Supporting Information: Design of Mixed PDMS-mPEG Slippery Covalently Attached Liquid-like Surfaces

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S1 Grafting conditions for PDMS and mPEG layers

S1.1 Topography of mPEG layers during screening of deposition methods

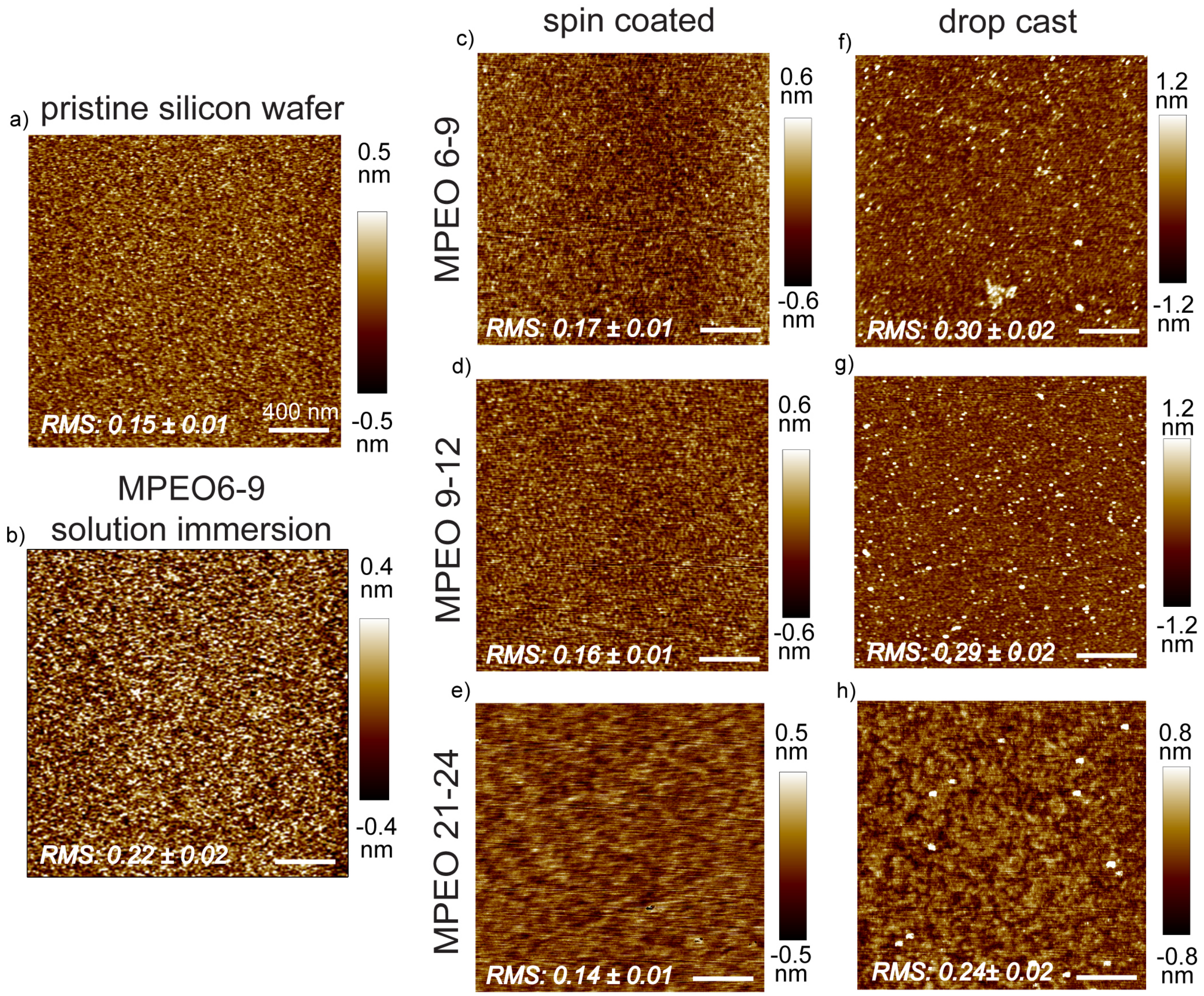

Figure S1: Topography of mPEG layers prepared by different methods. AFM micrographs of a) clean unmodified silicon wafer, and silicon wafer modified with b) mPEG$_{6-9}$ by solution immersion method, c) mPEG$_{6-9}$, d) mPEG$_{9-12}$, and e) mPEG$_{21-24}$ modified by spin coating and f) mPEG$_{6-9}$, g) mPEG$_{9-12}$, and h) mPEG$_{21-24}$ prepared by drop casting 5 v/v %. All surfaces displayed sub-nanometer RMS roughness (shown in each part). The scale bars are 400 nm.

