

Supporting Information for

**Shaped Films of Ionotropic Hydrogels Fabricated
Using Templates of Patterned Paper**

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Supplementary Experimental

General Conditions: All chemicals were purchased from Sigma-Aldrich, Fluka, Alfa Aesar, Fisher Scientific, or VWR and used without further purification. Whatman No. 1 chromatography paper was obtained from Sigma-Aldrich in square sheets measuring 20 x 20 cm. The sodium salt of alginic acid (AA) was obtained from Sigma, carboxymethyl cellulose was obtained from Calbiochem, and ι-carrageenan was obtained from Fluka. The strontium iron oxide powder used for the production of strongly magnetic hydrogels was purchased from Hoosier Magnetics (Ogdensburg, NY). Stock solutions of 1.5% AA (w/w), 2% CMC, and 2% CG were prepared with 18 MΩ·cm deionized water. For the production of colored films, a water soluble dye (~1 mg/mL) or a colored pigment (~2% by weight) was added to the polymer solution prior to the cross-linking step. The solutions used to wet the templates with multivalent ions were typically saturated or 2 M solutions of CaCl₂, Ni(NO₃)₂, Cu(NO₃)₂, FeCl₃, Ho(NO₃)₃, GdCl₃, or BaCl₂. The dimensions of the films were measured with a pair of digital calipers that recorded distances to the nearest hundredth of a millimeter. The final values are reported as 90% confidence intervals of the average of three trials.

Determination of the Capacity of the Paper for Aqueous Solutions of Cross-linking Ions: To determine the capacity of the Whatman No. 1 chromatography paper for the aqueous solutions of cross-linking ions, we cut a 2.0 cm x 2.0 cm square of paper template, massed it, and wet it with 100 μL of solution. The solution wicked into the template, and after the solvent front had reached every position along the edge of the paper, the excess solution was blotted away with a clean piece of paper and the wet template was massed. The difference in mass of the wet and dry templates was divided by the density of the solution to determine the volume of solution that entered the template. We repeated the experiment in triplicate for each solution and reported the volumes used to wet the paper as 90% confidence intervals.

Figure S1. Chemical structures of some polymers that form ionotropic hydrogels in the presence of multivalent cations.

