Reconfigurable Self-Assembly of Mesoscale Optical Components at a Liquid–Liquid Interface

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A method that uses magnetic fields to template the self-assembly and reconfiguration of 2D optical components with engineered surface wettabilities at a liquid–liquid interface is described. The optical components are mesoscale tiles of diffraction gratings each fabricated to contain a magnetic strip. Application of a magnetic field to the tiles, suspended at the interface between two immiscible liquids, assembles them into an array of gratings. The orientations of the tiles and the resulting optical effects are reconfigurable by a change in the magnetic field. It is possible to preserve the assembled patterns, if desired, by transferring them onto solid substrates. This procedure can be useful for generating coatings or films with interesting optical effects and for visualizing magnetic fields.

Self-assembly methods allow the distribution and alignment of small, preformed objects into desired patterns.[1–4] It is a potential alternative to conventional top-down techniques (e.g., photolithography) and serial processing steps (e.g., pick-and-place robotics) for scalable and low-cost fabrication of a wide range of structures with length scales from nanometers (e.g., self-assembly of diblock copolymers,[5–8] templated self-assembly using immunoglobulins,[9] DNA, and viruses[10–14]) to centimeters.[1,15] Self-assembly can generate materials with unique and useful optical properties: for example, 3D-assembly of colloids can form photonic crystals,[16,17] suspensions of silver nanoparticles[18] and gold-coated silicon hexagons[19] provide the reflective element for liquid mirrors, and selective wetting of polymers on long hydrophobic strips forms optical waveguides.[20] The organization of mesoscale (millimeter to centimeter) optical modules is less explored than that of nanoscale structures. Mesoscale structures offer the potential to generate regular arrays of functional optical elements over large areas. Some functions (e.g., diffraction, lensing) cannot be obtained easily (or at all) from the direct assembly of nanostructures.

The self-assembly of mesoscale plates into various arrays and porous structures using lateral capillary interactions between menisci at the edges of the plates has been previously demonstrated.[21–31] Most of these assemblies were static: once assembled, it was difficult to reconfigure the assembled pattern. There are few strategies that allow real-time reconfiguration of self-assembled mesoscale structures without requiring a change in the design and fabrication of individual components. Mao et. al. showed the reconfiguration of assembled structures by changing the center of mass of the plates suspended between two immiscible liquids: the assembled pattern changed from one where positive menisci dominated their self-assembly to one where negative menisci dominated.[28] This method was, however, limited: there were only two possible configurations and it also required a change of the liquids used. Magnetic-field-templated self-assembly provides real-time reconfigurability. Most of the previous work focused on the motion of small objects in response to magnetic fields[32–34] or the formation of structures that could not be changed once assembled.[35,36] The self-assembly of superparamagnetic particles has recently been used to modulate the transmission of light dynamically.[37,38] The generation of large-area materials with functional optical properties has not been reported.

This paper describes a simple approach to the dynamically reconfigurable self-assembly of more than 300 tiles of millimeter-scale diffraction gratings over areas greater than 10 cm^2. Changing the magnetic fields changes the patterns of the assembled structure and generates a range of optical effects. Anisotropic modification of the wettability of the top and bottom surfaces of the tiles locks them in the x-y plane at the interface between a hydrophobic liquid and a hydrophilic liquid with uniform top-down orientations. We did not modify the wettability of the side edges of the tiles using established methods.[21–31] Had we done so, the assembled structure could have been locked into a particular configuration by capillary interactions, or caused to have attractive or repulsive interactions. The aggregates of tiles with unmodified edges disassembled upon the removal of the magnetic field (by agitation, for example) and reconfigured into new structures upon the application of different patterns of magnetic fields.

This approach to the generation of reconfigurable optical films has five characteristics: i) The application of a magnetic field is required to assemble and orient the tiles. The orientation of the tiles in the assembled pattern follows the lines of the magnetic field. ii) Because there is no solid friction at the liquid–liquid interface, the optical elements are not subject to stiction or wear. iii) The assembled pattern could be reconfigured as many times as desired by a change in the magnetic field. iv) This method can, in principle, be used to organize and register large number of micro- to millimeter-scale components on surfaces (flat or curved). It is also interesting for its ability to generate colorful and changeable optical effects and to visualize magnetic field lines. v) Assembled patterns can be retained permanently by transferring the tiles onto a solid substrate, which makes this approach useful for the fabrication of optically functional coatings or films.

