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Electronic supporting information

Modulation of solid surface with desirable under-liquid wettability based on molecular hydrophilic-lipophilic balance

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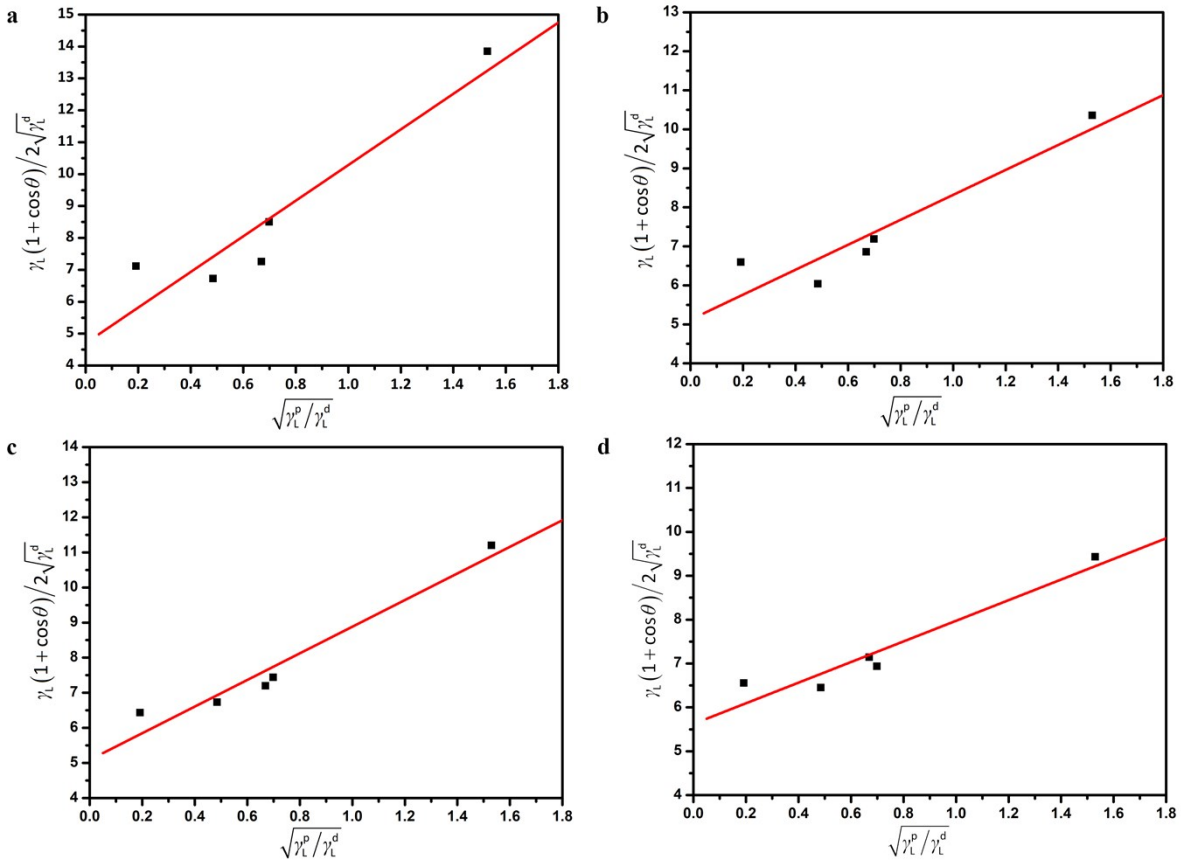


Fig. S1. Fitted curves of SE for four kinds of representative grafted surfaces by OWRK method. a) polydopamine, b) glycidyloxypropyl group, c) methacrylate group, d) phenyl group.

