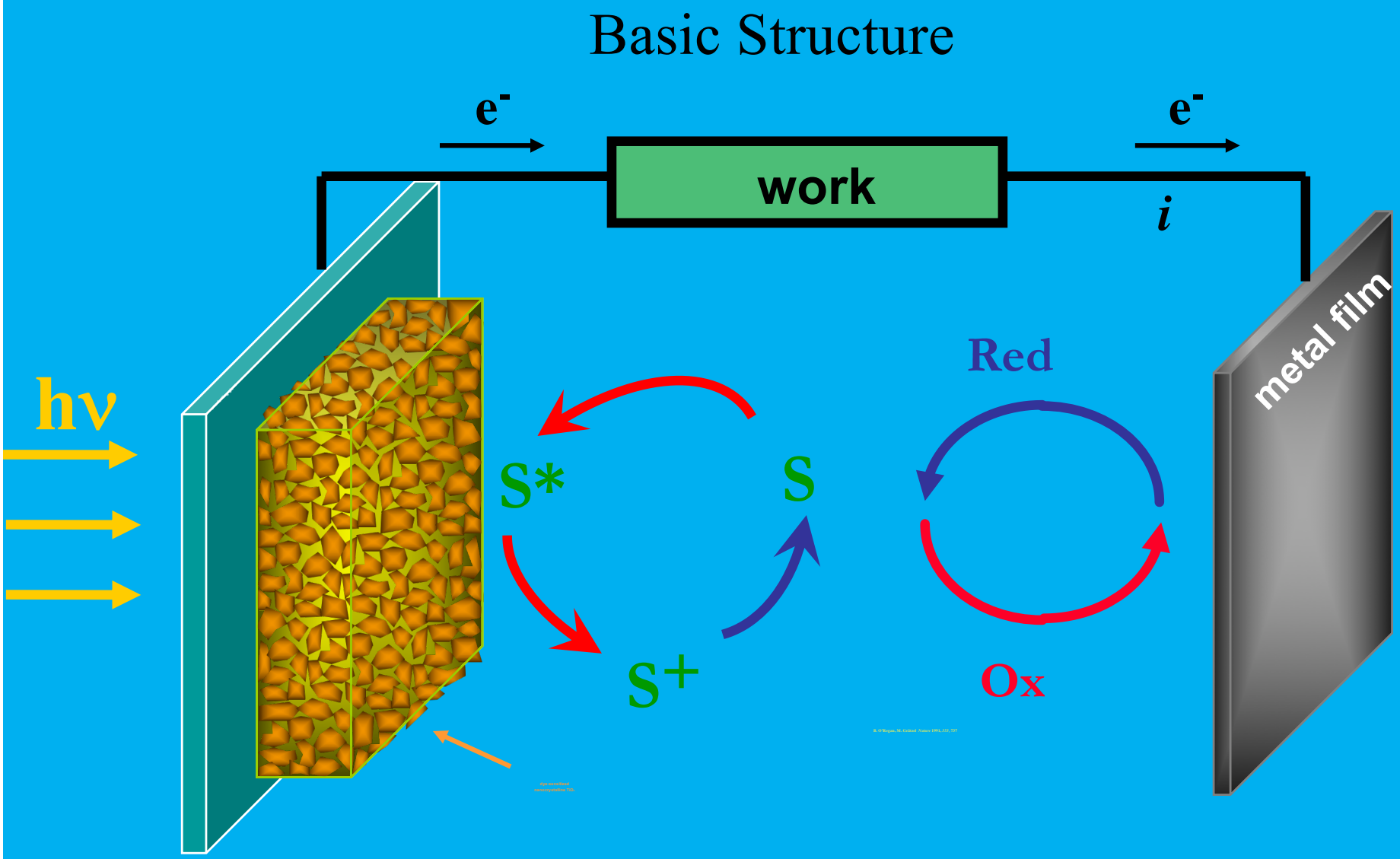
Solar Cell Technology	Max Lab Efficiency	Typical Cell Thickness	Si Use	Cost
Mono-crystalline Silicon (c-Si)	27.6%	~200µm	High	$$$
Poly-crystalline Silicon (p-Si)	20.4%	~200µm	Moderate	$$
Amorphous Silicon Thin Film (a-Si)	12.5%	<1µm	Low	$

