SUPPORTING INFORMATION

A periodic mixed gaussians-plane waves DFT study on simple thiols on Au(111): adsorbate species, surface reconstruction, and different thiols functionalization.

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Table S1. A summary of calculated and experimental energetics and geometrical parameters of Me-SH, Me-S$^-$ and Me-S• on Au(111). **D** is for S-Au(111) distance; **Au-S** is for the S distances from the closest Au atoms; **ζ** is for the complementary angle of C-S-Au(111) angle.

Species	Experimental/ Calculated	Attack Site	D, Å	Au-S, Å	ζ, degree	ΔE_f, kcal/mol	Ref.
Me-S•	PD	Atop	2. 42(3)	2. 42(3)	~ 50		32
Me-S•	BLYP	Fcc-bridge	2.09	2.56	46.97		73
Me-S•	PW91/PBE	Fcc-bridge	2.07			-39.66/-29.58	74
Me-S•	HREELS	not reported				-11.6/ -13.9	75
Me-S•	HREELS/PBE	Fcc-bridge	2.05	2.50	52.7		26
Me-S•	NIXSW	ontop	2.50(5)	2.50(5)			76
Me-S•	MP2	hollow	1.936		76		22
Me-S•	PW91/PBE	Fcc-bridge			58.5	-38.5/-26.0	29
Me-S•	PW91	Fcc-bridge	2.05	2.49		-21.8	27
Me-S•	BLYP	Fcc-bridge		2.68&2.85	65.8	-39.9	77
Me-S•	PW91	Fcc-bridge		2.510 unrelaxed 2.370 relaxed	56.4 62.7	-42.36 unrelaxed -52.99 relaxed	78
Me-S•	TDS and high-resolution soft X-ray photoelectron spectroscopy.					-34	79
Me-S•	STM/PW91	Fcc-bridge		2.452 2.467	52.9	-43.4	34
Me-S•	PW91	Fcc-bridge		2.52/2.49			34
Me-S•	Functional not reported	Fcc		1.788			24
Me-S•	NIXSW	On-top/adatom					33
Me-S•	PBE	Fcc-bridge		2.49	56	-35.6	37
Me-S•	PBE	on-top/adatom		2.30	72	-47.3	37
Me-S•	PBE	on-top/chain		2.44	46	-56.0	37
Me-S•	PBE	fcc-bridge	2.04	2.49	54.3	-38.0	80
Me-S•	Functional not reported				53-61	-37.1	81
MeSH	PBE	ontop		2.812		-10.1 (layers relaxed)	78
MeSH	STM/PW91	on-top		2.668	72	-8.6	34
Et-S•	B3LYP	fcc-bridge	-	2.634	67.1	-24.5 (cluster model)	83
Et-S•	PBE	-			53-61	-37.5	82
Et-SH	PBE	atop		2.799	-	-11.1 (layer relaxed)	78
Ph-S•	PBE	fcc-hollow		2.509	60.95	-31.6	84
Ph-S•	HF	-		2.500	37	-2.3	85
Ph-CH_2-S•	PBE	fcc-bridge	2.1	2.530	80	-	86
Ph-SH	HF	-	-	-	-	-1.6	85

Table S2. The NBO second order perturbation theory estimate of the Au-S bond strengths in different computed species and models.

