Electronic Supplementary Material (ESI) for Chemical Communications.

SUPPORTING INFORMATION

Synergistic Action of Thermoresponsive and Hygroresponsive Elements Elicits Rapid and Directional Response of a Bilayer Actuator

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Experimental methods

Preparation of the bilayer film. PVDF (1.5 g, Sigma Aldrich) was dissolved in 45 mL dimethylformamide (DMF) by vigorous stirring at 100 °C. A small amount of an azo-dye (4-aminoazobenzene, AAB) was added to the stirred solution for better visualization of the film. The mixture was cast onto glass slides that were pre-cleaned with acetone, and dried in oven at 90 °C until a homogenous film was obtained. An aqueous solution (10 mL) of PVA (2 g, Sigma Aldrich) and Ficoll 400 (0.1 g, Sigma Aldrich) was applied over the PVDF/AAB film to obtain the second layer, PVA/Ficoll. After drying at 25 °C over 24 h the bilayer film was cut into strips by using a razor.

Quantitative analysis of dehydration process of the bilayer strip. Thermogravimetric analysis (TGA) was performed with SDT Q600 thermal analyzer, using dry nitrogen as a carrier gas. Samples cut out from the same bilayer were used. The thermal decomposition was studied at heating rates 5, 10, 15, and 20 °C min^{-1} in the temperature range 25–150 °C. Tzero aluminum pans were used in all measurements. To confirm the cyclability, bilayer strips (4 mg) treated with water were first heated at a rate of 20 °C min^{-1} until it was completely dehydrated. The film was then taken out from the sample pan, placed on a moist paper containing 40% (w) water for 10 s, and analyzed again under identical conditions.

Measurement of curling speed. The instantaneous speed of one of the termini of the bilayer strip was analyzed using MATLAB R2012b[1] and ImageJ.[2,3] The motion traces of the terminus of the bilayer strip were tracked using DLTdv5, a MATLAB-based Digitizing program developed by the

Hedrick's Lab (released on 07.07.2014). While most of the data points were collected using the automatic feature and the extended Kalman filter, some data points were manually traced across each frame. The distance between two points was calculated using the general point distance formula, distance = $[(x_1 - x_2)^2 + (y_1 - y_2)^2]^{1/2}$. The instantaneous speed between two points at the terminus of the bilayer strip was calculated as distance/time. The pixel distances were then calibrated and converted to real distance using ImageJ.[2,3] The overlapped images shown in Figures S1A, 3F and 3G were also obtained by using MATLAB R2012b. After cropping the images, the individual images were fused and enhanced for clarity.

Nanoindentation measurements. Agilent G200 nanoindenter with an XP head and a Berkovitch diamond indenter with a tip radius of < 20 nm were used. The nanoindentation was first carried out while heating the sample from 25 to 105 ^{o}C, and on subsequent cooling to 25 ^{o}C. A 4 × 4 grid on the PVA/Ficoll side of the bilayer was sampled to record the loading/unloading curves at each temperature. The modulus was calculated using the Oliver–Pharr method where a fit of the unloading curve is used to determine the stiffness, contact depth, reduced modulus and modulus of the sample. The Poisson's ratio was set to 0.30. The hardness was calculated from the ratio of the peak load and the contact area.[4]

Scanning electron microscopy. Scanning electron microscopy (SEM) images were recorded with Quanta FEG 450 electron microscope with primary electron energy of 5 kV. The samples were attached directly to adhesive carbon tape. The micrographs were recorded at room temperature and pressure of 8.8×10^{-7} Pa.

Curling of the bilayer strips induced by heat. The temperature effect on the curling response of the bilayer strip was studied in two experiments. In the first experiment, the bilayer strip was heated by gradually increasing temperature from 25 to 105 ^{o}C at a heating rate of 4 ^{o}C s^{-1}. In the second series of experiments, the bilayer strip was quickly placed on a hotplate with constant temperatures set between 25 and 105 °C. The effects of thickness, length and width of the strip on the curling speed were studied at a constant temperature of 75 °C. In each case, the curvature was calculated as reciprocal of the radius, $\kappa = 1/R$. The radius R was extracted from the recordings using the software ImageJ (ver. 1.49). The movies were recorded with an iPhone 4 (Apple).

