

Week 9: Liquid Crystal Actuators

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Lecture Overview

- Topological defects and micromanipulation
- Liquid crystal polymers and elastomers

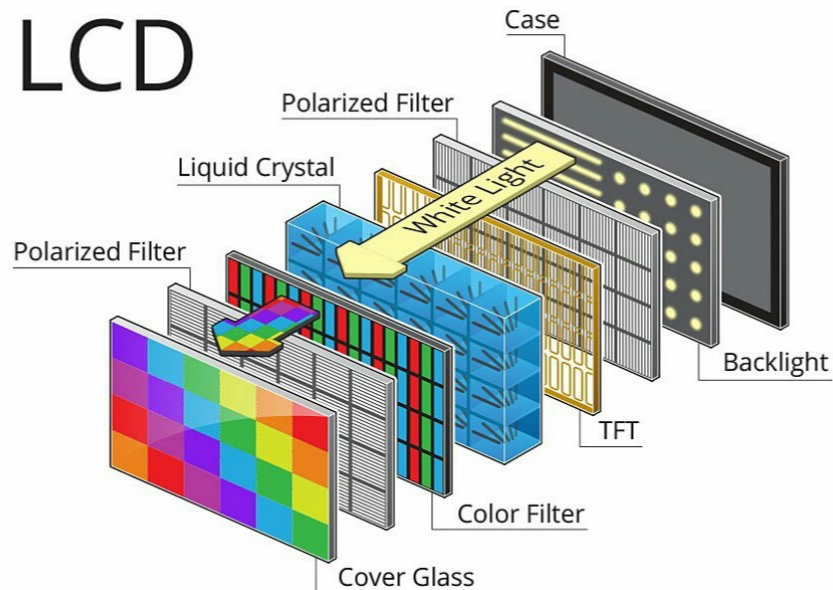
Liquid Crystals

- **Mesophase:** A state of a matter in between liquid and solid
- Combine the long-range order of crystals with the mobility of liquids (statistical arrangement of molecules)
- Orientational order, no positional order, anisotropy, still can flow
- Reconfigurable materials that optically report information about the environment
 - Electric fields (e.g. smart-phone displays)
 - Temperature (i.e. thermometers)
 - Mechanical shear
 - Sensors for chemical and biological stimuli

History

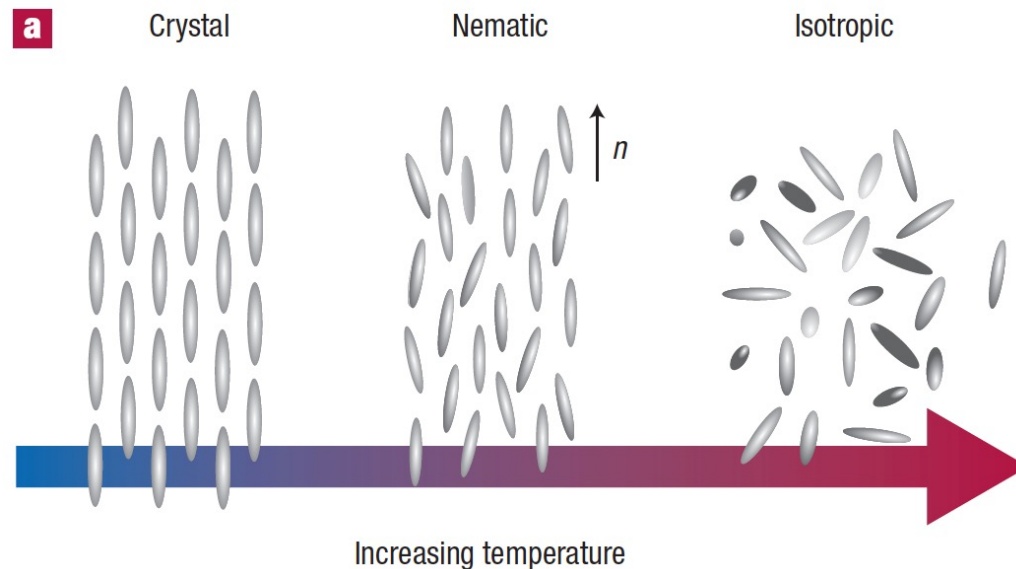
- 1890 Otto Lehmann identifies a new and distinct state of matter
- 1904 First commercially available LC (Merck)
- End of 1960s temperature indicators based on cholesteric LCs
- 1968 George Heilmeier builds first LCD prototype
- 1990s LCDs replace conventional display devices

LCD



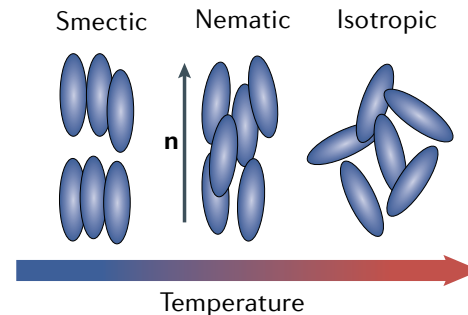
Terminology

- Formation of the mesophase
 - **Thermotropic**: temperature induced phase formation
 - If the temperature is too high, thermal motion will destroy the cooperative ordering of the LC phase, pushing the material into conventional isotropic liquid phase
 - May exhibit a variety of phases as temperature is changed
 - **Lyotropic**: Order depends on the concentration of the material



Terminology

- Mesogen: Un-crosslinked macromolecules that can organize into liquid crystalline phase through
 - Stiff molecular conformation
 - Intramolecular interactions such as hydrogen bonding
- Structure of the mesophase for rod-like molecules
 - Nematic (tread like)
 - Smectic (soap-like)
 - Cholesteric (chiral nematic)
- Structure of the mesogens
 - Calamitic (rod-like), discotic (flat, disc shaped), banana shape, conic



Mesogens: The subunits of liquid crystals

- Rigid molecule or molecule segment with anisometric (geometrical anisotropic) architecture that forms a mesophase

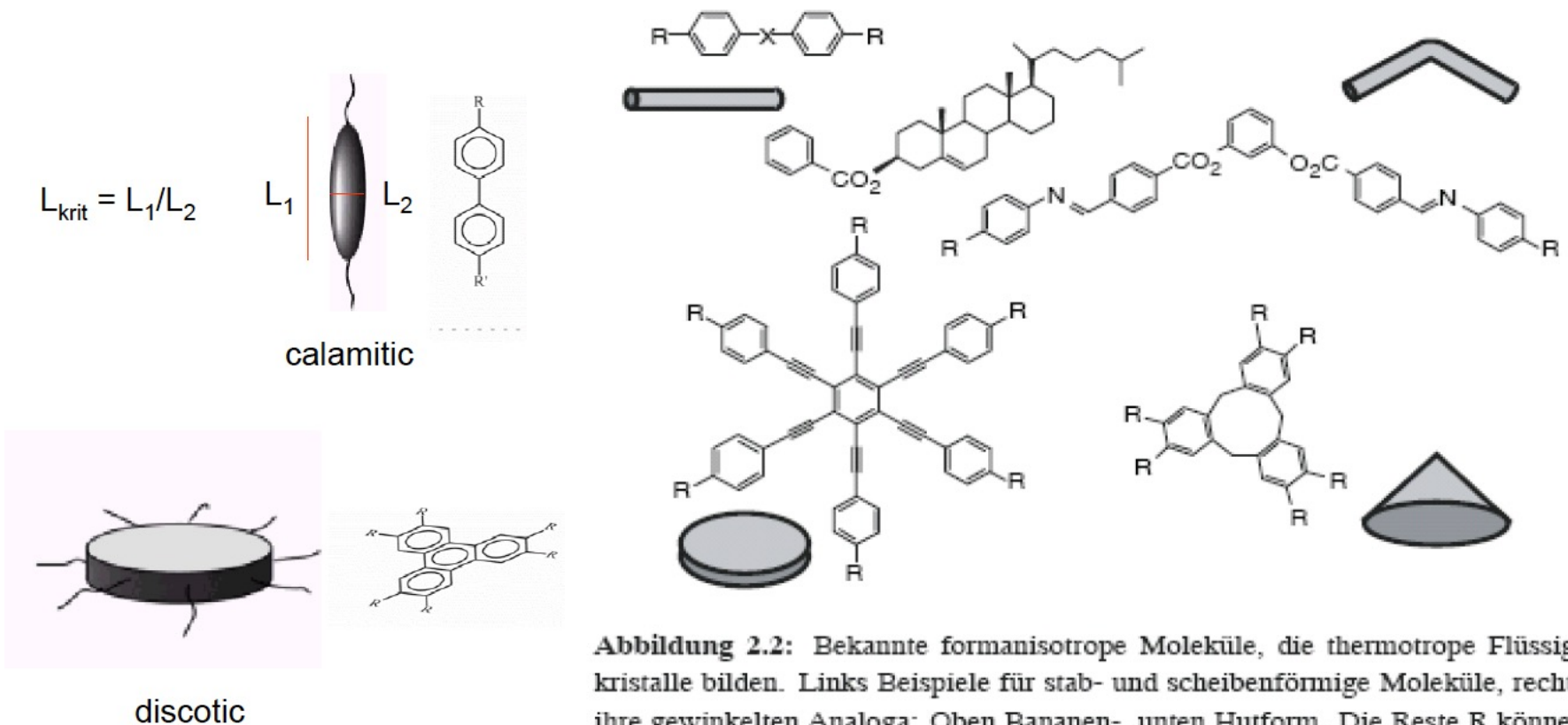
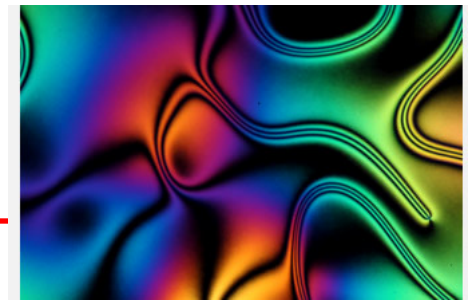
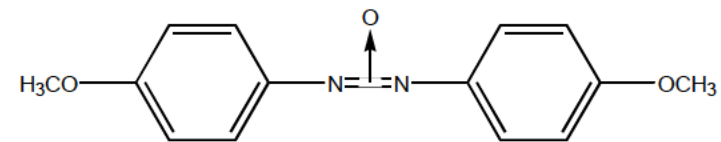
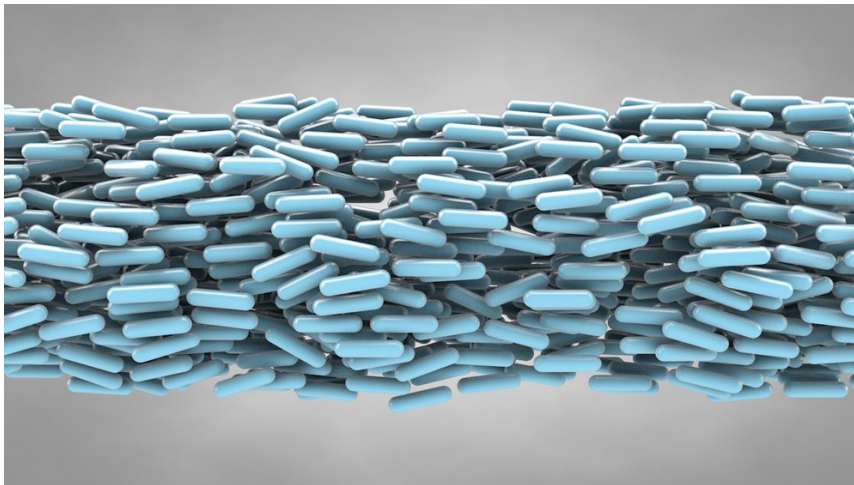


Abbildung 2.2: Bekannte formanisotrope Moleküle, die thermotrope Flüssigkristalle bilden. Links Beispiele für stab- und scheibenförmige Moleküle, rechts ihre gewinkelten Analoga: Oben Bananen-, unten Hutform. Die Reste R können Alkyl-, Alkoxy- oder komplexere, auch chirale Ketten, einzeln auch polare Gruppen wie CN oder NO₂ sein. Die Brückengruppe X kann z. B. eine Esterfunktion, eine Methylengruppe, eine Schiffsche Base oder eine Phenylgruppe sein.

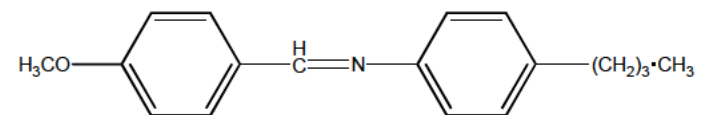
Nematic Liquid Crystals



- Comes from the Greek word for thread
- Preferred molecular orientation defines the director \mathbf{n}
 - Rod-like molecules are spontaneously and collectively aligned into a certain direction
- Director \mathbf{n} varies from point to point at macroscale
- 1D order where molecule centers are not oriented



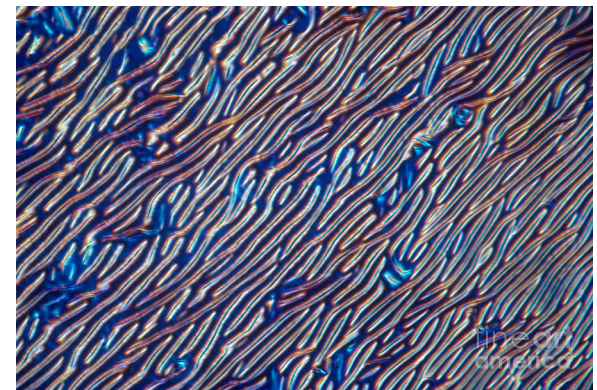
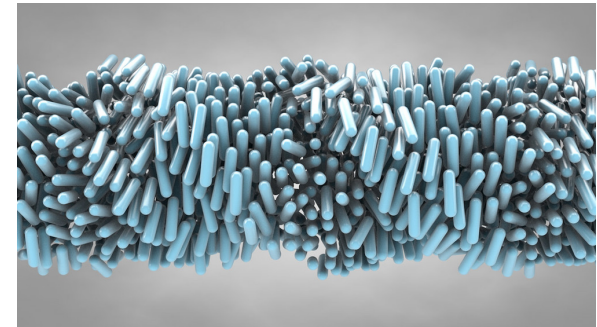
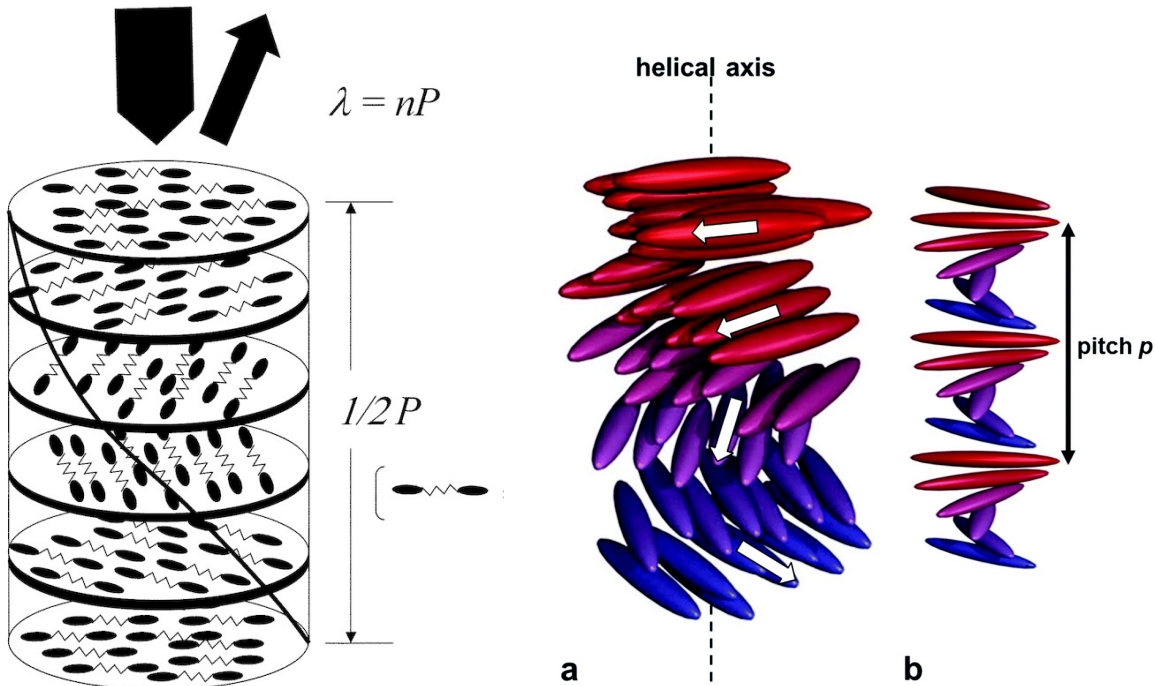
PAA: p-azoxyanisole



MBBA: n-(p-methoxybenzylidene)-
p-butylaniline

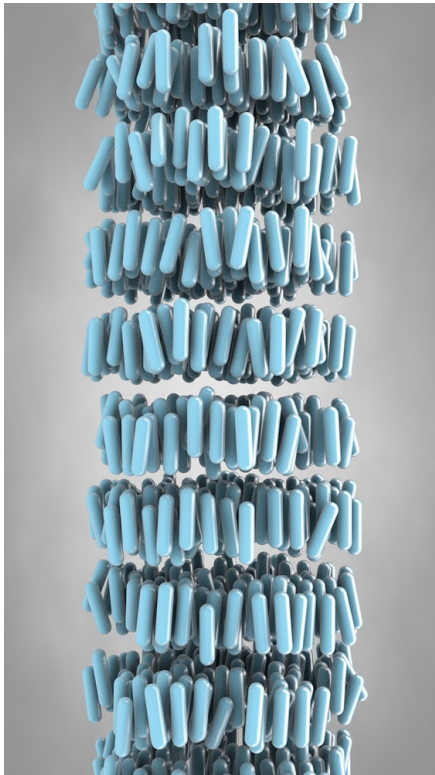
Cholesteric Phase

- The structure acquires a spontaneous twist about an axis perpendicular to the director
 - Also observed in cholesterol derivatives
 - Formed from chiral mesogenic molecules



Smectic Phase

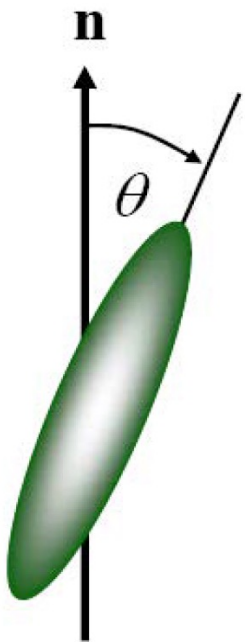
- Smectic phases exhibit a higher degree of order than nematics
- Molecule centers are oriented in the layers
- Mesogenic molecules with terminal alkyl or alkoxy chains



Order Parameter

- Quantitative description of the orientation of the mesogens
- Director **n**: Anisotropy is defined by the symmetry axis of the orientation distribution

$$S = (3\cos^2\theta - 1)/2$$



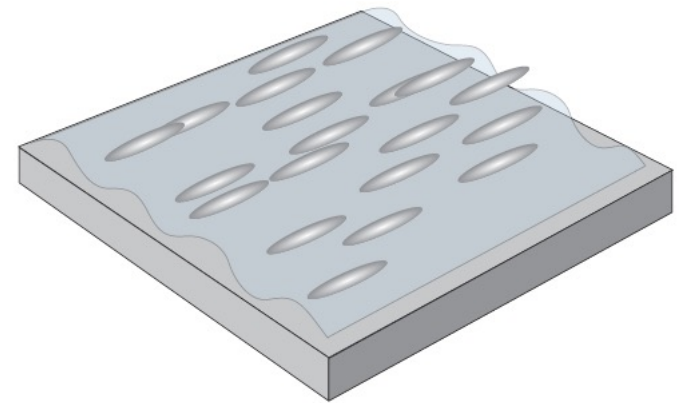
θ = Average deviation angle of the mesogen axes from the director

- All molecules aligned parallel to the director: $S = 1$
- Random distribution: $S = 0$
- Nematic phase: $0.45 < S < 0.65$
- Smectic phase: $0.85 < S < 0.95$

Hierarchy of Orientation

- Orientation of mesogens in domains
 - Domain size in the μm range
 - Orientation of the molecular axes with respect to the director inside each domain
- The directors of the domains are statistically distributed
- Uniform alignment of the domains
 - Rubbing
 - Aligned substrates
 - Application of magnetic or electric field
 - Viscous fingering

Planar alignment



Frank-Oseen Free Energy

$$g = \frac{1}{2}k_{11}(\nabla \cdot \mathbf{n})^2 + \frac{1}{2}k_{22}(\mathbf{n} \cdot \text{curl } \mathbf{n} + t_0)^2 + \frac{1}{2}k_{33}(\mathbf{n} \times \text{curl } \mathbf{n})^2$$

This is the famous Frank-Oseen elastic free energy density for nematics and cholesterics.

