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Supporting Information

Patterned Superomniphobic–Superomniphilic Surfaces: Templates for Site-Selective Self-Assembly**

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Section 1. Experimental methods

Electrospinning and spin-coating: 10 mg mL^{-1} solutions of 50 wt% 1H,1H,2H,2H-heptadecafluorodecyl polyhedral oligomeric silsequioxane (fluorodecyl POSS)[1] + poly(methylmethacrylate) (PMMA, M_w ~ 35,000, obtained from Scientific Polymer Products) were prepared in 95:5 vol:vol solvent mixture of Ashakilin AK-225 (Asahi Glass Co.):Dimethyl Formamide (Fisher Scientific). The solutions were electrospun onto silicon wafers using a custom-built setup, at flow rate, voltage and plate-to-plate distance of 0.03 mL min^{-1}, 15 kV and 25 cm, respectively. From Figure 1a in the main manuscript, we obtained the average size of the electrospun beads, $2R$ = 13.4 μm. We used equation (1) in the main manuscript, in conjunction with contact angle measurements (see SI section 3), to estimate the spacing ratio D^* = 15.9. Non-textured surfaces were prepared by spin-coating (Specialty Coating Systems Spincoater G3P–8) 10 mg mL^{-1} solutions of 50 wt% fluorodecyl POSS + PMMA in Ashakilin AK-225 on silicon wafers at 1500 RPM for 30 s. We used the Owens and Wendt approach[2] to estimate the solid surface energy.

Patterning with O$_2$ plasma treatment: The electrospun superomniphobic surfaces were exposed to O$_2$ plasma (Plasmatherm 790) at single bias RF source power of 100 Watt and a pressure of 10^{-2} Torr for 5 min. Stainless steel perforated mask (McMaster-Carr) with hole diameters of 840 μm and 150 μm and center to center spacings of 1400 μm and 280 μm respectively were used to obtain superomniphobic surfaces patterned with superomniphilic domains. We have also developed a novel photoresist mask transfer method (see supporting information section 5) to obtain superomniphobic surfaces patterned with superomniphilic domains of different shapes and sizes.

X-ray photoelectron spectroscopy (XPS): XPS analysis was conducted using a Kratos Axis Ultra X-ray photoelectron spectrometer. Monochromatic Al-Kα X-ray source was operated at 15 kV and 10 mA. Photoelectrons were collected at a takeoff angle of ~ 65° relative to the

sample surface. Wide-scan survey spectra were acquired at an analyzer pass energy of 160 eV and a step size of 1 eV. O 1s, F 1s and C 1s high-resolution spectra were collected at an analyzer pass energy of 60 eV and a step size of 1 eV. The peaks in the high-resolution C 1s spectra were indexed by comparing the binding energy at the peak maximum with standard spectra available for PMMA and poly(vinylidene fluoride).[3]

Contact angle measurements: The contact angle measurements were conducted using a Ramé-Hart 200-F1 goniometer. All contact angles reported in this work were measured by advancing or receding a small volume of liquid (~ 2 μL) onto the surface using a 2 mL micrometer syringe (Gilmont). At least three measurements were performed on each substrate. Typical error in measurements was ±2°.

Microscopy: The surfaces were imaged using a Hitachi SU8000 ultra-high resolution scanning electron microscope (SEM) at 5 kV and an Olympus BX 51 fluorescent microscope.

Fluorescent microsphere dispersions and polymer solutions: UV fluorescent red and green polyethylene microspheres (Cospheric LLC) of diameter 10-45 μm were dispersed in heptane and water, respectively, at 25 mg mL^{-1} using a vortexer. 50 mg mL^{-1} solution of poly(isobutylene) (PIB, M_w ~ 400,000, obtained from Scientific Polymer Products) in heptane containing a red fluorescent dye and 50 mg mL^{-1} solution of poly(vinyl pyrrolidone) (PVP, M_w ~ 1,300,000, obtained from Sigma Aldrich) in water containing a green fluorescent dye were prepared using a vortexer.

