

30 YEARS ANNIVERSARY

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Special Edition, in celebration of 30 years HRSMC
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PROGRAMME AND ABSTRACT BOOK

Meet the members of the HRSMC PhD Platform (Poster 0)

HOLLAND RESEARCH SCHOOL OF MOLECULAR CHEMISTRY | VU VRIJE UNIVERSITEIT AMSTERDAM | UNIVERSITY OF AMSTERDAM | Universiteit Leiden

The HRSMC PhD Platform

Who are we?



Ariba Adnan
Leiden University



Morgan Regnier
University of Amsterdam



Anissa Haim
VU Amsterdam



Pier Wessels
University of Amsterdam



Lin Xu
Leiden University



Yuman Hordijk
VU Amsterdam

Want to get to know us?

What are we doing?

The PhD Platform consists of PhD members of the HRSMC and contributes to the **education programme** and **network** that the HRSMC offers to young researchers. The PhD Platform is consulted on the subjects, quality and organisation of the HRSMC courses, schools and other activities. Furthermore, the PhD Platform organises the annual **Social Event** for PhD students and Postdocs.

Want to join?

We are always looking for new members! Are you interested or do you have questions? Contact us!

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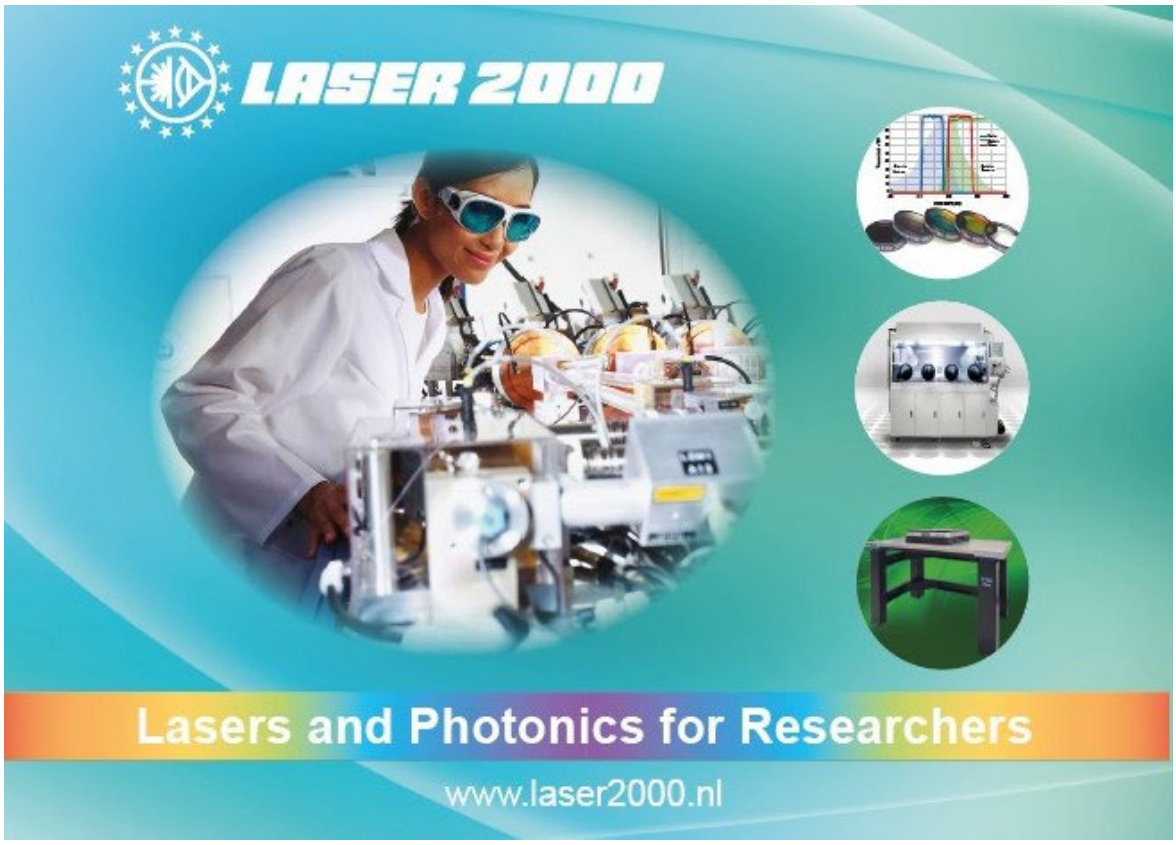
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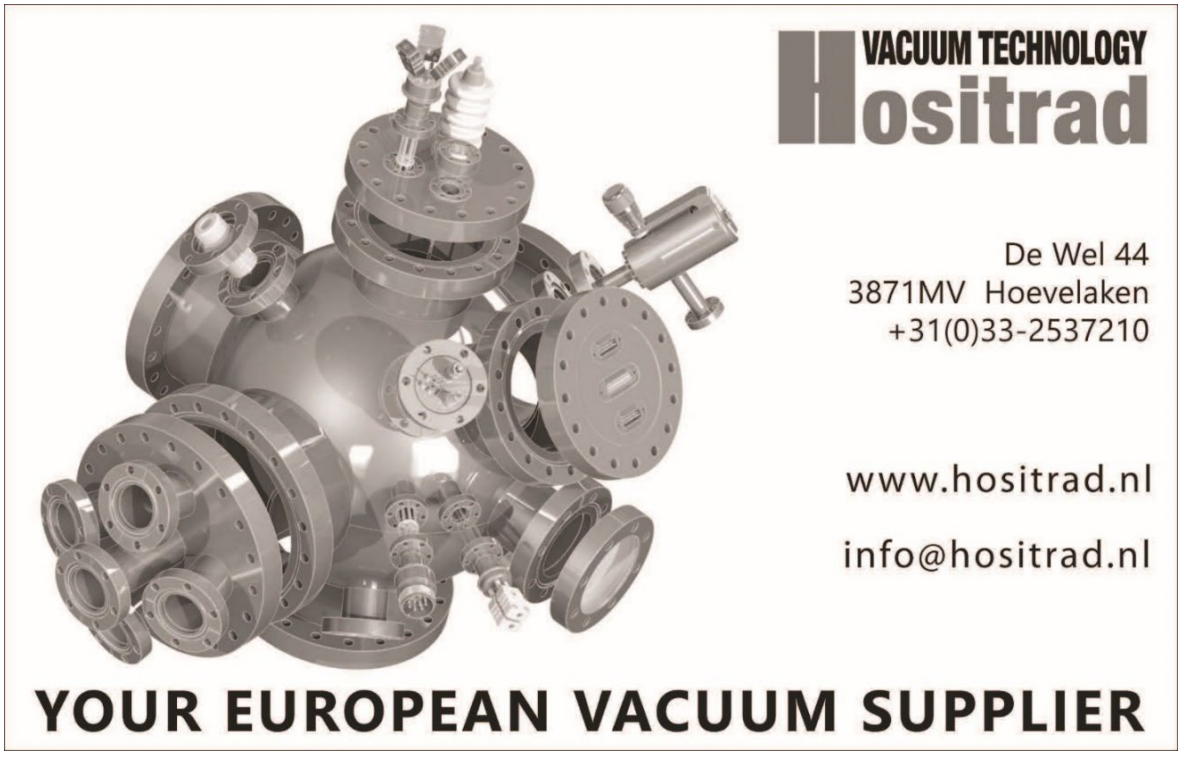
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WELCOME

On behalf of the Holland Research School of Molecular Chemistry, I am very pleased to welcome you all to this special 2024 HRSMC symposium. This year marks the 30th anniversary of our research school. This achievement has only been made possible through the combined efforts of all of us, and is one that we should treasure! To mark this occasion and to celebrate it with us we are very honoured to welcome Prof. Morten P. Meldal, Prof. Burkhard König, Prof. Richard Friend, Prof. dr. Hans Jakob Wörner and Prof. Kendall N. Houk as our plenary lecturers. And, equally important, we look forward to hearing the lectures of our own HRSMC staff members, postdocs and PhD students.

The HRSMC organizes this annual symposium to inform its members and other scientists from universities and industry about its research activities and novel trends in chemical research. The research topics of the HRSMC are collected in three themes: (1) 'Synthesis, Characterization, Reactivity and Properties of Molecules', (2) 'Physical Chemistry and Spectroscopy' and (3) 'Theoretical Chemistry'. Similar to the regular HRSMC symposia, PhD students, Postdocs and HRSMC staff members have been invited to give a lecture on their research, showcasing the state-of-the-art in these three themes. Since this is a special edition of the symposium, we give in this abstract booklet also an overview of the highlights and achievements of the HRSMC over these past 30 years.

For the sixteenth time, the Dick Stufkens Prijs will be awarded to the best PhD thesis that appeared under the auspices of the HRSMC. The 2024 laureate is Dr. Chao Chun Hsu. The prize will be presented by Prof. dr. Ronald Hage, chairman of the Jury and member of the External Advisory Committee of the HRSMC. After the award ceremony, Dr. Chao Chun Hsu will give a presentation of the work for which he has received the 2024 Dick Stufkens Prijs.

Finally, I would like to draw your special attention to the poster sessions where PhD students and Postdocs will present their research results and have the chance to learn about the work of others. The lectures, poster sessions and the reception afterwards will provide a good opportunity to become acquainted with new members of the HRSMC and their research activities.

I wish you all two very festive and inspiring days!

Prof. dr. Wybren Jan Buma
(Scientific Director HRSMC)

HOLLAND RESEARCH SCHOOL
OF MOLECULAR CHEMISTRY

Profile, reputation, highlights & achievements

Profile

The Holland Research School of Molecular Chemistry (HRSMC) is a consortium of:

- University of Amsterdam (UvA): Van 't Hoff Institute for Molecular Sciences
- Vrije Universiteit Amsterdam (VU): Department of Chemistry and Pharmaceutical Sciences
- Leiden University (UL): Leiden Institute of Chemistry, Leiden Observatory, Leiden Institute of Physics
- In 2016 and 2017 several groups of the Institute for Molecules and Materials (Radboud University, RU) became associated members of the school, while NIOK PhD members have joined as PhD-guest members.

The HRSMC is legally represented by the University of Amsterdam. The HRSMC was founded in 1994 and obtained accreditation by the Royal Netherlands Academy of Arts and Sciences (KNAW) from 1994-2018.

Mission

Provide excellent and extensive training for talented PhD and MSc students in molecular chemistry and physics. Initiate and foster top-level chemistry research projects and networks.

Philosophy

Advances and real breakthroughs in chemistry require a thorough understanding at the molecular level. To obtain the latter a concerted effort is paramount, both in research and education, combining synthesis, spectroscopic characterization and theoretical and computational description of molecular systems.

Reputation

The HRSMC is the only research school in the Netherlands with a mission in a broad field that addresses challenges society currently faces in areas like sustainability, energy, and health from a molecular perspective. Both in research and education the HRSMC efforts are internationally recognized. The highly challenging and exciting research- and educational environment attracts young and ambitious molecular scientists from all over the world. Especially the HRSMC schools have an impressive international character. For instance, of the twenty schools organized between 2005 and 2024, 105 of the 120 lecturers (88%) and 290 of the 1000 participants (29%) came from abroad. The status of HRSMC as a top leading research school is further underpinned by its track record in acquiring grants and awards, and by the very good to excellent scores in QANU and other research reviews.

In 2012 HRSMC was selected as one of only thirteen Dutch Graduate Schools to receive substantial funding from NWO. This enabled HRSMC to offer young

talented PhD students the opportunity to develop their own research ideas within the framework of the Graduate Programme "Sustainability, the Molecular Approach". This programme has now been developed and continued into the HRSMC Class of Excellence, a special inter-university (UvA-VU and UL) and multidisciplinary programme for highly talented chemistry MSc students. It guides them to become an expert in synthesis, spectroscopy and theory and helps them to build their network amongst staff members of three different Universities.

PhD output

In the thirty years of its existence a total of 699 PhD theses were published. In the last years the average number of HRSMC PhD graduates was approximately 11 per year.

Research output

The scientific output of the HRSMC is outstanding. In the past ten years, the total number of publications exceeded 3000 of which several were published in Science and in the Nature series, while more than 250 publications appeared in other high-impact journals such as Angewandte Chemie, JACS, and PNAS.

Fellowship programme

In 2015 the HRSMC Fellowship programme has been initiated. This programme finances visits from two weeks to six months by outstanding foreign researchers to HRSMC- affiliated research groups. Since 2015 52 Fellowships have been awarded for a total of 298 kEuro.
In 2020 the HRSMC PhD Mobility Programme has been initiated. The programme enables visits of HRSMC-affiliated PhD students to outstanding foreign research groups to perform research that is not possible to do within the HRSMC. Since 2020 22 PhD mobility grants have been awarded for a total of 70 kEuro.

Research network

The HRSMC has a prominent role in a number of important European collaborations like LaserLab Amsterdam (part of LaserLab Europe) and CECAM (Centre Européen de Calcul Atomique et Moléculaire) to which the Amsterdam Center for Multiscale Modeling (ACMM) belongs.
From 2001-2012, the HRSMC had an official collaboration with the WWU Münster, which resulted in the International Research Training Group (IRTG). This IRTG promoted and supported the exchange of guest lecturers and PhD researchers, as well as the organisation of joint courses and summer schools. For example, in the period 2007-2010, there were 22 research exchanges of PhD students and 22 joint activities. Even though the financial support by NWO and DFG ended in 2012, this collaboration is presently still very fruitful to both partners as evidenced by the number of joint studies.
Being part of the HRSMC consortium has benefits when applying for non-university funding with granting organisations such as the Netherlands Organisation for Scientific Research (NWO) and Technology Foundation STW, and for participation in programmes like NanoNed and IOP initiatives, and programmes within the

framework of the European Union, such as the Marie Curie Training sites. The HRSMC will continue to play an important role in obtaining such funding by facilitating existing and new collaborations between the different groups within the HRSMC.

People power

In the 30 years of HRSMC a significant number of graduates have acquired positions of relevance to science, industry or society in general. Some have been appointed at Dutch or foreign universities, while others now hold positions as leaders of research and innovation at large chemical and pharmaceutical companies. HRSMC PhD graduates have also found jobs at government agencies and last but not least, some have started their own companies.

Key educational activities since 1994

HRSMC Schools:

- Photochemistry (1998, 2003, 2008, 2012, 2016, 2022)
- Modern Developments in Spectroscopy (2001, 2003, 2006, 2009, 2012, 2015, 2018, 2023)
- Synthetic Bio-organic Chemistry (2001, 2005, 2009, 2013, 2017, 2021)
- Advanced Metal-Organic Chemistry and Catalysis (1998, 2002, 2006, 2010, 2014, 2018, 2022)

HRSMC Courses (interuniversity courses):

- Molecular Modeling (1998, 1999, 2000, 2001, 2002, 2003, 2004, 2005, 2006, 2008, 2013, 2016, 2019, 2022, 2024)
- Physical Methods in Inorganic Chemistry (1994, 1999, 2001, 2003, 2005, 2007, 2009, 2011, 2013, 2015, 2017, 2019, 2022)
- Photophysics, Photochemistry & Photobiology (1996, 1999, 2001, 2004, 2007, 2010, 2014, 2017, 2019, 2021, 2024)
- Molecular Simulations (2008, 2009, 2010, 2011, 2012, 2013, 2014, 2015, 2016, 2017, 2018, 2019, 2020, 2021, 2022, 2023, 2024)
- Targeted Synthesis Challenges (2017, 2018, 2019, 2021, 2022, 2023, 2024)

Other key activities:

- Annual HRSMC Symposium for all members with ca. 150-200 scientists attending
- Biannually scientific writing – high impact writing course (2015, 2017, 2019, 2021, 2023)
- Sustainability workshop (together with HIMS) organized by laureates of the "Sustainability, the Molecular Approach" Graduate Programme (2016, 2019)
- PhD/Postdoc Workshop on Science Communication (2023) organized by the HRSMC PhD Platform

Besides these activities, other educational activities were organised in the past 30 years to provide an excellent educational programme for PhD students which is also accessible to (advanced) MSc students.

Programme November 14, 2024

08:15 Coffee/ tea & registration

08:45 Opening by Prof. dr. Wybren Jan Buma *(Scientific Director HRSMC)* and Prof. dr. Marileen Dogterom *(President KNAW)*

09:05 The history of HRSMC: Prof. dr. Kees Elsevier *(Member External Advisory Committee HRSMC)*

Session 1: HRSMC theme 1 'Synthesis, Characterization, Reactivity, Properties of Molecules'

Chair: *Prof. dr. Bas de Bruin*

09:15 Prof. Morten P. Meldal (University of Copenhagen, Denmark)
"Molecular Click Adventures. A Leap from the Shoulders of Giants"

09:55 Lars van der Zee (University of Amsterdam)
"*Photoinduced Single Electron Transfer in Frustrated Lewis Pairs: An Investigation Along the Pnictogen Series"*

10:15 Coffee/ tea

10:45 Prof. Burkhard König (University of Regensburg, Germany)
"*Better Organic Synthesis with Light"*

11:25 Pim Broersen (University of Amsterdam)
"Emerging Strategies in Electrochemical C-N bond Forming Reactions"

Session 2: HRSMC theme 2 'Physical Chemistry and Spectroscopy'

Chair: Prof. dr. Sylvestre Bonnet

11:45 Prof. Richard Friend (University of Cambridge, UK)
"Spin Radical Organic Semiconductors"

12:25 Lunch – Poster session A

13:25 Adarsh Koovakattil Surendran (Radboud University)
"Integration of Mass Spectrometry in Electrochemical Research"

13:45 Prof. dr. Hans Jakob Wörner (ETH Zürich, Switzerland)
"Attosecond Spectroscopy: Observing Electrons in Motion"

14:25 Marlene Hoefnagel (Leiden University)
"Operando Characterization of the Cu-Catalyst Active Sites in Metal Organic Frameworks for Oxygen Reduction"

14:45 Coffee/ tea & Poster session B

Session 3: HRSMC theme 3 'Theoretical Chemistry'

Chair: *Prof. dr. Matthias Bickelhaupt*

15:45 Prof. Kendall N. Houk (University of California, CA)
"Frontiers of Pericyclic Reactions"

16:25 Dr. Celine Nieuwland (VU Amsterdam)
"Chalcogen Atom Size: A Key Parameter in Tuning Amide Hydrogen Bonding"

Session 4: Dick Stufkens Prize 2024

Chair: *Prof. dr. Wybren Jan Buma*

16:45 Dick Stufkens Prize winner introduction by Prof. dr. Ronald Hage (*Member External Advisory Committee HRSMC)*

16:55 Lecture by the winner of the Dick Stufkens Prize 2024: Dr. Chao Chun Hsu
"Mechanophore in Probing Local Information within Microscopic Mechanical Contacts"

17:25 Closure by Prof. dr. Peter van Tienderen (*Dean of the Faculty of Science, University of Amsterdam*)

17:35 Reception

18:30 End of day 1 and staff leaving for dinner

Programme November 15, 2024

08:30 Coffee/ tea & registration

Session 1: HRSMC theme 1 'Synthesis, Characterization, Reactivity, Properties of Molecules'

Chair: Dr. Bettina Baumgartner

08:45 Dr. Thomas Hansen (VU Amsterdam)
"Exploring Chemical Glycosylation Reactions: Can we Control Them?"

09:15 Dr. Irene Regeni (Leiden University)
"Ruthenium Peptide Bioconjugates for Photoactivated Chemotherapy"

Session 2: HRSMC theme 2 'Physical Chemistry and Spectroscopy'

Chair: Prof. dr. Irene Groot

09:35 Prof. dr. Katrien Keune (University of Amsterdam)
"Spectroscopic Imaging of Paintings from Macro- to Nanoscale"

10:05 Introduction PhD platform/PhD social activity

10:15 Coffee/ tea & Poster session C (End of the session: Voting for the best poster in research themes 1, 2 and 3)

11:10 Titus de Haas (Leiden University)
"Impact of Nuclear Dynamics on Photoinduced Hole Transfer in a P1/NiO Photocathode"

Session 3: HRSMC theme 3 'Theoretical Chemistry'

Chair: Dr. Pascal Vermeeren

11:30 Dr. Thanja Lamberts (Leiden University)
"Molecular Cocktails on the Rocks: Chemistry of Ices in Stellar Nurseries"

12:00 Massimiliano Paesani (University of Amsterdam)
"MetaParticles: Computationally Engineered Nanomaterials with Tunable and Responsive Properties"

12:20 Dr. Alexander Korotkevich (University of Amsterdam)
"AI for Development of Solid Salt Hydrates for Thermal Energy Storage"

Poster Prize Award and Closure

12:40 Poster Prize Award by Prof. dr. Matthias Bickelhaupt

12:50 Closure by Prof. dr. Wybren Jan Buma and lunch

13:45 Annual Staff Meeting

CV's and abstracts of invited lectures (in alphabetical order)

Prof. Sir Richard Friend



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Summary

Professor Sir Richard Friend is at the Department of Physics at the University of Cambridge, where he held the Cavendish Professorship of Physics from 1995 to 2020. He is currently a Director of Research in the Department of Physics, and has support for his research programme from the ERC, the EPSRC and the Simons Foundation. His research encompasses the physics, materials science and engineering of semiconductor devices made with carbon-based semiconductors, particularly polymers. His research advances have shown that carbon-based semiconductors have significant applications in LEDs, solar cells, lasers, and electronics. These have been developed and exploited through a number of spin-off companies. His current research interests are directed to novel schemes that seek to improve the performance and cost of solar cells.

Professor Friend is a Fellow of the Royal Society and of the Royal Academy of Engineering, and a Foreign Member of the US National Academy of Engineering. He has received many international awards for his research, including Laureate of the Millennium Prize for Technology (2010) the Harvey Prize (2011) of the Israel Institute of Technology and the von Hippel Award of the Materials Research Society (2015). He was knighted for "Services to Physics" in the Queen's Birthday Honours List, 2003.

SPIN RADICAL ORGANIC SEMICONDUCTORS

Richard Friend

Cavendish Laboratory, University of Cambridge, UK

We and others have recently reported that certain classes of radical organic semiconductors can be used as efficient light emitters in LED devices. We have found that structures where the lowest double excited state involves promotion of an electron from a HOMO level associated with a donor moiety such as carbazole to the radical SOMO level can show very high luminescence yield [1,2]. This is achieved by vibrational decoupling to high frequency modes, such as the phenylene ring stretch mode. We have optimised structures so that it is possible to electrically excite this doublet state, by sequential charge transfer of electron and hole. We have explored the use the radical semiconductor as the emissive 'guest' in a regular organic LED emissive layer 'host' where the radical semiconductor is able to harvest both singlet and triplet excitons formed in the host material [3].

I will also report on recent studies of photogeneration of high spin states in radical semiconductors. These include coupled doublet-triplet systems that evolve to quartets and quintets [4], and di-radical structures where both singlet and triplet spin states are optically accessible and luminescent. These provide opportunities for optical writing, manipulation and reading of spin states.

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Prof. dr. Kendall N. Houk



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Summary

K. N. Houk received his Ph.D. at Harvard, working with R. B. Woodward on experimental tests of orbital symmetry selection rules. He has taught at Louisiana State University, the University of Pittsburgh, and UCLA since 1986. From 1988-1990, he was Director of the Chemistry Division of the National Science Foundation. He was the UCLA Saul Winstein Chair in Organic Chemistry from 2009-2021, and is now Distinguished Research Professor. Beginning as an experimental organic chemist, he evolved over his career into a theoretical and computational organic chemist, involved in collaborations with groups all over the world. He is an elected member of the US National and Chinese Academies of Science. He has more than 1500 publications.

FRONTIERS OF PERICYCLIC REACTIONS

K. N. Houk[1], Q. Zhou[1]

[1]*Department of Chemistry and Biochemistry, University of California, Los Angeles, CA, USA*

The field of pericyclic reactions was named fifty years ago, but continues to be a fertile source of new chemistry. The theory of pericyclic reactions has advanced from the useful, but qualitative, model for allowed and forbidden reactions developed by Woodward and Hoffmann, through robust analysis tools such as the Distortion/Interaction – Activation Strain model of Bickelhaupt and Houk,[1] to quantitative methods to compute rates and selectivities, the results of the enormous advances in computational methods and computer power. Highlights from our UCLA laboratories and others around the world will be described for: 1. thermally forbidden pericyclic reactions that are nevertheless concerted,[2] 2. ambimodal cycloadditions that lead to multiple products from one transition state,[3] and 3. pericyclases, enzymes that catalyze pericyclic reactions.[4] Computational investigations from our laboratories, and collaborations with experimental groups, will be described.

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Summary

Prof. Burkhard König's scientific work is centered in the field of physical-organic chemistry and photochemistry. As one of the pioneers of chemical photocatalysis, he has significantly developed the field of light-driven organic synthesis in the past 20 years. He is one of the leading minds in this active research area in Germany and internationally. His contributions to the research area are ground-breaking and open new research directions.

Even before the methodology of photocatalysis received greater attention in synthetic chemistry, work by the König group on flavin photocatalysis began around 2000. The group reported the first photocatalytic variant of the Meerwein arylation and the first enantioselective heterogeneous photocatalysis with visible light. They introduced the concept of consecutive photo-induced electron transfer (conPET), established the redox-neutral utilization of carbon dioxide in synthesis via photogenerated carbanions, and used organic semiconductors and excited anions in photocatalysis. Recent contributions focus on dynamic photo-nickel catalysis and synthetic photochemistry at the water-oil interface. All projects combine synthetic methodology development with mechanistic investigations to pave the way for predictable applications in synthetic chemistry and industrial production processes. In close collaboration with groups from molecular biology, photoswitchable probes are developed that allow the reversible activation or inhibition of enzymes, GPCRs, and ion channels.

