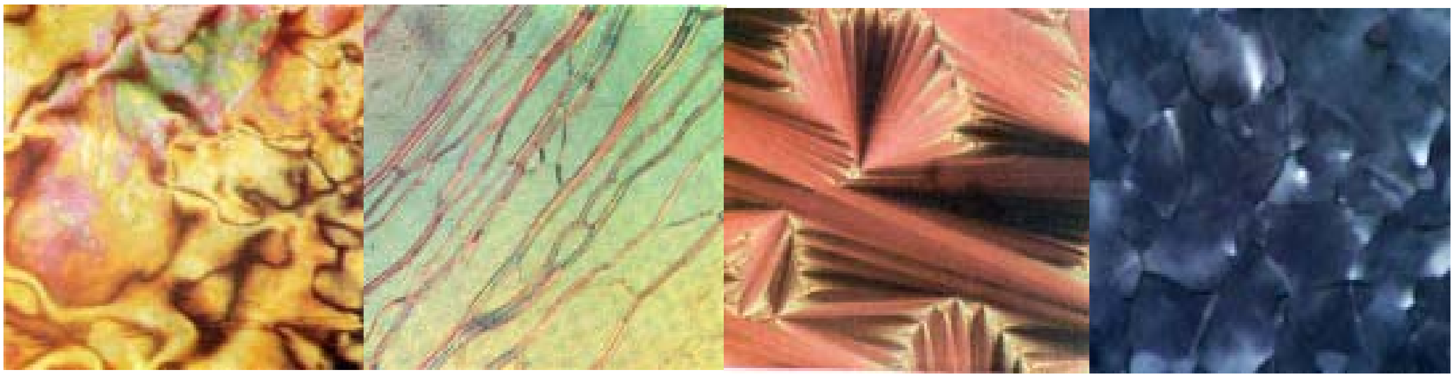
Liquid Crystals in Science and Technology

Class note for 9/13/2004



Huang-Ming Philip Chen

pchen@mail.nctu.edu.tw

National Chiao Tung University
Department Of Photonics and Display Institute

Part of slides are contributed from:
K. L. Marshall
Laboratory for Laser Energetics

The influence of the "liquid crystalline" mesophase extends far beyond the realm of information display

- **Liquid crystals are not a recently discovered phenomenon- they have been with us in the natural world from the very beginning**
- **The recent rapid advances in LC technology are a direct result of an interdisciplinary cooperation that dates back over 150 years**
- **The unique molecular orderings found in this "fourth state of matter" gives rise to a wide variety of physical and optical effects**
- **Liquid crystals constitute the basic structures of cell membranes in living organisms and play a vital role in many biological and natural processes**

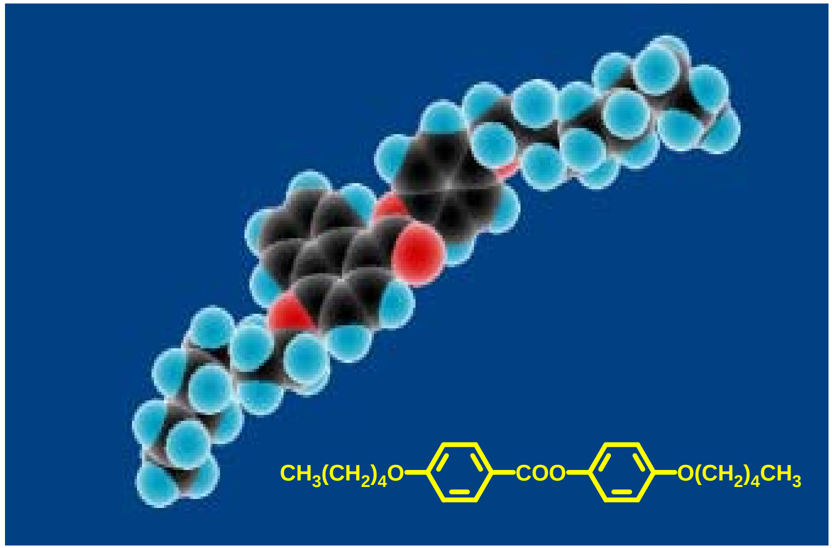
Liquid crystals have had a tremendous technological impact on science, technology, and everyday life

Thermography

bonding between metal surfaces
microwave field mapping

Biomedical

arteriosclerosis
bile fluid disorders
sickle cell anemia
cellular processes



Information display

calculators
watches, games
television, computers

High-performance materials

automobile tires
golf club shafts

Chemistry

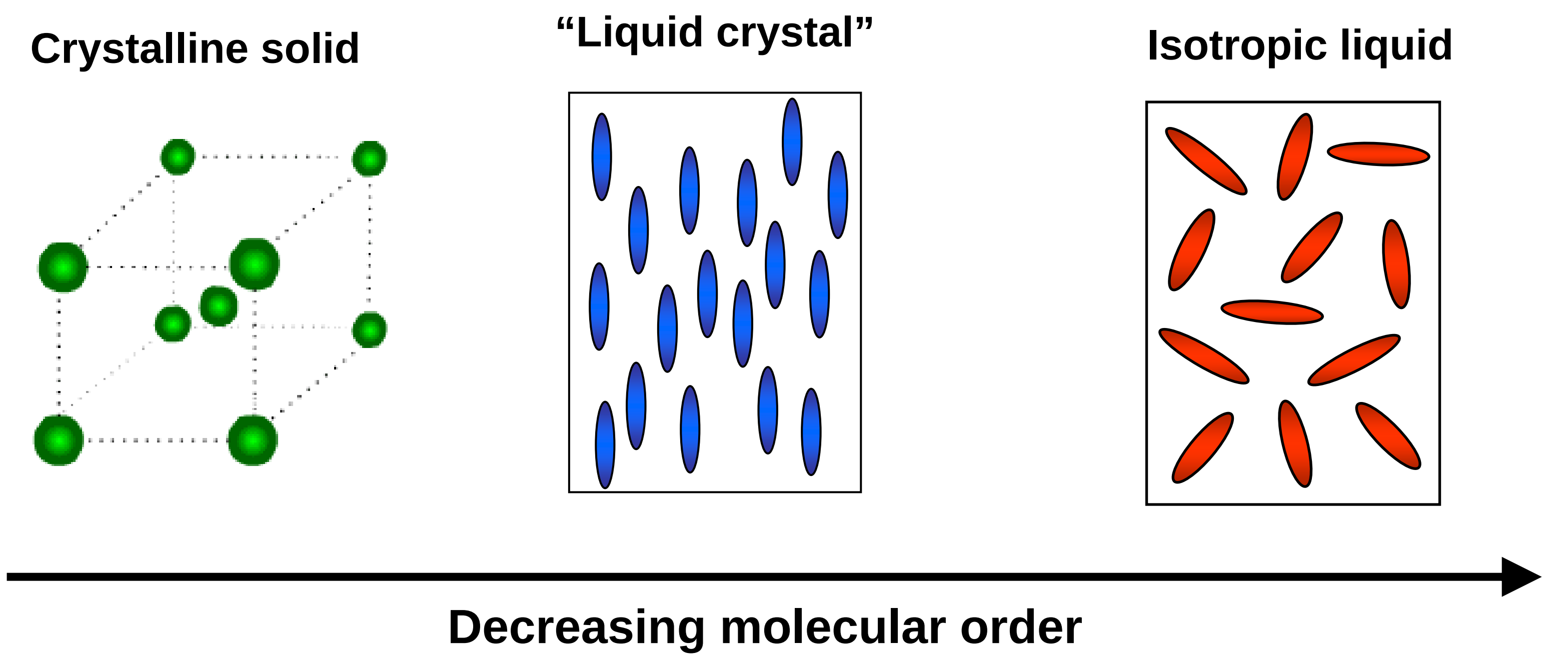
anisotropic solvents for chemical reactions and spectroscopy
stationary phases for gas chromatography

Lasers/photonics

image processing
optical modulators
circular polarizers
wave plates
apodizers

Liquid crystal science is one of the *oldest* interdisciplinary research areas

Liquid crystals are a form of condensed matter intermediate in order between the solid and liquid states



- Common materials that are liquid crystals include cholesteryl esters, lecithin, DNA, cellulose, and graphite
- Classified into different categories depending on their ***orientational*** (long-range) and ***positional*** (short-range) order

Terminology

Liquid crystal phases: also called ***Mesophases*** (*meso- from the Greek meso which means in between)*

Thermotropic:

Liquid crystal molecules which exhibit temperature dependent liquid crystalline behavior

- Enantiotropic: same mesophases reversibly upon heating and cooling
- Monotropic: mesomorphism upon cooling only

Lyotropic:

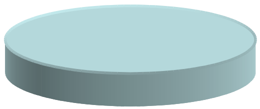
materials in which liquid crystalline properties appear induced by the presence of a solvent, with mesophases depending on solvent concentration, as well as temperature

Molecular shapes and their effects on molecular assembly

Calamitic (rod-like) mesogens

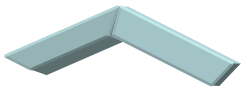
nematic, smectic, chiral nematic

Disk-like



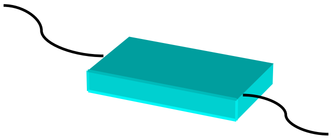
discotic

Bend-shape



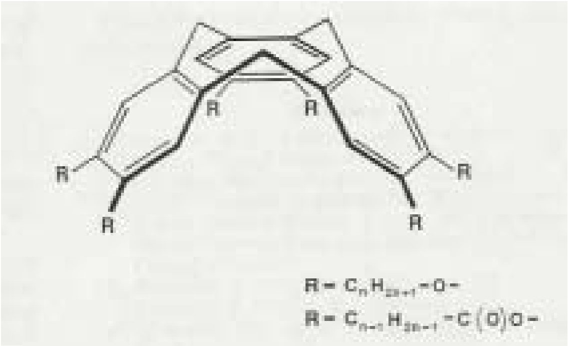
banana

Board-like

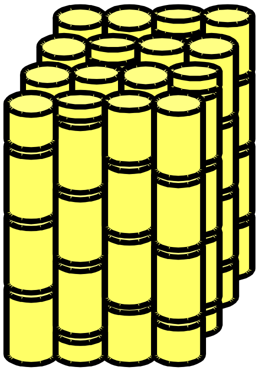


sandic

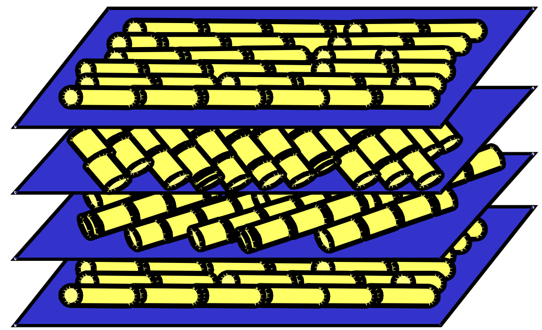
Pyramidic



Calamitic (rod-like) mesogens are the best known and most widely occurring class of liquid crystals . . . .

