Supporting Information

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SI Text

S1. Octadecyltrichlorosilane Self-Assembled Monolayer Coating

To form the octadecyltrichlorosilane self-assembled monolayer (OTS-SAM), a glass plate (25 × 15 cm) was rinsed with deionized water to remove water-soluble contaminants and dried with N_2. Next, the plate was rinsed with isopropyl alcohol (IPA), dried with N_2, and put in a base bath for about 3 h. After being removed from the base bath, the plate was rinsed thoroughly with deionized water and blow dried with N_2. The cleaned glass plate was dried further at 120 °C for about 3 h to ensure complete drying. After drying, the glass plate was immersed in a freshly prepared OTS solution (1 mM solution of OTS in toluene) and allowed to stay immersed for 30 min. The glass container containing the solution was sealed to minimize contact with atmospheric air and to avoid possible degradation of OTS. After 30 min, the plate was taken out of the solution and rinsed successively with toluene, acetone, chloroform, and IPA, and blow dried with N_2 between rinses. The SAM formed on the surface of the glass plate was annealed in a vacuum oven at ∼150 °C overnight.

S2.1. Dry Contact of Smooth Surfaces

The Dupré equation for calculating the work of adhesion between two surfaces, 1 and 2, in its general form is written as follows:

$$W_{dry} = A_C(\gamma_1 + \gamma_2 - \gamma_{1-2}). \quad \textbf{[S1]}$$

Here, W_{dry} is the work of adhesion between surfaces 1 and 2, A_C is the area of contact, and γ_1, γ_2, and γ_{1-2} are the surface energies of components 1 and 2 and the interfacial energy of the contact between 1 and 2, respectively.

We used Eq. **S1** to calculate the work of adhesion between each of our four surfaces [glass, PMMA, OTS-SAM–coated glass, and polytetrafluoroethylene (PTFE)] and the "gecko hair-like" *n*-hexadecane surface, assuming the contact interface formed as a result of contact between the two is flat (Table 2). The Young–Dupré equation for the dry contact between the two surfaces when air is the medium of contact may be written as follows (1):

$$W_{dry} = A_c(\gamma_{s-air} + \gamma_{h-air} - \gamma_{s-h}), \quad \textbf{[S2]}$$

where γ_{s-h} is the interfacial energy at the contact interface between the gecko hair-like surface and the contact surface (glass, PMMA, OTS-SAM–coated glass, or PTFE), γ_{h-air} is the surface energy of the gecko hair-like *n*-hexadecane surface, and γ_{s-air} is the surface energy of the contact surface.

Young's equation for the contact angle (θ_1) *n*-hexadecane makes on a given contact surface is

$$\gamma_{s-h} = \gamma_{s-air} - \gamma_{h-air}\cos\theta_1. \quad \textbf{[S3]}$$

Substituting Eq. **S3** in Eq. **S2** for γ_{s-h}, we get

$$W_{dry} = A_c\ \gamma_{h-air}(1 + \cos\theta_1). \quad \textbf{[S4]}$$

We measured the contact angle of *n*-hexadecane on all four surfaces we used for the gecko trials to obtain the value of θ_1 (see the second column of Table 1). The value of γ_{h-air} is known to be 25 mJ/m^2. Substituting all the known values in Eq. **S4** gives the work of dry adhesion (W_{dry}).

S2.2. Wet Contact of Smooth Surfaces

In the case of wet adhesion, i.e., the case in which water is the medium of contact, the work of adhesion (W_{wet}) is calculated using the following equation:

$$W_{wet} = A_c(\gamma_{s-water} + \gamma_{h-water} - \gamma_{s-h}). \quad \textbf{[S5]}$$

Here, W_{wet} is the work of adhesion between two surfaces contacting underwater. Similar to dry contact, $\gamma_{s-water}$ denotes the interfacial energy at the contact surface–water interface (contact surface is glass, PMMA, OTS-SAM–coated glass, or PTFE); $\gamma_{h-water}$ is the *n*-hexadecane–water interfacial energy; and γ_{s-h} is the interfacial energy at the surface–*n*-hexadecane contact interface.