- "Total installed [photovoltaic] capacity in the world now amounts to around 40 GW, producing some 50 terawatt-hours (TWh) of electrical power every year." – EPIA, May 2011

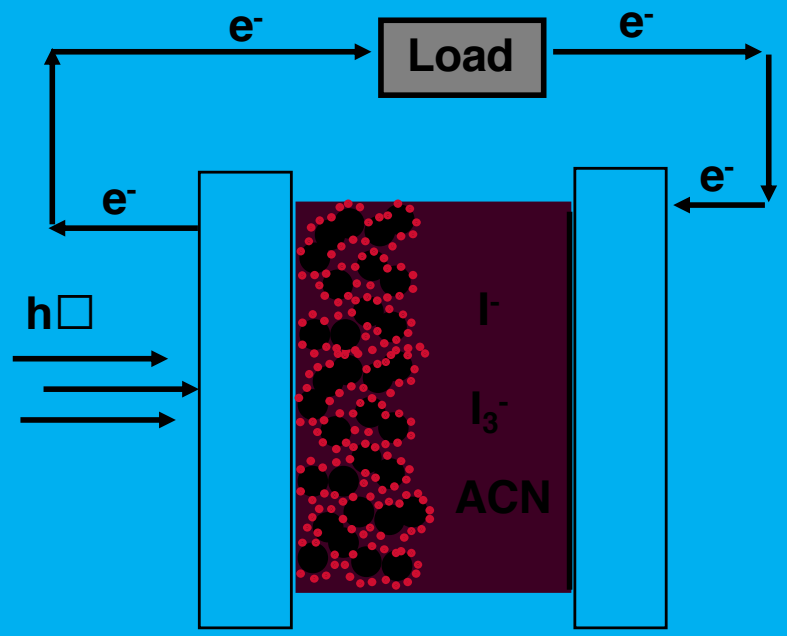
- Only about 0.2% of the total global generated electricity in 2010 comes from PV sources

- Solar will become increasingly important in the future as we begin to rely less on fossil fuels and turn to renewable energy sources for our power needs

Dye-sensitized Nanocrystalline Solar Cells



Dye Sensitized Solar Cells



- 8-10% Efficient
- >15% Efficiency Possible
- Stability

c&en
CHEMICAL & ENGINEERING NEWS
NOVEMBER 21, 2016

Obama's science policy: hits and misses
P.18

On the hunt for a human pheromone
P.23

Will the artificial leaf sprout?

Technology to turn sunlight into fuels struggles to prove its worth
P.32

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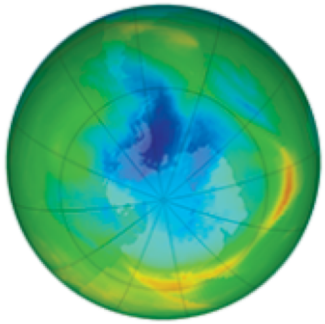
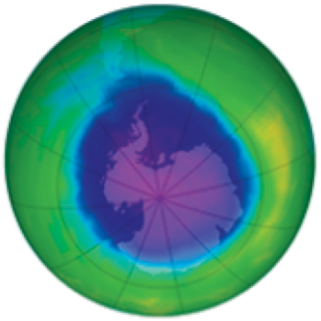
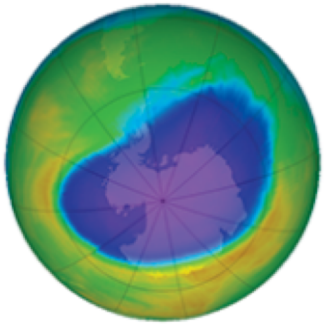


