BOOK OF ABSTRACTS

DOCDAYS 2021

13TH DOCDAYS

UNIVERSITY OF TECHNOLOGY GRAZ

APRIL 7TH – 8TH

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Online Registration

On the main slide of the event a QR code will be displayed that each participant has to scan in order to get the credits.

This has to be done daily in the morning (8:45-9:00) and before the start of the afternoon session (13:15-13:30).

The daily registration at the event is simple:

- Scan the QR code with your phone
- Open the link with your browser
- Enter your name and surname
- Confirm

INSTRUCTIONS FOR THE MEETING:

The meeting will be held via “Cisco WebEx”.For those of you who are presenting and have never used the platform before, download WebEx on your computer and create an account. More information can be found via the link: https://www.webex.com/de/index.html.

Please keep your microphone and camera off during the meeting, unless you are required otherwise.

During the presentation you need to share your screen and turn on your camera and microphone. Therefore, have your power point presentation ready and check the correct functioning of your camera and microphone before the meeting. You will share your screen during the whole duration of your presentation and questions time.

Every speaker has a slot of 20 minutes, which is composed of a maximum of 15 minutes presentation and 5 minutes of questions. Please keep your talk within the time limit.

During the 5 minutes of questions, every participant has to give feedback by filling out an online evaluation sheet. The poll will appear via WebEx after every talk. Every participant can express his/her feedback on the presentation but also on the design by a single vote in the form of 1 to 5 (1 being the highest score, 5 being the lowest) and a voluntary comment or suggestion. Please make sure to vote in the given time. It will not be possible to vote after the chair has closed the vote and has moved on with the schedule.

Additionally, there will be two sessions with so called poster presentations (PP), where first year students at the TU Graz doctoral school chemistry will present their thesis project in 5 minutes followed by a short question round. After these sessions every participant can leave comments for the speakers.

After every talk, questions can be asked by using the function “raise your hand” in the online chat. The chair of the session will then proceed by giving you the possibility to talk (according to the time schedule). Please speak clearly, loudly and be concise.

April 7th		April 8th	
08^{45}-09^{00}	**Online Registration**	08^{45}-09^{00}	**Online Registration**
09^{00}-09^{15}	**Opening, Welcome** Rector Prof. Martin Polaschek Dean Prof. Frank Uhlig	09^{00}-10^{00}	Chair: Weinberger IT02 Lam Research, I. Smolej, P. Dobrounig IT03 Patheon, P. Selig ST14 Lembacher-Fadum
09^{15}-10^{00}	Chair: Prof. Kroutil PL01 Prof. Thomas R. Ward, University of Basel IT01 Infineon Technologies, C. Koblinski		
10^{00}-10^{15}	**Coffee Break**	10^{00}-10^{15}	**Coffee Break**
10^{15}-11^{15}	Chair: Prohinig ST01 Breukelaar ST02 Püschmann ST03 Menzies	10^{15}-11^{15}	Chair: Menzies ST15 Müller ST16 Zukić ST17 Dalfen
11^{15}-11^{30}	**Coffee Break**	11^{15}-11^{30}	**Coffee Break**
11^{30}-12^{30}	Chair: Sorgenfrei ST04 Lainer ST05 Swoboda ST06 Burger	11^{30}-12^{30}	Chair: Wied ST18 Steiner A. ST19 Vakalopoulou ST20 Wintersteller
12^{30}-13^{30}	**Lunch Break**	12^{30}-13^{30}	**Lunch Break**
13^{30}-14^{30}	Chair: Rappitsch ST07 Wied ST08 Eggbauer ST09 Goni	13^{30}-14^{30}	Chair: Guttmann ST21 Rappitsch ST22 Prieschl ST23 Schuh
14^{30}-14^{40}	**Coffee Break**	14^{30}-14^{45}	**Coffee Break**
14^{40}-15^{10}	Chair: Grössl PP01 Natemeyer	14^{45}-15^{10}	Chair: Ladenstein PP05 Drusgala

	PP02 Wiesner PP03 Krammer PP04 Schmid		PP06 Zuccala PP07 Okorn
15^{10}-15^{25}	**Coffee Break**	15^{10}-15^{25}	**Coffee Break**
15^{25}-16^{45}	Chair: Prieschl ST10 Weinberger ST11 Pfleger ST12 Ladenstein ST13 Walenta	15^{25}-16^{45}	Chair: Wintersteller ST24 Sorgenfrei ST25 Redolfi ST26 Steiner L. ST27 Prohinig
		16^{45}-17^{00}	**Concluding remarks**

PLENARY LECTURE

PL01 Prof. Thomas R. Ward, University of Basel

Artificial Metalloenzymes for *in vivo* Catalysis: Challenges and Opportunities

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https://ward.chemie.unibas.ch/en/home/

Artificial metalloenzymes (ArMs) result from the incorporation of an abiotic metal cofactor within a host protein, Figure 1. Thanks to the remarkable supramolecular affinity of biotin for streptavidin (*K*D > 10-13 M), linking a biotin anchor to an organometallic catalyst ensures that, upon addition of streptavidin, the abiotic cofactor is quantitatively incorporated within the streptavidin. Alternatively, human carbonic anhydrase has proven equally versatile for the development of artificial metalloenzymes relying on aryl-sulfonamide anchors to ensure the localization of the abiotic metallocofactors within the host protein. The catalytic performance of the resulting ArMs can be optimized either by chemical (variation of the anchor-spacer-ligand moiety) or genetic- (mutation of the host protein) means. These chemogenetic schemes were applied to optimize the performance for thirteen different catalyzed transformations as well multiple reaction cascades in the presence of natural enzymes, either *in vitro or in vivo.* This presentation will highlight the group's effort to implement and evolve artificial metalloenzymes with activities that are complementary to natural enzymes. These include: C–H activation, hydroxylation, olefin metathesis, imine reduction, cross-coupling reactions etc.

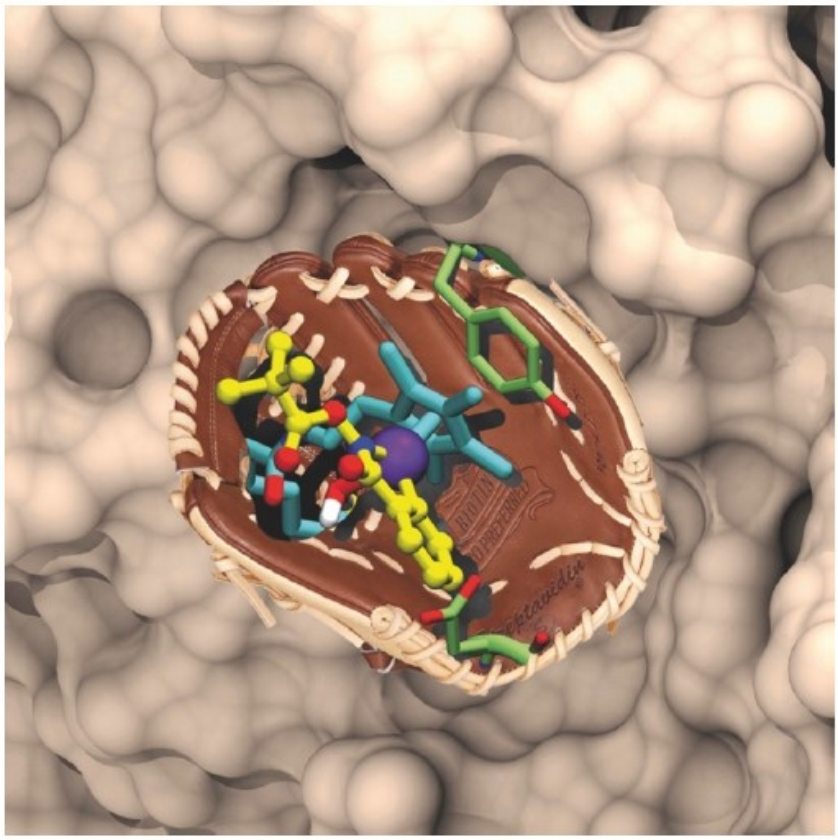

Figure 1. Endowing organometallic catalysis with a genetic memory. In a Darwinian spirit, anchoring an abiotic metal cofactor within a host protein allows to implement directed evolution schemes to optimize the performance of organometallic catalysts.

INDUSTRY TALK

IT01 Carsten Koblinski, Infineon Technologies AG

IT02 Irina Smolej, Patrick Dobrounig, Lam Research

IT03 Philipp Selig, Patheon, Thermo Fisher Scientific

Infineon Technologies Austria AG

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Company Introduction
Does contributing to cutting-edge technology AND to a better world sound interesting to you? That's exactly what we do at Infineon Technologies Austria AG: We make life easier, safer and greener – with technology that achieves more, consumes less and is accessible to everyone. Microelectronics from Infineon is the key to a better future. Efficient use of energy, environmentally-friendly mobility and security in a connected world – we solve some of the most critical challenges that our society faces while taking a conscientious approach to the use of natural resources.

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- Flexible working time models, teleworking options, comprehensive health programs and a healthy work-life balance.
- Training and continuing education, the inspiration of young talents for technology (STEM) and thus releasing diversity potentials.

Proudly ranked among the top 10 most attractive employers in Austria for the third time in a row!

In which area of study is Infineon particularly interested in?
Microelectronics, Electrical Engineering, Physics, Chemistry, Telematics, Material Science, Process Technology, Micro- & Nanotechnologies, Mechatronics, Mathematics, IT, etc.

Lam Research at a Glance

Irina Smolej, Patrick Dobrounig
Lam Research AG;
SEZ Strasse 1, 9500 Villach
Tel: +43 4242 204 0, www.lamresearch.com

Electronic devices are part of our everyday lives. From smartphones and tablets to wearables and automobiles, it's hard to go more than a few hours without using a semiconductor-enabled device. The semiconductor industry touches nearly every person on the planet as chipmakers continue to push the limits of what's possible and aspire to change the world through their products.
Lam Research, headquartered in the Silicon Valley in California, employs more than 12,000 employees worldwide and is one of the world's leading providers of semiconductor manufacturing equipment. In Villach, Lam Research employs around 550 employees and develops and manufactures the equipment for wafer cleaning.
Lam's wafer fabrication equipment and services allows chipmakers to build smaller, faster, and better performing electronic devices. Our broad portfolio of market-leading products for thin film deposition, plasma etch, photoresist strip, and wafer cleaning is one of the vital links between our customer's vision and the final product. **It's why nearly every advanced chip today is built with Lam Research technology.**
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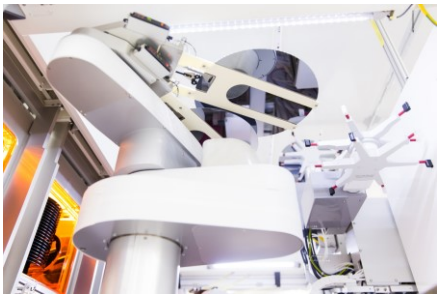

Key Facts
Founded: January 1980
Revenue: ~$11.9 Billion (CY 2020)
Employees: ~12,200 (CY 2020)
Headquarters: Fremont, California
Manufacturing: US, Austria, South Korea

Process Chemistry at Patheon, by Thermo Fisher Scientific

Philipp Selig
Patheon, by Thermo Fisher Scientific; Patheon Austria GmbH & Co KG
St.-Peter-Straße 25, 4040 Linz, Austria
philipp.selig@thermofisher.com

Process Chemistry is the art of developing a laboratory synthesis into a universally applicable, quality-controlled and safe large-scale production process.
Following a short presentation of our pharmaceutical production site in Linz, we will introduce you to some of the most important aspects of process chemistry (safety, operability, quality) and shed some light on the questions: Why do we need process chemistry, and what makes a good production process?

About Thermo Fisher Scientific

Thermo Fisher Scientific Inc. is the world leader in serving science, with revenues of more than $30 billion and approximately 80,000 employees globally. Our mission is to enable our customers to make the world healthier, cleaner and safer. We help our customers accelerate life sciences research, solve complex analytical challenges, improve patient diagnostics, deliver medicines to market and increase laboratory productivity. Through our premier brands—Thermo Scientific, Applied Biosystems, Invitrogen, Fisher Scientific and Unity Lab Services—we offer an unmatched combination of innovative technologies, purchasing convenience and comprehensive services.