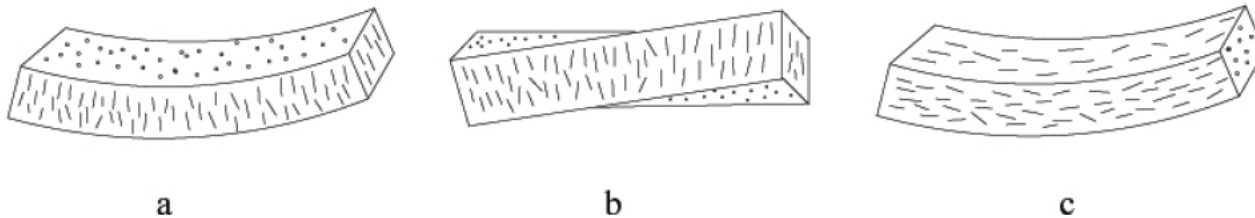


Figure: The three distinct curvature strains of a liquid crystal: (a) splay, (b) twist, and (c) bend.

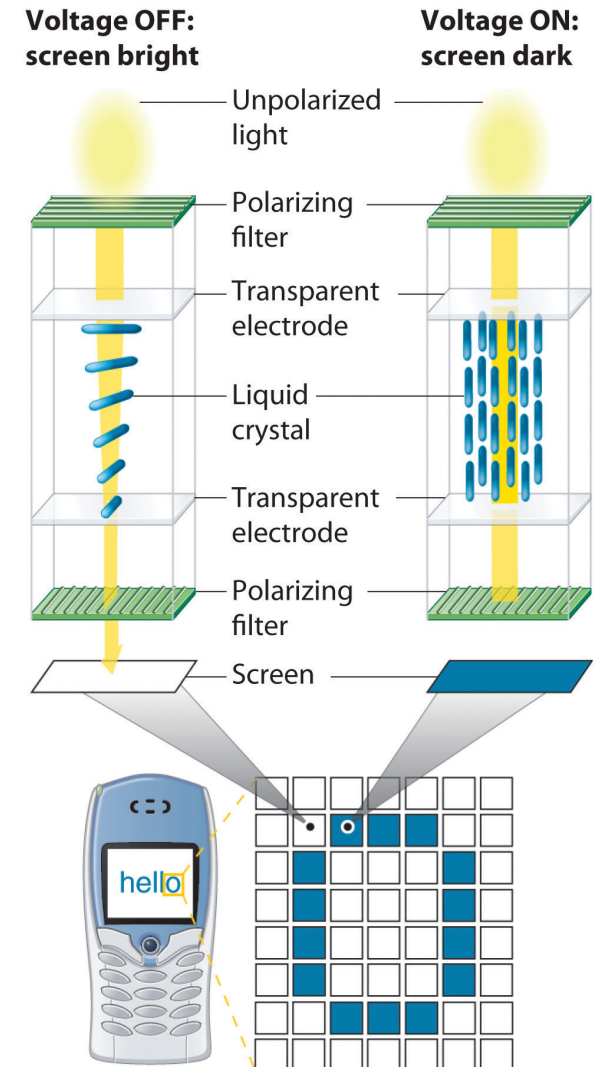
- A nonpolar LC with equal bend, splay, and twist constants

$$g = \frac{1}{2}k [(\nabla \cdot \mathbf{n})^2 + (\nabla \times \mathbf{n})^2]$$

- The equilibrium value of S is that which minimizes free energy

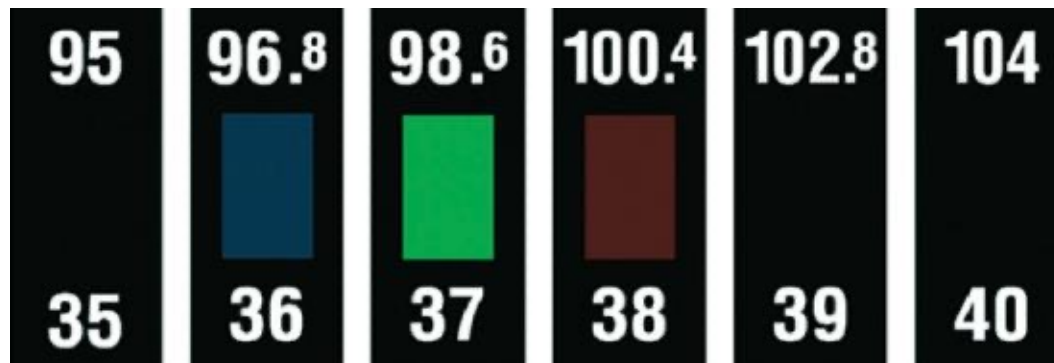
Liquid Crystal Displays

- Mesogens are polar,
 - interact with an electric field
 - change the orientation
- Nematic liquid crystals tend to be relatively translucent
- They become opaque when an electric field is applied and the molecular orientation changes
- This behavior is ideal for producing dark images on a light or an opalescent background



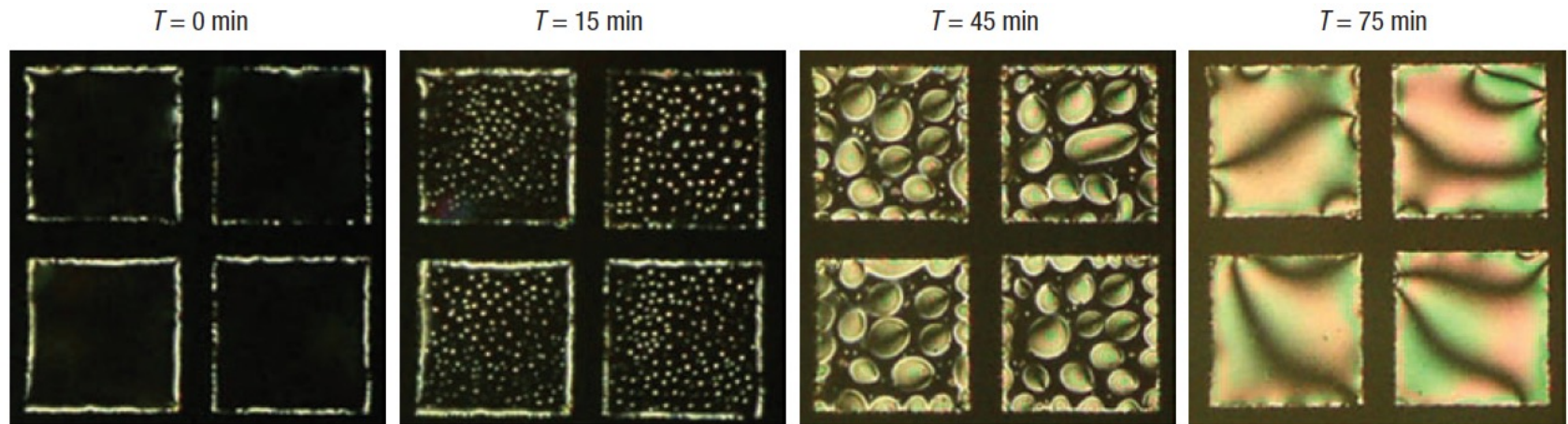
Liquid Crystal Thermometers

- Changes in molecular orientation that are dependent on temperature result in an alteration of the wavelength of reflected light.
- Changes in reflected light produce a change in color, which can be customized by using either a single type of liquid crystalline material or mixtures.
- An LC thermometer that indicates temperature by color

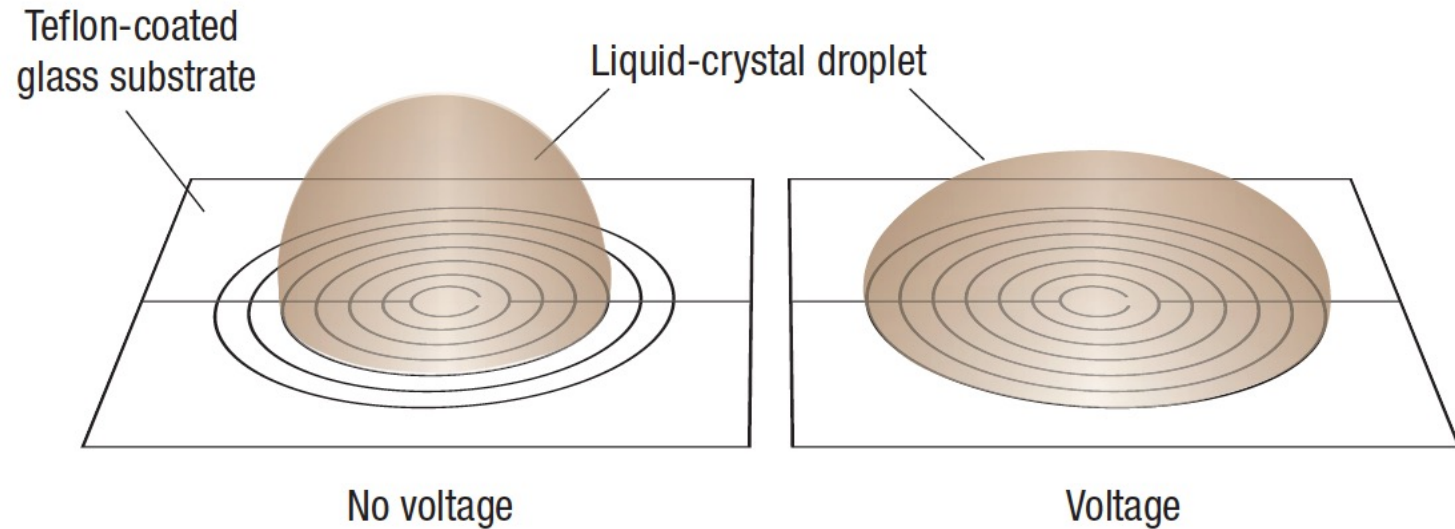


Biosensor

- Many biological systems, including cell membranes, phospholipids, cholesterol, DNA etc. exist in liquid crystal phases
- Liquid-crystal aqueous interface where chemical is applied
- Orientational change with the introduction of the chemical (enzymatic reaction)
- Label free detection



Dynamic Lenses

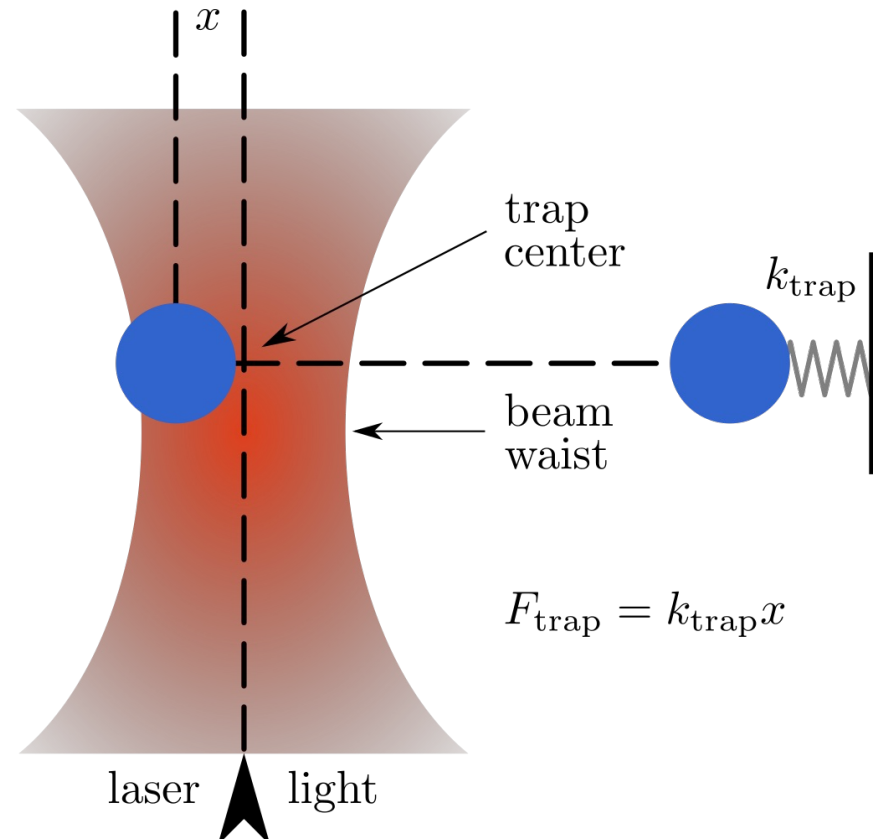
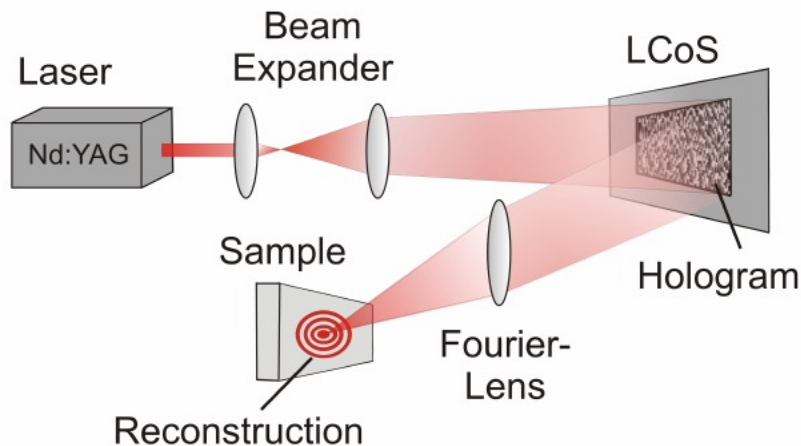


- Focal length of the lens is tuned with an electric field
- Microlens arrays similar to fly's eye
- Bifocal eyeglasses (near and far vision)

Spatial Light Modulators and Optical Traps

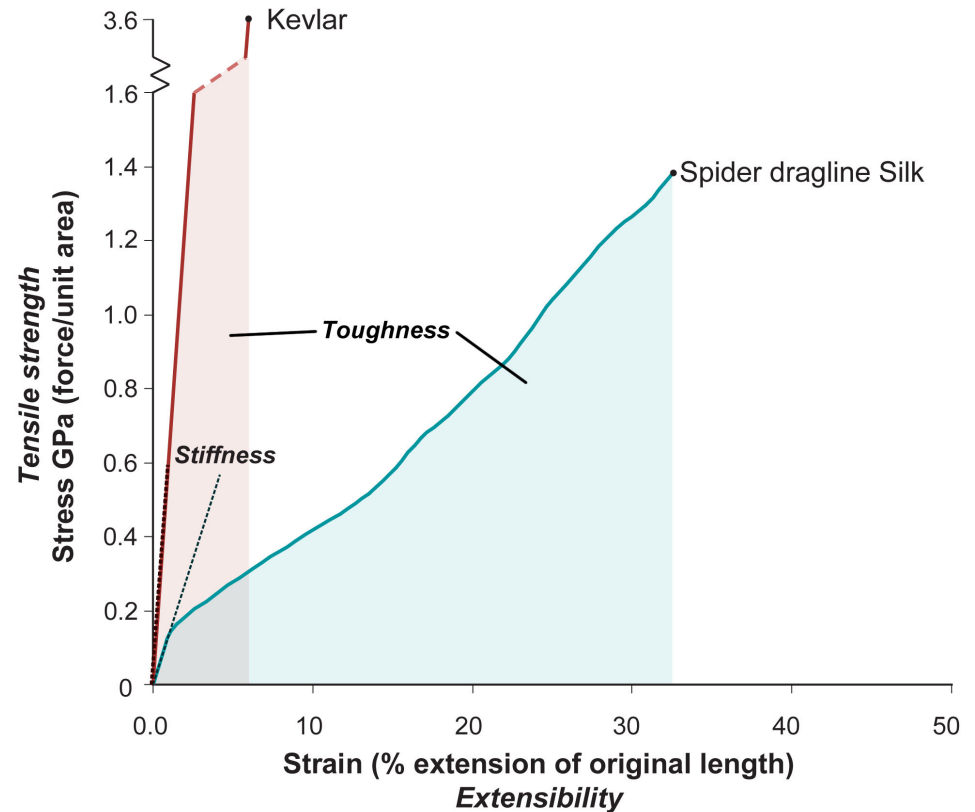
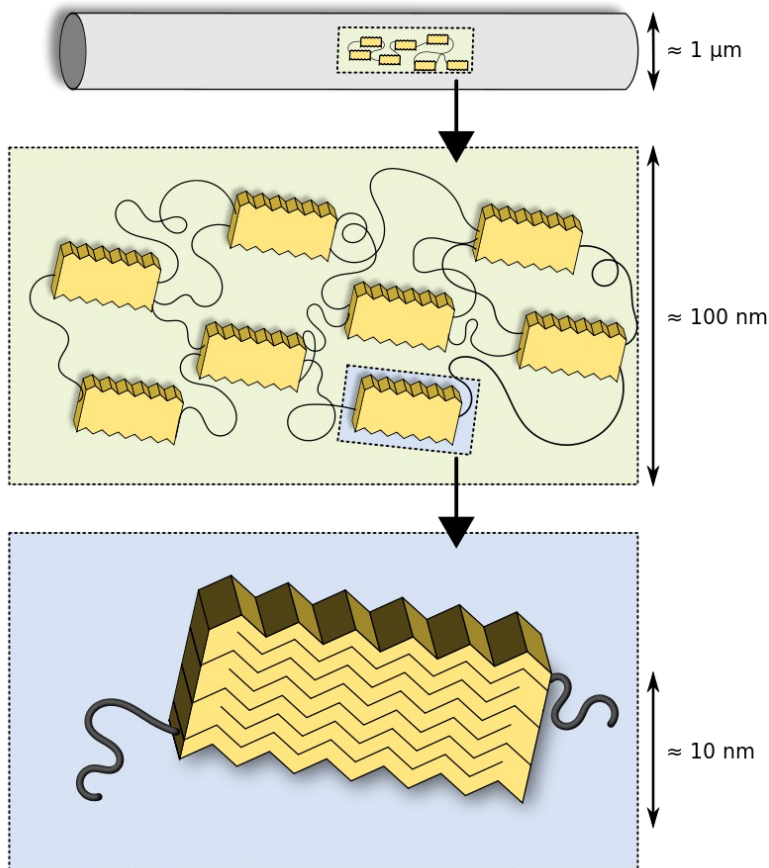
movie

- Spatially varying modulation of light intensity and/or phase
- Holographic display technology
- Holographic optical tweezers



