

**Annual Report 2017**

# Department of Chemistry



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*The DTU Chemistry Management Group 2017 (left to right) Klaus B. Møller, Inge Holkmann Olsen, Erling H. Stenby, Pernille Harris, Jens Ø. Duus.*

# Welcome to a new generation

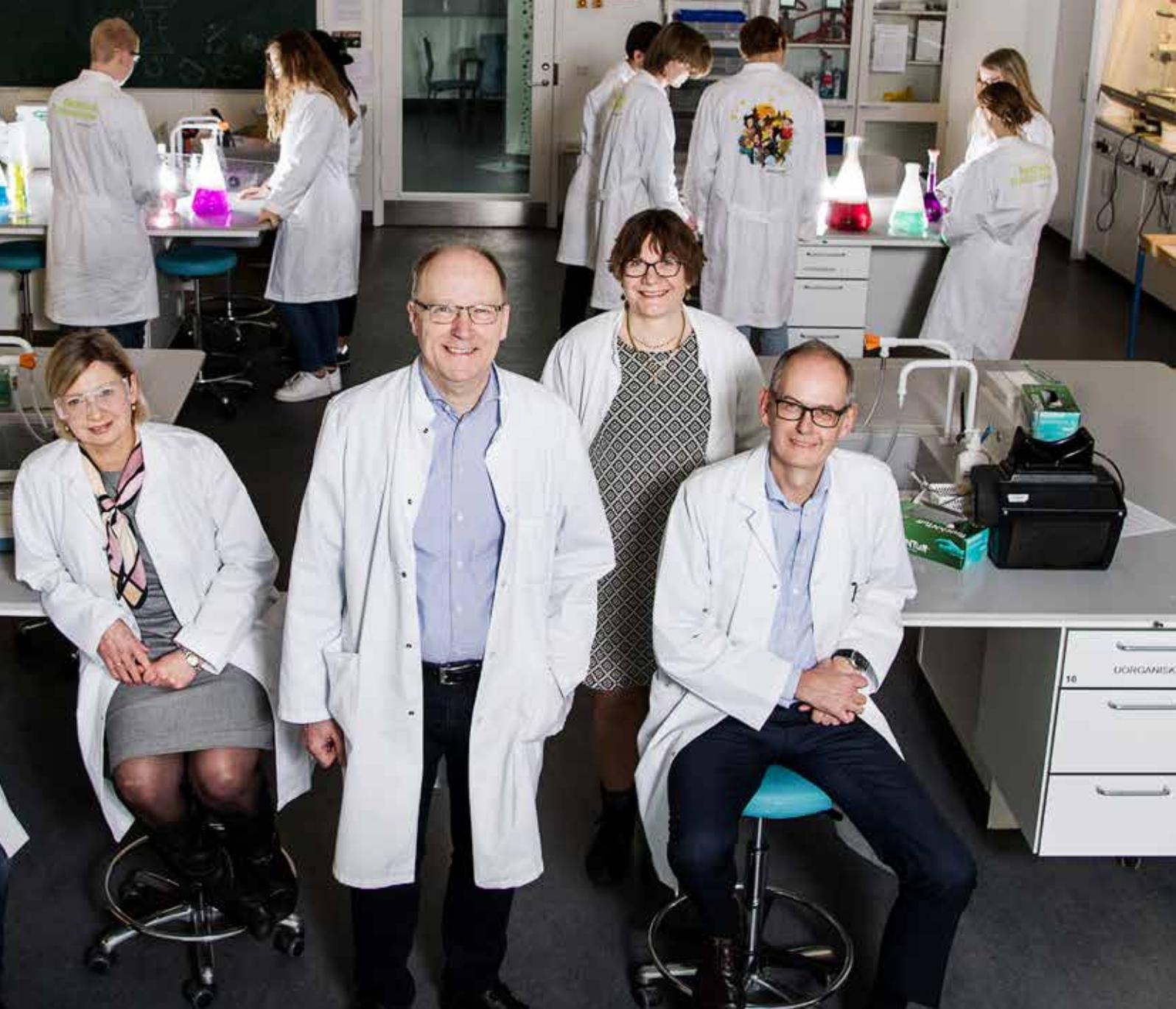
Welcome to the DTU Chemistry Annual Report 2017 – a year characterized by academic excellence and by young talented scientists.

## New faculty

DTU Chemistry appointed new professors in both 2016 and 2017. In 2017, we also invited a new generation of talented scientists in, as we asked six young researchers to join our faculty. Several of the new talents have already received significant grants and honours based on their scientific results.

With these new recruitments, the Department's expertise and research activities are strengthened, particularly within life science engineering and new materials. The new faculty contribute to our increasing teaching activities and give us the opportunity to develop the education programmes. We also have a solid base for enhanced cooperation with industry and other academic partners.

As international cooperation plays an important role in all research activities, I am proud to see that DTU Chemistry is considered an attractive partner also at the international level. Scientists from all over the world are approaching us for closer cooperation, and our international network is constantly expanding, as we are engaging in further cooperation with scientists, universities and other research institutions abroad. One of our new partners is Rensselaer



Polytechnic Institute in New York, USA, who invited us to join a long-term exchange agreement including research stays and increased exchange of students.

### **Record number of PhDs**

Education is one of the core tasks at DTU Chemistry, forming the next generation of researchers and engineers employed in industry.

I am pleased to notice, that our recruitment strategies towards coming students have led to increasing numbers of high level applicants for the BSc in Chemistry and Technology programme. In the years to come, we will intensify our focus on recruiting Danish and international graduate students for our Advanced and Applied Chemistry MSc programme.

Also at the PhD level, 2017 was a productive year. In 2017, a record number of 21 young talents obtained their PhD degree from DTU Chemistry. At the same time, 22 new PhD students were enrolled at the Department. Several of these will be performing their PhD in close cooperation with industry.

### **Academic excellence leads to external funding**

To my great satisfaction, in 2017 the Department attracted the highest amount of external funding ever. This reflects the level

of academic excellence amongst our researchers. The funding was obtained from both public and private sources and goes to cutting edge research, development of scientific talents, and new research infrastructure.

One of the larger grants has given us the possibility to establish a new national research facility, DK-OPENSREEN, which gives researchers access to chemical compounds and screening facilities. This is done in cooperation with the University of Copenhagen, Aarhus University and Aalborg University. Another grant from Haldor Topsøe A/S is strengthening the Department's focus on new materials for catalysis in sustainable chemistry and chemical production. It has made it possible to appoint a new Professor within the area. I invite you to learn more on these and many other intriguing projects in this year's annual report.

When looking ahead on the years to come, I am convinced that DTU Chemistry is in great shape to receive more talented students, to address the global grand challenges with innovative ideas, and to use our skills actively in collaboration with academic and industrial partners. I hope you will enjoy this report and that you will join forces with us in the future.

*- Erling H. Stenby*



## New faculty, new strengths

Since the summer of 2017, six young scientists have joined faculty and one member of faculty was appointed Professor (MSO).

The research groups at the department are organized in two major sections: Organic and Inorganic Chemistry with Professor Jens Ø. Duus as Head of Section and Physical and Biophysical Chemistry with Professor Klaus B. Møller as Head of Section.

DTU Chemistry has gained new strengths in the past year, particularly within the fields of chemical biology and materials chemistry.

“We were very excited when we got the opportunity to recruit six new faculty. Four of them work within chemical biology and two of them work within materials chemistry. We are glad to see how these young researchers have already strengthened the scientific expertise in the Department”, says Jens Ø. Duus.

Klaus B. Møller stresses another important positive impact that the recruitment has already had: “I am particularly happy about the new exciting collaborations between scientists from both sections that has emerged at an impressive speed following the appointment of the six new faculty members”.

### One new Professor

On December 15th 2017 Søren Kegnæs was appointed Professor (MSO) in Inorganic Chemistry. A grant from Haldor Topsøe A/S made the appointment possible. Just prior to the appointment, Søren Kegnæs was Associate Professor at the Department. His primary scientific field of interest is within the design of functional nanomaterials, their characterisation and application in heterogeneous catalysis with a specific focus on the synthesis of functional nanoparticles and high surface area materials with controlled porosity. Development of novel materials is of great importance for environmental protection and chemical production.

### Organic and Inorganic Chemistry

The Section of Organic and Inorganic Chemistry comprises activities within: Catalysis and Sustainable Chemistry, Materials Chemistry, and Organic Chemistry. Common themes are the synthesis and characterization of small to very large inorganic and organic molecules. The research areas are homogenous and heterogenous catalysis; gas separation and absorption; development of new materials; conversion of biomass, electrochemistry; bioelectrochemistry; graphene nanoparticles; coordination chemistry; chemical biology; NMR spectroscopy.

### Physical and Biophysical Chemistry

The Section of Physical and Biophysical Chemistry comprises activities within pure and applied physical chemistry. It covers both microscopic atomic-level descriptions and the macroscopic thermodynamic approach. Common themes are determination of structure and behaviour of small to medium-sized molecules as well as proteins, and many projects involve spectroscopy, scattering, and computer modelling. The research areas are Biophysical and Biomedical Chemistry; IR, THz, and Raman Spectroscopy; High Pressure Phase Behaviour for Oil and Gas Production; Protein and X-ray Crystallography; Polymers and Functional Interfaces; Theoretical, Computational, and Femtochemistry.

#### *Physical and Biophysical Chemistry:* ►

*Günther H. J. 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, Sonia Coriani, Pernille Harris and Kenny Ståhl.*



◀ **Organic and Inorganic Chemistry:** Jens Øllgaard Duus, David Tanner, Susanne Mossin, Robert Madsen, Hans Erik Molager Christensen, Charlotte Held Gotfredsen, Søren Kegnæs, Anders Riisager, Rasmus Fehrmann, Jingdong Zhang, Mads Hartvig Clausen, Qijin Chi, Kasper Steen Pedersen, Sophie Beeren, Katrine Qvortrup, Luca Laraia, Kira Astakhova and Martin Nielsen.

## Six new faculty

Associate Professor **Kira Astakhova**, Organic Chemistry. She is originally from Russia but just prior to her employment at DTU Chemistry she was Associate Professor at the University of Southern Denmark. She conducts research into synthetic biology in the cross-field between chemistry and biology. Part of her previous work has been centred on producing small pieces of fluorescent DNA – so-called probes – which adhere to the DNA strand and can reveal diseases. Another part of her work has focused on imitating the molecules of the body. This can help patients with autoimmune diseases such as rheumatoid arthritis.

Assistant Professor **Luca Laraia**, Organic Chemistry. Luca was born in Rome, Italy, but comes from the Max Planck Institute of Molecular Physiology in Germany, where he has worked as a postdoc and project leader. His research interests lie in the field of chemical biology and include the synthesis of compound collections, phenotypic screening, and target identification using chemical proteomics.

Assistant Professor **Sophie Beeren**, Organic Chemistry. She is from Australia, and before coming to Denmark, she was conducting research at the University of Cambridge. Her research in supramolecular chemistry utilizes non-covalent

interactions to create 'smart' materials and functional nanostructures, and she focuses on unconventional approaches to solving chemical synthesis issues. She is studying a new biotechnological approach to carbohydrate synthesis by combining molecular recognition and enzymology.

Assistant Professor **Katrine Qvortrup**, Organic Chemistry. Her research focuses on different areas of chemical biology, including the design and production of chemical compound libraries and of modified peptides and biomolecules, screening for biological activity and assay development, as well as identification of new biological targets.

Assistant Professor **Martin Nielsen**, Inorganic Chemistry. He works with homogeneous metal catalysis, where he studies hydrogen production from biomaterial, multi-metallic nanostructures, and synthetic enzyme models.

Assistant Professor **Kasper Steen Pedersen**, Inorganic Chemistry. Among other things, he is working to develop new two-dimensional material production methods by means of a chemical synthesis collection of molecular building blocks, allowing chemical encoding of specific properties. Two-dimensional materials are particularly relevant to advanced computer technology and spintronics.



# Tail-end NO<sub>x</sub> Abatement is within Reach

A novel ionic liquid (IL) catalytic system enables efficient oxidation of NO to NO<sub>2</sub> at temperatures down to room temperature. A patent is filed for the method which may enable tail-end deNO<sub>x</sub> of industrial off gases.

As nitrous oxides (NO<sub>x</sub>) are harmful to the environment and human health, emissions from ships, vehicles and industrial plants must be reduced. Ideally, catalytic NO<sub>x</sub> abatement should be placed at tail-end of the flue gas duct, allowing easy retrofitting to existing engine systems. However, this has traditionally been regarded as impossible since the temperature at tail-end would typically be too low for deNO<sub>x</sub> catalysts to work efficiently. But new results from DTU Chemistry suggest that tail-end NO<sub>x</sub> abatement is indeed realistic even at chimney temperatures, typically 60–80° C.

“We suggest a novel catalytic system, which performs well at the relatively low temperatures at tail-end. We have a patent application pending, and are already engaged in discussions with interested industry,” says Associate Professor Susanne Mossin.

NO<sub>x</sub> formation is inevitable during high temperature combustion processes utilizing air. NO<sub>x</sub> emissions cause acid rain, contribute to smog formation, induce respiratory diseases, and contribute to depletion of the ozone layer. Therefore, catalytic removal of NO<sub>x</sub> is installed in modern combustion driven vehicles, in power and waste incineration plants, and in other industrial facilities such as cement production.

The deNO<sub>x</sub> unit is usually placed in a high dust exposed position as the first emission

control unit. A placement at tail-end would be preferable since this would enable pre-removal of “poisons” by dust filters and the wet scrubber (removing sulphur oxides) – substances that hamper the catalytic effect.

## Intrigued by experimental results

As is often the case, the new concept is a spin-off from another project. Supervised by Susanne Mossin and Professor Rasmus Fehrmann, PhD Peter W. Jakobsen investigated deNO<sub>x</sub> catalyst systems of the SILP (supported ionic liquid phase) type.

An ionic liquid (IL) is defined as “a salt that is liquid below 100° C”. In other words, an ionic liquid has a low melting point and a high boiling point. This is attractive, because the amounts lost due to vaporization or decomposition are kept close to zero, which practically eliminates the need to add new ionic liquid to the system.

The PhD project of Peter W. Jakobsen – summarized at page 35 – investigates SILP catalytic systems for NO<sub>x</sub> removal. Overall, Peter W. Jakobsen

demonstrated these systems to be promising, while also noting that they are still quite far from becoming commercially attractive.

“During the experimental part of Peters’ project, we noticed remarkably high reactivity for NO oxidation to NO<sub>2</sub> at the beginning of the process. Unfortunately, the level dropped after just a few minutes. Still, we were intrigued, and further investigations attributed the effect to small amounts of alcohols present. Our idea was then to add an alcohol – we use methanol – and maintain continuous high reactivity,” Susanne Mossin explains.

As the IL was chosen 1-butyl-3-methylimidazolium nitrate, [BMIM][NO<sub>3</sub>].

## High stability towards humidity

Not only did the idea work. The reactivity proved so high that NO was oxidized to NO<sub>2</sub> at temperatures in the interval 30–120° C. This allows acceptable activity of a traditional catalytic deNO<sub>x</sub> system downstream at much lower temperatures than usual. In other words, the system is well suited for use at tail-end.



“We are helped by the fact that we do not need to oxidize NO completely. General experience from NO<sub>x</sub> abatement has established that a 50:50 mixture of NO and NO<sub>2</sub> is optimal for the following catalytic steps removing all types of NO<sub>x</sub>,” says Susanne Mossin.

The method has no harmful environmental effects as the required amount of methanol promoter is low and it is fully consumed in the process. The methanol achieves a turn over number of up to 30 before finally being oxidized to CO<sub>2</sub>.

A further advantage of the method is the stability of the catalyst towards humidity. It is difficult to avoid humidity in flue gas from engine systems. This will reduce the efficiency of most catalytic deNO<sub>x</sub> systems, but not of the new methanol promoted low temperature NO oxidation system which is able to tolerate a relative humidity of 100 %. Further, the system is able to tolerate very high flow rates. This makes the method potentially attractive for facilities such as power plants where the large flue gas volumes and high flow rates are challenging.

### Marine applications first in line

“Still, we imagine marine applications to be first in line,” says Susanne Mossin.

Why ships? Well, marine engines are generally fuelled with heavy oil types. These are cheaper than diesel for cars, but demand high combustion temperatures. To reach a high combustion temperature one needs to add more oxygen. And a high level of oxygen will again equal higher NO<sub>x</sub> emissions.

“When you have higher concentrations of NO<sub>x</sub>, the efficiency of a deNO<sub>x</sub> unit such as ours will also be higher. This makes marine applications attractive,” says Susanne Mossin.

Also, the timing is right in relation to marine applications, notes Rasmus Fehrmann:

“The International Maritime Organization (IMO) and various national authorities are beginning to impose NO<sub>x</sub> abatement regulation, but the vast majority of ships do not have any equipment yet. Obviously, it is easier to

introduce a new technology when the industry hasn't already invested in other types of equipment for the same purpose.”

### A new approach to NO<sub>x</sub> abatement

Another aspect of the method is that it could introduce a new approach to NO<sub>x</sub> abatement. If NO is oxidized quantitatively to NO<sub>2</sub> this could be absorbed efficiently downstream.

“Thus, we might have the oxidation and absorption as two separate processes. After oxidation, we may proceed with absorption of the NO<sub>2</sub> in order to target other nitrous oxide species such as HNO<sub>3</sub>. In other words, we could potentially create a better overall deNO<sub>x</sub> process turning a pollutant to a useful mineral acid with a market value,” says Susanne Mossin.

