SAND2018-11444C

Direct-write optical polarizers built from charge-transfer liquid crystals

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2. The Department of Chemistry and Biochemistry, Denison University, Granville, OH

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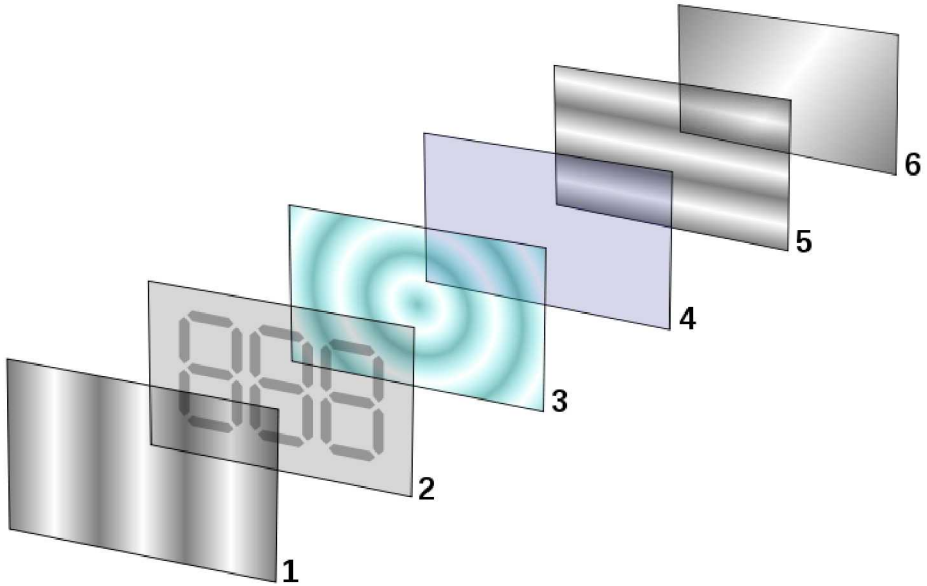
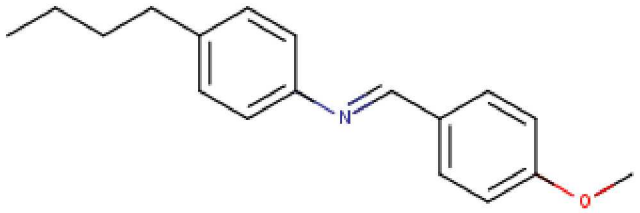
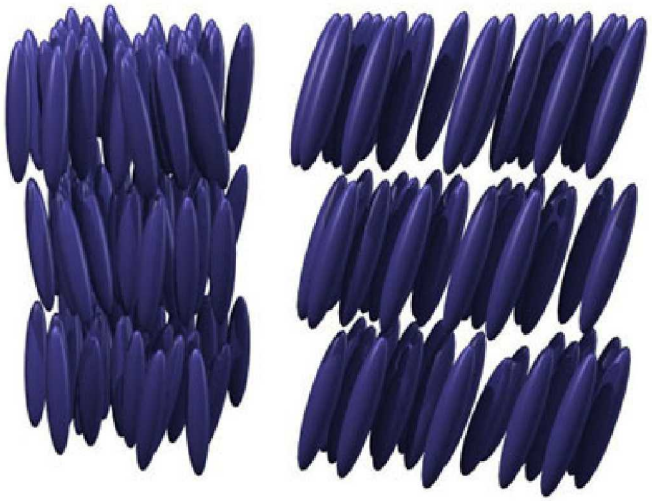
Liquid crystals are a ubiquitous optical technology





Chemical structure of N-(4-Methoxybenzylidene)-4-butylaniline (MBBA)



alignment in the smectic phases

Liquid crystal displays

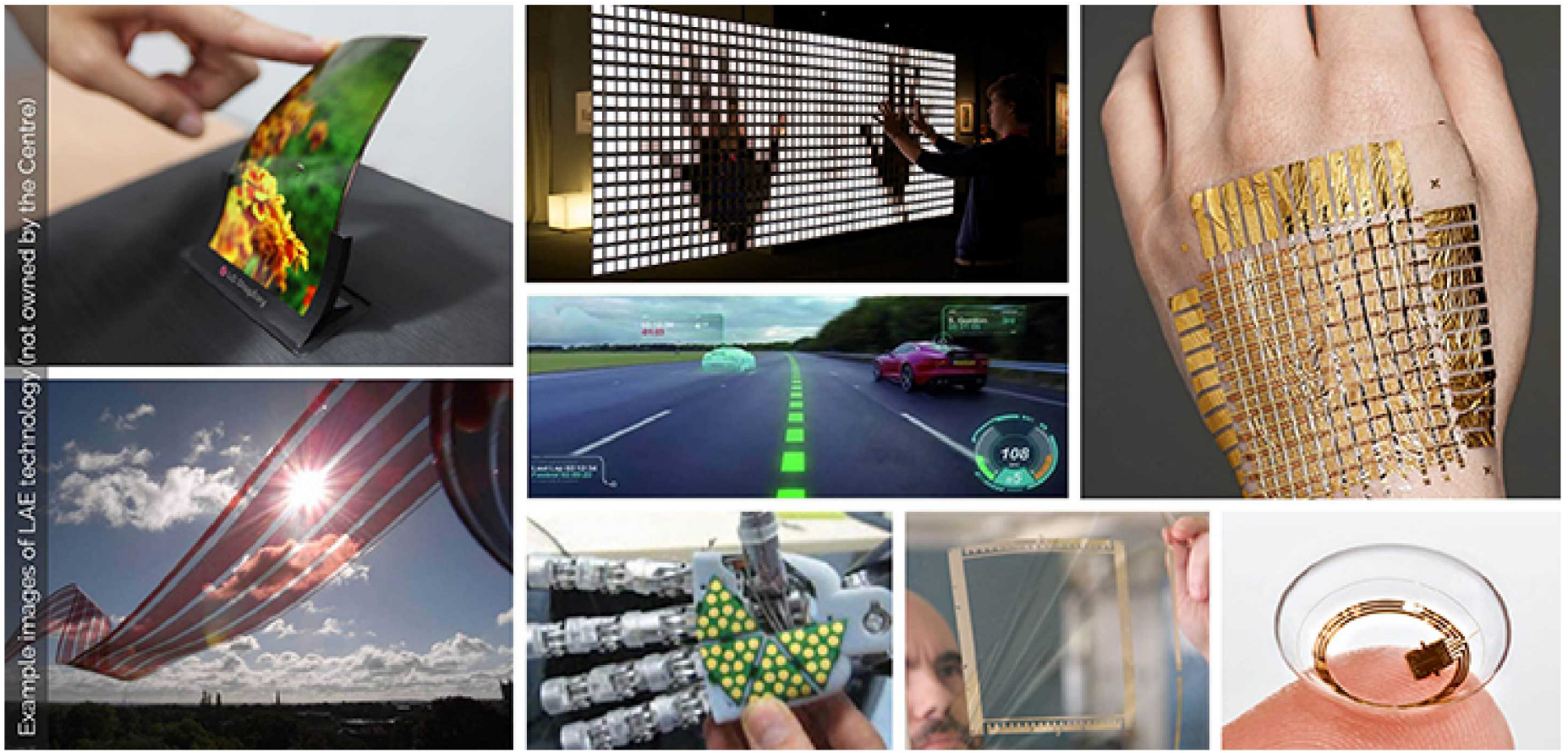
1.Polarizer with a vertical axis to polarize light as it enters.
2.Glass substrate with transparent electrodes . The shapes of these electrodes will determine the shapes that will appear when the LCD is switched ON.
3.Twisted nematic liquid crystal.
4.Glass substrate with common electrode film (ITO) with horizontal ridges to line up with the horizontal filter.
5.Polarizing filter film with a horizontal axis to block/pass light.
6.Reflective surface to send light back to viewer.

