Supporting Information:

“Encoding complex wettability patterns in chemically functionalized 3D photonic crystals”

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Movie M1: A live demonstration of a strip being immersed in 80% ethanol (aq, vol), displaying one pattern (Roman numeral “VIII”), which disappears upon air drying. It is then immersed in pure ethanol, displaying a different pattern (Roman numeral “III”), which again disappears upon air drying.

1. Materials and Methods:

IOF Synthesis:

Large-area, crack-free inverse-opal films (IOFs) were fabricated according to the procedure detailed in Ref. S1. Briefly, substrates of clean Si or glass were suspended vertically in an aqueous mixture containing 280nm diameter PMMA spheres and an acidic solution of tetraethyl orthosilicate (TEOS, Sigma-Aldrich). The temperature was fixed at 65C, allowing the solvent to evaporate slowly over a period of 1-3 days and depositing a highly ordered, crack-free PMMA colloidal FCC crystal with silica filling the interstitial sites. The organic species (PMMA colloids) were removed by heat treatment in air at 500°C for 5-8h leaving behind a porous inverse opal SiO₂ film.

Patterning of Surface Chemistry in IOFs:

The IOFs were exposed to vapors of 1H,1H,2H,2H-perfluorooctyl)trichlorosilane (13FS, Gelest, Inc.) in a vacuum chamber for 24h, followed by a 10 min bake at 150C. Polydimethylsiloxane (PDMS) masks (2-5mm-thick) were prepared by pouring a 10:1 (wt) mixture of PDMS resin and cross-linking agent (Sylgard 184, Dow Corning) into a clean, empty tissue culture dish and curing for 3-5h at 70C. Patterns were carved in freshly cured slabs using pre-shaped blades (e.g. cookie-cutter) or with a scalpel or razor-blade, and masks were discarded after one use. For IOFs containing *m* complex patterns (e.g. letters) with *n* different functionalities on an ROH background, the surface chemistries were first defined in a simple stripe pattern, where *m* large stripes to contain the final patterns of a given functionality were used. This allowed us to clamp large PDMS masks directly to the sample (with no overhanging cover slip) and ensuring that exposure to the oxygen plasma was the same for all mask heights and shapes. The mask could be peeled off after the exposure without damaging the structure. In each iteration of the patterning (see Fig. 1D, main text), the sample, with a PDMS mask clamped directly over the desired region is exposed to oxygen plasma (Diener Electric GmbH Femto-A plasma cleaner, O₂ flow rate 5-10sccm) for 3-10min. In the second step, the mask was removed and the sample was exposed to vapors of a different alkylchlorosilane, either n-decyltrichlorosilane (DEC, Gelest, Inc.), 3,3,3-trifluoropropyltrichlorosilane (3FS, Alfa Aesar) (each for 24h) or chlorotrimethylsilane (TMS, Alfa Aesar) (20 min). Exposure was done under vacuum for all alkylchlorosilane depositions except for highly volatile TMS, which was done at 1atm. All exposures were followed by a 10 min bake at 150C. In all experiments, we applied our functionalities in order of increasing wettability (13FS→DEC→3FS→TMS). After large regions containing each surface chemistry in the desired final pattern have been defined, the background was re-activated by one final exposure to oxygen plasma. To ensure good contact and a well-defined pattern, the PDMS masks (e.g. letters) were held under uniform pressure from a glass cover-slip. The sample was exposed in this state to oxygen plasma for 10-30min (5-10sccm) to impart ROH functionality on the background.

PDMS-filling:

For interface characterization and for the fabrication of visible fluidic channels, a IOF with regions of 13FS and ROH surface chemistries was fabricated as described above. 10:1 PDMS resin:cross-linker (Sylgard 184, Dow Corning) was poured over the sample until it was submerged. Penetration into the ROH pores was accelerated by placing IOF immersed in PDMS precursors under vacuum for 2-3h before curing for 2-5h at 70C. The vacuum step also served to remove any trapped bubbles. After curing the PDMS overlayer was peeled off manually, and was found to break naturally at the top-surface of the IOF in infiltrated regions.

2. Interface Characterization:

Interfaces were visualized by selective infiltration of PDMS resin then curing (see Materials and Methods). Interfaces were characterized by optical and scanning electron microscopy (JEOL, Zeiss) as well as via scanning optical spectroscopy (see Spectral Measurements). Figure S1 shows optical micrographs, spectral scans and SEM images of an interface visualized by selective infiltration of PDMS into the PC. All measurements show the presence of a transition, partially filled region, having a width varying from ~5-20 μm , separating the completely filled region and the completely unfilled region.

References:

S1. B.D. Hatton, L. Mishchenko, S. Davis, K.H. Sandhage, J. Aizenberg, Assembly of large-area, highly ordered, crack-free inverse opals, *Proc. Natl. Acad. Sci., U.S.A.* **107**, 10354-10359 (2010).

Figure S1. Optical characterization of a wetting interface visualized by the selective infiltration of PDMS into ROH-functionalized regions. Regions functionalized by 13FS were not infiltrated upon immersion in PDMS prepolymer. **A:** Optical micrograph of the interface with complete infiltration on the right. **B:** Cross-sectional SEM image of an interface corner, showing the boundary between regions filled with PDMS (ROH) and remaining empty (13FS). **C:** Scanning optical spectroscopy image at 494nm, clearly showing three distinct regions – the completely filled region, the partially filled transition region, and the completely empty region. **D-F:** A few representative spectra taken from points in each of the three regions showing the transition from a more pronounced reflection peak at ~530 nm in the non-infiltrated regions to a multi-peak thin-film interference pattern in the regions penetrated by PDMS, which is well index-matched with our sol-gel silica.