Supplementary Information

Friction of aromatic thiol monolayers on silver: SFA and AFM studies of adhesive and non-adhesive contacts

Y. Yang, J. Singh, and M. Ruths

Department of Chemistry, University of Massachusetts Lowell,
1 University Avenue, Lowell, MA 01854, USA.

CALCULATION OF SURFACE ENERGY

Experimental values of surface energies were calculated from measured contact angles using the Young–Dupré (YD) equation,[1] $W = \gamma_{\mathrm{LV}}\,(1 + \cos\theta)$, where γ_{LV} is the surface tension of the liquid, and W is the work of adhesion. Assuming that W is composed of the dispersion and polar components of the surface energy of the solid and surface tension of the liquid (the Owens–Wendt approach),[2] $W = 2\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}} + \sqrt{\gamma_{\mathrm{S}}^{\mathrm{p}}\gamma_{\mathrm{L}}^{\mathrm{p}}}\right)$, one obtains

$$2\left(\sqrt{\gamma_{\mathrm{S}}^{\mathrm{d}}\gamma_{\mathrm{L}}^{\mathrm{d}}} + \sqrt{\gamma_{\mathrm{S}}^{\mathrm{p}}\gamma_{\mathrm{L}}^{\mathrm{p}}}\right) = \gamma_{\mathrm{LV}}(1 + cos\ \theta) \qquad \text{(S1)}$$

Using eq. S1, the surface energy of the solid surface (i.e., the self-assembled monolayer), $\gamma_{\mathrm{YD}} = \gamma_{\mathrm{S}} = \gamma_{\mathrm{S}}^{\mathrm{d}} + \gamma_{\mathrm{S}}^{\mathrm{p}}$, was obtained from advancing contact angles of liquids with different surface tensions $\gamma_{\mathrm{LV}} = \gamma_{\mathrm{L}}^{\mathrm{d}} + \gamma_{\mathrm{L}}^{\mathrm{p}}$ (water: $\gamma_{\mathrm{L}}^{\mathrm{d}}$ = 21.8 mJ/m^2, $\gamma_{\mathrm{L}}^{\mathrm{p}}$= 51 mJ/m^2; methylene iodide:[2] $\gamma_{\mathrm{L}}^{\mathrm{d}}$ = 48.5 mJ/m^2, $\gamma_{\mathrm{L}}^{\mathrm{p}}$= 2.3 mJ/m^2). The resulting values of γ_{YD} for the three aromatic SAMS are listed in Table 2 of the main article ($\Delta\gamma_{\mathrm{YD}}$ = 1 mJ/m^2). $\gamma_{\mathrm{YD,ODT}}$ determined in a similar manner was 27 mJ/m^2. In all four SAM systems, the polar contribution to the surface energy of the solid was quite low, i.e., the surface energy of the monolayers arose mainly from dispersion intermolecular interactions.

FRICTION COEFFICIENTS

Friction coefficients μ were obtained from fits of straight lines to F vs. L data measured in ethanol (Tables S1 and S2). $\Delta\mu$ is the standard deviation in μ from the linear fit. Mean values of μ and the standard error (standard deviation of the mean) are given in bold font.

Table S1. Data from SFA experiments in ethanol. Radius of curvature R (if measured), sliding speed v, friction coefficient μ, and standard deviation in μ from linear fit, $\Delta\mu$.

Thiophenol, TP			
***R* (cm)**	***v* (μm/s)**	**μ**	**$\Delta\mu$**
	3.2	0.68	0.05
	3.2	0.59	0.01
	3.2	0.69	0.02
	3.2	0.52	0.08
	3.2	0.50	0.01
	3.2	0.43	0.02
	3.2	0.53	0.02
	3.2	0.51	0.01
2.53	1.6	0.63	0.04
2.31	1.6	0.73	0.09
4.69	1.6	0.53	0.02
4.69	1.6	0.52	0.04
4.69	1.6	0.52	0.03
	1.6	0.52	0.03
		0.56 ± 0.02	

Phenylthiophenol, PTP			
***R* (cm)**	***v* (μm/s)**	**μ**	**$\Delta\mu$**
	3.2	0.284	0.004
	3.2	0.26	0.01
	3.2	0.248	0.009
	3.2	0.26	0.08
	3.2	0.298	0.006
	3.2	0.246	0.003
1.97	1.6	0.22	0.02
4.41	1.6	0.242	0.009
	1.6	0.32	0.02
2.57	1.6	0.227	0.006
		0.26 ± 0.01	

