ASC Winter School 2023

Bologna (Italy), February 13th-17th, 2023

Spectroscopy at different length and time scales

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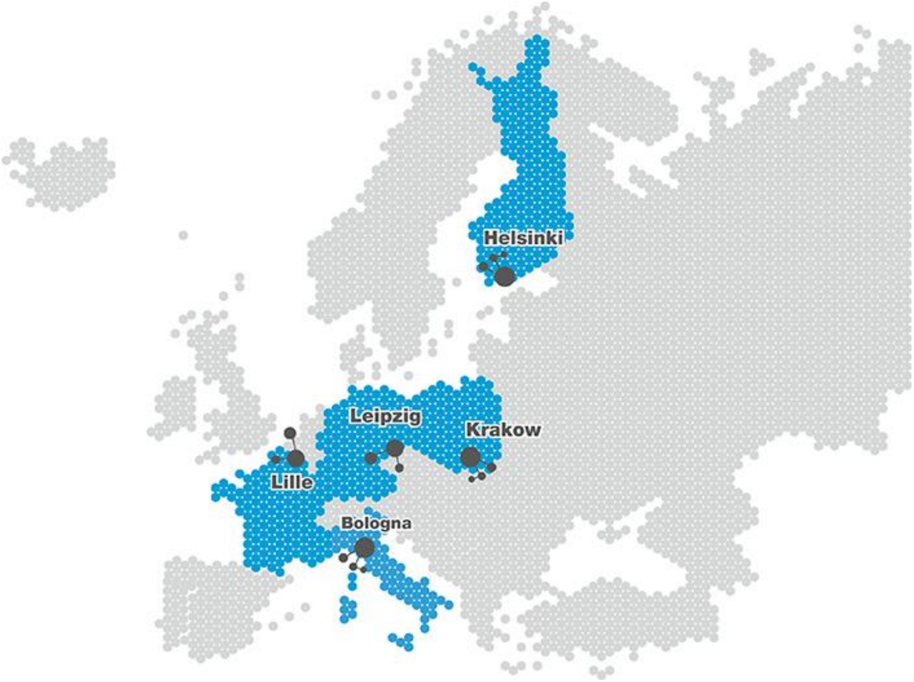

The Erasmus Mundus Master's Course «Advanced spectroscopy in chemistry» is a two-year (120 credits) programme within 5 European universities, providing students with a cross cultural education and expertise in state of the art spectroscopic techniques in a broad range of modern chemistry applications. A winter school is organized each year in a different location on a chosen topic to deepen one specific field of spectroscopy.

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Programme

Monday, February 13th

14:00-18:00
Registration ASC Winter School

20:30
Board dinner

Tuesday, February 14th

8:00 Registration

8:45 Opening
Andrea Mazzanti, head of Industrial Chemistry department "Toso Montanari"
Marco Giorgetti, chair of the ASC Winter School 2023

9:15-10.45
Edyta Beyer, SOLARIS National Synchrotron Radiation Centre (Poland)
"X-ray spectroscopy methods and applications using synchrotron light"

10:45-11:00 Coffee Break

11:00-12:30
Marco Garavelli, Industrial Chemistry department "Toso Montanari"- University of Bologna (Italy)
"Computational spectroscopy of photoactive biomolecules"

12:30-14:00 Lunch Break

14:00-15:30
Berthold Kersting, Institut für Anorganische Chemie, University of Leipzig (Germany)
"(Time-dependent) Luminescence and UV/VIS spectroscopy"

15:30-15:45 Coffee Break

15:45-17:15
ASC Alumni
"3 talks (20 min + 5 discussion)"

20:30 Social Dinner
"Sympo' ex-Chiesa, Via delle Lame, 83, 40122 Bologna"

Wednesday, February 15th

9:15-10.45
Vittorio Morandi, Istituto per la microelettronica e i microsistemi (IMM), Consiglio Nazionale delle Ricerche (CNR), Bologna (Italy)
"TEM microscopy"

10:45-11:00 Coffee Break

11:00-12:45
Ilaria Carlomagno, Elettra - Sincrotrone Trieste, Trieste (Italy)
"XRF mapping with SR"

12:30-14:00 Lunch Break

14:00-15:00
Simone Cailotto, *PerkinElmer S.p.A*
"Microscopy and FT-IR Imaging: advanced and innovative techniques for materials characterization"

15:00-15:15 Coffee Break

15:15-16:30
Mario Salvalaggio, ENI – Istituto Guido Donegani – Novara (Italy)
"Spectroscopic characterization in industry"

Thursday, February 16th

9:15-10.45
Ivana Hasa, Warwick Manufacturing Group WMG, The University of Warwick (UK)
"Electrochemical Impedance Spectroscopy"

10:45-11:00 Coffee Break

11:00-12:30
Matti Rissanen, Department of Chemistry, University of Helsinki (Finland)
"Chemical ionization mass spectrometry applied to atmospheric research"

12:30-14:00 Lunch Break

14:00-15:30
Michel Sliwa, Laboratoire de Spectrochimie Infrarouge et Raman (LASIR), University of Lille (France)
"Watching the photodynamics of photo-active nanosystems for advanced bioimaging"

15:30-15:45 Coffee Break

15:45-17:00
Poster session

Friday, February 17th,

9:15-10.45
Mika Pettersson, department of chemistry, University of Helsinki (Finland)
"Raman spectroscopy and its applications in characterization of 2D materials"

10:45-11:00 Coffee Break

11:00-12:45
Claudia Birkemeyer, Institute of Analytical Chemistry, Faculty of Chemistry and Mineralogy, University of Leipzig (Germany)
"Picture the world in molecular masses – mass spectrometry imaging with ambient ionization techniques"

12:30-14:00 Lunch Break

14:00-16:00
Meeting with local
coordinators

16:00-17:30
Questionnaire

17:30-18:00 Closing remarks

Invited Lecturers

Computational spectroscopy of photoactive biomolecules

Marco Garavelli

Dipartimento di Chimica Industriale "Toso Montanari" – University of Bologna, Viale del Risorgimento 4, 40136 Bologna, Italy

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The use of the computer to simulate light induced events in photoactive molecular materials has given access to a detailed description of the molecular motions and mechanisms underlying the reactivity of organic and bio-organic chromophores. Thus, different computational strategies and tools can now be operated like a "virtual spectrometer" to characterize and understand the photoinduced molecular deformation and reactivity of a given dye, allowing for an accurate description of photochemical/photobiological processes and a rational of the corresponding photophysical properties including time-resolved spectroscopy.

This contribution reviews recent advances in this field, by presenting methodological developments and applications in modeling the photophysical/photochemical properties of organic chromophores and complex photoactive molecular architectures, allowing for so far inaccessible descriptions and analysis. Retinal systems, visual proteins and genomic materials will be presented as a paradigmatic case.

Raman spectroscopy and its applications in characterization of 2D materials

Mika Pettersson

Nanoscience Center, Department of Chemistry, P.O. Box 35, FI-40014 University of Jyväskylä, Finland.

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In this lecture, I will focus on Raman spectroscopy. First, the concept of light scattering and the basic principle of the Raman effect will be explained, followed by the classical theory of Raman scattering. The main features of quantum theory of Raman effect will be very briefly introduced. Difference between non-resonant and resonance Raman scattering will be explained. Selection rules of rotational and vibrational Raman scattering will be handled including aspects of symmetry and group theory and effects of resonance Raman scattering. Modern special techniques including surface-enhanced and tip-enhanced Raman scattering and non-linear Raman techniques will be briefly introduced. Experimental features of Raman instruments will be handled, including discussion of properties of most important components. Raman microscopy and imaging will be included with some examples of applications. Finally, application of Raman spectroscopy and microscopy for analysis of 2D materials, especially graphene will be discussed including examples of some spectra.

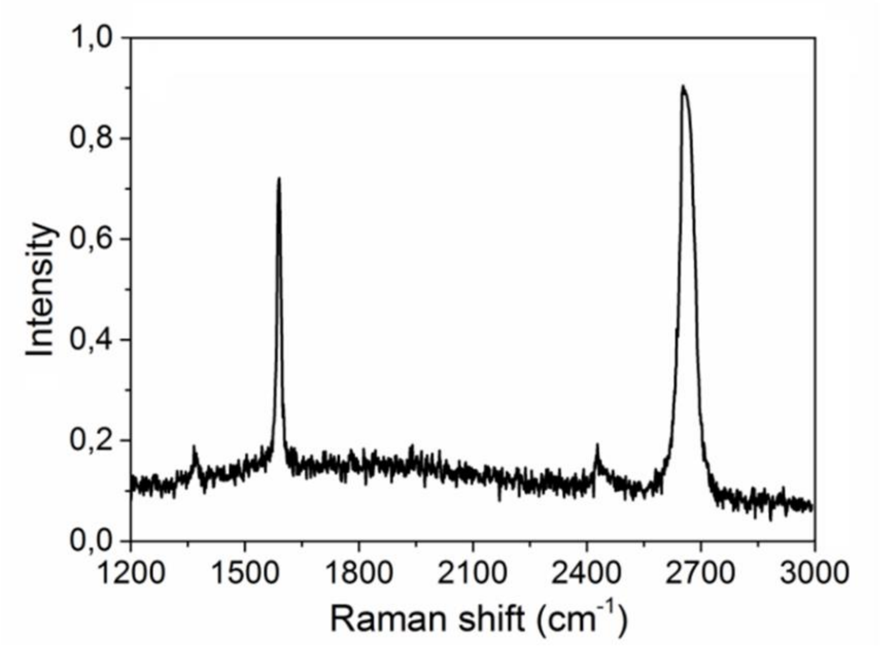

Fig. 1. Raman spectrum of graphene. Various information from the sample can be obtained from the spectrum including defect concentration, doping and number of layers, as will be discussed at the lecture.

Spectroscopic characterisation in industry

M. Salvalaggio, S. Zanardi, R. Marrazzo, S. Fanutti, A. Tacca, R. Paglino,
S. Spera, C. Carati and G. Marra

Eni S.p.A., R&D - Research & Technological Innovation Renewable, New Energies and Material Science Research Center, Novara Laboratories (CENTR), Physical Chemistry Laboratories. Via Fauser, 4 - 28100 Novara (NO) - Italy

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Eni is a global and integrated energy company with a high technological content, active at every stage of the entire value chain: from the exploration, development and extraction of oil and natural gas to the generation of electricity from co-generation and renewable sources, traditional and bio refining and chemicals, and the development of circular economy processes.
Eni contributes to a just transition, an energy transition to guarantee access to efficient and sustainable energy by achieving the goal of net zero emissions by 2050. This challenging energy transition is foremost driven by technological transformation through research, development and deployment of technologies on the basis of strategic drivers such as processes decarbonization, circular and bio-products, renewables and new energies, operational excellence. In this respect, the Renewable, New Energies and Material Science Research center in Novara is primarily focused on the development of innovative technologies in renewable energies.
In this lecture, after an overview of the ongoing activities conducted in the research center of Novara, a few practical applications of spectroscopic techniques to the development of solar energy technologies are presented.

