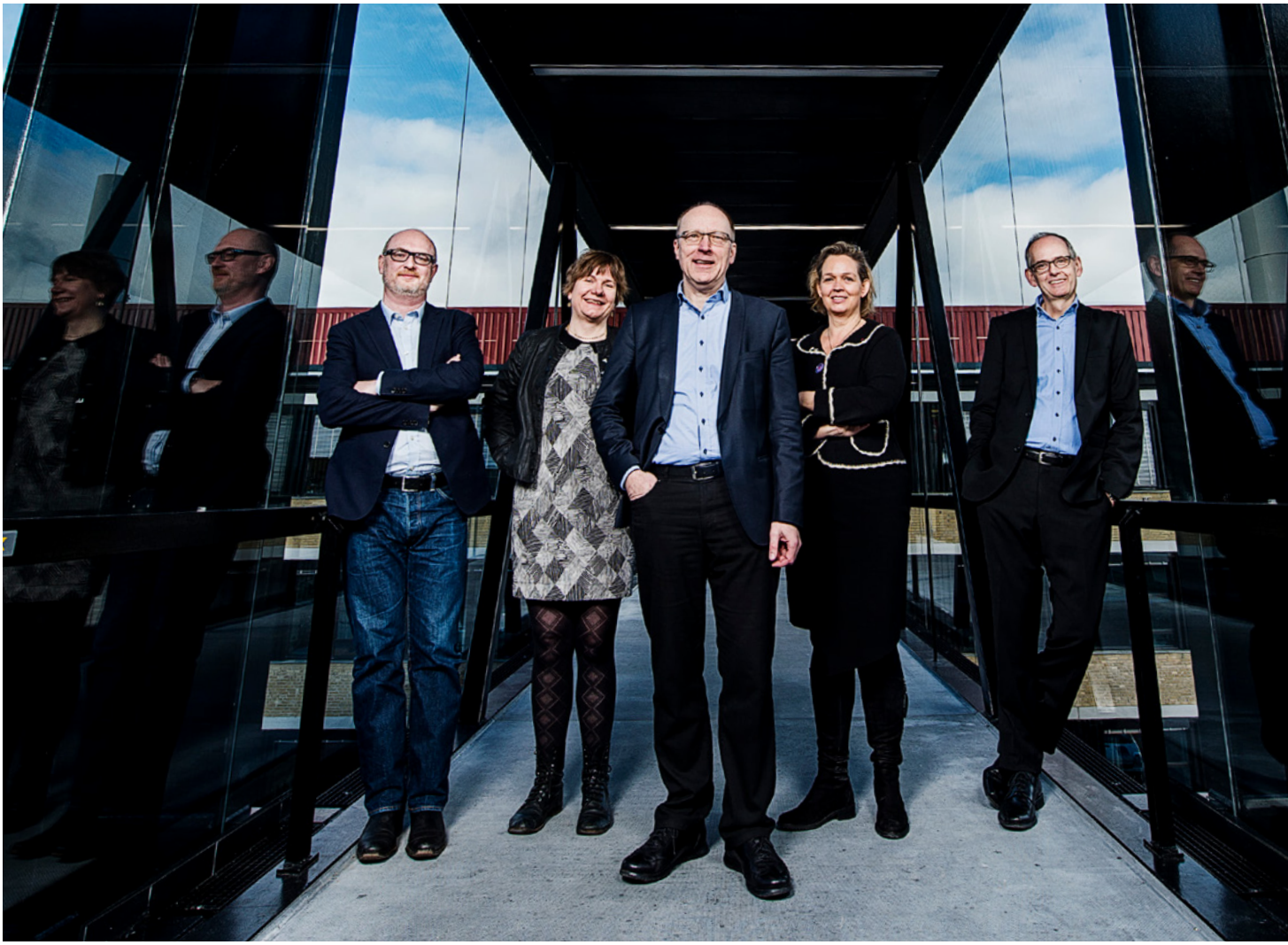
Technical University of Denmark

DTU

## Annual Report 2015

# Department of Chemistry



*The DTU Chemistry Management Group 2015*
*(left to right) Klaus B. Møller, Pernille Harris, Erling H. Stenby, Charlotte Mondrup and Jens Ø. Duus.*

# Moving forward - changing gear

Welcome to the DTU Chemistry Annual Report 2015 – an exciting year for the Department where we have finally moved in to the new DTU Chemistry building with state-of-the-art laboratories for research and teaching.

I can proudly say that our platform is now solid and ready to meet the challenges of chemistry for the future. We have the right infrastructure and skilled employees in all functions with a powerful blend of innovative scientists, a strong curriculum, and skilled support units. Together we are ready to find the best solutions by constantly thriving for excellence.

## Academic Excellence

The vision of DTU Chemistry is an internationally recognized department for advanced fundamental and applied chemistry that develops and transforms ideas to the benefit of sustainable societal development.

Our focus on EU collaboration is paying off and several larger projects were granted in 2015. The joint European project, PIPPI, is one example, where DTU Chemistry is the overall coordinator. Over the next four years, the project will develop a public database with cutting-edge knowledge about proteins in pharmaceutical formulations. You can read more about it in the article *Essential knowledge of proteins to guide pharmaceutical industry* in this Annual Report. It is our goal to increase the involvement in EU projects significantly over the next five years.

Signing of several framework agreements with industrial partners supports our knowledge sharing and collaboration, both within scientific work and education. The latest agreement is with Haldor Topsoe supporting catalysis and materials development. Our goal is to increase the number of such agreements in the future years.

Within the past five years, DTU Chemistry has been very successful in attracting young, talented researchers who have distinguished themselves with prestigious grants from the Sapere Aude, Ydun, and Villum Young Investigator programmes.

We are strengthening our Faculty further with addition of two new professor positions to be employed in 2016.

We are in the final stage of building the new NMR Center, funded by the Villum Foundation and DTU. DTU Chemistry has strong NMR competencies, and now we can make an even stronger contribution to the development of chemistry and biotechnology at DTU. NMR spectroscopy is one of the key techniques for studying organic molecules, and has therefore been chosen as a strategic initiative at DTU. The new center will allow DTU to conduct cutting-edge NMR research. It is to be inaugurated in the summer 2016.

Furthermore, we have a share in the new research center, the Center for Hyperpolarisation in Magnetic Resonance. My goal is that with the powerful blend of talent at the Department, DTU Chemistry will be able to attract funding for a Research Centre from the Danish National Research Foundation within the next five years.

## Educating the future

I'm also excited to note the continuous success in nursing scientific talent in a systematic approach to create a focused dialogue with the entire chain of talent from high school over BSc and MSc level and all the way to a PhD degree. We have been successful in attracting the very young talents and recruited the best for our BSc programmes in chemistry. In the coming years we will focus more on recruitment of graduate students as well as keeping on developing our teaching of chemistry students, for instance by focusing more on e-learning.

For the PhD School we thrive for Academic Excellence by recruiting the best Danish and foreign candidates. We offer them a good working environment, modern facilities, and we educate them to become excellent, young scientists. 14 young scientists got their PhD degree in 2015 – please have a look on their exciting projects in the chapter *PhD from DTU Chemistry.*

I see a hardworking Department focusing on academic excellence through people, projects, and results in order to keep our strong position in the future. Together with the rest of the DTU Chemistry Management Group, I invite you to get inspired to possible collaborations by this Annual Report 2015.

*– Erling H. Stenby*

# Two sections reinforcing the academic spirit

DTU Chemistry's trademark is scientific expertise founded in fundamental research in applied chemistry.

In 2015 The Department was organized in two major sections: Organic and Inorganic Chemistry with Professor Jens Ø. Duus as Head of Section, and Physical and Biophysical Chemistry with Associate Professor Klaus B. Møller as Head of Section – each section with underlying research areas.

For the Heads of the two Sections it is important to share knowledge, to listen to and to be inspired by each other – both within the entire Department, in between the sections as well as in smaller research groups. They both believe that this will reinforce the academic spirit throughout the Department and beyond.

The Section of Organic and Inorganic Chemistry covers four research areas:

Catalysis and Sustainable Chemistry (CSC) – NanoChemistry – Metalloprotein Chemistry – Organic Chemistry

The Center for Catalysis and Sustainable Chemistry is focusing at catalysis, gas separation and absorption, development of new materials, process design and conversion of biomass. NanoChemistry is focusing on electrochemistry and bioelectrochemistry with a long track record for applying electrochemical STM (Scanning Tunneling Microscopy) with prime focus on application of graphene nanoparticles. The Metalloprotein Chemistry combines diverse fields such as molecular biology, coordination chemistry, biochemistry, computational chemistry and biophysics. The focus of Organic Chemistry is Catalysis, Chemical Biology, and Spectroscopy. The core discipline is organic synthesis with interfaces to biology, medicine and natural products

**Organic and Inorganic Chemistry**

**Physical and Biophysical Chemistry**

chemistry. Computational chemistry and kinetic/mechanistic studies are also represented, as well as expertise in high-field NMR spectroscopy.

"The four areas are strong and well-functioning, and as Head of Section I wish to support and develop more synergy within the section, but also to the Section of Physical and Biophysical Chemistry," says Jens Ø. Duus.

The Section of Physical and Biophysical Chemistry comprises activities within pure and applied physical chemistry and analytical chemistry. It covers both micro-scopic atomic-level descriptions and the macroscopic thermodynamic approach. Common themes are the behavior of small to medium sized molecules as well as proteins, and many projects involve spectroscopy, crystallography and quantum chemical modeling. The research areas are Biophysical and Biomedicinal Chemistry; High Pressure Phase Behavior for Oil and Gas Production; Colloid Chemistry and Functional Interfaces; Theoretical, Computational and Femtochemistry; IR, THz, and Raman Spectroscopy.

"In 2015 The Department of Chemistry became physically united. We now sit closer together, and it can provide a more natural integration and knowledge sharing across the research groups. Today we have the best conditions for an open dialogue and greater knowledge sharing," explains Klaus B. Møller.

**Academic Excellence**

Another goal for Klaus B. Møller as Head of Section is to strengthen physical and biophysical chemistry in the education of the future chemists and raise the academic level even further.

"I want to ensure that DTU is the place for young students to find Academic excellence," he says.

To Jens Ø. Duus it is important to ensure the experimental infrastructure.

"We have both the facilities and the in-house workshop, but we need to secure that we'll continue to have state-of-the-art equipment," he explains.

Both Heads of Sections invite you to a new initiative with a joint seminar series in order to inspire and attract colleagues, students and other curious people. To follow the research at DTU Chemistry, please look at our website kemi.dtu.dk/english/Research

## DTU Chemistry Faculty

**Organic and Inorganic Chemistry**

Jingdong Zhang
Jens Ulstrup (Emeritus 2016)
Susanne L. Mossin
Robert Madsen
Hans Erik Mølager Christensen
Charlotte Held Gotfredsen
Søren Kegnæs
Rasmus Fehrmann
Peter Fristrup
Jens Øllgaard Duus
Mads Hartvig Clausen
Anders Riisager
Qijin Chi
David Tanner (Absent)
Jens H. von Barner
(Absent. Emeritus 2016.)