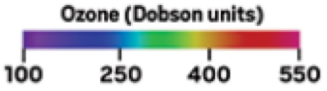
1979



1989



2016



The Nobel Prize in Chemistry 1995

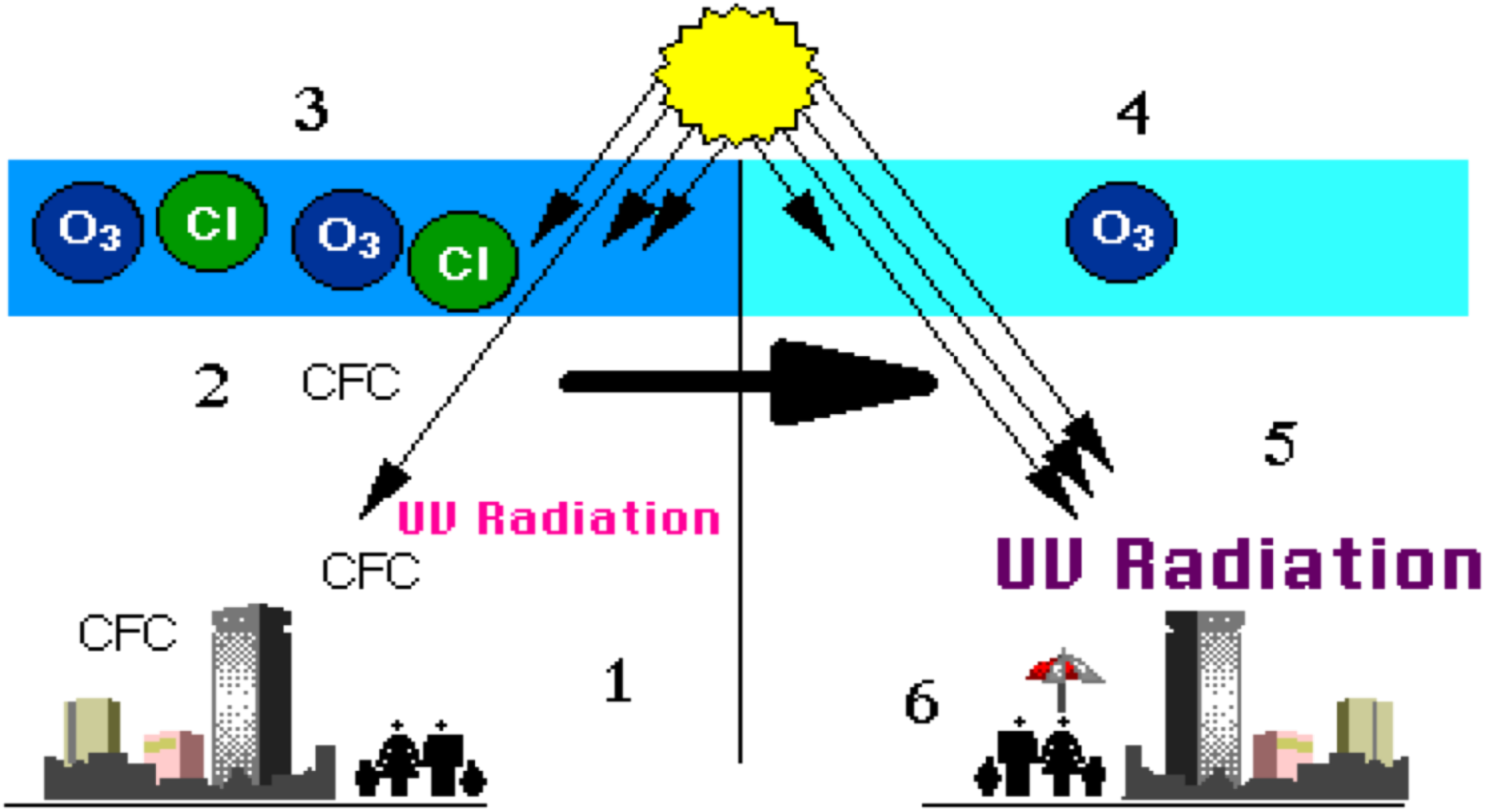
Paul J. Crutzen

Mario J. Molina

F. Sherwood Rowland

"for their work in atmospheric chemistry, particularly concerning the formation and decomposition of ozone"

