Supporting Information

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Liquid Wells as Self-Healing, Functional Analogues to Solid Vessels

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Table of Contents

Experimental ........................................................................................................................................ 2-3
Methods ............................................................................................................................................. 3-6
Table S1. Apparent contact angles of functionalized surfaces (values) ........................................... 6
Table S2. Physical properties of organic solvents used for confinement tests ................................... 6
Table S3. Water solubility and density of methacrylates used in this work ...................................... 6
Figure S1. Hydrophilic-hydrophobic chemical patterning .......................................................... 7
Figure S2. Apparent contact angles of functionalized surfaces (images) ....................................... 7
Figure S3. Raman mapping of a liquid well .................................................................................... 8-9
Figure S4. Confinement test with different organic solvents .................................................... 10
Figure S5. Confined aqueous droplets within water walls .......................................................... 10
Figure S6. Height of the water walls .............................................................................................. 11-12
Figure S7. Liquid well after being cut with a knife ......................................................................... 13
Figure S8. Liquid well extraction experiment ............................................................................. 13
Figure S9. Influence of the organic liquid on the lateral extensions ........................................... 14
Figure S10. Droplets of 1-nonanol in water ............................................................................. 15
Figure S11. Water-templated polymerization .......................................................................... 16
Videos S1-6. Description and experimental details ....................................................................... 16
References ......................................................................................................................................... 17
Experimental

Fabrication of patterned surfaces

Vinyl functionalized microscopy glass slides were provided by Aquarray (Eggenstein-Leopoldshafen, Germany). Microscopy glass slides were from Schott Nexterion (Jena, Germany). Modified microscopic glass slides from Aquarray were photopatterned by two consecutive thiol-ene reactions. In a first step, 200 µL of a solution of 1-dodecanethiol (10 vol%) in isopropanol was pipetted onto a modified glass slide. Then, a photomask was placed on top and the surface was irradiated with UV light for 2 min (16.0–17.0 mW cm\(^{-2}\)). For the second modification, 200 µL of a solution of 2-mercaptoethanol (10 vol%) a 1:1 solvent mixture of ethanol and water was pipetted onto the glass surface, which was then covered by a quartz glass plate. The surface was again irradiated with UV light for 2 min (16.0–17.0 mW cm\(^{-2}\)). Slides were rinsed thoroughly with isopropanol and dried after each modification step. An UVAcube 2000 from Dr. Hönle AG (Gräfelfing, Germany) was used for irradiation. The parts of the surface to become hydrophilic were modified with 2-mercaptoethanol while the parts of the surface to become oleophilic were modified with 1-dodecanethiol. Using this method, water patterns of various shapes and submillimeter resolution can be achieved (Figure S1). Chemicals were purchased from Sigma-Aldrich and used as received (Munich, Germany). Patterns were designed with the CAD software Rhinoceros 3D from Robert McNeel & Associates (Barcelona, Spain) and the respective photomask (chromium coated quartz glass) was fabricated by Rose Fotomasken (Bergisch-Gladbach, Germany).

Solvent confinement test

First the circle-shaped hydrophilic pattern was filled with 60 µL of water, which was dyed in blue. Then 20 µL of organic solvent were added in the middle of the pattern. To improve the visibility of the two phases, water was dyed with 10 w% of food blue ink from Dr. Oetker (Bielefeld, Germany) and the organic solvents were dyed with 10 w% of Oil Red O from Sigma Aldrich (Munich, Germany) to improve visibility of the phases.
Water-templated polymerization

A polymer precursor solution was prepared by dissolving lauryl acrylate (LA) in 1-nonanol in a mass ratio of 4:1. As a crosslinker, poly (propylene glycol) dimethacrylate (1 mol% relative to lauryl acrylate), the photoinitiator Irgacure 379 (4 wt% relative to lauryl acrylate), and Nile Red (0.036 wt% relative to the monomer) were added. The hydrophilic area of the pattern was filled with DI water. Then, the reaction mixture was poured into the hydrophobic surface area. The surface was then irradiated in the UV curing chamber UVAcube 2000 from Dr. Hönle AG (Gräfelfing, Germany) at a light intensity of 17-18 mW cm\(^{-2}\) for 3 minutes. The substrate was gently rinsed with 2-propanol to remove the water walls.

