# Table of Contents

Foreword ................................................................................................................. 3

Program/Schedule ................................................................................................... 4

Abstract of the Talk by Dr. Petra Neubauer-Guenther

Facing the challenge of ‘science management’ – How to hold the reins ............... 5

List of Posters ......................................................................................................... 6

Abstracts ............................................................................................................... 14

Special Thanks to our supporter: Frank Schneider, IMCD Deutschland .......... 76

Imprint ................................................................................................................... 77
Foreword

“Once per year a PhD symposium will be organized.” – so it reads in the rules of the Cologne Graduate School Chemistry.

It is a pleasure to chair the first PhD symposium on April 24th, 2018. This proves that the Graduate schools gets more and more alive. We hope that the symposium will foster the discussion between doctoral candidates from different research groups as well as with the supervisors, i.e. many different professionals inside and outside of academic research in Cologne.

Bringing together all doctoral candidates, who belong to the Department of Chemistry beyond the borders of disciplines, buildings and institutes is the mayor goal of this event. Nevertheless, the symposium offers a chance to train the presentation skills and provides an overview of all the thesis projects carried out at the department. In this way, the CGSC fosters the scientific exchange within the Department of Chemistry and beyond. We hope that after the starting phase the now “musts” for the doctoral candidates will turn into “likes” in the next years.

Many thanks to the organisation committee of this year’s symposium and Dr. Petra Neubauer-Günter, who will give the lecture on alternative career pathways. We are very grateful for the financial support donated by Dr. Schneider, CEO of IMCD Inc.

We are confident that the PhD symposium will become an important event in the academic calendar of the Department of Chemistry from now on.

Prof. Dr. Klaus Meerholz
Chairman of the CGSC Steering Committee
## Program/Schedule

**Tuesday I April 24, 2018 (14 – 18 pm)**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>14:00 – 14:10</td>
<td>Opening</td>
</tr>
<tr>
<td>14:10 – 15:10</td>
<td><strong>1. Poster session</strong> (first half of the participants will present)</td>
</tr>
<tr>
<td>15:10 – 16:00</td>
<td><strong>Talk:</strong> Petra Neubauer-Guenther</td>
</tr>
<tr>
<td></td>
<td>Facing the challenge of “science management” –</td>
</tr>
<tr>
<td></td>
<td>How to hold the reins</td>
</tr>
<tr>
<td>16:00 – 17:00</td>
<td><strong>2. Poster session</strong> (second half of the participants present)</td>
</tr>
<tr>
<td>17:00 – 18:00</td>
<td>Finger food</td>
</tr>
</tbody>
</table>
In this presentation, I will give you a short overview on my personal background as a PhD in Physics and my career path into the field of “science management”. You will get an impression not only of the working routine but also – and even more important - on the many different aspects of managing science (or scientists, to be precise). As indicated in the title, I will try to highlight the special challenges of this particular field of work.

**Keywords:** science management; personal experience; job description
List of Posters

CATALYSIS

CAT1
Catalytic Hydrogen Production from NADH in a Bio-Coupled System
Jessica E. Armstrong, Janne Naapuri, Jan Deska, Martin H. G. Prechtl*

CAT2
Photoswitchable Photocatalysts based on Phthalimides
Banu Öngel and Axel G. Griesbeck*

CAT3
Enantioselective Transition Metal Catalysis Using New Modular Chiral Diphosphine Ligands
Martin Reiher, Stephan Dohmen, Hans-Günther Schmalz*

CAT4
New Titanium Salalen Complexes for Non-Conjugated Terminal Olefin Epoxidation
Fabian Severin, Jörg.-M. Neudörfl, Albrecht Berkessel*

CAT5
Cyclodiphosphazanes as new hydrogen-bonding catalysts and its enantioselective catalysis
Xiaochen Wang, Florian Wolf, Bernd Goldfuß*

CAT6
Synthesis of organocatalysts bearing a London Dispersion element
Jonas König and Martin Breugst*

CAT7
The Breslow Intermediate of an Aromatic N-Heterocyclic Carbene (Thiazolin-2-ylidene)
Mathias Paul, Panyapon Sudkaew, Alina Wessels, Nils E. Schlörer, Jörg-M. Neudörfl, Albrecht Berkessel*

CAT8
Synthesis of high activity Ru nanocatalyst during hydrogenation of arene
Liu Si, Leo E. Heim, Martin H. G. Prechtl*
**CAT9**

Breslow Intermediates from Aromatic N-Heterocyclic Carbenes (Benzimidazolin-2-ylidenes)

Panyapon Sudkaow, Mathias Paul, Alina Wessels, Nils E. Schlörer, Jörg-M. Neudörfl, Albrecht Berkessel*

---

**CAT10**

Kinetic Studies on the Formation of Breslow Intermediates

Alina Wessels and Albrecht Berkessel*

---

**LIFE SCIENCE**

**LSC1**

Bimodal PET/MR tracers

Kai Giesen, Ingo Spahn, Bernd Neumaier*

---

**LSC2**

Preparation of $[^{18}F]$fluoroalkenyliodonium salts and their application for radiolabeling by Sonogashira coupling reactions

Swen Humpert, Boris D. Zlatopolskiy, Marcus Holschbach, Bernd Neumaier*

---

**LSC3**

Increasing a CPP’s target selectivity by conjugation of mitochondrial targeting sequences

Annika Klimpel and Ines Neundorf*

---

**LSC4**

Hollow Mesoporous Silica Capsules as Transporter for Drugs in Solution and on Surfaces

Eva Krakor, Isabel Gessner, Sanjay Mathur*

---

**LSC5**

Characterizing oxidative cysteine catabolism in health and disease

Anna-T. Mellis, Avadh Kumar, Sita Arjune, Guenter Schwarz*

---

**LSC6**

Designing elastic matrices for cardiomyocyte cell culture

Stephanie Pieroth, Carlos Heras-Bautista, Kurt Pfannkuche, Annette M. Schmidt*
LSC7 A New Cavity Ring-down Instrument for the Detection of Ambient HO₂ Radicals
*Michael Rolletter, Mathias Bachner, Andreas Hofzumahaus*, Hendrik Fuchs

LSC8 Big Data Approach for Small Molecules: Chemometrics & Metabolomics in a Liaison That’s Made to Last
*Benjamin Albrecht, Dolores Díaz Hernández, Niels E. Schlörer*

LSC9 Investigation of the seasonal dependency of photochemical processes in air with special emphasis on the contribution of nitrous acid to the formation of OH radicals
*Marvin Glowania, Frank Holland, Andreas Hofzumahaus*

LSC10 Sulfite oxidase-dependent nitric oxide synthesis mechanism and in vivo relevance
*Alexander Kaczmarek, Daniel Bender, Guenter Schwarz*

LSC11 Influence of sulfite on hydrogen sulfide metabolism in Isolated Sulfite Oxidase Deficiency (ISOD) / Molybdenum Cofactor Deficiency (MoCD)
*Joshua Kohl, Milos R. Filipovic, Guenter Schwarz*

LSC12 Alternative splicing controls mitochondrial targeting and FeS cluster insertion of human molybdenum cofactor synthesis 1 proteins
*Simon Mayr, Juliane Röper, Guenter Schwarz*

LSC13 *Arabidopsis thaliana* nitrate reductase isoform 1 is an important enzyme-source for nitric oxide
*Marie Mohn and Katrin Fischer-Schrader*

LSC14 Photochemical Oxidation of Organic Hydroperoxides and Epoxides (ISOPOOH and IEPOX) in the Atmospheric Simulation Chamber SAPHIR
*David Reimer, Hendrik Fuchs, Georgios Gkatzelis, Jean C. Rivera-Rios, Sergej Wedel, Astrid Kiendler-Scharr, Andreas Wahner, Andreas Hofzumahaus*, Ralf Tillmann*
| **MAT1** | First step towards the direct proof for the $\alpha$-decay of $^{209}\text{Bi}$ in old Bi minerals  
*Kevin Beu and Erik Strub* |
| **MAT2** | Single and double layered square arrays of cobalt ferrite nanoparticles  
*Dominique Dresen, Yannic Falke, Emmanuel Kentzinger, Sabrina Disch* |
| **MAT3** | Ascorbic Acid Based Synthesis of Copper Nanowires for Use as Transparent Back Electrodes in Perovskite Solar Cells  
*Robert Frohnhoven, Isabella Ahrens, Alexander Möllmann, Şenol Öz, Isabel Gessner, Sanjay Mathur* |
| **MAT4** | Mixed-Ligand Metal Arylalkenolates as New Family of Air Stable Molecular Precursors for the Gas Phase Deposition of Iridium-based Catalytic Coatings  
*Lasse Jürgensen, Michael Frank, Thomas Fischer, Sanjay Mathur* |
| **MAT5** | Analysis of guest materials in hole transport layers via mass spectrometry  
*Meike Körbitzer, Beatrix Bendler, Klaus Meerholz* |
| **MAT6** | Nitrogen-doping of freestanding reduced graphene oxide films for the application as anode material in lithium-ion-batteries  
*Tim Ludwig and Sanjay Mathur* |
| **MAT7** | Investigation of Molecular Properties for Organic Electronic Devices  
*Max Reimer, Thorsten Limböck, Laura Klask, Selina Olthof, Klaus Meerholz* |
| **MAT8** | Investigation of Hybrid Organic-Inorganic Perovskites for Light-Emitting Diodes  
*Ines Schmidt, Selina Olthof, Klaus Meerholz* |
| **MAT9** | External Magnetic Field Effects on Thin Films Formed by Chemical Vapor Deposition (CVD)  
*Daniel Stadler, Danny Bialuschewski, Thomas Fischer, Sanjay Mathur* |
MAT10  Electrospun Perovskite Fibers – New Flexible 1D Nanocomposites for Light Harvesting Applications  
*Christoph Bohr, Şenol Öz, Ashish Lepcha, Markus Schütz, Florian Staub, Thomas Kirchartz, Sanjay Mathur*

MAT11  Stabilized power output of Perovskite Solar Cells by Maximum Power Point Tracking  
*Simon Ewertowski and Klaus Meerholz*

MAT12  p-Type Transparent Conducting CuAlO₂ Thin Films by Atomic Layer Deposition  
*Michael Haiduk, David Graf, Aida Raauf, Sanjay Mathur*

MAT13  Efficient ferronematic coupling with polymer brush particles  
*Karin Koch, Matthias Kundt, Alexey Eremin, Annette M. Schmidt*

MAT14  Watching a single molecule walk into the hotspot of a plasmonic antenna  
*Mo Lu, Markus Pfeiffer, Klas Lindfors*

MAT15  Design and synthesis of DNA-flagellated nanostructures for locomotion in aqueous and confined media  
*Yeimy Martinez, Moritz Raphael, Annette M. Schmidt*

MAT16  3D-Printing of Photochemical Experiments  
*Melissa Renner and Axel G. Griesbeck*

MAT17  Hybrid elastomers with tuned particle-matrix interaction  
*Julian Seifert and Annette M. Schmidt*

MAT18  Towards full surface coverage of methylammonium bismuth halide (CH₃NH₃)₃Bi₂I₉ perovskite films via chemical and solvent engineering  
*Feray Ünlü, Şenol Öz, Sanjay Mathur*

MAT19  Electrospun Li₄Ti₅O₁₂ nanofibers as anode material for rechargeable lithium ion batteries  
*Valeria Weißbrot, Tim Ludwig, Mehtap Büyükyazı, Sanjay Mathur*
STRUCTURE

STR1  Size and concentration effects on particle diffusion in complex fluids as probed by Magnetic Particle Nanorheology  
*Melissa Hermes, Eric Roeben, Annette M. Schmidt*

STR2  How to derive the 3D structure of non-labeled peptides Protocol for NMR-based structural elucidation  
*Linda Jütten, Lucia Feni, Sara Parente, Ines Neundorf*, Niels E. Schlörer, Dolores Díaz Hernández*

STR3  Paving the Way to New Organic-Inorganic Hybrid Perovskites Containing Azobispyridines  
*Simon Schmitz and Axel Klein*

STR4  Synthesis of ternary acetylides with main group elements  
*Marc Hetzert and Uwe Ruschewitz*

STR5  Use of the ESA effect as a quantification method for nanoparticles  
*Alexander Renner, Markus Schütz, Daniel Moog, Thomas Fischer, Sanjay Mathur*

STR6  On the way to fluorous coordination polymers and metal-organic frameworks with alkaline earth and divalent rare earth metals  
*Daniel Smets and Uwe Ruschewitz*

SYNTHESIS

SYN1  Studies towards the synthesis of new proline-derived secondary structure mimetics  
*Judith Bruns, Ronald Kühne, Hans-Günther Schmalz*
SYN2 The Efficient Preparation of Radiolabelled Aromatic Amino Acids via Cu-Mediated Radiofluorination using Ni-Complex Frameworks

Austin Craig, Niklas Kolks, Elizaveta A. Urusova, Boris Zlatopolskiy, Bernd Neumaier*

SYN3 N4 Functionalization of Thiosemicarbazones for Catalytic and Nuclear Medical Purposes

Alexander Haseloer and Axel Klein*

SYN4 Direct carborane-peptide conjugates: Synthesis and evaluation as potential lipopeptides

Tamara Lützenburg, Matthias Scholz, Ines Neundorf*

SYN5 Novel Synthesis of Bio-Based Hydroxy Fatty Acids

Maresa Schröder, Christian Zerhusen, Marc C. Leimenstoll, Ulrich Schörken, Annette M. Schmidt*

SYN6 On the way to Bis-Cyclopalladation Pd(II)-Complexdimers of 2-phenylpyridine derivatives

René von der Stück, Sophie Zielke, Elisabeth J. Keloglu, Axel Klein*

SYN7 Singlet oxygen ene reaction of enoether-Michael systems

Diana But and Axel G. Griesbeck*

SYN8 Studies towards the total synthesis of Dysiherbol A

Julian Erver and Hans-Günther Schmalz*

SYN9 Luminescence and Electrochemistry of Platinum(II)-Complexes bearing tridentate C^N^C and C^N^N Ligands

Maren Krause and Axel Klein*

SYN10 An Atom-Economic and Stereospecific Access to Trisubstituted Olefins through Enyne Metathesis followed by 1,4-Hydrogenation and its Potential Application in the Total Synthesis of Vitamin E

Friederike Ratsch and Hans-Günther Schmalz*
SYN11 Studies Towards the Synthesis of Eurysterol A
Ömer Taşpınar and Hans-Günther Schmalz*

SYN12 Night-time chemistry in atmosphere by nitrate radical and detection by CRDS
Vaishali Vardhan, Hendrik Fuchs, Andreas Hofzumahaus*

THEORY

THE1 Interfacial properties of binary Lennard-Jones chains mixtures by molecular dynamics simulation
Eder L. Granados-Bazán, Sergio E. Quiñones-Cisneros, Ulrich K. Deiters*
Catalytic Hydrogen Production from NADH in a Bio-Coupled System

Jessica E. Armstrong, Janne Naapuri, Jan Deska, Martin H. G. Prechtl

Institute of Inorganic Chemistry, University of Cologne, jarmstr1@smail.uni-koeln.de
Department of Chemistry, Aalto University, Espoo, Finland, www.deskalab.com

With a rise in global population, worldwide demands for efficient energy storage systems are growing dramatically. Hydrogen gas presents an alternative to fossil fuels but is limited in mobility. In Nature, hydrogen is enzymatically transferred from formaldehyde to NAD+, yielding NADH.\textsuperscript{[1,2]} We have studied biomimetic catalysts for the oxidation of NADH to form NAD\textsuperscript{+}. These catalysts will be incorporated into a chemoenzymatic system using methanol, NAD\textsuperscript{+}, and NADH to generate H\textsubscript{2}.\textsuperscript{[1,2]} This system exploits the redox cycle of NADH/NAD\textsuperscript{+} to produce H\textsubscript{2} as a clean fuel.

