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-Supporting Information-

Hierarchical Chemomechanical Encoding of Multi-Responsive Hydrogel Actuators via 3D Printing

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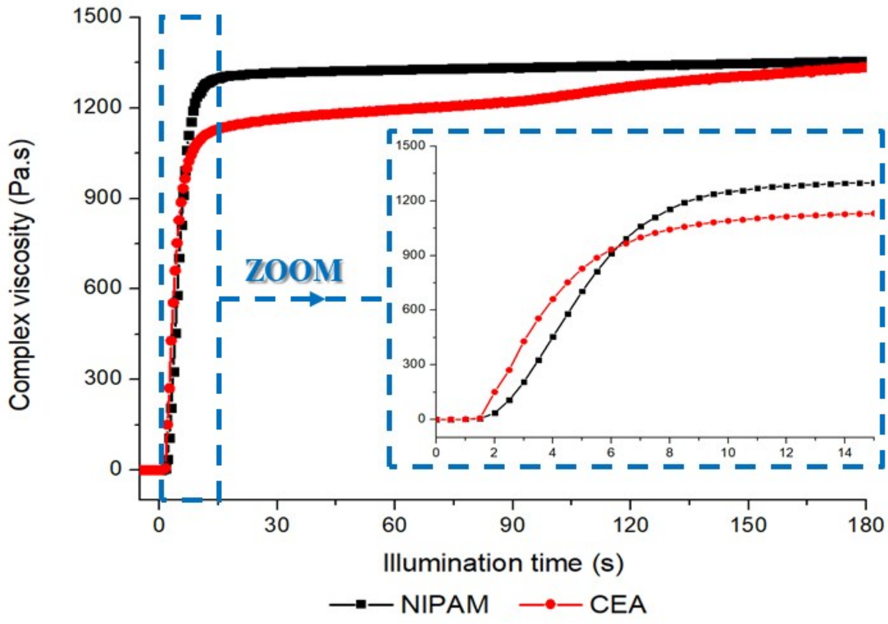


Figure S1. Complex viscosity with illumination time during photo-polymerization of NIPAM and CEA.

