# Preprogramming and Reprogramming Shape Morphing of Liquid Crystal Elastomer Membranes


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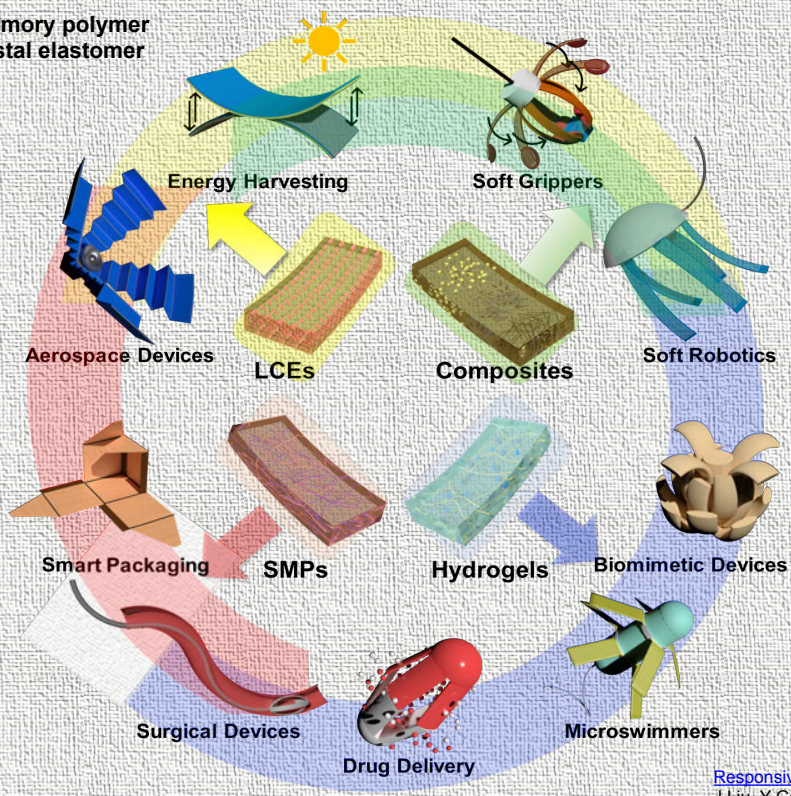
## Responsive and Foldable Soft Materials

SMP: shape memory polymer
LCE: liquid crystal elastomer

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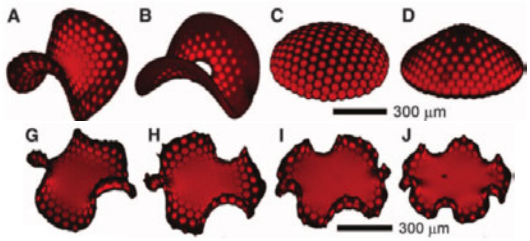
Responsive and Foldable Soft Materials
J Liu, Y Gao, YJ Lee, S Yang
Trends in Chemistry 2 (2), 107-122

# Examples of Shape Morphing Soft Material Systems

**Voxelated liquid crystal elastomers**

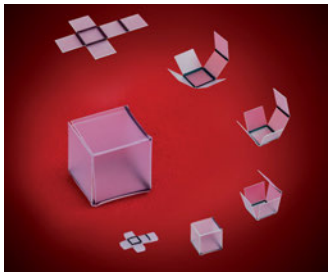
Ware, T. H., *et al. Science*, 2015, **347**, 982

**Thermoresponsive hydrogels with half-tone patterns**



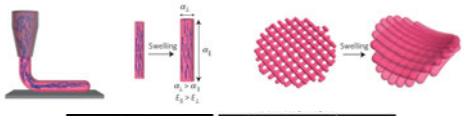

J. Kim, *et al.*, *Science*, 2012, **335**, 1201

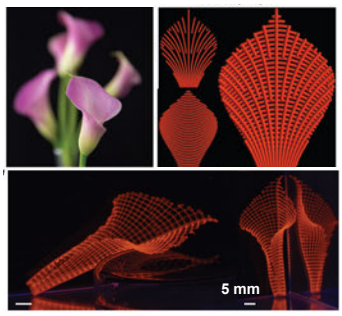
**Self-folding pre-strained polystyrene sheets**



Liu, Boyles, Genzer and Dickey, Soft Matter, 2012

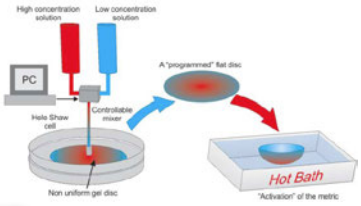
**4D Printed aligned hydrogels**

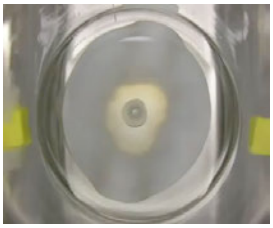





Sydney Gladman, A. *et al.* (2016) *Nat. Mater.* 15, 413

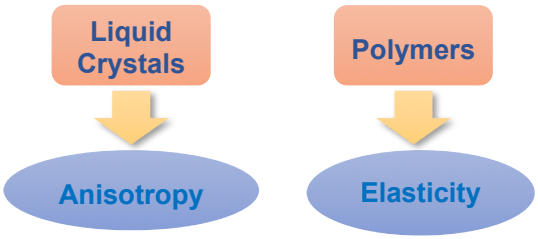
**Shaping Non-Euclidean hydrogel sheets with crosslinking gradient**

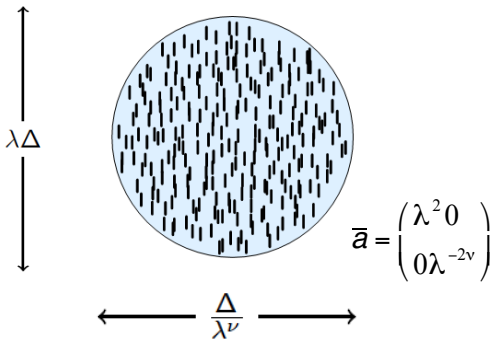


Yael Klein, *et al.*, *Science* **315**, 1116 (2007)