Precisely which applications and further developments are to be targeted will depend on the ongoing considerations with industry, she underlines:

“Also, we want to take development a bit further ourselves. We know the idea works, but we would like to get more experimental data in order to optimize the processes and also establish the exact ranges of temperatures and other conditions for which the method is suited.”

## CONTACT

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# Lasers Introduce “Magic” Chemistry

Selective conversion of a racemic mixture into a single enantiomer species can be achieved by laser pulses. The implications are huge for future chemistry.

Imagine a chemistry, where the structure of molecules can be changed at will. Does that sound futuristic? It still is, but efforts at the Theoretical, Computational and Femtochemistry Group at DTU Chemistry have taken a significant step in this direction. According to a study by PhD Student Esben Folger Thomas and Associate Professor Niels Engholm Henriksen it is possible to convert a racemic mixture selectively into a single enantiomer species by application of phase-modulated non-resonant laser pulses.

“Any traditional chemist will use a Bunsen burner to trigger or speed up reactions. However, that effect will not be selective but will apply to a range of reactions. In the case of a racemic mixture, the heat will cause individual enantiomers to assume the alternative shape, but reverse changes will occur at the same rate. As a result, the overall effect will be zero. So instead of a Bunsen burner we use laser light. By applying very specific laser pulses we can trigger only one of the two changes,” says Niels Engholm Henriksen.

The pulses need to be ultrafast, meaning in the femtosecond ( $10^{-15}$  second) range.

“This is the time scale of atomic motions. Here, it is possible to trigger an atom to “jiggle” in a very specific way by hitting it with complex laser pulse shapes,” says Esben Folger Thomas, adding that for some simple cases the situation can be compared to a kid sitting in a swing with a friend pushing:

“We all know that a push at the exact right time will increase the velocity, while a badly timed push will have almost no effect.”

## Too complex for the human brain

However, finding the optimal shape of a laser pulse is generally an immensely complex task.

“Luckily, we were able to have a computer find the solution for us,” says Niels Engholm Henriksen, smilingly. “The job would have been virtually impossible for any human brain.”

Even the computer cannot find the solution straight away. The group applied a machine learning technique known as a genetic algorithm. Just like in real-life natural selection, the rule of survival of the fittest is applied to candidate solutions, and after many repeated runs an optimal solution is found.

“Actually, we could not be sure from the outset, neither that a solution would exist, nor that the computer would be able to identify it. We have to credit our good fortune here,” says Esben Folger Thomas.

Changing a racemic mixture selectively into just one of the two enantiomer species has far more than academic interest. It is well known from the history of chemistry that two enantiomers can have significantly different properties. In some rare cases, a certain enantiomer can have adverse, even dangerous effects, while more often one of the enantiomers will be unwanted simply because it doesn't have the desired effect of the active compound. For example, in the pharmaceutical industry, extensive efforts are often applied to ensuring a pure result with only the desired enantiomer present in the final product.

“Changing the undesired enantiomers into the desired ones by application of laser pulses is a very satisfying solution, as we avoid throwing away half of the molecules,” says Niels Engholm Henriksen.

## Eagerly awaiting experimental confirmation

So then, why has the study – published in *The Journal of Physical Chemistry Letters* – not spurred extensive industrial interest and coverage in main stream media?

“At this point we have only shown that this can be done and how it should be done. We haven't done it experimentally, as we do not have access to the right type of powerful and accurate laser source,” answers Niels Engholm Henriksen. “However, discussions are ongoing with a group at Aarhus University. They are keen to do the experiment. Hopefully, we will get there. Once we have experimental results, I am confident the scene will change.”

While selective conversion of a racemic mixture into a single enantiomer species is highly interesting in itself, the perspective is actually much more exciting than that, according to Esben Folger Thomas:

“The possibility of changing the structure of a molecule by applying laser pulses, promises a new kind of chemistry. We may be able to make molecules that have never been seen before. This is actually the main motivation for me.”

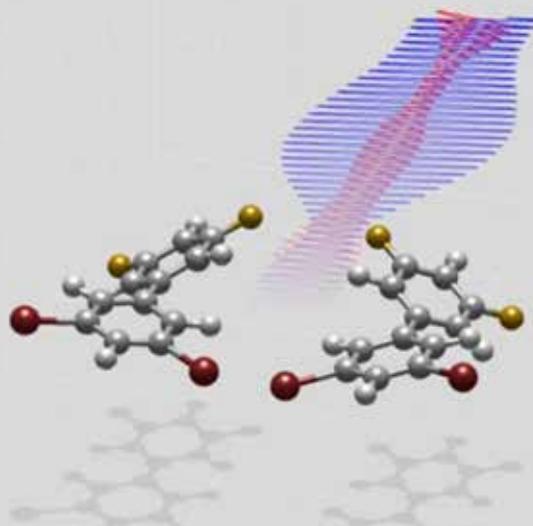
## Entirely new molecules in the horizon

An example is the ozone molecule ( $O_3$ ). Graphic illustrations always give the molecule in a V-shape – which it does indeed have – but in theory, the molecule could alternatively assume a triangular shape with each oxygen atom bonding to both its colleagues.

“While we know this structure to be theoretically possible, it has never been seen in practice. The energy input needed to create that extra bond is so big, that it by far exceeds what you can get from a Bunsen burner. But what if we could achieve the change with laser pulses?”, Esben Folger Thomas asks, noting that such futuristic chemistry could have vast implications: “As we haven't seen this type of molecule before, we cannot say what it could be used for. But its properties are likely to differ from the ozone we know.”



Esben Folger Thomas (left) and Niels Engholm Henriksen.



Niels Engholm Henriksen gives an example from catalysis:

“We already know that the position of the active site in a catalyst molecule is highly important. Today we are beginning to command the exact orientation of individual reactant molecules. But what if we could use laser pulses to make all the reactant molecules oriented and focused at the active site in the optimal position? This would enhance the catalytic performance greatly.”

#### Relevant in quantum computing

Also, Esben Folger Thomas sees a link to a very different field:

“The idea of using quantum computing attracts a lot of attention. It seems obvious to me, that you will need laser pulses to manipulate the states of the quantum computer in a controlled way.”

The quantum computing example stresses another point:

“The field is extremely interdisciplinary,” Niels Engholm Henriksen sums up. “To get this far we have already had to involve expertise in a range of disciplines like quantum mechanics, machine learning, laser optics, and scientific computing, just to mention some.”

*Phase-Modulated Non-Resonant Laser Pulses Can Selectively Convert Enantiomers in a Racemic Mixture*, Esben F. Thomas and Niels E. Henriksen, *The Journal of Physical Chemistry Letters*, 2017, 8, 2212-2219.

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## How the Magic is Done

A wide range of molecules exist in two forms with the same chemical formula, but with different physical structures that are mirror images of each other. A such molecule is known as chiral, and the different forms are called enantiomers. Further, a 50:50 mixture of the two enantiomers – which is normally found – is called a racemic mixture.

The two enantiomers mirror each other much like a persons’ left and right hand. Despite the similarity it is not possible to twist one of the hands to the exact same structure as the other. This would involve drastic surgery – in a chemical analogy this would mean breaking the chemical bonds and reconstructing the molecule entirely.

In their study, PhD Student Esben Folger Thomas and Associate Professor Niels Engholm Henriksen have shown that phase-modulated non-resonant laser pulses can selectively convert enantiomers in a racemic mixture. So far, their method is not universal but applies to a racemic mixture of 3D-oriented, 3,5-difluoro-3',5'-dibromobi-phenyl ( $F_2H_3C_6-C_6H_3Br_2$ ) molecules.

This molecule is a so called conformational isomer with properties that make it somewhat easier to manipulate compared with most other chiral molecules. The molecule has an axially chiral structure where simple torsional rotation around the stereogenic axis leads to transformations between left- and righthanded enantiomeric forms.

Furthermore, the laser-induced dynamics of  $F_2H_3C_6-C_6H_3Br_2$  are well studied experimentally. Notably, an extensive series of experiments conducted by a group at Aarhus University, has demonstrated that one or two

non-resonant femtosecond laser pulses can induce torsional vibration around the stereogenic axes of a Boltzmann population of aligned or oriented  $F_2H_3C_6-C_6H_3Br_2$  molecules in the gas phase.

In their study, Esben Folger Thomas and Niels Engholm Henriksen have used a machine learning tool, genetic algorithms, to identify the laser pulses and frequencies needed to achieve selective conversion of the enantiomers. The starting point is the time-dependent Schrödinger equation, which is universally used for prediction of the development in time of a quantum mechanical system.

By having the computer solve the Schrödinger equation repeatedly in numerous loops with application of a genetic algorithm, the optimal peak intensity and phase modulation of a pair of superposed, linearly polarized, non-resonant Gaussian laser pulses were found. The resulting solution increases the torsional oscillations of the molecules. Thus, a transfer of the molecular wave packet over the potential energy barrier separating the two enantiomeric forms is achieved. Moreover, the study shows how to limit this transfer so it occurs in only one type of enantiomer, leading to de-racemization.

A further advantage of the approach in the study relates to the way the laser pulses drive the molecular movement. This is done by way of the dynamic Stark effect, an effect which is also known from the shifting and splitting of spectral lines of atoms and molecules in an external electric field. The Stark effect is independent of the carrier frequency of the laser, which is practical from an experimental point of view, since it means that a wide range of lasers may be fitted for the task.

# Commitment to Energy Resources Chemistry

Through a range of oil and gas related projects, the Department is ready to contribute as industry looks into high pressure exploration at large depth and other advanced activities.

The hydrocarbon sector is characterized by a regime of price fluctuations, frequent shifts in public policies, and the dynamics of industry mergers and acquisitions. All these developments influence the possibilities for research funding, yet DTU Chemistry has managed to build an extensive portfolio of relevant projects over recent years.

“We can say with confidence, that we have the necessary resources to engage in future hydrocarbon projects both in terms of our academic staff and advanced equipment,” says Head of Department at DTU Chemistry, Professor Erling H. Stenby.

Not surprisingly, the majority of hydrocarbon related projects at the department have been focused on the Danish part of the North Sea.

“We have cooperation with the Danish and international corporations active in the North Sea. Still, we have also been able to create projects that are attractive to other companies. This funding has indirectly contributed to enhancing the knowledge base of the Danish energy sector,” says Erling H. Stenby. As examples he points to two PhD projects at the department, both funded jointly by ExxonMobil and ConocoPhillips. The subjects of the two projects are simulation of shale gas and heavy oil production respectively (for details see pages 26-27).

## Vast deep gas reserves

Both shale gas and heavy oil exploration has the oil and gas industry moving into new types of resources, that are often more complex to develop. Another example is oil and gas exploration at large

depths. This is known as HPHT – High Pressure, High Temperature – because both pressure and temperature increase with depth.

Several HPHT reservoirs are present in the Danish part of the North Sea. Of these, the Hejre field is under development, while the Svane field is on hold. This is probably the largest Danish gas discovery made so far, and could alone extend Denmark’s self-supply of natural gas for up to 30 years.

However, a number of technical challenges must be overcome in order to produce these fields in a safe and economically feasible way. These challenges have been addressed in a major project anchored at DTU, the NextOil project. Industrial partners were initially Maersk Oil and DONG Energy – in the future this would be Total and Ineos due to the acquisition by these companies of Maersk Oil and the oil and gas activities of DONG Energy respectively. Erling H. Stenby has recently accepted an invitation from Total to join the corporations’ Science Council.

“Due to the acquisitions combined with a prolonged period of relatively low oil and gas prices, exploration of the HPHT reserves in the Danish part of the North Sea has progressed at a slower pace than projected at the start of the project,” says Wei Yan, Senior Researcher at DTU Chemistry, and Project Manager for NextOil.

## Fluid compressibility is critical

“It remains likely that production of the significant HPHT reserves in the Danish part of the North Sea could commence in the near future. The NextOil project

has contributed strongly to this end by providing data, insight and simulation models, that were previously non-existent,” says Erling H. Stenby.

Feedback from the industry participants point to especially three valuable developments. Firstly, results on rock mechanics have already impacted well drilling processes at overseas fields by supplementing the existing geo-mechanical models.

Secondly, results on scaling have been highly useful in planning well design contingencies to deal with inorganic scale formation. Overall, scaling may not be larger problem in HPHT than in conventional oil and gas recovery but its nature is very different. The project has identified several “exotic” forms of scaling which are not normally seen in the industry, and this needs to be taken into account.

Thirdly, results on reservoir fluids help reducing uncertainty of production forecasts because the main driving mechanism in many HPHT fields is linked to fluid compressibility. The results from this work package furthermore help in reducing uncertainty on materials safety margins for the wells, as these are affected by flowing well temperatures.

## Equipped for high pressure experiments

The funding for the NextOil project allowed purchase of several types of advanced equipment.

“We are now able to do experiments at up to 200 °C and 1,500 bars. This allows us to do new types of science,” says Wei Yan, noting that the interest is not limited to HPHT applications. “For instance, in shale gas and heavy oil exploration high pressure phase behavior is also important, especially if Enhanced Oil Recovery methods are investigated.”



The experimental activities tie to comprehensive efforts in thermodynamic modelling.

“The leading role of DTU in development of phase equilibrium algorithms for process and reservoir simulation software can largely be attributed to Professor Emeritus Michael L. Michelsen, who founded this field here more than 30 years ago,” says Erling H. Stenby.

Since the retirement of Professor Michelsen, Wei Yan has “taken the torch”, as Stenby puts it. The current efforts within thermodynamic modelling for oil and gas applications are carried out in the COMPLEX project, led by Wei Yan.

“A lot of the developments in phase equilibrium calculation and thermodynamic modelling are actually quite generic,” says Wei Yan. “Adsorption of various compounds to different materials surfaces under high pressure is relevant to a range

of industrial and scientific applications. The new algorithms for calculating multiphase reaction equilibrium can be used in design and simulation of reactive distillation, heterogeneous organic synthesis, biofuel production, and underground CO<sub>2</sub> storage.”

#### **Interdisciplinary synergy**

Erling H. Stenby and Wei Yan are both members at the Center for Energy Resources Engineering (CERE) spanning across several DTU departments. Following the creation of the Danish Hydrocarbon Research and Technology Center (DHRTC) a few years ago, many projects at DTU with oil and gas applications are done in cooperation with DHRTC.

Currently, several groups within CERE are engaged in projects funded by DHRTC. Recently initiated projects focus on various aspects of improving oil recovery from the tight Lower Cretaceous formation in the Danish part of the North Sea.

Furthermore, some projects initiated by DHRTC involve groups at DTU Chemistry which are not normally associated with oil and gas research. Examples are efforts by the group of Associate Professor Esben Thormann on wettability, and by the group of Associate Professor René Wugt Larsen on the interaction between oil and various chemicals involved in oil and gas production.

“This is yet another example of the interdisciplinary synergy we see in this field,” Erling H. Stenby concludes.

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# New research infrastructure hosted at DTU Chemistry

Mads H. Clausen (left) and Faranak Nami beside the Compound Library.



This spring a unique kind of storage and laboratory facility starts to operate out of DTU Chemistry. Initially, the storage in form of a large freezer is up and running it will hold more than 30,000 small molecules. But the facility can hold up to 200,000 small molecules and fragments open for use by biologists and chemists engaged in medical, pharmaceutical and microbiological research.

Even though the appointed director of DK-OPENSREEN Professor Mads Hartvig Clausen from DTU Chemistry prefers to call it a research infrastructure, he politely accept the more mundane term Compound Library when talking about the new facility at DTU. In truth, it is both: A library built to store and distribute small molecules, and a research and screening infrastructure for chemical biology created in a joint venture between DTU, the University of Copenhagen, Aalborg University and Aarhus University, who funded the infrastructure with of 35 million kr. together with the Ministry of Higher Education and Science.

“The overall project is about facilitating that chemists and biologists can meet and work together in an easier and more productive way doing joint research. The purpose is to identify small molecules that in some productive way interfere with and modulate a biological system. That can be anything from an isolated enzyme where researchers look for a single inhibitor to a full cell system investigated for a more complex response to the small molecule. It is a continuous quest for so far undis-

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*The MALDI autoflex speed will be used for easy quality analysis and control.*

covered “hit compounds” with a desired biological activity, which can serve as starting point for additional research”, Mads H. Clausen explains.

Hit compounds are scientifically attractive partly because they through modification can be used to “interrogate” other biological systems by inducing an effect that disclose hitherto unknown aspects of the interrogated system. But they can also in their own right be used as starting points for drug discovery processes and help to validate biological targets as ‘druggable’ making them interesting to the pharmaceutical industry and startup ventures.

When the professor says small molecules, he really means small. The compounds in the library will be smaller than 500 Daltons equivalent to a hundredth of the weight of an ordinary enzyme. The small molecules are for the most parts synthesized although they in principle could be isolated from a natural biological system. The samples start off as solutions of single compounds with a purity of at least 95% as to ensure the robustness of the research done on the compound. The compounds will then be formatted in so-called assay-ready plates with 384 wells each holding a tiny amount of a unique compound. It is these plates that biologists can access like a “ready to eat” meal and use in their hunt for hit compounds. The system is in principle open access, but unlike a traditional public library not completely free. As user, you must pay a handling fee to help cover the running costs of the storage and the crucial quality control and formatting done at the facility.

