# From Interfaces to Cages - Confining Effects on Molecular Processes

730. WE-Heraeus-Seminar

27 – 30 September 2020
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

# Introduction

**The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de**

## Aims and scope of the 730. WE-Heraeus-Seminar:

The physicochemical properties of confined molecules within cavities, channels and interfaces are known to differ significantly from molecules in the bulk regime. Intensive research on the properties of physically nanoconfined fluids revealed a wide spectrum of emerging physical phenomena ranging from phase transitions and modified electronic structures to anomalous fluid dynamics. This anomalous behaviour of confined fluids can be exploited to open up new synthesis products and routes and to optimize reaction rates, yields and selectivities of chemical reactions. For decades, scientists have utilized geometrical confinement in order to develop efficient energy storage systems and catalysts based on (porous) solids and self-assembled (metal)organic cages. However, the impact of geometrical confinement on reactants, intermediates and products of chemical reactions is not yet understood on a fundamental level, probably due to the complex interplay between the geometry, size, surface texture and composition of confining systems.

Since a fundamental understanding of confinement-induced effects on molecular properties and reactions may contribute to optimize current chemical processes and to develop new research areas, the relevance of disentangling the different contributions to confining effects will be highlighted to a wider audience. In particular, the WE-Heraeus seminar aims at presenting and discussing the progress across disciplines. Furthermore, a common, unified understanding and new goals and challenges will be addressed in this interdisciplinary field of research. The complementary expertise of participants will cover experimental and theoretical work in the fields of physics, biophysics and chemistry.

## Scientific Organizerzationers:

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|---|---|
| Prof. Dr. Karina Morgenstern | Ruhr-Universität Bochum, Germany,<br>E-mail: karina.morgenstern@rub.de |
| Prof. Dr. Kristina Tschulik | Ruhr-Universität Bochum, Germany<br>E-mail: kristina.tschulik@rub.de |
| Dr. Sandra Jendrzej | Ruhr-Universität Bochum, Germany,<br>E-mail: sandra.jendrzej@rub.de |

# Program

# Program

## Sunday, 27 September 2020

| | | |
|---|---|---|
| 17:00 – 20:00 | Registration | |
| 19:00 | *BUFFET SUPPER and get-together* | |
| 20:30 – 20:40 | Karina Morgenstern | **Opening remarks** |

### Opening lecture

| | | |
|---|---|---|
| 20:40 – 21:40 | John Polanyi | **Chemistry in one-dimension** |

## Monday, 28 September 2020

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 09:45 | Makoto Fujita | **Self-assembly of Archimedean/non-Archimedean solids under mathematical restriction** |
| 09:45 – 10:30 | Anna McConnell | **The structural characterisation of paramagnetic metal-organic cages and their host-guest complexes** |
| 10:30 – 11:00 | *COFFEE BREAK* | |
| 11:00 – 11:20 | Sergi Ruiz-Barragan | **THz spectra of confined water** |
| 11:20 – 11:40 | David Van Craen | **Hierarchical helicates as solvent dependent reaction platform** |
| 11:45 – 12:30 | Xavi Ribas | **Supramolecular fullerene sponges as masks for regioselective functionalization of C60** |
| 12:30 – 12:40 | **Conference Photo** (in the front of the main building) | |

# Program

## Monday, 28 September 2020

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|---|---|---|
| 12:40 | *LUNCH* | |
| 14:00 – 14:15 | Stefan Jorda | **About the WE-Heraeus-Foundation** |
| 14:15 – 15:15 | **Flash talks 1** | |
| 15:15 – 16:00 | Vaidhyanathan Ramamurthy | **Medium matters: Dynamics of molecules in a confined space** |
| 16:00 – 16:30 | *COFFEE BREAK* | |
| 16:30 – 18:30 | **Poster session 1** | |
| 18:30 | *HERAEUS DINNER*<br>*(social event with cold & warm buffet with complimentary drinks)* | |
| 20:30 – 21:15 | Teresa Head-Gordon | **The role of interfaces for chemical transformations and transport under confinement** |
| 21:15 | **Discussions** | |

# Program

## Tuesday, 29 September 2020

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 – 09:45 | Lydéric Bocquet | **Water flows at ultimate scales and exotic ionic transport (towards an artificial ionic machinery)** |
| 09:45 – 10:30 | Friedrich Kremer | **Molecular dynamics in nanometric confinement as studied by Broadband Dielectric Spectroscopy** |
| 10:30 – 11:00 | *COFFEE BREAK* | |
| 11:00 – 11:45 | Ulrich Höfer | **Time-resolved spectroscopy of electron transfer processes at metal/organic interfaces** |
| 11:45 – 12:30 | Angelos Michaelides | **Interfacial water: from atmospheric ice nucleation to nano-confinement** |
| 12:30 | *LUNCH* | |

# Program

## Tuesday, 29 September 2020

| | | |
|---|---|---|
| 14:00 – 14:45 | Dominik Marx | **Prebiotic chemistry in nanometric confinement** |
| 14:45 – 15:45 | **Flash talks 2** | |
| 15:45 – 16:30 | *COFFEE BREAK* | |
| 16:30 – 18:30 | **Poster session 2** | |
| 19:00 | *DINNER* | |
| 20:30 – 21:15 | Iryna Zenyuk | **Confinement effects for nano-electrocatalysts for Oxygen reduction reaction** |
| 21:15 | **Discussion** | |

# Program

## Wednesday, 30 September 2020

| | | |
|---|---|---|
| 08:00 | *BREAKFAST* | |
| 09:00 - 09:45 | Mauricio Prieto | **Studying the effects of confinement in real time: water formation under ultra-thin silica films** |
| 09:45 – 10:15 | *COFFEE BREAK* | |
| 10:15 – 11:00 | Marialore Sulpizi | **Role of image charges on ionic liquids confined between metallic interfaces** |
| 11:00 – 11:45 | Antigoni Alexandrou | **Receptor confinement in membrane nanodomains: its role in signaling and disease** |
| 11:45 – 12:00 | Karina Morgenstern | **Closing remarks** |
| 12:00 | *LUNCH* | |

**End of the seminar and departure**

# Posters

# Posters Monday

| | | |
|---|---|---|
| 1 | André Platzek | **Coordination cage as photosensitizer and endrohedrally functionalized heteroleptic coordination cages** |
| 2 | Kristina E. Ebbert | **Systematic studies on heteroleptic coordination cages** |
| 3 | Kai Wu | **Backbone-bridging promotes diversity in heteroleptic cages** |
| 4 | Jacopo Tessarolo | **Steric hindrance: A tool for rational design of homo- and heteroleptic coordination cages** |
| 5 | Shota Hasegawa | **Heterodimerization of the bowl-shaped coordination cages leading to the pill-shaped dimer**<br>**Encapsulating the single $C_{70}$ molecule** |
| 6 | Maximilian Rüttermann | **Solvation dynamics of nanoconfined sodium hydroxide in reverse micelles** |
| 7 | Maximilian Jaugstetter | **The effects of 0D confinement on the nucleation behavior of metal salts confined in micelles. A point experimental and theoretical study** |
| 8 | Ellen Adams | **Nanoconfinement of acid inhibits proton hopping in non-ionic reverse micelles** |
| 9 | Lisa Schardt | **The response of amphiphilic hydrogels with varying hydrophilicity to the Hofmeister series** |
| 10 | Anna Selina Juber | **Free energy simulation of guest binding in a photoswitchable cage** |
| 11 | Julien Rowen<br>*(online via ZOOM)* | **Reactive molecules in confinement – from matrix cages to supramolecular host molecules** |

# Posters Monday

| | | |
|---|---|---|
| **12** | Luisa Weirich<br>*(online via ZOOM)* | **Prediction of the experimental IR and VCD spectra of crown ethers complexed with chiral ammonium salts by DFT calculation** |
| **13** | Kevin Scholten<br>*(online via ZOOM)* | **VCD studies of $C_3$-symmetric chiral thioureas** |

# Posters Tuesday

| | | |
|---|---|---|
| 1 | Inga Langguth | **STM investigations of insulating xenon interfaces on silver surfaces as low interaction substrates for advanced carbene studies** |
| 2 | John Thomas | **$D_2O$-$Cs^+$ complexes on Cu(111): An experimental study of real space structure and real time electron dynamics** |
| 3 | Vladimir Lykov | **Difference between $CO_2$ structures two-dimensional confined on a metal as compared to a salt surface investigated by STM.** |
| 4 | Federico Sebastiani | **An isolated water droplet in the aqueous solution of a supramolecular tetrahedral cage** |
| 5 | Saskia Körning | **Anisotropic dielectric tensor of nanoconfined water in graphene slit pores** |
| 6 | Henry Enninful | **A kernel-based approach to advanced thermoporometry characterisation of mesoporous solids** |
| 7 | Niclas Blanc | **The role of resistance and mass transport on the Tafel approach at composite catalyst thin-film electrodes** |
| 8 | Kevin Wonner | **Electrochemical studies of individual nanoparticles observed with dark-field microscopy** |
| 9 | Sarah Funke | **Using THz spectroscopy to investigate HCl in confined water systems** |
| 10 | Thorsten Ockelmann | **Understanding excited-state proton transfer and proton-confinement from the water perspective** |

# Posters Tuesday

| | | |
|---|---|---|
| 11 | Shadi Fatayer<br>*(online via ZOOM)* | **Molecular structure elucidation with charge-state control** |
| 12 | Patricia Gnutt<br>*(online via ZOOM)* | **Co-surfactant acrylamide: A study on size and stability of AOT reverse micelles incorporating acrylamide and polyacrylamide** |
| 13 | Prantik Saha<br>*(online via ZOOM)* | **Electrokinetic streaming current method to probe diffuse layer at externally polarized electrocatalyst-electrolyte interface** |

