

SYOP 1: On-surface Polymerization

Time: Monday 15:00–17:45

Location: H 0105

Invited Talk SYOP 1.1 Mon 15:00 H 0105
Formation mechanisms of covalent nanostructures — ●JONAS BJÖRK — Department of Physics, Chemistry and Biology, IFM, Linköping University, Linköping, Sweden

The on-surface reactions underlying the formation of covalent nanostructures are in many cases fundamentally different from their wet chemistry analogues. Furthermore, their mechanisms are often intractable from experiments due to short-lived intermediate and transition states, and to make use of the true potential of this approach we need to understand the factors controlling the on-surface reactions. Here, it will be demonstrated how density functional theory can be used as a powerful tool for gaining insight into the mechanisms of these reactions. Firstly, we will discuss the on-surface Ullmann coupling, where halogen-substituted molecules are used as the basic building blocks. The key aspects of this reaction scheme will be scrutinized for simple model systems, but we will also discuss the effect of increasing the complexity towards more realistic systems. In particular, it will be examined how metal adatoms affect the different reaction processes, as these have shown to play a pivotal role in experiments.

Secondly, we will briefly discuss the mechanisms of other coupling schemes presented during the last years, with focus on the homo-coupling of terminal alkynes. This reaction has a completely different mechanism than that of the on-surface Ullmann coupling, with the coupling preceding the release of any side-products. Furthermore, the on-surface chemistry of alkynes is extremely rich, with several possible reaction products depending on molecule and/or surface.

Invited Talk SYOP 1.2 Mon 15:30 H 0105
Selective C-H Activation and C-C coupling on Metal Surfaces — ●LIFENG CHI — Institute of Functional Nano & Soft Materials (FUNSOM), Soochow University, Suzhou 215123, P. R. China — Physikalisches Institut, Universität Münster, Wilhelm-Klemm-Strasse 10, 48149 Münster, Germany

Selective C-H bond activation is one of the most interesting and challenging topics in chemical synthesis. Recently, the development of the *on surface chemistry* provides an alternative strategy for the C-H activations. In this talk an overview for C-H activation and the following C-C coupling on metal surfaces will be given, together with detailed report on alkane homo-coupling and aryl-aryl coupling via the C-H activation by introducing OH group in phenyl rings. The influence of metal surfaces on reaction activation and selectivity will be discussed.

Invited Talk SYOP 1.3 Mon 16:00 H 0105
On-Surface Synthesis on Insulating Substrates — ●ANGELIKA KUEHNLE — Physical Chemistry, University Mainz, 55099 Mainz, Germany

On-surface synthesis has attracted great attention in recent years due to its promising potential for creating functional structures directly on surfaces [1]. An exciting aspect of on-surface synthesis is the capability to arrive at thermally stable molecular structures that might not be accessible by solution chemistry. Using tailored building blocks allows for tuning the electron transport properties of the resulting structure. Especially the latter is of tremendous interest when considering future applications in the field of molecular electronics. Having molecular electronics applications in mind requires decoupling of the electronic structure of the molecular network from the underlying support surface. Thus, it is highly interesting to transfer on-surface synthesis strategies from metallic to insulating surfaces. In this talk, recent results in on-surface synthesis on an insulating substrate carried out in ultra-high vacuum are reported [2-4].

[1] A. Gourdon, *Angew. Chem. Int. Ed.* 47 (2008) 6950; [2] M. Kit-

telmann, P. Rahe, M. Nimmrich, C. Hauke, A. Gourdon, A. Kühnle, *ACS Nano* 5 (2011) 8420; [3] R. Lindner, P. Rahe, M. Kittelmann, A. Gourdon, R. Bechstein, A. Kühnle, *Angew. Chem. Int. Ed.* 53 (2014) 7952; [4] M. Kittelmann, M. Nimmrich, R. Lindner, A. Gourdon, A. Kühnle, *ACS Nano* 7 (2013) 5614

15 min. break.

Invited Talk SYOP 1.4 Mon 16:45 H 0105
On-surface polymerization - a synthetic route to 2D polymers — ●MARKUS LACKINGER — Deutsches Museum, München, Germany — Technische Universität München, Physik Department, Garching, Germany

Flat surfaces appear to be the ideal template for the synthesis of regular 2D covalently cross-linked polymers. Surfaces can not only confine the reaction to two dimensions, but can also play an active chemical role during the polymerization. Hence, the material and crystallographic orientation of the surface can also be used to steer or even control the reaction. The main objective of the lecture is to critically discuss the status, the main challenges, and the potential of on-surface polymerization for the synthesis of 2D polymers.

Different coupling reactions were already employed in a surface-chemical approach, each with specific advantages and disadvantages. An important distinction is whether the reaction can be carried out under slightly reversibly conditions or necessarily remains fully irreversible. While polymerization close to thermodynamic equilibrium opens up ways to improved structural quality, purely kinetically controlled reactions apparently inevitably lead to highly defective networks. Using the example of on-surface Ullmann coupling a detailed view will be presented on the surface-dependence, possible reaction intermediates, and the relation between defects and kinetic reaction parameters. Finally, the potential of metastable intermediate organometallic networks to improve the structural quality of 2D polymers will be demonstrated.

Invited Talk SYOP 1.5 Mon 17:15 H 0105
On-surface azide-alkyne click chemistry and a novel metal-organic network based on Cu adatom trimers — ●TROLLE LINDEROTH — Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Denmark

Molecular nanostructures on solid surfaces are central to achieve advanced functional surfaces. Covalent synthesis with reactants adsorbed on surfaces has therefore been the focus of intense recent interest. In this context there is a need to identify suitable chemical reactions that will proceed under Ultra High Vacuum conditions. Early work in this direction from our group focused on the condensation reaction between aldehydes and amines to form imines [1-3]. Here, it was shown that the connectivity in two-dimensional surface polymeric networks could be controlled by kinetic parameters of the preparation procedure. More recently, we have explored the prototypical click-chemistry reaction of 1,3-dipolar Huisgen cycloaddition between azides and terminal alkynes to form a triazole product for reactants adsorbed on a Cu(111) surface (CuAAC reaction) [2]. Finally we have investigated the on-surface dehydrogenation reaction for tetra-hydroxy-benzene (THB) which enables formation of a novel metal-coordination network containing trimeric Cu-adatom clusters [3].

[1]: *Angew. Chem. Int. Ed.* 46 9227 (2007), *Angew. Chem. Int. Ed.* 47 4406 (2008).

[2]: *J. Am. Chem. Soc.* 135 2136 (2013).

[3]: *Chem. Comm.* 49, 9308 (2013), *Angew. Chem. Int. Ed.* 53 12995 (2014).