We have used UV/Vis spectroscopy to observe the degradation of NADH by various catalysts. Of the three catalysts discussed, Cp*Ru(phen)Cl is the most active for converting NADH. We must now verify the products of the NADH degradation. We hypothesize that the catalyst oxidizes NADH to NAD\textsuperscript{+} with a simultaneous release of hydrogen gas. Mass spectrometry will be used to test this hypothesis by determining the gasses produced during this process.

\textsuperscript{[1]} Heim, Leo E.; Thiel, Daniel; Geding, Christian; Deska, Jan; Prechtl, Martin H. G. Angew. Chem. Int. Ed. 2015, 54, 10308-10312.
\textsuperscript{[2]} Shen, Yangbin; Zhan, Yulu; Li, Shuping; Ning, Fandi; Du, Ying; Huang, Yunjie; He, Ting; Zhou, Xiaochun. Chem. Sci. 2017, 8, 7498-7504.

Keywords: chemoenzymatic, hydrogen, energy, NADH, ruthenium
Category: Catalysis
In recent years, the interest in the design, the synthesis and the characterization of fluorescent probes has increased.\[1\] With the aid of fluorescence probes, it is possible to determine specific analytes, whereby a change in the photophysical properties can be observed.\[2\]

Another important topic in photochemistry are photoswitches. The photoisomerization of azobenzenes provides a general lead example for the photocontrol of molecular structure and function.\[3\]

By combining such fluorescence probes with photoswitches, various processes can be determined. Depending on the switching state, the photophysical properties can be influenced. Thus, cis-trans photoisomerization results in a shift in absorbance or an increase or decrease in fluorescence intensity.

**Figure 1:** Cis-trans photoisomerization of different phthalimide coupled azobenzene photoswitches.


**Keywords:** fluorescence probes; photocatalysis; photoswitches

**Category:** Catalysis
Recently, a modular synthesis of chiral diphosphine ligands of type 1 was developed in our group.\textsuperscript{[1]} These ligands proved to be highly active in the asymmetric allylation of various amino substrates.\textsuperscript{[2]} Because of the great potential, especially of ligands of type 2, their synthesis was greatly improved with respect to both overall yield and structural scope, for instance regarding the sterical demand of R. Applications of these new ligands in Pd-catalysis will be presented.

\textbf{Keywords:} diphosphine ligand; transition metal; asymmetric allylation; TADDOL; C$_2$-symmetry

\textbf{Category:} Catalysis
New Titanium Salalen Complexes for Non-Conjugated Terminal Olefin Epoxidation

Fabian Severin, Jörg-M. Neudörfl and Albrecht Berkessel*

Institute of Organic Chemistry, Fabian.Severin@uni-koeln.de

In 2005, Katsuki et al. introduced the first titanium salalen complexes (such as 1) for hydrogen peroxide epoxidation with high enantioselectivities.[1] Our group improved the ligand for higher yields, enantiomeric excesses and lower catalyst loadings.[2] Until now, the diamine backbone (green) of these salalen ligands consisted of 1,2-diaminocyclohexane. The N-substituent (red) allowing the best results (2) was a fluorinated salicylic aldehyde derivative (quant., 94% ee).

In this study, the ligand backbone was varied with more easily accessible diamines.

The titanium salalen complex 3 gave high yields and high enantioselectivity. The reaction was optimized by varying the solvent and the use of additives.


Keywords: asymmetric epoxidation; salalen; hydrogen peroxid; titanium

Category: Catalysis
Cyclodiphosphazanes as new hydrogen-bonding catalysts and its enantioselective catalysis

Xiaochen Wang, Florian Wolf, Bernd Goldfuß*

Institute of Organic Chemistry, xwang9@uni-koeln.de

Cyclodiphosphazanes as new hydrogen-bonding catalysts can be applied for e.g. Michael addition for its LUMO lowering function. According to the structural property of the catalyst, further designs to a variety of its derivate is possible, including the chiral ones with the introducing of chiral units, which should also be effective for enantioselective catalysis.

Scheme 1. Chiral cyclodiphosphazanes as hydrogen-bonding catalysts and its enantioselective catalysis on Michael addition of hydroxynaphthoquinone and nitrostyrene.

Keywords: enantioselective catalysis; hydrogen-bonding catalysts; cyclodiphosphazanes

Category: Catalysis
Synthesis of organocatalysts bearing a London Dispersion element

Jonas König, and Martin Breugst*
Institute of Organic Chemistry, jonas.koenig@uni-koeln.de

London Dispersion interactions were first described by Fritz London in 1900 as the attractive part of the van-der-Waals interactions.[1] In the last couple of years they developed into an important tool in structural chemistry, catalysis, and the stabilization of reactive molecules.[2] In this study, the incorporation of a London Dispersion element as the chiral anchor in a L-proline-based molecule was investigated. To determine interactions between the catalyst and the substrate 2D and 1D NMR NOE measurements were conducted and first test reactions were performed.

Synthesis of the Catalyst:

Application:

(Synthesis of the desired organocatalyst and possible interaction in catalysis.)


Keywords: organocatalysis; L-proline; London Dispersion
Category: Catalysis
The Breslow Intermediate of an Aromatic N-Heterocyclic Carbene
(Thiazolin-2-ylidene)\(^{[1]}\)

Mathias Paul, Panyapon Sudkaow,† Alina Wessels,† Nils E. Schlörer, Jörg-M. Neudörfl, and Albrecht Berkessel* (†These authors contributed equally)

Institute of Organic Chemistry, Mathias.Paul@uni-koeln.de

Breslow intermediates, first postulated in 1958,\(^{[2]}\) are pivotal intermediates in carbene-catalyzed umpolung.\(^{[3]}\) Attempts to isolate and characterize these fleeting amino enol species first met with success in 2012 when we found that saturated imidazolidin-2-ylidenes react with aldehydes to form isolable, though reactive diamino enols that do not tautomerize.\(^{[4]}\) In contrast, aromatic thiazolin-2-ylidenes, upon stoichiometric reaction with aldehydes, yield the benzoin product and the recovered catalyst.\(^{[2b]}\) In some cases, the keto tautomer of the Breslow intermediate is observed, but not the enol itself.\(^{[5]}\)

The first generation and characterization of the elusive Breslow intermediate derived from aromatic N-heterocyclic carbenes (NHCs), namely thiazolin-2-ylidenes is reported.\(^{[1]}\)

\[ \text{The diaminoenol } E \text{ and its keto form } K \text{ were generated by reaction of the dimer of 3,4,5 trimethyl-thiazolin-2-ylidene (1) with pentafluorobenzaldehyde (2). The unambiguous NMR identification rests on double } ^{13}\text{C labeling of both the NHC and the aldehyde component. Acyl anion reactivity was proven by the formation of the enediol tautomer of the corresponding benzoin product } 2_2. \]


**Keywords:** organocatalysis, carbenes, Breslow intermediate, NMR, reaction mechanisms

**Category:** Catalysis
Homogeneous catalysts which generally need lower temperatures are not suitable for arene hydrogenation. Herein, we design a new way to prepare a kind of Ru nanocatalyst which is formed during the hydrogenation.

Scheme 1. a) Initial test system for the hydrogenation of arene. b) Postulated decomposition pathway of $\left\{ \left( p\text{-cymene} \right) \text{Ru}(\mu-\text{H})(\mu-\text{Cl})(\mu-\text{HCO}_2)\text{Ru}(p\text{-cymene}) \right\} \text{BF}_4$ without external reducing agents yielding Ru(0) which form nanoparticles

**Keywords:** catalysis; hydrogenation of arene; Ru nanoparticles;

**Category:** Catalysis
Breslow intermediates in NHC-catalytic cycle were first proposed in 1958.[2] In 2012, our research group prepared for the first time the 2,2-diamino enols generated from a non aromatic N-heterocyclic carbene (SIPr) and aldehydes.[3] For the first aromatic Breslow intermediates formation, benzimidazolin-2-ylidenes were employed. Therefore, the free \( N, N\)-bis-Mes and \( N, N\)-bis-Dipp-benzimidazolin-2-ylidene (1a-Mes/Dipp) were prepared from the corresponding anilines through a 3-step sequence\[4\] in order to serve as starting materials for the formation of the Breslow intermediates. The first generation and characterization of the elusive Breslow intermediates (3aa-3ad) derived from aromatic N-heterocyclic carbenes (NHCs), namely benzimidazolin-2-ylidenes is reported.[1]

The Breslow intermediates were formed smoothly and fully characterized by NMR and X-ray, by treating NHCs (1a-Mes/Dipp) with the aldehydes in THF-\( d_8 \) within 5-30 min.

The Breslow intermediates

\[
\begin{align*}
R & = 2,4,6\text{-trimethylphenyl} \\
& \quad 2,6\text{-di}(2\text{-propyl})\text{phenyl} \\
& \quad \text{3-step synthesis} \\
& \quad \text{THF-}d_8 \\
& \quad \text{r.t.}
\end{align*}
\]


Keywords: organocatalysis; carbene; Breslow intermediate; NMR
Category: Catalysis
Kinetic Studies on the Formation of Breslow Intermediates

*Alina Wessels and Albrecht Berkessel*

Department of Chemistry, Organic Chemistry, alina.wessels@uni-koeln.de

The Breslow intermediate, first postulated in 1958,[1] is the pivotal intermediate in carbene-catalyzed umpolung. Its formation and characterization by *in situ* NMR was accomplished from saturated imidazolidin-2-ylidenes (like SIPr) with aldehydes under aprotic conditions by our group in 2012.[2] However the mechanism of its formation is still not clarified. Therefore, computational studies were performed by Yates and Xue, taking aprotic conditions into account. However, it was found that the energy barrier of the assumed 1,2-proton shift is too high.[3]

Because of this a detailed kinetic study was conducted to investigate the mechanism.

![Image of reaction mechanism]

The reaction of the saturated N-heterocyclic carbene SIPr and aromatic aldehydes to the respective Breslow intermediates was monitored by NMR. To determine the kinetic orders in reaction components, two different methods were applied: i) the isolation method and ii) the variable time isolation analysis.[4]

Additionally, by exploiting the kinetic isotope effect, a proton inventory of the transferred protons was taken.


**Keywords:** Organocatalysis, carbene; Breslow intermediate; mechanism, NMR

**Category:** Catalysis
Bimodal PET/MR tracers

K. Giesen, I. Spahn, B. Neumaier*

Institute of Neuroscience and Medicine, INM-5: Nuclear Chemistry,

k.giesen@fz-juelich.de

Bimodal tracers combine high spatial resolution of magnetic resonance imaging (MRI) with high sensitivity of positron emission tomography (PET). Furthermore, the PET methodology enables an exact quantification of the contrast agent. The aim of this work is the synthesis of a radiolabeled PSMA-selective bimodal PET/MR contrast agent.

Figure 1: Synthesis of the bifunctional PSMA-selective chelating ligand via CuAAC-reaction.

For the synthesis of this bimodal probe, the production[1] and separation[2] of radio manganese, as well as the synthesis of a suitable bifunctional chelating ligand is required. $^{52}$Mn is produced via the $^{\text{nat}}$Cr(p,x)$^{52}$Mn nuclear reaction and separated chromatographically using the anion exchange resin Amberlite CG-400. The isolation yield of n.c.a. $^{[52\text{Mn}]}$MnCl$_2$ amounted to 95.5%. 1,2-Cyclohexandiaminetetraacetic acid (CDTA) is applied as the chelating agent. It has been shown previously that CDTA is suitable for in vivo imaging due to its high thermodynamic and kinetic stability.[3,4] Additionally, CDTA was equipped with a linking unit containing an alkyne moiety for Cu-catalyzed azide-alkyne cycloaddition (CuAAC). The CDTA moiety is coupled to the azide functionalized Glu-urea-Lys motif by using CuAAC. Glu-urea-Lys represents a pharmacophoric group with high affinity to the prostate specific membrane antigen (PSMA) facilitating the detection of prostate cancer metastases. Labeling of 2 with $^{52}$Mn was achieved in a radiochemical yield of > 99 %. PET/MR imaging of brain tumor mice models will be carried out in due course.


