

Additive manufacturing of intelligent light-responsive devices

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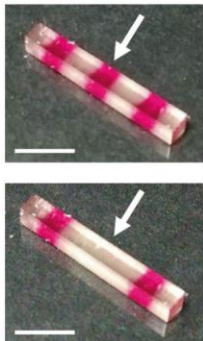


Dipartimento di Fisica "E. Fermi"
UNIVERSITÀ DI PISA



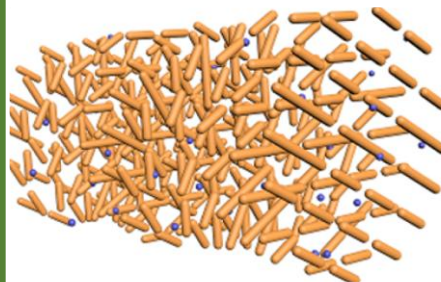
Soft Matter Nanotech group presentation

Photonics



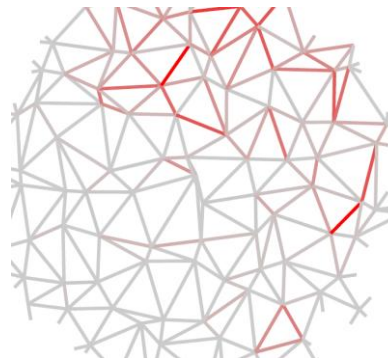
Light Sci. Appl.
2025, 14, 375

Spectroscopy



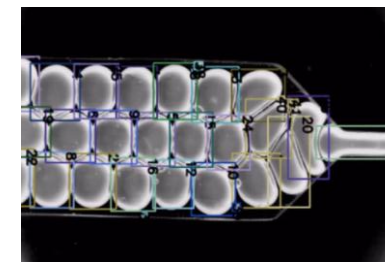
ACS Nano **2021**,
15, 8753-8760

Nano-networks



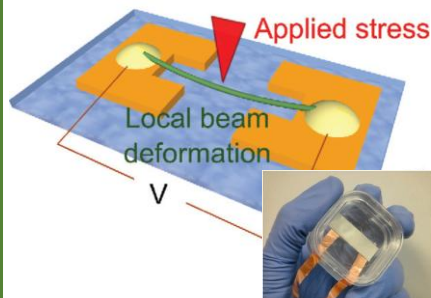
Nature Commun.
2022, 13, 6493

Advanced Lithographies and μ Fluidics



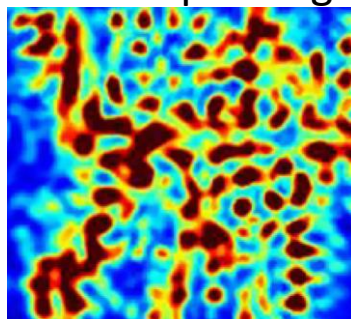
Appl. Phys. Rev.
2025, 12, 011306

Nanogenerators



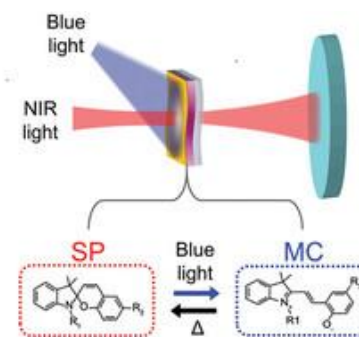
Adv. Mater. **2025**,
36, 2405363

Intelligent systems and 4D printing



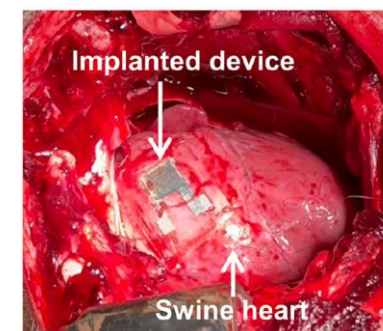
Nature Commun.
2020, 11, 5991

Optomechanics



Adv. Opt. Mater.
2025, 13, 2402883

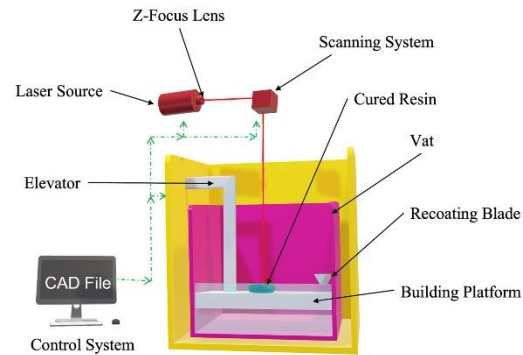
Nanobiotech



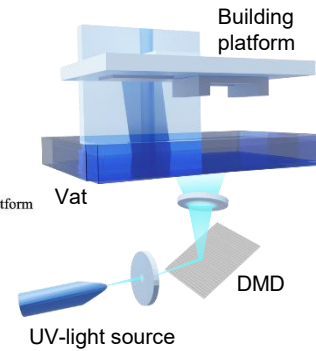
Sci. Adv. **2025**, 11,
eads0778

Additive manufacturing

Stereolithography

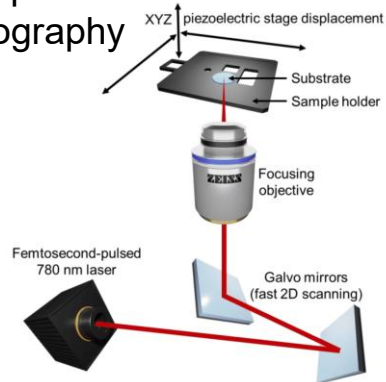


Digital Light Processing

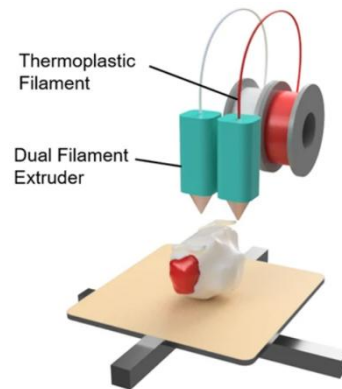


3D → 4D

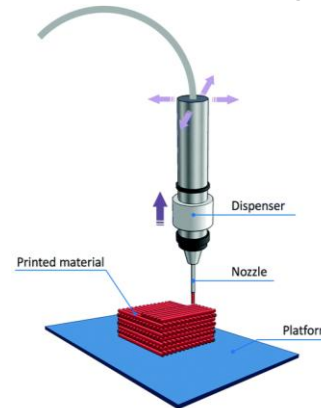
Two-photon Lithography



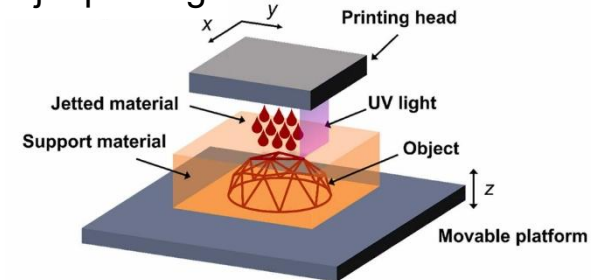
Fused deposition modeling



Direct ink writing



Inkjet printing

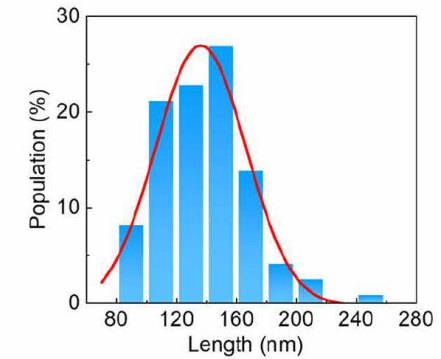
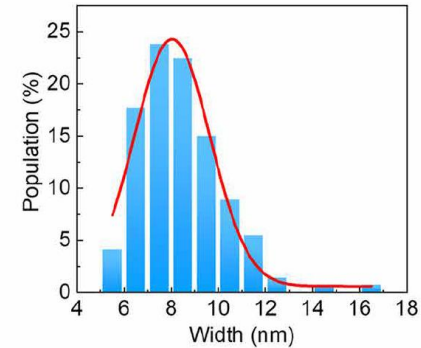
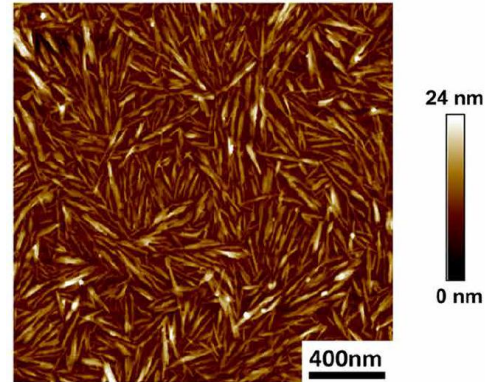


- ✓ Digital model
- ✓ Layer-by-layer fabrication
- ✓ Post-processing finishing

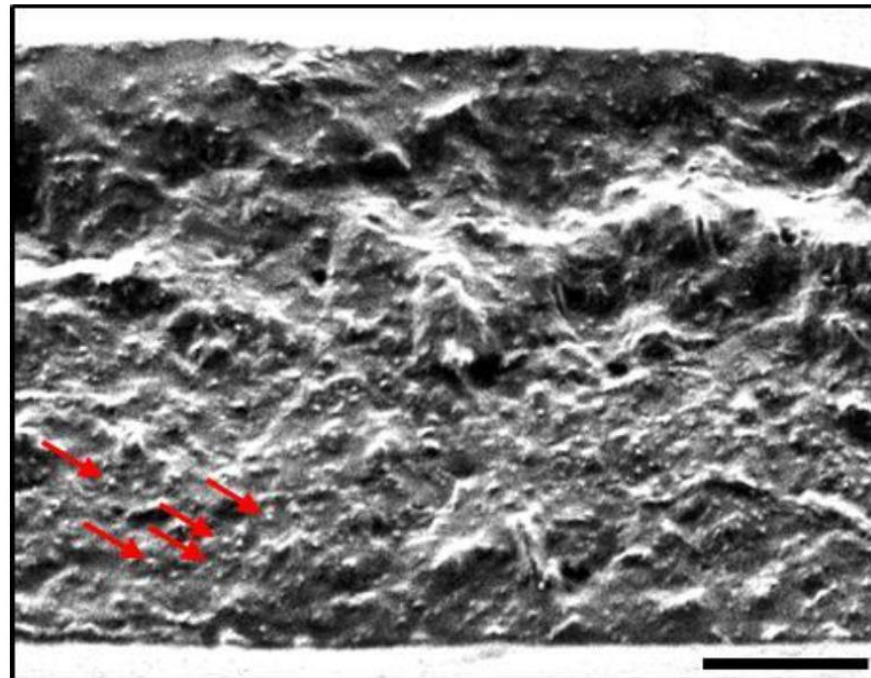
Hierarchically designed piezo-arrays

Cellulose nanocrystals

Alessandra Operamolla group,
Department of Chemistry
University of Pisa

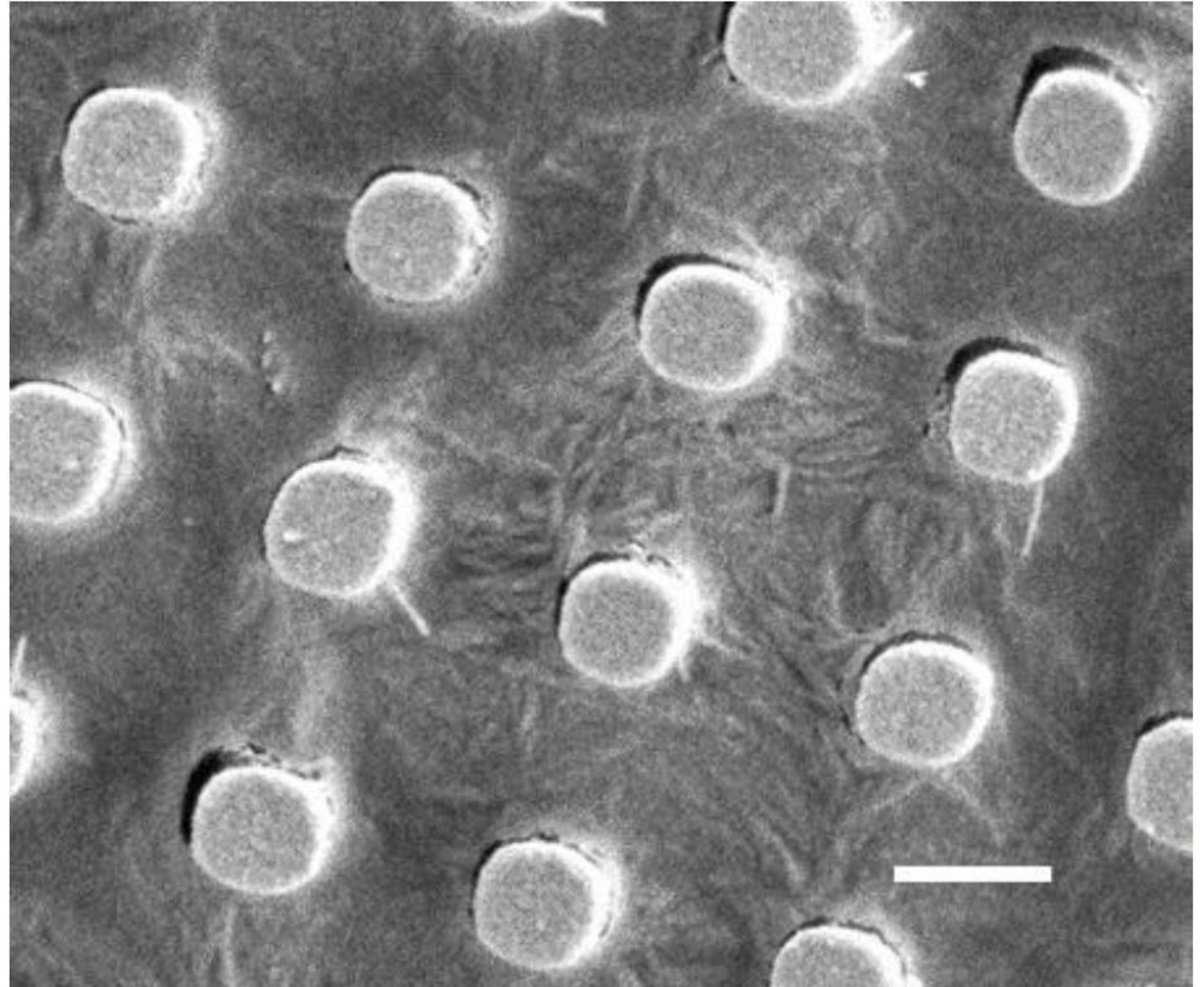
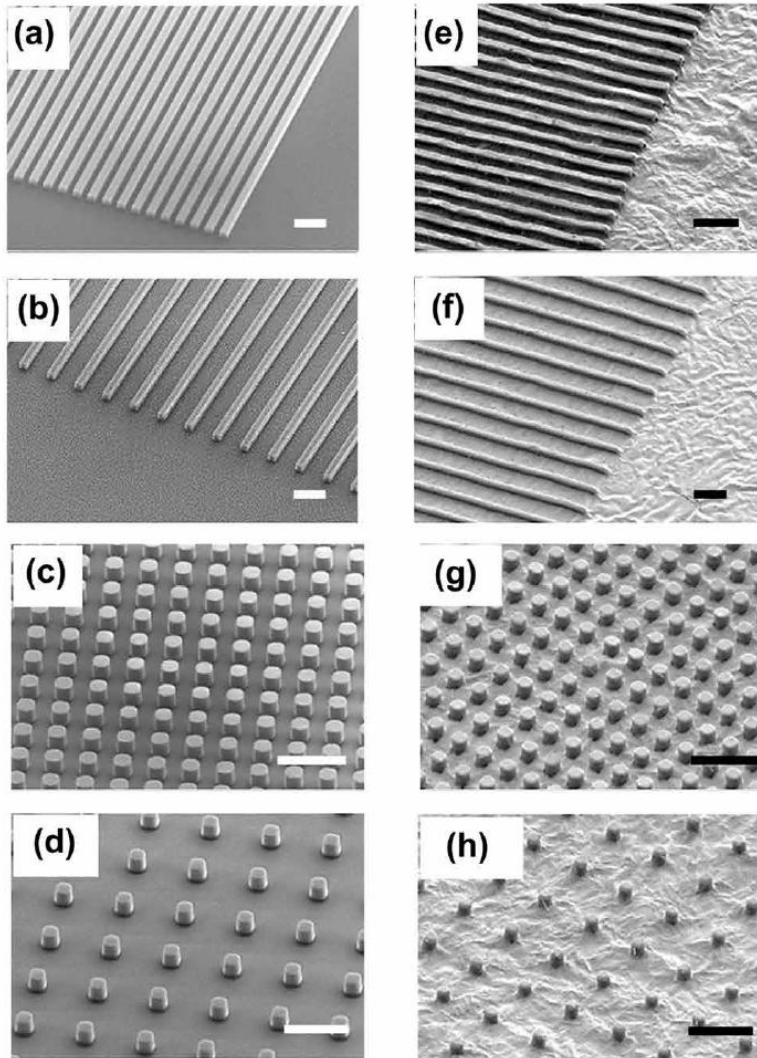