# Abstracts of Talks

(in chronological order)

# Chemistry in One-Dimension

**M.J. Timm, L. Leung, K.Anggara, and J.C. Polanyi**

*University of Toronto, Toronto, Canada*
*E-mail: john.polanyi@utoronto.ca*

Insight into reaction dynamics has been obtained by studies of single-collision events at the crossing point of molecular beams. This, however, left the collision geometry in the reactive encounter undefined. The present Symposium focuses on 'confining effects', which will aid in the selection of collision geometry. Such selection has been achieved previously by 'Surface Aligned Reaction', and by selection of the reactive 'Impact Parameter' ('b'; the collision miss-distance) using the atoms at an underlying surface as a molecular-scale collimator [1,2]. The present study employs impact parameter selection in combination with Scanning Tunneling Microscopy (STM) to image reagents and products in surface reaction. The reagents are directed energized F-atom 'projectiles' colliding with stationary chemisorbed CF3 'targets' on Cu(110) at 4.6K. The reagent F and product (F)' are seen by STM to move collinearly, evidencing one-dimensional reaction. This collinear event can be understood if the directed F-atom projectile 'knocks-on' the (F)' product, from the chemisorbed CF3 target. The STM images give direct evidence of umbrella-inversion of the CF3, concurrent with this F-atom 'knock-on'. The knock-on substitution reaction can be written as F + CF3 = (CF3)' + (F)', with primes indicating products. The 1-D momentum-transfer between the F and (F)' atoms is analogous to that between steel balls in Newton's cradle. The reactive case differs from Newton's due to some loss of momentum to (CF3)'. For this simple system of F + CF3 one-dimensional substitution reaction was observed for the majority (65%) of collisions examined by STM, at b=0 and a collision energy of ~1eV.

## References

[1] K. Anggara, L. Leung, M.J. Timm, Z. Hu, J.C. Polanyi; Sci. Adv., **4(10)**, eaau2821 (2018).

[2] K. Anggara, L. Leung, M.J. Timm, Z. Hu, J.C. Polanyi; Faraday Discuss., **214**, 89-103 (2019).

# Self-assembly of Archimedean/Non-Archimedean Solids under Mathematical Restriction

**Makoto Fujita**[a,b]
*aDepartment of Applied Chemistry, The University of Tokyo and*
*[b]Devision of Advanced Molecular Science Institute for Molecular Science (IMS)*
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**Abstract :** We and others have been intensively studying the self-assembly of coordination polyhedra whose framework topologies are described by Platonic or Archimedian solids.[1] The largest structure we have synthesized is $M_{30}L_{60}$ icosidodecahedron, one of the Archimedian solids.[2] Here, we unexpectedly obtained another $M_{30}L_{60}$ polyhedron that is NOT depicted in any elementary geometry textbook. Triggered by this observation, we mathematically rationalized the unexpected polyhedron based on a theory seldom discussed: the tetravalent Goldberg polyhedra. The common Goldberg polyhedra are made up of hexagons and pentagons with three edges meeting at every node of the polyhedron; well-known real-life examples include footballs and fullerenes. We simply extend this "trivalent" form to generate a new family of "tetravalent" Goldberg polyhedra, made up of squares and triangles.[3] These extended tetravalent Goldberg polyhedra are not described in the literature, presumably because nothing like them has ever been discovered in the real world. However, the square planar geometry of palladium(II) ions has the potential to direct the self-assembly of these unnatural polyhedra, allowing us to synthesize them in the laboratory. We further demonstrate the self-assembly of $M_{48}L_{96}$ (Figure 1), an extended Goldberg polyhedron, which was predicted by the theory.

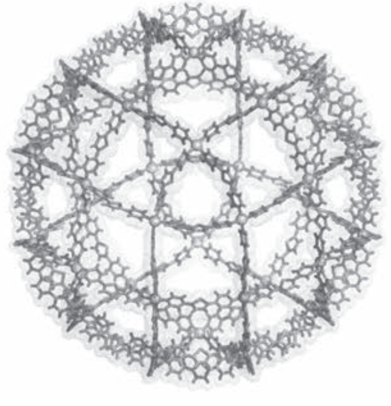

**Fig. 1**. X-ray structure of $M_{48}L_{96}$ complex

**Keywords:** Self-assembly, Archimedean Solids, Goldberg polyhedra, Palladium complexes

**References:**

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[2] D. Fujita, Y. Ueda, S. Sato, H. Yokoyama, N. Mizuno, T. Kumasaka, M. Fujita, *Chem* **2016**, *1*, 91.

[3] D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka, M. Fujita, *Nature* **2016**, 540, 563.

# The Structural Characterisation of Paramagnetic Metal-Organic Cages and their Host-Guest Complexes

**A. McConnell**[1]

[1] *Otto Diels Institute of Organic Chemistry, Christian-Albrechts-Universität zu Kiel, Kiel, Germany*

Supramolecular chemistry enables the self-assembly of larger architectures from relatively simple building blocks through reversible, weak interactions. Metal-organic cages can be readily assembled from metal ions and organic ligands and these cages can function as molecular containers since they possess well-defined three-dimensional cavities for the confinement of guest molecules. Since highly symmetric building blocks are typically used in the self-assembly process, the resulting cages and their cavities are often highly symmetric. Lower symmetry cages are appealing targets for not only the synthetic challenge but also for the potential to discriminate and confine more complex guest molecules. However, as the complexity of the cage architecture increases, structural characterisation of the cage in solution by NMR spectroscopy can become more challenging due to overlapping signals. While the use of paramagnetic instead of diamagnetic metal ions enables dispersion of the signals over a wider chemical shift range enabling sensitive detection of guest binding,[1] this leads to a number of challenges for structural characterisation of the cage. A paramagnetic NMR spectroscopy toolbox[2] for the characterisation of paramagnetic cages and their host-guest complexes will be presented.

## References

[1] A. McConnell, C. Aitchison, A. Grommet, J. Nitschke, J. Am. Chem. Soc. **139**, 6294-6297 (2017).

[2] M. Lehr, T. Paschelke, E. Trumpf, A.-M. Vogt, C. Näther, F. Sönnichsen, A. McConnell, Angew. Chem. Int. Ed. DOI: 10.1002/anie.202008439 (2020).

# THz spectra of confined water

**S. Ruiz-Barragan[1], D. Muñoz-Santiburcio[1,2], D. Marx[1]**

*[1]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum Germany*
*[2] CIC nanoGUNE, Tolosa Hiribidea 76, San Sebastiàn, Spain*

Water confined in rigid structures, such as graphene slit pores [1], currently generates enormous interest because of its greatly different properties with respect to the bulk phase of water [2-5]. We performed extensive ab initio molecular dynamics simulations which disclosed stark differences in H-bonding and electronic properties of nanoconfined water in very narrow graphene slit pores, thus forming mono- and bilayers only, versus less strongly confined water versus bulk water [2]. THz spectroscopy is known to be sensitive to the hydration dynamics and H-bonding, thus providing unique spectroscopic fingerprints of those. In this work, we introduce a machinery based on three key guidelines to rigorously compute THz spectra of water that is nanoconfined within slit pores: (1) Precise pressure control inside the slit pore; (2) applying an intrinsic density correction for ab initio water; (3) parameterizing an accurate water-graphene force field to allow for exhaustive QM/MM dynamics and thus for sampling the dipole time-correlation functions.

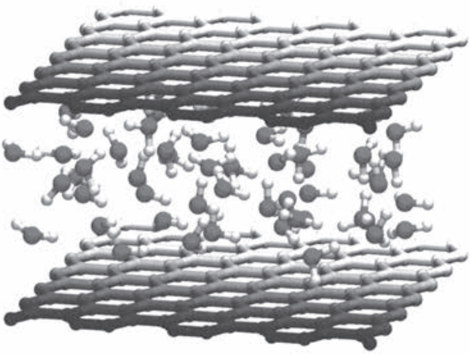

Fig. 1. Representative snapshot sampled from a water/graphene interface simulation.

