Adsorption and self-assembly of functionalized [5]helicene molecules on insulating ionic surfaces

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In recent years, organic thin films on insulating surfaces have become very important since they have the advantage of electronically decoupling molecules from the support, unlike metal surfaces. This leads to new phenomena of adsorption and self-assembly, which detailed mechanisms are studied on, e.g., the *model surfaces* of ionic alkali halides by noncontact atomic force microscopy (nc-AFM) and Kelvin probe force microscopy (KPFM) [1].
The current tentative picture for the adsorption considers a non-site specific van der Waals interaction between the molecule and the surface, but also an electrostatic interaction between the ionic lattice of the surface and functional groups of the molecule, which contain a partial charge or exhibit a local dipole. Although such two contributions explain to some extent experimental observations, many important questions remain still open – the current tentative model needs urgent further confirmation.
In this contribution, we focus on functionalized pentahelicene molecules, which are deposited in ultrahigh vacuum (UHV) onto (001) Suzuki surfaces of Cd^{2+} doped NaCl [2]. The local structure of the films and their dipole distribution are studied by UHV nc-AFM and KPFM, respectively, and DFT theory. The helicene molecules carry either one or two bromine atoms (MonoBromo, DiBromo) or one or two cyano groups (MonoCyano, DiCyano) (see Figure). We show that the adsorption and self-assembly of the molecules strongly depend on the number of functional groups, the type of group (dipole) and the adsorption site. In particular, the adsorption geometries (*charge matching*) and dipole strengths are of key importance. They all have an impact onto intermolecular interactions determining if self-assembly via π-π stacking of the helicene molecules is possible or not.

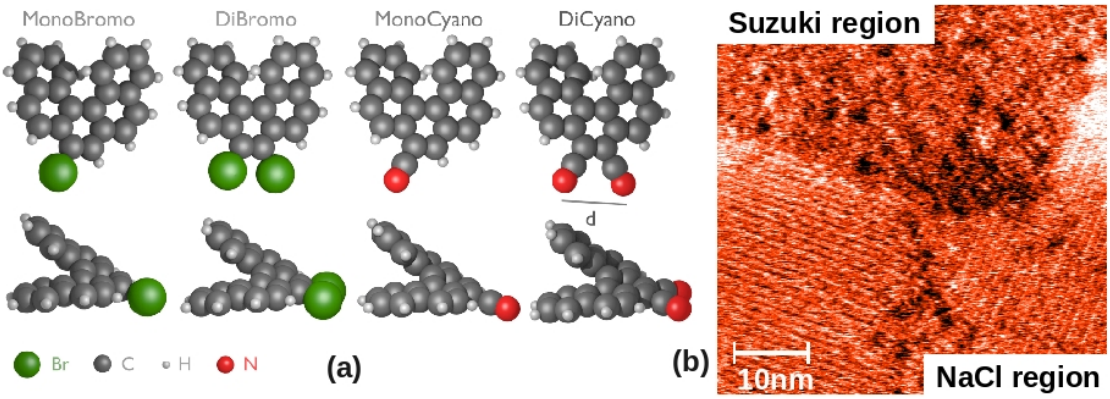

Figure: (a) The [5]helicene molecules used for the experiments. (b) DiCyano on the Suzuki surface. Only in the NaCl regions, self-assembly can be observed, but not in the Suzuki regions.

References

[1] C. Barth, A. S. Foster, C. R. Henry and A. L. Shluger, *Adv. Mater* **23**, 477 (2011)
[2] C. Barth, M. Gingras, A. S. Foster, A. Gulans, G. Félix, T. Hynninen, R. Peresutti and C. R. Henry, *Adv. Mater.* **13**, 2061 (2012).