In PVA:



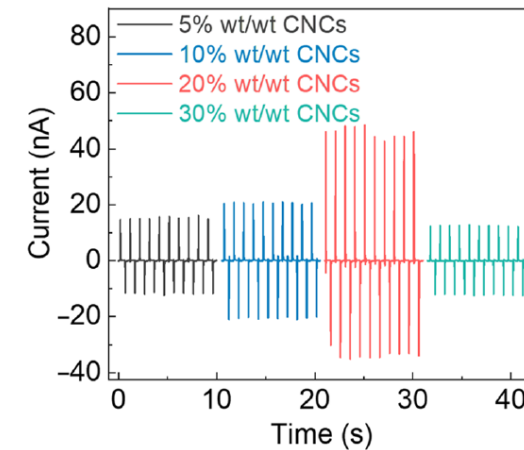
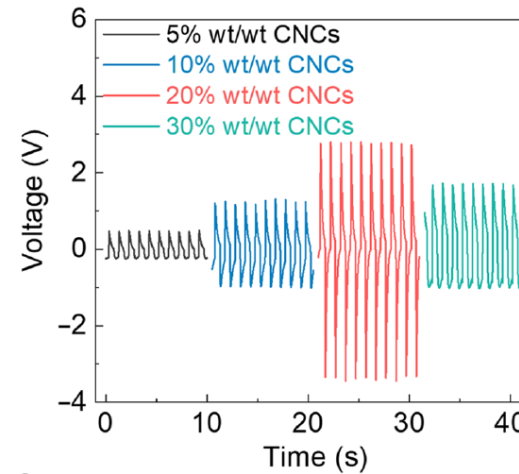
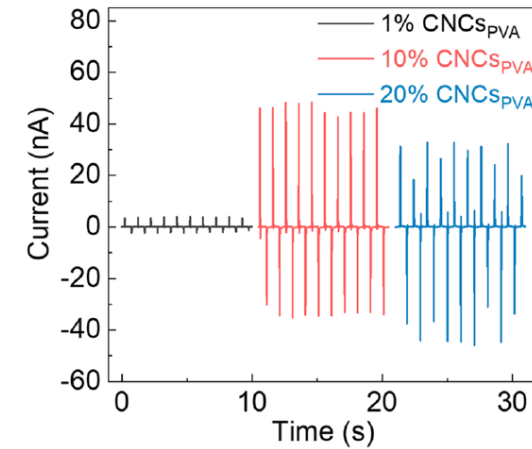
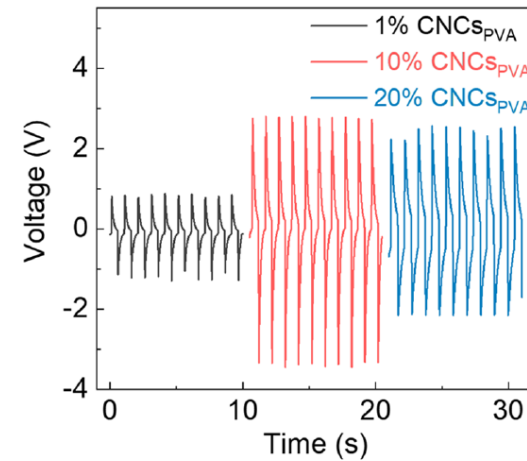
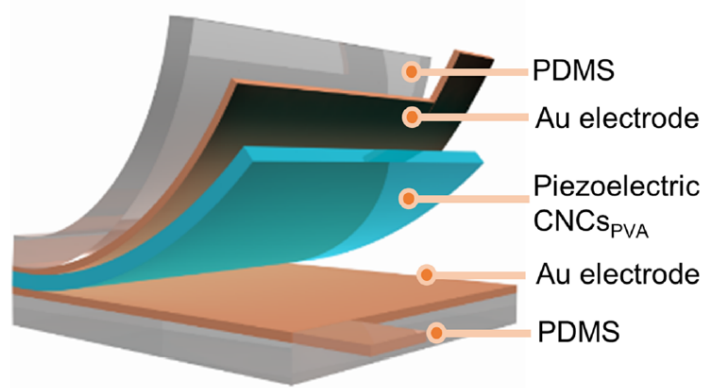
Scale bar 3 microns

Hierarchically designed piezo-arrays

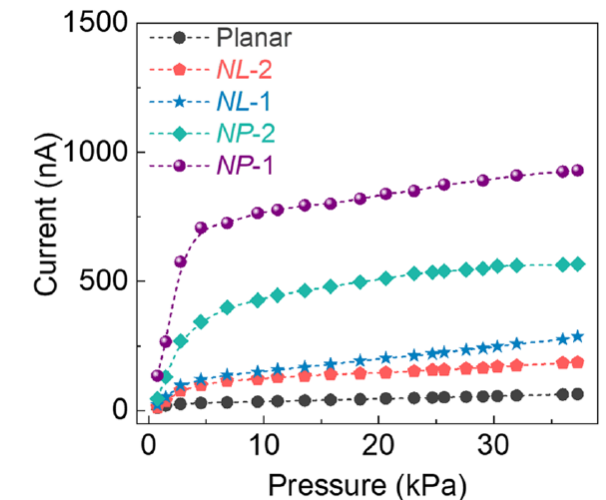
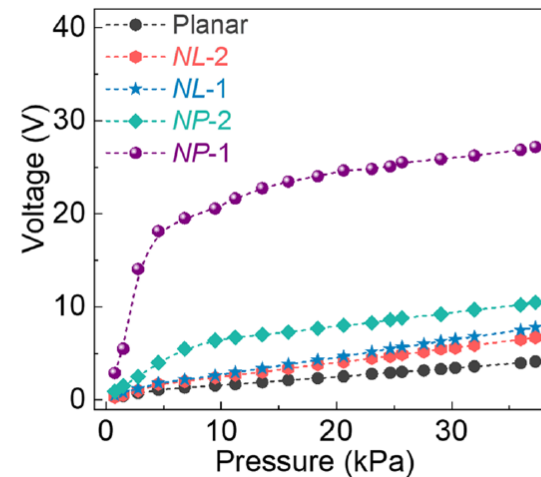
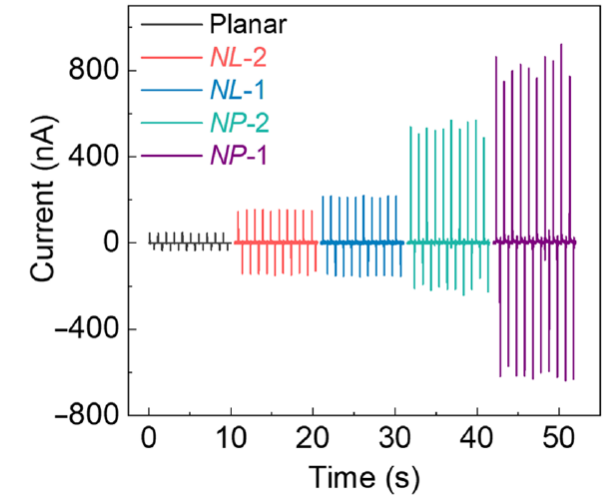
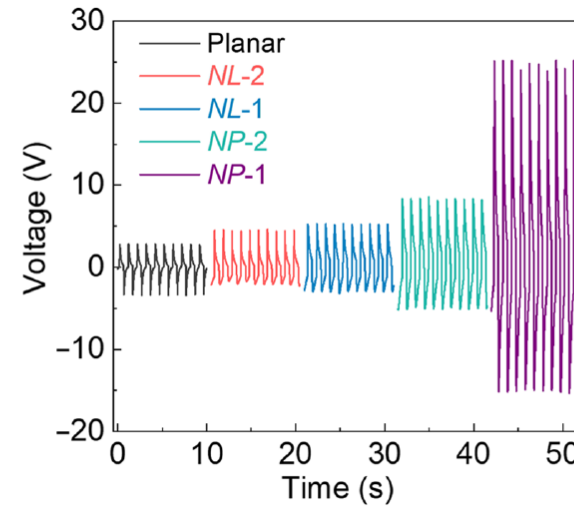
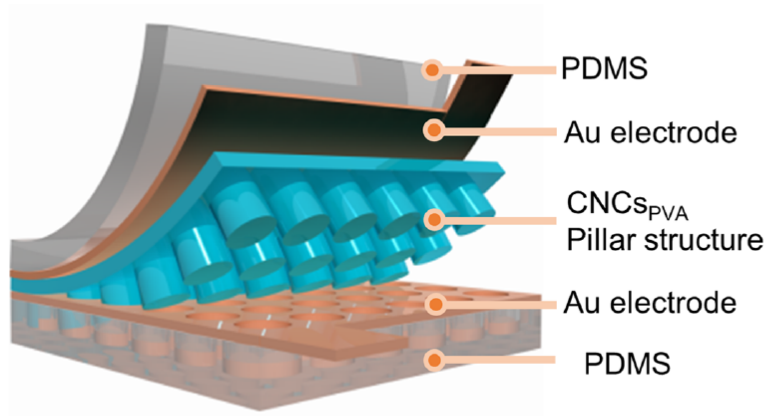




Hierarchically designed piezo-arrays

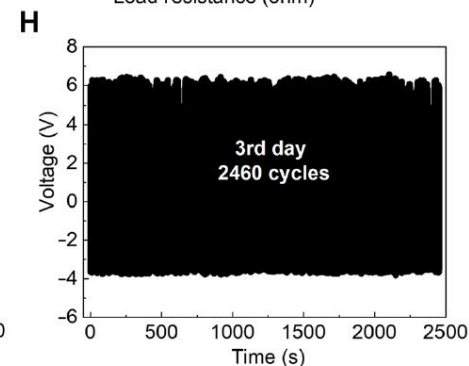
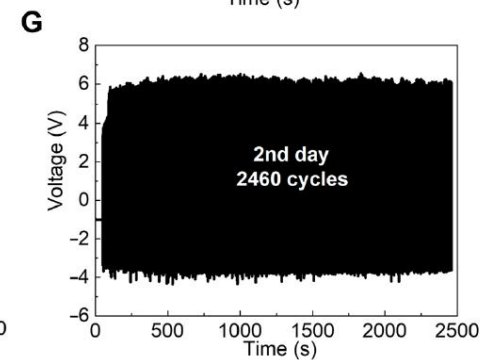
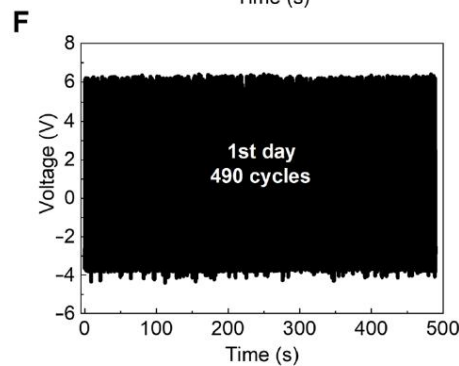
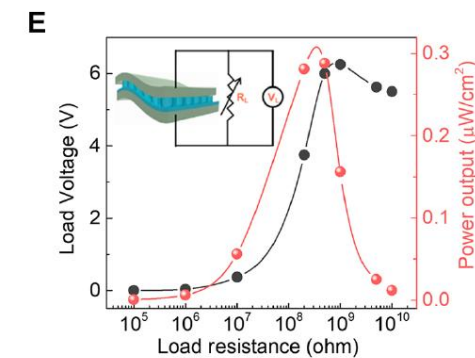
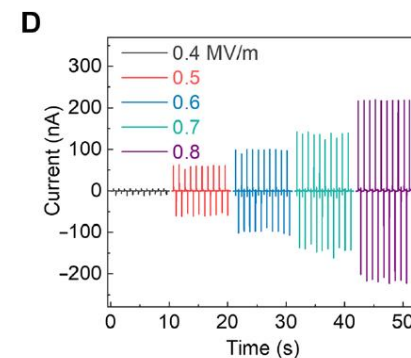
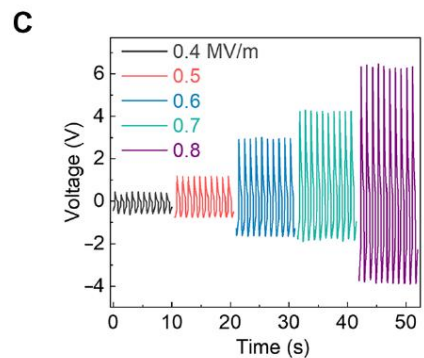
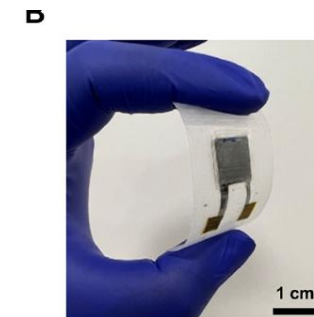
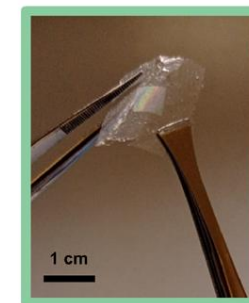
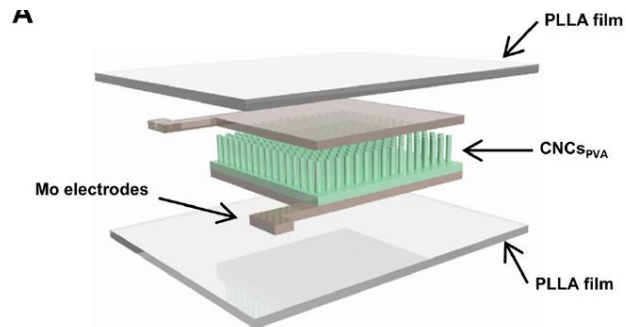
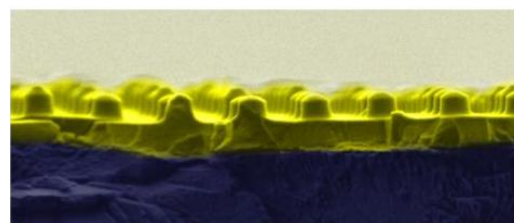
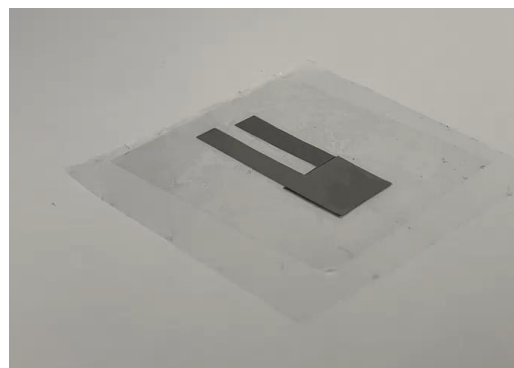
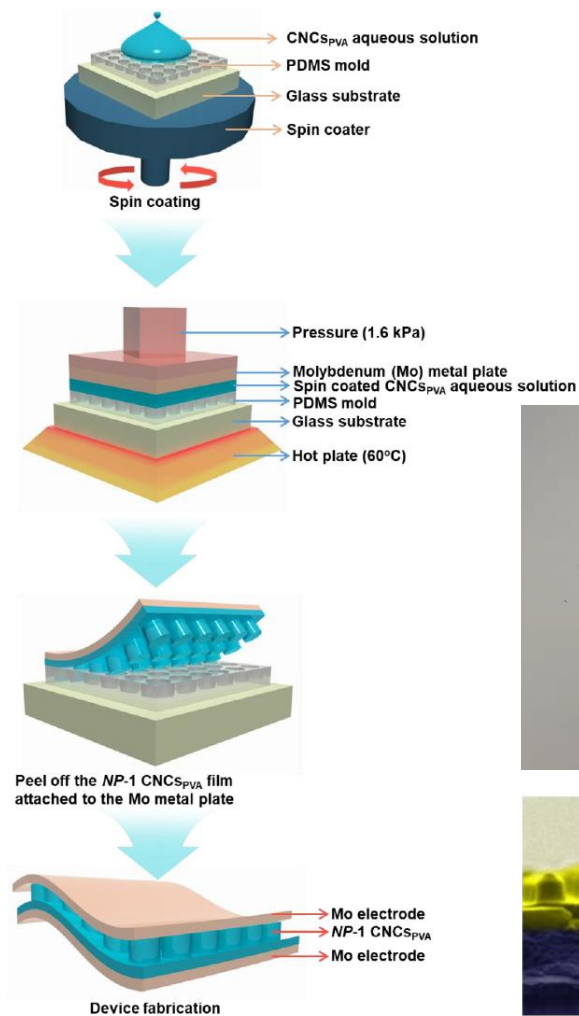


