Electronic Supplementary Information

Photo-tuning of highly selective wetting in inverse opals

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Fabrication of defect-free inverse opals

Large-area crack-free inverse opal films (IOFs) were fabricated as described in Ref. [S1,S2]. Briefly, monodispersed aqueous suspensions of polymethylmethacrylate (PMMA) microspheres (d~300 nm, ~3% standard deviation) were synthesized by surfactant-free emulsion polymerization [S1–S3]. Suspensions were cleaned using dialysis. Glass slides or Si strips, cleaned in acid piranha solution (3:1 concentrated sulfuric acid/30% hydrogen peroxide), were suspended in small vials containing 20 mL of deionized water, 0.1–0.5 mL of the colloidal suspension and 0.095–1.5 mL of a pre-hydrolyzed solution of tetraethyl orthosilicate (TEOS, Sigma-Aldrich) prepared as described in Ref. [S1]. The solution was left to evaporate in an oven held at 65 °C for 1-2 days, depositing a close-packed film of the PMMA spheres with SiO_2 from condensed TEOS filling the interstitial sites. After deposition, films were fired at 500 °C for 5 h to remove the polymer template and the resulting IOFs were cleaned in acid-piranha solution for 4 h.

Functionalization of inverse opals with chromophore-containing polyelectrolyte layers

Cleaned IOFs were immersed in a 2% w/v solution of (3-aminopropyl)trimethoxysilane (APTMS) in acetone for 30 minutes, followed by flushing with an excess of DI water before drying. The functionalized IOFs were then rinsed with DI water, followed by curing/drying in a 110 °C oven for 30 minutes. This protocol imparts a positive charge throughout the IOF when immersed in water, via protonation of the amine. The IOF was then immersed in a saturated (~10^{-2} M) solution of poly(Disperse Red 1 acrylate-*co*-acrylic acid) (p(DR1A-*co*-AA); 20 mol% Disperse Red 1 acrylate, determined by ^{1}H NMR [S4], see Fig. S1) dissolved in a 1:1 mixture of dimethylformamide (DMF) and water. This solvent blend serves the dual purpose of ensuring adequate polymer solubility, as well as completely wetting the IOF and allowing uniform polymer deposition. The IOF was immersed in the polymer solution for at least 8 hours to allow complete coating of the complex inverse-opal geometry, followed by two iterations of immersion for 1 hour in fresh DMF/water (1:1) mixtures to allow diffusion of unbound polymer from the structure.

Light irradiation, optical and wetting characterization

After functionalization, before and between uses, samples were stored at room temperature and away from ambient light in sealed drawers. Wetting response was characterized visually initially and after light exposure by imaging with a digital camera (Canon Rebel EOS) in air and immersed in water-ethanol mixtures ranging in 2.5% increments of ethanol concentration from 0% ethanol to 25% ethanol (v/v). Samples were imaged while submerged in 10 mL of liquid contained in a small dish. Samples were introduced to the liquids in the same order (starting with pure water and increasing ethanol concentration) and were dried under an air gun between successive immersions. All images were taken at a similar angle under ambient lighting conditions.

UV irradiation was performed by placing the sample directly at the end of a gooseneck fibre (1 cm diameter) connected to a UV lamp (Dymax®, 280–450 nm). A shutter attached to a timer was used to control exposure time. Lamp power was measured by placing a handheld power meter (Newport Co.) at the location of the sample. Visible irradiation was performed by placing the sample in front of the collimated output of a frequency-doubled Nd:YAG laser (Coherent, 532 nm, 73 mW). Microscope images and reflection spectra were recorded on a stereomicroscope (Leica) coupled to a fibre-based USB spectrometer (Ocean Optics).

Characterization of flat surfaces

Flat glass microscope slides (Fisher) were cleaned and functionalized with APTMS and then p(DR1A-*co*-AA) in the same manner as the IOFs. Water contact angles (advancing and receding) were measured on a goniometer (KSV) initially and following each flood exposure under the UV lamp. After each set of contact angle measurements and before the next UV exposure, samples were flushed with water to homogenize any possible water uptake in the film.

