HRSMC

SYMPOSIUM 2022



Holland Research School of Molecular Chemistry

Address:
University of Amsterdam
Science Park 904
1098 XH Amsterdam
P.O. Box 94157
1090 GD Amsterdam
The Netherlands

Phone: +31 20 525 6956 / 6454
E-mail: hrsmc-science@uva.nl
Homepage: http://www.hrsmc.nl

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WELCOME

On behalf of the Holland Research School of Molecular Chemistry, I am very pleased to welcome you to this 2022 HRSMC symposium. At this symposium we extend a special welcome to Prof. Fernando P. Cossio (Universidad del País Vasco, Spain), who will give this year's guest lecture. We furthermore look forward to hear the lectures of our own HRSMC staff members 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'*. PhD students, postdocs and HRSMC staff members covering the three themes have been invited to give a lecture on their research.

For the fourteenth time, the *Dick Stufkens Prize* will be awarded for the best PhD thesis that appeared under the auspices of the HRSMC. The 2022 laureate is Dr. Tessel Bouwens. The prize will be presented by Prof. dr. E.J.J. (Edgar) Groenen, chairman of the Jury and member of the External Advisory Committee of the HRSMC. After the award ceremony, Dr. Bouwens will give a presentation of the work for which she has received the 2022 *Dick Stufkens Prize*.

Finally, I would like to draw your special attention to the poster sessions where PhD students and postdocs will present their research results and get to know those 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, and to establish new collaborations.

Also, on behalf of the Board, I wish you all an inspiring day!

Prof. dr. Wybren Jan Buma

PROGRAMME

08:15 Coffee/ tea & registration
08:55 Opening by Scientific Director – Prof. dr. W.J. (Wybren Jan) Buma
09:10 Prof. Fernando P. Cossío (Universidad del País Vasco, Spain)
"*From particle physics to supramolecular chemistry: Barium tagging in neutrinoless double-beta decay nuclear reactions*"

Session 1: HRSMC theme 1: 'Synthesis, Characterisation, Reactivity and Properties of Molecules'
Chair: Dr. F. (Francesco) Mutti (University of Amsterdam, The Netherlands)

10:00 Prof. dr. S.A. (Sylvestre) Bonnet (Leiden University, The Netherlands)
"Photocatalysis at lipid bilayers for solar fuels: a multidisciplinary approach"
10:30 Coffee/ tea & Postersession 1
11:20 Verena Sukowski (University of Amsterdam, The Netherlands)
"S,O-ligand promoted meta-C–H arylation of anisole derivatives via palladium/norbornene catalysis"
11:40 Eva J. Meeus (University of Amsterdam, The Netherlands)
"*Enantioselective epoxidation of aromatic olefins by a Co(TAML)-based artificial metalloenzyme*"

Session 2: HRSMC theme 2: 'Physical Chemistry and Spectroscopy'
Chair: Dr. Rik Mom (Leiden University, The Netherlands)

12:00 Dr. C. (Charusheela) Ramanan (VU Amsterdam, The Netherlands)
"*Competitive photophysical pathways in molecular chromphore systems"*
12:30 Lunch - Postersession 2 starts at 13:00
13:45 Elahe Motaee (Leiden University, The Netherlands)
"*Unraveling the Fischer-Tropsch reaction at the atomic level*"
14:05 Nipon Deka (Leiden University, The Netherlands)
"*Direct probing of near-surface cations during the oxygen evolution reaction using operando XAS*"

Session 3: HRSMC theme 3: 'Theoretical Chemistry'
Chair: Dr. K.J.H (Klaas) Giesbertz (VU Amsterdam, The Netherlands)

14:25 Dr. D. (David) Dubbeldam (University of Amsterdam, NL)
"*Multi-scale modeling of adsorptive separation devices*"
14:55 Coffee/ tea & Postersession 3
15:45 Voting for best poster in session 1, 2 and 3
15:50 Daniela Rodrigues Silva (VU Amsterdam, The Netherlands)
"*Nature and strength of lewis acid–base pairs*"
16:10 **Dick Stufkens Prize Award Ceremony**
Introduction by chair of the jury (Prof. dr. E.J.J. Groenen, Leiden University, The Netherlands)
16:20 Lecture Winner Dick Stufkens Prize 2022: Dr. Tessel Bouwens
"*Using supramolecular machinery to enhance the efficiency of photoelectrochemical cells*"
16:50 Poster Prize and Closure
17:00 Reception
18:00 End of symposium and start Staff dinner

ABSTRACT INVITED SPEAKER

(PROF. FERNANDO P. COSSÍO)

FROM PARTICLE PHYSICS TO SUPRAMOLECULAR CHEMISTRY: BARIUM TAGGING IN NEUTRINOLESS DOUBLE-BETA DECAY NUCLEAR REACTIONS

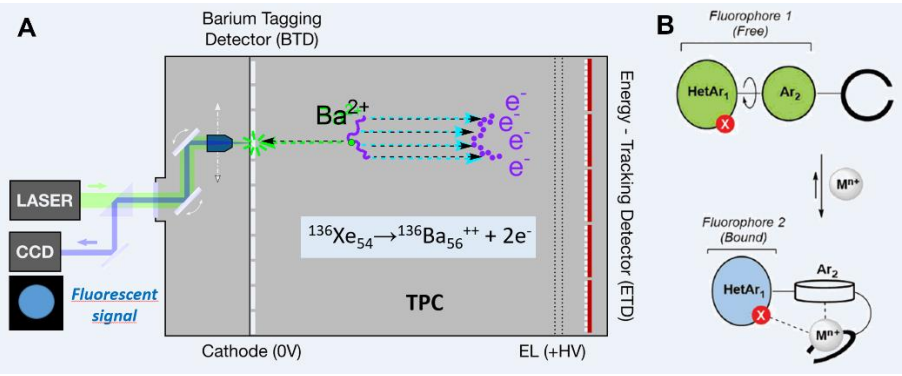
Fernando P. Cossío[1,2]

[1]Department of Organic Chemistry I and ORFEO-CINQA, University of the Basque Country (UPV/EHU), 20018 San Sebastian / Donostia, Spain University
[2]Donostia International Physics Center (DIPC), 20018 Sn Sebastian / Donostia, Spain

Neutrinoless double beta decay ($\beta\beta0\nu$) processes constitute a very promising method to find out whether neutrinos are they own antiparticles. Demonstrating this hypothesis would constitute a major discovery in physical sciences and cosmology. One useful $\beta\beta0\nu$ nuclear reaction involves the Xe-136 isotope and leads to the emission of two electrons, whose drift and energy can be monitored [1] in an ETD (Energy-Tracking Detector), together with a barium cation. Therefore, the second essential component of the TPC (Time Projection Chamber) to monitor this reaction is the BTD (Barium Tagging Detector).

The BTD must incorporate a fluorescent sensor [2] whose photophysical properties are adequate to distinguish the free and Ba^{2+}-bound states, thus giving rise to a bicolour fluorescent indicator (FBI) potentially useful for barium tagging [3]. The different emission spectra for the free and coordinated states stem from the decoupling between the aromatic components of the fluorophore upon barium coordination.

In this lecture, details about the design and chemical synthesis of FBIs, their photophysical properties and structure-activity relationships will be presented, with special emphasis on DFT and TD-DFT calculations that provide a rationale for the observed behaviour.



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ABSTRACTS OF STAFF LECTURES

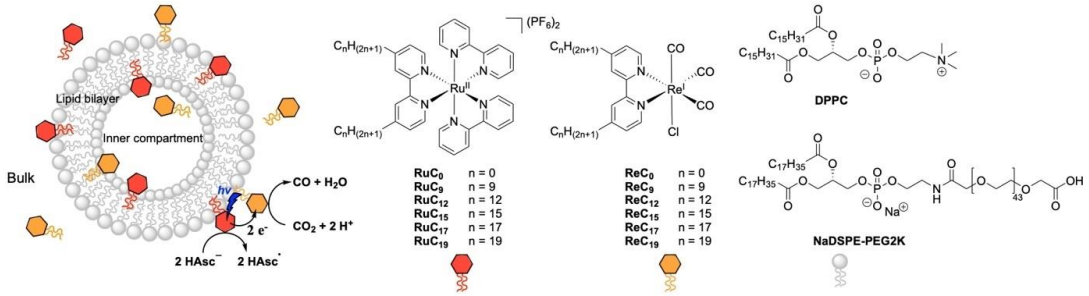
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PHOTOCATALYSIS AT LIPID BILAYERS FOR SOLAR FUELS: A MULTIDISCIPLINARY APPROACH

Sylvestre Bonnet[1]

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

Natural photosynthesis takes place at lipid bilayers. Although major progress has been achieved in understanding how it works, science is still unable to re-create an efficient, lipid-based photocatalytic membrane that can generate solar fuels. To understand what happens when a photocatalytic system is embedded in a membrane, a multidisciplinary approach is needed. First, photosensitizers and catalysts must be prepared that insert in the lipid bilayer at the right position. Second, these molecules need to be able to diffuse in the membrane and meet to exchange electrons or energy in the right direction. Finally, the rates of excited state generation, molecular collisions, and electron transfer, need to match, so that charge recombination is minimized and the photocatalysis works correctly. Understanding such intricate systems requires a multidisciplinary approach that is best provided by research networks such as the HRSMC and European networks. In this presentation, I will highlight a few of the recent progress made in my group on the making and understanding of photocatalytic liposomes that can generate solar fuel such as CO or H_2.



NWO is acknowledged for an HRSMC PhD fellowship to David Klein. This work was also supported by the EU FET Open programme project SoFiA (GAN 828838).

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COMPETITIVE PHOTOPHYSICAL PATHWAYS IN MOLECULAR CHROMPHORE SYSTEMS

Charusheela Ramanan[1,2]

[1]*LaserLaB Amsterdam, VU Amsterdam, Amsterdam, The Netherlands*
[2]*Max Planck Institute for Polymer Research, Mainz, Germany*

Molecular chromophores provide a broad range of possibilities for developing next-generation light-energy conversion applications. These π-conjugated materials exhibit high extinction coefficients, ease of synthetic tunability, and desirable semiconducting properties, which make them ideal for use in photovoltaics, solar fuel production, and energy storage. However, these materials exhibit complex potential energy landscapes and mixed electronic states. Photoactive processes such as light-harvesting, energy transport, and charge separation depends on factors such as structural disorder and intermolecular coupling interactions, which can furthermore be mediated by the environment. It is essential to understand the interplay between molecular structure and photophysical properties in order to design and optimize new materials for energy conversion applications.

Chromophore aggregation effects play a significant role in mediating competitive photophysical pathways and dynamics. Molecular chromophore systems aggregate via π-stacking interactions, leading to a mixture of Coulombic and charge-transfer couplings. Our work explores the relationship between interchromophore coupling and photophysical dynamics in a variety of systems, from the molecular scale to multichromophore assemblies, and also in optoelectronic devices.

MULTI-SCALE MODELING OF ADSORPTIVE SEPARATION DEVICES

David Dubbeldam[1]

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

The separation of mixtures, including enrichment, concentration, purification, refining and isolation are of extreme importance to chemists and chemical engineers. Pressure swing adsorption (PSA) is a non-cryogenic gas separation technology that achieves very high purity. Generally, the PSA process uses two or more adsorbent columns to avoid system downtime during the adsorption and desorption processes. The frequency of regeneration is an important parameter in the efficiency of the PSA unit and is a function of the adsorbent material, the selectivity, and operating conditions. Using molecular simulations, we efficiency screen possible nanoporous materials for their performance in PSA processes.

Using several levels of modeling (i.e., multi-scale modeling), we can accurately evaluate the efficiency of adsorptive separations. Using classical simulation techniques (i.e., Monte Carlo), we can compute adsorption isotherms for the crystalline nanoporous materials used in the adsorbent column. The next step/level, is to fit (using Genetic Algorithms), an isotherm model to the isotherm data. The isotherm model, and a model for the mixture adsorption, go into the higher-level modeling of the breakthrough apparatus. Hence, I will cover a wide variety of the techniques used at each level, and how they connect to each other. I will demo the modeling using computer codes.

ABSTRACTS OF PHD LECTURES

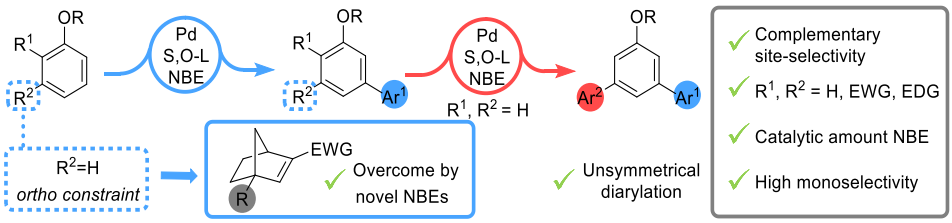
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S,O-Ligand Promoted meta-C–H Arylation of Anisole Derivatives via Palladium/Norbornene Catalysis

Verena Sukowski[1], Tati M. Ángeles Fernández-Ibáñez[1]

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

In the last decade metal-catalyzed C–H functionalization has become a powerful synthetic tool in organic synthesis since no prefunctionalization of the starting materials is required, leading to more sustainable and efficient methods. Nevertheless, the majority of the C–H functionalization reactions rely on the use of directing groups (DGs) to increase both the reactivity of the C–H bond and the selectivity of the process. An attractive alternative to the use of DGs is the use of ligands, allowing the direct functionalization of non-directed substrates. In this regard, we have discovered a new type of S,O-ligand, namely thioethercarboxylic acid, that enables palladium-catalyzed C–H olefination of simple arenes, thiophenes, anisole and aniline derivatives.[1] Using this catalytic system, high site-selectivity is typically observed for functionalization at the most electron rich position of the arene. Nevertheless, reversing the conventional site-selectivity, allowing for example the *meta*-functionalization of electron rich arenes, will have a tremendous impact in organic synthesis. One way to tackle this challenge is the use of palladium/ norbornene catalysis.[2] Here, we report a highly selective *meta*-arylation of a broad range of aryl ethers via Pd(S,O-ligand)/NBE cooperative catalysis. Insight in the mechanism is provided via isolation of palladium intermediates.



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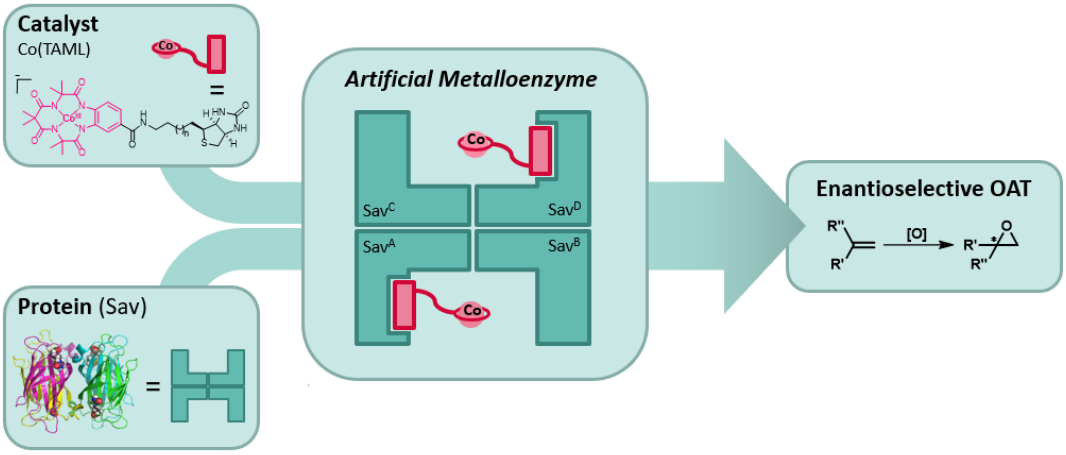
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ENANTIOSELECTIVE EPOXIDATION OF AROMATIC OLEFINS BY A CO(TAML)-BASED ARTIFICIAL METALLOENZYME

Eva J. Meeus[1], Nico V. Igareta[2], Iori Morita[2], Thomas R. Ward[2], Bas de Bruin[1], Joost N. H. Reek[1]

[1]Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands,
[2]Department of Chemistry, University of Basel, Switzerland

Second coordination sphere effects are crucial for the function of enzymes and hence laid the foundation for an intensive and thriving area of research devoted to catalysis in confined spaces. For instance, transition metal complexes can be placed inside synthetic cages to control their catalytic properties. Alternatively, encapsulation inside a protein also affords a well-defined secondary coordination sphere. The resulting artificial metalloenzyme offers means to optimize selectivity and activity towards a desired reaction. In this work, we incorporated a biotinylated Co(TAML)-complex (TAML = Tetra Amido Macrocyclic Ligand) into streptavidin (Sav) to assemble an artificial metalloenzyme, active in oxygen atom transfer (OAT) to aromatic olefins. After careful characterization of the host–guest system, initial screening of the Sav library – that included mutations at the positions Sav S112X and Sav K121X – demonstrated a positive effect on the selectivity, which is otherwise not achieved in absence of the protein. Hence, the Co(TAML)-catalyst proves amenable to the design and optimization of an artificial metalloenzyme active in enantioselective OAT, by means of the biotin-streptavidin technology.