# Liquid Crystal Elastomers (LCEs)

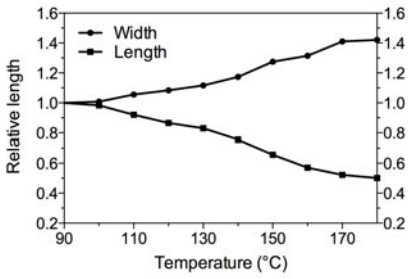



Warner M, Terentjev E M. Liquid Crystal Elastomers, Oxford Univ. Press, 2003; J. Mater. Chem., 2005,15, 2529

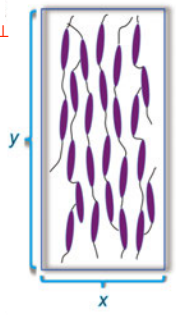
Hillel Aharoni

**Anisotropic stress/strain & reversible deformation**




$E_{\parallel} > E_{\perp}$

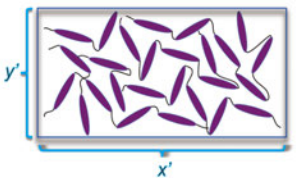
$\lambda_{\perp} > \lambda_{\parallel}$




**Actuated by heat, light, electric field…**

$T > T_{NI}$

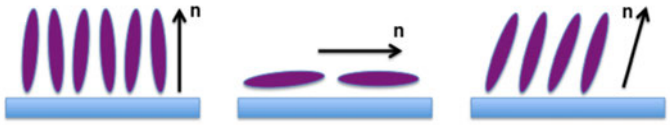
$T < T_{NI}$



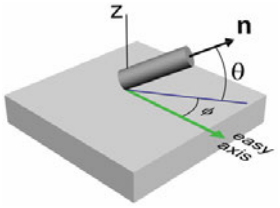

- Anisotropic strain: Up to 400%
- Reversible shape memory effect
- Load lifting 100-1000x of its own mass

# Surface Anchoring Effects

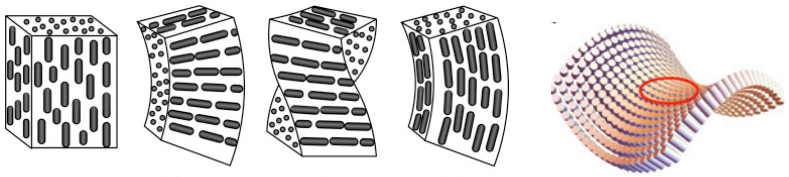
- **Surface Anchoring**




Homeotropic Planar Tilted




- **Elastic deformation**



Equilibrium Splay ($K_{11}$) Twist ($K_{22}$) Bend ($K_{33}$) Saddle-Splay ($K_{24}$)

**Frank-Oseen elastic energy**

$$F_V = \frac{1}{2}\int d^3r\{K_{11}(n\nabla\cdot n)^2 + K_{22}(n\cdot\nabla\times n)^2 + K_{33}[(n\cdot\nabla)n]^2 - K_{24}\nabla\cdot[n\times(\nabla\times n)+[(n(\nabla\cdot n)]\}$$

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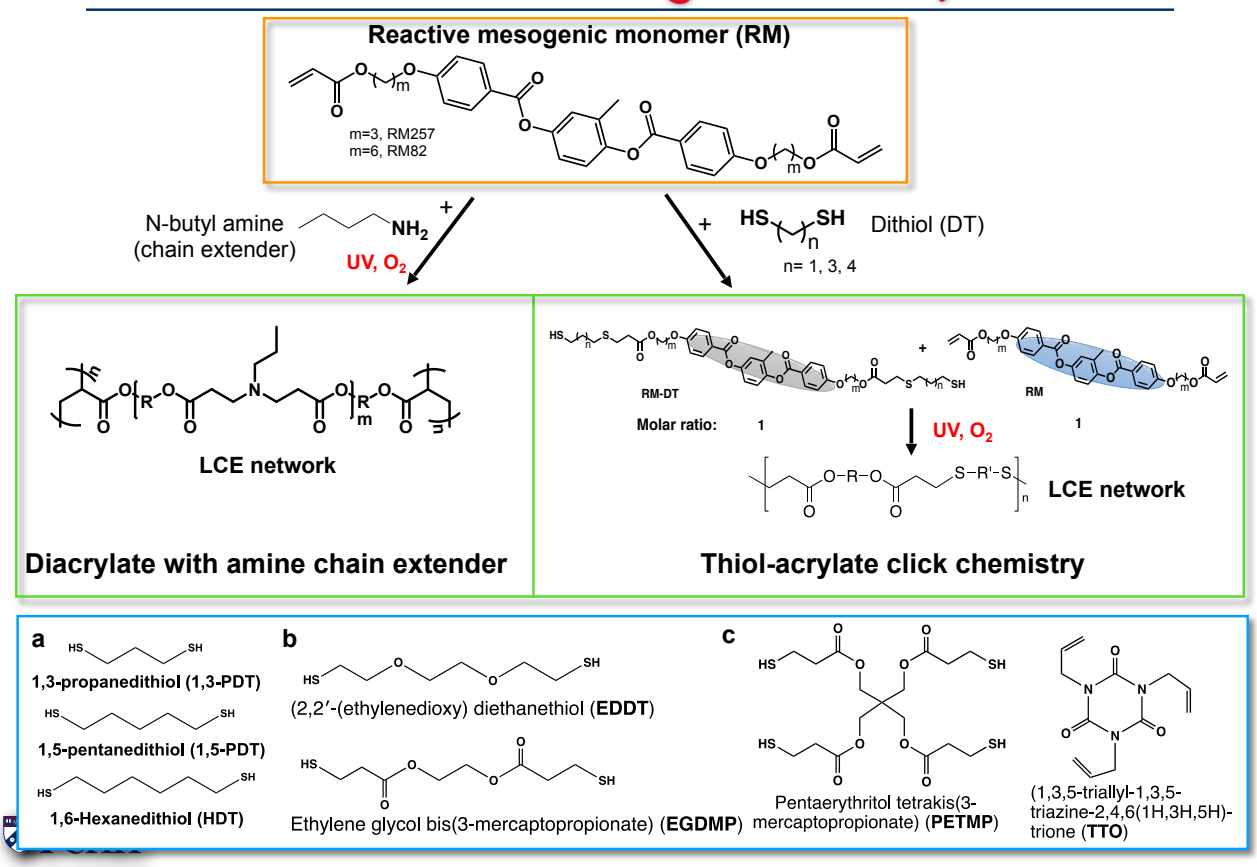
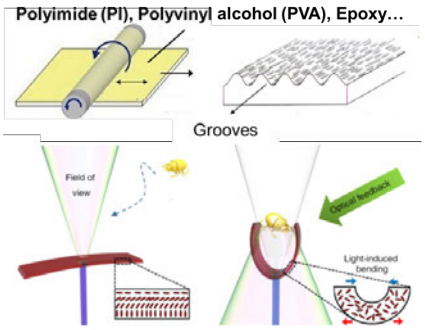
# LCE Crosslinking Chemistry



