

Supporting Information

Tracking down the Origin of Peculiar Vibrational Spectra of Aromatic Self-assembled Thiolate Monolayers

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Experimental vibrational band positions

Table S1: Vibrational modes observed in FTIR, IRRAS, or HREELS experiments for ATP in KBr matrix, ATP on graphite, ATP on ATP SAM, ATP SAM, NBPT in KBr matrix, NBPT SAM and H₂O on graphite. All SAMs were prepared on Au substrates. All values are given in cm⁻¹. The assignment is based on references listed below the table. Notation: ν = stretching modes (suffices s and a are symmetric and anti-symmetric), δ = deformation, β_{ip} = in-plan bending, γ_{oop} = out-of-plane bending, sh = shoulder, w = weak, free = hydrogen not engaged in hydrogen bonding, and H-bond = hydrogen engaged in hydrogen bonding.

Mode	ATP in KBr FTIR	ATP on graphite HREELS	ATP on ATP SAM HREELS	ATP SAM HREELS	ATP SAM IRRAS	NBPT in KBr FTIR	NBPT SAM HREELS	NBPT SAM IRRAS	H ₂ O on graphite HREELS
$\nu(\text{H}_2\text{O}_{\text{free}})$									3690
$\nu(\text{H}_2\text{O}_{\text{H-bond}})$									3395
$\nu_a(\text{NH}_2)$	3416								
$\nu_s(\text{NH}_2)$	3334 3208	3390	3390		3362 (w)				
$\nu(\text{CH})$	3022	3040	3040 2920	2920	2955 2929 2856	3076	2925	2957 2925 2853	
$\nu(\text{SH})$		2550	2550						
$\delta(\text{H}_2\text{O})$									1650
$\delta(\text{NH}_2)$	1622	1630	1630	1640 (sh)					
$\nu(\text{CC})$	1593 1495 1424			1425	1593 1495	1476			
$\nu_a(\text{NO}_2)$						1593 1507	1400	1607 1521	
$\nu_s(\text{NO}_2)$						1339		1346	
$\nu(\text{CN})$	1283			1295	1295	1294			
$\beta_{ip}(\text{CH})$	1176 1085 1007	1100	1100		1180 1080 1014	1002 1088 1108 1192	1080	1175 1115 1080	
$\delta(\text{NO}_2)$						855		855	
$\gamma_{oop}(\text{CH})$	821	815	815		821	822 753	820		
Frustrated rotation									830

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- 2 N.A. G. Al-Rawashdeh, W. Azzam, C. Wöll, *Z. Phys. Chem.*, 2008, **222**, 965.
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- 6 Q. Chen, A. Haq, B.G. Frederick, N.V. Richardson, *Surf. Sci.*, 1996, **368**, 310.
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Computational part

Glossary of structure notations

The following abbreviated structure notations have been used:

bridge-hcp ----- adsorption on near-bridge hcp sites, neighbor adsorbate molecules in a “herringbone arrangement” (nearly orthogonal to each other)

bridge-fcc ----- adsorption on near-bridge fcc sites, neighbor adsorbate molecules orthogonal to each other

top-adatom ----- adsorption on top sites, neighbor adsorbate molecules orthogonal to each other, one Au adatom between two adsorbate molecules

flat ----- adsorption on near-bridge fcc sites in flat orientation at low coverage (one adsorbate per $(2\sqrt{3}\times 2\sqrt{3})R30^\circ$ Au(111) surface unit cell

Table S2: Relative energies (kcal/mol) and adsorption energies per adsorbate molecule (kcal/mol) of various adsorption arrangements with two non-equivalent 4-aminothiophenol (ATP) molecules per $(2\sqrt{3}\times\sqrt{3})R30^\circ$ Au(111) surface unit cell.

