Self-protonating spiropyran-*co*-NIPAM-*co*-acrylic acid hydrogel photoactuators

Electronic Support Information

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Synthesis of BSP-acrylate

Acrylation of trimethyl-6-hydroxyspiro-(2H-1-benzopyran-2,2'indoline) (abb. BSP-OH) was done as follows. 500 mg of BSP-OH was dissolved in 20 mL of anhydrous dichloromethane in a 100 mL round bottom flask. The flask was placed in an ethanol bath to which liquid nitrogen was poured until bubbling stopped. To such cooled mixture under magnetic stirring, 0.6 mL of triethylamide was added followed by 0.2 mL of acryloyl chloride added dropwise. The reaction was allowed to stir for 48 hours during which the mixture warmed up to room temperature as the ethanol evaporated. The reaction mixture was washed with a saturated solution of $NaHCO_3$ and deionised water several times to remove the byproducts. The coloured water phase was also washed with dichloromethane. The combined organic phases were evaporated on a rotary evaporator with an addition of column silica powder. The BSP-acrylate was purified by column chromatography using ethyl acetate/hexane 1:8 mixture as the mobile phase. After evaporation of the solvent and vacuum drying (0.1 mBar), 400 mg of white powder was obtained. Yield 67 %

Gel shrinking measurements

Since the cut gel samples are never ideal circles several diameters were measured before the light irradiation. Then as the gel shrunk the ratio in shrinking separately for every diameter was expressed in percent. The standard deviations were then calculated between the shrinking ratios for the given time interval. A calculation of the relative swelling percent example for the 0-0 blank poly(NIPAM) gel is given below.

The ratio of the diameter of the dried gel and fully swollen gel is:

$$\frac{d_{\min}}{d_{\max}} = 0.66$$

The measured shrinking of 3 dimensions of the gel versus the light irradiation in µm is given:

	0min	5min	10 min	20 min
Diameter 1	3876	3845	3794	3721
Diameter 2	3526	3484	3464	3433
Diameter 3	3879	3802	3818	3770

For every diameter the swelling ratios are calculated for each time interval and expressed in %:

	0min	5min	10 min	20 min
Diameter 1	100.0%	98.8%	98.2%	97.4%
Diameter 2	100.0%	99.2%	97.9%	96.0%
Diameter 3	100.0%	98.0%	98.4%	97.2%

Then for every given time interval the average swelling percent is calculated along with the standard deviation:

	0min	5min	10 min	20 min
Average swelling	100.0%	98.7%	98.2%	96.9%
Standard deviation	-	0.5%	0.2%	0.6%

After applying the following formula $D = \left[1 - \left[\frac{(d_{\max} - d_x)}{(d_{\max} - d_{\min})}\right]\right] \cdot 100\%$ we obtain the following relative swelling values.

	0min	5min	10 min	20 min
Average swelling	100%	98.03%	97.27%	95.30%
Standard deviation	-	0.76%	0.30%	0.91%

The standard deviations were multiplied by $\frac{1}{\frac{d_{\min}}{d_{\max}}} = \frac{1}{0.66} = 1.5151$

Therefore, the relative swelling percent we use expresses the change in dimensions between the fully swollen state and the dried dehydrated state. See Figure S1 below.

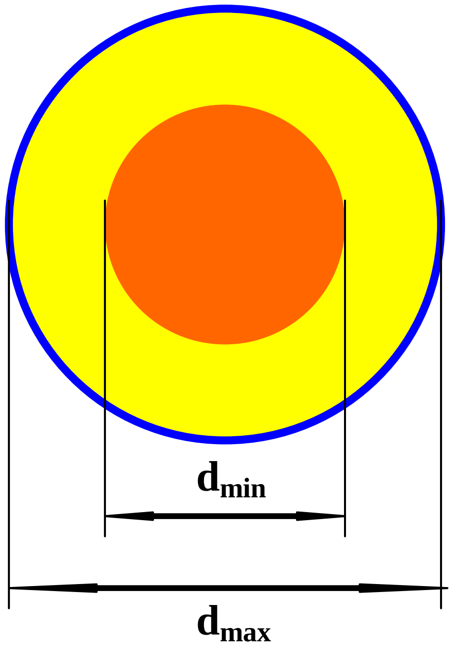

Figure S1: Graphical representation of the relative percent of swelling used. Blue represents the fully swollen diameter d_{max} (100 % relative swelling); orange represents the diameter of the dried gel d_{min} (0 % relative swelling); yellow colour is the actuator operating range.