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For further information please visit: https://www.thermofisher.com/patheon

STUDENT TALKS

April 7th

ST01 Breukelaar
ST02 Püschmann
ST03 Menzies
ST04 Lainer
ST05 Swoboda
ST06 Burger
ST07 Wied
ST08 Eggbauer
ST09 Goni
ST10 Weinberger
ST11 Pfleger
ST12 Ladenstein
ST13 Walenta

April 8th

ST14 Lembacher-Fadum
ST15 Müller
ST16 Zukić
ST17 Dalfen
ST18 Steiner A.
ST19 Vakalopoulou
ST20 Wintersteller
ST21 Rappitsch
ST22 Priesch
ST23 Schuh
ST24 Sorgenfrei
ST25 Redolfi
ST26 Steiner L.
ST27 Prohinig

POSTER PRESENTATION

April 7th

PP01 Natemeyer
PP02 Wiesner
PP03 Krammer
PP04 Schmid

April 8th

PP05 Drusgala
PP06 Zuccala
PP07 Okorn

Access to chiral Amines from Oximes using Ene-Reductases

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Flavin-dependent ene-reductases (EREDs), such as those of the Old Yellow Enzyme (OYE) family, are a well described and studied class of enzymes, mostly applied for the enantioselective reduction of electronically activated C=C double bonds (Figure 1, top). While a wide substrate scope has been established,[1] the enzymes are not known for the reduction of C=heteroatom bonds. Recent work in our group has shown that several ene-reductases reduce the oxime functionality of β-keto-α-oximo esters very efficiently, yielding tetrasubstituted pyrazines after non-enzymatic cyclisation and oxidation of the product formed in biotransformation (Figure 1, middle).[2] Now, we are working on new substrates (diester malonate-derived oximes) that do not cyclise, thus enabling an enzymatic route towards chiral amines (Figure 1, bottom). We quickly found that substrates derived from diester malonates were only converted when they contained a methyl ester (even the oxime derived from diethyl malonate was not converted), hinting at highly specific binding of the substrate.

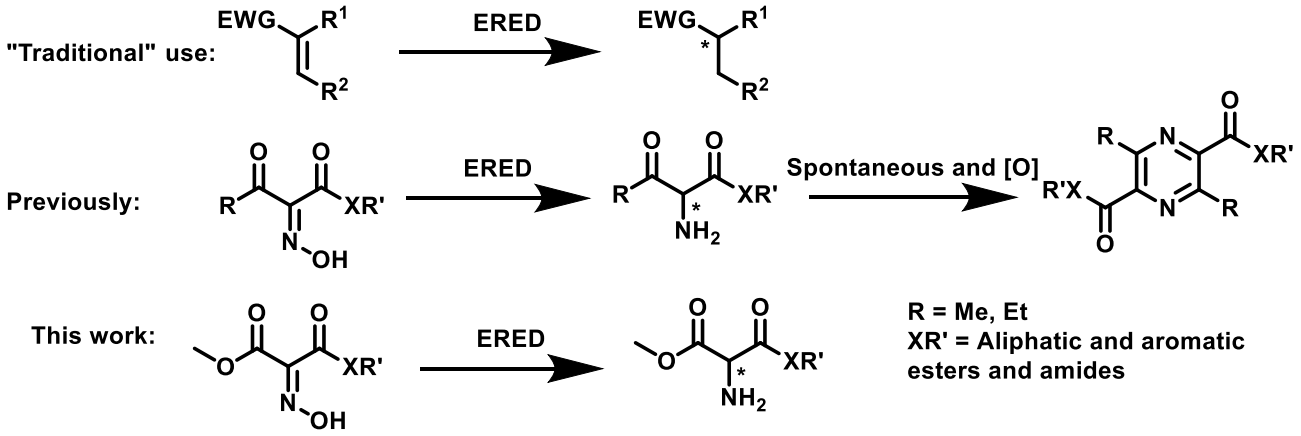

Figure 1. Reactions of EREDs. Top: well-established reduction of activated alkenes. Middle: reduction of oximes to pyrazines *via* ERED-catalysed amine formation. Bottom: reduction of malonic ester-derived oximes to aminomalonates.

A library of 15 oximes derived from malonic esters was synthesised to vary the "XR'" moiety with regard to sterics and electronics. Qualitative tests (formation of the amine was investigated by LC- or GC-MS) showed that biotransformation with eleven of the substrates yielded the corresponding amine. Current efforts focus on (chemical) synthesis of the racemic amines, establishing chiral LC-MS analytics to quantify conversion and enantiomeric excess, after which a more comprehensive screening can take place. Finally, it is our aim to show that these amines can be obtained on preparative scale (>100 mg) without racemisation of the compound.

References:

[1] Toogood, H. S.; Gardiner, J. M.; Scrutton, N. S. *ChemCatChem* **2010**, *2*, 892–914
[2] Velikogne, S.; Breukelaar, W. B.; Hamm, F.; Glabonjat, R. A.; Kroutil, W. *ACS Catal.* **2020**, *10*, 13377–13382

Synthesis of Mixed Functionalized Tetraacylgermanes

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Nowadays photoinitiators (PIs) are of high interest in different industrial application processes, like 3D printing, coatings and in the medical sector.[1] The design as well as the implementation of such PIs are very challenging, due to the fact that they need to fulfill a lot of requirements.[2] Recently, germanium-based photoinitiators have attracted higher attention, on account of their low toxicity and their bathochromic shift. For example, the commercial available Ivocerin, as well as, tetraacylgermanes are known as highly efficient photoinitiators. The drawback of Ivocerin is the complex multi-step synthetic route resulting in high costs. Tetraacylgermanes have the disadvantage of low solubility, which limits the field of applications.
Therefore, we introduce two one-pot synthetic pathways towards mixed functionalized acylgermanes, shown in Figure 1.[3]

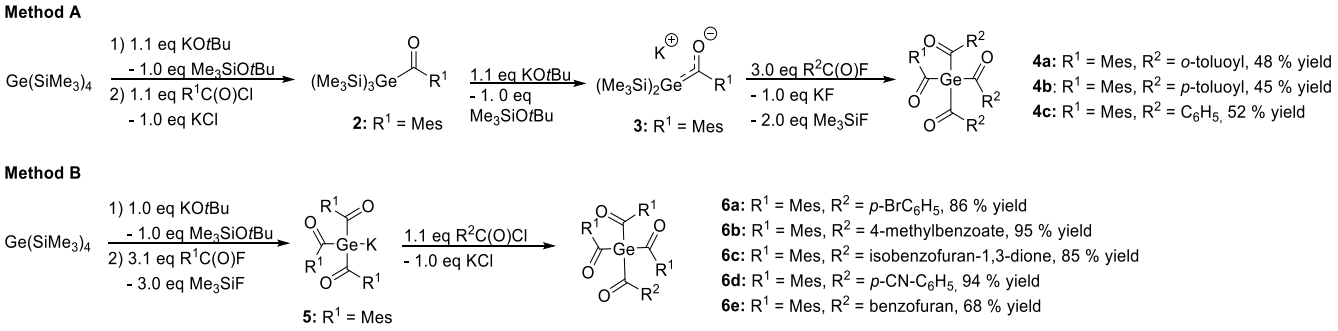

Figure 1. Two one-pot synthetic pathways towards mixed functionalized acylgermanes.

The introduction of different substituents on the germanium leads to an increased solubility compared to uniform tetraacylgermanes. These derivatives reveal broaded n-π* absorption bands, which is responsible for their photo-activity and are promising for a huge variety of applications.

References:

[1] a) L. R. Gatechair, D. Wostratzky, *Adhesive Chemistry: Developments and Trends*, Vol. 2, **1985**, 409.
b) A. Bagheri, J. Jin, *ACS Applied Polymer Materials* **2019**, *1*, 593. c) I. V. Khudyakov, M. B. Purvis, N. J. Turro*, Photoinitiated Polymerization*, Vol. 847, *American Chemical Society* **2003**, 113. d) N. Moszner, U. Salz, *Progress in Polymer Science* **2001**, *26*, 535.
[2] Y. Yagci, S. Jockusch, N. J. Turro, *Macromolecules* **2010**, *43*, 6245.
[3] S. D. Püschmann, P. Frühwirt, M. Pillinger, A. Knöchl, M. Mikusch, J. Radebner, A. Torvisco, R. C. Fischer, N. Moszner, G. Gescheidt, M. Haas, *Chem. Eur. J.* **2021**, *27*, 3338.

Arsenolipids in Marine Systems

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Heinrichstrasse 28, 8010 Graz, Austria
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The toxic properties of arsenic have been known for centuries. In recent decades there has been an increase in research and regulations surrounding arsenic in drinking water, and rice, two major sources of inorganic arsenic that can lead to poisoning. Despite many people receiving the majority of their arsenic intake from seafood, the toxicity has been widely dismissed due to the predominant form being organic arsenic, the most abundant of which – arsenobetaine – is non-toxic [1]. In many fatty fish and algae a large amount of the arsenic is actually present as arsenolipids, or lipid soluble arsenic species. Some of these, in particular arsenic-containing hydrocarbons (AsHC), have been found to exert at least equal cytotoxicity to human cells as inorganic arsenic[2], and they may even be able to cross the blood-brain barrier and placental barrier[3]. The exact modes of action are still unclear, and studies have been almost exclusively in vitro using synthesized arsenolipids. Developing a better understanding of these arsenolipids and improving quantification methods are therefore vital steps to evaluate the true toxicological risk of consuming seafood and algae to humans.

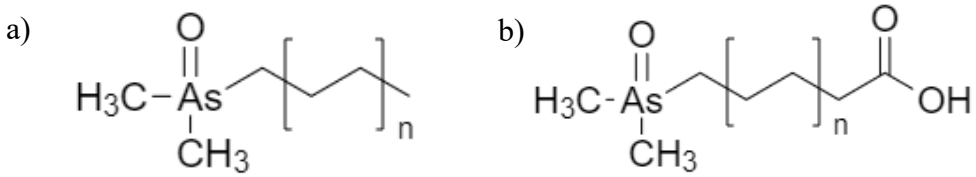

Figure 1. The structures of two of the main arsenolipid groups: a) arseno-hydrocarbons (AsHC), and b) arseno-fatty acids (AsFA)

Several main groups of arsenolipids have been identified, these are: arseno-hydrocarbons (AsHC), arseno-fatty acids (AsFA) and arsenophospholipids (AsPl). They have been found in a variety of fish, shellfish and algae. The main method to analyze them is currently high-performance liquid chromatography (HPLC) to separate the different arsenolipids, then ICP-MS/ES-MS to get both quantitative and qualitative data on the arsenolipids. There are issues around this analysis due to the requirement for organic solvents which cause disruptions in the ICP-MS detection. There is also a high level of matrix interferences from algae and fish oil samples, so this matrix has to be removed prior to analysis. We are working on optimizing this clean up procedure for fish oil with a variety of SPE materials, solvents and methods. The aim is to create a standard procedure that will work with a range of samples to get good quantitative recovery for further analysis. A screening method is also being developed using GC/MS to provide a faster and simpler overview of the arsenolipids present in a sample.

References:

[1] U. Arroyo-Abad, S. Lischka, C. Piechotta, J. Mattusch, T. Reemtsma, *Food Chemistry* **2013**, *141*, 3093–3102.
[2] B. Witt, F. Ebert, S. Meyer, K. A. Francesconi, T. Schwerdtle, *Molecular Nutrition and Food Research* **2017**, *61*, DOI 10.1002/mnfr.201700199.
[3] S. M. Müller, F. Ebert, G. Raber, S. Meyer, J. Bornhorst, S. Hüwel, H. J. Galla, K. A. Francesconi, T. Schwerdtle, *Archives of Toxicology* **2018**, *92*, 823–832.

The Chemistry of Dodecamethoxyneopentasilane: A New Building Block for Polysilane Chemistry[1]

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Although dodecamethoxyneopentasilane (**1**) was prepared decades ago,[1] a further functionalization was never accomplished. In close analogy to $Si(SiMe_3)_4$[2] and $Si(SiH_3)_4$,[3] we considered **1** as an ideal starting point for the synthesis of poylsilylanions. Thus, we now were able to achieve the synthesis of tris(trimethoxysilyl)silanides (M = Li, Na, K) **2** by reacting **1** with one equivalent of suitable bases. As depicted in Scheme 1, subsequent treatment of **2** with a variety of electrophiles gave the methoxypolysilanes **3**-**5**. Hydrogenation of the obtained products with *i*Bu_2AlH, furthermore, offers excellent possibilities for the synthesis of novel functionalized higher silicon hydrides.

