

Photoinduced, Charge-Driven, and Molecular Processes under Confinement

796. WE-Heraeus-Seminar

24 – 28 September 2023

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 796. WE-Heraeus-Seminar:

The geometric confinement to nanoscale dimensions has a significant impact on physical properties of molecules and transition states or pathways of molecular processes, enabling the formation of new species. Even though scientists are widely making use of molecular confinement in diverse fields such as material science, surface science, catalysis, and supramolecular chemistry, fundamental mechanisms that alter molecular processes are not fully explored yet. Especially different branches of science often relate the predominant impact of geometric confinement to different effective origins. Thus, we strive to establish a scientific, interdisciplinary community to foster fundamental research in this emerging field of confinement-controlled processes and to develop guidelines for a unified approach across disciplines of investigating and describing confinement effects to remove inconsistencies in their interpretation.

In this seminar, we will bring together an international group of established senior and early career researchers from the complementary fields of surface science, physical chemistry, physical organic chemistry, material science, and theory. We aim at unravelling the impact and underlying mechanisms of confinement-induced effects on molecular properties and transformations focusing on charge-driven and photoinduced processes under partially and fully confined environments including surfaces, nano and mesoporous materials, nanotubes, micelles, organic cages, helicates, and cell compartments.

Scientific Organizers:

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Introduction

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Registration:

Elisabeth Nowotka (WE Heraeus Foundation)
at the Physikzentrum, reception office
Sunday (16:00 h – 21:00 h) and Monday
morning

Program

Program

Sunday, 24 September 2023

| | | |
|---------------|----------------------|--|
| 16:00 – 21:00 | Registration | |
| 17:20 – 17:30 | Karina Morgenstern | Opening remarks |
| 17:30 – 18:30 | Miquel Salmeron | Structure and reactions at solid-liquid interfaces |
| 18:30 | <i>BUFFET SUPPER</i> | |
| 19:30 – 20:30 | Christiane Ziegler | Metallacrowns on Surfaces – how a multi-method approach reveals the details |

Program

Monday, 25 September 2023

| | | |
|---------------|--|---|
| 08:00 | <i>BREAKFAST</i> | |
| 09:00 – 10:00 | Kristina Tschulik | Utilizing single entity and spectro-electrochemistry to better understand electrocatalysis in confinement |
| 10:00 – 11:00 | Yi-Lun Ying | Looking at single-molecule reaction through a nanopore |
| 11:00 – 11:30 | <i>COFFEE BREAK</i> | |
| 11:30 – 12:30 | André Laschewsky | Polymer self-assembly driven by charge- or photo-induced processes, versus charge- or photo-induced processes driven by polymer self-assembly: Chicken or the egg? |
| 12:30 – 12:45 | Lidón Pruñonosa Lara | Controlled light induced switching of Co(II) coordination cage structures |
| 12:45 – 13:00 | Alexandre Walther | Guest-induced transformation and chiral self-discrimination in azulene-based coordination cages |
| 13:00 – 13:10 | Conference Photo (in the front of the lecture hall) | |
| 13:10 | <i>LUNCH</i> | |

Program

Monday, 25 September 2023

| | | |
|---------------|--|---|
| 14:30 – 14:45 | Julien Rowen | Heavy-atom tunneling in the ring expansion of fluorenylazirines |
| 14:45 – 15:00 | Chao-Nan Yang | Observing confined local oxygen-induced reversible thiol/disulfide cycle with a protein nanopore |
| 15:00 – 16:00 | Larissa von Krbek | Stimuli responsiveness in molecules, cages, and dynamic libraries |
| 16:00 – 16:30 | <i>COFFEE BREAK</i> | |
| 16:30 – 17:30 | Flash talks I | |
| | Iheb Baklouti Nicola Bogó Yuyin Du Kseniya Gorbatenko Guillaume Hoffmann Lea Klausfering Samantha Muhring-Salamone Maximilian Notheis David Ocklenburg Boutaina Rezki Philip Schreyer Marius Spallek Lion Luca Stiewe Gers Tusha Ertugrul Yalcin | |
| 17:30 | <i>DINNER</i> | |
| 18:30 | Poster session I | |

Program

Tuesday, 26 September 2023

| | | |
|---------------|---|--|
| 08:00 | <i>BREAKFAST</i> | |
| 09:00 – 10:00 | Amar Flood | Confining anions inside cyanostar macrocycles to stabilize, modify and amplify their reactivity |
| 10:00 – 11:00 | Gonzalo Abellan | Carbon nano-onions: Potassium intercalation and reductive covalent functionalization |
| 11:00 – 11:30 | <i>COFFEE BREAK</i> | |
| 11:30 – 12:30 | Angelika Kühnle | Hydration layers at surfaces: Attraction or confinement? |
| 12:30 – 12:45 | Michael Buchmeiser | Olefin metathesis under confinement in mesoporous supports |
| 12:45 – 13:00 | Lucy Zhao | Functional template for light-controlled charge regulation in confined mesopores |
| 13:00 | <i>LUNCH</i> | |
| 14:30 – 14:45 | Florian Albrecht | Selectivity in single-molecule reactions by tip-induced redox chemistry |
| 14:45 – 15:00 | Aisha Ahsan | Kinetically induced phase transitions for discrete numbers ($1 \leq n \leq 12$) of atoms inside quantum confinements |
| 15:00 – 19:00 | Excursion | |
| 19:00 | <i>HERAEUS DINNER</i> (social event with cold & warm buffet with complimentary drinks) | |

Program

Wednesday, 27 September 2023

| | | |
|---------------|---------------------|---|
| 08:00 | <i>BREAKFAST</i> | |
| 09:00 – 10:00 | Gregori Ujaque | Modelling reactivity in the confined space of metallocages |
| 10:00 – 11:00 | Rafal Klajn | Supramolecular machinery for disequilibrating azoarenes |
| 11:00 – 11:30 | <i>COFFEE BREAK</i> | |
| 11:30 – 12:30 | Gerhard Klebe | Drug-target mode-of-action analysis: A case of confinement-controlled chemistry? |
| 12:30 – 12:45 | Johanna Angona | Characterization and dealloying of single micelle-nucleated agau nanoparticles by scanning electrochemical cell microscopy |
| 12:45 – 13:00 | Fan Gao | Identification of chiral amino acids in a single peptide using an electrostatically asymmetric nanopore |
| 13:00 | <i>LUNCH</i> | |

Program

Wednesday, 27 September 2023

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|---------------|--|---|
| 14:30 – 14:45 | Robert Lehn | Automated local polymer writing into a mesoporous silica thin film using a commercially available fluorescence microscope and oxygen tolerant PET-RAFT |
| 14:45 – 15:00 | Elie Benchimol | Controlling self-sorting: stimuli responsive multi-cage systems |
| 15:00 – 16:00 | Marie-Laure Bocquet | Reactive liquid water with 2D materials from AIMD: water as a ion reservoir , a collective hydron and a molecular ligand |
| 16:00 – 16:30 | <i>COFFEE BREAK</i> | |
| 16:30 – 17:30 | Flash talks II | |
| | Mercè Alemany-Chavarria Dave Austin Frederike Beyer Adrian Buchmann Sebastian Hütgens Malavika Kalarikkal Clemens Müller Lilian Najm Alsaye Melinda Nolten Yong-He Pan Simon Christian Rickert Lisa Schardt Dipesh Somvanshi Rinshad VA Houyang Xu | |
| 17:30 | <i>DINNER</i> | |
| 18:30 | Poster session II | |

Program

Thursday, 28 September 2023

| | | |
|---------------|--------------------------|---|
| 08:00 | <i>BREAKFAST</i> | |
| 09:00 – 10:00 | Miguel A. Garcia-Garibay | Triplet quantum chain reactions in crystalline dewan benzenes |
| 10:00 – 11:00 | Yoko Sakata | Development of kinetically-controlled molecular recognition systems |
| 11:00 – 11:30 | <i>COFFEE BREAK</i> | |
| 11:30 – 12:30 | Talat Rahman | Confinement-induced enhanced reactivity of single atom catalysts: theory meets experiments |
| 12:30 – 13:00 | Karina Morgenstern | Closing remarks |
| 13:00 | <i>LUNCH</i> | |

End of the seminar and departure

NO DINNER for participants leaving on Friday; however, a self-service breakfast will be provided on Friday morning

Posters

Poster session 1

| | |
|---------------------------|---|
| Iheb Baklouti | On-surface synthesis of carbenes by dimerization on a metallic surface versus on an insulating layer |
| Nicola Bogo | Benchmarking DFT-based excited-state methods for intermolecular charge-transfer excitations |
| Yuyin Du | Redox-active coordination cages based on pentatopic diazobipyridine-containing ligands |
| Kseniya Gorbatenko | Matrix isolation of bistable carbene |
| Guillaume Hoffmann | Characterizing confinement effects on chemical reactions: Endofullerene as a case of study |
| Lea Klausfering | Two-dimensional porous fantrip network on the calcite(10.4) surface |
| Samantha Muhring-Salamone | Plasmonic Nanosensing in a polymer confinement at different hydration states |
| Maximilian Notheis | Allosterically controlled metallo-supramolecular spin crossover complexes |
| David Ocklenburg | Flexibility drives oxalate recognition with neutral L2Zn2 helicates |
| Philip Schreyer | In-situ deposition and characterization of 12-metallacrown-4 complexes on a graphene/Ni(111) substrate |
| Marius Spallek | Electrochemical aldehyde oxidation at gold electrodes: gem-diol, non-hydrated aldehyde, and diolate as electroactive species |
| Lion-Luca Stiewe | Observing coupled water and protein modes using nonlinear Terahertz spectroscopy |

Poster session 1

Gers Tusha

Stereoisomerism of a supramolecular cage: computations help to sort out the riddles of a self-sorting system

Ertugrul Yalcin

Towards coordination cages with catalytically functional ligands

Poster session 2

| | |
|-------------------------|--|
| Mercè Alemany-Chavarria | Molecular description of ligand encapsulation into metallocages |
| Dave Austin | Ligand coordinated Pt single-atom catalyst allows heteroatom bond formation during water-gas shift reaction |
| Frederike Beyer | Cryospectroscopic studies on the complexes of C₂F₃I and chiral tertiary amines |
| Adrian Buchmann | Pre-thermalization dynamics of [Ru(bpy)₃]²⁺ in water |
| Sebastian Hütgens | Synthesis of chromophore decorated Pd(II) based self-assembled coordination complexes |
| Malavika Kalarikkal | Chiroptical recognition of anions with neutral L₂Zn₂ helicates |
| Clemens Müller | Synthesis and chiroptical spectroscopy of chiral azacryptands |
| Lilian Najm Alsayed | Investigation of highly reactive azides on Ag(100) and low interaction walls such as NaBr(100) by infrared spectroscopy |
| Melinda Nolten | The influence of supramolecular hosts on nano confined and solvation water probed by THz spectroscopy |
| Yong-He Pan | Preparing CCSS surfaces for scanning tunneling microscopy |
| Simon Christian Rickert | Phenanthracene nanotubes for explosive detection |
| Lisa Schardt | Influence of the Cu nanoparticle formation in NaAOT reverse micelles on the size of the micelle |

Poster session 2

- Dipesh Somvanshi **Configurational bias Monte Carlo generalised for a multi-component high-density system**
- Rinshad VA **Confinement-driven enhanced photodynamic therapy of zinc phthalocyanine within metal-organic cage**
- Houyang Xu **A rational designed concave-convex switchable pseudo-cubic cage as a structurally adaptable supramolecular host**

Abstracts of Talks

(in alphabetical order)

Carbon Nano-Onions: Potassium Intercalation and Reductive Covalent Functionalization

María Eugenia Pérez-Ojeda¹, Matteo A. Lucherelli², Gonzalo Abellán²

¹ Department of Chemistry and Pharmacy, Chair of Organic Chemistry II, Friedrich-Alexander University of Erlangen-Nuremberg, Nikolaus-Fiebiger-Str. 10, 91058 Erlangen, Germany; Joint Institute of Advanced Materials and Processes (ZMP), Friedrich-Alexander University of Erlangen-Nuremberg, Dr.-Mack-Str. 81, D-90762 Fürth, Germany.

² Institute of Molecular Science (ICMol), University of Valencia, Catedrático José Beltrán 2, 46980 Paterna, Spain.

Functionalization of carbon nanomaterials is a promising approach to controllably engineer the band gap structure, create novel architectures, and manipulate the interfacial characteristics of graphene and carbon nanotubes, increasing their processability.[1,2] Herein we report the synthesis of covalently functionalized carbon nano-onions (CNOs) via a reductive approach using unprecedented alkali-metal CNO intercalation compounds. For the first time, an in-situ Raman study of the controlled intercalation process with potassium has been carried out revealing a Fano resonance in highly doped CNOs. The confinement of the alkali metal was further confirmed by electron energy loss spectroscopy and X-ray diffraction. Moreover, the experimental results have been rationalized with DFT calculations. Covalently functionalized CNO derivatives were synthesized by using phenyl iodide and *n*-hexyl iodide as electrophiles in model nucleophilic substitution reactions. The functionalized CNOs were exhaustively characterized by statistical Raman spectroscopy, thermogravimetric analysis coupled with gas chromatography and mass spectrometry, dynamic light scattering (DLS), UV–vis, and ATR-FTIR spectroscopies. Last but not least, we have developed a novel method for CNOs individualization, obtaining stable dispersions, as well as a characterization route based on DLS and ultracentrifugation. This work provides important insights into the understanding of the basic principles of reductive CNOs functionalization and will pave the way for the use of CNOs in a wide range of potential applications, such as energy storage, photovoltaics, or molecular electronics.[3]

References

[1] Abellán, G.; Schirowski, M.; Edlthammer, K. F.; Fickert, M.; Werbach, K.; Peterlik, H.; Hauke, F.; Hirsch, A. *J. Am. Chem. Soc.* 2017, 139, 5175.