The research received European (ERC) and national funding (Koselleck Award German Science Foundation; research clusters "Chemical Photocatalysis" and "Assembly control in photocatalysis") and was recognized by awards (most recent: Honda Award 2023 of the Japanese Photochemical Society).

BETTER ORGANIC SYNTHESIS WITH LIGHT

Burkhard König

Faculty of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germany

Over the last two decades, the use of light in synthetic organic chemistry has seen an enormous expansion. Photocatalysis and its combination with other catalytic principles, such as Brønsted- or Lewis-acid, organo-, metal- and bio-catalysis, are established tools in synthesis. Nevertheless, the unique ability of photocatalysis to enable chemical transformations by light energy that are difficult or impossible to achieve by other activation modes still provides many opportunities. Such reactions include energetically uphill acceptorless dehydrogenations, carbonyl Umpolung, and redox-neutral C-H carboxylations. Heterogeneous photocatalysts and photochemical reactions at oil-water interfaces facilitate reactions with ideal atom economy and high energy efficiency.

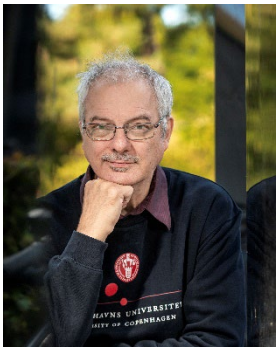
We discuss in the lecture some recent contributions from our laboratory to synthetic photocatalysis and give a perspective on where the field is heading and why the future of catalysis is bright.



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Summary

Morten Meldal is a Danish chemist and professor at the Department of Chemistry at the University of Copenhagen, Denmark. He was awarded the 2022 Nobel Prize in Chemistry, alongside Barry Sharpless and Carolyn Bartozzi, for the groundbreaking development of 'Click chemistry and biorthogonal chemistry'. He also received the 2009 American Chemical Society Ralph F. Hirschmann Award in peptide chemistry, as well as the 2011 Vincent du Vigneaud Award of the American Peptide Society.

Meldal obtained his MSc in chemical engineering and PhD, under the supervision of Klaus Bock, from the Technical University of Denmark (DTU). Meldal's PhD work focused on synthesis of carbohydrates, and after working as a postdoctoral fellow in organic chemistry at Cambridge University, he was professor and manager of a research synthesis group at Carlsberg Research Laboratory. In 2011, Meldal became professor at the Department of Chemistry at University of Copenhagen, where he headed the CECB research center within the field of chemical biology, with focus on peptide and combinatorial chemistry. Meldal co-founded three companies, Combio, Versamatrix, and Betamab Therapeutics ApS, which utilized the SPOCC and CECB platforms in biotechnological and pharmacological research and development.

Throughout Meldal's career, his research has had innovative influences on methods in peptide and combinatorial chemistry. His involvement in method development of solid-phase and combinatorial peptide synthesis, as well as development of the CuAAc Click reaction, have become mainstream methods for application in bioorganic and organic synthesis.

MOLECULAR CLICK ADVENTURES. A LEAP FROM THE SHOULDERS OF GIANTS.

Morten Meldal[1]

[1]*Department of Chemistry, University of Copenhagen, Denmark*

The concept of click chemistry matured simultaneously in different laboratories around the world in the 1990's. There was an urgent need for quantitative chemical reactions/molecular LEGO® to cope with the pressure from combinatorial science to synthesize, screen and identify one out of thousands – millions of compounds. We combined Peptide diversity with a variety of organic reactions including Diels Alder, Suzu-ki, INAIC and other reactions. During these investigations we more or less serendipitously discovered the CuAAC click reaction in 2001. The mechanism of the reaction will be discussed and its application in a varie-ty of studies involving immobilization, mimicry, structural control and protein ligation will be presented. Our investigations included the CuAAC reaction in synthesis of stable surrogates for disulfide bonds in anti-biotic 9, we produced a click protease with improved proteolytic activity and ligated the HIV fusion triple helix on to a fluorescent click template. The more existential aspects of our fundamental understanding of chemistry, the importance of serendipity to unravel the true complexity of our world at the molecular lev-el, the associated need for freedom of research, and our pledge to the young to study chemistry for a bet-ter future, will also be discussed.

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Summary

Hans Jakob Wörner has been a Professor at the Laboratory of Physical Chemistry at ETH Zurich since 2010. He was born in Freiburg, Germany, in 1981. Hans Jakob Wörner studied chemistry at EPF Lausanne and ETH Zurich, obtaining a doctorate in physical chemistry in 2007. He then worked as a postdoctoral fellow at the Laboratoire Aimé Cotton of the CNRS in Orsay, France, and at the National Research Council in Ottawa, Canada. His research interests are attosecond spectroscopy and its applications to chemical problems. He has pioneered the development of attosecond spectroscopy in the liquid phase, the measurement of charge migration and photoionization delays in molecules and the development of time-resolved table-top X-ray spectroscopy. His research group holds the world record for the shortest pulse of light (43 as) since 2017. He has received several awards and distinctions, including an ERC Starting Grant, the Grammaticakis-Neumann International Prize in Photochemistry, the Nernst-Haber-Bodenstein prize, the Broida Prize, the Klung-Wilhelmy Science Award, the Carus medal, an ERC Consolidator Grant and the Coblentz Award.

ATTOSECOND SPECTROSCOPY: OBSERVING ELECTRONS IN MOTION

Hans Jakob Wörner

Laboratorium für Physikalische Chemie, ETH Zürich, Zürich, Switzerland

Attosecond spectroscopy provides access to the ultrafast dynamics of electrons in matter, which take place on the extremely short time scale of attoseconds (1 as=10^{-18} s). These ultrashort time scales have become accessible through the development of attosecond pulses of light, which was recognized with the Nobel Prize in Physics in 2023. These light pulses, which have reached a duration of only 43 as in 2017 [1], have enabled the observation of electronic motion in atoms, molecules, liquids and solids on its natural time scale. Spectroscopic measurements with attosecond pulses have made the emission of electrons from matter, the transport of electrons and holes through molecules and the rearrangement of electrons during chemical reactions accessible to real-time measurements.

In this lecture, I will discuss recent results in the area of attochemistry, which studies the creation, the evolution and the influence of electronic coherences on chemical dynamics. Central to these concepts is charge migration, a purely electronic process that causes a periodic rearrangement of the charge distribution in molecules [2]. Charge migration usually couples to structural dynamics and can then result in permanent charge transfer. I will discuss the experimental observation of decoherence and revival of attosecond charge migration driven by nuclear motion, as well as the transfer of electronic coherence through conical intersections in the neutral silane molecule [3]. In an effort to extend the applicability of attosecond spectroscopy to complex, notably aqueous, systems I will discuss the development of table-top soft-X-ray spectroscopy, which has enabled the observation of the rearrangement of unoccupied molecular states during chemical reactions [4] and the fastest (<7 fs) electronic relaxation ever measured in molecules [5]. Turning from the gas phase to the liquid phase, I will discuss recent results on the observation of femtosecond proton transfer in ionized urea dimers in aqueous solution [6]. These results demonstrate the potential of attosecond soft-X-ray spectroscopy for studying electronic dynamics of chemically relevant systems under ambient conditions.

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Abstract
Winner Dick Stufkens Prize 2024

MECHANOPHORE IN PROBING LOCAL INFORMATION WITHIN MICROSCOPIC MECHANICAL CONTACTS

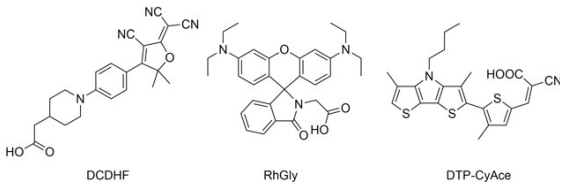
Chao-Chun Hsu

Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands

When two objects come into contact, friction—the tangential force—resists their relative motion. While friction can cause issues like machinery failure and wear, it also plays a crucial role in applications ranging from everyday tasks to high-precision technology. Controlling this "necessary evil" is key to achieving desirable properties. However, due to the lack of methods to probe mechanical forces at interfaces, scientists are often limited to two strategies: studying nanoscopic contact systems using atomic force microscopy, or examining macroscopic surface properties in relation to frictional forces, such as the coefficient of friction. No method has yet been able to directly link nanoscopic observations to macroscopic behavior in a single in-situ measurement, leading to inconsistent conclusions.

A major focus of my thesis is the design of mechanophores (Figure 1A), in combination with fluorescence microscopy, to simultaneously visualize both the microscopic contact (macroscale) and the local stress/pressure (nanoscale). These probes have attractive properties, as they adjust their geometry in response to external stimuli, such as shear (expansion)(1) and pressure (compression)(2), as shown in Figure 1B. Mechanical force can induce a reversible isomerization (activation), resulting in a significant shift in absorption and emission spectra. By selectively exciting the molecule in its activated state, we can visualize the real contact area at the microscopic level. Additionally, the activation process is force-sensitive, allowing us to quantitatively map the nanoscopic force distribution in both axial and tangential directions. This approach enables the unraveling of various tribological mechanisms and connects the fundamental origins of friction from the nanoscopic to the macroscopic scale.

A)



B)

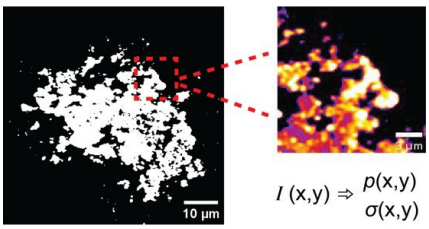


Figure 1 (A) Mechanophores for mechanical contact visualization. (B) Illustrations of using fluorescence microscopy to simultaneously acquire real contact area and local force information.

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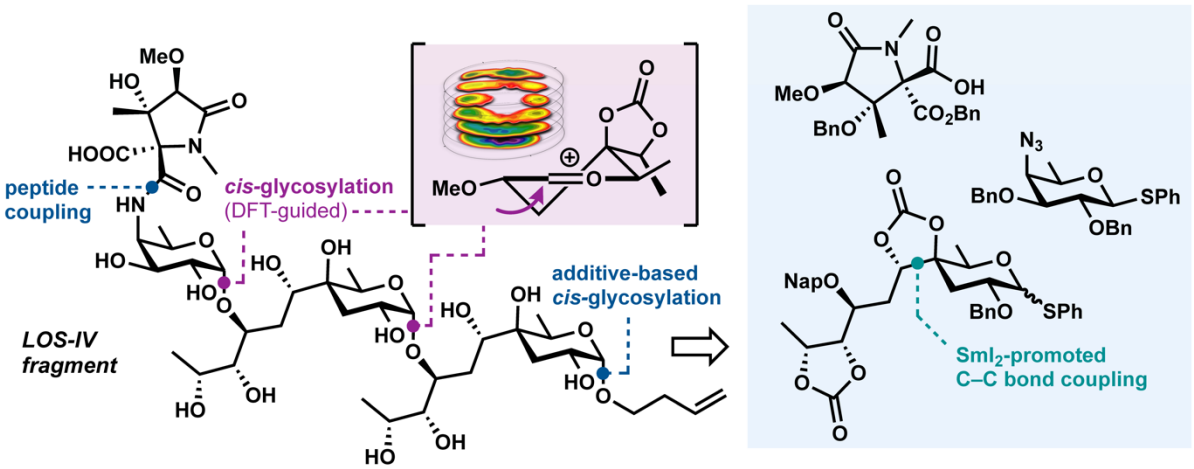
Abstracts of Staff Lectures
(in alphabetical order)

EXPLORING CHEMICAL GLYCOSYLATION REACTIONS: CAN WE CONTROL THEM?

Thomas Hansen[1]

[1] *Department of Chemistry and Pharmaceutical Sciences, AIMMS, Vrije Universiteit Amsterdam, The Netherlands*

Advances in the synthesis of complex carbohydrates and their conjugates continuously push the rapidly evolving field of glycoscience forward. Despite tremendous progress, the stereocontrolled construction of glycosidic linkages, typically through a transacetalization reaction, remains a formidable challenge in synthetic carbohydrate chemistry. Insufficient knowledge of the operative mechanism of the glycosylation reaction at the atomic level thwarts its rational development. Therefore, we used state-of-the-art computational and experimental techniques to obtain critical insight into the reaction mechanism.[1–3] We found that glycosyl cations can act as key reactive intermediates and mapped clear structure-reactivity-stereoselectivity relationships for these species. The insights gained in these studies paved the way to synthesize a set of highly complex mycobacterial glycolipids (see figure),[4] delivering more and more complex glycans to fuel glycobiological and glycomedical research.



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SPECTROSCOPIC IMAGING OF PAINTINGS FROM MACRO- TO NANOSCALE

Katrien Keune[1,2], Fréderique Broers[2,] Nouchka De Keyser[2], Annelies van Loon[2], Frederik Vanmeert[2], Petria Noble[2], Koen Janssens[3], Florian Meier[4].

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[2]*Conservation & Science, Rijksmuseum, Amsterdam, The Netherlands*
[3]*AXIS Research Group, University of Antwerp, Belgium*
[4]*Inorganic Chemistry & Catalysis, Utrecht University, The Netherlands*

Paintings are complex, heterogeneous systems that undergo chemical and physical changes from the moment they are created. To understand the artist's original intent, the techniques used, the current condition of the artwork, and how best to preserve it for future generations, paintings are studied at various length scales. This is achieved through a combined approach, utilizing non-invasive macroscale imaging technologies alongside micro- and nanoscale imaging analyses performed on embedded and loose microsamples.

In this presentation will highlight two studies that reveal new findings in Rembrandts' *The Night Watch* (1642), Rijksmuseum. The discovery of pararealgar (As_4S_4) and semi-amorphous pararealgar is a new addition to Rembrandt's pigment palette [1]. Macroscale X-ray fluorescence (MA-XRF) scan of the painting is combined with micro-Raman spectroscopy, electron microscopy and X-ray powder diffraction on microsamples. Supported by the study of related historical sources, it is concluded that Rembrandt deliberately combined these specific arsenic sulfide pigments with other pigments to achieve the golden luster. The second study presents the discovery of an unknown lead-containing "layer", which likely acts as a protective impregnation layer applied on the canvas before the quartz-clay ground was applied [2]. Three-dimensional synchrotron-based x-ray fluorescence mapping, revealing the distribution of lead within the paint sample, was combined with x-ray ptychographic nano-tomography. The latter visualizes and quantifies components not detectable by hard x-ray fluorescence such as the organic fraction and quartz.

The two highlights are discovered within the framework of *Operation Night Watch. Operation Night Watch* is the largest research and conservation project executed on this iconic work of art and was started in July 2019.

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MOLECULAR COCKTAILS ON THE ROCKS: CHEMISTRY OF ICES IN STELLAR NURSERIES

Thanja Lamberts[1,2] and team

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The darkness readily observed between the stars on a clear night sky is far from empty. In fact, a large variety of molecules has been detected in the gas phase. They make up about 99% of the total mass in the interstellar medium. The final 1% of mass is contained in micron-sized dust grains that once were expelled by dying stars.

In cold, dense interstellar regions, atoms and molecules adsorb, diffuse, and react on the surfaces of these dust grains, after which they can evaporate back into the gas phase. This leads to the build-up of molecular icy mantles of up to 100 monolayers thick. The interplay between the different surfaces processes determines which molecules are formed, where, and whether or not they are astronomically observable, either in the solid or gas phase. In order to quantitatively disentangle the relative importance on realistic amorphous ices one can make use of computational chemistry. This way me and my group aim to provide coarse-grained astrochemical models with crucial input parameters, such as branching ratios, binding energies, rate constants, and energy dissipation efficiencies.

I will focus on surface processes of molecules containing elements crucial to life, CHONS, and known to be present in cold interstellar regions to illustrate how binding, reactivity and dissipation go hand in hand. I aim to show the multi-faceted aspects of astrochemistry, linking our work to observational astronomy, and recent results obtained with the James Webb Space Telescope in particular.

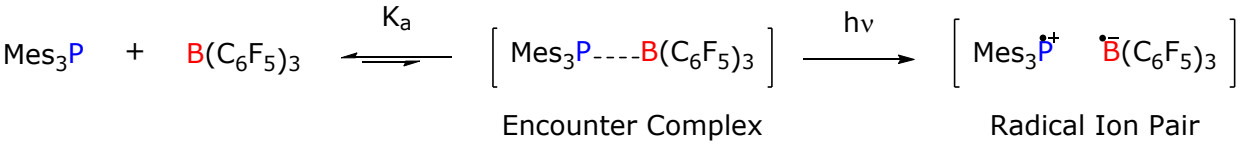
Abstracts of PhD Lectures
(Order based on programme)

PHOTOINDUCED SINGLE ELECTRON TRANSFER IN FRUSTRATED LEWIS PAIRS: AN INVESTIGATION ALONG THE PNICTOGEN SERIES

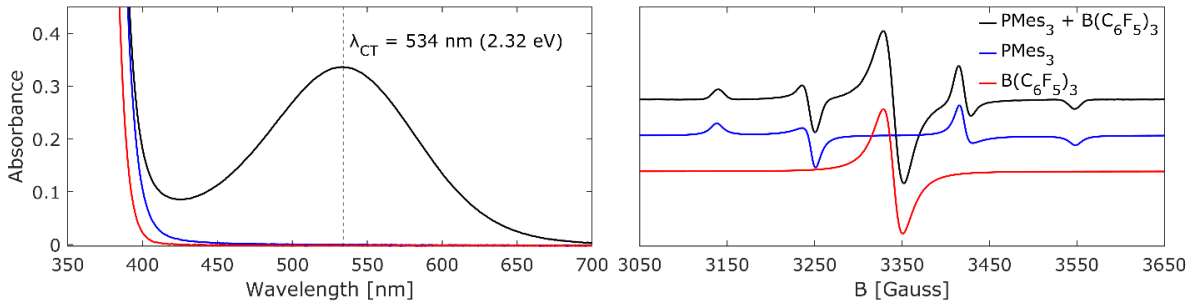
Lars J. C. van der Zee, Sven C. O. Dik, Chris. J. Slootweg

Synthetic Organic Chemistry (SOC), Van 't Hoff Institute for Molecular Sciences (HIMS), University of Amsterdam (UvA), Amsterdam, The Netherlands

Frustrated Lewis Pairs (FLPs), a combination of a sterically encumbered Lewis base and acid, such as $PMes_3$ and $B(C_6F_5)_3$, are well known to activate substrates like hydrogen and CO_2 in a two–electron fashion. Recently, the possibility of a photoinduced single-electron transfer (SET) from the Lewis base to the Lewis acid has been shown, generating a transient radical ion pair (RIP) which opens the opportunity for homolytic bond activation of more inert substrates like methane.[1,2]



Our group showed that the photoinduced SET takes place by initial assembly of the Lewis acid and base into the so-called encounter complex.[3] This complex has a new absorption band compared to the individual components called the charge transfer (CT) band. Irradiation of the CT band results in SET, which can be observed by, e.g., EPR spectroscopy.



In this lecture, we aim to explain the position and intensity of the CT band by employing the different pnictogen Lewis bases $NTol_3$, $PMes_3$, $AsMes_3$, $SbMes_3$ & $BiMes_3$ in combination with the Lewis acid $B(C_6F_5)_3$. We use a combination of spectroscopic tools (EPR, temperature-dependent and transient absorption UV–vis) and computations (TD–DFT, NBO analysis) to elucidate the factors influencing the CT band with the overall goal to enhance the development of new electron donor–acceptor (EDA) complexes in the field of photochemistry and to aid the formation of reactive radical pairs for the activation of inert substrates.

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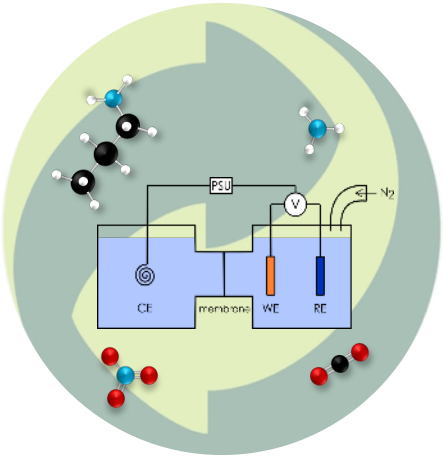
EMERGING STRATEGIES IN ELECTROCHEMICAL C–N BOND FORMING REACTIONS

Pim J. L. Broersen[1], Amanda C. Garcia[1]

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The formation of carbon-nitrogen (C–N) bonds is a fundamental reaction in organic chemistry, critical for producing pharmaceuticals, agrochemicals, and materials. Traditional methods of C–N bond formation often rely on harsh reagents, high energy input, and fossil-based feedstocks. Recent advances in electrosynthesis provide a sustainable alternative by using electricity to drive C–N bond formation under milder conditions.[1] Here, we present our research on novel electrochemical methods for C–N bond formation, focusing on the use of innovative electrocatalysts and green solvents.
We demonstrate the efficient electrosynthesis of glycine, a key amino acid, using a copper electrode modified with a lead monolayer ($CuPb_{1ML}$). This catalyst effectively inhibits the hydrogen evolution reaction (HER), a common parasitic reaction, and achieves a Faradaic efficiency (FE) of 57% for glycine production, with a glycine formation rate of 211 μmol h^{-1} cm^{-2}, outperforming both pure copper and lead electrodes.[2]

Additionally, we explore the electrosynthesis of various amines from alcohols using a TEMPO-based polymer electrode, achieving high selectivity and Faradaic efficiency (up to 97.5%) under optimized conditions. The use of electrochemistry enables us to replace traditional stoichiometric reagents and reduce the environmental impact of chemical synthesis by using renewable electricity. Our work demonstrates the potential of electrosynthesis to transform conventional C–N bond formation methods, offering a path toward greener and more sustainable chemical manufacturing.[3]
These findings highlight the importance of catalyst design and reaction environment optimization in advancing the field of electrosynthetic C–N bond formation, paving the way for industrial applications in sustainable chemical production.



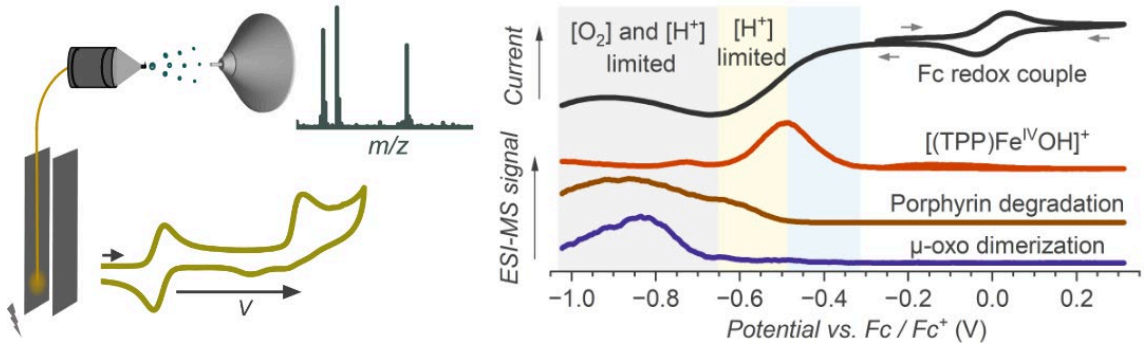
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INTEGRATION OF MASS SPECTROMETRY IN ELECTROCHEMICAL RESEARCH

Adarsh Koovakattil Surendran, Aleksandr Y. Pereverzev, Jana Roithová

Department of Spectroscopy and Catalysis, Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands

One of the fundamental difficulties in developing electrochemical processes is understanding the mechanism of complex reactions occurring at the electrode surface. These reactions are highly dynamic, influenced by the changing mass transport and kinetic conditions at the electrode−solution interface. Traditional analytical techniques often fail to capture the molecular details of these dynamic processes. Our study bridges this gap by developing an integrated approach combining voltammetry and electrochemical impedance spectroscopy with electrospray ionization mass spectrometry.[1] This integrated approach enables monitoring of the chemical processes at the electrode interface, tracking changes in intermediates and products in real-time during voltammetric scans and impedance measurements. Applied to the electrochemical reduction of oxygen catalyzed by the Iron(II)tetraphenyl porphyrin complex, the method reveals the critical role of mass transport in controlling reaction pathways.[2] We successfully detected various reaction intermediates and degradation pathways across different kinetic regimes. Our findings provide new insights into complex electrocatalytic processes and offer new ways to study them, enhancing our capacity to optimize electrochemical reactions for developing more sustainable chemical processes.