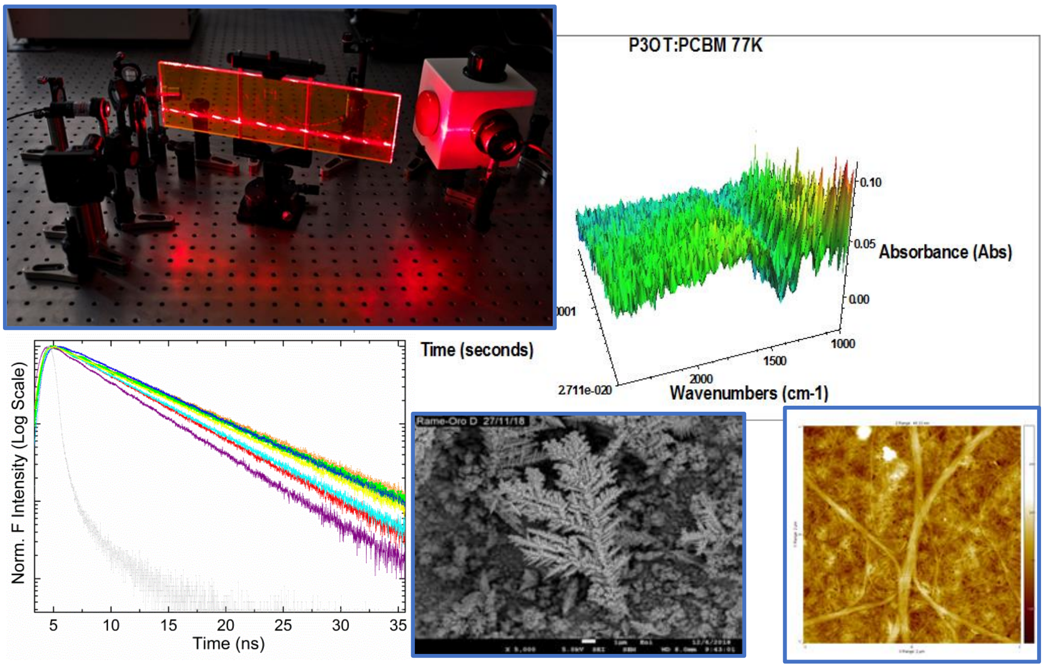

Fig. 1. Optical, spectroscopic and morphological investigation for solar technologies.

Concerning conventional PV, we work supporting the business with incremental innovation in silicon-based technologies. But we developed also innovative advanced PV, focusing on organic flexible PV module and perovskites for PV solar cells.
In an organic photovoltaic device, light absorption by the thin photoactive layer involves the photogeneration of tightly coupled electron-hole pairs (excitons). Then the excitons must diffuse towards the donor / acceptor interface and dissociate into free charge carriers, which can finally contribute to the photocurrent. Photoconversion process in OPV cells can be successful depending on the affinity of donor and acceptor in terms of electronic levels, proper morphology of the active layer, and so on[1]. To select promising donor/acceptor couples, a spectroscopic protocol has been developed to characterize these electronic materials, based also on measurement of quenching of fluorescence emission in the blend and on photoinduced absorption spectroscopies to verify the effective generation of free charge-carriers.

Luminescent solar concentrators are cost-effective complements to semiconductor photovoltaics that can boost the output of solar cells and allow for the integration of photovoltaic-active architectural elements into buildings[2]. Typical LSCs consist of plastic optical waveguide doped with chromophores, which absorb part of the incident light and emit a specific luminescent radiation. Due to the high refractive index of plastic matrix, the emitted light is wave-guided by total internal reflection towards the slab edges, thus realizing the concentration of solar light flux from the large surface of the slab into the small area of the photovoltaic cells. Hence, the understanding of the photophysical behavior of the chromophores, in terms of light absorption and emission, is of paramount importance. In particular, by acquiring the absorption and emission spectra and measuring the luminescence quantum yield (QY) - a pivotal parameter for the first evaluation of the chromophore as active site in an LSC device – and the real response curve of the PV cells on the slab edges, it is possible to completely predict the efficiency of an LSC device. Furthermore, the photostability of chromophores inside the plastic matrix must be deeply evaluated in order to prevent photodegradation phenomena which can jeopardize the device performances.

References

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[2] *B. McKenna and R. C. Evans., Adv. Mater.,* **2017**, 1606491.

Introduction to Time-resolved Absorption & Emission-Spectroscopy

Berthold Kersting

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This 90 min lecture gives an introduction into time-resolved absorption and emission spectroscopy. Specific emphasis is placed on the energetics and dynamics of photo-physical processes in small organic molecules, i.e. absorption and emission of UV and visible light in terms of their time-dependence and in terms of the underlying quantum mechanical principles. Important experimental aspects and typical applications are illustrated to highlight the importance of time-dependent spectroscopies in current scientific research and in technological development. The individual topics are grouped in five separate sections (~ 15-20 min duration), each focusing on well-investigated molecules such that the students can gain a qualitative understanding from the seminar, but may later consult the secondary literature to get a more detailed quantitative picture.

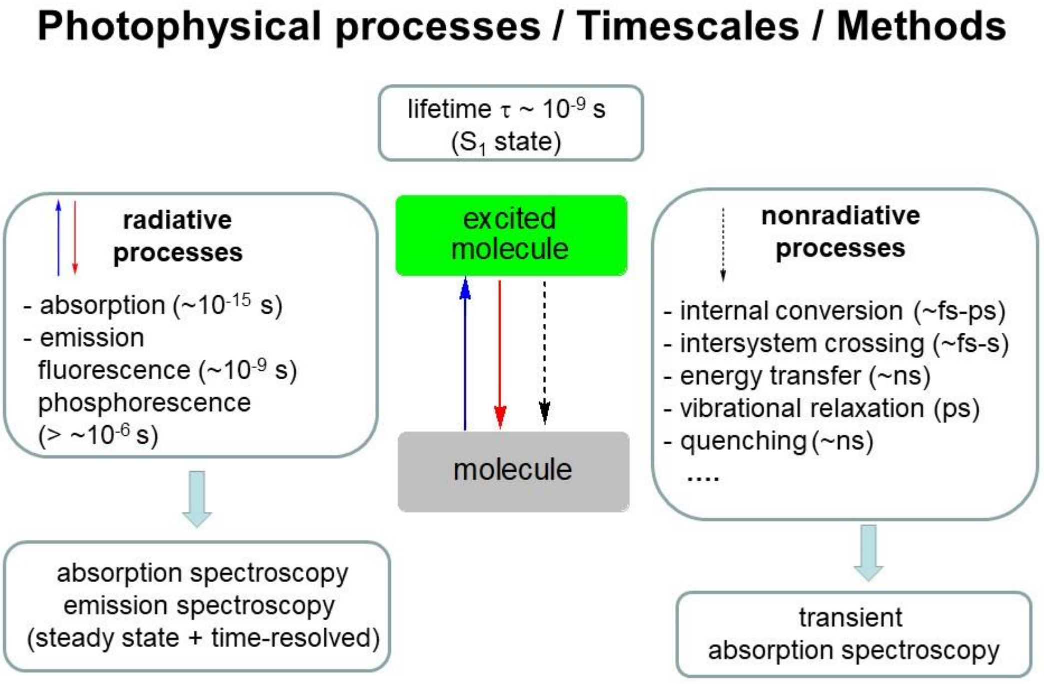
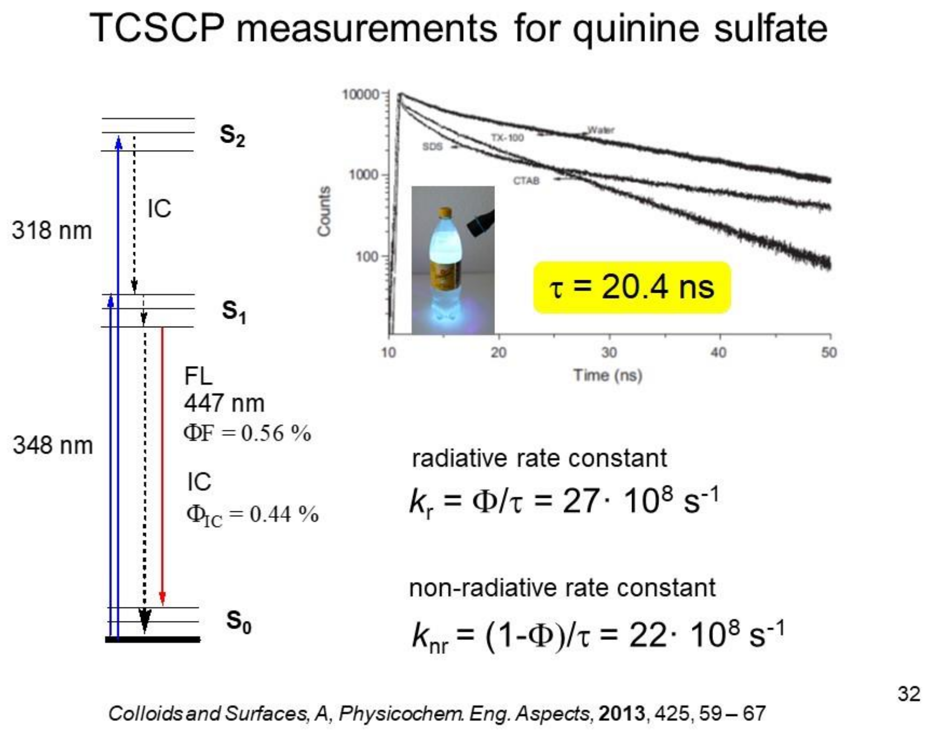


Fig. 1. Photophysical processes, timescales and methods presented in this seminar.

The lecture provides a systematic and rigorous introduction to the interaction of light with small organic molecules in terms of energy and timescale, beginning with the absorption of light by mauveine, the first synthetic dye stuff, and following to highly emissive compounds such as fluorescein and quinine sulfate (Fig. 2). The following topics are covered in this seminar: absorption spectroscopy, luminescence spectroscopy, time-resolved fluorescence spectroscopy, transient absorption spectroscopy.



TCSCP measurements for quinine sulfate

radiative rate constant

$k_r = \Phi/\tau = 27 \cdot 10^8\ s^{-1}$

non-radiative rate constant

$k_{nr} = (1-\Phi)/\tau = 22 \cdot 10^8\ s^{-1}$

Colloids and Surfaces, A, Physicochem. Eng. Aspects, **2013**, 425, 59 – 67

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Fig. 2. Determination of photophysical parameters of quinine sulfate, once used in the medication of malaria.

I thank the organizing committee for the invitation to this ASC winterschool.

References

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Picture the world in molecular masses – mass spectrometry imaging with ambient ionization techniques

Claudia Birkemeyer[1], Abigail Moreno-Pedraza[2], and Jürgen Schiller[3]

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[2] *Molecular Interaction Ecology group at the German Centre for Integrative Biodiversity Research (iDiv) Halle-Jena-Leipzig. Leipzig, Germany, abigail.moreno@idiv.de*
[3] *Instrumental Biomolecule Analysis at the Institute of Medical Physics and Biophysics, Medical Faculty, Leipzig University, Germany, juergen.schiller@medizin.uni-leipzig.de*

Mass spectrometry imaging (MSI) is currently receiving broad attention in the mass spectrometric community. The direct analysis of molecules from surfaces using surface ionization techniques such as desorption electrospray (DESI), direct analysis in real time (DART) or – most commonly – matrix assisted laser desorption ionization (MALDI) for mass spectrometry, enables the assessment of their spatial distribution and molecular patterns. Indeed, MSI allows label-free detection and mapping of a wide-range of organic and inorganic compounds and has the unique ability to identify structures and unravel molecular changes that occur in precisely defined parts of the sample [1]. The combination of molecular speciation with spatially resolved analysis renders a chemical microscope, which, for instance, makes MSI an ideal tool for material science, biomedical diagnostics [2], or ecologically relevant, molecular patterns in organisms. It is able to generate beautiful molecular images from a large variety of surfaces, ranging from cancer tissue sections to polished cross sections from old-master paintings [3]. What are the parameters that define and control the implications, challenges, opportunities, and possibilities associated with the application of MSI in diverse areas of research?

