

PROGRAMMED ASSEMBLY OF MOLECULAR FRAMEWORKS: A NEW CLASS OF DESIGNER SOLIDS?

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The demand for advanced materials with novel combinations of different functionalities requires the development of new types of solids. Self-assembly of one or different types of functional molecular units can be employed to fabricate crystalline arrangements, yielding complex but at the same time structurally well defined, highly ordered “Designer Solids”, which exhibit functionalities going well beyond that provided by the individual building blocks.

In this presentation, it will become evident that a recently introduced class of supramolecular materials, metal-organic frameworks, or MOFs, carry an enormous potential with regard to the fabrication of solids with unusual physical properties [1]. MOFs are stable materials, with decomposition temperatures well above 200°C (in some cases > 500°C). With selected examples, we will demonstrate the interesting, and often surprising (e.g. negative thermal expansion coefficient), mechanical, electronic, magnetic and optical properties of these molecular, crystalline materials.

We have developed a liquid phase epitaxy (LPE) process, which allows growing MOFs on modified substrates using a layer-by-layer procedure [1]. For the cm-sized, highly oriented MOF thin films with thickness in the micrometer-regime basic physical properties (mechanical [2,7], optical [3], electronic [4], magnetic [5]) of these porous, molecular solids can be determined using standard methods.

The porous nature of these crystalline solids opens up the prospect of adding additional functionality by placing molecules [8] or nanoobjects inside the voids within the MOFs, e.g. metal clusters or dye molecules [9].

Keywords: Designer Solids, Metal-Organic Frameworks, Organic Thin Films

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HIGH-RESOLUTION AFM/STM IMAGES: BEYOND IMAGING

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High-resolution AFM/STM images of molecules acquired functionalized tips [1,2] created a lot of excitement among researchers from many fields including material science, physics and chemistry. So far, the method has been mostly used to visualize chemical structures of molecules on surfaces, but quantitative information is mostly missing. Further proliferation of the technique depends critically on our ability to extract novel information or characterize/identify complex molecular structures.

In this talk, we will address both questions. First we will discuss a novel technique that maps out the electrostatic potential over a single molecule with unprecedented resolution [3]. The technique exploits the fact that image distortions typically observed in high-resolution atomic force microscopy images are for a significant part due to the electrostatic force acting between the tip and the charge distributed in the molecule of interest [4]. In addition, we report sub molecular resolution of water clusters achieved with AFM, which indicates that the H-bonded water systems remain intact during the high-resolution AFM imaging. What more, the AFM images provide information about chiral character of the electrostatic field of the water clusters.

In the second part, we will exploit the high-resolution images to identify the individual chemical products of on-surface reaction. What more, we will demonstrate chirality transfer from a homochiral helical precursor to enantiofacially adsorbed prochiral products through a cascade of stereoconservative on-surface reactions (see Fig.). We believe that the possibility to form globally enantiopure assemblies of prochiral molecules through on-surface synthesis opens a new way of expressing 2D chirality in so far unexplored types of organic-inorganic chiral surfaces.

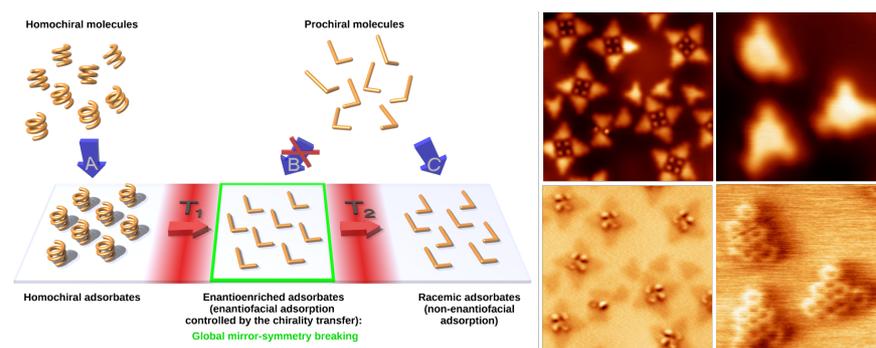


Fig. Right: The proposed concept of global mirror-symmetry breaking in the system of prochiral molecules on an achiral substrate through controlled on-surface chemistry reaction. Left: High-resolution AFM/STM images of different products of the chemical reaction.

