

Electronic Supplementary Material (ESI)

The Thermodynamics of Self-Assembled Monolayers Formation: A Computational and Experimental Study of Thiols on Flat Gold Surfaces.

Alberto Zoccante,^a Eleonora Cara,^b Federico Ferrarese Lupi,^b Philipp Honicke,^{c,e} Yves Kayser,^{c,f} Burkhard Beckhoff,^c Petr Klapetek,^d Davide Marchi,^a and Maurizio Cossi.*^a

a) Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale, via T. Michel 11, I-15121, Alessandria, Italy.

b) Istituto Nazionale di Ricerca Metrologica (INRIM), Strada delle Cacce, 91, I-10135, Torino, Italy.

c) Physikalisch-Technische Bundesanstalt (PTB), Abbestr. 2-12, 10587 Berlin, Germany.

d) Department of Nanometrology, Czech Metrology Institute (CMI), Okružní 31, 63800 Brno, Czech Republic.

e) Helmholtz-Zentrum Berlin, Hahn-Meitner Platz 1, 14109 Berlin, Germany.

Force-field parameters for sulfur/gold interactions.

As explained in the text, most force-field (FF) parameters used in the MD are taken from standard GROMOS 54A7 FF, except the Lennard-Jones parameters used to reproduce sulfur/gold interactions both for thiols and for thiylys. The latter parameters were optimized against quantum-mechanical calculations on small model systems in ref. E. Cara et al. *Journal of Materials Chemistry C*, 2020, **8**, 16513–16519. For the sake of the readers we report here these optimized parameters, taken from the ESI of the cited paper.

Table S1. Lennard-Jones parameters fitted on DFT calculations.

Pair	ϵ [kcal/mol]	σ [Å]
Physisorbed thiol S-Au	4.203	3.247
Chemisorbed thiylyl S-Au	24.50	2.495

DFT estimate of the S-H dissociation energy.

As explained in the text, the chemical potential of thiylyl SAMs depends on various contributions, among which the free energy change of the dissociation reaction:



Since the experimental values of ΔG_{diss} are not available for MMC or MPA, we resorted to DFT calculations to evaluate them. The bond dissociation energies (BDE) of thiol and molecular hydrogen can be directly computed (including semiempirical corrections for dispersion energy and counterpoise

corrections for the BSSE), then thermal contributions for enthalpies and entropies are added with Boltzmann averages referred to translational, rotational and vibrations motions. The last term requires the calculation of harmonic frequencies, at the same level as BDE.

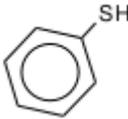
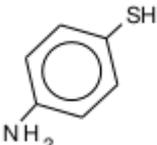
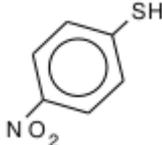
Before applying this procedure to the thiols of interest, the performance of different density functionals and basis sets has been tested against the experimental values of dissociation enthalpies (ΔH_{diss}): we used enthalpies rather than free energies for this trial because the former are more easily available in the experimental literature; once determined the best choice of functional and basis, ΔG_{diss} were computed at the same level.

For MMC, we considered some simple aromatic thiols, namely benzenethiol, *p*-aminobenzenethiol and *p*-nitrobenzenethiol to include both electron donating and electron withdrawing groups.

The results are collected below in Tables S2-S4: one can see that none of the tested functionals can reproduce all the experimental enthalpies fairly, but the best performance is obtained by B3P86 with the largest basis set, namely cc-pvtz.

Then the value of the free energy change for reaction 1 involving MMC was computed at the B3P86/cc-pvtz level, obtaining $\Delta G_{diss} = 130.0$ kJ/mol.

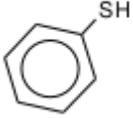
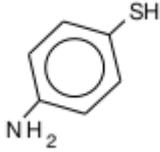
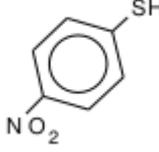
Table S2. Enthalpy change (kJ/mol) for reaction 1, computed for MMC at the B3LYP level with various basis sets, including thermal contributions at 298 K and Grimme's dispersion corrections, and compared to experimental values.

