

# Buckling-Induced Reversible Symmetry Breaking and Amplification of Chirality Using Supported Cellular Structures

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Robust routes to induce chirality in centrosymmetric systems are not only of fundamental interest in unraveling the origin of single chirality as found in nature, but also have a broad range of practical applications including optical devices,<sup>[1–3]</sup> sensors,<sup>[4]</sup> pharmaceuticals,<sup>[5]</sup> and advanced structural components.<sup>[6]</sup> Since many chiral systems show distinctive properties depending on their handedness,<sup>[4,7,8]</sup> elucidating routes to induce chiral symmetry breaking and to control the handedness across different length scales is crucial. In general, the emergence of chiral structures of single handedness relies on a two-step process: (i) spontaneous symmetry breaking, followed by (ii) full amplification of this chiral imbalance to yield a uniform configuration. On the molecular scale, experimental demonstrations of such processes have been reported only for few crystallizing systems and chemical reactions,<sup>[9–12]</sup> in which the amplification relies on activating and inhibiting interactions at the molecular scale.<sup>[13]</sup> Extending these principles to larger length scales requires fundamentally different concepts. Although centrosymmetric nanopost arrays<sup>[14–16]</sup> and swellable confined nanoscale gel films<sup>[17,18]</sup> were recently reported to form chiral structures in the absence of chiral induction, no study has been reported on the spontaneous and reversible chiral symmetry breaking and subsequent full amplification to yield large areas of ordered structures with single handedness.

Guided by a theoretical model, we here exploit buckling in rationally designed supported cellular structures at the mesoscale to reversibly switch between the initially achiral configuration and subsequent uniform left- or right- handed configurations. Moreover, we demonstrate that the underlying principles

can be generalized using different geometries, materials, stimuli, and length scales. Although buckling is often regarded as a failure mode that needs to be avoided in structural materials, there are numerous natural<sup>[19,20]</sup> and artificial<sup>[21–28]</sup> systems that use it to their advantage. Buckling of surface-attached strips<sup>[29]</sup> and free-standing structures<sup>[30]</sup> has been studied extensively, but little has been known about mechanical instabilities in surface-attached cellular structures. Moreover, while the deformation and unique mechanical properties of chiral cellular structures have been the focus of many studies,<sup>[31,32]</sup> here we demonstrate spontaneous and reversible chiral symmetry breaking in initially achiral structures followed by full amplification of the chiral imbalance across the entire structure to yield configurations of single handedness.

We start by recognizing that the formation of a chiral pattern, in which all vertices rotate in the same direction, requires that all the individual plates buckle in a higher mode comprising an integer number of complete sinusoids, as shown at the bottom of **Figure 1a** for a honeycomb as a model cellular structure. It is not sufficient to simply buckling a free-standing honeycomb structure to form a chiral structure, since this induces a first-order mode in all plates,<sup>[30,33]</sup> leading to an achiral configuration where adjacent vertices alternately rotate clockwise and counterclockwise, as shown at the top of **Figure 1a**. However, the attachment of the cellular structure to a rigid substrate allows higher order buckling modes, so that one can design architectures capable of deforming into either achiral or chiral configurations. Based on plate theory, we anticipate that the buckling mode can be controlled by carefully designing the dimensions of the cellular architecture. Furthermore, we expect that the connectivity of these cellular structures contributes to the uniform spreading of the chiral pattern once the symmetry is locally broken.

To define the design criteria and predict the deformation of the ensemble, we conducted elastic buckling analysis of an individual supported thin plate. Assuming that the thin plate of length  $l$ , height  $h$ , and thickness  $t$  may be described as a linear elastic material with Young's modulus  $E$ , Poisson's ratio  $\nu$ , and bending stiffness  $D = Et^3/12(1 - \nu^2)$ , its buckling behavior is described by<sup>[34]</sup>

$$\frac{\partial^4 w}{\partial x^4} + 2 \frac{\partial^4 w}{\partial x^2 \partial y^2} + \frac{\partial^4 w}{\partial y^4} + \frac{Et\varepsilon_{sw}}{D} \frac{\partial^2 w}{\partial x^2} = 0, \quad (1)$$

where  $w$  is the deflection in the out-of-plane direction and  $\varepsilon_{sw}$  denotes the differential swelling which is assumed to be uniform within the plate. To consider the effect of the