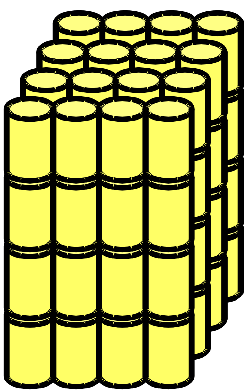


Nematic

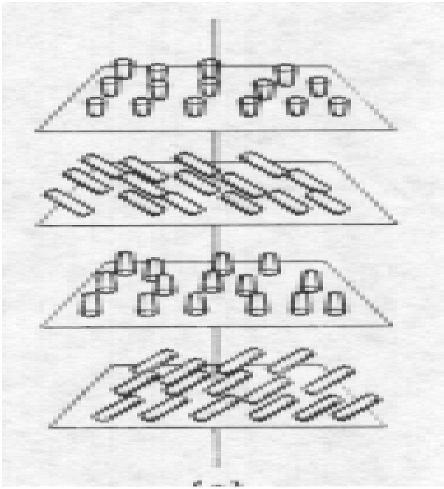


Cholesteric

- High orientational order
- Random positional order



Smectic



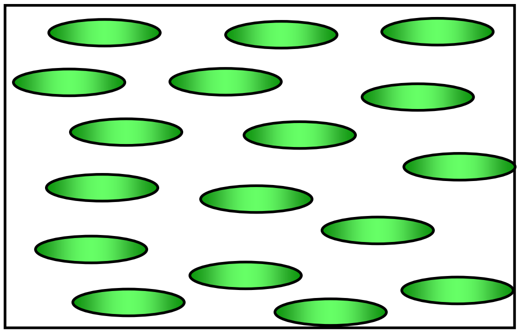
Smectic C*

- Both orientational
  <u>and</u>
  positional order

Unlike ordinary isotropic materials, the observed physical and optical properties of LC materials are dependent on "*orientation*"

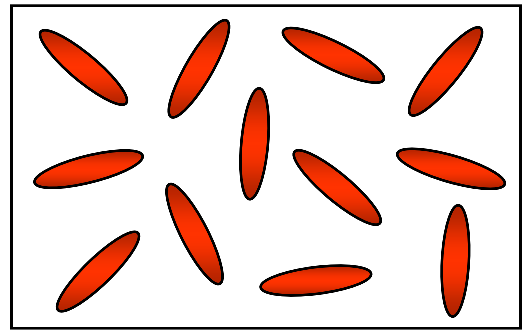
NCTU DI

Anisotropic



Physical and optical properties depend on orientation

Isotropic



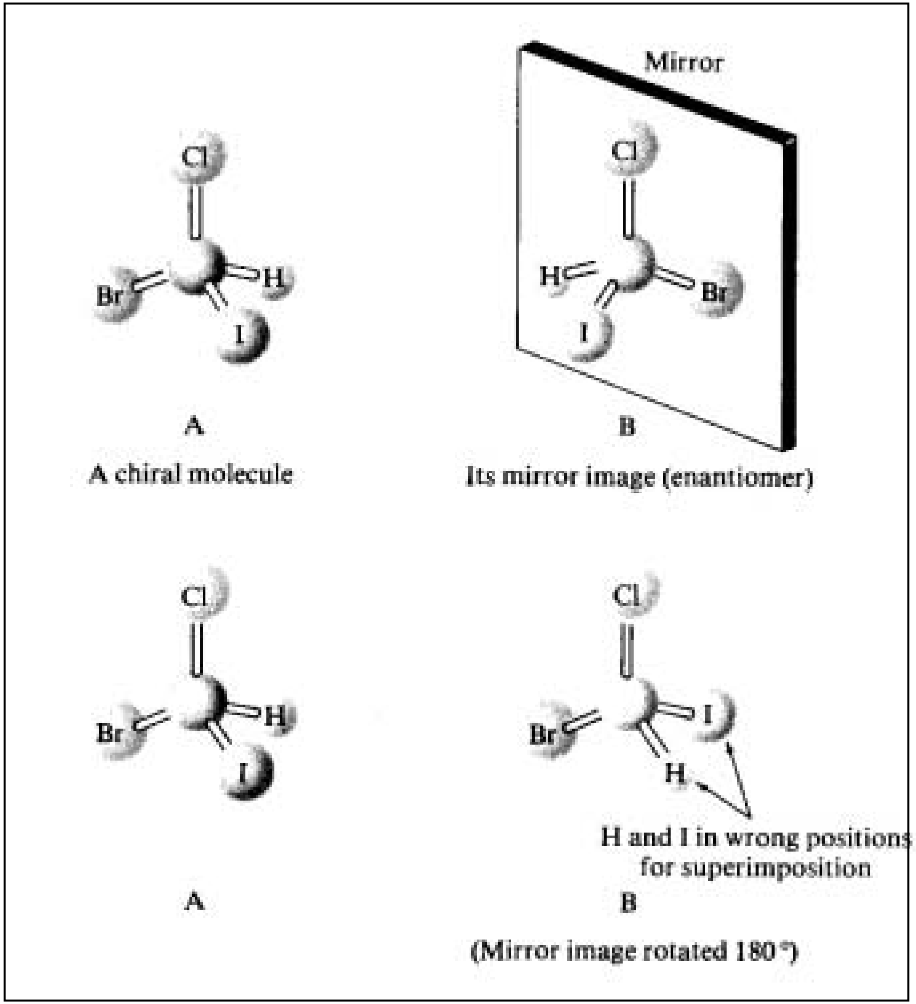
Physical and optical properties are invariant with orientation

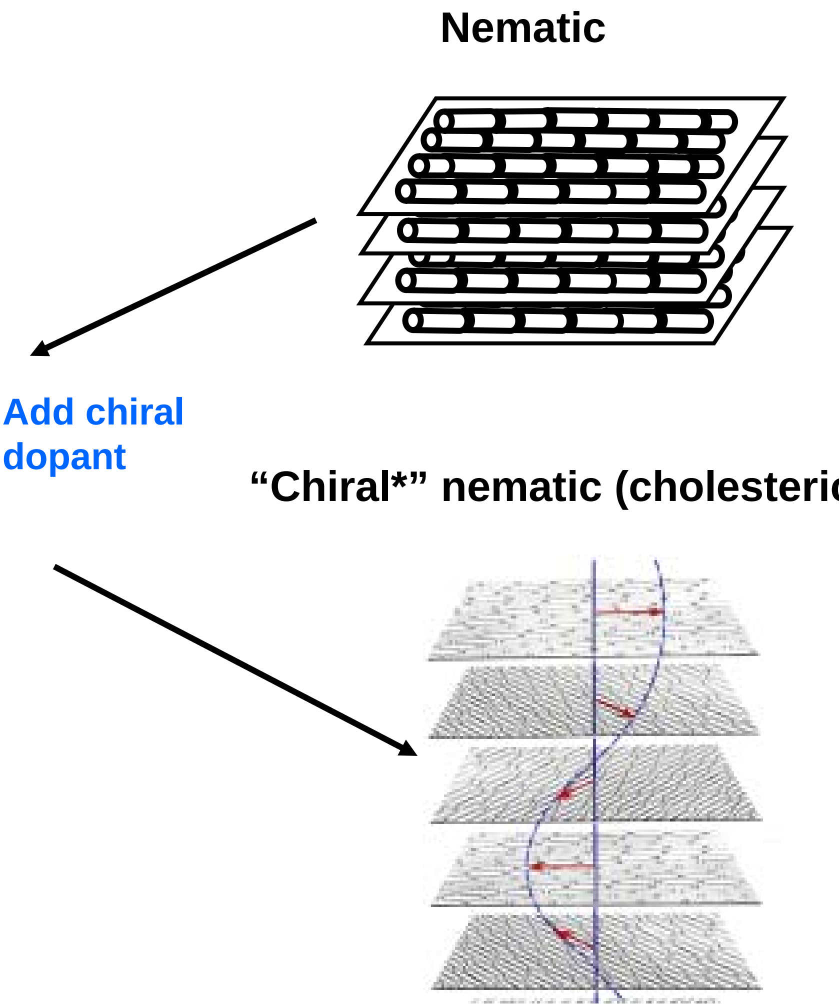
Δn = optical anisotropy (birefringence) = $n_e - n_o$

$\Delta\varepsilon$ = dielectric anisotropy = $\varepsilon_{\parallel} - \varepsilon_{\perp}$

Molecular reorientation induced by electromagnetic and optical fields can produce large effects

Introducing an "optically active" compound or group into an LC matrix induces mesophases with a helical structure





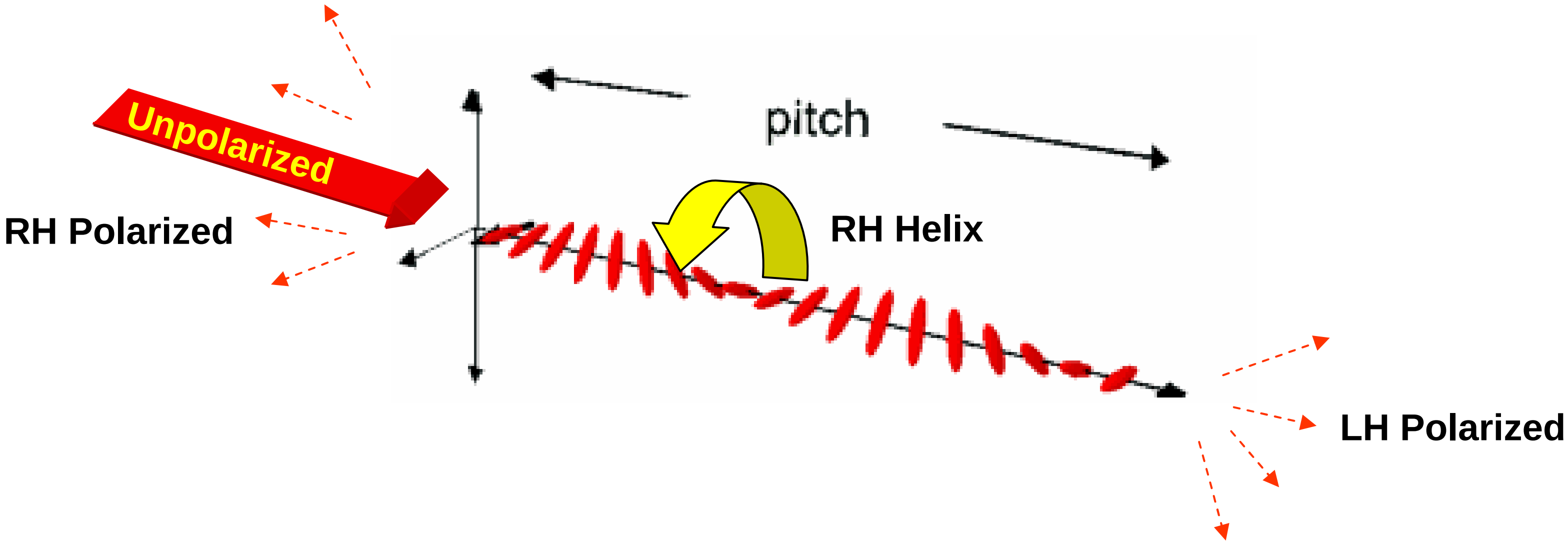
*** Derived from the Greek term "chiros" (hand)**

Selective reflection is an optical property unique to chiral liquid crystals

- **For incident wavelengths that satisfy the relationship**

$$\lambda = \bar{n}\, p$$

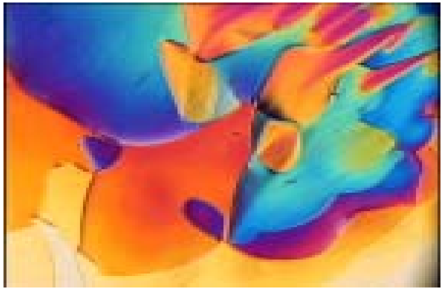
where $\bar{n}$ = average refractive index
p = pitch length



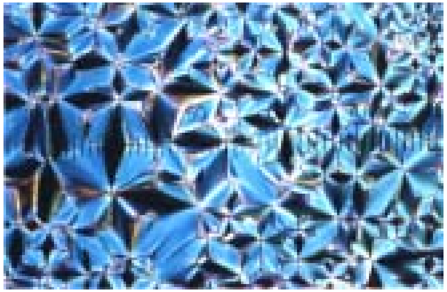
The pitch length is affected by the helical twisting power (HTP) and concentration of the chiral species as well as temperature

The interaction of polarized light with liquid crystals produces distinctive optical microscopic textures

