

Global Focus on Knowledge Production and Application of Materials

The University of Tokyo Hiroshi Komiyama

Lecture One: The production process of matter, e.g., metals
(iron and steel).

Lecture Two: Conjugation (device), e.g., semiconductors and
inorganic materials.

Lecture Three: Soft matter, e.g., liquid crystals.

Lecture Four: Matter in durable earth (device), e.g.,
fuel cells and biochips.

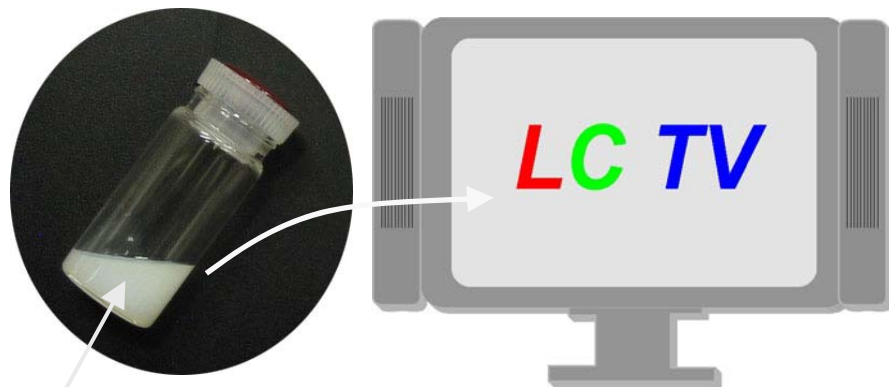
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1. Overview

- Examples of application : Liquid crystal displays, color films, color filters, and molecule sensors
- Materials (molecular structure and molecular design), structure (shape), velocity(multi-layer application and inkjet), and conditions
- Phenomena
Self-organization, chemical reaction, and (interfacial tension-driven) flow

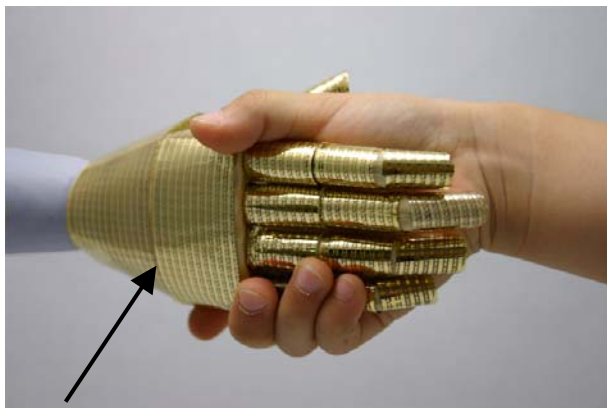
Soft Matter

Liquid crystal



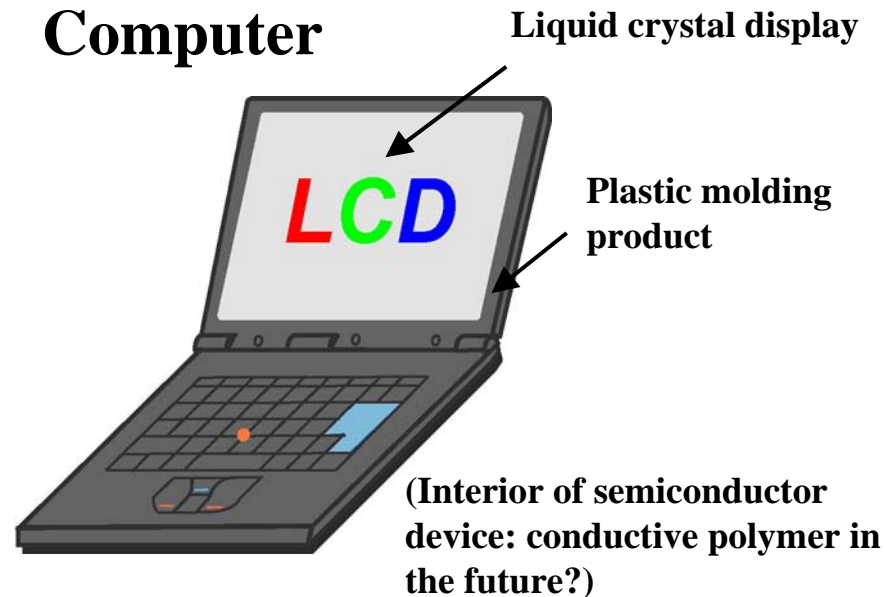
Organic low molecule

Robot

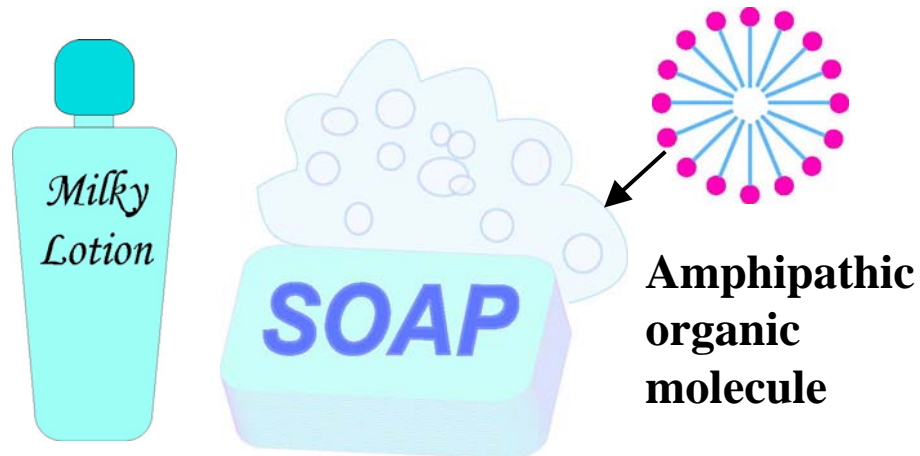


Conductive polymer

Computer



Micelle (soap and cosmetics)



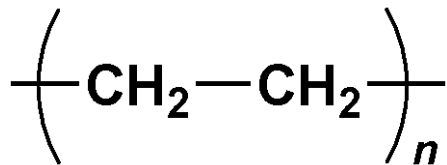
Properties of Soft Matter

	Organic material	Inorganic material	Metal
	Soft matter	Hard matter	
Structural unit	Molecule	Atom	
Functional expression	Monomolecular Molecular assembly	Atomic assembly	
Bonding force	Intermolecular force (relatively weak)	Covalent bond (relatively strong)	Metal bonding

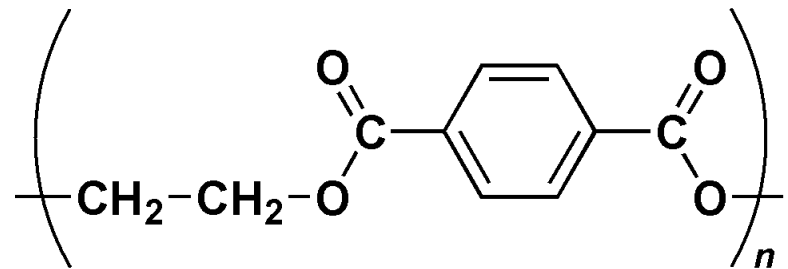
2. Soft Matter as Structural Materials

Polymer

Polyethylene



Polyethylene terephthalate (PET)



Injection Molding Process

Synthesis from petroleum (PET synthesis)



Thermal dissociation



Mold injection



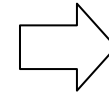
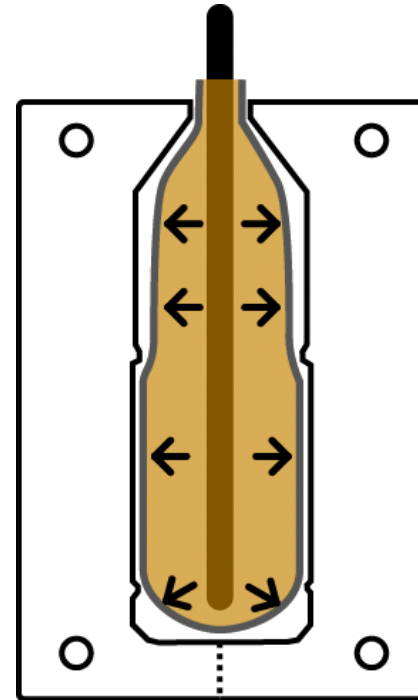
Air blow



Cooling



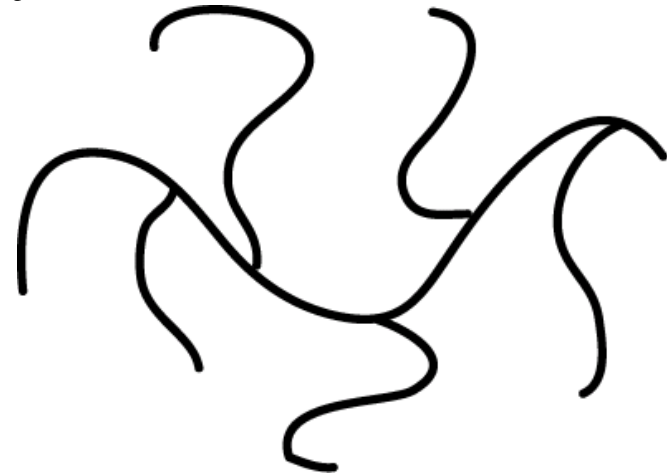
Removal



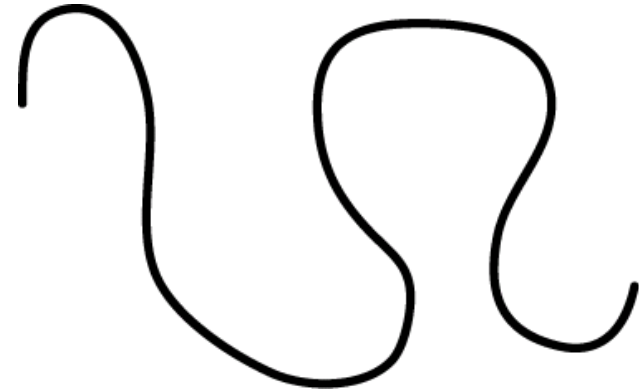
**Injection
molding**

Reaction Process and Molecular Structure

- High-pressure oxygen radical polymerization
→ Irregular structure
(cross-branch structure)



- Low-pressure catalytic polymerization
→ Regularly arrayed structure
(straight-chain structure)