Keywords: radiolabeling, PET, MR, bimodal imaging, $^{52}$Mn
Category: Life Science
Preparation of [\(^{18}\)F]fluoroalkenyliodonium salts and their application for radiolabeling by Sonogashira coupling reactions

S. Humpert, B. Zlatopolskiy, M. Holschbach, B. Neumaier*

Forschungszentrum Jülich, Institut für Neurowissenschaften und Medizin, INM-5: Nuklearchemie, S.Humpert@fz-juelich.de

**Aim:** Fluoroalkenyliodonium salts can be obtained by nucleophilic addition of fluoride to the triple bond of alkynyliodonium salts. They are valuable building blocks in palladium catalysed cross coupling reactions like Stille-, Heck- or Sonogashira couplings [1]. The aim of this work was the preparation of \(^{18}\)F-labeled fluoroalkenyliodonium salts. The feasibility of this prosthetic group for indirect radiolabeling by Sonogashira cross coupling reactions should also be evaluated.

**Methods:** Alkynyl(aryl)iodonium salts were radiolabeled with [\(^{18}\)F]fluoride in aqueous organic media in the presence of different bases and K[2.2.2]. The reaction parameters were optimized with respect to temperature, time, solvent and the amount of different bases and precursor. The effect of different substituents at the triple bond (\(R_1\)), counter ions (\(X^-\)) and aryl moieties (\(Ar\)) on the radiochemical conversions (RCCs*) was studied. One pot Sonogashira cross coupling of (\(Z\))-2-[\(^{18}\)F]fluorohexen-1-yl(phenyl)iodonium tosylate with several model compounds and potential linkers to biomolecules was evaluated.

**Results:** The nucleophilic addition of [\(^{18}\)F]fluoride to the triple bond furnished [\(^{18}\)F]fluorohexenyl(phenyl)iodonium salts in RCCs of up to 60 % using K[2.2.2]/KHCO\(_3\) in DMSO/water (2:1) at 75 °C within 10 min. Remarkably, the reaction afforded highest RCCs in aqueous media without time consuming azeotropic drying. Radiolabeling of phenylethynyl-derived iodonium salts generally resulted in lower RCCs of 20–30%. Different counter ions (OTs\(^-\), OMs\(^-\), BF\(_4^-\)) did not have a significant influence on RCCs. In the case of BF\(_4^-\) the molar activity of the resulting labeled iodonium salts decreased significantly (OTs\(^-\): 30 GBq/mmol vs. BF\(_4^-\):1.5 GBq/µmol, 100MBq isolated yield).

The one pot Sonogashira reaction at room temperature furnished the respective radiofluorinated compounds in RCYs of up to 88% within 10 min. The total synthesis time including HPLC purification amounted to 34 min.

**Conclusion:** [\(^{18}\)F]Fluorohexen-1-yl(phenyl)iodonium tosylate is a valuable and easily accessible prosthetic group for indirect radiolabeling of biomolecules using Sonogashira cross coupling.

*RCCs based on HPLC results


**Keywords:** Radiolabeling, positron emission tomography

**Category:** Life Science
Increasing a CPP’s target selectivity by conjugation of mitochondrial targeting sequences

**Annika Klimpel and Ines Neundorf**

*Institute of Biochemistry, aklimpel@smail.uni-koeln.de*

Mitochondria are, due to their role in the eukaryotic metabolism, often exposed to oxidative stress and participate in the scavenging of reactive oxidative species (ROS). In consequence, mitochondria are associated with many diseases, including diabetes, age-related neuro-degenerative diseases and cancer. For pharmaceutical approaches, a delivery system for the specific targeting of molecules, like DNA, antioxidants or proteins, to mitochondria becomes increasingly importance. One strategy implies the conjugation of cell-penetrating peptides to mitochondrial targeting sequences (MTS) to increase the target selectivity.

This work focusses on the conjugation of the cell-penetrating peptide sC18, to distinct MTS, which derived from mitochondrial proteins of the yeast genome (ALD5, BNA3 and HSP60). These sequences carry an information for the translocation across the mitochondrial membrane. The novel chimera are analyzed according to their secondary structure, their cellular response and their effect on the cell viability. Furthermore, the internalization, the sub-cellular localization and mitochondrial uptake are characterized. To verify the delivering ability of our constructs, the DNA intercalating compound chlorambucil was coupled to the peptides and cytotoxic effects were measured. Our results highlight that fusion of the cell-penetrating peptide sC18 to mitochondrial-targeting sequences is a promising tool for the development of a vector system for the delivery of therapeutic and diagnostic agents into mitochondria.


**Keywords:** mitochondrial targeting, cell-penetrating peptides, targeted drug delivery

**Category:** Life Science
One of the main problems regarding the efficient treatment of diseases like cancer, antimicrobial infections and diabetes is the low solubility of drugs under physiological conditions, which leads to low accumulation rates of the drug at the point of interest. However, if higher doses of the drug are administered, the systemic toxicity in the body is increased. Therefore, the development of new drug delivery vehicles has gained intense attention during the last years to enhance diagnosis and treatment of different diseases. In this regard, hollow mesoporous silica capsules are suitable candidates due to their biocompatibility and stability in biological milieu and their high loading capacity related to their inner core.

In this work, hollow ellipsoidal mesoporous silica capsules (HMSC) were synthesized through a hard template based method. Therefore ellipsoid-shaped hematite particles were used as template, coated with silica and the hematite core was removed by etching with hydrochloric acid leading to HMSC. Each synthetic step was analyzed via SEM, TEM, IR, BET and XRD proving the successful synthesis of HMSC.

It could be shown that hydrophobic as well as hydrophilic drugs could be loaded and the sustained release was monitored through UV-Vis measurements. HMSC were also deposited on glass substrates either through spin coating or by electrospinning and loaded with drugs, clearly demonstrating the possible application as an “active coating” for preventing the formation of biofilms on e.g. implants. With regard to an enhanced antimicrobial activity, HMSC were loaded with Ag or Cu nanoparticles. This study thus demonstrates the great variability and promising potential of HMSC particles for the efficient treatment of different diseases.

**Keywords:** Drug delivery, Silica

**Category:** Life Science
Molybdenum cofactor deficiency (MoCD) is an autosomal recessive disorder belonging to the large family of inborn errors in metabolism. Patients display symptoms early after birth and develop severe neurodegeneration within a few weeks. In the absence of therapy, death in early childhood is the usual outcome. Those symptoms appear to be mainly caused by excess amounts of sulfite that accumulate due to deficiency of the molybdenum dependent enzyme sulfite oxidase (SO). SO catalyzes the detoxification of sulfite to sulfate, which is the final step of oxidative cysteine catabolism. Therefore, the prevention of sulfite formation by blocking enzymes upstream of SO in the oxidative cysteine catabolism is of high therapeutic interest. However, in order to identify novel drug targets for the treatment of MoCD, the pathway upstream of SO must first be clarified. Sulfite could either be produced by the cytosolic isoform of aspartate aminotransferase (cAAT/GOT1) or the mitochondrial isoform (mAAT/GOT2). We thus determined the kinetic parameters for the different isoforms and found that both, cAAT and mAAT were relatively similar in their activity towards the upstream substrate cysteine sulfinic acid (CSA). To elucidate this pathway in a cellular context, we furthermore created GOT1 and GOT2 KO cell lines using the CRISPR/Cas9 system and will present a first characterization. We believe that deeper insight into the oxidative cysteine catabolism will be an important step towards finding a novel treatment for MoCD.

Keywords: molybdenum cofactor deficiency, sulfite oxidase, glutamate oxaloacetate transaminase, aspartate aminotransferase

Category: Life Science
Designing elastic matrices for cardiomyocyte cell culture

Stephanie Pieroth, Carlos Heras-Bautista, Kurt Pfannkuche, Annette M. Schmidt*
Institut für Physikalische Chemie, annette.schmidt@uni-koeln.de
Institut für Neurophysiologie, kurt.pfannkuche@uni-koeln.de

Since heart diseases belong to the most common causes of death in countries of the western world, there is strong demand for strategies for therapy and repair. Current studies reveal the principal option for in vitro differentiation and culture of cardiomyocytes (CMs) derived from human induced pluripotent stem cells (iPS-CMs). Due to their contractile behavior these muscle fiber cells have a limited survival on conventional tissue culture substrates. As biomimetic elastic matrices for culture, different (bio)gels are available with limited variability.

Our new approach is based on synthetic hydrogels offering the option of tailored mechanics and of functionalization for targets. Therefore, we employ a functionalized polyacrylamide hydrogel with customized mesh size and mechanical properties.[1] This allows to optimize Youngs modulus of the gels and to mimic the mechanical properties of native cardiac tissue in the range of 50-55 kPa. Further, the polyacrylamide hydrogels are functionalized with active ester groups to link protein ligands to the network and to allow cell attachment throughout the whole process of iPS cell expansion and cardiac differentiation. A microfluidic system is used to develop spheroids from polyacrylamide hydrogels in order to combine the technology with the scalability of suspension bioreactors. Ultimately, the goal is to develop a scalable, 3D cell culture system to perform stem cell expansion, cardiac differentiation and storage of differentiated cardiomyocytes in a continuous work flow inside a stirred bioreactor system.


Keywords: biomaterials, tissue engineering, cell culture, hydrogels, cell viability
Category: Life Science
A New Cavity Ring-down Instrument for the Detection of Ambient HO₂ Radicals

*Michael Rolletter, Mathias Bachner, Andreas Hofzumahaus and Hendrik Fuchs

Institute of Energy and Climate Research: Troposphere (IEK-8),
m.rolletter@fz-juelich.de

Measurement of hydroperoxy radicals (HO₂) in the atmosphere is essential for the understanding of the radical budget in the atmosphere. HOx (HOx = OH + HO₂) radical chemistry is responsible for the photochemical degradation of pollutants in the atmosphere impacting regional air quality and climate. Existing techniques measuring ambient HO₂ concentrations rely on chemical conversion of this radical species in hydroxyl (OH) radicals or sulfuric acid, which are subsequently detected by laser-induced fluorescence (LIF) or chemical ionization mass spectrometry (CIMS), respectively. The need of a chemical conversion step can lead to interferences from other radical species. In addition, all existing techniques require a difficult calibration procedure, while cavity ring-down spectroscopy (CRDS) is inherently calibration-free, because HO₂ can directly be detected in the infrared by absorption.

Current HO₂-CRDS instruments have a detection limit around 10¹⁰ molecules cm⁻³, while HO₂ concentrations in the lower troposphere are around 10⁸ molecules cm⁻³. The new instrument allows the quantitative detection of HO₂ radicals with high sensitivity suitable for ambient application. Utilising a distributed feedback laser diode (DFB) for a cw-CRDS, HO₂ radicals are detected in the first vibrational overtone of the OH stretch around 6638 cm⁻¹.

**Keywords:** spectroscopy, CRDS

**Category:** life science
Big Data Approach for Small Molecules: Chemometrics & Metabolomics
in a Liaison That’s Made to Last

B. Albrecht, D. Diaz* and N.E. Schlörer*

NMR Department, b.albrecht@uni-koeln.de

The use of NMR spectroscopy as a chemometric tool has opened a wide window of new applications.[1] Automatic analysis and high-throughput techniques, as well as improvements in instrumental resolution and sensitivity paved the way to collecting large amounts of (NMR) data in a short time. Simultaneous observation of ~10 to easily over 1000 characteristics (variables, e.g. frequencies) per object in a large pool of samples is a routine measurement – ‘big data’ is part of the daily lab routine.[2]

Improved instrumentation and statistical methods have benefitted the life sciences. Complex biological systems give rise to a wealth of information/data which is well met by a multivariate data analysis approach characterizing and attempting to make sense of (spectroscopic) data.

In the investigation of biological systems and the study of metabolism herein, the research topic was appointed the name metabolomics. The research area is devoted to characterizing and evaluating compounds of small molecular weight in bio fluids.[3]


Keywords: NMR spectroscopy, chemometrics, metabolomics, bio fluids

Category: Life Science
Investigation of the seasonal dependency of photochemical processes in air with special emphasis on the contribution of nitrous acid to the formation of OH radicals

Marvin Glowania, Frank Holland, Andreas Hofzumahaus*

Institute of Energy and Climate Research: Troposphere (IEK-8),

m.glowania@fz-juelich.de

Rising concentrations of man-made pollutants in the lower atmosphere have a large impact on human health and climate change. Current examples are, among many others, the elevated NO2 concentrations in several German cities or the continuously rising CH4 level worldwide. The fate of most trace gases in the atmosphere is determined by their reaction with the hydroxyl radical (OH) which initiates their chemical decomposition finally leading to their removal from the atmosphere. While the most important global source of OH is the photolysis of ozone and the subsequent reaction of O1D with water vapor it turned out that in polluted environments the photolysis of nitrous acid (HONO) can take over the major part of OH formation especially during wintertime. [1]

In my PhD thesis I will investigate the seasonal dependence of HONO photolysis as an OH source through field measurements of HONO within the framework of the “Jülich Atmospheric Chemistry Study” JULIAC.

With the so called LOPAP (= LOng Path Absorption Photometer), an instrument specially designed for high reaction efficiency and sensitivity, it is possible to extract and measure very low mixing ratios (LOQ: ~ 10 pptV) of HONO in the air. An online wet chemistry method including the formation of an intermediate diazonium salt and finally an azo dye (Griess reaction) implemented in a compact coil and debubbler system under constant air suction and reagents flow is the main concept of this method. The azo dye transported through a total reflective long-path Teflon tube constantly absorbs light in a specific VIS-wavelength range to provide the required sensitivity for detection in very low concentrations. By applying a two-channel system, possible interferences from NO2 or other compounds can be quantified and taken into account. [2]

First results of instrument tests will be presented.