	Adsorption arrangement	E_{rel}^a	E_{ads}
PBE with D3 dispersion correction	bridge-fcc-1	0.2	-30.6
	bridge-hcp-1	3.7	-28.8
	bridge-fcc-2	0	-30.7
	bridge-hcp-2	6.9	-27.2
	bridge-fcc-3	0.2	-30.6
	top-adatom	3.3	-29.0
PBE with Tkatchenko-Scheffler dispersion correction	bridge-fcc-1	0.4	-28.1
	bridge-hcp-1	3.6	-26.6
	bridge-fcc-2	0.1	-28.3
	bridge-hcp-2	0.1	-28.3
	bridge-fcc-3	0	-28.3
	top-adatom	0.3	-28.2

^a The relative energies are given with respect to the most favorable adsorption geometry for PBE calculations with D3 or Tkatchenko-Scheffler (TS) dispersion correction. Adsorption energy was calculated according to the equations given in the main text.

Table S3: Calculated frequencies (cm⁻¹) of N-H and C-H stretching vibrations of the free or adsorbed 4-ATP in various adsorption arrangements with two non-equivalent ATP molecules per (2√3×√3)R30° Au(111) surface unit cell and with one ATP molecule per (2√3×2√3)R30° unit cell.

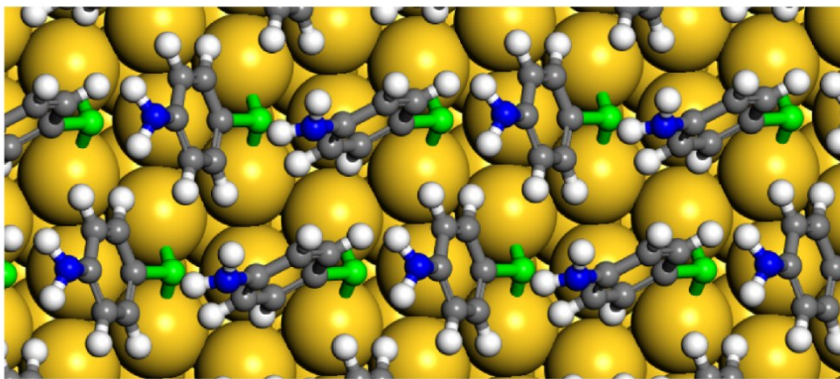
Adsorption sites	Method ^a	N-H				C-H							
bridge-fcc-1	D3	3567	3566	3474	3462	3152	3147	3119	3110	3096	3086	3085	3080
	TS	3572	3562	3470	3467	3160	3156	3130	3122	3108	3098	3094	3090
bridge-hcp-1	D3	3579	3573	3474	3470	3132	3126	3123	3118	3087	3083	3080	3078
	TS	3580	3574	3477	3474	3143	3136	3129	3120	3104	3102	3082	3080
bridge-fcc-2	D3	3578	3572	3475	3470	3130	3128	3127	3117	3083	3082	3077	3073
	TS	3575	3573	3475	3470	3139	3133	3126	3122	3105	3099	3082	3080
bridge-hcp-2	D3	3542	3539	3393	3327	3133	3127	3120	3118	3082	3082	3059	3052
	TS	3549	3548	3408	3360	3141	3137	3128	3126	3085	3084	3072	3066
bridge-fcc-3	D3	3542	3539	3393	3327	3133	3127	3120	3118	3082	3082	3059	3052
	TS	3546	3544	3403	3356	3141	3137	3130	3128	3086	3084	3076	3071
top-adatom	D3	3566	3559	3455	3410	3163	3155	3140	3099	3085	3084	3078	3053
	TS	3572	3562	3467	3426	3161	3155	3153	3110	3094	3085	3083	3074
Flat	D3	3587	3489	-	-	3123	3116	3104	3102	-	-	-	-
	TS	3597	3497	-	-	3127	3125	3111	3108	-	-	-	-
Free ATP	D3	3610	3510	-	-	3128	3126	3100	3097	-	-	-	-
	TS	3603	3501	-	-	3129	3127	3099	3098	-	-	-	-

^a Two methods for calculating the dispersion correction, DFT-D3 and Tkatchenko-Scheffler (TS), have been used for the calculation of vibrational frequencies calculations.

