Das Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien
Freiburg Center for Interactive Materials and Bioinspired Technologies

Report
2019

REPORT

2019

FIT

FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

FIT

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Georges-Köhler-Allee 105
79110 Freiburg
Germany

P: (+49) 761 203 67879
F: (+49) 761 203 4709
E: mail@fit.uni-freiburg.de
I: http://www.fit.uni-freiburg.de

Secretariat: Christian Neumann
Info Management: Manuel Birk
Managing Director: Prof. Dr. Jürgen Rühe
Administrative Management: Dr. Stefanie Meisen
Scientific Coordination: Dr. Olga Speck

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FOREWORD

FIT INTO THE ROARING TWENTIES

A new decade is dawning, with major new challenges for science and society ahead of us. Issues such as the creation of a sustainable society that uses its resources responsibly will challenge us in the coming years. This concerns issues such as material cycles, CO_2-neutral processes and avoiding the excessive use of natural resources. But this also applies to the creation of a society that not only tolerates and accepts the diversity of people in all areas, but actively uses and promotes it in order to create a breeding ground for a wide range of creative activities. Not only must outstanding work be done in the scientific field, but the results and findings of science must also be brought into society so that disinterest and "fake news" do not gain the upper hand. This will also place great demands on the work in FIT. With the excellent scientific climate and the established infrastructure at FIT, we will take advantage of the resulting opportunities and do our utmost to ensure that the twenties will be the "golden twenties" for FIT.

2019 was a year with many exciting new activities. The Cluster of Excellence "Living Adaptive and Energy-autonomous Materials Systems" is certainly the most significant development for FIT in the past year. After a successful project start at the beginning of 2019, which marks the beginning of the seven-year term, more than 80 people are now working in the cluster and are pursuing the vision of creating new materials systems that can adapt to a changing environment and "harvest" the energy required for this from their environment. The cluster is a prime example of interdisciplinary cooperation – even across organizational boundaries. Members of three non-university institutions and six faculties – from chemistry, physics, biology and engineering sciences to psychology and philosophy – are involved in the research network. A first impression of the cluster's research field was given at the official "Kick-off" event in September 2019, where international experts and researchers from FIT presented research work on the various cluster topics. In this year's report, the first reports on the results of research work carried out within the exciting project are now available. In addition to the increase in personnel, the expansion of the infrastructure has made great progress. The construction of the ideasFactory@FIT shared laboratories has begun and we hope to be able to officially open the laboratories at the end of the first quarter of this year.

Another highlight of last year at FIT was the acquisition of the ZEISS research cluster IPROM. IPROM stands for Interactive and Programmable Materials. The ZEISS Foundation supports investments and research projects in the program line "Breakthroughs in Research" for a period of five years with a high level of funding, which allows numerous research projects to be carried out and the infrastructure to be further expanded. The topic of the research cluster will be to generate materials with programmable properties. The official project start will be on Feb. 01, 2020.

Two further large projects have been acquired or started in 2019. One of these is the BioElast project on materials for adaptive architectures, which is a collaboration between the *liv*MatS excellence cluster in Freiburg and the architecture excellence cluster in Stuttgart. Another attractive project, which was also approved in 2019, is the establishment of a convergence center with Pennsylvania State University. This center will establish a German-American collaboration in the field of adaptive, sustainable materials. However, the focus is not exclusively on large collaborative projects. In addition to the afore-mentioned research networks, numerous excellent individual projects have also been started last year or have been continued. Many examples of these research projects can be found in this annual report.

We are pleased to welcome many more new members to FIT last year. This means that we are currently at an all-time high in the number of members! We are particularly pleased that we have once again been able to welcome a number of promising young scientists and researchers.

We would like to express our sincere thanks to all our employees for their outstanding achievements and services in the outstanding development of our FIT. Without the perpetual commitment of many hands, we would not be able to perform outstanding scientific work. We would like to thank all our administrative and technical staff, the FIT members, our in-house scientific staff, our Scientific Advisory Board, and the many supporters and sponsors inside and outside the university.

We have an exciting year and an exciting new decade ahead of us and look forward to many new challenges and opportunities. I hope you enjoy reading our annual report.

