Chemistry Materials for Memory and Display Systems

Syllabus

Memory Devices: Introduction, Basic concepts of electronic memory, History of organic/polymer electronic memory devices, Classification of electronic memory devices, types of organic memory devices (organic molecules, polymeric materials).

Display Systems: Photoactive and electroactive materials, Nanomaterials and organic molecules used in optoelectronic devices. Liquid crystals (LC's) - Introduction, classification, properties and application in Liquid Crystal Displays (LCD's). Properties and application of Organic Light Emitting Diodes (OLED's) and Quantum Light Emitting Diodes (QLED's).

Self-learning: Properties and functions of Silicon (Si), Germanium (Ge), Copper (Cu), Aluminum (Al), and Brominated flame retardants in computers.

Introduction, Basic concepts of electronic memory,

Basic Concepts of Electronic Memory

- The basic goal of a memory device is to provide a means for storing and accessing binary digital data sequences of "1's" and "0's", as one of the core functions (primary storage) of modern computers.
- An electronic memory device is a form of semiconductor storage which is fast in response and compact in size, and can be read and written when coupled with a central processing unit (CPU, a processor).
- In conventional silicon-based electronic memory, data are stored based onthe amount of charge stored in the memory cells.

History of organic/polymer electronic memory devices

- With the rapid development of the electronics industry in recent years, information technology devices, such as personal computers, mobile phones, digital cameras and media players, have become an essential part of our daily life. From both the technological and economic points of view, the development of novel information storage materials and devices has become an emergent issue facing the electronics industry.
- Due to the advantages of good scalability, flexibility, low cost, ease of processing, 3D-stacking capability and high capacity for data storage, organic-based electrical memory devices have been promising alternatives or supplementary devices to conventional inorganic semiconductor-based memory technology.
- The demand for more efficient and faster memory structures is greater today than ever before. The efficiency of memory structures is measured in terms of storage capacity and the speed of functioning. However, the production cost of such configurations is the natural constraint on how much can be achieved.

The advantages of organic and polymer electronic memory devices are:

a) They can be processed easily.
b) Structure of the molecule used can be designed through chemical synthesis,
c) Device structure is very simple.
d) Dimension of the device can be decreased (miniaturized).
e) Cost of production is less.
f) Power consumption during operation is low
g) They exhibit multiple state properties.
h) 3D stacking capability and
i) Data storage capacity can be increased to very large value.

CLASSIFICATION OF ELECTRONIC MEMORY DEVICES

1. TRANSISTOR-TYPE ELECTRONIC MEMORY

(It's a miniature device that is used to control or regulate the flow of electronic signals)

In order to store data in a memory device, it must have minimum two distinct electronic states. These states are assigned as "O" and "1" or "ON" and "OFF" respectively. A transistor-type semiconducting electronic memory device contains a fine electronic circuit, including a complementary metal oxide semiconductor (CMOS) transistor and capacitor (C). In this electronic circuit, "O" and "1" corresponds to the "discharged" and "charged" states of the C, respectively.

- Inorganic transistors are widely used in conventional semiconductor memory.
- Organic (including polymer) transistors are also of great potential for memory applications Organic field-effect transistor (OFET) type memory devices have attracted considerable research interest due to their easilyintegrated structure and the non-destructive reading of a single transistor.

2. CAPACITOR- TYPE ELECTRONIC MEMORY DEVICE

(It is a device used to store electric charge)

Organic and polymeric ferroelectric materials can be used in capacitor- type electronic memory device. Capacitors have two parallel plate electrodes and charges are stored in these electrodes under an applied electric field. Bistable states of capacitor is based on the amount of charge stored in the cell. Data can be stored in these devices based on different charge stored in the cell. Charges stored in the cell maintain electric polarization that can be switched between two stable states by an external electric field.

3. RESISTOR-TYPE ELECTRONIC MEMORY DEVICE

(It's a device having the resistance to the passage of electric current)

This type of memory device uses switchable resistive materials to store data. It is based on the change of the electrical resistivity of materials in response to an applied voltage (electric field). Electrical bistability arises in these materials due to different electrical resistivity which are assigned ON and OFF states.

4. CHARGE TRANSFER TYPE ELECTRONIC MEMORY DEVICE

This type of electronic device is based on the Charge Transfer Effects of a charge transfer complex. A charge transfer (CT) complex consists of two parts, one electron donor and other an electron acceptor. It is also called as a donor-acceptor (D-A) complex. The conductivity of a CT complex is dependent on the ionic binding between the D-A components. In CT complex, a partial transfer of charges occurs from donor part to the acceptor part. This results in difference in conductivity. CT complexes exhibit bistable states due to difference in conductivity. This behaviour is used to design molecular electronic devices.

Many organic CT systems, including organometallic complexes, carbon allotrope (fullerene, carbon nanotubes and graphene)-based polymer complexes, gold nanoparticle-polymer complexes, and single polymers with intra-molecular D-A structures are used for memory applications.