The sample and its chemistry determine what ionization source is more suitable for the analysis. [4] Successful detection of the analytes of interest at the desired spatial resolution requires careful attention to several steps in the mass spectrometry imaging protocol. MS images can be generated using vacuum or ambient ionization techniques; both have advantages and limitations. Thus, MALDI features a high spatial resolution but the success is crucially dependent on time-consuming sample preparation as it dictates the nature and mass range of detected molecules that can be imaged. In return, ambient techniques mostly rely on the direct chemical sampling with only few steps or even no treatment of the sample prior analysis and the viability of working under ambient conditions allows a particularly quick analysis: the sample can be set directly on the imaging platform, the target area is selected and analyzed.

However, arguably the greatest disadvantage of MSI is the difficulty in acquiring quantitative data. The development of quantitative MSI approaches would correspond to a quantum leap forward for the field and, is therefore a highly active area of current research [5,6]. Difficulties largely arise from the high dependence of the ion signal on the close chemical and morphological environment and the challenge associated with calibrating such signals. Consequently, at present MSI quantification is performed by signal comparison of relative intensities.

Within the past decade, MSI has been increasingly recognized as a valuable technique for studying the molecular morphology of complex systems. Its rapid evolution has resulted in an impressive array of instrument variations and sample applications, yet the tools and data are largely confined to specialists [7]. It is therefore important that at this junction the community further continue to integrate MSI into all branches of chemical and biological research.

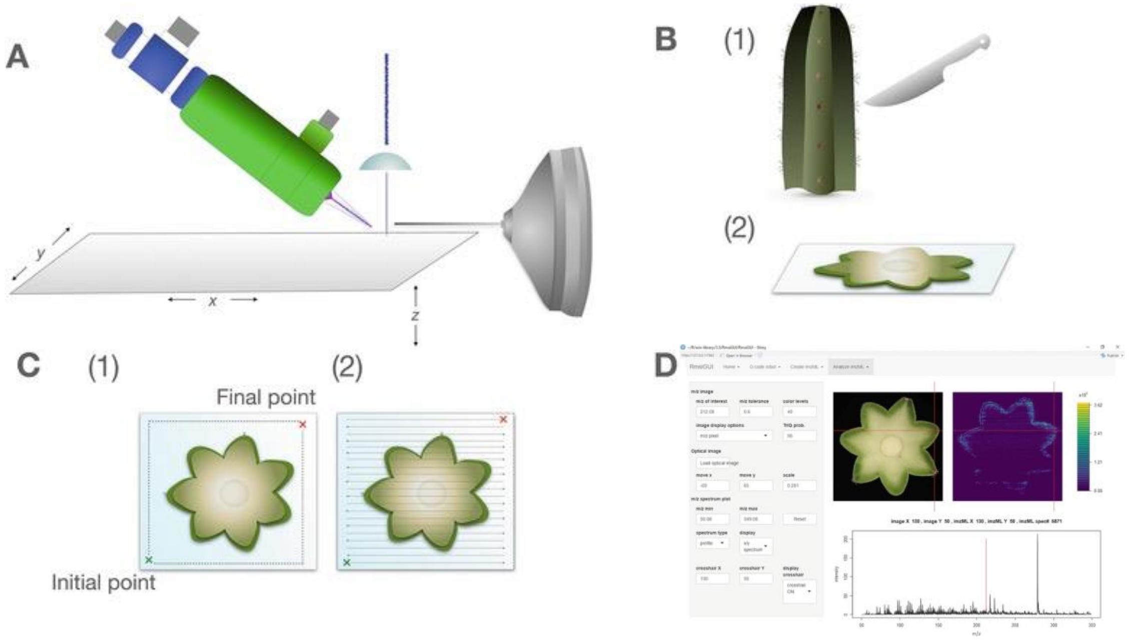

Figure. ***A****) Set up of LD-LTP in front of the MS inlet.* ***B****) Cut a flat sample slice.* ***C****) Delimitate the area of analysis, selecting the pixel size and the time.* ***D****) After the conversion the final image can be analyzed using specialized software in this example is shown the open-software RmsiGUI.*

References
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Watching photo-active systems at works: how to observe their ultrafast dynamics?

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The efficient use of photo-active systems is a prerequisite for our existence (e.g. solar cells) and the development of disruptive new technology. The best example is living systems that developed light adapted biological function. Among photo-active biological systems, photo-switchable proteins are key elements in different important biological functions for the vision, the protection or in the photosynthesis. They are also used in different applications such as opto-genetics and super-resolution bio-imaging. Their intrinsic properties of using in an efficient way the light is characterized by a photo-switching dynamics that takes place on several order time-scales, ranging from hundreds of femtoseconds to a few milliseconds. It involves several excited states and intermediates, and a complex interplay between the chomophore and 3D structural changes of the protein that guides efficiently the flow of energy to achieve reversibly the photo-modulation of different biological properties. However mechanistic details, in particular on the ultra-fast photochemical time scale, remain yet unclear. Another challenge in deducing the photo-switching mechanism is to create a uniform picture explaining both single pulse excitation experiments used in the study of ultrafast photo-dynamics, and continuous sun light irradiation experiments. I will discuss here on the different techniques allowing to probe and follow the photo-dynamics from femtosecond to minutes time scale. I will illustrate them on some dyes used in solar cells [1] and with our recent results on photo-switchable fluorescent proteins [2] and orange carotenoid protein [3], especially on how advanced time resolved techniques (time-resolved absorption spectroscopy and crystallography) and data analysis [4] could reveal some crucial parameters in the photo-switching dynamics and rationally tailor the development of efficient new photo-active proteins for bio-imaging [3] and optogenetics [2].

References

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X-ray fluorescence investigations with synchrotron radiation

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X-ray Fluorescence (XRF) is a powerful technique assessing the chemical nature of samples. Based on the X-ray interaction with matter, it is intrinsically non-destructive, element selective, and does not require any particular sample preparation procedure. Thanks to its high versatility, XRF is widely employed in different fields, ranging from fundamental physics to chemistry, from life science to cultural heritage, from geology to environmental sciences etc.

When coupled with synchrotron radiation (SR) sources, the limits of XRF can be pushed even further. This lecture aims to give a general overview of SR-XRF, providing the necessary tools to understand and exploit SR-XRF capabilities in real experiments. To this end, the physical phenomenon underlying the fluorescence emission will be described and the main potentialities of the technique will be explored [1]. In a similar fashion, synchrotron radiation sources will be outlined, focusing on the major advantages that synchrotrons offer with respect to the more common laboratory sources. After some theoretical background on X-ray production, beamline optics, detectors, and other devices will be described. The main differences between XRF and X-ray absorption spectroscopy will also be addressed and discussed, as well as the complementarity of the two techniques.

The discussion will then move to a few practical examples of setups typically used for XRF data collection including standard (45/45), grazing incidence/exit, and total reflection geometries. To this aim, the XRF beamline of the Elettra synchrotron [2,3] will be presented and discussed. Several case studies covering a broad range of applications will be presented to better explain some of the endless possibilities in a variety of fields.

The operation mode of beamlines and the access to synchrotron facilities will also be presented and the design of a realistic experiment with SR-XRF will be prepared with the active participation of the students, who will help in the evaluation of advantages and drawbacks of every choice.

Fig. 1 – The experimental hutch of the XRF beamline at the Elettra facility.

References

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Controlled ambient pressure chemical ionization mass spectrometry for quantifying the state of the environment

M. Rissanen[1,2], S. Iyer[1,2]

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[2]*Aerosol Physics Laboratory, Tampere University, Tampere, Finland*

For the last decade, ambient pressure chemical ionization mass spectrometry instruments with carefully controlled ion chemistries have offered an unprecedented detail into several key processes puzzling atmospheric scientist, perhaps most notably on the molecular steps leading to atmospheric particulate matter formation [1-4]. The technique can offer extreme sensitivity and selectivity by a careful choice of reagent ion chemistry [5,6] and the accompanying ion introduction methodology, and consequently several ionization inlet designs have been introduced in recent years [7-9]. By performing the sample ionization at the ambient pressure allows to target the trace gases with the smallest of concentrations, as the sample concentration does not decrease while pulling the sample to the low-pressure detection region of the mass spectrometer instrument. Coupled to careful selection of reagent ion chemistry, different chemical groups can be extracted for detection.

The methodology presented here is applicable for analyzing any gas-phase environment or any volatilized material thereof, yet the topical examples and detailed insight given are from studies relating to new particle formation in the ambient atmosphere.

References:

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Transmission Electron microscopy and spectroscopy

Matteo Ferroni[1,2], Raffaello Mazzaro[1,3], Vittorio Morandi[1]

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Transmission electron microscopy has become over the years a complex characterization method and a powerful support to the materials science community for synthesis, fabrication, and functional exploitation of nanostructures.

The improvement in electron optical systems as well as detector technology attained atomic resolution and high elemental sensitivity with controlled modification and damage imparted to the sample. X-ray and Electron Energy-loss spectrometers, two of the most performing attachments of the electron microscope, have increased their performance and production; in addition, computer-assisted techniques allow TEM imaging and spectroscopy to visualize a material’s structure and perform analytical determination of chemical species, their profiling, mapping and even three-dimensional reconstruction of the spatial arrangement.

Fig 1 shows the quantitative measurement by TEM of the atomic occupancy in a crystal structure, marking a significant accomplishment in the determination of the structure-property relationship for the functional class of insulating metal oxides.

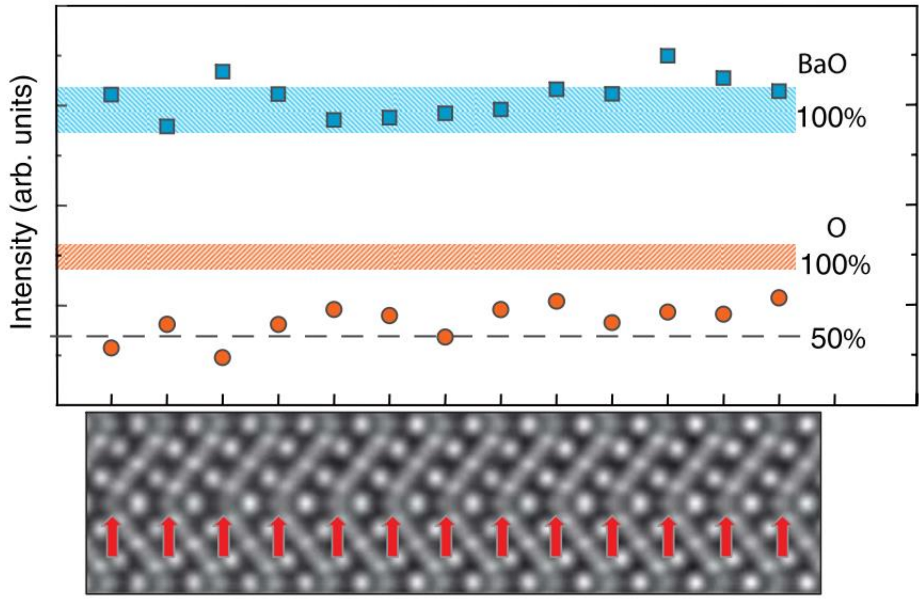

Fig. 1. Quantitative site-occupancy measurements in a BaTiO3 boundary (bottom image). Red arrows denote the appertaining oxygen sites. BaO columns in the boundary are stoichiometric, that is, 100% occupied. In contrast, the oxygen signal (red circles) is with 40%–70% occupancy, much lower than the bulk signal (red shaded band), indicating oxygen vacancies. From Ref [1]

The sub-eV energy resolution of Electron Energy-Loss spectrometers, operating in conjunction with the Scanning-Transmission imaging mode, combines the determination of structural, spectral, electronic and chemical properties of a material with a sub-nm resolution imaging and single-atom sensitivity for elemental identification. Fig.2 reports a STEM-EELS integrated approach to record an extensive spectral dataset processed in a tomographic three-dimensional reconstruction of a metallic silver nanoparticle.

