Nano Innovation 2020 Conference & Exhibition
Rome, 15-18 September

Direct Laser Writing

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School on nanotechnologies: processes and applications to sensors and actuators

lens European Laboratory for Non-Linear Spectroscopy

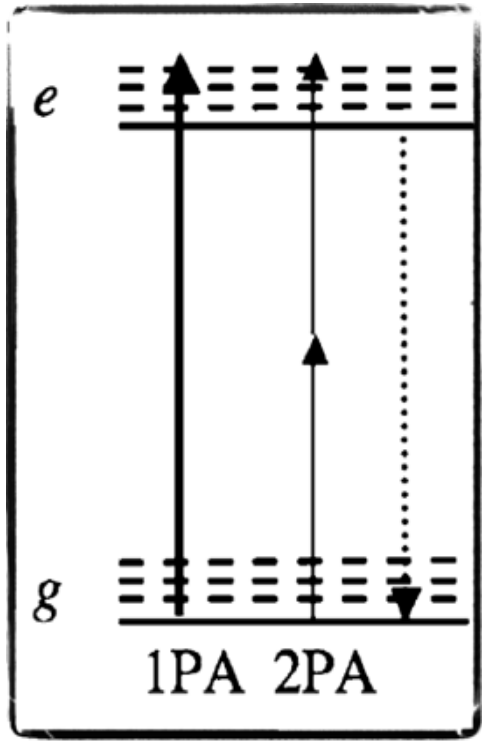
INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA

It-fab Italian Network for Micro and Nano Fabrication

Outlook

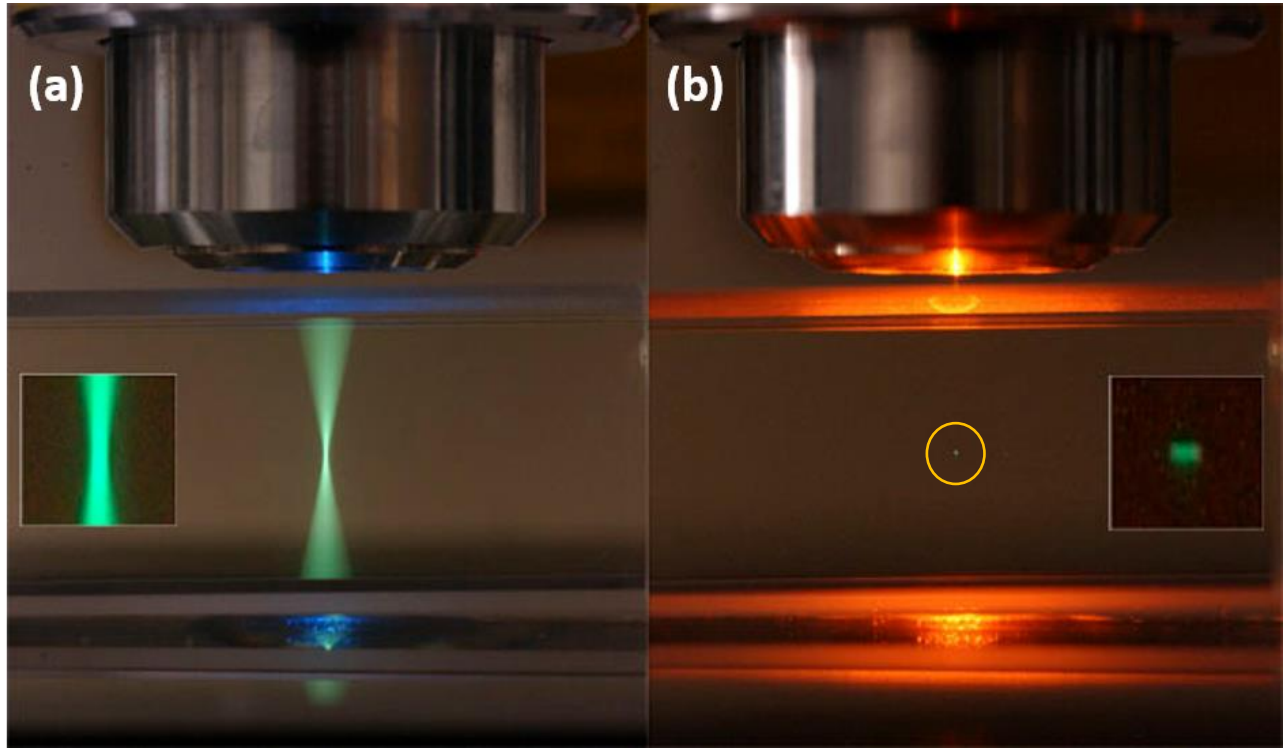
- Direct Laser Writing: principles
- Pros & Cons
- Applications
- Enhancing resolution: Stimulated emission depletion lithography
- Functional polymers

Two photon absorption



Single photon excitation

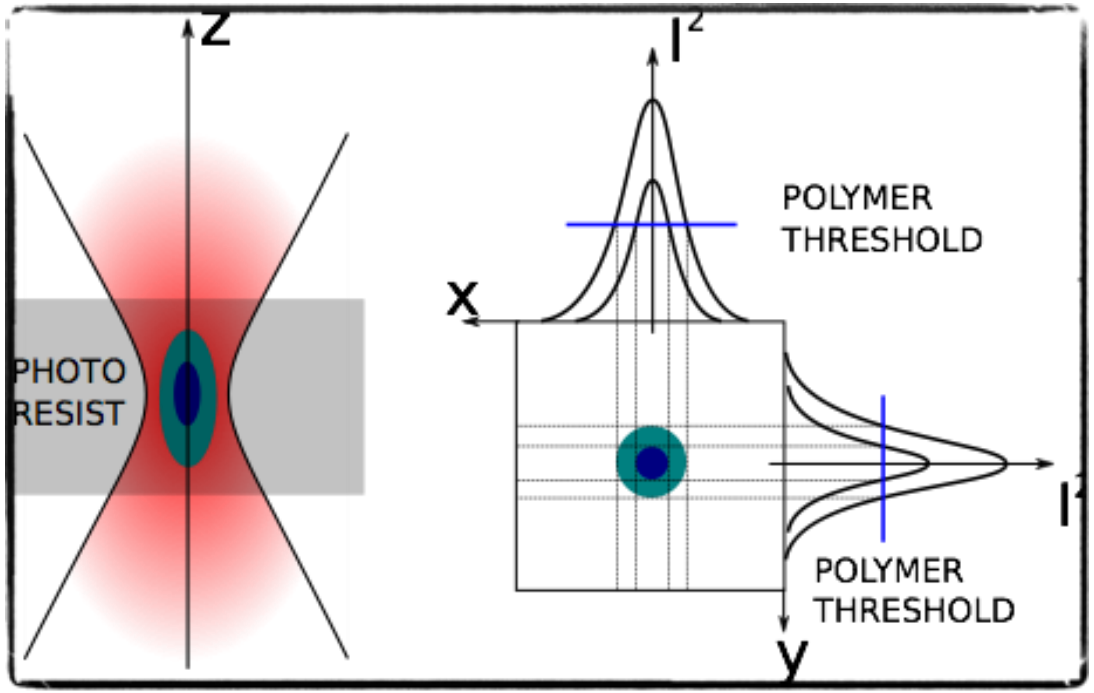
Two photon excitation



$$n^{(1)} = \sigma(\nu) N_g \frac{I}{h\nu}$$

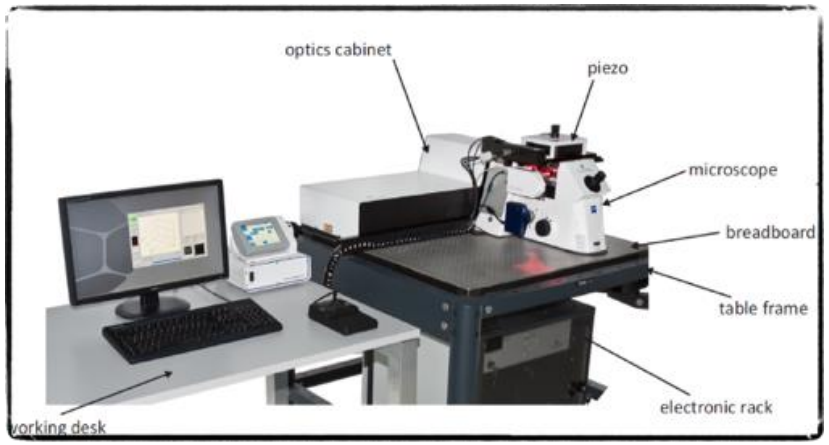
$$n^{(2)} = \frac{1}{2}\delta(\nu) N_g \left(\frac{I}{h\nu}\right)^2$$

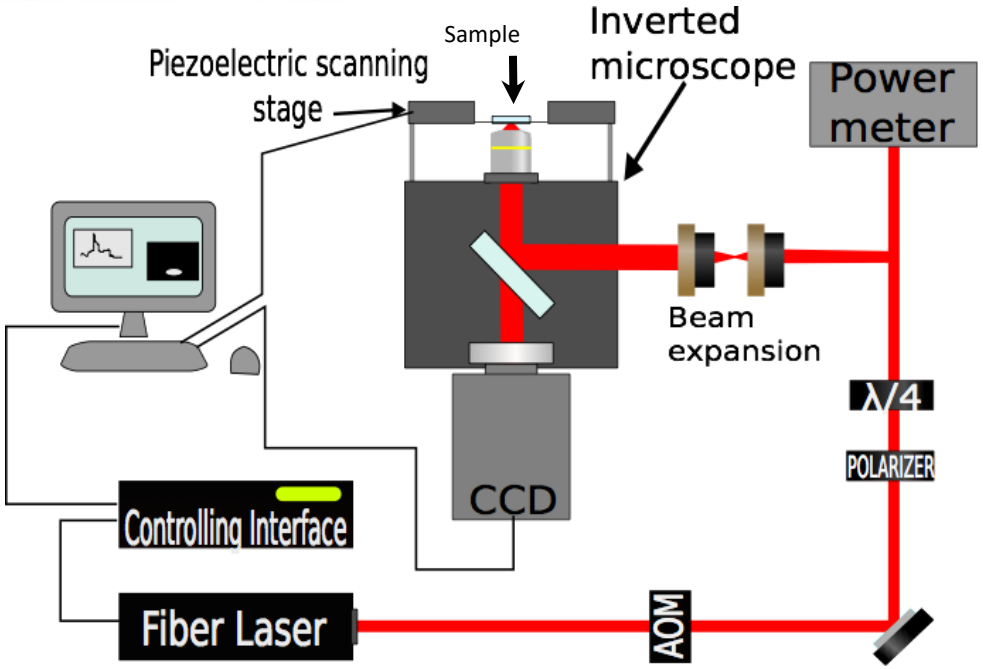
Two photon absorption polymerization

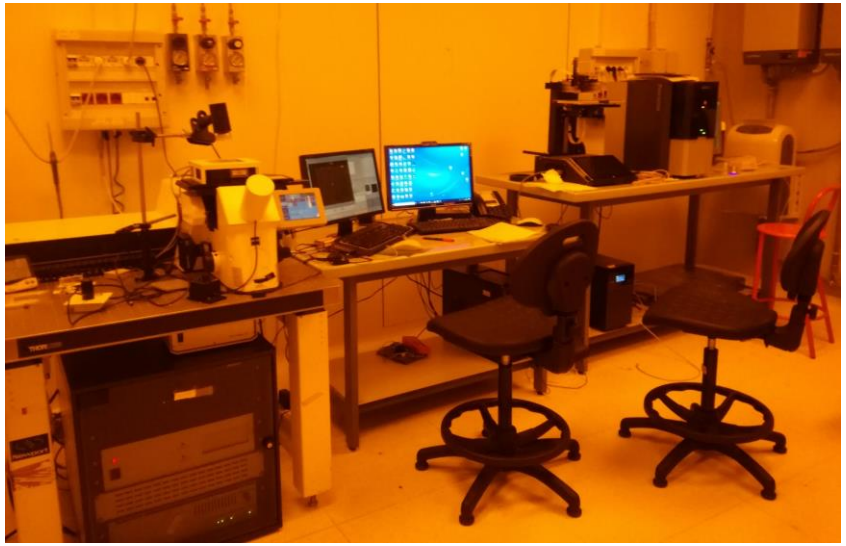


- Polymerization in the focus of the laser beam: 3D VOXEL
- Maskless process
- Positive and negative resists
- Typical resolution: 120 nm in xy plane
  250 nm in z direction
  (under diffraction limit)
- Development process with organic solvents

Direct Laser Writing (DLW)

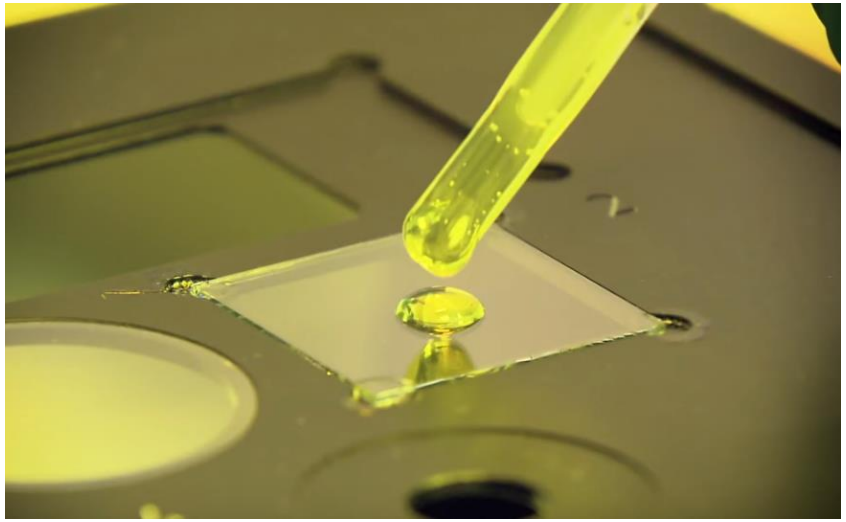


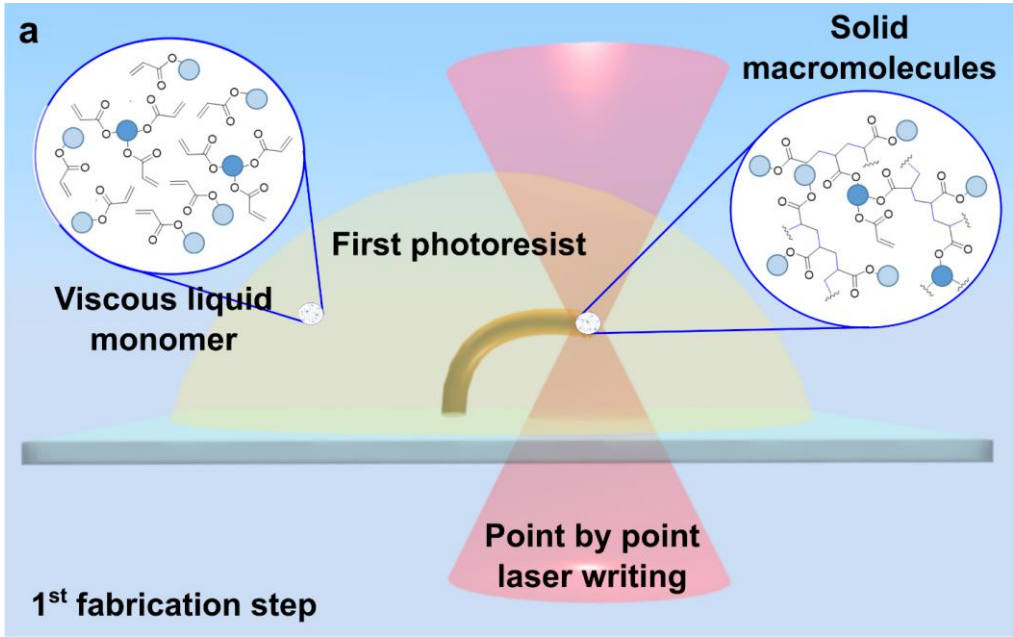




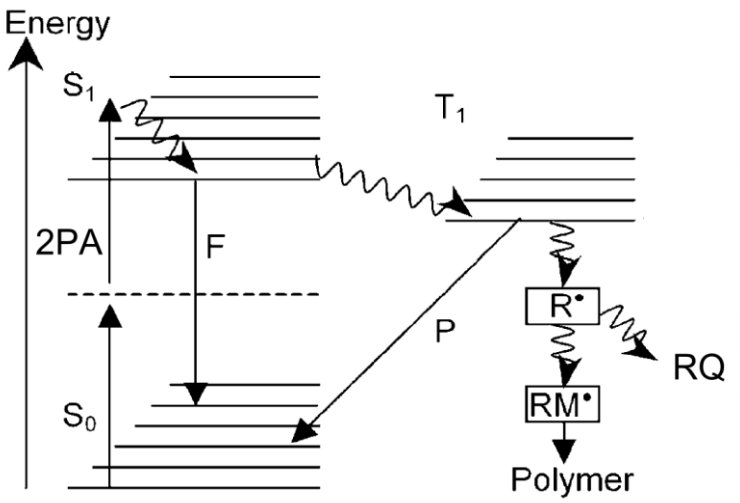
- Femtosecond Fiber Laser (150 fs)
- 780 nm
- Repetition rate 50 MHz

Direct Laser Writing (DLW)





