Dual Light and Temperature Responsive Cotton Fabric Functionalized with a Surface- Grafted Spiropyran- NIPAAM- hydrogel

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EQUIPMENTS

X-Ray Photoelectron Spectroscopy (XPS) was performed using a Thermo Scientific K-Alpha equipped with a monochromatic A1 K_α X-ray source operating at 200W. The base pressure was 1.6×10^{-8} Mbar. Wide energy survey scans were collected over the range of 0 to 1350 eV binding energy (BE).

Scanning electron microscopy (SEM) images were recorded on a FEI Quanta 3D FEG. The fibers were pulled out from the cotton fabric and coated with a ~5 nm layer of gold using a sputter coater (Quorum-Q300TD) equipped with a film thickness monitor (FTM) module.

All colour photographs of the macroscopic material were obtained by either snapshots of a movie (Figure 3) or photographs (Figure 2, SI-2 and SI-5) recorded with an iPhone 6, 64 GB model A1586.

The photographs displayed in Figure 3 were obtained by placing the cotton material in deionized water. After swelling for 2 hours, the material was illuminated by a Schott KL2500 LCD white light source at full power for 5 minutes at room temperature (black object in Figure 3a). Subsequently the material was allowed to recover in the presence of the background lighting in the laboratory.

Optical microscopy (OM) images were recorded with a Reichert Jung Polyvar microscope, equipped with a Lumenera Infinity 1 camera. The magnification was set to 200x and a green filter was used to avoid white light irradiation, which may cause the protonated merocyanine to isomerise. Individual fibers were pulled out from the fabric and suspended between two pieces of double sided tape on a glass slide, in such a way that the fiber was not in direct contact with the glass slide. This was placed in a closed, temperature controllable Linkam-cell (THMS600), through which high humidity air (~ 97 % RH) was flown to simulate fog conditions. The humid air was generated by a flowing a nitrogen stream through four flasks connected in series and filled with distilled water. The temperature was controlled with a Linkam TMS94 temperature-controller. The temperature program started at 15 °C and was held for 5 minutes to let the fiber absorb water. Then the temperature was increased to 50 °C at 5 °C/min. This temperature was also held for 5 minutes. Next, the temperature was decreased back to 15 °C at 5 °C/min, ending one temperature cycle. This was repeated for 5 cycles. For applying external light to isomerise the protonated merocyanine, a Schott KL2500 LCD white light source was used at full power.

The experiments in which the isomerisation was obtained with sunlight were performed on November 2th 2015 in Eindhoven. A thermometer was used to control if the temperature remained below the LCST, even if no heating of the sample was expected during the short time of illumination required to decolour the sample. The thermometer was placed several minutes before the sample to ensure a correct measurement of the temperature.

Differential scanning calorimetry (DSC) measurements were performed on a Q2000 from TA instruments. Heating and cooling rates of 5 °C/min were applied in the temperature range of 20 °C to 60 °C. Approximately 5 mg of the functionalized cotton fibers were placed in a T0-hermetic aluminium pan from TA instruments, to which ~ 30 μL water were added with a microsyringe to pre-wet the fibers, before sealing the capsule. Four heating cycles per sample were used for the measurements.

Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) was performed on a Varian 670-IR equipped with a Germanium crystal combined with a Varian 610-IR microscope. Before measuring, the samples were dried under vacuum in the oven at 40 °C. A piece of the woven fibers was placed on a glass substrate and the crystal was pressed on the samples to ensure good contact.

The water uptake experiments were performed by placing a pre-weighted amount of the cotton fabric inside a closed container. Before starting the experiment, the fibers were dried in vacuum for 24 hours at 40 °C to ensure the absence of water. Inside the closed container, there was a smaller container with water to create a high humidity environment. Care was taken to ensure that the cotton fabric was not in direct contact with the water.

TABLES

Table SI-1. Composition and weight increase determined by a gravimetric method, of the various materials synthetized.
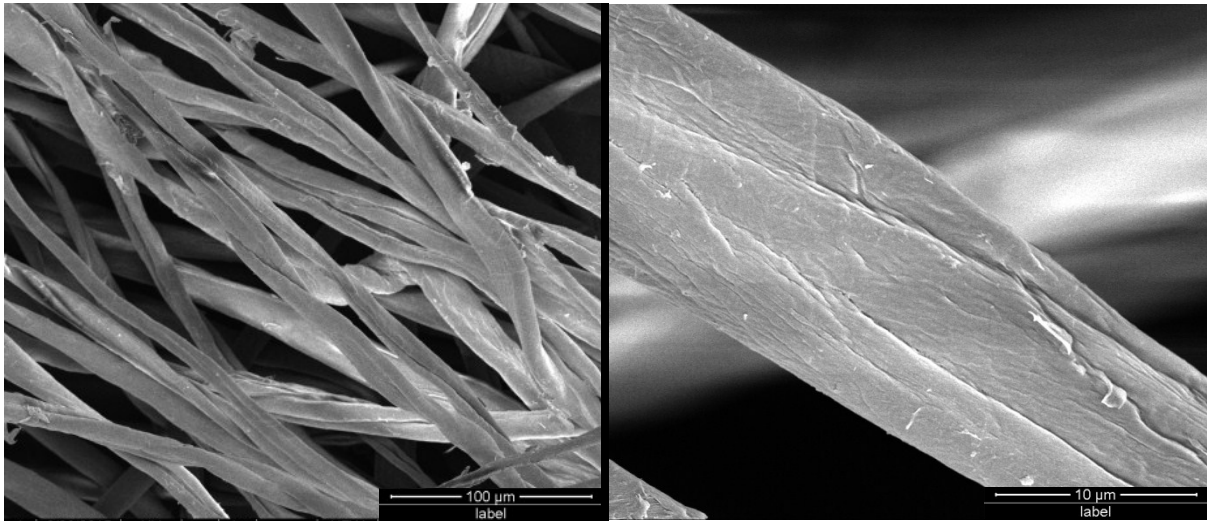
Sample	NIPAAm (mol%)	NaAc (mol%)	SpA	Weight-increase (%)
NIPAAm	100	0	0	100
NIPAAm+NaAc	95	5	0	188
NIPAAm+SpA	99	0	1	47
NIPAAm+NaAc+SpA (Complete mixture)	94	5	1	123