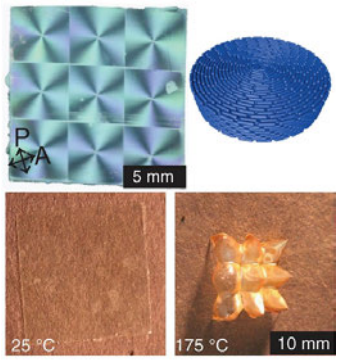
# Control of LC Alignment and LCE Actuation

- **Rubbing**



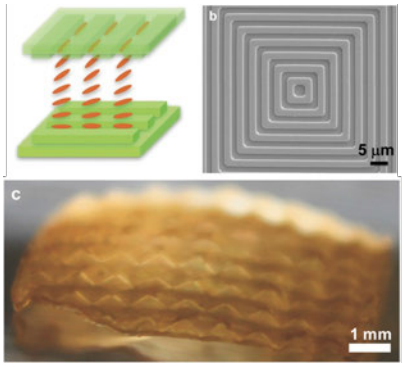

O.M.Wani, et al. *Nat. Commn.*, **2017**, *8:*15546.

- **Photoalignment**



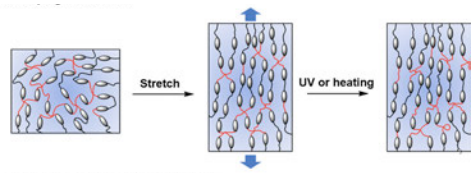

T. H. Ware, et al. *Science,* **2015**, 347, 982.

- **Microchannels**



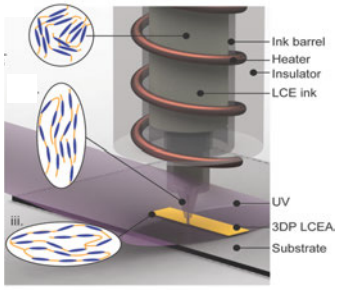

Y.Xia, et al. *Adv. Mater,* **2016**, *28*, 9637.

- **Mechanical stretching**

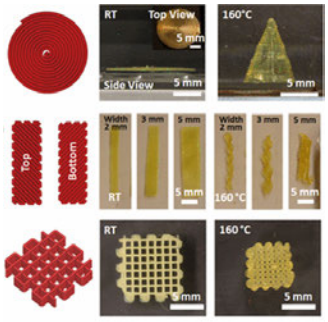



Wang et al. *ACS Appl. Mater. Interfaces* 2017, 9, 38, 33119

- **3D Printing**

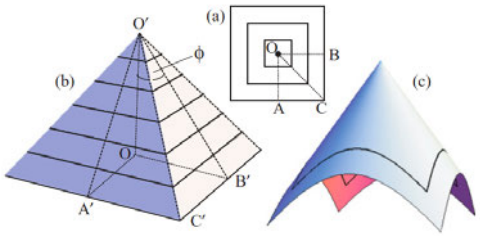



A. Kotikian, et al. *Adv. Mater,* **2018**, *1706164*

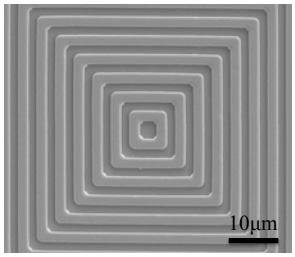



C.P.Ambulo, et al. *ACS Appl.Mater.Interfaces,* **2017**, 9, 37332.

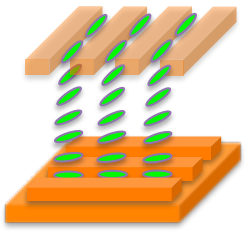
# Programmed Actuation in Liquid Crystal Elastomers



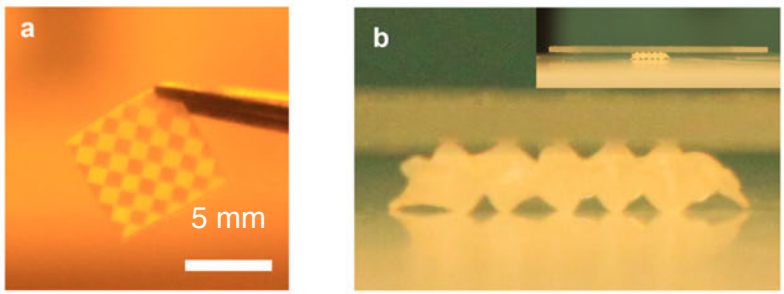

Modes, C. D. and Warner, M, **P***hys. Rev E* 2011, **84,** 021711




Epoxy pattern
(line width 2μm, spacing 2μm, depth 1.5-1.6μm)



Twisted cell

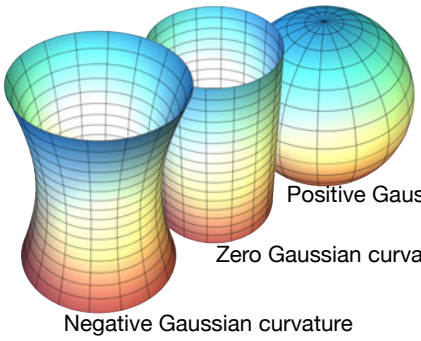



**Unusual weight lifting capacity:**
up to **734 x** its own weight by ~ 1mm vertically (stroke ~1000%)

**Work capacity**: **2.36J/kg**, or **~ 370 W/kg/m²**

Yu Xia, et al., SY, Adv. Mater. 2016, 28 (43), 9637

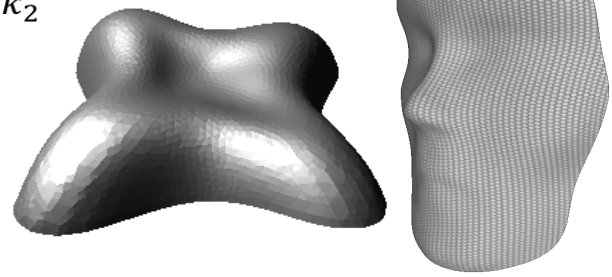
# Inverse Design of an Arbitrary 3D Shape




