SMARTER 8

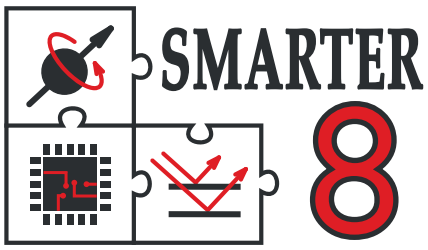
BOOK OF ABSTRACTS

September 22-25, 2024
Univ. Aveiro, Portugal

universidade de aveiro

SOCIEDADE PORTUGUESA DE QUÍMICA

CICECO



WELCOME

The SMARTER meeting brings together scientists in the areas of computation, diffraction, magnetic resonance and other spectroscopic techniques to promote and develop SMARTER approaches to optimally combine various techniques for structure elucidation of complex inorganic, organic and biological materials.

In 2024, SMARTER returns to Aveiro, between 22-25 September, continuing the tradition to encourage cross-fertilization between different fields, with invited speakers chosen to reflect recent experimental and computational advances for structural characterization as well as the diversity of approaches targeted, for example, to obtain crystal structures from powdered samples or understanding disordered systems.

The program consists of invited plenary and keynote lectures, oral and flash presentations.

Hope you enjoy SMARTER and being part of this collaborative effort to push the boundaries of materials science!

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INFORMATION

WELCOME RECEPTION

The welcome reception will occur at **Latina Pastry Shop and Winery,** at R. Dr. Alberto Souto 24-A, 3800-148 Aveiro. Registration can be completed during the welcome reception or on September 23rd or 24th in the atrium in front of the presentation auditorium.

PRESENTATIONS

Presentations will be held in the **José Grácio Auditorium**, located in the Mechanical Engineering Department, Building 22. The parallel flash sessions will take place in the same auditorium and in Room 22.3.6.

22 - Mechanical Eng. Depart
43 - NMR building
R - Rectory

INTERNET ACCESS

Network: eduroam

Username: smarterpanacea@visit.uaveiro.eu

Password: #Aveiro.2024#

LUNCHES

Lunches will be at the **Crasto Canteen** of the University.

22 - Mechanical Eng. Depart
43 - NMR building
R - Rectory
C - Crasto Canteen

DINNER

Conference Dinner: The conference dinner will take place at **Quinta do Éden**, located at Canto de Calvão 327, EN 109, 3840--061 (https://quintadoeden.com). A bus will transport participants from the Rectory to Quinta do Éden at 6:45 PM, with the return trip to the Rectory scheduled for 11:30 PM.

GETTING AROUND AVEIRO

Aveiro, known as the "Venice of Portugal," is famous for its canals, colorful boats, and Art Nouveau architecture.

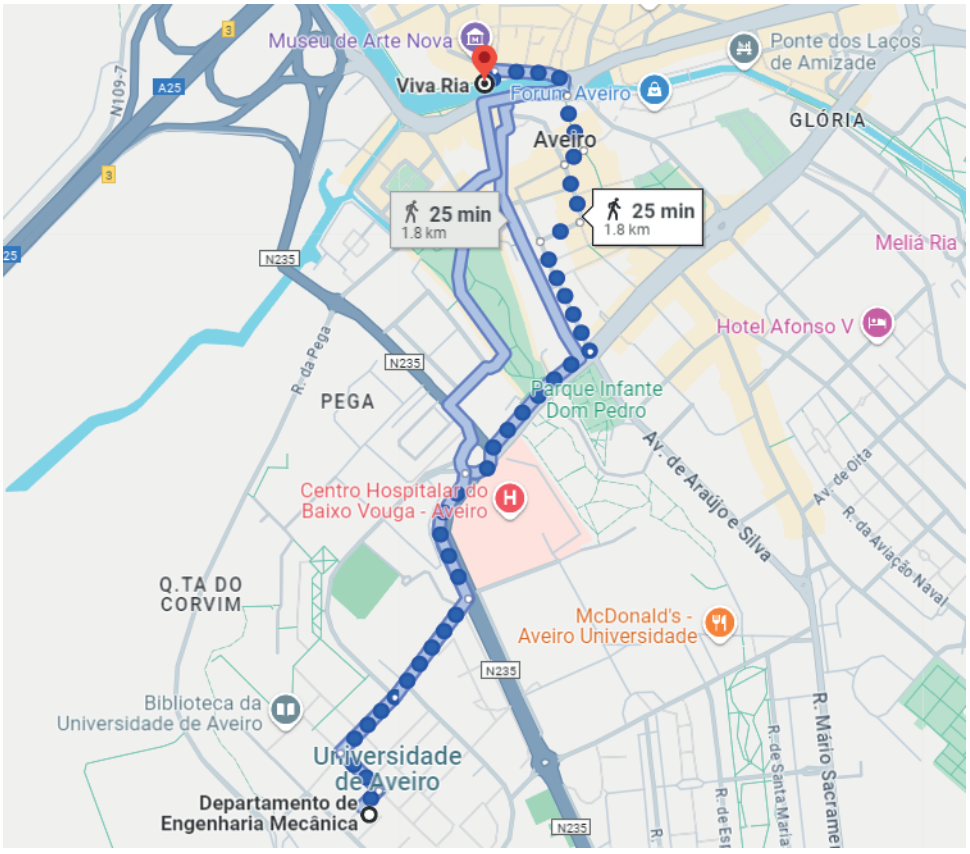
Walking: The compact city center makes it easy to explore on foot. Key attractions like the canals, moliceiro boats, and historic district are within walking distance, offering scenic views and cozy cafes.

Bicycles: Aveiro is also called the "City of Bicycles" due to its flat terrain and cycling culture. "BUGA" bikes are available, making it easy to explore the city and its natural reserves. https://buga.cm-aveiro.pt

Public Transport: The efficient bus system connects Aveiro with nearby beaches and the University of Aveiro. Single tickets and day passes are available. Aveiro's train station connects to Porto and Lisbon. It also features beautiful azulejo tiles, making it a point of interest itself.

MOLICEIRO RIDE

The **Moliceiro boat ride** will take place on September 23rd at 6:30 PM, departing from the **Viva Ria pier** at Cais: Jardim do Rossio, 3800--273 Aveiro.



PROGRAM

Sunday, September 22, 2024

18h30 - 20h30	Registration and Welcome Reception

Monday, September 23, 2024

08h30 - 09h00	Registration
09h00 - 09h30	Welcome Session
Session 1 Chair: João Rocha	
09h30 - 10h25	**PL1 - Alessandro Curioni** The future of computing and its impact on science: the era of accelerated discovery
10h25 - 10h55	Coffee Break
10h55 - 11h20	**OC 1 - Jonathan Yates**
11h20 - 11h45	**OC 2 - Philip Grandinetti**
11h45 - 12h25	**KN 1 - Carlos Bornes**
12h25 - 14h00	Lunch
Session 2 Chair: Giulia Mollica	
14h00 - 14h25	**OC 3 - Karsten Seidel**
14h25 - 14h50	**OC 4 - Jürgen Senker**
14h50 - 15h15	**OC 5 - Joana S. Figueiredo**
15h15 - 15h40	**OC 6 - Dmitry Chernyshov**

15h40 - 16h10	Coffee Break	
	Session 3 Chair: Mariana Sardo (Room 22.3.6)	Session 4 Chair: Ute Kolb (Auditorium)
16h10 - 17h30	**FC:** 1- T. Morais 2- A. Gaddam 3- P. Ouro 4- M. Shamzhy 5- A. Morena 6- R. Siegel 8- S. Brown 9- S. Varghese	**FC:** 10- D. Morineau 11- T. M Nguyen 12- D. Vandenabeele 13- V. Diez-Gómez 14- M. Bettermann 15- P. Länger 16- S. Radhakrishnan 17- I. Sobrados 18- T. Fischer
18h30 - 19h30	Moliceiro Ride	

Tuesday, September 24, 2024

Session 5 Chair: Luís Mafra	
09h00 - 10h00	**PL 2 - Bradley Chmelka** Correlated distributions of Pt guest species, exchangeable cations, and framework sites in Pt-zeolite catalysts
10h00 - 10h25	**OC 7 - Manjunatha Reddy**
10h25 - 10h55	Coffee Break
10h55 - 11h20	**OC 8 - Pavel Zelenovskii**
11h20 - 11h45	**OC 9 - Pooja Singh**
11h45 - 12h25	**KN 2 - Michal Leskes**
12h25 - 14h00	Lunch

14h00 - 14h25	**OC 10 - Yaroslav Khimyak**	
14h25 - 14h50	**OC 11 - Alysson Morais**	
14h50 - 15h15	**OC 12 - Rishit Yadav**	
15h15 - 15h40	**OC 13 - Giulia Mollica**	
15h40 - 16h10	Coffee Break	
16h10 - 16h50	**KN 3 - Diego Galvez Aranda**	
	Session 7 Chair: S. Radhakrishnan (Auditorium)	Session 8 Chair: P. Zelenovskii (Room 22.3.6)
16h50 - 18h00	**FC:** 19- D. Pereira 20- M. Soares 21- S. Vanlommel 22- Y. Kolyagin 23- H. Grüninger 24- S. Pappler 25- T. Insinna 7- E. Breynaert	**FC:** 26- T. Speelman 27- D. Marinheiro 28- J. Guest 29- M. Gabrijelčič 30- M. Švegovec 31- I. Shendorovich 32- A. Peach 33- F. Barzoki

Wednesday, September 25, 2024

Session 9 Chair: Yaroslav Khimyak	
09h00 - 10h00	**PL 3 - Ute Kolb** Nano crystal structure solution using three dimensional electron diffraction 3DED
10h00 - 10h25	**OC 14 - Janez Volavšek**

10h25 - 10h55	Coffee Break
10h55 - 11h20	**OC 15 - Daniel Dawson**
11h20 - 11h45	**OC 16 - Tiago Mendes Ferreira**
11h45 - 12h25	**KN 4 - Zhehao Huang**
12h25 - 14h00	Lunch
19h00 - 23h00	Conference Dinner

PL - Plenary, OC - Oral Communication, KN - Keynote, FC - Flash Communication

SCIENTIFIC PROGRAM

ALESSANDRO CURIONI

IBM Research, Zurich

Research interests: Vice President of IBM Europe and Africa and Director of the IBM Research Lab in Zurich, Switzerland. Dr. Curioni is an internationally recognized leader in the area of high-performance computing and computational science, where his innovative thinking and seminal contributions have helped solve some of the most complex scientific and technological problems in healthcare, aerospace, consumer goods and electronics. He was a member of the winning team recognized with the prestigious Gordon Bell Prize in 2013 and 2015. His research interests now include AI, Big Data and novel compute paradigms, such as neuromorphic and quantum computing.

BRADLEY CHMELKA

Chemical Engineering at UC Santa Barbara, USA

Research interests: correlation of macroscopic material properties and function with molecular structure and dynamics, particularly in heterogeneous macromolecular solids. Development and application of NMR methods for characterizing structure, dynamics, adsorption, transport, and reaction properties of new solid-state materials.

UTE KOLB

Johannes Gutenberg University Mainz, Germany

Research interests: structural characterization of nano crystalline materials. As a major tool we use transmission electron microscopy mainly collecting electron diffraction data sampling the three dimensional diffraction space. For this purpose we developed in 2007 the method automated diffraction tomography (ADT). It is applicable to a wide range of TEMs with different equipment and origin. Here we provide a short history and basic description of the method, a series of application cases together with hints how to access special crystallographic questions as well as a description of the data processing programs ADT3D and eADT.

DIEGO GALVEZ ARANDA

Université de Picardie Jules Verne, France

Research interests: Development of advanced deep learning models to simulate the operation principles of electrochemical energy materials, interfaces, components and full devices (batteries, fuel cells, electrolyzers...) as well as their manufacturing. Such multiscale models decribe mechanisms along different spatio-temporal scales. Their goal is to provide interpretation of experimental data, to optimize electrochemical energy devices and to provide advanced design guidelines.

CARLOS BORNES

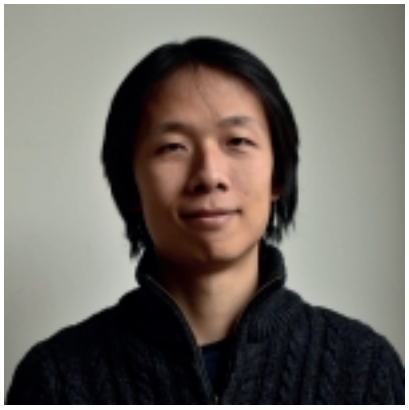
Faculty of Science, Charles University, Prague

Research interests: use of ab initio methods and neural network potentials to model the structure, reactivity, and dynamics of zeolites under operando conditions, and explore their impact on NMR spectroscopy.

MICHAL LESKES

Weizmann Institute of Science, Israel

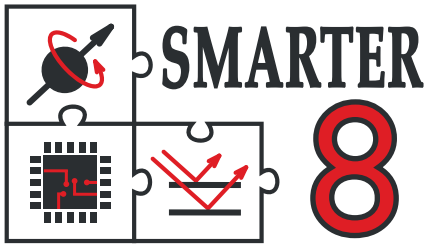
Research interests: materials for energy storage and conversion and in the effect of interfacial chemistry on the functionality of electrode and electrolyte materials, using a wide range of magnetic resonance techniques: solid-state NMR, EPR and DNP. In addition we employ common materials science characterization tools, including electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy.



ZHEHAO HUANG

Stockholm University, Sweden

Research interests: Three-dimensional electron diffraction (3DED) applied in the structural elucidation of nanoporous materials, advancing knowledge on structure-property relationships. The group is actively developing new 3DED techniques to reveal more details of functional materials, in particular metal-organic frameworks (MOFs). An important advantage of MOFs is the possibility to easily and systematically design and alter the structure and functionality at a molecular level. We are exploring the versatile structures of MOFs, as well as the closely associated properties, in view of applications in heterogeneous catalysis.



PLENARY

The future of computing and its impact on science: the era of accelerated discovery.

Alessandro Curioni

IBM Research, Säumerstrasse 4, 8803 Rüschlikon, Switzerland
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The future of computing holds immense potential for revolutionizing scientific discovery. This transformation is driven by two significant exponential technologies and their synergistic interaction: Artificial Intelligence (AI) and Quantum Computing.

As the world faces increasingly complex challenges, such as climate change, untreatable diseases, toxic substances in food and water, and plastic waste, traditional scientific methods prove insufficient. However, the recent shift in AI towards self-supervised learning on vast datasets has unlocked new possibilities. Foundation models, adaptable with minimal additional learning, can now address problems in material science, healthcare, and geospatial science. IBM, at the forefront of this revolution, recognizes the importance of responsible AI and collaborates with global partners from industry and academia to promote safe and trustworthy AI. This open innovation approach ensures that AI's impact on society remains positive and beneficial.

Furthermore, integrating quantum computing and AI can yield even more significant enhancements. For the first time in history, the way we compute has branched, providing unparalleled performance in various applications, including simulating nature, structuring data, and offering non-exponential speed-ups. In summary, the future of computing promises to significantly impact scientific discovery, addressing pressing global challenges and unlocking new possibilities for sustainable development. By embracing AI, quantum computing, and responsible innovation, we can harness the power of these technologies to create a better future for all.

Correlated distributions of Pt guest species, exchangeable cations, and framework sites in Pt-zeolite catalysts

Bradley F. Chmelka[1,*], Tsatsral Battsengel[1], Anna Pischer[1]

[1] *Dept. of Chemical Engineering, University of California, Santa Barbara, California 93106 U.S.A.*
** E-mail: bradc@ucsb.edu*

Understanding the atomic-scale compositions and structures of nanoporous Pt-zeolite catalysts is crucial to the development of strategies to improve and prolong activity, control metal dispersion, and reduce the amount of precious metal required. Detailed understanding of semicrystalline Pt-zeolite catalysts has been limited, however, by the non-stoichiometric compositions, distributions of the types and locations of Pt species and exchangeable cations, and their diverse interactions with different framework sites. Solid-state NMR, in combination with X-ray diffraction (XRD), high-resolution transmission electron microscopy (TEM), overcome many these challenges and yield detailed insights on the locations and interactions of Pt species and exchangeable cations, as functions of treatment conditions. $Pt(NH_3)_4^{2+}$, Pt^{2+}, Na^+ and H^+ cations compete to charge-balance different anionic framework sites, thereby influencing their mutual distributions. In particular, the influences of oxidative processes on the correlated locations of Pt and exchangeable cations in Pt-Na^+,H^+Y zeolite (Figure 1A) are revealed by 2D ^{27}Al–^{29}Si (Figure 1B), ^{23}Na–^{29}Si, and ^{29}Si-^1H NMR correlation spectra, which are sensitive to the interactions of Pt and Na^+ and H^+ ions with zeolite framework moieties. Distinct Na^+ cation sites are sensitively monitored by solid-state 1D ^{23}Na NMR spectra acquired at very high magnetic field, 35.2 T. Together with XRD and TEM results, the analyses enable the resolution, identification and quantification of different framework moieties, exchangeable cations, and Pt guest species at different sites within the nanoporous Pt-zeolite materials and the influences of treatment conditions on their respective distributions. In particular, the analyses show that the locations of Pt species in different zeolite cages depend strongly on calcination temperature over the range 200–600 °C, which influences the subsequent types and locations of Pt species within the zeolite nanopores. The atomic-level understanding of the treatment-dependent compositions and structures of Pt-zeolite materials yields design criteria for the distributions of Pt species in zeolite nanopores and insights on resulting adsorption, reaction properties and stabilities. The experimental approach and complementary spectroscopy and scattering techniques are expected to be generally applicable to other zeolite-supported metal systems for use in determining the composition-structure-function relationships that are central to understanding and improving macroscopic properties of heterogeneous catalysts.

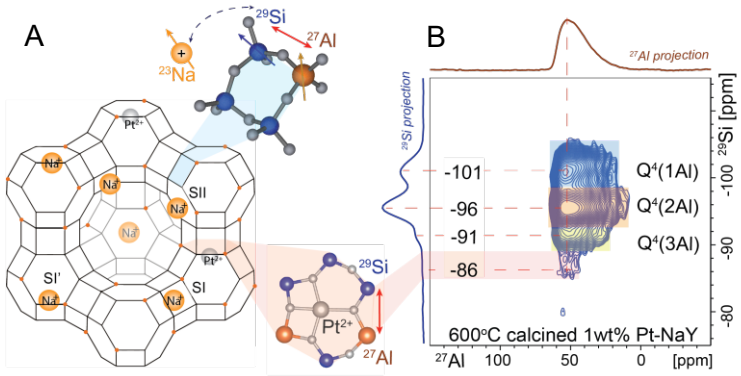

Figure 1 – Distributions of Pt species and Na^+ cations in zeolite nanopores revealed by solid-state NMR
(A) Schematic diagram of Pt-Na^+,H^+Y zeolite showing cation-exchange sites in supercage, sodalite cage, and hexagonal prism environments; (B) solid-state 2D $^{27}Al\{^{29}Si\}$ *J*-mediated NMR spectrum of 1 wt% Pt-Na^+,H^+Y calcined at 600 °C, which resolves signal intensity from distinct ^{29}Si sites that are directly bonded to different numbers of framework $^{27}Al^{IV}$ atoms and also manifests the influence Pt guest species.