Molecular Structure and Physical Properties

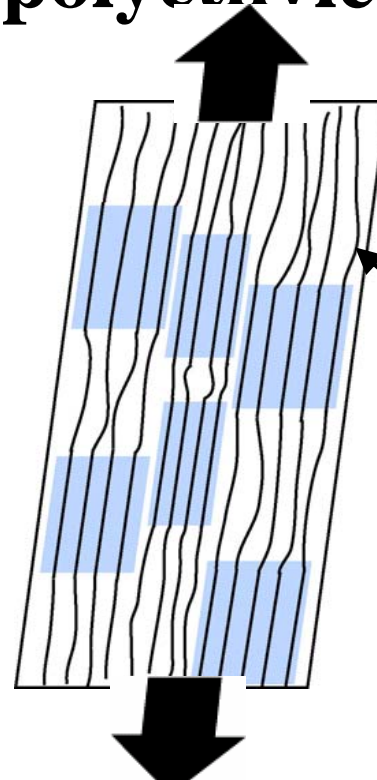
Cross-branch polyethylene



Difficult for molecules to arrange themselves

- **Soft (used for film)**
- **Transparent**

Straight-chain polyethylene

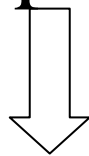
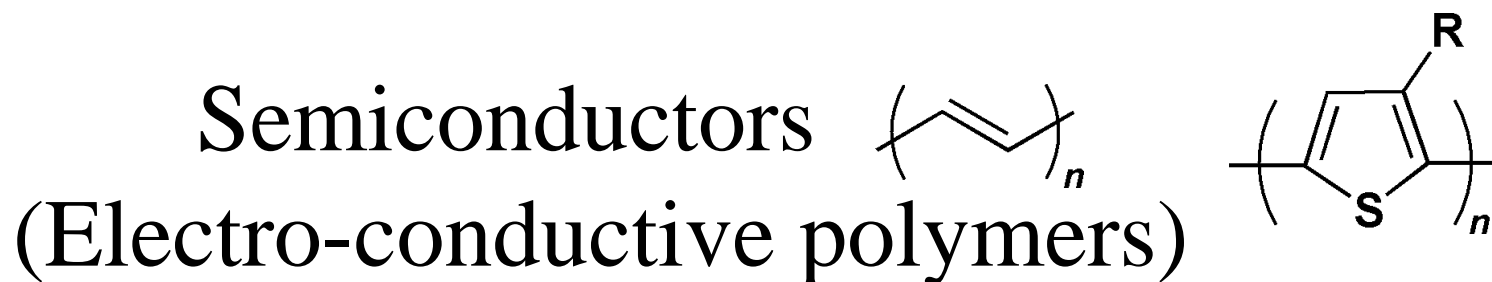
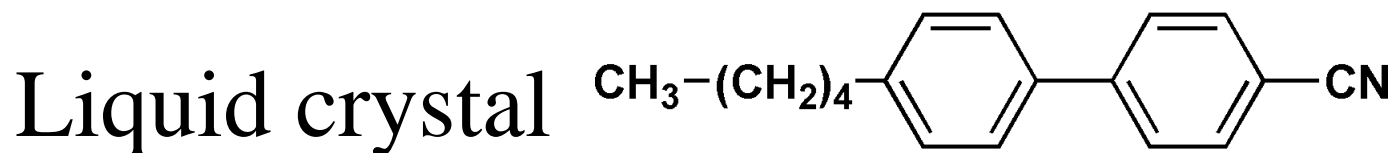


Spinning to give arrangement

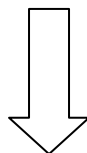
Crystalline region

- **High tensile strength (used for fibers)**
- **Opaque**

3. Functional Soft Matter



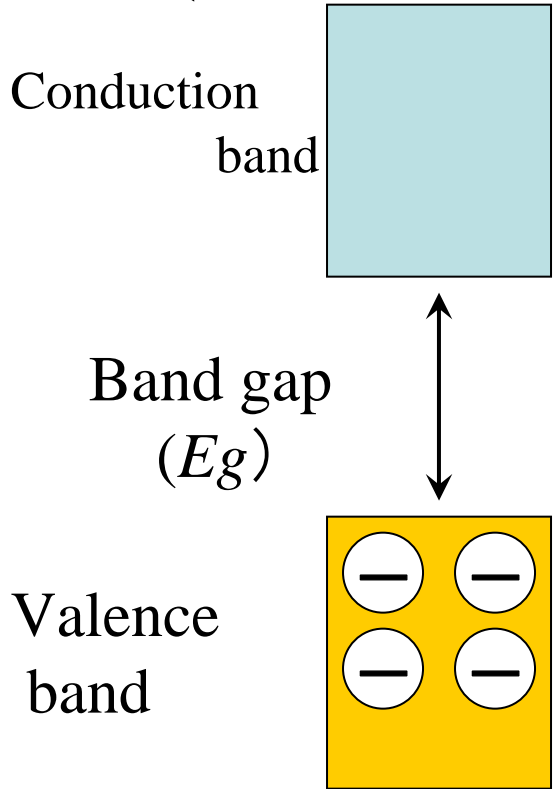
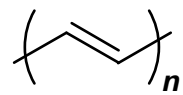
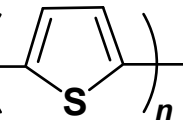
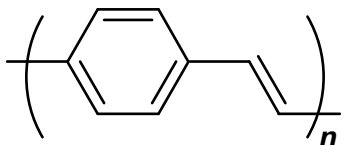
Functional devices (molecules)



Films (multi-layer and functionality), fibers,
and compound devices

Semiconductors

(Electro-conductive Polymers)

<div>Conduction band</div>  <div>Valence band</div>		Chemical compound	E_g (eV)
	Electro-conductive polymer	Polyacetylene 	1.4
		Polythiophene 	2.0
		PPV 	2.5
	Inorganic	Si	1.12
		GaAs	1.42

- Semi-conductive polymers enable molding processing approached easily.
- Tuning of E_g can be achieved by chemical modification.
- High conductivity appears by doping; high as metals.

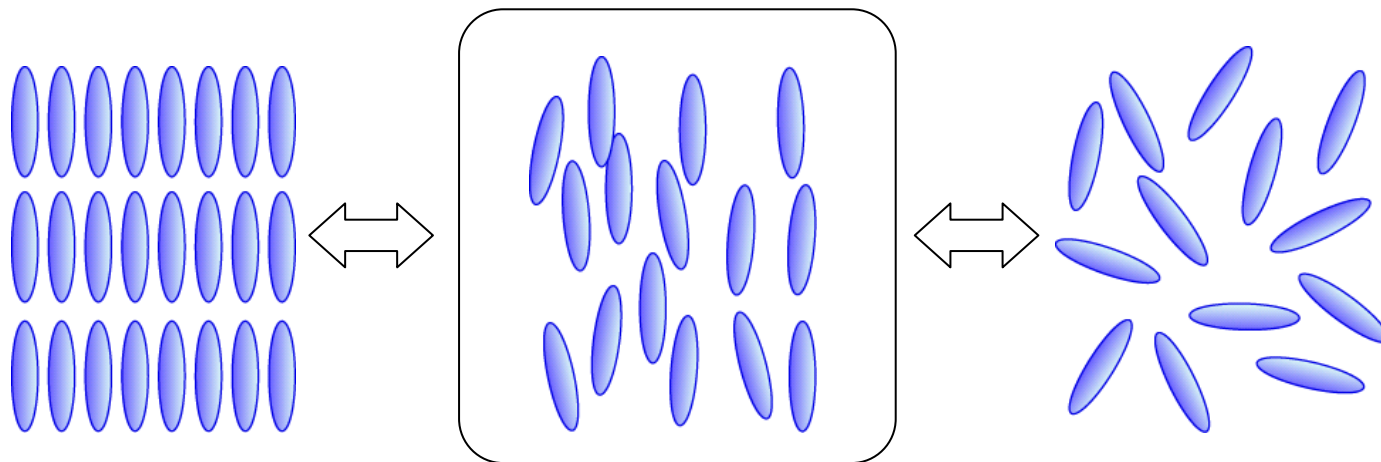
Polymeric Semiconductors

	Polymeric semiconductor	Silicon (inorganic) semiconductor
Basic characteristics	p-type and n-type semiconductors/pn junction Light emitting diode Field effect transistor	p-type and n-type semiconductors/pn junction Light emitting diode Field effect transistor
Advantageous characteristics	Soft, area enlargement, easy to control physical properties by changing the chemical structure, and light weight	Hard, outstanding durability High reliability

Capability of polymeric semiconductors:

- Bendable like paper, images depictable and erasable devices ➡ Electronic paper
- Molecular level (nano-size) ➡ Sensor systems such as ultra-micro complex devices and biomolecules.
- Structure similar to biomolecules ➡ Fault tolerance

Liquid Crystals

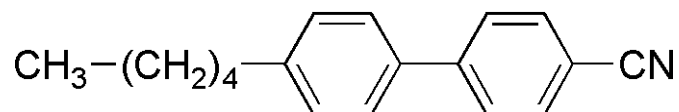


Crystal

Liquid crystal

Liquid

Temperature ——— 22.5°C ——— 35°C ———→



3.1 Process Example 1

Micrometer-sized Structure Making
in Direction of Thickness

Multi-layer Deposition of Photographic Films

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Images provided by Fuji Photo Film Co., Ltd.

Multi-layer Deposition by Multi-layer Coating

Factors:

- Laminar flow control
- Diffusion control of longitudinal direction
- Drying process control

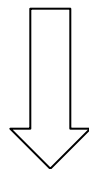
3.2 Process Example 2

Micrometer-size Structure Making in
Plane Direction

Top-down and Bottom-up

Scrape off from solid phase

“Top-down method”

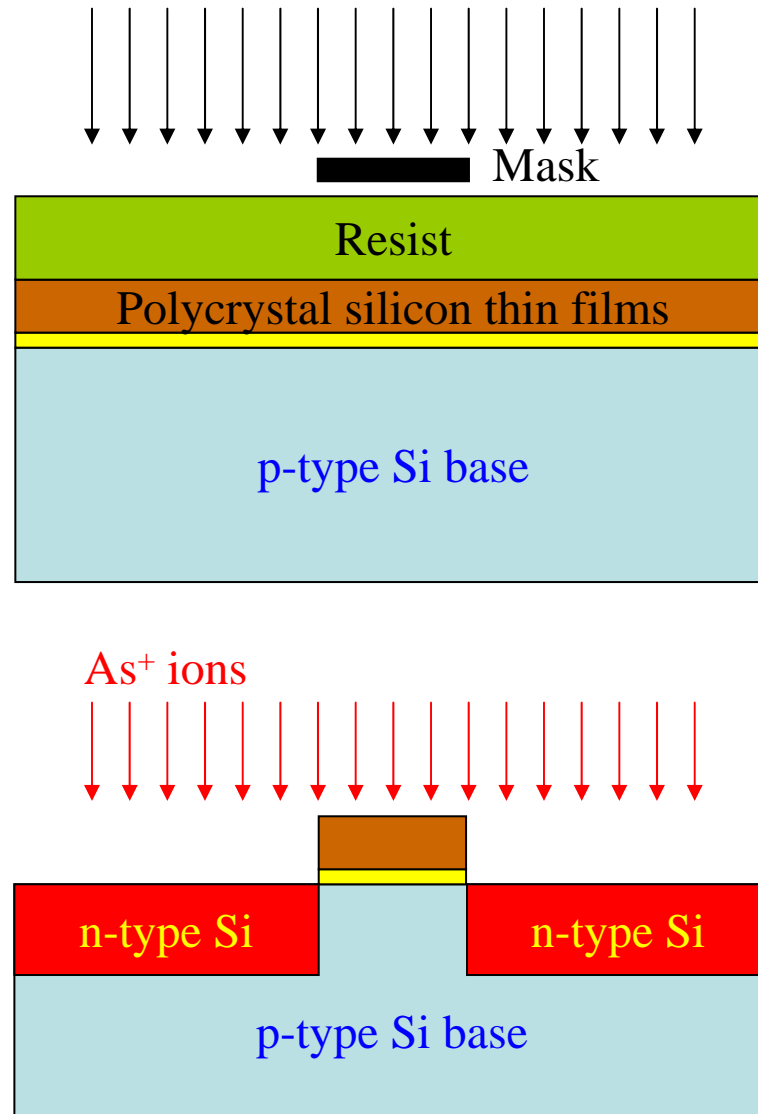


Assembling the molecule-by-molecule

“Bottom-up method”