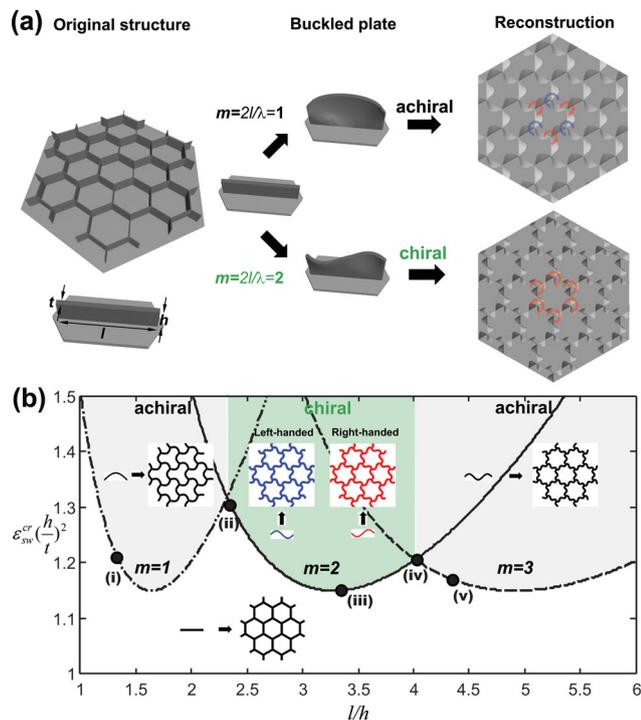
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DOI: 10.1002/adma.201300617



**Figure 1.** Design of structures. a) Schematic approach to the design of supported cellular architectures with buckling-induced chiral or achiral reconstructions. First, the cellular structure is deconstructed into individual supported plates and the wavelength  $\lambda$  of their buckling pattern is calculated. Then, the buckled pattern of the structure is reconstructed by connecting individual buckled plates. The color-coded arrows indicate the handedness of the vertices. b) Results of the buckling analysis for a single supported thin, elastic plate are plotted in a stability diagram. Upon reaching a critical swelling strain  $\epsilon_{sw}^{cr}$ , buckling modes of both half and full sinusoids can be achieved by adjusting  $l/h$  (the aspect ratio of the plate), resulting in respectively achiral and chiral patterns upon reconstruction of the cellular architecture. The circular black markers and corresponding Roman numbers indicate the aspect ratio  $l/h$  of macroscale honeycomb lattices ( $l = 5$  mm and  $t/l = 0.18$ , see Figure 2a) that were fabricated and tested to verify the validity of the analytical model.

neighboring plates in the lattice structures, we assume the two vertical edges at  $x = 0$  and  $x = l$  to be supported (i.e.,  $w = 0$  and  $\frac{\partial^2 w}{\partial x^2} + \nu \frac{\partial^2 w}{\partial y^2} = 0$ ), so that the solution of Equation 1 has the form  $w = f(y) \sin \frac{m\pi x}{l}$ ,  $m$  being an integer (see Supporting Information). For a plate attached to a rigid substrate (i.e., free at  $y = h$  and clamped at  $y = 0$ ), the critical swelling strain  $\epsilon_{sw}^{cr}$  and the wavelength  $2l/m$  of the corresponding mode can then be solved as a function of the aspect ratio  $l/h$ , as shown in Figure 1b. This stability diagram unambiguously reveals that in an initially straight plate with  $0 < l/h < 2.32$  a buckling pattern with half sinusoidal wavelength (i.e.,  $m = 1$ ) will emerge upon reaching a critical swelling strain, resulting in an achiral pattern (space group: P31m). Differently, if  $2.32 < l/h < 4.02$  the buckling will be a full sinusoid (i.e.,  $m = 2$ ), yielding a chiral pattern (space group: P6). To fully define the geometry of the supported cellular structure for experiments, we investigated the effect of the thickness of the plates using non-linear finite element analyses (see Supporting Information, Figure S1,S2). These numerical calculations show that the thickness only