Methods

Confocal laser scanning microscopy (CLSM)

Water-organic solvent interface on a pattern was investigated using confocal microscopy imaging (Leica Confocal Microscope SPE.). The fluorescence was observed for water stained with Rhodamine B (excitation/emission ~553/627 nm, 0.33 mg/ml) and 1-nonanol or \(n\)-hexadecane stained with Nile Red (excitation/emission ~552/636 nm, 0.33 mg ml\(^{-1}\)). LiCl (100 mg ml\(^{-1}\)) was added to the aqueous phase to prevent evaporation.

Fluorescence Microscopy

Fluorescence light microscopy images of liquid wells were recorded using a Keyence BZ-9000 fluorescence microscope from Keyence Corporation (Osaka, Japan).

Interfacial Surface Tension Measurement

The interfacial tension \(\gamma_{ow}\) (1-nonanol-water) was determined via ring tensiometry using a K11 Tensiometer from Krüss (Hamburg, Germany). The correction factor was chosen as described by Huh & Mason.\(^{[1]}\) The measurement can be described in brief: A ring is deposited at the interface of two liquids and is then lifted. When the ring is not wetted by the interface
anymore, the force exerted onto the ring decreases. Since this force is a function of the interfacial tension, the interfacial tension can be determined.

**Raman microscopy**

Raman 2D microscopy was performed on a Bruker Senterra instrument from Bruker Optic (Ettlingen, Germany). Excitation was performed with a laser beam at 532 nm at 2 mW output power. Spectra were collected from 70 – 4450 cm⁻¹. The Raman map consisted of 108 individual spectra over a surface area of ca. 3 • 5 mm². A chemical map was obtained by integration of the characteristic OH-stretching vibration from 3700 to 3140 cm⁻¹ and the CH-stretching vibration from 3020 to 2780 cm⁻¹. To minimize evaporation of the aqueous compartment, LiCl was added (0.5 g mL⁻¹). To 60 µL of this solution 1 mg of phosphoric acid was added to serve as an internal reference.

**Phase-field model for multiphase wetting systems**

To model multidroplet wetting phenomena with \( N \) phases, \( N \in \mathbb{N} \), we introduce a vector-valued order parameter \( \varphi(x,t) = (\varphi_1(x,t), ..., \varphi_N(x,t))^T \), where \( \varphi_i(x,t) \), \( i \in \{1, ..., N\} \), describes the state of the phase \( i \) at time \( t \) and position \( x \). The order parameter \( \varphi_i(x,t) \) varies continuously between two states, \( \varphi_i(x,t) = 0 \) (in gas) and \( \varphi_i(x,t) = 1 \) (in liquid). The phase-field model is a kind of diffuse interface model and based on the Ginzburg–Landau energy density functional, which is formulated as:

\[
F(\varphi) = \int_V \left( \varepsilon a(\varphi, \nabla \varphi) + \frac{1}{\varepsilon} w(\varphi) + g(\varphi) \right) dV + \int_S f_w(\varphi) dS,
\]

where \( V \) is the spatial domain, \( S \) indicates the solid-fluid boundary, and \( \varepsilon \) is related to the thickness of the diffuse interface. The first term \( a(\varphi, \nabla \varphi) \) is the gradient energy density and reads \( a(\varphi, \nabla \varphi) = \sum_{i<j} \gamma_{ij} (\varphi_i \nabla \varphi_j - \varphi_j \nabla \varphi_i)^2 \), with \( \gamma_{ij} \) denoting the surface/interfacial energy density of the \( ij \) phase boundary. The second term \( w(\varphi) \) denotes a multiobstacle potential of the form:
Here, the higher order term \( \sum_{i<j<k} Y_{ijk} \varphi_i \varphi_j \varphi_k \) is used to suppress artificial third phase contributions along binary phase boundaries.\(^1\) The third term \( g(\varphi) \) is formulated to ensure the volume conservation of respective phases.\(^2\) The last term \( f_w(\varphi) \) depicts the wall energy density, which constrains the Young’s wetting angles at the three-phase contact line on the substrate.