**Principal Curvatures, $\kappa_1$ and $\kappa_2$**

**Gaussian Curvature**

$$\kappa = \kappa_1 \kappa_2$$



- **General design problem:** Need to search for director field coordinates
- **Taking the design to practice:**
  - Accurately and faithfully imprint the design onto a thin LCE sheet
    - Top-down fabrication of micro-channels with strong surface anchoring
    - Nematic phase should be stable
    - Photochemistry needs to be efficient to lock the LC director field
  - Control over additional degrees of freedom
    - There are many possible isometric embeddings in space
    - The system might be stuck in a non-isometry or undesired configuration.

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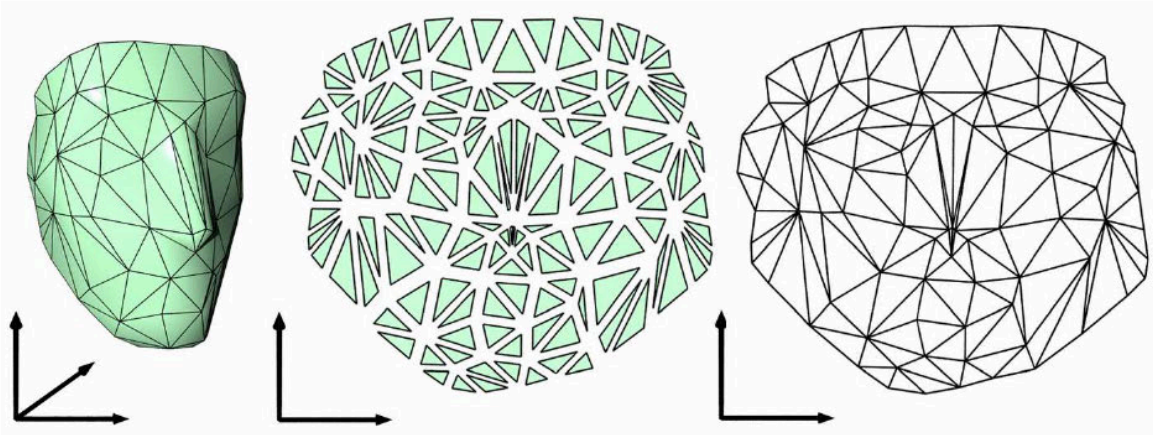
# A Local/Global Approach to Mesh Parameterization

**Original 3D mesh** **flattened triangles** **2D parameterization**



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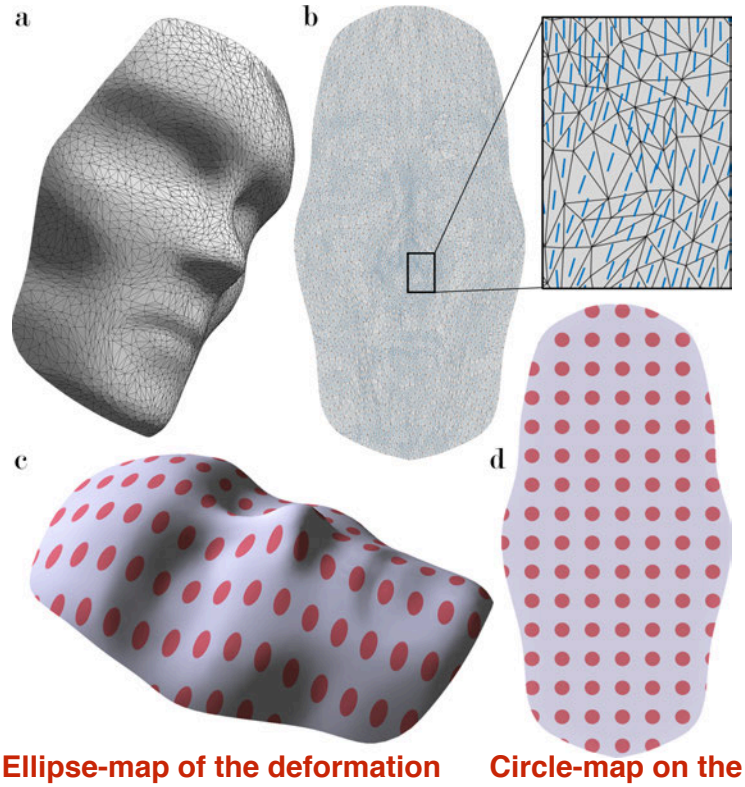
L. Liu, L. Zhang, Y. Xu, C. Gotsman, S. J. Gortler, Computer Graphics Forum, 27, 1495 (2008).

# Reserve Engineering of General Shapes

Input a 3D shape (face)

Numerical calculation of the 2D coordinates

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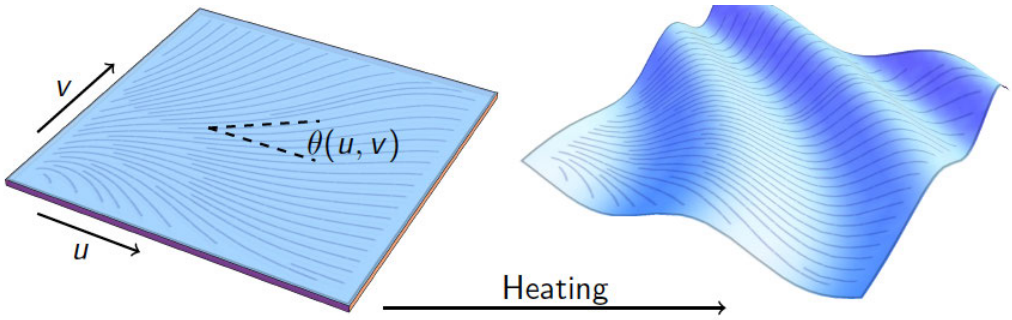
Ellipse-map of the deformation

Circle-map on the 2D film

# Search for Director Field Coordinates




assuming constant principal strains across the film

**Varying director field coordinates** $\theta(u,v)$

$$\bar{a}(u,v) = R[\theta(u,v)] \begin{pmatrix} \lambda^2 0 \\ 0 \lambda^{-2\nu} \end{pmatrix} R[\theta(u,v)]^T$$

Reference Gaussian Curvature:

$$\bar{K}_{\bar{a}} = (\lambda^{2\nu} - \lambda^{-2}) \left[ \left( [\theta_v^2 - \theta_u^2 - \theta_{uv}] \cos 2\theta + \left[ 2\theta_u \theta_v + \frac{\theta_{vv} - \theta_{uu}}{2} \right] \sin 2\theta \right) \right]$$

Hillel Aharoni, Sharon and Kupferman 2014.

