HRSMC

SYMPOSIUM 2023



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WELCOME

On behalf of the Holland Research School of Molecular Chemistry, I am very pleased to welcome you to this 2023 HRSMC symposium. At this symposium we extend a special welcome to Prof. dr. N.H. (Nathalie) Katsonis (*University of Groningen*), 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 fifteenth time, the *Dick Stufkens Prize* will be awarded for the best PhD thesis that appeared under the auspices of the HRSMC. The 2023 laureate is Dr. Arno Förster. The prize will be presented by Prof. dr. E.J. Baerends, chairman of the Jury and member of the External Advisory Committee of the HRSMC. After the award ceremony, Dr. Arno Förster will give a presentation of the work for which he has received the 2023 *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 HRSMC SYMPOSIUM
NOVEMBER 10, 2023, SCHELTEMA, LEIDEN

08:15	Coffee/ tea & registration
08:55	Opening by Scientific Director – Prof. dr. W.J. Buma
09:10	Prof. dr. N. H. (Nathalie) Katsonis (University of Groningen) *"On the Possible Origin of Lipids and Protocells in the Early Ocean"*
Session 1:	**HRSMC theme 1: 'Synthesis, Characterisation, Reactivity and Properties of Molecules'** *Chair: Dr. S. (Sonja) Pullen*
10:00	Prof. dr. ing. T. (Timothy) Noël (University of Amsterdam) *"RoboChem – The Chemical Robots are Coming"*
10:30	Coffee/ tea & Postersession 1
11:20	Zhiyuan He (University of Amsterdam) *"Iron-catalyzed Asymmetric Intramolecular Nitrene Transfer Reactions"*
11:40	Marvin A. Albers (VU Amsterdam) *"Environment-Responsive Peptide Dimers Bind and Stabilize Double-Stranded RNA"*
Session 2:	**HRSMC theme 2: 'Physical Chemistry and Spectroscopy'** *Chair: Dr. F. (Freek) Ariese*
12:00	Prof.dr. L.J.C. (Lars) Jeuken (Leiden University) *"Rational Design of Nanoparticle Biohybrids for Compartmentalised Photocatalysis"*
12:30	Lunch - Postersession 2 starts at 13:00
13:45	Robert Smit (Leiden University) *"Line-Narrowing Spectroscopy of Single Molecules on a Hexagonal Boron-Nitride Surface"*
14:05	Robert W. Schmidt (VU Amsterdam / University of Amsterdam) *"Raman Diffusion Ordered Spectroscopy"*
Session 3:	**HRSMC theme 3: 'Theoretical Chemistry'** *Chair: Dr. M.F. (Mark) Somers*
14:25	Dr. T.A. (Trevor) Hamlin (VU Amsterdam)
14:55	Coffee/ tea & Postersession 3 PLEASE REMOVE POSTERS AFTER SESSION
15:45	Voting for best poster in session 1, 2 and 3
15:50	Robert A.B. van Bree (Leiden University) *"Accurate but Efficient Calculations on a Tough Dissociative Chemisorption Reaction"*
16:10	**Dick Stufkens Prijs Award Ceremony** Introduction by chair of the jury (Prof. dr. E.J. Baerends)
16:20	Lecture Winner Dick Stufkens Prize 2023: Arno Förster "*Vertex Corrected GW-Bethe-Salpeter-Equation Calculations for Spectroscopy*"
16:50	Poster Prize and Closure
17:00	Reception
18:00	End of symposium and Scientific staff meeting (Expo 2)
19:00	Staff dinner at Scheltema

ABSTRACT INVITED SPEAKER

(PROF. DR. N.H. (NATHALIE) KATSONIS)

ON THE POSSIBLE ORIGIN OF LIPIDS AND PROTOCELLS IN THE EARLY OCEAN

Nathalie Katsonis[1]

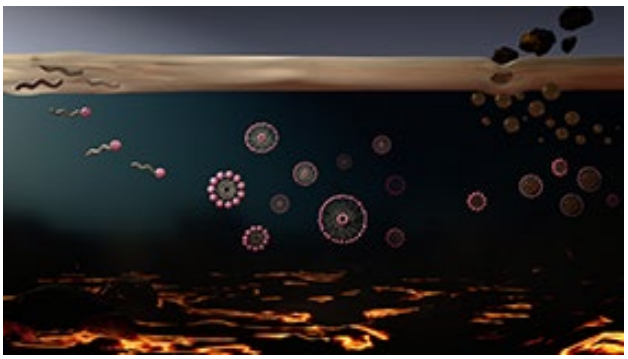
[1]*Stratingh Institute for Chemistry, University of Groningen, Groningen, The Netherlands*

The origin of life on Earth is one of science's great unresolved questions. The chemical and physical complexity of life, even early life, has arguably made this challenge all the greater since we cannot retrace the steps of life, beyond the fossil record.

Four billion years ago, the Earth was covered in water and devoid of life. Current thought holds that, during these early stages, molecules accumulated in early microscopic compartments called protocells. Protocells were probably made of lipids, in view of their self-assembling properties and their relatively simple structures. *However, where and how early lipids would have formed remains an unanswered question.*

I will present recent results indicating that primitive lipids – called fatty acids – could have formed by catalytic photo-oxidation of a thin layer of hydrocarbons that would have covered the ocean at that time [1]. These lipids would have stabilized microscopic droplets and provided them with motile behaviour, via Marangoni propulsion. The motile behaviour of water droplets in the oil slick would have had overarching consequences for the emergence of protocells [2] and leading to chemical complexity in System Earth.

We are concerned with providing new answers to open questions in research on the origins of life. But also, we foresee that our chemistry can find relevance in the remediation of the environment damage caused by polluting oil slicks.



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ABSTRACTS OF STAFF LECTURES

(ORDER BASED ON PROGRAMME)

ROBOCHEM – THE CHEMICAL ROBOTS ARE COMING

Timothy Noël[1]

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

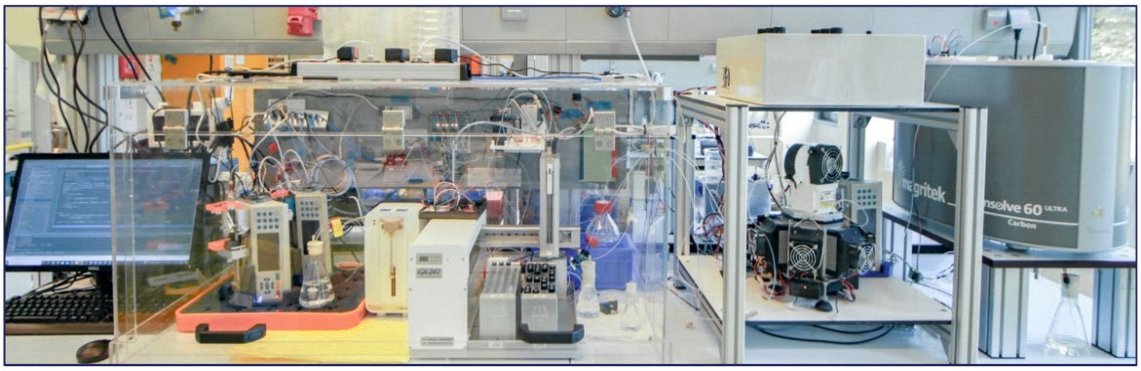
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As the chemical industry grapples with the challenges of optimizing, intensifying, and scaling up processes, we introduce a robotic solution called RoboChem.[1] This all-encompassing robotic platform seamlessly blends state-of-the-art hardware and software, enabling the autonomous enhancement of photocatalytic reactions in flow, presenting a more efficient alternative to traditional process development methodologies.

One of the standout features of RoboChem is its high-power continuous-flow capillary photoreactor. It not only ensures highly reproducible data but also adeptly tackles the prevalent issues tied to mass, heat, and photon transport. Moreover, a significant safety advantage of the platform is the ability to maintain a distance from potentially hazardous reactions, reducing direct human exposure and thereby enhancing laboratory safety protocols. Moreover, this technological intervention not only ensures precision but also dramatically reduces the margin for human errors, guaranteeing more consistent and reliable outcomes.

Our rigorous testing showcases the platform's unmatched efficacy, with observed enhancements in space-time yields far surpassing conventional methodologies. Further amplifying its merits, RoboChem's capability to autonomously curate extensive datasets points towards a transformative, digitally-informed future for synthetic chemistry.

In this talk, we will delve into the synergy between technology and organic chemistry, emphasizing the paramount importance of safety, precision, and the elimination of human fallibility as we venture forth into the realm of Industry 4.0.



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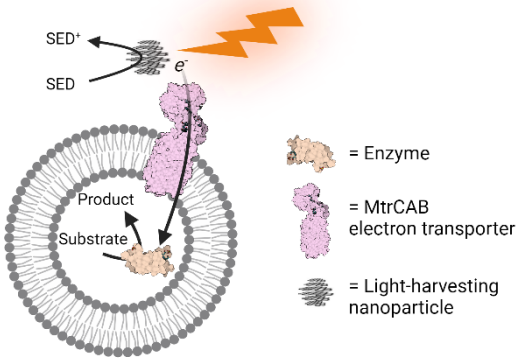
[1] Slattery, A; Wen, Z; Tenblad, P.; Pintossi, D.; Sanjose-Orduna, J.; den Hartog, T. and Noël, T. ChemRxiv, **2023**, DOI: 10.26434/chemrxiv-2023-r0drq.

RATIONAL DESIGN OF NANOPARTICLE BIOHYBRIDS FOR COMPARTMENTALISED PHOTOCATALYSIS

Lars J.C. Jeuken[1], Huijie Zhang[1], Imogen L. Robinson[1], Anna Stikane[2], Ee Taek Hwang[2], Erwin Reisner[3], Julea N. Butt[4]

[1]*Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands*
[2]*School of Biomedical Sciences, University of Leeds, Leeds, United Kingdom*
[3]*Yusuf Hamied Department of Chemistry, University of Cambridge, Cambridge, United Kingdom*
[4]*School of Chemistry, University of East Anglia, Norwich, United Kingdom*

In nature, charge recombination in photosystems is minimised by efficient charge separation across the thylakoid membrane. In a semi-artificial photosynthetic approach, we aim to mimic this principle by coupling photosensitising or photocatalytic nanoparticles (NPs) to lipid vesicles. Key to this approach has been an icosahaem membrane protein, MtrCAB from *Shewanella oneidensis* MR-1. In this protein, twenty haems form a ~15 nm long molecular wire, which efficiently transfer electrons across lipid membranes. The interaction between light-harvesting NPs and MtrCAB is confirmed by life-time fluorescence, X-ray footprinting mass spectrometry and photoelectrochemistry. Transmembrane photoreduction is observed in liposomes loaded with redox-active dyes and enzymes. We propose that these biohybrid systems can improve performance of whole-cell biophotocatalysts in the future.



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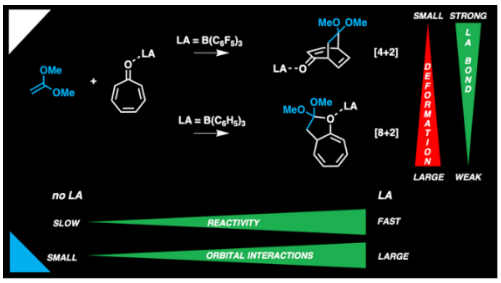
TEMPTING TROPONE IN CYCLOADDITIONS

Trevor A. Hamlin[1]

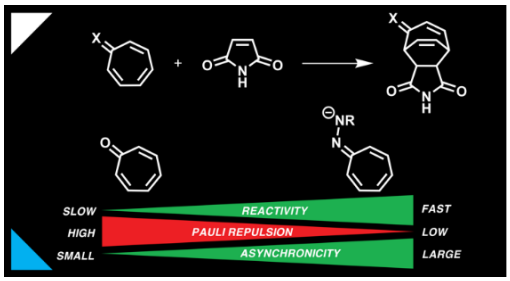
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In this talk, we scrutinize two methods employed to tempt the relatively unreactive tropone to react in cycloadditions using dispersion-corrected relativistic density functional theory. First, we study both uncatalyzed and Lewis acid (LA)-catalyzed cycloaddition reactions between tropone and 1,1-dimethoxyethene.[1] Our findings reveal that LA catalysts, namely BF_3, $B(C_6H_5)_3$, and $B(C_6F_5)_3$, significantly enhance reaction rates and lower reaction barriers by up to 12 kcal mol^{-1} through LUMO-lowering catalysis.[2] Furthermore, we explain how the judicious choice of the LA catalyst can effectively impart regiocontrol of the cycloaddition: $B(C_6H_5)_3$ furnishes the [8+2] adduct while $B(C_6F_5)_3$ yields the [4+2] adduct. Second, we explore how reversing the polarity of the carbonyl group (umpolung), *e.g.*, by converting tropone into its hydrazone analog, catalyzes the Diels-Alder reaction with maleimide.[3] We challenge the established explanation attributed to antiaromaticity-induced HOMO raising. Instead, we propose that the increased reactivity arises from enhanced asynchronicity, resulting in reduced strain and diminished destabilizing Pauli repulsion.[4] Our findings provide a deep understanding of the mechanism behind tropone activation.



Chem. Eur. J. **2023**, *29*, e202301223



Chem. Commun. **2023**, *59*, 3703

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ABSTRACTS OF PHD LECTURES

(ORDER BASED ON PROGRAMME)

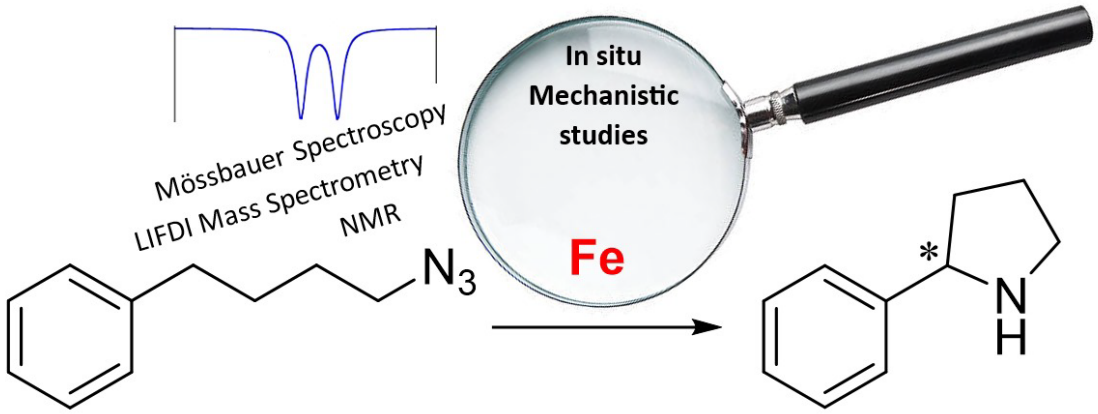
IRON-CATALYZED ASYMMETRIC INTRAMOLECULAR NITRENE TRANSFER REACTIONS

Zhiyuan He[1], Sam van der Loo[1], Rik Bennis[1], Stijn de Wit[1], Thomas Kwakkelstein[1], Bas de Bruin[1], Jarl Ivar van der Vlugt[1,2]

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

[2] *Institute of Chemistry, Carl von Ossietzky University Oldenburg, Germany*

N-heterocycles play a crucial role in the realm of bioactive molecules. The utilization of iron-catalyzed intramolecular C-H amination through organic azides offers an invaluable and sustainable approach for the targeted and atom-efficient synthesis of these heterocyclic motifs.[1] Following up on previous work from our group,[2] we herein investigate several iron-based catalysts capable of facilitating catalytic nitrene group transfer under mild reaction conditions, without the need for additives, while maintaining high chemoselectivity. Notably, by tuning the ligand, we are able to also achieve high levels of asymmetric induction in the resulting product - asymmetric C(sp^3)-H aminations are still scarce.[3,4] Furthermore, our study includes mechanistic investigations, employing several analytical techniques, including the *in-situ* freeze-quench Mössbauer spectroscopy, LIFID mass spectrometry and NMR.