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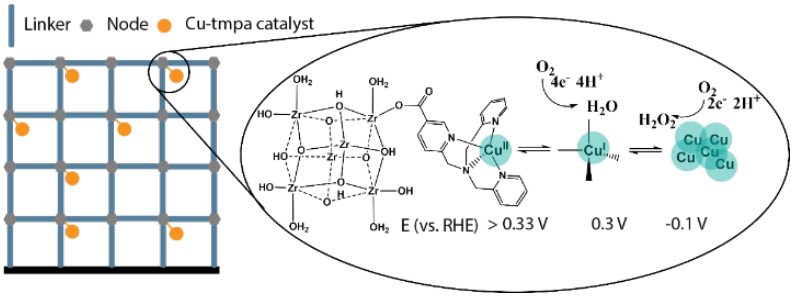
OPERANDO CHARACTERIZATION OF THE CU-CATALYST ACTIVE SITES IN METAL ORGANIC FRAMEWORKS FOR OXYGEN REDUCTION

Marlene E. Hoefnagel[1], Sascha Ott[2], Sheena Louisia[1] ,
Dennis G.H. Hetterscheid[1]

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[2]*Department of Chemistry, Ångström Laboratory, Uppsala University, Uppsala, Sweden*

Metal organic frameworks (MOFs) have been considered interesting materials for catalysis due to their high porosity (high active surface area), high stability and the confinement effects they impose on reactants. When immobilizing a catalyst in a MOF, catalysis becomes limited by the catalyst itself, electron transport through the framework or mass transport of reactants.We have found that incorporating a Cu-catalyst into a NU1000 MOF directed the selectivity of the oxygen reduction reaction (ORR) to water as the main product (FE_{H_2O} = 90%) and led to a significant improvement of the catalyst stability.[1] We attribute the selectivity for water to the retention and therefore overreduction of the H_2O_2 intermediate within the MOF pores, in close proximity to the catalyst. After controlled potential electrolysis (CPE) experiments a new species is formed. To investigate which species are formed during catalysis, we performed operando X-ray absorption spectroscopy (XAS). We monitored the potential dependent reversible changes in the structure and oxidation state of the copper catalyst. Initially, the embedded catalyst exhibits a Cu^{II} dominated character which is consistent with a Cu^{II}(tmpa) species (tmpa = tris(2-methylpyridyl)amine). During CPE, we observe a Cu species with an oxidation state distinct from the Cu^{II}(tmpa) catalyst. Finally, at more negative potentials, the catalyst takes on a Cu^0 dominated character as well as a more pronounced Cu-Cu scattering which we associate with the formation of Cu clusters.

To address potential electron transport issues related to the redox inert structure of the NU1000 MOF, we synthesized a new MOF with redox-active naphthalene diimide (NDI) linkers and incorporated the same Cu-catalyst. We show that the redox activity of the linkers does not contribute to higher catalytic activity, but does result in a smaller extend of Cu-cluster formation. Interestingly, we found higher selectivity for hydrogen peroxide (FE_{H2O2} = 75%) for the redox inert MOF compared to the redox active MOF (FE_{H2O2} = 60%), which indicates the selectivity is dependent on the extend of Cu-cluster formation.



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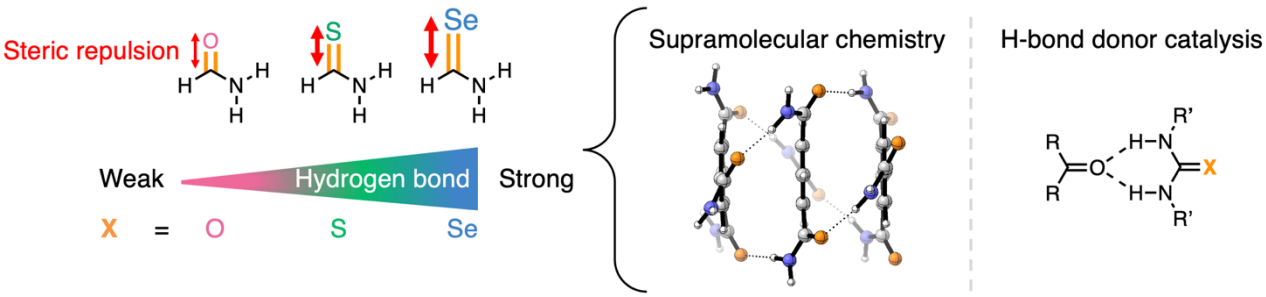
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CHALCOGEN ATOM SIZE: A KEY PARAMETER IN TUNING AMIDE HYDROGEN BONDING

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The hydrogen-bond donor strength of amides, $H_2NC(=X)R$, increases systematically as the chalcogen atom X descends in Group 16 of the Periodic Table. This trend appears counterintuitive because a reduced electronegativity of X down the group suggests, erroneously, a reduced C=X group electronegativity and, thus, a reduced hydrogen-bond donor strength. However, our quantum-chemical analyses reveal that the steric size of the chalcogen atom, and not its electronegativity, drives this experimentally observed phenomenon. Thus, a larger atom X pushes the C=X bond to a longer distance at which the $\pi^*_{C=X}$ molecular orbital drops in energy and becomes a better electron acceptor. This makes the C=X group effectively more electronegative in the sense that it accommodates more charge of the lone pair on the NH_2 group which becomes more positive and thus a better hydrogen-bond donor. In this talk, I show that this phenomenon and the steric mechanism behind it is not exclusive to Group 16 but can be generalized to varying X in the amide C=X moiety down Groups 14 and 15 of the Periodic Table.[2] Finally, I will discuss how the size of the chalcogen atom can be used as a key parameter to aid the design of hydrogen-bond donor catalysts and self-assembled polymers, highlighting its broader implications for material and catalyst design.[3–5]



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RUTHENIUM PEPTIDE BIOCONJUGATES FOR PHOTOACTIVATED CHEMOTHERAPY

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Anticancer peptides from natural sources are promising candidates for cancer therapy due to their biocompatibility, potent therapeutic effects, and low risk of inducing drug resistance in tumor cells. Despite these advantages, their clinical application has been hindered by susceptibility to proteolytic degradation and a lack of specificity for cancer cells, leading to severe side effects. A recognised strategy to increase the selectivity of the anticancer treatments is the local activation of drugs by light irradiation of the tumor. Polypyridyl-ruthenium complexes are well suited for photoactivated chemotherapy (PACT), since they exchange ligands upon visible light irradiation.[1]

In this work, we study the combination of biologically active anticancer peptides and photoactivatable Ru(II) complexes to achieve synergistic effects in a family of ruthenium-peptide bioconjugates for PACT treatment of cancer. By coordination of multiple Ru(II) complexes to the methionine residues of the peptide, the components cage each other in the dark, thus affording low toxicity, while light-induced cleavage of the ruthenium-thioether bonds releases two bioactive components, which kill cancer cells in a very efficient and side effect-free manner.

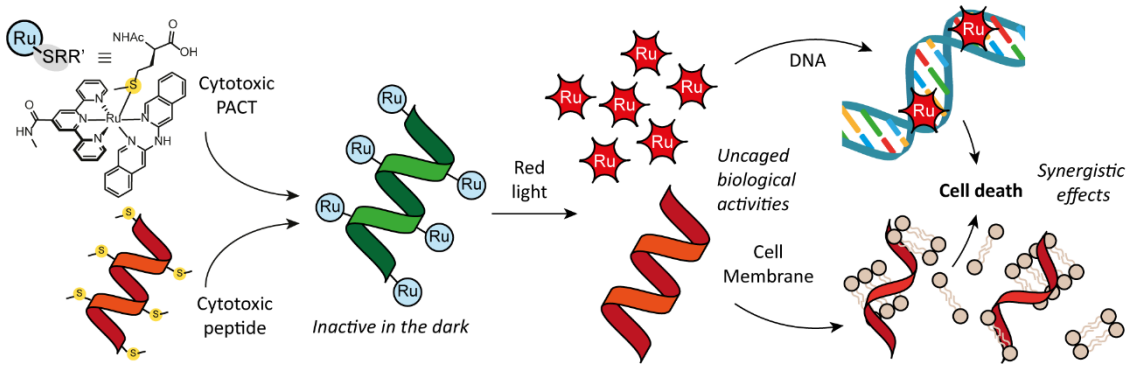


Figure 1: General concept of peptide-Ru(II) bioconjugates composition and action upon red light irradiation.

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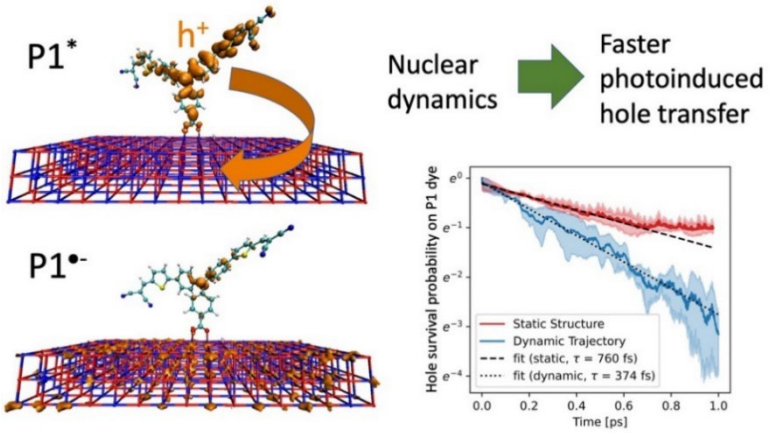
Acknowledgments
I.R. gratefully acknowledges the support of the European Commission through the MSCA Postdoctoral Fellowship project 101062229 — pepRu4PACT.

IMPACT OF NUCLEAR DYNAMICS ON PHOTOINDUCED HOLE TRANSFER IN A P1/NIO PHOTOCATHODE

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Dye-sensitized photoelectrochemical (DSPEC) cells show promise to directly store solar energy into chemical bonds. However, the performance of these cells is presently limited by the photocathode component. While extensive research has focused on optimizing semiconductor, dye and catalyst structures, the role of nuclear motion in the photoinduced charge separation dynamics remains largely unexplored. In this study, we investigate the impact of nuclear dynamics on the photoinduced hole injection of the benchmark NiO/P1 system (P1 = 4-(bis-4-(5-(2,2-dicyano-vinyl)-thiophene-2-yl)-phenyl-amino)-benzoic acid) through both theoretical and experimental approaches. In-situ transient absorption (TA) studies in aqueous environments with different viscosities show that the photoinduced hole injection either proceeds ultrafast (<100fs) or in a sub-ps time window. Interestingly, the slower component is slowed down considerably in more viscous media. Quantum dynamics simulations yield an injection lifetime remarkably close to the slow component from kinetic modelling of the TA results and highlight the critical role of thermal nuclear motion. Simulations including the nuclear thermal motion yield a twofold increase in hole transfer rate compared to simulations on fixed nuclei. Fourier analysis of the trajectories reveals resonances between the hole injection trace and the nuclear dynamics. Specifically, torsional motion around the dye's tails and aniline core appears to be strongly correlated with the hole dynamics. These results yield unprecedented insights into the photoinduced charge separation dynamics of the P1/NiO benchmark system and provide new design principles for improving dye-sensitized photocathodes.



METAPARTICLES: COMPUTATIONALLY ENGINEERED NANOMATERIALS WITH TUNABLE AND RESPONSIVE PROPERTIES

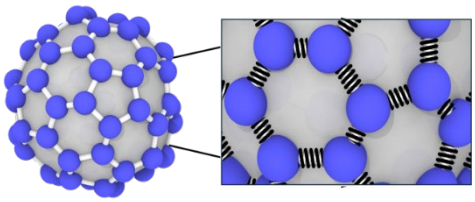
Massimiliano Paesani[1,2,3], Ioana M. Ilie[1,2,3]

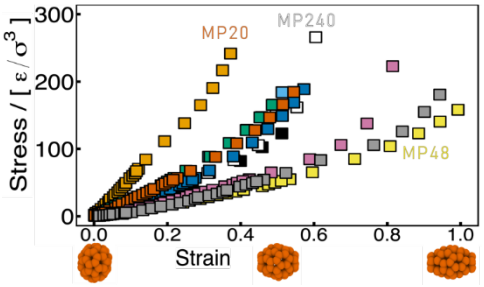
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In simulations, particles are traditionally treated as rigid platforms with variable sizes, shapes and interaction parameters. While this representation is applicable for rigid core platforms [1], particles consisting of soft platforms (e.g. micelles, polymers, elastomers, lipids) inevitably deform upon application of external stress.

We introduce a generic model for flexible particles which we call MetaParticles (MP) [2]. These particles have tunable properties, can respond to applied tension and can deform. A metaparticle is represented as a collection of Lennard-Jones beads interconnected by spring-like potentials. We model a series of metaparticles of variable sizes and symmetries, which we subject to external stress followed by relaxation upon stress release. The positions and the orientations of the individual beads are propagated by Brownian dynamics [3].
The simulations show that the mechanical properties of the metaparticles vary with size, bead arrangement and area of applied stress, and share an elastomer-like response to applied stress. Furthermore, metaparticles deform following different mechanisms, i.e., small MPs change shape in one step, while larger ones follow a multi-step deformation pathway, with internal rearrangements of the beads.

This model is the first step towards the development and understanding of particles with adaptable properties with biomedical applications and in the design of bioinspired metamaterials.





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AI FOR DEVELOPMENT OF SOLID SALT HYDRATES FOR THERMAL ENERGY STORAGE

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More than 50% of energy consumed in buildings is for thermal end use. Hence, in view of the global energy crisis there is urgency to develop technologies that efficiently store and reuse the available heat. A promising approach addressing this challenge is based on hydration reactions of solid salts:

$$MpXq \bullet (m-n)H2O + nH2O(g) \leftrightarrow MpXq \bullet mH2O + Q$$

This process is reversible, hydration reaction leads to release of heat, while the dehydration is endothermic. Such "heat batteries" have high energy densities (>1 GJ/m^3) and are environmentally benign. However, these materials need improvement in durability and operational conditions for real-life applications. We aim to discover new promising salt hydrates and optimize their design. This design space is however quite large (>10^8 reactions), making the conventional high-throughput screening unreasonable.

To approach this problem, we apply artificial intelligence. We fit machine learning models on thermochemical data for salt hydration reactions. As model input, we use reaction representations based on stoichiometry. Those simple representations are available for any hydration reaction however they encode only limited information about the reactants. We tackle this by introducing chemical contextual awareness, similar to context attention in natural language processing. Thanks to the attention mechanism, we can simultaneously learn information-rich graph-like representations of salt hydrates as well as predictive models directly from data. This way we developed models capable of predicting heat and energy density of hydration reactions with reasonable accuracies. We apply those models for virtual high throughput screening and identify a number of new hydration reactions promising for thermal energy storage. We believe that our work will benefit the community of material scientists by providing tools for smart choice of materials for experimental screening.

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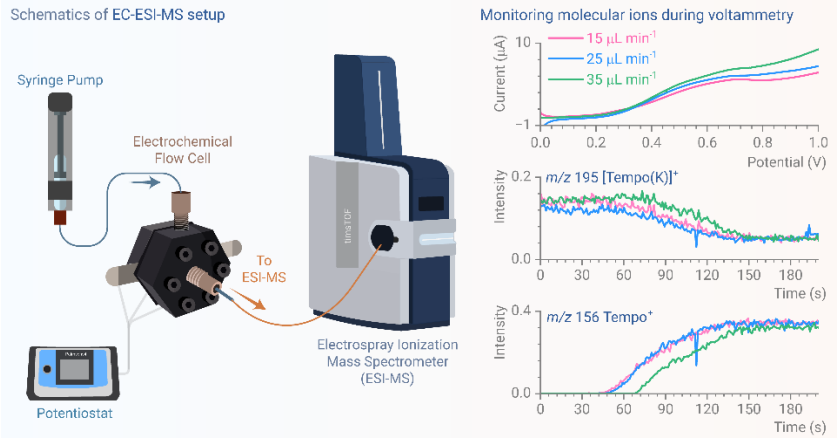
INTEGRATED ELECTROCHEMISTRY AND MASS SPECTROMETRY FOR MOLECULAR INSIGHTS INTO ELECTROCHEMICAL REACTION

Abhinav Bairagi[1], Max T. G. M. Derks[1], Alexandr Y. Pereverzev[1], Jana Roithová[1]

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Understanding electrochemical reaction mechanisms is essential for numerous applications, including the development of efficient electrocatalysts, redox flow batteries, and electrosynthesis processes. Conventional techniques like voltammetry and bulk electrolysis, while useful, offer limited molecular-level insights into these reactions. As a result, complementary spectroscopic methods are often needed to fully interpret the mechanisms of electrocatalytic reactions at the molecular level.

Online coupling of electrospray ionization mass spectrometric technique to the electrochemical methods provides a unique strategy in achieving the detailed molecular-level perspective in electrochemical reactions.[1] This poster presents electrochemistry-electrospray ionization mass spectrometry (EC-ESI-MS) as a powerful technique for studying electrochemical reactions. It focuses on specific examples, such as the electrocatalytic reduction of CO_2 and O_2, where EC-ESI-MS was instrumental in identifying reaction intermediates, tracking catalyst deactivation, and observing changes to the catalyst during the reactions.[2] The poster will also highlight the key advantages that make EC-ESI-MS an effective method for mechanistic studies of electrochemical reactions. These include: transferring reaction intermediates from solution to the gas phase, which eliminates solution-phase interference and enables the detection of short-lived species, using established mass spectrometric methods for complete characterization of intermediates; and allowing simultaneous monitoring of multiple interacting pathways in electrochemical reactions.



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"UNSEEN CHEMISTRY: UNVEILING THE ROLE OF RYDBERG EXCITED STATES IN CO_2 REACTIVITY ON INTERSTELLAR ICES"

Darío Barreiro-Lage[1], Gianluca Levi[2], Ivan Tambovtsev[2], Hannes Jónsson[2], Thanja Lamberts[1,3].

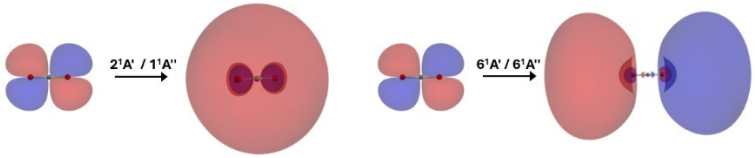
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Recent infrared ice observations in the birthplaces of stars with the James Webb Space Telescope (JWST) highlight the need for targeted studies on the formation and reactivity of interstellar solid-state molecules. Carbon dioxide (CO_2) is of particular interest as one of the main components of interstellar ices [1,2]. The ultraviolet (UV) photons emitted by nearby stars provide enough energy to excite molecular electronic states, which play a critical role in driving chemical reactions and facilitating energy redistribution processes. In light of this, we conduct a computational investigation on the electronically excited states of CO_2, specifically focusing on the low-lying Rydberg states in the **8-12** eV energy range. In the gas-phase, these states act as transient reservoirs with lifetimes extending beyond 100-150 femtoseconds, contrasting with the rapid dissociation typically seen in π-π* excitations [3].

Rydberg excited states, due to their unique electronic configurations, may influence desorption mechanisms, currently overlooked in astrochemical models. The extended lifetimes of Rydberg states could delay CO_2 dissociation and enable alternative pathways for energy redistribution, facilitating non-thermal desorption where molecules gain sufficient energy to escape from the ice surfaces. Our study employs a state-of-the-art computational approach involving variational density functional calculations of excited states, which are emerging as an attractive alternative to TDDFT. These calculations, similar in computational cost to ground-state methods, provide enhanced accuracy for long-range charge transfer, Rydberg, and core-level excitations [4,5]. By directly optimizing Rydberg states in a real-space grid representation and applying self-interaction corrections, this methodology is expected to enable precise characterization of the excited-state properties in CO_2 monomers and dimers. This approach has the potential to offer insights into astrochemical implications of CO_2 excited states stability and reactivity in the interstellar medium.



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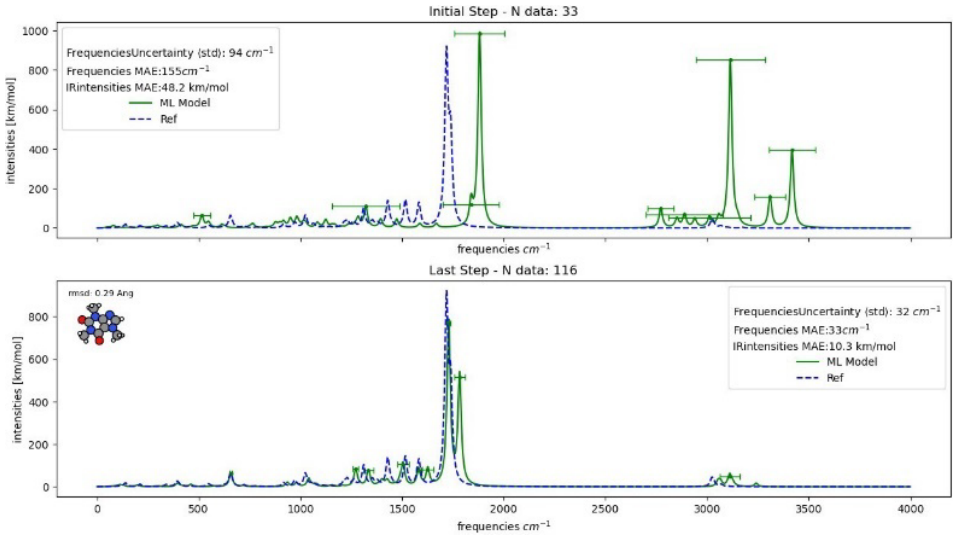
ACTIVE LEARNING FOR HARMONIC INFRARED SPECTRA

Giulio Benedini [1,2], Matti Hellström[1], Lucas Visscher[2]

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Infrared spectroscopy (IR) provides information on atomic structure while being a cheap and non-invasive technique. Its wide application is hindered by its spectra interpretation. Computational simulations could solve this problem but ab initio approaches have very high computational costs. The use of machine learning interatomic potentials (MLIP) can solve this problem.[1]

This work is about active learning workflow to train a committee of MLIPs tuned for IR spectra predictions. The workflow consists in two phases, each composed by three main steps that are repeated iteratively: sampling, training and testing phases. The initial phase of the active learning workflow is similar to previous works [2]. In a second phase the test step includes the calculation of infrared spectra with MLIPs. Displacing the optimized geometry along the normal modes evaluated by the MLIPs the next frames are chosen to be added to the training set. To further make the model more reliable the uncertainties over the frequecies are estimated. These ones correlates with the errors in the frequecies and they are informative of the MLIPs reliability. A preliminary result of this workflow is shown in the picture below. With less than 100 data points the error on the frequeices reduces from 155 cm-1 to 33 cm-1.



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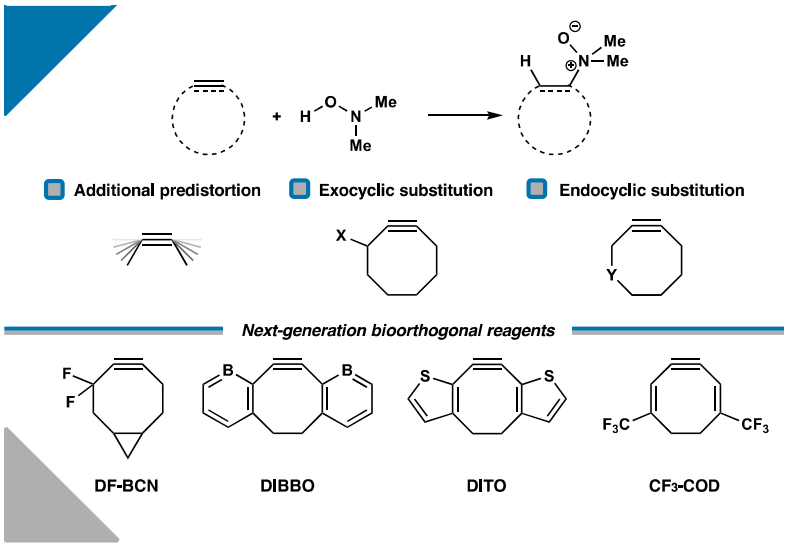
RETRO-COPE ELIMINATION OF CYCLIC ALKYNES: REACTIVITY TRENDS AND RATIONAL DESIGN OF NEXT-GENERATION BIOORTHOGONAL REAGENTS

Steven Beutick[1,2], Song Yu[1], Laura Orian[2], F. Matthias Bickelhaupt[1], Trevor A. Hamlin[1]

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[2]*Dipartimento di Scienze Chimiche, Università degli Studi di Padova, Padova, Italy*

The retro-Cope elimination reaction between dimethylhydroxylamine (**DMHA**) and various cyclic alkynes has been quantum chemically explored using DFT at ZORA-BP86/TZ2P. The purpose of this study is to understand the role of the following three unique activation modes on the overall reactivity, that is (i) additional cycloalkyne predistortion via fused cycles, (ii) exocyclic heteroatom substitution on the cycloalkyne, and (iii) endocyclic heteroatom substitution on the cycloalkyne. Trends in reactivity are analyzed and explained by using the activation strain model (ASM) of chemical reactivity. Based on our newly formulated design principles, we constructed a priori a suite of novel bioorthogonal reagents that are highly reactive towards the retro-Cope elimination reaction with **DMHA**.[2] Our findings offer valuable insights into the design principles for highly reactive bioorthogonal reagents in chemical synthesis.



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ON THE PATHWAY TO COMPLEXITY: MUTUAL AMINO ACID-CLAY INTERACTIONS IN ORIGINS OF LIFE

Orr Rose Bezaly[1,2], Helen E. King[2] , Annemieke Petrignani[1]

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[2]*Department of Earth Sciences, Utrecht University, Utrecht, The Netherlands*

The baffling nature of how life can emerge from otherwise non-living matter is one of the most intriguing open scientific questions. It is known that monomeric building blocks of life, such as amino acids that comprise proteins, are ubiquitous across the universe [1]. Off-world organics synthesized in space conditions can be delivered to rocky planets and enrich the local planetary reservoir [2]. Interactions of monomeric organics with clay minerals have been demonstrated crucial in complexifying this planetary reservoir, promoting the formation of biopolymers in warm pond conditions [3-5]. Research is however biased towards the incorporation of monomers of earth-like biopolymers, often dismissing the role of exogeneous species despite their universality. The study of mixtures of different-source organics and their interaction with critical mineral surfaces is therefore the immediate next step.

In this work, we examine adsorption interactions between calcium-montmorillonite and the strongly adsorbing proteinogenic L-lysine and L-arginine in the presence of the meteorite-common, non-proteinogenic gamma-aminobutyric acid. Single component vs. mixture adsorption behaviour is studied using attenuated total reflectance Fourier transform infrared spectroscopy, powder X-ray diffraction and transmission electron microscopy. The adsorption behaviour and the influence on the clay's structure is analysed and characterised [6-7]. It provides important insights on nanoscale effects that can govern non-enzymatic processes leading to chemical complexification on rocky planets.

