Atomic force microscopy images carry chemical information: Halogen bonds, Tautomerization, and molecular identification with deep learning

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High resolution non-contact atomic force microscopy (HR-AFM) with CO-functionalized metal tips reveals the internal structure of adsorbed organic molecules with unprecedented resolution, resolving intermolecular features, determining bond orders, and characterizing intermediates and final products generated in on-surface reactions [1].

Here, we show how the chemical information imprinted in HR-AFM images paves the way for understanding how the molecule-substrate interactions can be exploited to tune (i) the strength and the directionality of intermolecular halogen bonds [2], (ii) the nature and energy barriers for tautomerization in meso-Dibenzoporphycene (mDBPc) molecules [3], and (iii) the hydrogen bond driven molecular self-assembly in the paradigmatic case of trimesic acid (TMA) molecules [4]. Furthermore, we demonstrate that HR-AFM images contain enough information not only to reveal the molecular structure but also to identify each atomic species. This identification can be automated with machine learning techniques, using neural networks trained mainly with a large dataset of theoretical AFM images [5,6].

Regarding halogen bonds [2], we present an approach for controlling the 2D self-assembly process of halogenated compounds by adsorption on reactive metal surfaces. Molecule-substrate interactions modify the strength of the σ-hole, a positive region at the caps of the halogens, reversing the order of halogen bond strengths known from gas phase. Adsorption of mDBPc, dominated by the metal-coordination bond of the lone-pair electrons of the imine N atoms with the substrate, results, on NaCl films, in a new type of tautomerization process, where the transfer of H atoms within the porphycene cavity is accompanied by a significant displacement of the whole molecule [3]. Accurate comparison between modeled images and experiments on TMA on Cu(111) [4] allows us to identify key structural elements in the assembly in terms of the electron-withdrawing character of the carboxylic groups, their interactions with the surface, and the electron density in the region of the hydrogen bonds.

References

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