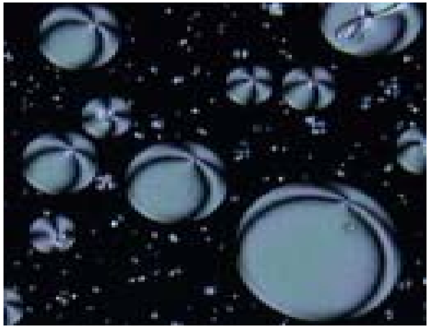
"Fingerprint" texture



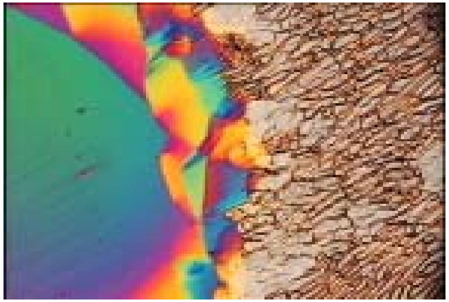
TGB- S_A* transition



Cholesteric "fan" texture

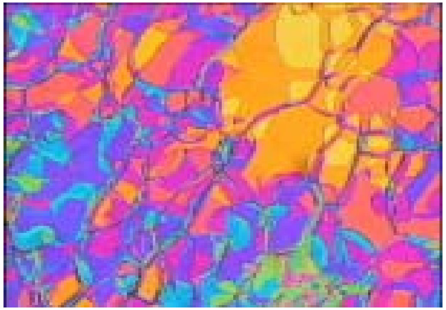


Cholesteric radial droplets



S_A – S_B transition

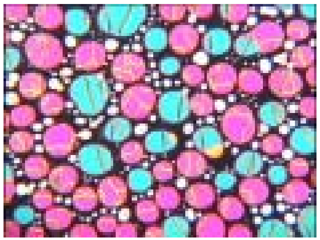
S*- cholesteric transition



TGB- l

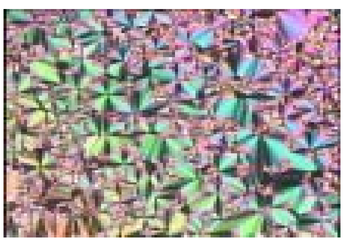
Thermotropic LC's are those in which the LC phase is produced by a change in temperature

N - I transition



Nematic (schlierien)

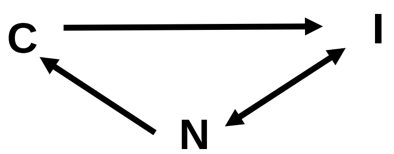
Smectic A



Enantiotropic ("reversible")

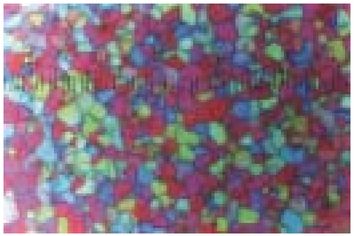
C ⟷ N ⟷ I

Monotropic ("irreversible")



Crystal

"Blue phase"

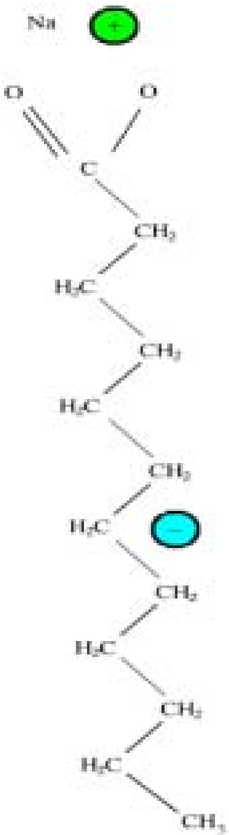


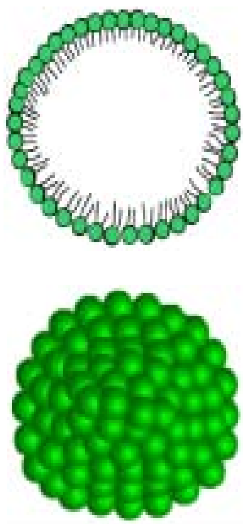
Cholesteric (Grandjean)

Smectic A*

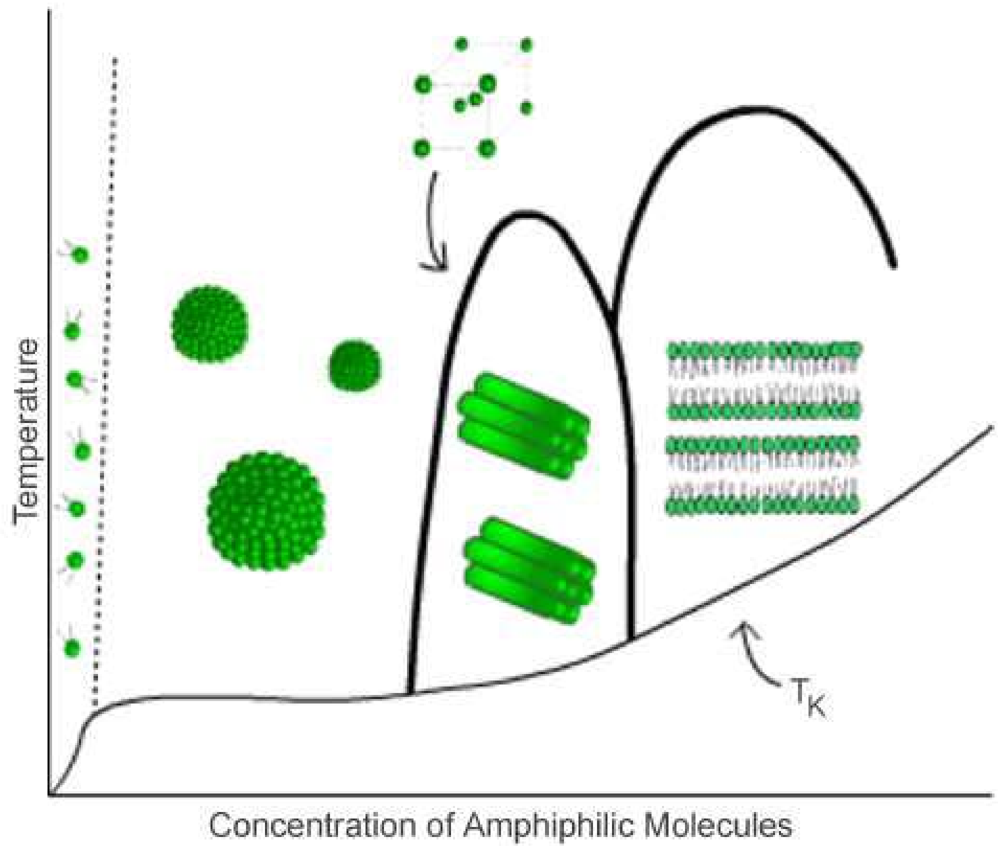
Lyotropic LC phases are formed when "amphiphilic" molecules interact with a solvent

- **Amphiphilic molecules have both polar and nonpolar character**





Micelle



http://plc.cwru.edu/tutorial/enhanced/files/llc/Intro/intro.htm

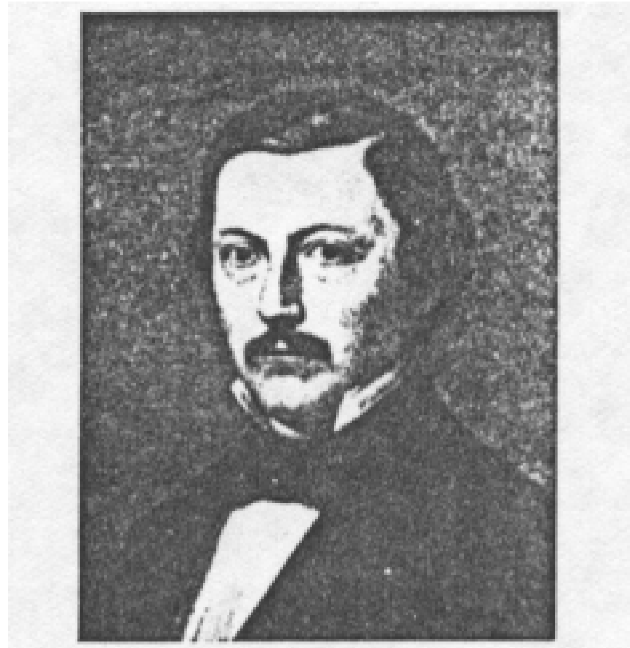
History shows that lyotropic liquid crystals were discovered around 30 years earlier

Rudolf Virchow (1821–1902).

- **Physician, pathologist, scientist, and social politician**

In the early *1850's* , Virchow described a soft, floating substance from nerve core he named "*Myelin*"

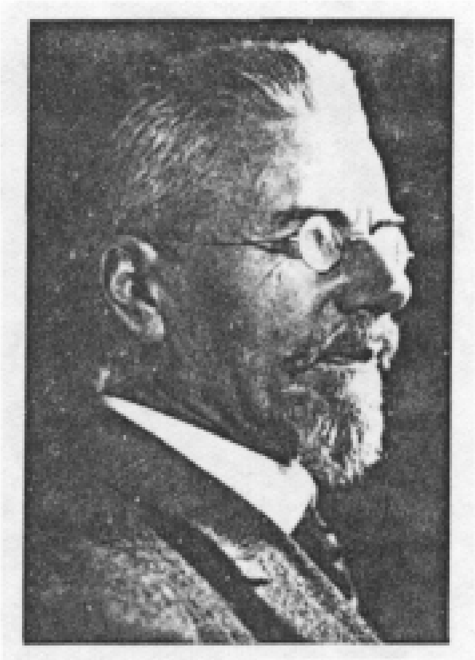
In *1857*, Metteneheimer discovered that Myelin was *birefringent*



C. Chr. Fr. von Mettenheimer (1824–1898).

- **Physician, opthamologist, microscopist**
- **Knighted for his work in anatomy, physiology, pathology, clinical medicine and public welfare**

In 1888, Friedrich Reinitzer observed "striking and marvelous apparitions" in his samples



Friedrich Reinitzer
(1857-1927)
Lecturer in Botany
German University of Prague

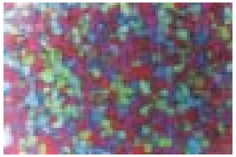
cholesteryl acetate and benzoate prepared from cholesterol

" . . .The substance exhibits two melting points, if one may say so. At 145.5^{o} , it melts to a turbid but absolutely fluid liquid which becomes suddenly clear not until 178.8^{o} . On cooling, violet and blue colors appear which quickly vanish with the sample leaving lactescently turbid but fluid. On further cooling the violet and blue colors reappear, but very soon the sample solidifies forming a white crystalline mass" . . . *

POM

crystal

Heating



145.5^{o}

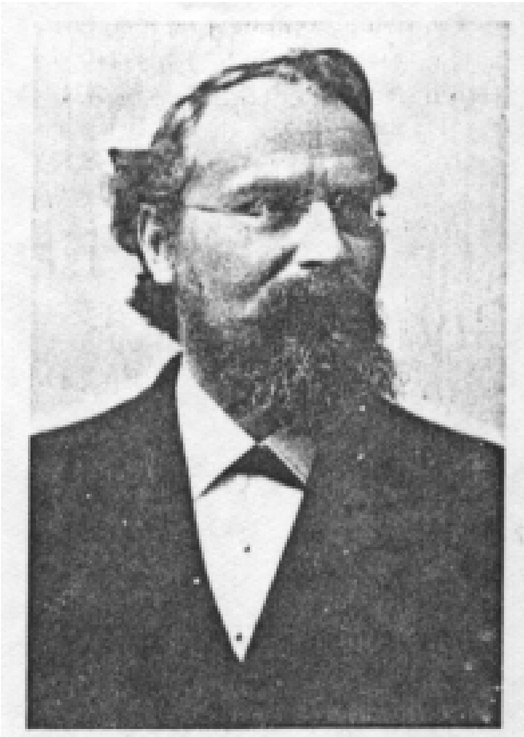
178.8

Cooling

crystal

***excerpt from a 16 page letter written to Prof. Otto Lehmann on March 14,1888**

Reinitzer sent his samples to Prof. Otto Lehmann for further investigations of his substances



Otto Lehmann
(1855-1922)
Professor of Physics
Technical University of Aachen

- **Appointed as assistant professor in 1885 after authoring 35 papers**
- **Research interest were phenomenon of phase transitions and what kind of "molecules" may be involved**
- **Well-known as an expert in phase transitions and crystal growth**
- **Coined the terms "enantiotropism" and "monotropism" to describe reversible and irreversible transitions**
- **Observed light scattering effects in cholesteric liquid crystals in an electric field**
- **Invented the heating-stage microscope and pioneered its use in experimental physics**

