



TECHNISCHE UNIVERSITÄT
CHEMNITZ

Faculty of Natural Sciences
Institute of Chemistry



A Concise Introduction

Impressum

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Preface

Regarding items with chemical background in daily press or TV reports, it's sometimes hard to believe we have actually arrived in times of modern chemistry. They rather remind us of alchemy with its beginnings in the 1st century A.D. in Egypt. In the alchemic philosophy, chemical-technological aspects like extractive metallurgy were interwoven with spiritual concepts. Additionally, these ideas were supported by secret alchemical symbols to obscure the divine chemical arts. However, we now live in times of modern chemistry, which has developed from the antique trial-and-error artistry through the age of enlightenment to a science of the modern era. Since the post-millennial reduction of the duplication rate of human knowledge to 3.65 years, more than 1 million new compounds are currently discovered every year in chemistry, in relation to more than 91 million organic and inorganic chemical substances actually registered at the Chemical Abstract Service (CAS, effective February 2015) and more than 600,000 publications every year in the chemical domain. Moreover, a 20th century trend in chemical history continues: the fusion of chemistry with the history of discoveries and inventions in production and analysis technologies (chemical industry, materials research, quality control) and the neighbouring sciences (biochemistry and biology, physical chemistry and physics, material sciences, geochemistry and geology, nanosciences etc.). This abundance of data cannot be overviewed by a single human being alone: CAS employs more than 400 scientists in order to archive all the data emerging every single day in science. A study program in chemistry intends to enable young people to identify, interpret, and apply those data to their own work.



Univ.-Prof. Dr. Klaus Dieter Stöwe
Professor for Technical Chemistry
and Managing Director of the Institute of Chemistry

For Chemnitz, chemistry has also had a special significance ever since the first science-oriented technical educational institution, the “Royal Industrial School of Chemnitz”, was founded in 1836, because it has been a major topic in the syllabi right from the beginning. At the Royal Industrial School in the mid-19th century, Julius Adolf Stöckhardt initially taught farmers in his “chemical field sermons” about new points of view on artificial fertilisation originally suggested by Justus von Liebig. In 1956, the Institute of Chemistry was founded in its present form and Ernst Altmann was assigned with the supervision of the institution.

These days, nine professors, two assistant professors, and two honorary professors reside in the chemical institute. Their research topics are highly interdisciplinary and there is an extensive network between the chemistry research groups and other groups of the Faculty of Natural Sciences, e.g. the Institute of Physics, as well as with other areas of the Chemnitz Technical University, for instance Mechanical Engineering, Electrical Engineering and Information Technology, and Computer Science. The institute's chemists contribute to the Cluster of Excellence “Merge Technologies for Multifunctional Lightweight Structures”, the first and only Federal Cluster of

Excellence on the topic of lightweight structures within Germany, and to the first interdisciplinary centre within Europe for the investigation of inorganic and hybrid nanomembranes, the “Centre for Materials, Architectures and Integration of Nanomembranes – MAIN”, with top level research for international competitiveness. Additionally, the institute’s chemists sustain and support several Research Units of the German Research Foundation DFG, e.g. the Research Unit 1497 “Twinpolymerisation of Organic-Inorganic Hybrid Monomers to Nanocomposites” and the Research Unit 1154 “Towards Molecular Spintronics”, as well as 1713 “Sensoric Micro- and Nanosystems”. The topics are oriented on basic as well as applied research and are characterized by a number of unique features. With the institute’s increasing emphasis on material science, these will become even more evident in the future. This booklet is to provide the interested reader with a first impression of the Institute of Chemistry.

Enjoy reading the contributions!

Chemnitz, December 2015.

A handwritten signature in black ink, appearing to read 'K. Stöwe', written in a cursive style.

Klaus Stöwe
(Managing Director of the Institute of Chemistry)

The development of the Institute of Chemistry

When the „Königliche Gewerbeschule zu Chemnitz“ was founded in 1836 as the first natural scientific educational establishment in Chemnitz, chemistry was one of the most important subjects. Knowledgeable teachers of the time instructed the basics of this rapidly developing science, besides the new knowledge in theoretical, organic, inorganic and technical chemistry. In the middle of the 19th century, the education of farmers gave Julius Adolf Stöckhardt the opportunity in his “chemical field sermons” to teach about new opinions of Justus von Liebig about artificial fertilization and to add his own findings. His book “Schule der Chemie” was one of the most widely spread textbooks in chemistry. One of the most famous pupils of this time was Clemens Winkler, who became Professor of Theoretical and Analytical Chemistry at the “Bergakademie Freiberg” and got famous for his discovery of the element germanium. With the announcement of the economic freedom in Saxony in 1862, the now “Höhere Gewerbeschule zu Chemnitz” developed into a technical educational institution under the influence of Theodor Böttcher.

For the education in the chemical department, technical and analytical chemistry was mostly taught according to the basics of chemistry, accompanied by a practical training in chemistry.

After the construction of the building next to the main station from 1867-1880, the chemical department was one of the best equipped departments in the „Höhere Gewerbeschule zu Chemnitz“ with its formidable collections and numerous working places.

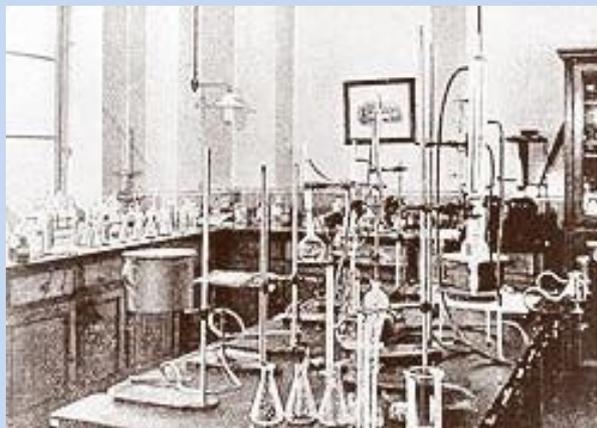


„Höhere Gewerbeschule zu Chemnitz“ 1880

A major characteristic of education in the „Technische Lehranstalten Chemnitz“, renamed in 1878, was the focus on practical education. This was and still is especially valid for chemistry. This was one of the reasons why graduates of the newly named „Königliche Gewerbeakademie“ (1900) were sought-after even outside of the saxonian industrial area.

After the World War I, several testing laboratories, like material testing and safety testing, were assigned to the institute. Especially the dyeing department gained high reputation under the leadership of Eugen Karl Emil Ristenpart. The book “Chemische Technologie der organischen Farbstoffe” and the publication “Die ostwaldsche Farbenlehre und ihr Nutzen für die Textilindustrie der Gespinnstfasern” demonstrated the high standards in education and research of the dyeing department and their growing importance on the textile industry in Saxony.

The further development of the chemical department was exceedingly determined through the research and teaching work of Paul Bernard Rother in the field of electrochemistry and electrochemical analysis.



Chemical laboratory around 1862

In the year 1947 after World War II the teaching program was reinitialized at the “Technische Universität zu Chemnitz” with a three yearlong study program in engineering with focus on chemistry at the newly founded Institute of Chemistry under the guidance of Paul Bernhard Rother, who’s specialty was the field of electrochemistry and electrochemical analysis.

A new stage of development for the technical school was reached in 1953. That year, when Chemnitz was given the name Karl-Marx-Stadt, the “Hochschule für Maschinenbau” was founded. In the transitional period most of the teaching in chemistry was done by part-time teachers. To fulfil the increasing demand in the educational and research work, it was necessary to create a separate structural unit for chemistry and so in 1956 the Institute of Chemistry was founded under the leadership of Ernst Altmann. In 1963, when the university of mechanical engineering received the status of “Technische Hochschule Karl-Marx-Stadt“, four departments (inorganic and technical chemistry, organic chemistry, physical and electro chemistry and macro molecular chemistry) were already working successfully in education and research.

In the year 1969, the section Material Science of the University of Technology, Chemical Department of the Engineer School for Mechanical Engineering and Textile Technology and Engineer School for Material Technology and Control were merged together into the “Sektion Chemie und Werkstofftechnik” at the University of Technology Karl-Marx-Stadt. This section consisted out of two major research areas: chemistry and materials technology.

In the turbulent times after the fall of the German wall and the re-unification of Germany on the October 3rd 1990, the Department of Chemistry succeeded in introducing chemistry as a full study program.

In the year 1994, today’s Institute of Chemistry was founded from the previous Department of Chemistry. The laboratories of the Institute of Chemistry were modernized from 1995 till 2004, which led to an excellent infrastructure. This was followed by providing more highly modern laboratories to the Institute of Chemistry in 2011.

Nine professorships, two junior professorships and two honorary professorships are working currently at the Institute of Chemistry. Despite the low number of professorships, compared to the national standard, the institute succeeded in having a broad spectra of research topics. Major key aspects are scientific work on short-lived intermediates, new functional heterocycles, molecular pincers and clamps, metal clusters, quantum chemical calculations, functional polymers, block polymers, twin polymerisation, hybrid materials, inorganic and organic nano composites, electric and magnetic metal-metal oxide nanoparticles, nano-tomography, self-assembling mono layers, liquid crystals, ionic liquids, dendrimers, coating methods, micro-structured membranes, homo- and heterogeneous

catalysis, new catalytic materials as well as new materials for energy storage and energy concepts.



Modern chemical laboratory 2015

These topics generate numerous connections for national and international contacts as well as cooperations of the Institute of Chemistry with other departments of the University of Technology Chemnitz. Therefore, the orientation of the research is interdisciplinary, interfacultary and interuniversity orientated with intensive cooperations with working groups from the Institute of Physics, the Faculty of Mechanical Engineering, Electro and Information Technology and Computer Science. This networking of the Institute of Chemistry within the University of Technology is reflected in the participation in several national and international research groups and competence networks.

This broad scientific line-up is to be focused further in the future and leads to a strong profile in material science related questions.

The Institute of Chemistry depicts itself as an independent educational and research institute with unique features, which

are visible in its basic and application driven research. Furthermore, it is an important scientific partner and service provider within and outside of the University of Technology Chemnitz.