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UNRAVELING THE FISCHER-TROPSCH REACTION AT THE ATOMIC LEVEL

Elahe Motaee[1], Irene M.N. Groot[1]

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

90% of all raw materials used today in the EU chemical industry are still of fossil origin. The energy transition, therefore, has far-stretching implications for chemical companies. The industry will need to replace its traditional energy sources with sustainable ones. This need is especially urgent in the Netherlands as it is striving to become CO_2-neutral by the year 2050. Therefore, finding technical solutions to decarbonize the chemical industry becomes more and more urgent.

The Fischer-Tropsch synthesis (FTS) process consists of multiple chemical reactions turning CO and H_2 into long-chain hydrocarbons that can be used as artificial fuels and chemicals. There are a variety of approaches to increase the yields of desired FTS products, e.g. by investigating active phases and sites, reaction mechanisms, and catalyst deactivation [1]. Active sites do not pre-exist but are constantly formed and consumed. The formation and abundance of active sites depend on the local chemical potential. Our approach is to acquire direct visualization at the atomic scale of the non-flat cobalt surface Co(10-12) during the reaction, mimicking industrially relevant conditions [2].

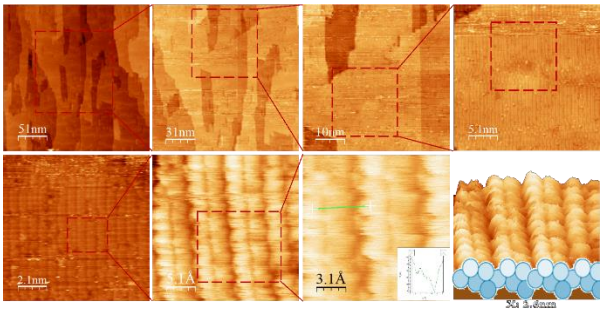


Figure 1: STM images of clean Co(10-12) showing the most stable surface termination, V_{bias}= -1 V, I_{tun}= 50- 100 pA

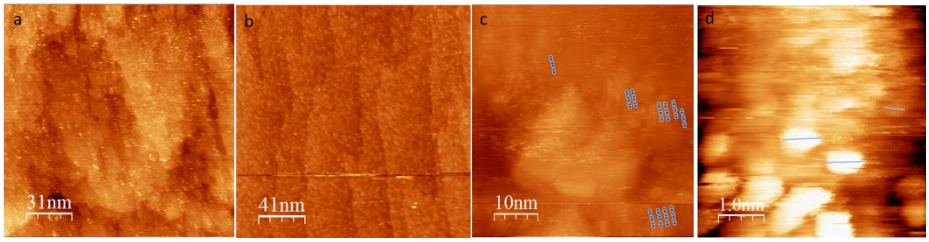


Figure 2: STM images of Co(10-12), (a) gradually forming cobalt oxide under H_2 at 220 °C, (b) spackle local roughening by molecular adsorbed CO, (c) linear feature growing on the surface under FTS reaction and (d) active steps sites on cobalt under FTS, V_{bias}= -1 V, I_{tun}= 50- 100 pA

References

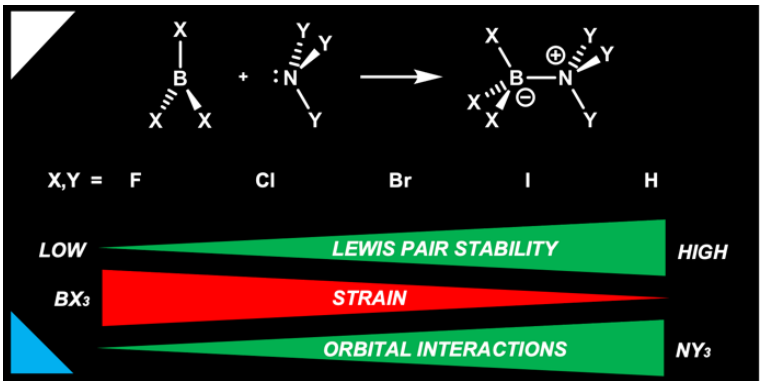
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NATURE AND STRENGTH OF LEWIS ACID–BASE PAIRS

Daniela Rodrigues Silva[1], Lucas de Azevedo Santos[1], Célia Fonseca Guerra[1], Trevor A. Hamlin[1]

[1]*Amsterdam Institute of Molecular and Life Sciences (AIMMS), Amsterdam Center for Multiscale Modeling (ACMM), VU Amsterdam, The Netherlands*

The fundamental concepts of Lewis acidity and basicity play a role in nearly all areas of chemistry.[1] Recently, our group has studied the most archetypal Lewis acid–base bonding of $X_3B{-}NY_3$.[2] Specifically, we evaluated the substituent effect on the Lewis acid and Lewis base by separately varying X, Y from H to F, Cl, Br, and I using the activation strain model and quantitative molecular orbital theory.[3] Unexpectedly, the bonding mechanism in the $X_3B{-}NH_3$ adducts is determined by the energy required to deform the BX_3 to the pyramidal geometry it adopts in the adduct. Thus, Lewis acids that can more easily pyramidalize form stronger bonds with Lewis bases. The decrease in the strain energy of pyramidalization going from BF_3 to BI_3 is directly caused by the weakening of the B–X bond strength, which stems primarily from the bonding in the plane of the molecule (s-like) and not in the p system, at variance with the currently accepted rationale. For the $H_3B{-}NY_3$ adducts, we show that the bonding trend is driven by the commonly accepted mechanism of donor–acceptor [HOMO(base)–LUMO(acid)] interaction. Our broad findings are relevant for chemists interested in synthesis, spectroscopy, and theory.



The support of the Netherlands Organization for Scientific Research (NWO) and the Brazilian agencies CNPq, CAPES, and FAPEMIG is gratefully acknowledged.

References

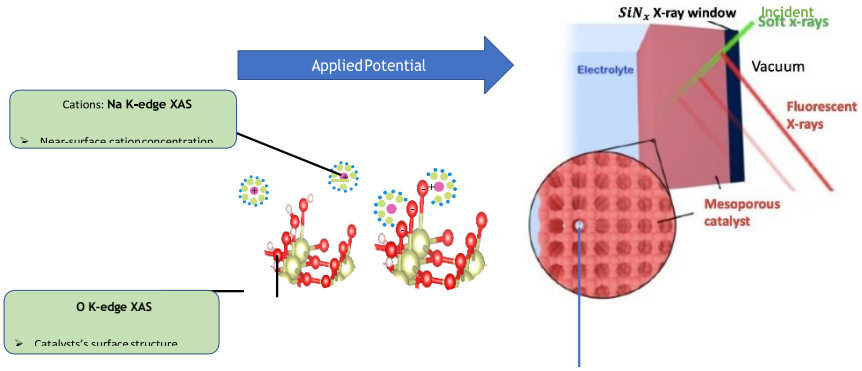
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DIRECT PROBING OF NEAR-SURFACE CATIONS DURING THE OXYGEN EVOLUTION REACTION USING OPERANDO XAS

Nipon Deka[1], Rik V. Mom[1]

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

Electrified solid-liquid interfaces are ubiquitous in technologies ranging from colloidal science to electrochemistry. Hence, an atomic-level characterization of the electrode-electrolyte interface is crucial for total control and optimization of the processes involved. While the electrode side of the interface has been quite extensively studied, the electrolyte side is comparatively poorly understood[1]. Specifically probing the near-surface electrolyte species during an electrochemical reaction is a major technical challenge in the field of catalysis and Surface chemistry. We have developed an interface-sensitive X-ray absorption spectroscopy (XAS) approach which allows us to directly probe the near-surface cations and anions of the electrolyte under applied potentials. In this approach, we employ a mesoporous electrocatalyst film coated on a $SiNx$ X-ray window. These mesoporous films exhibit an extremely high electrode- electrolyte interface area, enabling us to specifically probe the behavior of interfacial ions via their K-edge spectra. Using this approach, we have recently investigated the interaction of Na^+ cations with IrO_X during the oxygen evolution reaction (OER), which is a bottleneck in major electrochemical processes like green hydrogen production and CO_2 reduction. We used in-situ Na K-edge XAS to directly probe the concentration and coordination environment of the near-surface Na^+ cations. Simultaneously, in-situ O K-edge XAS monitored the interfacial water structure and the evolution of catalyst's surface structure. Contrary to expectations, we discovered that the positively charged Na^+ ions are drawn to the IrO_X surface by more positive potentials only at alkaline pH. This finding cannot be explained by any of the electrolyte theories[2] put up thus far, emphasizing the necessity of a detailed investigation of interfacial electrolyte structures.



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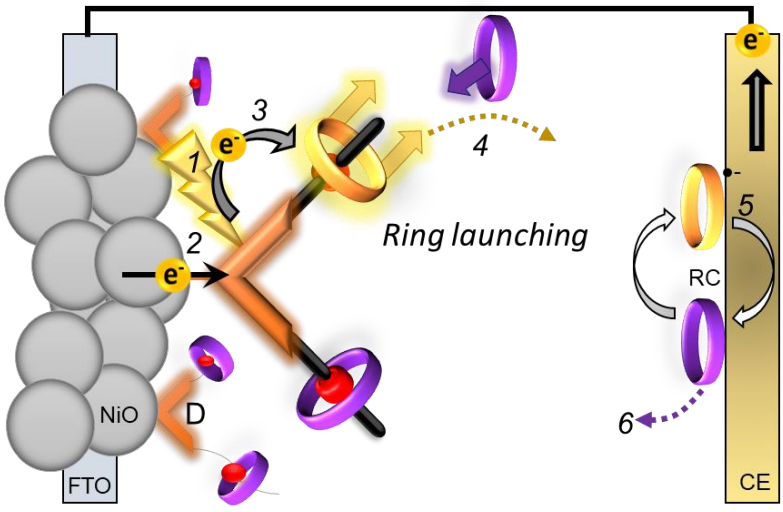
ABSTRACT WINNER DICK STUFKENS PRIZE 2022

USING SUPRAMOLECULAR MACHINERY TO ENHANCE THE EFFICIENCY OF PHOTOELECTROCHEMICAL CELLS

Tessel Bouwens

Yusuf Hamied Department of Chemistry, University of Cambridge, United Kingdom

The effects of global warming caused by the usage of fossil resources demand for a sustainable alternative. Inspired by nature's photosynthesis, scientist have developed devices, such as photoelectrochemical cells (PECs), that are able to use solar energy to generate electricity or solar fuels. However, PECs suffer from efficiency losses due to electron-hole recombination. Inspired by natural photosynthesis, we apply supramolecular machinery as a strategy to inhibit recombination through the organization of molecular components by making use of a (pseudo)rotaxane topology. Photoswitchable pseudorotaxanes are used to actively create a charge separated state by launching charged rings away from the surface that contain the holes. The PECs based on supramolecular machinery demonstrated a 16-fold and 5-fold increase in power conversion efficiency compared to devices featuring two control dyes that that do not facilitate pseudorotaxane formation. This bio-inspired approach to integrate supramolecular machinery in PECs demonstrates the impact of molecular organization on the performance of devices for solar conversion technologies.



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OVERVIEW POSTER SESSIONS

Session 1 10:30 – 11:20		
First name	Last name	Poster number
Valeriia	Andreeva	1
Suzanne	Assen	2
Lucas	de Azevedo Santos	3
Robert	van Bree	5
Emma	Caarls	7
Begum	Demirkurt	10
Hannah	Flerlage	13
Phebe	van Langevelde	19
Maximilian	Paradiz Dominguez	24
Cássia	Santana	29
Iuliia	Stroganova	32
Sjoerd	Verbeek	34
Lan	Wang	37

Session 2 13:00 – 13:45		
First name	Last name	Poster number
Timothy	Daas	8
Kezuan	Deng	11
Vladimir	Grigorescu	14
Brendan	Horst	15
Bas	Kreupeling	17
Martijn	Mekkering	20
Quynh	Nguyen	21
Celine	Nieuwland	22
Andre Nicolai	Petelski	25
Imogen	Robertson	27
Bauke	Smits	30
Wessel	Verbeet	35
Lars	van der Zee	38

Session 3 14:55 – 15:45		
First name	Last name	Poster number
Sjors	Bakels	4
Didjay	Bruggeman	6
Connor	Deacon-Price	9
Brian	Ferrari	12
Lukas	Hückmann	16
Pieter	Laan	18
Said	Ortega Rosales	23
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Thomas	Roose	28
Demi	Snabilié	31
Eveline	Tiekink	33
Rafaël	Vos	36

ABSTRACTS OF POSTERS

(IN ALPHABETICAL ORDER)

TURN-ON UPCONVERTED CALCIUM SENSOR

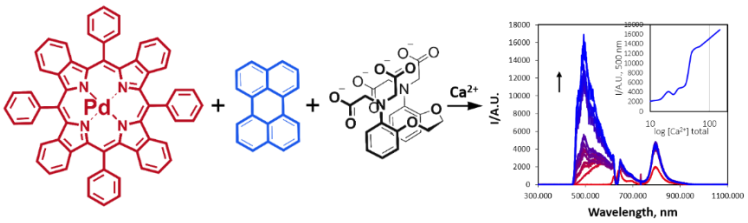
Valeriia D. Andreeva[1], Sylvestre Bonnet[1]

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

Calcium cation is one of the most popular analytes in biochemical studies because its concentration fluxes induce various processes in the body. Calcium sensors present on the market are sensitive and selective enough for this purpose but most of them work in blue and green light regions. That causes restrictions to the level of experiment complexity as green and blue light are not permeable through the tissue deep enough.

Recently, attempts to combine triplet-triplet annihilation upconversion (TTA-UC) with sensing towards Fe^{3+}[1], K^{+}[2] and Mg^{2+}[3] and other stimuli were published.[4]

Here we show calcium sensing via a triplet-triplet annihilation upconversion (TTA-UC) system. A classic TTA-UC couple[5] (PdTPTBP and perylene) was chosen as a reference system. Photo-induced electron transfer[6] (PET) based analyte recognition was introduced via chemical modification of the perylene annihilator. The modified annihilator showed calcium-dependent turn-on sensor behaviour both in water and in methanol. A combination of the annihilator with the porphyrine photosensitizer led to calcium-dependent upconversion emission.



Acknowledgements

This study was supported through LogicLab ITN, funded by the European Union's Horizon 2020 Research and Innovation Programme under Marie Sklodowska-Curie Grant Agreement 813920.

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AXIOMATIC DESIGN OF PEC CELLS FOR ETHYLENE PRODUCTION

Suzanne Assen[1], Agur Sevink[2], Huub de Groot[3]

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

Artificial photosynthesis of energy carriers and chemicals from abundant water and atmospheric CO_2 is one out of very few options to balance the supply of energy with the demand. A device that is able to use water, CO_2, and sunlight to make ethylene would help to store solar energy for long times. However, the light driven synthesis of fuel and chemicals has two critical hurdles, back reaction and recombination. We apply principles of axiomatic design (AD) to determine a rational path for the chemical engineering of complex photosynthetic device concepts for ethylene production. [1]

We find that for rational design, the OER and CO_2RR catalysts should be chosen first and the semiconductors that generate electron-hole pairs should be adjusted to these catalysts. In order to obtain the necessary potential and current to drive the oxygen evolution reaction and the CO_2 reduction reaction, tandem solar cells would be required to obtain solar to ethylene efficiencies over 1%.