S1.2 General reaction conditions for spin coating of PDMS and mPEG SCALS

General reaction conditions for the grafting of pure PDMS and mPEG SCALS on silicon wafers are shown in Table S1. The cleaned silicon wafer substrate is preheated to 150 °C for at least 1 min to reduce adsorbed water. The substrate is placed in the spin coater and the spin coater chamber is purged with N_2 until the relative humidity is below 10%. Next, 25 μL of the prepared polymer solution is applied to the substrate while it is spinning. The spin-coating is carried out for one minute; during which time the solvent evaporates, concentrating the reactive components of the solution. Spin coating times longer than one minute do not change the properties of the resulting film. If post-curing is required, the coated substrate is placed in an oven at the temperature indicted.

Table S1: Grafting conditions used to produce pure PDMS and pure mPEG SCALS. The concentration and solvents used for PDMS are shown in Table 2 and for mPEG in Table 1.

SCALS source	substrate area	preheat substrate	drop size	Coating condition				post curing	
				RH	temp.	spin rate	spin time	temp.	time
OH-PDMS	15 x 15 mm x mm	150 °C 1 min	25 μL	$< 10\%$	RT	2,000	60 s	-	-
mPEG$_{9-12}$								50 °C	20 hrs

S1.3 Effect of humidity control

When relative humidity was not controlled, the prepared layers were not reproducible in thickness and contact angle, as shown in Table S2. Layer thickness seemed to increase with catalyst concentration but the results were variable even when ambient RH was measured to be constant.

Table S2: Reaction conditions and physical properties of PDMS SCALS prepared using OH-PDMS without humidity control. Advancing (ACA) and receding (RCA) contact angle and contact angle hysteresis (CAH) are shown.

IPA (g)	OH-PDMS (g)	H_2SO_4 (g)	Coating conditions			Physical properties			
			Temp. (°C)	RH (%)	RPM	thickness (nm)	ACA (°)	RCA (°)	CAH (°)
1.0	0.1	4.8×10^{-5}	24.0	49	3,000	2.8	105.5	103.7	1.8
			24.0	49	3,000	1.1	103.2	97.4	5.8
		8.0×10^{-5}	24.0	49	3,000	1.4	104.4	98.9	5.5
			21.5	25	3,000	4.1	107.6	103.8	3.8
		1.2×10^{-4}	19.5	45	3,000	4.5	107.1	102.2	4.9
			19.5	45	3,000	10.0	112.2	102.1	10.1

S1.4 Effect of post-cure temperature on mPEG layers

A post-curing step was found to be necessary in order to graft mPEG layers that had slippery properties. Post-cure was conducted at 50 °C. To reduce the post-cure time, the post-cure temperature was increased to 90 °C. The thickness did not increase much but the contact angle hysteresis increased significantly from 0.6 to 9.1 ° and the surface was no longer slippery. It was found that mPEG cures differently with curing conditions, as shown in Table S3.

Table S3: Effect of post-curing temperature at 50 and 90 °C on the physical properties of mPEG SCALS produced.

