Growing molecular wires by polymerization on hydroxylated rutile surfaces

Marek Szymoński

Centre for Nanometer-Scale Science and Advanced Materials, NANOSAM, Faculty of Physics, Astronomy and Applied Computer Science, Jagiellonian University, Krakow

On-surface synthesis of covalently bound molecular nanostructures in a bottom-up approach has recently become very attractive in the field of nanoscience [1,2]. Such a strategy invokes functionalization of precursor molecules with specific linking sites, which are activated after molecule deposition on a surface [3]. So far, only surfaces of selected noble metals were used as substrates and the most popular method of activation was thermal triggering.

Recently we have reported on the covalent coupling of 10,10′-dibromo-9,9′-bianthryl (DBBA) molecules on a rutile TiO2(011) [4]. Low temperature STM (LT-STM) studies and DFT-D modelling showed that thermally activated DBBA molecules form polyanthrylene chains. In this context I would like to report on a comprehensive study concerning covalent coupling of diiodoterfluorene (DITF) and dibromoterfluorene (DBTF) molecules synthesized at Department of Chemistry of the Humboldt-Universität zu Berlin, into polyfluorene chains on a rutile TiO2 (011) and (110) surfaces prepared in different oxidation/reduction states. Our results, based on high resolution LT STM microscopy and parallel "in situ" mass spectroscopy of the reaction volatile products, show that presence of the surface hydroxyl groups is indeed crucial for the polymerization reaction. Moreover we demonstrate that reaction efficiency could be steered by varying the density of surface hydroxyls. The proposed C-C coupling mechanism involves proton transfer from a surface hydroxyl group to the precursor molecule and its preferred attachment to the halogen (X)-bearing carbon atom. This results in rehybridization and substantial weakening of the C-X bond and facilitates the C-C bond formation. Additionally, the titania surface reduction state may also influence the process.

[1] J. Cai, P. Ruffieux, R. Jaafar,M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Muellen, R. Fasel, Nature 2010, 466, 470.

[2] L. Lafferentz, V. Eberhardt, C. Dri, C. Africh, G. Comelli, F.Esch, S. Hecht, L. Grill, Nature Chemistry 2012, 4, 215.

[3] G. Franc,A. Gourdon, Physical Chemistry Chemical Physics 2011, 13 (32), 14283.

[4] M. Kolmer, A. A. A. Zebari, J. S. Prauzner-Bechcicki, W. Piskorz, F. Zasada, S. Godlewski, B. Such, Z. Sojka, M. Szymonski, Angewandte Chemie - International Edition 2013, 52, 10300.

Coarse-grained models for organic molecules at structured surfaces:

Coronene, C_{60} , and 6P

Sabine Klapp

Institut für Theoretische Physik, Technische Universität Berlin

We report about recent progress in modelling the structure and growth of organic molecules at surfaces using classical, coarse-grained models. To start with, we summarize kinetic Monte Carlo (kMC) simulation results for the growth of C_{60}/C_{60}, where we achieved excellent quantitative agreement with parallel real-time x-ray measurements. We then discuss extensions of these investigations towards the structure formation of para-sexiphenyl (6P) at ZnO surfaces. To this end we propose a new model which takes into account not only the steric and electrostatic interactions between the anisotropic molecules, but also the molecule-substrate interaction in presence of stripe-like electric surface potentials characterizing ZnO (10-10). Finally, we discuss the challenges in obtaining accurate coarse-grained potentials from atomistic trajectories, using the example of corone.