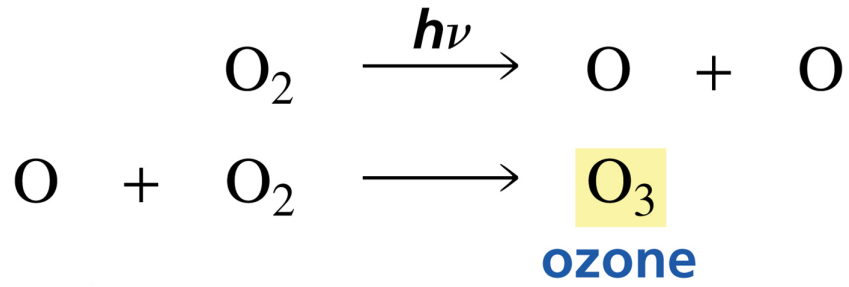
Ozone Depletion Process

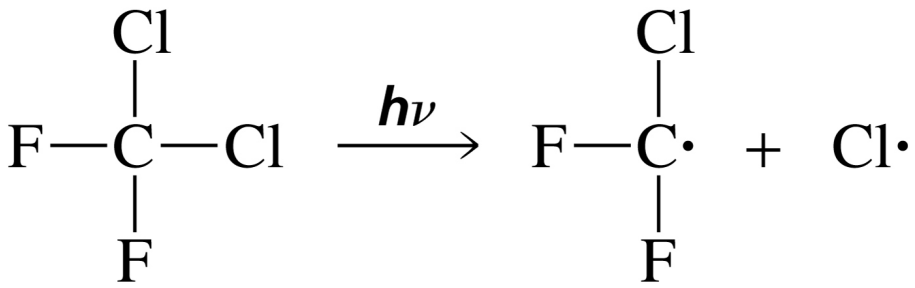


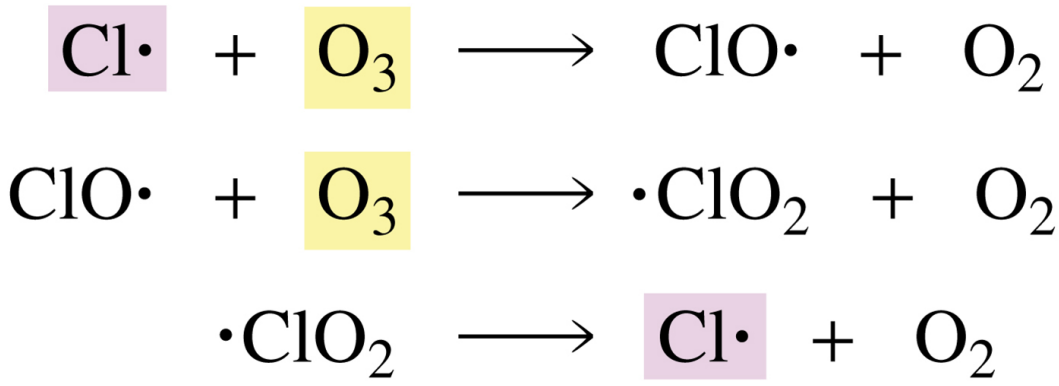
1 - CFCs released
2 - CFCs rise into ozone layer
3 - UV releases Cl from CFCs

4 - Cl destroys ozone
5 - Depleted ozone -> more UV
6 - More UV -> more skin cancer

Ozone hole


hν
O2
O + O
O + O2
O3
ozone


Cl
F—C—Cl
F
hν
F—C·
Cl
F
+ Cl·


Cl· + O3 → ClO· + O2
ClO· + O3 → ·ClO2 + O2
·ClO2 → Cl· + O2

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."