By coupling solar cell and catalyst equations [2], the bandgaps of semiconductors pair can be determined based on the chosen catalysts, giving a design range for the solar absorbers. Using these equations, we can predict that for a specific CO_2RR catalyst with a peak specificity of ca. 60% for ethylene [3], the optimum combination of bandgaps of the solar absorbers would be at 1.9 eV and 1.35 eV, in order to arrive at a maximum production rate of ca 31.2 µmol/cm2/h or an overall solar to ethylene efficiency of ca 11.5%.

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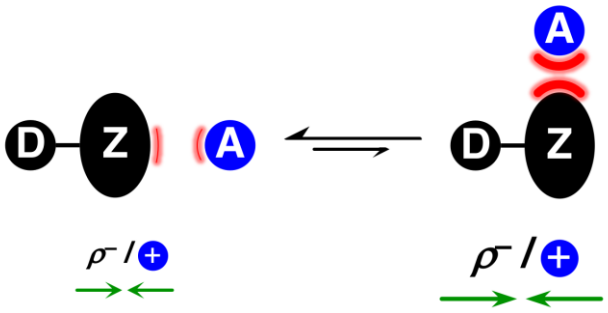
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INTERMOLECULAR COVALENT INTERACTIONS

Lucas de Azevedo Santos[1], Trevor A. Hamlin[2], F. Matthias Bickelhaupt[3]

[1]Amsterdam Institute of Molecular and Life Sciences, Amsterdam Center for Multiscale Modeling, VU Amsterdam, Amsterdam, The Netherlands

Pnictogen (PnB), chalcogen (ChB), halogen (XB), and hydrogen (HB) bonds are intermolecular interactions of the type $D_mZ\bullet\bullet\bullet A$, where Z = Pn, Ch, X, H (see figure below).[1] These intermolecular interactions play a crucial role in chemical reactivity, supramolecular materials, and drug design.[2] Typically, the s-hole model is invoked to rationalize the unexpected attraction between two partially negatively charged atoms and the geometry of these intermolecular interactions.[3] This model posits that the $D_mZ\bullet\bullet\bullet A$ complexes are bound and linear due to a Coulombic attraction between a positive electrostatic potential on the molecular surface of the bond donor (D_mZ) and the negative, point charge-like bond acceptor (A). We show how this treatment of atoms and molecules is oversimplified and unphysical. Not the Coulombic interactions, but the steric Pauli repulsion is the driving force preventing the bending of the bond acceptor away from D–Z•••A linearity. In fact, the Coulombic interactions favor (not oppose) bending. The cohesion in these interactions furthermore receives a major contribution from HOMO–LUMO orbital interactions. Therefore, we suggest abandoning the term non-covalent interactions for such bonds and instead using the designation intermolecular covalent interactions (ICI).



Acknowledgements

We thank the Netherlands Organization for Scientific Research (NWO) and the Brazilian agencies CAPES and FAPEMIG for financial support.

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HYPHENATION OF ION MOBILITY MASS SPECTROMETRY AND ACTION SPECTROSCOPY TO PROBE STRUCTURE AND KINETICS OF PEPTIDE AGGREGATION

Sjors Bakels[1], Steven Daly[2], Iuliia Stroganova[1], Agathe Depraz Depland[1], Melissa Baerenfanger[1], Berk Doğan[2], Jan Commandeur[2], Anouk M. Rijs[1]

[1]Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands
[2]MSVision, Almere, The Netherlands

A key physical process in the human body, the aggregation of peptides and proteins, is directly linked to age-related, neurodegenerative diseases, including Alzheimer´s and Parkinson´s Disease. Obtaining a full understanding of the early, neurotoxic steps of peptide aggregation is essential as this can lead to its control and prevention. However, this knowledge is obscured by a cascade of events occurring at various time and energy scales, producing complex and heterogenous mixtures of peptide aggregates. Therefore, we are developing a novel, multidimensional spectroscopy- and mass spectrometry-based method, that allows us to probe the structure and the kinetics of the initial steps of the aggregation process in a single measurement, see Figure 1.

This instrument, named the Photo-Synapt, involves the modification of a Waters Synapt G2 ion mobility – time-of-flight mass spectrometer, to allow for trapping and subsequent irradiation by UV or IR laser light of mass- and shape selected ions. In this way, we can measure an infrared spectrum from a selected, single species from the abovementioned complex mixture of aggregates. This will provide us with information on its secondary structure.

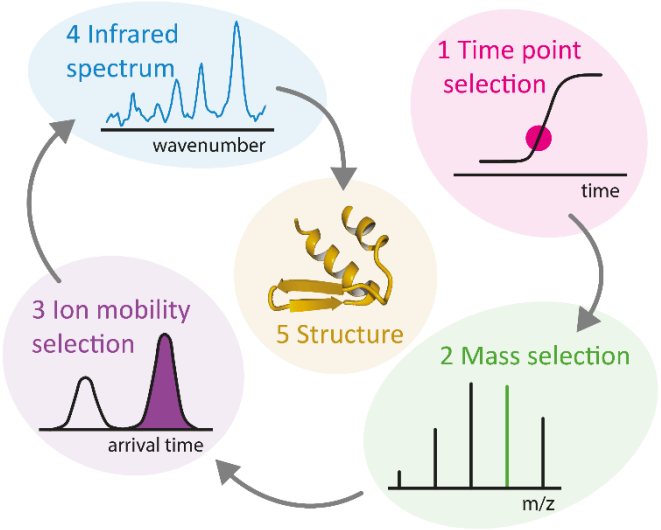


Figure 1: The 4D approach of the novel, multidimensional ion mobility mass spectrometer to probe the structure of peptide aggregates in a single experiment.

RESOLVING GGA-DFT FAILURE FOR MOLECULE METAL SYSTEMS.

Robert B. van Bree [1], Geert-Jan Kroes [1]

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

DFT at the GGA level is often considered the best compromise between feasibility and accuracy for reactions of molecules on metal surfaces. Recent work strongly suggests that specific reaction parameter (SRP) functionals based on GGA exchange are not able to describe gas-metal systems for which the work function of the metal surface (φ) minus the electron affinity of the molecule (EA) is less than 7 eV[1]. Systems with φ - EA < 7 eV exhibit an increased charge transfer from the metal to the molecule at the transition state (TS), increasing the delocalisation of the electron density. This enlarged delocalisation can cause GGA-DFT to underestimate the barrier height, similar to what has been observed for gas-phase reactions[1]. Examples of such systems are O2 + Al (111) and HCl + Au(111). The delocalisation problem was remedied in the gas-phase community by using hybrid functionals. However, even screened hybrid functionals are computationally expensive to use for metals. To resolve this, we attempted the use of the non-self-consistent field (NSCF) screened hybrid functionals. These functionals compute hybrid DFT energies based on SCF-GGA electronic densities. This poster presents results and progress on developing an NSCF HSE03-1/3x@RPBE PES for the O2 + Al(111) system and compares reaction probabilities to that of an SCF HSE03-1/3x PES[1], Embedded cluster calculations[2], and experimental reaction probabilities[3].

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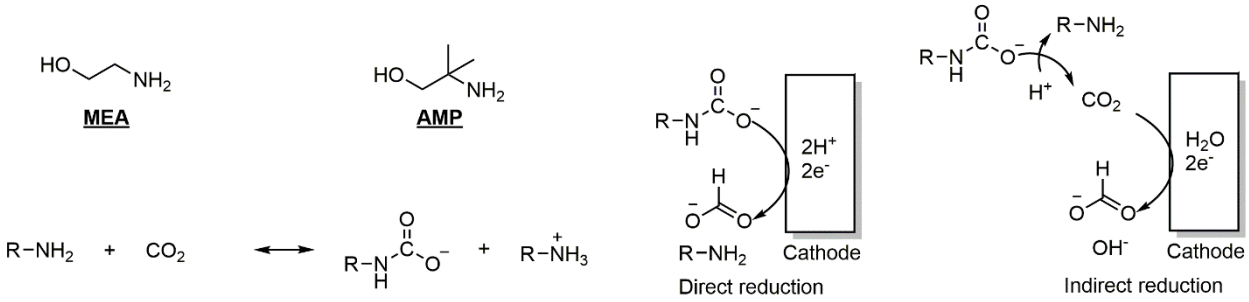
AMINES FOR CARBON CAPTURING AND UTILIZATION

Didjay.F. Bruggeman[1], Amanda. C. Garcia[1]

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

Carbon Capture and Utilization (CCU) technologies is a promising strategy to introduce a carbon cycle between fossil-generated CO_2 and useful carbon building blocks. Industrial CO_2 capturing involving amines has existed for many decades. CO_2 can be chemisorbed on amines ($R–NH_2$) *via* a nucleophilic reaction to yield the corresponding carbamates ($R–NHCO_2$). A promising route to utilize CO_2 is using an electrolyzer powered by renewable electricity to produce valuable feedstocks.[1] Recent work by Khurram *et al.* proves that carbamates can be directly used as the carbon source in electro-reduction when using non-aqueous electrolytes.[2] The integrated capture–electrolysis process might lead to a lower energy cost.

Inspired by the concept of direct electro-reduction of carbamates, we wanted to investigate the influence of amine properties on CO_2 to formic acid conversion using lead (Pb) and copper (Cu) working electrodes (WE).[3] We compare freely dissolved CO_2 with two popular CO_2 scrubbing amines: the sterically unhindered monoethanolamine (MEA) and the sterically hindered 2-amino-2-methylpropanol (AMP). Experiments with a Pb-WE give a reductive onset potential trend of $MEA–CO_2$> Free CO_2> $AMP–CO_2$, while the Cu-WE trend is $MEA–CO_2$> $AMP–CO_2$> Free CO_2. Interestingly, long-term electrolysis on Pb-WE gives a 50% Faradaic efficiency in formic acid (FE_{FA}) for both the free CO_2 and $AMP–CO_2$, while $MEA–CO_2$ has 0% FE_{FA}. In contrast, the Cu-WE gives ~100% FE_{FA} for the free CO_2, but 0% FE_{FA} for both $AMP–CO_2$ and $MEA–CO_2$. This hints that the amines play an active role in the CO_2 reduction mechanism on the electrode materials. We aim to take advantage of *in situ* spectroscopy technologies to gain fundamental mechanistic understandings during electrochemical conditions. We surmise that distributions of carbon products can be tuned with the help of carefully chosen amines when performing direct carbamate reduction.



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ELECTROCATALYTIC C-N BOND FORMATION: SYNTHESIS OF GLYCINE

Emma Caarls[1], Pim Broersen[1], Amanda C. Garcia[1]

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

A circular approach is the way forward in a system confronted with the limits of growth by the climate crisis. The valorisation of waste products is an important step in this development, and an especially interesting challenge for the field of chemistry. At the same time, chemical synthesis needs to transition towards safer and less polluting practices. The electrocatalytic synthesis of the amino acid glycine combines these two goals in one approach.

The aim of the presented work is the valorisation of CO_2 and nitrate through C-N bond formation. In order to focus the research efforts, investigations started from oxalic acid and hydroxylamine, reduction products of CO_2 and nitrate respectively. Previous efforts had shown that Cu-Hg electrodes can be suitable for the electrochemical synthesis of glycine in aqueous electrolyte. The mercury is incorporated to supress the hydrogen evolution reaction (HER).[1] Our work follows this approach, but replaces the mercury by lead, also a known HER suppressor and less toxic than mercury.[2] We investigated how the behaviour of a Cu electrocatalyst for glycine synthesis, from oxalic acid and hydroxylamine, is affected by the deposition of a Pb protective layer. For this, we used the conventional electrochemical methods of cyclic voltammetry and chronoamperometry, with a copper electrode, a lead electrode, and a copper-lead electrode.

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NONCOVALENT INTERACTIONS FROM MODELS FOR THE MØLLER-PLESSET ADIABATIC CONNECTION

Tim Daas[1], Eduardo Fabiano[2], Fabio Della Sala[2], Paola Gori-Giorgi[1], Stefan Vuckovic[3]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*

[2]*Insititute for Microelectronics and Microsystems, Unisalento, Italy*

[3]*Department of Chemistry, University of California, Irvine, United States of America*

Noncovalent interactions (NCIs), such as dispersion interactions, play an important role in many chemical and biological processes but are a challenge for quantum chemistry. In wavefunction based theories MP2, which is the first meaningful order correction to the Hartree-Fock energy, has been used to approximate dispersion interactions, although it overestimates the weak additive correlation effects that are important to describe the interactions between, for example, benzene dimers [1]. Furthermore, it has recently been shown that MP2 also has diverging errors for large molecular systems [2]. Density Functional Theory (DFT), the workhorse of quantum chemistry, runs into issues when describing dispersion interactions too. Normally, empirical D3/D4 dispersion corrections are added to standard DFT functionals when dispersion plays a role, although they could affect the accuracy for other NCIs [3]. Therefore, it would be useful to have a functional that can accurately describe all NCIs at the same time.

We have introduced a new set of functionals [4] that directly approximate the Møller-Plesset Adiabatic Connection (MP AC), that has as weak-interaction expansion the MP perturbation series, by interpolating between MP2 and the large-coupling strength limit [5,6]. These functionals have the same cost as double hybrids and greatly reduce the large MP2 errors for typical pi-stacking complexes (e.g., benzene-pyridine dimers) and for the large molecular systems, while keeping the same good performance for systems for which MP2 is accurate. Furthermore, they are also competitive with state-of-the-art dispersion enhanced functionals and can even significantly outperform them for a variety of NCIs such as hydrogen bonds, charge-transfer interactions, and dipole interactions.

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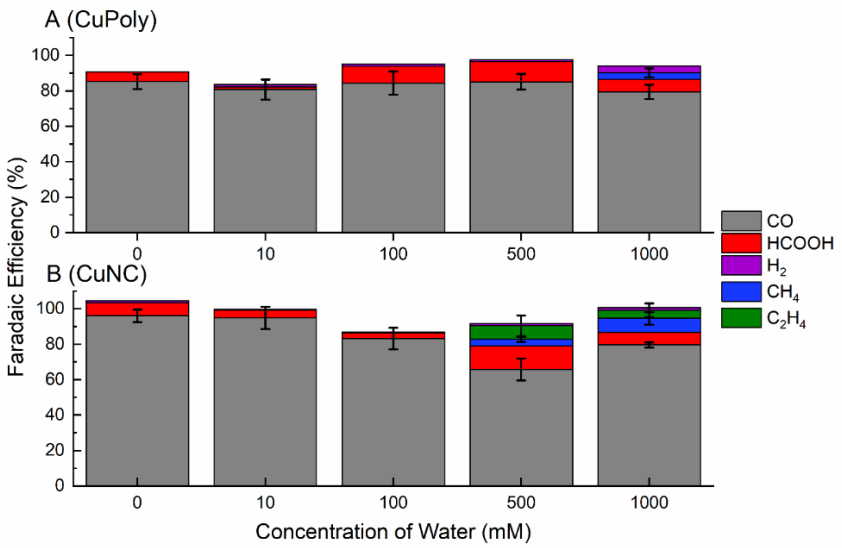
ELECTROCHEMICAL CO_2RR IN ORGANIC ELECTROLYTE: IMPACT OF THE WATER CONTENT AND CU MORPHOLOGY IN PRODUCT DISTRIBUTIONS

Connor Deacon-Price[1], Alisson. H. M. da Silva[2], Cássia. S. Santana[1], Marc. T.M. Koper[2], Amanda. C. Garcia[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

[2]*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands*

CO2 can be recycled to valuable multi-carbon products via electrochemical reduction of CO2 (CO2RR) on copper electrodes[1]. Product distributions and faradaic efficiencies can be tuned via organic electrolytes and nanostructured catalysts. An acetonitrile electrolyte system with different amounts of H2O (0 – 1000 mM) and shape-selective Cu*x*O-derived nanocube catalysts are used to investigate these features in tandem. Increasing the amount of H2O in acetonitrile is found to only slightly influence CO2RR activity, even when present in significant concentrations. Online gas chromatography analyses show that across all measured H2O concentrations CO is formed as a major product whilst HER is significantly suppressed. Ethylene was observed at water concentrations of ≥ 500 mM and only over CuNC catalyst, but at much lower faradaic efficiencies in comparison to pure aqueous electrolyte analogue systems. This research reveals fundamental aspects of the CO2RR in non-aqueous media which may aid rational design of future related system.