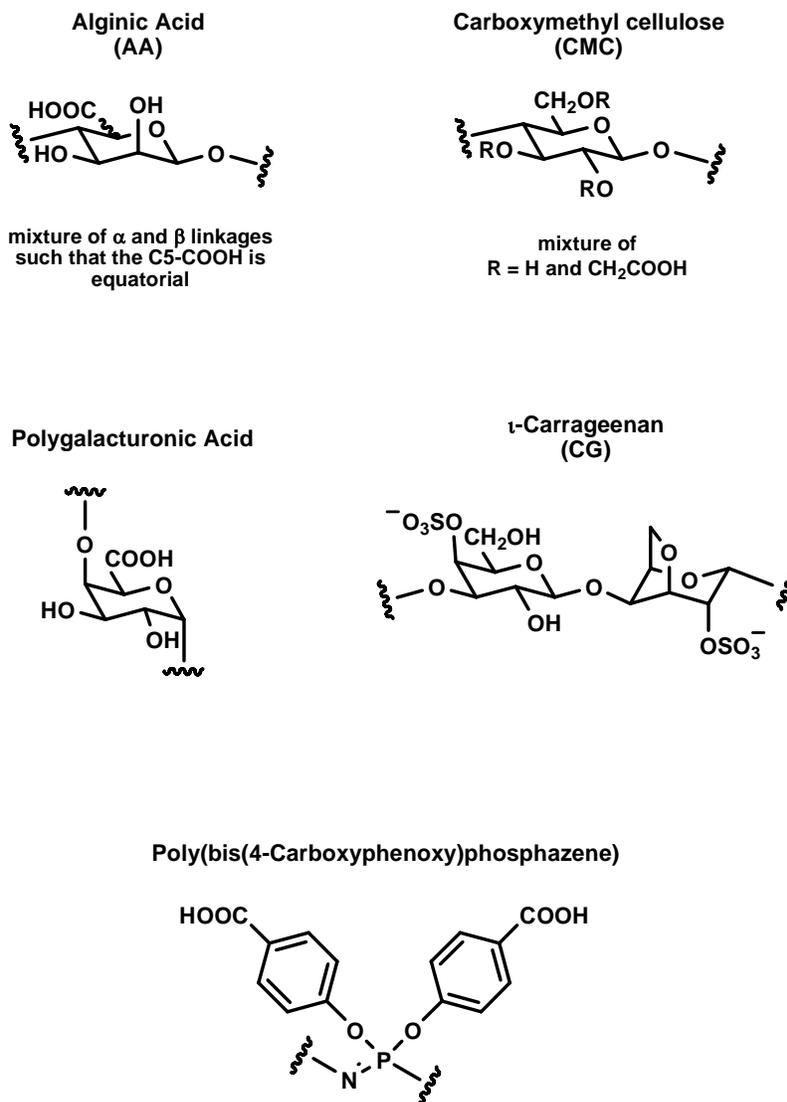


Figure S2. (Figure 2 in color). A schematic diagram that depicts the procedure for making shaped films of Fe^{3+} -AA using a template of patterned paper. In this process, we wet the shaped regions of paper with a saturated solution of FeCl_3 (b). Next, a solution of sodium alginate containing a red dye (to improve contrast) was applied to a glass slide and the slide was pressed against the template (c) to form hydrogel films after the ions left the paper and cross-linked the polymer (d). Gently prying at the edges of the shapes with a spatula freed the films from the template (e).