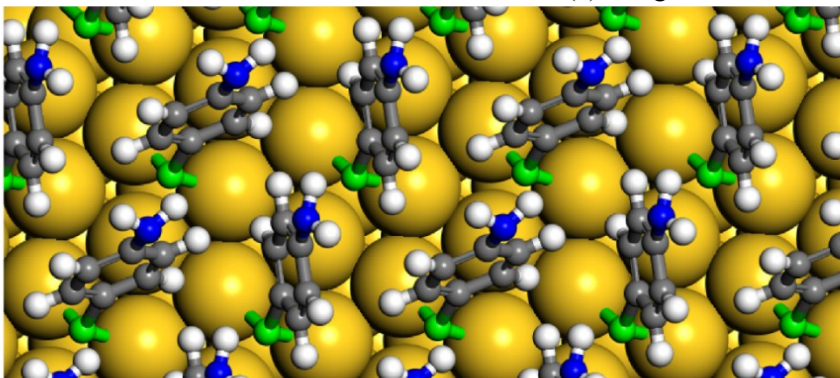
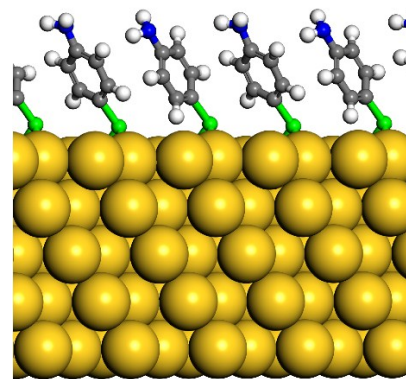
Table S4: Structural parameters of ATP in most stable adsorption arrangements with two non-equivalent ATP molecules per (2√3×√3)R30° Au(111) surface unit cell.

Adsorption sites	Molecule ^a	d_{S-Au}^b			$d_{S-added\ Au}^c$	d_{H-bond}^d	$\theta_{NH_2-surface}^e$	$\theta_{Benzene-surface\ normal}^f$
bridge-fcc-1	mol1	2.42(2.43)	2.43(2.44)	3.02(3.08)	-	-	21.2(21.9)	26.9(25.8)
	mol2	2.46(2.47)	2.49(2.50)	2.99(3.02)	-	-	42.8(43.5)	16.3(17.2)
bridge-hcp-1	mol1	2.45(2.46)	2.47(2.47)	3.03(3.05)	-	-	43.8(41.9)	16.9(17.2)
	mol2	2.44(2.45)	2.47(2.48)	3.01(3.06)	-	-	37.5(37.2)	20.6(19.5)
bridge-fcc-2	mol1	2.44(2.45)	2.46(2.47)	2.93(3.00)	-	-	38.5(38.2)	19.3(18.5)
	mol2	2.44(2.45)	2.47(2.47)	2.97(3.00)	-	-	42.4(41.1)	17.1(17.0)
bridge-hcp-2	mol1	2.42(2.45)	2.57(2.48)	3.09(2.97)	-	2.3(2.3)	55.3(56.6)	7.9(2.9)
	mol2	2.37(2.48)	3.24(2.48)	3.39(3.06)	-		63.6(60.4)	0.1(1.3)
bridge-fcc-3	mol1	2.44(2.45)	2.48(2.49)	2.93(2.98)	-	2.2(2.3)	57.1(56.8)	1.6(2.6)
	mol2	2.47(2.48)	2.48(2.48)	3.05(3.06)	-		61.6(60.7)	3.0(1.2)
top-adatom	mol1	2.53(2.47)	3.45(3.58)	3.64(3.66)	2.31(2.31)	2.4(2.5)	64.6(63.0)	0.6(1.5)
	mol2	2.47(2.50)	3.58(3.66)	3.66(3.69)	2.30(2.30)		36.8(36.2)	20.7(21.0)

