Genarris 4.0: Random Structure Generator for organic/inorganic Interfaces

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INTRODUCTION

Functional hybrid inorganic-organic systems(HIOSs)

- Molecular thin films on inorganic substrates material have critical applications : organic solar cells (OSCs), organic field effect transistors (OFETs), organic light emitting diodes (OLEDs) and sensors.
- Understanding the structure and electronic properties of HIOSs is key to enhance the performance of organic electronic devices. The interfacial structure directly affects properties through changes in the intermolecular electronic coupling, dipole formation, polarization induced gap narrowing, and charge transfer (CT).

Experimental characterization & Limitation

- Experimental characterization of HIOSs is performed through surface science techniques: topographic surface imaging (STM), spectroscopy (UPS), surface scattering (NIXSW), and thermodynamic measurements ((TPD)).
- Limitation: indirect information like spectra, hard to directly associate with geometry. The exact adsorption site is undetermined

Computational study

- Complement spectroscopy experiments by assigning the observed spectral features to specific atomic configurations and electronic state
- Access the vast configuration space of possible interface structures and compositions and explore materials that have not been made yet
- Help determine the energetically most favored adsorption site

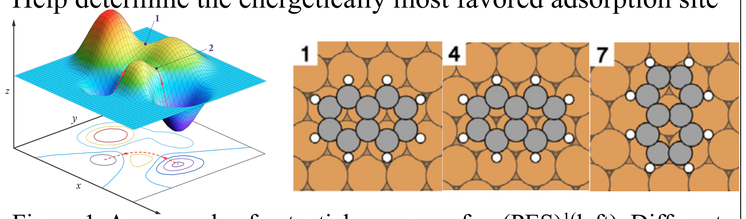


Figure 1. An example of potential energy surface(PES)[1](left). Different absorption sites of naphthalene molecule on Cu(111)[2](right).

METHOD

Genarris 4.0

- A random structure generator for organic/inorganic interfaces
- Genarris 4.0 is written in python and interface with FHI-aims for interface energy evaluation and geometry relaxation.
- 1st step: film lattice generation

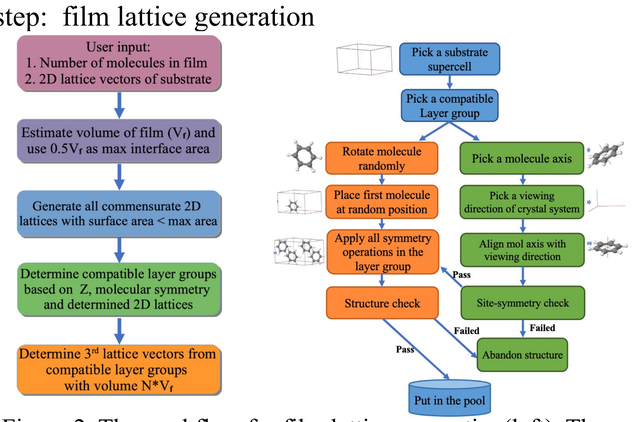


Figure 2. The workflow for film lattice generation(left). The workflow for molecule placement in lattice (right).

- 2nd step: film slab generation by Ogre

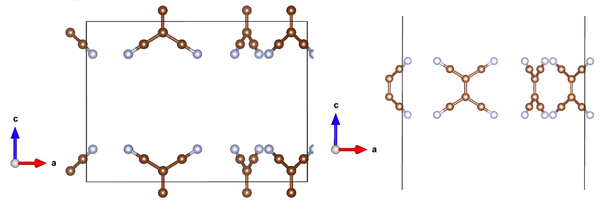


Figure 3. Film lattice (left). Film slab (right)

- 3rd step: clustering and down-selection

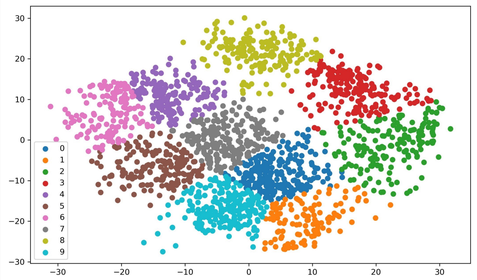


Figure 4. An illustration of grouping interface structures into different clusters, based on geometric descriptors.[3]

- 4th step : surface geometry matching

$$S = \bar{A} - c(1+\bar{R})^2 \qquad \bar{A} = \frac{V_a}{\sum_{atoms} V_{at}} \qquad r_a = r_{vdw} + \alpha$$

RESULT

TCNE/Au(111)

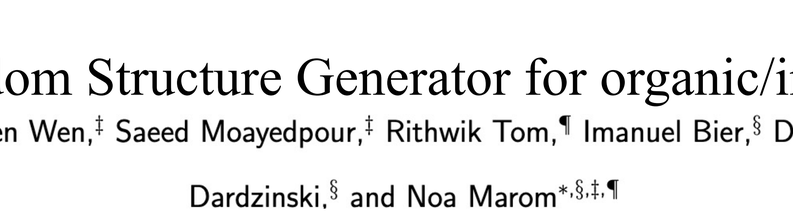


Figure 5. TCNE/Au(111) interface area, gamma angle and their joint distribution in the final relaxed pool. Exp value is in red.

