On-Surface Site-Selective Chemical Conversions -- Corroles on Ag(111)

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The electronic structure of flexible macromolecules like corroles promotes the stabilization of metal ions in exceptionally high oxidation states. This makes them distinctive candidates for various biomedicine, catalysis, as well as solar cell applications.
Combining *first-principles* calculations, temperature-programmed desorption (TPD) measurements, scanning tunneling microscopy (STM), X-ray spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy measurements and simulations, we characterize the chemical state and the conformation of the free-base corrole 5,10,15-tris(pentauorophenyl)corrole (3H-TpFPC) adsorbed on Ag(111) surface and unravel annealing induced chemical reactions. With our novel method to simulate the XPS and the angle dependent NEXAFS signatures of the C1s and N1s edges, we can interpret the spectral features and predict the temperature induced new molecular chemical states. [1]
We reveal a formation of on-surface stable corrole radicals by a site-specific cleavage of a pyrrole N-H bond triggered by annealing to 330 K. The molecular species adsorb with their macrocycle tilted approximately 20° with respect to the surface plane contrasting the typical saddle-shape conformation of related porphyrin species. The tilted adsorption geometries enable the molecules to aggregate in non-trivial interwoven monolayer structures. [1,2] After annealing to 430 K, a thermally induced regioselective cyclization (ring closure) reaction, between the phenyl ring and the pyrrolic moiety, mediated by the radical cascade has been reported. The ring-closed radicals form a highly symmetric hexagonal monolayer structure. [3] Our calculations resolve the packing motif and predict the molecular conformations within the structure, which might offer exciting areas of application.

References

[1] H. Aldahhak, et al., J. Phys. Chem. C, 121, 2192, 2017.
[2] S. Tebi et al., ACS nano 11, 3383, 2017.
[3] H. Aldahhak, et al., Chem. Euro. J. 24, 6787, 2018.

Figures

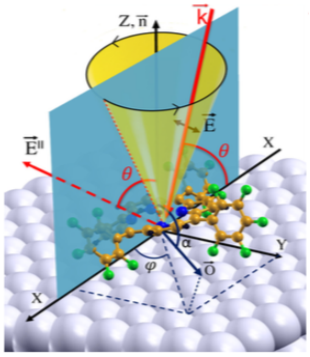

Figure 1. NEXAFS in experiment and simulations for structure identification