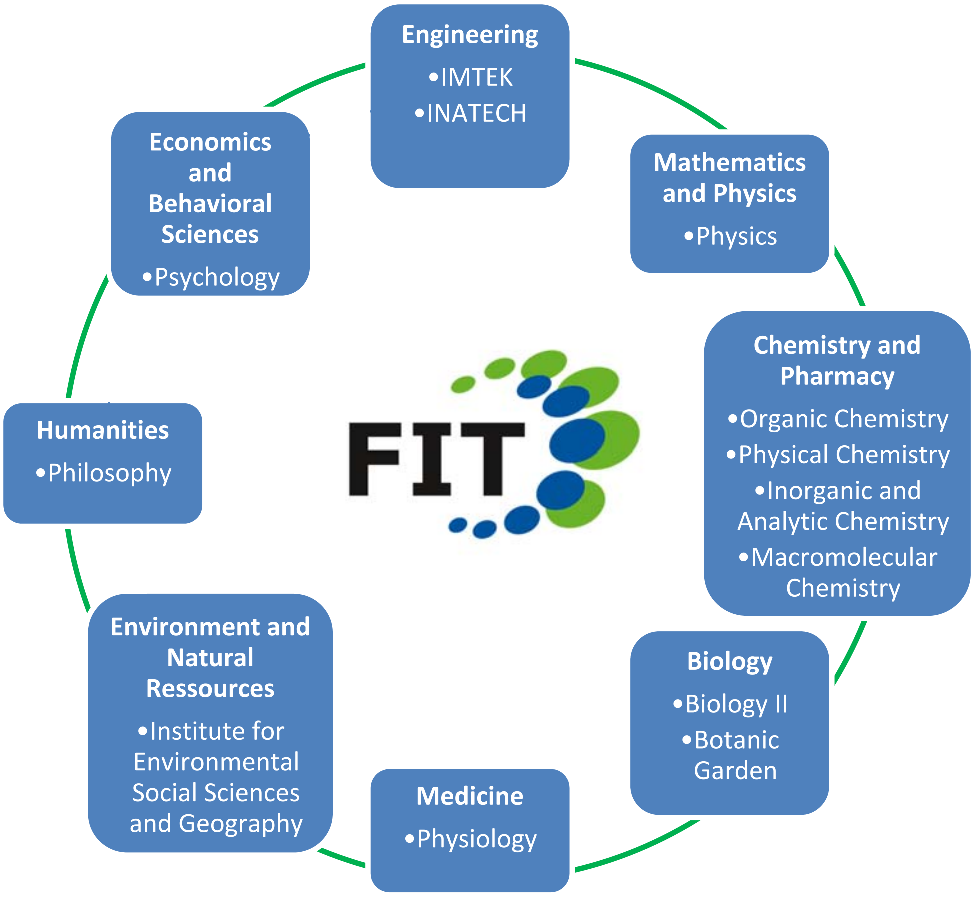
J. Ruhe

Jürgen Rühe

(Executive Director FIT)

THE CENTER

STRUCTURE

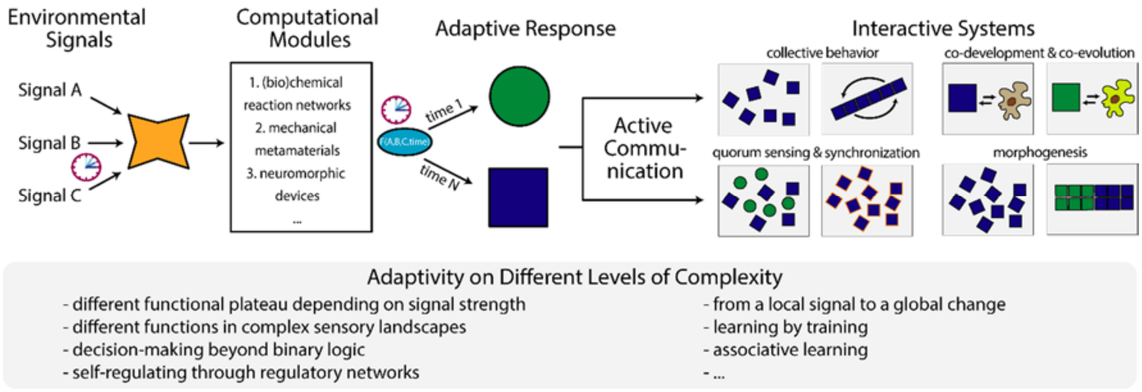


Overview of the various faculties and institutes that carry out disciplinary and interdisciplinary projects within the framework of basic research at FIT. A list of current and completed projects is available on the FIT website.

The FIT is a research institution of national and international importance for the development of future-oriented, innovative materials and materials systems. Special focus is placed on materials systems that react to changes in the environment and thus, inspired by plants and animals, have life-like functions.

Following the model of living nature, these "vital" materials systems are interactive, adaptive, energy-autonomous, self-repairing, self-improving or even learning. These extraordinary properties and functions make them a decisive advance in the sustainable development of technology and society.

Adaptive and Active Polymer Materials



Pathways towards adaptive and interactive behavior. Reprinted with Permission from Wiley VCH 2019 (Walther, 2019)

Adaptive, Active and Interactive Materials and Systems – a fascinating terminology for future soft materials systems with unprecedented opportunities. But what are adaptive materials? What are interactive materials or systems? How do they contrast present-day responsive and switchable materials?

If we want to answer this question, we need to get increasingly inspired from the dynamics and behavior of living biological systems. For instance, cepaholopods exhibit adaptive camouflaging to protect them against predators. Interestingly enough this camouflaging is only provided through a local sensor-processor-actor system, that is disconnected from the brain of the organism as cephalopods are color blind. Hence there is a local embodied intelligence that organizes the adaptation in a complex sensory landscape, and energy is needed to provide this adaptation through muscle contraction around chromophore cells. Similarly, stem cells are able to probe a complex sensory landscape, such as static and dynamic mechanical properties, topography, biological signals and matrix degradability to guide differentiation into different lineages. Here we learn that different signals must be weighed against each other and computed, also in a time correlated manner. Biological systems organize this through (bio)chemical reaction networks. Therefore such reaction networks are a tool to provide soft matter systems with increased adaptation capabilities. Additionally, training and learning are classical examples of adaptive behavior. For instance, muscles adapt their performance through metabolic growth, but they can also loose their mechanical memory when the exercise is stopped. Besides, Pavlovian adaptation is the classical example where a dog learns to connect an unconditioned neutral stimulus to exhibit new behavior. This means that signal processing routines need to be intertwined and that a memory module needs to be built up.

Form these considerations it becomes evident that we have to think about adaptive materials as materials that are able to process a complex sensory landscape and that are able to change their behavior over time, not in the sense of fatigue, but in the sense of being able to process signals differently over time. How do we reach there? We need to empower soft materials systems with computational elements to provide local embodied intelligence. The correct tools are there, such as in the case of chemical reaction networks, mechanical metamaterials or neuromorphic devices. In the future we need to connect progress in these domains to the materials world, which requires to overcome disciplinary boundaries.

Finally, if we want to move in the direction of interactive systems, then we need to establish active communication channels between adaptive entities, so that two adaptive entities actively cross-regulate each other. Ultimate goals may be a biosynthetic hybrid co-evolution in which synthetic and biological entities adapt towards each other, actively. These fields are truly at the infancy and it will be exciting to see where we are standing in 10 years from now.

FIT targets such disruptive concepts and the new *liv*MatS Cluster and the ETN Creanet Project are important project lines in this context.