Top-down Method (Review)

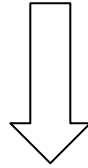
(Silicon Semiconductor Lithography)



Bottom-up Morphogenesis

Example 1: Color Filter

Micro-size dot alignment



Inkjet printing

Color Filter Making by Inkjet (Bottom-up Process)

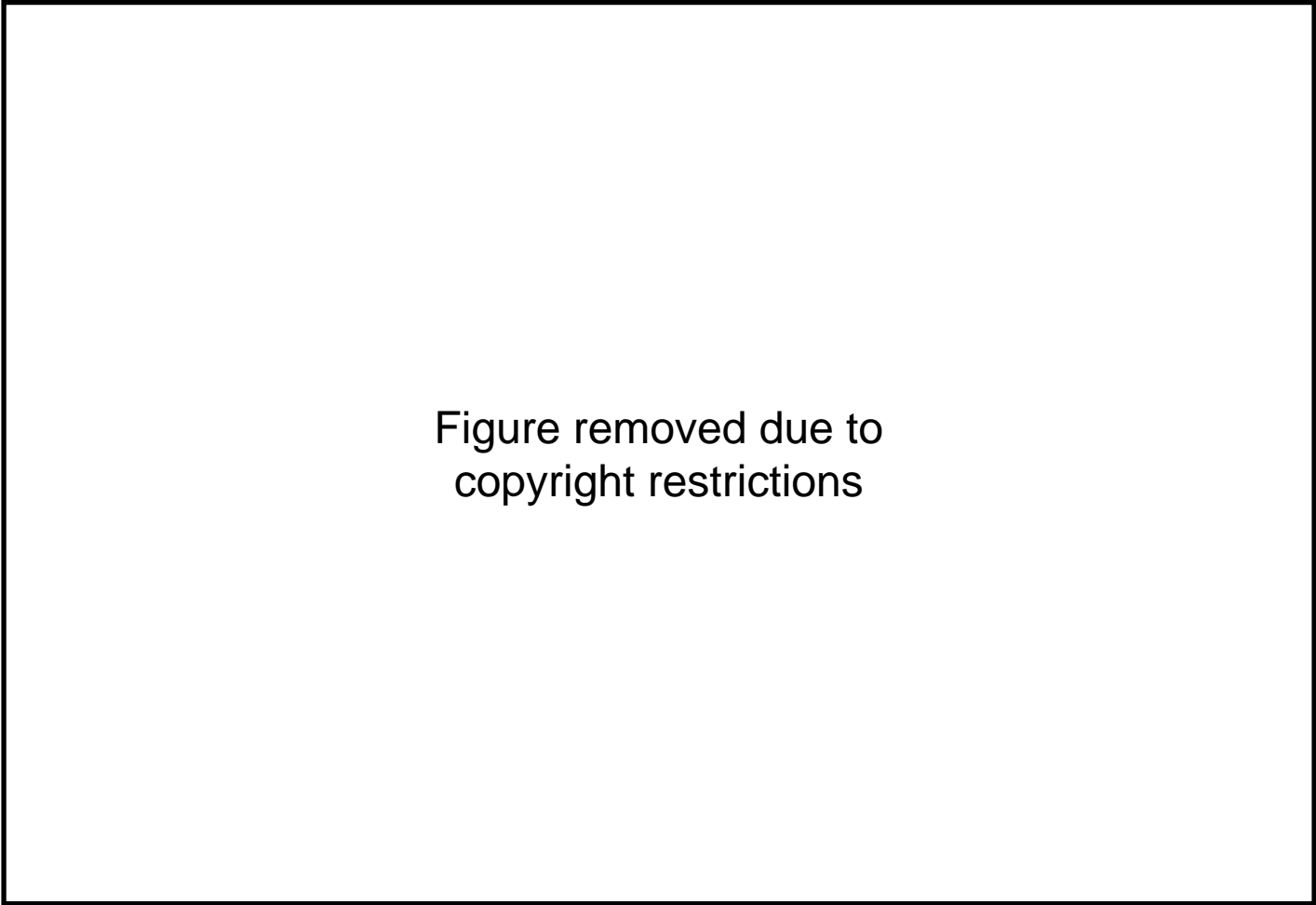
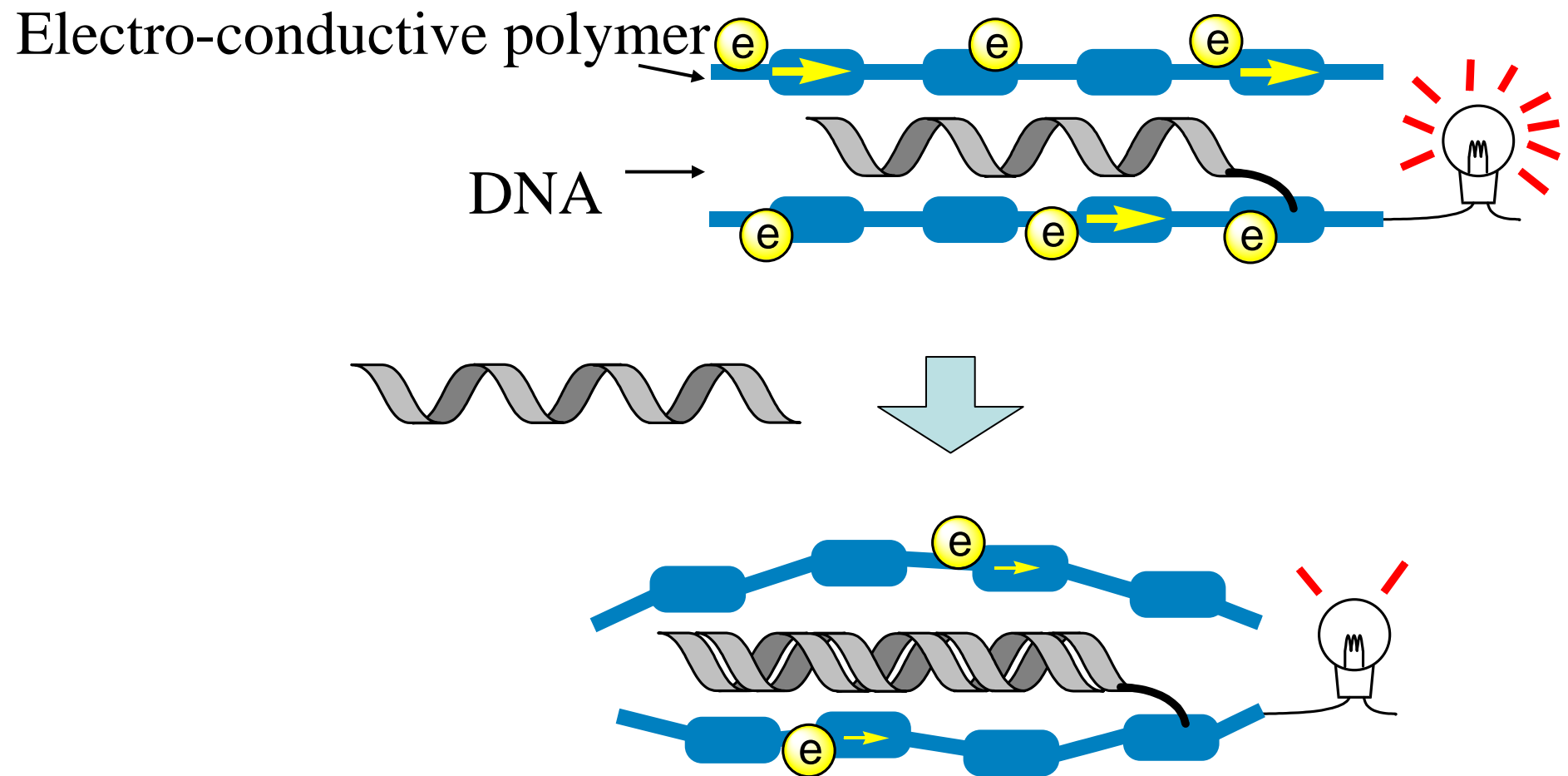


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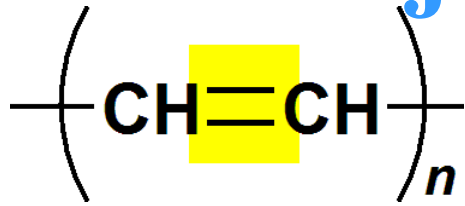
4. Functional Devices and their Formation Process

E.g., DNA sensors



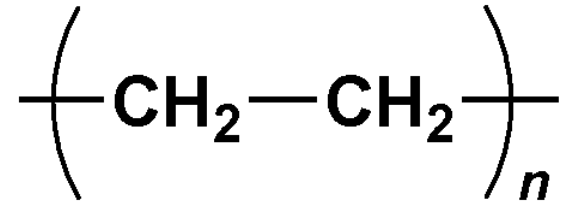
Chemical Structure of Soft Matter with Semi-conductive Properties

Conjugated Structure



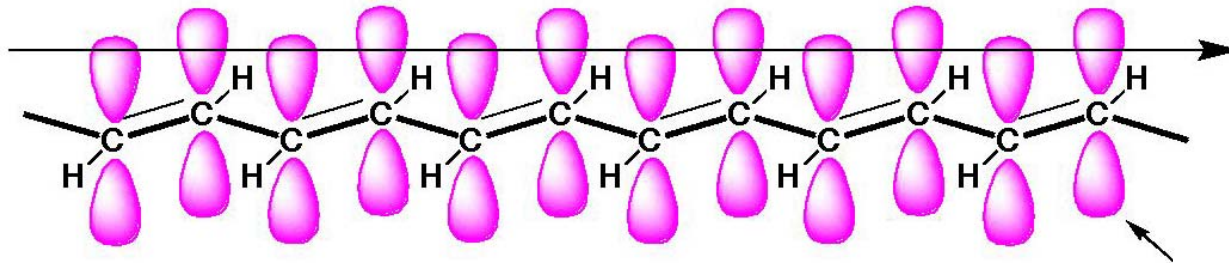
Polyacetylene
(conductor)

(Conjugated structure)



Polyethylene
(insulator)

(No conjugated structure)