Keywords: Atmospheric Chemistry, Climate Research, Analytics, Photometry

Category: Life Science
Sulfite oxidase (SO), a mitochondrial enzyme that belongs to the molybdenum enzyme family, catalyzes the reaction of sulfite to sulfate. Sulfite is derived as the terminal product of the catabolism of cysteine. Individuals lacking in functional SO accumulate toxic sulfite, leading to severe neurological damages and early childhood death. Recent studies revealed a novel function of SO as a nitrite reductase, thereby generating nitric oxide (\(\cdot\text{NO}\))\(^1\). Since NO is a gaseous radical with respective functions in the human body e.g. the regulation of blood pressure or the nitrosylation of proteins, SO might have putative roles in the respective NO-mediated regulations. In SO, nitrite is reduced at the molybdenum cofactor (Moco) domain. However, nitrite is only able to accept the first of the two electrons from a fully reduced Moco, leading to a semi-reoxidized Mo(V), indicating towards a higher complexity of the NO-synthesis reaction. Since this novel function of SO was recently discovered and is not yet fully understood, two major questions have to be answered in the future: What is the reaction mechanism and is the SO-mediated NO-synthesis physiological relevant? Rapid kinetics using a Stopped-Flow Machine have been performed to determine electron transfer rates occurring during the catalysis. Furthermore, the artificial electron donor benzyl viologen (BV) was utilized to characterize the steady-state nitrite reduction kinetics of SO. To investigate the physiological relevance of the NO-synthesis function in vivo, SO-deficient human embryonic kidney (HEK) cells was generated using the CRISPR/cas system. These cells were genetically modified to stably express the soluble guanylate cyclase (sGC), an enzyme which catalyzes the conversion of guanosine triphosphate (GTP) to cyclic guanosine monophosphate (cGMP) upon activation by NO, thereby enabling the indirect determination of NO production in living cells. We will present \textit{in vitro} and \textit{in vivo} results further strengthening the hypothesis that SO contributes significantly to nitrite-dependent NO synthesis in vertebrates.

\[1\] Wang J, Krizowski S, et al., Antioxidants & Redox Signaling, 2015, 23(4), 283-294

**Keywords:** sulfite oxidase; nitrite-nitric oxide synthesis

**Category:** Life Science
Isolated sulfite oxidase deficiency (ISOD) and Molybdenum Cofactor Deficiency (MoCD) are rare inherited metabolic disorders characterized by severe neurological abnormalities, brain dystrophy, intractable seizures, feeding difficulties and early death. MoCD is caused by mutations in genes involved in molybdenum cofactor (Moco) biosynthesis while ISOD is based in the isolated loss of sulfite oxidase (SO) activity. SO, a mitochondrial enzyme, is responsible for the detoxification of sulfite to sulfate during the catabolism of cysteine, and is considered to be the most important Moco-dependent enzyme. A loss of SOX activity causes severe neurological symptoms in MoCD and SOD with death in early childhood as usual outcome. At biochemical level, sulfite, thiosulfate, S-sulfocysteine, and taurine are highly accumulated, while glutathione, cystine and sulfate levels are below normal range in both diseases[1]. Recently, we quantified thiol levels in ISOD patients urine using monobromobimane-derivatization and HPLC-based analysis. In cooperation with the laboratory of MR Filipovic at the University of Bordeaux, we investigated the persulfidation levels in SUOX-/- fibroblasts using a newly developed tag-switch technique. Furthermore, we used in vitro approaches to study the effect of sulfite on persulfidated model proteins and small molecular persulfides. In addition to this, we investigated the effect of hydrogen sulfide on S-sulfonated compounds. Currently, we are establishing a SUOX-/- mouse line using the Crispr/Cas9 system in order to further study the changes in hydrogen sulfide metabolism.

The thioredoxin (Trx) system has recently been identified as a de-persulfidating system in mammalian cells[2]. We have studied in vitro the effect of Trx on the proposed final oxidation product of persulfides, S-sulfonates, using both tryptophane fluorescence and a combined, Trx reductase-based assay.


**Keywords**: life sciences; hydrogen sulfide; sulfite; persulfides; isolated sulfite oxidase deficiency

**Category**: Life Science
Alternative splicing controls mitochondrial targeting and FeS cluster insertion of human molybdenum cofactor synthesis 1 proteins

**Simon Mayr, Juliane Röper and Guenter Schwarz***

Institute of Biochemistry, smayr@smail.uni-koeln.de

The molybdenum cofactor (Moco) is essential for nearly all forms of life and is synthesized in an ancient multistep pathway\(^1\). Moco biosynthesis in humans requires at least four genes, of which the MOCS1 locus, encoding for proteins catalyzing the first two steps of Moco synthesis\(^2\), is the product of a gene fusion. Alternative splicing of the MOCS1 transcript in exon 9 generates three different C-terminal products (splice types I-III). Type I splicing produces the two [4Fe4S] cluster containing radical-SAM enzyme MOCS1A. Type II and III splicing on the other hand produces multi-domain MOCS1AB-proteins with an inactive MOCS1A- and a functional MOCS1B-domain\(^3\). Functionality and iron-sulfur cluster content of the fusion-protein remain unknown.

Here, we report and characterize the maturation of alternatively spliced MOCS1-proteins. We found utilizing fluorescence microscopy, cellular fractionation and partial proteolysis experiments that MOCS1A-proteins require exon 1a for translocation to the mitochondrial matrix, where assumingly the [4Fe4S] clusters are incorporated. MOCS1AB-proteins target to the matrix via an independent internal motif, during which the entire non-functional MOCS1A-domain of MOCS1AB is proteolytically cleaved resulting in active MOCS1B-protein not harboring any [4Fe4S] cluster. The *in vivo* activity of non-fused MOCS1B was confirmed by a recent patient case, where we found a solely separate expression of MOCS1A and MOCS1B, yet were able to detect MOCS1B activity via the Moco degradation product urothione. In conclusion we uncovered that alternative splicing controls maturation of MOCS1-proteins regarding the cellular localization, as well as the iron-sulfur cluster content.


\[^3\] Gray TA and Nicholls RD; Diverse splicing mechanisms fuse the evolutionarily conserved bicistronic MOCS1A and MOCS1B open reading frames. RNA. 2000 Jul;6(7):928-36.

**Keywords:** alternative splicing/iron-sulfur cluster/mitochondrial translocation/molybdenum cofactor

**Category:** Life Science
Arabidopsis thaliana nitrate reductase isoform 1 is an important enzyme-source for nitric oxide

Marie Mohn and Katrin Fischer-Schrader*
Institute of Biochemistry, mmohn@smail.uni-koeln.de

Plant nitrate reductase (NR) is the first and rate-limiting enzyme in nitrate assimilation. Each 100 kDa subunit of the homodimer contains an N-terminal molybdenum cofactor, a central cytochrome $b_5$ and a C-terminal FAD cofactor. Many plants, including the model plant Arabidopsis thaliana (At) express two genes (NIA1 and NIA2) encoding two functional NR isoforms. NR isoform 2 is responsible for 90% of NR activity as was found by enzyme activity analysis of nia1 deficient plants, while the nia2 mutant plants retain only 10% NR activity [1]. Plant NR can also catalyse the reduction of nitrite to generate the signalling molecule nitric oxide (‘nitrite reductase activity’). To date biochemical studies are lacking to determine the relative importance of the individual NR isoforms in this physiological role.

Both C-terminal truncated Arabidopsis thaliana NR isoforms carrying the molybdenum and heme cofactors were recombinantly expressed and purified. Subsequently, the nitrite reducing activity of both enzymes was assessed and compared by using a benzyl viologen:nitrite activity assay for steady-state analysis, using rapid kinetic stopped-flow measurement for pre-steady state analysis and using an an NO-anlyazer to monitor NO generation.

Accumulating evidence points to differential nitrite-reductase activity for the two NR isoforms suggesting that NR1 plays a more important role in physiological NO-generation.


Keywords: Nitrate reductase, nitric oxide, NO, steady-state kinetics, benzyl viologen
Category: Life science
Volatile organic compounds (VOCs) are atmospherically oxidized by the hydroxyl radical OH that is part of the catalytic cycles of hydrogen oxides (OH, HO₂) and nitrogen oxides (NO, NO₂). Isoprene, predominantly emitted from vegetation, accounts for one third of global nonmethane VOC emissions.[2] Due to strongly varying nitrogen oxide concentrations, oxidation mechanism pathways under pristine and urban conditions differ considerably. The major first-generation oxidation products under pristine conditions (low NO case) are isoprene hydroxyl hydroperoxides (ISOPOOHs), which are further predominantly oxidized by the OH radical to epoxydiols (IEPOX).[3] By employing authentic ISOPOOH and IEPOX standards their photochemical OH oxidation was investigated in the atmospheric simulation chamber SAPHIR utilizing proton transfer reaction mass spectrometry (PTR-MS). Measured trace gas and radical concentrations are compared to a state-of-the-art model (MCM 3.3.1).

References:

Keywords: Synthesis, Organic Hydroperoxides, Isoprene Oxidation, Simulation Chamber, PTR-MS
Category: Life Science
First step towards the direct proof for the α-decay of $^{209}$Bi in old Bi minerals$^{[1]}$

Kevin Beu, Erik Strub*

Division of Nuclear Chemistry, kbeu@small.uni-koeln.de

In 2003 de Marcillac et al. reported their observations of α-particles during background measurements using scintillating bolometers, which were attributed to the decay of $^{209}$Bi$^{[1]}$. The α-decay of $^{209}$Bi leads to the stable decay product $^{205}$Tl, which shifts the natural isotopic composition $^{203}$Tl (29.52%) and $^{205}$Tl (70.48%) towards $^{205}$Tl$^{[2]}$. This aspect was not further investigated at that time, but it would be a direct proof for the instability of $^{209}$Bi. An analysis should be possible using a specific separation technique for the system Bi/Tl and analytical methods to observe an isotopic shift of $^{205}$Tl in samples of old $^{209}$Bi minerals. Ongoing works deal with the development of a chemical separation procedure, as well as the acquisition and pre-testing of suitable Bi raw materials.

- For separation, an established separation technique$^{[3]}$ for the system Pb/Tl was adapted on the system Bi/Tl. This technique was applied as a proof of principle on n.c.a. amounts of $^{204}$Tl, using liquid scintillation counting for analysis.
- Several mineral (bismuthinite) samples were analyzed for their natural Tl content using LA-ICP-MS. Only at very low Tl concentrations it can be expected that the isotopic signature of Bi decay can be unambiguously identified.


Keywords: analysis; separation; bismuth; thallium; minerals

Category: Materials
Single and double layered square arrays of cobalt ferrite nanoparticles

Dominique Dresen¹, Yannic Falke¹, Emmanuel Kentzinger², Sabrina Disch¹*

¹Institute of Physical Chemistry, dominique.dresen@uni-koeln.de
²Jülich Centre for Neutron Science, Forschungszentrum Jülich

Magnetic nanostructures receive great attention currently as they are interesting both due to potential applications, e.g. in information technology and spintronics [1] and for the fundamental investigation of dipolar/exchange coupling [2]. In particular stacked structures of ordered magnetic nanoparticle monolayers are interesting due to their potential for highly structured 3D devices and as model systems for the study of nanoscale magnetism. Here, we present ongoing studies on the preparation and characterization of single domain magnetic nanoparticles arranged in a dense square lattice. The nanostructures are characterized structurally by electron microscopy, grazing-incidence small-angle x-ray scattering and x-ray reflectometry, and magnetically by vibrating sample magnetometry. The results are compared to the individual nanoparticle properties and approve the successful preparation of single and double layered square arrays. As a result, this work presents a way to a high quality model system for future studies of dipolar magnetic interaction on the nanoscale.


Keywords: magnetic nanoparticles; self-assembly; monolayers; x-ray scattering
Category: Materials
Ascorbic Acid Based Synthesis of Copper Nanowires for Use as Transparent Back Electrodes in Perovskite Solar Cells

Robert Frohnhoven, Isabella Ahrens, Alexander Möllmann, Senol Öz, Isabel Gessner, and Sanjay Mathur*

Institute of Inorganic Chemistry, robert.frohnhoven@uni-koeln.de

In the past decade, the synthesis of metallic nanowires and nanofibers as an alternative material for Indium Tin Oxide (ITO), the market leading material for transparent conductive electrodes (TCEs), became a field of research interest, since the metallic nanostructures are easily accessible via wet chemical routes and can be used for flexible optoelectronic device applications, which is not the case for brittle ITO. In this work, the combination of the mild and non-toxic reducing agent ascorbic acid[1] and the oleylamine/oleic acid ligand system[2] is introduced for the solvothermal and microwave assisted synthesis of Copper nanowires (CuNWs) with high aspect ratios up to 165. The synthesized CuNWs are then spin coated onto flexible plastic substrates to obtain transparent conductive layers. After treatment with glacial acetic acid in order to remove surface oxides and residual surfactant molecules, these conductive layers are then transfer laminated with a ball bearing pen[3] onto regular stacked perovskite solar cells as a transparent back electrode.


Keywords: material, nanowire synthesis, transparent conductive electrode, perovskite solar cells
Category: Materials
Investigation of the interplay of metal-organic chemistry will enrich the state-of-the-art of CVD and ALD technology and open new possibilities for the applications of new Ir-based materials. Therefore heteroleptic mixed-ligand complexes exhibiting manifested Janus-type reactivity are under investigation to elaborate the precursor chemistry – materials synthesis – functional property chain. Physico-chemical studies (thermal degradation behavior, volatility), gas phase deposition studies have been carried out to elucidate the adsorption behavior (sticking coefficient) of new molecules. Finally, the CVD- and ALD-grown materials were tested towards their (electro)catalytic applications, particular in the oxygen evolution reactions. In this work synthetic preparation and structural characterization of precursors will be reported and their thermal decomposition behavior is examined.