[2] Schirowski, M.; Abellán, G.; Nuin, E.; Pampel, J.; Dolle, C.; Wedler, V.; Fellinger, T. P.; Spiecker, E.; Hauke, F.; Hirsch, A. *J. Am. Chem. Soc.* 2018, 140, 3352.

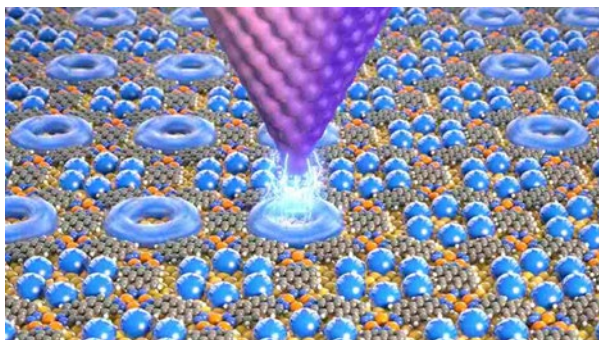
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Kinetically induced phase transitions for discrete numbers (1 \leq n \leq 12) of atoms inside quantum confinements

Aisha Ahsan^a, S. Fatemeh Mousavi^a, Thomas Nijs^a, Sylwia Nowakowska^a, Olha Popova^a, Aneliia Wäckerlin^a, Jonas Björk^b, Lutz H. Gade^c, Thomas A. Jung^{a,d}

^aDepartment of Physics, University of Basel, 4056 Basel, Switzerland. ^bDepartment of Physics, Chemistry and Biology, IFM, Linköping University, Linköping 581 83, Sweden. ^cAnorganisch-Chemisches Institut, Universität Heidelberg, Im Neuenheimer Feld 270, 69120 Heidelberg, Germany. ^dLaboratory for Micro- and Nanotechnology, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland.

We report about our investigations of condensation processes inside quantum confinements formed by on-surface coordination networks interacting with an electronic surface state. We produce periodic 2D quantum-well arrays with 1.6 nm pore dimensions containing a unique well characterized confined quantum well state. In well-controlled exposure experiments, such quantum well arrays are filled to different degrees. We then use the atomically resolving Scanning Tunneling Microscopy and Spectroscopy to investigate the number of atoms in each of the confining pores as well as the – typically shifted -- quantum state associated with the specific occupancy. In histogram plots we identify peaks giving us the ‘magic numbers’ for particularly stable occupancies and associate them with the one-by-one filling behaviour of the quantum wells. Further, we perform experiments at controllably varied temperatures and observe how the filling statistics of the quantum wells with condensates evolves. In our in-depth studies we can identify and reproducibly investigate (i) the thermally induced phase evolution of the populated quantum wells, (ii) the locally induced phase transformation between ‘solid’ and ‘fluid’ condensates inside the confinements by electric field ramping and (iii) the on-set of diffusion and coarsening at elevated temperatures as well as the real-time monitoring of the evolution of the filling levels. In addition to providing a showcase for ‘single-digit’ nanoscale data storage in a cheaply fabricated self-assembled matrix, this work is of fundamental interest as it paves the way to real space investigations of condensation processes in quantum confinements built by thermodynamic equilibration with sub-atomic precision.



A graphic animation of a possible data storage device on the atomic scale: A data storage element – consisting of only few (1-12) xenon atoms – is liquefied by a voltage pulse.

References

- [1] Nature Communications, 6, 6071 (2015) [\[DOI: 10.1038/ncomms7071\]](https://doi.org/10.1038/ncomms7071)
- [2] Small, 15, 1803169 (2018) [\[DOI: 10.1002/sml.201803169\]](https://doi.org/10.1002/sml.201803169)
- [3] Nanoscale (2019) [\[DOI: 10.1039/c8nr09163c\]](https://doi.org/10.1039/c8nr09163c)

Selectivity in single-molecule reactions by tip-induced redox chemistry

**Florian Albrecht¹, Shadi Fatayer^{1,2}, Iago Pozo³, Ivano Tavernelli¹,
Jascha Repp⁴, Diego Peña³, Leo Gross¹**

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² Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), Thuwal, Saudi Arabia

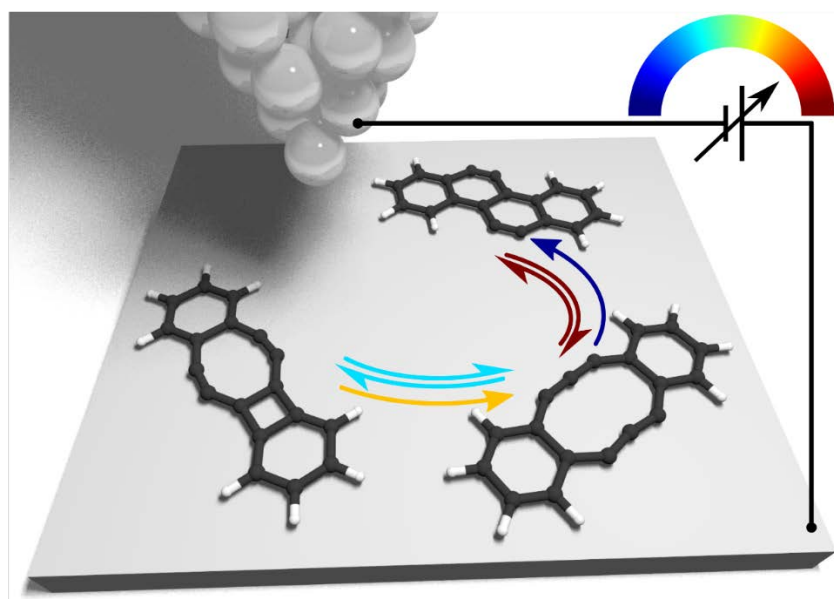
³ Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela, Spain

⁴ Institute of Experimental and Applied Physics, University of Regensburg, Regensburg, Germany

Since the first experiments by S.-W. Hla in 2000 [1], tip-induced on-surface synthesis is an active field. Not only in on-surface chemistry, selective control over the outcome of a reaction is a major quest. Here, we activate a molecule adsorbed on ultrathin insulating films by dehalogenation and perform selective constitutional isomerization reactions in a low temperature UHV combined STM and AFM. The selectivity is controlled by the polarity and amplitude of applied voltage pulses. The insulating films stabilize the isomers in different charge states and allow for their characterization. The importance of molecular charge state on the reaction is supported by DFT-derived isomerization energy landscape [2].

[1] S.-W. Hla et al., *Phys. Rev. Lett.* **85**, 2777 (2000)

[2] F. Albrecht et al., *Science* **377**, 298 (2022)



Characterization and Dealloying of Single Micelle-Nucleated AgAu Nanoparticles by Scanning Electrochemical Cell Microscopy

J. Angona^{1,2}, D. Valavanis², D. Houghton², T. Schroeder Rossi¹, F. Yang³, B. Roldan Cuenya³, J. V. Macpherson², P. R. Unwin², K. Tschulik¹

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Bimetallic nanoparticles (NPs) are highly interesting electrocatalyst materials due to synergistic effects generated by their additional active sites [1], and a capacity for tuning their activity by dealloying-treatment [2]. Synthesis routes using 0D confinement in micelles give enhanced control over composition and morphology of these bimetallic NPs [3]. However, a certain unavoidable distribution of catalytic performances and abilities for dealloying remains among the NPs. This calls for electrochemical tools that offer activity measurements at the single-entity level. Scanning electrochemical cell microscopy (SECCM) is such a tool, probing electrocatalytic current locally in a nanodroplet cell, and collecting many data points on one sample that can be post-characterized by e. g., scanning electron microscopy (SEM). This allows a direct correlation between NP activity and morphology/composition. The great potential of SECCM to probe single entities has already been demonstrated in correlative multi-microscopy studies [4] and the technique is being continuously developed further. In this work, precursor-loaded reverse block co-polymer micelles are electrodeposited on a conductive substrate forming AgAu alloy NPs. Electrochemical dealloying of these bimetallic NPs is used to tune their electrocatalytic activity for the hydrogen evolution reaction. At different states of dealloying, the NPs are characterized individually as to their specific activity and Ag: Au ratio using SECCM, followed by co-located SEM. This is linked with identical-location TEM (transmission electron microscopy) and EDX (energy-dispersive x-ray spectroscopy) at different dealloying states. Thus, the correlation of morphology and composition with the specific activity of dealloyed bimetallic nanocatalysts is enabled at a single-catalyst level, by statistical analysis, paving the way towards a knowledge-based design of electrocatalysts.

References

- [1] J.-H. Liu et al., *J. Phys. Chem. B*, **109**, 1, 40–43 (2005)
- [2] C. Rurainsky et al., *J. Mater. Chem. A*, **8**, 19405-19413 (2020)
- [3] H. Mistry et al., *Catalysis Today*, **288**, 30-36 (2017)
- [4] S. C. S. Lai et al., *J. Am. Chem. Soc.*, **133**, 28, 10744–10747 (2011)

Controlling self-sorting: stimuli responsive multi-cage systems

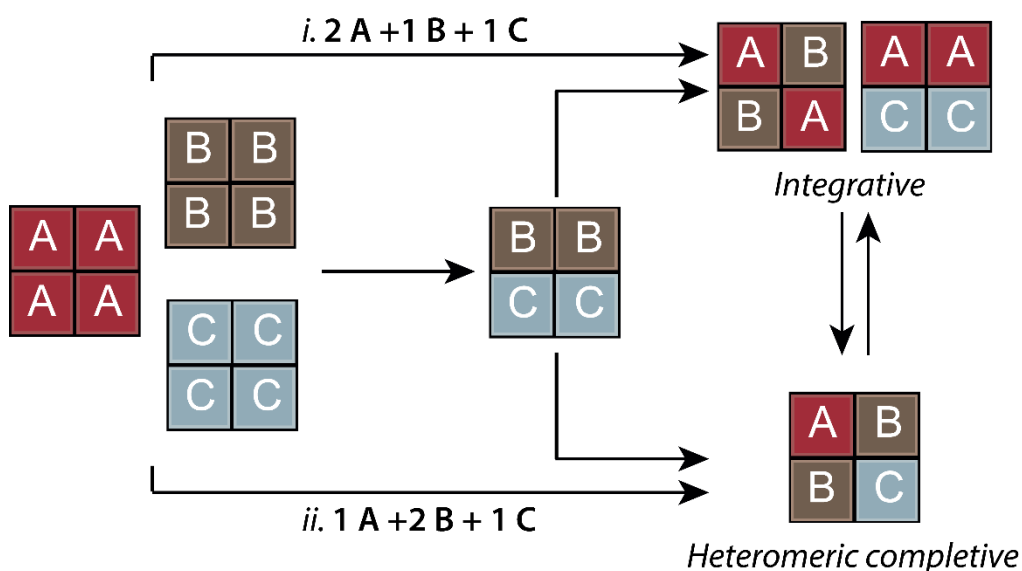
Elie Benchimol, Guido Clever

Dept. of Chemistry and Chemical Biology, TU Dortmund University,

While the majority of studies on heteroleptic assembly was aimed at producing a single discrete species in solution, biological systems are composed of a multitude of complex assemblies in mixture that either act together or perform separate functions. This requires multiple non-covalent assemblies to coexist under the same set of conditions and in an orthogonal fashion. Mimicking such a level of complexity has proven to be one of the most difficult tasks in supramolecular chemistry, in particular in dynamic equilibria.

We report the first example of “heteromeric complete” self-sorting in coordination cage systems. Two heteroleptic assemblies coexist in solution and the system can be controlled by mean of the ligand stoichiometry. Furthermore, it is possible to switch between either a Pd₂AB₂C heteroleptic cage through integrative sorting assembly or a mixture of two architectures Pd₂A₂B₂ and Pd₂A₂C₂.

Eventually, using multicomponent systems where several assemblies coexist independently can be exploited to transfer specific information from an assembly to another through stimuli responsiveness.



Reactive liquid water with 2D materials from AIMD: water as a ion reservoir , a collective hydron and a molecular ligand

Benoit Grosjean¹, Felix Mouhat¹, Nikita Kavokine³, Laura Scalfi², R. Netz², N., L. Bocquet¹ and M.-L. Bocquet¹

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²*Department of Molecular Spectroscopy, Max Planck Institute for Polymer Research,, Mainz, Germany*

³*Fachbereich Physik, Freie Universität Berlin, Berlin, Germany*

Nanoscale fluid dynamics or nanofluidics, is an emerging field of research where the continuum of hydrodynamics meets the atomic nature of the confining surface. When the surface is a 2D material like graphene the high performance of water flows at the nanoscale has long defied a rational understanding. Since 2D carbon materials can form large-scale membranes, rationalizing such performance is of utmost importance to facilitate water remediation. In this talk I first explain why the ideal 2D materials (graphene and hBN) acquire large surface negative charges, when immersed into aqueous solutions and rationalize the origin of this surface charge by means of *ab initio* MD (AIMD) simulations [1]. Second I propose an explanation for a sharp radius-dependent reduction of water friction inside multiwall carbon nanotubes, which cannot be accounted for with AIMD. Hence our group has derived an out-of-equilibrium theory beyond Born-Oppenheimer unveiling a quantum coupling between electronic excitations in the solid and molecular excitations in the liquid in the terahertz regime - coined “hydrons”- [2]. Finally I will explain why molecular water do react on a series of defective 2D materials like graphene oxide [3], a boron-vacancy in hBN and a Fe-N₄ Single Atom Catalyst defect in graphene, pointing out the necessary inclusion of water explicitly in the quantum simulations. As a key result, such interfacial chemical reactions fuel spontaneously neat liquid water with protons, which is highly needed for green heterogenous catalysis.