We fabricated tiles (squares with edges of 2 mm and circles with diameters of 2 mm) of reflective diffraction elements with the top surface made hydrophilic and the opposite face made

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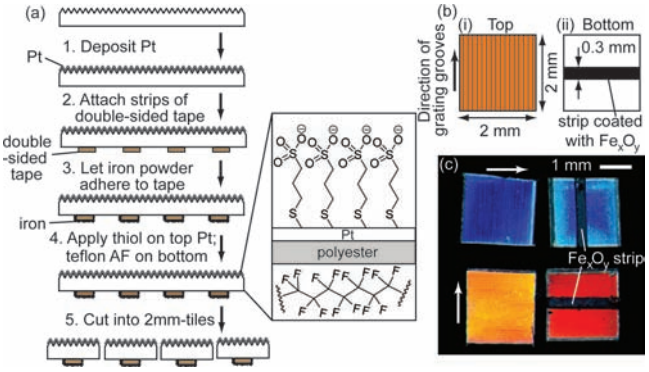

Figure 1. a) Fabrication of grating tiles. 150-nm-thick platinum was deposited on a transmission-type polyester film of grating. Strips of double-sided tape were attached to the bottom face of the gratings and coated them with iron powder to make them responsive to magnetic fields. The Pt-coated side of the grating was rendered hydrophilic with 3-mercapto-1-propanesulfonic acid and the opposite side was rendered hydrophobic with Teflon AF. The tiles were then cut into square (length = 2 mm) or circular shapes (diameter = 2 mm) manually using scissors or a hole puncher. b) Scheme showing the top and bottom of the tile. c) Optical microscopy image of four tiles. The left shows the top face of the tiles, and the right shows the bottom face of the tiles. The white arrows indicate the direction of the grating grooves. The reflected colors from the top and bottom surfaces of the tiles differed because the tiles on the left were tilted slightly into the plane relative to the tiles on the right.

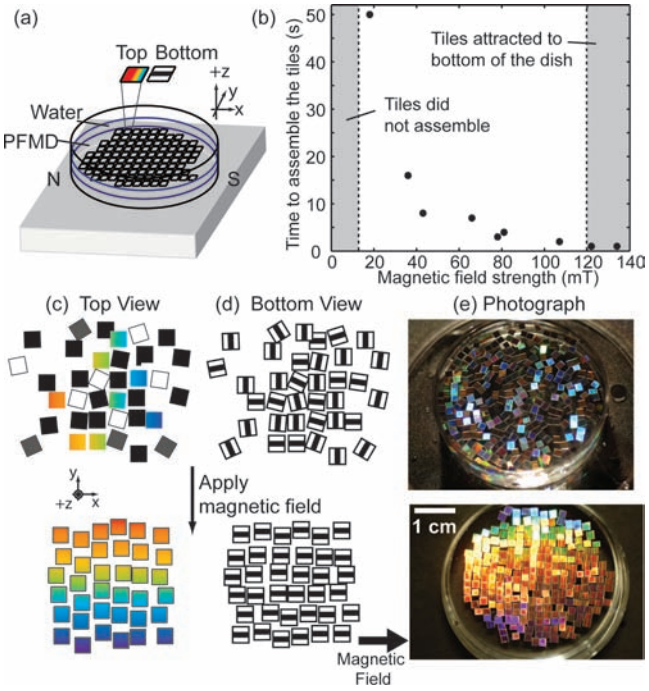

Figure 2. a) Scheme of the positioning of the tiles at the water–PFMD interface. b) The time needed to assemble the tiles into the final pattern as a function of the strength of the magnetic field. c–e) Schemes and photographs showing the orientation and alignment of the tiles with an external magnetic field.

hydrophobic (**Figure 1**; see Experimental Section for details). We dispersed the tiles in a Petri dish containing perfluoro-1-methyldecalin (PFMD) and water (**Figure 2**a). The density, ρ, of the polyester tiles was about 1.4 g cm^{-3}, which is intermediate between that of PFMD ($\rho \approx 2$ g cm^{-3}) and water ($\rho \approx 1$ g cm^{-3}). The tiles self-assembled at the interface of the two liquids with an orientation driven by the pattern of hydrophilic and hydrophobic surface modification on the two faces of the tiles. After shaking or stirring the suspension for a few seconds, ≈99% of the tiles settled into the correct up-down orientation, in which the hydrophilic side faced the water phase and the hydrophobic side faced the PFMD. Additional shaking did not flip upside-down tiles into the proper orientation. More vigorous agitation may help, but excessive shaking might cause the tiles to overlap.