Nano crystal structure solution using three dimensional electron diffraction 3DED

U. Kolb[1,*]

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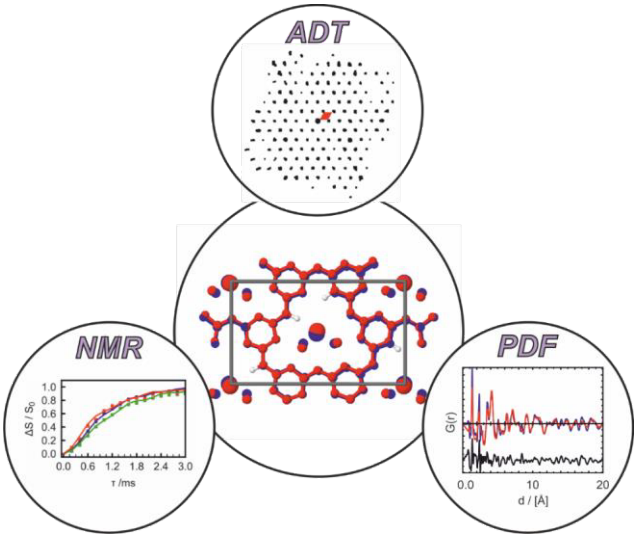
More than a decade after the development of automated diffraction tomography (ADT)[1,2] allowing for the direct solution of crystal structures based on electron diffraction data taken from nano crystals a variety of data collection protocols exist[3]. The approaches have in common that they tilt a non-oriented crystal in the electron beam but use for integration of the reciprocal space either a defined tilt step combined with electron beam precession or a continuous tilt movement with a high speed camera. As an overarching term three dimensional electron diffraction (3DED) was chosen. Nowadays, dedicated electron diffractometers are on the market, but many groups use as well the possibility to upgrade existing transmission electron microscopes. This talk will cover advances in data acquisition and processing[4] and will discuss important tricks and pitfalls for the method using a few showcases. It points out new approaches to enable a wide community to use 3DED as well as new tracking routines allowing to take datasets from nano crystals of around 20nm with a 25nm probe from highly agglomerated crystals or the investigation of vacuum sensitive hydrated samples with a high water content[5,6]. The 3DED method especially combined with XRPD and NMR is extremely powerful (Scheme 1). Several examples will be provided where this combination is of significant benefit[7]. For example the structural characterization of two blue-emitting OLED materials designed to eliminate charge carrier trapping[8] revealed two polymorphs each and a unexpected side product supporting a better understanding of materials properties.



Scheme 1: Combination of 3DED with XRPD and NMR,

References

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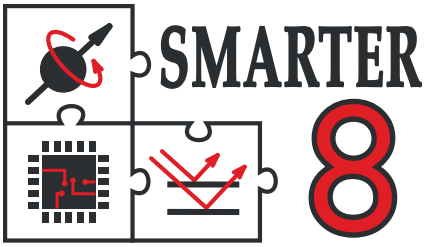

KEYNOTE

Operando simulation of zeolites using machine-learning methods

C. Bornes[1,*], A. Erlebach[1], C. J. Heard[1], L. Grajciar[1]

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Zeolites are nanoporous aluminosilicates that have been used in a wide range of industrial applications for decades, primarily as sorbents and catalysts. Despite their long-standing use, many challenges remain in achieving an atomistic understanding of zeolite structure, dynamics, and reactivity. Computer simulations and solid-state NMR are often combined to provide insights into these aspects. Computer simulations and solid-state NMR are often combined to gain insights into zeolite structure, dynamics and reactivity. However, this approach typically involves comparing experimental data obtained from samples with defects, varying degrees of hydration, and diverse chemical compositions at moderate temperatures with simplistic models. Computational studies often rely on static simulations at 0 K in high vacuum, or very short dynamic simulations, of models with few or no defects and a narrow range of chemical compositions. This disparity between the samples experimentally and computational models hinders the development of a true atomic-level understanding of zeolites.

We addressed this limitation by combining reactive neural network potentials (NNPs), that produce nanosecond-long trajectories, with regression methods that can time-average NMR chemical shifts. This enables modelling zeolites at *operando* conditions, replicating the conditions used in experimental setups. Our reactive NNPs offer a computational speedup of 10^3 compared to standard ab initio methods. This increase in efficiency enables us to explore a wider range of chemical compositions, including variations in Si/Al ratios, hydration levels, and defects. Additionally, it allows us to perform extended dynamical simulations, far surpassing the typical tens of picoseconds achieved by conventional methods, thereby approaching the timescales relevant to NMR measurements. We have successfully developed NNPs for siliceous and Al-containing H- and Na-exchanged zeolites, which accurately interpolate the potential energy surface, including reactive events and counterion migrations, and can be extended to other systems such as 2D and amorphous (alumino)silicates. Regression methods like LASSO and KRR have enabled us to bypass the time-consuming step of calculating NMR chemical shifts using ab initio methods, particularly when dealing with multiple structures over a nanosecond-long simulation. We have recently shown that these methods accurately predict the chemical shifts in zeolites for ^{23}Na, ^{27}Al, and ^{29}Si nuclei.[1–4]

Acknowledgements
The authors acknowledge the Czech Science Foundation (LG, AE, CJH: GAČR standard project 23-07616S). Charles University Centre of Advanced Materials (CUCAM) (OP VVV Excellent Research Teams, project number CZ.02.1.01/0.0/0.0/15_003/0000417) is acknowledged. This work was supported by the Ministry of Education, Youth and Sports of the Czech Republic through the eINFRA CZ (ID:90254) and ERC_CZ project LL 2104 (CJH). CB acknowledges funding from the European Union's Horizon 2020 research and innovation programme under grant agreement no. 101180584.

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Elucidating the Structure and Composition of Buried Interfaces with New Solid-State NMR Methods

Michal Leskes
Department of Molecular chemistry and Materials Science, Weizmann Institute of Science, Rehovot, Israel
E-mail: michal.leskes@weizmann.ac.il

Buried interfaces play a central role in the function of energy storage and conversion materials. Some examples include the catalytically active interfaces formed between different oxides or charge transfer processes across heterogenous interfaces formed in solar, fuel and battery cells. As such there is great interest in probing the chemical composition and structure of such interfaces. However, the limited quantity, inaccessibility, heterogeneity and disorder of buried interfaces limit our ability to characterize them by conventional diffraction and microscopy tools.
Solid state NMR spectroscopy is one of the best tools to determine the chemical composition of solids, yet the inherent low sensitivity of NMR prevents the detection of interfaces. In recent years, the development of Dynamic Nuclear Polarization (DNP), a process in which the high electron spin polarization is transferred to surrounding nuclear spins thereby increasing NMR sensitivity by orders of magnitude, has completely transformed the breadth of applications and systems that can be studied with solid state NMR.
In this talk I will survey recent developments in the field, focusing on the development and application of DNP from endogenous polarization sources such as paramagnetic metal ions. I will describe the basic principles of the approach and demonstrate how it can be applied to selectively probe buried interfaces with high sensitivity. I will show how we can gain unique chemical and structural information on nanometer thick interfacial layers and the application of the approach to obtain unprecedented atomic-scale insight into heterogenous native and artificially formed surface layers in battery materials.

Computational modelling and Machine Learning to assist battery manufacturing processes

Diego E. Galvez-Aranda[1,2], Alejandro A. Franco [1,2,3,4,*]

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[2] *Reseau sur le Stockage Electrochimique de l'Energie (RS2E) FR CNRS 3459, Hub de l'Energie 15 rue Baudelocque, Amiens Cedex 80039, France*
[3] *ALISTORE-European Research Institute FR CNRS 3104, Hub de l'Energie 15 rue Baudelocque, Amiens Cedex 80039, France*
[4] *Institut Universitaire de France 103 Boulevard Saint Michel, Paris 75005, France*
* *E-mail: alejandro.franco@u-picardie.fr*

We present here an innovative integration of computational modeling and machine learning (ML) techniques to assist battery manufacturing processes. This transformative approach aims at enhancing production efficiency, optimizing material usage, and improving the overall performance at the different stages of the battery manufacturing process. In this lecture, we describe the fundamentals and application examples of our approach, starting with our physics-based models able to predict how manufacturing parameters impact the properties of electrodes and cells. These physics-based models are supported on methods such as Coarse-Grained Molecular Dynamics (CGMD) and Discrete Element Method (DEM)We discuss their capabilities and limitations and our methods for their experimental calibration and validation.

Additionally, we also present the integration of ML algorithms with physics-based models, highlighting the advantages in the simultaneous employment of both techniques. We use ML to provide advanced solutions for forecasting, monitoring and optimization, to help on the design of better electrodes, maximizing and minimizing certain properties to enhance their performance.[1-2] For forecasting we use ML to explore different formulations based on datasets constituted by both experimental and/or simulation data.[3] For monitoring, when new materials want to be tested at the different manufacturing stages, we use a ML model trained on a physics simulation-based dataset, to predict the dynamics occurring during the compression of the electrode (in the so-called calendering stage) in a fraction of time compared to the original physics-based model.[4] We present our findings arising from a an innovative multidisciplinary approach that bridges materials science, engineering, computational science and artificial intelligence, paving the way for next-generation battery technologies capable of meeting the increasing demands of electric vehicles and renewable energy systems.

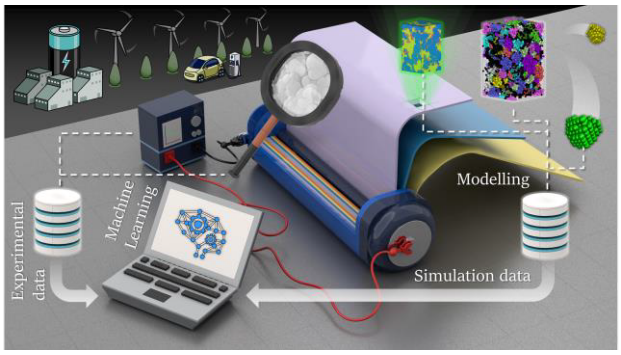

Figure 1: Schematic representation of the simultaneous use of Machine Learning techniques fed by experimental and simulation data applied to the battery manufacturing process.

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Structure elucidation of complex materials by three- dimensional electron diffraction

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Metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) are known for their versatile physicochemical properties, which offers immense opportunities in a wide range of applications. However, MOFs and COFs are often synthesized as nanocrystals, which are challenging for studies by single crystal X-ray diffraction methods. Moreover, their complex structures result in severe peak overlapping in powder X-ray diffraction patterns, which hinders their structure elucidation. Three-dimensional electron diffraction (3DED) has been developed to tackle these challenges. By taking advantage of the strong interaction between electrons and matter, 3DED allows single crystal structural analysis even when the crystal sizes are down to the range of nanometers.

In this talk, I will give an overview of the development of low-dose 3DED method for analyzing MOFs and COFs, where we overcome the challenges of electron beam damage to these compounds[1]. Using 3DED, I will give an example of studying structure-property relationship of PCN-226 as an electrocatalyst[2]. Furthermore, I will talk about the high-throughput advantage of 3DED on discovery of new MOF materials among phase mixtures[3], and discovery of unknown layer stacking behavior in a 2D COF4. Last but not least, I will present our recent development by using 3DED to probe molecular motions in MOF nanocrystals[5] and using 3DED to study host- guest interactions[6]. We believe that using 3DED as a powerful analytical tool for discovering new MOFs and COFs and revealing their unique properties at an atomic level would help to accelerate research in this community.

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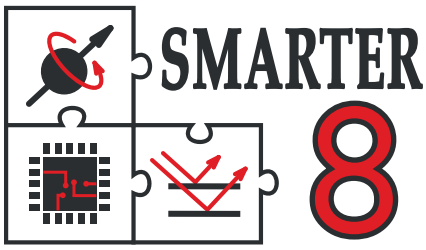

ORAL COMMUNICATION

A Computationally Efficient Approach to Model the Effects of Dynamics on NMR parameters in Solid Electrolytes

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Solid-state NMR is a sensitive probe of both atomic scale structure and dynamics. In many materials, first principles calculations of NMR parameters using a static crystal structure do a very good job of reproducing experimental measurements. However, in materials which feature ionic mobility (e.g. solid electrolytes) simulations based on static structures can spectacularly fail to reproduce experiment.
To address this issue we introduce a computationally efficient method to obtain time averaged NMR parameters. This uses machine-learned potentials to access long-time dynamics. The trajectory is analyzed such that time-converged NMR parameters are computed using a minimum number of DFT simulations. We distinguish between the effects of local vibrations which occur at short time-scales, and ion-hops which occur on longer time-scales. The final results are in excellent agreement with experiment.

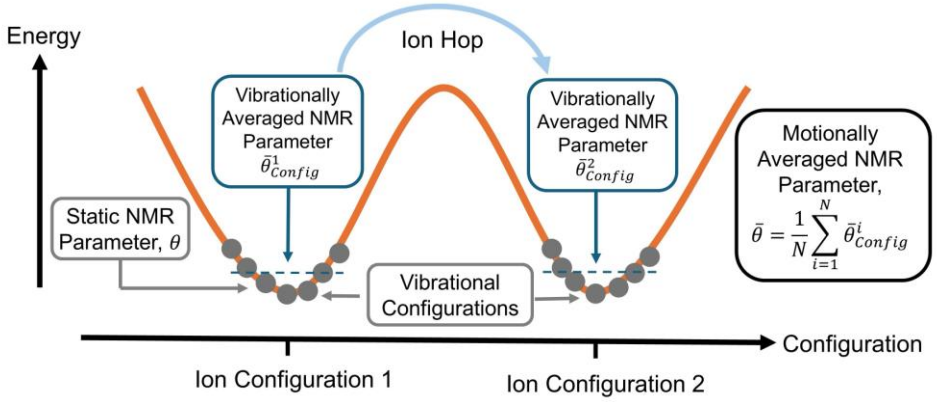

Figure 1:

Acknowledgements
We thank Collaborative Computational Project in NMR Crystallography (www.ccpnc.ac.uk) for support.

Refining siliceous zeolite framework structures with ^{29}Si 2D *J*-resolved NMR Spectroscopy

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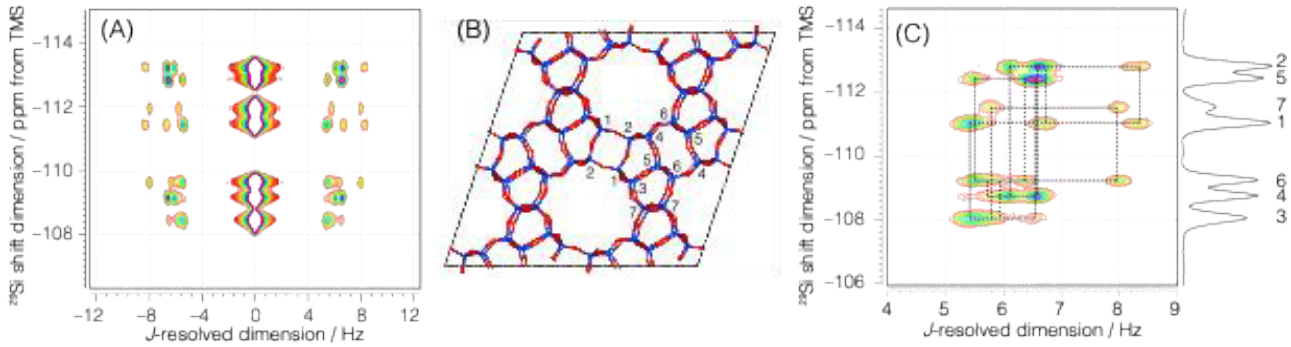
A modified shifted-echo Phase-Incremented Echo-Train Acquisition (SE-PIETA) pulse sequence is developed for the acquisition of natural abundance ^{29}Si 2D *J*-resolved spectra in crystalline silicates. The sequence is applied to the highly siliceous zeolites Sigma-2 and ZSM-12. The 2D *J*-resolved spectra are used to develop a silicate framework structure refinement strategy based on the known correlations of Si-29 chemical shifts and geminal $^2J_{Si\text{-}O\text{-}Si}$ couplings to local structure and Si-O, O-O, and Si-Si distance restraints.



(A) Experimental 2D *J*-resolved ^{29}Si NMR spectrum of siliceous zeolite ZSM-12 showing contributions from both coupled and uncoupled ^{29}Si resonances. Numbered isotropic chemical shift peaks are assigned to the corresponding numbered sites in the ZSM-12 framework structure shown in (B). (C) Region of the experimental 2D *J*-resolved ^{29}Si NMR spectrum of siliceous zeolite ZSM-12 showing positive *J* splittings of the coupled ^{29}Si resonances. Numbered isotropic chemical shift peaks are assigned to the corresponding numbered sites in the ZSM-12 framework structure shown in (B).

Acknowledgments
This material is based upon work supported by the Chemical Measurement and Imaging program in the National Science Foundation Division of Chemistry under Grant No CHE-2107636 (with partial co-funding from the Ceramics program in the Division of Materials Research).

Structure of a crystalline zinc-coordination complex with amorphous side phase

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The Great Famine, which occurred in Ireland during the mid-19th century, resulted in the devastating loss of nearly one million lives and compelled an equal number of people to emigrate. This tragic event was triggered by the uncontrollable outbreak of a plant disease known as late blight, which is caused by a fungus-like microorganism.
Nowadays, infections such as late blight in potatoes and powdery mildew in vines can be prevented by applying substances belonging to the class of ethylene bis(dithiocarbamates) (EBDTCs). Despite being available since the 1940s, the molecular structure of the metal complexes of EBDTCs was not described in very detail until the crystal structure of Zineb, a single-phase crystalline material, was published in 2020[1].
In this study[2], we present a comprehensive multi-method structural characterization of an EBDTC with zinc, which is the active ingredient of a highly effective and plant-compatible organic contact fungicide. We applied a combination of elemental analysis, thermogravimetry, ^{1}H and ^{13}C solution-state NMR spectroscopy, mass spectrometry with different modes of ionization, chemical reduction assay, IR- and Raman spectroscopy, scanning transmission electron microscopy including energy dispersive spectroscopy, micro electron diffraction, powder X-ray diffraction at lab and synchrotron sources, including total scattering with pair distribution function analysis, ^{1}H, ^{13}C, ^{15}N, and ^{67}Zn solid-state NMR spectroscopy, as well as Zn and S K-edge X-ray absorption spectroscopy.
Our findings reveal that this EBDTC with zinc comprises two distinct phases. The primary phase is a zinc-coordinating crystalline phase. The secondary phase is amorphous and does not coordinate zinc. We reveal the crystal structure of the primary phase and infer the primary structure of the secondary constituent. We wish to share our experience from this approach to provide learnings towards similar objectives.