The evolution of the phase order parameter \( \varphi_i(\mathbf{x}, t) \) is such as to minimize the free energy functional:

\[
\tau \varepsilon \partial_t \varphi_i = \varepsilon \left( \nabla \cdot a_{\varphi \varphi_i} (\varphi, \nabla \varphi) - a_{\varphi \varphi_i} (\varphi, \nabla \varphi) \right) - \frac{1}{\varepsilon} w_{\varphi \varphi_i} (\varphi) - g_{\varphi \varphi_i} (\varphi) - \lambda_1
\]

in \( V \) with the natural boundary condition

\[-\varepsilon a_{\varphi \varphi_i} (\varphi, \nabla \varphi) \cdot \mathbf{n} - f_w(\varphi_i) - \lambda_2 = 0\]

on \( S \). Here, \( \mathbf{n} \) is the normal vector of the substrate and \( \tau \) is a pseudo time variable. This pseudo time relaxation is used to effectively find the equilibrium state following the gradient descent path. The notations \( a(\varphi, \nabla \varphi), w(\varphi), g(\varphi), \) and \( f_w(\varphi) \) describe the partial derivatives \( \partial / \partial \varphi_i \) and \( \partial / \partial \varphi_i \) of the functions \( a(\varphi, \nabla \varphi), w(\varphi), g(\varphi), \) and \( f_w(\varphi) \), respectively. \( \lambda_1 \) and \( \lambda_2 \) are Lagrange multipliers to ensure the constraint \( \sum_{i=1}^N \varphi_i (\mathbf{x}, t) = 1 \) in the domain \( V \) and on the substrate \( S \), respectively. The Lagrange multipliers \( \lambda_1 \) and \( \lambda_2 \) are found to read:

\[
\lambda_1 = \frac{1}{N} \sum_{i=1}^N \left( \varepsilon \left( \nabla \cdot a_{\varphi \varphi_i} (\varphi, \nabla \varphi) - a_{\varphi \varphi_i} (\varphi, \nabla \varphi) \right) - \frac{1}{\varepsilon} w_{\varphi \varphi_i} (\varphi) - g_{\varphi \varphi_i} (\varphi) \right),
\]

\[
\lambda_2 = \frac{1}{N} \sum_{i=1}^N \left( -\varepsilon a_{\varphi \varphi_i} (\varphi, \nabla \varphi) \cdot \mathbf{n} - f_w(\varphi_i) \right).
\]

**Water contact angle measurements**

Measurements were performed with a DSA 25 contact angle goniometer from Krüss (Hamburg, Germany) using the sessile drop technique. Apparent contact angles were determined by depositing 5 \( \mu L \) droplets of 1-nonanol, \( n \)-hexadecane, or water onto the surface. The droplet shape was fitted with a Young-Laplace fit. Apparent contact angles were determined on
surfaces coated completely with either the hydrophobic, the hydrophilic, or the omniphobic surface modification.