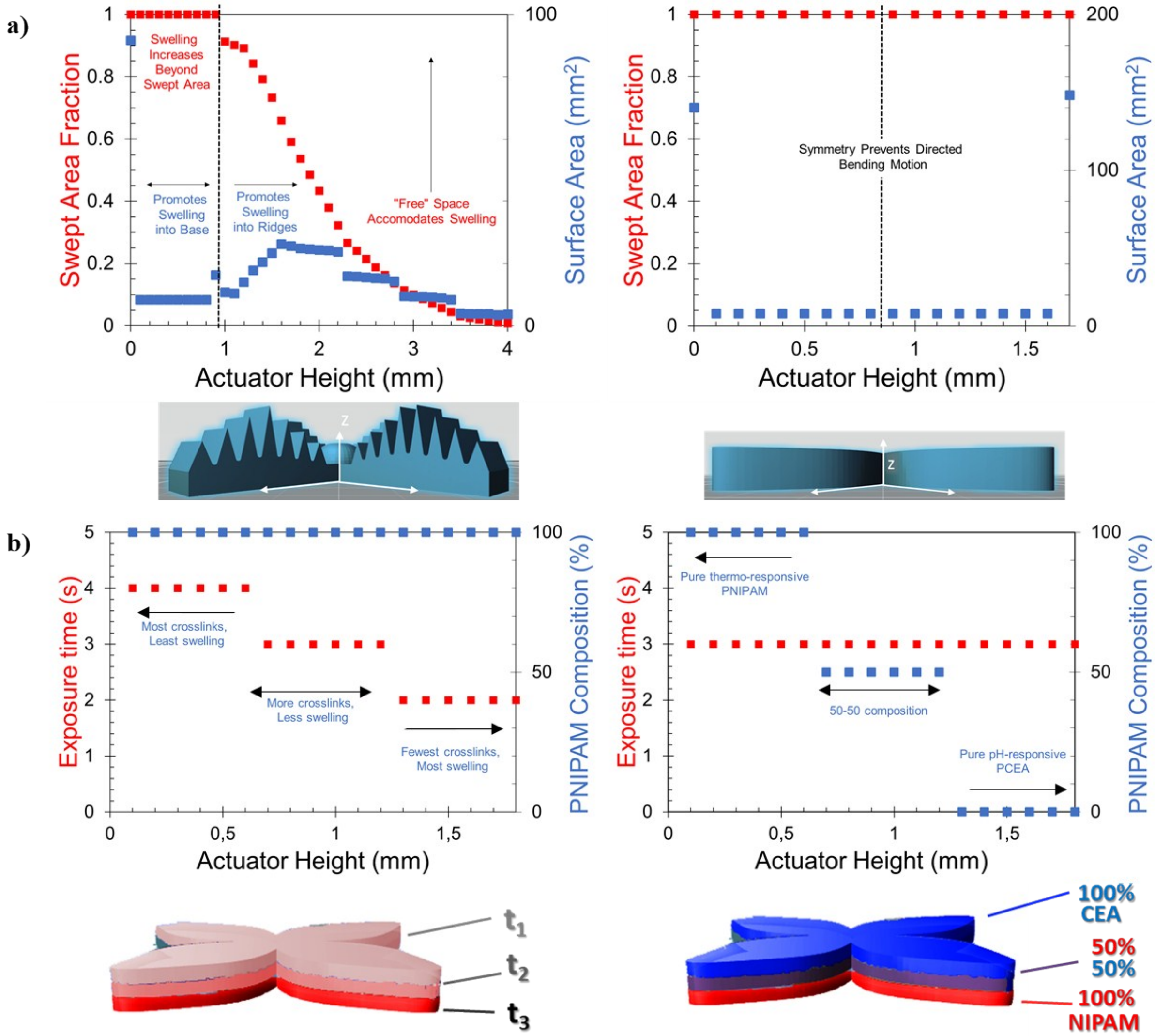


Figure S2. Schematic of the three separate 3D-printed chemomechanical gradients. (A) Distribution of the calculated surface area to volume ratio via mechanical design into the multi-armed gripper (left) and the flower-like (right) structures as a function of Z-height in the hydrogel actuator. (B) Distribution of the crosslinking density via different UV photo-exposure time (left) and the chemical composition via resin vat exchange (right) as a function of Z-height in the hydrogel actuator.