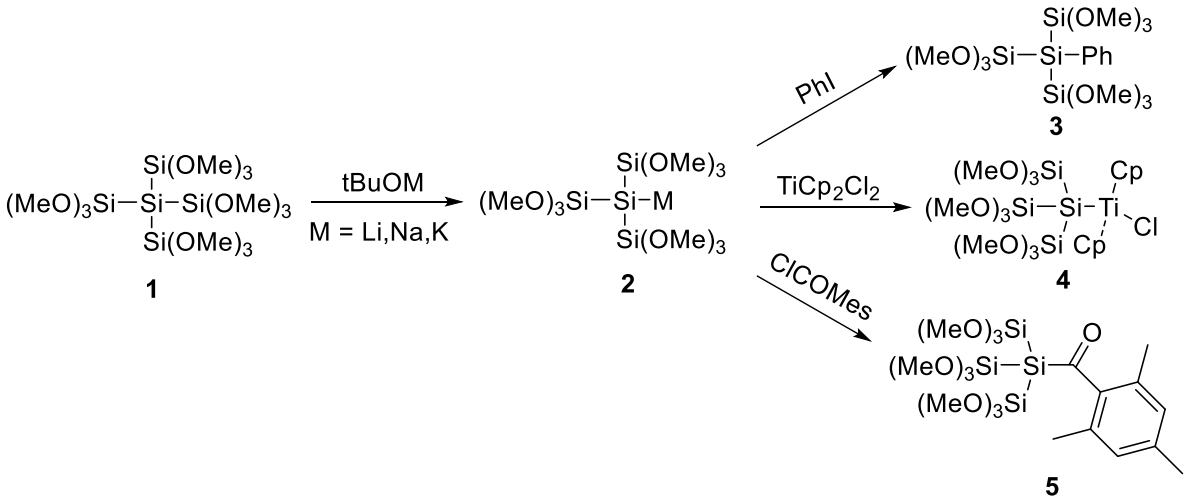

Figure 1. Reaction of 1 with various electrophiles

References:

[1] T. Lainer, M. Leypold, C. Kugler, R.C. Fischer, M. Haas, *Eur. J. Inorg. Chem.* **2021**, 529-533
[2] F. Höfler, R. Jannach, *Z. anorg. Allg. Chem*. **1975**, 413, 285-292
[3] C. Marschner, *Eur. J. Inorg. Chem*. **1998**, 221-226
[4] H. Stueger, T. Mitterfellner, R. Fisch, C. Walkner, M. Patz, S. Wieber, *Chem. Eur. J*. **2012**, 18, 7662-7664

Investigation of unspecific Peroxygenases (UPOs): Biocatalytic C-H Oxyfunctionalization using H_2O_2 as an Oxidant

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Unspecific Peroxygenases (UPOs, EC.1.11.2.1) present promising biocatalysts, which can catalyze a diversity of oxygenation reactions including hydroxylation of alkanes and aromatics, epoxidation of alkenes, heteroatom oxygenation as well as C-C and C-S bond formation.[1] Since UPOs are heme-thiolate dependent enzymes, they share common reaction chemistry and active site characteristics with P450 monooxygenases but are biotechnologically more attractive as they do not rely on nicotinamide cofactors and complicated electron transport chains.[2] UPOs take a step into a terrain where chemical alternatives are rarely efficient or even impossible. Despite this great potential, the present challenge is to identify activity on non-natural substrates and tame their chemo- regio- and stereoselectivity.[3]

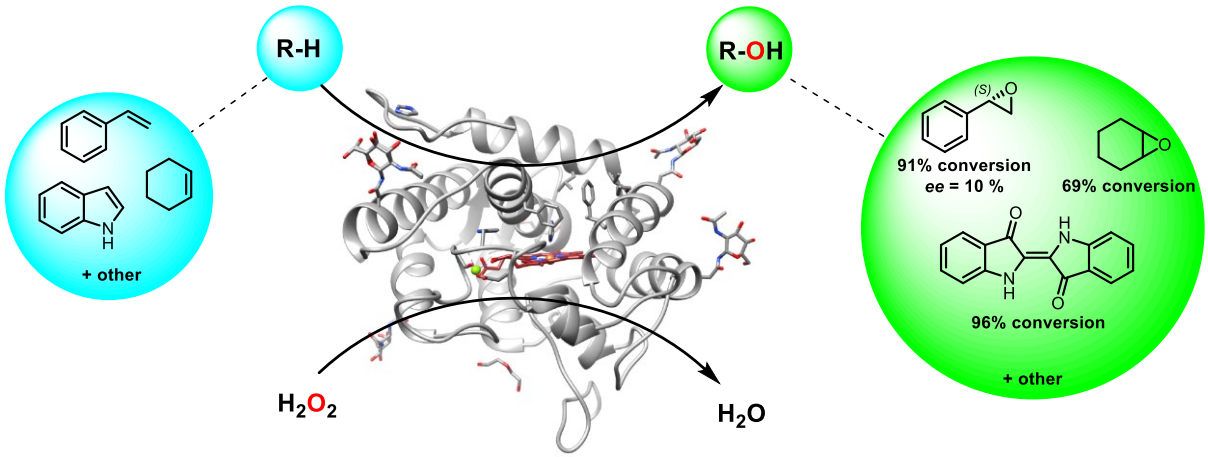

Figure 1. General reaction scheme C-H oxyfunctionalization reactions catalyzed by UPOs (embedded in the structure of the peroxygenase from *Hypoxylon sp*.)

We here report the successful C-H oxyfunctionalization of various small molecules by a set of novel peroxygenases including an unspecific peroxygenase from *Hypoxylon sp.* which showed notable thermal stability and efficiently produced the natural dye indigo through the oxidation of indole with conversion of up to 96 % and less than 1 % side oxidation products. Further endeavors focus on assay design to identify new UPOs as well as on broadening their substrate scope.

References:

[1] M. Hobisch, D. Holtmann, P. Gomez de Santos, M. Alcalde, F. Hollmann, S. Kara, *Biotechnology advances* **2020**, 107615.
[2] S. Chakrabarty, Y. Wang, J. C. Perkins, A. R. H. Narayan, *Chemical Society reviews* **2020**, *49*, 8137.
[3] Y. Wang, D. Lan, R. Durrani, F. Hollmann, *Curr. Opin. Chem. Biol.* **2017**, *37*, 1.

Porous, Crystalline Oxygen Sensors: PCN-224 MOF

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Optical sensing of oxygen is of great importance in research and industry[1]. These sensors rely on quenching of luminescence of an indicator by molecular oxygen. Among numerous phosphorescent indicators explored, porphyrin derivatives are probably the most popular representatives[2].These materials are also excellent building blocks for metal-organic frameworks (MOFs) since they have a rigid and defined geometry as a tetra-dentate ligand. MOFs are crystalline materials that generally consist of metal nodes and organic linkers and are characterized by extremely high porosity. Due to this permanent porosity and high accessibility to gases in the framework, these materials are promising for sensing applications including oxygen sensing [3].

One well-described porphyrin-based MOF is PCN-224. It consists of Zr_6 clusters which are connected with tetrakis-(4-carboxyphenyl) porphyrin (H_2TCPP) as an organic linker. This MOF has a permanent porosity with a reported BET surface of 2600 m²/g and large pore sizes of 1.9 nm [4]. This leaves the individual porphyrin units as organic linkers well isolated from each other while being extremely well accessible for guest materials, such as oxygen. At 20 kPa oxygen in the gas phase, 4.2-fold quenching compared to nitrogen atmosphere (with $\tau_0 \sim 6.8$ ns) is observed for fluorescent PCN-224 MOF. Apart from the free-standing crystals, also MOFs supported on different substrates (poly(acrylonitrile) nanofibers, glass fibers, porous glass and TLC silica-gel) have been prepared and show sensitivity only slightly below that of the free crystals.

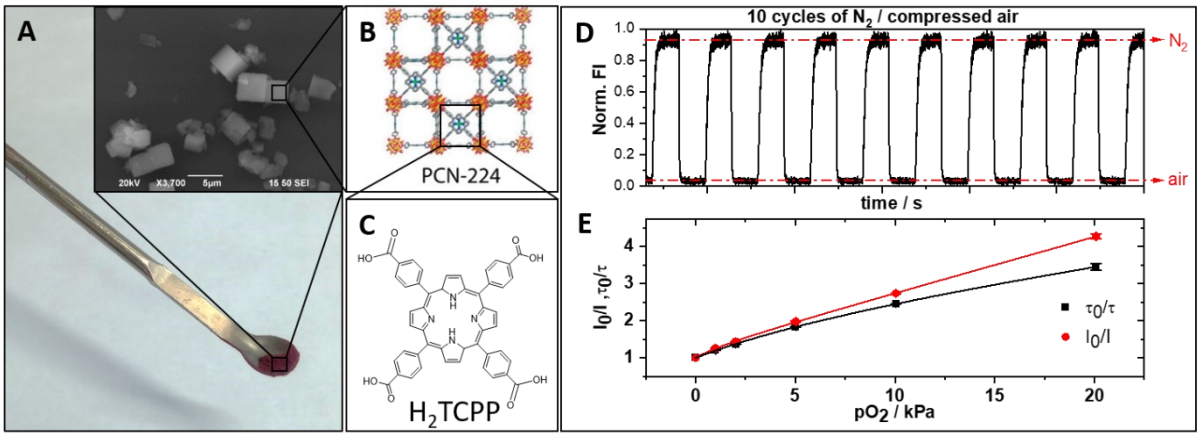

Figure 1. A: Image of the red PCN-224 free powder with a SEM image of single crystals. B: Structure of PCN-224 MOF. C: Structure of tetrakis-(4-carboxyphenyl) porphyrin (H_2TCPP), the organic linker in the PCN-224 MOF. D: Dynamic response of the PCN-224 powder to alteration of gas atmosphere between nitrogen and air. E: Stern Volmer plots for PCN-224 at 25 °C and dry gas atmosphere.

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Exploring MOFs and HOFs for Enzyme Immobilization

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Metal-organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs) belong to a class of extended materials which can be constructed using a modular approach.[1,2] Thus, allowing for precise tuning of porosity and material characteristics. These traits make them promising candidates for enzyme immobilization.[3–5] In addition to protecting the biocatalyst from harsh conditions, they may also increase their long-term stability and enable biocatalyst recycling.[6] Herein, we examine the immobilization of the D-amino acid oxidase (DAAO) from *Trigonopsis variabilis* to create biocomposite materials using zeolitic imidazolate framework-8 (ZIF-8), metal-azolate framework-7 (MAF-7) and a hydrogen-bonded organic framework (CC44).[2,7,8] Furthermore, the assessment of immobilization parameters allows us to gain insight on the interaction between framework material and biocatalyst performance.

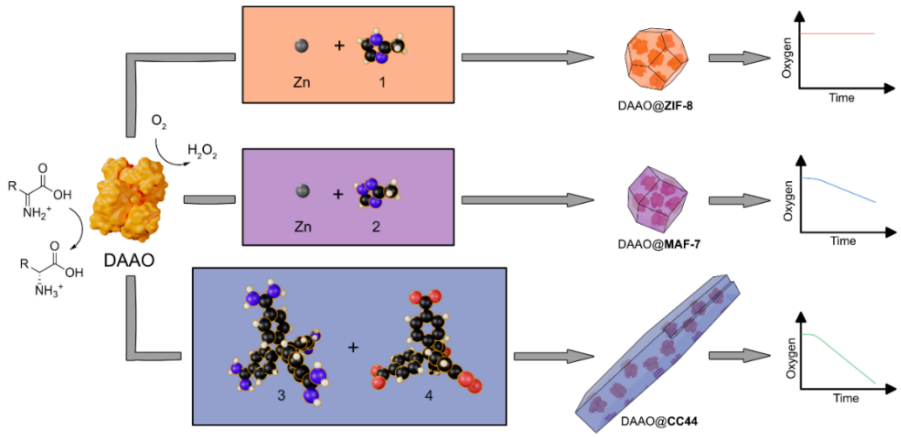

Figure 1. Overview of DAAO immobilization in ZIF-8, MAF-7 and CC44. 1…2-methyl-1*H*-imidazole, 2…3-methyl-1*H*-1,2,4-triazole, 3…(methanetetrayltetrakis(benzene-4,1-diyl))tetrakis(aminomethaniminium), 4…4,4',4",4'"-methanetetrayltetrabenzoate

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Exploring Chanoclavine Synthesis in Ergot Alkaloid Pathway

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Ergot alkaloids constitute a group of indole-derived mycotoxins that are produced in various filamentous fungi. Due to their potential pharmacological activities, the chemical nature of these biomolecules and their biosynthetic routes have been studied for a long time.[1,2]

The biosynthesis of these diverse compounds follows a route via the intermediate chanoclavine-I, which is produced from Me-DMAT through two enzymes, an FAD-dependent (EasE) and a heme-dependent oxidoreductase (EasC) after prenylation via a prenyltransferase (DmaW) (Figure 1). Previous studies on these key enzymes, revealed EasE to be responsible for 1,3-diene formation and EasC the essential enzyme for oxidative ring closure.[3,4] Here we present characterization and optimization trials for implementation of an *in vitro* production platform by reconstitution of the early steps in the pathway.

First characterization of DmaW revealed L-tryptophan and L-abrine (N-methyl-L-tryptophan) to be preferred substrates for prenylation by the prenyltransferase from *A. japonicus*. Site-directed mutagenesis at position Y195 to serine increased the activity towards 5-substituted tryptophan derivative, 5-hydroxy-L-tryptophan. By optimization of conditions successful scale-up of prenylation could be achieved and isolation was performed for proper characterization.