Keywords: AFM; STM; Chirality; water; electrostatic field; DFT; sub molecular resolution

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SNOM SPECTROSCOPY FOR TISSUE IMAGING AND CANCER DIAGNOSTICS

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We present a fully implemented Infrared (IR) Scanning Near-field Optical Microscopy (SNOM) in spectroscopic mode for tissue imaging and early cancer diagnostics. The SNOM has been coupled with an infrared light source, based on Free Electron Laser at the ALICE facility in Daresbury [1]. The potential of IR spectroscopy to characterise cancerous tissues has long been recognised and studies of various cancers by many groups have established that regions of malignant tissue can be easily identified on the basis of its IR spectrum. The oesophageal adenocarcinoma, the cancer with the fastest rise in incidence in the Western world, requires an instrument providing specific chemical images at sub-cellular level of oesophagus tissue.

Preliminary results of IR-SNOM on oesophageal adenocarcinoma have shown that the system can operate at nanometer resolution and has been able to distinguish between healthy and malignant tissues [2]. The optical fibre has been driven in particular areas of the oesophageal tissue and topographical and optical images have been collected simultaneously at different wavelengths. In particular, SNOM images were collected at wavelengths of 7.0 μm (no strong biomarker), 7.3 μm (protein/glycoprotein), and 8.05 μm (DNA). Figure 1 shows 40 μm x 40 μm optical SNOM images for two samples, labelled Cancer and Benign: the colour maps show the location of intense DNA (red), intense protein/glycoprotein (blue) and of strong overlap of DNA and protein/glycoprotein (orange). As clearly visible, Cancer sample shows a large spread of intense signal from DNA whereas Benign sample shows a lower overall density of DNA, which is more dispersed and exhibits more localised centres. This approach demonstrates the potential of the IR-SNOM spectroscopy for yielding an accurate diagnostic test for oesophageal and other types of cancers.

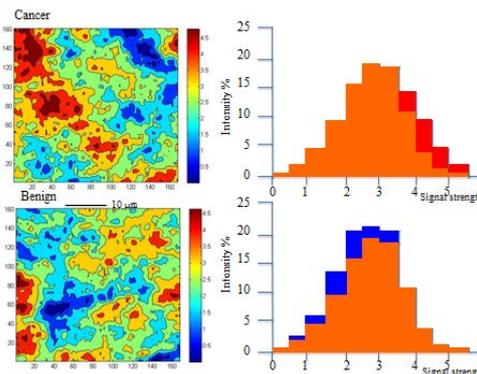


Fig. 1. IR-SNOM image maps .

Keywords: Nanophonics; cancer diagnostics

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PROBING THE UNOCCUPIED BAND STRUCTURE WITH LOW-ENERGY ELECTRON MICROSCOPY

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The properties of any material are fundamentally determined by its electronic band structure. While the occupied bands can be routinely measured, it is remarkably difficult to characterize the empty part of the band structure experimentally. We now introduce a technique to measure these bands from nanoscopic samples [1]. It relies on the dependence of the reflectivity of low-energy electrons on their incidence angle on the sample and their kinetic energy. Since this angle-resolved reflected-electron spectroscopy (ARRES) is based on state-of-the-art low-energy electrons microscopy it has a spatial resolution 10nm, which is five orders of magnitude better than other techniques. We use ARRES to study the unoccupied band structure of so-called van der Waals crystals. Those custom made materials are built up by stacking layers of two-dimensional materials, such as graphene, boron nitride, or transitionmetal dichalcogenides, on top of each other. This allows it to construct crystals with specific properties that are not available in conventional materials. We also show how this novel technique can be used to shed light on the interaction between electronic states of individual layers. This knowledge is crucial for the understanding of how to tailor the properties of Van der Waals crystals in a LEGO-like fashion.

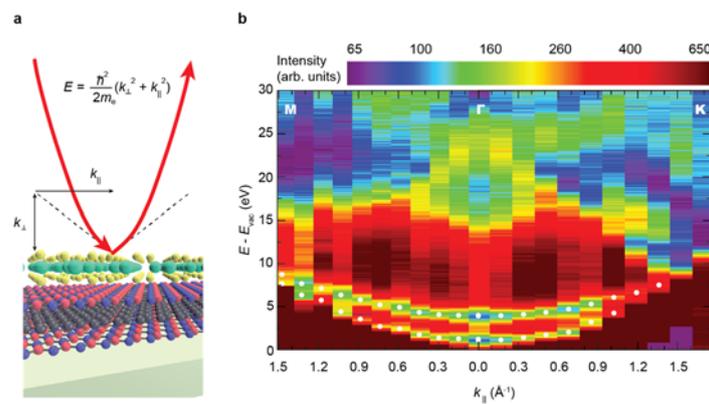


Fig. 1. **a**, Changing the angle of incidence of low-energy electrons onto a surface while recording their energy and reflected intensity yields insights into the materials unoccupied band structure. **b**, This ARRES measurement reveals, e.g., the bands of bilayer graphene and shows clear band quantization at low energies.

Keywords: Band structure; Low-energy electron microscopy; Van der Waals material

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