Section 2. Estimation of solid surface energy

We used the Owens and Wendt approach[2] to estimate the surface energy γ_{sv} of the 50 wt% fluorodecyl POSS + PMMA blend surface before and after O$_2$ plasma treatment. We used heptane (γ_{lv} = 20.1 mN m^{-1}) as the non-polar liquid to estimate the dispersive component of the solid surface energy γ_{sv}^d and water (γ_{lv}^d = 21.1 mN m^{-1} and γ_{lv}^p = 51.0 mN

m^{-1}) as the polar liquid to estimate the polar component of the solid surface energy γ_{sv}^p. The solid surface energy values were estimated by using the advancing contact angles measured on spin-coated surfaces before and after O$_2$ plasma treatment (Table S1). The calculated surface energies are reported in Table S1.

Table S1. Estimated solid surface energies for 50 wt% fluorodecyl POSS + PMMA blend before and after O$_2$ plasma treatment.

	Surface energy (mN m^{-1})		
	Polar component (γ_{sv}^p)	Dispersive component (γ_{sv}^d)	Total ($\gamma_{sv} = \gamma_{sv}^p + \gamma_{sv}^d$)
Before O$_2$ plasma treatment	11.08	0.02	11.1
After O$_2$ plasma treatment	19.8	48.0	67.8

Section 3. Table of contact angles

Table S2. Contact angles on electrospun surfaces composed of 50 wt% fluorodecyl POSS + PMMA before and after O$_2$ plasma treatment.

	Electrospun surface					
	Water		Heptane		Methanol	
	θ_{adv}^*	θ_{rec}^*	θ_{adv}^*	θ_{rec}^*	θ_{adv}^*	θ_{rec}^*
Before O$_2$ plasma treatment	162°	160°	151°	141°	153°	145°
After O$_2$ plasma treatment	0°	0°	0°	0°	0°	0°

Table S3. Contact angles on spin-coated 50 wt% fluorodecyl POSS + PMMA surfaces before and after O$_2$ plasma treatment.

	Spin-coated surface					
	Water		Heptane		Methanol	
	θ_{adv}^*	θ_{rec}^*	θ_{adv}^*	θ_{rec}^*	θ_{adv}^*	θ_{rec}^*
Before O$_2$ plasma treatment	123°	110°	61°	38°	64°	43°
After O$_2$ plasma treatment	20°	0°	10°	0°	11°	0°

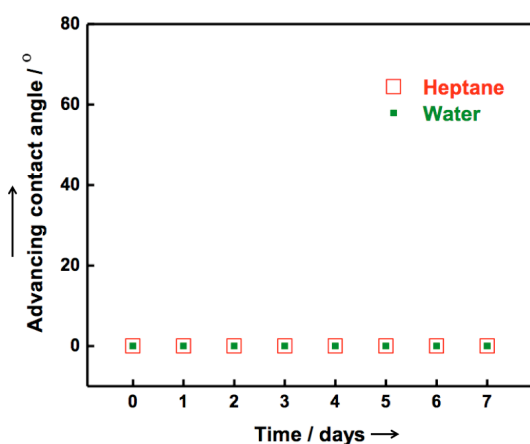## Section 4. Stability of superomniphilic surfaces

Figure S1. The apparent advancing contact angles of water and heptane on the superomniphilic surface at various times after O_2 plasma treatment.