Two photon polymerization

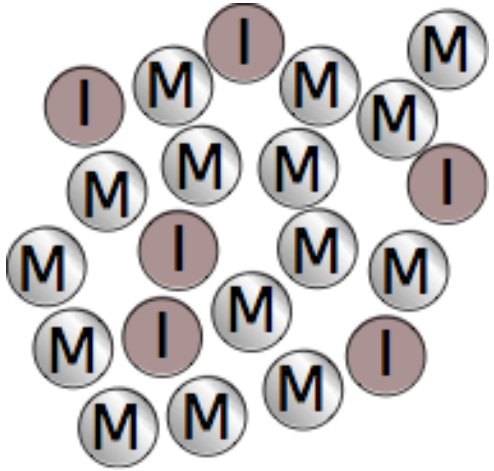


Radical polymerization

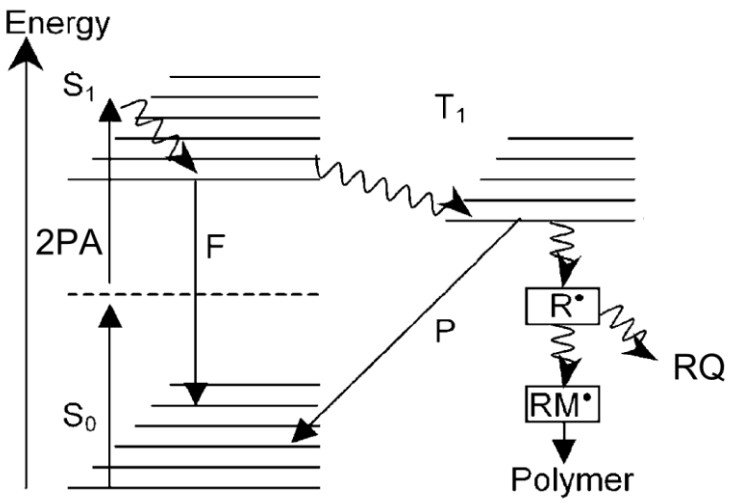
$$I \xrightarrow{2h\nu'} I^* \longrightarrow R\cdot$$

$$R\cdot + M \rightarrow RM\cdot \xrightarrow{M} RMM\cdot \ldots \rightarrow RM_n\cdot$$

$$RM_n\cdot + RM_m\cdot \rightarrow RM_{m+n}R$$



Two photon polymerization



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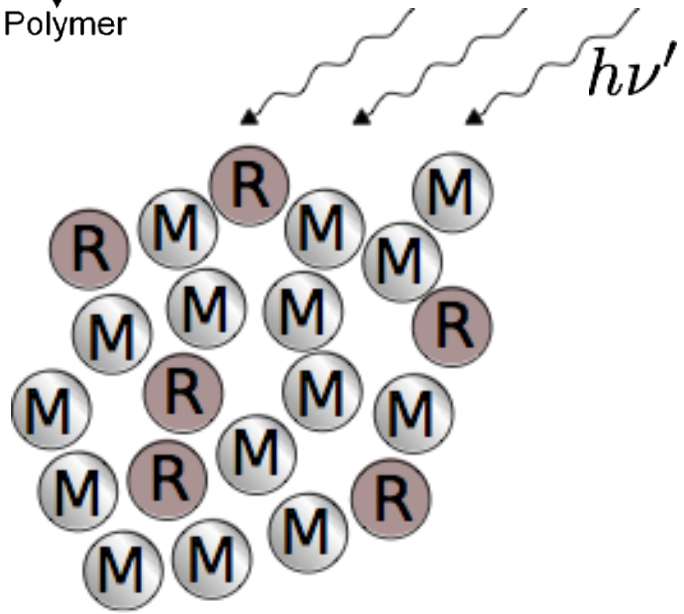
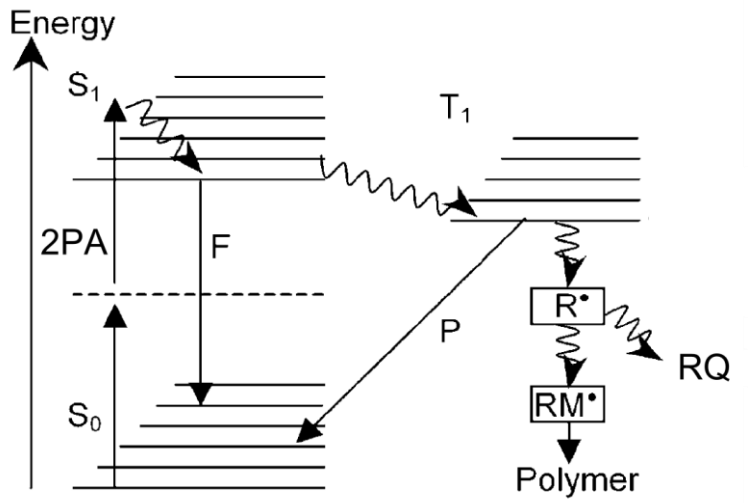


Two photon polymerization



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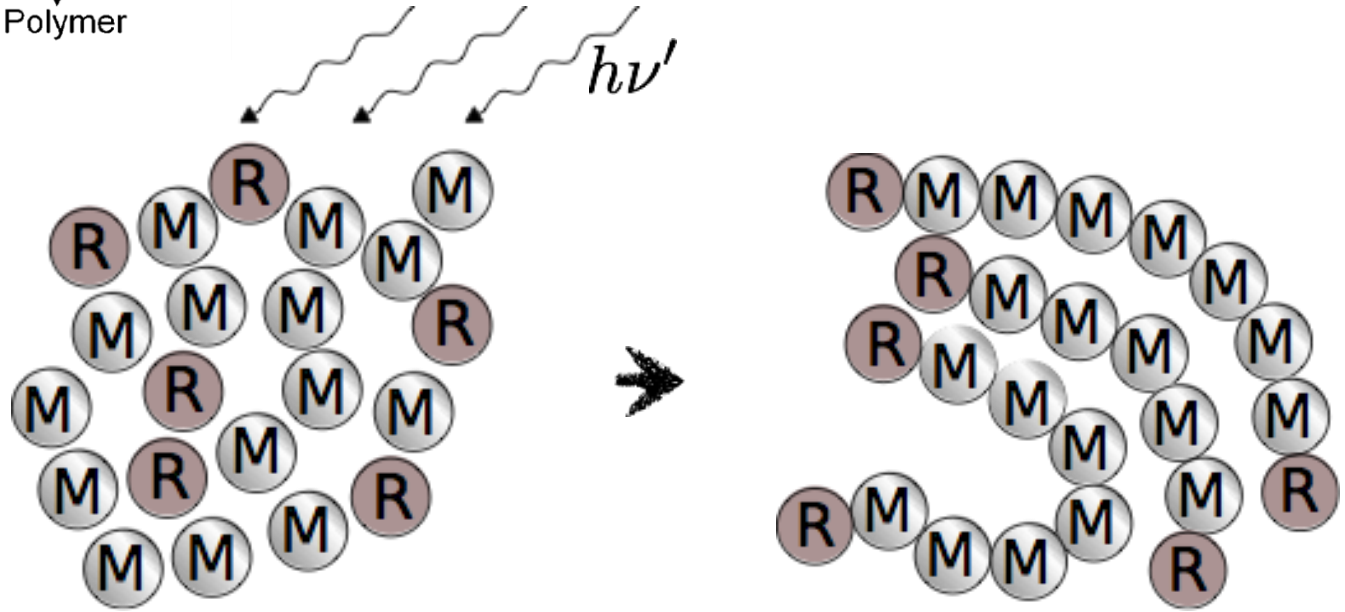


Direct Laser Writing (DLW): Parameters

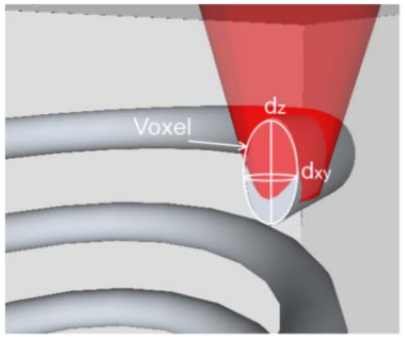
Parameters

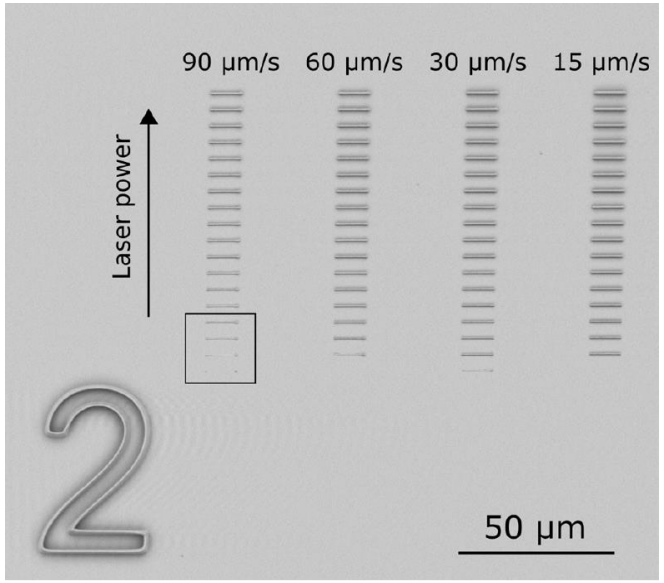
- 3D position
- Laser power
- Writing speed

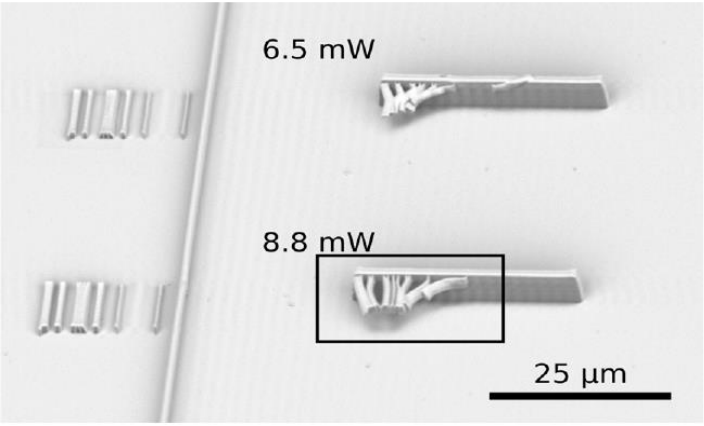
Dose

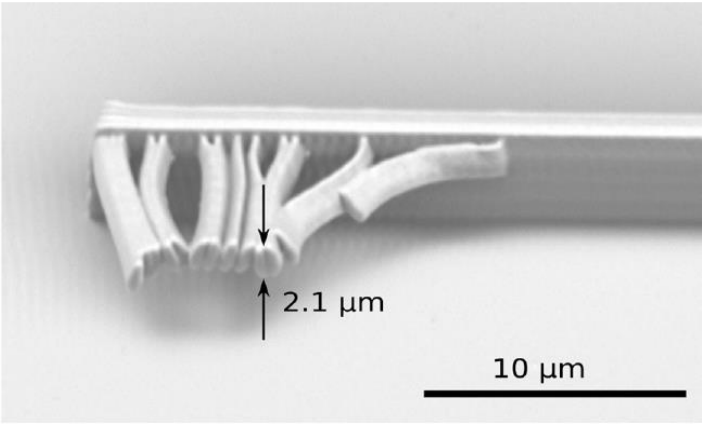
Features

- Polymerization Threshold
- Voxel dimension
- Cross-linking degree → UV curing









Direct Laser Writing (DLW): Pros & Cons

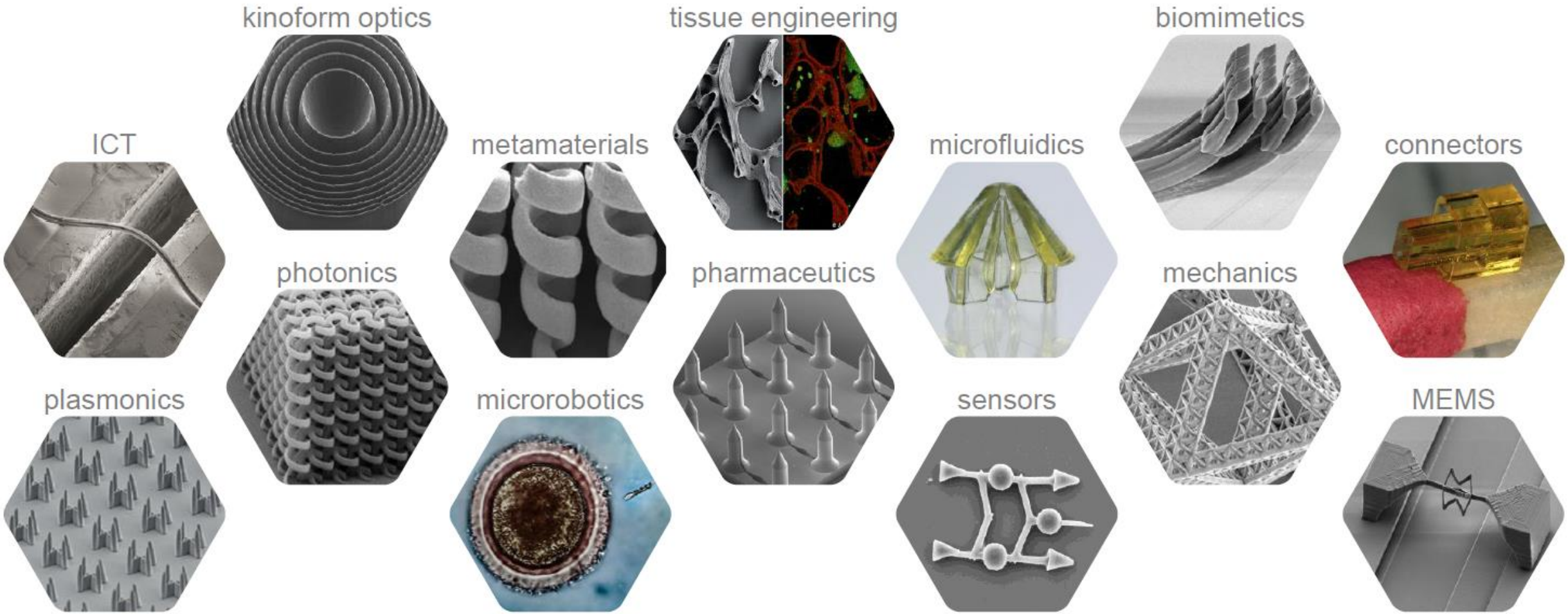
PROS

- 3D designs
- Maskless process
- Low cost
- Versatility of polymers
- Easy integration of different materials

CONS

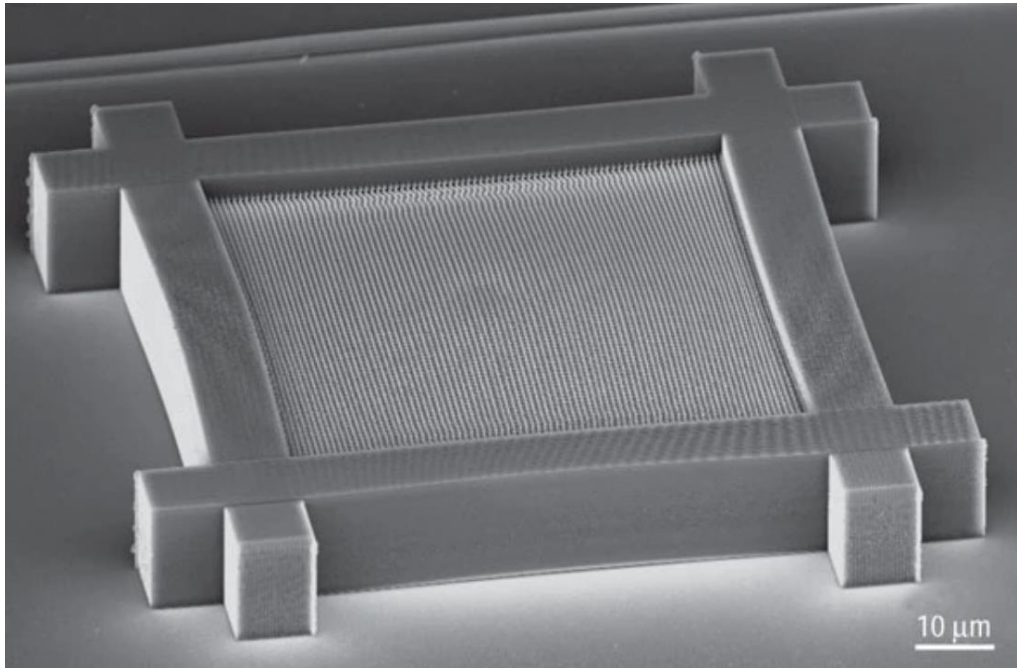
- Limited resolution
- Serial Fabrication
- Low refractive index of polymers