„Whenever science is able to enlighten wide circles but only allowed to enlighten a narrow study room, whenever science may be beneficial for life but does nothing, then its dignity seems to be far more at risk than if we let its sphere of influence spread in all directions simultaneously, according to the current status of knowledge. This way, a dead dignity turns into a living one.“

Julius Stöckhardt, 1855

Degree programs

Graduates from the chemistry study programs will acquire fundamental practical and theoretical skills for a rapid transition into their future working field, like industry, administration and research with specialization like development, production, analytics, assessment, management, patent right, documentation, sales or customer support. A master degree also opens the possibility for graduates to aim for a PhD degree. To prepare the graduates for the huge variety of possible working fields, the studies are structured with an emphasis on general education and strong interdisciplinary cooperation with the department of physics, engineering etc. A bachelor degree can be achieved within six semesters following a ready planned course schedule, while courses in the master studies can be chosen freely and should be finished within four semesters. Both degrees are concluding with the writing of a thesis within three or six months respectively. The bachelor degree enables students get into the working life within just three years, but it also serves as the foundation for the following master program. The master studies are based on the knowledge and skills gained within the bachelor program, which are further enhanced with methods of problem solving concerning complex scientific chemical questions. This brings the students closer to the standards of international research. As a result of the specialized education, graduates from master studies possess a trained analytical way of thinking and the ability to develop rational problem solving strategies. These belong to the outstanding qualities of a chemist.

Starting with the winter term 2015/16 the master study program „Advanced Functional Materials“ is offered by the Institute of Chemistry and the Institute of Physics both being located at the Faculty of Natural Sciences. The program can be studied in English but additionally modules in German language are offered and thus, bilingual studies are possible. The study program is based on advanced skills in Chemistry and Physics with regard to materials sciences, and the transfer of knowledge in synthesis, development, analysis, and manufacturing of functional materials.

Further Information can be found at: <https://www.tu-chemnitz.de/chemie/studium.html>.

Bachelor of Science Chemistry

Duration of studies: 6 semesters

Taught topics:

- General and inorganic chemistry
- Organic chemistry
- Physical chemistry
- Mathematics and physics
- Chemical technology
- Polymer chemistry

Graduating with a bachelor thesis

Master of Science Chemistry

Duration of studies: 4 semesters

Taught topics:

- Scientific discussion of current research topics
- Scientific working methods
- Specialized courses:
 - Catalysis and surface-interface-chemistry
 - Synthesis chemistry
 - Processes and modelling
 - Material science
 - Modelling and simulation
- Interdisciplinary courses

Graduating with a master thesis

Advanced functional Materials

Duration of studies: 4 semesters

Taught topics:

- **Material Chemistry**
 - Synthetic methods
 - Materials for innovative energy concepts
 - Sustainable production technologies
- **Material Physics**
 - Surfaces, thin films & interfaces
 - Semiconductor physics
 - Photovoltaics
- **Compulsory Subjects**
 - Nanophysics
 - Microscopy and analysis on the nanoscale
 - Surface spectroscopies
 - And others....
- **Advanced Practical Training in Methods of Modern Materials Science**

Graduating with a master thesis

Methods at the Institute of Chemistry

The following methods are available for research, education and external service.

Spectroscopic methods

- NMR-spectroscopy
- Atomic emissions spectroscopy (AAS)
- UV/Vis-spectroscopy
- IR/Raman-spectroscopy
- FT-IR-spectroscopy
- Energy dispersive X-ray spectroscopy (EDXS)

Optical methods

- Powder X-ray diffraction
- Single crystal X-ray structure determination
- Fluorescence microscopy
- Determination of refraction index

Electrochemical methods

- Cyclic voltammetry
- Impedance measurements
- Spectroelectrochemistry
- Rotary electrodes
- Zeta-potential determination

Adsorption and chromatographic methods

- Gas chromatography
- BET-porosimetry
- Chemical vapour deposition (CVD)

Thermal analysis

- Calorimetry
- Thermal gravimetry (TG)
- Differential thermal analysis (DTA)
- Dynamic differential calorimetry (DSC)

Microscopy

- Optical and fluorescence microscopy
- Confocal laser-scanning-microscopy (in reflected light or fluorescence mode)
- Scanning electron microscopy
- Reflected light microscopy

Miscellaneous

- Particle size determination by differential sedimentation
- Mass spectrometry (ESI, FI)
- Karl-Fischer-titration
- Atomic force microscopy (AFM)
- Catalytic investigations in several industrially relevant reactions
- Metallographic preparations
- Roughness determination
- Dynamic light scattering
- Coupled gas chromatography-mass spectrometry
- Metallographic preparation

International Cooperation



Working Groups

Inorganic Chemistry

Chemical Technology

Coordination Chemistry

Materials for Innovative Energy Concepts

Organic Chemistry

Physical Chemistry

Physical Chemistry/Electrochemistry

Polymer Chemistry

Supramolecular Chemistry

Theoretical Chemistry and Applied

Quantum Chemistry

Computational Quantum Chemistry

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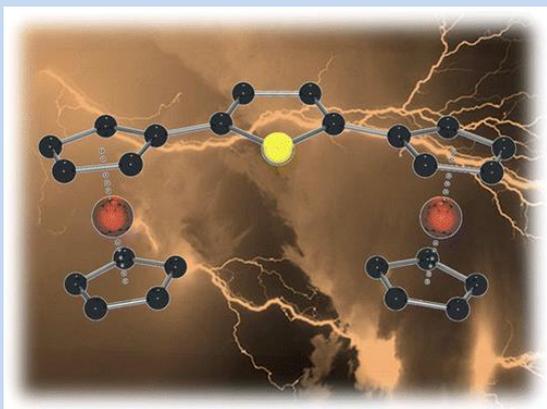


Inorganic Chemistry

The research topics of the professorship of Inorganic Chemistry are focused in the border area of fundamental research and industrial application.

Electron Transfer

The investigation of electron transfer processes in multimetallic compounds provides important basics for the development of new sensor systems and molecular electronic devices. In this respect, our research focuses on the investigation of metal-metal-interactions across π -conjugated bridging ligands and on the possibility to influence the electron transfer behaviour of the connecting unit by variation of steric and/or electronic factors. [1-3]

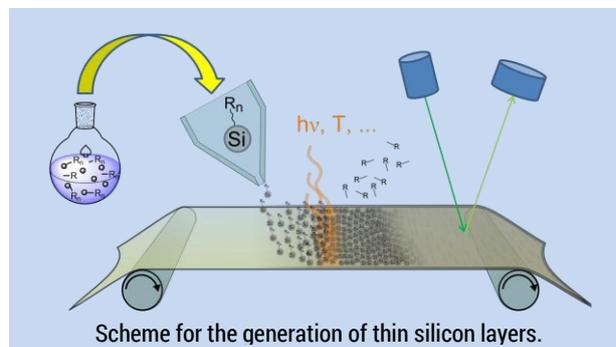


Electron transfer processes in homobimetallic transition metal complexes. [3]

Catalysis

The investigation of transition metal catalyzed C,C cross-coupling reactions is of great importance for the development of sustainable and environmentally friendly synthesis methodologies of fine chemicals and pharmaceuticals. Our group mainly focuses on the use of planar-chiral ferrocene-based phosphines as steering ligands. By modifying the phosphines it is possible to increase the catalytic activity and to exert a strong influence onto the regio- and stereoselectivity of these transformations. [4,5]

Photovoltaic



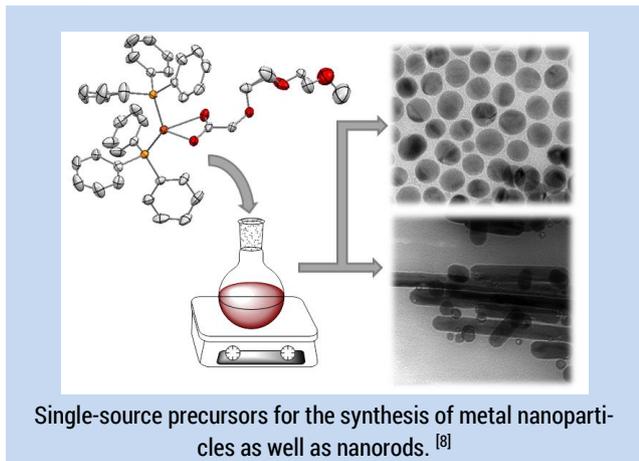
The development of a new process for the production of thin silicon layers from solution requires novel silanes. The respective starting material will be deposited by spray coating on (flexible) substrates and thereafter metallization will be initiated by energy impact (ΔT and/or $h\nu$). By optimization and advancement of the process conditions a cost-effective material

production of thin photovoltaic-active silicon layers is feasible. [6]

Nano-Materials

For the synthesis of many different metal and metal oxide nanoparticles and nanorods mainly metal carboxylate-based single-source precursors are used. These complexes also act as metal sources in ALD, CVD and spin-coating deposition processes and inkjet printing. By the application of these techniques, dense and homogeneous conductive metal layers on the nanometre scale are available.

The functionalization and preparation of hybrid materials with metal or metal oxide nanoparticles is the main topic of twin polymerization. The obtained twin polymers yield, after carbonization or oxidation, highly microporous carbon or mesoporous silica materials, which were in situ functionalized with metal or metal oxide nanoparticles. The key application area is catalysis. [7,8]



Services

- ESI/APCI/APPI-TOF mass spectrometry
- X-ray diffraction
- Investigation of the thermal behaviour of compounds with TG/DSC and TG-MS
- Shimadzu gas chromatography/mass spectrometry
- Elemental analysis (CHN analyser) Thermo, FlashEA 1112
- SonoTek ultrasonic spray system
- DTF FLA100PA flash lamp annealing
- CVD, ALD reactors
- (Spectro)electrochemistry
- Dynamic light scattering
- NMR spectroscopy

Selected Publications

- [1] K. Kaleta, A. Hildebrandt, F. Strehler, P. Arndt, H. Jiao, A. Spannenberg, H. Lang, U. Rosenthal, *Angew. Chem. Int. Ed.* **50**, **2011**, 11248.
- [2] U. Pfaff, G. Filipczyk, A. Hildebrandt, M. Korb, H. Lang, *Dalton Trans.* **43**, **2014**, 16310.
- [3] J. M. Speck, R. Claus, A. Hildebrandt, T. Ruffer, E. Erasmus, L. van As, J. C. Swarts, H. Lang, *Organometallics*, **31**, **2012**, 6373.
- [4] D. Schaarschmidt, H. Lang, *Organometallics* **32**, **2013**, 5668
- [5] M. Korb, H. Lang, *Organometallics* **33**, **2014**, 6643.
- [6] B. Büchter, F. Seidel, R. Fritzsche, I. Toader, R. Buschbeck, A. Jakob, S. Schulze, H. Freitag, H. Lang, M. Hietschold, D.R.T. Zahn und M. Mehring, *J. Mater. Sci.* **49**, **2014**, 7979.
- [7] C. Schliebe, K. Jiang, S. Schulze, M. Hietschold, W. B. Cai, H. Lang, *Chem. Commun.* **49**; **2013**, 3991.
- [8] D. Adner, S. Möckel, M. Korb, R. Buschbeck, T. Ruffer, S. Schulze, L. Mertens, M. Hietschold, M. Mehring, H. Lang, *Dalton Trans.* **42**, **2013**, 15599.

