Taking on-surface polymerization to the next level: Hierarchical and substrate-directed covalent assembly of complex nanostructures

One of the key challenges in current science and technology is to assemble functional nanostructures and exploit them in miniaturized devices and various applications. Covalent molecular nanoarchitectures offer the advantage of inherent stability, functional tunability, and increased charge transport capability. The method of on-surface polymerization, which allows the bottom-up construction of these nanoarchitectures, has been pioneered by the groups of Stefan Hecht (**IRIS Adlershof**, member of the CRC 951) and Leonhard Grill (FHI Berlin, member of the CRC 951) a few years ago (see Nature Nanotechnol. 2 (2007) 687) and was later used to prepare and characterize conjugated molecular wires (see Science 323 (2009) 1193). However, the degree of sophistication was rather limited thus far due to the involvement of single step processes only.

The same research team has now been able to greatly improve their method. In their most recent article in Nature Chemistry the authors demonstrate that the polymerization process can be carried out in a hierarchical fashion and further be directed by the underlaying substrate. On the one hand, the chemists designed suitable monomers, which carry two types of reactive groups allowing for sequential activation. These monomers with "programmed" reactivity initially form one-dimensional chains, which subsequently "zip up" in the second dimension (see Figure). On the other hand, the physicists utilized corrugated surfaces to orient monomers and intermediate chains and therefore direct the growth process. The new method greatly improves the quality of the formed nanostructures with regard to increased size as well as decreased defect density and allows for the construction of more complex structures from more than one type of building block.

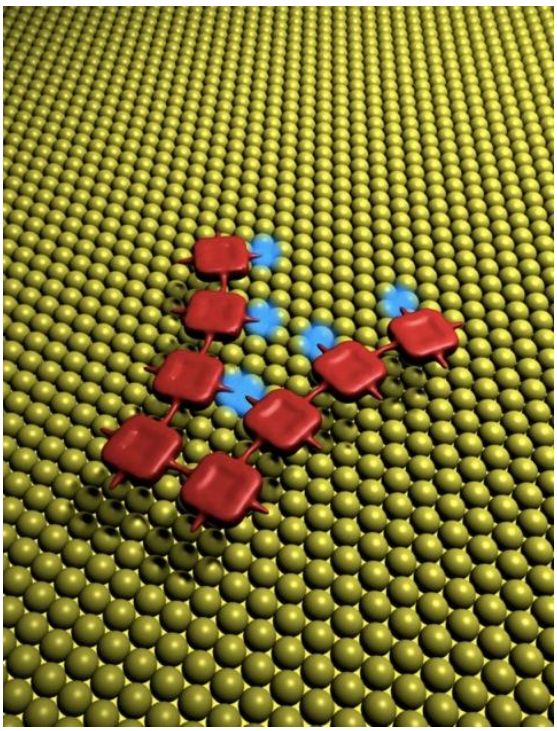

Fig.: "Molecular zipper": Monomers (red) initially polymerize at low temperatures into linear polymer chains, which subsequently interconnect at higher temperatures to a two-dimensional network. The "zipping" step is facilitated by the pre-orientation of the activated groups (blue). (Image © by L. Lafferentz)

This work was carried out in the framework of the EU-Project AtMol and the CRC 951 and published on: 15 January 2012 in: Nat. Chem. 2012, 4, DOI: 10.1038/nchem.1242