## References

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[3] L. Fumagalli, et al., Science **360**, 6395, 1339 (2018)
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[5] D. Muñoz-Santiburcio, et al., Phys. Rev. Lett. **119**, 5, 056002 (2017)

# Hierarchical Helicates as Solvent Dependent Reaction Platform

**David Van Craen,[1] Markus Albrecht*,[2]**

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[2]*Institut für Organische Chemie, RWTH Aachen University, Aachen, Germany*

Since the beginning of life, helical structures such as DNA play a fundamental role in the chemistry of nature. On a macroscopic level this structural motif is found in springs, screws and even winding stairs to benefit from its unique properties. J.-M. Lehn defined the term "helicate" in 1987 and introduced this longstanding motif in chemistry.[1]

Hierarchically assembled lithium-bridged titanium helicates were developed by our group two decades later using catechols with keto or ester functionalities in the 3-position.[2] Since then a great variety of ligands were used to observe the equilibrium between a "Werner"-type triscatecholate complex and the corresponding dimer bridged by lithium cations. Bulky chiral ligands lead to stereochemically locked helicates (dimers) while the monomers are stereochemically labil due to Bailar twist or Ray-Dutt twist rearrangements.[3]

Utilizing helicates consisting of chiral ligands and a diene ligand allows us to perform stereoselective Diels-Alder reactions in a post-functionalization process.[4,5] The monomer-dimer equilibrium enables an on/off-switching of the stereoselectivity via the choice of solvent.[4] Enantioselectivities up to 58 % *ee* are achieved depending on the choice of chiral ligand and solvent. The induction pathway is elucidated and diastereoselectivity is observed for nitro-Michael reactions utilizing similar helicates containing secondary amines as catalytic ligands.[5]

## References

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# Supramolecular Fullerene Sponges as Masks for Regioselective Functionalization of $C_{60}$

**Xavi Ribas**

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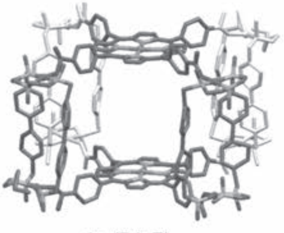
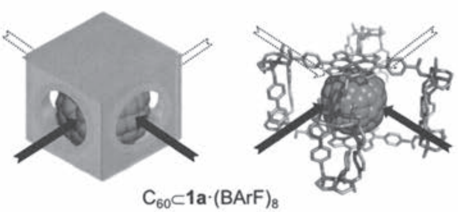
The regioselective functionalization of fullerenes and the control of the number of adducts is highly important to release the current brake in the development of fullerene chemistry. Nowadays, easy-accessible $PC_{60}BM$ and $PC_{70}BM$ are mainly used as electron transport material in solar cell prototypes,[1] due to the hampered accessibility to pure alternative fullerene poly-adduct derivatives. In a general basis, multi-adduct mixtures with uncontrolled regioselectivity are obtained, and chromatographic purification is too costly and time consuming to be used in the bulk production of solar cells. Herein, a porphyrin-based supramolecular tetragonal prismatic capsule[2,3] is used as a mask to tame the over-reactivity of Bingel-Hirsch-type cyclopropanation reactions and, more importantly, to have full control on the equatorial regioselectivity and on the number of additions.[4] Thus, exclusively equatorial bis-, tris- and tetrakis-$C_{60}$ adducts using ethyl-bromomalonate are obtained in a stepwise manner and fully characterized (NMR, UV-vis and XRD). Furthermore, fully equatorial hetero-tetrakis-adducts are easily synthesized at will in one pot for the first time. These results, fully attributed to the confinement control imposed by the capsule's cavity, represent a novel and unique strategy to infer exquisite regio-control to the synthesis of fullerene equatorial poly-adducts. We envision that the described protocol will produce a plethora of new candidates for testing in solar cell devices.



**1a**·(BArF)$_8$

**Supramolecular Mask**



$C_{60}$⊂**1a**·(BArF)$_8$

## References

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# Medium Matters: Dynamics of Molecules in a Confined Space

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## Abstract

From time immemorial it is well known that curtailment of freedom often leads to changes in the behaviour of living beings. Similar restriction of freedom leads to selectivity in the chemical behavior molecules embedded in biological systems. Extending these well-known concepts supramolecular chemists have established that even small molecules upon confinement in synthetic hosts exhibit behaviour distinctly different from the ones in an isotropic solution.

In this lecture the role a "Medium" in bringing about changes in the well-established behaviour of excited molecules would be illustrated with select examples. Results of steady state and ultrafast experiments will be presented that highlight how the confinement alters the excited state dynamics of anthracene, stilbenes and azobenzenes, the molecules that act as triggers in various biological systems and man-made devices. Another reaction to be discussed concerns with electron transfer (eT) that plays a fundamental role in a number of biological events including photosynthesis. Examples and ultrafast dynamics of donors, imprisoned within an organic capsule, transferring an electron to an acceptor across a molecular wall would be presented.

The main message of the talk is that molecules like humans behave differently when confined within synthetic cages.

## References

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# The role of interfaces for chemical transformations and transport under confinement

Teresa Head-Gordon

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Chemical transformations, selectivity, and transport rarely occur in a single homogeneous aqueous phase, but instead occur in niches, crevices, and impurity sites at confining interfaces between two or more phases of gases, liquids or solids. The effects of confinement are ubiquitously present across diverse fields spanning nanochemistry and chemical catalysis, environmental and energy sciences, geosciences, and functional materials. Fundamentally, confinement at interfaces alters water and solution compositions and phases to reformulate the thermodynamics of selectivity, transition states and pathways of chemical reactions, nucleation events, and kinetic barriers for transport. I will provide three different examples of theoretical studies of confinement around anhydrous clays, natural enzymes, and a general non-equilibrium phenomena of confinement which we refer to as dynamical inversion of the energy landscape.

# Water flows at ultimate scales and exotic ionic transport (towards an artificial ionic machinery)

**L. BOCQUET**[1]

*[1]CNRS and ENS, Laboratoire de Physique,*
*24 rue Lhomond, 75005 Paris France*

Ion transporters in Nature exhibit a wealth of complex transport properties such as voltage gating, activation, or mechano-sensitive behavior. When combined, such processes result in advanced ionic machines achieving active ion transport, high selectivity, etc. On the artificial side, there has been recent progress in the design and study of transport in ionic channels at nanoscales, but mimicking the advanced functionalities of ion transporters remains as yet out of reach [1].

In this talk, I will highlight various examples of strongly non-linear ionic transport in 1D and 2D nanofluidic channels, leading to mechano-sensitive ion conduction. I will first discuss experiments on ionic transport across 1D and 2D channels with sub-nanometer dimensions: 2D systems show non-linear voltage control of the streaming currents, while 1D carbon nanotubes with sub-2 nanometer size highlight a pressure-dependent conductance, which mimics very closely the response of biological mechano-sensitive ion channels [2,3]

Beyond I will show how the specificities of advanced transport at these scales constitute building block which allow creating basic neuronal functionalities. In this context, I will in particular discuss theoretical developments of Coulomb blockade in ionic transport, demonstrating single ion transport and quantized ionic conduction at room temperature, based on a fractional Wien effect [4]. In 2D, we show theoretically that this leads to ionic memristors functionalities and Hodgkin-Huxley dynamics.

## References

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[3] "*Mechanically activated ionic transport across single digit carbon nanotubes*", A. Marcotte, T. Mouterde, A. Nigues, A. Siria and L. Bocquet, to appear in **Nature Materials** (2020)

[4] "*Ionic Coulomb blockade as a fractional Wien effect* " N. Kavokine, S. Marbach, A. Siria, L. Bocquet, **Nature Nanotechnology 14**, 573–578 (2019)

[5] "*Artificial nanofluidic memristors and Hodgkin-Huxley dynamics in two-dimensional angstroslits*", P. Robin, N. Kavokine, and L. Bocquet, in preparation

# Molecular dynamics in nanometric confinement as studied by Broadband Dielectric Spectroscopy

F. Kremer

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The question on what length-scale molecular and especially glassy dynamics of low molecular liquids and polymers takes place is of fundamental importance and has multifold practical implications. Recent results based on Broadband Dielectric Spectroscopy [1] for nanometric thin (≥5 nm) layers of a variety of polymers [2-6] and even for isolated chains [7] will be presented, delivering the concurring result that deviations from glassy dynamics of the bulk never exceed margins of ±3 K *independent* of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. - The experiments lead to the conclusions that glassy dynamics takes place on the length scale a few polymer segments ($\leq \sim$ 1nm), while the conformation of the chain as a whole is strongly modified by the geometrical confinement [8,9].

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# Time-resolved spectroscopy of electron transfer processes at metal/organic interfaces

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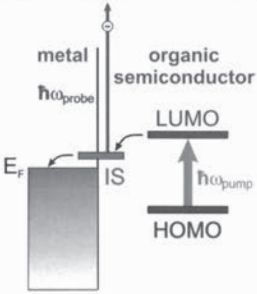
Interfaces between ordered organic thin films on single-crystal metals constitute well-defined model systems for electrical contacts of organic semiconductor devices. Time-resolved two-photon photoemission (2PPE), a method that combines femtosecond laser pump-probe techniques with photoelectron spectroscopy, can provide detailed microscopic information about electron transfer processes at such model contacts. Specific emphasis of this talk will be on the role of interface-specific electronic sates for the charge transfer.

Experiments with organic bilayer systems, such as CuPc/PTCDA/Ag(111) or PCTDA/TiOPc/Ag(111), unambiguously show that normally unoccupied interface states (IS) can be optically excited from the metal side as well as from the LUMO of the second and even third organic monolayer. Transfer times of electrons from the LUMO into the IS and from the IS to the metal range from 20 to 100 fs. These values indicate that the IS wave function has good overlap with both, the delocalized electron system of the metal and the relevant molecular orbitals. Interface states located between the Fermi level of the metal and the molecular LUMOs are thus able to mediate the charge transfer. The results show that not only the molecular level alignment at the interface, but also the properties of interface-specific electronic states play an important role for the efficiency of organic/metal contacts.



Work performed in the framework of the Collaborative Research Centre "Structure and Dynamics of Internal Interfaces" (SFB 1083).

# Interfacial water: from atmospheric ice nucleation to nano-confinement

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Research in my group focusses mainly on understanding chemical reactions and physical processes at surfaces. This includes the application and development of a variety of state of the art computer simulation methods as well as strong collaborations with experiment. In this talk I will discuss some of our recent work on water and ice. This will include new insights into the mechanisms of homogenous [1] and heterogenous ice nucleation [2-6] and the structure and dynamics of water at solid surfaces [7] and when confined within 2-dimensional membranes [8]. Methodological developments aimed at providing more accurate treatments of adsorption on and bonding within solids will also be covered [9-10].