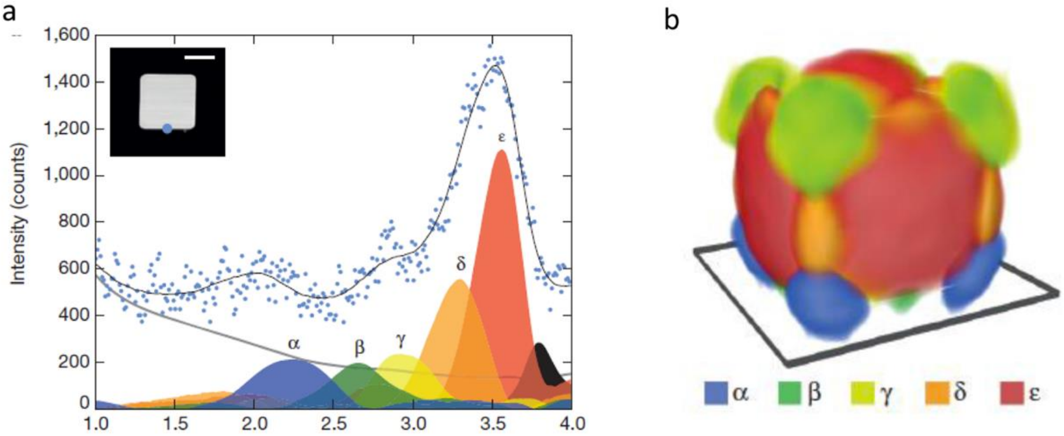

Fig. 2. 3D-EELS tomographic mapping of the localized surface plasmon resonances (LSPR) on a 100nm Ag nanocube: (a) EELS spectrum recorded for the probe position marked in blue on the HADF image and identification of the spectral components (α, β, γ, δ, and ε) to be attributed to LSPRs on the cube, also visible are the zero-loss tail and the bulk silver plasmon (in black); (b) the 3D map of the identified specific components. From Ref [2] and references therein.

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X-Ray Spectroscopy Methods and Applications using Synchrotron Light

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The SOLARIS synchrotron, located in Krakow, Poland, is a third-generation light source operating at medium electron energy. The first synchrotron light was observed in 2015 and the consequent development of infrastructure led to the first user experiments at soft X-ray energies in 2018. The SOLARIS synchrotron is composed of a 600 MeV linear accelerator and a vertical transfer line that is used as an injector into the storage ring. The storage ring with a circumference of ninety-six meters and 1.5 GeV maximum energy consists of 12 Double-Bend Achromat cells. Presently, SOLARIS Centre delivers experiments with five beamlines (overall six end-stations) and a cryo-microscopes facility, while three additional beamlines are under construction, and several more are in conceptual preparations. The SOLARIS National Synchrotron Radiation Centre currently operates beamlines at photon energies ranging from VUV to hard X-rays and provides different photon- and electron-based techniques for sample investigations. From the currently operating beamlines, all facilitate spectroscopy methods, i.e. X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence analysis (XRF) [1].

Spectroscopy methods are based on the photoelectric effect, which was first observed by Heinrich Hertz and eventually described in quantum-mechanical terms by Albert Einstein. The effect occurs if atoms are excited with radiation of a sufficient photon energy. The primary photons transfer their energy to the electrons of an atom, which causes an emission of the said electron from the atom shell. These photoelectrons have a specific kinetic energy, whose analysis is the basis for X-ray photoelectron spectroscopy (XPS). The kinetic energy of a photoelectron is specific to the element and the binding energy of the electron as well as the energy of the excitation. The emitted electron creates a vacancy in the atom shell, and an electron from an energetically higher shell fills this vacancy. During transition, the filling electron releases its excess energy in the form of a fluorescence photon or an Auger electron. Fluorescence photons have an energy that is element and transition specific. The detection of fluorescence photons gives the basis for X-ray fluorescence analysis (XRF).

An application example for combined X-ray spectroscopic measurements is given: Since the introduction of the revised SI on the 20th of May 2019, the kilogram is no longer defined as the mass of the international prototype of the kilogram but is instead derived from a fixed numerical value for the Planck constant. One of the two independent primary methods that allow a realisation of the definition of the kilogram with relative uncertainties of a few parts in 10^{-8} is the X-ray-crystal-density (XRCD) method. This method uses silicon spheres. By determining the number of atoms in a sphere, its mass is established. Silicon spheres that are currently used for the practical realisation of the definition of the mass unit are primary mass standards and are produced from nearly perfect isotopically enriched ^{28}Si crystals [2]. However, the spheres have an always present surface layer of silicon dioxide, water, and carbonaceous contaminations. Therefore, the surface layer needs to be quantified for realisation.

The surface layer of silicon spheres was characterised and quantified by combined X-ray spectroscopy, using X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence analysis (XRF) [3]. In addition, the mass stability of silicon spheres was investigated, including silicon oxide growth behaviour, since knowledge of sphere mass stability is required for uncertainty analysis, drift corrections, and determination of appropriate realisation intervals. An ultrahigh vacuum instrumentation for XPS and XRF was developed for measurement, especially on spheres, to access the mass of the overall surface layer and the sublayers. The investigation gives answers to the central question of the suitability of silicon spheres as novel mass standards. The oxide layer of silicon spheres follows a logarithmic growth function, creating a self-limiting layer. As a result, spheres are ready for measurements and suitable for a stable realisation with small measurement uncertainties already three months after the end of the polishing process. Moreover, the spheres of ^{28}Si and natural silicon are equal when it comes to surface properties, such as growth of the oxide layer or adsorption of water or carbonaceous contaminations. Concerning the handling of the spheres, current cleaning techniques are sufficient for a realisation with highest accuracy, as they produce reproducible results. Thus, the influence of cleaning procedures on the short-term mass stability of silicon spheres is negligible [4].

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Poster Contributions

Identification and discrimination of chelated metals in oil-based paint tubes and dryers explored by ultra-high resolution MALDI FT-ICR mass spectrometry

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Introduction & experimental

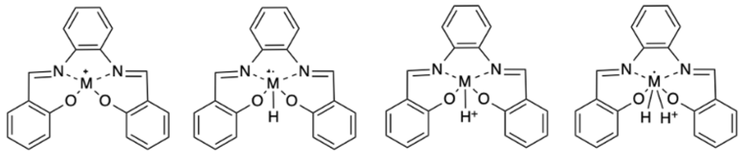
Louis Pasteur, at the end of the 19th century, was one of the first chemists to attempt to rationalize the role of metals in the drying of oil paintings [1]. These studies, and many others since, have shown that metal complexes play a fundamental role in the process of oxygen uptake, followed by the of hydroperoxides into free radicals, which leads to the binding of the pigment to the paint support, resulting in cured cross-linked polymer networks. The present study aims to answer the questions opened by Pasteur and to find a suitable protocol for the analysis of metals in oil art paint tubes and dryers using ultra-high resolution mass spectrometry. Initially, analytical grade metal solutions including Co(II), Cu(II), Fe(II), Fe(III), Mn(II), Pb(II), Ti(IV), Zn(II), Zr(IV) were reacted with five different chelating agents, commercially available or that we synthetized, in order to find the most suitable one. Mass spectrometry measurements were performed with a MALDI ionization source on a Bruker Solarix XR 9.4 Tesla FT-ICR instrument and with optimized conditions and parameters.

Results

Schiff base tetradentate (salen) N,N'-bis(salicylidene)-1,2-phenyldiamine was found to be the best ligand in terms of metal specificity and signal intensity. FT-ICR mass spectrometry proved to be a powerful tool due to its resolution of more than 1 million at 100 m/z, which allows to clearly distinguish the different chemical compositions of the complexes. Oxidation, protonation, or radical reactions occur and are evidenced by the presence of the corresponding ions in the spectra. Their presence and intensity depend on the possible oxidation states of the target metal and of the substitution on the salen. Thus from Cu(II), the native species salen-$Cu^{2+} + H^+$, the oxidized species salen-Cu^{3+} and the one having added a radical hydrogen [salen-Cu^{2+} + H°] + H^+ are observed. The dissolution of pigments required harsh conditions. To work on these more complex samples, a solid extraction protocol with a reverse phase SPE column was optimized. In a second step, we determined the relative sensitivity of the metals in mixture and showed that they can be distinguished. We then applied this workflow to pigments extracted from modern and historical paint tubes and dryers, such as Kortrijk dryer samples. We are currently downscaling our approach to work on cultural heritage samples.

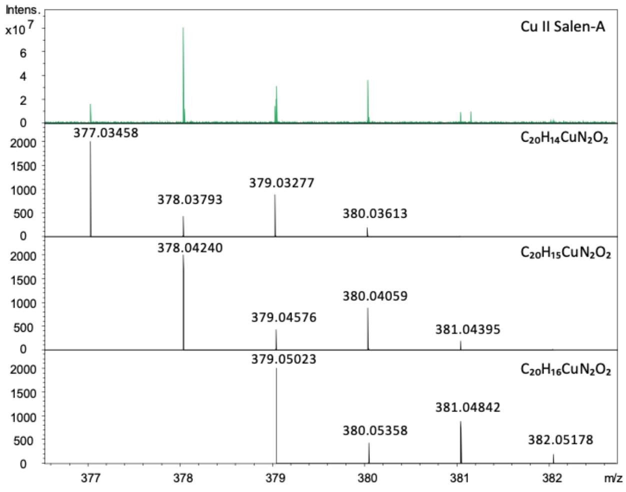
Conclusions

The present study lays the foundation for future research on determining the origin of pigments by measuring metal isotope ratios and determining trace metal contaminants. The MALDI FT-ICR spectra were obtained with only 0.1 μg of metals which opens the way for its application on paint samples on the solution obtained by the polymerization methods we developed for the organic part.



1 2 3 4

Fig. 1. 1 oxidated specie $C_{20}H_{14}MN_2O_2$, 2 radical specie $C_{20}H_{15}MN_2O_2$, 3 protonated specie $C_{20}H_{15}MN_2O_2$, 4 radical specie $C_{20}H_{16}MN_2O_2$, 8 doubly chelated metal $C_{40}H_{29}MN_4O_4$



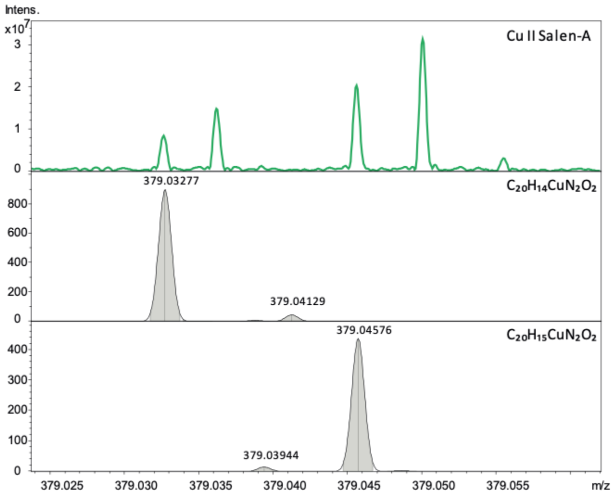


Fig. 2a. MALDI FT-ICR of Cu(II). The figure shows the measured isotopic pattern (top) and the calculated isotopic pattern (bottom) for the species H-14, H-15 and H-16
Fig. 2b. MALDI FT-ICR spectrum of Cu(II) Salen-A complex showing the zoom of the measured peak at 379 m/z (top) and the calculated peak (bottom) for the species H-14 and H-15

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Electrochemical and Structural Characterization of Nickel Nitroprusside as a Potential Cathode Material for Batteries

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We report the electrochemical performance and structural studies on nickel nitroprusside (NiNP) as a prospective cathode material in a Li-ion battery. The electrochemical performances are studied using half-cell cyclic voltammetry (CV). The working electrode materials were prepared by mixing the NiNP with carbon active and binder, wrapped by aluminum foil. The structural characterizations were preliminary carried out using X-Ray Absorption Spectroscopy (XAS), X-Ray Fluorescence (XRF), and X-Ray Diffraction (XRD) techniques.