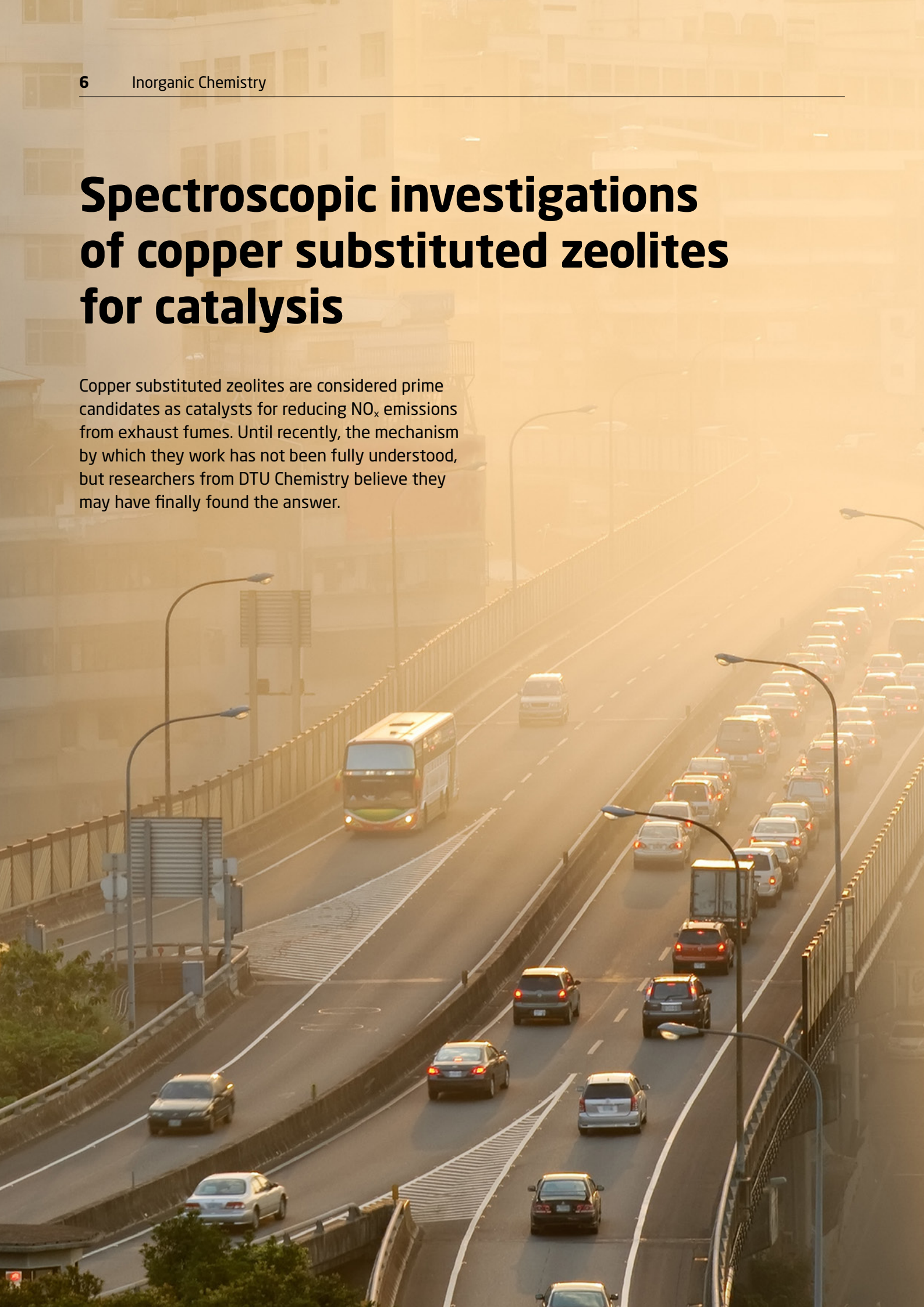
**Physical and Biophysical Chemistry**

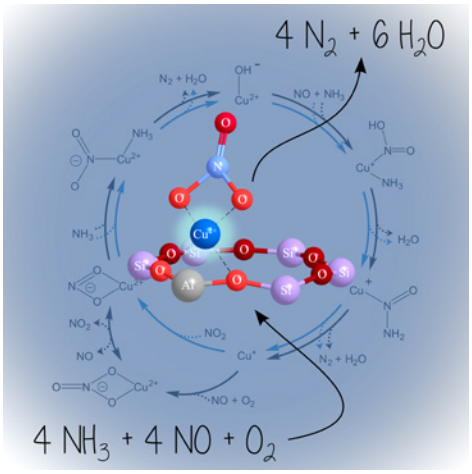
Günther H. Peters
Wei Yan
Rolf W. Berg
Irene Shim
Niels Engholm Henriksen,
René Wugt Larsen
Klaus Braagaard Møller
Esben Thormann
Jonas Rosager Henriksen
Kasper Planeta Kepp
Pernille Harris
Kenny Ståhl

Read more about us:

# Spectroscopic investigations of copper substituted zeolites for catalysis

Copper substituted zeolites are considered prime candidates as catalysts for reducing $NO_x$ emissions from exhaust fumes. Until recently, the mechanism by which they work has not been fully understood, but researchers from DTU Chemistry believe they may have finally found the answer.






*The catalytic cycle. For the first time a chemically consistent reaction cycle is suggested for the environmentally important selective catalytic reduction (SCR) reaction for removal of harmful NO and $NO_2$ from exhaust gases. Illustration by PhD Anita Godiksen*

Stricter laws regarding emission requirements for exhaust gases are being introduced in many countries around the world as concern for the environment increases. Reducing $NO_X$ emissions from the exhausts of diesel engines and power plants is an important part of this, which can be achieved through the selective catalytic reduction of NO to $N_2$ by ammonia. Copper substituted zeolites have been shown to be effective catalysts for this reaction. Especially copper chabazite has been proven to be particularly useful for application in diesel engines.

These catalysts will no doubt see widespread use in the future, although a problem facing scientists studying them has been understanding the reactant mechanisms by which the catalysis occurs. Suggestions have been put forward and all have had shortcomings, but Associate Professor Susanne Mossin from DTU Chemistry believes that she, collaborators at Haldor Topsøe A/S and the University of Turin have now solved the conundrum.

A specialist in electron paramagnetic resonance (EPR) spectroscopy, Susanne Mossin originally approached the task by evaluating the existing literature. "I could see that the suggestions put forward for the mechanism did not seem right," she explains. "I tend to approach these challenges from an inorganic chemistry perspective, so in the end, rather than try and find fault in these suggestions, we tried to come up with a solution working from the very beginning, writing down all the possible reactions that could take place between the molecules involved. After working on it for a while, everything suddenly fell into place and I could see straight away that we had something promising."

According to the scheme, which was recently published in the journal ACS Catalysis, the reaction can be very simply divided into a reduction of the catalyst by by NO + $NH_3$ and an oxidation either by NO + $O_2$ or by $NO_2$. $N_2$ and water are produced in both the oxidation and reduction steps. Together these constitute a complete catalytic cycle. Every step of the cycle uses only common stable molecules, eliminating the issues of charged or "half molecules" present in other suggestions.

Since finding a solution to the catalytic cycle, Susanne Mossin, and her PhD student Anita Godiksen have been performing *in situ* EPR spectroscopy to back up their work. "Catalysts do not enter their active state until you expose the catalyst system to the conditions of the reaction," says Susanne Mossin. "It is therefore not good enough to investigate these materials with *ex situ* methods – you need to look at them under *in situ or operando* conditions." EPR spectroscopy is undemanding instrument-wise compared to other advanced spectroscopic methods, making it particularly suited for *in situ* and *operando* investigations for systems containing EPR active species. Collaborators from the University of Turin have provided extra experimental evidence in the form of *in situ* X-ray absorption spectroscopy and Fourier transform infrared spectroscopy.

With the framework for the catalysis mechanism now in place, Susanne Mossin will spend the remainder of the three-year project confirming the individual steps, investigating differences between the different types of active sites as well as looking for deactivation mechanism investigating differences between the different types of active sites of the catalyst system. "Knowing what makes a catalyst work and what stops it working is useful," she explains. "Catalysts must be designed to fit specific criteria such as lifespan and stability, so the more knowledge you have about how they work, the more you can tweak them to work more efficiently in certain conditions."

## Published article

T. V. W. Janssens, H. Falsig, L. F. Lundegaard, P. N. R. Vennestrøm, S. B. Rasmussen, P. G. Moses, F. Giordanino, E. Borfecchia, K. A. Lomachenko, C. Lamberti, S. Bordiga, A. Godiksen, S. Mossin, P. Beato, A Consistent Reaction Scheme for the Selective Catalytic Reduction of Nitrogen Oxides with Ammonia *ACS Catal.* **2015**, *5*, 2832-2845.

## Next step ...

... is twofold: To use the unrivaled sensitivity of EPR spectroscopy to investigate the reactivity and rate of the individual active sites and to investigate the mechanism of catalyst deactivation.

## CONTACT

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# Essential knowledge of proteins to guide pharmaceutical industry

Knowledge of the properties of proteins right down to atomic level is essential for making it easier and faster for the pharmaceutical industry to manufacture protein-based drugs in liquid form. Over the next four years, a joint European project, PIPPI, with DTU Chemistry as the overall coordinator, will develop a public database with cutting-edge knowledge about the properties of proteins in pharmaceutical formulations.

Although, a variety of new therapeutic proteins has been developed showing benefits in the treatment of ailments like diabetes and cancer, obtaining physical stability in formulations still remains one of the biggest challenges to pharmaceutical scientists. This is mainly due to the limited knowledge of the way these proteins interact in the solutions in which they are marketed.

The European Horizon2020 programme has funded € 4 M to develop a database over a four-year period, which shall ensure more efficient development of the very extensive and protracted screening process that protein drugs, e.g. next generation treatments of cancer, autoimmune- and metabolic diseases, undergo before being put on the market.

**Towards protein-based drugs**

The healthcare sector is challenged as the average age of Europe's population is rising. Greater focus is being devoted to manufacturing safe and risk-free drugs, while the requirements for evaluating new drugs and their possible side effects are becoming stricter. All of this has moved the pharmaceutical industry towards protein-based drugs, which have high specificity and relatively few side effects. But there is very little knowledge of the way these proteins behave in the solutions in which they are sold.

**The Scientific challenge**

"Drugs as we know them from the pharmacy typically consist of an active substance such as paracetamol in painkillers. In addition to the active substance, there are other substances in the finished tablet, for example, excipients facilitating that the tablet is dissolved in the right way and stabilizing the active substances. Similarly, excipients are added to protein solutions to increase the stability of proteins," explains Pernille Harris, Associate Professor at DTU Chemistry, who is the overall coordinator for the entire project, which has a large number of partners from both the pharmaceutical industry, European universities, and other stakeholders.

"Today, the pharmaceutical industry carries out very extensive screening of all these excipients to test their performance with the active substance. It is this screening process that we hope to be able to streamline with this project," she says.

Few universities in Europe have formulation of biologics as a scientific subject. Consequently, the pharmaceutical industry is required to train hired scientists.

Jens Bukrinski, senior scientist from Novozymes A/S says: "We are proud to be part of a consortium comprising leading researchers in protein and pharmaceutical science in Europe. We have high expectations that PIPPI will help boosting the knowledge in the field. Furthermore, we hope that PIPPI will result in increased focus to the field."

**15 new PhD positions from 2016**

While e.g. a substance like paracetamol is a small organic molecule, which will be stable for a long time in a tablet, protein-based drugs are very sensitive and the challenge in respect of

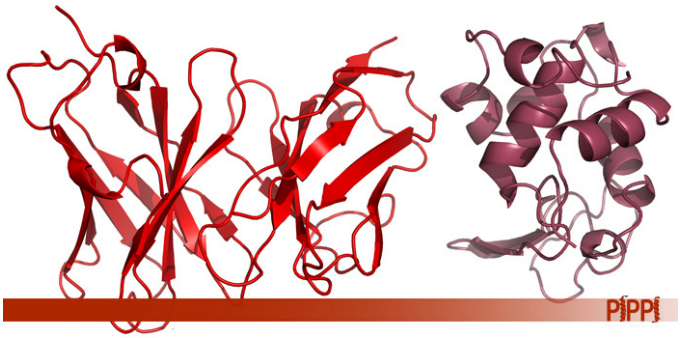
protein drugs is to eliminate the risk of their degradation in aqueous solution or even of precipitating out from the solution.

"The idea of the project is to establish a comprehensive protein library, representing the different properties that proteins can have, for example in terms of size, charged distribution, hydrophobicity and flexibility," explains Pernille Harris.

"Subsequently, they will be studied using state-of-the-art techniques from the pharmaceutical industry and finally their abilities to interact with various substances at the atomic level will be characterized. Then everything will be gathered in a database," she continues.

In the project 15 new PhD positions will be created and the students will work towards this goal with the various partners. Ultimately, knowledge right down to the atomic level on a variety of protein may make it easier to predict the behaviour of a similar, new protein targeted for use by the pharmaceutical industry. The aim is for the protein to be stable in the solution, and although this result can be achieved today, getting there may be a long and hard process.

"And at the end of the day, you may still not be completely certain why it actually works," says Pernille Harris.




**The Consortium PIPPI**
Scientists in the field of structural and computational biology, biophysics, protein formulation and stability have formed the consortium 'Protein-excipient Interactions and Protein-Protein Interactions in formulation', PIPPI.

PIPPI, funded under the European Horizon2020 programme, is an Innovative Training Network (ITN) concerning the challenges in formulation of protein-based drugs. PIPPI will combine systematic investigations of the physicochemical behavior of a number of proteins with an in-depth understanding of the molecular interactions behind the macroscopic behavior. The overall objective is to develop methodologies, tools and databases to guide the formulation of robust protein-based therapeutics in the future.

The consortium consists of both academic and industrial partners located in Denmark, Sweden, Germany and United Kingdom. Each of the project partners contributes excellent competence in their particular areas.

**PIPPI and DTU Chemistry**
The overall project coordinator Associate Professor Pernille Harris as well as Associate Professor Günther Peters from DTU Chemistry contribute to PIPPI. The core research in the group is in the area of Structural and Computational Biology. Our contribution to PIPPI will be studies of the overall atomic structure of the proteins and their intermolecular interactions. Pernille Harris is working with protein crystallography, small-angle X-ray scattering and X-ray absorption spectroscopy. Günther Peters, leader of the Chemistry at the Interface to Biology research group at DTU Chemistry, has extensive expertise in in-silico modelling techniques.

## *Partners*

Technical University of Denmark
University of Copenhagen
University of Manchester
Ludwig-Maximilians-Universität München
Lund University
Max IV Laboratory
MedImmune Ltd., Cambridge, UK
Novozymes A/S
Wyatt Technology Europe GmbH
NanoTemper Technologies GmbH

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Read more on pippi-itn.eu by using this QR-code

# A radical change in the form of teaching

Associate Professor Günther Peters from DTU Chemistry has turned the course Physical Chemistry for biological sciences upside down. For several years, the average grades have been too low and the failure rate too high.

