ELECTRONIC SUPPLEMENTARY INFORMATION FOR

Is there a Au-S bond dipole in self-assembled monolayers on gold?

LinJun Wang,[a,c] Gerold M. Rangger,[b] ZhongYun Ma,[c] QiKai Li,[c] Zhigang Shuai,*[a,c]
Egbert Zojer,*[b] and Georg Heimel,[d]

[a] *Department of Chemistry, Tsinghua University, 100084 Beijing, PR China. Fax: +86 10 6279 7689; Tel: +86 10 6279 7689; E-mail: zgshuai@tsinghua.edu.cn*
[b] *Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria. Fax: +43/(0)316/873-8466; Tel: +43/(0)316/873-8475; E-mail: egbert.zojer@tugraz.at*
[c] *Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Sciences (BNLMS), Institute of Chemistry, Chinese Academy of Sciences, 100190 Beijing, PR China*
[d] *Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, D-12489 Berlin, Germany*

Contents

1. Computational methods

All calculations were performed at the density functional theory level using the PW91 exchange-correlation functional, as it has been (empirically) found to perform slightly better for van-der-Waals bonded systems than other typical (semi)local functionals.[1] Spin-restricted calculations were performed for all closed-shell systems and spin-unrestricted calculations for the radical molecular monolayers. We used a plane-wave basis set with a cutoff energy of 20 Ryd to expand the valence Kohn-Sham orbitals and the projector augmented-wave method[2,3] to describe the valence-core interactions. An 8×5×1 Monkhorst-Pack grid[4] was employed for the *k*-point sampling of the 2D Brilluoin zone, together with a first-order Methfessel-Paxton smearing[5] with a broadening of 0.2 eV.

Calculations were performed with periodic boundary conditions using the repeated slab approach, where five layers of gold atoms model the Au(111) substrate. For reasons of consistency, all thiols are arranged in the same $p(\sqrt{3}\times3)$ surface unit cell containing two molecules with sulfur atoms bonded at *fcc*-hollow sites slightly shifted to the bridge site.[6] The molecular packing assumed in the calculations is experimentally found for biphenylthiols on Au(111)[7] and is consistent with the surface area per molecule found for alkanethiols on Au(111).[8,9] A vacuum gap (> 20Å) is introduced between the uppermost SAM atom and the subsequent periodic image of the slab to exclude spurious electronic interaction; a dipole layer in the middle of the vacuum region compensates for the net-dipole moment of the asymmetric slabs (molecules adsorbed only on one side).[10] The absorption structures of the thiols on the gold surface were obtained through a geometry optimization in internal coordinates[11] where the bottom three gold layers were fixed at their equilibrium positions in the bulk (lattice constant 4.175 Å[6]), while the top two gold layers and all SAM atoms were fully optimized until the remaining forces were smaller than 0.01 eV/Å.

2. Additional electronic parameters related to the saturated and the radical scenarios

Table S1. DFT-calculated vacuum-level difference, ΔE_{vac}, between the head-group side and the thiol-group side of the free-standing molecular monolayer; left-sided ionisation potential, IP_{left}, right-sided ionisation potential, IP_{right}, of the free-standing monolayers; and the difference between IP_{right} and the IP of the SAM bonded to gold, E_{corr}. Only those values are listed that are not already contained in the main paper.

	saturated scenario						radical scenario	
	I	I	II	II	II	II		
system	ΔE_{vac} [eV]	IP_{right} [eV]	IP_{left} [eV]	E_{corr} [eV]	ΔE_{vac} [eV]	IP_{right} [eV]	ΔE_{vac} [eV]	IP_{right} [eV]
C1-NH_2	-0.62	7.12	9.19	0.01	-2.05	7.14	-1.85	7.10
C1-CN	1.99	10.16	9.23	-0.10	0.86	10.09	1.03	10.10
C2-NH_2	-1.30	3.73	5.47	0.11	-1.76	3.71	-3.56	2.51
C2-CN	3.81	8.94	5.46	0.16	3.47	8.93	1.65	7.73
C3-NH_2	-0.84	3.05	4.96	0.13	-1.93	3.03	-4.04	2.07
C3-CN	3.60	7.34	4.92	0.14	2.42	7.34	0.26	6.40
T1-NH_2	-1.34	2.92	4.79	0.12	-1.87	2.92	-4.16	1.73
T1-CN	3.98	8.28	4.79	0.14	3.48	8.27	1.22	7.10
T2-NH_2	-0.90	3.14	4.81	0.11	-1.67	3.14	-3.83	1.98
T2-CN	3.63	7.73	4.85	0.11	2.87	7.72	0.75	6.56
T3-NH_2	-0.95	3.04	4.71	0.12	-1.67	3.04	-3.93	1.96
T3-CN	3.59	7.60	4.72	0.12	2.88	7.60	0.64	6.53