Polyacetylene

Electron cloud

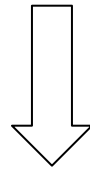
Characteristics of Functional Soft Matter

- Flexible
- Large area
- Bio-interface

Pending problems:
durability and stability

4.1 Bottom-up Process

Printing technology



Painting directly by ink

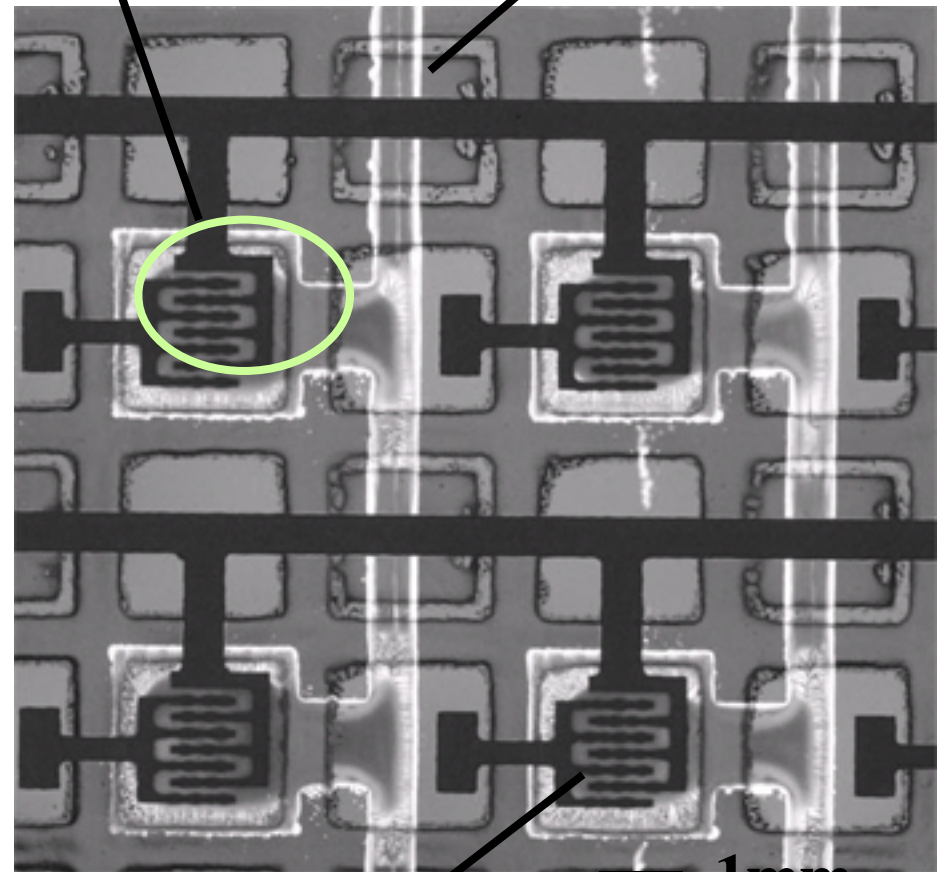
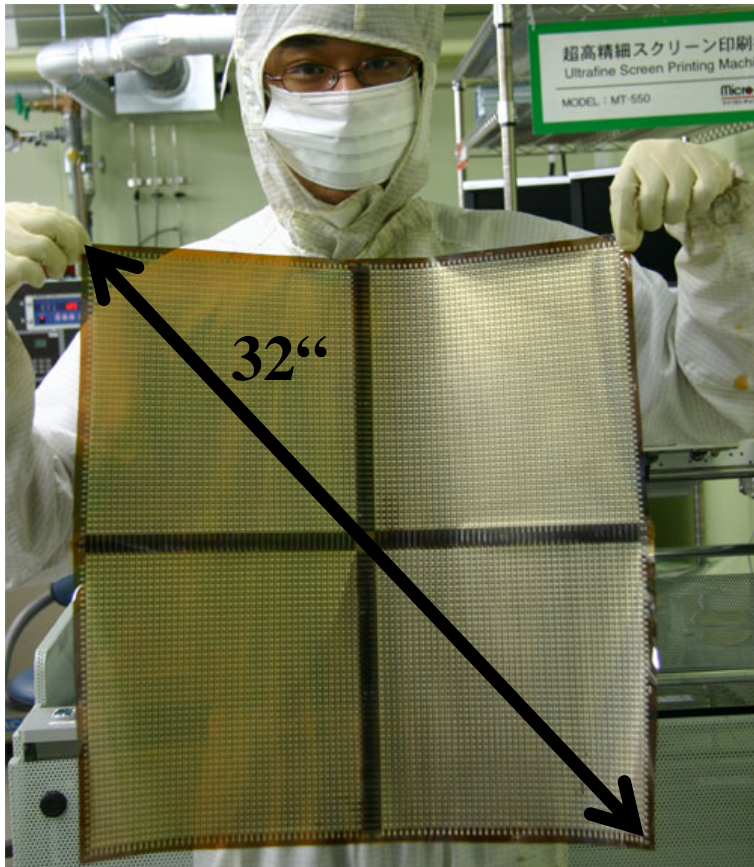
Printing (Circuit Making)

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Images provided by Seiko Epson Corporation

4.2 Application to Artificial Electronic Skins

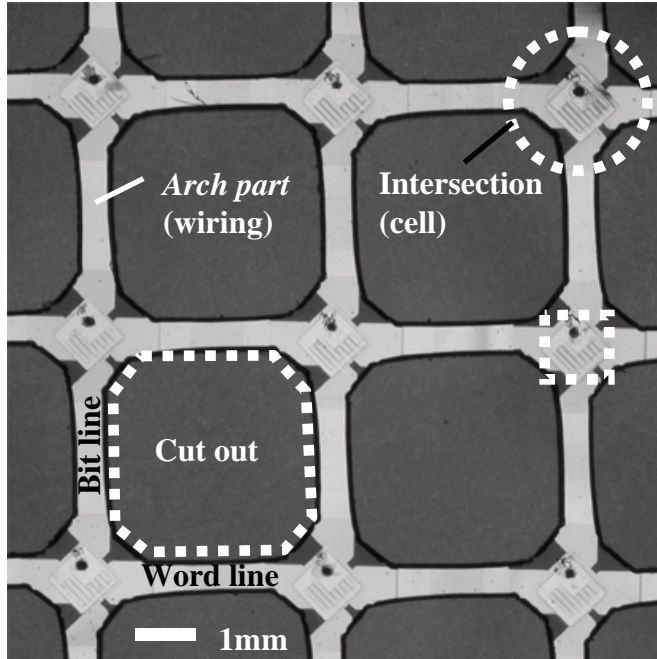
Channel length $L=50\text{ }\mu\text{m}$ Electro-conductive polymer Wiring (silver nano-particle)



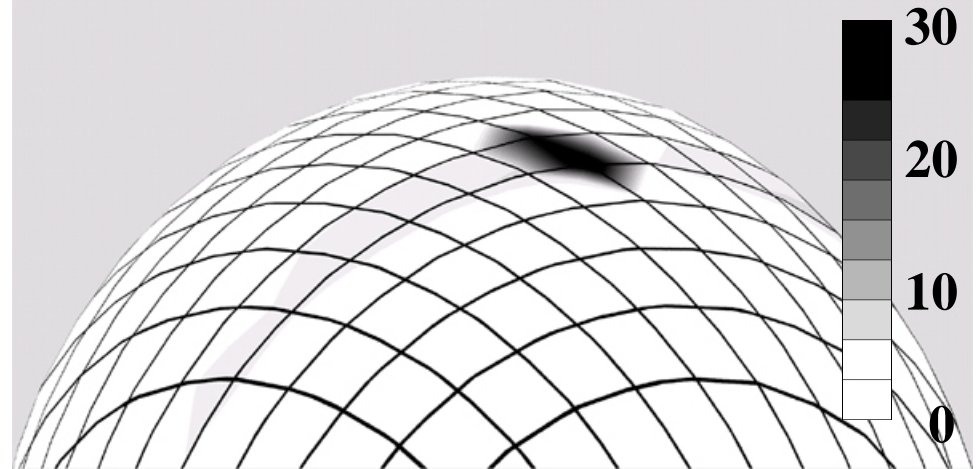
Department of Applied Physics School of Engineering, The University of Tokyo:
Someya Laboratory

Gate insulator (polyimide)

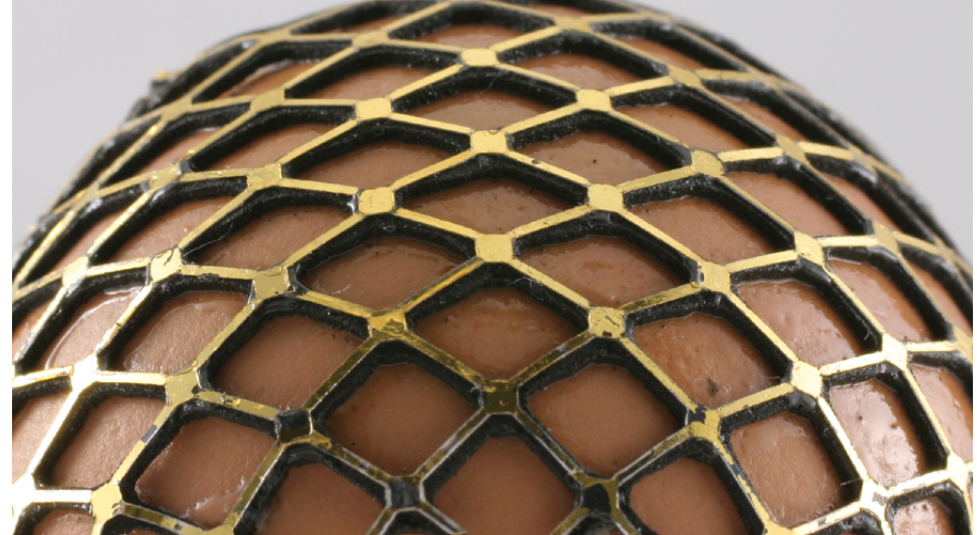
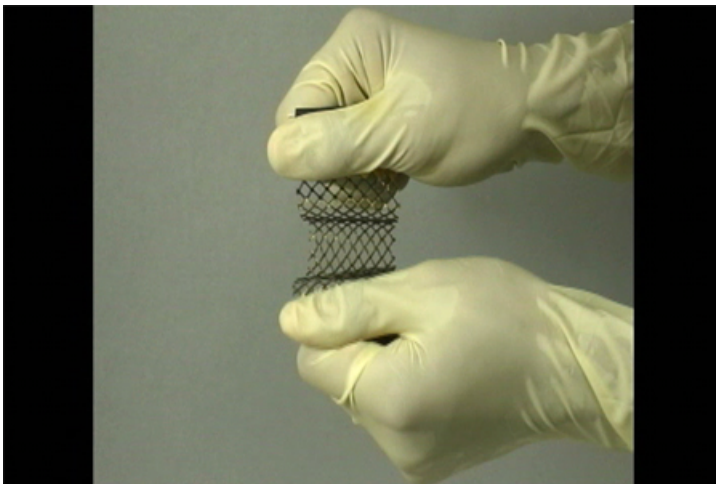
Stretchable Artificial Electronic Skins



Pressure distribution measurement Pressure (kPa)



Artificial skin attached to the surface of an egg



A Robot Hand with Human Cutaneous Sense



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(*TIME*, November 21, 2005)

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(*TIME*, November 21, 2005)

4.3 High Speed Process

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Images provided by Toppan Printing Co., Ltd.

