SUPPORTING INFORMATION

Chemistry of Cysteine Assembly on Au(100): Electrochemistry, in situ STM and Molecular Modeling

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Cysteine monolayers on Au(100), adsorption dynamics, network assembling, electrochemical interface, DFT

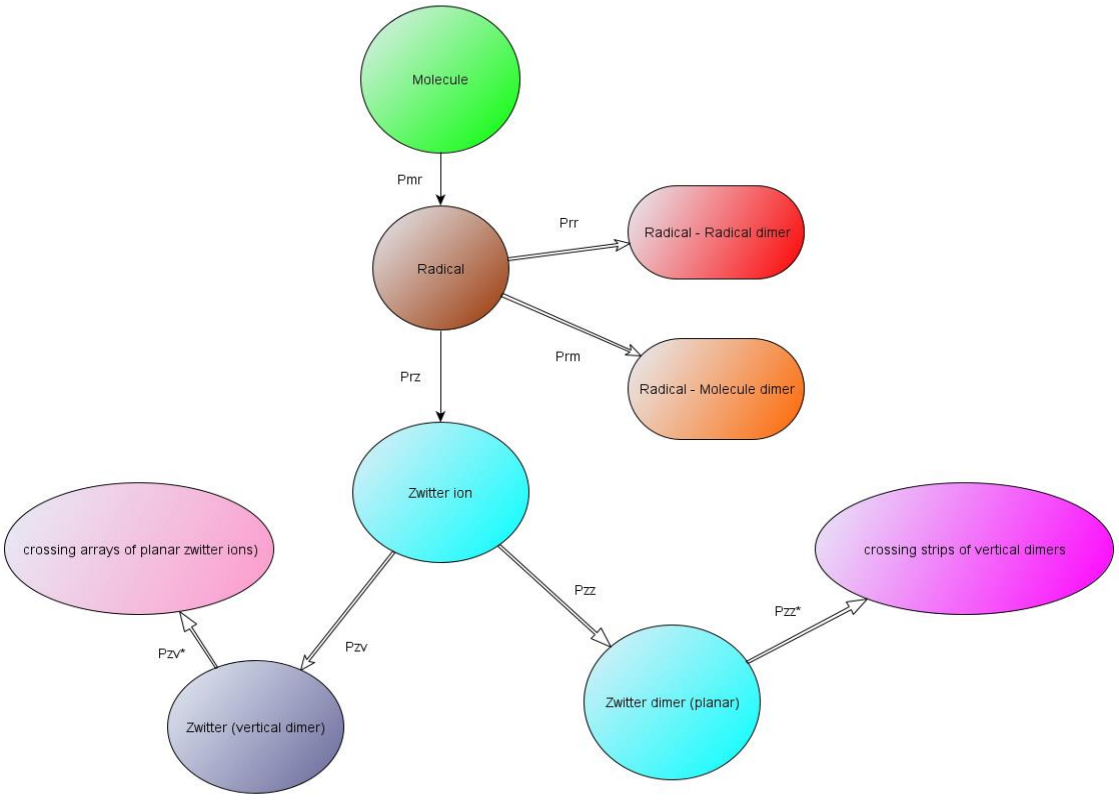

Figure S1. A tree of probabilities used in the kinetic MC simulations (Values for Au(100): Pmr = 0.125, Prz = 0.711, Prr = 0.638, Pzz = 0.113, Pzv = 0.004, $P^{*}zv$ = 0.2, $P^{*}zz$ =0.02).

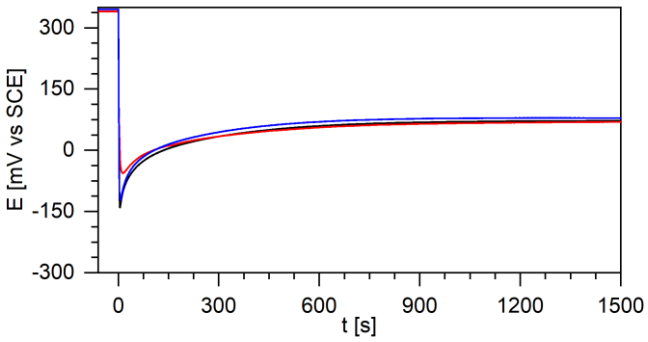

Figure S2. Reproducibility of chronopotentiometric data. Repeat measurements on different single-crystal Au(100) electrodes with 250 µM L-Cys injected in 0.25 mM KH_2PO_4 (pH4.66) at t=0.