Associate Professor Günther Peters had a hard time accepting that students found Physical Chemistry so difficult. He therefore decided to do something about it. It would, however, require a radical change in the form of teaching.

Günther Peters applied for funds for this process and was granted financial support from the pool for special input in the field of e-learning at DTU, and received help from DTU LearningLab.

**A different form of teaching**

It has, however, not been straightforward for the visionary professor to transform the type of teaching on a traditional course where the students are used to attending lectures and then working together in groups. Many of the students felt that they lost their grasp of the course contents when the weekly lectures were replaced by group work, for example, where the different groups themselves were responsible for studying their areas of theory in depth and then presenting their work to each other.

But Günther Peters' whole idea is that the students must take responsibility themselves for learning the theory, with the lecturer and the assistant teachers offering assistance, that is meeting the students where they are in terms of scientific knowledge and providing the support they need to increase their level of understanding.

Following the reorganization, 'Physical Chemistry for biological sciences' now consists of just four lectures and two experimental studies that conclude with a report.

A number of videos related to the learning outcomes have been prepared, and all are available on Coursera. Here the students can also find quizzes supporting the theory.

Finally, the course comprises a major project that requires students to study theory in depth and present their research to each other. They are subsequently to apply this theory to working with interdisciplinary problem issues.

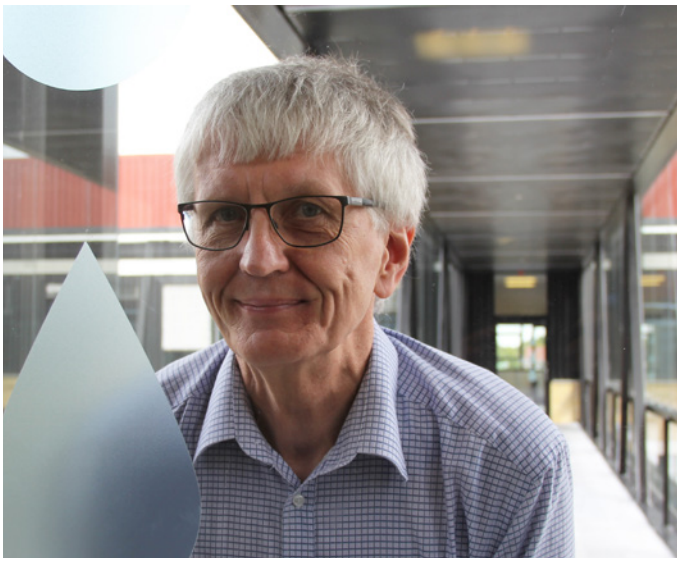
The course as a whole concludes with an oral exam, where the students are given the questions in advance.

**Student experiences**

Michelle, Anjila, Martina, Jian Gui, and Stephane are sharing experiences over lunch. They have all followed and completed the Physical Chemistry for biological sciences course despite their frustrations—especially the feeling of not having had an overview of the syllabus during the course.

"Project work requires that your group discusses theory and plans presentations. This is a good thing, as it increases your understanding of and commitment to the course," says Michelle.

"But you end up only focusing on your own group's area of theory, which makes it hard to subsequently understand the other groups' areas of theory," several of the students agree. On the other hand, they feel that they have become more independent when it comes to acquiring knowledge and thinking for them selves, and they have had a lot of practice in doing oral presentations.

"I think it's a cool subject. It opens your eyes to what the world looks like and provides an understanding of the mechanisms behind physical chemistry," says Anjila, putting a lid on her coffee to keep it heated.

"However, I've missed a common thread in the course and an overview of the syllabus, which has been frustrating," says Martina. This criticism has been noted and taken seriously by both lecturers, teaching assistants, and the study board, and Martina therefore believes that future students will learn much more on the course.

Tine Frederiksen, a teaching assistant who has just finished her MSc in Advanced and Applied Chemistry, is also convinced that these wrinkles will have been ironed out the next time the course is taught.

"The students have been brilliant at providing constructive criticism about the course, which is sure to help the next batch of students," she says. She herself has also contributed to estimating what the students can and cannot reasonably be expected to achieve in the way of assignments, and to ensuring that they remain motivated and challenged throughout the course.

Tine also thinks it is very positive that Günther Peters has chosen to react to the high failure rate and the previous course evaluations. She has previously seen other course supervisors who did nothing, and who expressed the view that it is simply a matter of the students being less gifted. But not Günther Peters from DTU Chemistry.

"But with this new form of teaching on the course, he's chosen to do something different to increase the knowledge of physical chemistry for the students," she says smiling.

**The common thread**

In spite of the fact that the students on the reorganized course have felt a bit like guinea pigs, they all praise Günther Peters for his great commitment, because they really feel that he wants the best for them and has been highly responsive to both their frustrations and their constructive feedback.

Associate Professor Günther Peters says that the new form of teaching on the course has given him better one-on-one time with the students and that the students have become better. The oral exam has just been completed, and it turned out to be a good experience for both the lecturer and the students—the grade point average was an impressive 7.1.

Günther Peters has used the past months to clarify the common thread in the course, so that the students get a better overview of the course from day one. He has received many new ideas, based on the constructive feedback from the students, both during the course and from the course evaluation.

## *Follow the course*

You can follow the lectures by using the QR-code below

Or watch an experiment: Eksperiment - Nulstroemspotentialet

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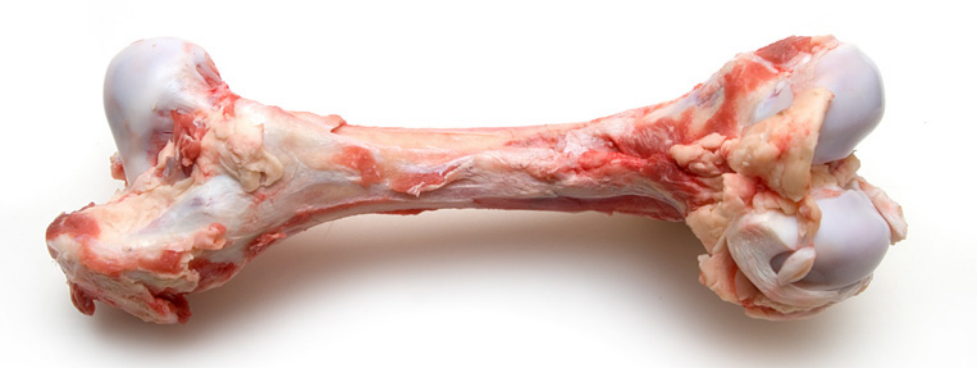
# Waste product becomes bio-plastic

Glycerol is a low-value byproduct from bio-diesel production. A new process patented by DTU Chemistry can convert glycerol into the monomer allyl alcohol which can be polymerized into plastic.



Production of bio-diesel by trans-esterification of sorted household garbage and waste from the meat industry is already a large step forward for sustainability. However, trans-esterification also yields about 10% glycerol. Presently bio-diesel producers can sell this byproduct at symbolic prices only – hardly covering the cost of capturing and purifying the glycerol. Now, researchers at DTU Chemistry has found a feasible route for turning glycerol into allyl alcohol. Allyl alcohol is a valuable raw product in the fine chemicals industry, where this monomer – normally produced from crude oil – is polymerized into a range of polymers.

"A catalytic route was identified about five years ago, but that was relying on the rare and expensive element Rhenium as catalyst. We have shown that the same result can be achieved using Molybdenum instead. Since the cost of Rhenium is about 100 times higher than the cost of Molybdenum, this is a significant step towards a process which can be implemented by industry," says Associate Professor Peter Fristrup, DTU Chemistry. "A further practical advantage of the new process is that it will be pretty straightforward to add to the existing glycerol purfication process."

**Zero is left for the landfill**

The plant operated by Daka near Horsens produces about 5,000 tons of glycerol annually as a byproduct from bio-diesel production. The process developed by Peter Fristrup's group will be able to convert at least 25% of the glycerol into allyl alcohol.

Allyl alcohol can be converted into a wide range of chemical building blocks – for example into acrylic acid which can be polymerized to give the super-absorbent polymer known from diapers.

"The remaining fraction can be processed further, and the end product here is a dark, robust substance which can be burned - so at least you will get energy from it. One of the possible solutions for the surplus of glycerol is to burn it – but glycerol burns notoriously badly. Our technology actually solves this problem by generating a much more easily flammable product through water removal. In this way the entire raw material will have been used, leaving nothing to be deposited at a landfill," says Peter Fristrup. "This will be a fine example of the circular economy where byproducts are seen as a resource rather than waste."

DTU Chemistry is currently discussing further cooperation with Daka as well as other partners interested in 100% bio-based allyl alcohol, acrylic acid or 1,4-butane diol.

**More economic than fermentation**

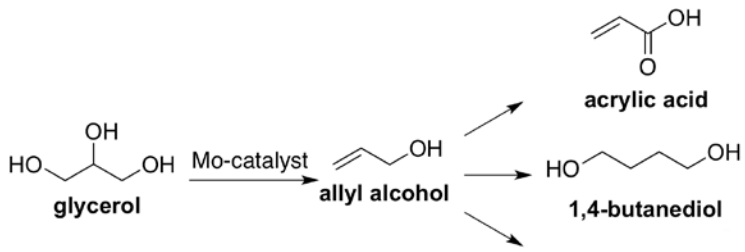
The group has filed several patents concerning the Molybdenum-catalyzed process and similar processes for bio-mass conversion.

A different application is being pursued in collaboration with industry partner Haldor Topsoe as part of the national BIOVALUE-initiative (total budget DKr. 170 mio.). Specialized in catalysis the company has developed several catalysts for production of lactic acid from sugar.

"I cannot reveal the details yet, but in general terms I can say that the perspective is that Topsoe is able to obtain other products than lactic acid using the same catalysts. These products may be processed into new bio-based polymers – hopefully in a more efficient way than alternative routes – or they may find completely new applications," states Peter Fristrup.

Lactic acid can be polymerized into PLA, Poly Lactic Acid. PLA has several applications. One example is as a benign matrix for 3D printers, another one is for bio-degradable disposable cups and plates.

"I would like to stress that one should not always assume that products originating from biomass sources are more biodegradable than similar products from crude oil. This is a widespread




*Dethlefsen, Fristrup, WO 2015/028028 A1*


misunderstanding. However, in the case of PLA the biodegradability is actually very good, making this polymer highly suitable for disposable products."

Lactic acid is traditionally produced by fermentation. The Topsoe process are more direct, chemical routes to the end product. Unlike fermentation they do not involve tanks with water and microorganisms and thus avoids amounts of slurry which needs to be treated afterwards. Further, the catalytic processes can run at elevated temperatures, since no microorganisms need to be nursed, which will speed up processes and improve economy.

**Mimicking oil formation**

Besides patent applications, the group has a steady production of scientific articles. Peter Fristrup is confident that this situation will continue despite an overall backlash for bio-plastics:

"The price of crude oil is currently very low. This has made it harder for companies to create good business cases for bio-plastics. Still, it is beyond doubt that bio-plastics will play a major role in the future. After all, crude oil is a non-renewable source with high $CO_2$ burden, while straw, food waste and a number of other bio-materials are renewable, cheap, and $CO_2$ neutral raw materials. In one case we can even incorporate $CO_2$ into the product and if surplus electricity from wind power is used this could potentially make the bio-plastic $CO_2$ negative!"

Research at DTU Chemistry has shown that a number of products produced from crude oil today can also be produced from biomass, he notes:

"As chemists we are extremely proud of these achievements. One prominent challenge is the fact that biomass has a much higher oxygen content than crude oil. Removing this oxygen is tricky, since the processes needed typically have very high activation energies – meaning they would not occur spontaneously or only very slow in nature. In fact, nature has spent millions of years removing this oxygen under the extreme conditions which prevail in the crude oil reservoirs. We are now able to mimic these processes in our laboratories – only at much, much higher rates. It may well be that these processes are not in high demand just now, because we cannot compete with the current low prices for crude oil, but I am confident that they will find applications. This could either be in contexts where a higher price is acceptable due to the better climate protection properties of biomass-derived products, or it could be because different products are accessible such as for example PLA which cannot be produced from crude oil."

Until the end of 2015, the research described in the article was mainly financed by a Sapere Aude Research Leader Award obtained by Peter Fristrup from the Danish Council for Independent Research and has resulted in 3 patent applications and more than 10 research publications. The activities with Haldor Topsoe continue under a new grant from the Danish Innovation Fund. Professor Robert Madsen coordinates DTU Chemistry participation in the new project, which also involves industry partners Haldor Topsoe (Denmark) and Perstorp (Sweden).

## Published articles

*ChemCatChem* **2015**, *7*, 1184 - 1196.
*Chem. Eur. J.* **2015**, *21*, 3435-3442.
*ChemSusChem* **2015**, *8*, 613 - 617.
*Inorg. Chem.* **2015**, *54*, 11031-11036.
*ACS Catalysis* **2015**, *5*, 3638-3647.

## Patent applications

Dethlefsen, Fristrup, Process for reducing the oxygen content of biomass using vanadium-based catalysts, filed December 22, 2014.