Component		Post-curing condition		Physical properties			
Solvent system (g)	$mPEG_{9-12}$ (g)	Temp. (°C)	Time (hrs)	Thickness (nm)	ACA (°)	RCA (°)	CAH (°)
EtOH(95) + H_2O(5) → AA(pH4): 1.0	0.1	50	20	1.9	41.5	40.9	0.6
		90	20	2.0	42.3	33.2	9.1

S2 Synthesis of mixed SCALS from a single solution

S2.1 Selection of a common solvent for grafting of mPEG and PDMS layers

The grafting of PDMS and mPEG chains from a single solution required optimization of solvent, catalyst and post-curing step. To identify the most appropriate solvent for both

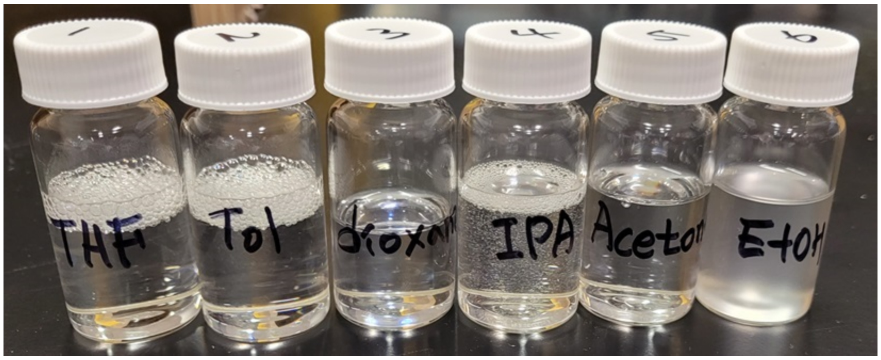

Figure S2: Photo demonstrating the solubility of a 50:50 mixture of PDMS oil (20 cSt) and PEG1,000 (Mn 1,000) in a range of solvents: tetrahydrofuran (THF), toluene (Tol), dioxane, isopropyl alcohol (IPA), acetone, and ethanol (EtOH). A clear solution indicates complete compatibility, while an opaque solution suggests some aggregation due to poor compatibility.

PDMS and mPEG, PDMS oil (20 cSt, Mn 2,000, Sigma-Aldrich) and PEG1,000 (Mn 1,000, i.e. of higher molecular weight than those of SCALS source used) were used. Solutions were prepared according to the ratios shown in Table S4; when IPA was used, the solution appeared transparent, whereas with EtOH, it appeared opaque (Figure S2). This difference is attributed to the fact that IPA allows complete mixing of PDMS and PEG1,000, resulting in a transparent solution, while EtOH does not achieve full miscibility, leading to aggregation and an opaque appearance.[1,2] As a result, IPA was selected instead of EtOH for the production of a more homogeneous solution. Other solvents were also tested (tetrahydrofuran, toluene, dioxane and acetone), but they have issues related to hazard, evaporation rate, and solubility, as shown in Table S4.

Table S4: Formulation of PDMS and PEG1,000 for visual miscibility test, evaporation rate (ER) and hazards. The values presented in the table for each solvent represent their weight ratios in the formulation. The evaporation rates are based on butyl acetate as a reference point. The E/R values indicate how quickly each solvent evaporates compared to butyl acetate, providing insight into their volatility. The higher the E/R value, the faster the evaporation rate. The hazard information is derived from Material Safety Data Sheets (MSDS) for each solvent.

THF	Toluene	dioxane	PDMS	PEG1,000	Appearance	ER	Hazards	Usage Recommendations
9.0	-	-	0.5	0.5	transparent	6.3	flammable, CNS depressant	Use in a fume hood
-	9.0	-			transparent	2.0	neurotoxic, flammable	Use in a fume hood
-	-	9.0			transparent	2.2	carcinogenic, skin irritant	Use in a fume hood
IPA	Acetone	Ethanol	PDMS	PEG1,000	Appearance	ER	Hazards	Usage Recommendations
9.0	-	-	0.5	0.5	**transparent**	**1.7**	**skin irritant**	**can be used relatively safely**
-	9.0	-			transparent	14.4	flammable, relatively low toxicity	can be used relatively safely
-	-	9.0			opaque	2.7	flammable	can be used relatively safely

S2.2 Optimized procedure to obtain mixed surfaces

A procedure was optimized to produce mixed layers from a single solution of PDMS and mPEG, as shown in Table S5, but mixed surfaces could not be obtained at any mixing ration, as mPEG dominated the coverage, as determined from the value of water contact angle. The developed 2-step spin coating procedure used the same solutions shown in Table S5 but they were applied in two successive steps, first PDMS followed by mPEG, with the timing explained in the main text and Section S3.