Hierarchically designed piezo-arrays



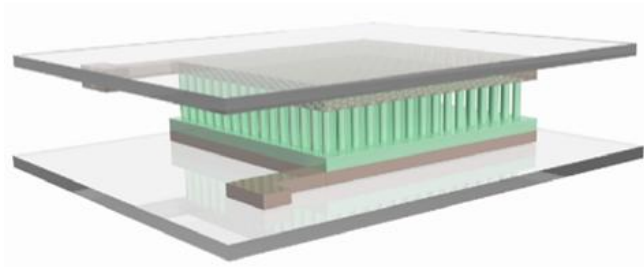
d_{33} of the composite: up to 35 pC/N

Hierarchically designed piezo-arrays

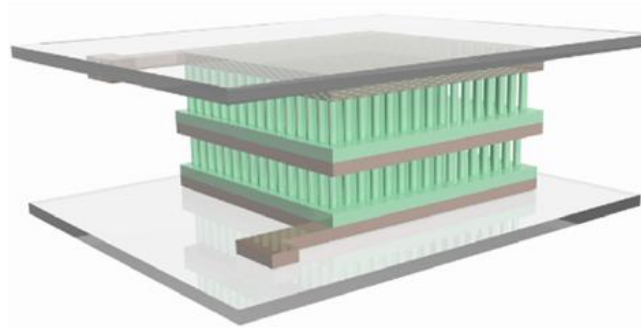


Hierarchically designed piezo-arrays

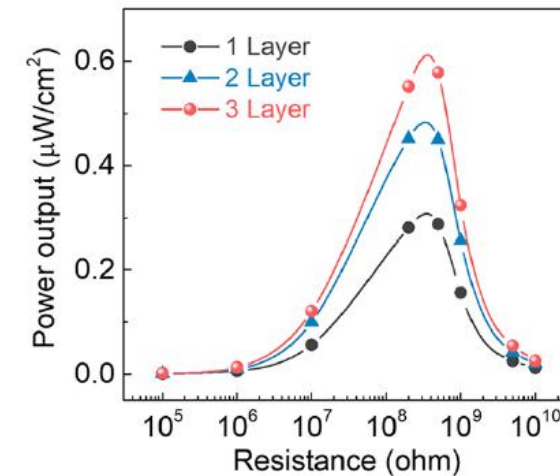
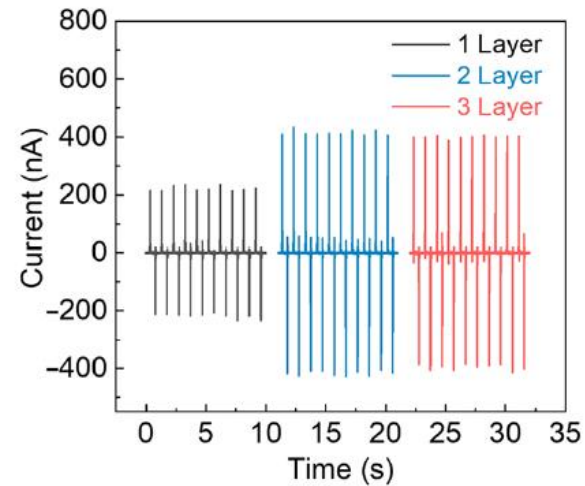
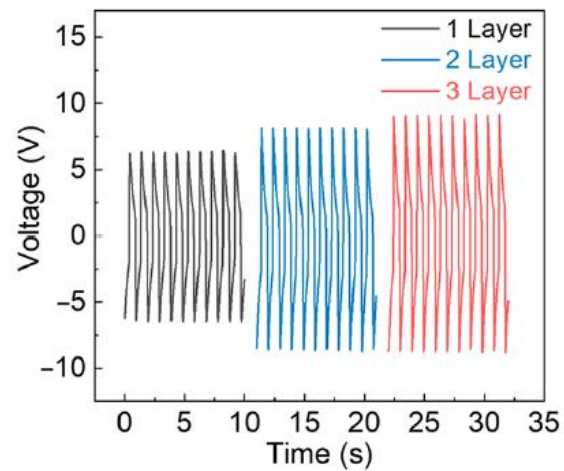
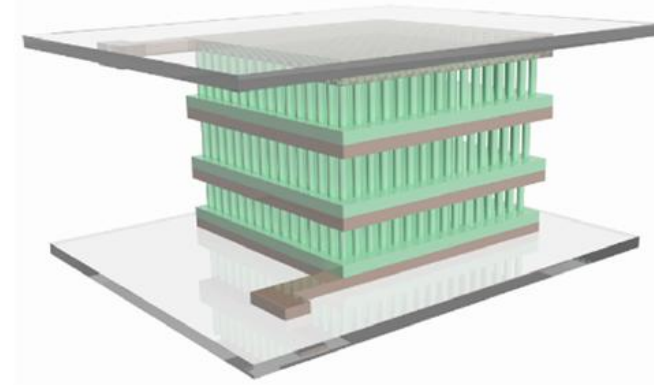
1 Layer device



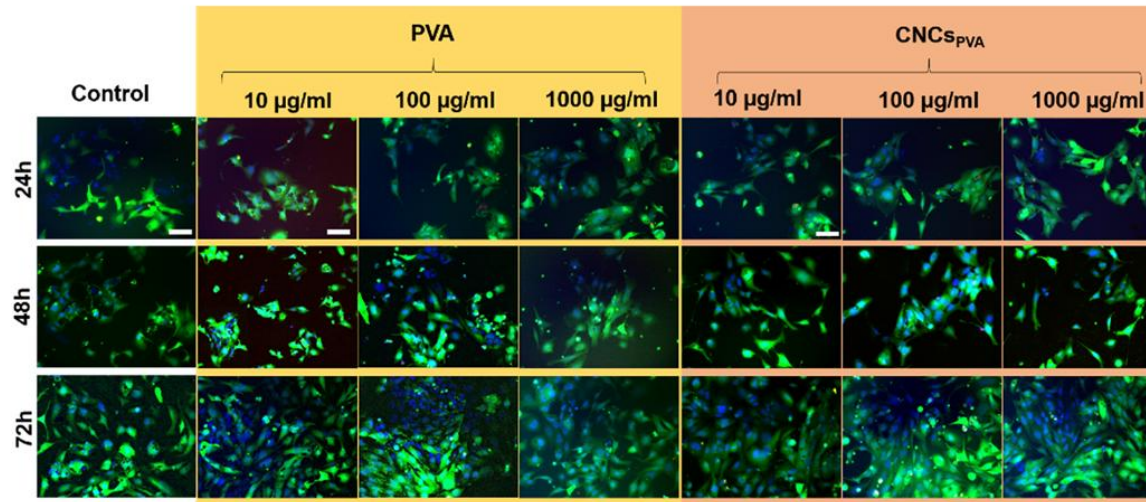
2 Layer device



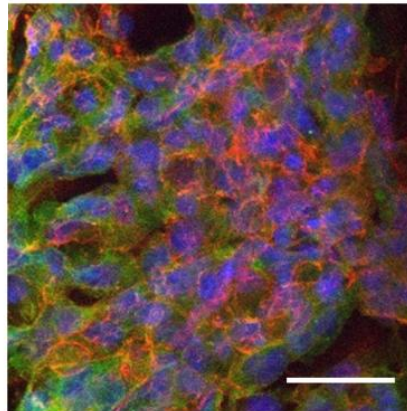
3 Layer device



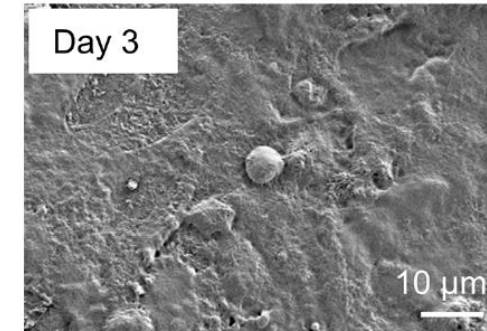
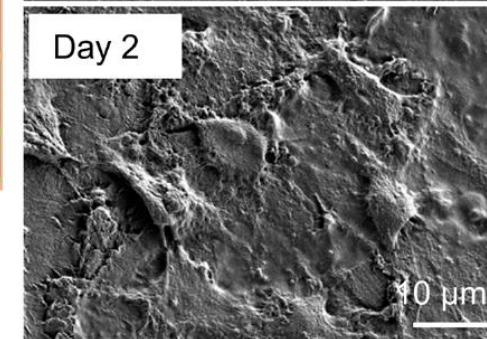
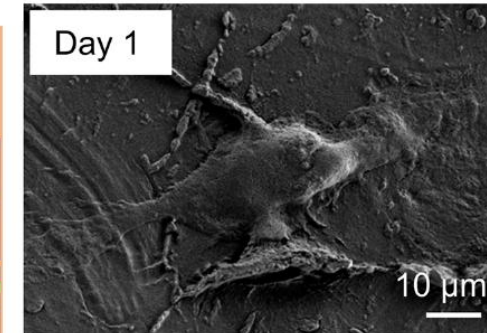
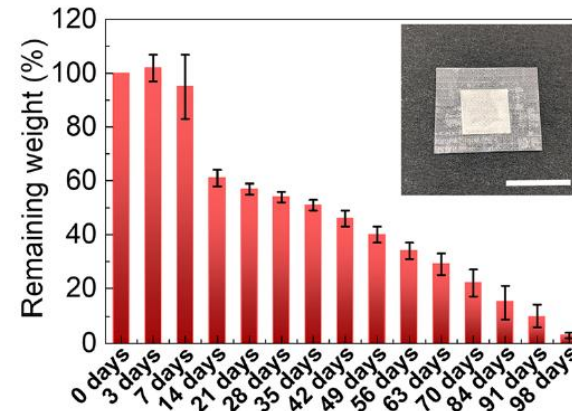
Hierarchically designed piezo-arrays



Calcein/Propidium Iodide

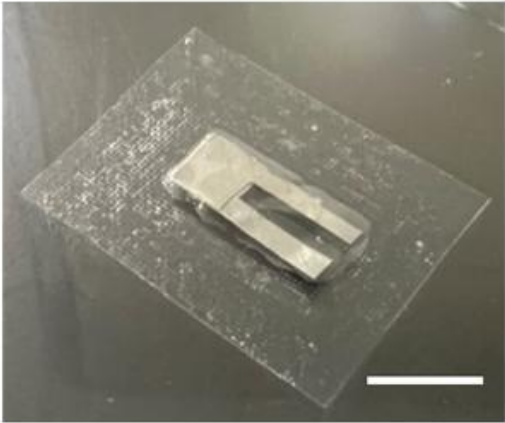


Tubulin/Actine

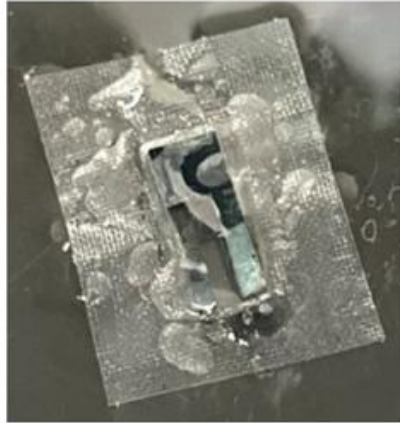


Hierarchically designed piezo-arrays

0 day



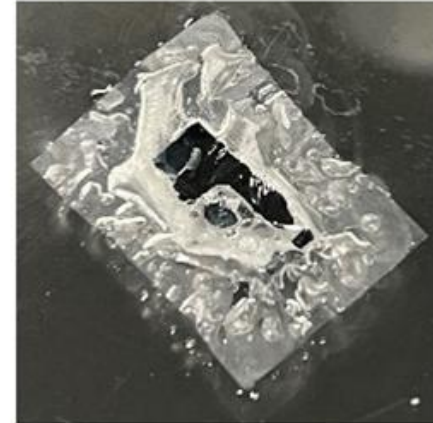
14 days



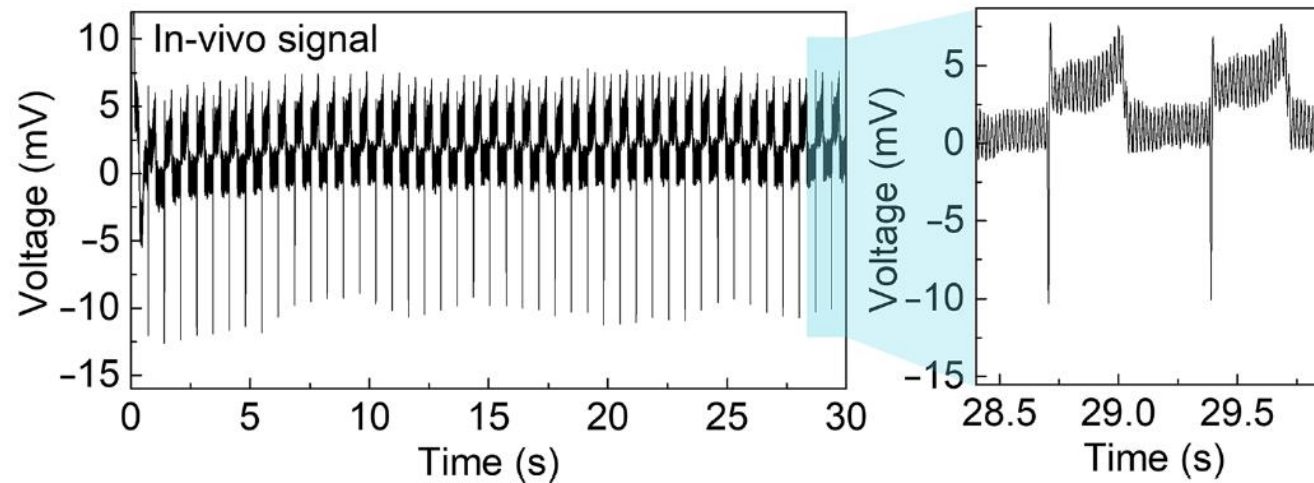
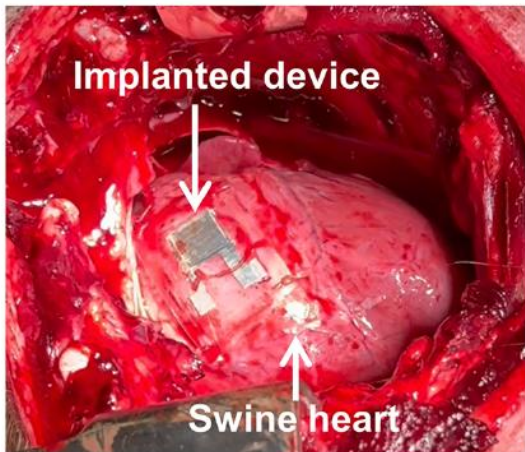
42 days



56 days



70 days



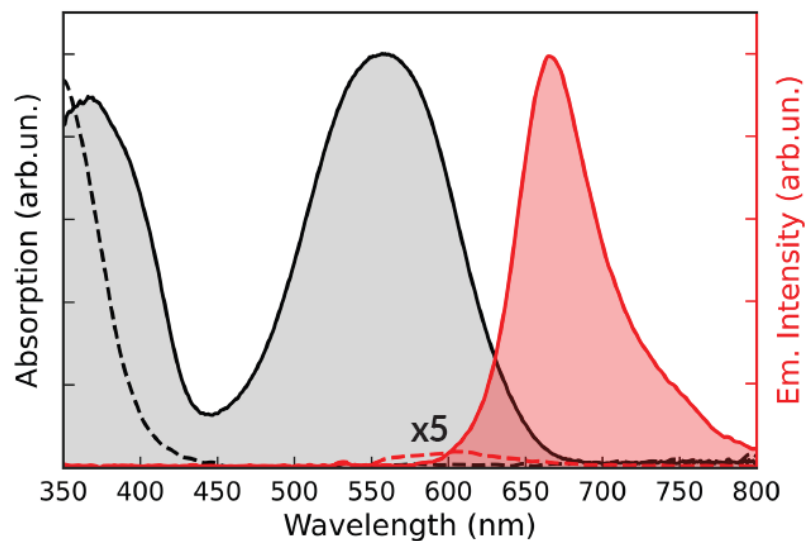
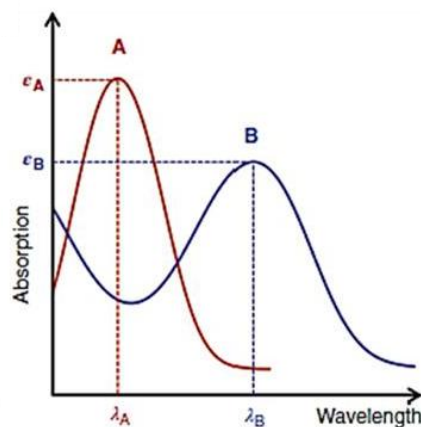
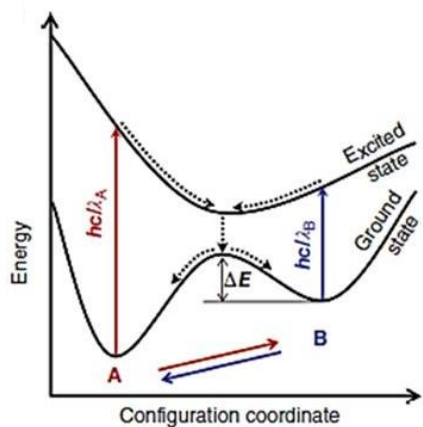
Xudong Wang group,
Department of Materials Science and Engineering,
University of Wisconsin-Madison

Why 4D in Photonics?