Dethlefsen, Fristrup, Process for reducing the oxygen content of biomass using molybdenum-based catalysts, filed November 20, 2014.

Dethlefsen, Fristrup, Process for functionalizing biomass using molybdenum catalysts, filed August 29, 2014. WO 2015/028028 A1.

## CONTACT

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# DTU Chemistry heading for the future

Since the inauguration of the new building 211 in the fall 2015, DTU Chemistry is now physically a unified department able to provide even more sublime research and teaching results.

The new Building 211 provides DTU Chemistry with absolutely firstclass laboratory facilities, a host of support functions, and a new shared foyer area where students, lecturers and researchers can meet and mingle in an informal setting.

**The biggest fume cupboard in Denmark**

On the ground floor, there are four large teaching laboratories, each with room for up to 24 students, while the first floor houses eight research laboratories for exploring various areas of organic chemistry.

The laboratories also feature a large and technologically advanced machine: 110 fume cupboards distributed over an area of 3,200 $m^2$, that need to be able to handle the special requirements posed by state-of-the-art chemistry education and research.

The ceiling height of more than six metres ensures sufficient air flow to the labortories' 110 fume cupboards. A specially future-proofed system for piped gases is to supply the laboratories with gases, while a central vacuum and cooling system services all fume and ventilation cupboards.

The new Building 211 is built at the end of the existing buildings 206 and 207 and is a direct extension of the renovated Building 209, which now serves as the central chemical handling unit.

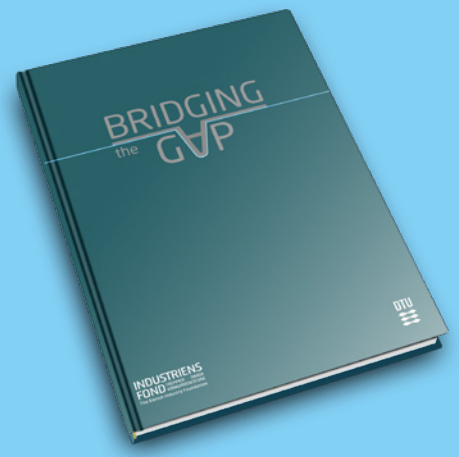
**DTU Chemistry Support Units**

To support state-of-the-art facilities, research and teaching, DTU Chemistry continues to offer the right support and complementary skills. The central administrative and technical staff functions at the Department – being Laboratory Technicians, Machine Center, IT Support, Communication & Graphic Design, Administrative Support, Project and Innovation Support, Reception and Service Center – keep adding value to the researchers in educational and scientific matter making the unified Department prepared for the future challenges in chemistry.

**FACTS ABOUT BUILDING 211**

- Size: 3,200 $m^2$
- Budget: DKK 111.5 million
- Client: DTU
- Turnkey consultant: COWI
- Architect: Rørbæk & Møller Arkitekter
- Constructed: 2011-2015

# The bridge is built – a new innovation model




The idea of starting your own company is plausible and the entrepreneurial spirit is vibrant. DTU Chemistry together with DTU Photonics have been the driving force in the Bridging the Gap-project – a new innovation model to increase the rate at which Danish universities can spinout new technology ventures.

The BtG-model is a generic tool guiding users from the earliest phases of match making between researchers and industry experts all the way – over the bridge – to the successful establishing of a new company spun out from the university and on to the market with new customers and growing revenue.

**Spinouts from DTU Chemistry**
Specshell and GlycoSpot are examples of two companies spun out from DTU Chemistry, proving that the BtG model is one useful way to move forward if you want to bring knowledge from universities and introduce it to the market in the hands of competent entrepreneurs.

Today Specshell ApS is an engineering company specialized in development, design, manufacturing and operation of advanced analytical systems based on Infrared spectroscopy. The company is based on years of research and development, resulting respectively in a Master Thesis and a PhD dissertation for the founders of the company at DTU Chemistry.

The initial basis for Specshell was the development of specialised test cells to be used for in-line IR spectroscopy. The focus has since been extended to the development of a complete in-line IR Spectroscopic system, which is expected to provide radical new opportunities for process control and analytical work in the brewing industry.

GlycoSpot is a biotechnology company specializing in the development and production of assay kits for carbohydrate active enzymes based on the industry-standard 96 well format. GlycoSpot enzyme screening kits provide high-throughput, reproducible solutions for enzyme screening in a simple 4 step procedure.

Enzymes are essential components of many industrial processes and are increasingly regarded as attractive alternatives to traditional chemical-based processing since they are effective, environmentally benign, cost effective, and precise in their mode of action.

The company is based on knowhow developed at the University of Copenhagen (KU) and the Technical University of Denmark (DTU).

**Bridging the Gap Model**
The BtG model deploys a systematic, decentralized approach to collaboration with experienced, external entrepreneurs who have successful spinout experience and detailed market insight. The results from BtG show that experienced entrepreneurs and researchers working together improve the commercialization process. The model opens up the research process to include external knowledge about markets and industries together with the technical focus of the research teams.

Student involvement has had a positive effect on the spin-out cases, so future perspectives of BtG include a strengthened link to the educational systems.

## *Next step ...*

Bridging the Gap (BtG) was a 2-year project funded by The Danish Industry Foundation. The goal of Bridging the Gap has been to create a new innovation model which will increase the rate at which Danish universities can spinout new technology ventures. The BtG model serves now as best practice in the knowledge exchange established between Danish universities (DTU, ITU, AAU and CBS) and is a default tool for spinning out companies.

## CONTACT

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# PhD from DTU Chemistry

DTU Chemistry takes pride in educating PhDs at the highest international level. We present a diverse research education in modern chemistry which contributes to the development of cutting edge science at the Department. The goal for all PhD-students is to publish in leading journals and participate in leading international conferences during their three year long research education.

**PhD ChemClub**
The main purpose of the PhD ChemClub at DTU Chemistry is to strengthen the professional and social network between PhD-students at the Department. The PhD ChemClub is run by PhD-students and they arrange several annual events: PhD Symposium, Post-graduate career events with experts from industry and academia, Inspiring talks by invited speakers, Social gatherings. We invite interested candidates to have a look at our website kemi.dtu.dk/English where you can read more about our PhD programme as well as the DTU Chemistry research areas.

**Power Performance**
Excellent scientists must also be able to communicate their research results efficiently. DTU Chemistry offers each PhD-student an intensive communication course (1,5 ECTS) to practice their presentation techniques to perfection. A cornerstone in this regard is the annual PhD Symposium at which stakeholders from the industry are invited to attend both oral presentations and a postersession by the Departments PhD-students.

**Contact us!**
In the following you can witness the diverse DTU Chemistry PhD Defences 2015. All supervisors invite you to get in touch, if you are interested in the full thesis, in further information or in possible collaboration.

You are also welcome to contact the Head of the PhD School, Professor Erling H. Stenby, Head of Department, ehst@kemi.dtu.dk

# Synthetic Molecules with Protein-like Folds

Since naturally occurring proteins and peptides are most often rapidly metabolized, synthetic peptide analogs are of increasing pharmacological interest.

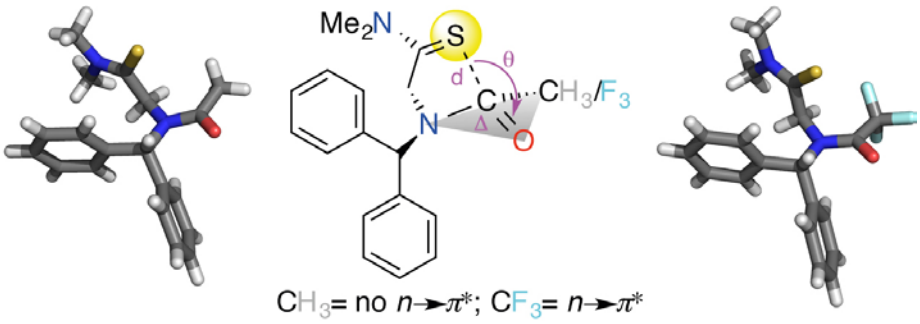
As proteins and peptides are responsible for countless processes in living organisms, they are attractive lead compounds for development of drugs to treat a variety of diseases. A prime example is the administration of insulin to treat diabetes. However, naturally occurring proteins and peptides are often unfit as drugs for a number of reasons, including short half-lives in the body. It would thus be highly attractive to manufacture synthetic molecules that mimic the structure and function of proteins or peptides but with improved pharmacokinetic properties. This thesis presents progress in techniques designed for this purpose.

The activity and distinct selectivity of proteins and peptides are highly dependent on the accurate three-dimensional presentation of functional groups. Modulation of these properties is desired in development of pharmaceutical agents. However, due to proteolytic instability and poor cell permeability, peptides have traditionally been considered unsuitable as drug candidates. Synthetic peptide analogs are suggested as a tactic to bypass these undesired properties. Specifically, so-called peptidomimetics with the ability to mimic the structural elements in proteins are of interest.

A prominent type of peptidomimetics is α–peptoids (N-alkylglycines or simply peptoids) which are able to fold into helical and sheet-like arrangements. However, their backbone flexibility is increased due to presence of tertiary amides. In this project, backbone interactions that possibly account for stability of peptoid secondary structures were probed. Stereoelectronic modifications such as thioamidation and trifluoroacetylation were applied to a series of peptoid monomer model compounds. It was demonstrated that carbonyl-carbonyl interactions could be probed in peptoids by trifluoroacetylation.

Synthesis of backbone-fluorinated oligopeptoids proved unsuccessful, but an intermediate was effectively utilized in the synthesis of fluorinated triazoles as amide bond surrogates via copper(I)-catalyzed azide-alkyne cycloaddition. The fluorine-containing triazole motifs were incorporated in both linear and cyclic peptide targets. In silico studies support this new fluorinated moiety as a viable bioisostere of the amide group.

Further, a small series of backbone-fluorinated α,β-hybrid and β,β–peptoid dimers were analyzed by NMR-spectroscopy, and the results complemented the conformational behaviour of their monomeric counterparts. Synthesis of backbone-fluorinated β–peptoid oligomers was commenced and initial strategies showed promising results for further investigation.




Published: Engel-Andreasen et al. *J. Org. Chem.* **2015**, *80*, 5415-5427.

**Jens Engel-Andreasen**
**PhD**

*"Peptidomimetics with new Backbone Architectures"*

## CONTACT

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Funded by:
**The project was funded by DTU Chemistry.**

**The project included a stay in The Kirshenbaum Laboratory at New York University, NY, USA.**

# Synthetic Studies of Bio-active Molecules

The thesis describes tools for the development of the complicated three-dimensional structure of drug candidates inspired by naturally occurring bio-active molecules.

**Lasse Bohn Olsen**
**PhD**

*"Synthetic Studies of Bio-active Molecules"*

## CONTACT

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**Thomas E. Nielsen, now Director of Protein and Peptide Chemistry, Novo Nordisk**

Funded by:
**The project was funded by the DTU Chemistry Academic Excellence Scholarship. The project included a stay at University of Cambridge, UK.**

Plant extracts have been used for treating ailments for several thousand years. It is known today that the effect of many historical plant-based remedies can be ascribed to certain biologically active compounds. For instance, salicylic acid is the active component of willow bark, which has been used by Native Americans to lover fever, while quinine from bark of the quina tree counteracts malaria. The thesis describes several findings related to drug discovery inspired by such naturally occurring bio-active molecules.

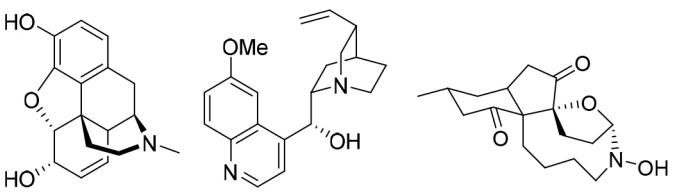
Most approved drugs have simple and easy-to-synthesize structures. However, with the constant evolution of existing diseases and the emergence of new ones, more complicated three-dimensional structures are in demand. For industry to embark on this path, academia has a responsibility to develop new tools and methodologies and to set an example by carrying out synthesis of complicated bio-active compounds.

Firstly, a photo-labile protecting group for hydroxylamines was developed. This is a tool which allows chemists to carry out more types of transformations. The optimized synthesis of this photo-protected hydroxylamine proceeds in 50 % overall yield over four steps, and is ideal for multi-gram scale synthesis.

Secondly, an asymmetric variant of a newly developed method for synthesizing 1,2,3,4-tetrahydrocarbazoles was developed. In this variant of the reaction chiral phosphoric acids are used to induce chirality. It was found that indoles carrying large substituents in the 2-position gave excellent enantiomeric access when employed as the external nucleophile, but at the cost of lower yield due to a decline in reactivity. The final products were obtained in yields ranging from 12 % to 72 % over three steps, with antiomeric excess in the range of 18-98 %.

Thirdly, a number of different routes for synthesis of the bioactive natural product (+)-Sieboldine A were explored with the purpose of testing the practical usefulness of existing methodology known in literature and developed in-house at DTU. An effective way of carrying out the key 1,4-addition using a Hosomi-Sakurai type reaction was identified.