The contact angle of water (θ_2) also was measured on all four surfaces (first column of Table 1), giving the following relationship:

$$\gamma_{s-water} = \gamma_{s-air} - \gamma_{water-air}\cos\theta_2, \quad \textbf{[S6]}$$

where $\gamma_{water-air}$ is the surface tension of water. Substituting Eqs. **S3** and **S6** in Eq. **S5** for γ_{s-h} and $\gamma_{s-water}$ gives the following equation:

$$W_{wet} = A_c(\gamma_{h-water} + \gamma_{h-air}\cos\theta_1 - \gamma_{water-air}\cos\theta_2). \quad \textbf{[S7]}$$

The values of $\gamma_{h-water}$ and γ_{h-air} are known to be 50 mJ/m^2 and 25 mJ/m^2, respectively. θ_1 and θ_2 were determined experimentally, as discussed in *SI Text*, section 3. Table 1 summarizes the contact angles of water and *n*-hexadecane on different test surfaces. Substituting all the values in Eq. **S7** gives the value of wet adhesion. Thus, knowing all the parameters, we can estimate $W_{wet} : W_{dry}$ using Eq. **S8** below (derived from Eqs. **S4** and **S7**):

$$\frac{W_{wet}}{W_{dry}} = \frac{\gamma_{h-water} + \gamma_{h-air}\cos\theta_1 - \gamma_{water-air}\cos\theta_2}{\gamma_{h-air}(1 + \cos\theta_1)}. \quad \textbf{[S8]}$$

Ratios are reported in Table 2.

S3. Contact Angle Measurements

Samples of about 1 × 1 cm were cut from the actual test surfaces used for whole-animal adhesion trials. Surfaces were rinsed with ethyl alcohol, because ethyl alcohol is the only cleaning step between trials, followed by blow drying. The contact angle of deionized water and *n*-hexadecane was measured using Ramé–Hart Instruments Advanced Goniometer 500 F1 with Drop Image Advanced software. A droplet of 10–12 μL of the given test liquid was deposited on the surface and the contact angle was measured. At least three measurements were taken for each sample, and the average and SEM were calculated to estimate the deviations in the measurements.

S4.1. Dry Contact for a Tetrad-Patterned Surface

In the case of a tetrad-patterned surface in dry contact with different surfaces, Eq. **S4** may be used to calculate W_{dry}. A_C in this case is only a fraction of the total surface area that forms a contact interface.

S4.2. Wet Contact for a Tetrad-Patterned Surface

In the case of contact between the tetrad-patterned gecko hair-like surface and the contacting surface (glass, PMMA, OTS-SAM–coated glass, or PTFE), there are four possible cases, as shown schematically in Table 2. The ratio $W_{wet} : W_{dry}$ for all the cases may be estimated as follows (final ratios are reported in Table 2).

Case 1.

$$W_{wet} = A_C\gamma_{h-water} + A_2\gamma_{s-water} - A_C\gamma_{s-h} - (A_2 - A_C)\gamma_{s-air} \quad \textbf{[S9]}$$

A_1 and A_2 in the case of patterned surfaces correspond to total surface areas of the gecko hair-like n-hexadecane tetrad-patterned unit cell and the surface with which it is in contact (glass, PMMA, OTS-SAM–coated glass, or PTFE), respectively. Further simplification of Eq. **S9** and appropriate substitutions give an equation to calculate W_{wet} for case 1 (below):

$$W_{wet} = A_C(\gamma_{h-water} + \gamma_{h-air}\cos\theta_1) - A_2\gamma_{water-air}\cos\theta_2. \quad \textbf{[S10]}$$

$W_{wet} : W_{dry}$ thus is calculated using Eqs. **S4** and **S10**:

$$\frac{W_{wet}}{W_{dry}} = \frac{\gamma_{h-water} + \gamma_{h-air}\cos\theta_1 - (A_2/A_C)\,\gamma_{water-air}\cos\theta_2}{\gamma_{h-air}(1+\cos\theta_1)}. \quad \textbf{[S11]}$$