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L. Piveteau and L. Emsley (EPFL) for 900 MHz spectrometer access. R. Hellmann (BASF SE) for sample management. J. Senker (U Bayreuth) for providing an implementation of the MULTI-CP NMR pulse sequence. S. Hirth and P. Mühlbeier for additional mass spectra using ToF-SIMS. O. Safonova and S. Phadke (SLS, PSI, Villigen, Switzerland) for additional Zn-EXAFS measurements (data not shown). European Synchrotron Radiation Facility (ESRF) for provision of synchrotron radiation facilities. Jakub Drnec for assistance and support in using beamline ID31. The ESRF measurement setup was developed with funding from the European Union's Horizon 2020 research and innovation program under the STREAMLINE project (grant agreement ID 870313).

Conflict of interest statement
BASF SE funded work to authors directly affiliated with it and co-funded work of the other authors. BASF is a producer of the product Polyram® WG.

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Understanding Guest-Host Materials for Gas Storage, Photocatalysis and Ion Conduction using the SMARTER Approach

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Porous materials offer potential for applications as diverse as gas storage and separation, catalysis, electronic and ionic transport, and sensor design. In particular, porous materials become relevant in the context of current efforts to turn to a sustainable economy. For example, they are investigated as separators in electrochemical energy storage and conversion devices and as heterogeneous photo- and photoelectro-catalysts that can improve the efficiency and atom economy of essential reactions like water splitting and carbon dioxide utilisation.

The spatial and chemical constraints of the structured hosts enforce a shape to the adsorbed fluid phases and impose interactions at the guest-host interfaces. If the dimension of the constraints reaches the nanometre scale, confinement effects on properties like mass and charge transport and the catalytic reactivity emerge. Recent results suggest that the complex interplay between the confinement-induced guest-host interactions and the mobility of the mass and charge carriers can lead to exceptional properties of the guest-host materials.

The lecture will provide an overview of our recent advancements in synthesizing and post-synthetic modification of porous polymers and metal-organic frameworks to understand and use these confinement effects.[1-4] We apply an integral approach to analyse structural details, local dynamics, long-range transport and catalytic activity simultaneously. For this, we combine techniques like powder X-ray diffraction, sorption measurements, solid-state NMR, diffuse reflectance, Mößbauer, and impedance spectroscopy, NMR diffusometry and quantum chemical calculations.

Acknowledgements
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SMARTER approach to 4-MPy adsorption onto zinc chalcogenide-based substrates

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Raman spectroscopy is a technique with great potential for molecular detection, but whose low sensitivity renders its use impractical in trace chemical analysis. Taking advantage of the surface-enhanced Raman scattering (SERS) effect, some materials can provide strong signal enhancement, hence making this spectroscopic technique useful in sensing applications. Although SERS has been mainly applied onto plasmonic metal substrates, most notably gold and silver, recent developments have shown that other types of materials can be explored as SERS active substrates, including semiconductor and 2D nanostructures of distinct morphologies and compositions.[1,2] Fully understanding non-plasmonic SERS can expand the application of this technique to materials that are cheaper and tailorable for a multitude of purposes.[2]
In this communication, we explore the properties of ZnO particles and their interaction with 4-mercaptopyridine (4-MPy) through first principle calculations and compare it with those of ZnS. The basis for these studies was our recent research on ZnS/GO, which was found to enhance the Raman signal of chemisorbed 4-MPy, compared to isolated ZnS or GO flakes. Via computational methods, we concluded that the observed synergistic effect was the result of the appearance of intragap energy levels upon adsorption of ZnS on GO, assisting charge-transfer mechanisms and resulting in signal enhancement.[3] Our findings show that ZnO behaves differently to ZnS powders, leading to Raman signal enhancement of chemisorbed 4-MPy both when isolated and supported on GO. The influence of diverse parameters in the morphological and electronic characteristics of the substrates is discussed, thereby gaining a better understanding on the application of zinc chalcogenide semiconductors as SERS substrates.

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Crystallography with synchrotron light - an old wine into new wineskins

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Bright synchrotron light offers many new options for scattering experiments, first of all thanks to the high intensity and ability to tune the energy of penetrating radiation. Here we focus on advantages and pitfalls of crystallographic measurements at modern source of synchrotron radiation, and discuss good and not-so-good practices of doing small molecule crystallography at synchrotrons. We also review some recently developed tools dealing with the large volumes of data produced at synchrotron experiments. Finally, we consider two phenomena frequently seen at synchrotrons, diffuse scattering and radiation damage, as well as corresponding methods of extracting useful information on the structural disorder.

High field NMR crystallography sheds light on efficiency-durability tendencies in organic solar cells

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In the past 5 years, organic solar cells have enabled high-performance (OSCs) achieving over 19% power conversion efficiency (PCE, compared to the theoretical limit of ~33%). In such devices, thin films of 100-200 nm consisting of phase separated small molecule acceptors, A (M_w = 1-2kDa) and donor polymers, D (M_w = 50-100kDa) are used as photoactive layers – also referred to as bulk-heterojunction (BHJ) morphology – which govern performance and durability.[1] Efforts have been expended to facilitate the structure-based understanding of key optoelectronic properties that contribute to high performance, however, little is known about the molecular origins of large variations in performance, spanning from 5% to 18% PCE. This is due, in part, to the compositional and structural heterogeneities associated with D and A molecules at different length scales.[1,2] We present the combined use of solid-state NMR, crystallography, and molecular modeling to elucidate the atomic-scale interactions in OSC thin films.[2] In so doing, we will present NMR crystallography which help explain polymorphic behaviour of acceptor molecules (Figure 1: Y6) in the BHJ blends that are not always followed/governed by the packing interactions viewed in their single crystals. Notably, 2D ^{13}C-^{19}F and ^{19}F-^{1}H correlation spectra acquired high fields (18.8-28.2T) enables the local structures of D and A molecules to be resolved and distinguished in thin films and powder forms. These findings indicate that the PM6:Y6 solar cells processed from different solvents self-assemble into different structures and morphologies, whereby the relative orientations of the sidechains and end groups of the Y6 molecules to their fused-ring cores play a crucial role in determining the resulting morphology and overall performance of the solar cells. The molecular-level understanding of the D:A BHJ morphology enabled by this approach will guide the engineering of next-generation D and A molecules for developing stable and efficient organic photovoltaics.[3,4]

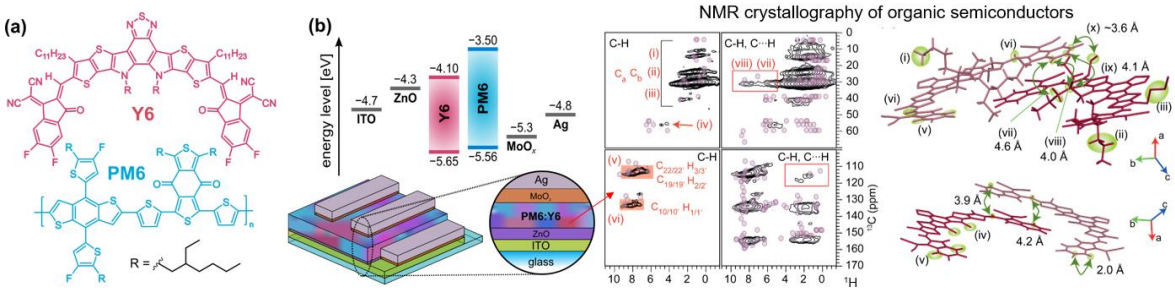

Figure 1: (a) Chemical structures of PM6 and Y6 molecules. **(b)** Energy levels of the OSC device, and 2D ^{1}H-^{13}C HETCOR spectra for **Y6** films processed with aliphatic (top) and aromatic (bottom) regions, acquired with 0.1 ms (left panels) and 4 ms (right panels) CP contact times, depicting the directly bonded C-H and through-space C···H interactions, respectively. The overlaid dots in the 2D spectra correspond to the GIPAW DFT calculated ^{1}H and ^{13}C chemical shifts (C…H <2.5 Å).

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^{2}H NMR study of water dynamics in dipeptide nanochannels

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Self-assembling peptide nanotubes can serve as effective channels for the small molecules or ions transportation[1]. Charged amine and carboxylic functional groups covering the internal surface of the nanochannels affect the organization of ions and molecules therein resulting in their intricate motion. In this work, we present a study of water motion through several dipeptide nanotubes with the pore size below 1 nm (Figure 1). We used a combination of single crystal X-ray diffraction, quadrupolar solid-state nuclear magnetic resonance (NMR) spectroscopy, and dynamic vapour sorption (DVS) measurements to analyze water diffusion inside the nanochannels.

The obtained results indicate several types of water molecules in the nanochannels differ in their dynamics and the diffusion character. In diphenylalanine (Phe-Phe) channels, two independent flows were revealed: a conventional axial flow located around the nanotubes axis and a helical flow located near the peptide shell[2]. These two flows are independent of each other and their diffusion coefficients differ by several orders of magnitude (1.5×10^{-10} m^2s^{-1} and 4×10^{-12} m^2s^{-1}, respectively). The molecular dynamics simulations have confirmed the trajectory of the helical flow being dictated by the screw-like distribution of the functional groups within the channel walls, while its flux is governed by external water vapour pressure.

The obtained results demonstrate a great potential for peptide nanotubes use for transportation of small molecules and ions, such as lithium, in energy storage devices and micro- and nanofluidic systems.

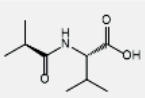
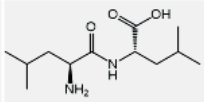
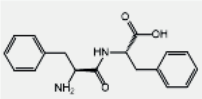
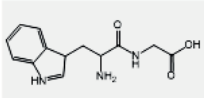
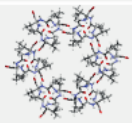
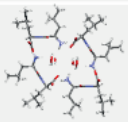
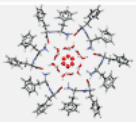
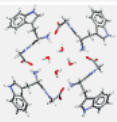
Peptide	Ala-Val	Leu-Leu	Phe-Phe	Trp-Gly
Structural formula				
Structure of the nanochannel				
Space group	$P6_1$	$P2_12_12_1$	$P6_1$	$P4_1$
Pore size	6 Å	5×7.5 Å	9 Å	6 Å

Figure 1: Structural characteristics of the peptide nanochannels studied in this work.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials (UIDB/50011/2020, UIDP/50011/2020, and LA/P/0006/2020), the project UniRCell (SAICTPAC/0032/2015, POCI-01-0145-FEEDER-016422), and the project "BioPiezoSensor" (2022.03781.PTDC) financed by national funds through the FCT/MEC (PIDDAC). NMR spectrometers are part of the National NMR Network (PTNMR) and are partially supported by the Infrastructure Project 022161 (cofinanced by FEDER through COMPETE 2020, POCI, PORL, and FCT through PIDDAC). This work has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (Grant Agreement 865974). The authors are also grateful for the financial support granted by Agenda and Resilience Plan (PRR) and by the Next Generation European Funds to University of Aveiro, through the Agenda for Business Innovation "NGS – Next Generation Storage" (Project n°2, application C05-i01.01/2022). The authors are grateful to ALPACA for the providing computing resources. P.Z. is grateful to the Royal Society of Chemistry for the RSC Research Fund grant (R23-8379659473).

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Probing DNP Driven Transitions in Methyl Rotors using 2-^{13}C Acetate Carbon NMR Spectra

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Dynamic Nuclear Polarization (DNP) has emerged as a powerful technique to enhance NMR signals, significantly improving the sensitivity and resolution of NMR spectroscopy. In present study, we focus on the simulation of the acetate carbon spectrum, specifically examining the influence of the methyl rotor on the lineshape under different DNP conditions. Using quantum mechanical simulations, we model the dipolar couplings and Zeeman interactions of the methyl group rotor.
Experimental observations reveal a noticeable distinction between positive and negative DNP enhancement spectra of 2-^{13}C labeled acetate [1,2]. Our simulations elucidate the significant differences in the NMR spectra, demonstrating how the population distribution of the methyl rotor states varies with the DNP condition. In the positive DNP-enhanced spectra, the A state of the methyl rotor is predominantly populated, while in the negative DNP-enhanced spectra, the E state shows higher population.This disparity in state populations can be attributed to the underlying tunneling splitting of the methyl rotor, which is more pronounced in molecules like acetate. Our findings corroborate previous studies that have reported similar phenomena in systems with significant tunneling splitting[2,3,4]. These results underscore the critical role of methyl rotor dynamics in interpreting DNP-enhanced NMR spectra and provide a deeper understanding of the molecular behavior under different polarization conditions.

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In-situ CLASSIC NMR spectroscopy providing a molecular-level understanding of assembly of multi-component pharmaceuticals

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Pharmaceutical cocrystals are multicomponent materials prone to exhibit polymorphism. The polymorphic outcome could be controlled using mechanochemical cocrystallisation techniques *via* the addition of solvents or polymers of different properties.[1,2] *In-situ* monitoring methods, such as synchrotron TRIS-PXRD, are used to gain knowledge of the mechanisms of such phase transitions. However, this methodology is limited in focussing exclusively on solid-state components of the reaction.

We have used CLASSIC (*Combined Liquid- And Solid-State In-Situ Crystallisation*) NMR[3] as a versatile *in-situ* monitoring technique to gain a molecular-level understanding of crystallisation pathways during liquid- and polymer-assisted mechanochemical cocrystallisation processes. As models, cocrystals of theophylline and benzamide (TP:BZ 1:1) and metronidazole and gallic acid (MNZ:GAL 1:1) were selected due to their known polymorphism.[1,4] This methodology was also applied to investigate the crystallisation processes of cocrystals of nicotinamide and isonicotinamide with 3-hydroxybenzoic acid (3HBA), 2-hydroxybenzoic acid (2HBA), and 2,3-dihydroxybenzoic acid (2,3-DHBA), of varying stoichiometry. The selection of these compounds is driven by their isomeric relationships yet stark difference in hydrogen bonding patterns, providing a platform to investigate the influence of molecular structure on cocrystal formation.

The acquired data enabled us to observe phase transitions of neat compounds and polymorphs of cocrystals forming *in-situ* when the starting physical mixtures were subjected to mechanochemical force arising from the spinning of the sample at the magic angle. The APIs and coformers could be characterised by different interactions with the additives used depending on the cocrystal system, polarity of the solvent or temperature of the reaction in the case of polymers as well as different kinetics of the cocrystal assembly. In summary, CLASSIC NMR spectroscopy can be successfully utilised for *in-situ* monitoring and understanding the mechanism of solvent- or polymer-mediated mechanochemical reactions. We proved it to be an effective tool for following the solid-state phase evolution in time, comparable to synchrotron TRIS-PXRD.

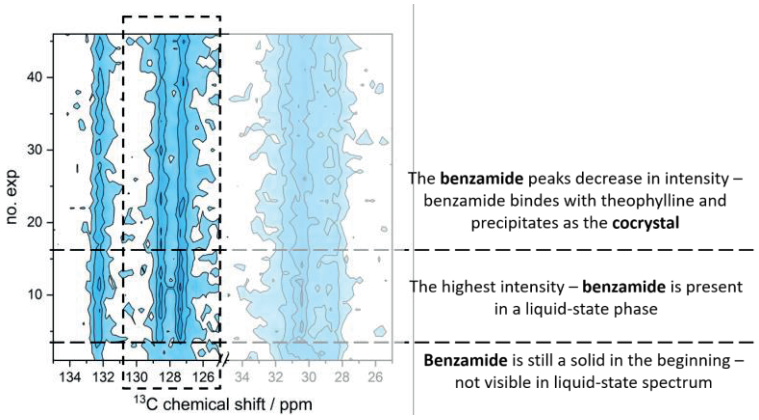

Figure 1: The phase behaviour of benzamide in TP:BZ system based on time-resolved ^{13}C {^{1}H} spectra

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The UK 850 MHz solid-state NMR Facility used in this research was funded by EPSRC and BBSRC (projects no. 220128, 220733). The assistance of Dr. Dinu Iuga is highly acknowledged.

A grasp into the molecular organization of nanoconfined water and its unconventional properties

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Water is a key player in many chemical, biochemical and physical processes. The way it interacts with other molecules and materials defines solubility constants, reaction speed, reaction routes and supramolecular arrangement. At interfaces, where surface interactions strongly influence the intermolecular organization of the surrounding molecules, water presents unconventional properties. Near surfaces, water can form a low-density state with a high degree of hydrogen bonding frustration.[1–3] Stabilized by a high electrical potential barrier preventing reorientation of its dipole moment, water molecules tend to align parallel to the surface forming ordered (ice-like) phases.[2,4] Such ordered water exhibits very low polarizability, since the reorientation upon applying an electric field is limited by the surface interaction. This results in permittivity values as low as 2.[4] Confined in hydrophobic nano-pores ice melts at -65 °C.[5] While this unconventional behavior very much attracts scientific curiosity, it also impacts technological, biological, chemical and physical processes. In hydrophilic nanopores, phase-pure cubic ice I_c is observed at moderate pressure and temperature, owing to the stabilizing influence exerted on the molecular organization by the solid-water interface.[6] This contribution discusses the properties of water confined in the pores of micro- and mesoporous silicate materials with tuned surface chemistry. In these materials, water adsorbs to defects and Brønsted acid sites, which is directly probed by NMR spectroscopy. The nanoconfinement also affects the hydrogen bonding properties of water, which in turn causes a drastic decrease in its dielectric permittivity and is reflected in the dielectric data recorded using the NMR probe head (**Figure 1**).[7] Water fractions occupying different positions inside the pores can also be observed via NMR and dielectric relaxation spectroscopy (DRS) spectroscopy.

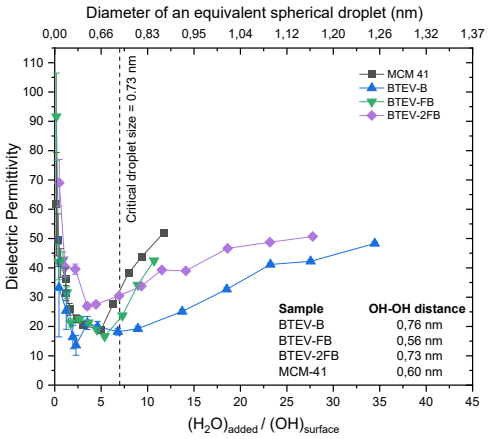

Figure 1: Dielectric permittivity of water confined in the mesopores of silicate materials of different surface chemistry. Different amounts of water - $(H_2O)_{added}$, in mol - were added to the sample. The amount of hydroxyl groups – $(OH)_{surface}$ - in the surface of each solid was quantified using NMR.