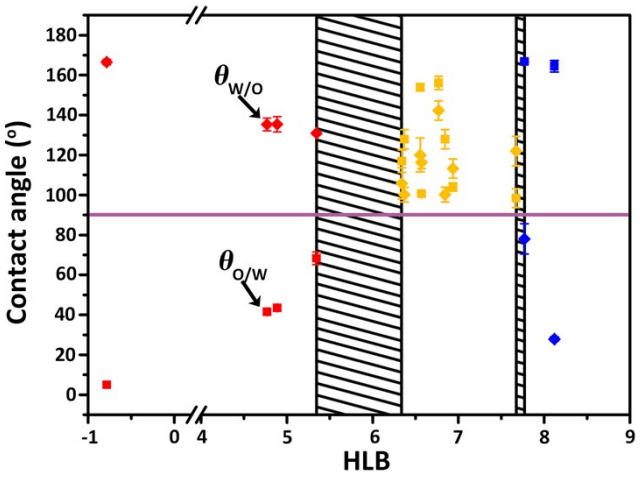


Fig. S2. Relationship between under-liquid wettabilities of solid surfaces with their *f* values in hexadecane-water system. ■: $\theta_{o/w}$, ♦: $\theta_{w/o}$, red: under-water oleophilic and under-oil hydrophobic, yellow: under-water oleophobic and under-oil hydrophobic, blue: under-water oleophobic and under-oil hydrophilic. Black shaded regions in the figure are the transition regions.

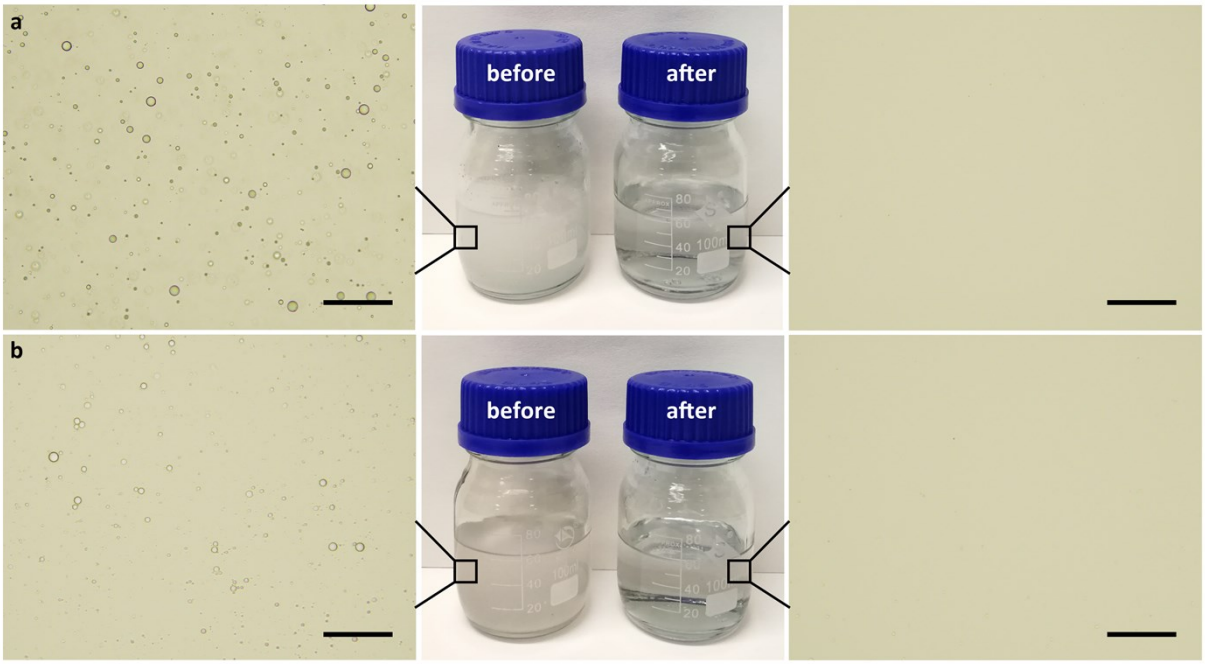


Fig. S3. The emulsion separation of CSTPNM. a) Oil-in-water emulsion, cyclohexane/water, stabilized by surfactant CTAB. b) Water-in-oil emulsion, water/cyclohexane, stabilized by surfactant SDBS. Scale bar, 100 µm. The emulsions were prepared by mixing liquids with a volume ratio of 1:100, and then 2 mg/mL of surfactant was added under high stirring. 60 mL emulsion could be separated within 10 minutes.