UV-Vis Spectroscopy

Changes in the absorbance spectra of the spiropyran hydrogels under different illumination conditions were recorded in reflectance mode using two fiber-optic light guides connected to a Miniature Fiber Optic Spectrometer (USB4000 - Ocean Optics) and aligned using an in-house made holder (Fig. S1). The in-house-designed holder was fabricated using a 3D printer (Dimension SST 768) in black acrylonitrile butadiene styrene co-polymer (ABS) plastic in order to minimise interferences from ambient light. The two parts of the holder (one to be placed underneath the hydrogel, the other one on top (Figure S1A) were designed using ProEngineer CAD/CAM software package and fixed together to ensure no interferences from ambient light

(Fig. S1B). The light source was a LS-1 tungsten halogen lamp (white light) obtained from Ocean Optics, Inc. The spectra were calibrated with a white standard WS-1-SL provided also by Ocean Optics Inc. Data from the spectrometer was processed using Spectrasuite software provided by Ocean Optics Inc. For clarity, the absorbance spectra recorded were smoothed using Origin software using Savitzky–Golay algorithm.

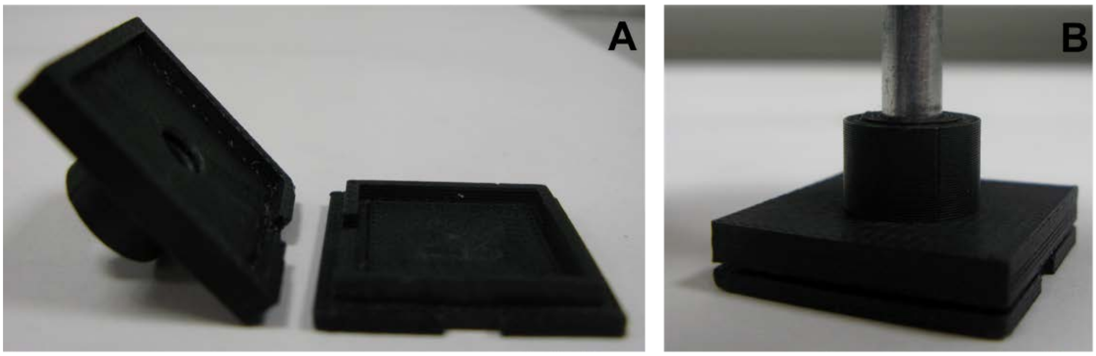

Figure S2. In house designed holder used for absorbance measurements of the spiropyran hydrogels.

Gel protonation study

A separate set of gels containing only 5% of AA were prepared and placed in solutions of varying pH. Solutions of HCl were used to adjust the pH. As it can be seen in Figure S3 below the pH of 4 the gel maintains a constant size but above the pH matching the pK_a of the acrylic acid (pH = 4.2) the gels exhibit increased swelling due to the hydrophilic nature of the deprotonated $–COO^-$ groups.