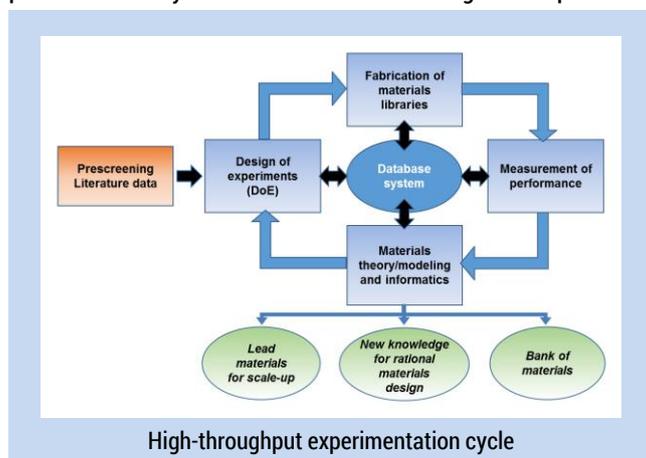


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Chemical Technology

According to the bridging function between fundamental and application of functional materials of the newly established chair for Chemical Technology at the Technical University Chemnitz, the research topics are located in the area of material synthesis and characterisation with focus on combinatorial chemistry and high-throughput technologies.

Traditional materials development is characterized by an „one-after-the-other“-principle; this process is slow and ineffective. The parameter spaces in the search for new materials are extremely huge; especially in chemistry the main variational parameter is the composition of compounds of the approximately 70 useable chemical elements of the periodic system. High-Throughput Technologies provide means for a much more effective search. A modern High-Throughput Experimentation cycle consists of the following sub steps:



This process is iteratively repeated until a specific, predefined objective of the whole procedure is established. With each iteration the number of samples is reduced, but correspondingly the information depth of the measurement data for all samples within each cycle is increased. At the end of the process only a few new materials have been discovered or just an optimized lead compound, which will be synthesized later on in larger amounts.

This procedure was used in the past successfully for the discovery and optimization of heterogeneous catalysts for a number of processes, as e.g. emission reduction of Diesel soot, Selective Catalytic Reduction of nitrous gases with ammonia (NH₃-SCR), reduction of methane slip in biogas engines, efficiency increase in chlorine production, electrocatalyst testing for fuel cell applications or synthesis of nano-scaled chalcogenide materials.

Selective Catalytic Reduction with Ammonia

In the field of automobile exhaust gas catalysis the challenge for the development and optimization of appropriate catalysts is given by the circumstances that under the non-steady-state operational conditions of a power-driven vehicle the catalysts have to reveal high activities over a huge temperature range, very different exhaust gas compositions and oxygen concentrations as well as after long operational lifetimes. For the removal of nitrous gases from the off-gas stream several different approaches have been proposed including storage and reduction of nitrous gases (NO_x Storage and Reduction – NSR)

and the Selective Catalytic Reduction with ammonia (NH₃-SCR). Especially in the low temperature operation range the catalysts actually used have still to be improved. Via a fast scanning stage setup coupled with a gas flow cell of an FTIR spectrometer as high-throughput characterisation method, vanadium-based catalyst libraries synthesized by impregnation techniques and doped with different metals were tested for their activity on nitrous gas reduction and optimized according to the experimentation cycle shown in the figure above.

Fuel Cell Catalyst Support Materials

In Polymer Electrolyte Membrane Fuel Cells, hydrogen and oxygen are converted into water and electrical power. For these catalytic processes most commonly platinum supported on carbon is used. Under the potentials and oxidizing conditions of the fuel cell the support material is not stable against conversion into carbon monoxide, carbon dioxide and formic acid, so that alternatives for carbon have to be discovered. The challenge here is the development of catalyst support materials with sufficient chemical stability at the low pH-values established by the membrane materials revealing additionally the necessary electrical conductivity. This is achieved by doping of acid-stable metal oxides as tantalum or niobium oxide with metal ions of various valences using different charge compensation mechanisms generating crystal lattice defects in the host lattice.

Micro-structured reactors

In micro-structured reactors characterised by dimensions at least in one direction below one millimetre and an extraordi-

narily large heat exchange surface area to reaction volume ratio up to 50 000 m²/m³, extremely active porous catalyst layers were successfully applied. With these highly active wall catalysts reactions with very large reaction heats can be run with very high conversions and product selectivities because of the large heat dissipation efficiency and the isothermal reactor operation in contrast to conventional catalysts which would result in a runaway scenario.



Setup of a micro-structured reactor and reactor walls coated with catalyst

Additional Research Topics

- Energy storage materials
- Photovoltaic and thermoelectric materials
- Resource- and energy-efficient processes
- Reaction technological investigation of heterogeneously catalysed processes
- Migration in print processes

Selected Publications

- [1] W. F. Maier, K. Stöwe, S. Sieg, *Ang. Chem. Int. Ed.* **46**, **2007**, 6016.
- [2] B. Weidenhof, M. Reiser, K. Stöwe, W. F. Maier, M. Kim, J. Azurdia, E. Gulari, E. Seker, A. Barks, R. Laine, *J. Am. Chem. Soc.* **131**, **2009**, 9207.
- [3] K. Stöwe, M. Hammes, M. Valtchev, M. Roth and W. F. Maier, in: *Modern Applications of High Throughput R & D in Heterogeneous Catalysis* (Ed. A. Hagemeyer, A. Volpe), Ebook-Chapter, Bentham Science, 2014, ISBN: 978-1-60805-873-0, S. 118-172.
- [4] T. Schwarz, S. Schirmeister, H. Döring, E. Klemm, *CIT* **82**, **2010**, 921.



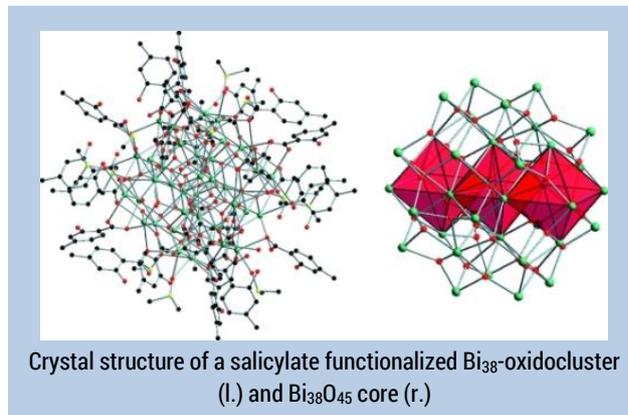
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From Molecules to Materials

The chemistry of main group metals of the 14th and 15th group constitutes our research with focus on synthesis, structure and characterization. The topic of molecular chemistry is complemented by several aspects of materials science such as heterogeneous photocatalysis, porosity of metal oxides, energy storage and conversion as well as properties of hybrid materials. Currently, our research projects concentrate on photocatalysis with oxides of the environmentally benign heavy metal bismuth, hydrolysis processes of bismuth oxido clusters and structure formation by dispersion type interaction with heavy main group elements. In addition we study the synthesis and properties of organic-inorganic hybrid materials as well as porous metal oxides, nanoparticles and nanocomposites.

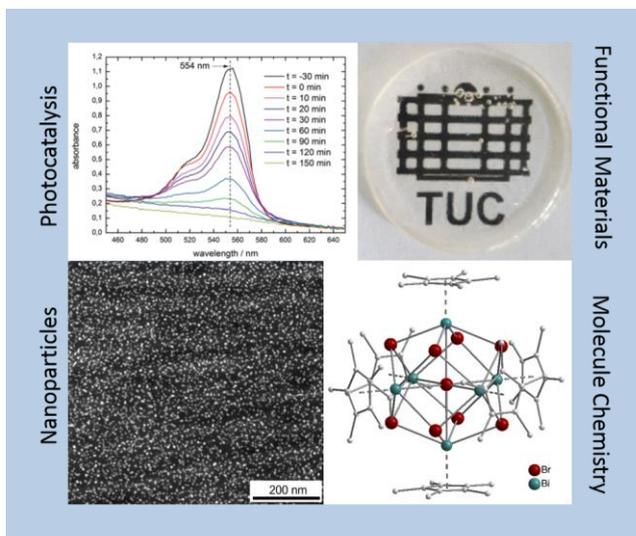
Metaloxido clusters and Nanoparticles

Molecular precursors and especially metal oxido clusters hold great potential for the controlled production of monodisperse nanoparticles. In addition, the clusters offer the possibility for functionalization at the cluster periphery and thus to tune physical properties. With respect to applications for example in the field of biomaterials we investigate modification of the clusters with e.g. amino acids, antibiotics or fluorescent markers prior to implementation into a polymer. The modified nano-scaled oxido clusters might act as radiopacifiers or depot for antimicrobial agents.



Photocatalysis

Bismuth-containing photocatalysts are of great interest with respect to their activity for photocatalytic water splitting and water purification using visible light. Currently we concentrate on improving the catalyst performance and investigate novel concepts for the deposition of catalysts on substrates using ultrasonic spray coating starting from molecular precursors and metal oxido clusters. Recently, thin films with thicknesses in the micrometre range were produced based on metastable bismuth oxides on diverse substrates which show promising photocatalytic activity.