References

- [1] B. Grosjean, M.-L. Bocquet, R. Vuilleumier, Nat. Comm. **10**, 1656 (2019).
- [2] N. Kavokine, M.-L. Bocquet, L. Bocquet, *Nature* **602**, 84–90 (2022).
- [3] F. Mouhat, F.X. Coudert, M.-L. Bocquet, Nat.Comm. **11**, 1566 (2020)

Olefin Metathesis Under Confinement in Mesoporous Supports

M. R. Buchmeiser¹

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Stereoselective macrocyclization reactions offer access to a large variety of high-value chemicals and are nowadays preferably accomplished by olefin or alkyne ring-closing metathesis. Due to competing oligomerization reactions, however, high dilution is usually required, resulting in substrate concentrations of 5 mM or less. Also, high catalyst loadings up to 25 mol-% are necessary. To overcome these issues, we developed a biomimetic approach to macrocyclization, which uses well-defined organometallic catalysts selectively confined within the mesopores of a support material.^[1] This allows the use of substantially higher substrate concentrations up to 100 mM with macrocyclization selectivities up to 98%. Particularly the use of recently developed, highly active but functional group tolerant, air stable, cationic Mo and W imido/oxo alkylidene N-heterocyclic carbene complexes^[2-8] provides, apart from high macrocyclization selectivity, access to high Z-selectivity in olefin bond formation and high productivity. An extension of this concept to ring-expansion metathesis polymerization yielding cyclic polymers will be presented, too.

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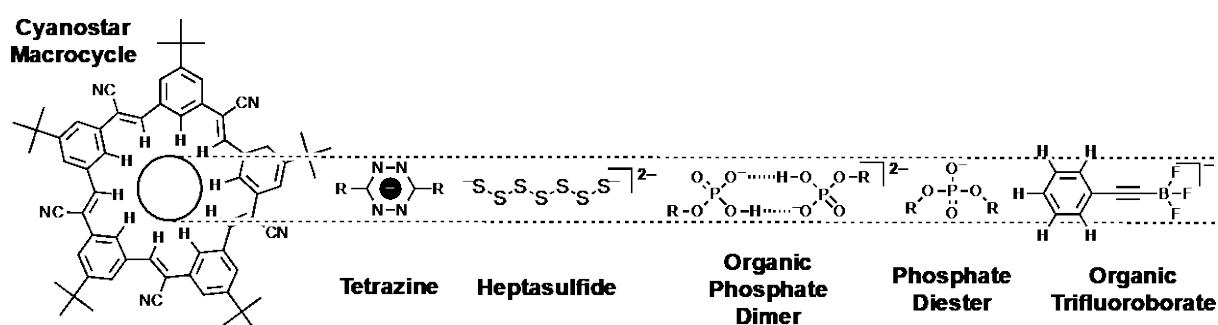
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Confining anions inside cyanostar macrocycles to stabilize, modify and amplify their reactivity

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Confining guests inside hosts has long been considered a mechanism to stabilize, modify and amplify the reactivity of the bound guests. The binding of small molecules to proteins provides ideal exemplars of the variety of functions that can be achieved using this principle. We are exploring these ideas using anions as guests when they are encapsulated inside short and large π -stacked and donut-shaped, cyanostar macrocycles. The central cavity is large enough to confine a cross section of anions. Using specific examples, we will showcase stabilization by protecting tetrazine radicals (Tz^{\bullet}) from oxidation, polysulfide dianions ($-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-\text{S}-$) from shuttling in rechargeable LiS batteries, and dimers of organic phosphates (aryl-OPO₃H⁻) from Coulomb repulsion. We will highlight a modification of Brønsted–Lowry acid-base properties of the phosphates in dimers and interlocked rotaxanes (R–OPO₃⁻–R). In unpublished work, we will present how stabilization of organic trifluoroborates (R–BF₃⁻) can modulate and potentially amplify their Lewis acid-base properties.



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Identification of Chiral Amino Acids in a Single Peptide Using an Electrostatically Asymmetric Nanopore

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Chirality widely exists in chemical and biological processes. In view of the great importance of chiral amino acids, many sensing technologies have been developed. However, existing approaches including mass spectrometry and optical methods encounter great challenges in amino-acid chiral discrimination due to the similar molecular weight and the absence of the overall molecule chiral center. Recently, the single-molecule method based on nanopore has shown the ability of sensing chiral molecules by designing a specific chiral environment, but it is hard to generalize towards peptides containing chiral amino acids. Herein, we established an asymmetrically stereo-confined space employing OmpF, an outer membrane porin from *E. coli* with an electrostatically asymmetric constriction zone (CZ). The extremely narrow sensing region of OmpF with a diameter of 0.7 nm matches the amino acid volume. And the heterogeneous distribution of charged residues in OmpF forms a strong lateral electrostatic field at CZ. This laterally asymmetric electrostatic field forces the sidechains of amino acids to specific orientations within OmpF, causing distinct ionic current fluctuations. Statistical analysis of the respective ionic current variations allows distinguishing the presence and position of a single amino acid with different chirality. Furthermore, the disease-related peptide β -Amyloid and its D-Asp¹ mutant and a mixture of the icatibant peptide drug and its D-Ser⁷ isomer have been discriminated, which demonstrates the potential application of OmpF chiral sensor. Our studies highlight a novel sensing mechanism for identifying single chiral amino acids in peptides and even for single-molecule proteomic studies.

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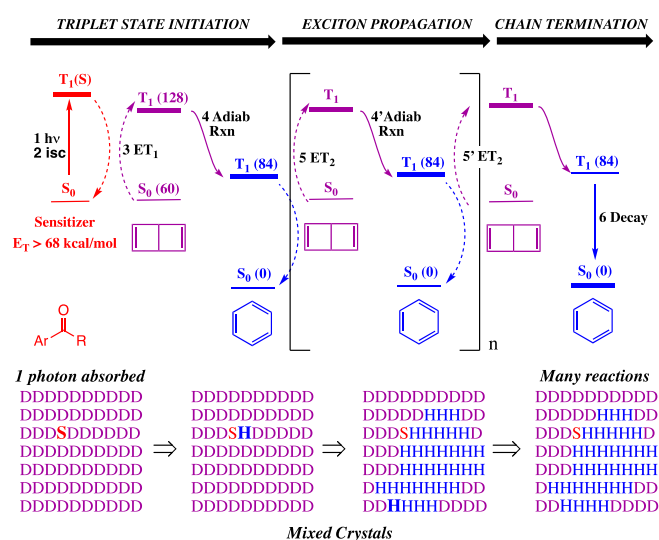
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Triplet Quantum Chain Reactions in Crystalline Dewar Benzenes

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Quantum chain reactions are characterized by the formation of more than one photoproduct per photon absorbed ($F > 1$) and constitute a promising signal amplification mechanism. Quantum chain reactions occur via an adiabatic excited state reaction where the excited photoproduct transfers energy to a new ground state reactant that is able to propagate the chain. The number of reactions per photon is determined by (1) the quantum yield per step, (2) the efficiency of energy transfer, and (3) the lifetime of the excited state. We have previously shown that crystals can enable quantum chain reactions from very short excited states by an efficient exciton-delocalization mechanism [1]. Now, with the purpose of exploring much greater amplification values, we have analyzed the triplet-sensitized isomerization of Dewar benzene to Hückel benzene as a promising model system [2]. Knowing that diffusion-mediated energy transfer can be the chain-limiting event in solution, we demonstrate a long-lived triplet state chain carriers in a crystalline solid can be more efficient by taking advantage of energy transfer by a triplet exciton delocalization mechanism. Using Dewar benzenes with either covalently attached or co-crystallized triplet sensitizers we have shown the amplification of large quantum yields of ca. $\Phi_{QC} \approx 10$ -50 in saturated solutions to values that increase to as much as ca. $\Phi_{QC} \approx 500$ in the crystalline state.



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Supramolecular machinery for disequilibrating azoarenes

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DisEquilibration by Sensitization under Confinement (DESC) is a supramolecular approach to isomerize photoswitchable molecules from the ground state to the metastable state using visible light of the desired wavelength (including red light). I will show that a combination a coordination cage and a visible-light sensitizer can act together to selectively bind and sensitize the *E* isomer of various azoarenes. Upon switching to the metastable *Z* isomer, the azoarene loses its affinity to—and is expelled from—the cage, which can then convert additional copies of *E* into *Z*. In this way, the cage·sensitizer complex acts as a light-driven supramolecular machine, converting light energy into chemical energy in the form of out-of-equilibrium photostationary states that cannot be accessed directly using visible light [1].

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Drug-Target Mode-of-Action Analysis: A Case of Confinement-Controlled Chemistry?

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Drug molecules usually evolve their activity through the binding to a macromolecular receptor. These receptors are biopolymers, composed by amino acids, nucleobases or sugar molecules. They provide a structured environment to which a drug molecule can bind. Once bound, the drug molecule, particularly if we consider small molecules, is in a highly confined environment, that modulates the properties of both binding partners. In case of enzymes, the drug molecules, often do not deviate strongly from natural substrates, however important chemical modifications morph them from being a reacting substrate to an inhibitor that blocks the enzyme reaction. What kind of confinement-controlled chemistry is required to morph a substrate into an inhibitor? Other biopolymers operate in signal transduction cascades and transmit through small but essential structural changes an information flow between the exterior and interior of cells. Cells have to change their functional status to perform and govern biological processes which, on macroscopy scale, make organs to fulfil a particular task. Mostly, these changes of the functional status of a cell are triggered by the binding of a small molecule ligand to a macromolecular receptor. In consequence of this binding of the small molecule to the confining architecture of the biopolymer, the macromolecule experiences important changes which initiate a cascade of subsequent processes that finally transform the cell in the modified state.

Using some examples the principle of drug-target interactions will be explained and how the mutual binding of a drug molecule to a biopolymer can accomplish its functional task in a highly confined environment.

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Hydration Layers at Surfaces: Attraction or Confinement?

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Dynamic atomic force microscopy (AFM) is a versatile tool for investigating surfaces at the atomic level. When performed at the solid-liquid interface, information about the solvation structure at the interface can be obtained [1].

At solid-water interfaces, hydration layers typically form [2-4]. The physical origin of these layers is usually ascribed to (i) confinement of the water at the interface and (ii) attraction of the water to the surface. While confinement is a general property at any solid surface, attraction is specific to the given system. In this talk, layer formation by confinement will be discussed in general, *i.e.*, it is explained how layer formation can be explained even in the absence of attraction. With the help of molecular dynamics simulations, it is shown that confinement alone does not cause the layer formation in the specific case of graphite surfaces. Thus, attraction between water and graphite is required to explain the layers observed on graphite at ambient conditions.

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Polymer Self-assembly Driven by Charge- or Photo-induced Processes, versus Charge- or Photo-induced Processes Driven by Polymer Self-assembly: Chicken or the egg?

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By virtue of their cooperative behavior, amphiphilic polymers can self-assemble in aqueous media into a multitude of stable supramolecular and colloidal structures, which are governed by a delicate balance of hydrophilic and hydrophobic interactions [1]. The formation of such structured systems results not only in major changes of the physical properties, but may also profoundly alter their chemical behavior, for instance due to compartmentalization, pre-organization or confinement effects. In reverse, processes that modulate the hydrophilicity (or alternatively, the hydrophobicity) of specific building blocks will unbalance the polymers' hydrophilic and hydrophobic interactions, thus changing their self-assembly processes as well as the resultant supramolecular structures. This can be exploited to create so-called responsive systems, in which small changes of a selected system parameter result in big changes of their properties. In extreme cases, both the amphiphilicity and the self-assembled structures are turned upside down, for which the term "schizophrenic self-assembly" had been coined [2]. Often, both phenomena, the modulation of the system's chemical behavior by the self-assembly process, and the modulation of self-assembly behavior by a dynamically tuned hydrophilic-hydrophobic balance, are closely interwoven. In this contribution, possible approaches to such "schizophrenic systems" will be presented [3,4], and the appropriate design of suited polymers elucidated making use of charge- and photo-induced processes.

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Automated local polymer writing into a mesoporous silica thin film using a commercially available fluorescence microscope and oxygen tolerant PET-RAFT

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Functionalization of mesoporous material with polymers to modify its attributes e.g. ion transport or wettability is a much-studied field. A localized functionalization can then be used for e.g. lab-on-a-chip devices with hydrophobic barriers and hydrophilic reaction chambers or janus membrane-like structures for fluid-based material separation. One way to produce locally confined polymer functionalization is to use light-induced polymerization in combination with local illumination. The use of photomasks allows for locally restricted illumination and is well suited for mass production but lacks flexibility when developing new patterns. A direct “writing” of polymer with a precisely controlled local illumination is needed for rapid prototyping in research and development. The development of a visible light-induced method made the usage of commercially available fluorescence microscopes with laser illumination for polymer writing possible.

Here, we present an adaptation of an oxygen tolerant photoinduced electron/energy transfer reversible addition–fragmentation chain transfer polymerization (PET-RAFT) to work under confinement in mesoporous silica films. In combination with a commercially available fluorescence microscope (Nikon Ti2-E) automated, precise and flexible micrometer-scale polymer writing in mesoporous silica thin films was achieved. Optimization of illumination time and power led to the ability to “write” any given monochromatic pixel image with a chosen polymer into the mesoporous silica film within a reasonable time frame. Three monomers with varying attributes were tested with the system (DMAEMA, MEP, METAC). Consecutive polymerization, as well as re-initiation for the functionalization with block-copolymers was successfully performed.

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Controlled light induced switching of Co(II) coordination cage structures

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Self-assembled metallo-supramolecular coordination cages and their host-guest chemistry have been of interest for decades due to their potential applications in areas such as medicinal and environmental chemistry, e.g., for drug delivery and as gas capture agents. However, controlling the ingress and egress of guest molecules into the cage's cavity can be challenging. Various external stimuli, such as temperature, pH, and light, have been used to regulate host-guest interactions. Amongst those, light is a particularly versatile stimulus for *in-situ* manipulation, because it can be controlled spatiotemporally, its wavelength and intensity can be precisely regulated, it is waste-free, and it avoids introducing further chemicals.

A photoswitchable cage, which undergoes structural transformations upon irradiation with light, would allow the cavity size to be easily modulated for controlled ingress and egress of guests. Using ligands with photoswitchable building blocks enables the formation of such light responsive cages. Azobenzenes, a well-established class of photosensitive chromophores, undergo controllable and reversible structural transformations *via* nitrogen double bonds.