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Charge-Transfer Complexes: Implementation in solution-processed Organic Field-Effect Transistors

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Organic Field-Effect Transistors (OFETs) represent an indisputable core element of organic electronics. During the last decades, a concerted effort has been engaged in improving their performances and ripening their applicability. While doping still represents a key methodology to fabricate high performing devices, Charge-Transfer Complexes (CTCs) [1] have become extremely attractive thanks to their tunable nature [2] ranging from unipolar [3] and ambipolar [4] [5] semiconductors to metals and even superconductors. Moreover, the demanding low cost and large area fabrication has highlighted the importance of solution processing approaches that additionally enable the control of the charge carrier concentration and distribution in organic semiconductors. The current implementation of CTCs is more commonly restricted to the form of single crystals produced via drop casting methods and co-evaporation of the parent materials, far from the industry applicability purposes. We report a study of CTCs of (C_8O-BTBT-OC_8)(F_4-TCNQ) [6] and (Ph-BTBT-C_{10})(F_4-TCNQ) deposited as thin films by a solution processing technique named Bar-Assisted-Meniscus Shearing (BAMS) [7] [8]. The devices were electrically analyzed, while the structure and morphology of the films were determined by optical Microscopy, X-rays diffraction and Atomic Force Microscopy. Raman and IR spectroscopy were employed as well to study the CTCs.

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Hydrogel for Energetic and Sensor Applications

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Hydrogel exists in the form of soft matter with a 3D crosslinked hydrophilic polymer as the backbone, so it's able to hold large amounts of water [1]. A lot of natural and synthetic polymers can turn into hydrogels and take shape in 3D network structures by diverse crosslinking mechanisms. Because of the variety of preparation methods, hydrogels have broadly tuneable physical and chemical properties, which bring about value of applications in different situations: wet adhesives, photo/thermo/electrochromic devices, wound dressings, flexible sensors, and electronics [2]. Hydrogel flexible electronics consist of physiological signal electrodes, supercapacitors, actuators, triboelectric nanogenerators, and so on. In this contest it will be prepared and studied hydrogel based on PVA and conducting polymers with the aim to use them in energetic and sensor applications (Fig.1).

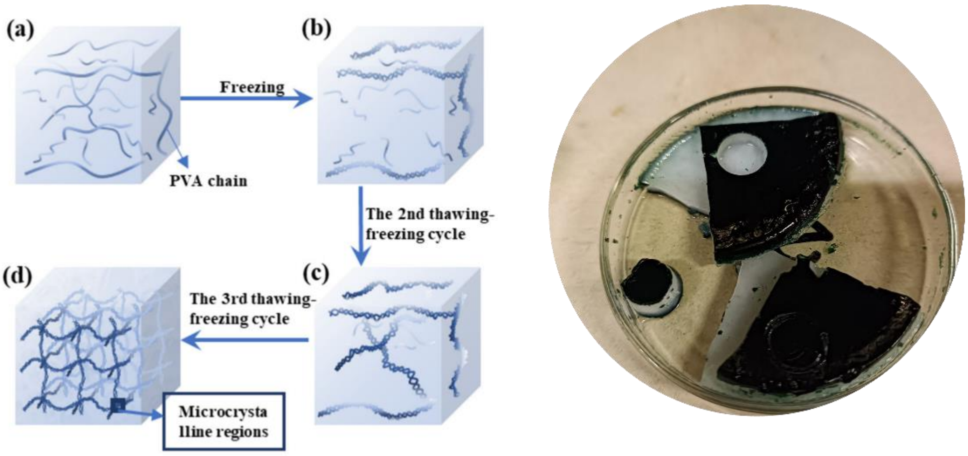

Fig. 1 Hydrogel preparation

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Cryo-EM sample preparation for virus research. Methods and obstacles.

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Viruses are a major safety concern worldwide and understanding how they function is crucial for the addressing this problem. One of many techniques that allows for the in-depth investigation into the structure of viral particles, cryo-electron microscopy (cryo-EM), has recently gained wider recognition, since the development and improvement of cryo-EM methodology were recognized by the Nobel Prize in 2017.[1] However, the implementation of cryo-EM in structural biology involves many individual experiments, each facing its own obstacles.

Members of the genus *Flaviviridae* are the cause of many severe diseases transmitted by insects, such as Yellow fever, Dengue fever, West Nile and Zika virus, spread by mosquitoes, and several types of encephalitis, transmitted by ticks.[2] One of the barriers to the investigation of the abovementioned viruses is also the underlining factor behind the importance of the research on them – the severity and mortality of the diseases caused by them.[3] In the frame of our current project, we are exploring the means of circumventing this problem, by using the chimeric species of the Langat virus, which is BSL2 safe. The chimera is provided by our collaborators from Umea University.

Our goal is the characterization of this model, and its assessment for the role of studying tick-borne encephalitis (TBEV). To achieve this goal using cryo-EM, the viral sample has to be monodisperse and pure.

Commonplace techniques for virus purification include ultra-centrifuge filtration, virus pelleting, gradient centrifugation can produce significantly different outcomes, even for highly similar viruses. A prominent example of this phenomenon was observed in our current work – an optimized protocol to produce the TBEV, used in our group to achieve atomic resolution models of said virus, did not yield similar results in the framework of our current project, both in terms of virus concentration, and in virion quality.[4]

Here, we present our progress with the optimization of the virus production, purification, and cryo-EM sample preparation – stages that are often overlooked in discussions of the results of viral structure studies.

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Electropolymerization of N,N’-bis-[2,2’;5’,2’’]tert-thiophen-5-ylmethylcyclohexane-1,2-diamine: focus on the reaction mechanism elementary steps.

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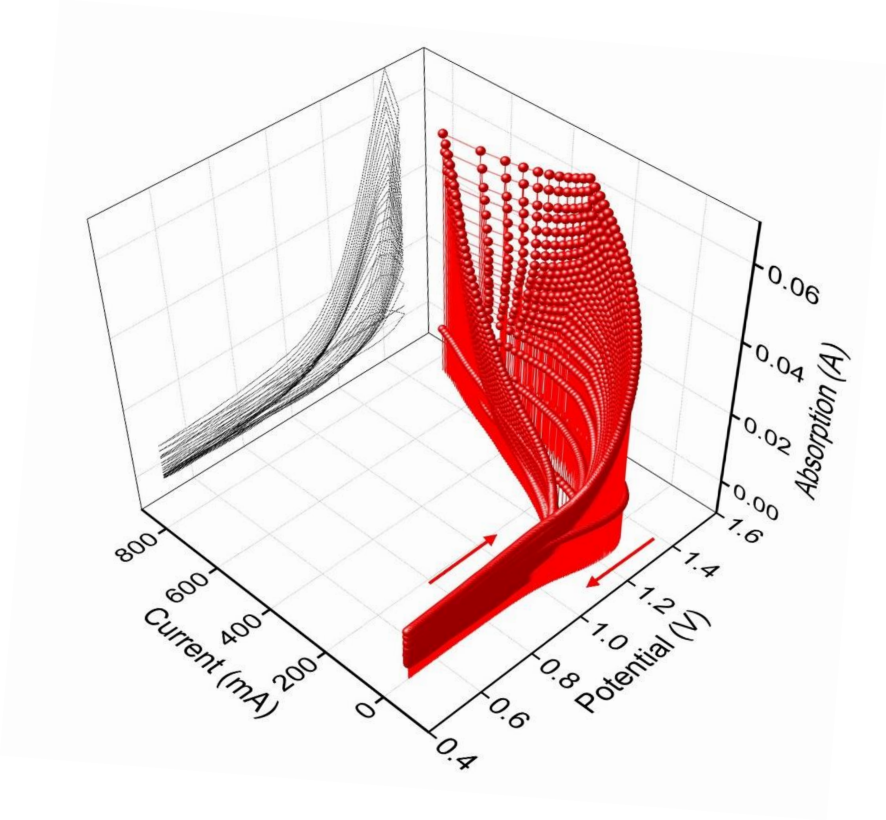
N,N’-bis-[2,2’;5’,2’’]tert-thiophen-5-ylmethylcyclohexane-1,2-diamine) (2T3N)[1], a chiral oligothiophene derivative, is polymerized electrochemically on indium-tin oxide (ITO) surface. The electro-polymerization mechanism is probed by tight comparison of electrochemical and “in-situ” spectro-electrochemical measurements. Theoretical



calculations of UV-Vis spectra allow to rationalize the experimental outcome, and show that a "sigma" complex involving a 2T3N dimer plays a key role in the overall polymerization mechanism[2],[3].

Fig. 1. 2T3N spectro-electrochemical polymerization 3D representation. Polymerization was achieved via 20 CV scans between 0.5 and 1.5 V in a 2T3N 5 mM, TBATFB 0.1 M ACN solution (0.05 V s^{-1} potential scan rate). ITO coated glass was the WE, Pt and Ag/AgCl/KCl_{sat} were the CE and RE, respectively. The CVs' recorded current is plotted on the y-axis, while the imposed potential is reported on the x-axis. During the electro-polymerization, the adsorption was recorded at 680 nm and it is plotted on the z-axis.

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Ionic plastic crystals: harnessing Raman spectroscopy for phase transition identification

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Plastic crystals (PCs) comprehend a group of materials owning long-range order while conserving some degrees of rotational freedom. This seemingly conflicting high crystallinity and plasticity properties in PCs have made them an active field of research in the past years [1].

Specifically, in our research we have focused on the study of the so-called ionic PCs, standardly comprised by a globular-shaped cation and small anion [1]. Three cations were studied, namely: 3-quinuclidonium, $[QH_{co}]^+$, and both enantiopure and racemic mixtures of 3-hydroxyquinuclidinium, $[QH]^+$, cations. These were synthesized as methanesulfonate, $[MS]^-$, salts derivatives; this was done so as to study the role of the cation in PC forming phases, since interesting previous results were obtained varying the anion in hydroxyquinuclidinium salts derivatives [2].

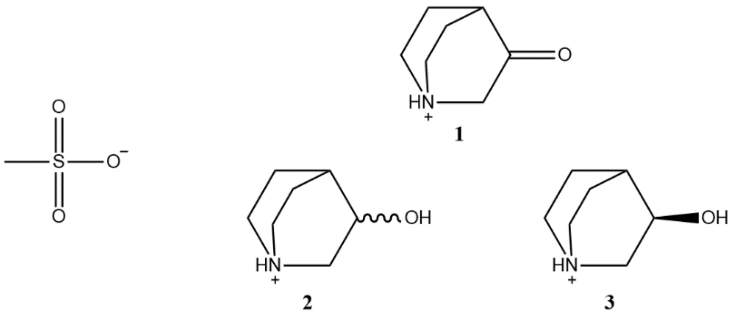

Figure 1. Molecular structures of the employed compounds for Raman measurements. Methanesulfonate salts varying the cation enumerated as: 1 (3-quinuclidonium), 2 (racemic 3-hydroxyquinuclidinium) and 3 (enantiopure R-3-hydroxyquinuclidinium).

Raman spectroscopy allows us to investigate the vibrations of both inter- and intra-molecular vibrations of a crystal. As a result, it has been shown to be a valuable tool for phase transition identification [3]. Particularly, temperature dependent Raman studies, ranging from -120 °C to 200 °C, were performed to investigate the plastic phase transition following the lattice phonons dynamics, below 150 cm^{-1}, and the molecular dynamics for all the three systems. A plastic phase transition was successfully identified for QHMS chiral compound, while direct solid-to-liquid transitions were identified for the $QH_{co}MS$ and racemic QHMs counterparts, using complementary information coming from differential scanning calorimetry (DSC) and X-Ray diffraction (XRD) measurements.

