Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supplemental Information for

Identification of Au-S complexes on Au(100)

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1. Tunneling conditions for STM images in the main text.

Figure	Image size (nm^2)	Tunneling current (nA)	Sample Bias (V)	θ_S
1a	30 x 30	0.915	-0.516	
1b	10 x 10	8.72	-0.002	
1c	5 x 5	13.91	-0.002	
2a	8 x 8	2.19	-0.456	0.009
2b	10 x 10	1.83	-0.500	0.009
2c	10 x 10	2.63	-0.002	0.009
2d	10 x 10	2.85	-0.002	0.009
3a	15 x 15	1.72	-0.085	0.024
3b	15 x 15	1.94	-0.052	0.032
3c	15 x 15	2.38	-0.078	0.055
3d	15 x 15	1.01	-0.061	0.115
4a	15 x 15	1.68	-0.135	0.009
4b	15 x 15	2.104	-0.038	0.032
6a	5 x 3.3	3.03	-0.023	0.055
6b	10 x 10	1.91	-0.229	0.009
6c	10 x 10	1.00	-1.000	0.009
6d	10 x 10	3.03	-0.023	0.055
6e	10 x 10	1.68	-0.253	0.055
6f	10 x 10	1.79	-0.168	0.055
6g	10 x 10	2.10	-0.038	0.055
8e	3.6 x 4	0.468	+1.000	0.115
9a	2 x 2	2.91	-0.033	0.055
9b	2 x 2	3.03	-0.023	0.055
9c	2 x 2	2.10	-0.038	0.055
12	30 x 30	1.75	+0.092	0.115

2. Details of determining Au mass balance.

The density of atoms in the hex reconstruction, N_{hex}, is 15 nm^{-2}, while in the unreconstructed layer the density, N_{1x1}, is 12 nm^{-2}. To determine the number of ejected Au atoms, we first determine the area of the unreconstructed regions and multiply this by the density difference, ΔN = 3 nm^{-2}. This gives the density of Au atoms released, N_{rel}. Then, we evaluate the density of Au atoms contained in complexes and rafts, N_{cr}. If there were perfect mass balance on the terrace (and within the scope of the imaged regions), the difference N_{rel} - N_{cr} would be zero.

The fraction of Au atoms released but not accounted for in complexes and rafts, shown in Fig. 13(b), is calculated as $F = (N_{rel} - N_{cr})/ N_{rel}$. A positive value of F indicates that more Au atoms are ejected than consumed, as is true at 0.009 ML. A large negative value of F would indicate the reverse. We estimate that the small deviations of F from zero, at 0.024, 0.032, and 0.055 ML in Fig. 13, are within experimental uncertainty.

3. Details of DFT results for the chemisorbed phases.

Energetics of single S adsorbed on 4fh sites of Au(100) in 9 different supercells from DFT-PBE calculations, averaging from L = 7 to 12. Uncertainties, in parentheses, represent the variation in μ_S between individual slab thickness values. The index j is the separation between nearest-neighbor S atoms in units of a, for each supercell. The three values in boldface define the convex hull shown in Fig. 4 in the text.

j	θ_S	k-points grid	Supercell	μ_S (eV)
1	1	(12 x 12)	(1 x 1)	0.169(4)
2	**1/2**	**(17 x 17)**	**(√2 x √2)R45°**	**-0.834(2)**
3	**1/4**	**(12 x 12)**	**(2 x 2)**	**-1.273(2)**
4	1/5	(11 x 11)	(√5 x √5)R26.6°	-1.219(4)
5	1/8	(8 x 8)	(2√2 x 2√2)R45°	-1.282(5)
6	1/9	(8 x 8)	(3 x 3)	-1.268(2)
7	1/10	(8 x 8)	(√10 x √10)R18.4°	-1.281(2)
8	**1/13**	**(7 x 7)**	**(√13 x √13)R33.7°**	**-1.294(5)**
9	1/16	(6 x 6)	(4 x 4)	-1.285(3)

4. Other configurations evaluated with DFT.

Figures S1-S9 show some of the other S atom arrays tested in DFT. Each panel contains a schematic of the repeating structure within the unit cell, slab thickness (L), and the chemical potential of sulfur, μ_S. Many panels also include a simulated STM image, in shades of orange. The supercell is given in each figure caption.