References:

Walther, A. (2019). From Responsive to Adaptive and Interactive Materials and Materials Systems: A Roadmap. *Advanced Materials* 1905111.

Andreas Walther

Biomimetic, Biobased and Bioactive Materials Systems

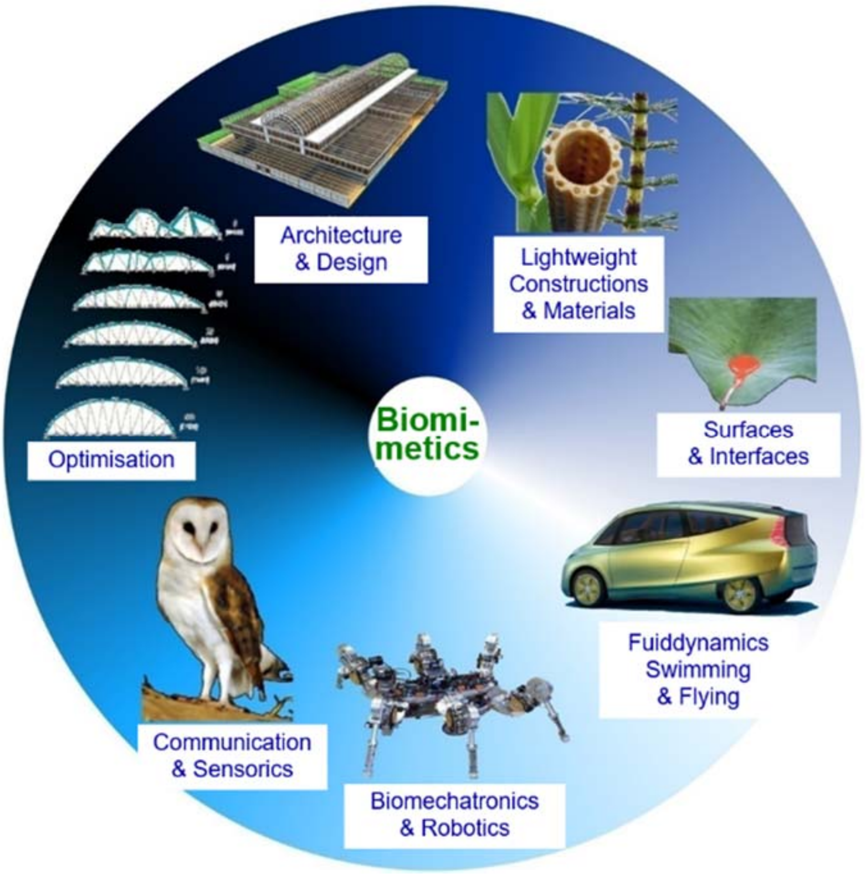


Fig. 1: Different fields of biomimetic research. © Plant Biomechanics Group Freiburg

The research focuses in this future field deal with the development and construction of bio-inspired, biomimetic, biobased and bioactive material systems. In addition to the transfer of functional principles from living nature to technical systems, this also includes the development of new active hybrids by the integration of synthetic and biological components, and the bioactive functionalization of materials and (micro)systems to enable them to interact with proteins, cells and tissues.

Biomimetic materials systems @ FIT

During the last decades biomimetics has attracted increasing attention as well from basic and applied research as from various fields of industry and building construction. Biomimetics has a high innovation potential and offers the possibility for the development of sustainable technical products and production chains. The huge number of organisms with the specific structures and functions they have developed during evolution in adaptation to differing environments represents the basis for all biomimetic R&D-projects. Novel sophisticated methods for quantitatively analyzing and simulating the form-structure-function-relation on various hierarchical levels allow new fascination insights in multi-scale mechanics and other functions of biological materials and surfaces. Additionally, new production methods enable for the first time the transfer of many outstanding properties of the biological role models into innovative biomimetic products for reasonable costs. In the FIT we concentrate on the development of biomimetic materials systems with various self-x-properties including self-repair, self-adaptation, self-cleaning and self-organization. Other research topics deal with bioinspired materials systems with pronounced energy dissipation, trainable materials systems, and the usage and development of 4D-printing technologies for the production of novel bioinspired materials systems.

Biobased materials @ FIT

In the biobased materials research @ FIT, we try to use biomimetic approaches to design novel materials from renewable resources. Our efforts particularly focus on the utilization of lignocellulosic biopolymers towards the design of advanced materials and materials systems. One such project has attempted to develop novel processing approaches of lignin, the second most abundant biopolymer on earth, by utilizing a liquid crystalline cellulosic polymer as processing aid and lubricant. This processing approach is inspired by the biosynthesis and the morphogenesis of the plant cell wall. During the plant cell wall morphogenesis, a liquid crystalline cellulose / hemicellulose network serves as a host structure for the in-situ polymerization of monolignols. The monolignols polymerize into a 3D highly branched lignin biopolymer, which consolidates the composite structure to finally deliver a high-strength, high toughness composite lignocellulosic material. The resulting lignocellulosic blends can be processed in solution by direct ink writing. This research paves the way to new processing avenues for lignocellulosic polymers and thus novel applications.

Thomas Speck & Marie-Pierre Laborie

(Micro)Systems for Energy Conversion, Storage and Energy-autonomy

In this future field, the research focuses on the development and construction of material systems for energy conversion and storage. As such, inspired by nature, materials and systems are developed for the conversion of solar energy (solar cells and photoelectrochemical cells for artificial photosynthesis), chemical energy (fuel cells), thermal energy (thermoelectric generators) and vibrational energy (triboelectric generators). One aspect thereby aims to realize material systems with an embedded energy autonomy, i.e. materials systems which are ideally able to harvest the required energy from the ambient. In that sense, the materials and systems developed in this future field range from macro to highly embedded micro systems. As most ambient energy forms are intermittent, systems for energy storage must also be developed, so that the required energy is available on demand. Breaking with classical modular approaches, one vision is hereby to develop multifunctional conversion and storage systems at the highest level of integration, realizing a seamless integration of both functions. In this context, advanced multifunctional material processing techniques are of highest importance to realize this integration challenge.