A magnetic field was applied to the system of tiles at the liquid–liquid interface using a rectangular NdFeB bar magnet (4 cm × 4 cm × 1 cm, in the *x*-, *y*-, and *z*-directions), placed a few centimeters beneath the liquid–liquid interface. Upon application of this magnetic field, the tiles self-assembled into a structure such that the strips of iron powder on their bottom side aligned with the direction of the magnetic field (Figure 2c–e). The tiles, thus, mapped the lines of the field produced by the magnets. The time necessary to assemble the tiles into the final pattern increased as the strength of the magnetic field decreased (Figure 2b). For field strengths <10 mT (measured using a Hall-effect gauss meter, Sypris Model 6010), the tiles did not assemble into a close-packed structure. For field strengths >120 mT, the tiles were no longer fixed at the interface between water and PFMD; they were instead pulled through the interface to the bottom of the Petri dish closest to the magnets. For the experiments that involved orienting the tiles at the interface, applied field strengths were between 80 and 100 mT.

After some agitation (e.g., gentle tapping on the Petri dish for 5 s), the tiles assembled into a structure that was 80–90% close-packed. This number was estimated from the ratio of the area of a perfect close-packed structure that contains the same number of components to the area of the assembled structure. The theoretical maximum packing density of tiles is 90.67% in a close-packed hexagonal lattice composed of circular tiles, while the theoretical maximum packing density is 100% in a square lattice composed of square tiles. The patterns of colors reflected from square tiles assembled in a square lattice therefore appeared more uniform than the patterns reflected from assemblies of circular tiles (compare Figure 2e, bottom with Figure 6b).

Figure 3 shows the assembled tiles of gratings upon the application of a magnetic field. The field lines were parallel in the *x*-direction over the whole area of the Petri dish. The long axis of the grooves on the gratings was in the *y*-direction. The angle of observation was varied in the *x*-*z* plane and the colors reflected were examined. Due to the diffraction of light by the grating elements, the colors observed at different angles follow that given by the grating equation (Equation 1):[39]

$$d(\sin\theta_r - \sin\theta_i) = m\lambda \quad (1)$$

where d (=1 μm) is the spacing between the grooves in the grating, θ_i (≈30°) is the angle of the light source, θ_r is the angle of reflection of diffraction order m, and λ is the wavelength of light ($\lambda \approx$ 400–700 nm for the visible wavelengths). At $\theta_r \approx 30°$, diffraction of order $m = 0$ occurred; no dispersion of color could be observed (Figure 3b-ii, c-ii). When the observation angle was ≈5°

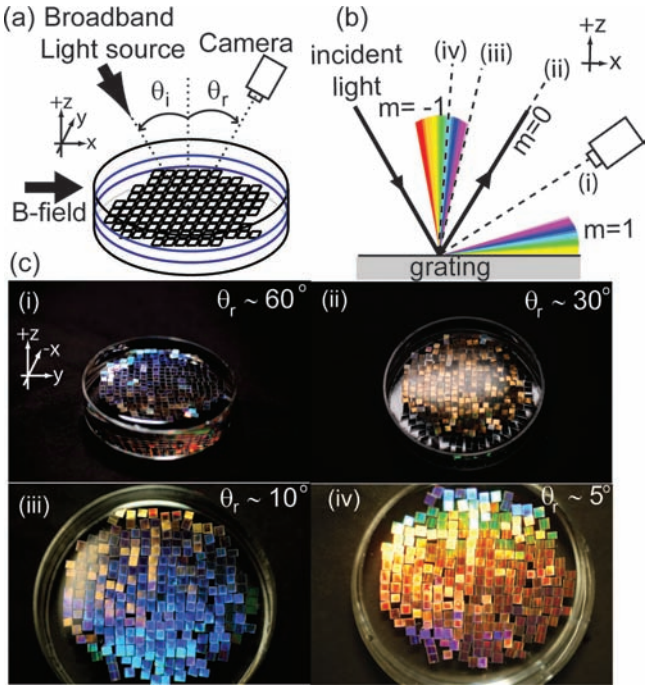

Figure 3. a) Scheme showing the conditions under which the optical microscopy images in (c) were obtained. The angle of the incident light (θ_i) was fixed and the angle of observation (θ_r) varied from ≈5° to 60°. A uniform magnetic field was applied in the *x*-direction. b) A simplified scheme of the diffraction of visible light from a small area on the grating. The actual light source was not collimated. Numbers (i–iv) indicate the approximate angles of the camera in (c). c) Photographs of the assembled tiles imaged at different observation angles. The magnetic field was fixed in all cases. The length and width of the tiles were both 2 mm.