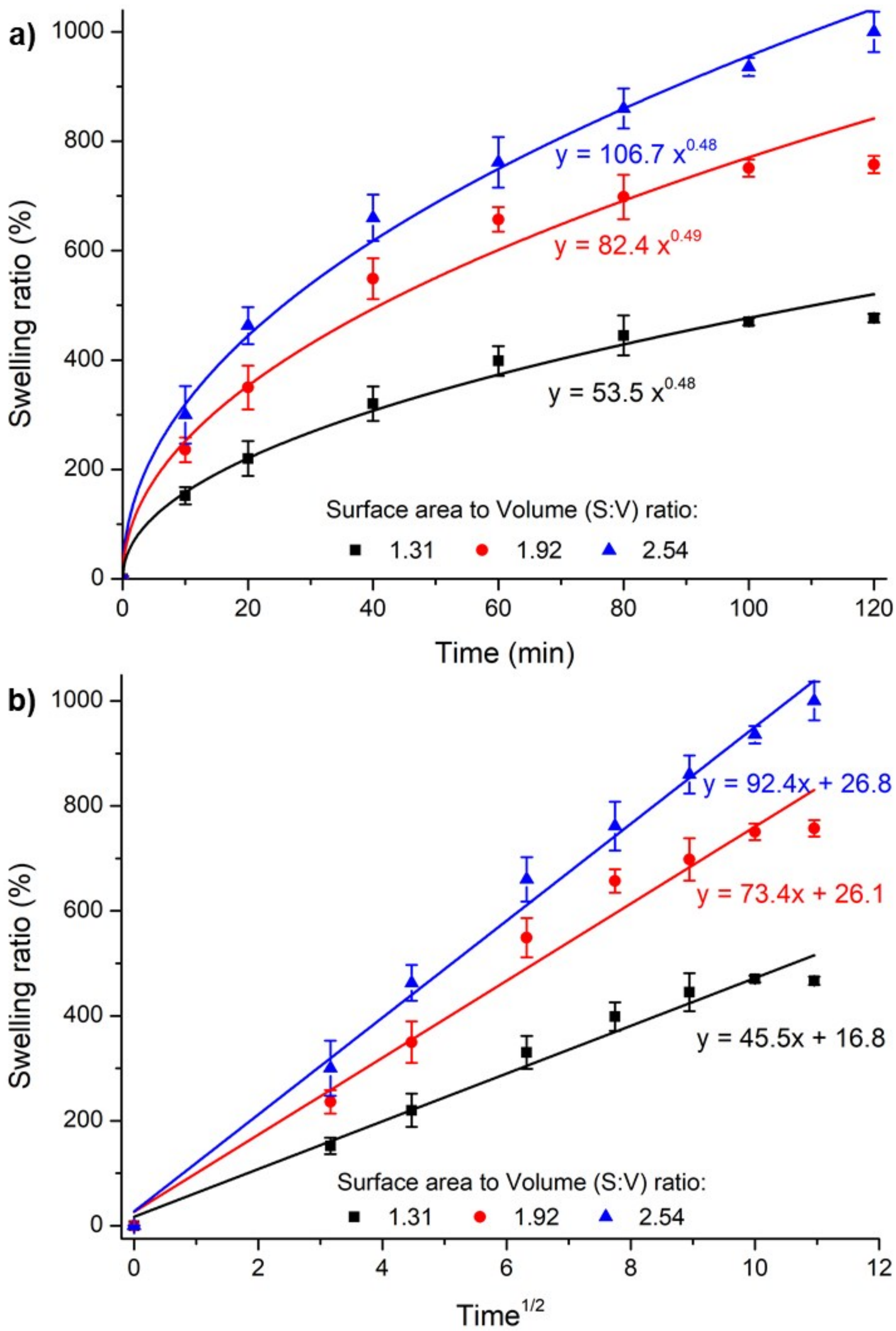


Figure S3. Power-Law fits (a) and swelling *vs*. the square root of immersion time plots (b) of the osmotic swelling rate of PNIPAM cubic lattices with different designed S:V ratios.

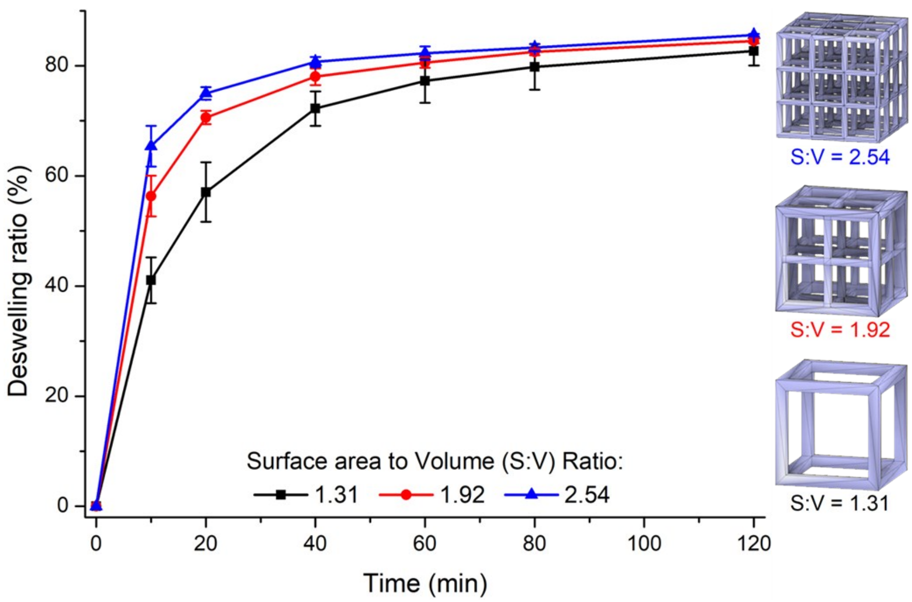


Figure S4. Deswelling performance of 3D-printed PNIPAM cubic lattices with different S:V ratios.