Material systems for energy conversion and storage @ FIT

The largest activites in the future field are presently associated with the research activities in research area A of the livMatS Cluster in which novel concepts and systems for energy autonomous materials systems are developed.

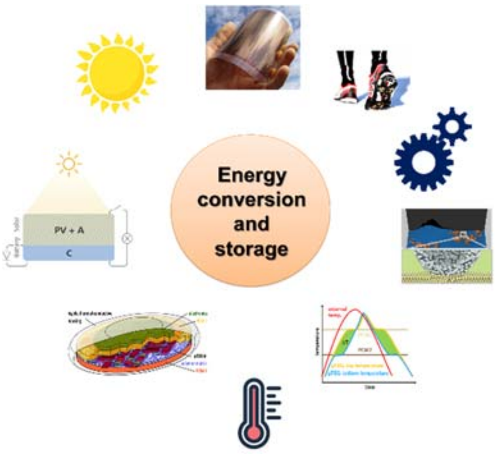


Fig.1: Different forms of energy conversion and storage and associated materials and systems. © Area A of the *liv*MatS Cluster.

Solar energy conversion and storage

Solar energy is converted and stored as electrical charges in SolStore devices; devices, which fuse the function of light-induced charge carrier generation/separation and charge carrier storage at different levels of integrations, ranging from 3 electrode systems, in which a solar cell shares an electrode with an electrochemical energy storing system (supercapacitor or battery) to 2 electrode systems, in which the light-induced charge carrier generation/separation and charge carrier storage are truly embedded in one multifunctional material system.

This central *liv*MatS research is complemented by other FIT research projects in the future field related amongst others to a) solar energy conversion with novel tandem solar cells or photoanodes for photoelectrochemical water splitting, b) electrochemical energy conversion with bioinspired materials for Pt-free fuel cells as well as c) improved electrochemical energy storage with novel battery concepts and materials and interfaces.

Thermal energy conversion and storage

This area is anticipated by the development of highly efficient thermoelectric generators (TEGs) with integrated phase shift materials to be used as a storage unit for thermal energy. The corresponding project ThermoBatS is therefore again aiming at an intricate fusion of energy conversion and storage. The thermoelectric materials chosen are fabricated as highly nano-micro scale powders and formulated as thermoelectric inks or pastes. Fabrication of TEGs happens via dispensing or printing into flexible substrate materials, thus creating a versatile multi-material system suitable for the ambient temperature range. Other projects outside of livMatS will tackle the area of high-temperature energy harvesting using powder-pressed and sintered or electroplated thermoelectric materials. A third direction to be followed in all projects is the characterization of thermoelectric materials and systems.

Mechanical energy conversion

In livMatS, triboelectric generators are the actual main topic of research in the project TriboGen. Here, we will do an extensive study on the fundamental physical effects of triboelectric charge generation, to gain more insight into this phenomenon, which is known for thousands of years but still a matter of scientific debate. As a result, optimized materials and suitable surface topologies will be developed for highly efficient triboelectric generators. Charge extraction will happen through innovative concepts and automatic frequency tuning will be performed through the mechanical design of self-adaptive triboelectric vibration harvesters.

These named projects are exemplary for the trend of energy research followed in FIT. Aside of the mentioned activities additional related projects are planned to widen the research platform with additional and highly innovative concepts for energy conversion, storage and transfer.

Anna Fischer & Peter Woias

Core Facilities

Imaging of Materials Systems

- Scientific heads: Prof. Dr. Anna Fischer and Prof. Dr. Andreas Walther
- Responsible manager: Dr. Yi Thomann

This Core Facility represents a specialized laboratory for microscopy and tomography. On the basis of existing and additionally procured equipment the facility has established advanced expertise especially in the field of high performance electron microscopy. It provides service measurements with high resolution TEM/STEM, FIB/SEM, EDX and their 3D visualization, in order to investigate complex functional principles in technical as well as in biological systems as role models for new technological developments.

At the end of May 2019, we introduced also a new usage concept that allows now more users access to our services, as long as their research works are bound to the condition of a non-profit status.

The current terms of use can be found on our homepage:

http://www.fit.uni-freiburg.de/Dateien/device-rules

http://www.fit.uni-freiburg.de/Dateien/Device-fees

Highlights of research works accomplished in the core facility in the year of 2019:

1) 3D investigation of oxygen reduction catalysts consisting of mesoporous N-doped carbon nanoballs and supported finely divided Pt nanoparticles (AK Anna Fischer, FIT)

2) Host-guest mediated self-assembly of 3D DNA Origami cuboids (Andreas Walther, FIT)

3) Structural and functional imaging of large and opaque plant specimen (Hesse, Bunk, Speck, Masselter, FIT)

4) Double-tilt TEM Tomography on Pt nanoparticles supported on TRGO (graphene) sheets (Thomann, FIT; Mülhaupt, FMF)

5) FIB/SEM Tomography of nacre-mimetic hydrocarbon composites (Thomann, FIT; Fan Zhong FMF)

6) HR-TEM/STEM investigation on polymer solar cells – enhancement of the material contrast in the polymer active layer (Fig. 1).