Table S1. Surface groups and the corresponding molecular formula.

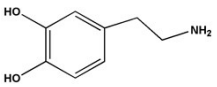
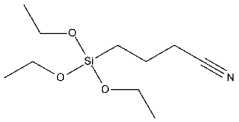
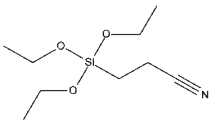
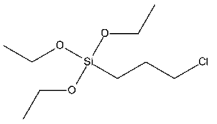
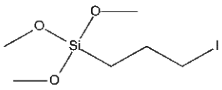
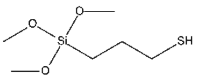
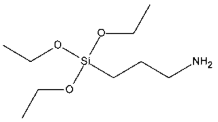
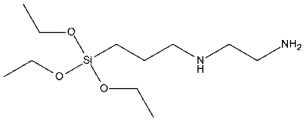
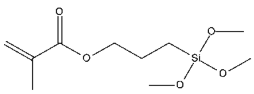
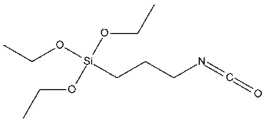
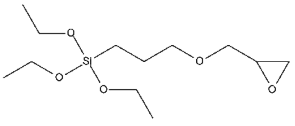
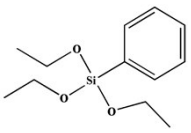
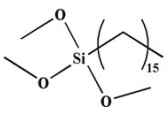
Surface group	Regent	Structural formula
Polydopamine	Dopamine	
Cyanopropyl	3-Cyanopropyltriethoxysilane	
Cyanoethyl	2-Cyanoethyltriethoxysilane	
Chloropropyl	(3-Chloropropyl)triethoxysilane	
Iodopropyl	(3-Iodopropyl)trimethoxysilane	
Mercaptopropyl	(3-Mercaptopropyl) trimethoxysilane	
Aminopropyl	(3-Aminopropyl)triethoxysilane	
Diamino	N-(2-Aminoethyl)-3-aminopropyltriethoxysilane	
Methacrylate	3-(Trimethoxysilyl)propyl methacrylate	
Isocyanate	3-(Triethoxysilyl)propyl isocyanate	
Glycidyloxypropyl	Triethoxy(3-glycidyloxypropyl) silane	
Phenyl	Triethoxyphenylsilane	
Hexadecyl	Hexadecyltrimethoxysilane	

Table S2. Components of SEs for various liquids.

Liquid	SE (γ) mJ m^{-2}	DSE (γ^d) mJ m^{-2}	PSE (γ^p) mJ m^{-2}
water	72.80	21.80	51.00[1]
diiodomethane	50.80	49.00	1.80[2]
ethylene glycol	48.80	32.80	16.00[3]
N, *N'*-dimethylformamide	36.50	25.20	11.30[4]
hexadecane	27.47	27.47	0[1]
cyclohexane	25.24	25.24	0[1]

Table S3. Components of SEs of the grafted surfaces, and the corresponding *f* values.