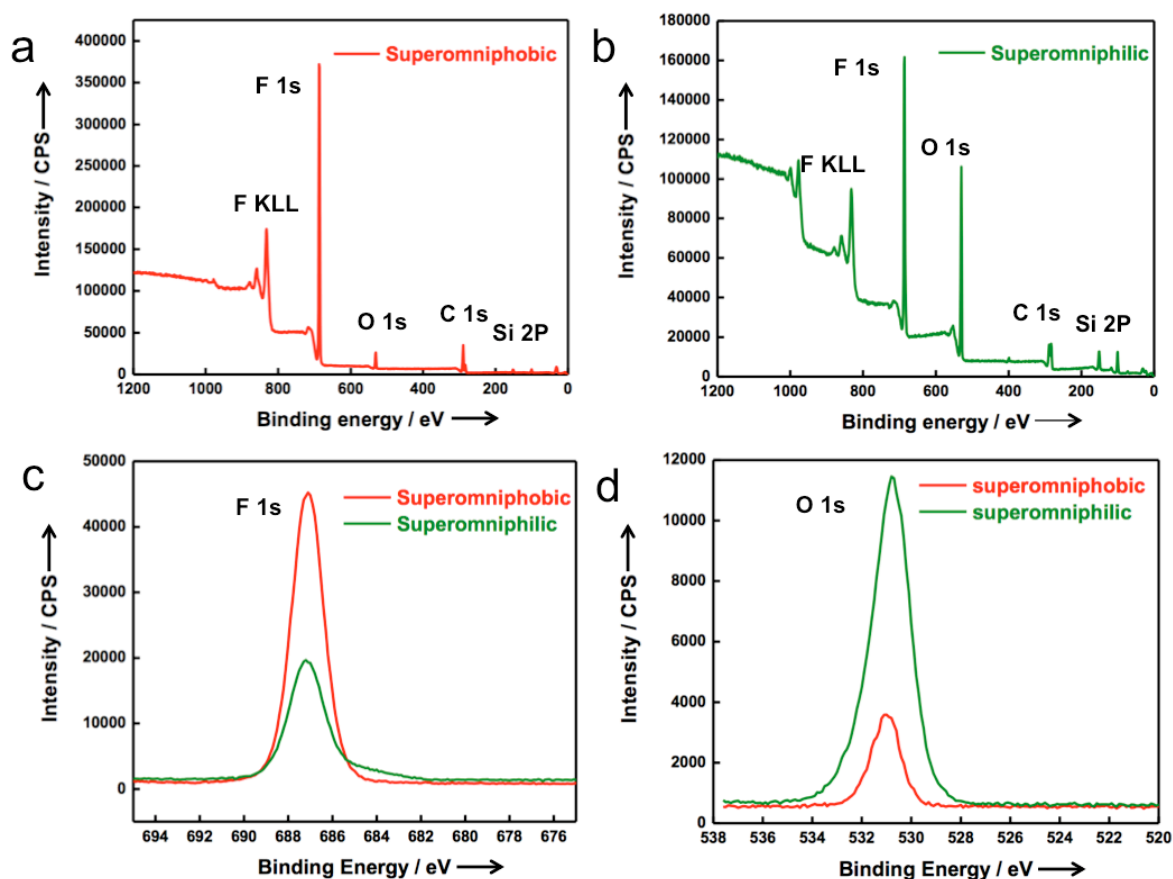## Section 5. XPS data for superomniphobic and superomniphilic surfaces

Figure S2. a) and b) Survey spectra for a superomniphobic surface and a superomniphilic surface, respectively. The characteristic peaks for carbon, fluorine, oxygen and silicon within the spectra are labeled. c) and d) High-resolution fluorine 1s spectra and oxygen 1s spectra,

respectively. These spectra compare the corresponding peak intensities for the superomniphobic and the superomniphilic surfaces.