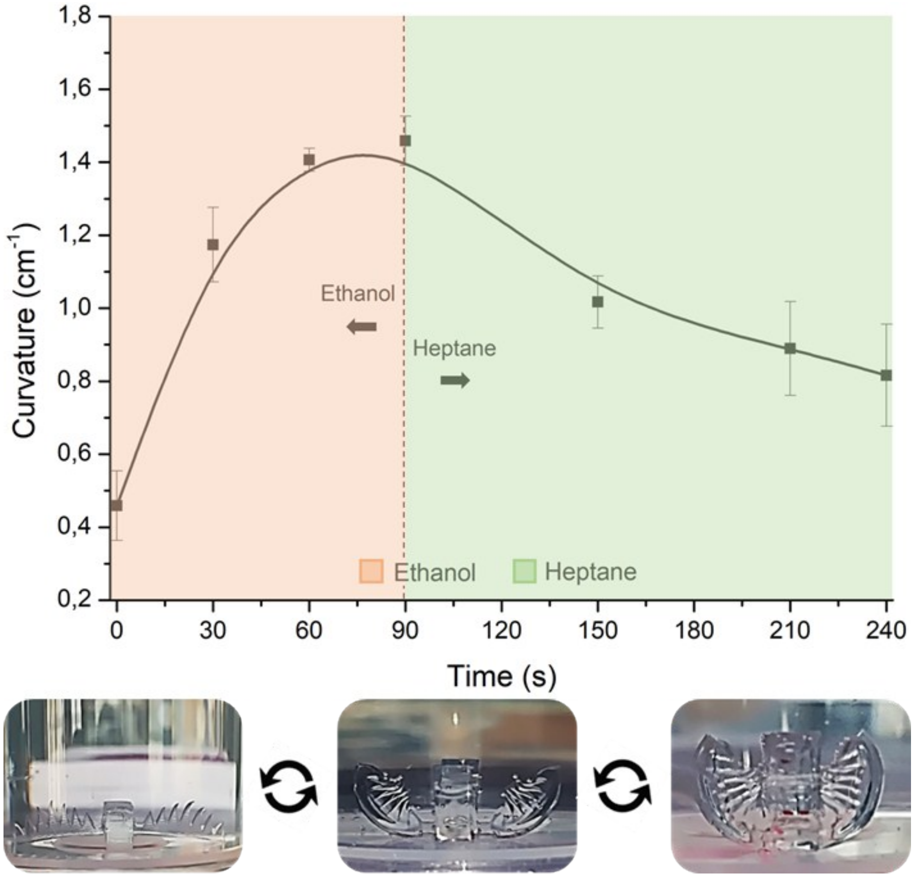
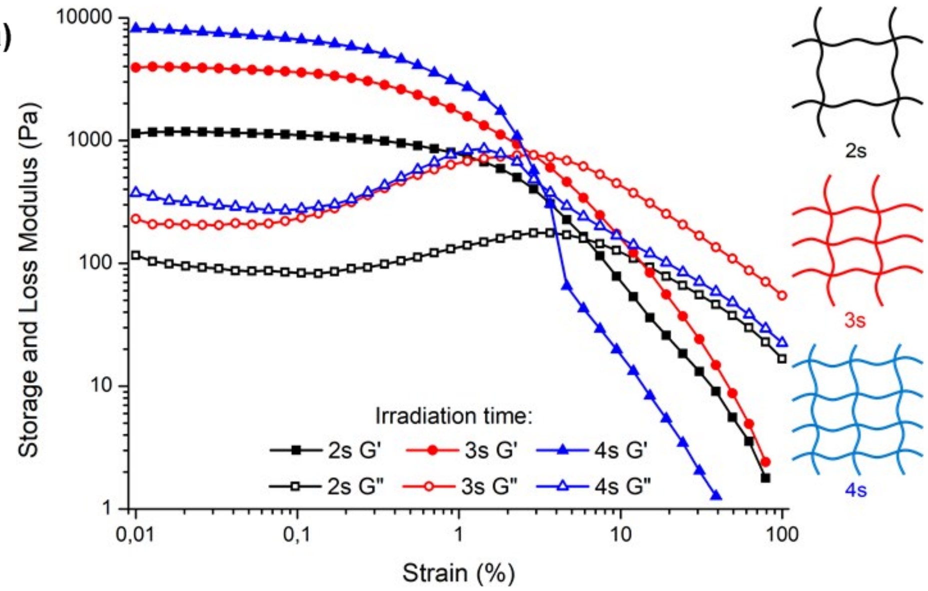


