# Communication Poster
# 247th ACS National Meeting&Exposition
# 16-20 march 2014, Dallas USA

**Experimental and theoretical studies of supramolecular self-assemblies on a silicon surface**

Guillaume Copie[1], Christophe Krzeminski[1], Fabrizio Cleri[1], Bruno Grandidier[1], Younes Makoudi[2], Frank Palmino [2], Frederic Chérioux [2]

[1] IEMN, UMR-CNRS 8520, Avenue Poincaré, 59650 Villeneuve d'Ascq.
[2] Institut FEMTO-ST, Université de Franche-Comté, CNRS, ENSMM, 32 Avenue de l'Observatoire, 25044 Besancon cedex France.

We report the experimental and theoretical study of the self-assembly of planar organic molecules of the type tris-1,3,5-(4'-X-biphenyl)benzene (with X=H, Br and CN) on a passivated, boron-doped Si(111)-B $\sqrt{3}x\sqrt{3}R=30°$ surface. Ordered molecular structures are observed by high-resolution STM. We perform multi-scale atomistic simulations, by DFT structure relaxation (Gaussian03), metadynamics, molecular dynamics (MD) with empirical forces, and kinetic Monte Carlo with condensed degrees of freedom. At low coverage, we identify by metadynamics the lowest-energy adsorption sites consistently with the STM images. Upon increasing molecular coverage, structural phase transitions of the molecular network are observed, in excellent agreement with experimental STM data. Our theoretical models allow to elucidate the subtle interplay between dispersion forces and hydrogen bonding, leading to some unexpected phenomena. Biasing the MD by a simple elastic-band constraint method, we identify the kinetic path leading from a high-density to a low-density ordered phase. Next, kinetic Monte Carlo simulations over a frozen Si(111)-B surface, with energy parameters derived from the MD, help explaining the apparently striking experimental observations, according to which lower-density phases are favored over higher-density phases.