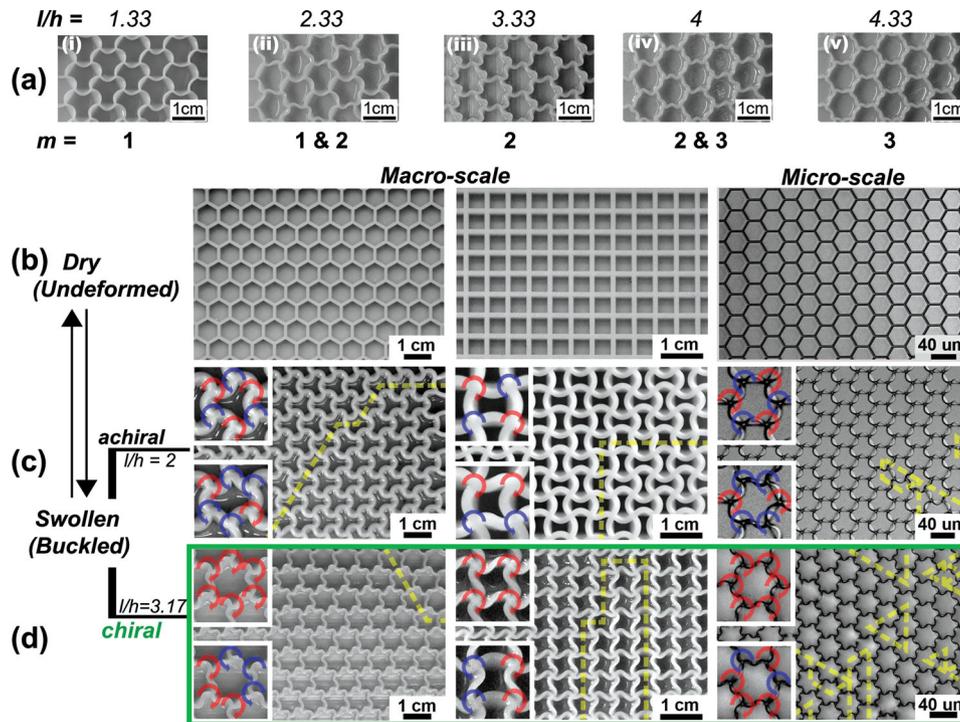
marginally affects the buckling modes (Supporting Information, Figure S2), confirming that the buckling-induced pattern of supported cellular structures is dictated by the aspect ratio  $l/h$  of the individual plates.

Having ascertained the critical design parameters, we validated our analytical model by fabricating surface-attached cellular structures with aspect ratios  $l/h$  that correspond to different regimes in the stability diagram, as indicated by the circular markers in Figure 1b. We started with macroscale honeycomb structures ( $l = 5$  mm) comprising a few unit cells and made from silicone rubber (see Experimental Section). When swelled, the structures yielded either chiral, achiral or mixed patterns (Figure 2a and Supporting Information, Figure S3), exactly as predicted by our analysis (Figure 1b). We then fabricated samples comprising a larger number of unit cells with geometries corresponding to both the achiral ( $l/h = 2$ ,  $t/h = 0.37$  and  $l = 5$  mm) and chiral ( $l/h = 3.17$ ,  $t/h = 0.40$  and  $l = 5$  mm) regime in the stability diagram. Furthermore, since the analytical model is not limited to a specific cellular geometry, we also fabricated macroscale ( $l = 5$  mm) square lattices comprising plates with the same aspect ratio (Figure 2b). Again all the samples buckled as predicted by the analytical model (Figure 2c,d – left/center), showing that the design principles can be applied to different geometries.

Because the pattern formation exploits a mechanical instability that is scale-independent (where the continuum assumption holds), we extended the principle to microscale honeycombs ( $l = 20$   $\mu$ m) made from epoxy resin (see Supplementary Methods). The structures buckled upon immersion in *N*-methyl-2-pyrrolidone, and the stability diagram again correctly predicted the emergence of either chiral or achiral patterns (Figure 2c,d – right). Subsequently evaporating the solvent led to reconversion of the buckled structures back into the original configurations, demonstrating that the controlled pattern formation is fully reversible.

