Hybrid Inorganic/Organic Systems for Opto-Electronics

Collaborative Research Centre 951

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"Hybrid Inorganic/Organic Systems for Opto-Electronics"

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Surfaces with a twist: Stereoselective chemistry, aperiodic tiling and electron spin filtering of helical aromatic hydrocarbons

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Surfaces with a twist: Stereoselective chemistry, aperiodic tiling and electron spin filtering of helical aromatic hydrocarbons

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Surfaces functionalized with helically shaped aromatic hydrocarbons, so-called helicenes, are of interest for chiroptical electronic devices or for electron-spin filtering. While self-assembled layers facilitate studying interesting phenomena, covalently linked chiral modified materials would be much more robust and therefore better suited for applications. For that matter, on-surface chemistry has become an important approach towards new functional interfaces that are hardly available by solution chemistry. We briefly report stereoselective chemistry of different helicene species on noble metal surfaces. The stereochemical analysis of diastereoisomers formed on the surface is performed by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (ncAFM). Depending on the site of bromination at the helical backbone, the Ullmann coupling reaction of different bromohelicenes proceeds stereospecifically to heterochiral or homochiral products. The diastereoselective chemistry is explained by topochemical effects due to the on-surface alignment of the helicenes during reaction. Moreover, stereospecific transmission from helical to planar chirality by cyclodehydrogenation and Diels-Alder cycloaddition will be discussed.

In the second part we report a unique transmission of chirality from single molecule into two-dimensional self-assembled monolayers on a silver surface. The relatively high molecular flexibility of 1,3,5-tristetrahelicenebenzene allows adaptation of handedness during crystal growth which is governed rather by entropy than by enthalpy. The 2D crystal is a solid solution with domains of opposite enantiomeric excess and supramolecular handedness. The layer is dominated by motifs, such as nodes of different topology, i.e., two-armed and three-armed spirals, and by enantiospecific lateral offset of oligomeric triangles. To our knowledge such chiral self-assembly phenomenon has been neither reported previously nor has such aperiodic tiling of the plane been previously described by mathematical analysis.

Finally, we will report different studies in order to shine light into the so-called chirality-induced spin selectivity (CISS) effect. Our experiments include approaches, such as spin-selective analyses of photoelectrons, spin-polarized low-energy electron microscopy and enantioselective adsorption on ferromagnetic surfaces.