FlexEnable's glass-free organic LCD (OLCD)

Source: wikipedia.org

Printable, flexible, large-area electronics

Flexible electronics: Flexible, light and thin, robust, cost, innovation and prototyping

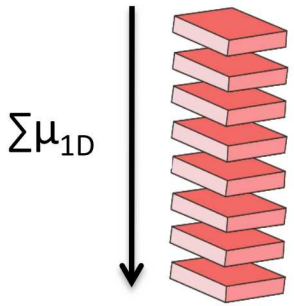


EPSRC Centre for Innovative Manufacturing in Large-Area Electronics (UK)

Organic photovoltaics, OLEDs (lighting, displays), (bio)sensors, distributed intelligent systems

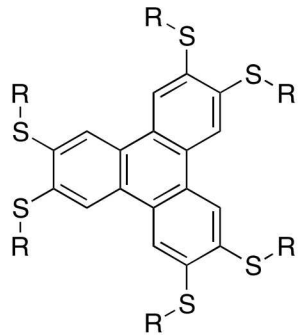
Organic Electronic Materials

Organic π-Stacked Semiconductors



Charge mobility

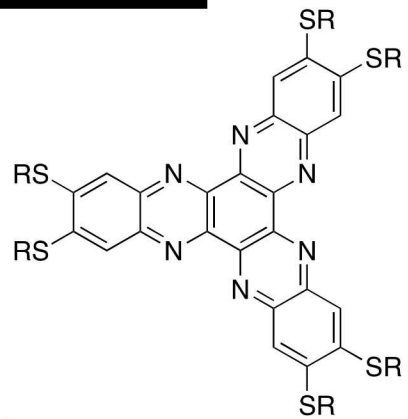
Time Of Flight (TOF)



Kato

λ_{onset} = 360 nm

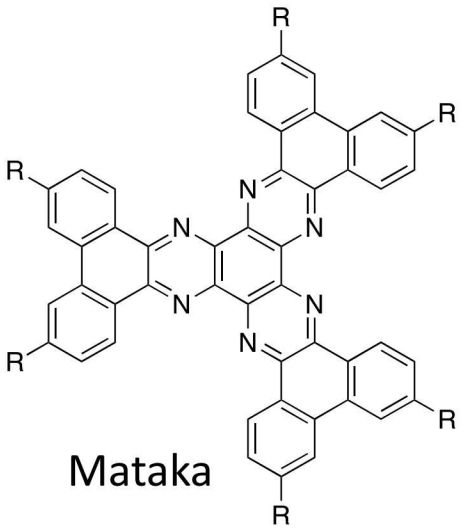
0.1 $cm^2\ V^{-1}\ s^{-1}$



Geerts

λ_{onset} = 430 nm

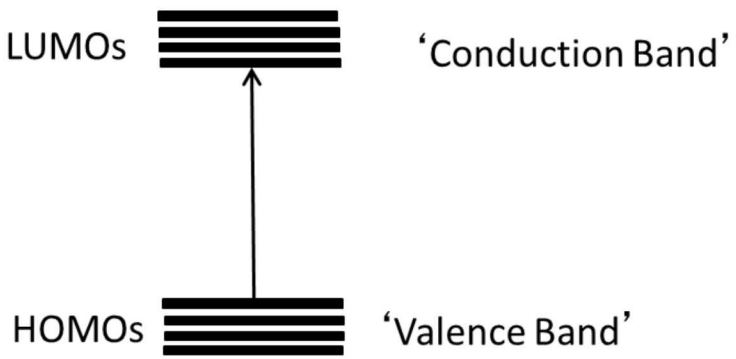
0.3 $cm^2\ V^{-1}\ s^{-1}$



Mataka

λ_{onset} = 520 nm

10 steps, 13% yield

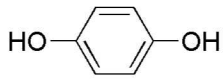


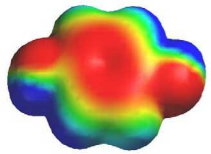
Amorphous Si: 0.5 – 1.0 $cm^2\ V^{-1}\ s^{-1}$

λ_{onset} = 1100 nm

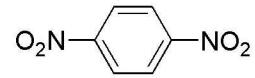
Lehmann, M., et al. *Chem. Eur. J.*, **2005**, *11*, 3349-3362; Hirai, Y., et al. *Adv. Funct. Mater.*, **2008**, *18*, 1668-1675; van Herrikhuyzen, J., et. al. *J. Am. Chem. Soc.*, **2004**, *126,* 10021-10027

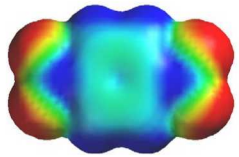
Reczek Lab (Denison): Aromatic-Aromatic Donor-Acceptor Interactions





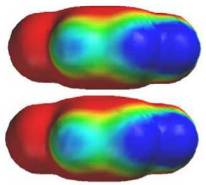
Electron-rich ‘Donor’



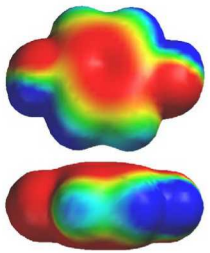


Electron-deficient ‘Acceptor’

Stacking:

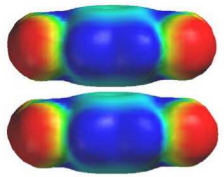


Face-centered
repulsive

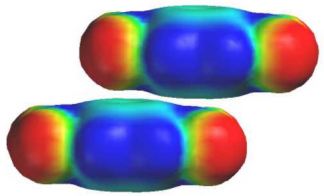


Herringbone
ok

Stacking:

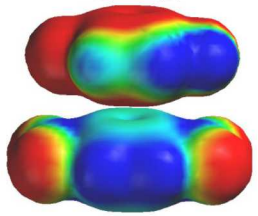


Face-centered
repulsive



Off-set
slightly attractive

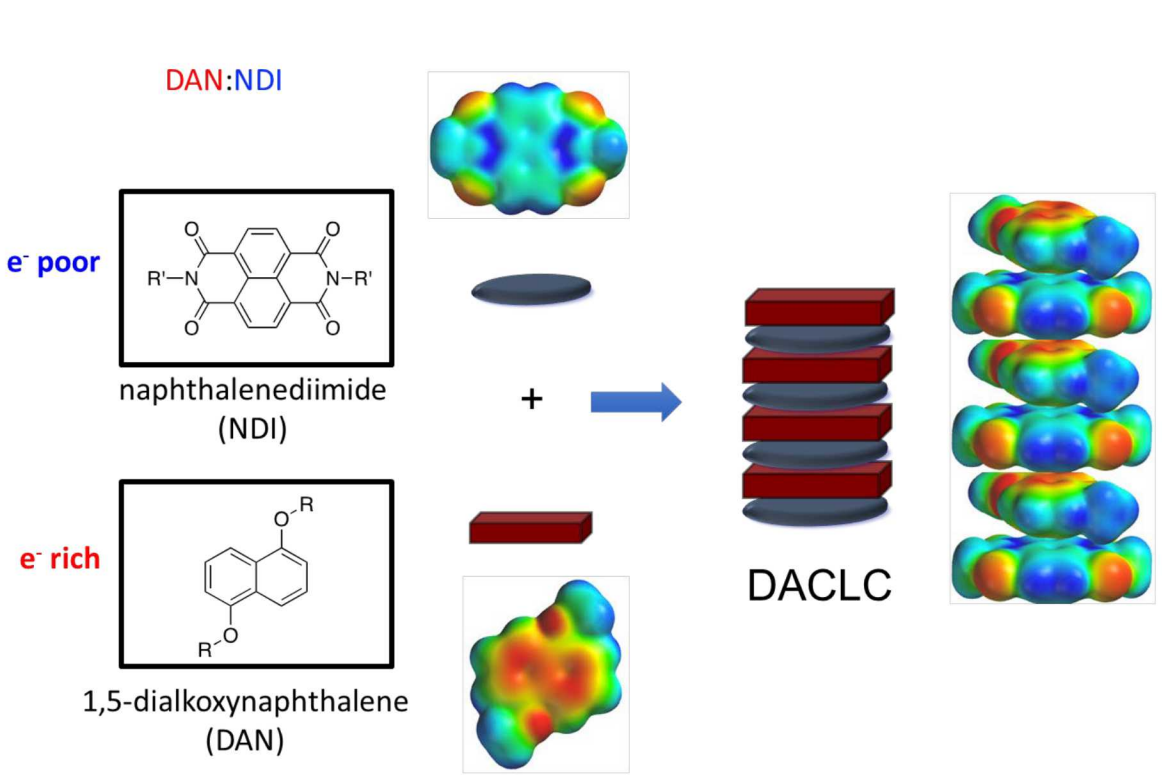
Advantage to stability
and orbital overlap!



