Supporting Information

The phenylalanine ligands effect on the chiral-selective oxidation of glucose on Au(111)

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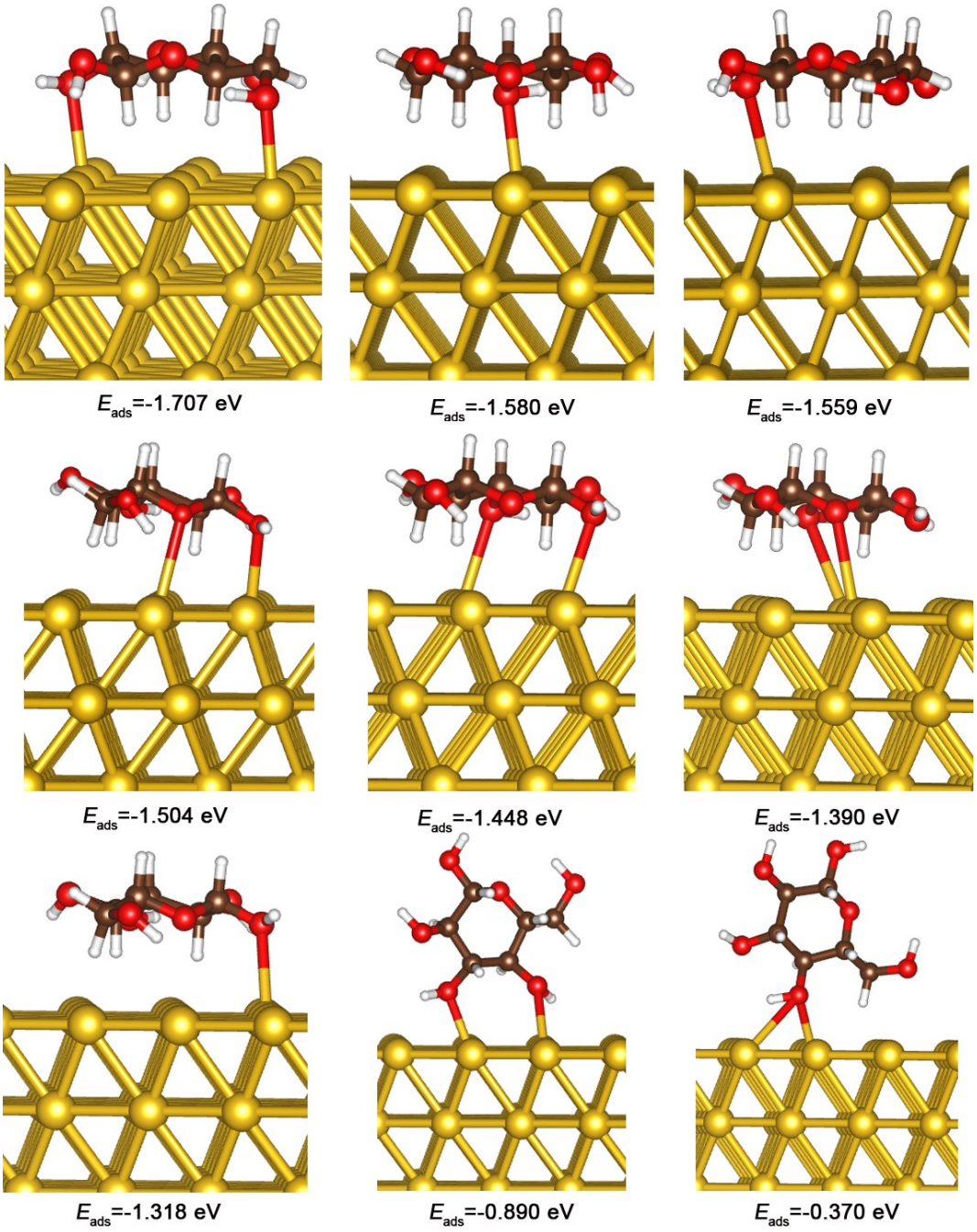

Figure S1 The optimized adsorption configurations of D-glucose on Au(111). The corresponding adsorption energies are also listed in the figure. The adsorption energies of glucose are calculated by $E_{ads}(\text{glucose}) = E_{\text{Au(111)-glucose}} - E_{\text{Au(111)}} - E_{glucose}$.