As coming platform manager of the library, Dr. Faranak Nami from DTU Chemistry is busy getting the storage freezer and laboratory ready. Right now, setting up the database, trimming the robot preparing the plates and getting the

right equipment on board and operational is very much top of mind for her, but besides that she sees achieving sufficient diversity in the collection of compounds as an important and challenging task.

“We need a collection of maybe a 100,000 compounds, and there’s no way we can synthesize that amount ourselves. Some of the compounds we are going to buy, of course, but at the same time, we have to reach out to chemists from other research institutions and ask them to donate compounds to the library. It is very important to focus on a strong diversity and therefore I have to do a lot of PR and persuade external researchers to help us build the collection,” she explains.

Mads H. Clausen explains the donation part of the project as a win-win situation for the donors. “We would like to reach out to chemists and universities locally and outside DK and say: This is an opportunity! Donate your compounds instead of sticking them in the back of a freezer and forgetting about them when your initial research project is over. We make sure the exact structures of donated compounds are kept confidential, that they are screened by capable biologists and ultimately this might generate new knowledge. Then you might want to move forward and work with the biologists, but you may also be content in adding value to society by getting extra value out of a compound that is already funded”.

Intellectual property rights are essential when asking people to donate their compounds. Mads H. Clausen admits that it is a delicate balance between being truly open-access and altruistic to the benefit of society as the university partners and the Ministry of Higher Education and Science aim for, but at the same time to protect the IP rights of the people using and donating to the infrastructure. To ensure the confidentiality, DTU Chemistry anonymize the structures, so the biologist

using the library have to get in contact with the chemist donating the compound if he or she gets a hit. The resulting project will be a co-op between the chemist and the biologist as long as they want to work together. If the latter is not the case, Dr. Faranak Nami and DTU Chemistry can assist the biologist in moving forward with the resulting research project with due respect and reference to the chemist who donated the compound. “We act as an honest broker bringing the parties together without interfering unless invited”, Mads H. Clausen explains. In his opinion that extra level of confidentiality makes DK-OPENSREEN a bit more attractive than other public domain infrastructures where everything is open for scrutiny from the outset, and intellectual property rights thus difficult to protect.

The research infrastructure outside of DTU Chemistry consists of a chain of research laboratories hosted by the partners conducting systematic screenings and isolations of small molecules. At the outset focus will be on new strategies in the fight against infectious diseases, resistant bacteria and chronic ailments, but with time, other fields might very well join the venture and contribute to the library based research. So far no great results loom in the horizon with everything under construction, but Mads H. Clausen and Faranak Nami both expect 2019 to hold some exciting perspectives. “I’m convinced we will see a number of new collaborations between chemists and biologists utilizing this infrastructure next year. It’s premature to guess what comes out of it, but the amount of interest we’ve been met with tells us, that we bring something to the field that a lot of researches need to move forward”, Mads H. Clausen states.

# The Protein Hit Squad

Down the hall on the second floor at DTU Chemistry, the offices of Associate Professor Günther H.J. Peters and Associate Professor Pernille Harris lie but a few meters apart.

Pernille Harris is working with protein crystallography, small angle X-ray scattering and relationships between protein structures and physicochemical properties of them. Günther Peters is an expert in macromolecular modeling and bioinformatics with extensive expertise in molecular modelling techniques. His research involving interdisciplinary approaches are applicable in the pharmaceutical and biomedical field. They share a deep interest and extensive knowledge about proteins in all forms, varieties and structures. Both researchers have substantial experience with leading interdisciplinary research groups, formulating research programs, and initiating and developing collaborative contacts with other academic and industrial research groups nationally as well as internationally. The two seasoned researchers constitute what you could call a Protein Hit Squad in their close investigative collaboration dating more than 10 years back, targeting protein structures relevant to the pharmaceutical industry and the quest for new drugs. Even though Günther H.J. Peters early in his career worked with proteins in the lab as well, these days it is Pernille Harris who does the experiments.

“At one point I had to choose. You can’t be an expert in everything and mastering both experimental and computational studies of proteins is challenging. I therefore chose to work with the modelling and leave most of the

experimental work being carried out by collaborators. However, my experience in the lab is very useful when supervising my students,” Günther H.J. Peters explains.

There is no fixed working order between the two researchers, but basically Pernille Harris experimentally finds the shape of the protein, or a variety of shapes, from the same protein or group of proteins. She then gives these shapes to Günther H.J. Peters, who finds the shape that fits his atomic model best. Sometimes it is the other way around, but the point is, that without the experimental work to back his models, Günther H.J. Peters’s predictions could be far from reality, and without the computer modelling, Pernille Harris would have difficulties extracting the necessary details about the proteins.

These days the hit squad epithet it is very much true for the largescale PIPPI research project named by project coordinator Pernille Harris who has always had a weak spot for Swedish author Astrid Lindgrens famous free spirited Pippi Longstocking character. And as it is with the freckled redhead with the exorbitant muscle strength, the PIPPI project is very much alive and kicking with an abundance of interesting results flowing from the project.

PIPPI is an acronym for “Protein-excipient Interactions and Protein-Protein Interactions in formulation”. Funded under the European Horizon2020

programme, the consortium running PIPPI consists of both academic and industrial partners located in Denmark, Sweden, Germany and United Kingdom. The overall goal is to develop a public database with detailed knowledge about the properties of proteins in pharmaceutical formulations through systematic investigations of the physicochemical behavior of carefully selected proteins combined with a deep understanding of the molecular interactions behind the observed behavior.

Protein based drugs, or biologics, as they are called in the trade, are increasingly popular in pharmaceutical industry due to their higher specificity and fewer, less severe side effects compared to drugs based on small molecules. Biologics have proven to be successful in high profile treatment regimens targeting serious diseases as cancer, autoimmune deficiencies, hemophilia and diabetes. More than 250 different biologic medicines is on the market right now, and at least three times that amount are in the pipelines around the world. It has been called the biologics revolution and expectations for future advances in individual treatment of diseases like HIV with carefully designed protein drugs is high, even though the biologics current market share is less than 5% of the total pharmaceutical market.

However, proteins are big, complex and unruly, and their interactions often poorly understood. It is difficult and sometimes



impossible to characterize them in a laboratory. To complicate matters further, small differences in the immensely complex industrial production processes can generate damaging variations in the resulting protein causing individual variations in the patients' responses to the drug. To minimize the risk, the producers must implement strict control with purity and composition of every component of the drug, including the chemistry of the vaccine solvent or pill. And this is where PIPPI is coming to the rescue:

"When you take a pill or inject a drug, it's a lot more than just the active protein. There is the stuff you use to actually make the pill or the solvent for the vaccine, and there is additives you need to make the drug last on the shelves in the pharmacy. PIPPI is making systematic investigations into these additives to see how they affect the stability and how they interact with the drug protein," Pernille Harris explains.

To make these investigations as diverse and thorough as possible, the PIPPI consortium has recruited a small army of 15 PhD students distributed between members of the PIPPI consortium studying the same 20 carefully selected proteins with a variety of laboratory and computer modelling techniques such as light scattering techniques, stability screening assays state-of-the-art computer simulations. Through this multifaceted biophysical and structural

*DTU Chemistry hosted a workshop for the members of the international PIPPI consortium in October 2017. Günther H.J. Peters front row, far left. Pernille Harris in the back, second from the left (black jacket).*

characterization of the proteins in a pharmaceutical setting, the young investigators are able to correlate structure with stability and thus create a catalogue or library of protein behavior under different solution conditions. The rich database is important for future drug developers when deciding how to administer and store the drugs.

According to Pernille Harris, the coordination of the young researchers' effort is the most challenging but also the most rewarding part of the program:

"We're not their supervisors, but naturally there has to be a certain measure of coordination to keep PIPPI on track and ensure coherency in the process. We also have to bring all results together and extract all the proper information. The workload and hence timeframe differ from technique to technique, so it is no small task getting everybody in sync on the program" she explains.

Never the less, she expect to see more of this kind of multinational and multi methodology projects in the future:

"It is very efficient and we get so many interesting results much faster than we had anticipated. At the same time, the PhD students get an encouraging feeling of belonging to something bigger than

their own project, a scientific community of sorts. They experience a unique possibility to discuss their projects with other researchers who have the same interests and gather inspiration and support from the partner companies. And the companies get a chance to meet and recruit the young researchers they are interested in", Pernille Harris explains.

Despite the obvious need and possibilities, skilled researchers in the field is still very much in demand. One of the focus areas of PIPPI therefore, is to facilitate a strong network among the young researchers across sectors, traditions and topics. The partners in the consortium behind PIPPI hope these investigators evolve into the key opinion leaders of the future. In that effort, they could not have chosen stronger allies and role models than Pernille Harris and Günther H.J. Peters.

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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 PhD-students at DTU Chemistry is strengthening their professional and social network at the Department. They do this through the PhD ChemClub. 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](http://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 poster session by the departments PhD students.

## Contact us!

In the following you can get acquainted with the diverse DTU Chemistry PhD Defences 2017. 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](mailto:ehst@kemi.dtu.dk)



# Design of porous nanostructured solid catalysts

Synthesis of novel porous materials for catalysts.

Solid catalysts have numerous applications in areas such as energy production, petroleum industry, the production of chemicals and pharmaceuticals, and environmental technologies. The project focuses on improvement of nano-structured materials for solid acid catalysts and for catalysts for fuel cells. The improvements aim to increase the activity and stability of the catalysts in order to minimize waste of precious elements, starting materials, and energy, for a more sustainable chemical industry.

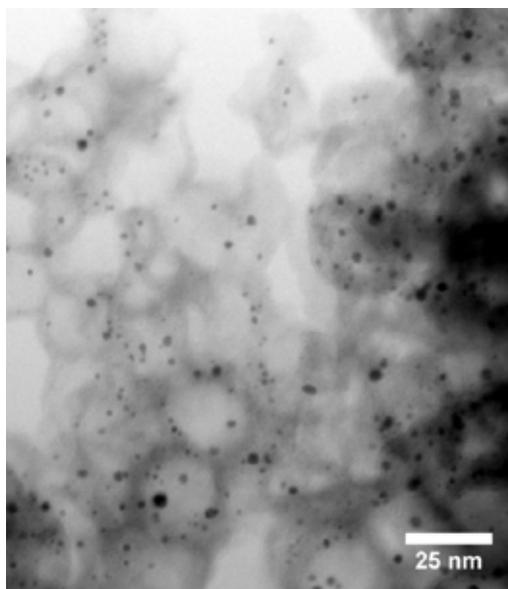
Zeolites, a class of porous materials, are becoming increasingly important in catalysis as solid acids. Their usefulness originates from their structure which contains a large pore volume based on micro-pores and possible acid sites. However, the micro-pores may decrease the diffusion of reactants and products. This potential drawback can be countered by generating additional porosity. In the project, a novel method for preparation of meso-porous zeolites with a carbon secondary hard template was developed. The carbon is generated through the decomposition of methane over nickel nanoparticles. This is done as an in situ process, directly upon the silica source for the zeolite.

As the new method is significantly cheaper than previously reported for carbon templates, it increases the feasibility of using meso-porous zeolites for various applications. The developed zeolite possesses a greater total pore volume, while still matching its conventional counterpart in terms of crystallinity and acidity. Further, it exhibited much higher conversion, which is attributed to the enhanced diffusion. The method was able to create varying porosity and it was applied successfully to a number of different zeolites.

*STEM image of the Pt nanoparticles encapsulated in hollow carbon spheres.*

Fuel cells are expected to become important in future energy systems, as they are able to convert hydrogen-containing feedstock into electricity with high efficiency and extremely low environmental impact. The project focuses on fuel cells of the proton exchange membrane type (PEMFC). For PEMFC to move from niche to large scale applications, a highly active and stable catalyst is needed. In this project, platinum nano-particles were successfully encapsulated in hollow nitrogen doped carbon spheres. The catalyst was employed in the electro-oxidations of methanol, ethanol, and formic acid.

Electro-chemical results showed that the activity of the material was hindered by the low porosity of the shell. Consequently, the carbon shell was activated with potassium hydroxide to generate some micro-porosity in the thin carbon shell in order to improve the diffusion of reactants. While initial catalytic testing showed some drawbacks, the sample displayed great promise and further optimization for applications in sustainable production of electricity could be interesting.



**Jacob Oskar Abildstrøm**  
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*"Design of Porous Nano-structured Solid Catalysts"*

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Funded by:  
**The Danish National Research Foundation and DTU Chemistry.**

# Towards better Treatment of Rheumatoid Arthritis

Promising prodrug candidates for safe and efficient treatment of Rheumatoid Arthritis (RA) are presented.



**Jorge Peiró Cadahía**  
PhD

*"Novel Strategies for the Synthesis, Evaluation, and Delivery of Biologically Active Molecules"*

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Funded by:  
**DTU Chemistry**

Rheumatoid Arthritis (RA) is an autoimmune disease and chronic inflammatory disorder associated with progressive disability and reduced life time expectancy. Affecting around 1% of the world's population, RA has large socio-economic costs. The project presents new prodrug candidates for RA treatment.

RA is characterized by synovial inflammation and tissue damage. The origin and cause are unknown, and no cure exists. However, treatments that reduce the symptoms and the activity of the disease have appeared over the last three decades. The standard of care treatment is by disease-modifying anti-rheumatic drugs (DMARDs), where methotrexate (MTX) is the frontline drug.

A characteristic of the inflammatory tissue associated with RA is known as oxidative stress. A number of reactive oxygen species (ROS) are found, e.g. hydrogen peroxide ( $H_2O_2$ ), in up to 100-fold increase when compared to healthy tissue. As ROS are cytotoxic to invading bacteria, they are a cornerstone in the human immune system. However, sustained elevated ROS levels unrelated to infections are harmful, and it is an obvious ambition to reduce the oxidative stress in RA patients.

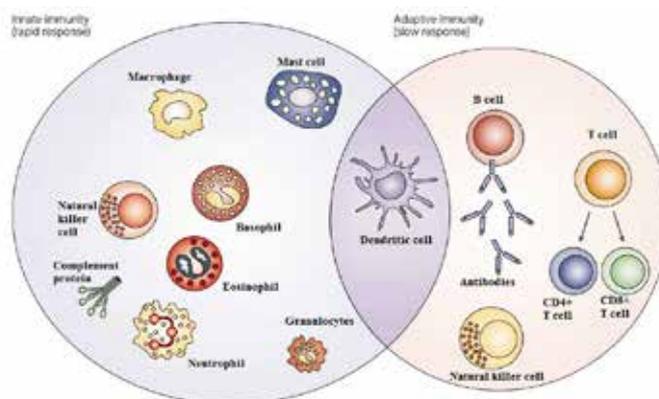
In the project, novel  $H_2O_2$ -sensitive prodrugs of MTX and the related aminopterin (AMT) were synthesized. The strategy was based on  $H_2O_2$ -triggered pro-moieties attached to the drugs via

different linkers. Proof-of-principle was achieved, as in vitro activation of the prodrugs proved to be effective under pathologic concentrations of  $H_2O_2$  reported for inflammatory tissues.

The solubility and chemical stability of the synthesized prodrugs were evaluated. Further, selected candidates were assessed in pharmacokinetic assays. The prodrug candidates showed moderate to good solubility, high chemical and enzymatic stability, and biological activity comparable to that of the parent drugs. Additionally, the in vivo efficacy and preliminary toxicity in the type-II collagen-induced arthritis murine model were assessed, verifying the potential use of the prodrug candidates in RA therapy.

In a separate part of the project, a novel methodology for selective activation of classically unreactive methyl-C(sp<sup>3</sup>)-H bonds in aliphatic amines was developed. A diverse range of substrates were able to undergo unprecedented regioselective methyl-C(sp<sup>3</sup>)-H carbonylation, forming the corresponding  $\gamma$ -lactams in good yields and high diastereoselectivities under optimized reaction conditions.

In conclusion, a site-selective  $H_2O_2$ -sensitive prodrug strategy has been applied to MTX and AMT, and data was collected to prove the potential use of the prodrug candidates for a safer and efficient treatment of RA when compared to the parent drugs, showing very promising results, which encourage further studies.



*The innate immune system is constituted of soluble factors and distinct cellular components including granulocytes (neutrophils, eosinophils, and basophils), mast cells, macrophages, natural killer cells, and dendritic cells. The adaptive immune system consists of B-cells, T-cells (T-helper or CD4+ and T-cytotoxic or CD8+), and antibodies.*

# Design of Sintering-stable Heterogeneous Catalysts

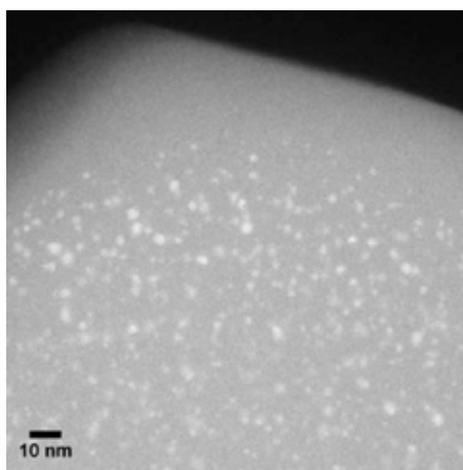
Sintering-stability is a key feature for nanoparticle catalysts. Two promising protocols have been developed.