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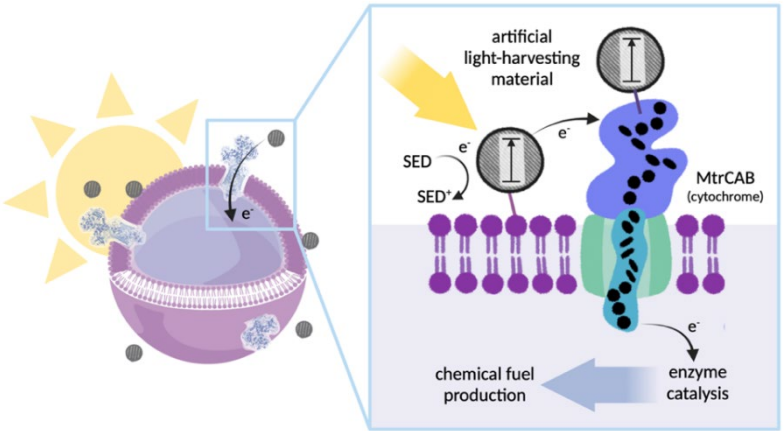
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DEVELOPMENT OF BIOHYBRID NANOREACTOR SYSTEMS FOR SOLAR-DRIVEN FUEL PRODUCTION

Imogen L. Bishara-Robertson[1] Huijie Zhang[1], Lars J. C. Jeuken[1]

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There is an urgent need for sustainable energy sources such as solar fuels to replace the reliance of humanity on fossil fuels. Biological catalysts, which provide unparalleled catalytic specificity, can be integrated with durable inorganic light-harvesting materials in photosynthetic 'biohybrid' systems for solar-driven fuel production. Here, we seek to compartmentalise such photosynthetic systems by coupling synthetic light-harvesting materials, such as carbon dot (CD) nanoparticles and tris(bipyridine)ruthenium complexes, with the transmembrane cytochrome 'nanowire' protein MtrCAB from *Shewanella oneidensis* MR-1. Reconstituted into vesicle-based systems, which we call nanoreactors, MtrCAB can transport photoelectrons into the vesicle lumen for compartmentalised redox catalysis.[1] Our work includes: the encapsulation of hydrogenase enzymes within nanoreactors for H_2 fuel production, the reinforcing of lipid-based nanoreactors with synthetic amphipathic polymers to increase stability, the chemical conjugation of CDs directly with the MtrCAB protein,[2] and use of a membrane-anchored Ruthenium photosensitiser.[3] We hypothesise that optimising materials used within these nanoreactors, and thus enhancing the defined pathway of photoelectron transfer, will increase the potential longevity and scalability of these systems and help improve quantum yield by stabilising the charge separated state. We further propose that elements of this research can be used as a proof-of-principle for application in whole-cell biohybrid systems, in which the bacteria *Shewanella oneidensis* MR-1 could be directly sensitised with light-harvesting material and used as a biological catalyst.[4]



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SEPARATING ACID FROM SUGARS IN HYDROLYSATE FROM (LIGNO)CELLULOSIC WASTE STREAMS – A HISTORY

Emma Sarah Caarls[1], Jorge Bueno Moron[2], Gerard van Klink[1,2], Gert-Jan Gruter[1,2]

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Saccharides are excellent precursors for generating building blocks typically derived from fossil resources.[1,2] To enable this transition, technological advancements are imperative to ensure an adequate supply of sugars for the chemical industry. The sugar market is expected to increase, also due to the necessary shift away from fossil towards renewable resources. Efficient bio-refinery of lignocellulosic (waste) streams can provide the necessary carbon sources of tomorrow's chemical industry.

The Dutch sustainable chemistry company Avantium developed poly(ethylene 2,5-furandicarboxylate) (PEF), a new bio-based plastic.[3] For this product sugars are converted to 5-methoxymethylfurfural (MMF), which is converted to furan-2,5-dicarboxylic acid (FDCA), the key monomer for PEF. This technology is being implemented at industrial scale in an FDCA flagship plant opened in October 2024. This factory will run on commercially available sugars. Currently, these sugars compete with those intended for human consumption. If the choice is presented between food and its plastic packaging, the preference is clear. Instead of edible plants, the future of biorefinery lies in non-edible, lignocellulosic biomass like wood and other cellulosic (waste) streams, like textiles.

The hydrolysis of lignocellulosic material is achieved using highly concentrated mineral acids at low temperatures and ambient pressures. This process leads to the breakdown of cellulose and hemicellulose, to obtain glucose and other lignocellulosic sugars. Avantium's Dawn Technology™ consists of a two-stage HCl treatment to obtain sugar-containing hydrolysate from wood chips.[4,5] However, the acid-sugar separation required to utilise these saccharides for the production of PEF remains commercially challenging. Here, we present preliminary results from a literature study into the history of chemical biomass hydrolysis at (pilot) plant scale and the corresponding separation methods, as well as potential alternatives not yet implemented at larger scale.

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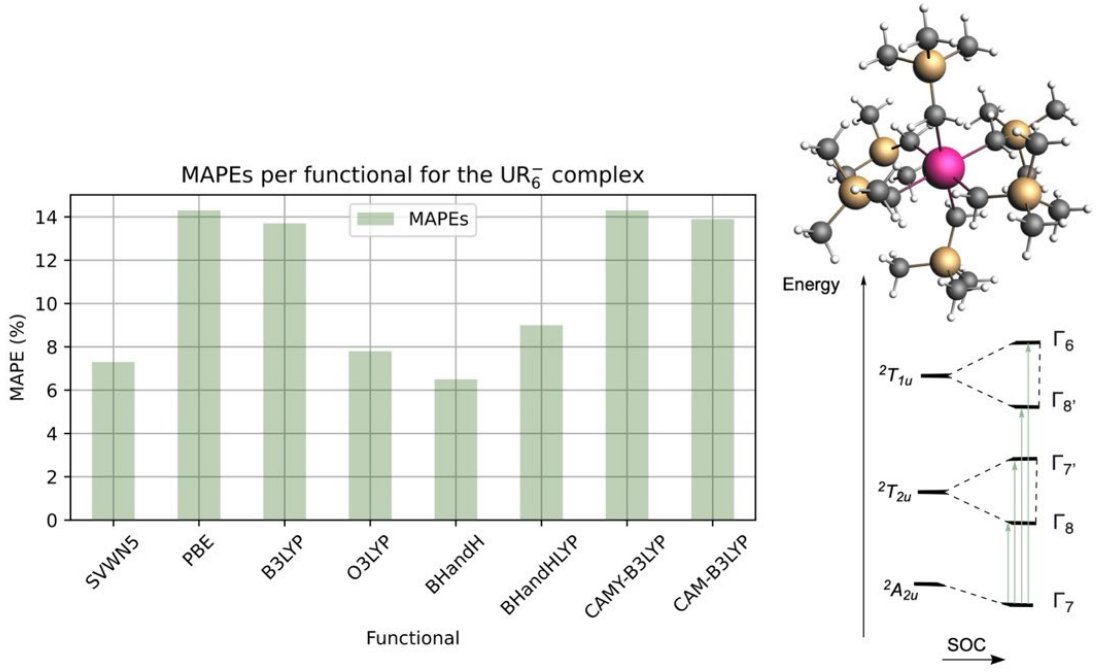
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OPEN-SHELL TIME-DEPENDENT DENSITY FUNCTIONAL THEORY WITH SPIN-ORBIT COUPLING

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When using quantum chemical methods to study electronically excited states of open-shell molecules, it is often beneficial to start with wave functions that have well defined spin. For excited states of molecules containing heavy elements, spin–orbit coupling (SOC) is important and needs to be included as well. An efficient approach is to include SOC perturbatively on top of a restricted open-shell Kohn–Sham (ROKS) time-dependent density functional theory, which can be combined with the Tamm–Dancoff approximation (TDA) to suppress numerical instabilities. We implemented and assessed the potential of such a ROKS-TDA-SOC method, also featuring the possibility of calculating transition dipole moments between states to allow for full spectrum simulation. Our study[1] shows that the ROKS-TDA-SOC formalism yields a clear and easy-to-use method to obtain electronically excited states of open-shell molecules that are of moderate size and contain heavy elements.



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CHEMICAL RECYCLING OF HDPE AND LDPE FROM MUNICIPAL WASTE STREAMS USING HYDROTHERMAL LIQUEFACTION PROCESS

Shih-Chieh Chien[1], Roni Mallick[1], Shiju N Raveendran[1]

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Plastic waste is a significant environmental issue in modern society [1]. Traditional mechanical recycling has been addressing this problem but has intrinsic limitations: it requires cleaner feedstock and allows a limited number of cycles. Chemical recycling holds considerable potential as a supplementary method. Hydrothermal Liquefaction (HTL) is an emerging chemical recycling technique for plastics.

As part of the EU project, PLASTICE (https://plastice.eu/), we studied the HTL of mixed plastic waste containing predominantly HDPE and LDPE, from municipal plastic waste streams in batch reactors. Experiments were conducted at varying temperatures, durations, stirring speeds, water-to-plastic ratios, and plastic granule sizes. The three main product groups, gas, oil, and char were analyzed to determine their yield under different reaction conditions and to understand the composition of each phase. Results indicate that lower temperatures (around 430°C) and shorter reaction times yield higher amounts of oil and less gas. However, the oil produced is viscous with longer carbon chains, sometimes even waxy. Conversely, higher temperatures (450 or 460°C) and longer reaction times result in less oil but shorter carbon chains and a higher proportion of aromatic compounds in the oil. The composition of the oil at different temperature is shown in ***figure 1***. A higher water-to-plastic ratio led to more gas and less oil production, while the oil phase has longer carbon chain and higher selectivity to alkene. This means that the reaction mechanism is influenced by reaction conditions. According to our results [2], HTL shows promising potential in processing mixed municipal plastic waste streams. The oil resulting from our HTL process satisfies the requirements for feeding into the downstream cracker unit for producing olefins such as ethylene and propylene. These olefins can then be used to synthesise fresh polymers. The results will be discussed in detail in the meeting.

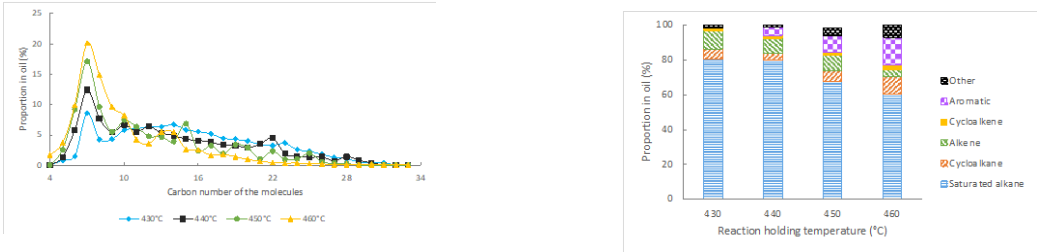


Figure 1. Left: carbon chain length distribution of the oil; Right: the composition category of the oil, at different reaction temperatures. 35 g of post-consumer HDPE plastic was ground into small pieces and liquefied with 50 ml of water for 15 minutes.

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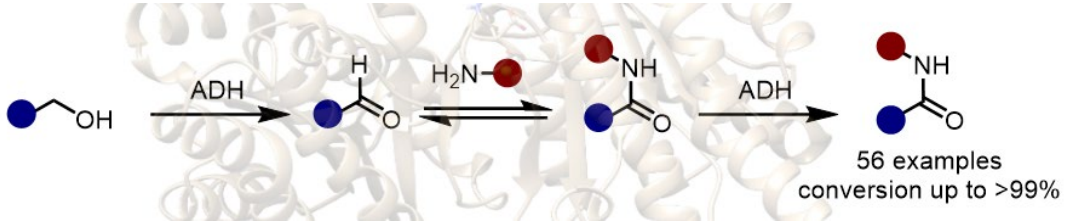
CATALYTIC PROMISCUITY OF ALCOHOL DEHYDROGENASES: A MILD SYNTHESIS OF AMIDES VIA OXIDATIVE COUPLING OF ALCOHOL AND AMINES

Matteo Damian,[1] Patrick Peters,[1] Vasilis Tseliou,[1] Tanja Knaus,[1] Francesco G. Mutti[1]

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In biocatalysis, catalytic promiscuity is defined as the ability of an enzyme to catalyze a reaction that is different from its natural one. In this context, over the past years, our group has revealed novel enzymatic promiscuous activities, one notable example being the conversion of alcohols to nitriles catalyzed by alcohol oxidases using air and ammonia.1 Inspired by this work, we have investigated promiscuous activities of alcohol dehydrogenases that, in nature, catalyze the reversible oxidation of alcohols to carbonyl compounds at the expense of nicotinamide adenine dinucleotide [NAD(P)H] as cofactor. In this work, we devised a new enzymatic method to produce amides from alcohols and amine-rich buffers by harnessing an unprecedented catalytic promiscuity of alcohol dehydrogenases (ADHs). Among the alcohol dehydrogenases tested—NAD dependent and NADP dependent, Prelog and anti Prelog—five of them showed activity toward the formation of the amide. The reaction work with benzyl, aromatic, linear aliphatic and branched aliphatic alcohols with conversion up to 99%.

Notably, the synthesis of amides stands as a cornerstone in chemistry, also bearing significance in biology, a fact underscored by their prevalence in patents within medicinal chemistry.2 Despite numerous approaches for amide synthesis documented in the literature, many suffer by inadequate atom efficiency and the generation of wasteful byproducts.3 Therefore, our biocatalytic approach for amide synthesis paves the way to a promising sustainable methodology to access these compounds.



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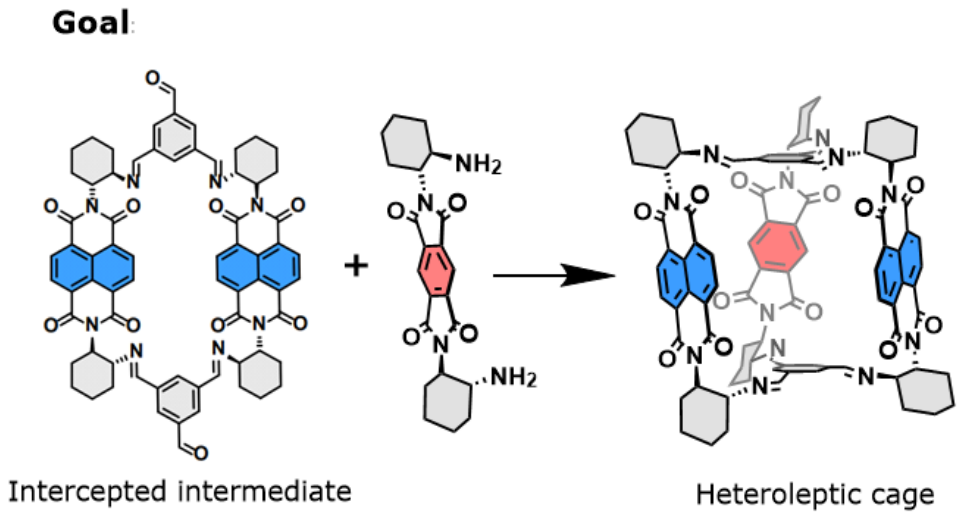
TOWARDS HETEROLEPTIC COVALENT ORGANIC CAGES

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Porous organic cages (POCs) provide access to diverse microporous materials. Despite their three-dimensional structure, they can be obtained in one step via reversible dynamic covalent chemistry. The combination of porosity, optoelectronic properties, and solubility represents an excellent platform for variety of applications.[1] However, POCs predominantly possess high symmetry, and it is challenging to reduce it. Yet, POCs with lower symmetry considerably extend the material space to achieve new applications in catalysis, photochemistry, and more.

Here, we will report the synthesis of rylene diimide POCs under kinetic control.[1,3,4] We investigated the reaction mechanism to identify crucial synthetic intermediates that we intercepted and fully characterized during the cage synthesis. We will present how these intermediates can be successfully employed in the synthesis of low-symmetry POCs. Such stepwise approach facilitates a modular synthesis and enables introduction of diverse chromophores into POCs endowing them on-demand with customizable physical properties.



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MACHINE LEARNING FOR CLASSICAL DFT

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Classical density functional theory (cDFT) is concerned with finding the equilibrium particle distribution for a classical interacting particle system without the need for simulation. Although cDFT has contributed to understanding the behavior of molecular systems, its progress has been held back by the need for approximations to render the framework analytically feasible. We have developed a neural network model that can find the particle distribution of a simple interacting particle system using the cDFT framework. Traditional molecular simulations can be computationally expensive and time-consuming when screening numerous large structures, but utilizing cDFT with neural networks has the potential to bypass these limitations

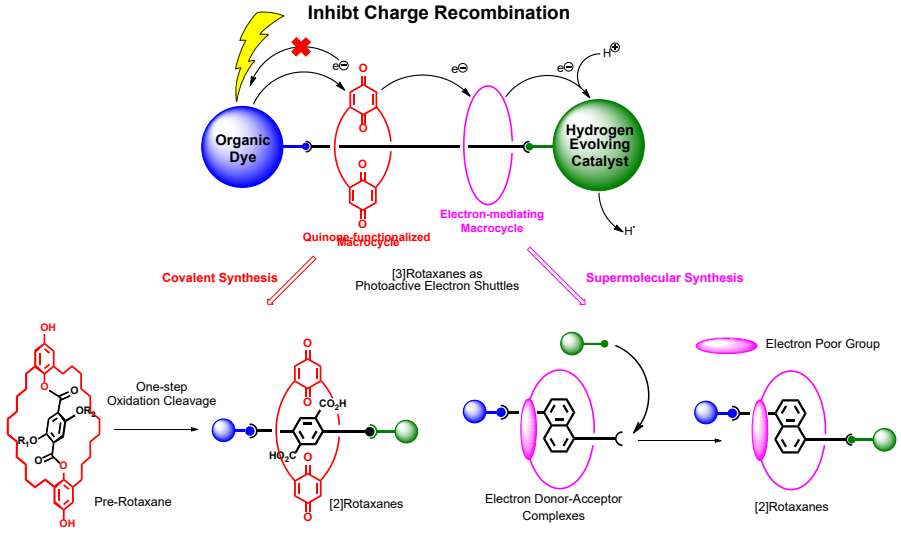
HYBRID COVALENT/ SUPRAMOLECULAR SYNTHESIS OF [3] ROTAXANES AS PHOTOACTIVE ELECTRON SHUTTLES

Zezhong Dong[1], Milo Cornelissen[1], Jennifer Munro[1], Nick Westerveld[1], Alessandro Mantoani[1], Joost Koning[1], Clea Mellbourn[1], Simon Mathew[1] , Jan H. van Maarseveen[1].

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Addressing the challenge of avoiding electron recombination in artificial photosynthetic devices necessitates innovative solutions.[1] Our proposed strategy involves the integration of redox mediators within the macrocycles of [3]Rotaxanes to serve as efficient electron transporters. This approach aims to facilitate unidirectional electron flow from the dye to the hydrogen evolving catalyst, thereby mitigating the issue of rapid recombination.

The design encompasses two key components. Firstly, a quinone-functionalized macrocycle, synthesized via covalent templated methodology, offers the unique capability to neutralize negative charges through protonation of the quinone radical anion [2], thereby enhancing electron transfer efficiency and stability. Complementing this, the second macrocycle, engineered through supramolecular synthesis, features redox-active properties with a lower reduction potential and ensures the unidirectional transport of electrons. By combining these specialized macrocycles within the [3]Rotaxanes framework, we envision a novel approach to circumvent electron recombination, ultimately advancing the efficacy of artificial photosynthetic systems.



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RU-BASED CAGES FOR PHOTOREDOX CATALYSIS FOR *IN VIVO* APPLICATIONS

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Employment of transition metal catalysts in a cellular environment has advanced to a variety of new-to-nature reactions, enabling profluorophore and prodrug deprotection reactions, synthesis of biomolecules or (protein) labelling.[1,2] Photoredox catalysis can have an additional advantage in this area, since light as external stimuli allows improved spatio-temporal control over the desired catalytic reaction. Especially in the dilute and complex cellular environment, this type of catalysis is limited by diffusion of the reactants, and the (triplet) lifetime of the often transition-metal based photosensitizer or photocatalyst.[3,4]

A strategy to tackle these limitations is to integrate the photocatalyst into a supramolecular coordination cage. [1,3,4] This supramolecular strategy creates a *micro-environment* in the solution in which the local concentration of catalyst is possibly increased and/or the substrate can preorganize. These effects might enhance both the efficiency as the selectivity of the photoredox catalysis *in vivo*. For that reason, we investigated the influence of integrating the commonly employed photocatalyst $Ru(bpy)_3$ into M_6L_4-cage structures, such as the previously established Ru-TT cage,[5] for Ru-photoredox catalysis in a cellular environment.

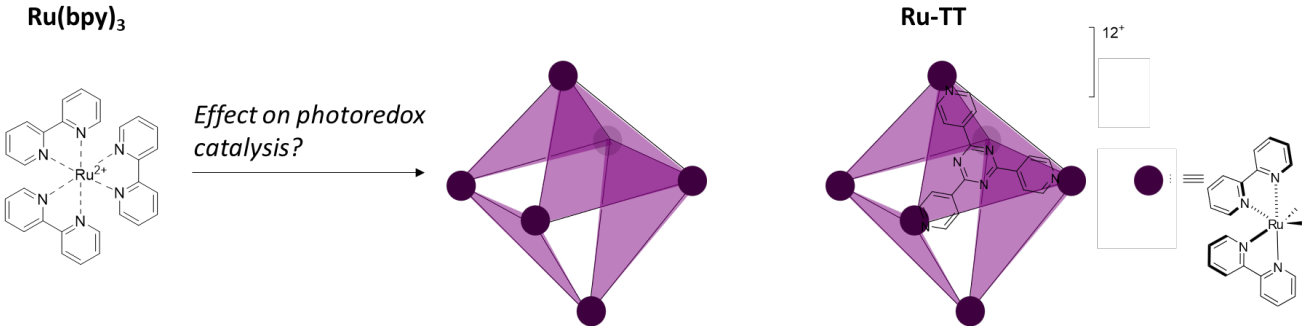


Figure 1. Schematic drawing of integrating the commonly employed photocatalyst $Ru(bpy)_3$ into M_6L_4-cage structures, such as the Ru-TT cage[5] where the ruthenium metal functions as a node in the supramolecular structure.

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RU-BASED A HEMI-INDIGO PROTON INFORMATION RATCHET

Nol Duindam[1], Albert M. Brouwer[2], Sander J. Wezenberg[1]

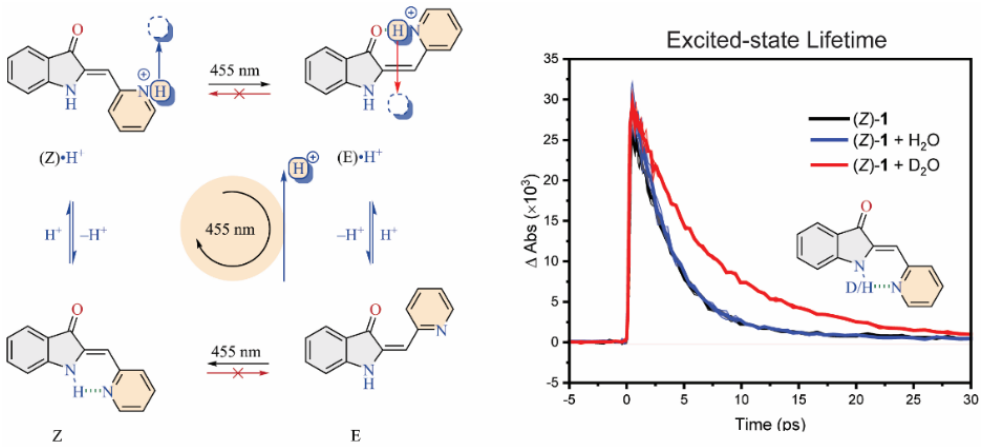
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Photoisomerization of retinal in bacteriorhodopsin is at the basis of proton pumping across the bacterial membrane. Synthetic systems capable of directionally moving macrocyclic rings over a nonsymmetric axle[1] have been developed, but analogous light-driven pumping of small biologically relevant substrates, including protons and ions, has not been achieved and remains a fundamental challenge.

We previously described *N*-heterocyclic hemi-indigos of which the direction of photoisomerization is fully dictated by the protonation state,[2] thus operating according to an information ratchet mechanism.[3] This gives rise to a unique monodirectional interconversion cycle that drives proton translocation with respect to the scaffold; forward photoisomerization solely occurs with the proton associated whereas the backwards isomerization occurs only after proton disassociation.

Transient absorption spectroscopy was performed in order to elucidate the mechanism of this selective inhibition of photoisomerization. Isotope studies confirm the involvement of the intramolecular hydrogen bond in the ultrafast deactivation of the excited state, outcompeting productive photoisomerization.

We envision that rational design of such selective inhibition of either forwards or backwards photoisomerization paths by binding of a substrate can be applied as a general approach for directional transport of that substrate.