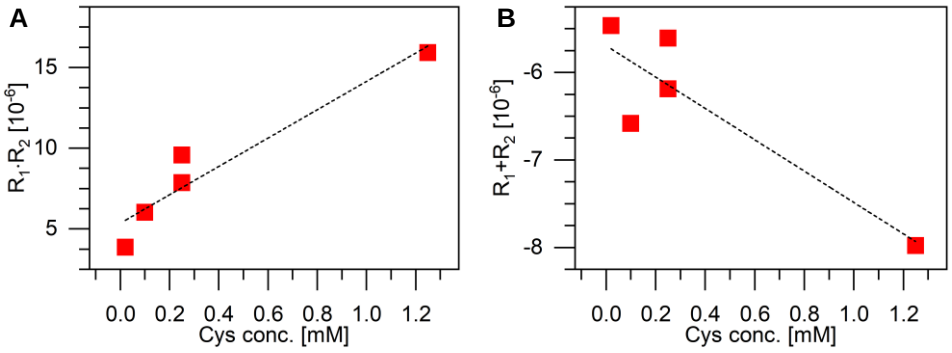

Figure S3. Plots of R_1 X R_2 (left) and R_1+R_2 (right), from the chronopotentiometric data shown in Figure 3, against the Cys concentration (mM) in solution. 25 mM KH_2PO_4.

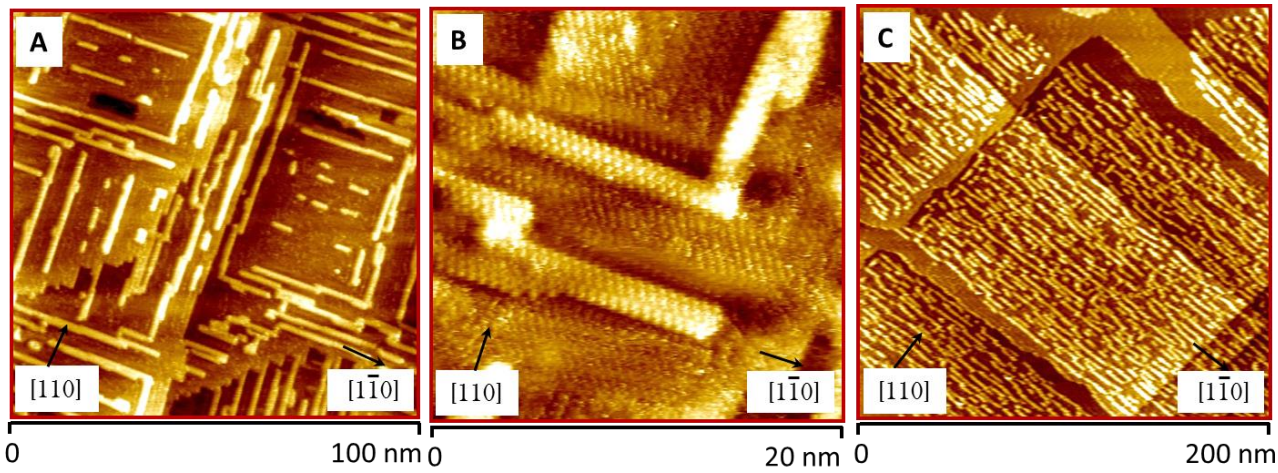

Figure S4. *In situ* STM images of L-Cys adlayer on Au(100), I_t=0.20 nA, V_{bias}= -0.10 – -0.24 V. E_W=-0.5 – -0.20 V. (A) and (B) *in situ* adsorption for 60 µM L-Cys in 20 mM KH_2PO_4 (pH4.6). 3.5 hours (C) pre-adsorption of 0.5 mM L-Cys on Au(100) for 20 hours.