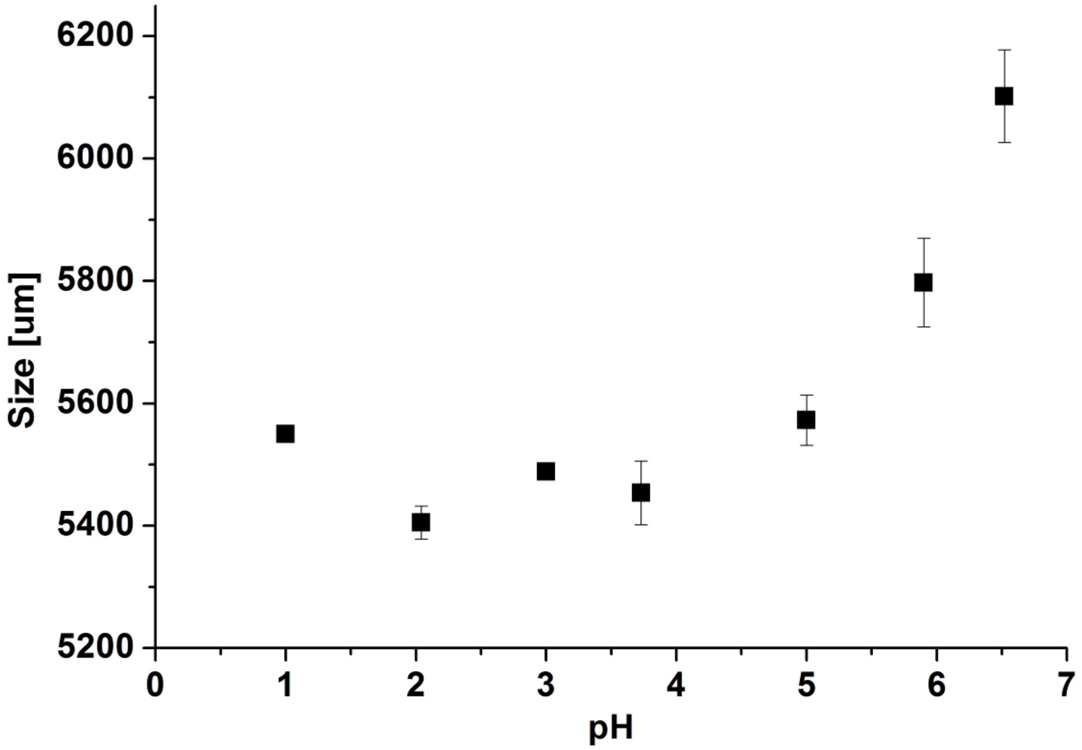

Figure S3. Diameter of poly(NIPAM) gels containing 5 mol% acrylic acid in solutions of varying pH.

FT-IR spectroscopy of gels

The gel ATR-FTIR spectra were collected on a Perkin-Elmer Spectrum 100 in the range of 650–4000 cm^{-1} and were obtained from 4 scans with a resolution of 2 cm^{-1}. Complete characterisation and assignments are listed in Table S1. The samples analysed were the BSP acrylate powder, hydrated gel 5-3 and hydrated blank poly(NIPAM) gel. Characteristic peaks of poly(NIPAM) can be seen in both the blank and gel 5-3: C=O stretch at ~1630 cm^{-1},[1] N-H in plane bending at 1552 cm^{-1},[1] and the symmetry vibrations of isopropyl methyls C-$(CH_3)_2$ at 1388 cm^{-1} and 1370 cm^{-1}.[1] Spiropyran presence is confirmed by bands at 1484 cm^{-1} (CH_3 assymetric bending)[2] and 1607 (aromatic ring).[2] A new band appearing at 1020 cm^{-1} can be assigned to the C-O(H) stretching vibration from the carboxylic acid.[3]

Table S1. Characteristic functional groups found in the hydrogels

Assignment	Poly(NIPAM)	BSP	5-3 gel	References
C=O	-	1740	1740 (sh)	4
aromatic ring	-	1607	1607 (sh)	2, 4
C=O (stretch)	1631	-	1629	1, 5
N-H (in plane bending)	1552 (sh)	-	1552	1, 5
CH_3 assymetric bending)	-	1484	1484	2
N-H (stretch)	1462	-	1460	5
C-CH_3 (symmetric bending)	1389		1388	1
C-CH_3 (symmetric bending)	1370		1370	1
C–N stretching	-	1291	-	2
-CO(H) (stretching)	-	-	1215	3
C-O ester stretch	-	1159	-	4, 6
C-H (out of plane)	-	1020	1020 (weak)	2
C-H symmetric stretching	-	1012	1012 (weak)	2
O–C–N stretching		967	-	2
Benzene ring		914	-	2

*sh - shoulder

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