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ENVIRONMENT-RESPONSIVE PEPTIDE DIMERS BIND AND STABILIZE DOUBLE-STRANDED RNA

Niall McLoughlin[1,2], Marvin A. Albers[1,2], Estel Collado Camps[3], Jannik Paulus[1,2], Youri A. Ron[1], Saskia Neubacher[4], Sven Hennig[1,2], Roland Brock[3,5] Tom N. Grossmann[1,2]

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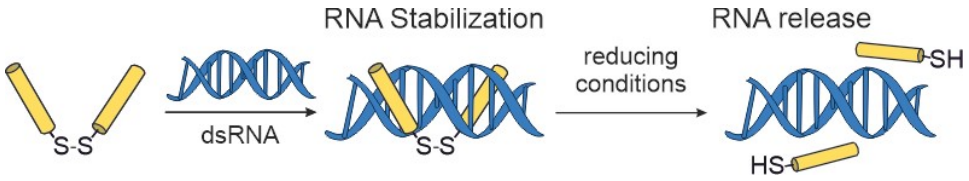
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Double-stranded RNAs (dsRNA) possess immense potential for biomedical applications.[1] However, their therapeutic utility is limited by low stability and poor cellular uptake.[2] Different strategies have been explored to enhance the stability of dsRNA, including the incorporation of modified nucleotides, and the use of diverse carrier systems.[3] Nevertheless, these have not resulted in a broadly applicable approach thereby preventing the wide-spread application of dsRNA for therapeutic purposes. Herein, we report the design of dimeric stapled peptides based on the RNA-binding protein TAV2b.[4] These dimers are obtained via disulfide formation and mimic the natural TAV2b assembly. They bind and stabilize dsRNA in the presence of serum, protecting it from degradation. In addition, peptide binding also promotes cellular uptake of dsRNA. Importantly, peptide dimers monomerize under reducing conditions which results in a loss of RNA binding. These findings highlight the potential of peptide-based RNA binders for the stabilization and protection of dsRNA, representing an appealing strategy towards the environment-triggered release of RNA. This can broaden the applicability of dsRNA, such as short interfering RNAs (siRNA), for therapeutic applications.



Acknowledgements:

This work was supported by the European Research Council (ERC starting grant number 678623, and ERC proof of concept grant 101112973) and Instruct-ERIC (PID26489). E.C.C. received funding from the Radboudumc.

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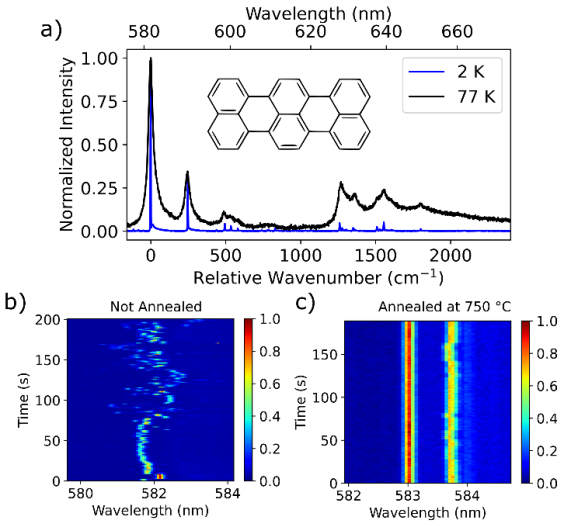
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LINE-NARROWING SPECTROSCOPY OF SINGLE MOLECULES ON A HEXAGONAL BORON-NITRIDE SURFACE

Robert Smit[1], Arash Tebyani[1], Jil Hameury[1], Sense Jan van der Molen[1], Michel Orrit[1]

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

Single organic molecules embedded in an organic crystalline matrix can, with a right choice of matrix, possess narrow (tens of MHz) and stable zero-phonon lines at low temperature. However, once the molecules are located closer to the ill-condensed boundaries of the matrix, the zero-phonon lines are found to be intensely broadened and subject to spectral diffusion, while no zero-phonon lines of single molecules have been detected directly at the surface. In this work, we study a new and unconventional matrix for single molecules: two-dimensional hexagonal boron-nitride (hBN). We show for terrylene molecules that we can deposit them at the surface of hBN by spin-coating or sublimation. Contrary to observations with three-dimensional matrices, we can record the molecule's zero-phonon lines at low temperature (Figure a) on hBN and we show presence of spectral diffusion (Figure b). We compare measurements with hBN that was either annealed or not annealed, prior to molecule deposition, and we find remarkable differences. After annealing, the spectral stability of single molecules is significantly improved (Figure c) and this may point to organic contamination as a potential source for the spectral diffusion. Moreover, after annealing, we find that some terrylene molecules have a significantly shifted electronic transition frequency and possess an altered spectrum. The combination of low-temperature spectroscopy of single molecules and hBN as a substrate for them provides new ways of studying the interaction of molecules with surfaces. This novel matrix has the potential to be applicable to a broad range of fluorescent molecules, which are not always easy to incorporate in standard matrices, and study them one-by-one.



RAMAN DIFFUSION ORDERED SPECTROSCOPY

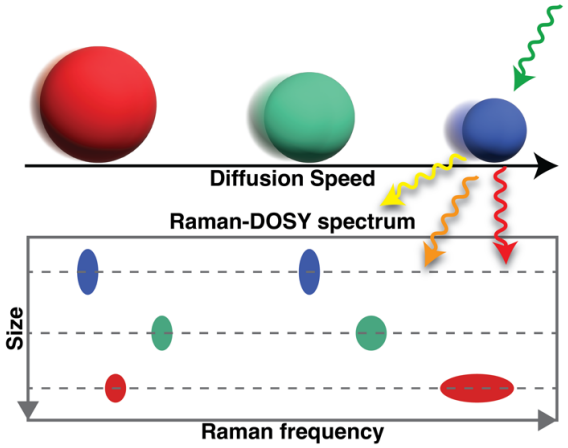
Robert W. Schmidt[1,2], Giulia Giubertoni[2], Federico Caporaletti[2], Paul Kolpakov[2], Noushine Shahidzadeh[2], Freek Ariese[1], Sander Woutersen[2]

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Measuring the diffusion constant is a well-known method to determine the size (hydrodynamic radius) of molecules, aggregates and particles. Here, we combine the size sensitivity of such diffusion-based methods with the structure sensitivity of Raman spectroscopy by performing Raman diffusion-ordered spectroscopy (Raman-DOSY), the Raman analog of NMR-DOSY. We demonstrate this new method on samples containing small molecules, proteins, and supramolecules (micelles).[1]

The core of the Raman-DOSY setup is a flow cell with a Y-shaped channel containing two inlets: one for the sample solution and one for the pure solvent.[2] The two liquids are injected at the same flow rate, giving rise to two parallel laminar flows in the channel. After the flow is stopped, the solute molecules diffuse from the solution-filled half of the channel into the solvent-filled half at a rate determined by their hydrodynamic radius. Their arrival is recorded in a spectrally resolved manner by Raman micro spectroscopy. From the time series of Raman spectra, a two-dimensional Raman-DOSY spectrum is obtained, which has the Raman frequency on one axis and the diffusion coefficient (or equivalently, size) on the other. In the case of mixed samples, the Raman-DOSY spectrum cleanly separates overlapping Raman peaks arising from molecules of different sizes, and we obtain size and structural information of all compounds in the mixture.

Raman-DOSY is label-free, does not require deuterated solvents, and can thus be applied to samples that might be difficult to investigate with other diffusion-based spectroscopy methods.



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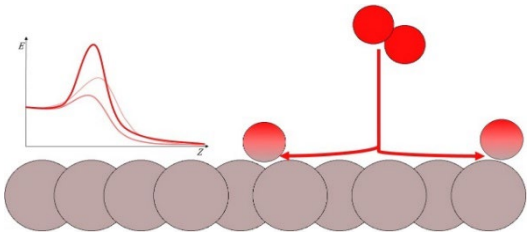
ACCURATE BUT EFFICIENT CALCULATIONS ON A TOUGH DISSOCIATIVE CHEMISORPTION REACTION

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

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

In the theory of molecule-on-metal interactions, density functional theory (DFT) at the generalized gradient approximation (GGA) level is usually considered a good compromise between feasibility and accuracy. Recent work, however, strongly suggests that density functionals (DFs) based on GGA exchange are not able to describe gas-metal systems if the charge transfer energy (i.e., the work function of the metal surface minus the electron affinity of the molecule) is less than 7 eV [1]. An infamous molecule-metal system showing such a low charge transfer energy is O_2 on Al(111). Historically, theoretical studies have had difficulties in accurately describing the O_2 + Al(111) reaction using conventional (GGA-based) methods. Systems with low charge transfer energy are hard to describe because they exhibit enlarged delocalisation of the electron density at the transition state. This delocalisation causes GGA-DFT to underestimate the reaction barrier energy, leading to overestimated reaction probabilities [1]. Gas phase reactions have suffered similar difficulties, suggesting that one should adopt the same strategy leading to success for gas phase systems. In line with this, results of increased accuracy were obtained with a (screened) hybrid density functional for O_2 on Al(111) [1].

However, no solution is free and (even screened) hybrid DFs in plane-wave-based DFT have exceptionally high computational costs. We attempt to reduce these costs along two lines of approach. First, we show that using a non-self-consistent DFT approach to developing a screened hybrid DF potential energy surface leads to an accuracy comparable to that of the fully self-consistent screened hybrid method for the reaction of O_2 on Al(111), at an order of magnitude lower computational cost. Second, we investigate the accuracy of the hole model [2] as a possible screening tool for DFs to describe gas-metal systems. In the hole model, barrier heights are sampled at a large (in principle complete) set of barrier geometries to compute an approximate reaction probability for a given DF. This method thus results in an overview of the corrugation and anisotropy of the reaction barrier as described by a specific DF. Since the hole model does not require a global PES its use leads to substantial savings in computational costs. Our results suggest that both lines of approach investigated can be used to reduce computational costs of future projects involving screened hybrid functionals for gas metal systems.



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ABSTRACT WINNER DICK STUFKENS PRIZE 2023

VERTEX CORRECTED GW-BETHE-SALPETER-EQUATION CALCULATIONS FOR SPECTROSCOPY

Arno Förster[1]

[1]*VU Amsterdam, Amsterdam, The Netherlands*

The *GW* approximation (*G*: single-particle Green's function, *W*: screened Coulomb interaction)-Bethe-Salpeter Equation (BSE) approach is a promising method for the calculation of optical excitations in complex systems. The *GW* approximation approximates Hedin's equations[1] by neglecting the so-called vertex corrections. Hedin's equations provide all single- and two-particle dependent properties of many-particle systems, including total energies, charged, and optical excitations.

In this contribution I will introduce Hedin's equations in an alternative form, which highlights their physical content[2]. I will then introduce the *GW*-BSE approximation, explain the underlying approximations, and discuss how it can be used to describe optical properties of molecules. Finally, I will discuss possibly strategies to improve over the *GW* approximation by calculating vertex corrections and discuss reasons why previous attempts to include vertex corrections for molecules failed[3–6].

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OVERVIEW POSTER SESSIONS

Session 1 10:30 – 11:20		
First name	Last name	Poster number
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Anna	Chernysheva	6
Nick	Gerrits	11
Vladimir	Grigorescu	12
Lukas	Hückmann	14
Andy	Jiao	16
Filipp	Kolomeichuk	18
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Juraj	Malinčík	23
Martijn	Mekkering	24
Quynh	Nguyen	25
Dana	Rademaker	29
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Session 2 13:00 – 13:45		
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Indigo	Bekaert	2
Steven	Beutick	3
Jasper	Bos	4
Sergey	Fisher	10
Matteo	Damian	7
Hassan	Javed	15
Jorn	de Jong	17
Remigiusz	Krecijasz	19
Sabine	Langens	21
Pan	Li	22
Leonardo	Passerini	28
Morgan	Regnier	30
Rafaël	Vos	40
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Session 3 14:55 – 15:45		
First name	Last name	Poster number
Pim	Broersen	5
Titus	de Haas	13
Nol	Duindam	8
Laura	Finazzi	9
Celine	Nieuwland	26
Imogen	Robertson	31
Said	Ortega Rosales	27
Edoardo	Spadetto	35
Jens	Tolboom	37
Lennard	Tweel	38
Daniela	Rodrigues Silva	32
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ABSTRACTS OF POSTERS

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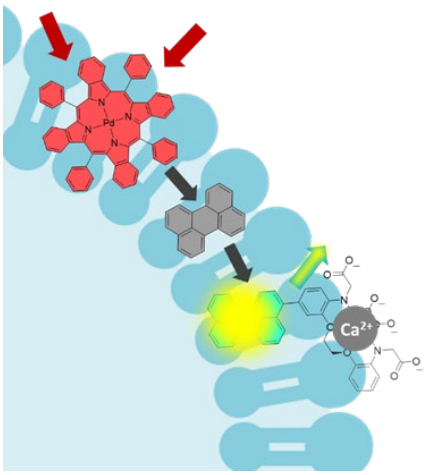
UPCONVERTING LIPOSOMES FOR CALCIUM SENSING IN CYTOSOLIC CONDITIONS

Valeriia D. Andreeva[1], Ilse Roosen[1], Sina K. Götzfried[1], Amrutha Prabhakaran[2], Haley Ehlers[3], Lenie van den Broek[3], Tia Keyes[2] Sylvestre A. Bonnet[1]

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Triplet-triplet annihilation upconversion-based (TTA-UC) metal cation sensors are potential *in vitro* and *in vivo* imaging agents because of background-free upconverting imaging and the use of tissue-penetrating red light. However, the application of these molecular systems in biology is limited by the low solubility of TTA-UC photosensitizers in water and the need for high annihilator concentrations to reach high upconversion quantum yields. Here, we report the first liposome-based TTA-UC system that, upon red light excitation, emit blue light in a calcium-dependent manner in aqueous solutions that model the cytosol. To prepare such liposomes we functionalized the lipid membrane of liposomes with a combination of the Pd(II)-tetraphenyltetrabenzoporphyrine – perylene TTA-UC couple and a perylene-based calcium chelator. The nature of the lipid mixture composing the membrane was found to strongly influence calcium sensing by upconversion in such liposomes, while mixing perylene with the perylene-BAPTA in the membrane was found critical for the sensitivity of the sensing system.