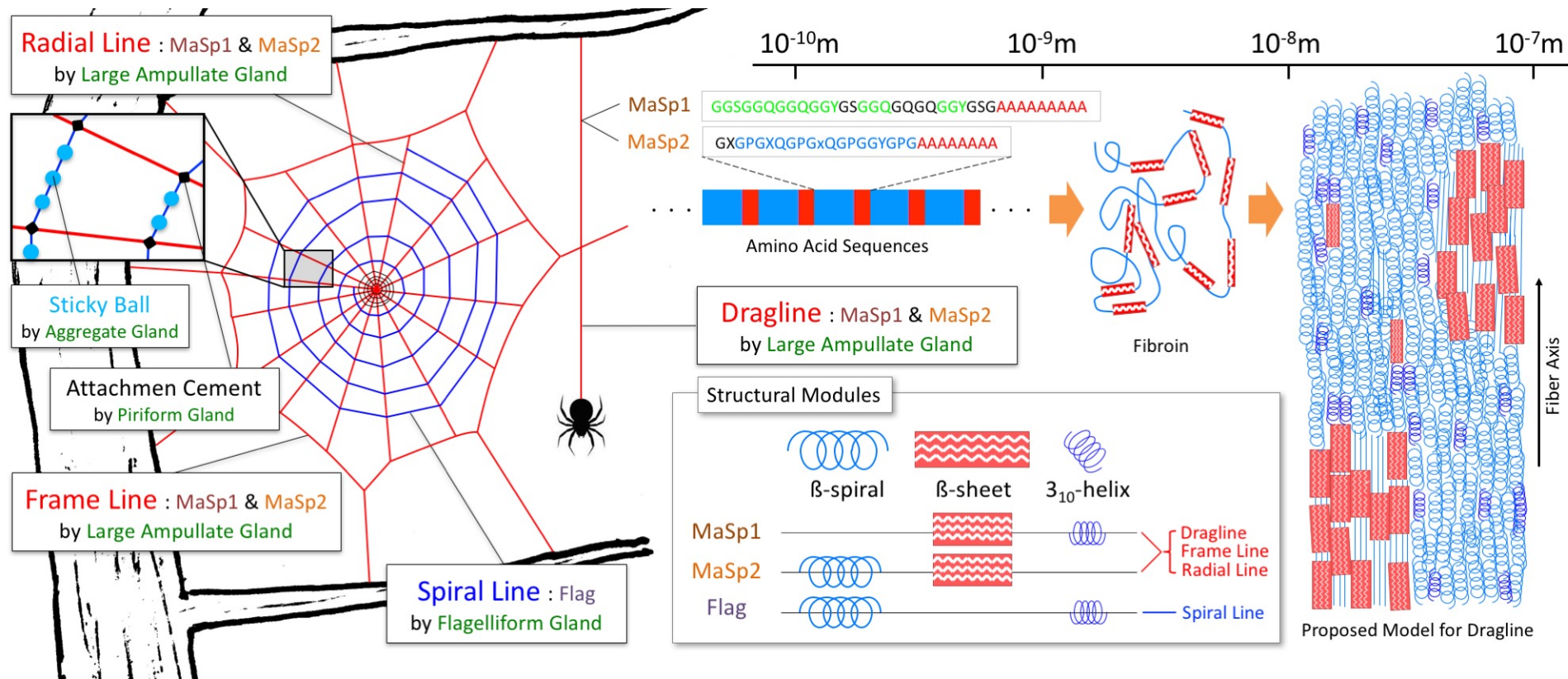
Structural Elements

- Extrusion of fibers with aligned rod shaped mesogens
 - Kevlar, spider silk



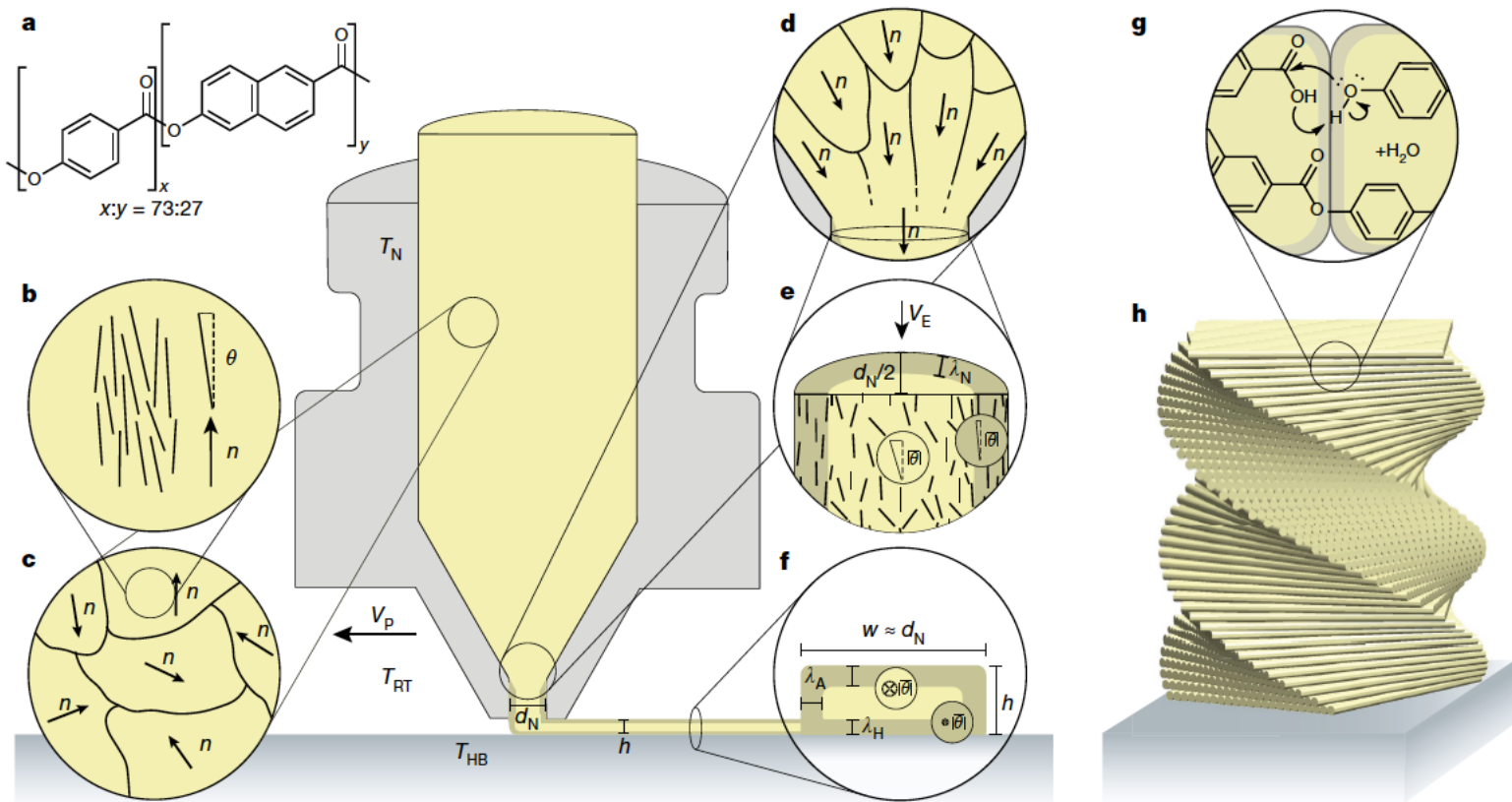
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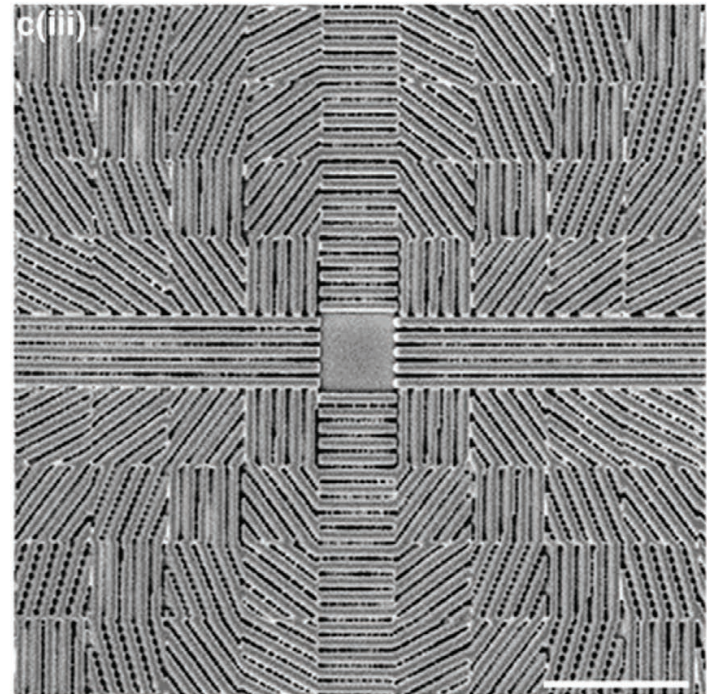
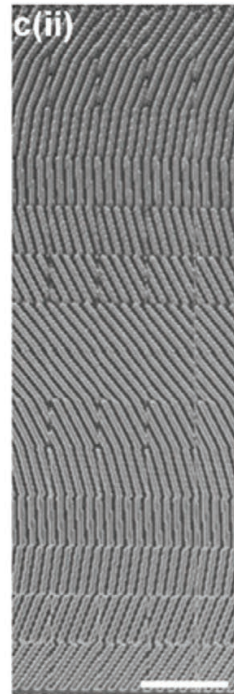
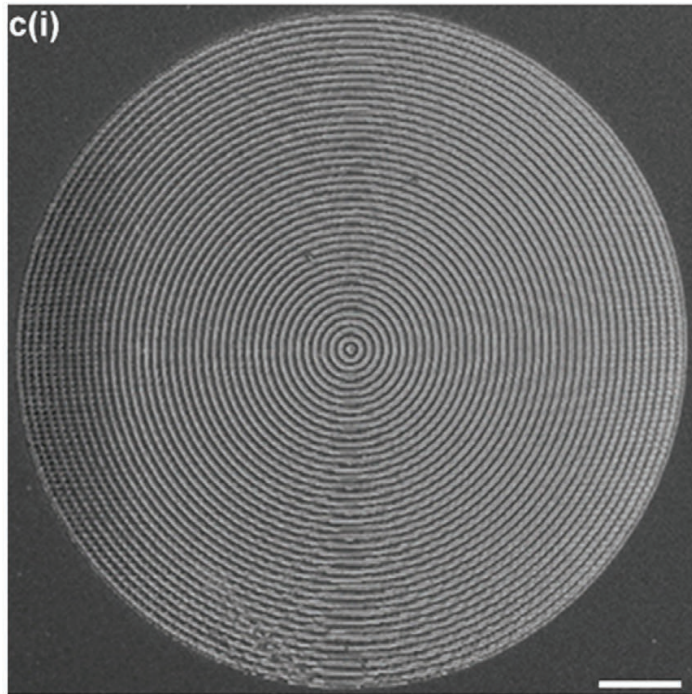
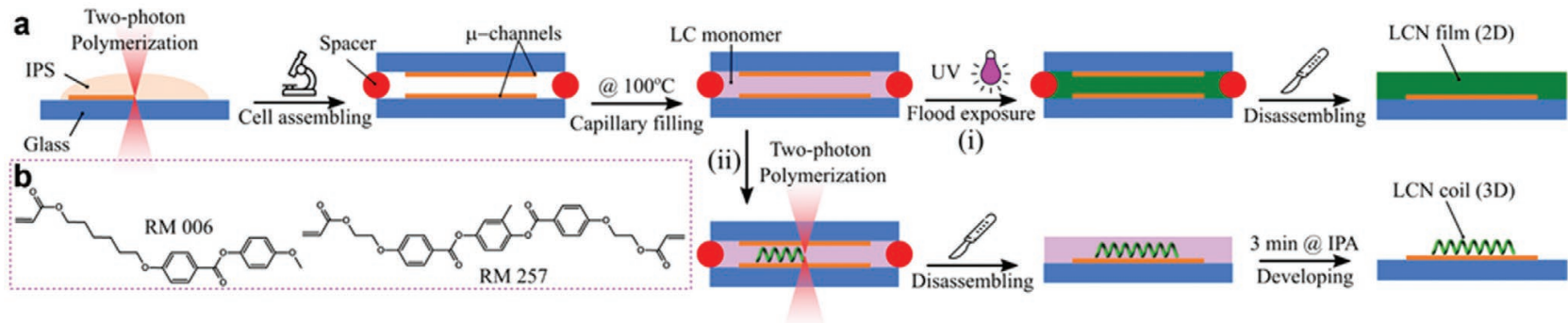


3D printing of liquid crystal networks

- The directors are subjected to elongational and shear forces during the extrusion through the heated nozzle
- Solidification front freezes the nematic order in place

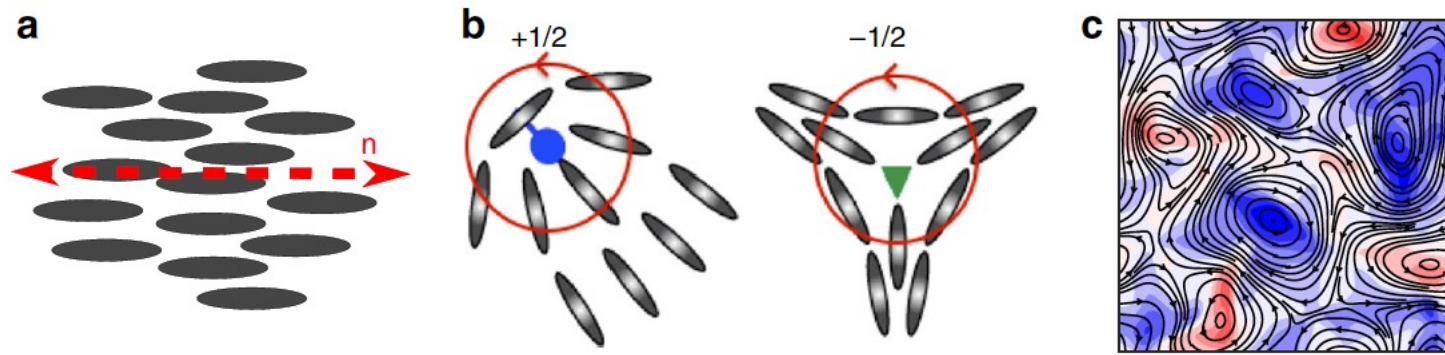


3D printing of liquid crystal networks

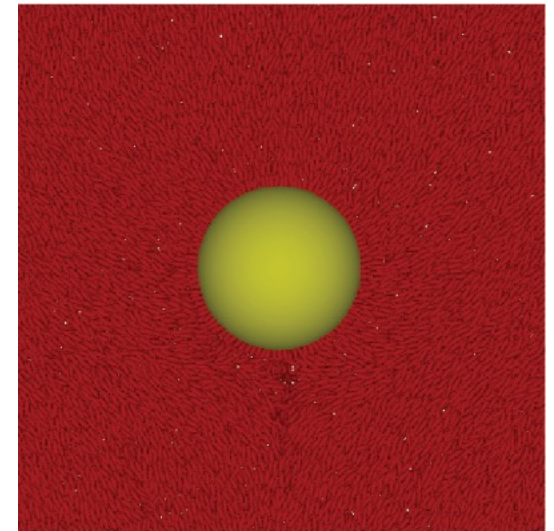
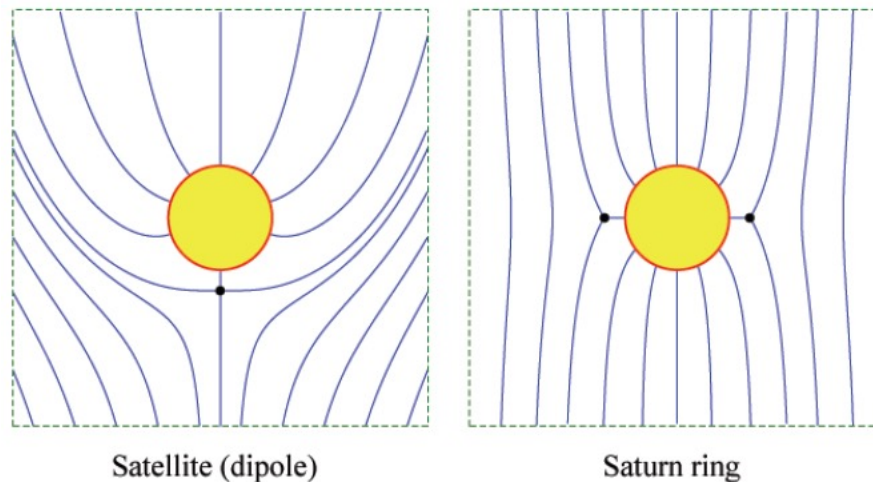


Topological Defects in Nematics

- Active nematic turbulence

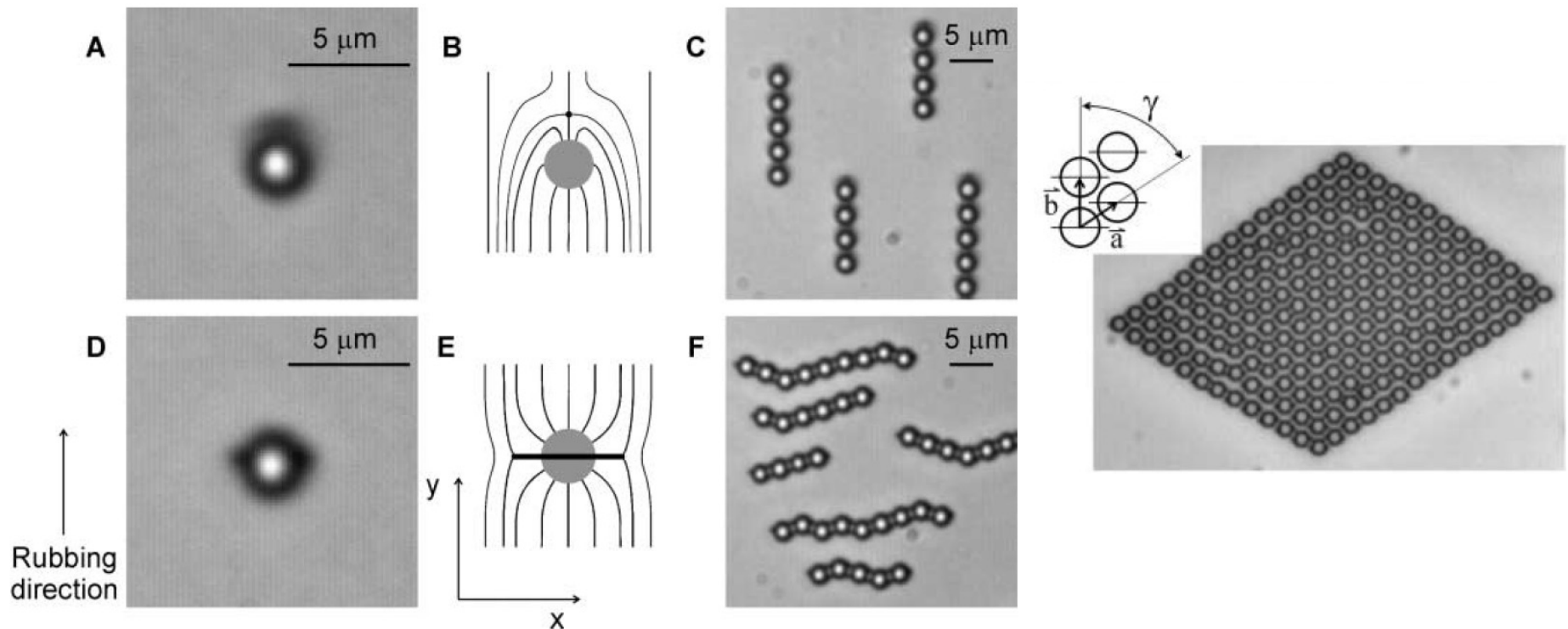


- Topological defects induced by colloidal particle

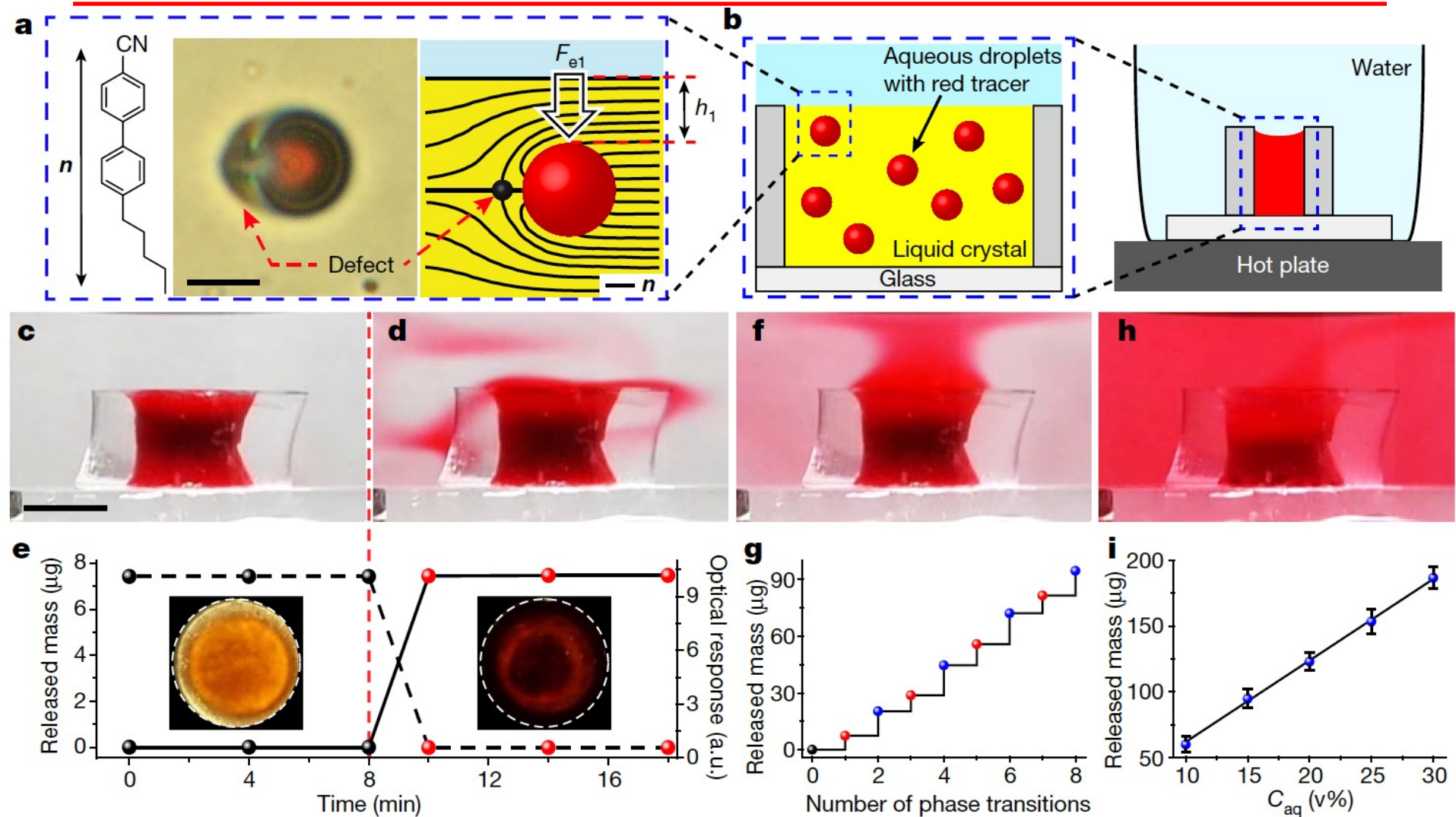


Nematic-mediated interactions

- The orientation of nematic molecules is locally disturbed because of their interaction with microparticle surfaces
- The disturbance can be considered as elastic deformation at microscale
- 2.3 μm silica spheres in 5 μm or 2.5 μm LC layer