Catalysis is widely used by industry to convert raw materials into chemicals and fuels in an economical way with low environmental impact. Nanoparticles are attractive as catalysts, since the nanoparticles have much higher surface-to-volume ratio than bulk materials. However, nanoparticles can easily agglomerate. This phenomenon, known as sintering, may reduce and eventually block the catalytic activity. The project demonstrates the ability of two different synthesis methods to create sintering-stable nanoparticle catalysts.

Nanoparticles of noble metals are often effective catalysts. However, noble metals like gold, palladium and platinum are expensive raw materials, and it is highly desirable to preserve the catalytic capability of the nanoparticles for as long as possible. The project investigates two experimental protocols for encapsulation of metal nanoparticles inside porous materials.

The first method applied was the pressure assisted impregnation and reduction method (PAIR). Here, a porous material is impregnated with a solution of a metal precursor, and its reduction is performed under elevated pressure. The procedure was successfully used to synthesize 2-3 nm gold nanoparticles inside porous silicas. The synthesized samples showed increased stability towards sintering.

As the second method, in situ incorporation was chosen. This is a one-pot procedure based on simultaneous growth of a porous silica and entrapment of a metal precursor in the form of an ethylenedia-mine complex inside the forming crystalline network, leading to encapsulated metal nanoparticles after reduction in hydrogen. The in situ incorporation method produced single metal palladium and



STEM image of the Pd-Pt nanoparticles encapsulated in porous silica.

platinum nanoparticles, 2-3 nm in size, and bi-metallic palladium/platinum nanoparticles inside silica.

The synthesized catalysts were able to decompose formic acid with 85 % selectivity towards hydrogen at temperatures around 100 °C. Encapsulated palladium catalysts were shown to be very active in Suzuki cross-coupling reaction.

In conclusion, both the PAIR method and in situ incorporation were shown to be feasible and easy protocols for synthesis of metal nanoparticles inside a zeolite matrix. Small size, high catalytic activity and stability towards sintering make both protocols promising for further research.



**Agata Gallas-Hulin**  
PhD

*"Design of Sintering-stable Heterogeneous Catalysts"*

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# Catalytic Treatment of Diesel Engine Exhaust Gas

Copper exchanged onto chabazite (CHA) zeolite is an efficient catalyst in the removal of nitrogen oxides from diesel engine exhaust. This project contributes to a better understanding of the catalytic mechanism.



**Anita Godiksen**  
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*"Spectroscopic Investigations of Copper Exchanged Zeolites"*

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Funded by:

**The Independent Research Fund Denmark (FTP).** The project was carried out in close collaboration with Haldor Topsøe A/S.

Nitrogen oxides (NO<sub>x</sub>) is a collective term for nitric oxide (NO) and nitrogen dioxide (NO<sub>2</sub>). These are harmful substances emitted from combustion processes including diesel engines. NO<sub>x</sub> emissions contribute to ozone depletion, smog formation, and human health problems. Therefore, increasingly stringent emission legislation has been introduced over the last decades, to ensure only limited amounts of NO<sub>x</sub> are released to the atmosphere. Catalytic NO<sub>x</sub> removal is often carried out through selective catalytic reduction (SCR), using ammonia (NH<sub>3</sub>) as the reductant. NH<sub>3</sub>-SCR is an efficient method to convert NO<sub>x</sub> to nitrogen and water. It is a challenge to ensure catalytic efficiency over the entire range of operating conditions. This is especially true for automotive applications since fluctuations in the operating temperature are inevitable.

CHA zeolite is an artificial silica-aluminate mineral with ion-exchange properties. Over just a few years the copper exchanged version, Cu-CHA has been successfully commercialized as an SCR catalyst. This catalyst is especially attractive for NH<sub>3</sub>-SCR due to its high stability at operating conditions. However, the catalytic mechanism is not fully understood. This is an obstacle for further development of the catalyst.

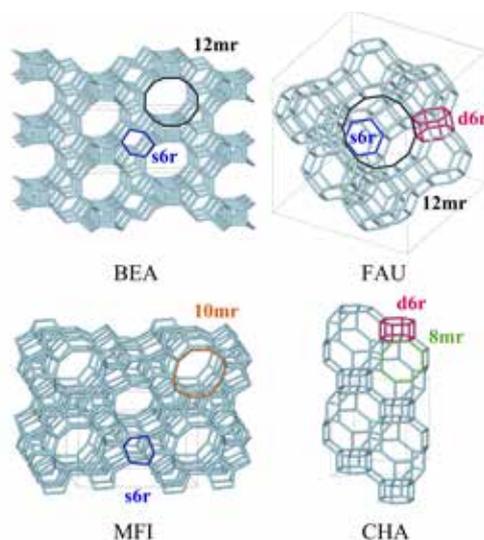
In this project, both in-situ electron paramagnetic resonance (EPR) spectroscopy and ex-situ ultraviolet-visible (UV-Vis) spectroscopy were applied to examine the coordination environment of copper in the zeolite structure under dehydration and during exposure to SCR relevant gasses. Results from the UV-Vis investigations were found to be in agreement with the EPR results.

Several copper sites were found in CuCHA after activation at elevated temperatures. They were assigned to separate Cu<sup>2+</sup> locations in the zeolite structure. From analysis of EPR spectra of dehydrated CuCHA with different Cu loading, the distribution of Cu sites was assigned and quantified.

Copper prefers to be in the vicinity of two aluminium in the zeolite framework structure but can also be found in less preferred sites with only one aluminium in the vicinity. The reactivity of copper is known to be different depending on the number of aluminium in the proximity. The surprising result of this project is that the oxidation reactivity can be further differentiated. Conditions can be chosen where only one type of sites will react with the oxidizing gas. Thus, the site preferred by copper upon ion exchange was shown to be the least reactive whereas the less preferred exchange site was shown to be the most reactive site for reaction with SCR relevant gasses, NH<sub>3</sub>, NO and O<sub>2</sub>.

The project has revealed how EPR spectroscopy can be applied at catalytic relevant temperatures (100 -300 °C) and gas flow rate and compositions without compromising spectral quality. It has revealed how formation and decomposition of copper coordinated to ammonia or nitrate can be followed in real time.

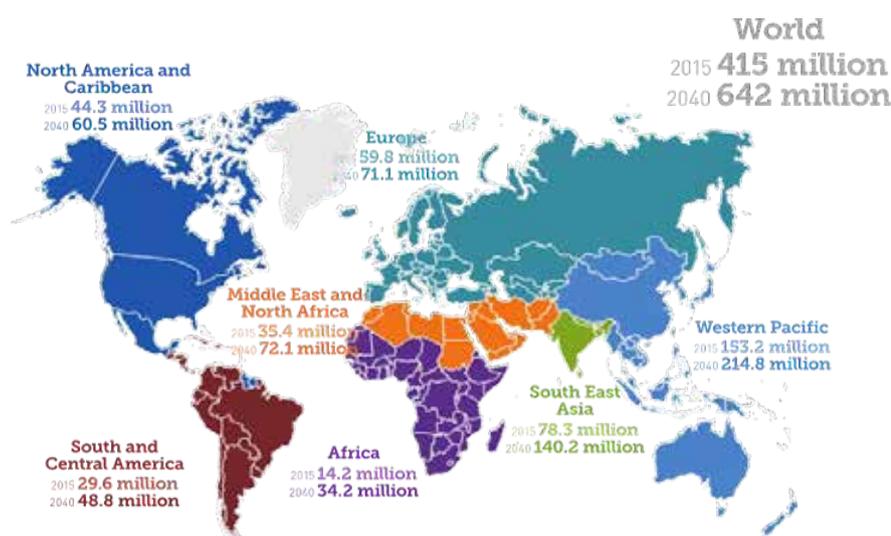
Based on these findings, mechanistic details of the interaction between the active copper and the gasses could be revealed and a new suggestion for the mechanism of the SCR reaction on these materials were proposed.



*Drawing of the four zeolite frameworks: BEA, FAU, MFI and CHA. Important structure sites are marked and labeled. s6r: single 6 membered ring. d6r: double 6 membered ring. Xmr: X membered ring.*

# Nano-sensors for Healthcare and Food Quality Control

High sensitivity and low price make sensor candidates based on functional graphene nanomaterials attractive for a range of emerging applications.



Estimated number of diabetic population worldwide in 2015 and 2040 (20-79 years) (adapted from idf.org)

In the near future, simple and inexpensive sensor devices will permit citizens to perform a range of self-diagnostic analyses without professional training or expensive laboratory facilities. Also, similar sensors are in demand to cope with the increasing challenges in detection of food contaminants and in environmental monitoring. Nano-sensors can be highly sensitive, and at the same time cheap due to the small amount of raw material needed. This project designs several such sensor candidates based on nanostructured graphene materials.

Graphene, an atomically thick layer of graphite, can be engineered to obtain the biocompatible properties in demand for chemosensor and biosensor applications.

Firstly, graphene was functionalized with the small bio-molecule dopamine and used for detection of melamine. Melamine is a well-known food contaminant, i.e. found in low-quality dairy products. The developed sensor was capable of detecting melamine in extremely low quantities – with a lower detection limit of 0.4 nM.

Secondly, twenty different amino acids were used for the green synthesis of nitrogen doped

graphene. The amino acid lysine was found to be most efficient. The resulting nitrogen doped graphene was used for dopamine chemo-sensing.

For other graphene-based bio-sensing applications, graphene was first functionalized with a branched polymer to derive a biocompatible graphene matrix for stable accommodation of more complex bio-recognition elements such as enzymes. The graphene was used for novel glucose sensing. In the next step, the pre-synthesized biocompatible graphene was functionalized with a redox active molecule, ferrocene. The engineered graphene was further functionalized with enzymes and used for glucose and cholesterol bio-sensing.

Finally, the bio-functionalized graphene was step-wise converted to a printable ink and further used for fabrication of flexible and screen-printed bio-sensing devices. The screen-printed electrodes were tested for glucose level measurements in real human serum samples, and found to be closely comparable with the results obtained by the standard clinical methods in a hospital.



**Arnab Halder**  
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*"Biocompatible Nano-engineering of Graphene-based Materials for Sensor Applications"*

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# Synthesis of useful Algae Compounds

The project showcases a promising strategy for synthesis of carrageenan oligosaccharides, which are useful tool compounds for biological studies.



**Christine Kinnaert**  
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*"Towards the Synthesis of Carrageenan Oligosaccharides"*

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Funded by:

**DTU Chemistry**

Carrageenans are a type of polysaccharides found in certain seaweeds. They are widely used as gelling and viscosity-enhancing agents in the food industry. Further, carrageenans are being investigated for drug delivery applications. Oligosaccharides are useful model compounds for the highly complex carrageenan polysaccharides – but since the currently available extraction methods require extensive purification it has been suggested to instead produce them by chemical synthesis. The project showcases a promising synthetic strategy.

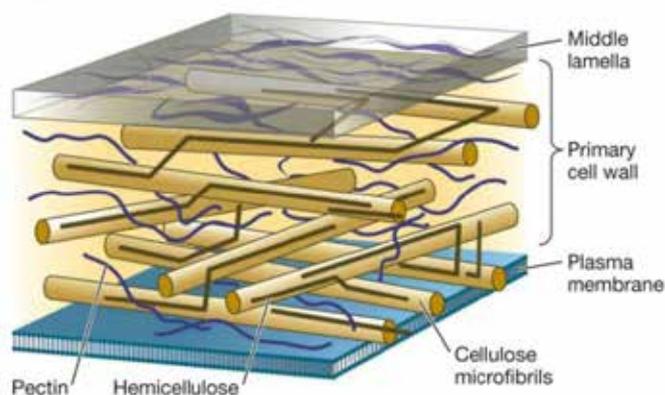
Carrageenans are a family of highly sulfated galactans found in the cell walls of certain red seaweeds of the Rhodophyceae class. They are able to form thermo-reversible gels or viscous solutions when added to salt solutions, and therefore serve as gelling, stabilizing and texturizing agents in the food industry. Further, carrageenan oligosaccharides are suggested for drug delivery applications, as they can be used as a matrix for preparation of extended-release tablets. Their application in polymeric microspheres for delivery of drugs in a rate-controlled manner is also explored.

Although several studies have been conducted, only a limited range of oligosaccharide structures are available and these require extensive purification. The key aim of this project therefore was to synthesize carrageenans, while a further ambition was to synthesize all ten known carrageenans from one single precursor.

A modular approach relying on the synthesis of a key  $\beta$ -1,4-linked digalactoside building block carrying suitable protecting groups was chosen. Each disaccharide was  $\alpha$ -1,3-linked to each other to build up the carrageenan backbone consisting of D-galactose with alternating  $\beta$ -1,4 and  $\alpha$ -1,3 glycosidic linkages.

After other methods proved unsuccessful, a set of orthogonal protecting groups was found to be surprisingly effective, affording the desired tetrasaccharide by forming the regioselective  $\alpha$ -1,3-linkage in 55 % yield through a glycosylation between a 2,3-OH disaccharide acceptor and a trifluoroacetimidate disaccharide donor. When tested, the deprotection and sulfation steps gave the G-D6S disaccharide carrageenan successfully in 70% yield followed by debenzoylation and hydrogenation. The protection groups performed well and could be successively removed. The deprotection steps prior to the sulfation as well as the selective C-6 sulfation step were translated successfully to the tetrasaccharide. Further debenzoylation and hydrogenation will afford the G-D6S tetrasaccharide.

Once further development reaches the tetrasaccharide targets, they will serve as model compounds for structural analysis to help our understanding of the gelation process at a molecular level. This will improve fundamental knowledge about the polymer, which could pave the way for industrial applications. Further, the synthesized carrageenan oligosaccharides could help in characterization of enzymes involved in their biosynthesis and increase the understanding of algae cell wall biosynthesis.



*Schematic model of the primary cell wall of an angiosperm cell.*

# Synthesis of an Important Constituent of the Plant Cell Wall

A developed protocol affords substrates that are highly useful for pectic enzyme studies.

Massive investments are made in utilization of biomass for fuel and chemicals. Still, a range of processes need to be optimized. To this end, characterization of enzymes involved in degradation of the plant cell wall is important. However, the plant components of interest are highly complex structures, which complicates their isolation from biological sources. Therefore, chemical synthesis stands as the method of choice. The project presents routes to synthesize key fragments found in the plant cell wall.

The plant cell wall is a complex amalgam of polysaccharides and proteins, embedded in a highly hydrated matrix. While cellulose and hemicellulose are the most abundant polysaccharides, the project focuses on one group of non-cellulosic polysaccharides, namely pectin. Pectic polymers play crucial roles in signaling and in defense responses against herbivores and pathogens.

Rhamnogalacturonan II (RG-II) is a highly conserved cell wall pectic oligosaccharide. In industry, RG-II is mainly obtained from red wine after extractions and purification in several steps. In recent years, RG-II has attracted considerable interest due to potential desirable effects in human nutrition and health.

RG-II is composed of six structurally different oligosaccharides referred to as side chains A-F, which are attached to a linear homogalacturonan (HG) backbone. In the project, a pentasaccharide portion of the RG-II polysaccharide was synthesized. The synthesis commenced with commercially available D-galactose pentaacetate from which four discrete galactose building blocks were prepared. In this way, the synthesis of a HG backbone with the possibility to install branching was successfully accomplished by iterative glycosylations of these monosaccharide building blocks. To this end, a 3-deoxy-D-manno-2-octulosonic acid (Kdo) residue derived from side chain C was specifically targeted.

Furthermore, the optimal conditions for each glycosylation step was established. These achievements allowed for the assembly of tetra-galactoside with good to excellent yields (68 to 85%) in the glycosylation steps and high selectivity for the desired  $\alpha$ -(1 $\rightarrow$ 4)-linked products. The target oligo-galacturonate was finally obtained after chemoselective deprotection of the 6-positions, followed by oxidation of the corresponding primary alcohol and introduction of the benzyl esters.

Moreover, the synthesis of Kdo on large scale was accomplished via a base-catalyzed aldol condensation between D-arabinose and oxaloacetic acid. In turn, this result enabled the development of a new shorter and higher-yielding protocol to prepare a benzyl ester fluoride donor from the ammonium salt of Kdo. Finally, this donor was coupled to the HG backbone affording the desired pentasaccharide with high  $\alpha$ -selectivity.

In conclusion, the developed protocol will allow for the introduction of other side-chains derived from RG-II, and could potentially be expanded to prepare a longer backbone chain via the iterative coupling of versatile monosaccharide building blocks. All the substrates that will be accessible after the final deprotection steps will prove to be useful for pectic enzyme studies.



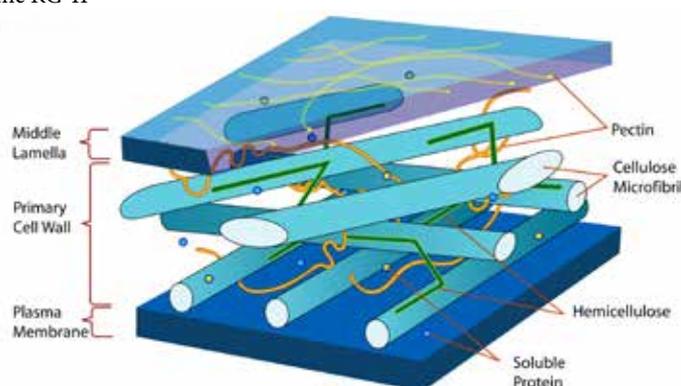
**Enzo Mancuso**  
PhD

*"Chemical Synthesis of a Rhamnogalacturonan II Fragment"*

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Funded by:  
**The Independent Research Fund Denmark (FTP)**



Section of a wall in growing plant cells.