Supplementary Figures:

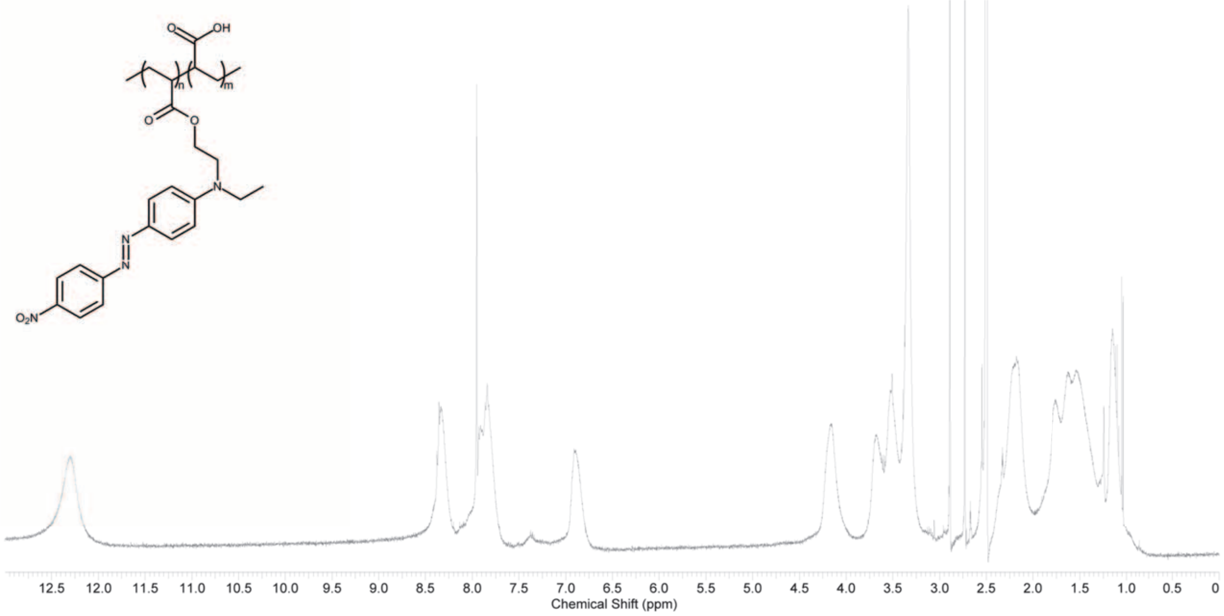

Figure S1. ^{1}H NMR spectrum of poly(Disperse Red 1 acrylate-*co*-acrylic acid) in DMSO-d$_6$. Broad features from 1.5–2.2 ppm correspond to the acrylate backbone; peaks at 1.14 and 3.5–4.2 ppm represent the alkyl groups bound to the amine in the DR1 chromophore. The aromatic features fall in the region of 6.9–8.4 ppm, and the broad feature at 12.3 ppm corresponds to the acrylic acid protons. Sharp features correspond to solvent impurities trapped in the polymer matrix: 1.02 and 1.04 (diisopropyl ether), 2.50 (residual DMSO), 2.73, 2.89, 7.95 (N,N-dimethylformamide), and 3.33 (water).

