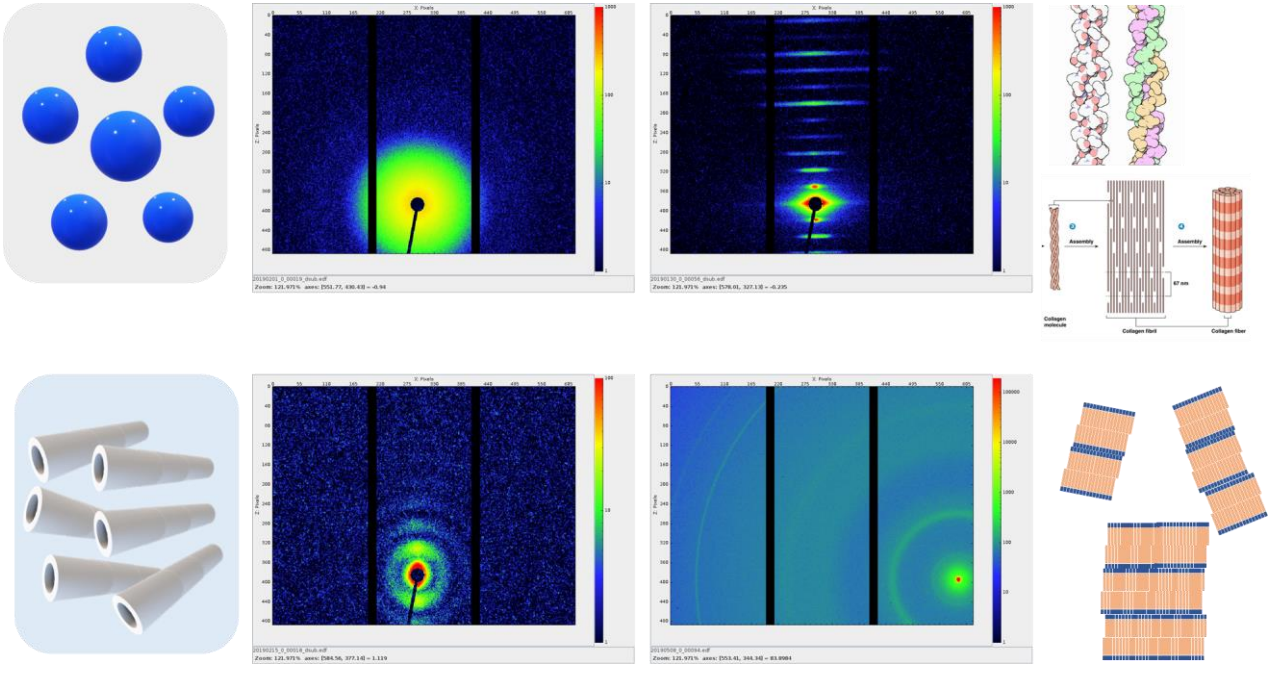
SAPIENZA
UNIVERSITÀ DI ROMA

Alessandra Del Giudice, PhD
Department of Chemistry
alessandra.delgiudice@uniroma1.it

X-ray scattering based methods for industrial applications – a focus on the small angles



Overview

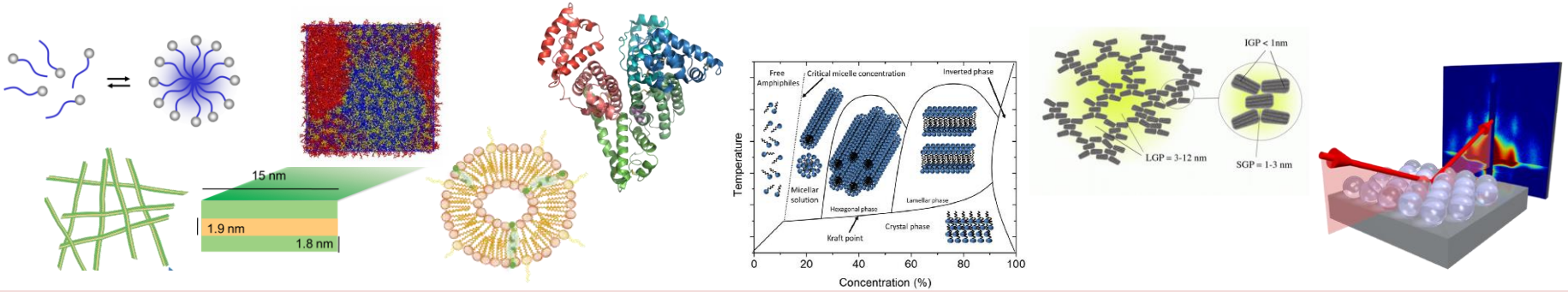
- X-ray scattering techniques within the **ATOM** project

  X-ray diffraction at CNIS
  X-ray tomography at Sapienza
  SAXSLab Sapienza

- **Small angle X-ray scattering**: what is it? and why is it useful?

- Examples of **applications** of possible interest in different industrial fields:

  biopharmaceutical industry
  formulation of consumer products
  development of hierarchical and hybrid materials



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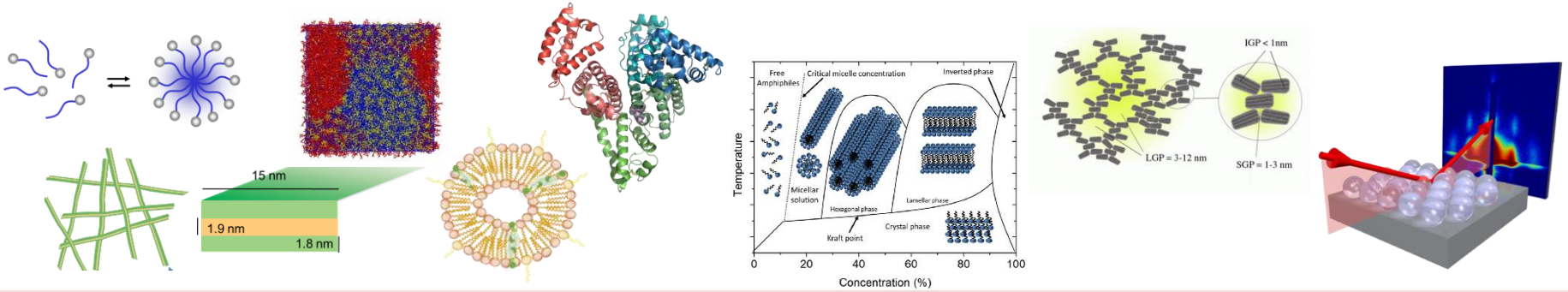

X-ray scattering techniques within the ATOM project

Aim: Build an open infrastructure for material and device characterization at the nanoscale

X-ray diffraction at CNIS

- Bruker D8 Advance diffractometer

- Mo-anode tube, delivering high energy X-ray beam

- The instrument is designed for delivering ultimate quality diffraction data, combined with ease of use and ample flexibility in order to quickly switch to different operative options.

- it can operate both in transmission and reflection modes

Responsible: Prof. Olga Russina (olga.russina@uniroma1.it)

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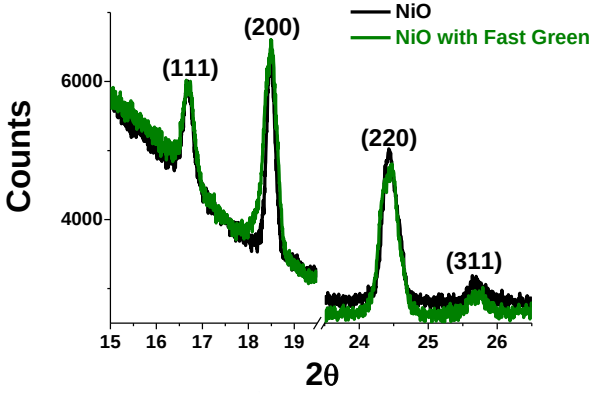

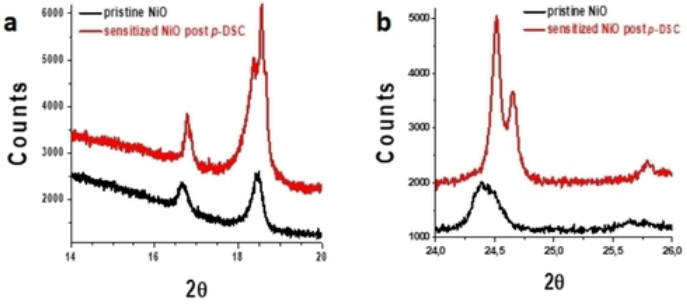

- Example: dye-sensitized solar cells

  - XRD analysis of the μm-thick film of mesoporous NiO of the electrode: comparison between bare film, "Fast-green"-sensitized film, and the sensitized film after use as photoctaode of the cell

  - the occurrence of peak broadening and splitting testifies surface reconstruction of the NiO phase during the photooxidation of iodide