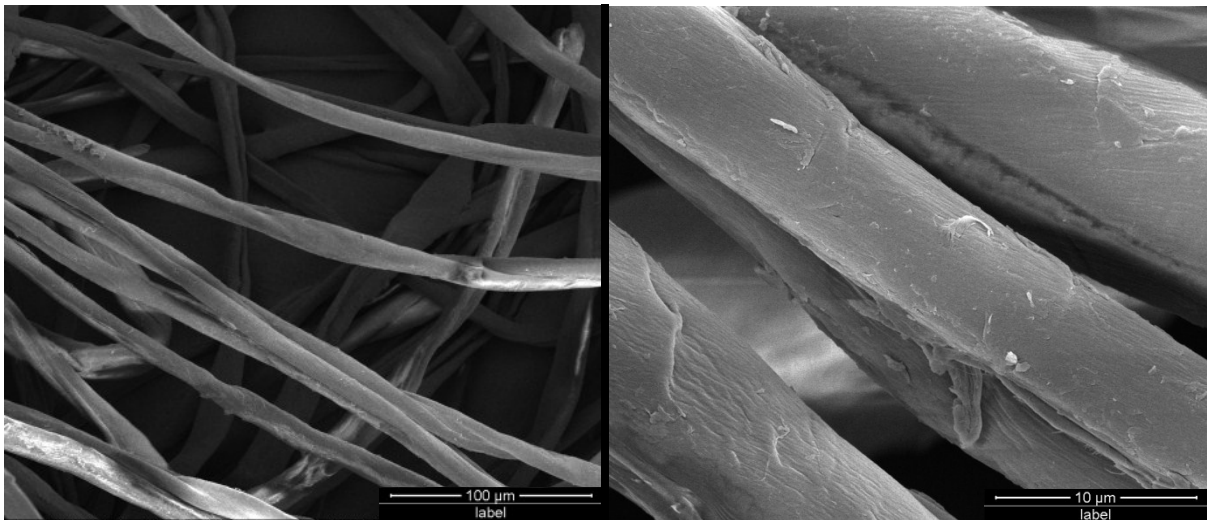**Table SI-2.** Number of data points and the length of fiber measured for each sample.

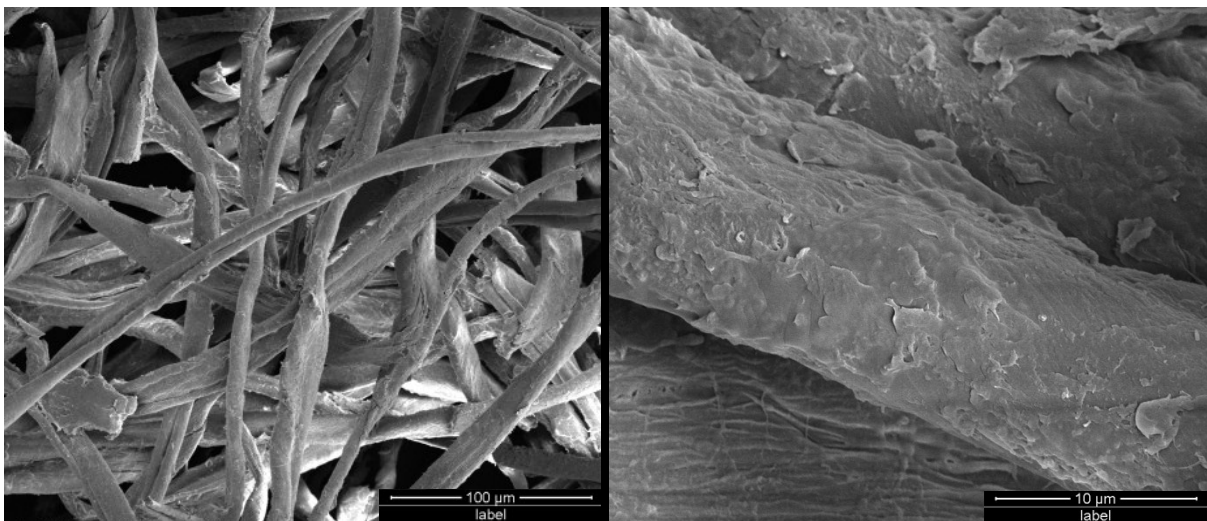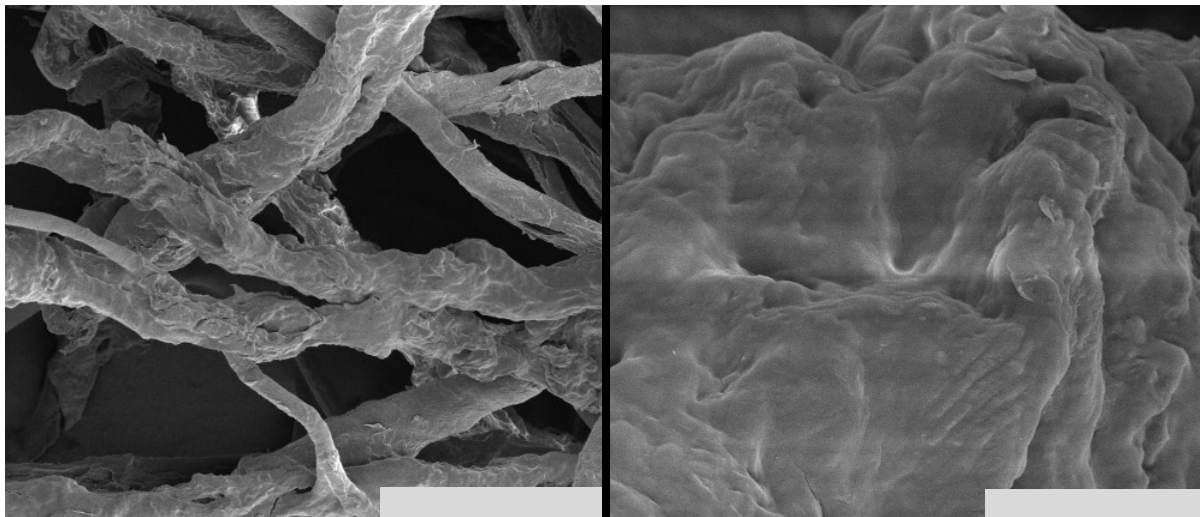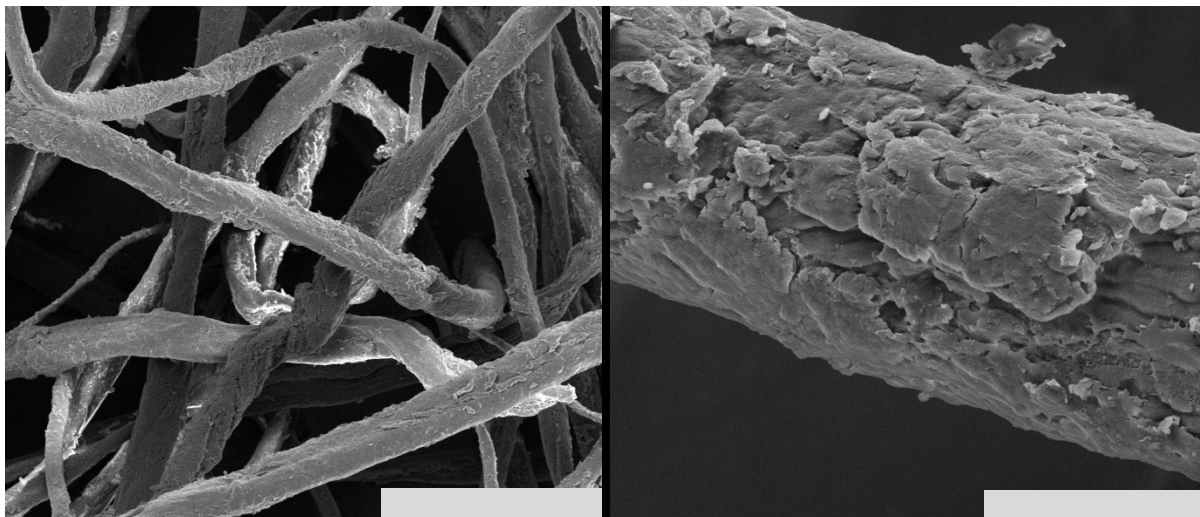|	Data points	Length (μm)
a	2360	147.5
b	2861	178.8
c	1876	117.3
d	1654	103.4
e	1684	105.3