Acknowledgements
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NMR Crystallography Study of ^{17}O-labeled L-Proline Enabled by Mechanochemical Enrichment

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Amino acids are an important class of small organic molecules made up of three functional groups: a carboxylic group (-COOH), an amine group (-NH_2) and a side chain (-R). They serve as building blocks for peptides and proteins, which can arrange themselves to form more complex structures (*i.e.* triple helix, β-sheets). Generally, these structures are stabilized by inter- and intra-molecular hydrogen bonding networks involving oxygen. So far, these systems have mainly been studied using ^{1}H, ^{13}C, and ^{15}N solid-state nuclear magnetic resonance (ssNMR). However, the literature on ^{17}O ssNMR of amino acids and proteins is scarce, despite its unique ability to probe subtle changes and provide crucial information about its local environment.[1]

Over the last decades, ^{17}O ssNMR has garnered increasing interest due to significant advancements in NMR methodology and instrumentation, making it feasible to study the ^{17}O nucleus.[2] However, the very low natural abundance of ^{17}O (0.04%) is still a major roadblock in its development and accessibility. To address this issue and further push the limits of ^{17}O NMR, recent developments have been made in isotopic labeling, thanks to fast, efficient and cost-effective procedures employing mechanochemistry.[3,4]

In this work, we use mechanochemistry for the ^{17}O enrichment of L-Proline (L-Pro). The labeled compound was characterized using ^{1}H and ^{13}C solution-state NMR, mass spectrometry, and powder X-ray diffraction to confirm its purity, enrichment level, and crystallinity. This is followed by multinuclear ssNMR analyses of L-Pro, including its first ^{17}O ssNMR study (Figure 1), and a spectrum recorded at 100 K. These observations for L-Pro highlight the sensitive nature of ^{17}O ssNMR, and its unique ability to probe subtle changes in the local environment resulting from the dynamics in the crystal structure (ring puckering and/or H-bonding). The experimental data is further confronted with DFT calculations performed on an L-Pro crystal structure. Finally, this work helps pave the way for NMR crystallography to study complex biological systems, by introducing ^{17}O-labeled L-Pro into them, to provide a better insight into molecular dynamics and bonding motifs.

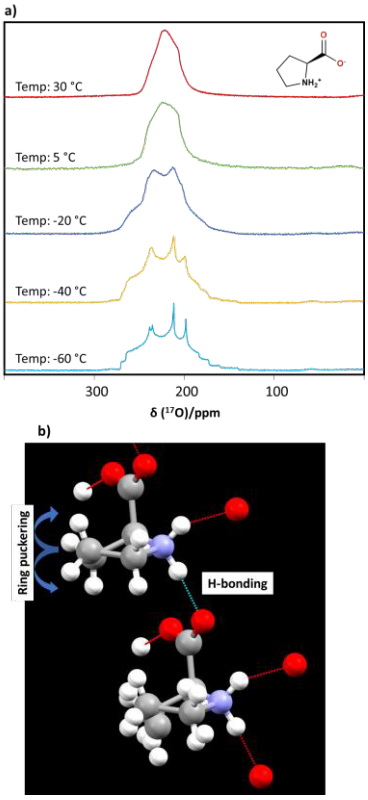

Figure 1: a) Molecular dynamics revealed for L-Pro by ^{17}O VT MAS NMR acquired at 14.1 T, b) Partial representation of the disordered L-Pro crystal structure recorded at room temperature (CCDC: 1537419).

Acknowledgements

We thank the European Research Council under the European Union's Horizon 2020 research and innovation program (Grant Agreement No. 772204; 2017 ERC-COG, MISOTOP project). Financial support from the IR INFRANALYTICS FR2054 for conducting part of the research is also gratefully acknowledged.

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Crystallization in confinement studied by solid-state NMR and MAS DNP

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Crystallization plays an important role in many areas of biology, chemistry and materials science, but the underlying mechanisms that govern crystallization are still poorly understood because of experimental limitations in the analysis of such complex, evolving systems. To derive a fundamental understanding of crystallization processes, it is essential to access the sequence of solid phases produced as a function of time, with atomic-level resolution. Rationalization of crystallization processes is particularly relevant for polymorphic functional materials, for which manufacture or storage-induced, unexpected, polymorph transitions can compromise the end-use of the solid product. Interestingly, these transformations often imply the formation of metastable forms. Today, detection and accurate structural analysis of these – generally transient – forms remain challenging, essentially because of the present limitations in temporal and spatial resolution of the analysis. These experimental barriers prevent the rationalization – and hence the control – of crystallization processes.
In the attempt of better understanding the mechanisms underlying crystallization, we recently introduced cryogenic solid-state NMR and MAS DNP strategies enabling time-resolved investigation of crystallization of polymorphic organic solids from bulk and confined solutions.[1,2] The use of confinement is a particularly interesting strategy as it allows to slow down crystallization by reducing the probability of nucleation events.3 Focusing on hyperpolarizing porous matrices based on silica[4] and polymers[5], I will discuss how the use of confined environments, combined with the sensitivity enhancement of DNP, allows metastable forms produced along crystallization pathways to be revealed and characterized.[6,7]

Acknowledgements
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Unraveling the Disorder in Microporous $AlPO_4$-LTA•$(H_2O)_w$

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Heat storage and reallocation are increasingly important in our developing society. Hydrophilic porous solids, such as microporous aluminophosphate with Lind Type-A topology ($AlPO_4$-LTA), play a significant role due to their promising properties for various technological applications. $AlPO_4$-LTA stores energy in its dry state and releases it upon hydration through a process of water sorption.[1]

To enhance the development of such materials, it is vital to have an accurate description of their atomic structure. While structure of crystalline materials can be solved by using classical crystallography, partially or fully disordered systems present a greater challenge.[2] Advanced experimental methods combined with state-of-the-art computer simulations are essential for deeper understanding.

In our research we sought to develop an accurate structural model of this complex material. We employed water uptake measurements, X-ray diffraction crystallography, high-energy X-ray and neutron total scattering, solid-state nuclear magnetic resonance spectroscopy, first-principles calculations, and molecular dynamics simulations. These techniques provide comprehensive insight into the material's dry state and enabled us to propose the first approximate structural model of its hydrated state.

Our findings reveal previously overlooked disordered motifs in a dry microporous $AlPO_4$-LTA and the detailed structure of its hydrated state, which exhibits both long- and short-range order (Figure 1).[3]

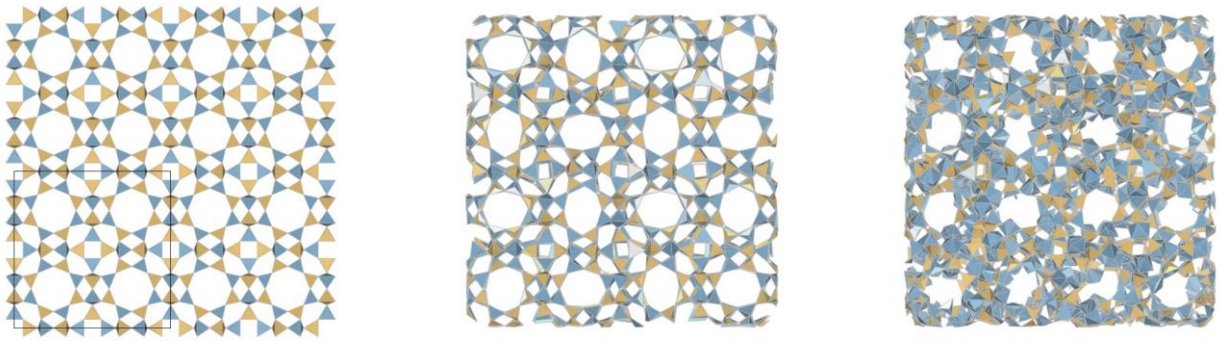

Figure 1: Structural models of 2x2x2 framework supercell representing microporous $AlPO_4$-LTA. Structural disorder within framework is increasing from left to right.

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We extend our gratitude to the late Prof. Dr. Gregor Mali for his invaluable discussions. We also thank Diamond Light Source synchrotron (proposal CY26689) and Institut Laue-Langevin nuclear reactor (proposal DIR-230) for beamtime. This research was funded by the Slovenian Research Agency (ARRS) through the research grants P1-0010 and P1-0021.

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NMR crystallographic characterisation of mixed-metal aluminogallophosphate framework materials

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Microporous phosphate-based zeotypes have been investigated for various applications including as catalysts, catalyst supports, and guest storage/release systems. Many useful properties such as Lewis or Brønsted acidity and redox behaviour can be introduced by doping the framework with other species. Even the framework structures that are accessible can depend on their compositions.

Our recent work has involved characterisation of both aluminophosphates and gallophosphates through an NMR crystallographic approach, with a particular focus on the chabazite-type (CHA) system AlPO-34 and GaPO-34, as these are useful model systems in many experiments. However, as is so often the case, even these "model" systems show surprising complexity. The organic templates in AlPO-34 display microsecond timescale dynamics,[1] GaPO-34[2] has a complex gel aging process that can lead to the alternative phase, GaPO-34A with shorter aging times,[3,4] and calcination of GaPO-34 can (with 1-methylimidazolium as the template) proceed via an intermediate dehydrofluorination step.[5] The lessons learned from characterising and understanding these model systems have allowed us to prepare and characterise mixed-metal γ-$(Al,Ga)_2O_3$ oxide precursors[6] and convert these to "AlGaPOs".[7] Here, we focus on the characterisation of the AlGaPO-34 solid solution, including combining NMR spectroscopy and DFT calculations to quantify and rationalise the non-random distribution of Al and Ga within the framework and understand the different orientations of the 1-methylimidazolium template molecules.

Finally we demonstrate that the NMR crystallographic approach applied to the AlGaPO-34 solid solution can further be applied to gain insight into other, more complex AlGaPOs.

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Towards highly realistic molecular models of complex lipid membranes using solid-state NMR and MD simulations

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A wide diversity of complex lipid membranes is found in nature with lipid compositions varying over different cell types and organelles. It is expected that such variations relate to an optimisation of the functions of the distinct membranes. However, a clear picture of such molecular dependencies has not been yet reached. Understanding such dependencies is of interest, not only in fundamental lipid biophysics, but also for the design of lipid-based systems with biomedical applications e.g. the design of lipid nanoparticles (LNPs).
One important step towards such goal is to improve the molecular-level characterisation of biological membranes. This is challenging because the number of different lipids in any given biological membrane is high, and because lipids are small and only partially disordered. The most powerful experimental technique for characterisation lipid membranes is arguably solid-state NMR spectroscopy which has been used since the 1970's to characterise these systems, starting with ^{2}H NMR to more advanced approaches using dipolar recoupling methods under magic angle spinning.
Here, I present our most recent work combining solid-state NMR methods and molecular dynamics (MD) simulations towards characterising complex lipid membranes. Namely, I will: Present how to successfully analyse dipolar recoupling data measured from complex membrane systems using NMR numerical simulations that account for RF inhomogeneity[1]; Present the latest progress in the NMRlipids open collaboration project, from which resulted the NMRlipids databank (www.databank.nmrlipids.fi), which includes now more than 800 simulation trajectories of lipid membranes that we have been validating with solid-state NMR data[2]; And show preliminary results on myelin models to be used towards studying myelin directly from nerve tissue.

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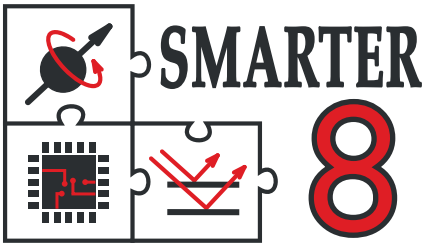

FLASH PRESENTATIONS

Ph-PMO with wall-embedded nitroxide radical for DNP-NMR

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Solid-state Nuclear Magnetic Resonance (ssNMR) is a powerful technique for analyzing the structure and dynamics of solid materials. However, its sensitivity is often limited by low spin polarization and weak signals. Dynamic Nuclear Polarization (DNP) NMR can enhance the NMR signal by several orders of magnitude by combining microwave (MW) irradiation and free radical polarization. This improvement is influenced by several factors such as MW frequency and power, temperature, magnetic field strength, sample geometry and the nature and concentration of polarizing agent. However, typical DNP-NMR sample preparation is a time-consuming process that may lead to poor homogeneity, reduced DNP enhancement, instability and sample contamination. Regarding the study of the surface of porous materials DNP-NMR there are also some specific drawbacks such as: limited polarization transfer to the surface of materials, surface/volume ratio is often large and radicals are sometimes larger than pore size hindering sample polarization homogeneity. Other disadvantage is the use of polarized solvents, which should be avoided for gas adsorption studies.[1]

To overcome these disadvantages, alternative methods for introducing polarizing agents to study porous materials are being pursued. Herein, we aim at inserting radical molecules into the structure of porous sorbents through the synthesis of Periodic Mesoporous Phenylene-silica (Ph-PMO) with a wall-embedded monoradical. PMOs have a unique hybrid nature, featuring a high concentration of organic groups in the wall. Despite its potential suitability to work as a model material for CO_2 adsorption studies, there is limited research on PMOs in the literature, particularly with regards to NMR studies to characterize their pore surface chemistry. To reach our goal, an isoindoline nitroxide monoradical was first silylated and then co-condensated with the 1,4-bis(triethoxysilyl)benzene precursor in the presence of a structural directing agent. The different synthesis steps were followed by Electron Paramagnetic Resonance (EPR) to understand the radical behaviour since the moment it was added to a solution until being bound to the silica-based matrix. EPR measurements combined with X-ray diffractometry and -196 °C N2 adsorption-desorption isotherms showed the success of the radical incorporation on the Ph-PMO pore walls. Although the incorporation of radicals into porous materials is being studied[2,3], optimization studies are needed. This study helps to fill a gap in the existing literature regarding the incorporation of radicals in PMOs, laying the foundation for further research in this area.

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Advanced NMR Investigation of the Effect of P/Na Content in Bioactive Glasses

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Commercially available silicate-based bioactive glasses (BGs) are predominantly used in powder form due to their susceptibility to crystallization. These limitations hinder the advancement of BGs for soft-tissue applications, where high-temperature processes like fiber-drawing are required, which can induce partial crystallization or melt phase-separated glass, compromising their properties. To address these challenges, we investigated the effects of various alkaline and alkaline-earth oxides on the structure and formation of LLPS within the SiO_2–P_2O_5–CaO–MgO–Na_2O–K_2O–SrO–ZnO system with varying P and Na contents. Our study employs a comprehensive set of solid-state nuclear magnetic resonance (NMR) experiments, supported by classical molecular dynamics (MD) and Monte Carlo (MC) simulations.

The ^{31}P Spin Echo Decay (SED) and Dipolar Re-coupling Effects Nuclear Alignment Reduction (DRENAR) techniques reveal the clustering of phosphates into nanoscale domains. Additionally, ^{23}Na{^{31}P} Rotational Echo DOuble Resonance (REDOR) and ^{31}P{^{23}Na} Rotational-Echo Saturation Pulse DOuble Resonance (RESPDOR) experiments show that Na preferentially associates with phosphate species. Microscopy further confirmed the presence of liquid-liquid phase separation (LLPS), which increases with higher P content. The ^{29}Si NMR spectra indicate increased polymerization of the silicate network with rising phosphate content, while the phosphate predominantly remains in the orthophosphate (P^0) form. LLPS increases with increasing phosphate content glasses destabilizing the glass network.

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Revealing the potential of poly(heptazine imides)-based adsorbents for CO_2 capture

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A promising new class of polymeric carbon nitrides (PCNs), the poly(heptazine imides) (PHIs), has emerged as a potential candidate for CO_2 adsorption due to its cost-effectiveness, stability at temperatures up to 450 °C, and moisture-resistance (e.g., not observed in MOFs, leading to structural collapse). PHIs present a facile and rapid synthesis, via molten-salt approach, a microporous structure, and show a high CO_2 adsorption capacity (~ 4 mmol/g), according to preliminary results. However, the semi-crystalline nature of these materials has made it challenging to establish the mechanisms of CO_2 uptake, unclear to this date. In this work, an in-depth study of PHIs for application in CO_2 adsorption is showcased. Solid-state nuclear magnetic resonance (ssNMR) helped characterizing the structure and adsorption mechanism (unveiling interactions between the framework and ^{13}C-enriched CO_2, at an atomic-level), leading to a clear understanding of PHIs and consequentially the potential for fine tuning towards CO_2 adsorption.
PHIs were synthesized through a rapid and tunable molten-salt approach, using low-cost precursors and a salt (**Figure 1**).

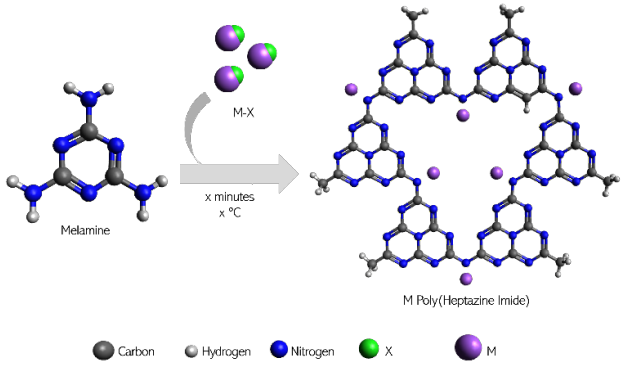

Figure 1. Synthetic pathway of PHIs

By varying the precursor's concentration, and temperature setup, control over crystallinity and textural properties (surface area, porous structure, etc.) were achieved.

The obtained results show (i) an increase in crystallinity when comparing PHIs to traditional PCNs, (ii) an increase in CO_2 adsorption capacity with an increase in dwell time under certain temperatures during synthesis, (iii) higher CO_2 adsorption than any other PHIs reported for the purpose of CO_2 capture (as per our knowledge), (iv) high selectivity for CO_2 in binary gas mixtures (CO_2/N_2), and (v) an adsorption mechanism comprised of physisorption, with mostly solid-like physisorbed CO_2 species.

The main conclusions of the work and its most relevant contributions consist of unveiling of the most accurate CO_2 adsorption mechanism for this material up to date, the establishment of a direct link between crystallinity and CO_2 adsorption capacity, which can be easily tuned during the synthesis, and the highest CO_2 adsorption capacity registered for PHIs to date.

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In situ infrared spectroscopy for understanding new zeolite catalysts

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In situ infrared spectroscopy stands as a powerful characterization technique, offering important information on the surface chemistry of zeolite catalysts. This contribution exemplifies the key role of this technique in understanding the structure-performance relationships in recently emerged germanosilicate zeolites with extra-large pores,[1,2] "isoreticular" zeolites with continuously variable micropore sizes,[3] and hierarchical micro-mesoporous zeolites.[4]

Recently, germanosilicate zeolites with weak Lewis acid centers were found to catalyze reactions relevant for the valorization of biomass-derived compounds. A spectroscopic study of germanosilicate catalysts in glycerol ketalization[1] and sucrose-to-hydroxymethyl furfural transformation[2] revealed *in situ* evolution of Ge Lewis acid sites into more active Brønsted acid centers during catalytic operation (Figure 1, top). These findings illuminate the functionality of zeolite catalysts with uncharacteristic chemical compositions in the demanding applications of biomass valorization.