Herein, we present the synthesis of a photoswitchable ligand containing an azobenzene moiety that undergoes *E*-to-*Z* isomerisation upon exposure to UV light. The ligand self-assembles into a photoswitchable M₄L₆ coordination cage in the presence of Co(II). As envisioned, irradiation of the Co^{II}₄L₆ structure led to its structural rearrangement, thereby completely changing its cavity size and shape. Synthesis and investigation of such stimuli-responsive cages will allow for controlled guest binding and release by modulating the cavity size of the cage for future applications.

Confinement-induced enhanced reactivity of single atom catalysts: theory meets experiments*

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Singly dispersed transition metal atoms on oxide surfaces, the so-called single atom catalyst, have recently been shown to attain chemical activity and selectivity for several technologically important reactions that surpass those of Pt single crystal surfaces, the prototype exemplary catalyst but with a large price tag. Apart from being cost-effective, single atom catalyst offer excellent opportunities for tuning their local environment and thereby their oxidation state, local coordination, and electronic structure. In this talk, I will present results of collaborative work of our research group with several experimental groups on single transition metal atoms anchored on oxide surfaces, with and without ligands, that have the potential to be cost-effective catalysts with high activity and product selectivity. Examples will include Pd and Pt atoms anchored on ZnO that form a bimetallic local environment consisting of one Pd and three Zn atoms with high catalytic activity for generation of H₂ through methanol partial oxidation (MPO) [1] and Pt atoms stabilized in specific fine-tuned local coordination environments that exhibit strikingly distinct, local coordination dependent catalytic propensity in reactions as varied as CO oxidation and NH₃ oxidation [2]. I will also pay attention to the special role played by ligands (1,10-phenanthroline-5,6-dione (PDO)) in enhancing selective hydrogenation of acetylene to ethylene of Pd single atoms stabilized on ceria surfaces [3]. Emphasis in each case will be on the electronic structural changes brought about by the characteristic local environment of the transition metal atoms that promote the activity and product selectivity of these novel nanocatalysts. I will also draw attention to some descriptors that may define the emerging functionalities of the above materials which are great examples of systems in controlled confinement.

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Heavy-Atom Tunneling in the Ring Expansion of Fluorenylazirines

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Nitrenes, the nitrogen analogues of carbenes, are highly reactive species and therefore possess only short lifetimes under normal conditions. Confining these species in cages of inert gases such as argon at cryogenic temperatures enables the investigation of these molecules by conventional FTIR, UV/Vis and EPR spectroscopy. A phenomenon that can only be studied at low temperatures are tunneling reactions where a molecule undergoes rearrangement despite lacking the energy to overcome the associated reaction barrier.

When 2-azidofluorene was deposited in an argon matrix at 3 K and irradiated with UV light, the corresponding triplet nitrene was formed. In contrast to time-resolved solution studies, the nitrene is stable under the applied confinement and its photochemistry can be investigated. Upon further photolysis, similar to experiments in solution at room temperature, two isomeric ketenimines are formed. This transformation is a two-step process via the corresponding benzazirines, but in contrast to previous measurements in solution, only one of the isomeric benzazirines was found. Additionally, this benzazirine was found to undergo heavy-atom tunneling to its ketenimine and the reaction rate was measured. A good agreement with estimated rates based on DFT calculations was found, showing a much higher rate constant for the other isomer that likely leads to this reaction not being detectable by (slow) matrix isolation measurements, but by time-resolved spectroscopy in solution. Thus, this investigation highlights the influence of position isomerism on quantum tunneling rates under these special confining conditions.

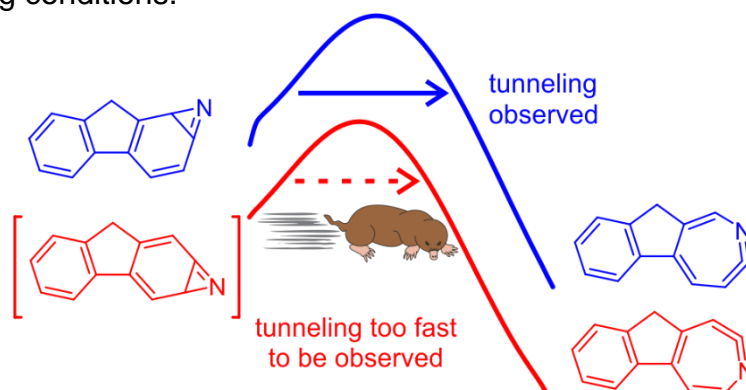


Figure 1. Schematic drawing of the heavy-atom tunneling processes occurring in cryogenic matrices.^[1]

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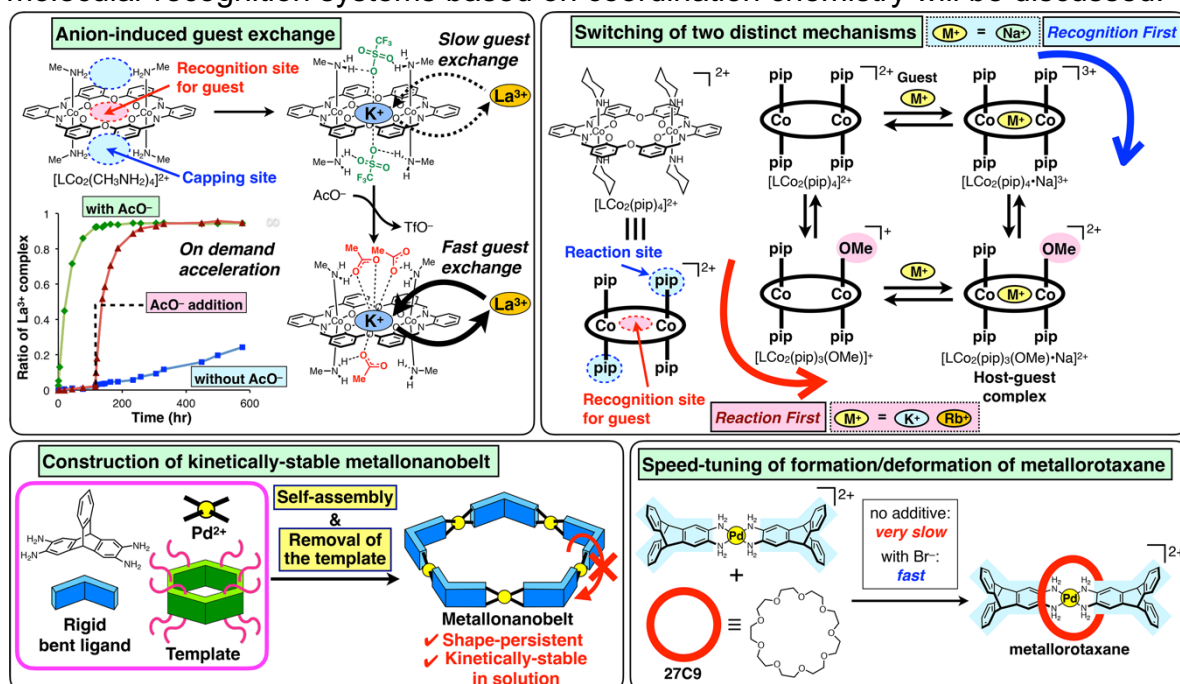
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Development of Kinetically-Controlled Molecular Recognition Systems

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Molecular recognition is generally a thermodynamically controlled event where the recognition ability is governed by the binding constants. Beside these thermodynamic parameters determined under equilibrium conditions, control of kinetic parameters such as guest inclusion/exchange rate or kinetic pathways is also important for the development of new host-guest system in which a desired function is driven and controlled by guest recognition. However, the strategy for the precise control of these kinetic process have rarely been reported. In this presentation, kinetically-controlled molecular recognition systems based on coordination chemistry will be discussed.



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Structure and Reactions at solid-liquid interfaces

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A detailed knowledge of the molecular structure of the interface between Electrodes and Electrolytes is crucial for solving fundamental problems in fields like electro-catalysis, wetting, corrosion, photochemistry, batteries and many others. The atomic/molecular structure of the electrode and that of the electrolyte, the so-called electrical double layer, in operation conditions, has eluded detailed study with spectroscopy due to the scarcity of surface-sensitive microscopy and spectroscopy techniques that can operate under liquid phases. My group in Berkeley has developed methodologies, techniques, and reaction cells that break this barrier. These techniques include optical vibration spectroscopies, including nano-Infrared, Raman, Sum Frequency generation, and X-ray and XPS and NEXAFS spectroscopies. I will show examples of recent results where we determined the double layer structure on Cu, Au, Pt, TiO₂, and graphene electrodes, in various electrolytes, and the molecular evolution of adsorbates in the presence of electric fields.

Utilizing single entity and spectro- electrochemistry to better understand electrocatalysis in confinement

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Over the past two decades, electrochemistry transformed into a widely utilized toolbox for basic physicochemical studies, sustainable synthesis approaches, and renewable energy technologies, ranging from batteries and supercapacitors to water electrolyzers and fuel cells. Since electrochemical reactions usually occur at complex, often porous and inhomogeneous electrodes, identifying confinement effects on reaction kinetics and product selectivity is usually not possible. Nano-electrochemical methods probe the kinetics of a full electrode, that is, a multi-component system composed of binders, conductive additives, a current collector and the catalytically active nanomaterial under investigation. Accordingly, both, separating mass transport from kinetic effects to extract and quantify the intrinsic nanocatalyst activity and identify degradation phenomena of the catalyst instead of the full composite, is extremely difficult by traditional electrochemical concepts.^[1] This inhibits the characterization - and thus the targeted exploitation - of confinement in electrocatalysis, and the comparability of data obtained in different laboratories or even with theoretical studies. Overcoming this limitation can be achieved via the development of novel electrochemical methods. Single entity electrochemistry, i.e. electrochemistry of or at single nanoparticles, spectro-electrochemical and in situ/operando microscopy investigations will be showcased in this talk as examples of such methods.

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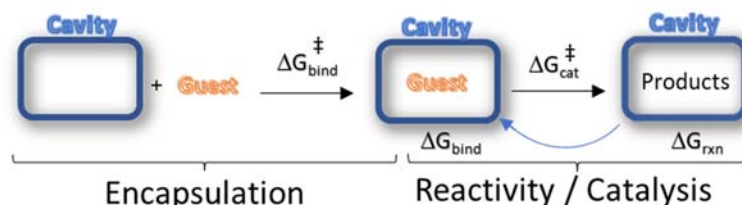
Modelling Reactivity in the Confined Space of Metallocages

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Reactivity inside cavities refer to chemical and physical processes that occur within confined spaces. When the cavities are generated by metallocages it merges host-guest chemistry with catalysis.¹ The process starts by the encapsulation of molecular guests (reactants) into the host (cavity), followed by the reaction itself. The computational study is very challenging, however, having a molecular/computational description should provide valuable insights into the physicochemical properties that guide such processes.

Chemical reactions can be faster inside cavities compared to solvent. What are the factors that govern such reaction rate increase? Here we will present a multiscale computational investigation. Some of the most relevant reactions catalyzed by the Raymond's² tetrahedral $[Ga_4L_6]^{12-}$ metallocage and the Fujita's octahedral $[Pd_6L_4]^{12+}$ metallocage³ will be presented. We will evaluate how the physicochemical properties (nature of the guest, motion of the species, solvent, etc.) affect encapsulation and reactivity.⁴



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Stimuli responsiveness in molecules, cages, and dynamic libraries

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Photoswitchable molecules can reversibly interconvert between two different isomers. We have developed a versatile synthesis for macrocyclic azobenzenes, which allows for facile modification of these photoswitches. One example shows high chemical stability, long half-life of its *Z*-isomer, quantitative *Z*→*E* conversion under white light, and excellent separation of the excitation bands to address either the *E* or *Z*-state selectively. Almost quantitative *Z*→*E* conversion, even under white light, is a unique feature with an important impact on applications, in which the configuration under ambient light needs to be close to 100%.^[3]

Spin-crossover (SCO) metal-organic cages are capable of switching between high-spin and low-spin states, which enables these molecular containers to be used as magnetic sensors and switches. A SCO tetrahedral Fe^{II} cage is capable of encapsulating various guests, which stabilize different cage spin states depending on guest size. Conversely, the SCO tetrahedron exhibits different affinities for the guests in different spin states, which is inferred to result from the subtle structural differences of the cavity caused by the change in metal centre spin state.^[2]

A dynamic library of metallo-supramolecular assemblies formed from a bis-urea-functionalized subcomponent reconfigured in response to the addition of monosaccharide derivatives, which served as guests for specific library members. The (*P*) enantiomer of the Fe^{II}₂L₃ helical structure bound β-D-glucose selectively over α-D-glucose. As a consequence, the library collapsed into the (*P*)-Fe^{II}₂L₃ helicate following glucose addition.^[3]

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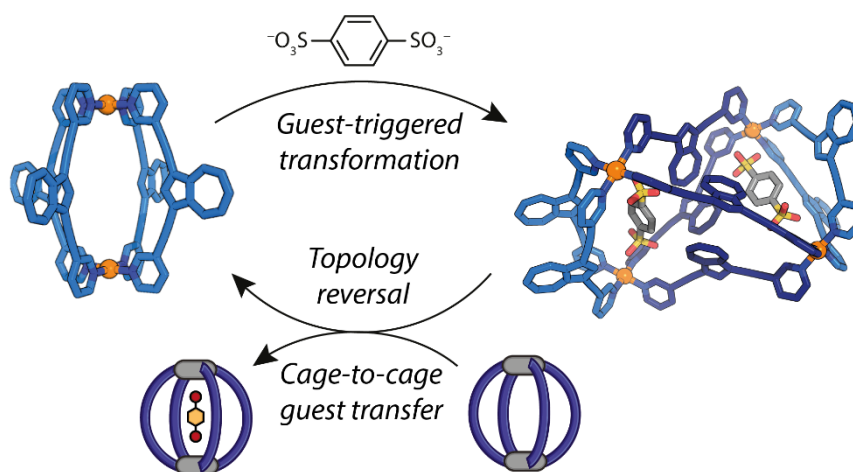
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Guest-induced transformation and chiral self-discrimination in azulene-based coordination cages

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The topology of coordination cages depends on several factors, notably the coordination geometry of the metal centres and the shape of the organic ligands constituting the walls of the cages. Based on these parameters, it is possible to predict the final structure of the final assembly. However, introducing guest species to the coordination assemblies' cavities can trigger unpredictable transformations to different shapes and topologies, a feat enabled by the labile nature of the coordination bond. From the first example shown by the lab of Ken Raymond [1] to the recent work of our group, this talk will explore the different structures and transformation pathways that were uncovered, turning seemingly simple systems into more complex ones as they react to guest binding. In particular, we will explore the halide-triggered dimerization of lantern-shaped Pd₂L₄ cages,[2][3] or a more recent example of the reversible transformation from a Pd₂L₄ cage to a Pd₄L₈ tetrahedron by the recapture of the guest by a second lantern-shaped cage.[4] We will also touch on chiral systems self-discriminating based on solvent H-bonding.