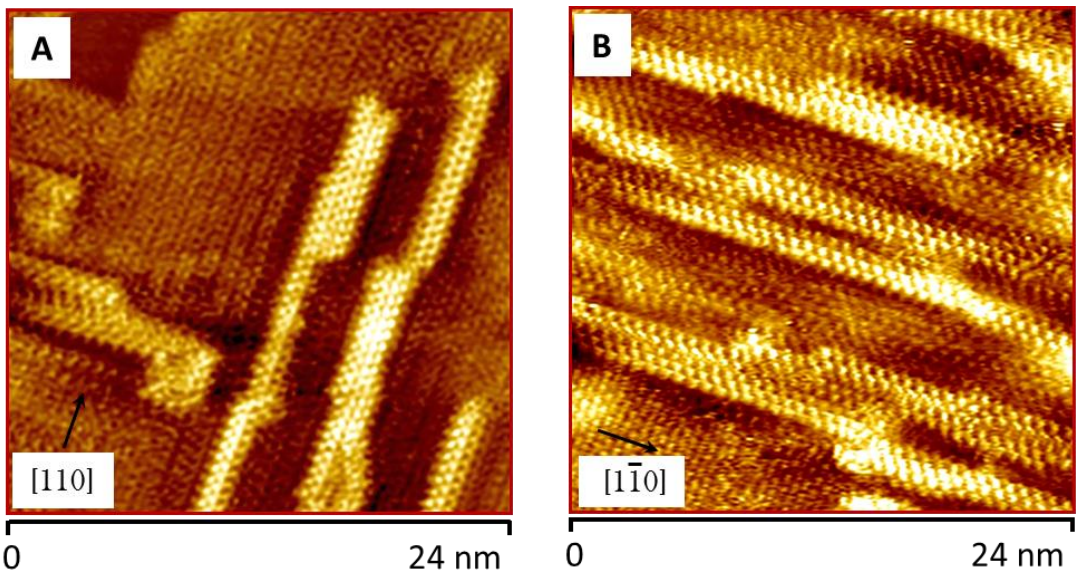

Figure S5. *In situ* STM images of L-Cys adlayer on Au(100), I_t = 0.06 – 0.20 nA, V_{bias} = 0.10- -0.40 V. E_W=-0.25 – - 0.15 V, 200 µM L-Cys in 25 mM KH_2PO_4 (pH4.66).