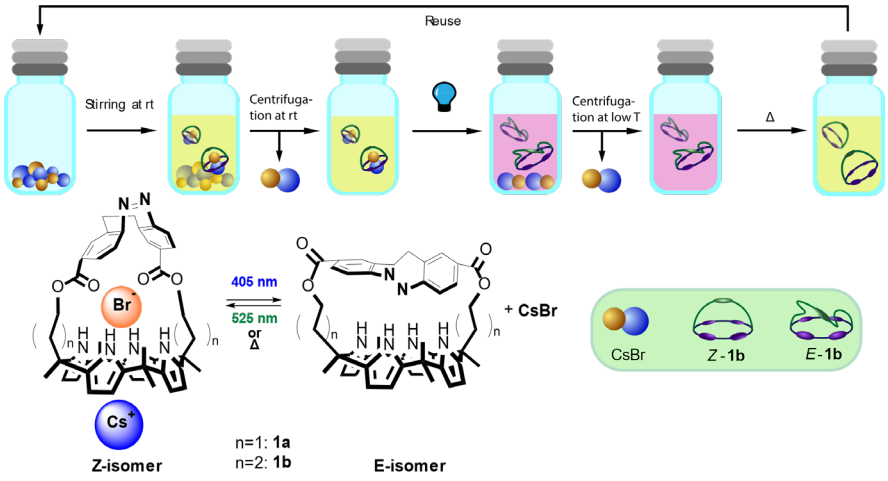
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CESIUM SALT EXTRACTION AND DEPOSITION BY A PHOTOSWITCHABLE CALIX[4]PYRROLE RECEPTOR

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Selective removal of cesium salts from wastewater remains a significant challenge in industry. Calix[4]pyrrole macrocycles are promising extracting agents as they show high binding affinity and selectivity towards anions and cesium ion pairs.[1] Nevertheless, while very high affinity is desired for efficient extraction, it hampers recyclability and recovery of the subbstrate. An effective strategy to overcome this issue, [2] recently developed in our group, is to introduce a photoresponsive strap such that low-affinity and high-affinity states can be addressed by light.[3] A drawback of the current system is the use of damaging UV light and low photo-stationary state ratios, which hamper its efficiency as an extractant. To address these issues, we have introduced Z-diazocine as a bridging unit. Here, we present two diazocine-strapped calix[4]pyrrole receptors, which can be switched over multiple cycles between high and low binding affinity states using visible light irradiation. Both Z-isomers strongly bind chloride and bromide anions in 1:1 stoichiometry. Exposure of the host-guest complexes to 405 nm, leading to formation of the respective E-isomer, results in anion release. The receptor with a longer spacer is shown to function as an effective extractant of cesium bromide. This work opens up a new photo-modulable approach to extraction and deposition of cesium salts, which eventually will help to reduce the volume of waste streams.



Acknowledgments
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SUPRAMOLECULAR INTERACTIONS FOR $C0_2$ HYDROGENATION TO CH_3OH

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The hydrogenation of CO_2 and CO_2-derivatives using a homogeneous, molecularly defined catalyst has been widely explored in recent years, but most examples are limited to low TONs, which limit their applicability compared to heterogeneous catalysts for the same reaction. This is mostly due to two different slow steps in the catalysis, namely H_2 splitting and the hydrogenation of the metal-formato species. In this project each of these two slow steps are tackled using supramolecular interactions. In the case of H_2 splitting, Ir- and Co-based homogeneous catalysts bearing a pendant base in the ligand backbone were synthesized. The protonation of this pendant base would aid H-H splitting by metal-ligand cooperation, which would allow for facile hydride formation. In the case of the hydrogenation of the metal-formato species, Ir- and Co-based homogeneous catalysts were synthesized bearing H-bonding moieties on the ligand backbone. These H-bonding moieties would allow for supramolecular interactions between the catalysts, ideally accessing a bimetallic mechanism which would speed up the hydride transfer to the metal-formato species, as was suggested in previously reported literature. Preliminary results involving this latter strategy show not only an increase in TON for formic acid hydrogenation to CH_3OH in the case of some H-bonding catalysts, but also the possibility for this catalyst to perform catalyst in the presence of no additives. While these first results are promising, more studies need to be conducted to test this catalytic system and to verify if both of these strategies can not only speed up catalysis, but also access for different hydrogenation states, which wouldn't be possible without these supramolecular interactions.

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EXPLORING THE PROPERTIES OF ELECTROCHEMICAL INTERFACES AT THE ATOMIC SCALE

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The structural and electronic properties of electrochemical interfaces are of paramount importance for understanding the mechanisms of electrocatalytic reactions and therefore designing efficient electrode materials. Despite tremendous efforts dedicated to this topic, a complete picture of the electrochemical double-layer (EDL) is still lacking. Experimentally, the voltametric currents and their dependency on the interface environment constitute a primary source of information to investigate the structure and reactivity of electrified interfaces. Nonetheless, these electrochemical signals are often constituted by multi-component responses due to the complexity of processes occurring at electrochemical interfaces, making them hard to deconvolute and relate to EDL microscopic structures and properties [1].

In recent years, ab initio molecular dynamics (AIMD) has become an important tool to complement experiments for investigating interfacial properties as it allows to capture the electronic structure and chemical interactions of the interface at the atomic scale [2-3]. In this work, a potential-dependent AIMD approach is employed to simulate electrified metal/water interfaces and investigate their electronic and structural properties in realistic conditions. The potential of zero-charge and double-layer capacitance, which can be considered as fingerprints characteristic of the microscopic properties of an electrochemical interface, are computed at a quantum level. Notably, the influence of the hydrogen coverage on the double-layer capacitance of platinum surfaces is rationalized. Thermodynamic properties of ions in their solvation spheres are analyzed and consistently compared to experimental measurements. Such calculations can be of great help not only to rationalize phenomena experimentally observed in electrocatalysis but also to develop an EDL model going beyond the classical Gouy-Chapman-Stern theory.

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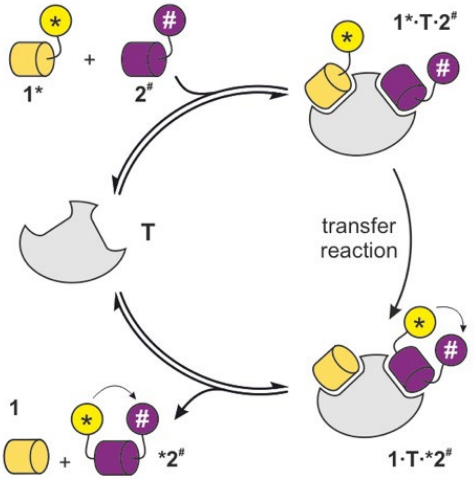
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NON-ENZYMATIC PROTEIN TEMPLATES AMIDE BOND FORMATION AND PROVIDES CATALYTIC TURNOVER

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The spatial alignment of functional groups is a central aspect of most catalytic processes. Protein scaffolds with their exceptional molecular recognition properties have evolved into powerful biological catalysts. However, the rational design of artificial enzymes starting from non-catalytic protein domains proved challenging. Herein, we report the use of a non-enzymatic protein as template for amide bond formation. Starting from a protein adaptor domain capable of simultaneously binding to two peptide ligands, we designed a catalytic transfer reaction based on the native chemical ligation. This system was used for the selective labelling of a target protein validating its high chemoselectivity and potential as a novel tool for the selective covalent modification of proteins.



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TRANSFER LEARNING FOR THE PREDICTION OF PROTEIN-LIGAND BINDING AFFINITIES OF METAL COMPLEXES

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Machine learning methods have been successfully applied to predicting the binding affinity of organic inhibitors to proteins, thanks to the abundance of data available for these systems. However, the limited data available for metal complex inhibitors, makes the application of such methods challenging. For instance, PDBbind[1] contains binding affinities for about 20,000 protein-ligand complexes, but only around 100 data points correspond to metal containing inhibitors, with no single metal type being represented by more than 15 data points. To address this data limitation, transfer learning presents itself as an effective solution. It can be used to obtain knowledge from a larger dataset and apply it to a smaller one, if the descriptors in both sets are relatively similar. Given that the interaction between a fully coordinated metal ion and the protein is primarily determined by the organic linkers coordinated to the metal, the marginal distributions of the descriptors for metal complex and organic inhibitors should not differ too much.

In this contribution, we apply transfer learning using a large organic dataset and a small ruthenium inhibitor dataset. Our findings indicate that applying various machine learning algorithms solely to the smaller dataset does not yield satisfactory results. However, by incorporating information from the larger organic dataset within a transfer learning framework, significant improvements are observed. In particular, when using a contrastive semantic alignment algorithm.

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MODIFYING THE LOCAL PH ON AU-ELECTRODES DURING HYDROGEN EVOLUTION BY POLYMER-COATINGS

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Regarding current efforts to decrease society´s dependence on carbon-based fuels, the electrochemical hydrogen evolution reaction (HER) is of outstanding importance. Despite its technological maturity, many aspects of this reaction remain poorly understood, especially regarding its dependence on the local chemical environment. Recently, the interdependence of the local cation concentrations and the local pH-value under operating conditions has been demonstrated applying rotating disc gold electrodes. Increasing the rotation rate led to a surprising decrease in HER current density explained by a decrease of the local pH causing a decrease in the local cation concentration.[1] Herein, we investigate the influence of polymer- coatings on the pH/cation concentration interdependence in buffered and non-buffered K^+, Na^+ and Li^+-containing solutions. The local pH-values inside the polymer-coatings are determined by confocal fluorescence microscopy (CFM) after equipping the polymer with fluorescent pH reporters. The results are compared to those obtained from non-coated Au- electrodes emphasizing the crucial role of the polymer in tuning the local environment for improved electrochemical HER.

Concerning the sensitivity of other electrochemical reactions like CO2 or N2 reduction on the local environment[2,3], polymer-coatings have a great potential to optimize electrocatalysts in general.

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TOWARD A TOTAL SYNTHESIS OF (+)-PEROPHORAMIDINE TROUGH A CARBOPALLADATION APPROACH

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Perophoramidine is a complex polycyclic alkaloid isolated from the marine ascidian *Perophora namei* showing promising anticancer activity. These medicinal properties, together with its two vicinal quaternary spiro stereocenters, make it a popular target for total synthesis.

Here, we report a novel synthetic strategy toward the regio- and stereoselective construction of (+)-(dehalo)perophoramidine through an asymmetric carbopalladation approach. In the key step, we envision a Heck – Suzuki coupling cascade to construct the two required vicinal quaternary stereocenters of (+)- (dehalo)perophoramidine. We report our progress in synthesizing suitable substrates and investigating conditions for the envisioned cascade cyclization.

MDNA: SOFTWARE MODULE FOR DNA STRUCTURE ANALYSIS AND GENERATION

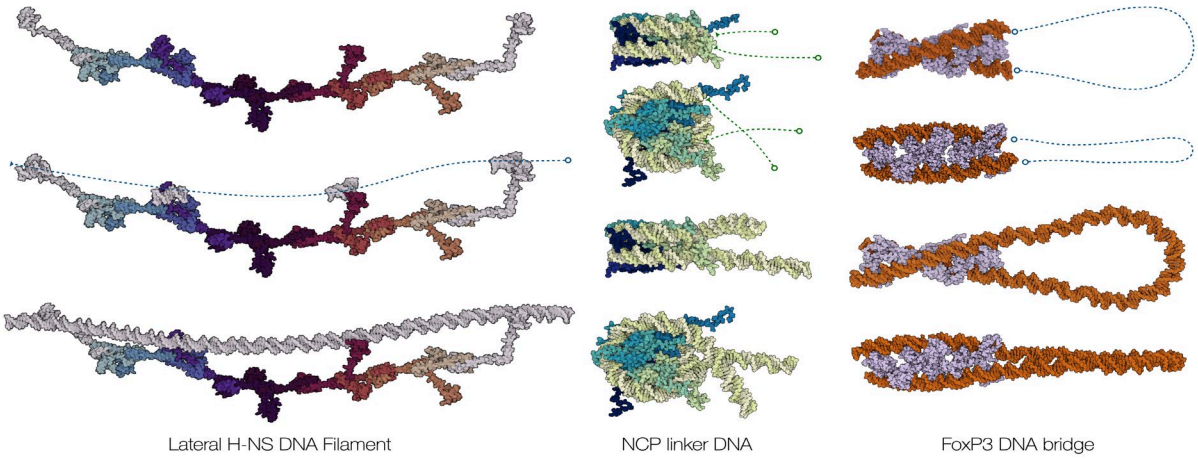
Thor van Heesch[1], Enrico Skoruppa[2], Jocelyne Vreede[1]

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We introduce MDNA, a Python-based molecular modelling toolkit specifically designed to address the limitations of current tools in generating accurate DNA configurations for molecular dynamics (MD) simulations, particularly in complex DNA and DNA-protein assemblies. Traditional methods often rely on experimental data and oversimplified, linear B-DNA models, which are insufficient for representing curved structures, non-canonical modifications, or protein-DNA interactions.

MDNA overcomes these challenges by employing a flexible spline-based mapping technique and a rigid body approach for DNA bases, enabling the construction of arbitrary DNA shapes. Key features include support for (non-)canonical base modifications, such as Watson-Crick-Franklin to Hoogsteen transitions, DNA methylation, and the ability to refine structures using Monte Carlo minimisation. Additionally, MDNA provides tools for analysing DNA structures and trajectories by calculating geometric properties using a rigid body formalism. MDNA fills critical gaps in existing methodologies by combining the generation, refinement, and analysis of DNA structures in a single platform. Its versatility and precision make it an essential tool for exploring DNA dynamics and complex biological systems involving DNA-protein interactions. Real-world examples of constructing large biomolecular configurations using MDNA will be discussed.

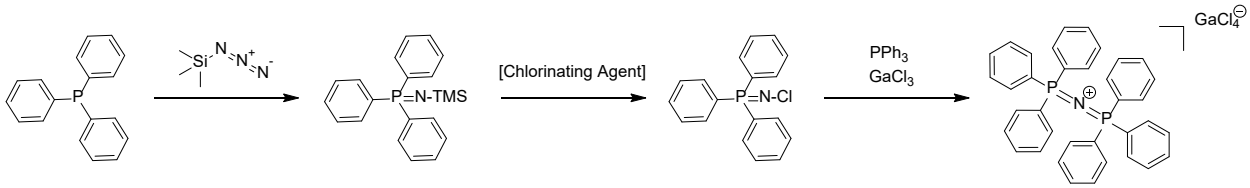


INVESTIGATING A NOVEL ROUTE TOWARDS $R_3P{=}N[ED]^+$ SPECIES USING $R_3P{=}N^+$ LEWIS ACIDS

Jelle Hofman[1], Francesco Cirigliano[1], Carlijn Pool[1], Chris Slootweg[1]

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Phosphorus compounds have garnered significant interest due to their potential as ligands and their involvement in various chemical processes. However, the synthetic pathways to these desired compounds are not always environmentally benign. A prime example is the synthesis of $[Ph_3P{=}N{=}PPh_3]Cl$, which frequently employs chlorine or bromine and generates considerable waste.[1] A more sustainable approach would involve the synthesis of the Lewis acidic species $Ph_3P{=}N^+$, which can be readily attacked by nucleophilic donors such as PPh_3. Although nitrogen-based species are typically classified as Lewis basic due to the presence of a lone pair, Gandelman and colleagues have demonstrated that cyclic triazanes exhibit electrophilic behaviour around the central nitrogen atom, attributable to the localisation of a positive charge.[2] A key challenge in this methodology lies in the stabilization of the highly reactive $Ph_3P{=}N^+$ species. Our current investigation focusses on employing the Staudinger reaction to introduce nitrogen into triphenylphosphine, followed by chlorination and a chloride abstraction (see Scheme 1).



Scheme 1 General synthesis approach used for the synthesis of $R_3P{=}N{=}[ED]^+$ species.

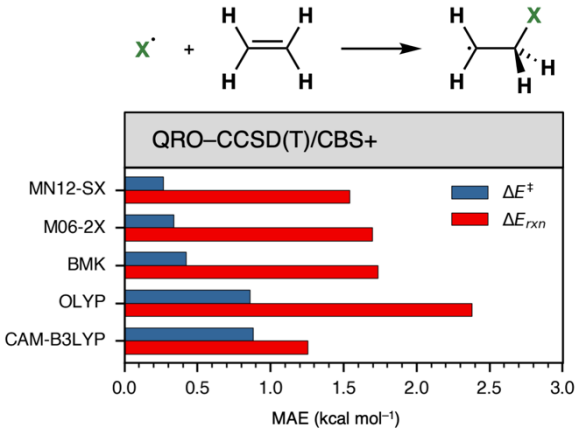
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RADICAL ADDITION REACTIONS: HIERARCHICAL *AB INITIO* BENCHMARK AND DFT PERFORMANCE STUDY

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Benchmarking is an important topic in all of computational chemistry. It is the one way to figure out if your methodology is accurate and reliable for a given chemical system. In this talk I will talk about the do's and don'ts of our benchmark on radical addition reactions.[1] We used a hierarchical[2] series of *ab initio* methods (HF, MP2, CCSD, CCSD(T)) paired with a hierarchal series of Dunning basis sets with and without diffuse functions ((aug)–cc–pVDZ, (aug)–cc–pVTZ, (aug)–cc–pVQZ). Since we work with radical systems we transformed the HF ground-state wavefunctions into quasi-restricted orbital (QRO) reference wavefunctions to address spin contamination. Following extrapolation to the CBS limit, we determined that the energies from our highest- QRO–CCSD(T)/CBS+ level were converged with respect to the *ab initio* method and basis set, respectively. Our QRO–CCSD(T)/CBS+ reference data was used to evaluate the performance of 98 density functional theory (DFT) approximations for both energetics and key geometrical parameters of the stationary points.



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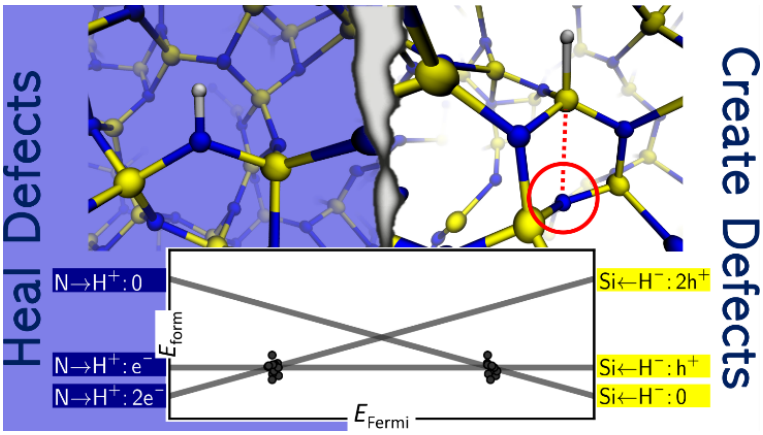
CHARGE TRAPPING IN SILICON NITRIDE: HYDROGEN AS SAVIOR AND SABOTEUR

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[1]*Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, The Netherlands*

Amorphous silicon nitride (a-Si_3N_4) is an essential material in nanoelectronics, particularly for charge trapping in flash memory devices. EPR experiments combined with electronic structure calculations suggest that undercoordinated Si atoms (K-centers) are responsible for this phenomenon; however, the propensity of such defects towards hydrogen passivation raises the question of the completeness of this picture.

In this work, we combine force field (FF) simulations with hybrid density functional theory (DFT) calculations. Using the MG2 force field, we generated a statistically significant ensemble of a-Si_3N_4 structural models via the melt-quench method. Upon adding charges to those models, we perform structural optimization using the HSE06 hybrid DFT-functional to accurately describe band edges and defect trapping energies. We identify a hitherto unknown mode of intrinsic polaronic trapping of electrons in a-Si_3N_4: Charging can generate either a K-center or Si-Si-type defect while discharging recovers the amorphous network's original structure.[1] Crucially, this study bridges the previously fragmented understanding of charge trapping and hydrogen incorporation. We demonstrate that hydrogen plays a dual role: It can repair coordination defects, healing the network, yet also promotes Si-N bond breaking in strained areas, thus compromising the network integrity.[2] Our findings offer a unified perspective on the interplay between defect formation, hydrogen behavior, and charge trapping, providing insights critical for optimizing a-Si_3N_4's electronic properties in nanoelectronic applications.



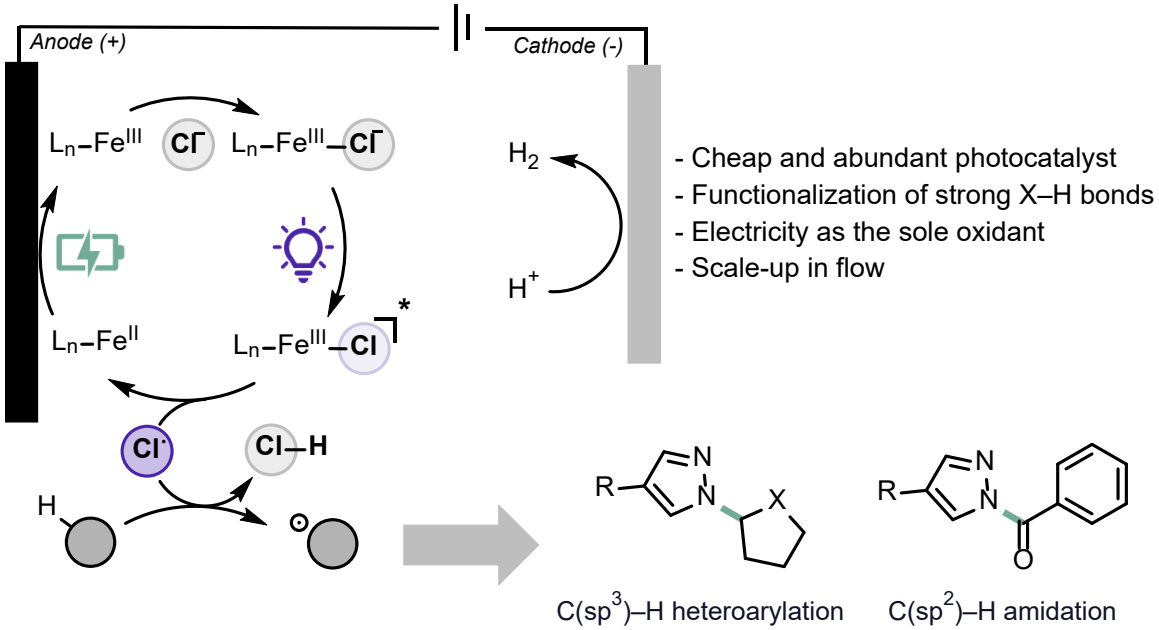
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OXIDANT-FREE FUNCTIONALIZATION OF C–H BONDS ENABLED BY IRON ELECTROPHOTOCATALYSIS IN BATCH AND FLOW

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ElectroPhotoCatalysis (EPC) is gaining attention in organic synthesis due to its ability to enable novel dehydrogenative processes without the need for sacrificial oxidants. We leveraged this technology, combined with iron catalysis, to efficiently develop an electrophotocatalytic method for the direct functionalization of various C–H bonds with *N*-nucleophiles, using electricity as the sole oxidant.[1] The products are generated through an electrochemically induced radical-polar crossover (RPC) mechanism involving hydrogen atom transfer (HAT) photocatalysis, all under remarkably mild conditions. Finally, we integrated these methodologies to continuous-flow systems, known as flow ElectroPhotoCatalysis (*f*-EPC), highlighting the potential for scalable processes due to improved irradiation, increased electrode surface area, and enhanced mixing of the reaction mixture.[2] This versatile approach supports late-stage functionalization, making it highly applicable in drug development.



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PREDICTING RIGIDITY RESPONES OF NATURAL POLYELECTROLYTES: A BAYESIAN APPROACH

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The mechanical properties of charged polymers are strongly influenced by the presence of ions. For instance, experimental and computational studies have found that calcium ions weaken the intramolecular hydrogen-bond network of the natural polysaccharide hyaluronan, leading to a decrease in rigidity. Since hyaluronan is crucial for many physiological processes, including the development of cancer and osteoarthritis, it is important to predict its mechanical responses to different environments. To accomplish this, one needs to explore the bending free energy, or persistence length, of hyaluronan in various ion concentrations. However, this involves a prohibitive number of expensive and time-consuming experiments or simulations. To tackle this, we use Bayesian approaches to explore the bending free-energy landscape via enhanced sampling simulations. Each sample provides a free-energy gradient estimation, which we can use directly in Bayesian optimization to find free-energy extrema, or in Bayesian quadrature to directly calculate the integrand, i.e., the free energy. Both approaches focus the expensive calculations on the most informative samples of the free-energy landscape, which are iteratively selected based on a probabilistic model. With this approach, we can efficiently identify different regimes of polyelectrolyte rigidity, predicting mechanical responses in various conditions, comparable with experiments.