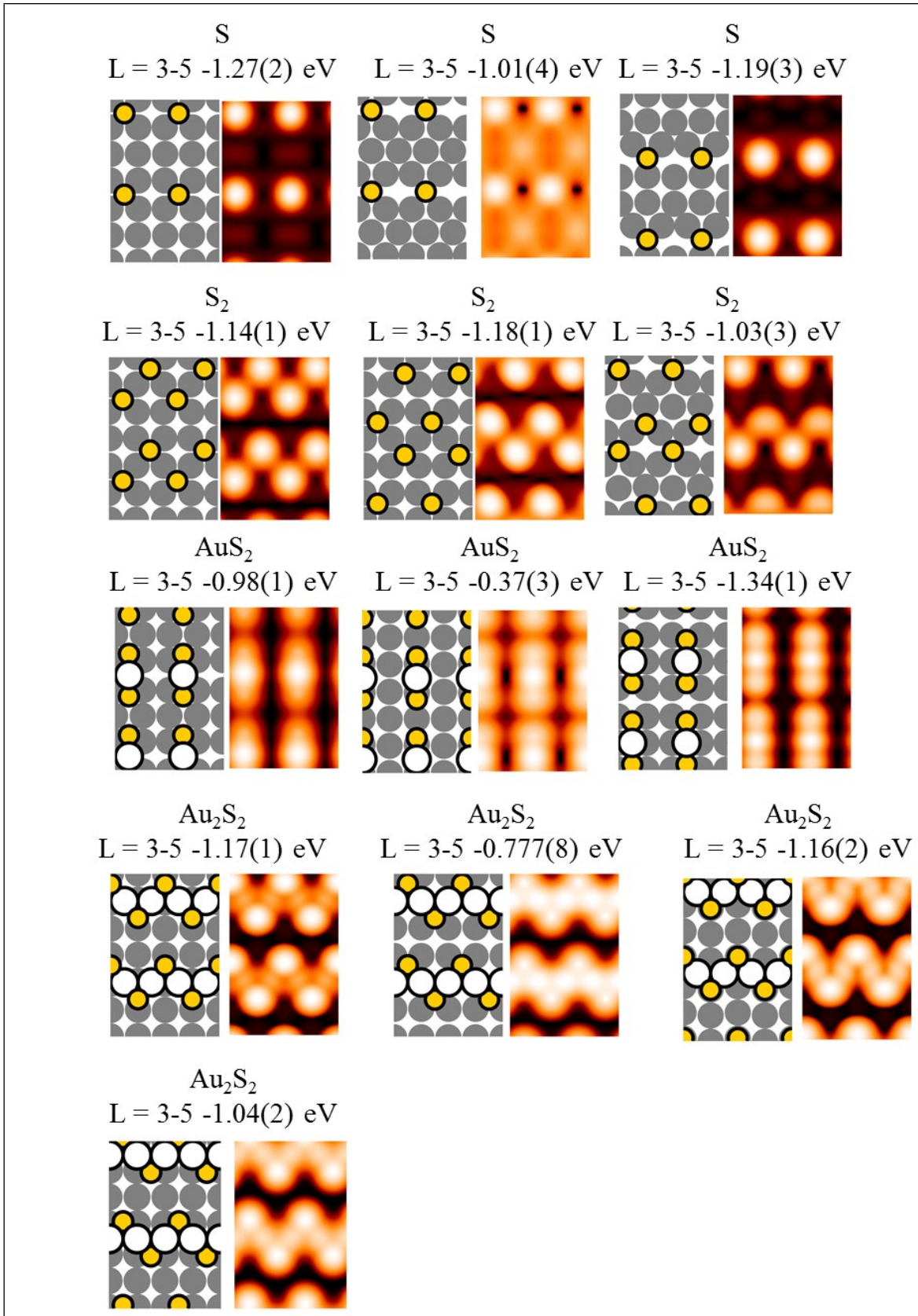

Figure S1. (2 x 3) supercell.