# Effective Upgrading of a Biomass By-product

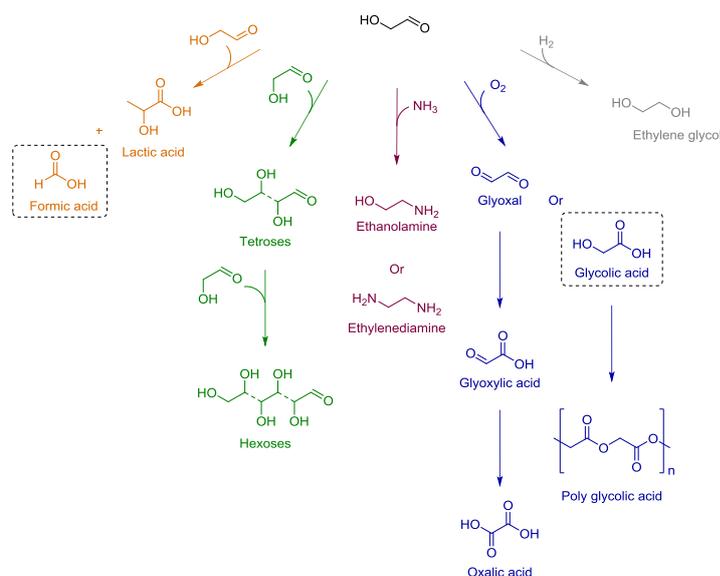
Glycolaldehyde can be selectively converted into either glycolic acid or formic acid under mild conditions. The procedure is relevant for industrial use.



**Amalie E. Modvig**  
PhD

*"Selective Oxidation of Biomass-derived Chemicals"*

With typical carbon contents ranging from 42-54 %, biomass is a promising renewable carbon source. However, new sustainable industrial processes for conversion of biomass are required. This project presents such processes for upgrading of glycolaldehyde (GAD), which is a common by-product from degradation of larger biomass-derived compounds. Also, similar processes are investigated for some simple alcohols.



*Conversions of glycolaldehyde into various biomass derived chemicals.*

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Funded by:

**The Danish Council for Strategic Research and the Danish Council for Technology and Innovation. The project was carried out in collaboration with Haldor Topsøe A/S.**

GAD is the smallest sugar, consisting of two carbons containing both an aldehyde and a hydroxyl group. Several studies on conversion of GAD into useful products have been reported, suggesting GAD to be a potential platform molecule. Still, new and sustainable protocols for the required conversion are needed.

In the project, heterogeneous supported gold nanoparticle catalysts were utilized to catalyze selective oxidation of GAD to glycolic acid, which has found applications in various industries. Up to 68 % glycolic acid was obtained at high catalyst loading, limited by CO<sub>2</sub> formation. At a catalyst loading more fitting for industrial application, 57 % glycolic acid was obtained.

As an alternative, GAD was instead oxidized to formic acid utilizing a ceria-supported ruthenium hydroxide catalyst. Formic acid is a well-known industrial platform chemical. Recently, it has been suggested that formic acid may facilitate safe transportation and storage of hydrogen, as hydrogen can efficiently be released from formic acid. Hydrogen has multiple applications, one of them being energy conversion by fuel cells.

81 and 88 % formic acid was obtained at low and increased surface catalyst areas, respectively. Degradation of formic acid was observed for the low-surface area catalyst over time, whereas the higher-surface area catalyst was found to yield high substrate stability over time.

Oxidations of GAD at high temperatures generally resulted in over-oxidation products. However, reduced conversion was observed if temperatures were decreased too much. The optimal temperature range was found to be 80-90 °C for aqueous, base-free oxidations of GAD.

In conclusion, the project has shown that GAD can be selectively converted into either glycolic acid or formic acid, depending on the catalyst applied, under mild, aqueous and base-free conditions. High product stability in the ceria-supported ruthenium hydroxide catalyzed oxidation to formic acid, together with good catalyst activity observed when reusing the catalysts, renders the developed procedure for formic acid production highly applicable for industrial use.

# Vanadium-catalyzed Conversion of Biomass

Ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) is shown to be an efficient and sustainable catalyst for several reactions relevant to conversion of biomass.

Biomass is the most abundant renewable carbon resource, and it is most likely that fuels and chemicals obtained from biomass will play a major part in tomorrow's society. However, for the necessary conversion of biomass, new and improved technology has to be developed. A major difference between fossil and biomass feedstock is the presence of oxygen in the biomass. The focus of the project was the study of reactions which remove oxygen from molecules in order to increase the value of biomass components.

More specifically, vanadium catalyzed deoxydehydrogenation (DODH) was applied to conversion of vicinal diols (characteristic of biomass materials) to alkenes. Initial experiments found the DODH reaction to proceed in an autoclave at 230 °C, when 1,2-decanediol was allowed to react with 5 mol% ammonium metavanadate ( $\text{NH}_4\text{VO}_3$ ) in isopropanol. After 17 hours, a yield of 1-decene that corresponded to 50 mol% of the starting substrate was achieved.

A further goal was to use an alcohol as both the solvent and as the reductant. Secondary alcohols were found to give much better yields than their primary analogues, and isopropanol was selected for further research.

Most of the screened catalysts gave the same yields, and  $\text{NH}_4\text{VO}_3$  was judged to be a good choice based on its availability and ease of handling. Further, this catalyst proved to be more sustainable if reused before it gets deactivated.

Vanadium catalyzed DODH was found to have unique selectivity towards substrates containing exactly one primary and one

secondary hydroxyl group. In contrast, internal diols such as 3,4-hexanediol gave no yield of alkene and both stereoisomers of 1,2-cyclohexanediol were almost completely unreactive. However, substrates that are stabilized by conjugation, such as hydro-benzoin, were found to undergo oxidative cleavage to form two aldehydes. The reactivity of the diols also depends strongly on the orientation of the hydroxyl groups. A sharp decline in product yield was thus observed when cis-1,2-cyclohexanediol was added to a reaction of 1,2-hexanediol, which was in contrast to addition of the trans stereoisomer. A possible reason is that the trans isomer cannot simultaneously coordinate to the metal with both hydroxyl groups and thereby inhibit the reaction. Glycerol proved to be unreactive as well, whereas 1,2-propanediol and 3-isopropoxy-1,2-propanediol did undergo DODH to yield propene and 3-isopropoxy-1-propene, respectively.

In a related but separate project, vanadium catalyzed reactive distillation of glycerol was developed. The reaction setup and conditions were optimized to ensure a quick separation of the products from the mixture. Here, just 1 mol%  $\text{NH}_4\text{VO}_3$  was enough to achieve up to 22 mol% of allyl alcohol and 4 mol% acrolein from 23 g of glycerol, when heated to 275 °C for 5 hours. This was done in an optimized setup in which a short-range distillation centerpiece allowed for a fast separation of the alcohol.

The catalytic performance of  $\text{MeReO}_3$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  was compared, and vanadium was found to give more allyl alcohol than rhenium, which is surprising due to the increased DODH reactivity of rhenium.



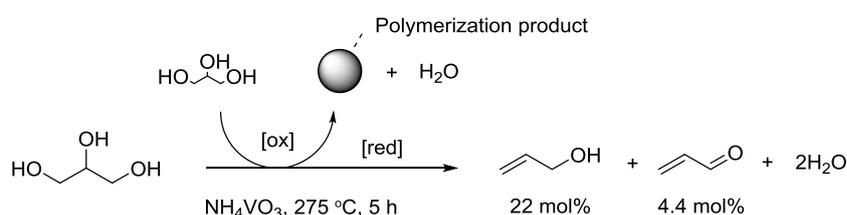
**Lasse Bo Nielsen**  
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*"Sustainable Chemistry for Biomass Utilization"*

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Funded by:  
**The Independent Research Fund Denmark, Sapere Aude.**



*Proof of concept: Use of vanadium catalysts for conversion of biomass-related molecules to value-added organic products.*

# Simulation of Flow in Heavy Oil Reservoirs

Heavy oil reservoirs undergo large changes in temperature and pressure depending on the applied production strategy. The project presents tools for thermal simulation.



**Duncan Paterson**  
PhD

*"Flash Computation and EoS Modelling for Compositional Thermal Simulation of Flow in Porous Media"*

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**ExxonMobil,**  
**ConocoPhillips.**

Of the total known world oil reserves only 30 % are conventional sources, while 70 % are heavy oil, extra heavy oil, oil sands and bitumen. Presently, the cost of producing heavy oil is often close to the sale price of the oil. Therefore, the cost of production needs to come down. To that end, better understanding of the production processes is required. The focus of the project is thermodynamic description of the oil.

Heavy oil is a viscous and dense substance, which flows very slowly under gravity at atmospheric temperature. Most often it is necessary to use steam to reduce the viscosity and enhance oil production. Production can be further enhanced with a light hydrocarbon solvent.

Simulation of heavy oil reservoirs is not trivial, as they undergo large changes in temperature and pressure depending on the applied production strategy. Furthermore, the use of a light hydrocarbon solvent can lead to highly asymmetric mixtures and the appearance of a second oleic phase.

A number of possible equations of state (EoS's) were evaluated. It was found, that if the interaction between the water and hydrocarbon phases is not considered important, then the commonly used cubic EoS's with the van der Waals mixing rules are suitable. If more complex interactions are considered important, then the cubic EoS's can be used with the Huron-Vidal type mixing rules. More complex EoS's such as cubic plus association (CPA) or PC-SAFT can also be used.

For thermal simulation it is necessary to add an energy balance to the system. Commonly, the temperature is used as an additional primary variable. The resulting isothermal flash specification can lead to some problems during transient simulation. The fluid in some grid-blocks may become narrow boiling. The enthalpy of a narrow boiling mixture changes rapidly due to very small changes in temperature or pressure.

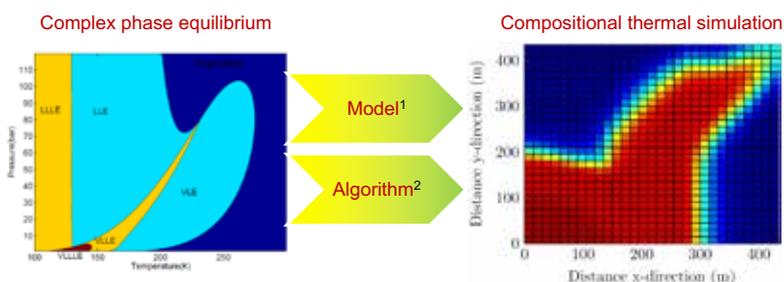
An approach using the energy directly in the flash calculation (e.g. isobaric, isenthalpic flash) is explored in this work and an algorithm presented which takes only slightly more computational resources than the conventionally used isothermal flash. This is demonstrated to be robust for a number of mixtures, and an approach tailored for the flash calculation of mixtures containing water is described.

The conventional isothermal flash framework is cumbersome when dealing with more than two or three phases. A new method – modified RAND – is presented. The method is primarily examined for multiphase isothermal flash, with a robust implementation described. Furthermore, the conventional method of solving an EoS at a specified temperature and pressure is abandoned and a method which co-solves the EoS with the equilibrium equations is described – vol-RAND.

Finally, a thermal EoS based reservoir model is developed from an isothermal simulator. The energy balance partial differential equation is added, and the temperature used as an additional primary variable. The EoS's compared for heavy oil related fluids are implemented in the simulator. Also, a multiphase flash algorithm using modified RAND and stability analysis skipping is added to the simulator.

With the thermal reservoir simulation tool developed it is possible to carry out further comparisons and add more complexity in future work.

*Handling complex equilibrium in compositional simulation through advanced thermodynamic models and efficient equilibrium calculation algorithms: The RAND-based formulations provide a new framework for multiphase flash w/ or w/o reactions.*



1. G<sup>E</sup>-type mixing rules and association models

2. Multiphase PH flash and new RAND formulations

# Simulation of Production from Shale

The project has developed robust calculation tools for phase equilibrium in porous media with capillary pressure and adsorption effects.

Production of oil and gas from shale reservoirs has become a reality over the past few decades. As shale reservoirs are much tighter than conventional reservoirs, with pore sizes ranging in the nanometer scale, they were previously considered technically unviable to produce. New technologies such as horizontal drilling and multistage fracturing have changed the scene, but forecasting of the production remains a challenging task. The project presents models and algorithms for the purpose.

Especially in USA, production from shale has grown fast and partly substituted electricity from coal-fired power plants. However, current recovery factors are low ranging from 20-30 % for shale gas and 3-7 % for shale oil. A better understanding of the processes involved is likely to lead to higher recovery factors.

The confined nature of shale reservoirs introduces challenges in the understanding of the fluid phase behavior. High capillary forces can be experienced between the liquid and vapor, and selective adsorption of components onto the rock becomes relevant.

The project presents an efficient algorithm for phase envelope calculations in the presence of capillary pressure. It is used to analyze the main changes on the phase boundary for several fluids

of interest. The results show changes in the saturation pressure and temperature along the phase envelope, except at the critical point. A linear analysis explains such changes. As a result, useful mathematical relationships that estimate the magnitude of these changes were obtained. Moreover, a flash algorithm that accounts for capillarity was developed.

Since capillary pressure and adsorption occur simultaneously in shale, its combined effect was studied. A model comparison for high-pressure adsorption in shale is presented. As adsorption data in shale are scarce, additional capabilities besides the accuracy were considered. The multicomponent potential theory of adsorption yields the best results. Moreover, it is useful to extrapolate adsorption data for hydrocarbons that are not available in the literature. An algorithm for phase split calculations considering both capillary pressure and adsorption was developed. The results show that adsorption and capillary pressure can significantly change the phase behavior. In general, a shrunk phase envelope with a shifted critical point is obtained for hydrocarbon mixtures. This behavior is mainly caused by compositional changes in the bulk phase due to selective adsorption of the heavier components onto the rock, while the change in bubble point pressure is mainly due to capillary pressure.

In conclusion, the project has developed several robust calculation tools for phase equilibrium in porous media with capillary pressure and adsorption effects. Analysis based on use of these tools shows capillary pressure and adsorption to have non-negligible effects on phase equilibrium in shale.

*Effect of capillary pressure and adsorption on phase equilibrium of fluids with different GORs (gas oil ratios)*



**Diego Sandoval**  
PhD

*"Phase Equilibrium Modeling for Shale Production Simulation".*

## CONTACT

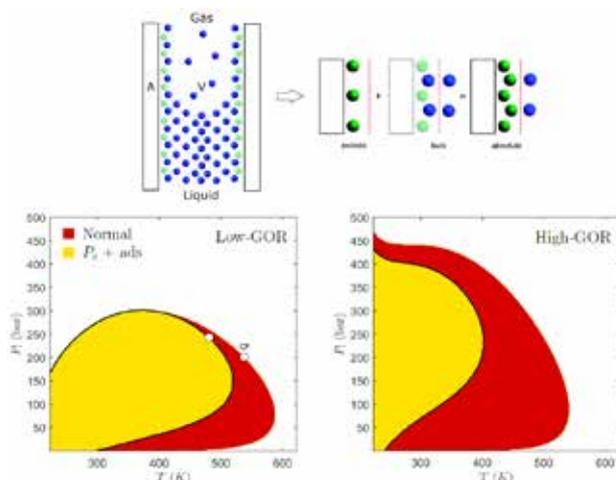
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**ExxonMobil.**



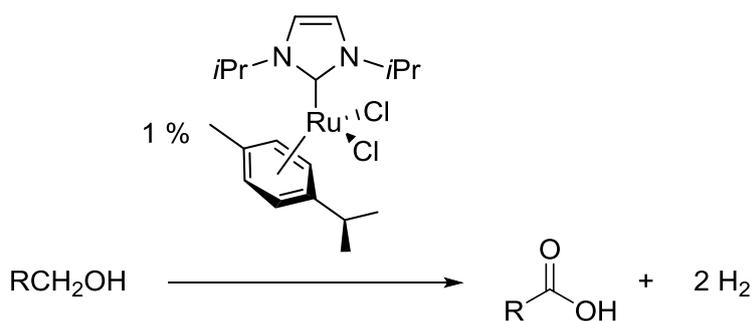
# Better Catalysis in Organic Chemistry

Carboxylic acids, imines, and biaryls are important compounds in organic chemistry. Suitable catalysts for their synthesis are presented.



**Carola Santilli**  
PhD

*"Transition Metal Catalyzed  
Synthesis of Carboxylic Acids,  
Imines, and Biaryls"*



*Dehydrogenation of a primary alcohol to the carboxylic acid.*

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Funded by:  
**DTU Chemistry**

Several transition metals are known for their ability to catalyze chemical reactions. The right choice of both the transition metal and the specific synthesis method for the catalyst is crucial to the efficiency for any given reaction. The project suggests suitable catalysts for synthesis of three groups of important compounds in organic chemistry; namely carboxylic acids, imines, and biaryls.

The efficiency of a catalyst is expressed through its capability to enhance both the kinetics of the reaction and the selectivity towards the desired product. A further property in high demand is the ability of the catalyst to be swiftly regenerated.