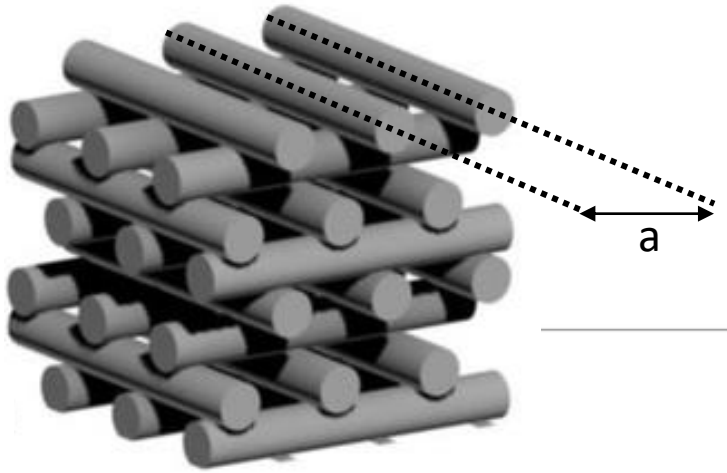
Applications

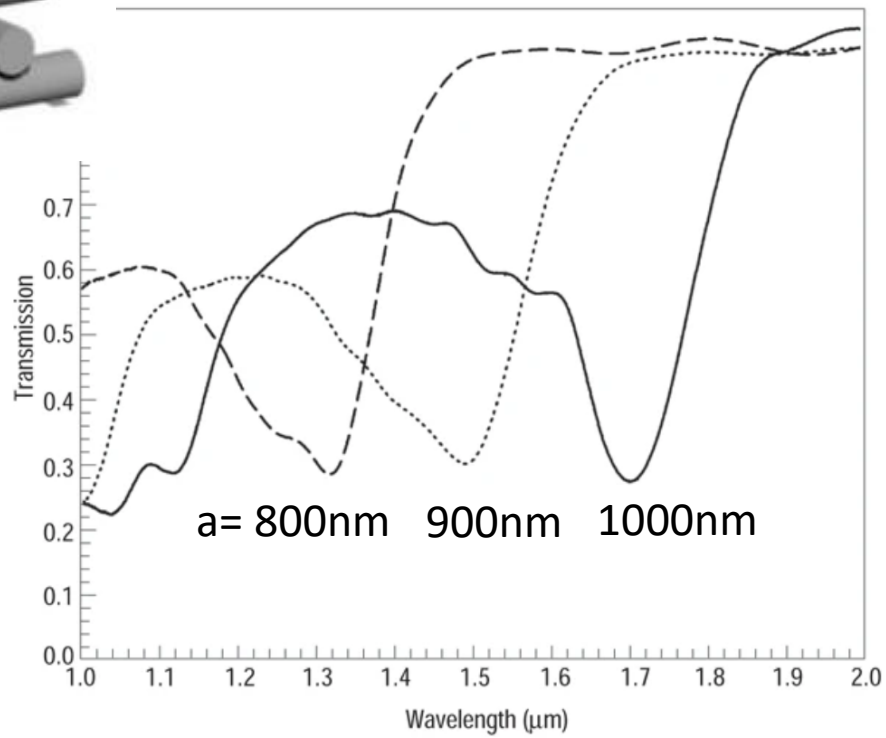


Direct Laser Writing (DLW): Photonic crystals

3D photonic crystals: woodpile structure

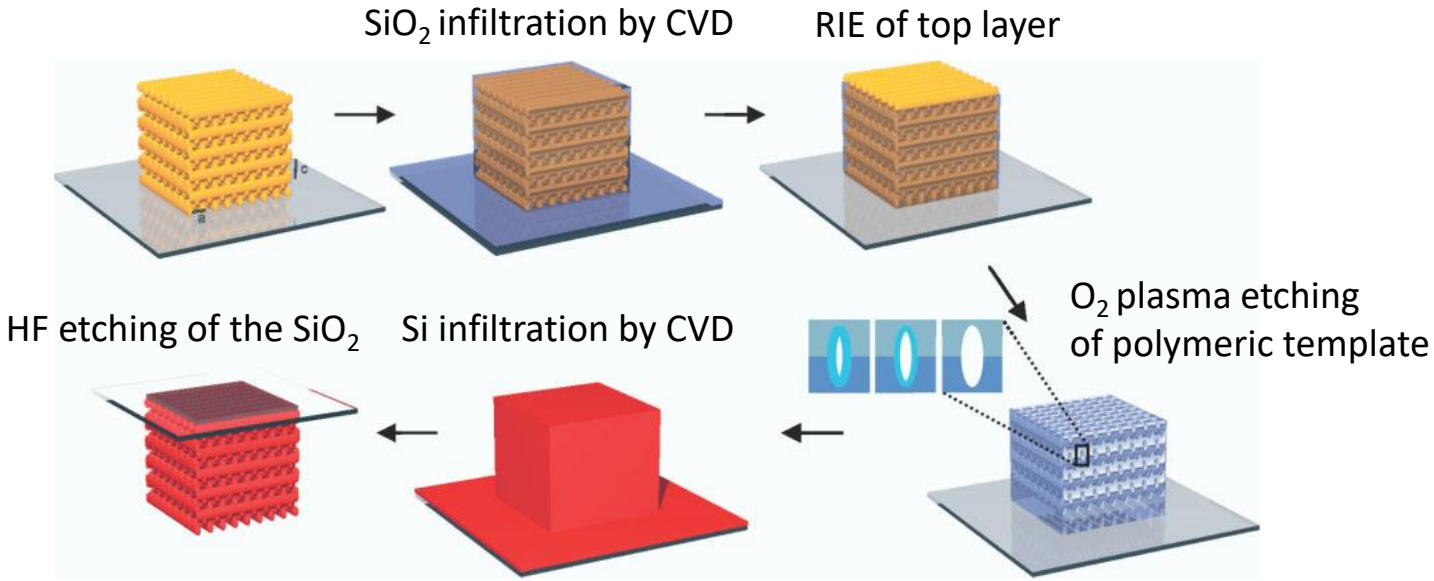


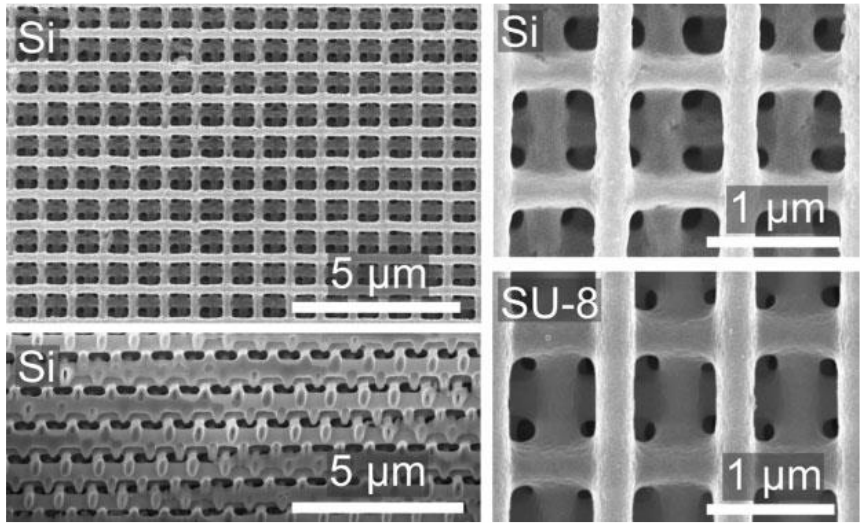


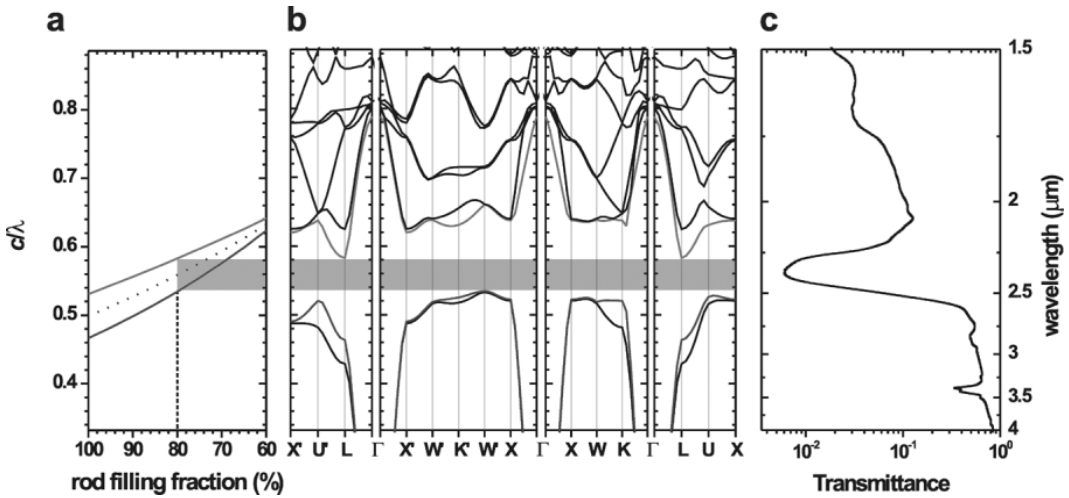


M. Deubel, …M. Wegener et al., *Nat. Mater.* **2004**, *3*(7), 444.

Single and double inversion of 3D polymeric templates

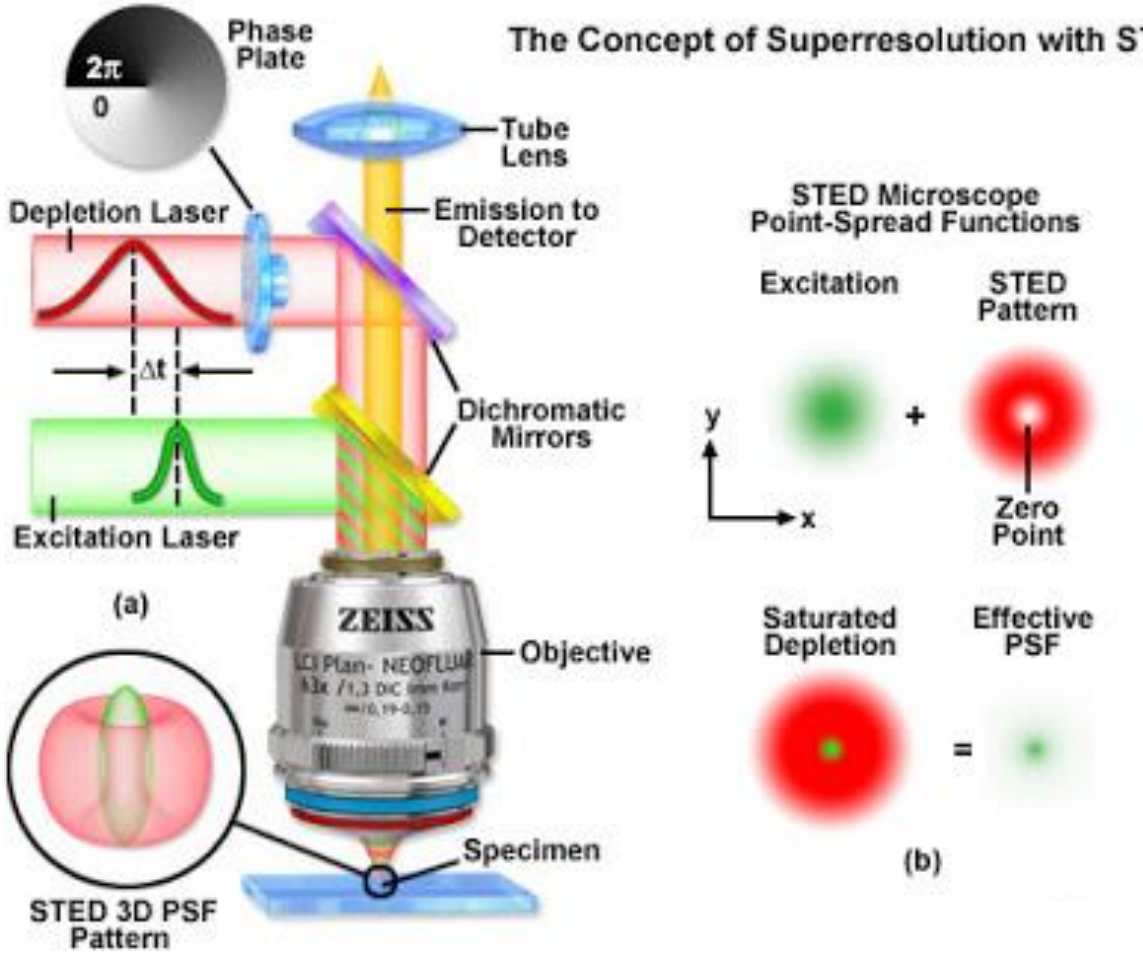


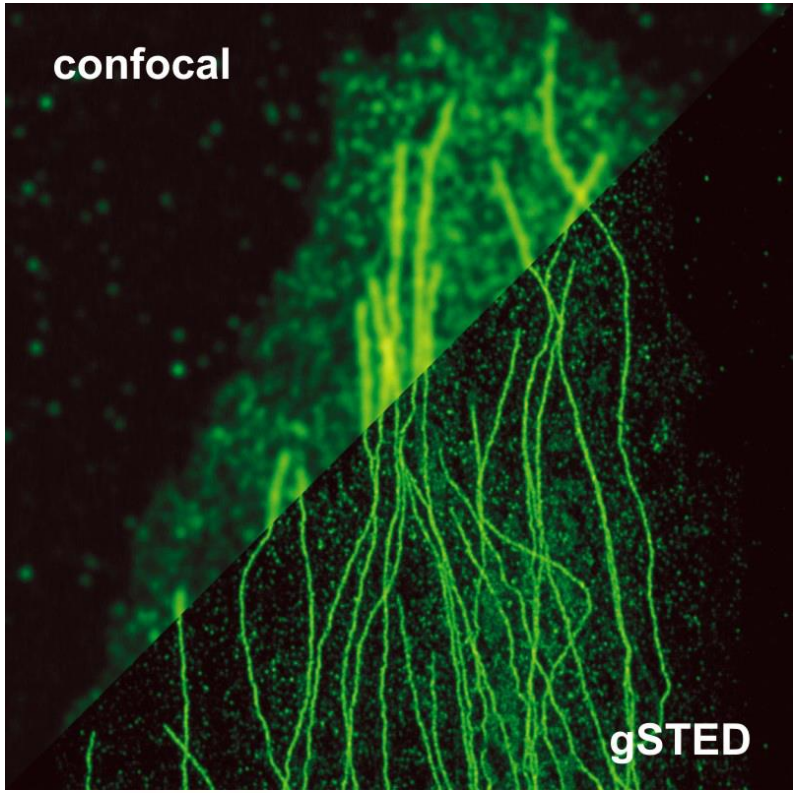




Tétreault N. et al. *Advanced Materials* **2006,** 18.4 , 457.

Enhancing resolution: from STED fluorescence microscopy

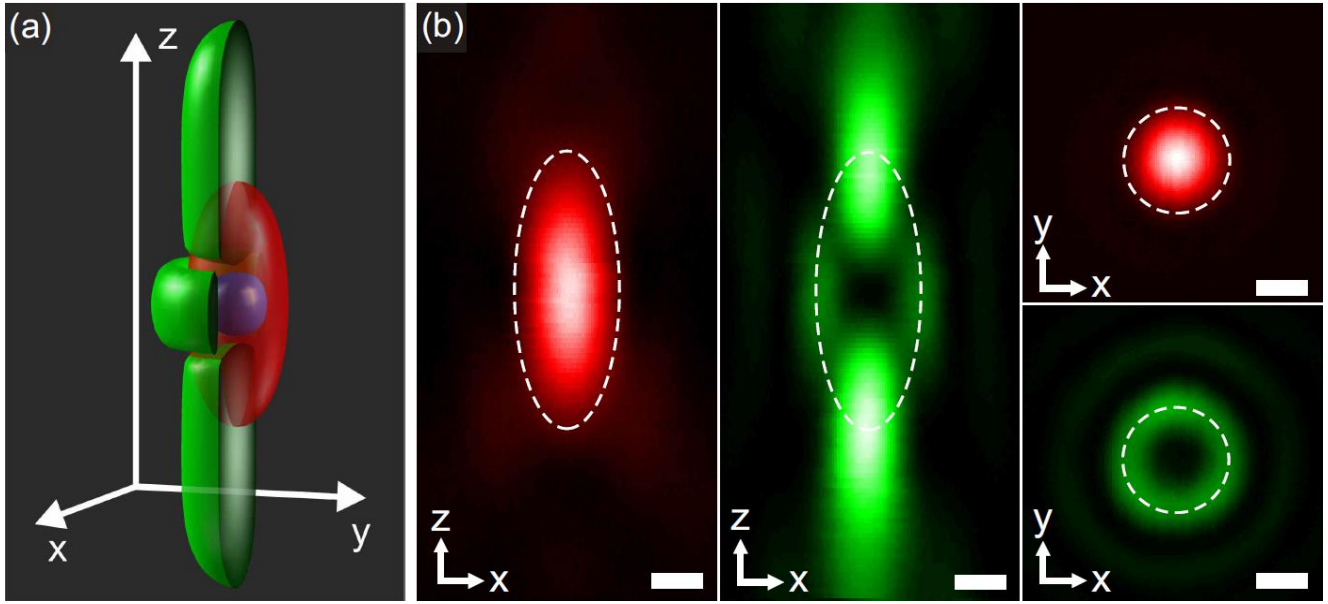


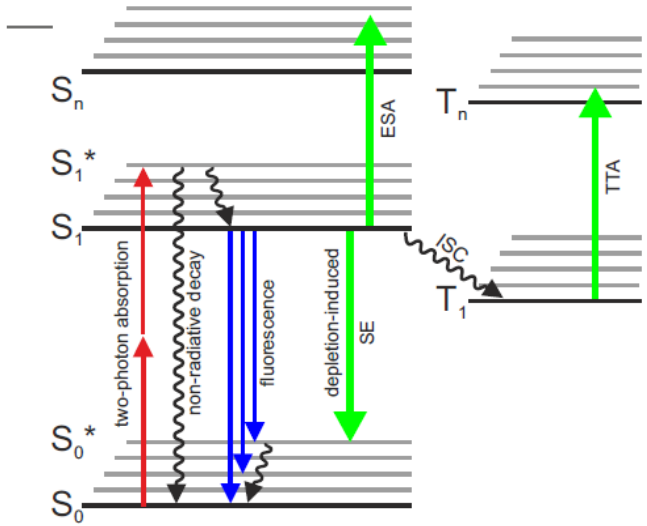


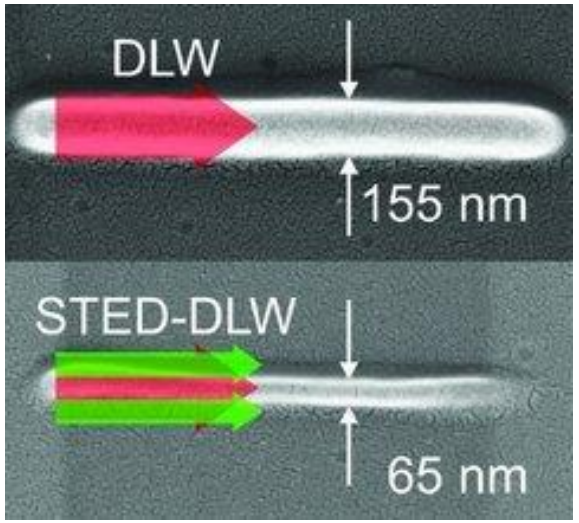
5.6 nm resolution using visible light

Hell, Stefan W., and Jan Wichmann, *Optics letters* **1994,** 19.11, 780.