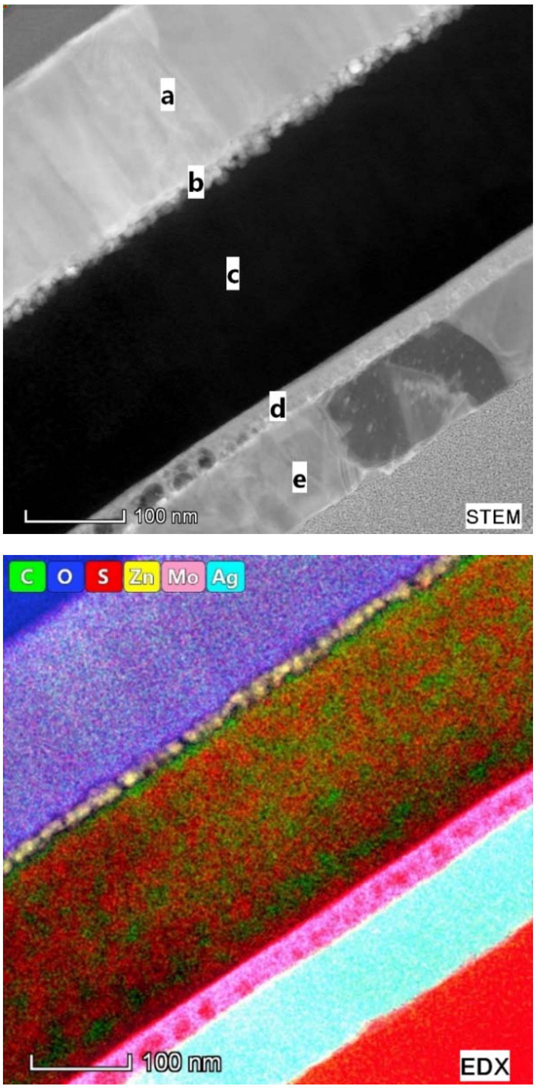


Fig. 1: Layered structure of an organic solar cell. Cross section visualized by STEM (upper) and EDX (lower). The about 15 nm thick slice for HR-TEM and STEM was prepared with our FIB/SEM technique. It was possible to visualize the acceptor and donor components in the active layer (c in the STEM and red/green mixed layer in the EDX image), which is very important for the understanding of the efficiency of energy harvesting. Layers: a: ITO; b: ZnO2; c: P3HT/PCBM, d: MoOx and e: Ag. © Thomann

Functional Processing

Manufacturing technique for bioinspired materials with focus on nanolithography, film technology, and generative processes

- Scientific head: Prof. Dr. Claas Müller[1,2]
- Responsible manager: Dr. Jing Becker[1]

[1]FIT Core Facility "Functional Processing",
[2]IMTEK Department of Microsystem Engineering,
Laboratory for Process Technology

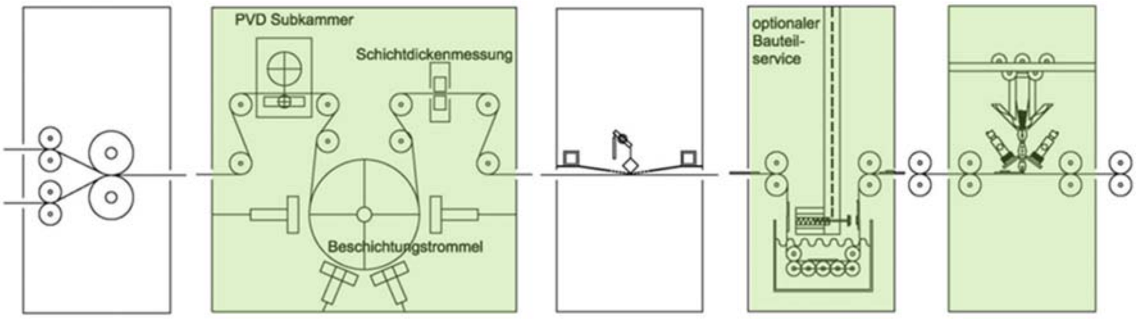


Fig. 1: Arrangement of the process modules in the technology platform 2 (from left): roll laminator, PVD & PECVD system, screen printer, electrophoretic deposition system and aerosol jet printer. © Core Facility 2, FIT, Freiburg

Short description of research goals: Manufacturing technique for bioinspired materials with focus on nanolithography, macromolecular foil technology, and 3D-printing technology

In order to support the research projects running in FIT, a powerful technology department, Core Facility "Functional Processing", is established for functional design and efficient manufacturing of (micro-) systems and adaptive bioinspired materials.

The Core Facility "Functional Processing" concentrates particularly on the fabrication of nano- and micro-structures on macromolecular foils. Besides UV-NIL (UV-nanoimprint-lithography) as well as HE-NIL (hot-embossing-nanoimprint-lithography) technologies, various novel manufacturing technologies, such as roll lamination, thin film deposition, surface modification, aerosol jet printing technology, electrophoretic deposition, as well as screen printing technology are developed for special applications on polymer foils.

The equipment installed in the Core Facility "Functional Processing" is divided into two different categories according to the operation complexity. The category 1 includes the Cryomill system for material grinding with its integrated liquid nitrogen cooling system, the Stork roll laminator and the electrophoretic deposition system (EPD) from Permatecs. For this equipment category, after the application from the users and the evaluation by Core Facility "Functional Processing" group, the applicants would receive a clearly defined training course offered by the CF 2 stuffs. Following the training activities, the applicants will be issued a permit to work on the system. For the other system in CF 2, due to the operation complexity and the maintenance requirements, the users outside the CF 2 group are not allowed to perform alone on the systems. The equipment in this category could only be operated by the CF 2 stuffs.

From the beginning of year 2019, Core Facility “Functional Processing” has cooperated with research group Prof. Dr. Wolfgang Kowalsky (Technische Universität Braunschweig) on the topic of fabrication and investigation of polymer-based optical sensor platform with integrated light source. This project is financed by Deutsche Forschungsgemeinschaft DFG (Project-ID: KO1040/22-1). In this project, a planar optical sensor platform with integrated organic laser as optical light source, single-mode waveguide structures, sensor systems and organic photodiodes will be fabricated on a flexible polymer foil. A novel electrically tuned laser concept will be developed for the optically pumped organic laser source which is very important for the polymer sensor systems. In this project, in order to realize the integration purpose, novel manufacturing processes will be developed and optimized in Core Facility 2. By applying such kind of manufacturing methods, polymer-based optical sensor platforms could be fabricated cost effectively with high precision.

