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Supporting Information

3D Shape Change of Multi-Responsive Hydrogels Based on Light-Programmed Gradient in Volume Phase Transition

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Experimental

Materials: All chemicals were obtained from Sigma Aldrich and used as received unless otherwise specified. Deionized water was produced by an ELGA Laboratory water station and had a resistivity of 18.2 m/cm. To remove inhibitors, oligoethyleneglycol methyl ether methacrylate [300 g mol^{-1},OEGMA], 4-acetoxystyrene (AOST) and ethyleneglycol dimethacrylate (EGDMA) were passed through a basic alumina column immediately before use. Membranes for dialysis (molecular weight cut-off of 3500 Da) were purchased from Thermo Fisher Scientific.

Preparation of the hydrogels: As a representative example, 0.38 mL AOST monomer, 0.724 mL OEGMA monomer and 23 µL EGDMA crosslinker were mixed in a glass vial. 33 µL of IRGACURE 2959 photoinitiator was then added. The vial was shaken by hand to make a homogeneous solution mixture. Two pieces of glass slides were separated by a spacer with a thickness of 1 mm. Then the solution was injected into the holder. The photopolymerization was conducted by irradiation with UV light for 30 mins (unfiltered spectrum of Uvitron SunRay 600 UV Light Curing Flood Lamp System, 40 mWcm^{-2} intensity in the range 320-390 nm). Other hydrogels with different molar ratios of AOST to OEGMA were prepared using the same method. The crosslinker content was fixed at 2.5 mol% for all of the samples. After completion, the hydrogels were dialyzed against DI water (24 h) and acetone (24 h). Finally, the gels were dried under high vacuum at 45 °C for two days. To simplify the discussion, “H0X0Y” refers to the hydrogel with a 4-acetoxystyrene/OEGMA molar ratio of x/y. Monomer conversions were calculated gravimetrically by measuring the weight of the purified dry gel. The monomer conversions were calculated to be 80%, 78%, 77% and 74% for H0406, H0505, H0604 and H0703, respectively.

Measurement of water uptake:
To measure the water uptake values by gravimetric analysis, a small piece of hydrogel was taken in a beaker and immersed in DI water at different temperatures for 24 h to attain the maximum swelling ratio. Three duplicate samples of each hydrogels hydrogel were prepared for swelling experiment to guarantee the reproducibility. Then, the swollen hydrogels were taken out of the water and weighed after removing the excess water on the surface. The ESR was calculated from the following equation.
Water uptake(%) = (Ws –Wd)/Wd× 100
where Ws and Wd are the weights of swollen hydrogel in equilibrium and the corresponding dried hydrogel, respectively.

UV irradiation of hydrogels
UV irradiation experiments were carried out with an unfiltered high-pressure UV lamp (220 nm-450 nm). For these experiments, the light intensity (power density) at the sample surface was measured with a spectroradiometer. The integrated power density at 254 nm was measured to be 20 mW/cm^2. The hydrogel sheets with prescribed sizes were deposited on a glass plate and immersed in aqueous media with 0.005 mM NaOH, which was then exposed to UV light.

Patterned UV light irradiation were performed using various photomasks (Cr pattern on quartz) directly onto the hydrogel sheets (2cm×1cm×1mm). The mask contains black stripes with different sizes passing at a certain angle θ with respect to the long axis of the mask. The angle between the stripes and the long axis of the mask (300 µm in width and 300 µm in distance) was varied from 0 ˚, 60 ˚ and 90˚.

Characterization
Infrared spectra of the hydrogels were acquired using a Nicolet 5700 Fourier transform infrared (FTIR) spectrometer fitted with an attenuated total reflectance (ATR) accessory that used a diamond internal reflection element (IRE) and the angle of incidence of the beam was fixed at 45˚ relative to the IRE. Thirty-two scans were averaged over a range of 500 to 4000 cm^{-1} at a resolution of 4 cm^{-1}. The yield of hydroxyketone groups was calculated as described in previous work.[1]

The absorption spectra of 4-acetoxystyrene (1×10^{-6} mol mL^{-1}) was recorded on a Varian UV-Vis Cary 4000 spectrophotometer over a wavelength range of 200-500 nm.