Upconverting liposomes for calcium sensing in cytosolic conditions preparation strategy.



Acknowledgements:
This project has received funding from the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 813920

ANION-INDUCED HELICAL FOLDING REMOTELY CONTROLLED BY LIGHT

Indigo M. Bekaert[1], Suchismita Saha[1], David Villarón[1], Maxime A. Siegler[1], Sander J. Wezenberg[1]

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

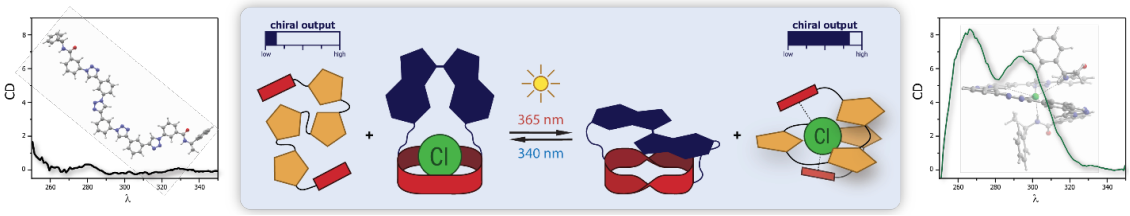


Figure 1**:** A stiff-stilbene strapped calix[4]pyrrole receptor and a chiral triazole foldamer are combined to form a rudimentary communication-type system with chloride functioning as the messenger.

An important aspect of living organisms is their ability to receive and respond to signals from the environment – a process that involves a complex network of signaling pathways. Mimicking these events in artificial molecular systems would offer fundamental understanding of biological communication processes, assist in efforts to emulate the complexity of life and allow for new routes to smart materials and pharmaceuticals.

We envisioned that synthetic photoresponsive receptors could be a powerful tool in the processing of information in such emulative supramolecular systems. Through irradiation with light a guest may be ejected, which can then function as a messenger to activate a secondary process.[1] Few artificial communication-type systems are known and guest variety is low.[2] Even though anionic species play an important role in signal processing and information storage in biology, they have not yet been used as messengers in this context.

In this work, a stiff-stilbene strapped calix[4]pyrrole receptor and a newly developed chiral oligo(aryl-triazole) foldamer that both bind chloride, are combined.[3,4] Light-induced isomerization of the photoreceptor releases chloride, which then functions as messenger to trigger helical folding of the oligo(aryl-triazole), generating a circular dichroism (CD) output. Back isomerization of the receptor with light of a different wavelength allows reuptake of the anion by the receptor and unfolding of the foldamer. A rudimentary communication-type process is thus created.

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UNDERSTANDING THE RETRO-COPE ELIMINATION REACTIVITY OF LINEAR ALKYNES

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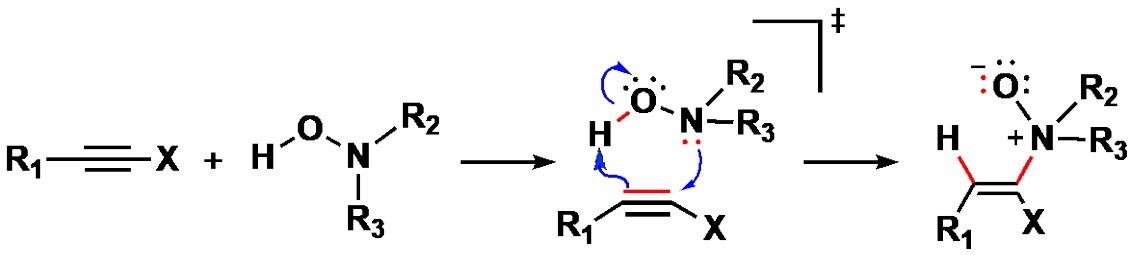
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We have quantum chemically investigated the bioorthogonal retro-Cope reaction of linear alkynes $R_3C{-}C{\equiv}C{-}X$ (R_3 = combinations of H, MeO, F; X = H, F, Cl, Br, I) with N,N-dimethylhydroxylamine using relativistic density functional theory at ZORA-BP86/TZ2P. This novel reaction can be tuned through judicious substitution of the alkyne at both the terminal and propargylic position to render second-order kinetics that rival and out-compete strain-promoted variants.[1] Using our activation strain and quantitative MO analyses, we are the first to tease apart the physical factors at the root of this reactivity enhancement upon terminal or propargylic substitution of propyne.



Aknowledgments

We would like to thank the Fondazione Cassa di Risparmio di Padova e Rovigo (Cariparo) and the Netherlands Organization for Scientific Research (NWO) for financially supporting this work.

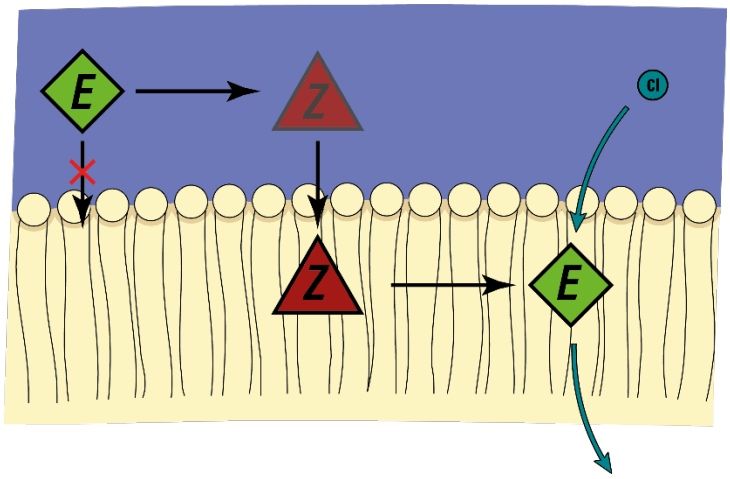
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PHOTOCONTROL OVER TRANSMEMBRANE ANION TRANSPORT THROUGH MODULATION OF MEMBRANE INCORPORATION AND MOBILITY

Jasper E. Bos[1], Maxime A. Siegler[2], Sander J. Wezenberg[1]

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The transport of anions across the cell membrane underlies many important regulatory functions in biology, and is controlled by proteins that respond to external stimuli. In recent years several artificial transporters have been developed,[1] of which a few can be controlled by modulation of their binding affinity in response to stimuli,[2] e.g. light.[3,4]

However, differences in transport activity between photoaddressable states were found to be much larger than what can be explained based on the difference in binding affinity alone, indicating that additional factors related to the photoswitching process played an important role. We show here that the activity of an anion transporter can be controlled by changing both membrane solubility and mobility using light, while the anion binding site remains virtually unaltered. This study will be of great importance to the future design and improvement of anion transport systems and is an important step towards their application in biological systems.

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SELECTIVE ELECTROCHEMICAL METHANOL OXIDATION TO FORMALDEHYDE

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Amanda C. Garcia[1]

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Formaldehyde is one of the most important bulk chemicals with a high market share. Traditional synthesis of formaldehyde is achieved via selective oxidation of methanol over a silver or iron oxide catalyst. This is an energy intensive process as it requires temperatures of 250 °C or higher. An electrochemical approach that can perform this reaction at room temperature is therefore an interesting approach to make this process greener.

Most research into the electrochemical oxidation of methanol focusses on fuel cell applications, whereby the full oxidation of methanol to CO_2 is desired.[1] Therefore, formaldehyde is an unwanted side product. Formaldehyde electrosynthesis from methanol is therefore rather unexplored. We thought a heterogeneous molecular approach could achieve selective methanol oxidation. Therefore, we synthesized a TEMPO polymer that has been used in previous alcohol oxidation reactions.[2] Using neat methanol as our solvent and reactant, the TEMPO polymer performs the electrooxidation of methanol to formaldehyde with Faradaic Efficiencies higher than 90%. Since methanol also acts as a formaldehyde stabilizer, this prevents both overoxidation and evaporation of the methanol, making the product easier to handle and analyze.

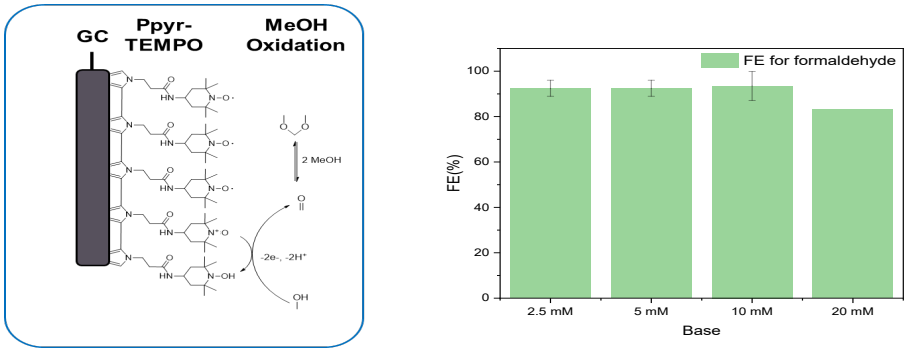


Figure 1: General design of the Methanol oxidation catalyst (left) and Faradaic efficiency (right).

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FROM INORGANIC PHOSPHATES TO ORGANIC: HOW TO IMPROVE THE PHOSPHORUS INDUSTRY?

Anna Chernysheva[1], C. Lillian Bisschop[1,2], G. Bas De Jong[1], J. Chris Slootweg[1]

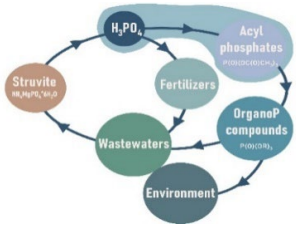
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Currently, the phosphorus industry is a complex and energy-consuming process, which involves non-renewable resources, such as phosphate rock (mostly fluorapatite, Ca5(PO4)3F) located mainly in Morocco [1]. For example, to make pure organophosphorus compounds with flame-retardant properties, now it is necessary to reduce phosphate rock to toxic white phosphorus P4. The next step includes phosphorus oxidation and the production of halogenated phosphorus compounds, such as PCl3, PCl5, etc. Only after this reduction-oxidation cycle, it is possible to obtain benign organophosphorus compounds [2].

Now it is necessary to think about this problem because of the expected crisis. The population of our planet is growing and this growth should decline only after 60 years [3]. In order to meet both the growing demand for phosphorus-containing products and to reduce the amount of phosphorus ending up in the environment after use, it is interesting to use wastewater as a renewable source of phosphorus. This approach will also help to avoid such a negative phenomenon as eutrophication – excessive growth of algae on the water surface which is dangerous for fish and other living creatures [4].

It is already known how to make phosphoric acid from the wastewater. But how to obtain benign organophosphorus compounds from the phosphoric acid avoiding unnecessary reduction-oxidation cycles? The idea of this project is trying to answer that question. The aim of that project is to find a lost chain between phosphoric acid and benign organophosphorus compounds.



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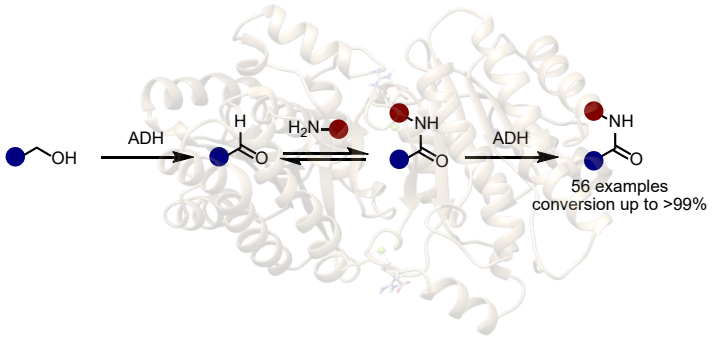
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A New Reaction with a Known Enzyme: Enzymatic Coupling of Alcohols and Amines to Synthesize Amides

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The synthesis of amides is of great significance in both chemistry and biology as especially evidenced in medicinal chemistry patents.[1] Despite numerous approaches are described in the literature, many of them suffer from poor atom efficiency and wasteful byproduct generation.[2] Inspired by *i)* the pioneering work of Milstein on amide synthesis through the coupling of alcohols and amines,[3] *ii)* our group's research on nitrile synthesis which highlighted an interesting hemiaminal intermediate[4] and *iii)* the remarkable activity exhibited by one alcohol dehydrogenase (ADH) in accessing lactams,[5] we devised a method to produce amides from alcohols and amine-rich buffers using ADHs. Initially, we tested Cm-ADH and Pf-ADH, which we have previously investigated in-depth for the selective reduction of prochiral ketones due to their anti-Prelog selectivity and NAD dependency. Pf-ADH exhibited the desired activity, successfully transforming the corresponding alcohol into the amide. Subsequently, we assessed five additional ADHs, and notably, five out of seven demonstrated the ability to catalyze the coupling of alcohols and amines, thereby opening the door to a promising new synthetic methodology.



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MONODIRECTIONAL PHOTOCYCLE DRIVES PROTON TRANSLOCATION

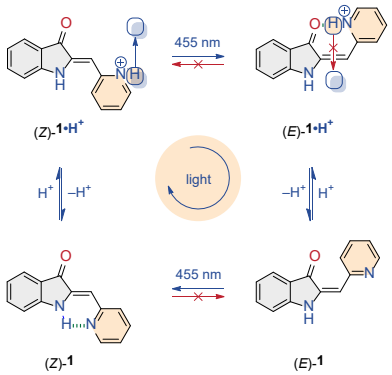
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Photoisomerization of retinal in bacteriorhodopsin is at the basis of proton pumping across the bacterial membrane. Synthetic systems capable of directionally moving macrocyclic rings over a nonsymmetric axle[1] have been developed, but analogous light-driven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

We describe unique protonation-controlled isomerization behavior for hemi-indigo dyes bearing N-heterocycles[2], featuring intramolecular hydrogen bonds. Light-induced isomerization from the Z to E isomer is unlocked when protonated, while reverse E → Z photoisomerization occurs in the neutral state. Since in the presence of acid the neutral and protonated hemi-indigo species are in equilibrium, they are interchanged photochemically in a specific order under irradiation with a single wavelength of light, giving rise to a unique monodirectional photocycle of interconversion.[3] As a consequence, associated protons are displaced in a preferred direction with respect to the photoswitchable scaffold.