Enhancing resolution: STED lithography



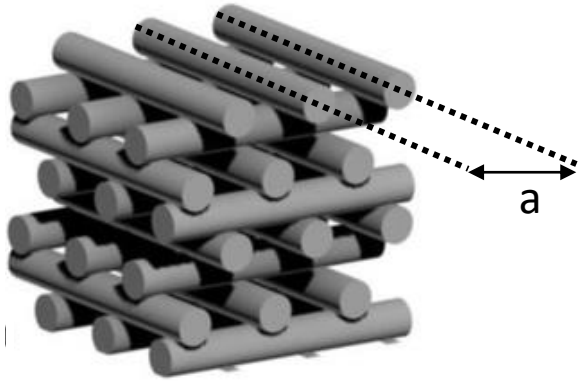


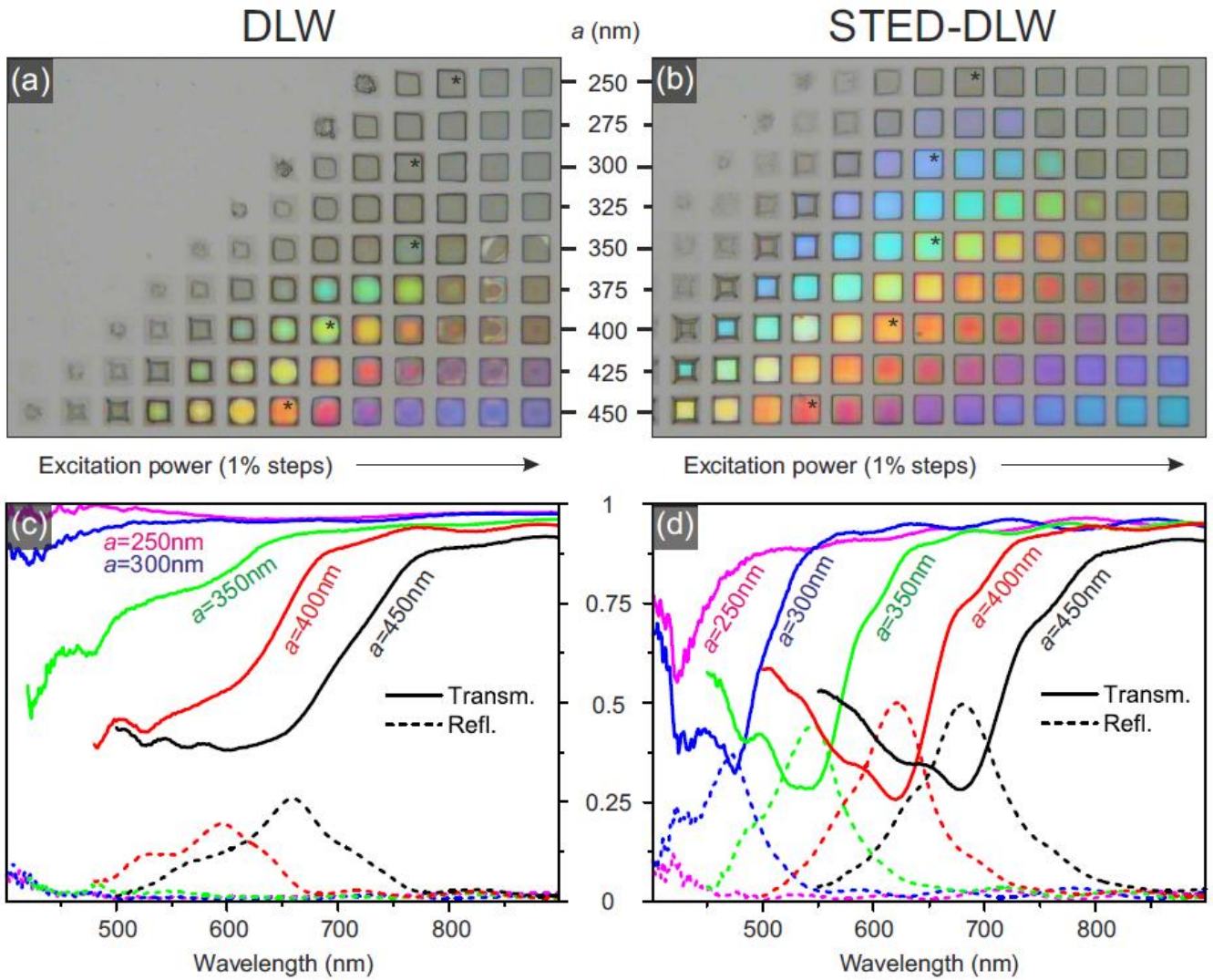


Diffraction unlimited lithography

Fischer J.,… Wegener M., *Advanced materials* **2010,** 22.32, 3578.

Enhancing resolution: STED lithography

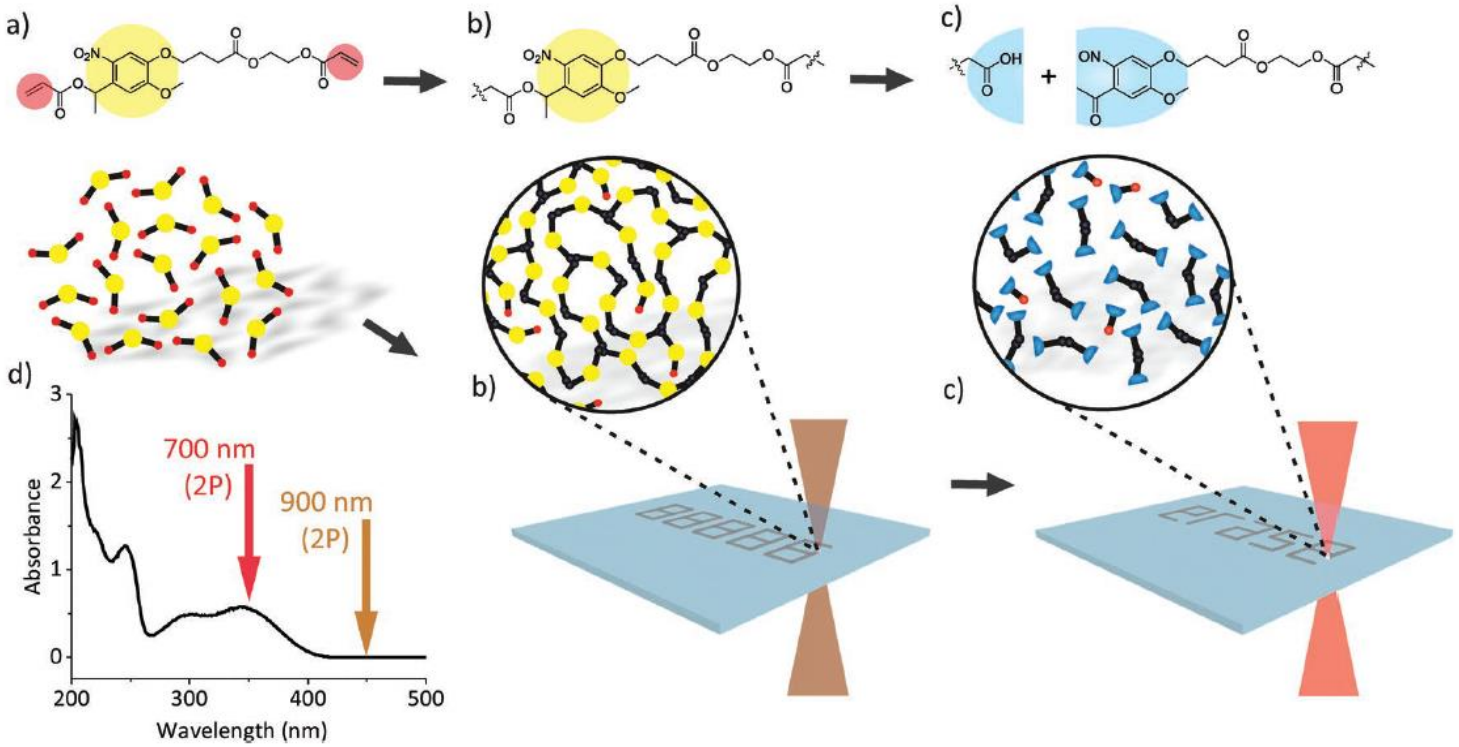




Fischer J., Wegener M., *Optical Materials Express* **2011,** 1.4, 614.

Functional polymers: Printing and erasing by light

photocleavable
o-nitrobenzyl group



Batchelor R., et al., Advanced *Materials* **2019,** 31.40, 1904085.

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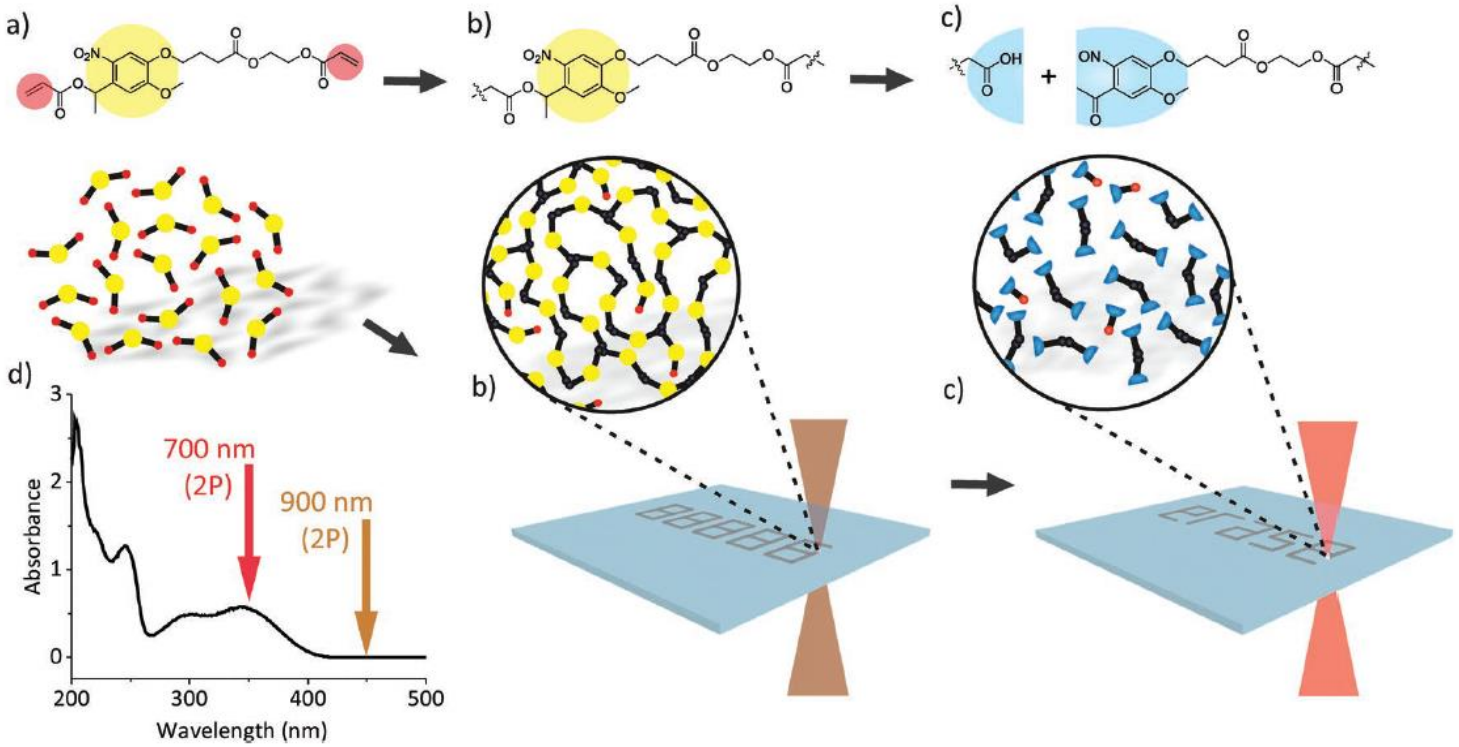
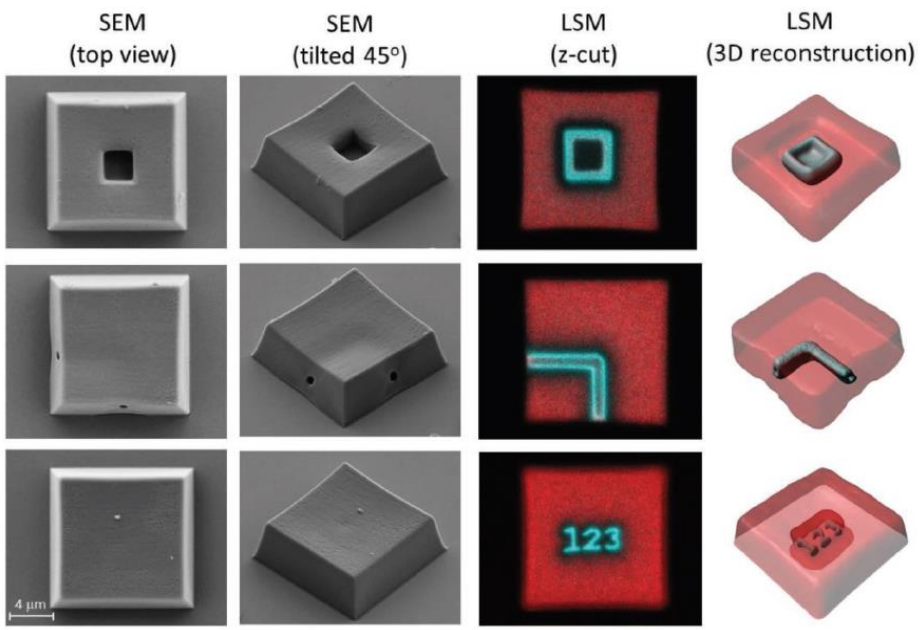
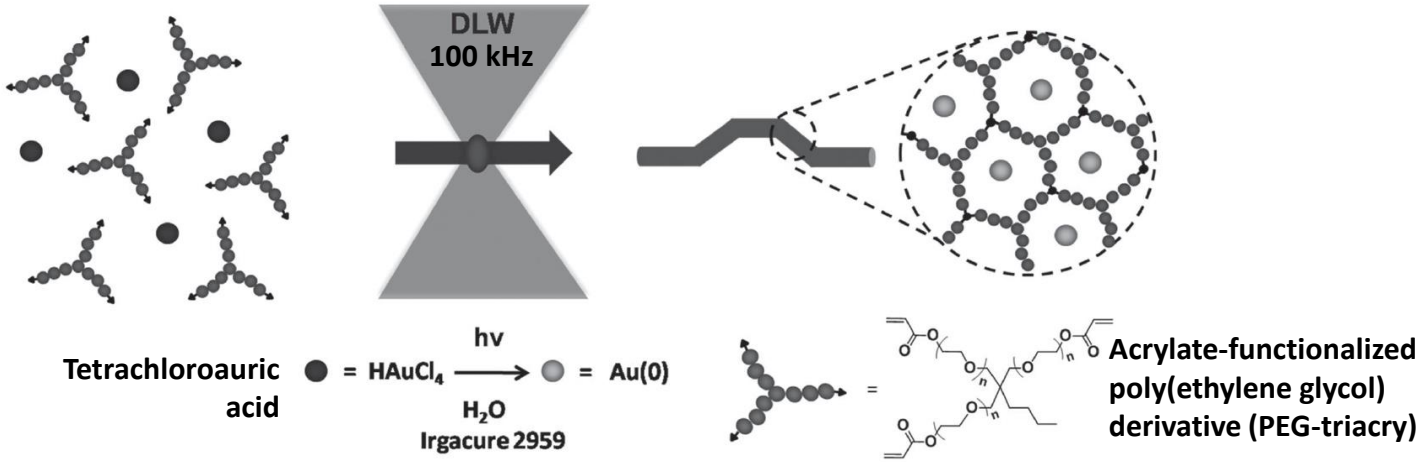


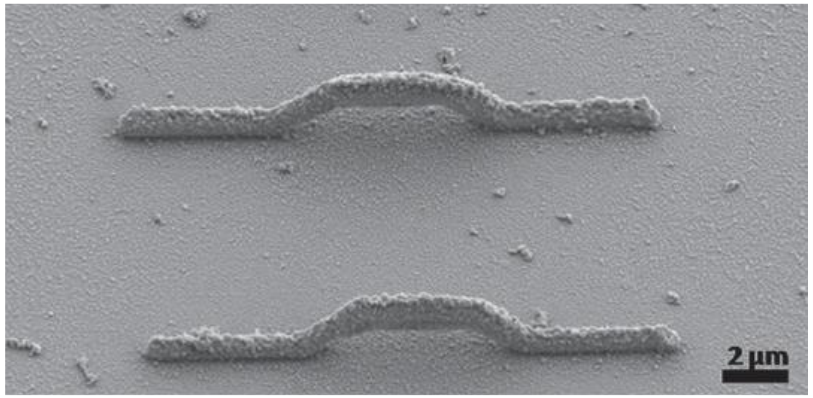


Batchelor R., et al., Advanced *Materials* **2019,** 31.40, 1904085.

Functional polymers: Conductive polymers

simultaneous photopolymerization and photoreduction of metallic salts





Blasco E., et al. " *Advanced Materials* **2016,** 28.18, 3592

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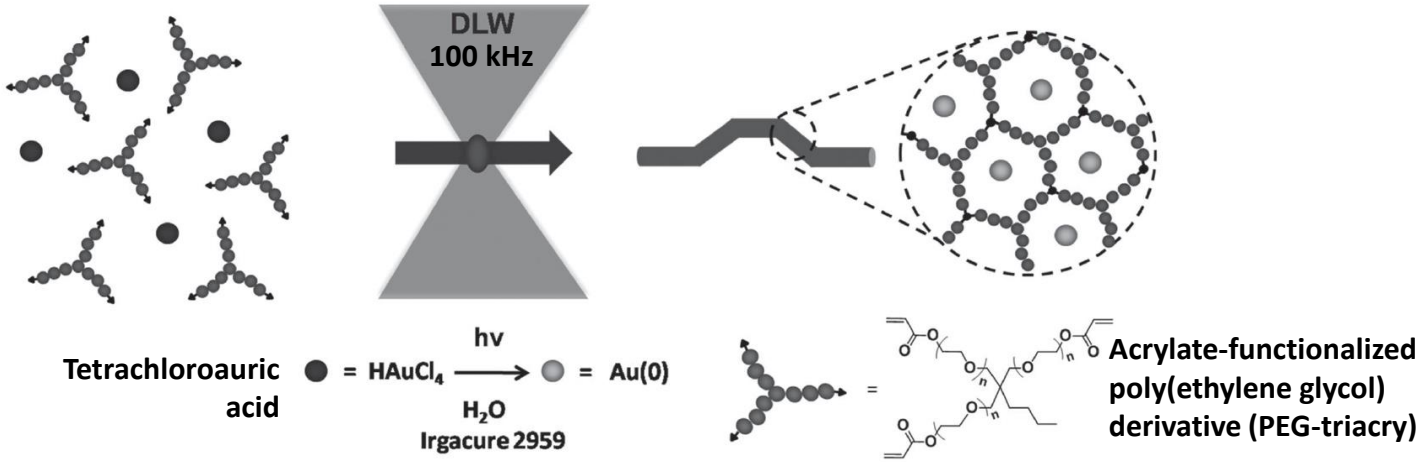
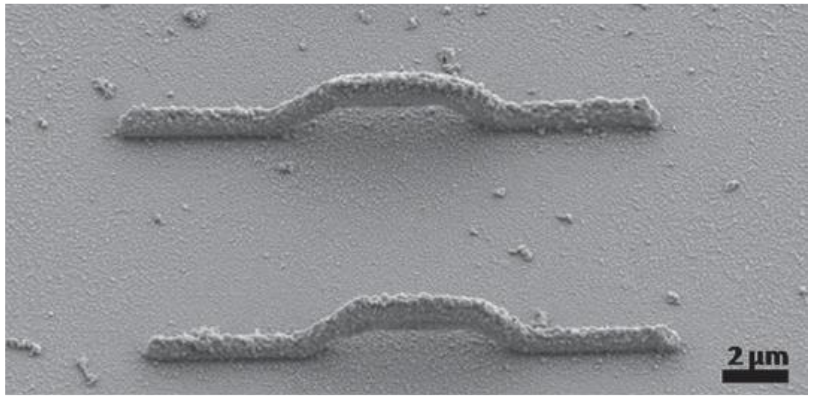
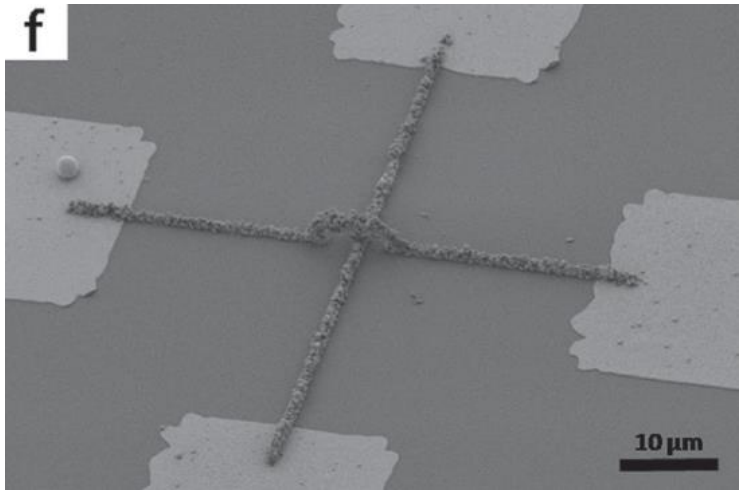
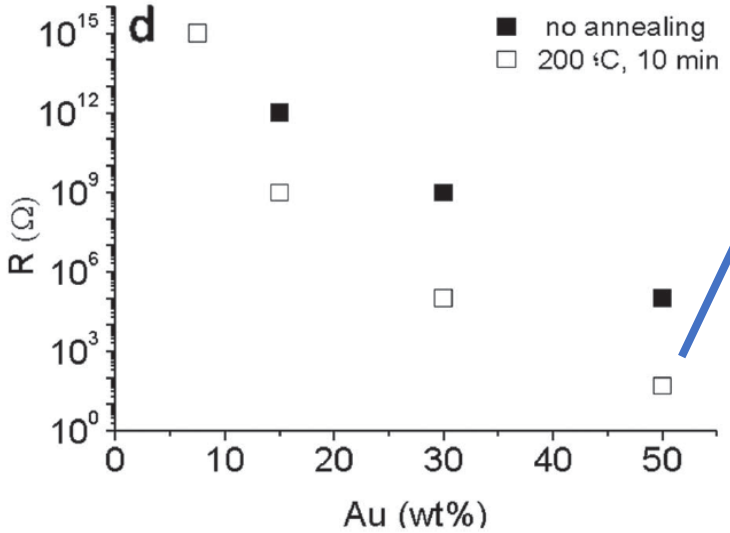