Raman spectra were collected using a Thermo-Fisher Almega dispersive Raman spectrometer. Spectra were collected of the hydrogels using a microscope accessory with a 503 objective, and the liquids/solutions were typically measured using the 180˚ backscatter accessory. The instrument was fitted with both 633 nm and 780 nm lasers. The spectra were collected using a single grating between 90 and 3900 cm^{-1}. An acquisition time of 1 s was used and at least 256 scans were averaged.

Microscopic deformations were recorded using a digital camera. Before studying the deformation, the H0X0Y hydrogel sheets were equilibrated at room temperature of 20 ^{o}C for 30 min to reach its equilibrium swelling state. After the UV irradiation, the temperature of the aqueous media and salt concentration were varied to study the bending behaviour of the irradiated hydrogels under different conditions.

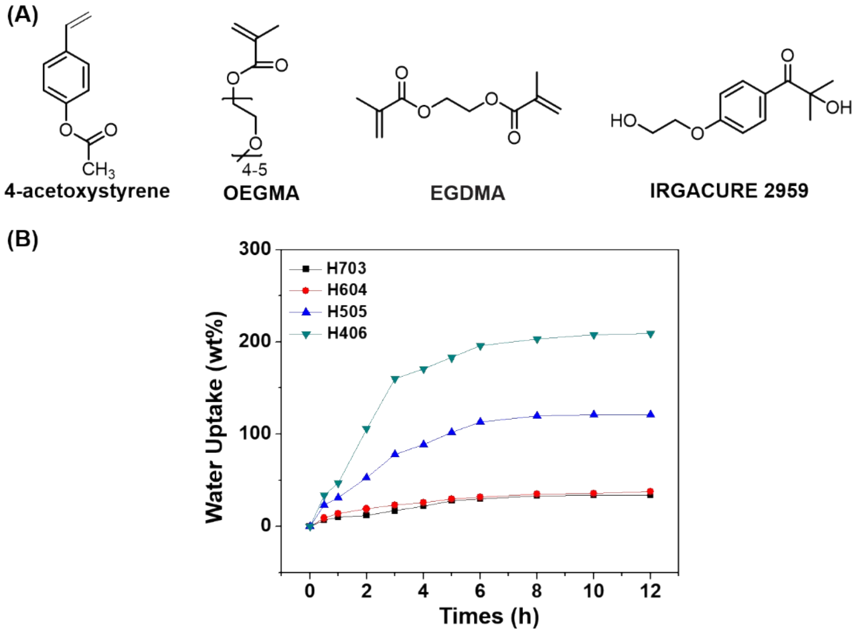

Figure S1. (A) Molecular structures of monomers, crosslinker and photoinitiator used for the preparation of crosslinked polymer hydrogel networks. (B) Water uptake curves of hydrogels with different AOST: OEGMA ratios as a function of swelling time.

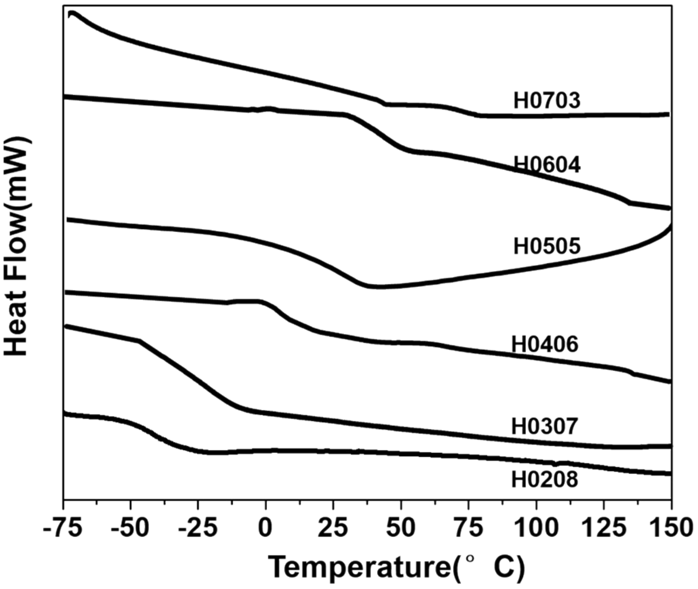

Figure S2. DSC traces for the hydrogel samples.

A single T_g was observed for all of the hydrogel samples in scanning the temperature range from – 75 to 150 ^{o}C, suggesting lack of blockiness in the hydrogel structure. The T_g of H0208 to H0703 were measured to be -29.1, -10.7, 12.1, 31.4, 48.3 and 64.9 ^{o}C, respectively.