(Figure 3c-iv), a large range of colors spanning from blue to red could be imaged with the camera. These colors originated from the diffraction of visible wavelengths with order $m = -1$ ($\theta_{r,m=-1;\,\lambda=400\text{ nm}} \approx 5°$, and $\theta_{r,m=-1;\,\lambda=700\text{ nm}} \approx -11°$) (Figure 3b-iv).[40]

Although optimizing order in the assemblies was not our highest priority, defects in the assembled structures were noticeable based on the profiles of the light reflected. First, there were voids among the tiles. For square tiles, these voids came, at least in part, from differences in the dimensions of the manually cut tiles. The magnetic strips were also not always centered (±0.2 mm from the center of the tile). Second, the colors and intensities of light reflected were not uniform. These non-uniformities arose from small tilts of the tiles at the liquid–liquid interface, probably due to small irregularities at the edges of the tiles formed in fabrication, and consequent irregularities in the forces produced by the meniscus. For circular tiles, the puncher used to cut the tiles also caused the tile to curve. Third, tiles occasionally overlapped if agitation was too rigorous.

Many of these defects can be minimized by improving the fabrication of the tiles. The most difficult issue with fabrication here was the cutting of uniformly shaped gratings with no curl or deformities around the edges. These difficulties can, in part, be mitigated using existing methods in microfabrication, laser-cutting, or custom-machined dies. Bucaro et. al. demonstrated that standard lithographic and dry-etching techniques are capable of creating 8-μm micromirrors with smooth surfaces and uniform hexagonal shapes.[19] Using a similar procedure, it should be possible to pattern grooves to form a diffraction grating that contains a strip of magnetically responsive material (Fe_xO_y or Ni) formed by evaporative deposition of these materials onto the grating. This method should allow the generation of tiles with uniform square or hexagonal shapes to improve the efficiency of packing at the liquid–liquid interface.

Figure 4, **5** show that the pattern of the assembled tiles depended on the pattern of the applied magnetic field. The tiles assembled into structures in which the magnetic strips under each tile were aligned with the component of the local magnetic field lines projected in the plane of the liquid–liquid interface. Since the gratings consisted of linear grooves, the diffraction of light, and therefore the distribution of reflected colors from the tiles, occurred at a relatively narrow range of angles when the grooves on the grating were perpendicular to the direction of observation. When the applied magnetic field lines were not unidirectional (Figure 5), the orientations of the gratings on the tiles were not uniform throughout the whole assembly. Only a small fraction of tiles reflected bright colors under these magnetic field patterns.

To obtain a reflection of colors from a large range of angles, other designs of diffraction gratings can be used (e.g., one that consists of a regular array of posts). Alternatively, the use of photonic crystals with complete band gaps[41] allows the reflection of light in all directions at fixed wavelengths. To achieve changeable optical effects by a rotation in the magnetic field, the tile element should also display rotational asymmetry in its optical properties. So long as magnetically responsive components can be incorporated into these optical elements, the same strategy can be used to assemble the elements using a magnetic field.

One disadvantage of the assembly of these tiles at a liquid–liquid interface is that it is difficult to preserve the patterns

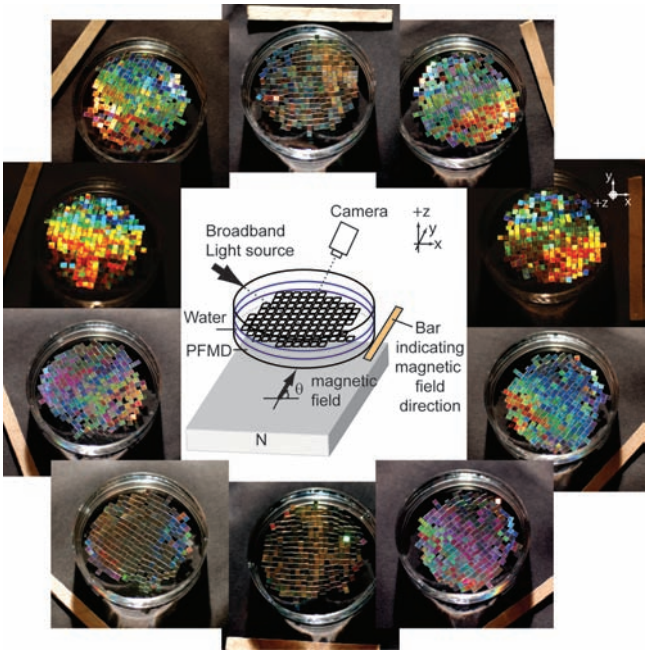

Figure 4. Optical images of the tiles oriented under different directions (θ) of the magnetic field. The length and width of the tiles were both 2 mm.