Case 2. Similar to case 1, the equation for W_{wet} for case 2 is derived as

$$W_{wet} = A_1\gamma_{h-water} + A_2\gamma_{s-water} - A_C\gamma_{s-h} - (A_1 - A_C)\gamma_{h-air} - (A_2 - A_C)\gamma_{s-air}. \quad \textbf{[S12]}$$

Further simplification gives Eq. **S12** in terms of parameters measurable experimentally:

$$W_{wet} = A_1(\gamma_{h-water} - \gamma_{h-air}) - A_2\gamma_{water-air}\cos\theta_2 + A_C\gamma_{h-air}(1+\cos\theta_1). \quad \textbf{[S13]}$$

$W_{wet} : W_{dry}$ for this case is derived using Eqs. **S4** and **S13**:

$$\frac{W_{wet}}{W_{dry}} = \frac{(A_1/A_C)(\gamma_{h-water} - \gamma_{h-air}) + \gamma_{h-air}(1+\cos\theta_1) - (A_2/A_C)\gamma_{water-air}\cos\theta_2}{\gamma_{h-air}(1+\cos\theta_1)}. \quad \textbf{[S14]}$$

Case 3. W_{wet} for case 3 is derived in a way similar to that of cases 1 and 2 above:

$$W_{wet} = (2A_C - A_1)\gamma_{h-water} + (A_1 - A_C)\gamma_{h-air} + A_C(\gamma_{s-water} - \gamma_{s-h}). \quad \textbf{[S15]}$$

Simplification and substitution reduces Eq. **S15** in the following form:

$$W_{wet} = A_C[2\gamma_{h-water} + \gamma_{h-air}(\cos\theta_1 - 1) - \gamma_{water-air}\cos\theta_2] + A_1(\gamma_{h-air} - \gamma_{h-water}). \quad \textbf{[S16]}$$

Using Eqs. **S4** and **S16**, the ratio $W_{wet} : W_{dry}$ may be calculated as shown below:

$$\frac{W_{wet}}{W_{dry}} = \frac{2\gamma_{h-water} + \gamma_{h-air}(\cos\theta_1 - 1) - \gamma_{water-air}\cos\theta_2 + (A_1/A_C)(\gamma_{h-air} - \gamma_{h-water})}{\gamma_{h-air}(1+\cos\theta_1)}. \quad \textbf{[S17]}$$

Case 4. The equation for W_{wet} in case 4 is calculated as follows:

$$W_{wet} = A_C(\gamma_{h-water} + \gamma_{s-water} - \gamma_{s-h}). \quad \textbf{[S18]}$$

Simplification on substitution gives Eq. **S18** in terms of $\theta_1$and θ_2:

$$W_{wet} = A_C(\gamma_{h-water} + \gamma_{h-air}\cos\theta_1 - \gamma_{water-air}\cos\theta_2). \quad \textbf{[S19]}$$

The equation for the ratio $W_{wet} : W_{dry}$ is derived below:

$$\frac{W_{wet}}{W_{dry}} = \frac{\gamma_{h-water} + \gamma_{h-air}\cos\theta_1 - \gamma_{water-air}\cos\theta_2}{\gamma_{h-air}(1+\cos\theta_1)}. \quad \textbf{[S20]}$$

A_1, A_2, and A_C here represent the total surface area of the tetrad unit cell, the total surface area of the test surface, and the contact area, respectively. We calculated the areas using the dimensions of a unit cell we estimated from SEM images. For the tetrad-patterned unit cell, A_1 = 3,961 μm^2, A_2 = 121 μm^2, and A_C = 64 μm^2. The respective ratios of areas for $W_{wet} : W_{dry}$ were calculated based on these values and substituted.

