Electronic Supplementary Information

Surface-Mediated Ordering of Pristine Salen Molecules on

Coinage Metals

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Content

Geometry optimization of different Salen isomers	S2
Conformational isomers of CI _C	S2
Adsorption configurations of Salen on surface	S3
Synchrotron XPS measurements of Salen on Cu(111)	S3
Possible intermolecular configurations between a pair of Cl _c isomers	S4
Possible intermolecular configurations between a pair of CI _c isomers	S5

1. Geometry optimization of different Salen isomers

The geometry optimization of the Salen molecule in free space was completed by MM2 method in Chem3D. The calculated conformations of the Salen molecules were initialized by rotating the molecular segments around three types of intramolecular σ bonds (marked by red, yellow and blue arrows), starting from Cl₀. More than 30 initial conformations were optimized with MM2, and three optimized conformations were found, as shown in Figure S1 a-c. The calculation results revealed that Cl₀ (Figure S1c) was the most energetically favorable conformation (5.31 kcal/mol) in free space, compared with other typical conformations.



Figure S1. Calculated structures for the Salen molecule in free space. The total energy is given under each structure.





Figure S2. Eight conformational isomers of CI_c on surface; Four structural isomers are marked as A-D, and their surface enantiomers are correspondingly marked as A'-D'.

3. Adsorption configurations of Salen on surface

The N atoms in Salen form a stronger interaction with the Cu(111) surface than to the Au(111) surface, leading to that the apparent height of inside ethyl group becomes higher than other parts of the molecule.



Figure S3. Tentative models of the Salen molecule on (a) Cu(111) and (b) Au(111).

4. Synchrotron XPS measurements of Salen on Cu(111)

In the synchrotron XPS measurements of Salen on Cu(111), 100 K (the lowest temperature being achieved in synchrotron XPS setup) was employed to avoid (albeit not completely] the surface reaction between Salen and Cu(111). To calibrate the BE in XPS, Au 4f7/2 (84 eV) was used as the reference. For O1s, there exist two peaks where the dominating one locates at 533.2 eV and the small one, at 530.8 eV. The main peak stems from the OH group interacting with the Cu(111) surface, while the small one (530.8 eV), from the partial dehydrogenation of the OH group at the experiment temperature. For N 1s, there also exist two peaks where the major one locates at 399.3 eV and the minor one, at 403.2 eV. The major peak is due to the N 1s signal from the molecule, while the minor one at 403.2 eV, due to the π - π * electron transition because of the extra π bond between the nitrogen and carbon atoms (C–N*) (ref. 41). As discussed in the text, the XPS data are compared with those for Salen powders in previous report (Ref.41 in the text where C1s, 285 eV, was used as a BE reference) where the strongest features for N 1s and O 1s were reportedly located at 399.0 eV and 532.9 eV, respectively. Meanwhile the smaller peaks for N 1s and O 1s were located at 403.0 eV and 531.1 eV, respectively. A chemical shift of 0.3 eV in both N1s and O1s is likely due to the systematic calibration error.



Figure S4 (a) N 1s and (b) O 1s features for Salen on Cu(111) at 100 K. The N 1s and O 1s XPS spectra were acquired with a photon energy of 480 eV and 600 eV, respectively.

5. Possible intermolecular configurations between a pair of CI_c isomers

The possible intermolecular binding modes between two out of the eight isomers of Cl_c (A, B, C, D, A', B', C' and D') are summarized in Figure S5. Firstly, we propose that both molecules be parallel to each other because nearly all molecules are parallel in the self-assembly structure, according to the STM observations. Secondly, we build two parallel conformers in the modeling software which are forced to be co-planar. One of the molecules is dragged up and down until a hydrogen bond is established, as indicated by the software. The corresponding configurations are recorded and shown below. Thirdly, we superimpose the recorded 36 configurations on the experimental observed STM images. It turns out that three of them (Cl_c-D&Cl_c-D, Cl_c-D', Cl_c-D'&Cl_c-D') well match the STM-observed self-assembly structures. The proposed models are utilized in the text.

	CI _c -A	CI _c -B	Cl _c -C	CI _c -D	Cl _c -A'	Cl _c -B'	Cl _c -C'	Cl _c -D'
Cl _c -A	and	and	and	and	ando	and	and	and
CI _c -B		and	and	and	ang	and	ang	and
Cl _c -C			and	and	durp	and	drub	and
CI _c -D				ofilo	durp	dirb	gung	and
CI _c -A'					dup	dino	and	and
CI _c -B'						ding	and	and
Cl _c -C'							durb	and
CI _c -D'								and

Figure S5. Possible binding conformations for two Cl_c isomers.

6. The orientations of the Salen chains on Ag(111)

As shown in Figure S6a and S6b, the self-assembled Salen chains on Ag(111) are rotated by about 10° clockwise or anticlockwise with respect to the <110> lattice direction of the substrate surface. In total, there exist six chain orientations. For example, the direction in Figure S6d is in accordance with the <451> lattice direction of the Ag(111) surface, which is about 10° clockwise from the <110> direction (Figure S6c). The distance between each pair of the Salen molecules (1.30 nm) is close to the lattice distance along the <451> direction (1.32 nm) as well.



Figure S6. (a) STM image of the self-assembled Salen chains on Ag(111) (coverage = 0.34 ML). (b) The molecular model of the Salen chains in different orientations. Each chain is rotated +10° or -

10° with respect to <110>; (c) Atomically resolved STM image of the Ag(111) surface; (d) STM image of a Salen chain on Ag(111). The orientations of the molecular chains and lattice directions are marked by the arrows in the panels.