Finally, so-called stapled peptides were explored. The thesis describes the development of stapling linkers designed to increase cell permeability, and the development of a photo-crosslinking moiety, which is applicable in photo-affinity labeling. It is demonstrated that a fragment from a larger protein can be used to selectively label other proteins, even in complicated mixtures. The technique ca easily be employed in assays to determine overexpression of certain genes.




**Morphine (1.1)** **Quinine (1.2)** **(+)-Sieboldine A (3.1)**

*Early bioactive compounds.*

# Chemical Biology of Dietary Fibers

Dietary fibers are known to benefit human health. Synthetic analogs of the natural fiber compounds are attractive for research purposes as their properties can be controlled.

Dietary fibers have gained considerable interest due to their proven beneficial effects on human health. Plant fibers are mainly located in the plant cell wall and consist of many complex and heterogeneous polysaccharides. A number of techniques have been developed for the study of these substances. However, these techniques demand well-defined and pure oligosaccharides. This is traditionally obtained by purification of natural fibers, but this process is highly time-consuming. Therefore, chemical synthesis is currently regarded as superior. The thesis describes a new preparative synthesis method for building blocks related to one large type of dietary fibers, hemicellulose.

During the last decade a range of biotechnological methods have been developed for the study of dietary fibers, including specific monoclonal antibodies, which are a key tool in protein-carbohydrate interactions, enzyme-linked immunosorbent assay (ELISA), and carbohydrate micro-arrays. These all depend on acceptable quantities of specific and pure oligosaccharides. An alternative to isolation of oligosaccharides from the plant cell wall is chemical synthesis.

The thesis describes a new preparative synthesis method for d-xylose and d-xylobiose building blocks through carbohydrate interconversion of d-glucose and d-cellobiose. Both building blocks are intermediates for synthesis of polysaccharides found in arabinoxylans, which is one of the major dietary fiber types in the primary cell wall of a number of plants.

A partly protected d-cellobiose was obtained from cellobioside octaacetate in 37 % yield through eight optimized synthetic steps and subsequently oxidized to β–d-glucuronic acid-(1→4)-thio-β-d-glucuronic acid. The resulting diasaccharide was subjected to catalytic dehydrogenerative decarbonylation, where implementation of an in situ generated iridium catalyst gave the best results after optimization. Using a hydrogen scavenger in the presence of trace amounts of water, the desired xylobioside was achieved in good yield.

As proof-of-concept, the protected xylobioside glycosol donor was applied in the synthesis of oligoxylans, where an octasaccharide was assembled using only three glycosylation steps. Furthermore, the method proved to be an alternative route for selective equatorial deuterium labeling of d-xylose by retention of stereochemistry in the carbon-carbon bond scissoring step.

**Martin Jæger Pedersen**
**PhD**

*"Stereoselective Conversion of Glucosides into Xylosides"*

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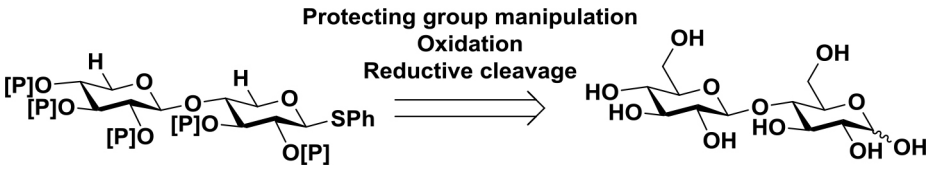
Funded by:
**The project was funded by The Danish Research Council for Strategic Research. The project included a stay at the University of Leeds, UK.**




*Building blochs for synthesis.*

# Identification of Targets for Cancer Treatment

Generation of small molecule libraries by diversity-oriented synthesis (DOS) may reveal the expression of proteins by genes and thereby provide new targets for pharmaceutical treatment.

**Mette Ishoey**
**PhD**

*"Metal-catalyzed Tandem and Multicomponent Reactions: From Library Design to Screening of Epi-genetic Targets"*

## CONTACT

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Funded by:
**The project was funded by DTU. The project included a stay at the Harvard Medical School, USA.**

Cancer and several other severe illnesses are related to genetics. Of interest here are not only the genes themselves but even more so the expression of their products, i.e. proteins. The field is called epi-genetics. A sub-field is reverse chemical genetics in which small molecules are screened against isolated proteins in order to modulate the protein function. The thesis presents novel strategies for synthesis of compound collections for this purpose.

The publication of the human genome sequence in 2001 provided scientists with the opportunity to understand the role of all genes in normal physiology as well as pathology. However, the gene sequence in itself does not provide information on the dynamic expression of proteins which is of key interest to a number of drug discovery applications.

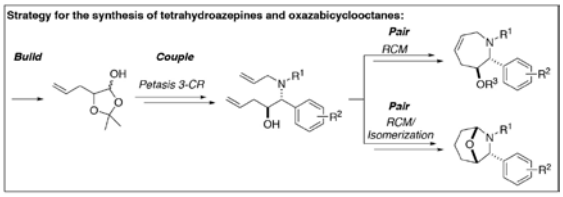
It has been estimated that 10-14 % of the human genome encodes proteins that are likely to be modulated by existing drug-like small molecules. Nonetheless, only around 1,000 of these approximately 30,000 genes have known chemical modulators. As a consequence many human disease-related targets are currently "undruggable".

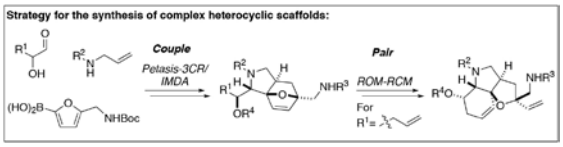
In order to identify more targets, the need for generation of structurally diverse compound collections is apparent. Diversity-oriented synthesis (DOS) aims at efficient generation of small molecule libraries with a high degree of complexity and scaffold diversity. Multi-component, tandem and cascade reactions are ideally suited for DOS since they provide complex frameworks in few steps. Compounds originating from DOS campaigns have been identified as potent and selective inhibitors of protein-protein interactions (PPIs) implicated in different types of cancers.

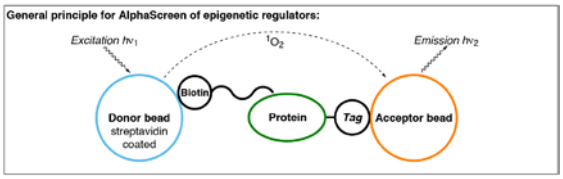
In the project, a tandem RCM/isomerization/nucleophilic addition reaction formed the basis for a library of medium-sized heterocycles. Further, a novel Petasis 3-CR/IMDA reaction cascade in combination with a ROM-RCM sequence provided access to a library of complex sp3-rich heterocycles.

Efficient and high-yielding diversification reactions enabled the introduction of appendage and functional group diversity around the common scaffolds, and library members were synthesized in 5-6 operations. Target-based assays for high-throughput screening were developed for two epi-genetic regulators, namely the bromodomain-containing ATAD2 and the histone methyltransferase NSD1.

In conclusion, epi-genetic regulators are promising drug targets due to the potential of reverting malignant cell-states into more benign phenotypes. In this context, libraries of structurally diverse small molecules hold the potential of providing novel chemical probes for targets previously deemed undruggable. Ultimately such probes could lead to the treatment and prevention of severe diseases such as cancer.



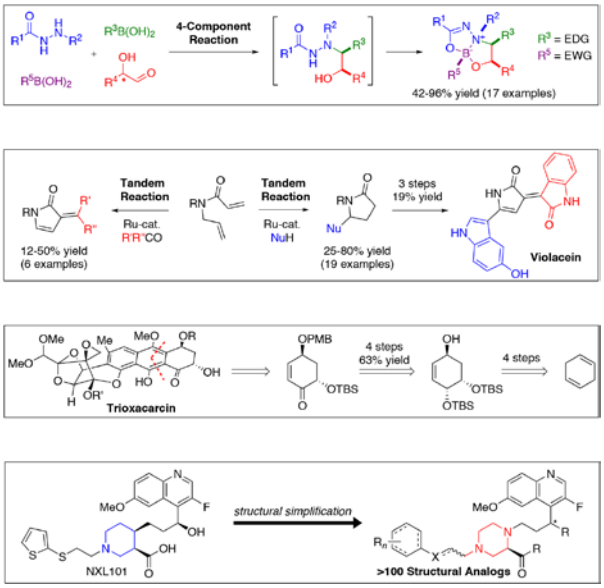



# Efficient Short-cuts in Drug Discovery

Rather than a linear path of consecutive reactions, application of two or more simultaneous reactions can be more effective. Such tandem reactions can open new doors in drug discovery, and facilitate the total synthesis of complex molecules.

Synthesis of large and complex molecules in drug discovery and other organic chemistry involves multiple individual reactions. Traditionally these have been carried out in a linear fashion, where the product of one reaction becomes the starting material for the next. However, it would be faster and more efficient in terms of the resources needed if two or more reactions could be performed simultaneously. This has spurred an interest in tandem reactions and even total synthesis. The thesis contributes with new methodology in this field.




A total of five main contributions are presented.

In the first project, a novel 4-component reaction of hydrazides, α-hydroxy aldehydes and two orthogonally reactive boronic acids, yielding distinct dioxadiazaborocines (DODA borocines) in a highly stereoselective fashion, has been developed. The products have yet to find an application, but may be interesting as pharmaceuticals or as inducers of stereoselectivity in enantioselective reactions.

Secondly, ruthenium-catalyzed tandem reactions combining ring-closing metathesis (RCM), isomerization of double bonds, and either aldol condensation or nucleophilic addition afforded a series of 5-substituted 2-pyrrolidinones and 3-substituted 2-pyrrolones.

Further, tandem methodologies provided a new entry to the total synthesis of the bioactive natural product violacein, which was synthesized in four steps with an overall yield of 13 %.

A fourth project investigated total synthesis of the antitumor antibiotic trioxacarcin. An efficient stereoselective route to a key cyclohexanone fragment was devised. The route featured an enantioselective epoxide rearrangement and proceeded in eight steps from 1,4-cyclohexadiene. This holds promising perspectives for research on trioxacarin structure-activity relationship and in drug discovery.

Finally, an efficient synthetic route to piperazine-based structural analogs of the antibiotic NXL101 has been developed. This substance has been withdrawn from clinical phase I trials due to an off-target interaction. In the project more than 100 structural analogs were synthesized and several of these showed promising antibiotic activity along with a reduced off-target interaction compared to NXL101.

Overall, the five projects have contributed with new knowledge on tandem and multicomponent methodologies and access to scaffolds of interest in drug discovery.

**Mette Terp Petersen**
**PhD**

*"Multicomponent Reactions, Metal-catalyzed Tandem Reactions, and Total Synthesis: Development and Applications in Drug Discovery"*

## CONTACT

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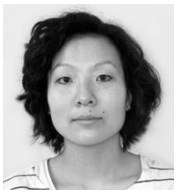
Funded by:
**The project was funded by DTU. The project included a stay at The Scripps Research Institute, USA.**

# Tandem Reactions in Organic Chemistry

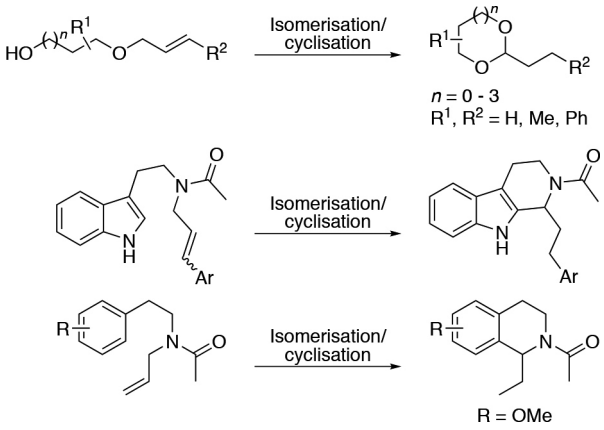
By replacing multistep procedures with cooperative catalytic systems, more selective and efficient synthesis can be obtained.



**Ragnhild Gaard Ohm**
**PhD**

*"Tandem Transition Metal Catalysis and Organo-catalysis for the Synthesis of Aza- and Oxacycles"*

An ideal chemical reaction is efficient, selective and "atom-economical", meaning that the participating atoms end up in the resulting product(s) to the highest possible degree. By replacing multistep procedures with one-pot catalytic systems, a high degree of selectivity and efficiency can be obtained. Compared to traditional methods, which often generate side products such as salts, catalysts may activate otherwise inaccessible functionalities, thus leading to more efficient and atom-economical reactions. The thesis presents new such catalytic reactions in organic chemistry.

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Funded by:
**The project was funded by The Lundbeck Foundation.**

Tandem reactions are consecutive chemical transformations combined into one synthetic operation. The idea is to achieve a cooperative catalytic system. When subjecting an appropriate substrate to the system, the capability of two catalysts can be exploited in an efficient manner, resulting in remarkable transformations. Optimization of reagent compatibility is often required in order to succeed.