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Observing Confined Local Oxygen-Induced Reversible Thiol/Disulfide Cycle with a Protein Nanopore

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Disulfide bonds are of significance in thiol-based redox regulation ^[1,2]. However, due to the lack of analytical tools, there is still little knowledge about how local O₂ under protein confinement mediates the reversible thiol/disulfide cycle ^[3,4]. Herein, a protein nanopore reactor inside a glove box was developed for acting as O₂ confinement as well as a single-molecule sensor for real-time monitoring of the reversible thiol/disulfide cycle. Results demonstrated that the presence of local O₂ molecules in protein nanopores can facilitate the redox cycle of disulfide formation and cleavage by promoting a higher fraction of effective reactant collisions due to nanoconfinement. The further kinetics calculation described that the negatively charged residues near reactive sites facilitate proton-involved oxygen-induced disulfide cleavage under protein confinement. The unexpectedly strong oxidation ability of confined local O₂ may play essential roles in cellular redox signaling and enzyme reactions.

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Single-Molecule Reaction in a Protein Nanopore

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Chemical bonding plays a pivotal role in the field of chemistry. The ability to observe covalent and non-covalent bonds at the single-molecule level in real time provides valuable insights into the behavior of intermediates. Biological nanopores, which are intricate and well-ordered nanomachines, offer a unique platform for studying single-molecule chemistry.^[1-2] These nanopores consist of membrane proteins that form singular channels with distinct geometric and chemical properties, enabling the investigation of reactions at the single-molecule level. By tracking individual intermediates as they occur, we can visualize each step of a reaction or interaction and understand the underlying dynamics. Herein, we engineered an aerolysin nanopore reactor to elaborate the single-molecule reaction kinetics under nanoconfinement.^[3-4] By identifying the bond-forming and non-bond forming events directly, a four-state kinetics model is proposed for the first time.^[4] By combining with an N₂ glove box, we precisely control the local oxygen concentrations and monitor the reversible thiol/disulfide cycling process in real time.^[3] The results demonstrate that the local O₂ molecules in protein nanopores could facilitate the redox cycle of disulfide formation and cleavage by promoting a higher fraction of effective reactant collisions owing to nanoconfinement. Further kinetic calculations indicate that the negatively charged residues near reactive sites facilitate proton-involved oxygen-induced disulfide cleavage under protein confinement. Our work enables control over reaction pathways at the single-molecule level using emerging nanopore techniques, offering valuable insights for the design of single-molecule reactors. By continuously adjusting conditions accordingly and improved reaction selectivity, the synthesis of fine chemicals can be fine-tuned, leading to improved yields and reduced waste production. This advancement represents a significant step toward the development of sustainable and efficient manufacturing processes for fine chemicals.

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Functional template for light-controlled charge regulation in confined mesopores

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Biological pores provide a precise nanopore architecture and technologically unreached transport performance including gated, directed, selective transport. Directed transport through nanopores has been achieved by symmetry breaking. While structural asymmetry has been experimentally demonstrated to direct transport using conical ion track etched pores^[1], this has only been theoretically demonstrated for asymmetric functionalization^[2]. Asymmetric nanoporous material design needs new material fabrication and functionalization approaches. Here, we present an approach for *in-situ* polymer functionalization of mesopores developing functional block copolymer templates for sol-gel chemistry and evaporation induced self-assembly. For example, using PS-*b*-PAA *in-situ* functionalized silica films with pH responsive ionic permselectivity under highly filled conditions have been fabricated.^[3] Light-controlled charge regulation can be achieved with PEO-*b*-PNBA as mesopore template, which time-dependently releases pH responsive groups upon irradiation. Cyclic voltammetry measurements provide insights into the ionic permselectivity and its correlation to film structure, pore filling and gating of transport. The advantages of using functional block copolymers for *in-situ* functionalization include the one-step synthesis of functional hybrid silica films which then could be fabricated easily with e.g. high-throughput printing techniques such as gravure printing^[4] and the potential of realizing complex architectures consisting of different polymer-functionalized parts in a precisely designed manner on the nanoscale^[5]. This direct and simple approach for *in-situ* functionalization anticipates to enhance the achievable transport control and is thus relevant for technologies based on molecular transport in nanoscale pores such as sensing, separation, catalysis, drug-release and energy conversion.

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Metallacrowns on Surfaces – how a Multi-method Approach Reveals the Details

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Surface-attached molecules containing multiple magnetic ions often show excellent magnetic molecular properties. In particular, transition metal complexes containing exchange-coupled open-shell metal ions have attracted attention in the last decade. In such systems, spin relaxation time enhancement can provide a route to nanoscale spintronic devices.

We here report on the metallacrown complexes CuCu₄ and CuFe₄. Their preparation on reactive surfaces is delicate because of their low thermal stability. We thus use solvent-based methods (e-spray, liquid jet) applied in UHV for their deposition. In a multi-method approach, we utilize scanning tunneling microscopy, IR-spectroscopy, and in particular X-ray, UV- and inverse photoemission spectroscopy to prove the intactness of the complexes and to study their interaction with Au, SiO₂, and Ni/graphene surfaces.

In order to be able to use these complexes in practical applications, the magnetic states of the molecular spin systems on surfaces must be clarified. This is particularly important in contact with a metallic substrate to which the molecules are to be applied in devices. Spin-flip inelastic tunneling spectroscopy (SF-IETS) at low temperatures is an excellent tool for the detection of spin excitations and correlations of metal-organic complexes adsorbed on surfaces. After an introduction to this method, it will be shown that the two complexes CuCu₄ and CuFe₄ exhibit different spin-flip mechanisms correlated with their ligand sphere and their spin state. In particular, CuCu₄ may open a route to manipulate spins in non-magnetic metals confined to the molecular scale.

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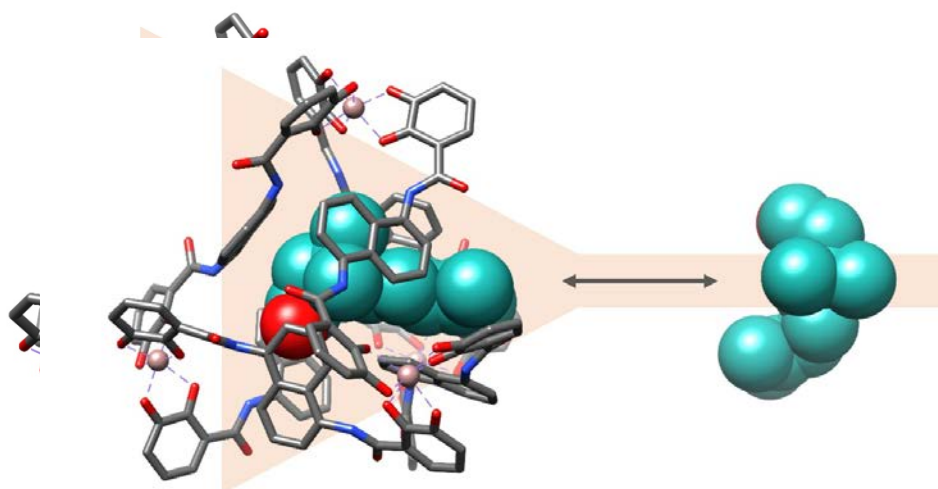
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Molecular Description of Ligand Encapsulation Into Metallocages

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Metallocages are self-assembled supramolecular structures that act as hosts for small molecules and have proven the ability to catalyze various reactions, mirroring the catalytic activities observed in many biological enzymes [1]. In this work, we study the encapsulation process of molecular guests into metallocage hosts at theoretical level. In recent years, several computational methods have been employed to unravel the intricate aspects of host-guest binding energies. However, these methods exhibited different degrees of success [2,3]. In the present work we propose a protocol using Well-Tempered Funnel Metadynamics that provides a significant advancement in the study of encapsulation processes of ligands into metallocages [4]. In addition, this protocol offers valuable insights into the characterization of ion-pair complexes, encapsulation barriers, and a complete description of the free energy profile for the host-guest binding process. Several tests,



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Ligand Coordinated Pt Single-Atom Catalyst Allows Heteroatom Bond Formation During Water-Gas Shift Reaction

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Abstract

Hydrogen is a promising renewable and environmentally friendly fuel to meet future global energy needs. An important reaction to produce hydrogen is the water-gas shift reaction (WGS), ($CO + H_2O \rightarrow CO_2 + H_2, \Delta H = -41.1 \text{ KJ/mol}$). Interest in the use of single-atom catalysts (SACs) for facilitating these reactions has grown. This project explores a new strategy that can create a metal-ligand single-site on a metal oxide support. 1,10-phenanthroline-5,6-dione (PDO), was chosen as the ligand for its oxidative potential for stabilizing metal cations in two bidentate sites. The single-atom nature of the Pt is characterized by EXAFS, XPS, XRD, DRIFTS, and TEM. The catalytic activity is evaluated for the WGS reaction, and it is discovered that Pt-ligand SAC supported on defective TiO_2 shows higher inherent catalytic activity than Pt NPs with significantly lower activation energy which is generally desirable for the redox mechanism. Using density functional theory (DFT) to simulate the Redox, associative, and single Pt atom WGS reaction on defected TiO_2 surface. The DFT calculations further confirm that the redox mechanism has a lower energy barrier than the associative mechanism for Pt-ligand SAC. A microkinetic study was also performed to obtain the theoretical turnover frequency for all three reactions. The microkinetic study shows that the Redox mechanism has a higher turnover frequency than that of the associative and single Pt atom reactions.

On-surface synthesis of carbenes by dimerization on a metallic surface versus on an insulating layer

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A carbene is a key intermediate in organic chemistry in reactions such as cyclopropanations[1], insertion reactions[2], and the olefin metatheses[3]. However, despite their importance in homogeneous and heterogeneous catalysis, their reactivity on surfaces with different interactions has not been explored yet. Here we reveal the on-surface reaction of the precursor 9-diazofluorene to bifluorenylidene on the Cu(111) surface and NaBr(100) layer. The reaction on surfaces is followed by Infrared Reflection Absorption Spectroscopy (IRRAS) analysis. Cu(111) is catalytically active, such that 9-diazofluorene is dissociated into fluorenylidene upon deposition at liquid nitrogen temperature. The carbene creates a copper-carbene complex on the first layer, which decouples the carbenes in higher layers from the copper surface. By illuminating the surface at a wave length of 365 nm, the fluorenylidene reacts and creates bifluorenylidene and other species. In order to increase the yield of bifluorenylidene, a low interaction wall of NaBr(100) is introduced. The formation of bifluorenylidene is preferred when the reaction with the Cu(111) surface is hindered. Understanding those reactions between carbenes and low interaction walls opens the way to develop novel catalytic systems. This will be discussed in this poster.

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Cryospectroscopic Studies on the Complexes of C₂F₃I and Chiral Tertiary Amines

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Using the matrix isolation technique,¹ we investigated weak intermolecular interactions in complexes of trifluoroiodoethene C₂F₃I (ITFE) and chiral tertiary amines of various steric demand. High resolution FT-IR spectroscopic studies revealed not only the formation of halogen-bonded C-I...N complexes - depending on the steric shielding of the nitrogen center - but also the less thermodynamically favourable C-I... π interactions. Furthermore, based on the prominent C=C stretching vibration of the well-studied halogen-bond donor ITFE,² experimental halogen-bond strengths could be determined.

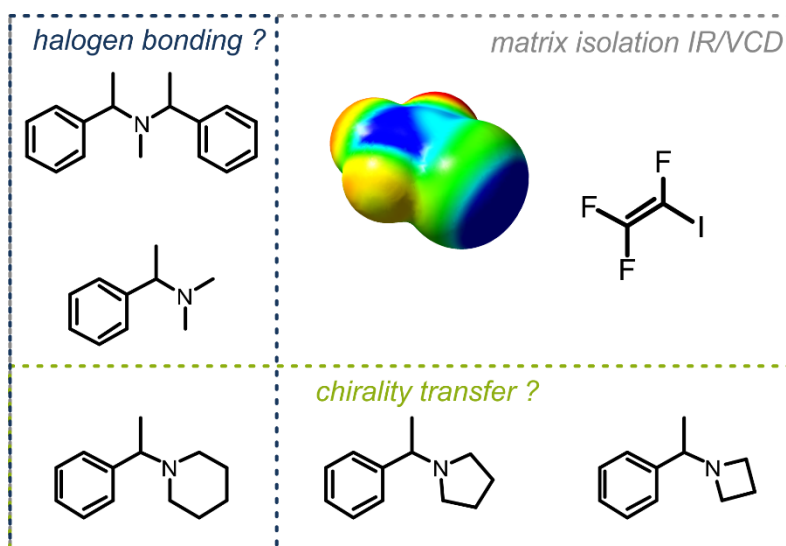


Figure 1: Chiral tertiary amines and halogen-bond donor ITFE whose complex formation was studied by chiroptical spectroscopy under matrix isolation conditions.

FT-IR data were complimented by Vibrational Circular Dichroism (VCD) measurements to test for a chirality transfer from the chiral tertiary amines towards the achiral ITFE. In this context, a good optical quality of the matrix is essential to unambiguously assign an induced VCD signature to ITFE due to complexation and is therefore an imperative objective of all our matrix isolation studies.