Moreover, a chemo-enzymatic route to the essential 1,4-diene intermediate is desired. By performing two consecutive Wittig reactions and a tryptophan synthase catalyzed reaction the intermediate was successfully synthesized.

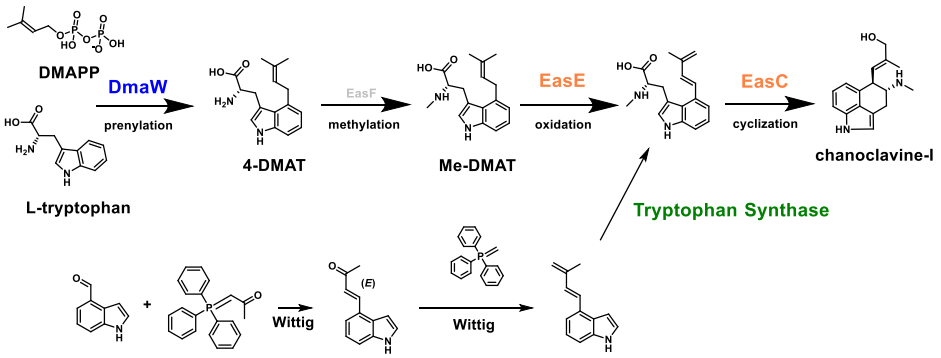

Figure 1. Early steps in the ergot alkaloid pathway and alternative approach to the 1,4-diene intermediate.

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Towards large – Scale Production of 2D Materials

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Two-dimensional (2D) materials have gained worldwide attention in recent years because of their outstanding properties due to their structure and dimensionality. Graphene was the first 2D material that was isolated and studied in 2004 by Andre Geim and Konstantin Novoselov.[1] During the last decade there has been an increasing interest on other 2D materials such as boron nitride (BN),[2] transition metal dichalcogenides (TMDs, such as MoS_2, TiS_2, TaS_2, WS_2 etc.),[3-4] layered metal oxides [5] and many others. However, the large – scale production of these materials still remains a major challenge. A very promising and widely used method is the liquid phase exfoliation (LPE), because it can be scaled up relatively easily.[6-10] Despite it being scalable, the yields of obtained 2D nanosheets vary between 2 – 3 %.[11-13] We investigated the cause of the low yields by examining the LPE production of graphene, boron nitride nanosheets (BNNS) and molybdenum disulfide (MoS_2 NS). Our results show that these low yields are caused by an equilibrium that is formed between the exfoliated nanosheets and the bulk material during the sonication process. By shifting this equilibrium, we were able to upscale the production and increase the yields of graphene, BNNS and MoS_2 NS up to 13%, 26% and 32%, respectively.

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Syntheses of 2,4-functionalized Diphosphapentasilanes as Precursors for low-valent Tin and Germanium Compounds

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In contrast to diphosphanes with carbon backbones, the number of 1,2 diphosphadisilanes is rather small.[1] Diphosphasilanes with longer chain lengths do not exist with the exception of three 1,3-diphosphatrisilanes.[2-3] However, similar to their carbon analogues, diphosphatrisilanes are expected to offer a wide range of uses in organometallic synthesis and as ligands in complex chemistry.
Our main interest is their possible application for the formation of low-valent group 14 compounds, namely diphosphagermylenes and -stannylenes.[4]

The aim of the presented work is the preparation and characterization of 2,4 diphosphapentasilanes, $SiMe_2[Si(SiMe_3)_2PRR']_2$ with R,R' = H, Ph, $SiMe_3$, and R = $SiMe_3$, R' = $Si(SiMe_3)_3$, and $C(SiMe_3)_3$. The reaction behaviour of these silanes is compared to behaviour of related carbon compounds, namely 1,2-diphosphaethanes and 1,3-diphosphapropanes. Experimental work is accompanied by DFT calculations aiding the characterization of these compounds and supporting a better comprehension of the reaction mechanism depending on the substitution pattern on the phosphorus atoms.
Molecular structures obtained by single crystal X-Ray diffraction, where feasible, and DFT calculations show an optimal preorientation of the diphosphapentasilanes regardless of the size and kind of the substituents. This characteristic qualifies them as ideal candidates for the formation of monomeric cyclic diphosphatetrylenes.

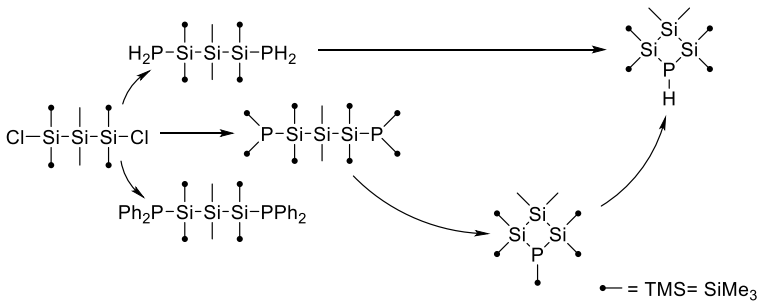

Figure 1. Reaction Pathways

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Determination of the Hydrocarbon Composition in exhaust Gases of renewable Fuels used in internal combustion Engines

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Due to legal requirements the share of renewable fuels in the transport sector must be increased to an equivalent of 14 % of the consumed energy until 2030.[1] This presents a big challenge due to strict sustainability criteria (greenhouse gas savings of at least 70 % compared to conventional fuels when using renewable fuels) which pose high requirements on feedstocks as well as production processes.[2] An additional challenge is caused by different physicochemical properties of many renewable fuels compared to conventional fuels, which are mainly caused by their high oxygen content. These fuels often show different combustion behavior which leads to an altered hydrocarbon composition of their exhaust gases when being burned. Therefore, the exhaust gases of fuels with varying shares of renewable components were investigated via gas-chromatography.

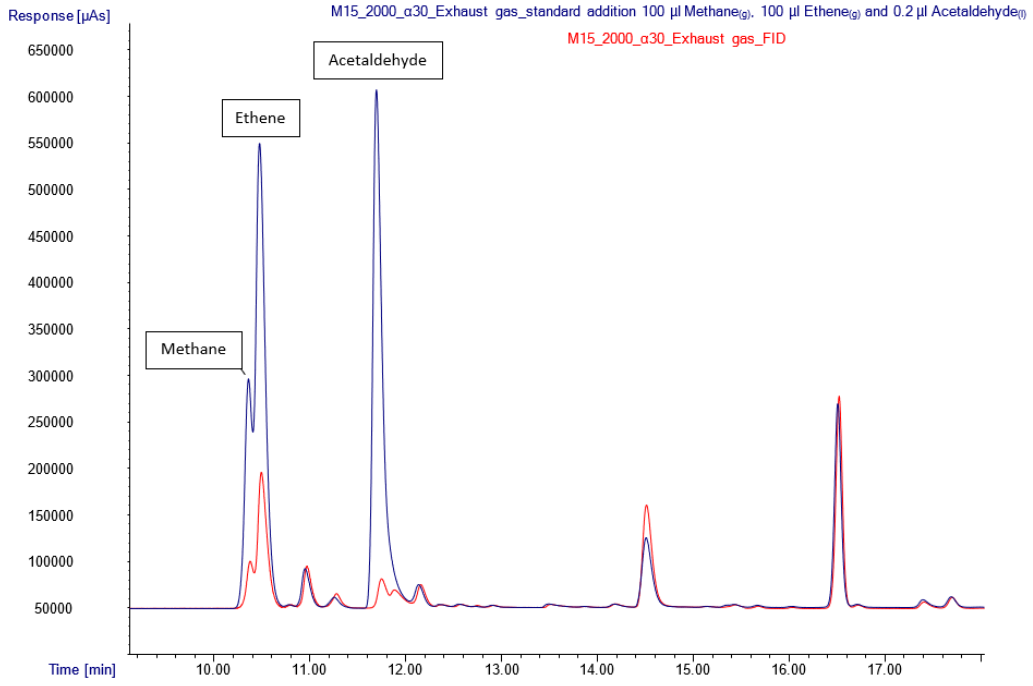

Figure 1. High volatile fraction of hydrocarbons of an exhaust gas when using a blend of 15 vol.-% Methanol in conventional gasoline. Standard addition was performed for selected analytes of interest. The chromatogram of the exhaust gas is overlaid with the chromatogram of the exhaust gas including the added analytes.

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On the electrical Transport Properties in NaSICON-type $Na_3M_2(PO_4)_3$ (M = Fe, Cr)

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NaSICON-type solid electrolytes enable sodium-ion conductivities exceeding 10^{-3} S·cm^{-1}, hence, they are ranked as top candidates for post Li-ion battery technologies. Such high conductivities can be found for NaSICONs with Na contents ≥ 3 parts per formula unit and a mean ionic radius of the M-cations around 0.72 Å. This value corresponds to the ionic radius of $^{[6]}Zr^{4+}$. Similar values are found for $^{[6]}Hf^{4+}$ (0.71 Å) and $^{[6]}Sc^{3+}$ (0.745 Å).[1,2] Compounds with M = $^{[6]}Fe^{3+}$ (0.645 Å) or $^{[6]}Cr^{3+}$ (0.615 Å) seem to behave, however, distinctly different than other NASICON-type materials showing an unexpected high ionic conductivity in combination with a high pre-exponential factor and a high activation energy.[1] It is hypothesized that this could be related to the remaining d-electrons in the valence shell having an impact on the crystal structure and ionic conductivity.[1] To study the origin of this anomaly we synthesized flux-grown $Na_3Fe_2(PO_4)_3$ (NFP) and $Na_3Cr_2(PO_4)_3$ (NCP) single crystals to investigate the interrelation of electrical properties and phase behavior as a function of orientation along [100] and [001] and temperature using electrochemical impedance spectroscopy, single crystal XRD and DSC. Our preliminary data identified a very complex phase behavior for NFP and NCP with up to three order-disorder phase transitions between 350 and 440 K. These are strongly linked to the ionic conductivity mechanism. However, further studies on the electronic contribution to the total conductivity are needed before a conclusive explanation about the anomalous conduction behavior of NFP and NCP can be provided.

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Investigation of the Amavadin Distribution in *Amanita muscaria* with a newly developed HPLC-ICPMS Method

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One of the most famous mushrooms is *Amanita muscaria*, also known as the fly agaric mushroom. With its characteristic red cap and white dots, it can be found in the forests of northern Eurasia. This vanadium (V) accumulator mushroom can easily take up more than 100 mg V/kg dry mass (dm), whereas other mushrooms typically contain less than 0.5 mg V/kg dm.[1] Around half a century ago the chemical form of V in this mushroom was identified as a complex called amavadin,[2] but until now no method is available to investigate this V-compound systematically in other mushrooms species and to prove if this is the only vanadium-complex in *Amanita muscaria.*

Therefore, a new element-selective method was developed by utilizing high performance liquid chromatography (HPLC) coupled to inductively coupled mass spectrometry (ICPMS). For chromatography a strong anion-exchange column in combination with an aqueous mobile phase containing an ammonium citrate buffer and ethylenediaminetetraacetate (EDTA) was used.

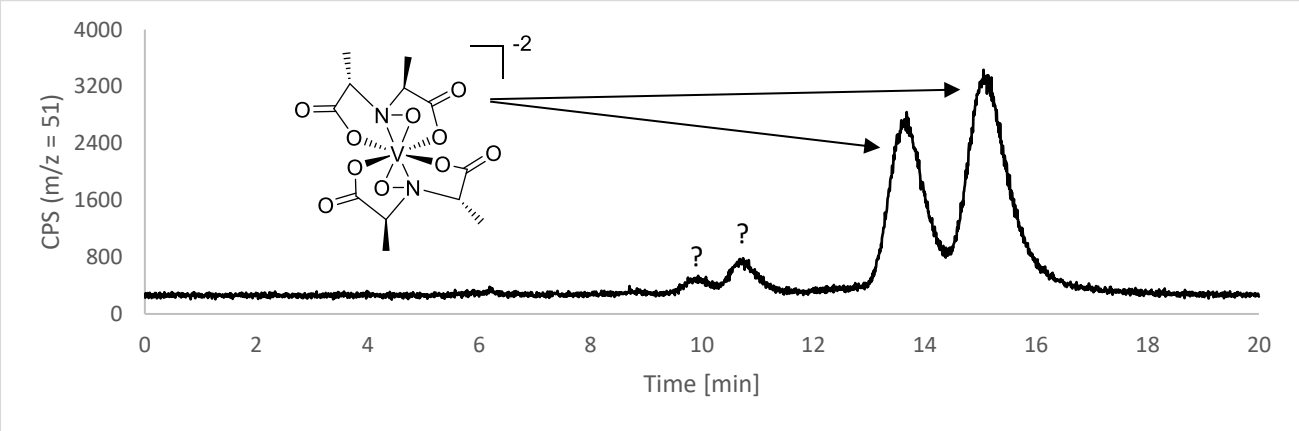

Figure 1 HPLC-ICPMS chromatogram of V monitored @ m/z 51 in an Amanita muscaria gill sample**.**

With the optimized method the extraction efficiency of fruit-body samples was 74 ± 12 % and the two isomers of amavadin eluted in less than 17 minutes. Surprisingly, other vanadium species than amavadin were also detected at significant concentrations (Figure 1). Our results demonstrate that the V-speciation in *Amanita muscaria* is more complex than thought until now. Further investigation of the V uptake, metabolism and distribution[3] of vanadium is required to elucidate the accumulation and role of vanadium in this mushroom.