Table S5: Optimized solutions and process to spin coat mixed layers of PDMS and mPEG. In the unsuccessful 1-step process, a solution of PDMS in IPA and one of mPEG in EtOH were mixed according to the ratios in the main text. In the successful 2-step process, the 2 solutions were successively dispensed on the spinning substrate on the spin coater.

Type	Reactant solution			Coating condition			Post-cure
	SCALS source (g)	Solvent (g)	Catalyst (g)	pre-heat	RH (%)	RPM	
PDMS	OH-PDMS (0.1)	IPA (1.0)	H_2SO_4 (8.0×10^{-5})	150 °C for 1 min	< 10	2,000	-
mPEG	mPEG$_{9-12}$ (0.1)	EtOH(0.95) + H_2O(0.05)	→ AA(pH4): (1.0)				50 °C × 20 hrs

S2.3 Adjustment of the PDMS SCALS process for combining in a single solution with mPEG

To implement a single solution method to graft PDMS and mPEG at the same time, a post-cure step was needed and a mixture of both catalysts (H_2SO_4 and acetic acid) was found necessary. Post-curing of PDMS SCALS without a catalyst resulted in a thickness of 0.6 nm (Table S6) after 20 hours at 50°C, which was below the 3 nm target. This indicated that the catalyst system was needed even under heat curing conditions. When acetic acid, a weaker catalyst than H_2SO_4, was applied alone with post-cure, a thickness of 0.7 nm was obtained. The acetic acid catalyst is too weak to obtain proper thickness for PDMS SCALS. A bi-catalyst system was then introduced to achieve a thickness of 3 nm target. The pH was adjusted to 4 with acetic acid and H_2SO_4 was gradually added at 1.2×10^{-5} g, 1.6×10^{-5} g and 3.3×10^{-5} g (Table S6). A thickness of 3.0 nm was obtained at 1.6×10^{-5} g of H_2SO_4. As observed in previous PDMS optimization experiments, the thickness of SCALS increased with the amount of H_2SO_4, but the concentration could be decreased from 8.0×10^{-5} g to 1.6×10^{-5} g due to the effect of the bi-catalyst system, with the addition of acetic acid at pH = 4 and post-cure condition.

Table S6: Adjusted conditions tested to obtain PDMS layers, designed to match those used for mPEG, for deposition from a single solution

components				post-curing		property			
IPA (g)	OH-PDMS (g)	H_2SO_4 (g)	acetic acid	Temp.(°C)	Time(hrs)	thickness	ACA	RCA	CAH
1.0	0.1	-	-	50	20	0.6	93.3	87.4	5.9
		-	pH4	50	20	0.7	95.3	89.6	5.7
		8.0×10^{-5}	-	-	-	2.9	106.5	104.8	1.7
		1.2×10^{-5}	pH4	50	20	2.1	104.3	100.4	3.9
		1.6×10^{-5}	pH4	50	20	3.0	102.8	101.1	1.7
		3.3×10^{-5}	pH4	50	20	10.9	112.9	98.6	14.3

S2.4 Adjustment of the mPEG SCALS process for combining in a single solution with PDMS

To integrate into a single solution, the mPEG SCALS process required replacing EtOH as a solvent with IPA and applying a bi-catalyst system. If H_2SO_4 achieved the desired mPEG SCALS thickness, the bi-catalyst system or post cure may have not been necessary. When ethanol was replaced with IPA, the thickness of mPEG SCALS was reduced. When the catalyst was changed to H_2SO_4 (at the optimum concentration for PDMS SCALS) without post-cure, the thickness was only 0.8 nm, and even with post-cure, it was 0.9 nm, indicating that H_2SO_4 did not work properly for mPEG. In the same way as the adjusted PDMS SCALS recipe, the pH4 solution with acetic acid was constantly used, while H_2SO_4 was added at amounts of 1.2×10^{-5} g and 1.6×10^{-5} g. A layer of thickness 1.2 nm was measured at 1.6×10^{-5} g, which was lower than the 1.4 nm measured at 1.2×10^{-5} g. It is believed that H_2SO_4 catalyst might have damaged the mPEG SCALS.[3,4] This also explains why H_2SO_4 is not ideal for use with mPEG SCALS. The optimum catalyst content in the bi-catalyst system for mPEG SCALS was 1.2×10^{-5} g as shown in Table S7.