In the project a tandem isomerization/cyclisation reaction sequence initiated by a dual transition metal/Brønsted acid catalytic system has been developed. The methodology was applied on allylic ethers and amides where the transition metal catalyst initiates olefin migration to the corresponding enol ether or enamide. Subsequent Brønsted acid catalyzed tautomerisation results in oxocarbenium and N-acyliminium ions, which are trapped by tethered nucleophiles. Cyclic acetals, tetrahydro-β-carbolines and tetrahydroisoquinolines have been synthesized through this tandem reaction with yields ranging from 13 to 95 %.

Further, investigations were made into possible generation of iminium ions via a transition metal catalyzed photoredox reaction and also into possible synthesis of BINOL-peptide phosphoric acids.

Finally, a number of enantiomerically enriched tetrahydrocarbazoles have been synthesized via a novel Friedel-Crafts-type cyclisation/substitution reaction sequence. 4-(Indol-3-yl) butanal can undergo a 6-exo-trig cyclisation to form 2,3,4,9-tetrahydrocarbazol-1-ol. Under acidic conditions, the hydroxyl group can be substituted by an external indole nucleophile via a benzyl stabilized carbocation. The stereoselectivity of the reaction is dictated by a chiral phosphoric acid and enhanced by the presence of a bulky auxiliary attached to the nucleophile. The tetrahydrocarbazoles were isolated in 33-70 % yield and 18 to 97 % ee.

# Fuel and Fuel Additives from Biomass

Catalyzed conversion of bio-oil into transportation fuel, fuel additives and other higher value products is one of the renewable energy solutions of the future.

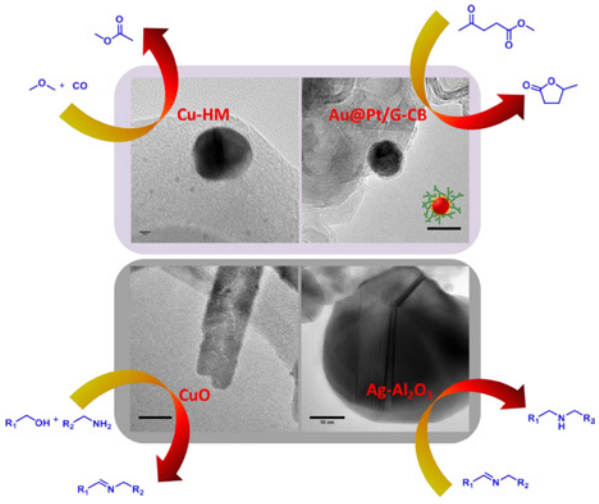
Synthesis of transportation fuel or fuel additives from straw and other agricultural and forestry waste products is a green and sustainable energy solution. The thesis presents a series of new catalytic technologies for this purpose.

Ethanol is already widely used as a renewable fluid transportation fuel, but predominantly produced from corn and sugar cane which may also be used as food. In this project, a catalytic system for synthesis of methyl acetate (MA) from ligno-cellulosic biomass, obtained from agricultural waste products, was developed. MA is a precursor for production of ethanol. More specifically, the porous catalyst H-mordenite catalyzed dimethyl ether (DME) carbonylation to yield MA. Improved activity of the catalyst was observed with optimal loading (1 wt%) of copper impregnated onto the H-mordenite. This improved activity from 65 to 81 % in two hours with about 97 % selectivity. A known drawback of H-mordenite as a catalyst is deactivation by pore filling, but here the active lifetime of the catalyst was increased by desilication followed by recrystallization.

Another renewable bio-fuel is γ–valerolactone (GVL). In the project, GVL was synthesized from levulinic acid (LA) and its methyl ester (MLA) using a novel bimetallic catalyst consisting of Au-core Pt-shell nanoparticles supported on graphitized carbon black (Au@Pt/G-CB). The catalyst efficiently catalyzed the LA to GVL reaction under relatively mild conditions in water to give quantitative yields of GVL.

A well-known initial treatment of ligno-cellulosic biomass is pyrolysis which gives pyrolysis liquid, also known as bio-oil. Bio-oil is a dark brown fluid with a strong smoky odour. It is not directly usable in its initial form but contains more than 300 compounds, the majority being aldehydes. These can be a source of carbonyl compounds as an alternative to using fossil based feedstocks. In the project, an inexpensive copper oxide catalyst was developed and tested for the aerobic oxidation of alcohols to carbonyl compounds. A reaction mechanism involved in the oxidation process was also proposed and experimentally supported. Further, imination of these carbonyl compounds with primary amines using copper oxide and silver nanoparticles supported on alumina ($Ag/Al_2O_3$) is presented.

Finally, hydrogenation of imines was studied with $Ag/Al_2O_3$ to obtain the corresponding secondary amines. The prepared nanocatalyst proved highly efficient, yielding excellent conversion and selectivity towards the reduction of both aromatic and aliphatic imines under relatively mild reaction conditions. The versatility of the nanocatalyst is demonstrated by application to synthesis of secondary amines via a tandem reaction with high selectivity (up to 98 %) towards the targeted product.




*Catalyst systems examined for production of transportation fuel additives and other higher value chemicals.*

**Raju Poreddy**
**PhD**

*"New Catalytic Technology for Conversion of Biomass-derived Oxygenates into Bio-fuels and Imines/Amines"*

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**Anker Degn Jensen, aj@kt.dtu.dk**

Funded by:
**The project was funded by The Danish Ministry for Science, Technology and Development through the UNIK initiative Catalysis for Sustainable Energy (CASE).**

# Green Routes to Acrylic Plastics

Novel ionic liquid catalysts can be applied to the synthesis of methyl propionate, which is an important precursor for production of acrylic plastic.

**Santosh G. Khokarale**
**PhD.**

*"New Catalytic Routes for Methyl Propionate Synthesis"*

## CONTACT

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Funded by:
**The project was funded by The Danish Council for Independent Research.**

Methyl propionate (MeP) is an important chemical in the synthesis of acrylic plastics. Traditionally, MeP is produced from fossil crude oil, but it can also be produced from biomass. Thus, MeP can be part of the transition to renewable raw materials in the fine chemicals industry. The thesis investigates new routes for synthesis of MeP. If such routes prove more efficient than existing ones, they can be considered green, as they will yield more product relative to the amounts of raw material and energy used.

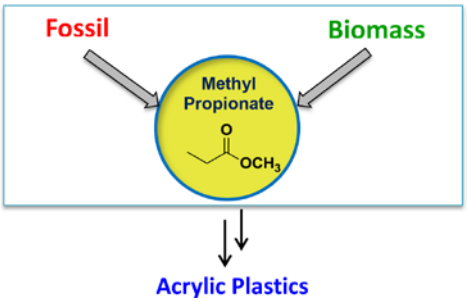
MeP is a methyl ester of propionic acid. It occurs naturally as a volatile component of kiwi fruit and strawberries. The main industrial application of MeP is as a precursor for the production of acrylic plastics. More specifically, MeP is a chemical platform for the synthesis of methyl methacrylate (MMA). MMA is further polymerized to give poly-methyl methacrylate (PMMA); a strong, durable and transparent plastic sold under the trade marks Perspex and Plexiglas.

In the fine chemicals industry MeP is synthesized in mainly three ways. These are methoxycarbonylation of ethylene, oxidative esterification of propanal, and Baeyer-Villager oxidation by enzymatic catalysis.

The project focused at new approaches to these processes. A suggested new approach is the use of ionic liquids as catalysts. An ionic liquid is defined as "a substance composed of two distinct ions that is liquid below 100 °C". Application of Brønsted acid modified ionic liquids as acidic promotors and reaction media in methoxycarbonylation of ethylene to methyl propionate synthesis was investigated. Ionic liquid comprising liquid-liquid biphasic media encourages efficient methyl propionate separation and Pd-biphosphine complex catalyst recyclability.

Further, an advanced ionic liquid catalyst concept was investigated. The supported ionic liquid phase (SILP) catalyst technology was used for vapour phase continuous flow process for methyl propionate synthesis. SILP can be considered as "heterogenization of a homogeneouos catalyst". The approach was shown to bring new opportunities for implementing homogeneous catalysts in industrial processes.

Finally, synthesis of methyl propionate from hydrogenolysis of methyl lactate derived from biomass was investigated. Various supported bimetallic catalysts were synthesized comprising precious and non-precious metals. The catalyst composition and its relationship with activity in the process were investigated.



# Ionic Liquids for $CO_2$ Capture

The project indicates that ionic liquids can be used in $CO_2$ capture both in their neat form and – more commercially relevant – as supported ionic liquid phase (SILP) materials.

The need for reductions in atmospheric $CO_2$ levels in order to mitigate climate change is widely accepted. For instance, the EU has a goal to emit 40 % less $CO_2$ in year 2030 compared to year 1990. It is possible to remove $CO_2$ from flue gases, but the cost is currently high. The thesis investigates innovative capture techniques based on ionic liquids.

Ionic liquids are salts that are liquid under 100 °C. Unlike molecular solvents, ionic liquids consist of ions – just like more common salts – but they are thermodynamically more stable in the liquid phase due to a high degree of disorder, low ion density and high degree of asymmetry. This is practical since these conditions are unfavourable to crystal packing.

In the project, ionic liquids were tested as $CO_2$ absorbents both in their neat form and as so called supported ionic liquid phase (SILP) materials. A SILP material consists of an ionic liquid deposited in the pores of an inorganic or organic porous support material.

Firstly, $CO_2$ absorption in amino acid-based ionic liquids was studied. The amino acids glycine and proline yielded the best ionic liquids for reversible $CO_2$ capture. Water in ionic liquid significantly enhanced both the total $CO_2$ uptake and the rate of uptake. Both ammonium and phosphonium cations were investigated. The tetrahexyl phosphonium yielded the highest $CO_2$ uptake: 1.55 mole $CO_2$ per mole of ionic liquid.

SILPs were found to absorb slightly less than the corresponding neat ionic liquids. This was attributed to passivation of a small portion of the ionic liquid by the support surface. Supports with high surface area were preferred, and of the studied materials ordinary $SiO_2$-60 gave the highest $CO_2$ uptake. The SILP materials were selective towards $CO_2$ uptake at low partial pressure.

*Stationary appearance of [N6666][Orn] after CO2 absorption for 1 min.*

In another part of the project, methyltrioxirhenium was tested as a catalyst for the commercially interesting propene to propene oxide reaction. The catalyst was very selective towards the desired oxide and could be recycled with moderate success.

Overall, the project has shown that ionic liquids are versatile both as reactant and as solvent, and that both neat ionic liquids and SILP materials can be used in $CO_2$ capture. Only the SILP materials have commercial interest. Further engineering development is necessary after this proof-of-concept.

**Helene Kolding**
**PhD**

*"Catalysis and Selective Gas Absorption in Ionic Liquids"*

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**The project was funded by the DTU Chemistry Academic Excellence Scholarship. The project included stays at The Technical University of Munich (TUM), Germany, and at the University Aix-Marseille, France.**

# Green Production of Nitriles

Alternative, ruthenium-catalyzed paths to acetonitrile, benzonitrile and other industrially important nitriles are presented.

**Emily Catherine Corker**
**PhD**

*"Catalytic Synthesis of Nitriles in Continuous Flow"*

Nitriles are an important class of compounds that find applications as solvents, intermediate compounds and pharmaceutical molecules. Current nitrile synthesis methods rely on petrochemical starting materials. This is in itself not ideal in a world where fossil resources are becoming scarcer. The thesis presents an alternative, catalyzed process. An attractive feature of the new process is that it can be run at much milder conditions compared with traditional methods. This reduces energy consumption during manufacture considerably and also carries various practical advantages.

The most important industrial nitrile process is ammoxidation of propene to acrylonitrile. Annual production exceeds 5 million tons of acrylonitrile. The dominant concept is the Sohio process which was introduced in 1960 and soon became successful due to high conversion rates (98 %) and good yields. The process produces both acrylonitrile and acetonitrile, which can be seen as an advantage. However, in the event that acrylonitrile production drops for economic or political reasons, this could lead to a shortage of acetonitrile – as occurred in 2009. Furthermore, the Sohio process relies on petroleum based feedstocks and has relatively harsh operating conditions, including temperatures in the range 400-450 °C. A more energy efficient process is therefore in demand.

The thesis presents a new, alternative path to acetonitrile from ethanol via the oxidative dehydrogenation of ethylamine. High conversion rates (up to 100 %) and selectivities (80-90 %) are reported.

Further, $RuO_2/Al_2O_3$ catalysts are applied to the oxidative dehydrogenation of benzylamine in air, utilizing a new reaction setup. Moderate benzonitrile yields (up to 62 %) and high conversions (up to 100 %) are reported. After optimization of the catalysts, benzonitrile yields were improved (up to 82 %).

Finally, oxidative dehydrogenation of amines using air and $RuO_2/Al_2O_3$ catalysts was applied to a range of substituted aromatic amines and longer chain aliphatic amines. Substituent groups of aromatic amines are found to affect both the rate of amine conversion and nitrile production. Novel attempts are made to apply the Hammett relationship to the oxidative dehydrogenation of amines using air and $RuO_2/Al_2O_3$ catalysts in continuous flow.