Although all the experimental results show an excellent agreement with the analytical predictions, we observed a racemic mixture of chiral domains displaying both right- and left-handedness evolved from several nucleation events. At the boundaries of these domains (shown as yellow lines in Figure 2), the plates buckled either in the 1st or 3rd mode. Avoiding such racemic mixtures and making defect-free patterns with a single-handedness thus requires the prevention of multiple nucleation sites. We therefore gradually wetted the samples from a single location. This approach induced a unique nucleation event that propagated over the entire sample to yield uniform buckling patterns (Figure 3a). Remarkably, we observed that during the spreading of the pattern some plates initially buckled either in the wrong direction or with an unpredicted mode (Figure 3b). These defects were, however, repaired upon propagation of the swelling front through the defect site when the majority of the plates connected to the defect buckled correctly. The interconnected cellular architecture is thus crucial for conserving the propagation of a single handedness over the entire substrate (Figure 3d) by allowing a self-repair mechanism through connected plates.

While instabilities can be induced by a number of stimuli, including thermal, electrical, and mechanical loadings (Supporting Information, Figure S4), the convenience, versatility



**Figure 2.** Verification of the stability diagram. a) Buckling patterns of macroscale honeycombs with different aspect ratio  $l/h$  ( $t/l = 0.18$  and  $l = 5$  mm for all samples). The Roman numerals indicate the corresponding marker in the stability diagram (Figure 1b). The observed buckling mode ( $m$ ) is shown below each image. Note that a mixture of modes is found for geometries lying on the boundary of adjacent regimes. b–d) Buckling-induced reversible pattern formation in a supported macroscale honeycomb lattice (left), macroscale square lattice (center) and microscale honeycomb lattice (right) upon rapid swelling: b) Optical images of original, undeformed structures; c) For  $l/h = 2$ ,  $t/h = 0.37$ , buckling induces an achiral pattern; d) For  $l/h = 3.17$ ,  $t/h = 0.40$ , a chiral pattern is observed. These buckling patterns are in agreement with the analytical predictions, but multiple domains with different chirality are observed, whose boundaries are highlighted by the yellow dashed lines. The insets show magnified images of the buckled patterns within the domains (top) and at the domain boundaries (bottom). The color-coded arrows indicate the handedness of the vertices.