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# Prebiotic Chemistry in Nanometric Confinement

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The exploration of possible scenarios for prebiotic molecular synthesis, including biopolymers such as peptides, is paramount to understanding how primitive life emerged on young Earth. Amongst a vast number of different hypotheses, evidence accumulated that iron-sulfur minerals in conjunction with water at elevated temperatures and pressures might offer favorable reaction environments. In particular, aqueous solutions confined between mineral surfaces, thus forming ultra-narrow slit pores, are increasingly discussed to serve as nanoreactor environments. After some words about prebiotic chemistry, I will review some of our purely computational insights into chemical processes taking place in nanometric slit pore environments as offered by the layered mineral mackinawite [1-4]. In an effort to control more stringently the confinement conditions and, moreover, to eliminate as much as possible non-generic confinement effects due to chemical water-wall interactions, we introduced recently water-filled graphene slit pores of varying widths, hosting mono- and bilayer water lamellae up to much thicker multilayers [5], while still allowing for "full QM" ab initio molecular dynamics simulations [7]. Having constructed an accurate water-graphene force field, which needs to depend on the confinement width to be reliable, we are able to quantitatively compute the symmetry-adapted anisotropic dielectric tensor profiles across graphene-water-graphene slit pores as a function of their width [6].

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# Confinement Effects for Nano-Electrocatalysts for Oxygen Reduction Reaction

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Oxygen reduction reaction (ORR) is one of the most technologically relevant reactions. It occurs at the interface of electrocatalyst and electrolyte, where oxygen reacts with protons and electrons to form water. Because electrocatalyst is dispersed on a high surface area supports, morphological confinement becomes critical, as it dictates proton and oxygen transport. Up to 62 % of Pt nanoparticles can be buried in interior of the meso- and larger micropores [1]. Furthermore, confinement is induced by ionomer, ionic liquids or molecular additives and its impact on electrocatalyst reactivity and transport properties is currently not well understood. We present here an overview of electrostatics and mass transport induced confinement and its relevance for ORR.

Using two-dimensional electric double layer models of water-filled meso-pores, we show the proton expulsion in the pores due to positively charged Pt surface, and explore the design space of local conditions to promote ORR. We further attempt to validate the model via electrokinetic experiements, measuring zeta potential for Pt surface under applied potentials. These studies motivate the experimental work of using ionic liquids to enhance proton transport to the electrocatalyst sites. Figure 1 shows the cyclic voltammetry and electrochemical impedance spectroscopy (EIS) for high surface-are Pt/C and for Pt/C with various ionic liquids.

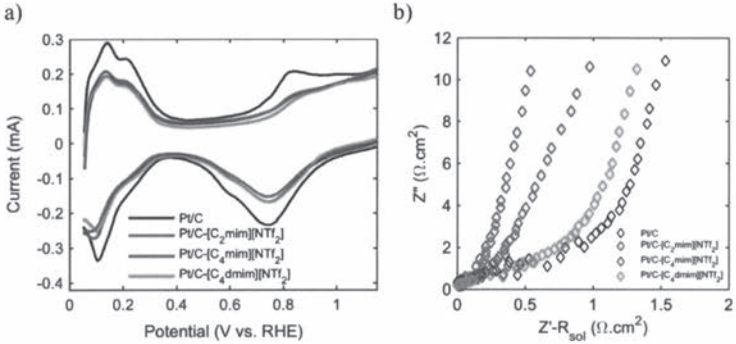

**Figure 1. a) Cyclic voltammetry of Pt/C and b) EIS measurements in $N_2$ using rotating disc electrode.**

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# Studying the effects of confinement in real time: water formation under ultra-thin silica films

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Thin oxide films are interesting model systems for the assessment of the fundamental properties of real catalysts.[1] Among them, $SiO_2$ has been the subject of many studies in the last decades due to its relevance in the field of heterogeneous catalysis either as a support or active component.[2-3] Moreover, $SiO_2$ thin films supported on Ru(0001) have shown the ability of intercalating molecules into the gap existing between the crystal surface and the oxide film.[4] In this presentation, I will address the possibility of studying the effect of confinement under different silica films by assessing, in-situ and in real time, the oxidation of $H_2$ with the aberration corrected spectro-microscope SMART[5] at the synchrotron light source BESSY-II, by means of µXPS, µLEED and LEEM. As an example, Figure 1 shows snapshots taken during the water formation in confinement under a $SiO_2$ bilayer film. As seen from the snapshots the reaction occurs as a front and causes a sudden change in contrast in LEEM. Finally, possible effects on the energetics of the process will be discussed based on the direct determination of the apparent activation energy for the reaction in different scenarios.[6-8]

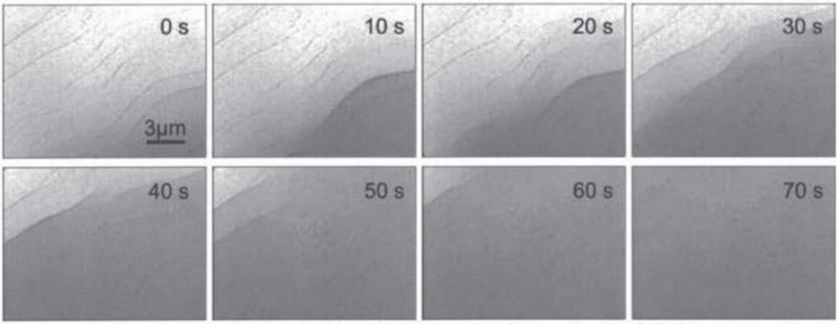

Fig. 1: LEEM snapshots showing the $H_2$ oxidation reaction front under the $SiO_2$ film supported on Ru(0001). $E_{kin} = 14$ eV

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# Role of image charges on ionic liquids confined between metallic interfaces

**S. Ntim**[1] **and** **<u>M. Sulpizi</u>**[1]

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The peculiar properties of ionic liquids in confinement are not essential for energy storage, catalysis and tribology, but interesting still pose fundamental questions. Recently, an anomalous liquid–solid phase transition has been observed in atomic force microscopy experiments for 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM][$BF_4$]), the transition being more pronounced for metallic surfaces [1]. Image charges have been suggested as the key element driving the anomalous freezing. Using atomistic molecular dynamics simulations, we investigate the impact of image charges on structure, dynamics and thermodynamics of [BMIM][$BF_4$] confined between gold electrodes. Our results not only unveil a minor role played by the metal polarisation, but also provide a novel description of the interfacial layer [2]. Although no diffuse layer can be defined in terms of the electrostatic potential, long range effects are clearly visible in the dynamical properties up to 10 nanometers away from the surface and are expected to influence viscous forces in the experiments.

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# Receptor confinement in membrane nanodomains: its role in signaling and disease

**T.-T. Hoang[1], C. Yu[1], N. Olivier[1], C. I. Bouzigues[1], A. Alexandrou[1]**

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The cell membrane separates the cell interior from the cell exterior. Protein molecules, receptors, inserted in the cell membrane detect external signals by binding ligand molecules which induces receptor conformational changes that activate the receptor and trigger a signaling cascade of molecular interactions finally leading to a cell response. It is broadly assumed that the efficiency of such signaling process is optimized by confining these receptors in membrane nanodomains. However, the nature of these nanodomains is still not fully elucidated.

We will focus on receptors confined in membrane nanodomains rich in cholesterol and saturated sphingolipids, often termed "rafts", and in tetraspanin-enriched nanodomains. For receptors that need to dimerize to be activated, like the epidermal growth-factor receptor, EGFR, the confinement in nanodomains increases the local receptor concentration and the encounter probability. When these nanodomains are disrupted, this influences the signaling efficiency and may even impede receptor overactivation which can be correlated with the alleviation of disease symptoms.

We will show how single-molecule tracking and super-resolution microscopy help shed light into the nanodomain environment by providing complementary information. Using long single-molecule trajectories containing a large amount of information, the confining potential felt by the receptors could be determined using a Bayesian inference approach. We could moreover follow the softening of the confining potential as cholesterol-rich nanodomains were depleted from cholesterol. With super-resolution microscopy, on the other hand, we could visualize the characteristics of receptor clusters and how they vary when tetraspanin is depleted.

Receptor confinement in membrane nanodomains thus dictates both cell-level signaling processes and organism-level pathological situations.

# Abstracts of Posters
# Monday

(in chronological order)

# Coordination Cage as Photosensitizer and Endrohedrally Functionalized Heteroleptic Coordination Cages

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From the vast variety of structures derived from supramolecular assembly, coordination cages formed by banana-shaped ligands and Pd(II) cations are of special interest in our group.[1] These cages consist of two geometrically well-defined metal centers and four ligands with coordinating pyridine functionalities. Aside from the coordinating pyridine moiety, the ligand backbone can easily be modified and functionalized yielding diverse molecular assemblies. Certain $Pd_2L_4$ cages are known to form interpenetrated double cages with three distinct cavities that can incorporate anionic and neutral guest molecules as well.[2] An acridone-based, interpenetrated double cage [$3BF_4@Pd_4L_8$] acts as a photosensitizer for generating singlet oxygen which adds to 1,3-cyclohexadiene in a [2+4] Hetero-Diels-Alder reaction to form 2,3-dioxabicyclo[2.2.2]oct-5-ene. Photocatalytic activity was exclusively observed for the assembled cage, whereas free organic ligand L decomposes upon irradiation. While cage [$3BF_4@Pd_4L_8$] does not accept any organic guests, NMR, MS and single crystal X-ray results reveal that both substrate and product are readily encapsulated in the central pocket of its chloride-activated form [$2Cl@Pd_4L_8$]. The system combines multiple functions (photosensitization, allosteric activation and guest uptake) within a structurally complex, mechanically-bonded self-assembly built up from a simple and readily accessible ligand.[3]

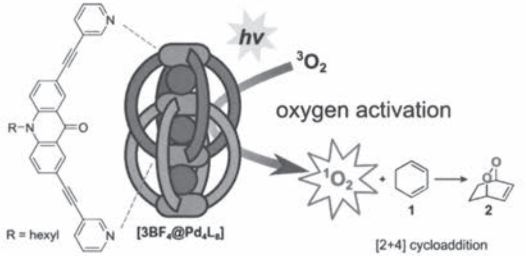

**Fig. 1.**: Acridone-based interpenetrated coordination cage acts as a singlet oxygen photosensitizer to form the product of a [2+4] cycloaddition.