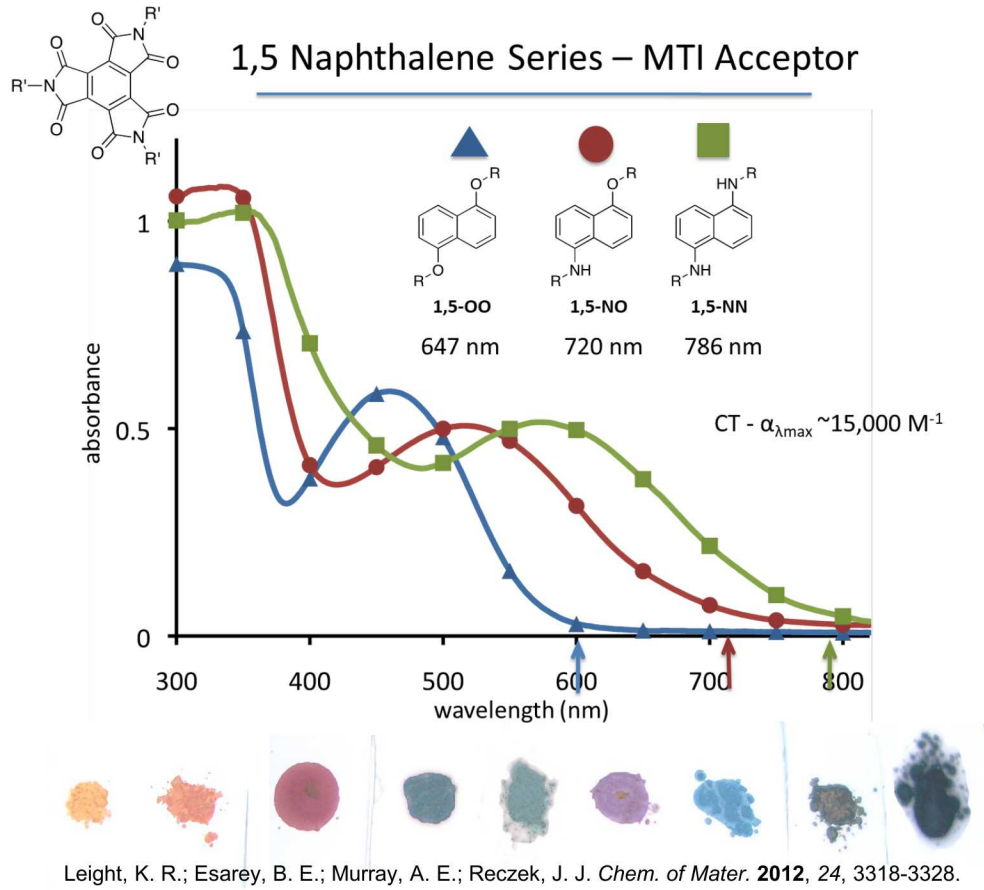
Alternating face-centered
attractive!

Hunter, C. A.; Sanders, J. K. M. *J. Am. Chem. Soc.* **1990**, *112*, 5525

Tuning the Charge-Transfer Absorbance of DACLCs



Reczek, J. J., et. al., *J. Am. Chem. Soc.* **2006,** *128,* 7995-8002



Leight, K. R.; Esarey, B. E.; Murray, A. E.; Reczek, J. J. *Chem. of Mater.* **2012**, *24*, 3318-3328.

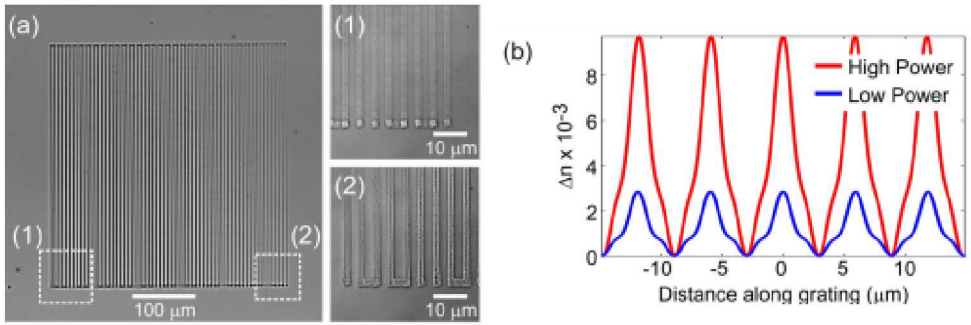
Donor-acceptor columnar liquid crystals (DACLCs): Self assembling 1D structures comprised of electron-rich and electron poor molecular precursors

DACLCs optical/electronic properties result from charge-transfer energy band following assembly and can be modulated via pendant groups to tune, for example, bandgap.

Directing the alignment of DACLCs is challenging

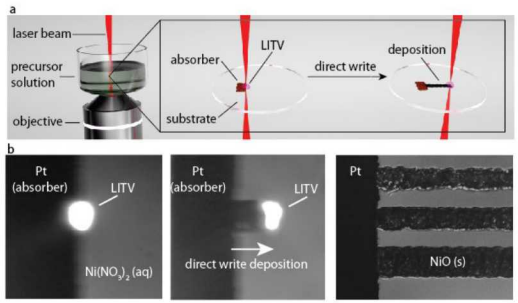
Kaehr Lab (Sandia): Laser direct write (LDW) of metals, metal oxides, semiconductors, graded materials…

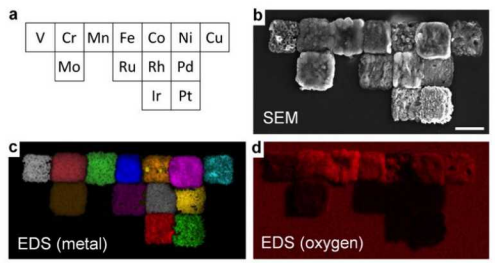
Graded index materials



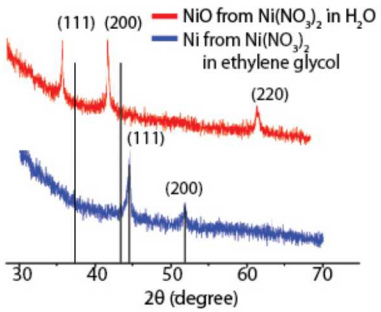
Appl. Phys. Lett., (2016) 109, 123701.

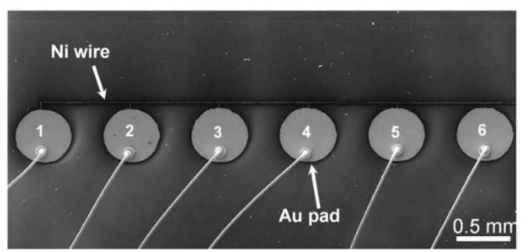
Sequential deposition of diverse materials into arbitrary patterns

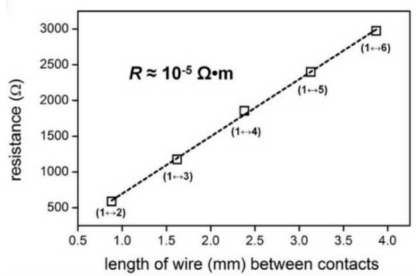




One step LDW-induced reduction to form Ni structures

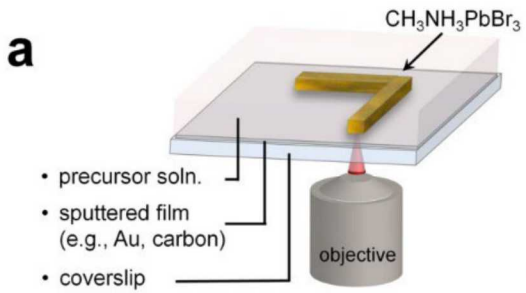


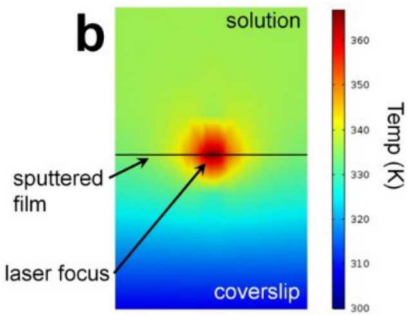


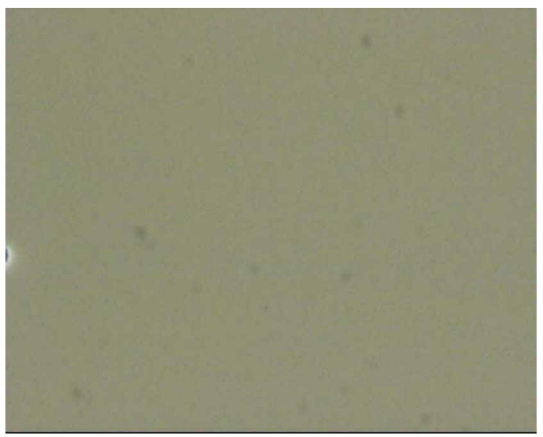


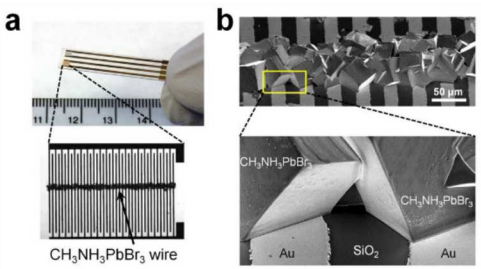
ACS Appl. Mater. Interfaces, (2016) *8* (33), pp 21134–21139.