Faradaic efficiencies of CuPoly (A) and CuNC (B) at varying concentrations of water determined by online gas chromatography at -2.0 V vs. Ag/Ag+ for 90 min.

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SUPER - RESOLUTION OPTICAL IMAGING DOWN TO NANOSCALE ASPERITIES OF MECHANICAL CONTACTS

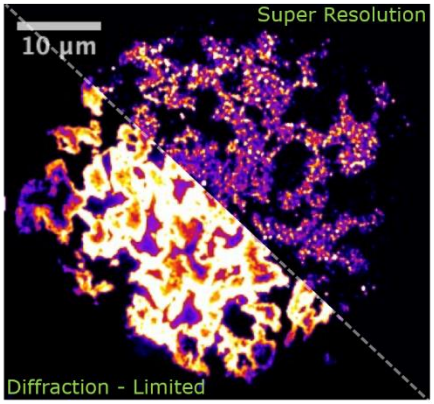
Begüm Demirkurt[1], Fred Brouwer[1], Daniel Bonn[2]

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

[2]Van der Waals – Zeeman Institute, University of Amsterdam, Amsterdam, The Netherlands

Fluorescent molecules from the special group called molecular rotors have been used as sensors to measure local viscosity, and real contact area recently[1]. We present a method for super - resolution imaging of mechanical contact between objects by means of a fluorescence blinking of rigidochromic molecular rotor and widefield fluorescence microscopy. After partial photobleaching of a monolayer of rotor molecules covalently attached onto a glass coverslip, the remaining molecules show on/off switching on a timescale of ~450 ms under contact. Both the fluorescence and millisecond - ON times during blinking cycles of the single molecules are observed to enhance in the contact.

This combination of properties allows us to use the molecular rotor for super-resolution imaging. Using this new method, we improve the lateral contact imaging resolution of a rough polystyrene and glass spheres on glass by a factor of three with respect to the diffraction limited technique, to ~80 and 70 nm, respectively. This improvement in resolution revealed an important observation coming from the different deformation characteristics: real contact area values of rough and purely elastic objects would be biased by the imaging resolution.



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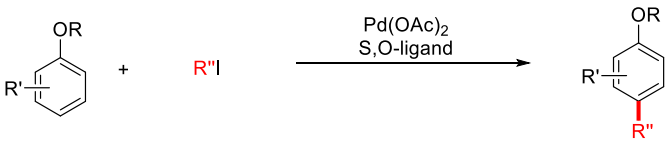
NON DIRECTED C–H ARYLATION OF ANISOLES VIA PALLADIUM/S,O-LIGAND CATALYSIS

Ke-zuan Deng[1], Tati M. Á. Fernández-Ibáñez[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Biaryl compounds are one of the most common and versatile skeletons in organic synthesis present in bioactive molecules, synthetic intermediates, functional materials and reagents.[1] Thus, developing efficient methodologies to prepare various biaryl compounds is of great importance. Traditionally, biaryl compounds are synthesized *via* cross coupling, which requires a pre-halogenated starting arenes.[2-3] On the other hand, C–H arylation is a greener alternative to the cross coupling since no pre-functionalization of the starting arene is required.

Here, we present a novel nondirected C–H arylation of anisole derivatives *via* Pd/S,O-ligand catalyst. The reaction proceeds under mild reaction conditions with a wide range of anisoles providing the *para*-arylated products in good yields.



R' = EDG/EWG; R" = aryl.

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FLOATING IN SPACE: HOW TO TREAT THE WEAK INTERACTION ENERGY OF INTERSTELLAR CO ICES

Brian C. Ferrari[1], Germán Molpeceres[2], Jörg Meyer[1], Johannes Kästner[3], Yuri Aikawa[2], Marc C. van Hemert[1], Thanja Lamberts[1,4]

[1]*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands*
[2]*Department of Astronomy, The University of Tokyo, Tokyo, Japan*
[3]*University of Stuttgart, Stuttgart, Germany*
[4]*Leiden Observatory, Leiden University, Leiden, The Netherlands*

A plethora of molecules have been detected in the interstellar medium, some of which are expected to form through surface reactions on interstellar ices. It is generally thought that interstellar ices are layered, with an amorphous polar water-rich layer and then an amorphous CO-rich layer. However, recent studies have suggested that the CO-rich layer should be crystalline and possibly even segregated as a single crystal atop the water-rich layer. If so, there are far-reaching consequences for the formation of complex organic molecules, such as sugars that use CO as a backbone. To supplement these studies we calculate the binding energies of CO on crystalline α-CO, along with a more atomistic and in depth study of the binding energy of CO on amorphous CO ices. Furthermore, we benchmark the performance of various DFT methods when treating surface processes on CO ices. We find that CO has a large distribution of binding energies (100 - 1200 K with ZPE corrections) on amorphous CO, including a significant amount of weak transient. This is a first step towards understanding the possible crystallization of amorphous CO into α-CO. Lastly, we find that CO binding energies are dominated by dispersion (~ 90%), as such, functionals need dispersion corrections to accurately treat it. In particular, we find the ωB97V-M functional to be a strong candidate for simulation surface processes on CO ices.

SAFE AND SUSTAINABLE-BY-DESIGN: COMPUTER-BASED REDESIGN OF PERSISTENT CHEMICALS

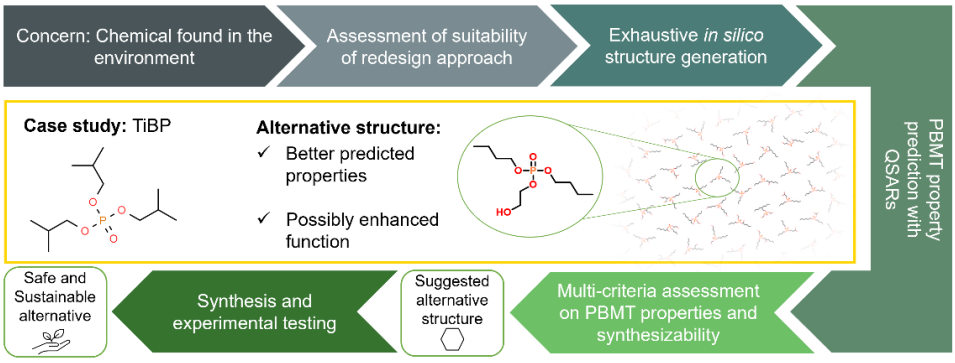
Hannah Flerlage[1], Joanke van Dijk[2,3], Steven Beijer[1], Annemarie P. van Wezel[2], J. Chris Slootweg[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

[2]*Institute for Biodiversity and Ecosystem Dynamics, University of Amsterdam, Amsterdam, The Netherlands*

[3]*Copernicus Institute of Sustainable Development, Utrecht University, Utrecht, The Netherlands*

Persistent chemicals can be an asset in a well-functioning circular economy where products are more durable and can be reused or recycled. However, this objective cannot always be fulfilled as release of chemicals from products into the environment can be inherently coupled to their use. For chemicals in the environment, persistency is seen as a major concern due to their accumulation over time which exacerbates potential risks. In these situations, chemicals should be designed for degradation. In this study, a systematic and computer-aided workflow was developed to facilitate the chemical redesign for reduced persistency [1]. The organophosphate flame retardant tri-*iso*-butylphosphate which has been detected in environmental monitoring studies was used as a case study for exploration of the approach. Flame retardants provide important functions for fire safety, but are also a significant class of environmental contaminants. Over 6.3 million alternative structures were generated *in silico* and filtered based on QSAR model outputs to remove structures predicted to be non-readily biodegradable. With a multi-criteria analysis based on predicted properties and synthesizability, a top 500 of the most desirable structures was identified. The target structure di-*n*-butyl (2-hydroxyethyl) phosphate was manually selected and synthesized. The approach is currently being expanded and experiments are carried out for further verification to reach its full potential in the mitigation of chemical pollution and to help enable a safe circular economy.



Systematic, computer-aided approach to redesign for less persistent chemicals

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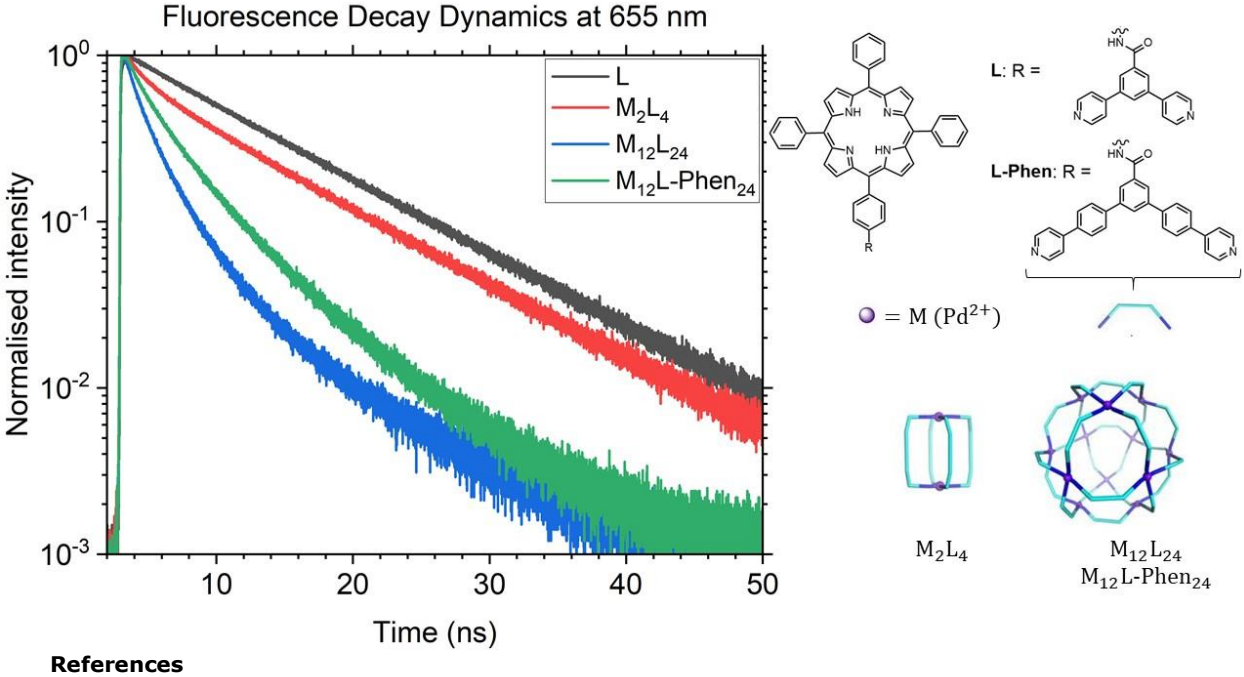
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EXCITON DIFFUSION AND ANNIHILATION IN PORPHYRIN/METAL-ORGANIC CAGE STRUCTURES

Vladimir Grigorescu[1], Tom Keijer[2],
Joost N. H. Reek[2], Charusheela Ramanan[1]

[1]*VU Amsterdam, Amsterdam, The Netherlands*
[2]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Light harvesting in natural photosynthetic systems relies on precise organisation of the chromophores in an antenna complex *via* its protein scaffold. We explore a biomimetic approach to light-harvesting, where metal-organic cages self-assemble to act as the scaffold to organise porphyrin chromophores in well-defined arrangements.[1] Porphyrins are useful chromophores to employ in such systems, as they are synthetically accessible structural analogues to the chlorophylls found in nature. Three configurations of porphyrins on metal-organic scaffolds are analysed here: 4 molecules in a self-assembled Chinese lantern configuration (M_2L_4) or 24 molecules as the sides of cuboctahedra of two different sizes ($M_{12}L_{24}$ and M_{12}L-Phen$_{24}$)[2]. These compounds feature the same steady-state absorption and emission bands as the model ligand. However, the intermolecular coupling introduced by the proximity and orientation of neighbouring porphyrins results in various degrees of fluorescence quenching. The photophysical dynamics of this assembly are investigated on the fs to ns timescale using visible time-resolved spectroscopy. The fluorescence quenching is dependent on the dimensions of the cages and the structural isomerism of the ligands. These results are modelled within the context of exciton diffusion and annihilation in molecular aggregates.



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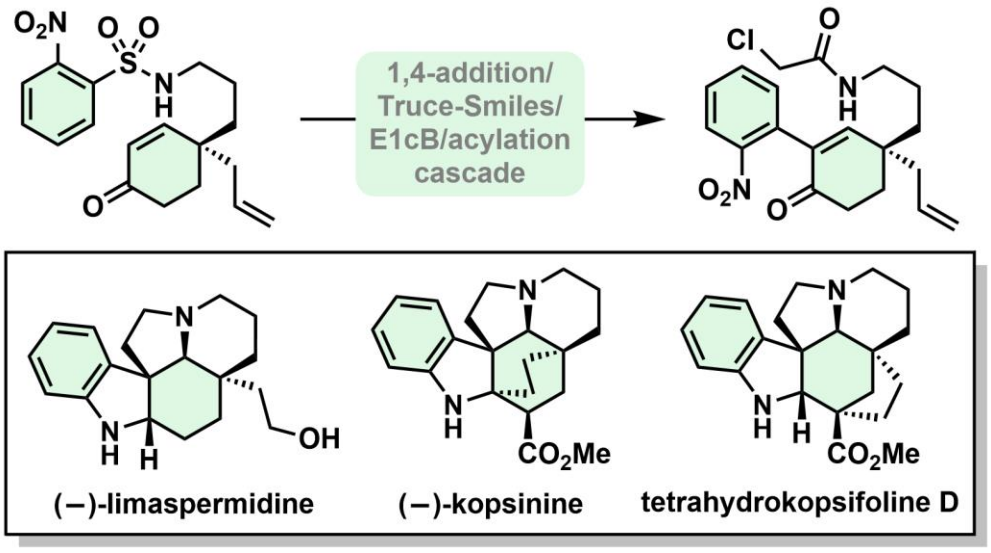
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TOTAL SYNTHESIS OF COMPLEX INDOLE ALKALOIDS BY A NITROARYL TRANSFER CASCADE REACTION

Brendan Horst[1], Daniël S. Verdoorn[1], Eelco Ruijter[1]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*

The medicinally relevant alkaloids of the Aspidosperma and Kopsia genera of flowering plants show high structural complexity, thus forming a challenging target for synthetic chemists.[1] Most syntheses rely on an indole starting material, necessitating the use of protecting groups. An alternative approach involves a late-stage Fischer indole synthesis, which may, however, result in low yields due to poor regioselectivity. In this work, we present a solution to both problems by making use of cascade chemistry.[2] This allows the combination of multiple elementary reaction steps in a single process, and thus inherently contributes to enhanced synthetic efficiency.



We report an intramolecular conjugate addition/Truce-Smiles/E1cB cascade of 2-nitrobenzenesulfonamide-functionalized cyclohexenones as a new entry to the core scaffold of monoterpene indole alkaloids. The method was applied to the asymmetric total synthesis of (−)-limaspermidine, (−)-kopsinilam, and (−)-kopsinine, as well as the framework of the kopsifoline alkaloids. Furthermore, we show that the cascade tolerates various substituents on the nitroarene, opening the way to other natural products as well as non-natural analogues.