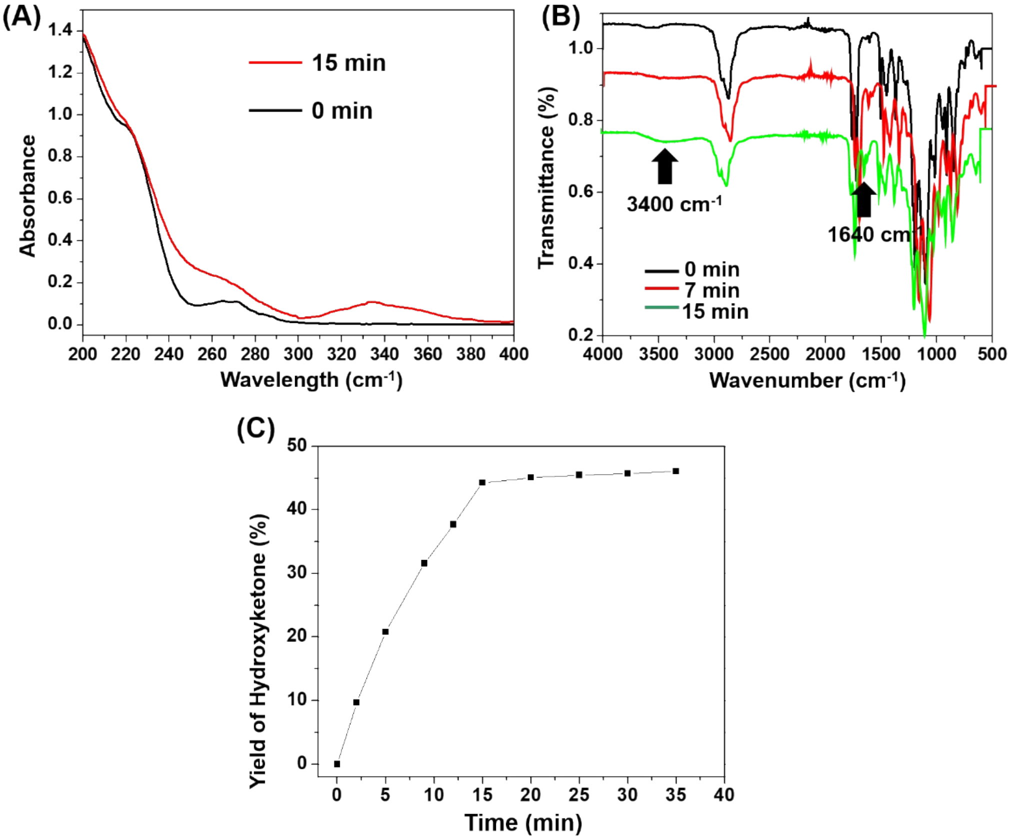

Figure S3. (A) UV-vis spectra of AOST in chloroform 1×10^{-7} mol.L^{-1}. The UV-Vis spectrum of AOST monomer in chloroform shows that the unexposed sample has an absorbance band near 270 nm, which corresponds to the n-π^* transition of the phenyl chromophore. A significant increase in UV absorption was observed after UV irradiation. Two new absorbance maxima located at ca. 255 nm and 340 nm were observed after irradiation. (B) ATR-FTIR spectra of the dry network polymer after different UV irradiation time. (C) The yield of hydroxyketone groups as a function of UV irradiation time (power density = 20 mW/cm^2). The hydrogels were dried before measurement in order to minimize the peak at 1640 cm^{-1} due to hydrogen bonds between ester carbonyl groups and water, which overlaps with the peak from the photo-rearrangement product. Longer irradiation times did not generate additional hydroxyketone units, indicating the maximum yield of hydroxyketone was achieved after 15 mins of UV irradiation under these conditions.