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# Systematic Studies on Heteroleptic Coordination Cages

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In supramolecular chemistry, coordination cages of the $[Pd_2L_4]$ type represent a family of diverse metallo-supramolecular structures with rich host-guest chemistry.[1] To achieve greater structural complexity and functionality, heteroleptic $[Pd_2L^A{}_2L^B{}_2]$ cages, containing two different ligands, have been achieved in the next step.[2] While there have been diverse approaches on heteroleptic cage design, this work focusses mainly on the shape-complementary approach utilizing complementary binding angles and the entropic penalty the system has to overcome forming larger structures.[3,4] Focus of this work is the design of shape complementary ligands that carry functional groups for hydrogen bonding pointing to the inside of the final cage. The cages are then analyzed with regard to their ability to bind neutral guests and finally finding suitable reactions to carry out inside the cage to obtain a supramolecular artificial enzyme.

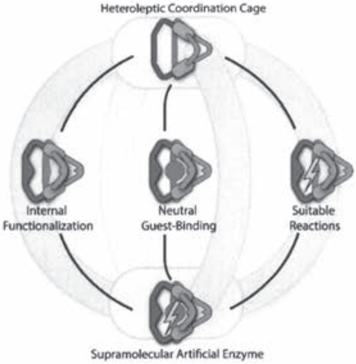

**Fig. 1.**: Schematic overview of this project addressing internal functionalization, neutral guest-binding and finding suitable reactions for catalysis in heteroleptic coordination cages.

Analytical procedures include basic 1D and 2D NMR experiments, ESI-MS and X-ray analysis. Furthermore, we started to analyze complex mixtures of up to ten different heteroleptic cages using trapped-ion-mobility spectrometry (TIMS) measurements, proving it to be a valuable addition to our standard analytic procedures.[5]

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# Backbone-Bridging Promotes Diversity in Heteroleptic Cages

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Most biological multitopic assemblies are low symmetric, usually hetero-multimeric.[1] Mimicking such asymmetrical biological systems by artificial supramolecules poses challenges to the employed assembly strategies. Recently, the exclusive formation of coordination cages with an asymmetric cavity has been pioneered in a variety of studies either by exploring the role of interligand, host-guest π-π interactions, implementing subtle donor-site modifications or utilizing a feasible and versatile "shape-complementarity".[2] While construction of self-assembled multi-cavity cages were realized by two major strategies: i) Utilization of multitopic e.g. tris- or even tetrakis-monodentate ligands,[3] ii) Catenation of single-cavity cages to give interpenetrated cages with three or more cavities of rather small size, rational construction of coordination cages containing multiple cavities of different sizes with the potential to differentiate guest species has been rarely studied.[4]

Here we report the non-statistical self-assembly of a heteroleptic cage cis-$[\mathrm{Pd}_2\mathbf{L}^{\mathbf{A}}{}_2\mathbf{L}^{\mathbf{B}}{}_2]$ by combination of shape-complementary bis-monodentate ligands $\mathbf{L}^{\mathbf{A}}$ and $\mathbf{L}^{\mathbf{B}}$ with Pd(II) cations. Furthermore, we show how such assemblies can be diversified by introduction of covalent backbone bridges between two $\mathbf{L}^{\mathbf{A}}$ units. Together with solvent- and guest-effects, the flexibility of these linkers is shown to modulate the nuclearity, topology and number of distinguishable cavities in a family of four structurally highly diverse supramolecular assemblies. We show how the interplay of few factors, controlling a ligand's coordination mode, can trigger structural differentiation and open new paths to push complexity in metallo-supramolecular assemblies and their properties to a higher level.

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# Steric hindrance: a tool for rational design of homo- and heteroleptic coordination cages

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Metal-mediated self-assembly of supramolecular assemblies has been proven to be an efficient tool for developing new materials with well-defined shapes and geometries. Among this, banana-shaped bis-monodentate ligands react with Pd(II) cations to achieve a broad range of topologies from small $Pd_2L_4$ cages, their interpenetrated dimers, rings of various size up to large spheres.[1] Besides the structural properties, appropriate choice of the building blocks allows to introduce functions in the system. However, most of the reported examples are highly symmetric structures carrying only one functionality. Introducing more properties (i.e. different building blocks) often lack of control over stoichiometry and stereochemistry. To overcome this, recently we started to develop rational design strategies to assemble heteroleptic cages in a non-statistical fashion.[2] We successfully used coordination-sphere engineering,[3] geometric shape-complementarity,[4] and ring-embedded-metal approaches to obtain integrative self-sorting of multicomponent $M_2L_4$ cages. In this work we report a new approach based on steric hindrance, to gain control over the nuclearity of the metal-mediated architectures, and as a strategy to form new $Pd_4L_8$ heteroleptic cages towards multifunctional coordination cages.

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# Heterodimerization of the Bowl-Shaped Coordination Cages Leading to the Pill-Shaped Dimer Encapsulating the Single C70 Molecule

**Shota Hasegawa[1] and Guido. H. Clever[1]**

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The physical properties of fullerenes confined in a defined space are of great interest as they can show, for example, metallic behavior and even superconductivity.[1] Such intriguing properties may be the result of a close contact between multiple fullerenes, encapsulated in close proximity within the same confinement. Solution-phase host-guest chemistry can be used to bring multiple fullerenes closely together, using hosts with specific cavity dimensions. So far, investigations of such multi-fullerene complexes have been limited to aggregates of only the same fullerenes. Therefore, the development of nano-arrays able to encapsulate different fullerenes on selected positions has come into the focus of our interest. To address this challenge, we design host molecules, able to bind several fullerenes of different sizes, based on self-assembled coordination cages, composed of curved ligands offering $\pi$ -surfaces. Recently, we reported formation of a pill-shaped coordination cage by coordination-sphere engineering a nanoscopic bowl, followed by bridging two bowls with anionic linkers.[1] We assumed that the pill-shaped cage is a good candidate to realize selective encapsulation of two different fullerenes as this host can encapsulate $C_{60}$ and $C_{70}$. On this poster, the synthesis of coordination cages consisting of Pd(II) cations and novel triptycene-based organic ligands and their encapsulation ability towards concave carbon-rich guests will be disclosed. Furthermore, single $C_{70}$ molecule encapsulating pill-shaped dimer formation by heterodimerization of bowl-shaped coordination cages will be shown (Figure 1). We believe that the $C_{70}$ encapsulating pill-shaped dimer is a good candidate to realize the rational heteromultimeric encapsulation of different fullerenes.

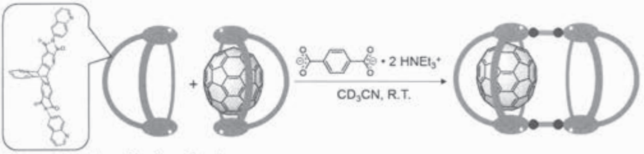

Figure 1. Heterotic dimerization

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# Solvation Dynamics of Nanoconfined Sodium Hydroxide in Reverse Micelles

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The hydrogen-bonding network of aqueous sodium hydroxide (NaOH) confined inside non-ionic reverse micelles (RMs) was characterized spectroscopically via dielectric relaxation, TeraHertz-time domain (THz-TDS), and THz-FTIR experiments. Measurements reveal distinct solvation dynamics of basic RMs with solvation of NaOH that is different from that observed in bulk solution. Relaxation times indicate movement of solvated ions from the micelle/water interface to the inner micelle core with increasing micelle size. Surprisingly, movement of the solvated ions to the micelle core causes a 4x decrease of the relaxation time of inner core water, in which times are consistent with pure water RMs, suggesting bulk-like solvation occurs. This effect is accompanied by a blue shift of the hydrogen-bond stretch band at 200cm$^{1}$ in FTIR spectra with increasing size. These results show a size-dependent solvation of confined NaOH, where solvent dynamics indicate inner core solvation of dissolved $Na^+$ and $OH^-$ ions in large RMs.

# The effects, of 0D confinement on the nucleation behavior of metal salts confined in micelles. A point experimental and theoretical study.

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Many recent works in the fields of material science, electrochemistry and industrial chemistry revolve around the synthesis of single metal and bimetal nanoparticles in micellar conditions.[1] With its 0-D confinement of the reaction space this method provides an outstanding control over size and shape of the resulting particles by variation of the micellar material, the solvent and the precursor. In a well-known synthesis the precursor is reduced by a chemical reducing agent introduced into the micelle, using the micelle as micro reactor.[2] More recent publications reveal a multitude of suitable nucleation procedures for micelle confined metal salts (i.e. electrochemical, plasma treatment).[3][4] However, the interfacial conditions these micelles could introduce within the bulk phase and the changes in nucleation behaviour that may arise from them are still mostly unknown.