M. Bonomo, S. Sheehan, D. P. Dowling, L. Gontrani, D. Dini, *ChemistrySelect* **2018**, *3*, 6729.

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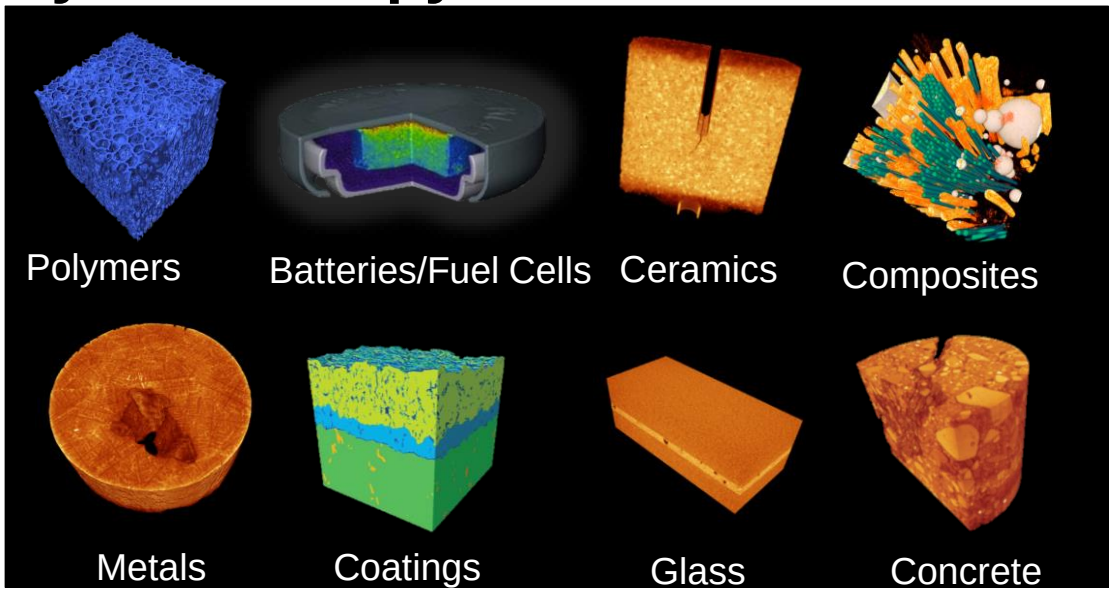
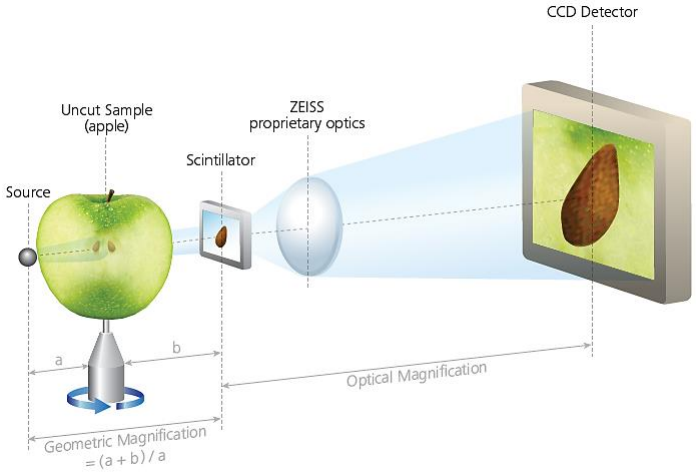
X-ray Computed Tomography
X-ray Microscopy





X-ray scattering techniques within the ATOM project

Aim: Build an open infrastructure for material and device characterization at the **nano- and meso-scale**

Small Angle X-ray Scattering

https://www.chem.uniroma1.it/saxslab/

Responsible: Prof. N. V Pavel (now Prof. L. Galantini)

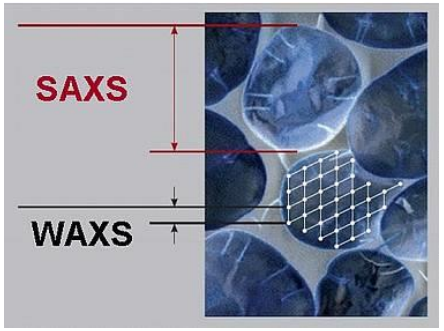
Post-doc: Dr. Alessandra Del Giudice (alessandra.delgiudice@uniroma1.it)

A multifunctional instrument to carry out measurements of:

Small Angle X-Ray Scattering (**SAXS**)

Wide Angle X-Ray Scattering (**WAXS**)

Grazing Incidence Scattering (**GI-S/WAXS**)



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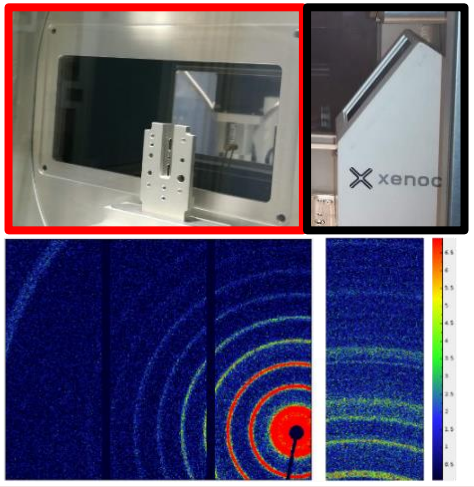

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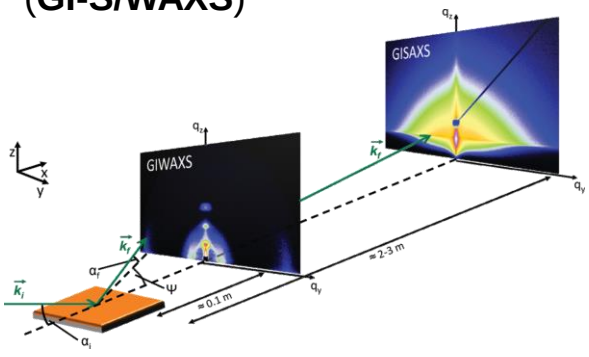

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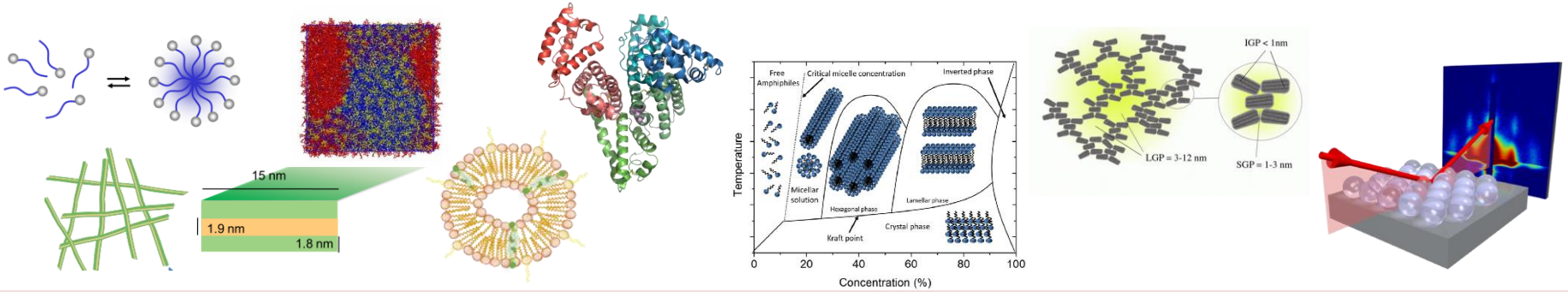
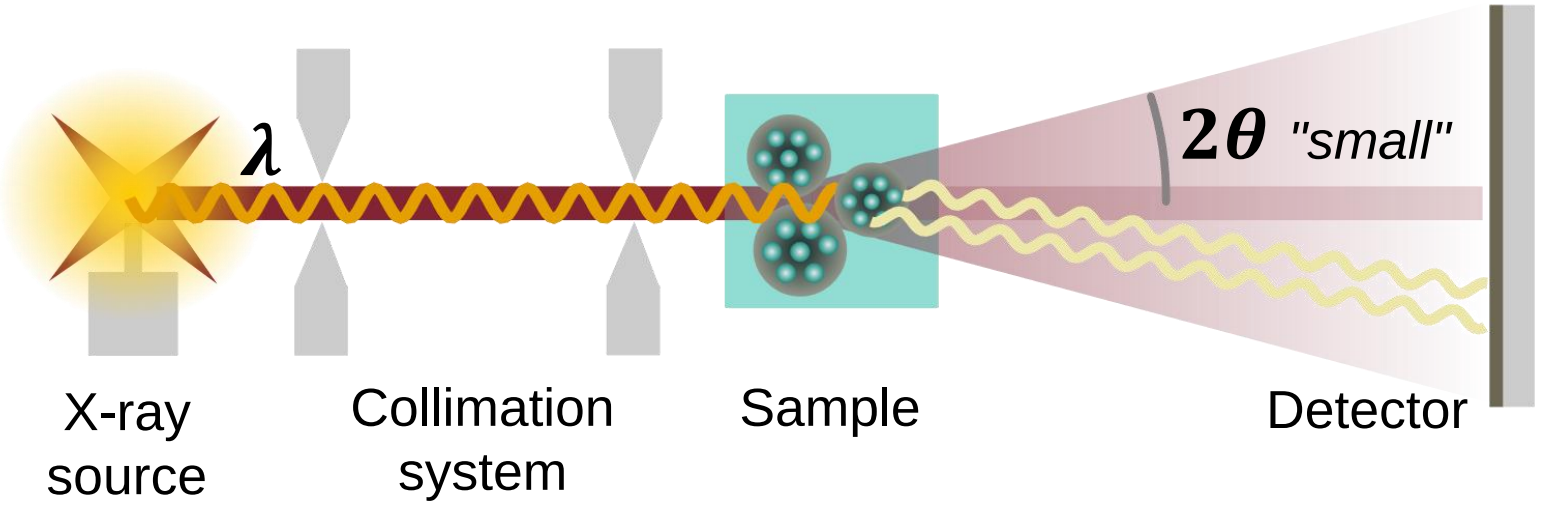


Small Angle X-Ray Scattering

what is it?