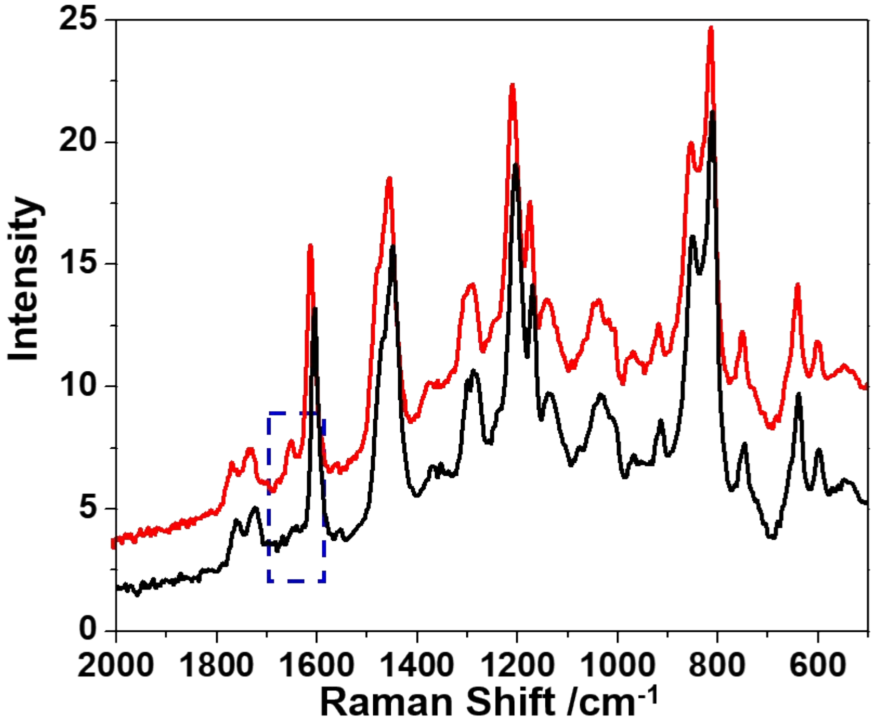

Figure S4. Raman spectra of H0505 hydrogels before (black) and after (red) UV irradiation.

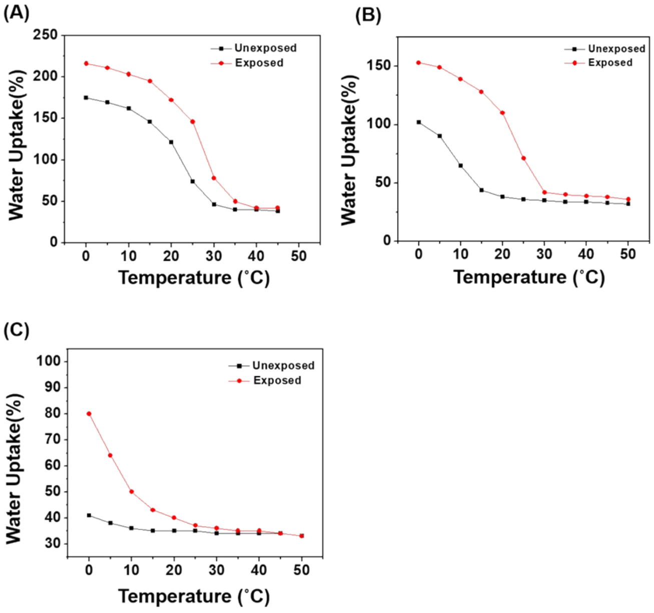

Figure S5. Temperature dependence of the water uptake of unexposed and exposed hydrogels (A) H0505, (B) H0604, (C) H0703.

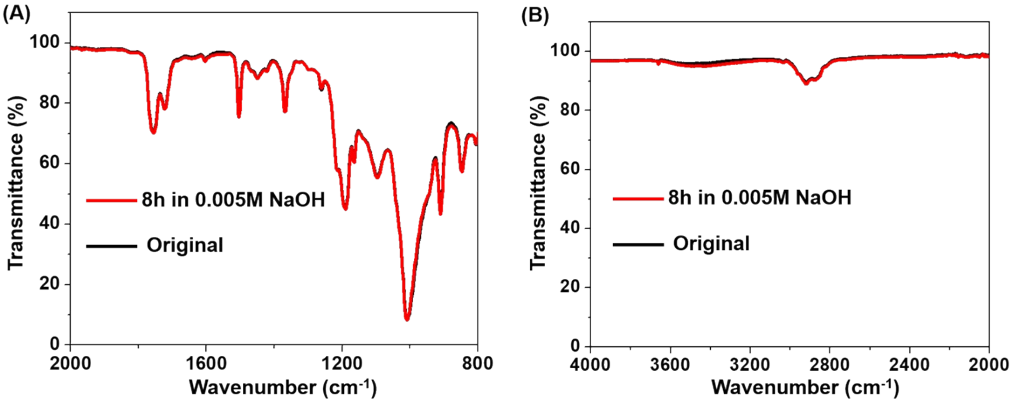

Figure S6. ATR-FTIR spectra of dehydrated hydrogel before and after immersion in 0.005M NaOH solution. The FTIR spectra of the hydrogels displayed no obvious change over 8 h.