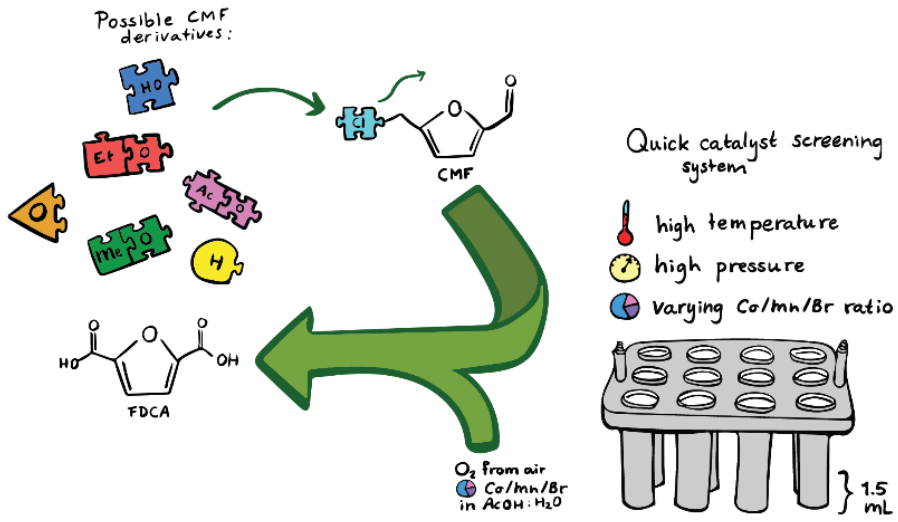
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FROM POLYCOTTON WASTE-DERIVED PLATFORM CHEMICAL TO MONOMER FOR BIO-BASED PLASTIC

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PET and cotton are the most broadly used fibre materials in textile industry, making up more than 75% of global fibre production. The majority of textiles consists of a blend of multiple materials, hampering the recycling of these materials.
In this study, cotton present in polycotton textile waste (a blend of cotton and polyester) is depolymerised to glucose and separated. Glucose is in-situ converted to 5-(chloromethyl)furfural (CMF), while the PET fibres present in the blend textile stay intact. CMF can be converted to various furfural derivatives, that subsequently can be oxidatively converted to furan-2,5-dicarboxylic acid (FDCA), one of the two monomers for polyethylene furanoate (PEF). This research compares different furfural derivatives, their reaction pathways and how suitable they are as an intermediate for the conversion of CMF to FDCA. The authors have found that 2,5-diformylfuran and 5-hydroxymethylfurfural can be oxidized to FDCA with the highest yield, compared to four other promising furfural derivatives. Working towards a conversion process with industrial application, the goal of this research is to find the 'winning bridge' between CMF and FDCA, aiming to unlock a new waste feedstock for large scale production of bio-based monomers for plastics.



EXPLORING CO(10-12) SURFACE REACTIONS VIA OPERANDO STM DURING FISCHER-TROPSCH SYNTHESIS

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Fischer-Tropsch synthesis [1] is a feasible method for sustainable fuel generation, capable of reducing atmospheric CO_2 emissions and reliance on crude oil. Designing more efficient catalysts to make Fischer-Tropsch synthesis (FTS) industrially viable requires a further understanding of the catalytic processes at the nanoscale and Co(10-12) model catalysts hold significant potential in this regard. Metallic and oxidized Co(10-12) surfaces were analyzed before, during, and after exposure to 0.3 mbar/min CO and 0.7 mbar/min H2, and 0.3 mbar/min CO only, at both room temperature (RT) (300 K) and high temperature (HT) (493 K) for this study. The temperature, pressure, and ratio of CO and H2 influenced the reaction pathways. To observe the reaction mechanisms taking place under realistic conditions, we used various methods that provide morphological and chemical information on the catalytic surface, which include the operando scanning tunnelling microscopy (STM) that is suitable for the FTS reaction conditions up to 6 bar and 600 K combined with Auger electron spectroscopy, low-energy electron diffraction, and quadrupole mass spectrometry [2].

This study revealed a novel oscillation process linked to surface reconstruction initiated by carbon presence and the temporary inhibition of catalytic active sites caused by oxygen. A new oscillation could commence probably due to the desorption of reaction products. These insights will advance the Co(10-12) catalyst, offering promise for producing value-added hydrocarbons by supporting the development of more efficient and cost-effective FTS catalysts and procedures. However, more studies, comprising validation and investigation of oscillation behavior triggers and the impact of oxygen enhancement, are crucial for thoroughly understanding these processes.

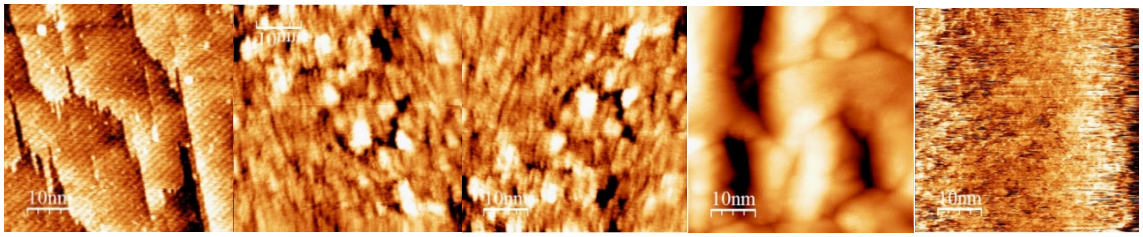


Fig. STM images of (a) clean Co(10-12), (b) Co(10-12) after exposure to CO and H_2 at RT, (c) Co(10-12) after exposure to CO and H_2 at HT, (d) oxidized Co(10-12) after exposure to CO and H_2 at RT, (e) oxidized Co(10-12) after exposure to CO and H_2 at HT.

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ROLE OF EXCITON DELOCALIZATION IN CHIROPTICAL PROPERTIES OF BENZOTHIADIAZOLE CARBON NANOHOOPS

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The development of chiral organic materials with a strong chiroptical response is crucial for advanced technologies such as circularly polarized luminescence (CPL), enantioselective sensing or security. [1] Chiral carbon nanohoops, known for their curved, cyclic structures offer a unique platform to achieve strong chiroptical properties with visible-light fluorescence and high quantum yields. [2]

However, the absence of clear design principles due to lacking structure–property relationships for these chiral emitters hinders the progress in the field. [3] To address this, we synthesized two chiral macrocycles, integrating a pseudo-meta [2.2]paracyclophane with planar chirality and a fluorescent benzothiadiazole unit. These macrocycles display red-shifted fluorescence with high fluorescence quantum yields, and large Stokes shifts and differ in the extent of π-electron conjugation. This enabled a systematic investigation of the role of exciton delocalization on chiroptical properties of carbon nanohoops. By combining steady-state spectroscopy with quantum chemical calculations, we uncovered a unique structure–property relationship, offering valuable insights for the design of materials with enhanced electronic circular dichroism or exceptional CPL brightness.

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LIGHT-RESPONSIVE FERROCENE MOLECULAR NANOHOOP

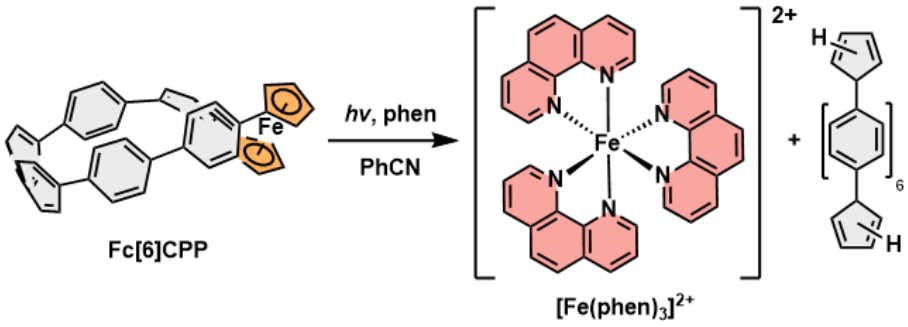
Remigiusz B. Kręcijasz[1], Juraj Malinčík[1], Simon Mathew[1], Peter Štacko[2*], Tomáš Šolomek[1*]

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Ferrocene-based macrocycles emerge as an interesting family of compounds with applications in molecular electronics,[1] redox-active systems[2] and host-guest chemistry.[3] In particular, [*n*]ferrocenophanes, wherein both cyclopentadienyl rings are bridged by a few atoms, exhibit a highly tilted ferrocene unit prone to dissociate the otherwise rock-stable Fe–Cp bond upon irradiation due to strain.[4] This allowed for unprecedented, photocontrolled access to novel functional polymers.[5] Moreover, similarly weakened Fe–Cp bond in ferrocenophanes may act as a mechanophore in mechano–responsive polymers.[6]

In this work, we induced strain to ferrocene by incorporating it into the backbone of highly strained [*n*]cycloparaphenylenes,[7] the shortest *(n,n)* armchair carbon nanotubes. Thereby, we obtained the first metallocene-based light-responsive carbon nanohoop that can release Fe^{2+} ions with spatial and temporal control triggered by benign blue or green light. The ferrocene nanohoop is over 1'000-fold more photoreactive than ferrocene itself and demonstrates how delicate strain control using the curved nanotube-derived nanohoop may impart reactivity to inert metallocenes. The newly designed metallamacrocycle open routes to develop new photocaged metal ion carriers, like ferritin, responsive, shape-adaptable supramolecular materials, or metallocene polymers.



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Acknowledgements

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SEMI-EMPIRICAL MD SIMULATIONS TO UNRAVEL GLYCOSYLATION REACTION MECHANISMS

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Synthetic oligosaccharides are indispensable tools in chemical glycobiology, to unravel and manipulate the role of these important biomolecules in biological processes. However, the synthesis of oligosaccharides is an arduous and labor-intensive process, requiring a significant amount of time-consuming trial-and-error to optimize the glycosylation reaction used to build the target oligosaccharide. Several reaction paths can be followed in the chemical union of two carbohydrate building blocks and these pathways determine the overall stereoselectivity of the glycosidic bond forming process.

In this research, front- and backside glycosylation reactions between a glucose donor and ethanol-derived acceptors with varying nucleophilicities have been investigated *in silico*. Density functional tight binding-based (GFN-xTB) molecular dynamics simulations have been performed to capture the full complexity of the reaction systems by including dynamical and solvent effects explicitly. Moreover, these simulations are combined with multiple replica metadynamics in order to accelerate the crossing of free energy barriers. Contrary to general expectations, we find that the front- and backside reaction paths are both viable for the systems under investigation, and show a similar free-energy activation barrier.

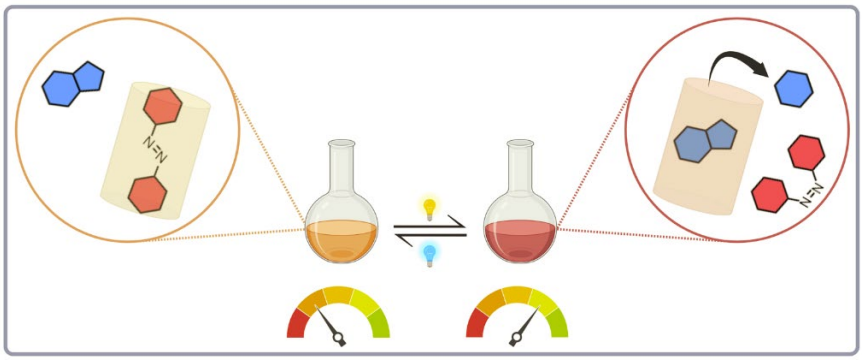
SUPRAMOLECULAR CONTROL OVER PILLARARENE-CATALYZED KEMP ELIMINATION WITH A PHOTORESPONSIVE INHIBITOR

Sabine G.H.A.V. Langens[1], Sander J. Wezenberg[1]

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Chemical transformations in biological systems are catalyzed in a highly efficient manner by enzymes, which are able to respond to environmental stimuli. Chemists have developed efficient and advanced artificial catalysts, however, little effort has been targeted towards controlling catalytic activity dynamically.[1] Nevertheless, dynamic control over catalysis is of high interest, for example, for tandem and relay catalysis. This dynamic control is typically achieved by introducing responsive motifs into catalyst backbones, which has drawbacks such as tedious synthesis and potential loss of catalytic function. This limits broader application. Competitive, non-covalent binding of a light-switchable inhibitor to regulate catalytic activity could offer a waste-free solution. Nevertheless, this concept has only been demonstrated successfully once for a specific organocatalyzed Michael addition in organic solvent.[2]

We present the regulation of pillar[5]arene catalytic activity by light-controlled binding of azobenzene-4,4-dicarboxylate in aqueous solutions. This system present a basis to modularize the design of non-covalent dynamic catalytic systems. Pillar[5]arene was previously shown to catalyze Kemp elimination reactions.[3] Here, we show that binding of the azobenzene (*E*)-isomer to pillar[5]arene blocks substrate binding and hence, diminishes catalytic conversion. UV-light irradiation yields the azobenzene (*Z*)-isomer, which results in its expulsion from the pillar[5]arene cavity. Consecutively, substrate binding is allowed, leading to accelerated conversion. Blue light irradiation can reinstate the inactive catalyst-azobenzene complex. Finally, we show that reversible control is achieved *in situ* over multiple irradiation cycles. We envision that our system can be implemented in chemical reaction networks and will assists in the development of tandem and relay catalytic processes.



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IN VIVO CONVERSION OF AZIDE-PROTECTED PRODRUGS

Annechien A. H. Laporte,[1] Tom Keijer,[2] Gabriel Forn-Cuní,[2] Dennis Aschmann,[1] Jianghua Liu,[1] Martina Färber,[3] Thijs van Schaik,[3] Leila Akkari,[3] Alexander Kros,[2] Joost N.H. Reek[1]

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Glioblastoma, one of the most aggressive forms of brain cancer, continues to have a dismal prognosis despite the standard treatment regimen of maximal surgical resection, temozolomide chemotherapy, and radiation therapy. Over the past three decades — despite substantial scientific efforts — there has been minimal improvement in patient outcomes. A critical hurdle in developing novel therapies is minimizing off-target effects while enhancing treatment selectivity. One promising approach involves the administration of prodrugs, followed by bioorthogonal activation at the tumor site. Although several bioorthogonal protecting groups have been identified, their stability and cleavage mechanisms in complex biological systems remain poorly understood. While azide-based protecting groups have shown promise *in vitro*, recent studies indicate that their metabolic stability *in vivo* is limited. Our current research focuses on evaluating the stability, toxicity, and cleavage behavior of various protecting groups, both *in vitro* and in animal models. Additionally, we are investigating how different cleavage mechanisms respond to physiological conditions, aiming to enhance the efficacy and precision of prodrug-based therapies.



Figure 2 Glioblastoma is characteristically challenging to treat as a low percentage of the total drug dose reaches the brain, leading to systemic toxicity. Selective activation of a prodrug at the site of interest (e.g., the brain) can lead to increased therapeutic doses while decreasing systemic toxicity.

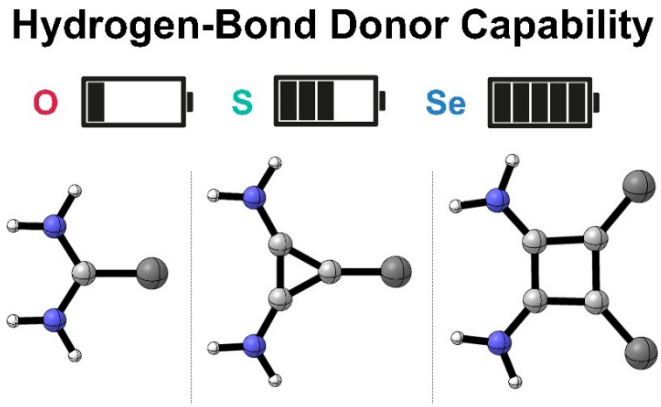
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EFFECT OF CHALCOGEN ATOM SIZE ON HYDROGEN BOND STRENGTH IN AMIDE-BASED LINEAR POLYMERS

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Supramolecular linear chains of urea, deltamide, and squaramide have the potential to form complex supramolecular structures due to their capability of forming hydrogen bonds[1], but what are the implications considering their sulfur and selenium analogues? Previous work with urea showed that substituting sulfur and selenium for oxygen leads to an unexpected increase in hydrogen-bond donor strength[2]. Our current work extends these insights to the supramolecular realm, utilizing dispersion-corrected density functional theory (ZORA-BLYP-D3(BJ)/TZ2P) to explore how these chalcogen substitutions influence hydrogen bonding in linear chains composed of urea, deltamide, and squaramide building blocks[3]. We reveal that as the chalcogen size increases, the larger chalcogen withdraws more charge from adjacent amino groups, amplifying the positive character of hydrogen donors and strengthening their interaction with negatively charged acceptors. This nuanced interplay of forces expands the toolkit for designing supramolecular assemblies with tailored properties.



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EFFECT OF STEPS AND OH ADSORBATES ON THE POTENTIAL OF ZERO CHARGE OF PT ELECTRODES

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Understanding the potential of zero charge (PZC) and the structure of stepped Pt/water interface is crucial for comprehending the reaction environment in realistic catalysis [1-2]. However, the values and even the trend of PZC changes with step density vary across different experimental techniques and computational methods. Moreover, spectroscopy and computational results indicate the presence of OH adsorbates at the step sites even in H adsorption region [3-4]. Therefore, it would be interesting to investigate how step density and OH adsorbates influence the PZC and double layer structures of stepped Pt electrodes.

In this poster, we discuss how ab initio molecular dynamics (AIMD) can be used to investigate the PZC and the structure of the stepped Pt/water interface. We found that an additional dipole forms at the step due to smoluchowski effect, decreasing the work function and PZC. OH adsorbates also form a dipole, which quenches the step dipole and increases the PZC. Water molecules act as a dielectric buffer, adsorbing and orienting according to the dipoles formed by the step and OH adsorbates.

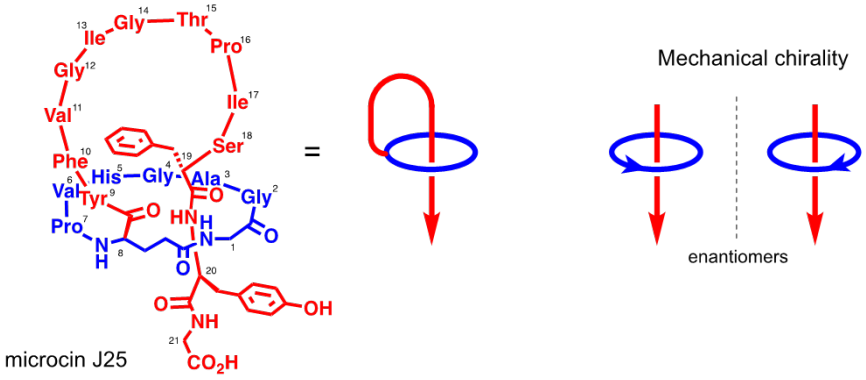
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DESIGN AND COVALENT SYNTHESIS OF MECHANICAL CHIRAL MOLECULES

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Mechanical chirality is a fascinating molecular physical property that is also found in the natural lasso peptides. This phenomenon appears when two achiral subcomponents incorporating directionality such as the amide bonds in a peptide chain become mechanical interlocked to give rotaxanes or catenanes. An example of mechanical chirality would be a rotaxane composing of an all glycine peptide macrocycle and a thread with two different stoppers. We aim at the stereoselective synthesis of mechanically chiral rotaxanes in order enable in the future the synthesis of optically active lasso peptide analogs.



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LABORATORY ASTROCHEMISTRY: ELECTRONIC PHOTOABSORPTION OF INTERSTELLAR OXYGENATED PAHS

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Polycyclic aromatic hydrocarbons (PAHs) are found everywhere in space and could contain up to 15% of the total carbon of the universe [1]. For this reason, they stand as potential candidates for being carrier of the observed UV-visible absorption lines in the InterStellar Medium (ISM), the Diffuse Interstellar Bands (DIBs) [2], which are mostly still unidentified. Within this context, our research seeks a deeper understanding of the electronic characteristics of PAHs, particularly when functionalized with oxygen(s). Our approach involves both an experimental and a theoretical study. Experiments are performed by using a high-resolution gas phase setup aiming to recreate the conditions that space telescopes might encounter in the ISM. The UV-visible absorption spectrum is probed to study the electronic behaviour of the oxygenated (O)PAH and is compared to Time-Dependent Density Functional Theory (TDDFT) calculations, aiming to correlate experimental spectra with theoretical models. Our specific focus on OPAHs not only aims to understand the influence of heteroatom(s) on PAH's electronic behaviour in the ISM, but also to gain insight into understanding the nature of DIB carriers.

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GRAPHITIC CARBON NITRIDE AS A PHOTOCATALYST FOR DECARBOXYLATIVE COUPLINGS VIA NICKEL CATALYSIS

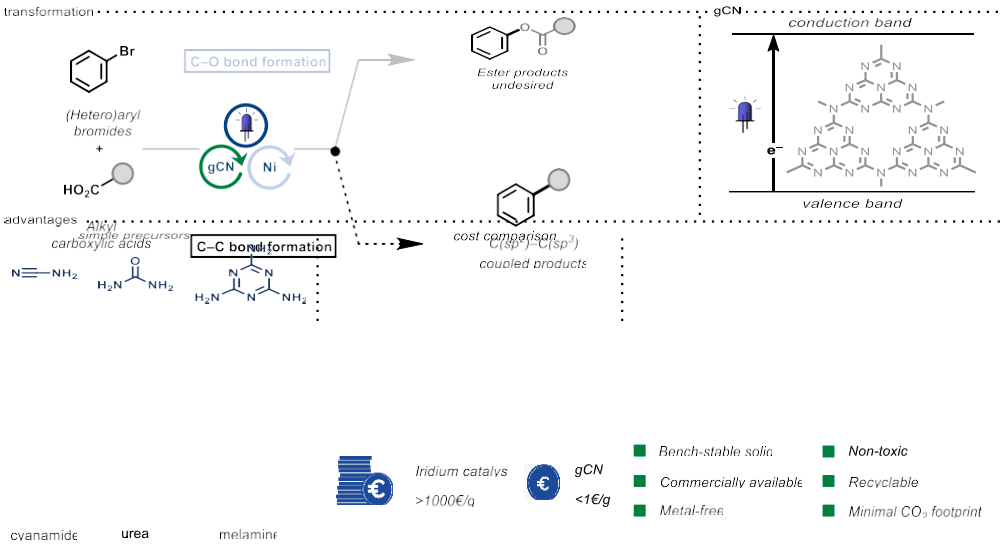
Florian Lukas[1], Michael T. Findlay[1], Timothy Noël[1]

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The development of robust and reliable methods for the construction of $C(sp^2)$-$C(sp^3)$ bonds is vital for accessing an increased array of structurally diverse scaffolds in drug discovery and development campaigns. While significant advances towards this goal have been achieved using metallaphotoredox chemistry, many of these methods utilise photocatalysts based on precious-metals, exploiting their efficient redox processes and tuneable properties.[1] However, due to the cost, scarcity, and toxicity of these metals, the search for suitable replacements should be a priority.[2]

We explored the use of commercially available heterogeneous semiconductor graphitic carbon nitride (gCN) as a photocatalyst, in combination with a nickel catalyst, for the cross-coupling between aryl halide and carboxylic acid coupling partners.[3] gCN has already been shown to engage in single-electron-transfer and energy-transfer processes for the formation of C–X bonds, and as part of a dual-catalytic system for the formation of C–O.[4]

In our work, we managed to overcome previous limitations to furnish C–C over C–O bonds using carboxylic acid coupling partners and explored a broad scope of both aryl halides and carboxylic acids, as well as α-keto acid coupling partners. It was demonstrated that gCN is easily recycled and drastically reduces Total Carbon Release (TCR) in comparison to procedures that rely on Iridium photocatalysts.



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TOPOLOGICAL π-SYSTEM BISTABILITY DETERMINES THE CHIROPTICAL PROPERTIES IN HELICENE CARBON NANOHOOPS

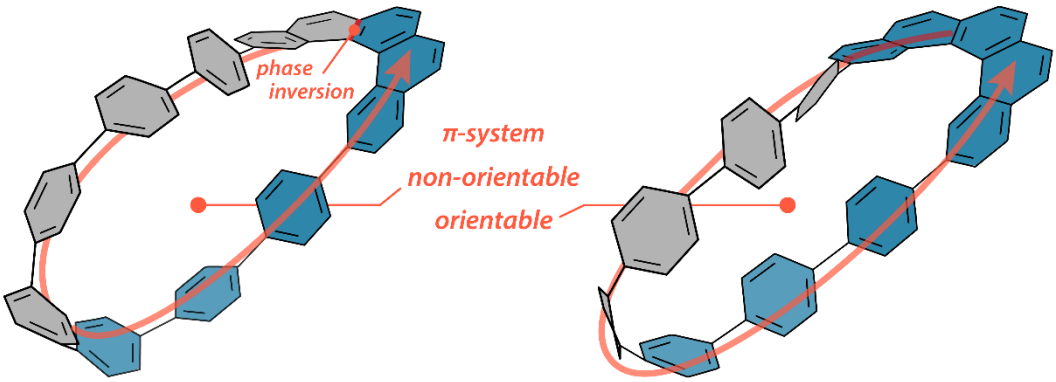
Juraj Malinčík[1], Carlos M. Cruz[2], Araceli G. Campaña[2], Tomáš Šolomek[1]

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A cyclic π-conjugated system with (4*n*+2) electrons can be aromatic or antiaromatic depending on its topology. In general, π-systems that can be mapped on an orientable surface follow classic Hückel aromaticity rules [1] while π-systems that can be mapped on a non-orientable surface, like a Möbius strip, follow Möbius aromaticity rules.[2] Such an antithetical outcome emerging from the π-system topology for an optical property is currently unknown.

In this contribution, we demonstrate for the first time that the topology of the molecular π-system in chiral helicene carbon nanohoops [3] significantly affects their interaction with circularly polarized light. This results in simultaneous emission of both right- and left-handed circularly polarized light at different wavelengths from a single enantiomer. Helicene carbon nanohoops adopt conformations that possess either an orientable or a non-orientable π-system which then determines the handedness of the emitted circularly polarized light. Therefore, the origin of this phenomenon is the topological bistability of the π-system. Furthermore, the bistability can be controlled by molecular strain allowing to turn one of the emissions off. Our work is the first to show that the topological bistability of π-electron system can determine the chiroptical properties.



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TECHNO-ECONOMIC ASSESSMENT OF HYDROTHERMAL LIQUEFACTION OF MIXED PLASTIC WASTE

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Catalysis Engineering, Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands

United Nations Sustainable Development Goals (SDGs) 7, 11, 12 and 13 deal with responsible consumption of materials for a better livelihood [1]. However, plastic production and its management have become a concern in the past few decades causing serious ecological and human health problems. In the last 70 years, plastic waste generation has increased by 225 times [2]. Polyolefins (a type of plastics) contribute to almost one-half of plastic waste production and because of high chemical stability, it remain in the environment for centuries. Thermo-chemical recycling of plastic waste has the potential to depolymerize plastics into chemicals/materials including monomers and fuel molecules [3-5]. Therefore, in this study, hydrothermal liquefaction (HTL) of mixed plastic waste is considered for the production of high-grade gas and oil. The techno-economic assessment of HTL using mixed plastic waste is performed for technical and economic feasibility, within the framework of the Horizon Europe project, Plastice (https://plastice.eu/). Accordingly, the energy efficiency (η_{energy}) and cost of oil production (COO) are estimated for the overall process.