Figure 5. Packing structures of the tiles differed according to the pattern of magnetic field applied. a) The tiles in the absence of magnetic fields. The length and width of each tile were both 2 mm. b–e) The assembly of tiles in response to different patterns of magnetic fields.

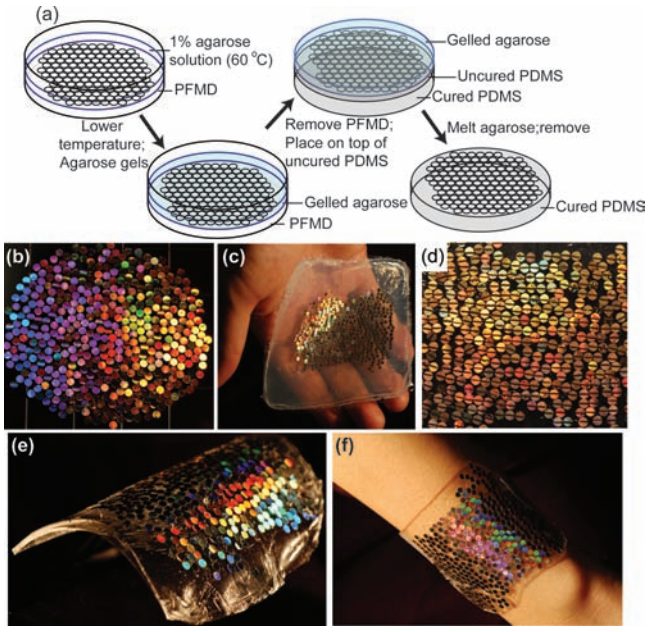

Figure 6. a) Scheme showing the transfer of the tiles from the liquid–liquid interface to a solid substrate. b) Assembled circular tiles at the liquid–liquid interface. The diameter of the tiles was 2 mm. c,d) The bottom of the tiles after the agarose gelled. Some tiles were displaced and lost when the gel was transferred between different surfaces by hand (for photography). These displacements can be avoided by transferring the gel directly onto PDMS. e,f) Photographs of tiles transferred onto a film of PDMS that was curved and wrapped around a wrist, respectively.

permanently or to integrate them with other materials or devices. Here we demonstrate an approach that transfers the assembled pattern onto solid and flexible substrates.

The tiles were assembled at the interface of PFMD and an agarose solution (1 wt%) at ≈60 °C (**Figure 6**). After the agarose cooled to 20 °C and gelled, the tiles were fixed on the surface of the gel. Upon draining the PFMD, the bottom surface of the tiles became exposed. Curing polydimethylsiloxane (PDMS) on this surface, and subsequent melting the agarose and pouring it off, transferred the tiles onto PDMS. Figure 6e,f show that it was possible to bend the PDMS film or wrap it around a wrist. In principle, it is possible to suspend the tiles at the interface of PDMS and PFMD or PDMS and water directly. Curing the PDMS after the tiles assembled under a magnetic field could generate a film of PDMS consisting of the assembled tiles. This strategy was not practical using the materials we had available because PDMS was more viscous than water and PFMD, and the time for the tiles to assemble was >10 times longer than that needed for PFMD–water system.

We demonstrated a new method for the assembly and registration of optical components with small footprints using surface forces and magnetic forces. To obtain different optical responses (reflected colors here) from these components, magnetic fields were applied in different orientations relative to the light source. We have shown the manipulation of the orientation of the tiles in the plane of the liquid–liquid interface (x-y plane) only. It should also be interesting to control the tilting angle of these tiles (in the x-z or y-z planes) as the tilt of the grating element determines the color reflected at fixed angles of the light source and observation. If the tilting of individual elements can be addressed separately, this system can be applied towards constructing a reflection-based color display.