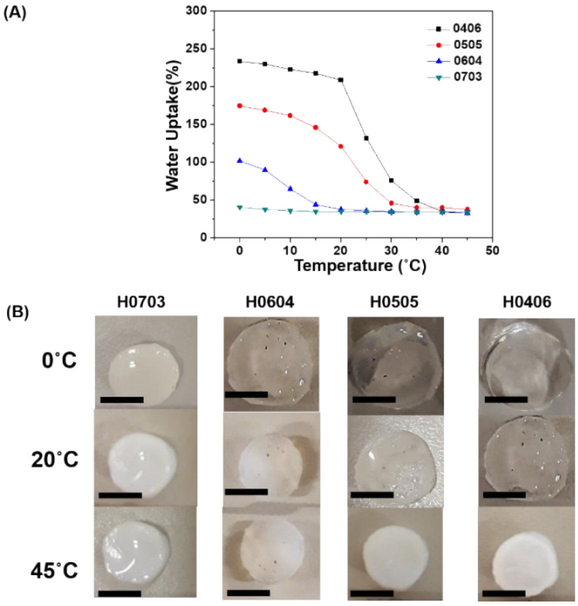

Figure S7. (A) Temperature dependence of the water uptake of hydrogels with different AOST: OEGMA ratios. (B) Photographs of the gel disks with different AOST: OEGMA ratios at different temperatures. Scale bars: 1.5 cm.

The 2D dimensions of all the hydrogels exhibited strong dependence on temperature (except for H0703 hydrogel with the highest AOST content). There was only a slight change in size and transmittance of H0703 as the temperature of the aqueous medium changed from 0 ^{o}C to 45 ^{o}C. At all temperatures this hydrogel was above the VPTT. In contrast, the other three samples were transparent and swollen at an initial temperature of 0 ^{o}C. When the temperature was increased to room temperature, H0604 immediately became opaque and the hydrogel disk was significantly reduced in size. This change in transmittance is attributed to disruption of the hydrophilic/hydrophobic balance when the temperature was higher than the VPTT. H0505 and H0406 remained transparent at room temperature, even though the disk diameters were reduced by 26% and 14%, respectively. Moreover, all of the hydrogels became opaque and significantly smaller at a temperature of 45 ^{o}C.

Table S1. The measured volume phase transition temperature of hydrogels before and after UV irradiation. The VPTT was estimated from plots of the water uptake vs. temperature.

Code	Unexposed	Exposed
H0703	-	11 ^{o}C
H0604	14 ^{o}C	25 ^{o}C
H0505	25 ^{o}C	34 ^{o}C
H0406	32 ^{o}C	39 ^{o}C