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Synthesis and Isotopic Labelling of Tilimycin and Tilivalline, Cytotoxic Secondary Metabolites of *Klebsiella Oxytoca*

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In some cases, antibiotic therapy can lead to antibiotic-associated hemorrhagic colitis (AAHC), which is caused by rapid overgrowth of the enteric bacterium *Klebsiella oxytoca*.[1] The pyrrolobenzodiazepine tilivalline (**1**) was the first identified metabolite of *K. oxytoca*, which is secreted into the intestinal lumen causing epithelial apoptosis and leading to AAHC.[2] However, the unexpected cytotoxic activity of a non-tilivalline-producing mutant strain on HeLa cells suggested that *K. oxytoca* might be able to produce another, even more cytotoxic metabolite, which we named tilimycin (**2**). For further studies, we were searching for a synthetic access to tilimycin and its derivative. Starting with 3-hydroxyanthranilic acid, we were able to synthesize the desired compound in a simple three-step procedure. Furthermore, it could be demonstrated that tilimycin is the precursor in the biosynthesis of tilivalline, which is spontaneously formed by a nucleophilic attack of free indole.[3,4] Recently, we synthesized ^{15}N-labelled tilimycin and tilivalline, which successfully have been used as internal standards for simultaneous quantification of both metabolites in complex biological matrices.[5]

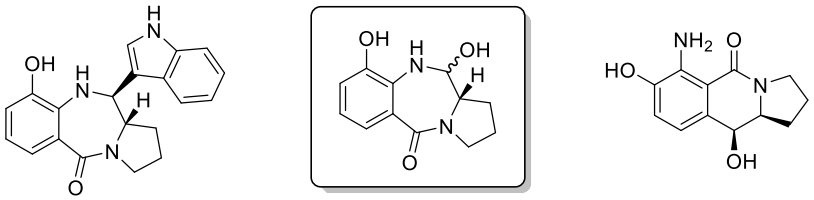

Figure 1. Metabolites of *K. Oxytoca*: Cytotoxic tilivalline (**1**) and tilimycin (**2**); non-cytotoxic culdesacin (**3**).

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Catalytic Active Aminopropyl Tin Compounds

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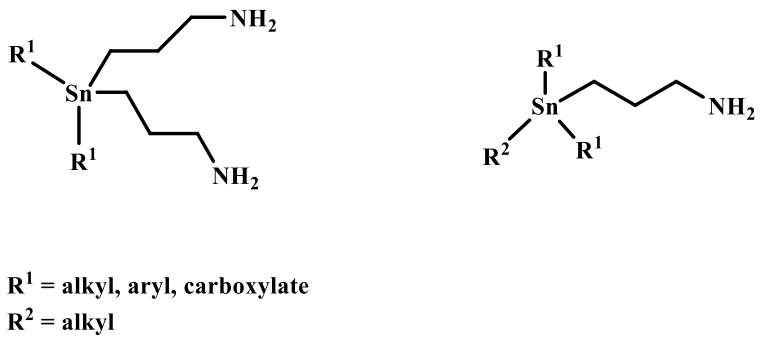
Organotin compounds have been extensively investigated for their catalytic activity in polymer synthesis. The well-established common industrial catalyst is dibutyltin dilaurate (DBTDL). The main problem that occurs by using DBTDL as a catalyst in polyurethane synthesis is the leach out effect of the catalyst from the polymer due to weathering. Resulting in a lack of chemical bonding of the catalyst within the polymer bulk material.
Therefore, our aim is to synthesize organotin derivatives[1,2] which display corresponding catalytic activity as DBTDL, but lack the negative effects associated with their use, by introducing aminopropyl side chains into the catalytically active molecules, with which the catalyst is bound covalently into the Polymer. In this respect we describe the catalytic behavior in model reactions depending of the catalyst structure.



R^1 = alkyl, aryl, carboxylate
R^2 = alkyl

Figure 1. Investigated catalysts structures, differing in structure and number of alkyl, aryl and carboxylate residues.

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Biocatalytic Access to Amides

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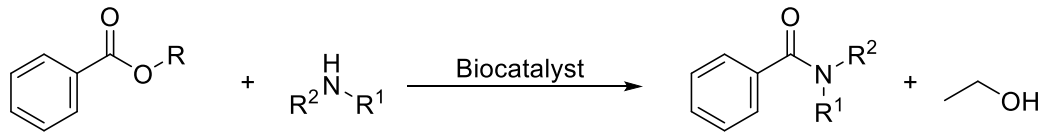
Amide formation is one of the most important reactions in industrial pharmaceutical synthesis.[1] Although the synthetic approaches appear to be simple, they suffer in fact from many drawbacks. The synthesis requires toxic or hazardous reagents to activate the ester or acid component and having a poor atom economy.[2] So far, many strategies to obtain amides have been published, but several problems have not been solved yet.[3,4] Challenges are for example the direct transformation of carboxylic acids or esters with amines. Known chemical strategies require the activation of the substrate via $SOCl_2$ leading to a reactive acyl chloride which reacts with the amine. The reaction suffers from poor atom economy, danger and racemization of the α-center in the acid. For these challenges biocatalysis may provide a solution, especially because biocatalysis is known for using harmless reagents and working under mild conditions.



R= Me or Et

Figure 1. Amide formation from esters in organic solvent by a hydrolase in a single step.

Our aim is to identify a biocatalytic access to amide formation, especially by the help of hydrolases starting from bulky acyl donors. Screening several hydrolases, one promising candidate has been discovered so far, the lipase from *Sphingomonas sp.* HXN-200 also known as SpL.[5] The lipase was discovered and expressed by Li and co-workers in 2018. SpL shows high activity in aminolysis towards various acid and esters with amines in organic solvents. New substrates have been tested and functional studies on this protein shall be conducted to understand its reaction behavior.

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Porous Materials under high hydrostatic Pressure

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Luminescence based optical chemical sensors for gasses rely on a matrix material, that is highly permeable for gasses.[1] Such materials typically include porous silicas and glasses as well as polysilsesquioxanes.[2,3] Recently metal organic frameworks (MOF), another class of porous materials, have gained increasing attention. Due to their tuneable pore size and chemistry they can be tailored to selectively adsorb certain gasses.[4] One field of application where the versatility of optical sensors poses a great advantage is deep sea measurements.[5] Until now, there are no studies that investigate the stability of porous materials under high hydrostatic pressures as would be required for marine applications at great depths.

In this study, different porous materials (MOFs, poly(silsesquioxanes), silica gels) have been equipped with an oxygen indicator dye and dispersed in different hydrophobic polymeric matrices. The stability of the porous host material under high hydrostatic pressures has been investigated in a specially designed pressure chamber (Fig. 1). This was achieved via measurement of the luminescence of the O2 indicator during the pressurization and depressurization process. It was found that most of the materials survive exposure to high hydrostatic pressure, however the heightened pressure leads to material specific, systematic errors that need to be corrected for when deploying them in the field.

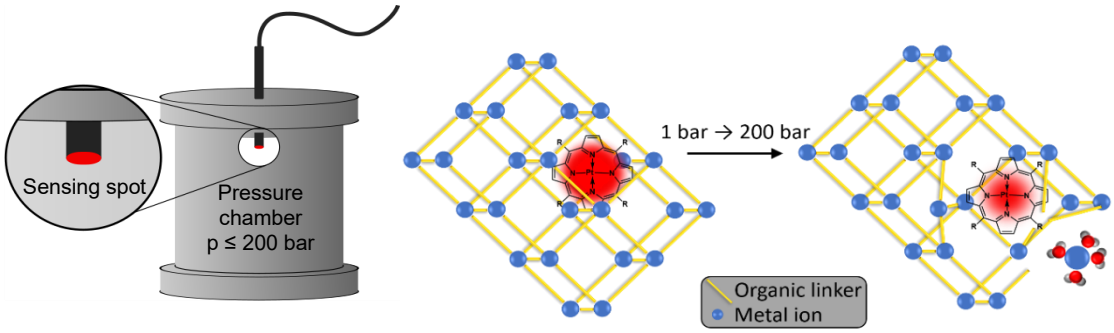

Figure 1. Left: Schematic representation of the pressure chamber; Right: Possible lattice distortion of a MOF due to high pressure causing change in luminescence properties of dye molecule

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Photochemical Chloramination of Olefins in continuous Flow

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A chloramination reaction adds an amine moiety and a chlorine atom across an olefin, yielding β-chloro amines in an atom-economical manner. These products are important for applications including medicinal chemistry. Thus far, only limited examples of this reaction exist, generally using metal catalysts. The photochemical transformations have been restricted to *N*-chlorosulfonamides[1] in presence of an Ir photoredox catalyst, until last year's publication by the Leonori group.[2] There, they demonstrated the chlorination of dialkyl amines using *N*-chlorosuccinimide (NCS), followed by photochemical chloramination of olefins under photoredox conditions, employing $Ru(bpy)_3$ as photoredox catalyst. Although they demonstrate on their model substrate, that the reaction is possible under continuous flow conditions, they rely on prior batch formation of the chloramine with NCS (low atom economy), the use of chlorinated solvents (environmental issue), trifluoroacetic acid (TFA, more expensive) and a complex protocol to perform the reaction (poor scalability).

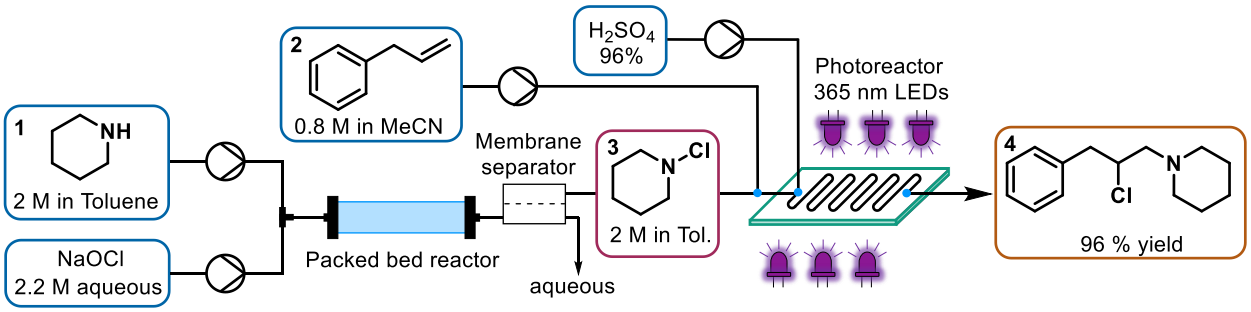

Figure 1. Schematic representation of the experimental chloramination setup: Aqueous bleach is mixed with an amine in a packed bed reactor. After separation of the organic stream using membrane technology, the *N*-chloramine is combined with an olefin and sulfuric acid in the photoreactor, where upon 365 nm irradiation, the desired β-chloro amine is formed.

With our strong interest in scalable photochemistry toward manufacturing of active pharmaceutical ingredients (APIs), we opted to develop a new procedure, to overcome these issues. Due to the unstable nature of chloramines, it was clear that a fully telescoped process, omitting the isolation of this species, would be advantageous. We established the formation of the *N*-chloramine by reacting aqueous bleach, prepared from $NaOCl{\cdot}5H_2O$, with the amine (**1**) dissolved in toluene. Efficient mixing of the biphasic system in a packed bed reactor and subsequent phase separation using membrane technology yields a 2 M solution of the chloramine (**3**) in toluene.
For the subsequent photochemical transformation, we confirmed that protonation of the chloramine is necessary, but sulfuric acid can replace TFA. The reaction proceeds efficiently in acetonitrile, replacing chlorinated solvent. Interestingly, the radical aminochlorination reaction does not require photoredox catalysis. Direct irradiation of the chloramine with 365 nm light (or triplet sensitization by an organic dye using visible light) is sufficient to generate the amino radical. The β-chloro amine (**4**) could be isolated in 96% yield translating to a productivity of 19 g/h in the 2.8 mL lab scale photoreactor. Reaction development toward a scalable and widely applicable process will be discussed.