Keywords: Mixed-ligand iridium precursor, CVD/ALD, iridium oxide, nanostructured films, water splitting
Category: Materials
Analysis of guest materials in hole transport layers via mass spectrometry

*Meike Körbitzer, Beatrix Bendler and Klaus Meerholz*

Institute of Physical Chemistry, meike.koerbitzer@uni-koeln.de

The properties of organic electronic devices, such as organic light emitting diodes (OLEDs), organic solar cells (OSCs) or organic field-effect transistors (OFETs), are strongly influenced by electronic defects of structural or contaminational origin in their layers. Impurities may occur due to residues from material synthesis or device fabrication, selectively added as dopants or by degradation of any of the above or the device material itself. It is important to understand the influence of these intrinsic and extrinsic defects on the electronic properties of the materials and the devices, as to date it is not understood well.[1] Especially impurities with lower LUMO energies or higher HOMO energies than the materials are expected to have a high influence on device properties, as they can act as electron or hole traps and may influence the charge carrier efficiency.[2] As charges are expected to use these energetically favoured states more often, it may lead to earlier deterioration and degradation of the molecule and thus a change of the layer composition. With the concentration of foreign molecules usually being very low, sensitive analytic procedures need to be used and optimized for further analysis of the traps. Therefore, non-crosslinkable guest molecules were added to an organic crosslinkable material used as charge transport layer and afterwards easily extracted by the laser beam of LDI-MS (Laser Desorption Ionization Mass Spectrometry). It proves to be a reliable analysis method for those molecules.[3] However, as the mass spectrum of the host matrix shows many mass signals over a large range, it will be a challenge to analyze molecule degradation products in crosslinked materials.


Keywords: organic electronics, LDI-MS
Category: Materials
Nitrogen-doping of freestanding reduced graphene oxide films for the application as anode material in lithium-ion-batteries

Tim Ludwig and Sanjay Mathur*
Institute of Inorganic Chemistry, sanjay.mathur@uni-koeln.de

Since its discovery in 2004, graphene has received enormous scientific interest due to the remarkable two-dimensional structure, making it highly promising for numerous applications. Electrodes in lithium-ion-batteries (LIBs) are one of these applications that could benefit from mechanical strength, high surface area and electrical conductivity of graphene. For the integration in commercial LIBs, it is important to develop simple, cost effective and scalable methods for the production of graphene-like structures. Due to the good dispersibility in water and other polar solvents, graphene oxide easily forms multi- and monolayers and therefore offers advantageous properties for a green and simple wet-chemical synthesis. Therefore, in this work graphene oxide was synthesized and further processed by liquid and gas phase approaches to obtain reduced graphene oxide films via pressure filtration with superior mechanical properties. These paper-like structures of regularly arranged reduced graphene oxide flakes are mechanically stable, scalable to mass production and can be used as flexible ultrathin electrodes in LIBs.

Besides a flexible electrode design, these films enable an increased volumetric energy density due to a reduction in weight, as additional battery paste components such as current collector, carbon black and binding agent, are no longer necessary. This is attended by the smaller preparative effort of the freestanding electrode design.

Moreover, nitrogen doping of these graphene-like structures has been proven successful to increase the storage capacity of LIBs. The integration of N-atoms increases the electrical conductivity and offers a higher theoretical storage capacity because of the higher energy of the Li-N-bonding in comparison to the Li-C-bonding. Different approaches to integrate nitrogen into the carbon structure, e.g., via thermal reduction or microwave assisted methods, have been performed in this work focusing on their influence on electrical and electrochemical properties. As-prepared films were subsequently integrated into LIB half-cells to demonstrate their application potential.

Keywords: Reduced Graphene Oxide, Lithium-Ion-Batteries, Nitrogen-Doping; Categories: Materials
Investigation of Molecular Properties for Organic Electronic Devices

Max Reimer, Thorsten Limböck, Laura Klask, Selina Olthof and Klaus Meerholz*
Institute of Physical Chemistry, max.reimer@uni-koeln.de

Electrical and optical properties of many organic semiconducting molecules are highly anisotropic. Hence they depend on the packing and ordering motif in materials. Nowadays such molecules are already being used in organic electronic devices. Being able to grow layers with an engineered order could dramatically improve their properties such as absorption, emission and conductivity. Therefore we investigate a certain merocyanine whose ordered growth was previously observed and that is evaporated on highly ordered substrates. These substrates act essentially as templates that do not change the properties of the device. Useful materials for the template can be monolayers of graphene or hexagonal boron nitride [1,2]. Here the first aim is to relate the packing motif of the molecules to the width of their energetic levels. At the moment atomic force microscopy (AFM) is used to determine the order of the molecules. In the future the packing motif will be observed additionally with low energy electron diffraction (LEED). The width of the energetic levels is measured with ultra-violet photoelectron spectroscopy (UPS) which can provide information on the density of states in the region of the highest occupied molecular orbital (HOMO). The obtained knowledge should then be used to fabricate optimized organic electronic devices such as field effect transistors (FETs), light emitting diodes (LEDs) or solar cells.


Keywords: materials; crystallinity; molecular order
Category: Materials
Investigation of Hybrid Organic-Inorganic Perovskites for Light-Emitting Diodes

Ines Schmidt, Selina Olthof and Klaus Meerholz*
Institute of Physical Chemistry, ines.schmidt@uni-koeln.de

Perovskite materials are of considerable interest, due to their unique semiconducting properties. They exhibit a high charge carrier mobility, broad absorption range, small exciton binding energy and long-range exciton diffusion length. Hybrid perovskites are mainly used as solar cells where the efficiency increased from 3.8% to over 22% in the last seven years.[1,2]

Hybrid inorganic/organic perovskite materials have the general formula ABX\textsubscript{3}, where A is a monovalent cation (Cs, methylammonium (MA) or formamidinium (FA)), B is a divalent metal cation (Sn or Pb) and X is a halide anion (I, Br or Cl). The combination of these results in 18 different perovskites. These can be prepared by spin coating or evaporation, but to gain high efficient perovskite layers the crystal formation during the preparation must be controlled.

Due to their facile fabrication, their outstanding charge transporting properties, easy bandgap (E\textsubscript{g}) tuning and high colour purity, perovskite are promising for light-emitting applications.

<table>
<thead>
<tr>
<th></th>
<th>Pb</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>CsPbI\textsubscript{3}</td>
<td>CsSnI\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>MAPbI\textsubscript{3}</td>
<td>MASnI\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>FAPbI\textsubscript{3}</td>
<td>FASnI\textsubscript{3}</td>
</tr>
<tr>
<td>Br</td>
<td>CsPbBr\textsubscript{3}</td>
<td>CsSnBr\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>MAPbBr\textsubscript{3}</td>
<td>MASnBr\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>FAPbBr\textsubscript{3}</td>
<td>FASnBr\textsubscript{3}</td>
</tr>
<tr>
<td>Cl</td>
<td>CsPbCl\textsubscript{3}</td>
<td>CsSnCl\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>MAPbCl\textsubscript{3}</td>
<td>MASnCl\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td>FAPbCl\textsubscript{3}</td>
<td>FASnCl\textsubscript{3}</td>
</tr>
</tbody>
</table>

Absorption onset and bandgap of different perovskites, measured with UV-Vis absorption spectroscopy.

In my thesis the optical and electrical properties of different perovskite should be investigated and the application of perovskite layers for charge transport in OLEDs as well as emissive layers should be studied.


Keywords: organic-inorganic hybrid perovskite, light-emitting diodes, charge transport
Category: Materials
Magnetic materials are one of the most important pillars of our nowadays society. Without these materials – the fundament of modern microelectronics - we would have to write this proposal by hand. Coexisting with electricity, magnetic phenomena are exploited in data storage devices, control systems, sensors and music instruments. However, if it comes to the nano regime, magnetism is rather unexplored. While we gain more and more informations on the influence of external fields on e.g. the orientation of magnetic nanoparticles during drying processes, the influence of magnetic fields on magnetic thin film formation and their potential for growth control during thermal CVD is not investigated yet. By a combination of external magnetic fields and conventional CVD, we created a specialized setup, which allows the investigation of magnetic field effects on thin film formation, delivering an additional possibility to transfer molecular properties to nano scaled materials. Depending on the oxidation state of the central atom, an interaction between clustered molecules and an applied magnetic field, depending on the number of unsaturated electronic spins and cluster size can be studied. While decomposing during CVD process, small clusters are formed, which - if consisting of a magnetic material - might interact with an applied external magnetic field. First results of these studies will be demonstrated.

**Figure 1:** Iron films deposited in a) the presence and b) the absence of an externally applied magnetic field. While anisotropic film growth is observed in magnetic field assisted CVD, homogeneous film formation is measured in zero field deposition.

**Keywords:** Magnetic Materials, Chemical Vapor Deposition, Nanostructured Films

**Category:** Materials
Electrospun Perovskite Fibers – New Flexible 1D Nanocomposites for Light Harvesting Applications

Christoph Bohra, Senol Öz, Ashish Lepcha, Markus Schütz, Florian Staub
Thomas Kirchartz, Sanjay Mathur

aInstitute of Inorganic Chemistry, C.Bohr@uni-koeln.de
bIEK-5 Photovoltaik, Forschungszentrum Jülich GmbH

Due to their high efficiencies (up to 22%, comparable to established thin-film solar cells like Cu(In,Ga)Se₂ or CdTe), interest in perovskite solar cells is growing rapidly. In contrast to the high quantity of publications dealing with planar, rigid solar cells, one dimensional, fiber like solar cells have not been focused. Therefore, single step fabrications of phase-pure organic-inorganic lead and tin halide perovskite (MeNH₃MI₃; M= Sn,Pb) fibers are presented. The experimental results demonstrate first comprehensive data on inert electrospinning of an air sensitive organic-inorganic hybrid material. X-ray diffraction and steady state photoluminescence data confirmed the phase purity, as well as photonic properties. Planar heterojunction solar cells prepared by direct electrospinning of composite fibers onto compact TiO₂ coated FTO substrates showed a photoelectric response under simulated sunlight conditions. Despite their lower efficiencies (compared to planar PV cells), 1D hybrid perovskite fibers are potential elements for flexible optoelectronics.

Keywords: Perovskites; Electrospinning; Nanofibers; Photovoltaic
Category: Materials
Perovskite Solar Cells (PSCs) attracted much attention in the last decade due to their rapid enhancement in power conversion efficiencies (PCE), today exceeding 22%.[1] Appropriate characterization techniques remain a key issue in order to determine the power output of the solar cells. This becomes especially important in cells which show hysteresis in their current-voltage characteristics regarding opposite scan directions.

In this work a program for Maximum Power Point Tracking (MPPT) was designed to get insight into the performance during the early stage of power conversion. We tested solar cells with three different perovskites, showing various behaviors until they reach a stabilized power output under working conditions.


**Keywords:** MPPT; Perovskites; hysteresis

**Category:** Materials
Abstract. The use of renewable energy is becoming increasingly important since energy requirement as well as greenhouse gases are increasing. Among hydro and wind power, solar energy is a further key element to mitigate further emissions. Transparent Conductive Oxides (TCO’s) will increasingly move to the fore due to their high potential as material for renewable energy. In this class Delafossite type oxides, CuMO2, are highly investigated candidates as p-type TCO materials. The fabrication of transparent solar cells by the combination of n- and p-type transparent oxides into p-n junctions can be used for the functionalization of available surfaces. Atomic layer deposition (ALD) becomes attractive for TCO’s and transparent solar cells due to their unique ability to generate pinhole-free, continuous and dense films with precise thickness control.

**Keywords:** Transparent Conductive Oxide, Atomic Layer Deposition, Delafossite, Thin Films, Nanostructured Films

**Category:** Materials
The ability to control nematic phases in thermotropic liquids by external fields is of great importance for their application, e.g. in optical devices. While it is common to use electric voltage in such devices, the employment of magnetic fields is less straightforward due to the low magnetic anisotropy of the mesogens. However, as already predicted by deGennes and Brochard in 1970, the incorporation of dipolar magnetic particles is expected to result in nematic phases that are readily manipulable at moderate magnetic field strength.[1] Nonetheless, one of the main challenges for the experimental realization is strong tendency to agglomerate of the nanoparticles, as a consequence of the strong molecular interactions of the mesogens and the dipolar interactions between the particles.[2] Thus, up to now, experimental evidence for such coupling is rare.

Our new approach to circumvent this problem, and to achieve ferromagnetically doped liquid crystals with enhanced volume fraction and stability, is based on nanoparticles that are surface-modified with a side-chain LC polymer brush. Thereby, a variation of shell thickness, mesogen density and the spacer length is possible. With this approach, a higher compatibility between the particle surface and the mesogenic matrix, and an effective steric stabilization of particles against agglomeration is obtained. The impact of the doped particles on the phase behavior of 5CB is investigated with respect to particle concentration. By addition of 9OCB-PHMS functionalized magnetic particles, the order parameter of the system increases, indicating an effective coupling between the particles and the LC matrix. The magnetic response of the ferronematic phase is investigated by capacitance measurements in a magnetic field (Figure 1b).


Keywords: materials, liquid crystals, ferronematics, magnetic particles
Category: Materials
Metal nanoparticles can serve as optical antenna to enhance the reception and emission of light from quantum emitters such as a quantum dots or dye molecules. The coupling efficiency of a quantum emitter and a plasmonic antenna depends strongly on their relative positions. One of the challenges in studying emitter-plasmon coupling is the required positioning accuracy. In our work, we study an active plasmonic system based on DNA origami nanotechnology. This structure consists of two 60 nm gold spheres, which act as a gap antenna and a DNA walker carrying a single Atto 647N dye. After addition a trigger molecule, the dye molecule will be transported autonomously into the hotspot of the plasmonic antenna.