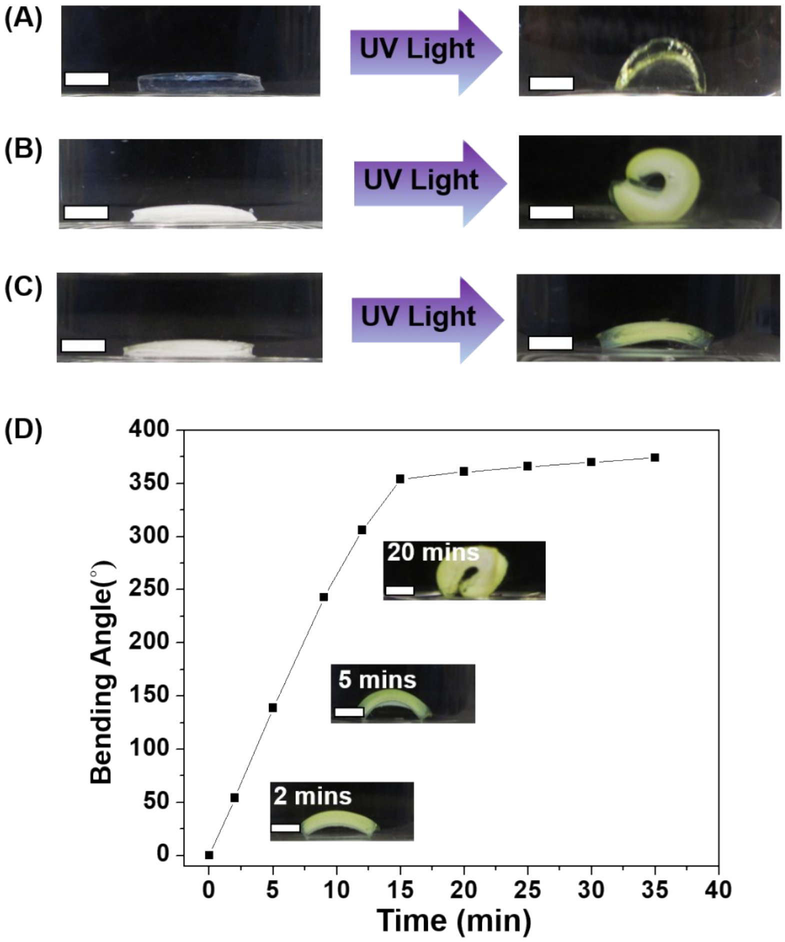

Figure S8. Photographs of the hydrogels with different AOST: OEGMA ratios (A) H0505, (B) H0604, (C) H0703 bending backward towards the irradiated part at 20 °C. (D) Bending angle of the H0604 hydrogel as a function of irradiation time.

It was found that the bending angle increased with the increase in irradiation time and finally reached a stable bending angle. The bending angle did not change significantly on further irradiation.

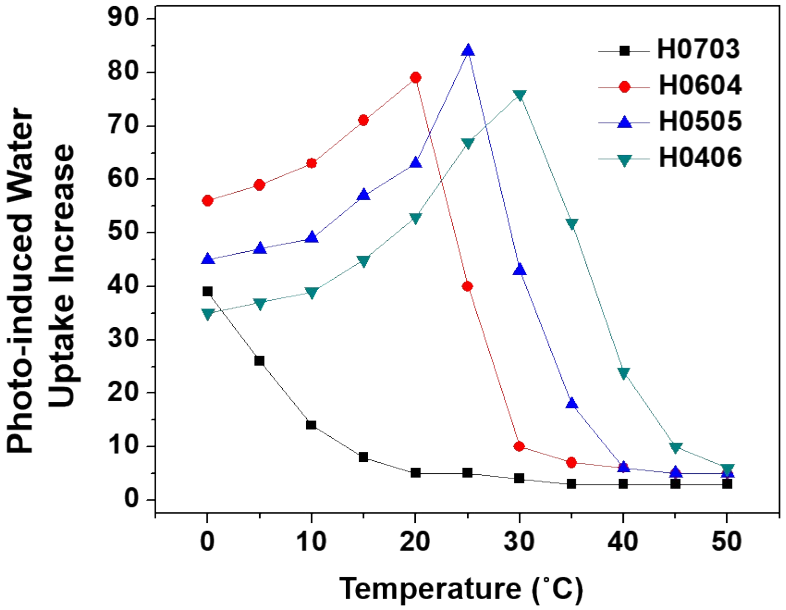

Figure S9. The photo-induced increase in water uptake (water uptake of unirradiated hydrogel minus water uptake of the irradiated hydrogel) for different samples as a function of temperature.

It was observed that the water uptake in all the samples was significantly increased after illumination in 0.005 mM NaOH aqueous solution with UV light for 15 mins. For example, from 0 ^{o}C to 20 ^{o}C both the unexposed and exposed H0406 hydrogels were swollen, and the water uptake of the exposed sample was approximately 35% higher. The difference in water uptake increased with increasing temperature and approached a maximum at 30 ^{o}C (77% wt). However, the difference in water uptake between unexposed and exposed sample significantly decreased from 35 ^{o}C to 50 ^{o}C. Such dependence of change in photoinduced water uptake on temperature is due to different thermal properties of unexposed and exposed sections of the samples. The unexposed H0406 hydrogel undergoes a volume phase transition from 20 ^{o}C to 35 ^{o}C and consequently the water uptake rapidly reduced, while the exposed region was still in a relatively highly swollen state at this temperature range in which the water uptake only undergoes a slight reduction, due to increased hydrophilicity and VPTT. Both the unexposed and exposed hydrogels were highly dehydrated at higher temperatures from 35 ^{o}C to 50 ^{o}C, resulting in negligible increase in water uptake.