Models/Species	Interaction	Energy (Kcal/mol)	
Au36	MeSH	$3p_z$(S)-6s(Au)	19.7
		3s(S)-6s(Au)	4.8
		$3p_z$(S)-6s(Au)	
	MeS^-	3s(S)-6s(Au)	14.8; 16.2
		3s(S)-$6p_z$(Au)	4.8; 2.9
		$3p_x$(S)-6s(Au)	3.1; 2.5
			3.1, 2.3
		$3p_z$(S)-6s(Au)	
	MeS•	3s(S)-6s(Au)	17.8; 17.9
		3s(S)-6 p_z(Au)	5.2; 3.3
		$3p_x$(S)-6s(Au)	4.1; 2.8
			3.0; 3.1
Au37	MeSH	$3p_z$(S)-6s(Au)	36.5
		3s(S)-6s(Au)	2.7
	MeS^-	$3p_z$(S)-6s(Au)	102.0
		3s(S)-6s(Au)	6.5
	MeS•	$3p_z$(S)-6s(Au)	105.6
		3s(S)-6s(Au)	7.3
Au38	Au_{ad}-MeSH-Au_{ad}	3s(S)-6s(Au)	9.7; 8.4
		$3p_x$(S)-6s(Au)	4.7; 7.8
	Au_{ad}-MeS^--Au_{ad}	$3p_z$(S)-6s(Au)	20.1; 33.6
		3s(S)-6s(Au)	3.6; 3.7
		$3p_x$(S)-6s(Au)	22.8; 7.0
	Au_{ad}-MeS•-Au_{ad}	$3p_z$(S)-6s(Au)	26.9 ; 29.6
		3s(S)-6s(Au)	4.1 ; 3.8
		$3p_x$(S)-6s(Au)	19.3 ; 13.5
Au37	MeSH-Au_{ad}-	3s(S)-6s(Au)	2.2 ; 2.4
	MeSH	$3p_x$(S)-6s(Au)	21.1 ; 21.0
		3s(S)-6s(Au)[a]	4.7 ; 3.9
	MeS^--Au_{ad}-MeS^-	$3p_x$(S)-6s(Au)[a]	2.6 ; 4.4
		$3p_z$(S)-6s(Au)[a]	10.4 ; 7.4
		3s(S)-6s(Au)[b]	5.0 ; 4.8
		$3p_x$(S)-6s(Au)[b]	84.7 ; 80.0
		$3p_x$(S)-$6p_x$(Au)[b]	4.1 ; 3.7
		$3p_x$(S)-$6d_{xz}$(Au)[b]	3.4 ; 3. 0
		$3p_x$(S)-$6d_{xy}$(Au)[b]	4.2 ; 3. 9
		3s(S)-6s(Au)[a]	6.2 ; 4.3
	MeS•-Au_{ad}-MeS•	$3p_x$(S)-6s(Au)[a]	5.8 ; 5.2
		$3p_z$(S)-6s(Au)[a]	15.0; 8.6
		3s(S)-6s(Au)[b]	6.2 ; 5.0
		$3p_x$(S)-6s(Au)[b]	73.1; 70.3
		$3p_z$(S)-6s(Au)[b]	2.5 ; 0.9
		$3p_x$(S)-$6p_x$(Au)[b]	3.9; 3.4
		$3p_x$(S)-$6d_{xz}$(Au)[b]	3.0; 2.8
		$3p_x$(S)-$6d_{xy}$(Au)[b]	3.9 ; 3.7

a) bond corresponds to that of sulphur gold atom in the Au(111)

b) bond corresponds to S-Au_{ad} atom.

Table S3. The experimental from ref 105 and B3LYP/LACV3P**++ computed bond dissociation energy (in vacuum and in kcal/mol) of different sulphur compounds studied here.

Species	Experimental BDE	cal. BDE
MeS-H	92±1.5	82.5
MeS-Me	77±1.5	54.5
EtS-Et	74±2	49.8
PhS-Ph	-	54.2
PhS-Me	67.4±1.5	44.3
MeS-Ph	89.2±2	62.2

Table S4. DFT Computed energetics and structural information for the substituted long alkylthiols on Au(111). **D** is for S-Au(111) distance; **Au-S** is for the S distances from the closest Au atoms; **ζ** is for the complementary angle of C-S-Au(111) angle.