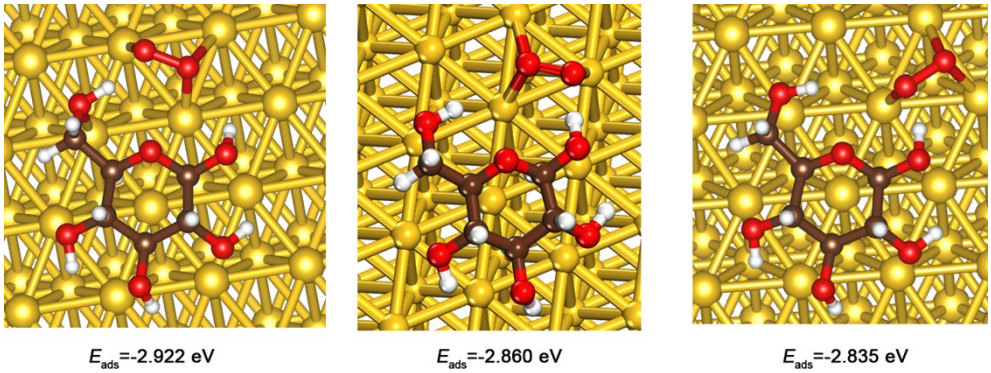

Figure S2 The optimized configurations of D-glucose and O_2 co-adsorbed on Au(111). The total adsorption energies of D-glucose and O_2 are also listed in the figure. The adsorption energies of are calculated by $E_{ads}(\text{glucose}^*\_O_2^*) = E_{\text{Au(111)}-\text{glucose}-O2} - E_{\text{Au(111)}} - E_{glucose} - E_{O2}$

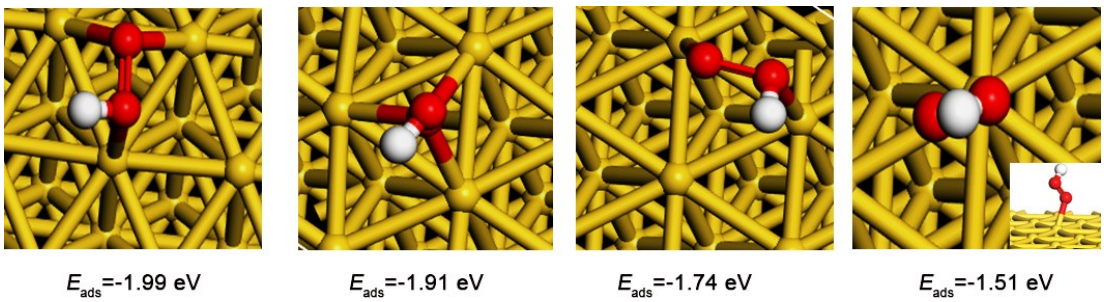

Figure S3 The optimized adsorption configurations of OOH on Au(111). The corresponding adsorption energies are listed in the figure.

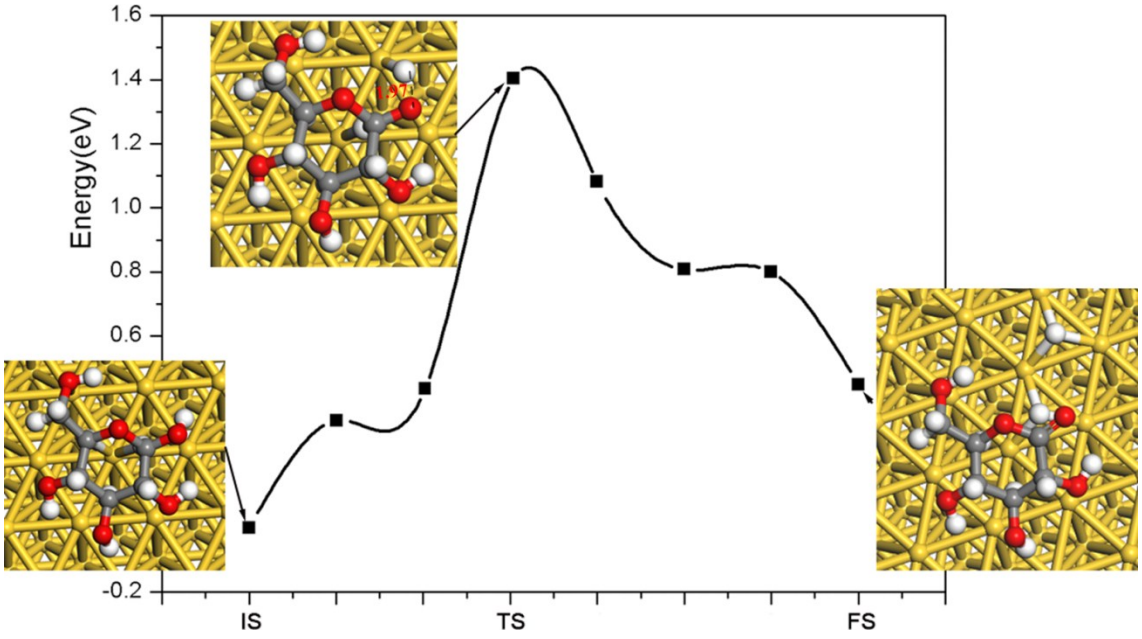

Figure S4 Potential energy profile for removing two H atoms from glucose directly to the Au(111) surface.