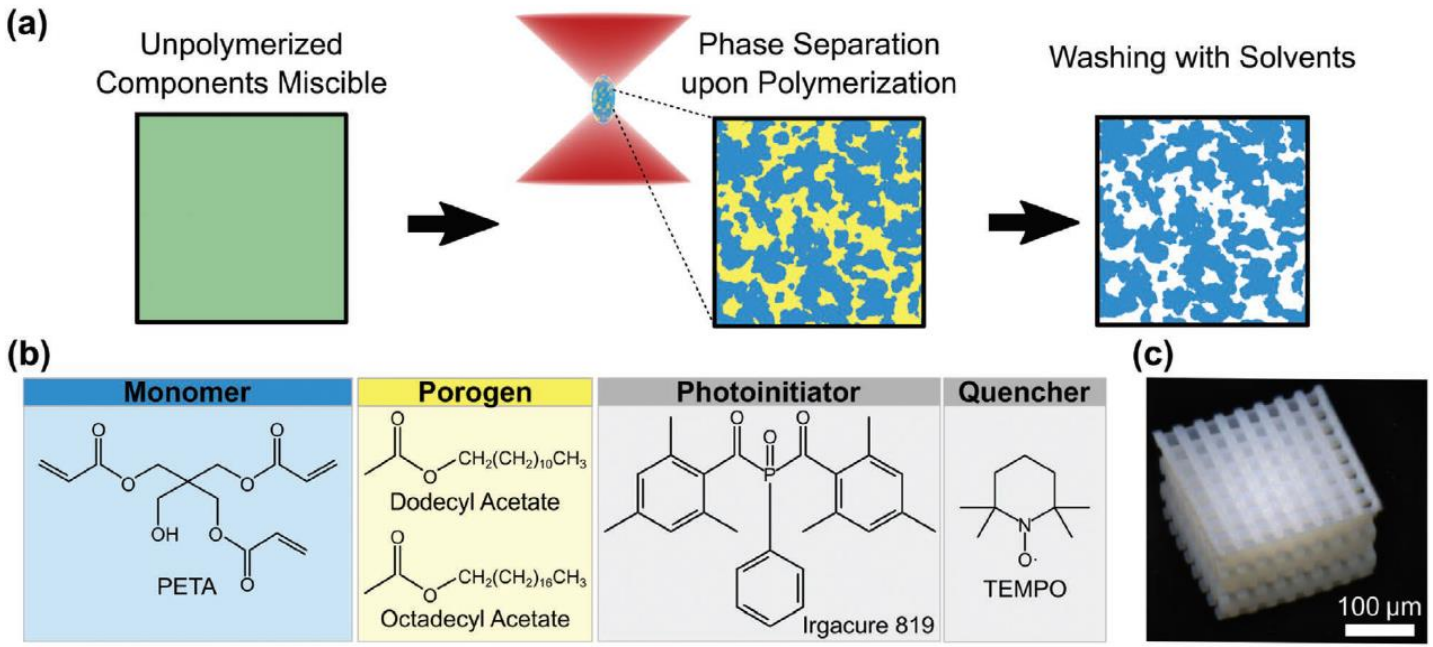


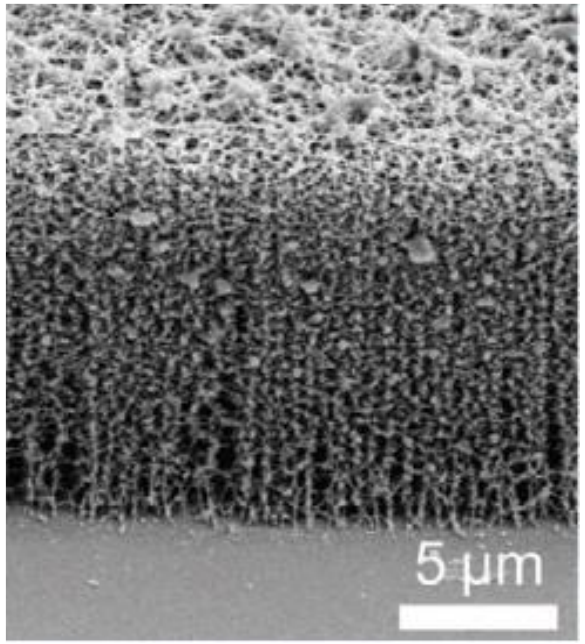


$\sigma = 2.2 \cdot 10^6$ S m^{-1}
20 times < bulk gold

Blasco E., et al. " *Advanced Materials* **2016,** 28.18, 3592

Functional polymers: Porous structures





Mayer F. et al., *Advanced Materials* **2020,** 32.32, 2002044.

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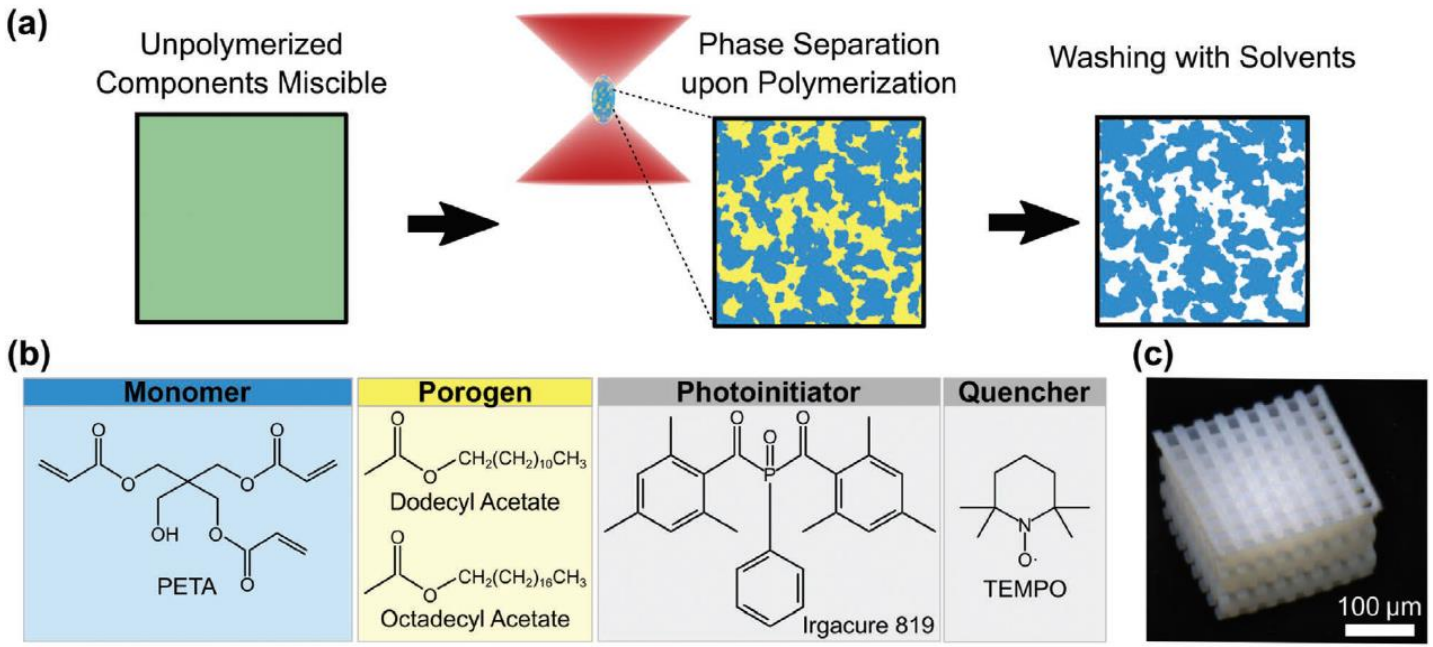
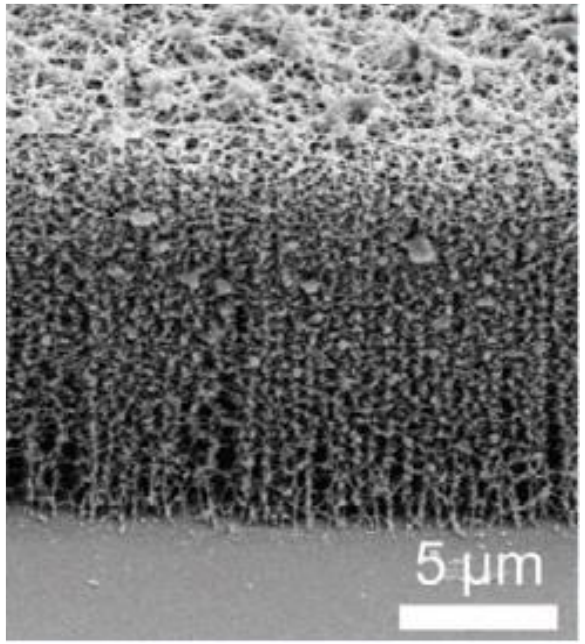
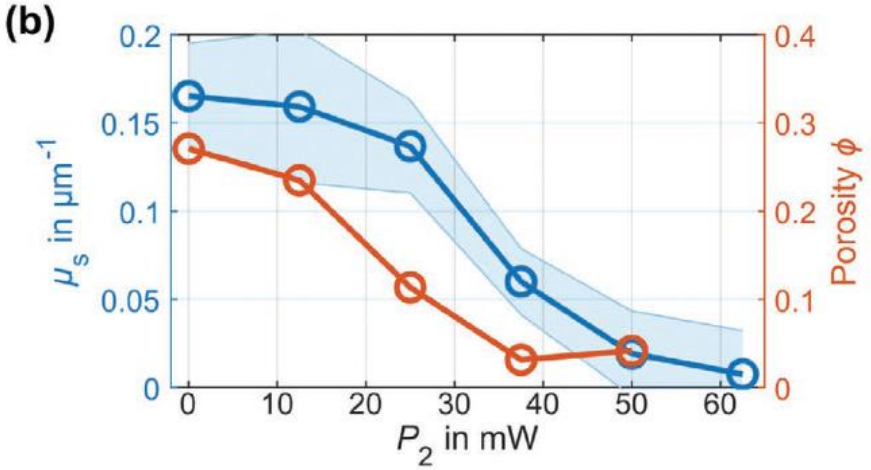
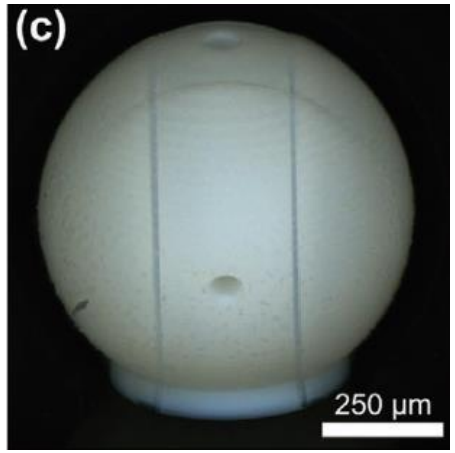


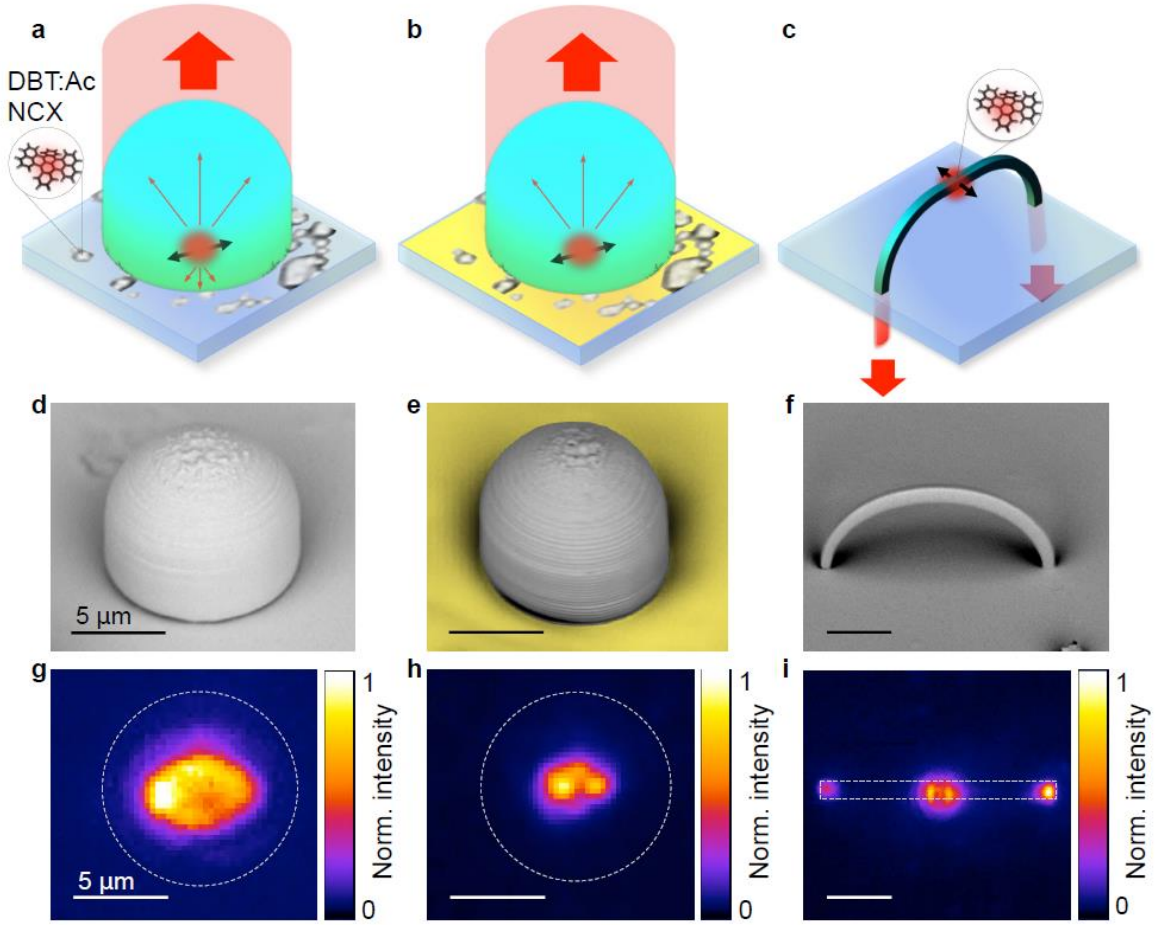


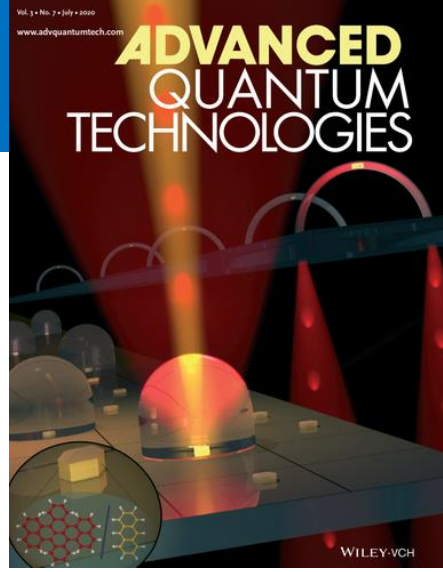




Mayer F. et al., *Advanced Materials* **2020,** 32.32, 2002044.