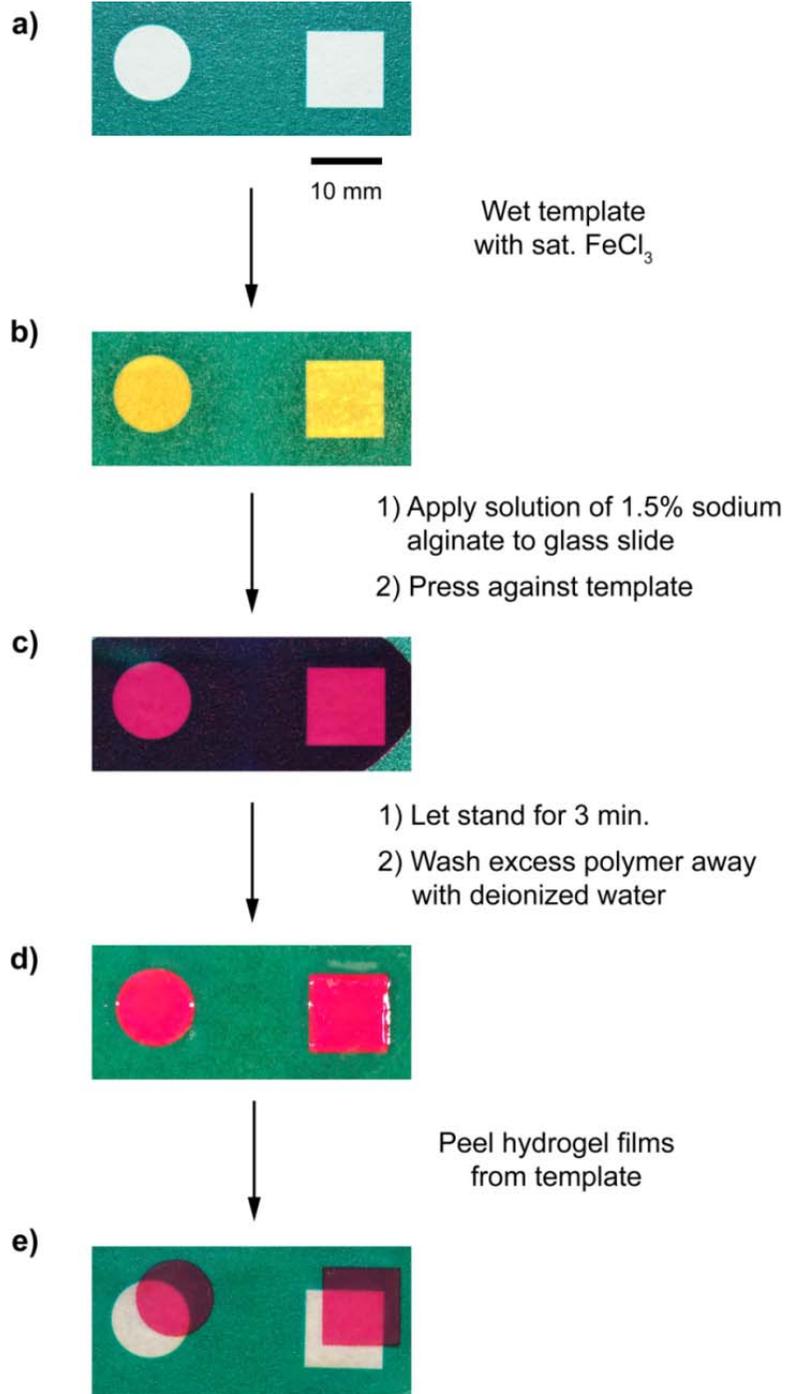


Figure S3. (Figure 3 in color). Schematic depicting the formation of hydrogel films on paper templates wetted with cross-linking agent. a) Preparation of a film through unconstrained growth. The ions spread isotropically from the exposed regions of paper into the uncross-linked aqueous solution of anionic polymer such that the thickness of the film matched the distance the sides extended past the edge of the shaped template. b) Preparation of a film with a textured top surface using a molded plate. The plate controls the shape of the surface, and the spacer units (typically, layers of tape) control the thickness of the film.