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Honeycomb-Structured Metal Sulfide Thin Films via a Nanosphere Lithography Method

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The metal sulfides show an increased interest and they have been employed in a broad area of applications, including solar cells, light-emitting diodes, lithium-ion batteries and other.[1] In literature, there are many reports for the synthesis, characterization and application of metal sulfide films, but few deal with structured metal sulfide films. The main route towards structured metal sulfides employs templates. Two are the main template-assisted methods, the soft-templating with directing agents, such as lyotropic liquid crystalline templates,[2] and the hard-templating with templates such as mesoporous silica.[3] Nanosphere lithography is a technique that is classified in the soft-templating technique and utilizes monodispersed colloidal particles, such as polystyrene microspheres (PS-MS), as template for the formation of periodically ordered arrays.[4]
Our research is focused on the novel synthesis of honeycombed-structured metal sulfide films via the nanosphere lithography technique. As shown in Figure 1, the process consists of three steps, the PS-MS template formation, the metal sulfide infiltration and formation and finally, the template removal. The properties and features of films are studied via several techniques such as Profilometry, FT-IR spectroscopy, X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM).

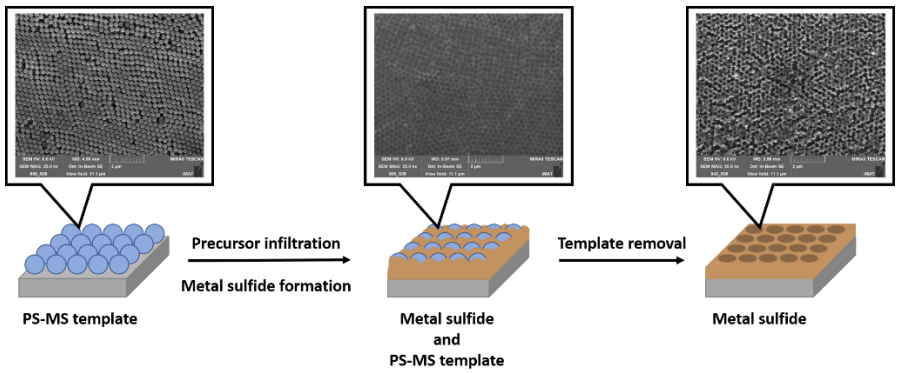

Figure 1. Preparation process including SEM images of the $CuInS_2$ example for the formation of highly structured porous metal sulfide with the use of PS-MS template.

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Hydrocolloidal Qualities of Xanthan: A Handbook for a Microbially Produced Commodity

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Xanthan is a material that in many ways can be considered a model substance for molecular level tailored materials: twisting a cellulose-type backbone from basically beta-sheet conformation into a helical conformation by introducing charged tri-saccharide branches. Additionally, xanthan is a microbial exo-polysaccharide, and hence, produced on micro-scale by bacteria open for tuning by specific breeding or genetic modifications of these organisms. In aqueous media xanthan forms hydrocolloidal systems and the focus of the Doctoral Thesis is screening of aqueous xanthan-systems on polymer- and hydrocolloidal characteristics to correlate molecular-level and hydrocolloidal characteristics with controlled material performance.[1]

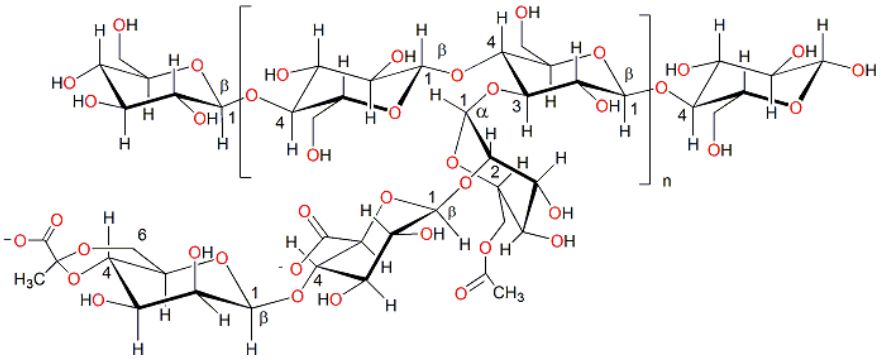

Figure 1. Xanthan repeating unit: β (1→4) D-glucoses with α (1→3) linked triose-branches consisting of a partially (60-70%) C6-acetylated mannose β (1→2) connected glucuronic acid and another optionally (30-40%) C4-pyruvate derivatized β (1→4) linked mannose.

Xanthan shows up with the pronounced capability as a viscosity control agent in aqueous media and therefore is used in a range of food (E415) and non-food (CAS 11138-66-2) applications. Stability/Instability of xanthan/water-modifier-systems (XWM-systems) is a key issue in such applications and therefore, response capability and collapsing conditions due to applied stress will be investigated by rheology/viscosimetry. With respect to polymer characteristics such as distributions of dimensions, conformation, diffusive and electrokinetic mobility investigations by separation techniques, photon-correlation spectroscopy and zeta-potential are supposed to be performed. Surface/Interface-energy in interaction of aqueous xanthan systems with selected solid surfaces/interfaces will be determined by contact angle. To obtain information on the kind of resulting associates when xanthan polymers aggregate to form colloidal objects calorimetric data will be correlated with apparent degree of polymerization distributions obtained at various conditions by AF4 (asymmetric flow field flow fractionation) and SEC (size exclusion chromatography) for the heterogeneous and homogeneous partitions of the aqueous xanthan-system.[2]

References:

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Bright, Stable Fluorene- and Carbazole-fused Aza-BODIPYs Absorbing/Emitting in the Near-Infrared Spectral Region

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BODIPY dyes have been studied extensively in the past decades due to their outstanding properties, including sharp absorption and fluorescence bands, high fluorescence quantum yields and molar absorption coefficients, and excellent photostability.[1] Structurally related aza-BODIPY dyes possess a nitrogen atom in the *meso*-position and are characterized by bathochromically shifted absorption and emission spectra. Most of the aza-BODIPY derivatives have four phenyl groups directly substituted on the 1,3,5 and 7 position of the core and the simplest of them, called tetraphenyl aza-BODIPY (**TPAB**, see Figure 1), has its absorption and emission maxima below 700 nm. However, for medical and biological applications, absorption and emission in the near-infrared (NIR) spectral region is preferred due to lowest autoabsorption and autofluorescence of biomolecules (optical window), deep penetration of the NIR light and significant reduction of light scattering. Common strategies to obtain NIR absorbing aza-BODIPYs include: (i) introduction of donor groups or (ii) π-extension with large aromatic substituents either only partly conjugated or fully condensed.
Here we present three new aza-BODIPY dyes, fused with fluorene or carbazole moieties. The spectroscopic studies of the aza-BODIPYs showed that absorption and emission maxima were bathochromically shifted up to 139 nm, relative to the parent **TPAB**. Moreover, these dyes exhibit strong absorption (absorption coefficients up to 237 000 $M^{-1}cm^{-1}$), emission in the near-infrared range (741-800 nm) with exceptional high quantum yields (up to 0.66) and excellent photostability. Owing to their outstanding properties, the new aza-BODIPY dyes belong to the brightest NIR dyes reported and can represent an excellent platform for further exploration in biomedical and material research. A pH indicator containing only one fused carbazole unit is also prepared and in terms of photophysical properties occupies an intermediate position between the classical tetraphenyl aza-BODIPYs and the new fused compounds. Furthermore, a proof-of-concept study shows that the synthesized aza-BODIPYs have potential in material-based application as anti-counterfeiting dyes.

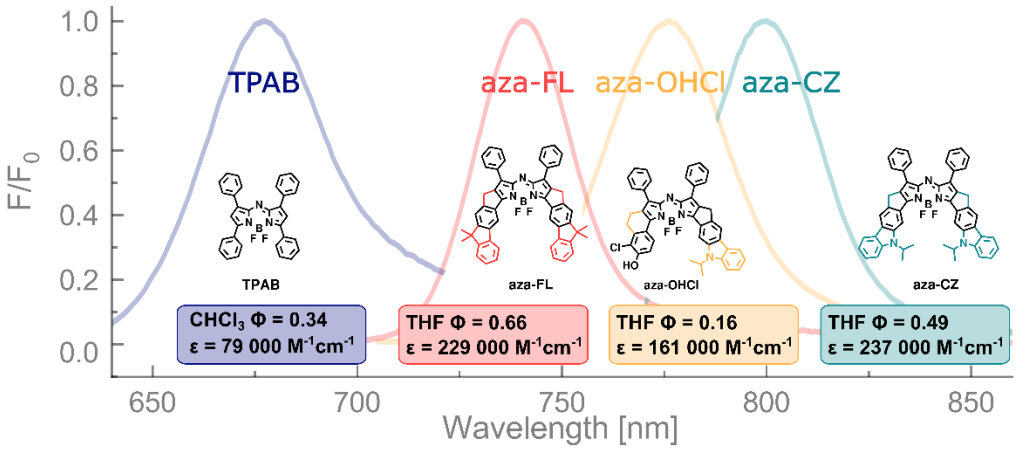

Figure 1. Emission spectra, photophysical properties and chemical structure of the synthesized aza-BODIPYs **aza-FL**, **aza-OHCl** and **aza-CZ** compared to the parent **TPAB**.

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Chemical Generators for the Utilization of BDMS and Performic Acid in Continuous Flow

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The concept of chemical generators describes the in-situ, on-demand generation and consumption of highly reactive reagents. The use of such highly reactive chemicals often enables the use of more direct and atom-economic routes, which are often underutilized because of safety concerns. Generating these highly reactive reagents in continuous flow mode makes the safe handling and utilization of these reagents possible.[1]

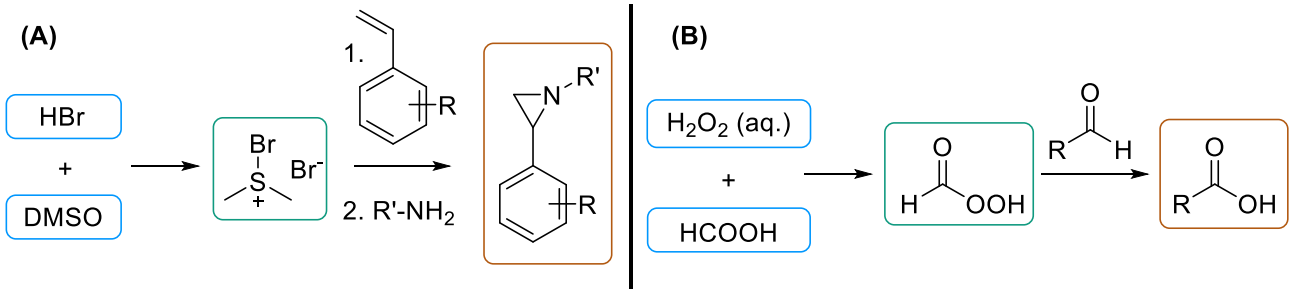

Figure 1. (A): Chemical generator for the generation of bromodimethylsulfonium bromide (BDMS) and the consecutive reaction of styrenes to aziridines. (B): Performic acid generator for the oxidation of aldehydes.

Bromodimethylsulfonium bromide (BDMS) is a versatile reagent which is usually prepared from Br_2 and dimethyl sulfide. The compound can also be generated in-situ by mixing HBr and DMSO. We managed to establish a continuous flow BDMS generator, where HBr was mixed with DMSO in presence of a styrene to generate the corresponding 1,2-bromodimethylsulfonium bromides.[2] Finally, these intermediates were combined with primary amines to generate 2-aryl aziridines. This concept was used to synthesize a small scope of 2-aryl aziridines in synthetically useful yields after total residence times as low as 7 minutes. The whole system was set up using only simple PFA tubing as residence time units.

We further explored the chemical generator concept for the formation of peroxy carboxylic acids from hydrogen peroxide and the corresponding carboxylic acids. The in-situ generation of performic acid was previously explored in our group for the hydroxylation of alkaloids.[3] Despite the unstable nature of peracids they can be handled safely under continuous flow conditions, even at elevated temperatures.

We investigated the in-situ generation of performic acid and peracetic acid for the oxidation of aldehydes to the corresponding carboxylic acids. The reaction proofed to be very efficient for a number of aliphatic and aromatic aldehydes giving almost quantitative yields in the best cases. Additionally, the reaction was shown to be very sustainable with E-Factors as low as 5.2.

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Reaction of Cyclic Silanides with Ketones

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The Sila-Peterson type reaction established by Oehme, Apeloig and Ishikawa had a huge impact on the synthesis of new silenes.[1] With only a few exceptions most stable silenes described in the literature so far are acyclic molecules. In this contribution we investigated the Sila-Peterson reaction of the alkali metal substituted cyclohexasilanes (1a, M = Li; 1b, M = K)[2] with the primary aim to synthesize Apeloig-Ishikawa-Oehme-type silenes with exocyclic structures. We observed that the obtained products strongly depend on the used ketone component.[3] Treatment of 1b with the non-aromatic and non enolizable 2-adamantanone lead to the moderately stable silene 2 which could be characterized by NMR and UV spectroscopy as well as by trapping reactions. The reaction of 1b with aromatic ketones also follows a Sila-Peterson type mechanism. However, instead of the corresponding silenes, carbanionic species such as 3, 4 and 5 were obtained.