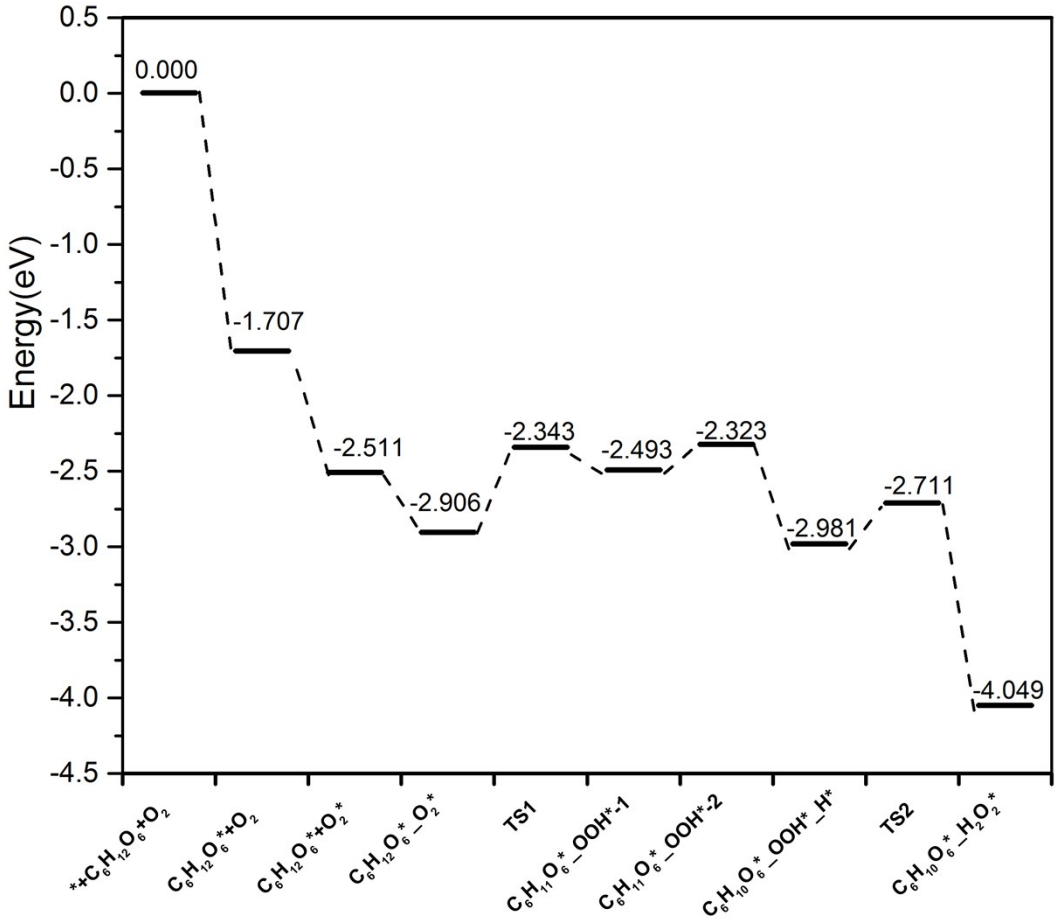

Figure S5 Potential energy profile along the MEP of the first half-reaction of L-glucose oxidations on clean Au(111).