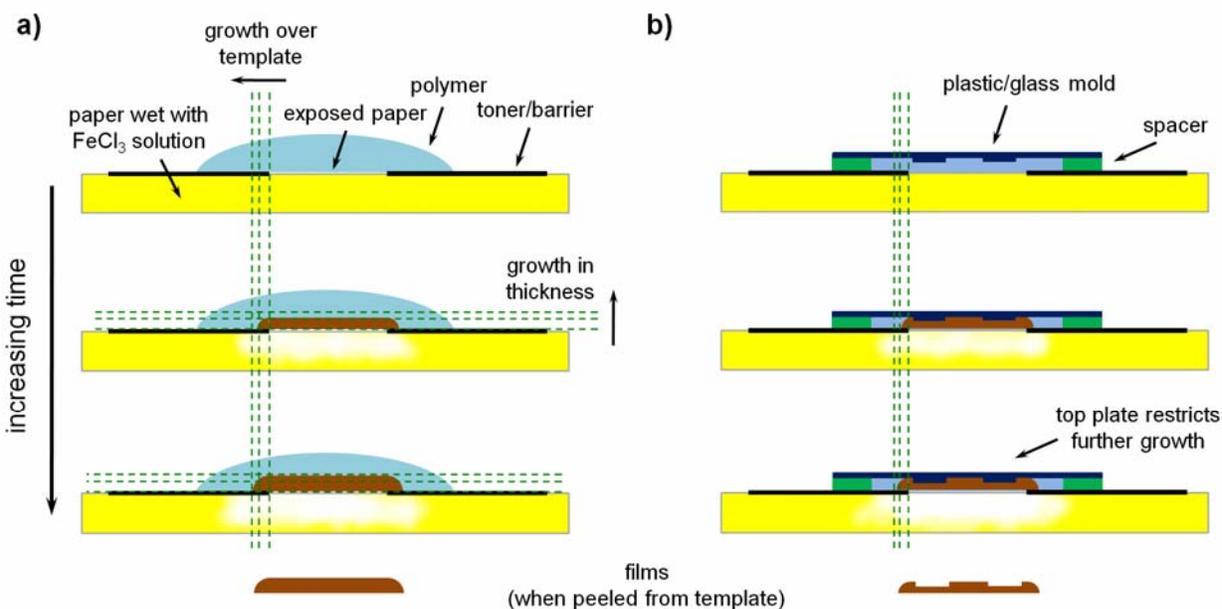


Figure S4. (Figure 4 in color). Hydrogel films patterned in various complex structures and schematic representations of the paper templates used to make them. a) Strips of Gd^{3+} -AA colored with Cibacron Brilliant Red 3BA suspended over a Petri dish (thickness = 0.70 ± 0.06 mm). b) “Short” 2-D rings of Fe^{3+} -AA colored with activated carbon (thickness = 0.85 ± 0.03 mm). c) “Tall” 3-D ring of Gd^{3+} -AA colored with Cibacron Brilliant Blue F3GA (thickness = 0.21 ± 0.06 mm). d) Interlocking “tall” rings of a mixture of 1% AA and 0.6% ι -carrageenan cross-linked with Gd^{3+} (thickness = 0.44 ± 0.20 mm). e) A Möbius strip of 1% AA/0.6% CG cross-linked with Fe^{3+} (thickness = 0.90 ± 0.08 mm).

Hydrogel Structure

Associated Template

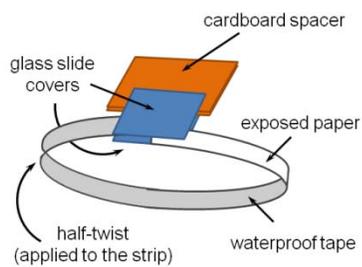
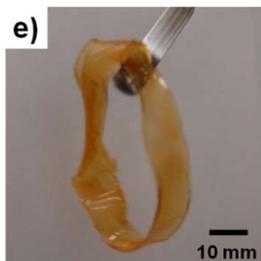
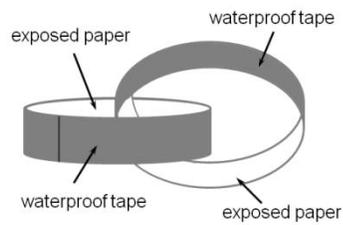
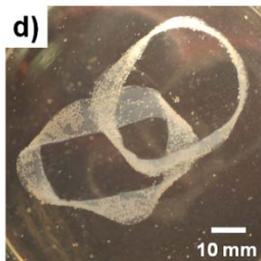
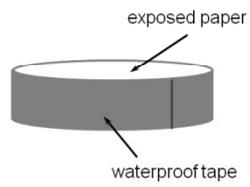
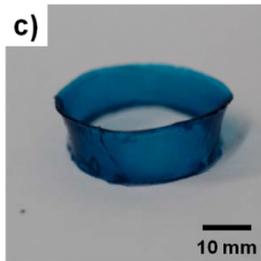
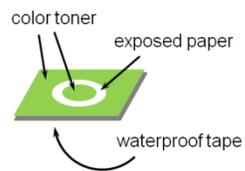
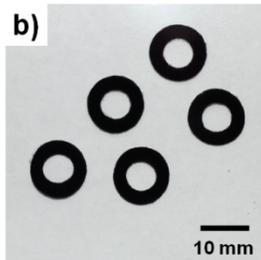
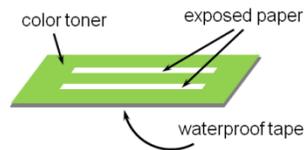
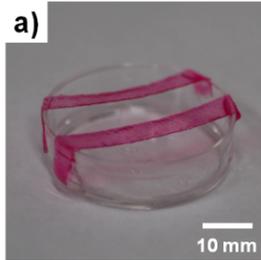


Figure S5. (Figure 5 in color). A photograph that depicts the ability of a rare-earth bar magnet to selectively attract films of ionotropic hydrogels cross-linked with Ho^{3+} cations. The Ho^{3+} -cross-linked ring contains activated carbon (2% by weight) as a black pigment to distinguish it from the orange Fe^{3+} -cross-linked alginate films.