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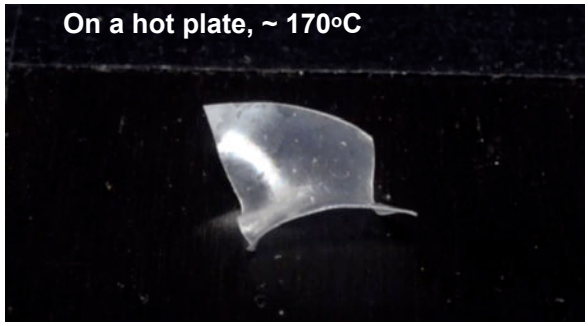
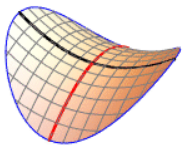
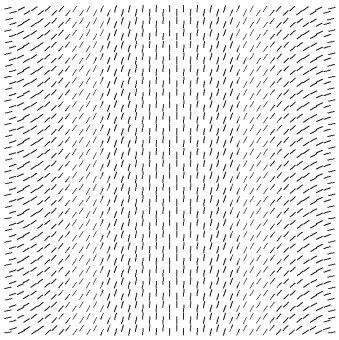
# Achieving Simple Gaussian Curvatures

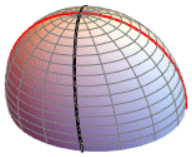
## Negative Curvature

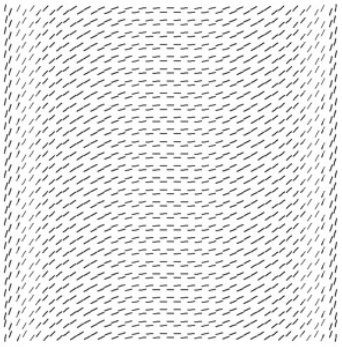




## Positive Curvature





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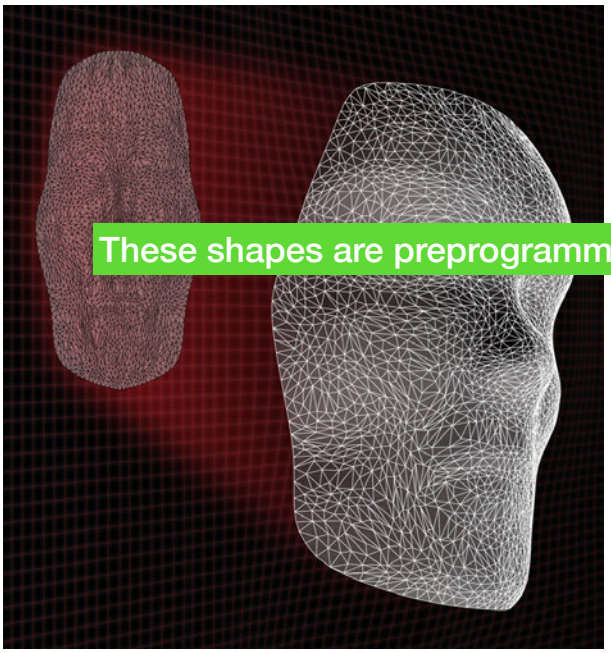
Yu Xia, Xinyue Zhang, Hillel Aharoni, Randall Kamien, SY, PNAS 2018, 115 (28) 7206

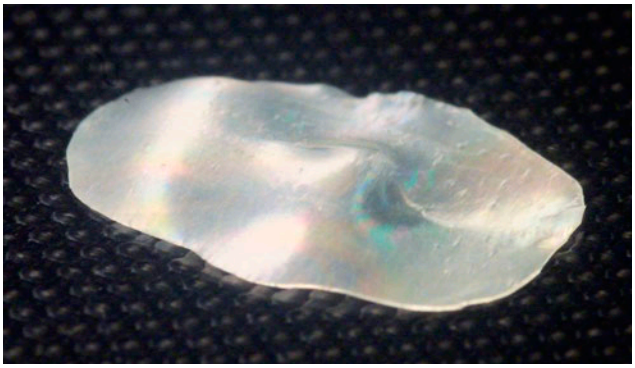
# Combination of Gaussian Curvatures

**Leaf: combination of negative curvatures**



These shapes are preprogrammed, reversible, NOT reprogrammable

**Face: positive + negative + zero curvatures**



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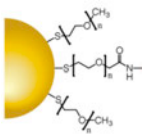
Yu Xia, Xinyue Zhang, Hillel Aharoni, Randall Kamien, SY, PNAS 2018, 115 (28) 7206

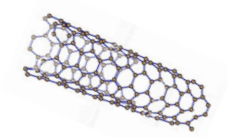
# Fascinating 1D and 2D, Anisotropic Nanomaterials

**The offer**

- High mechanical strength
- High thermal and electrical conductivity
- Photothermal, electrothermal responsiveness



**0D metallic nanoparticles; photothermally responsive**

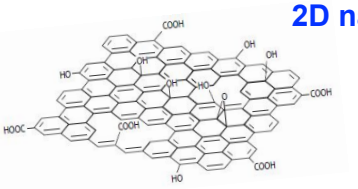


**1D nanorods, tubes**

**Carbon nanotubes (CNTs)**
E ≈60 GPa for multi-walled CNTs

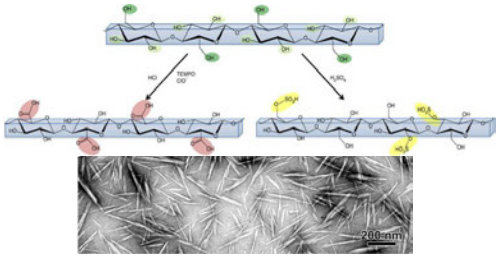
**Au nanorods**
Photothermally responsive