Surface group	Surface energy (mJ m^{-2})			
	DSE	PSE	SE	*f*
Silicon hydroxyl	12.18	54.61	66.79	4.484
Polydopamine	22.10	31.16	53.26	1.410
Cyanoethyl	22.65	23.48	46.13	1.037
Isocyanate	21.20	21.06	42.26	0.993
Mercaptopropyl	25.27	23.32	48.59	0.923
Cyanopropyl	23.52	20.60	44.11	0.876
Diamino	26.19	19.08	45.28	0.729
Methacrylate	25.91	14.38	40.30	0.555
Aminopropyl	27.62	15.12	42.74	0.547
Glycidyloxypropyl	26.23	10.23	36.46	0.390
Chloropropyl	29.34	7.46	36.80	0.254
Phenyl	31.63	5.52	37.15	0.175
Iodopropyl	38.47	2.37	40.84	0.062
Hexadecyl	26.20	0.01	26.21	~0

Table S4. Wettabilities of surfaces with varied kinds of groups.

Surface group	Contact angle (°)		
	θ_{w}	$\theta_{o/w}$	$\theta_{w/o}$
Silicon hydroxyl	<5	164.4 ± 2.9	27.9 ± 1.1
Polydopamine	39.1 ± 3.8	166.8 ± 0.4	78.0 ± 7.6
Cyanoethyl	51.7 ± 0.8	127.9 ± 4.8	100.2 ± 3.7
Isocyanate	56.8 ± 3.7	116.9 ± 5.6	105.8 ± 7.8
Mercaptopropyl	48.9 ± 2.8	98.4 ± 4.7	122.0 ± 7.4
Cyanopropyl	56.0 ± 1.3	115.2 ± 1.8	97.4 ± 5.0
Diamino	56.4 ± 3.2	156.1 ± 3.4	142.3 ± 4.8
Methacrylate	64.1 ± 0.6	100.6 ± 0.5	116.3 ± 3.1
Aminopropyl	61.5 ± 2.6	153.9 ± 1.8	120.0 ± 8.5
Glycidyloxypropyl	70.8 ± 2.4	104.0 ± 2.1	113.2 ± 4.8
Chloropropyl	75.4 ± 1.5	68.3 ± 3.2	130.9 ± 0.9
Phenyl	77.9 ± 0.7	41.5 ± 1.3	135.3 ± 3.2
Iodopropyl	81.9 ± 2.0	43.5 ± 1.1	135.4 ± 3.8
Hexadecyl	109.1 ± 2.6	<5	166.5 ± 1.4

Table S5. Characteristic volumes for atoms V_x (m^3 mol^{-1}) ($\times$ $l0^{-5}$).[5]

H	C	N	O	F
0.871	1.635	1.439	1.243	1.048
	Si	P	S	Cl
	2.683	2.487	2.291	2.095
	Ge	As	Se	Br
	3.102	2.942	2.781	2.621
	Sn	Sb	Te	I
	3.935	3.774	3.614	3.453

Note: For any bond between two atoms, whether it is single, double or triple bond, the V_x should be diminished value of $0.656 \cdot 10^{-5}$ m^3 mol^{-1}.[6]

Table S6. Calculated group numbers of some lipophilic fragments.

Fragment	V_x	*n*	Group number
>C<	0.323	0	-0.109
-CH<	0.866	0	-0.292
$-CH_2-$	1.409	0	-0.475
$-CH_3$	1.952	0	-0.658
=CH-	1.194	0	-0.402
-CCl<	2.09	0	-0.704
-CI<	3.448	0	-1.162
C_6H_5-	6.621	0	-2.231
=C<	0.651	0	-0.219
$=CH_2$	1.737	0	-0.585
$-CF_2-$	1.761	0	-0.593
$-CF_3$	2.48	0	-0.836
$-C_6H_4-$	6.078	0	-2.048

Note: For lipophilic fragments, $n = 0$.

Table S7. Calculated group numbers of some hydrophilic fragments.

Fragment	V_x	*n*	Group number
-C≡N	2.09	1	0.796
-N=C=O	2.677	2	2.098
-SH	2.178	1	0.766
$-NH_2$	1.541	1	0.981
>NH	0.998	1	1.164
$-COOCH_2-$	3.562	2	1.800
-O- (ether)	0.587	1	1.302
-OH	1.13	1	1.119

Table S8. HLB values of surfaces with varied kinds of groups.