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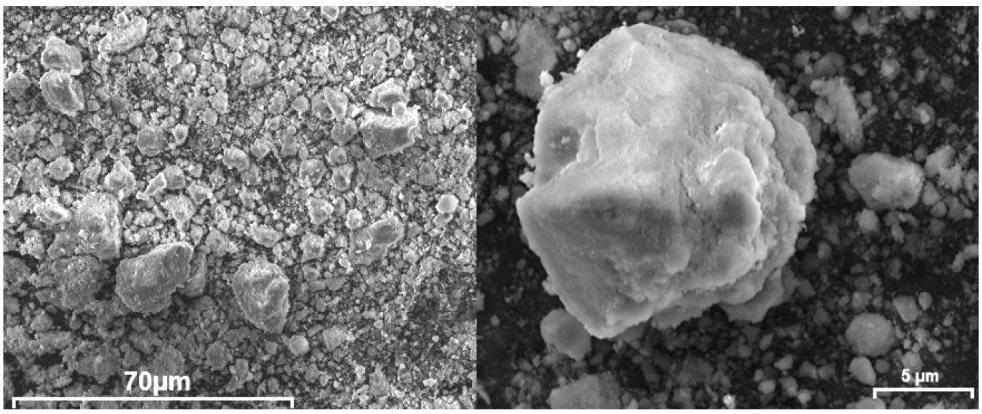
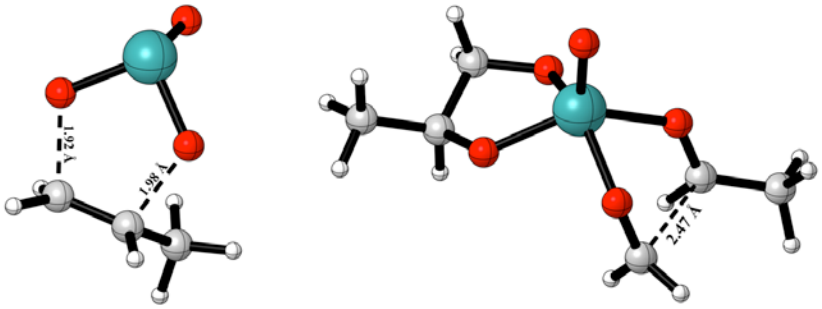



*FSecondary electron SEM images of the RuO2/Al2O3 catalyst.*

# Systematic Innovation in Organic Chemistry

Computational methods can accelerate screening campaigns in organic chemistry.




*Transition states for alkene extrusion (left) and diol oxidation (right) catalysed by Molybdenum.*

**Daniel Lupp**
**PhD**

*"Mechanistic Studies with Density Functional Theory Methods"*

The dominant method for discovering drug candidates and other new organic chemistry compounds is through extensive screening regimes, often involving tens of thousands of structurally similar molecules. This is both laborious and costly. The thesis investigates how such screening programs can be assisted by computational methods that strongly limit the number of potential candidates.

The thesis describes four projects using density functional theory (DFT) for mechanistic studies of organic reactions. The key parameter in DFT is the electron density, which can be described as the likelihood of finding an electron within a certain volume of space around the atom nucleus. A large advantage of DFT is the relatively low computational costs compared with other theories. This had led to application in a variety of fields. Examples include materials science, organometallics, and the study of drug metabolism.

In the first project, a mechanism for the molybdenum-catalyzed deoxydehydration of vicinal diols was suggested and compared to other possible mechanisms. It was furthermore applied to the Mo-catalyzed reduction of sulfoxides. The mechanism consists of two main steps, the diolate-cleavage from a bisdiolate Mo(VI) complex and the alkene extrusion from a monodiolate Mo(IV) complex.

In the second project, a mechanism consisting of oxidative addition, addition of hydrogen and reductive elimination was suggested for the nickel-catalyzed hydrogenolysis of aryl ethers. Good agreement between experimental and computational results supports the assumption of a selectivity-determining oxidative addition step.

The third project addresses the palladium-catalyzed C-H activation reaction of aryl sulfonamides. A mechanism involving an intramolecular proton abstraction by an acetate followed by coordination and insertion of methyl acrylate was suggested. Further, a possible pathway for the oxidation of the palladium catalyst was suggested.

Finally, in the fourth project it was attempted to find a mechanism for a chiral Brønsted acid-catalyzed cyclization reaction and to predict the enantio-selectivity of the reaction.

The conclusions drawn from all four projects were tested by comparison with experimental evidence and can hopefully be used to improve the efficiency and applicability of the examined reactions. Through this process, computational chemistry should be able to contribute to moving the field of organic chemistry away from its serendipitous nature and towards a more exact science that relies less on extensive screening.

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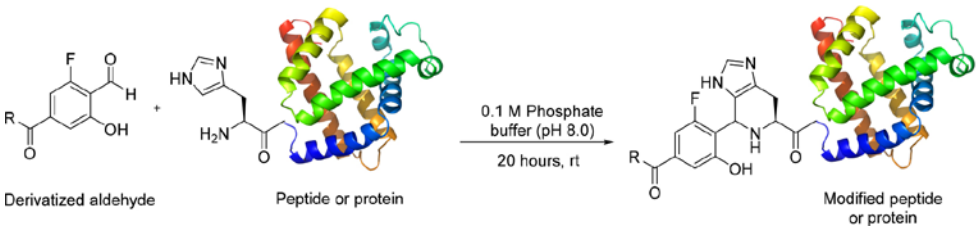
Funded by:
**The Danish Council for Independent Research.**

# Site-specific Modification of Proteins

While naturally occurring proteins often inspire drug discovery, modifications are necessary for proteins to become actual drug candidates.

**Claus Gunnar Bang**
**PhD**

*"Site-selective Modification of Peptides and Proteins"*




Proteins are becoming increasingly more interesting as pharmaceuticals. While proteins found in nature often serve as inspiration in drug discovery they can normally not be used directly for various practical reasons. The need to identify novel reactions and develop protein modification protocols is therefore growing. Moreover, there is a need for such modifications to be site-specific. If the goal is related to a change of the protein's working mechanism, the modification should be at the active site of the molecule. If, however, the modification seeks to alter the pharmacological properties of the protein without hampering the working mechanism, it is desirable to modify an area of the surface far away from the active site. The project deals with novel synthetic pathways which are able to modify proteins in a site-specific manner.

A series of peptide based ligands was synthesized and their usability was confirmed via photo induced conjugation to the protein human serum albumin.

Simultaneously, a novel hypothesis of neighboring group assisted acylation reagents was tested. While testing a small series of acylation reagents on the peptide hormone GLP-1 (37) it was observed that some specific aldehydes reacted selectively with the N-terminal histidine of the peptide. Screening revealed that the aldehydes required specific properties to perform the reaction. It was shown that complete conversion was only obtained with electron deficient aldehydes bearing a hydrogen bonding substituent in one ortho position and often a halogen in the second.

The reactivity of histidine versus tryptophan was tested. The reaction displayed a large degree of chemo-selectivity towards histidine in a competitive environment a very mild conditions at pH 8. The pattern changes in acidic buffer, where the reactivity of histidine is almost completely absent.

In a final experiment, a 10 kDa PEG Pictet-Spengler reagent was synthesized and used to modify the N-terminal of human antithrombin III, a glycosylated 57 kDa protein from the coagulation cascade.

The Pictet-Spengler reaction with N-terminal histidine adds a very useful reaction to the bio-conjugate toolbox. The method does not require any preceding modification of the native peptide or protein. It involves a canonical amino acid and the optimal conditions are very close to the physiologic N-terminal histidine containing bio-molecules. The method will hopefully be a novel reliable tool for protein modification.

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**Thomas E. Nielsen,**
**now Director of Protein and Peptide Chemistry, Novo Nordisk**

Funded by:
**The project was funded by Novo Nordisk, Innovation Fund Denmark.**

# New Routes in Drug Discovery

Compound libraries inspired by serotonin and other pharmacologically relevant indole alkaloids have been developed via novel catalytic reactions.

Alkaloids are compounds which contain nitrogen atoms. They constitute a class of compounds that generally shows interesting pharmacological properties. Alkaloids are produced by many organisms in nature, e.g. bacteria, fungi, plants, and animals, but they can also be produced synthetically. The biosynthetic route to indole alkaloids generally starts from the amino acid L-tryptophan. The thesis focusses on indole alkaloids which are one of the largest sub-groups. Examples of naturally occurring indole alkaloids are serotonin, harmine, heptaphylline, and lysergic acid, all of pharmacological relevance.

The pursuit of new synthetic methodologies for the next generation of compound libraries is ongoing. In particular, incorporation of scaffolds which are inspired by naturally occurring products is of high interest. The project investigates new routes for the synthesis of indole-containing small molecules that carry structural features similar to or reminiscent of naturally occurring alkaloids.

Synthesis of 1,2,3,4-tetrahydro-β-carbolines (TBHCs) was based on a transition metal/ Brønsted acid-catalyzed tandem isomerization/N-acyliminium ion cyclization of N-acylated allylic tryptamines. In order to optimize reaction conditions a ruthenium hydride catalyst $RuHCl(CO)(PPh_3)_3$ was combined with diphenyl phosphate at elevated temperature (refluxing tolune). This led to good yields (68-96 %) of the desired products. Further, the substituent α to the nitrogen in the allylic system proved to be highly important for the enantio-selectivity. Enantiomeric excesses up to 57 % were obtained.

Further, 1,2,3,4-tetrahydrocarbazoles were synthesized using three different types of novel Brønsted acid- catalyzed Friedel-Crafts-type reactions. Type 1 reactions involved direct intramolecular cyclization from an indole moiety to an aldehyde resulting in the corresponding alcohols. Type 2 reactions were based on addition of nucleophiles, either to cyclized alcohols or directly to the carbonyl followed by cyclization. In type 3 reactions organometallic reagents were added to the carbonyl with subsequent cyclization.

A two-step synthetic route via the alcohols was investigated. The route was found to be most efficient when carbocation stabilizing groups were present around the alcohol, favoring type 3 reactions. Three final type 3 products were synthesized in good yields (64-95 %).

**Casper Lykke Hansen**
**PhD**

*"Combining Organometallic Catalysis and Organocatalysis for the Synthesis of Heterocyclic Scaffolds"*

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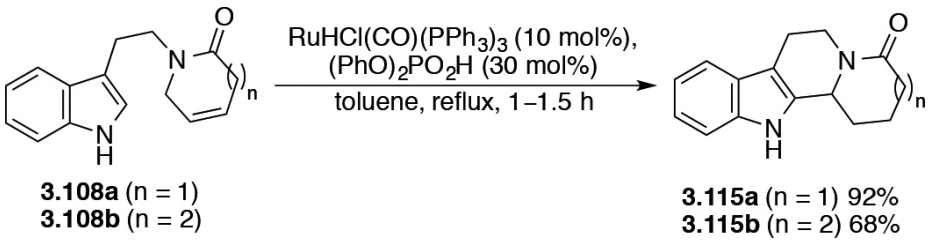
Funded by:
**The project was funded by the DSF Center for Antimicrobial Research (CAR). The project included a stay at the University of Cambridge, UK.**




*Ru hydride/Brønsted acid-catalyzed synthesis of tetracyclic THBCs.*

# New Weapons against Multi-resistant Bacteria

Multi-resistant bacteria such as MRSA are an increasing problem. The project has identified several promising antibiotics candidates.

**Thomas Flagsted**
**PhD**

*"Synthetic Methodologies for the Generation of Focused and Diverse Molecular Libraries"*

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**Thomas E. Nielsen, now Director of Protein and Peptide Chemistry, Novo Nordisk**

Funded by:
**The project was funded by the Center for Antimicrobial Research (CAR). The project included a stay at the University of Cambridge, UK.**

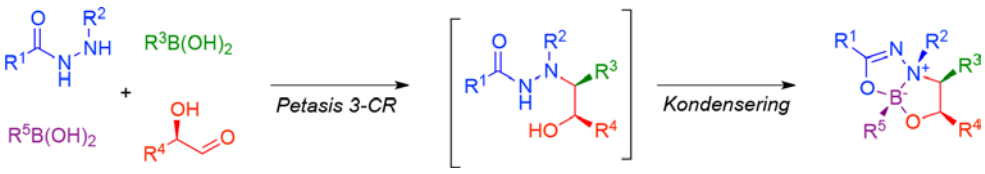
As multi-resistant bacteria are a growing concern worldwide there is a need for new effective antibiotics. Preferably their effect should be due to other mechanisms than traditional antibiotics, which bacteria such as MRSA (Methicillin-resistant Staphylococcus aureus) currently seem to be able to resist. The thesis presents several novel antibiotics candidates.

In recent years interest in bacterial topoisomerase inhibitors (NBTIs) has increased. Their mode of action is distinctively different from the dominant type of antibiotics, the fluoroquinolones. NBTIs target the vital bacterial enzymes DNA gyrase and topisomerase IV. Unfortunately, several NBTIs have been associated with undesired inhibition of the hERG potassium channels in humans, which can lead to cardiac arrhythmia. One NBTI, NXL101, was withdrawn from clinical phase I trials for this reason.