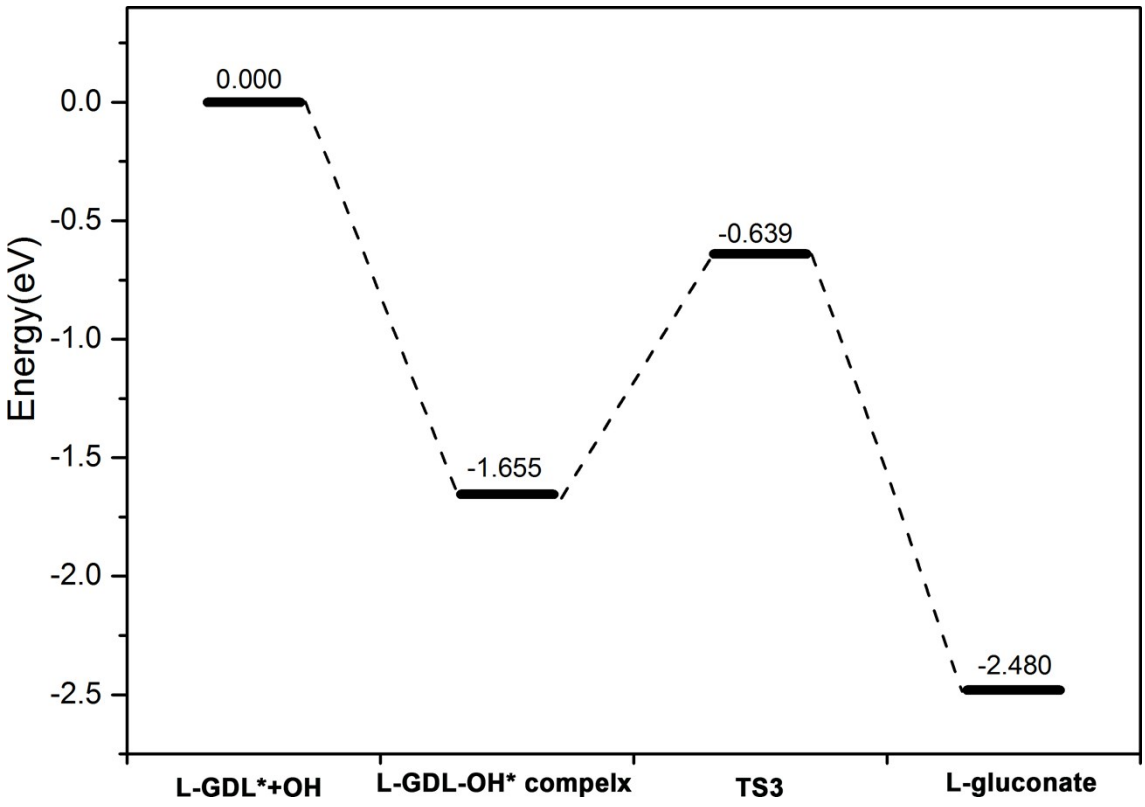

Figure S6 Potential energy profile along the MEP of the second half-reaction of L-glucose oxidations on clean Au(111). All the energies were given with respect to the energy of D-GDL*+OH state.

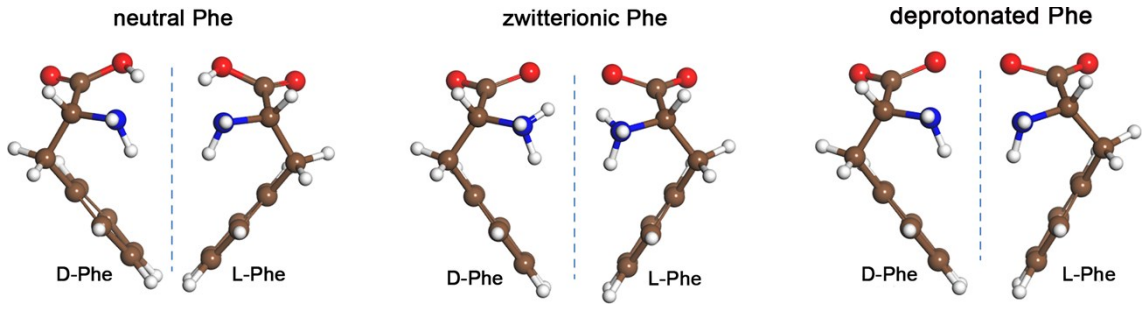

Figure S7 Structures of the three forms of Phe used in this study. The yellow, blue, red, brown, and white balls correspond the Au, N, O, C, and H atoms, respectively.

