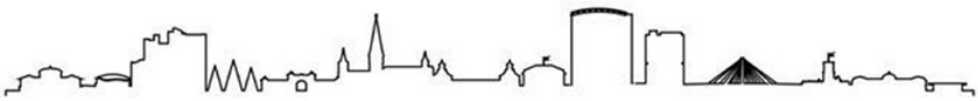
BOOK OF ABSTRACTS

GDCh

Gesellschaft Deutscher Chemiker



46th FGMR Annual Discussion Meeting

International Conference of the German Magnetic Resonance Community

September 15 – 18, 2025 Bonn, Germany

UNIVERSITÄT BONN

www.gdch.de/fgmr2025

www.fgmr2025.uni-bonn.de

Division of Magnetic Resonance
of the German Chemical Society

Opening remarks and organization

We are pleased to welcome you to Bonn for the 46th FGMR Annual Discussion Meeting of the Division of Magnetic Resonance (FGMR) of the German Chemical Society (GDCh).

The program will cover all topics where resonances of electron and/or nuclear spins are detected, including solution- and solid-state NMR/EPR as well as all types of other related topics like hyperpolarization, dynamics and diffusion, imaging, instrumentation, exotica, and much more. Besides three tutorials, 10 plenary lectures, and 15 invited talks over three parallel sessions, we will additionally select 43 of the contributed abstracts as promoted talks. Plenty of opportunities for in-depth discussions will be available during two extended poster sessions.

We hope that all participants will engage in intense knowledge exchange for jumpstarting novel developments within the magnetic resonance community all over the world.

Sincerely yours,
The scientific and organizing committees

Scientific Committee

Prof. Dr. Björn Cirzilius – University of Rostock

Dr. Guinevere Mathies - University of Konstanz

Prof. Dr. Jörg Matysik - University of Leipzig

Prof. Dr. Ann-Christin Pöppler - University of Würzburg

Prof. Dr. Olav Schiemann - University of Bonn

Prof. Dr. Monika Schönhoff - University of Münster

Dr. Karsten Seidel - BASF SE, Ludwigshafen

Prof. Dr. Thomas Wiegand - RWTH Aachen University

Local Organizing Committee

Dr. Dinar Abdullin

Hamed Alaei

Jonas Büger

Alina Geis

Kevin Kopp

Prof. Dr. Olav Schiemann

Yuliia Zuieva

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Acknowledgement

We thank our sponsors for supporting the conference:

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Prizes and Awards

Felix-Bloch Lecture:

Prof. Dr. Torsten Gutmann

Overhauser Award:

Dr. Vindra Sant

Ernst Awards:

Dr. Melina Daniilidis
Marvin Lenjer
Dr. Markus Matz

Otto-Stern Prize:

Prof. Dr. Paul Heitjans

Mo 15.9.	Tue 16.9.	Wed 17.9.	Thu 18.9.
	Chair T. F. Prinser	**Chair E. Bordignon**	**Chair R. Bittl**
	9:00 PL 1 F.H.T Allain **HS2**	9:00 PL 5 G. Jeschke **HS2**	9:00 PL 9 G. Buntkowski **HS2**
	9:30 PL 2 M. Lerche **HS2**	9:30 PL 6 O. Lafon **HS2**	9:30 PL 10 H. Sun **HS2**
10:00 onwards Registration	10:00 Coffee (**Foyer**)	10:00 Coffee (**Foyer**)	10:00 Coffee (Foyer)
	Chairs H. Schwalbe/C. Kay/B. Meier	**Chairs K. Seidel/J. Matysik/A. Blank**	**Chairs G. Mathies/D. Abdullin/O. Schiemann**
	10:30 Il 1/2/3 **HS3,5,7**	10:30 IL 7/8/9 **HS3,5,7**	10:30 IL 13/14/15 **HS3,5,7**
	10:55 L1/2/3 **HS3,5,7**	10:55 L19/20/21 **HS3,5,7**	10:55 L37/38/39 **HS3,5,7**
	11:15 L4/5/6 **HS3,5,7**	11:15 L22/23/24 **HS3,5,7**	11:15 L40/41/42 **HS3,5,7**
	11:35 L7/8/9 **HS3,5,7**	11:35 L25/26/27 **HS3,5,7**	
12:00-15:00 FGMR Board Meeting (**Bibliothek PC**)			**Chair B. Corzilius**
	11:55 Lunch & Poster (**Mensa**)	11:55 Lunch & Poster (**Mensa**)	11:35 HighQ **HS2**
Chair Kevin Kopp			11:40 Otto Stern Preis, Paul Heitjans **HS2**
12:30 T1 "Paramagnetische NMR" J. Koppe **HS2**	**Chairs D. Hinderberger/M. Schönhoff/A. Pöppl**	**Chairs R. Carmieli/C. Schmidt/U. Scheler**	
13:10 T2 "Liquid-State DNP" A. Kuzhelev **HS2**	13:30 IL 4/5/6 **HS3,5,7**	13:30 IL 10/11/12 **HS3,5,7**	12:40 Concluding (10 min) **HS2** O. Schiemann
13:50 T3 "In Cell EPR" M. Kasanmascheff **HS2**	13:55 L10/11/12 **HS3,5,7**	13:55 L28/29/30 **HS3,5,7**	
	14:15 L13/14/15 **HS3,5,7**	14:15 L31/32/33 **HS3,5,7**	15:00 Peldor Data Base Meeting **HS2**
Chair O. Schiemann	14:35 L16/17/18 **HS3,5,7**	14:35 L34/35/36 **HS3,5,7**	
15:00 Opening (Schiemann) **HS2**			
15:30 Ilya Kuprov "100 years of Spin" **HS2**	14:55 Coffee & Poster (odd) (**Mensa**)	14:55 Coffee & Poster (even) (**Mensa**)	
Chair B. Corzilius	**Chair B. Corzilius**	**Chair B. Corzilius**	
16:00 Intro Awards **HS2**	16:30 Bloch Lecture, Torsten Gutmann **HS2**	16:30 Overhauser Award, Vindra Sant **HS2**	
16:15 Ernst Awards **HS2**			
Melina Daniilidis, Marvin Lenier, Markus Matz	**Chair F.H.T. Allain**	**Chair G. Jeschke**	
	17:30 Magritek **HS2**	17:15 Bruker **HS2**	
Chair Corzilius	17:35 PL 3 J. Jelonnek **HS2**	17:20 PL 7 E. Bordignon **HS2**	
17:00 FGMR Member Assembley **HS2**	18:05 PL 4 R. Bittl **HS2**	17:50 PL 8 B. Diehl **HS2**	
19:00 Welcome Mixer (**Mensa**)	19:00 Young Scientists' Program **HSPC**	19:30 Boarding Ship	
	18:35 Subgroup AK EPR meeting **HS3**	20:00 Departure Ship/ Banquet	
	18:35 Subgroup Small Molecules meeting **HS5**		
	20:30 Schließung		

Scientific Programme

Monday, September 15, 2025

Registration

Foyer

11.00 a.m. **Registration (open until end of conference)**

FGMR Board Meeting

Library

12.00 p.m. **FGMR Board Meeting**

Tutorials

Chair: K. Kopp — Lecture hall 2

12.30 p.m.	**Paramagnetic Solid-State NMR: Challenges and Advances** J. Koppe, Lyon/FR
01.10 p.m.	**Basics of Dynamic Nuclear Polarization in Liquids** A. Kuzhelev, Frankfurt/DE
01.50 p.m.	**In-cell EPR** M. Kasanmascheff, Dortmund/DE

Opening Ceremony

Chair: O. Schiemann — Lecture hall 2

03.00 p.m.	**Opening** O. Schiemann
03.30 p.m.	**“Eine neue Kopenhagener Irrlehre”: 100 Years of Spin** I. Kuprov, Rehovot/IL

Ernst Awards

Chair: B. Corzilius — Lecture hall 2

04.00 p.m.	**Intro Awards** - B. Corzilius
04.15 p.m.	**Ernst award** - M. Dainiilidis
04.30 p.m.	**Ernst award** - M. Lenjer
04.45 p.m.	**Ernst award** - M. Matz

FGMR Member Assembley

Chair: B. Corzilius — Lecture hall 2

05.00 p.m. **FGMR Member Assembley**

Welcome Mixer

Mensa

07.00 p.m. **Welcome Mixer (open end)**

Scientific Programme

Tuesday, September 16, 2025

Plenary Session 1

Chair: T. F. Prisner — Lecture hall 2

09.00 a.m.	Plenary Lecture 1 **Molecular Basis for Primer Synthesis Initiation by DNA Primase** F. H.-T. Allain, Zürich/CH , P. Wu, Zürich/CH, F. F. Damberger, Zürich/CH, J. Zehnder, Zürich/CH, N. Schröder, Aachen/DE, N. Senning, Zürich/CH, G. Lipps, Muttenz/CH, T. Wiegand, Aachen/DE
09.30 a.m.	Plenary Lecture 2 **M. Lerche (tba)**

10.00 a.m. Coffee break — Foyer

Parallel Session 1
Conductors/Electrolytes

Chair: H. Schwalbe — Lecture hall 3

10.30 a.m.	Invited Lecture **Charge, ligand binding and chain dynamics of macromolecules** U. Scheler, Dresden/DE
10.55 a.m.	Speakers: J. Koch & A. Römer **Selective Excitation near Conductive Material Surfaces and Interfaces with Optimal Control** J. Kochs, Jülich/DE , A. Römer, Jülich/DE, M. Schatz, Jülich/DE, M. Streun, Jülich/DE, S. Jovanovic, Jülich/DE, S. Köcher, Jülich/DE, J. Granwehr, Jülich/DE
11.15 a.m.	**Exploring photo- and electrochemically induced paramagnetic ionic states in organic semiconductors by EPR spectroscopy** M. Mayländer, Oxford/GB , M. Ladwig, Oxford/GB, N. Curwen, Oxford/GB, C. Tait, Oxford/GB
11.35 a.m.	**Electrophoretic NMR-based Characterization of Charge and Mass Transport in Polymer Electrolytes** M. Schönhoff, Münster/DE , S. Buyting, Münster/DE

Parallel Session 2
Biosystems 1: Integrated Methods

Chair: C. Kay — Lecture hall 5

10.30 a.m.	Invited Lecture **Towards Understanding the Molecular Choreography of Proteins and Lipids in Myelin** D. Hinderberger, Halle (Saale)/DE , P. Kursula, Bergen/NO, S. Michler, Halle (Saale)/DE, E. Hingst, Halle (Saale)/DE, C. Schwieger, Halle (Saale)/DE, H. Hashemi Haeri, Halle (Saale)/DE
10.55 a.m.	**Integrative NMR Reveals an Intrinsically Disordered and Dynamic N-Terminus in SARS-CoV-2 NSP3** N. A. Lakomek, Düsseldorf/DE , K. Vormann, Jülich/DE, T. Tobias , Jülich/DE, F. T. Tucholski, Düsseldorf/DE, A. Cukkemane, Düsseldorf/DE, L. Nagel-Steger, Düsseldorf/DE, R. Bartenschlager, Heidelberg/DE, R. Biehl, Jülich/DE
11.15 a.m.	**Design of New Antimicrobial Peptides Guided by NMR-based Structural Analysis** D. Friedrich, Cologne/DE , M. Quagliata, Florence/IT, G. C. Petti, Cologne/DE, J. Grabeck, Cologne/DE, K. König, Cologne/DE, A. Rout, Lübeck/DE, A. M. Papini, Florence/IT, A. Mallagaray, Lübeck/IT, B. P. H. J. Thomma, Cologne/DE, I. Neundorf, Cologne/DE
11.35 a.m.	**Protein Folding at All Stages Observed by DNP-Enhanced Solid-State NMR** H. Heise, Düsseldorf/DE , L. Levorin, Jülich/DE, N. Becker, Düsseldorf/DE, B. Uluca-Yazgi, Jülich/DE, L. Gardon, Düsseldorf/DE, M. Kraus, Jülich/DE, P. Neudecker, Düsseldorf/DE, L. Gremer, Jülich/DE

Parallel Session 3
Hyperpolarization

Chair: B. Meier — Lecture hall 7

10.30 a.m.	Invited Lecture **Photo-CIDNP NMR in liquid and solid state** J. Matysik, Leipzig/DE
10.55 a.m.	**Mapping the Influence of Orientation and Distance of SCRP on solid Photo-CIDNP effect in a Multi-Tyrosine Flavoprotein System** R. Qin, Leipzig/DE , J. Hungerland, Oldenburg/DE, V. Rohr, Leipzig/DE, L. Gerhards, Oldenburg/DE, I. Solovyov, Oldenburg/DE, J. Matysik, Leipzig/DE
11.15 a.m.	**Magnetic Field-Dependent CIDNP in Biomimetic Flavin–Tryptophan Dyads** G. Musabirova, Leipzig/DE , T. Theiss, Leipzig/DE, A. Kyruitin, Novosibirsk/RU, I. Zhukov, Novosibirsk/RU, O. Morozova, Novosibirsk/RU, T. Gulder, Leipzig/DE, A. Yurkovskaya, Novosibirsk/RU, J. Matysik, Leipzig/DE

11.35 a.m.	**Polarizing Small Molecules via Parahydrogen-Induced Polarization and Spin Diffusion** B. Uluca-Yazgi, Jülich/DE , A. Singh, Jülich/DE, T. Karakaya, Jülich/DE, T. Chaloyard, Jülich/DE, J. Eills, Jülich/DE

11.55 a.m. Lunch / Poster — Mensa

Parallel Session 4
Polymers

Chair: D. Hinderberger — Lecture hall 3

01.30 p.m.	Invited Lecture **Wettability of mesoporous materials** C. Schmidt, Paderborn/DE , I. Lamata-Bermejo, Paderborn/DE, N. Lopez-Salas, Paderborn/DE, W. Keil, Paderborn/DE, Y. Zhao, Paderborn/DE
01.55 p.m.	**Exploring the Potential of ^{19}F NMR Spectroscopy for Determining Per- and Polyfluoroalkyl Substances (PFAS).** T. Zorn, Ludwigshafen am Rhein/DE , T. Schwidetzky, Ludwigshafen am Rhein/DE, T. Grün, Ludwigshafen am Rhein/DE
02.35 p.m.	**Solid-State NMR Studies of Intracrystalline Chain Dynamics in Ketone-Functionalized Polyethylene** K. Saalwächter, Halle/DE , A. Anuar, Halle/DE, A. Edalat, Halle/DE, L. Ringelhan, Halle/DE, Q. Yu, Halle/DE, A. Petzold, Halle/DE, T. Thurn-Albrecht, Halle/DE, M. Baur, Konstanz/DE, S. Mecking, Konstanz/DE

Parallel Session 5
Biosystems 2: Complexes

Chair: M. Schönhoff — Lecture hall 5

01.30 p.m.	Invited Lecture **Unique features of NMR of RNA** H. Schwalbe, Frankfurt/DE
01.55 p.m.	**Spotlight on the nucleotide: Phosphorus-31 solid-state NMR for the investigation of ATP hydrolysis in ATPases** N. Schröder, Aachen/DE , K. Sengupta, Mülheim/DE, L. Decamps, Mülheim/DE, S. De Beer, Mülheim/DE, T. Wiegand, Mülheim/DE
02.15 p.m.	**Unraveling the structure of the YopO-$(SycO)_2$ complex using pulsed dipolar EPR spectroscopy** A. Reuter, Bonn/DE , O. Schiemann, Bonn/DE
02.35 p.m.	**The coming of age of the DNA enzymes technology** M. Etzkorn, Düsseldorf/DE , J. Schmuck, Düsseldorf/DE, J. Borggräfe, Düsseldorf/DE, C. Ruth, Düsseldorf/DE, J. Victor, Düsseldorf/DE, A. Viegas, Düsseldorf/DE

Scientific Programme

Parallel Session 6
Hardware & AI

Chair: A. Pöppl — Lecture hall 7

01.30 p.m.	Invited Lecture **Recent trends in compact pulsed ESR systems and their applications** A. Blank, Haifa/IL
01.55 p.m.	**Dipstick EPR-on-a-chip sensors achieving sub-µM/G/√Hz sensitivity** A. Chu, Stuttgart/DE , M. Segantini, Berlin/DE, B. Alnajjar, Stuttgart/DE, M. Kern, Stuttgart/DE, K. Lips, Berlin/DE, J. Anders, Stuttgart/DE
02.15 p.m.	**Helium-3 magnetometers for high fields** P. Blümler, Mainz/DE , M. Fertl, Mainz/DE, H. Grafe, Dresden/DE, R. Graf, Mainz/DE, W. Heil, Mainz/DE
02.35 p.m.	**Ultrabroadband 1D and 2D NMR Spectroscopy** B. Luy, Karlsruhe/DE

Poster session - Coffee

Mensa

02.55 p.m. **Poster Session, combined with coffee**

Felix-Bloch Lectureship

Chair: B. Corzilius — Lecture hall 2

04.30 p.m.	**Intro Award** - B. Corzilius
04.45 p.m.	**Felix-Bloch Lectureship**

Industry Sponsor

Chair: F. H. T. Allain — Lecture hall 2

05.30 p.m. **Magritek**

Plenary Session 2

Chair: F. H. T. Allain — Lecture hall 2

05.35 p.m.	Plenary Lecture 3 **From Megawatt-Class Gyrotron Oscillators for Nuclear Fusion Devices to High-Power Microwave Sources for DNP-NMR Applications** J. Jelonnek, Karlsruhe/DE , M. Vöhringer, Karlsruhe/DE, K. Balaban, Karlsruhe/DE, A. C. Ulusoy, Karlsruhe/DE, A. Marek, Karlsruhe/DE, M. Thumm, Karlsruhe/DE
06.05 p.m.	Plenary Lecture 1 **Gadolinium Retention in Brain Tissue after in-vivo Injection of Contrast Agents** R. Bittl, Berlin/DE , L. Anderhalten, Berlin/DE

Scientific Programme

Subgroup Meeting

06.35 p.m. **Subgroup Meetings AK EPR (Lecture hall 3)**

06.36 p.m. **Subgroup Meeting Small Molecules (Lecture hall 5)**

Young Scientists

Lecture hall PC

07.00 p.m. **Young Scientists' Program**

08.00 p.m. Closing

Scientific Programme

Wednesday, September 17, 2025

Plenary Session 3

Chair: E. Bordignon — Lecture hall 2

09.00 a.m.	Plenary Lecture 5 **The EPR Hunter's Guide to Active Centres of Catalysts** G. Jeschke, Zürich/CH, M. Agrachev, Zürich/CH, K. Raue, Zürich/CH, J. W. A. Fischer, Sapporo/JP
09.30 a.m.	Plenary Lecture 6 **NMR observation of quadrupolar nuclei in materials using ultra-high magnetic fields, DNP and advanced experiments** O. Lafon, Lille/FR, Y. Kolyagin, Lille/FR, M. Hamdouna, Lille/FR, C. Moussa, Lille/FR, H. Nagashima, Tsukuba/JP, A. Rankin, Lille/FR, J. Trébosc, Lille/FR, F. Pourpoint, Lille/FR, L. Delevoye, Lille/FR, J.-P. Amoureux, Lille/FR

10.00 a.m. Coffee Break — Foyer

Parallel Session 7
Relaxation

Chair: K. Seidel — Lecture hall 3

10.30 a.m.	Invited Lecture **Miscible liquids experience phase separation in confinement: An NMR relaxation and diffusion study of binary fluids in mesoporous glass** S. Stapf, Ilmenau/DE, N. Siebert, Ilmenau/DE, B. Gizatullin, Ilmenau/DE, C. Mattea, Ilmenau/DE, P. Merle, Ilmenau/DE, A. Sara, Ilmenau/DE, C. Dreßler, Ilmenau/DE
10.55 a.m.	**Mechanistic Understanding of Polyester Hydrolases through Isotope-labelled Polyethylene terephthalate using MAS NMR.** E. Butenschön, Leipzig/DE, J. Matysik, Leipzig/DE, D. Huster, Leipzig/DE, C. Song, Leipzig/DE
11.15 a.m.	**Transverse Relaxation Optimized Spectroscopy in the Presence of Chemical Exchange at 1200 MHz** P. Neudecker, Düsseldorf/DE, A. Dingley, Jülich/DE, D. Willbold, Düsseldorf/DE
11.35 a.m.	**$R_{1\rho}$-relaxation at the rotary resonance condition** A. Krushelnitsky, Halle/DE

Scientific Programme

Parallel Session 8
DNP

Chair: J. Matysik — Lecture hall 5

10.30 a.m.	Invited Lecture **The Rise and Fall of Nuclear Spin Polarization** B. Meier, Karlsruhe/DE
10.55 a.m.	**Simulation of pulsed dynamic nuclear polarization in the steady state** S. A. Jegadeesan, Konstanz/DE , Y. Zhao, Massachusetts/US, G. Smith, St Andrews/GB, I. Kuprov, Rehovot/IL, G. Mathies, Konstanz/DE
11.15 a.m.	**Investigation of a Partially Fluorinated Matrix and Exploration of ^{19}F-^{13}C Cross Relaxation for Enabling ^{19}F MAS DNP** E. R. Bensons, Rostock/DE , A. C. Pinon, Gothenburg/SE, B. Corzilius, Rostock/DE
11.35 a.m.	**Spin-spin interaction in Conjugated Trityl Biradicals: A journey through different coupling regimes** K. L. Kopp, Bonn/DE , F. Herpell, Bonn/DE, O. Schiemann, Bonn/DE

Parallel Session 9
Quantum Sensors & Information Technology

Chair: A. Blank — Lecture hall 7

10.30 a.m.	Invited Lecture **From EPR Spectroscopy to MASERs: A Dielectric Journey** W. M. Kay, Saarbrücken/DE
10.55 a.m.	**Quantum sensing with spin defects in boron nitride nanotubes** R. Rizzato, Munich/DE , A. Hidalgo, München/DE, L. Nie, München/DE, E. Blundo, München/DE, N. R. von Grafenstein, München/DE, J. J. Finley, München/DE, D. B. Bucher, München/DE
11.15 a.m.	**Development of a microscale NV-NMR spectroscopy at 1 T** U. Banerjee, Munich/DE , J. C. Hermann, Munich/DE, R. D. Allert, Munich/DE, A. Blank, Haifa/IL, D. B. Bucher, Munich/DE
11.35 a.m.	**EPR Studies of Molecular Qubit Assemblies** J. van Slageren, Stuttgart/DE , J. Wischnat, Stuttgart/DE, L. Tesi, Stuttgart/DE, P. Thielert, Frankfurt/DE, J. Werner, Karlsruhe/DE, A.-N. Unterreiner, Karlsruhe/DE, S. Richert, Frankfurt/DE

11.55 a.m. Lunch / Poster — Mensa

Parallel Session 10
Methods

Chair: R. Carmieli — Lecture hall 3

01.30 p.m.	Invited Lecture **Understanding Homogeneous Catalysis with high-resolution operando Flow NMR Spectroscopy** U. Hintermair, Bath/GB
01.55 p.m.	**IltPy : A python library for inverse Laplace transform of magnetic resonance data** D. T. Daniel, Jülich/DE , C.H. Bartsch, Jülich/DE, F.P. Bereck, Jülich/DE, R.A. Eichel, Jülich/DE, S. Köcher, Jülich/DE, C. Scheurer, Jülich/DE, J. Granwehr, Jülich/DE
02.15 p.m.	**Robust Bilinear Rotations and the HUGE-BIRD** Y. T. Woordes, Eggenstein-Leopoldshafen/DE , T. Reinsperger, Ettlingen/DE, S. Ehni, Fallanden/CH, B. Luy, Eggenstein-Leopoldshafen/DE
02.35 p.m.	**Identifying and overcoming resolution barriers in ^{19}F ENDOR** A. Meyer, Göttingen/DE , A. Kehl, Göttingen/DE, L. Sielaff, Göttingen/DE, M. L. Rämisch, Göttingen/DE, M. Bennati, Göttingen/DE

Parallel Session 11
Phases, Biometerials

Chair: C. Schmidt — Lecture hall 5

01.30 p.m.	Invited Lecture **In situ NMR Spectroscopy – A Versatile Tool to Study Framework Flexibility in Materials** E. Brunner, Dresden/DE
01.55 p.m.	**Phase separation in supercooled water/glycerol mixtures probed by ih-RIDME** M. Yulikov, Zurich/CH , S. Kuzin, Göttingen/DE
02.15 p.m.	**Phase Transition of PBLG: Characteristics and Usefulness for Structure Determination** F. Hoffmann, Karlsruhe/DE , G Guthausen, Karlsruhe/DE, Y Woordes, Karlsruhe/DE, B Luy, Karlsruhe/DE
02.35 p.m.	**On the brink of collapse – interior design of thermo-responsive multicompartment micelles shown by NMR spectroscopy** J. Żmuda, Würzburg/DE , A.-C. Pöppler, Würzburg/DE

Scientific Programme

Parallel Session 12
Biosystems 3: In Membrane & In Cell

Chair: U. Scheler — Lecture hall 7

01.30 p.m.	Invited Lecture **Multi-Contrast MRI: A Comprehensive Window into Brain Microstructure** S. Boretius, Göttingen/DE
01.55 p.m.	**Towards investigation of protein conformations in cells with EPR spectroscopy** Y. Limbach, St Andrews/GB , B. E. Bode, St Andrews/GB, O. Schiemann, Bonn/DE
02.15 p.m.	**Structural basis of apoptosis induction by the mitochondrial voltage dependent anion channel** F. Hagn, Garching/DE , M. Daniilidis, Garching/DE, U. Günsel, Garching/DE, G. Broutzakis, Münster/DE, R. Janowski, Neuherberg/DE, K. Leitl, Garching/DE, D. Niessing, Neuherberg/DE, C. Gatsogiannis, Münster/DE
02.35 p.m.	**Characterisation of a fold in TANGO1 evolved from SH3 domains for the export of bulky cargos** R. Stoll, Bochum/DE , J. Auch, Bochum/DE, O. Arnolds, Bochum/DE

Poster session - Coffee

Mensa

02.55 p.m. **Poster Session, combined with coffee**

Overhauser Award

Chair: B. Corzilius — Lecture hall 2

04.30 p.m.	**Intro Awards** - B. Corzilius
04.45 p.m.	**Overhauser Award** - V. Sant

Industry Sponsor

Chair: G. Jeschke — Lecture hall 2

05.15 p.m. **Bruker**

Scientific Programme

Plenary Session 4

Chair: G. Jeschke — Lecture hall 2

05.20 p.m.	Plenary Lecture 7 **An integrative approach to unveil the structural basis of the indirect inhibition of apoptosis** E. Bordignon, Genf/CH
05.50 p.m.	Plenary Lecture 8 **HEteronuclear Referencing for METRologic Isotope Calibration (HERMETRIC)** B. W. K. Diehl, Köln/DE , J. Waldthausen, Köln/DE

Conference Dinner - Ship Cruise

07.30 p.m. **Baording Ship**

08.00 p.m. **Departure Ship / Banquet**

Scientific Programme

Thursday, September 18, 2025

Plenary Session 5

Chair: R. Bittl — Lecture hall 2

09.00 a.m.	Plenary Lecture 9 **Parahydrogen Induced Polarization of Biomolecules – From Amino Acids to Mini-Proteins and Biopolymers** G. Buntkowsky, Darmstadt/DE
09.30 a.m.	Plenary Lecture 10 **Configurational and conformational analysis of cyclic peptides and flexible natural products using anisotropic NMR spectroscopy and density functional theory** H. Sun, Berlin/DE , A. F. Ketzel, Berlin/DE, C. J. Schattenberg, Berlin/DE

10.00 a.m. Coffee BreakFoyer

Parallel Session 13
Molecules

Chair: G. Mathies — Lecture hall 3

10.30 a.m.	Invited Lecture **EPR Study of charge transfer co-crystals Structure/Function Relationship** R. Carmielli, Rehovot/IL , K. Kopp, Bonn/DE, O. Cohen, Rehovot/IL, E. Edinach, Rehovot/IL, C. Fontanesi, Modena/IT, L. Shimon, Rehovot/IL, O. Schiemann, Bonn/DE
10.55 a.m.	**Probing the Magnetic Susceptibility Tensor of an Europium(III) complex by Paramagnetic Solid-state NMR** H. Busch, Aachen/DE , C. Zocher, Leipzig/DE, L. Günzel, Leipzig/DE, E. Bartalucci, Aachen & Mühleheim/DE, J. Koppe, Lyon/FR, B. Kersting, Leipzig/DE, T. Wiegand, Aachen & Mühlheim/DE
11.15 a.m.	**A Monosubstituted C(0) Atom in its Triplet State: Expanding the Family of Carbon-centered Diradicals** Y. Kutin, Dortmund/DE , T. Koike, Sendai/JP, M. Drosou, Mülheim/DE, A. Schnegg, Mülheim/DE, D. A. Pantazis, Mülheim/DE, M. M. Hansmann, Dortmund/DE, M. Kasanmascheff, Dortmund/DE

Parallel Session 14
Solid Materials

Chair: D. Abdullin — Lecture hall 5

10.30 a.m.	Invited Lecture **An EPR Study of the Incorporation of Paramagnetic Divalent Metal Ions in Solids** A. Pöppl, Leipzig/DE
10.55 a.m.	**In situ EPR Spectroscopy for the Detection of Dihydrogen Isotopes Adsorbed on Metal-Organic Frameworks** M. F. Lukman, Leipzig/DE , S. Schlayer, Leipzig/DE, A. Pöppl, Leipzig/DE
11.15 a.m.	**Zero-Field Splitting and Electric Field Effects in Fe^{3+} Centers in Quantum Paraelectrics** I. Zdeg, Brno/CZ , O. Laguta, Brno/CZ, V. Laguta, Prague/CZ, P. Neugebauer, Brno/CZ