During 2019, important research results from Core Facility 2 have been submitted to international peer-reviewed journals. The breakthroughs have also been presented on international conferences to a broader scientific community. The relative information is shown below:

1. J. Becker, M. Čehovski, R. Caspary, H.-H. Johannes, W. Kowalsky und C. Mueller: Polymer-basierter wellenleiterintegrierter DFB Laser, MST Kongress 2019 Berlin
2. J. Becker, M. Čehovski, H.-H. Johannes, W. Kowalsky und C. Mueller: Bragg Grating Integrated Waveguide Structures Fabricated by CNP Process, Microelectronic Engineering (submitted)
3. Marko Čehovski, Jing Becker, Ouacef Charfi, Hans-Hermann Johannes, Claas Mueller, Wolfgang Kowalsky: Single-mode Polymer Ridge Waveguide Integration of Organic Thin-Film Laser, Microelectronic Engineering (submitted)

Modelling and Simulation of Materials Systems

- Scientific head: Prof. Dr. Michael Moseler
- Responsible manager: PD Dr. Michael Walter

[1]Institute of Physics, University of Freiburg, [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

FIT supports materials development and system integration through modelling and simulation. The funding granted by the Landesstiftung and the German Research Foundation for this purpose was used in 2017 for an extension of the NEMO-cluster located at the University of Freiburg, where FIT participates in a “shareholder” principle. Due to synergy-effects additional 1000 cores (therefore approx. 20% more than were granted) were included to the cluster corresponding to a 5.6% of the full extended cluster. The “shareholder”-status allowed to use the computational resources already before this extension, a possibility that was used extensively by the simulation group of FIT. As shown in fig. 1, the actual use of the computational resources summed up to 6.3%of the full NEMO-Cluster.

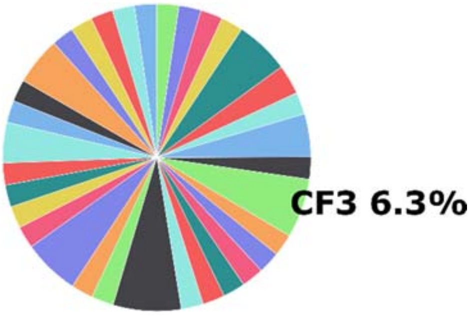


Fig. 1: Partition of computational time used on the full NEMO-cluster in the year 2019. The fraction used by CF3 is highlighted. © RZ University of Freiburg

These calculations performed and models developed allowed addressing current problems in tribology, polymer chemistry, organic photovoltaics and catalysis in simulation as well as modelling of materials based on natural resources. This work resulted in 10 peer-reviewed publications during the year 2019. These studies are possible due to the co-development of the internationally developed software packages ASE and GPAW.

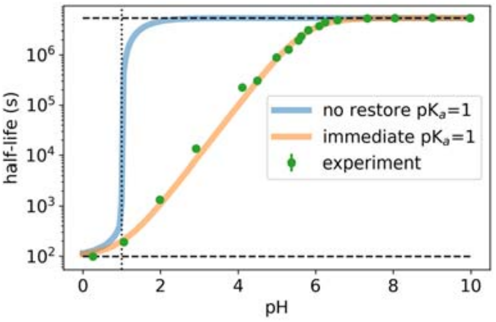


Fig. 2: Comparison of the modeled and measured half-lifes for the thermal spontaneous transition back-transition of AAP (see text) from the Z-form to the E-form. The model uses the experimental half-lives $\tau_{1/2}$ (pH > 7) = 5.40 · 10^6 s (upper dashed line) and $\tau_{1/2}$ (pH 0.3) = 98.5 s (lower dashed line) as well as a numerically optimized pK_a (Z) of 1 (dotted line). Experimental data from S. Ludwanowski, group Andreas Walther (© core facility 3).

The outcome of one of our activities in direct collaboration at FIT is depicted in Figure 2 as an example. We have investigated the thermal transition of arylazopyrazole (AAP) from the Z-form to the energetically lower E-form. AAP is similar to azobenzene, the prime example of a photoswitch molecule that changes conformation under irradiation, a property that allow its use as molecular machine. Experimental results of the group of Andreas Walther showed a strong pH dependence in the thermal back-reaction in AAP. The half-lives cover the range from ~100 seconds to more than 60 days at room temperature. Our modeling activities not only helped to reveal a pH-dependent chance in the transition path from density functional theory calculations of the corresponding barriers, but also helped to understand the exact dependence of the half-life with pH. An effective rate model developed by us furthermore reveals that the protonation is practically immediate at the timescale of these transitions in AAP. The figure shows the excellent agreement between model and measurements.

MANAGEMENT

Prof. Dr. Jürgen Rühe
(Managing Director)
IMTEK
Department of Microsystems Engineering
Chemistry and Physics of Interfaces

Prof. Dr. Thomas Speck
(Deputy Managing Director)
Plant Biomechanics Group
Botanic Garden
Faculty of Biology

Dr. Stefanie Meisen
(Administrative Director)
FIT

Dr. Olga Speck
(Scientific Coordinator)
FIT

DIRECTORATE

The Board of Directors of the FIT consists of five full-time professors from the participating faculties of the University of Freiburg that must also be members of the FIT. These professors are appointed by the Rectorate for a term of three years on the recommendation of the general meeting. The Directorate elects the Managing Director and the Rectorate appoints him for a term of three years. The Board of Directors is responsible for managing the business and decides on all matters that are not assigned to another body of the university. It coordinates the tasks to be performed within the FIT and draws up an annual research and financial plan. The members of the Directorate also include the respective Managing Director of the FMF and a representative of the young scientists. In 2019, members of the Directorate were:

Prof. Dr. Jürgen Rühe
(Managing director)
Faculty of Engineering

Prof. Dr. Thomas Speck
(Deputy managing director)
Faculty of Biology

Prof. Dr. Anna Fischer
Faculty of Chemistry and Pharmacy

Prof. Dr. Andreas Walther
Faculty of Chemistry and Pharmacy

Prof. Dr. Peter Woias
Faculty of Engineering

Prof. Dr. Rolf Mülhaupt
(Managing director of the FMF)
Faculty of Chemistry and Pharmacy

Dr. Can Dincer / PD Dr. Karen Lienkamp
(Representative of young scientists)
Faculty of Engineering

MEMBERS

Laboratories with the corresponding infrastructure and office space are made available to members for a limited period of time. The members have access to the three Core Facilities. In 2019, the members included (in alphabetical order):

Prof. Dr. Jan C. Behrends (Faculty of Medicine)

Dr. Witali Beichel (Faculty of Engineering)

Ludmila Cojocaru, PhD (Faculty of Engineering)

Dr. Can Dincer (Faculty of Engineering)

Prof. Dr. Christoph Eberl (Faculty of Engineering)

apl. Prof. Dr. Christian Elsässer (Faculty of Mathematics and Physics)

Prof. Dr. Birgit Esser (Faculty of Chemistry and Pharmacy)

Prof. Dr. Anna Fischer (Faculty of Chemistry and Pharmacy)

Prof. Dr. Stefan Glunz (Faculty of Engineering)

Dr. Frank Goldschmidtböing (Faculty of Engineering)

Prof. Dr. Rainer Grießhammer (Faculty of Environment and Natural Resources)

Dr. Dorothea Helmer (Faculty of Engineering)

Prof. Dr. Lore Hühn (Faculty of Humanities)

Prof. Dr. Thorsten Hugel (Faculty of Chemistry and Pharmacy)

Prof. Dr. Henning Jacob Jessen (Faculty of Chemistry and Pharmacy)

Prof. Dr. Andrea Kiesel (Faculty of Economics and Behavioral Sciences)

Dr. Peter Koltay (Faculty of Engineering)

Prof. Dr. Ingo Krossing (Faculty of Chemistry and Pharmacy)

Prof. Marie-Pierre Laborie, Ph.D. (Faculty of Environmental and Natural Resources, until 10.01.2019)

PD Dr. Karen Lienkamp (Faculty of Engineering)

Dr. Tom Masselter (Faculty of Biology)

Prof. Dr. Michael Moseler (Faculty of Mathematics and Physics)

Prof. Dr. Rolf Mülhaupt (Faculty of Chemistry and Pharmacy, until 30.09.2019)

Prof. Dr. Claas Müller (Faculty of Engineering)

Prof. Dr. Lars Pastewka (Faculty of Engineering)

Dr. Uwe Pelz (Faculty of Engineering)

Prof. Dr. Bastian E. Rapp (Faculty of Engineering)

Prof. Dr. Günter Reiter (Faculty of Mathematics and Physics)

Prof. Dr. Ralf Reski (Faculty of Biology)

Prof. Dr. Winfried Römer (Faculty of Biology)

Prof. Dr. Jürgen Rühe (Faculty of Engineering)

Dr. Olga Speck (Faculty of Biology)

Prof. Dr. Thomas Speck (Faculty of Biology)

Dr. Simon Thiele (Faculty of Engineering, until 30.06.2019)

Dr. Severin Vierrath (Faculty of Engineering)

Prof. Dr. Andreas Walther (Faculty of Chemistry and Pharmacy)

Prof. Dr. Peter Woias (Faculty of Engineering)

Dr. Uli Würfel (Faculty of Mathematics and Physics)

Prof. Dr. Roland Zengerle (Faculty of Engineering, until 31.01.2018)

SCIENTIFIC ADVISORY BOARD

The Scientific Advisory Board accompanies the scientific work of the FIT and shall provide the directorate with suggestions for its further development. Members of the Advisory Board are external university professors whose research focus lies in the field of activity of the FIT. They are appointed by the Directorate for a period of five years. Since June 2019, the following professors belonged to the newly nominated Scientific Advisory Board:

Spokesperson: Prof. Dr. Ingo Burgert (ETH Zurich, Switzerland)

Deputy spokesperson: Dr. Karine Anselme (Institut de Science des Materiaux de Mulhouse (IS2M), France)

Prof. Dr. Eduard Arzt (Saarland University and Leibniz Institute for New Materials, Germany)

Prof. Dr. Clothilde Boulanger (Université de Lorraine, France)

Prof. Dr. Peter Fratzl (Max Planck Institute of Colloids and Interfaces, Potsdam, Germany)

Prof. Dr. Oskar Paris (University of Leoben, Austria)

Prof. Dr. Christoph Weder (Adolphe Merkle Institute, Fribourg, Switzerland)

Prof. Dr. Eric Yeatman, Imperial College London, UK)

INTEGRATIVE BOARD

The Integrative Board is set up as a university-internal advisory body and monitors the development of the FIT. It works towards the reconciliation of interests of the faculties and institutions involved in FIT. In 2019 the following persons were members of the Integrative Board, with the deans always changing to the winter semester.