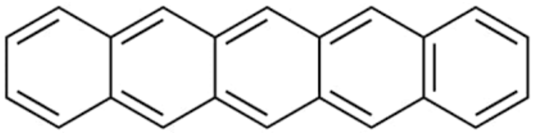
TYPES OF ORGANIC MEMORY MATERIALS

There are two classes of materials which can exhibit bistable states and are used in organic memory devices. They are:
1) Organic molecules,
2) Polymeric materials,
Under each category, lot of different types of molecules exhibiting memory effect are available. Few of them are described here:

1. ORGANIC MOLECULES

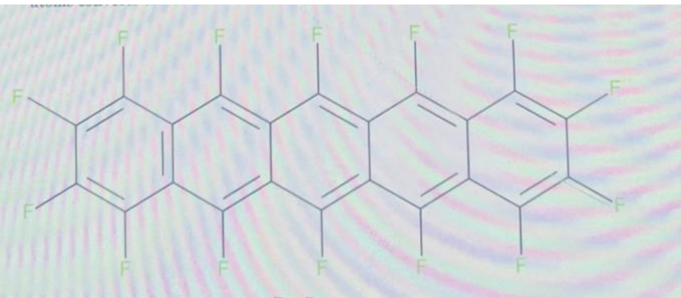
There are different category of organic molecules which show bistable or multistable states when external field is applied. When a threshold voltage is applied they undergo a transition from the OFF state to the ON state, or from the ON state to the OFF state. All these materials can be used in organic electronic memory devices. Few of them are mentioned here.

a) Acene derivatives: Acenes are the polycyclic aromatic compounds consisting of linearly fused benzene rings. They are the very first discovered organic memory devices because of their high charge carrier mobility. Exapmles for acenes are pentacene, perfluoropentacene, naphthalene, anthracene, tetracene, The most important member of the acene family is pentacene. It is a linearly-fused aromatic compound with five benzene rings. It can be obtained in crystal and thin film form. Both forms exhibits a very good hole mobility and hence it behaves as a p-type semiconductor.



Pentacene

When all the hydrogen atoms of pentacene are replaced by fluorine atoms the resulting molecules is perfluoropentacene. Strongly electron withdrawing nature of fluorine atoms converts this molecule in to n-type semiconductor.



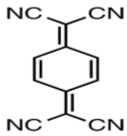
Perfluoropentacene

Pentacene and Perfluoropentacene, both have similar structure and similar crystal packing but former behaves as p-type semiconductor and latter behaves as an n-type semiconductor. Therefore, these molecules together exhibit charge-transfer processes that are useful for memory applications.

b) Devices exhibiting bistable negative differential resistance (NDR): These devices exhibit two stable

NDR states when placed between two ITO electrodes and external field is applied. This property was used to switch between the ON state and the OFF state and hence as a memory device.
Example: N'-diphenyl-benzidine(NPB) embedded between two IT electrodes.

c) Charge transfer complexes: These molecules have two parts, one is electron donor and second is electron acceptor. Donor is an organic molecule. Acceptor can be either metal or organic molecule. These devices exhibit two stable charge states which arise due to transfer of electrons from donor to acceptor under the influence of external field and this principle is used in memory device.
Examples:
a) Copper and 7,7,8,8-tetracyanoquinodimethane (TCNQ) complex (Cu TCNQ)



d) Organic memory devices with a triple-layer structure sandwiched between two outer metal electrodes.
Example: 2-amino-4,5-imidazoledicarbonitrile (AIDCN)trilayerstructure interposed between an anode and a cathode. This device shows two bistable conductivity states on applying voltage. This memory device is non-volatile and rewritable.

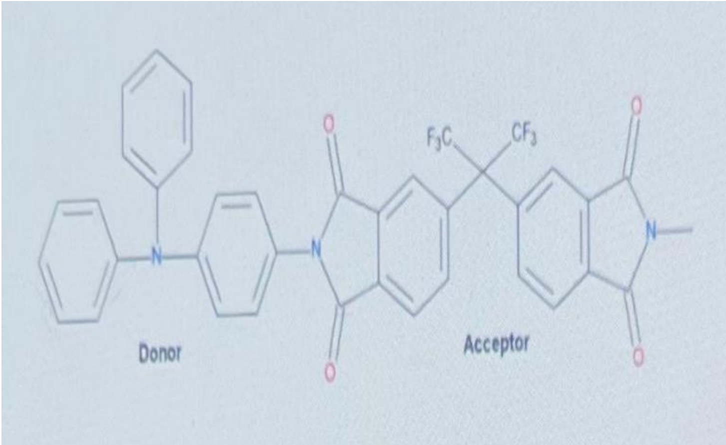
e) Small organic molecules containing both an electron donor and an electron acceptor in a single molecule (D-A molecules): They exhibit bistable conductivity states due to electron transfer from Highest Occupied Molecular Orbital (HOMO) to Lowest Unoccupied Molecular Orbital (LUMO). They are known as Donar-Acceptor molecules (DA molecules).
Example: DRAM device where the electron acceptor naphthalimide (NA) and electron donor carbazole (CA) were linked by hydrazone bond.

f) Small D-A molecules with multilevel stable states: These molecules exhibit multilevel stable states and can be used to increase device capacity by three times. This type of device is called as ternary memory device.
Examples:
a) ITO device demonstrated a typical non-volatile ternary WORM memory behaviour.