Lehmann's "Kristallisations-Mikroskop", the forerunner of the modern-day hot-stage for polarizing microscopy

NCTU DI

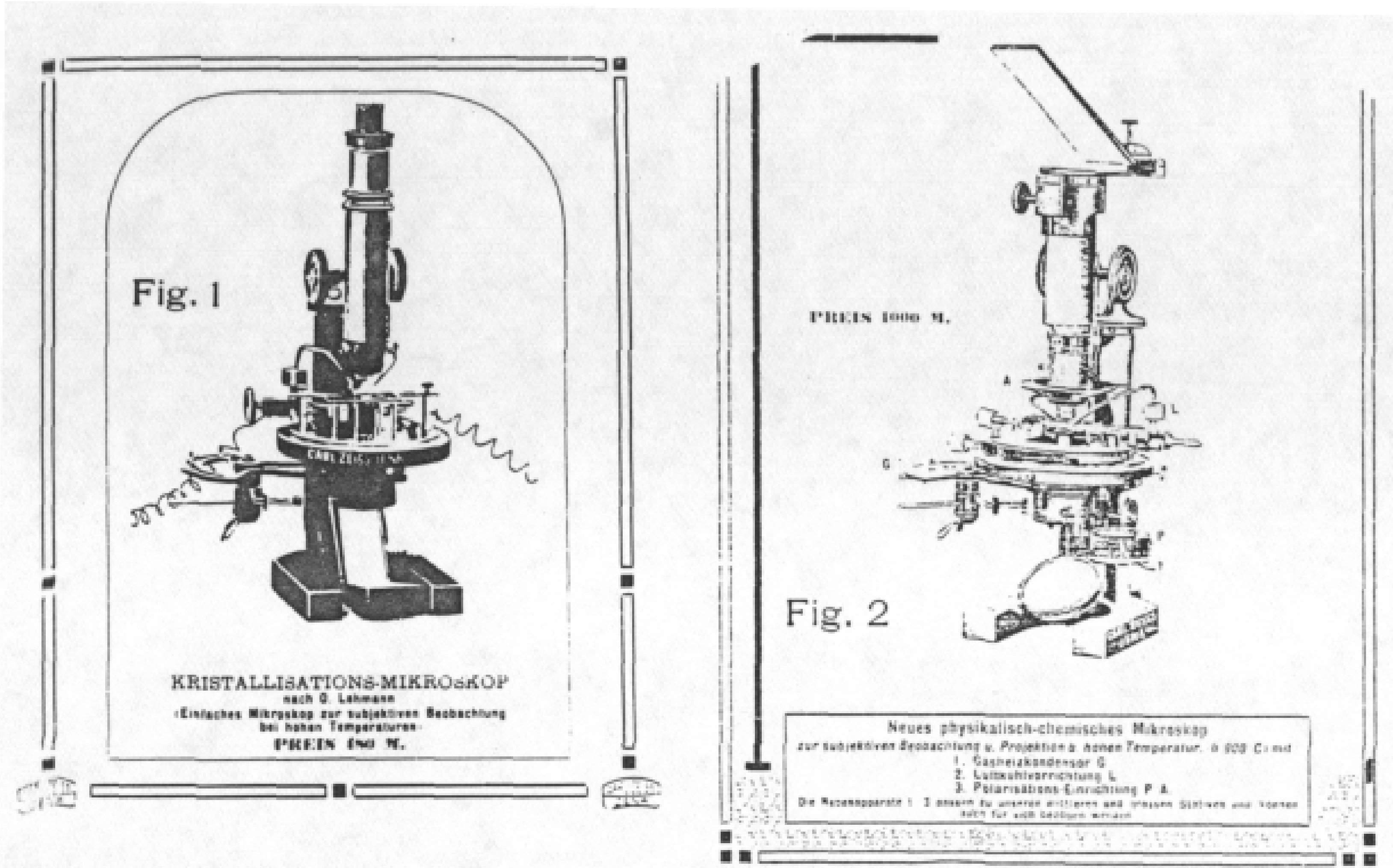


FIGURE 15 Later types of heating-Microscopes, as manufactured by Zeiss-Jena. The polarizing unit was either a reflecting glass plate, or a Nicol-prism.

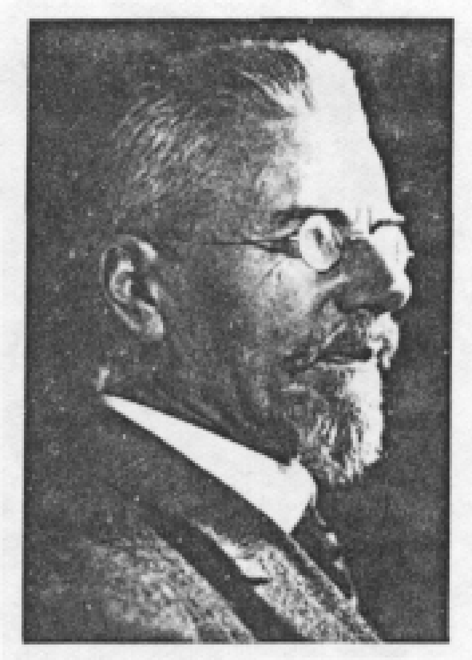
Lehmann confirmed the existence of a "flowing, soft crystalline state " in Reinitzer's samples

Otto Lehmann

Lehmann writes to Reinitzer on August 20,1889:

" … And so my new results confirm your already in good time declared view, that the "Griess" (the substance that causes the turbidness) consists of *very soft crystals,* that are to be considered as a physically isomeric modification of the substance. It is absolutely homogeneous, and another liquid- as you assumed formerly- is not present. . . .

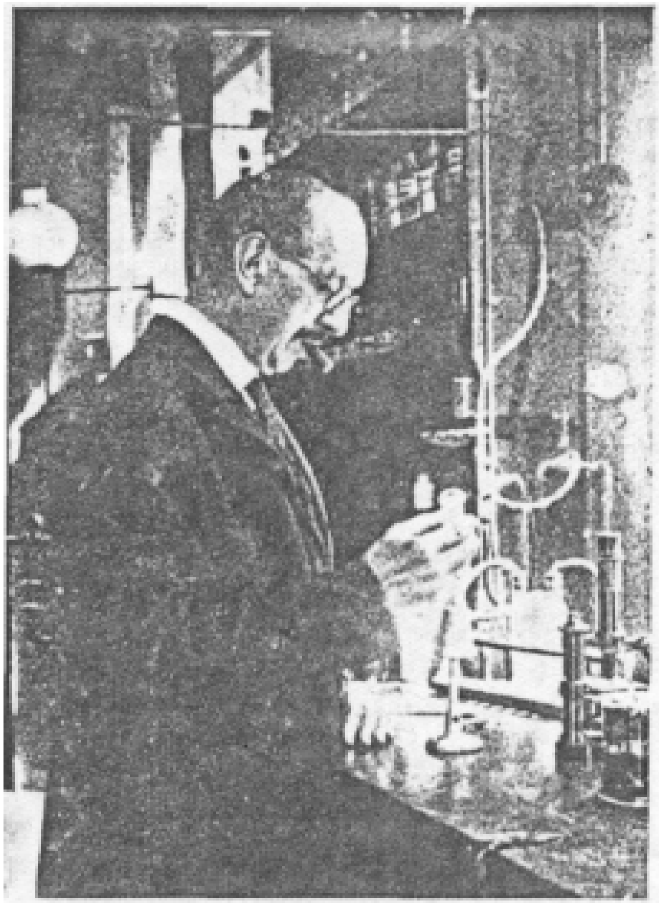
. . . It is of a high interest for the physicist that crystals exist that are of such a considerable softness that one could almost call them liquid."



Friedrich Reinitzer

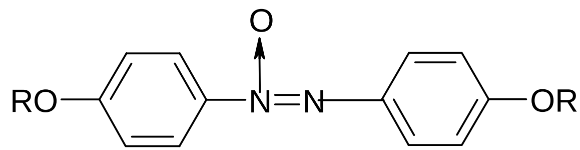
Lehmann's article entitled "Uber Fliessende Krystalle" (On Floating Crystals) submitted to Zeitschrifte fur Physikalishe Chemie on August 30, 1889 is the first published work to introduce the concept of a "liquid crystal"

In 1889, Gatterman and Ritschke synthesized the first liquid crystals not derived from natural products

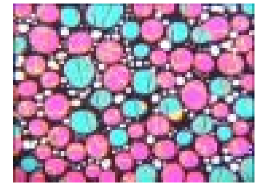


Ludwig Gatterman
(1860-1920)

Assistant Professor of Chemistry
Heidelberg University



Azoxy ethers

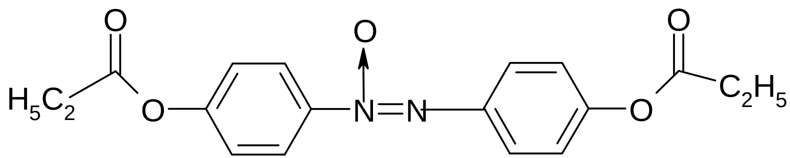


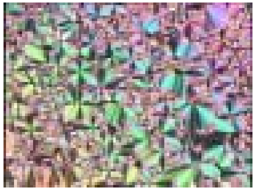
- **Observed two phase transitions and "floating turbid melts" under the microscope**
- ***Published the synthesis details on June 11,1890***
- **Lehman confirms behavior, and terms them "*Krystalline Flussigkeiten*"* because their viscosity was much lower than the cholesterics**
- **Lehmann publishes "The Structure of Crystalline Liquids" on March 24, 1890**

The chemist Daniel Vorlander dominated the liquid crystal research scene for three decades beginning in 1905

Daniel Vorlander
(1867-1941)
“Ordinarius” fur Chemie
University of Halle

- **In 1902, he found that one of the compounds he had synthesized**

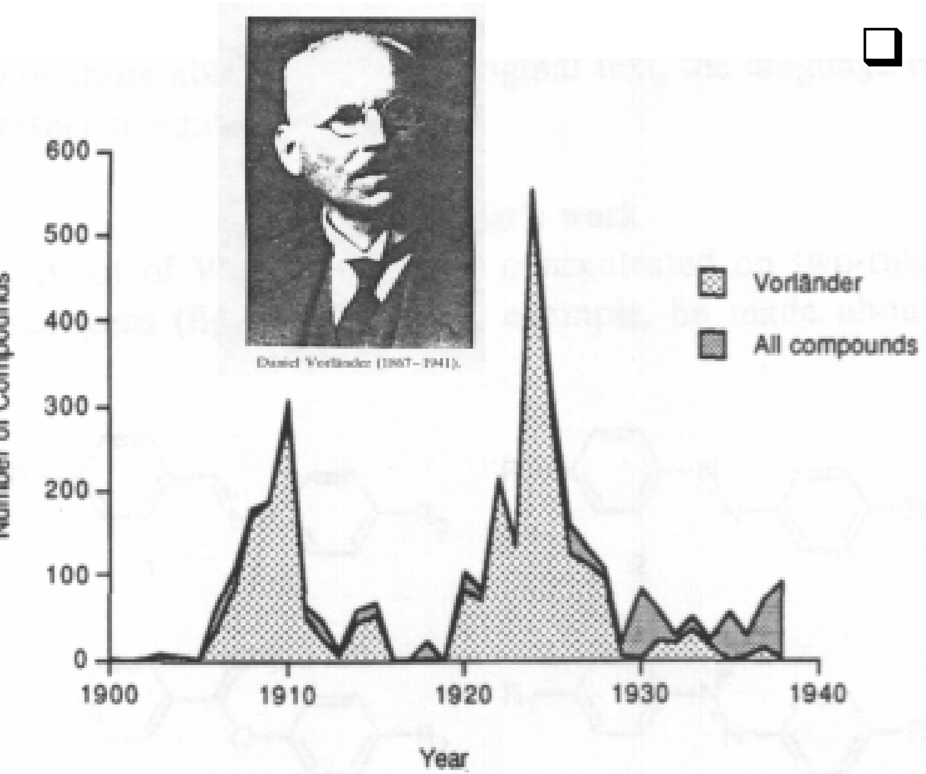




was also a liquid crystal (smectic)