FIGURES

Cotton

Cotton-BIB

Cotton-NIPAAM

Cotton-NIPAAm-acrylic acid

Cotton-NIPAAm-spiropyran

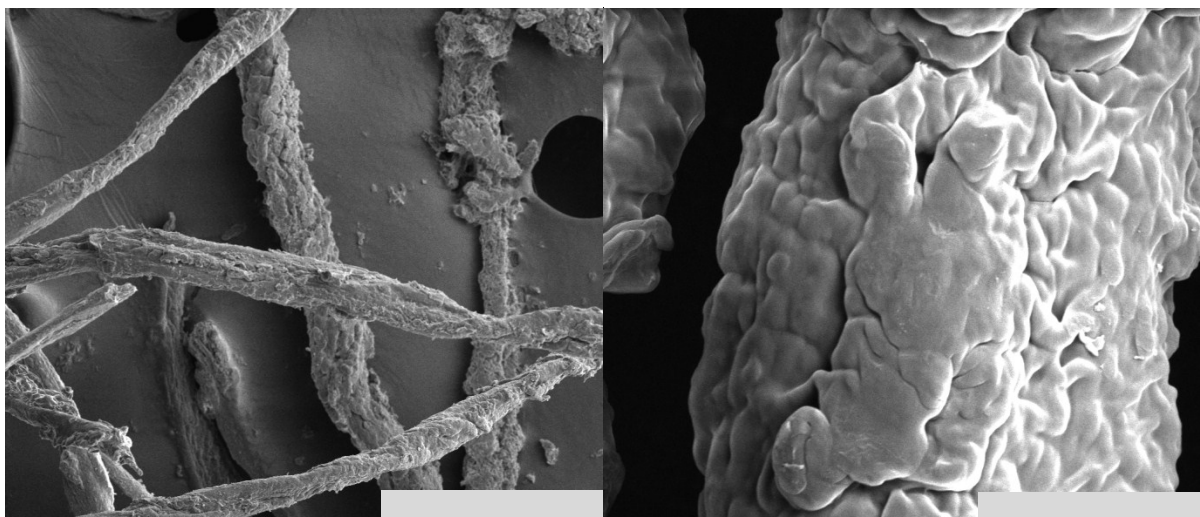Cotton-NIPAAm-spiropyran- acrylic acid

Figure SI-1. Scanning electron microscopy (SEM) micrographs taken on locations representative of the overall morphology of the samples: Cotton, Cotton-BIB, Cotton NIPAAm, Cotton-NIPAAm-acrylic acid, Cotton-NIPAAm-Sp and Cotton-NIPAAm-Sp-acrylic acid.
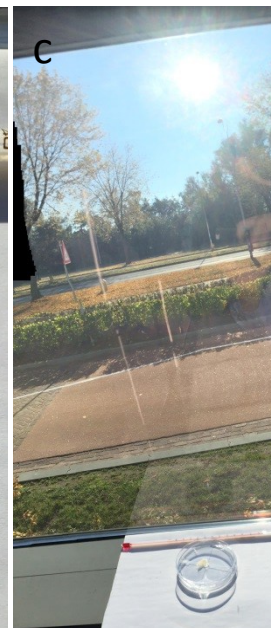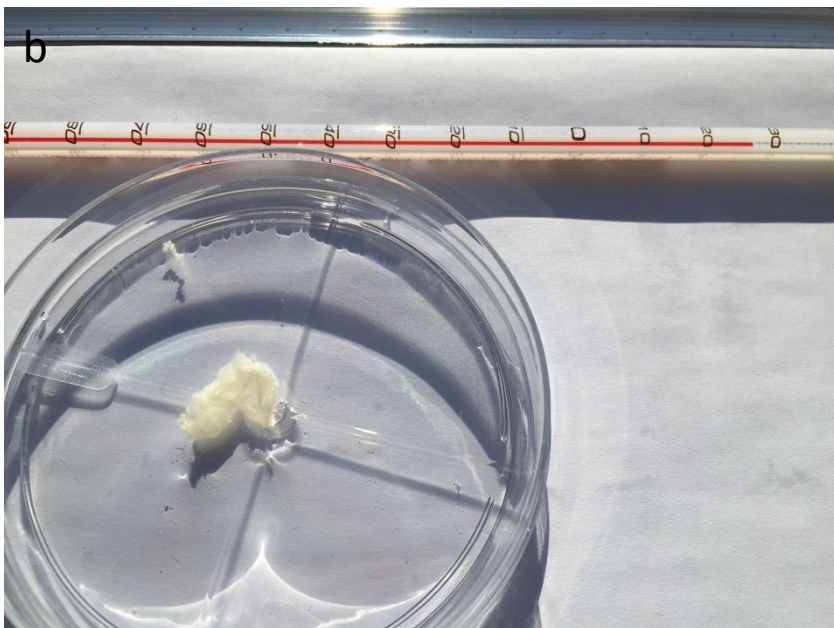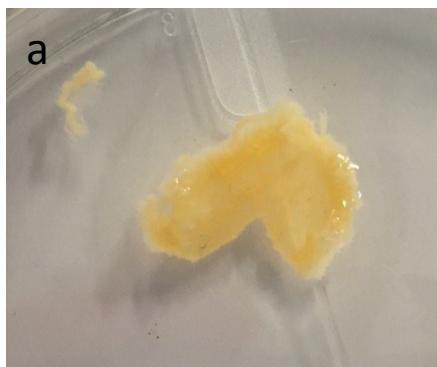
Figure SI-2. The functionalised cotton material in the laboratory (under a fluorescent tube light) showing the yellow/orange colour (a) corresponding to protonated merocyanine. The material was placed in sunlight (b) (behind a window (c)) and within 60 seconds the material completely lost the colour.