2. POLYMER MOLECULES

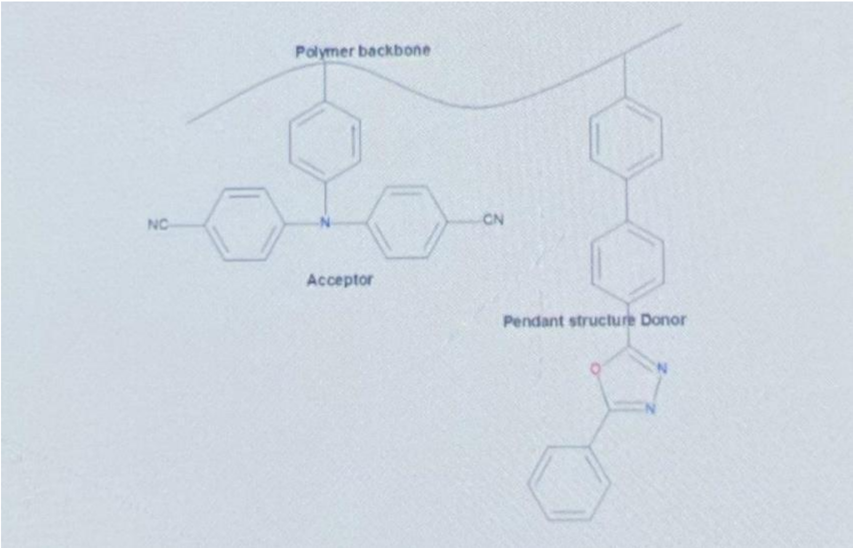
There are five classes of polymers which exhibit memory effect and are used in electronic memory devices.

a) Functional polyimides (PIs):
Functional polyimides (Pls) are one of the most commonly used polymeric materials for organic electrical memory applications. They have high thermal stability and mechanical strength and can be easily processed from solution. In functional PIs, phthalimide acts as the electron acceptor, and triphenylamine acts as an electron donor to form a Donor-Acceptor structure. They exhibit two stable charge states under applied electric field. These states arise due to transfer of electrons from donor to acceptor. This bistability is used to store data in memory device.



b) Non-Conjugated Polymers with Pendants

Non-conjugated polymers with pendent electroactive donors and acceptor are another kind of polymer materials which exhibits electronic memory effect.



c) Conjugated Polymers

Conjugated polymers are rich in pi electrons and they can be made to show charge states by incorporating electron acceptor groups in their back bone. This induced charge transfer channel determines volatility of the memory device. D-A type conjugated polymers are used to fabricate different types of memory device, such as volatile DRAM and SRAM devices, and non-volatile WORM and Flash devices.

d) Polymers with fullerenes or graphene: Carbon nanomaterials such as fullerenes, graphene and their derivatives have good optoelectronic properties. Polymer with covalently attached fullerene, in which the carbazole group of polymer serves as the electron donor and C60 serves as the electron acceptor, has been synthesized.

e) Polymers Containing Metal Complexes:

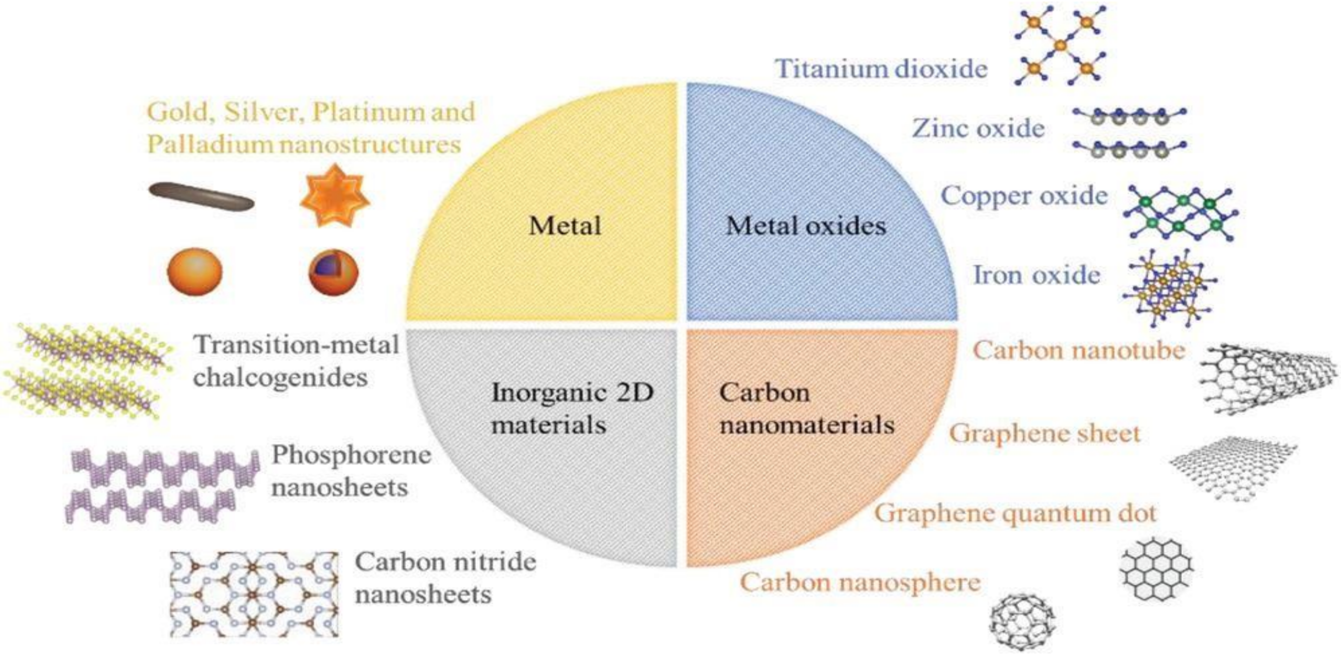
Transition-metal complexes exhibits reversible redox properties. When these are introduced into polymer backbones, they can improve the stability of conductive states. Ferrocene (Fe) is the commonly used metal complex. It exhibits non-volatile memory when introduced in to polymer.