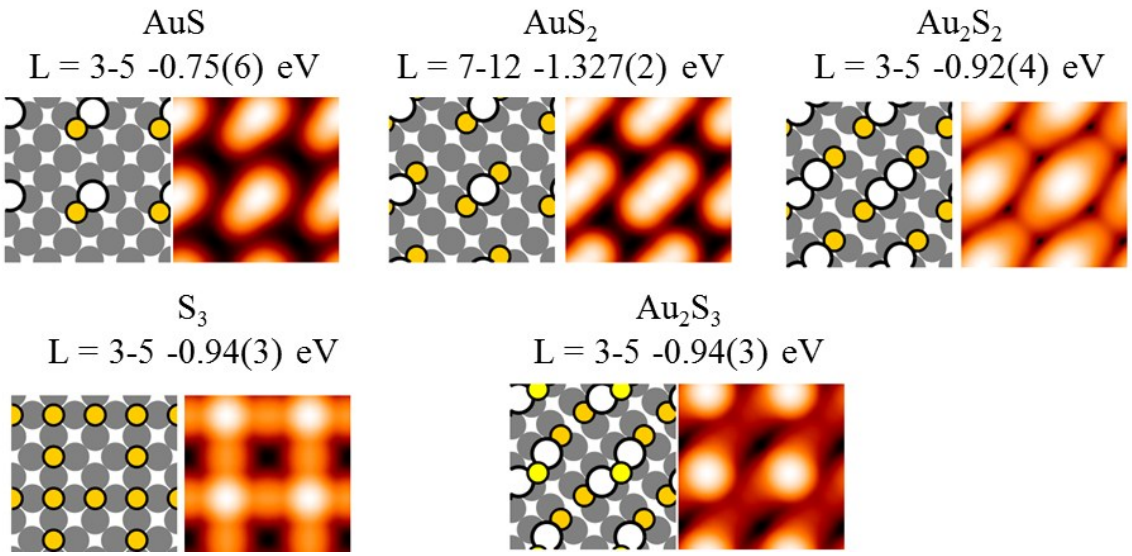

Figure S2. (2√2 x 2√2)R45° supercell.