Surface group	HLB
Silicon hydroxyl	8.119
Polydopamine	7.770
Mercaptopropyl	7.673
Glycidyloxypropyl	6.937
Cyanoethyl	6.846
Diamino	6.770
Methacrylate	6.571
Aminopropyl	6.556
Cyanopropyl	6.371
Isocyanate	6.341
Chloropropyl	5.346
Iodopropyl	4.888
Phenyl	4.769
Hexadecyl	-0.783

Table S9. The relationship between the reported wettabilities of surfaces with known chemical compositions and the predicted results based on the HLB values.

Surface group	HLB	Prediction	Correctness[a]	Ref.
Hydroxyl (plasma)	8.119	Under-water lipophobic/	Y	7
Polydopamine	7.770	Under-oil hydrophilic	Y	7
Cyanopropyl	6.371	Under-liquid dual-lyophobic	Y	7
Perfluorooctyl	2.243		Y	7
Perfluorodecyl	1.055	Under-water lipophilic/	Y	8
Octadecyl	-1.733	Under-oil hydrophobic	Y	7
SU8	-4.881		Y	7

[a] Y: yes, the prediction is in accordance with the experimental result. N: no, the prediction is different from the experimental result. All the data are measured on the smooth solid surface.

Table S10. Under-liquid wettabilities of two rough substrates.

Surface group	SiNWs		STPNMs		HLB
	$\theta^*_{o/w}$	$\theta^*_{w/o}$	$\theta^*_{o/w}$	$\theta^*_{w/o}$	
Mercaptopropyl	160.5 ± 2.7	166.3 ± 1.6	162.6 ± 2.1	158.9 ± 2.7	7.673
Glycidyloxypropyl	162.3 ± 2.0	161.2 ± 7.8	158.1 ± 2.5	157.3 ± 0.7	6.937
Cyanoethyl	161.0 ± 1.3	129.6 ± 5.8	159.2 ± 1.9	151.2 ± 1.5	6.846
Diamino	165.2 ± 4.1	153.5 ± 5	163.3 ± 3.6	155.7 ± 4.2	6.770
Methacrylate	166.4 ± 0.4	168 ± 1.7	160.7 ± 2.3	155.2 ± 3.8	6.571
Aminopropyl	164.7 ± 2.1	163.6 ± 1.4	162.5 ± 3.2	154.2 ± 3.4	6.556
Cyanopropyl	163.5 ± 2.2	150.2 ± 3.7	159.4 ± 2.7	157.4 ± 2.6	6.371
Isocyanate	163.4 ± 1.9	164.7 ± 1	160.7 ± 3.1	162.6 ± 2.4	6.341

Note S1. The OWRK (Owen, Wendt, Rabel and Kaelble) method.[9,10]

For the interface of solid surface and liquid, the work of adhesion can be expressed as follows:

$$W_a = \gamma_S + \gamma_L - \gamma_{SL} \quad \text{(S1)}$$

The adhesion can be divided into polar and dispersion parts. As proposed by Fowkes, the polar and dispersive interfacial attractions can be treated independently, and the polar-dispersive interactions can be neglected.

$$W_a = W_a^d + W_a^p = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right) \quad \text{(S2)}$$

where W_a^d and W_a^p are the dispersive and polar component of W_a, and γ_S^d, γ_S^p, γ_L^d, γ_L^p are DSE and PSE of solid and liquid, respectively.