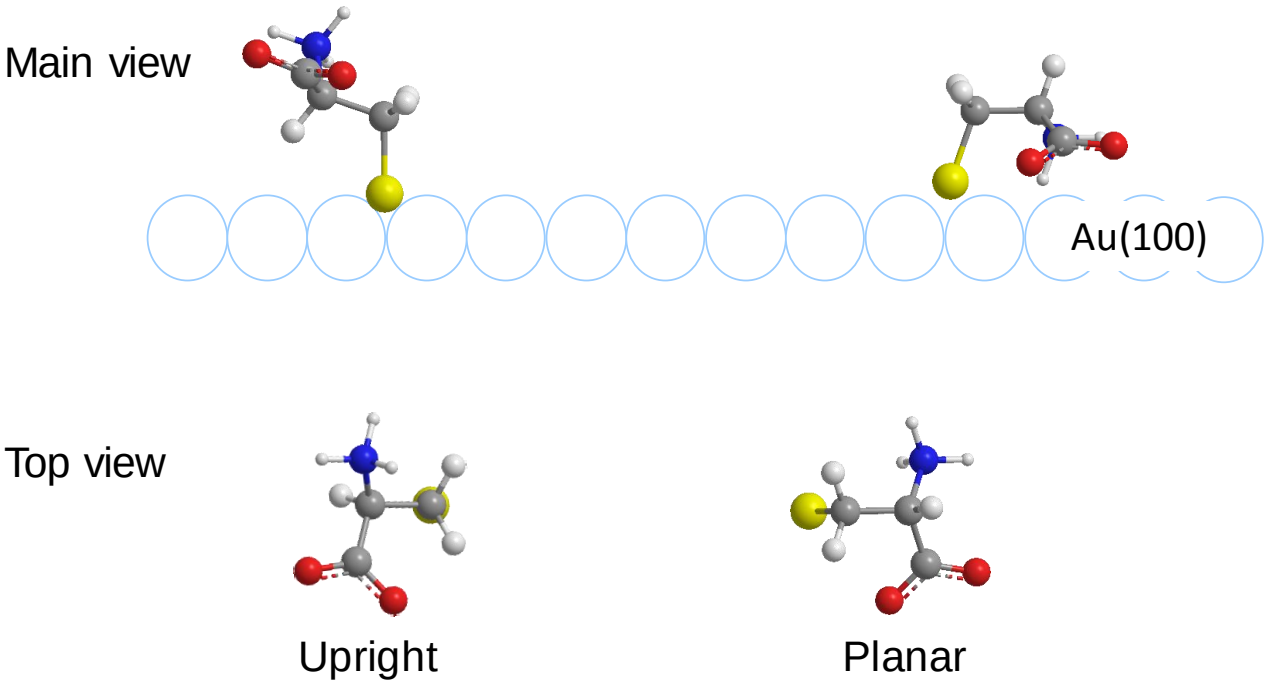

Figure S6. Main (upper) and top (bottom) view of planar (right) and upright (left) L-Cys molecules. The same code for Figure 7C.

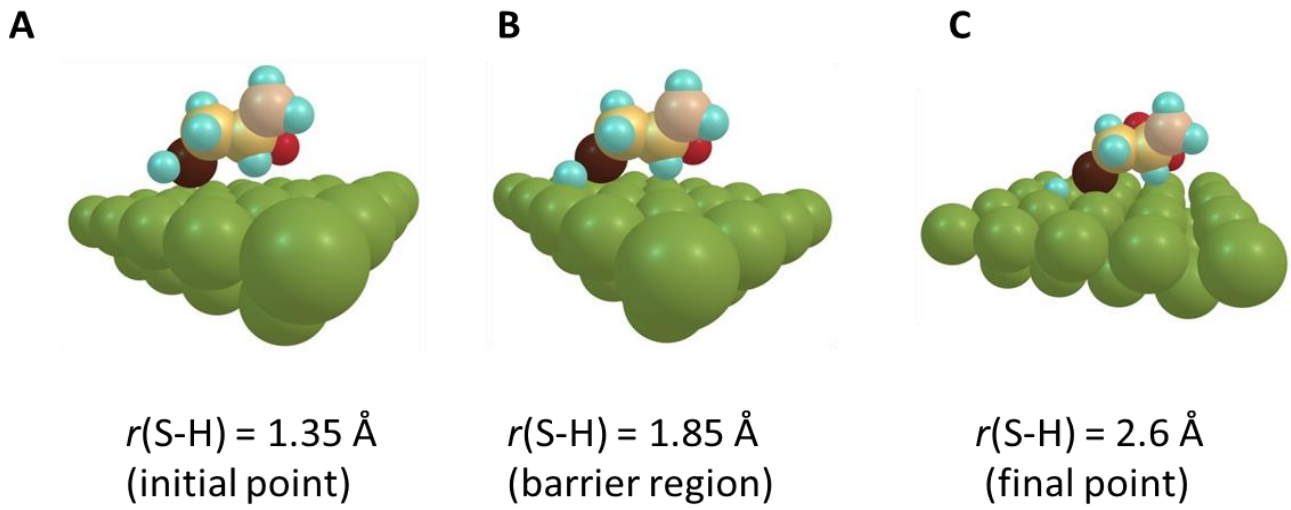

Figure S7. Selected structures of a Cys molecule dissociatively adsorbed at the Au(100) surface (with –S-H bond cleavage) corresponding to three points at the potential energy surface (see Figure 10A)**.**