Species	Attack site	D (Å)	Au-S, Å	ζ, degree	ΔE_f, kcal/mol
Au_{36}-Au_{ad}MeSH (hcp)	atop	2.44	2.44	107.1	-42.7
Au_{36}-Au_{ad}-MeS^-(hcp)	atop	2.35	2.35	103.3	-52.1
Au_{36}-Au_{ad}-MeS•(hcp)	atop	2.31	2.31	105.0	-22.4
Au_{36}-MeSH-Au_{ad}-MeSH	atop	2.56	2.56, 2.56	76.7, 77.4	-17.2
Au_{36}-MeS^--Au_{ad}-MeS^-	atop- atop	2.71 ; 2.78	2.36, 2.71 ; 2.36, 2.78	76.3, 78.5	-7.3
Au_{36}-MeS•-Au_{ad}-MeS•	atop- atop	256 ; 2.58	2.36, 2.56 ; 2.35, 2.58	72.6, 73.0	-47.2
Au_{36}-Au_{ad}-MeSH-Au_{ad}	Bridge	1.95	2.52, 2.54	645	-23.3
Au_{36}-Au_{ad}-MeS^--Au_{ad}	Bridge	1.95	2.46, 2.47	54.7	-65.9
Au_{36}-Au_{ad}-MeS•-Au_{ad}	Bridge	1.87	2.42, 2.42	69.1	-70.0
Au_{36}-MeSMe	*quasi*-atop	2.76	2.84	81.3, 75.6	-3.3
Au_{36}-Au_{ad}-MeSMe	*quasi*-atop	2.43	2.43	68.9, 76.0	-23.4
Au_{36}-EtSEt	*quasi*-atop	2.78	2.81	80.9, 73.4	-12.9
Au_{36}-Au_{ad}-EtSEt	*quasi*-atop	2.43	2.43	67.7, 77.1	-24.6
Au_{36}-EtS•	fcc-bridge	2.07	2.54, 2.52	64.2	-38.1
Au_{36}-Au_{ad}-EtS•	*quasi*-atop	2.31	2.31	71.5	-43.0
Au_{36}-EtS•-Au_{ad}-EtS•	atop-atop	2.55 ; 2.59	2.36, 2.55 ; 2.36, 2.59	72.5 ; 73.2	-47.8
Au_{36}-PhSPh	*quasi*-atop	2.8	2.88	78.7, 45.3	-7.8
Au_{36}-PhS•	fcc-bridge	2.13	2.59, 2.56	48.5	-26.2
Au_{36}-Au_{ad}-PhSPh	*quasi*-atop	2.48	2.48	69.4, 65.6	-19.7
Au_{36}-Au_{ad}-PhS•	*quasi*-atop	2.30	2.30	72.1	-20.6
Au_{36}-PhS•-Au_{ad}-PhS•	atop- atop	2.63 ; 2.63	2.36, 2.63 ; 2.37, 2.63	102.9 ; 110.5	-38.5
Au_{36}-PhSMe	fcc-bridge	2.48	2.88, 2.87	75.5 (Me), 16.2 (Ph)	-5.9
Au_{36}-Au_{ad}-PhSMe	*quasi*-atop	2.44	2.44	89.5 (Me), 62.5 (Ph)	-20.8

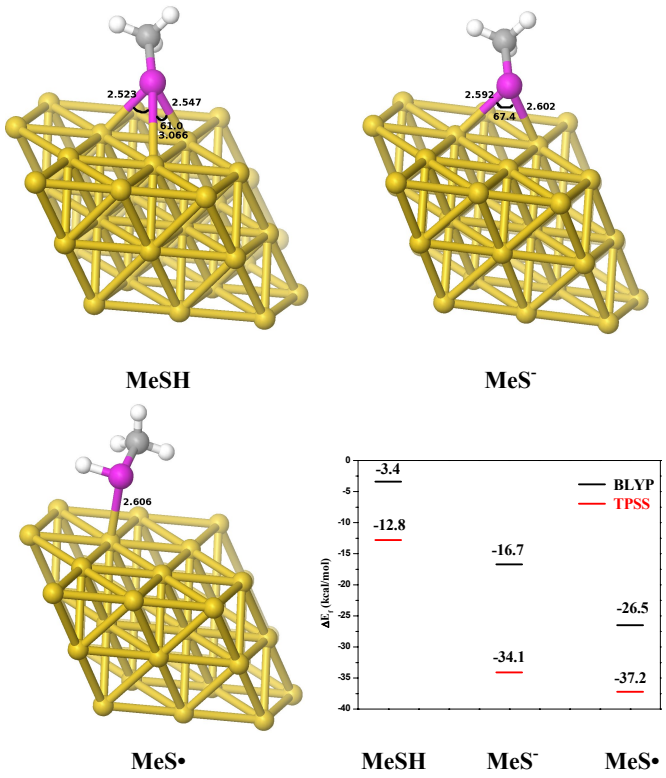


Figure S1. The DFT computed formation energies of the three different species on the Au(111) using TPSS and BLYP functionals. The optimized structures are of TPSS functional.