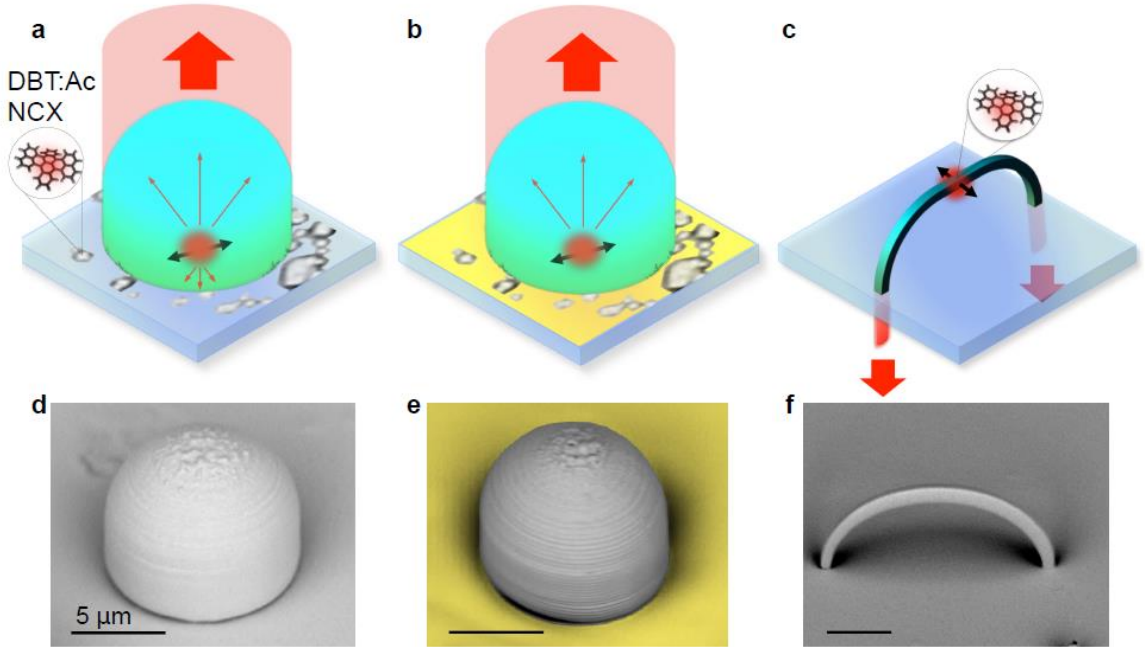
Functional polymers: Integration of quantum emitters

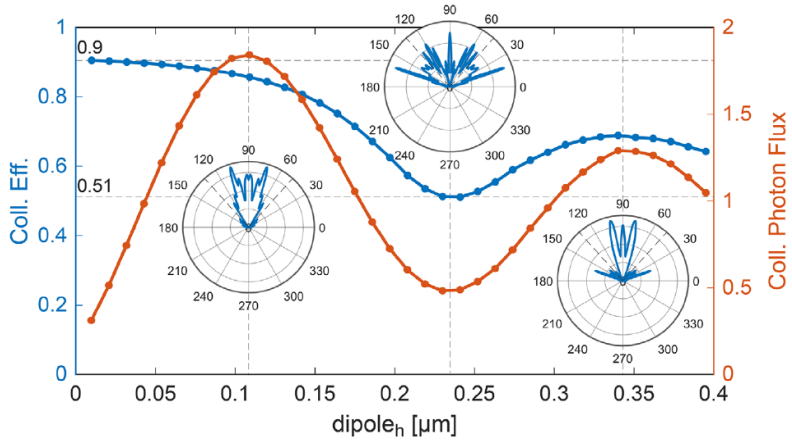


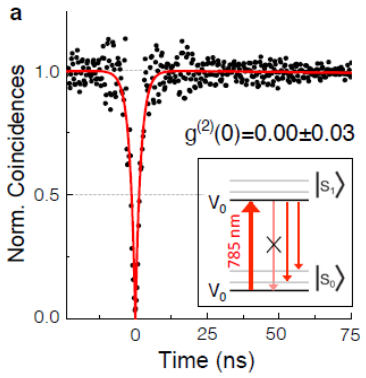


Colautti M., et al., *Advanced Quantum Techologies* **2020,** 2000004

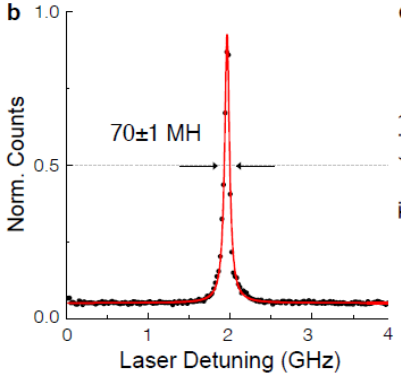
Functional polymers: Integration of quantum emitters



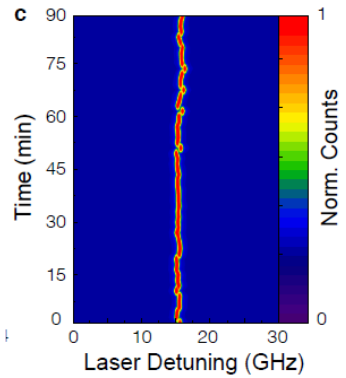




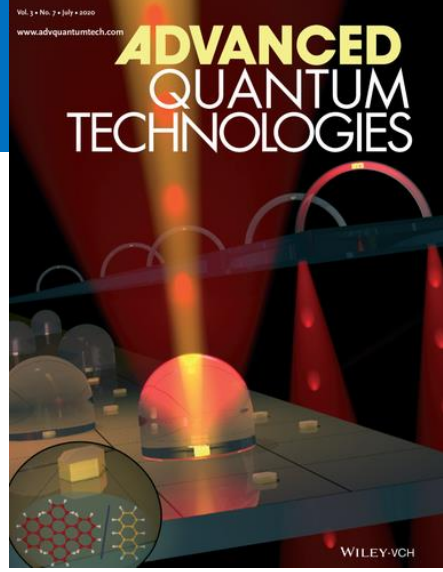
II order autocorrelation function



Life-time limited linewidth

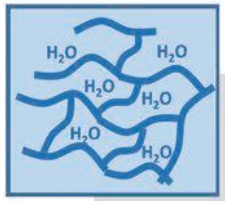


Photostability of molecule emission



Colautti M., et al., *Advanced Quantum Techologies* **2020,** 2000004

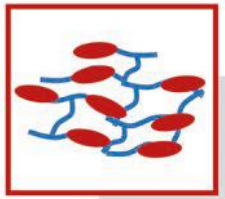
Functional polymers: 4D Microprinting



Hydrogel-based Microstructures

Photoresists:
- Acrylate-based hydrogels
- Acrylamide-based hydrogels
- Protein systems

Applications:
- Soft Microrobotics: microactuators, microgrippers
- Microfluidics



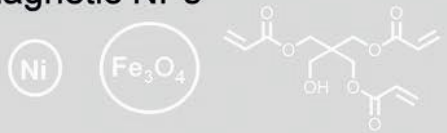
Liquid Crystalline Microstructures

Photoresists:
- Liquid crystalline monomers

Applications:
- Microrobotics
- Tunable optics

Composite Microstructures

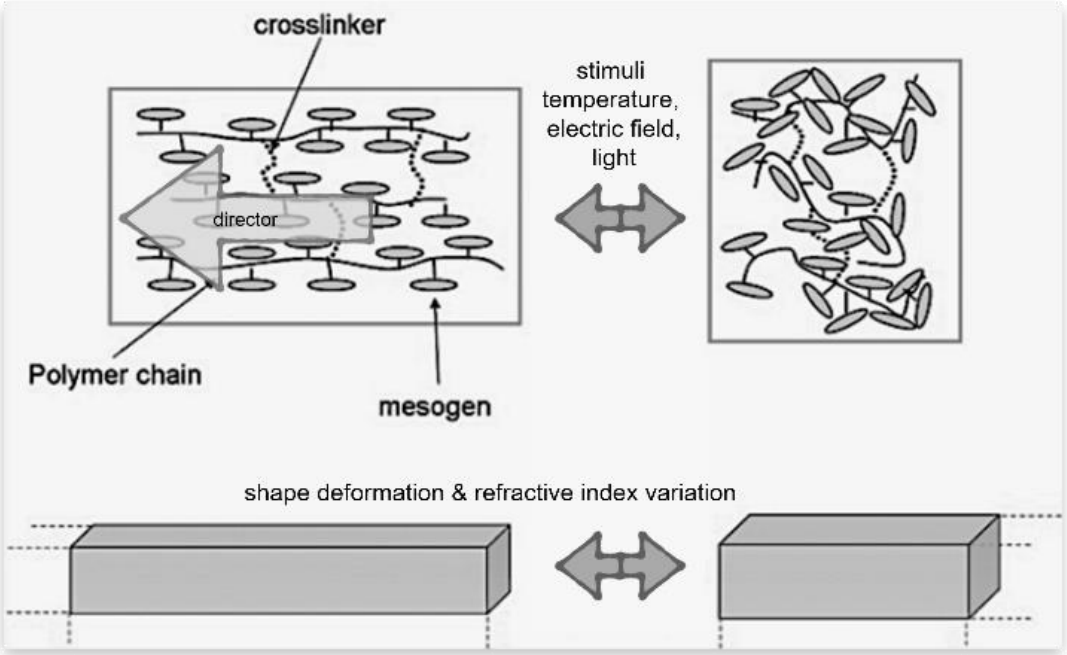
Photoresists:
- Acrylate-based monomers (+ post-metallization)
- Dispersion of acrylate-based monomers and magnetic NPs

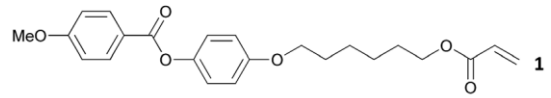


Applications:
- Microswimmers
- Microobject manipulation
- Drug and cell delivery

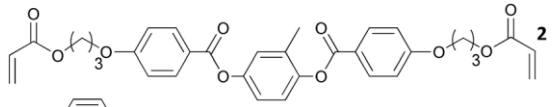
Spiegel C., et al., *Advanced Functional Materials* **2019,** 1907615

Liquid crystalline networks

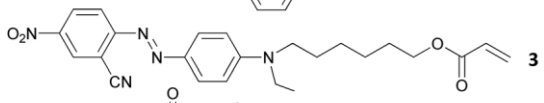




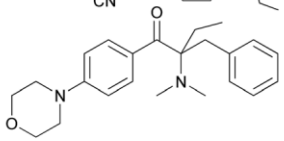
Mesogen



Cross-linker

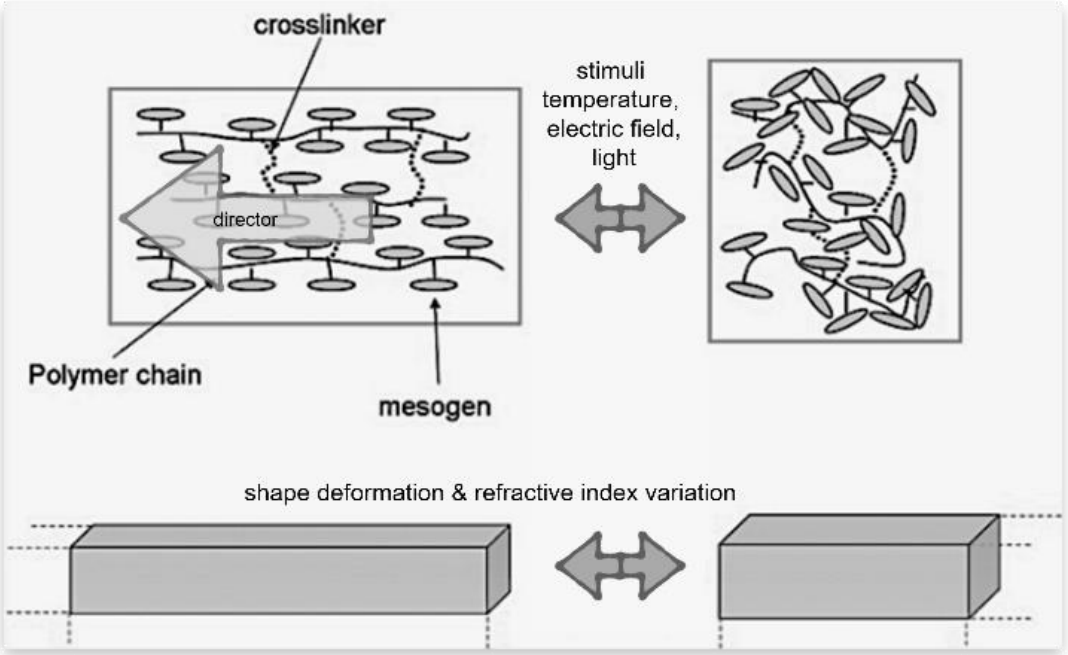


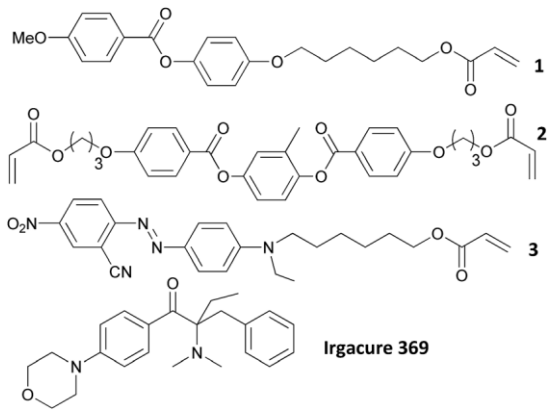
Azo-dye



Photoinitiator

Liquid crystalline networks





Mesogen

Cross-linker

Azo-dye

Photoinitiator

LIGHT

Local stimulus

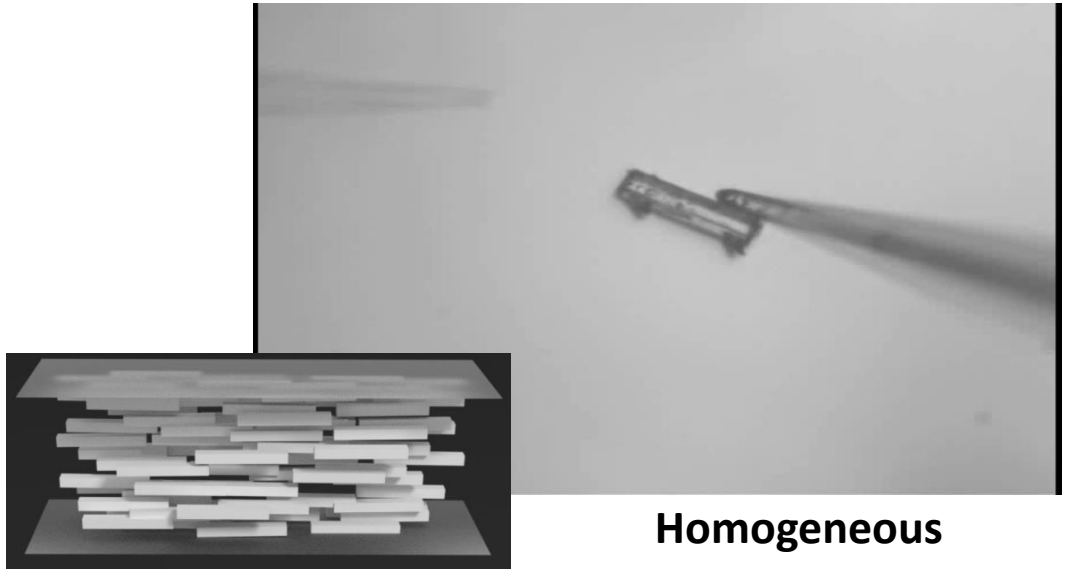
Space and time modulation

Multi-parametric control

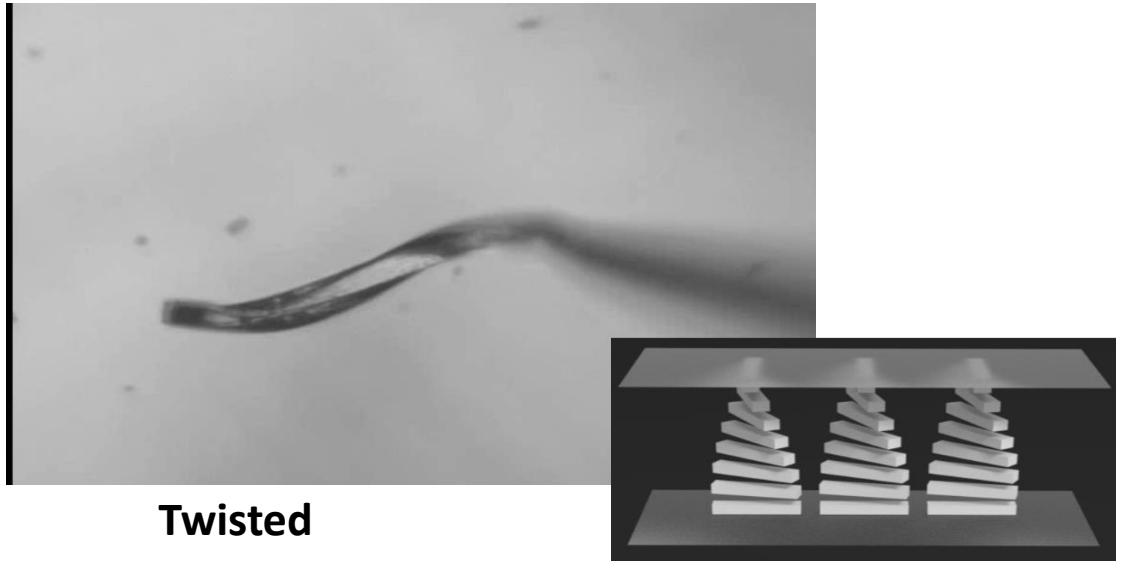
Non-invasive and remote actuation

Dry environments

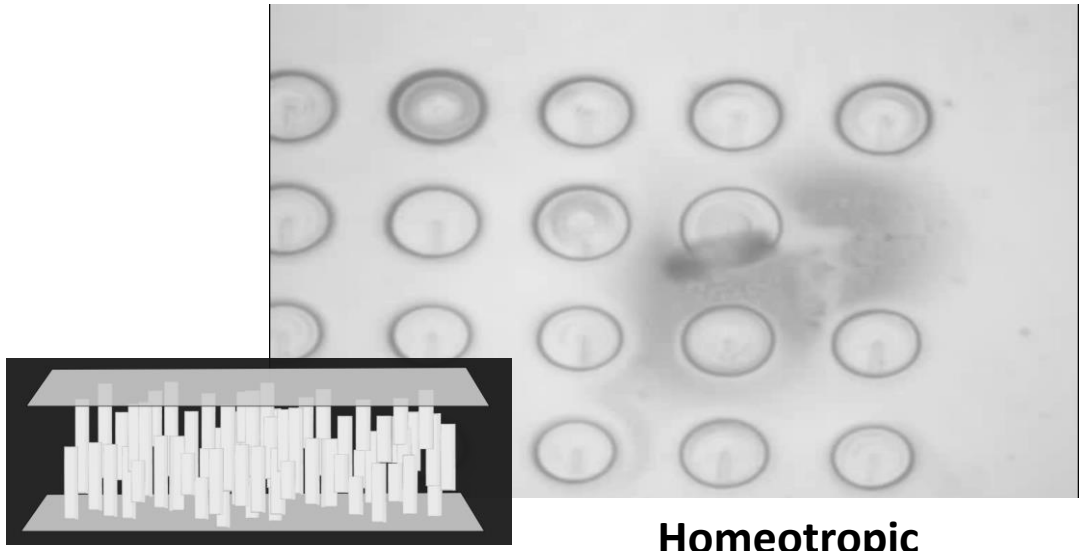
Liquid crystalline elastomer: alignments and deformations