Firstly, a new methodology for the synthesis of carboxylic acids from primary alcohols and hydroxide was developed. The reaction is catalyzed by the ruthenium N-heterocyclic carbene complex [RuCl<sub>2</sub>(I/iPr)(p-cymene)] where dihydrogen is generated as the only by-product. Various substituted benzyl alcohols smoothly undergo transformation. Fast conversion to the carboxylic acids was achieved. The kinetic isotope effect of the reaction was determined to be 0.67 using 1-butanol as the substrate. A plausible catalytic cycle was characterized by DFT/B3LYP-D3 and involved coordination of the alcohol to the metal, β-hydride elimination, hydroxide attack on the coordinated aldehyde, and a second β-hydride elimination to furnish the carboxylate.

Secondly, the reaction between aryl halides and aryl Grignard reagents catalyzed by MnCl<sub>2</sub> was extended to several methyl-substituted aryl iodide reagents by performing the reaction at 120 °C. A limitation of the hetero-coupling process is the concomitant dehalogenation of the aryl halide and homo-coupling of the Grignard reagent, which result in low to moderate yields of the desired hetero-coupling product. The mechanism of the cross-coupling process was investigated in two radical trap experiments. The employment of radical scavengers such as 1,4-cyclohexadiene and 4-(2-bromophenyl)-but-1-ene revealed the presence of an aryl radical intermediate. This leads to the proposal of an SRN1 pathway for the coupling.

Finally, a study of the dehydrogenative synthesis of imines catalyzed by simple and commercially available manganese complexes was conducted. Originally, the low valent CpMn(CO)<sub>3</sub>, Mn(CO)<sub>5</sub>Br, and Mn<sub>2</sub>(CO)<sub>10</sub> complexes were employed for the coupling reaction between benzyl alcohol and cyclohexylamine. These displayed poor or no reactivity. Surprisingly, when the Jacobsen complex is used as the catalyst, the reaction between benzyl alcohol and cyclohexylamine resulted in 77 % yield of the corresponding imine. Moreover, gas evolution confirmed that the reaction occurs by dehydrogenation.

# Novel Tools for Medical Imaging

Several new diagnostic methods with applications in cancer diagnostics and in blood pool imaging have been developed.

Accurate diagnostics can improve therapeutic outcome as well as patient compliance. In the project, several new diagnostic tools were developed for medical imaging with applications in cancer diagnostics and in blood pool imaging.

Approximately 50% of all cancer patients receive radiotherapy. As tumors rarely display a fixed position during therapy, it is desirable to use an injected marker as a point of reference to secure that the radiation dose targets the tumor rather than the surrounding sound tissue. In the project, a fiducial marker based on encapsulated gold nanoparticles (AuNPs) within a gelation matrix of sucrose acetate isobutyrate (SAIB) was developed. The marker was tested in vivo in mice and a canine dog, displaying contrast in the range of 1200 HU which decreased to 800 HU over 8 weeks indicating potential aggregation of AuNPs within the SAIB formulation.

A tissue marker for surgical guidance of non-palpable tumors in breast cancer was also developed. As radioactive tracer, radio-iodinated SAIB-derivatives were developed based on the regio-selective ipso-iodination of aryl-TMS moieties. The radiochemical yield was 83% with a radiochemical purity of 95%. The formulation was tested in vivo as a potential tissue marker in mice, showing excellent stability and contrast properties. A dosimetric

calculation for human patients indicated that vital organs and tissues would not be considerably affected by the radiation dose.

Further, a small library of iodide-based contrast agents for remote loading in liposomes was synthesized for blood pool imaging. Long circulating contrast agents for blood pool imaging by CT-imaging are of interest due to the current limitations of short retention times and the considerable amounts needed to achieve a proper contrast. Remote loading of one candidate was successful; however, the proper contrast level was not sufficient to be visible by CT-imaging.

Finally, site-specific radio-iodination of peptides and proteins was performed. To achieve a conclusive outcome in radio-immuno-assays as well as retaining a high binding affinity of receptor binding peptides, regioselective radioiodination is crucial. Therefore, a TMS-substituted tyrosine was synthesized via the Negishi coupling to test if regioselective iodination could be obtained. The tyrosine derivative was used in the synthesis of dipeptides of phenylalanine, tyrosine and tryptophan respectively in order to evaluate the selectivity towards ipso-substitution of the TMS in the iodination reaction. First proof-of-concept experiments using aryl-TMS as placeholder in the site-specific iodination of peptides and proteins were demonstrated.



**Henrik Schaarup-Jensen**  
PhD

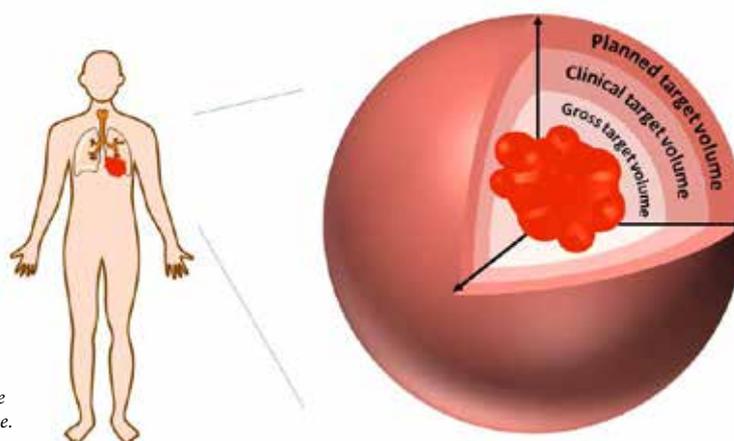
*"Synthesis and Development of Diagnostic Tools for Medical Imaging"*

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Funded by:  
**The Danish Council for Strategic Research and DTU Chemistry.**



*Schematic representation of the different kinds of target volume.*

# Novel Graphene Catalysts for Fuel Cells

Electrocatalysts which are efficient relative to their consumption of both energy and platinum (Pt) hold new promise in polymer electrolyte membrane fuel cell applications.



**Nedjeljko Seselj**  
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*"Chemical Production of Graphene Catalysts for Electrochemical Energy Conversion"*

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Funded by:

**The Independent Research Fund Denmark (FTP).**  
The project was carried out in collaboration with the company Danish Power Systems.

Fuel cells are regarded as an important part of the future energy system, since they provide clean energy with low pollution. However, fuel cells depend on expensive catalyst materials such as platinum (Pt). The project presents a new kind of graphene based catalysts with high catalytic performance and stability and minimal Pt content.

Fuel cells convert chemical energy stored in fuel molecules into electrical energy via electrochemical reactions. Basic elements of a fuel cell are cathode, anode and electrolyte. Commonly used fuels are dihydrogen, methanol, ethanol and formic acid. While several types of fuel cells exist, the focus of this project is polymer electrolyte membrane fuel cells (PEMFCs) that employ small fuel molecules and dioxygen to produce electrical energy.

PEMFCs offer high specific energy density, but the technology is not widely available, primarily due to the expensive catalyst employed. Highly active catalysts, such as Pt are required, since the mild operating conditions (up to 100 °C) do not contribute significantly to elevating the reaction-driving forces. Pt is a scarce element in the Earth's crust, and only a few hundred tons are produced annually, leading to high and increasing prices. Extensive studies have therefore been undertaken to synthesize Pt nanocrystals in order to maximize the catalytic surface area, and thereby the catalytic effect, while minimizing platinum consumption.

In the project, Pt nanoparticles were synthesized. Next, bimetallic Au@Pt nanoparticles were synthesized with atomically thin Pt shells, further increasing the Pt utilization. Graphene was chosen as support due to its unique properties, such as high charge carrier mobility, high conductivity, mechanical strength, and high surface area. A further advantage is the chemical inertness under PEMFC operating conditions.

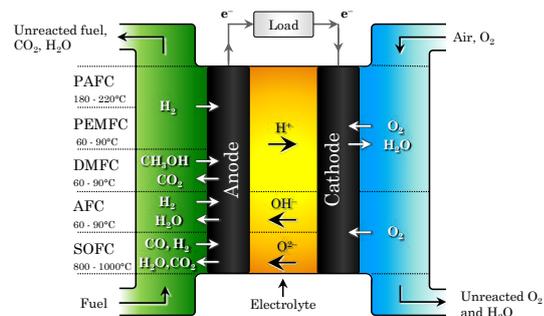
Chemical anchoring of Pt and Au@Pt nanoparticles was achieved via L-cysteine linker molecules that provide pathways for fast

electron transfer during the electro-catalytic reactions. Electrochemical properties of self-assembled L-cysteine monolayers immobilized on single-crystal Au(111) surfaces in ionic liquids were studied and their structures imaged by scanning tunneling microscopy (STM), to investigate the nature of L-cysteine bonds on Au.

Au increases the Pt d-band energy, resulting in stronger bonding to fuel molecules, and higher current densities and power densities in PEMFCs. Furthermore, Au cores protect Pt atomic layers from poisoning. A G-Cys-Au@Pt electrocatalyst in the PEMFC anode setup exhibited superior performance compared to the commercial catalyst used in industry. This was mainly attributed to unique behavior of water while interacting with hydrophobic graphene.

Finally, a direct formic acid, methanol, and ethanol PEMFC station was established. Here, as-synthesized graphene-immobilized Au@Pt nanoparticles exhibit high electrocatalytic performance as anode materials with long stability.

In conclusion, electrochemical power sources pose a promising alternative in a time of depleting fossil fuels. Electrocatalysts which are efficient relative to their consumption of both energy and Pt offer here new perspectives in PEMFC applications.



*Scheme of representative FC systems: AFC, PEMFC, DMFC, PAFC, and SOFC. The fuel oxidation occurs at the anode while oxygen is reduced to water at the cathode. Ionic species involved in the reactions of different FC technologies is noted as the electrolyte.*

# Closing in on the Causes of Alzheimer's

Improved understanding of the structural and chemical origins of Alzheimer's disease may lead to new structure-based strategies for treatment.

Alzheimer's disease (AD) affects millions of people worldwide. Currently, no cure exists. The project aims to improve understanding of the structural origins of the disease by studying the structural changes occurring in the key proteins A $\beta$  and presenilin involved in the disease.

WHO estimates that more than 30 million people worldwide suffer from AD, a devastating neuro-degenerative disease that involves loss of memory, mood swings, changes in behavior, and loss of bodily functions. Despite the impact of the disease and extensive research efforts, no efficient cure has yet been developed, and it is expected that more molecular mechanism-based strategies are necessary.

Brains of Alzheimer's patients contain large amounts of aggregated misfolded protein deposits known as "senile plaques". These are mainly composed of metal ions and A $\beta$  peptides organized as  $\beta$ -sheet structured fibrils.

AD mainly occurs sporadically, but a small portion (3-5 %) of cases are connected to genetic mutations. These familial AD (FAD) cases provide a strong basis for studying the structural causes of the disease. The FAD cases are generally characterized by early onset and display a purer form of the structural deviations than the sporadic cases where a mix of several age-related effects is often seen.

FAD is typically associated with genetic mutations in the genes coding for amyloid precursor protein (APP), presenilin 1 (PSEN1) and presenilin 2 (PSEN2). These mutations are all related to A $\beta$ .

In the project, fundamental structural origins of A $\beta$  and PSEN1 that drive disease severity were identified. Using different force field methods and molecular dynamics simulations the project defined the most important structural types of A $\beta$  and correlated these against experimental data to define the structures that explain experimental data relevant to disease. The project shows that simple, specific conformational features such as coil, helix and solvent availability of

genetic A $\beta$  variants correlate with their toxicity, and these hotspots are thus of interest as new targets of more specific, tailored antibodies.

Using EPR, CD, NMR, and fluorescence spectroscopy techniques, the normal and two mutant A $\beta$  forms were studied that are protective and pathogenic, respectively, to enable a model system of the disease. Distinct structural and aggregation behavior was observed that correlates with disease manifestation. The Cu $^{2+}$  binding site of A $\beta$  was studied and shown to enforce the differences, consistent with a known role of copper-A $\beta$  interactions as probably central to the disease.

The project also studied PSEN1, the catalytic subunit of  $\gamma$ -secretase which is responsible for releasing A $\beta$  peptides into the extracellular space of neurons.

Using meta-analysis, the project found significant correlations between clinical patient data and specific changes in fundamental structural and chemical properties such as hydrophobicity and stability of the PSEN1 mutants. Also, major structural changes were discovered in the PSEN1 subunit which controls access to the enzyme that produces A $\beta$  and aids in positioning and cleavage of substrates, and this led to a new model of how long vs. short A $\beta$  peptides are formed, and the classification of three conformation states of the protein that directly controls the ratio of their production (the longer forms are considered to be more pathogenic).

Hopefully, the research findings presented will be helpful in designing new strategies for treating AD.



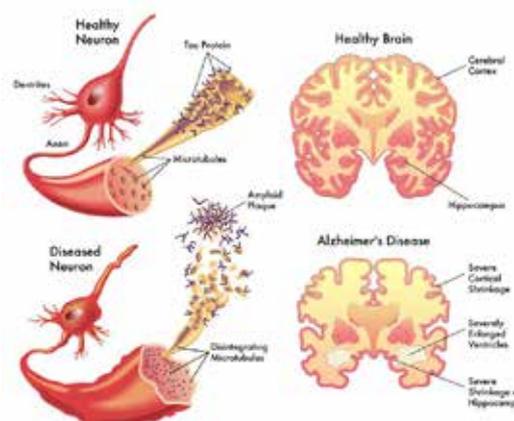
**Arun Kumar Somavarapu**  
PhD

*"Structural Dynamics and Pathogenicity of A $\beta$  and Presenilin1 Variants: Towards a Mechanistic Understanding of Alzheimer's Disease"*

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Funded by:  
**The Independent Research Fund Denmark (FNU)**  
and the **Danish Center for Scientific Computing**.



Graphic representation of healthy and Alzheimer's disease brain showing amyloid beta plaques and tau protein.

# Synthesis of Anti-Cancer Candidates

Strategies for high-throughput generation of hydroxamic acids relevant in treatment of a variety of diseases, including cancer, are presented.



**Kim Thollund Mortensen**  
PhD

*"Development of a UV-Cleavable Protecting Group for Hydroxylamines, Synthesis of a Structurally Wide Variety of Hydroxamic Acids, and Identification of Histone Deacetylase Inhibitors"*

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Funded by:

**The Independent Research Fund Denmark (FTP)**

Hydroxamic acids are an important class of organic compounds owing to their presence in numerous biologically active molecules. Several hydroxamic acids are regarded as potential drugs, mainly for treatment of cancer but also a number of other diseases. The project suggests chemical strategies for high-throughput generation of structurally diverse hydroxamic acids.

A hydroxamic acid bears the functional group  $RC(O)N(OH)R'$ , with R and R' as organic residues and CO as a carbonyl group. Some hydroxamic acids (e.g. vorinostat, belinostat, and trichostatin A) are histone deacetylase inhibitors (HDIs) meaning they inhibit the enzyme histone deacetylase (HDAC). HDIs have long been used in psychiatry as mood stabilizers. More recently, several HDIs have entered clinical trials for treatment of various types of cancer. Furthermore, individual HDAC enzymes have been linked to a variety of other diseases, including chronic pain and cystic fibrosis. The project presents mild and reliable chemical strategies for synthesis of a range of structurally diverse hydroxamic acids.

In order to synthesize molecules with various functional groups, the ability to block and unblock reactivity in a controlled way is essential.

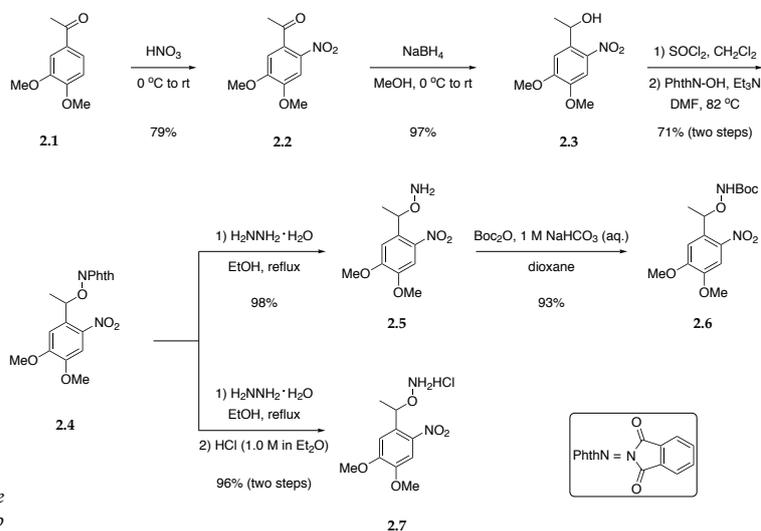
Therefore, the use of so-called protecting groups is a vital tool in organic chemistry. However, some disadvantages are inevitable when using protecting groups. Firstly, two steps are added to the total step count, protection and deprotection. Secondly, the protecting groups limit the types of chemistry that can be performed as too harsh treatment, such as acidic- and basic-catalyzed hydrogenation, may damage the target molecule.

In contrast, removing protecting groups by UV-light is a mild method. Thus, photo-cleavable protecting groups are highly applicable for the synthesis of structural complex and sensitive compounds, including biologically important molecules. The project presents the development of a novel O-hydroxylamine photo-cleavable protecting group, based on the methyl-6-nitroveratryl moiety. Application of the protected hydroxylamine derivative for the synthesis of a broad range of N-alkylated hydroxamic acids was demonstrated.

Importantly, the construct is shown stable towards a diverse set of reaction conditions, as well as orthogonal with conventional protecting groups. The O-protected hydroxylamine derivative was applied to synthesize

a small collection of N-alkylated suberanilohydroxamic acid as subtype selective HDAC inhibitors.