Organic-Inorganic Hybrid Materials

The synthesis of porous and nano-scaled metal oxides is carried out following the novel concept of twin-polymerization for organic-inorganic hybrid materials (DFG research unit 1497) starting from well-defined metal alkoxides with polymerisable ligands. In this process, the polymerization of the organic component and the inorganic material are mechanistically coupled and start from a single precursor. Thus, the hybrid material is composed of interpenetrating networks with dimensions on the nanometre scale down to 1 to 3 nm. The organic component might be regarded as structure-directing matrix and can be removed to give inorganic nanoparticles or mesoporous metal oxides. The novel concept of twin polymerization is currently extended to produce porous metal(oxide)@SiO₂ nanocomposites for energy storage and gas sensing, and heterometallic oxides with photocatalytic activity.

Molecular Precursors

We focus on the synthesis and characterization of metal alkoxides and metalorganic compounds with elements of group 14 and 15. Many of these molecules might be used as molecular precursors for diverse materials including films with photovoltaic or photocatalytic activity. In addition, compounds with metal-bismuth bonds within compounds which might serve as molecular precursors for heterometallic oxides such as multiferroic BiFeO₃ are studied. Other research activities on the synthesis and characterization of new organometallic compounds with unusual bonding situations including dispersion type interactions are also part of this research topic.

Services

- Powder X-ray diffraction (PXRD)
- Photocatalytic studies
- Synthesis of metal oxides, organic-inorganic hybrid materials and nanoparticles

Selected Publications

- [1] M. Schlesinger, S. Schulze, M. Hietschold, M. Mehring, Metastable β -Bi₂O₃ nanoparticles with High Photocatalytic Activity from Polynuclear Bismuth Oxido Clusters, *Dalton Trans.* **42**, **2013**, 1047.
- [2] L. Miersch, T. Ruffer, M. Mehring, Organic-inorganic hybrid materials starting from the novel nano-scaled bismuth oxido methacrylate cluster [Bi₃₈O₄₅(OMc)₂₄(DMSO)₉] \cdot 2DMSO \cdot 7H₂O, *Chem. Commun.* **47**, **2011**, 6353.
- [3] C. Leonhardt, S. Brumm, A. Seifert, A. Lange, S. Csihony, M. Mehring, Tin Nanoparticles in Carbon / Silica Hybrid Materials by the use of Twin Polymerization, *ChemPlusChem* **10**, **2014**, 1440.
- [4] D. Mansfeld, L. Miersch, T. Ruffer, D. Schaarschmidt, H. Lang, T. Böhle, R. W. Troff, C. A. Schalley, J. Müller, M. Mehring, From {Bi₂₂O₂₆} to chiral ligand-protected {Bi₃₈O₄₅}-based bismuth oxido clusters, *Chem. Eur. J.* **17**, **2011**, 14805.



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Materials for Innovative Energy Concepts

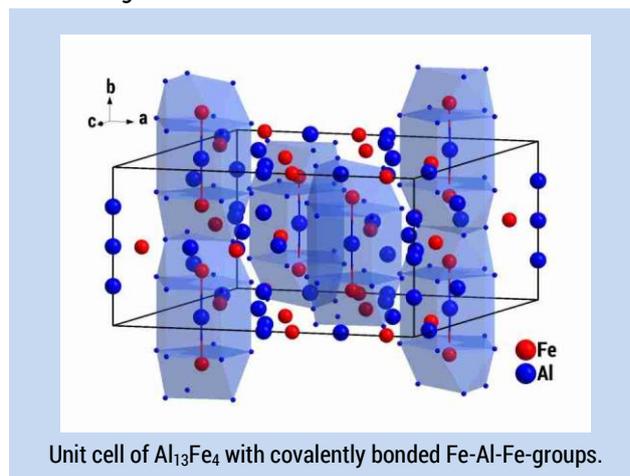
Intermetallic compounds are a highly interesting yet somewhat neglected class of compounds. They consist of at least two metallic elements and combine electric conductivity as well as ionic and covalent shares in bonding. In contrast to alloys, the crystal and electronic structures of intermetallic compounds differ greatly from those of the constituent elements. Thus, these materials exhibit very peculiar physical and chemical properties which can be employed for energy-relevant catalysts, structural or energy conversion materials.

[1]

Semi-Hydrogenation of Acetylene

The semi-hydrogenation of acetylene is an industrial scale process to remove traces of acetylene from ethylene, since even smallest amounts of acetylene poison the catalysts used for the oxidation to ethylene oxide ($15 \cdot 10^6$ t/a) or the polymerisation of ethylene to polyethylene ($80 \cdot 10^6$ t/a). Industrial hydrogenation catalysts mostly use palladium or palladium-based alloys as active components. However, palladium features a number of side reactions like the formation of carbides and hydrides, which may strongly modify the catalytic properties and lead to a loss of selectivity and/or activity. Catalyst materials containing the intermetallic compounds GaPd, GaPd₂, or Ga₃Pd₇ as active species do not exhibit these disadvantages due to the high stability of the compounds.^[2] Our knowledge-based research subsequently led to the discovery

of the noble metal-free hydrogenation catalyst Al₁₃Fe₄.^[3] Current work is concerned with broadening the portfolio of substrates and compounds in order to reach a more extensive understanding.

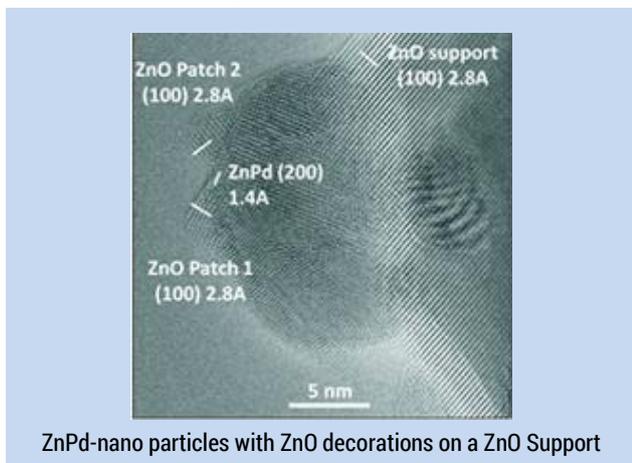


Methanol Steam Reforming

Methanol is a promising molecule for future hydrogen storage. Besides the easy storage, a further advantage is the releasing of the entire chemically bound hydrogen from a water/methanol mixture via methanol steam reforming under mild conditions ($\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow 3 \text{H}_2 + \text{CO}_2$).^[4] A high selectivity for CO₂ is important here in order not to poison the downstream fuel cells for power generation with CO. Our research has permitted us to show that the intermetallic compound ZnPd in teamwork with ZnO is able to conduct methanol steam reforming

with high selectivity.^[5] As in the semi-hydrogenation of acetylene, the focus is on the development of a noble metal-free catalyst.

Nanoparticulate Synthesis



Catalytic high performance materials call for a systematic nanoparticulate synthesis of supported intermetallic compounds – whereas to date there is no general approach to this end. The development of customised processes succeeds with the help of the acquired understanding in inert atmosphere and water-free media. Catalytic investigations can thus be conducted on materials with high surface area and, e.g., the influence of the supporting material can be examined.^[6] This allows conducting catalytic investigations on materials with high specific surface area and, e.g. by supporting the particles after synthesis, exploring the influence of the supporting material. However, the synthesis protocols are for the most part too complex for industrial scale production, therefore innovative procedures are currently being developed to enable a water-based synthesis.

Services

- synthesis of alloys and intermetallic compounds
- particle size determination by differential sedimentation
- thermal behaviour of materials in inert and reactive atmosphere via DTA/TG/MS
- determination of catalytic properties
- elementary analysis via ICP-OES and REM/EDXS

Selected Publications

- [1] M. Armbrüster, R. Schlögl, Yu. Grin, Intermetallic Compounds in Heterogeneous Catalysis – A Quickly Developing Field Sci. Technol. *Adv. Mater.* 15, **2014**, 034803.
- [2] M. Armbrüster, M. Behrens, F. Cinquini, K. Föttinger, Yu. Grin, A. Haghofer, B. Klötzer, A. Knop-Gericke, H. Lorenz, A. Ota, S. Penner, J. Prinz, C. Rameshan, Z. Révay, D. Rosenthal, G. Rupprechter, P. Sautet, R. Schlögl, L. Shao, L. Szentmiklósi, D. Teschner, D. Torres, R. Wagner, R. Widmer, G. Wowsnick, How to Control the Selectivity of Palladiumbased Catalysts in Hydrogenation Reactions: The Role of Sub-Surface Chemistry, *ChemCatChem* 4, **2012**, 1048.
- [3] M. Armbrüster, K. Kovnir, M. Friedrich, D. Teschner, G. Wowsnick, M. Hahne, P. Gille, L. Szentmiklósi, M. Feuerbacher, M. Heggen, F. Girgsdies, D. Rosenthal, R. Schlögl, Yu. Grin, Al₁₃Fe₄ as a low-cost alternative for palladium in heterogeneous hydrogenation, *Nat. Mater.* 11, **2012**, 690.
- [4] M. Armbrüster, M. Behrens, K. Föttinger, M. Friedrich, É. Gaudry, S.K. Matam, H.R. Sharma, The Intermetallic Compound ZnPd and Its Role in Methanol Steam Reforming, *Catal. Rev.: Sci. Eng.* 55, **2013**, 289-367.
- [5] M. Friedrich, S. Penner, M. Heggen, M. Armbrüster, High CO₂ Selectivity in Methanol Steam Reforming through ZnPd/ZnO Teamwork, *Angew. Chem. Int. Ed.* 52, **2013**, 4389.
- [6] Y. Luo, Y. Sun, U. Schwarz, M. Armbrüster, Systematic Exploration of Synthesis Pathways to Nanoparticulate ZnPd, *Chem. Mater.* 24, **2012**, 3094.



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Organic Chemistry

Frequently, efficient optimization of the reaction conditions regarding the yield and chemo-, regio-, and stereoselectivity is only possible in organic chemistry if some knowledge of the mechanisms of the processes is available. On the other hand, the generation of molecules with unusual bonding properties or new arrangement of functional groups, although at first only an academic question, often leads to useful reactions of synthetic organic chemistry.