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



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PREFERRED PROTONATION SITE OF AROMATIC AMINES: ELUCIDATION VIA IR ION SPECTROSCOPY

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Aromatic amines, such as aniline and its polycyclic derivatives, present basic characteristics leading to two possible distinct protonation sites: the amino group or one of the carbons of the ring(s). However, the preferred protonation sites in the gas phase may differ from the ones in solution as the solvation energy is typically much larger for the charge-localized amine-protonated tautomer as compared with charge-delocalized ring protonated tautomers. For this reason, the structural elucidation of protonated aniline and substituted anilines has been a topic of extensive theoretical[1] and experimental work[2], which led to the conclusion that proton affinities are highly dependent on experimental conditions and level of theory employed. In this work, we carry out spectroscopic studies on aromatic amines to assess the specific protonation sites, in particular, the research question we want to tackle is how the presence of additional aromatic rings influences the favoured protonation site. The candidates that we propose to study for this project are two possible constitutional isomers of aminonaphthalene and aminoanthracene.

The spectroscopic characterization of these species is carried out combining mass spectrometry (MS) and infrared (IR) spectroscopy techniques. MS is an effective tool for ion formation and their preliminary characterization; however, it does not provide detailed structural information, e.g. to distinguish the various isomers. IR spectra of mass-selected ions provide the unique fingerprint of each molecular system, enabling to discern one isomeric structure from the other. Comparison of the experimental IR spectra with quantum chemical calculations allows to precisely assign the ion molecular structure and assess the impact of electronic and steric effects on the protonation site. The IR spectra of 1-aminonaphthalene, 2-aminonaphthalene, 1-aminoanthracene and 2-aminoanthracene have been recorded on an ion trap mass spectrometer coupled with the free-electron laser for infrared experiments (FELIX) and revealed the presence of multiple isobaric species contributing to the observed bands. Determining which isomer gives rise to the observed features will be carried out on a FTICR mass spectrometer equipped with a trapped-ion mobility spectrometry (TIMS) unit, which not only can measure mobilities and collisional cross sections but also might be used as a filter to record IR spectra of mobility-selected ions. Preliminary TIMS studies revealed the presence of distinct mobility peaks for each molecule. We aim to repeat these measurements and record mobility-selected IR spectra of all the isobaric species.

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TOWARDS HETEROLEPTIC COVALENT ORGANIC CAGES

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Over the past decade, the field of porous organic cages (POCs) has emerged, providing access to a diverse array of microporous materials. Despite the intricate three-dimensional structure of POCs, these compounds can be readily obtained in a single step via reversible dynamic covalent chemistry (DCC) under conditions of thermodynamic control, ensuring high yields. With their combination of diverse optoelectrical properties, shape-persistent porosity, and ease of handling, POCs present an intriguing platform for a variety of applications.[1,2] Nevertheless, instances of POCs in literature predominantly feature highly symmetrical architectures, making the reduction of symmetry a challenging endeavour. POCs with lower symmetry possess the potential to introduce desirable attributes for photochemistry and catalysis, capitalizing on the directional electronic field between meticulously arranged donoracceptor interfaces.

Our experiments reveal that the formation of our rylene diimide cages does not rely on thermodynamic control, but instead on kinetic reaction control, leading to the formation of cages as a metastable state being deep kinetic traps.[1,3–5] By comprehending the reaction pathway and the stabilities of crucial synthetic intermediates during the synthesis of the cages, a strategy for selective creation of lower symmetry POCs can be proposed. We successfully isolated and characterized pivotal intermediates using NMR, high-resolution MS, and single-crystal x-ray diffraction, which were subsequently employed in the synthesis of lower symmetry cages. This step-wise approach facilitates a modular synthesis, enabling the introduction of diverse chromophores that result in POCs with new physical properties which are customizable for specific applications.

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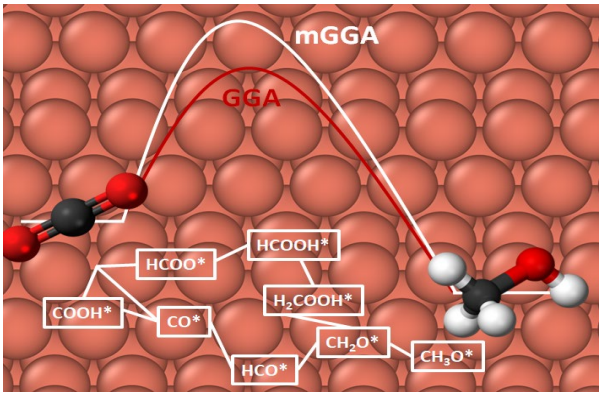
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IMPROVING MOLECULE-METAL SURFACE REACTION NETWORKS USING THE META-GENERALIZED GRADIENT APPROXIMATION: CO_2 HYDROGENATION

Nick Gerrits[1,2]

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[2]*Research group PLASMANT, Department of Chemistry, University of Antwerp, Antwerp, Belgium*

Density functional theory (DFT) is widely used to gain insight in molecule-metal surface reaction networks, which is important for a better understanding of heterogeneous catalysis. However, it is well known that generalized gradient approximation (GGA) density functionals (DFs), most often used for the study of reaction networks, struggle to correctly describe both gas-phase molecules and metal surfaces. Also, GGA DFs typically underestimate reaction barriers due to an underestimation of the self-interaction energy. Screened hybrid GGA DFs have been shown to (partially) solve this problem, but are currently intractable for wide usage in molecule-metal surface studies.[1] In this work we use a more affordable meta-generalized gradient approximation (mGGA) DF in combination with a non-local correlation DF for the first time to study a catalytically important surface reaction network, namely CO_2 hydrogenation on Cu.[2] We show that the mGGA DF used, namely rMS-RPBEl-rVV10, outperforms GGA-vdW DFs, especially in describing gas-phase molecules and predicting barriers. We demonstrate that this mGGA DF is also a better choice for constructing molecule-metal surface reaction networks.



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PROBING THE PHOTOREDOX CATALYSIS MECHANISM OF PERYLENE DIIMIDE CAGES WITH ULTRAFAST VISIBLE SPECTROSCOPY

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Photocatalysis offers the possibility of novel reaction pathways for the cost-effective production of valuable chemicals with various applications. For example, a photosensitiser can yield a strongly reducing anionic radical, which can then react with a large variety of commercially available substrates under mild conditions [1]. Perylene diimides (PDIs) are a well-studied class of dyes that feature strong, tuneable absorption in the visible range and chemical stability. They also exhibit excited states with reductive properties suitable for photocatalysis. They have therefore been used as single-molecule catalysts for this type of reaction [2]. Supramolecular assemblies containing PDI centres can advance these materials by increasing selectivity through pre-organisation of the photosensitiser and substrate [3]. Here we apply femtosecond transient absorption spectroscopy to investigate the photocatalytic mechanism of a single-molecule PDI photosensitiser (PDI-Pyr2) and compare it to a supramolecular square assembly (PDI-C) which contains two such chromophores.

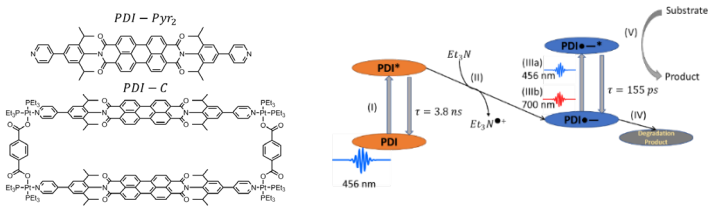


Figure Left – structures of PDI-Pyr$_2$ and PDI-C; Right – Schematic catalytic mechanism

Our preliminary results agree with literature that the mechanism whereby PDIs catalyse this reaction involves an initial excitation at 456 nm to a singlet excited state (I), which is reduced by Et_3N, yielding a stable radical (II). The suggested subsequent steps are in question, as the $PDI^{\bullet-}$ does not absorb 456 nm (IIIa), while excitation under radiation >650 nm (IIIb) is possible, but too short-lived to react in solution [4, 5]. Finally, a photodegradation product (IV), which then performs the dehalogenation (V) is possible, but this species has not been characterised [6]. This suggests that the proposed mechanism still contains many open questions that need to be addressed.

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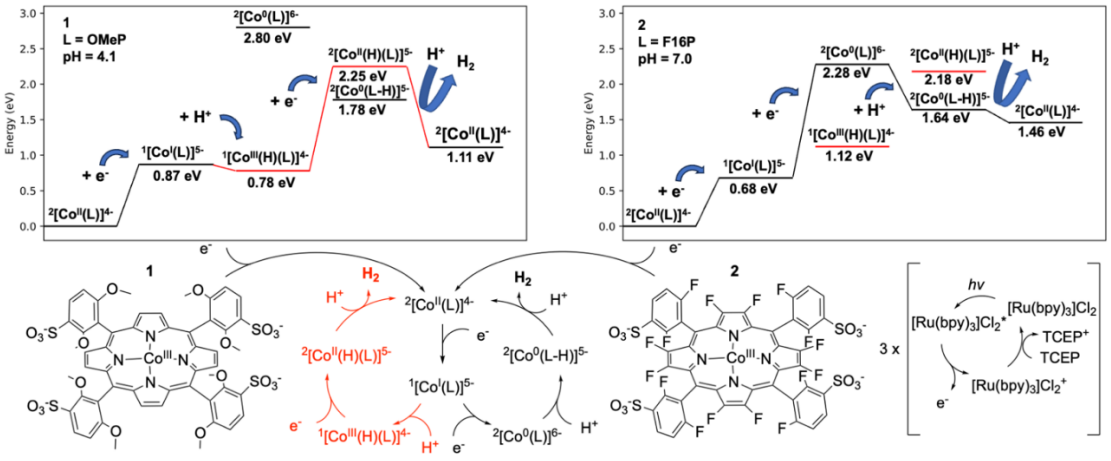
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TUNING THE CATALYTIC MECHANISM IN COBALT PORPHYRIN COMPLEXES TO ENHANCE PHOTO-INDUCED H_2 EVOLUTION

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Light-induced H_2 evolution in aqueous solutions has garnered considerable attention for its potential use in solar-to-energy production. For a practically useful hydrogen evolution process, catalysts capable of operating at a low overpotential and in mild conditions are essential. In this study, a series of four cobalt porphyrin complexes was synthesized, in which the electron density on the cobalt center was tuned by introducing both electron-donating and electron-withdrawing groups onto the porphyrin macrocycle. Subsequently, the complexes were studied for their light-induced hydrogen evolution activity in aqueous solutions at pH 4.1 and pH 7. Interestingly, the catalyst with the most electron donating substituents (**1**) performs best in acidic conditions, while the catalyst with electron withdrawing substituents (**2**) performs better in neutral conditions.[1] Based on DFT calculations and electrochemical experiments, we propose two distinct catalytic cycles for these two catalysts. After reduction of the active $^2[Co^{II}(P)]^{4-}$ catalyst, **1** undergoes oxidative protonation at the metal center, followed by concerted electron and proton transfer to form H_2 and recover the initial catalyst. In contrast, **2** undergoes protonation only after a second reduction. Because the second reduction is mostly porphyrin based, a ligand-based mechanism is now more favorable (see figure below).[2] This work offers fundamental insights into the catalytic mechanism of water-soluble hydrogen evolution catalysts, with potential implications for solar-to-fuel conversion.



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INTRINSIC CHARGE TRAPPING AND REVERSIBLE CHARGE INDUCED STRUCTURAL MODIFICATION IN AMORPHOUS SILICON NITRIDE

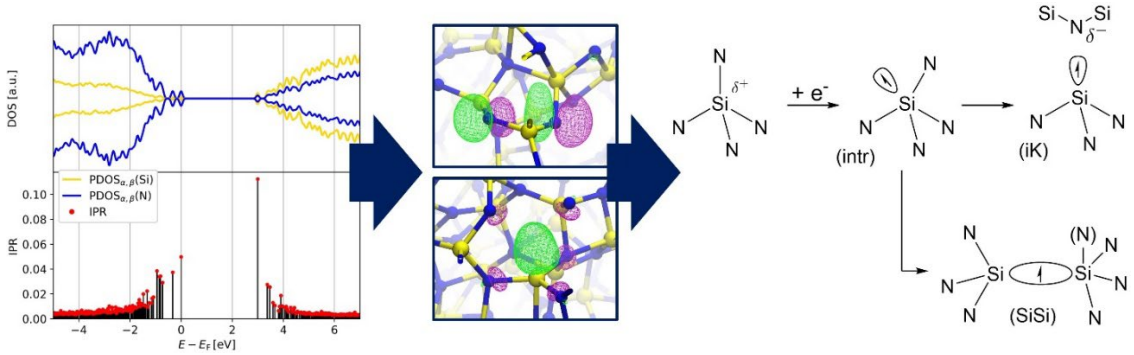
Lukas Hückmann[1], Jonathon Cottom[1], Jörg Meyer[1]

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Amorphous silicon nitride (a-Si_3N_4) is an essential material for nanoelectronics due to its unique ability to trap charges long-term, which is prominently used in flash memory devices. Photoemission and EPR experiments combined with electronic structure calculations suggest Si-centered defects (K-centers) being responsible for this phenomenon.[1-3] The propensity of such defects towards passivation, oxidation, and annealing, however, raises the question of the completeness if this prevalent picture.

In this work,[4] we combine simulations at force field (FF) and density functional theory (DFT) level. Hundreds of structural models for a-Si_3N_4 are created with the melt-quench procedure using the MG2-FF. Adding charges to those models, we perform structural optimization and electronic characterization using the PBE and HSE06 density functionals, respectively. Combined with a new compact descriptor to characterize local distortions, this holistic approach facilitates to generate statistically meaningful distributions of "defects" in amorphous materials.

We identify a hitherto unknown mode of intrinsic polaronic trapping of electrons in a-Si_3N_4: Charging can generate either a K-center or a Si-Si-type defect. At the same time, discharging recovers the amorphous network's original ("defect-free") structure. Such significant and reversible structural modifications upon charging offer a new understanding of discrepancies between charge-trapping and defect concentrations observed experimentally.



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A Structural Model For Transient Pt Oxidation During Fuel Cell Start-Up Using Electrochemical X-Ray Photoelectron Spectroscopy

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Potential spikes during the start-up (SU) and shutdown (SD) of fuel cells are a major cause of platinum (Pt) electrocatalyst degradation, which limits the lifetime of the device[1]. The electrochemical oxidation of Pt that occurs on the cathode during the potential spikes plays a key role in this degradation process[2]. However, the composition of the oxide species formed, as well as their role in catalyst dissolution remains unclear. In this study, we employ a special arrangement of XPS (X-ray Photoelectron Spectroscopy), in which the Pt electrocatalyst is covered by graphene, making the in situ examination of the Pt oxidation/reduction under wet conditions possible. We use this assembly to investigate oxidation state changes of Pt within fuel cell relevant potential window. We show that above 1.1 VRHE, a mixed Ptδ+/Pt2+/Pt4+ surface oxide is formed, with an average oxidation state that gradually increases as the potential is increased. By comparing a model based on the XPS data to the oxidation charge measured during potential spikes, we show that our description of Pt oxidation is also valid during the transient conditions of fuel cell SU/SD. This is due to the rapid Pt oxidation kinetics during the pulses. As a result of the irreversibility of Pt oxidation, some remnants of oxidized Pt remain at typical fuel cell operating potentials after a pulse.