Table S7: Adjusted conditions tested to obtain mPEG layers, designed to match those used for PDMS, for deposition from a single solution

Components					Post-curing		Property			
EtOH (g)	IPA (g)	mPEG	H_2SO_4 (g)	acetic acid	Temp.(°C)	Time(hrs)	Thickness(nm)	ACA(°)	RCA(°)	CAH(°)
1.0	-	0.1	-	pH4	50	20	1.9	41.5	40.9	0.6
	1.0		-	pH4	50	20	1.6	40.3	38.3	2.0
-			8.0×10^{-5}	-	-	-	0.8	38.8	27.4	11.4
-			8.0×10^{-5}	-	50	20	0.9	36.8	34.1	2.7
-			1.2×10^{-5}	pH4	50	20	1.4	38.1	36.7	1.4
-			1.6×10^{-5}	pH4	50	20	1.2	40.5	36.4	4.1

S3 A 2-step grafting method for mixed SCALS

To fabricate PDMS and mPEG SCALS, a new 2-step grafting approach was introduced. Optimized solutions for PDMS and mPEG were prepared as shown in Table S5. Firstly, the PDMS solution was applied on the spinning substrate; then, after a set reaction time, the mPEG solution was applied and the spinning was maintained for 60 seconds; finally a post-cure step at 50°C for 20 hours and washing were performed (Figure S3).

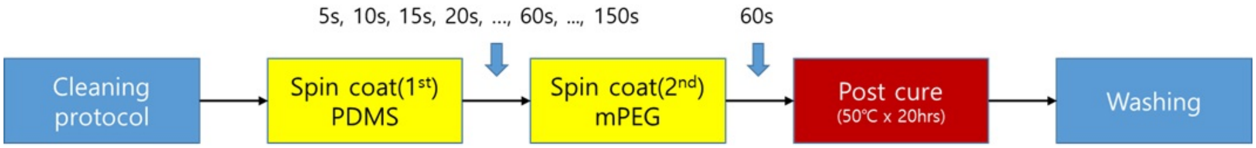

Figure S3: Schematic illustration of the 2-step spin coating procedure to prepared mixed PDMS-mPEG layers. The order of deposition and the duration of PDMS reaction (spinning time) were crucial to obtain the desired wettability.

Figure S4 shows the relationship between average contact angle, contact angle hysteresis (CAH), and thickness as a function of PDMS reaction time. The contact angle generally rises with the reaction time. The CAH increases until approximately 20 seconds, after which it begins to decline. The CAH starts to increase again after 60 seconds due to the formation of thick layers that develop roughness.

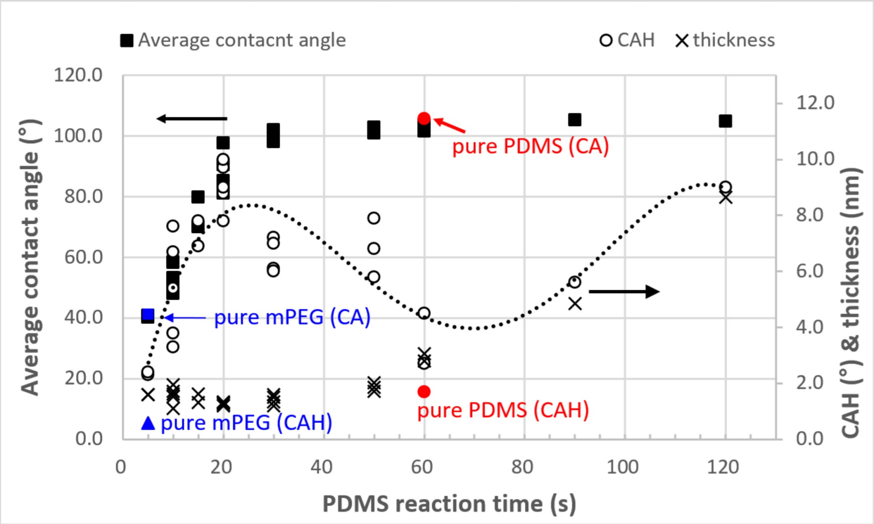

Figure S4: Mixed mPEG-PDMS layers prepared with the 2-step method. Average contact angle (solid square, left), contact angle hysteresis (CAH, empty circle, right), thickness (cross symbol, right) obtained by varying spin-coating time of PDMS from 5 to 120 s. The line is a guide to the eye which represents a cubic fit. The red symbol represents pure PDMS SCALS, and the blue symbol represents pure mPEG SCALS.