Basic research in the group of Organic Chemistry at the University of Technology Chemnitz is focussed on the following themes:

- new and short-lived azides
- compounds with ring strain
- unusual cycloaddition reactions

The boundaries between the interrelated topics are fluid as shown by the subsequent examples.

The isolation of short-lived azidoacetylene is a particular challenge, also because of its explosive properties.^[1] The compound does not lead to a nitrene as previously claimed; instead liberation of dinitrogen produces cyanocarbene.^[1,2] Some of the energetic azides with the formula C_2N_4 are similarly short-lived.^[3] However, formyl azide can be handled more easily and has recently been isolated for the first time, although it undergoes a very rapid Curtius rearrangement.^[4]

Novel α -azido alcohols have been utilized in synthetic chemistry. Such azides were overlooked for a long time although they can be prepared by simple hydroazidation of aldehydes.^[5]

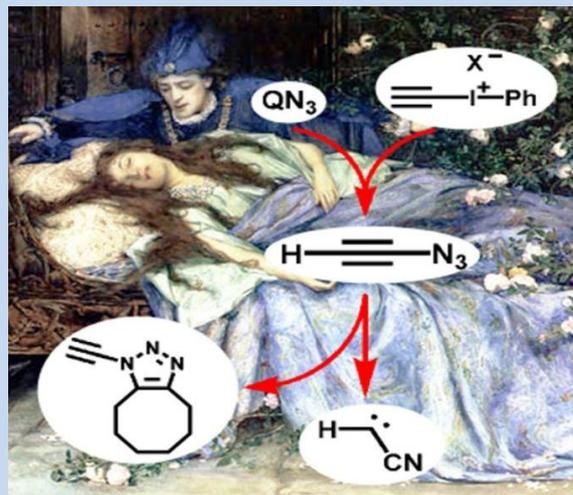
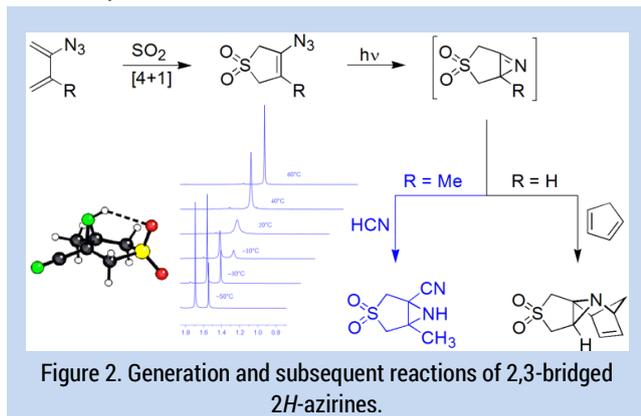


Figure 1. After 102 years of unsuccessful attempts to synthesize azidoacetylene, spectroscopic evidence (NMR, IR) of this elusive compound has been shown.

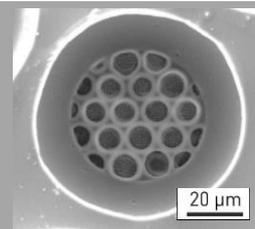
The ring strain of 2,3-bridged 2*H*-azirines enables addition and cycloaddition reactions, which are not possible for simple imines.^[6] In the case of cyclooctyne, the ring strain is used to overcome the notoriously low reactivity of N_2O (laughing gas). This leads under mild conditions to a 1,3-dipolar cycloaddition and subsequent ring opening with formation of α -diazo ketones or the corresponding (nitrogen including) secondary products.^[7] Another 1,3-dipolar cycloaddition is in the center

of interest, when cyclooctyne surprisingly reacts with acetylenedicarboxylates to generate furan derivatives already at room temperature.^[8]



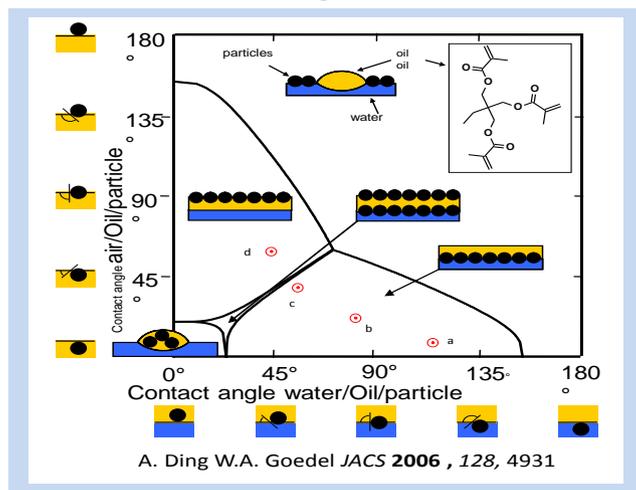
Selected Publications

- [1] K. Banert, R. Arnold, M. Hagedorn, P. Thoss, A. A. Auer, Reactions of Unsaturated Azides, Part 30. 1-Azido-1-alkynes: Synthesis and Spectroscopic Characterization of Azidoacetylene, *Angew. Chem.* 124, **2012**, 7633; *Angew. Chem. Int. Ed.* 51, **2012**, 7515.
- [2] X. Zeng, H. Beckers, J. Seifert, K. Banert, The Photochemical and Thermal Decomposition of Azidoacetylene in the Gas Phase, Solid Matrix, and Solutions, *Eur. J. Org. Chem.*, **2014**, 4077.
- [3] K. Banert, S. Richter, D. Schaarschmidt, H. Lang, Reactions of Unsaturated Azides, Part 32. Well Known or New? Synthesis and Structure Assignment of Binary C₂N₁₄ Compounds Reinvestigated, *Angew. Chem.* 125, **2013**, 3583; *Angew. Chem. Int. Ed.* 52, **2013**, 3499.
- [4] K. Banert, C. Berndt, M. Hagedorn, H. Liu, T. Anacker, J. Friedrich, G. Rauhut, Reactions of Unsaturated Azides, Part 29. Experimental and Theoretical Studies on the Synthesis, Spectroscopic Data, and Reactions of Formyl Azide, *Angew. Chem.* 124, **2012**, 4796; *Angew. Chem. Int. Ed.* 51, **2012**, 4718.
- [5] K. Banert, C. Berndt, S. Firdous, M. Hagedorn, Y.-H. Joo, T. Ruffer, H. Lang, Extremely Simple but Long Overlooked: Generation of α -Azido Alcohols by Hydroazidation of Aldehydes, *Angew. Chem.* 122, **2010**, 10404; *Angew. Chem. Int. Ed.* 49, **2010**, 10206.
- [6] K. Banert, A. Ihle, A. Kutzt, E. Penk, B. Saha, E.-U. Würthwein, Reactions of Unsaturated Azides, Part 31. Generation of highly strained 2,3-bridged 2H-azirines via cycloaddition reactions of 2-azidobuta-1,3-dienes and photolysis of the resulting cyclic vinyl azides, *Tetrahedron* 69, **2013**, 2501.
- [7] K. Banert, O. Plefka, Synthesis with Perfect Atom Economy: Generation of Diazo Ketones by 1,3-Dipolar Cycloaddition of Nitrous Oxide at Cyclic Alkynes under Mild Conditions, *Angew. Chem.* 123, **2011**, 6295; *Angew. Chem. Int. Ed.* 50, **2011**, 6171.
- [8] K. Banert, S. Bochmann, A. Ihle, O. Plefka, F. Taubert, T. Walther, M. Korb, T. Ruffer, H. Lang, Synthesis with Perfect Atom Economy: Generation of Furan Derivatives by 1,3-Dipolar Cycloaddition of Acetylenedicarboxylates at Cyclooctynes, *Molecules* 19, **2014**, 14022.



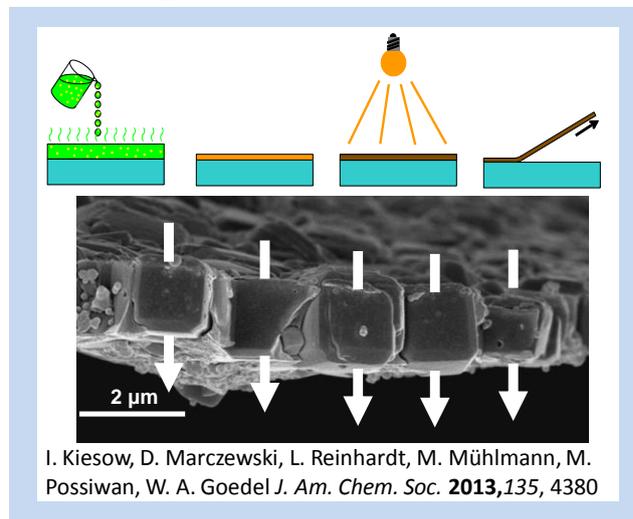
Physical Chemistry

Particle-Assisted Wetting

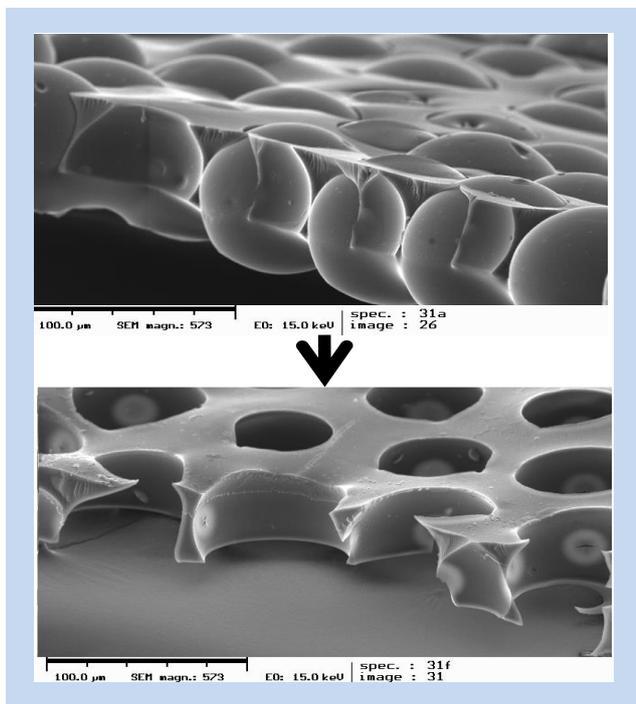


If a liquid does not wet a surface, wetting may be induced via addition of suitable particles. We describe this phenomenon theoretically and via experiments and utilize it for the preparation of composite membranes and micro sieves via float casting.