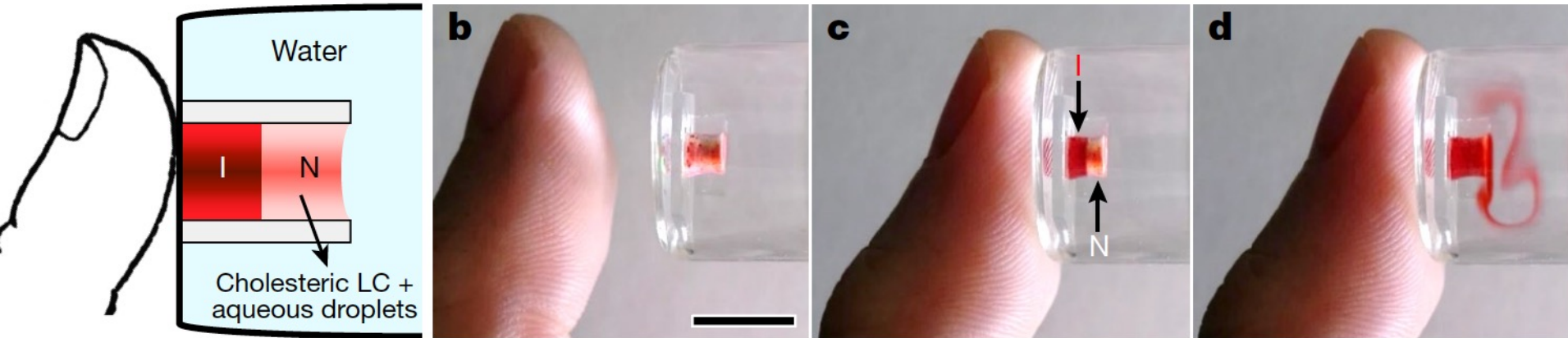


Pulsatile ejection of microdroplets from LCs



Pulsatile ejection of microdroplets from LCs

- Heat released from the human finger

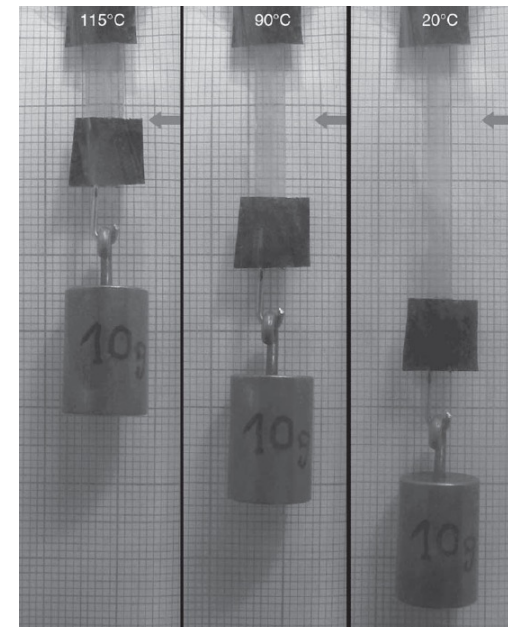
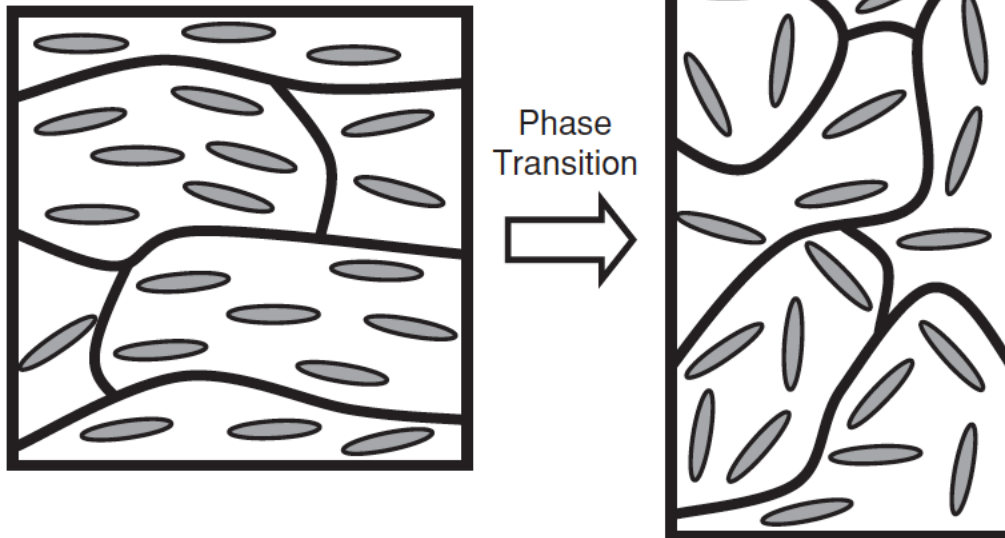
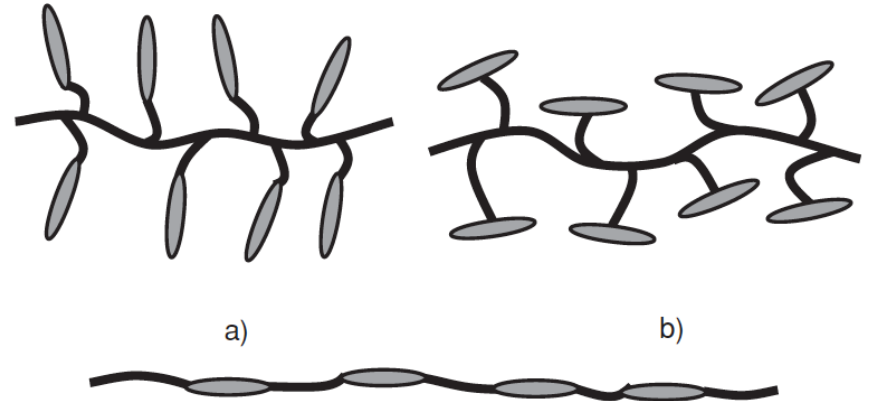


Liquid Crystal Elastomers

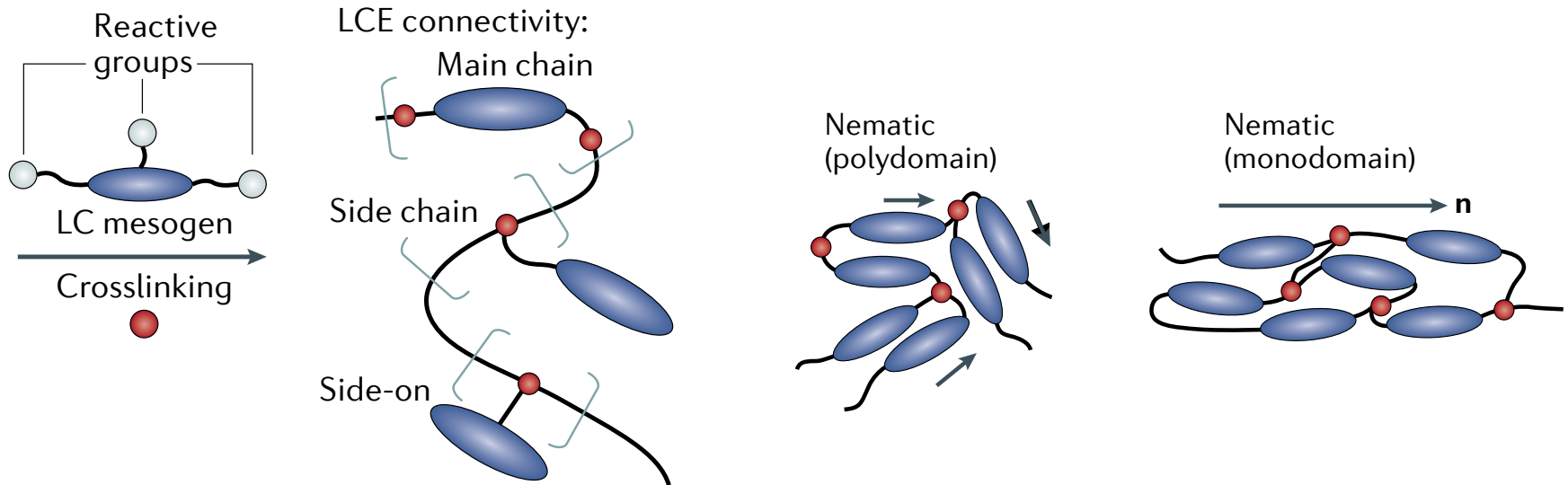
- Mesogenic monomers incorporated into the backbones or sidechains of weakly crosslinked long flexible polymers (i.e. polysiloxane)
 - Anisotropy and large susceptibility of low-molecular mass LCs with rubber elasticity
- Strong coupling between the orientational order and mechanical strain
 - Changing orientation order gives rise to internal stresses
 - Deformation and change of shape
- Molecular structure corresponds to traditional rubber
 - Long chains of molecules that can easily slip past one another
 - Enable the material to be expanded with very little force
 - Strains of several 100 per cent
 - Mechanical response depends on alignment direction and phase

Liquid Crystal Elastomers

- Coupling between the mesogens and polymer chains
 - (a) end-on
 - (b) side-on
 - (c) main-chain

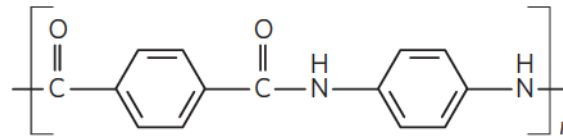
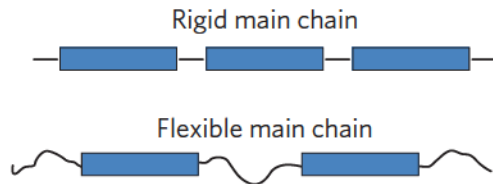


Liquid Crystal Elastomers



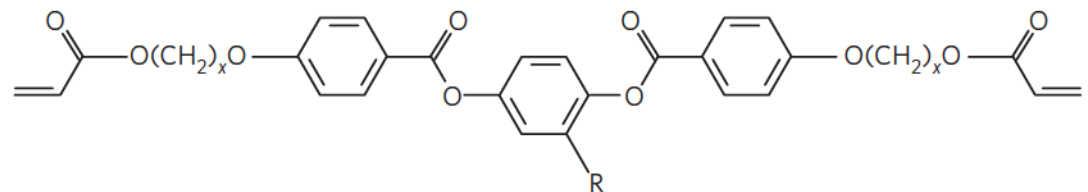
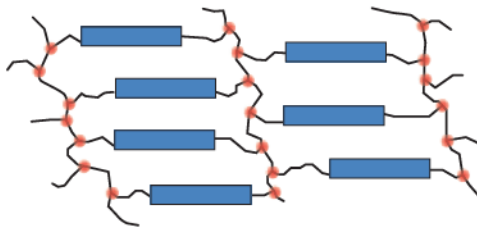
Liquid Crystal Elastomers

Liquid crystal main-chain polymers (LCPs)



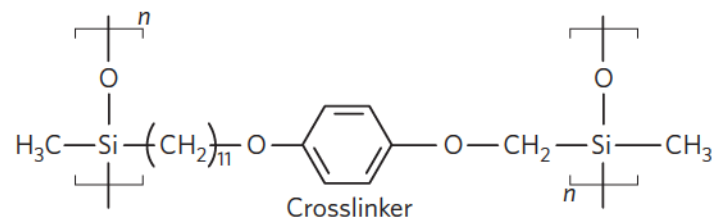
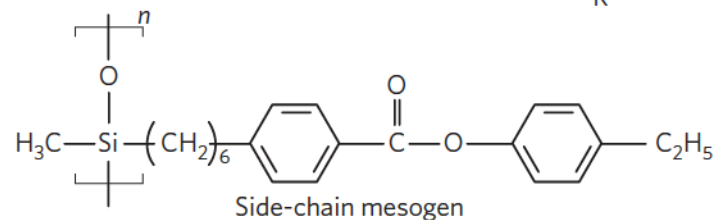
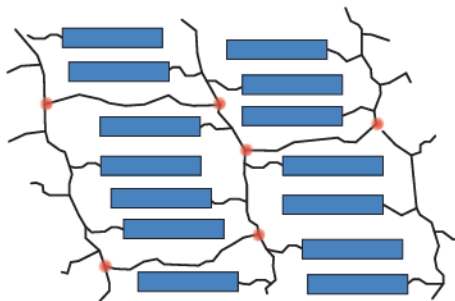
$T_m \sim >300^\circ\text{C}$
 $E \sim >100\text{ GPa}$
 $\Delta S \sim 0\%$

Glassy liquid crystal polymer networks (LCNs)



$T_g \sim 40\text{--}120^\circ\text{C}$
 $E \sim 0.8\text{--}2\text{ GPa}$
 $\Delta S \sim 5\%$

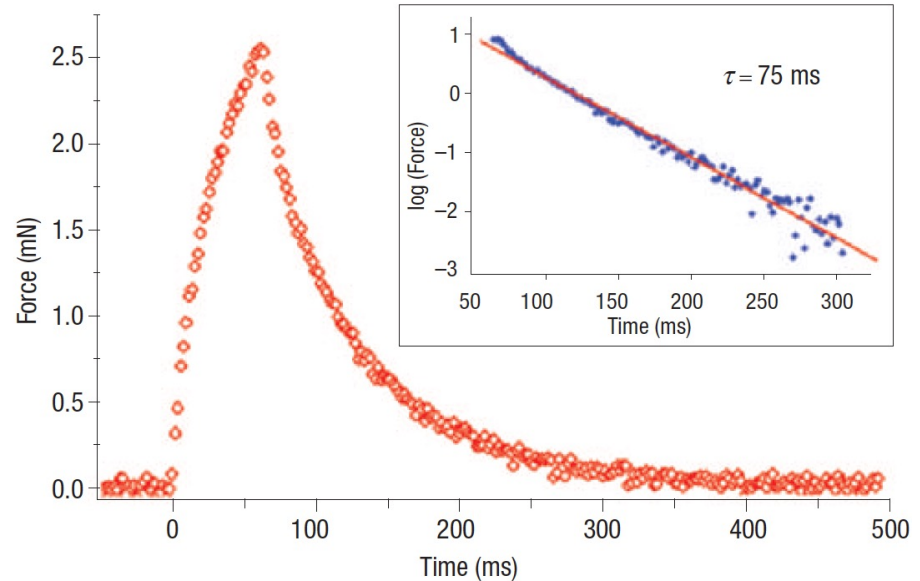
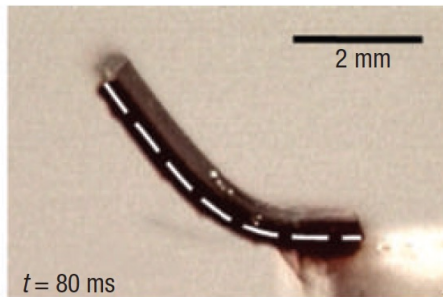
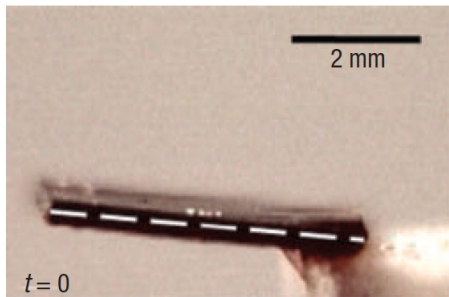
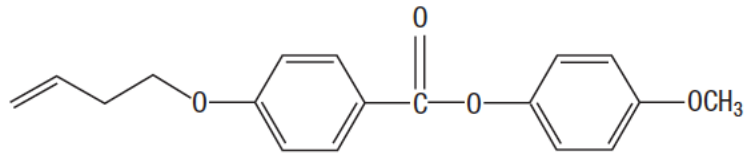
Liquid crystal elastomers (LCEs)



$T_g \sim <20^\circ\text{C}$
 $E \sim 0.1\text{--}5\text{ MPa}$
 $\Delta S \sim 90\%$

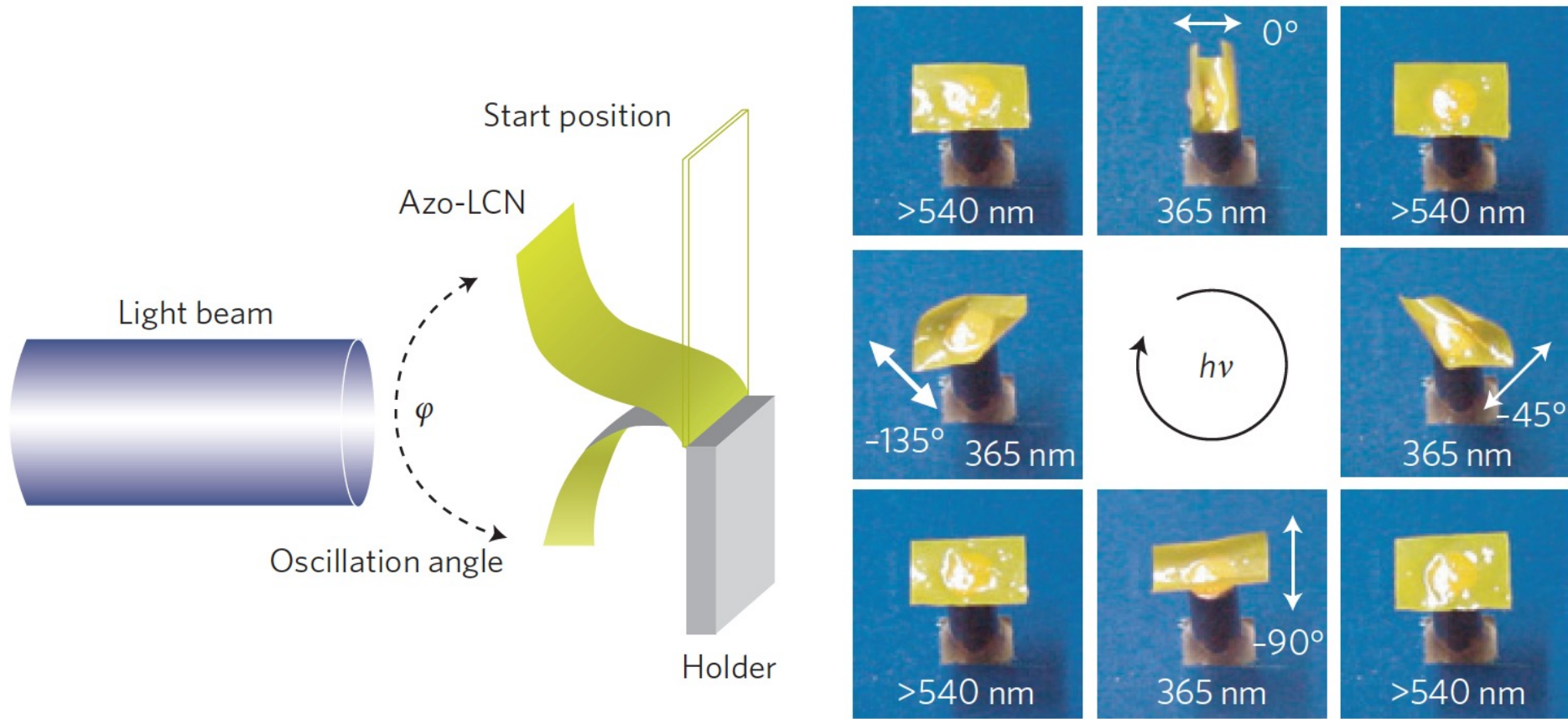
Wireless control with light

- Dopants containing azobenzene moieties: covalent bonding or dissolving
- Change in the degree of order
 - Photoisomerization of the dissolved dye
 - Photoisomerize between trans- and cis-states in the presence of linear polarized light at specific wavelengths