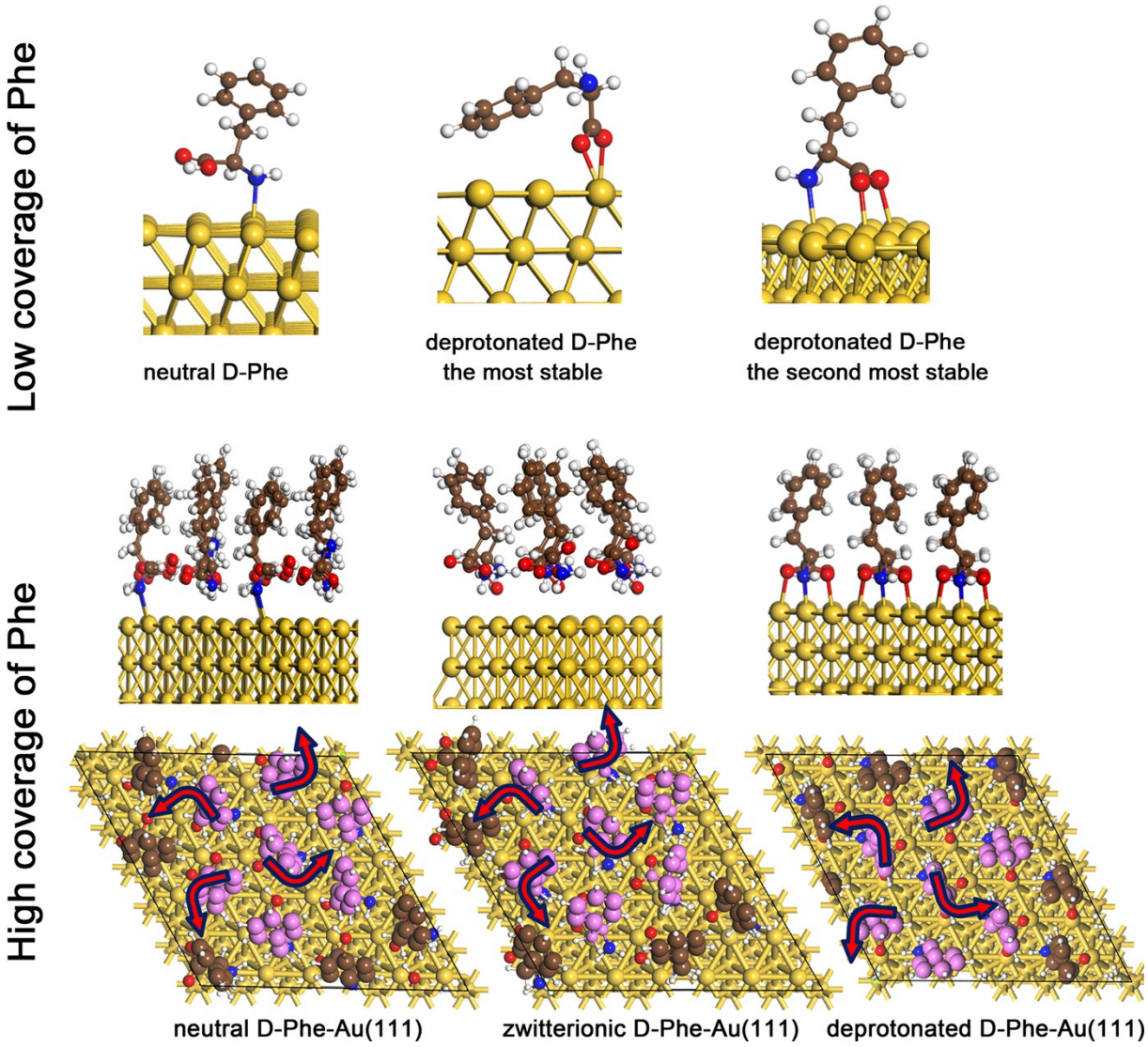

Figure S8 The adsorption structures of D-Phe on Au(111) at the coverage of 3/16 and the self-assembled structures of neutral, zwitterionic, and deprotonated D-Phe on Au(111) at the saturate coverage. The yellow, blue, red, brown, and white balls correspond the Au, N, O, C, and H atoms, respectively. To highlight the chiral structures, some of the C atoms in Phe molecules were shown in pink balls in the top views.

