Exploring on-surface structural transformation using DFT

Throw this molecule on Cu(111) surface...

Once deposited, the molecule reacts immediately with the copper surface...

...and interesting things happen
☆ it undergoes several on-surface reactions, changing its structure considerably
☆ final and intermediate structures show self-assembly!

...after annealing at 200°C, first stable transformation happens...

...further annealing at 400°C yields the final structure.

1 H or no H? Although the low-temperature AFM images reveal the molecular geometries with high precision, hydrogen atoms are difficult to identify.

We used DFT calculations to investigate the problem:

the structures without...

...and with “extra” H atoms clearly differ in geometry...

...the structure with two “extra” hydrogen atoms (C_{24}H_{14}) matches the experiments!

0 H or no H? – prequel Perhaps the “extra” hydrogen atoms are already present in the first reaction?

According to DFT calculations this is indeed plausible:

the geometry is stable enough to exist...

...it fits both to AFM and STM characteristics...

...and it suggest a realistic pathway leading to the first stable structure

2 H or no H? – sequel To obtain the final structure, two hydrogen atoms need to be removed.

Experimentally this is observed after annealing at 400°C, in accordance with DFT energetics.

These results demonstrate the potential of on-surface reactions as a route for chemical synthesis – and the necessity of computations.

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