Terphenylthiol, TPT			
***R* (cm)**	***v* (μm/s)**	**μ**	**$\Delta\mu$**
	3.2	0.237	0.002
	3.2	0.237	0.003
	3.2	0.245	0.003
	3.2	0.313	0.005
	3.2	0.245	0.004
	3.2	0.271	0.005
	3.2	0.198	0.006
	3.2	0.221	0.002
3.13	1.6	0.29	0.02
3.13	1.6	0.278	0.009
3.13	1.6	0.28	0.01
3.13	1.6	0.25	0.01
	1.6	0.263	0.007
	1.6	0.30	0.01
2.25	1.6	0.290	0.005
2.25	1.6	0.269	0.006
2.25	1.6	0.294	0.003
2.25	1.6	0.263	0.003
		0.263 ± 0.007	

Octadecanethiol, ODT			
***R* (cm)**	***v* (μm/s)**	**μ**	**$\Delta\mu$**
2.9	3.2	0.079	0.007
	3.2	0.060	0.001
	3.2	0.094	0.004
	3.2	0.132	0.007
	3.2	0.095	0.003
		0.09 ± 0.01	

A total of 25 different pairs of surfaces were used for SFA experiments (Table S1), in each pair one surface was a SAM on template-stripped silver and the other was bare mica. In some experiments, more than one contact position was investigated and/or a second loading-unloading cycle was done on the same contact position. The results were reproducible as long as the surfaces were undamaged. In Table S1, *R* is the radius of curvature of the surfaces when undeformed (not in contact). In some cases, *R* was not measured due to surface damage at the end of the experiment or low contrast in the interference pattern when the silver thickness was higher than 50 nm, which was the case in some early experiments.

Eight SAM-covered surfaces were investigated with AFM (Table S2). Also here, several positions were investigated on some of the surfaces. Si tips with a native oxide layer were used as the opposing surface. In Table S2, *R* is the tip radius determined by reverse imaging of a calibration sample (TGT01, MikroMasch) in air.

Table S2. Data from AFM experiments in ethanol. Tip radius *R*, sliding speed *v*, friction coefficient μ, and standard deviation in μ from linear fit, $\Delta\mu$.

Thiophenol, TP			
***R* (nm)**	***v* (μm/s)**	μ	$\Delta\mu$
56	2	0.73	0.06
56	2	0.56	0.03
		0.64 ± 0.08	

Terphenylthiol, TPT			
***R* (nm)**	***v* (μm/s)**	μ	$\Delta\mu$
56	2	0.28	0.01
69	2	0.32	0.03
		0.30 ± 0.02	

Phenylthiophenol, PTP			
***R* (nm)**	***v* (μm/s)**	μ	$\Delta\mu$
56	2	0.34	0.03
69	2	0.31	0.02
69	2	0.25	0.06
69	2	0.28	0.02
		0.29 ± 0.02	

Octadecanethiol, ODT			
***R* (nm)**	***v* (μm/s)**	μ	$\Delta\mu$
69	2	0.075	0.003
69	2	0.085	0.006
159	2	0.071	0.005
		0.077 ± 0.004	

CRITICAL SHEAR STRESSES

Critical shear stresses $S_c = F/A$ (Tables S3 and S4) were determined from measured values of F in dry N_2 gas and nominal contact areas A. In the SFA experiments, A was directly measured from the interference pattern in adhesive contact, whereas for the AFM studies, A was calculated using the TCCM model described in the main article. Mean values of S_c and the standard error (standard deviation of the mean) are given in bold font.

Eleven different pairs of surfaces (SAM against bare mica) were studied in N_2 with the SFA (Table S3), and 14 SAM surfaces were used in the AFM. Commonly, more than one contact position was studied. Some of these pairs or surfaces were also used for experiments in ethanol (Table S1 and S2). In such cases, the experiments in N_2 were done first to avoid contamination.

Table S3. Data from SFA experiments in dry N_2 gas. Radius of curvature R (if measured), sliding speed v, critical shear stress $S_c = F/A$, and its standard deviation ΔS_c.