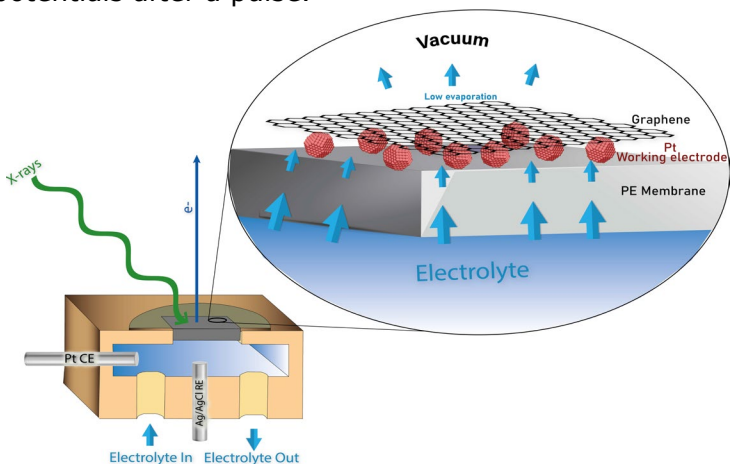


Figure 1: Schematic diagram and functioning of the in situ XPS cell

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BINDING OF FLAT PAHS AND GRAPHENE WITH MOLECULAR TWEEZERS

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Graphene is atomically thin and conductive, which makes it an interesting material for molecular sensing such as DNA sequencing.[1] However, applicability of graphene remains limited due to the difficulties in functionalizing the graphene edges, as many impurities and defects can be introduced during sculpting and electrografting of graphene. The introduction of impurities and defects can be avoided by functionalizing the graphene edges using non-invasive supramolecular forces. To this end, defect-free graphene functionalization is envisioned to be possible using molecular tweezers as graphene edge clamps. One such molecular tweezer has been synthesized, which is shown to bind polycyclic aromatic hydrocarbons (PAHs) such as pyrene and coronene with binding constants in the order of 10^4 M^{-1}.[2] The next challenge is how to determine the exact binding mode of the molecular tweezer with larger PAHs and graphene.

References

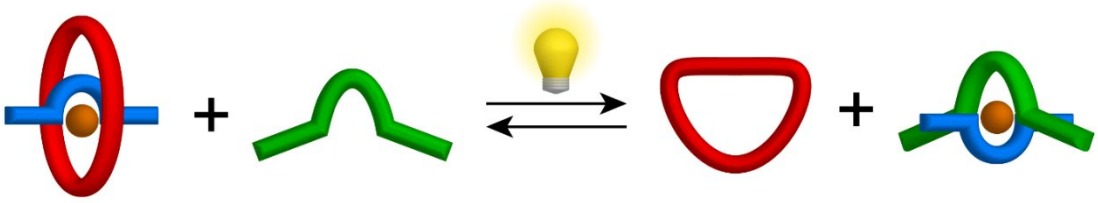
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PHOTOCONTROLLED THREADING OF ANION-TEMPLATED PSEUDOROTAXANES

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In recent years, the use of molecular machines to control motion on the nanoscale has gained significant interest.[1] Several approaches have been taken to create new types of molecular machines able to perform specific functions. Herein, pseudorotaxanes have played an important role, e.g. in the development of supramolecular pumps and ratchets, where an external stimulus can be used to regulate threading.[2] While reported examples are still limited, notable current strategies have made use of light as a stimulus to control binding affinity and kinetics of crown ether-ammonium complexes.[3] To extend the versatility and modularity of such systems, we have developed photoresponsive pseudorotaxanes making use of the anion-templated approach reported by Beer.[4] Our design is based on stiff-stilbene light-switchable macrocycles of which the *Z*-isomer is able to form a pseudorotaxane structure upon addition of a pyridinium halide axle, *via* anion binding between the three components.[5] Photoisomerization to the *E*-isomer leads to contraction of the macrocycle and concomitant dethreading. Interestingly, addition of a secondary host to the pseudorotaxane system allowed for light-triggered translocation of the axle between the macrocycle and this secondary host. The presented approach opens up new opportunities towards the development of molecular machines and stimuli-responsive mechanically-interlocked anion receptors.

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INVESTIGATION OF THE ROLE OF TRIPHENYLPHOSPHINE OXIDE AS AN ELECTROLYTE ADDITIVE FOR LI-ION BATTERIES

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Recently triphenylphosphine oxide (TPPO) was shown[1] to be a viable electrolyte additive to enhance the safety and performance of Ni-rich cathodes in Li-ion batteries. Ni-rich cathodes offer increased specific capacity at higher voltages compared to the conventional Li-ion batteries, making them attractive for energy storage applications. However, their practical utilization is hindered by safety and thermal stability concerns that traditional additives (vinylene carbonate, trimethylsilyl phosphate[2]) fail to mitigate.

Electrolyte additives play a critical role in Li-ion battery performance, influencing factors such as ionic conductivity and the formation of the solid-electrolyte interphase (SEI). TPPO, in particular, has shown promise as an SEI modifier, addressing the shortcomings associated with Ni-rich cathodes.

This research seeks to uncover the underlying chemical mechanisms at the cathode-electrolyte interface when TPPO is introduced as an additive. By elucidating these mechanisms, the study aims to contribute to a deeper understanding of Li-ion battery operation and facilitate the safe integration of Ni-rich cathodes into next-generation energy storage solutions.

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STIMULI-RESPONSIVE FERROCENE MOLECULAR NANOHOOPS

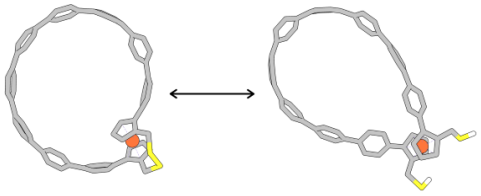
Remigiusz Krecijasz[1], Tomas Solomek[1]

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[*n*]Cycloparaphenylenes ([*n*]CPPs) are macrocycles consisting solely of *n* benzene rings connected via their para positions. They represent the shortest armchair carbon nanotubes. Although envisioned decades ago, the first synthesis of these strained molecules was accomplished only in 2008[1] and opened new frontiers in aromatic hydrocarbons research. Small [*n*]CPPs (*n* = 5–12) exhibit unique size-dependent optoelectronic properties with applications in bioimaging, sensing and optoelectronic materials.[2]

[*n*]CPPs possess a rigid cavity with a high electron density making them excellent hosts for electron-poor guests. As an example, fullerene C_{60} is encapsulated by [10]CPP with impressive $K_a = 2.79 \times 10^6$ L^{-1} mol in toluene, due to the matching size and curvature of the host and the guest.[3] However, C_{60} cannot be easily released because it is not yet possible to adjust the shape of the cavity. Controlling the shape of the cavity reversibly, e.g., through an external stimulus, would open new avenues to govern the [*n*]CPP–guest interactions. To this date, there is a single attempt to achieve such control by incorporating azobenzene photoswitch into [*n*]CPP structure.[4] However, the switching is strongly limited by the [*n*]CPP size.

In this work, I use ferrocene as a molecular hinge in the [*n*]CPP backbone to alter the macrocycle curvature reversibly. The control over the geometry of the cavity will thus allow for uptake and release of guests, such as fullerenes, at will. Moreover, since ferrocene is a known mechanophore,[5] incorporation of ferrocene–[*n*]CPPs into polymers will allow to tailor their macroscopic response to mechanical stress.



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Acknowledgements

We thank European Research Council (ERC) (Grant Agreement No. 949397) for the funding of this research.

AB INITIO MOLECULAR DYNAMICS SIMULATIONS TO UNRAVEL GLYCOSYLATION REACTION MECHANISMS

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Synthetic oligosaccharides are indispensable tools in chemical glycobiology, to unravel and manipulate the role of these important biomolecules in biological processes. However, the synthesis of oligosaccharides is an arduous and labor-intensive process, requiring a significant amount of time-consuming trial-and-error to optimize the 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*. DFTbased 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, and that unlike static calculations a decrease of acceptor nucleophilicity is associated with a shift towards S_N1-type mechanisms.

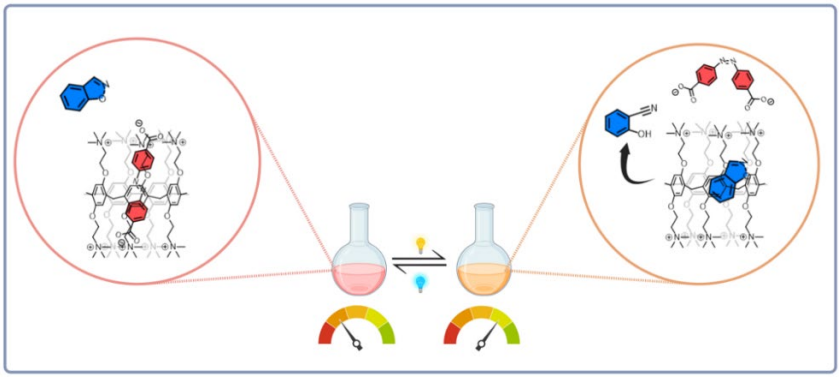
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SUPRAMOLECULAR CONTROL OVER PILLARARENE-CATALYZED KEMP ELIMINATION WITH A PHOTORESPONSIVE INHIBITOR

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Chemical transformations in biological systems are catalyzed in a highly efficient manner by enzymes, which are able to respond to stimuli in their environment. Chemists have developed efficient artificial catalysts for advanced chemical conversions, however, little effort has been targeted towards controlling catalysis in a dynamic fashion.[1] Nevertheless, dynamic control over catalysis is of high interest for tandem and relay catalysis. Dynamic control is typically achieved by introducing responsive motifs into the catalyst backbone. This approach has drawbacks, however, including tedious syntheses and loss of function, limiting broader application. Competitive, non-covalent binding of a switchable inhibitor to regulate catalytic activity could offer a solution, but has only been demonstrated successfully once for a specific organocatalyzed Michael addition in organic solvent.[2]

Here, we present catalytic activity modulation of a more versatile catalyst, pillar[5]arene, by light-controlled binding of azobenzene-4,4-dicarboxylate in aqueous conditions. Pillar[5]arene was shown to catalyze Kemp elimination reactions.[3] We show that binding of the (*E*)-isomer to pillar[5]arene blocks substrate binding and hence, diminishes catalytic conversion. UV-light irradiation yields the (*Z*)-isomer, resulting in its expulsion from the cavity. This allows for substrate binding, which leads to accelerated conversion. Blue light irradiation can reinstate the inactive form of the catalyst. We envision that our system can be expanded towards feedback control. Additionally, it assists the development of modular dynamic tandem and relay catalysis towards chemical reaction networks.

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Keywords: Stimuli-control, supramolecular chemistry, photoswitch, catalysis, anion binding, dynamic molecular systems

NANOSCALE THERMOMETRY OF PLASMONIC STRUCTURES VIA RAMAN SHIFTS IN COPPER PHTHALOCYANINE

Pan Li[1,*], Sven H. C. Askes[1,*], Esther del Pino Rosendo[2], Freek Ariese[1], Charusheela Ramanan[1, 2], Elizabeth von Hauff[1, 3, 4], Andrea Baldi[1]

[*]equal author contribution

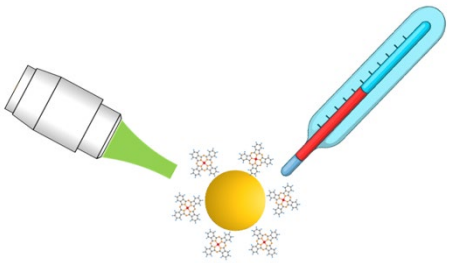
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Temperature measurements at the nanoscale are vital for the application of plasmonic structures in medical photothermal therapy and materials science, but very challenging to realize in practice. In this work, we exploit a combination of surface enhanced Raman spectroscopy together with the characteristic temperature dependence of the Raman peak maxima observed in β-phase copper phthalocyanine (β-CuPc) to measure the surface temperature of plasmonic gold nanoparticles (NPs) under laser irradiation. We begin by measuring the temperature dependent Raman shifts of the three most prominent modes of β-CuPc films coated on an array of Au nanodisks over a temperature range of 100 K to 500 K. We then use these calibration curves to determine the temperature of an array of Au nanodisks irradiated with varying laser powers. The extracted temperatures agree quantitatively with the ones obtained via numerical modelling of the electromagnetic and thermodynamic properties of the irradiated array. Thin films of β-CuPc display low extinction coefficients in the blue-green region of the visible spectrum as well as exceptional thermal stability, allowing a wide temperature range of operation of our Raman thermometer, with minimal optical distortion of the underlying structures. Thanks to the strong thermal response of the Raman shifts in β-CuPc, our work opens the opportunity to investigate photothermal effects at the nanoscale in real-time and over single-nanoparticles.



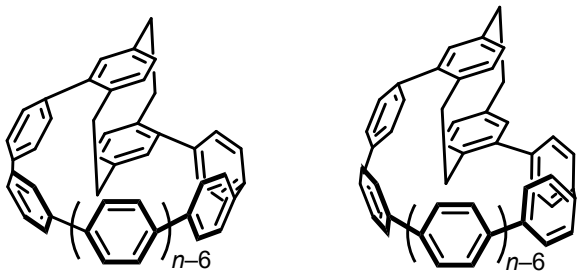
CRITICAL EVALUATION OF SPIRAL *PARA*-PHENYLENES AS CIRCULARLY POLARIZED LUMINOPHORES

Juraj Malinčík[1], Tomáš Šolomek[1]

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Materials that exhibit circularly polarized luminescence (CPL) are desirable for the development of optoelectronic devices, such as circularly polarized light-emitting diodes and photodetectors. Furthermore, CPL has the potential to provide new insights into the mechanism of photoluminescence and to develop new materials for advanced technologies. Cycloparaphenylenes ([*n*]CPPs), are excellent candidates for CPL materials due to their favorable luminescence properties, such as visible-light fluorescence with a high quantum yield and large Stokes shifts, as well as good processability.[1] However, CPPs are achiral which prevents them from displaying CPL. The issue could be circumvented by introducing a stereogenic unit into the structure of CPPs.[2]

In this contribution, we present a series of carbon nanohoops that incorporate a [2.2]paracyclophane (PCP) moiety into the structure of [*n*]CPPs. We name the resulting carbon nanohoops as spiral *para*-phenylenes, abbreviated as [*n*]SPPs, where *n* defines the number of phenylenes. These compounds could be utilized as chiral luminophores because PCP moiety becomes chiral when incorporated into a macrocycle. We investigated the electronic structure of [*n*]SPPs with both *para*- and *meta*-connection to the PCP moiety in both their ground and excited states to rationalize the design of chiral carbon nanohoops with a high quantum yield and emission dissymmetry factor. *p*[9]SPP was synthesized recently by Du group.[3] Therefore, we are also comparing our computational results with the known experimental data.