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Benchmarking DFT-based excited-state methods for intermolecular charge-transfer excitations

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In the pursuit of predicting the energetics of intermolecular charge-transfer (CT) excitations in supramolecular assemblies, we face the challenge of identifying reliable, accurate and reasonably inexpensive DFT-based methods. Many approximations influence the performance of such methods, among them the choice of a semi-empirical range-separated exchange-correlation functional (XCF), which must be capable to accurately describe long-range interactions^[1]. On top of that, the XCF should reproduce the exact derivative discontinuity for the addition and removal of an electron to the system. This can be achieved by tuning the range-separation parameter in the XCF, which is now a system-specific property^[2]. A second, yet fundamental approximation resides in the formalism employed for excited-states electronic-structure calculation. We here compare two such formalisms: the first is time-dependent DFT^[3] (TD-DFT), where the response of the system to an electric field is studied to capture the energies of electronic excitations. TD-DFT is well known for its deficiencies when it comes to CT excitations, especially when the Tamm–Dancoff approximation is applied and molecular orbitals (MOs) are not reoptimized in the excited state. The second approach employed for the calculation of excited-state energetics is a state-specific Δ SCF calculation, in which the MOs are optimized to achieve a stationary energy under a set of constraints^[4]. Due to the formation of a Zwitterion in the CT states, the orbitals are expected to change significantly.

Multiple XCFs and excited-state methods are tested against highly accurate reference data for small molecular dimer systems, with the goal to identify the best strategy for the calculation of intermolecular CT energetics using a low-scaling method that can then be applied to the large supramolecular assemblies.

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Pre-thermalization dynamics of $[\text{Ru}(\text{bpy})_3]^{2+}$ in water

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In the present study, we focus on the energy release of a chromophore subsequent to photoexcitation into the solvent. Recent breakthroughs in nonlinear THz techniques have enabled the observation of a dynamic solvent response on a picosecond timescale [1], [2]. We have employed optical pump terahertz (THz) probe spectroscopy to investigate $[\text{Ru}(\text{bpy})_3]^{2+}$ in an aqueous solution. $[\text{Ru}(\text{bpy})_3]^{2+}$ is of central importance because of its use as a photosensitizer in photocatalytic processes [3]. This importance originates from the metal-ligand charge transfer it undergoes upon optical excitation [4]. This charge rearrangement induces a response of the water network. Because the excitation process is well defined in time, it enables the observation of the reorganization of the water network subsequent to the initial disturbance. The response of the water network is expected to start in the immediate proximity of the $[\text{Ru}(\text{bpy})_3]^{2+}$ molecule and then travel spatially outwards into the bulk form there. In our optical-pump THz-probe experiments, we can see the frequency-resolved reaction of the water network to the metal-ligand charge transfer excitation of $[\text{Ru}(\text{bpy})_3]^{2+}$ in the range from 50 to 200 cm^{-1} . We will present results that can be attributed to the suspected initial directed network reaction within the first 2 ps as a red shift of the THz signal. The signal grows in magnitude on a timescale between 1 ps and 20 ps, indicating the involvement of an increasing number of hydrogen bonds as it would be expected from a disturbance traveling into the bulk solvent. It finally settles into a THz signal that remains constant until the end of our observation time at 300 ps. This signal is slightly blue-shifted from the difference in linear THz signal when observing water at different temperatures [5]. These findings tie initial solvent motions to, and give an indication of, the properties of the hot ground state in an aqueous solution.

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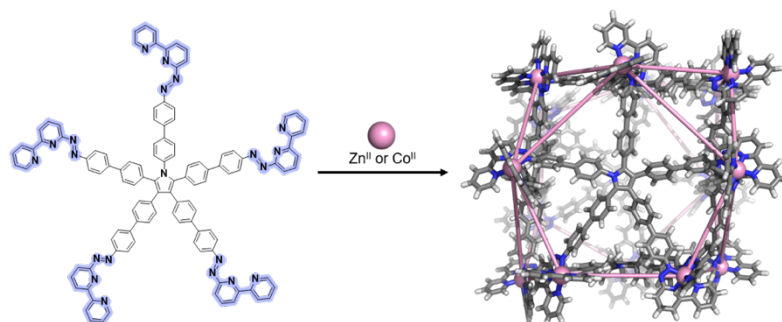
Redox-active Coordination Cages Based on Pentatopic Diazobipyridine-Containing Ligands

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Metal-organic cages featuring internal cavities can effectively accommodate diverse guest molecules. The controlled release and uptake of guest molecules can be regulated by diverse stimuli. For instance, incorporating redox-active diazopyridine motifs into metal-organic cages could render the cage with reversible redox-controlled guest release and uptake abilities.¹ However, it is also important to endow the redox active properties to larger complex architectures, as cages with augmented structural complexity have increased chances of encapsulating more low-symmetry and information-rich guest molecules.

Herein, we have designed a novel pentatopic pyrrole-based ligand by upgrading diazopyridine groups with diazobipyridine groups to construct a large truncated rhombohedral $M_{15}L_6$ cage ($M = Zn^{II}$ or Co^{II}), since our previous study suggested that iminobipyridine-contained ligands can provide tridentate coordination abilities to metal ions, resulting in much larger architectures.² In comparison to previously reported diazopyridine-contained tetrahedral or cubic cages, this newly formed truncated rhombohedral cage with diazobipyridine groups boasts a significantly larger internal cavity, with the potential to accommodate larger guest molecules, including dimethoxypillar[5]arenes, calix[6]arenes, and tert-butylcalix[5]arenes. In addition, the diazobipyridine groups of this ligand can reversibly accept and donate electrons, thus functionalizing the cage with redox properties. As a result, guest molecules are expected to be released upon reduction and subsequent decomposition of the cage and can be encapsulated again upon oxidation and the reformation of the cage.



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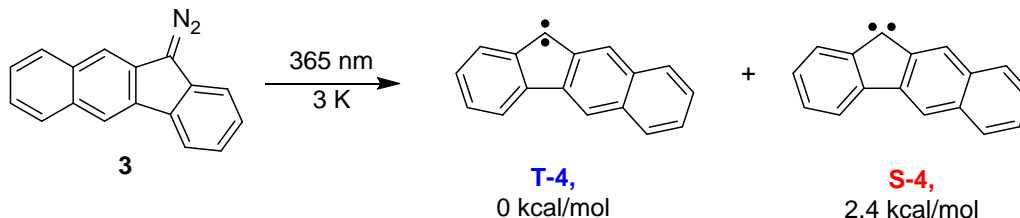
Matrix isolation of bistable carbene

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This project aims to synthesize and characterize a bistable carbene confined within a matrix cage, investigate its reactivity with small molecules, and examine the modulation of the singlet-triplet ratio induced by confinement. Some carbenes exhibit a small energy gap between their singlet and triplet states, leading to a switch between these spin states. This phenomenon challenges the expectation of rapid intersystem crossing and can be observed under matrix isolation at cryogenic temperatures.

The magnetic bistability of confined carbenes holds potential for information storage. Benzo[b]fluorenylidene is a molecule of interest in this context. The choice of matrix host influences the observed spectra and singlet-triplet ratio. Experimental findings reveal the carbene's magnetic bistability and absence of thermo- or photo-induced spin conversion. Reactivity investigations involve introducing small molecules and studying the carbene's behavior in pure hydrogen and deuterium matrices using IR, UV-vis, and EPR spectroscopy.



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Characterizing confinement effects on chemical reactions: Endofullerene as a case of study

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Both literature and experimental work concur that confinement modulates chemical reactivity in four different ways [1-2]

- By influencing chemical kinetics
- By influencing selectivity
- By influencing the establishment of transition states or reaction intermediates
- By altering the physico-chemical properties of confined molecules

But remarkably very few theoretical works on confinement effects have been carried out. The literature is mostly limited to confinement effects involving small molecules and simple reactions, such as the decomposition of carbonic acid trapped in fullerene-type cages by Mallick et al. [3]. Yet the results obtained are quite interesting, as they show that there is a significant correlation between strength of confinement and enthalpy of reaction. In fact, by decreasing the size of the molecular cage cavity, i.e., by using smaller fullerenes, the reaction becomes increasingly endothermic. Whereas without confinement, the reaction is highly exothermic.

Thus, our work was aimed at modelling and investigating confinement effects on larger scaled chemical reactions. The inquiry was done on a set of classical organic chemistry reactions. Two monomolecular reactions were modeled in the gas phase and inside of different fullerene cages (C60, C70 and C80). Interesting results were obtained and they will be presented in the poster presentation.

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Synthesis of Chromophore Decorated Pd(II) Based Self-Assembled Coordination Complexes

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The organization of individual chromophores on a molecular scale is a challenge to be overcome in controlling intermolecular photoinitiated processes such as charge or energy transfer. Self-assembled coordination complexes (SCCs) are constructed from relatively simple molecular building blocks, which are incorporated into fixed positions in the SCCs framework. Thus, they may be used as a scaffold to attain exact control over chromophore positioning. Furthermore, SCCs are widely used in host/guest chemistry based applications which may be enhanced by the presence of photoactive groups.

Following such considerations we decided to introduce BODIPY and anthracene as chromophoric groups to the *exo* position of bispyridyl ligands, which then self-assemble with Pd(II) cations into Pd₂L₄-cages, {[Pd₂L₄]@[Pd₄L₈]} cage-in-ring complexes^[1] and Pd₁₂L₂₄ molecular spheres, where the chromophores are arranged in fixed positions and relative orientations. In the literature, introduction of functions to the *endo* position was used to induce Pd₂(L^A)(L^B)₃ self-sorting, or to attain catalytically active molecular spheres. Thus, we developed a synthetic route to both BODIPY and anthracene decorated ligands featuring a final stage diversification of the *endo* position, enabling the facile synthesis of desired ligands. For the attained complexes, we envision applications as fluorescent drug delivery vectors, supramolecular photo-redox catalysts or light harvesting antenna systems featuring a directional multi step energy transfer.

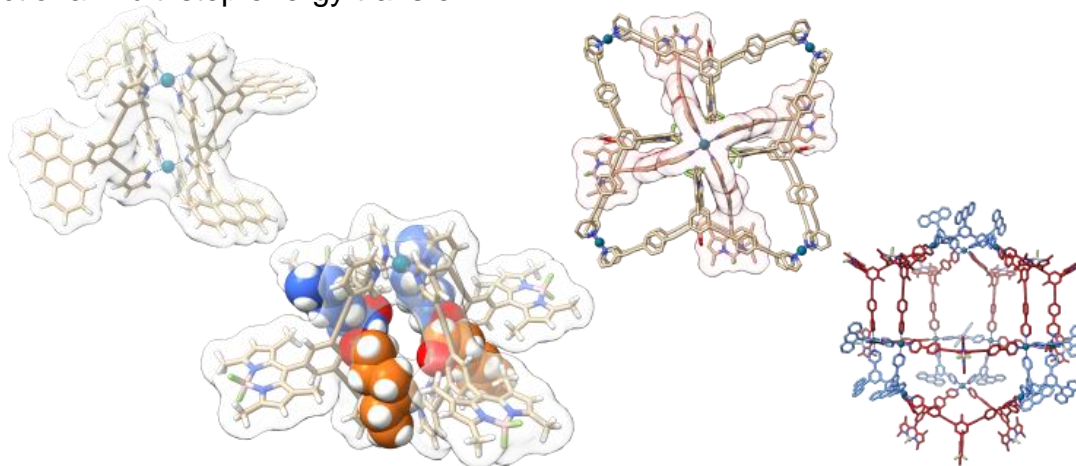


Fig. 1: Left to right: Model of an anthracene decorated [Pd₂L₄] cage, X-ray structure of an *exo*-BODIPY, *endo*-alkoxy decorated Pd₂L₄ cage, X-ray structure of a BODIPY-decorated {[Pd₂L₄]@[Pd₄L₈]}^[1] cage-in-ring complex, model of a self-sorted Anthracene/BODIPY decorated [Pd₁₂(L^A)₁₂(L^B)₁₂] molecular sphere.

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Chiroptical recognition of anions with neutral L_2Zn_2 helicates

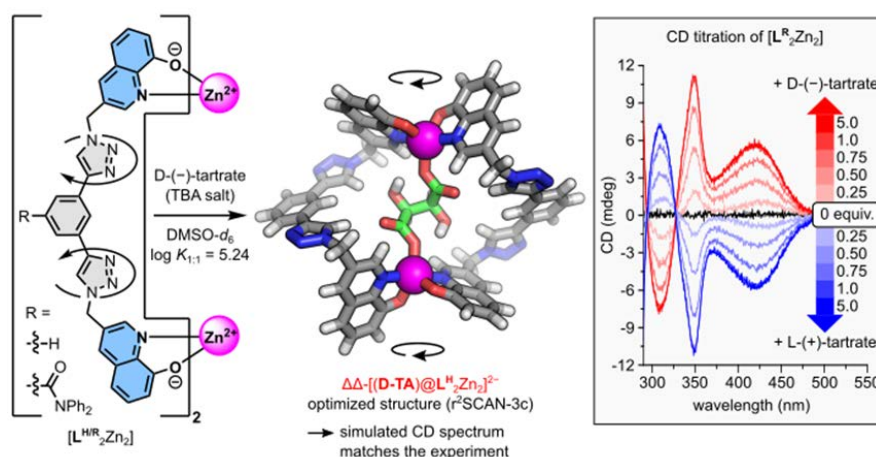
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Chirality analysis of small molecules is crucial for determination of their enantiopurity. Current methods utilize streamlined chromatographic techniques with chiral stationary phases. However, chiroptical probes based on host-guest interactions offer an alternative approach, using common spectroscopic techniques like CD spectroscopy to distinguish enantiomers and quantify their ratio.^[1]

Aiming at this, we explored the potential of charge-neutral double-stranded zinc(II) helicate-based anion receptors, incorporating triazole units that can rotate and give rise to a meso structure or a racemic mixture of the right- and left-handed complex. This receptor was proved to have high binding affinities towards dicarboxylates with association constants ranging up to $10^8 M^{-1}$ in DMSO as shown in previous study.^[2] By utilizing chiroptical responses upon recognition of chiral mono- or dicarboxylates, we conduct chirality analysis of tartrate using CD spectroscopy. Enrichment of one of the enantiomers of the racemic helicate occurs upon chiral guest binding which results in cotton effects.^[3] This receptor-based approach offers high-throughput screening capabilities with minimal waste production and provides an alternative to current methods in chiral analysis.