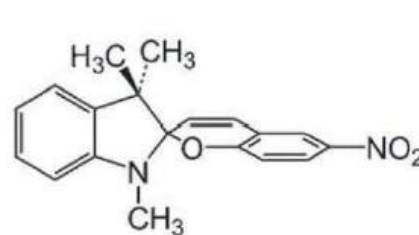
- ✓ Accumulation properties for excitational events → Storage and computation in the same location
- ✓ Precise definition of optical access points and coupling efficiency, and high potential for non-destructive reading
- ✓ Satisfactory versatility of available polymers and photochromic dopants in terms of transparency, mixing, control of refractive index and roughness, achievable on-off ratios etc.
- ✓ Potential for long-term full-organic computing interfaces with bio-systems
- ✓ Potential of photochromic systems as initiators for polymerization



Photochromic molecules



Spiropyran (SP)



Colourless
Non polar
3D structure

UV irradiation of the spiropyran:

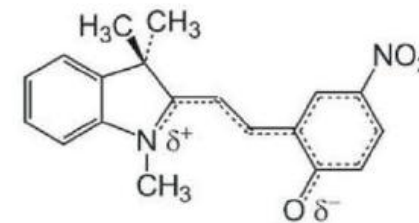
- Cleavage of the C-O bond
- Open-form merocyanine isomer

UV (365-405 nm)



Green (532 nm)

Merocyanine (MC)



Coloured
Polar
Planar structure

Visible irradiation of the merocyanine:

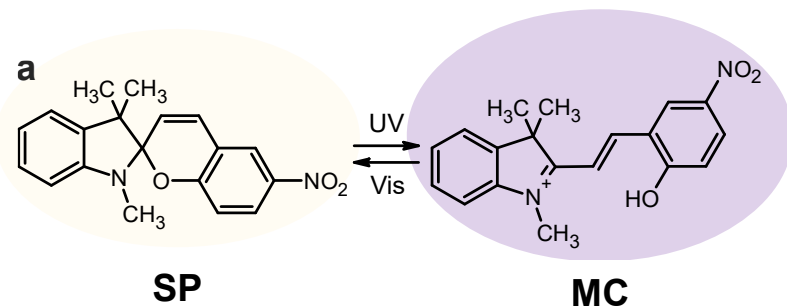
- Closure of the C-O bond
- Close-form spiropyran isomer

Changes Abs, refractive index, and polarity

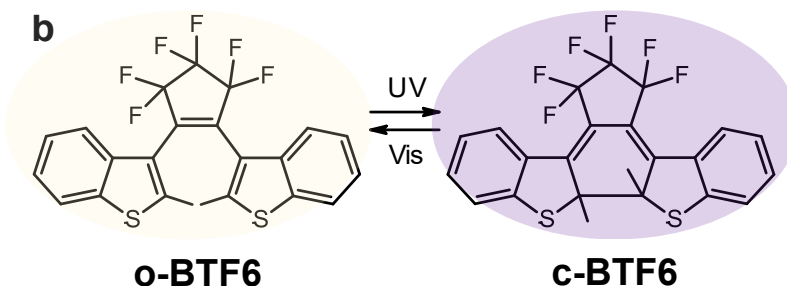
3D printing of photochromic devices

Photochromic molecules

T-type (can undergo thermal decoloration)



P-type (basically thermally-irreversible)

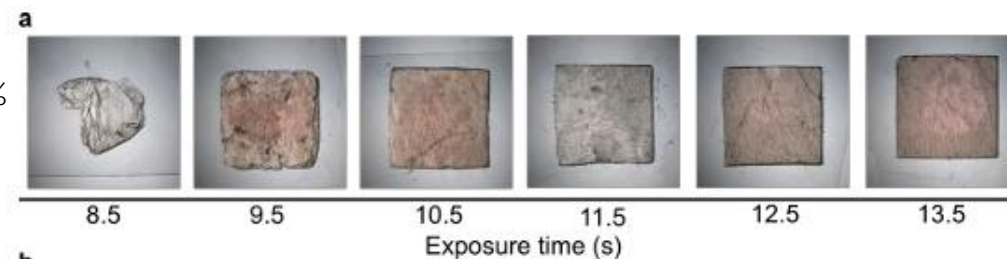


The optimal DLP UV exposure time is of
12 s for samples with $\chi_{TPO} = 0.5\%$ and $\chi_{SP} = 3.5\%$ pre-polymer
6 s for $\chi_{TPO} = 0.5\%$ and $\chi_{BTF6} = 3\%$ pre-polymer

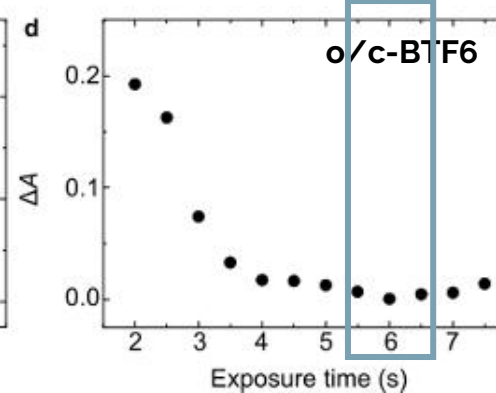
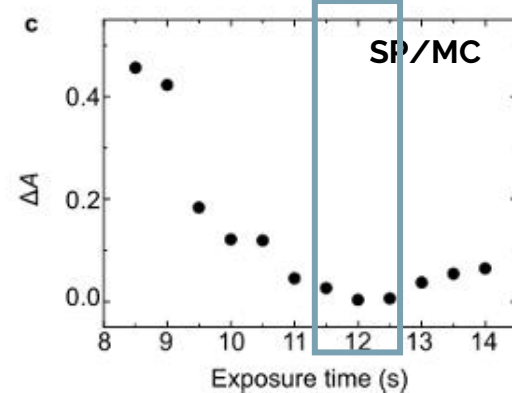
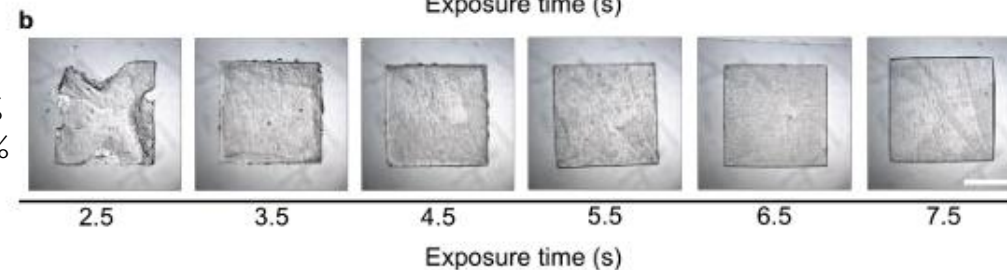


Optimization of the DLP printing processes (Micro Plus HD (Envisiontec, 405 nm, cw, $\sim 1 \text{ mJ/cm}^2$))

SP/MC
 $\chi_{TPO} = 0.5\%$
 $\chi_{SP} = 3.5\%$



o/c-BTF6
 $\chi_{TPO} = 0.5\%$
 $\chi_{BTF6} = 3.5\%$

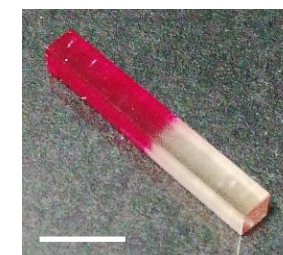
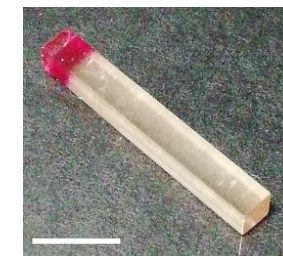
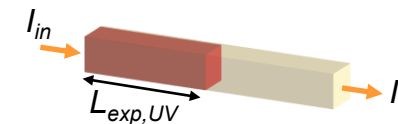
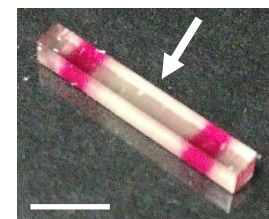
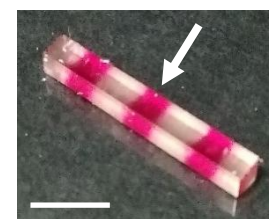
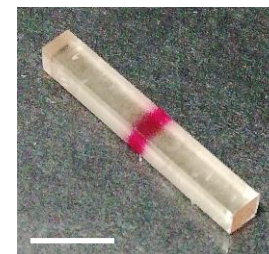
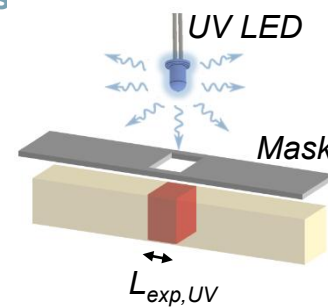
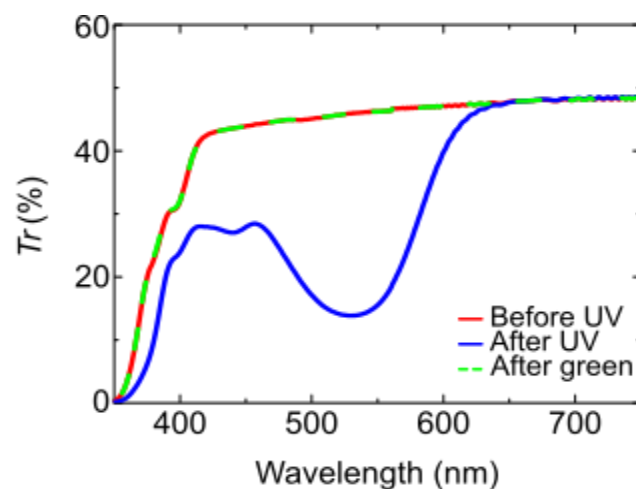
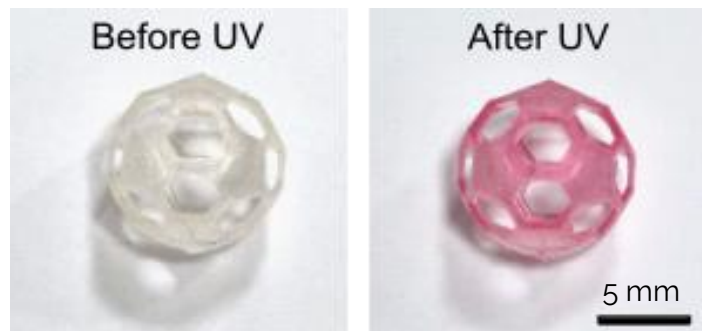
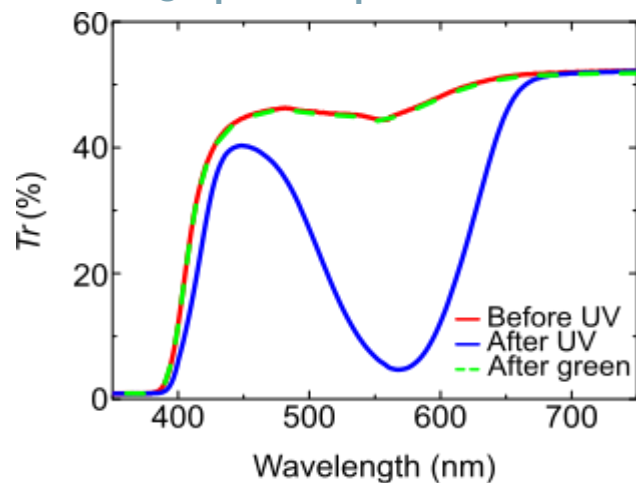
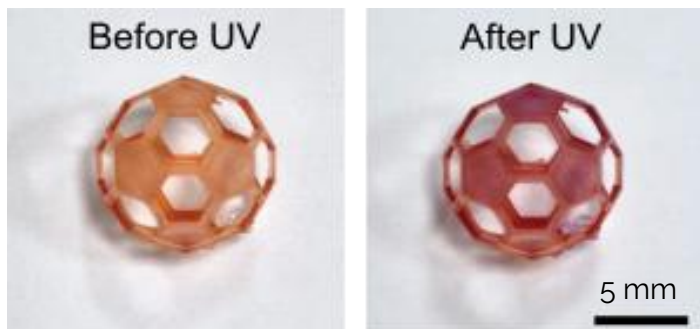


$$\Delta A = |(AD - AM) / AD|$$

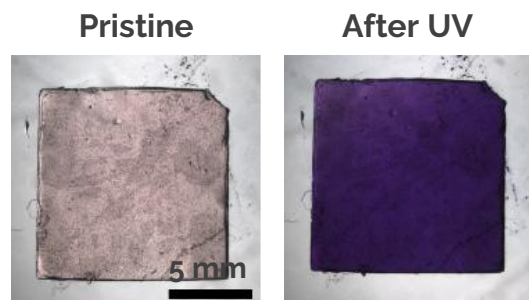
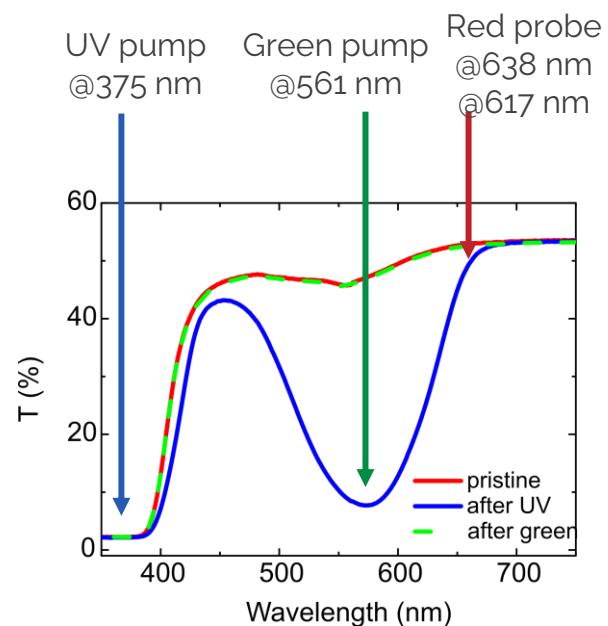
AM: area of the printed structures
AD: area of the designed structure