***In situ* measurement of the thermally induced tension.** The mechanical properties of strips of the bilayer, PVA/Ficoll and PVD/AAB were performed with a tensile tester (MTI Instruments, MTII/Fullam). A strip of the sample (2 cm × 0.5 cm × 42 μm) was gripped between two sample holders, and the gauge length was adjusted to 1 cm while keeping the strip straight. The gauge length was maintained fixed throughout the measurement. Electrically heated rod was used to heat the strip. When approached by electrically heated rod, the strip was instantly heated to about 70 °C, as determined by using Infrared Thermographic Camera (Image IR, Germany). After the rod was removed, the strip quickly cooled to room temperature (~25 °C).

Fabrication of soft robots. Two, three, four or more bilayer strips were joined together with an adhesive tape to prepare actuators with varying number of mechanically active parts. The mechanical response from these dynamic elements was recorded on a hotplate at 85 °C.

Supplementary Figures

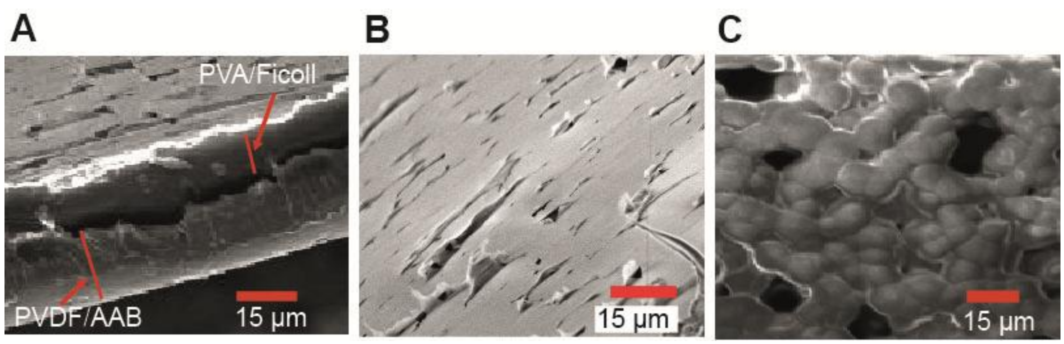

Figure S1. (A) Scanning Electron Microscopy (SEM) images of a cross-section of the bilayer strips showing the average thickness of the two layers. (B,C) SEM images of the surface on the PVA/Ficoll (B) and PVDF/AAB (C) side of the bilayer.

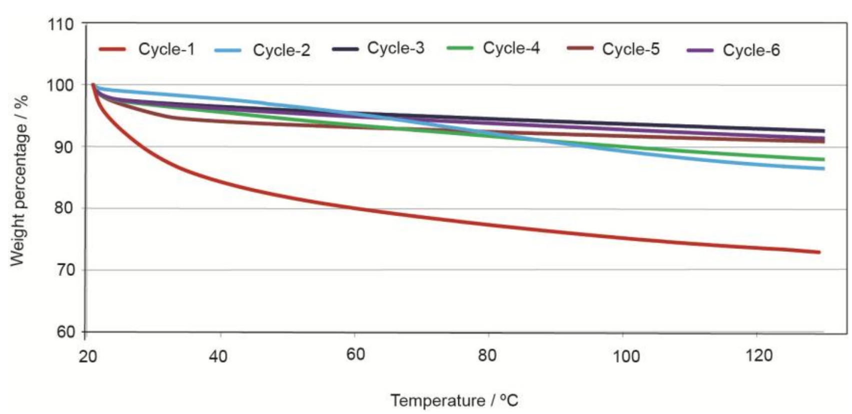

Figure S2. Thermal analysis of the reversibility of hydration. A bilayer strip (4 mg) that was hydrated by being placed in contact with a moist paper for 10 s, was subjected to thermogravimetric analysis at a heating rate of 10 °C min^{-1} until 130 °C. Six hydration–dehydration cycles are shown.