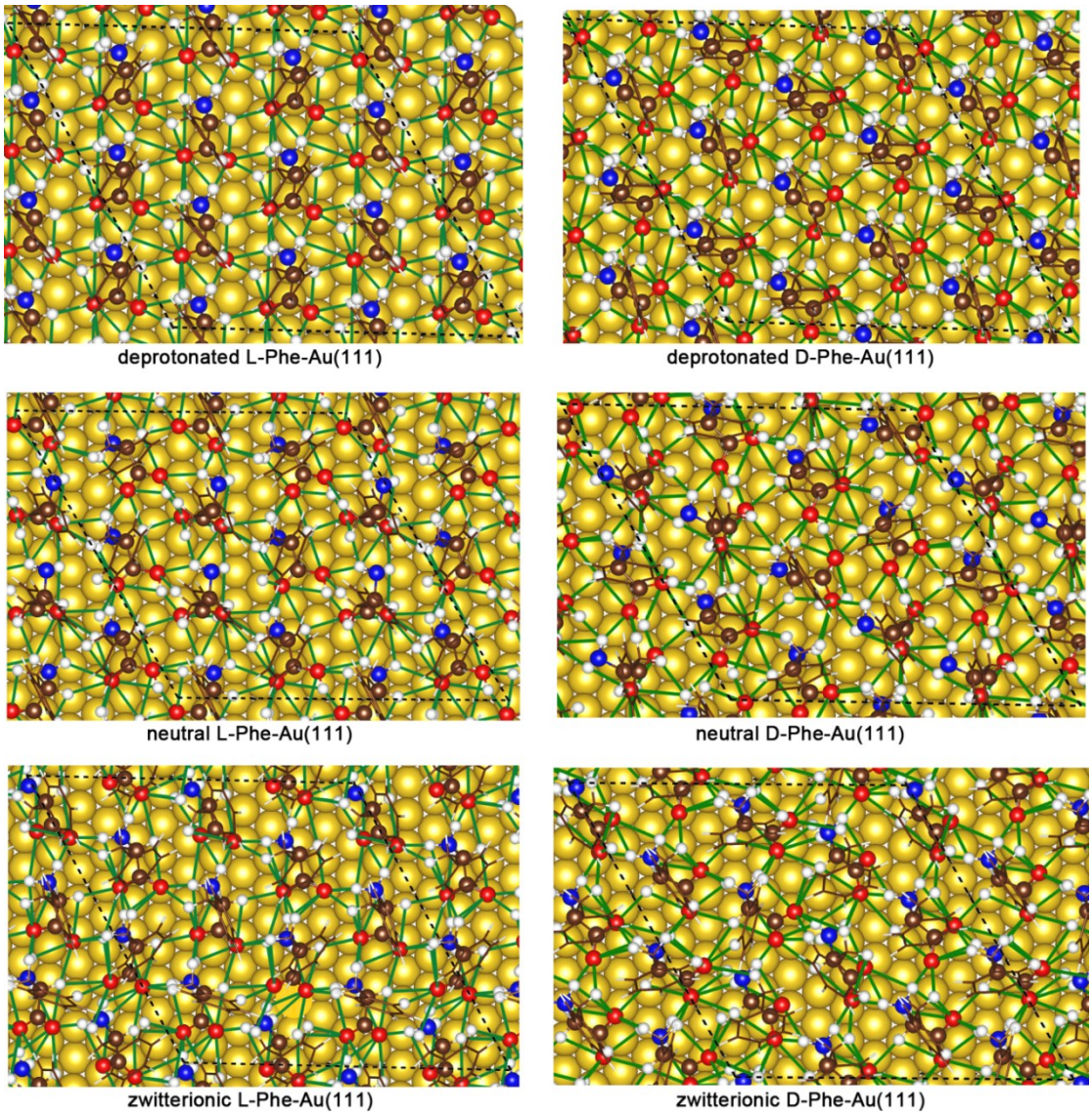

Figure S9 The hydrogen bond network of Phe molecules on Au(111) at the saturate coverage. For clarity, some C atoms and the H atoms that do not form hydrogen bonds are shown in the line model.

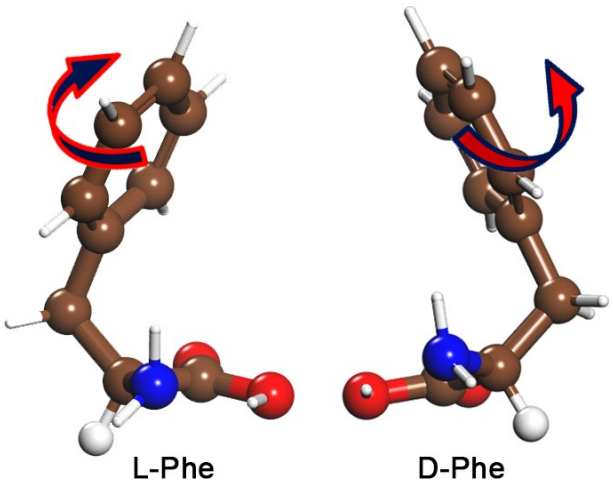

Figure S10 The defined rotation direction of benzene ring: from amino to the H atom which bonds to the chiral carbon and then to carboxyl.