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BOTTOM-UP SYNTHESIS OF STABLE PLATINUM DIMERS ON CERIUM OXIDE

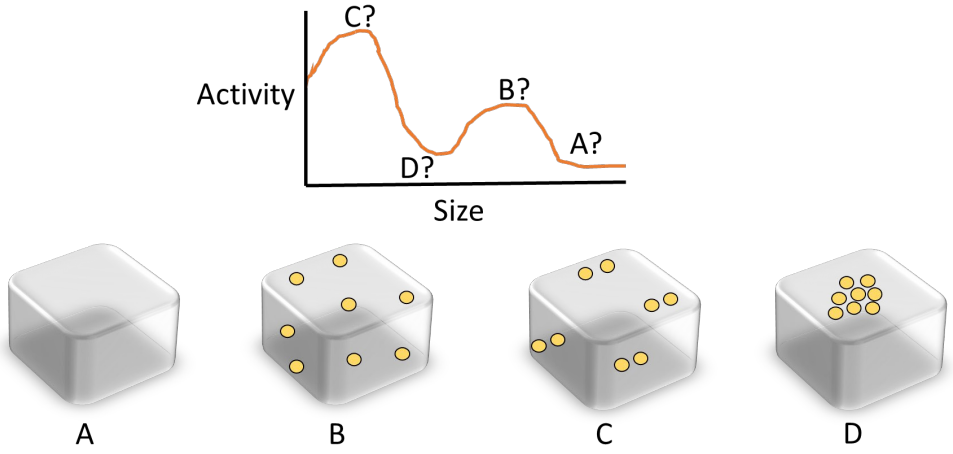
Martijn J. Mekkering[1], Petrus C. M. Laan[1], Alessandro Troglia[2], Roland Bliem[2], Gadi Rothenberg[1*], Ning Yan[3*]

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Analogous to the well-known single-atom catalysts (SACs) we present here the synthesis and performance testing of dual-atom catalysts (DACs). These feature sites containing pairs of metal atoms, and can outperform SACs thanks to their additional binding possibilities. Yet quantifying the improved catalytic activity in terms of proximity effects is difficult, as it requires both an understanding of the reaction mechanism and high-resolution kinetic data. Here we use an automated bubble counter setup to compare the catalytic performance of ceria-supported platinum SACs and DACs in ammonia borane hydrolysis. The catalysts are characterised using XPS, SEM and CO-DRIFTS. Kinetic studies of the SACs show two temperature-dependent regions, with a transition point at 44 °C. Conversely, the DACs, that can activate the water molecules also at low temperatures, show only one regime. The additional proximal Pt atom improves the reaction rate three-fold, enabling faster reactions at lower temperatures. Importantly, both the energy of activation and the pre-exponential factor are affected. The former is lowered as the DACs enable the activation of the water O–H bond, while the latter is increased thanks to an improved hydrogen spillover effect due to the adjacent Pt site. Interestingly, using ammonia borane hydrolysis as a benchmark reaction gives further insight with regard to spilllover mechanisms, above that which is available from traditional CO oxidation studies.

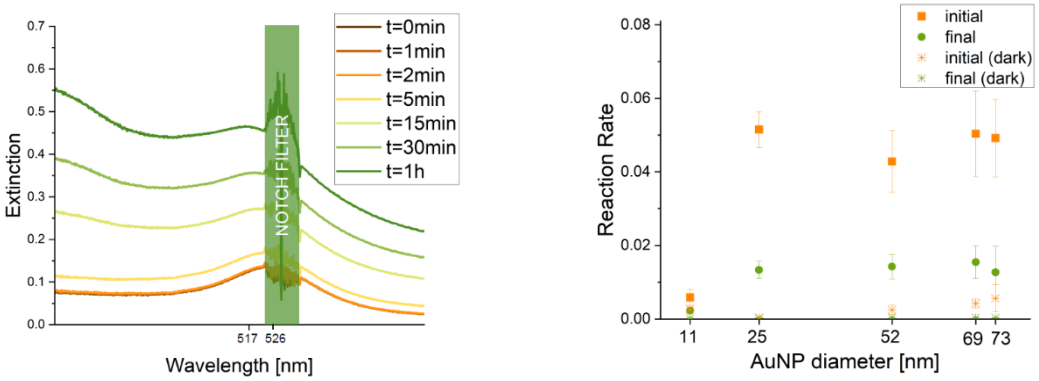


HARVESTING PLASMONIC HOT HOLES

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Noble metal nanoparticles (NPs) exhibit exceptional light scattering and absorption, thanks to so-called localized surface plasmon resonances (LSPRs). These resonances originate from light-driven oscillations of free electrons and can be used in a variety of applications, from opto-electronics to photochemistry and optical sensing.
Recently, plasmonic nanostructures have been thoroughly investigated for their potential application in photocatalysis thanks to their ability to generate hot electrons and hot holes upon excitation with light. These non-thermalized charge carriers can be harvested to drive redox reactions at the surface of the metal, but it remains unclear how efficient this process is, particularly considering their very short lifetime.
In this study, we investigate the light-driven synthesis of Au@Ag core@shell structures, where the growth of the Ag shell is facilitated by hot holes originating from interband transition in the Au cores. Previous studies have suggested that the mean free path of a d band hole is limited to 4 nm, which makes the growth of the Ag shell challenging, particularly for large Au NPs and thick Ag shells.[1-3]
To elucidate the photochemical role of the mean-free path of d-band holes, we study the Ag shell growth over Au nanoparticles of varying sizes and compare the rates in the dark and under plasmon excitation.
Our results show surprisingly similar reaction rates on AuNPs of different diameters.



(Left) Time evolution of Ag-shell growth on 25nm AuNPs. The LSPR shifts from 526 nm to 517 nm after a reaction time of 1h. (Right) Initial and final reaction rates of the Ag shell growth on AuNP different diameters during plasmon excitation using a 532 nm CW laser and in the dark.

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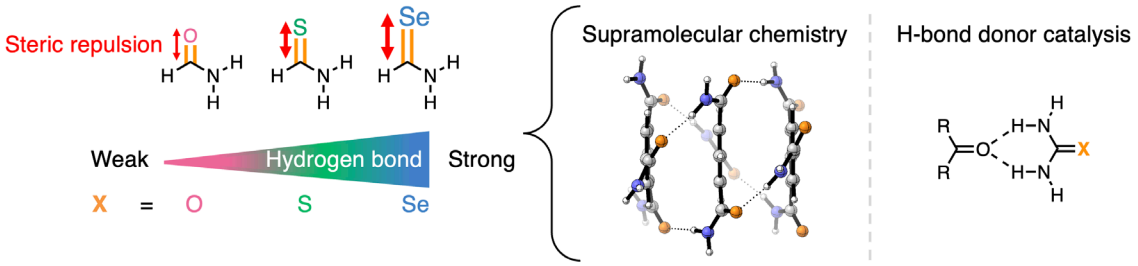
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How the Chalcogen Atom Size Dictates the Hydrogen-Bonding Capability of Amides

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Thioamides ($H_2NC(=S)R$) and selenoamides ($H_2NC(=Se)R$) can form stronger hydrogen bonds (H-bonds) than carboxamides ($H_2NC(=O)R$), despite the lower electronegativity of S and Se compared to O. This counterintuitive phenomenon has been experimentally explored, particularly in H-bond donor organocatalysis[1] and supramolecular chemistry,[2] but an sound explanation to this is lacking. In this talk, I will demonstrate that the NH_2 groups in thio- and selenoamides are despite the lower electronegativity of S and Se, more positively charged than in carboxamides, and thus better H-bond donors.[3] This originates from the larger electronic density flow from the nitrogen lone pair of the NH_2 group into the lower-lying $\pi^*_{C=S}$ and $\pi^*_{C=Se}$ orbitals than to the high-lying $\pi^*_{C=O}$ orbital. The relative energies of the $\pi^*_{C=X}$ levels follow from the p_π–p_π overlap between the chalcogen *n*p and carbon 2p atomic orbitals, which is set by the carbon–chalcogen (C=X) distance, a consequence of the steric Pauli repulsion between the two bonded atoms. Thus, our quantum-chemical analyses reveal that not the electronegativity but the *steric size* of the chalcogen atom determines the amide's hydrogen-bond donor strength. Finally, I will discuss the overlooked role of the chalcogen atom size on the suitability of the amide geometry for intermolecular H-bonding in supramolecular systems.[4]



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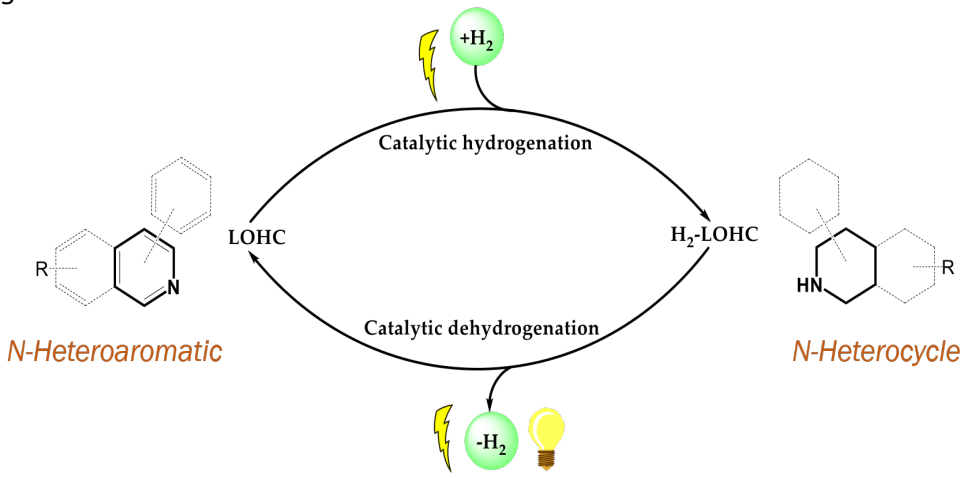
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LIQUID ORGANIC MOLECULES FOR SUSTAINABLE HYDROGEN STORAGE

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As our current hegemonic system and its reckless exploitation of fossil fuels, ecosystems, bodies and lives continue to sink us into a planetary crisis; it is increasingly more urgent to find strategies to ameliorate the negative consequences of this dominant way of life. Shifting from fossil fuels to more benign sources of energy is one of the key aspects that could potentially reduce the burden on our planet (as long as this change would be embedded in a broader systemic transition). For this endeavor, the sun and the wind emerge as vital allies, providing potentially sufficient energy for the systemic and human needs. Nevertheless, these types of energy are intermittent in nature, and to ensure a steady and reliable supply, that is also compatible with the demands and power relations of the globalized world-system, 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 potentially renewable energy. Nevertheless, its effective, safe, user friendly and economical storage are still an important challenge. To contribute to tackle this, we envision the synthesis and reversible catalytic hydrogenation-dehydrogenation of suitable aromatic heterocycles. These heterocycles act as "rechargeable" fuels, or Liquid Organic Hydrogen Carriers (LOHCs), which chemically bond and stabilize hydrogen until the moment to use it comes.



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AMYLOID AGGREGATION BY ELECTRON PARAMAGNETIC RESONANCE

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Amyloid aggregation is a process connected to neurodegenerative diseases such as Parkinson's and Alzheimer's diseases. In general, intrinsically disordered proteins fold into beta sheet aggregates called fibrils, and the oligomers formed during this process are considered the toxic species taking part in neurodegeneration. Characterization of oligomers is difficult with conventional techniques, due to their structural heterogeneity and transientness, which hampers the study of neurodegenerative diseases themselves. We are studying alpha Synuclein aggregation, a central process in Parkinson's disease.

By means of site directed spin labeling (SDSL) coupled to continuous wave-electron paramagnetic resonance (CW-EPR), the aggregation process can be followed, in situ and at room temperature.

This approach allows for the study of alpha Synuclein aggregation without the need for chemical separation of monomers and aggregates. The CW-EPR spectrum will thereby be composed of a superposition of components, namely monomers, oligomers and fibrils. Simulation of the EPR spectrum allows for the quantification of the amount of aggregates and of monomers in the sample.

This approach coupled to a fluorescent-based assay specific for amyloid fibrils allows for the evaluation of the aggregation curves, including the toxic oligomers.

We show that in the first hours of incubation, non-fibrillary aggregates are formed and can be detected, allowing for preparation of oligomer-enriched sample and evaluation of aggregation rates [1,2].

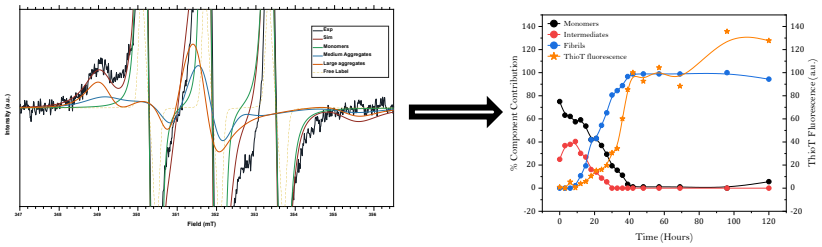


***Figure 1**: From simulation components to aggregation curves*

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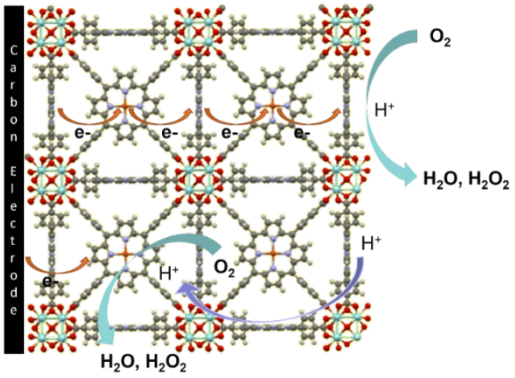
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INVESTIGATION OF THE ELECTROCHEMICAL OXYGEN REDUCTION REACTION OF COBALT PORPHYRIN METAL ORGANIC FRAMEWORKS

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The use of fossil fuels is leading to drastic climate changes. Therefore, development of renewable fuels such as hydrogen is needed. Hydrogen can be consumed in fuel cells in which the oxidation of hydrogen is coupled to the oxygen reduction reaction (ORR).[1] A well-defined, durable and economically viable catalyst is needed to catalyse this ORR. One class of catalysts that fit these requirements are metal-organic frameworks with an active catalyst incorporated in the structure. In comparison to other heterogeneous catalyst, MOFs are highly modular in nature, which leads to the possibility for easy alteration of the catalytic site. Moreover, due to the porous structure of the framework, the density of active catalytic sites at the electrode is extremely high. However, the porous structure of these frameworks can also lead to limitations in catalysis due to poor charge transfer in the framework.[2] Moreover, selectivity of the reaction can change upon using a porous environment.[3] In this work we have set out to systematically study the effects of the heterogenization of a cobalt porphyrin catalyst in the MOF PCN-224(Co). Assessment of the ORR activity and selectivity indicated that catalysis in the MOF is slower due to limited diffusion in the pores. Moreover, by creating a single site metal catalyst in the MOF, the selectivity of the ORR for H2O2 is 80% in the MOF compared to 30 % in the porphyrin. These results indicate a strong influence of the framework on the ORR catalysis and the realization of single site catalysts within the porous structure.