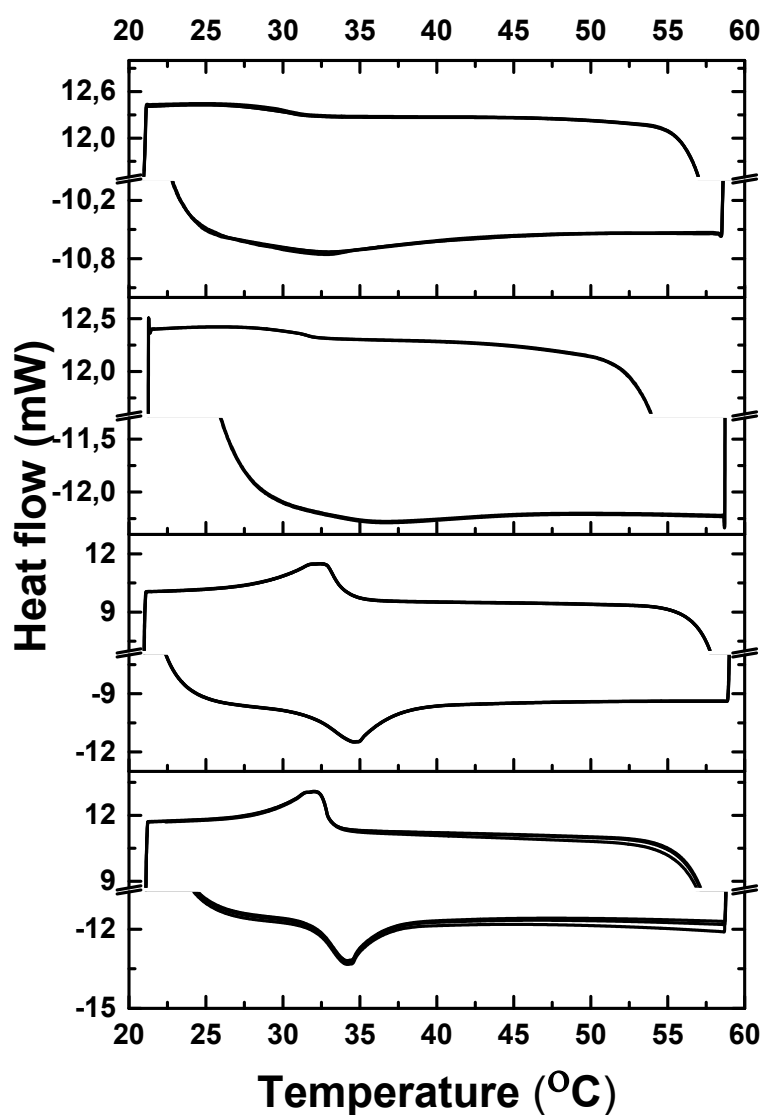
Figure SI-3. Differential scanning calorimetry thermographs of the cotton functionalized material. From bottom to top: NIPAAm, NIPAAm-acrylic acid, NIPAAm-spiropyran and NIPAAm-spiropyran-acrylic acid.
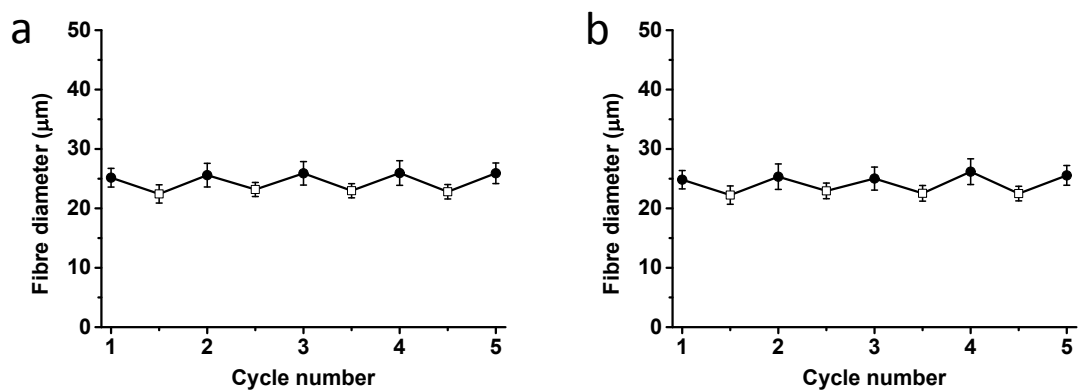
gure SI-4. Light-responsive behaviour (a) and temperature responsive behaviour (b) of the reference cotton fibers, functionalized in the absence of acrylic acid units (NIPAAm-Sp, Table S1) upon 5 consecutive cycles of illumination (open squares) and dark conditions (closed circles) (a) or 50 °C (open squares) and 15 °C (closed circles), below and above PNIPAAm LCST, respectively (b).
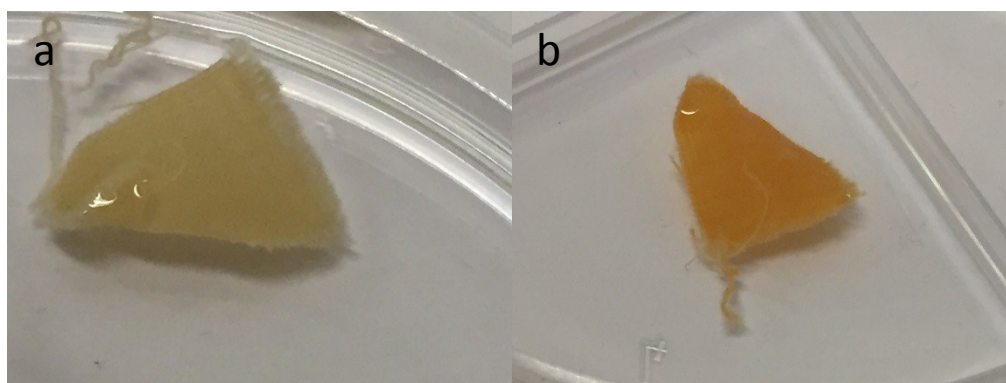

