Molecular reactions, charge transitions and excited states investigated by AFM

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Atomic force microscopy (AFM) with functionalized tips achieves atomic and bond-resolved resolution providing insights into the structure, aromaticity, charge states and bond-order relations of individual molecules [1]. Importantly for on-surface synthesis, the products and intermediates of chemical reactions can be identified and characterized. Recently, we generated by atom manipulation the elusive carbon allotrope cyclo[18]carbon and resolved its debated structure [2].

On insulating substrates, we can control the charge states of molecules. With ultra-high-resolution imaging we resolve how the charge state of molecules affects their structure [3], see Figure. By alternatively attaching and detaching single charges from a molecule on an insulator, we probe transitions between different charge states including neutral excited states and quantify the reorganization energy [4] and singlet and triplet excitation energies [5]. Accessing excited states this way, recently triplet lifetimes and their quenching by molecular oxygen have been measured by Peng *et al.* [6].

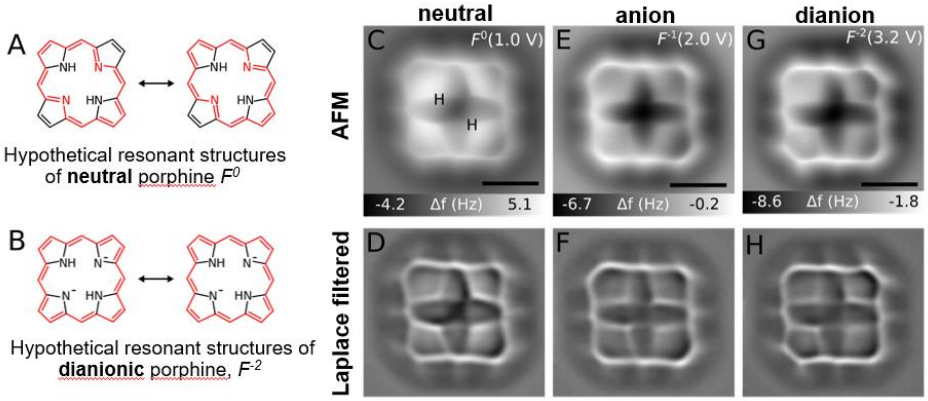

Figure: Porphine on NaCl, imaged in different charge states (neutral, negative and doubly negative) by AFM with CO tip functionalization. Bonds of increased bond order appear shorter, which allows us to draw conclusions about the structure, aromaticity and conjugation pathway (indicated red in A and B) in different charge states [4].

References

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[6] J. Peng *et al. Science* **373**, 452 (2021)