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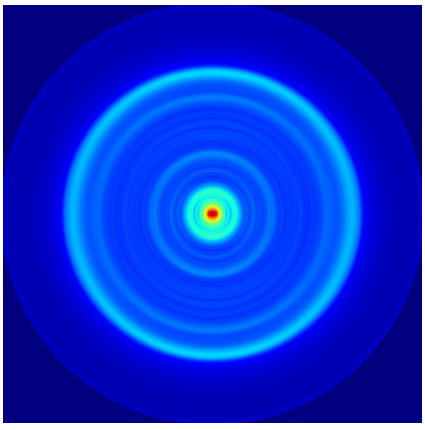
HIGH-RESOLUTION SPECTROSCOPY IN FREQUENCY AND TIME DOMAINS OF NOVEL NATURE-BASED PHOTOTHERMAL MATERIALS

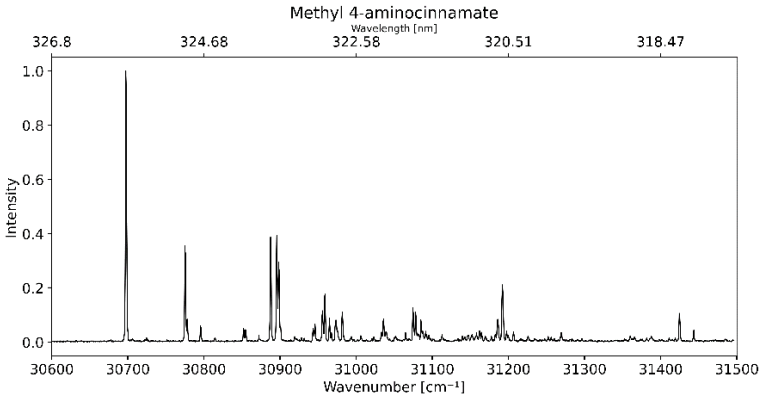
Hugo Maurer[1], Wim Roeterdink[1], Wybren Jan Buma[1]

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Photothermal compounds are molecules that efficiently convert light into heat. They are employed in a wide range of applications ranging from sunscreens in health care to crop boosters in agriculture. As far as their use sunscreens is concerned, there is currently a steeply increasing concern related to their impact on health[1] and environment.[2] Here, we report a spectroscopic study of methyl para/ortho-amino-cinnamate, a novel nature-inspired system that features favourable photochemical and photophysical properties for such applications.

These studies start with high-resolution gas phase spectroscopic studies including Resonance Enhanced Multiphoton Ionization (REMPI), pump-probe and high-resolution electron Velocity Map Imaging (VMI) spectroscopies that provide a detailed characterization of the spectroscopy and decay dynamics of the isolated molecule. Para- and ortho-substituted amino-cinnamates have been investigated, revealing a surprising difference in their spectroscopic properties. All the experimental results have been backed up by state-of-the-art theoretical quantum calculations.





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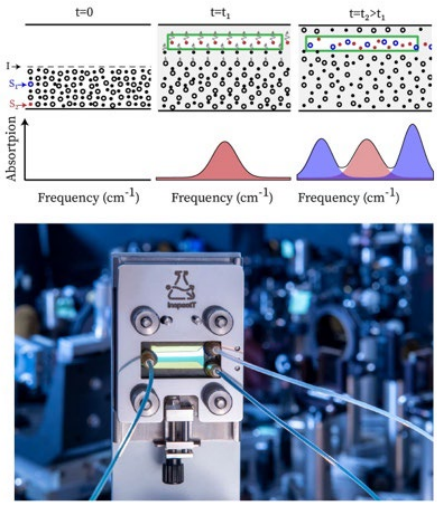
IR-DOSY (INFRARED- DIFFUSION ORDERED SPECTROSCOPY): ADDING THE SIZE DIMENSION TO SPECTROSCOPY

Carolyn J. Moll[1], Giulia Giubertoni[1] , Sander Woutersen[1]

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Characterizing the size and the chemical structure of molecules and particles is essential in many research fields, including chemical synthesis, and quality control in pharmaceutical companies. Infrared (IR) spectroscopy is widely used as an analytical tool for chemical analysis due to its affordability and wide applicability. While IR spectroscopy provides information about the chemical structure of molecules, it lacks information about the size. Inspired by Nuclear Magnetic Resonance Diffusion-Ordered Spectroscopy (NMR-DOSY), which relies on the Stokes–Einstein relation that links the molecule's diffusion coefficient with its size, we have invented IR Diffusion-Ordered Spectroscopy (IR-DOSY).

Using this technology, we can simultaneously characterize the molecular structure and the size of molecules and particles, thus adding another dimension to traditional one-dimensional infrared spectroscopy. The combined IR-frequency and diffusion-coefficient sensitivity is achieved by creating a concentration gradient within a newly developed sample cell, and tracking its equilibration in an IR-frequency resolved manner. From the acquired data a two-dimensional IR-DOSY spectrum can be constructed that has the IR-frequency on one axis and the diffusion coefficient (or equivalently, size) on the other axis. The IR-DOSY sample-cell can be easily integrated in any IR-spectrometer, transforming it into a size-sensitive tool.



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A SUPRAMOLECULAR APPROACH OF UTILIZING NAPHTHALENE MONOIMIDES IN (ENANTIO)SELECTIVE CATALYSIS OF DIBENZOHYDROFURANS AND INDOLINES

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Dibenzohydrofurans and indolines are classes of molecules that are widely present in pharmaceuticals. Current synthetic pathways involve either a multistep Diels-Alder reaction or reduction with H_2 from benzofuran or indole, requiring harsh conditions and precious transition metals.[1,2] An additional synthetic pathway is single electron reduction of the *ortho*-halide allyl phenol ether or allylaniline, which is followed by 5-*exo*-*trig* ring closure and hydrogen atom transfer (Figure 1). Involving a radical mechanism, this pathway has been demonstrated by electrochemically mediated photoredox catalysis under mild conditions.[3,4] Drawbacks however are that high reduction potentials are required due to the electron donation nature of the allyloxy/allylamine function, and that enantioselectivity remains a challenge in electro- and photoredox catalysis.

In the last decade, polycyclic aromatic heterocycles (PAC), such as naphthalene monoimide (NMI), have gained a lot of interest in photoredox chemistry. While the neutral species of NMI only absorbs light in the UV region, the singly and doubly reduced feature a red-shifted λ_{max} to the visible region. Both species exhibit good luminescent lifetimes and high excited state reduction potentials, making them suitable candidates for visible light photoredox catalysis.[5-7] We explore the potential of introducing NMI in a supramolecular, chiral moiety, to achieve the required reduction potentials while inducing enantioselectivity on the reaction.

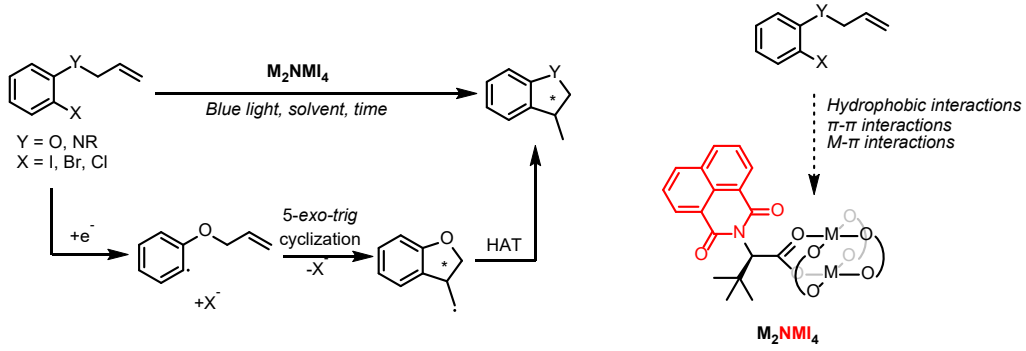


Figure 1. Showing reaction and structure of the NMI catalyst.

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BIOREFINING HARDWOOD WOOD CHIPS TO FDCA

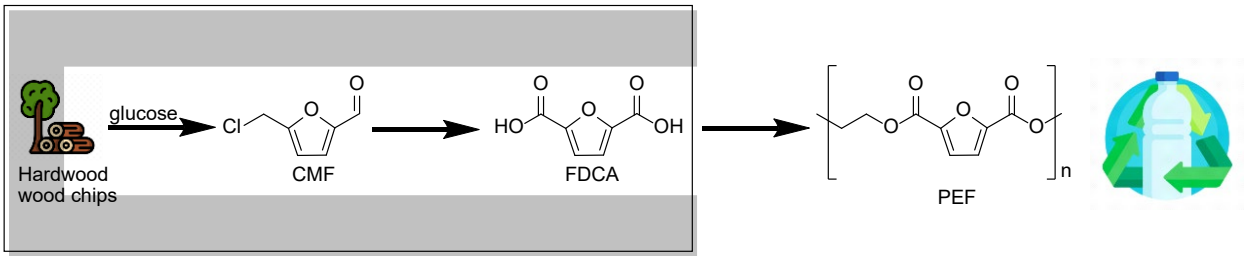
Vasileios Papadopoulos[1,2], Jorge Bueno Morón[1,2], Gerard van Klink[1,2], Gert-Jan Gruter[1,2]

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The ever-growing use of plastics and their participation in environmental pollution demand drastic change.[1] Avantium and the Industrial Sustainable Chemistry group at the UvA, pioneers in Renewable Chemistry, are actively contributing towards this direction. Avantium is currently constructing the world's first 2,5-furandicarboxylic acid (FDCA) plant in Delfzijl, the Netherlands, by converting high-fructose syrup to 5-methoxymethylfurfural (MMF), followed by oxidation to FDCA and purification. FDCA is the key monomer of poly(ethylene furanoate) (PEF), a 100% plant-based polymer with superior barrier priorities to poly(ethylene terephthalate) (PET). Regarding its recyclability, the same polyester hydrolysis principles that are currently used for PET can be successfully applied.

Upgrading this technology to non-edible feedstocks demands an alternative procedure. 5-Chloromethylfurfural (CMF), which can be derived from lignocellulosic biomass, can provide a new approach. Avantium's DAWN™ and YUKON technologies enable the hydrolysis of lignocellulosic biomass, specifically hardwood wood chips, into monomeric C_5 and C_6 sugars. These sugars can subsequently be converted into furfural and CMF, respectively, in a thermochemical manner.[2] After separation of these two components, CMF can be converted either to MMF, utilized in FDCA production, alternative intermediates or directly oxidised into FDCA.[3] This concept can be extended to alternative feedstocks, such as the cellulosic fraction of textile waste, cleaning wipes or cigarette filters, diminishing the requirement of separation because of the absence of C_5 sugars.[4] Preliminary results of hardwood transformations to FDCA will be presented.



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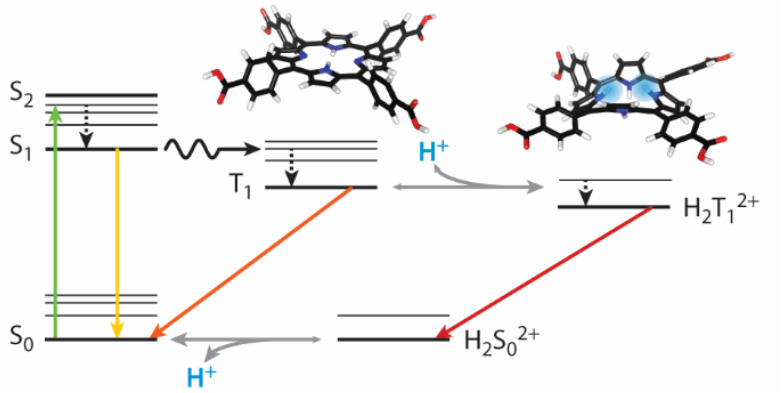
PORPHYRINS ON ACID: KINETICS OF THE PHOTOINDUCED-PROTONATION

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Free-base porphyrins can be protonated, which significantly impacts their electronic and excited state properties. While excited state dynamics are well explored for either neutral or fully protonated porphyrins, the intermediate region has not yet been explored, although their potential implications for photocatalytic reactions are evident. This study explores how partial protonation affects the nature and properties of photoexcited states of tetrakis(4-carboxyphenyl)porphyrin (TCPP) using steady-state and nanosecond transient absorption spectroscopy. Global-fit analysis of the decay curves revealed the formation of a protonated excited triplet state from the neutral triplet state, as well as the long lifetimes of these species of up to 120 µs. The photoexcited triplet state of TCPP functions as a photobase, which was confirmed by computational analysis of the electron density of the exited states showing increased nucleophilicity at the unprotonated nitrogen atoms of the porphyrin core. These findings indicate that photoinduced protonated excited triplet states can function as electron acceptors with anodically shifted redox potentials, opening new pathways for porphyrin-based photoreactions.[1]



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REVERSE WATER GAS SHIFT REACTION OVER ACTIVE, STABLE METAL-FREE BOROPHENE OXIDE CATALYST

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Two dimensional and layered materials are receiving increased attention nowadays in several fields including catalysis. We have recently shown that MAX phases and MXenes exhibit interesting catalytic properties in oxidative dehydrogenation and CO_2 conversion. Following these, we have recently started studying boron-based layered and two-dimensional materials including borophene. Several theoretical calculations have shown that borophene, with numerous active sites and pronounced electron deficiency, can act as a superior catalyst for CO_2 reduction reactions, reduction of dinitrogen, hydrogen evolution reactions and many more[2]. Additionally, borophene's low dimension makes it easier to redistribute its electron density to perform as a catalyst or a support in various reactions. However, there are very few experimental realizations yet, due to (i) the lack of facile, low-cost and efficient synthetic methods and (ii) stability issues associated with free standing borophenes. Therefore, we aimed at developing a simple and novel route to stable borophene or its derivatives, including borophene oxide (BO, oxidised borophene) and borophanes (BH, reduced borophene)[3]. After several attempts, thin sheets of boron-containing materials with surface -ONa/-OK groups were prepared *via* the stepwise heating of borohydrides ($NaBH_4$/ KBH_4) in presence of potassium formate under different conditions[3]. Further, we tested them as catalysts in Reverse Water Gas Shift (RWGS) reaction for the conversion of CO_2 to CO. The results reveal an interesting structure sensitivity of the catalytic activity. While a high activity and selectivity towards CO was observed for a certain composition, other types of boron-structures were largely inactive. Details of catalyst synthesis, structure-activity correlation, insights on the mechanism and key active species of RWGS reaction will be presented.

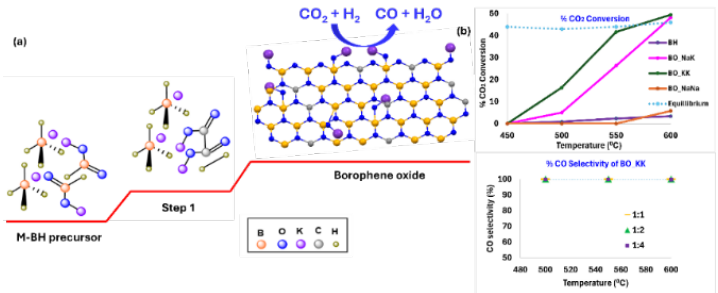


Figure 1: Schematic illustration of synthesis borophene oxide and its catalytic activity towards RWGS reaction; (b) results showing % CO2 conversion and % CO selectivity.

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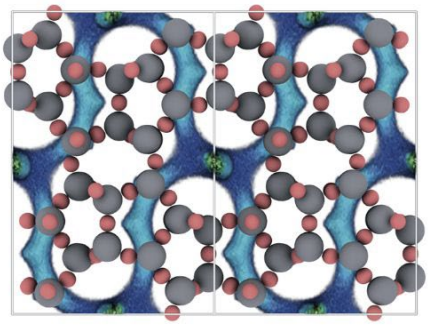
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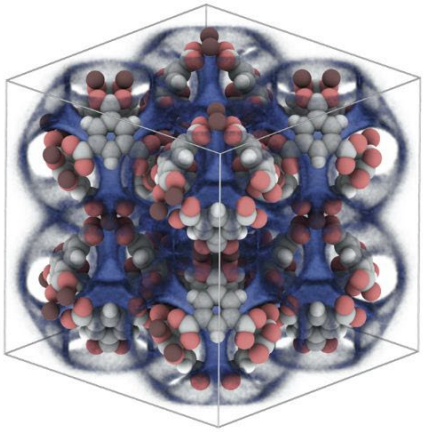
RASPA3: A MONTE CARLO CODE FOR COMPUTING ADSORPTION AND DIFFUSION IN NANOPOROUS MATERIALS AND THERMODYNAMICS PROPERTIES OF FLUIDS

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We present RASPA3, a molecular simulation code for computing adsorption and diffusion in nanoporous materials, and thermodynamic and transport properties of fluids.[1] It implements force field based classical Monte Carlo/Molecular Dynamics in various ensembles. In this article, we introduce the new additions and changes compared to RASPA2. RASPA3 is rewritten from the ground up in C++23 with speed and code readability in mind. Transition-Matrix Monte Carlo is added to compute the density of states and free energies. The Monte Carlo code for rigid molecules is based on quaternions and the atomic positions needed in the energy evaluation are re-created from the center of mass position and quaternion orientation. The expanded ensemble methodology for fractional molecules with a scaling parameter λ between 0 and 1 now also keeps track of analytic expressions of dU/dλ, allowing independently verification of the chemical potential using thermodynamic integration. The source code is freely available under the MIT license on GitHub. Using this code, we compare four Monte Carlo (MC) insertion/deletion techniques: unbiased Metropolis MC, Configurational-Bias Monte Carlo (CBMC), Continuous Fractional Component MC (CFCMC), and the CB/CFCMC technique. We compare particle distribution shapes, acceptance ratios, accuracy and speed of isotherm computation, enthalpies of adsorption, and chemical potentials, over a wide range of loadings and systems, for the grand canonical ensemble and for the Gibbs ensemble.





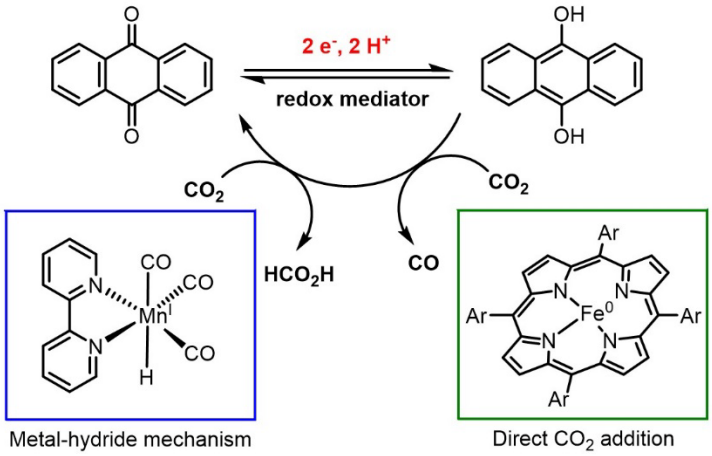
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IMPROVED ELECTROCATALYTIC CO2 REDUCTION BY MOLECULAR CATALYSTS THROUGH ANTHRAQUINONE REDOX MEDIATOR

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Homogeneous electrocatalysis is a continuously developing field that is very suitable for improving, controlling and understanding small molecule conversions. Amongst the environmentally relevant and simultaneously challenging conversions, the reduction of carbon dioxide to value-added chemicals is not yet applied at relevant scales. State-of-the-art systems lack in applicability, activity and stability. Inspired by nature, these electrocatalytic systems can be improved significantly by the addition of proton and electron transfer mediators.[1] The presence of these relatively simple molecules enhance the activity of electrocatalytic conversions by improving the proton and electron transfer to the intermediates in the catalytic cycle.[2] This work describes a simple, but elegant strategy to improve the CO_2 reduction reaction catalysed by two different molecular catalysts, namely an FeTPP-Cl and a $Mn(bpy)(CO)_3Br$ complex. Through the addition of organic, commercially available redox mediator anthraquinone, the catalysis is improved for these two system which operate via two distinct mechanisms. These results demonstrate the simplicity of bio-inspired catalysis and provide a starting point for further envisioned systems where catalyst and mediator are organized in even more efficient ways.



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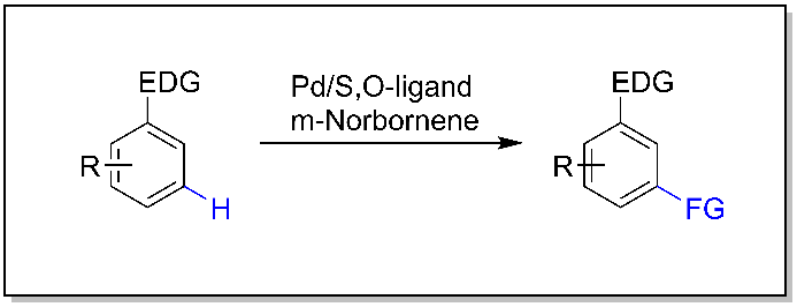
NON-DIRECTED META C–H FUNCTIONALIZATION OF ELECTRON RICH ARENES VIA PD/S,O-LIGAND/NORBORNENE COOPERATIVE CATALYSIS

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The direct C–H functionalization of aromatic substrates without the need for chelating directing groups could allow for the efficient synthesis of complex organic structures including a number of medicinally relevant compound. Using the palladium/S,O-ligand system developed in our group, it is possible to perform various functionalizations directed solely by the electronics of the substrate. By using a catalytic norbornene mediator together with the palladium/S,O-ligand system, the natural site selectivity of the C–H functionalization can be reversed and the electronically disfavoured meta position of electron rich arenes can be functionalized. This orthogonal site selectivity can provide a simple, one-step route towards the functionalization of positions that would otherwise be challenging to directly access.

Recently, our group has published an efficient method for the non-directed meta C-H arylation of aniline and anisole derivatives however, the introduction of other functionalities remains challenging. Here, we aim to expand the reaction scope of norbornene mediated meta C-H functionalizations.



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TOWARDS DFT STUDIES OF ENHANCED VCD SPECTRA

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Vibrational circular dichroism (VCD) spectroscopy is a powerful tool for the characterization of the absolute configuration and structural features of chiral molecules. The applicability of VCD is, however, limited by its low signal intensities, which are typically four to six orders of magnitude smaller than those of the infrared absorption itself [1].
The amplification of VCD intensities up to 2 orders of magnitude have been observed for metal complexes of transition metals such as Co(II) or Ni(II). The theoretical explanation of the observed phenomena was suggested by Nafie et al. based on vibronic coupling theory [2] and was attributed to the presence of low-lying electronic excited states [3]. However, as yet no calculations following Nafie formalism have been reported that reproduce the observed large enhancement and proper signs of the peaks.
In the present work we calculate the VCD enhancement as a correction to magnetic field perturbation theory (MFP) intensities following Nafie's approach [2]. We apply the approach to calculate the enhancement for sparteine complexes with Co(II) and Ni(II). We demonstrate that the density functionals overestimate the low-lying excited states of the complexes significantly, which hinders reproducing the enhanced VCD spectra. We show that multiconfigurational methods are required to properly describe the low-lying d-d transitions.
We introduce a practical approach which combines DFT calculations with separate optimization of significant state energies for interpreting the experimental spectra. Our combined approach allows to reach the spectra similarities of the calculated enhanced and experimental spectra to more than 50% and successfully reproduces the significant bands and features of the experimental spectra.

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RAMAN DIFFUSION ORDERED SPECTROSCOPY

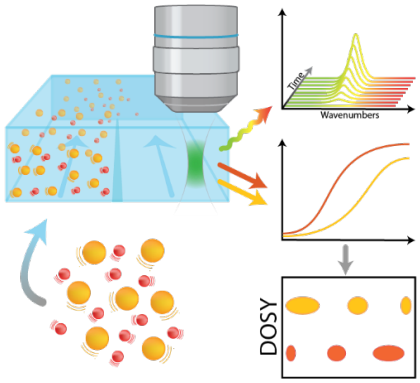
Robert W. Schmidt[1,2], Giulia Giubertoni[2], Federico Caporaletti[2], Paul Kolpakov[2], Noushine Shahidzadeh[2], Freek Ariese[1], Sander Woutersen[2]

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Size plays a pivotal role in chemistry, influencing various properties and behaviors of substances. Smaller molecules or particles often react more quickly due to their increased mobility and larger surface area relative to their volume. In nanomaterials, size can determine toxicity, as smaller particles can penetrate biological membranes more easily, potentially causing harm. Understanding these size-related effects is essential for predicting and controlling chemical reactions, leading to more effective and safer applications in various fields.
Raman spectroscopy is a label-free method that measures the vibrational modes of molecules, enabling the identification and characterization of the chemical composition and molecular structure of a sample. It primarily relies on lasers and spectrometer components, making it relatively inexpensive compared to other size-determining methods that require more complex and costly equipment, such as NMR, SEC, and SEM. However, Raman spectroscopy itself lacks the ability to measure the sizes of molecules or small particles.

Here, we present Raman diffusion-ordered spectroscopy (Raman-DOSY), a method to measure the diffusion of molecules in a liquid. The central component of the setup is a flow cell, where we measure the time it takes for molecules to diffuse from one side of the cell to the other. The arrival of the molecules is recorded spectrally by Raman spectroscopy, which simultaneously allows for the identification of the compounds and the estimation of the diffusion coefficient which can be correlated to the hydrodynamic radius of the compounds.