Charles H. Townes

Nicolay G. Basov

Aleksandr M. Prokhorov

Nobels in Photochemistry

Development of Flash Photolysis and Femtosecond Chemistry

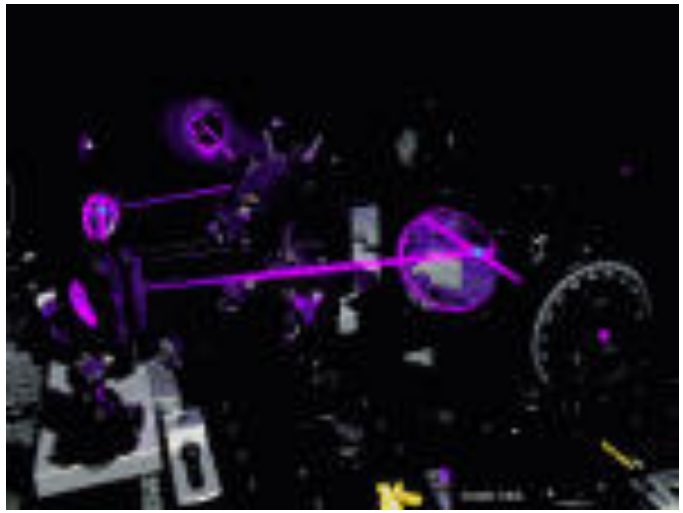
Norrish

Porter

Zewail

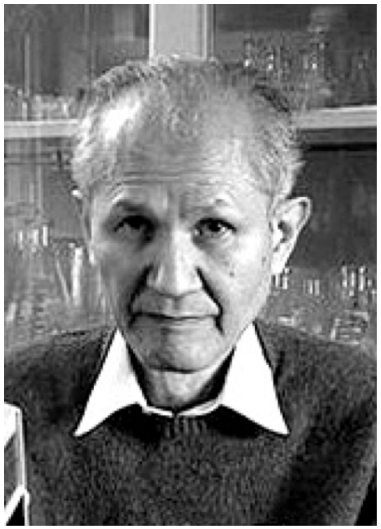
The Nobel Prize in Chemistry 1967

The Nobel Prize in Chemistry 1999

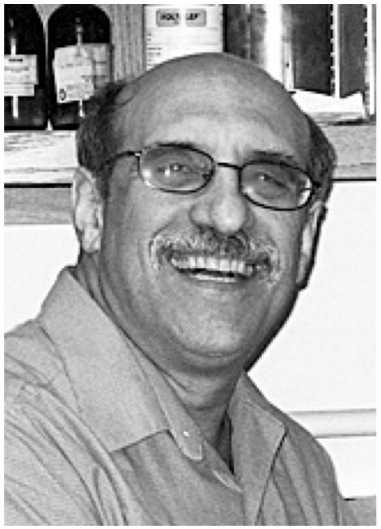


The Nobel Prize in Chemistry 2008

"for the discovery and development of the green fluorescent protein, GFP"

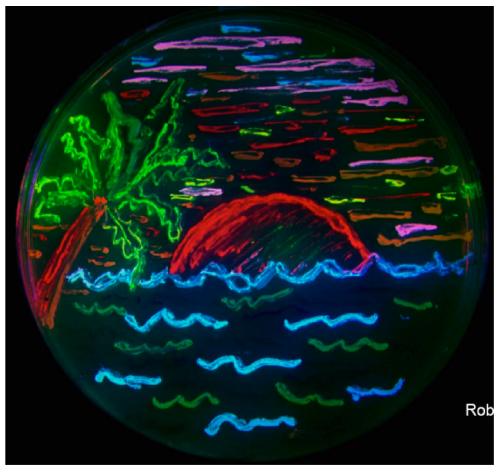


Osamu Shimomura



Martin Chalfie

Roger Y. Tsien



The Nobel Prize in Physics 2014

"for the invention of efficient blue light-emitting diodes which has enabled bright and energy-saving white light sources."

Isamu Akasaki

Hiroshi Amano

Shuji Nakamura

Our fore-fathers knew it, time for us to harness it

Surya

From the Sun arise all beings.
The Sun sustains them all.
Into the Sun they all vanish.
What the Sun is,
that I am.

—Surya Upanishad