The *in situ* techniques like liquid cell TEM, Darkfield Microscopy and surface sensitive spectroscopic techniques paired with a controlled nucleation (i.e. by electrochemical means) enable a time resolved capture of the nucleation process, as the change in chemical composition and absorptivity is monitored. Combined with concise state-of-the-art simulations a nucleation mechanism in regard to concentration gradients, liquid/liquid interfaces and surfactant nucleus interactions can be drawn.

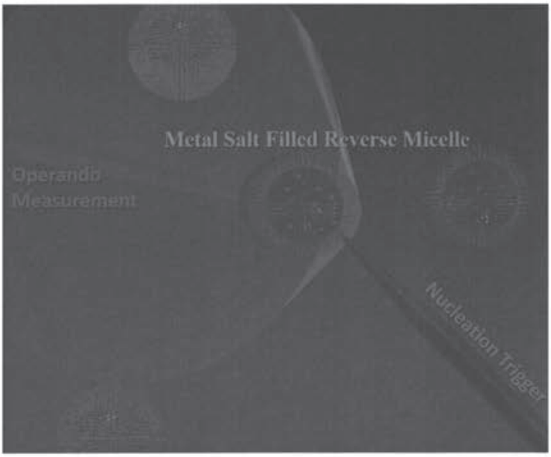

Fig. 1. Schematic illustration of the nucleation process occurring confined within the liquid pocket of a single micelle, triggered by a controlled process, while screened via *operando* measurements.

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# Nanoconfinement of Acid Inhibits Proton Hopping in Non-ionic Reverse Micelles

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Here the hydrogen-bonding network of water confined within neutral (water) and acidic (HCl) non-ionic Igepal reverse micelles was probed with THz absorption spectroscopy and dielectric relaxation spectroscopy. Characterization of the micelles as a function of size shows that the dissociated $H^+$ proton and $Cl^-$ anion preferentially adsorb to the water/micelle interface independent of micelle size. The Debye relaxation times of both interfacial and inner core water is retarded by the HCl and depends on micelle size. $W_0=9$ ($r$ = 2.41 nm) was identified as critical size for a turnover in structural and dynamical solvent properties. Below this size interfacial water dynamics are not retarded and a conductance band in the dielectric spectra is not observed. Above this size, a conductance band appears, formation of Eigen-like complexes occurs, and a 4 times retardation of inner core water is observed. The results presented here indicate that proton hopping (Grotthuss mechanism) and formation of solvated proton complexes is inhibited for micelles smaller than $W_0=9$.

# The response of amphiphilic hydrogels with varying hydrophilicity to the Hofmeister series

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Hydrogels exhibit excellent biocompatibility and resistance against nonspecific attachment of proteins most likely due to their stable hydration shell [1]. The properties of hydrogels made from crosslinked polymer chains can be altered by changing the pore size, attaching side chains with different functionalities and modification of the polymer backbone. All these alterations have a significant influence on the interaction with aqueous salt solutions. Copolymers of the sulfobetaine N-(2-methacryloxy)-ethyl-N,N-dimethylammoniopropansulfonate (SPE) with n-butyl methacrylate (BMA) and the photocrosslinker 2-(4-benzoylphenoxy)ethyl methacrylate (BPEMA) were used to tune the hydrophilicity of the hydrogels by varying the SPE:BMA ratio. The mechanical properties and the response of the polymer networks with salt solutions were characterized by surface plasmon resonance spectroscopy (SPR). Swelling and diffusion in the confined space of the pores is strongly influenced by the anions and salt concentrations in saline solutions. Moreover, there is no linear correlation between the hydrophilic content in the hydrogels and their swelling.

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## Free Energy Simulation of Guest Binding in a Photoswitchable Cage

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Photoswitchable hosts that confine small guest molecules inside of their cavities offer a way to control the binding/unbinding process through light. However, a detailed characterisation of the structural and thermodynamic consequences of photoswitching is very challenging to obtain by experiment alone. Thus, all-atom molecular dynamics (MD) simulations were carried out to gain insight into the relationship between structure and binding affinity.

Binding free energies of the $B_{12}F_{12}^{2-}$ guest were obtained for all photochemically accessible states of a photoswitchable dithienylethene (DTE) based coordination cage synthesized by Clever et. al. [1]. The MD simulations show that successive photo-induced closure of the individual ligands that form the cage decreases the binding affinity, thus offering a microscopic explanation for experimental findings.

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# Reactive Molecules in Confinement – from Matrix Cages to Supramolecular Host Molecules

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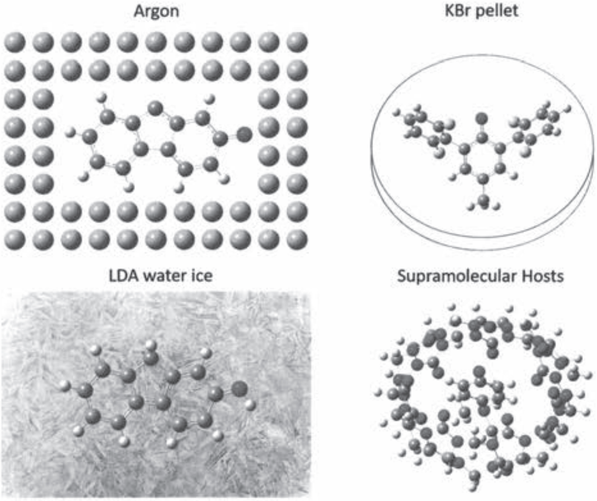
Reactive intermediates such as carbenes and nitrenes, due to their unpaired electrons in the triplet state, might serve as promising candidates for the development of organic magnets.[1] However, this is accompanied by high reactivity and thus low lifetime of the intermediate under normal conditions. Therefore, there is a need for increasing their stability in order to make them suitable for future applications.

This is performed by comparing results of interesting new reactive species formed in inert (Ar) and reactive matrices (low-density amorphous water ice) at cryogenic temperatures with attempts to stabilize reactive intermediates beyond cryogenic temperatures. Hereby, preliminary results on two routes regarding the stabilization are pursued. The first one is the internal stabilization by substitution with inert and sterically bulky groups near the reactive center and the second one consists of external stabilization by confining the intermediate in supramolecular host molecules.



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# Prediction of the experimental IR and VCD spectra of crown ethers complexed with chiral ammonium salts by DFT calculation

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Supramolecular chemistry is a fast-growing field and due to its interdisciplinary character, of great interest in many research areas. The influences on the preferred conformation by the complexation of the host and guest molecules are investigated for many supramolecular systems. Often for complexes only the binding affinity, binding constants and the crystal structure is studied by $^1$H-NMR spectroscopy, X-ray spectroscopy, fluorescence spectroscopy, UV/VIS spectroscopy. [1] While these techniques mainly focus on the stability in solution, resp. on the structure in the solid state, no information are received about the structure and binding situation in solution. Since VCD spectroscopy is very sensitive to even small conformational changes and non-covalent binding events[2], it should be implemented as technique for the analysis of host guest systems. Due to the combination of experimental data and theoretical spectra obtained by DFT calculations, a very detailed understanding of the binding situation and the conformational preferences of the complex is possible. In former studies the complexation of the crown ethers 18Crown6 and 15Crown5 with chiral ammonium salts, e.g. Methylbenzyl ammonium chloride, was investigated by IR and VCD spectroscopy. Thereby we noticed, that the prediction of the pure ammonium salts in chloroform and the prediction of the complex of 15Crown5 with Methylbenzyl ammonium chloride is far more complicated than expected. In this poster contribution the attempts for the correct prediction of the experimental spectra are presented.

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# VCD studies of C3-symmetric chiral thioureas

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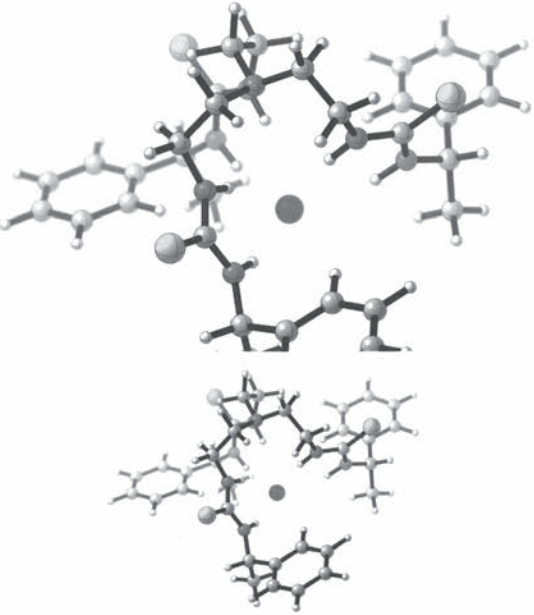
Thioureas are well known for their ability to form hydrogen bonds via their NH-protons, promoted by the electron withdrawing effect of the thionylgroup and further substituents. This also makes them able to bind different anions such as halides, nitrates, sulfates or organic carboxylates.[1] Therefore a wide range of application fields, from anion exchange to catalysis, is reported in literature and many more can



Chiral Thiourea **2**, upon binding a chloride anion

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# Abstracts of Posters
# Tuesday

(in chronological order)

# STM Investigations of Insulating Xenon Interfaces on Silver Surfaces as Low Interaction Substrates for Advanced Carbene Studies