S4 Effect of humidity on mPEG layer thickness

Neutron reflectometry (NR) was used to characterize the nanostructure of coatings prepared by spin coating mPEG solutions in different humidity conditions, in order to establish their swelling in water. The air measurements were carried out in a sealed stainless steel sample chamber equipped with an in situ humidity/temperature sensor (JIHAI, KSID. The temperature was maintained at 21 ±1 °C. For dry measurements (0 % RH), the environmental chamber was purged of moisture using pure N_2. For saturated measurements (100 % RH), a vessel of D_2O was placed next to the sample to increase vapor saturation; for submerged measurements, the samples were fully immersed in D_2O for 10 minutes prior to start of measurement. Film thickness and volume fraction were fitted from the data and the results are shown in Figure S5. Data analysis was carried out in the refnx reflectometry package,[5] as described in previous work.[6] The thickness of mPEG6-9 and mPEG9-12 layers increased by about 0.5 - 1 nm between the dry (0 % RH) and the saturated measurements (100 % RH).

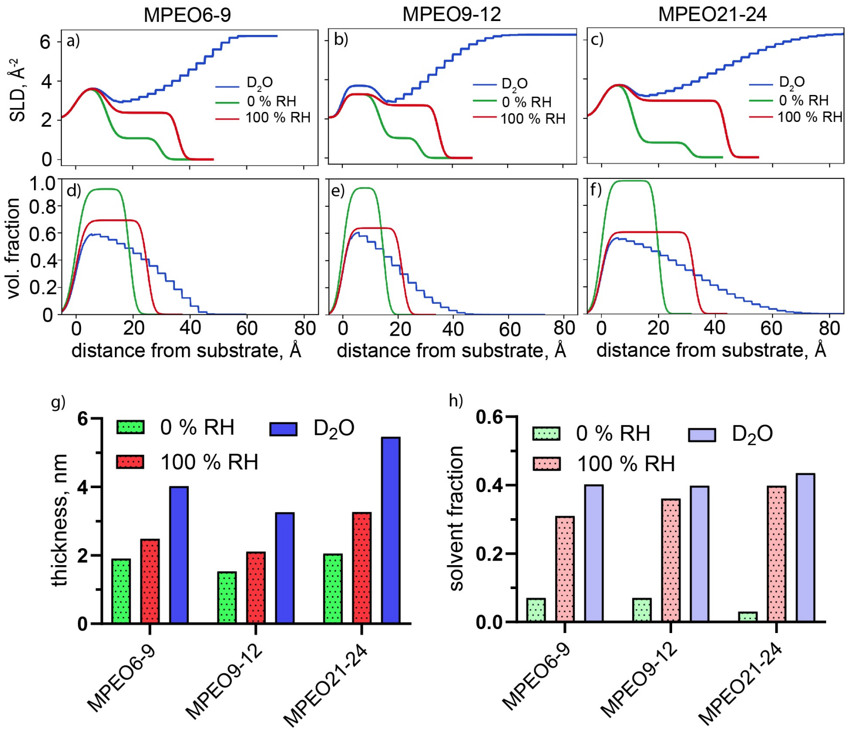

Figure S5: Neutron reflectometry data on mPEG layers. (a-c) Scattering length density (SLD) profiles for (a) mPEG$_{6-9}$, (b) mPEG$_{9-12}$, and (c) mPEG$_{21-24}$ when dry (0 % RH, green), saturated by vapor (100 % RH, red) and when submerged in D_2O (blue). SLD profiles were used to derive volume fraction profiles for (d) mPEG$_{6-9}$, (e) mPEG$_{9-12}$, and (f) mPEG$_{21-24}$. (g) Film thickness when mPEG layers were dry (green), saturated by vapor (red), and submerged in D_2O (blue). (h) Changes in solvent fraction in the same conditions reflect the fraction of water retained by each coating when dry (green), saturated by D_2O vapor (red), and liquid D_2O (blue). Error bars are too small to be visible.