DISPLAY SYSYTEMS:

<u>Photoactive and Electroactive materials:</u>

<u>Photoactive materials</u>: These are the substances which are capable of responding to light or other electromagnetic radiation.

<u>Electroactive materials</u>: These are the substances which are capable of responding to an applied electric field.



Nanomaterials and organic molecules used in optoelectronic devices:

Nanomaterials can be **defined** as **materials possessing, at minimum, one external dimension measuring 1-100nm**

Organic molecules used in optoelectronic devices are referred to as photoactive and electroactive organic materials. They are also called as **organic semiconductors**. When these materials are used in devices, they exhibit **opto-electronic phenomena** and properties are given below:

a) Absorption and emission of light radiation in the wavelength region from ultraviolet to near infrared region.

b) Photo generation of charge carriers.

c) Transport of charge carriers.

d) Injection of charge carriers from the electrode.

e) Exhibit excellent nonlinear optical properties.

Organic molecules used in optoelectronic devices:

Organic compounds with extensive conjugation and pi-electron systems are capable of exhibiting above mentioned set of properties. Those organic materials can be broadly classified into three categories:

a) Small organic molecules

b) Conjugated oligomers

c) Polymers

a) Small organic molecules are crystalline in nature examples for this class of molecules are poly-condensed aromatic hydrocarbons like anthracene, pentacene and fullerenes.
b) Conjugated oligomers are a new family of organic pi-electron systems, with well-defined structures, whose properties and functions can be controlled by varying the conjugation length. Few examples for this class are, pentacene and oligothiophenes.
c) Polymers are bad conductors of electrons. But, conducting polymers with extensive conjugation and pi-electron system exhibit above mentioned electro-optical behavior and they are excellent functional materials. Examples of this class of polymers which find extensive application as organic semiconducting materials are, polyacetylene, polythiophenes, polypyrroles and polyanilines.

NANOMATERIALS USED IN OPTOELECTRONIC DEVICES

Nanomaterials with opto-electrical properties can help in size reduction of future opto-electronic devices. Graphene, fullerenes, carbon nanotubes (CNTs) are carbon based materials which show good electrical, electronic and optical properties. Semiconducting materials are fundamental to opto electronic devices, Quantum dot (QDs) materials including silicon, germanium & different semiconductors such as Sulphides, Phosphides, Selinides of Gallium, Indium, Cadmium (GaS, GaN, GaP, InP, InS, CdSe) and Semiconducting oxides such as TiO2, ZnO, SiO2 shows good opto-electrical properties. These materials along with low-dimensional structures also exhibit unique kind of light-matter interactions like surface plasmon resonance, spintronics, plasmonics etc. They can be used in future photonic and electronic devices.

LIQUID CRYSTAL DISPLAYS

LIQUID CRYSTALS

INTRODUCTION

Liquid crystals find application in the areas of science and engineering, particularly in display systems of modern electronic gadgets. Devices using liquid crystal displays have the advantage of low power consumption and hence are widely used in display devices of mobile communication appliances, aircraft cockpit, laptops and related electronic equipment’s.

Definition of Liquid Crystals: A liquid Crystals is a Phase between Solid and Liquid States.

Example: Cholesteryl Benzoate (145.5º to 178.5ºC)