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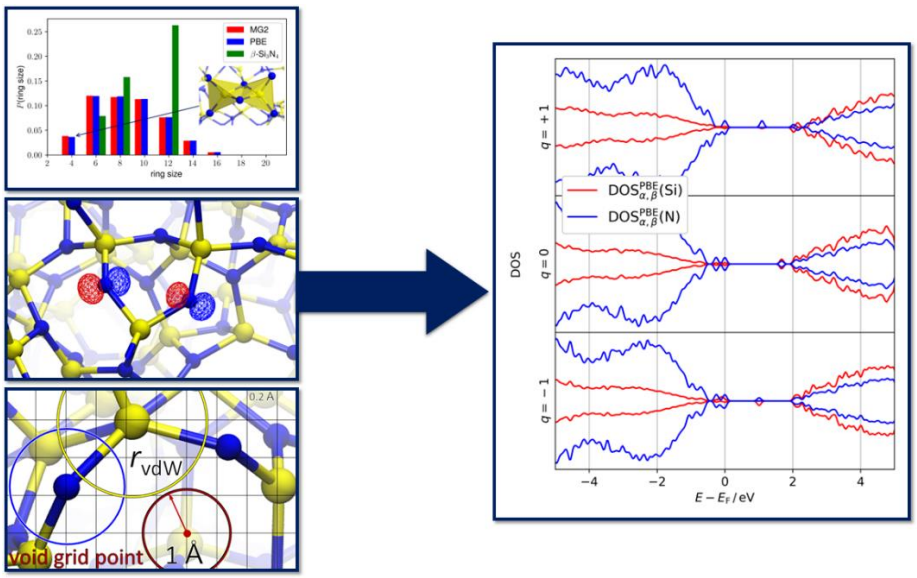
The Role of Morphology in Amorphous Silicon Nitride (Si_3N_4)

Lukas Hückmann[1], Jonathon Cottom[1], Jörg Meyer[1]

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

Amorphous silicon nitride (Si_3N_4) is an essential material for nanoelectronics due to its excellent mechanical and electrical properties. A unique feature of silicon nitride-based memory devices is long-term charge trapping, but how this phenomenon impacts the structure, including any charge-induced breakdown, is an open question. Photoemission and EPR experiments provide a valuable snapshot of the N- and Si-centered defects, their geometry, and associated electronic defect states.[1,2] In combination with electronic structure calculations, structural defects are considered responsible for charge trapping.[3]

This work combines simulations at force field (FF) and density functional theory (DFT) level. Hundreds of structural models are created with the melt-quench procedure using the MG2-FF,[4] followed by further refinement using the PBE functional.[5] This work identifies and examines characteristic local structural motifs only found in the amorphous Si_3N_4 phase, e.g., distorted coordination spheres, rings, off-coordinated atoms, and voids. Subsequently, their cross-relations and their influence on the electronic structure are investigated. It is shown that distorted SiN_4-tetrahedra act as precursors for electron trapping, whereas undercoordinated nitrogen atoms feature the hole polarons.



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AB INITIO MOLECULAR DYNAMICS SIMULATIONS TO UNRAVEL GLYCOSYLATION REACTION MECHANISMS

Bas Kreupeling[1], Francesco Buda[1], Jeroen D.C. Codée[1]

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

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 reaction used to build the target oligosaccharide: the glycosylation reaction. 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. Recently, ab initio molecular dynamics (AIMD) simulations have shown the necessity of explicit solvation in predicting the correct transition state structures of some glycosylation reactions.[1]

In this research, glycosylation reactions between a methylidene glucose donor and several simple alcohol acceptors with varying nucleophilicity have been investigated *in silico*. DFT-based Born-Oppenheimer molecular dynamics (BOMD) simulations have been performed to capture the full complexity of the reaction systems by including dynamical and solvent effects explicitly. Moreover, these simulations have combined with enhanced sampling techniques such as metadynamics in order to accelerate the crossing of free energy barriers, and to map out the free energy profiles. It was found that the obtained results are in line with experiment, where the decrease of acceptor nucleophilicity is associated with a shift towards S_N1-type mechanisms.

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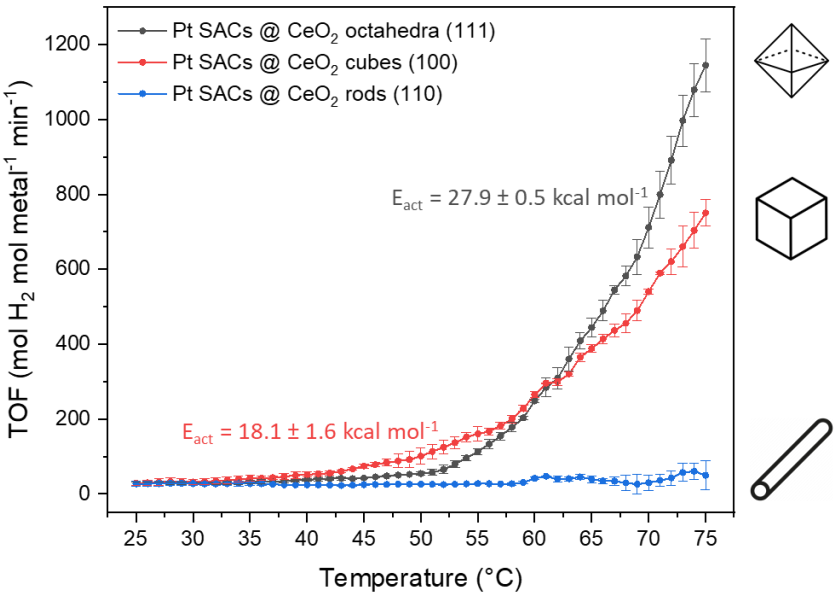
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METAL OXIDE SUPPORTED SINGLE ATOM CATALYSTS – DOES THE FACET MATTER?

Petrus C. M. Laan[1], Martijn J. Mekkering[1], Joost N. H. Reek[1], Gadi Rothenberg[1], Ning Yan[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Single-atom catalysts can be supported on a wide variety of metal oxides. Previous work showed that variations in metal oxides have a tremendous effect on catalytic performance. However, there is far less known about if the exposed crystal facet itself can have an effect too. Therefore, we selectively prepared cerium oxide (CeO_2) -rods, -cubes and -octahedra, exposing solely (110), (100) and (111) facets, respectively. This was followed by deposition of platinum single-atoms on these materials, resulting in a set of model catalysts that allowed us to study and understand facet-dependent chemical reactivity. To do so, the catalytic activity of these materials was studied with fast and precise online measurements by using the hydrolysis of ammonia borane as a probe reaction. We found the following trend: Pt_1@CeO_2-cubes > Pt_1@CeO_2-octahedra >> Pt_1@CeO_2-rods. These results reveal that crystal-facet engineering is an effective strategy to further finetune catalytic properties of atomically-dispersed supported metals. Further studies into the exact origin of the observed differences are currently performed in our labs.

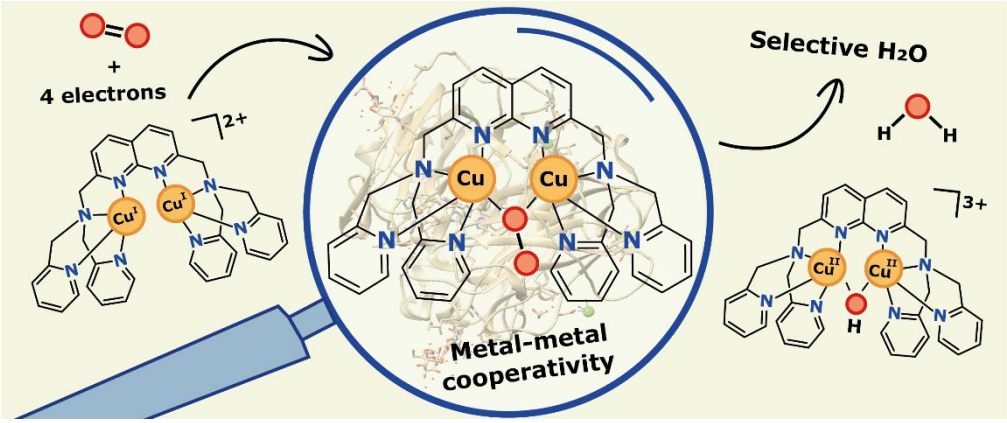


MECHANISTIC INVESTIGATIONS INTO THE SELECTIVE REDUCTION OF OXYGEN BY A MCO T3 SITE-INSPIRED COPPER COMPLEX

Phebe H. van Langevelde[1], Errikos Kounalis[2], Lars Killian[2], Emily C. Monkcom[2], Daniël L. J. Broere[2], Dennis G. H. Hetterscheid[1]

[1]*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands*
[2]*Institute for Sustainable and Circular Chemistry, Utrecht University, Utrecht, The Netherlands*

Understanding how multicopper oxidases (MCOs) efficiently and selectively reduce oxygen in the trinuclear copper cluster (TNC) is of great importance. Previously it was reported that when the T2-site is removed from the TNC, all O_2 binding activity at the dinuclear T3-site is lost. To address the question if and how a more constrained T3-site will catalyze the reduction of oxygen, we herein report a mechanistic investigation into the oxygen reduction reaction (ORR) activity of the dinuclear copper complex **[Cu₂L(μ-OH)]³⁺** (**L**=2,7-bis[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine). This T3-inspired complex confines the Cu centers in a rigid scaffold in close proximity and we demonstrate that under these constraints the dinuclear copper site displays ORR activity. By identification of key intermediates along the catalytic cycle of **[Cu₂L(μ-OH)]³⁺** we provide for the first time evidence that metal-metal cooperativity takes place during electrocatalysis of the ORR by a copper-based catalyst, which also results in an improved selectivity for the four-electron ORR. Electrochemical measurements show that the mechanisms of the ORR and hydrogen peroxide reduction reaction (HPRR) found for **[Cu₂L(μ-OH)]³⁺** are different from the ones found for analogous mononuclear copper catalysts. Overall, the mechanism of the **[Cu₂L(μ-OH)]³⁺**-catalyzed ORR in this work gives insight into the ORR activity of a T3-site and contributes to understanding of how the ORR activity and selectivity are established in MCOs.

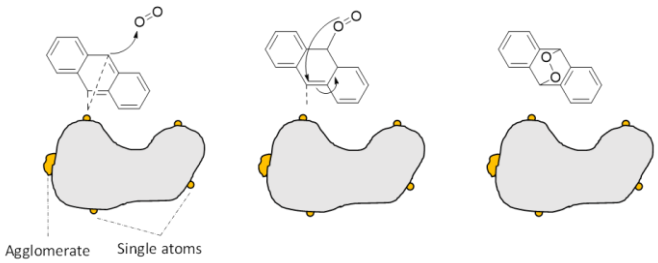


SELECTIVE ANTHRACENE PHOTO-OXIDATION OVER TITANIA-EMBEDDED SINGLE ATOM CATALYSTS

Martijn J. Mekkering[1], Gadi Rothenberg[1], Ning Yan[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Single-atom catalysts (SACs) often show exceptionally high performance per metal loading. [1] Besides benefiting from a better atom-economy, the metal support interaction is more pronounced in SACs compared to traditional catalysts. [2] Photochemical conversions rely much on the interaction of the active site with the photoactive support. In this work we show exactly the importance of this interaction by minimizing the distance of the active site with the support, by using SACs. We use anthracene as an example for the oxidation reaction to anthracene-9,10-endoperoxide. We observed a four-fold improvement compared to dense packed nanoparticle catalysts. SACs therefore take advantage of using less expensive material and an improved catalytic activity. Moreover, we show compelling evidence that photocatalytic conversion is possible with photons carrying an energy of 2.7 eV, which is *less* than the bandgap of TiO_2 (E_g = 3 eV).



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BOTTOM-UP AND TOP-DOWN SYNTHESIS OF AU@AZO CORE@SHELL NANOMATERIALS

Quynh Nguyen[1], Attilio Zilli[2], Agostino di Francescantonio[2], Michele Celebrano[2], Andrea Baldi[1]

[1]VU Amsterdam, Amsterdam, The Netherlands
[2]Politecnico di Milano, Milano, Italy

Aluminium doped zinc oxide (AZO) is a cost-efficient, highly earth-abundant, conductive, transparent and chemically-, mechanically- but most importantly photo-stable material which additionally exhibits nonlinear optical phenomena such as third- and second harmonic generation. These properties make it an attractive material for photocatalysis, optoelectronic devices and nanolasers [1].

Plasmonic systems such as gold nanoparticles (Au NPs) can amplify the optical response of a photonic material as the localised surface plasmon resonances (LSPRs) strongly enhance the near-field. This phenomenon is for example taken advantage of in photo-detectors with an increase in their photo-sensitivity [2].

In this project we develop the synthesis of Au@AZO core@shell nanomaterials using both a bottom-up colloidal method and a top-down single-particle approach.
The colloidal synthesis is based on a modified hydrothermal procedure used to prepare Au@ZnO nanoparticles [3]. The top-down approach exploits the plasmonic photothermal heating of a gold nanoparticle under focused laser irradiation while being immersed in an aqueous AZO precursor solution. We follow the shell formation by monitoring the increase in the scattering cross-section of the nanoparticles and a red-shift in their resonance wavelength [4].

Our approach has the potential to generate highly tuneable hybrid plasmonic nanostructures with controlled levels of aluminium doping and tailored shell thicknesses for opto-electronic applications.

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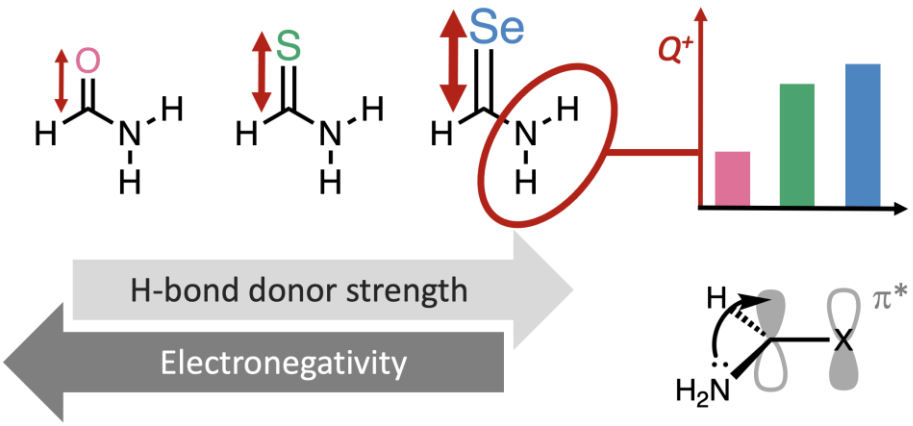
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How the Chalcogen Atom Size Dictates the Hydrogen-Bond Donor Capability of Amides

Celine Nieuwland[1], Célia Fonseca Guerra[1]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*

The amino groups of thio- and selenoamides can act as stronger hydrogen-bond donors than that of carboxamides, despite the lower electronegativity of S and Se compared to O. This phenomenon has been experimentally explored, particularly in organocatalysis[1] and supramolecular chemistry,[2] but a sound electronic explanation is lacking. In this talk, I will demonstrate that the NH_2 groups in thio- and selenoamides are more positively charged than in carboxamides, and thus better hydrogen-bond donors.[3] Our quantum chemical analyses reveal that this originates from the larger electronic density flow from the nitrogen lone pair of the NH_2 group towards the lower-lying $p^*_{C=S}$ and $p^*_{C=Se}$ orbitals than to the high-lying $p^*_{C=O}$ orbital. The relative energies of the p* levels follow from the mutual overlap between the chalcogen *n*p and carbon 2p atomic orbitals, which is set by the carbon–chalcogen equilibrium distance, a consequence of the steric Pauli repulsion between the two bonded atoms. Thus, not the electronegativity nor the often-suggested polarizability but the *steric size* of the chalcogen atom determines the amide's hydrogen-bond donor capability.