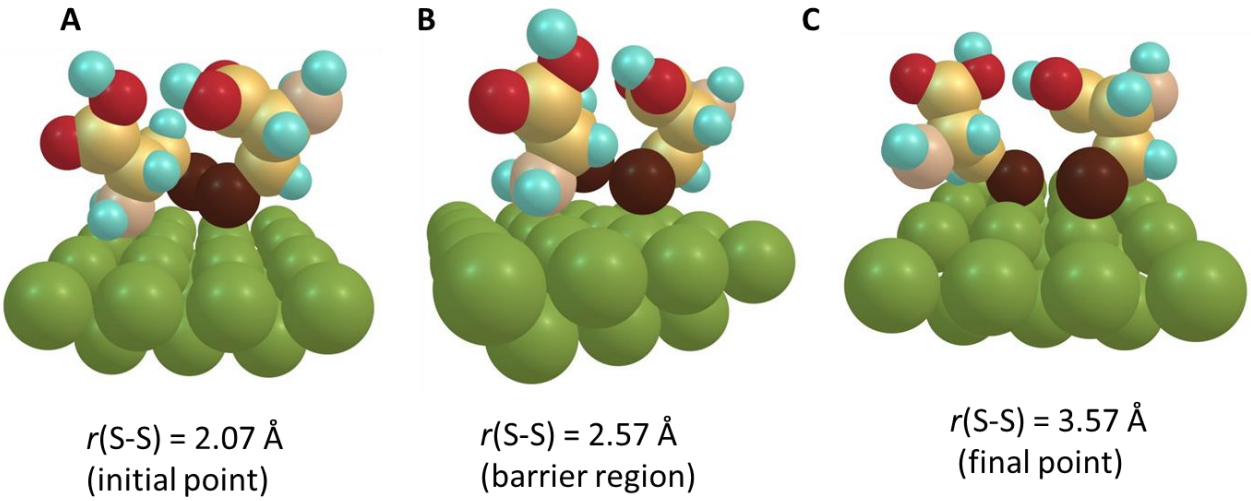

Figure S8. Selected structures of a cystine molecule dissociatively adsorbed at the Au(100) surface (accompanied by –S-S– bond cleavage) corresponding to three points at the potential energy surface (see Fig. 10B).

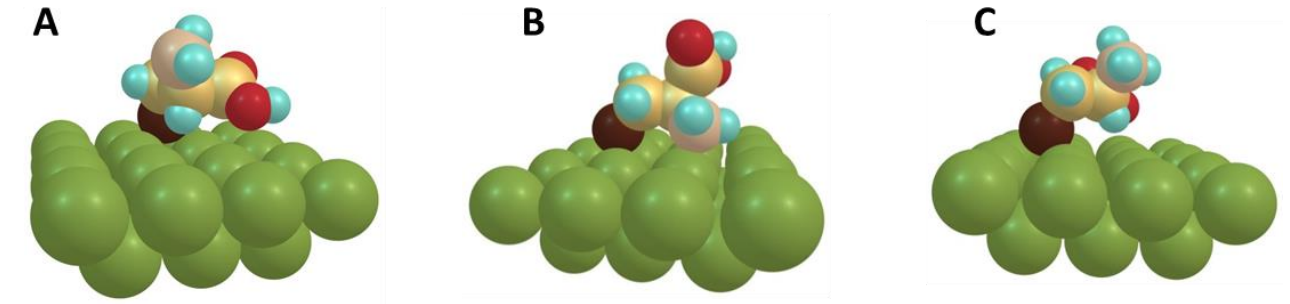

Figure S9. Optimized orientations of selected L-Cys radical forms adsorbed at the model Au cluster; (A) R with carboxylic acid group down, *r*(Au-S) = 2.46 Å, *r*(Au-O) = 2.89 Å; (B) R with amino group down, *r*(Au-S) = 2.43 Å, *r*(Au-N) = 2.31 Å ; (C) Zwitterionic R_Z, *r*(Au-S) = 2.47 Å.