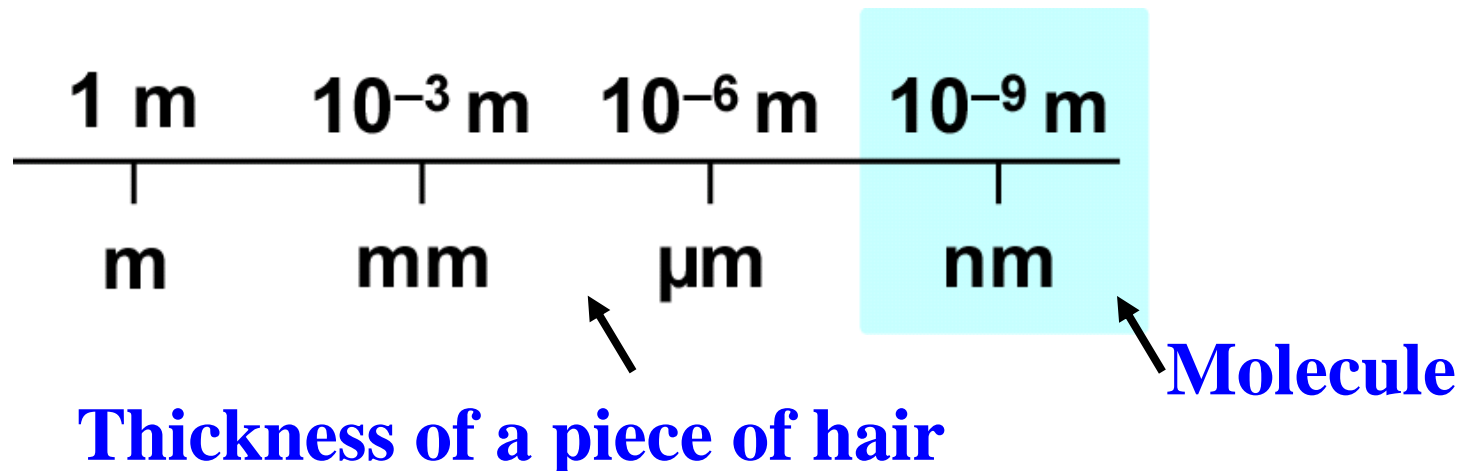
5. Manufacturing at the Nanometer Level

Functional expression by molecular designing

Nano-size device integration

Self-organizational structure formation process

Large area and flexible devices



5.1 Self-organization Phenomenon

Molecules and atoms (cluster) spontaneously form the structure while maintaining the unit of the structure.

Future expectations:

- Accurate formation of the structure
- Energy conservation process
- Low environmental burden

Categories and Examples of Self-organization phenomenon

Thermo-dynamics	Equilibrium	Non-equilibrium open system
Examples	Crystal Liquid crystal Self-organization of membranes Phase separation	Turing model Belousov-Zhabotinsky reaction Liesegang ring Wind-ripples formed on sand Stripe patterns of tropical fish Forests

Examples of Self-organization

- Thermodynamically-non-equilibrium systems
(Sand dunes, forests, and oscillation in chemical reactions)

Grow as solvent evaporates.
Crystal of ascorbic acid
(Liesegang ring)



Wind-ripples formed on Tottori Sand Dune



Source: Prof. Mitsugu Matsushita, Faculty of Science and Engineering, Chuo University

Photo: Prof. Yoshihiro Yamazaki, Department of Physics, Waseda University

Examples of Self-organization

- Thermodynamically-non-equilibrium systems
(Sand dunes, forests, and oscillation in chemical reactions)

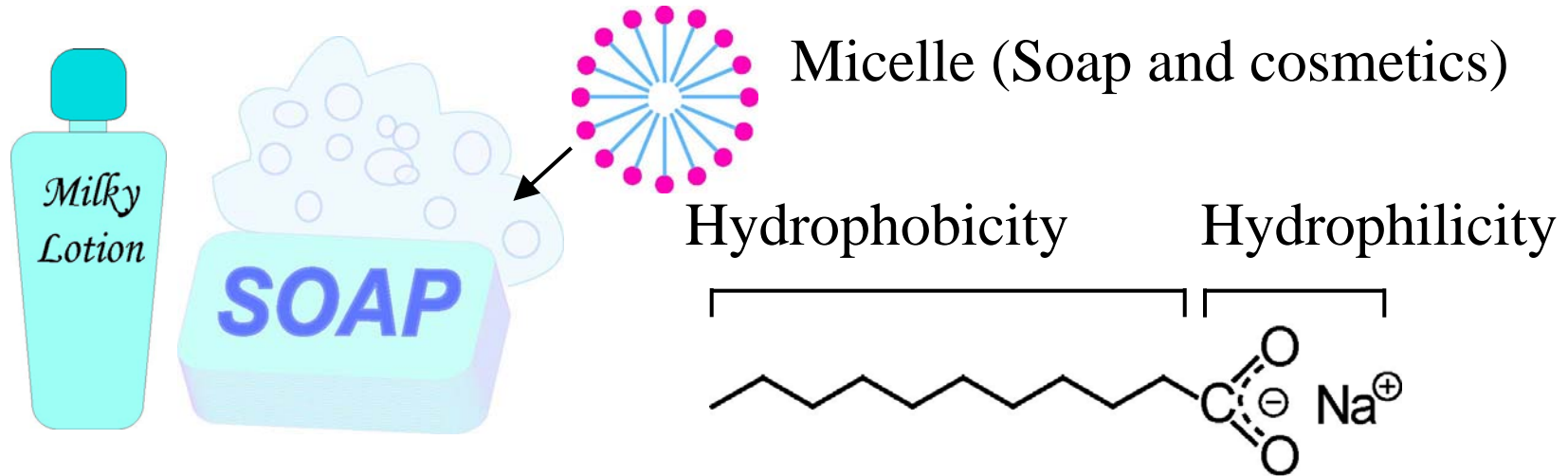
Forest (Mt.Shimagare, Tateshina)



PENSION RADISH-GARDEN

<http://www.p-rg.com/n/nanafushigi.html>

5.2 Self-organization of Amphipathic Molecules



Self-organization at surface of the base

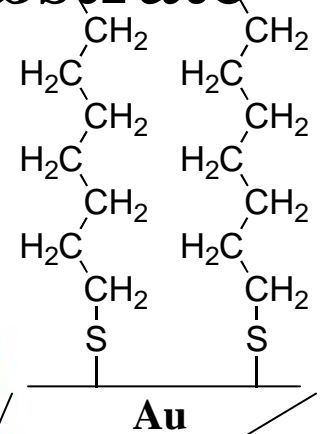
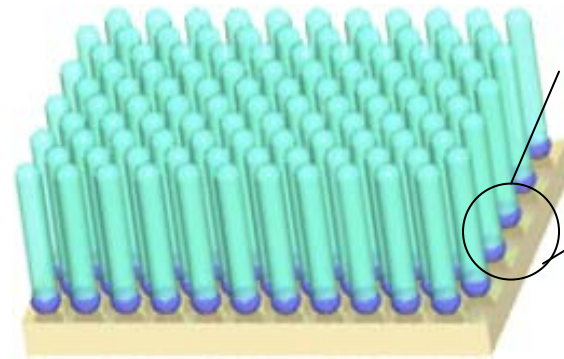
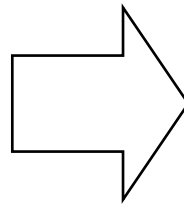
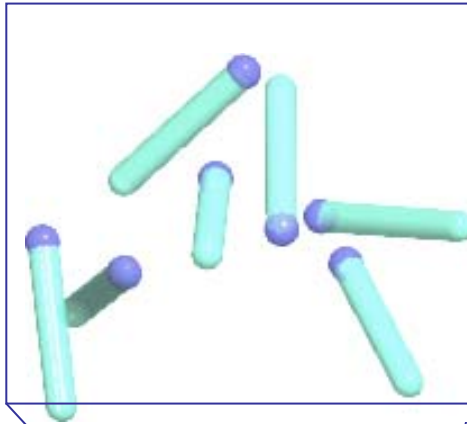
Functionalization at the molecular level
(Self-assembled monolayer)

Self-assembled Monolayer (SAM)

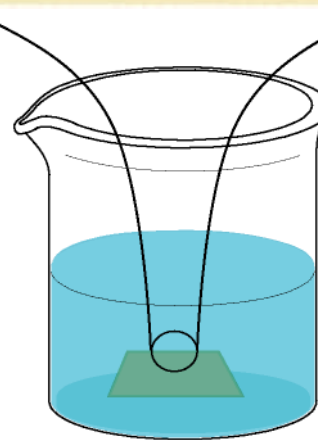
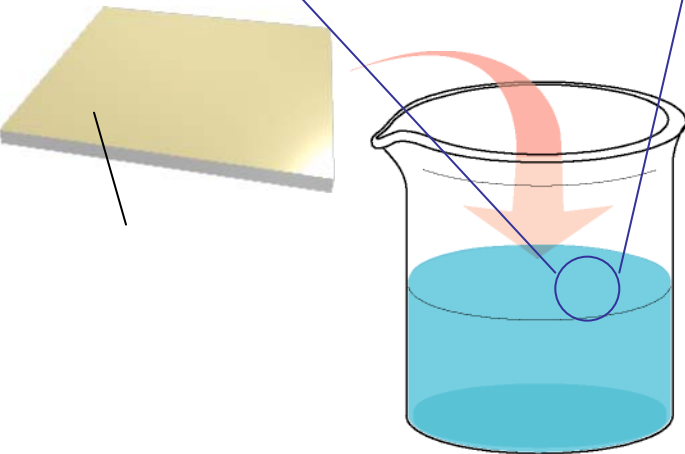
Two-dimensional Crystallization on Substrate