We use fluorescence microscopy to track the motion of the dye molecule. After triggering the walker, fluorescence lifetime and brightness of each molecule is measured at regular time intervals. Our key observation is that the devices show a clear reduction of fluorescence lifetime as a function of time from start of walking. The change of lifetime agrees well with the value obtained from finite element method calculations, and the speed of the motion also matches with ensemble fluorescence assay of walking. In summary, our result shows that the walker structure undergoes a unidirectional walk and we observe an increase of fluorescence decay rate when it enters the plasmonic hotspot. This demonstrates a promising approach to develop novel plasmonic devices where a single quantum emitter can be dynamically positioned.

Keywords: Plasmonic antenna; DNA origami; Single molecule microspectroscopy
Category: Materials
Design and synthesis of DNA-flagellated nanostructures for locomotion in aqueous and confined media

Yeimy Martinez, Moritz Raphael, Annette M. Schmidt*

Institut für Physicalische Chemie, annette.schmidt@uni-koeln.de

Developing artificial swimmers at the nanoscale has emerged as a new class of active matter over the past decade. These mobile nanostructures are opening up novel applications ranging from biosensing to targeted drug delivery in fluid environments dominated by a low Reynolds number regime. While keeping complexity low, such systems should also overcome the influence of Brownian collisions, viscous drag and various surface phenomena. Taking inspiration from nature, the mobility strategies of biological swimmers provide thus a plethora of inspiration to create similarly performing artificial systems. In this regard, we present here the design and synthesis of DNA-flagellated nanostructures based on the general arrangement of flagellated bacteria and sperm cells. Mimicking this pattern, the nano-head is prepared through the seed-mediated growth of CoFe₂O₄ onto platinum nanoparticles, whereas the flexible tail is achieved by the selective attachment of DNA strands to the platinum counterpart. This investigation includes the systematic synthetic approach to prepare the nanostructures by thermolysis in solid phase and the further transfer and stabilization in aqueous phase. Moreover, a study on the attachment of DNA to platinum is judiciously implemented using two model DNA sequences. Finally, the induced mobility is preliminarily evaluated in confined media using agarose gel electrophoresis by pointing out the role of the surface charge of the DNA-flagellated nanostructures.


Keywords: material, artificial swimmers, DNA flagella, low-Reynolds number, mobility

Category: Materials
3D-Printing of Photochemical Experiments

Melissa Renner, Axel G. Griesbeck*

Institute of Organic Chemistry, mrenner@small.uni-koeln.de

Because of a drastic decrease in cost and commercial availability, 3D-printing is a technology with enormous future potential for pure and applied chemistry. In chemistry it opens the opportunity to print custom-made reactors, such as (micro-)flow reactors.[1] Though there are some examples for 3D-printed reactors in organic synthesis, such as from Cronin and coworkers[2], so far there is only one for photochemistry applications.[3]

The concept for this work is to develop a continuous-flow reactor, which is easy to print and to use and where the catalyst or sensitizer is already immobilized. Our prototype is a flow reactor printed from polypropylene, where TPP as a dye-sensitizer is immobilized through adsorption on the surface and the light exposure is enabled through a glassfront. As a model reaction the photooxygenation of citronellol was used and showed comparable yields as the batch-reaction with the sensitizer in solution.

Furthermore, the immobilization of the catalyst through covalent-bonding with the to-be printed polymer is investigated.


Keywords: 3d-printing; photochemistry; flow chemistry; catalysis

Category: Materials
Hybrid elastomers with tuned particle-matrix interaction

Julian Seifert, Annette M. Schmidt*

Institut für Physikalische Chemie, email: annette.schmidt@uni-koeln.de

Hybrid materials that combine magnetic nanoparticles with complex matrices such as gels and elastomers can be manipulated by external magnetic fields. By employing magnetic nanoparticles as multifunctional, inorganic crosslinkers, magnetic node networks with a direct covalent coupling between magnetic and elastic component are obtained. These materials show a novel type of particle-matrix interaction.[1]

Here, we present the synthesis of magnetic node networks based on spindle-like $\alpha$-Fe$_2$O$_3$ particles and an elastomeric matrix. This new type of magnetically manipulable elastic material is expected to have promising applications for dampers or in robotics, where the mechanic properties need to be reversibly altered. By the incorporation of spindle-like hematite particles, showing magnetic as well as geometric anisotropy, we induce direction dependent properties in the magnetic node networks, as one of the key steps to the realization of actuators showing a reversible contraction along one axis.[2]

The prepared magnetic node networks show the typical viscoelastic behavior of particle filled elastomers. Due to the covalent attachment of the magnetic nanoparticles to the elastic matrix, high particle contents of up to 30 m% can be employed without observing particle agglomeration, leading to structures with decent magnetic properties. The occurring magnetic hysteresis in the reversible elastomers is attributed to a reorientation of the magnetic moment within the particle at high fields. In ongoing experiments, we intend to maximize the direction dependent magnetic properties by aligning the magnetic nanoparticles in a magnetic field and conserving the magnetic order through the crosslinking process.


Keywords: materials, ferroelastomer, stimuli-responsive, magnetic nanoparticles, crosslinking

Category: Materials
Towards full surface coverage of methylammonium bismuth halide \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) perovskite films via chemical and solvent engineering

**Feray Ünlü, Senol Öz, Sanjay Mathur** *

*Institute of Inorganic Chemistry, sanjay.mathur@uni-koeln.de*

Recently, low dimensional bismuth halide perovskites emerged as a promising alternative to lead based 3D hybrid perovskites in the field of optoelectronics, including solution processable thin film solar cells. Lead based metal halide perovskite solar cells have already achieved 22.7% certified solar to electric power conversion efficiency for small area devices (<1 cm²). However, one of the major problems encountered with this new technology, apart from structural and chemical stability, is the toxicity associated with heavy metal lead. Potentially less toxic bismuth halide perovskites semiconductors possess promising optoelectronic properties including a high absorption coefficient on the order of \(10^4 \text{ cm}^{-1}\) and can be processed from solution using a variety of wet chemical deposition techniques and additives. Achieving full surface coverage along with precise control over nucleation sites has proven to be difficult by employing techniques, derived from the lead halide perovskite counterpart.

In this study, we investigated the influence of bismuth xanthate precursor and various solvents for the single-step deposition of methyl ammonium bismuth iodide perovskite \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) thin-films with full surface coverage. The use of acetonitrile solvent in the perovskite synthesis led to pinhole-free absorber layers. Solar cell in \(n-i-p\) stack configuration \((\text{FTO/c-TiO}_2/\text{mp-TiO}_2/(\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9/\text{Spiro-OMeTAD/Au})\) achieved a remarkably high fill factor of 0.74-0.77 with negligible hysteresis in the current-voltage sweep. Bismuth ethyl xanthate was used as a non-halide precursor additive for the deposition of \((\text{CH}_3\text{NH}_3)_3\text{Bi}_2\text{I}_9\) films. Additionally, a small amount of cesium iodide was incorporated in a multi cation approach to benefit from its known effects such as improvement of stability and phase-pure crystallization. The addition of bismuth ethyl xanthate led to solar cells with improved current density (0.7 mA/cm²), fill factor (0.63) and power conversion efficiency (0.26%) compared to devices fabricated without bismuth ethyl xanthate \((\text{J}_{\text{SC}} = 0.5 \text{ mA/cm}^2, \text{ FF}= 0.58, \text{ PCE}= 0.17\%\)).

**Keywords:** organic inorganic perovskite, solar cell, chemical engineering, solvent engineering

**Category:** Materials
Electrospun Li$_4$Ti$_5$O$_{12}$ nanofibers as anode material for rechargeable lithium ion batteries

Valeria Weißbrot, Tim Ludwig, Mehtap Büyükyazi, Sanjay Mathur*
Institute of Inorganic Chemistry, sanjay.mathur@uni-koeln.de

Lithium titanate based systems (Li$_4$Ti$_5$O$_{12}$, LTO) provide a promising platform as efficient anode materials for rechargeable lithium ion batteries. In this work LTO nanofibers were produced by electrospinning and tested in lithium half-cells. Further, previously synthesized reduced graphene oxide (rGO) was added to the nanofiber matrix in order to increase the specific capacity and cycle stability of the LTO by improving its electronic conductivity. Phase-pure crystalline LTO fibers were obtained, which exhibited a good reversible specific capacity of 133.1 mAhg$^{-1}$ and an excellent cycle stability with a capacity loss of 4.5% after 100 cycles. Addition of rGO as conducting agent to the nanofibers provided a 17% higher reversible specific capacity with a maintained cycle stability. The simple and cost-efficient modification with rGO can be applied in commercial LTO batteries instead of the acetylene black for a superior electrochemical behavior.

Keywords: Lithium-ion batteries, electrospinning, anode material
Category: Materials
Size and concentration effects on particle diffusion in complex fluids as probed by Magnetic Particle Nanorheology

**Melissa Hermes, Eric Roeben and Annette M. Schmidt***

*Institute of Physical Chemistry, annette.schmidt@uni-koeln.de*

Rheology allows to access information on the (quasi-)continuous properties of bulk materials, and a few methods have been developed to investigate the flow in microstructured materials (e. g. complex fluids) on the micro- or nanoscale with spatial resolution. By employing magnetic particles as probes in soft hybrid systems, the possibility to investigate the self-assembly and dynamic interactions systematically by means of dynamic susceptibility is given. In this study, we perform nanorheological experiments using the method of Magnetic Particle Nanorheology,[1,2] and systematically vary the size of the tracer particles. The experiments are analyzed by paying pronounced attention to the ratio of structural length scales within the investigated material and the probe size. Besides the analysis of size effects, special attention is payed to the influence of the particle fraction on the subsequent rheological properties. It is expected that at higher particle fraction structure formation occurs that leads to interesting viscoelastic properties.

![Fig. 1. TEM images of CF@SiO₂ nanoparticles with increasing shell thickness.](image)

As magnetic phase, CoFe₂O₄ (CF) nanoparticles (d_TEM = 17.3 nm ± 14 %) are used and these particles are systematically coated with a silica (SiO₂) shell to obtain tracer particles with variable hydrodynamic size (see Fig. 1). The Brownian relaxation of the tracer particles in complex fluids is investigated by means of AC susceptometry in the range of 1 Hz – 250 kHz and the use of theoretical models gives access to rheological properties. The viscosity, storage and loss moduli and diffusion properties are analyzed. The results show systematic deviations from macroscopic behavior in the higher frequency range that are caused by the varying hydrodynamic diameters of the tracer particles. The size- and concentration-dependent particle diffusion is evaluated further considering the scaling theory of De Gennes and by comparison to theoretical predictions.


**Keywords:** structure; synthesis, rheology; nanoparticles, magnetism

**Category:** Structure
How to derive the 3D structure of non-labeled peptides

Protocol for NMR-based structural elucidation

L. Jütten¹, L. Fenì², S. Parente², I. Neundorf*², N. E. Schlörer¹, D. Diaz*¹

¹ NMR facility, Department of Chemistry, University of Cologne, 50939 Cologne, Germany, ljuetten@smail.uni-koeln.de
² Institute of Biochemistry, University of Cologne, 50674 Cologne, Germany

NMR spectroscopy is one of the most powerful analytical techniques suitable not only for characterization of chemical compounds but also for investigation of chemical reactions. Even though, from a historical perspective, NMR spectroscopy has been typically associated to chemical research, in the last decades the use of NMR-based methods in biology has been boosted as the technique provides important information on both, the shape of large biomolecules¹ and the molecular recognition processes involved in biological events.²

The so-called BioNMR field has been firmly settled into structural biology although some restrictions apply, concerning e.g. molecular weight of the studied systems³ and the almost imperative need of isotopically labeled material (i.e. ¹³C, ¹⁵N)⁴. Nevertheless, research for drug design has extensively profitted from the latest developments in this area and, nowadays, a kit of very well documented NMR experiments can be successfully employed to explore novel biological/medical applications.⁵

Herein we present a step-by-step guide of the basic experimental and computational methods required to derive the 3D structure of short, non-labeled peptides in solution.


Keywords: NMR Spectroscopy, Solution NMR, Structural Biology, Molecular Recognition, Ligand-protein interactions

Category: Structure
From reaction mixtures containing azobis(n-pyridine) derivatives (azpy; n = 2, 4) and Cu(NO$_3$)$_2$ or Bi(NO$_3$)$_3$ in the presence of HX (X = I, Cl) we obtained new 1-D and 0-D lead-free pseudo-perovskite structures. In the presence of HI we received (4,4’azpy)[Cu$_2$I$_4$] and the isomer (2,2’azpy)[Cu$_2$I$_4$] as well as the polyiodide-containing structures (4,4’azpyH)$_2$[Cu$_2$I$_4$(I$_3$)$_2$]$_2$ and (4,4’azpyH$_2$)[BiI$_6$]I$_3$. From HCl we received the analogue compounds (4,4’azpyH$_2$)[CuCl$_4$] and (4,4’azpyH$_2$)[BiCl$_5$].

We reported six novel structures with azpy as a partially protonated organic counterpart. For most of the copper containing structures, EPR measurements confirmed the oxidation state of +II that determine the amount of hydrogens at the azpy molecule. An occurring problem during crystallization is the formation of polyiodide species that hinder a direct connection of the metal halide coordination polymers needed to build a perovskite-like network.

**Keywords:** Single crystal XRD; solid-state chemistry; crystallization  
**Category:** Structure
Synthesis of ternary acetylides with main group elements

Marc Hetzert, Uwe Ruschewitz*
Institute of Inorganic Chemistry, marc.hetzert@uni-koeln.de

Ternary acetylides with alkali and transition metals like Na$_2$PdC$_2$ and Na$_2$PtC$_2$ are known for more than 20 years.[1] But it was only in 2015 that the first ternary acetylides Li$_2$TeC$_2$ and Na$_2$TeC$_2$ containing just main group elements were reported.[2] Since solid state reactions at elevated temperatures were not successful to produce Li$_2$TeC$_2$ and Na$_2$TeC$_2$ their syntheses were performed in liquid ammonia at -60 °C.[2]

As our group has a long-standing expertise with reactions in liquid ammonia to synthesize (hydrogen)-acetylides, we have tried to reproduce the results given in ref. 2 and to expand them to the other alkali metals like potassium, rubidium and cesium. For each alkali metal we obtained a new compound, but due to the low crystallinity of the resulting materials their crystal structures still have to be solved. In a next step we reacted selenium and sulfur with alkali metal (hydrogen)-acetylides in liquid ammonia according to:

$$A_2C_2 + Se_{\text{NH}_3(\text{liq.})} \rightarrow A_2SeC_2 \quad (A = \text{Li-Cs})$$

$$AC_2H + Se_{\text{NH}_3(\text{liq.})} \rightarrow ASeC_2H \quad (A = \text{Na-Cs})$$

The syntheses with sulfur and selenium led to orange, brown or yellowish crystalline powders. XRD analyses showed new crystalline phases in all products (Fig. 1).