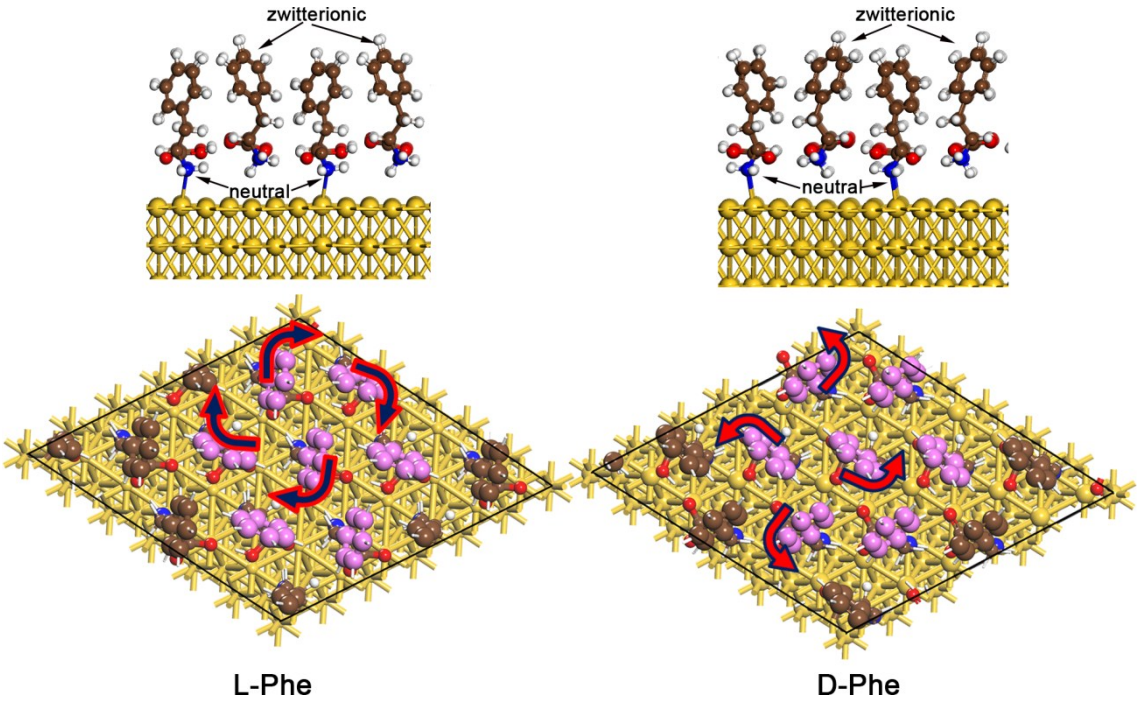

Figure S11 The mixture of neutral and zwitterionic Phe molecules co-adsorbed on Au(111) surface at the saturate coverage. The mixture can self-assemble into the "windmill-like" chiral pattern.