Figure S5. Detailed first cycle of the osmotically driven actuation of 3D-printed gradient-like PNIPAM structures of varying S:V ratio along the printing Z-axis.

a)



b)

t (s)	G' (Pa)	G'' (Pa)	ν_e (10^{-6} mol/cm³)
2s	930	110	0.375
3s	2475	495	0.998
4s	4340	540	1.751

Figure S6. Oscillation amplitude sweeps of PNIPAM-based hydrogels with different crosslinking density by means of controlling the near-UV exposure time (a) ; An estimation of the effective crosslinking density as determined by modulus measurements in the rubbery plateau (b).

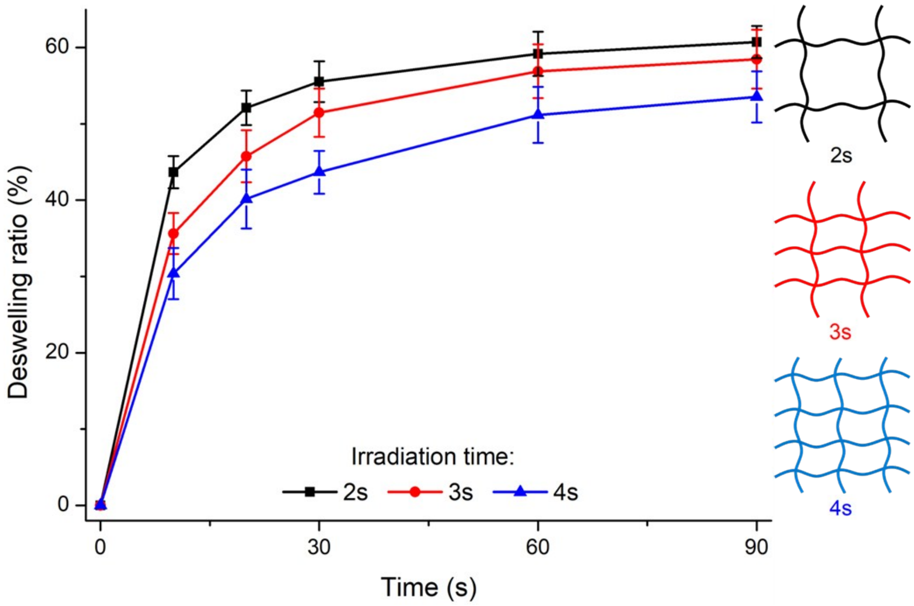


Figure S7. Deswelling performance of 3D-printed PNIPAM-based hydrogels with different crosslinking density by means of controlling the near-UV exposure time.