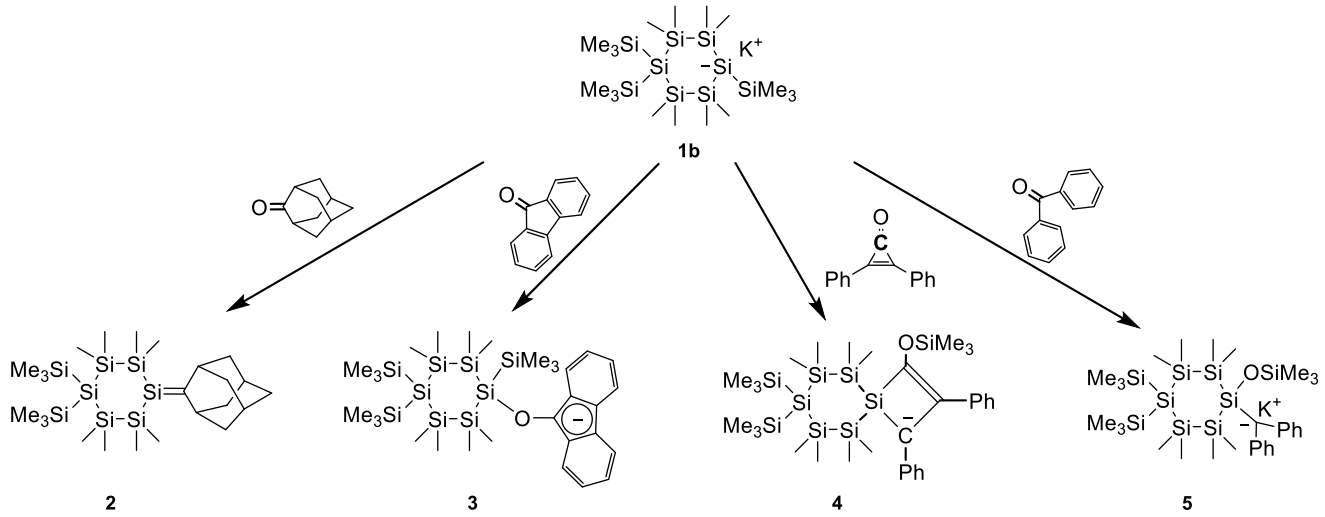

Figure 1. Synthesis of a Cyclic Silanide with different Ketones

References:

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The Influence of Co-Solvents on Biocatalyst Stability

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After establishing a biotransformation on laboratory scale the addition of organic co-solvent during process intensification might be needed.[1] A poor substrate solubility or needs to simplify downstream processing might require the solvent as additive. Consequently, the biocatalyst is exposed to organic solvents which might reduce its activity or even lead to a complete inactivation. Why one enzyme can tolerate a co-solvent while another one loses its activity entirely is not understood in detail, yet. We aim to decipher the solvent resistance of different biocatalysts towards different solvents and shed light onto enzyme and solvent features that define the (in-)stability. To achieve this, we combine experimental evaluation of stability with computational methods. In order to have a good data set for the computational analysis we have identified a representative set of ene-reductases for which solvent stability was assessed.[2] We have measured the thermal stability in the presence of co-solvents and the influence of the co-solvents on the initial activity. The addition of the tested organic solvents led to a decrease of the melting temperature in all cases. The degree of destabilization seems to be dependent on the solvent type and concentration while the initial activity under the same conditions behaves different. In some cases, the addition of the co-solvent led to an increase in the initial activity while it led to a decrease for other ene-reductases or in combination with other co-solvents. Thus, a thermal destabilization does not necessarily go together with a reduction of the initial activity. This variability within the experimental stability data is a good starting point for further computational analysis. The detailed analysis of this data set will give evidence on properties of solvent and enzyme that determine stability or instability. This opens possibilities to optimize the tolerance of enzymes towards solvents.

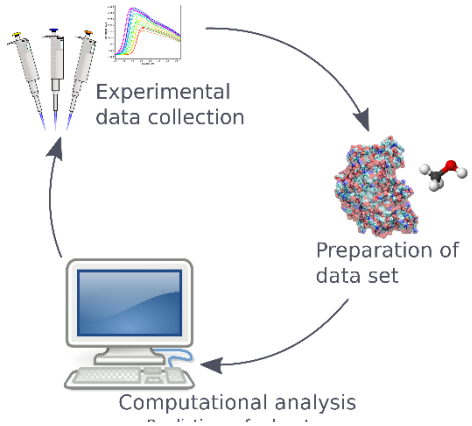

Figure 2. Strategy of stability analysis.

Acknowledgement: BASF SE

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Thermodynamics and electrical Properties of Spinel-Structure NTC thin Films fabricated by chemical Solution Deposition

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Negative temperature coefficient (NTC) thermistors are fundamental components for temperature sensing in a broad variety of applications. The majority of commercial NTC thermistors available are fabricated by traditional powder processing routes. Thin films offer a route to further device miniaturization. In addition, due to their unique properties, they provide a different perspective to gain a more detailed insight into the charge transport and degradation mechanisms of NTC materials.

Nickel-manganite and nickel-cobalt-manganite thin films were prepared by chemical solution deposition from nitrate and acetate precursors on polished alumina and oxidized silicon substrates. The morphology, phase formation, and electrical properties of the films were investigated by variation of crystallization temperature, atmosphere during cooling and film thickness. The electrically conductive spinel phase was formed as a main phase independent of processing conditions and all fabricated thin films exhibited NTCR characteristics. Special focus was put on the investigation of the degradation of the NTC thin films which leads to a drift of the electrical resistance with time. It was found that cooling in reducing atmosphere favors the partial decomposition of the spinel phase, but it also reduces the resistance drift of the samples. From this finding it can be deduced that an increased oxygen vacancy concentration from the redox reaction decreases cation vacancy concentration via Schottky equilibrium. This supports the assumption that cation redistribution by a cation vacancy diffusion mechanism is the relevant mechanism of resistance drift in such thin films.

Exploring the Importance of the second Coordination Sphere in Acetylene Hydratase

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Our group has been heavily invested in modelling the active site of acetylene hydratase (AH), a W-dependent enzyme naturally occurring in *Pelobacer acetylenicus*. AH is employed in the bacterium to convert acetylene into acetaldehyde *via* hydration of the triple bond. In spite of all the effort put into the development of a bioinspired acetylene hydration catalyst based on tungsten, no functional system has been reported in literature so far.[1,2] The group of Kroneck *et al* investigated the importance of selected amino acids located in close proximity to the W-center in the enzyme.[3] Their results suggest a carboxylate residue in the second coordination sphere is necessary for enzyme activity. Based on these results I am exploring the possibility to introduce a second coordination sphere tethered to the ligand coordinated to W.

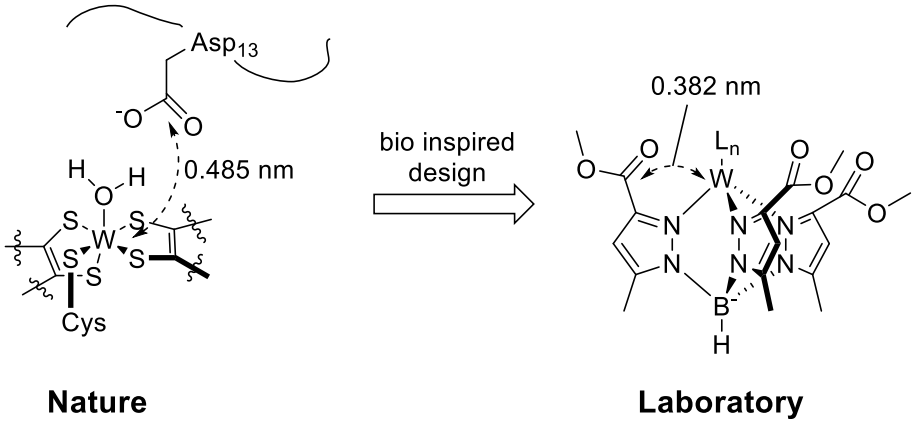

Figure 1. Model W complexes inspired by the tungsten-carboxylate distance in acetylene hydratase.

The introduction of a second coordination sphere might enable us to successfully carry out a W-coordination complex catalyzed hydration of acetylene and other alkynes.

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The Role of SiO_2 in semiconducting $BaTiO_3$-based Ceramics: Extension of the Jonker Model and Effect on the electrical Properties

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$BaTiO_3$-based ceramics with positive temperature coefficient of resistance (PTCR) recently gained in significance due to their application as cabin heating elements in electrical vehicles. [1] Although used as a sintering aid in $BaTiO_3$ ceramics for decades, the effect of SiO_2 on electrical properties as well as the underlying physical mechanisms have not been investigated in detail. [2,3] In this work, we systematically study the influence of SiO_2 on PTCR properties, but also on the resistance development at temperatures below the PTC regime, which has been hardly ever given attention to so far. Using capacitance-voltage measurements, we determine temperature dependent grain boundary potential barrier parameters. By combining these results with x-ray diffraction measurements and resistance-temperature properties, we propose a new model describing the resistance evolution throughout the whole temperature range from room-temperature up to the PTCR regime. Further, we show that electrical field strength increases with higher SiO_2 content, accompanied by a reduction in voltage sensitivity of resistance.

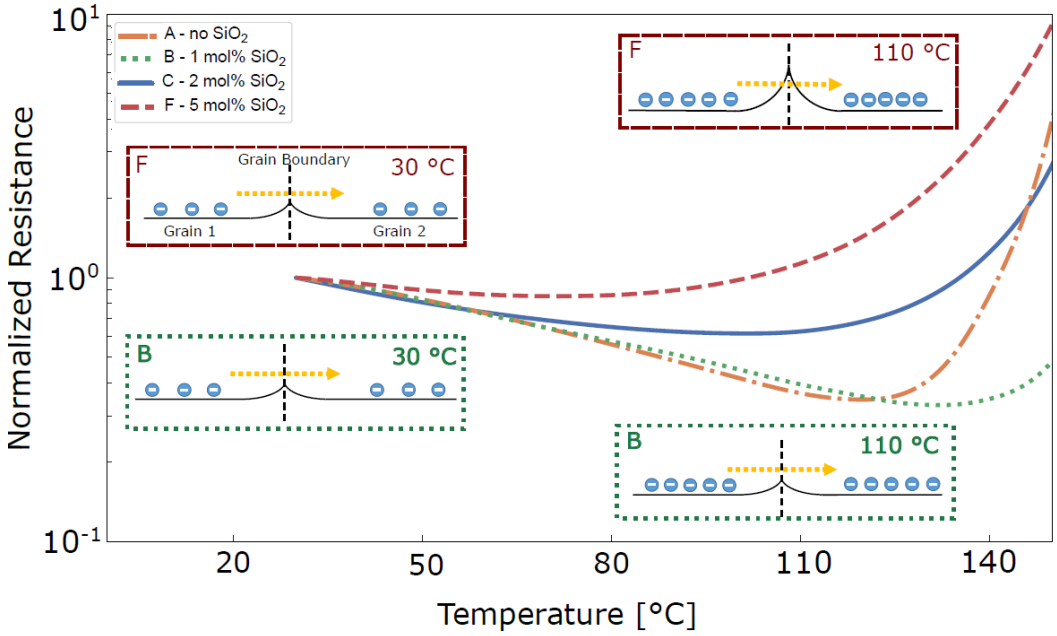

Figure 1. Resistance-temperature characteristics of $BaTiO_3$-based ceramics with varying SiO_2-content. Insets schematically show the temperature evolution of grain boundary potential barriers for the two extreme samples B and F.

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Surface Characterisation and the Effects of wet Chemistry on GaN Semiconductors

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The technology evolved fast with the development of the semiconductors. For many years, silicon has been used as single element semiconductors but the development of new technologies (E-mobility, high-power devices, etc.) require semiconductors with a higher bandgap and better electron mobility than silicon can provide. In the recent years another class of semiconductors started to grow beside the silicon semiconductor. Now a combination of elements of the third and fifth period opened new ways to form semiconductors with a high bandgap which are very promising to fulfill the needs of the new technologies and the change in the energy transmission.[3]

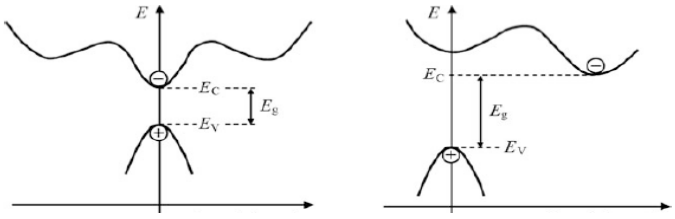

Figure 3 Difference between direct (left) and indirect (right) semiconductor with the dependency of the impulse [1]

Gallium nitride is one of the new 3/5 semiconductors. Whereas silicon is an indirect semiconductor with a quite small bandgap of 1,1 eV, gallium nitride is a direct semiconductor with a high bandgap of 3,4 eV. This difference concerning the bandgap and the change from an indirect to a direct semiconductor now gives new fields of application. In direct semiconductors the electron can be excited directly into the conduction band leaving a hole in the valence band without changing its impulses. This change of the impuls needs energy so the indirect semiconductor cannot be as effetive as the direct semiconductor.[1]
But the gallium nitride semiconductor is coming with new challenges. Are state of the art processes from the silicon semiconductor production working for gallium nitride? How are different wet chemistry agents used for the different processes effecting the surface, the structure and the defects on the surface? These questions are the main aspect of this dissertation, to create fundamental knowledge about how the chemistry effects the upper layers of the semiconductor and how the impact of the chemistry may result in a change of the device behaviour in the end of the process.