Float Casting of Membranes and Micro Sieves

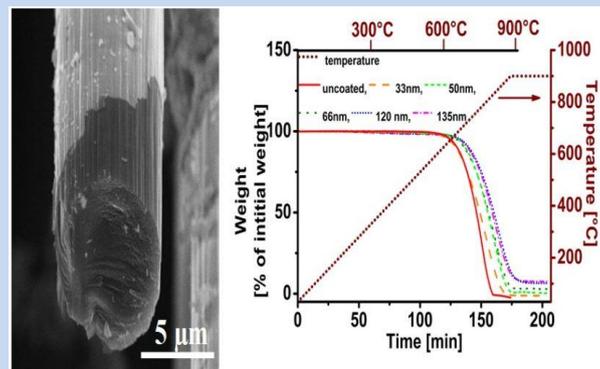


Mixtures of hydrophobic particles and water insoluble liquids are applied to a water surface. These mixtures spontaneously spread to form mixed layers. The water insoluble liquid is solidified via photo polymerisation and we obtain thin composite membranes which are subsequently lifted off the water surface. The membranes thus obtained combine the advantageous permeability and selectivity of the particles with the advantageous mechanical properties of the polymer matrix.



In another approach we use particles of narrow size distribution to create float cast composite membranes and dissolve the particles after solidification of the hydrophobic liquid. This way we finally obtain micro sieves: porous polymer sheets with uniform holes. These micro sieves have a low flow resistance and a sharp size selectivity in filtration applications and therefore are well suitable for the purification of liquids and gases.

Chemical Vapour Deposition - Atomic Layer Deposition



A. K. Roy, W. Baumann, S. Schulze, M. Hietschold, T. Mäder, D. J. Nestler, B. Wielage, and W. A. Goedel, *J. Am. Ceram. Soc.*, **2011**, *94*, 2014-2022

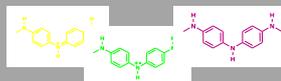
We coat, predominately fibres for the reinforcement of composites, via Chemical Vapour Deposition and Atomic Layer Deposition with thin inorganic layers, which protect the fibres from reaction with the matrix of a composite from oxidation by air at elevated temperatures and optimize the mechanical coupling between fibres and matrix.

Selected Publications:

- [1] I. Kiesow, D. Marczewski, L. Reinhardt, M. Mühlmann, M. Possiwan, W. A. Goedel, Bicontinuous zeolite-polymer-composite membranes prepared via float-casting, *J. Am. Chem. Soc.* **135**, **2013**, 4380.
- [2] S. Stöckel, S. Ebert, M. Böttcher, A. Seifert, T. Wamser, W. Krenkel, S. Schulze, M. Hietschold, H. Gnaegi, W. A. Goedel, Coating of Alumina Fibres With Aluminum Phosphate by a Continuous CVD Process, *Chem. Vap. Deposition* **20**, **2014**, 388.



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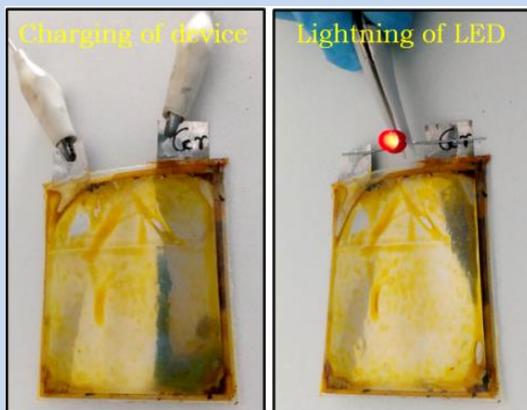


Electrochemistry

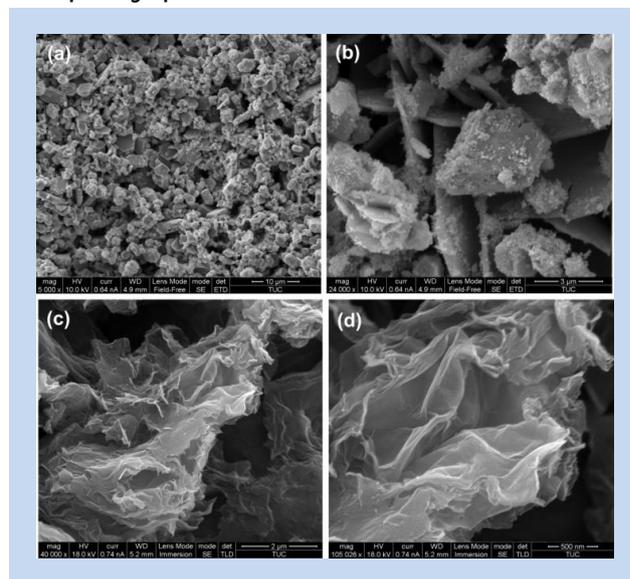
Knowledge of structures and dynamics at the phase boundary electrode/electrolyte solution and identification of species in the interphase close to the interface are essential for revealing the mechanism of many electrochemical processes. Because even many biological processes (e.g. photo-synthesis) and processes in the environment (e.g. corrosion) can be considered as electrochemical reactions the results of related studies have a strong impact. Systems and processes studied in our group include:

Electrochemical Energy Conversion and Storage

Storage in particular of electric energy is essential for a functioning industrial society, even at locations far away from the electric grid communication, medical primary care and daily life are hardly conceivable without electric energy.



Our studies of materials for sodium and lithium ion batteries, of electrolyte systems, of materials and systems for supercapacitors provide contributions toward further development of components and systems. The previous picture shows a supercap driving a light emitting diode, the following one shows microphotographs of the active materials.



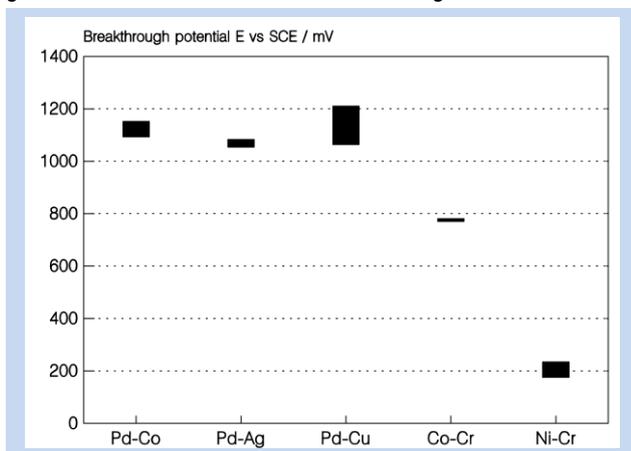
Intrinsically Conducting Polymers

Numerous organic molecules (e.g. aniline, pyrrole, thiophene and their substituted relatives) can be transformed electrochemically into intrinsically conducting polymers, they can also be modified and characterized with electrochemical methods. The easily visible color change induced by electrode

potential changes (Electrochromism, see pictures in page header) is one of the spectacular properties, further applications in electrochemical energy technology, corrosion protection, sensors and surface modification are also promising. Our group provides contributions ranging from fundamental studies to investigations of applications.

Corrosion

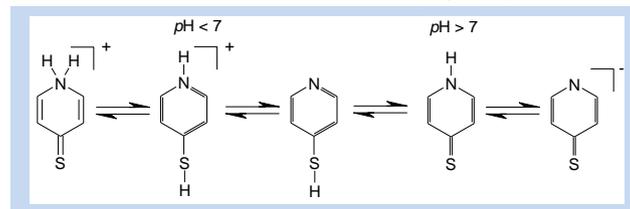
The large economic impact of corrosion of particularly metals and its consequences already justifies intense research into its understanding and prevention. Biological effects of corrosion products of e.g. corrosion of metals in dentistry suggest experimental studies of the influence of alloy composition, processing conditions, and *in vitro*-environment. Our studies of palladium-based alloy, non-precious metal alloys and amalgams contribute to a better understanding.



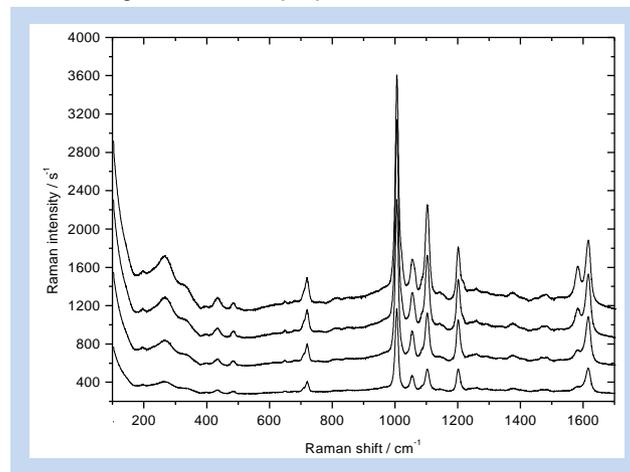
Self-Assembled Monolayers

Numerous molecules adsorb at the phase boundary solid / gas phase or / liquid and form more or less well-organised adlay-

ers. Strong interactions of the adsorbed molecules with surface and between the molecules are of major importance.



With electrochemical, in particular *in situ*-spectroelectrochemical studies of such layers we contribute to a deeper understanding of formation, properties and behavior.



Selected Publications

- D.P. Dubal, R. Holze, *Pure & Appl. Chem.* **86**, **2014**, 611.
- R. Holze, Y.P. Wu, *Electrochim. Acta* **122**, **2014**, 93.
- D.P. Dubal, R. Holze, P. Gomez-Romero, *ChemPlusChem* **80**, **2015**, 944.
- M. Bron, R. Holze, *J. Solid State Electrochem.* **19**, **2015**, 2673.
- F. Wang, Y. Liu, X. Wang, Z. Chang, Y. Wu, R. Holze, *ChemElectroChem* **2**, **2015**, 1024.
- R. Holze, *Phys. Chem. Chem. Phys.* **17**, **2015**, 21364.
- Z. Chang, Y. Yang, X. Wang, M. Li, Z. Fu., Y. Wu, R. Holze, *Sci. Rep.* **5**, **2015**, 11931.