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Two-dimensional porous fantrip network on the calcite(10.4) surface

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The triptycene derivate fantrip (fluorinated triptycene anthracene) has three fluorinated anthracene blades. Due to its structure, fantrip can form a two-dimensional porous network by self-assembly. This network structure was observed on graphite(0001) [1] and Au(111) [2] surfaces under ultrahigh vacuum conditions. However, in both cases, passivation of the surface is necessary to reduce the molecule-substrate interactions. Here we show that the porous fantrip network can be achieved without surface passivation when using calcite(10.4) as substrate. We have analyzed the formed structure using atomic force microscopy (AFM) and present possible arrangements of the molecules on the surface. This network is interesting in the view of an on-surface polymerization by [4+4] photocycloaddition.

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Plasmonic Nanosensing in a polymer confinement at different hydration states

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Gold nanoparticles (NPs) absorb light in the visible wavelength range due to plasmon excitation. As this absorption is sensitive to the optical properties of the surrounding environment, they are widely used as plasmonic nanosensors.[1] The energy required to excite the plasmon resonance of the particles depends on their size, morphology, and the surrounding medium [2,3], and any change causes a shift of the resonance energy.[4] For thin film coatings, SPR experiments with thin gold films as sensors are the gold standard for the investigation of thin polymer films (<100 nm)[7]. Recently it was shown that if plasmonic biosensors are incorporated into thicker polymers, they sensitively respond to the polymer and convert small changes in the local refractive index into a spectral shift.[5] Here, we integrated NPs as local spectator probes into a polymer and the response of the plasmon resonance to changes of the local optical properties enabled the investigation of changes of confined polymer networks during hydration in aqueous media. Different hydrophilic methacrylate-polymers that contain the gold nanoparticles were synthesized by grafting-through polymerization [6] and the change of the plasmon resonance in the polymer confinement during the hydration and dehydration of the polymers was determined by UV-Vis spectroscopy. The results enable a correlation of the polymer chemistry, structure, and their hydration/dehydration behavior, which motivates further experiments exploring polymer properties and their responses to external cues.

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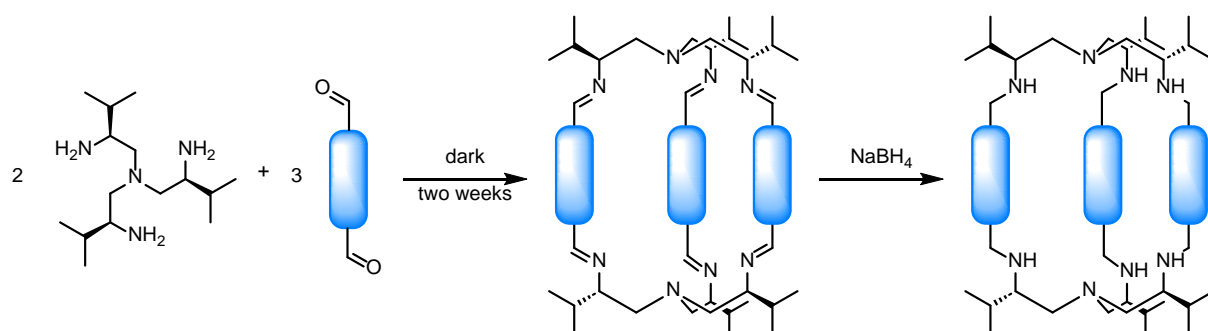
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Synthesis and Chiroptical Spectroscopy of Chiral Azacryptands

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Azacryptands are macrocyclic cage compounds first synthesized by Lehn and co-workers.^[1] In this work, we present the synthesis of novel chiral azacryptands obtained by condensation of chiral TREN (tris(2-aminoethyl)amine)^[2] units, derived from valine, with different dialdehydes. Vibrational circular dichroism (VCD) spectroscopy was employed to characterize the structural preferences of the cage compounds. VCD spectroscopy is the IR version of CD spectroscopy and the difference between left and right circularly polarized light is measured. It is highly sensitive to, for instance, solvent-induced conformational changes.^[3]



Literature precedence for VCD spectra of cage compounds is scarce.^[4] The VCD spectra of the novel azacryptand cages have been recorded and compared with spectra obtained by DFT-based methods. While the Boltzmann weighted spectra fit for the small *p*-phenyl linker system, the conformer distribution fails to predict the VCD spectra for systems with longer linker groups (*p*-biphenyl and *m*-biphenyl). Despite being higher in energy, conformers where the cavity has collapsed reproduce the experimental spectra better.

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Investigation of highly reactive azides on Ag(100) and low interaction walls such as NaBr(100) by infrared spectroscopy

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Organic azides are essential to click chemistry, which has applications in many fields such as synthetic chemistry, medicine, biochemistry, pharmacology, and catalysis [1]. The key to these applications is that organic azides form free nitrene intermediates upon annealing or exposure to ultraviolet radiation [2]. Despite such importance, their reactivity on surfaces has rarely been studied.

Therefore, we study the photoinduced reaction of the organic azide 2-azidofluorene (2AF) on a Ag(100) surface and a NaBr(100) decoupling layer at cryogenic temperature (110 K) under ultra-high vacuum conditions. Via the analysis method infrared reflection absorption spectroscopy (IRRAS) crucial information about intermediates and products formed during the photolysis can be gained. Since nitrene formation is prevented by charge transfer between Ag(100) and 2AF, the use of a NaBr decoupling layer is important to suppress the influence of Ag(100). During the photolysis with UV light ($\lambda = 254$ nm), the molecule releases the azido group and forms the reactive intermediate 2-fluorenylnitrene. From these intermediate, different products were formed upon illumination with different wavelengths. The products and their dependence on wavelength will be discussed in this poster.

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The influence of supramolecular hosts on nano-confined and solvation water probed by THz spectroscopy

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Metal cages of the $M_4L_6^{12-}$ type form self-assembled tetrahedra in which the naphthalene-based ligands span each edge, while metal ions (e.g., gallium or indium) occupy the vertices. The cavity can embed a guest molecule upon de-solvation which will undergo a follow-up reaction due to the metal ionic field. Thus, the cavity as host acts similar to an active site of proteins. [1, 2]

Our previous studies using THz spectroscopy and ab initio molecular dynamics revealed the role of encapsulated water in supramolecular catalysis and its thermodynamic properties in a $Ga_4L_6^{12-}$ host. [3] In presence of the strongly binding cationic salt tetraethylammonium chloride ($[Et_4N]^+Cl^-$), all cations are trapped and displace water due to a higher binding constant compared to the trapped water. We proposed that the solvated cavity hosts a dynamically and structurally distinct water network that is different from any known water phase and can be viewed as a low-entropy, low-enthalpy water droplet that acts as a thermodynamic driving force and supports the encapsulation of guest molecules in aqueous solutions.

Our latest results address the question of whether changes in host, guest, and solvent composition affect the thermodynamic properties of the encapsulated water and thus the overall catalytic properties. We present here first THz measurements on an $In_4L_6^{12-}$ cage and the spectroscopic changes due to the addition of a fixed amount of DMSO to water in direct comparison with $Ga_4L_6^{12-}$ to show the thermodynamic differences and possible changes in catalytic activity.

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Allosterically controlled metallo-supramolecular spin crossover complexes

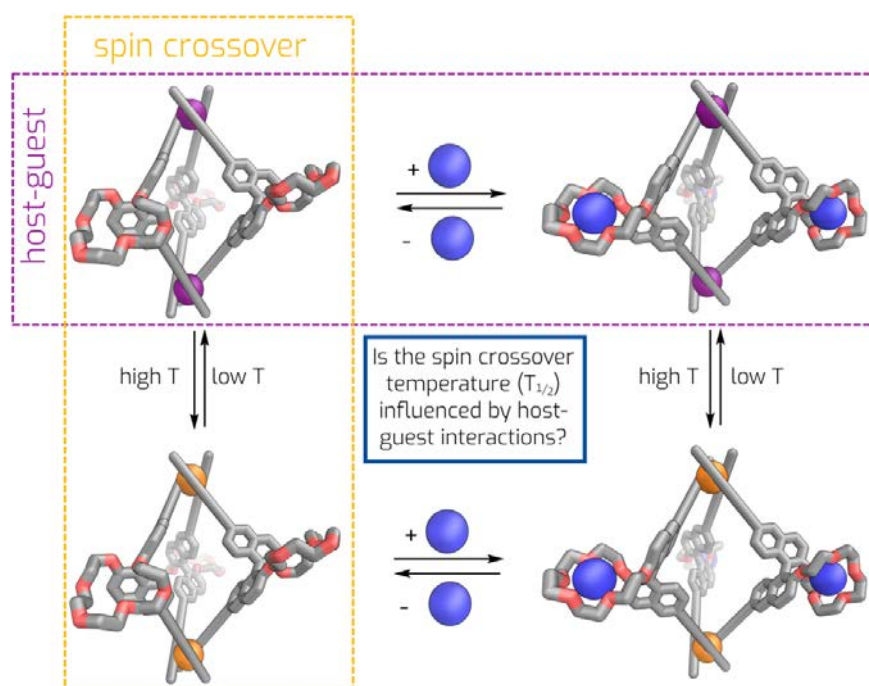
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Bistable materials are an exciting area of research as they can be used as molecular switches and in molecular machines. One example can be found in supramolecular spin-crossover (SCO) complexes, which contain metal ions which can exist in two spin states.^[1] The ligands for these SCO capable complexes must hit a sweet spot where both spin states are accessible, resulting in an easily disturbed balance. Small covalent changes can result in a complex which can only exist in one spin state. Minute changes in electronic and geometric structure can have drastic effects, hence, coupling SCO molecules with a secondary switchable unit, such as an allosterically controlled switch, opens the potential for a double action switch in which four discrete states are accessible in just one (supra-)molecule.^[2]



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Flexibility drives oxalate recognition with neutral L2Zn2 helicates

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Topic: host-guest chemistry

Dicarboxylic acids and their corresponding anions are involved in several industry processes and are omnipresent in nature. Many dicarboxylic acids are, for example, intermediates in the biosynthesis of proteins and environmental metabolites.[1,2] Oxalic acid, the simplest dicarboxylic acid, may cause a multitude of health problems including kidney stones and liver damage.[3-4] Thus, research tackling new receptors for especially oxalate is of great importance. Recently, our group published the first version of a charge-neutral metal-based self-assembled L2Zn2 helicate with the capability of binding dicarboxylates with astonishing binding affinities in competitive media.[5] Inspired by its size selectivity regarding the dicarboxylate length with naphthalene-2,6-dicarboxylate as aromatic and pimelate as aliphatic analyte being ideal matches for the receptor, the goal of this project is to bind now even shorter dicarboxylates. By modulation of the planar backbone with rather rigid bond angles to a more flexible backbone based on dipropargylamine, the host-system increases its degree of freedom. Hence the system is capable of binding oxalate.[6] Overall, the synthesis of the more flexible ligand is easy to handle, as the dipropargylamine is commercially available and it only takes one classic Schotten-Baumann-Reaction for its derivatization and a copper(I) catalyzed alkyne-azide cycloaddition to connect the backbone with the coordination units based on 8-hydroxyquinolines.

Keywords: metal-driven self-assembly, neutrally charged receptor, helicates, oxalate

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Preparing CCSS Surfaces for Scanning Tunneling Microscopy

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Compositionally complex solid solution (CCSS) provide different adsorption sites for simultaneously multiple reactions steps at the same surface and are a promising way to improve catalysts [1][2][3]. In this study, Au, Ag, Cu, Pt, and Pd are chosen as candidates for a quinary alloy ($\text{Cu}_{22}\text{Pd}_{18}\text{Ag}_{27}\text{Pt}_{13}\text{Au}_{19}$) to understand the resulting surface structure.

These five elements are designated as targets and are evaporated onto the Au(111)/Mica in room temperature chamber under vacuum conditions. The intermediate goal is to find a sample preparation to allow atomic resolution with a STM. To prepare a clean, flat enough surface several steps of flashing annealing process, which were performed under a vacuum of 10^{-7} mbar.

The resulting sample surface was investigated by AFM on air. The changes of the surface structure are monitored in relationship with the annealing temperature to establish the preparation parameters for atomically flat surfaces. This then will be the first stepping stone for an atomic resolution of the surface composition achieved by STM.

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Phenanthracene Nanotubes for Explosive Detection

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The template-assisted self-assembly of organic molecules can optimize the performance of organic electronic devices, such as sensors. Here we present insights on template-assisted self-assembly of phenanthracene nanotubes (PNTs), which can be perceived as an expansion to the third-dimension of molecular polygons investigated before.^[1]

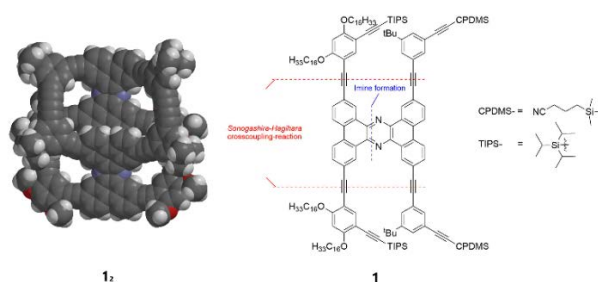


Figure 1: Structure of phenanthracene nanotube **12** (dimer of the H-shaped precursor **1**; only the cavity is shown) optimized at the *GFN2-xTB* level of theory (left); retrosynthetic approach to the H-shaped precursor **1** (right).