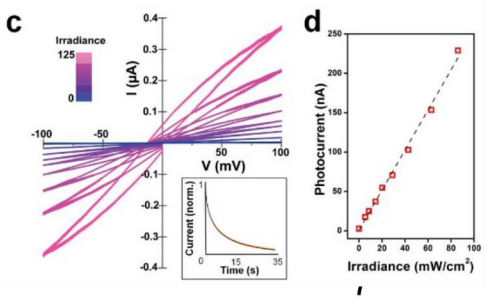
LDW of semiconductors







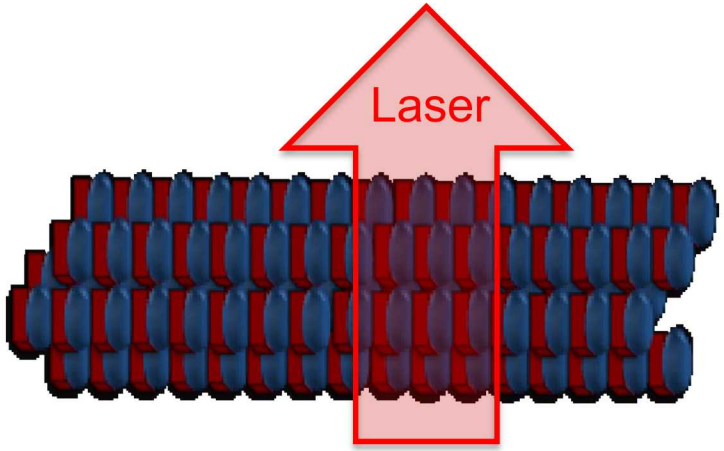




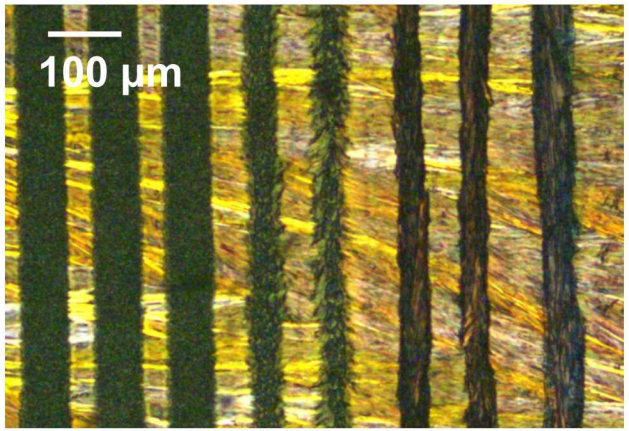
J. Phys. Chem. Lett., (2016) 7, pp 3736–3741.

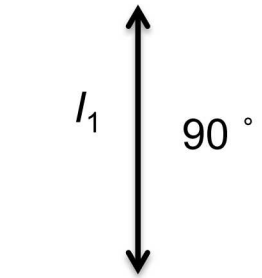
Laser light interactions with DACLC films

Region of horizontally aligned DACLC film

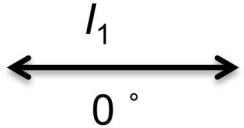


750 (NIR) nm laser passed over film at varying speed

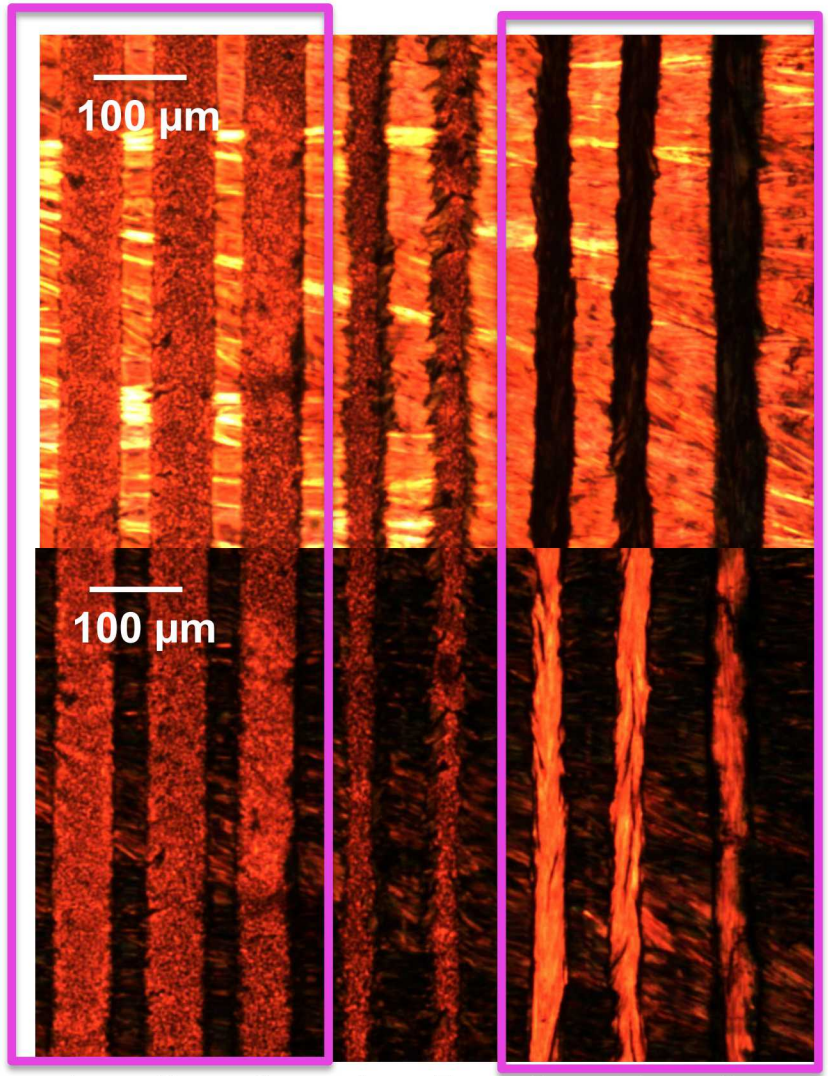




Plane polarized light



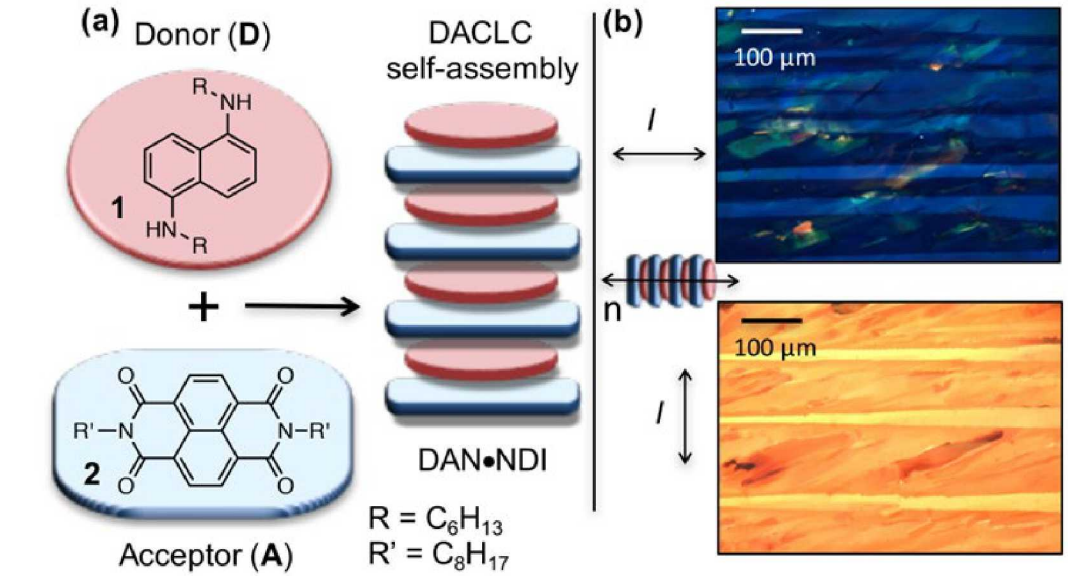
isotropic



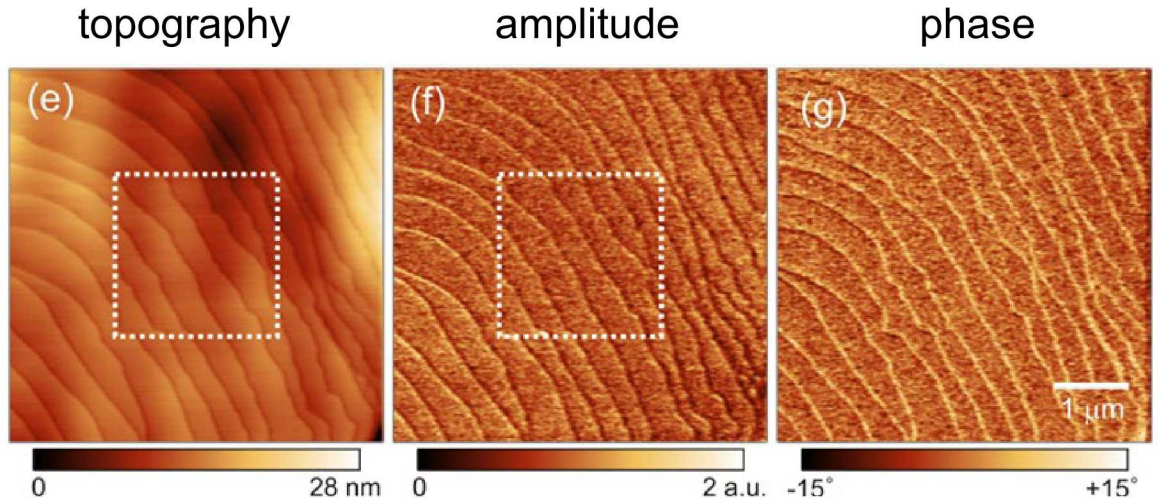
anisotropic and reoriented

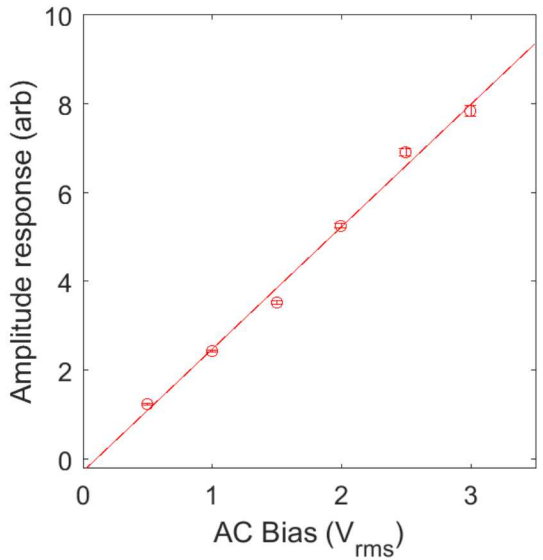
Dichroic/Piezoelectric Properties of DACLC films