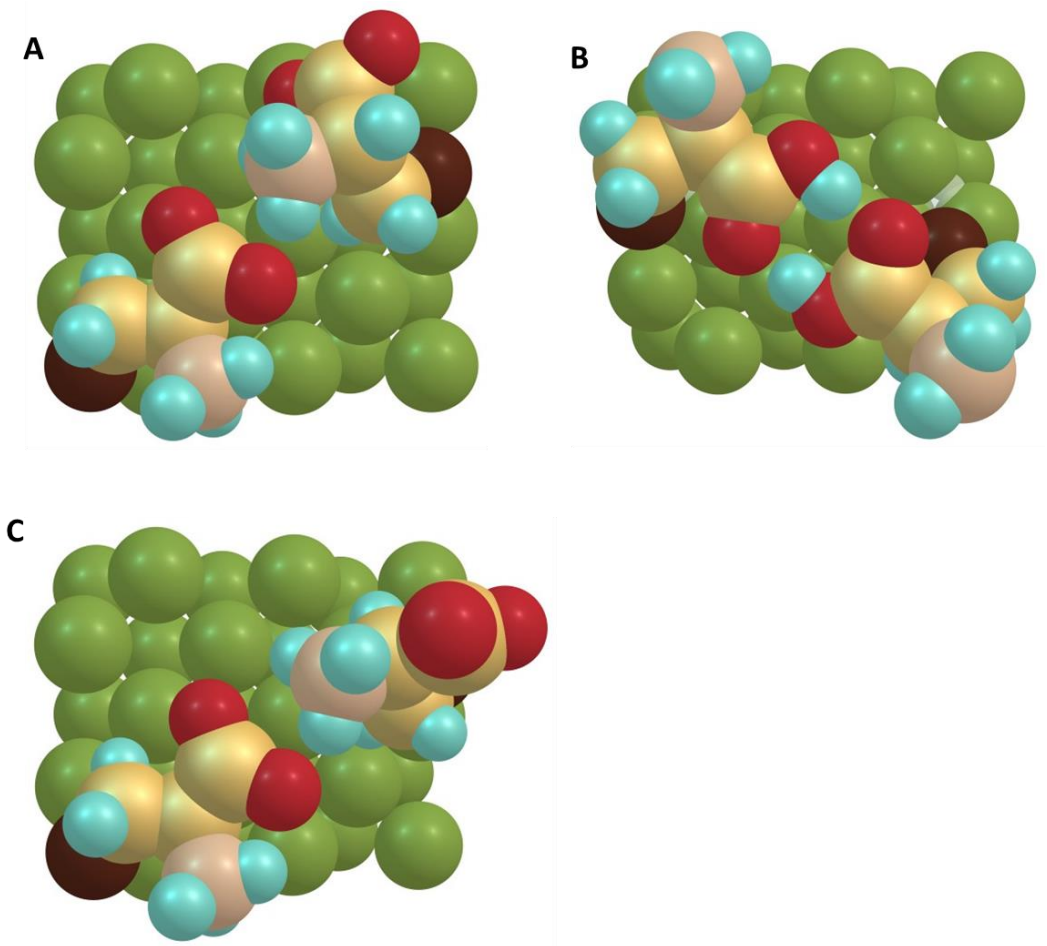

Figure S10. Optimized structures of three Cys radical dimers adsorbed at the Au(100) surface in planar (horizontal) orientation; L,L (A); D,D (B); L,D (C). (A) *r*(S-S) = 7.35 Å; (B) *r*(S-S) = 8.36 Å; (C) *r*(S-S) = 9.92 Å

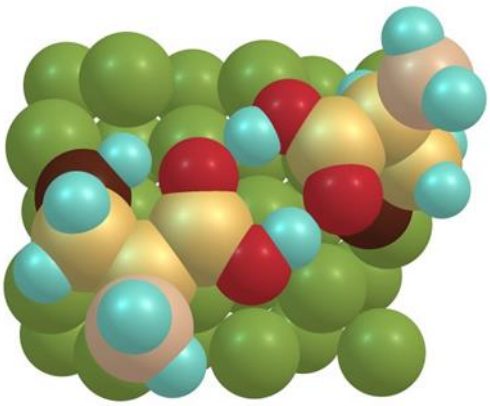

Figure S11. Optimized orientation of an L-Cys R-M dimer in planar (horizontal) orientation adsorbed at the Au(100) surface.

Table S1. Adsorption energy of some L-Cys forms from aqueous solution at the Au(100) surface.

	Radical Figure S9A	Radical Figure S9B	Radical zwitter ion Figure S9C
ΔE_{ads}, eV	-1.2	-1.34	-0.48

Table S2. Formation energy (ΔE_f^{dim}), the Au-S bond length and S-S distances calculated for three different Cys radical dimers, R-R, adsorbed at the Au(100) surface in planar (horizontal) orientation.