OR

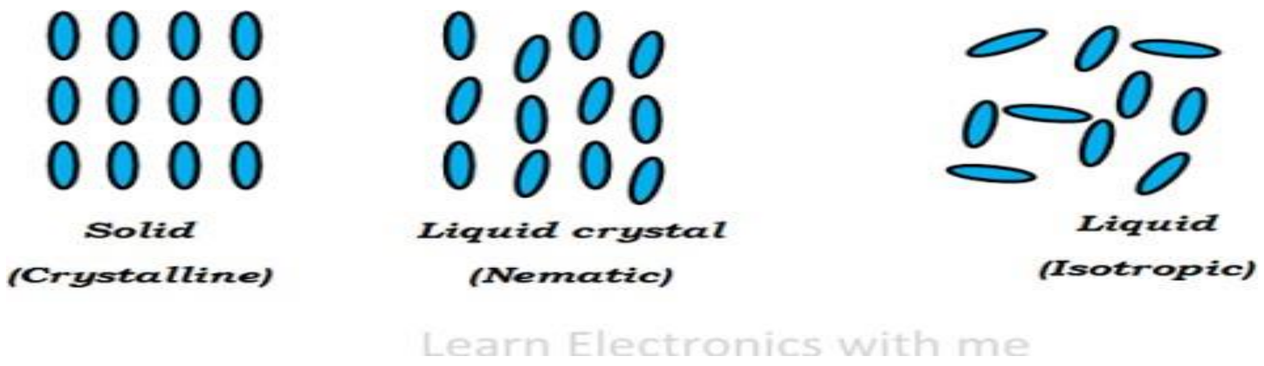
Liquid crystal may be described as a distinct state of matter in which the degrees of molecular ordering lie intermediate between the ordered crystalline solid state and the completely disordered liquid state. The liquid crystal state is also referred to as **mesophase**.

What is Liquid Crystal Display?

- Liquid Crystal Display (LCD) is a flat display screen used in electronic devices such as laptop, computer, TV, cellphones and portable videogames.
- As the name says liquid crystal is a material which flows like a liquid and shows some properties

of solid. These LCD are very thin displays and it consumes less power than LEDs.

- As the name says the molecular structure of liquid crystal is in between solid crystal and liquid isotropic.
- Liquid crystal display(LCD) example when we increase the temperature the ice cube melts and liquid crystal is like the state in between ice cube and water.
- Liquid Crystal Display(LCD)is a flat display screen used in electronic devices such as laptop, computer, TV, cell phones and portable videogames.



The liquid crystal state was first discovered by an Austrian botanist, Freidrich Reinitzer in 1888 in cholesteryl benzoate molecule. He observed that solid cholesteryl benzoate on heating becomes a hazy liquid at 145.5°C which on further heating turns into a clear, transparent liquid at 178.5°C (as if it had two melting points). On cooling, similar phase change was observed at same temperature. Liquid crystal phase is also called as **mesophase.**

Classification of Liquid crystal

Liquid crystals are classified into two main categories, namely
1. Thermotropic liquid crystals
2. Lyotropic liquid crystals

1. Thermotropic Liquid Crystals

The class of compounds that exhibit liquid crystalline behavior on variation of temperature alone are referred to as thermotropic liquid crystals. The temperature range at which some liquid crystals are stable are given below:

Cholesteryl benzoate	145.5 ^{o}C to 178.5 ^{o}C
p-azoxyphenetole	137 ^{o}C to 167 ^{o}C
p-azoxyanisole	116 ^{o}C to 135 ^{o}C
Anisaldazine	165 ^{o}C to 180 ^{o}C

Thermotropic liquid crystals may be further classified as:

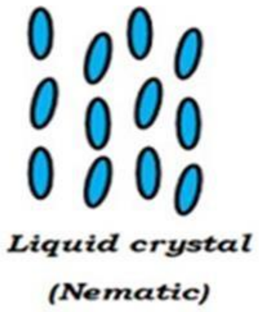
a) Nematic liquid crystals

b) Chiral(Twisted)Nematic liquid crystals
c) Smectic liquid crystals

a) Nematic liquid crystals:

Nematic (Greek nematos = thread like) liquid crystals are formed by compounds that are optically inactive. The
molecules have elongated shape and are approximately parallel to one another. In this phase the molecules maintain a preferred orientational direction but no positional order and they can diffuse throughout the sample.

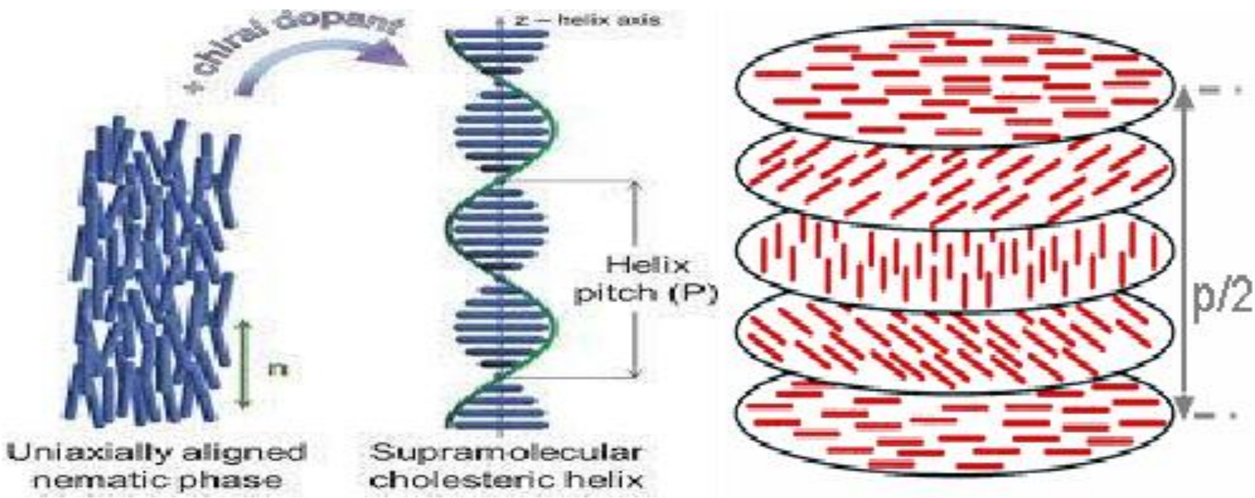
Ex: Para-azoxyanisole (PAA) which exhibits liquid crystalline behavior in the temperature range of 118°C to 135°C.