**I. Langguth[1], M. Quack[1], I. Trosien[2], W. Sander[2], and K. Morgenstern[1]**

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The outstanding high reactivity of carbene molecules is of central interest in catalysis and basic research. For the understanding of these reactive intermediates, scanning tunneling microscopy (STM) is a highly favorable technique to gain locally resolved insight into the electronic structure of carbenes and their precursors. For an unperturbed characterization of these molecules, advanced surface decoupling methods are needed, to exclude dominating surface influences. Hence, the strategy of this work is to mimic the low interaction conditions between carbenes and their chemical environment as present in rare gas matrices by preparation of an ultra-thin non-conducting rare gas interface. Thus, the consecutive adsorption of xenon (Xe) followed by fluorene based carbene precursors on silver single crystals is investigated by low-temperature STM in ultra-high vacuum. Kinetically restricted precursor molecules are found to dictate the rotational orientation of Xe domains. Preliminary results for an evident molecular adsorption on top of the Xe layer are presented. This work was supported by the Research Training group 'Confinement-Controlled Chemistry', funded by the Deutsche Forschungs-gemeinschaft (DFG) under Grant GRK2376 / 331085229

# $D_2O$-$Cs^+$ complexes on Cu(111): An experimental study of real space structure and real time electron dynamics

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We aim at electron transfer processes at interfaces involving (1) photoinjection of electrons to solvated $D_2O$-Cs complexes from a metal electrode, (2) (de)solvation processes driven by the changed Cs charge count, and (3) back transfer of electrons to the metal. By combining Scanning Tunneling Microscopy (STM) and time-resolved Two-Photon Photoelectron Spectroscopy (2PPE) we investigate the microscopic structure and the ultrafast dynamics driven by photo-induced electron transfer at $D_2O/Cs^+/Cu(111)$. In time-resolved 2PPE we can follow the journey of the electron at the interface (1-3) in real time. Cs/Cu(111) exhibits an anti-bonding resonance (AR) feature upon photoexcitation at 3.1 eV which induces nuclear motion of the Cs ion core normal to the surface [1,2]. We perform static 2PPE experiments on Cs/Cu(111) while coadsorbing $D_2O$ and observe that the AR peak energy shifts from 2.71 eV to 2.76 eV above the Fermi energy of Cu(111) and the photoelectron intensity recedes at a coverage > 2 $D_2O$ per Cs ion. A new water-induced state emerges at 2.55 eV which we identify for 1 – 3 $D_2O$ per Cs. In time-resolved 2PPE experiments we find that this state stabilizes upon electron transfer from 2.42 eV to 2.24 eV at a rate of 1.0 eV/ps. Analysis of autocorrelation traces reveals an increase of decay time from 12 ± 3 fs to 52 ± 10 fs upon adsorption of $D_2O$. Furthermore, STM results show that Cs ions solvated with few $D_2O$ molecules exhibit an increase in apparent height and formation of $D_2O$ – Cs complexes for a coverage > 10 $D_2O$ molecules in which the effective distance between Cs ions are smaller than for dry Cs ions on surface. We demonstrate the microscopic nature of alkali solvation at interfaces and emphasize that coadsorption of water screens the interaction of alkalis with the environment while the alkali motion along the surface normal persists.

This work was supported by RESOLV, funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2033 - Projektnummer 390677874.

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# Difference between $CO_2$ structures two-dimensional confined on a metal as compared to a salt surface investigated by STM.

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Confinement increases the collision probability, but it might limit the flexibility of reactants during a chemical reaction. This effect of the confinement to one or two dimensions can be studied in a surface science approach. In this project, we use low temperature (T = 7 K) scanning tunneling microscopy (STM) in ultra-high vacuum (UHV) conditions (base pressure > $10^{-10}$ mbar) to study the effect of confinement dimensionality by consecutive adsorption of sodium bromide (NaBr) layers, carbon dioxide ($CO_2$), and electron-rich phosphines [1,2] onto a Ag(100) single crystal. Thereby, NaBr layers serve to electronically decouple the adsorbate molecules from the metallic substrate. The NaBr on Ag(100) is forming as quadratically-shaped islands, that are growing initially as a double layer followed by third and fourth layers. Further, the structures formed by $CO_2$ on pristine Ag(100) surface [3] are compared to those on a decoupling NaBr double layer. On Ag(100), the $CO_2$ monolayer consists mainly of domains with a quadratic symmetry. The geometry of $CO_2$ on the NaBr double-layer will be discussed in this presentation.

This work was supported by the Research Training group ´Confinement-controlled Chemistry´, funded by the Deutsche Forschungsgemeinschaft (DFG) under Grant GRK2376 / 331085229.

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# An Isolated Water Droplet in the Aqueous Solution of a Supramolecular Tetrahedral Cage

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Supramolecular capsules create internal cavities that act like enzyme active sites [1] and can confine water as well. The $Ga_4L_6^{12-}$ tetrahedral assembly by Raymond and co-workers represents an excellent example of a water-soluble supramolecular cage, which, using steric interactions and electrostatic charge to chemically position the substrate while shielding the reaction from solvent, has been shown to provide enhanced reaction rates that approach the performance of natural biocatalysts [2]. In particular, the driving forces that release confined water from the nanocage host to favour the direct binding with the substrate is thought to be a critical factor in the catalytic cycle, but is challenging to probe directly.

Here, we used THz absorption spectroscopy [3] and ab initio molecular dynamics [4] to characterize low-frequency vibrations and structural organization of water in this nanoconfined environment. We determined that a dynamically distinct network of 9±1 water molecules is present within the nanocavity of the host. The low-frequency absorption spectrum and theoretical analysis of the water in the $Ga_4L_6^{12-}$ host demonstrate that the structure and dynamics of the encapsulated droplet is distinct from any known phase of water. A further inference is that the release of the highly unusual encapsulated water droplet creates a strong thermodynamic driver for the high affinity binding of guests in aqueous solution for the $Ga_4L_6^{12-}$ supramolecular construct.

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# Anisotropic dielectric tensor of nanoconfined water in graphene slit pores

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Water that is nanoconfined within rigid structures, such as graphene slit pores [1], features different properties from bulk water [2] which directly impact on applications [3]. Recently, we discovered substantial differences in H-bonding and electronic properties between nanoconfined water in graphene slit pores when forming mono- and bilayers versus less strongly confined water versus bulk water [2]. Interestingly, the dielectric constant of water has been probed experimentally which offers some surprising results [4,5]. In an effort to shed light on these findings, we computed the local dielectric tensor across water lamellae in graphene-based slit pores subject to the symmetry restrictions imposed by planar confinement. Our previous *ab initio* simulation results [2] were used to parameterize a consistent water-graphene force field for the present simulations. Our results [6] show distinct confinement effects in the two components of the dielectric tensor. While the parallel component increases strongly at the confining walls, the distance-dependence of the perpendicular component is more intricate, yet points to a low value after averaging it within the water lamellae. We have additionally studied the impact of different flexibilities of the graphene sheets, from highly flexible to completely fixed in space. Simulations with restricted graphene sheet movement suggest that the water density distribution and dielectric response is rather independent of graphene fluctuations.

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# A Kernel-Based Approach to Advanced Thermoporometry Characterisation of Mesoporous Solids

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Detailed determination of the pore structure of mesoporous solids offers important guidance towards optimal design of various applications such as molecular separations, adsorption, gas storage, catalysis, among others.

Customarily used characterisation tools, such as thermoporometry and gas sorption, typically utilise the general adsorption isotherm (GAI) equation derived for ordered pore systems. However, the complex morphology of disordered porous solids, with its attendant cooperativity effects in thermodynamic phase transitions, renders characterisation more complex than what the GAI or Gibbs-Thomson equation presents.

Herein, a novel approach involving the recently developed serially connected pore model (SCPM), which extends the GAI by incorporating cooperativity effects in phase transitions arising from pore complexity. Additionally, variation of the molten liquid layer thickness which exists between a solid core and the pore walls and the removal of metastability in very small pores are incorporated into the creation of kernels for analysis with the SCPM.

The kernels are employed to study the structure of mesoporous MCM_41 and SBA_15 samples.

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# Stratification of Electrolyte Solutions in Graphene Nanoconfinement

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Electrolytes in nanoconfined water shows very interesting as well as puzzling behavior. Investigations of these electrolyte solutions can shed light on some of the modern day's problems like electrochemical energy storage, desalination nanodevices, or chemical reactions in nanoreactors. Force field molecular dynamics (FFMD) is helpful to understand nanoconfined ionic solutions in terms of their structural and dynamical properties like density profiles or diffusion coefficients. A key issue of any such FFMD simulations is the selection of the force field parameters for the studied system. For water in graphene slit pores, our group optimized accurate interfacial force fields for graphene slit pores filled with water [1] based on RPBE-D3 density functional theory and ab initio molecular dynamics [2]. Moreover, controlling the thermodynamic conditions is not straightforward in confined systems. In the same work [1], a new methodology for controlling pressure in slit pores has been developed, called piston approach. Based on these methodological advances, we have performed a series of FFMD simulations of aqueous ionic solutions inside graphene slit pores systematically as a function of water filling while keeping the applied pressure at 1 bar. The main differences between cations and anions as well as fully flexible and frozen graphene confinement will be outlined.

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# The role of resistance and mass transport on the Tafel approach at composite catalyst thin-film electrodes

**N. Blanc**, C. Rurainsky, K. Tschulik

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Electrocatalysts play a major role in the development of energy storage and conversion technologies, necessary for a transition from fossil fuels to renewable energy sources. To characterize such catalysts, the use of rotating disk electrodes, which are modified with multicomponent catalyst inks is common practice. These consist of a catalytically active material, a conductivity enhancing supplement and a binder, which confines the mixture to build the electrode. In this work, we present a numerical model to simulate the effect of altered mass transport and conductivity inside a catalyst film that consists of catalytically active nanoparticles, a chemically inert binder material and pockets of electrolyte. Implications for the classical Tafel analysis, which is the standard for comparison of different catalysts, are evaluated at various combinations of film resistances and mass transport properties. We show that for some combinations, linear Tafel-like responses may occur that would interfere with a sound catalyst activity evaluation, as the obtained voltammograms would not contain actual kinetic information.