S5. Non–Tetrad-Patterned Surface in Wet and Dry Contact

A schematic of a non–tetrad-patterned surface is shown in Fig. S1. One unit cell is boxed. Similar to a tetrad-patterned unit cell, dimensions of this type of gecko toe morphology were estimated using SEM imaging. For this type of unit cell, A_1 = 996 μm^2, A_2 = 36 μm^2, and A_C = 16 μm^2. $W_{wet} : W_{dry}$ ratios thus were calculated using the values and equations derived above for four different cases of wet contact. The results are shown in Table S1.

S6. Hamaker Constant Calculations

The parameters used for Hamaker constant calculations and the values obtained for different substrates are tabulated in Tables S3 and S4, respectively.

1. Chaudhury MK (1996) Interfacial interaction between low-energy surfaces. *Mater Sci Eng Rep* 16(3):97–159.

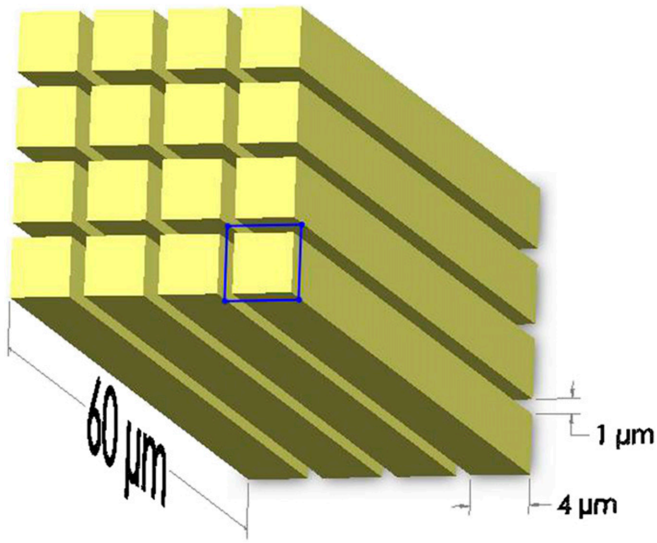

Fig. S1. Schematic representation of the non–tetrad-patterned unit cell morphology. One unit cell is boxed in blue. Columns are 60 µm tall and 4 µm wide. Each column is separated by 1 µm.

Table S1. $W_{wet} : W_{dry}$ **ratios for the non–tetrad-patterned surface in each of the four wetting cases and on each test surface**

	$W_{wet} : W_{dry}$			
Surface	Case 1	Case 2	Case 3	Case 4
Glass	−0.62	30.39	−30.45	0.56
PMMA	1.23	32.04	−29.43	1.38
OTS-SAM	1.78	34.37	−30.95	1.64
PTFE	1.98	34.83	−31.12	1.74

Table S2. Multivariate ANOVA showing a significant difference in shear adhesive force across surfaces

Effect	Wilks' lambda	Exact *F*	Numerator df	Denominator df	*P* value
Treatment	0.163	1.628	1	10	0.2309
Surface	19.896	53.057	3	8	<0.0001*
Surface × treatment	3.308	8.821	3	8	0.0064**

This table shows a significant difference (*$P < 0.0001$) in shear adhesive force across surfaces (glass, PMMA, OTS-SAM–coated glass, and PTFE), and this difference is a result of the interaction between surface and treatment (wet or dry; **$P = 0.0064$). The *F*-statistic is from the Wilks' lambda test.

Table S3. Parameters used to calculate Hamaker constants for the absorption frequency (ν_e) of 3×10^{15} s^{-1}

Medium	Dielectric constant, ε	Refractive index, *n*
Water	80	1.33
n-Hexadecane	2.05	1.42
Glass	3.7	1.54
PMMA	2.6	1.5
PTFE	2.1	1.36

Table S4. Hamaker constant values calculated for different contact surfaces

Surface	Hamaker constant, J	
	$A_{132(air)}$ ($\times 10^{-20}$J)	$A_{132(water)}$ ($\times 10^{-20}$J)
Glass	6.53	0.75
PMMA	6.16	0.68
PTFE	4.59	0.34

Subscripts 1, 2, and 3 correspond to gecko hair-like *n*-hexadecane, substrate (glass, PMMA, and PTFE), and air (or water), respectively.