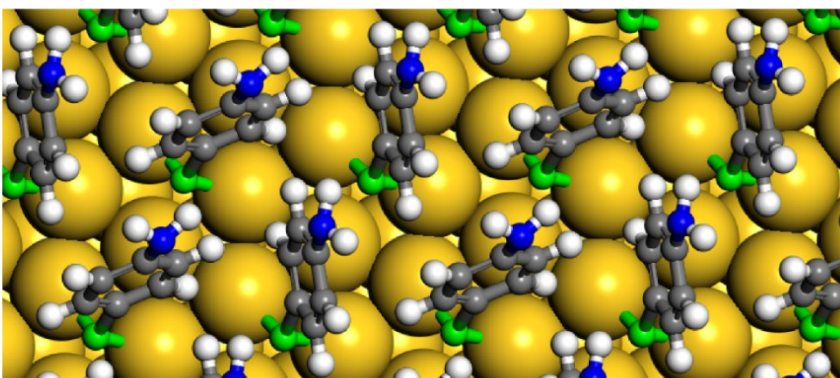
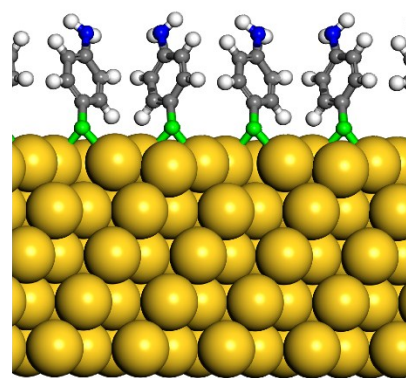
^a Structural parameters calculated at the PBE+D3 or PBE+TS (in parentheses) level for the two non-equivalent adsorbed molecules are given separately. ^b d_{S-Au} is the bond length between the S atom and the nearest Au atoms. ^c d_{H-bond} is the length of the hydrogen bond present in some of the adsorption complexes. ^d $d_{S-added\ Au}$ is the bond length between the S atom and the added Au atoms. ^e $\theta_{NH_2-surface}$ is the angle between the NH₂ group and Au(111) surface. ^f $\theta_{Benzene-surface\ normal}$ is the angle between the benzene ring and the Au(111) surface normal.



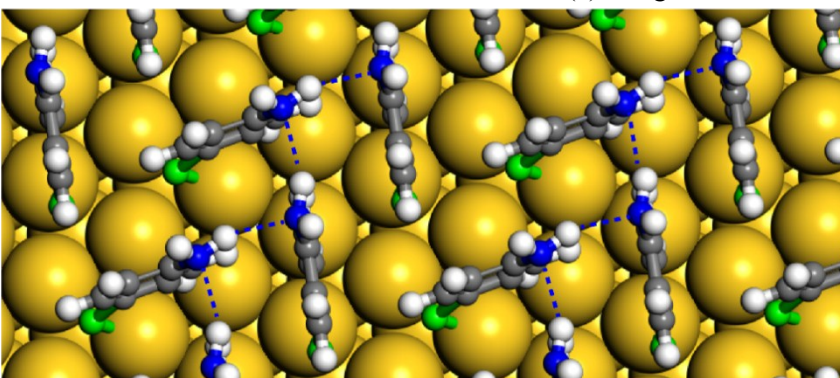
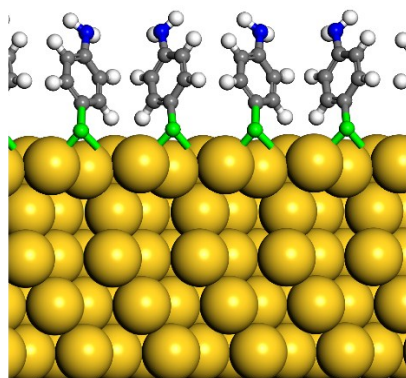
(a) bridge-fcc-1