Dichroic



Piezoelectric



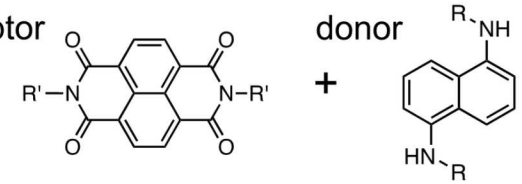


The piezoelectric response is linear with applied voltage, indicative of a piezoelectric material. The white box was scanned while applying a DC bias of +8V. The lack of change of contrast in the amplitude signal observed under these conditions indicates a true piezoelectric response and not interaction with injected charges or other electromechanical coupling.

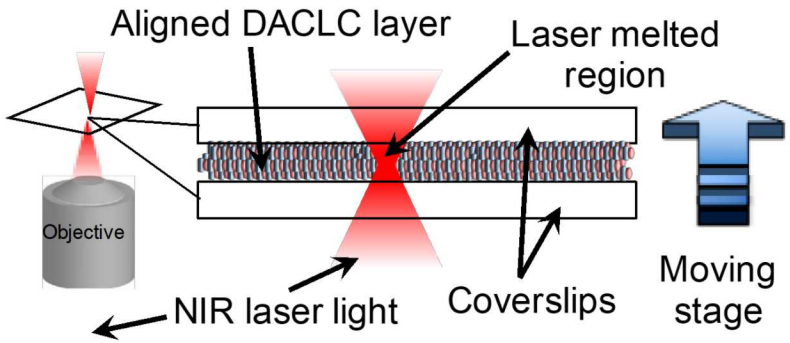
Process for rewritable dichroic materials

Laser Heating

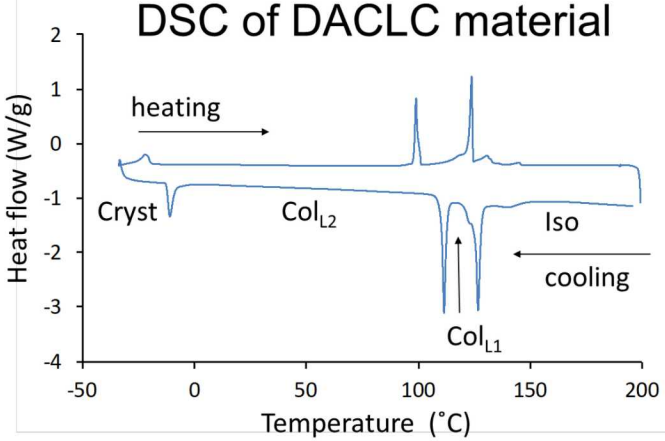
acceptor + donor



Setup for writing with Red/NIR laser



DSC of DACLC material

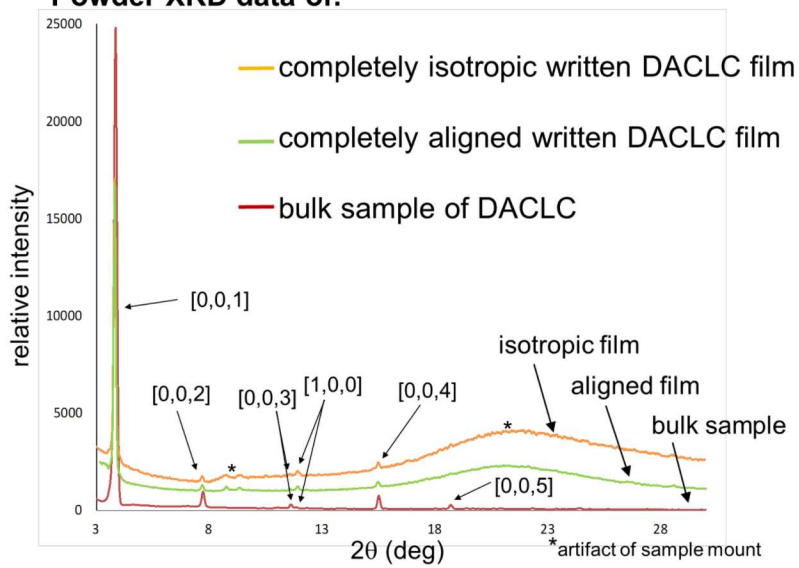


Supramolecular structure

➢ **Writing rate does *not* affect phase identity**

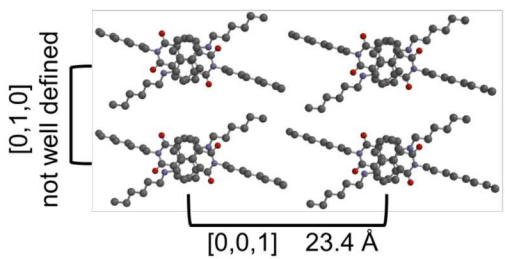
Powder XRD of films shows written regions that are isotropic verses re-aligned have the *same* phase structure.

Powder XRD data of:

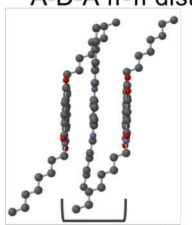


Packing structure (powder data and modeling)

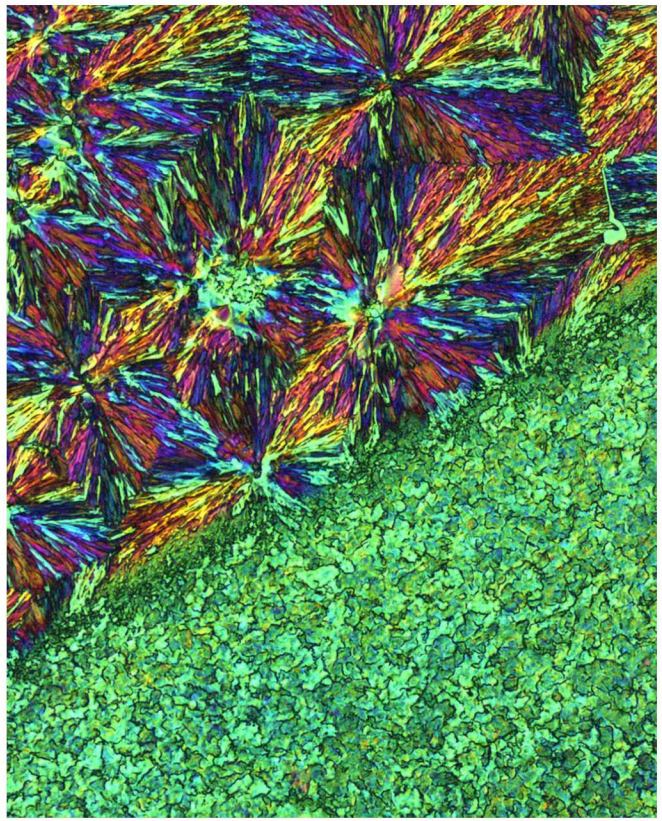
Top-view (down columns) of Col$_L$ phase



A-D-A π-π distance

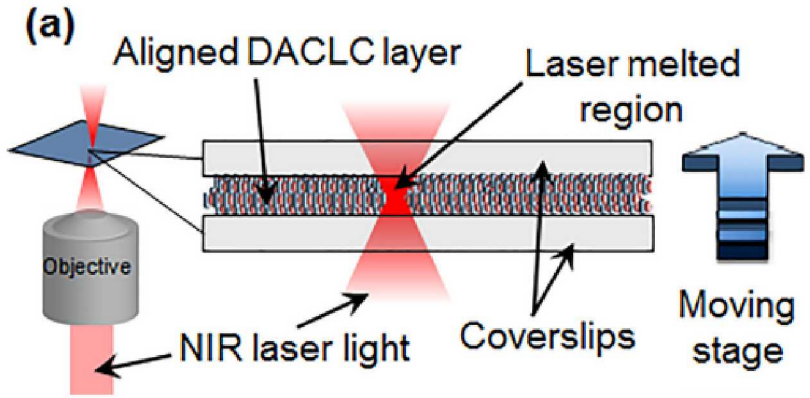


Anisotropic (bulk sample)