Parallel Session 15
Batteries

Chair: O. Schiemann — Lecture hall 7

10.30 a.m.	Invited Lecture **Solid-state NMR of Li-ion batteries: Applications to self-healing binders and aqueous cells** K. Märker, Grenoble/FR , T. Patranika, Uppsala/SE, L. Abboud, Grenoble/FR, K. Lahtinen, Uppsala/SE, S. Paul, Grenoble/FR, G. De Paëpe, Grenoble/FR, A. J. Naylor, Uppsala/SE, J. Mindemark, Uppsala/SE, K. Edström, Uppsala/SE, G. Hernández, Uppsala/SE
10.55 a.m.	**From Model Systems to Real Cells: Investigating Lithium Equilibria in Batteries Using T_1 NMR** P. Schleker, Jülich/DE , B. Wolff, Jülich/DE, V. Barysch, Jülich/DE, D. Daniel, Jülich/DE, P. Jakes, Jülich/DE, R.-A. Eichel, Jülich/DE, J. Granwehr, Jülich/DE
11.15 a.m.	**Understanding the behaviour of $LiCoO_2$ positive electrodes in aqueous lithium-ion batteries using solid-state NMR spectroscopy** L. Abboud, Grenoble/FR , G. De Paëpe, Grenoble/FR, K. Märker, Grenoble/FR

Industry Sponsor

Chair: B. Corzilius — Lecture hall 2

11.35 a.m. **High Q**

Scientific Programme

Otto Stern Awards

Chair: B. Corzilius — Lecture hall 2

11.40 a.m.	**Intro Awards** - B. Corzilius
11.55 a.m.	**Otto Stern Award** - P. Heitjans

Concluding

Chair: O. Schiemann — Lecture hall 2

12.40 p.m. **Concluding**

01.00 p.m. End of Conference

Meeting

Lecture hall 2

03.00 p.m. **Peldor Data Base Meeting**

List of Posters

P01 **Investigating the Protein-RNA Dynamics of CRISPR Cas13a using EPR Spectroscopy**
C. Allar, Bonn/Deutschland, F. Zahnen, Bonn/DE, A. Zalfen, Bonn/DE, O. Schiemann, Bonn/DE

P02 **Development of a High Temperature Operando NMR Probe Head for Electrochemical Applications**
S. Amanzadeh Salout, Dresden/Deutschland, S. Paasch, Dresden/DE, E. Brunner, Dresden/DE, O. Pecher, Erfurt/DE, P. Lepucki, Erfurt/DE, M. Braun, Erfurt/DE

P03 **Engineering Flavoprotein-Based Tags for Enhanced Sensitivity in Hyperpolarized EPR Spectroscopy**
V. Apet, Leipzig/Deutschland, S. Krebs, Leipzig/DE, F. Engelberger, Leipzig/DE, M. Elgeti, Leipzig/DE, J. Meiler, Leipzig/DE, I. Coin, Leipzig/DE

P04 **The effect of acquired mutations on the structure and function of viral potassium ion channels**
P. Asrani, Bochum/Deutschland, A. Elgendy, Bochum/DE, A. Zeipelt, Bochum/DE, L. Schäfer, Bochum/DE, G. Seebohm, Münster/DE, R. Stoll, Bochum/DE

P05 **Characterization of a fold in TANGO1 evolved from SH3 domains for the export of bulky cargos**
J. Auch, Bochum/Deutschland, O. Arnolds, Stockholm/SE, S. Pütz, Bochum/DE, R. Stoll, Bochum/DE

P06 **DNP at 0.34 T for the Investigation of Batteries**
V. M. Barysch, Jülich/Deutschland, B. Wolff, Jülich/DE, M. Streun, Jülich/DE, P. Jakes, Jülich/DE, P. P. M. Schleker, Jülich/DE, J. Granwehr, Jülich/DE, R. A. Eichel, Jülich/DE

P07 **Investigations on Exchange Kinetics in a multivalent Xenon Host for 129Xe HyperCEST MRI**
V. Bayer, Heidelberg/Deutschland, J. Jayapaul, Heidelberg/DE, L. Schröder, Heidelberg/DE

P08 **NMR studies of a new RNA alkylating ribozyme**
I. Bessi, Würzburg/Deutschland, C. P. M. Scheitl, Würzburg/DE, E. Dorinova, Würzburg/DE, C. Höbartner, Würzburg/DE

P09 **Halbach 2.0 – Creating homogenous fields with finite size magnets**
P. Blümler, Mainz/Deutschland, I. Rehberg, Bayreuth/DE

P10 **Distinct Valence States in Minimal FeFe-Hydrogenases**
S. Boschmann, Dortmund/Deutschland, M. Heghmanns, Dortmund/DE, S. Yadav, Mülheim/DE, C. Brocks, Bochum/DE, T. Happe, Bochum/DE, D. Pantazis, Mülheim/DE, M. Kasanmascheff, Dortmund/DE

P11 **Selective Labeling and Measurement of Biomolecules for Multi-Spin EPR Distance Analysis**
J. Bürger, Bonn/Deutschland, O. Schiemann, Bonn/DE

P12
Ç Dağ, Istanbul/Türkei, M. Lambert, Frankfurt/DE, F. Löhr, Frankfurt/DE, P. Güntert, Frankfurt/DE, V. Dötsch, Frankfurt/DE

List of Posters

P13 **Solvent-Dependent Photo-CIDNP Effects in Synthetic Donor-Acceptor Diads**
D. Denisov, Leipzig/Deutschland, A. Sajadi, Leipzig/DE, G. Musabirova, Leipzig/DE, T. Theiss, Leipzig/DE, L. Gerhards, Oldenburg/DE, I. Solov'yov, Oldenburg/DE, T. Gulder, Leipzig/DE, J Matysik, Leipzig/DE

P14 **Electrophoretic NMR-based Determination of Transference Numbers in Polymer and Post-Li Electrolytes**
D. M. Feld, Münster/Deutschland, M. Schönhoff, Münster/DE

P15 **Evaluating Site-Specific Isotopic Labelling Strategies for the Solid-State NMR**

Analysis of Polymeric Micelles with Low Guest Loadings
A. Fleck, Würzburg/Deutschland, A.-C. Pöppler, Würzburg/DE

P16 **A Superconducting Resonator-Based Platform for Advanced EPR Distance Methodology and Applications**
A. Gamble Jarvi, Waterloo/Kanada, T. Borneman, Waterloo/CA

P17 **Solid-State NMR Investigation of Volatile Organic Compounds Adsorption in DUT-134 (Cu)**
B. Gao, Dresden/Deutschland, R. Engemann, Dresden/DE, S. Kaskel, Dresden/DE, E. Brunner, Dresden/DE

P18 **Amyloid fibril formation kinetics of low-pH denatured bovine PI3K-SH3 monitored by three different NMR techniques**
L. Gardon, Düsseldorf/Deutschland, N. Becker, Düsseldorf/DE, N. Rähse, Düsseldorf/DE, C. Höbling, Düsseldorf/DE, A. Apostoldis, Düsseldorf/DE, C. M. Schulz, Düsseldorf/DE, K. Bochinsky, Jülich/DE, L. Gremer, Düsseldorf/DE, N. L. Lakomek, Düsseldorf/DE

P19 **19F MAS NMR Spectroscopy for Structural Elucidation of Novel TADF Materials**
R. Graf, Mainz/Deutschland, C. Haese, Ludwigshafen/DE, O. Sachnik, Mainz/DE, P. V. M. Blom, Mainz/DE

P20 **Structural Characterization of Phases in Synthetic Apatites and Mouse Bone Using 43Ca DNP NMR Correlation Experiments at 30 K**
Z. Grilli, Grenoble/Frankreich, S. Paul, Grenoble/FR, A. Nelson, Paris/FR, W. Papawassiliou, Grenoble/FR, C. Gervais, Paris/FR, D. Laurencin, Montpellier/FR, G. De Paëpe, Grenoble/FR

P21 **Study of nuclear magnetization transfer between water and ice phases in nanoporous solids**
A. Gutierrez, Leipzig/Deutschland, R. Valiullin, Leipzig/DE

P22 **Following the Binding of crRNA to Cas13a in the Time Domain by Pulsed Electron-Electron Double Resonance**
A. Haardt, Bonn/Deutschland, O. Schiemann, Bonn/DE, U. B. Kaupp, Bonn/DE

P23 **The tale of a stable phenoxazine radical: EPR and X-ray studies with application perspectives**
M. Hryniuk, Wrocław/Polen, A. Białońska, Wrocław/PL, M. Witwicki, Wrocław/PL

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P24 **Solid-State NMR Insights into the Structure-Property Relationship in Hybrid Perovskites**
F. Hu, Berlin/Deutschland, P. B. Groszewicz, Berlin/DE, K. Lips, Berlin/DE

P25 **There and Back Again - the journey of a magnetic transfer between 1H and 14N nuclei under fast MAS.**
L. Kiesewalter, Würzburg/Deutschland, A-C. Pöppler, Würzburg/DE

P26 **Rotational Resonance for the Selective Acceleration of Spin Diffusion Pathways under Site-Specific DNP**
J. Klütz, Rostock/Deutschland,

P27 **NMR-based analysis of the structure and dynamics of cargo-binding domain of TANGO1 from Drosophila melanogaster**
E. Kriukov, Bochum/Deutschland, O. Arnolds, Bochum/DE, R. Stoll, Bochum/DE

P28 **Isoleucine Side Chains as Reporters of Conformational Freedom in Protein Folding Studied by DNP-Enhanced NMR**
L. Levorin, Düsseldorf/Deutschland, N. Becker, Düsseldorf/DE, B. Uluca-Yazgi, Düsseldorf/DE, L. Gardon, Düsseldorf/DE, M. Kraus, Düsseldorf/DE, P. Neudecker, Düsseldorf/DE, L. Gremer, Düsseldorf/DE, H. Heise, Düsseldorf/DE

P29 **Unraveling the Internal Dynamics of p38α through Stereospecific Methyl Labeling in Solid-State NMR**
F. Lindemann, Dortmund/Deutschland, S. Vasa, Dortmund/DE, R. Linser, Dortmund/DE

P30 **Investigation of the Role of Histidines in the inward directed proton-pump Xenorhodopsin**
A. Mayer, Frankfurt/Deutschland, J. Fischer, Frankfurt/DE, S. Lentge, Frankfurt/DE, J. Becker-Baldus, Frankfurt/DE, C. Glaubitz, Frankfurt/DE

P31 **In situ Monitoring of Lithium Metal Dendrites using EPR-on-a-Chip (EPRoC)**
M. Perez, Berlin/Deutschland, A. Freytag, Berlin/DE, M. Kern, Stuttgart/DE, J. Anders, Stuttgart/DE, P. B. Groszewicz, Berlin/DE, K. Lips, Berlin/DE

P32 **Exploiting Eddy Currents – Optimal Control in NMR for Conductive Surface-Selectivity**
A. J. Römer, Jülich/Deutschland, J. F. Kochs, Jülich/DE, M. Schatz, Jülich/DE, M. Streun, Jülich/DE, S. Jovanovic, Jülich/DE, S. S. Köcher, Jülich/DE, J. Granwehr, Jülich/DE

P33 **Very Fast Bioorthogonal Spin Labeling with Tetrazin-Substituted Gd3+ Complexes**
J. Rüter, Bielefeld/Deutschland, A. Godt, Bielefeld/DE

P34 **X-band and Q-band EPR studies of multi-nitroxide adducts as potential MRI CAs**
E. Shirdel, Bellatera/Spanien, D. Abdulin, Bonn/DE, X. Wang, Bellatera/ES, A. Puig Martin, Bellatera/ES, H. Alaei, Bonn/DE, V. Lloveras, Bellatera/ES, O. Schiemann, Bonn/DE, J. Vidal Gancedo, Bellatera/ES

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P35 **Investigating 1H Polarization transfer via Spin Diffusion in PHIP Experiments**
A. Singh, Jülich/Deutschland, B. Uluca-Yazgi, Jülich/DE, T. Karakaya, Jülich/DE, J. Eills, Jülich/DE

P36 **Heterocyclic Staudinger ligation for spinlabelling with GdIII-complexes**
E. Stratmann, Bielefeld/Deutschland, X. Yao, Bielefeld/DE, M. Qi, Bielefeld/DE, E. Landwehr, Konstanz/DE, M. Drescher, Konstanz/DE, A. Godt, Bielefeld/DE

P37 **DCODE- a modern HOSE Code alternative?**
S. Thomas, Potsdam/Deutschland, H. M. Möller, Potsdam/DE

P38 **Very fast spinlabeling with GdIII complexes of different line widths**
S. Tönsing, Bielefeld/Deutschland, X. Yao, Bielefeld/DE, J. Bohm, Bielefeld/DE, M. Qi, Bielefeld/DE, E. Stratmann, Bielefeld/DE, E. Landwehr, Konstanz/DE, M. Drescher, Konstanz/DE, A. Godt, Bielefeld/DE

P39 **Advanced Analysis of Parabens via HPLC-HSQC on a Benchtop NMR**
J. Tratz, Karlsruhe/Deutschland, M. Gaborieau, Karlsruhe/DE, M. Matz, Karlsruhe/DE, M. Pollard, Karlsruhe/DE, M. Wilhelm, Karlsruhe/DE

P40 **Covalent doping for compartment-selective DNP-NMR analysis of polymer micelles**
K. Ulrich, Würzburg/Deutschland, A.-C. Pöppler, Würzburg/DE

P41 **Effect of Pore Hierarchy on Transport of Methane in Carbon Material**
J. Wang, Leipzig/Deutschland, Y. Cheng, Xuzhou/CN, R. Valiullin, Leipzig/DE

P42 **Exploring acetylene bridged Bis-Trityls as possible candidates for J-driven Dynamic Nuclear Polarization**
L. Westhofen, Bonn/Deutschland, K. Kopp, Bonn/DE, T. Hett, Bonn/DE, O. Schiemann, Bonn/DE

P43 **Evaluation of 13C Satellite Decoupling Techniques for Accurate Quantitative 1H NMR spectra**
T. Zorn, Ludwigshafen am Rhein/Deutschland, C. Adam, Ludwigshafen am Rhein/DE

Lecture Abstracts

Paramagnetic Solid-State NMR: Challenges and Advances

Jonas Koppe
Centre de RMN à Très Hauts Champs de Lyon (UMR 5082 – CNRS, ENS Lyon, UCB Lyon 1), Université de Lyon, 5 Rue de la Doua, 69100 Villeurbanne, France.

Solid-state nuclear magnetic resonance (NMR) studies of paramagnetic materials generally pose several theoretical and experimental challenges. Hyperfine couplings between unpaired electrons and surrounding nuclei are complex to describe and often result in fast-decaying signals as well as broad resonances. However, the field has seen tremendous progress over the past decades, driven in particular by technological advances that now allow the routine application of magic-angle spinning (MAS) at and beyond 100 kHz, new excitation and inversion radio-frequency pulses relying on amplitude and phase modulation, and the development of new theoretical frameworks that enable a comprehensive description of the effects of hyperfine coupling.

This tutorial will cover the theoretical foundations of paramagnetic NMR, including the origins and modeling of the various contributions to the paramagnetic shift and shift anisotropies. Interpretation of these spectral features heavily relies on quantum-chemical computations, the most promising approaches of which will also be discussed. Furthermore, strategies for tailored broadband pulse schemes incorporated into one- and two-dimensional NMR experiments under ultra-fast MAS conditions will be presented. Examples from recent work on catalysts, battery materials, spin-crossover complexes, and molecular machines will illustrate the application of these methods in practice.

Basics of Dynamic Nuclear Polarization in Liquids

A. Kuzhelev, Frankfurt/Germany

Dr. Andrei Kuzhelev, Goethe University Frankfurt am Main, Institute of Physical and Theoretical Chemistry, Max-von-Laue-Str. 7, 60438 Frankfurt am Main, Germany

Dynamic Nuclear Polarization (DNP) is a powerful technique that significantly enhances the sensitivity of NMR spectroscopy by transferring substantial polarization from electron spins to nuclear spins. While DNP has been successfully applied to solid-state systems, its use in liquid environments remains limited, which presents challenges for researchers, especially at high magnetic fields.

This tutorial aims to provide a comprehensive understanding of liquid-state DNP. It will begin with a definition of its core principles and an exploration of the constraints that currently hinder its widespread application. The presentation will include an examination of the current applications of liquid-state DNP at both low and high magnetic fields, with an emphasis on the effectiveness of various polarizing agents and the crucial role of molecular diffusion. Additionally, it will discuss the DNP mechanisms applicable to liquid systems, including the Overhauser effect and the solid effect.

In conclusion, the future of liquid-state DNP will be addressed, highlighting its potential applications across diverse fields such as biology, catalysis, and materials science.

In-cell EPR

M. Kasanmascheff, Dortmund/DE

TU Dortmund University, Otto-Hahn-Str. 4a, 44227 Dortmund/DE

Achieving high resolution in structural biology within the native environment of biomolecules—specifically, within living cells—remains one of the most significant challenges faced by researchers today. Among the various techniques employed to tackle this issue, electron paramagnetic resonance (EPR) spectroscopy has emerged as a powerful tool for in vivo studies. This tutorial aims to provide participants with a comprehensive understanding of site-directed spin labeling and pulsed dipolar spectroscopy, particularly in the context of cellular investigations.

Throughout the session, we will explore different methodologies utilized in EPR spectroscopy, highlighting their unique advantages and potential applications in studying biomolecular interactions and dynamics within living systems. We will also address the challenges associated with these techniques, such as optimizing experimental conditions and interpreting data in complex biological environments.

With this tutorial, I aim to give valuable insights into how EPR spectroscopy can be effectively harnessed for in-cell studies, paving the way for advancements in our understanding of biomolecular behavior in their native contexts.

Molecular Basis for Primer Synthesis Initiation by DNA Primase

Pengzhi Wu[1], Fred F. Damberger[1], Johannes Zehnder[2], Nina Schröder[3], Niklas Senning[1], Georg Lipps[4], Thomas Wiegand[3,5], Frédéric H.-T. Allain[1]

[1]Institute of Biochemistry, Department of Biology, ETH Zürich, Switzerland
[2]Laboratory of Physical Chemistry, ETH Zürich, Switzerland
[3]Institute of Technical and Macromolecular Chemistry, RWTH Aachen University, Germany
[4]Institute of Chemistry and Bioanalytics, University of Applied Sciences Northwestern Switzerland, Muttenz, Switzerland
[5]Max Planck Institute for Chemical Energy Conversion, Mülheim (Ruhr), Germany

DNA primases synthesize short primers required for DNA polymerases to initiate replication, yet the mechanism of the initial dinucleotide formation remains poorly understood. Using structural NMR, we show that the ancillary domain of the archaeal pRN1 primase binds both the DNA template and the initiating NTPs. Unexpectedly, only the second NTP initially base-pairs with the template, while the first remains unpaired, causing its corresponding template base to flip out and contact the interdomain linker. This interaction partially unwinds the ancillary domain's N-terminal helix, allowing the catalytic domain to engage. In the resulting closed conformation, the base-paired second NTP is transferred from the initiation to the elongation site, while the first NTP pairs with its template in the initiation site—placing both base pairs in the active site for catalysis. These findings reveal how the full-length primase coordinates template recognition, stepwise NTP assembly, and proofreading—an initiation mechanism likely conserved across all primases.

“Long-Lived ^{15}N-Betaine Enables Multi-Phase Hyperpolarized MRI"

M. Lerche, Kopenhagen/DNK

Hyperpolarized magnetic resonance imaging (HypMRI) with ^{13}C-labeled substrates has enabled insigths into dynamics of fast metabolism, but its short signal lifetime restricts observations to the first 1–2 minutes post-injection. To overcome this limitation, we developed ^{15}N,d_9-betaine as a long-lived endogenous molecular contrast agent, combining high polarization efficiency (~27%), excellent aqueous solubility, and a ~7-minute T_1 in vitro. This extended lifetime supports multi-phase imaging strategies, including sequential injections from a single hyperpolarized dose to capture both rapid dynamics and delayed distribution.

We demonstrate the methodological potential of ^{15}N,d_9-betaine in rodents by achieving high temporal resolution of perfusion imaging in the kidneys, followed by delayed-phase and high-resolution acquisitions, all within a single experiment. Importantly, the long signal lifetime and favorable spectral properties also enabled us to detect metabolic conversion of betaine to dimethylglycine in the liver.

The results establish ^{15}N,d_9-betaine as a versatile molecular imaging agent that extends HypMRI capabilities across time scales. By enabling both dynamic perfusion studies and metabolic readouts from one hyperpolarized preparation, this work highlights new methodological avenues for long-lived ^{15}N agents in physiological and disease-relevant imaging.

Charge, ligand binding and chain dynamics of macromolecules

U. Scheler, Dresden /DE

Dr. Ulrich Scheler, Leibniz-Institut für Polymerforschung Dresden e.V., Hohe Str. 6, 01069 Dresden /DE

Charge and electrostatic interaction play an important role in biological and technological processes. The effective charge of macromolecules, proteins or polyelectrolytes, often is considerably smaller than the nominal charge because of the condensation of counterions reducing the effective charge and thus the potential experienced by the free counterions.
Applying an electric field results in electrophoretic motion of charged moieties. From the electrophoretic mobility and the self-diffusion coefficient measured on the same time and length scales the effective charge of the molecule or complex under study is calculated without any model. Thus the counterion condensation on proteins and synthetic macromolecules has been quantified. Small molecules may bind as ligands to macromolecules in a similar way. Electrophoretic NMR has shown that the electrostatic interaction is the Major interaction behind the weak or temporal binding of ligands to charged macromolecules but not the only driving force. Diffusion NMR provides higher precision in the determination of the binding constant. The design of a probehead for the application of strong electric fields in a dilute aqueous solution are discussed as well.
Polymer chain dynamics under external shear is investigated in a Searle cell in-situ in the NMR spectrometer. The spin-spin relaxation time T_2 is a good measure for the polymer chain dynamics. Restricted mobility due to entanglements leads to a shortened T_2. For entangled polymers under the loss of entanglements is the dominating effect. The charge on the chains of polyelectrolytes results in stiffer chains with less entanglements. Manipulating the electrostatic repelling force along the chain e.g. by adding salt allows to shift the balance between chain ordering and loss of entanglements under shear.

Selective Excitation near Conductive Material Surfaces and Interfaces with Optimal Control

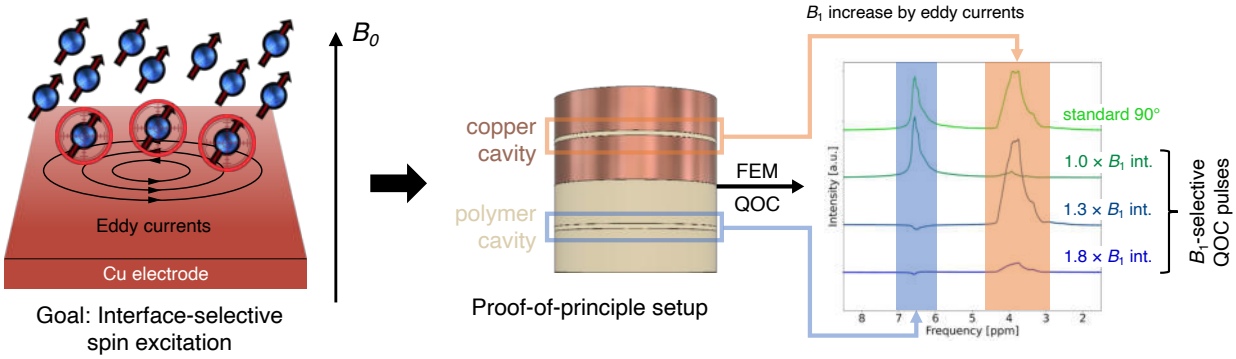
J. F. Kochs, Jülich/GER, A. J. Römer, Jülich/GER, M. Schatz, Jülich/GER, M. Streun, Jülich/GER, S. Jovanovic, Jülich/GER, S. S. Köcher, Jülich/GER, J. Granwehr, Jülich/GER

Johannes F. Kochs, Forschungszentrum Jülich GmbH & RWTH Aachen University, Wilhelm-Johnen-Straße, 52428 Jülich/GER

The electrochemical conversion of CO_2 from exhaust gases of industrial processes to C_{2+} products like ethylene or ethanol, is typically conducted in complex aqueous reaction systems. Product distributions are affected by multiple factors including electrochemical cell setup, local reaction conditions, catalyst composition and structure as well as dissolved CO_2 availability.

NMR spectroscopy is a powerful, non-invasive method to investigate electrochemical processes *in operando*. Local reaction conditions in an electrochemical cell, such as pH value, can be imaged indirectly by quantifying pH dependent equilibrium concentrations of electrolytes [1]. However, shielding effects, susceptibility gradients and eddy currents caused by conductors in electrochemical cells lead to inhomogeneous B_0- and B_1-fields. The magnetic field distortions produce artifacts in complex pulse sequences, compromising solvent suppression and spatially-encoded imaging.

In this study, we deliberately exploit inhomogeneities to design spatially selective shaped pulses. Finite element method (FEM) simulations are used to accurately predict magnetic field distortions induced by eddy currents near conductive surfaces [2]. Predicted B_0- or B_1-distortions can subsequently be incorporated in a quantum optimal control (QOC) workflow. In a proof-of-concept experiment, QOC-NMR pulses selectively address designated Larmor (B_0) and nutation (B_1) frequencies in a custom-made model setup holding liquids in a conductor- and insulator-enclosed cavity. The signal of each cavity is selectively enhanced or suppressed based on their local B_0- or B_1-field intensity. The results demonstrate how QOC-NMR can substitute conventional selective signal excitation and suppression as well as avoid drawbacks of gradient-based imaging experiments, establishing fast and surface-selective NMR in catalysis, electrochemistry and material sciences.



Literature:

[1] M. Schatz, S. Jovanovic, R.-A. Eichel, J. Granwehr, *Sci. Rep.* **2022**, 12, 8274.

[2] M. Schatz, M. Streun, S. Jovanovic, R.-A. Eichel, J. Granwehr, *Magn. Reson.* **2024**, 5, 167.

Exploring photo- and electrochemically induced paramagnetic ionic states in organic semiconductors by EPR spectroscopy

M. Mayländer, Oxford/GB, M. Ladwig, Oxford/GB, N. Curwen, Oxford/GB, C. Tait, Oxford/GB

Dr. Maximilian Mayländer, University of Oxford, S Parks Road, OX1 3QZ Oxford/GB

Paramagnetic ionic states in organic semiconductor materials play a significant role in the operation of many organic electronic devices. A deeper understanding of the charge and spin density distribution in these states can help establish structure–property relationships that are key to improving device efficiencies.[1] EPR spectroelectrochemistry is a powerful tool for the investigation of radical ions of organic donor and acceptor molecules in different chemical environments, such as in solution and in thin films, in particular if combined with hyperfine spectroscopy to study their spin density distribution. Interpretation of the experimental EPR results with aid from DFT calculations, allows us to gain insight into the influence of the chemical environment and molecular structure on the electronic properties of the molecule.
Using a three-electrode setup in an EPR tube, we generate radical ions of organic electron-donor and electron-acceptor molecules for organic photovoltaics (e.g. PTB7-Th and EH-IDTBR), enabling us to characterise the radical ions in situ with continuous wave EPR and UV-vis spectroscopy.[2] Trapping the radical ions by flash freezing then allows us to investigate the spin density distribution in greater detail using a series of hyperfine spectroscopic techniques (Q-band ^{1}H Davies ENDOR, ^{14}N ESEEM, and HYSCORE). Comparison of the results with measurements on photoexcited donor: acceptor blends revealed differences in spin density distributions attributed to a pronounced dependence of spin delocalization on the molecular environment.

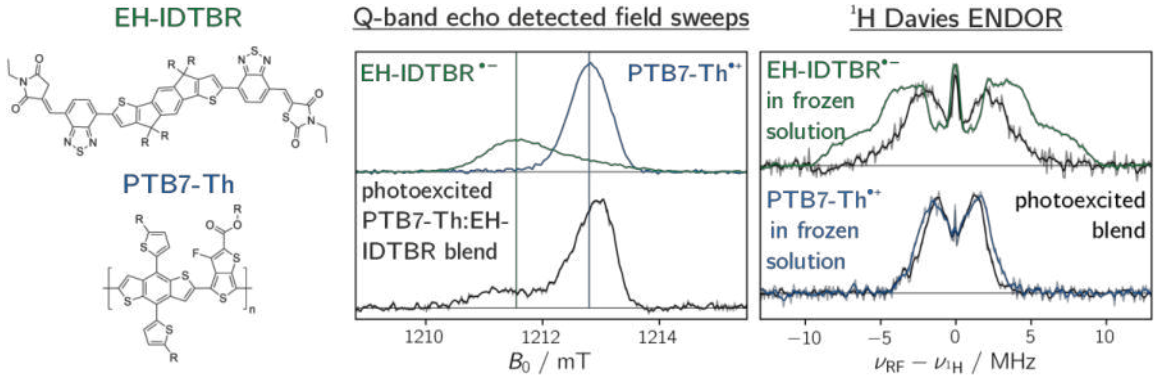


Figure 1. Comparison of echo-detected field sweeps and Davies ENDOR spectra of the EH-IDTBR anion and PTB7-Th cation in frozen solution with the photoexcited PTB7-Th:EH-IDTBR blend. The molecular structures of the donor and acceptor molecules are also shown.

Literature:

[1] T. M. Clarke, J. R. Durrant Chem. Rev. 2010, 110, 6736–6767.
[2] S. A. Bonke, T. Risse, A. Schnegg, A. Brückner Nat. Rev. Methods Primers 2021, 1, 33 1–20.