**2D nanosheets**



**Graphene**
E ≈130 GPa

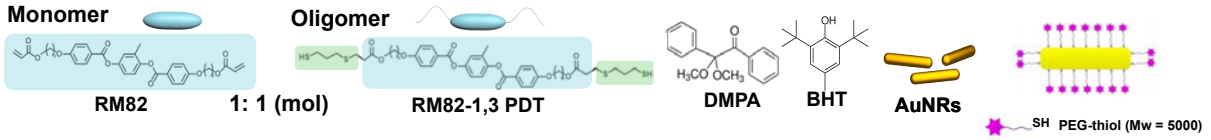
**Cellulose Nanocrystals (CNCs)**
Biobased, abundant

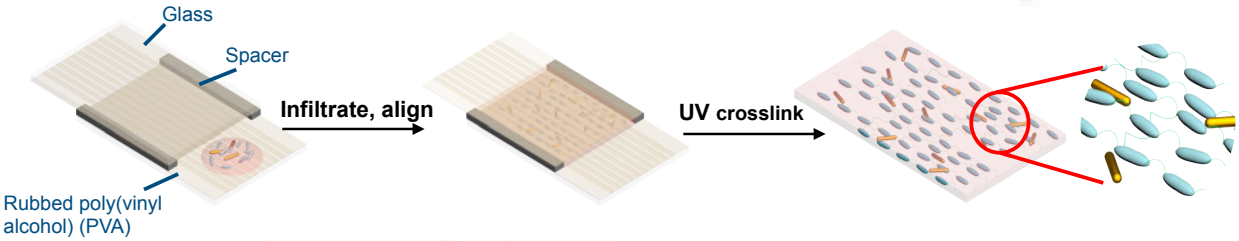


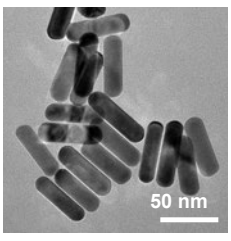
Y. Habibi, et al. J. Mater. Chem. 18 (2008) 5002.

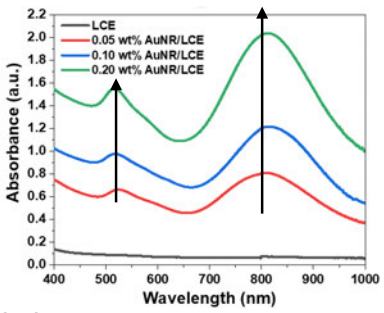
- **Graphene and CNCs are lyotropic (conc. dependent) liquid crystals that can be pre-aligned in solutions**

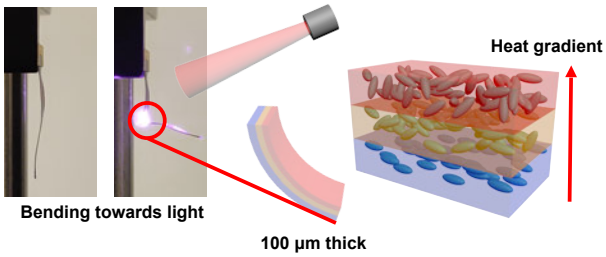
# Near-IR Responsive LCE/Au Nanorods (AuNRs)



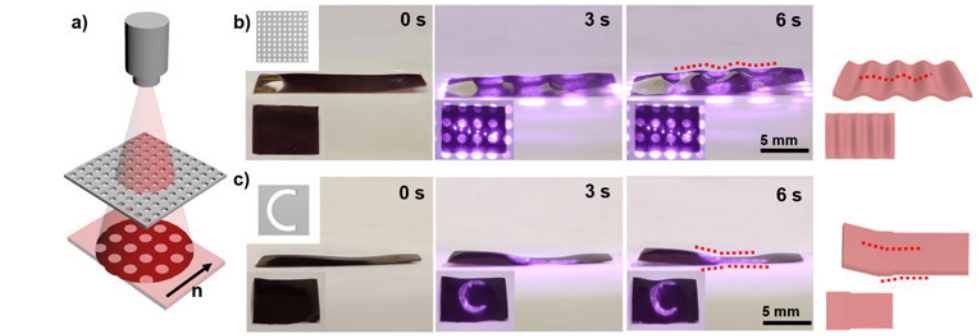




**L = 52.3 nm and d = 15.1 nm**

**Repeated actuation > 50 times**

Wang, Yuchen; Dang, Alei; Zhang, Zhifeng; Yin, Rui; Gao, Yuchong; Feng, Liang and Yang, Shu*, *Adv. Mater.* **2020**, 202004270

# LCE/AuNR Film is Reprogrammable



- Shapes can be reprogrammed indefinitely using photomasks on the same film
  - No need to pre-program the alignment of the LCEs.
  - More complex actuation can be realized by light modulator.

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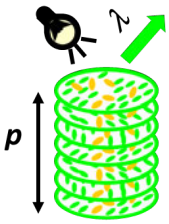
Wang, Yuchen; Dang, Alei; Zhang, Zhifeng; Yin, Rui; Gao, Yuchong; Feng, Liang and Yang, Shu*, *Adv. Mater.* **2020**, 202004270

# Chiral Nematic (or Cholesteric) Liquid Crystals (CLCs)




**helical rotation of birefringence makes structural colors**

$\lambda = npsin\theta$ $\lambda_o = (n_o + n_e)P/2$

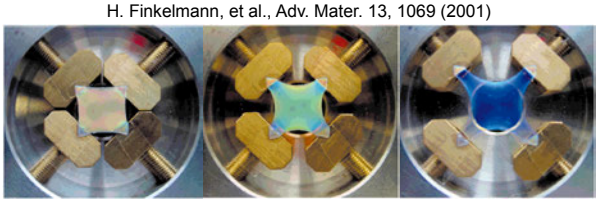
***n:*** average refractive index

***p:*** helical pitch

θ: reflection angle with respect to surface

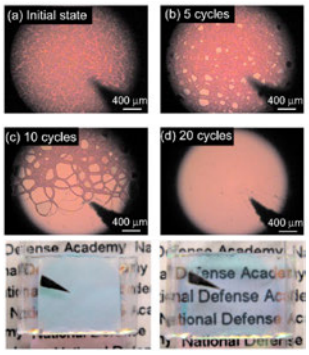
**Stretchable side-chain CLCEs**

H. Finkelmann, et al., Adv. Mater. 13, 1069 (2001)



**a large monodomain formed in small molecule LCs**

R. Ozaki, et al., Appl. Phys. Lett. 92, 163304 (2008)




- LC small molecules self-organize in a long-range order (good uniformity);
- It is not easy to create a uniform monodomain in LCEs
  - monomomers and oligomers are much more viscous to infiltrate into a LC cell
- For a broadband switch, a large strain is needed, but the film is limited by the geometric confinement
  - a minimum tensile strain of 75 % or a compressive strain of 42 % along the on-axis is necessary to switch between 400 and 700 nm