Electrons in the sample scatter monochromatic X-rays and a pattern is generated by the interference of the scattered waves which contains information about the relative positions among scatterers.



Small Angle X-Ray Scattering

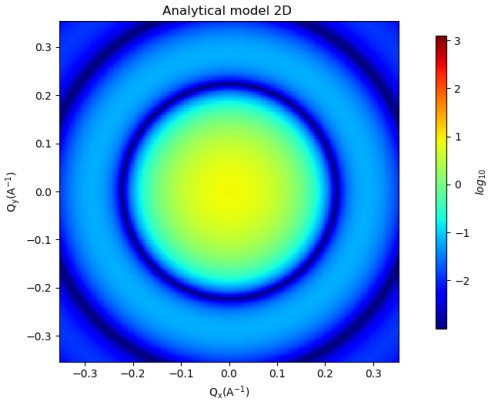
what is it?

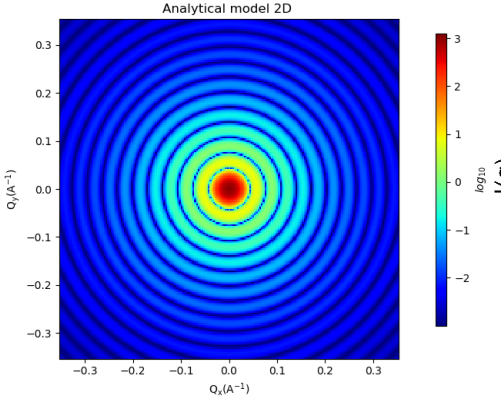
Every technique based on scattering follows a reciprocity law: at fixed λ, the **larger the dimensions** of the inhomogeneities, the **smaller the angles** from the incident beam at which the scattered intensity can be seen.

real space **FT** *reciprocal space*

2 nm

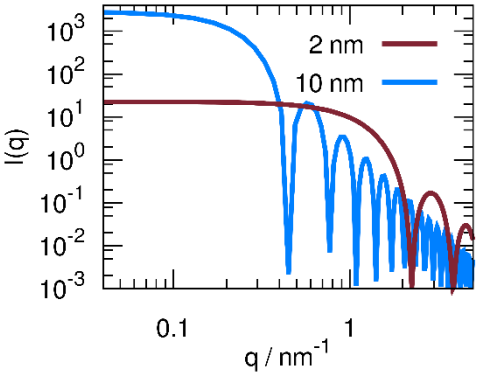
10 nm





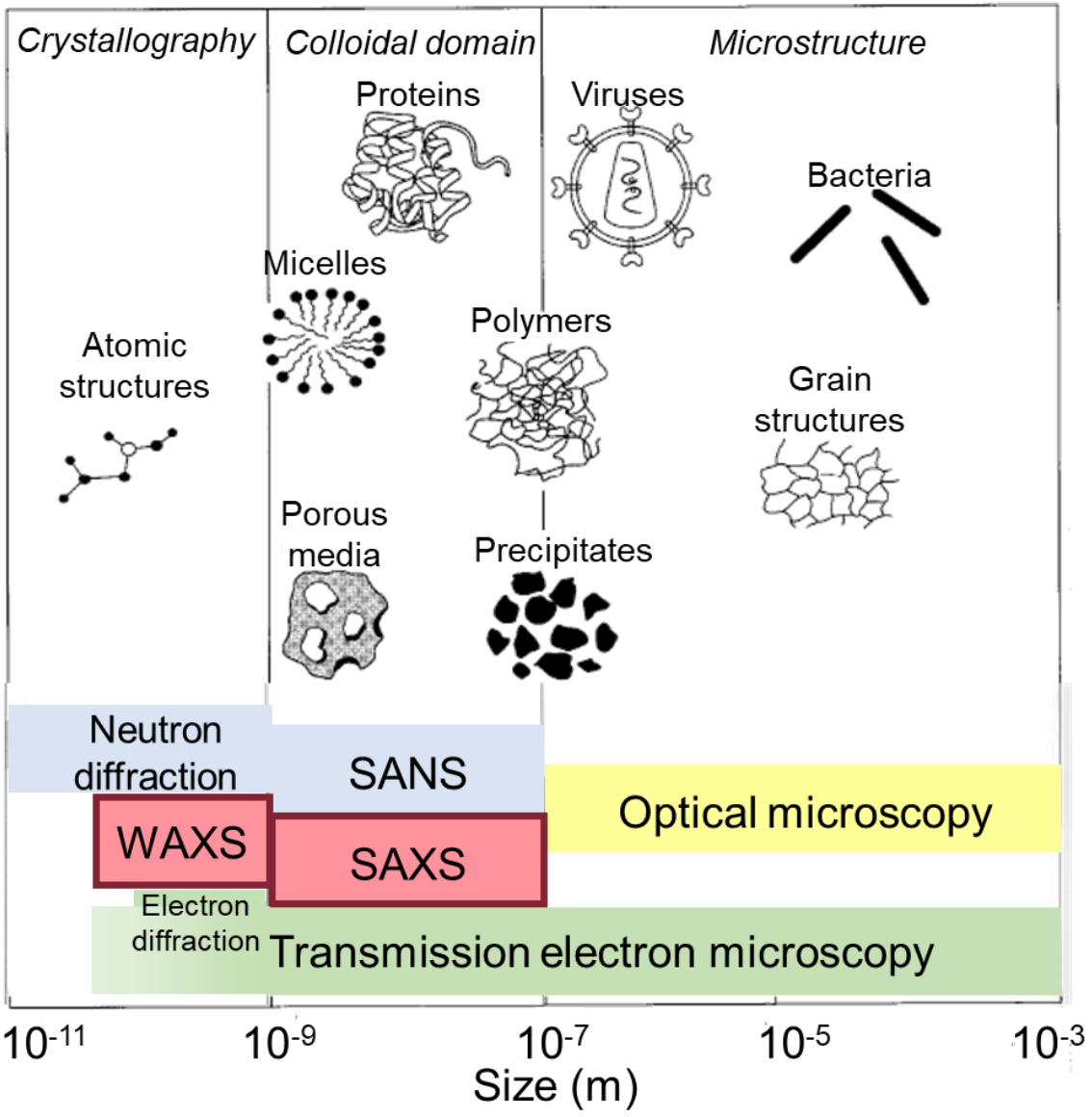
$$q = \frac{4\pi \sin\theta}{\lambda}$$

Units size^{-1}



Small Angle X-Ray Scattering

what is it useful for?



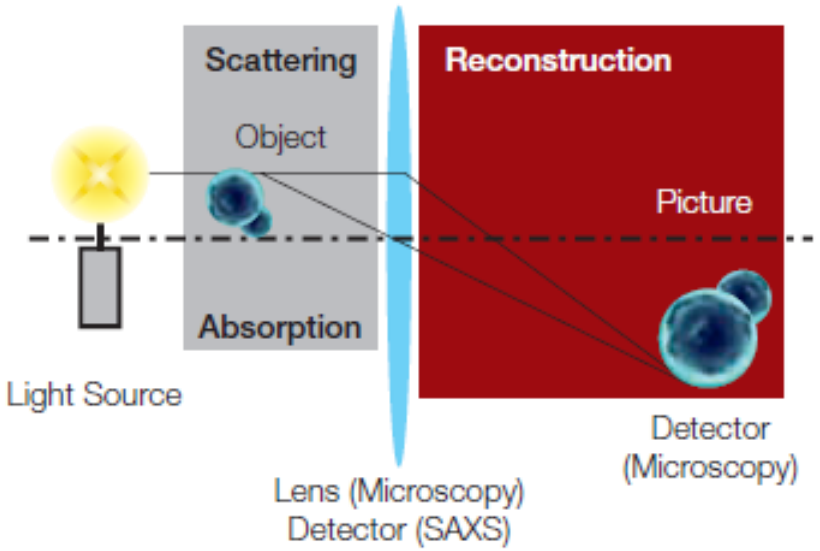
Why small angles?

Structure in the colloidal domain

Small angle X-ray scattering probes the size and shape of **electron density inhomogeneities** ranging in the 1 nm – 300 nm scale.

Small Angle X-Ray Scattering

what is it useful for?



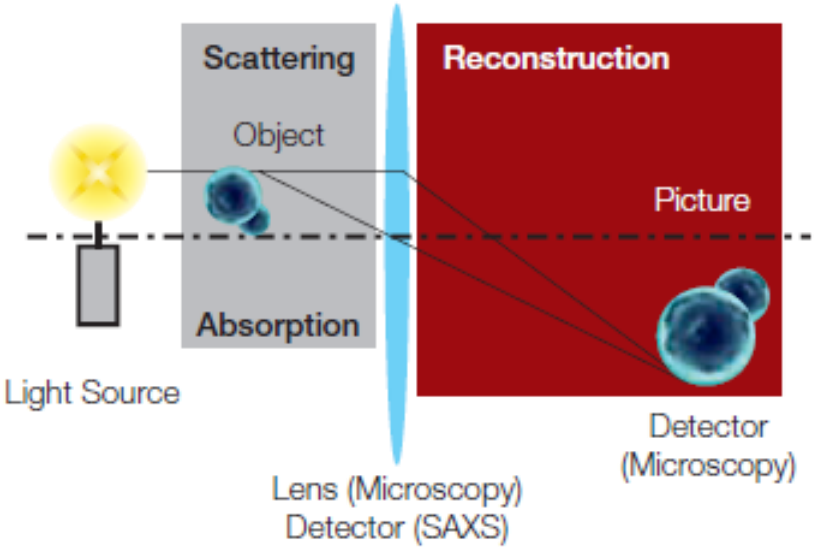
Complementary to microscopy

in scattering techniques the "reconstruction" of the structural information needs the Fourier Transform

	Microscopy	Scattering
Structural information	Non-ambiguous but also not representative of the whole sample	Representative but ambiguous
Avarage data	Require a lot of work	Always obtained
Artifacts due to sample preparation	Unavoidable	Scarce (experiments «in situ»)

Small Angle X-Ray Scattering

what is it useful for?