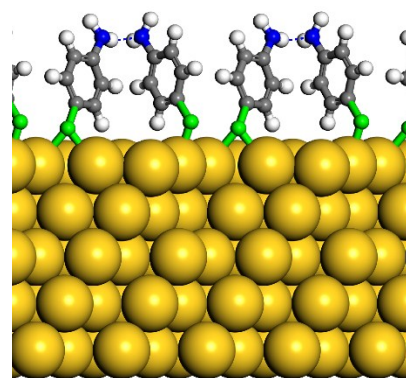
(b) bridge-hcp-1



(c) bridge-fcc-2



(d) bridge-hcp-2



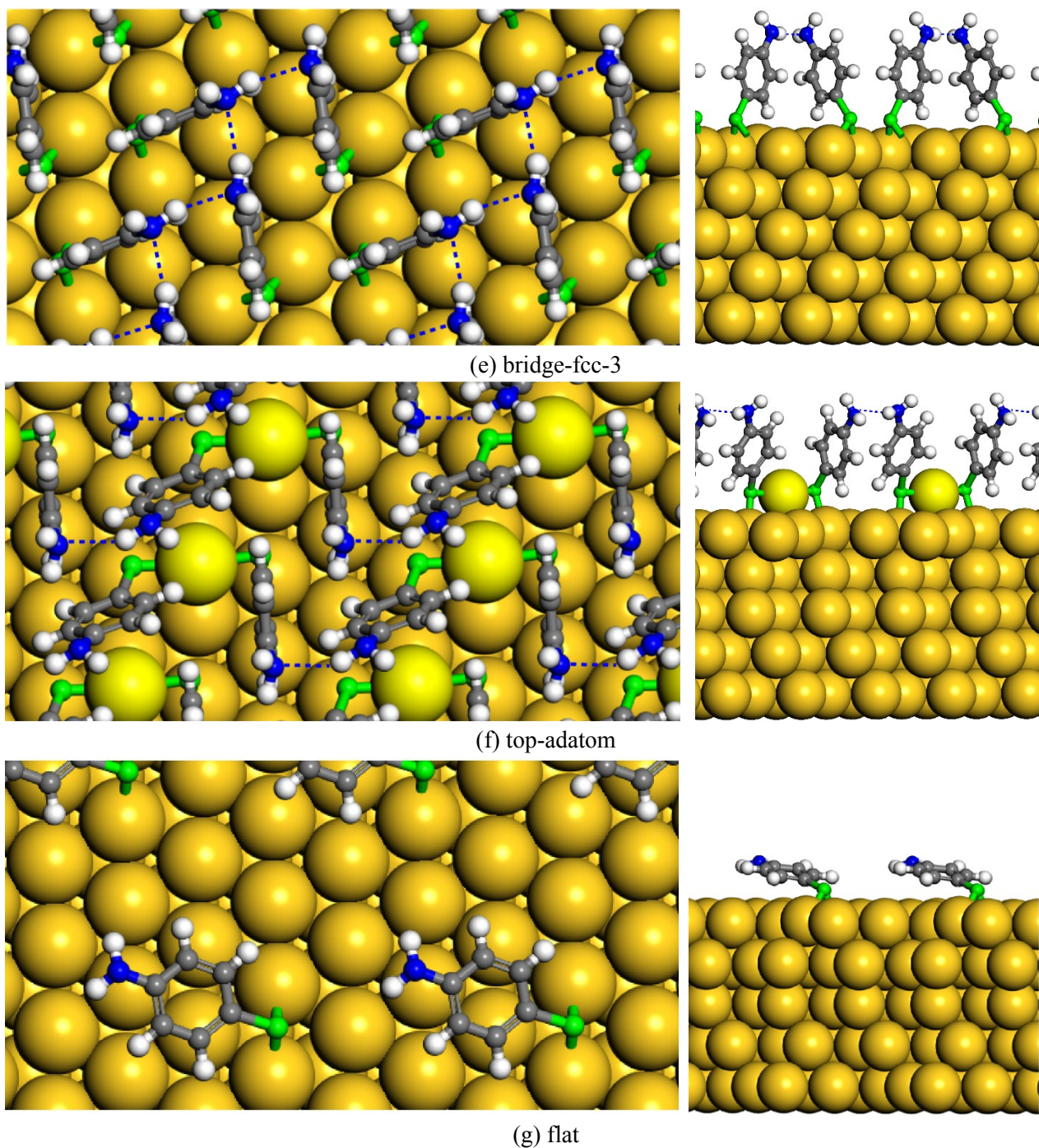
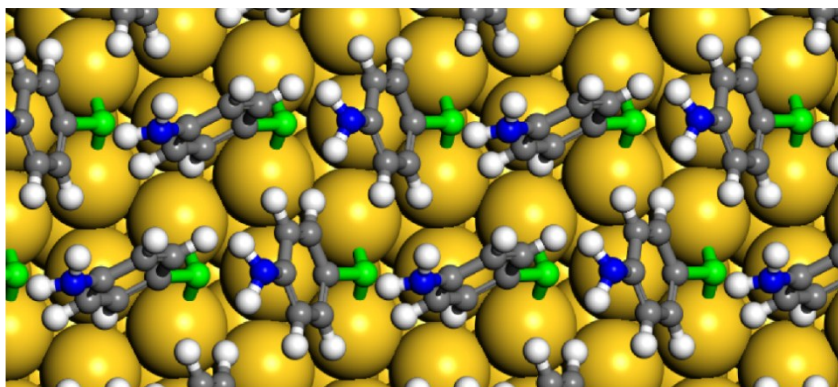
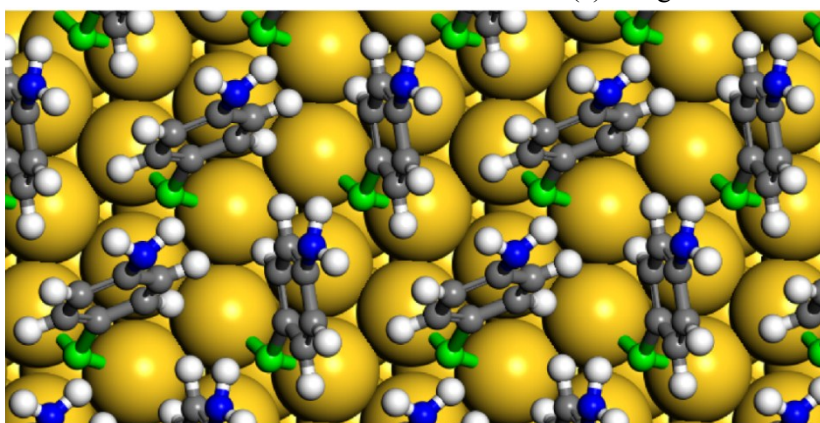
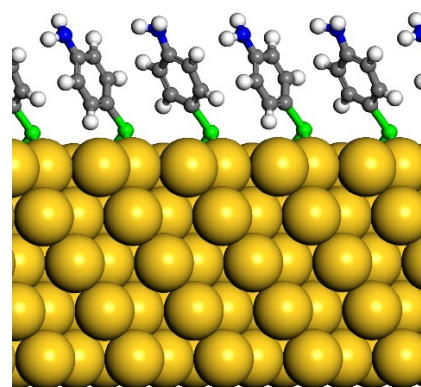