New "isoreticular" zeolites created by the top-down synthesis approach feature the same structure of crystalline layers, but different interlayer connectivity and thus gradually variable micropore sizes. Through FTIR-monitored co-adsorption of molecular probes of different sizes across a series of "isoreticular" zeolites coupled with kinetic analysis of their performance in a model ethanol-to-diethyl ether dehydration reaction, these recently developed materials have demonstrated their suitability as model catalysts for evaluating the confinement effect in Brønsted acid-catalyzed reactions.[3]

Medium-pore aluminosilicate MFI zeolite was recently shown as selective catalyst of the cross-etherification reaction, yielding valuable cyclopentyl methyl ether. Combined catalytic and *in situ* FTIR spectroscopic analyses of both conventional and hierarchical MFI zeolites have revealed the Eley- Rideal mechanism of the reaction (Figure 1, bottom)[4] and highlighted the key role of prevailing surface adducts in determining catalyst selectivity, which can be tuned based on the zeolite type.[5] These findings provide a guide for tailoring efficient solid acid catalysts for the selective synthesis of cyclopentyl methyl ether.

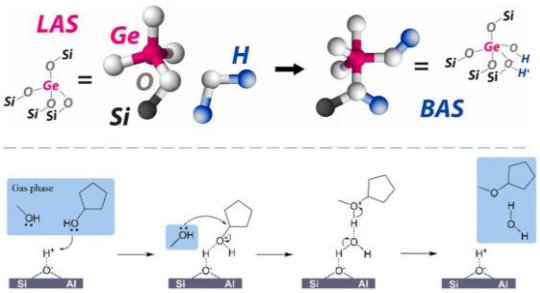

Figure 1: (top) *In situ* evolution of Ge-associated Lewis acid sites (LAS) into Brønsted acid sites (BAS) detected during glycerol ketalization[1] and sucrose-to-hydroxymethyl furfural transformation.[2] (bottom) Eley-Rideal mechanism of cyclopentyl-methyl ether formation detected over the MFI zeolite catalysts.[4,5]

Designing zeolite catalysts for specific applications is important, but practically impossible without understanding the active sites and their interaction with the reactants, intermediates, and products of a catalytic process. By uncovering the intra- and intermolecular interactions of molecules on the catalyst surface, *in situ* FTIR spectroscopy remains the core method for studying emerging zeolite catalysts.

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Understanding the acidity properties of different silica-based materials via ^{31}P ssNMR using TMP as probe molecule.

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Nowadays, various industrial processes are performed with the aid of acid catalysts. In the past decades Brønsted acid such as H_2SO_4, H_3PO_4 and HF have been broadly used as homogeneous catalysts due to their acidic strengths. Despite their excellent catalytic performances, these homogeneous catalysts display serious drawbacks mainly related to equipment corrosion, difficult waste treatment and high toxicity. To solve the above-mentioned problems, solid heterogeneous acid such as zeolites, functionalized silica and supported heteropolyacids (HPAs) have been developed and largely employed in various catalytic chemical processes.[1] In general, the heterogeneous solid acids display two different kinds of acidity: Lewis (L) and Brønsted (B). Silica-based materials are among the most used heterogeneous catalyst due to high specific surface area and pore size distribution. Moreover, the L/B acid balance can be tuned via the insertion of a metal cation in the structure or modifying the ratio between silicon and the selected metal cation. In this context, different analytical methods based on well known spectroscopic techniques have been developed with the aim to characterize these acidic features. Indeed, the overall acidity can be studied via the use of probe molecules (e.g. pyridine and ammonia) in combination with temperature programme desorption approach (TPD) or coupled to infrared spectroscopy (FT-IR).[2] Recently, it has emerged that detailed acid features such as nature, concentration, and strength of acid sites can be investigated by solid state nuclear magnetic resonance (ss NMR) selecting a suitable probe molecule containing NMR-sensitive nucleus such as ^{13}C, ^{15}N, or ^{31}P. Among all the possible probe molecules, trimethylposphine (TMP) and trimethylposphine oxide (TMPO) are largely employed in this field (Figure 1). The use of these two molecules is quite advantageous due to the wide chemical shift range of ^{31}P NMR allowing the clear identification of the different acid sites, and because ^{31}P is a dipolar nucleus with an abundance of 100%.[3]
Herein, we show the characterization of the L and B acidity of different silica-based materials using TMP as probe molecule. Initially, a comparison between Hf, Ga and Sn silica hallow nanotubes is done. Afterwards, Ga and Sn nanotubes are compared with the respective silica hollow nanospheres, to evidence a possible modification on the acid properties due to the different morphology of the solids. Finally, an oxidation treatment in air allows converting TMP in TMPO which can employed to better understand the strength of the different acid sites.

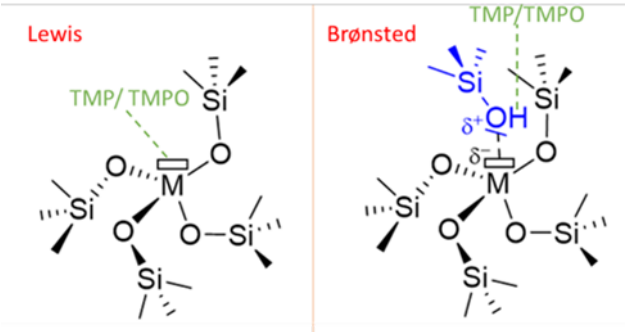

Figure 1. General schematic representation of Lewis (left) and Brønsted (right) acid active site on silica-based materials.

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Local structure of solid-state electrolyte investigated via solid-state NMR spectroscopy

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All-solid-state lithium-ion batteries have become increasingly important in recent years due to their potential to offer higher energy density and enhanced safety compared to conventional liquid electrolyte-based lithium-ion batteries. In this context, solid-state electrolytes such as the garnet-type solid electrolyte LLZO are under high scrutiny due to their high ionic conductivity at room temperature.[1] In particular, the Al-doped cubic form of $Al_{0.2}Li_{6.025}La_3Zr_{1.625}Ta_{0.375}O_{12}$ (ALLZTO, space group $Ia\bar{3}d$) is a very promising candidate. One of its two Li sites is not fully occupied, creating some Li vacancies and thus favouring Li-ion conduction. However, its local structure (Li vacancies/defects) is still not well understood, and neither is the influence of Al-doping. Solid-state NMR is the method of choice to investigate the local defects within the structure created by the Al-doping, Li vacancies and the Zr/Ta site shared occupancy.
Using NMR crystallographic strategies, we analyse electric field gradient (EFG) and chemical shift (CSA) tensors derived from $^{6/7}$Li, ^{27}Al, ^{91}Zr and ^{139}La MAS and static NMR spectra. While the EFG is sensitive to local distortions and missing atoms, the CSA is susceptible to X-O bond (X = Al, La and Zr) alterations. Those experimental values are compared to ab initio CASTEP calculations for different defect models. Additionally, $^{6/7}$Li T_1 and T_2 relaxation measurements were carried out to probe the Li^+ ion dynamics and ^{7}Li NMR PFG diffusion measurements provided information on the long-range transport.

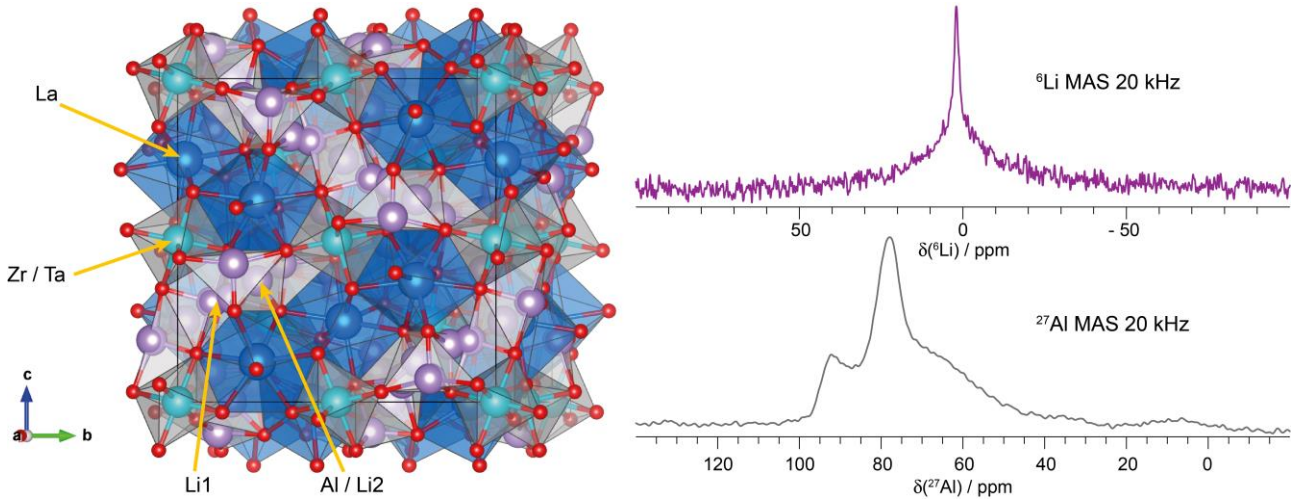

Figure 1: LLZO structure (left) along with ^{6}Li (top right) and ^{27}Al (bottom right) MAS spectra of $Al_{0.2}Li_{6.025}La_3Zr_{1.625}Ta_{0.375}O_{12}$.

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Disentangling spaghetti: SMARTER crystallography strategies to reveal supramolecular assemblies in porous functional materials

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The majority of industrial-scale chemical processes rely on the complex interplay between metal cations, anions, water, organics, and framework atoms of porous functional materials. While a molecular-level understanding of what exactly is happening in the pore systems is critical for advancing the synthesis and applications of these materials, investigating the interactions of molecular compounds within the pore system remains a challenge, typically not achievable using a single characterization technique.

Combination and optimal integration of solid-state magnetic resonance with other diagnostics like spectroscopic techniques, diffraction, scattering and modelling provides unprecedented opportunities to resolve guest structures and assemblies in pore systems of functional porous materials.
Using mainly porous zeolite materials as examples, this contribution will outline a general approach to tackle the characterization of porous functional guest host assemblies, with a specific focus on the pore content and supramolecular organization of molecular species residing in the pore system.
In a first example, the combination of in situ NMR and IR spectroscopy identified specific aspects of hydrogen bonding between aliphatic alcohols and high-silica ZSM-5 zeolites (Figure 1). This insight allowed to detailed description of the relevant sorption mechanism based on hydrogen bonding of the alcohol function of the guest with siloxane bridges of purely silicious sections of the host. This mechanism coexists with traditionally accepted alcohol adsorption mechanisms like Brønsted acid site adsorption and adsorption at framework defects (i.e., silanols).[1]

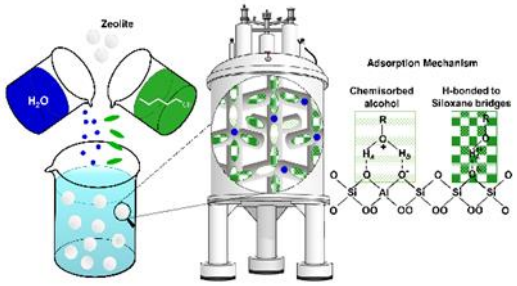

Figure 1: *Hydrogen bonding to oxygen in siloxane bonds drives liquid phase adsorption of primary alcohols in high-silica zeolites*

This first example will then be extended to the adsorption of water in the same series of zeolites, combining multi-diagnostic quantitative MAS NMR and permittivity spectroscopy to demonstrate how water, in contrast to alcohol, selectively adsorbs on Brønsted acid and defect sites, forming small clusters with size-dependent dielectric properties and hydrogen bonding behavior. The insights provided by these studies are not only relevant for rationalizing adsorption but present a foundation for understanding solvent effects in liquid-phase reactions catalyzed by such microporous materials.

Moving towards the identification of larger supramolecular examples, inorganic supramolecular assemblies consisting of 4 sodium cations bound by hydrated hydroxide species were identified in the pore systems of hydroxy-sodalite by combining multi-dimensional multi-nuclear NMR spectroscopy and X-ray diffraction.[2] This identified super-ion is recognized as a structure-directing agent during the formation of this zeolite but is irreversibly destroyed once the as-made zeolite is removed from its synthesis medium and contacted with water.

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NMR Crystallography of Pharmaceuticals

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The NMR crystallography approach is applied to characterize two active pharmaceutical ingredients, Lorlatinib[1] and Ritlectinib[2]. Specifically, GIPAW calculations of chemical shifts for ^{1}H, ^{13}C, $^{14/15}$N and ^{19}F as well as of electric field gradients for ^{14}N complement magic-angle spinning (MAS) solid-state NMR experiments. Specifically, ^{14}N-^{1}H heteronuclear multiple-quantum coherence (HMQC) and ^{1}H-^{1}H double-quantum (DQ) single-quantum (SQ) correlation experiments are presented at a ^{1}H Larmor frequency of up to 1 GHz and a MAS frequency of up to 60 kHz. A full assignment of the ^{1}H and ^{13}C chemical shifts is achieved using also ^{1}H-^{13}C cross polarization (CP) HETCOR spectra. A particular focus is on probing key hydrogen bonding interactions that drive the adopted molecular packing in a specific polymorph.

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Structural Characterization of Porous Covalent Organic Frameworks using DNP enhanced Solid-State NMR and Computational Modeling

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Determining the precise structural features of complex, amorphous and polycrystalline powdered solids remains a significant challenge in the scientific community. This holds true particularly for porous covalent organic frameworks (COFs) and polycatenanes, where the conventional methods of structural elucidation (single-crystal X-ray diffraction, solution-state NMR etc.) cannot be readily employed to obtain detailed three-dimensional structures. COFs are an important class of porous materials with diverse applications in areas like gas storage, catalysis, and sensing, but their structural characterization has been hindered by their inherent disorder and lack of long-range crystalline order. This work explores the use of advanced solid-state nuclear magnetic resonance (ssNMR) spectroscopy techniques, including dynamic nuclear polarization (DNP) combined with computational modeling, to elucidate the local and intermediate-range structures of COFs. Solid-state NMR provides unique structural information by probing the chemical environments and connectivity of individual atoms within the amorphous COF frameworks. By integrating experimental ssNMR data with theoretical calculations, such as density functional theory (DFT) calculations, to develop structural models that account for the local bonding arrangements, intermolecular interactions, for the interaction studies of COF materials with various substrates and ligands. The findings from this study demonstrate how the synergistic application of experimental solid-state NMR and theoretical DFT calculations can provide unprecedented insights into the structural features of these complex, amorphous polymers. This powerful approach overcomes the limitations of traditional diffraction-based techniques, paving the way for a deeper understanding of the structure-property relationships in COFs and enabling the rational design and optimization of these porous materials for diverse applications. Herein, I will be presenting our latest research results on gas sensing iCOFs (ionic covalent organic frameworks)[1], solid-state photoluminescent COFs[2], humidity responsive COFs[3], and also mechanically interlocked molecules such as catenanes and polycatenanes.

Acknowledgements

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Water Dynamics in Porous Materials: What can we learn from Quasielastic Neutron Scattering?

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Water confined in nanoporous materials is ubiquitous in many applications related to energy and environment. This includes porous solids for water purification, solid electrolytes, membranes for proton exchange fuel cells,[1] nanofluidic devices and desalinization technology.
Under these conditions, the structure and dynamics of water molecules is significantly altered with respect to the corresponding bulk state.[2,3] This is a direct consequence of spatial restriction and liquid-surface interactions which become more prominent the smaller the pore size is. These effects obviously depend on the pore surface chemistry and the morphology (shape) of the material porosity. Interestingly, the water dynamics also depend on the length scale that is probed. For instance, different translational diffusion can be expected if it is monitored along a trajectory that is smaller than the pore size, that exceeds the diameter or even the grain size of nanoporous powder.
To resolve this problem, a multi-scale experimental approach is an asset. In the present communication, we will discuss the opportunity offered by quasielastic neutron scattering methods to characterize the dynamics of confined water at the nanoscale,[4] that is to say for a molecular displacement equal to or less than the pore size, which can therefore be considered as a complementary tool to NMR that accesses longer scales. Our talk will be illustrated by recent studies carried out on water-filled porous silicas, organosilicas and sulfonated porous aromatic framework.

Acknowledgements
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Studying pharmaceutical cocrystals obtained by mechanochemistry by means of 3D electron diffraction and solid-state NMR spectroscopy

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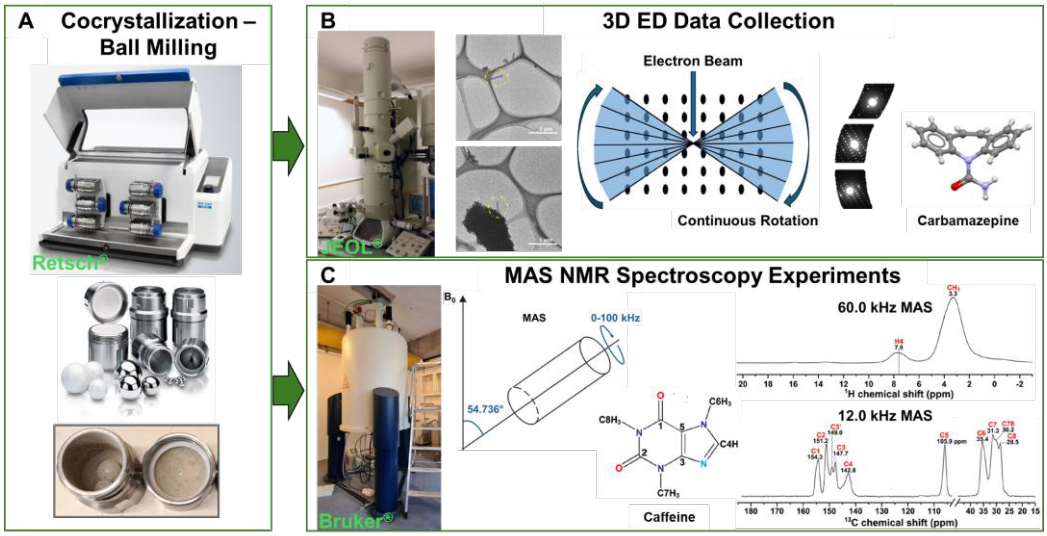
Mechanochemistry has recently emerged as a promising method to complement state-of-the-art crystal engineering and crystallization processes aimed at optimizing the physico-chemical properties of active pharmaceutical ingredients (APIs).[1] Multicomponent pharmaceutical solids, such as cocrystals and salts, are increasingly being used as an alternative solid form of the parent drug due to their enhanced physico-chemical properties, in particular improved solubility profiles and dissolution rates.[2]

Here, we demonstrate based on mechanochemically obtained cocrystals of two different APIs how three-dimensional electron diffraction (3D ED) and solid-state nuclear magnetic resonance (NMR) spectroscopy can be efficiently used as analytical tools to investigate and extract diverse information from such nano-sized pharmaceutical cocrystallites. Three-dimensional electron diffraction (3D ED), also referred to as microcrystal electron diffraction (MicroED), has proven to be a powerful tool for crystal structure determination of solid forms in the pharmaceutical industry.[3] The method complements established techniques by opening up the possibility of studying small organic molecules from crystals that are too small for conventional single-crystal X-ray diffraction and too complex for powder X-ray diffraction. In this study, we demonstrate the crystal structure determination of a novel cocrystalline form of the anticonvulsant and antiepileptic drug carbamazepine[4] by 3D ED. In addition, we used magic-angle spinning (MAS) NMR spectroscopy experiments to examine the chemical-shift/structure trends of a series of four caffeine cocrystals and all corresponding precursors.[5]



Scheme: (**A**) Cocrystal preparation through ball milling and their study by (**B**) 3D ED and (**C**) MAS NMR spectroscopy.