Complementary to microscopy

Main Disadvantage

- Hard to interpret data

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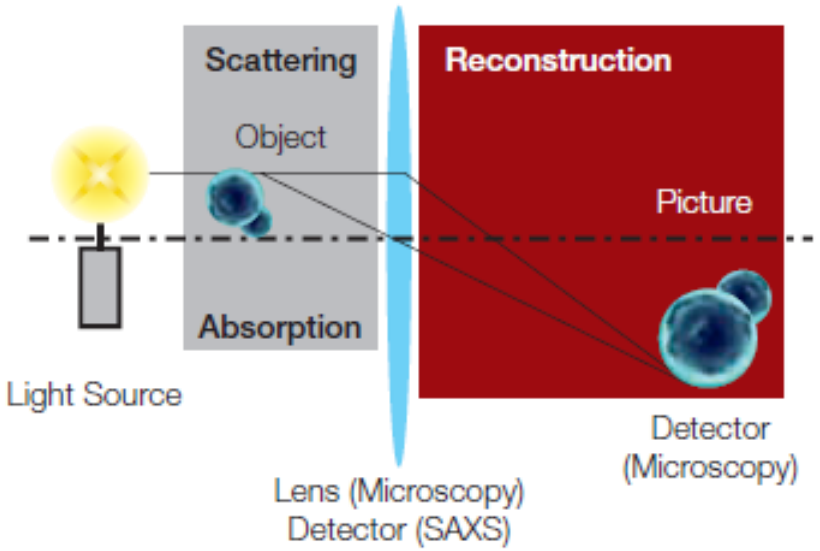

Complementary to microscopy

Advantages

- Average information
- Non-destructive
- Minimal sample preparation («in-situ»)
- Large range of sizes probed (0.2-100 nm)
- Variable sample states (solution, powder, gel,…)

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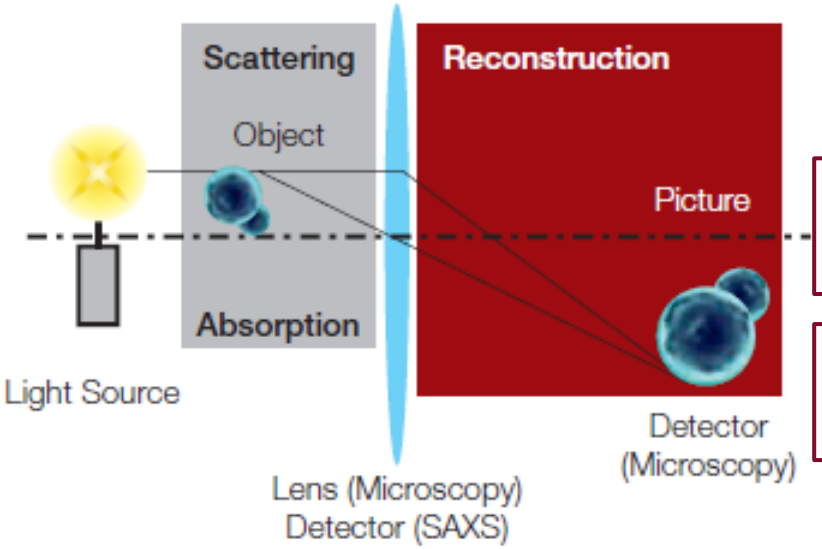


Complementary to microscopy

- SAXS helps TEM for significant sampling and quantitative statements

- TEM helps SAXS for clues about the shape of particles for use in data analysis

TEM good for:

- Direct and detailed image
- Local details
- Local surface
- Faithfully represents local complexities

SAXS good for:

- Statistically significant average info
- Global parameters and distribution
- Different sample states
- No artifacts in sample preparation
- In situ transition study

Small Angle X-Ray Scattering

what is it useful for?

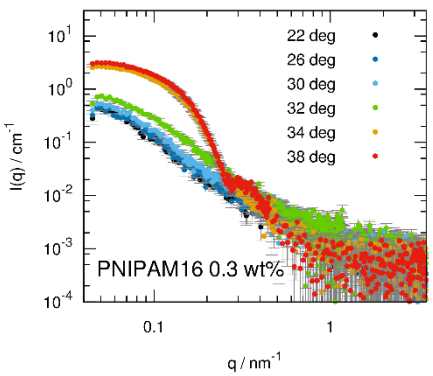
SAXS is particularly useful to characterize **soft-matter systems** at **different length scales** and their **changes as a function of several parameters**

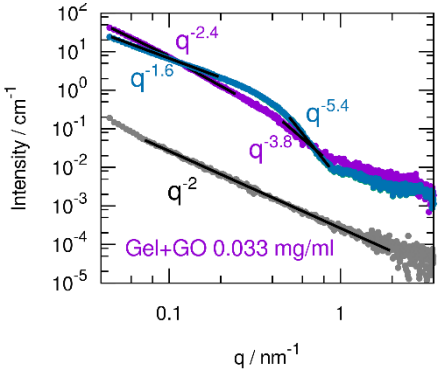
For example:

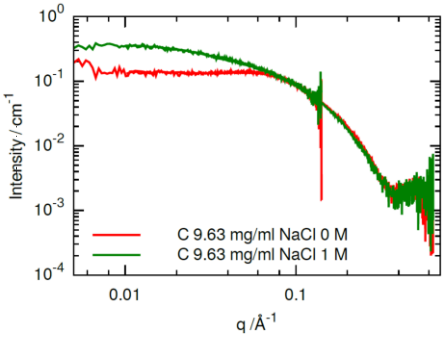
- Concentration
- Chemical composition
- Preparation protocol
- Temperature
- pH
- Ionic strength

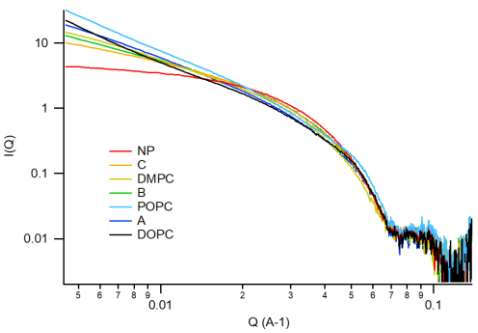
Multiple samples can be easily analyzed and compared in highly reproducible conditions to discover the effects of several variables on the structure and monitor them in a quantitative and statistically significant way.

This can help elucidating the underlying mechanism of complex processes and **linking structure to function**.









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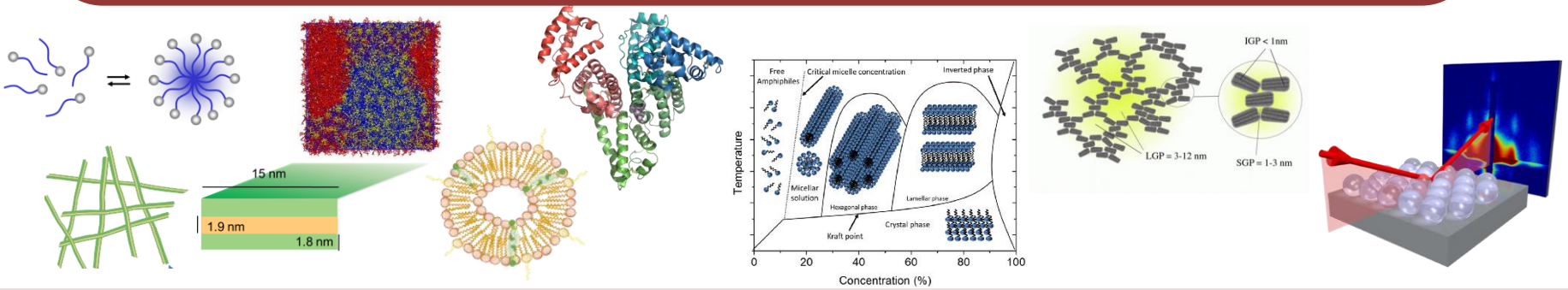
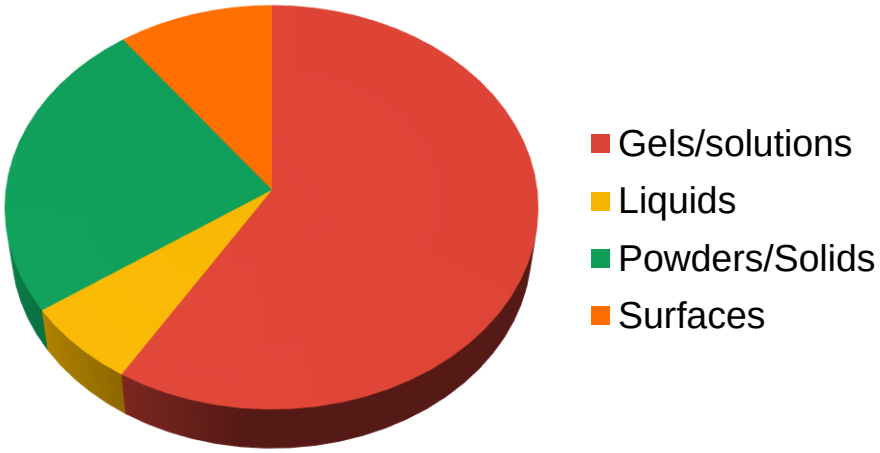
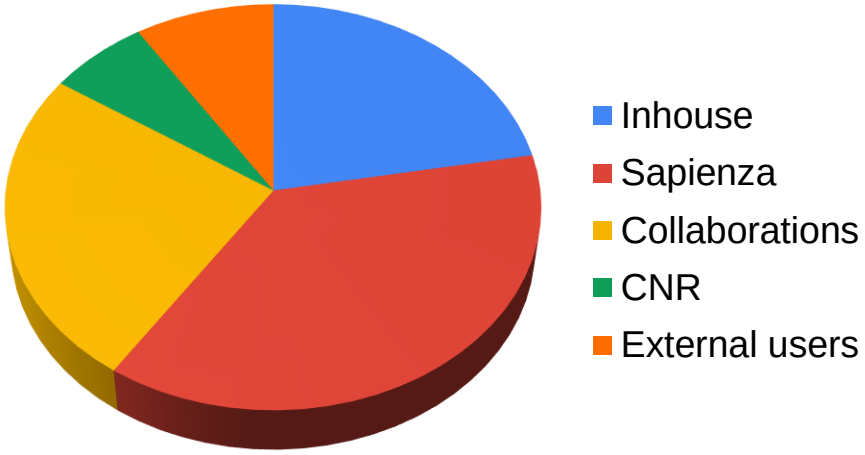