S5 Mixed layers are still relatively slippery

Although the mixed layers prepared here have a higher CAH than either of the pure SCALS systems, they would be considered slippery in most other contexts. For instance, alkane self-assembled monolayers typically have CAH of between 3 and 20°.[7] Even self-assembled monolayers that were optimized for minimum contact line friction by Lepikko *et al.*[8] have CAH values that are higher than the mixed layers prepared here in the range of contact angle between 40 and 85 ° and around 105°.

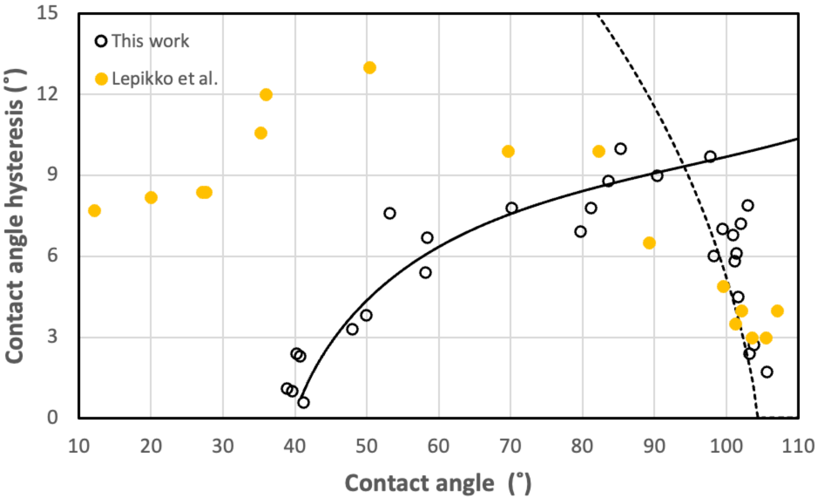

Figure S6: Comparison of the data presented in Figure 5b) with the self-assembled alkane monolayers of different surface density prepared by Lepikko et al. (data taken from Figure 4 in reference[8]).

References

1. ASTM Standard Test Method for Appearance of Clear, Transparent Liquids (Visual Inspection Procedure). ASTM Standard E2680-23, 2023; `https://www.astm.org/e2680-16.html`.

2. ASTM Standard Test Method for Testing Alkyd Compatibility with Resin or Resin Solutions. ASTM Standard D6887-03, 2020; `https://www.astm.org/d6887-03r13.html`.

3. Burwell, R. L. The Cleavage of Ethers. *Chem. Rev.* **1954**, *54*, 615–685, 25.

4. Burwell, R. L.; Fuller, M. E. The Cleavage of Ethers by Hydrogen Bromide. *J. Am. Chem. Soc.* **1957**, *79*, 2332–2336, 26.

5. Nelson, A. R. J.; Prescott, S. W. refnx: neutron and X-ray reflectometry analysis in Python. *J. Appl. Cryst.* **2019**, *52*, 193–200.

6. Katselas, A.; Gresham, I. J.; Nelson, A. R. J.; Neto, C. Exploring the water capture efficiency of covalently attached liquid-like surfaces. *J. Chem. Phys.* **2023**, *158*, 214708.

7. Fadeev, A. Y.; McCarthy, T. J. Self-Assembly Is Not the Only Reaction Possible between Alkyltrichlorosilanes and Surfaces: Monomolecular and Oligomeric Covalently Attached Layers of Dichloro- and Trichloroalkylsilanes on Silicon. *Langmuir* **2000**, *16*, 7268–7274.
8. Lepikko, S.; Jaques, Y. M.; Junaid, M.; Backholm, M.; Lahtinen, J.; Julin, J.; Jokinen, V.; Sajavaara, T.; Sammalkorpi, M.; Foster, A. S.; Ras, R. H. A. Droplet slipperiness despite surface heterogeneity at molecular scale. *Nat. Chem.* **2024**, *16*, 506–513.