	L,L Figure S10A	D,D Figure S10B	L,D Figure S10C
ΔE_f^{dim}, eV	-0.65	-0.99	-0.89
r(Au-S), Å	2.47; 2.55	2.4; 2.57	2.52; 2.58
r(S-S), Å	7.35	8.36	9.92

Table S3. Formation energy (ΔE_f^{dim}), the Au-S bond length and S-S distances calculated for three different Cys dimers in zwitterionic form, R_Z-R_Z, adsorbed at the Au (100) surface in planar (horizontal) orientation.

	L,L Figure 11B	D,D Figure 11B	L,D Figure 11C
ΔE_f^{dim}, eV	-3.62	-2.7	-3.3
r(Au-S), Å	2.54; 2.55	2.48; 2.52	2.52; 2.55
r(S-S), Å	9.94	6.4	10.1

Table S4. Formation energy (ΔE_f^{dim}), the Au-S bond length and S-S distances calculated for three different Cys dimers[#], R_Z-M_Z, adsorbed at the Au(100) surface in vertical orientation.

	L,L Figure 12B	D,D Figure 12B	L,D Figure 12C
ΔE_f^{dim}, eV	-1.15	-1.05	-1.11
r(Au-S), Å	2.5; 2.52	2.39; 2.48	2.52; 2.55
r(S-S), Å	7.08	8.2	9.15

[#]R_Z is adsorbed at the Au(100) surface, while M_Z is located on top (from the solution side).

Table S5. Probabilities used in additional kinetic MC simulations (the meaning of probabilities is illustrated in Fig. S1)[#].

Metal surface	P_{mr}	P_{rz}	P_{rr}	P_{zz}	P_{zv}	P^*_{zz}	P^*_{zv}
Au(110)	0.74	0.84	0.34	0.83	$4\ 10^{-2}$	0.91	0.02

[#] P^*_{zz} describes the probability of event, when an array of Cys zwitterionic species adsorbed in planar orientation crosses a strip formed by Cys dimers in vertical orientation and continues its growth.

P^*_{zv} corresponds to the probability of event, when a stripe formed by Cys dimers in vertical orientation crosses an array of Cys zwitter ionic forms in planar orientation and continues its growth.

Table S6. Fractions of some species and structures in the Cys SAM on Au(110) estimated for different stages of the monolayer formation based on kinetic MC simulations. (*A*) 2.25 10^4 steps, (*B*) 9 10^4 steps, (*C*) 2.75 10^5 steps, (*D*) 2.25 10^6 steps.

Stages of the SAM formation	M	R	R_Z	R-M	R_Z-R_Z planar arrays	$[R_Z\text{-}M_Z]_n$ vertical rows
(*A*)	0.4	0.48	0.	0.12	0	0
(*B*)	0.015	0.035	0.18	0.02	0.74	0.01
(*C*)	0	0.005	0.02	0.012	0.93	0.033
(*D*)	0	0	0.018	0	0.96	0.022

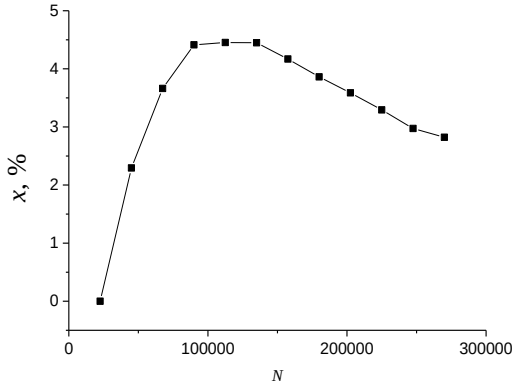

Figure S12. Fraction of all "vertical" Cys dimers in the SAM at the Au(110**).** (*x*) as a function of the number of MC steps (*N*).