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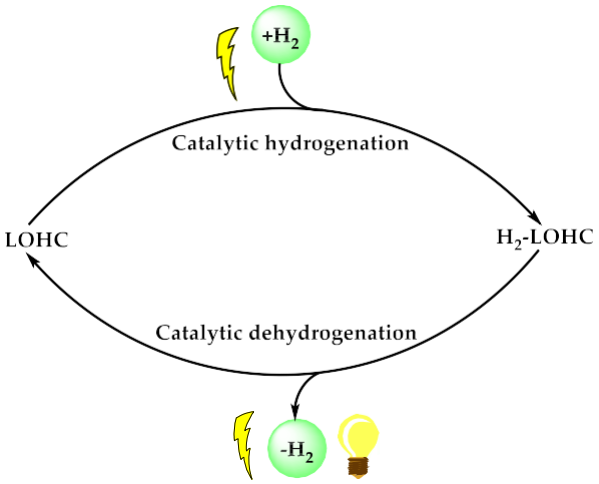
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LIQUID ORGANIG MOLECULES FOR SUSTAINABLE HYDROGEN STORAGE

Said Ortega Rosales[1], Pim Linnebank[1], Mike Hopman[1], Sebastiaan Mellema[1], Mirte van der Voort[1], J. Chris Slootweg[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

The world around us, and our history within it, have been shaped by the development of technologies that allow us to efficiently access the abundant energy that surrounds us. From storing energy through agriculture, to releasing it using the internal combustion engine, these innovations represent tipping points in human society. And now, another tipping point is needed. As our current system and its reckless exploitation of fossil fuels, ecosystems, and lives continue to sink us into an environmental and humanitarian crisis; it is increasingly more urgent to find strategies to ameliorate the negative consequences of this way of life. Shifting from fossil fuels to more benign and abundant sources of energy is a key aspect to reduce the burden on our planet. For this endeavour, the sun and the wind emerge as vital allies, providing potentially sufficient energy for the human needs, which can be easily converted to electricity, and with only minor disruptions to the ecosystem. Nevertheless, these types of energy are intermittent in nature, and to ensure a steady and reliable supply it is necessary to harvest, store, and distribute them. Hydrogen offers the possibility to act as an energy carrier for transportation and long-term storage of renewable energy. But there is a catch; its effective, safe, user friendly and economical storage is still an important challenge. A challenge for which circular liquid organic hydrogen carriers (LOHCs) offer a solution.



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TIME-RESOLVED NEAR-EDGE SOFT X-RAY ABSORPTION SPECTROSCOPY AS A NEW TOOL IN ORGANIC PHOTOCHEMISTRY

Maximilian Paradiz Domínguez[1], Lars B.M. Fondell[2], R. Büchner[2], Alexander Föhlisch[2], Fred A.M. Brouwer[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*
[2]*Helmholtz-Zentrum Berlin für Materialien und Energie, Berlin, Germany*

We report on time-resolved NEXAFS experiments on liquid samples.[1] Changes in X-ray absorption following UV excitation are measured as a function of time in a ps to ns timescale, providing us with information about changes in core electron binding energies and orbital occupations.

We have used this technique to study the light-driven dynamics of pyridine N-oxide and of pyridazine N-oxide. Despite being well-represented in the photochemistry literature for their unique synthetic capabilities,[2] the excited state dynamics as well as the exact nature of the photogenerated intermediates of the aromatic N-oxides remain open questions.[3] The sensitivity of this technique to the presence of holes allows us to separate the dynamics that occur in the excited surface from those that occur in the ground state surface. The X-ray chemical shifts, in combination with (TP)DFT calculations, allow us to track changes in the N-O, C-O, and N-N bonding patterns during their structural evolution.

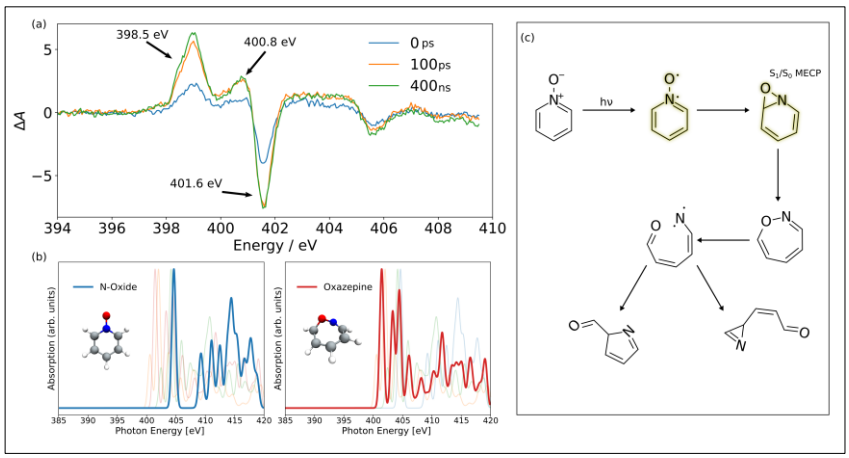


Figure 1: Pyridine N-Oxide. (a) Time-resolved N-edge spectrum (b) Calculated spectra of two species (c) Proposed scheme

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UNDERSTANDING THE INFLUENCE OF ALKALI CATIONS AND HALOGEN ANIONS ON THE COOPERATIVITY OF CYCLIC HYDROGEN-BONDED ROSETTES IN SUPRAMOLECULAR STACKS

Andre Nicolai Petelski[1,2], Célia Fonseca Guerra[1]

[1]Amsterdam Center for Multiscale Modeling (ACMM), Amsterdam Institute of Molecular and Life Sciences (AIMMS), VU Amsterdam, Amsterdam, The Netherlands
[2]Universidad Tecnológica Nacional, Chaco, Argentina

Hydrogen-bonded supramolecular systems are known to obtain extra stabilization from the complexation with ions, like guanine quadruplex (GQ).[1] They experience strong hydrogen bonds due to cooperative effects.[2] To gain deeper understanding of the interplay between ions and hydrogen-bonding cooperativity, relativistic dispersion-corrected density functional theory (DFT-D) computations were performed on triple-layer hydrogen-bonded rosettes of ammeline derivatives interacting with alkali metal cations and halides, as shown in **Figure 1a**. Our results show that when ions are placed between the stacks (see **Figure 1b**), the hydrogen bonds are weakened but, at the same time, the cooperativity is strengthened. This phenomenon can be traced back to the shrinkage of the cavity as the ions pull the monomers closer together and therefore the distance between the monomers becomes smaller. On one hand this results in a larger steric repulsion, but on the other hand, the donor-acceptor interactions are enhanced due to the larger overlap between the donating and accepting orbitals leading to more charge donation and therefore an enhanced electrostatic attraction.

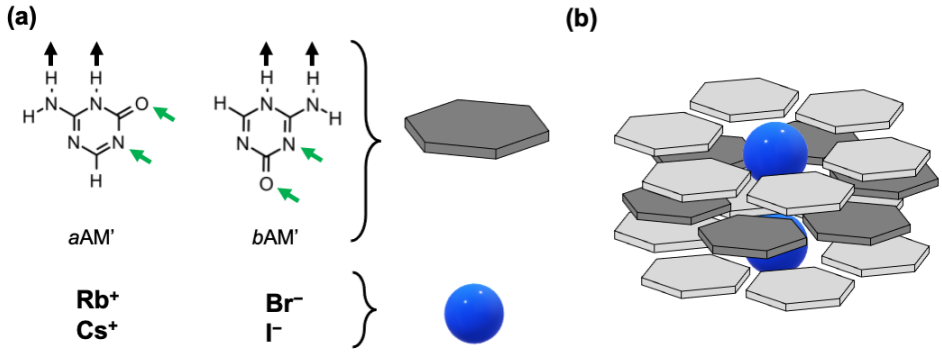


Figure 1: (a) Molecular structures of ammeline derivatives. Black and green arrows indicate the hydrogen bond donors (D–H) and acceptors (A) respectively. **(b)** Schematic representation of a hydrogen-bonded supramolecular stack.

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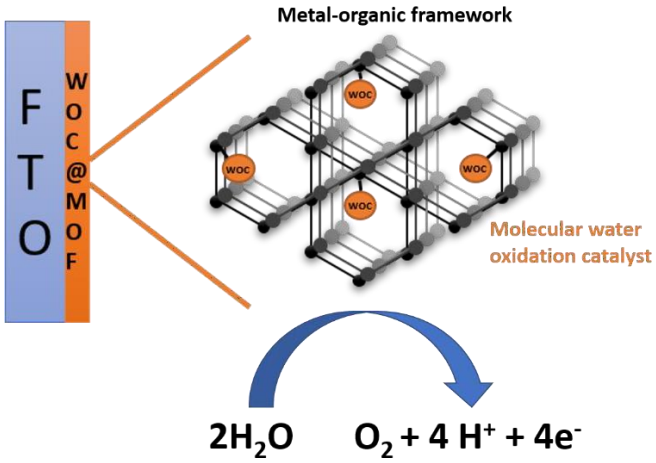
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HETEROGENIZATION OF MOLECULAR WATER OXIDATION CATALYSTS IN METAL-ORGANIC FRAMEWORKS

Dana Rademaker[1], Dennis G.H. Hetterscheid[1]

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

Hydrogen gas is seen as the green fuel of the future. Hydrogen gas can be made by water splitting, during which the proton reduction reaction is coupled to the oxygen evolution reaction (OER) in which water is oxidized to form oxygen. In this reaction, the energetics of the OER are the main bottleneck and require a large energy input. However, this reaction can be efficiently and selectively catalysed by electrochemical homogenous water oxidation catalysts (WOCs). Limitations of these homogeneous catalysts in electrochemical set-ups are the limited availability of the complex in solution near the surface and the instability of the catalyst over time due to an oxidative bimolecular pathway. In this work we aim to concentrate the complex near the electrode and prevent the deactivation of molecular complexes by heterogenizing the catalyst molecules in a metal-organic framework (MOF). MOFs have a highly porous and modular structure, which makes them ideal hosts for molecular catalysts. In this way, the molecular catalyst molecule can retain its selectivity and activity while gaining in stability.



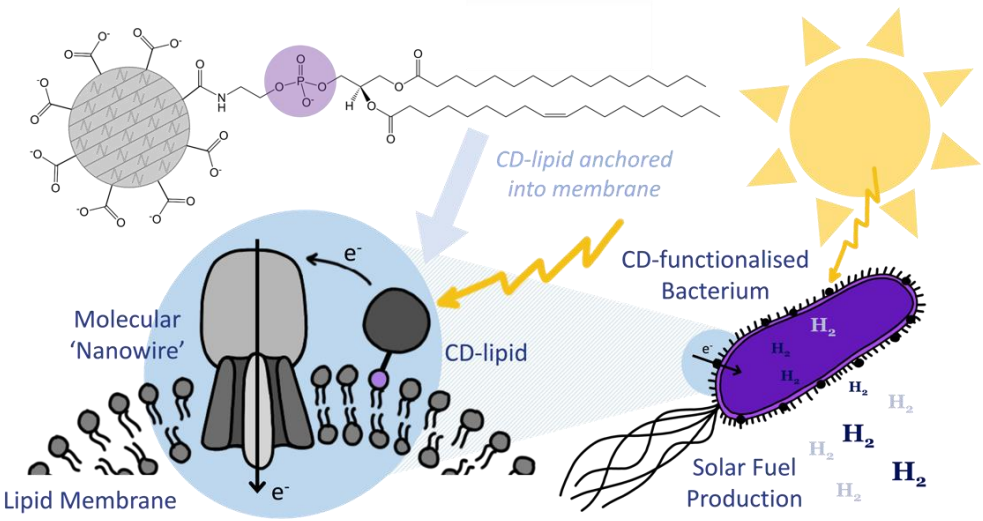
DEVELOPING LIPID-FUNCTIONALISED CARBON DOTS TO FACILITATE TRANSMEMBRANE PHOTOELECTRON TRANSFER

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

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

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 specifity for the production of desirable chemicals, can be integrated with durable inorganic light-harvesting materials to create solar-powered biohybrid systems for functions such as fuel production. Here, we aim to couple light-absorbing carbon dots[1] (CD) to non- photosynthetic bacteria[2] to create semi-artificial photosynthetic systems.

CDs are fluorescent semi-conducting nanoparticles which absorb broadly in the UV-visible range. In this work, graphitic nitrogen-doped CDs (g-N-CD) are chemically modified to improve their functionalisation of exoelectrogenic bacteria through covalent coupling to phospholipids. It is hypothesised that a phospholipid anchor would allow attachment of CDs to the outer membrane of these bacteria, transferring photoelectrons directly to the transmembrane molecular 'nanowires' that naturally function in the exchange of electrons between intracellular electron-transport proteins and the extracellular environment. To create a CD-phospholipid bioconjugate, carboxylic acid groups on the surface of g-N-CDs are reacted with the primary amine groups of phosphoethanolamine (PE) lipids to form amide bonds, using carbodiimide-containing compound EDC to activate crosslinking. The functionality of the bioconjugate is tested firstly through ability to attach to model lipid membranes, and secondly through facilitation of photoelectron transfer across a 'nanowire'- containing lipid membrane when under illumination.



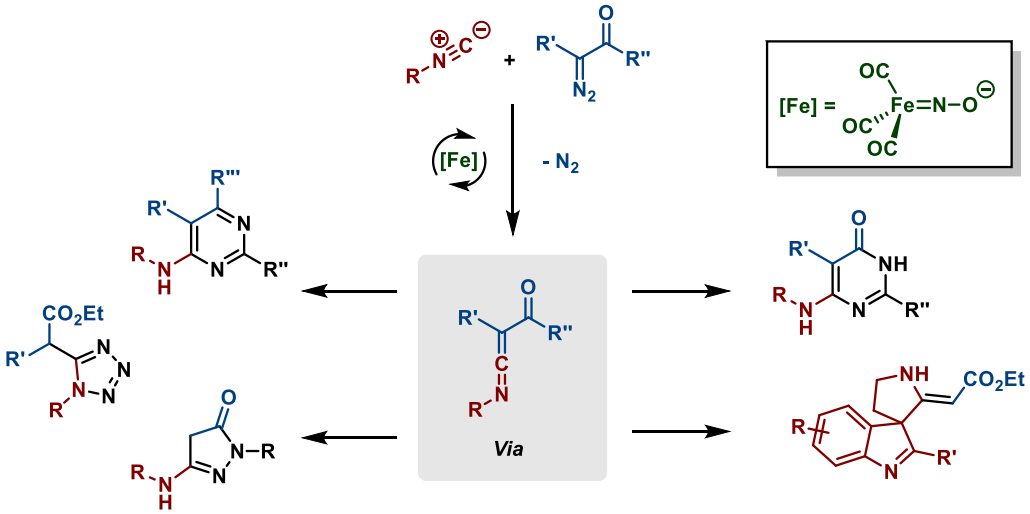
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IRON-CATALYZED CARBENE TRANSFER TO ISOCYANIDES APPLICATION IN THE SYNTHESIS OF HETEROCYCLES

Thomas. R. Roose[1], H. Daniel Preschel[1], Trevor A. Hamlin[1], Bert U.W. Maes[1], Eelco Ruijter[1], Romano V. A. Orru[1]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*



Isocyanides display unique reactivity as is evident by their use in cascade chemistry, multicomponent reactions, and transition metal catalysis. In the latter field, isocyanides have predominantly been used as inputs for Pd-catalyzed imidoylative cross-coupling reactions.[1] A new, less explored reactivity involves carbene transfer reactions, via *in situ* generated transition metal-carbenoids. The coupling of carbenes and isocyanides leads to ketenimines, which have proven to be versatile synthetic intermediates.[2] To date, only a handful of cascade processes based on transition metal-catalysed transfer of carbenes to isocyanides has been reported.[2] Unfortunately, these methods often use rare and precious noble metals such as Pd or Rh, while base metal-catalysed processes remain scarce. We now report the use of the electron rich ferrate complex $[Fe(CO)_3NO]N(n\text{-}Bu)_4$[3] in the carbene transfer reaction of α-diazo esters to isocyanides to form ketenimine intermediates, which can be transformed *in situ*. For example, addition of amidines as 1,3-bisnucleophiles results in medicinally relevant 4-aminopyrimid-6-ones.[3]. In addition, we applied this methodology in the formal total synthesis of (±)-aspidospermidine, (±)—aspidofractinine and (±)-limaspermidine.