Acknowledgements
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SYSTEMATIC FRAMEWORK VACANCIES IN CESIUM ZEOLITES JEOPORDIZES ITS USE FOR NUCLEAR WASTE STORAGE

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The nuclear accident in Fukushima in 2011 promoted the scientific quest to safely capture and store harmful radioactive nuclei, Cs in particular. One of the most promising strategies involves the hydrothermal synthesis of pollucite (Cs-ANA), in which aluminosilicates capture the radioactive Cs in their framework while forming. Pollucite has the structural advantage of having framework windows smaller than the ionic diameter of Cs, theoretically preventing the Cs from escaping the porous material. This work, however, reports systematic framework defects, jeopardizing the Cs-retaining capacity and diminishing their potential for the storage of nuclear waste.

Cs-ANA has a unique mechanism to modulate its framework composition. Employing SMARTER crystallography, it was proven that instead of a virtual substitution of an Al-cation pair for a silicon atom, the Cs-content is kept constant, incorporating systematic T-site vacancies, which in the most extreme cases account for up to 13% of the possible T-sites. The resulting silanol nests are partially deprotonated to accommodate the perceived charge imbalance. Interestingly, the degree of vacancies is shown to increase over time. Despite the defects, all materials show high crystallinity in both X-ray and neutron diffraction. Additional analysis using quantitative multinuclear (^{1}H, ^{27}Al, ^{29}Si, ^{133}Cs) NMR crystallography allows closer investigate the architecture, hydrogen bonding patterns and distribution of the silanol nests in the framework, leading to a structural model, agreeing with spectroscopic and structural data. Our results highlight the structuring role of inorganic cations for porous materials using Cs-ANA as an extreme example.

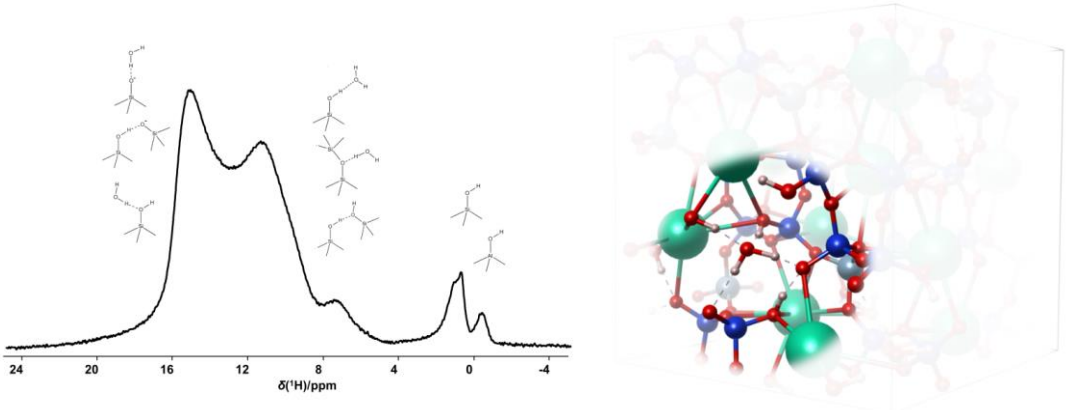

Figure 1. (left) ^{1}H MAS NMR spectrum of pollucite (Si/Al = 4), with assignment of resonances. (right) Hydrogen bonding pattern of a water molecule centered inside a tetrahedral silanol nest.

Structural evolution of layered $H_2V_3O_8$, a high-capacity lithium-storing cathode, during lithium intercalation

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$H_2V_3O_8$ is a promising high-capacity cathode material for lithium-ion batteries (LIBs). It allows reversible two-electron transfer during electrochemical lithium cycling processes, showing high-capacity (378 mAh g^{-1}) and high-energy (945 Wh kg^{-1} at an average voltage of 2.5 V).[1,2] While a considerable number of research works have demonstrated the exceptional electrochemical lithium storage properties of $H_2V_3O_8$, the structural changes that occur during the intercalation process have not been studied and the crystallographic positions occupied by the guest species have not been revealed before. The objective of this study is to gain insights into the lithium storage mechanism of $H_2V_3O_8$. A combination of Density Functional Theory (DFT) calculations with high-resolution synchrotron X-ray and neutron diffraction studies is employed to accurately describe the crystal structures of both pristine and lithiated $H_2V_3O_8$.[3]
In $H_2V_3O_8$, combined results of synchrotron X-ray and neutron diffraction show a *P*nma structure with hydrogen atoms located on a single-crystallographic site in a waterlike arrangement, through which bent asymmetric hydrogen bonds across adjacent $V_3O_8^{2-}$ chains are established. DFT energy calculations show this is the most stable conformation of hydrogen atoms in the *P*nma space group.
For $LiH_2V_3O_8$, synchrotron X-ray diffraction data were used as a starting model for DFT calculations. Geometry optimization predicts a hydrogen-bonding switch of structural water upon lithium intercalation, which was subsequently validated by neutron diffraction. In addition, DFT studies suggest a reduction in symmetry from *P*nma to $P2_12_12_1$ to achieve a more stable structure with enhanced hydrogen and lithium bonding. Further ab initio molecular dynamics studies show that vibrations around more stable sites for lithium and hydrogen atoms lead to a mean structure with *P*nma symmetry.

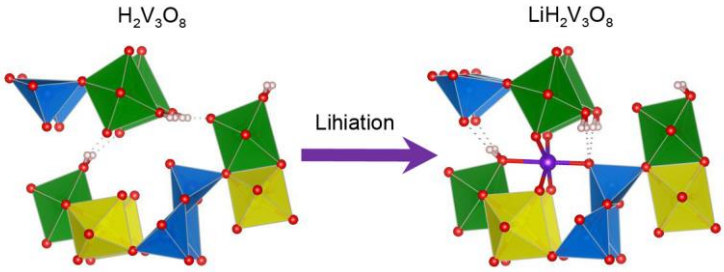

Figure 1: Structural change from $H_2V_3O_8$ to $LiH_2V_3O_8$.

Acknowledgements
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Investigations of translational movement for charge carrier transport in nano-confined environments of porous polymers

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To address the current challenges in energy storage and conversion, particularly those related to the time-scale issues of charge carrier transport and hosting, functionalized porous polymers have emerged as promising materials. Sulfonated polyaromatic frameworks (SPAFs) have demonstrated a broad stability window across various temperature, electrical, and chemical conditions, together with competitive conductivity values, making them suitable for battery and fuel cell applications.[1,2] Since porous systems should not just provide a sweet spot for host molecules regarding accessibility and higher pore volumes, sufficiently confined area is required to avoid bulk-properties for those hosts.[3–5] The SPAF-2 system has been extensively studied under specific humidity conditions due to its three-dimensional open porosity and nanoscale confinement, which are believed to create optimal conditions for charge carrier transport.[1] Proton exchange capacities up to 6 mequiv·g^{-1} and conductivities of about 1 S·cm^{-1} were discovered on high humidity levels.[1] Additionally, XRD, NMR, EDX and IR measurements have shown, that synthesis optimizations led to a more even distribution of sulfonic acid groups, higher degrees of cross-linking, and reduced paramagnetic centers from catalyst residues within the framework. Variations in sulfonation degrees and humidity, and the resultant properties like rising water-sorption and diffusion-constants, have been verified using quasi-elastic neutron scattering (QENS) and water-physisorption experiments. Furthermore, pair distribution function (PDF)-XRD has been employed to determine the intrinsic distances within the framework and the attached sulfonic acid groups. Finally, water diffusivity was investigated utilizing PFG NMR.

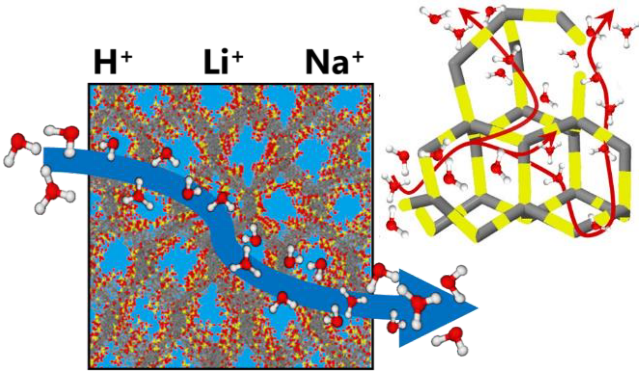

Figure 1: Illustration of energetically favorable charge-carrier transport through the three-dimensional pore channels of the framework.[1]

Acknowledgements
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A comparative structural study on metal disorder in a series of of bimetallic M,Mg-MOF-74 (M = Co, Cu)

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Nowadays, humanity is confronted with several challenges caused by man-made climate change.[1] Major factors are carbon dioxide emissions[2] e.g., from industrial processes and transport, inducing storms and global temperature rises.[3] To mitigate these effects, capturing carbon dioxide and its sequestration to fine chemicals is vital. A possible route can be via the CPO-27/MOF-74 metal-organic framework, as it shows promising results for CO_2 uptake thanks to its coordinatively unsaturated metal site[4].
The framework consisting of chains of edge-connected metal oxygen octahedra[5] shows intriguing chemical and physical behaviors for the mixed metal variants. In this study, the crystallinity, specific surface area, band gap and disorder were investigated for the Cu,Mg and Co,Mg mixed-metal systems. The frameworks were synthesized with magnesium ratios ranging from 0 to 100 at.% without loss of crystallinity, whereas the lattice parameters don't behave according to Vegard's law[6]. Additionally, their specific surface areas and band gaps are in disagreement with the general rule of mixtures. This suggests a homogeneous distribution of metals in the chains over the complete range of metal ratios for both Cu,Mg-CPO-27 and Co,Mg-CPO-27..

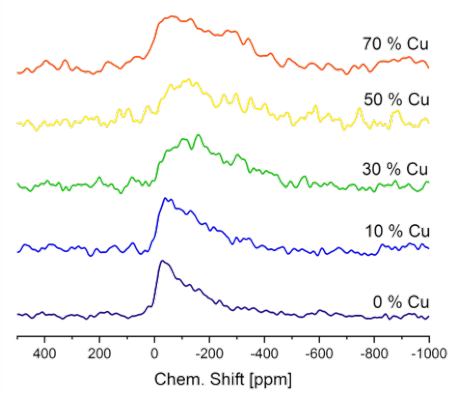

Figure 2: ^{25}Mg NMR spectra of several Cu,Mg-CPO-27 samples.

By analyzing the stress and strain inside the crystallites, as provided by PXRD, the interactions with polar and non-polar solvents within the frameworks were investigated as well as possible displacements of metal centers caused by the metal mixing.
The successful mixture of metals in MOF-74 for Mg ratios spanning from 0 to 100 % opens the materials for possible applications in e.g. CO_2 capture and sequestration processes.

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SMARTER crystallography elucidating the role of water in zeolite crystallization

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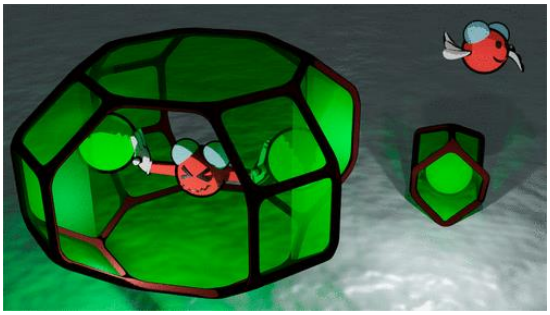
Zeolites, incredibly versatile nanomaterials, hold immense significance in our society, playing pivotal roles in various industries, including petrochemical, catalysis, and environmental applications. Despite decades of research, the intricate mechanisms governing zeolite formation still remain largely elusive, with synthesis protocols largely relying on trial-and-error methods. Conventional methods involve hydrothermal gel conversion, hindering in-depth in situ characterization. To address these limitations, we developed a novel synthesis approach utilizing Hydrated Silicate Ionic Liquids (HSILs), enabling zeolite formation from a homogenous phase.[1] HSILs, composed of ions and trace amounts of water, have demonstrated remarkable potential in producing highly crystalline zeolites spanning a diverse range of frameworks. This controlled chemistry facilitates comprehensive in situ multidiagnostic characterization using SMARTER crystallographic approaches combining advanced techniques such as NMR, MEEIS, and XRD, unravelling the intricate relationships between initial precursor speciation, cation variations, water content, basicity, and the resulting zeolite framework type, formation kinetics, and potential for industrial scale-up. Two examples of SMARTER crystallography elucidating the role of supramolecular complexes of water in templating and directing the porosity of zeolites.

Example 1.[2] A direct link between the sodium speciation in the synthesis mixture and the pore structure and content of the final zeolite is demonstrated in the example of hydroxysodalite. Super-ions with 4 sodium cations bound by mono- and bi-hydrated hydroxide are identified as structure-directing agents for the formation of this zeolite. This documentation of inorganic solution species acting as a templating agent in zeolite formation opens new horizons for zeolite synthesis by design.

Example 2.[3] Variation of water content of the initial HSIL based synthesis mixture yields porous merlinoite (MER) zeolite when H_2O/KOH exceeds 4 and dense, anhydrous megakalsilite when H2O/KOH is lower. SMARTER crystallography revealed the role of cation hydration on phase selectivity, allowing a spatial cation arrangement enabling the formation of pores. Under water deficient conditions, the entropic penalty of cation hydration in the solid is large and cations need to be entirely coordinated by framework oxygens, leading to dense, anhydrous networks. Hence, the water activity in the synthesis medium and the affinity of a cation to either coordinate to water or to aluminosilicate decides whether a porous, hydrated, or a dense, anhydrous framework is formed.



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Acknowledgements

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Microstructure of Kaliophilite: a ^{29}Si and ^{27}Al MAS NMR study and CASTEP analysis

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Kaliophilite, discovered in 1839, was the first among 12 polymorphs with compositions near to K[AlSiO4] to be identified. It is a very rare mineral of the feldspathoid (framework silicate) group, but this is a surprisingly challenging crystal structure to determine.
Kaliophilite has a complex and intriguing framework structure with several different silicate tetrahedra–based rings and the potential for very large cavities topology.
Nevertheless, initial attempts to resolve the kaliophilite structure were unsuccessful and, based on synchrotron data from micro-crystals, it was concluded that pseudo-symmetry and twinning were possible issues. This challenge could now be overcome using the recently developed electron diffraction tomography (EDT) technique (see e.g. Mugnaioli *et al.*, 2009) that allowed collecting data from a single crystal of a few hundred nanometers in size.
In this work, ^{29}Si and ^{27}Al MAS NMR spectroscopy were used to confirm the framework topology (connection between tetrahedra through Al-O-Si bonds), which can be defined by six-membered rings of alternating Si and Al tetrahedra forming a 6^3 net perpendicular to **c**. In tridymite, all rings are equivalent with vertices 1-3-5 pointing upwards and the remainder downwards, connecting to the adjacent sheets. Kaliophilite is the first case where three different types of ring topology coexist: 1-3-5, 1-2-3 and 1-2-4.
DFT was used to optimize the geometry of the cell and the positions of the atoms forming its basis. CASTEP DFT calculations predict chemical shifts and chemical shielding, to compare with the experimental ones. ^{29}Si MAS-NMR spectrum indicates a main component with a pronounced doublet assigned to Q4(4Al) single environment of Kaliophilite; the comparison with ab initio calculations, explains the observed unfolded central peak because of the crystallographically distinct Si-sites.
This discovery opens the door to developing other useful topologies for applications such as catalysis, photonics, and more.

Acknowledgements
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Structure and electrolyte-host interactions for a series of TpPa based covalent organic frameworks using NMR crystallography

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Electrolyte-host systems based on structured materials are promising candidates for various applications like separators in electrochemical energy storage devices. Covalent organic frameworks (COFs) have gained significant interest as hosts for electrolyte materials due to their large surface area and tuneable pore surface. The spatial constraints in the pores enforce a confinement effect onto the electrolyte and impose additional electrolyte-host interactions resulting in changed properties like lower crystallisation temperature, suppressed phase transformation and changed transport mechanism. These changes are highly dependent on the structure and surface functionalities of the host.[1] Here, we used a combination of NMR spectroscopy, XRD and quantum chemical modelling to elucidate the underlying transport processes for the COFs[2–5] TpPa-SO_3X with $X=H^+/Li^+$ loaded with H_2O.

NMR spectroscopy allowed an unambiguous assignment of the signals to the TpPa structure. The pore space was probed with physisorption and ^{129}Xe NMR spectroscopy. XRD and NMR data showed that AA stacking creates hexagonal channels with a layer distance of 3.3 Å. This stacking is disrupted for dry systems due to a twisting of the layers, as shown by DFT calculations. Adding sulfonic acid groups to the system increases the hydrophilicity but also, as seen from broader NMR signals, introduces disorder, which could hinder a high proton conductivity. Correlation experiments like $^1H^1H$ DQ-SQ and $^{13}C\{^7Li\}$ REDOR further probed the cation influence. Improved ^{13}C NMR resolution was observed with increasing water uptake. The water uptake leads to a higher ordered system, providing a better framework for mass and charge transport.

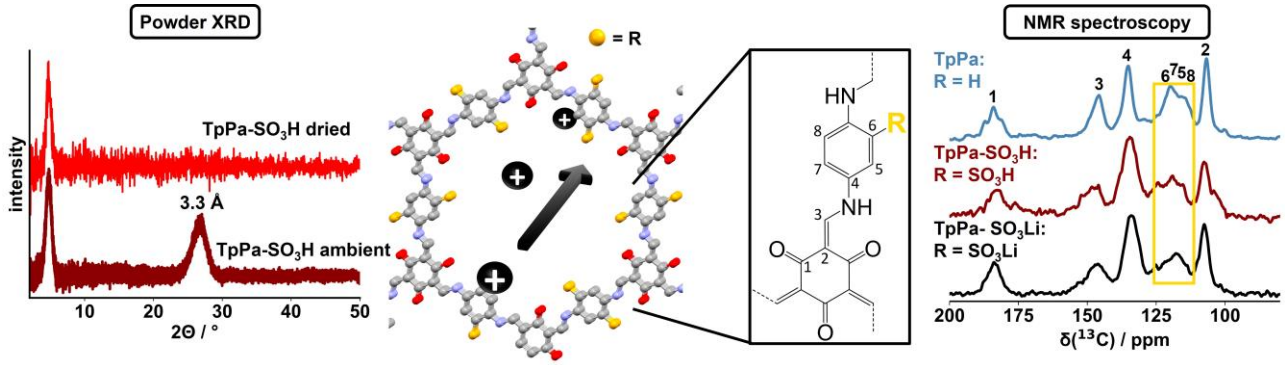

Figure 1: Powder XRD of TpPa-SO_3H dry and ambient relative humidity (left); Scheme of proton transport and structure for TpPa-R (middle) and their ^{13}C NMR spectra with the respective assignment (right).