Basis set	B3LYP		
			
6-31G(d)	90.3	69.3	103.0
6-31G(d,p)	94.9	73.5	107.4
6-31+G(d,p)	96.6	76.2	109.6
6-311G(d,p)	*	77.7	109.8
6-31G(2d,2p)	99.6	78.3	111.8
cc-pvdz	92.5	71.6	105.2
cc-pvtz	94.0	81.8	115.6
Exp. ^(a)	113.0	75.3	125.6

(a) Bond dissociation enthalpies: ref. 1 for thiols, 2 for H₂.

* Convergence problems.

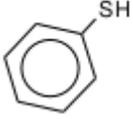
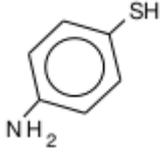
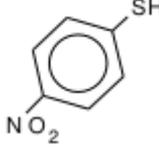
Table S3. Enthalpy change (kJ/mol) for reaction 1, computed for MMC at the B3P86 level with various basis sets, including thermal contributions at 298 K, and compared to experimental values.

B3P86			
Basis set			
6-31G(d)	98.4	76.9	111.3
6-31G(d,p)	103.1	81.1	115.8
6-31+G(d,p)	104.8	83.7	117.9
6-311G(d,p)	106.5	86.1	119.0
6-31G(2d,2p)	108.4	86.5	120.8
cc-pvdz	110.2	87.9	121.3
cc-pvtz	112.0	89.7	124.5
Exp. ^(a)	113.0	75.3	125.6

(a) Bond dissociation enthalpies: ref. 1 for thiols, 2 for H₂.

* Convergence problems.

Table S4. Enthalpy change (kJ/mol) for reaction 1, computed for MMC at the BLYP level with various basis sets, including thermal contributions at 298 K, and compared to experimental values.

BLYP			
Basis set			
6-31G(d)	82.0	56.7	94.6
6-31G(d,p)	86.6	61.0	98.0
6-31+G(d,p)	88.7	64.0	*
6-311G(d,p)	89.4	65.0	101.3
6-31G(2d,2p)	91.5	66.1	103.5
cc-pvdz	95.1	69.3	106.2
cc-pvtz	95.9	70.1	107.7
Exp. ^(a)	113.0	75.3	125.6

(a) Bond dissociation enthalpies: ref. 1 for thiols, 2 for H₂.

* Convergence problems.

For MPA, we followed the same approach (limiting the test calculations to B3LYP and B3P86 functionals, given the results obtained for MMC). In this case, many fonts report similar dissociation enthalpies for different alkyl thiols, i.e. 146 kJ/mol. The computed dissociation enthalpies are reported in table S5: also in this case, the comparison with the experiment indicates that the most reliable level is B3P86/cc-pvtz.

At this level, the best estimate for MPA dissociation free energy is $\Delta G_{diss} = 119.6$ kJ/mol.

Table S5. Enthalpy change (kJ/mol) for reaction 1, computed for MPA with various basis sets, including thermal contributions at 298 K, and compared to experimental values.

Basis set	B3LYP	B3P86
6-31G(d)	121.9	129.2
6-31G(d,p)	125.7	133.1
6-31+G(d,p)	125.8	133.3
6-311G(d,p)	130.2	138.1
cc-pvdz	129.3	136.4
cc-pvtz	130.0	138.0
Exp. (a)	146	146

Averaged free energies.

In the text we mentioned that the SAM insertion free energies, computed by GROMACS with the BAR method, have been obtained for five random thiols/thiyls in each monolayer, to account for layer inhomogeneities.

In Tables S6-S9 we report the computed Helmholtz free energies for all the samples considered, along with the mean free energy and the corresponding Standard Error of the Mean (SEM).

Table S6. Helmholtz free energy of insertion (kJ/mol) for physisorbed thiol MMC.