3D printing of photochromic devices

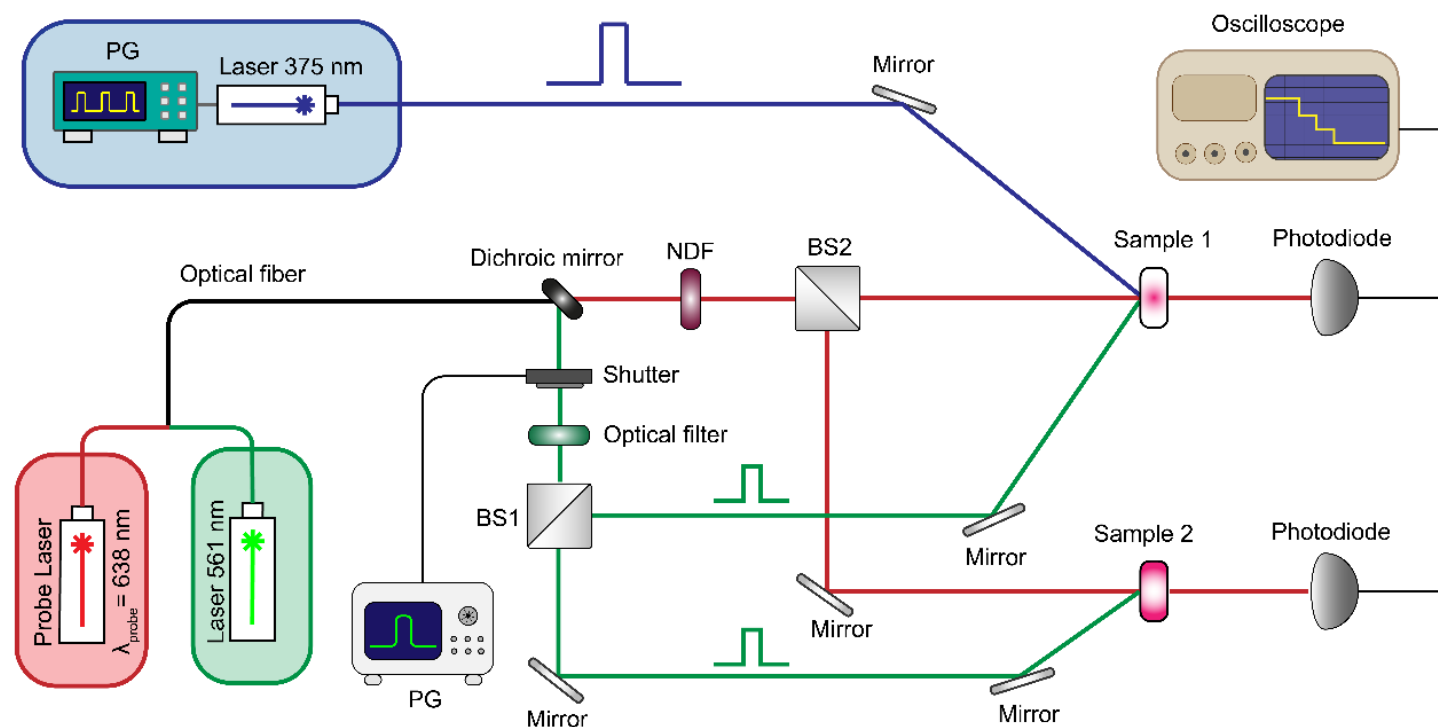
3D printed photochromic structures



Set-up

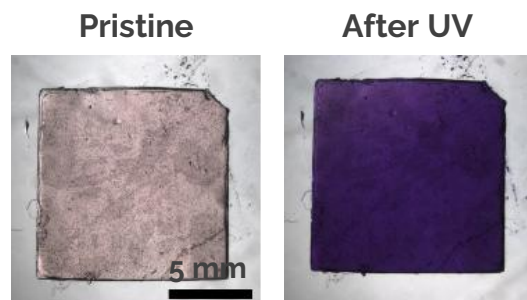
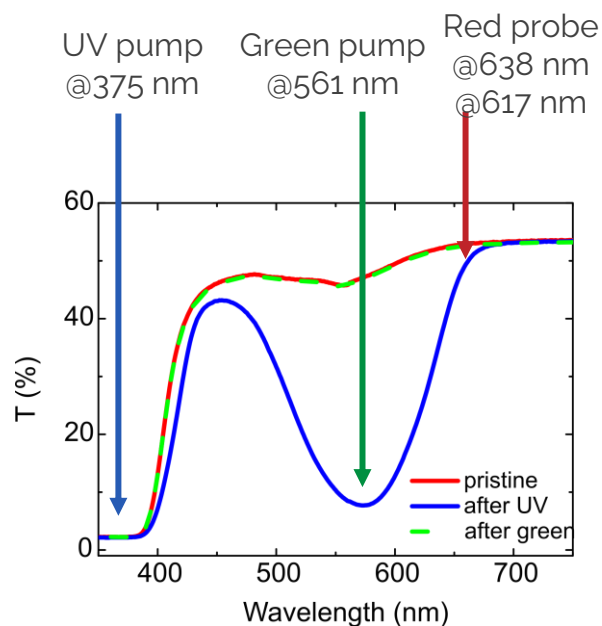


BEDMA + 0.5 %w/w TPO + 3.5 %w/w SP/MC

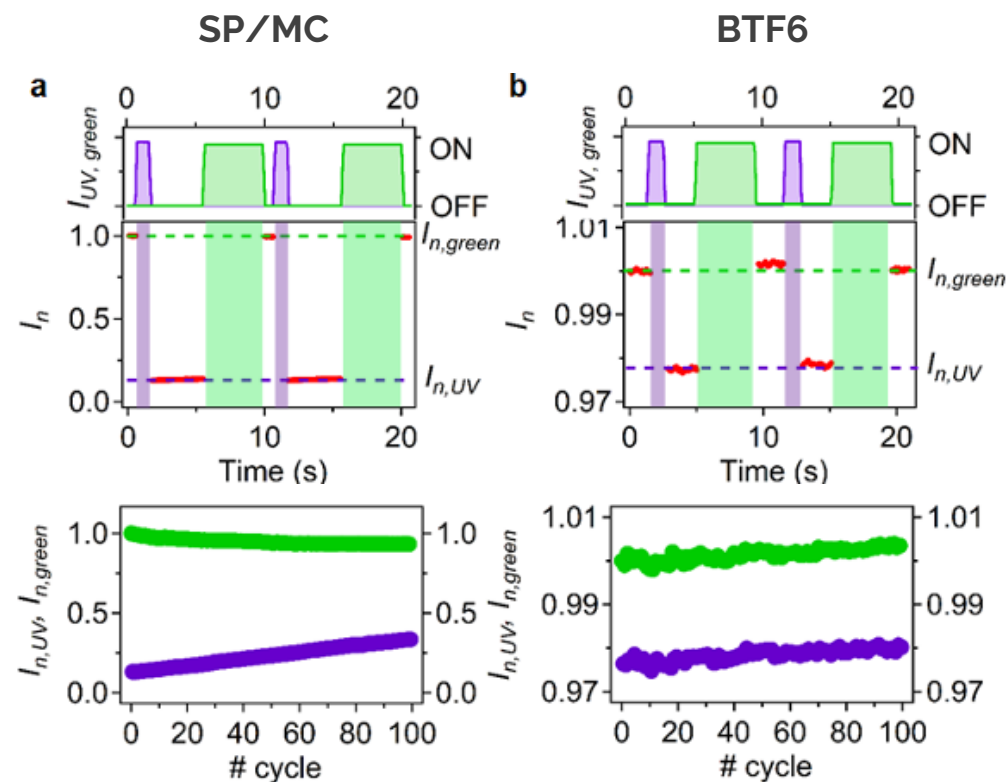




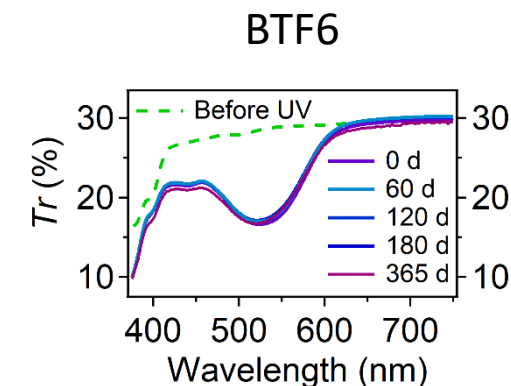
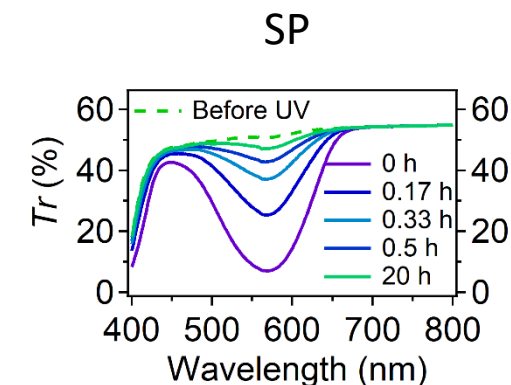
Cyclic conversion and thermal relaxation



BPA + 0.5 %w/w TPO + 3.5 %w/w SP/MC



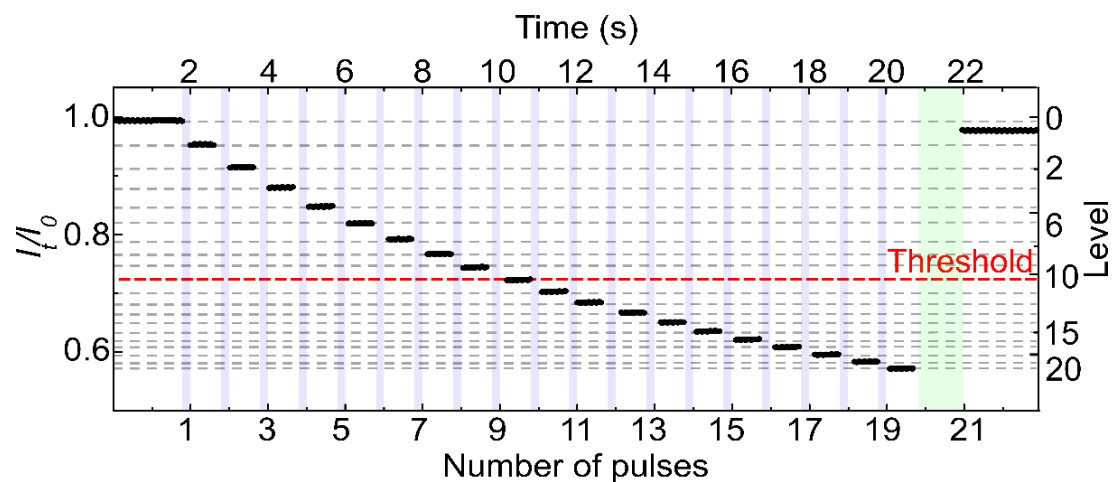
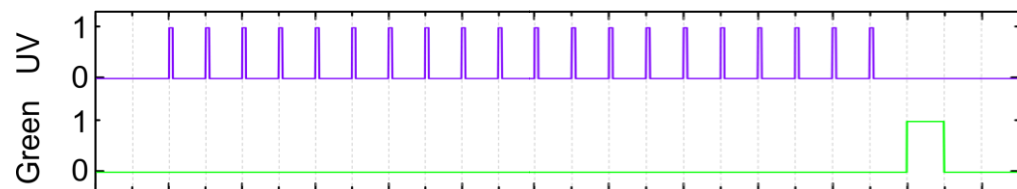
- For SP/MC ΔI_n decreases to 70% of the initial value
- For BTF6 ΔI_n is decreased to 85% of the initial value



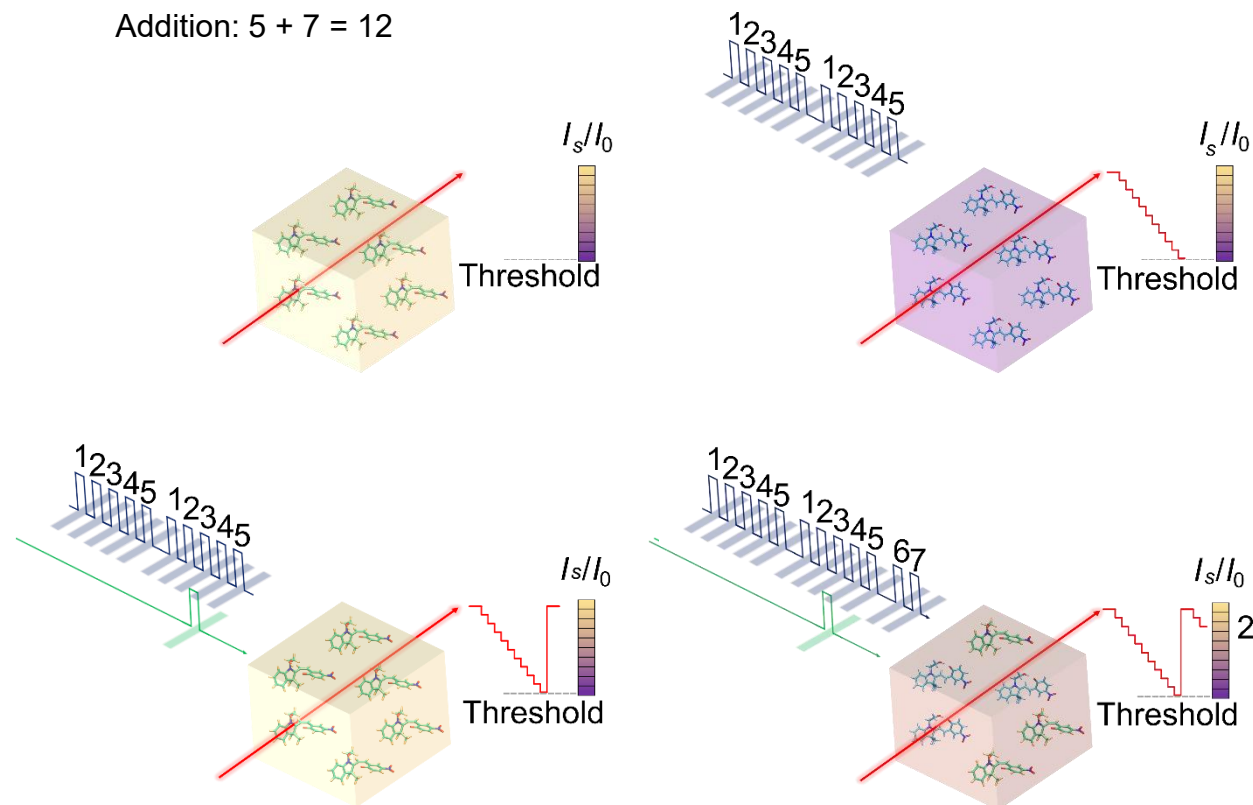
Conversion and reversion with UV/green pulses