Acknowledgements
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Exploring CO_2 Sorption Mechanisms in Green Cellulose and Chitosan Aerogels using solid state NMR and DFT calculations

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Carbon dioxide (CO_2) is the most greenhouse gas emitted by human activities and one of the biggest responsible for climate changes. Thus, CO_2 emissions must be dramatically reduced to mitigate global warming. Several technologies have been proposed to remove CO_2 from the air or flue gases, but amine-scrubbing is currently the most used method to remove CO_2 at industrial-scale applications. Amine-based liquid absorbents suffer from several limitations such as poor chemical stability, environmentally unfriendly, and demand high-energy regeneration stages[1]. Alternatively, the adsorption technology uses solid adsorbents, which are promising candidates for large-scale carbon capture due to their lower regeneration energy requirements and durability over many cycles, two of the main cost drivers in CO_2 capture technologies [2].

The practical implementation of large-scale carbon capture technologies requires the availability of CO_2 selective and low-cost materials that are renewable. Polysaccharide-based adsorbents are abundant, renewable and biodegradable, making them a promising candidate for this use. However, the CO_2 capture mechanisms in these materials remain largely unknown.

In this work, CO_2 sorption mechanisms on cellulose and chitosan aerogels were studied by solid-state NMR spectroscopy and DFT calculations. A combination of 1D ^{13}C cross-polarization (CP), 2D ^{13}C-{^{1}H} LG-CP HETCOR and CP kinetics NMR experiments were performed to characterize confined chemisorbed and physisorbed CO_2 adsorbed species. First-principle DFT calculations were used to aid the NMR assignments of the different types of adsorbed CO_2 species. We show, for the first time, that while cellulose aerogels adsorb CO_2 purely via physisorption processes, chitosan aerogels instead capture CO_2 via chemisorption and physisorption processes. The chemisorbed species in chitosan aerogels were assigned as ammonium carbamate and carbamic acid species. These results contribute towards a better understanding of the adsorption processes in these materials, and it is a steppingstone for future improvements in the performance of these sustainable solid sorbents.

Acknowledgements
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Unravelling Gas Adsorption Behaviour in Porous Materials: A Computational Approach

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Global warming poses a significant threat to our planet, requiring urgent measures to mitigate its effects. Among the most promising strategies to tackle this pressing issue is the reduction of CO_2 emissions by capturing this greenhouse gas, whether directly from the atmosphere or from flue gas. While amine-based solvents have traditionally dominated industrial applications in post-combustion CO_2 capture, their environmental drawbacks and energy-intensive regeneration processes underscore the need for more sustainable alternatives. Solid sorbents, such as covalent organic frameworks (COFs) have emerged as promising candidates for efficient carbon capture, with modified amine-bearing functional groups that provide tailored sorption properties.

Numerous experimental studies have examined these classes of porous sorbents, with recent solid-state NMR investigations uncovering CO_2 speciation under different adsorption conditions.[1-3] Nevertheless, comprehensively understanding the structural intricacies and underlying gas adsorption mechanisms remains a huge challenge. An in-depth comprehension of the molecular-level interactions governing sorption processes is crucial for advancing beyond the status quo, optimizing the design and utilization of porous media for gas storage, separation, and catalysis.

In this study, we explore computational methodologies to probe gas adsorption behaviour within different porous materials, namely COFs. Our extensive computational simulations include grand canonical Monte Carlo (GCMC) simulations to investigate CO_2 and H_2O adsorption in COFs with varying pore sizes and geometries, and molecular dynamics (MD) simulations to examine time-dependent molecular properties within these materials, employing reactive force fields to better describe molecular interactions. Our findings, supported by experimental evidence from solid-state NMR and gas adsorption analysis, contribute to the fundamental understanding of gas adsorption phenomena in porous media. Importantly, they offer invaluable insights for the rational design of materials tailored for efficient gas adsorption, thereby advancing the pursuit for sustainable solutions in CO_2 capture and global warming mitigation.

Acknowledgements

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Combined computational-experimental NMR for the structural investigation of complex materials

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Solid-state NMR spectroscopy is routinely used to further the understanding of the structure of nanoporous materials and the dynamic phenomena taking place within. The correct interpretation of experimental NMR spectra is not always a straightforward procedure, due to overlapping contributions, limited resolution and overall complexity of the system under investigation. Combining computational modeling with experimental techniques can provide insight otherwise inaccessible to these techniques on their own. This work describes a computational protocol that may be used for the theory-backed assignment of solid-state NMR spectra in crystalline materials which exploits the symmetry of either the framework or its underlying secondary building units to connect the experimental spectrum to theory.[1,2] We apply variations of the protocol to different systems, both zeolites[3] and covalent organic frameworks, and show that, in spirit of the SMARTER approach, the combination of experiment and theory is a true asset in solid-state NMR of complex materials.

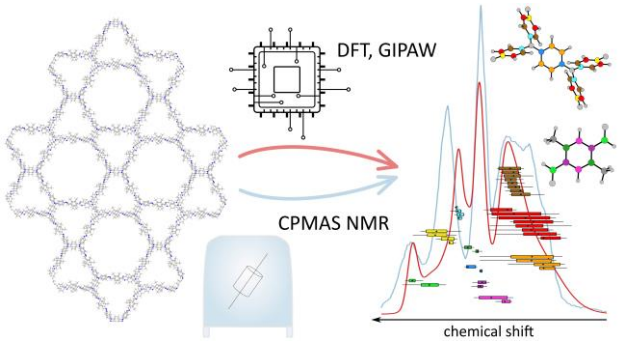

Figure 1: One example of the combined computational-experimental NMR approach is the classification and assignment of carbon-13 resonances in covalent organic frameworks (Figure reproduced from Ref. [1]).

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Observation of covalent connectivities in crystalline compounds: Pure-shift INADEQUATE with improved sensitivity and resolution

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2D NMR homonuclear correlation is a powerful tool to determine the structure of crystalline samples. In compounds with minimal dipolar couplings and relaxation rates, through-bond refocused-INADEQUATE is the optimal choice to identify the covalent connectivities between identical nuclei. However, the resolution of this method is limited by *J*-coupled doublets along the direct dimension. Also, the method's sensitivity is often low, notably for unlabelled samples, where the concentration of spin pairs is small. These limitations can prevent resolving crystallographic sites in different polymorphs with similar structures or identifying crystal lattices with low levels of symmetry.

Here, we report on a series of 2D phase-sensitive INADEQUATE pulse sequences (Figure 1a,b), which give pure-shift singlet-line DQ-SQ homonuclear correlation spectra with improved sensitivity. This was achieved by incorporating a composite refocusing (CR) block[1] and a z-filter into the pulse sequence and employing bi-exponential non-uniform sampling ($NUS_{bi\text{-}exp}$).[2]

The methods were tested for three distinct isotopes, ^{29}Si, ^{13}C and ^{31}P, on four crystalline compounds: intergrown polymorphs of ^{29}Si-enriched pure-silica β zeolite, SnP_2O_7, and uniformly ^{13}C-labelled glycine and histidine.

Applying a constant-time INADEQUATE-CR version for zeolite β allows us, for the first time, to distinguish and identify all 21 non-equivalent Si crystalographic T-positions in the three co-crystallized polymorphs.[3] In the case of SnP_2O_7, the z-filtered version resolved more than 115 individual ^{31}P signals, allowing us to attribute the P1 symmetry to the structure, not $P2_1$ or Pc, as suggested earlier. A 7.5 reduction of the experimental time was achieved using a 33% $NUS_{bi\text{-}exp}$.

We also analyzed possible artifacts originating from J-mismatching, differences in relaxation times between coupled nuclei, strongly coupled protons and multi-spin systems. According to the type of studied compound, we explain which INADEQUATE-CR sequence must be employed.

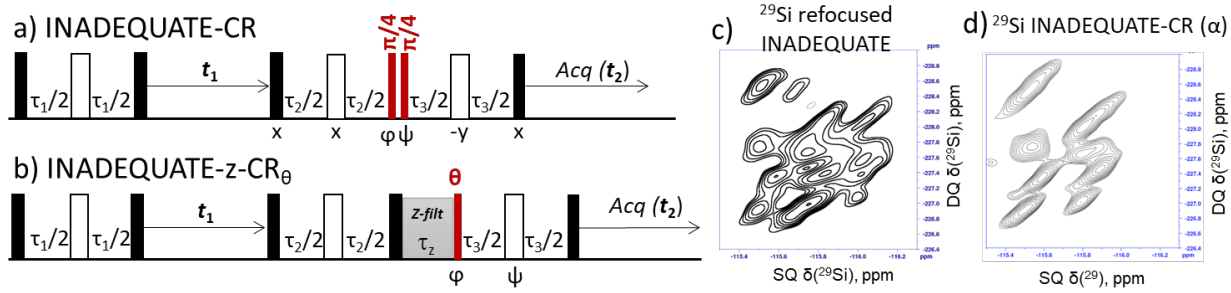

Figure 1: (a) INADEQUATE-CR and (b) INADEQUATE-z-CR_θ pulse sequences. Fragments of 2D ^{29}Si (c) refocused INADEQUATE and (d) pure-shift INADEQUATE-CR_α spectra of ^{29}Si-enriched β zeolite.

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A combined NMR, XRD and DFT study on Al^+-substituted $Na_{2-x}Zn_{1-x}Al_xCl_4$ with enhanced sodium ionic conductivity for solid-state batteries

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The high demand for lithium-ion batteries and potentially improved alternatives is fueling significant research in academia and industry. Sodium-based solid-state batteries (SSBs) are promising candidates, offering reduced cost (when selecting, other than Na, abundant raw materials) and improved safety.
The critical component of sodium SSBs is the solid sodium ion electrolyte. Metal halides have emerged as materials combining excellent mechanical processibility and electrode compatibility.[1] However, the low ionic conductivity problem remains unsolved (10^{-6}~10^{-5} S/cm). One possibility is the targeted introduction of vacancies, for example, via aliovalent substitution, to directly influence the ionic conductivity of solid ion conductors.[2–4]

In this work, we synthesized a series of Al^+ substituted $Na_{2-x}Zn_{1-x}Al_xCl_4$ with nominal x=0-1 using a mechanochemical approach to introduce Na^+ vacancies in the crystal lattice. We studied the influence of Al substitution on the Na^+ ionic conductivity using impedance spectroscopy (EIS), revealing a sudden increase above x=0.25 with a maximum at x=0.5 followed by a linear decrease for higher Al contents (Figure 1). In order to investigate this unexpected behavior for Na^+ conductivity in a solid solution of $NaAlCl_4$- Na_2ZnCl_4 we used a combined analytical approach of powder X-ray (and Neutron) diffraction, solid-state NMR spectroscopy and DFT calculations. In this way, the formation of different phases, Na^+ vacancy, and Al cation distribution are disentangled, as well as their contribution to the ionic conductivity. Indeed, the Rietveld refinements confirm that a two-phase system is forming to overcome a miscibility gap between Al and Zn. Furthermore, NMR and DFT revealed preferential ordered Na vacancy structures in layers for low Al contents in $Na_{2-x}Zn_{1-x}Al_xCl_4$ (x<0.25), while Al contents between x = 0.3-0.5 result in partially occupied layers. This indicates that Al contents can be tuned in order to maximize ionic conductivity by manipulating the vacancy-assisted Na migration pathways.

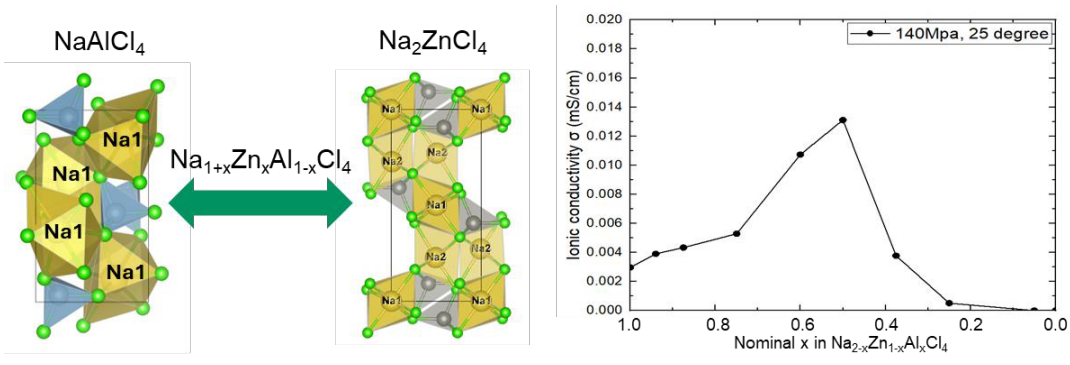

Figure 1: Left: crystal structures of $NaAlCl_4$ and Na_2ZnCl_4. Right: Na ionic conductivity as a function of nominal Al content x in $Na_{2-x}Zn_{1-x}AlCl_4$.

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Influence of Surface Chemistry on Water Diffusion Behavior in Hydrated Functionalized Mesoporous Organosilicates

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Water, one of the most significant substances on Earth, still exhibits some properties and behaviors that are not fully understood.[1] This includes its behavior in confinement.[2] Periodic mesoporous organosilicates (PMOs) are highly valuable for mimicking naturally confined environments and, therefore, with their tunable porosity and pore properties exploring water behavior under diverse conditions.[3]

PMOs are organic-inorganic hybrid materials composed of polysilsesquioxanes uniformly bridged by organic linkers. This unique structure enables the integration of the advantages of a highly ordered mesoporous framework with the tunability of the material's chemical and physical properties.[4] In this study, we investigated divinylbenzene-bridged PMO (DVB-PMO) and fluorinated divinylbenzene-bridged PMO (DVF-PMO) (Figure 1). Both materials exhibited a pore size of approximately 4 nm. Compared to MCM-41, which has similar pore dimensions, both PMOs demonstrated increased hydrophobicity. Notably, DVF-PMO showed greater hydrophobicity than DVB-PMO, as evidenced by water adsorption isotherms (Figure 1).

To investigate the behavior of water under confinement as a function of pore properties, diffusion measurements were conducted using ^{1}H pulsed-field gradient nuclear magnetic resonance (PFG-NMR) experiments and compared with those of pure MCM-41. The samples were examined at 95% relative humidity (RH) to ensure that the pores in all samples were completely filled with water. The measurement revealed a strong dependence of the diffusion coefficient on the hydrophilicity of the pore surface in the material.

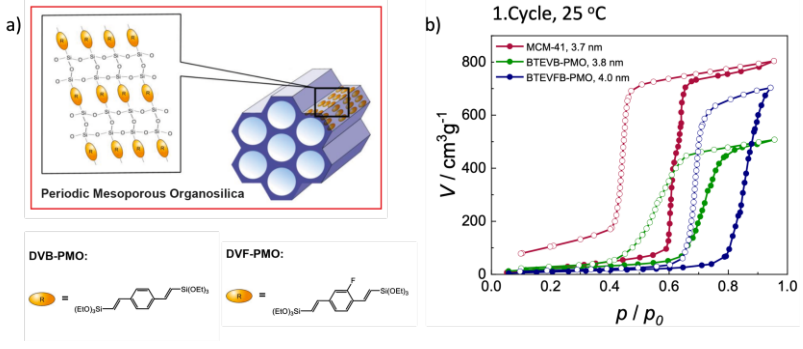

Figure 1: General structure of periodic mesoporous organosilica (PMOs) and definition of the two examined products DVB-PMO and DVF-PMO (a) with corresponding water sorption data (b) .[5]

Acknowledgements
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Probing the electronic structure of $LiCoO_2$ *via* variable temperature and *operando* NMR

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Since their introduction to the market in 1990, Li-ion batteries (LIBs) have revolutionised energy storage for devices, electric vehicles and on the grid. One of the most commercially successful cathode materials to date is lithium cobalt oxide (LCO), whose layered structure enables fast charge-discharge rates and high gravimetric capacities. As soon as LCO is delithiated, it undergoes an insulator-to-metal transition, attributed to the holes generated in the t_{2g} states on Co. Whilst this phenomenon has been investigated many times –*via* diffraction, Raman and optical spectroscopies, nuclear magnetic resonance (NMR) spectroscopy and magnetometry– a complete understanding of the charge distribution and compensation mechanism during charge has not yet been fully achieved, despite LCO's status as a model compound. Here, we present a novel methodology for studying LCO non-invasively using variable-temperature, *ex situ* and *operando* NMR, *operando* synchrotron X-ray diffraction and *ex situ* magnetometry, with the aim of understanding which sites the conduction electrons occupy and the role itinerant electrons play in charge compensation, structural distortions and degradation mechanisms. We leverage the presence of all three NMR-active nuclei in LCO to investigate the insulator-metal transition *via ex situ* ^{7}Li, ^{59}Co and ^{17}O variable temperature NMR, with *operando* NMR providing time resolution to local structural changes during the insulator-metal transition. The local structure obtained was combined with bulk electronic structural information provided by magnetometry and *operando* X-ray diffraction, resulting in an electronic picture where conduction holes are delocalised over Li and O ions and more localised over the Co ions.

Spin-Orbit Coupled GIPAW Calculation of NMR Chemical Shieldings

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Relativistic effects are crucial for calculating the chemical shielding of heavy elements. Effects are considerable from the fifth row of the periodic table[1,2] and essential for sixth row elements[3,4] and beyond. Such nuclei are ubiquitous in modern energy materials, necessitating an appropriate theoretical description for the solid-state.

Our work builds upon Yates *et al.*[5], who demonstrated a scalar relativistic ZORA[6] (Zeroth Order Relativistic Approximation) implementation within the Gauge-Including Projector Augmented Wave (GIPAW) method[7,8]. We are in the process of developing our method within the Vienna Ab Initio Simulation Package (VASP)[9].

Preliminary results on ^{119}Sn, ^{199}Hg, and ^{207}Pb systems confirm the importance of relativistic description for these nuclei[1,3,4] and reveal directions for further improvement of our method. Once complete, we are confident our method will substantially improve the support theory can offer to experiment for materials such as perovskites and III-V semiconductors.

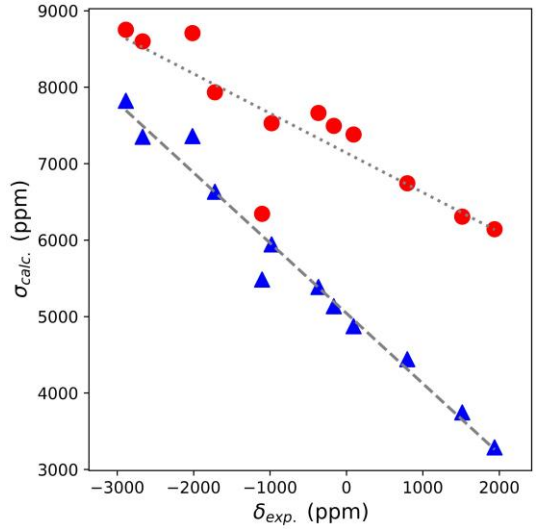

Figure 1: Correlation diagram for calculated versus experimental isotropic shielding of a ^{207}Pb-series[4]. Scalar ZORA results (l) with linear correlation $\sigma_{calc} = -0.52\ \delta_{exp} + 7140.43$ with $R^2 = 0.74$ (grey dotted). Spin-Orbit Coupled ZORA results(p) with linear correlation $\sigma_{calc} = -0.92\ \delta_{exp} + 5043.60$ with $R^2 = 0.97$ (gray dashed).