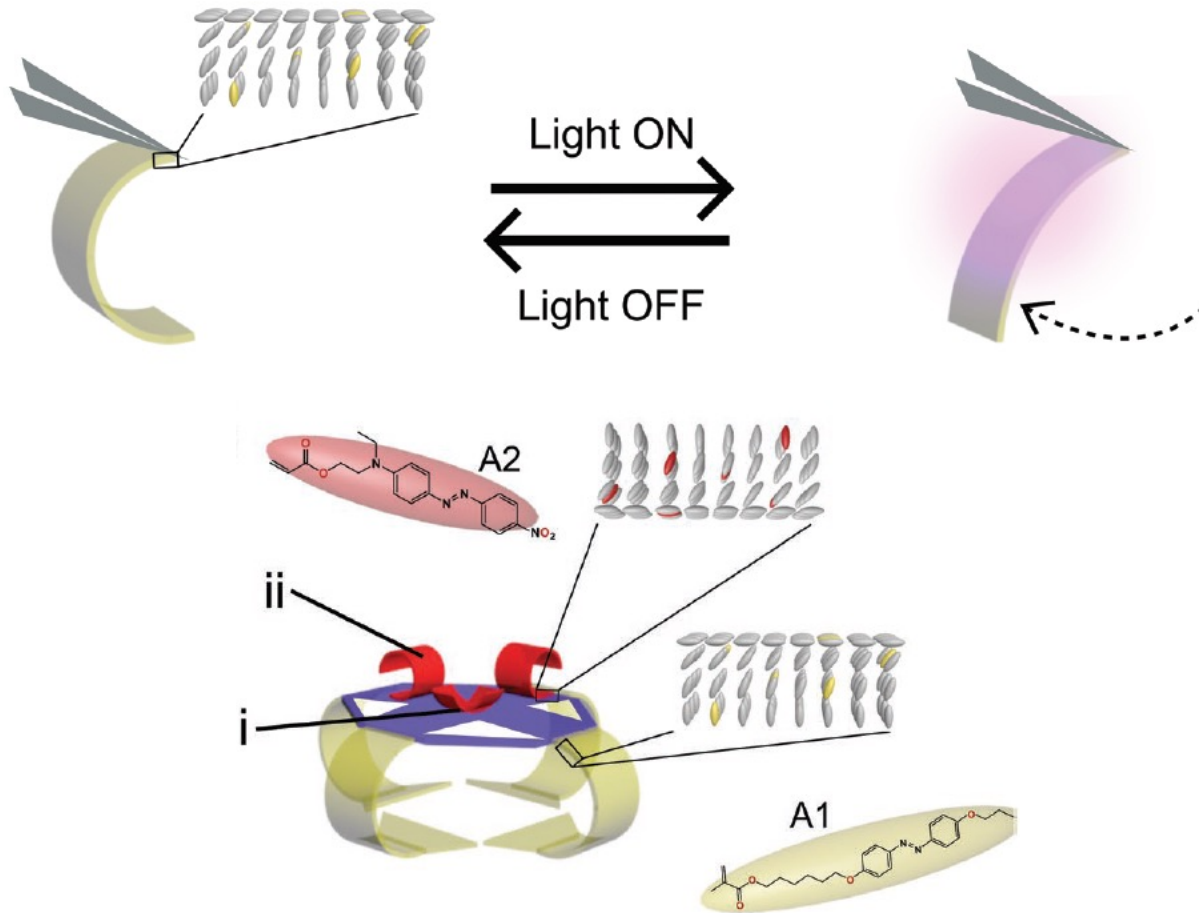
Wireless control with light

- Intensity, polarization, and wavelength of light



Soft robot

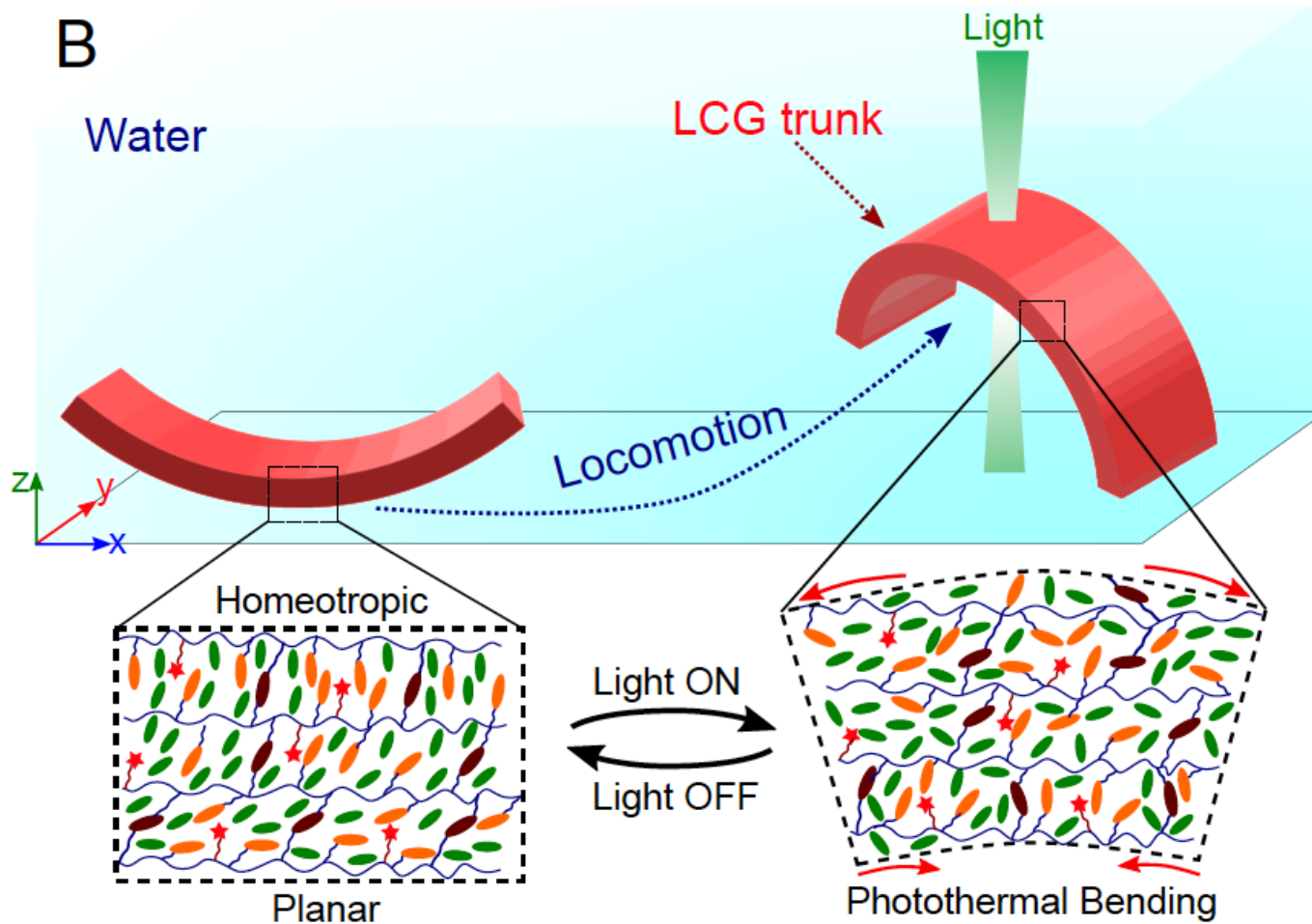
- Two different materials for the legs and the grippers



Soft robot



Soft robot



Light-fueled Oscillation

Frequency: 1 Hz

Sample size: 9 x 1.5 x 0.1 mm³

The playback speed is 1X.

Swimming in Vertical Direction based on Undulatory Light-fueled Bending

Light source: Arc Lamp

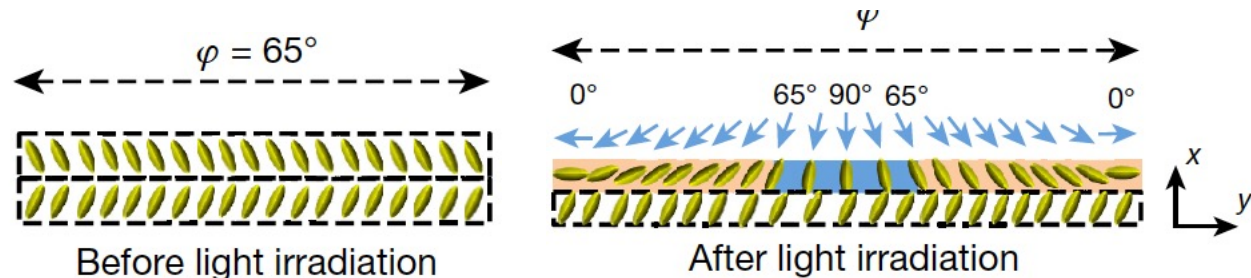
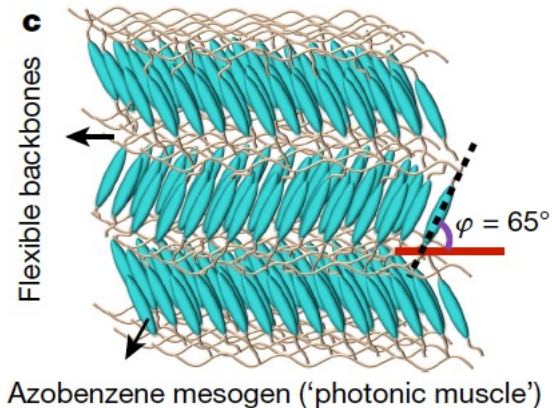
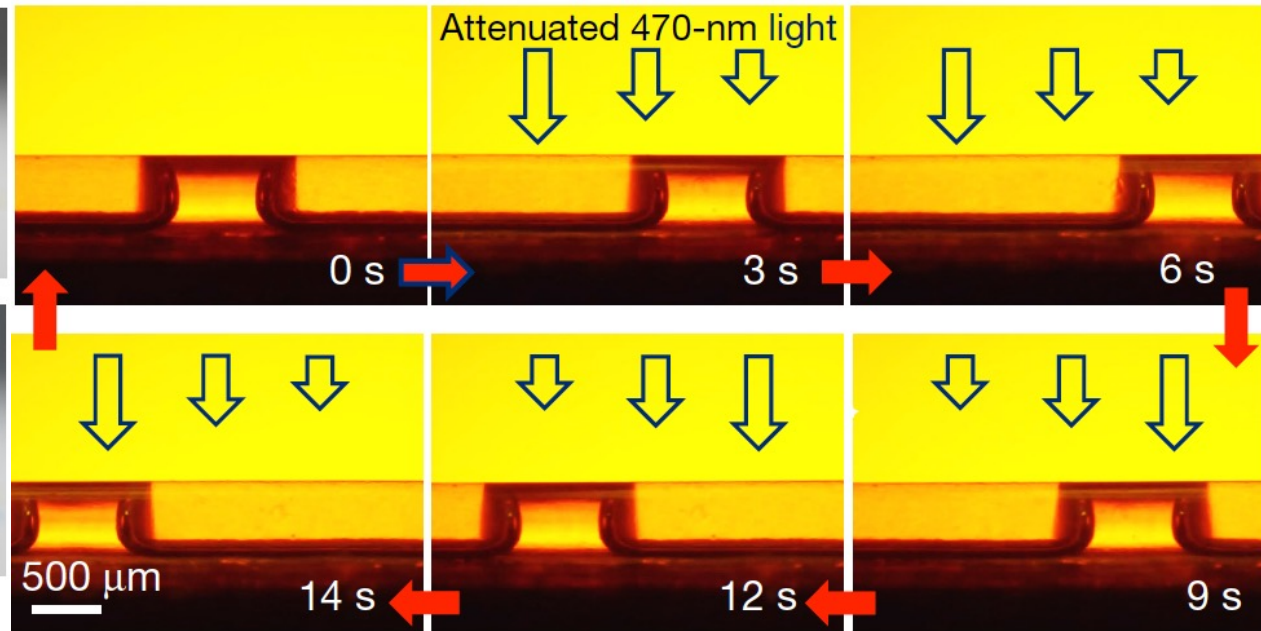
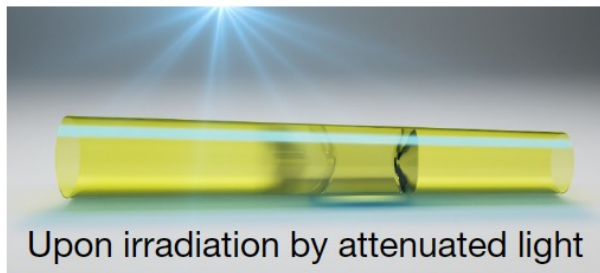
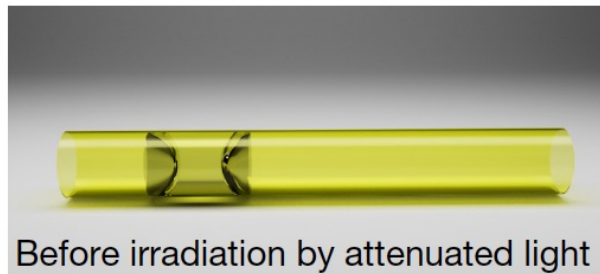
Light intensity: $< 1.8 \text{ W cm}^{-2}$

Sample size: $16 \times 3 \times 0.1 \text{ mm}^3$

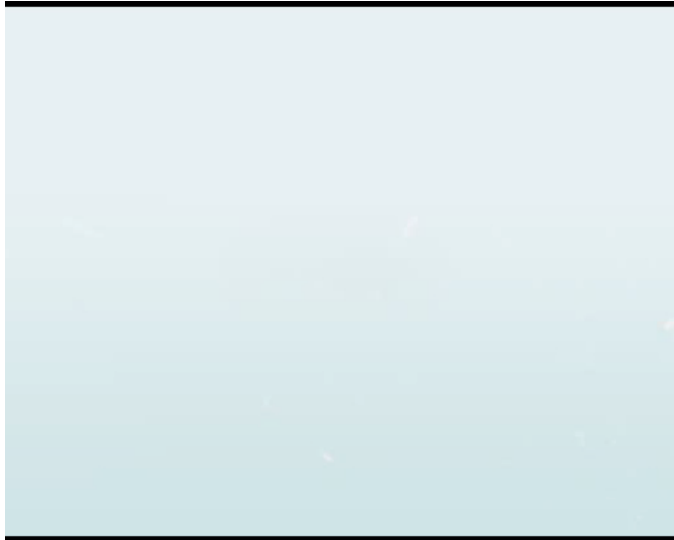
The playback speed is 1X.

Pumping and transport

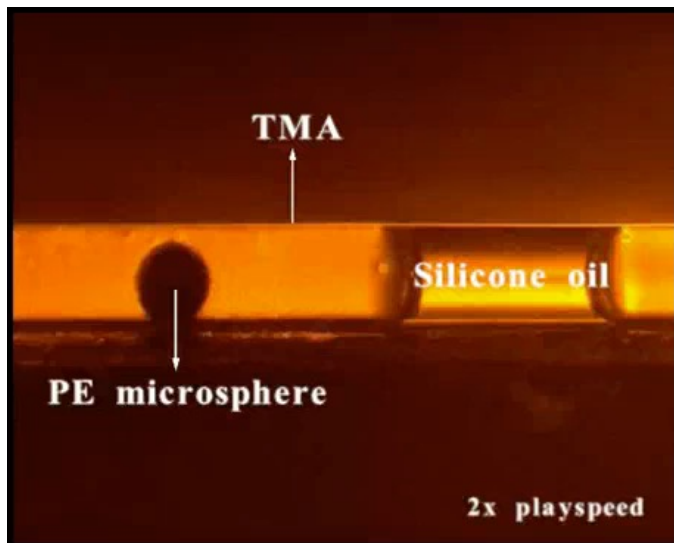
- Deformation into a cone-like geometry: capillary force



Pumping and transport

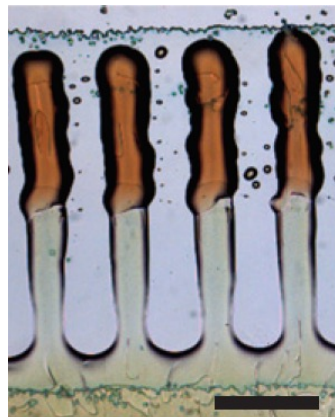
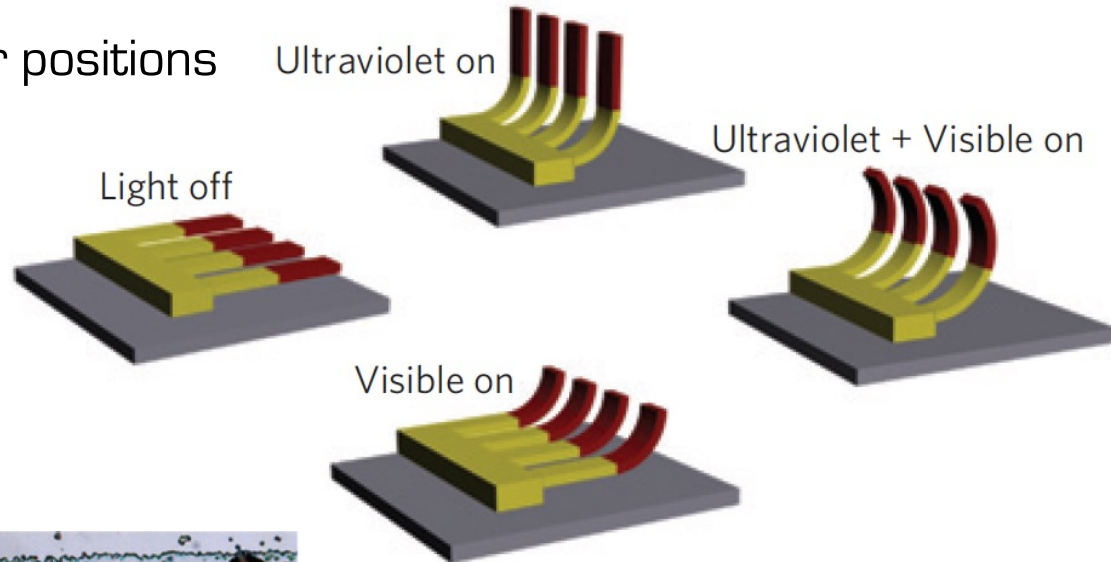
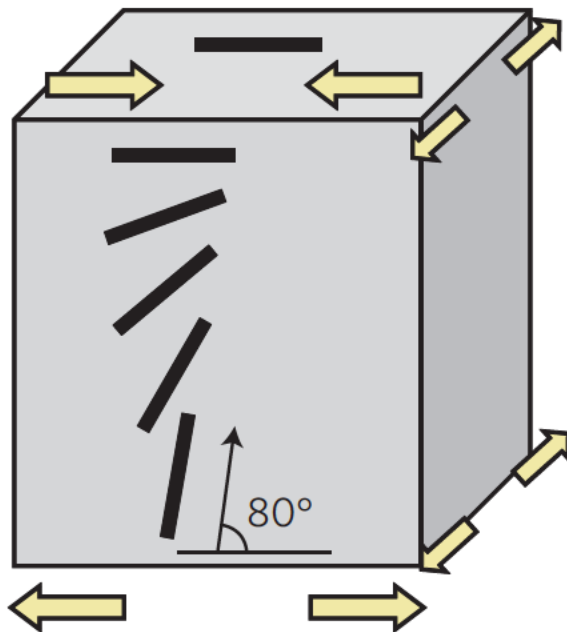


