Ordering of Phthalocyanines on Thallium-Pasivated Silicon Surfaces: Influence of Fluorination

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Ordering of planar organic molecules on metal-passivated surfaces is influenced by two crucial factors: 1) Surface periodicity serves as a grid for the adsorbed molecules and thus dictates possible separations of them. 2) Atomic structure of the molecules, especially chemical properties of molecular periphery drives interaction between the molecules.

Previously we have shown [1] that fluorinated copper phthalocyanines (F_{16}CuPc) on Si(111)-Tl(1x1) do not tend to self-order and instead form a 2D gas allowing to observe pair-correlation function by the scanning tunneling microscopy (STM). On the other hand, non-fluorinated copper phthalocyanines (F_0CuPc) form ordered structures but only at close-to-monolayer coverage or in a strong field of an STM tip [2]. Importantly, the latter can be used to manipulate the ordered structures.

The home-made room-temperature STM is used to study ordering of the phthalocyanines on the Si(111)-Tl(1×1) surface and stability of the ordered islands with respect to the field of the STM tip. Ab-initio calculations with included van-der-Waals interaction and spin-orbit coupling show the lowest-energy arrangements and the charge transfers induced by presence of the molecules. Finally, kinetic Monte Carlo simulations give insight into mechanisms of ordering-disordering observed on the surfaces.

We will present results of study extended to molecular mixtures of F_{16}CuPc and F_0CuPc and to the molecules fluorinated just partially (F_8CuPc). In both cases, forces of electrostatic origin stabilize ordered structures of these molecules. Information about influence of fluorination will be dervied from comparison of different molecules forming simillar structures but with very different behaviours.

References:
[1] P. Matvija, F. Rozbořil, P. Sobotík, I. Ošťádal, and P. Kocán, J. Phys. Chem. Lett. **8**, 4268 (2017).
[2] P. Matvija, F. Rozbořil, P. Sobotík, I. Ošťádal, B. Pieczyrak, L. Jurczyszyn, Scientific Reports **7**, 7357 (2017).

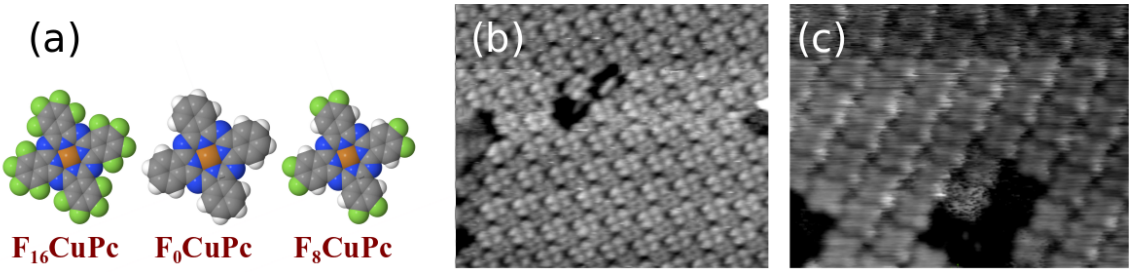

Figure: (a) structural models of used phthalocyanines. (b) STM image of F_{16}CuPc+ F_0CuPc mixture, (c) island of ordered F_8CuPc molecules.