3. Effect of spin polarisation on the total energy and the total dipole moment along the surface normal

Table S2. DFT-calculated total energy and total dipole moment per unit cell along the surface normal of the combined C2-CN thiol-gold system, the pristine gold slab, the free-standing molecular monolayers of unsaturated and H-saturated species, and the layer of saturating H-atoms at the two positions illustrated in Fig. 1c in the main text. The results for spin-polarised and non spin-polarised (*i.e.*, spin-restricted) calculations are given. Regarding the total energy, spin polarisation affects only the radical monolayer and the isolated hydrogens. The dipole moment, which is the most important quantity in the present study, is influenced by spin-polarisation only for the free-standing radical monolayer, *i.e.*, spin-polarised calculations are recommended there to obtain reliable results.

single point calculations	total energy [eV]		dipole moment [eÅ]	
	no spin polarisation	with spin polarisation	no spin polarisation	With spin polarisation
SAM/Au(111) total system	-406.13	-406.13	0.655	0.654
pristine gold slab	-91.84	-91.84	0.001	0.000
radical monolayer	-311.20	-311.44	0.390	0.414
saturated monolayer I	-320.95	-320.95	0.955	0.955
saturating hydrogen I	-0.57	-2.79	0.000	0.000
saturated monolayer II	-320.89	-320.89	0.868	0.868
saturating hydrogen II	-0.17	-2.2	0.000	0.000

4. Effect of the position of the saturating hydrogen atoms on IP_{left}

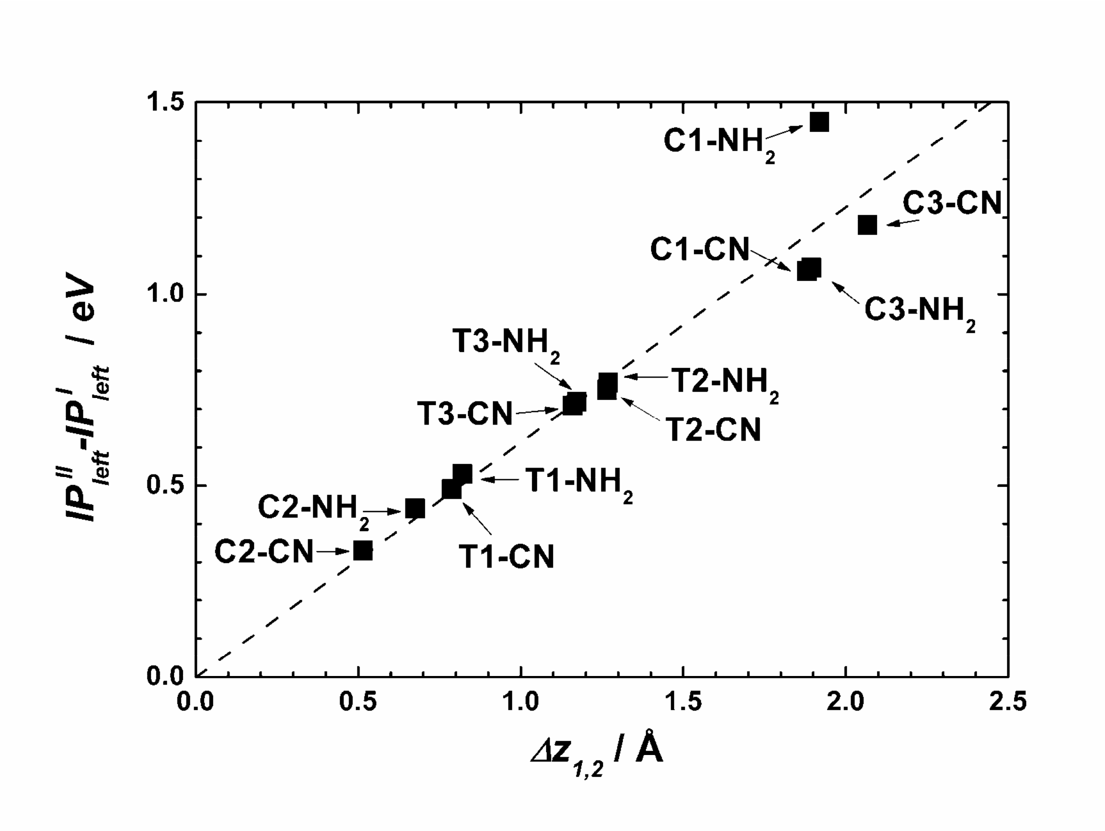

Figure S1. Difference between the DFT-calculated IP_{left} values for saturating hydrogen positions I and II as a function of the difference in the corresponding hydrogen *z*-coordinates. The dashed line is a linear fit through the origin.

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