- **As principal teacher of organic chemistry for all science students in Halle, he held each lecture as a “special event” with visual demonstrations**
- **Was the first to study the influence of molecular structure on the appearance of liquid crystalline phases**
- **Developed synthesis of “homologous series” of compounds for studying structure-property relationships**

During his tenure at Halle, Vorlander synthesized over 2700 liquid crystal compounds



igure 1. Number of liquid crystal materials reported by Vorländer and in total in each year from 1900 to 1950.

about 5% of all compounds made to date

❑ ***First to synthesize:***

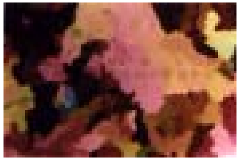
- **Metallomesogens**
- **Polymer mesogens ("suprakristallin")**
- ***Banana-shaped mesogens***
- **Heterocyclic mesogens**
- **Mesogens with lateral groups**
- **Thermotropic ionic mesogens**
- **Columnar (discotic) mesogens**
- ***Ferroelectric mesogens***
- **"Siamese-twin" mesogens (flexible dimers)**

Georges Friedel develops a classification system for liquid crystal phases in 1922

Georges Friedel
(1865-1933)
University of Strasbourg

- The son of the famous chemist Charles Friedel
- Described liquid crystal phases as "crystalline-amorphous" rather than "solid-liquid"
- Coined the term "mesomorphic" to describe liquid crystals as a new state of matter
- Used the Greek terms "nematic" ("thread")

and smectic ("soap")



instead of "schlierien" and "rod" to classify non-chiral liquid crystal phases

Friedel did not take the possibility of smectic phase polymorphism into account

The 1960's mark the beginning of a period of "re-awakening" of interest in liquid crystals

- Prior to 1965, liquid crystals were considered an unimportant, "niche" research area

  "*Whilst liquid crystals are uncommon and of no practical importance, they are of interest for the light they throw on the conflict between order and disorder.*"
  - M. J. S. Dewar (1967)

  "Herr Schenck, leave this stupid stuff!"
  - J. Vollhard to his then research assistant R. Schenck (circa 1890)

- Extensive synthesis work by George Gray (University of Hull) and researchers at the Halle school under the direction of Sackmann yielded a host of new compounds for experimentation of physical and optical properties

- The First International Liquid Crystal Conference was held at Kent State University in 1965, with an attendance of 90 delegates

- By the Fourth ILCC in held in Stockholm in 1972, device applications were being discussed and presented openly

Thermal mapping using selective reflection was the first practical application for cholesteric LC's

- Initial research begun at Westinghouse Electric by J. L. Fergason in the late 1950's
- First applications were for non-destructive thermal testing of turbine blades for cracks and defects
- Numerous other thermography applications were explored, as well as research in color mapping of electric, magnetic, and microwave fields
- Later applications in the field of biomedicine included placental location, mammography, and study of blood flow

Termed the "Chameleon Chemical" in the popular press, cholesteric LC's were applied to human thermography

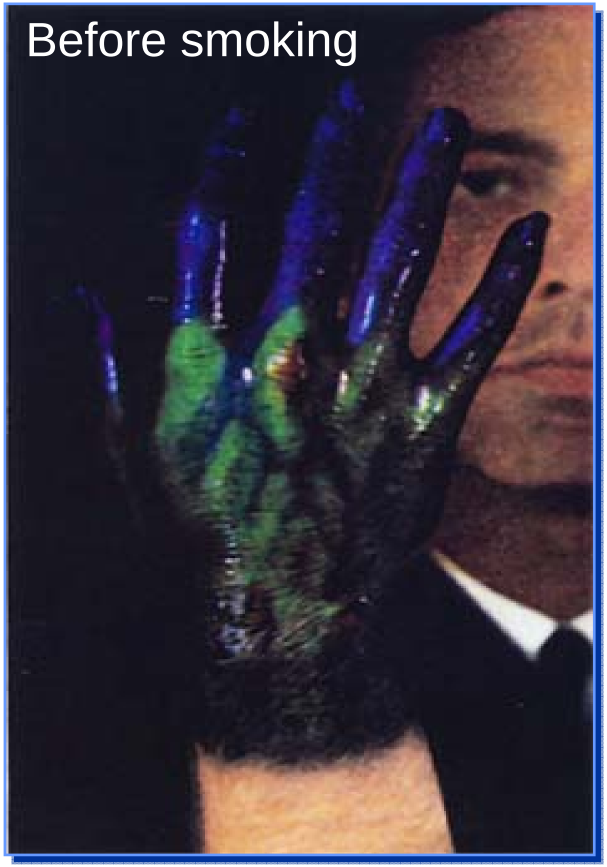
Sprayed onto the body, liquid crystals map out temperature

– warmest: blue

– cooler: green → red

January 12, 1968

Cholesteric liquid crystal thermography was promoted as a cost-effective way for doctors to see beneath the skin



Blue (warm) fingers for normal blood flow

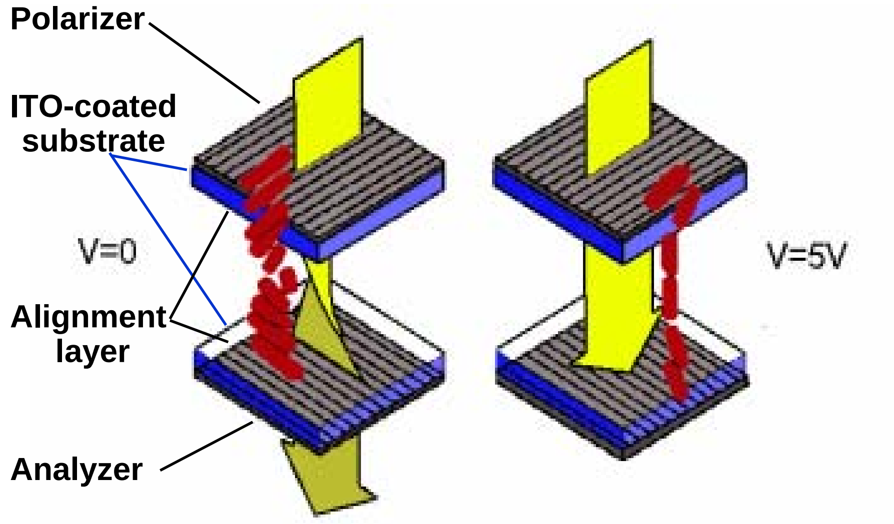
Green (cooler) fingers from nicotine in cigarettes that restricts flow to extremities

Do not smoke! It reduces your blood flow!!!

The invention of the "twisted nematic" LC display marks the birth of the modern LCD industry

- **Helfrich and Schadt (Europe) and Fergason (USA) apply separately for patents on the twisted nematic (TN) display concept**
- **LCD manufacturing for watch and calculator displays begins in the U.S. (RCA and ILIXCO)**
- ***The US was the dominant manufacturer of LCD displays during this period***
- **Japanese companies acquired the technology through licensing agreements**

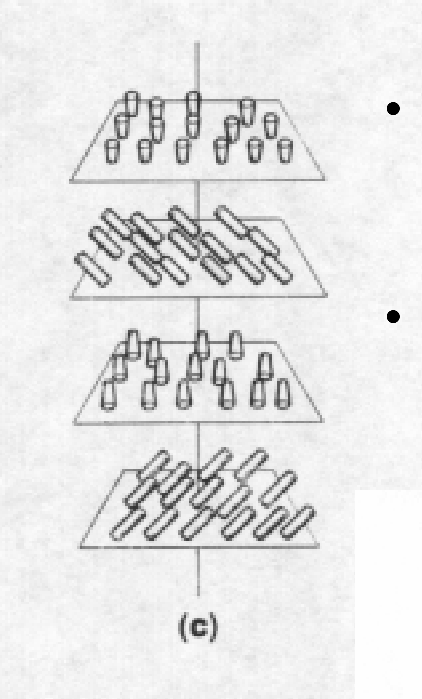
Twisted Nematic (TN)



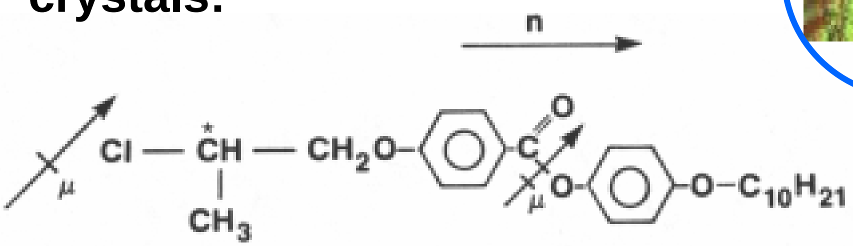
Acts as a voltage-controlled *polarization rotator* (light valve)

Question: *Where is the LC display research now?*

R.B. Meyer observed the first evidence of ferroelectric switching in the chiral smectic C* phase



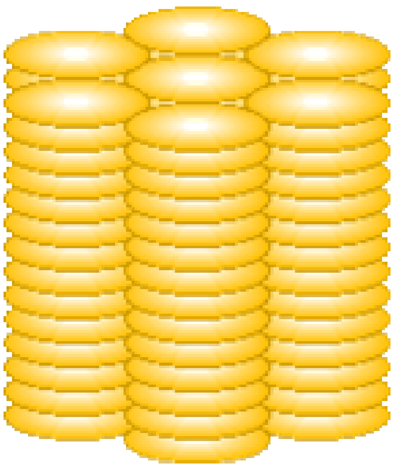
- Observed field-linear helix unwinding in the chiral smectic C (SmC*) material DOBAMBC
- Postulated that three elements were required for ferroelectric effects to be seen in liquid crystals:



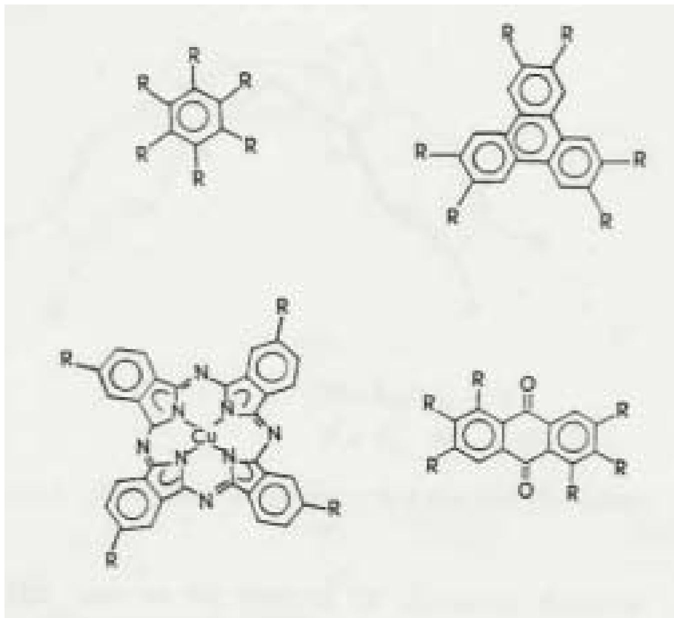
- ❑ Molecular tilt (produced by alkyl tail and small transverse dipole moment
- ❑ A chiral center (noncentrosymmetric)
- ❑ Large transverse dipole moment coupled rigidly to the chiral center

Discotic liquid crystals represent the first mesophases obtained "by rational design"

- **Hexahydroxbenzene-n-alkanoates first synthesized by *Chandresekhar's* research group in 1977**