**It will be ideal to**

1) Create a uniform CLCE and
2) CLCE has large biaxial Poisson's ratios

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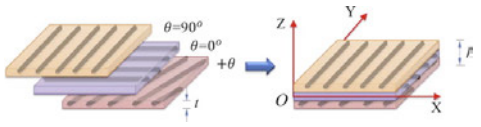
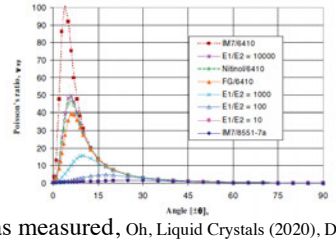
# Poisson's Ratio in Anisotropic Materials

**Isotropic material**

$0.2 < \nu < 0.5$ $\quad k_i = \frac{2\nu}{1-\nu} \le 2$

- Poisson's ratio ν(n,m) for anisotropic elastic materials can have no bounds.
  Ting, T. C. T. & Chen, T. *Q. J. Mech. Appl. Math.* **58**, 73 (2005).
- Poisson's ratio ν(n,m) for graphite /epoxy laminates > 1 & lay-up angle dependent, Peel, L. D. *Phys. status solidi* **244**, 988 (2007)



- Anisotropic poisson's ratio of azo-acrylate LCE was measured, Oh, Liquid Crystals (2020), DOI: 10.1080/02678292.2020.1790680

**a**) the ratios of transverse to longitudinal strains

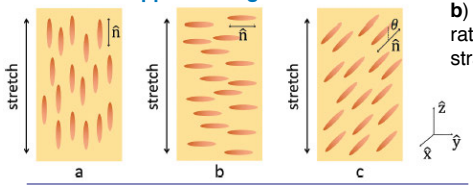
$$\nu_{31} = -\frac{\varepsilon_{xx}}{\varepsilon_{zz}}$$

$$\nu_{32} = -\frac{\varepsilon_{yy}}{\varepsilon_{zz}}$$

**For a transversely isotropic material:** due to uniaxial symmetry

$\nu_{31} = \nu_{32}$, $\nu_{23} = \nu_{13}$, $\nu_{12} = \nu_{21}$

**stresses are applied along the z direction**




| sample | molar ratio: acrylate/amine | molar ratio: 2Azo/total reactive agents | $T_g$ [°C] | S | Thickness [μm] |
|---|---|---|---|---|---|
| A | 1.1 | 1 | − 5.3 | 0.435 | 55 |
| B | 1.1 | 2 | 7.6 | 0.345 | 61 |
| C | 1.1 | 4 | 9.3 | 0.335 | 51 |

**b**) the ratio of two transverse strains and the ratio of one longitudinal and one transverse strain

$$\nu_{21} = -\frac{\varepsilon_{xx}}{\varepsilon_{zz}} \qquad -1 \le \nu_{21} \le 1$$

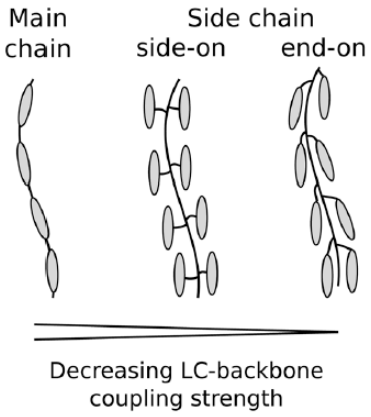
$$\nu_{23} = -\frac{\varepsilon_{yy}}{\varepsilon_{zz}}$$

$\nu_{ji} > 0.5$ with nearly conserved volume ($\nu_{ji} + \nu_{jk} \sim 1$) upon application of $\varepsilon_j$,

Table 2. Poisson's ratios of the three samples determined from tensile tests.

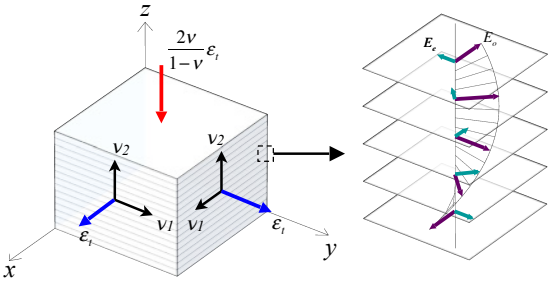
| Sample | $\nu_{32}$ | $\nu_{31}$ | $\nu_{21}$ | $\nu_{23}$ |
|---|---|---|---|---|
| A | 0.515 ± 0.012 | 0.496 ± 0.032 | 0.984 ± 0.048 | 0.111 ± 0.058 |
| B | 0.535 ± 0.011 | 0.480 ± 0.091 | 0.875 ± 0.020 | 0.147 ± 0.017 |
| C | 0.508 ± 0.019 | 0.518 ± 0.029 | 0.929 ± 0.034 | 0.118 ± 0.020 |

# Different Types of LC Polymers



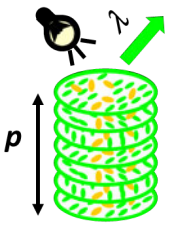

Mistry, D. *et al. Nat. Commun.* **9**, 5095 (2018)

MCLCE can be considered effectively isotropic in the transverse plane (*xy*-plane)




$$\varepsilon_z = -k_t(\varepsilon_x + \varepsilon_y) = -\frac{2\nu_2}{1-\nu_1}(\varepsilon_x + \varepsilon_y) = \Delta\lambda / \lambda_o$$