During an external stay at Nanyang Technological University, Singapore, compounds targeting the quorum sensing network in *Pseudomonas aeruginosa*, important for the treatment of bacterial infections, was also synthesized.



*Synthesis of O-hydroxylamine protecting group*

# From Biomass-sugars to Chemicals

Several promising tin-catalyzed reactions for conversion of biomass-derived sugars into chemicals are presented.

Most chemicals are currently produced from fossil resources like natural gas or oil. As we slowly transition from these finite sources of carbon to more renewable resources, new catalytic systems are needed. The project presents tin-based catalysts for conversion of sugars substrates into chemicals of high value.

Biomass is one of the most readily available carbon sources. However, mainly due to its content of oxygen, biomass is so different in its chemical structure from oil that many existing technologies fall short. Not only will new catalysts and processes have to be developed, entirely new chemicals will result.

In the project, several tin-silicate materials were prepared. These tin-containing catalysts are recognized for their ability to transform carbohydrates into different valuable products.

Sn-Beta is known to be a highly active zeolite catalyst for conversion of sugars. It was shown that the active component tin changes the growth of crystals. Just a small increase in tin content was enough to cause longer crystallization times (up to 60 days). Addition of small amounts of alkali metal salts could counter this effect. The effect of alkali was found to transcend to a variety of sugars, solvents and other tin-silicates such as Sn-MCK-41 og Sn-Beta prepared by a post-synthesis methodology. The latter makes it possible to use industrially relevant tin-containing catalysts to achieve high yields of methyl lactate.

In the absence of alkali, instead of retro-aldol reaction, hexoses and pentoses were found to undergo  $\beta$ -dehydration leading to several new and highly functional products. These include the trans-2,5,6-trihydroxy-3-hexonic acid methyl ester (from hexoses) or trans-2,5-dihydroxy-3-pentenoic acid methyl ester (from pentoses) in acceptable yields (18-33 %).

By using a zeolite with narrow channels (Sn-MFI), shape selectivity could be exploited for the valorization of small sugars. Glycolaldehyde (GA) could selectively undergo aldol condensation to give high yields of the rare tetroses (74 %). With larger pore systems and channels substantial yields of hexoses were formed from subsequent condensation reactions (Sn-MCM-41 and Sn-Beta). In the particular case of Sn-MFI and Sn-Beta, additional conversion of the tetroses lead to vinyl glycolic acid (VGA) and  $\alpha$ -hydroxy- $\gamma$ -butyrolactone (HBL). Changing the conditions, it was possible to form up to 44 % of VGA directly from GA using Sn-MFI.

In conclusion, all the prepared tin-silicate materials were found to form desirable, potential high-value products from sugars such as methyl lactate, methyl vinyl glycolate and previously unknown  $\alpha$ -hydroxy- $\beta$ ,  $\gamma$ -unsaturated esters. These reactions and catalysts are very promising for conversion of abundant biomass-derived sugars into chemicals.



**Søren Tolborg**  
PhD

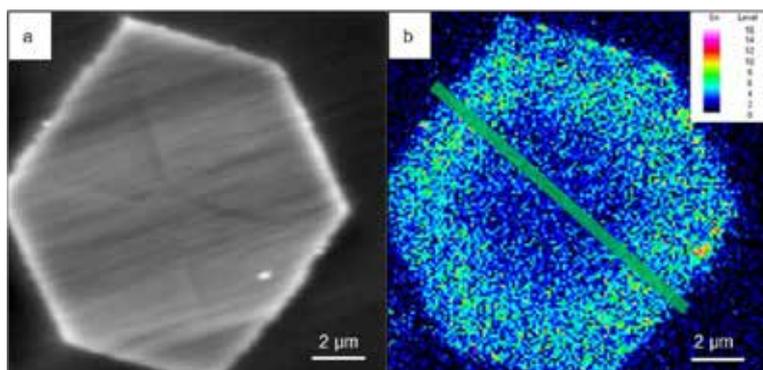
*"Synthesis, Characterization and Evaluation of Tin-containing Silicates for Biomass Conversion"*

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Funded by:  
**The SPIR initiative by the Danish Council for Strategic Research and the Danish Council for Technology and Innovation. The project was done in collaboration with Haldor Topsøe A/S.**



Scanning electron microscopy image of synthesized Sn-Beta catalyst with the Sn X-ray intensity highlighted.

# Models for Deep Oil Exploration

The accuracy of existing thermodynamic models under HPHT (High Pressure, High Temperature) conditions is evaluated, and improvements are suggested.



**Farhad Varzandeh**  
PhD

*"Modeling Study of High Pressure and High Temperature Reservoir Fluids"*

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Funded by:

**Innovation Fund Denmark, Maersk Oil and DONG E&P as part of the NextOil (New Extreme Oil and Gas in Denmark) project.**

With dwindling easily accessible oil and gas resources, the industry is driven towards deeper geological formations. In deep reservoirs, temperature and pressure can become extremely high, e.g. up to 250 °C and 2,400 bars. It is well known that established thermodynamic models have shortcomings when applied to such extreme conditions. The thesis evaluates the accuracy of existing models for HPHT (High Pressure, High Temperature) exploration, while also suggesting improvements.

HPHT reservoirs are technologically and economically risky to develop, but highly rewarding if successfully produced. A critical parameter is the length of time which equipment must withstand the HPHT conditions. Therefore, accurate knowledge of the reservoir fluid behavior is required, including density and viscosity of oil and gas at reservoir conditions. Also compressibility is critical, as compression is necessary for HPHT production.

Currently, there are neither accurate databases for these fluid properties, nor adequate equations of state (EoSs) for density and compressibility able to predict these properties at extreme conditions. Presently, oil companies use correlations based on lower temperature and pressure databases despite their unsatisfactory predictive capability at extreme conditions – with margins of error as large as +/- 50%.

The project evaluated both cubic and non-cubic EoSs. It was found that the non-cubic models are much better than the cubics for density, com-

pressibility, heat capacity, and Joule-Thomson coefficient calculation of both light and heavy components in reservoir fluids over a wide temperature and pressure range. The GERG-2008 model gave the lowest deviations of all. Still, this model gave large deviations for bubble point pressure calculation on certain heavy and asymmetric binary systems, suggesting that the model may still be improved for some binary pairs.

Soave-BWR gave the closest prediction of the thermal properties to that of GERG-2008 among the other EoSs tested.

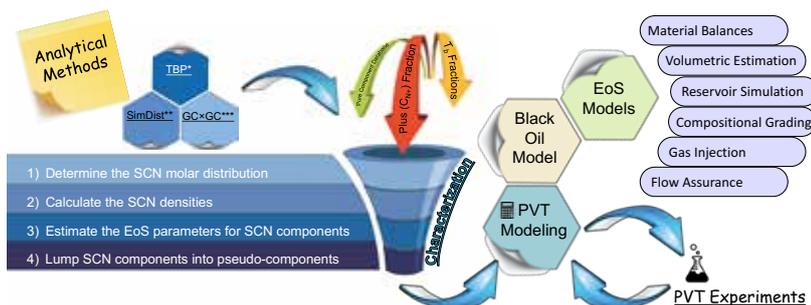
For non-cubic models like PC-SAFT, the characterization method is less mature than cubic models. Therefore, a new reservoir fluid characterization method for PC-SAFT is proposed. In addition, this method was improved by adjusting the correlations with a large PVT database.

Importantly, a general approach to characterizing reservoir fluids for any EoS has been established. The approach consists in developing correlations of model parameters first with a database for well-defined components and the adjusting the correlations with a large PVT database. It is shown that this approach can be applied to PC-SAFT, and to classical cubic models like SRK and PR.

With the developed methods, a comparison in PVT calculation involving 17 EoS-characterization combinations and 260 reservoir fluids was made.

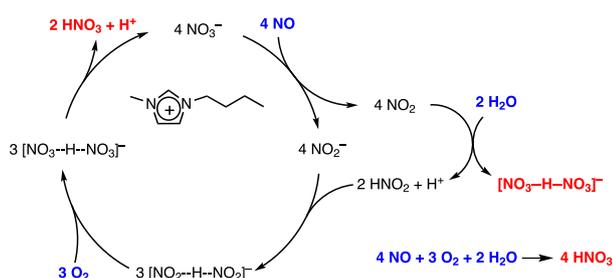
Finally, several new sets of mixing rules were developed for Soave-BWR for mixture calculation to improve the value of this model. It was shown, that some problems with the original Soave-BWR can be fixed by the new mixing rules. However, the overall performance was not significantly improved. Development of mixing rules for non-cubic EoS models is still a semi-empirical process, requiring extensive testing.

*In addition to non-cubic EoS models, advanced characterization of heavy fractions is crucial to HPHT PVT modelling.*



# Cleaner Incineration of Biomass and Waste

Tail-end solutions for efficient NO<sub>x</sub> abatement in biomass and waste incineration plants have been developed.



Proposed catalytic cycle for the absorption and oxidation of NO to HNO<sub>3</sub> by [BMIM][NO<sub>3</sub>]. Blue species are reactants, red species are the products, and black species are intermediates.

The share of biomass and waste incineration in our energy supply is growing steadily. This is a key factor in the ongoing transition away from fossil fuels. However, these feedstocks come with new challenges. The project presents strategies for post-combustion removal of nitrogen oxides (NO<sub>x</sub>) which is a health and environmental concern.

Formation of NO<sub>x</sub> is inevitable during high temperature combustion processes in air. NO<sub>x</sub> emissions cause acid rain, contribute to smog formation, induce respiratory diseases, and contribute to depletion of the ozone layer. Therefore, catalytic removal of NO<sub>x</sub> is installed in modern power plants. The deNO<sub>x</sub> unit is usually placed in a very exposed position as the first emission control unit. However, this is not ideal when biomass and municipal waste are used, as these feedstocks contain levels of catalyst poisons such as potassium and hydrochloric acid. This problem must be solved, as it hinders a more widespread use of alternative fuels.

The project approach is to aim for a tail-end de-NO<sub>x</sub> unit. At tail-end, the level of potential catalyst poisons is expected to be insignificant, because the gas has passed through a wet scrubber. Furthermore, a tail-end unit is typically more easily installed in existing power plants.

The focus is on ionic liquids (ILs), which have been shown as possible effective and selective absorbers. Due to the high viscosity of ILs it is feasible to disperse them onto a porous support

in so-called supported ionic liquid phase (SILP) materials. The ILs facilitate oxidation of NO<sub>x</sub> to nitric acid, HNO<sub>3</sub>, by oxygen and water present in the exhaust. HNO<sub>3</sub> is retained in the IL until it is released by heating the IL above 130 °C.

Dimensioning of an absorber unit for retrofitting into a cargo ship was performed. It was found, that in order for the SILP absorbers to become viable for marine applications, the absorption

capacity had to be increased by a factor of 30-50.

Further, hollow-sphere silica (HS) was applied for the purpose. SILP formulations utilizing the HS-support material performed significantly better than other SILP formulations. An improvement with a factor of 4-6 was found when the SILP materials were compared volumetrically. At this level of efficiency, NO<sub>x</sub> absorption and oxidation may be applied for specialized purposes like nitric acid production. Presently, however, for large scale application in flue gas cleaning the absorption strategy would need improvement by at least a factor of 10.

Another highly promising approach for tail-end deNO<sub>x</sub> is to utilize the efficient oxidation of NO over the IL based material to higher nitrogen oxides and acids (NO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>) to boost the rate of known deNO<sub>x</sub> catalyst technology. This effect can be sustained in steady state at low temperature and at significantly higher volumetric rates than those found in the literature. Also, unlike other low-temperature oxidation methods, this method is not affected negatively by the presence of water in the flue gas. Thus, the requirements needed for large scale installations are within reach.

In conclusion, the results are very encouraging. Tail-end NO<sub>x</sub> abatement seems more attractive than ever. This will allow for retrofitting of deNO<sub>x</sub> units in existing plants and consequently for much more efficient NO<sub>x</sub> abatement in biomass and waste incineration plants.



**Peter Westergaard Jakobsen**  
PhD

"Low-temperature DeNO<sub>x</sub> Technologies for Power and Waste Incineration Plants"

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Funded by:  
**energinet.dk (PSO)**

# Tuning the Behaviour of Polymers in Water

A range of specific ion effects in polymer solutions have been studied.



**Saeed Zajforoushan  
Moghaddam**  
PhD

*"Specific Ion Effects  
in Thermo-Responsive  
Polymer Solutions"*

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Funded by:

**The Swedish Research  
Council (VR)**

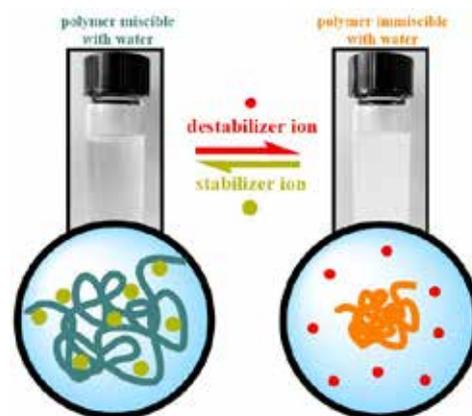
Thermo-responsive polymers are macromolecules that undergo a sudden change in their physical properties and miscibility with water in response to temperature change. In addition to temperature effect, the addition of salts can also affect the behaviour of these polymers in water. It has been demonstrated that different ions do not have the same effect on polymer properties, thus the term specific ion effects (also known as the Hofmeister effect) has been introduced.

The mechanisms through which various ions can affect the polymer properties are still under active debate, which form the framework of this PhD project. Understanding the fundamentals of ion-specificity can be of great importance from two standpoints. First, it can help us to better understand the functioning of biological systems where a mixture of different biomacromolecules and ions exist, as many diseases and disorders have been speculated to originate from changes in the composition of ions present in human body fluids. On the other hand, getting to know how ions can affect the micro- and macroscopic properties of thermo-responsive polymer solutions, we can more effectively control and adjust the performance of these polymers for applications such as tissue engineering and drug delivery.

Considering the significance of this phenomenon, different aspects of specific ion effects in polymer solutions have been studied in this project.

In the first part, specific ion effects in salt mixtures are studied. Firstly, to assess the previously reported mechanisms for the specific ion effects. Secondly, to investigate the Hofmeister effect under a condition that is more similar to the physiological and biological systems.

In the second part, the role of polymer properties on the Hofmeister effect are investigated. For a given polymer, various parameters such as the molecular weight can affect the solubility and properties in water.



*Stabilizer ions make the polymer more miscible with water, while destabilizer ions give rise to phase separation and cloudiness.*

The experimental approach here is to fix the salt type, then see how the corresponding Hofmeister effect can be affected by changing the polymer molecular weight and concentration in the solution.

The third part aims to study how changing the solvent properties can affect the Hofmeister effect. Therefore, the polymer and the salt entities are fixed and the Hofmeister effects in light (H<sub>2</sub>O) and heavy (D<sub>2</sub>O) water are compared.

In the fourth part of the project, the Hofmeister effect of different salts on a model thermo-responsive polymer in bulk solution and at the gold/aqueous interface are closely examined. This helps to perceive how different salts can affect the conformation and interactions of polymers confined at a solid surface. In the last experimental part, the properties of two cationic block copolymers at the silica/aqueous interface are scrutinized, in order to better understand the adsorption of polymers at the solid/aqueous interfaces.

The work is finally concluded by a review on the previous studies on the Hofmeister effect and then suggesting the future research steps.

# Graphene Paper supported Sensors and Energy Conversion Devices

Graphene paper is a layered assembly of graphene nanosheets. This paper-like material is well suited for fabrication of disposable, low-cost sensors, and energy storage and conversion devices.

Graphene nanosheets are single-atom-thick sheets of carbon. Soon after the first synthesis of graphene in 2004, this novel nanomaterial was identified as a strong candidate for a range of applications. The project presents methods for fabrication of sensors and energy converters based on graphene papers, a layered material made of graphene oxide (GO) or reduced GO (RGO) nanosheets.

Graphene, a two-dimensional (2D) material with carbon atoms arrayed in a honeycomb pattern, displays a number of outstanding physicochemical properties. These include excellent conductance for both heat and electricity, and high mechanical strength. For practical applications, graphene will need to be assembled into macroscopic architectures. To this end, graphene oxide (GO) is well suited due to its notable number of oxygen-containing groups on the planar surface and at the edges. These provide possibilities for the functionality and assembly of GO nanosheets into 2D graphene paper with different macroscale shapes through various fabrication techniques. Graphene paper can be used as ideal scaffolds for the incorporation of functional materials with specific functionality.

In the project, GO was modified by nano-structured Prussian Blue (PB) in the form of nanoparticles and cubes. Several advanced techniques (e.g. XRD, XPS, TEM, SEM) were applied for characterization of the nano-composites. The results confirmed that all PB nanostructures were combined well with the graphene nanosheets. Furthermore, PB nanostructure functionalized graphene materials were fabri-

cated into disposable paper sensors and supercapacitor electrodes. For example, Au@PBNPs hybrid GO suspension was filtered by layer-by-layer into functional GO paper, which was further converted into electrically conductive reduced GO (RGO)/Au@PB paper via hydrazine vapor reduction.

The resulting graphene papers had sufficient conductivity and flexibility, and robust mechanical strength to be cut into free-standing electrodes. With low cost and scalable production capacity, such electrodes are highly interesting as flexible, disposable, simple and low-cost sensors. In the project, their efficiency as sensors for detection of H<sub>2</sub>O<sub>2</sub> was demonstrated.

