BP 33: Focus Session Chemical Imaging for the Elucidation of Molecular Structure II (joint session O/BP)

Unravelling the multiscale molecular heterogeneity at interfaces is one of the main challenges in modern biophysics and surface science due to the major role specific structural properties play in determining their macroscopic function and behavior. In the last few decades, several specialized chemical imaging techniques have been developed that can reveal many of these crucial structural details, representing an enormous advance in our elucidative capabilities. Clear examples of this range from super-resolution and 3D tomography to tag-free characterization down to the single-molecule level. This focus session will explore the vast range of methods and possibilities for characterizing the different structural aspects in heterogeneous molecular systems and specifically highlight the potential complementarity of the different techniques through multi-modal approaches. Overall, by bringing together different communities, this session aims to foster scientific exchanges that could spark the next major developments in chemical imaging.

Organized by
Martin Thämer (FHI Berlin), Alexander Fellows (FHI Berlin), and Kerstin Blank (University Linz)

Time: Friday 10:30–12:45 Location: H24

Invited Talk BP 33.1 Fri 10:30 H24

Multidimensional Super-resolution Imaging: Wasting Light to Learn New Things — •Steven Lee — University of Cambridge

The talk will outline two single-molecule fluorescence approaches that can be used to determine orthogonal metrics about a single emitter.

The first half introduces "POLCAM," a simplified single-molecule orientation localization microscopy (SMOLM) method based on polarised detection using a polarisation camera. POLCAM's fast algorithm operates over 1000 times faster than the current state-of-the-art, allowing near-instant determination of molecular anisotropy. To aid adoption, open-source image analysis software and visualization tools were developed. POLCAM's potential was demonstrated in studying alpha-synuclein fibrils and the actin cytoskeleton of mammalian cells. (Nature Methods 2024). The second approach focuses on "Single-Molecule Light Field Microscopy" (SMLFM), encoding 3D positions into 2D images for volumetric super-resolution microscopy. SMLFM shows an order-of-magnitude speed improvement over other 3D PSFs, resolving overlapping emitters through parallax. Experimental results reveal high accuracy and sensitivity in point detection, enabling whole-cell imaging of single membrane proteins in live primary B cells and high-density volumetric imaging in dense cytosolic tubulin datasets. (Nature Comms 2024)

Invited Talk BP 33.2 Fri 11:00 H24

MALDI mass spectrometry imaging: application examples ranging from food analysis to pharmaceutical research — •Andreas Römpp — Bioanalytical Sciences and Food Analysis, University of Bayreuth, Bayreuth, Germany

Mass spectrometry imaging is an analytical technique that provides spatially-resolved molecular information for a wide range of compound classes. In contrast to many histological methods, it does not require labeling. The capabilities and limitations of MS imaging will be discussed on the basis of several application areas with a focus on food analysis and pharmaceutical research. In our study 'MALDI mass spectrometry imaging: from constituents in fresh food to ingredients, contaminants and additives in processed food' (https://doi.org/10.1016/j.foodchem.2022.132529) we analyzed a range of plant-based and meat-based food. The analysis of natamycin in cheese and acrylamide in gingerbread constitute the first mass spectrometry imaging measurements of a food additive and a food contaminant, respectively. MS imaging is the only method that can analyze the distribution of drug compounds in animal models or human tissue (without labeling). This is exemplified on the detection of anti-tuberculosis drugs in mouse model tissue including our most recent study on the clinical stage antibiotic BTZ-043 which has just been accepted for publication in Nature Communications (https://doi.org/10.1038/s41467-025-56146-9).

BP 33.3 Fri 11:30 H24

On-Surface Synthesis and Characterization of a Nitrogen-Containing Heterocycle — •Marco Thaler[1], Ricardo Ruvalcaba Briones[2], Matthias Zeilerbauer[1], Shadi Fatayer[2], and Laerte Patera[1] — [1]University of Innsbruck, Austria — [2]King Abdullah University of Science and Technology, Thuwal, Saudi Arabia

Nitrogen-containing heterocycles are fundamental building blocks in nature, forming the core of essential biomolecules and pharmaceuticals. This study demonstrates the on-surface formation of an N-heterocyclic organic compound via thermal activation of a tailored precursor. High-resolution non-contact atomic force microscopy (nc-AFM) provides bond-level resolution of the synthesized structures. Complementary scanning tunneling spectroscopy visualizes changes in the electronic structure resulting from the formation of the heterocycle. Density functional theory calculations (DFT) reveal the most probable reaction mechanism, highlighting the critical role of hydrogen release as the driving force of the reaction. These findings emphasize the versatility of on-surface synthesis as a powerful tool for creating complex organic compounds.