Photocontrol of fluid slugs

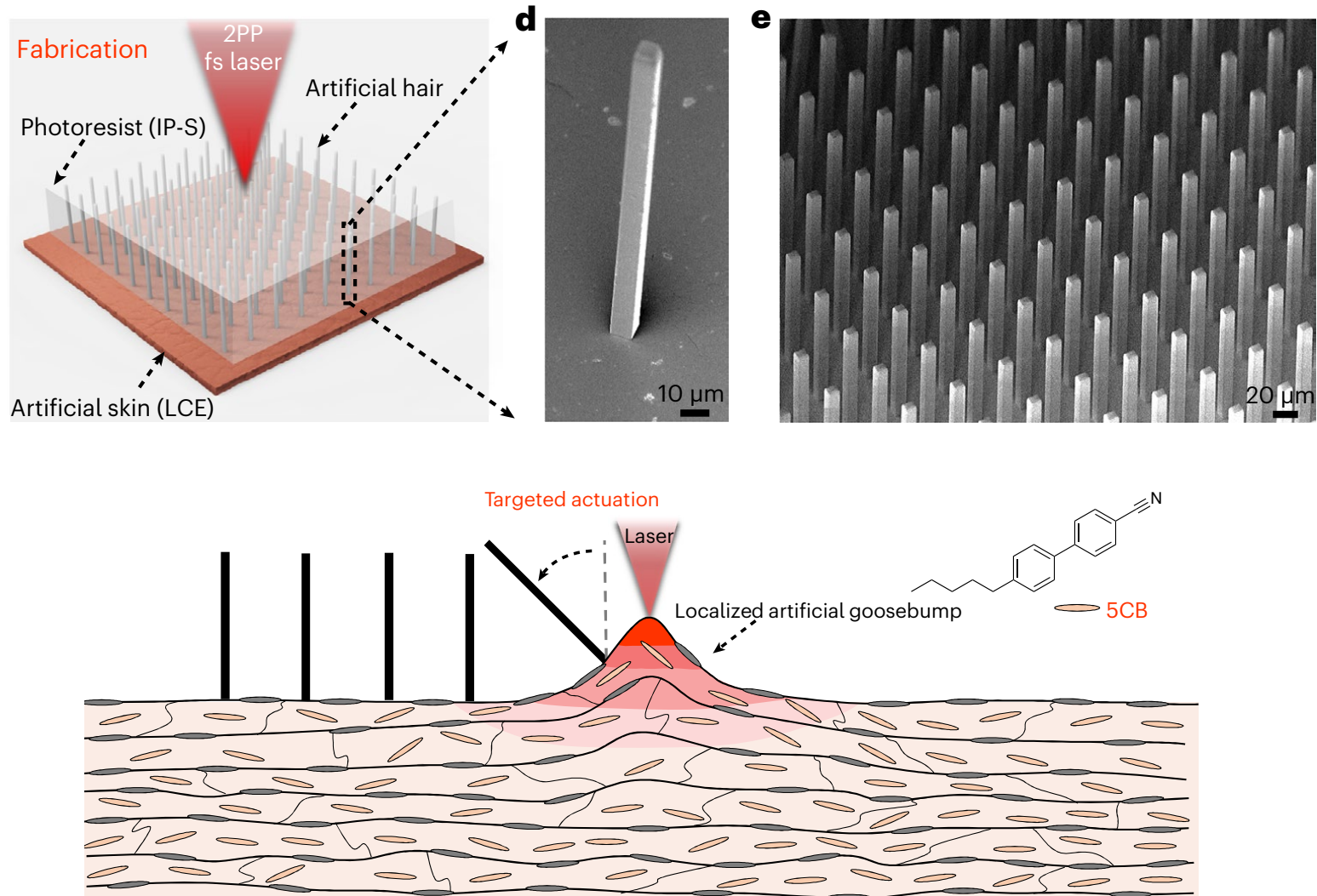


Artificial Cilia

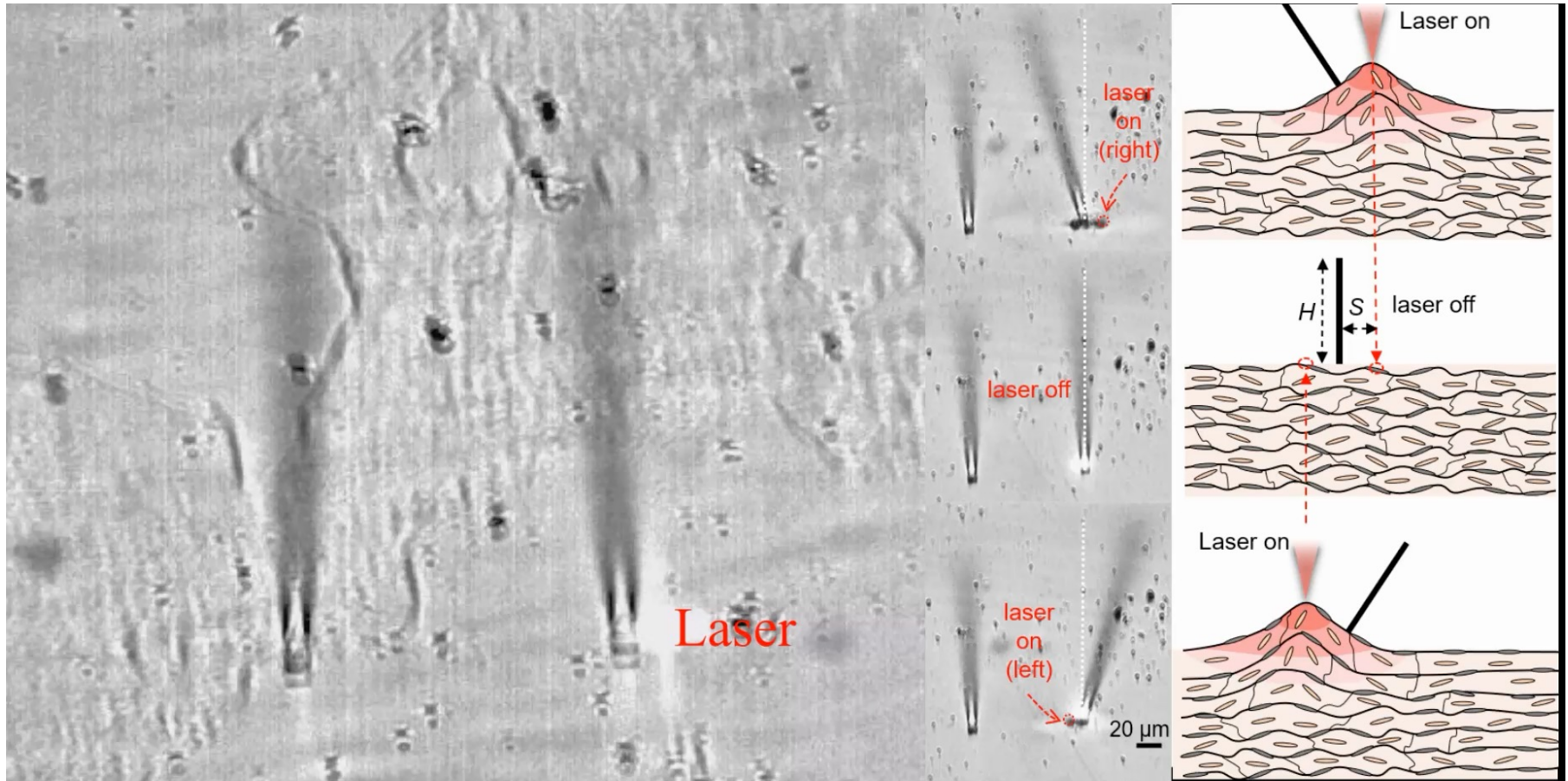
- Asymmetric motion controlled by the spectral composition of light
 - Two different dyes
 - Switching between four positions



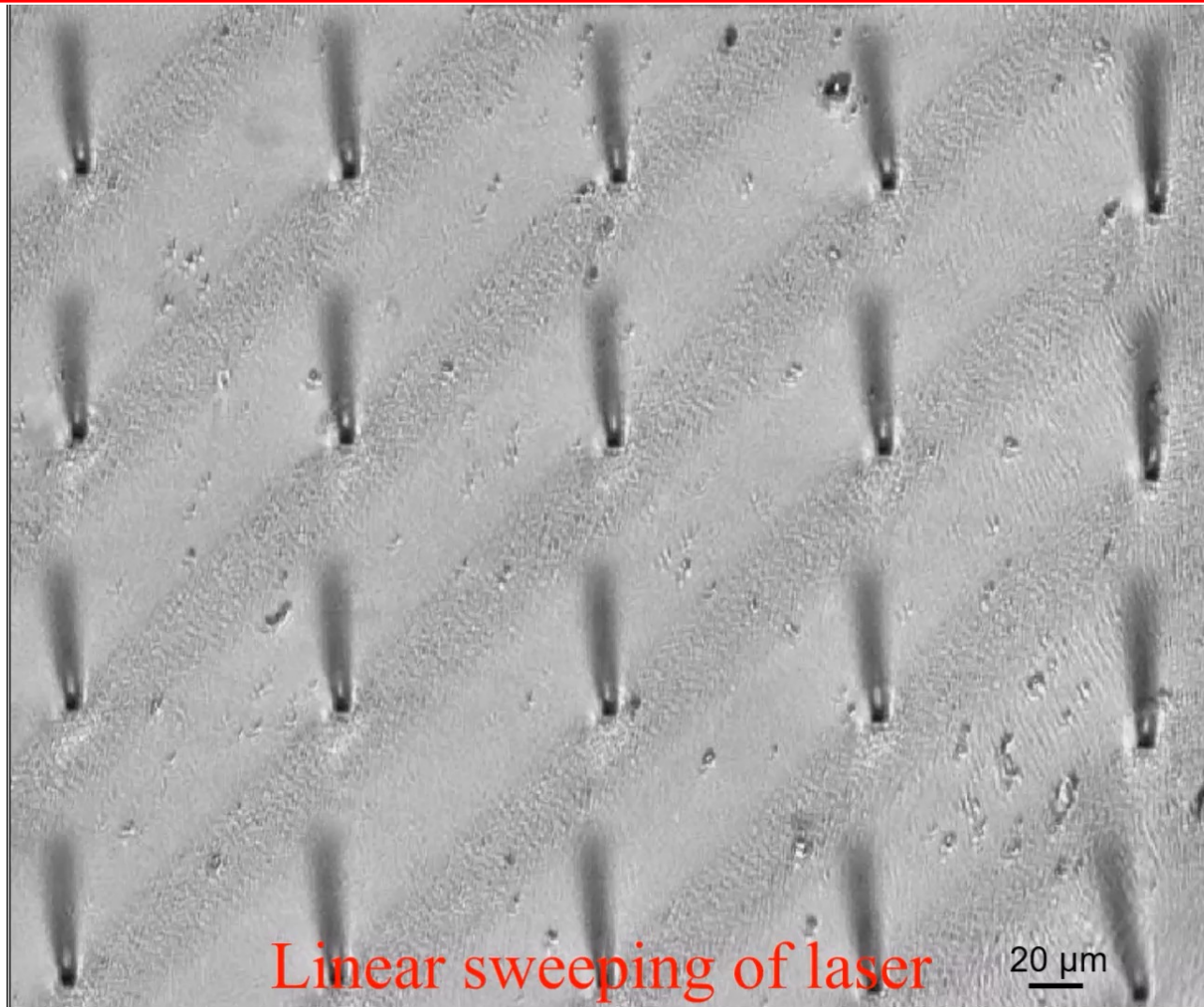
LCE Skin



LCE Skin

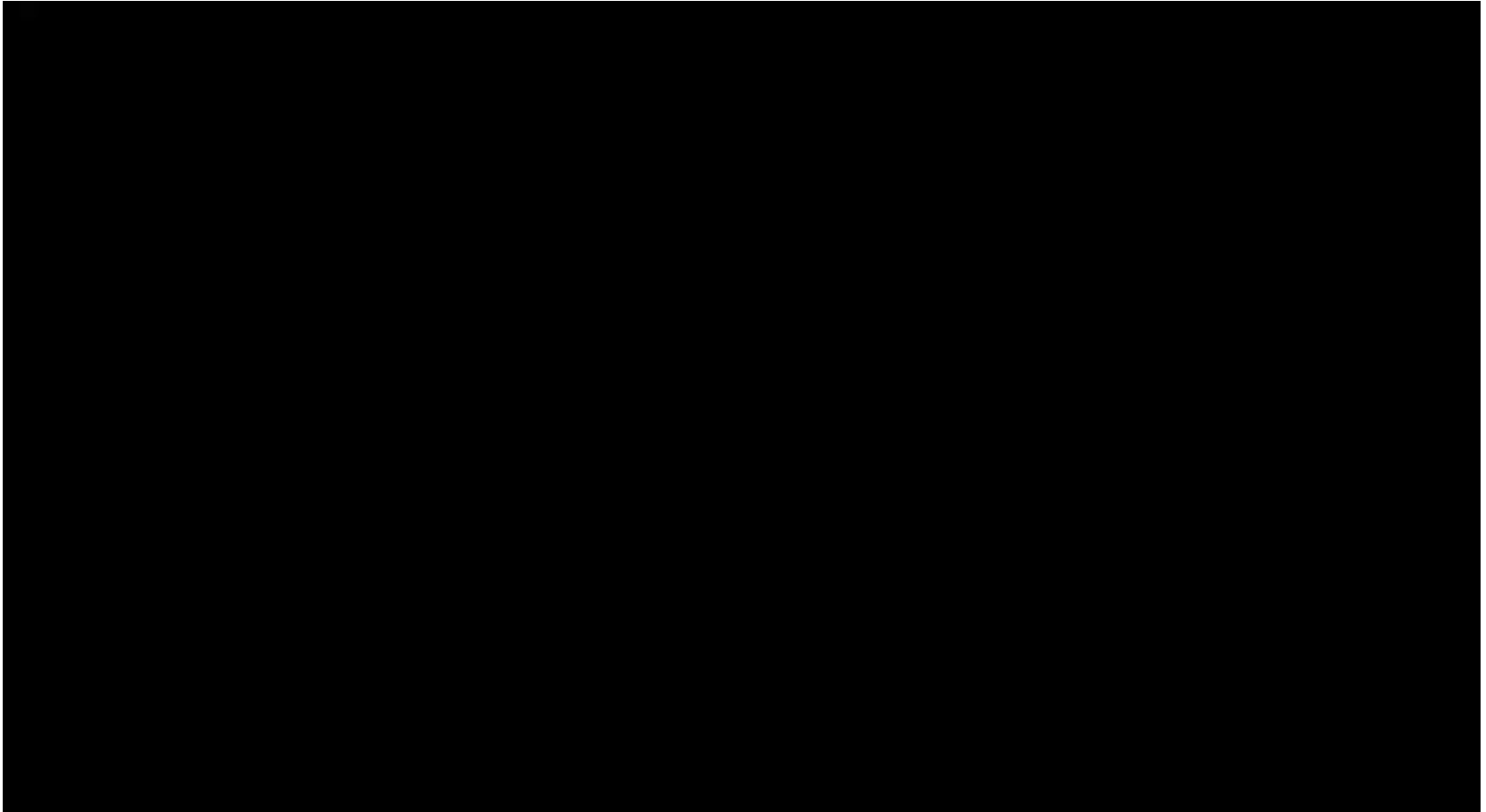


LCE Skin



Rotation and rolling

- Shear stress gradients through the thickness



Making waves in a photoactive polymer film

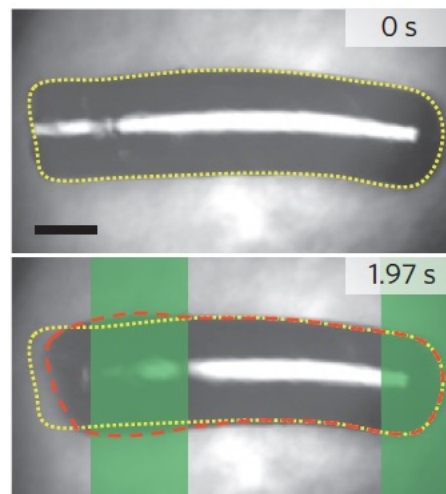
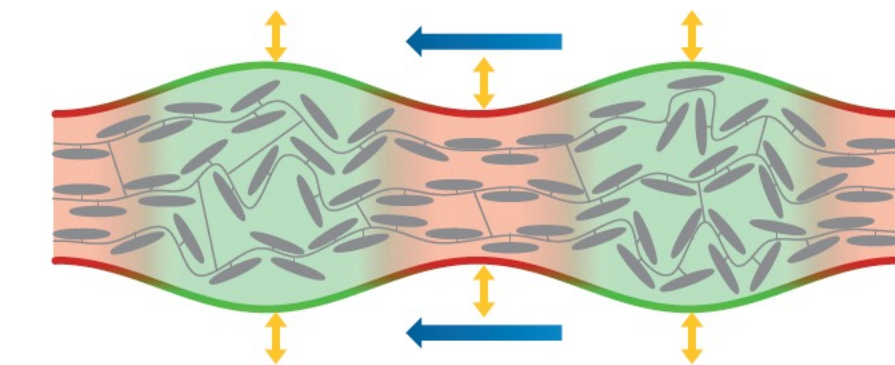
- continuous, directional, macroscopic mechanical waves under constant light illumination