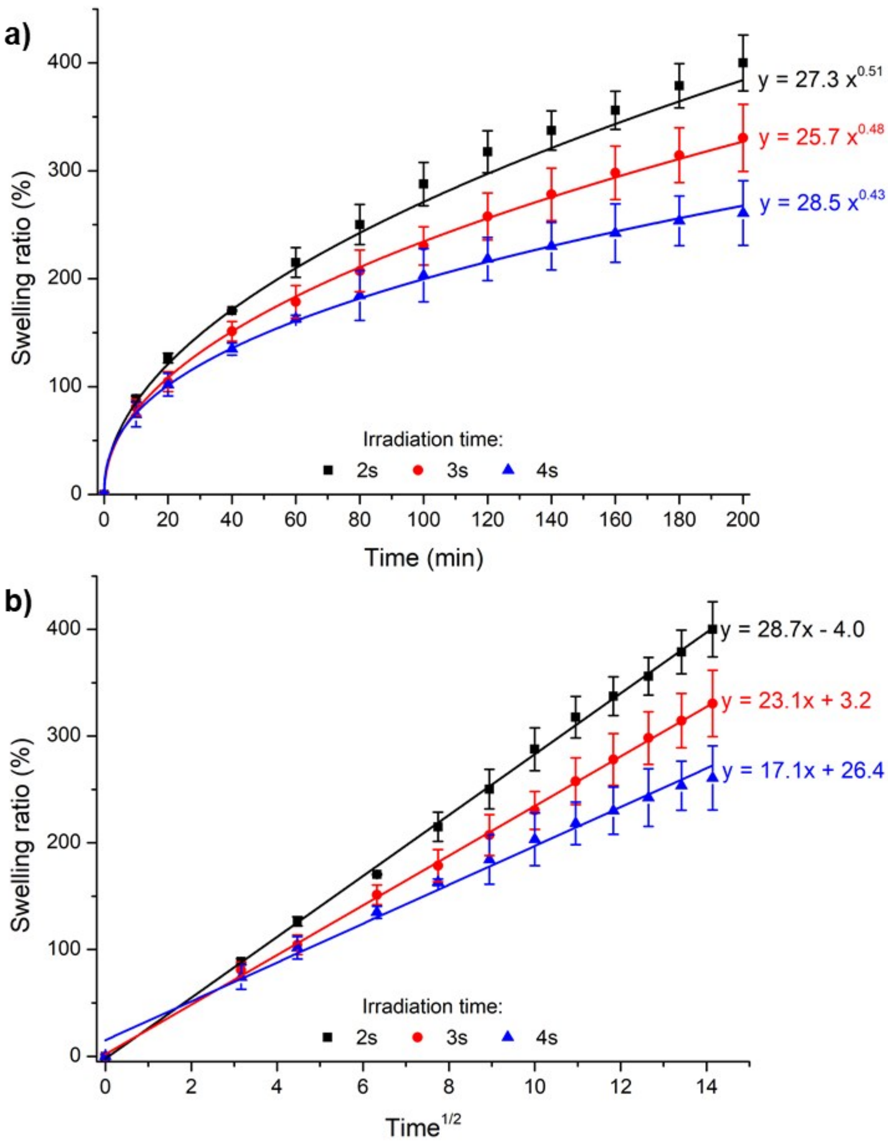


Figure S8. Power-Law fits (a) and swelling *vs*. the square root of immersion time plots (b) of the swelling rate of PNIPAM-based hydrogels with different crosslinking density by means of controlling the near-UV exposure time.