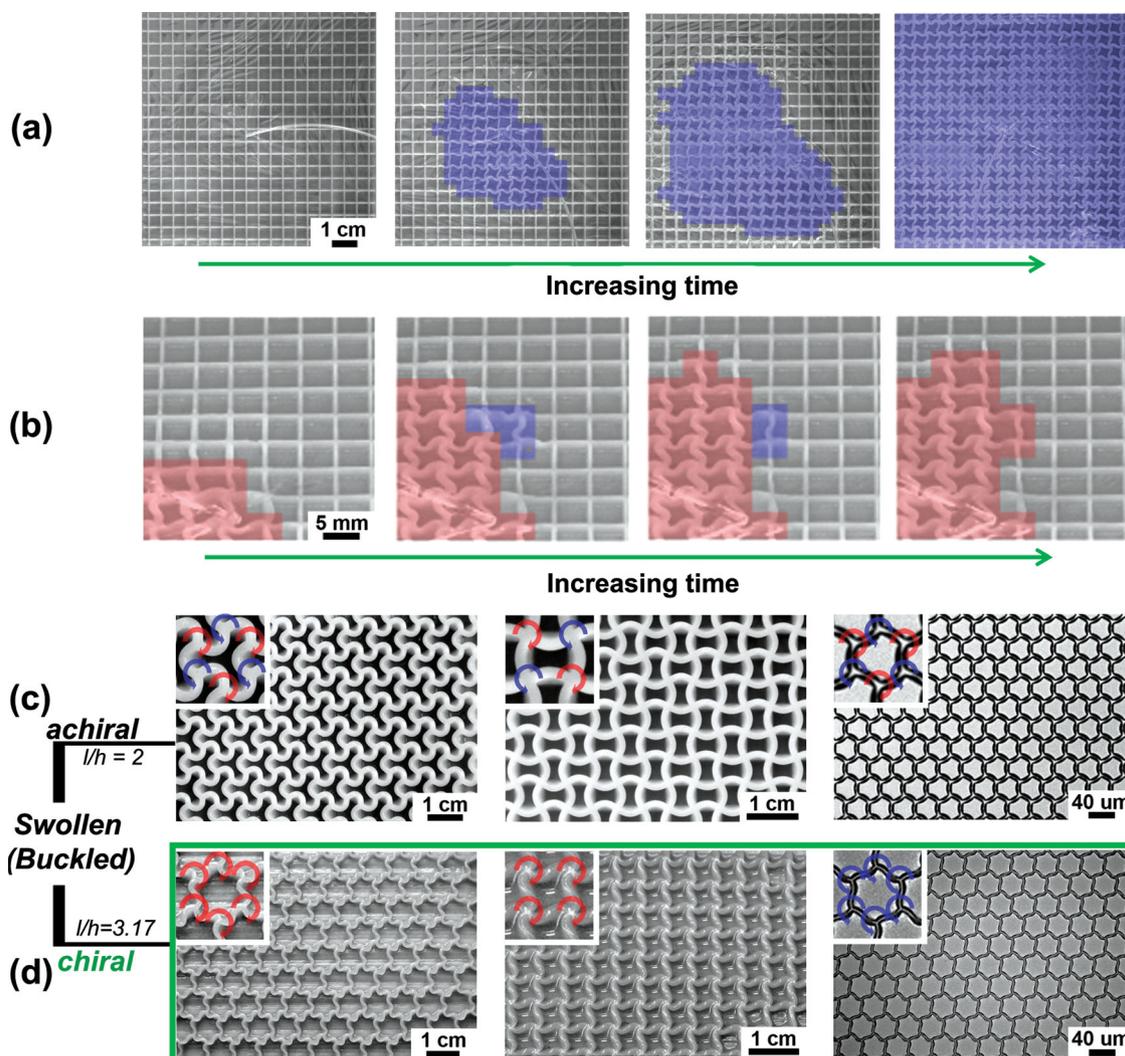
and, most importantly, the reversibility and directionality of the reconfiguration process that arises from swelling-induced buckling enables a unique mechanism where chirality can be chosen, reversibly written and amplified as described below.

Repeated swelling-unswelling revealed that the same buckling pattern reoccurred every time. The structure thus possesses memory of deformation, likely embedded in a previous reorganization of the polymeric network, which can steer the chiral outcome in a subsequent symmetry breaking event. This memory effect can be used to select the handedness of the chiral patterns at will. Since statistical analyses showed equal probability of left-handed and right-handed patterns in rapidly swollen structures (Figure 4a,b), one can map the domains of different handedness and choose a region of desired handedness as a seed. After unswelling the structure back into the initial pattern, we can initiate the slow, directional swelling of the structure starting from one of the mapped domains (Figure 4c). Remarkably, when the progressing pattern reached the previously identified domain boundaries, the handedness of the spreading pattern was still preserved, thereby overwriting the memory of these domains to yield patterns of uniform handedness by the repair mechanism discussed above. When the structure subsequently was unbuckled by drying and rapidly swollen again, we recovered the single-chirality pattern, confirming that the memory of initially racemic domains was

indeed overwritten. This chiral memory is also durable: even after four months the memory is still preserved. Information on the handedness can thus be stored, read out, and overwritten, providing a versatile programmable mechanism.

Guided by an analytical model and numerical calculations, here we show a proof of principle of buckling-induced local symmetry breaking and subsequent spreading of a chiral pattern to yield globally uniform configurations of single handedness in supported cellular structures. We experimentally demonstrate that this strategy offers a unique range of advantages: i) it can be applied to structures with various length scales (where the continuum hypothesis holds); ii) the reconfiguration occurs upon application of different stimuli and using different materials, so that it can be used to dynamically alter surface properties and morphology; iii) the transformation can be made fully reversible; and iv) most importantly, it can be controlled to yield either uniform achiral or chiral configurations with user-defined handedness.