Good fatigue properties

Arithmetic operations

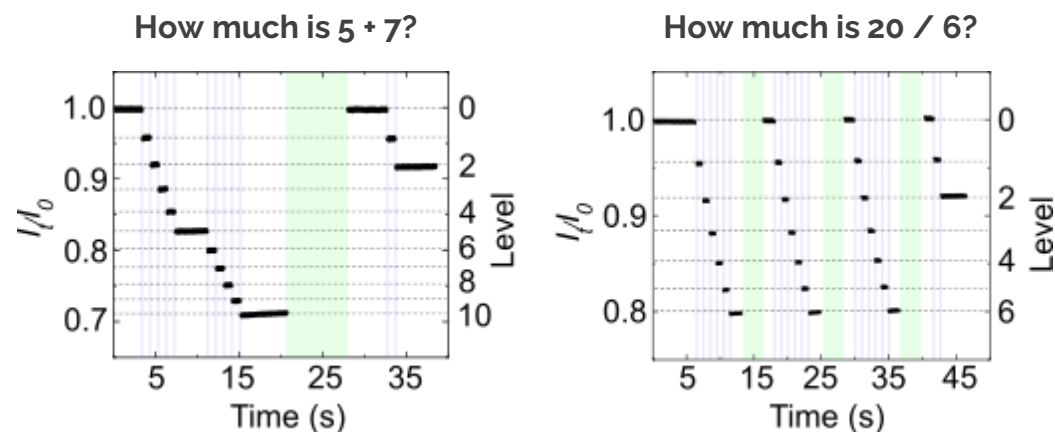


Addition: $5 + 7 = 12$

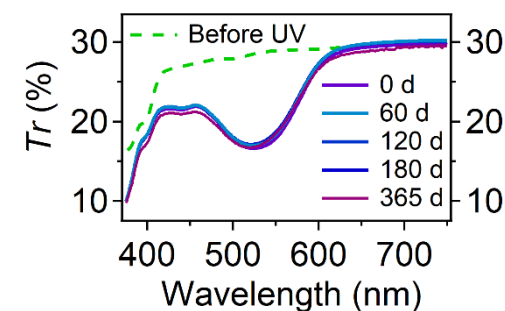
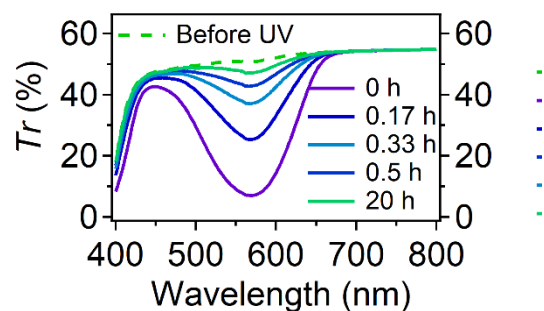
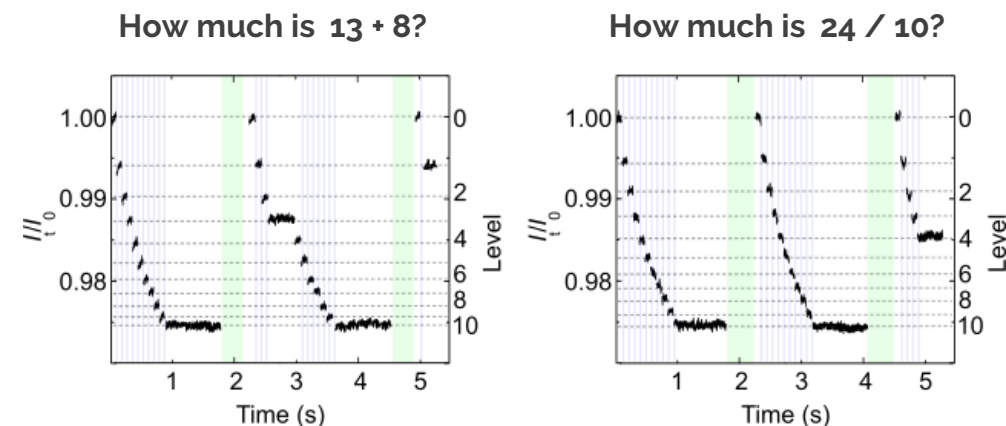


Arithmetic operations

3D printed slab made of TPO/BEDMA and 3.5%w/w SP

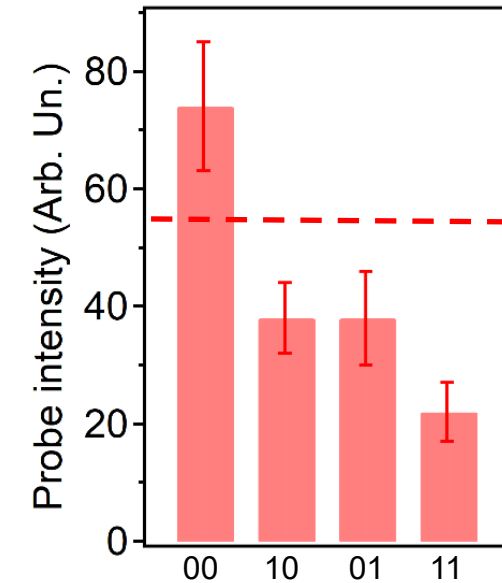
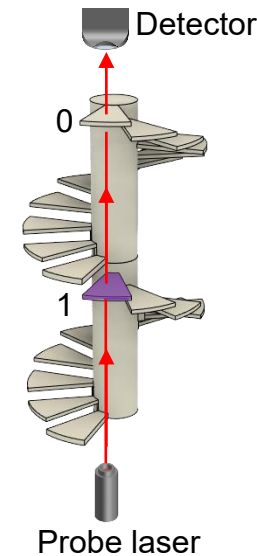
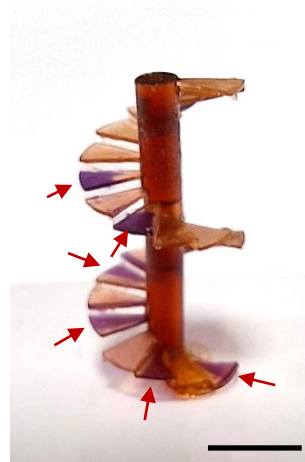
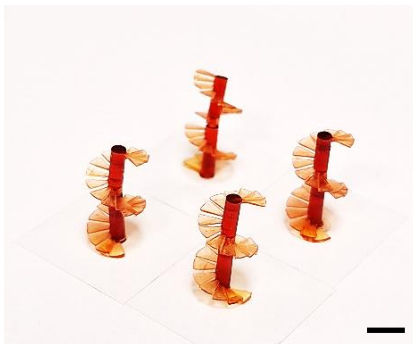
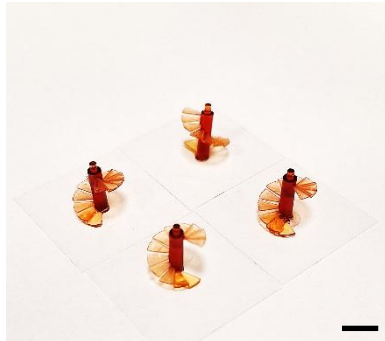
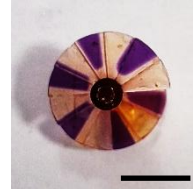
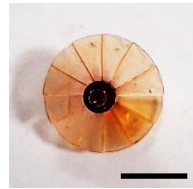


3D printed slab made of TPO/BEDMA and 3% w/w BTF6



Stable, long term storage

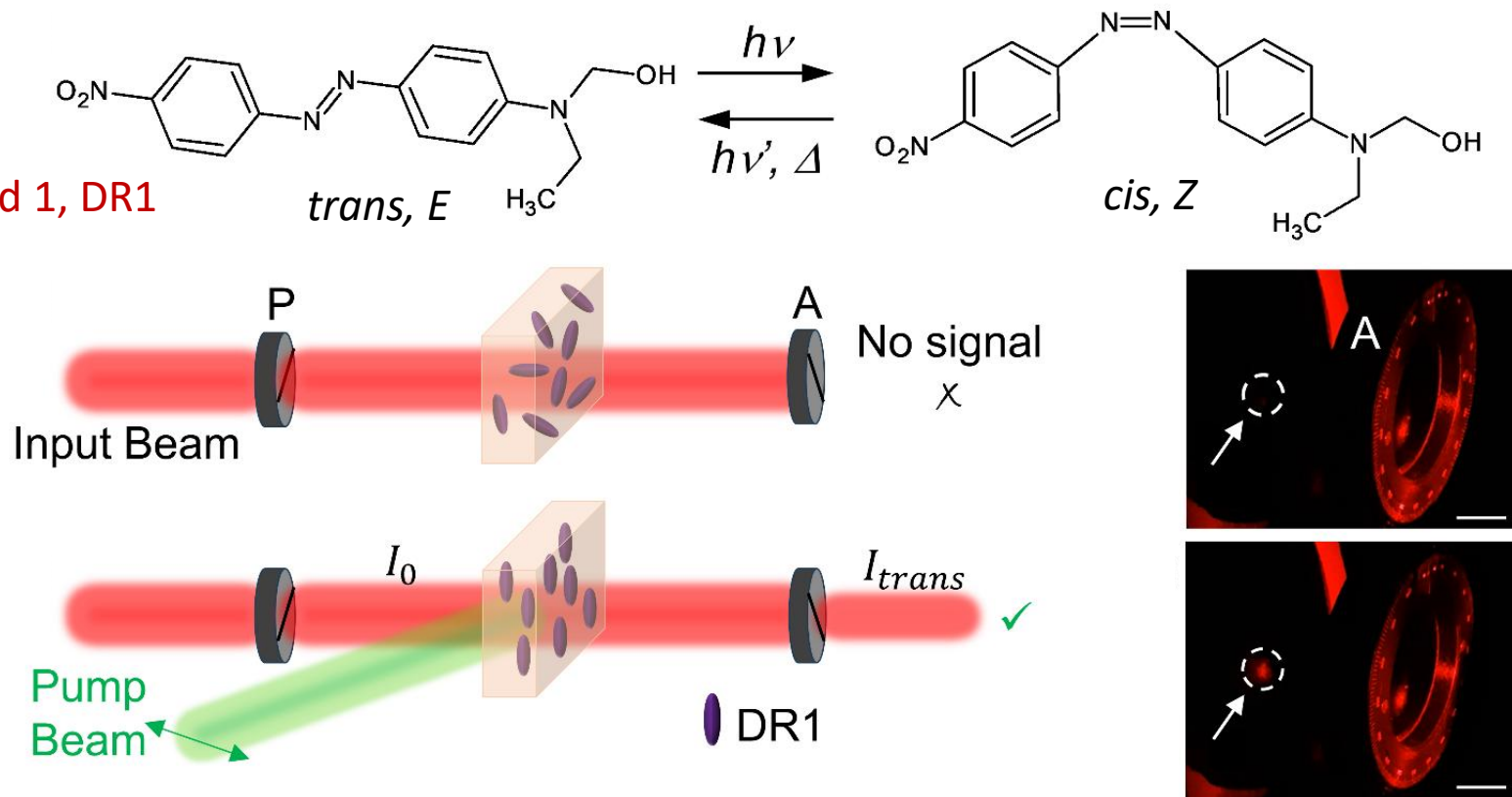
Logic operations



Multiple photochromic systems
integrated by using 3D spiral-shaped
components for parallel processing

Photoinduced birefringence

Disperse Red 1, DR1

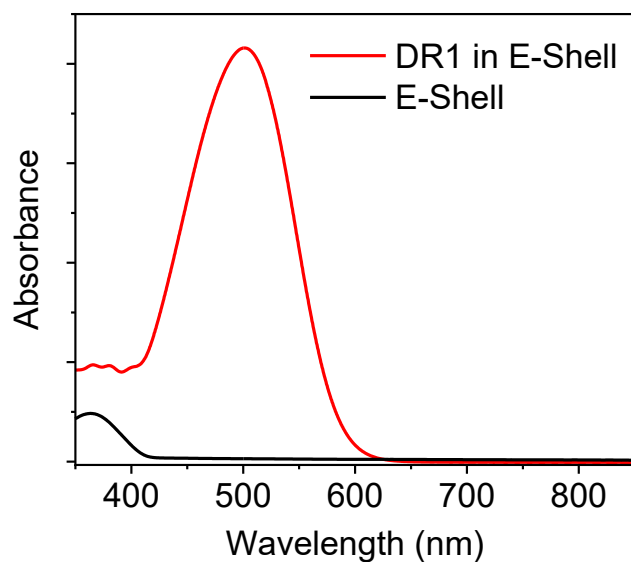


Matrix: E-shell[®] 600
DR1/E-shell: 1% w/w

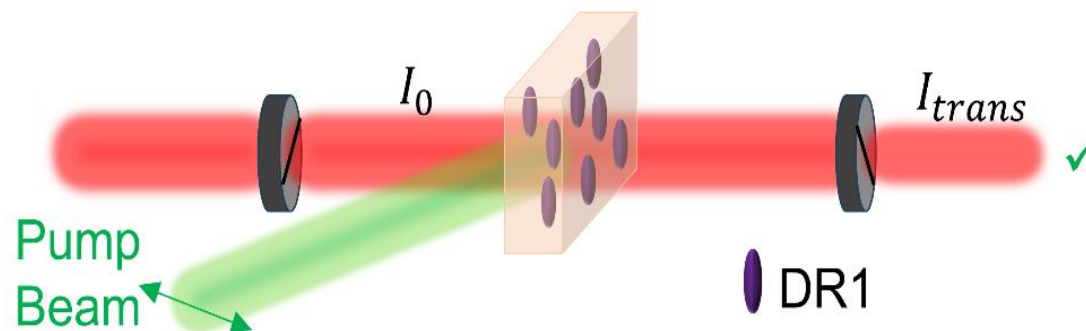
Additive manufacturing by
SLA and DLP

Molecules can be driven across repeated photo-isomerization cycles, ultimately leading to significant alignment perpendicular to the polarization direction of incident light. Such anisotropic molecular arrangement might lead to optical birefringence and dichroism, with magnitude precisely tunable by varying the light intensity