Electrophoretic NMR-based Characterization of Charge and Mass Transport in Polymer Electrolytes

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The transference number T_+ of the active ion, for example Li^+, is one of the most decisive figures to describe the transport properties in a battery electrolyte. Its measurement by electrochemical methods is impeded by the challenge to control interfacial resistances. Therefore, electrophoretic NMR (eNMR), which provides the drift velocities of all constituents of an electrolyte in an electric field via a ^7Li, ^{19}F and ^1H flow experiments, has become a valuable alternative. There, the transference number is directly calculated from the electrophoretic mobilities. [1]

Here, we present a study of the influence of various co-solvents on charge and mass transport in salt-in-polymer electrolytes based on poly(ethylene oxide). Strong influences of the nature of the co-solvent are observed and attributed to the fact that the neutral co-solvents exhibit a drift velocity in the electric field as well. The origin of this drift of neutral species is the need to compensate the volume flux of large anions towards the anode. It is found that smaller or no co-solvents are more beneficial in enhancing T_+, as in this case the chain and the Li^+ drift velocity are enhanced, increasing T_+.[2]

Furthermore, a systematic variation of the type of anion of a Li salt in PEO reveals that Li^+ ion drift velocities can be boosted by employing large anions. We show that the benefit of large anions is not merely an effect of their large Stokes radius, reducing their migration velocity to the benefit of Li^+ migration. Instead, testing for a scaling relation of Li^+ flux with anion radius reveals a far stronger effect of large anions boosting Li^+ transference. This effect is again attributed to the volume flux of large anions, which occurs in the opposite direction and requires compensation. [3]

These findings provide new guidelines for battery electrolyte design, as they show that the migrative flux of all constituents needs to be considered and affects the performance in terms of T_+.

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Wettability of mesoporous materials

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Mesoporous materials are used in many fields, for example, in catalysis and energy conversion and storage. These applications require that small molecules, such as solvents, reactants, or electrolytes, can enter the pores. The interaction of the guest molecules with the pore walls strongly affects their NMR spectra. Hence, the distinct changes in the NMR spectra of small guest molecules can in turn be used to probe the pore system and its wetting by small molecules. For the investigation of host systems that contain no or only a small amount of protons, an ideal probe molecule is water: its single proton site leads to high sensitivity and simple NMR spectra. Magic angle spinning (MAS) is required to remove residual anisotropies due to interaction with the surface.

In this contribution, ^{1}H MAS spectroscopy of water in different host systems will be discussed. The first class of materials are mesoporous silicas. It had previously been found that the pore-filling mechanism in these materials depends on the pore diameter and is different for MCM-41 (small mesopores) and SBA-15 (somewhat larger mesopores) [1]. We have investigated if the polarity of the pore walls affects the filling mechanism by comparying MCM-41 with a hydrophobically modified MCM-41. Although there are differences in the structure of water [2], our NMR findings indicate that the filling mechanism is not affected. The second class of materials are carbons. Due to ring currents in the aromatic pore surface, guest molecules show strongly up-field shifted NMR signals [3]. This nucleus-independent chemical shift (NICS) depends on the average distance between the observed spins in the guest molecules and the pore walls, and is most pronounced in small micropores and nanopores. Our comparison of a pure carbon material [4] and highly nitrogen-doped one revealed interesting differences in the wetting of these materials [5].

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Exploring the Potential of ^{19}F NMR Spectroscopy for Determining Per- and Polyfluoroalkyl Substances (PFAS).

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Per- and polyfluoroalkyl substances (PFAS) are used in consumer products and industrial applications due to their desirable properties including oil and water repellence, fire retardance, and durability.[1-2] However, the regulation and monitoring of PFAS are currently being discussed.[1-2]

Various targeted and non-targeted analytical approaches have been developed to determine the total PFAS amount, and the specific chemical identities present in biological and environmental matrices.[3-4] Nevertheless, the structural diversity of PFAS continues to pose challenges for a comprehensive and quantitative analysis. [3-4]

^{19}F nuclear magnetic resonance (NMR) spectroscopy benefits from minimal sample preparation and a high tolerance to complex matrices. Moreover, carefully optimized one-dimensional ^{19}F NMR acquisition parameters and advanced techniques such as steady-state free precession (SSFP) NMR, can achieve detection-limits in the nanomolar range.[5]

Building on these optimized ^{19}F NMR methods, this study evaluates various reference compounds and external calibration techniques for their suitability to quantify PFAS at low concentrations. To further improve sensitivity, different relaxation agents are investigated to reduce T_1 relaxation times and pushing the limits of detection. A reference database of known PFAS is also being expanded to facilitate compound identification in biological and environmental samples.[6] Special attention is given to matrix-induced chemical shift variations and the resulting challenges in the unambiguous assignment of ^{19}F-containing compounds.

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Solid-State NMR Studies of Intracrystalline Chain Dynamics in Ketone-Functionalized Polyethylene

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Ketone-functionalized polyethylene (KetoPE) [1] containing randomly distributed carbonyl moieties is a promising alternative to high-density polyethylene (HDPE) with regards to its improved potential for functionalization and chemical recycling. KetoPE is here investigated using the solid-state NMR methodology established in our group to determine whether the semicrystalline structure and molecular dynamics of HDPE are preserved upon carbonyl incorporation.

Temperature-dependent ^{1}H free-induction-decay (FID) measurements, analysed using a three-component fit, were employed to determine the crystallinity and semicrystalline thermal properties of the samples. The corresponding second moments extracted from the crystalline component were evaluated to probe the presence and extend of fast intracrystalline dynamics (ICD). Structural assignments of KetoPE were established by combining ^{13}C CP-MAS and DP-MAS experiments, which enabled the identification of keto groups residing in crystalline and amorphous regions and allowed assessment of their incorporation into crystalline lamellae. With the ^{13}C resonances identified, ^{13}C T_1-relaxation measurements using a *z*-filtered sequence were applied to quantitatively analyse chain diffusion using the one-dimensional free-diffusion model, revealing an only minor impact of keto incorporation on molecular mobility [2]. Complementary Goldman–Shen ^{1}H spin-diffusion experiments showed a faster magnetization build-up for the isolated carbonyl signal compared to crystalline CH_2, indicating that the majority of isolated keto groups preferentially localize at the crystal–amorphous interphase, consistent with an earlier report [3].

Overall, this study demonstrates the application of solid-state NMR techniques to elucidate the structural and dynamic effects of low-level, randomly distributed keto groups in polyethylene, aiding in the quest for more sustainable polymers while preserving the essential semicrystalline features of HDPE.

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From Megawatt-Class Gyrotron Oscillators for Nuclear Fusion Devices to High-Power Microwave Sources for DNP-NMR Applications

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Dynamic Nuclear Polarization (DNP) has proven to be a highly effective method for enhancing the performance of Nuclear Magnetic Resonance (NMR) systems by leveraging the electron magnetic moment. It requires microwave sources that generate high-power electromagnetic fields in the frequency range from approximately 100 Gigahertz (GHz) up to 1 Terahertz (THz). Although there are several sources available that can produce electromagnetic waves at a few milliwatts (mW), it is difficult to find sources that produce output power levels from a few watts up to several hundred watts. DNP methods typically fall under one of two categories: continuous wave (CW) DNP (CW-DNP) and pulsed DNP. Those methods differ in whether the sample is irradiated by CW sources or with coherent pulses, typically with microwaves from amplifiers. Today, there is a growing shift towards pulsed operation, offering much broader flexibility for DNP-NMR. The only known microwave source capable of delivering output power levels ranging from around 10 W up to several 100 W at around 263 GHz, for 400 MHz DNP-NMR systems, and above is the gyrotron [1]. The gyrotron, is an electron vacuum tube originally developed for output power levels up to above one megawatt and for operation as microwave source for nuclear fusion devices and long-range radar systems. It is a specific form of the electron cyclotron maser that uses a simple tapered cylindrical cavity as its main interaction circuit. The cavity is oversized, typically several wavelengths in diameter. The gyrotron is an oscillator that operates in CW at a free-running frequency. Despite being possible to be tuned by a few MHz and injection-locked from an additional source it lacks the capability to produce coherent pulses. To address these needs, within the German DFG CRC project HyPERiON, KIT is performing R&D into a new type of hybrid amplifier system building on the long-term experience in the design of megawatt-class gyrotrons for nuclear fusion, its latest research on helical-type gyro-travelling wave tubes (gyro-TWT) and the research on solid-state microwave amplifiers.
The presentation will start with an introduction into gyrotrons and the related R&D at KIT, originally targeting for nuclear fusion. It will finish with the fundamentals of the research work ongoing for a new type of hybrid amplifier system for DNP-NMR.

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Gadolinium Retention in Brain Tissue after *in-vivo* Injection of Contrast Agents

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We use magnetic resonance techniques to assess the potential retention of gadolinium [1] after intravenous injections of gadolinium-based contrast agents (GBCA) for enhancing the diagnostic value of magnetic resonance imaging (MRI). Representatives of either linear or macrocyclic GBCA were administered to mice with experimental autoimmune encephalomyelitis (EAE), a common animal model of multiple sclerosis. We detected varying amounts of Gd^{3+} in the µM range in sub-mm biopsy samples from different regions of inflamed brains by high-frequency continuous wave electron paramagnetic resonance (EPR) at 94 GHz (3.3 T). Deconvolution of the cwEPR spectra recorded on the specimen treated with the linear GBCA gadopentetate revealed two components with characteristics of both GBCA-bound Gd^{3+} and Gd^{3+} in aqueous solution in a 7:3 ratio, indicating that *in vivo* some Gd dissociates from this linear GBCA.
To further explore the local molecular environment of the retained Gd, we employed electron-nuclear double resonance (ENDOR) measurements. Gd-specific pulse ENDOR on tissue samples is hampered by strong signal contributions from endogenous paramagnetic species, in particular Mn^{2+}. We developed ENDOR sequences with tailored flip angles for different spin states, e.g. $S_{Mn^{2+}} = 5/2, S_{Gd^{3+}} = 7/2$, based on [2], to efficiently suppress the unwanted signal contributions. Again, ^{1}H ENDOR measurements exhibited spectral features consistent with a partial Gd^{3+} release in case of the linear GBCA gadopentetate. No release was observable for macrocyclic GBCA.
Furthermore, ^{31}P ENDOR spectra provided evidence for binding of retained Gd^{3+} to endogenous phosphate-containing species. Based on the Gd-P distance determined from the hyperfine coupling, we attribute the observed ^{31}P ENDOR signals to phosphorus containing molecules directly ligating released Gd^{3+} in case of the linear GBCA. No ^{31}P ENDOR signal was observable in the case of macrocyclic GBCA.
In some conditions, the Gd concentrations detected by EPR were significantly lower than those determined by mass spectrometry (MS) earlier [3]. Therefore, we utilized quantitative MRI as a second magnetic resonance method to determine the amount of retained Gd. For this, the *in vivo* T_1 relaxation times and corresponding relaxivities r_1 in the different brain regions of GBCA-treated mice and reference values obtained on mouse brain tissue homogenates spiked with specific GBCA concentrations were compared to the Gd concentrations detected with MS. Again, the *in vivo* relaxivities underestimated the actual amount of retained Gd in the same cases as EPR measurements did, and agreed otherwise. Thus, we conclude that part of the Gd is retained in insoluble deposits, e.g. Gd-phosphates, invisible in both EPR and MRI.

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Towards Understanding the Molecular Choreography of Proteins and Lipids in Myelin

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Myelin is a complex, fascinating biomembrane: a compact multilamellar structure formed by lipids and proteins in the vertebrate nervous system. The self-assembly of myelin-like structures is intriguing for physical chemists and structural biologists alike; high-order lipid structures can be induced by myelin proteins in the test tube, allowing a study of this unique process at multiple levels. We have started a multi-method approach that aims at understanding the molecular interactions between all myelin components simultaneously at different levels of maturation and organization, comprehending the forces that drive this self-assembly, and reconstruction of fully controlled synthetic myelin in vitro.
This multi-method-approach combines expertise in physical chemistry, EPR spectroscopy, structural biology, scattering methods with synchrotron radiation, and polymer science, as well as protein production and membrane models. Key aspects include kinetic and spectroscopic analyses of protein insertion into lipid membranes, imaging of lipid structures induced by myelin proteins, characterisation of adhesive proteolipid surfaces before assembly into multilayers, estimation of interaction forces, as well as high-resolution analysis of structure, dynamics, and physicochemical properties of assemblies made from pure components in the laboratory. We aim at unraveling how non-covalent interactions lead to the formation of nanoscale nuclei for the self-assembly of functional supramolecular biostructures.
The first step towards this consists of *deconstructing myelin*, i.e. reaching an overarching physicochemical description of myelin and a fundamental understanding of the synergy between myelin molecules in adequate model systems. In this presentation, I will mainly introduce the complex system of myelin and the use of EPR and IR-based methods to study these proteolipid systems in model systems that we developed for multi-protein studies like lipid monolayers [1], unilamellar lipid vesicles [2] and lipid nanodiscs. [3]

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Integrative NMR Reveals an Intrinsically Disordered and Dynamic N-Terminus in SARS-CoV-2 NSP3

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The rise of AI-based structural model prediction tools, such as AlphaFold, has revolutionized current structural biology; yet, experimental validation remains indispensable. Here, we present an integrative NMR-based pipeline for obtaining experimentally validated structural information, as well as insights into structural dynamics, on a small, soluble protein. Using the N-terminal ubiquitin-like domain 1 (Ubl1) of SARS-CoV-2 non-structural protein 3 (NSP3) as a model, we assess the secondary structure content by CD spectroscopy for overall and by NMR secondary chemical shifts for residue-specific information. NMR residual dipolar couplings (RDCs) verify the validity of the AlphaFold3 structural model in comparison to existing X-ray structures. Small-angle X-ray scattering (SAXS), analytical ultracentrifugation, and calibrated size exclusion chromatography provide information on the overall shape of the protein. NMR ^{15}N relaxation experiments yield residue-specific insights into structural dynamics [1,2]. A model-free analysis of the NMR relaxation data delivers amplitudes of motions and their corresponding timescales.

We identify a globular fold of Ubl1, comprising four α-helices and four β-strands, in agreement with two recent X-ray structures and the AlphaFold3 structural model. Unlike the X-ray structure, we observe only a weak, presumably transient, β-sheet propensity for the very N-terminus. Secondary chemical shifts suggest a high intrinsic disorder of the N-terminal region, in agreement with the AlphaFold3 structural prediction for the N-terminus (which, nonetheless, shows only a low confidence level). Magnetic-field-dependent NMR relaxation data (at 600, 900, and 1200 MHz) and their analysis using an extended model-free approach reveal a highly flexible N-terminus of approximately 15 amino acid residues in length, underscoring its disordered character.

Since the intrinsically disordered N-terminus of Ubl1 constitutes the N-terminus of the NSP3 on the rim of Sars-CoV-2 double membrane vesicle (DMV) pore, we hypothesize that the N-terminus of NSP3 may be involved in forming biomolecular condensates. A comparison to the Ubl1 domain from Sars-CoV-1 indicates a similar fold and a flexible N-terminus. Therefore, the structure and dynamics of the NSP3 N-terminus appear to be conserved across different coronaviruses, highlighting the N-terminal Ubl1 domain of NSP3 as a potential drug target. Preventing an interaction between Ubl1 and its interaction partners would impede viral replication and, consequently, viral infection.

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Design of New Antimicrobial Peptides Guided by NMR-based Structural Analysis

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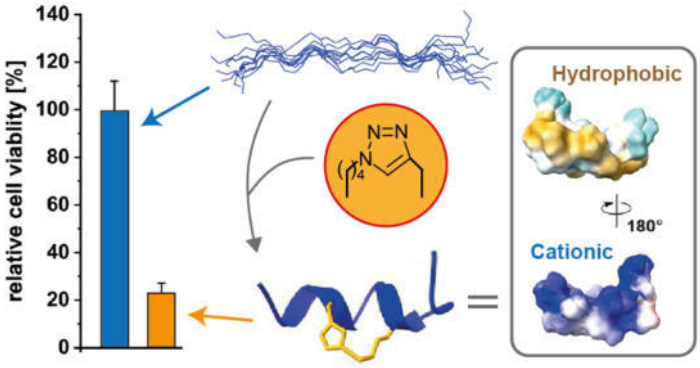
The increase in antibacterial resistance is one of the greatest challenges in modern medicine driving an urgent need to develop new drugs to combat resistant pathogens. A promising class of molecules represent peptides that can be efficiently designed to exhibit high antimicrobial efficacy. As we show by NMR, incorporation of a triazolyl-bridge modification induces a well-defined α-helical structure in a newly designed antimicrobial peptide with enhanced efficacy, resulting in improved positive electrostatic surface potential on one side of the peptide and clustering of hydrophilic and hydrophobic residues on opposite surface areas of the molecule. As highlighted by micelle-bound peptide structures determined by NMR and systematic alanine substitution, we identify arginine 3 and asparagine 11 as presumable membrane-interacting residues. Collectively, our NMR-based analysis provides evidence that an α-helical structure enhances antimicrobial activity by creating positively charged and hydrophilic, and hydrophobic areas as molecular surface signatures, potentially promoting the interaction of the peptide with the cellular target membrane.



In search for new antibiotics, we further uncover the mode of action of the recently identified bactericidal protein Ave1. Using NMR, we solved its three-dimensional structure, revealing a six-stranded β-barrel fold and show that Ave1 disrupts microbial membranes. Furthermore, we demonstrate that synthetic peptides corresponding to positively charged regions of Ave1 exhibit antimicrobial activity. By characterizing the interaction of Ave1 with lipoteichoic acid, a major component of the gram-positive cell wall, our findings support a model how Ave1 associates with the bacterial surface, from where it perturbs the plasma membrane, ultimately leading to membrane dissipation and cell death. This opens new routes to develop novel antimicrobial peptides based on Ave1.

Protein Folding at All Stages Observed by DNP-Enhanced Solid-State NMR

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Protein folding, misfolding and aggregation is a hallmark of a variety of neurodegenerative diseases. Therefore, a better understanding of the protein folding landscape is of paramount interest. Backbone conformations as well as side chain torsional angles are closely linked to NMR chemical shifts in proteins, and thus directly report on conformational preferences with site-specific resolution. In disordered proteins or protein regions with high intrinsic flexibility, motions of the backbone and side chain rotations lead to averaging over all conformations sampled.
Recently, several approaches have been developed to experimentally determine conformational ensembles directly in fully or partly disordered proteins in frozen solution. Upon freezing in a cryoprotectant medium, the exchange between different conformations is stopped, and all conformations sampled by each nucleus are present with their respective probability. Combination of frozen solution NMR with dynamic nuclear polarization (DNP) makes it possible to study distributions of conformations in large proteins with high sensitivity.

In the present study, we employed two-dimensional DNP-enhanced ssNMR to get detailed insights into backbone as well as side chain conformations of isoleucine to follow protein folding and aggregation.
We investigated different amino-acid selectively labelled model proteins for intrinsically disordered proteins (IDPs), denatured and well-folded proteins, and amyloid fibrils, in particular the model protein PI3K SH3, which is well-folded at neutral pH and unfolds and aggregates at low pH.
Line-shape analysis by integration of representative peak areas in 2D spectra provides an accurate overview of the distribution of side-chain conformations. For well-folded proteins, most Ile chemical shifts in frozen solution are well resolved and similar to those observed in solution. For unfolded proteins and IDPs, all Ile sidechains have full conformational freedom, and, therefore, inhomogeneous line broadening dominates the cryogenic spectra. Moreover, we demonstrate that conformational ensembles of proteins strongly depend on solvent and buffer conditions. This allowed different unfolded structures for chemical and acidic pH denaturing of the PI3K SH3 domain to be distinguished. In amyloid fibrils from PI3K SH3 chemical shifts typical for β-strand like secondary structure dominate the spectra, whereas Ile residues belonging to the fuzzy coat still add the IDP-type line shapes.

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Unique features of NMR of RNA

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The importance of RNAs is increasingly recognized. Yet, structural biology of RNA lacks behind protein structural biology. The conformational dynamics of RNAs are part of the reason for this disparity between protein and RNA structural biology.

NMR spectroscopy in solution is well suited to deal with conformational dynamics of RNA. In this contribution, we will introduce methodological advances that include novel methods to study RNA dynamics, especially for RNA-ligand complexes, to detect RNA hydrogen bonds and temperature-dependent RNA conformational transitions. The lecture will include discussion of model systems and of viral RNA elements. Combined MD and NMR studies will be shown to be key to understand and describe the conformational dynamics of RNA.

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Spotlight on the nucleotide: Phosphorus-31 solid-state NMR for the investigation of ATP hydrolysis in ATPases

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The Sms-system is an ancient minimal version of Suf, which is responsible for the biogenesis of iron-sulfur clusters. [1] Those are important in various biological processes for instance in the respiratory chain or in the nitrogen fixating enzyme nitrogenase. [2] The Sms-system consists of the proteins SmsC and SmsB, where SmsB is performing the biogenesis of the iron-sulfur cluster and SmsC has an ATPase activity. [1]

We herein present a solid-state NMR strategy for the investigation of ATP hydrolysis in the ATPase SmsC by detecting the fate of the nucleotide. Based on ^{31}P-detected NMR experiments it is possible to obtain an in-depth understanding of the ATP hydrolysis process in a protein. The different stages of the ATP hydrolysis can be mimicked by using stable and non-hydrolysable ATP-analogues. ^{31}P-based solid-state NMR experiments reveal atomic-level insights into ATP binding and hydrolysis without the need for an expensive ^{13}C and ^{15}N labelled protein and time demanding sequential resonance assignment. This enables the investigation of even larger and more complex protein systems, where a resonance assignment in the solid state becomes increasingly difficult or even entirely impossible. ATP analogues are not only useful for probing the nucleotide binding conformation, but in the case of choosing a slowly hydrolysable ATP analogue, also enable the measurement of real-time NMR experiments, following ATP hydrolysis directly within the NMR rotor. This real-time data can give additional valuable information about the ATP hydrolysis mechanism. A further rarely explored property is the homonuclear ^{31}P-^{31}P dipolar coupling among the phosphorus spins of the nucleotide, which can be measured for instance by Dipolar Recoupling Enhanced Nuclear Alignment Reduction (DRENAR) experiments. [3] The measured dipolar couplings directly reveal both, structural and dynamic insights in ATP binding. SmsC was found to be a very promiscuous enzyme, which is not only able to hydrolyze ATP, but also ADP, the transition-state analogue ADP:AlF_x and the ATP analogue AMPPNP. For the hydrolysis of AMPPNP two different products were observed depending on the reaction conditions.

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Unraveling the structure of the YopO-$(SycO)_2$ complex using pulsed dipolar EPR spectroscopy

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The *Yersinia* outer protein O (YopO) is one of six effector proteins of the pathogenic *Yersinia* bacteria, including the plague-causing *Yersinia pestis* bacteria. It is a key component in the suppression of the hosts' immune response upon infection. YopO is comprised of three domains, a GDI, a kinase, and a membrane localization domain. During the infection process, the specific Yop chaperone O (SycO) is hypothesized to bind as a dimer to the membrane anchor thereby masking it and aiding to the solubility of full-length YopO. While structures of YopO without the membrane anchor have been solved [1,2], this is neither the case for full-length YopO nor for the YopO-$(SycO)_2$ complex. We therefore aim here to gain insights into the structure and formation of the full-length YopO-$(SycO)_2$ complex.

We combine for this site directed spin labeling and EPR spectroscopy, especially pulsed electron electron double resonance (PELDOR or DEER) [3]. We were able to express, purify and label isolated SycO and the YopO-$(SycO)_2$ complex. This enabled us to identify structural changes in SycO upon YopO-$(SycO)_2$ complex formation and furthermore, to gain insights into the architecture of the complex.

Our results demonstrate a dimer formation of SycO in the absence of YopO. Additionally, SycO was found to bind YopO as a dimer in the YopO-$(SycO)_2$ complex. We will present results on the temperature dependence of the binding of SycO by YopO and the conformational changes in SycO upon binding. *In-silico* distance calculations of the complex, based on AlphaFold3, were in close agreement with the experimental data.

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The coming of age of the DNA enzymes technology

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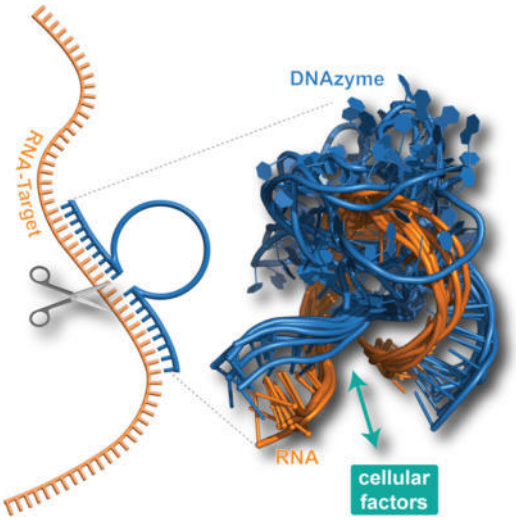
DNA-based enzymes, also known as DNAzymes, possess an exciting biotechnological and therapeutic potential. However, persisting limitations in their application are accompanied by insufficient insights into their mode-of-action.



We have carried out NMR-focused integrative structural studies of a number of different DNAzymes and found one unifying feature: An exceptionally strong link between structure, function, dynamics, and environmental parameters. Thus, NMR-based structural biology is key to a mechanistic understanding of the system. In this regard, we could obtain time-resolved insights into one of the most prominent DNAzymes[1,2]. We could further show that our insights enable rational-designed improvements of the system, providing new means to unravel the full potential of the DNAzyme technology.

Here an overview of the integrative structural biological approach required to assess such dynamic nucleic acid systems is provided and results on different systems are discussed[1-5]. Furthermore, progress in identifying and overcoming limitations and translating the system towards the desired cellular applications are presented.

Due to its inherent advantages over other established gene-editing tools, the upcoming next-generation of DNAzymes may become a generalized platform technology to address a wide range of therapeutic and biotechnological needs. It seems that decades after its discovery and driven by NMR-based structural biology, the DNAzyme technology is finally coming of age.

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Photo-CIDNP NMR in liquid and solid state

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) occurs as nuclear hyperpolarization upon light-induced radical-pair dynamics. In the liquid state, the radical-pair dynamics is described by the classical “radical-pair mechanism” (RPM). Here, the chemical fate of the reaction process depends on the nuclear spin states. Under solid-state conditions, anisotropies become relevant, as specified in the “three-spin mixing” (TSM). Presently, the number of systems which have been demonstrated to show photo-CIDNP, is significantly increasing.

The presentation will provide an update on recent developments in liquid- and solid-state NMR, with time-resolution and field-dependence [1], on specifically designed samples (proteins [2,3] and synthetic diads [4]) as well as on micro-MRI applications.

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Mapping the Influence of Orientation and Distance of SCRP on solid Photo-CIDNP effect in a Multi-Tyrosine Flavoprotein System

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Photo-Chemically Induced Dynamic Nuclear Polarization (Photo-CIDNP) is one of the hyperpolarization methods that enhances NMR signals by generating non-Boltzmann nuclear spin magnetization through spin-correlated radical pairs (SCRP) created by photoexcitation [1]. Flavoproteins have served as valuable models in previous studies exploring the mechanisms underlying the Photo-CIDNP effect [2][3][4][5].The light-oxygen-voltage (LOV) domain 4511 from *Methylobacterium radiotolerans* (*Mr*4511) is a flavoprotein with multi-tyrosine as electron donners and FMN as electron receptor, which shows significant solid-state Photo-CIDNP signal enhancement in ^{13}C natural abundance. By applying site-directed mutagenesis to the system, different hyperpolarization enhancements with varying orientations and distances relative to SCRP were mapped, showing orientations and distances between electron donner and electron receptor playing crucial roles in the efficiency of the solid-state Photo-CIDNP effect.

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Magnetic Field-Dependent CIDNP in Biomimetic Flavin–Tryptophan Dyads

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We investigated magnetic field-dependent photo-chemically induced dynamic nuclear polarization (photo-CIDNP) in a series of biomimetic flavin–tryptophan dyads connected via rigid oligoproline linkers of variable length (3–12 prolines). These model systems were designed to mimic donor–acceptor geometries in photoreceptor proteins and allow systematic tuning of intramolecular distance and flexibility [1]. The study employed ^{1}H field-cycling NMR, time-resolved CIDNP, relaxation and diffusion measurements to understand how linker structure affects spin dynamics.

Across the magnetic field range from 1 mT to 9.4 T, we observed distinct CIDNP behavior depending on the linker length. Longer linkers (6–12 prolines) produced CIDNP profiles characteristic of bimolecular electron transfer dominated by Δg-mechanism at high field. In contrast, shorter dyads (3–4 prolines) showed additional field-dependent features, including CIDNP maxima at intermediate fields (5–20 mT), suggesting the presence of intramolecular biradical pathways governed by exchange interactions.

High-resolution NMR experiments further revealed the presence of slowly interconverting conformers in short linkers, likely resulting from cis–trans isomerization of the polyproline backbone. These minor conformers displayed different diffusion coefficients, correlation times, and polarization behavior, and appear to be the origin of exchange-driven CIDNP observed at low and intermediate fields.

Our findings demonstrate that even in structurally constrained donor–acceptor systems, conformational heterogeneity may significantly modulate spin dynamics. Magnetic field-dependent photo-CIDNP is thus a powerful probe of structural and dynamic effects in biomimetic electron-transfer models.

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Polarizing Small Molecules via Parahydrogen-Induced Polarization and Spin Diffusion

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Parahydrogen-induced polarization (PHIP) overcomes the inherently low sensitivity of magnetic resonance methods by incorporating the spin order of parahydrogen into target molecules via chemical reactions and interactions. Compared to other signal enhancement methods, PHIP is relatively inexpensive and can be easily implemented into standard NMR equipment, and is particularly well-suited for benchtop NMR spectroscopy. PHIP has been extensively optimized for polarizing specific molecules such as [1-^{13}C] fumarate [1], [1-^{13}C] pyruvate [2], and specific amino acids [3]; however, its wider applicability is restricted because it requires substrates that directly interact with H_2.