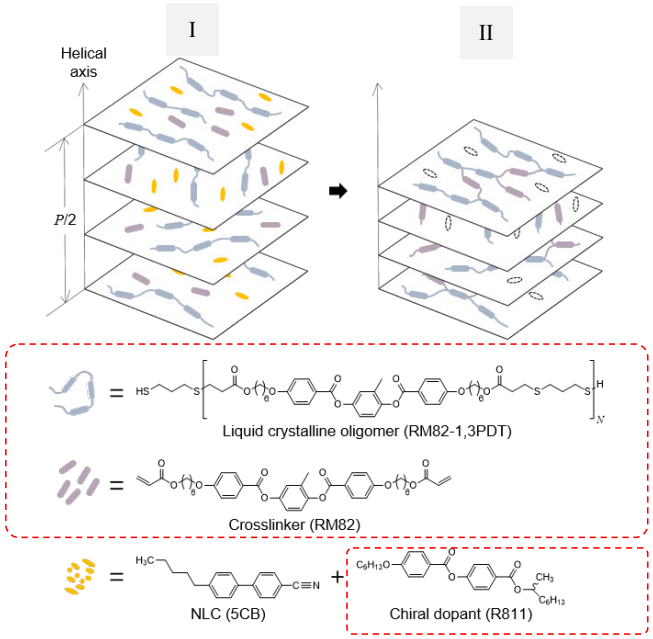
- Side-chain CLCEs have isotropic backbones
- Main-chain CLCEs (MCLCEs) could have a large elasticity anisotropy between the direction of the helix and the plane normal



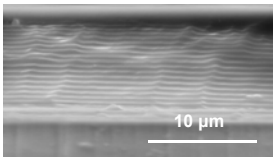

$$\lambda_o = (n_o + n_e)P/2$$

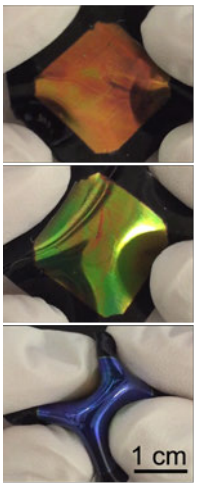
$n_o$ and $n_e$ are the ordinary and extraordinary refractive indices of LCs, respectively

# Fabrication of Main-chain CLCE (MCLCE) Membrane




**Large chiral monodomain & uniform color shift**



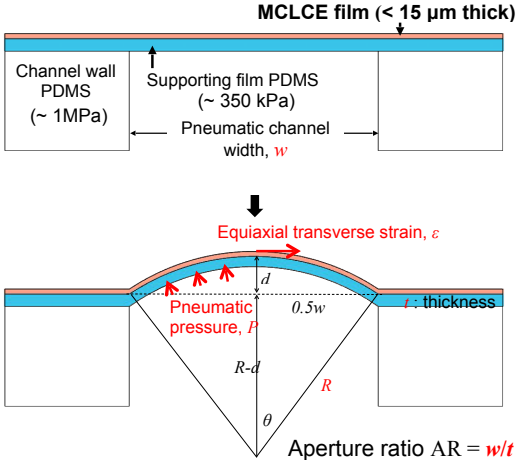

**I** *Phase stabilization of prepolymer of LCEs (PLCEs) in small molecular CLCs*
- Decrease of the viscosity and the working temperature
- Stable mono-domain chiral nematic phase

**II** *Deswelling of CLCEs after removal of the CLCs*

Se-Um Kim, Young-Joo Lee, et al. SY, submitted

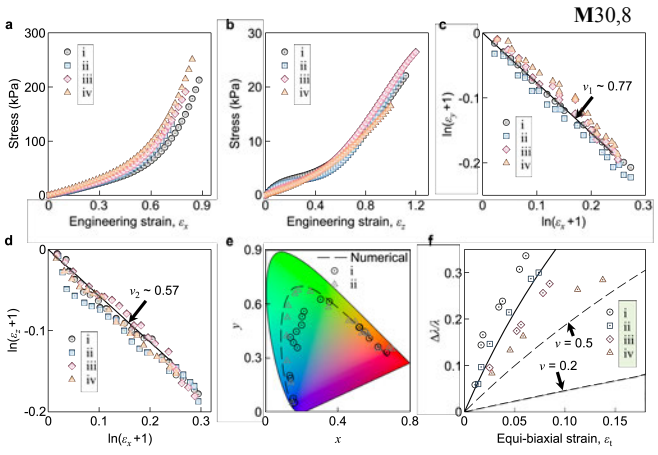
# Main-Chain Cholesteric LCE (MCLCE) Membranes: Elasticity Anisotropy

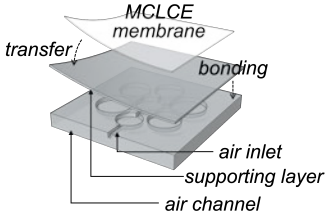
(Young's modulus $E_1$ ~ 94.3 kPa)
**MCLCE film (< 15 μm thick)**

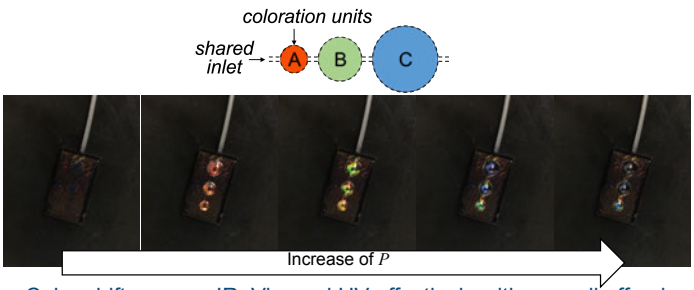



Aperture ratio AR = *w/t*

Se-Um Kim, Young-Joo Lee, et al. SY, submitted




Color shifts across IR, Vis. and UV effectively with a small off-axis strain due to the large Poisson's ratio

# Summary

- Using top-down fabricated 1D microchannels, we can guide the alignment of LC monomers or LCOs within the channels arbitrarily
  - **We than inverse designed to pre-program shape morphing of 2D membranes into different Gaussian Curvatures**
- By introducing photo thermally responsive inorganic nanofillers (e.g. Au nanorods) in LCE matrix, we demonstrate post-programming of shapes using photomasks
- Lastly, we fabricated highly deformable MCLCEs that have large biaxial Poisson's ratios (> 0.5) and demonstrate broadband switch in the visible wavelength with ~ 20% strain

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