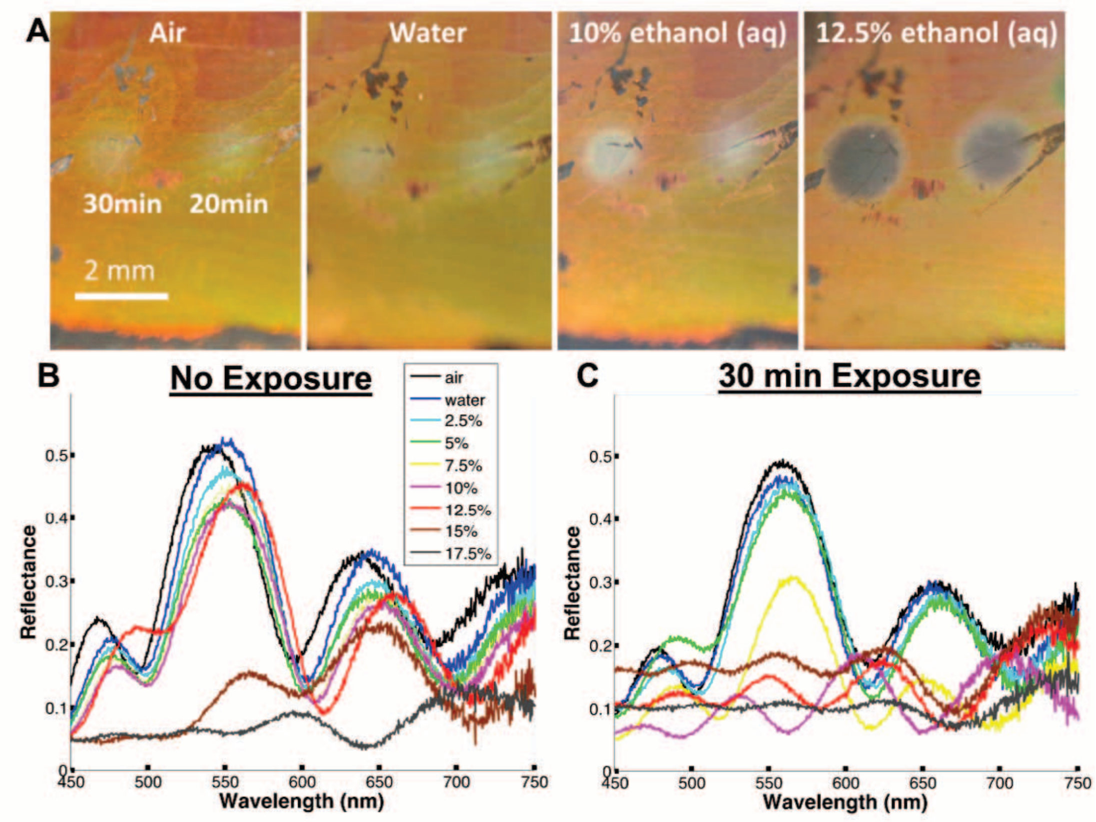

Figure S2. (A) Photographs of a p(DR1A-*co*-AA)-functionalized IOF after exposure of two regions for 20 min and 30 min to a collimated laser spot (532 nm, 73 mW, ~1 mm in diameter), showing colour change due to photobleaching in air and increased wettability in water-ethanol mixtures. (B,C) Reflectance spectra in water and various ethanol-water mixtures (ethanol concentration, v/v, listed in the legend) of two regions of the IOF, one taken in an unexposed region (B) and the other taken at the centre of the spot having had 30 min of laser exposure (C). Both regions have the same thickness (12 layers).