b) Chiral (Twisted) Nematic liquid crystals:

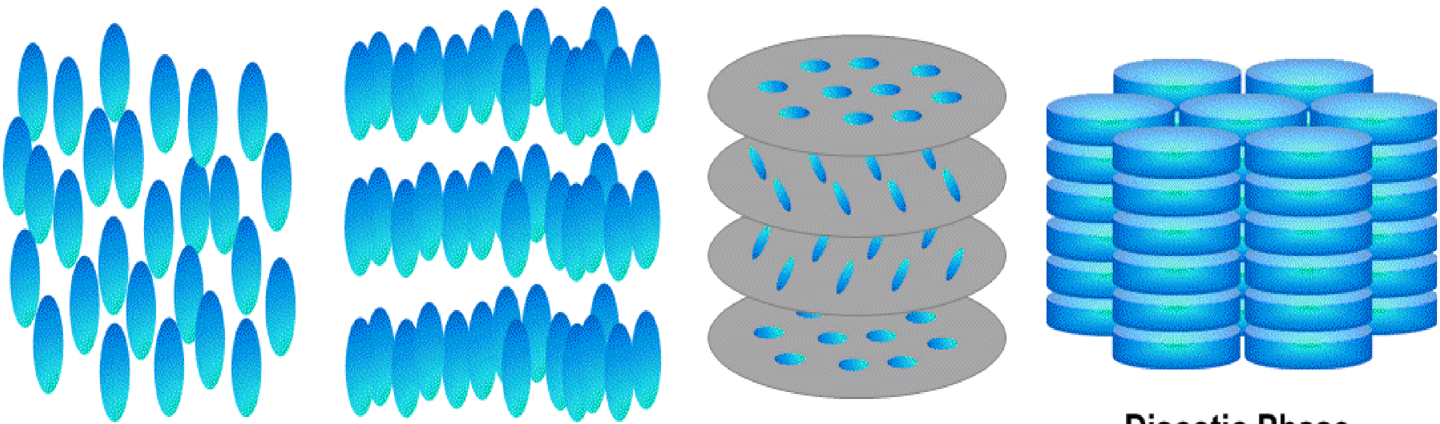
Chiral nematic or twisted nematic liquid crystals (TNLC) are formed from optically active compounds having chiral centres. Compared to nematic liquid crystals, all the molecules are approximately parallel to one another, but in Chiral nematic phase, the molecules arrange themselves so as to form a Helical structure. In this mesophase, the director is therefore not fixed in space as in a nematic phase, but rotates throughout the sample forming a helical pattern as it changes its direction just like the motion of a nut on a screw. The distance travelled by the director as it completes one full turn is called the **pitch** of the liquid crystal. In other words, the pitch length is the distance travelled by the director when it gets turned by 360°. The twist present in chiral nematic liquid crystals make them to exhibit spectacular optical properties.

Ex: Cholesteryl benzoate (145.5 ^{o}C to 178.5 ^{o}C), Cholesteryl myristate, Cholesteryl formate



c) Smectic Liquid Crstals:

Substances that form smectic phases are soap-like (in Greek, smectos means soap) Infact, the soft substance that is left at the bottom of a soap dish is a kind of smectic liquid crystal phase. In smectic mesophase, there is a small amount of orientational order and also a small amount of positional order. The molecules are arranged in regularly spaced layers (positional order). Within the layer they tend to point along the director (orientational order) Based on the orientation of the director there are two types of smectic phases. If the director is perpendicular to the planes it is called smectic A and smectic B if the director makes an angle other than 90°.



2. Lyotropic Liquid Crystals

Some compounds transform to a liquid crystal phase when mixed with a solvent They have both polar (lyophilic) and a non-polar (lyophobic) end. They are amphiphilic compounds. Such amphiphilic molecules form ordered structures in both polar and non-polar solvents. They are usually obtained by mixing the compound in a solvent and increasing the concentration of compound till liquid crystal phase is observed. Such liquid crystals are called lyotropic liquid crystals. The formation of lyotropic liquid crystals is dependent on the concentration of either the component or the solvent.