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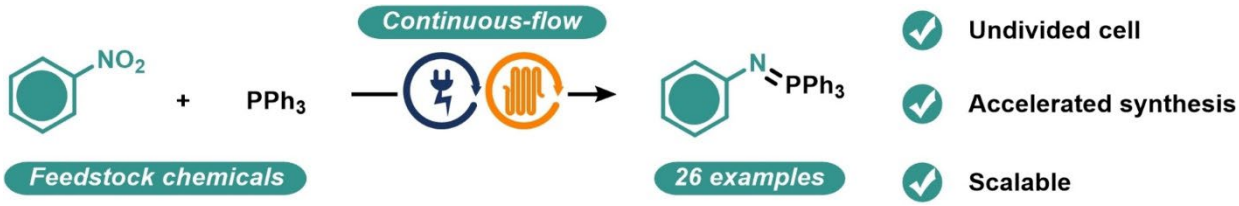
FLOW ELECTROSYNTHESIS OF IMINOPHOSPHORANES FROM NITRO (HETERO)ARENES

Morgan Regnier[1], Rodrigo Costa e Silva[1,2], Clara Vega[1], Luca Capaldo[1], Lars Wesenberg[1], Grace Lowe[1], Kleber Thiago de Oliveira[2], Timothy Noël[1]

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Iminophosphoranes hold significant potential in the field of synthetic chemistry as essential precursors for a wide range of organic compounds.[1] However, as of today, a safe and scalable method for their synthesis has not been established. Therefore, a practical electrochemical method for synthesizing aryliminophosphoranes from widely available nitro(hetero)arenes in a continuous-flow system is presented. The utilization of flow technology offers several advantages to our approach, including the elimination of the need for a supporting electrolyte, and enhanced scalability.[2] Our method demonstrates good tolerance towards various functional groups, with electron-deficient nitroarenes being particularly suitable for this strategy. In addition, we have demonstrated the versatility of aryliminophosphoranes as intermediates in synthesizing anilines, amines, and amides. To further enhance the utility of our approach, we have developed a telescoped method that utilizes a tube-in-tube setup for the in-situ production of isocyanates.



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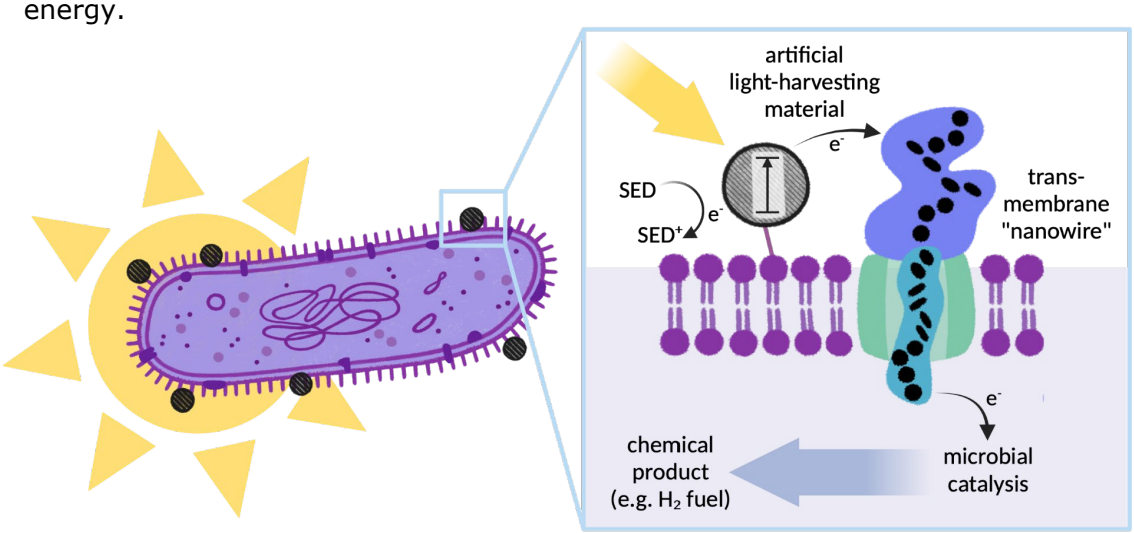
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MEMBRANE-ANCHORED NANOPARTICLES TO FACILITATE TRANSMEMBRANE PHOTOELECTRON TRANSFER

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There is an urgent need for sustainable energy sources such as solar fuels to replace the reliance of humanity on fossil fuels. Biological catalysts, which provide unparalleled catalytic specificity for the production of desirable chemicals, can be integrated with durable inorganic light-harvesting materials to create solar-powered biohybrid systems. It is possible to design these systems to have functions such as sustainable fuel production. In this work we investigate the direct attachment of light-harvesting nanoparticles, such as carbon dots (CDs), to the outer membrane of exoelectrogenic bacteria. We hypothesise that this will establish a defined pathway of photoelectron transfer across the cell membrane of exoelectrogens, which naturally contain transmembrane molecular 'nanowires' that function to exchange electrons between the intracellular and extracellular environment. CDs are fluorescent semi-conducting nanoparticles which absorb broadly in the UV-visible range. Carboxylic acid groups available at their surface allow for chemical modification, and thus conjugation with membrane components. The functionality of a modified nanoparticle is tested firstly through ability to attach to lipid membranes, and secondly through facilitation of photoelectron transfer across a 'nanowire'-containing membrane. A membrane-anchored photosensitiser such as this could allow whole-cell (or liposome-based) fuel production systems to be driven by solar energy.



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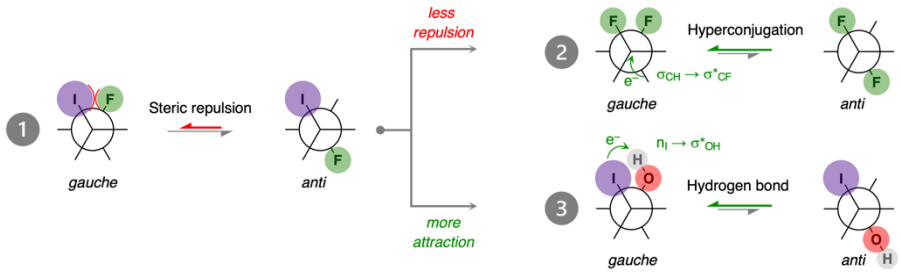
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REVISITING ROTATIONAL ISOMERISM OF ORGANIC COMPOUNDS

Daniela Rodrigues Silva[1], Trevor A. Hamlin[1], Célia Fonseca Guerra[1], F. Matthias Bickelhaupt[1]

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A firm grasp of the driving forces behind conformational isomerism is crucial for the rational design of molecules with tailor-made properties. With this in mind, we reinvestigate the rotational isomerism around the C–C bond in archetypal organic compounds within the framework of Kohn-Sham molecular orbital (KS-MO) theory. Our bonding analyses reveal that overall rotational energy profiles are always set by steric repulsion between occupied–occupied orbitals. However, the conformational preferences can be shifted if one of the two requirements are met: i) if the relative steric repulsion is too weak and thus easily counteracted by subtle attractive interactions (*e.g.*, hyperconjugation[1]; **1** → **2**, Fig. 1); or ii) if stronger intramolecular interactions take place (*e.g.*, hydrogen bonding[2]; **1** → **3**, Fig. 1). Our analyses lead to a novel, fundamentally revisited picture of the physical mechanisms behind well-known conformational effects in organic chemistry.



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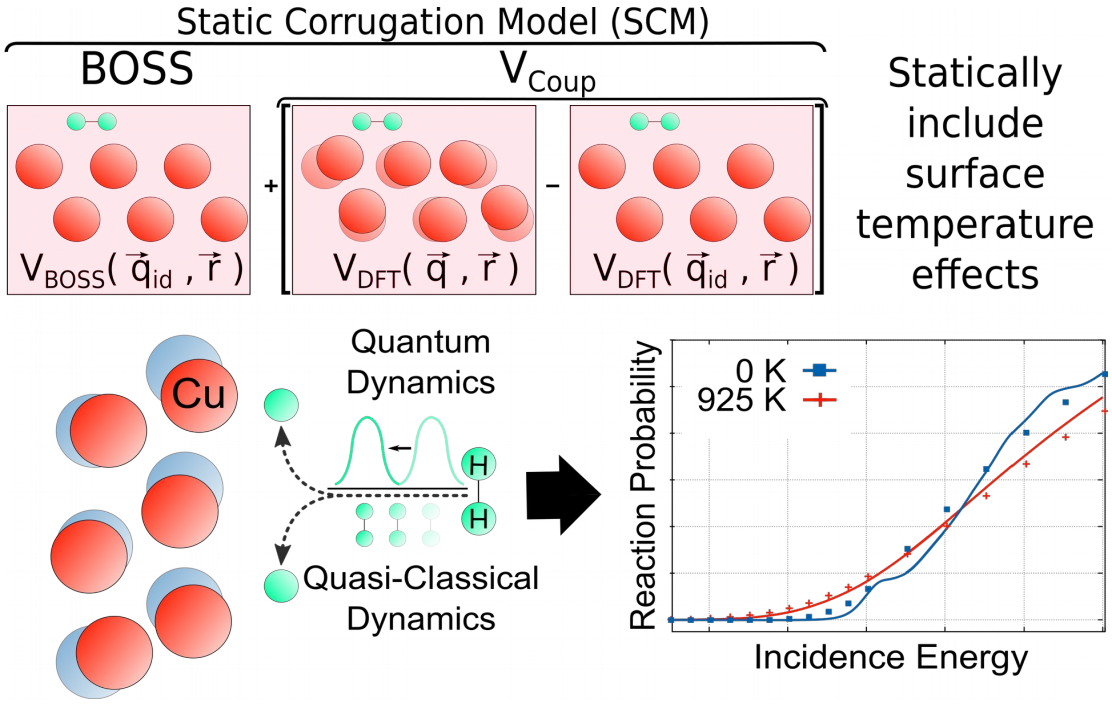
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Accurate Description of Surface Temperature Effects for the Quantum Dynamics of H_2 on a Metal Surface

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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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LIGHT INDUCED COBALT(III) CARBENE RADICAL FORMATION FROM MALONIC ESTERS

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Carbene transfer catalysis enables the direct functionalization of C–H or C=C bonds, which is of great importance for the pharmaceutical and chemical industry. However, pre-activated reagents, such as iodonium ylides or diazo compounds, 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 non-prefunctionalized reagents, such as malonic esters, using photochemistry. First, a cobalt-malonate adduct is formed under basic conditions. Upon irradiation of light, this intermediate can undergo hydrogen atom abstraction, forming a cobalt(III) carbene radical complex. In presence of styrene, cyclopropanation occurs leading to direct C=C bond functionalization, although with stochiometric yields only. This work demonstrates that the desired cobalt(III) carbene radical complex can be formed from commercially available and bench stable malonic esters, replacing the detrimental pre-activated reagents that are commonly used.

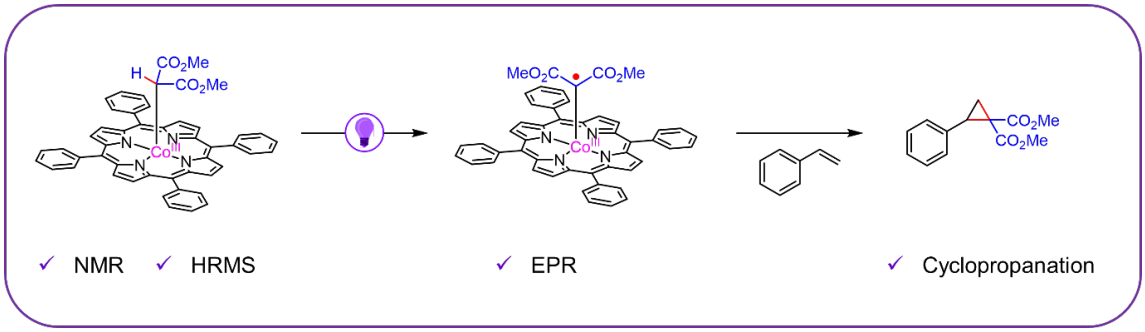


Figure 1. Cyclopropanation reaction via a cobalt(III) carbene radical complex that is generated from the cobalt-malonate adduct upon irradiation of light.

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PERSPECTIVE ON MANY BODY PERTURBATION THEORY CORRELATION ENERGY METHODS

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Moller-Plesset 2nd order perturbation theory (MP2) and the Random Phase Approximation (RPA) are two well-established quantum chemical perturbation theory methods, utilized for calculating correlation energies in molecular systems including, for instance, non-covalent interactions. Nevertheless, their computational demands can become prohibitive, especially when dealing with larger systems.

A strategy to reduce the computational cost of these methods consists of downsizing the many basis functions products, which appear in such methods, into a more compact auxiliary function set. One of the most effective variants of this technique known as Pair Atomic Resolution of Identity (PARI) was already explored by Baerends in the 70's, allowing simulations of larger chemical systems. Nevertheless, achieving chemical accuracy remains an ongoing challenge when RI is applied to perturbation theory methods.

We aim to present RI-MP2 and RI-RPA procedures and to discuss their best-suited applications and their capabilities in comparison to other high-reference methods. Moreover, we show how novel stabilization approaches can allow Numerical Atomic Orbital (NAO) based RI-MP2 and RI-RPA to reach accuracies close to Gaussian atomic orbital implementations employing exact math and more expensive compression procedures.

In summary, RI-MP2 and RI-RPA approaches are precise and cost-effective methods that, when employed appropriately, can yield accurate estimates of molecular energy. That in principle can have far-reaching applications in various chemistry fields, such as revealing unknown molecular binding affinities or for instance explaining still unclear catalytic mechanisms.