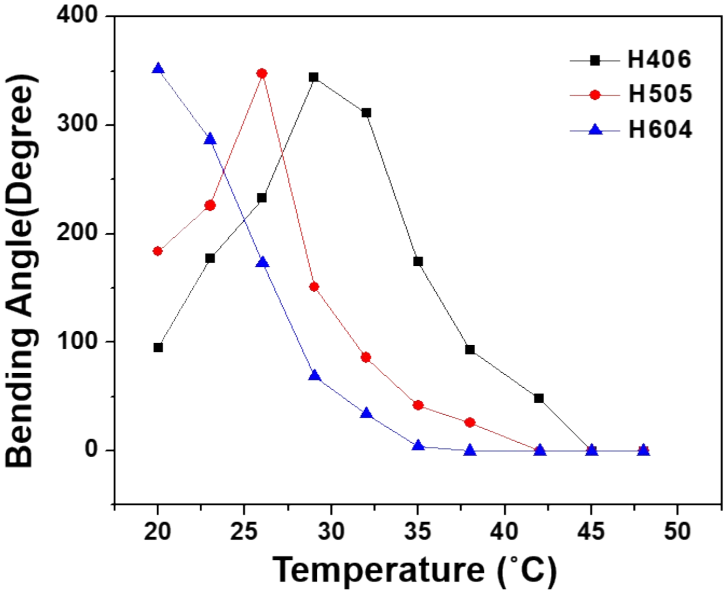

Figure S10. The bending angles of hydrogels of different compositions measured as a function of temperature.

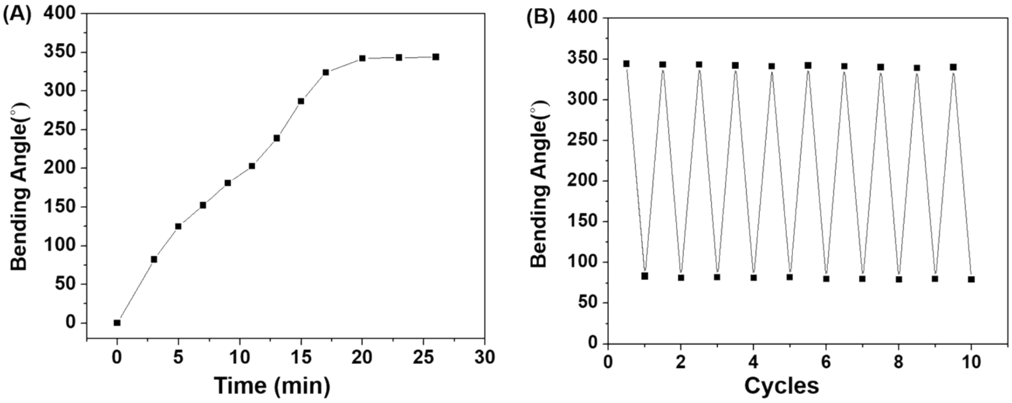

Figure S11. (A) Kinetic of bending of H0406 hydrogel under the stimulus of a temperature change from 20 °C to 29 °C. (B) The reversible shape change of H0406 hydrogel during cycles of temperature increase and decreases.