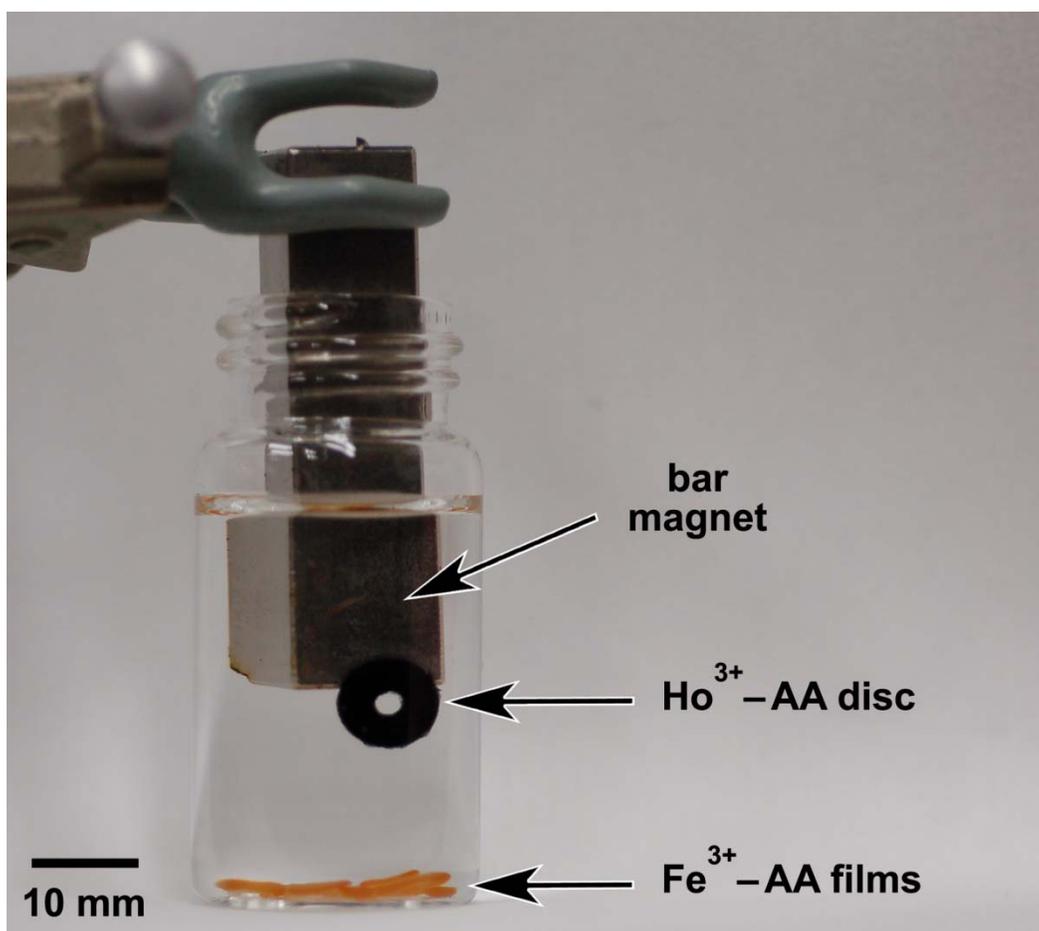
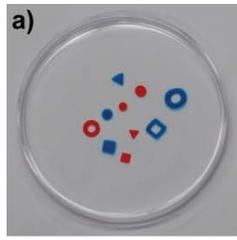
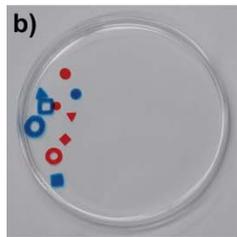


Figure S6. A sample demonstration of the separation of magnetic films from a mixture of alginate films. a) A starting mixture of Gd^{3+} -AA films (colored red with Pigment Red 4) and Ca^{2+} -AA (colored blue with Pigment Blue 15) of various shapes (rings, discs, triangles, and squares). b) The mixture shifted to one side of the Petri dish when the dish was tilted. c) A bar magnet positioned near the mixture of films selectively attracted the Gd^{3+} -AA shapes such that they could be dragged to the other side of the dish. Shaking the magnet released the films. d) Repetition of this process effected the complete separation of the Gd^{3+} -cross-linked films from the initial mixture.