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POLYMER
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Polymer Chemistry

The working group is focused on the synthesis and characterization of novel complex organic/inorganic or organic /organic hybrid materials and macromolecular architectures.

Furthermore, we are interested in functional dyes which are suitable to empirically measure the polarity of Ionic Liquids or metal oxide surfaces. Novel initiators for radical polymerization and reversible switchable polymers are a focus of our research as well.

Due to the interdisciplinary research profile, the polymer chemistry group cooperates with theoretical chemists, physicists and engineers.

Twin Polymerization

The greater goal of this cooperative research project is the development of a new concept in the field of material science which allows the generation of two or more different polymers within one procedure. To obtain a material with the desired properties, the fundamental understanding of the interrelation between reactivity and electronic structure of the monomeric building blocks has to be gained and the reaction pathway for the polymerization and the required composition has to be known. The greater synthetic strategy of twin polymerization involves the integration of polymerization processes derived from step-growth and ring opening polymerization as well as combination with chain polymerization of vinyl monomers.



Nanocomposites in shape of owl-figurines produced by simultaneous twin-polymerization of non-shrinking twin monomers in melt (middle, right); fabricated in a silicone rubber mould intended for tin casting (left).

Functional Dyes

Chromophoric/fluorophoric systems bearing certain functional moieties, like boronic acids, amino acids, barbiturates or diols allow the incorporation in supramolecular structures and the detection of biologically relevant compounds.

Surface Functionalization and Surface Polarity

The polymer chemistry group has developed a UV/Vis spectroscopic methodology which is able to measure surface polarity of surfaces by means of solvatochromic probes. The intelligent combination of different probes enables the separate determination of acidity, basicity and dipolarity/polarizability of surfaces, organic solvents and room temperature ionic liquids.



Solvatochromic dye molecule adsorbed on different inorganic oxides are used to probe surface polarity

Ionic Liquids and Polyelectrolytes

The influence of the molecular structure of more than 120 various imidazolium, pyridinium, tetraalkylammonium and phosphonium ionic liquids with different anions on hydrogen bond acidity and basicity as well as dipolarity and polarizability has been examined.

The water born polyelectrolyte polyvinylamine has been used as component for surface functionalization and for hybrid material synthesis. Due to widespread applications and post-derivation reactions it can be considered as a chemical chameleon.

Radical Polymerization

Imine bases have proven to be novel co-initiators for controllable radical polymerization of acrylate monomers when combined with ionic liquids or isocyanates. By means of this

new technology, the chemistry of radical acrylate polymerization and isocyanates can be tied together.

Services

- solid state NMR spectroscopy
- surface polarity measurements using solvatochromic dyes
- UV/VIS and fluorescence measurements

Representative References

- [1] T. Löschner, A. Mehner, S. Grund, A. Seifert, A. Pohlers, A. Lange, G. Cox, H.-J. Hähnle, S. Spange, A Modular Approach for the Synthesis of Nanostructured Hybrid Materials with Tailored Properties: The Simultaneous Twin Polymerization. *Angew. Chem. Int. Ed.* 51 **2012**, 3258.
- [2] M. Göring, A. Seifert, K. Schreiter, P. Müller, S. Spange, A non-aqueous procedure to synthesize amino group bearing nanostructured organic-inorganic hybrid materials. *Chem. Commun.* 50, **2014**, 9753.
- [3] S. Seifert, S. Höhne, F. Simon, C. Hanzelmann, R. Winkler, T. Schmidt, R. Frenzel, P. Uhlmann, S. Spange, Adsorption of Poly(vinylformamide-co-vinylamine) Polymers (PVFA-co-PVAm) on Copper. *Langmuir* 28, **2012**, 14935.
- [4] A. Schade, N. Behme, S. Spange, Dipolarity versus Polarizability and Acidity versus Basicity of Ionic Liquids as Function of their Molecular Structure. *Chem. Eur. J.* 20, **2014**, 2232.
- [5] I. Polenz, A. Laue, T. Uhrin, T. Ruffer, H. Lang, F. G. Schmidt, S. Spange, Thermally cleavable imine base/isocyanate adducts and oligomers suitable as initiators for radical homo- and copolymerization. *Polym. Chem.* 5, **2014**, 6678.



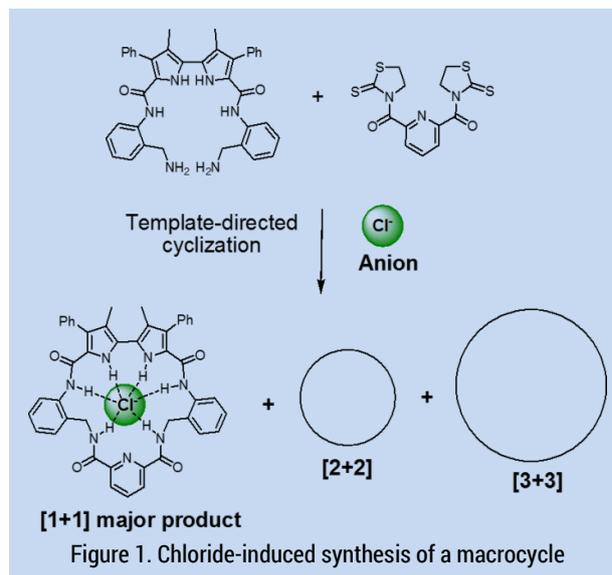
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Supramolecular Chemistry

The research interests of the laboratory encompasses supramolecular synthesis and self-assembly, molecular recognition, colorimetric and fluorometric probes for anions, molecular switches and devices.

Control of Self-Assembly

One of the biggest challenges in supramolecular chemistry is the control of self-assembly in order to obtain desired structures with desired properties. Nature can easily perform this with the help of templates, namely it builds functional molecules in response to external stimuli or environmental factors. Our work aims at mimicking this adaptive behaviour of biological systems, namely transfer molecular information stored in the interacting species to the functions of self-assembled architectures (receptors, sensors or catalysts). Such an approach allows us to construct new receptors for anions (Figure 1). Knowing the structure of selective receptors we design molecular probes by modifying the structure with an appropriate fluorophore that can transfer the information about the binding to a fluorescent answer.

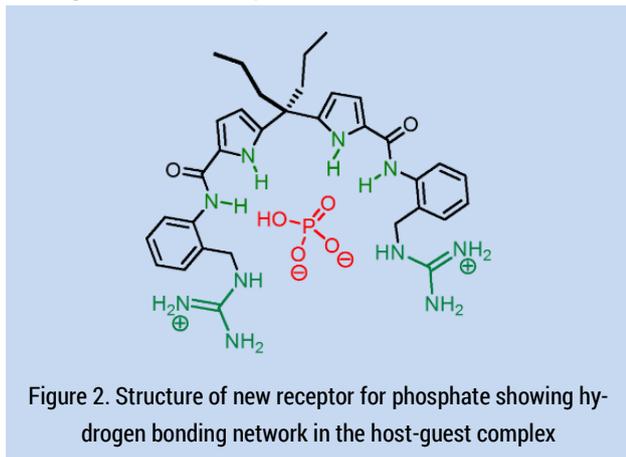


Molecular Recognition of Phosphates

We focus on recognition and sensing of phosphate primarily because phosphates are an essential part of nature and living organisms. Recent prognoses predict dramatic decrease and even exhausting of phosphor-containing mineral resources during the next ca. 40 years.

Thus, understanding principles how to bind and detect phosphate in water is of great fundamental and technological significance. We investigate various approaches how to design receptors that bind phosphates selectively. One of the approaches involves the combination of binding sites of different nature in one receptor.

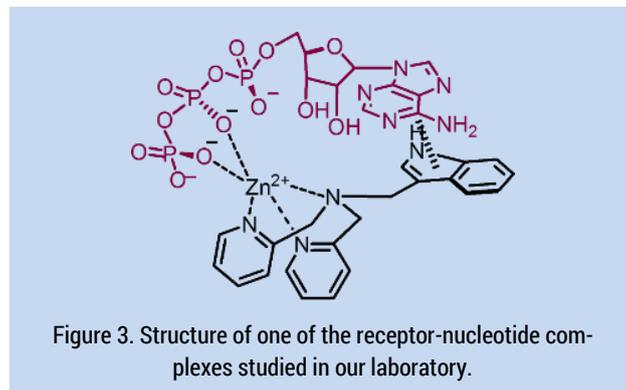
For example, a recently developed receptor for phosphate (Figure 2) combines dipyrrolylmethane- and guanidinium binding sites in the receptor structure.



Fluorescent Probes for Nucleotide

Non-covalent interactions between nucleobases and aromatic amino acids are essential to life. They take part in stabilization of natural DNA-protein complexes, and recent investigations demonstrate that they are as important as hydrogen bonding. Understanding non-covalent interactions between nucleobases and aromatic compounds, especially aromatic dyes, will open the door to new developments in rational drug design, control of gene expression and artificial receptors and/or fluorescent probes for nucleotides and short DNA or RNA sequences. In this project, we investigate model receptors for nucleotides, containing a Zn(II) site that provides strong coordination of a nucleotide through Zn(II)-phosphate electrostatic interactions. Our model receptors for nucleotides also contain an aromatic compound that interacts with a nucleobase through non-covalent interactions. We try to understand

the selectivity of these receptors for a particular nucleotide based on characterization of the nucleobase-aromatic compound interactions with the help of experimental and theoretical tools.



Selected Publications

- [1] E.A. Kataev, C. Müller, G.V. Kolesnikov, V.N. Khrustalev, Guanidinium-based Artificial Receptors for Binding Orthophosphate in an Aqueous Solution, *Eur. J. Org. Chem.*, **2014**, 2747.
- [2] E.A. Kataev, C. Müller, Recent advances in molecular recognition in water: artificial receptors and supramolecular catalysis, *Tetrahedron*, **2014**, 137.
- [3] E.A. Kataev, G.V. Kolesnikov, R. Arnold, H.V. Lavrov, V.N. Khrustalev, Templating Irreversible Covalent Macrocyclization by Using Anions, *Eur. J. Chem.*, **2013**, 3710.
- [4] E.A. Kataev, R. Arnold, T. Rüffer, H. Lang, Fluorescence Detection of Adenosine Triphosphate in an Aqueous Solution Using a Combination of Copper(II) Complexes, *Inorg Chem.* 51, **2012**, 7948.