SAXSLab Sapienza statistics

Type of sample/setup

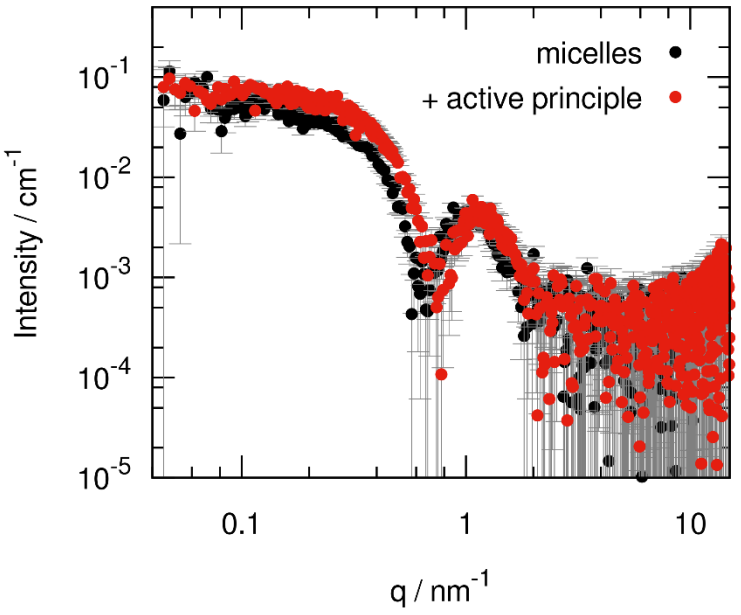


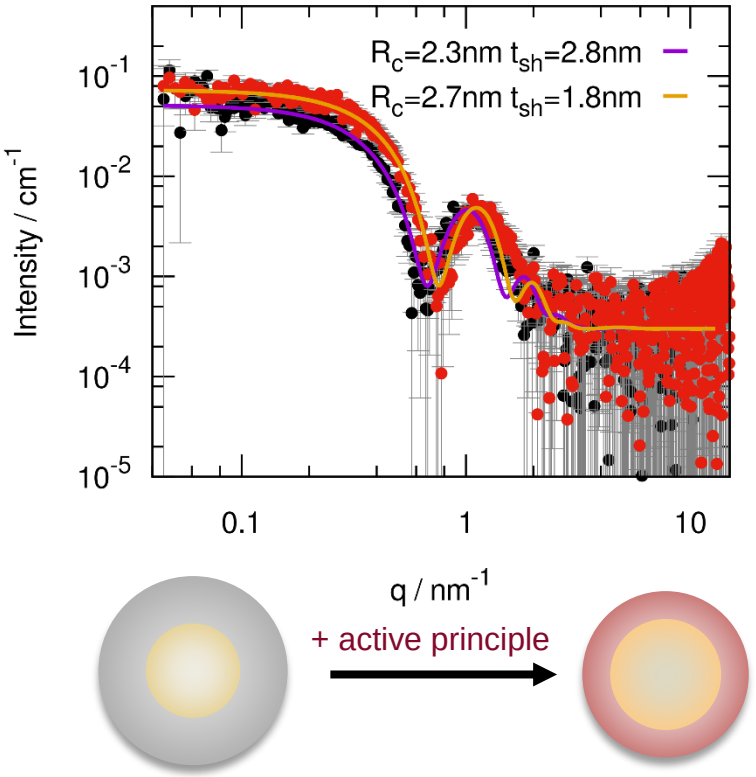
Users



Micelles

Formulation with a Vitamin-E-based surfactant for delivery of an active ingredient





core-shell sphere model fit

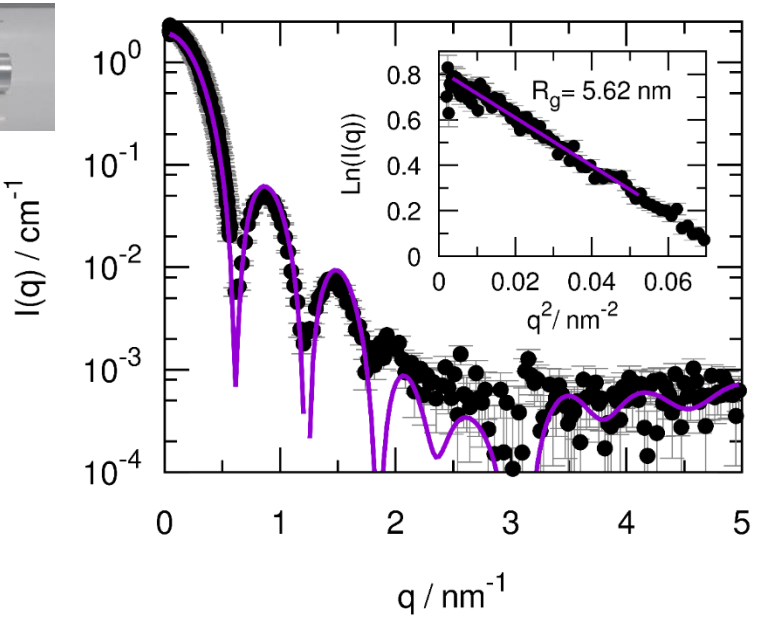
Thanks to:

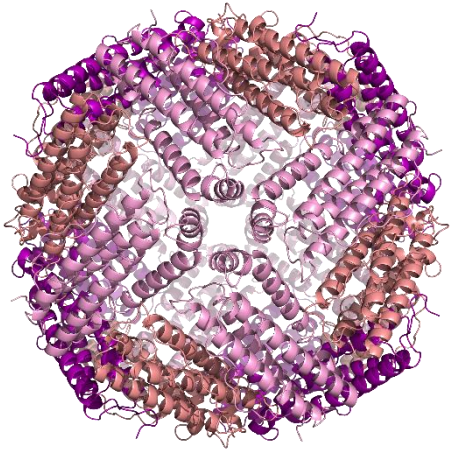
Cinzia Giannini (Istituto di Cristallografia, CNR Bari), Fabia Gozzo (Excelsus Structural Solutions SPRL)

Proteins in solution

SAXS can help in the characterization of purified samples of biological macromolecules:

- average size and shape
- oligomeric state
- quality assessment
- degree of flexibility
- conformational changes
- oligomerization equilibria and complex formation





pdb 3AJO

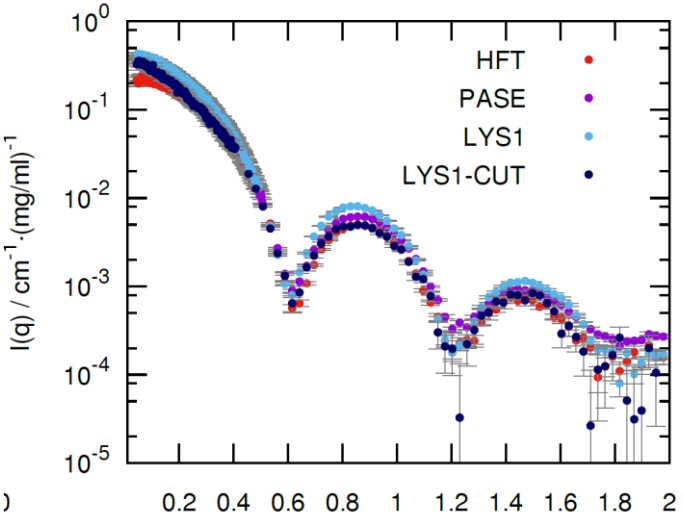
Recombinant Human Ferritin self-assembles in the expected 24-mer «hollow sphere» form and the scattering profile is in agreement with the crystal structure.