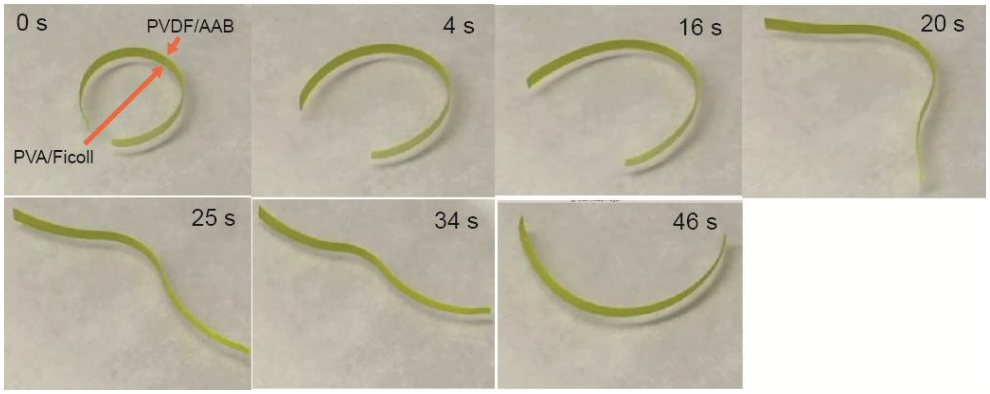

Figure S3. Snapshots of the curling of a bilayer strip induced by hydration. A bilayer that was curled by heat (panel labeled 0 s) was immersed in water at 22 °C. The film absorbs water and swells, whereupon it curls toward the PVDF/AAB layer. This curling process is very slow compared to the curling induced by heat.

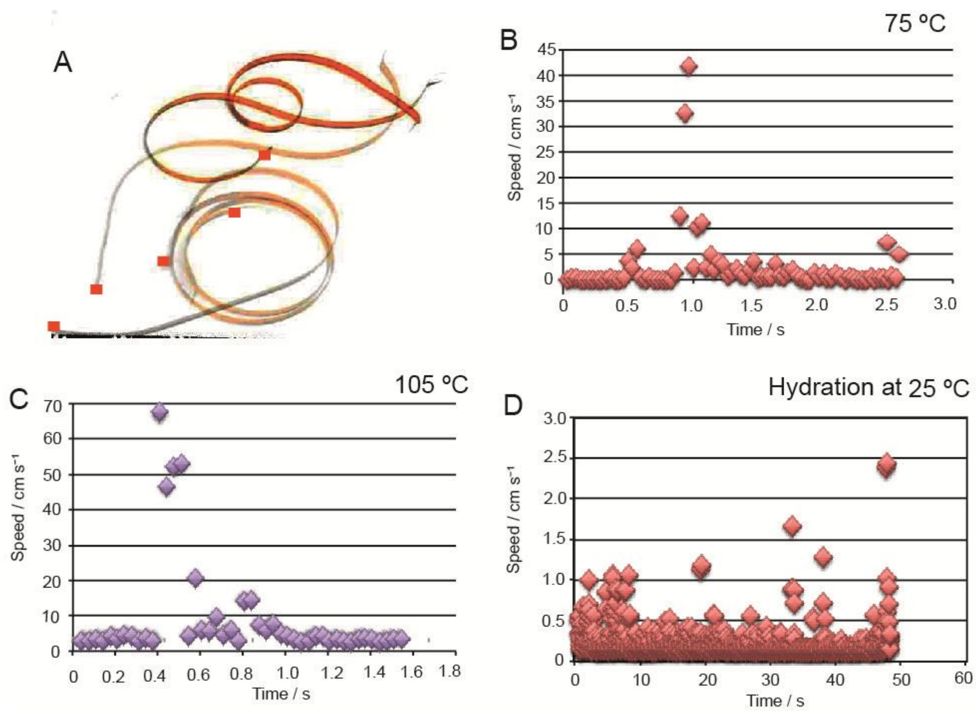

Figure S4. Analysis of the motion of a bilayer strip induced by heat. (A) Overlapped snapshots of the curling motion of the bilayer strip on a hotplate at 75 °C. (B,C) Time-dependent profiles of the speed of the terminus of the strip recorded during curling at 75 °C (B), and 105 °C (C). (D) Time-dependent profile of the speed of the terminus during curling induced by hydration at 25 °C.