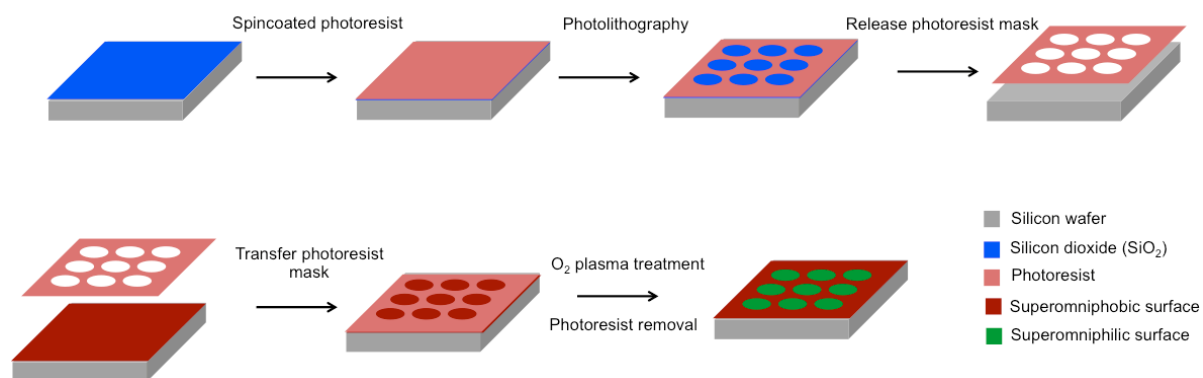## Section 6. Photoresist mask transfer (PRMT) method

Figure S3. Schematic showing the steps of the photoresist mask transfer (PRMT) method.

In order the make the fabrication of patterned superomniphobic-superomniphilic surfaces with different sizes and shapes easier and more universal, we have developed the photoresist mask transfer method, as shown in Figure S3. Since the photoresist cannot be spin-coated on a superomniphobic surface due to its extreme non-wettability, we used an alternative technique to transfer the photoresist mask onto the superomniphobic surface. In this method, a 1 μm thick layer of silicon dioxide (SiO_2) is deposited on a silicon wafer using plasma enhanced chemical vapor deposition (PECVD). The photoresist (SPR 220 3.0) is spin-coated at 3000 rpm on the SiO_2 surface. This resulted in a 3 μm thick photoresist film. The photoresist film is then patterned with the desired geometry using photolithography and developed (in AG 300 MIF, manufacturer). The developed photoresist film is then lifted off from the silicon wafer by dissolving SiO_2 in dilute hydrofluoric acid and transferred onto the electrospun superomniphobic surface. Using the developed photoresist film as a mask, the electrospun superomniphobic surface is exposed to O_2 plasma. After O_2 plasma exposure, the photoresist mask is removed by degrading with ultraviolet light (365 nm) and dissolving in the photoresist developer (AG 300 MIF). Thus, patterned superomniphobic-superomniphilic

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surfaces are obtained. Overall the PRMT methodology allows us to easily fabricate superomniphilic domains of different sizes and shapes.

Section 6. Comparison of nucleation rates for heptane condensation in the superomniphobic regions and the superomniphilic regions.

We used the setup shown in Figure S2 to expose the superomniphobic surface patterned with superomniphilic domains to heptane vapors. The reservoir of liquid heptane was heated to 50°C using a hot plate and the patterned substrate was at room temperature (~ 25°C). For this system, we estimate below, the ratio of nucleation rates for heptane condensation in the superomniphobic region and the superomniphilic regions.
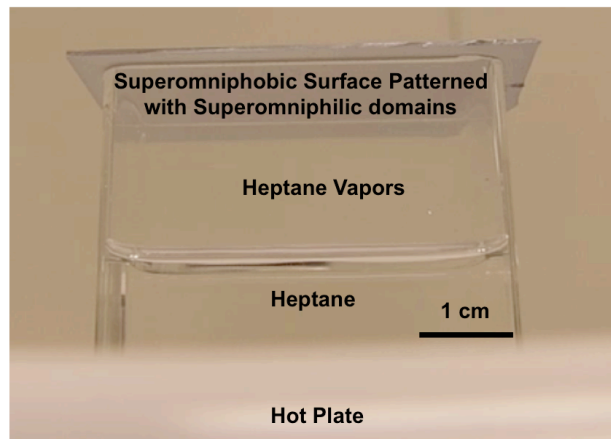

Figure S4. Experimental setup used for the condensation of heptane on superomniphobic surface patterned with superomniphilic domains.