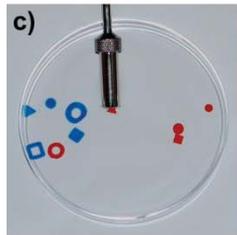


30 mm

Tilt dish



- 1) Attract Gd^{3+} -AA films with magnet
- 2) Move magnet to desired location
- 3) Release films



Repeat until separation
is complete

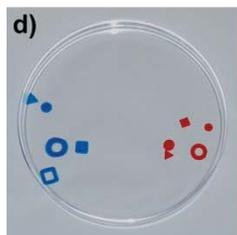


Figure S7. A ribbon of ferrimagnetic hydrogel formed by suspending micron-sized particles of strontium iron oxide in the solution of uncross-linked polymer prior to gelation. The ribbon, made from a mixture of 1% AA and 0.6% ι -carrageenan, was strongly attracted to a bar magnet and could wrap around sharp corners or fold back on itself without fracturing.

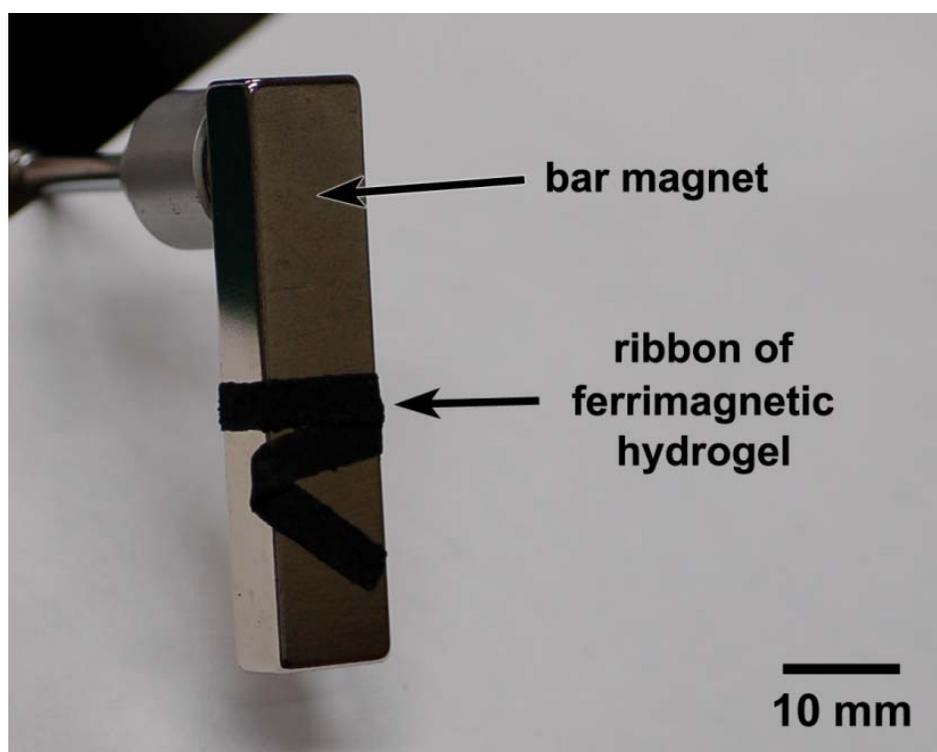


Figure S8. Hydrogel discs formed by cross-linking 2% (w/w) solutions of AA, CMC, and CG with a saturated solution of FeCl_3 . a) Disc of Fe^{3+} -AA (thickness = 1.04 ± 0.13 mm). b) Disc of Fe^{3+} -CMC (thickness = 0.81 ± 0.03 mm). c) Disc of Fe^{3+} -CG (thickness = 1.26 ± 0.20 mm).