In this work, we are constructing a PHIP system to polarize a wider range of small molecules using parahydrogen. After polarizing a source molecule using PHIP, it is solidified with a target, and spin diffusion in the solid state leads to polarization of the target species. [4] To investigate this phenomenon further, we have developed a home-built setup for PHIP experiments, featuring custom electronic circuitry to control a hydrogen gas channel via computer-operated valves, and electromagnets for low-field polarization transfer. The hydrogenation reaction takes place in a stainless steel reactor, and the hyperpolarized product is then rapidly moved into a magnetic shield for polarization transfer, and then to a benchtop NMR spectrometer for ^{13}C or ^{1}H signal acquisition. This integrated and automated workflow minimises signal loss and improves reproducibility. We have successfully hyperpolarized proton sites via PHIP and transferred the polarization efficiently into magnetization on ^{1}H and ^{13}C nuclei. The combination of PHIP with spin diffusion offers a strategy for relaying hyperpolarization to molecular sites that are not directly involved in the hydrogenation reaction. This approach has the potential to overcome the substrate specificity of conventional PHIP and extend its applicability to more complex systems, including protein–ligand complexes and small molecules.

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Recent trends in compact pulsed ESR systems and their applications

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Electron spin resonance (ESR) spectroscopy is a powerful tool used across a wide range of scientific, technological, and medical applications. While most ESR instruments rely on continuous-wave (CW) detection—offering relative simplicity in both design and operation—pulsed ESR systems remain significantly more complex. These systems are typically bulky, expensive, and often require specialized expertise to operate, which limits their broader adoption.

In contrast to the long-standing availability and growing popularity of compact CW ESR systems, compact **pulsed** ESR instruments are still rare. Our research group has been actively working to overcome this limitation by developing a new generation of compact, cost-effective, and user-friendly pulsed ESR platforms. This effort encompasses all critical subsystems of pulsed ESR, including the core spectrometer for pulse generation and signal detection, the microwave bridge, high-power amplifiers, modular control software, compact magnet designs, and integrated cryogenic cooling solutions.

In this talk, I will present our recent progress in miniaturizing and streamlining these components, and demonstrate how they can be combined into a complete high-performance system that maintains the capabilities of full-scale laboratory instruments. I will also highlight several applications of these compact pulsed ESR systems, including:

- Structural biology, with systems tailored for distance measurements using DEER spectroscopy,
- Chemistry, for in-line reaction monitoring and transient radical detection, and
- Medical diagnostics, particularly for non-invasive quantification of tissue oxygenation via in vivo oximetry.

Finally, I will offer perspectives on the future of compact pulsed ESR technology and its potential to expand the accessibility and utility of ESR in both research and applied domains.

Dipstick EPR-on-a-chip sensors achieving sub-$\mu M/G/\sqrt{Hz}$ sensitivity

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EPR-on-a-chip (EPRoC) sensors have demonstrated their unique features in realizing truly portable EPR spectrometers with excellent spin sensitivities of approximately 1e9 $spins/\sqrt{Hz}$ at $14\ GHz$ [1]. Here, the full portability is made feasible by an on-chip voltage-controlled oscillator for EPR sensing, which allows simultaneous frequency sweep and frequency modulation. This, in turn, enables the use of a small permanent magnet in combination with several custom-designed circuit boards for frequency reference and lock-in detection. Towards the use of EPRoC sensors for liquid samples, there are several technical challenges that need to be addressed. First of all, the sensing volume of an inductor loop inside a VCO is tiny in the range of $\sim 8-10nL$ for $14\ GHz$, rendering poor concentration sensitivity (c_{min}). Secondly, the chip sensors must be protected against damage as well as from introducing contamination while being in contact with the liquid samples. To address these challenges, several sensor topologies and post-processing steps have been proposed in recent years. These topologies include a VCO-array to lower the noise floor and c_{min} by $\sqrt{N_{VCO}}$ [2], and the arrangement of multiple VCOs to form a large, multiple-segment composite VCO whose coil perimeter can be arbitrarily large while still minimizing radiation loss [3]. Laser and focus ion beam (FIB) were used to drill a hole through the chip coil to enable a perpendicular mounting of sample-containing capillaries [4]. Last but not least, a chemical inert layer was coated on the chip surface to enable dipstick-style liquid measurements [5].

This talk summarizes these developments and presents measurement evidence of their effectiveness. For the first time, EPR experiments prove the $\sqrt{N_{VCO}}$ enhancement in concentration sensitivity of the VCO-array. A VCO-array prototype operating at $14\ GHz$ is shown to achieve a sub-$\mu M/G/\sqrt{Hz}$ sensitivity, on par with commercial EPR setups. We present the first 8-segment VCO chip prototype operating at 13.5 GHz, featuring a large 2 mm coil diameter and a 1.5 mm laser-drilled hole for through-coil capillary insertion. The chip's inert coating enables both capillary and dipstick measurements. Sensitivity tests with solvents such as water and ethanol confirm a performance of $2\mu M/G/\sqrt{Hz}$. Furthermore, we introduce a second-generation large-coil chip, designed in 65 nm CMOS, with simulated EPR sensitivity reaching $0.1\mu M/G/\sqrt{Hz}$. The presentation concludes by highlighting joint developments under SpinMagIC, our spin-off project aimed at commercializing EPRoC technology. Key achievements include a compact, highly homogeneous permanent magnet, and the development of ultra-low-noise signal generators and lock-in amplifiers—all at significantly reduced cost compared to existing commercial solutions. Altogether, we are approaching the realization of the first fully functional, highly sensitive EPRoC system—poised to meet the demands of both scientific research and industrial applications.

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Helium-3 magnetometers for high fields

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While low magnetic fields (< 10^{-2} T) can be measured extremely precisely (ca. 10^{-13}) using SQUID or SERF, nuclear magnetic resonance (NMR) offers the highest precision at high fields. Moreover, the highest metrological accuracy is achieved through continuous measurements of frequencies. This demands a sample with long coherence times, as it is the case for motionally averaged signals of gases. A state that requires only a few millibar of the gas, hence necessitates hyperpolarization of the nuclear spins even at high fields. For this reason, ^{3}He is the ideal candidate due to its ability to be hyperpolarized – either via metastability optical pumping (MEOP) [1] or the PAMP-effect [2]. Furthermore, it shows only minimal interactions with the environment and its gyromagnetic ratio has been determined independently using Penning-traps [3]. Another requirement to obtain such extremely long lasting signals (T_2* times in the order of 100 – 200s) the sample has to be kept in suitable containers to minimize susceptibility effects [4] and allow even for absolute field measurements [5].

While low-pressure and hyperpolarized ^{3}He enables extreme precision magnetometry (< 10^{-12}), we recently also produced high pressure (up to 50 bar) ^{3}He samples for applications in which optical polarization is impractical. Such thermally polarized samples can serve as very simple and robust NMR-magnetometers and may be used over a very broad temperature range (1-300 K). Their production and strategies to adjust T_1 for rapid sampling are presented for a temperature range from 5 to 300 K. [6]

Taken together, ^{3}He-magnetometers have the potential to become the new standard for high precision magnetometry at high magnetic fields.

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Ultrabroadband 1D and 2D NMR Spectroscopy

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The chemical shift range of many NMR-active isotopes cannot be excited in a single experiment by classical hard pulse high resolution spectroscopy. Such nuclei can be addressed by specifically optimized saturation pulses, which are derived from linear frequency sweeps that are further optimized using methods derived from optimal control theory. A multi-isotope 1D experiment covering 6 MHz as well as homonuclear COSY and heteronuclear HMBC experiments covering more than 100 kHz are demonstrated, which can be adapted to fit any needs for specific isotopes at any spectrometer field.

The EPR Hunter's Guide to Active Centres of Catalysts

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Catalysts change chemical state during reactions, with many catalytic cycles going through more than two states. Heterogeneous catalysts, in particular, are complex solid-state materials that usually feature a variety of defect and dopant centres that are potentially catalytically active and may also act in concert. In many cases, an active site goes through a paramagnetic state during the catalytic cycle, which makes EPR spectroscopy an attractive technique for identifying active sites, elucidating kinetics, and understanding mechanisms. Given the need to transform the chemical industry to employ renewable carbon feedstock and to further improve energy economics and clean-up of exhaust gases, there is great scope for EPR spectroscopy in catalyst research.

Coming to reliable conclusions on industrially relevant catalysts is complicated by the fact that they often contain several paramagnetic centres, with some of them being bystander species and some active sites. To tell them apart, one needs to measure EPR spectra while the catalysed reaction is going on and correlate the observed spectral changes to product formation or reactant consumption. We have built an operando setup for high-temperature gas reactions over heterogeneous catalysts [1] as well as a droplet-based system for observing homogeneous and dispersed heterogeneous catalysts in liquid solution [2]. By modulating the reaction gas stream and performing lock-in detection post-processing (modulation-excitation spectroscopy), we can improve signal-to-noise ratio and suppress contributions from bystander species [3]. Because of the complexity of the materials, EPR spectroscopy is usually applied in concert with complementary characterization techniques, as we illustrate on the example of single-atom catalysts [4]. For such catalysts, support materials may not be innocent, but rather contribute to catalysis via a pool of oxygen vacancies [5]. Coupled oxygen vacancies can make a material semi-conductive, also in the microwave range, which can then be detected via the off-resonance diode current of an EPR spectrometer. We have observed a correlation between EPR signal intensity and microwave conductivity upon reducing and oxidizing materials of interest in the context of heterogeneous catalysis.

These concepts will be illustrated on the examples of batch oxidation of methane to methanol over Cu(II) loaded zeolites [6], methanol synthesis from CO_2 over reducible metal oxide catalysts [5], and simultaneous conversion of nitrous oxide and nitric oxide over an industrial iron-exchanged zeolite catalyst [7].

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NMR observation of quadrupolar nuclei in materials using ultra-high magnetic fields, DNP and advanced experiments

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Solid-state NMR spectroscopy can provide unique insights into the atomic-level structure of defects in materials, which have a major influence on the optoelectronic and chemical properties. Nevertheless, major limitations of this technique remain its lack of resolution and sensitivity for quadrupolar nuclei with spin $I \geq 1$, which represent over 74% of NMR-active isotopes and are the only NMR-active isotopes to observe the majority of chemical elements, including O, Al, Na, S, Zr, Cl, etc [1].

We show how recent instrumental and methodological developments open new avenues for the observation of these quadrupolar isotopes. In particular, we have leveraged the gain in resolution provided by 1.2 GHz NMR spectrometer (B_0 = 28.2 T) to obtain novel insights into the local environments of quadrupolar nuclei, such as ^{17}O, ^{27}Al, ^{63}Cu or ^{67}Zn, in solids. This approach has been applied to shed light on the mechanisms operating in the mechanosynthesis of organometallic complexes. We have also developed advanced NMR experiments to improve further resolution and sensitivity for the detection of quadrupolar nuclei at 28.2 T. We have especially introduced techniques for the indirect detection via protons of spin-3/2 nuclei, such as ^{23}Na, ^{11}B and ^{35}Cl, under high resolution [2]. We have also explored how the signals of nearby distinct quadrupolar isotopes, such as ^{27}Al and ^{11}B, can be correlated in 2D spectra using continuous wave recoupling (see Fig. 1). The resolution of these 2D heteronuclear correlation spectra between half-integer quadrupolar nuclei can be proportional to B_0^4, when their linewidths are dominated by second-order quadrupolar interaction.

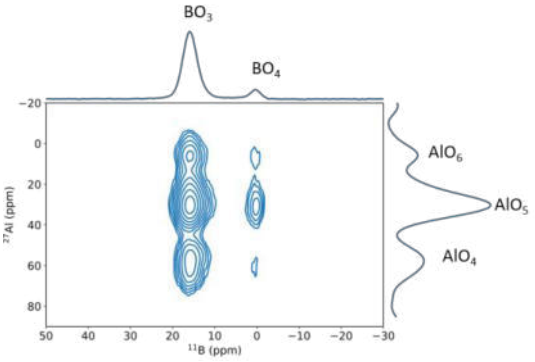

Figure 1. ^{27}Al-^{11}B 2D through-space HMQC spectrum of a glass at 28.2 T.

We have also leveraged the sensitivity gain provided by indirect DNP relayed by protons to detect half-integer quadrupolar nuclei near surfaces of inorganic materials with high resolution and sensitivity [3, 4]. This technique has notably been applied to observe oxygen vacancies near the surface of ZnO nanoparticles used in optoelectronics and active sites of heterogeneous catalyst for the oxidative dehydrogenation of propane.

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Miscible liquids experience phase separation in confinement: An NMR relaxation and diffusion study of binary fluids in mesoporous glass

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The distribution of mixtures of fluids in geometric confinement is affected by the interaction of the individual components with the interface. Radial density functions of the molecular distribution reveal that, depending on fluid combinations, density variations occur from between one to several molecular diameters away from the surface. Molecular dynamics are therefore significantly affected in mesoporous materials with pore diameters below 50 nm. Important factors that affect the molecular distribution are predominantly polarity of both the surface and the molecule, but also molecular shape, size and proticity. It is well known that, for untreated glass and silica surfaces, the molecular polarity leads to variations in T_2 by up to three orders of magnitude, an observation that is matched by T_1 at low magnetic field strength and T_1 dispersion in general. Diffusion, on the other hand, of sufficiently small molecules is independent of polarity and is only governed by the tortuosity of the matrix. A comparison of relaxation and diffusion of liquid mixtures in confinement and in the bulk thus serves as a suitable test for anomalies in the mixing behavior.

Binary mixtures of liquids were prepared with one component perdeuterated, and were filled into Vycor porous glass as well as several types of silica gels. Samples included acetone/cyclohexane, THF/cyclohexane and acetone/water, all of them being fully miscible in the bulk. Relaxation times T_1 and T_2 of ^{1}H as well as ^{2}H were determined for Larmor frequencies between 1 kHz and 300 MHz employing field-cycling relaxometry. Diffusion coefficients were determined by PFG methods on 1T and 7T scanners. For selected fluids, MD simulations were carried out for cylindrical silica pores of similar size, from which radial density profiles and diffusion coefficients were computed.

For acetone/cyclohexane, a pronounced reduction of the apparent tortuosity – the ratio of bulk to confined diffusivity – was found in acetone but was absent in cyclohexane [1,2]. Similar observations were made for water and acetone, suggesting a trend of surface affinity in the order water>acetone>cyclohexane. Very long NMR relaxation times confirm that cyclohexane is removed from the silica surface unless it constitutes the only phase present [3]; the effect is also apparent for water/acetone. MD radial density profiles clearly confirm the preferred adsorption of the more polar liquid. At very low acetone concentration in the mixture with cyclohexane, we found evidence for a reduction of D of 1-2 orders of magnitude, suggesting that the acetone phase close to the surface falls beyond the percolation threshold.

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Mechanistic Understanding of Polyester Hydrolases through Isotope-labelled Polyethylene terephthalate using MAS NMR

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With global plastic production steadily increasing,[2] enzymatic recycling of polymers such as polyethylene terephthalate (PET) is being explored as a promising, energy-saving alternative.[1] Understanding the mechanisms underlying this biocatalytic recycling process may enable rational protein engineering and thus launch a new and more efficient technical opportunity to amplify the extent of plastic waste recycling. The polyester hydrolase PHL7 and its recent mutants have been shown to degrade amorphous PET films at a rate that surpasses all other PET-hydrolysing enzymes reported to date.[3-5] However, enzymatic degradation of crystalline PET still poses a significant challenge.
Recent advances in solid-state NMR spectroscopy have enabled the study of enzyme-substrate binding sites through the establishment of different matrices.[6] These techniques will be used to study the binding mode of various isotope-labelled PET oligomers with PET-Hydrolases via solid-state NMR. While ^{13}C-labelling of the PET ligand reveals distance-dependent information with the active site, ^{2}H-labelling shows changes in dynamics of mobile, amorphous and crystalline PET throughout the process of enzymatic degradation. These results further elucidate the role of hydrophobic subsite II between different polyester hydrolases and provide a better understanding of the biocatalytic PET degradation. Molecular dynamics and docking simulations, assisted by the NMR data, can provide atomic-level insight and guide the engineering of polyester hydrolases with improved function in the future.

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Transverse Relaxation Optimized Spectroscopy in the Presence of Chemical Exchange at 1200 MHz

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Chemical exchange on the chemical shift time scale contributes to transverse relaxation and can be measured in spin-lock- or CPMG-based relaxation dispersion experiments to quantify micro- to millisecond dynamics [1], which allows the determination of the 3D structure of transiently populated protein conformations [2,3]. The advent of 1200 MHz NMR spectrometers extends the range of chemical shift time scales to faster dynamics. Unfortunately, higher sensitivity to fast chemical exchange is associated with fast transverse relaxation and severe exponential signal loss, which makes detection of affected resonances increasingly difficult.

We have used Nedd4-1 WW3, a 41-residue domain in a folding-unfolding equilibrium [4], and the 411-residue transpeptidase domain of PBP3 [5] to develop and evaluate different 2D ^{1}H-^{15}N detection schemes at 1200 MHz. Transverse relaxation optimized (TROSY) schemes are generally superior or at least competitive to HSQC spectra, even for smaller proteins. The absence of ^{15}N decoupling in TROSY also frees up duty cycle load that can be used for ^{15}N CPMG sequences. We have therefore developed 2D ^{1}H-^{15}N TROSY experiments [6] with CPMG transfer periods to refocus chemical exchange signal loss [7] without compromising coherence selection and water flip-back. On our inverse 3 mm triple-resonance cryogenic probe, these transfers provide sufficient bandwidth to cover the typical spectral range at 1200 MHz. We have also been able to incorporate CPMG transfers into 2D ^{1}H-^{15}N BEST-TROSY [8] and ^{15}N TROSY-CPMG relaxation dispersion [2] experiments at 1200 MHz, suggesting that CPMG-TROSY has the potential to serve as a general-purpose amide detection scheme with increased sensitivity for exchanging systems at high magnetic fields.

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$R_{1\rho}$-relaxation at the rotary resonance condition

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Quantitative analysis of $R_{1\rho}$ relaxation rates in solid-state NMR faces several methodological challenges, notably B_1 field inhomogeneity (typically 10–20%). Under MAS, $R_{1\rho}$ rates depend on the spectral density function $J(\omega_{MAS}-\omega_{SL})$, where $\omega_{MAS}/2\pi$ and $\omega_{SL}/2\pi$ are the MAS and spin-lock frequencies, respectively. To access slow molecular motions, the condition $\omega_{MAS} \sim \omega_{SL}$ is required. In this case, the distribution of ω_{SL} across the sample introduces severe uncertainty, making accurate data interpretation impossible without knowing the exact ω_{SL} distribution.

The spin-lock field distribution function $\rho_{inhom}(\omega_{SL})$ can be directly measured from the Fourier transform of the nutation curve [1,2]. This distribution is significantly asymmetric, exhibiting a long low-frequency tail and an abrupt cutoff near the maximum ω_{SL} from the high-frequency side. Additionally, $R_{1\rho}$ decay amplitudes show a pronounced V-shaped dependence on ω_{SL}, with a minimum at the rotary resonance condition ($\omega_{SL} = \omega_{MAS}$) [3,4]. Unlike prior studies, our approach quantitatively accounts for both field inhomogeneity and V-shaped amplitude modulation. The experimentally measured $R_{1\rho}$ rate is expressed as:

$$\langle R_{1\rho} \rangle = \int_{low\_limit}^{high\_limit} R_{1\rho}(\omega_{SL})\,\rho_{inhom}(\omega_{SL})\rho_V(\omega_{SL})d\omega_{SL},$$

where $\rho_V(\omega_{SL})$ describes the V-shaped amplitude modulation. Furthermore, under the rotary resonance condition, recoupling of weak homonuclear dipolar interactions (e.g. ^{15}N–^{15}N coupling) can distort the shape of relaxation decays. While this can hardly be treated analytically, the effect becomes irrelevant when analysis is confined to $\omega_{SL} < \omega_{MAS}$, due to the sharp cutoff in $\rho_{inhom}(\omega_{SL})$.

This integrated approach was applied to analyse ^{15}N proton-decoupled [4] $R_{1\rho}$ rates in a solid protein under various proton decoupling strengths. Despite these complications, the method enables reliable, high-precision $R_{1\rho}$ data analysis even at very small difference $\omega_{MAS}-\omega_{SL}$ (almost zero), unlocking access to molecular dynamics over an exceptionally broad frequency range.

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Understanding Homogeneous Catalysis with high-resolution *operando* FlowNMR Spectroscopy

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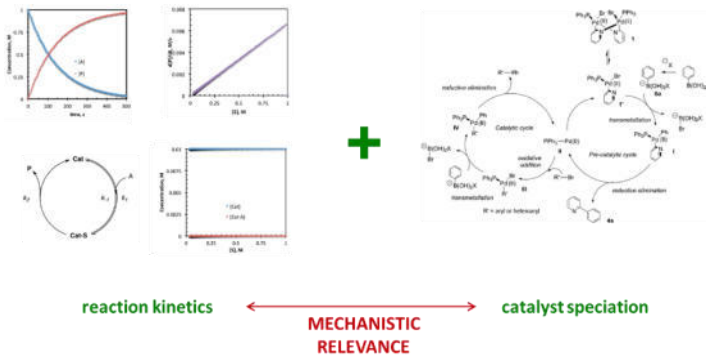
The development of efficient catalytic processes is often hampered by limited insights into the mechanism of the reaction and the transformation of the catalyst during turnover, typically requiring empirical optimisation. Rational catalyst development based on detailed understanding of activation and de-activation mechanisms, potential resting or dormant states, and the kinetics of the productive cycle can be tedious and often inaccurate by traditional ex-situ approaches.

We have built a setup in which a reaction vessel is coupled to an NMR flow tube via small diameter air-tight HPLC tubing. With this we can continuously circulate a reaction mixture through a high-resolution spectrometer to simultaneously follow the reaction progresses and catalyst transformation under realistic conditions in real time.[1] We have characterised flow effects on continuous NMR acquisition[2] and optimised mass and heat transport aspects of such setups[3] to ensure accurate and relevant data is collected. Multiple solvent suppression and selective excitation techniques allow the detection of minor intermediates even in non-deuterated solvents,[4] and the use of paramagnetic relaxation agents can greatly improve heteronuclear NMR sensitivity and quantification.[5] Complementary techniques such as UV-vis, HPLC, MS and GPC can be added to the sample flow path which has allowed the comprehensive analysis of asymmetric hydrogen transfer catalysis[6] and dynamic organometallic catalysis in solution[7] and under gas pressure.[8, 9] This setup is also useful for interrogating photocatalysis,[10] carrying out chemical shift titrations in complex mixtures,[11] and special FlowDOSY techniques[12] allow following molecular weight evolution during polymerization reactions.[13]



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IltPy: A python library for inverse Laplace transform of magnetic resonance data

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Relaxation and diffusion processes offer rich information about interactions and dynamics in materials and can be correlated to chemical composition and structure. [1] Experimental magnetic resonance data obtained from relaxation and diffusion measurements are often analysed by fitting a suitable mathematical function to the data for extracting underlying relaxation time and diffusion rate constants. However, depending on the compositional heterogeneity, processes may exhibit functional dependencies which are not governed by a single characteristic parameter but a distribution. Therefore, experimentally measured data may feature a superposition of different contributions, and their disentanglement becomes challenging by conventional data analysis methods. In such cases, inversion algorithms allow for quantitative analysis by inverting the data with a suitable kernel, mitigating the need for possibly ambiguous assumptions regarding the number of components or the shape of the underlying distribution. Herein, *IltPy*,[2] an open-source python library is introduced for performing regularized inverse Laplace transforms (ILT) of one- and multi-dimensional data. Conventional approaches to ILT of magnetic resonance data require an assumption of signal contributions to be strictly positive. [3] However, this approach suppresses negative contributions which may be physically relevant, particularly in systems undergoing chemical exchange or cross-relaxation.[4]
IltPy implements regularized inverse Laplace transform (ILT) without requiring non-negativity (NN) constraints.[5] Tikhonov regularization in its generalized form is used, and the solution is stabilized with a uniform penalty and a zero-crossing penalty allowing for extraction of parameter distributions preserving both positive and negative features in the data without preferring one of the signs. *IltPy* supports user-defined kernels and validity of NN constraint can be tested by comparing inversions with and without NN. For large data sets, singular value decomposition is used to compress data. For experimental data with non-uniform noise or oscillatory features, such as ESEEM, *IltPy* supports weighted inversions. Furthermore, resolution of multi-dimensional data may be improved by regularization of non-inverted dimensions.[2] *IltPy* is particularly suited for EPR and NMR spectroscopic data. The performance of the library is demonstrated using application examples from relaxation and diffusion data sets, revealing insights into interactions and environments in complex systems.

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Robust Bilinear Rotations and the HUGE-BIRD

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Bilinear rotations form an essential tool in modern pulse sequence design as it allows the manipulation of spins based on their specific bilinear interactions. The original Bilinear Rotation Decoupling (BIRD) element [1] effectively applies a universal π-rotation when heteronuclear one-bond coupling is allowed to evolve and leave spins untouched for couplings close to zero. The main drawback of the BIRD element is that delay mismatch, and – more importantly – coupling variation within the sample, leads to dissipation of magnetization and this may make signals become uninterpretable and unphaseable. Using the COB approach [2], we optimized the BIRD element to be robust over Coupling, Offset and B1-variations into the new COB-BIRD. We apply this new sequence in a {1H}13C 2D-INEPT type experiment on partially aligned (–)-nicotine with total coupling values ranging from 71 Hz to 253 Hz. We then design a new homonuclear BIRD into the Homonuclear Universal Gyration or Excitation Bilinear Rotation Differentiation (HUGE-BIRD) and apply this to an S/N optimized INADEQUATE sequence for effective 13C-13C spin system selection.

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Identifying and overcoming resolution barriers in ^{19}F ENDOR

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In 2020, we introduced the strategic use of bioisosteric ^{19}F labels in combination with pulsed electron nuclear double resonance (ENDOR) for measuring biomolecular distances in paramagnetic systems on the low nanometer range.[1] Measurements on small nitroxide models allowed estimating an accessible distance range of 0.5 – 1.5 nm, for which dipolar Pake patterns were obtained. The upper distance limit was imposed by low sensitivity and, more importantly, a lack of spectral resolution. The low resolution was caused by an ENDOR line width of ~20 kHz, which is nearly equal to the dipolar coupling constant at 1.5 nm. Limiting line widths of 20 – 30 kHz were reproducibly found by us and others in subsequent years, but no physical explanation for the origins of this parameter were given.

Here, we present the results of our most recent studies. First, we could identify different contributions to the intrinsic ENDOR line width,[2] with inter-nuclear dipole coupling between the ^{19}F nucleus and nearby protons playing a particularly important role. Knowledge about the importance of this nuclear dipole broadening mechanism aided in the investigation of a nitroxide labelled riboswitch. In this case, fluorine/proton nuclear dipolar couplings were practically absent, which enabled ENDOR measurements and analyses at a ^{19}F-nitroxide distance exceeding 2.0 nm,[3] i.e. > 30 % above the previously estimated distance limit. Furthermore, we also found experimental ways to suppress the nuclear dipole broadening using a novel, time-domain ENDOR experiment called pulsed dipolar hyperfine spectroscopy (PDHS).[4] This experiment reduces the ENDOR line width to about 3 kHz and could thus enable measurements at distances exceeding 2.5 nm.

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An integrative approach to unveil the structural basis of the indirect inhibition of apoptosis

Apoptosis, a form of programmed cell death, is a key mechanism in multicellular organisms that requires strict regulation. Cells that cannot perform apoptosis can grow unhindered, leading to tumors, while cells that perform apoptosis unnecessarily contribute to degenerative diseases, such as Alzheimer's disease. [1]

The mitochondrial pathway of apoptosis in cells is performed and regulated by the Bcl-2 protein family, consisting of the proapoptotic effector proteins (e.g. Bax) which form pores at the outer mitochondrial membrane, the BH3-only activator proteins (e.g. Bid) which trigger the effectors' activation, and the antiapoptotic proteins (e.g. Bcl-xL) which inhibit the effectors (direct mode) and/or the activators (indirect mode. The structural basis of the inhibition is still unresolved, but it is crucial for understanding the regulation of apoptosis and for developing potent apoptotic modulators.

Here, using an integrative modeling approach that combines site-directed spin labeling EPR spectroscopy with molecular simulations, we describe the structure, interaction interfaces, and dynamics of the inhibitory complex between Bcl-xL and tBid at the mitochondrial membrane. The dynamic ensemble model, validated by DEER distance constraints obtained in liposomes and in mitochondria and by HDX-MS, provides new insights in the mechanism of indirect inhibition of apoptosis [2,3].

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HEteronuclear Referencing for METRologic Isotope Calibration (HERMETRIC)

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This work presents the concept of HEteronuclear Referencing for METRologic Isotope Calibration (HERMETRIC) as an innovative approach to quantitative NMR (qNMR) spectroscopy. The aim is to establish a metrologically based fundamental understanding that goes beyond traditional homonuclear NMR methods. In comparison to established quantitative methods — such as weighing, titration, chromatography, and complexometry — it is demonstrated that qNMR, as a primary method, can determine absolute amounts of substance directly without external calibration. At the same time, heteronuclear quantification opens new perspectives by enabling the direct traceability of all active nuclei to a universal qNMR primary standard. The concepts are intended to encourage the further establishment of qNMR as a powerful instrument in analytical chemistry and its incorporation into pharmacopoeias and other official standard protocols.