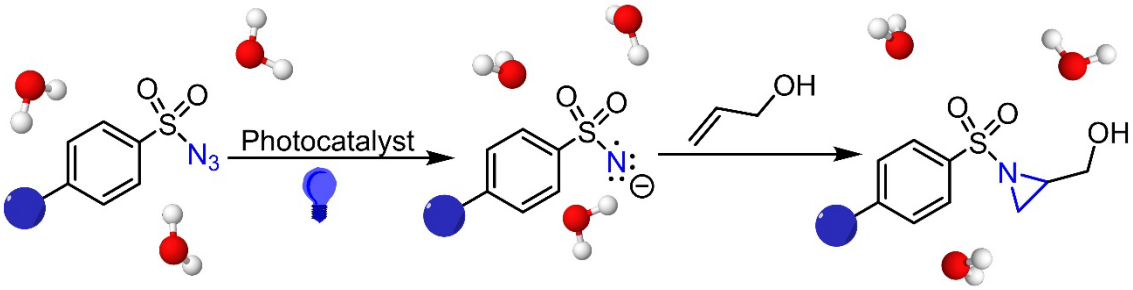
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NITRENE GENERATION FOR OLEFIN AZIRIDINATION UNDER AQUEOUS CONDITIONS

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Aziridines, which are three-membered heterocycles consisting of one nitrogen and two carbon atoms, have shown to be useful functional groups both in synthetic intermediates and biologically relevant molecules. Despite their broad applicability, the synthesis of these moieties is considered a challenge. Therefore, multiple photocatalytic aziridination methodologies have been developed over the past few years. In these reactions, nitrenes are generated by electron or energy transfer from a photosensitizer such as a cyanoarene[1,2] or ruthenium complex[3], to an organic azide or iminoiodinane. These methodologies have shown to be effective for the aziridination of a broad range of olefin substrates. However, due to their hydrophobic conditions these methodologies have shown to be less successful for polar substrates. To resolve this limitation, we designed a photocatalytic aziridination methodology under aqueous conditions. During this process, a range of sulfonyl azides and water soluble photosensitizers were screened, mainly focusing on achieving a high yield, catalytic efficiency and preventing the formation of a hydroxyamination product. This aqueous aziridination methodology may allow for the synthesis of complex, polar aziridines, in which multiple protection and deprotection steps can be avoided.



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ELECTROCATALYTIC C–H AMINATION FROM PRIMARY AMINES

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Metal nitrene transfer catalysis is an efficient method for the direct formation of C–N bonds, which is important for the pharmaceutical industry.[1] Currently, metal nitrene intermediates are formed from high-energy nitrene precursors, such as azides or iminoiodinanes (Figure 1, top). These nitrene precursors require additional synthetic steps, have an explosive nature, or generate halogenated waste. Moreover, the formation of C–N bonds via this methodology is limited by these specific nitrene precursors.

Therefore, our aim is to generate metal nitrene intermediates from primary amines using electrochemistry.[2,3] In this work, we present our recent findings in the electrocatalytic intramolecular C–H amination reaction from 4-phenylbutylamine (Figure 1, bottom), with the aid of a first-row transition metal catalyst. By using spectroscopic techniques, including electron paramagnetic resonance (EPR) spectroscopy, we postulate that the primary amine can be oxidized and further react to form the desired C–N bond. With this study, we demonstrate that primary amines can be used as a safer alternative nitrene precursor.

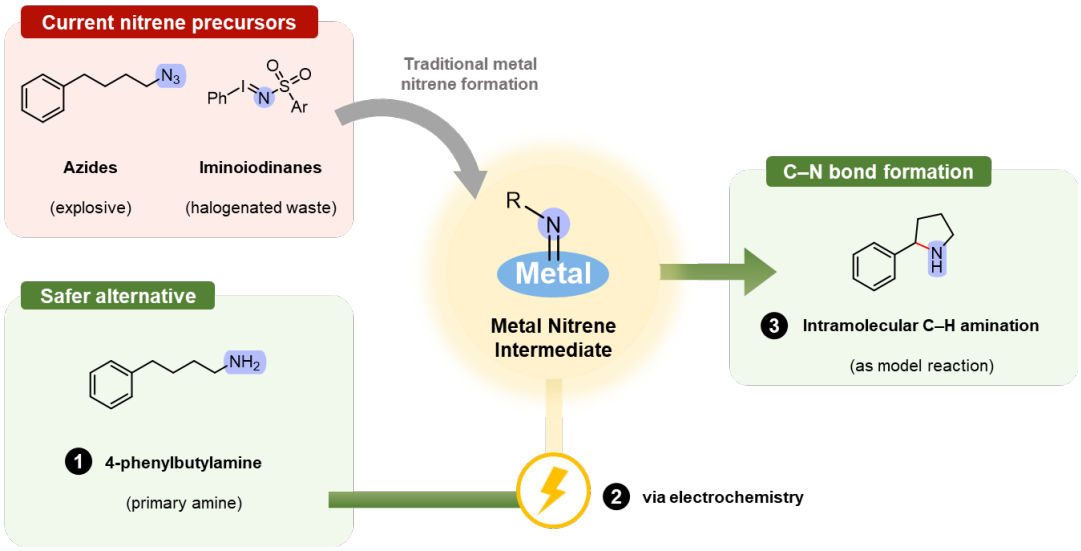


Figure 1. Schematic scheme of current nitrene precursors and the electrochemical C–H amination from 4-phenylbutylamine.

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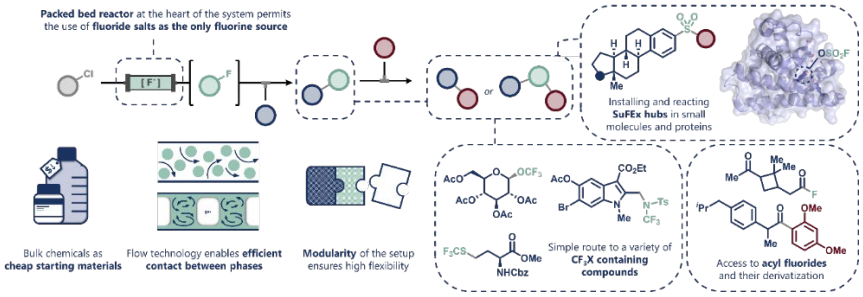
FLOW CHEMISTRY AS AN ENABLING TOOL FOR PFAS-FREE ACCESS TO FLUORINATED MOTIFS

Jelena Stanić[1], Timothy Noël[1]

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Fluorine is prized for introducing unique properties to molecules, making it ubiquitous in products from clothing and kitchenware to drugs and pesticides.[1] Unfortunately, many fluorinated compounds degrade into persistent per- or polyfluoroalkyl substances (PFAS), raising environmental concerns. While this led the EU to propose a ban on most PFAS, fluorinated drugs and agrochemicals will be out of its scope due to their high importance.[2] This makes finding alternatives for their synthesis, omitting the commonly used organofluorine reagents, one of the essential research challenges.

Fluoride salts are the most environmentally benign source of fluorine, entirely avoiding the use of PFAS-forming reagents. However, their poor nucleophilicity has long limited their synthetic potential. We envisioned that improving the contact between fluoride salts and the reagents could overcome that obstacle. This was accomplished by flowing the reagent solution through a packed bed reactor (PBR) containing alkali fluoride salt. This method provided access to the various CF_3-heteroatom building blocks[3], SuFEx hubs[4] and acyl fluorides[5] starting from bulk chemicals. The high modularity of the PBR allows easy handling of gaseous or moisture-sensitive intermediates, and flow technology ensures increased process safety and scalability. We believe our approach is a significant step forward in fluorine chemistry, providing an on-demand method for producing valuable fluorinated compounds.



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STEREOSELECTIVE ACCESS TO BICYCLIC SCAFFOLDS VIA ONE-POT CU-PD SEQUENTIAL CATALYSIS

Sebastian Strähler[1,2], Rens Clijnk[1], Anthony Kromodimedjo[1], Olivier Riant[2], Eelco Ruijter[1]

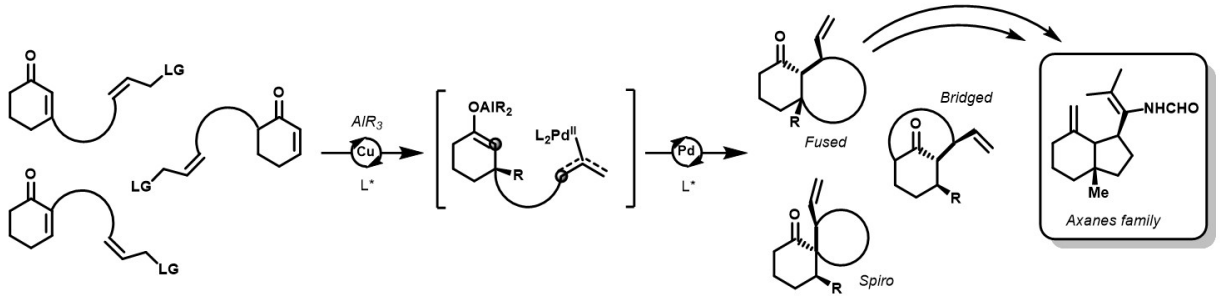
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One-pot sequential catalysis refers to catalytic transformations in which the catalysts for each step are added sequentially into the same reaction vessel. Each catalytic step produces an intermediate that serves as the substrate for the next one, allowing for the efficient formation of multiple bonds and stereogenic centers in one single synthetic operation, without the need for costly and tedious isolations of potentially unstable intermediates.[1,2]

Cu-catalyzed conjugate addition of nucleophiles to cyclic enones generates a metal enolate intermediate that can subsequently participate as a nucleophile in Pd-catalyzed asymmetric allylic alkylation.[3] While the amalgamation of these two independent reactions in an intermolecular fashion has already been reported, no example of an intramolecular version has yet been developed.[4–6]

Our strategy is based on the enantioselective Cu-catalyzed conjugate addition of organoaluminium reagents to cyclic enones bearing a tethered allylic group for subsequent intramolecular asymmetric Pd-catalyzed allylic alkylation. Depending on the position and the length of the tethered chain, bridged, fused, and spirocyclic scaffolds of different ring sizes can be obtained. Many of these bicyclic scaffolds being present in nature, the strategy could be applied to the synthesis of biologically active natural products such as axanes.[7]



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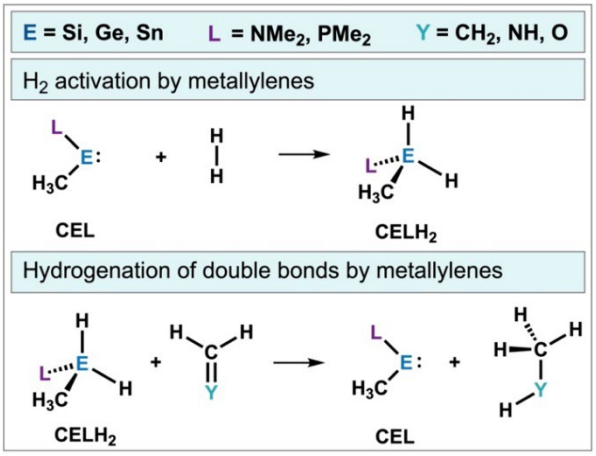
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RATIONAL DESIGN OF METALLYLENES FOR HYDROGENATION REACTIONS

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Heavier main-group elements have emerged in the past two decades as suitable alternatives to transition metals.[1] Main-group chemistry was originally considered to be limited by large energy gaps leading to weak interactions with small molecules, such as H_2. Transition metal complexes, by contrast, exhibit varied bonding due to their diverse electronic structure. However, it was recently shown that compounds with heavier main-group elements could mimic transition metal catalysts, for instance, the heavier analogue of carbenes known as metallylenes with larger Group 14 elements such as Si, Ge, and Sn. In our group, we have focussed on how metallylenes can activate H_2 and subsequently hydrogenate alkenes, alkynes, carbonyls, and imines.[2,3] We studied the effect of changing the main-group element and ligand of the metallylene (H_3C–E–L, CEL; E = Si, Ge, Sn and L = NMe_2, PMe_2) by using density functional theory. Our findings show that the activation of dihydrogen decreases from Si to Sn down Group 14, while the reactivity of hydrogenation with the activated species increases. These opposite trends stem from the weakening of the bonds between the hydrogen atoms and the Group 14 atom from Si to Sn. Changing the ligand from NMe_2 to PMe_2 also has opposite effects on H_2 activation and the following hydrogenation. We now understand why reactivity increases for H_2 activation from NMe_2 to PMe_2 while it decreases for hydrogenation. By combining our insights, we rationally designed an optimally tuned catalyst considering the overall catalytic cycle of metallylenes.



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BUILDING A TRANS HETEROLEPTIC RUTHENIUM(II) COMPLEX FOR SEQUENTIAL LIGAND PHOTOSUBSTITUTION

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Ligand photosubstitution by irradiation of a ruthenium(II) polypyridyl complex has been applied in photoactivated chemotherapy (PACT) to trigger the photorelease of biologically active compounds.[1] While the majority of PACT complexes photorelease a single ligand, incorporation of two different photolabile ligands may afford PACT compounds for combination therapy that can selectively and sequentially photorelease two different drugs from a single heteroleptic octahedral Ru(II) complex. To obtain such control over photosubstitution, *trans* ruthenium complexes are ideal as they allow using the *trans* effect in the excited triplet state to release two ligands using light of different wavelengths.

In this study we report a series of *trans* Ru(II) complexes $[Ru(MeL)(\mathbf{X})(\mathbf{Y})]^{2+}$ based on a tetrapyridyl scaffold MeL that coordinate the metal in the basal plane, thus leaving 2 trans axial positions for monodentate ligands **X** and **Y**. First, thermally stable homoleptic complexes (**X** = **Y**) were prepared and their photochemistry quantified under light irradiation with different colors demonstrating excitation wavelength dependency on the photosubstitution quantum efficiency. Using these results, we could prepare photochemically a heteroleptic *trans*-Ru(II) complex (**X** ≠ **Y**). Strikingly, this complex showed sequential photorelease of ligand **X** with red light, followed by ligand **Y** with green light. These results allowed us to establish the first quantitative description of the *trans* effect in the triplet excited state.

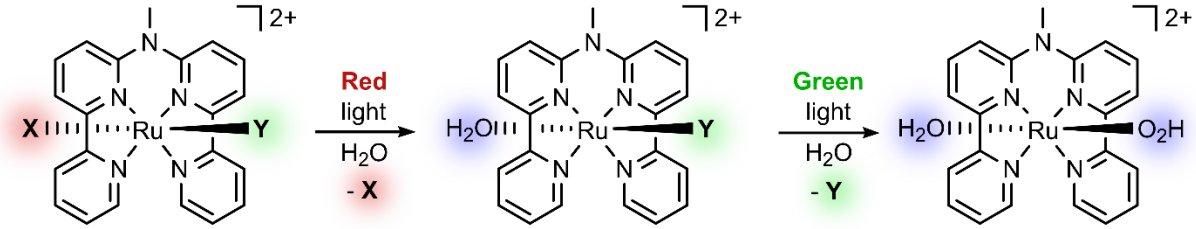


Figure 1: A *trans* heteroleptic ruthenium(II) polypyridyl complex which allows for sequential photosubstitutionof ligand **X** upon irradiation with red light, followed by ligand **Y** with green light.

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PHOTOCATALYTIC WATER SPLITTING OVER MOF-ON-MOF DERIVED HETEROSTRUCTURE

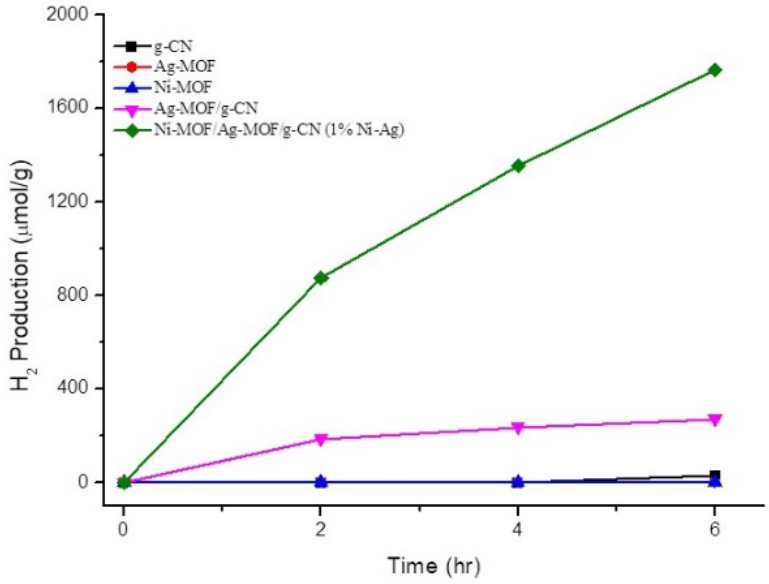
Pankaj Verma[1], Maartje van Rijn[2], Sonja Pullen[2], Jan van Maarseveen[3], Shiju N. Raveendran[1*]

Catalysis Engineering[1], Homogeneous, Supramolecular & Bio-inspired Catalysis[2] and Synthetic Organic Chemistry

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Given the finite nature of resources and the carbon emissions associated with fossil fuels, hydrogen generation via photocatalytic water splitting has emerged as a prominent solution to meet future energy demands[1]. Semiconductors, with suitable band gaps, play an important role in capturing and converting solar energy into valuable products such as hydrogen, carbohydrates, and methane[2]. Among these, graphitic carbon nitride (g-CN) is a commonly used semiconductor but the performance is hindered by limited light absorption and fast recombination of photogenerated electron-hole pairs.

To address these limitations, integrating g-CN with metal-organic frameworks[3] (MOFs) offers many possibilities, including extending the visible light response, suppressing electron-hole recombination, and enhancing hydrogen generation efficiency. We synthesized a MOF-on-MOF/g-CN based heterostructure aimed to improve photocatalytic water splitting activity in the visible range (440 nm). The synthesized Ni-MOF-on-Ag-MOF/g-CN heterostructure achieved a significant hydrogen generation of 1765 μmol g^{-1}, which is 61-fold compared to that of g-CN and 6.5-fold to that of Ag-MOF/g-CN. The results will be presented in detail at the HRMC symposium.



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THE METALLOPHILIC SELF-ASSEMBLY OF RED-SHIFTED CYCLOMETALATED PALLADIUM PHOTOSENSITIZERS

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Photodynamic therapy is a non-invasive and targeted way to treat tumors. Photosensitizers (PSs) have low dark cytotoxicity and good biosafety, and then show light cytotoxicity after light irradiation.[1] Cyclometalated palladium (Pd) PSs were reported that have excellent singlet oxygen or reactive oxygen species generation.[2] [3] The series of cyclometalated Pd(II) complexes with square planar structure can form nano aggregates in cell culture medium with fetal calf serum based on metallophilic interaction and pi-pi stacking. On one hand, the carrier-free nano PSs aggregates with good stability and proper size distribution are proven that have high cellular uptake and tumor therapy efficacy *in vitro* and *in vivo*.[3] On the other hand, the metallophilic interaction is also helpful to redshift the compounds absorption. However, the blue or green light absorption limits the light penetration depth and hinders the application of these compounds toward solid tumor treatment. Here, we introduce electron-withdrawing groups (EWGs) to the pyridine part of the ligand to lower the LUMO energy of the metal complex to red-shift. For example, the HOMO-LUMO energy gap reduces from PdLF (ΔE= -3.49 eV) to $PdLCF_3$ (ΔE= -3.30 eV). Besides, to improve the water solubility, triethylene glycol monoethyl ether (TEG) was introduced, $PdLCF_3TEG$ was obtained. $PdLCF_3TEG$ shows a very high photo index (PI > 240) with green light PDT for melanoma A375 cells, which largely improves the PDT efficacy of previous PdL (PI = 72).

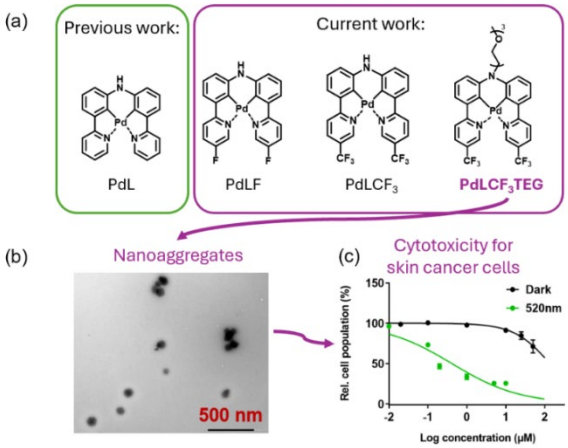


Figure. The molecular structures(a); and nano aggregates morphology by TEM (b) and the dark and light cytotoxicity results (520 nm, 8min, 13 J/cm^2) of $PdLCF_3TEG$ (c)

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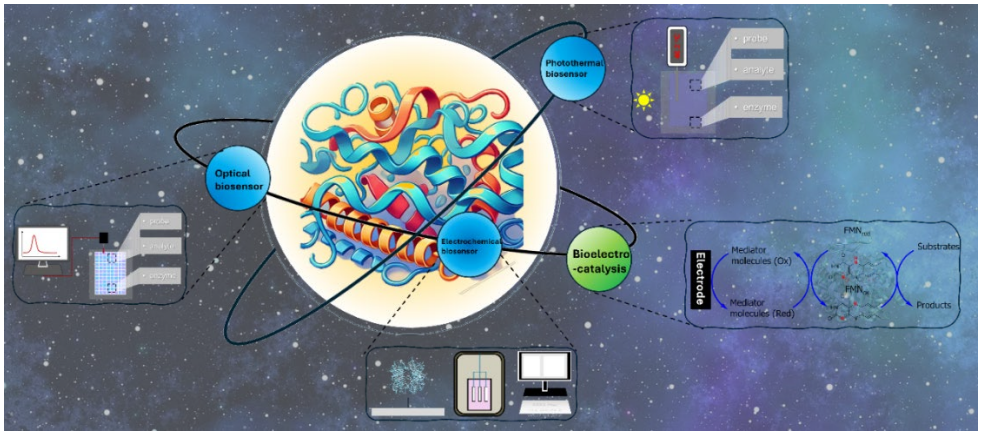
DESIGNING MULTIFUNCTIONAL ENZYMATIC DEVICES FOR BIOSENSING AND CHEMICAL CONVERSION

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Enzymes are ideal catalysts for performing sustainable and green chemical reactions because they operate in aqueous buffers under mild reaction conditions, display high catalytic efficiency as well as chemo-, regio-, and stereoselectivity, and are inherently biodegradable. A current trend is the combination of biocatalysis and electrochemistry to generate bio-electrochemical systems applicable to biosensing and chemical conversion. In particular, the exceptional substrate selectivity of some enzymes makes them an excellent choice for the construction of novel, highly sensitive, and selective biosensors. Therefore, in our group, we aim to leverage enzyme engineering to develop enzyme-based biosensors that are also stable and recyclable. Another ambitious objective is the development of integrated multi-signal enzymatic biosensors, which combine multiple measurements in a single device, such as optical, electrochemical, and photothermal readouts. This feature leads to a significant reduction in the false-negative/false-positive rates currently associated with disease diagnosis. We are exploring the use of different enzymes to develop a broad range of biosensors. Finally, we are investigating the potential of combining biocatalytic and electrochemical reactions to enhance the performance and applicability of biocatalysis in organic synthesis.



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ION-ASSISTED CO2ERR IN METAL PORPHYRIN CAGE: A DFT STUDY COMBINING STATIC AND DYNAMIC MODELLING

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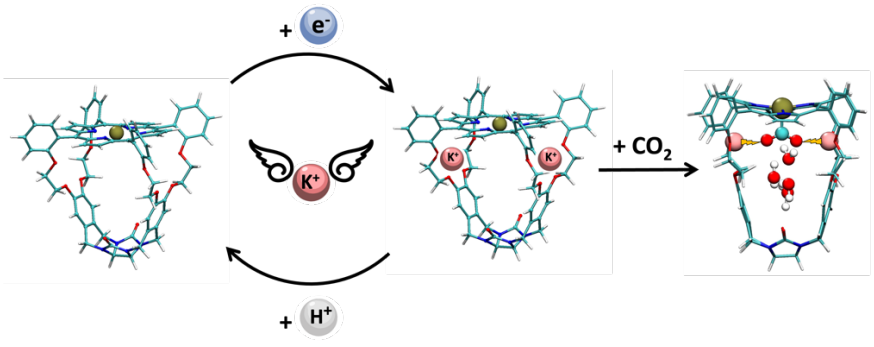
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A cage-embedded metal-porphyrin catalyst inspired by reaction pocket in enzymes, where CO_2-to-CO electroreduction is enhanced by hosting cations from electrolyte, is synthesized. Our DFT study combines static and dynamic modelling to investigate cation's promoting effects such as a lowered overpotential and an increased activity. Static theoretical calculation explores two possible pathways for electron transfer and CO_2 binding to cobalt-porphyrin cages, elucidating how cations impact catalyzed CO2ERR overpotential.

On the other hand, Ab initio molecular dynamics simulations were employed to demonstrate the behavior of cations and cage structural dynamics, incorporating the aqueous solvent by a micro-solvation along the catalytic cycle. Notably, MD simulation not only shows that the presence of potassium introduces an alternative cation direct assisted pathway during C-O scission, complementing the conventional proton-assisted pathway, but also reveals that its assistance to CO_2 reduction functions through a dynamical host-guest chemistry.



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