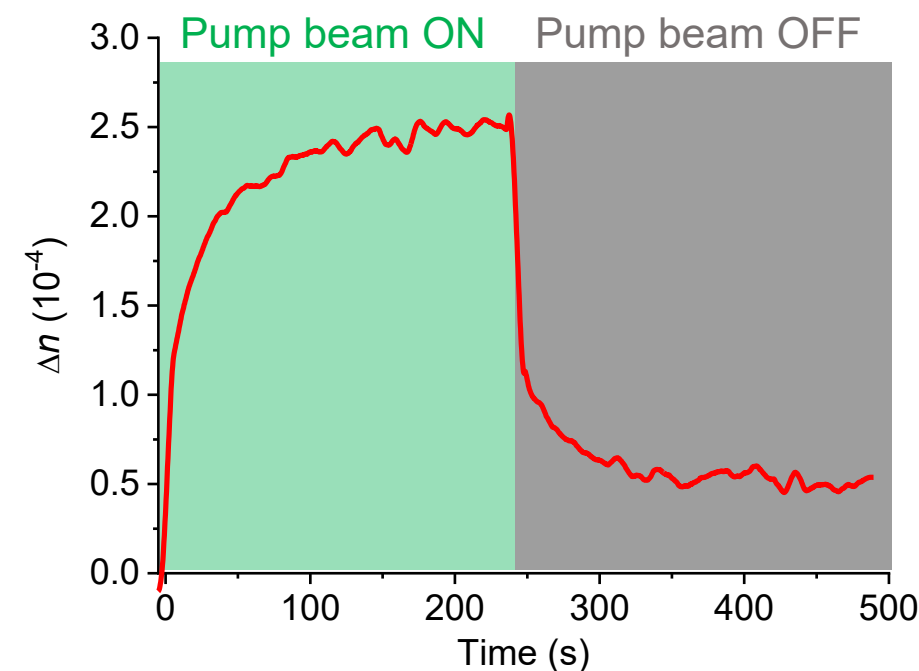
Photoinduced birefringence



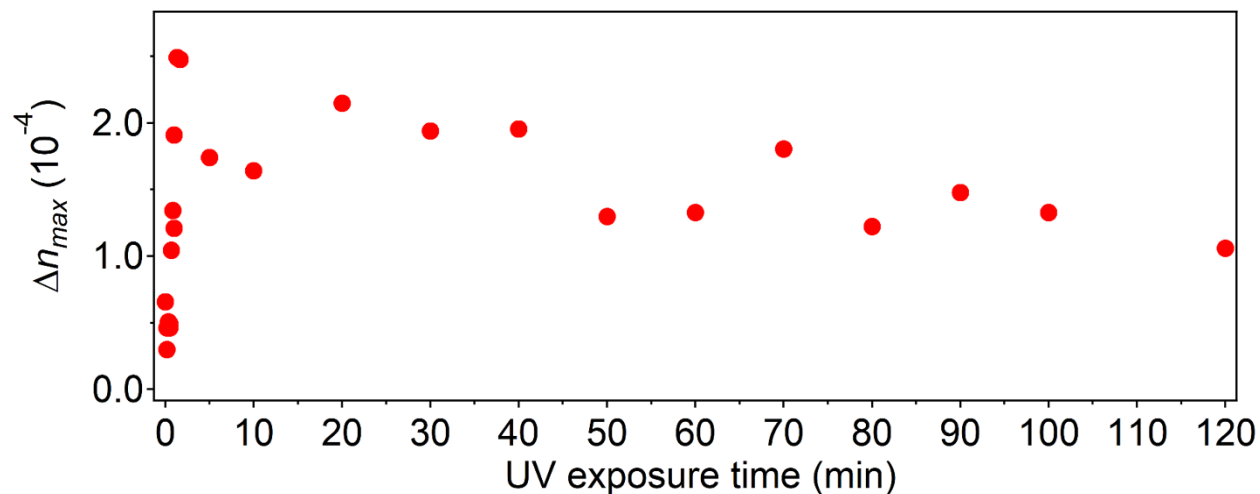
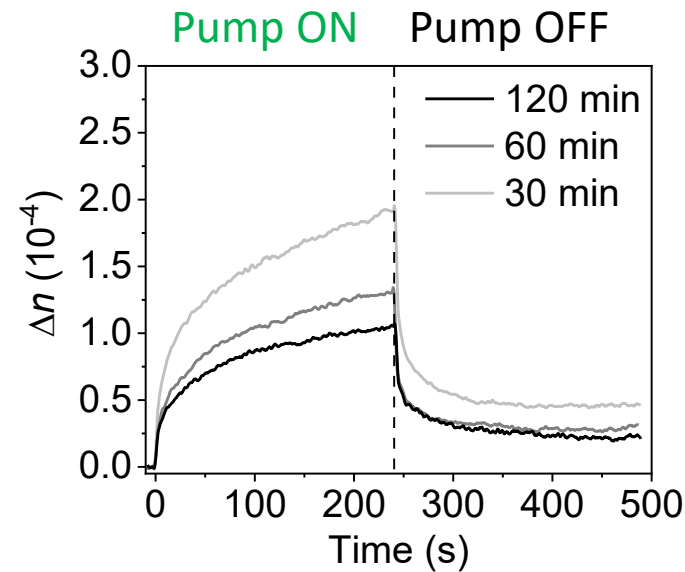
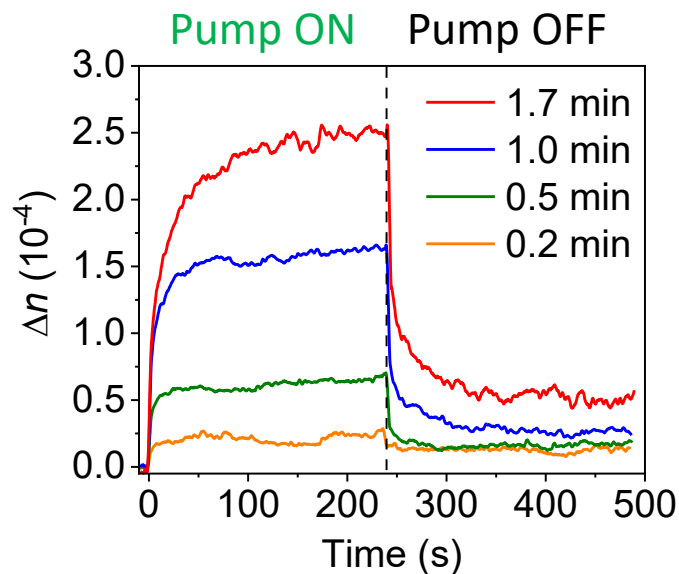
↑ Pump
↑ Probe



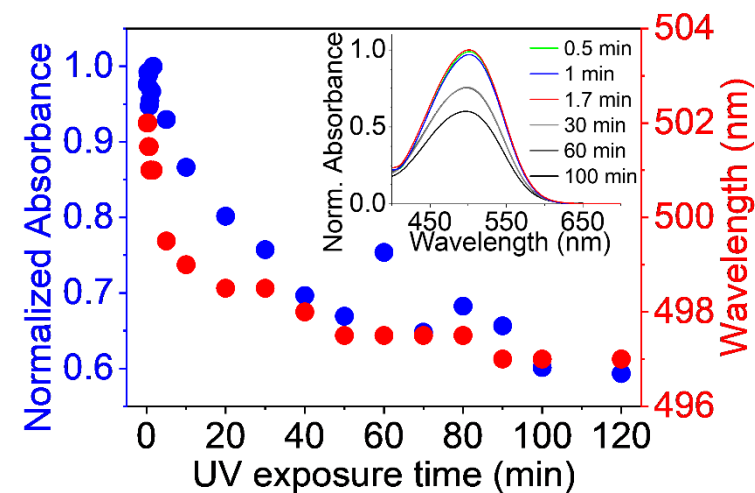
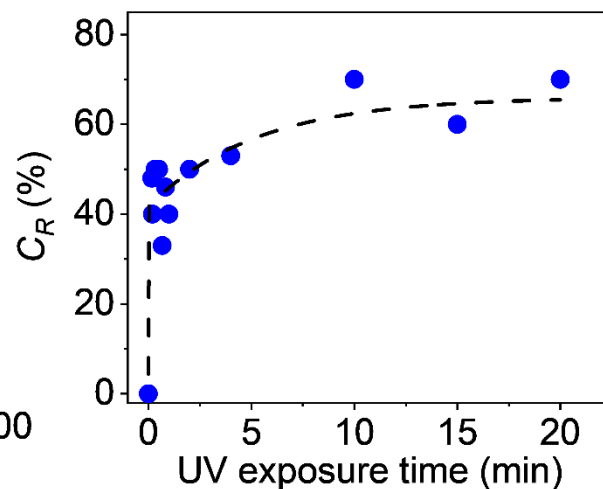
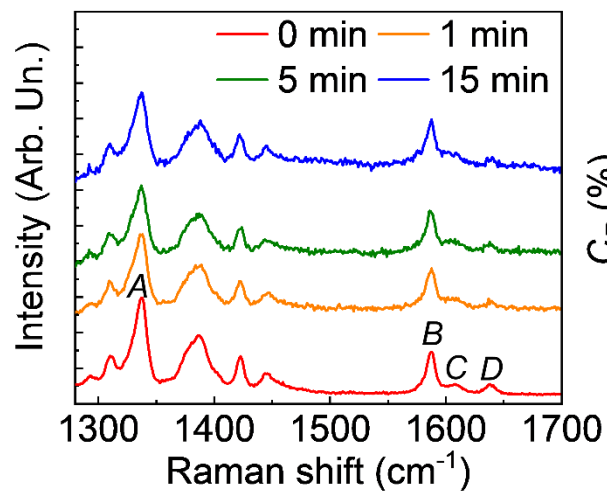
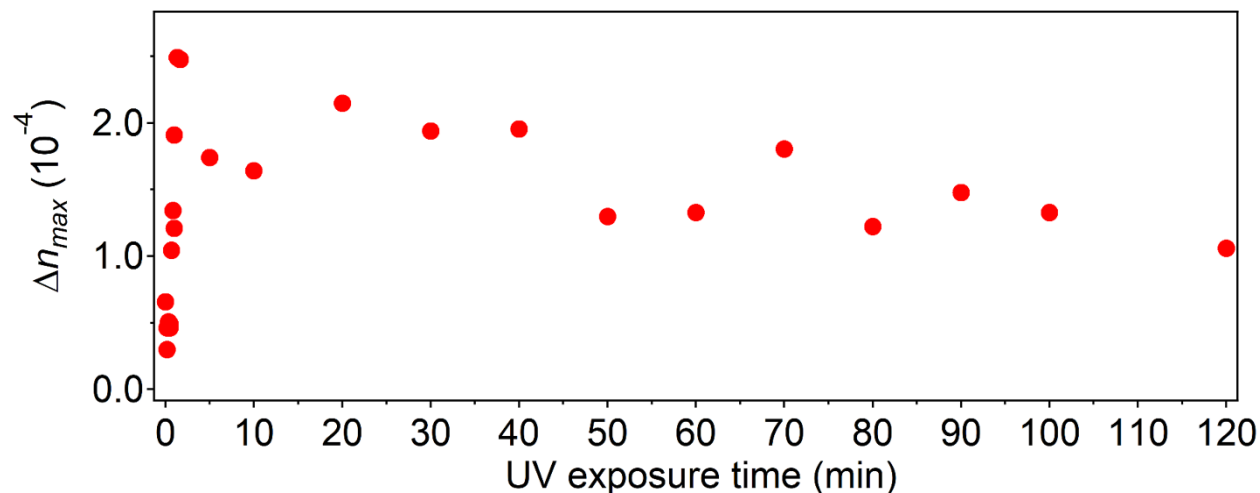
$$\frac{I(I_{pump}, t)}{I_0} = \sin^2 \left(\frac{\pi |\Delta n| d}{\lambda_{probe}} \right)$$



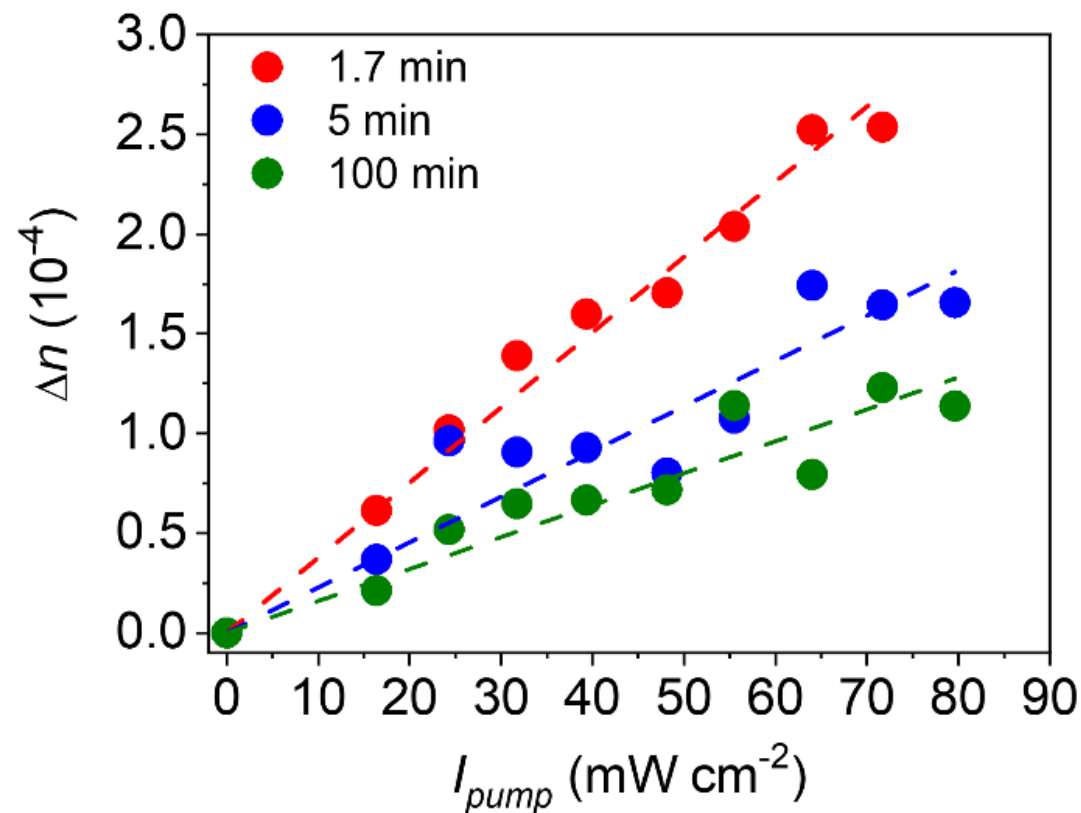
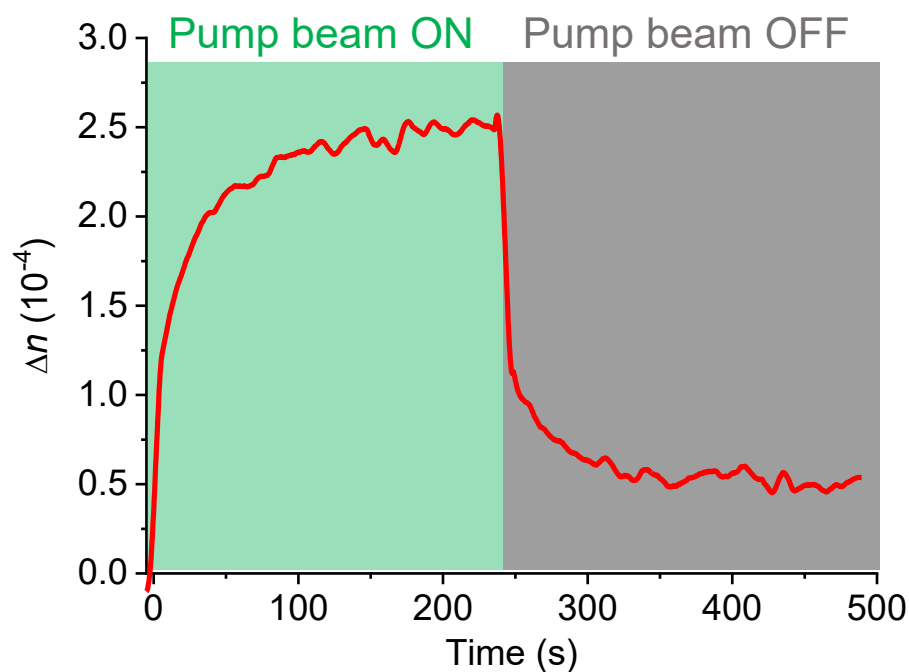
Birefringence vs. UV polymerization



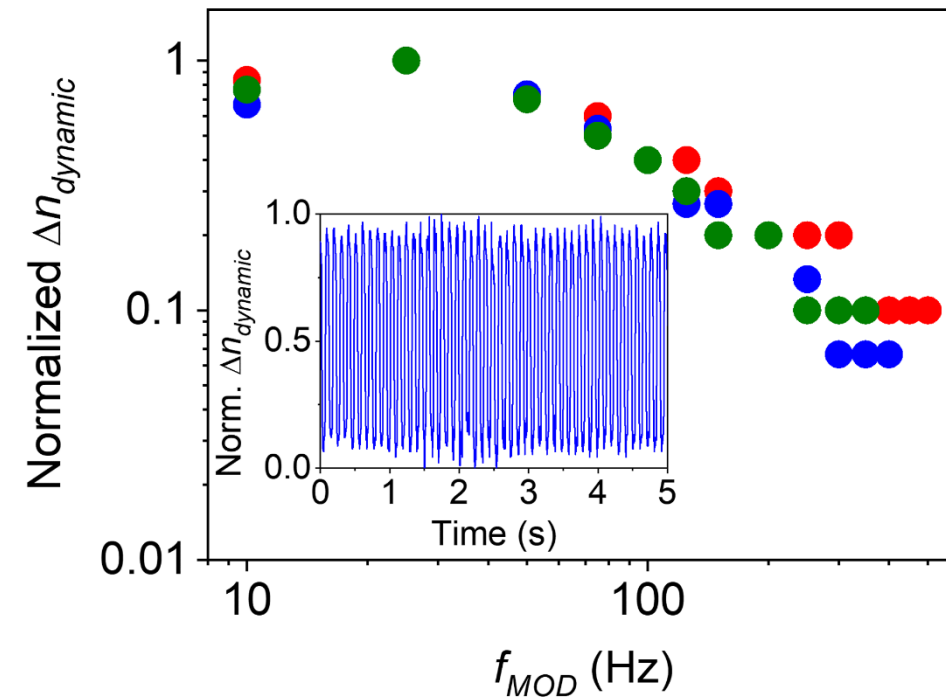
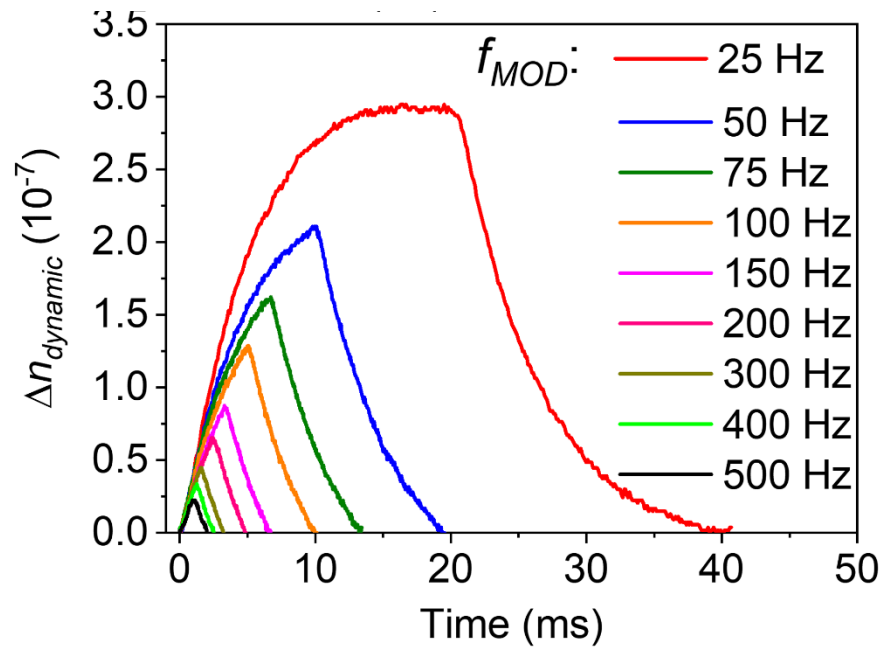
Birefringence vs. UV polymerization