Keywords: Heteronuclear Quantitative NMR Spectroscopy, Isotopic Analysis, Analytical Principles, Methods Comparison, Weighing, Titration, Complexometry

The Rise and Fall of Nuclear Spin Polarization

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Achieving and preserving high nuclear spin polarization is essential to spin hyperpolarization. In bullet-DNP the balance of hyperpolarization build-up (facilitated by the presence of radicals) and preservation (hindered by the presence of radicals) differs from ordinary dissolution-DNP. I will show how this balance can be optimized, and how the gains in proton polarization can be applied in drug screening.

In the second part of the talk, I will reverse gears and describe how a new type of magnetic resonance, so-called nonsecular resonances (NSRs) can be used to saturate the nuclear spin polarization by irradiation far off the Larmor frequency. With the existence of NSRs established, I will then show how they can be used for hetero-nuclear polarization transfer using radio-frequency excitation at a single frequency.

Simulation of pulsed dynamic nuclear polarization in the steady state

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Simulation of pulsed dynamic nuclear polarization (DNP) is a valuable tool to identify good conditions for experiments and give insights into their behavior. Numerical simulations based on the kernel of Spinach [1], previously carried out for single polarization transfer from 1 electron to 2 protons were useful in predicting the conditions for experimental field profiles with DNP pulse sequences: time-optimized pulsed (TOP), X-inverse-X (XiX), and two-pulse phase modulation (TPPM) [2]. However, deviations between simulations and experiments were observed. Moreover, optimization of repetition time is not possible with the single transfer simulation. Simulating the complete pulsed DNP process to polarize the bulk nuclei is complex, requiring hundreds and thousands of polarization transfers for the spin system to reach the steady state. We have a solution to quickly compute the steady state using Newton-Raphson's root-finding algorithm [3]. This algorithm is numerically stable and is three times faster than brute force propagation for a 9-spin system.
Steady-state simulations at 0.34 (X), 1.2 (Q), and 3.4 T (W band) accurately reproduce the experimental field profiles, optimization of repetition times, and electron nutation frequency dependence, even with a simple spin system of 1 electron and 1 proton. Polarization transfer curves indicate that the steady orbits differ from the orbits of the spin system during single transfer. Agreement with experiments further improves when including electron-proton distance and electron nutation frequency distributions. Nuclear spins close to the radical have a fast longitudinal relaxation rate, which is incorporated into our relaxation model. The steady-state simulations are also useful in predicting the experimental behaviour with DNP pulse sequences that induce polarization transfer via adiabatic passage (Fig. 1), and hence, shall be used for designing efficient pulse sequences.

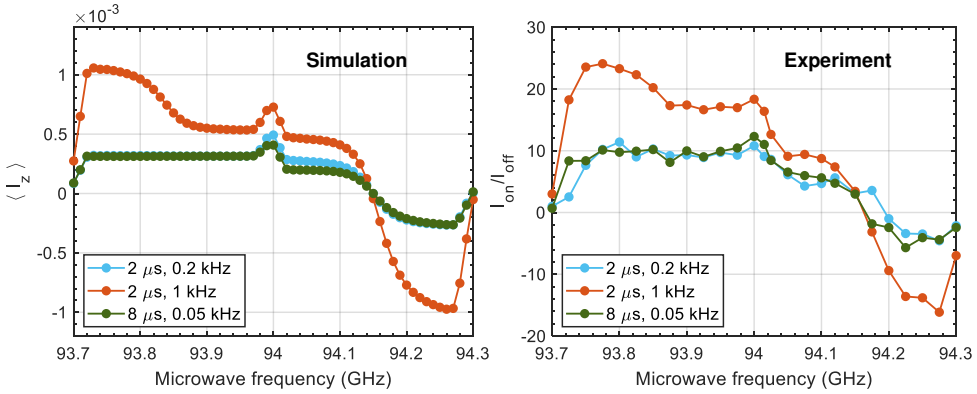

Fig. 1. Field profiles showing the effect of repetition rates with chirp pulses of 300 MHz bandwidth.

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Investigation of a Partially Fluorinated Matrix and Exploration of ^{19}F-^{13}C Cross Relaxation for Enabling ^{19}F MAS DNP

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Magic-angle spinning (MAS) solid-state NMR is a unique technique among the toolbox of analytical methods. Its sensitivity is constrained by the thermal polarization of nuclear spins; consequently, in many challenging systems, the implementation of hyperpolarization methods can often emerge as the only feasible option. The most promising method for MAS NMR is dynamic nuclear polarization (DNP), which utilizes the transfer of the large electron polarization to nuclei during microwave irradiation. DNP has been successfully applied in many areas, enabling otherwise unfeasible experiments such as in-cell applications.[1]

A notable development in recent years is the heightened interest in ^{19}F NMR. Due to its absence in all biological building blocks, fluorine atoms can be invoked as spin-tags to gain site-specific structural insights into biological complexes. Moreover, the ^{19}F nucleus is prevalent in active pharmaceutical ingredients (API), opening the distinctive ability to study APIs by ^{19}F NMR. In the pioneering works of Emsley *et al*.[2] and Polenova *et al*.[3] ^{19}F MAS DNP was first demonstrated for each of the above applications. Furthermore, recent studies employing ^{1}H-^{19}F cross polarization (CP) experiments have shown the remarkable potential of ^{19}F DNP.[4] Despite recent efforts, the advancement of the field of ^{19}F DNP is currently constrained by the limited availability of dedicated MAS DNP probes capable of irradiating ^{1}H and ^{19}F resonances simultaneously.

The objective of this study is to explore alternative approaches for making ^{19}F DNP accessible even in light of the limited availability of such dedicated H/F probes. In one direction, we have systematically investigated partially fluorinated glycerol/water/DFIP (1,3-difluoro-2-propanol) DNP matrices to facilitate relayed polarization transfer through a denser ^{19}F spin network. In this regard, we demonstrate that with such an approach a fourfold increase in the sensitivity of direct ^{19}F and ^{19}F-^{13}C CP experiments on fluorinated model compounds can be attained. In addition, we have observed ^{19}F-^{13}C cross relaxation (CR) under cryogenic DNP conditions, thereby establishing an alternative ^{19}F DNP pathway. We show that this CR pathway can be invoked for SCREAM-DNP (Specific Cross-Relaxation under Active Motions under DNP)[5] to site-specifically investigate ^{13}C nuclei that are in proximity to trifluoromethyl groups.

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Spin-spin interaction in Conjugated Trityl Biradicals: A journey through different coupling regimes

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Organic radicals are important intermediates in many chemical reactions and are rather unstable and reactive species. However, in some cases, these radicals can be sufficiently stabilized. Nitroxide and Trityl radicals are prominent and strongly represented examples in this context. Trityl radicals are particularly fascinating structures, because of their rather encapsulated and purely carbon-centred radical moiety, resulting in high chemical stability, narrow EPR linewidths, and long coherence times. Hence, they are used for applications such as spin labels for EPR based distance determination, magnetic resonance imaging, or dynamic nuclear polarization. Despite their favourable characteristics, examples of chemically coupled multi-spin systems based on Trityl radicals – other than labelled proteins – are rather scarce, and the scope of studied spin-spin interactions is still limited.[1-5] A deeper understanding of these interactions is crucial in the rational design of new model systems in fields such as DNP, molecular magnetism, and spintronics. In this work we investigate a series of Trityl biradicals covalently linked via polyphenylene bridges of varying length. Depending on the strength of the electronic coupling – ranging from weak to strong exchange/dipolar interactions – valuable insights into the radical properties can be obtained. By combining continuous-wave and pulsed EPR at room and low temperatures, we access both dipolar and isotropic exchange interactions. Furthermore, we demonstrate that dipolar coupling remains detectable even at room temperature, for biradicals with shorter bridges. Finally, high-field EPR experiments (at W-band) provide access to the relative orientations of the trityl moieties, enabling detailed structural characterization of the biradical systems.

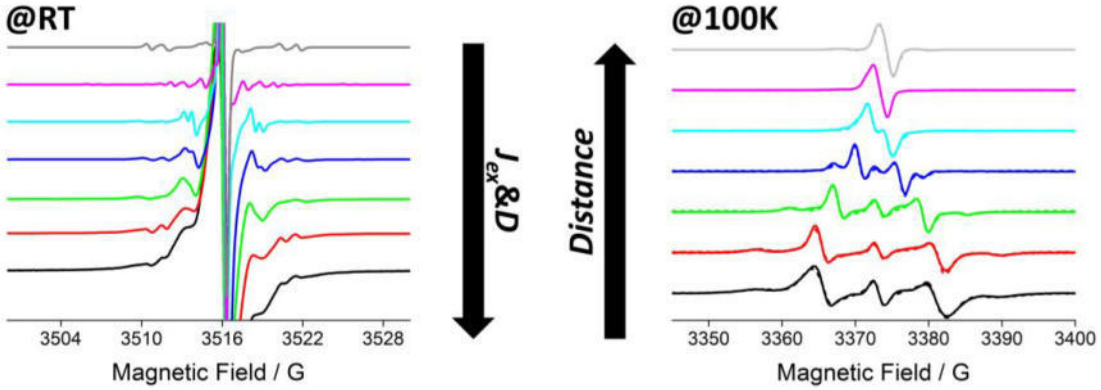

***Figure 1**: cw EPR spectra of investigated Trityl biradicals.*

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In situ NMR Spectroscopy – A Versatile Tool to Study Framework Flexibility in Materials

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Porous materials like metal-organic frameworks (MOFs) or covalent-organic frameworks (COFs) can exhibit structural flexibility. That means, pronounced structure transitions are induced by external stimuli like adsorption of certain molecules from surrounding gases or liquids, temperature or pressure changes, and others. [1] Such stimuli-responsive, flexible MOFs and COFs are attractive candidates for applications in gas adsorption and separation, in catalysis, as well as for sensing purposes. Hence, the characterization and basic understanding of these structural transitions is an important research topic. [1]

In situ NMR spectroscopy of adsorbed molecules allows to characterize the host-guest interactions which can induce structural transitions by determining NMR parameters of the adsorbed species. For *in situ* gas adsorption studies, we have developed special equipment [2] enabling *in situ* high-pressure NMR studies. Variable gas pressures up to 100 bar can be applied at variable temperatures down to 190 K inside the NMR spectrometer. The influence of framework flexibility upon the adsorption selectivity from gas mixtures (^{129}Xe/Kr) was studied in detail by *in situ* high-pressure ^{129}Xe NMR spectroscopy. [2] Carbon dioxide is another suitable probe to study flexible frameworks. *In situ* high-pressure ^{13}C NMR spectroscopy of $^{13}CO_2$/$^{13}CH_4$ mixtures was applied to study the selectivity of gas uptake by flexible MOFs. [3] Notably, covalent CO_2 binding to certain defects in MOFs and MOF glasses was observed during CO_2 adsorption studies. [4] *In situ* ^{129}Xe NMR spectroscopy also served to study the influence of defects and the crystallite size upon the framework flexibility of the unique, pressure-amplifying framework material DUT-49. [5] Finally, liquid-state adsorption of alcohols can be studied by solid-state NMR spectroscopy of samples soaked with defined amounts of solutions. For example, an unexpected adsorption-induced phase transition was detected by time-resolved ^{13}C MAS NMR spectroscopy in ZIF-11. [6]

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Phase separation in supercooled water/glycerol mixtures probed by ih-RIDME

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Intermolecular hyperfine relaxation-induced dipolar modulation enhancement (ih-RIDME) technique has been developed over the last few years. [1] The ih-RIDME technique is sensitive to proton spins at distances from 1 nm to 3 nm and at some conditions beyond these limits. Changes in the local proton density as well as the 'connectivity' of proton cloud around spin labels can be quantitatively described, which opens new perspectives in the soft and unstructured matter research. Here, we demonstrate the capabilities of ih-RIDME on a practically important example of frozen water-glycerol mixtures serving as popular cryoprotectors in biological study. Storing homogeneous water-glycerol mixtures at -80°C, which is above the glass transition temperature, but which is a typical storage condition for biological samples,[2] leads to a liquid-liquid phase separation into water-rich phase and glycerol-rich phase.[3] The ih-RIDME data confirm strong preference of nitroxide probes to stay in the glycerol rich phase and allow evaluation of the phase composition. No bulk isotope effect on the composition of the glycerol-rich phase was observed upon deuteration of water or glycerol. These experiments also suggest applicability of ih-RIDME technique for studying solvation shell effects in macromolecular systems, such as proteins, nucleic acids as well as natural and synthetic polymers.

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Phase Transition of PBLG: Characteristics and Usefulness for Structure Determination

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The liquid crystal Poly-γ-benzyl-L-glutamate (PBLG) is a well-known alignment medium for organic molecules. It shows a pure anisotropic phase above a critical concentration and below it is purely isotropic. But in a small concentration range at the transition from isotropic to anisotropic both phases coexist. The behavior of this phase transition is investigated by conventional and rheological NMR, as well as MRI. The co-existence of both phases is studied with kinetic experiments and applications regarding residual anisotropic parameters are given particular consideration.

On the brink of collapse – interior design of thermo-responsive multicompartment micelles shown by NMR spectroscopy

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Polymeric micelles, consisting of a hydrophobic core and a hydrophilic corona, are widely researched carriers for poorly water-soluble drugs. These nanostructures provide many advantages such as improved bioavailability, drug solubility, targeting, improved blood circulation times, and more [1]. The introduction of a compartmentalized core enables advantageous co-delivery of drugs within one carrier [1]. However, in many cases, the investigation of their structure and dynamics is challenging, particularly in complex polymer systems. Conventional techniques such as microscopy or light scattering, although invaluable, cannot unravel what is happening beneath the micellar surface [2]. NMR spectroscopy has been emerging as a powerful tool for the investigation of these intricate nanostructures [3]. How is each layer organized? How do the micelles interact with the environment? How do varying chain mobilities affect the structure? NMR with its wide array of different techniques helps answering these questions. In turn, this allows us to learn more about the interior design of polymeric micelles.

Taking inspiration from the work of A. Walther et al. [4], different block copolymers were synthesized and assembled into micelles. The copolymers consisted of poly(butyl/benzyl) acrylate, polyethylene glycol, and poly(n-isopropyl) acrylamide (PNIPAM), incorporated for its thermo-responsive properties. Known for having a lower critical solution temperature slightly below body temperature, PNIPAM transitions from hydrophilic to hydrophobic and collapses into the micellar core, compartmentalizing it. The self-assembled structures were investigated under various conditions, from variable temperature or use of cryoprotectant, to drug encapsulation. Peak analysis and relaxation data were used to probe the rigidity of each micellar component, while NOESY and DOSY aided in the investigation of the intermolecular and intramolecular interactions. This work aims to expand the current knowledge by elucidating the architecture, dynamics and interactions of multicompartment polymeric micelles.

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From EPR Spectroscopy to MASERs: A Dielectric Journey

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Molecular systems containing unpaired electron spins may be prepared in a non-Boltzmann state, resulting in spectra showing enhanced absorption or emission, as originally – and unexpectedly – observed in NMR and ESR spectra following flash-photolysis, and given the acronyms: CIDNP and CIDEP, respectively. Non-Boltzmann spin populations (*usually)* increase the sensitivity of the experiment, and allow, for example, the use of direct detection, continuous-wave EPR without the use of magnetic field modulation, for example for the investigation of photo-generated species such as spin-correlated radical pairs and triplet states.

Another technological development that enhances the sensitivity of EPR spectroscopy is the use of dielectric resonators. A typical example is the use of Corundum, a crystalline form of Al_2O_3, commonly known as sapphire.

The use of both electron spin-polarization and optimization of dielectric resonators [1] was fundamental for our realization [2] and optimization [3] of a solid-state, room-temperature, continuous-wave MASER, using NV- centers in diamond.

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Quantum sensing with spin defects in boron nitride nanotubes

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Spin defects in semiconductors are widely investigated for various applications in quantum sensing. Conventional host materials such as diamond and hexagonal boron nitride (hBN) provide bulk or low-dimensional platforms for optically addressable spin systems, but often lack the structural properties needed for chemical sensing. Here, we introduce a new class of quantum sensors based on naturally occurring spin defects in boron nitride nanotubes (BNNTs) [1, 2], which combine high surface area with omnidirectional spin control—key features for enhanced sensing performance. First, we present strong evidence that these defects consist of weakly-coupled spin pairs, akin to recently identified centers in hBN [3], and demonstrate coherent spin control over ensembles embedded within dense, microscale BNNTs networks. Using dynamical decoupling, we enhance spin coherence times by a factor exceeding 300x and implement high-resolution detection of radiofrequency signals. By integrating the BNNT mesh sensor into a microfluidic platform we demonstrate chemical sensing of paramagnetic ions in solution, with detectable concentrations reaching levels nearly 1000 times lower than previously demonstrated using comparable hBN-based systems [4,5]. This highly porous and flexible architecture positions BNNTs as a powerful new host material for quantum sensing.

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Development of a microscale NV-NMR spectroscopy at 1 T

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Nitrogen-vacancy (NV) centers in diamond have emerged as a powerful platform for quantum sensing, offering high sensitivity and spatial resolution for magnetic field detection under ambient conditions. One of their most promising applications is microscale nuclear magnetic resonance (NMR) spectroscopy [1], particularly for small-volume and surface-sensitive chemical analysis. To date, most NV-NMR experiments have been conducted at magnetic fields between 100–200 mT [2,3]. However, accessing higher magnetic fields is crucial for improving chemical resolution and spectral information.

In this work, we report on recent progress toward implementing an NV-NMR system operating at magnetic fields near 1 T, supported by preliminary experimental results. Operating at this regime introduces several technical challenges, including the need for high NV drive frequencies (~30 GHz) and strong B1 fields to achieve short π and $\pi/2$ pulse durations. To address these, we developed a custom-designed probehead that integrates efficient microwave delivery, optimized light collection, and microfluidic sample handling.

Our initial experiments demonstrate successful NV spin control at 1.12 T, marking a critical step toward high-field NV-NMR. This platform opens new possibilities for microscale chemical analysis with a level of spectral information comparable to benchtop NMR spectrometers. Future applications may include single-cell analysis [4] and lab-on-a-chip technologies.

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EPR Studies of Molecular Qubit Assemblies

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Paramagnetic molecules that may be employed as molecular qubits have been shown to possess long coherence times in the three digit microsecond regime, in nuclear-spin-poor and dilute matrices, such as doped solids and frozen solutions.[1] To make progress toward implementing quantum technologies with such molecules, a long road lies ahead.

A first step is the preparation of two- and other few-qubit assemblies.[2] This is essential for the implementation of two-qubit gate operations. Ideally, the interaction between the two qubits should be switchable, e.g., by light excitation. To this end, we have prepared dimers of the TEMPO radical which are bridged by anthracene moieties, using different coupling strategies.[3] Time-resolved absorption measurements reveal different intersystem crossing efficiencies. The coupled nature of the photoexcited three-spin system was unambiguously demonstrated by time-resolved EPR measurements.

For quantum computing and quantum simulation, extended two-dimensional arrays of qubits are required. As a first step in this direction, we have prepared self-assembled monolayers (SAMs) of TEMPO-molecules using a modular approach.[4] Careful analysis demonstrated clean SAM formation. EPR measurements on intact SAMs revealed sizable coherence times. Recent investigations with other radicals substantiated and enhanced on these findings.[5]

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Multi-Contrast MRI: A Comprehensive Window into Brain Microstructure

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Magnetic Resonance Imaging (MRI) has become an indispensable tool in clinical diagnostics owing to its non-ionising nature, exceptional soft tissue contrast, and virtually unlimited penetration depth. These characteristics enable the acquisition of high-resolution images from deep within the body, supporting a wide range of medical applications.

Although conventional MRI techniques are highly sensitive to changes in tissue structure and composition, they often lack specificity regarding the underlying biological or pathological mechanisms driving the observed signal changes. Clinically relevant parameters, such as cell density, myelin content, or protein aggregation, do not necessarily correspond directly to MRI-accessible quantities like relaxation times (T1, T2). As a result, similar contrast alterations may originate from distinct microstructural or biochemical processes, complicating interpretation and limiting the diagnostic and prognostic utility of standard MRI protocols.

To overcome these limitations, a range of advanced MRI techniques has been developed to probe additional biophysical and biochemical properties of tissue. These include, but are not limited to, diffusion-weighted imaging (DWI), magnetisation transfer imaging (MTI), and susceptibility-based imaging. Each of these modalities provides complementary insights into tissue microstructure, composition, and function.

Multi-contrast MRI approaches aim to combine these diverse contrasts to enhance the specificity of tissue characterisation. By leveraging the complementary information offered by different MRI contrasts, such frameworks can improve the differentiation of pathophysiological processes that may appear similar on conventional images.

This presentation will examine the advantages and limitations of individual MRI contrast mechanisms, as well as their synergistic potential when combined in a multi-contrast framework. By correlating MRI findings with histological analyses and employing animal models with well-characterised tissue properties, we aim to refine our understanding of the biological correlates of MR signal changes. Ultimately, this knowledge may inform the development of more specific and biologically meaningful imaging biomarkers.

Towards investigation of protein conformations in cells with EPR spectroscopy

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To understand biomolecular function within native environments, structural information should ideally be acquired directly within the relevant context to reveal the complex interactions that take place e.g., inside living cells. The emerging field of pulsed dipolar electron paramagnetic resonance spectroscopy (PDS) enables studying biomacromolecular structures in vitro and more recently in their natural environment. Triaryl methyl (TAM)[1], gadolinium [2] or copper based spin labels [3] that are persistent against reduction under the studied conditions, have been exploited to study the behaviour of the Yersinia outer protein O (YopO) from *Yersinia enterocolitica* as well as the group G protein G, domain B1 (GB1) from *Streptococcus sp* inside cells.

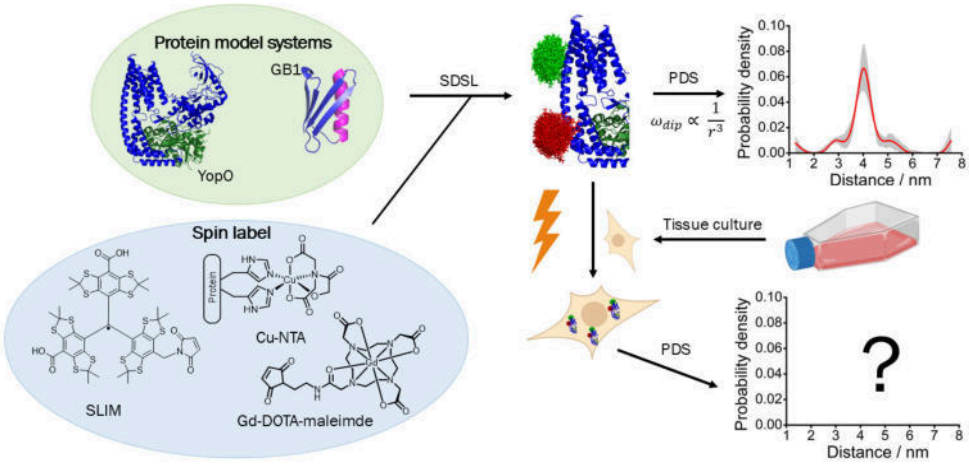

Figure 1: Protein model systems YopO (PDB-ID: 4CI6) and GB1 (PDB-ID: 4WH4) and a variety of spin labels for in cell applications, in vitro and in cells.

Here, I will report on experiments with YopO and GB1 screening different spin labels, cell types as well as delivery methods to optimise the resulting PDS data quality. YopO yielded data consistent with aggregation in combination with TAM radicals and to a lesser extent with gadolinium based spin labels. In contrast, GB1 with either TAM or gadolinium spin labels did not aggregate under the examined conditions and is currently being investigated in HeLa and *E. coli* cells. More recently the applicability of Cu-NTA for in cell experiments was demonstrated and could be applied to the studied systems, in combination with relaxation induced dipolar modulation enhancement (RIDME) which provides a significantly increased sensitivity. The acquired data highlights that the combinations of spin label, protein, and PDS method are of essential importance for the stability of the systems studied and quality of the resulting PDS data.

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Structural basis of apoptosis induction by the mitochondrial voltage dependent anion channel

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The voltage-dependent anion channel (VDAC) is the main gateway for metabolites across the mitochondrial outer membrane. VDAC oligomers have been associated with apoptosis at mitochondrial stress conditions. However, the mechanistic and structural basis of VDAC's capability to induce apoptosis pathways remains poorly understood. Here, we show with biochemical and structural methods that VDAC1 oligomerization triggers the dissociation of its N-terminal α-helix (VDAC1-N) from the channel interior. We used advanced lipid nanodiscs [1,2] as a tool to selectively trap VDAC1 in its canonical helix-inserted or helix-exposed state to probe its conformational changes by NMR spectroscopy and cryo-electron microscopy. The results show that once trapped in a small and confined lipid nanodisc – a proxy for the oligomeric state - the VDAC1 β-barrel changes its shape leading to the release of the N-terminal α-helix to the channel exterior. VDAC1-N can then engage in the interaction with partner proteins, such as the apoptosis inhibitor protein BclxL. We performed interaction studies between VDAC1 in both conformational states and BclxL using NMR spectroscopy and could detect binding only for the helix-exposed state. These insights facilitated the structure determination of the BclxL-VDAC1-N complex at high resolution and provided atomistic details on the VDAC1 binding mode at the canonical BH3-groove in BclxL. Biochemical assays showed that VDAC1-N can promote pore formation of the pro-apoptotic protein Bak [3] by neutralizing BclxL's inhibitory activity. These findings suggest that stress-induced oligomerization of VDAC can trigger the exposure of its N-terminal α-helix leading to the neutralization of anti-apoptotic Bcl2 proteins. This mode-of-action is reminiscent of BH3-only sensitizer Bcl2 proteins that are efficient inducers of Bax/Bak-mediated mitochondrial outer membrane permeabilization and ultimately apoptosis [4].

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Characterisation of a fold in TANGO1 evolved from SH3 domains for the export of bulky cargos

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Bulky cargos like procollagens, apolipoproteins, and mucins exceed the size of conventional COPII vesicles. During evolution a process emerged in metazoans, predominantly governed by the TANGO1 protein family, that organises cargo at the exit sites of the endoplasmic reticulum and facilitates export by the formation of tunnel-like connections between the ER and Golgi. Hitherto, cargo-recognition appeared to be mediated by an SH3-like domain. Based on structural and dynamic data as well as interaction studies from NMR spectroscopy and microscale thermophoresis presented here, we show that the luminal cargo-recognition domain of TANGO1 adopts a new functional fold for which we suggest the term MOTH (MIA, Otoraplin, TALI/TANGO1 homology) domain. These MOTH domains, as well as an evolutionary intermediate found in invertebrates, constitute a distinct domain family that emerged from SH3 domains and acquired the ability to bind collagen. [1]

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Parahydrogen Induced Polarization of Biomolecules –
From Amino Acids to Mini-Proteins and Biopolymers

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Nuclear Magnetic Resonance (NMR) spectroscopy is one of the most powerful tools for elucidating the structural and dynamic features of biomolecules and their biochemical interactions. However, the inherently low sensitivity of NMR remains a significant limitation, primarily due to the low population differences (spin polarization) between spin states at thermal equilibrium. To overcome this challenge, a number of complementary hyperpolarization techniques were developed, which, by physical or chemical techniques, create spin-polarization far away from thermal equilibrium and boost the NMR signals by several orders of magnitude. Parahydrogen Induced Polarization (PHIP) and its reversible variant SABRE (Signal Amplification By Reversible Exchange) are among the most versatile and cost efficient hyperpolarization techniques for NMR signal enhancement in solution NMR.
The talk will first give a short introduction to PHIP and SABRE, followed by an overview of our special PHIP set-ups. Then some examples from our recent work on bioactive or biological molecules will be presented. The first example shows the results of our studies on a bioactive derivative of sunflower trypsin inhibitor-1 (SFTI-1), which inhibits matriptase, a colon cancer-related enzyme. The PHIP activity of the inhibitor was achieved by labeling the tetradecapeptide with O-propargyl-L-tyrosine. By using a carefully optimized automated PHIP setup in 1D PHIP experiments, an amplification of up to approximately 1200 was found compared to normal NMR. This enormous amplification factor enabled ultra-fast single-scan detection of 2D TOCSY spectra of micromole solutions of the PHIP-labeled inhibitor. We then present recent results on the hyperpolarization of fumarate and eptifibatide, a platelet aggregation inhibitor derived from the venom of certain rattlesnakes, and octreotide, a somatostatin analogue used in the diagnosis and treatment of various cancers. While the previous examples used rather small target molecules, the two remaining examples show the application of PHIP to a 236 kD biopolymer and a disulfide-rich mini-protein.

Configurational and conformational analysis of cyclic peptides and flexible natural products using anisotropic NMR spectroscopy and density functional theory

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Configurational and conformational analysis of drug-like small molecules and peptides is essential for understanding their biological activity and cellular uptake properties. However, experimental methods for precisely determining the stereochemistry and conformation of flexible organic molecules remain limited.

In this talk, I will first introduce experimental approaches that enable the straightforward extraction of anisotropic NMR parameters—such as residual dipolar couplings (RDCs) and residual chemical shift anisotropies (RCSAs)—in both aqueous and organic solvents using oligopeptide-based liquid crystalline phases [1,2]. Next, I will present our recent comprehensive benchmark of carbon shielding anisotropies based on coupled-cluster reference tensors and evaluate the influence of various density functional theory (DFT) methods on RCSA-based stereochemical and conformational analysis of organic molecules [3]. Building on these advancements, I will showcase several examples where the combination of anisotropic NMR spectroscopy and advanced computational methods has enabled successful determination of the configuration and conformation of flexible natural products and cyclic peptides. In particular, we demonstrate that integrating independent NMR observables with state-of-the-art DFT calculations significantly enhances the accuracy and efficiency of structural determination [4–6]. Finally, I will illustrate our recent efforts in predicting anisotropic NMR parameters using atomistic molecular dynamics simulations.