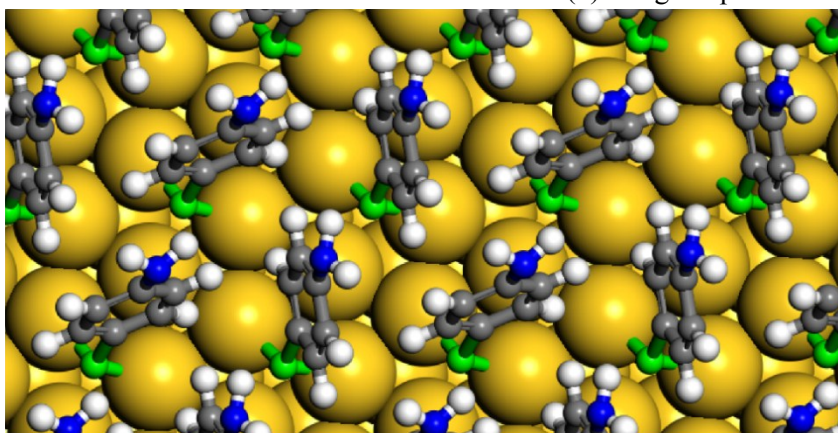
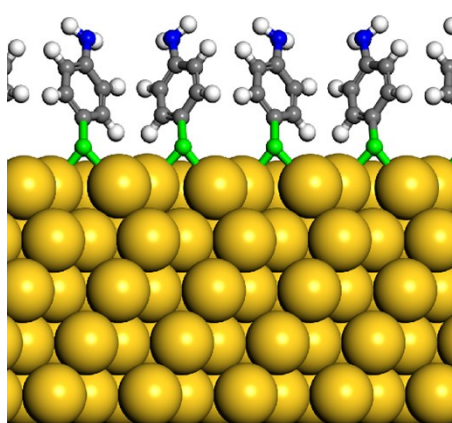
Figure S1: Top (left) and side (right) views of the equilibrium adsorption geometries without (a-c, g) and with intermolecular H-bonds (d-f) obtained at the PBE level by taking D3 dispersion correction into consideration. Element color coding: Au, gold; Au adatoms, yellow; S, green; C, grey; H, white; N, blue. The H-bonds are indicated with blue dashed lines.