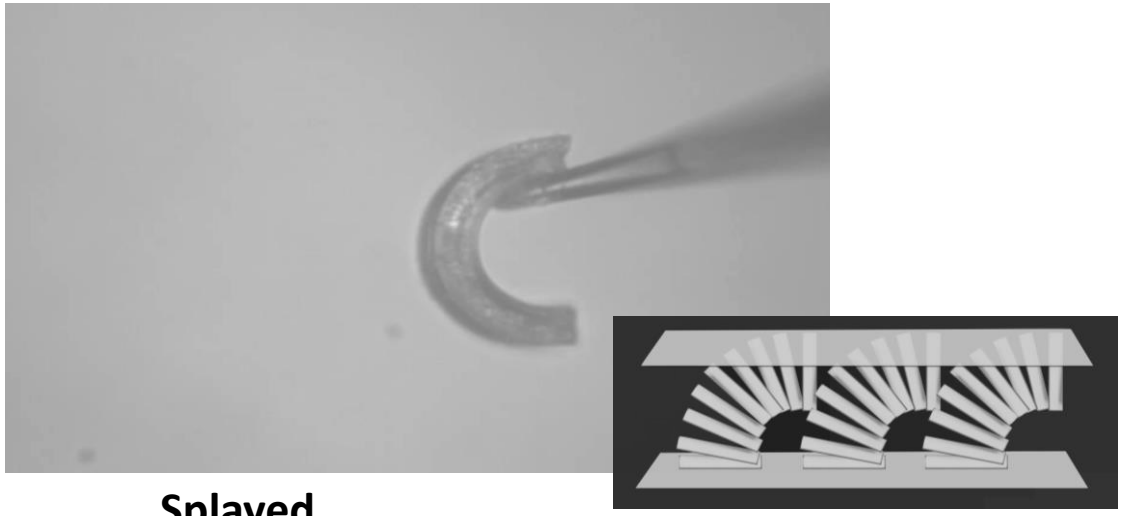
Homogeneous



Twisted

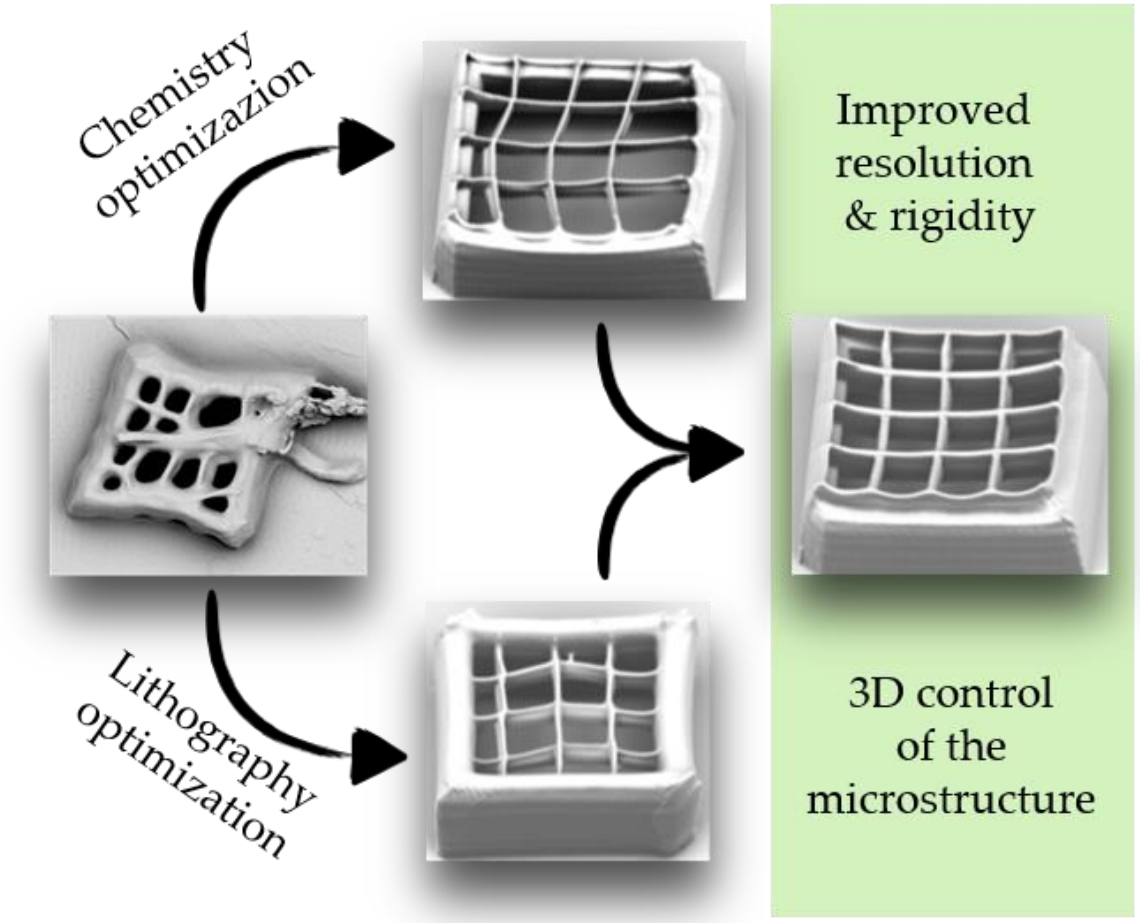


Homeotropic



Splayed

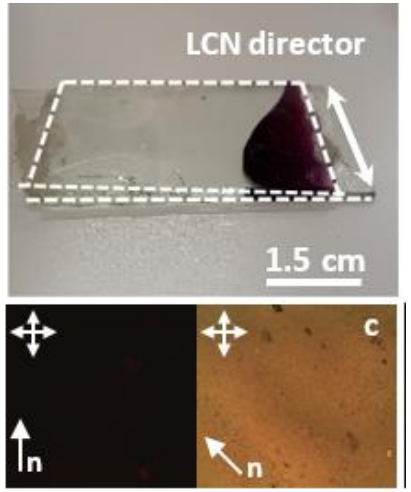
New mixtures and DLW



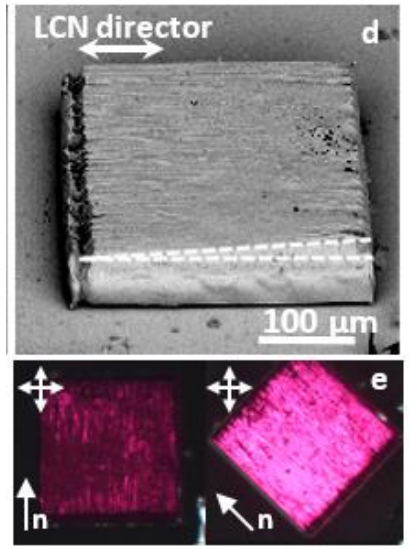
Nocentini S., et al., *Materials* **2016,** 9.7, 525.

Liquid crystalline mixtures: Refractive index characterization

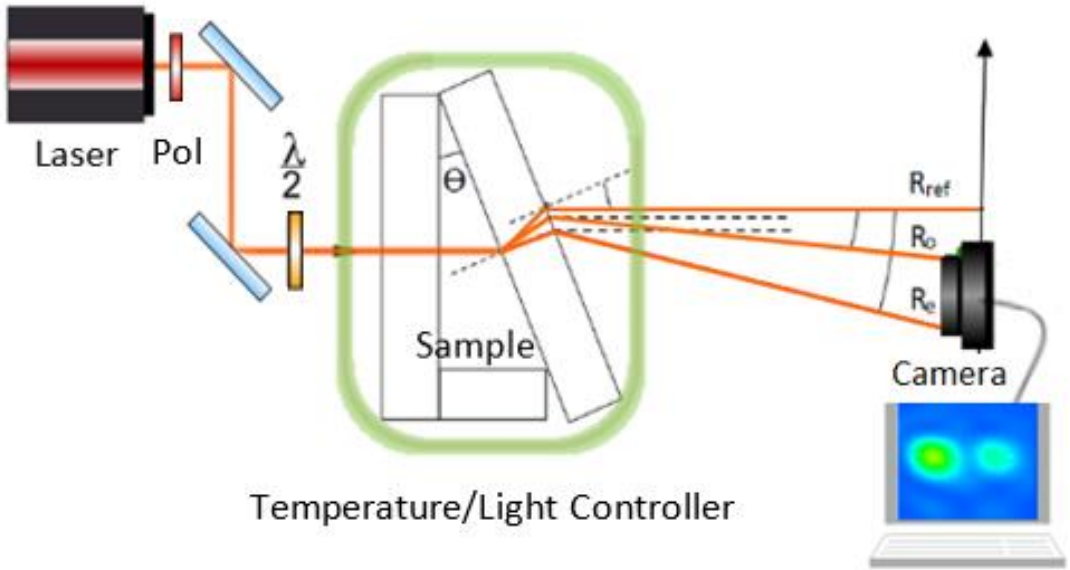
Macroscopic wedge

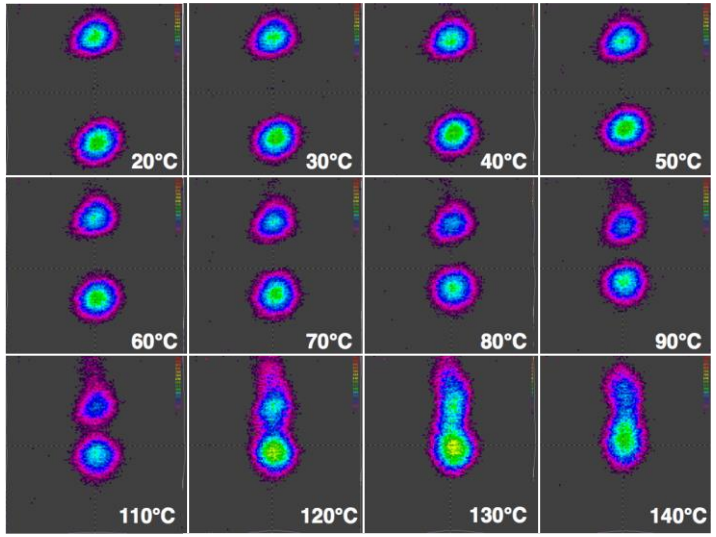


Microscopic wedge



Refractometer method



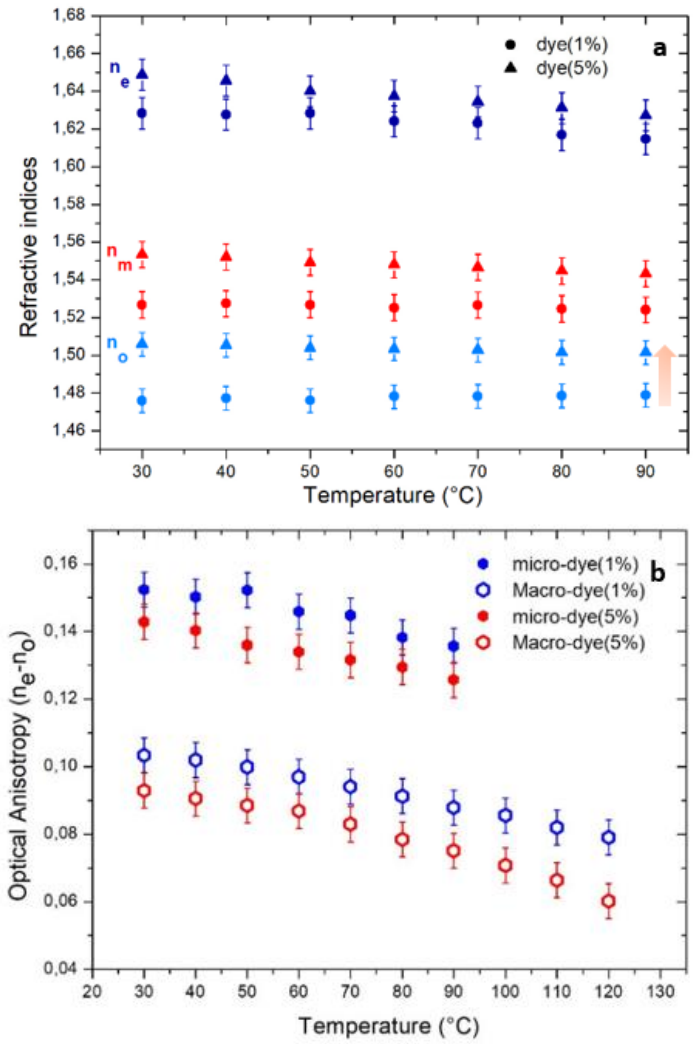


De Bellis I., et al., *Journal of Physical Chemistry C* **2019,** 123.43, 26522

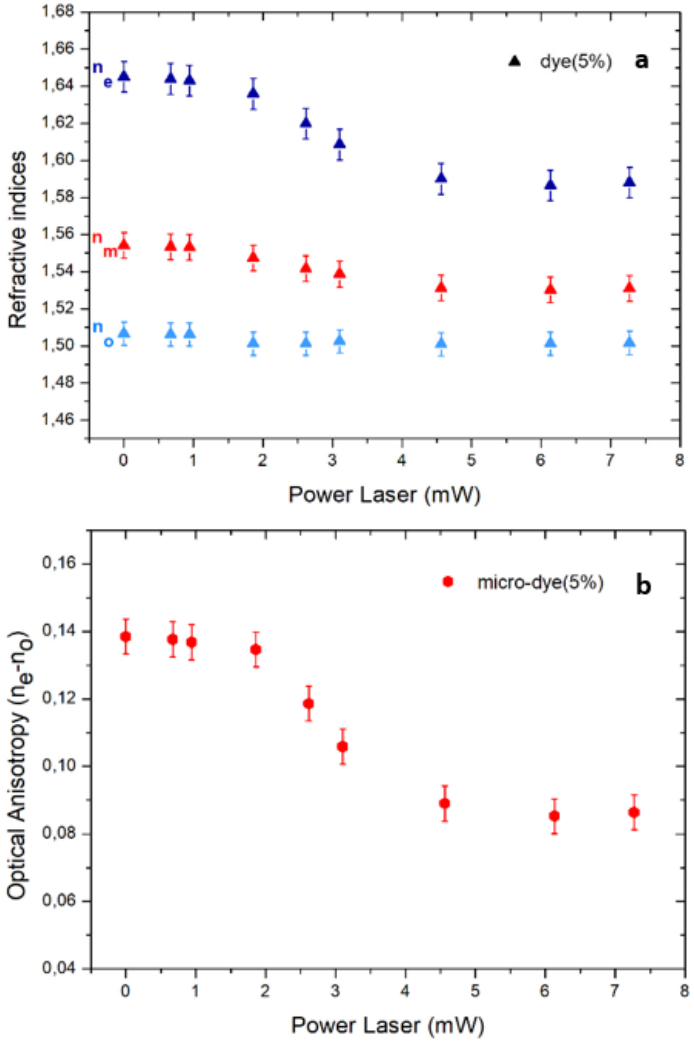
Liquid crystalline mixtures: Refractive index characterization

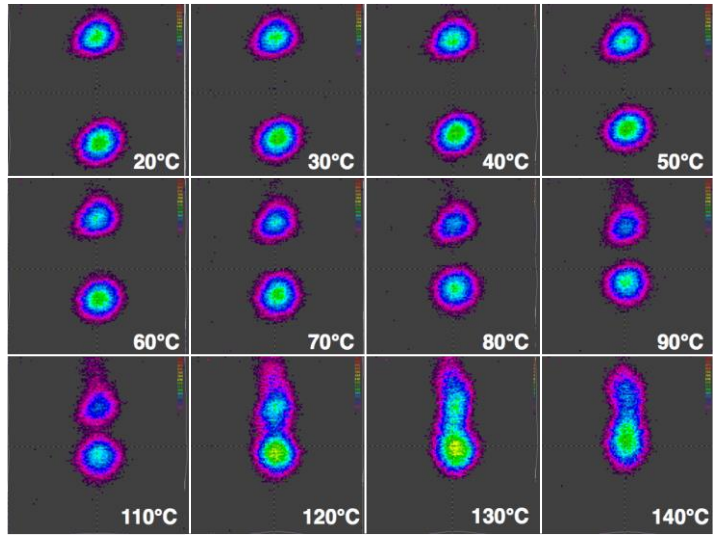
Refractometer method for the MICRO wedge

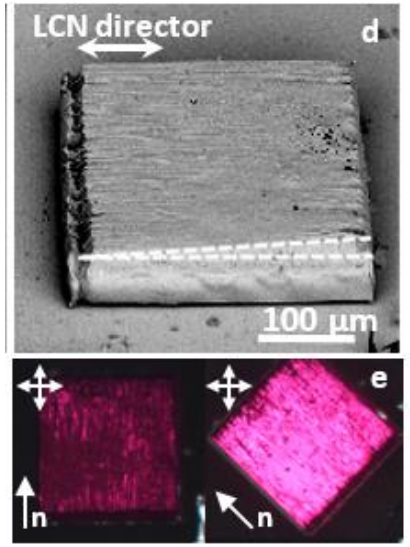
Temperature tuning



Light tuning

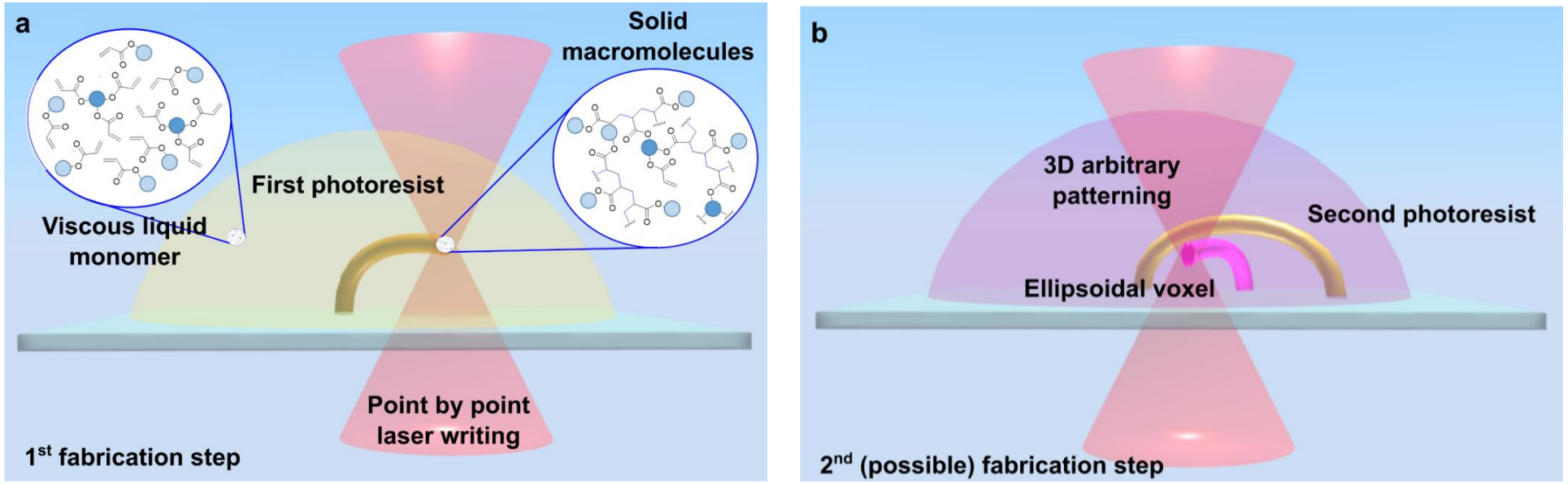






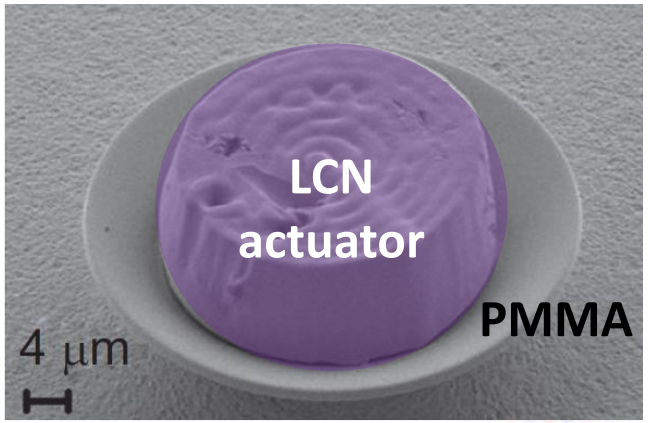
De Bellis I., et al., *Journal of Physical Chemistry C* **2019,** 123.43, 26522