Thiophenol, TP			
***R* (cm)**	***v* (μm/s)**	**S_c (MPa)**	**ΔS_c (MPa)**
	~3	23.6	ca. 3
	~3	20.6	ca. 3
	~3	25.3	ca. 3
		23 ± 1	

Terphenylthiol, TPT			
***R* (cm)**	***v* (μm/s)**	**S_c (MPa)**	**ΔS_c (MPa)**
	9	10.4	1.6
	9	9.7	1.6
2.25	3.9	12.0	0.6
2.25	3.9	13.9	0.4
		11.5 ± 0.9	

Phenylthiophenol, PTP			
***R* (cm)**	***v* (μm/s)**	**S_c (MPa)**	**ΔS_c (MPa)**
2.84	5.9	7.1	0.6
2.84	5.9	8.9	0.6
	4.4	6.5	0.6
	4.4	4.7	0.3
3.95	2.7	8.79	0.08
2.57	3.2	7.8	0.3
		7.3 ± 0.6	

Octadecanethiol, ODT			
***R* (cm)**	***v* (μm/s)**	**S_c (MPa)**	**ΔS_c (MPa)**
2.9	~3	5.5	0.3
2.9	~3	3.3	0.2
	~3	2.5	0.2
	~3	2.8	0.2
	~3	1.99	0.07
	~3	2.7	0.1
2.8	~3	3.7	0.1
1.55	3.8	2.97	0.06
	4.6	2.9	0.2
	3.6	2.1	0.2
	3.2	1.79	0.09
		2.9 ± 0.3	

Table S4. Data from AFM experiments in N_2 gas. Tip radius R, sliding speed v, monolayer thickness h, work of adhesion W, Young's modulus E, critical shear stress S_c, standard deviation ΔS_c, and transition parameter ζ.

Thiophenol, TP							
***R* (nm)**	***v* (μm/s)**	***h* (nm)**	***W* (J/m^2)**	***E* (GPa)**	***S*$_c$ (MPa)**	**Δ*S*$_c$ (MPa)**	ζ
56	2	0.6	0.055	7	750	150	0.0044
69	2	0.6	0.055	7	700	140	0.0044
69	2	0.6	0.050	7	600	120	0.0040
			0.053±0.002		**683±44**		

Phenylthiophenol, PTP							
***R* (nm)**	***v* (μm/s)**	***h* (nm)**	***W* (J/m^2)**	***E* (GPa)**	***S*$_c$ (MPa)**	**Δ*S*$_c$ (MPa)**	ζ
69	2	1.2	0.075	3	400	52	0.0280
56	2	1.2	0.065	7	410	53	0.0104
56	2	1.2	0.067	7	330	43	0.0107
69	2	1.2	0.045	7	400	52	0.0072
			0.063±0.006		**385±18**		

Terphenylthiol, TPT							
***R* (nm)**	***v* (μm/s)**	***h* (nm)**	***W* (J/m^2)**	***E* (GPa)**	***S*$_c$ (MPa)**	**Δ*S*$_c$ (MPa)**	ζ
56	2	1.6	0.068	7	550	72	0.0145
56	2	1.6	0.067	7	480	62	0.0143
56	2	1.6	0.060	7	400	52	0.0128
56	2	1.6	0.060	7	570	74	0.0128
69	2	1.6	0.050	7	520	68	0.0107
69	2	1.6	0.060	7	380	49	0.0128
69	2	1.6	0.065	7	380	49	0.0139
69	2	1.6	0.060	7	440	57	0.0128
			0.061±0.003		**465±27**		

Octadecanethiol, ODT							
***R* (nm)**	***v* (μm/s)**	***h* (nm)**	***W* (J/m^2)**	***E* (GPa)**	***S*$_c$ (MPa)**	**Δ*S*$_c$ (MPa)**	ζ
69	2	2.4	0.045	0.2	13	1.7	0.504
69	2	2.4	0.060	0.2	26	3.4	0.672
			0.053±0.008		**19.5±6.5**		
372	2	2.4	0.057	0.5	4.0	0.4	0.255
372	2	2.4	0.060	0.2	3.0	0.3	0.672
372	2	2.4	0.052	0.5	5.5	0.6	0.233
372	2	2.4	0.060	0.2	3.8	0.4	0.672
372	2	2.4	0.057	0.5	9.0	0.9	0.255
			0.057±0.001		**5.1±1.1**		

REFERENCES

1. J. N. Israelachvili, *Intermolecular and Surface Forces*. 3rd ed., Elsevier, Amsterdam, 2011.

2. H. Y. Erbil, *Surface Chemistry of Solid and Liquid Interfaces*. Blackwell, Oxford, 2006.