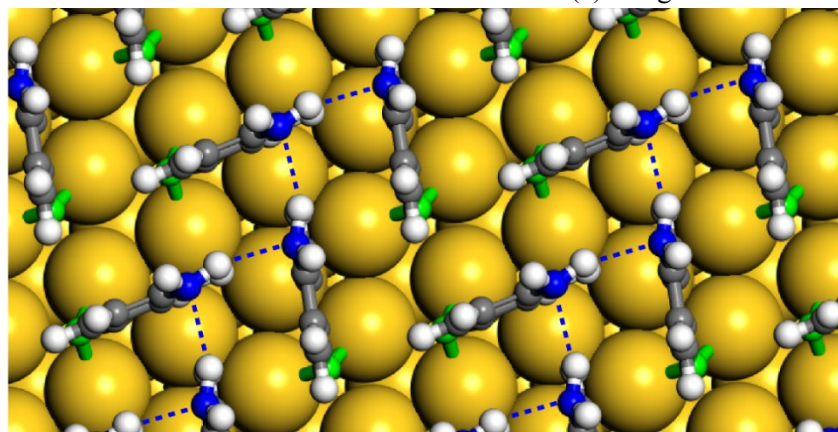
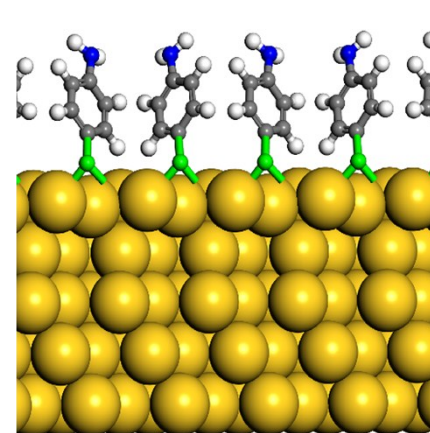
(a) bridge-fcc-1