In contrast to molecular symmetry-breaking reactions and crystallization systems, both the nucleation and propagation of chirality can be visualized directly to unravel the underlying mechanisms and fully control the pattern formation. This process not only provides a remarkable example of spontaneous symmetry breaking, but also outlines a general strategy in which a judicious choice of dimensions, materials, stimuli and



**Figure 3.** Uniform pattern formation by controlling nucleation. a) Time-lapse series showing a single nucleation event and subsequent slow spreading of a buckling-induced chiral pattern by gradually wetting from a single location. b) Time-lapse series of the self-repairing process. The initial defect in the form of a few clockwise vertices (blue) is overwhelmed by the surrounding counterclockwise vertices (red), thus amplifying the chiral patterns of the nucleus. c,d) The combination of the unique nucleation event and amplification mechanism results in either uniform achiral ( $l/h = 2$ ) (c) or chiral ( $l/h = 3.17$ ) (d) patterns. Higher-magnification images of the buckled patterns are shown in the insets; the color-coded arrows indicate the handedness of the vertices.

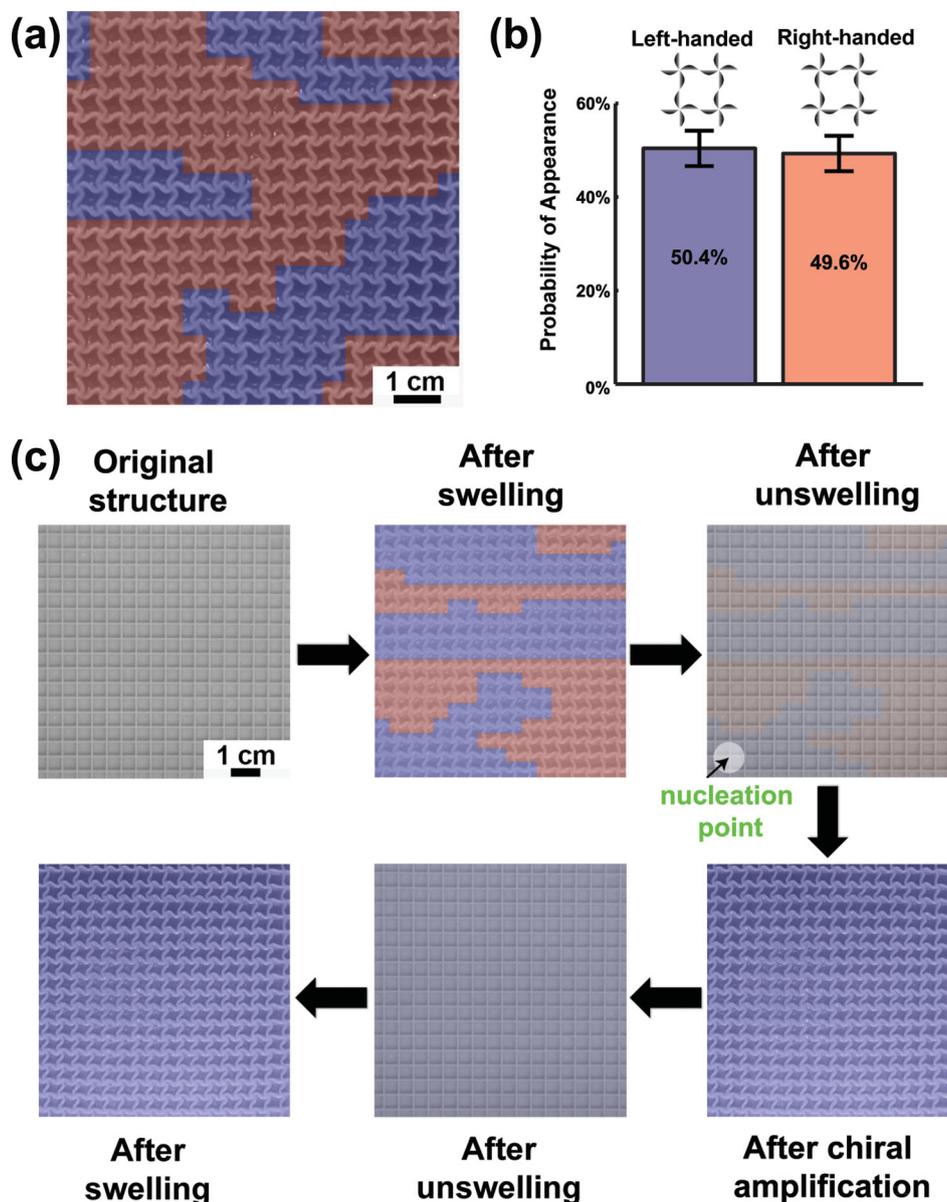
architectonic designs provides a foundation for a wide range of multidisciplinary basic and applied studies. For example, our results could be used to design templates to facilitate fabrication of free-standing chiral structures. Moreover, in structures with sizes comparable to the wavelength of the light, our approach could lead to the design of novel thin film polarization converters, waveguides and circular dichroism spectroscopy substrates.