Liquid crystalline mixtures & DLW for photonics and microrobotics

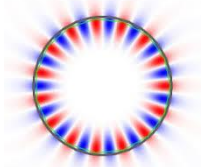


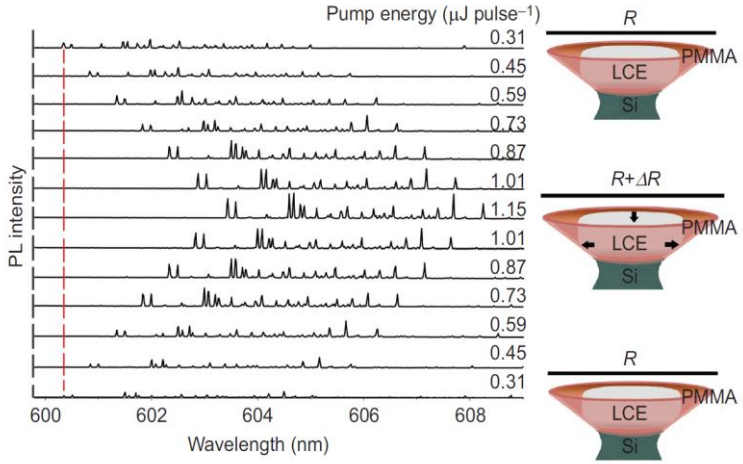
Liquid crystalline mixtures & DLW for photonics

A light tunable microlaser

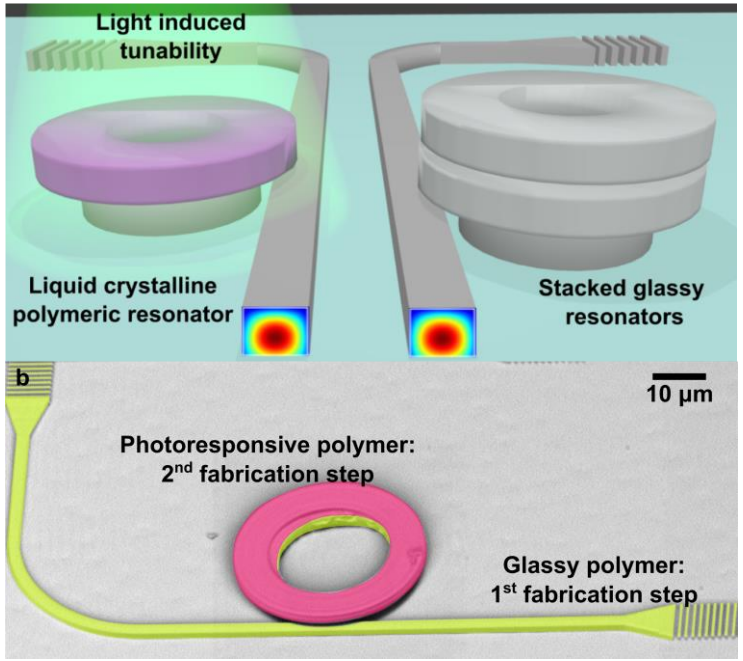


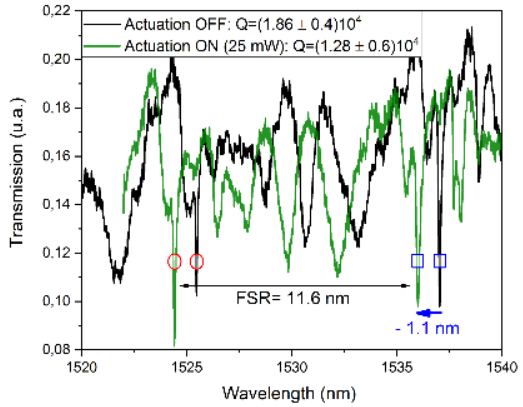
$$2\pi R\, n_{eff} = m\lambda$$



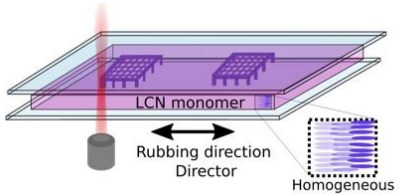


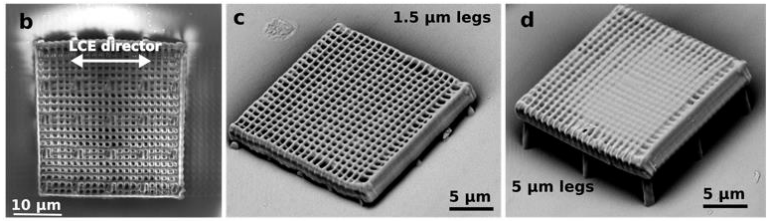
Optically controlled 3D photonic circuits

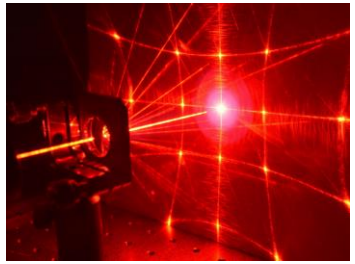


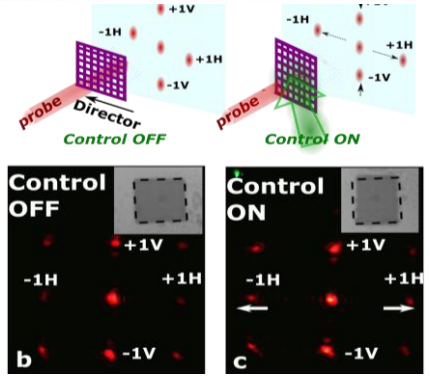


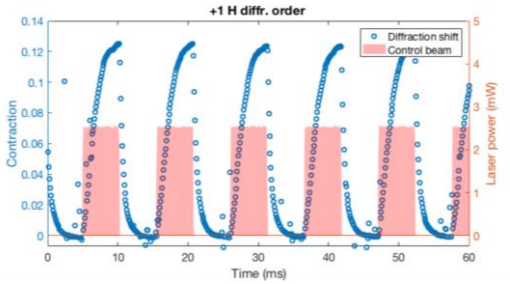
A light controlled beam steerer





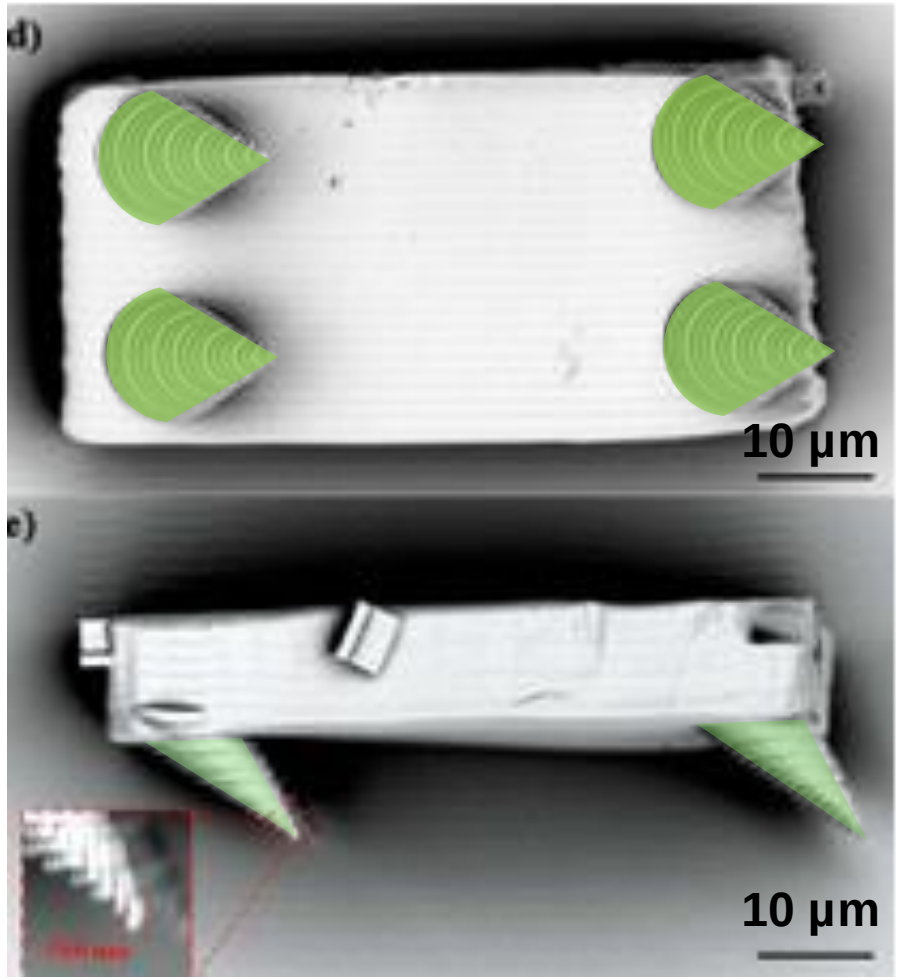






Flatae A. M., et al. "*Light: Science & Applications* **2015,** 4.4, e282; Nocentini S., et al., *ACS Photonics* **2018** 5.8, 3222; Nocentini S., et al., *Advanced Optical Materials* **2018,** 6.15, 1800167

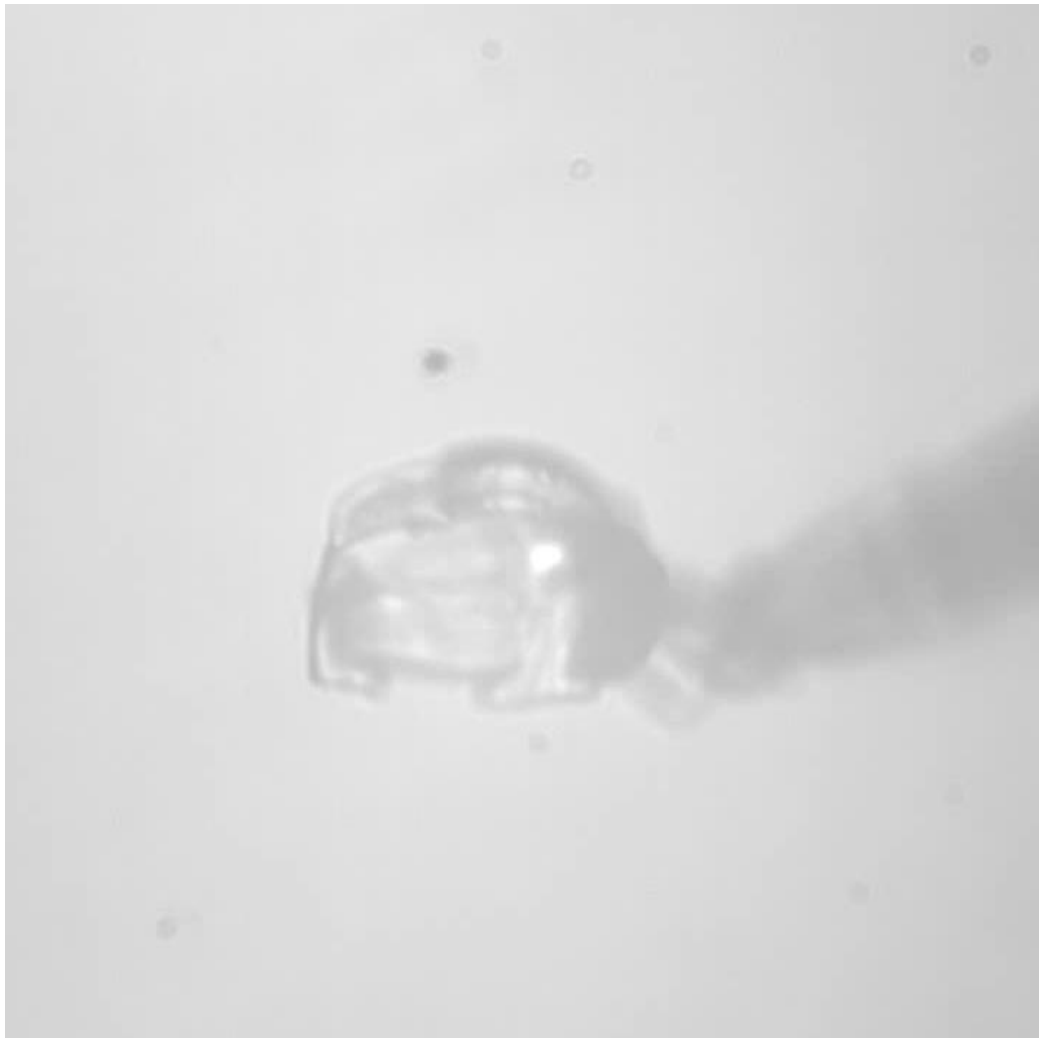
Liquid crystalline mixtures & DLW for microrobotics

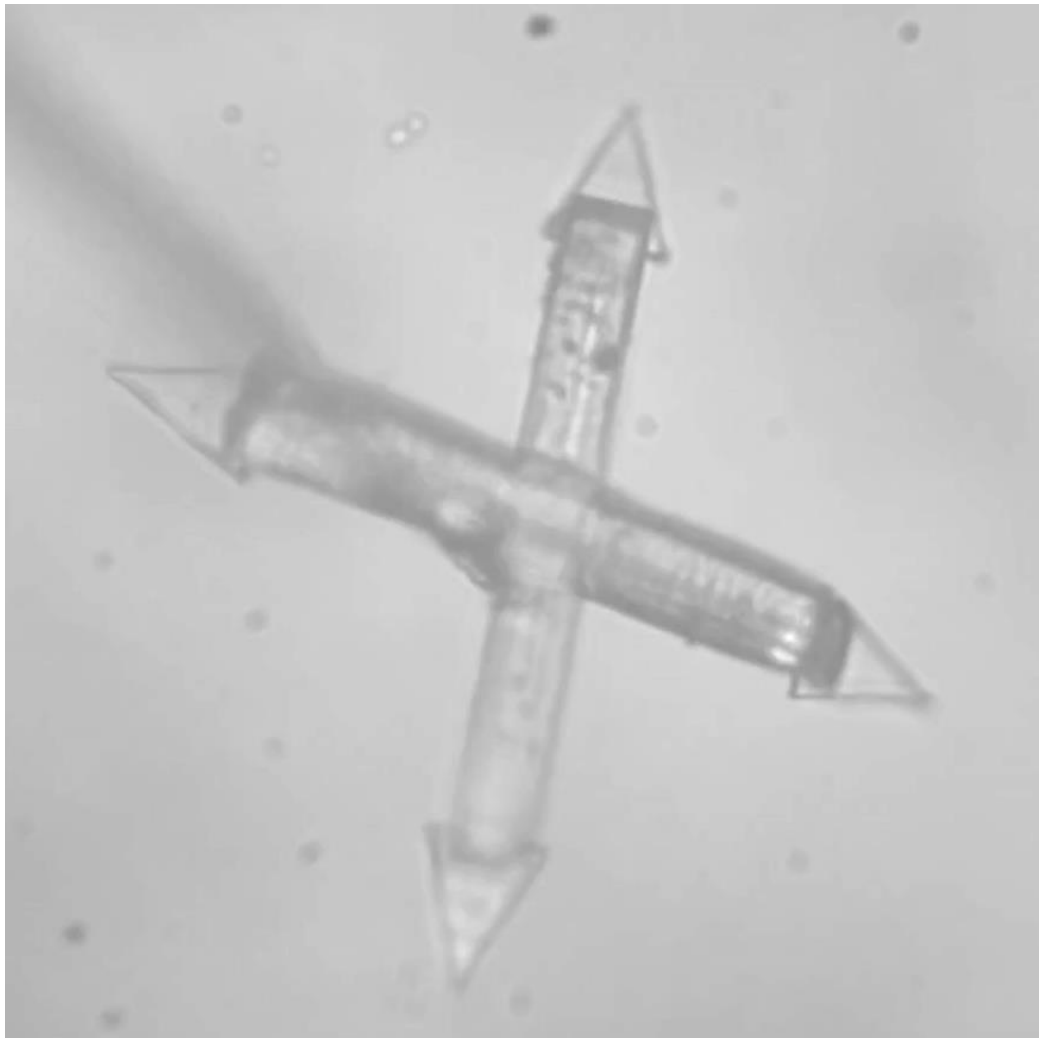


The light fueled micro walker

Zeng H. et al., *Advanced Materials* **2015,** 27.26, 3883.

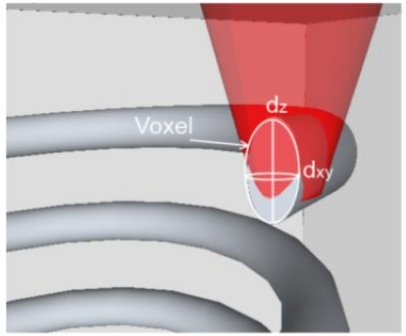
Liquid crystalline mixtures & DLW for microrobotics





D. Martella, S. Nocentini et al., *Adv. Mater.* **2017**, *29.42: 1704047*

Direct laser writing



3D photolithography based on two photon absorption polymerization

- Arbitrary 3D design (CAD models)
- Different applications
- Large choice of materials
- Tailor the polymer properties
- 4D microprinting
- ….new ideas?!….

Thank you for your attention

Time for questions!

INRiM ISTITUTO NAZIONALE DI RICERCA METROLOGICA

Lens European Laboratory for Non-Linear Spectroscopy

KIT Karlsruhe Institute of Technology

CNR-INO ISTITUTO NAZIONALE DI OTTICA CONSIGLIO NAZIONALE DELLE RICERCHE