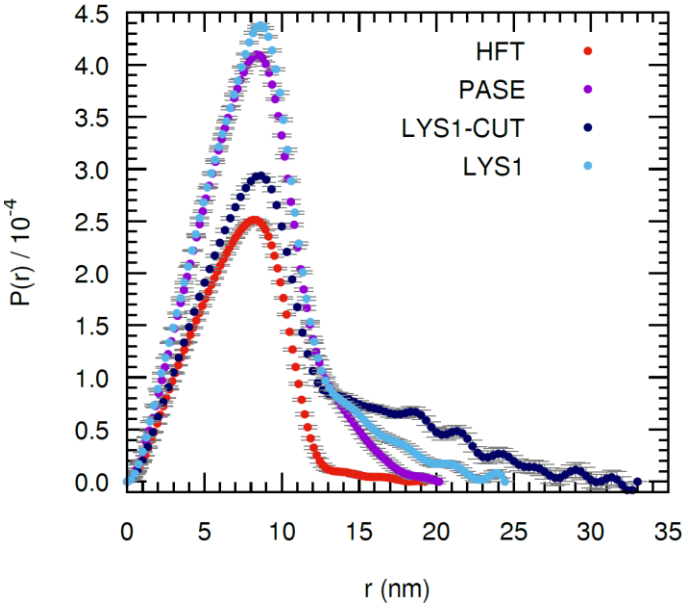
Thanks to:

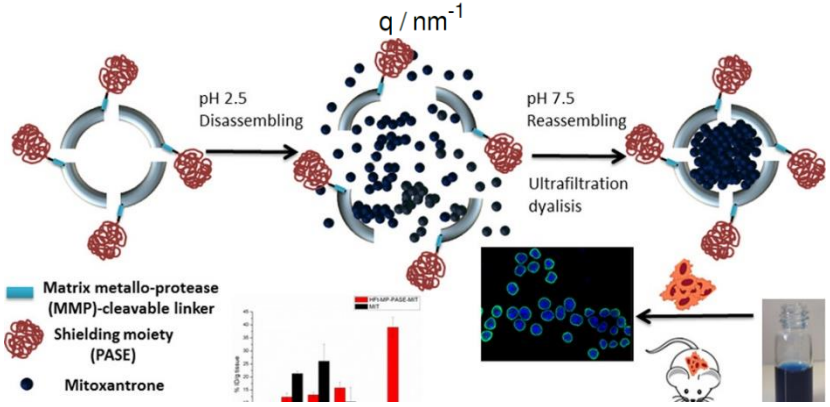
Annarita Fiorillo (Dept. of Biochemical Sciences, Sapienza)

Proteins in solution

Engineered Ferritin sequences can be used to build nanocages for drug delivery with stimuli-responsive and stealth properties







"PASE"= Proline-Alanine-Serine-Glutammate polymeric chains

E. Falvo et al. J. Control. Release. 275 (2018) 177–185.

Thanks to:

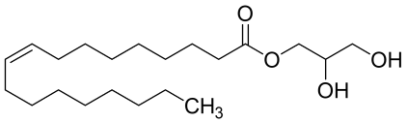
Annarita Fiorillo (Dept. of Biochemical Sciences, Sapienza)

biopharmaceutical industry

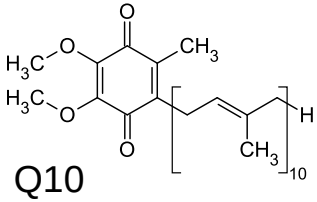
consumer products

Liquid crystalline phase formulations

lipid-based liquid crystalline phases dispersed in the form of nanoparticles thanks to surface-active stabilizers can be used for the encapsulation and delivery of active molecules

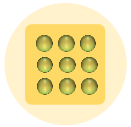


Monoolein



Q10

Hexosomes

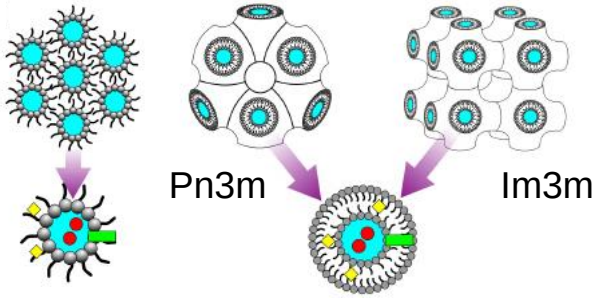


Cubosomes

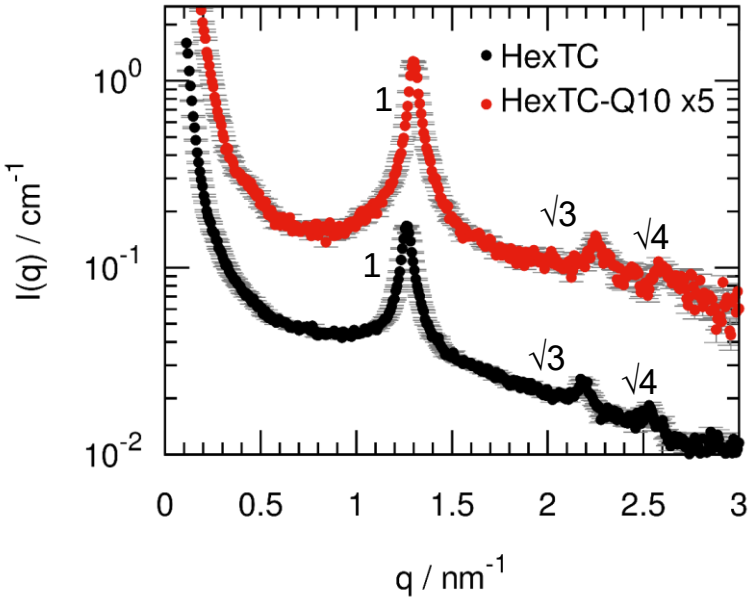
SAXS peaks allow for **phase identification** and measure of the lattice parameter, from which the **size of water channels** can be inferred.

The hexagonal phase of the hexosomes formulation is retained when encapsulating the Q10 coenzyme

Hexagonal Bicontinuous cubic



Lattice parameter:
5.74(1) nm
5.59(2) nm



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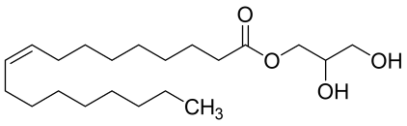

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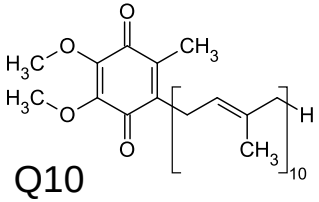
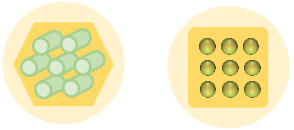


Q10

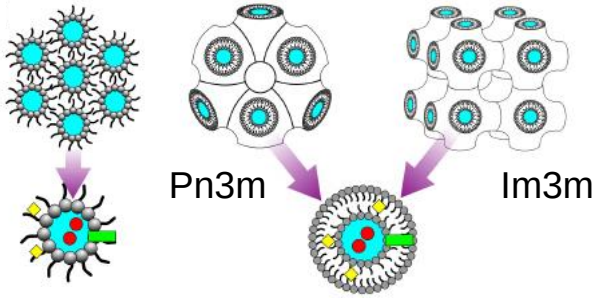


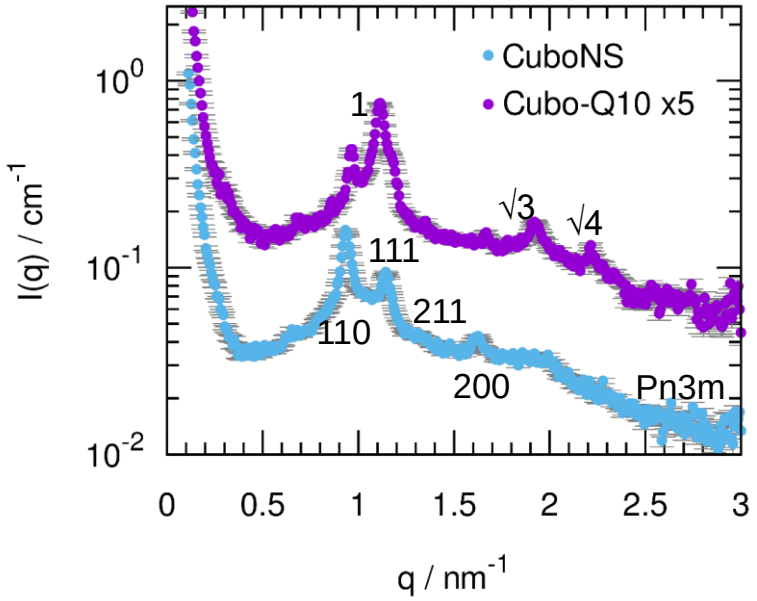
Hexosomes Cubosomes

SAXS peaks allow for **phase identification** and measure of the lattice parameter, from which the **size of water channels** can be inferred.

For another formulation in which a cubic phase was aimed at, the data suggest that by adding Q10 a hexagonal phase is present, too.