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EPR Study of charge transfer co-crystals Structure/Function Relationship

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Organic charge-transfer (CT) co-crystals exhibit unique electronic and magnetic properties depending on their molecular packing structures and aggregate states which exhibit a variety of novel properties through multicomponent synergistic and collective effects. Previously we presented that Anthracene/ tetracyanoquinodimethane (TCNQ) charge transfer co-crystals have a localized spin with a unique long relaxation times as a results of its mixed stack packing in the crystal.

Here we present the results of our charge transfer co-crystals screening study, which resulted with three more charge transfer co-crystals having mixed stack packing and long spin relaxation times: Tetramethylphenylenediamine (TMPD)/ tetracyanoquinodimethane (TCNQ), Naphthalene/1,2,4,5-Tetracyanobenzene (TCNB) and perylene/2,2'-Benzo[1,2-b:4,5-b']dithiophene-4,8-diylidene-bis-propanedinitrile (DTTCNQ).

In this study we were able to determine the criteria for charge transfer co-crystals with long spin relaxation times.

In addition, EPR study upon photoexcitation of Anthracene/TCNQ co-crystals showed the formation of spin polarized radical-pair spectrum. Its EPR phase pattern indicates it is a triplet born radical pair.

Probing the Magnetic Susceptibility Tensor of an Europium(III) complex by Paramagnetic Solid-state NMR

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A variety of materials ranging from inorganic battery materials, catalysts to metalloproteins feature unpaired electrons and can thus be classified as "paramagnetic". Solid-state NMR is the method-of-choice to study their structural and dynamic properties in the solid state, particularly in cases where standard X-ray crystallographic characterization techniques reach their limit. For NMR investigations, the paramagnetic nature of a sample can be a double-edged sword. On the one hand, the hyperfine interaction between the unpaired electrons and the nuclear spins encodes structural information through additional contributions to the isotropic chemical shift (contact and pseudo-contact shifts, PCSs), as well as to the shift anisotropy. In addition, paramagnetic relaxation enhancements modulate the nuclear relaxation times as a function of the distance between the metal centre and the nucleus-of-interest [1]. On the other hand, these effects lead to NMR spectra spanning a very wide chemical-shift range and shorten the relaxation times significantly, which requires the use of adiabatic pulse schemes, like in the adiabatic magic angle turning experiment [2,3].

In this study, a paramagnetic Europium(III) calix[4]arene complex has been investigated, which allows for trapping of small guest molecules in the calixarene cavity. An essential parameter to quantify the paramagnetic effects of the lanthanoid centre is the magnetic susceptibility tensor χ. By trapping either K^+/H_2O or a guanidinium cation in the cavity of the complex, the magnetic susceptibility tensor has been probed by solution- and solid-state NMR. Proton-detected 1D and 2D NMR spectra employing fast magic-angle spinning (MAS) frequencies were performed and revealed strongly shifted resonances experiencing significant PCSs. The influence of intermolecular effects on such strongly shifted resonances is discussed, as well as the impact of the MAS frequency on the spectra. Additionally, selective ^{13}C and ^{15}N isotope labelling was utilized to probe noncovalent fixation of the guanidinium cation to the complex.

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A Monosubstituted C(0) Atom in its Triplet State: Expanding the Family of Carbon-centered Diradicals

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Among carbon-centered diradicals, carbenes—featuring a disubstituted carbon atom—form the most extensively studied class, with applications in various fields of chemistry. In contrast, monovalent carbon compounds are largely underrepresented. Recent advances in organic synthesis [1, 2] have enabled us to pursue novel classes of triplet-state molecules, such as triplet vinylidenes. [3] Here we present an EPR/ENDOR characterization of $Ph_3P{\rightarrow}C$ (**1**, inset in Fig. 1, left), a novel compound photochemically generated from the recently synthesized diazophosphorus ylide Ph_3PCN_2. [4, 5]

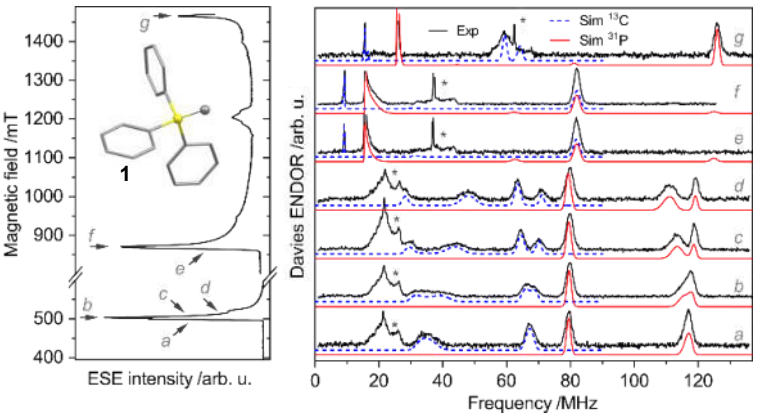

Figure 1: Q-band EPR spectrum of **1** (left); ^{13}C and ^{31}P ENDOR spectra of **1** recorded at the marked field positions with simulations (right).

A triplet ground state of this monovalent diradical species was elucidated by multi-frequency temperature-dependent EPR spectroscopy (Q-band data in Fig. 1, left). A positive ZFS parameter $D = +0.543\ cm^{-1}$ and a vanishingly small rhombicity $|E|/D = 0.002$ were obtained from spectral simulations. Since the D value is in the range typical for some carbenes, orientation-selective ENDOR (Fig. 1, right) was used to constrain the electronic structure based on the purely axial ^{13}C and predominantly isotropic ^{31}P HF tensors.

The P−C bond is best described as dative. The bonding can be understood in terms of a triplet C atom in its ground ^{3}P state (arising from the $2s^2 2p^2$ configuration) accepting the lone pair from Ph_3P, which straightforwardly explains the triplet ground state of the monovalent carbon adduct.

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An EPR Study of the Incorporation of Paramagnetic Divalent Metal Ions in Solids

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In many applications of electron paramagnetic resonance (EPR) spectroscopy for the investigations of solids paramagnetic ions are present as minor doping impurities or are introduced as paramagnetic local probes into the otherwise diamagnetic host materials. Then, in order to utilize the full potential of EPR, a major prerequisite is the identification of the incorporation site of the paramagnetic ion. In particular, if the paramagnetic ions are employed as local probes in crystalline solids the verification of the desired incorporation at framework sites and the investigations of possible distortions of the coordination geometry of the substitution site is of high relevance for further investigations of local properties of the solid in the vicinity of this site. In many cases, a thorough characterization of the incorporation site with its coordination requirement requires a combined continuous wave (cw) EPR and pulsed EPR (hyperfine) spectroscopy approach supported by quantum chemical computations.

In the presentation we will present examples for EPR investigations of the incorporation of mainly divalent paramagnetic ions at framework sites in crystalline solids. The work ranges from paramagnetic ion doping into ionic hydrites [1] with application potential for hydrogen storage materials to metal organic frameworks [2] for gas storage and separation applications.

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In situ EPR Spectroscopy for the Detection of Dihydrogen Isotopes Adsorbed on Metal-Organic Frameworks

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For the first time, *in situ* continuous wave (CW) EPR spectroscopy has been successfully applied to selectively monitor dihydrogen isotopologues (DHI) adsorption on flexible metal-organic frameworks (MOFs), particularly DUT-8 ($Ni_{0.98}Co_{0.02}$), from the perspective of its selective framework responses towards H_2 and D_2 adsorption [1]. This approach provides a non-destructive, highly sensitive method to observe isotopologue-selective gate-opening transitions, where D_2 triggers framework expansion (closed pore → open pore phase), whereas H_2 remains ineffective due to nuclear quantum effects. As another proof of detection reliability, *in situ* CW-EPR spectroscopy was also implemented to directly monitor the selective adsorption of DHI on flexible MIL-53 ($Al_{0.99}Cr_{0.01}$) and MIL-53 ($Al_{0.99}V_{0.01}$) via the breathing transitions of these MOFs. EPR parameters, including zero-field splitting (for the Cr^{3+} probe), *g*-tensors and hyperfine coupling (for the V^{4+} probe) serve as indicators of breathing transitions induced by DHI adsorption and desorption processes on MIL-53 (Al) [2].

In addition, we have implemented the *in situ* hyperfine spectroscopy setup as a novel approach in this field [3] with comparable measurement conditions and results as for the already established (thermal desorption spectroscopy) TDS method. Furthermore, *in situ* electron spin echo envelope modulation (ESEEM) extends the high-resolution advantage of ESEEM to explore the pore fillings by D_2 and HD during the adsorption and desorption processes. In this context, *in situ* ESEEM measurements were implemented for the ZIF-8 system as a first application example employing two distinct spin probes with different perspectives: Cu^{2+} at framework sites (as comprehensively investigated through multifrequency EPR and DFT predictions) and TEMPO radicals within the pores. The *in situ* ESEEM results for both probes successfully mapped the D_2 or HD density in the pores of ZIF-8 during the adsorption-desorption processes, in agreement with previous volumetric adsorption data.

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Zero-Field Splitting and Electric Field Effects in Fe^{3+} Centers in Quantum Paraelectrics

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We present high-field EPR investigations of Fe^{3+} centers in the quantum paraelectric materials $SrTiO_3$ and $KTaO_3$, known for their strong dielectric response and the suppression of ferroelectric order due to quantum fluctuations. These materials, though extensively studied, continue to reveal novel properties relevant for spintronics and quantum technologies [1]. Using single crystals and operating at microwave frequencies above 100 GHz over a temperature range of 5–300 K [2] , we identify Fe^{3+}–oxygen vacancy centers exhibiting strong axial zero-field splitting (D ≈ 44 GHz for $SrTiO_3$ and 43.5 GHz for $KTaO_3$ at 5 K). The ZFS shows a monotonic decrease with temperature. Notably, the structural phase transition in $SrTiO_3$ at 105 K does not produce detectable changes in ZFS, in contrast to prior results for Mn^{2+} centers. Finally, the application of static electric fields up to 30 kV/cm induces a measurable shift in the EPR spectra, demonstrating spin-electric coupling significantly stronger than typically observed in conventional dielectric hosts [3]. Such strong spin–electric field coupling in quantum paraelectric hosts is especially promising for the development of electrically addressable spin qubits operating at frequencies above 100 GHz.

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Solid-state NMR of Li-ion batteries:
Applications to self-healing binders and aqueous cells

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The importance of Li-ion batteries (LIBs) is undisputed, with applications ranging from portable electronic devices and large electric vehicles to grid storage of renewable energy. As global demand continues to grow, further advancements of battery technology are required as well, such as improvements in energy density and in safety. Such developments require tailored characterisation methods to monitor and understand the underlying processes. In this presentation, I will discuss two examples where we employ solid-state NMR for this purpose.

Self-healing binders have been proposed to improve the cycling stability of silicon electrodes. Their “self-healing” behaviour relies on dynamic bonds that break during the lithiation of silicon, allowing for volume expansion, and form again during delithiation when the silicon particles shrink.[1] However, it is challenging to confirm this mechanism experimentally, which hinders the rational optimization of such binders. In this talk, we investigate a cross-linked polymeric binder system containing dynamic covalent bonds and employ solid-state NMR to detect the presence or absence of cross-linking, using ^{1}H-^{13}C 2D correlation spectra as well as ^{11}B 1D and MQMAS spectra.[2] First results from ex situ high-field solid-state NMR measurements on cycled silicon electrodes with this binder will be discussed as well.

A major safety concern with LIBs arises from the flammability of their organic electrolyte, which is why the use of aqueous electrolytes has been proposed as a safer alternative.[3] However, most aqueous LIBs use electrode materials that have been developed for use in traditional organic electrolytes, meaning that their interaction with water is not well understood. A common assumption is that H^+ can replace Li^+ in the electrode materials, but direct experimental evidence remains scarce. With solid-state NMR being well suited to detect, localise, and quantify protons, we employ it to study electrodes cycled in aqueous electrolytes under different conditions, utilizing ^{1}H and ^{7}Li 1D NMR spectra as well as ^{1}H-^{7}Li dipolar recoupling experiments.

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From Model Systems to Real Cells: Investigating Lithium Equilibria in Batteries Using T_1 NMR

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Nuclear Magnetic Resonance (NMR) provides unique access to the dynamic chemical equilibria inside battery materials. In particular, ^{7}Li longitudinal relaxation times (T_1) can be used to probe the interaction between lithium ions in the solid electrode and the surrounding electrolyte, a key factor in fast-charging capability and electrochemical performance.

Here, we investigate the equilibrium between bulk lithium in $Li_4Ti_5O_{12}$ (LTO) and various electrolytes using ^{7}Li T_1 relaxation measurements.[1,2] Static NMR experiments on LTO nanopowder saturated with different electrolytes reveal a pronounced dependence of T_1 on electrolyte composition—up to an order of magnitude change. By applying inverse Laplace transformation without non-negativity constraints [3], we separated bulk and electrolyte contributions and attribute the observed T_1 shortening to the release of pinned surface polarons [4] upon contact with lithium-containing electrolytes. These polarons become mobile and contribute to bulk relaxation, highlighting a previously underappreciated charge-equilibrium mechanism at the solid–liquid interface.

Motivated by this, we are developing NMR-compatible in-operando cell architectures to apply this relaxation-based probe in real battery systems. We demonstrate the adaptation of a quartz-glass EPR cell [5] for in-operando NMR, enabling ^{7}Li measurements under operational conditions. Furthermore, we explore a resonant circuit design where the battery itself acts as a component of the RF resonator. This concept allows NMR access even in high-field environments and metallic-cased commercial cells such as 18650 formats [6,7].

While T_1 measurements in full cells remain a future goal, these developments pave the way for probing interfacial equilibria and ion–electron dynamics in real batteries using NMR, from model powders to industrial formats.

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Understanding the behaviour of $LiCoO_2$ positive electrodes in aqueous lithium-ion batteries using solid-state NMR spectroscopy

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Battery technology plays an ever-growing role in our daily lives. Li-ion batteries are the most widely used rechargeable batteries, but have safety issues due to the flammability of their organic electrolyte. Aqueous Li-ion batteries (ALIBs), which use water-based electrolytes, are emerging as safer, non-flammable alternatives.[1] Nevertheless, they suffer from several limitations that currently prevent commercial exploitation, among them the narrow electrochemical stability window (ESW) of water, which results in comparably low energy density. Furthermore, even when cycled within the ESW, ALIBs still show poor cycling stability due to the degradation of the electrodes, which are often not specifically designed for use in aqueous media. As the nature of this degradation remains poorly understood, further investigation of ALIBs and the behaviour of their electrodes are required.

In our work, solid-state nuclear magnetic resonance (NMR) is used for the first time to study the behaviour of positive electrodes in aqueous electrolytes and to detect if protons intercalate into the active material, as hypothesized in literature. [2,3] The positive electrode used in this study is lithium cobalt oxide ($LiCoO_2$, LCO). In this presentation, we will compare the electrochemical behaviour of ALIBs in acidic, neutral and basic electrolytes and present ex-situ ^{1}H and ^{7}Li NMR spectra of LCO as well as ^{1}H-^{7}Li dipolar recoupling experiments (REDOR, TEDOR). The ^{7}Li NMR spectra inform us about Li content in the electrode and are sensitive to the oxidation state of cobalt, approximating the state of charge of the material. Interestingly, the ^{1}H NMR spectra and ^{1}H-^{7}Li recoupling experiments show the intercalation of protons into the layered LCO electrode - an important information that is difficult to obtain with other analytical techniques. Using this result, we compare the intercalation of protons into the LCO electrodes in the three different electrolytes and relate this to the performance of the ALIBs. The results highlight the power of solid-state NMR in investigating the behaviour of cathode materials in ALIBs and the proton intercalation into these materials.

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Poster Abstracts

Investigating the Protein-RNA Dynamics of CRISPR Cas13a using EPR Spectroscopy

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The class 2, type VI ribonuclease CRISPR-Cas13a is known for its diagnostic application and already in use in nucleic acid detection. [1] However, the mechanism for its function and the involved conformational changes are not fully resolved. Only a few experimental structures along its mechanistic pathway from the apo, via the pre-crRNA- and crRNA-, to the target—crRNA-bound [2] state are known, and these structures stem from multiple different bacteria and contain different levels of truncation. Our aim is to resolve the mechanistic pathway of Cas13a from *Leptotrichia buccalis* without any cut-offs, using cw and pulsed EPR spectroscopy. While data from previous projects of our group focused on the Cas13a protein, here we emphasize the RNA aspect of the protein-RNA interaction.

To do so, we combine Site-Directed Spin Labeling (SDSL) [3] with continuous wave (*cw*) EPR spectroscopy and Pulsed Electron-Electron Double Resonance Spectroscopy (PELDOR or DEER) [4] by attaching nitroxide spin labels site-specifically to both Cas13a and the binding RNAs. To label the RNA, we developed an azide-bearing nitroxide that was “clicked” to an alkyne-modified nucleotide.

We address questions regarding the efficiency of the protein-RNA complex formation, and whether the protein binds pre-formed crRNA–target RNA structures. Further, we investigate the position of the RNAs within the complex in vitrified solution and compare them to crystal- and cryoEM structures to obtain a complete picture of the RNA-Cas13a complex.

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Development of a High-Temperature Operando NMR Probe Head for Electrochemical Applications

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Nuclear Magnetic Resonance (NMR) spectroscopy is an effective technique for investigating electrochemical processes in energy storage devices. *Operando* NMR measurements provide real-time, straightforward insights into electrochemical reactions taking place within electrochemical cells, including batteries and supercapacitors. However, investigation of next-generation solid-state batteries and high-temperature ionic liquid electrolytes presents considerable challenges due to their required operating temperature up to 300°C. Existing NMR equipment, dependent on superconducting magnets inside helium-cooled environments (~-270°C), experiences critical thermal limitations when incorporating high-temperature electrochemical cells. To address this limitation, we introduce the creation of a high-temperature operando NMR probe head (HOToperandoNMR), designed for conducting electrochemical studies at temperatures up to 300°C. Considerable innovations include the following: 1. A high temperature operation with precise temperature control, 2. Effective thermal insulation to protect the magnet bore, 3. Implementation of high temperature electrochemical cell, and the development of novel cell designs for studying battery materials and electrochemical reactions in ionic liquids. The system is designed by NMR Service GmbH and developed in collaboration with the TU Dresden. This novel design combines advanced thermal management techniques, real-time temperature monitoring with an of ±1°C, and automated optimization of measurement parameters. The commercialization of HOToperandoNMR will make this method available for both, academic and industry research, as a result considerably advancing the investigation of next-generation energy storage systems.

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Engineering Flavoprotein-Based Tags for Enhanced Sensitivity in Hyperpolarized EPR Spectroscopy

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The inherently low polarization of magnetic resonance techniques limits the sensitivity of both EPR and NMR, despite their central role in structural biology. To address this challenge, we aim to develop high-sensitivity spin tags tailored for hyperpolarized EPR spectroscopy. Our approach utilizes flavoprotein domains—such as LOV, BLUF, and cryptochromes—that generate spin-correlated radical pairs (SCPRs) upon photoactivation between a flavin cofactor and an aromatic residue. These SCPR-containing proteins will be employed as fusion tags for GPCRs, enabling enhanced DEER measurements. Sensitivity and performance will be further optimized through the site-specific incorporation of non-canonical amino acids (ncAAs) to modulate radical pair dynamics. Ultimately, we aim to design a *de novo* “maquette” spin tag with simplified architecture and robust functionality. This system is intended for *in cell* EPR applications, particularly under conditions of low concentration, and will provide a platform for probing electron transfer and hyperpolarization mechanisms in defined secondary structures.

The effect of acquired mutations on the structure and function of viral potassium ion channels

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Abstract

Hosts often search for strategies to defend themselves from viral infections either mediated at transcription level or by introducing mutations in these viral genes. Here, we report two orthologue sequences of potassium ion channel protein Kesv encoded by *Ectocarpus siliculosus* virus (EsV-1) namely, Kesv 1^{1} and Kesv 2^{2}. Functionally, both variants differed by only seven residues in their protein sequence and yet showed significant differences in the ion conductance rate.

Structural models were generated by both AlphaFold 2 (AF2) and Alphafold 3 (AF3) with AF3 displaying superior geometric validation and more stable tetrameric structures. A notable difference was observed in the N-terminal α-helix region which was variable across all the structural predictions. Mechanistic investigations using ion conduction-simulations revealed distinct conduction modes in which Kesv 1 favoured a soft-knock-on (water-mediated) and Kesv 2 exhibited a hard-knock-on (ion-driven) conduction pathway. Among all seven mutations, the double mutation in the pore region (Q61H and T66A) experimentally resulted in a significantly reduced functional expression of this channel in *Xenopus laevis* oocytes. Thus, Kesv channel proteins – harbouring the minimalist design to form an active ion channel opens possibilities to understand their structures on an atomic level through NMR spectroscopy.

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Characterization of a fold in TANGO1 evolved from SH3 domains for the export of bulky cargos

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The Melanoma Inhibitory Activity (MIA) protein family is characterized by featuring a SH3-like domain, for which the name MOTH (*MIA, Otoraplin, TALI/TANGO1 Homology*) domain was suggested.[1] Unlike classical SH3 domains, it does not bind proline-rich ligands. Instead, the MOTH domain developed the ability to bind collagen, except for MIA, which features a fibronectin binding site.[1]
New artificial intelligence-based methods predict that the MOTH domain of the protein *Transport And Golgi Organization 1* (TANGO1) is elongated by a C-terminal α-helix; which would be an unknown extension conserved throughout vertebrates.[1] Using microscale thermophoresis (MST) and solution state NMR spectroscopy we gain insights into the function of the domain's modification.
Our MST experiments demonstrate that the elongated TANGO1's MOTH domain binds type IV collagen, in contrast to its SH3-like core domain without helix extension.[1,2] Comparing the predicted structure to our experimental structure based on $^{13}C/^{15}N$-NOESY experiments, an influence of the helix on the conformation of the aromatic network in the domain's core and the surface area can be seen.[1,3-4] The latter could be one of the reasons for TANGO1's ability to bind collagen. By NMR titration experiments using the TANGO1's SH3-like core domain and a synthetic peptide corresponding to the predicted α-helix, we could determine a dissociation constant of 320.8 ± 4.1 µM with a dissociation rate k_{off} of $1.1 \times 10^3 \pm 29.1$ s^{-1} at the predicted interaction site, indicating binding.[1]
Due to the α-helix conservation throughout vertebrates and its necessity to bind collagen, it seems to be essential for the protein's functionality.[1] Currently NMR titration experiments are being used to identify the collagen-binding residues and determine the dissociation constant K_D.

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DNP at 0.34 T for the Investigation of Batteries

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The performance and lifespan of rechargeable lithium batteries are largely determined by intricate interfacial phenomena occurring at the electrode-electrolyte interface. A key element in this process is the solid electrolyte interphase (SEI), a passivating layer that develops on the electrode surface during battery cycling. Despite its importance, the SEI structure and composition remain difficult to characterize.[1] To achieve higher energy densities, battery designs are increasingly exploring anode-free configurations, where lithium is deposited directly onto a current collector like copper, rather than relying on a conventional lithium-based anode. While this approach holds significant promise, it also presents new challenges — most notably, the formation of lithium dendrites. These needle-like structures can pierce the separator, potentially leading to short circuits or battery failure.[2] Despite extensive research on lithium plating and dendrite formation, the molecular formation processes are not yet fully understood.

Dynamic nuclear polarization (DNP) provides a powerful means to gain deeper insight into this phenomenon. By transferring polarization from electron spins to nuclear spins, DNP significantly enhances the sensitivity of NMR, particularly under low magnetic field conditions. We present combined EPR and DNP-enhanced ^{7}Li NMR measurements of lithium on copper, performed using a custom-built setup operating at 0.34 T.[3] The resulting enhanced ^{7}Li NMR signal allows for the observation of electrochemically deposited lithium on copper, harvested from a Cu vs. Li cell, with an enhancement larger than 400. Additionally, upon saturation of the lithium electron resonance, the ^{1}H signal from the nearby electrolyte exhibited approximately a twofold enhancement, suggesting the capability to probe the SEI. These measurements utilized a battery cell housing specifically designed for EPR,[4] highlighting its suitability for future in operando studies.

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Investigations on Exchange Kinetics in a multivalent Xenon Host for ^{129}Xe HyperCEST MRI

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^{129}Xe HyperCEST imaging offers a promising approach for targeted molecular imaging, overcoming the inherently low sensitivity of conventional MRI. The incorporation of liposomes as multivalent nanocarriers functionalized with lipopeptides that carry cryptophane-A (CrA) cage molecules has demonstrated a biocompatible and versatile platform. This system enables significantly enhanced signal generation, requiring up to 17-fold lower saturation pulse powers compared to free CrA hosts [1]. However, the exchange kinetics of this two-step Xe exchange, which features multiple tuneable parameters, remain insufficiently understood and have not yet been systematically characterized. To address this, the Xe exchange rate k_{BA} and the bound Xe pool fraction f_B was quantified in a sample containing CrA-functionalized liposomes, using a methodology proposed recently [2]. This provides the first analysis of Xe exchange kinetics in a liposomal nanocarrier host system, enabling the optimization of saturation parameters for future imaging applications.

Liposomes were prepared with extrusion, comprising 87.8 mol% 1-palmitoyl-2-oleoyl-sn-glycero-3-phosphocholine (16:0-18:1 PC; Avanti Research, Alabaster, AL), 10 mol% cholesterol (Sigma-Aldrich, St. Louis, MO), 2 mol% CrA-lipopeptides (synthesized as described in [1]), and 0.2 mol% rhodamine-labeled phosphoethanolamine (18:1 Liss Rhod PE; Avanti Research, Alabaster, AL), resulting in a final liposome concentration of 100 µM dissolved in Dulbecco's phosphate-buffered saline (DPBS; Sigma-Aldrich). Measurements were conducted using a Bruker 9.4 T MRI system. A gas mixture of 2% Xe (natural abundance), 10% N_2, and 88% He was bubbled into a 1 mL sample at 80 mL/min, 20 °C with an operating pressure of 3.5 bar. Z-spectra were acquired using the HyperCEST method with a saturation pulse length t_{sat} of 2 s and saturation powers P_{sat} ranging from 1 mW to 60 mW to determine k_{BA} via changes in the linewidth Γ. Additionally, depolarization rates λ were measured for t_{sat} between 0.1 s and 20 s across the same P_{sat} range to evaluate f_B.

The experimental data showed agreement with theoretical models, yielding $R^2 > 0.99$ for the fitted functions describing both Γ and λ as functions of P_{sat}. From these fits, we determined $k_{BA} = 633 \pm 28\ s^{-1}$ and $f_B = 0.276 \pm 0.015$. These findings represent the first quantification of exchange kinetics in CrA-functionalized liposomes and establish a basis for comparative studies with other liposomal formulations or Xe host systems.

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NMR studies of a new RNA alkylating ribozyme

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Catalytically active RNAs (ribozymes) capable of post-transcriptional site-specific labelling have been emerging as powerful tools for biophysical and structural studies of RNA structure and dynamics. The first methylating ribozyme (MTR1) was discovered in our laboratory through *in vitro* selection, [1] and its mechanism of action elucidated by X-ray crystallography. [1,2] A new family of RNA alkylating ribozymes is currently investigated for its ability to install a variety of functional groups on the N1 of the target adenine using O^6-benzylated guanine (Bn^6G) variants as cofactor. The pH rate profile resembles that of MTR1, suggesting the involvement of protonated residues in the catalysis. However, the new ribozyme engages its RNA target via a substantially different mechanism, enabling recognition of a broader range of sequence motifs.

Here, we present preliminary results from our NMR investigations of the new ribozyme using Bn^6G as cofactor. The RNA construct was engineered for facilitating the NMR assignment using a “divide and conquer” approach. The resulting construct retained catalytic activity, albeit with a slightly reduced alkylation rate. 1D ^{15}N-filtered ^{1}H experiments, 2D ^{1}H,^{1}H-NOESY, 2D ^{1}H,^{15}N-HSQC and 2D ^{1}H,^{15}N-BEST-TROSY-HNN-COSY were performed on a trans-active construct consisting of a uniformly ^{15}N-labelled ribozyme hybridized to a substrate RNA at natural abundance. These experiments enabled us to characterize the mode of target RNA engagement and confirm biochemical mutational studies. Furthermore, multiple conformational states of the ribozyme were detected, possibly including kinetic traps. Our ongoing work aims at elucidating the ribozyme’s structure and mechanism, with focus on the pH-dependence of its activity.

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Halbach 2.0 – Creating homogenous fields with finite size magnets

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Homogenous magnetic fields can be created by suitable arrangements of permanent magnets, with Halbach rings being a well-established approach [1,2]. These rings are most effective when composed of very long (theoretically infinite) magnetic rods, modeled as line dipoles.

However, the classical Halbach concept is inherently limited when dealing with finite-sized permanent magnets. To overcome this, three-dimensional configurations of such magnets have been explored. In [3], optimal designs for both single and stacked rings of point dipoles are presented, achieving superior field strength and homogeneity compared to the original Halbach design and previous numerical approximations [4].

The key innovation is the so-called *focused configuration*, achieved by tilting the dipoles out of the plane of the ring. This design enables highly homogeneous fields that are shifted out of the magnet plane – an essential feature for single-sided magnetic resonance applications [5].

Furthermore, rotating these tilted rings relative to one another further enhances field homogeneity, albeit at the expense of a uniform field direction. However, such configurations remain suitable for NMR, as the field vector rotates only within the transverse plane of the rings, while the axial direction remains stable and can be used for rf excitation.

The theoretical predictions are validated through experimental realizations of various magnet arrangements using cuboid magnets. The results demonstrate that these novel configurations effectively overcome the limitations of finite-sized magnets in Halbach arrays, providing enhanced field strength and homogeneity. This makes them particularly well-suited for applications in mobile magnetic resonance.

All configurations can be explored, analyzed, and exported for 3D printing via a dedicated Python GUI [6].