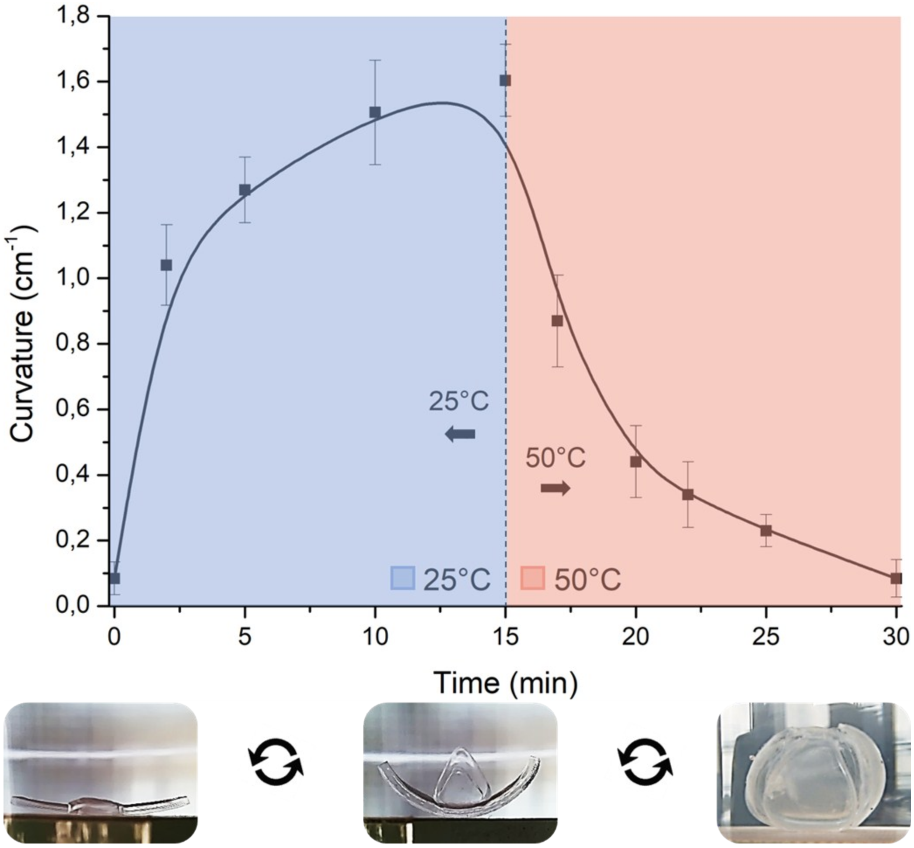


Figure S9. Detailed first cycle of the thermally driven actuation of 3D-printed gradient-like PNIPAM structures of variable crosslinking density along the printing Z-axis.

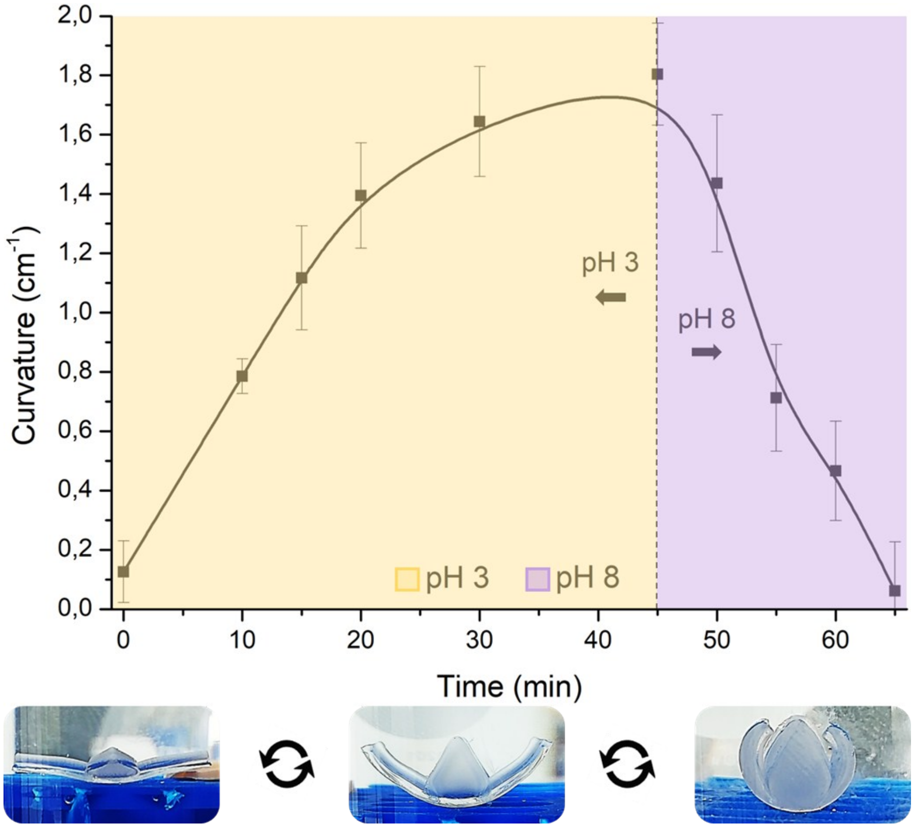


Figure S10. Detailed first cycle of the pH-controlled actuation of 3D-printed gradient-like structures of varying layer's composition along the printing Z-axis.

Table S1. Characteristics and bending performances of the three separate synthetic strategies for programming in chemomechanical gradients.

Strategies	Surface Area to Volume Ratio	Crosslinking Density	Chemical Composition
Geometries			
Dimensions	2 cm length 0.4 cm thickness	2 cm length 0.18 cm thickness	2 cm length 0.18 cm thickness
Stimuli	Osmotic pressure	Temperature	pH
Time of actuation	90 sec in ethanol (from flat to curved) 150 sec in heptane (from curved to flat)	15 min in distilled water at 25°C (from flat to curved) 15 min in distilled water at 50°C (from curved to flat)	45 min in citrate-phosphate buffer at pH 3 (from flat to curved) 20 min in citrate-phosphate buffer At pH 8 (from curved to flat)
Curvature upon actuation	1.4 cm^{-1} 	1.55 cm^{-1} 	1.75 cm^{-1}