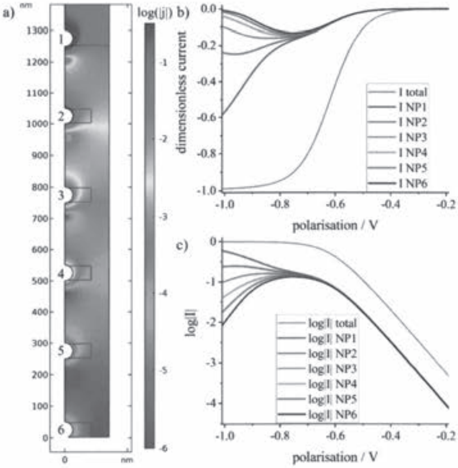

*Figure 1. a) The logarithm of the total flux magnitude at an electrode polarisation at large overpotentials is plotted. Catalytically active nanoparticles confined in a binder are acting as electrodes. b) The current distribution of an LSV in this system is shown. c) The corresponding Tafel plots of the dimensionless currents allow to determine the kinetic parameters at polarisations larger than -0.6 V. [1]*

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# Electrochemical Studies of Individual Nanoparticles Observed with Dark-Field Microscopy

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Single metallic nanoparticles, especially silver and gold, are nowadays frequently used in medicine or sportswear due to their antibacterial and anti-inflammatory properties, their physical properties, chemical reactivities and degradation. However, those nano-entities are still poorly understood and explored. Single noble metal nanoparticles can be studied with dark-field microscopy based on their localized surface plasmon resonance.[1] Using this methodology, it is possible to observe their optical appearance, thus color, and scattering spectrum. Hyperspectral imaging can be used to observe a change of the localized surface plasmon resonance *in situ* and *operando* due an applied potential and a subsequent electrochemical reaction, which is monitored by change of the scattering intensity and spectrum.[2,3]

With this new method, further insights into reaction processes and dynamics or structural transformations of nanoparticles during various electrochemical reactions can be observed. Thus, this knowledge can be used to gain more information about the *in vivo* and *operando* properties of nanoparticles itself, possible confinement effects at the particles or the impact of a dielectric environment at the particle surface or in the vicinity of it.

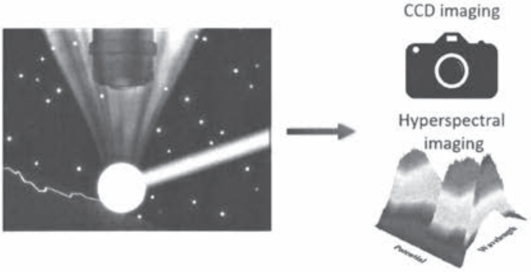

*Figure 1: Schematic illustration of an individual plasmon active nanoparticle during an electrochemical reaction at an electrode observed with dark-field microscopy.*

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# Using THz spectroscopy to investigate HCl in confined water systems

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Water is a ubiquitous molecule, which occurs in nature not only in bulk form but also in confined environments. Especially in biological cells with 40% of the volume being occupied by macromolecules, water molecules are not present in their usual tetrahedral form, as seen in bulk water. Instead, it strongly interacts with the confining interface [1,2]. This results in a perturbed hydrogen-bond network and retarded dynamics of confined water in comparison with bulk water. Reverse micelles like AOT (sodium bis(2-ethylhexyl)sulfosuccinate) are commonly used as model systems to investigate confined water. As a result of their amphiphilic character, nanometer-sized water pools become encapsulated by surfactants in a nonpolar solvent. These characteristics predestinate reverse micelles as a perfectly fitting model system to investigate the behavior of water systems within confined spaces. The size of micelles can be varied easily by altering the ration of water to surfactant, which is named the $W_0$ value. The collective hydrogen-bond network itself can easily be probed using THz spectroscopy. THz/FIR absorption spectroscopy is extremely sensitive to the changes in the structure and dynamics of the intermolecular hydrogen-bond network of water and aqueous solutions. In our setup, we can operate in the frequency range of 1 to 20 THz, corresponding to 30-700 $cm^{-1}$. [3] Here, we recorded THz spectra of nanoconfined water with HCl in micelles to investigate charge transport under confinement conditions.

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# Understanding Excited-State Proton Transfer and Proton-Confinement from the Water Perspective.

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It has come to a recent understanding, that the solvent and its attributes substantially affect chemical or biological processes [1]. Modelling the properties of the solvent by geometric confinement, e.g. along interfacial water or by frictional confinement in binary solutions, can alter the direction and outcome of these reactions [2,3]. Inside reverse micelles for example, the proton transfer rates are proven significantly slower than in the bulk [4]. Proton transfer takes often a part in the mechanism of reactions and thus demands further investigation. In the case of excited state proton transfer (ESPT), photoacids such as Pyranine have been investigated a number of times to give insight into temporal dynamics of proton transfer. By an increased acidity in the excited state, photoacids are ideal substances to probe the temporal evolution of ESPT. However, most techniques employ spectroscopic methods observing the ESPT from the perspective of the solute instead of the solvent where the proton is transferred to as final product. Here we present a novel technique of optical-pump Terahertz-probe spectroscopy where we trigger the photoacid and monitor the response in the THz frequency range, related to the hydrogen bond motions und thus water solvation dynamics. By observing the THz transmission changes, we were able to describe the dynamics upon photoexcitation within three distinct regimes. The signal consists of the energy release in the excited state of Pyranine, diffusive proton hopping and the final energy dissipation into the bulk. With the basic understanding of ESPT from the solvent perspective, we have derived a fitting model in accordance to literature that we seek to expand and extend by altering or confining the solvent geometry. For this instance, we present in addition first results from the Pyranine acetate system in which the acetate acts as a proton catcher surrounding the Pyranine. Further measurements will be addressed by the investigating ESPT in nanoconfined water inside reverse micelles.

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# Molecular structure elucidation with charge-state control

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The charge state of an adsorbed molecule significantly affects its physical as well as its chemical properties, for example, adsorption position, molecular conformation and aromaticity. The proven capabilities of single-electron sensitivity [1,2] and atomic-resolution [3] of atomic force microscopy (AFM) make it an ideal tool to perform charge-state manipulation experiments while atomically resolving the induced changes within the molecule. Here, we present AFM-based results that simultaneously demonstrate both the control in charge-state and the capability of resolving the atomic structure of a single molecule for different molecules [4].

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# Co-surfactant Acrylamide: a study on size and stability of AOT reverse micelles incorporating Acrylamide and Polyacrylamide

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Assemblies of nanoscale water pools solubilized by a layer of surfactants in nonpolar solvents are generally called reverse micelles (RMs) and find application in many areas of science and technology. For instance, they can be employed as chemical and enzymatic nanoreactors[1], in nanoparticle synthesis[2] or as experimental models for physically confined systems with limited amounts of water[3]. Understanding the composition, size and morphology of micellar structures can improve the applications further. Initially, we were interested in the effects of reverse micelle confinement upon the polymerisation of Acrylamide, but observed the effect of Acrylamide (AM) acting as a co-surfactant in AOT reverse micelles by the AM concentration dependent increase in micellar size has been observed previously [4,5]. Therefore, in this work the interactions between AM as well as PAM and the AOT reverse micelles are investigated and compared to effects on size at different water loading ratios of AOT reverse micelles incorporating varying molar amounts of AM as well as PAM by Dynamic light scattering (DLS) and FTIR measurements.

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# Electrokinetic Streaming Current Method to Probe Diffuse Layer at Externally Polarized Electrocatalyst-Electrolyte Interface

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We developed a novel technique, combining electrochemistry and electrokinetics, to understand the structure of electric double layers (EDL) at an electrocatalyst-electrolyte interface. It was applied to polycrystalline Au and Pt interfaces. Traditional electrochemical methods are used to study externally polarized electrode-electrolyte interfaces and Faradaic reactions. Electrokinetic methods (streaming current/potential) are used to study ion distribution and ionic conductivity in the diffuse layer at the interface of unpolarized (externally) solid material and electrolyte. We combined a 3-electrode electrochemical setup and a pressure regulated electrokinetic setup to apply potential on a planar electrode and measure streaming current for different pressures. Zeta potential at different applied potentials is calculated from the streaming current vs pressure data. Experimentally obtained zeta potential values are substituted into the exact analytical solution of Poisson-Boltzmann distribution in the diffuse layer to explicitly calculate ion density and ionic conductivity in this layer. This is a direct experimental method to calculate diffuse layer charge density at polarized interface using the well-established Gouy-Chapman-Stern (GCS) theory. The measured zeta potential vs applied potential data follows an approximate linear relationship in the capacitive potential window, and deviation from linearity is observed during specific adsorption of ions at the interface. In future, the knowledge of ion distribution and ionic conductivity in the diffuse layer calculated using this method will be applied to understand the ion-conduction mechanism inside the micro (< 2 nm) and mesopores (2-50 nm) of PEM fuel cell electrodes, where enhanced double layer conductivity is presumed to transport $H^+$ ions to Pt particles. The model will also require a detailed knowledge of pore-space geometry. This method can also be extended to understand the Platinum-ionic liquid interface.

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