Columnar phase

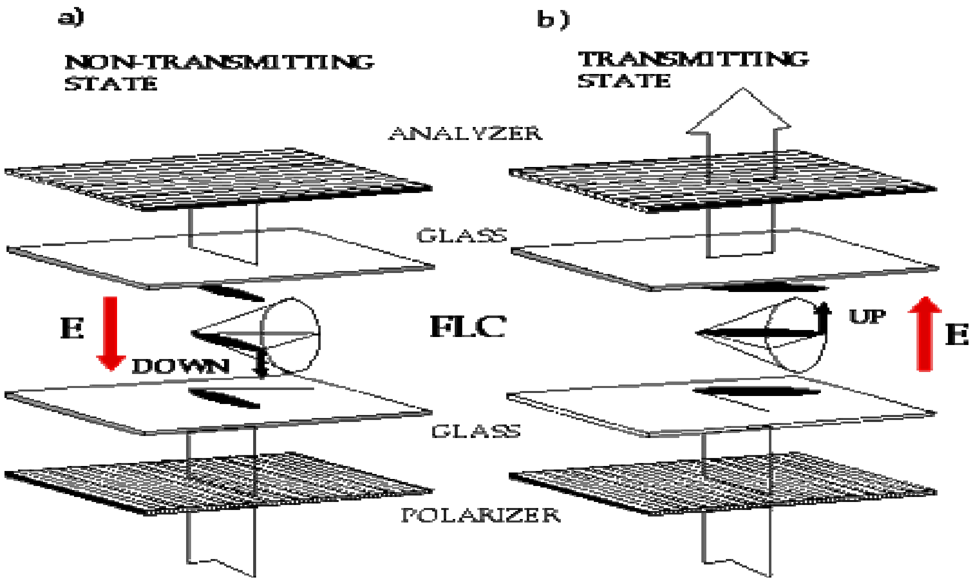


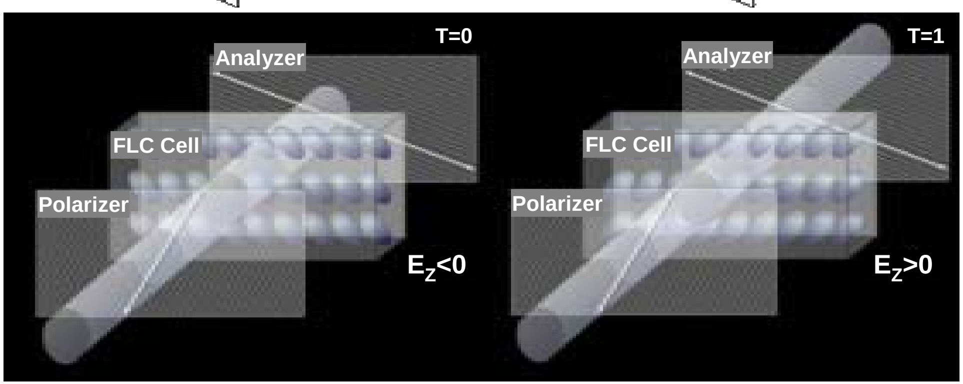
Nematic discotic phase

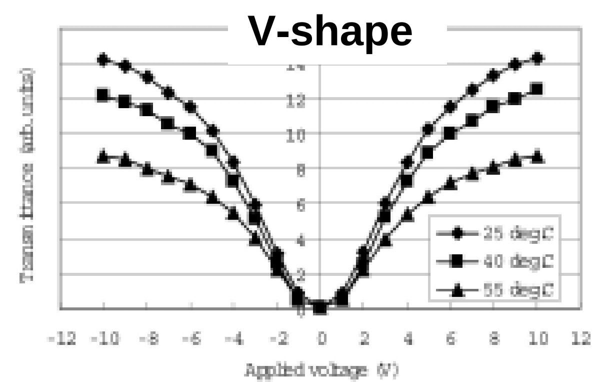
Applications in optical storage media, displays, nonlinear optics, and as anisotropic semiconductors have been explored

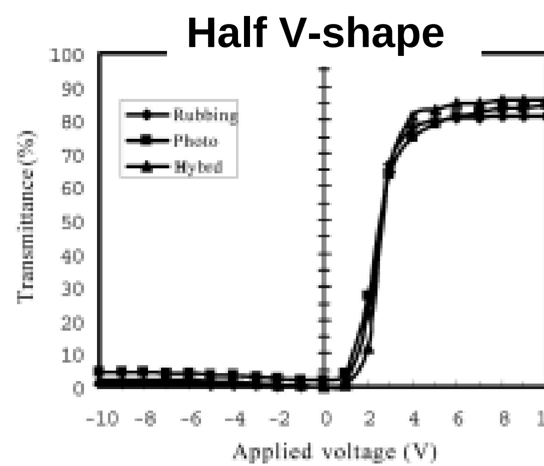
Ferroelectric LC's brought the promise of "bistable switching and broke the millisecond response time barrier

- Surface-Stabilized Ferroelectric Liquid Crystal (SSFLC) device (Clark and Lagerwall)



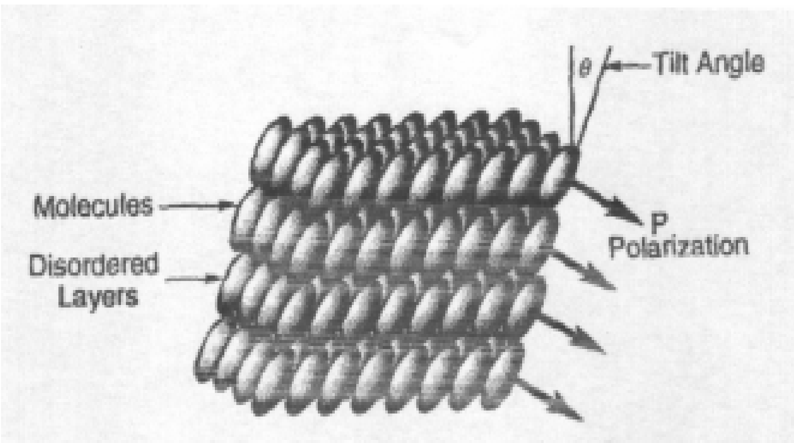




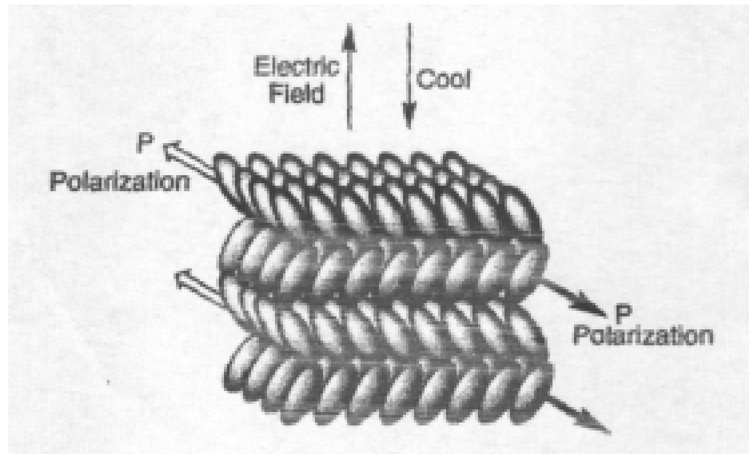


Helix-unwinding by surface forces and thin cell spacing

The discovery of antiferroelectric LC phases by Fukuda opened new possibilities for device applications



Ferroelectric LC

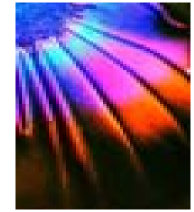


Antiferroelectric LC

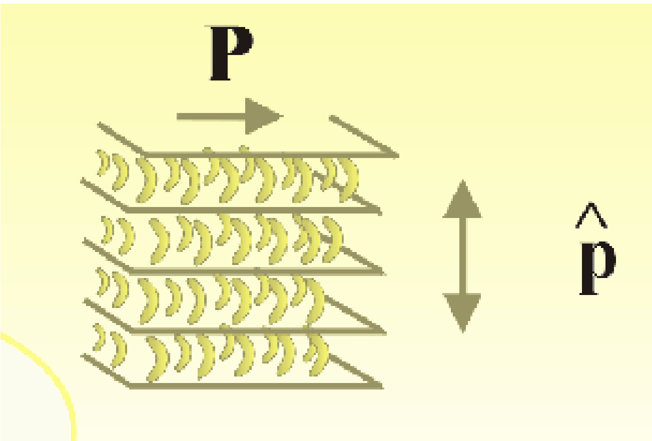
The energy barrier between the ferroelectric and antiferroelectric states is very small and molecular switching occurs at very low voltages

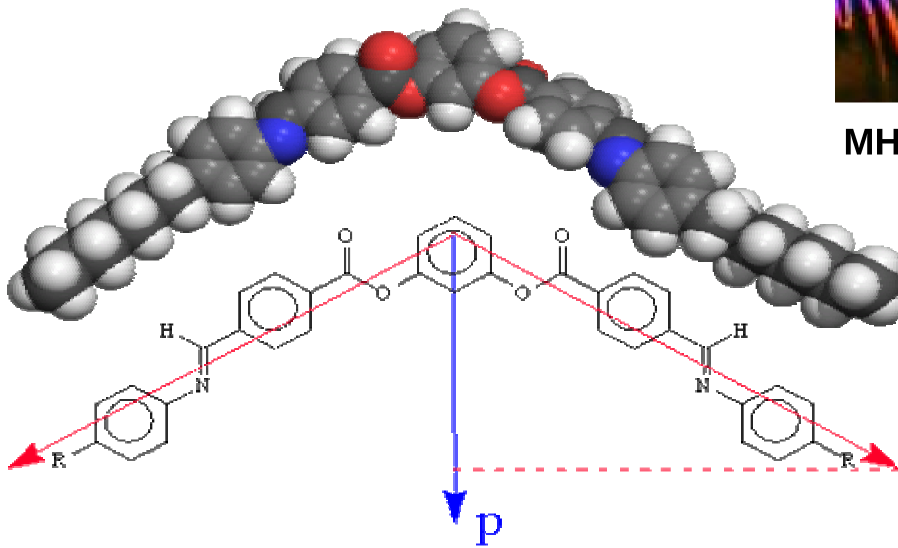
Banana-shaped mesogens show ferroelectric properties even though the constituent molecules are achiral

- **Banana LC's were first reported by Vorlander as "bad rods"**



MHOBOW

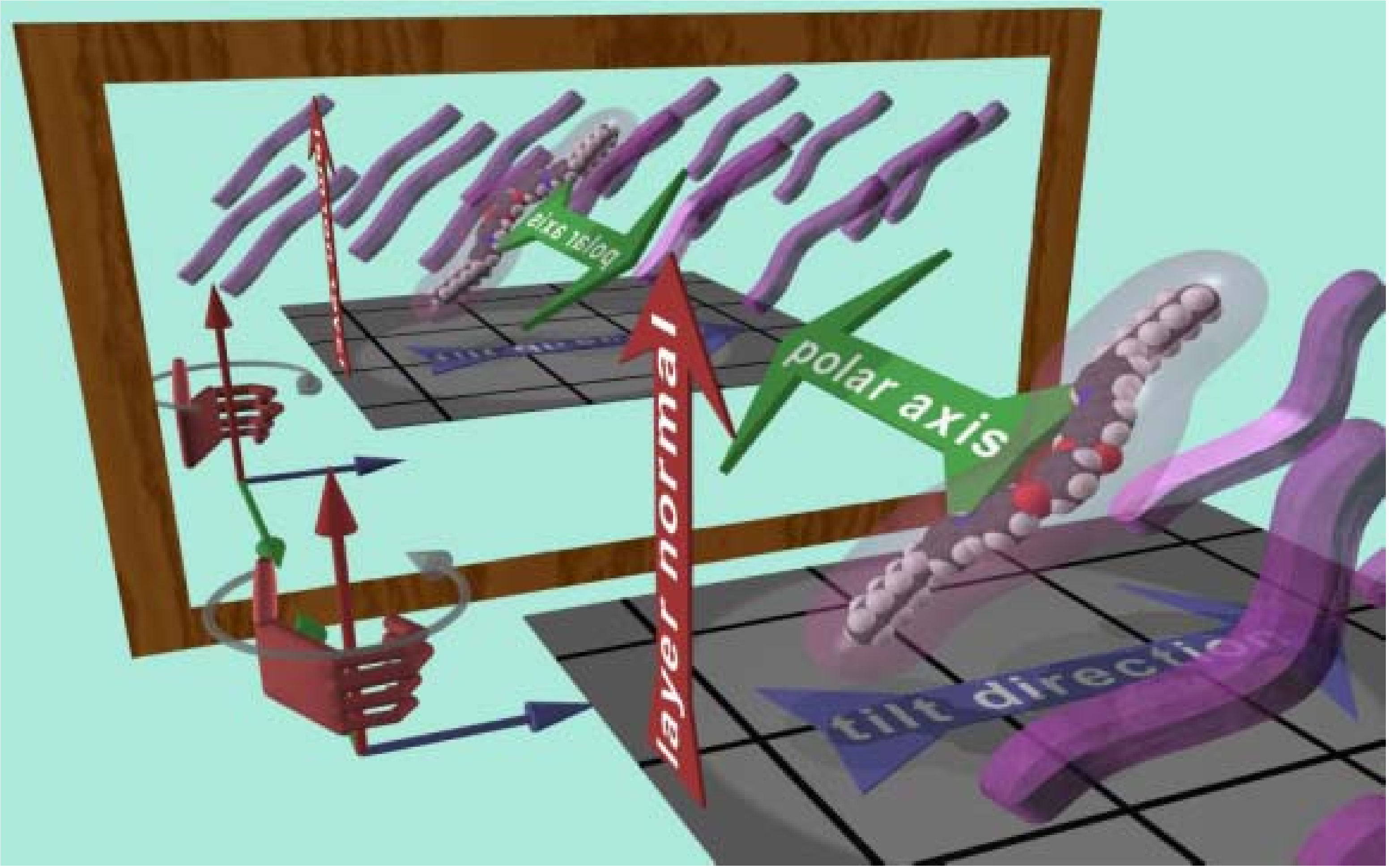




- **Antiferroelectric switching demonstrated by Takazoe in 1996**
- **MHOBOW synthesized by the Walba group (U. Colorado) (2002)**
- **ODBP mesogens (biaxial nematics) synthesized by Madsen in 2004**