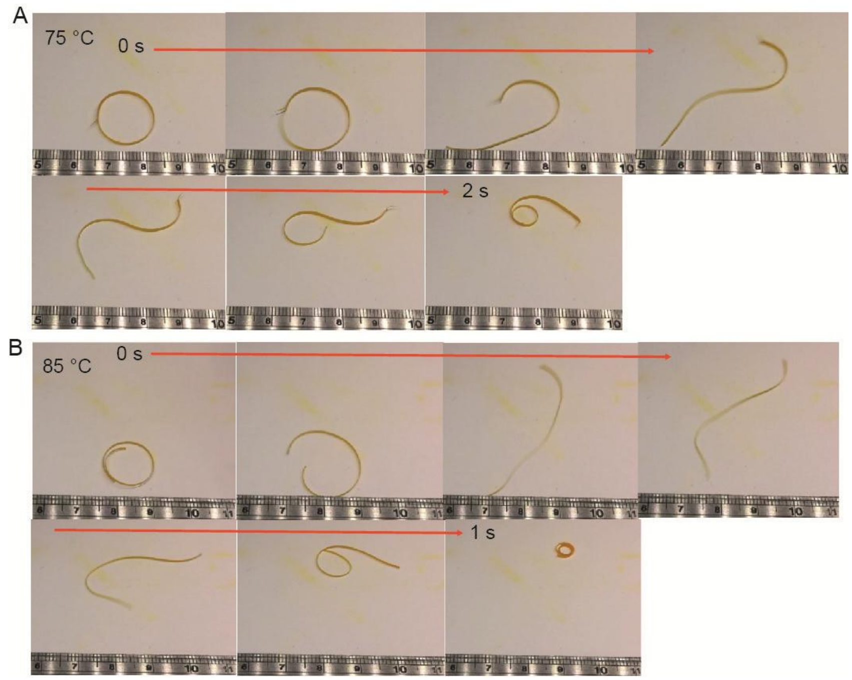

Figure S5. Snapshots of the fast curling motion of a bilayer strip placed on a heated hotplate. The strip is curling and moving away from its initial position across the surface at 75 °C (A) and 85 °C (B). A steel ruler was used as a support from which the film sprang off.