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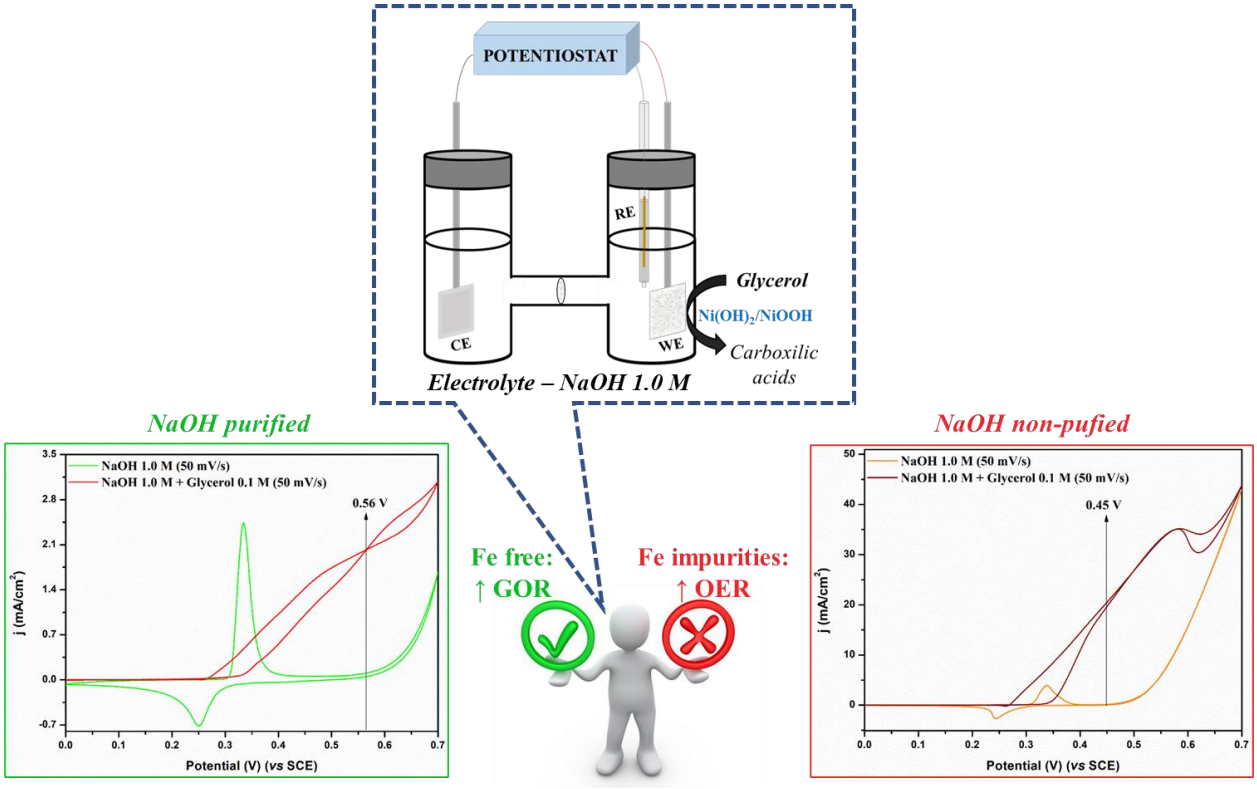
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THE EFFECT OF FE INCORPORATION INTO $NI(OH)_2$/NIOOH FILM TO BE APPLIED TO GLYCEROL ELECTROOXIDATION

Cássia S. Santana[1], Elvisona Gjonaj[1], Amanda C. Garcia[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Electrochemical glycerol oxidation reaction (GOR) has received a great attention in the past years as it can be coupled to renewable sources of electricity to produce compounds that are more valuable than glycerol itself. Among non-precious metals, nickel-based electrocatalysts, in addition to low price and large sources, have an anti-poison ability and long-term stability in alkaline solutions, making them attractive candidates for GOR. Under alkaline conditions it has been shown that that Fe impurities readily incorporate into $Ni(OH)_2$/NiOOH films during electrochemical experiments [1]. Taking this into account, here we investigate the influence of the electrolyte purification to minimize the effects of Fe impurities into $Ni(OH)_2$/NiOOH to be applied to GOR. Our major finding is that there is Fe incorporation into $Ni(OH)_2$/NiOOH film electrode when the electrolyte is not purified. As a result, it increases the NiOOH activity to parallel oxygen evolution reaction, OER ($4OH^- \rightarrow O_2 + H_2O + 4e^-$), and therefore decreases the faradaic efficiency to valuable chemicals that can be obtained from GOR.



References

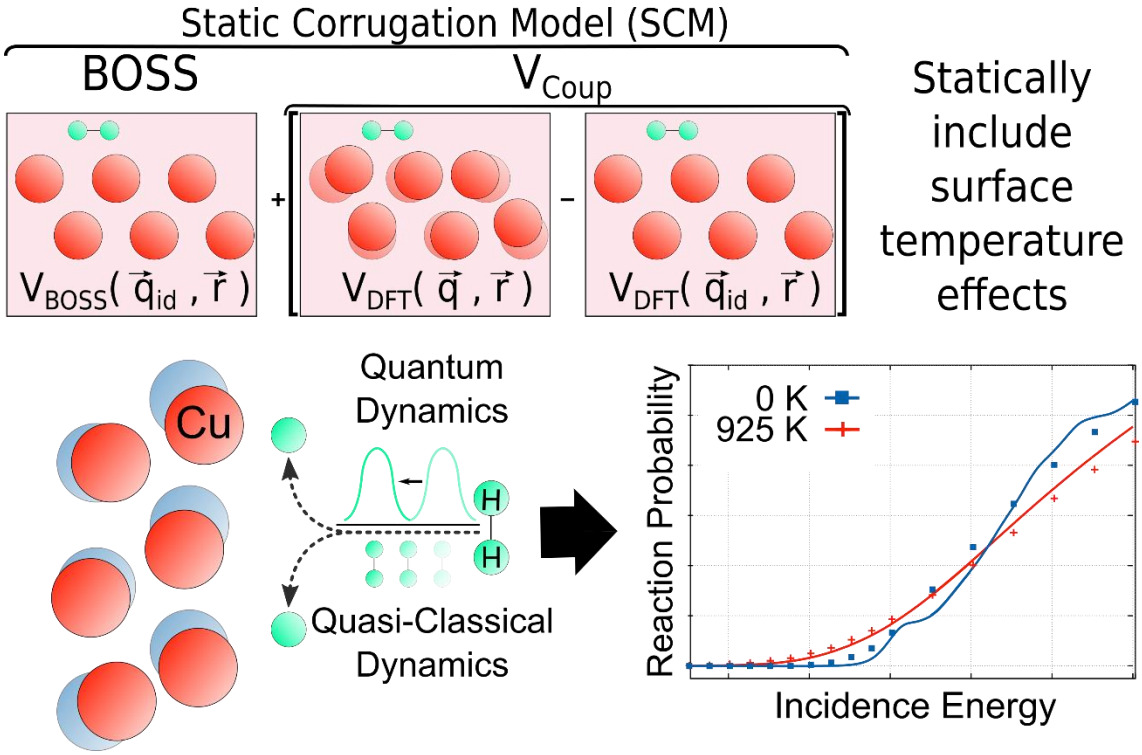
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ACCURATE DESCRIPTION OF SURFACE TEMPERATURE EFFECTS FOR THE QUANTUM DYNAMICS OF H_2 ON A METAL SURFACE

Bauke Smits[1], Mark Somers[1]

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

Surface temperature effects are an important topic for the dissociative chemisorption of H_2 on a metal surface. We present our use of the static corrugation model to accurately reproduce experimental dissociation curves using full 6D quantum dynamics simulations. We further discuss the agreement (and differences) in obtained results when using (quasi-)classical methods instead.



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CARBENE TRANSFER CATALYSIS VIA ELECTROCHEMISTRY

Demi D. Snabilié[1] and Bas de Bruin[1]

[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

The direct functionalisation of C–H or C=C bonds is of great importance for the pharmaceutical and chemical industry, but traditional methods often require multiple steps, harsh conditions or scarce second-row transition metals. Carbene transfer catalysis enables this direct functionalisation and can be performed under mild conditions with abundant first-row transition metals. However, "high-energy" reagents are often used as carbene precursors, which generate halogenated waste, are dangerous to work with or limit the scope of the reaction. Therefore, our aim is to generate a carbene radical complex from low-energy reagents, such as malonic esters, via electrochemistry. In this way, direct functionalization is achieved without the need of pre-activated reagents or high temperatures.

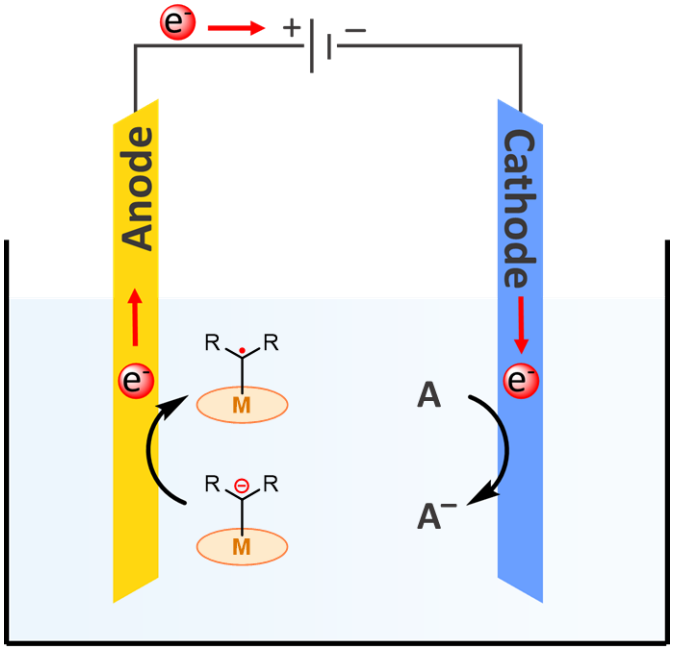


Figure 1: Generating a carbene radical complex via electrochemistry.

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UNRAVELLING PEPTIDE AGGREGATE FORMATION USING ION MOBILITY-MASS SPECTROMETRY

Iuliia Stroganova[1], Kevin Hes[1], Thaleia Tente[1], Agathe Depraz Depland[1], Sjors Bakels[1], Anouk M. Rijs[1]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*

Peptide and protein aggregation is one of the key physical processes in the human body. The incorrect folding of a protein and resulting exposure of the hydrophobic protein core can result in formation of aggregates, which have typical cross-β-sheet rich structures [1]. These amyloid structures are well-known for their association with a variety of human neurodegenerative diseases. In our work we focus on the tau protein segment PHF6 which is associated with Alzheimer's Disease (AD) and several other neurodegenerative diseases, known as "tauopathies".

Currently, we are working with two types of mass spectrometers, where we interface droplet-based microfluidic electrospray ionization (ESI) and ion mobility-mass spectrometry (IM-MS) with IR and UV photodissociation spectroscopy (Figure 1).

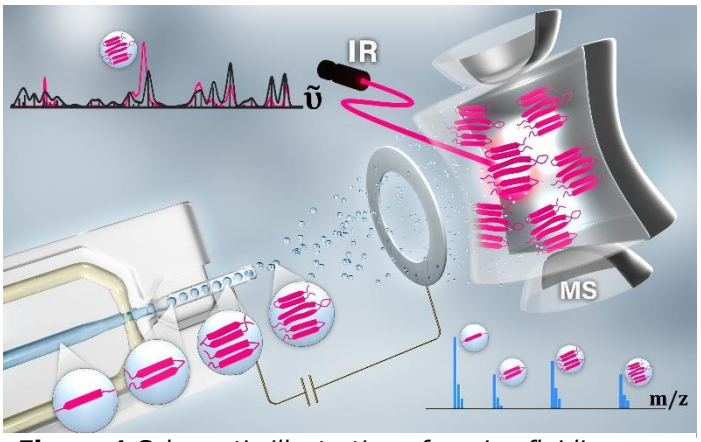


Figure 1 *Schematic illustration of a microfluidic source coupled to MS.*

This combination allows us to obtain both structural and kinetic information on peptide aggregation in a single experiment. The species that are formed during aggregation are very complex and heterogeneous. IM-MS enables us then to discriminate between different aggregate sizes with the same mass-to-charge ratio. Additionally, it provides structural information on the formed aggregates by determining their collision cross sections (CCS). IR spectroscopy can help to distinguish between different types of secondary structure. And finally coupling a microfluidics source (generating picolitre droplets) with IM-MS, allows us to study peptide aggregation in a more controlled environment and to probe the effect of confinement.

We would like to thank dr. E. Kempa and prof. dr. P. Barran (University of Manchester) and dr. A. Piruska and prof. dr. W.T.S. Huck (Radboud University).

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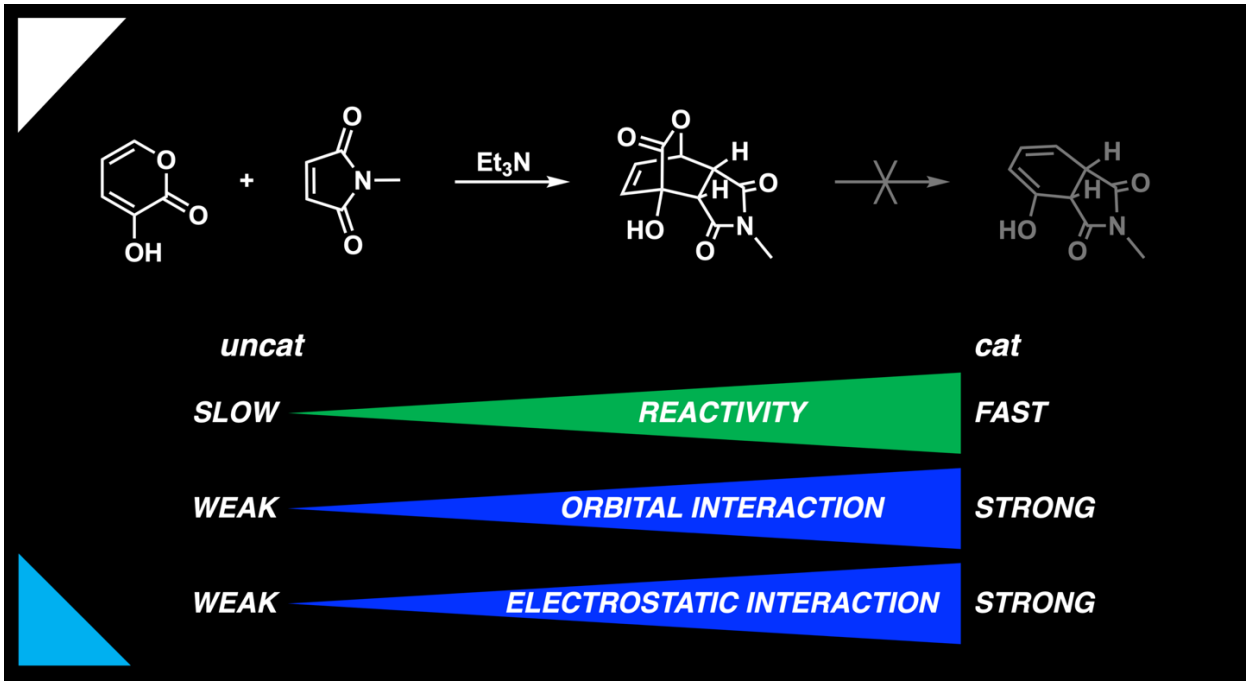
How Bases Catalyze Diels-Alder Reactions

Eveline H. Tiekink[1], Shihao Yu[1], Pascal Vermeeren[1], F. Matthias Bickelhaupt[1,2], Trevor. A. Hamlin[1]

[1]*Amsterdam Institute of Molecular and Life Sciences, VU Amsterdam, Amsterdam, The Netherlands*

[2]*Institute for Molecules and Materials, Radboud University, Nijmegen, The Netherlands*

We have quantum chemically studied the base-catalyzed Diels-Alder reaction between 3-hydroxy-2-pyrone and N-methylmaleimide using density functional theory. The uncatalyzed reaction is slow and is preceded by the extrusion of CO_2 via a retro-Diels-Alder reaction. Base catalysis, *e.g.*, by triethylamine, lowers the reaction barrier up to 10 kcal mol^{-1}, causing the reaction to proceed smoothly at low temperature, which quenches the expulsion of CO_2, yielding efficient access to polyoxygenated natural compounds. Our activation strain analyses reveal that the base accelerates the Diels-Alder reaction via two distinct electronic mechanisms: (i) by the *HOMO-raising* effect, which enhances the normal electron demand orbital interaction; and (ii) by donating charge into 3-hydroxy-2-pyrone which accumulates in its reactive region and promotes strongly stabilizing secondary electrostatic interactions with N-methylmaleimide.