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Theoretical Chemistry and Applied Quantum Chemistry

Development of New Efficient Correlation Methods

It is well-known that a quantitative description of the electronic structure in molecules is usually not possible with the Hartree-Fock (HF) method. One way to achieve higher accuracy in electronic structure calculations is to improve the wavefunction, which can be routinely done by many-body perturbation theory (MBPT), configuration interaction theory (CI), or coupled-cluster theory (CC). The major drawback of these approaches is their strong dependence of the computational effort on the size of the one-particle basis set. This means that these approaches depend heavily on the system size, if atom-centered basis functions are used. Since for large systems the canonical HF orbitals are not necessarily the best choice for a PT-, CI-, or CC-expansion of the wavefunction, many groups use a local orbital basis instead, to include electron correlation. This allows to screen out insignificant contributions to the energy and therefore the computational cost is reduced. Conceptually different approaches divide the total system into parts and then perform a perturbation expansion to obtain the total correlation energy. An approach designed in this way is the incremental scheme of Stoll. It is based on the Bethe-Goldstone expansion which was introduced to quantum chemistry by Nesbet more than 40 years ago. The correlation energy is

expanded in the incremental series:

$$E_{corr} = \sum_i \Delta\varepsilon_i + \sum_{i>j} \Delta\varepsilon_{ij} + \sum_{i>j>k} \Delta\varepsilon_{ijk} + \dots$$

The first order terms correspond to the correlation energy of the domains:

$$\Delta\varepsilon_i = \varepsilon_i$$

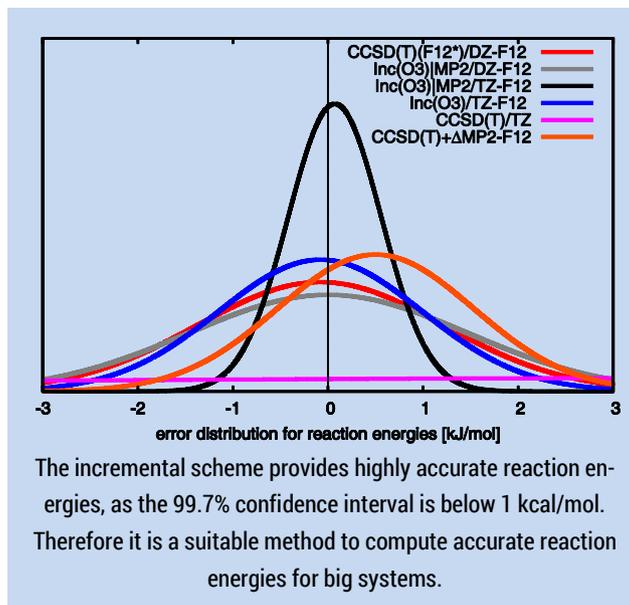
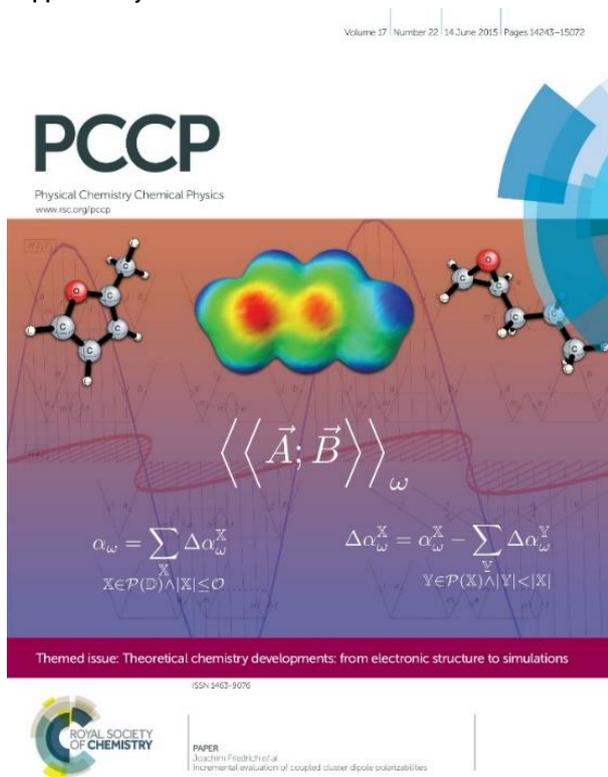
The second order increments are defined as a two-body correction:

$$\Delta\varepsilon_{ij} = \varepsilon_{ij} - \varepsilon_i - \varepsilon_j$$

Higher orders are calculated analogously. The incremental scheme was successfully applied during the last 15 years to various periodic systems and molecules. Recently we proposed a fully automated implementation of the incremental scheme for CCSD(T), CCSD and MP2 energies, implemented an automatic distance screening, extended the approach for the usage of symmetry and to the UCCSD method for open-shell calculations. In order to account for the local character of the core electrons, we introduced an efficient scheme to treat the core and core-valence correlation. With the approach developed in the group of Prof. Friedrich it was possible to compute the binding energy of $[\text{Al}(\text{H}_2\text{O})_{25}]^{3+}$ with CCSD(T) close to the basis set limit using a basis set of quintuple zeta quality with about 6000 basis functions. A few years ago it was impossible to perform coupled cluster calculations for systems of this size together with a basis set of this quality.

Incremental Expansions in Property Calculations – Dipole Polarizabilities

Recently we were the first group in the world to set up a fully automatic and efficient property treatment in the framework of the incremental scheme. Using this code we investigated the accuracy of the incremental expansion for frequency dependent dipole polarizabilities and due to the importance of this work got a title page in PCCP. This development is the starting point for a new generation of quantum chemical methods providing high accuracy together with a wide range of applicability.



Selected Publications

- [1] T. Anacker, D. P. Tew, J. Friedrich, First UHF Implementation of the Incremental Scheme for Open-Shell Systems, *J. Chem. Theory Comput.*, **2015**, accepted.
- [2] J. Friedrich, Efficient calculation of accurate reaction energies - Assessment of different models in electronic structure theory, *J. Chem. Theory Comput.* **11**, **2015**, 3596.
- [3] J. Friedrich, H. R. McAlexander, A. Kumar, T. D. Crawford, Incremental evaluation of coupled cluster dipole polarizabilities, *Phys. Chem. Chem. Phys.* **17**, **2015**, 14284.
- [4] T. Anacker, J. Friedrich: New Accurate Benchmark Energies for Large Water Clusters -- DFT is Better Than Expected, *J. Comput. Chem.* **35**, **2014**, 634.
- [5] J. Friedrich, J. Hänchen, Incremental CCSD(T)(F12*)IMP2 - A black box method to obtain highly accurate reaction energies, *J. Chem. Theory Comput.* **9**, **2013**, 5381.
- [6] J. Friedrich, K. Walczak, Incremental CCSD(T)(F12)IMP2-F12 - A method to obtain highly accurate CCSD(T) energies for large molecules, *J. Chem. Theory Comput.* **9**, **2013**, 408.



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Computational Quantum Chemistry

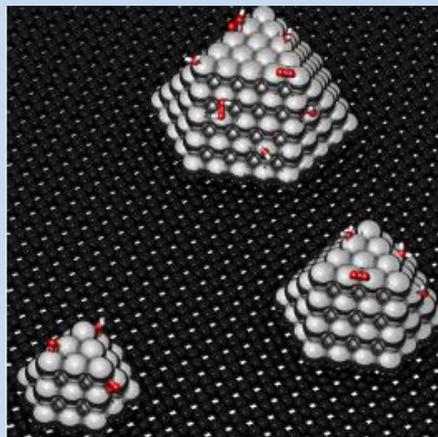
Our group is located at the Max-Planck Institute for Chemical Energy Conversion in Mülheim an der Ruhr and our work focusses on method development and application of quantum chemical tools in materials science and catalysis.

Method Development in Quantum Chemistry

Method development in our group includes new algorithms for existing schemes like the computation of parameters of the NMR spectroscopy, the extension of existing methods like DFT algorithms for systems under electrochemical potential^[1] or the development of novel approaches like tensor decomposition in quantum chemistry.^[2] Our development platform is the ORCA program package which is being developed at the MPI CEC.^[3]

Applications in Materials Science and Catalysis

Our group is involved in the activities of the FOR 1497 "Twin Polymerization". Within this project, we simulate details of the cationic and thermal twin polymerization of various precursors to yield organic/inorganic nanocomposites.^[4] In the framework of the MAXNET-Energy research initiative of the MPG we carry out electronic structure calculations on systems of relevance in electro catalysis. This includes the oxygen reduction and evolution on platinum nanoparticles or properties of carbon materials as catalyst support or electrode materials.^[5]



Computational model of different platinum nanoparticles and oxygen species on a carbon support

Selected Publications

- [1] W.B. Schneider, A.A. Auer, Constant Chemical Potential Approach for Quantum Chemical Calculations in Electrocatalysis. *Beilstein J. Nanotechnol.* 5, **2014**, 668.
- [2] U. Benedikt, K.-H. Böhm, A.A. Auer, Tensor Decomposition in Post-HF Methods, *J. Chem. Phys.* 139, **2013**, 224101. Computational model of different platinum nanoparticles and oxygen species on a carbon support.
- [3] ORCA - an ab initio, DFT and semiempirical SCFMO package, see <https://orcaforum.cec.mpg.de/>.
- [4] A.A. Auer, A. Richter, A.V. Berezkin, D.V. Guseva, S. Spange. Theoretical Study of Twin Polymerization - From Chemical Reactivity to Structure Formation, *Macromol. Theor. Sim.* 21, **2012**, 615.
- [5] W.B. Schneider, U. Benedikt, A.A. Auer, Interaction of Platinum Nanoparticles with Graphitic Carbon Structures: A Computational Study. *ChemPhysChem* 14, **2013**, 29.