Ex: (i) Soap (soap - water mixture) molecules

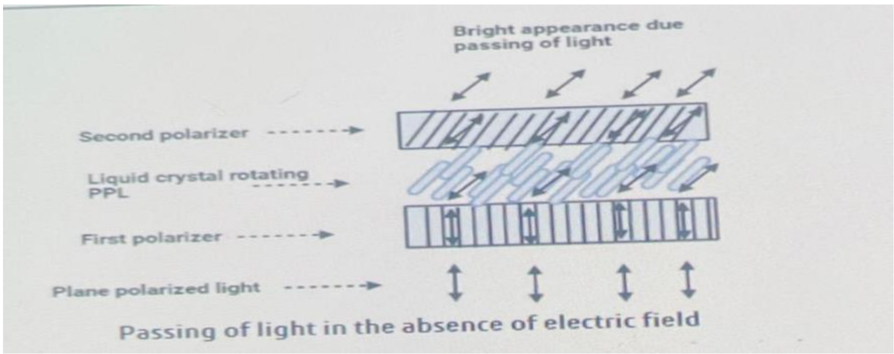
(ii) Phospholipids which are biologically important molecules where each cell membrane owes its structure to the liquid crystalline nature of the phospholipid - water mixture.

EFFECT OF LIGHT AND ELECTRIC FIELD ON LIQUID CRYSTALS

Effect of light

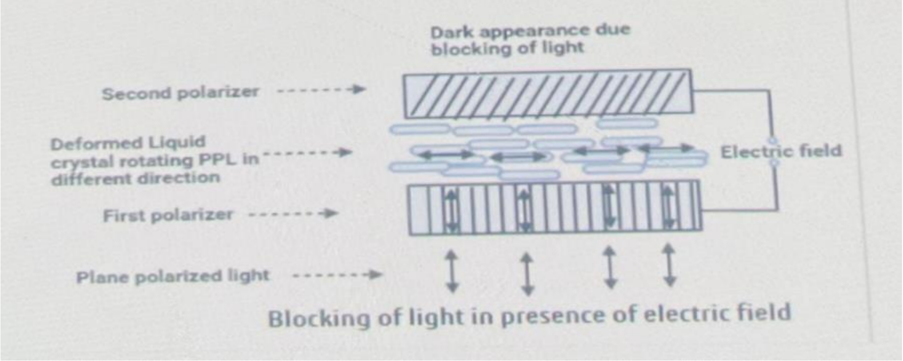
When plane polarized light is made to pass through two crossed polarizer's, no light emerges out. This is because, the light emerging from the first polarizer is completely absorbed by the second polarizer and hence appears dark.

Now, if a display is obtained by placing liquid crystal in between two polarizers and the two polarizers are placed inclined to each other at an angle similar angle of rotation by liquid crystal (twisted nematic liquid crystal which is optically active). If a source of light radiation is kept below first polarizer, it passes through it and rotated by liquid crystal and passes through the second polarizer. Hence, it gives bright appearance to display.



Effect of Electric Field

Now, if an electric field is applied between two polarizers, then liquid crystal molecules will rearrange themselves to applied field and hence the rotation of plane of the polarized light is also affected. Thus, light passing through first polarizer cannot pass through second polarizer and it gives dark appearance to display.



Thus, display appears bright in the absence of electric field and appears dark in the presence of an electric field. This combination of optical and electrical properties of liquid crystals are used in Liquid Crystal Displays.

Properties of Liquid Crystals:

- Light weight and compact
- Low power consumption
- High resolution
- Easy to manufacture
- Less heat is emitted during operation.

Applications of Liquid Crystal Displays:

- Used in TV, Computer Monitor, Mobile Phones, Watches, calculators etc.
- Used in Medical Equipment's like Blood pressure instruments, X-ray and Patient monitoring systems
- Used in Automotive Industry. Example: GPS System, Electronic Displays in car etc.
- Used in Gaming Display devices.

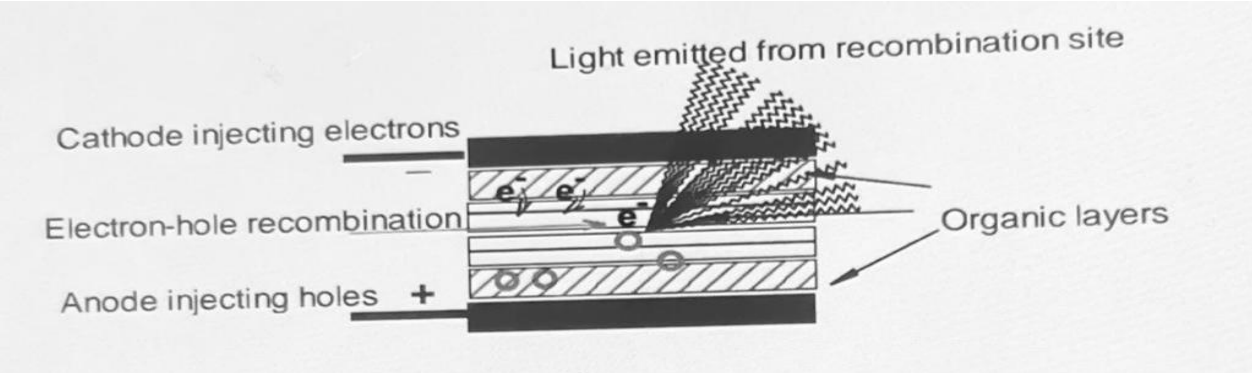
- Used in Analytical instruments like Colorimeter, pH meter, Potentiometer, Conductometer etc.
- Used in Traffic Signals, Thermometers, Petrol Pump indicators, airplane cockpits, advertisement boards etc.