Table S1. Apparent contact angles of 1-nonanol and \( n \)-hexadecane for different parts of the patterned surface.

| Area of the pattern              | Contact Angle ['] |
|----------------------------------|-------------------|
|                                  | water             | \( n \)-hexadecane | 1-nonanol  |
| Hydrophilic (2-mercaptoethanol)  | 0                 | 0                   | 0          |
| Hydrophobic (1-dodecanethiol)    | 157 ±7            | 0                   | 0          |
| Omniphobic (PFDT)\( ^a \)        | 167 ± 3           | 55 ± 8              | 70 ± 7     |

\( ^a \)1H,1H,2H,2H-perfluorodecanethiol

Table S2. Physical properties of the solvents used in this work.

| Solvent                   | \( \gamma_{oa} \) [mN m\(^{-1}\)] (20 °C) | Dielectric constant\[2\] (20 °C) | Boiling Point\[3\] [°C] | Density (20°C) [g ml\(^{-1}\)] | Water solubility (20°C) [g L\(^{-1}\)] |
|---------------------------|---------------------------------------------|----------------------------------|-------------------------|-------------------------------|----------------------------------------|
| ethanol                   | 22.1                                        | 24.5                             | 78.3                    | 0.789                         | Miscible                               |
| ethyl acetate             | 23.2                                        | 6.02                             | 77.1                    | 0.902                         | 83                                     |
| 1-butanol                 | 24.2                                        | 17.8                             | 117.7                   | 0.81                          | 73\(^a\)                               |
| 1-nonanol                 | 28.0                                        | 8.83                             | 215.0                   | 0.827                         | 0.3                                    |
| 1-decanol                 | 28.8                                        | 7.81                             | 230.0                   | 0.830                         | 0.04                                   |
| tetrahydrofuran           | 26.4                                        | 7.58                             | 66.0                    | 0.889                         | Miscible                               |
| dichloromethane           | 26.5                                        | 9.08                             | 39.8                    | 1.325                         | 17.5\(^a\)                             |
| \( n \)-hexadecane        | 26.95                                       | 2.05                             | 287.0                   | 0.773                         | 2.3 \times 10^-5                       |
| toluene                   | 28.4                                        | 2.44                             | 110.6                   | 0.865                         | 5.2 \times 10^-1                       |
| N,N-dimethylformamide     | 37.10                                       | 36.7                             | 152                     | 0.95                          | Miscible                               |
| \( n \)-hexane            | 18.43                                       | 1.89                             | 68.7                    | 0.672                         | 9.5                                    |
| \( n \)-octane            | 21.62                                       | 1.95                             | 125.0                   | 0.7                           | 7 \times 10^-4                         |
| iso-octane                | 18.77                                       | 1.94                             | 99.0                    | 0.69                          | -                                      |

\(^a\)25 °C

Table S3. Physical properties of the methacrylates used in this work.

| Methacrylate              | Solubility in water at 25 °C [g ml\(^{-1}\)] | Density at 25 °C [g ml\(^{-1}\)] |
|---------------------------|-----------------------------------------------|-----------------------------------|
| Butyl methacrylate        | 0.08                                          | 0.894                             |
| 2,2,2-Trifluoroethyl methacrylate | 0.0029                                   | 1.181                             |
| Lauryl methacrylate       | 4 \times 10^-8                               | 0.868                             |
| 1H,1H,2H,2H-Perfluorodecyl methacrylate | 0                                    | 1.59                              |
Figure S1. Optical microscopy images of hydrophilic surface areas filled with water. Water was dyed with Rose Bengal. The patterns display flawless round shapes, edges, and borders on the submillimeter scale. Scale-bars are 1 mm. The hydrophilic areas are functionalized with 2-mercaptoethanol, whereas the hydrophobic surface areas are modified with 1-dodecanethiol.