Figure SI-5. Reference cotton fabric functionalized without the acrylic acid units (NIPAAm+Sp, Table S1), before (a) and after (b) immersing it in a 0.1M HCl aqueous solution.
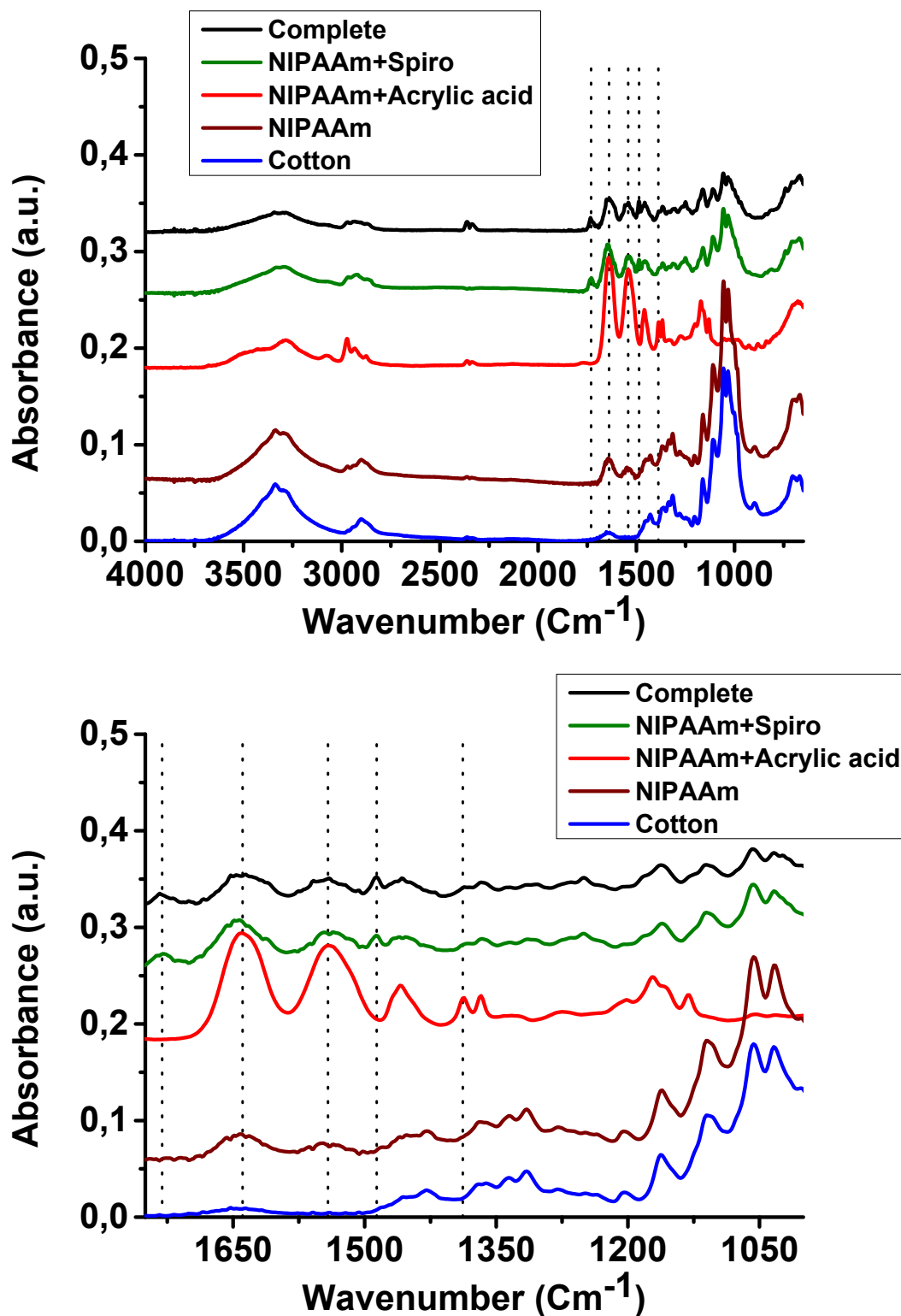
Figure SI-6. ATR-IR spectra of all the functionalized cotton fabrics prepared (Table S1). The graph in the bottom is an expansion of the one above, showing the main bands of interest.
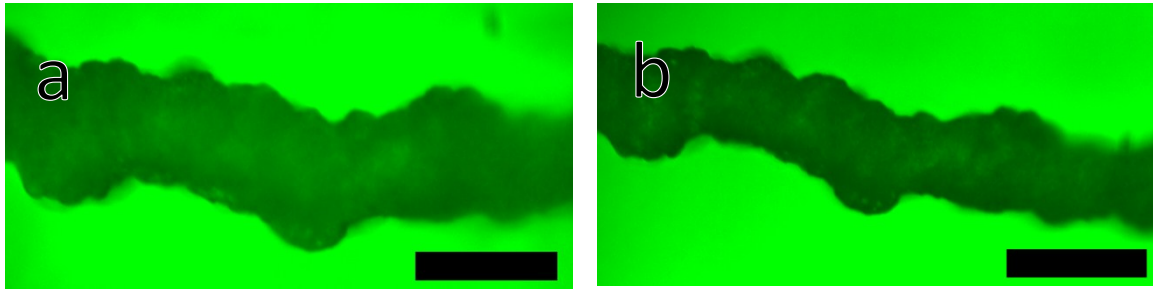
Figure SI-7. Optical microscopy micrograph of the functionalized fibers used in Figure 4 at 15 °C (a) and 50 °C (b). The black scale bar represents 50 μm.
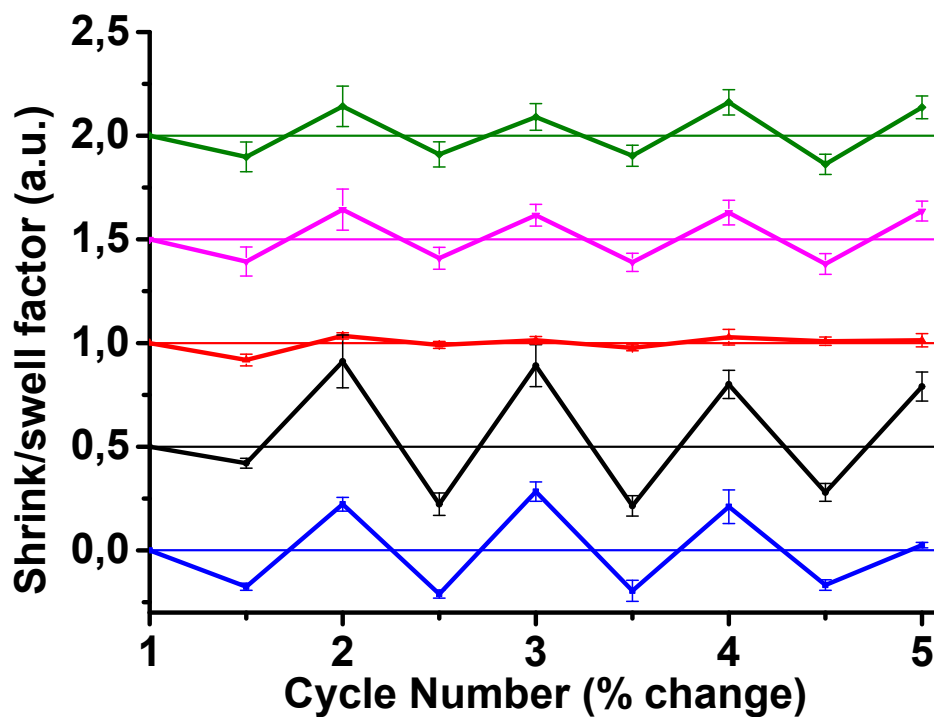

Figure SI-8. Plot of the shrink/swell factor ($[w_i-w_{i-1}]/w_{i-1}$), measured using a point-by-point comparison, where the width of the fiber is measured at nearly identical points along the length of each fiber during swelling and shrinking. Negative values indicate shrinking of the material compared to the previous image, whereas positive values indicate swelling of the material. The horizontal lines for each data series depict no change (shrink/swell factor = 0); the graphs are offset by 0.5 increments.

