

MS38-O4 Charging fragments of fullerenes with multiple electrons: remarkable structural transformations and metal binding records from X-ray crystallography and ⁷Li NMR

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Non-planar carbon allotropes, such as fullerenes and nanotubes, attract significant interest due to their outstanding properties and potential applications as lightweight carbonaceous materials for microelectronics and energy storage. Open geodesic polyarenes, representing fragments of fullerenes and caps of nanotubes, are broadly used for theoretical and experimental studies of curved π -surfaces. Their excellent electron accepting abilities have been the focus of our attention in the last several years. We investigate redox properties of the bowl-shaped corannulene (C₂₀H₁₀) that is able to accept up to 4 electrons in step-wise reduction reactions. We isolated crystalline products of various reduced states of corannulene and accomplished their first X-ray crystallographic characterization. This allowed us to reveal remarkable structural transformations of π -bowl upon addition of multiple electrons. Moreover, the resulting carbanions were shown to serve as unique bowl-shaped aromatic ligands for metal coordination. The highly reduced corannulene was confirmed to form fascinating supramolecular aggregates with multiple lithium ions encapsulated between non-planar decks.^[1] The use of single crystal X-ray diffraction was crucial for this work as previous NMR investigations failed to provide correct structural assignments. Next, we pushed further the coordination limit of the tetrareduced bowl having one electron per five C-atoms and being more electron rich than the fullerene-hexaanion. We used the concomitant alkali metal reduction reactions that resulted in the isolation of a new class of triple-decker sandwich structures with a record number of alkali metals encapsulated. A synergistic use of X-ray crystallography, NMR spectroscopy and DFT calculations was required in order to rationalize the electronic structures and dramatic ⁷Li NMR shifts shown by these unprecedented mixed alkali metal supramolecular aggregates.^[2,3] These novel results establish a new paradigm in alkali metal binding for curved polyaromatic surfaces, allowing to further advance carbon-based materials for energy-storage applications.

References

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Keywords: curved polyarenes, stepwise reduction, crystal structures, NMR spectroscopy, DFT calculations

MS38-O5 Crystallisation in-situ - and much more - at the ESRF BioSAXS BM29 beamline

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BioSAXS, or macromolecular solution scattering, plays an ever-increasing role in structural evaluation in biology since the introduction of dedicated synchrotron beamlines. A number of robots have been developed to offer high throughput and automation. The combination of SAXS with size exclusion chromatography (SEC), where the eluted sample is exposed to X-rays immediately after separation, is also explored. The ESRF BioSAXS beamline BM29 provides routinely two experimental modes: i) STATIC mode using a sample changer and ii) HPLC mode with SEC on line. Automatic switching between these two modes is done by remote control allowing optimal use of available beamtime. Dedicated beamline control and data acquisition software allows sample-changer control and real-time data display (two-dimensional and one-dimensional). It is connected to a data processing pipeline, providing automatic data processing up to *ab initio* models for both modes. Data collection parameters and results are logged and stored in the modified ISPyB database (a laboratory information management system that combines sample tracking and experiment reporting).

Recently, within a Long Term Project cooperation, droplet microfluidics devices were introduced to the beamline. The figure shows the current set-up on the beamline with the inset photograph of droplet generation in the microfluidics chip. The droplets (containing buffer, protein in solution and crystallisation agent) are driven by an oil phase and exposed to X-rays in a fused silica capillary of 300 μ m diameter in vacuum. The capillary is connected directly to the exit of the microfluidic chip and sealed into BM29 standard sample holder. Thanks to an external trigger signal, data are recorded only when droplets cross the X-ray beam to avoid radiation damage of oil and total reflection on droplet walls. With help of such a device crystallisation studies in situ of *glucose isomerase* were carried out.

In the presentation, an overview of macromolecules in solution experiments and possibilities at BM29 will be given, together with the description of latest results with digital microfluidic devices.

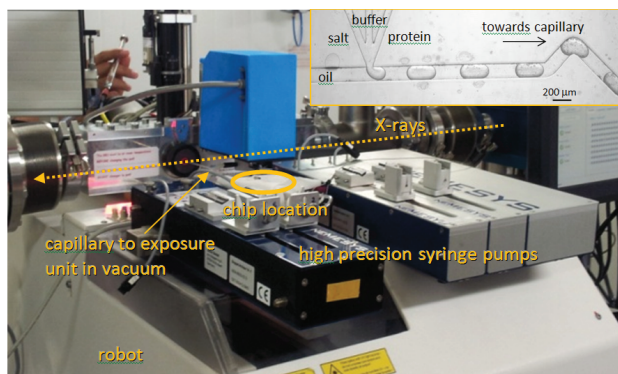


Figure 1. Photograph of microfluidics set-up at BM29 beamline. Inset represents a screen snapshot of droplet generation during crystallisation experiment. Small black dots appearing in droplets on right side are first crystals.

Keywords: small angle X-ray scattering, microfluidics, proteins in solution

MS39. Recent advances in diffraction instruments, detectors and data processing

Chairs: Trevor Forsyth, Rosanna Rizzi

MS39-O1 Updates in single-crystal neutron diffraction

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Single-crystal neutron diffraction is represented all over the world by a small set of instruments operated by specialists at large-scale facilities. In addition, very often every neutron diffraction instrument has a unique setup with dedicated hardware and software and, most of the time, an in-house made detector with in-house software for both data collection and data treatment. This situation has relegated neutron diffraction in a niche of experimental techniques to be used only when unavoidable. New materials combining inorganic and organic moieties, especially developed for exhibiting multiple physical properties, present nowadays a challenge to structural analysis, requiring more and more to combine x-rays and neutron data in order to obtain a more thorough description of the systems under study. In this talk, a survey on the actual possibilities and some outlooks in single-crystal neutron diffraction will be given, in particular touching upon 2D detectors, data collection and data processing software.

Keywords: neutron diffraction, single-crystal, 2D detectors