Figure S2. Droplet shapes for water, \textit{n}-hexadecane and 1-nonanol on surfaces modified with (i-iii) 1-dodecanethiol and (iv-vi) 1\textit{H},1\textit{H},2\textit{H},2\textit{H}-perfluorodecanethiol. Determined water contact angles are tabulated Table S1. Scale-bars are 1 mm.
Figure S3. Raman mapping of the liquid-liquid interface between an organic liquid trapped in a ring of water. (A) Schematic illustration and chemical composition of the analyzed patterns. (B) Raman mapping results with 1-nonanol as organic core. Raman spectra (i) obtained on different spots (ii) around the liquid-liquid interface. The spectra measured on spots in the 1-nonanol phase (orange, averaged) can be clearly distinguished from those spectra measured on spots in the aqueous phase (blue, averaged). Integration and color coding of the OH-stretching scattering intensity yields a chemical map (iii). (C) Raman mapping results with n-hexadecane as organic core. Raman spectra (i) obtained on different spots (ii) around the
liquid-liquid interface. The spectra measured on spots in the $n$-hexadecane phase (orange, averaged) can be clearly distinguished from those spectra measured on spots in the aqueous phase (blue, averaged) or outside of the liquid-liquid pattern, where no liquid was present (green, averaged). Integration and color coding of the OH-stretching scattering intensity yields a chemical map (iii). After the measurement, the liquid-liquid compartment with $n$-hexadecane as core was destroyed, presumably due to the Raman laser induced heat and the movement of the sample platform. For this reason, the chemical map (iii) of the liquid-liquid interface between water and $n$-hexadecane appears to be distorted.
Figure S4. Confinement test for different organic solvents (red) with a ring of water (blue). Scale-bar: 5 mm. The volume of water is 60 µL and the volume of the organic liquid is 20 µL.

Figure S5. Water droplets confined within a water-barrier mediated by the organic liquid in the core. Both the droplet and the ring consist of water. Water droplets were dyed with blue ink to identify the contact time, which was defined as the time required for a water droplet to merge with the water wall after getting in contact with each other. The organic liquids within the water-ring shown were (i) butyl methacrylate (BMA) and (ii) 1\textit{H},1\textit{H},2\textit{H},2\textit{H}-perfluorodecyl methacrylate (PFDM). Scale-bar: 5 mm. (iii) Average contact time of droplets with the water-ring in dependence of the different methacrylate added into the liquid well. The contact time increased from butyl methacrylate (-C\textsubscript{4}H\textsubscript{9}), 2,2,2-trifluoroethyl methacrylate (-CH\textsubscript{2}CF\textsubscript{3}), dodecyl methacrylate (-C\textsubscript{12}H\textsubscript{25}), to 1\textit{H},1\textit{H},2\textit{H},2\textit{H}-perfluorodecyl methacrylate (-CH\textsubscript{2}H\textsubscript{4}C\textsubscript{8}F\textsubscript{17}), respectively. Error bars are standard deviations (n=3).
Figure S6. (A) Height of a ring-shaped water wall as a function of the water volume. The maximum height ($h_{\text{max}}$) of the water wall was 1.95 mm for 210 µL of water. The decrease in the height of the water wall for a volume of 220 µL is due to an anisotropic distribution of the water within the ring, thus no meaningful value for the height can be derived anymore. Error bars are standard deviations (n=3). (B) Height of ring-shaped water walls as a function of the 1-decanol volume. An initial decrease of the height of the water wall can be observed, presumably due to the interaction of water and 1-decanol. Addition of 1-decanol up to a volume of 60 µL increased the height of the water wall, due to the increase in the height of the 1-decanol trapped in the liquid well. Error bars are standard deviations (n=3). (C) Height measurements of water walls via image analysis for (i) 100 µL and (ii) 180 µL. (iii) Height measurement of 1-
decanol (60 µL water, 330 µL 1-decanol). As in the case of 1-nonanol, the meniscus of the 1-decanol is above that of the water wall (1.97 mm). The height of 1-decanol in the liquid well exceeds the capillary height of 1-decanol (1.83 mm) as calculated from its density (0.83 g mL⁻¹), surface tension (28.5 mN m⁻¹) and the gravitational acceleration g (9.81 m s⁻²) according to the expression \( \lambda_c = \left(\frac{\gamma_{ao}}{\rho_w g}\right)^{1/2} \). A water contact angle measurement device was used to capture the profile images. The dimensions of the image were calibrated onto a needle of known thickness. Scale-bars: 2 mm.
**Figure S7.** Picture (top view) of a ring-shaped water wall (60 µL) confining 1-nonanol (20 µL) after being cut by a knife multiple times. Some 1-nonanol was transported outside of the liquid well as a result of the cutting and formed droplets. The shape of the 1-nonanol droplets still indicates the direction of cutting. The structural integrity and confining ability of the water wall remained intact. Water was dyed blue to improve the visibility. Scale-bar: 3 mm.