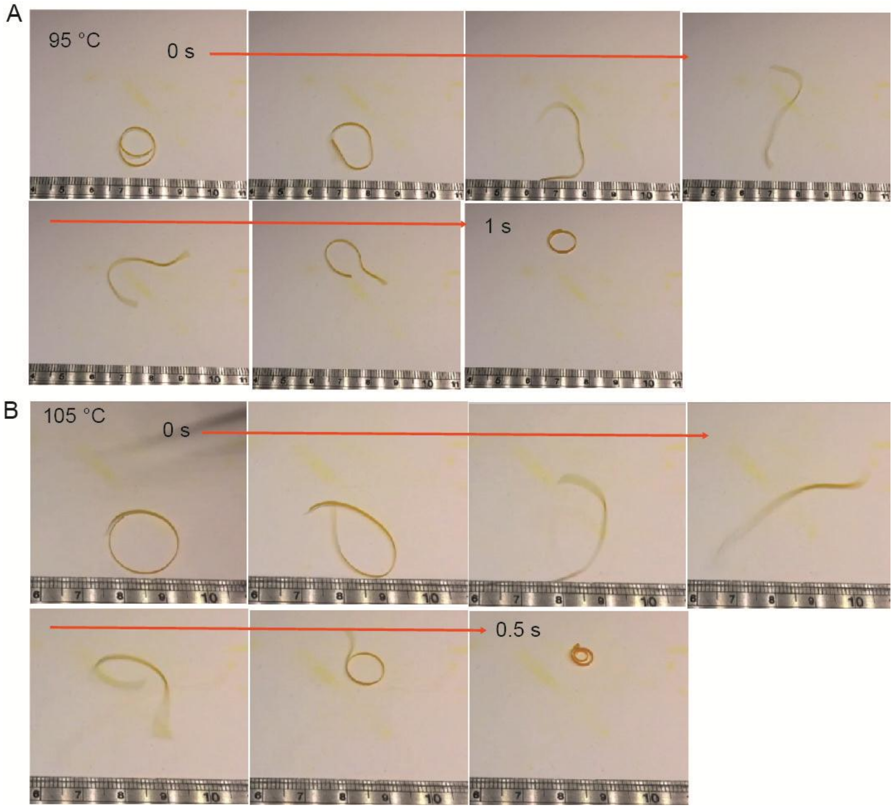

Figure S6. Snapshots of the fast curling motion of a bilayer strip placed on a heated hotplate. The bilayer strip curls and moves away from its initial position across the surface at 95 °C (A) and 105 °C (B). A steel ruler was used as a support from which the film sprang off.

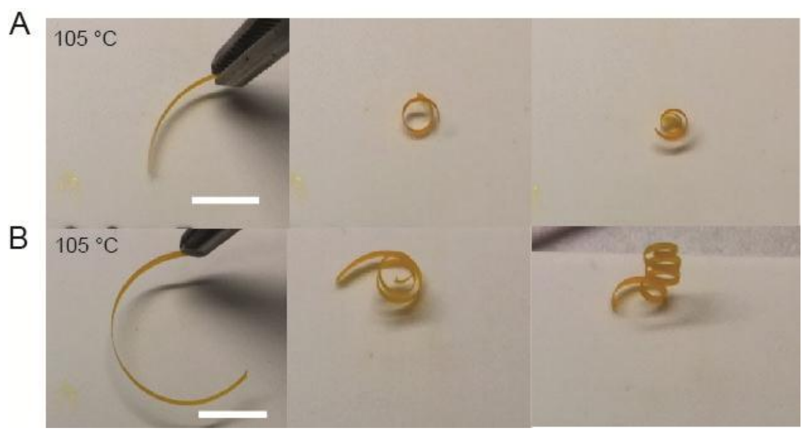

Figure S7. Effect of the length on the curling of the strip induced by heat. (A,B) At lengths > 3 cm, the strip coils into a helix instead of a multilayer spiral when the temperature is higher than 105 ºC. The length of the scale bar is 1.5 cm.

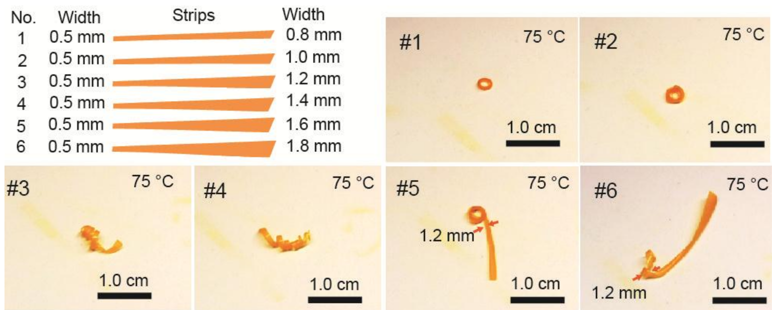

Figure S8. Effect of the width on the curvature of strips with non-uniform width curling at 75 °C. The panel on the top left shows the non-uniform width of the strips. To investigate the effect of non-uniform width on the curling behavior of the bilayer strip, six ribbons of identical length (6.0 cm) that taper from the same width at one end (0.5 mm) to a varying width on the opposite end in increments of 0.2 mm were prepared. Ribbons having similar width at both ends curled into flat multilayered spirals. Increased difference of the width at the two ends resulted in coiling into a helix.