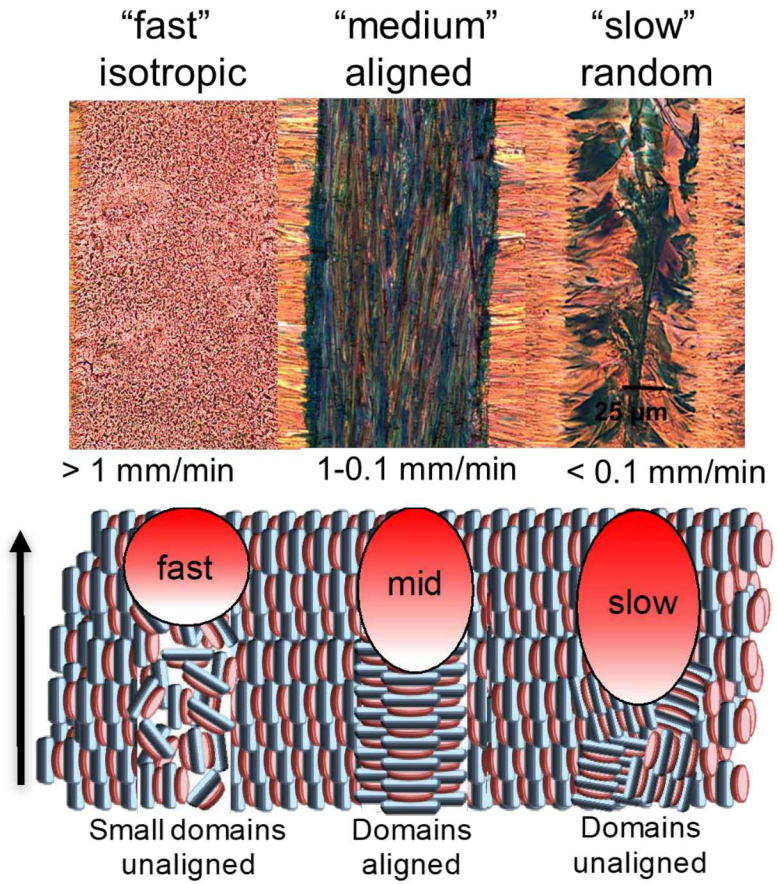
Isotropic

DACLC Reconfigurable Optical Polarizers

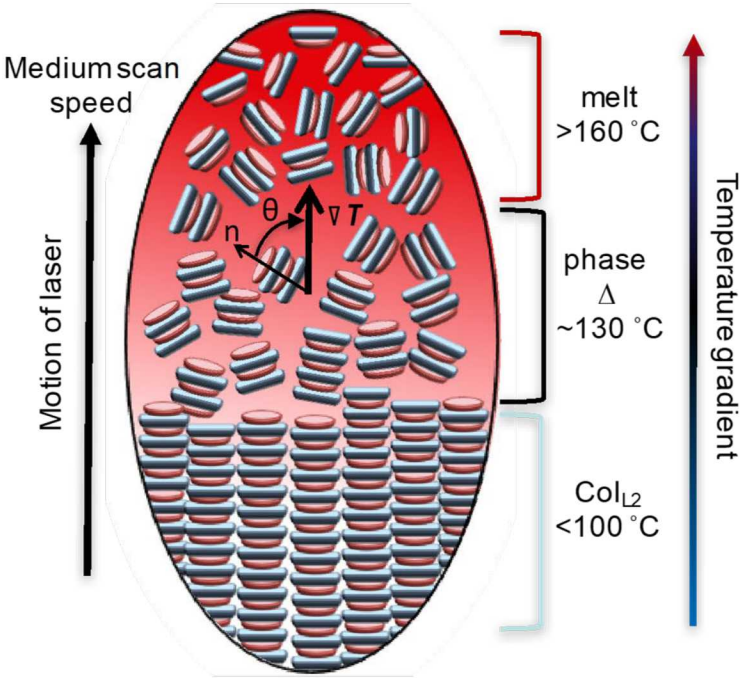


Laser heating is used to induce a directional thermal gradient that results in an ability to orient DACLCs into patterned regions of dichroic films. Fast cooling results in isotropic regions.

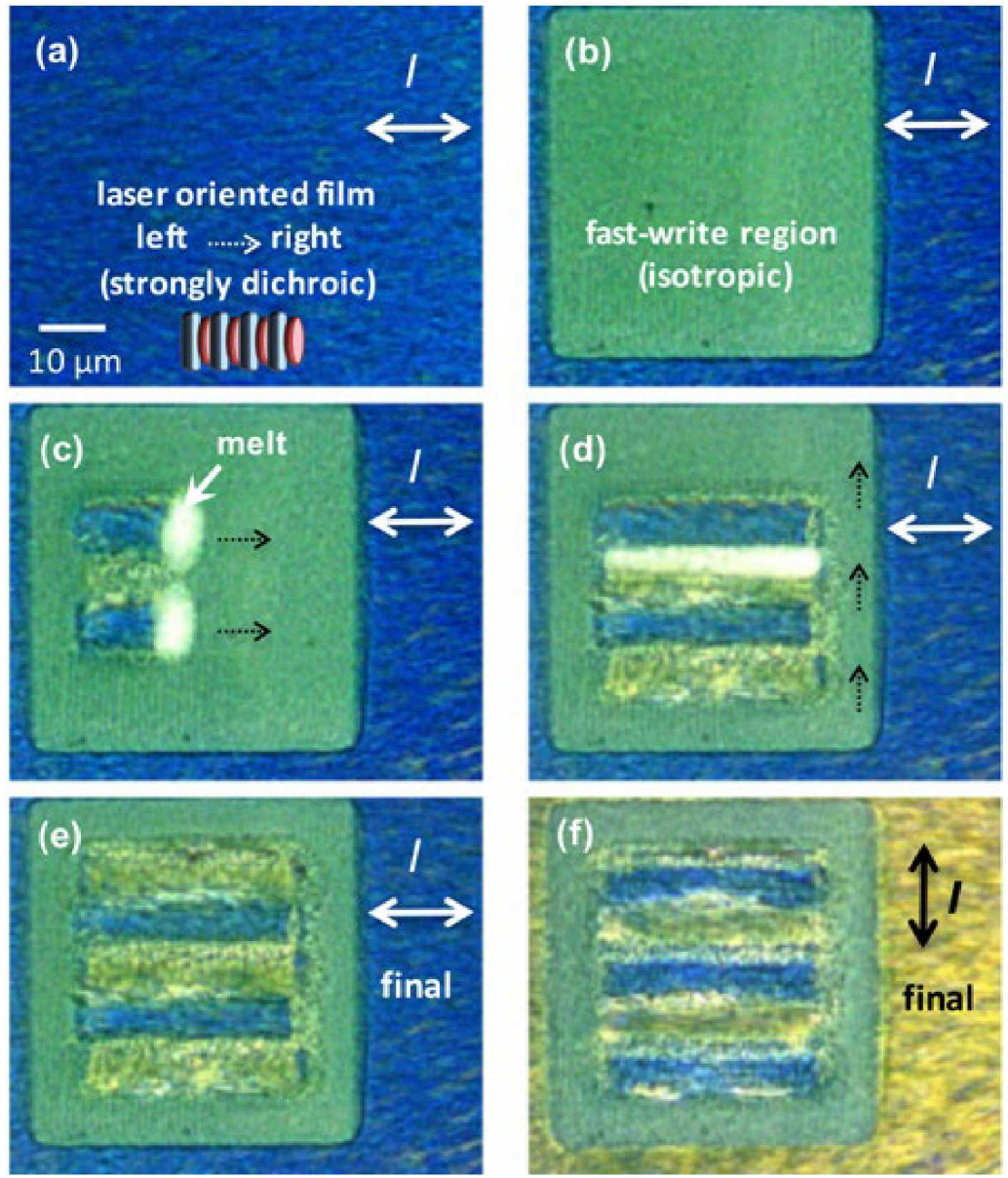
➢ **Rate affects cooling time and thermal gradient**