Note that the standard deviations do not overlap from one measurement to the next, hence there are significant transitions occurring in the material. Moreover, the swelling is occurring uniformly in proportion to the thickness of the fiber. The data series correspond to the following graphs: Figure 3 (blue), Figure 4 black (black), Figure 4 red (red), Figure SI-4a (magenta), and Figure SI-4b (green).
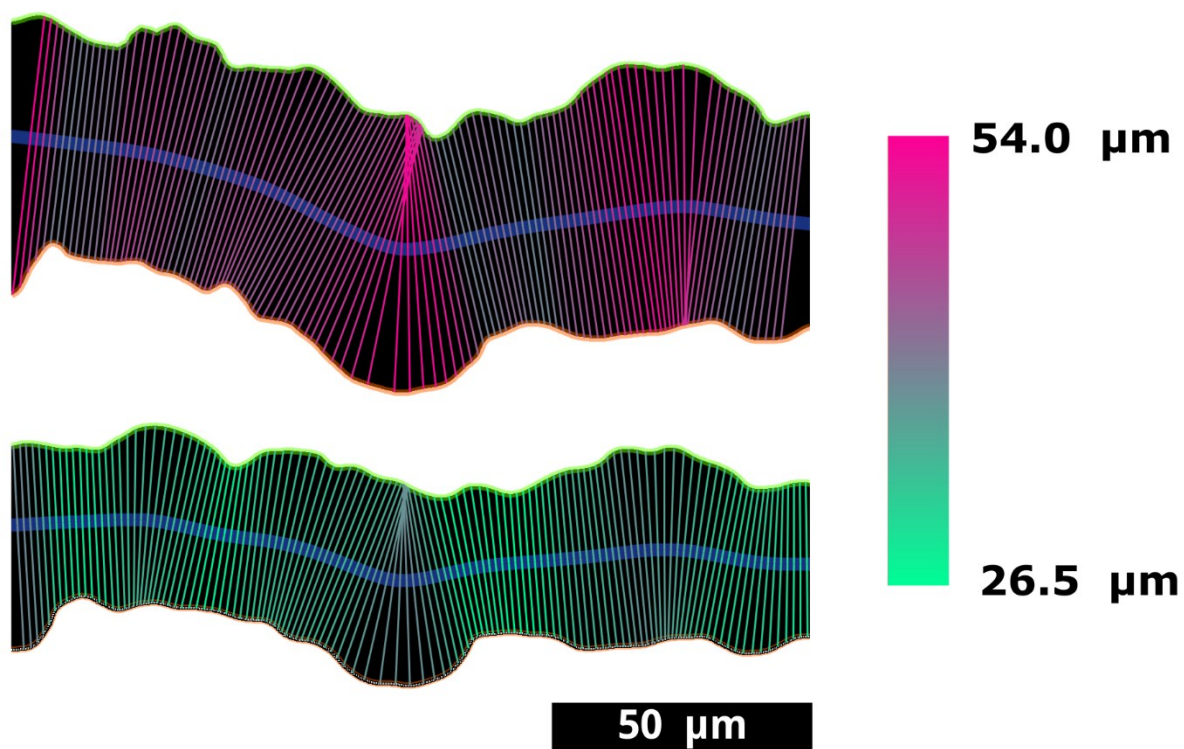
Figure SI-9. Visualization of the measurements used for determining widths and width changes in fiber structures used to construct Figure 4 and Figure SI-8 (black line in both images) in swollen (top) and shrunk (bottom) states; analogous measurements were performed for all plots. Masks derived from the optical microscope images are shown (black) with widths measured orthogonal to the centre line (blue). The lines (every 20th line shown) are indexed as a function of position, allowing changes at each point along the length of the fiber to be tracked. The colour shows the width of each measurement, as indicated by the gradient to the right.
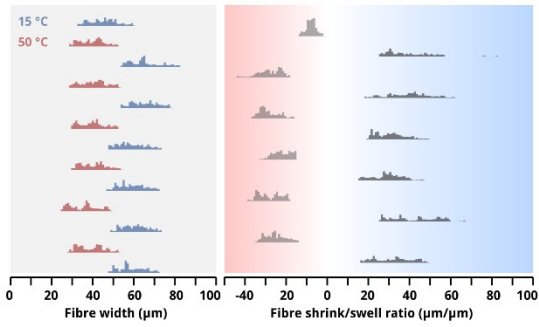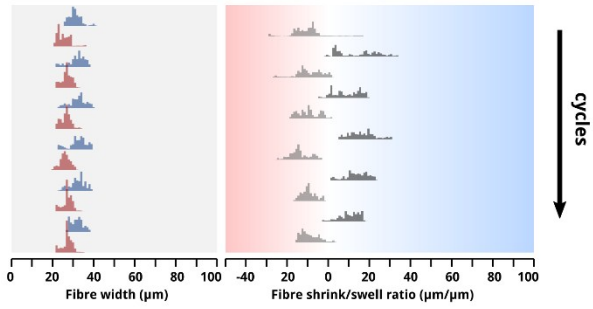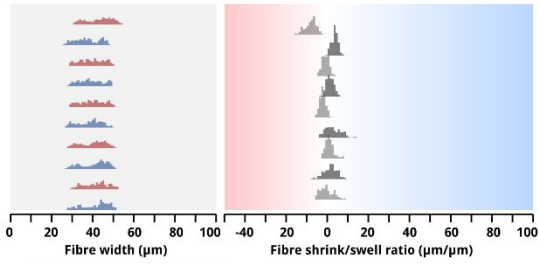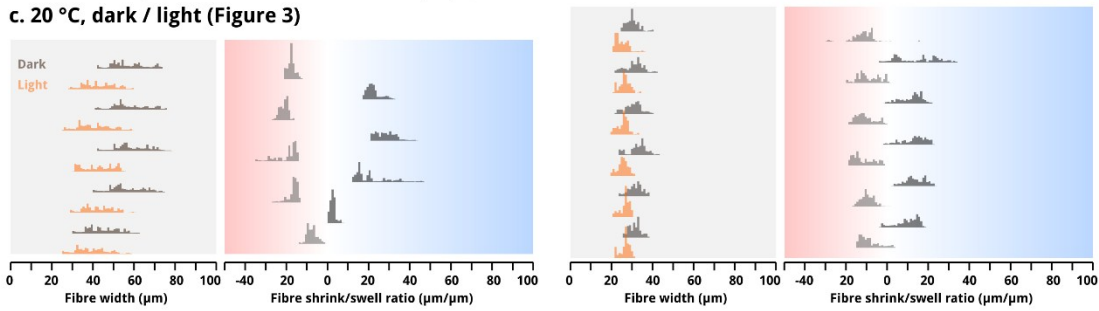
Figure SI-10. Distributions of fiber widths (μm) and shrink/swell ratios (%), measured using a point-by-point comparison, where the width of the fiber is measured at identical points along the length of each fiber in both swollen and shrunken states. Grey panels show width distributions, while the corresponding red/blue panels show the distributions of shrinking and swelling from one state to the next. All distributions are normalized for constant area.