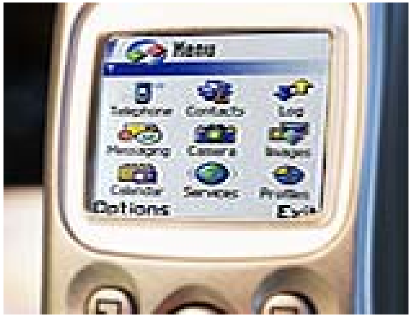
Because they are noncentrosymmetric (C_2 symmetry), banana LC's can show nonlinear optical properties (SHG)

Banana mesogens meet the C_2 symmetry requirement for ferroelectricity *without a chiral center*



Molecules are *not* superimposable on their mirror image!

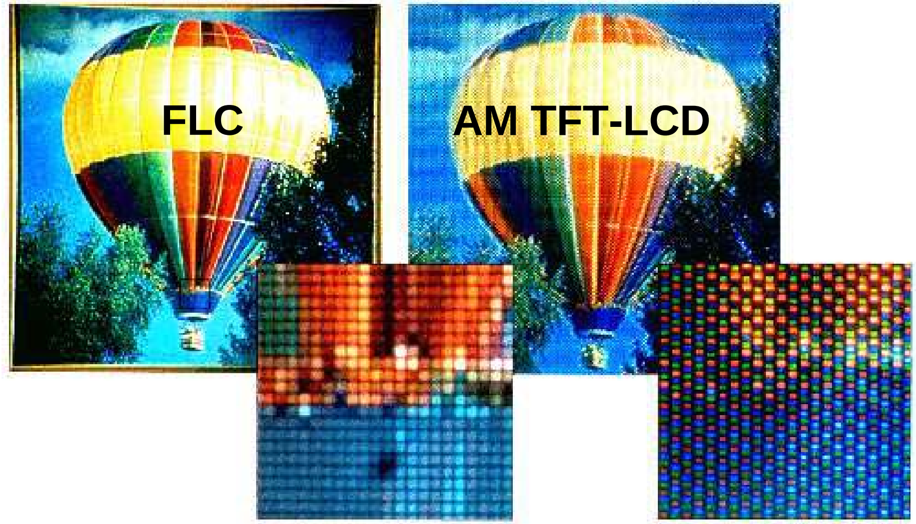
Nematic liquid crystal displays have become ubiquitous in the flat-panel display market



From a "niche" research area in 1950 to a multi-billion dollar industry today!

Ferroelectric LC devices have now matured to the point of demonstrable commercial products

Canon SSFLC display panel



Displaytech “FLC on Silicon” technology

Advantages of FLC Cell:

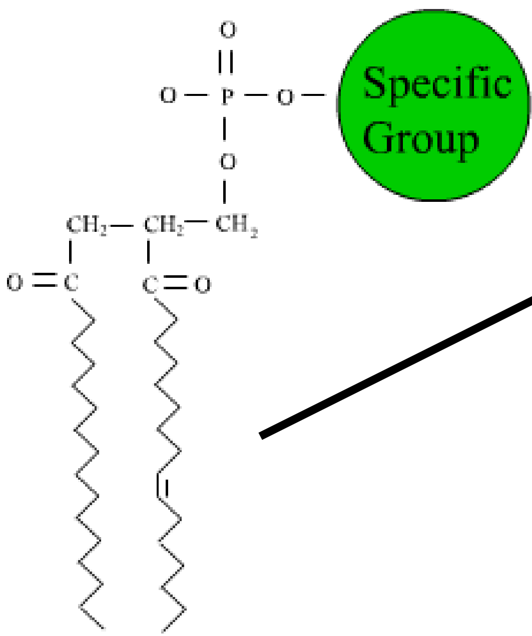
- **Fast response time:** 10^1~10^2 μsec
- **High contrast ratio:** 300~700:1 (*under bright ambient*)
- **Memory effect:** Bi-stable / Multi-stable
- **Higher resolution:** 3x of conventional LCD
- **Wide viewing angle:** Without compensation film

Liquid crystals play a vital role in many aspects of life processes and the natural world

- Lyotropic and thermotropic liquid crystalline structures play an important role in biophysics, cell biology, and reproduction of DNA
- All cell membranes are lyotropic liquid crystals
- The outermost layer of skin is primarily a lyotropic liquid crystal made of fatty acids
- The brain and nerve endings are particularly rich in mesogens (cerebrosides)
- Diseases such as arteriosclerosis and sickle cell anemia are related to liquid crystal transitions

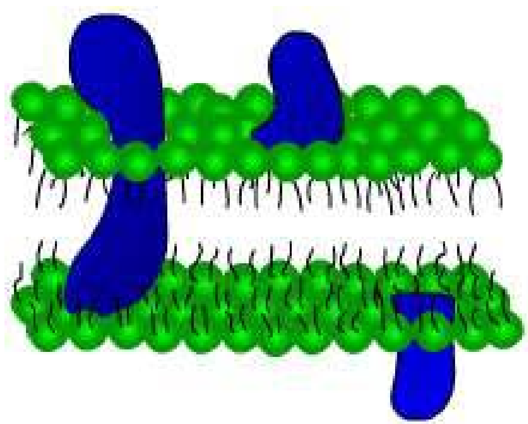
Lyotropic liquid crystals constitute the basic structures of cell membranes in living organisms

- Phospholipids and cholesterol form lyotropic bilayers, the basic structure of a cell membrane

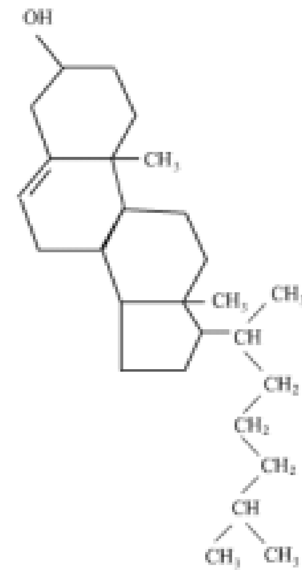


Phospholipid

Protein



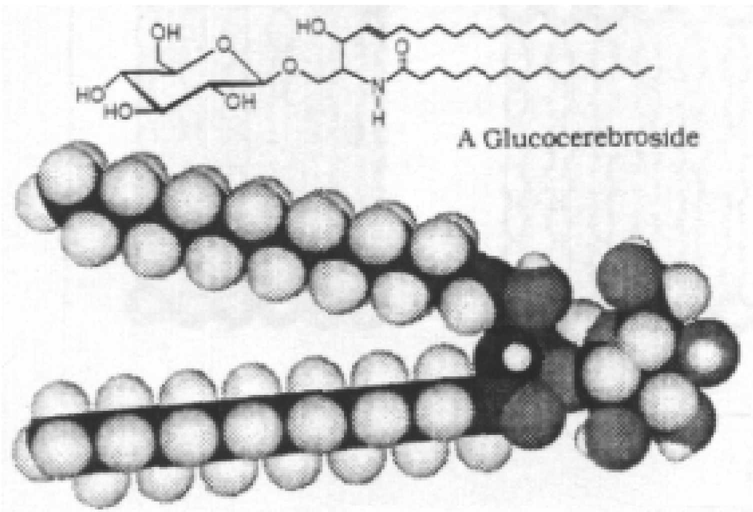
Cell membrane

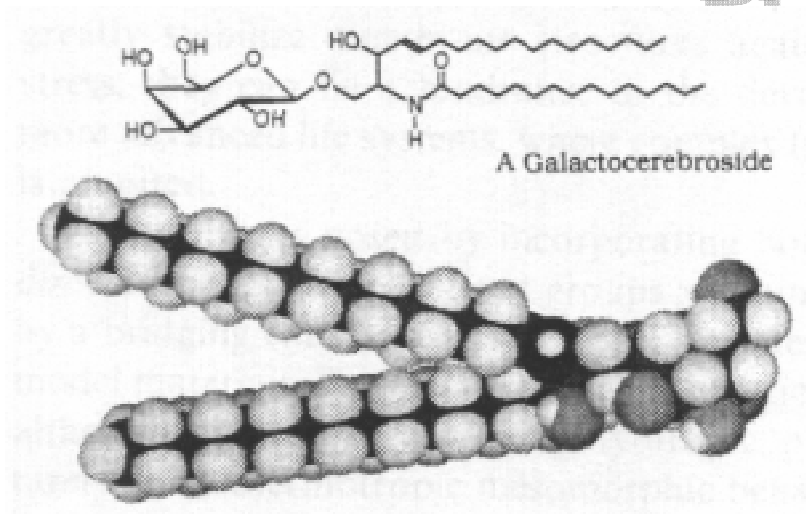


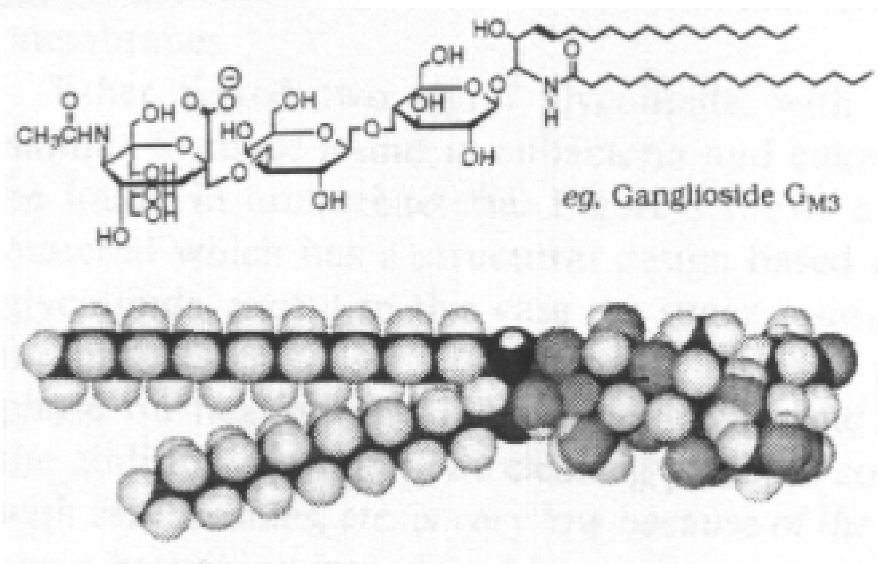
Cholesterol

http://plc.cwru.edu/tutorial/enhanced/files/llc/Apps/apps.htm

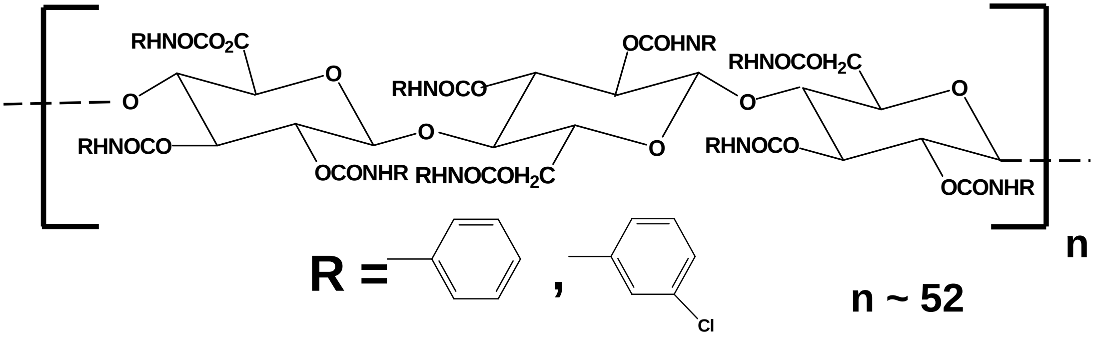
Lyotropic cerebrosides and gangliosodes play an important role in brain and nervous system functions