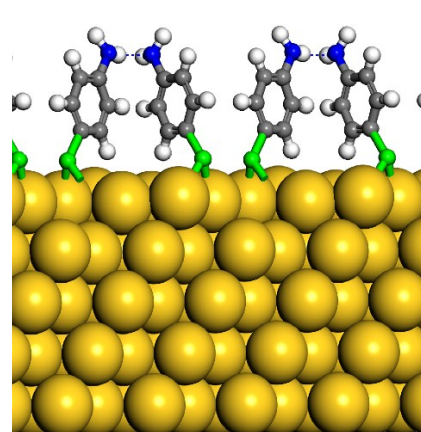
(b) bridge-hcp-1



(c) bridge-fcc-2



(d) bridge-hcp-2



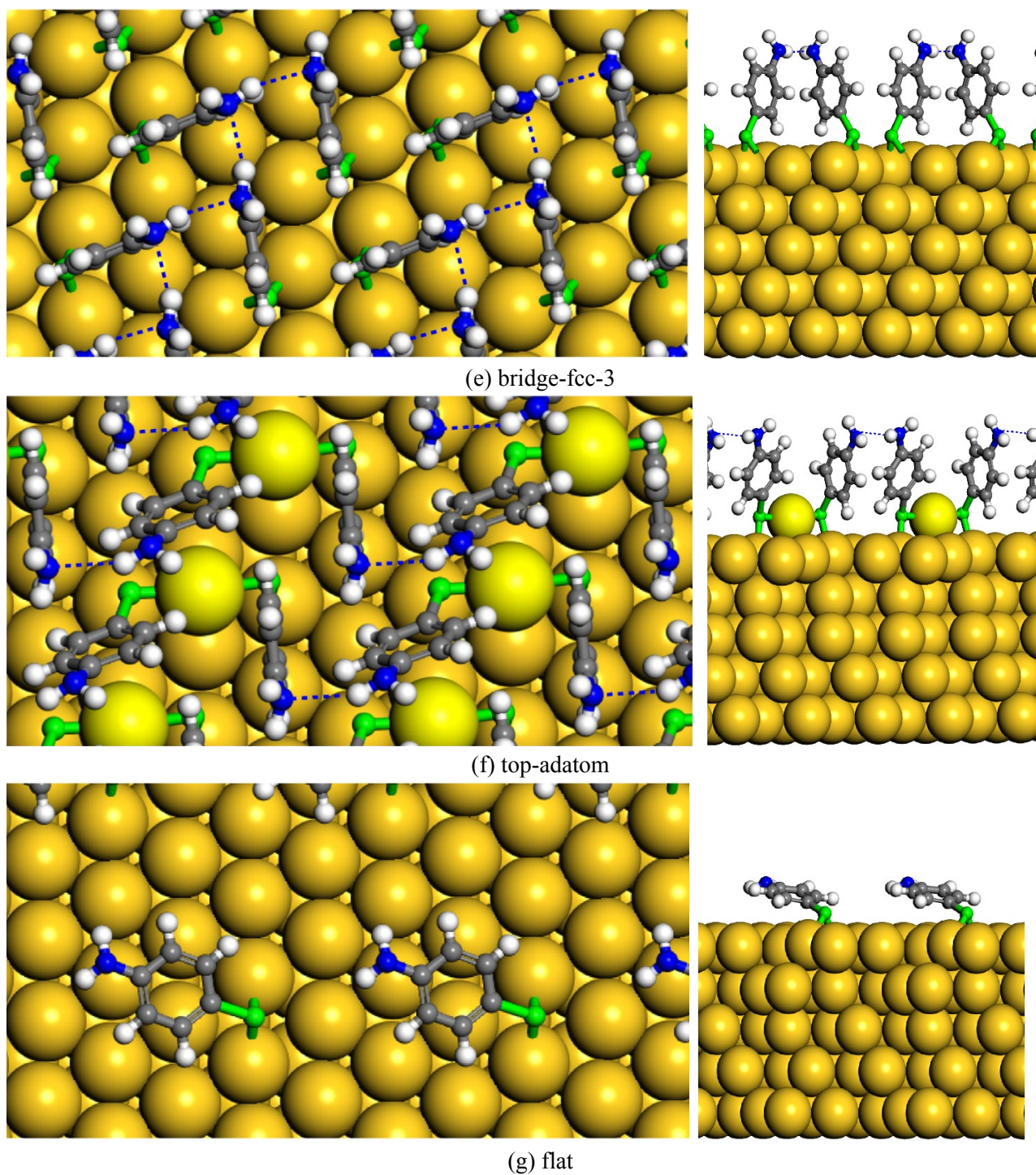


Figure S2: Top (left) and side (right) views of the equilibrium adsorption geometries without (a-c, g) and with intermolecular H-bonds (d-f) obtained at the PBE level by taking Tkatchenko-Scheffler dispersion correction into consideration. Adsorbates in the neighboring cells have been removed for clarity. Element color coding: Au, gold; Au adatoms, yellow; S, green; C, grey; H, white; N, blue. The H-bonds are indicated with blue dashed lines.