According to Young's equation， when contact angle $\theta > 0$,

$$\gamma_S = \gamma_{SL} + \gamma_L \cos\theta \quad \text{(S3)}$$

Combine these equations,

$$\frac{\gamma_L(1+\cos\theta)}{2\sqrt{\gamma_L^d}} = \sqrt{\gamma_S^d} + \sqrt{\gamma_S^p}\frac{\sqrt{\gamma_L^p}}{\sqrt{\gamma_L^d}} \quad \text{(S4)}$$

The polar and dispersive components of the solvent are known, thus plotting the left side of Equation (S4) against $\sqrt{\gamma_L^p} / \sqrt{\gamma_L^d}$ will theoretically produce a linear line of data points. Then $\sqrt{\gamma_S^d}$ and $\sqrt{\gamma_S^p}$ can be calculated with more than two liquids with given surface tension components (water, ethylene glycol, *N*, *N'*-dimethylformamide, nitromethane, and diiodomethane are used in this work).

Note S2. Comparison of the adhesion work (W_a).

In the OWRK method, the interaction between liquid and solid surface, called adhesion work (W_a), can be expressed as following equation:[9,10]

$$W_a = W_a^d + W_a^p = 2\left(\sqrt{\gamma_S^d \gamma_L^d} + \sqrt{\gamma_S^p \gamma_L^p}\right) \quad \text{(S5)}$$

where W_a^d and W_a^p are the adhesion work generated by the DSE-DSE and PSE-PSE interfacial attractions, respectively. γ_S^d, γ_S^p, and γ_L^d, γ_L^p represent DSE and PSE of solid surface and the liquid, respectively. By introducing the concept of *f*, the above equation can be evolved into:

$$W_a = 2\sqrt{\gamma_S^d \gamma_L^d}\left(1 + \sqrt{f_S f_L}\right) \quad \text{(S6)}$$

where f_S and f_L are the *f* values of the solid surface and the liquid, respectively. In the cyclohexane–water–solid system, the adhesion work between cyclohexane and solid surface is determined by the DSE-DSE interfacial attraction because of the *f* value of cyclohexane (denoted as f_O) is approximately equal to 0 due to the nonpolar property (Supporting Information, Table S2), and $\sqrt{f_S f_L}$ in Eqation (S6) can be neglected.

The ratio of W_a at water–solid interface (W_{aSW}) to that at nonpolar oil–solid interface (W_{aSO}) that can reflect the competitive affinity of solid surface to water and oil is expressed as the following equation:

$$W_{aSW} / W_{aSO} = \sqrt{\gamma_W^d \gamma_O^d}\left(1 + \sqrt{f_S f_W}\right) \quad \text{(S7)}$$

where the γ_W^d and γ_O^d are the DSE of water and oil, respectively. f_W is the *f* value of water, which is a constant value of 2.34 (Supporting Information, Table S2). In the cyclohexane–water–solid system, Eqation (S7) can be converted into:

$$W_{aSW} / W_{aSO} = \sqrt{21.80 / 25.24}\left(1 + \sqrt{2.34 f_S}\right) \approx 0.929\left(1 + \sqrt{2.34 f_S}\right) \quad \text{(S8)}$$

Therefore, the ratio of W_{aSW} to W_{aSO} is proportional to the square root of f_S value. Specifically, solid surfaces with higher f_S values exhibit stronger interfacial affinity to water; conversely, lower f_S means a stronger interfacial affinity to oil.

On the contrary, the ratio of W_a at water–solid interface (W_{aSW}) to that at polar oil–solid interface (W_{aSO}) is expressed as the following equation:

$$W_{aSW} / W_{aSO} = \sqrt{\gamma_W^d \gamma_O^d}\left(1 + \sqrt{f_S f_W}\right) / \left(1 + \sqrt{f_S f_O}\right) \quad \text{(S9)}$$

Since both the numerator and denominator contain f_S value in this equation, the change of W_{aSW} /W_{aSO} with f_S is complex, not monotonically increasing or decreasing. Therefore, it can be inferred that the effect of f_S on the under-liquid wettability of the solid surface should be different in the polar oil/water/solid and non-polar oil/water/solid systems.

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