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Distinct Valence States in Minimal FeFe-Hydrogenases

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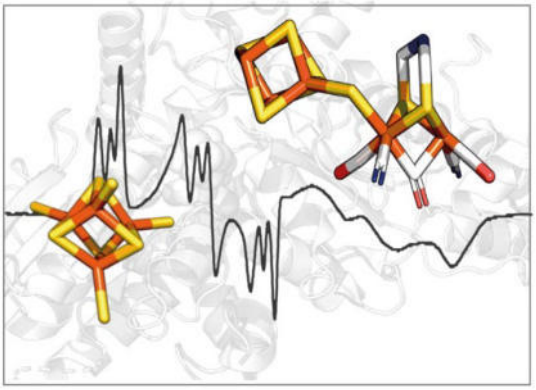
Redox-active enzymes often rely on metallocofactors to mediate complex oxidative and reductive transformations. Understanding the electronic structure of metallocofactors is key to manipulating these enzymes. By applying advanced EPR techniques, we can characterize paramagnetic states and track their evolution. Combined with biochemical and theoretical approaches, this enables new insights into the fundamental mechanisms of metalloenzymes.

A prominent example is the FeFe-hydrogenase family, whose unique active site is called the H-cluster, which comprises a [4Fe4S] cubane linked via a conserved cysteine to a [2Fe] subcluster. In addition to that, many FeFe-hydrogenases utilize accessory FeS clusters to support intricate electron transfer chains. In contrast, some minimal FeFe-Hydrogenases manage without any accessory clusters throughout.



To explore alternative mechanisms of electron transfer regulation, we investigated the minimal FeFe-hydrogenase *Cr*HydA1, which lacks accessory FeS clusters.[1] There we could demonstrate the existence of distinct valence states arising from a single FeS-cluster. This concept is now being extended to a growing set of novel minimal hydrogenases. Based on this shared feature, we propose a new “redox switch” mechanism that operates in the absence of accessory FeS clusters. Our data suggest that structural heterogeneity and valence isomerism within the cubane cluster itself can serve as a regulatory element, tuning electron transfer and catalytic bias.

Our work on these distinct enzymes offers new insights into FeS cluster interactions and their role in enzymatic electron transfer, contributing to a broader understanding of FeFe-hydrogenases.

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Selective Labeling and Measurement of Biomolecules for Multi-Spin EPR Distance Analysis

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Measuring precise distances throughout biomolecules is crucial to understand their structure, dynamic, and function. Since Electron Paramagnetic Resonance (EPR) spectroscopy is a powerful tool to determine nanometer-scale distances between spin labels, it is commonly utilized in structural biology, by inserting spin labels into the biomolecule of interest [1]. However, the distance analysis of systems containing more than one pair of spin labels can prove to be challenging due to multi spin effects [2]. Our approach to solve this drawback is to utilize a combination of multiple light-induced spin labels (LISL) and a stable radical/metal. Using LISL with separated UV/Vis absorption spectra enables us to attach multiple labels into one system, while being able to excite only specific pairs.

Our results show the successful production of Heme-free myoglobin. We inserted a cysteine residue via site-directed mutagenesis, which we labelled with MTSL. We investigated its properties using cw-EPR and UV/Vis spectroscopy. Currently we aim to insert the Zinc-protoporphyrin IX chromophore into the free binding pocket of myoglobin. This protein will then be employed as a test system for light induced distance measurements.

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Unveiling Dual E2 Binding Sites of the HECT Ligase by NMR

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E6-associated protein (E6AP), also known as ubiquitin-protein ligase E3A (UBE3A), is a multifaceted enzyme crucial for regulating cellular processes via the ubiquitin-proteasome system (UPS). Initially identified as a binding partner for the human papillomavirus (HPV) E6 oncoprotein, E6AP has emerged as a key player in diverse cellular pathways, including cell cycle control, transcriptional regulation, and tumorigenesis. Consequently, elucidating the structure, function, and regulation of E6AP offers valuable insights into its roles in health and disease, potentially leading to novel therapeutic strategies targeting this enzyme for various disorders. Although the crystal structure of E6AP depicts a trimeric form, the prevailing belief suggests that HECT E3 enzymes function as monomers, aligning with observations of other HECT-type enzymes in their crystal structures. Additionally, recent research proposes the presence of two distinct E2 (UbcH7) binding sites on E6AP, designated Site 1 and Site 2, which cooperate in polyubiquitin chain assembly. Site 2, also known as the cryptic binding site due to its low affinity, presents challenges for structural elucidation using crystallography [2]. To address this limitation and investigate the oligomerization dynamics of the E6AP HECT domain and its UbcH7 binding region, we employed cutting-edge solution-state NMR techniques. Additionally, TRACT analysis was performed to investigate the protein's oligomerization state at 90 µM and 500 µM concentrations. The calculated TauC values (44.7 ns and 45.48 ns) suggest that the protein exists in a dynamic equilibrium between dimeric (36.78 ns) and trimeric (54.79 ns) states. In conclusion, this study reinforces the concept of distinct E2 interaction regions on E3 enzymes, critical for E2-E3 interactions and the overall mechanism of action within the Ubiquitin and ubiquitin-like systems. Furthermore, the findings support the notion that E3 HECT ligases may function in an oligomeric state, challenging the prevailing belief of their exclusively monomeric nature.. Text of the abstract. Text of the abstract. Text of the abstract.

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Solvent-Dependent Photo-CIDNP Effects in Synthetic Donor–Acceptor Diads

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Photochemically induced dynamic nuclear polarization (photo-CIDNP) enhances NMR signals by generating non-equilibrium nuclear spin populations via photochemical reactions. First observed in solid-state systems in 1994 [1], the effect has since been widely studied in photosynthetic reaction centers using magic angle spinning (MAS) NMR. In solids, mechanisms such as three-spin mixing (TSM), differential decay (DD), and differential relaxation (DR) transfer electron spin polarization from spin-correlated radical pairs to nearby nuclear spins through hyperfine interactions [2]. Extending this phenomenon to artificial systems remains an ongoing challenge.

In this study, we investigate photo-CIDNP in synthetic donor–acceptor diads connected by polyproline helices. These diads are biologically compatible and well characterized, with PPII helical motifs, common in collagen and other proteins. Each diad combines a flavin acceptor with an aromatic amino acid donor, with distances of 3–18 Å.

Although our long-term goal is to study these diads under solid-state conditions, this work focuses on the liquid state, where solvent effects and molecular dynamics are easier to control. While previous studies [3] examined structural and electronic factors in photo-CIDNP, here we investigate solvent-dependent effects in liquid-state NMR. We aim to identify solvents that promote strong photo-CIDNP signals and are compatible with future solid-state applications. Our results show that solvent choice significantly affects polarization patterns. Notably, DMF produced strong signals primarily from the solvent itself, suggesting unexpected interactions.

These findings highlight the critical role of solvent selection in designing photo-CIDNP experiments, particularly for transitioning to solid-state MAS NMR. Ongoing studies aim to optimize conditions that yield diad-specific signals under immobilized conditions by examining the effects of solvent and polyproline linker length.

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Electrophoretic NMR-based Determination of Transference Numbers in Polymer and Post-Li Electrolytes

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Understanding ion transport in electrolytes is key to improving electrochemical storage technologies. Electrophoretic NMR (eNMR) is a useful method for investigating charge transport with species-selective information. This method enables the determination of electrophoretic mobilities μ through the application of electric voltage pulses during pulsed-field gradient NMR (PFG-NMR) experiments, followed by an evaluation of the drift velocity-induced phase shifts of the echo signal. These mobilities can be used to determine the transference numbers T_i of the respective species, offering detailed insight into charge transport processes. [1] It can therefore help to clarify current discrepancies and challenges in the literature regarding T_i, which arise from its determination by different methods (electrochemical, thermodynamic, theoretical, etc.) with various assumptions, which are not always fulfilled by real electrolytes. For example, electrochemical methods are impeded by the challenge to handle interfacial resistances of metal electrodes, in particular with post-Li-based electrolytes. The objective of this study is to highlight the efficiency of eNMR as a tool for charcterising ion transport in different electrolyte systems.

Here, we study poly(ethyleneoxide) (PEO) in combination with lithium bis(trifluoro-methanesulfonyl)imide (LiTFSI), which is a common standard system for polymer electrolytes. [2] We show that recent advancements in eNMR methodology can provide a more precise and reliable T_+ determination, yielding slightly larger mobilities for all electrolyte components, as well as higher T_+. In particular, the positive mobility of PEO is consistent with the expected migration of the polymer to maintain local volume neutrality during ion migration. [3]

We further investigate different concentrated liquid organic electrolytes containing TFSI salts of Na^+, K^+, Mg^{2+}, Ca^{2+}, and Zn^{2+}. Analysis of T_+ in post-lithium electrolytes, where the cation either lacks an NMR-active nucleus or suffers from rapid spin relaxation, become feasible by the recently introduced combination of impedance spectroscopy (IS) with anion mobility measurements via eNMR. [4] The results show that especially K^+ exhibits the largest mobilities and T_+ (T_{K+} = 0.68), surpassing Li^+ (T_{Li+} = 0.51). These findings reveal that cations with lower charge density demonstrate larger T_+, due to a reduced coordination strength with their solvation shells, enabling enhanced ion transport.

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Evaluating Site-Specific Isotopic Labelling Strategies for the Solid-State NMR Analysis of Polymeric Micelles with Low Guest Loadings

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The rational design of micellar drug carriers requires a clear understanding of how molecular motifs influence loading, stability, and release.[1] However, amorphous hosts prevent complete structural elucidation by classical diffraction methods, and low guest concentrations in drug-delivery systems or theranostic nanocarriers limit the sensitivity of conventional NMR spectroscopy[2]. This challenge can be addressed by using NMR signal-enhancement strategies, such as isotopic labelling[3] or dynamic nuclear polarisation[4], to reveal polymer-guest interactions.

Three site-specific labelling strategies in a curcumin–poly(2-oxazoline) model system were compared by synthesising four curcumin isotopologues varying only in the methoxy group: unlabelled, ^{13}C-labelled, D_3-labelled, and $^{13}CD_3$-labelled. They were encapsulated with 5-50 % w/w into the polymer micelles via thin-film hydration. For ^{1}H-^{13}C HETCOR spectra at 50 % loading, unlabelled curcumin micelles showed extensive interaction patterns and isotopic editing helped disentangle overlapping signals and assign distinct contacts. At 5 % loading, detectable intermolecular cross-peaks appeared only in the labelled samples: ^{13}C-methoxy labelling revealed polymer-methyl contacts, while deuteration enabled observation of ^{1}H-^{2}H interactions.

Site-specific labelling thus provides complementary insights into host-guest interactions under realistic, low-concentration conditions, enabling direct, site-resolved mapping of drug-polymer contacts and aiding structural elucidation. However, it should be noted that synthesising isotopically labelled analogues requires additional effort and may provide only a narrow, potentially biased view of the host-guest interactions. DNP provides more uniform, yet less selective, sensitivity enhancements. Additionally, it carries a risk of altering the micellar structure during sample preparation.[4] The next step will be a more detailed comparison of the two different approaches.

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A Superconducting Resonator-Based Platform for Advanced EPR Distance Methodology and Applications

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Electron Paramagnetic Resonance (EPR) spectroscopy remains a powerful tool in the determination of biophysical information on a wide array of sample types. Specifically, EPR based distance measurement techniques provide valuable data on the structure and dynamics of biologically relevant macromolecules such as proteins, DNA, and RNA. Additionally, advancements in EPR sensitivity continue to propel the field forward to applications that were previously untenable. One such advancement that has recently made significant strides forward is the use of superconducting microresonators for EPR measurements. These devices possess a compact mode volume and thus a high filling factor, combined with a high internal quality factor for enhanced noise rejection. Such aspects enable unprecedented absolute spin sensitivity. However, such devices often require sample concentrations and volumes unsuitable for biological EPR measurements. Recently we demonstrated a microstrip resonator design that enables biologically-relevant sample sizes with a resonator bandwidth sufficient to perform Double Electron Electron Resonance (DEER) distance measurements. This device serves as a highly stable and sensitive platform for simple implementations of advanced techniques and methodologies, enabling specialized and/or difficult biological applications. The results shown here continue to advance the scope of applications for superconducting resonators, and EPR at large.

Solid-State NMR Investigation of Volatile Organic Compounds Adsorption in DUT-134 (Cu)

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The effective capture of volatile organic compounds (VOCs) such as formaldehyde [1] or 1,4-dioxane [2] is essential for air or water purification aimed at protecting human health. Two-dimensional (2D) metal-organic frameworks (MOFs) represent promising materials for this application [3], offering highly accessible surfaces and tunable pore environments. In this work, we investigate the adsorption of formaldehyde and 1,4-dioxane in DUT-134(Cu) ($[Cu_2(dttc)_2]_n$, dttc = dithieno [3,2-b:2′,3′-d] thiophene-2,6-dicarboxylate), a 2D MOF that can be hierarchically assembled into well-defined, large-area carpets and tubular structures to maximize the accessibility of open metal sites [4].
We employed advanced solid-state nuclear magnetic resonance (NMR) spectroscopy to explain the molecular-scale mechanisms of adsorption within these frameworks. Cross-polarization (CP) build-up curves were systematically measured for pristine and formaldehyde (20% wt water solution as well as paraformaldehyde) and 1,4-dioxane-loaded DUT-134(Cu) samples. Analysis of the CP build-up kinetics revealed significantly shorter time constants upon exposure to VOCs, indicating enhanced dipolar coupling between the adsorbed VOCs and the framework sites. This quantitative parameter serves as a sensitive probe of adsorption strength, providing direct evidence for strong host–guest interactions at open Cu (II) sites.
Additionally, two-dimensional ^{1}H–^{13}C heteronuclear correlation (HETCOR) experiments with variable contact times were performed to resolve the spatial proximities and binding environments of VOCs within the MOF structure. The observed contact-time dependence of cross peaks confirmed localized, site-specific adsorption near the metal centers, supporting a mechanism dominated by Lewis's acid-base interactions. These NMR findings were corroborated by Raman spectroscopy, which revealed characteristic vibrational modes.
This study highlights the power of solid-state NMR spectroscopy- through CP kinetics and HETCOR analysis-as a non-destructive, site-specific approach for quantifying and mapping gas adsorption in MOFs. The insights gained provide critical design principles for optimizing 2D MOF architectures for efficient VOC capture in real-world air filtration applications.

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Amyloid fibril formation kinetics of low-pH denatured bovine PI3K-SH3 monitored by three different NMR techniques

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Amyloid fibril formation is involved in several neurodegenerative diseases like Alzheimer's or Parkinson's disease. To develop therapeutic approaches, it is crucial to study the aggregation process and fibril formation of the underlying amyloidogenic peptides and proteins. The PI3K-SH3 domain has been used as a model system for studying protein folding and fibrilization due to a transition of a folded native state at neutral pH to an unfolded state and, ultimately, fibrillar state at low pH. [1]

In order to understand this transition, we include solution NMR, high-resolution magic angle spinning (HR-MAS) NMR, and solid-state NMR using the nuclear spins as intrinsic probes to monitor fibril formation [2]. Solution NMR provides high sensitivity for recording two-dimensional spectra but can only track the decay of monomeric species via scalar coupling based experiments. Solid-state NMR, though less sensitive, can detect both monomers in INEPT and aggregated species via cross polarization based experiments. HR-MAS NMR acts as a hybrid method combining MAS spinning like in solid-state NMR while applying solution NMR spectroscopy experiments (e.g. HSQC).

We find consistent decay rate constants of monomeric SH3 among all NMR methods used which can be fit by a simple mono-exponential decay function suggesting fibril elongation as the primary growth mechanism. Moderate MAS spinning at 8 kHz seem to have a minor influence on the seeded fibril formation kinetics. Solid-state NMR reveals the disappearance of monomers corresponds to aggregated species with no substantial mass difference. Atomic force microscopy confirms the presence of fibrils at the end of each series of measurements.

Subsequent follow up studies suggest a major influence of pH and aggregation conditions in the fibrillation and molecular details of the fibrillar structure as seen by solid-state NMR. We also present novel insights through solvent paramagnetic relaxation enhancement (sPRE) data of both the native and fibrillar states of PI3K-SH3 mapping the surface of both protein conformations.

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^{19}F MAS NMR Spectroscopy for Structural Elucidation of Novel TADF Materials

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Highly efficient organic electronic devices with excellent external quantum yields can be achieved following the concept of thermally activated delayed fluorescens, where the designed small energy gap between the singlet and the triplet excited state allows for a thermally activated back transfer of the non-radiative triplet excitons to the fluorescent singlet state. Most the developments of these materials and designs of TADF organic LED devices were aiming for the ultimate external quantum efficiency (EQE). Despite the TADF design, however, the novel materials have to provide a long term stable and well-balanced charge transfer in order to ensure a durable efficient functionality of the devices. In many cases, small parasitic molecules like water or oxygen can penetrate the crystalline structures of the materials and reside in the materials acting locally as hole or electron traps, respectively, spoiling the initially balanced charge transfer, which is essential for the homogeneous and efficient operation of the TADF layer in an OLED device.[1]

Solid state NMR measurements can provide some insight into the local molecular packing arrangement of the new TADF molecules, even if the materials cannot be crystallized from solution as required for x-ray diffraction studies.[2] Due to the poor spectral ^{1}H MAS NMR resolution, ^{19}F MAS NMR methods are essential for the solid state NMR characterization of these materials. In particular, simple ^{19}F T_1 relaxation time and double-quantum filtered ^{19}F MAS NMR measurements help to distinguish signals of crystalline and amorphous molecular packing of the TADF molecules, while two dimensional ^{1}H-^{19}F HETCOR and ^{19}F-^{19}F double quantum correlation experiments allow to explore the local molecular packing in more detail. Moreover, the ^{19}F MAS NMR spectra indicate in many substantial differences in the molecular packing of solution crystallized material used for diffraction studies and gas phase deposited TADF material utilized as light emitting layer in electronic devices.

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Structural Characterization of Phases in Synthetic Apatites and Mouse Bone Using 43Ca DNP NMR Correlation Experiments at 30 K

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Accurate structural characterization of bone mineral at the atomic scale presents a significant challenge due to the low sensitivity of key nuclei such as 43Ca. Previous research has explored dynamic nuclear polarization (DNP) [1],[2], and high-field NMR to enhance 43Ca detection [3]; however, sensitivity limitations due to low natural abundance and large quadrupolar coupling, have hindered 2D 1H - 43Ca correlation spectroscopy and determination of quadrupolar coupling constants—crucial parameters that provide insight into the calcium environments. In this study, we combine magic angle spinning (MAS) DNP with dipolar recoupling DR–INEPT [4] to efficiently polarize 43Ca nuclei and alleviate the sensitivity issues.

We will demonstrate a significant fold increase in sensitivity in both synthetic hydroxyapatite (HAp) and real mouse bone samples, making direct observation of 43Ca at natural isotopic abundance feasible in biologically relevant samples. As a next step, we aim to perform experiments at ultra-low temperatures (~30 K) to assess whether reduced thermal motion enhances polarization transfer and enables 2D 1H–43Ca HETCOR experiments in other HAp, and its precursor phase like octacalcium phosphate (OCP). Enhanced sensitivity at 30 K [5] might also enable determination of quadrupolar parameters of nuclei. The ability to perform such experiments would open new possibilities for probing the coordination environments of calcium in pathological versus healthy bone, determining the different calcium sites present from their correlation to OH groups, and providing structural insight into bone quality and disease mechanisms.

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Study of nuclear magnetization transfer between water and ice phases in nanoporous solids

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The study and characterization of nanoporous solids is of great importance and to this end the usage of nuclear magnetic resonance has been developing as a promising tool. By introducing water into nanoporous structures, liquid and frozen phases develop at low temperatures, which can then be identified due to their vastly different transverse relaxation rates. By exploiting the high contrast of the water and ice phases, information on the morphology and pore structure can be extracted [1].

For the correct characterization of nanoporous materials, the description of different nuclear magnetic relaxation mechanisms, in particular of the magnetization transfer between these phases, as well as their dependence on various parameters such as temperature and pore size, will be beneficial. This can be most efficiently done using materials with ordered pore structures in which well-defined geometries of ice and water phases can be created.

In this contribution we explore the magnetization transfer between water and ice in porous silica, the pore structure of which is composed of spherical nanopores connected by micropores. This was achieved using the Goldman-Shen pulse sequence [2], which initially suppresses the transverse magnetization originating from the ice phase and then allows for the re-equilibration of the magnetization. The studies were performed at different temperatures and over various time scales in order to identify the various transfer mechanisms that are present, and the results were compared to theoretical predictions.

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Following the Binding of crRNA to Cas13a in the Time Domain by Pulsed Electron-Electron Double Resonance

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In this study, the binding of CRISPR-RNA (crRNA) to the protein Cas13a in low RNA excess is investigated in a time resolved manner. Cas13a is expressed heterologically and labeled site specifically via reaction of the nitroxide spin label MTSSL with two cysteine residues that are introduced at two positions in the protein. Pulsed electron-electron double resonance (PELDOR) is then measured to obtain the dipolar coupling between the two unpaired electrons of the nitroxides. [1]

Labeled protein and crRNA are mixed and frozen after a defined aging time, and via preparation of multiple samples, each frozen after a different aging time, a discrete time series is generated. From the PELDOR signal of each sample in the series, the population of the apo state and the crRNA bound state of Cas13a can be calculated. [2]

The dependency of the crRNA bound state population and the aging time gives rise to kinetic information about the Cas13a-crRNA complex formation. Preliminary experiments utilizing a microsecond freeze hyperquenching device [3] revealed that after 668 µs, around 10% of the holo state was formed at a crRNA excess of 1.2. Based on this finding, larger aging times such as milliseconds and even seconds to minutes are investigated in this study.

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The tale of a stable phenoxazine radical: EPR and X-ray studies with application perspectives

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Organic radicals, due to their open-shell structure, have promising applications in various fields of material science. Some are used in OLED displays [1], others exhibit electrical conductivity making them suitable for flexible electronics [2], or display magnetic properties that make them candidates for building blocks of single-molecule magnets [3]. At the same time, phenoxazine derivatives are widely utilized in medicine (e.g., as anticancer and antidiabetic agents) and in technology [4]. Our long-term goal is to combine the unique features of radicals and phenoxazines in a single molecular system. To this end, we developed a synthetic procedure that yields a stable phenoxazine radical. The resulting product crystallizes from ethanol or methanol as small oblong crystals, suitable for X-ray diffraction studies.

Structural analysis revealed the formation of two distinct 10H-phenoxazine derivatives: 2,4,6,8-tetra-tert-butyl-10H-phenoxazine (molecule A in Figure 1.a) and 1-hydroxy-2,4,6,8-tetra-tert-butyl-10H-phenoxazine (molecule B in Figure 1.a), linked by hydrogen bonds. Electron paramagnetic resonance (EPR) spectroscopy revealed that the radical centre is located on the nitrogen atom of molecule A, with the unpaired electron delocalized across the molecular framework (Figure 1.b). In line with current research trends, this stable radical system is a promising candidate for further investigation as a magnetic or luminescent material.

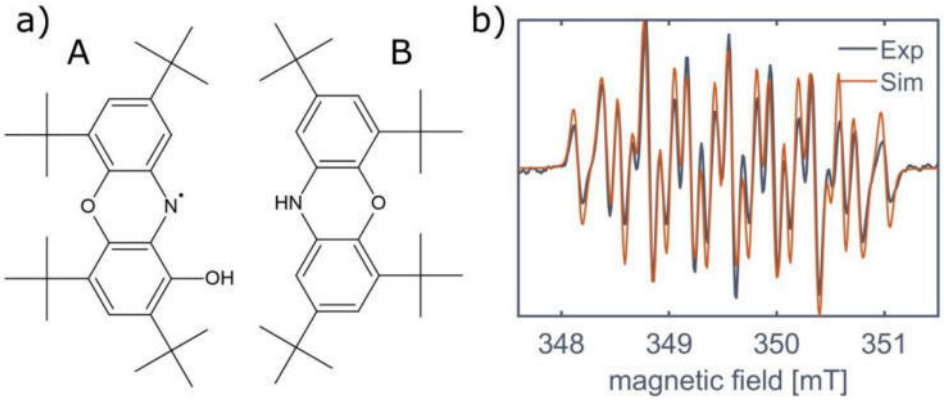

Figure 1. a) The schematic structure and b) EPR spectra of obtained radical system

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Solid-State NMR Insights into the Structure-Property Relationship in Hybrid Perovskites

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Perovskite solar cells represent one of the most promising photovoltaic technologies, with certified power conversion efficiencies now exceeding 27.3%. To fully realize the potential of halide perovskites, it is critical to probe and understand their atomic-level microstructures and structural dynamics, which govern their macroscopic optoelectronic performance and long-term stability.

Solid-state nuclear magnetic resonance (SSNMR) spectroscopy, as a powerful characterization technique, offers unique capabilities to resolve local environments, dynamic processes, and weak interactions within perovskite lattices. Importantly, it allows for the direct quantification of cation reorientational dynamics and lattice fluctuations, which are now increasingly recognized as key factors influencing charge carrier lifetime, trap state density, and phase stability.

Recent results concerning the application of NMR of solids and liquids will be presented. This will focus on the detection of ^{207}Pb and ^{1}H NMR signals from perovskites in polymeric membranes, as well as liquid state NMR of reaction adducts, which are generated during ink preparation and might have a significant role in cell performance.

By correlating NMR observables with macroscopic device performance metrics, we aim to establish a comprehensive structure–dynamics–property relationship that bridges atomic-scale processes with photovoltaic functionality. This approach will provide new insights for rational perovskite material design and offers atomic-level understanding to guide the further optimization of device performance.

There and Back Again - the journey of a magnetic transfer between ^{1}H and ^{14}N nuclei under fast MAS.

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NMR spectroscopy using the ^{14}N nucleus has a wide range of applications as nitrogen occurs in many organic, biological or medical systems. Due to its spin of ½, the ^{15}N nucleus is often preferred over the spin-1 nucleus with its quadrupolar interactions, although the natural abundance of 99.64% clearly favours ^{14}N. The challenges of quadrupole interactions and the low gyromagnetic ratio of the nitrogen nucleus can be overcome by using fast MAS and magnetization transfer from ^{1}H to ^{14}N.[1] Hydrogen-nitrogen interactions, particularly those involving intra- or intermolecular hydrogen bonds, can contribute to our understanding of structure and function, clearly worth a closer look.

Two types of ^{1}H-^{14}N correlation experiments were compared: the ^{1}H-^{14}N HMQC (Heteronuclear Multiple Quantum Coherence) experiment and the ^{1}H-^{14}N DCP (Double Cross Polarization) experiment. In the HMQC experiment, two-way magnetization transfer occurs through dipolar recoupling of ^{1}H and ^{14}N nuclei, which generates heteronuclear coherence.[2] In the DCP experiment, the magnetization is transferred from ^{1}H to ^{14}N, and back again using two optimized CP pulses.[3] Both methods can be used to determine direct NH, as well as longer-range ^{1}H-^{14}N correlations.

The two experiments were implemented and thoroughly optimized using crystalline histidine and the dipeptide AspAla. They were then applied to systems with different levels of crystallinity, rigidity, and size, such as the small molecule drug atorvastatin (crystalline as well as amorphous) and self-healing ureidopyrimidinone (UPy) containing polymers.[4] Based on this set of samples similarities, differences, and respective advantages and disadvantages will be discussed. For instance, a specially optimized DCP could be tailored to focus on specific ^{1}H-^{14}N correlations, whereas the HMQC would examine all correlations observable at a given recoupling time.

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Rotational Resonance for the Selective Acceleration of Spin Diffusion Pathways under Site-Specific DNP

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In solid-state NMR magic-angle spinning (MAS) is used to average the anisotropic parts of the chemical shielding and dipolar coupling to approach the spectral resolution obtainable in liquid-state NMR. The sensitivity of MAS NMR can be enhanced by the application of dynamic nuclear polarization (DNP). However, the spectral overlap of chemically similar species in biomolecular samples presents a challenge in the resonance assignment. To distinguish between different residues SCREAM-DNP (Specific Cross Relaxation Enhancement by Active Motions under DNP) is used as a method to introduce site-specificity. In this approach, polarization is transferred from hyperpolarized ^{1}H to methyl group carbons by heteronuclear cross-relaxation. Via carbon-carbon spin diffusion (SD) the polarization can then spread to further carbons in the vicinity.[1]

A notable strength of MAS NMR is its ability to measure the dipolar coupling between a spin pair through recoupling techniques. The dipolar coupling is selectively reintroduced, thereby enabling the determination of the distance between two spins. Rotational resonance (R^2) recouples the dipolar interaction for homonuclear spin pairs when the MAS frequency is matched to their isotropic chemical shift difference.[2] Distance information can be obtained by lineshape analysis or exchange curve experiments. Additionally, R^2 can be implemented in SCREAM-DNP experiments during their polarization time to selectively increase the coherent dipolar SD process.[3]

So far, the compatibility of R^2 with SCREAM-DNP was studied in a selectively ^{13}C-labelled model compound. While the prior investigation served as a proof of concept this work focuses on the detailed analysis of the exact MAS frequency match and the decline of the SD-rate dependent on the MAS frequency. We now specifically observed the n=1 R^2-condition under SCREAM-DNP. For this purpose, we recorded the MAS profile for two model compounds of different ^{13}C-distance and qualitatively compared the decrease in dipolar coupling with the variation of the MAS frequency. Furthermore, we measured the R^2-width profiles which yield the MAS dependence of the dipolar coupling through an exchange experiment at a constant mixing time.[4] By the comparison of the two profiles, we aim to obtain information about distances from SCREAM-DNP rate constants.