Hexagonal Bicontinuous cubic

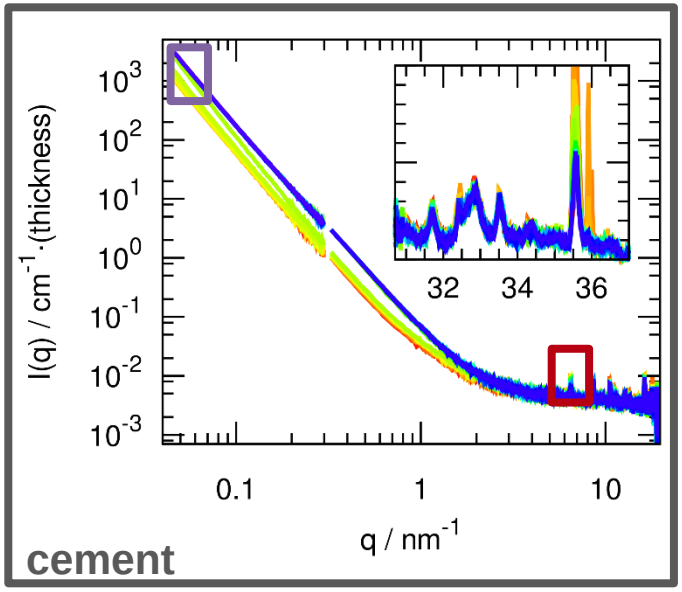


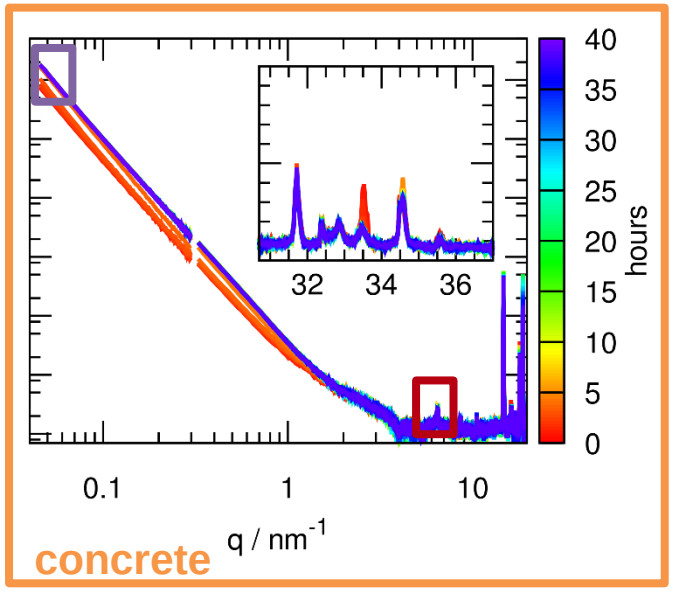


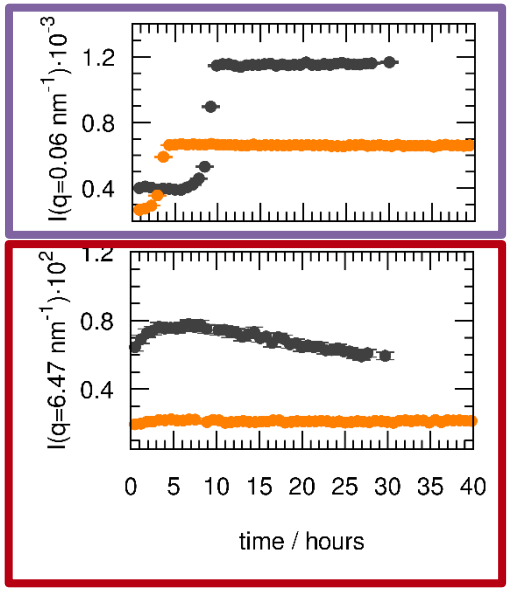
Thanks to:

Marco Fornasier (Dept. of Chemistry, Università di Cagliari)

Cement and concrete setting







Thanks to:

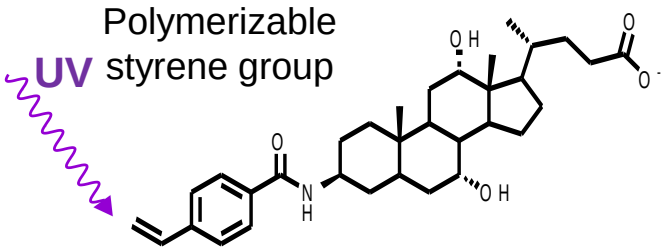
Greg Chass (Dept. of Chemistry, Queen Mary University of London)

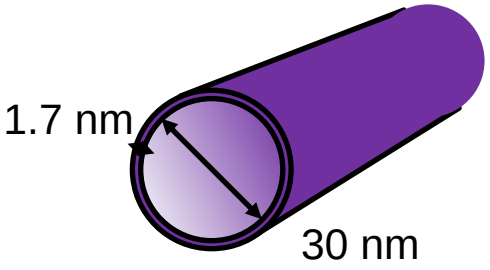
materials development?

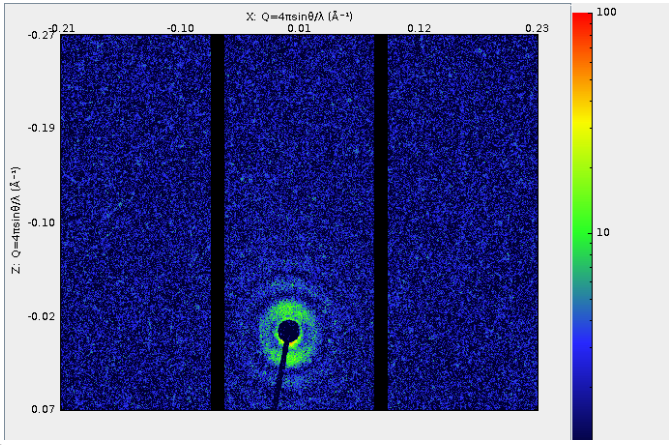
biopharmaceutical industry?

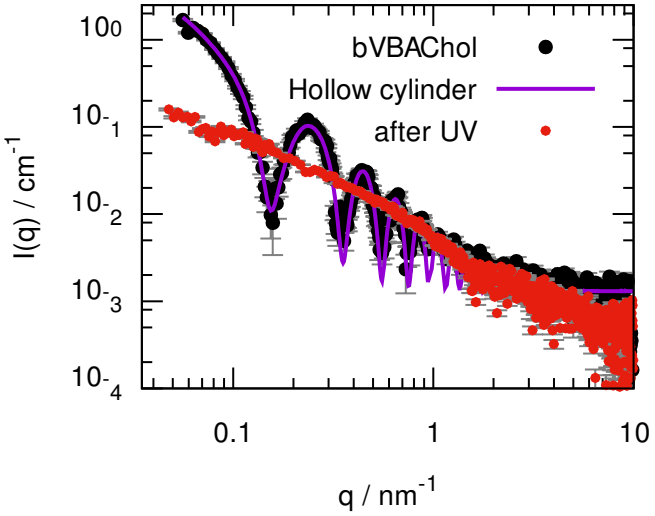
stimuli-responsive self-assembled nanotubes

A **bile salt derivative** bearing a styrene moyety self-assembles in long hollow cylinders. The polymerization by UV-light irradiation destroys the nanotube structure.









Thanks to:

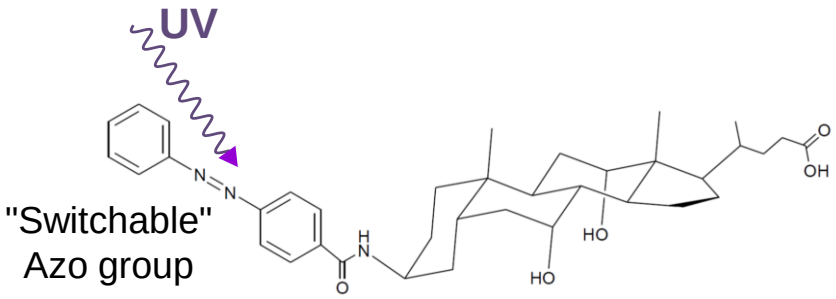
M. Alfonsini (Dept. of Chemistry, Sapienza)

materials development?

biopharmaceutical industry?

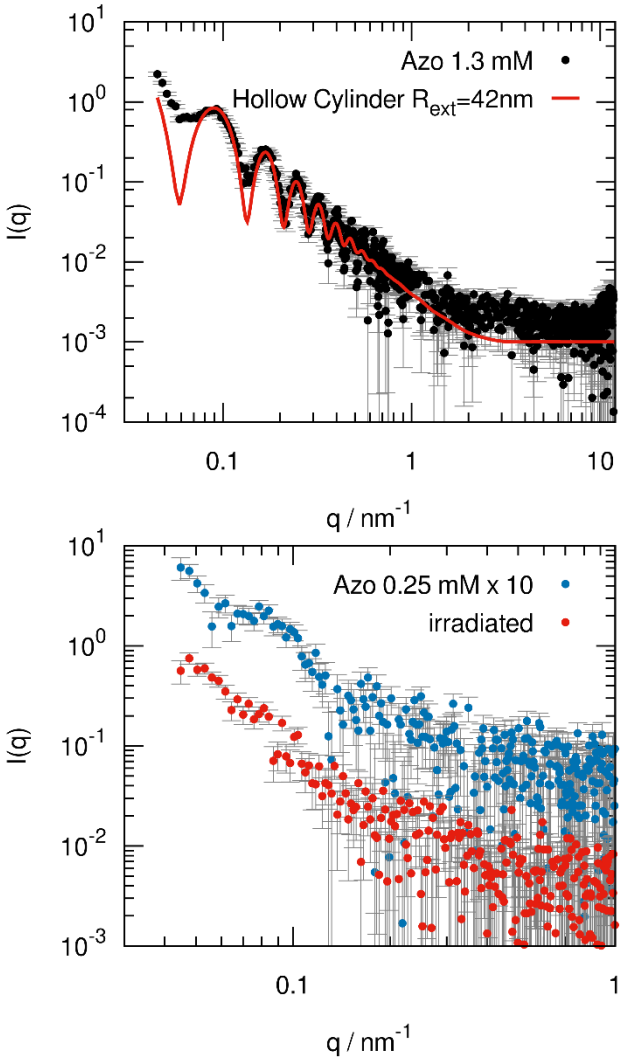
stimuli-responsive self-assembled nanotubes

A **bile salt derivative** bearing an "Azo" group could switch upon irradiation from the trans to the cis form, which should be more soluble as a monomer. The stable trans stereoisomer self-associates in hollow cylinders with a rather monodisperse diameter.