Additionally, factor group analyses in each salt were conducted to try predicting and disentangling the lattice phonon spectra via polarized measurements.

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Computational evaluation and design of Vorinostat derivatives - HDAC inhibitors and their synthesis.

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Histone deacetylase (HDAC) inhibitors are a class of drugs used in the cancer treatment [1]. The first successful HDAC inhibitor with hydroxamic acid moiety, Suberanilohydroxamic acid, also known as Vorinostat, was already used for the treatment of cutaneous T-cell lymphoma [2]. The search for other drugs of this family is reasonable due to the success of Vorinostat and his known binding motif.

To analyze the large number of possible inhibitors, the most efficient way is to apply computational methods. We developed the docking protocol with Biochemical Library (BCL) [3], used for substructural manipulation and generation of ready to screen structures of ligands, and Rosetta Software [4] for protein-ligand docking. We analyzed the pharmacophore of Vorinostat, and used the known desired binding pose from previous docking results of ligand with the same warhead to make further docking in Rosetta more precise. Further, the interface score values were compared and the ligands were synthesized through the two-step reaction, using Suberic acid and Aniline derivatives as starting material.

The protocol developed allows to use BCL to align the specific atoms, in our case, metal binding site of the ligand, in a desired way. Our pipeline can dock in constrained manner: based on the knowledge of the ligand interactions, it is possible to partially conserve the structure and sample only other part of the ligand. This approach reduces the amount of sampling, as well as giving superior results than classic way of docking and can be used for many similar cases leading to more precise docking models.

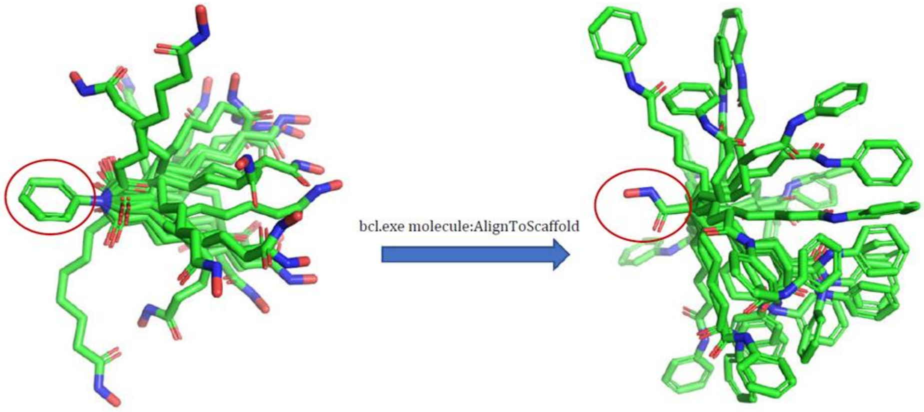

Fig. 1. Conformations created with and without alignment of zinc-binding site

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Plastic Phase Transition Behaviors of Quinuclidinolium Salts of Various Counter-Anions

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Plastic Crystals are materials in which the molecules or ions occupy the exact center of mass as in regular crystal lattice but have freedom of rotation. They show typical disorder-order transitions that lead to realizing various sorts of functional materials. Especially organic ionic plastic crystals (OIPCS) have gained much attention over the past years thanks to their potential usage as solid-state electrolytes [1-2].

The aim of this work was threefold: (i) we were interested in investigating the counter-anion dependence of the plastic phase transitions in a series of R-(+)-(3)-hydroxyquinuclidinium salts [QH]X. By varying the size, shape, and charge of the anion, we expected to obtain different behaviors in terms of plastic phase transition and type; (ii) we wanted to explore the possibility of preparing crystalline solid solutions, studying how the composition of the resulting materials further affects the phase transition compared to the pure parent systems, and (iii) we intended to analyze the ionic conductivity behavior of these salts especially by comparing in their ordered and disordered phases.

To this end, we synthesize a series of [QH]X salts with various counter-anions, including the tetrahedral anions sulfate (SO_4^{2-}), tetraphenylborate (BPh_4^-), tetrafluoroborate (BF_4^-), octahedral hexafluorophosphate (PF_6^-), and methanesulfonate ($SO_3CH_3^-$) by the metathesis of [QH]Cl using metal salts of the corresponding anions. A combination of solid-state techniques, including variable temperature XRD, thermal analyses, multinuclear (^{11}B, ^{13}C, ^{15}N, ^{19}F, and ^{31}P) solid-state NMR spectroscopy, variable temperature wide-line ^{19}F T^1 relaxation measurements, micro-Raman spectroscopy, and electrochemical impedance spectroscopy (EIS) are used to elucidate crystal structures, phase transition behavior and ionic conductivity of the so-obtained materials. [3].

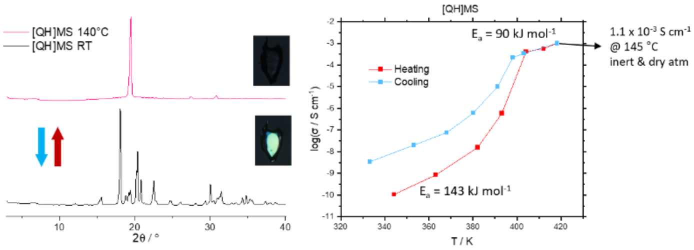

Fig. 1. *VT-PXRD and trend of the ionic conductivity of [QH]MS.*

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H_2 Production by Methane Oxy-Reforming: Effect of Catalyst Pretreatment on the Properties and Activity of Rh-$Ce_{0.5}Zr_{0.5}O_2$ Synthetized by Microemulsion

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In recent years, hydrogen has been thought to be a key green fuel and feedstock to meet the Paris agreement's climate goals [1],[2]. However, one of the main obstacles for the introduction of sustainable hydrogen production processes is represented by the cost of substituting steam reforming (SR) plants [3] which are energy intensive processes due to the intrinsic endothermicity of the reaction involved. In this work, we propose the substitution of SR with oxy-reforming, i.e., the coupling of SR with catalytic partial oxidation (CPO), the latter has indeed the role of exchanging in a better way the heat through the catalyst bed through its exothermicity.

With this aim, we prepared different Rh-based catalysts were synthesized by impregnation of the metal over a $Ce_{0.5}Zr_{0.5}O_2$ support obtained by inverse microemulsion synthesis. The supports were then calcined at 750 or 900°C and the catalysts were reduced at 750 or 500 °C. The systems have been then fully characterized by means of XRD, nitrogen physisorption, TPR and TEM (*Fig. 1.*) to verify the production of the desired phases and the active phase dimension and dispersion.

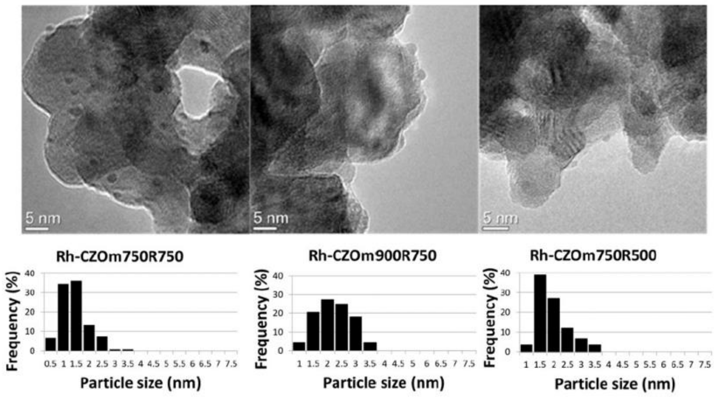
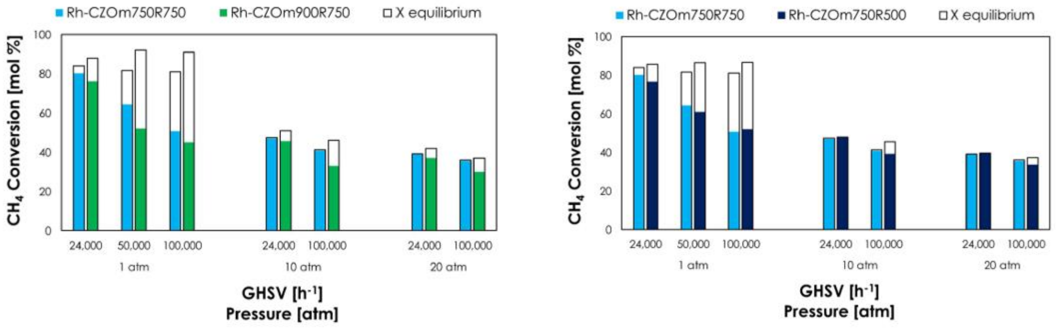


Fig. 1. TEM images and particle size distribution of the different Rh-CZO catalysts.

In particular, we observed that a lower calcination temperature allowed for an increase in the support surface area, and, hence, resulting in well-dispersed Rh species that provided a high reducibility for both the metal active phase and the Ce-based support.

Afterwards, the prepared catalysts were tested in the methane oxy-reforming reaction at 750°C, feeding sub-stoichiometric oxygen and steam together with methane.

We found that the catalyst calcined at 750°C and reduced at the same temperature provided not only high methane conversion (*Fig. 2.a and 2.b*), but also the best stability towards deactivation phenomena thanks to an enhanced metal-to-support interaction (MSI) that hindered carbon deposition over the catalyst, as evidenced by the characterization of the spent catalyst performed via XRD and Raman spectroscopy (*Fig. 3.*).



a. **b.**

Fig. 2. Experimental and equilibrium methane conversion at 750°C, S/C 0.7; O/C 0.2 and different pressures and GHSVs for (a) Rh-CZOm750R750 and Rh-CZOm900-R750; and (b) Rh-CZOm750R500 and Rh-CZOm750-R750

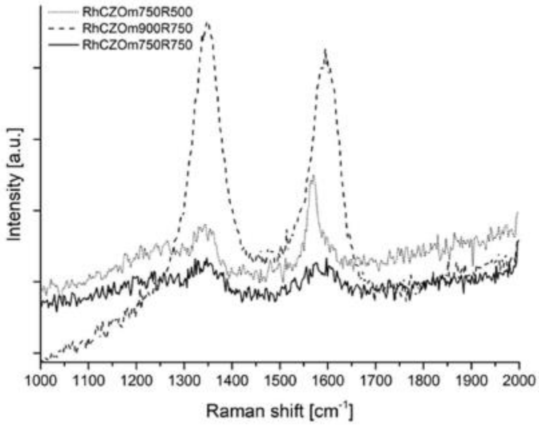


Fig. 3. Raman analysis of the spent catalysts.

Finally, considering the temperature profile along the reactor length, the catalyst calcined and reduced at 750°C was responsible for the smoothest thermal profile, presumably due to the anticipation of the SR reaction given by the improved reducibility of the catalytic system which increased methane dissociation and allowed the process to run with less sharp temperature gradients over the catalyst bed.

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Characterisation of recycled carbon fibres

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Carbon Fiber Reinforced Composites (CFRCs) are increasingly replacing conventional materials in application requiring high mechanical performance, due to their light weight and excellent mechanical properties.[1,2] As a result, the global demand for CFRCs grew from 2018 to 2019 from 128.500 to 141.500 tonnes/year and is expected to be around 197.000 tonnes/year in 2023.[3,4] European legislation has imposed more stringent controls on the management of CFRC waste.[5]
In this context, this works deals with the optimization of the pyro-gasification process of CFRP scraps, according to the scheme in **Figure 1**, in order to obtain recycled carbon fibers (rCFs) of good quality.