We have also demonstrated a way to transfer assembled materials from liquid interfaces onto solid substrates. This method can, therefore, be compatible with micro- or nanofabrication procedures where the components were formed in a liquid. Nanoscale optical structures (e.g., metamaterials with a negative index of refraction) fabricated using nanoskiving,[42,43] for example, are suspended at the interface of water and air after being sliced with a microtome. The footprint of these elements is small (a few hundreds of μm^2). While this size is sufficient for characterization, it would be very difficult to fabricate these components in the large areas necessary for applications in coatings or films, e.g., construction of an invisibility cloak[44] directly from micrometer-sized samples with negative index properties would be very challenging. If magnetic

components can be incorporated into these elements, however, the assembly of these elements into large areas should be possible using the procedure we have described. We have shown the assembly of hundreds of structures over areas of square centimeters using commercially available permanent magnets; electromagnets can potentially generate fields over much larger areas than permanent magnets for the assembly of many elements over much larger areas (square meters). We believe that this assembly method can bridge the gap between nanofabrication (where sample sizes are usually small) and the generation of large-surface-area materials for end use.

Experimental Section

Fabrication of Tiles of Gratings: One side of a 100-μm-thick transmission-type polyester diffraction grating film (1000 grooves mm^{-1}, Edmund Optics) was coated with 150 nm of platinum to make the grating reflective (Figure 1). Using Pt was advantageous because: i) it was possible to form self-assembled monolayers (SAM) of thiols on them to modify the wettability of the surface;[45] ii) Pt adhered to the surface of polyester without the need of an adhesion layer; iii) among metals on which self-assembled monolayers of thiols (Au, Ag, Pt, Pd)[45] could be formed, the reflectivity of light from Pt was relatively uniform in the visible wavelength region. Au has low reflectivity at wavelengths <500 nm, and therefore possesses a yellow reflected color. Reflectivity from Ag degraded over time due to the formation of silver oxide.

To fabricate magnetic strips on the opposite face of the grating, 0.3-mm-wide strips of double-sided tape (indoor carpet tape, 3M), generated using a laser cutter, were attached. To simplify the transfer of double-sided tape to the tiles, the double-sided tape was first attached to a substrate of Teflon, strips were laser cut through this double-sided tape but not the Teflon. Excess tape was removed and the uncoated side of the polyester diffraction grating was then pressed against the strips of double-sided adhesive on Teflon. Double-sided tape adhered more strongly to polyester than to Teflon, and the construct of double-sided tape and diffraction grating could be removed from the original substrate of Teflon. Pressing the side of the sheet with double-sided adhesive against a plate covered with loose iron powders coated the strips of double-sided tape with a sufficient quantity of the ferromagnetic powders to make them strongly responsive to magnetic fields. The incorporation of these magnetic strips allowed the position and orientation of the gratings to be manipulated using an external magnetic field.

Immersion of the samples in a solution of 3-mercapto-1-propanesulfonic acid (1 mM in ethanol, 5 min) formed hydrophilic SAMs on the Pt-coated side. The contact angles of water and perfluoro-1-methyldecalin (PFMD) on this surface were both <10°. A pipette was used to apply amorphous fluoropolymer (Teflon AF 400S1–100-1, Du Pont) to the opposite surface; the fluoropolymer spread evenly and dried to form a continuous hydrophobic film. The contact angles of water and PFMD on this surface were 120° and <10°, respectively. These grating components therefore had a strong orientation preference when suspended and agitated at the interface between water and perfluorocarbon: they oriented spontaneously in such a way that the hydrophilic side, which contained the grating structure, was in contact with water, while the Teflon-coated side, which contained the magnetic strip, was in contact with the perfluorocarbon.

Tiles also spontaneously oriented themselves at the interface of water and some hydrocarbons (e.g., hexane), with the hydrophobic side facing the top hydrocarbon phase and the hydrophilic side facing the bottom water phase. If this hexane–water system were to be used, the surface wettability of the tiles would have to be reversed so that the grating elements would face up.[46] Organic solvents (e.g., dichloromethane) that are denser than water tend to dissolve these tiles; by working with a crosslinked polymer, it would be possible to make them much more solvent resistant. For all the self-assembly experiments, perfluorocarbons were used instead of hydrocarbons because perfluorocarbons are nontoxic and chemically inert.

The grating was cut into square shapes (2 mm × 2 mm) using scissors or into circular shapes (diameter 2 mm) using a hole puncher (McMaster). This size was selected because tiles of larger footprint did not orient spontaneously at the liquid–liquid interface and tiles of smaller size were challenging to fabricate manually.

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