Disadvantages of liquid crystals:

- Speed of operation is low
- Lifespan is less
- Restricted viewing angles

ORGANIC LIGHT EMITTING DIODES (OLED's):-

Definition: OLED's are the type of display technology that uses thin organic layers to emit light, when current is applied.



Construction of an OLED

PRINCIPLE AND WORKING OF OLED:

OLED devices consists of two electrodes, an anode and a cathode and organic layers are placed between two electrodes. Multiple organic layers are used, in which each layer plays an intrinsic role. When a voltage is applied to an OLED device through anode and cathode, charge carriers are injected from the electrodes to the organic layers. Anode injects holes (positive charges) and cathode injects electrons (negative charges) to the system. The holes and electrons are transported to an emission site and recombined. Organic materials in the emission site are excited by recombination of holes and Electrons. When the excited organic materials returns to its ground state, then the emission occurs. The emission frequency in an OLED depends upon the energy gap between the excited and ground states. Emission colors can be controlled by the energy gap between the excited and ground states

PROPERTIES OF OLED:

- They are Thin and Flexible, Light Weight.
- High Contrast ratio & wide viewing angles.
- Produce more accurate color.
- Low Power Consumption.
- Fast response time.
- They produce sharp moving images.
- Using variety of different organic materials various colors can be generated.

APPLICATIONS OF OLED's:

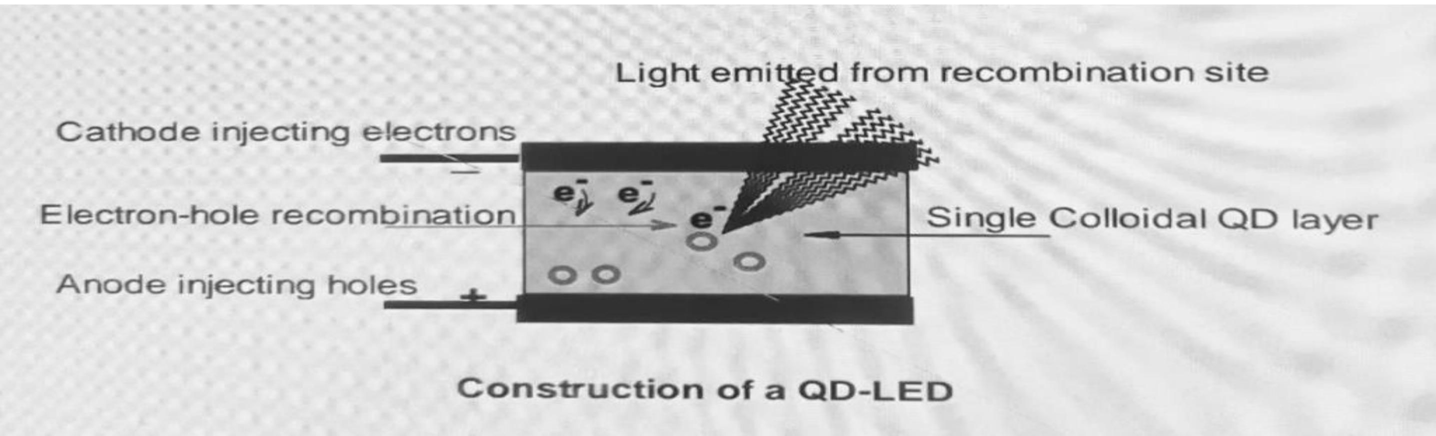
- Used in Consumer Electronics like TV, Computer Monitor, Mobile Phones, etc.,
- Used in Automotive Industry.**Example:** Dashboard Displays, Lighting Systems, Electronic Displays in car, etc.,
- Used in Wearable devices like Smart Watches, Fitness Trackers, etc.,
- Used in Medical instruments like Surgical lights, Diagnostic Equipment's, etc.,

DRAWBACKS OF OLED:

An important drawback of the OLED technology is the lack of trust and cheap patterning methods for various color pixels. Because OLEDs are composed of small molecule organics, they are not consistent with the classical lithographical patterning techniques that necessitate exposure to solvents which completely deteriorate the structures of OLED.

QUANTUM DOT LIGHT EMITTING DIODES (QD-LEDS)

Definition: QD-LEDs are the type of display technology that uses Quantum dots layers to emit light, when current is applied.



PROPERTIES OF QD-LEDS:

- High color accuracy
- High Brightness
- Produces more color accurately
- Low power Consumption
- Long life span and High efficiency
- More flexibility
- High quantum yields.
- Will not deteriorate as easily as OLEDs

APPLICATIONS OF QD-LEDS:

- Used in large, flat TV Screens, Digital Cameras, Mobile Phones, etc.
- Used in Personal Gaming Equipment's.
- Used in Digital Signal Displays.

- Used in electronic Displays in Automobiles.
- Used to backlight technology.

Sony manufactured first TV using this new type of technology called Triluminos quantum dot display technology in 2013.