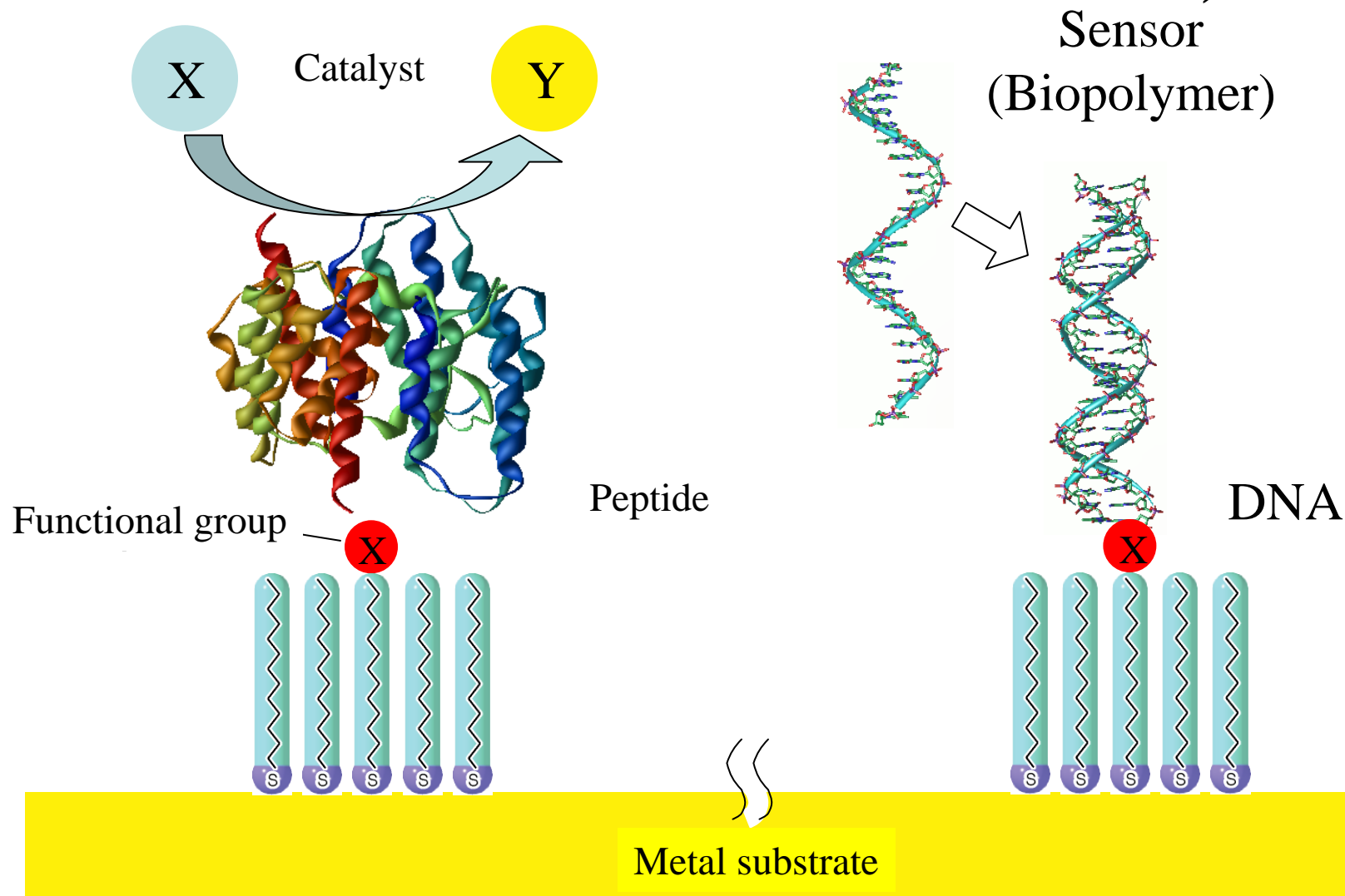
(Amphipathic molecule)



Au

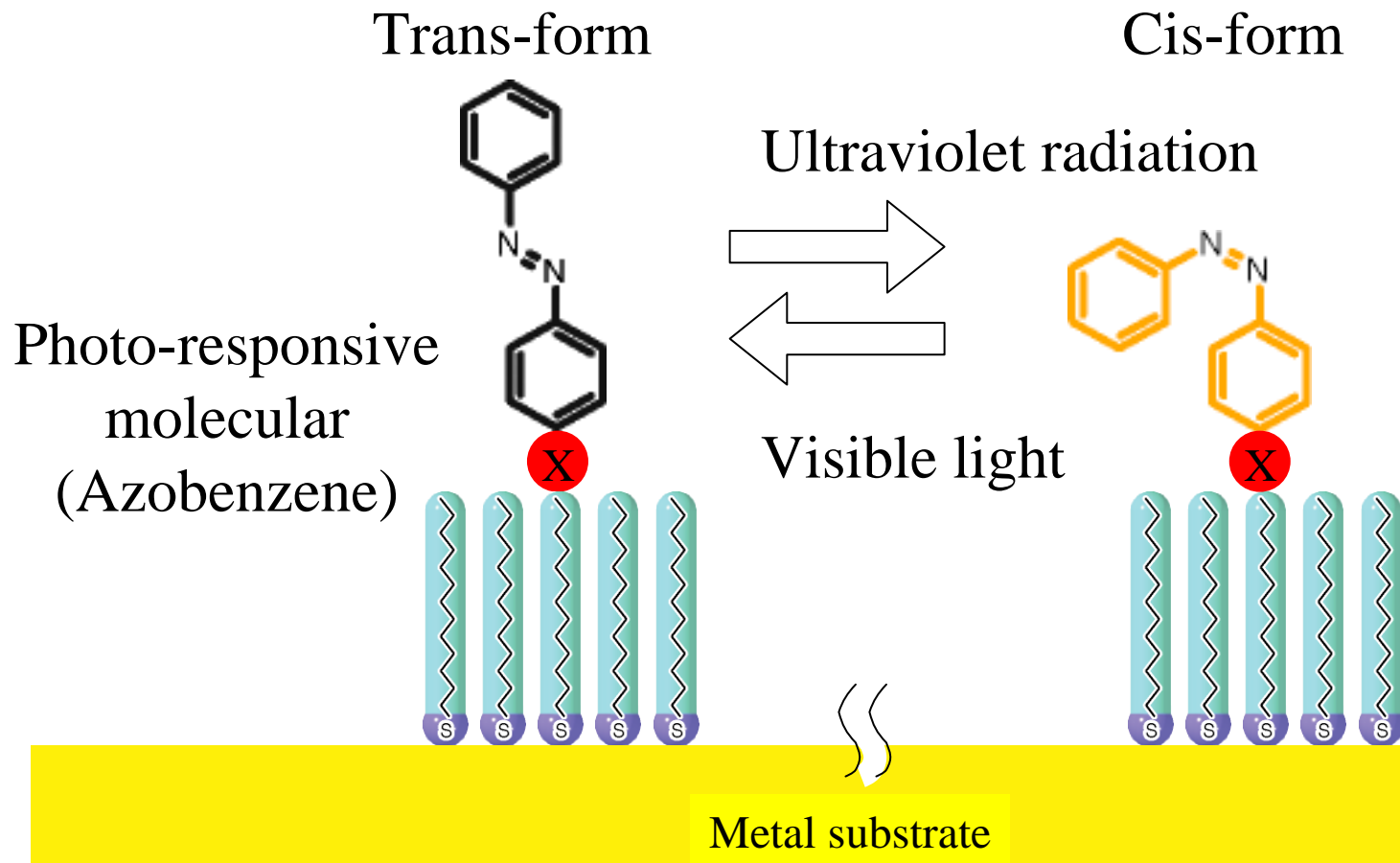


Application of Self-assembled Monolayer (1) (Monomolecular Catalyst and Monomolecular Sensor)



Application of Self-assembled Monolayer

(2) (Optical Memory and Sensor)



Phenomenon Highlighted by Ultra-fine (1)

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Images provided by Seiko Epson Corporation

Phenomenon Highlighted by Ultra-fine (2)

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Images provided by Seiko Epson Corporation

Governed by Interfacial Tension

- Interfacial tension/ gravity

$$\frac{\sigma \times \text{Circumference}}{g \rho \times \text{Volume}} = \frac{\sigma}{g \rho r^2}$$

1 micron-radius
water droplet
can yield 10^7 !

σ : Interfacial tension [N m^{-1}]

g : Gravitational acceleration [m s^{-2}]

ρ : Density [kg m^{-3}]

r : Droplet radius [m]