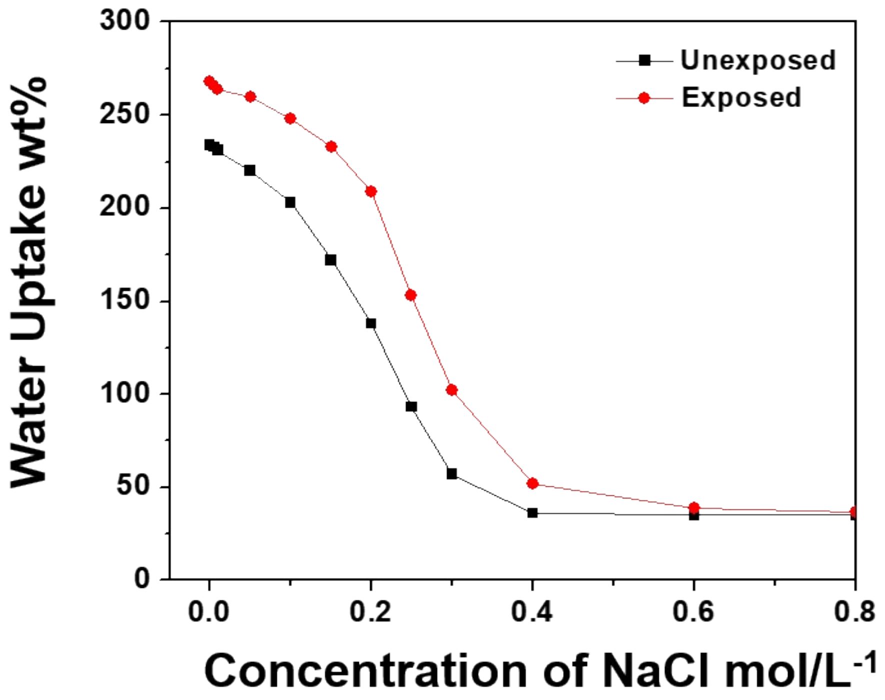

Figure S12. The water uptake of unexposed and exposed H0406 hydrogel at different NaCl concentrations at room temperature (20 °C).

The unexposed sample showed a drastic decrease in water uptake when the NaCl concentration increased from 0.1 M to 0.4 M, due to the salting out effect. The exposed sample showed a higher water uptake in solution with a NaCl concentration from 0 to 0.4 M. The sample was still in the highly swollen state when the concentration of NaCl was from 0.2-0.3 M while the unexposed sample exhibited significant water loss.

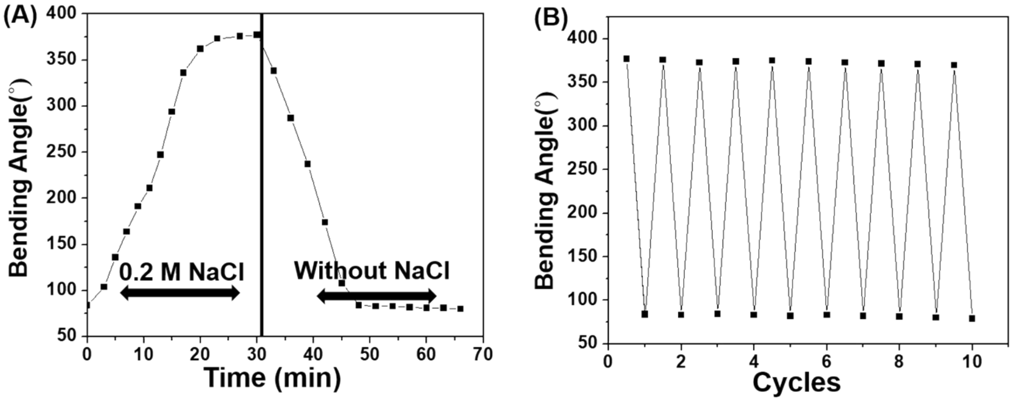

Figure S13. (A) Bending angle as a function of time in 2 wt% NaCl solution and aqueous medium without NaCl. (B) The reversible shape change of H0406 hydrogel in aqueous media with and without NaCl.

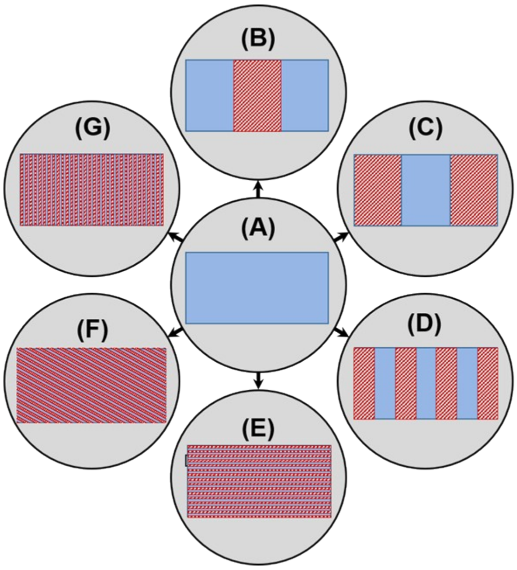

Figure S14. Schematic illustration of patterns of UV irradiation corresponding to images in Figure 3 of the main manuscript. A: no UV irradiation; (B) 3-segment patterned hydrogel with irradiation in the middle segment, (C) 2 light-exposed segments at each end, (D) 7-segment hydrogel with 4 unexposed segments; (E-G) 300 µm-wide exposed stripes and 300 µm-wide unexposed stripes oriented at (E) 0˚ (F) 60˚ (G) 90˚.

Reference

1. T. Höfler, T. Grießer, X. Gstrein, G. Trimmel, G. Jakopic and W. Kern, *Polymer*, 2007, **48**, 1930-1939.