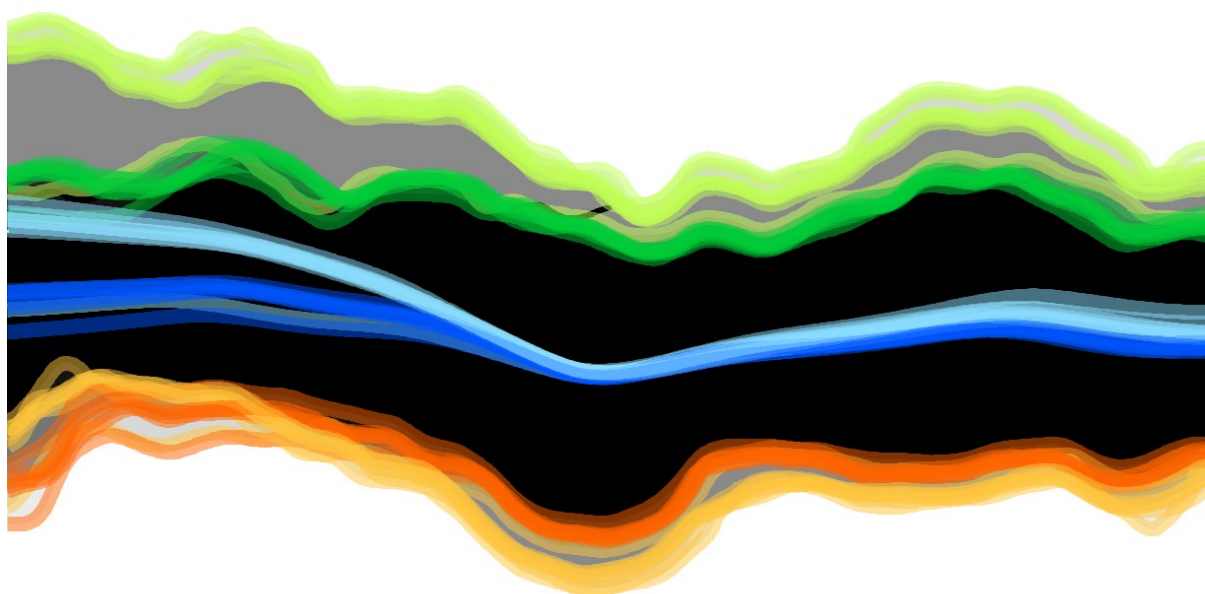
Figure SI-11. Overlaid outlines from the fiber mask showing the positions of the edges and the centre line through the image sequence. Darker colours correspond to the shrunk state, while the lighter colours correspond to the swollen state. Orange and green lines overlay the edge positions for the bottom and top edge, respectively. The blue/cyan centre line shows a reversible bending motion, becoming straighter in the shrunk state and more bent in the swollen state by about 10°.
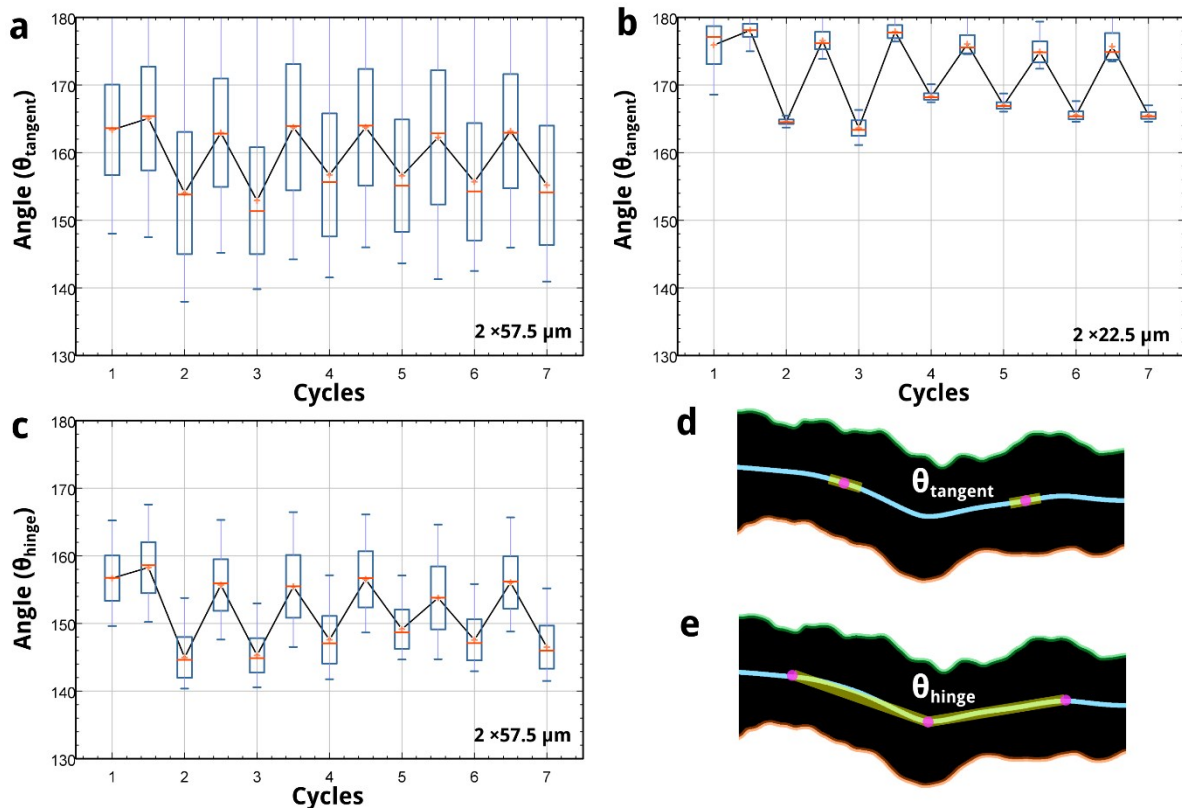
Figure SI-12. Changes in the bending angle of the fiber (see Figure 4) are measured *via* two methods: (a,b,d) Using the centre line tangents at a series of paired points, from which the angle can be calculated, or (c,e) selecting a "hinge" point, from which relative angles can be calculated for paired x,y points on the centre line. In all cases the two series of points are taken from opposite sides, and all pair permutations (a [Set 1] × [Set 2] matrix) are evaluated when calculating the statistics. Plots (a,b,c) are boxplots, with min, max, standard deviation (y-axis of the box), mean (light orange cross), and median (orange-red line) depicted. a. Measured using tangents, two 57.5 µm regions show cycling of the bending angle. b. Two narrower sections (22.5 µm each) show narrower distributions in the bending angle. c. The bending angle measured relative to a selected "hinge" point (a maximum in the distance map from which the images were aligned). d. Fiber mask, with two points with tangents drawn. e. The selected "hinge" point, along with two points along the centre line are shown on the fiber mask.