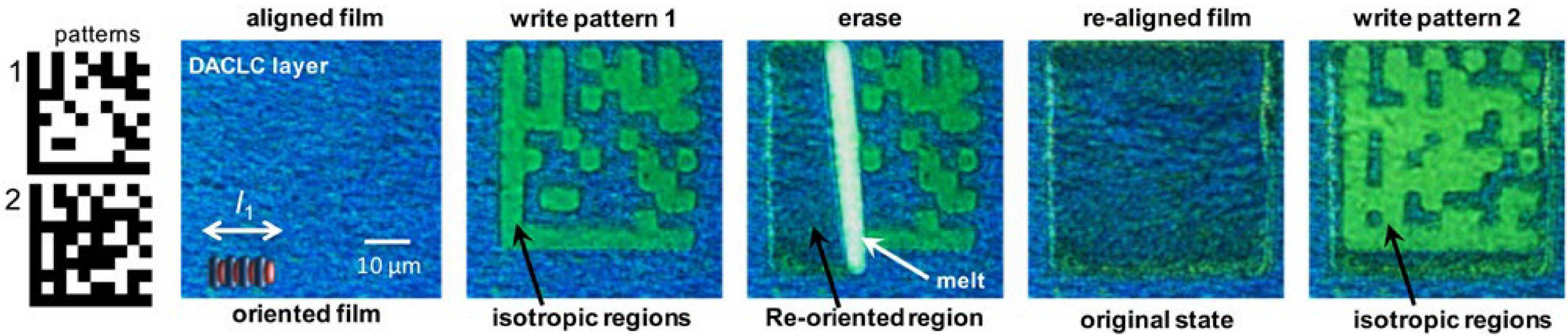
Thermal gradient orients the Col director (n)