5.4 Self-assembled Soft Matter: Liquid Crystals

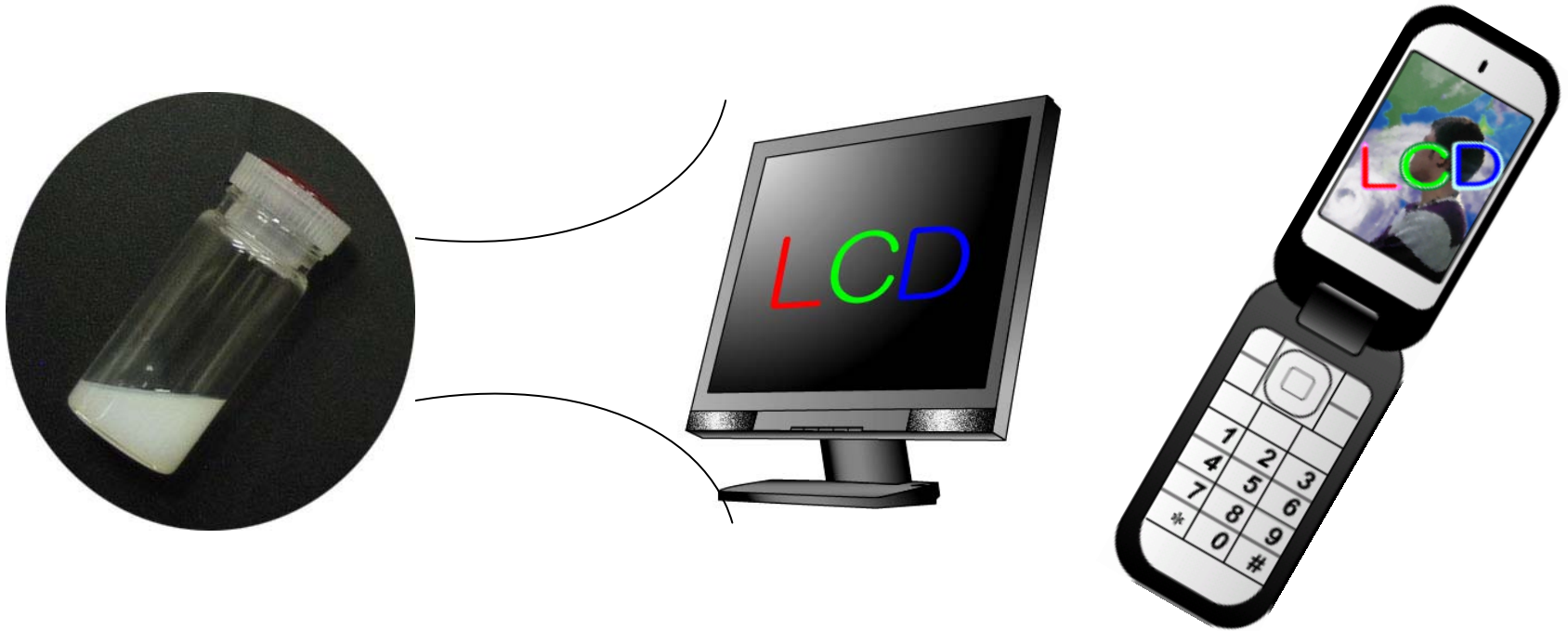
- The fourth state of matter

Solid, liquid crystal, liquid, and vapor



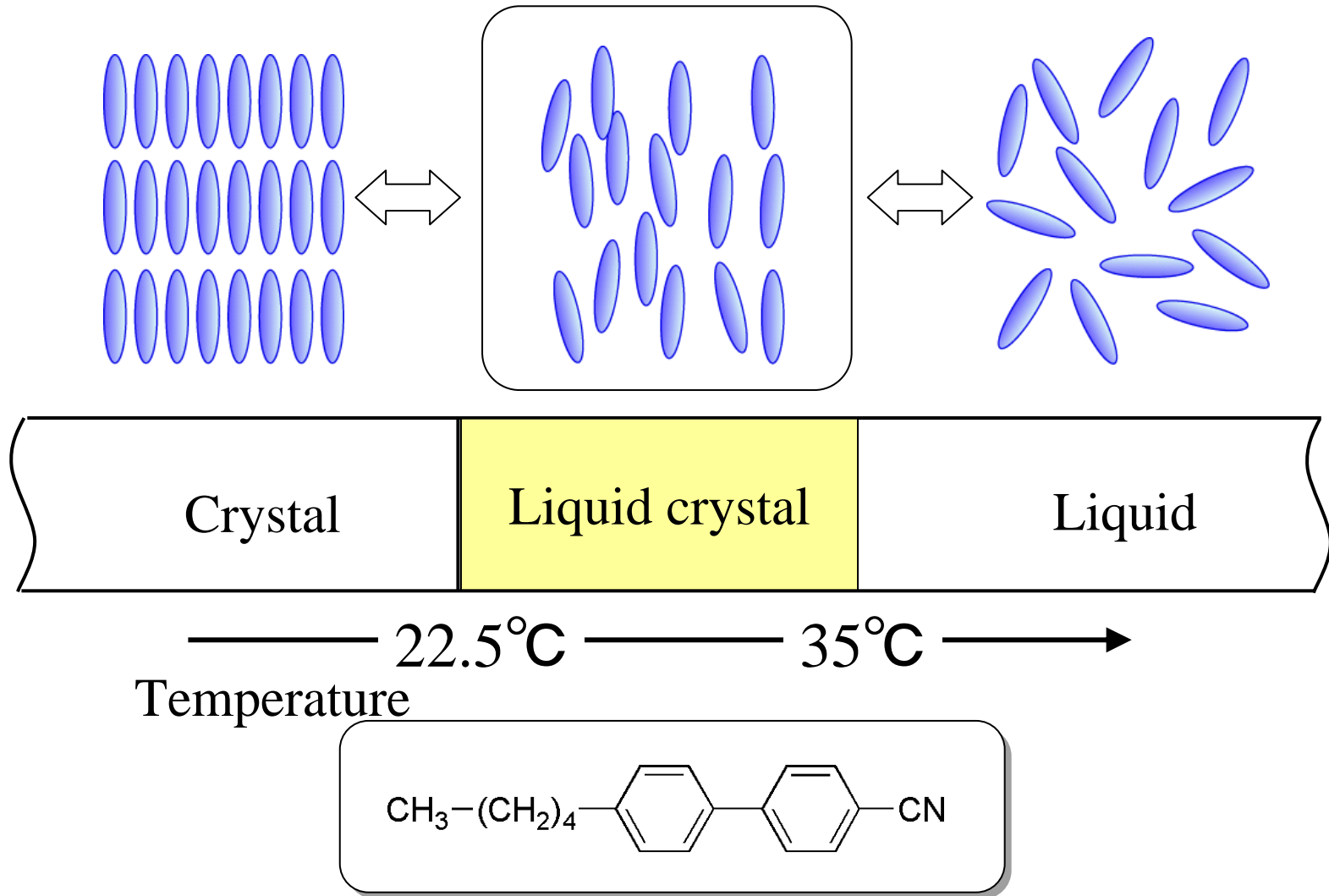
Examples of Liquid Crystal Applications

Liquid crystals are used in the displays.