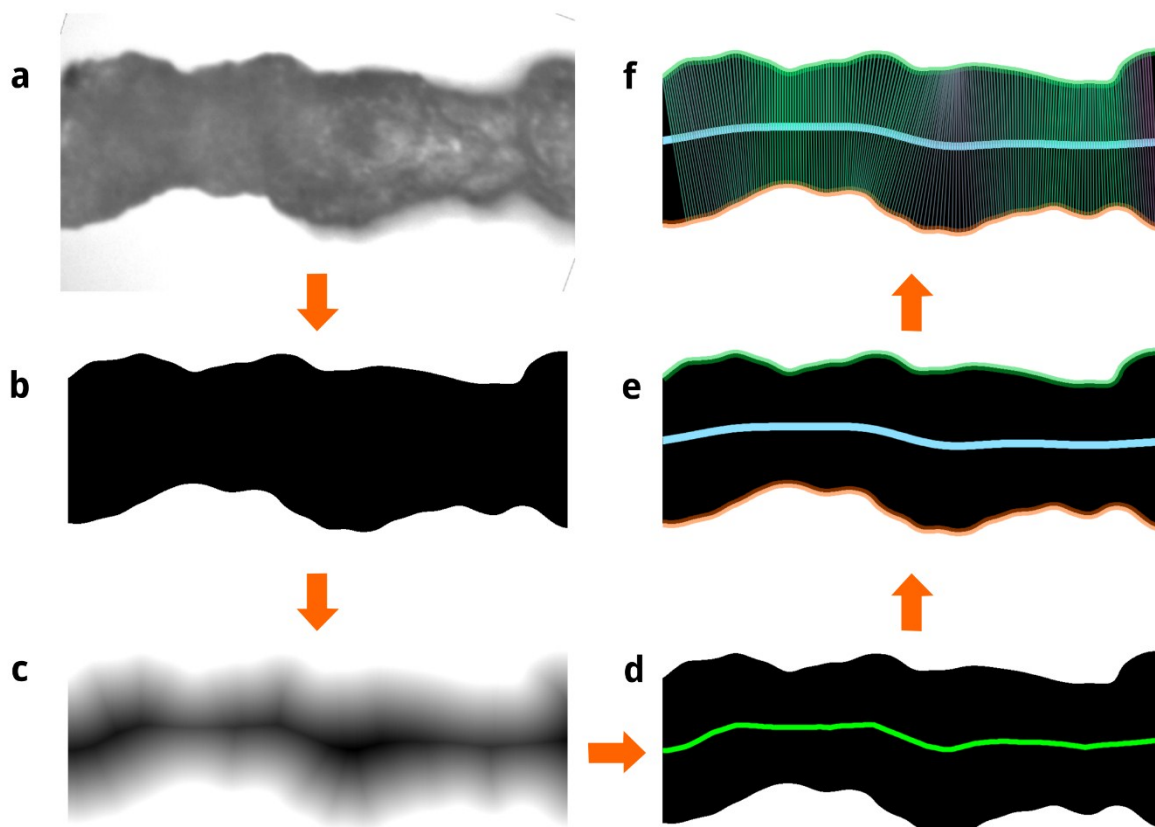
Figure SI-13. Schematic outline of the width analysis using an image from Figure 3. These steps follow the alignment and registration steps necessary to obtain a stack of corresponding segments. a. Original microscope image, with green channel extracted. b. Binary image following Otsu Auto Local Thresholding with ImageJ. (Note: For images with poor background contrast due to condensation on the windows, the threshold was subsequently edited manually to trace the fiber.) c. Distance map used to calculate, d. the initial position of the centre line (green). e. Centre line (cyan) following force-directed smoothing, where the edges (shown in green and orange), marked with equidistantly spaced points, repel points in the centre line, thus smoothing the curve. f. Edge-to-edge lines, perpendicular to the centre line, used to calculate the fiber width and shrinking/swelling statistics.
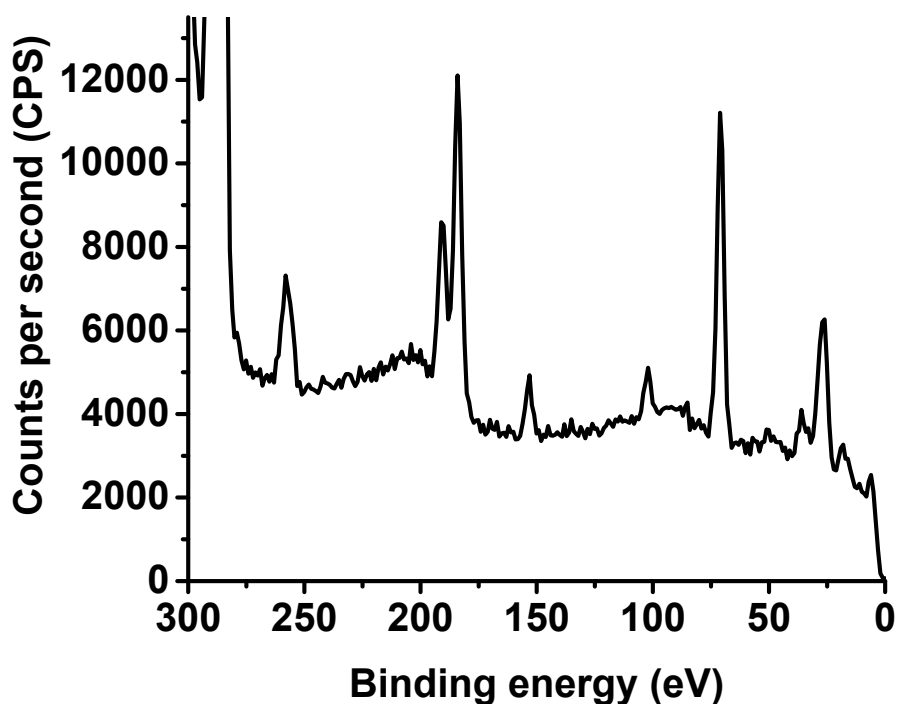
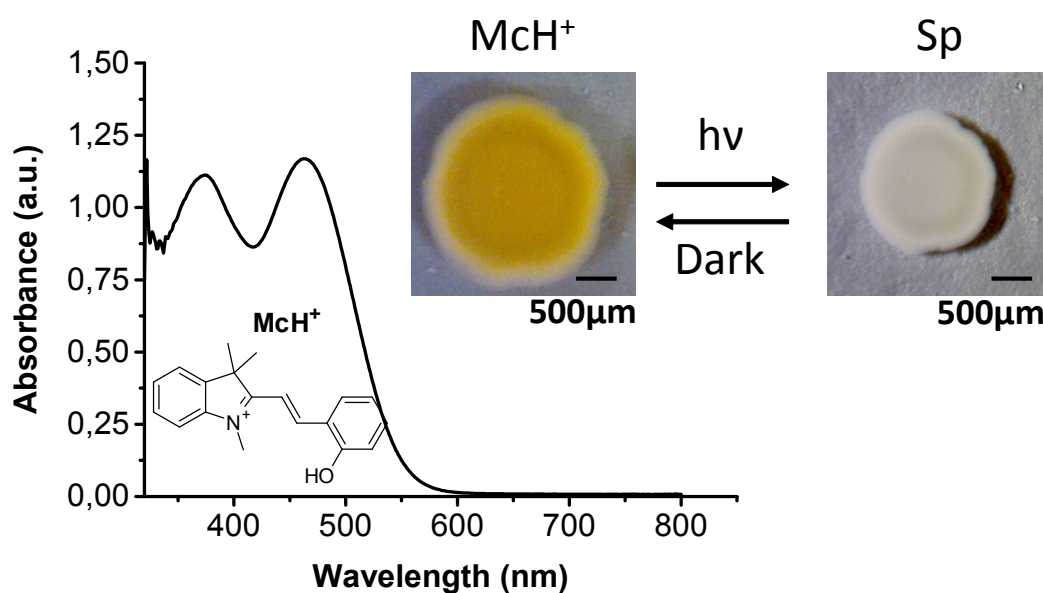**Figure SI-14.** XPS spectrum of the BiB functionalised cotton fibres.

Figure SI-15. A gel disk composed of 91 mol % NIPAM, 5 mol % acrylic acid, 2 mol % N,N'-methylenebis (acrylamide) (MBIS), 1 mol % Irgacure 819 and 1 mol % spiropyran, showing the spectrum of the merocyanine form (McH⁺) combined with the macroscopic effect of color and size of a hydrogel disk. The gel on the left is the gel containing protonated merocyanine (McH⁺). Upon illumination with white light, the gel loses its colour and shrinks, comparable with the gel formed on the cotton fibre (Sp). Partially reproduced from J. ter Schiphorst *et al.*, Chem. Mater., 2015, 27, 5925–5931. For more details, see original work.