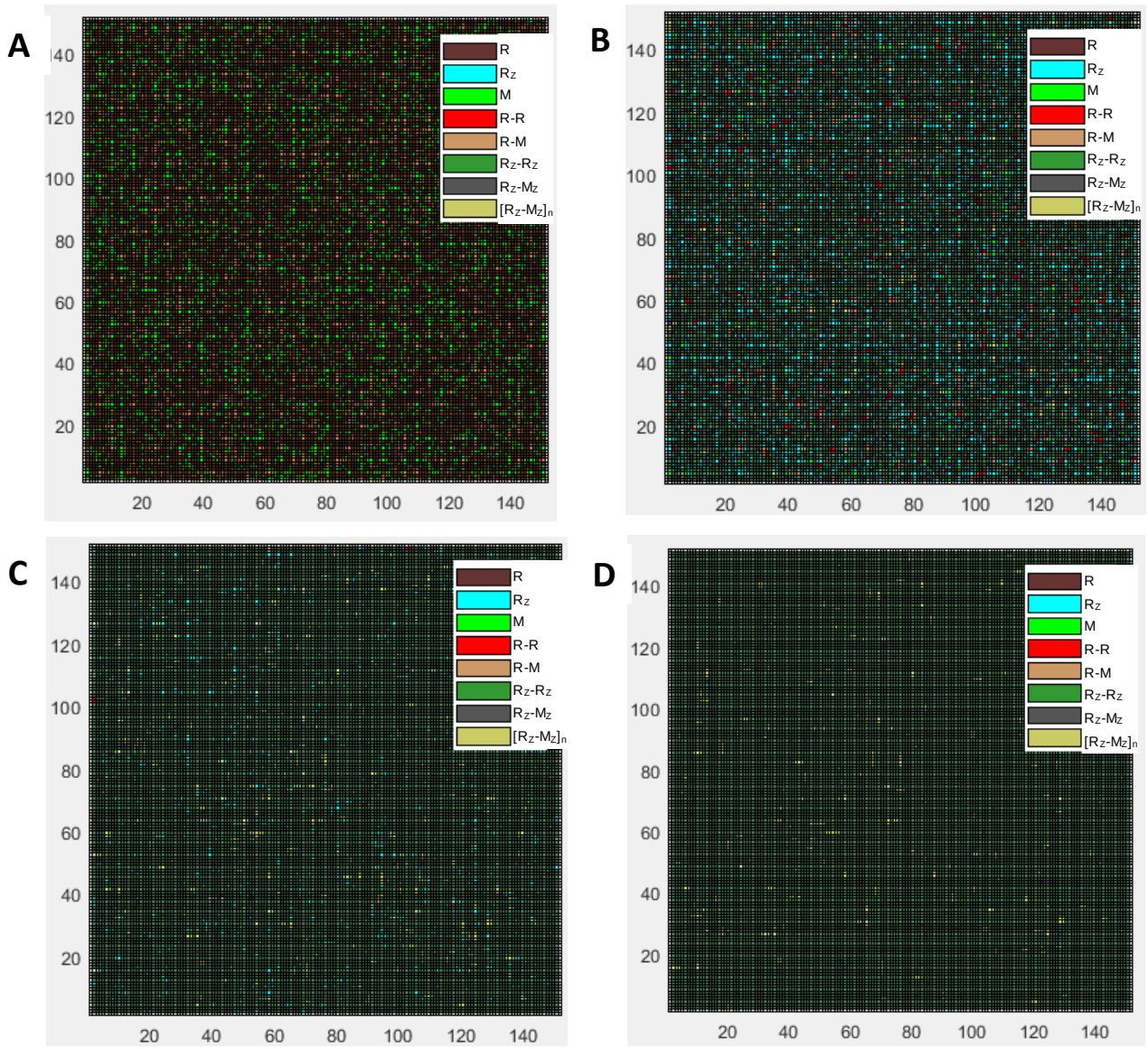

Figure S13. 2D-pictures illustrating four different stages of the formation of Cys SAM on Au(110) (see Table S6) built using the data of kinetic MC simulations. M, R, R_Z are Cys molecules, radicals, and radical zwitter ions, respectively. R-R, R-M, R_Z-R_Z, R_Z-M_Z are dimer species. $[R_Z\text{-}M_Z]_n$ indicates rows of vertical dimers.