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Nanoencapsulation of metal complexes with antidiabetic properties. Characterization of the materials and loading challenges

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Diabetes mellitus is a major global health issue with increasing prevalence, prompting the need for innovative therapeutic solutions.[1] In response, we proposed the development of metal complexes comprised of chrysin, a natural flavonoid with antidiabetic properties[2], as complexation with metal ions is known to enhance the therapeutic potential of certain drugs.[3] Hereupon, Cu(II)- and Co(II)-chrysin metal complexes were synthesized and characterized using X-ray diffraction (XRD), infrared and UV-VIS spectroscopy to assess their structural integrity and composition. *In vitro* assays were done on Caco-2 and Hep-G2, respectively intestinal epithelial and hepatocyte cell lines, to evaluate the antidiabetic potential and the cytotoxicity of the synthesized compounds. Remarkably, the metal complexes significantly reduced intestinal glucose absorption and increased hepatic glucose uptake (Fig.1). However, the low water solubility of the metal complexes might limit their therapeutic efficacy. For that reason we encapsulated them into mesoporous silica nanoparticles. Different loading approaches were tested, followed by the characterization of the nanosystems as well as the integrity of the loaded compounds. In summary, this study provides valuable insights on the development and characterization of nanoencapsulated coordination compounds as novel therapeutic agents for managing illnesses as diabetes mellitus.

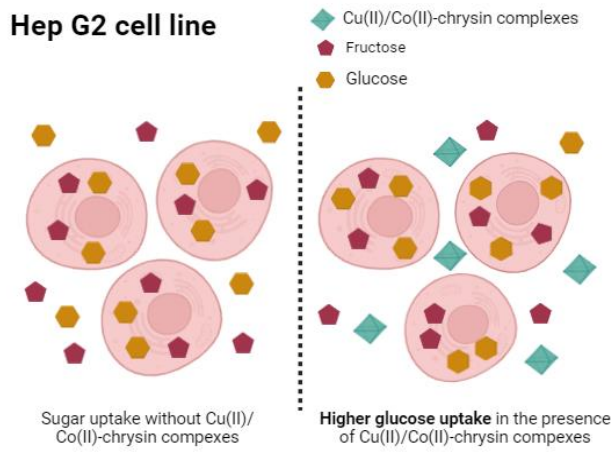

Figure 1: A schematic representation illustrating the impact of Cu(II)- and Co(II)-chrysin complexes on enhancing hepatic glucose uptake.

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The use of MD simulation and ML-predicted chemical shifts in understanding amorphous drugs

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Amorphous materials generally have very different physical properties to their crystalline forms, which poses a potentially major issue in developing active pharmaceutical ingredients (APIs). The higher free energy associated with amorphous materials can cause physical instability, leading to unwanted crystallisation. On the other hand, the higher solubility of amorphous forms compared to crystalline materials can be highly desirable, especially for APIs with poor aqueous solubility.

Although solid-state NMR spectroscopy can be readily applied to amorphous materials, the spatial disorder results in broad, often undistinctive line shapes that limit the usefulness of traditional "NMR crystallography". 2D experiments can be used to significantly reduce the overlap of individual resonances. However, in this work, we focus on key distinctive regions in 1D NMR spectra, associated with, (for example) tautomerisation in irbesartan. We compare 1D experimental NMR ^{1}H, ^{13}C and ^{15}N spectra with predicted spectra, demonstrating how these distinctive features can be effectively simulated and understood using molecular dynamics (MD).

The major challenges of predicting NMR spectra from disordered materials are firstly in producing models of disordered materials, and secondly computing chemical shifts for large, disordered models. A protocol has been developed that uses MD simulations to generate models of amorphous structures, while the second challenge has been addressed using a machine learning algorithm (ShiftML2[1]) to predict chemical shifts from snapshots of the MD simulations. We highlight the presence of significant dynamics in these amorphous models, and the need to average over the snapshots of the simulation to produce a reasonable chemical shift range at a given atomic site.

This work, which has been submitted to Faraday Transactions[2], will demonstrate (amongst other features) the influence of the torsion angle behaviour on the chemical shift of the carbon in the tetrazole group in the amorphous form of irbesartan, as well as the role of inter/intramolecular H-bonding in the chemical shift of the H atom in that same tetrazole group. This information can be readily extracted from the MD simulations and correlated directly with the chemical shift. Variable temperature production runs have also been performed, above and below the glass transition, to further analyse the dynamics in the system via the calculation of the mean diffusion coefficient.

NMR is a powerful probe of local chemical environments; it is however hampered in its utility by the high degree of molecular mobility in the amorphous forms of molecular drug materials. MD simulations provide a route to constructing and understanding these materials and ML facilitates rapid acquisition of precise chemical shift data, that would be computationally prohibitive to achieve via DFT calculations.

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Investigating Hard Carbons in Na-Ion Batteries Through X-ray Raman Scattering and *Operando* NMR Spectroscopy

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Current research efforts in the field of energy storage are focused on finding alternatives to lithium-ion batteries (LIBs). Among these are sodium-ion batteries (SIBs) due to the high availability of sodium, its low cost, and suitable redox potential.[1] Hard carbons, which are suitable for anodes in SIBs, exhibits good electrochemical performance and cyclic stability.[2] However, the exact mechanism of their operation remains unknown.[3] Unfortunately, the C and Na K-edges fall in the soft X-ray region (below 1 keV), where the penetration depth of X-rays is limited to about 10-100 nm. This limitation restricts characterization primarily to the surface of the samples. The low penetration depth, combined with the need for an in-vacuum setup, makes soft X-ray absorption spectroscopy (XAS) unsuitable for bulk studies in batteries. However, this challenge can be overcome by X-ray Raman Scattering (XRS), which uses hard X-rays to measure the absorption spectrum at the C and Na K-edge allowing analysis of the chemical state of C and Na and their interaction deep within the bulk material.[4] NMR spectroscopy is also a very powerful tool and can provide complementary information to that obtained by XRS.[5] The combination of XRS and NMR characterization offers a unique and comprehensive approach to the study of SIBs investigating not only the active material but also changes in the carbon anode structure and their impact on sodium insertion.

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Deciphering the Puzzle of Copper Integration in Imidazole-Based Systems and Their Amorphous Counterparts

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In this study, we delve into the fascinating world of Zeolitic Imidazolate Frameworks (ZIFs) and their glassy counterparts, exploring their unique structural properties and potential applications. ZIFs are a subclass of metal-organic frameworks (MOFs) with exceptional structural diversity and tuneable porosity, which makes them interesting materials for a variety of applications including gas separation and catalysis[1,2]. Their capacity to undergo transitions from crystalline to glassy states—a phenomenon that has attracted a lot of interest in materials science[3,4]—is especially intriguing. Furthermore, it has been demonstrated[5,6] that altering the synthetic conditions and substituting metal nodes can fine-tune the structure, melting behaviour, and mechanical properties of ZIFs.

This study explores the complex process of integrating copper into zinc-based ZIFs through both solvothermal and mechanochemical synthesis methods. $Cu(OAc)_2 \cdot 2H_2O$ was introduced during mechanochemical synthesis in an attempt to incorporate Cu^{2+} ions into the ZIF framework. The synthesis of copper-doped ZIFs with uniform copper distribution was confirmed by extensive characterization using a variety of analytical and spectroscopic techniques, such as energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), thermogravimetric and calorimetric analysis (TGA/DTA, DSC), diffuse reflectance ultraviolet–visible spectroscopy (DR UV–Vis) inductively coupled plasma optical emission spectroscopy (ICP-OES), and X-ray diffraction (XRD). Nevertheless, other spectroscopic methods, including solid-state nuclear magnetic resonance (ssNMR), Fourier Transform Infrared Spectroscopy (FTIR), and Raman spectroscopy, provided mixed results regarding the integration of copper into the framework. Furthermore, the quest for a reagent that enables the mechanochemical synthesis of higher percentages or pure copper ZIFs continues. As a result, our focus turned to solvothermal synthesis using various copper salts as metal sources. Leveraging insights from prior studies on copper-imidazole complexes and our own findings concerning mixed metal ZIFs, we explore the intricate structural dynamics of copper-based frameworks.

In conclusion, by unravelling the relationship between composition, structure, and thermal properties, we want to open up new avenues for the development and deployment of ZIF-based materials with tailored properties for gas storage and catalysis. Through the lens of solid-state NMR spectroscopy, we gain unprecedented insights into the intricate interplay between structure and function, paving the way for innovative advancements in materials science and beyond. Our comprehensive methodology, integrating solid-state NMR with various techniques like powder XRD (as well as non-ambient XRD), DSC, simultaneous TGA/DTA, SEM, Extended X-ray Absorption Fine Structure (EXAFS), X-ray Absorption Near Edge Structure (XANES), not only deepens our understanding of ZIFs but also holds promise for the development of next-generation materials with improved functionality and performance.

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Exploring Non-Covalent Structures from NMR Chemical Shifts in Solution and Solid States

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This presentation addresses the utilization of NMR chemical shifts to investigate noncovalent interactions in both solutions and solid states, Figure 1. The exploration of these interactions through experimental NMR chemical shifts, coupled with DFT calculations, reveals several key challenges.

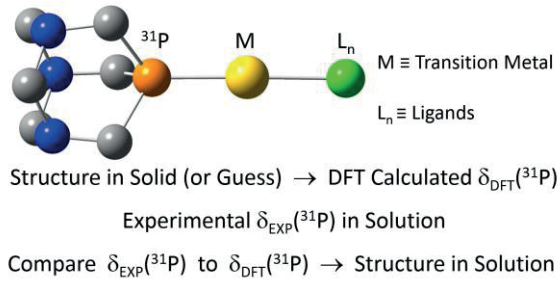

Figure 1: From NMR Chemical Shift to Structure in Liquid and Solid States.[1]

Firstly, the conversion of theoretically calculated NMR shieldings into the experimental chemical shift scale requires knowledge of the absolute shielding of a reference molecule. This issue is discussed using examples from ^{31}P and ^{15}N NMR.[2,3]

Secondly, determining the minimum needed size of model systems for calculations and accounting for external environmental influences are crucial aspects. For most systems, clear requirements exist, including an accurate geometry, the utilization of the Polarizable Continuum Model approximation, and consideration of all direct non-covalent interactions involving the NMR-active nucleus or fragments electronically conjugated with it. However, for molecular systems with highly polarizable electron density, these criteria prove insufficient. The addition of an external electric field becomes necessary, albeit its value must be determined through alternative means.[4,5]

Finally, the presentation addresses the need for relativistic corrections in DFT calculations of NMR chemical shifts, specifically in coordination complexes involving heavy metals. Such corrections are unnecessary for elements from the first to the third rows of the periodic table, provided they are not covalently bonded to heavy elements. However, for elements from the fifth period and beyond, these corrections are deemed indispensable, Figure 2.[6]

Figure 2: Applicability of Non-relativistic DFT Calculations of NMR Chemical Shifts in Pyridine-Metal Complexes.[6]

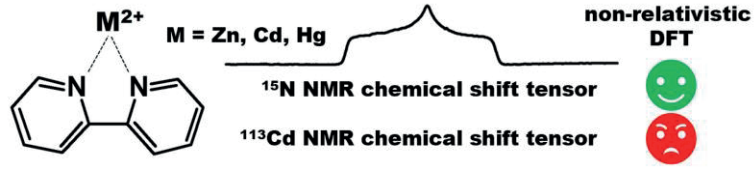

Figure 2: Applicability of Non-relativistic DFT Calculations of NMR Chemical Shifts in Pyridine-Metal Complexes.[6]

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Oxygen-17 Solid-State NMR Enables New Insights Into the Structure and Reactivity of Carbonate Salts

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Geological carbon sequestration is a viable climate change mitigation strategy for the safe and permanent storage of carbon dioxide (CO_2).[1,2] It relies on the formation of carbonate minerals, *e.g.* by reaction of CO_2 with phases containing alkali and alkaline-earth metal ions (Mg^{2+}, Ca^{2+}, or Na^{+}).[1,2] To better understand this process and identify the many potential carbonates that can form (*e.g.,* carbonates, bicarbonates, anhydrates, and hydrates) requires a detailed characterization. Solid-state nuclear magnetic resonance (ssNMR) is particular well-suited for the characterization of carbonates, since it can be used to study both crystalline and amorphous solids.

Recently, ^{17}O ssNMR has shown to be an exquisite probe of both the molecular-level structure and dynamics of CO_2 capture materials,[3] making it an attractive tool for studying the structures, properties, and reactivities of carbonate salts, using NMR-crystallography approaches. Despite these advantages, it remains a challenge due to the markedly low natural abundance of ^{17}O (0.04%), which usually necessitates isotopic enrichment prior to experimental acquisition, and is scarcely used due to the limited number and high-cost of ^{17}O-enriched precursors, like ^{17}O-labeled CO_2.

Herein, we demonstrate for the first time the mechanochemical oxygen-17 enrichment of carbonates and their detailed characterization using ATR-IR, powder X-ray diffraction (pXRD), and multinuclear ssNMR, with a particular emphasis on ^{17}O ssNMR.[4] First, we describe a novel, efficient, and inexpensive approach for the enrichment of carbonates using ^{18}O-labeled or ^{17}O-labeled water. Second, the successful synthesis and incorporation $^{18}O/^{17}O$ into the carbonates is demonstrated using ATR-IR, with their crystallinity and purity assessed by pXRD. Third, ^{17}O ssNMR spectra act as a unique spectral fingerprint able to distinguish between anhydrous and hydrated carbonates, and bicarbonate salts, providing information on the local structural environment and hydrogen-bonding. Finally, ^{17}O *in-situ* ssNMR experiments were performed, revealing new insights into the structure and reactivity of metal carbonates (Figure 1), crucial for the rational design, understanding, and NMR crystallographic refinement and prediction of hitherto carbon capture materials.

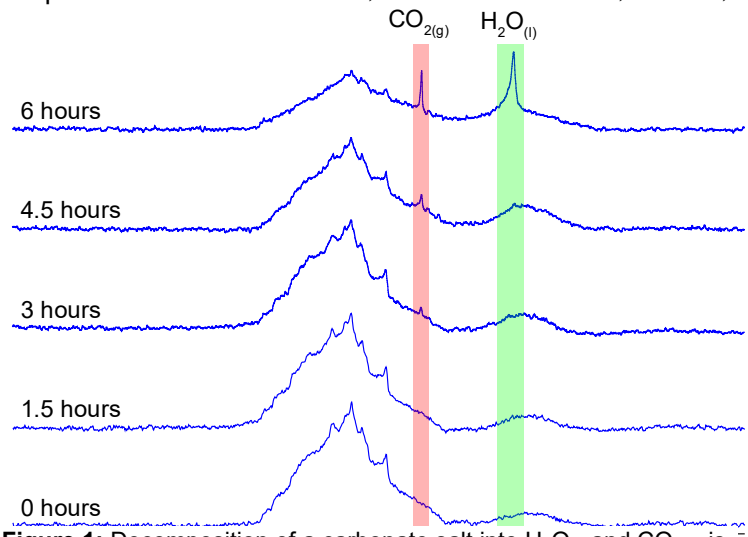

Figure 1: Decomposition of a carbonate salt into $H_2O_{(l)}$ and $CO_{2(g)}$ is revealed by *in-situ* ^{17}O MAS ssNMR spectra acquired at 14.1 T.

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Do looks matter? Impact of Morphology on Light-Induced Halide Segregation in Mixed Halide Perovskite Powders

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Lead halide perovskites, with their versatile ABX_3 lattice structure, have rapidly reached the efficiency of silicon solar cells, approaching the theoretical limit for single-junction cells[1]. They are also prime candidates for multi-junction solar cells due to the tunability of their band gap energy by adjusting the halide composition of e.g. iodide (I) and bromide (Br) in solid solutions forming mixed halide perovskites[2]. However, mixed halide perovskites, e.g. $MAPbI_{3-x}Br_x$, possessing band gap energies optimal for tandem solar cells, exhibit rather low phase stability. Light-induced halide segregation results in heterogenous compositions and in a deterioration of optoelectronic performance of solar cells.[3,4] Therefore, an understanding of halide migration kinetics and pathways, essential for the segregation process under illumination, as a function of perovskite morphology is crucial for a stability improvement.

In this study, we synthesized a suit of $MAPbI_{1.5}Br_{1.5}$ powders by a mechanochemical approach[5] following different synthesis strategies. We have used as educts either the precursors MAX and PbX_2 (X=I or Br) or parent perovskites $MAPbI_3$/$MAPbBr_3$, with and without the addition of additives, such as ionic liquids or bulky ammonium cations, during syntheses. The resulting powder perovskite properties were analyzed using complementary methods such as SEM, X-Ray diffraction, photoluminescence, and solid-state NMR spectroscopy, revealing apparently similar structural and optical characteristics among the different powders. However, the powders exhibit distinct morphologies, strongly affecting their response to light-induced halide segregation. In-situ XRD under 1 sun illumination reveals significant differences in halide segregation kinetics and recovery times between the different powders. This is emphasizing the pivotal role of morphology and different additives in governing the behavior of mixed halide perovskite powders under light exposure. These insights offer valuable guidance for the development of improved perovskite materials for solar energy conversion.

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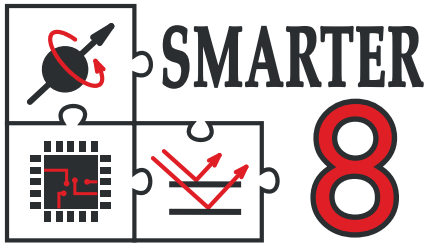

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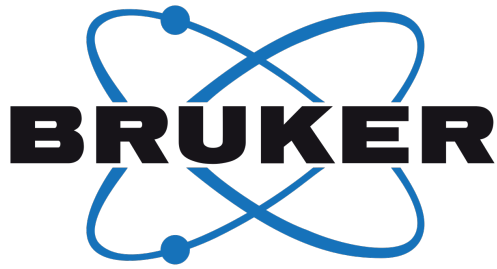
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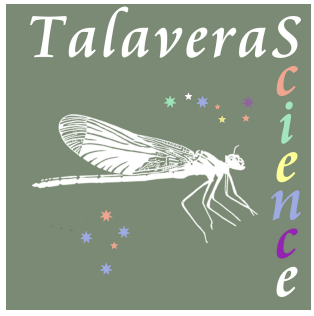
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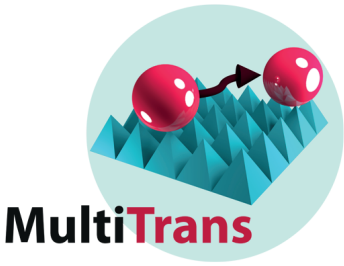
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