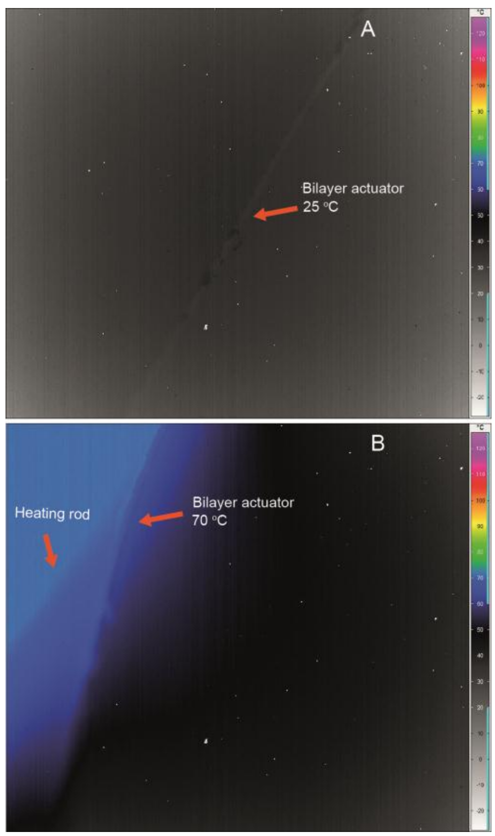

Figure S9. Temperature of the bilayer strip during measurement of the heating-induced contraction/expansion response. Electrically heated rod was used to heat the strip during the measurement. The temperature of the strip is determined with an Infrared Thermographic Camera (Image IR, Germany). The strip was initially at 25 °C (A), but was heated to 70 °C when it was approached with a heated rod (B).

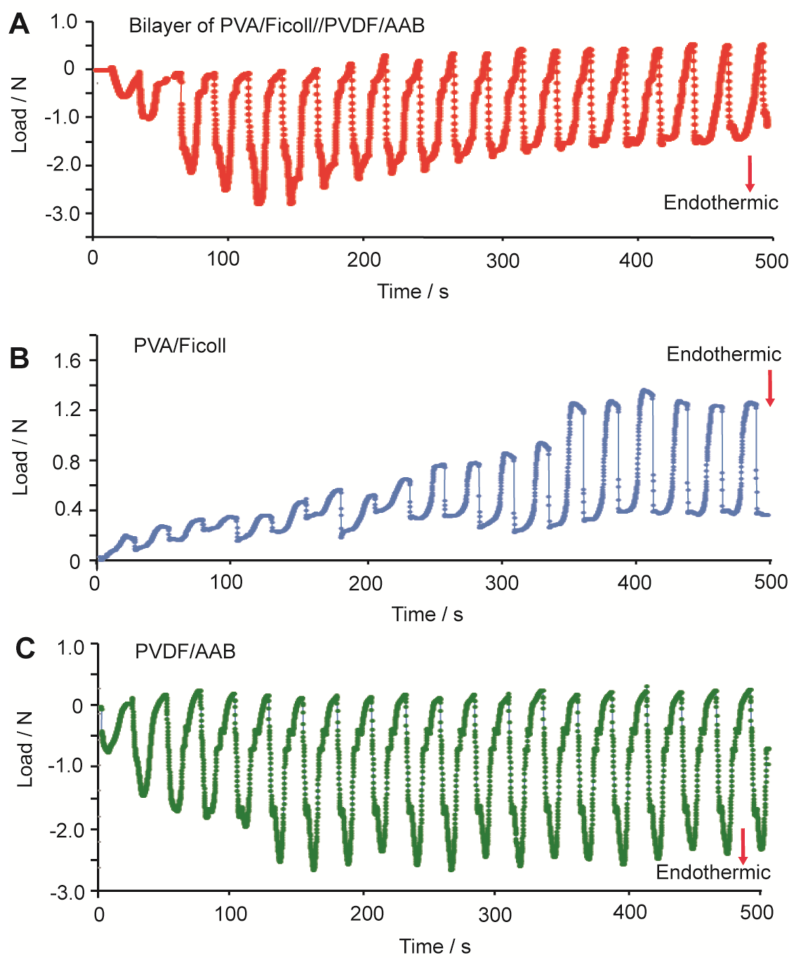

Figure S10. Contraction/expansion force and reversibility of operation of the bilayer actuator and its components during heating/cooling. Time profiles of periodic contraction and expansion of the bilayer actuator (A), single layer of PVA/Ficoll (B), and single layer of PVDF/AAB (C) are shown. The 10-s intervals of heating were separated with 17-s intervals for cooling.