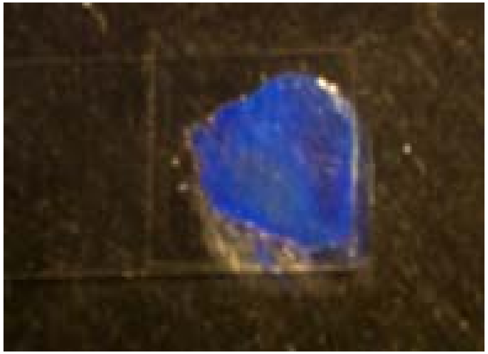




Derivatives of cellulose can form both thermotropic and lyotropic liquid crystals



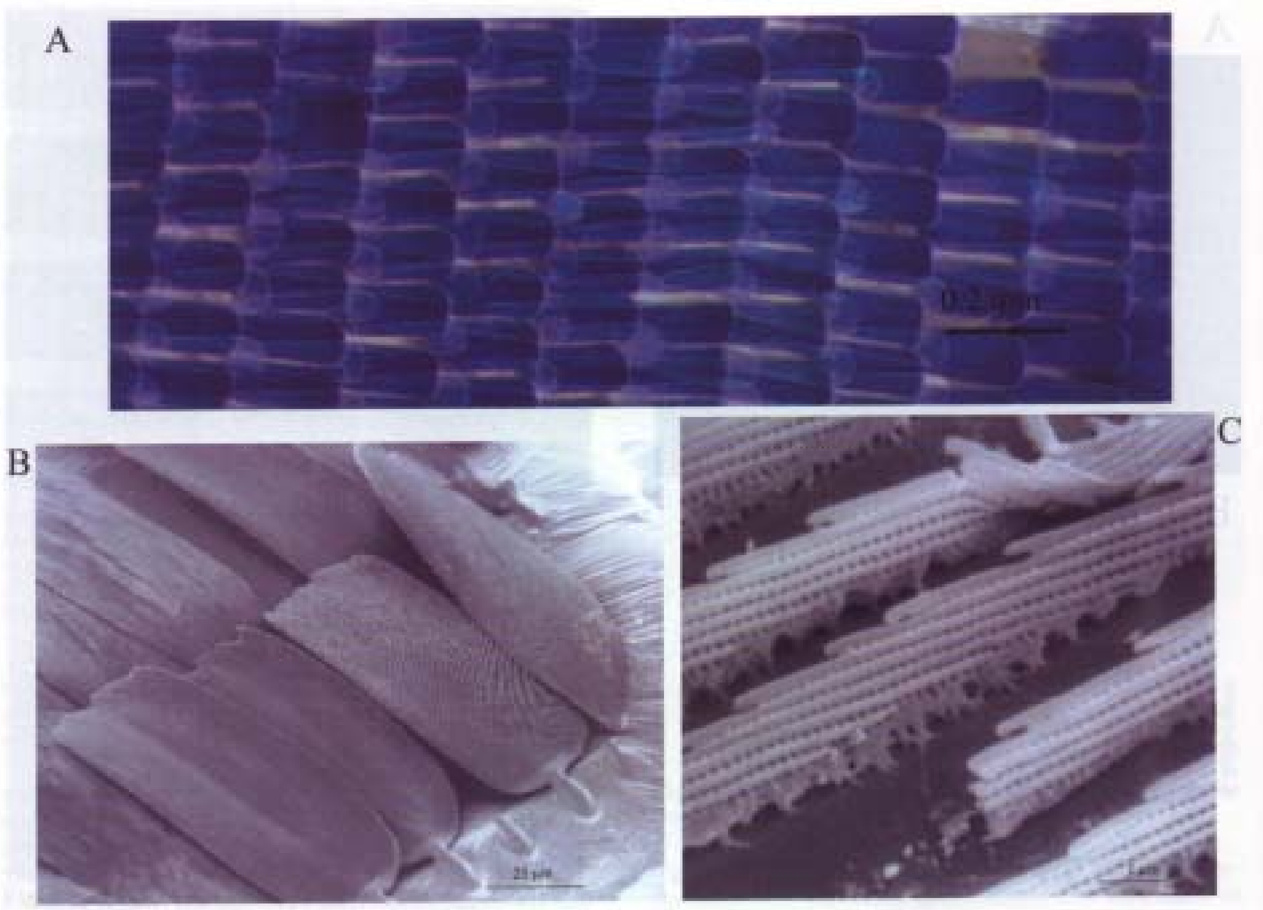
Cellulose Tricarbanilate (a *urethane*)



Cross-linked cellulose urethane lyotropic LC film

- When dissolved in a suitable photopolymerizable host (e.g, an acrylate), temperature-insensitive, robust films with selective reflection can be obtained for optical applications
- Starting materials (cellulose) are extremely low-cost and plentiful

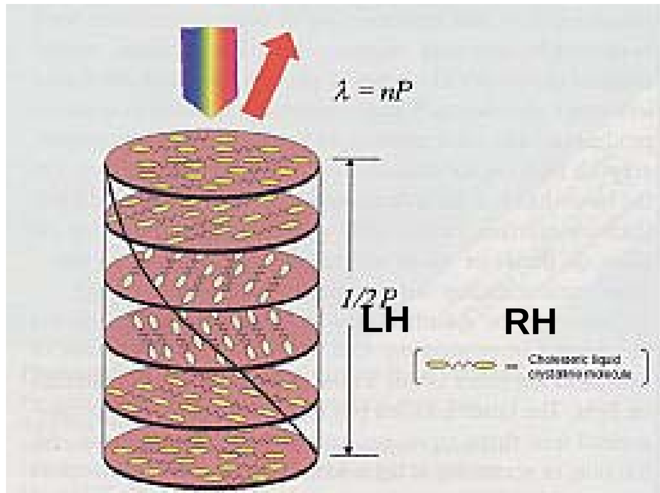
The irridescent colors in the wings of many birds and butterflies are due to an interference effect and not pigmentation

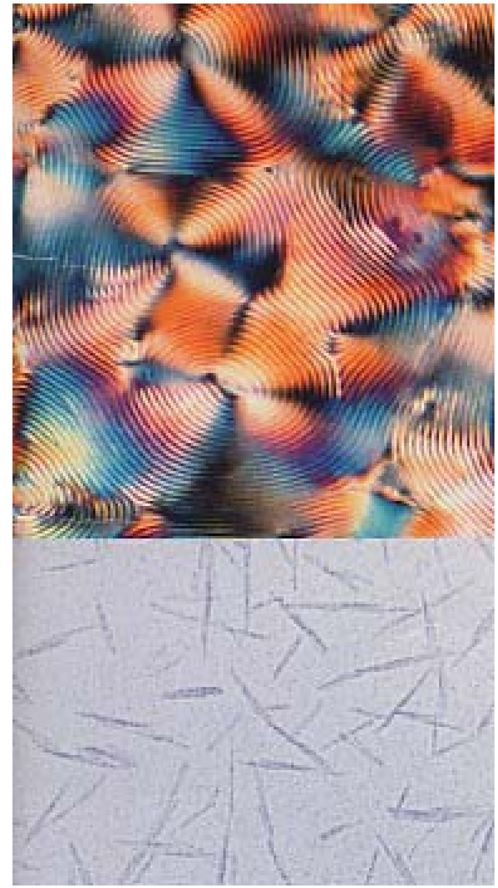


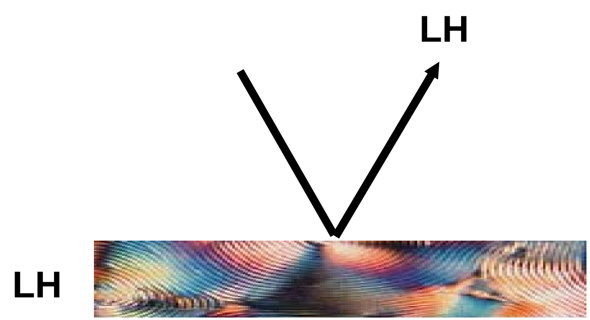
Butterfly wing

Ostroverkhova, Oksana ,and Moerner, W. E. *Chem. Rev.* **2004,** *104,* 3267-3314

The exocuticles of beetles contain layers of *chitin*, a naturally occurring polysaccaride that possesses a cholesteric liquid crystal structure







P. Optima

$_{max}$ = broad, with peak at 560 nm (LH)

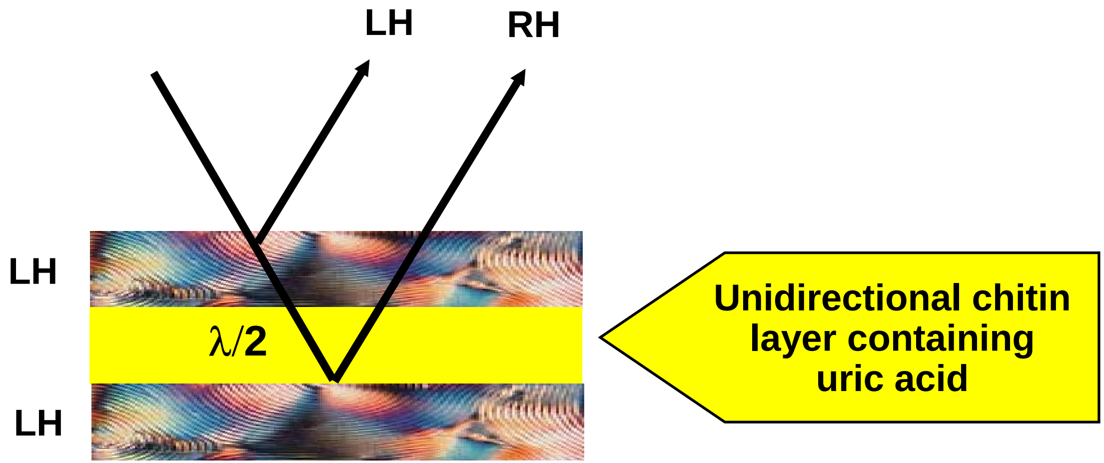
Chitin crystals

A "unidirectional" birefringent layer between the helical chitin layers in *P. Resplendis* acts as a l/2 plate!

P. Resplendis

λ_{max} = ***560 nm (LH)***

λ_{max} = ***575-624 nm (RH)***



S. Caveney, "Cuticle Reflectivity and Optical Activity in Scarab Beetles: The Role of Uric Acid", *Proc. Roy. Soc. Lond*. B, **1971**, *178*, 205-225

Liquid crystal research has a rich past and a bright future

NCTU DI

- **Despite competition from new technologies in the information display area, liquid crystal research remains a vibrant and growing area**
- **Close collaboration between scientists and engineers from inter-disciplines between physics, chemistry, materials science, optics and electrical engineering continues to be a train of the liquid crystal research**
- **New mesophases continue to be discovered and exciting new applications for these materials are being conceived**