DACLC Reconfigurable Optical Polarizers

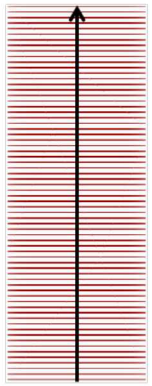


DACLC Reconfigurable Optical Polarizers

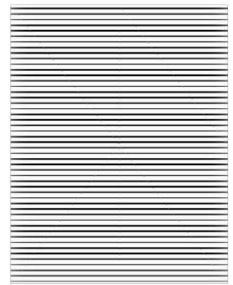


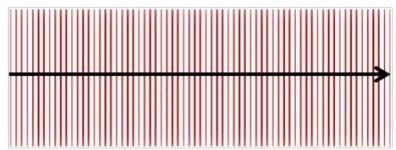
Controlling Pixel Alignment

Nanoscribe

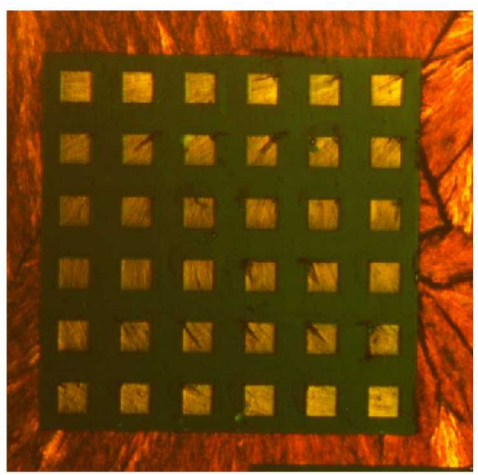


Hatching

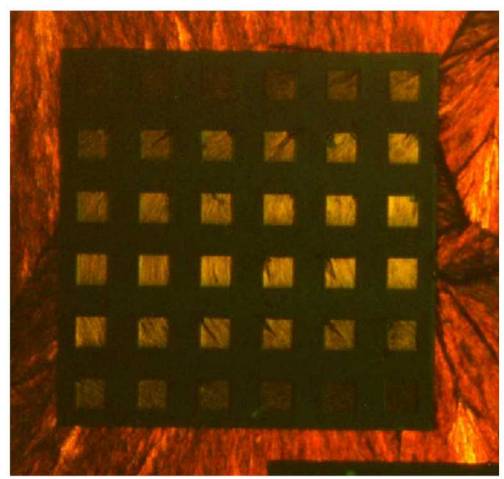




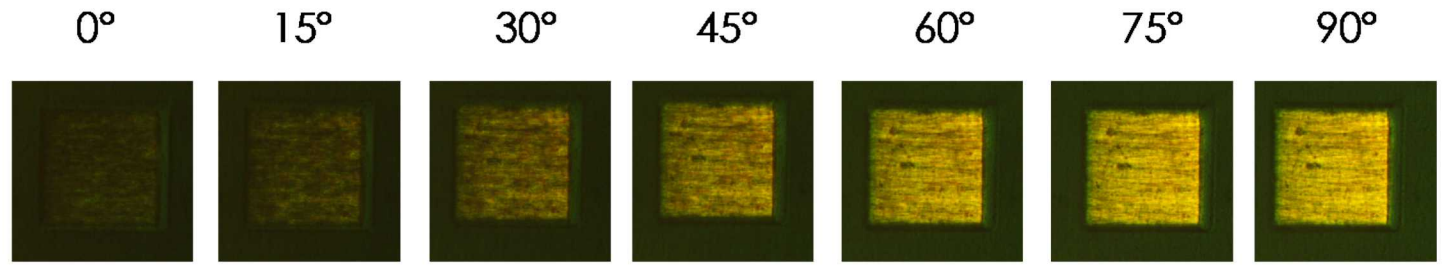
Varying hatching angle from 0-175°



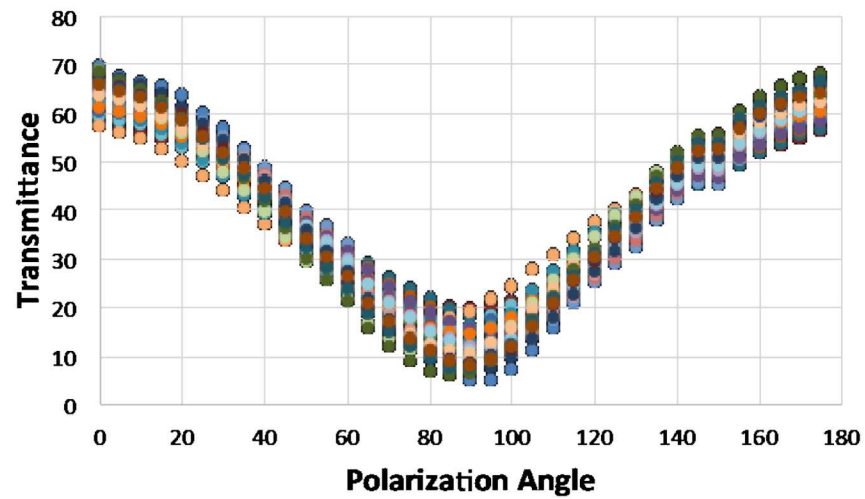
Not polarized



Polarizer at 0°



0° hatching angle, varying polarization angle



Grayscale images

Original image

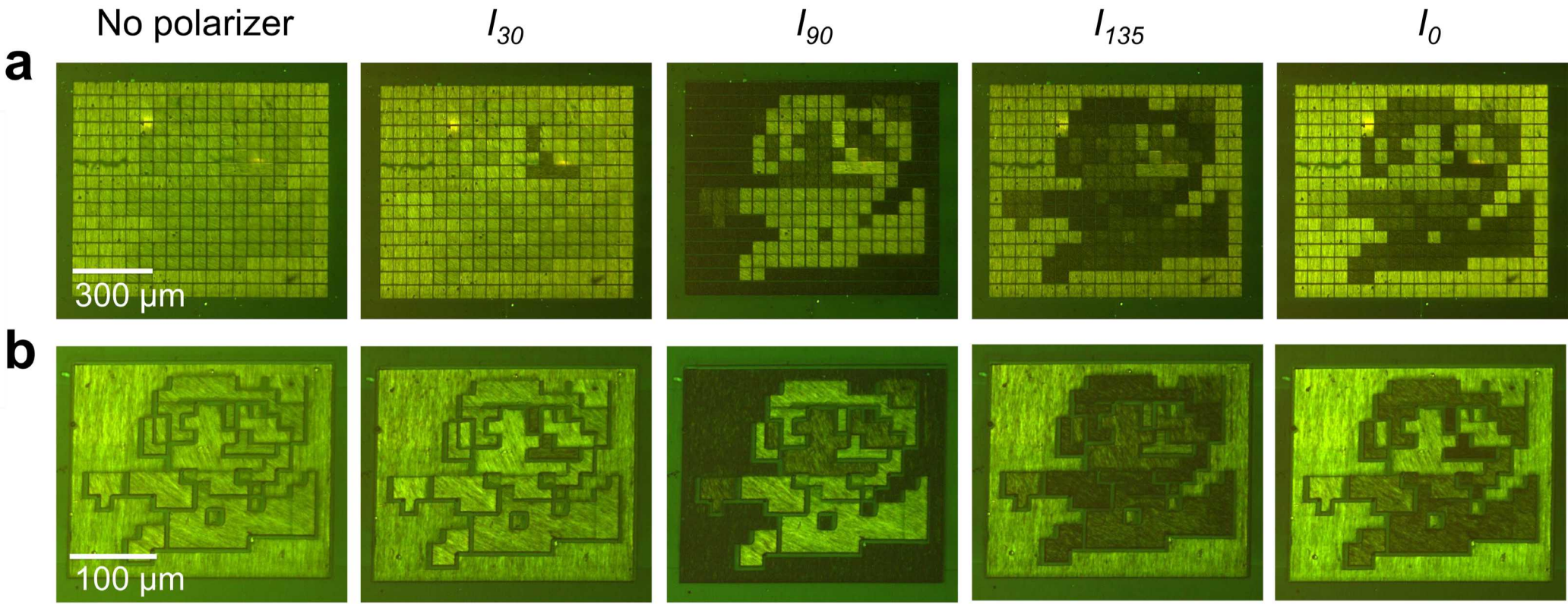
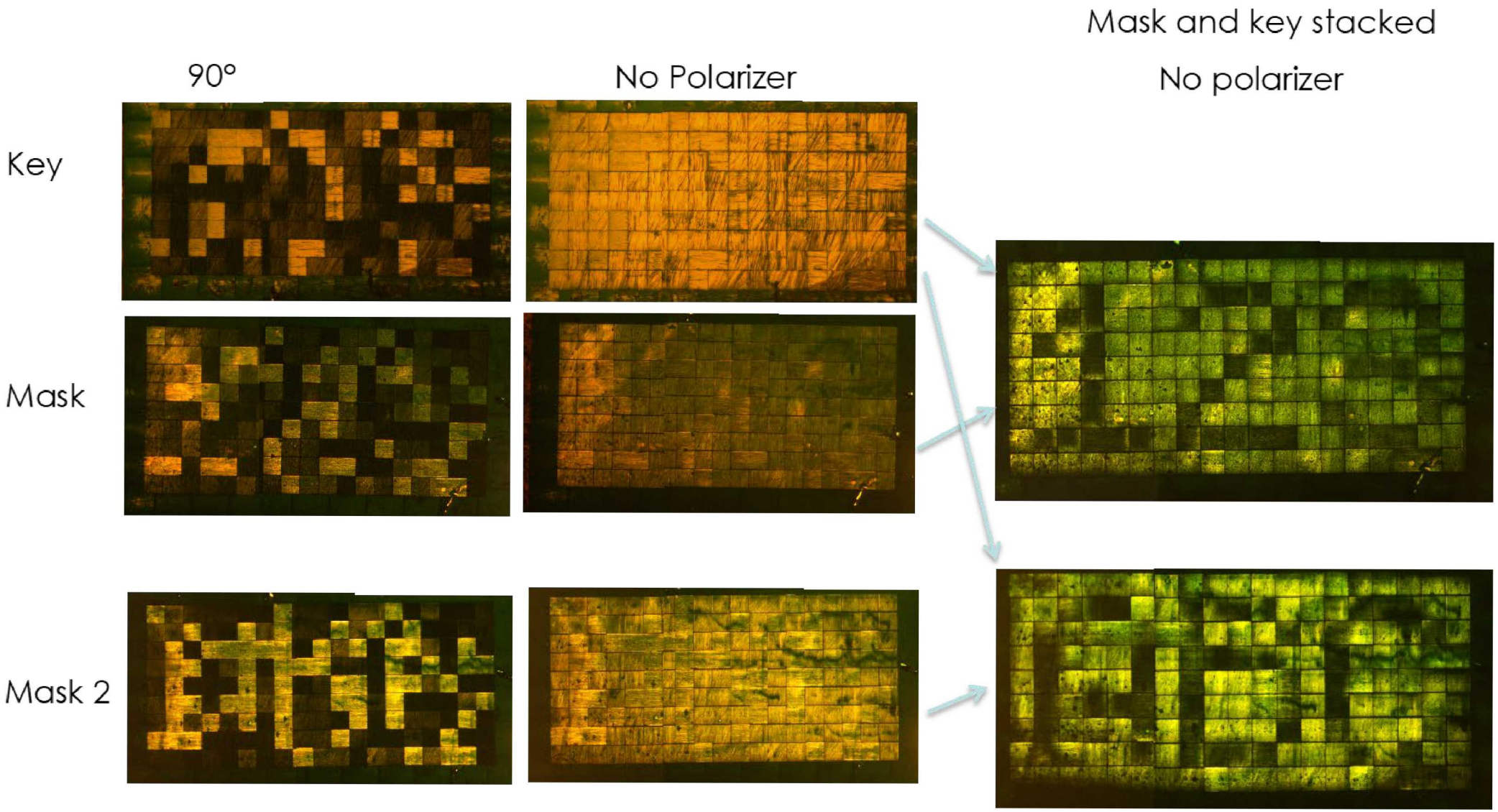


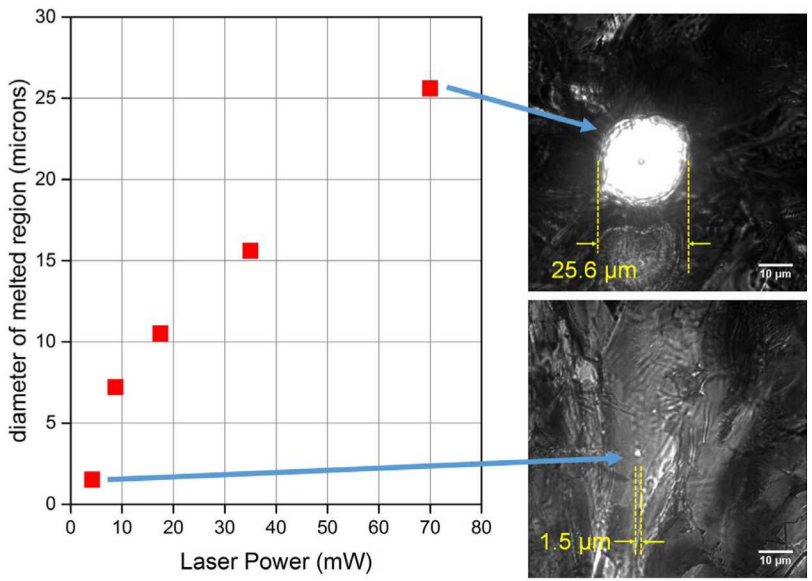
Image encryption



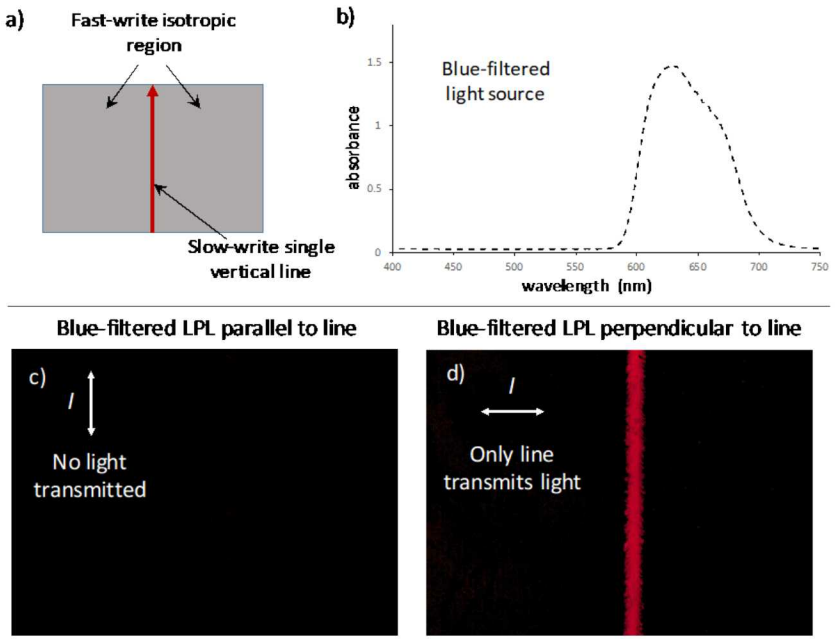
Conclusions

- Demonstration of an optical write/rewrite (OWR) material system comprised of modular, donor acceptor columnar (piezoelectric) liquid crystals.
- Laser-directed assembly combined with the self-healing characteristics of DACLCs provide for limitless rewriting.
- High dichroic ratio provides analogue-like readout. Using polarization-dependent transmittance coupled with the ability to define the input polarization orientation increases the possible permutations for a patterned area—advantageous for data storage, authentication and cryptography applications.

resolution



output filtering



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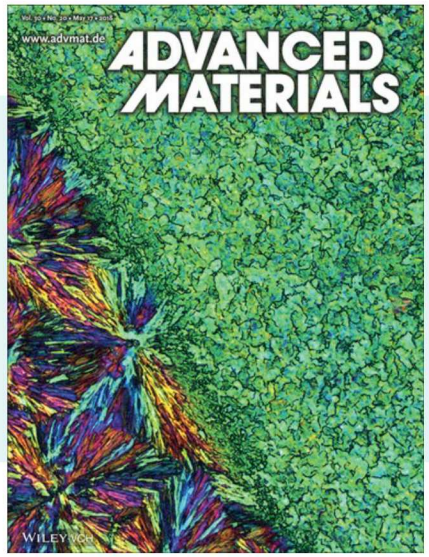
Van Winkle et al, "Laser Rewritable Dichroics through Reconfigurable Organic Charge-Transfer Liquid Crystals", **2018**, *Adv. Mater.* 1706787.



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