The free energy barrier for the nucleation of a liquid droplet on a flat surface is strongly dependent on the Young's contact angle θ. According to Volmer's classical nucleation theory, the free energy barrier for nucleation is given as:[4]

$$\Delta G = \pi \gamma_{lv} r *^2 \left(2 - 3\cos\theta + \cos^3\theta \right) / 3 \tag{S3-1}$$

Here, γ_{lv} is the surface tension of the liquid, and $r*$ is the critical radius. The critical radius is given by Kelvin's classical equation:[4]

$$\ln\left(p/p_o \right) = 2\gamma_{lv} M_v / RTr * \tag{S3-2}$$

Here, p_o is the vapor pressure over the flat surface of the liquid, p is the vapor pressure over a curved surface of a condensed liquid droplet with radius r^*, M_v is the molar volume of the liquid, T is the temperature and R is the universal gas constant. The vapor pressure over the flat surface of a liquid at a given temperature T (in °C) is given by the Antoine equation:[5]

$$\ln p_o = A - \frac{B}{T+C} \qquad (S3\text{-}3)$$

Here, p_o is in kPa. A, B and C are the parameters for Antoine equation. For heptane, A =13.86, B = 2910.26 and C = 216.43.[5] From equation (S3-3), the vapor pressure p_o = 5.2 kPa at 25°C (substrate temperature). Assuming equilibrium between the reservoir of liquid heptane (at 50°C) and the heptane vapors, the vapor pressure over the curved surface of a condensed heptane droplet p = vapor pressure of heptane p_o at 50°C. Thus, from equation (S3-3), we obtain p = 18.9 kPa. Substituting the values of p and p_o into equation (S3-2), we estimate the critical radius of nucleation for heptane r^* = 2.1 nm. The nucleation rate J is related to the free energy barrier ΔG by the relation:[4]

$$J = J_o \exp\left(\Delta G/kT\right) = J_o \exp\left[\pi\gamma_{lv} r^{*2}\left(2 - 3\cos\theta + \cos^3\theta\right)\big/3kT\right] \qquad (S3\text{-}4)$$

Here, k is the Boltzmann's constant. From equation (S3-4), we obtain the ratio of nucleation rates for heptane condensation in the superomniphilic regions (with θ_{adv} = 10°) to that in the superomniphobic regions (with θ_{adv} = 61°) to be ~10^5.