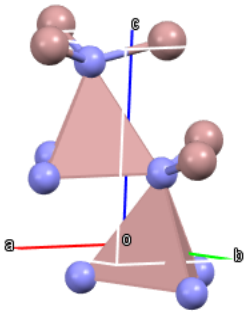

Figure 4 GaN unit cell, designed with Mercury

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Synthesis and Characterization of Group 14 Photoinitiators

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Photoinduced free radical polymerization is an important method for a variety of industrial processes such as microelectronics, coatings, adhesives, inks, microlithography, optics, medicine, 3D object manufacturing and many more. In this process, a liquid monomer or a soft film is easily converted into a solid material when exposed to light. The photoinitiator, labelled A-B in Figure 1, is homolytically cleaved by light, visible or UV, generating radicals. This leads to the addition of monomers, which in turn leads to the formation of a polymer through further propagation. For an efficient photopolymerization reaction, a photoinitiator system, a polymerizable medium and a light source must be compatible. The photoinitiator is particularly important as it absorbs the light, converts the energy into reactive species and starts the reaction.[1]

Figure 1. General reaction scheme of free radical photopolymerization

In collaboration with Evonik Creavis GmbH, the synthesis and characterization of new group 14 photoinitiators for photoinduced free radical polymerization will be investigated in the course of this dissertation. The declared aim of this project is to synthesize a suitable photoinitiator that meets today's high requirements, such as low to no toxicity of the photoinitiator itself and the photoproducts formed, good storage stability, high efficiencies, good photobleaching, etc. Once promising compounds are prepared and fully characterized, they will be tested for their photoreactivity. Since the entire project is confidential, the planned synthesis route and the target molecules cannot be disclosed.

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Activity-based Protein Profiling of Oxidoreductases

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Activity-based Protein Profiling (ABPP) represents an intriguing method for the identification and evaluation of target proteins in its active state.[1] In this specific case, oxidoreductases (e.g. ALDH2) should be addressed. For this purpose, small molecule probes, carrying an iodonium warhead and a linker (e.g. equipped with an azide) for the biorthogonal reporter tag ligation (e.g. affinity tag, fluorescent tag), are synthesized. These compounds should then be tested in ABPP experiments with various enzymes and proteins and will hopefully add a new class of probes to the rather limited set of ABPP probes that have been developed to investigate oxidoreductases.[2]

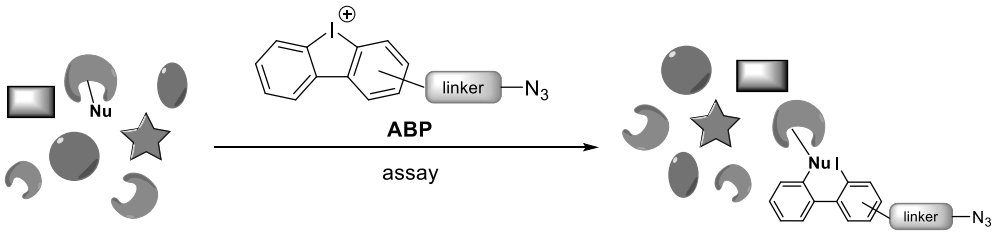

Figure 1. Concept for ABPP labeling with an activity-based iodonium probe.

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Synthesis and Characterization of Group 14 Nanoparticles

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Hydrides of higher group 14 elements are often highly reactive molecules that undergo dehydrogenative coupling reactions. Depending on the degree of hydrogenation, as well as the other substituents, this leads to the formation of dimers, oligomers or three-dimensional polymeric nanomaterials. These materials present new avenues for potential energy storage and conversion (Sn) and optoelectronic (Ge) applications.
Previous research in our group showed that the size and morphology of tin nanoparticles can be controlled *via* the reaction conditions resulting in materials with varying properties.[1-3] Further characterization efforts utilizing impedance spectroscopy and TEM will complement the existing research over the course of this dissertation. However, the analysis of these materials is severely limited by their lack of solubility, and their low stability, preventing common characterization techniques from being used.
In contrast to their tin counterparts, the corresponding germanium nanoparticles can be dissolved in common solvents such as THF,[4] allowing for full characterization of these polymeric materials with applicable analytical techniques such as NMR, GPC, SEM, EDX, TEM, SAXS, WAXS and MALDI-TOF.
The optimized preparation and characterization of novel higher group 14 metal based materials and evaluation of their potential applications will thus be the goal of this dissertation.

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Single Electron Transfer (SET) Reactions of Acyl Group 14 Compounds

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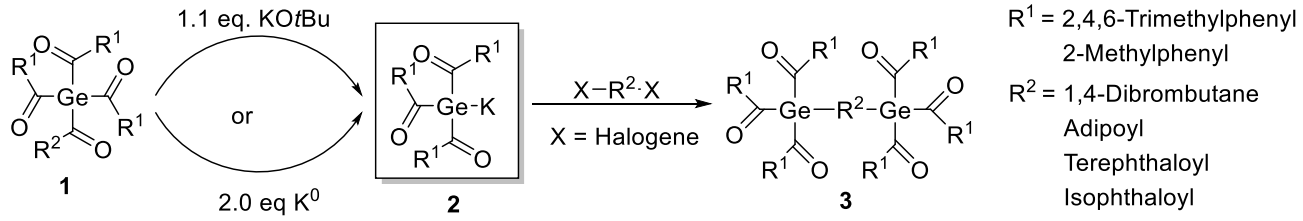
Due to their outstanding photochemical properties, germanium-based photoinitiators are well established on the market. High addition rates to the monomer, high absorption intensities together with a low toxicity predestines acylgermanes as ideal photoinitiator for medical purposes, as well as for various other applications. Recent research in this field revealed their superior reactivity upon reduction with potassium *tert*-butoxide (KO*t*Bu).[1,2] As explored by Murphy et al.,[3] this type of reaction involves a single electron transfer triggered by the addition of a base. In the case of acylgermanes, the compounds obtained represent highly reactive precursors for further functionalization.



Scheme 1
Reduction of a Tetraacylgermane with KO*t*Bu or K^0 with further functionalization

The aim of this PhD thesis is a detailed investigation of photo-induced and ground-state electron transfer reactions. Herein, the focus lies on the characterization and functionalization of group-14 acyl-derivatives. The research strategy itself includes a careful examination of synthetic and spectroscopic as well as mechanistic aspects implying the well-established collaboration between the Gescheidt and the Haas group

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Investigation on hybrid Devices comprising organic Solar Cells and alkali ion Battery Materials

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The concept of combining an energy harvesting and an electrochemical energy storage component into an integrated compact device exhibits significant advantages: besides the space-saving aspect, a device of this kind could not only find its application in small self-powering sensors, but also serve as a stable additional power supply on larger scales.[1]

This work will be concentrating on the development of a fully operating photo-rechargeable hybrid system coupling a single-junction organic solar cell with a low-voltage alkali ion battery.

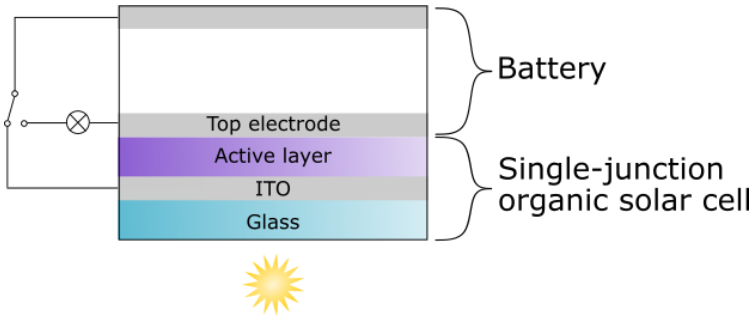

Figure 1. Schematic representation of the structure of an integrated photo-rechargeable hybrid device, where the battery is installed on top of the PV module. The top electrode of the solar cell represents the contact point between the two components.

The fabrication process reveals structural challenges that need to be addressed.
First, the material blend selected for the photovoltaic module needs to provide high voltages (> 1.3 V), to allow the charge of the low-voltage battery. Similar performances should be reached also after increasing the solar-cell active area from 0.09 cm^2 up to 1 cm^2. Scaling up the area is a fundamental step for the assembly of the hybrid device, since it allows to contact the battery with the top electrode of the solar cell. Additionally, the compatibility of the top-electrode material with the battery represents a crucial point. The presence of chemical interactions between the two parts would degrade the whole system and reduce its lifetime.

Finally, the hybrid system should be able to provide the needed energy supply on demand, i.e., guarantee a good reliability. Therefore, a detailed investigation of the stability of the assembled device proves to be of great importance. Referring to a previous work of Sebastian Höfler,[2] the current-voltage response will be tested under illumination (charging) and discharging conditions, as well as under different irradiances. Repeated surveys of the device performance will give relevant information about its stability over longer periods of time.

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Anisotropic etching of Copper via corrosion Inhibition

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Metallic copper was first introduced as an interconnect metallization material for semiconductor device processing in 1997, the change from aluminum required significant adaptations in processing techniques. Since then the so-called scaling of devices has been continuously progressing, with the number of interconnect layers rising rapidly. To achieve the optimum electron conductivity within the copper lines and fitting the form factors given by the device design rules, electrochemical deposition of Cu ("dual-damascene plating") has been found to be the enabling deposition technology. Still after so many years of copper deposition learning for nano-scale dimensions, significant challenges still exist especially related to ever more stringent requirements on the material e.g., deposition with better uniformity, higher conformality within small device features, etc.[1]
On the other hand, also the controlled removal of copper has become a more and more critical process steps to build these devices. Wet chemical etching is the process of choice when working with copper since copper cannot be effectively etched by gas/plasma-based processes, as no useable, highly volatile species are formed by copper. However, wet chemical etching processes are by default isotropic. With the scaling of device features further down into the nano scale level, anisotropic wet chemical etching is a much sought-after process, as it would simplify many processing sequences.[2] Therefore, in this work we will focus on investigating the use of localized corrosion inhibition and directed light in combination with various chemical environments (pH, ionic activity, oxidizing strength, …) to achieve anisotropic etching profiles.

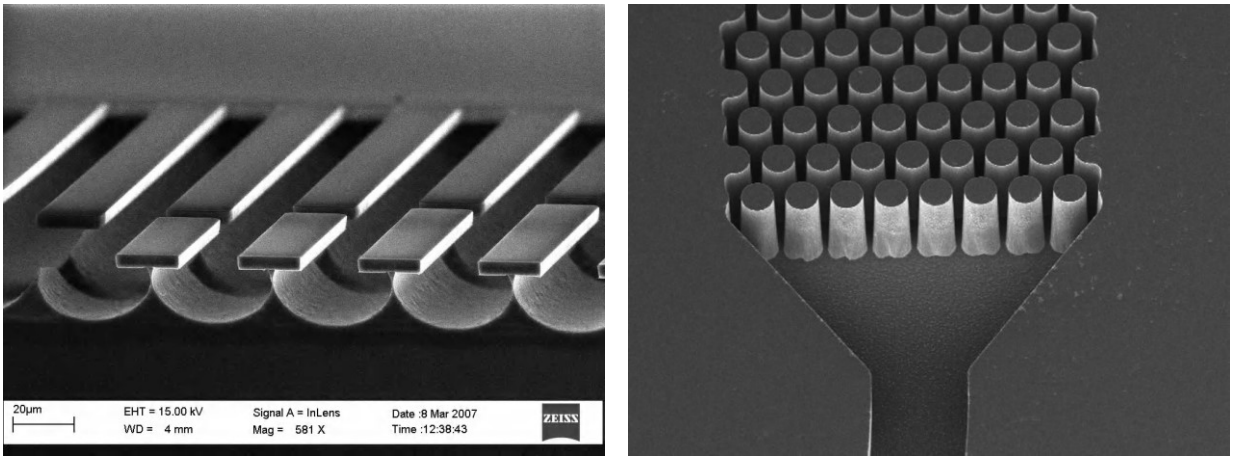

Figure 1. Isotropic (left) and anisotropic etch profiles (right) **Es ist eine ungültige Quelle angegeben.**

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