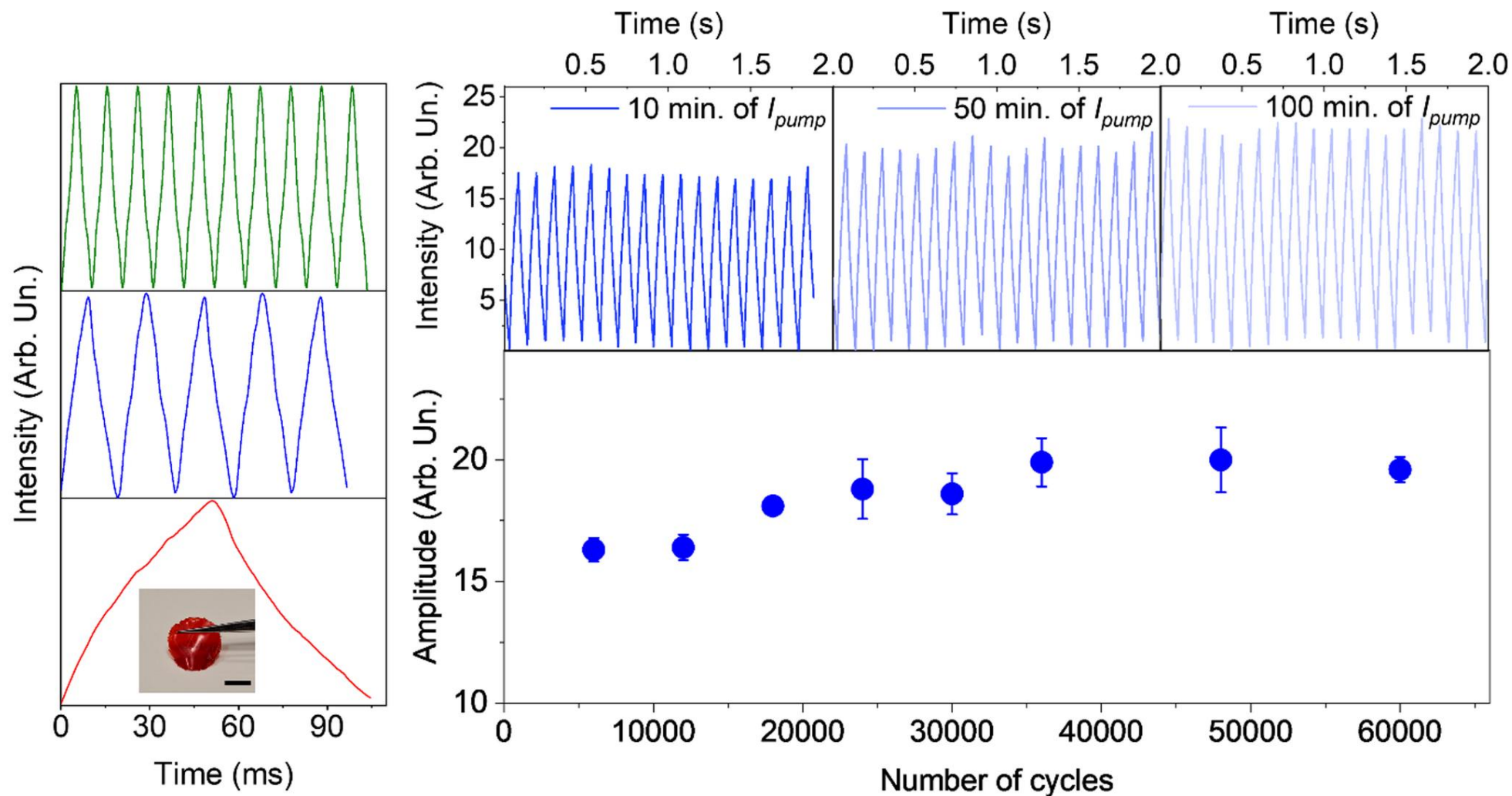
Dependence on pump intensity



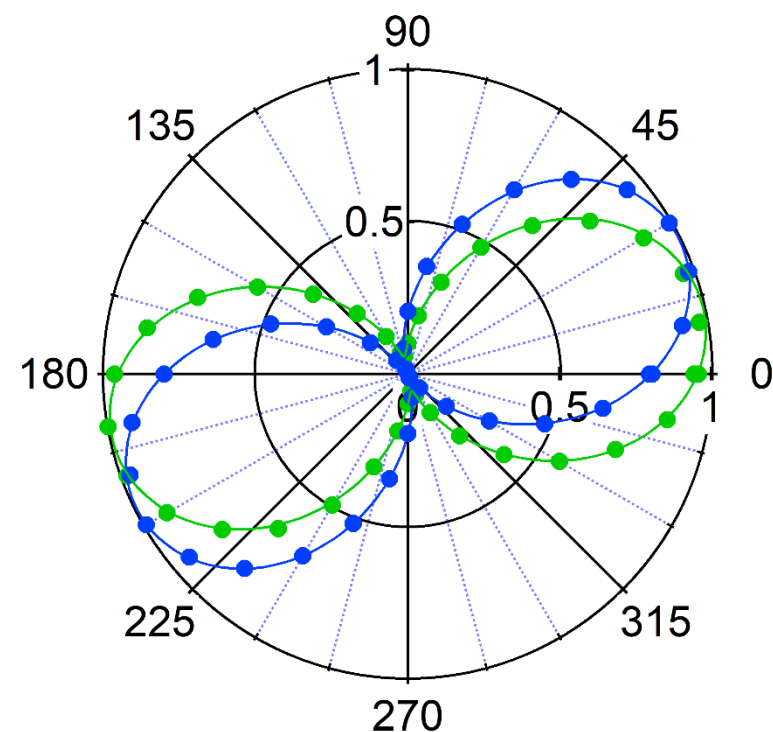
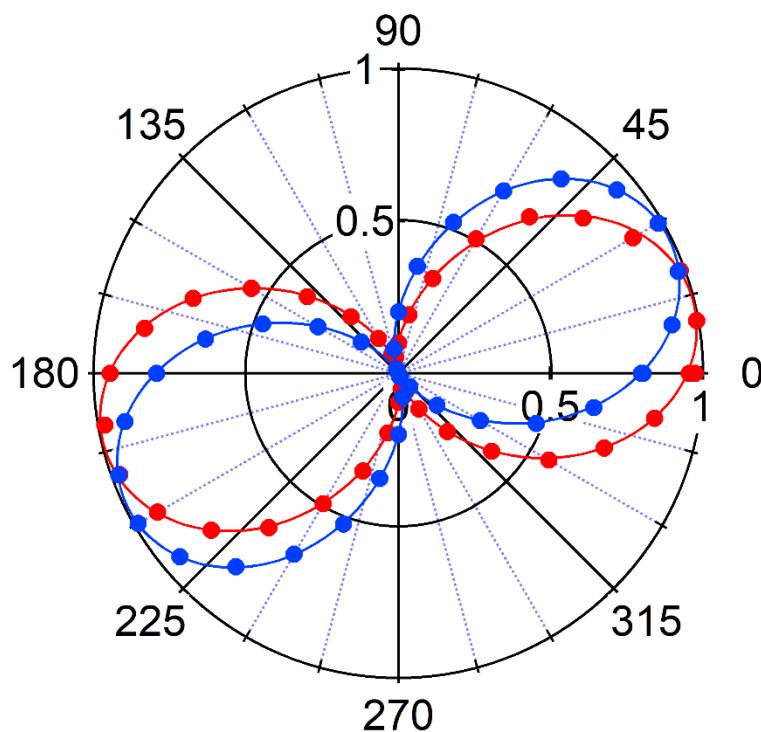
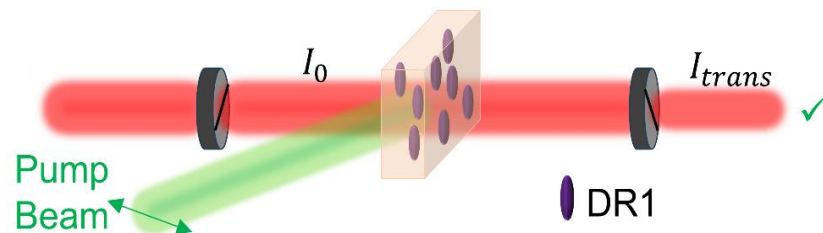
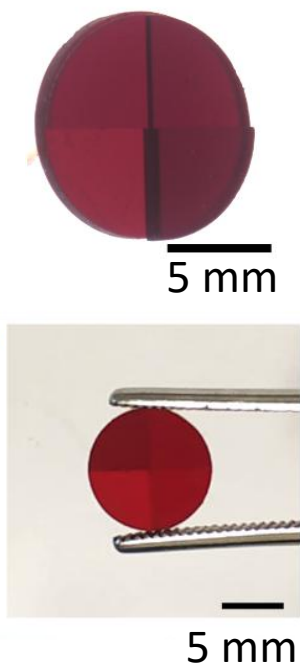
Light-by-Light modulation



Device operation

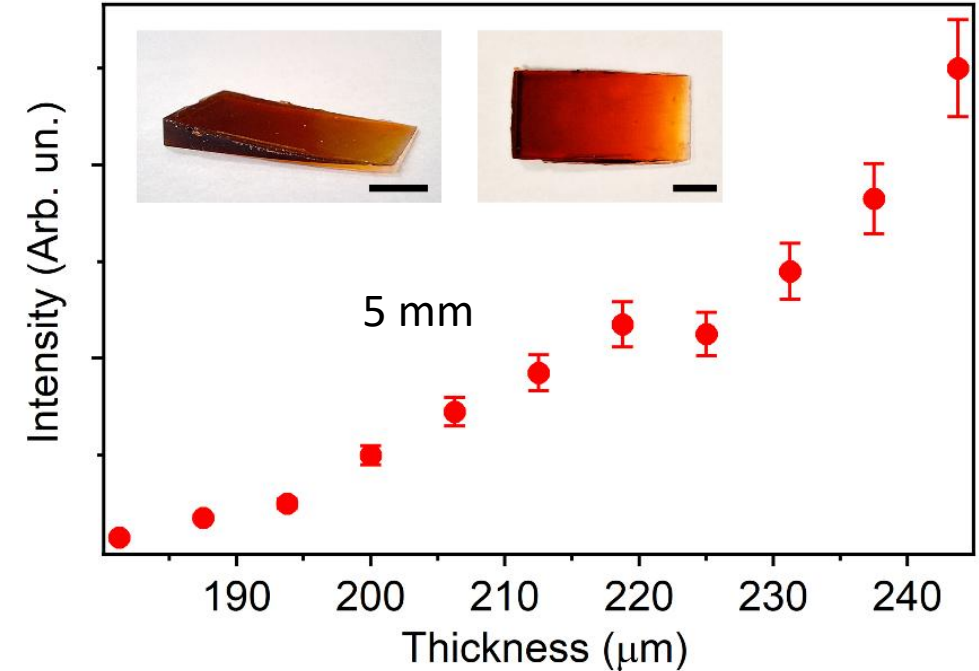
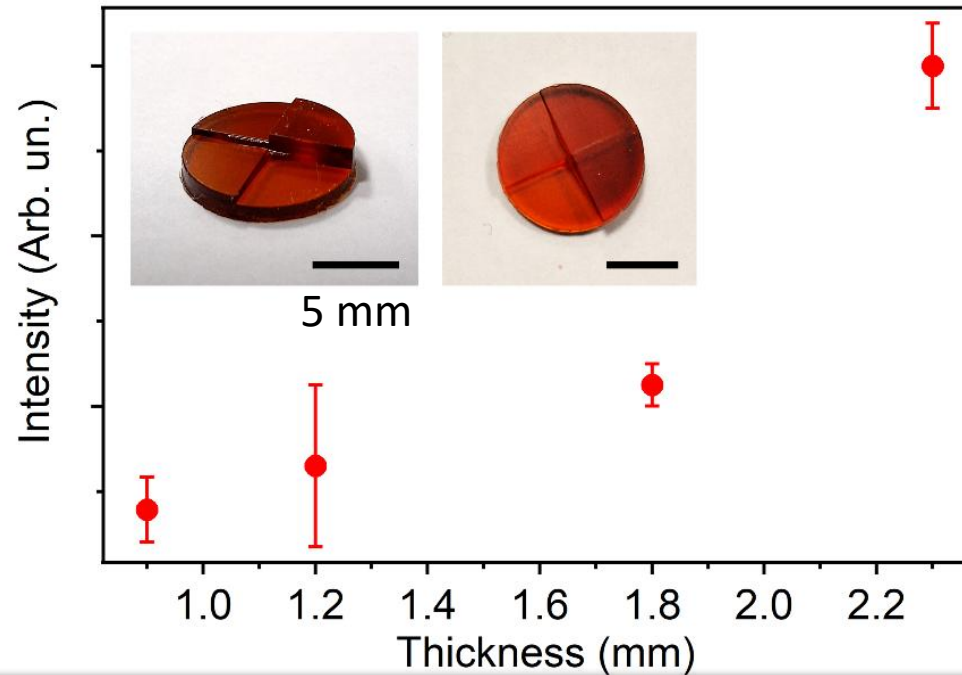


Polarization properties



3D printed devices

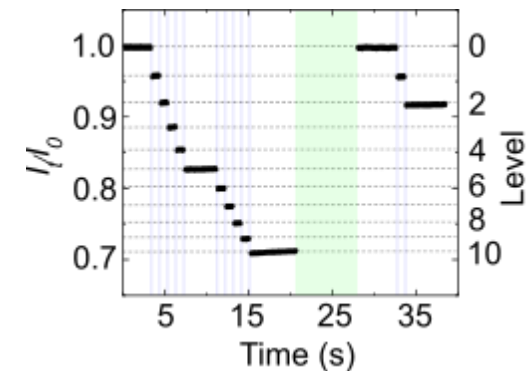
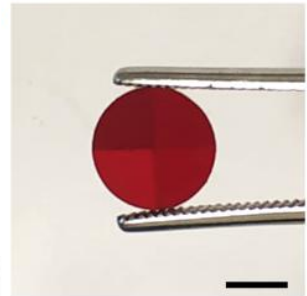
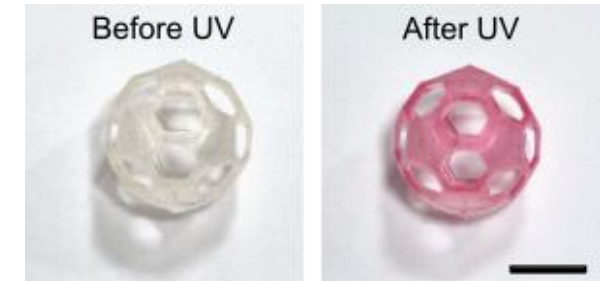
$$\frac{I(I_{pump}, t)}{I_0} = \sin^2 \left(\frac{\pi |\Delta n| d}{\lambda_{probe}} \right)$$



3D printed devices with photo-responsive molecules can be used effectively to optically modulate the intensity of light beams. The combination of 3D structures and photo-induced birefringence might enable exceptional spatio-temporal control of input beam intensities.

Conclusions

- ✓ Demonstrated practicability of 4D printing for photonics, controlling the propagation (intensity, polarization...) of light by external optical stimuli
- ✓ By combining input data processing and memory capabilities, photochromic materials are interesting for all-organic and all-optical operations to be integrated in 3D architectures
- ❑ Further integration of active and nonlinear materials and components for a truly automated operation, enhance photo-conversion rates and yield.



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