The research focus was set on host-guest chemistry of the PNTs, enabling the manufacturing of chemiresistive sensors based on single-walled carbon nanotubes. This way, novel sensors for nitroaromatic explosives detection were made. Regarding the synthesis, a modular approach inspired by preliminary work on the oligomerization of H-shaped molecules via a *Glaser-coupling*, was used.^[2]

This work has been funded with support of the DFG via “TIDE-Template-designed Organic Electronics” (RTG-2591).

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Influence of the Cu Nanoparticle Formation in NaAOT Reverse Micelles on the Size of the Micelle

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The confinement of micelles aids the synthesis of uniform metallic nanoparticles (NPs) and prevents agglomeration.^[1] However, not only the micelle influences the properties of the formed NP, but a feedback interaction between the micelle and formed particle develops.^[2] Consequently, the micelle participates in the NP formation and needs to be considered when studying such reactions. However, the impact of the NP formation on the size of reverse micelle is not well understood. To gain insight how the confinement of the copper to either the aqueous core or the core-surfactant interface in the micelle and the reduction reaction influence the micellar size, we used Cu(AOT)₂ containing reverse micelles and compared them to CuSO₄-containing and pure NaAOT micelles. The micelle size was studied by dynamic light scattering (DLS) and small angle x-ray scattering (SAXS) while the water loading, organic solvent, and Cu concentration were systematically varied to study the influence of these parameters on the change of the micellar size during the reduction.

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In-situ deposition and characterization of 12-metallacrown-4 complexes on a Graphene/Ni(111) substrate

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Since the discovery of single-molecule magnets (SMM), which are characterized by their axial magnetic anisotropy and a high spin ground state, suitable molecules have been researched to enable their application as memory devices in spintronics and in quantum computing.

The {Cu(II)[12-MCCU(II)N(shi)-4]} metallacrown (CuCu4-MC), deposited on a surface, is a good candidate for such a system since the symmetry and correlation of its multiple spins enable interesting high or low spin ground states. The adsorption of the CuCu4-MC has been investigated on diamagnetic Au(111) surfaces, and spin-flip excitations have been observed.

Using a Ni(111) single crystal with a single layer of epitaxial graphene promises an interesting interaction of the metallacrowns with the substrate since the nickel has ferromagnetic properties for which the diamagnetic graphene can serve as a mediating layer.

The successful in-situ deposition (via methods based on liquid-jet and electrospray) and characterization using scanning tunneling microscopy (STM), UV, X-ray, and inverse photoemission spectroscopy (UPS, XPS, IPES) of single CuCu4-MC is the basis for further investigations into the magnetic and electrical properties using Spin-Flip Inelastic Tunneling Spectroscopy (SF-IETS).

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Configurational bias Monte Carlo generalised for a multi-component high-density system.

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Molecular overlaps during the insertion step of Monte Carlo prevent the application of grand canonical Monte Carlo to condensed systems due to large rejection rates, also known as the high-density problem. The configurations sampled must be biased towards low-energy (non-overlapping) structures to prevent overlap. The Rosenbluth method[1] is one such configuration-biased method used to avoid the high-density problem for chain molecules. In this contribution, we aim to develop a general method based on Rosenbluth's method, which applies to all chemical systems.

We implement a solvent repacking scheme: removing multiple molecules to form a cavity and packing them more efficiently. We ensure efficient packing with the help of an auxiliary potential with a smoothly adjustable parameter that allows us to interpolate from high-density to low-density regions. Kindt's method[2] accommodates the special case when solute molecules are much larger than solvent molecules for 2D bicomponent hard disk mixtures. Kindt's was extended to realistic 3D multi-component size-variant flexible molecules while maintaining strict, detailed balance. Our Monte Carlo implementation is parallelised, including a fast neighbour lists algorithm and various interfaces to forcefield and DFT-B programs. The program has its own integrated molecular viewer as well.

Our method extends the grand canonical Monte Carlo method to high-density systems. Potential applications include the study of explicit solvation phenomenon and confined systems such as carbon nanotubes/cages, micelles and surfaces.

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Electrochemical Aldehyde Oxidation at Gold Electrodes: gem-Diol, non-Hydrated Aldehyde, and Diolate as Electroactive Species

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Electrocatalytic aldehyde oxidation is a highly relevant process for upgrading biomass-derived platform chemicals to value-added products.^[1] A commonly used electrode material to oxidize aldehydes selectively to carboxylates in alkaline media is gold.^[2] To this date, it is assumed that the electroactive species in this reaction is the diolate.^[2] It forms in solutions at high pH values when hydroxide binds to the carbonyl carbon atom. Accordingly, a high electrolyte pH is aspired for the electrolysis of biomass at many electrode materials. However, such conditions also facilitate the hydroxide induced aldehyde decomposition, forming various unwanted by-products and polymers that block the electrode surface.^[3] In this work, we demonstrate the successful oxidation of aliphatic aldehydes at a rotating gold electrode (RDE) at a relatively low pH value of 12.^[1] At this pH, the diolate constitutes less than 1% of the total aldehyde content. The appreciable currents (that is, reaction rates) obtained despite this low diolate concentration strongly indicate that other aldehyde forms (i.e., the geminal diol and the non-hydrated aldehyde) are also electroactive species in aldehyde oxidation. The possibility to selectively oxidize aldehydes at lower pH values is of great significance, as it allows us to develop strategies to achieve high current densities while avoiding aldehyde decomposition. This paves the way for possible future applications in industrial electrolyzers.

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Observing coupled water and protein modes using nonlinear Terahertz spectroscopy

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Proteins are highly dynamic structures. It is becoming apparent that the well-established picture of proteins exerting their function through switching between a limited number of structurally and functionally distinct conformations – a process taking place at the μs to ns time scale – needs to be complemented by the inclusion of faster long-ranged protein vibrational modes happening on a ps time scale [1]. It is suspected that such motions play a decisive role in the functionality of proteins in general as well as in the catalytic activity of enzymes [2,3]. While under physiological conditions these modes are strongly coupled to vibrational modes of the solvent, most methods used to investigate long-ranged protein vibrational modes require a crystalline sample and are therefore unable to capture this coupling [1]. Optical pump-Terahertz probe (OPTP) spectroscopy can be used on liquid samples and therefore evades this limitation. Its specificity for ps time scale processes renders it ideal for probing long-ranged protein vibrations, intermolecular water network dynamics, and their coupling modes [4,5]. Allowing to catch the dynamics following photoexcitation of an optically excitable system, time scales and associated spectral features of the energy transfer from the chromophore across its protein environment toward the surrounding solvent network can be monitored with a temporal resolution of hundreds of fs. Through polarization-resolved measurements, additional information on energy transfer directionality and the involvement of protein modes in that process may be gathered. First results from measuring aqueous solutions of the model protein myoglobin indicate a short-lived (few ps) anisotropic response and the emergence of a broad absorption feature within a few tens of ps that remains throughout the following measurement window of up to 300 ps, potentially associated with sustained protein-water coupled modes.

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Stereoisomerism of a supramolecular cage: computations help to sort out the riddles of a self-sorting system

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Self-assembled metal-organic cages have gained significant attention in the field of supramolecular chemistry due to their multiple interesting properties, which have potential applications in various areas, including selective recognition and confinement of guest molecules and stimuli-responsive systems[1,2].

Recently, the Clever Lab has successfully extended the pool of supramolecular cages with a Pd₂L₄^[4+] topology[3] by using a new ligand that bears a bi-azulene moiety in its backbone. The hindered rotation of the bi-azulene moiety results in two atropisomeric forms of the ligand: R and S. Consequently, the chiral information is transferred during the formation of the cage, resulting in the generation of distinct isomers. Specifically, four diastereoisomeric supramolecular cages can be identified: RRRR, RSRS, RRSS, and RRRS. Moreover, experimental evidence shows that the isomerization rate of the ligand (R to S) after the cage formation is considerably higher with respect to the isomerization rate of the ligand in solution.

In this study, we perform electronic structure calculations using both density functional theory[4] and accurate wavefunction methods[5] to investigate the structure and the relative energies of the different diastereoisomers as well as the above-mentioned isomerization process. Our work displays the importance of explicit solvent in the energetic ranking of the isomers. Additionally, we identify the preferred isomerization pathway of the ligand. Relying on a reduced model of the supramolecular cage, we point out that the observed rate acceleration has a more complex origin than the perturbation exerted by the palladium atoms on the electronic structure of the ligand. Moreover, our calculations show that the counterion of the cationic cage does not play a significant role in the isomerization process.

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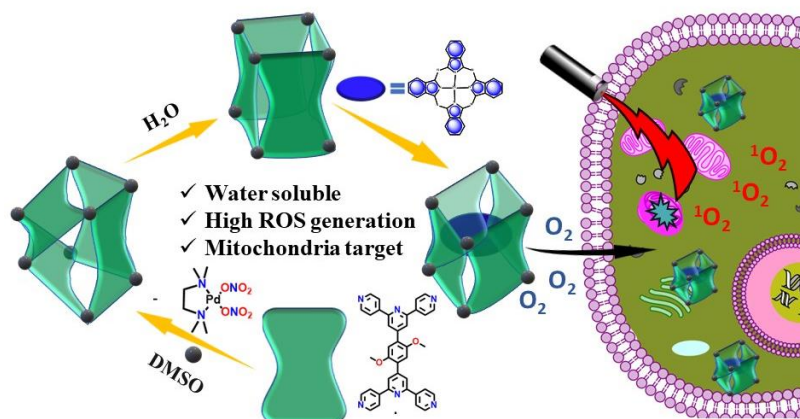
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Confinement-Driven Enhanced Photodynamic Therapy of Zinc Phthalocyanine within Metal-Organic Cage

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Zinc Phthalocyanine (**ZnPc**) has shown great potential applications as a photosensitizer (PS) in photodynamic therapy (PDT) owing to its strong absorption in the red-light region (660-720 nm) and biocompatibility. However, suboptimal PDT performance is observed for **ZnPc** due to the poor solubility and tendency to form aggregates in aqueous media. Herein we report, the effective solubilization of **ZnPc** in aqueous media through the encapsulation of **ZnPc** within a water-soluble barrel (**MB**). A rare gyrobifastigium structure was constructed by the coordination-driven self-assembly and converted to its isomeric Pd₈ tetragonal barrel (**MB**) by simple treatment with water. The confinement of the **ZnPc** within the cavity of the **MB** (**ZnPc**⊂**MB**) enhanced the singlet oxygen quantum yield in water. The enhanced cellular uptake and cytotoxicity of **ZnPc**⊂**MB** compared to **ZnPc** in HeLa cells showed that encapsulation of **ZnPc** within a water-soluble cage is an efficient method for the enhancement of PDT.¹



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A Rational Designed Concave-Convex Switchable Pseudo-cubic Cage as a Structurally Adaptable Supramolecular Host

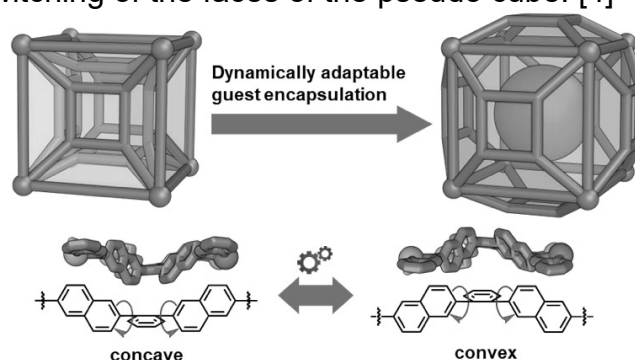
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A main current challenge in the research on supramolecular hosts is to enhance their binding abilities. Metal-organic cages generally possess well-defined shapes and interior voids, making them excellent candidates for guest binding. However, due to the entropic requirements for metal-ligand assemblies, rigid ligands are often necessary for creating these cages. As a result, the robust shapes of the resulting hosts limit the range of potential target molecules, thereby restricting the application of the cages in related areas. Therefore, the development of structurally flexible and adaptable cages has become a crucial problem in the studies of these self-assembled structures. [1-3]

In this work, we present a pseudo-cubic cage assembled from a tetratopic pyridyl-imine ligand with 2,6-naphthalenes as rotary units. We hypothesise that its faces could switch between concave and convex conformations to accommodate different guests, due to the rotational freedom imparted by the naphthalene groups. The empty cage was found to exhibit an all-concave conformation. We found that a wide range of hydrocarbons, chlorocarbons, and fluorocarbons can be encapsulated within its cavity. Evidence in NMR and ion-mobility mass spectrometry experiments further suggested the potential concave-convex switching of the faces of the pseudo cube. [4]



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Towards Coordination Cages with Catalytically Functional Ligands

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Inspired by the high selectivity and reaction rate of enzymatic catalyst in nature we study the incorporation of catalytic functionality in the ligand backbones of coordination cages, aimed at the realization of discrete nanoscale molecular flasks to perform reactions under nano-confinement.

To achieve greater structural complexity and functionality in metallocsupramolecular cages, the use of $[Pd_2L_2L'_2]$ heteroleptic cages composed of two different ligands is envisioned as a promising milestone towards mimicking enzymatic activity. Introducing hydrogen-bonding functions in coordination cages enables various catalytic reactions. The first aim of this study was to form a coordination cage with squaramide-based ligands and square-planar Pd(II) cations. Formation of homo- and heteroleptic cages were analyzed by NMR spectroscopy in solution, mass spectrometry in the gas phase and by single crystal X-ray in the solid state.

Solvents have a crucial effect on hydrogen bonding properties in solution and DMSO is a competitive hydrogen acceptor, therefore increasing Squaramide's solubility is fundamental for the host-guest and catalysis studies.

Squaraine dyes are also derivatives from squaric acid and have a zwitterion property. Squaraine-based ligands have been studied with respect to cage formation and then host-guest chemistry. Formation of Squaraine-based coordination cage were analyzed by NMR spectroscopy in solution, mass spectrometry in the gas phase and by single crystal X-ray in the solid state. Host-guest interaction of Allura Red AC with a Squaraine-based coordination cage was studied by NMR and UV-Vis spectroscopy.