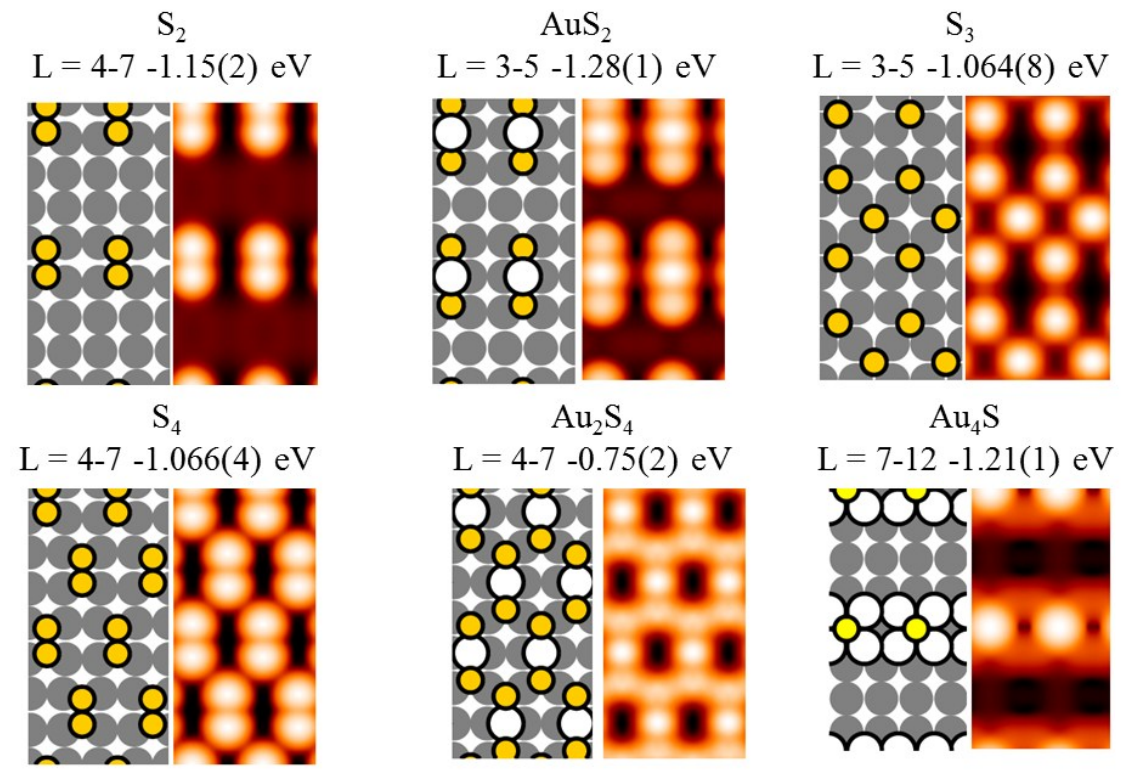

Figure S3. (2 x 4) supercell.

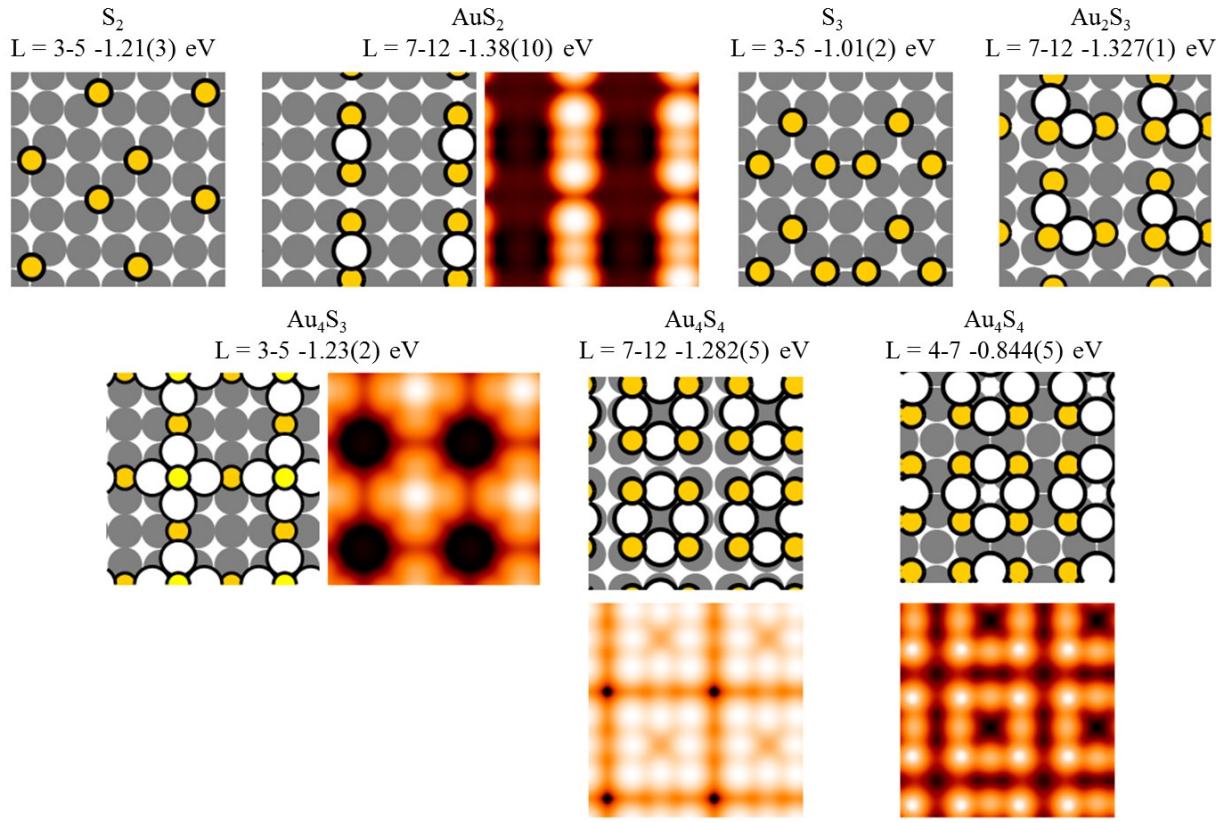

Figure S4. (3 x 3) supercell.