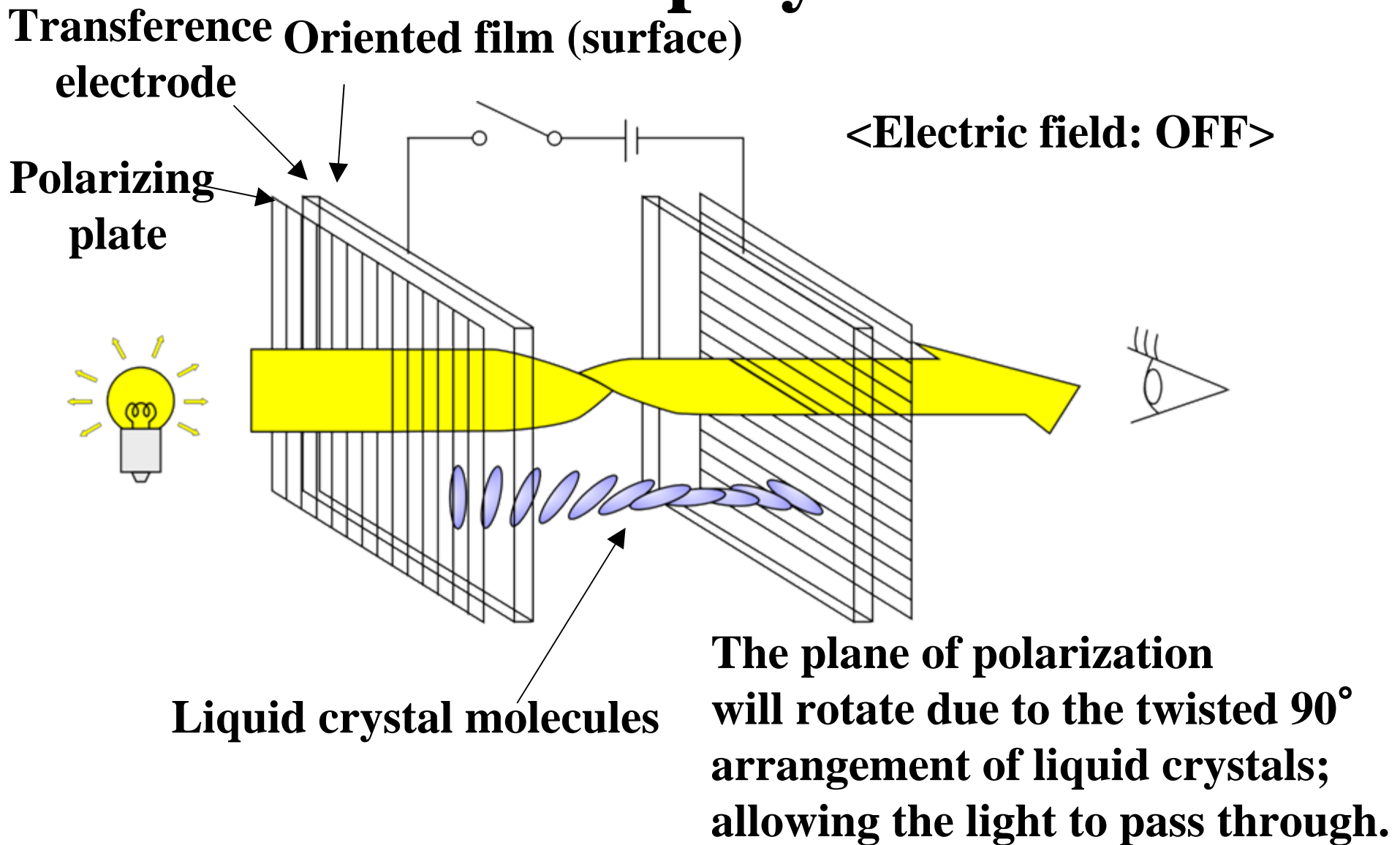


Displays for PCs and cell phones

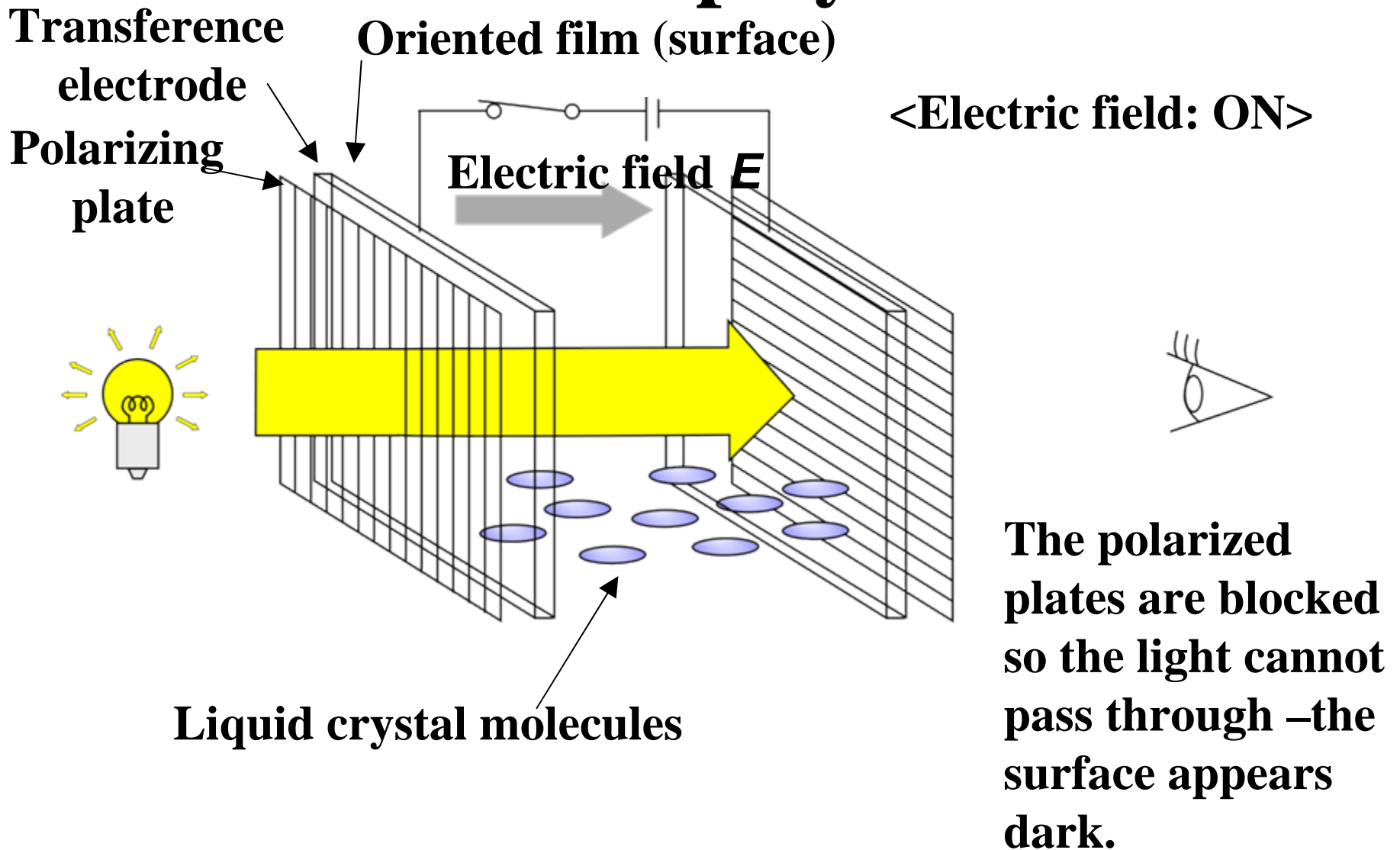
Phase Transition of Liquid Crystals



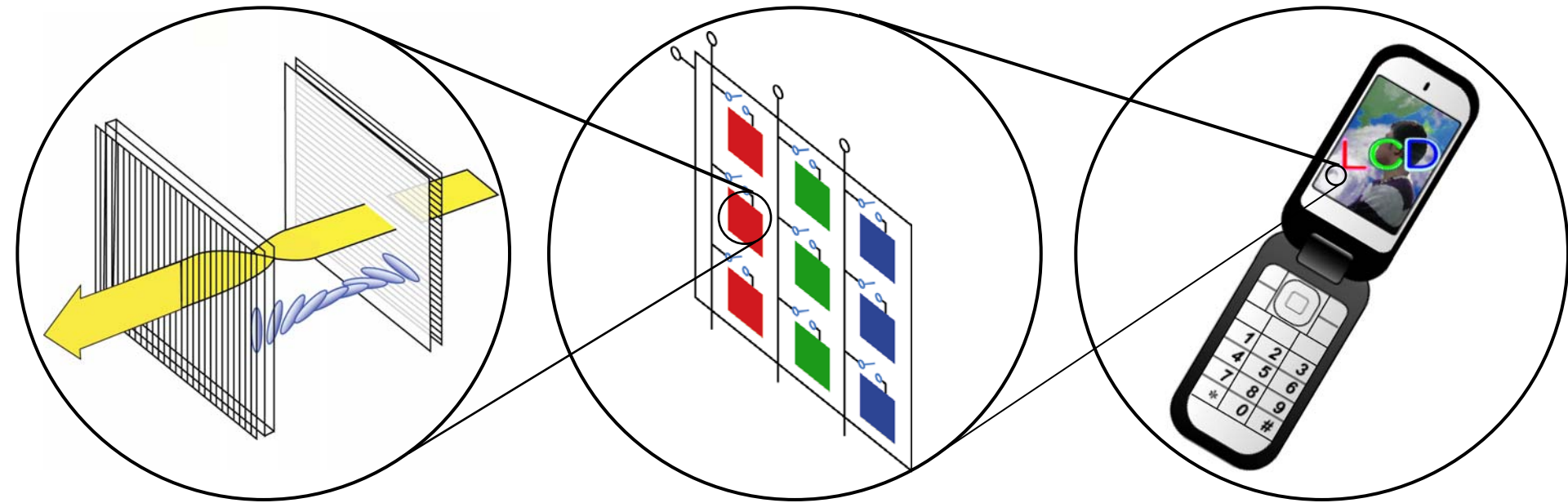
Mechanism of Liquid Crystal Displays



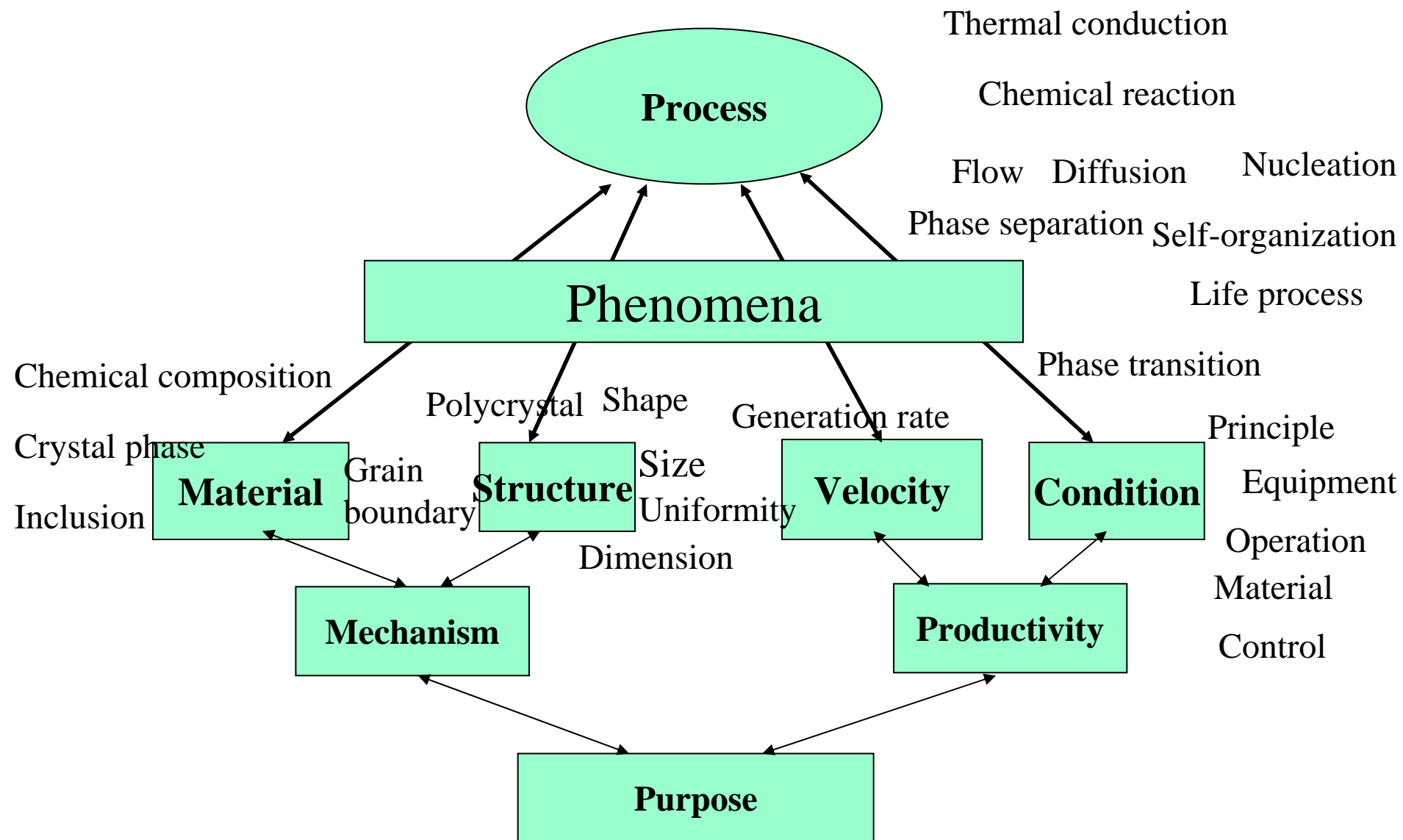
Mechanism of Liquid Crystal Displays



Color Liquid Crystal Displays



Each segment is controlled by a transistor.



6. Matter, Physical Properties, Structure, Functions, and Applications For Liquid Crystal Displays:

Matter: rod-shaped and electronically-polarized molecules are weakly arranged.



Physical properties: polarization in the substance may shift the arrangement.

Structure: 10 micron films are filled in between the plane electrodes.

Functions: Alter the arrangement of molecules in response to the state of the electric field.

Change from transparent to opaque.

Applications: Displays can be achieved if every pixel is controlled.
Color displays can be obtained by enabling the polarized light to pass through a color filter.

7. The Latest Research

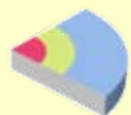
Molecular design and high-level functional expression based on the reaction design

High-level control and applications of self-organization

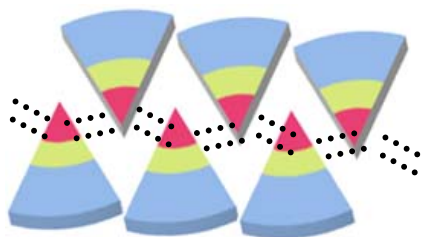
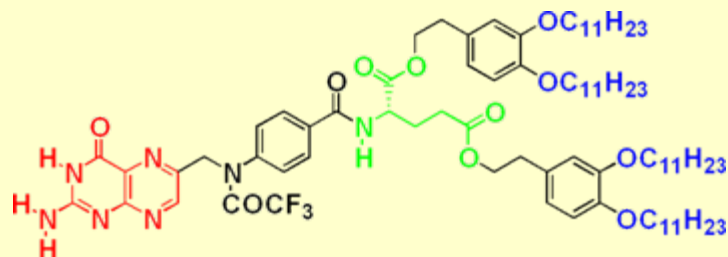
Multi-function integration

Replication and integration of organisms

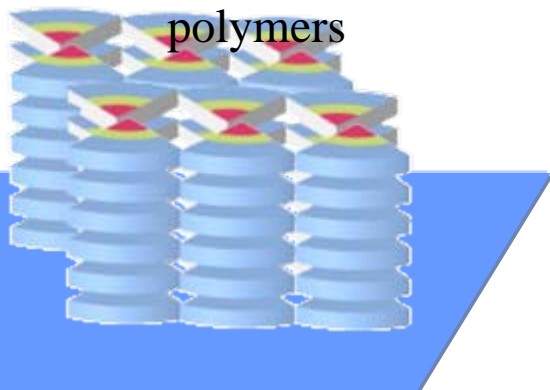
Development of Liquid Crystal Based Ion Sensors



Supramolecular
liquid crystal



Super-molecular
polymers



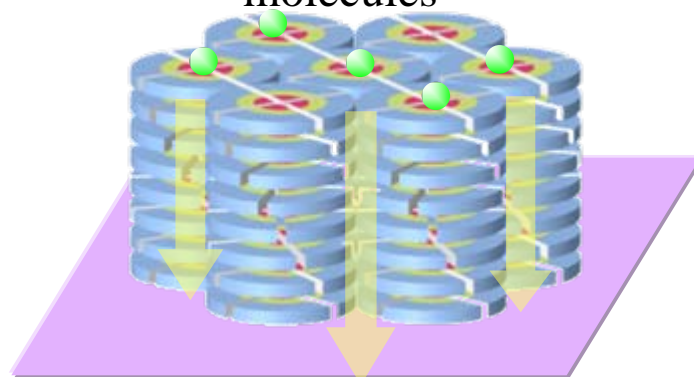
Hydrogen bond
switching



Disc-shaped
molecules



Ions
(stimulus)



**Self-organization structures are changed and ion signals
are sent in response to the stimulus.**

8. Summary of Soft Matter

Applications:

Structural materials (general-purpose plastics, high-performance plastics, general-purpose films, and fibers)

Functional materials (liquid crystals and semiconductors
=electro-conductive plastics)

Matter (designs of molecules and their assembly), structure, velocity, and conditions

Functionalized by particular matter and its structure

Phenomenon (interfacial tension and Marangoni convection)

Next lecture topics: Earth-friendly durable materials (devices), fuel cells, and micro-chemical chips