Also, graphene paper was designed as a sacrificial template for preparation of 2D nano-porous metal oxide (MO). 2D MO structures demonstrated superior catalytic, photovoltaic and electrochemical performance due to their large surface-to-volume ratio and nanometer scale thickness. Nano-porous structured MO is therefore promising in applications such as adsorption, catalysis, energy conversion and storage, optoelectronics, and as biological sensing platforms.

In particular, a novel method for preparation of 2D nano-porous structural MO by directly annealing GO paper with metal ions was developed. Furthermore, layer-by-layer, nano-porous 2D CuO nanosheets were assembled into photocanodes for photo-electrochemical water splitting to generate hydrogen.

Finally, CuO/ZnO hybrid nanosheets and NiO nano-sheets were designed as a non-enzymatic sensor for high-performance detection of glucose and urea.



**Minwei Zhang**  
PhD

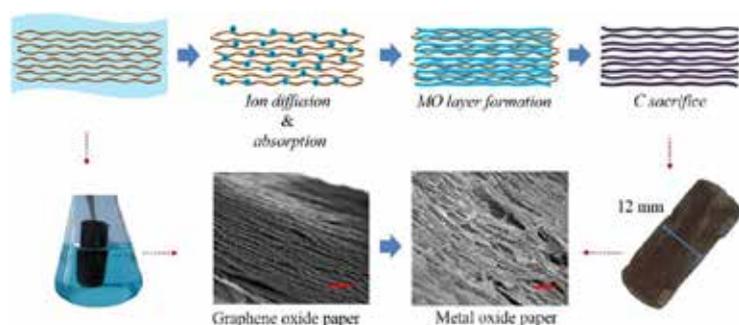
*"Graphene Paper based Nanomaterials for Electrochemical Sensing and Energy Conversion"*

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Funded by:  
**The Independent Research Fund Denmark (FTP), China Scholarship Council (CSC) and DTU Chemistry.**



*Highlight figure of part 3*

# Master Theses 2017

## Adrienna Francesca Marie Hofmann

*Synthesis of native and isotopically labelled New Psychoactive Substances (NPS) for forensic analysis.*

## Ahmed Acharkau

*Hydrothermal stability of Cu-CHA based NH<sub>3</sub>-SCR catalysts*

## Aleksandra Anna Fraczek

*Synthesis of Polychlorinated Alkanes (PCAs) as Reference Materials for Environmental Analysis.*

## Alexandre Paolo Voute

*Quantum tunneling in chemical reactions described by semi-classical methods*

## Andreas Juul Jacobsen

*Low Temperature Sulfur Resistant DeNO<sub>x</sub> Technologies*

## Aske Lundbo Andersen

*Heterogeneous molybdenum-catalyzed reactions of biomass-based materials*

## Charlotte Busk Magnus

*Enantioselective synthesis of a 3-carbon ring-closed Nicotine analogue*

## Christian Sørensen

*In Silico Investigation of Ligand Binding Sites in Dopamine  $\beta$ -Hydroxylase Using Schrödinger Suites*

## Daniel Nikolaus Rainer

*Study of silicic acid polymerization in the presence of transition metals*

## David Gottfried Bording

*A computational simulation of a pump-probe experiment on the femtosecond timescale*

## David Nielsen

*Dependence of the properties of Cu-zeolites on synthesis method studied by in-situ EPR*

## Fatima Hejjo

*Nanoparticle-catalyzed fluorination and fluoroalkylation*

## Frederik Bojsen Kværndrup

*Low Temperature Sulfur Resistant DeNO<sub>x</sub> Technologies*

## Gerard Montserrat Siso

*Light-driven evolution of gold nanoparticle morphology and properties*

## Johannes Eiler

*Surface Activity of Particles in a Hydrophobic Polymer Matrix*

## Kasper Spanggård Buss

*Carbon encapsulated nickel/cobalt nanoparticle catalysts for double bond migration of allylbenzenes*

## Katja Desiree Pedersen

*Structural studies of autoinducing peptides*

## Kristian Weber Pedersen

*Determination of formaldehyde levels and source in pharmaceuticals*

## Lars Bo Jannik Ehlers Bjerrum

*Investigation of the structural determinants that regulate the catalytic efficiency of cellobiohydrolase (Cel7A) studied by enzymatic characterization and molecular dynamics simulations*

## Lina Adil Abdulrahim Al-Naama

*The project will produce graphene by chemistry methods and study its properties using Raman spectroscopy*

## Lærke Kjeldsen

*Mutations in Parkinson's disease: From protein to patient*

## Marcin Adam Sawczuk

*Development of the nanomaterial for the naphthenic acid extraction from the heavy crude*

## Maria-Lito Glykioti

*Density and heat capacity measurement of reservoir fluid related systems at high pressures*

## Michael Agerup Mortensen

*Synthesis of small-molecule modulators of GPCR activity*

## Mikkel Undall-Behrend Christiansen

*Functionalization of nanoporous gold films via chemical modification*

## Niklas Rosendal Bennedsen

*Encapsulated nickel/cobalt nanoparticle catalysts for hydrosilylation*

## Nomikh Kottaki

*PVT study of reservoir fluids at HPHT conditions*

## Oliver Lynggaard Isaksen

*In-situ investigations of iron substituted zeolites*

## Panagiota Kalomoiri

*Characterization of Carbohydrate-Active Enzymes*

## Rasmus Egekjær Jensen

*Mutations in Parkinson's disease: From protein to patient*

## Rikke Rud Christiansen

*A computational study of Sn-beta catalysed reactions*

## Simone Louise Zacho

*Hydrolytic Dehydrogenation of Ammonia Borane over MOF Derived Cobalt Nanoparticles Catalysts*

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Find DTU Chemistry Students at:  
facebook.com/DTUChemistryStudents  
For more information: Teaching Administrator  
Mette Christine Møller, mcmo@kemi.dtu.dk

# Publications 2017

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 Department's exciting results and projects during 2017. 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 2017, please scan the code or see: [kemi.dtu.dk/Omos/Publikationer](http://kemi.dtu.dk/Omos/Publikationer).



# A Leading Research Department

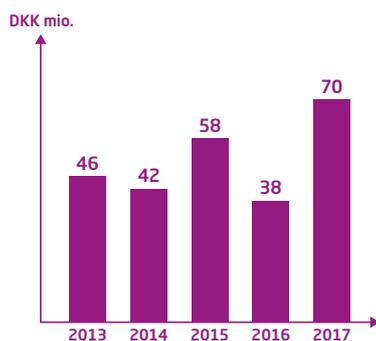
DTU Chemistry focuses on scientific excellence through people, projects, and results in order to stay a leading research department. DTU Chemistry is still very successful in attracting scientific talent. We keep on having a very high number of applicants for the BSc in Chemistry and

Technology exceeding the number of applicants, we can actually accommodate.

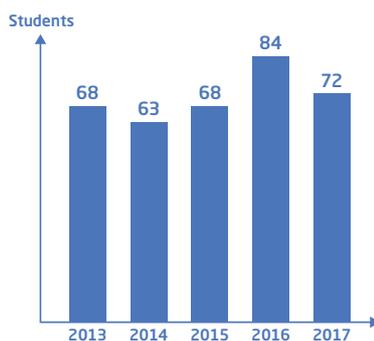
Once again the Department had a high success rate in applications for external funding in 2017. We are pleased to find

that sources outside DTU as public funds, private companies, and private foundations take increasing interest in our Department.

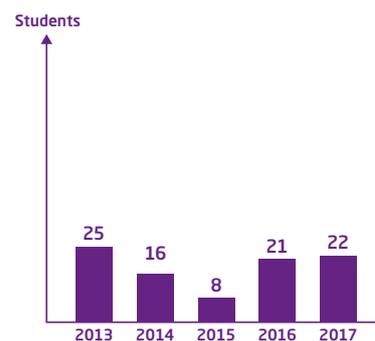
External funding



BSc admission



PhD admission



# Acknowledgement

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

Christine Weber  
Lundbeck A/S

Hanne B. Rasmussen  
Novo Nordisk A/S

Tue Johannessen  
Amminex A/S

Ole Kirk  
Novozymes A/S

Jesper Nerlov  
Haldor Topsoe A/S

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## DTU Chemistry has a wide cooperation with industry.

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

Albeda Research

Albumedix

Amminex

Arla

Arrayjet

Bayer

Bioenergy 2020+

Biolin Scientific

Carlsberg

Coloplast

Niels Clauson-Kaas

ConocoPhillips

CP Kelco

Danish Power System

Edelris

European Membrane House

Evonik Industries

ExxonMobil

Ferring

GlycoSpot

Grundfos

Haldor Topsøe

Hempel

Johnson Matthey

Junckers Industrier A/S

LAB

Leapcraft

Leo Pharma

Linde

Liqtech

Lloyds Register Consulting

Lundbeck

MedImmune

NanoTemper Technologies

Novo Nordisk

Novozymes

Perstorp

PlantProbes

Pharmacosmos

Puregas Solutions

QuantiBact

Riemann

Scandinavian Micro Biodevices

SSI Diagnostica

Total

Veloxis

Welltec

Wyatt Technology Europe GmbH

Ørsted

# Events

## Open House event

Once again, the Department was very active during the annual DTU Open House event. Our guided tours broke all records in 2017 with around 200 interested high school students taking part in them. The efforts appear not to be in vain. This year 72 students signed up for the BSc programme in Chemistry and Technology, which is headed by Professor Klaus B. Møller, who also grabbed a unique opportunity to promote this education in the evening news on DR1 television just a few weeks before the application deadline.

## The Torkil Holm Symposium

The winner of the Nobel Prize in Chemistry in 2016, the Dutch professor Ben L. Feringa, was first on the podium at the international Torkil Holm Symposium in Copenhagen. More than 300 chemists from both industry and academia participated. The event is sponsored by The Torkil Holm Foundation and arranged by ATV – the Danish Academy of Technical Sciences. Professor David Tanner from DTU Chemistry is chairman of the ATV Scientific Organizing Committee.

## The 4th EuCheMS Inorganic Chemistry Conference

The conference had more than 260 international participants, it covered all aspects of inorganic chemistry, and it was held in Copenhagen. The 4th EuCheMS Inorganic Chemistry Conference was organized by Professor Søren Kegnæs and Associate Professor Susanne Mossin, both from DTU Chemistry, along with colleagues from the University of Copenhagen and from Haldor Topsøe A/S.

## The SLAS Nordic Chemical Biology Meeting

Professor Mads H. Clausen from DTU Chemistry welcomed 130 engaged participants to the SLAS Nordic Chemical Biology Meeting 2017 in Copenhagen. Mads H. Clausen organized the conference in cooperation with Professor Christian A. Olsen from the University of Copenhagen.

*Top: DTU ScienceShow at the DTU Open House event.  
Left: The Torkil Holm Symposium. Right: Interested high school students at the DTU Open House event.*



Credit: Tom Jersø/ATV



# Highlights 2017

DTU Chemistry has selected various highlights from 2017 to supplement the articles on pp 6-15. You can read more at our website [kemi.dtu.dk/English/Nyheder](http://kemi.dtu.dk/English/Nyheder), or follow our activities on Facebook/Kemi på DTU.

## GRANTS & HONOURS

### Villum Fonden, Young Investigator

Assistant professor Martin Nielsen from DTU Chemistry received a DKK 10 million grant from the Villum Fonden. He will now initiate a project related to one of the most important tasks of our time, namely the transition from a polluting energy system based on fossil fuels to an environmentally-friendly alternative based on sustainable resources. The project will contribute to achieving this objective by developing catalytic processes, which effectively extract hydrogen from renewable organic material. The grant is provided under the Villum Fonden Young Investigator Programme, 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, two new postdoc positions and a position as laboratory technician.

### Grants from Independent Research Fund Denmark (DFR)

Researchers from DTU Chemistry received a series of grants from Independent Research Fund Denmark (DFR), summing up to more than DKK 19 million.

Senior Researcher Kaibo Zheng has received DKK 5.9 million for a project on quantum dots — which are tiny semiconductor nanocrystals having the potential to be used in solar cells as they are far better at absorbing the sun's energy than the existing standard silicon materials. Professor Sonia Coriani has

received DKK 5.6 million for a project with the aim to develop new theory and new calculation methods to predict and interpret results of advanced spectroscopic experiments. Professor Mads Hartvig Clausen has received DKK 2.6 million for a project on selective prodrugs for the treatment of Rheumatoid Arthritis. Associate Professor Qijin Chi has received DKK 2.6 million for a project on optimization of assembly and photoinduced charge transfer of quantum dot/perovskite-graphene nanosystems. Professor MSO Kasper Planeta Kepp has received DKK 2.5 million for a project, which aims at earlier and more targeted treatment of Alzheimer's disease.

### Other grants and honours

A new European network with strong DTU Chemistry participation has been launched. The initiative is called COSINE (COmputational Spectroscopy In Natural sciences and Engineering). Professor Sonia Coriani heads the work package on modeling of advanced spectroscopies, and Professor Klaus B. Møller is also participating in it. Of the total budget, 580.000 EUR (DKK 4.3 million) are allocated to DTU Chemistry.

Professor Jingdong Zhang has been appointed a member of the exclusive, independent think tank ATV – the Danish Academy of Technical Sciences.

Professor MSO Rasmus Fehrmann has received DKK 1 million from The Danish Maritime Fund to a project which aims at developing simple, safe and cheap measuring equipment to monitor sulphur emissions from ships.



Left: Assistant Professor  
Martin Nielsen. Right:  
Professor Jingdong Zhang.



Two young researchers, Mariusz Kubus from Poland and Diptesh Dey from India, have been granted a H.C. Ørsted COFUND fellowship and will thus spend the next years at the Department of Chemistry advancing their scientific careers. Mariusz Kubus will work on design, synthesis and characterization of 2D metal-organic framework materials, and Diptesh Dey will work on laser-induced control of molecules and chemical reactions.

A sculpture more than three metres high has been inaugurated. The sculpture between two of DTU Chemistry's buildings in Lyngby is the visible proof that Associate Professor Günther H. J. Peters from DTU Chemistry is the first ever to receive the DTU Award for Development of Teaching and Learning.

A poster made by postdoc Søren Kramer won "Chemistry – A European Journal Poster Prize" among 900 other posters. It happened at the 13. "European Congress on Catalysis" in Florence, Italy.

Postdoc Jerrick Jørgen Mielby from DTU Chemistry was on board when the sailing ship "Thor Heyerdahl" was on a ten day scientific voyage of discovery with a group of talented scientists from around the Baltic Sea. Jerrick Jørgen Mielby was invited by Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU). PhD student Tine Maja Frederiksen has received an Elite Research travel grant of DKK 200,000. Elite Research travel grants are given to very talented PhD students in order for them to perform longer-term studies in some of the best research environments in the world.

## REACHING OUT

### DTU ScienceShow

DTU ScienceShow is a group of students who deliver a professional science show with show elements from chemistry and physics. DTU ScienceShow is a part of DTU's branding and recruiting strategies. 2017 was the first full year where DTU ScienceShow was hosted by DTU Chemistry, and it was also a busy year for DTU ScienceShow. There were 99 shows in 2017 and 91 shows in 2016. Professor Anders Riisager from DTU Chemistry is heading the DTU ScienceShow advisory board.

### DTU Chemistry in Newsweek

A scientific article by Associate Professor Rolf W. Berg from DTU Chemistry has created international media attention. In the article in "Applied Spectroscopy Reviews" Rolf W. Berg proposes a brand new and better way to handle the dangerous roads in winter, and Newsweek is just one example of the international mass media, that wrote about it.

## HIGH-IMPACT PUBLICATIONS

A fruitful collaboration bridging DTU Chemistry and DTU Chemical Engineering and combining theory and experiments has resulted in a front page article in an important catalysis journal. Associate Professor Günther H. J. Peters and Postdoc Sindrila Dutta Banik from DTU Chemistry have, together with two colleagues from DTU Chemical

Engineering, published an article in the scientific journal "Catalysts". In the article "Effects of Water Clustering on the Activity of *Candida antarctica* Lipase B in Organic Medium", they present the findings from their study of enzyme activity effects in an organic medium at different water contents.

Professor MSO Kasper Planeta Kepp from DTU Chemistry has written a review article in the high-profile journal "Coordination Chemistry Reviews". Alzheimer's disease is increasingly recognized to be linked to the function and status of metal ions, and recently, the amyloid hypothesis has been strongly intertwined with the metal ion hypothesis; in fact, these two hypotheses fit well together and are not mutually contradictory. In the article "Alzheimer's disease: How metal ions define  $\beta$ -amyloid function", Kasper Planeta Kepp focuses on the essential coordination chemistry and biochemistry that relate transition metal ions iron, copper, and zinc to  $\beta$ -amyloid (A $\beta$ ) and most likely define the peptide's roles in neurons.

Formic acid has recently attracted considerable attention as a safe and convenient source of hydrogen for sustainable chemical synthesis and renewable energy storage. In an article in the high-impact publication, Journal of Catalysis, three researchers from DTU Chemistry – Professor Søren Kegnæs and Postdocs Jerrick Jørgen Mielby and Andreas Jonas Kunov-Kruse – show that silica encapsulated and amine functionalised gold nanoparticles are highly active catalysts for the production of hydrogen by vapour phase decomposition of formic acid.

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