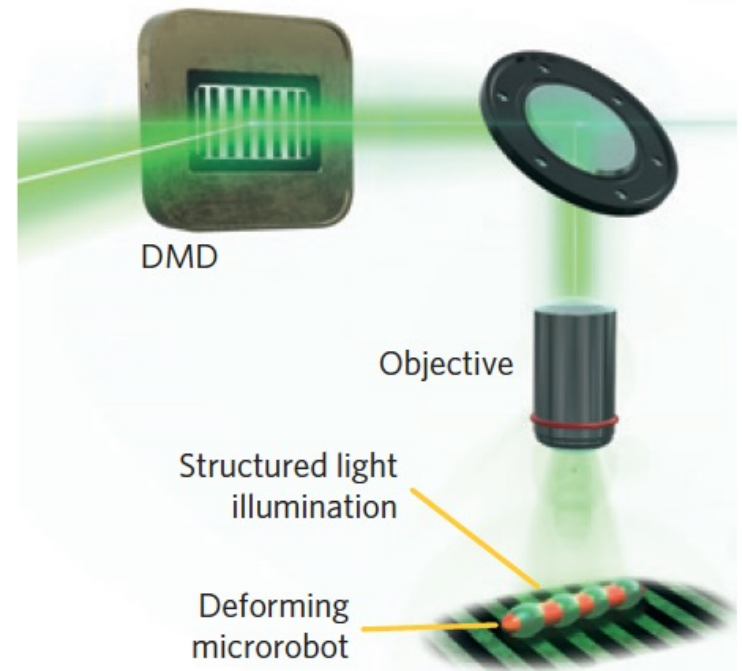
Planar side up

Biomimetic Swimming

- Generating of a travelling wave under periodic light pattern

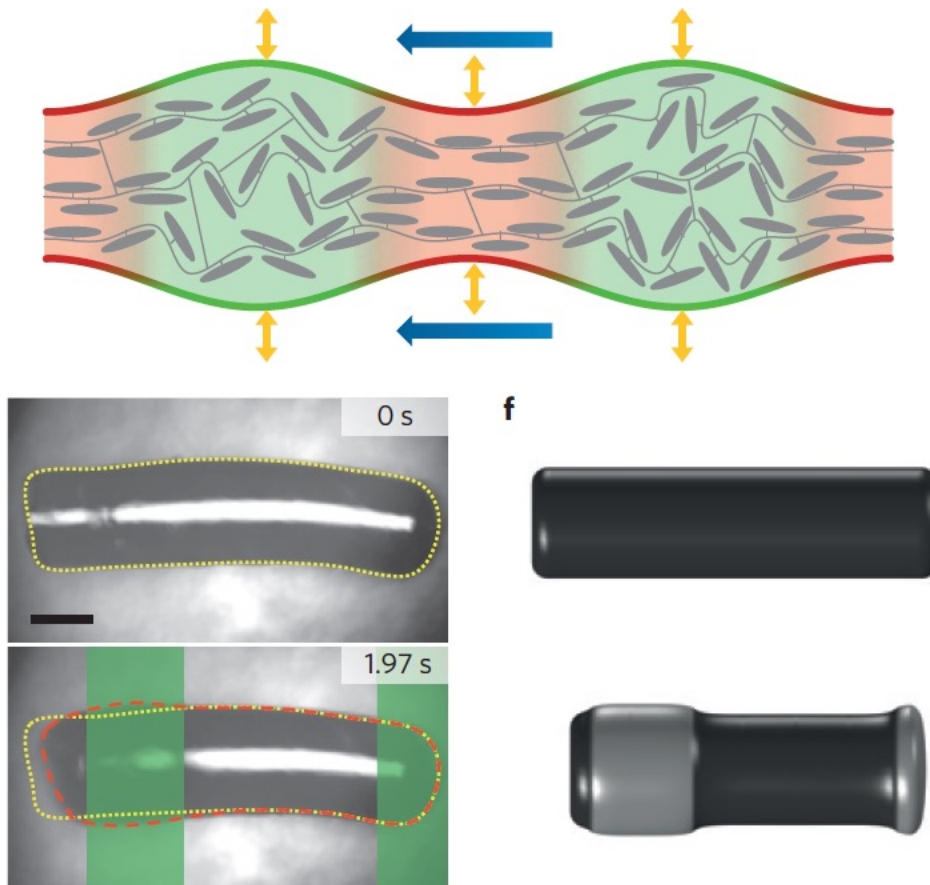


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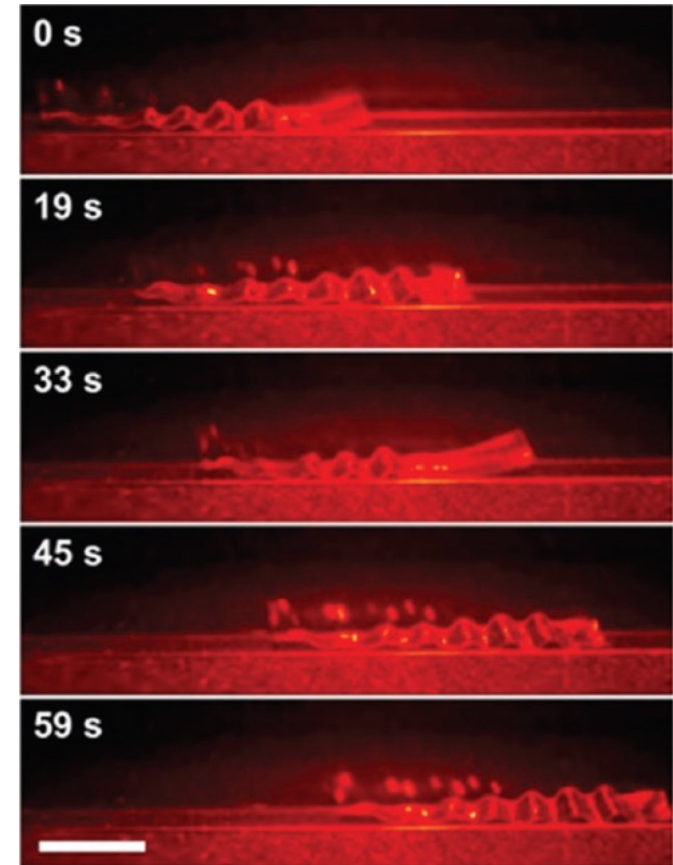
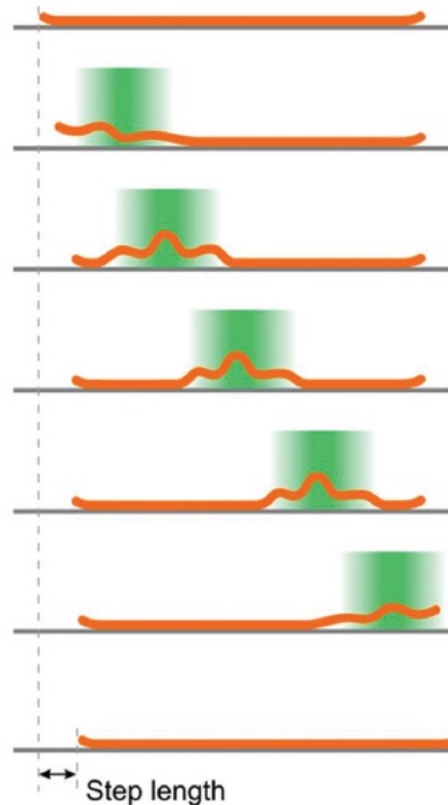
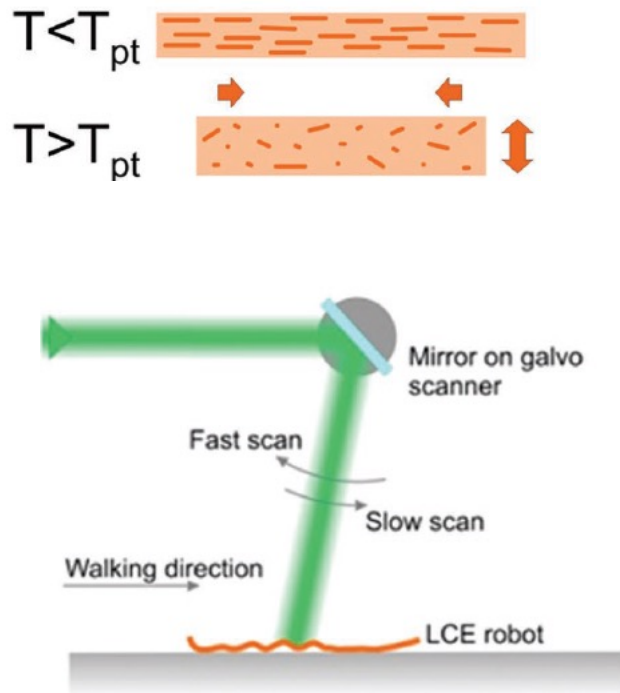
Biomimetic Swimming

- Generating of a travelling wave under periodic light pattern



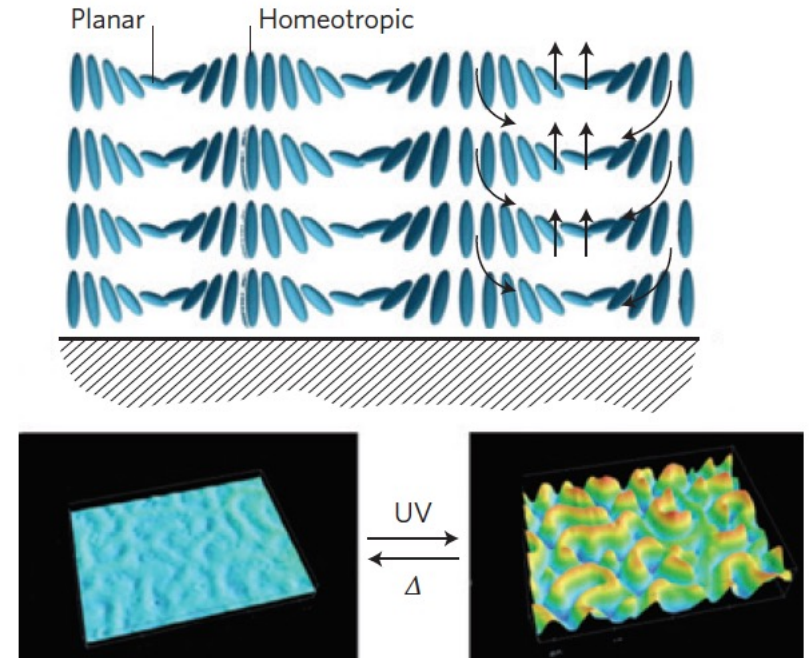
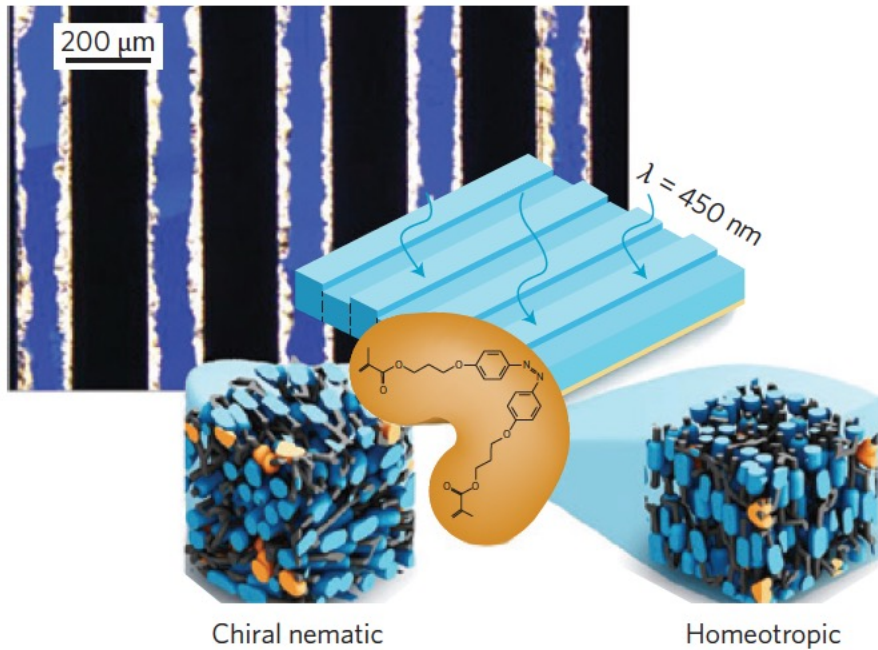
Biomimetic Crawling ([movie](#))

- Spatially modulated light field to trigger synchronized, time-dependent body deformations
- Scanning a laser beam

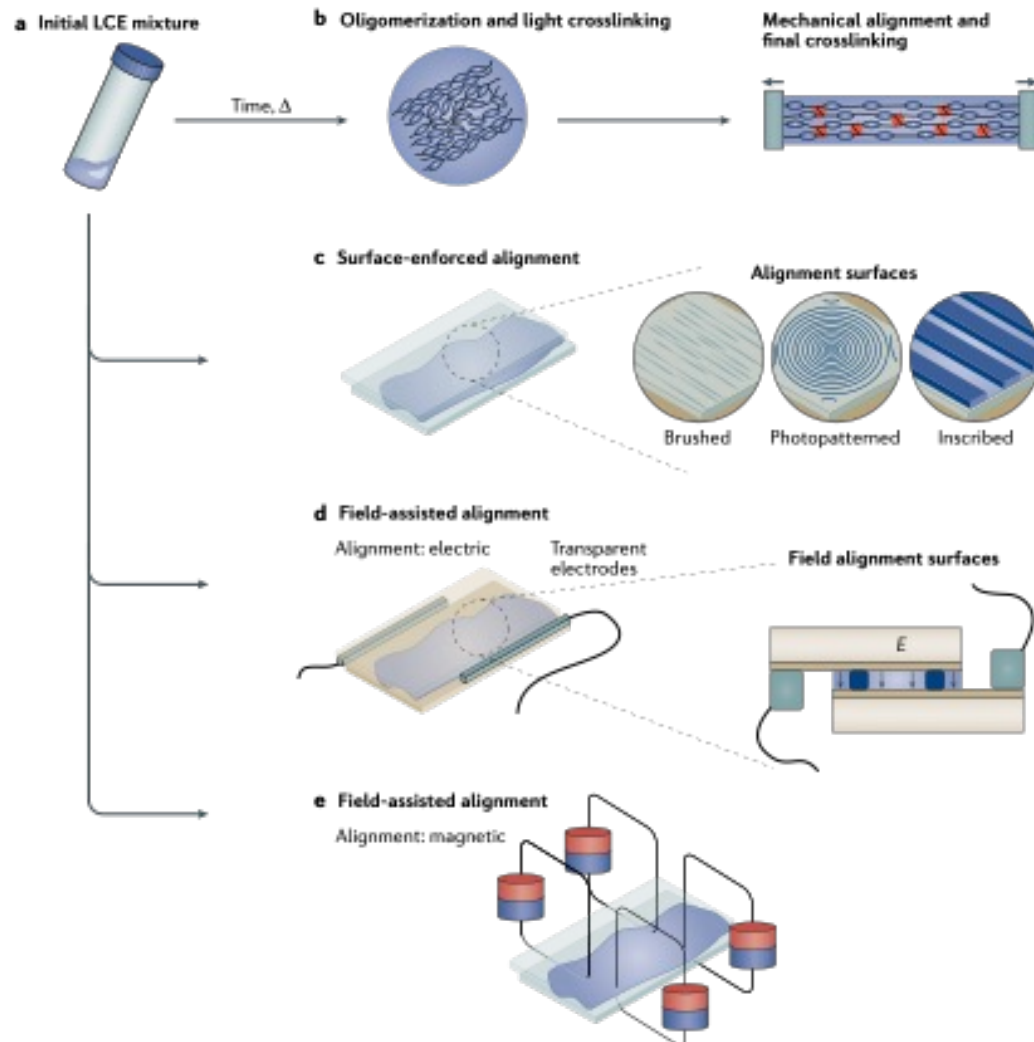


Programming local anisotropy

- Spatially complex shape changes or surface variations
- Electric, magnetic or photoalignment prior to polymerization
- Lock complex orientation in the polymer

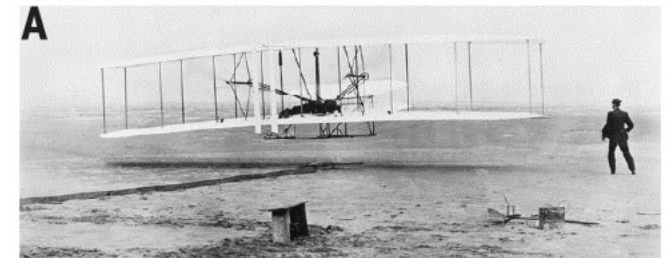
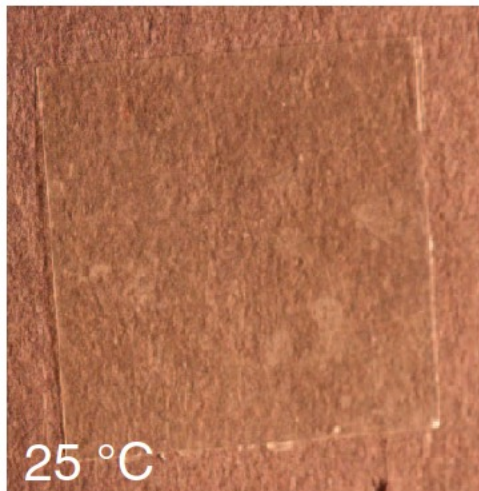


Programming local anisotropy



Voxels

- Complex director profiles within LCE
- Spatial control with high resolution
- Photoalignment surface

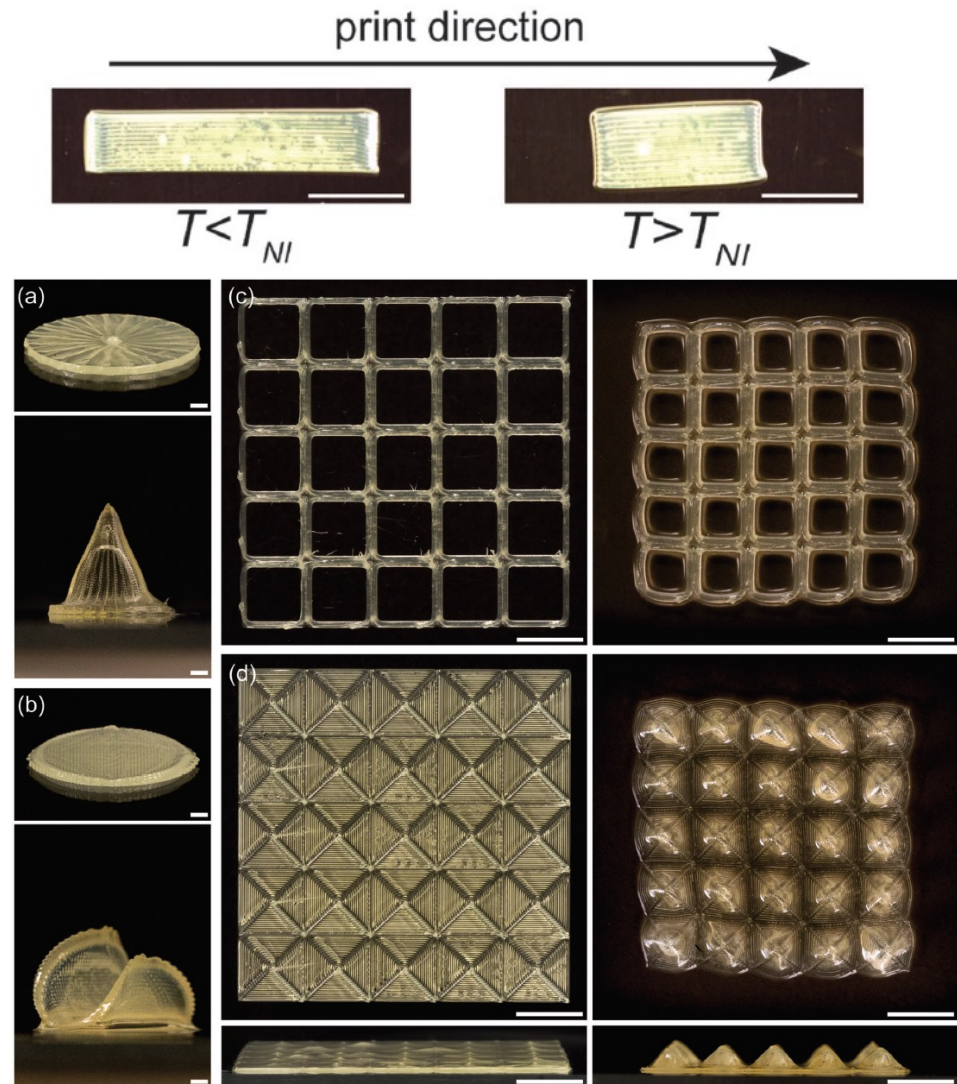
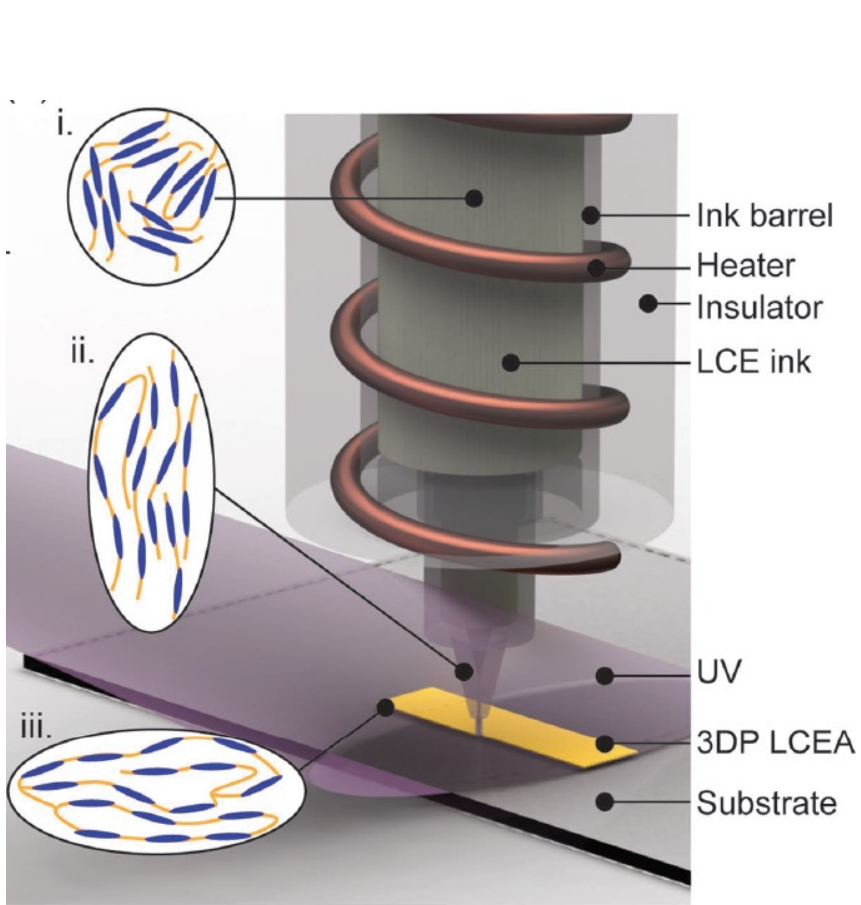