The main focus of the project has been redesign of NXL101 to facilitate synthesis of related NBTIs with the idea of preserving the antibacterial activity without having the undesired hERG inhibition. For this purpose a new piperazine-based NBTI template was developed, and more than 100 analogs were synthesized. The most potent analog displayed higher antibacterial activity against MRSA (and MSSA) than NXL101, while the hERG affinity was decreased. A study showed that no resistance was developed over the course of 22 days, during which time the reference ciprofloxacine developed high resistance (from a MIC = 1.6 to ›25 µg/mL).

In a second part of the project, strategies to access structurally diverse compound collections were addressed. Firstly, the Petasis 3-component reaction was used for creation of a densely functionalized hydrazido-alcohol template, which was further transformed into an array of skeletally diverse compounds via multiple modes of cyclization. Secondly, a novel 4-component reaction was developed based on the Petasis 3-component reaction employing an additional boronic acid to afford a diversely substituted bicyclic boronate. Thirdly, a strategy for the synthesis of spiro- and macrocycles was devised. The strategy relies on an intramolecular Diels-Alder reaction to create a complex scaffold, incorporating three new stereogenic centers, two of which are quaternary.

Overall, the project gives reason to assume that further molecules displaying desirable pharmacological properties can be found through the outlined strategies, notably via discrete structural modifications of the piperazine-based NBTI template.




*Reactionscheme: Development of a novel 4-component reaction.*

# Master Theses 2015

Jonas Oldenburg Jørgensen
*Development of a Multiple-use Formulation for an Anti-TFPI Monoclonal Antibody (Concizumab) Using Preservatives*

Rikke Mia Grave Kølgaard
*Investigating adhesives used in ostomy products – A study of adhesive forces and the effect of ileostomy-output on adhesion, using a 'Skin/adhesive/output'-model system*

Pernille Schiødt Vase
*Optimization of clearance protocol for more robust determination of intrinsic clearance for metabolically stable compounds*

Saima Sharif Chaudhry
*Improving a PBPK model of the CYP3A4 inhibitor itraconazole by including the co-inhibitory metabolites hydroxy-itraconazole, keto-itraconazole and N-desalkyl-itraconazole*

Arta Aslani
*Improving a PBPK model of the CYP3A4 inhibitor itraconazole by including the co-inhibitory metabolites hydroxy-itraconazole, keto-itraconazole and N-desalkyl-itraconazole*

Cecilie Drobek
*Analysis of impurity forming reactions in solid state pharmaceuticals*

Jenny Kim Bathke
*Effects of the linker on the adsorption and catalytic properties of the Cellulases Cel6A and Cel7A from Trichoderma reesei*

Tine Maja Frederiksen
*Structure of a Glucagon-like peptide-1 analogue and its interaction with the endogenous receptor*

Sara Westergaard Olsson
*Deglycosylation of whey protein isolates and their effect on gel formation in fermented milk products*

Kadri Alasepp
*Metalloproteins involved in neurological disorders*

Nanna Sloth Møller
*Investigations and alternatives in crosscoupling chemistry by formation of enzymatic nano agglomerates for application in biosensors*

Thomas Christian Vaarby
*Synthesis of homocarboxypiperazines*

Daniel Madsen
*In-Bead High-Throughput Screening Technology for Profiling of Substrates for Histone Deacetylase Enzymes*

Esben Folger Thomas
*A theoretical investigation of laser pulse shaping with application to the control of quantum molecular dynamics*

Jacob Seneca Nielsen
*A theoretical investigation of intense non-resonant laser-molecule interactions with application to the control of H+OD <- HOD -> D + OH*

Kaywan Javanmiri
*Fibrillation of insulin*

Fabian Barrientos Garcia
*Pre-formulation and stability characterization of therapeutic peptides*

Ulf Molich
*X-ray Crystallography and Molecular Modelling – a Comparative Study Using OPRTase as Model System*

Samuel Gilbert Elliot
*Zeotype-catalyzed conversion of carbohydrates to lactic acid derivatives*

Søren Jønck
*Molybdenum-catalyzed degradation of lignin model compounds*

Andreas Moesgaard Christiansen
*Methods to functionalize beta-peptoid helices*

Daniel Bo Larsen
*Theoretical and Experimental Studies of the Transannular Mannich Reaction*

Susanne Helene Jensen
*Polymer functionalized graphene nanocomposites for controlling super-hydrophobic or hydrophilic properties*

Jonas Hagel Thorn
*Two-dimensional metal oxide and graphene nanocomposites for supercapacitor electrodes*

Katrine Elsøe
*In situ spectroscopy of catalysts during activation and operation*

Frederick Stappen Nielsen
*In-situ investigations of deactivation of DeNOx catalysts*

Peter Andreas Boeg
*Investigations of fundamental physicochemical properties of ionic liquids*

Jeppe Lunde Schmidt
*Bimetallic zeolite materials for deNOx aftertreatment systems*

Mindaugas Genys
*Wettability alteration using nanotechnology*

Hilmar Mar Einarsson
*Simulation of Reservoir Processes with CFD Tools*

Athanasios Stefanakis
*PVT in Shale Gas Production: Modelling and Simulation*

Georgia Pantelide
*Phase behavior study of hydrocarbon mixtures with an HPHT PVT apparatus*

Antonios Pantelakis
*Phase behavior study of hydrocarbon mixtures with an HPHT PVT apparatus*

Ioannis Chasomeris
*Density and viscosity of hydrocarbon mixtures at high pressures and high temperatures*

Vasos Vasou
*Density of oil-related systems at high pressures*

Susanne Voss
*Experimental determination of fetal hemoglobin in the blood*

Sidsel-Maria Glasdam
*Development of Reference Method for determination of ionized Magnesium in Whole Blood*

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# Acknowledgement

**DTU Chemistry highly appreciates the active involvement of our Advisory Board:**

Kim Andersen
Lundbeck A/S

Thomas Högberg
Leo Pharma A/S

Tue Johannessen
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Ole Kirk
Novozymes A/S

Jesper Nerlov
Haldor Topsoe A/S

**DTU Chemistry has a wide cooperation with industry.**

**Among the Department's industry partners are:**

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# Publications 2015

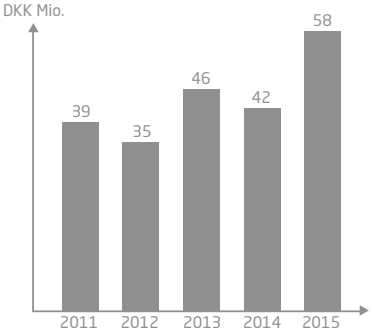
DTU Chemistry has a high performance in the world of chemical science. This is reflected in all the publications produced and published in high impact journals every year. In this Annual Report you can find examples of some of the Departments exciting results and projects during 2015. The Department has a strong track record in scientific publications and we keep on increasing the ISI publications. For a complete list of DTU Chemistry's publications in 2015, please scan the code or see: kemi.dtu.dk/Omos/Publikationer

# A Leading Research Department

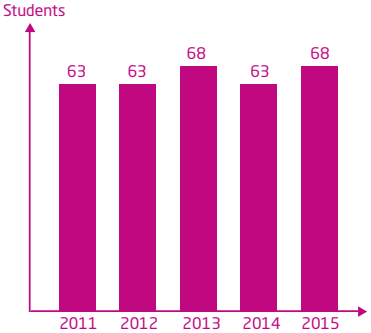
DTU Chemistry focuses on scientific excellence through people, projects, and results in order to stay a leading research department. DTU Chemistry is still very successful in attracting scientific talent. We keep on having a very high number of applicants for the BSc in Chemistry and Technology exceeding the number of applicants, we can actually accommodate.

Once again the Department had a high success rate in applications for external funding in 2015. We are pleased to find that sources outside DTU as public funds, private companies, and private foundations take growing interest in our Department.

External funding exclusive overhead




BSc admission



*The Torkil Holm Symposium, Copenhagen. Credit: Tom Jersø/ATV*

# Highlights 2015

DTU Chemistry has selected some diverse highlights from 2015. You can read more at our website kemi.dtu.dk/english/Nyheder or follow our activities at facebook/DTUKemi.

## GRANTS & HONORS

### Donations from Carlsberg

The Carlsberg Foundation's Distinguished Postdoc Fellowship goes to Yong Xiao under the supervision of Associate Professors Jingdong Zhang and Hans Erik Mølager Christensen. The grant will be used on in-situ nanoscale investigation of microbial extra-cellular electron transfer. Senior Researcher Katrine Qvortrup receives DKK 350,000 for her project aiming at developing novel antibody-drug conjugates designed as a targeted therapy for the treatment of cancer. Associate Professor Jonas Rosager Henriksen receives DKK 150,000 for a project on gold-liposomal nanoparticle synthesis investigated using UVvis and fluorescence spectroscopy. DTU Chemistry is co-financing 1/3 of the project.

### Villum Foundation Young Investigator

Associate Professor Søren Kegnæs has received a DKK 7 million grant from the Villum Foundation. He will now initiate a project on design of heterogeneous nano-particle catalysts. The grant is provided under the Villum Foundation Young Investigator Program aiming to support talented younger researchers in the technical and natural sciences. Besides the purchase of new equipment, the donation will enable two new PhD positions and two new Postdocs- positions.

### Grants from Independent Research Council (DFF)

Researchers at DTU Chemistry receive a series of grants from The Danish Research Council for Independent Research (DFF),


summing up to more than DKK 12 million Postdoc Jerrik Jørgen Mielby receives DKK 3.9 million for a project on production of substitute natural gas using encapsulated metal nanoparticle catalysts. Postdoc Christian Engelbrekt receives 3.5 million kr. for development of new metal oxide/noble metal hybrids as plasmonic bi-functional nanocatalysts for solar energy. Postdoc Roberto Ortiz receives DKK 2.5 million for a project on anti-fouling bio-active surfaces. In addition to their Postdoc grants, Jerrik Jørgen Mielby and Roberto Ortiz receive DKK 0.5 million from DFF's prestigious Sapere Aude program aimed at talented younger scientists.

Associate Professor Jonas Rosager Henriksen is granted 2.6 million kr. for a project on novel bio-materials for brachytherapy.

### Other Grants & Honors

Industrial PhD-student Amanda Sølvhøj is awarded the years' Outreach Award from the Academy of Technical Sciences (ATV). She works partly at Haldor Topsøe A/S, partly at DTU Chemistry.

Dr. Thomas S. Kuhlmann receives the Molecular Spectroscopy Prize at the annual congress of the Danish Chemical Society.

Postdoc Asmus O. Dohn receives the prestigious Springer Thesis Award for his PhD thesis on modeling of transient changes in molecular geometries.

Students Andreas Juul Jacobsen and David Nielsen took 1st prize in the DTU competition "Green challenge". Their project was on low temperature DeNOx with supported ionic liquid phase materials.

Associate Professor Jingdong Zhang receives DKK 36,500 from the foundation of A.N. Neergaard and Wife for purchase of a quartz-crystal microbalance (QCM) instrument.

Professor Mads Hartvig Clausen and Associate Professor Qijin Chi each receive donations of a total of DKK 0.5 million from the international networking program of the National Board of Research and Innovation.

## EVENTS

### New Center Inaugurated

The new DTU Center for Hyperpolarization in Magnetic Resonance is carried out in cooperation between DTU Electrical Engineering and DTU Chemistry. The Danish Foundation for Fundamental Research has enabled the new entity through a DKK 55 million grant over six years.

### Reaching out to High School Students

180 high school students from Espergærde visit DTU Chemistry during a day of introduction to the natural sciences at the university. Further, the Department is always very active during DTU's annual Open Door event. More than 600 leaflets were handed out to the many young, interested visitors. The efforts appear not to be in vain. This year 68 freshmen set out to become bachelors of Chemistry & Technology.

### The Torkil Holm Symposium

More than 300 leading chemists from both industry and academia participated in the international Torkil Holm Symposium in Copenhagen. The event is sponsored by the Torkil Holm Foundation and the Academy for the Technical Sciences (ATV).

### High-impact Publications

Associate Professor Qijin Chi and Postdoc Ramendra S. Dey from the NanoChemistry Group at DTU Chemistry have worked out a cost-effective way to assemble 3D graphene nanomaterials. Their article *Approaching the Theoretical Capacitance of Graphene through Copper Foam Integrated Three-dimensional Graphene Networks* was chosen as cover article in *Journal of Materials Chemistry.*

Associate Professor Anders Riisager, Senior Researcher Saravana Shunmugavel and PhD Mayra Melian-Rodriguez published an article on inorganic zeolites in *ChemSusChem*. The three scientists from the Centre for Catalysis and Sustainable Chemistry (CSC) at DTU Chemistry find that inorganic zeolites are excellent non-enzymatic catalysts for interconverting sugars used to produce important bio-platform chemicals such as furfural.

For the first time beta-peptoids are made to fold into a spiral—a so-called helix which is a stable structure. Beta-peptoids are imitations of the body's natural amino acids, the so-called peptides. Behind the achievement is a cooperation between four DTU Chemistry scientists: Associate Professor Pernille Harris, Associate Professor Peter Fristrup and Professor Christian Adam Olsen (now with University of Copenhagen) and PhD student Jonas S. Laursen. Their findings were published in *Nature Communications*.

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