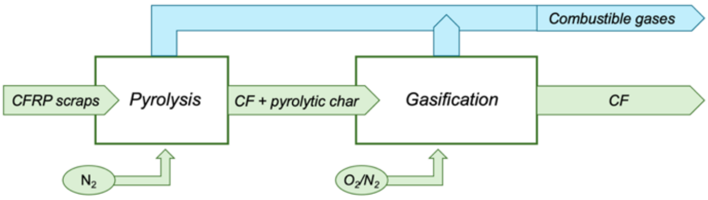

Figure 2. *Pyro-gasification process scheme*

The process was carried out on pristine and cured prepregs. Preliminary characterisation of the available materials was carried out through FT-IR spectroscopy (ATR mode) in order to investigate the nature of the polymer matrix of the prepregs, which turned out to be epoxy resin.
Thermogravimetric analysis (TGA) was carried out in order to investigate the degradation kinetics of the polymer matrix and the trend of weight loss as a function of time and temperature. In particular TGA allows to optimized the process conditions in terms of temperature (T>400°C) and residence times. The degradation process was carried out in a pilot plant involving first of all a pyrolysis step in an inert environment (N_2) and then a gasification step in an oxidizing athmpsphere (O_2/N_2).
Recovered CFs were analyzed by SEM in order to assess, helped by a visual inspection, the condition of the fibers after pyrolysis. In particular it was verified the absence of char and possible degradation on their surface (**Figure 2**).

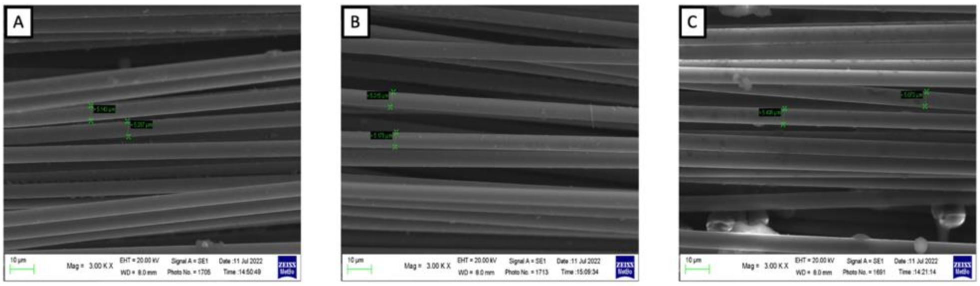

Figure 23. *SEM images of CFs recovered from: (A) prepreg, (B) cured material, and (C) virgin fibres. (3000X)*

Single-fibre tensile tests were performed with the aim of investigating the effect of pyrogasification treatment on the mechanical properties of recycled fibres compared to virgin fibres (**Figure 3**).

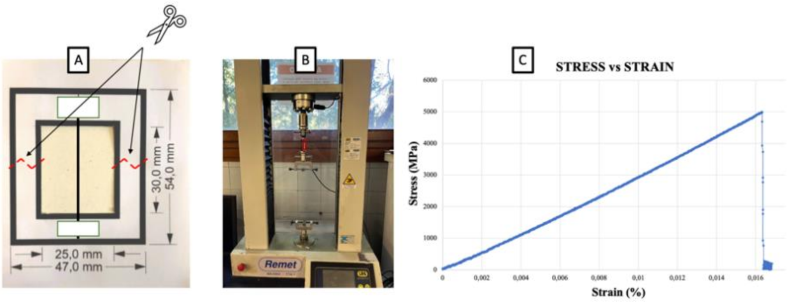

Figure 3. *Single-fibre tensile test: A) paper frame for fibre fixing; B) dynamometer; C) stress vs. strain graph of a rCF recovered by cured prepreg*

Finally, in order to verify both the quality of the fibre surface and the possible presence of small amounts of amorphous char, the rCFs and virgin ones were analyzed by Raman spectroscopy.

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Thermal pyrolysis of rubber materials

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Waste management is a global issue which impacts the sustainability of environmental and economic developments. In particular rubber waste in the forms of tyres, gloves, polymer composites or others are problematic materials for treatment as they are highly resistant to biodegradation [1]. These wastes which are conventionally disposed of in landfills and incinerators, are an eyesore and can serve as habitats for vermin and mosquitoes. In addition, their combustion releases pollutants such as polycyclic aromatic hydrocarbons (PAHs), benzene, styrene and phenols, which are harmful to human health [2]. Among rubber recycling methods, such as tire retreading, reclaimed rubber, rubber powder and pyolysis [3], the latter is preferred because of its environmental friendlier character and its potential of material and energy savings [4]. Pyrolysis technology thermally decomposes rubber or other organic wastes (e.g., biomass), in an inert atmosphere at temperatures of about 350–550°C or higher, to obtain liquid pyrolysis oil, solid char and pyrolytic gas as products. The resulting products can be further and selectively upgraded to fuels or value-added chemicals [1].

In this context, we considered of interest to evaluate the possibility of recycling rubber products of different formulations by pyrolysis process (Figure 1). A particular attention was given to the study deals with the pyrolysis of chlorine-containing rubbers. In order to optimize the process conditions, a preliminary study of the thermal degradation of each sample was performed by thermogravimetric analysis (TGA). Following these preliminary analyses, it was decided to conduct pyrolysis tests at 500°C.

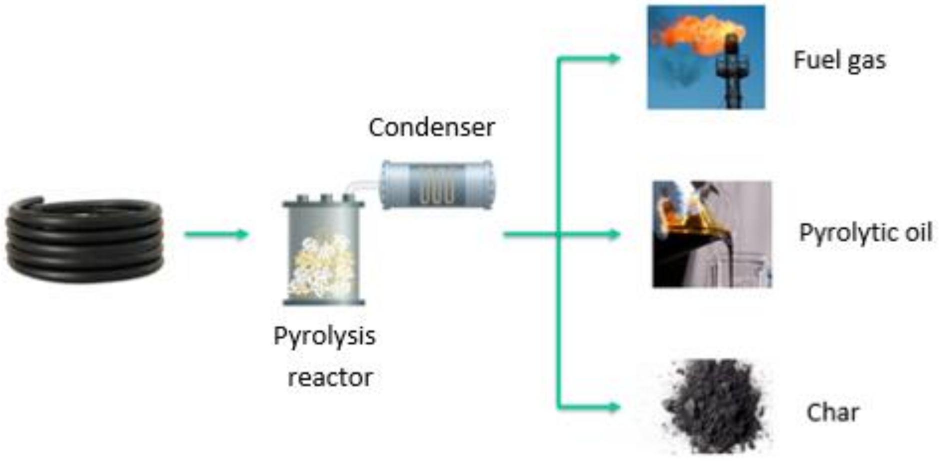

Fig. 1. Pyrolysis process of rubber products.

The solid residue (char) and oil obtained from the pyrolysis process were analyzed by X-ray fluorescence (XRF) to evaluate the distribution of heteroatoms (Chlorine, Sulfur, Silicon, Aluminum...) among the fractions.

This analysis highlighted that the oil obtained by chlorine-containing rubber shows a non-negligible content of Chlorine, which compromises its quality. As reported in literature, stepwise pyrolysis is an effective method to reduce the chlorine content in pyrolysis liquids [5], so the process was repeated performing an initial step of dehydrochlorination at 360°C, and then completing the degradation at 500°C.

The gases evolved during the process, sampled at different times, were analyzed qualitatively by GC-MS. The chromatograms obtained (Figure 2), in agreement with the literature [6], revealed the presence of hydrogen and light hydrocarbons (C1-C3). Such a composition gives the product a high calorific value which makes it suitable for applications as a fuel, for example, for the energy self-maintenance of the pyrolytic process itself. It can also be exploited as a source of H_2.

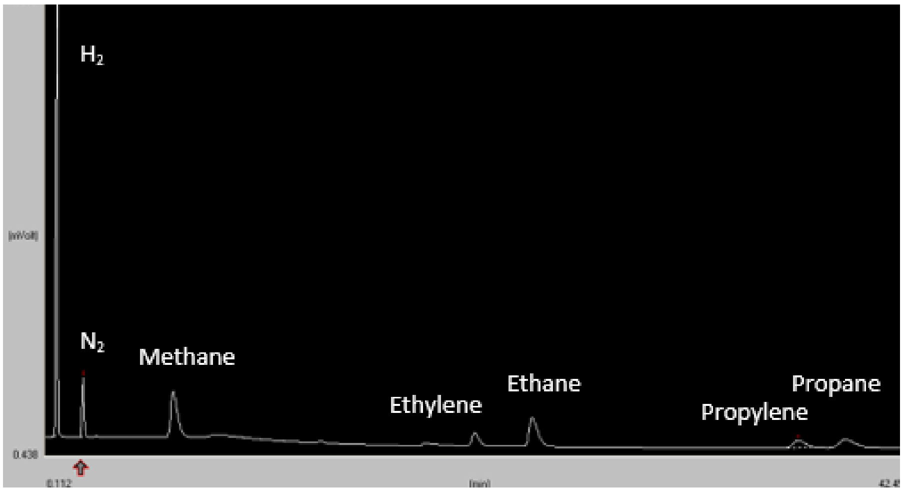

Fig. 2. GC-MS chromatogram of gas phase.

The obtained pyrolysis oils were analyzed by GC-MS. They are mixtures of C4-C20 hydrocarbons (and heavier fractions not identifiable by this analysis), whose ratio of aliphatic to aromatic compounds varies according to the nature of the polymer. SBR-based rubbers degrade by producing an oil rich in aromatic compounds such as styrene and alkylated benzenes; Natura Rubber-based objects degrade by producing more aliphatic compounds. If the rubber, on the other hand, contains Chlorine, as in the case of polychloroprene, chlorinated hydrocarbons are formed among the products.

Compounds containing Nitrogen and Sulfur are also present, probably resulting from the degradation of additives (e.g., vulcanization agents) and accelerator materials.

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Development of a biocomposite for additive manufacturing

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The growing environmental global regulations directed scientific research towards more sustainable materials, even in the field of composite materials for additive manufacturing. In this context, the present research aims at the development of thermoplastic composites for FDM application with a low environmental impact, focusing on the possibility to use wastes from different industrial processes as filler to produce composite filaments for FDM 3D printing. Poly(lactic) acid (PLA) is one of the most widely used materials obtained from renewable resources. The biofillers, instead, are that particular category of reinforcement that derive from biomass, usually from food wastes (third generation resources) since they are cheap and abundant, but can derive also from primary/secondary generation resources such as cotton, flax, hemp or wood [1]. Cellulose is the most abundant biopolymer in the biosphere,with a high crystallinity. For these reason, materials based on this are widely utilized as biofiller. The employment of natural materials as biofiller for PLA allows to develop a specific class of green composite materials, also known as biocomposite, bringing several advantages, such as full circularity of the resources, biodegradability, low specific gravity, high specific strength, and reduction of whole material cost. Implementing this new class of composite material to AM technique would allow to dramatically reduce the environmental impact of 3D printed products. [2] The purpose of this work is to study the possibility of using different amount of two agricultural wastes, i.e. wheat milling waste and rice husks, both rich in cellulose, as bio-fillers of PLA to produce biocomposites for FDM, hereafter define as PLA-F and PLA-L respectively. Mechanical characterization was carried out by DMA to evaluate the thermomechanical effect of the specific biofiller on conservative Modulus (E') and peak temperature of *tanδ* **-** the latter indicates the temperature at which viscous behaviour is at its maximum. The results of dynamic mechanical analysis (Fig.1) showed that the addition of the wheat waste and rice husk led to variations in the modulus values of the biocomposites, both in relation to the nature of biofiller and its amount. In particular, it was observed that in PLA-L the addition of rice husks leads to significantly higher modulus values (measured at 30°C) than pure PLA. On the other hand, in the case of PLA-F, E' in the 10% formulation is the same as that of pure PLA, whereas up to 20% wt biofiller leads to E' drop. This decrease in modulus can be caused by the formation of voids within the extrudate (intrabead voids) caused by the high biofiller content, but also by the increase in melt viscosity because of the addition of the highly porous wheat milling.