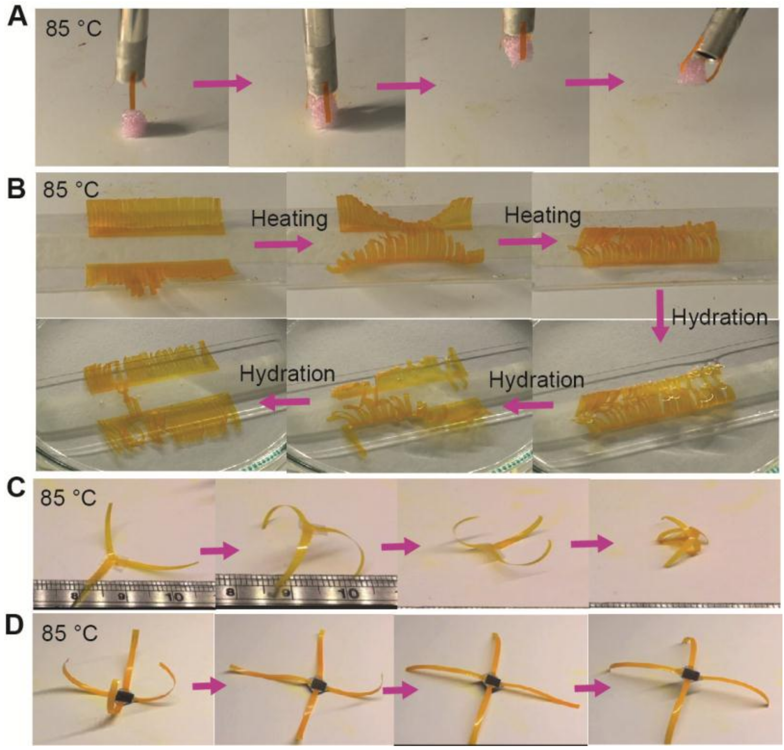

Figure S11. Simple demonstration of possible applications of the bilayer actuators. (A) A soft robot fabricated of three bilayer strips affixed to a metal tube lifts a lightweight object from hot surface. The bilayer "tentacles" bend in response to heating. (B) A pair of soft actuators that mimic the hygro/thermoinduced curling of the stems of *S. lepidophylla* by reversible response to external heating/hydration stimuli. The soft robot was first placed on a hotplate to curl, and then it was immersed in water at 22 °C to uncurl. (C) Three-arm soft actuator jumps when exposed to heat. (D) Four-arm soft actuator stands up by heating.

Legends to the Supplementary Movies

Movie S1. Reversible curling of a bilayer strip induced by heating/hydration. The video is shown at twice the real speed

Movie S2. Switching of the handedness of a right-handed actuator to a left-handed by instantaneous heating at 85 °C.

Movie S3. Curling of the bilayer strip induced by gradual heating at a rate of 4 °C s^{-1}.

Movie S4. Fast curling and motility of the bilayer strip induced by instantaneous heating at temperatures from 75 to 105 °C. The thickness of the strip is 30 μm.

Movie S5. Bilayer strip with one end fixed to a support shows uniform curling induced by heat at 75 °C.

Movie S6. A soft robot made of three bilayer strips affixed to a metal tube lifts a lightweight object from a hotplate at 85 °C. The strips bend due to heating. The video is shown at twice the real speed.

Movie S7. A pair of soft actuators made of bilayer strips that mimic the hygro/thermoinduced curling of the stems of *Selaginella lepidophylla* by reversible response to heating/hydration. The video is shown at four times the real speed.

Movie S8. Three-arm soft actuator made of the bilayer strips jumps, and four-arm soft actuator stands up when they are exposed to heat.

Supplementary references

1 The MathWorks, Inc., MATLAB and Statistics Toolbox Release 2012b, 2012.

2 C. A. Schneider, W. S. Rasband and K. W. Eliceiri, *Nat. Methods*, 2012, **9**, 671–675.

3 T. L. Hedrick, *Bioinspir. Biomim.*, 2008, **3**, 034001–7.

4 W. C. Oliver and G. M. Pharr, *J. Mater. Res.*, 2004, **19**, 3–20.