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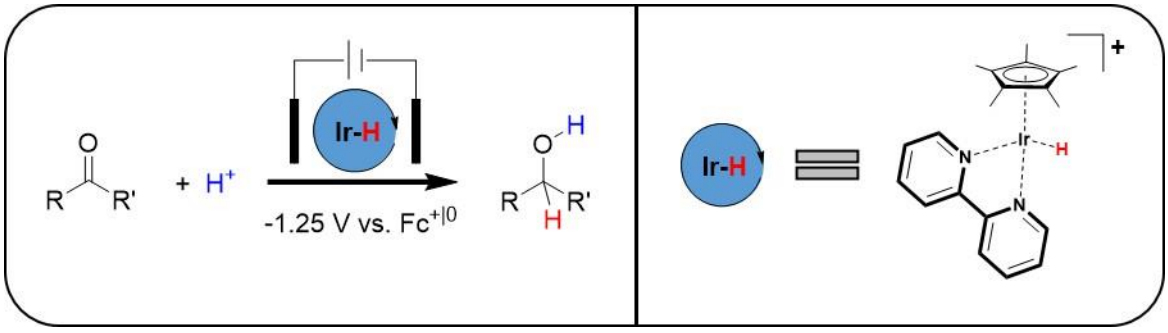
ELECTROCATALYTIC HYDROGENATION OF CARBONYLS WITH AN IRIDIUM COMPLEX

Sjoerd Verbeek[1], Dennis Hetterscheid[1], Elisabeth Bouwman[1]

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

Metal-based homogeneous catalysis plays a key role in several chemical industries, for the production of pharmaceuticals, flavours, or fragrances, as well as in the fine chemicals industry where catalysts are used to produce enantiomerically pure organic compounds. Enantiomerically pure alcohols, for example, can be synthesized through asymmetric hydrogenation. This catalytic process is usually performed by using dihydrogen gas in the presence of a molecular catalyst. A breakthrough was found by R. Noyori who used 2-propanol as a sacrificial hydrogen donor in a process named transfer hydrogenation [1]. Another way we envision to perform hydrogenation without using dihydrogen gas is by generating the required hydride *in situ*, using molecular catalysts that are capable of reducing protons to hydrides when an electric potential is applied. [2]

The development of molecular electrocatalysts capable of performing simple organic reactions has gained renewed interest in recent years. Several review papers have highlighted the importance of finding suitable electrocatalysts for the hydrogenation of carbonyls, imines and alkenes. Our approach is to use an iridium catalyst known for its ability to perform asymmetric (transfer) hydrogenation and evaluate it for electrocatalytic hydrogenation reactions. [3] Our results show that the iridium catalyst is capable of forming an iridium hydride species under electrocatalytic conditions, hydrogen evolution can be suppressed by exclusion of light, since this compound is a known photoelectrocatalyst. [4] When a carbonyl substrate is present in solution the hydride can be transferred to the carbonyl forming an alcohol molecule, this was confirmed by analysis after bulk electrolysis of the solution. The results of this study are expected to contribute to further development of molecular catalysts capable of hydrogenating more complex organic molecules.



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TETRAPYRIDINE LIGAND FOR RUTHENIUM-BASED PHOTO-ACTIVATED CHEMOTHERAPY

Wessel Verbeet[1], Sylvestre Bonnet[1]

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

Photo-activated chemotherapy (PACT) is a new anticancer treatment modality where a biologically active compound is released from a prodrug upon visible light irradiation.[1] In recent years, this method has shown great potential for delivering an enzyme inhibitor or a DNA-binding ruthenium-based agent.[2, 3] However, PACT compounds may also deliver multiple biological active components sequentially (Figure 1).

This study investigates a series of photosubstitutionally active ruthenium complexes based on the tetrapyridyl bis(bipyridyl)amine (bbpya) scaffold bearing various monodentate ligands (sulfoxides, nitriles, pyridines, thioethers) in axial positions. The complexes were synthesized and their photosubstitution properties investigated, including light absorption properties, activation wavelength, and photosubstitution quantum yield. Our results showed a significant effect of the nature of the axial ligands on the photosubstitution properties of the complex, and wavelength-selective photosubstitution reactions that allowed for removing one or both monodentate ligands. These investigations open new routes towards light-controlled multi-targeted ruthenium-based PACT compounds.

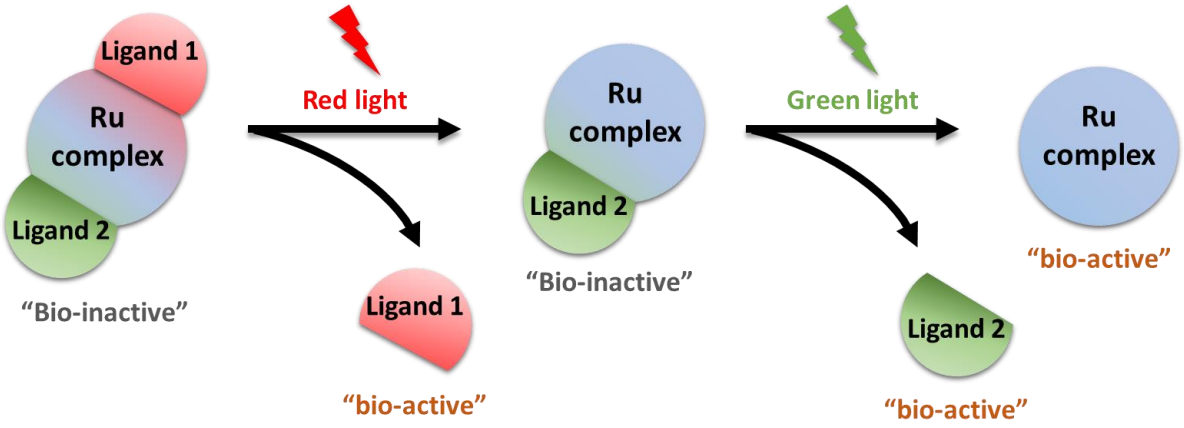


Figure 1: A multi-targeted ruthenium-based PACT compound: two different monodentate axial ligands are sequentially released upon light irradiation at two different wavelengths.

Acknowledgements

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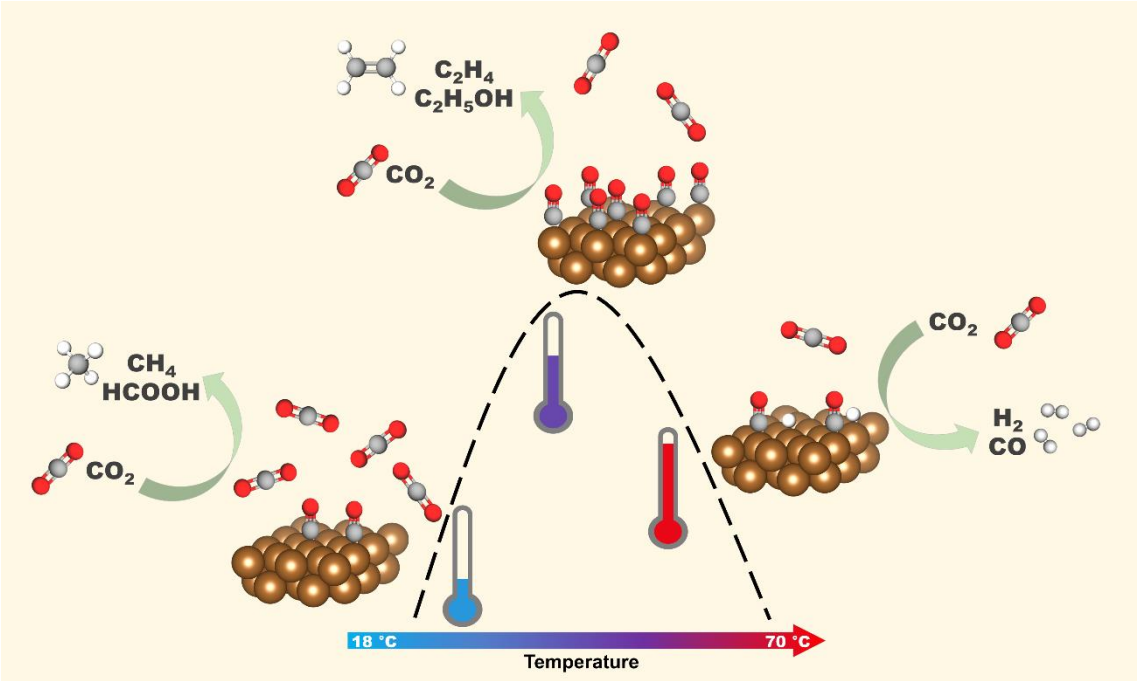
OPTIMUM, INCREASE OR DECREASE;HOW TEMPERATURE AFFECTS THE SELECTIVITY OF ELECTROCHEMICAL CO_2 REDUCTION ON COPPER

Rafaël E. Vos[1], Kees E. Kolmeijer[1], Marc T.M. Koper[1]

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

Electrochemical reactions in general, and the CO_2 reduction reaction (CO2RR) in particular, are commonly studied at room temperature. However, it is important to elucidate the effect of temperature on the product distribution and activity of CO2RR on copper as practical electrolyzers will operate at elevated temperatures. Copper is hereby specifically interesting as it is an unique catalyst for CO2RR capable of producing a variety of products including multi-carbon products such as ethylene and propanol.

In this study, we have performed electrolysis experiments at different temperature and potentials. We show that there are two distinct temperature regimes. From 18 up to ∼ 48 °C, C2+ products are produced with higher Faradaic efficiency, while methane and formic acid selectivity decreases, and hydrogen selectivity stays approximately constant. From 48 to 70 °C, we observe that hydrogen evolution dominates and the activity of CO2RR decreases. Moreover, the CO2RR products produced in this higher temperature range are mainly the C1 products CO and HCOOH. We argue that CO surface coverage, local pH and kinetics play an important role in the first regime, while the second regime appears most likely to be related to changes in the copper surface.



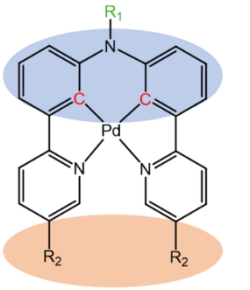
SELF-ASSEMBLY OF PUSH-PULL CYCLOMETALATED PD PHOTOSENSITIZER FOR PHOTODYNAMIC THERAPY UNDER RED LIGHT IRRADIATION

Lan Wang[1], Sylvestre Bonnet[1]

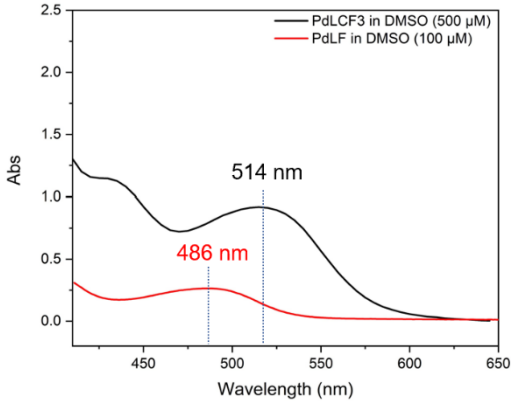
[1]*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands*

Photodynamic therapy (PDT) is a non-invasive and targeted treatment for cancers. When photosensitizers (PS) accumulate in the tumor tissue, they can be excited by light to generate phototoxicity, while in the dark toxicity is negligible and they do not damage tissues. The ideal wavelength of light for PDT is red or NIR light because longer wavelengths penetrate deeper in biological tissues [1]. Many d^8 or d^{10} metal complexes have been studied as PS for PDT because they easily generate singlet oxygen ($^1O_2$) [2]. However, many of these complexes are lipophilic and lose their photodynamic properties upon aggregation in aqueous solution.

In this research, we designed new cyclometalated Pd PS's based on the push-pull strategy, to achieve red light absorption and aggregation altogether without losing photodynamic properties. Electron-withdrawing R_2 groups were introduced to the known PdL complex to lower its LUMO energy, while cyclometalation serves as electron-donating group. Besides, due to the metalophilic interaction these monomers easily forms PDT-active nanoaggregates in solution [2], which is beneficial for cellular uptake. According to the absorption results, the $PdLCF_3$ shows better maximum absorption (514 nm) than PdLF (486 nm) and previous PdL (481 nm).



PdLF: R_1 = H, R_2 =F;
$PdLCF_3$: R_1 = H, R_2 =CF_3



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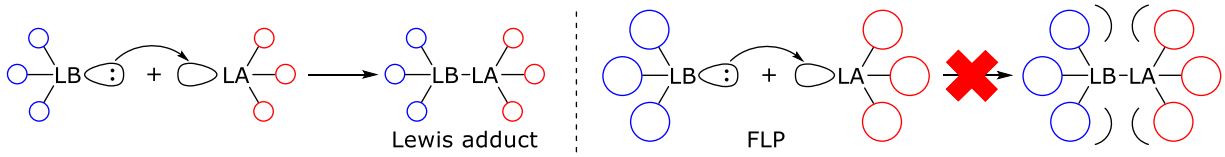
A Radical Approach To Methane Activation

Lars J.C. van der Zee[1], J. Chris Slootweg[1]

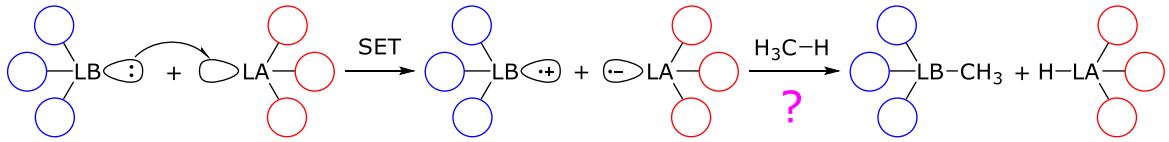
[1]*Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, Amsterdam, The Netherlands*

Methane is an interesting building block for many chemicals, for example for the direct production of methanol. However, the C–H bond of methane is one of to the most difficult bonds to activate, making the activation a big challenge. The goal of this project is to develop a new, metal free approach for the activation of methane.

Our approach originates from the frustrated Lewis pair (FLP) chemistry. Typically Lewis acids and Lewis bases form unreactive Lewis adducts, however, in FLPs steric bulk prevents the formation of these Lewis adducts.[1] This makes the empty orbital of the Lewis acid and lone pair of the Lewis base are still available for reactivity. Since the discovery of FLPs, the activation of several small molecules, for example dihydrogen, has been demonstrated. However, there are small molecules such as methane, for which the activation with FLPs is still illusive.



Recently our group showed that in FLP systems a photoinduced single electron transfer (SET) from Lewis base to Lewis acid can occur, leading to a radical ion pair.[2,3] The principle of single electron transfer will be used to design, synthesis and characterize new radical ion pairs with the aid to activate methane or other challenging substrates.



Acknowledgements

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INVESTIGATING THE FATE OF NANOPLASTICS IN AQUATIC ENVIRONMENTS

Tycho Roorda[1], Alexandra Gandea[1], Irene M.N. Groot[1]

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

Plastic particles in the ocean have become a contaminant of emerging concern due to their damage to humans and marine life[1,2]. Of all plastic production, which is increasing still, it has been shown that more than 99% of plastic waste which ends up in the oceans can not be accounted for[2,3]. The belief is that part of all this missing plastic degrades to a micro- and nano-sized scale which had not yet been detected[4,5]. Nanoplastics have also been shown to promote the spreading of toxins, such as heavy metals, which would otherwise sink to the ocean floor at their source[6,7]. In order to understand the fate of nanoplastics in aquatic environments, we must have a better understanding of the degradation mechanisms at an atomic and chemical level. In this project, we have successfully deposited nanoplastics onto a substrate in UHV by physical vapor deposition for degradation studies and to investigate their binding mechanism to other toxins in the ocean. The deposition of nanoplastics is confirmed by mass spectrometry, Auger electron spectroscopy and X-ray photoelectron spectroscopy. The degradation mechanisms which will be studied are oxygenation, hydrogenation, UV exposure and thermal annealing which will be investigated in ultra-high vacuum with atomic force microscopy and combined scanning tunneling microscopy. This combination allows for the identification of individual particles by conductivity making it possible to study the binding mechanism between nanoplastics and certain toxins. In this project, we aim to investigate the binding mechanism between nanoplastic particles and heavy metals as well as the nanoplastics' degradation by operando dosing of gases and heating to real world conditions.

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