From X-ray powder diffraction data the crystal structures of ASeC$_2$H ($A = \text{K, Rb, Cs}; \text{Cmc}_2_1, Z = 4$) were solved and refined. They contain the unusual and unprecedented $[\text{Se-C≡C-H}]^-$ anion, which was confirmed by IR spectroscopic data. Upon heating obviously $C_2H_2$ is released leading to cubic phases with diffraction patterns similar to those obtained with tellurium. These cubic phases have yet to be investigated.


Keywords: Selenium, syntheses in liq. ammonia, ternary acetylides, XRPD
Category: Structure
Use of the ESA effect as a quantification method for nanoparticles

*Alexander Renner, Markus Schütz, Daniel Moog, Thomas Fischer and Sanjay Mathur*

Institute of Inorganic Chemistry, sanjay.mathur@uni-koeln.de

In the recent years, nanotechnology became a promising field in cancer research by using hyperthermia behavior of magnetic nanoparticles in cancer treatment as well as the usage of mesoporous silica (SiO$_2$) nanoparticles as biocompatible drug carrier. Thereby, surface functionalization is one of the most important techniques enhancing the specific uptake of cancer cells and their treatment. Nevertheless, surface group and ligand quantification is still one of the biggest challenges in nanoparticle modification but indispensable in regard of their possible medical applications. Nearly all known quantification methods of surface-bound ligands including direct and indirect methods are affected by size or charge distributions of particles, resulting in scattering of measurement results.

To close this knowledge gap, we report a novel quantification method of freely accessible hydroxide groups located on the particle surface of SiO$_2$ nanoparticles, utilizing the electrokinetic sonic amplitude (ESA) effect supported by simultaneous conductivity measurements. Furthermore, the degree of surface functionalization of phase-pure quasi-cubic hematite (α-Fe$_2$O$_3$) particles having a zeta potential of about +50 mV was monitored through their reaction with 10-undecynoic acid and citric acid as ligand molecules, paving a profound way of ligand quantification. Thereby, all results highlight the usage of ESA techniques by its high potential as quantification method in nanoparticle surface modification.

**Keywords:** Nanoparticles, Zeta potential, Electrokinetic sonic amplitude, Silica, Hematite

**Category:** Structure
On the way to fluorous coordination polymers and metal-organic frameworks with alkaline earth and divalent rare earth metals

**Daniel Smets, Uwe Ruschewitz**

_Institute of Inorganic Chemistry, daniel.smets@uni-koeln.de_

Although the CSD database lists over 70,000 crystal structures of coordination polymers (CPs) and metal-organic frameworks (MOFs), to the best of our knowledge only very few examples with divalent lanthanides are published up to now.[1] It is the aim of my work in this field to synthesize and characterize divalent CPs and MOFs with ligands with different degrees of fluorination.

Further, our group tries to evaluate the influence of fluorination on the thermal stability and functionality of the resulting CPs and MOFs, e.g. compounds with trimesate ligands (BTC\textsuperscript{3-}) with different degrees of fluorination are investigated. We were able to establish routes for the synthesis of mono-, di-, and perfluorinated trimesate precursors as mono-potassium salts.[2,3] Up to now I was able to successfully synthesize and characterize two isostructural MOFs with Eu\textsuperscript{II} and Sr\textsuperscript{II} as metal centers and further MOFs with mono- and difluorinated trimesate and alkaline earth metals. First investigations point a surprising stability of the Eu\textsuperscript{II} compound to air, obviously caused by the “shielding” chemical environment in the coordination network, which seems to be a promising option to obtain other coordination polymers with even less stable, divalent rare earth metal cations. The stabilization of metals like Sm\textsuperscript{II} or Yb\textsuperscript{II} in CPs or MOFs requires the synthesis in inert organic solvents.[4] However, trimesic acid and their fluorinated analogues as mono-potassium salts are typically only soluble in polar solvents like water, which in turn would lead to an oxidation of the divalent lanthanides to their stable trivalent oxidation state.

To increase the solubility of the organic linker molecules in organic solvents I have tried to synthesize compounds with large organic cations like tetrabutylammonium ((Bu)\textsubscript{4}N\textsuperscript{+}) of these linkers. Details of my first synthetic approaches and the properties of the resulting compounds with fluorinated trimesate anions will be presented as well as first reactions with Ln\textsuperscript{II} salts.


**Keywords:** coordination polymers, linker design, metal-organic frameworks, structure and function

**Category:** Structure
Studies towards the synthesis of new proline-derived secondary structure mimetics

Judith Bruns, Ronald Kühne and Hans-Günther Schmalz*

Institute of organic Chemistry, Judith.bruns@uni-koeln.de

Designed peptide mimetics interfering with relevant protein-protein interactions represent potentially powerful drugs for the treatment of cancer and other diseases.[1,2] In this context, the Schmalz-group is focusing on the interaction between proline rich motives (PRMs) and specific binding domains (PRDs, e.g. the EVH1 domain) to prevent the invasion and migration of cancer cells. In order to do so, the research concept aims at the synthesis and use of proline derived dipeptide modules (ProMs) which are structurally rigidified in a PRD-recognizing conformation.

By proper combination of such ProM units, low-molecular weight PRD-inhibitors can be developed to potentially modulate key physiological processes in a therapeutically useful fashion.

As a proof of concept, we designed and synthesized a novel class of pentapeptidic ligands, containing ProMs as diproline mimetics. Binding studies on those molecules revealed their powerful inhibitory properties towards the EVH1-domain: besides surpassing the wildtype ligand in terms of binding affinity, these inhibitors also showed antimeatalastic behaviour in in vivo investigations.


Keywords: Peptide chemistry
Category: Synthesis
The Efficient Preparation of Radiolabelled Aromatic Amino Acids via Cu-Mediated Radiofluorination using Ni-Complex Frameworks

A. Craig¹, N. Kolks¹, E. Urusova¹, B. Zlatopolskiy¹,², B. Neumaier*¹,²

¹Institute for Radiochemistry und Experimental Molecular Imaging (IREMB), University Clinic Cologne.
²Institute for Neuroscience and Medicine, INM-5: Nuclear Chemistry, Forschungszentrum Jülich.
austin.craig@uk-koeln.de

The aim of this project was to study the feasibility of Ni-BPB auxiliaries as easily-removable dual-protecting group functionalities for the facile preparation of radiofluorinated aromatic amino acids (AAA) via alcohol-enhanced Cu-mediated [¹⁸F]fluorination.¹ Target AAA tracers include 2-/4-[¹⁸F]Phe, and 2-[¹⁸F]Tyr, which could be applied for tumor detection, 6-[¹⁸F]FMT, clinically used for imaging of the dopaminergic brain areas/neuroendocrine tumors, and 4-[¹⁸F]FTrp, potentially suitable for visualization of Trp metabolism. The flexibility of the synthetic approach allowed for a range of corresponding and novel α-methyl [¹⁸F]AAA derivatives to be accessed.₈

A number of Bpin-substituted Ni-complexes of AAA have been successfully radiolabelled according to the established alcohol-enhanced Cu-mediated radiofluorination.¹ The attractiveness of this methodology is highlighted by the commercial availability/facile preparation of the requisite compounds for precursor synthesis and the correspondingly high ¹⁸F-incorporation rates (RCCs). For example, 4-[¹⁸F]FTrp was prepared in an unoptimized RCY of 25% and in excellent radiochemical and stereochemical purity.ᵇ,c The procedure was successfully implemented to an automated module furnishing 4-[¹⁸F]FTrp in 16% RCY.ᵈ


Keywords: Nuclear chemistry; Positron Emission Tomography, organic chemistry; radiolabelling
Category: Synthesis

<table>
<thead>
<tr>
<th>(S)-Ni-XBX-[¹⁸F]AAA醀</th>
<th>RCC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-[¹⁸F]FPhe</td>
<td>57</td>
</tr>
<tr>
<td>2-[¹⁸F]FPhe</td>
<td>60</td>
</tr>
<tr>
<td>α-Me-2-[¹⁸F]FPhe</td>
<td>59</td>
</tr>
<tr>
<td>6-[¹⁸F]FMT</td>
<td>53</td>
</tr>
<tr>
<td>α-Me-6-[¹⁸F]FMT</td>
<td>38</td>
</tr>
<tr>
<td>2-[¹⁸F]FTyr</td>
<td>66</td>
</tr>
<tr>
<td>4-[¹⁸F]FTrpb²</td>
<td>93 (25,c 16ᵈ)</td>
</tr>
</tbody>
</table>

⁸ SYN2
Functionalization of Thiosemicarbazones for Catalytic and Nuclear Medical Purposes

Alexander Haseloer, Axel Klein*

Institute of inorganic Chemistry, ahaseloe@mail.uni-koeln.de

Thiosemicarbazones are very good chelating ligands due to their thion–thiol tautomerism. They form complexes with various transition metals that are interesting for catalysis like nickel, iridium and platinum, and metal isotopes for nuclear medicine like $^{52}$Mn, $^{61}$Cu and $^{188}$Re. But despite the successful coordination of these metals very few ligands of thiosemicarbazones have been optimized for such specific tasks.$^{[1,2]}$

Air stable cyclometallated iridium hydrides of the type $[\text{Ir}^{\text{III}}\text{H}(\text{PPh}_3)_2\text{L}_C]$ (see Scheme) could be synthesized and tested in the oxidation of formaldehyde in order to gain knowledge about the role of the structural backbone of the ligand. Our results show that the thiosemicarbazone ligand needs to contain an acidic proton ($= R^3$) to perform the oxidation.

For nuclear medicine several amino acid conjugated thiosemicarbazones were synthesized by transformation of the N–α position of amino acids. Thiosemicarbazones from Lysine were synthesized at the sidechain. These were generated in order to label peptides with radioactive isotopes. The thiosemicarbazides were condensed with 2-carbonyl pyridines to generate 1-N-heterocyclic thiosemicarbazones. These were shown to coordinate Rhenium carbonyls to form complexes of the type $[\text{Re}^{\text{(CO)}_3}\text{Ln}]$ (see Scheme).$^{[3]}$


Keywords: Nuclear Medicine, Coordination Chemistry, Organometallic Chemistry, C–H activation
Category: Synthesis
Herein, we report the synthesis and characterization of direct carborane-peptide conjugates. Carboranes are non-natural and extremely hydrophobic compounds and turned out to be suitable pharmacophores for diverse biological applications [1]. In this work, we established an efficient procedure for the coupling of carboranes to peptides on solid support. The carborane-peptide conjugates showed remarkably prolonged, and carborane isomer dependent chromatographic retention times. This effect can be used to generate non-natural lipopeptides with fine-tuned properties. This fine-tuning might be interesting for biologically active peptides, such as cell-penetrating peptides (CPPs). CPPs are still of great interest in biological applications, especially considering drug delivery systems. Regarding this, we further demonstrate the coupling of carboranes to the cell-penetrating peptide sC18, which was developed in our working group [2]. The carborane-sC18 variants turned out to enhance the cell-penetrating abilities and are therefore an interesting candidate for several applications.


Keywords: Synthesis; carborane; boron; solid-phase peptide synthesis; cell-penetrating peptides; amphipathic peptides

Category: Synthesis
Due to the worldwide shortage of petrochemical based resources, the usage of renewable bio-based raw materials for established and novel products becomes increasingly important.[1] Such bio-based resources are already used for the fabrication of a variety of products, e. g. paper, lubricants, detergents or cosmetics. In the future they are expected to emerge in many more applications in industry and household.[1]

A very promising approach relies on the use of glycolipids as a source of hydroxy fatty acids.[2] Microbial glycolipids are produced for instance via fermentation from natural resources such as plant oils and sugar.[3] After fermentation, complex product mixtures are obtained with the composition depending on the microorganism, substrate and fermentation time.[3]

The successful use of microbial glycolipids and hydroxy fatty acids derived therefrom as bio-based intermediates requires reliable analytical methods as well as robust manufacturing processes for the synthesis and cleavage of bio-based molecules. In order to obtain hydroxy fatty acids as bio-based intermediates, the acidic cleavage of microbial derived glycolipids was investigated by HPLC-, NMR- and IR-measurements.

A reliable synthesis route was developed and the product was thoroughly characterized.


Keywords: sustainable; synthesis; hydroxyl fatty acid; characterization
Category: Synthesis
On the way to Bis-cyclopalladation
Pd(II)-Complexdimers of 2-phenylpyridine derivatives

René von der Stück, S. Zielke, E. J. Keloglu, A. Klein*
Institute of Inorganic Chemistry, rene.vonderstueck@uni-koeln.de

Since almost 20 years bis-cyclometallated platinum(II)complexes of the type [(dphpy)PdX] (dphpy = 2,6-Diphenylpyridin) are known and well characterized. Their synthesis is straight forward and works out for a variety of different ligand systems.[1] After a first cyclometallation leading to µ-dichlorobridged dimers a second cyclometallation in boiling dmso is performed leading to bis-cycloplatinated monomers. Despite all chemical and physical similarities between palladium and platinum no bis-cyclopalladation of tridentate C^N^C ligands could be performed yet and bis-cyclometallated compounds in general are still very scarce.[2] In order to provide a better understanding of these compounds and to finally obtain a successful bis-cyclopalladation a variety of 2-phenylpyridine derivatives was synthesized and their optical and electrochemical properties investigated.