BP 33.4 Fri 11:45 H24

Elasticity Mapping of Nonahelicene with Submolecular Resolution by NC-AFM — •Max Halbauer[1], Takashi Kumagai[2], Martin Wolf[1], and Akitoshi Shiotari[1] — [1]Fritz-Haber-Institute, Faradayweg 4-6, 14195 Berlin, Germany — [2]Institute for Molecular Science, 38 NishigoNaka, Myo-daiji, Okazaki 444-8585, Japan

Controlled modification of atomic configurations of molecules and materials is an exciting goal for non-contact atomic force microscopy (NC-AFM). Certain changes like shifts of the electronic energy gaps may be expected, but are not well explored and not established on the molecular scale. Here we report quantitative measurement of atomic-scale deformation in single molecules with NC-AFM. Individual molecules of nonahelicene ([9]H) and coronene (Cor) were studied on a Ag(110) surface under ultrahigh vacuum and cryogenic conditions by the measurement of frequency-shift distance curves for this. The molecular responses can be replicated with an empirical Lennard-Jones model, but for [9]H an elastic contribution is required to account for its elastic nature. Furthermore, a 3D-force mapping technique, termed molecular deformation mapping (MDM), allows to study the lateral position dependence of the elastic response. The MDM of [9]H reveals a spatially strongly anisotropic behaviour for the elasticity, interaction forces, elongation and binding energy of the tip to the molecule. The result is rationalized in terms of an aromaticity model.

BP 33.5 Fri 12:00 H24

Detection and control of quantum proton ordering in hydrogen bonds at the atomic scale — •Yiqi Zhang — Institute of Physics, Chinese Academy of Sciences, Beijing 100190, China

Directly probing the spatial arrangements and quantum nature of protons in hydrogen-bonded (H-bonded) materials and biosystems is the key to understand their macroscopic properties and functions. Here, exploiting bond-resolved atomic force spectroscopy (BR-AFS) combined with path-integral molecular dynamics method, we demonstrate for the first time that BR-AFS measurements along the apparent H-bond between proton donor and acceptor atoms allows the identification of both classical H-bonds with inherent directionality and non-classical H-bonds with quantum proton delocalization in self-assembled imidazole derivatives on surfaces. Unlike the conventional unidirectional H-bonding in linear chains, chiral cyclic hexamers exhibit unique quantum proton ordering in their ground states, which contain a mix

of classical and non-classical H-bonds, breaking rotational symmetry. Furthermore, we show the capability to switch the quantum-proton-ordering state on and off by altering the adsorption registry coupled with a collective transfer of six protons within the cyclic H-bonds. These findings open new pathways for detecting and controlling complex proton orders and for engineering proton-based quantum states with atomic-level precision.

BP 33.6 Fri 12:15 H24

Imaging of the conformations of individual β-cyclodextrins with non-contact AFM — Marko Grabarics[1], •Benjamin Mallada[1,2,3], Shayan Edalatmanesh[2,3], Stephan Rauschenbach[1], Pavel Jelinek[2,3], and Bruno de la Torre[2] — [1]Kavli Institute for Nanoscience Discovery, University of Oxford, UK — [2]CATRIN, Palacký University Olomouc, CZ — [3]Institute of Physics, Czech Academy of Sciences, CZ

Glycans, biopolymers essential to biology and materials science, are highly complex due to their structural diversity, conformational flexibility, and numerous possible isomers. Conventional methods often struggle to resolve these structures with atomic precision, especially under solvent-free conditions. We employ nc-AFM under UHV to determine the atomic structure of β-cyclodextrin (β-CD), a cyclic glucose molecule.

Our results reveal the adsorption geometries, hydroxy group positions, and stabilizing hydrogen bonds on a Au(111) surface. The primary face forms a closed hydrogen-bond network, while the secondary face exhibits pairwise interactions between OH groups of the same glucose monomer. DFT calculations validate these findings, enabling precise structural assignment and capturing subtle conformational differences.

This work highlights nc-AFM's capability to overcome the limitations of conventional sequencing techniques and represents the first application of nc-AFM to glycans. Future integration with ion deposition techniques could extend its utility to more complex glycans.

BP 33.7 Fri 12:30 H24

Domain size effects in the spectra of micro-heterogeneous samples — •Thomas Mayerhöfer[1,2] and Jürgen Popp[1,2] — [1]Leibniz Institute of Photonic Technology (IPHT), Albert-Einstein-Str. 9, 07745 Jena, Germany — [2]Institute of Physical Chemistry and Abbe Center of Photonics, Friedrich Schiller University, Helmholtzweg 4, 07743 Jena, Germany

Samples are often not composed of a single pure compound but are instead mixtures of different substances. Under the Bouguer-Beer-Lambert approximation, the absorbance spectra of such mixtures can be simply derived by summing the spectra of the individual components, with each spectrum weighted by the molar fraction of the corresponding compound.

In the context of wave optics, the resolving power of light at a given wavelength becomes crucial. If a microscope using light at this wavelength can distinguish structural details within the sample, the sample is classified as micro-heterogeneous. In this case, spatial averaging occurs at the intensity level, involving reflectance and transmittance rather than absorbance.

The shift from micro-heterogeneity to macro-heterogeneity is gradual and cannot be described by an analytical formula due to the wave nature of light. This has significant implications for spectrum interpretation, as it can lead to substantial variations in peak shapes, positions, and intensities, e.g., during mitosis.