An increase in melt viscosity leads to a change in the cross-sectional area of the deposited layer, which assumes a more circular shape, in contrast to a lower viscosity extrudate, which has an oval

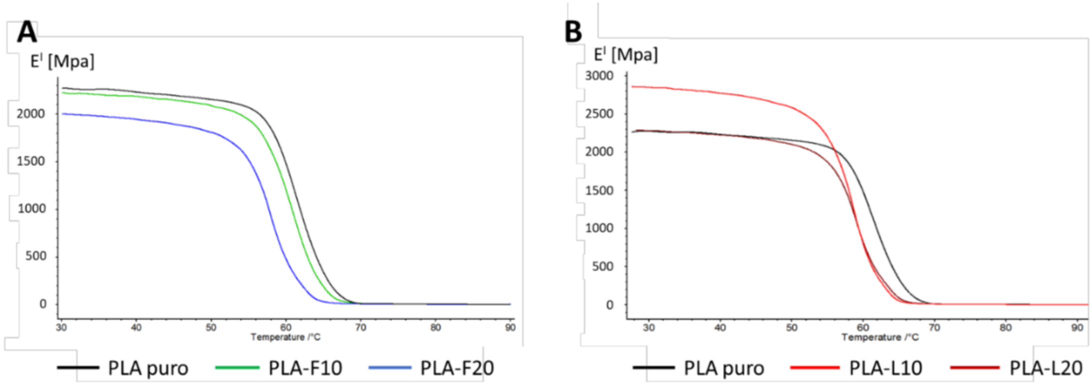

Fig.1. DMA plots of PLA-F (A) and PLA-L (B) biocomposites. The curves show: Pure PLA (black curve), PLA-F10 (green curve), PLA-F20 (blue curve), PLA-L10 (red curve) and PLA-L20 (brown curve).

cross-sectional area. The extrudates with a circular cross-section lead, in turn, to an increased formation of voids between the extruded material (interbead voids), which similarly to intrabead voids promote crack formation and propagation and lead to a decrease in mechanical properties. Finally, we proceeded to determine the peak temperature of tanδ, al known as 'damping factor', which represents the ratio between the dissipative modulus E'' and the conservative modulus E', a parameter that takes on different values depending on the type of biofiller. In the case of PLA-F, the tanδ value decreases in relation to the amount of biofiller from 68°C for PLA-F10 to 65°C for PLA-F20, and this decrease can also be caused by the low adhesion between filler and matrix. on the other hand, in the case of PLA-L, it can be observed that in both the L10 and L20 formulations, the tanδ value corresponds to 66°C, a decrease of approximately 3°C compared to pure PLA. The decrease in tanδ measured in biocomposites with rice husk could be caused not only by the low adhesion between the two phases but also by the different chemical nature and smaller grain size of this biofiller.

The results show that the biocomposites produced exhibit slightly lower mechanical properties than pure PLA, due to the non-optimal interaction between the matrix and the biofillers. In order to increase the properties of the materials produced, alternative strategies need to be evaluated, including the possibility of subjecting the biofillers to surface treatments, or the use of compatibilizers.

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Eosin Y intercalated Layered Double Hydroxides as photoactive material for solar energy conversion in Dye Sensitized Solar Cell (DSSC)

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Dye-Sensitized Solar Cells (DSSCs) are photoelectrochemical cells able to convert solar energy into electricity. They are composed by a photoanode, usually a thin nanocrystalline semiconductor film of TiO_2, supported on a transparent conductive oxide (TCO) layer, and a counter-electrode (Pt). An electrolytic solution containing a redox mediator (I^-/I_3^-) keeps in contact the two electrodes providing ionic conductivity to the system. A photosensitive pigment (dye) is adsorbed onto the surface of the semiconductor, with the aim of absorbing light to produce free charge carriers. The system is closed by an external electrical circuit.

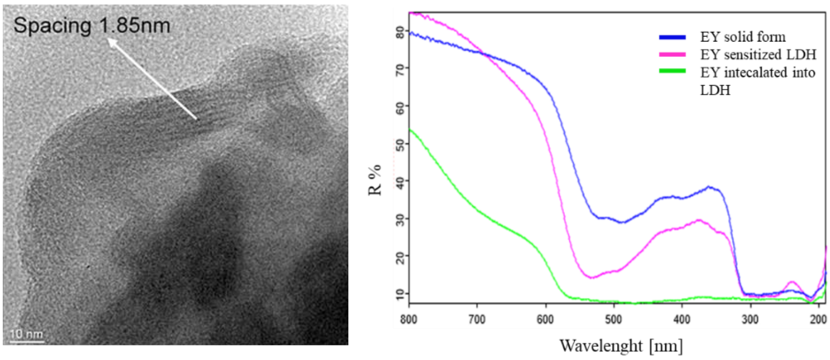

Figure 4. TEM image of EY intercalated into ZnAl LDH (left). Solid UV-Vis-NIR DRS analysis of pure EY, ZnAl LDH sensitized (LDH-S) and intercalated (LDH-I) with EY (right).

Electron transfer processes at dye/semiconductor interface, including electrons migration into semiconductor structure and easy diffusion of electrolytes molecule toward oxidised dye, have a key role for a high efficiency [1]. However, the sensitization approach suffers from the limited support surface area available for dye loading, dye deactivation, detouchment and photodegradation. These issues may be partially overcome by employing Layered Double Hydroxides as photoanode material.

Indeed, in this work we aim to exploit a unique characteristic of layered double hydroxide, namely the presence of an interlayer, to host and protect Eosin Y dye (EY).

LDH are anionic clays made of layered hydroxides sheets positively charged due to the partial substitution of divalent cation with a trivalent one, in which the charge neutrality is provided by anions located in the interlayer domain.

Here a hybrid organic-inorganic material based on LDH was obtained by coprecipitation under inert atmosphere of a Zn^{2+} and Al^{3+} solution into a EY aqueous solution, keeping pH 9 by addition of NaOH.

sample	Jsc (mA cm^{-2})	Voc (mV)	FF (%)	PCE (%)	IPCE [a] (%)
LDH-S	0.08	532	46	0.019	0.11
LDH-I	0.11	568	30	0.019	0.21

[a] calculated at 534 nm.

Table 1 - photovoltaic parameters and efficiencies of tested DSSCs.

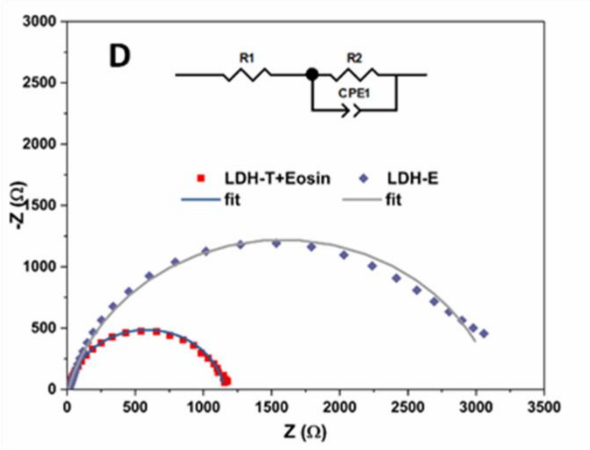

Figure 2 - Nyquist plots acquired in the dark and equivalent circuit used to fit the experimental points.

The dye intercalation was proved both by the shift of XRD diffractogram peaks (00l) toward lower angles, indicating larger *d* spacing, and by TEM images which reported a layered structures with interplanar distances compatible with EY intercalation. Interestingly, UV-Vis analysis displayed a higher absorption of light by the intercalated material (LDH-I) compared to the LDH sensitized (LDH-S) or to the pure EY, which was attributed to a synergic effect of the hybrid material and an higher amount of dye loaded onto the support by thanks to interlayer space exploitation. Current-Voltage curves were performed to evaluate the photovoltaic perfomances of the produced devices (Table 1). Both current density and open circuit voltage (Jsc and Voc) parameters were found to increase for LDH-I respect to LDH-S. Higher Jsc was assigned to the enhanced light harvesting ability of LDH-I while higher Voc value was ascribed to low recombination rate between photoanode and electrolyte. To further confirm this hypothesis EIS analyses in the dark were done on the same devices (Figure 2). The Nyquist plots showed for each DSSC a single semicircle at high and medium frequency due to the high impedance of the devices tested. The main components were related to the photoanode and the photoanode/electrolyte interfaces. In the equivalent circuit, R1 described the electrical resistance of substrate and film while R2 and CPE1 described the charge-transfer resistance and charge accumulation at the photoanode/electrolyte interface. R2 values of 1148 Ω, and 3139 Ω were obtained for LDH-S and LDH-I respectively, suggesting for the latter a higher resistance, thus a lower rate, for charge recombination between electrode/electrolyte. However, low overall photovoltaic efficiencies (PCE%) were shown by the tested devices. Indeed PCE is affected by Fill Factor (FF), that are in turn related to internal electrical resistance. This seemed to be high for the constructed devices, probably as a result of poor film adhesion and/or poor conductivity of the photoanodic material [2]. For this reason further improvements of intercalated material morphology and chemical composition have been attempted and investgated to overcame the limitations while exploiting the advantages provided by dye intercalation rather that surface sensitization.

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Influence of small molecules at CMKLR1 and GPR1 Receptors

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Chemerin is an immunomodulatory factor which plays a major role in several inflammatory process. It activates GPCR receptors and leads into downstream signaling which can undergo different pathways, including Ca^{2+} mobilization and arrestin recruitment (*Figure 1*). [1] This activation can be modulated by using small molecules which culminates in a reduced stimulation of such pathways. At the present work, the negative modulation of GPR1 and CMKLR1 receptors was tested through BRET and Ca^{2+} assay, in order to assess the negative modulation of small test molecules. [2] [3] The results obtained for the first receptor can be used as preliminary data to improve the assay set-up and achieve more relevant results. For the CMKLR1 receptor experiments, the negative modulation of the compounds at CMKLR1 could be determined in terms of inhibitory and effective concentration, and a superficial structure-activity relationship could be evaluated.

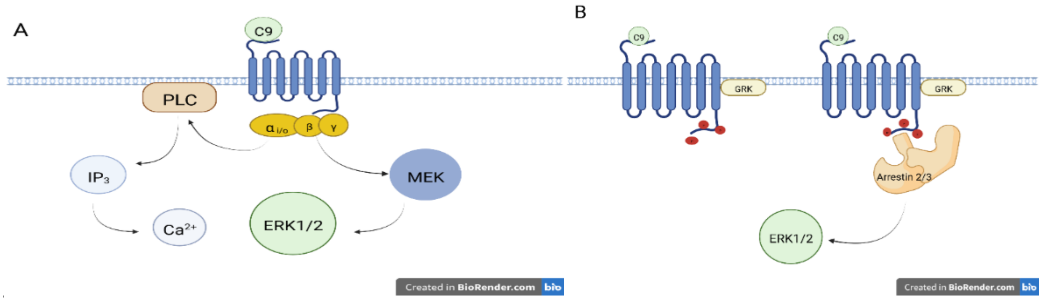

Fig. 5. Activation pathway of CMKLR1 and GPR1 receptors. A – Activation of CMKLR1. Dissociation of the α from the βγ subunits leads to phosphorylation of the mitogen-activated protein kinases and further phosphorylation of the ERK1/2, which can activate transcription factors. As well as that, activation of PLC leads into the decomposition of membrane lipids into Inositol Phosphate 3 (IP3), which binds into the endoplasmatic reticulum of the cell promoting calcium release. CMKLR1 can also undergo downstream signaling trough arrestin-3 recruitment, as described for GPR1 in Figure B. B – Activation of GPR1. The dissociation of G protein's subunits promotes the activation of GRK's, which culminates into Arrestin 2 or 3 recruitment by receptor's phosphorylation. Arrestin can lead to downstream signaling by activating ERK1/2.

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