Image

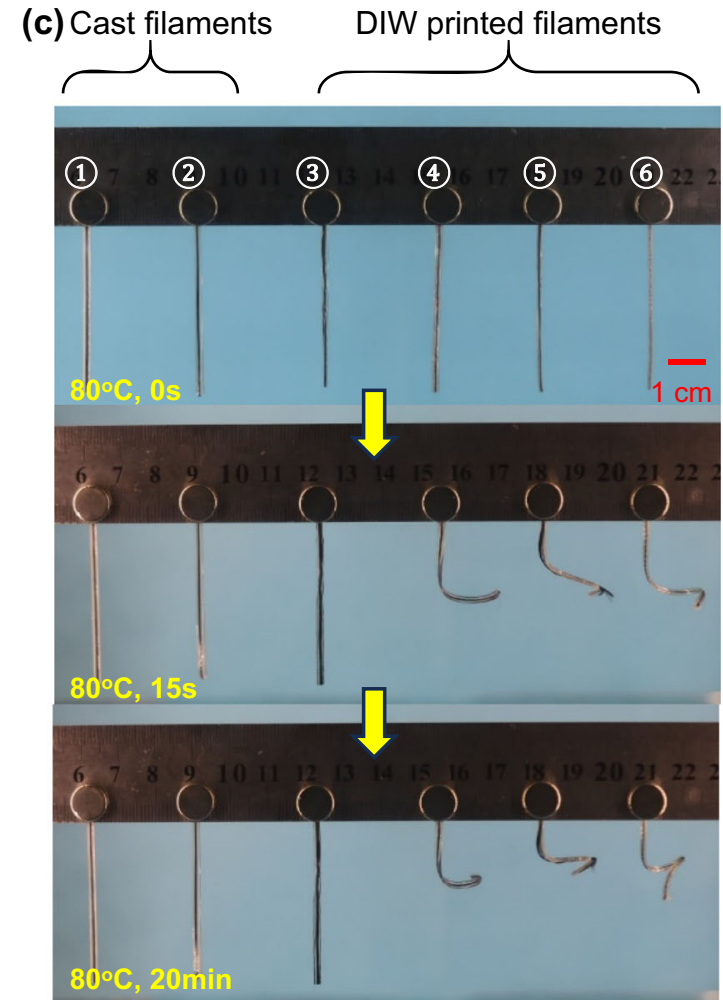
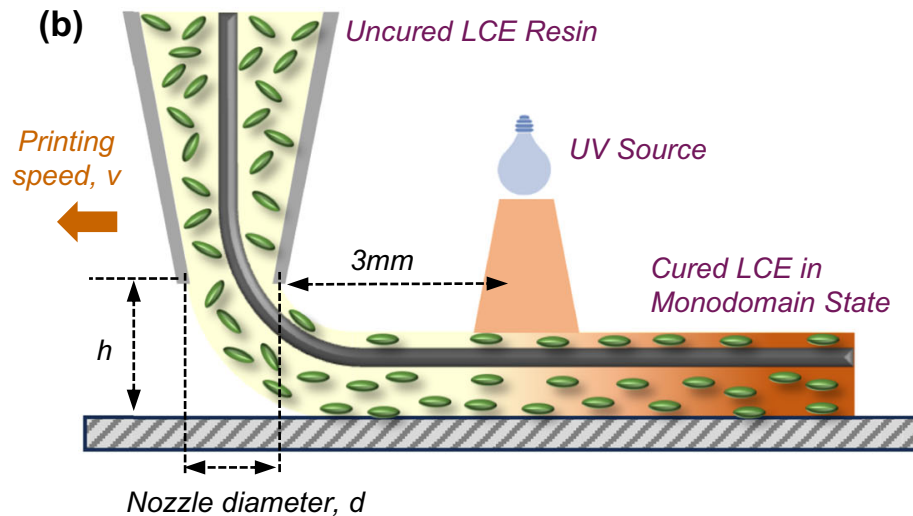
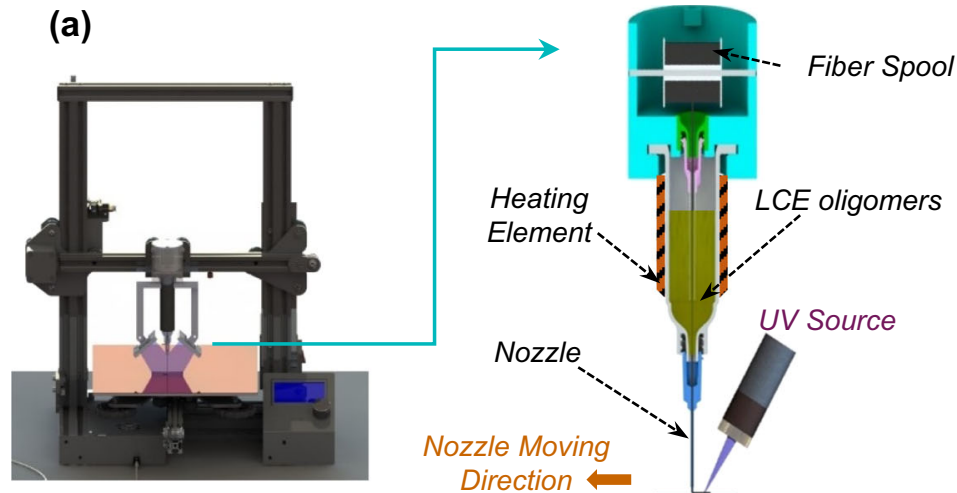


Liquid Crystal Elastomer

3D Printing LCE Actuators



3D Printing LCE Actuators



3D Printing LCE Actuators



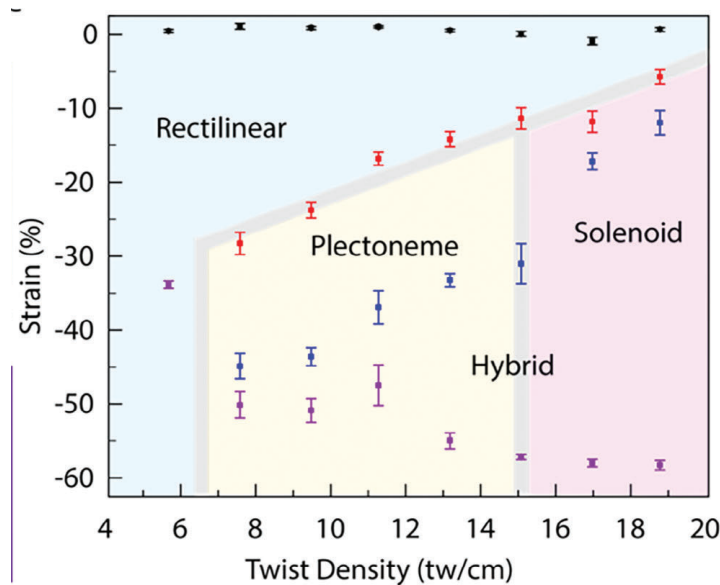
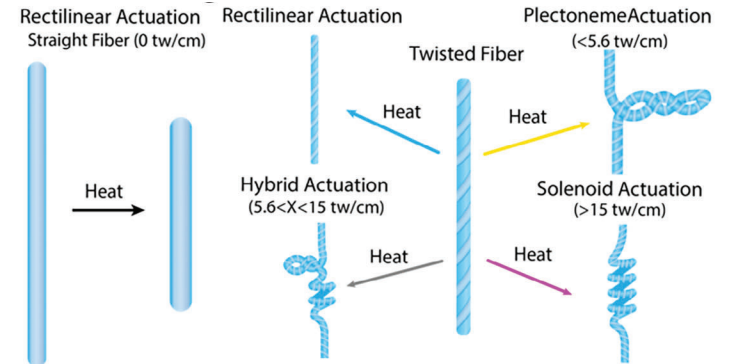
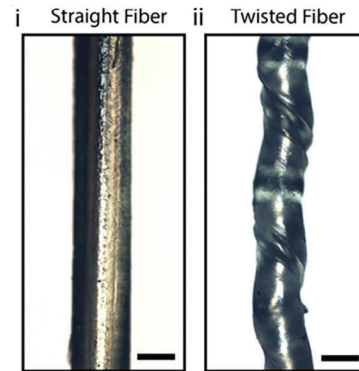
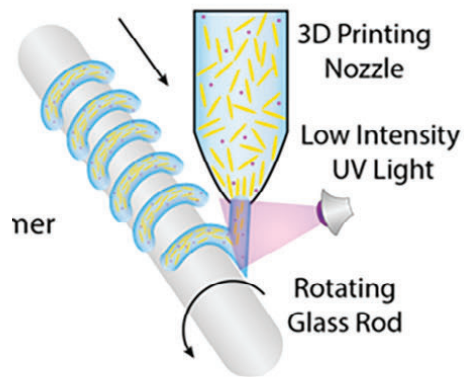
3D Printing LCE Actuators

3x

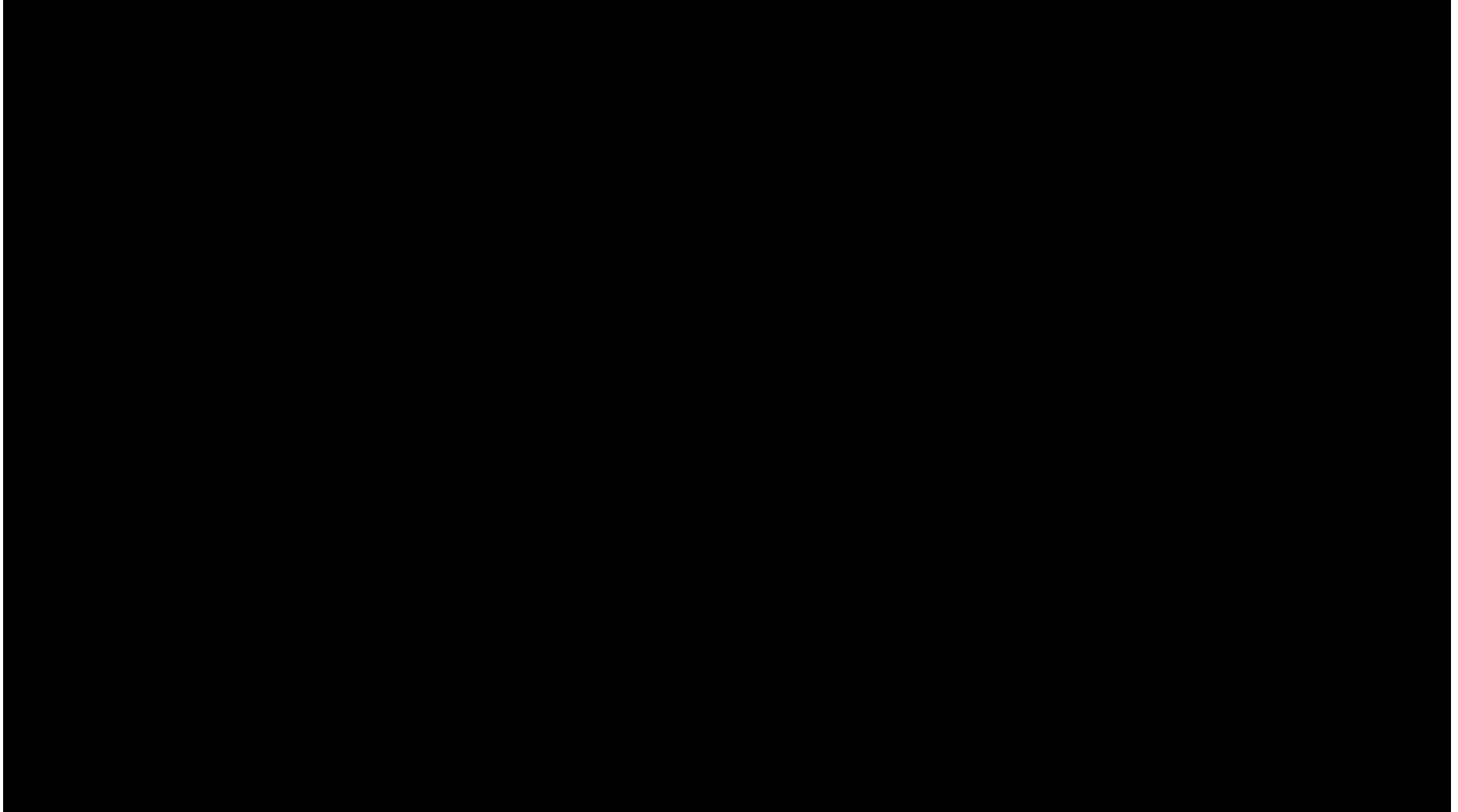
Electricity On



Twisted Liquid Crystal Elastomer Fibers

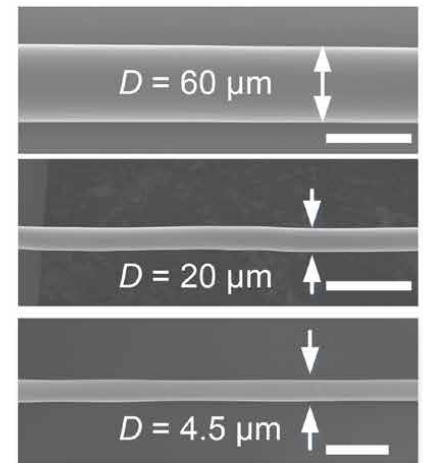
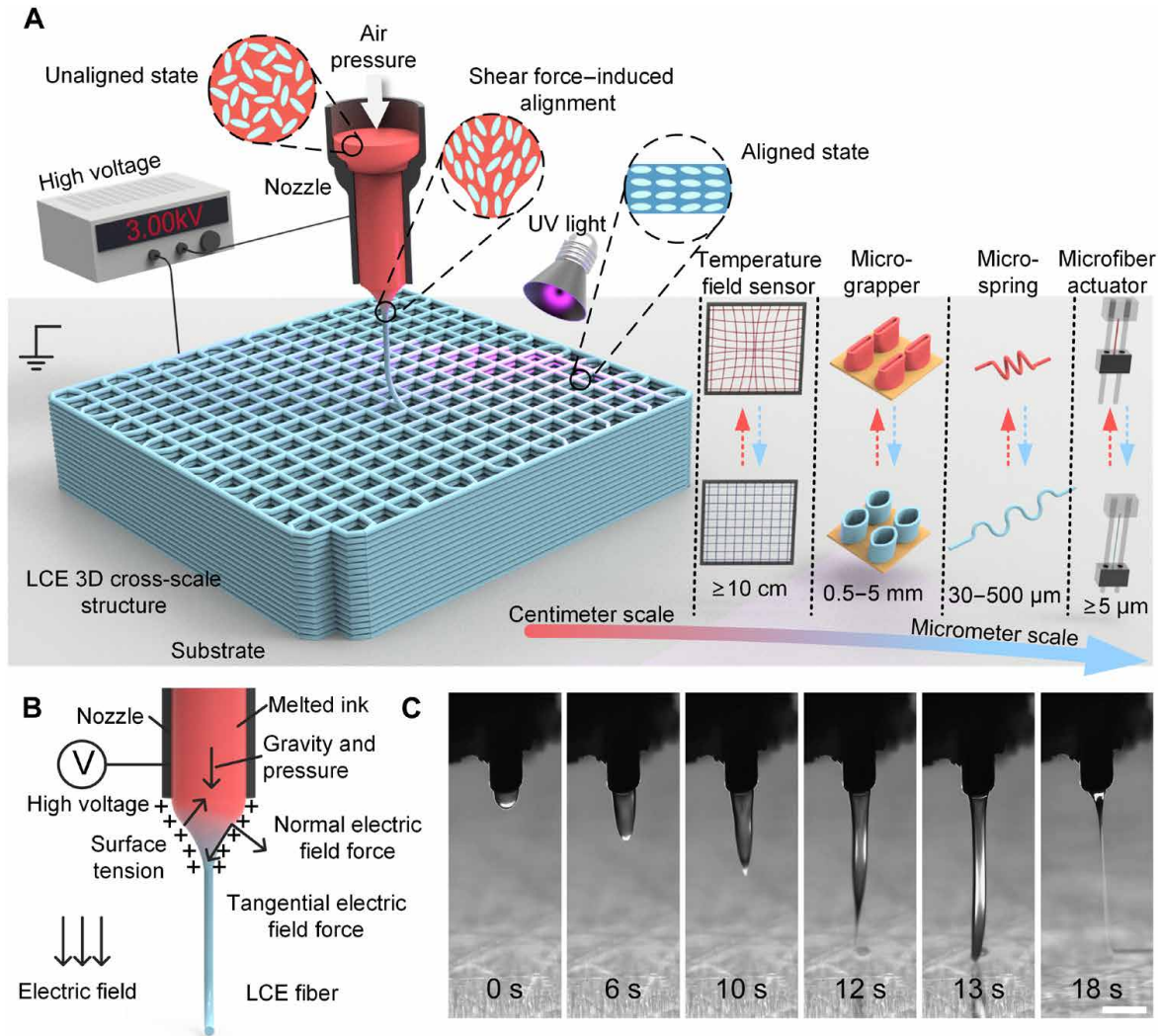


Twisted Liquid Crystal Elastomer Fibers



Twisted Liquid Crystal Elastomer Fibers

Melt electrowriting

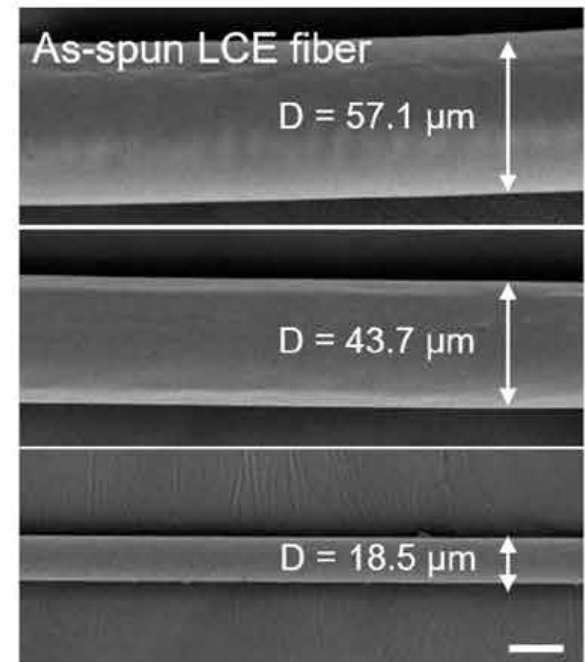
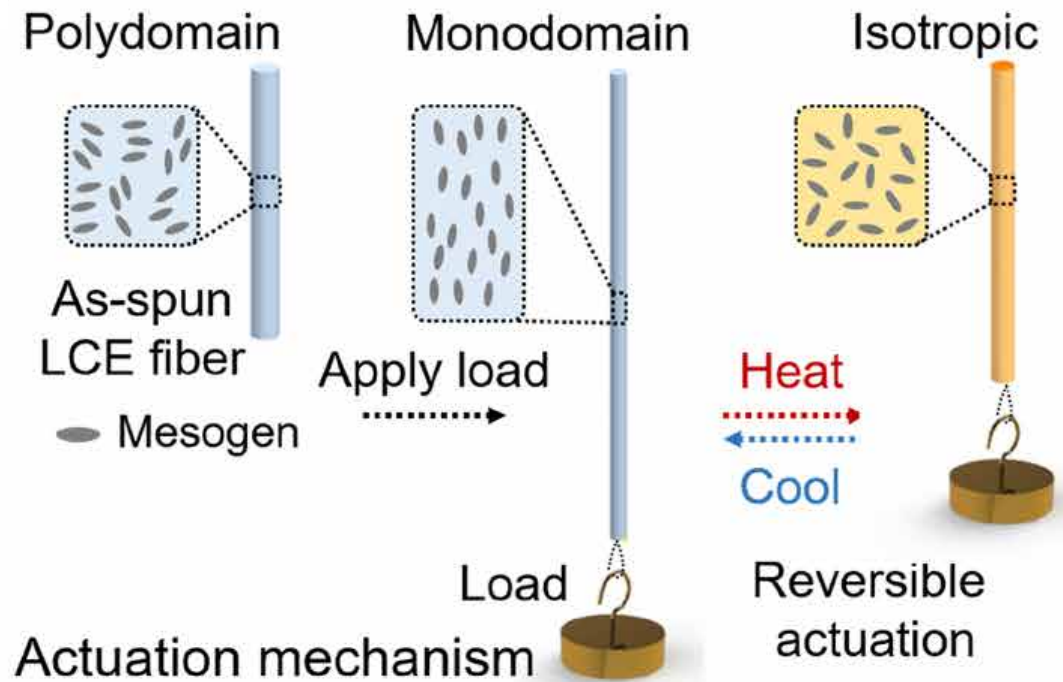


Melt electrowriting

- Melt electrowriting (MEW) is a polymer melt processing technique which involves formation of polymer fibres and their controlled deposition to create complex architectures following additive manufacturing
- A high voltage (up to 10 kV) applied across the nozzle-collector gap (0 – 10 mm) leads to the formation of a Taylor cone at the tip of the nozzle which forms into a stable polymer jet
- The electrical forces acting on the jet lead to its thinning as it travels from the nozzle to the collector and fibres in the range of 5 – 50 μm can be formed depending on the parameters used
- Once a stable jet is formed, the nozzle can be moved with respect to the collector at pre-defined speeds to deposit fibres in controlled and layer-by-layer manner

Electrospun LCE Microfiber Actuators

- Large actuation strain (60%), fast response ($< 0.2\text{s}$), and high power density (400 W/kg)
- Nematic isotropic phase transition of mesogens



Electrospun Liquid Crystal Elastomer Microfiber Actuator

Qiguang He¹⁾, Zhijian Wang¹⁾, Yang Wang²⁾, Zijun Wang²⁾, Chenghai Li¹⁾, Raja Annapooranan²⁾
Jian Zeng¹⁾, Renkun Chen¹⁾, Shengqiang Cai^{1, 2 *)}

¹ Department of Mechanical and Aerospace Engineering, University of California, San Diego

² Materials Science and Engineering Program, University of California, San Diego

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