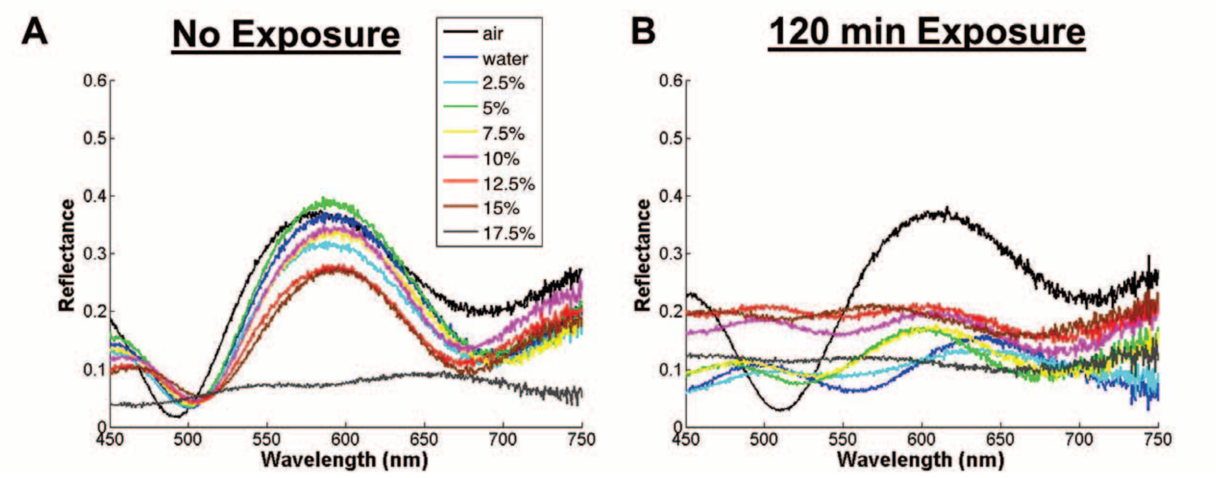

Figure S3. Reflectance spectra of a p(DR1A-*co*-AA)-functionalized IOF (7 layers) in water and various ethanol-water mixtures (ethanol concentration, v/v, indicated in legend) in an unexposed spot (A) and at the centre of the laser spot (532 nm, 73 mW, ~1 mm in diameter, collimated) after irradiation for 120 min (B). These spectra show that after sufficient exposure, wetting in water can be achieved, just as was observed for UV-induced photobleaching.

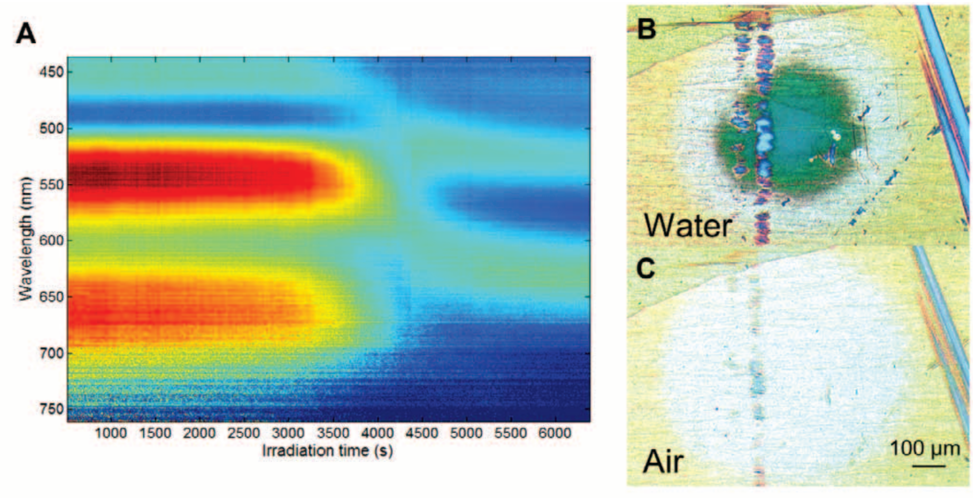

Figure S4. *In situ* photo-induced wetting through exposure of a p(DR1A-*co*-AA)-functionalized IOF to visible light while submerged in water. The IOF, submerged in water, was placed under illumination from a 75 W Xenon lamp (LEP Ltd.) under a microscope objective (1000x magnification) and the reflection spectrum was continuously monitored to track changes in wetting behavior. (A) Temporal evolution of the reflection spectrum showing the onset of wetting (~4000 s). (B,C) Images of the IOF taken afterwards while still in water (B) and then after drying (C), showing the spatial correlation between the photobleached region (indicated by the bright spot in C) and the wetted region (dark spot in B).

References:

S1. Hatton, B.; Mishchenko, L.; Davis, S.; Sandhage, K. H.; Aizenberg, J. *Proc. Nat.Acad. Sci. U.S.A.,* **2010**, *107*, 10354–10359.

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S4. Ahmad, N. M.; Saqib, M.; Barrett, C. J. *Journal of Macromolecular Science, Part A* **2010**, *47*, 534-544.