"Azo"- cholate

Cis-trans isomerization of the Azo group detectable from UV spectra

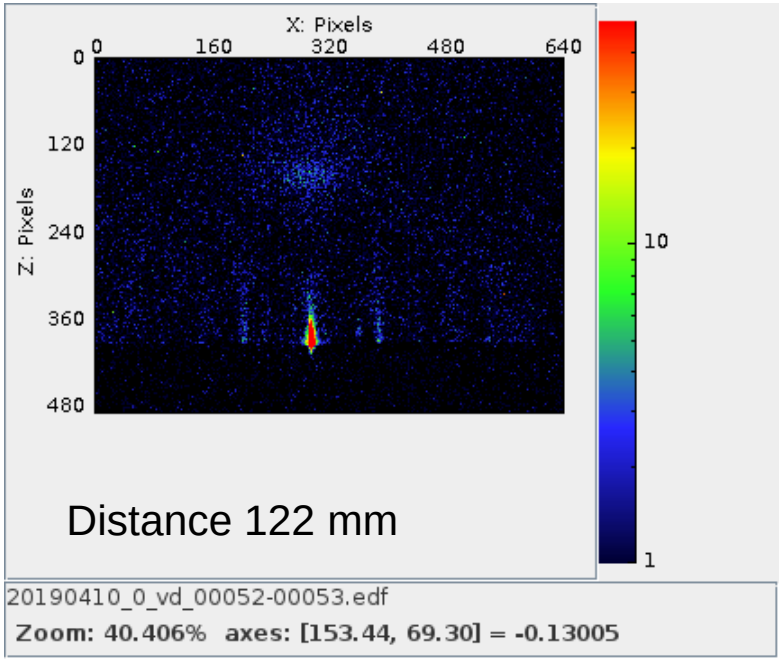


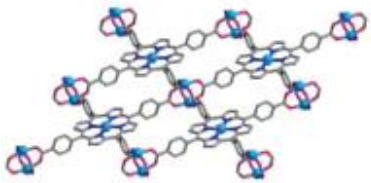
Thanks to:

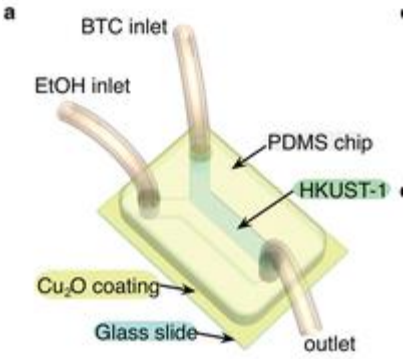
J. Cautela (Dept. of Chemistry, Sapienza)

development of materials technologies

metal-organic frameworks as thin films





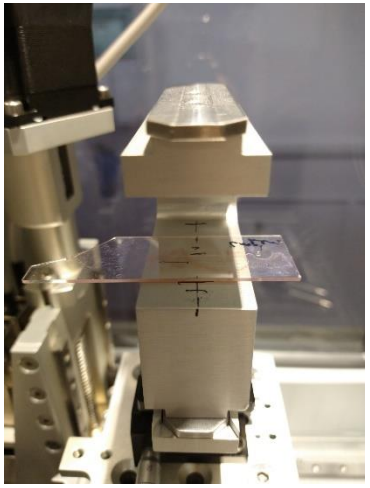


In-Flow MOF lithography
Sevim, S et al. *Adv. Mater. Technol.* 2019, 4, 1800666.

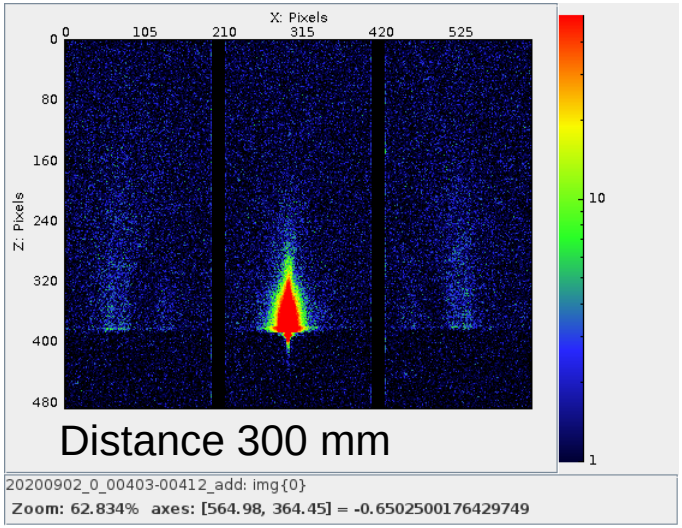
Thanks to:
Carlos Franco (ETH Zuerich), Luis Puigmarti (University of Barcelona)

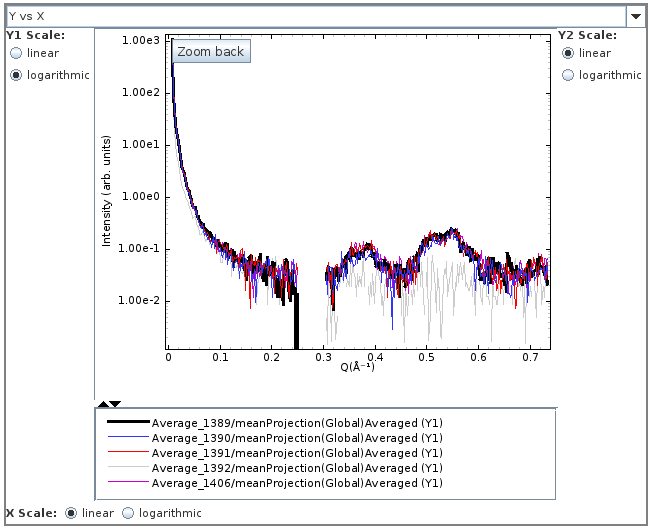
development of materials technologies

metal-organic frameworks as thin films



post-synthesis metallation with microfluidics





Thanks to:

Carlos Franco (ETH Zuerich), Luis Puigmarti (University of Barcelona)

SAXSLab Sapienza Technical Features

Xeuss 2.0-QXoom in operation since November 2018

- Microfocus Cu kα X ray source (λ=0.154 nm)
- Single reflection multilayer optics monochromator
- «Scatterless» slits collimation

SAXSLab Sapienza Technical Features

Xeuss 2.0-QXoom in operation since November 2018

- Microfocus Cu kα X ray source (λ=0.154 nm)
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- Flexible motorized sample stage
- Possibility of reflection geometry for surfaces (GISAXS and GIWAXS)
- Evacuated chamber (p~0.2 mbar), possibility of in-air setup

Thermalized capillary cells

Solids holders

Disposable capillaries

Gels/powders/ slurries capsules

GISAXS stage for flat surfaces

SAXSLab Sapienza Technical Features

Xeuss 2.0-QXoom in operation since November 2018

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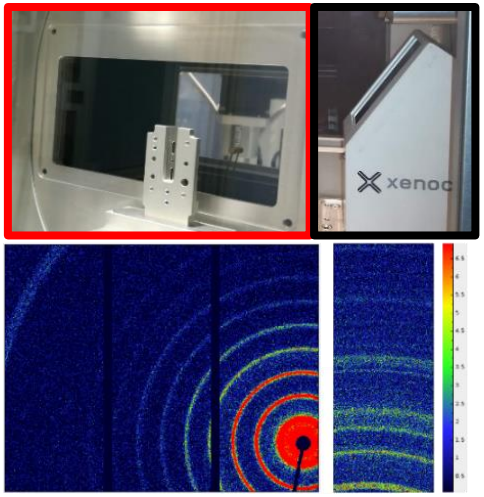

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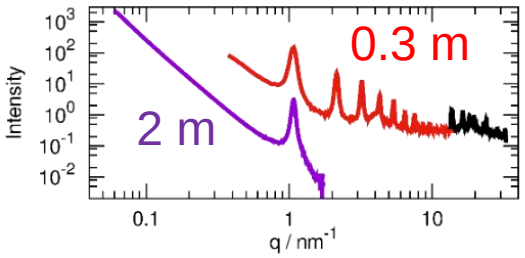

- Pilatus single-photon counting detector (high dynamic range, direct beam measurement)
- SAXS detector variable distance (overall q-range 0.04-16 nm^{-1})
- Simultaneous WAXS detector (13-33 nm^{-1})
- Intensity on absolute scale

Thank you for the attention ☺

SAXSLab Sapienza

Looking forward to seeing you

- ***SAXSLab Sapienza***

Dipartimento di Chimica, Ed. Cannizzaro, St. 058

https://www.chem.uniroma1.it/saxslab/home

- Alessandra Del Giudice

alessandra.delgiudice@uniroma1.it

- Luciano Galantini

luciano.galantini@uniroma1.it