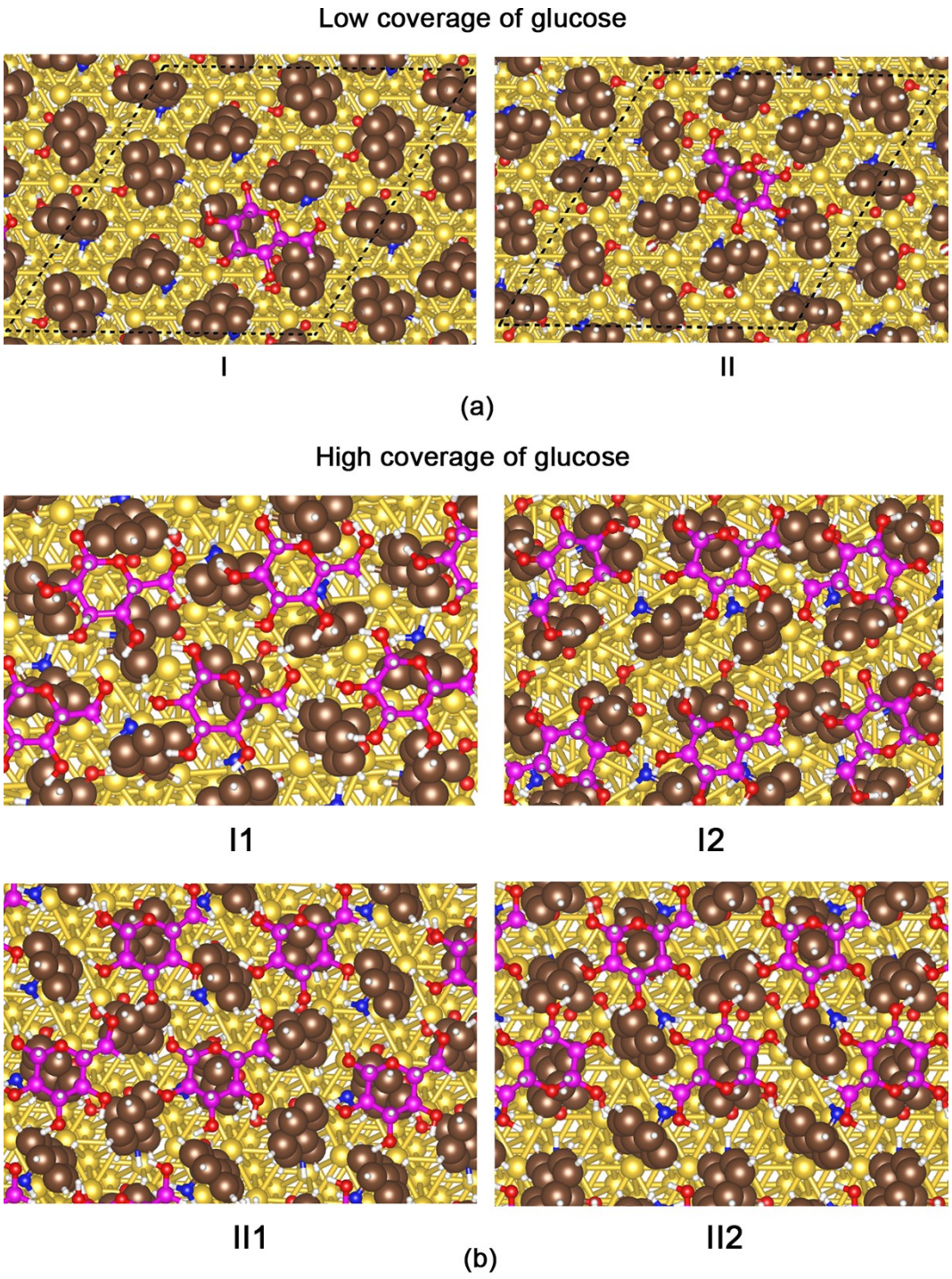

Figure. S12. The configurations of D-glucose adsorption on chiral neutral L-Phe-Au(111) surface (a) at the coverage of 1/4 and (b) at the saturate coverage. The blue, red, and white balls correspond the N, O, and H atoms, respectively. The brown and pink balls correspond the C atoms in Phe and C atoms in glucose.

For low coverage of glucose (the coverage of 1/4), two stable structures (labeled as "I" and "II") are obtained as shown in Figure S8a. In both structure I and II, the molecular plane of glucose is almost parallel to the chiral surface. The difference is that in structure I the glucose molecule is located above the crack formed between the "stamen" and two petals, whereas in structure II, the glucose molecule is located above the "stamen". Accordingly, four stable configurations of glucose the saturate coverage are obtained on each Phe-Au(111) surface (Figure S8b). In structures I1 and II1, all glucose molecules have the same orientation, and in structures I2 and II2, glucose molecules have two opposite orientations.

For glucose molecules adsorption the saturate coverage on Phe-Au(111) surface, new hydrogen bond formed between glucose and Phe molecules and formed between glucose molecules. For the most stable adsorption structure, the adsorption energies per glucose are larger at high coverage than at low coverage (Table 2), which is owing to the hydrogen bond formed between glucose molecules. These hydrogen bond effect is more prominent when glucose adsorption on clean Au(111) surface. The adsorption energy per glucose on clean Au(111) is 0.243 eV higher at higher coverage than at low coverage.

Table S1 The adsorption energies per Phe molecule for the most stable structure of neutral, zwitterionic, and ionic D-Phe on Au(111).

	form of Phe	E_{ads} (eV)
Low coverage	deprotonated	-0. 215
	neutral	-0.803
	zwitterionic	unstable
High coverage	deprotonated[a]	-0.471
	neutral	-1.035
	zwitterionic	-1.528

Table S2 At the $\frac{1}{4}$ coverage of glucose, the adsorption energies of L- and D-glucose molecules on deprotonated, neutral, and zwitterionic L- and D-Phe-Au(111) surfaces (eV)

form of Phe	structure	L-Phe-Au(111)-D-glucose	L-Phe-Au-(111)-L-glucose	D-Phe-Au(111)-L-glucose	D-Phe-Au(111)-D-glucose
deprotonated	I	-0.545	-0.529	-0.542	-0.529
	II	-0.580	-0.490	-0.579	-0.489
neutral	I	-1.023	-0.927	-1.018	-0.921
	II	-0.995	-0.941	-0.996	-0.940
zwitterionic	I	-1.033	-0.945	-1.031	-0.945
	II	-1.006	-0.904	-1.003	-0.901

Table S3 at the saturate coverage of glucose, the adsorption energies of L- and D-glucose molecules on deprotonated , neutral, and zwitterionic L- and D-Phe-Au(111) surfaces (eV)

form of Phe	structure	L-Phe-Au(111)-D-glucose	L-Phe-Au-(111)-L-glucose	D-Phe-Au(111)-L-glucose	D-Phe-Au(111)-D-glucose
deprotonated	I1	-3.323	-3.255	-3.323	-3.255
	I2	**-3.861**	**-3.392**	**-3.858**	**-3.393**
	II1	-3.604	-3.506	-3.602	-3.503
	II2	-3.800	-3.609	-3.799	-3.608
neutral	I1	-4.060	-3.877	-4.056	-3.876
	I2	-3.873	--3.612	-3.868	-3.611
	II1	**-4.340**	**-3.895**	**-4.337**	**-3.892**
	II2	-4.191	-3.903	-4.192	-3.903
zwitterionic	I1	**-3.952**	**-3.585**	**-3.948**	**-3.581**
	I2	**-4.135**	**-3.638**	**-4.126**	**-3.633**
	II1	-3.983	-3.834	-3.979	-3.830
	II2	-4.404	-4.252	-4.400	-4.250

Table S4 The comparison of the adsorption energies of Phe and glucose on clean Au(111) at their low and high coverage.

	Phe	E_{ads} (eV) of Phe	E_{ads} (eV) of glucose
Low coverage	deprotonated[a]	-0.208	-1.707
	neutral	-0.797	
	zwitterionic	unstable	
High coverage	deprotonated[a]	-0.470	-1.950
	neutral	-1.034	
	zwitterionic	-1.527	