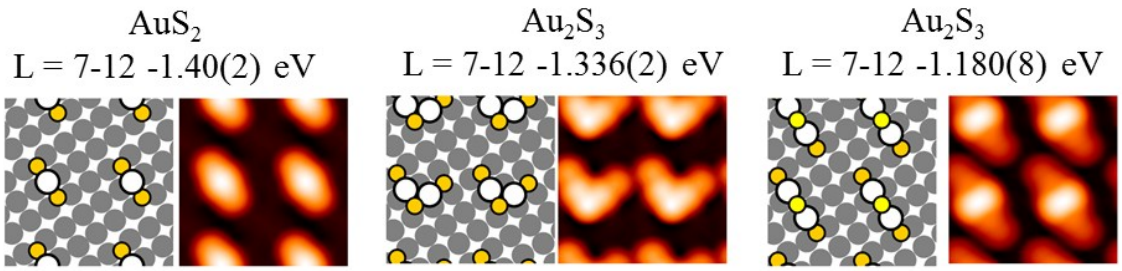

Figure S5. (√13 x √13)R33.7° supercell.

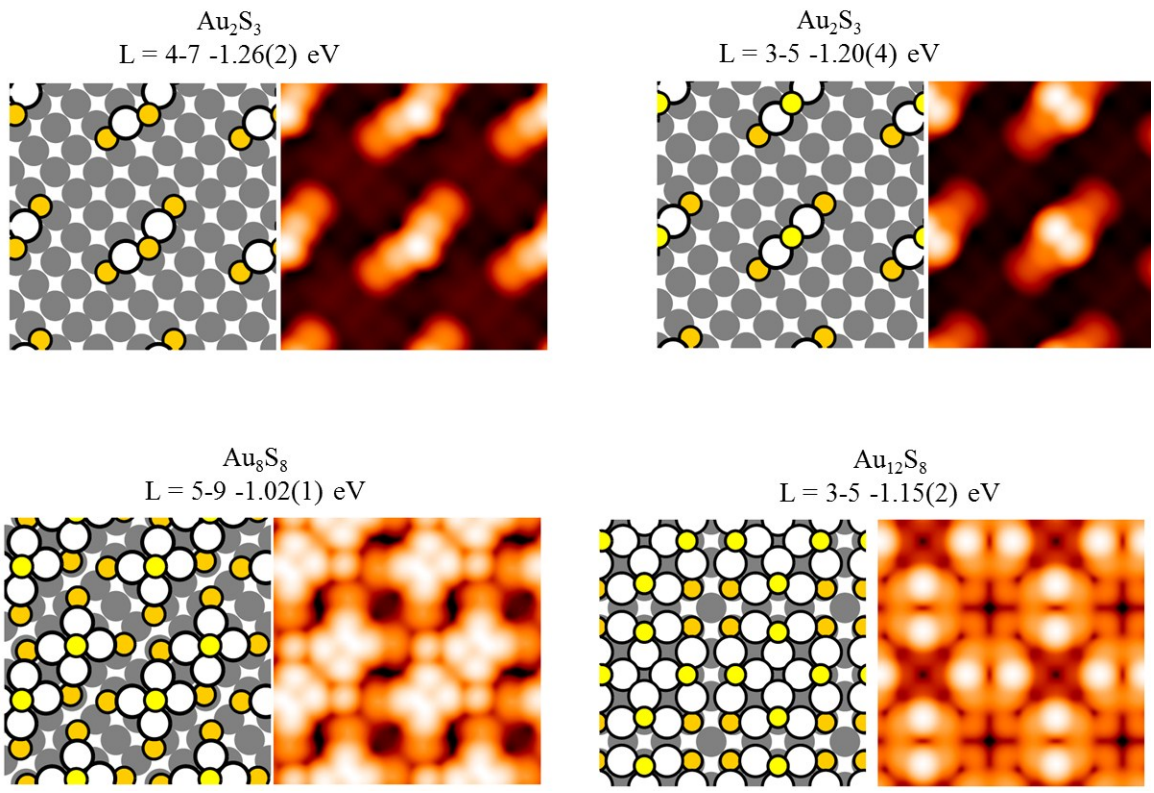

Figure S6. $(3\sqrt{2} \times 3\sqrt{2})R45^{\circ}$ supercell.