(Figure 1: Synthesis of cyclometallated platinum(II)- and palladium(II)dimers and subsequent bis-cyclometallation in the case of platinum.


Keywords: organometallics; cyclometallation; synthesis; catalysis
Category: Synthesis
Singlet oxygen ene reaction of enolether-Michael systems

**Diana But, Axel G. Griesbeck**

*Institute of Organic Chemistry, diana.but@uni-koeln.de*

Organic peroxides exhibit a variety of biological activities.[1] Because of their high antimalarial, antibacterial, cytotoxic, and other pharmacological properties, they present an important source of lead structures for drug development. The role model for peroxide drug research and the most prominent example is the natural sequiterpene artemisinin, which has high antimalarial properties.[2] Several synthetic peroxides have been synthesized over the last decades and some of them were tested successfully for their antiparasitic activities.[3] One approach for synthesizing peroxides is the photooxygenation of olefins with singlet oxygen. The singlet oxygen ene reaction has been studied on a range of olefins with different substituents, regarding their reactivity and regioselectivity.[4] So far, the reaction of olefins with two substituents with opposite electronic properties, has not been studied. In this work, the singlet oxygen ene reaction of enolether-Michael systems has been investigated.

![Singlet oxygen ene reaction of an enolether-Michael system to its hydroperoxide.](image)

**Figure 1**: Singlet oxygen ene reaction of an enolether-Michael system to its hydroperoxide.


**Keywords**: singlet oxygen, organic peroxides, pharmacological activities

**Category**: Synthesis
Studies towards the total synthesis of Dysiherbol A

**Julian Erver and Hans-Günther Schmalz**

*Institute of Organic Chemistry, jerver@smail.uni-koeln.de*

Dysiherbol A (1), a representative of the hydroquinone-sesquiterpenes, was recently isolated from a marine sponge. The natural product features a novel tetracyclic carbon skeleton and three adjacent quaternary carbon centers. Interestingly, Dysiherbol A shows submicromolar inhibitory activities towards the cancer cell line NCI-H929 and the protein complex NF-κB, regulating inflammatory, immunological and carcinogenic processes. Because of the potent bioactivity and intriguing structure, Dysiherbol A is both an attractive and challenging target compound for total synthesis.\[1\]

In this work, the carbon skeleton of Dysiherbol A shall be constructed through an intramolecular Friedel-Crafts acylation, using enone 3 as a precursor.\[2\] With ketone 2 in hand, Dysiherbol A (1) should be accessible via α-methylation and Grignard reaction. The synthesis of enone 3 shall be realized using the building blocks 4-6, featuring an enantioselective one-pot 1,4-addition / α-alkylation.\[3\]

![Chemical structures](image)


**Keywords:** Natural product synthesis, Friedel-Crafts reaction, enantioselective 1,4-addition

**Category:** Synthesis
Luminescence and Electrochemistry of Platinum(II)-Complexes bearing tridentate \( C^{\text{N}\text{C}} \) and \( C^{\text{N}\text{N}} \) Ligands

Maren Krause and Axel Klein*

Institute of Inorganic Chemistry, maren.krause@uni-koeln.de

Luminescent platinum complexes attracted huge interest over the last years. For example they can be used as dopants for optoelectronic devices like organic light-emitting diodes (OLEDs).[1] Platinum(II) complexes are square planar with \( d^8 \) configuration. Thus, the \( d_{x^2-y^2} \) orbital is strongly antibonding. During d-d transition population of these orbital causes a significant distortion of the excited state geometry which favors non-radiative decay. Strong field ligands, e.g. carbanionic ligands, can enhance the luminescence properties: The strongly antibonding \( d_{x^2-y^2} \) orbital is raised in energy, therefore non-radiative decay via the d-d excited state is suppressed and emission predominantly occurs through MLCT (metal-to-ligand charge-transfer) states.[2] Tridentate cyclometalating \( C^{\text{N}\text{N}} \) or \( C^{\text{N}\text{C}} \) ligands additionally benefit of huge rigidity.

However, the exact influence of the molecular structure on the luminescence quantum yield is still not fully understood. Therefore, we designed new ligands starting from the elementary structures shown in Fig. 1 and investigated the photophysical and electrochemical behavior of the corresponding platinum complexes.

![Figure 1: Structures of C^{\text{N}\text{C}} (2,6-diphenyl-pyridine) and C^{\text{N}\text{N}} (6-phenyl-2,2'-bipyridine) platinum(II) complexes with anionic coligands X⁻ (e.g. halides). Note, that a neutral coligand leads to non-charged C^{\text{N}\text{C}} complexes.](image)


Keywords: complexes, organometallics, phosphorescence, electrochemistry

Category: Synthesis
The development of a new, efficient synthetic strategy for the stereoselective synthesis of trisubstituted olefins represents an important challenge in synthetic organic chemistry. As the established methods have several drawbacks and cannot be considered to be atom-efficient\(^1\), we investigated the so far never described combination of intermolecular enyne cross metathesis followed by 1,4-hydrogenation. We investigated the scope and limitations by choosing different functionalized alkynes and alkenes as substrates. 15 successful examples delivering exclusively the trisubstituted \(E\)-alkene in moderate to good overall yield proved the broad applicability of our reaction sequence.\(^2\)

An application of our methodology in the synthesis of a late stage precursor of \(\alpha\)-Tocopherol (Vitamin E\(^3\)) showed already promising results and we hope for further application of our methodology in other organic syntheses in the future.

\[\text{[1]} \quad \text{Sheldon, R.A. Pure Appl. Chem.} \quad \text{2000}, \quad 72, \quad 1233.\]
\[\text{[2]} \quad \text{Ratsch, F., Schmalz, H.-G. Synlett} \quad \text{2018}, \quad 29, \quad 785.\]
\[\text{[3]} \quad \text{Schlundt, W., Dissertation, Universität zu Köln, Köln 2017.}\]

**Keywords:** Ru catalysis, enyne cross metathesis, 1,4-hydrogenation, synthesis of alkenes, diastereoselectivity

**Category:** Synthesis
Eurysterols A and B are cytotoxic and antifungal sulfated sterols from an undescribed sponge of the genus *Euryspongia* collected in Koror, the capital of Palau, in 2000. Both compounds were isolated as colorless oils, elucidated and tested for biological activities by Boonlarppradab from the Scripps Institute of Oceanography in California in 2007. Eurysterol A possesses a cholastane skeleton consisting of 27 carbon atoms, which is substituted by two hydroxy groups, a pentacyclic ether bridge between the C-8 and C-10 positions and a sodium sulfate group at C-3. Compared to A, Eurysterol B differs only by a double bond at C-22 at the side chain. Both compounds were tested for their cytotoxic activities against human colon tumor cell lines (HTC-116) and for fungal inhibition against wild-type and amphotericin B-resistant strains of *Candida albicans*. Eurysterol A was the more active compound in both cytotoxicity and fungal inhibition assays with an IC$_{50}$ value of 2.9 µg/mL and MIC values of 15.6 µg/mL, respectively.

The combination of their interesting and useful bioactivity and structural uniqueness make Eurysterols worthy candidates for synthesis. Therefore, the aim of my thesis is to synthesize Eurysterol A, the most active and structural simple member of the Eurysterol family. The main strategy contains inter alia: a Mukaiyama hydration and hypoiodite reaction as key steps.


**Keywords:** steroids; natural products; synthesis; cobalt catalysis; hypoiodite reaction

**Category:** Synthesis
Night-time chemistry in atmosphere by nitrate radical and detection by CRDS

Vaishali Vardhan, Hendrik Fuchs and Andreas Hofzumahaus
Institute of Energy and Climate Research-8, v.vardhan@fz-juelich.de

A large number of trace gases are released into the atmosphere by anthropogenic activities and also by plants. During daytime, OH oxidizes the pollutants such as volatile organic compounds which further form particles and ozone is also produced in a quasi-catalytic reaction chain. During nighttime, there are no primary photolytic sources of OH. Instead, higher nitrogen oxide species, the nitrate radical NO₃, can be formed in the reaction of NO₂ with ozone. NO₃ can further react with NO₂ during night to form di-nitrogen pentoxide (N₂O₅), which is in thermal equilibrium with NO₃, because it is thermally labile. The formation of these nitrogen oxides during nighttime can be regarded as a nocturnal reservoir for ozone, because NO₃ is rapidly photolyzed by sun-light on the next morning leading to the reformation of NO and NO₂, which is further photolyzed and reforms O₃. However, the nocturnal reservoir can be reduced by several processes. On the one hand, N₂O₅ can be hydrolyzed in heterogeneous reactions on aerosol surfaces leading to the formation of nitric acid (HNO₃) that cannot easily reform NOX species. On the other hand, NO₃ can also oxidize air pollutants like organic compounds similar to OH during the day.

In comparison to daytime oxidation by the hydroxyl radical, much less research on nighttime chemistry by NO₃ has been done in the past. Therefore, the impact of this chemistry on the oxidative capacity of the atmosphere and on the formation of secondary pollutants is not well known. This is partly due to lack of sensitive instrumentation that allows for routine measurements of NO₃ concentrations in the atmosphere. We have developed a custom-built instrument at Forschungszentrum Juelich which is based on cavity ring down spectroscopy. NO₃ can be detected by absorption spectroscopy, because it has a strong absorption at 662nm. The challenges of detection are due to low mixing ratios of NO₃ in the atmosphere (parts per trillion range) and the potential loss of NO₃ on instrument surfaces. The sum of NO₃ and N₂O₅ can be simultaneously observed in a second, heated cavity in which N₂O₅ is thermally decomposed to N₂O₅. First results of the instrumental characterization will be presented.

Keywords: Quasi-catalytic reaction, heterogeneous reaction, nocturnal reservoir, cavity ring down spectroscopy.
Category: Synthesis
Interfacial properties of binary Lennard-Jones chains mixtures by molecular dynamics simulation

Granados-Bazan, E.L.; Quiñones-Cisneros, S.E.; Deiters, U.K.*
Institute of Physical Chemistry, egranad1@smail.uni-koeln.de

Systems of linear tangent chains composed of bonded Lennard-Jones interaction sites (monomers) are being studied using Molecular Dynamics simulation in the NVT ensemble. As its name suggests, the molecules of this model have no restriction neither for bonding or torsional angles. The vapor-liquid interface is studied through direct simulation of an explicit liquid film varying the temperature and molar composition of the system. Janeček’s [1] long-range corrections (LRC) have been added to address cutoff radius effects; density profiles, surface tension as well as the microscopic components of the pressure tensor are calculated using the mechanical definition.

The intention is to study the \{C_2+C_1\}, \{C_6+C_2\}, \{C_8+C_2\}, \{C_{10}+C_2\}, \{C_{10}+C_1\}, \{C_{20}+C_1\}\footnote{The notation \(C_n\) refers to chains composed of \(n\) monomers or interaction sites.} systems to gain a deeper insight into density profiles behavior as the asymetry of the molecules increases. So far, the systems have been simulated using about 2250 interaction sites and \(4\times10^6\) integration steps. Although mixtures with short molecules like \{C_2+C_1\} and \{C_6+C_2\} show good results with acceptable statistical noise, systems involving longer molecules need much more molecules and time to reach an equilibrium state [2], making the problem suitable for a high performance computing system.


Keywords: Molecular dynamics; Lennard-Jones chains; surface tension.
Category: Theory
Special Thanks to our supporter:
Frank Schneider, IMCD Deutschland

IMCD Deutschland has more than 50 years of experience in the sales, marketing and distribution of specialty chemicals and food ingredients in Germany, actively serving the German chemical industry. Their team of experienced technical sales specialists passionately strives for a second to none service to guarantee rapid successes for both their principals and customers alike.

Principals working with IMCD Deutschland can expect maximum flexibility and devotion to grow their business: from providing a fully centralised international set-up to a more intimate local approach depending on the specific requirements.

Their customers profit from tailor-made solutions from our comprehensive and complementary product portfolio. Understanding and fulfilling their needs from supply chain to technical support is paramount for their dedicated sales teams.

IMCD Deutschland also operates two Technical Service Centres in Cologne- one Coatings and one Pharmaceutical laboratory- offering new product development and formulation support as well as practical and theoretical training to ensure the continued improvement of their strong technical service for customers. In addition, IMCD Deutschland also operates a HSEQ lab in Hürth, providing a quality control service for re-filled or mixed products and managing samples sent to customers worldwide, as well offering additional technical support for IMCD.

Frank Schneider
Country Manager of IMCD
Imprint

University of Cologne
Department of Chemistry
Greinstr. 4-6
50939 Cologne, Germany
Email: heike.henneken@uni-koeln.de
Web: http://www.cgsc.uni-koeln.de

Limit of Liability/Disclaimer of Warranty: The current publication was carefully worked and produced with best efforts in preparing. Nevertheless, the authors and publisher do not accept any liability for the accuracy of the information, instructions and for mistakes within.

© University of Cologne, Department of Chemistry, Germany, April 2018.

All rights reserved (including those of translation into other languages). No part of this publication may be reproduced or transmitted in any form or by any other means, electronic or mechanical, including photocopy, recording, or any information storage and retrieval system, without permission in writing from the publisher. Registered names, trademarks, etc. used in this booklet, even when not specifically marked as such, are not to be considered unprotected by law.

Coverdesign: Ömer Taşpınar

Editors/Production: Ömer Taşpınar, Dr. Heike Henneken (CGSC coordinator)

Organizational team: Kay Merkens, Ines Schmidt, Sarah Segieth, Ömer Taşpınar, René von der Stück, and Dr. Heike Henneken (CGSC coordinator)
1st PhD Symposium
April 24, 2018
Present your research!

POSTER ABSTRACT SUBMISSION DEADLINE
March 29, 2018