## Experimental Section

**Fabrication of Samples:** Macroscale ( $l = 5$  mm) surface-attached hexagonal and square cellular structures were fabricated by first making negative molds using a 3D printer (Connex 500 available from

Objet, Ltd.) and were subsequently used to make positive structures from a silicone rubber (Elite Double 32 available from Zhermack). The structures were attached to rigid back plates. Two microscale surface-attached hexagonal structures ( $l = 20$   $\mu\text{m}$ ) were fabricated for this study. The aspect ratios of the macroscale and microscale plates are ( $l/h = 2$ ,  $t/h = 0.37$ ) and ( $l/h = 3.17$ ,  $t/h = 0.40$ ) for achiral and chiral structures, respectively. The microscale structures were first fabricated in  $\langle 100 \rangle$  Si wafers. Replicas of the silicon masters were fabricated using soft lithography-based methods<sup>[35]</sup> with commercially available UV-curable epoxy (UVO-114 from Epoxy Technology, Billerica, MA).

**Buckling-Induced Pattern Formation:** Buckling was induced by swelling, using hexane and N-methyl-2-pyrrolidone (NMP) for silicon rubber and epoxy structures, respectively. The resulting patterns were recorded using a Nikon D90 digital SLR camera for the macroscale samples and a Leica DMRX microscope connected to a QImaging Evolution VF cooled color CCD camera for the microscale samples.



**Figure 4.** Memory effect allowing readout, selection and overwriting of the handedness of the chiral pattern. a) An example of a rapidly swollen macroscale square lattice structures, showing a racemic mixture of left- and right-handed domains. b) Statistical probabilities of the vertices rotate into right- and left-handed configurations from nine independent experiments using different samples. The error bars indicate the standard deviation of the respective probability. c) These chiral domains can be selected and amplified. For this, we first map the chiral domains upon rapid swelling. Subsequently the structure is reconverted into the unbuckled configuration, where the handedness map is given in faded red and blue. Buckling is then initiated at a location selected from the chirality map to induce a uniform pattern of the desired handedness. If the structure is subsequently unbuckled and rapidly swollen, the uniform pattern is recovered, demonstrating that the chiral memory of the original racemic pattern is overwritten.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

This work was supported by Army Research Office MURI award W911NF-09-1-0476 and the Materials Research Science and Engineering Center under NSF Award No. DMR-0820484. K.B. acknowledges support

of the Wyss institute through the Seed Grant Program and NSF-CMMI-1149456-CAREER. We acknowledge the use of the facilities at the Harvard Center for Nanoscale Systems supported by NSF Award No. ECS-0335765 and MIT Microsystems Technology Laboratories. W.L.N. acknowledges the Netherlands Organization for Scientific Research for financial support. We thank Dr. James Weaver for help with macroscale structure preparation, Tom de Geus and Bas Overvelde for discussions, and Dr. Jayson Paulose and Dr. Andrej Kosmrlj for helpful comments.

Received: February 5, 2013

Revised: April 3, 2013

Published online:

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