Figure 6. Comparison between results from geometric score function(left) and energy computed by PBE + TS^{surf} (middle) for TCNE/Au(111). Comparison between experimental structure and generated structure in the present work. (right)

PTCDA/Ag(111)

Figure 7. PTCDA/Ag(111) interface area, gamma angle and their joint distribution in the final relaxed pool. Exp value is in red.

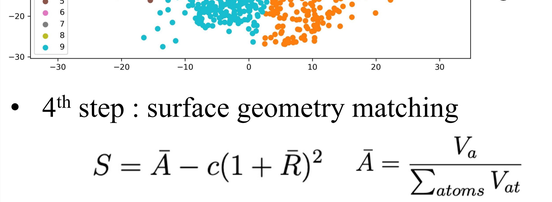


Figure 8. Comparison between geometric score (left) and energy computed by DFT for PTCDA/Ag(111).

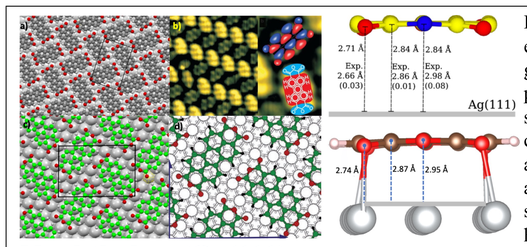
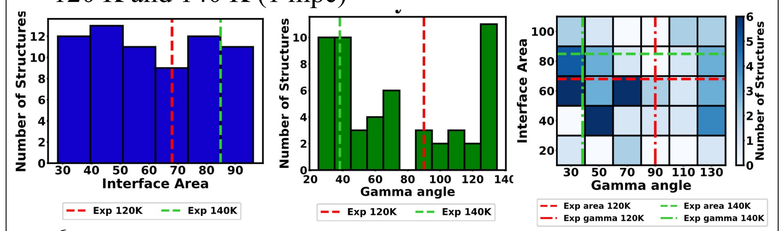


Figure 9. Comparison between experimental structure and generated structure in the present work. a) Generated structure b) Experimental STM c)A close-up on generated adsorption site. D) Experimental adsorption site. Fig on the right shows agreement in adsorption height

Naphthalene/Cu(111)

- Three kinds of ordered phases are identified depending on substrate temperature and adsorbate concentration.
- 120 K and 140 K (1 mpc)



- 6 mpc

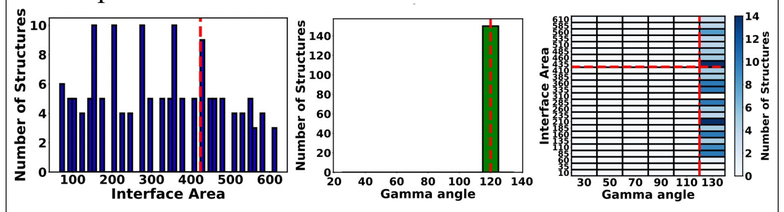


Figure 10. Naphthalene/Cu(111) interface area, gamma angle and their joint distribution in the final relaxed pool for Z=1 (above) and Z=6 (below).

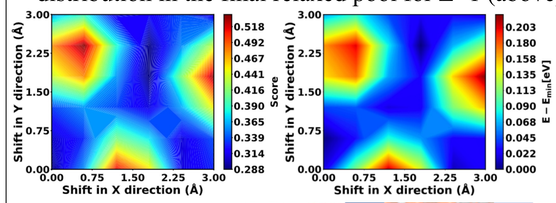


Figure 11. Comparison between geometric score (left) and energy computed by DFT for naphthalene/Cu(111).

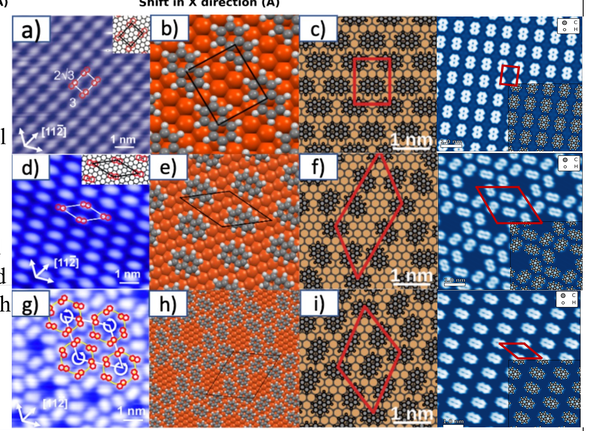


Figure 12. Comparison of a), d), g) Experimental structure, c), f), i) Simulated structure from previous study and b), e), h) Generated structure along with their STMs in the present work.

CONCLUSION

- In summary, we have presented Genarris 4.0 and demonstrated its application with TCNE on Au(111), PTCDA on Ag(111) and naphthalene on Cu(111)
- Besides experimental structure, other promising low-energy structures are also identified (details in paper)

References

1. CC BY-NC; Ümit Kaya via LibreTexts.
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3. Wikipedia, 2021, K-Means Clustering From Scratch in Python, https://www.askpython.com/python/examples/k-means-clustering-from-scratch
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