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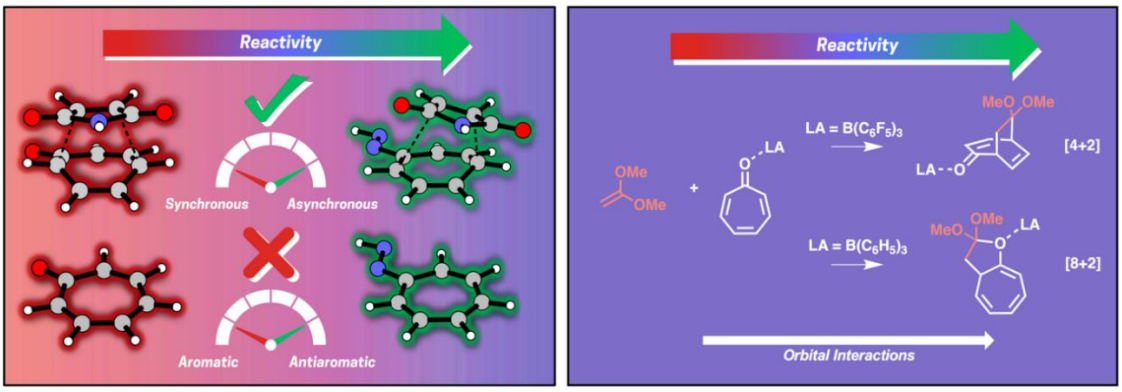
ENHANCING THE REACTIVITY OF TROPONE

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Tropone is an aromatic compound that has a low reactivity in cycloaddition reactions, such as the Diels-Alder reaction. Its reactivity can be accelerated by using i) Lewis acid catalysts or ii) carbonyl umpolung. Lewis acids promote cycloaddition reactions via LUMO-lowering catalysis. Lewis acids can even cause total regiocontrol in cycloaddition reactions between tropone and 1,1-diethoxyethene: the Lewis acid $B(C_6H_5)_3$ furnishes the [8+2] adduct while $B(C_6F_5)_3$ yields the [4+2] adduct.[1] We discovered that the regioselectivity shift finds its origin in the ability of the Lewis acid to absorb distortion by adopting a trigonal pyramidal geometry around the boron atom.[2]

Tropone can be activated via carbonyl umpolung by using hydrazone ion analogs. Recently, the higher reactivity of hydrazone ion analogs was ascribed to a raised HOMO energy induced by antiaromaticity.[3] This dearomatizing HOMO-raising rationale is frequently used to explain observations in the laboratory. We, however, show that the correlation between a raised HOMO energy and a higher reactivity is not causal.[4] Instead, the lowering of the reaction barrier is caused by an amplified asynchronicity of the reaction mode that results in less deformation of the reactants, and a relief in destabilizing Pauli repulsion between the deformed reactants.



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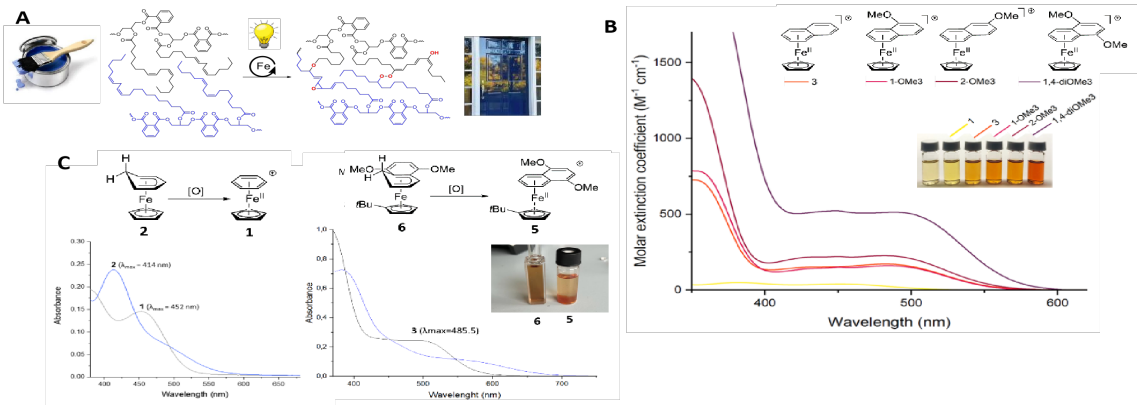
LIGHT TRIGGERED CURING OF PIGMENTED ALKYD PAINTS USING IRON CONDENSED ARENE COMPLEXES – THE RISKIEST WAY TO MAKE PAINT

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Previously, our group demonstrated that photoactive complexes $[(Cp)Fe(arene)]^+$ can serve as latent catalysts, enabling photochemical control over the initiation of alkyd paint curing. This catalyst offers an alternative to traditional cobalt salts, eliminating the need for antiskinning agents. These catalysts exhibit exceptional activity when excited by blue light and performs effectively in transparent and light-coloured paints. However, its drying performance in paints of other colors is suboptimal due to its low extinction coefficient, posing a significant challenge that needs to be resolved.

$[(Cp)Fe(naphthalene)]^+$ derivatives have a higher photo lability which results in a faster drying process. However, the low solubility of these iron-salt complexes in the hydrophobic alkyd resin medium necessitates a solution. One possible approach is to reduce the Naphthalene ring through an elegant reaction involving *tert*-butyllithium. This modification improves the catalysts' solubility whilst retaining a high molar extinction coefficient, making it easier to activate substrates of color and thus enhancing its applicability.



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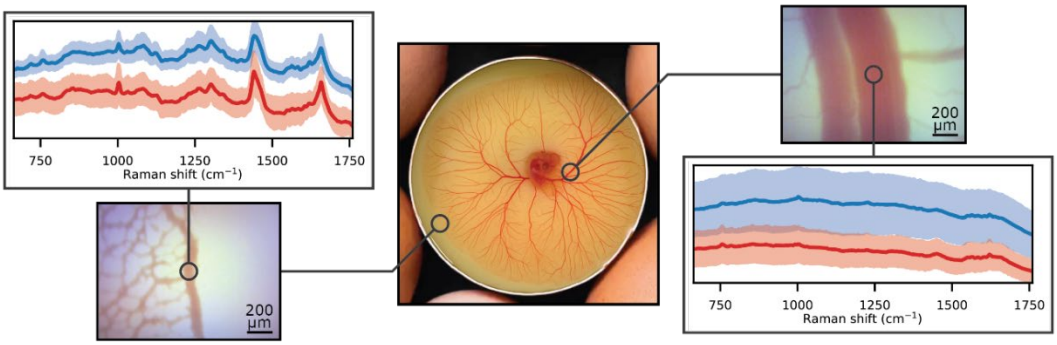
EXPLORING SUBSURFACE RAMAN SPECTROSCOPY FOR NON-INVASIVE SEX DETERMINATION OF CHICKEN EGGS

Lennard van den Tweel[1], Freek Ariese[2], Carla Van der Pol[3], Henry van den Brand[1]

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In order to meet the demand for consumption eggs, billions of specially bred layer chickens are hatched every year. Serving no purpose in the industry, over 372 million one-day old male chickens are culled every year in Europe. Current, commercial in-ovo sexing techniques are unfit for sexing before day 9 of incubation (E9) and their invasive nature imposes a risk for bacterial infection. Thus, there is a need for scalable, accurate (>98.5%) and non-invasive techniques for in-ovo sexing, with the potential for application before the onset of nociception at E7. Fluorescence and Raman spectroscopy were recently demonstrated as promising techniques for the retrieval of sex-related biomarkers from embryonic blood for early and accurate in-ovo sexing.[1,2] However, the high optical scattering of the eggshell has so far proven an insurmountable challenge in the application of these techniques in a non-invasive manner.

This work assesses the suitability of subsurface Raman spectroscopy techniques for the non-invasive retrieval of known sex-related biomarkers from extra-embryonic tissues. *Ex-ovo* backscatter Raman microscopy of extra-embryonic blood vessels on E3.5-4 confirmed a significant increase in haemoglobin and near-infrared autofluorescence in blood of male embryos. Limited success in the retrieval of the same biomarkers in smaller blood vessels reveals the considerable challenges for *in-ovo* sexing using Raman spectroscopy. Other techniques, such as time-domain diffuse optical spectroscopy are currently being explored.



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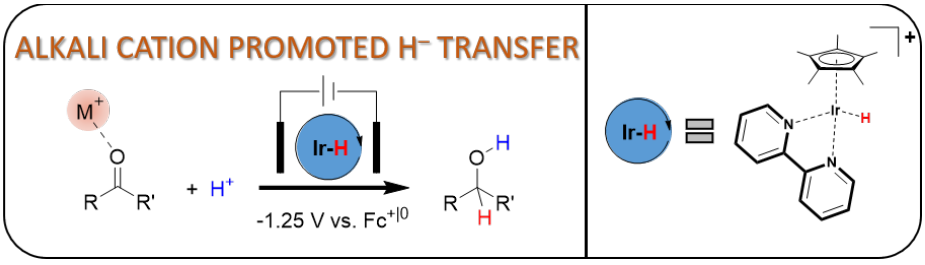
ELECTROCATALYTIC HYDROGENATION OF CARBONYLS WITH AN IRIDIUM COMPLEX

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

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Metal-based homogeneous catalysis plays a key role in several chemical industries, 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]. In (transfer) hydrogenation reactions usually a large amount of alkali metal alkoxides are present, which are believed to aid in catalyst activation and/or substrate activation through C=O-M^+ non-covalent interactions (where M^+=alkali metal cation) [2]. We envision another way to perform hydrogenation without using dihydrogen gas, namely by generating the required metal-hydride *in situ*, using molecular catalysts that are capable of reducing protons to hydrides when an electric potential is applied [3].

In our approach we synthesised an iridium catalyst which is known to perform hydride transfer under acidic aqueous conditions [4], and we were able to generate the reactive iridium hydride via electrochemical reduction in acidic water and perform hydride transfer. However, when we switched to an organic solvent the (electro)chemically generated iridium hydride was not capable of hydride transfer. The iridium hydride was chemically synthesized and we found that hydride transfer does occur when alkali metal cations are present in solution. In our poster we show with ^{1}H NMR spectroscopy the reactivity of the iridium hydride with several alkali metal cations in acetonitrile. We then show that the iridium hydride can be generated electrochemically at a relatively mild potential in organic solvent and through bulk electrolysis we show that hydride transfer occurs only with alkali metal cations present.



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How Temperature Affects the Selectivity of the Electrochemical Reduction of CO_2 at Au, Cu and Ni

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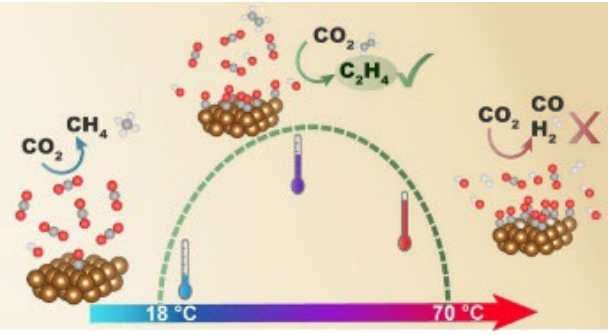
Electrochemical reactions in general, and the CO_2 reduction reaction (CO2RR) in particular, are commonly studied at room temperature. However, it is important to elucidate the effect of temperature on the product distribution and activity of CO2RR as practical electrolyzers will operate at elevated temperatures. We studied the effect of temperature on various metals.

Gold as it is a relatively simple electrode material only producing CO and H_2. We showed that increasing temperature leads to both an increase in activity and selectivity of the CO2RR towards CO. However, at higher temperatures mass transport limitations due to the lower CO_2 availability and higher local pH become more important.[1]

Copper is studied as it is an unique catalyst for CO2RR capable of producing a variety of products including multi-carbon products such as ethylene and propanol. We showed that at ambient pressures Cu has 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.

These trends can be explained by a combination of factors such as local pH, CO surface coverage and changes in the copper surface.[2]

Ni is capable of producing longer hydrocarbon chains via a Fischer-Tropsch like mechanism. It shows increasing activity with temperature at ambient pressures, but the chain growth probability is intrinsically not much affected by the temperature. This means that the product distribution does not significantly change with temperature. However, we do observe that at higher temperatures, faster degradation takes place, probably due to coking of the catalyst.



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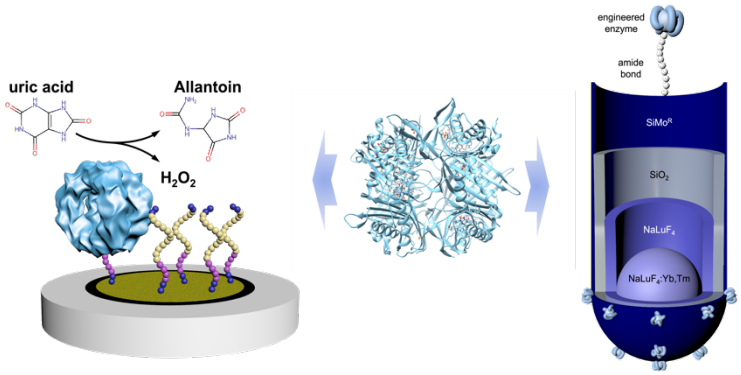
ENGINEERED ENZYMES ENHANCED BIOSENSING PROPERTY

Zheng Wei[1], Yuxin Liu[2], Tanja Knaus[1], Gadi Rothenberg[1], Hong Zhang[1], Felix F. Loeffler[2], Francesco G. Mutti[1]

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Biosensors utilising oxidoreductase enzymes have undergone extensive research over the past decade, primarily motivated by the demand for swift and accurate diagnostic procedures. The cost and application landscape of these sensors have been notably influenced by their properties and thermal stability. In response to this, we have developed a thermally stable electrochemical biosensor and reusable fluorescent nanoprobes using engineered and thermally stable enzymes, aimed at enhancing disease diagnosis. The commendable detection accuracy and long-term stability exhibited by these biosensors demonstrate the potential for creating cost-effective and efficient biosensors through strategic enzyme engineering.



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A QUINONE-AMINE RADICAL ION PAIR FOR HOMOLYTIC BOND ACTIVATION

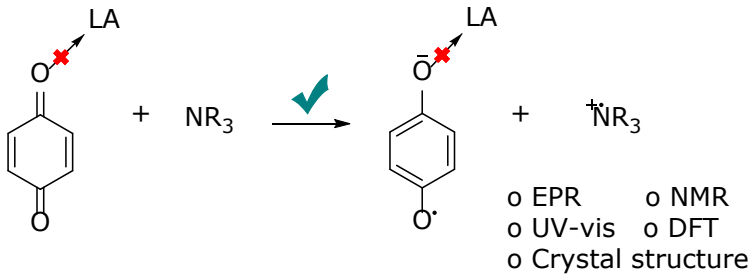
Lars J. C. van der Zee[1], Jelle Hofman[1], Simon Mathew[1], J. Chris Slootweg[1]

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The activation of small molecules is typically performed in an heterolytic fashion. Homolytic splitting, on the other hand, could be advantages for splitting strong covalent bonds. For this, the use of radical ion pairs (RIPs) is of interest as they provide simultaneously two radicals and thus the potential for cooperative reactivity. To date, only two groups of stable organic RIPs are known, one based on tetracyanoethylene (TCNE)[1] as electron acceptor, and one all boron-based RIP.[2]

The development of novel RIPs has recently been made possible due to the discovery of single electron transfer within Frustrated Lewis Pairs (FLPs).[3] The SET occurs from a Lewis base to a Lewis acid, yielding often a RIP as fleeting intermediate. Recent activities focused on the formation of stable RIPs, e.g. based on quinones as the electron acceptor and amines and phosphines as the electron donor.[4] For almost all the quinone-based RIPs investigated, the SET is facilitated when the quinone is converted into a stronger acceptor by coordination of a Lewis acid or the RIP is only short lived.

To simplify the quinone-based RIPs, we developed a class of stable RIPs without the need of activating the quinone. Careful design let to a new set of RIPs, which were characterized using multiple methods (UV-vis, EPR, DFT, NMR, crystal structure) and its reactivity explored for homolytic bond activation.



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