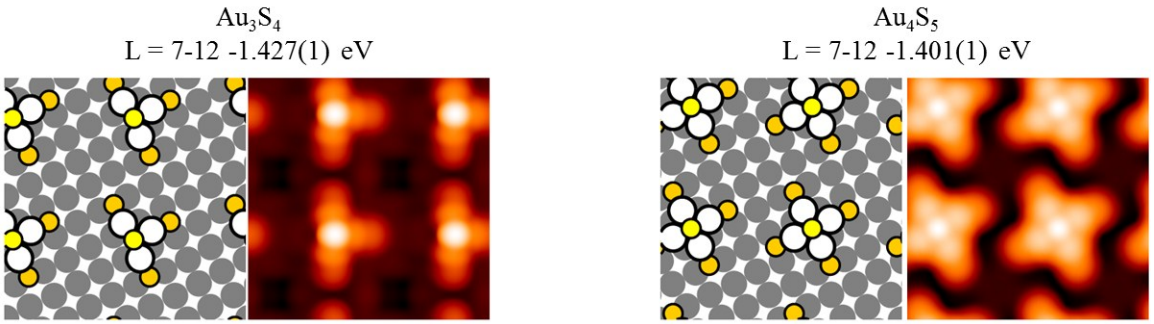

Figure S7. $(2\sqrt{5} \times 2\sqrt{5})R26.6^{\circ}$ supercell.

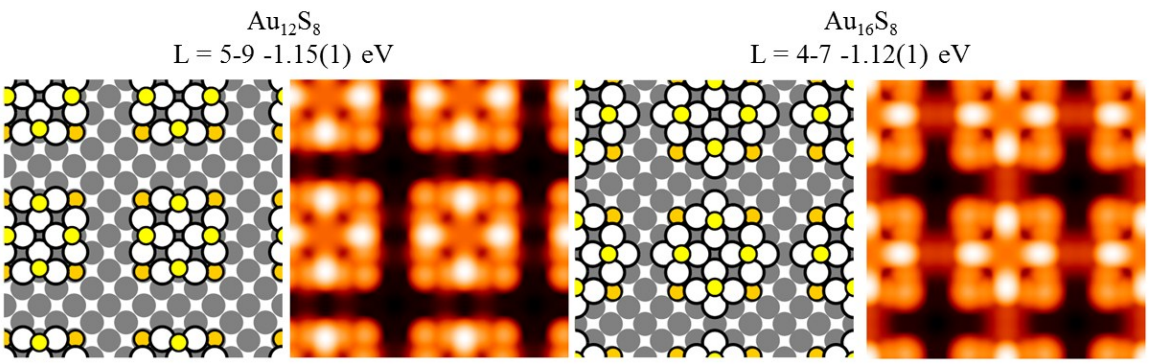

Figure S8. (4√2 x 4√2)R45◦ supercell.

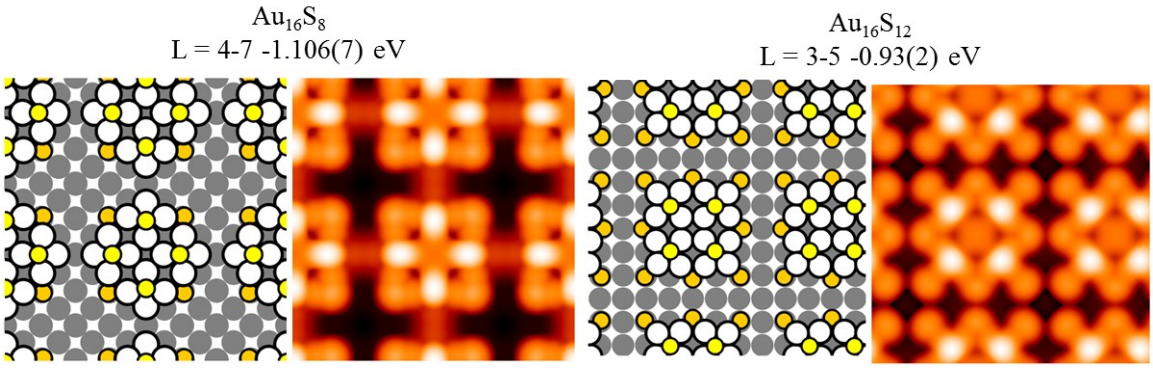

Figure S9. (6 x 6) supercell.