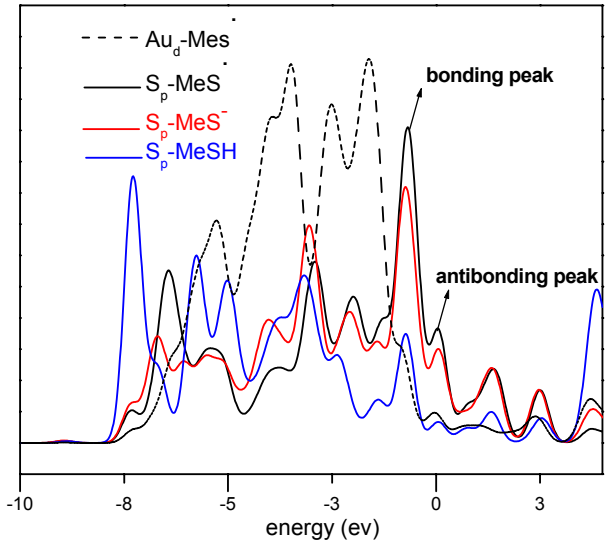
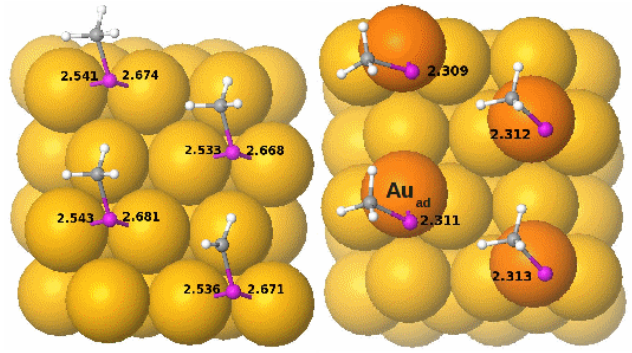


Figure S2. The DOS plot for selected electronic states of the three species. The origin of the energy scale is set at the system Fermi level.



a) b)

Figure S3. The (√3 x √3)R30° surface structure of MeS• species on a clean (a) and reconstructed (1:1 ratio model) (b) Au(111) surface. Gold adatoms are dark-yellow coloured

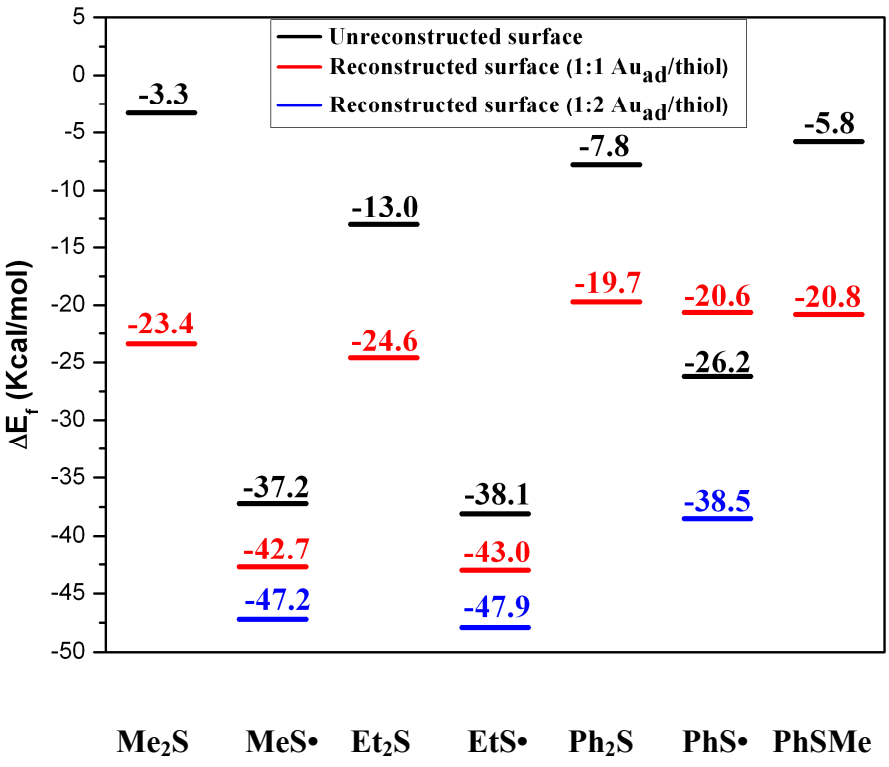


Figure S4. The formation energies of the substituted alkylthiols on the Au(111).