**Figure S8.** Liquid-liquid extraction experiment. A solution of methylene blue (0.1 vol%) and Oil Red O (0.1 vol%) in 1-decanol (30 µL) was deposited inside the water wall (100 µL). Over time, methylene blue diffused into the aqueous phase, whereas Oil Red O remained in the organic phase.
Figure S9. Comparison of the influence of the organic liquid on the hydrophobic surface area on the dimensions of the organic and aqueous phase in a ‘matryoshka’ pattern. The dimension of the photomask used for the hydrophilic-hydrophobic patterning of the surface can be seen on the left. For the inner and outer water barrier, 20 and 60 µL of water were added, respectively. The inner and outer organic layer were brought in contact with 8 and 40 µL of either \(n\)-hexadecane or 1-nonanol, respectively. Apparently, \(n\)-hexadecane takes up a larger share of the surface area relative to the total surface area covered by liquids than 1-nonanol. Both 1-nonanol and \(n\)-hexadecane were dyed with 0.5 mg ml\(^{-1}\) Oil Red O to improve the visibility of the boundaries.

Total surface area (\(d = 22 \text{ mm}\)): \(380.1 \text{ mm}^2 (100\%)\)

Surface area covered by \(n\)-hexadecane: \(148.5 \text{ mm}^2 + 30.2 \text{ mm}^2 = 178.7 \text{ mm}^2 (47\%)\).

Surface area covered by 1-nonanol: \(124.7 \text{ mm}^2 + 14.5 \text{ mm}^2 = 139.2 \text{ mm}^2 (37\%)\)
Figure S10. Images of 1-nonanol droplets (dyed with Oil Red O) in petri dishes filled with DI water. For all volumes tested (10 - 50 µL), 1-nonanol formed droplets which did not spread over the surface of the water. The same result was obtained for pure droplets of 1-nonanol.
Figure S11. Pictures of the products of the water-templated polymerization taken at an angle of 45°. After the polymerization, the water barriers were washed away, leaving a free-standing polymer in the form of a film with a thickness of 150-200 µm. Scale-bars: 5 mm.

Video S1. Formation of a water-confined organic liquid on a glass slide with a hydrophobic-hydrophilic core-shell patterning. Upon addition of water, a circle forms on the hydrophilic part of the substrate. Then, 1-nonanol (dyed red) was added in between the water walls. The video speed is accelerated 5x.

Video S2. Comparison of the spreading behavior of dyed- and pure solvents. Drops of 1-nonanol or \( n \)-hexadecane with and without Oil Red O (0.8 mol L\(^{-1}\)) are dropped onto the surface of water in a petri dish.

Video S3. Cutting of a liquid well with a knife. The organic solvent is 1-nonanol. The ring-shaped water wall water contains a blue dye.

Video S4. Extraction experiment in a liquid well. The organic phase consists of 0.1 vol% methylene blue (water soluble) and 0.1 vol% Oil Red O (not water soluble) in 30 µL 1-decanol. The ring-shaped water wall consists of 100 µL water.

Video S5. Agitation experiment of a liquid well. Parts of the liquid wall recede and reform upon mechanical agitation.

Video S6. Water droplets confined within the liquid well. The hydrophobic liquids in the core are methacrylates with different ester group chain lengths. The ring-shaped water wall consists of 60 µL water. Water droplets were dyed blue.
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