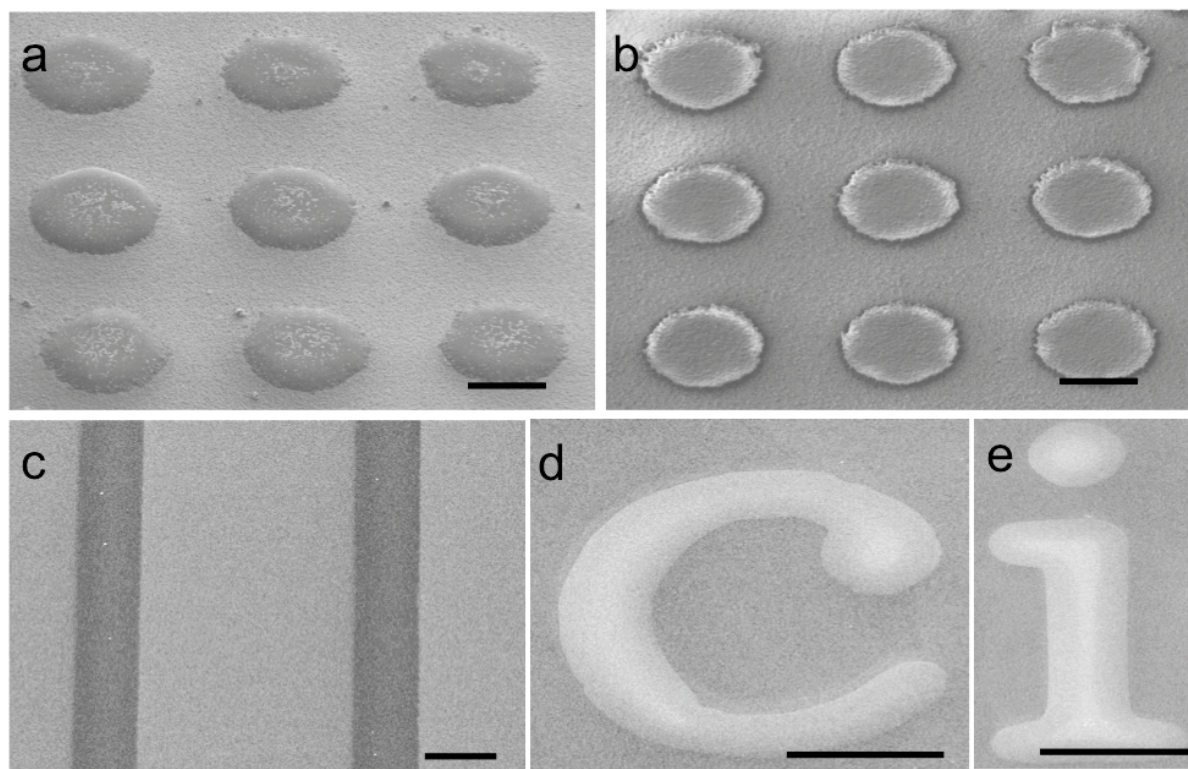**Section 7. SEM images showing site-selective self-assembly**

Figure S5. SEM images showing the site-selective self-assembly of a) circular poly(vinyl pyrrolidone) (PVP) films, b) circular poly(isobutylene) (PIB) films, c) striped PIB films, and d) and e) c-shaped and i-shaped PIB films, respectively. The scale bars represent 500 μm.

References:

[1]   A. Tuteja, W. Choi, M. Ma, J. M. Mabry, S. A. Mazzella, G. C. Rutledge, G. H. McKinley, R. E. Cohen, *Science* **2007**, *318*, 1618.
[2]   D. K. Owens, R. C. Wendt, *J. Appl. Polym. Sci.* **1969**, *13*, 1741.
[3]   G. Beamson, D. Briggs, *High resolution XPS of organic polymers : the Scienta ESCA300 database*, Wiley, Chichester [England]; New York, **1992**.
[4]   a)R. A. Sigsbee, (Ed.: A. C. Zettlemoyer), M. Dekker, New York, **1969**; b)K. K. Varanasi, M. Hsu, N. Bhate, W. Yang, T. Deng, *Appl. Phys. Lett.* **2009**, *95*; c)M. Volmer, *Kinetik der Phasenbildung*, Steinkopff, Dresden and Leipzig, **1939**.
[5]   B. E. Poling, J. M. Prausnitz, J. P. O'Connell, McGraw-Hill, New York, **2001**.

Movie Captions

Movie S1. A superomniphobic surface patterned with superomniphilic domains is dipped in a beaker filled with heptane (dyed red). This results in the site-selective self-assembly of heptane droplets within the superomniphilic domains.

Movie S2. A superomniphobic surface patterned with superomniphilic domains is sprayed with heptane (dyed red). This results in the site-selective self-assembly of heptane droplets within the superomniphilic domains.

Movie S3. A superomniphobic surface patterned with superomniphilic domains is exposed to heptane vapors. Heptane vapors preferentially condense on, and wet, the superomniphilic domains.

Movie S4. A superomniphilic surface patterned with superomniphobic domains is immersed in boiling methanol. Methanol vapor bubbles preferentially nucleate on the superomniphobic domains (black circles).