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NMR-based analysis of the structure and dynamics of cargo-binding domain of TANGO1 from *Drosophila melanogaster*

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The efficient secretion of large extracellular proteins such as collagen requires specialised mechanisms in the secretory pathway. TANGO1 (Transport ANd Golgi Organisation 1) is a a multidomain transmembrane key protein in this process and mediates the packaging of large cargo molecules at the ERES (Exit Site of Endoplasmatic Reticulum) by interacting with both the cargo on the lumenal side and the COPII machinery on the cytoplasmic side. The luminal N-terminal cargo-binding domain of TANGO1, a modified SH3-like domain, plays a central role in the recognition and binding of secretory cargo. Despite its biological relevance, the structural and dynamic properties of this domain have so far been insufficiently characterised.[1],[2],[3]

In this study, the structure and dynamics of the cargo-binding domain of TANGO1 from *Drosophila melanogaster* was analysed using multidimensional NMR spectroscopy in solution. The complete assignment of the backbone and side chain resonances formed the basis for the determination of the three-dimensional solution structure, caalculated by ARIA. The resulting structure shows a modified SH3-like fold with characteristic β-sheet motifs, but without classical proline-rich binding pockets typical for canonical SH3 domains.[4]

In addition, dynamic properties of the domain were characterised by 15N relaxation measurements (R1, R2 and heteronuclear NOE). These analyses revealed a predominantly rigid core structure with increased flexibility in the terminal regions and potential functional surfaces. The structural and dynamic information obtained provides valuable insights into the molecular properties of cargo recognition of TANGO1 in *Drosophila melanogaster* and contributes to a better understanding of the evolutionary diversity of this conserved domain.[5]

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Isoleucine Side Chains as Reporters of Conformational Freedom in Protein Folding Studied by DNP-Enhanced NMR

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Understanding the dynamic conformations of protein side-chains is essential for deciphering protein function. We employed DNP-enhanced solid-state NMR (ssNMR) at cryogenic temperatures to dissect isoleucine (Ile) side-chain dynamics across diverse protein states. We examined three Ile labeled proteins, representing key biological states: intrinsically disordered (α-synuclein), well-folded (GABARAP), and the whole folding/unfolding/misfolding transition (PI3K SH3).

By analyzing 13C chemical shifts, which reflect Ile side-chain angles, and performing line-shape analysis of 2D spectra, we obtained comprehensive information about secondary structure and protein mobility. Furthermore, through peak volume integrations, we could quantify the prevalence of specific conformations.
Our results revealed that in well-folded proteins, Ile residues exhibit well-resolved chemical shifts, reflecting structural rigidity. Here, residue-specific conformations could be identified and quantified. In contrast, unfolded and intrinsically disordered proteins displayed significant line broadening, as consequence of higher conformational freedom. We demonstrated that solvent conditions profoundly influence conformational ensembles, distinguishing different unfolded states of PI3K SH3. In amyloid fibrils, β-sheet-like chemical shifts dominated, indicating restricted conformations. Concurrently, broad signals were observed, reflecting the residual disorder of Ile within the fuzzy coat surrounding the fibril core.

Our research demonstrates the capability of DNP-enhanced ssNMR to overcome limitations in studying (partially) disordered biomolecules. Freeze-trapping physiological exchange provides a precise ensemble snapshot, representing each conformation's probability, offering a more accurate representation than time-averaged data. This approach is a significant advancement in structural biology.

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Unraveling the Internal Dynamics of p38α through Stereospecific Methyl Labeling in Solid-State NMR

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The protein kinase p38α (MAPK14), a highly conserved 41 kDa enzyme, plays a pivotal role in the MAPK/ERK signaling pathway where it translates external stimuli into cellular responses. It is essential for key processes such as proliferation, differentiation, and cell division. Dysregulation of p38α has been linked to inflammatory diseases, neurodegenerative disorders, and cancer, making it a promising therapeutic target.

We aim to characterize the effects of two known p38α-binders—sorafenib, an approved anti-cancer drug known to inhibit multiple kinases, and β-OG, an amphiphilic molecule often used for membrane protein stabilization—on the global and local dynamics of p38α. To achieve this, we combine NMR of p38α in either solution or a crystalline environment with a stereospecific isotope-labeling approach that enables analysis of methyl groups in a highly deuterated environment. This technique generates very well-resolved C-H correlations that allow rapid peak assignment and facilitate quantitative comparison between conformational-exchange dynamics in solids and in solution.

To facilitate characterization of p38α by solid-state NMR, we are establishing a protocol for detecting CHD2 methyl groups in paramagnetically doped p38α crystals using solid-state NMR. The size-independence of solid-state NMR, as well as slight shifts for the timescales of internal dynamics, offers unique advantages for studying large complexes and may ultimately provide insights into regions of the enzyme that are obscured in solution NMR. By integrating solution and solid-state NMR techniques, our work aims to deepen understanding of p38α dynamics and interactions at both molecular and systemic levels.

Investigation of the Role of Histidines in the inward directed proton-pump Xenorhodopsin

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The regulation of ion gradients across cell membranes is essential for life. In archaea, bacteria, and unicellular eukaryotes, one mechanism of regulation involves microbial rhodopsins (MRs), photosensitive retinylidene membrane proteins. Xenorhodopsin from Nanosalina sp. (NsXeR) is a light-driven inward proton pump [1, 2] with an unusual transport direction that may protect against alkaline environments or regulate intracellular signalling [3].

Histidine has unique properties due to its versatile interaction capacity, tautomeric variability, and pH sensitivity of the imidazole group [4, 5]. In some MRs, it participates in hydrogen bonds or salt bridges near the retinal Schiff base (RSB), acts as part of proton donor/acceptor complexes [6, 7, 8], and can function as a pH sensor or ion selector [9, 10].

In NsXeR, H48 is part of the RSB hydrogen bond network and may function as its proton acceptor. H94 likely belongs to the proton release group at the cytoplasmic side [2], while H225 is also located towards the cytoplasmic side [1] but with unclear function. We investigated the histidine residues in *Ns*XeR using solid-state NMR at ambient temperatures as well as under frozen conditions to enable DNP enhanced data acquisition and cryo-trapping.

Dark-state data show that all three histidines respond differently to pH changes in terms of imidazole protonation. Our current work focuses on the role of H48, highlighted in the literature for its essential functional contribution [1, 2], with previous observations and our data also indicating structural relevance. We study this through site-directed mutagenesis and analysis of the hydrogen bond network and dipolar coupling patterns in the dark state, and will assess how these features evolve during the photocycle by examining individual photointermediates.

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In situ Monitoring of Lithium Metal Dendrites using EPR-on-a-Chip (EPRoC)

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Batteries based on lithium metal anodes offer a significantly higher specific capacity when compared to the graphite anodes currently used in lithium-ion batteries. However, lithium metal exhibits inhomogeneous plating during charging that leads to the growth of dendritic microstructures, causing short-circuits and preventing its commercial use. To properly understand its growth mechanism, characterization methods that are particularly sensitive to lithium metal are advantageous.

Several approaches based on electron paramagnetic resonance (EPR) spectroscopy have been recently demonstrated using commercial EPR systems for monitoring the growth and presence of lithium metal dendrites, but these systems require the design of intricate *in situ* cells. Our approach of using EPR-on-a-chip (EPRoC), however, allows the use of simple electrochemical cells and an active volume comprising only the plated lithium, thereby greatly simplifying the acquired signals and facilitating their analysis.

In addition to its compact nature, EPRoC has great potential in terms of sensitivity, ease of use, price, and *in situ* compatibility. Using an EPRoC, we designed a simple electrochemical cell comprised of lithium metal and a copper current collector and monitored its EPR signal while charging. Employing a physical model for conduction EPR (CEPR), we modeled the plated lithium metal and deduced a specific charging stage that exhibited clear signs of dendritic growth, and offered a deeper insight into the growth mechanism. This EPRoC proof of concept in the characterization of battery materials could open the door to many new research and industrial possibilities, considering its advantages over commercial EPR systems.

Exploiting Eddy Currents – Optimal Control in NMR for Conductive Surface-Selectivity

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With the growing importance of *in operando* nuclear magnetic resonance (NMR) spectroscopy of electrochemical systems, such as electrolysis or battery cells, complex setups give rise to new experimental challenges that are difficult to address with standard NMR experiments. Particularly, conductive cell components cause magnetic field distortions due to shielding and eddy current effects, leading to reduced resolution, non-quantitative results, and potential artifacts. However, these local distortions can also be selectively addressed using shaped pulses tailored by quantum optimal control (QOC).

We show how finite element method (FEM) simulations accurately predict distortions of the oscillating magnetic field amplitude B_1 in NMR setups containing conductive materials, most notably in proximity of conductive surfaces [1, 2]. The distortions can be well approximated as a linear scaling of the local nutation frequency. The information can be utilized in ensemble QOC workflows, where it is conventional to model B_1 inhomogeneities as linear scalings of the nutation frequency to design B_1-robust or B_1-selective pulses [3].

In a proof-of-principle setup, we demonstrate how B_0-robust, yet B_1-selective pulses enable spatially selective NMR excitations between copper disks without the need for pulsed field gradients. The selective excitation is shown to be independent of the compound in-between the disks. The approach suggests a yet unexplored potential of *in operando* NMR in electrochemistry, material sciences, and heterogeneous catalysis.

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Very Fast Bioorthogonal Spin Labeling with Tetrazin-Substituted Gd^{3+} Complexes

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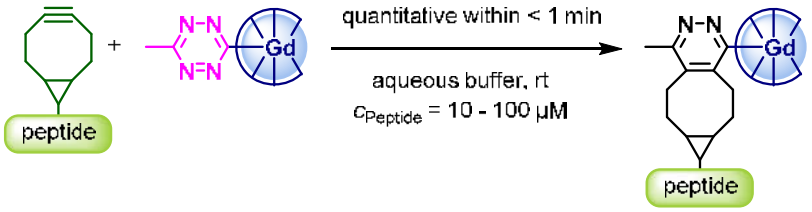
The reaction sequence consisting of an inverse electron demand Diels-Alder cycloaddition (IEDDA) between a 1,2,4,5-tetrazine (Tz) and a strained alkyne or alkene and a cycloreversion with nitrogen elimination, can proceed very fast and bioorthogonally and is therefore interesting for spin labeling of biomolecules.[1–3] Here we report on Gd^{3+} complexes ready-made for spin labeling of peptides which provide bicyclo[6.1.0]non-4-yne or *trans*-cyclooctene in their side chains. Such non-canonical amino acids have been genetically incorporated into proteins.[4] Our design of the Tz-substituted Gd^{3+} complexes is based on the idea to make use of the pyridine ring, a frequently occuring structural unit in transition metal complexes, as an IEDDA-accelerating substituent. Indeed, the complexes were found to react highly chemoselective and within seconds. The design of the Gd^{3+}-based spin label minimizes conformational variety. Furthermore, the progress of the reaction can be simply monitored with standard UV-Vis spectroscopy.



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X-band and Q-band EPR studies of multi-nitroxide adducts as potential MRI CAs

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Introduction of new alternatives for MRI contrast agents is in high demand due to the commercial ones based on Gd (III) ions suffer from issues such as accumulation in different parts of body along with their side effects. [1] Although nitroxide radicals are well-known in different research area such as DNP, protein spin labelling and etc. Their potential applications as MRI contrast agents have been limited due to their weak contrast property and rapid bio-reduction in biological systems. To overcome their mentioned issues, we have introduced water-soluble organic radical dendrimers. [2] However, step by step synthesis and tedious purification process cause the synthesis of such macromolecules become rather challenging. Therefore, by exploiting the approach of Multi Component Reactions (MCRs) in organic synthesis, di- and tri-nitroxide radicals were synthesized. Ultimately, this leads to more efficient organic radical dendrimers with the same size but more radical centres.

Due to the intrinsic magnetic property of such systems, besides other characterization techniques, EPR spectroscopy plays a crucial role in identifying as well as studying radical-radical interactions. In that regard, CW-X band measurements are conducted at room temperature, 100 K and up to 370 K to extract isotropic and anisotropic as well as gaining insight about flexibility of the systems, respectively. Q-band pulsed measurements are conducted at 70 K to obtain relaxation times (T_1, T_m) and also spin state distributions by running nutation experiments. The EPR results reveal that diradical and triradical posse strong exchange coupling between two radicals, then the third radical in the triradical mostly acts as an individual radical centre.

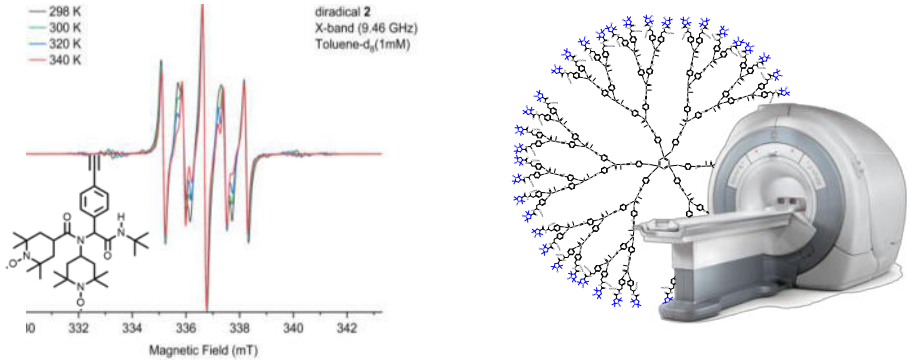

Figure 1: **left:** Experimental EPR spectra of diradical 1mM in toluene-d8 at variable temperatures at X-band CW-EPR spectrometer (9.46 GHz). **right:** 3rd generation of a radical dendrimer

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Investigating ^{1}H Polarization transfer via Spin Diffusion in PHIP Experiments

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Parahydrogen-Induced Polarization (PHIP) is a time-efficient and inexpensive hyperpolarization method that uses the *para* spin isomer of hydrogen in chemical reactions for enhancing NMR signals. But PHIP is limited to polarizing specific molecules, and in the liquid phase the polarization does not effectively spread to other molecules. In the solid-state, nuclear polarization spreads through dipolar couplings in a process known as spin diffusion, enabling indirect polarization transfer to distant spins. The combination of PHIP with spin diffusion (PHIP-SSD) can help transfer polarization from the hyperpolarized source to non-polarized target molecules, even those not directly involved in the initial reaction. PHIP-SSD has been demonstrated for ^{13}C spins previously but it is not yet explored for ^{1}H spins. [1] In this work, we are attempting to observe whether ^{1}H hyperpolarization survives liquid–solid–liquid phase transitions, and ^{1}H polarization of target molecules via PHIP-SSD.

Fumarate was synthesized via trans-hydrogenation of a precursor molecule acetylene dicarboxylic acid (ADC) in presence of a ruthenium catalyst, using parahydrogen. [2] The reaction yielded ~160 mM fumarate with the two ^{1}H nuclei in the spin-singlet state. To facilitate conversion of the singlet spin order into magnetization of ^{1}H and ^{13}C nuclei in the 2.2% natural abundance of [1-^{13}C]fumarate, the sample was placed within a magnetic shield, where a controlled magnetic field (B_0) sweep was applied along the z-axis. [3] Crystallization of fumarate was carried out in a 400 mT Halbach magnet by adding sulfuric acid to the reaction product mixture and subsequently re-dissolving the precipitate in alkaline D_2O. [4] Hyperpolarized ^{13}C NMR signals were observed, with 15% polarization before crystallization and 6% afterwards. We observed 2.6% ^{1}H polarization on [1-^{13}C]fumarate in solution before precipitation. After precipitation, we also detect 0.14% ^{1}H hyperpolarization on fumarate molecules lacking ^{13}C (which are not polarized in the liquid state by the field sweep), suggesting that they were polarized via solid-state spin diffusion. Since we solidified the hyperpolarized ^{13}C-fumarate with the non-polarized ^{12}C-fumarate together, we believe the ^{1}H polarization diffuses from the ^{13}C-fumarate (hyperpolarized source molecules) to the ^{12}C-fumarate (non-polarized target molecules) in solid-state.

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Heterocyclic Staudinger ligation for spinlabelling with Gd^{III}-complexes

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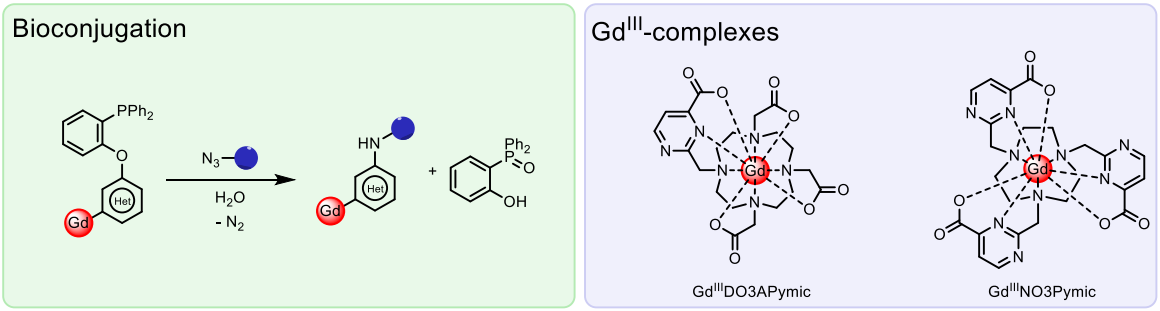

The Staudinger ligation[1] is a bioconjugation reaction which is rather slow and usually too slow to be used for spinlabelling. We expanded this reaction to aryloxy substituted heterocycles as the electrophile. With a model compound we determined for this heterocyclic Staudinger ligation a rate constant of $k = 0.05\ M^{-1}s^{-1}$ which is 25 times as high as those reported for the Staudinger ligation by Bertozzi et al. ($k = 0.002\ M^{-1}\ s^{-1}$).

A comparison of pyridine and pyrimidine as the heterocycle proved pyrimidine to be the best choice. Because for the application of a Gd^{III}-complex as a spinlabel its linewidth is of high relevance, we investigated how the exchange of pyridine for pyrimidine effects the linewidth. The pyrimidine containing complex Gd^{III}DO3APymic shows a smaller linewidth than Gd^{III}DO3APic while the linewidth of Gd^{III}NO3Pymic is about the same as that of Gd^{III}NO3Pic. Therefore, we expect these complexes to be good candidates for EPR spectroscopic distance determination: Gd^{III}DO3APymic for DEER spectroscopy and Gd^{III}NO3Pymic for cw spectroscopy.

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DCODE- a modern HOSE Code alternative?

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In 1978, W. Bremser published the first version of the HOSE Code (Hierarchical Ordered description of the Substructure Environment) for the "Characterization of the spherical environment of a single atom and complete ring systems". (Bremser, 1978)
This made it possible, for example, to store the chemical shift of an atom and its chemical environment together in data processing systems and to use it to predict NMR spectras for new compounds. Therefore, the HOSE code has found its way into various applications for the storage and prediction of chemical shifts. As an example, reference should be made to the NMRShiftDB2, as it is of particular importance as a data source for the work presented here. (Kuhn & Schlörer, 2015)
Since the original HOSE code does not contain stereochemical information, there may be problems with the coding of constitutopice, and especially with coding of diastereotopice atoms and groups, and consequently also with the calculation spectroscopic parameters for these. Consequently, various extensions of the HOSE Code have been developed. In the NMRShiftDB, for example, the extension described by Kuhn and Johnson can be used. (Kuhn & Johnson, 2019)
However, since the HOSE code is based on the chemical bond between two atoms as a neighborhood criterion, it cannot necessarily detect neighbors in the vicinity of the encoding atom purely by chance. Therefore, we had the idea of redesigning the linear coding of the chemical environment of an atom from scratch a while ago. Our approach is based on geometric distance as a measure of spatial proximity. It is then irrelevant whether two atoms are connected to each other via one, two, three or more bonds or not. And this is the basis of DCODE (for DistanceCODE), which we would like to introduce in more detail here in a first version. A preliminary test with 48 randomly selected compounds resulted in a MAE of 1.95 ppm. And the use of the DCodes as an assignment tool resulted in a matching assignment consistent with the experiment in more than 80% of cases.

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Repository: https://github.com/steto123/dcode

Very fast spinlabeling with Gd^{III} complexes of different line widths

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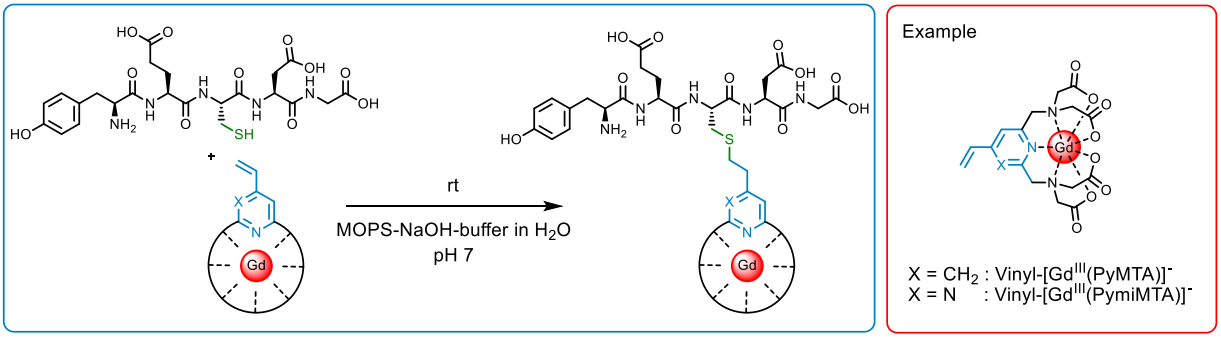

We are investigating the thiol-ene-reaction for bioconjugation of Gd^{III} complexes which are of interest as spin labels.[1] The thiol-ene reaction between a protein-embedded cysteine and ligand 4-vinyl-PyMTA was found to be too slow to be of broad applicability.[2] Furthermore, the corresponding Gd^{III} complex $[Gd(PyMTA)]^-$ did not react.[2] Substituting pyridine for pyrimidine led to a huge increase in reactivity. With a complex of similar structure, we determined a reaction constant of k_2 = 6 $M^{-1}s^{-1}$. This exceeds the reaction rate of 1 $M^{-1}s^{-1}$ that is required for acceptable conversion within 24 h according to SAITO *et al.*[3]

Following EPR spectroscopic investigations of the corresponding unsubstituted complexes to examine the influence of the substitution of pyridine for pyrimidine revealed that the substitution did not influence the narrow line width. Therefore, we expect the vinyl-substituted complexes to be suitable for efficient spin labelling.

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Advanced Analysis of Parabens via HPLC-HSQC on a Benchtop NMR

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Two-dimensional NMR spectroscopy offers improved spectral resolution and increased structural information compared to 1D NMR. Especially Heteronuclear Single Quantum Coherence (HSQC) provides significant advantages over 1D $^{13}C/^{15}N$ NMR by having a better signal-to-noise ratio (SNR) per square root of measurement time. Coupling HSQC to HPLC introduces a third dimension, enabling concerted chromatographic separation and spectral NMR analysis for enhanced characterization.
Using a 90 MHz benchtop spectrometer for this purpose offers several benefits, like smaller space requirements, an easier coupling to the HPLC system, and no cryogenic liquids needed in comparison to high field NMR. However, benchtop spectrometers generally exhibit lower SNR and reduced resolution, which necessitates extensive optimization of both measurement parameters and data processing protocols [1, 2, 3].
As a model system, parabens, commonly used as preservatives in cosmetics, were investigated. Building on our previous work, which successfully coupled 1D ^{1}H NMR and 2D COSY with HPLC in both stop-flow and on-flow modes [2, 4], our optimized HSQC method allows the acquisition of HSQC spectra in approximately 6 minutes, a substantial improvement compared to the several hours typically required for HSQC measurements. The method was developed using continuous flow analysis of stock solutions, and methylparaben as well as propylparaben could be characterized following chromatographic separation in stop-flow mode.

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Covalent doping for compartment-selective DNP-NMR analysis of polymer micelles

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Block copolymer micelles represent a diverse platform for drug delivery systems, potentially including targeting moieties or stimuli-responsive elements to control cargo release.[1] Structural characterization of such complex particles is essential for their development but remains challenging, especially if low-concentration species such as surface groups or active ingredients need to be detected. Solid-state NMR combined with hyperpolarization techniques such as Dynamic Nuclear Polarization (DNP) provides a solution to this problem.[2]

We are functionalizing polymer end-groups with biradical polarizing agents (PAs) to selectively direct the PAs to specific micellar compartments. Thereby we can detect low amounts of drug in MAS DNP experiments. While the DNP-induced signal enhancement occurs throughout the entire sample, depolarization and bleaching effects are restrained to the close vicinity of the PAs.[3] By analyzing these localized signal changes, we can generate spectra that highlight only the molecular components in close proximity to the PAs.

This approach can be used to specifically analyze the drug-rich domain in the micellar core or the excipients outside of the nanoparticles. As a result, detailed information on the spatial arrangement of the individual constituents within the micelles and their environment can be obtained.

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Effect of Pore Hierarchy on Transport of Methane in Carbon Material

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Coalbed methane (CBM), a byproduct of coalification, is primarily stored as adsorbed methane within micropores. Due to strong spatial confinements, methane diffusion in these micropores is significantly hindered, often leading to difficulties in gas extraction and gas outburst incidents during engineering applications. As a typical porous medium, coal possesses a rich distribution of micropores, mesopores, and macropores. Although the multiscale pore structure of coal is known to influence gas transport, the individual contributions of mesopores and macropores to transport efficiency from micropores remain poorly quantified due to the complex and heterogeneous pore network in coal. This study aims to isolate and evaluate these effects within a controlled system.

To achieve this goal, we constructed a synthetic analogue using activated carbons with hierarchically-organized controlled pores, enabling systematic comparison of diffusion behaviour across distinct structural types. These samples featured varying combinations of micropores, mesopores, and macropores. Low-temperature nitrogen adsorption experiments were conducted to determine pore volume, surface area, and pore size distribution. Methane diffusion behaviour was assessed using pulsed field gradient nuclear magnetic resonance (PFG-NMR) under various equilibrium pressures. Additionally, tracer-desorption experiments were performed by following NMR free induction decay signal variation in response to stepwise pressure changes. These data were fitted with diffusion models to obtain transport diffusion coefficients.

Interestingly, methane diffusion rates increased linearly with pressure in samples containing mesopores. This trend is primarily governed by the ratio of micropore to mesopore volumes and the intrinsic diffusion coefficients within the mesopores, suggesting favorable transport enhancement effect likely governed by strong connectivity between micro- and mesopores. At equal pressures, materials with higher mesopore content consistently exhibit enhanced overall diffusion efficiency. These findings suggest that highly permeable mesopores provide critical transport pathways, enabling methane to more readily escape microporous confinement. Although the effect of pore connectivity remains an open question, our study demonstrates that hierarchical pore structure alone can significantly influence diffusion dynamics. This work offers new insights into gas transport in complex porous systems and may inform the design of materials for enhanced CBM recovery.

Exploring acetylene bridged Bis-Trityls as possible candidates for *J*-driven Dynamic Nuclear Polarization

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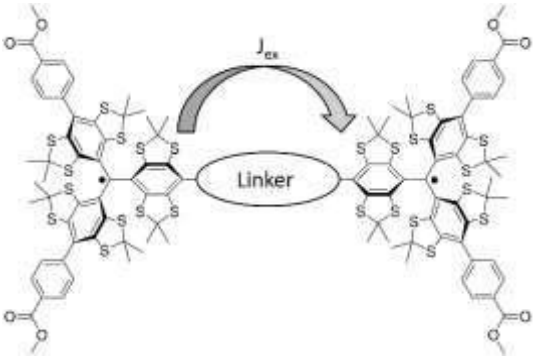
To enhance the sensitivity of solution state NMR, among the multitude of possible dynamic nuclear polarization methods a new approach was proposed. Here, the polarization agent needs to have an interelectron exchange coupling $J_{ex,}$ which matches the electron Lamor frequency. To achieve exchange couplings in the upper gigahertz region, short, covalently linked biradicals need to be employed.[1]

A multitude of short, covalently linked Bis-Trityl compounds were synthesized to be investigated as possible polarizing agents. Using Trityl radicals has several advantages, such as ease of modification, small EPR linewidths and their long relaxation times.[2] While the narrow signal allows for easy analysis of the resulting spectrum, the long relaxation times are especially useful as to not interfere with the cross-relaxation pathways required for J-DNP.

In this work, acetylene bridged Bis-Trityls were synthesized and investigated by cw-EPR, DFT and UV-Vis spectroscopy to gain further insight into their electronic structure and reactivity.



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Evaluation of ^{13}C Satellite Decoupling Techniques for Accurate Quantitative ^{1}H NMR spectra

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^{13}C satellite signals naturally occur in ^{1}H NMR spectra adjacent to each parent signal with an intensity of approximately 0.5%.[1] These satellites pose a significant risk of masking or overlapping with signals from minor components, thereby limiting the quantitative analysis of mixtures using NMR spectroscopy. Suppressing ^{13}C satellite signals can therefore improve the accuracy of both qualitative and quantitative analyses of minor components.[2]

Common broadband ^{13}C decoupling techniques include globally optimized rectangular pulses (GARP) and bilevel adiabatic (BILEV) decoupling.[3-4] If not carefully optimized, these sequences can lead to sample heating, decoupling sidebands and signal broadening.[1-2] The destruction of interfering satellites by perfect echo low-pass filtration (DISPEL) sequence offers an alternative broadband suppression method that is effective across a wide range of coupling constants.[1] This advantage, however, comes at the cost of slightly reduced sensitivity and potential relaxation bias.[1]

This study aims to evaluate broadband ^{13}C decoupling schemes and DISPEL pulse sequences for their suitability in generating quantifiable ^{1}H NMR spectra.[2, 5] The reliability of the ^{13}C satellite suppression techniques is compared to conventional ^{1}H NMR spectra in the context of qNMR. Validating these methods will enhance the overall effectiveness of qNMR analysis, enabling clearer and more reliable results when examining complex mixtures.

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