SAM density (nm ⁻²)	Sample # 1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	$\langle \Delta A \rangle$	SEM
0.56	-228.00	-251.07	-228.28	-234.69	-236.07	-235.62	4.19
2.05	-117.89	-89.84	-108.96	-80.58	-88.17	-97.09	6.99
3.16	-133.48	-121.91	-67.73	-80.70	-80.85	-96.93	12.91
3.35	-79.54	-77.24	-77.32	-62.32	-67.72	-72.83	3.33
3.54	-109.58	-104.21	-152.61	-109.11	-103.21	-115.74	9.30
3.72	-38.75	-79.47	-78.06	-65.32	-66.47	-65.61	7.31
4.47	17.79	41.50	44.25	13.24	21.98	27.75	6.34
4.84	157.70	196.12	97.97	109.31	105.72	133.36	18.88
5.03	219.97	269.26	340.01	207.63	176.64	242.70	28.54

Table S7. Helmholtz free energy of insertion (kJ/mol) for chemisorbed thiol MMC.

SAM density (nm ⁻²)	Sample # 1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	$\langle\Delta A\rangle$	SEM
0.50	-354.58	-355.22	-356.90	-347.49	-345.07	-351.85	2.34
2.12	-299.34	-317.82	-282.49	-365.36	-284.26	-309.85	15.26
3.53	-255.03	-261.24	-249.86	-248.14	-261.15	-255.08	2.74
3.93	-187.39	-207.63	-183.00	-169.34	-232.90	-196.05	11.07
4.00	-173.42	-176.90	-169.70	-171.17	-172.56	-172.75	1.21
4.06	-77.75	-134.47	-137.90	-155.22	-177.31	-136.53	16.54
4.11	-83.09	-132.33	-95.30	-67.31	-99.72	-95.55	10.78
4.24	-66.66	-89.53	-74.31	-127.26	-72.81	-86.11	10.95
4.45	23.55	21.32	8.21	38.16	17.96	21.84	4.85
4.84	198.62	288.41	307.48	316.22	381.72	298.49	29.49

Table S8. Helmholtz free energy of insertion (kJ/mol) for physisorbed thiol MPA.

SAM density (nm ⁻²)	Sample # 1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	$\langle\Delta A\rangle$	SEM
0.56	-136.15	-135.48	-137.13	-138.66	-135.03	-136.49	0.65
1.86	-139.52	-145.66	-147.25	-149.43	-147.44	-145.86	1.69
2.61	-142.67	-148.11	-141.37	-142.12	-141.87	-143.23	1.24
3.54	-68.36	-80.24	-101.77	-105.91	-92.47	-89.75	6.93
3.72	-97.44	-113.78	-96.88	-78.50	-109.88	-99.30	6.18
3.91	-81.48	-52.64	-70.01	-77.88	-82.98	-73.00	5.56
4.09	-80.40	-76.22	-93.80	-95.90	-91.24	-87.51	3.89
4.28	-60.62	-72.19	-86.44	-74.68	-47.96	-68.38	6.55
5.21	-31.43	-39.40	4.57	-14.02	1.28	-15.80	8.69
6.51	43.78	14.37	44.81	6.78	25.98	27.14	7.64
7.45	211.55	232.88	231.21	224.61	288.58	237.77	13.25

Table S9. Helmholtz free energy of insertion (kJ/mol) for chemisorbed thiol MPA.

SAM density (nm ⁻²)	Sample # 1	Sample # 2	Sample # 3	Sample # 4	Sample # 5	$\langle\Delta A\rangle$	SEM
0.50	-217.49	-219.79	-217.48	-219.31	-217.43	-218.30	0.52
1.74	-218.39	-220.99	-221.12	-221.23	-227.37	-221.82	1.48
2.56	-221.11	-222.40	-220.37	-222.26	-225.41	-222.31	0.86
3.40	-211.47	-214.34	-209.06	-199.56	-202.37	-207.36	2.78
3.80	-183.08	-172.85	-182.25	-154.57	-196.01	-177.75	6.87
4.22	-181.09	-152.55	-161.73	-156.17	-181.98	-166.70	6.23
5.21	-130.65	-120.26	-119.82	-111.20	-135.05	-123.40	4.24
6.51	23.60	-5.09	-40.70	-9.11	-6.64	-7.59	10.19
7.24	156.84	184.53	145.60	219.06	108.98	163.00	18.53