Prof. Dr. Jürgen Rühe (Managing Director of FIT)

Prof. Dr. Thomas Speck (Deputy Managing Director of FIT)

Prof. Dr. Daniela Kleinschmit / Prof. Dr. Heiner Schanz (Dean of the Faculty of Environmental and Natural Resources)

Prof. Dr. Wolfgang Driever / Prof. Dr. Dierk Reiff (Dean of Biology)

Prof. Dr. Gregor Herten / Prof. Dr. Wolfgang Soergel (Dean of Faculty of Mathematics and Physics)

Prof. Dr. Oliver Einsle / Prof. Dr. Oliver Einsle (Dean of Faculty of Chemistry and Pharmacy)

Prof. Dr. Hannah Bast / Prof. Dr. Rolf Backofen (Dean of Faculty of Engineering)

Prof. Dr. Norbert Südkamp (Dean of Faculty of Medicine)

Prof. Dr. Eberhard Schockenhoff (Management Director of the Interdisziplinäres Ethikzentrum)

Dr. Bruno Ehmann (Management Freiburg Research Services)

Dr. Stefanie Meisen (Administrative Management of FIT)

Prof. Dr. Ingo Burgert (Spokesperson of the Scientific Advisory Board)

FIGURES AND FINANCES

The FIT members were and are actively involved in the acquisition of projects in line with FIT's research priorities. The number of projects could be increased by nine projects to 40, which have provided a total of 2.4 million euros for research. In this context, 84% of the funds were spent on personnel. This in turn led to an enormous increase in the number of employees from 190 to 244. 30 postdocs, 108 doctoral students, 30 master students and 13 bachelor students were supervised in 2019. They were all able to look beyond the faculties and experience a culture of cooperation at FIT. At the same time, FIT only has two budgeted positions: The head of administration with 25% and an assistant with 100%.

Furthermore, 13% was spent on material resources and only 3% on investments. This shows that the basic investments have finally been completed and that the budget is thus set up purely through project financing. From this point of view, a comparison of the budget for 2018 with 2019 shows a minimal increase. In order to be able to understand the figures accordingly, please refer to the following graphs and tables for further details.

In addition to the existing third-party funding, FIT was successful in the 2018 Excellence Initiative and was thus able to start with the *liv*MatS cluster in 2019. Within the cluster, 927 k€ were spent as direct project costs, 541 k€ for the creation of new shared laboratories and 495 k€ for strategic measures and administration. 14 projects started within the cluster in 2019 with 42 project leaders and 48 employees.

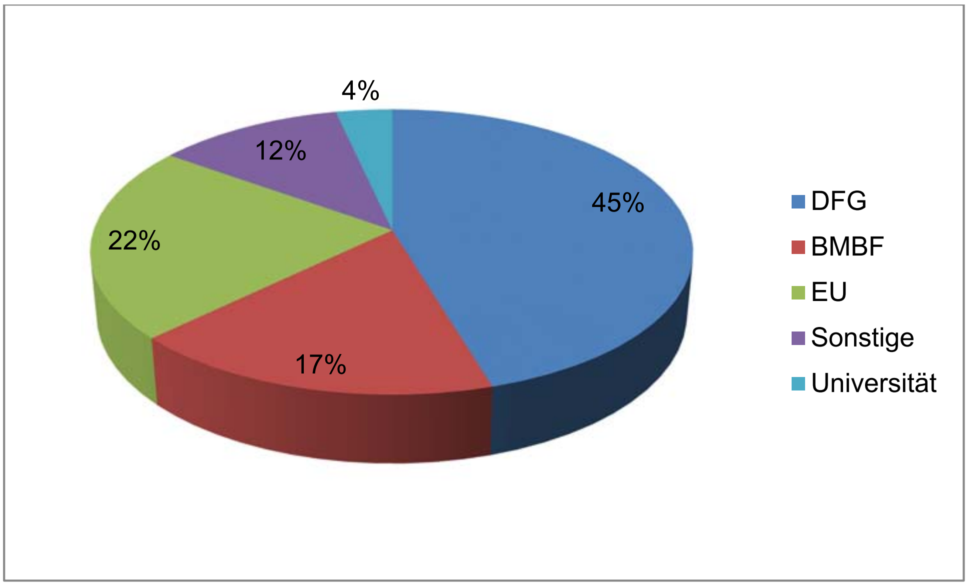


Fig. 1: Percentages participation of the FIT-budget 2019

Tab. 1: Budget from 2016 until today in €

	2016	2017	2018	2019
DFG	874.430	986.267	1.055.197	1.062.597
Land	2.468.606	4.048.018	928.292	0
BMBF	0	69.121	409.381	407.970
EU	202.420	288.415	355.219	518.315
Other	0	62.672	189.235	270.947
University	93.657	75.200	75.200	82.000
Total	3.639.113	5.529.693	3.012.525	2.341.829

Tab. 2: Projects in 2019

Projektleitung	Projekt	Gesamtprojekt	Verausgabt 2019
Behrends	IRTG SoMaS	191.100	59.576
Beichel	Vectorstiftung LIM-Mobil	465.032	94.923
Dincer	DFG miPAT	300.450	82.829
	DFG miRNAs	303.200	10.578
Fischer	DFG SPP 1613	155.200	30.785
	Vectorstiftung AlkaCell	201.644	16.812
	BMBF TEMCat3D	106.334	17.776
Glunz	DFG OPoSiT	142.400	54.468
Goldschmidtböing	DFG Adaptive	157.400	19.138
Krossing	EU ERC UnipHied	265.000	47.578
Lienkamp	BMBF ANTIBUG	1.174.040	324.457
	BMBF BioMAMPs	316.400	65.736
	EU ERC Regenerate	1.498.987	117.705
Masselter	SFB TRR 141 A06	239.300	35.522
Mülhaupt	IRTG SoMaS	239.925	35.247

Projektleitung	Projekt	Gesamtprojekt	Verausgabt 2019
Müller/Becker	DFG Polymerbasierte	165.300	89.220
Rapp	EU ERC CaLa	1.999.750	39.077
Reiter	IRTG SoMaS	3.722.074	110.428
Römer	IRTG SoMaS	93.600	36.318
	DFG Energetische	168.155	8.879
Rühe	IRTG SoMaS	188.000	68.121
	DFG Polymer	211.400	39.758
	DFG PAK	165.800	19.173
	DFG Dynamisches	202.500	11.115
	DFG KOMMA	246.250	3.677
Rühe, Speck, Reiter	EU Marie Curie PlaMatSu	747.649	92.506
Speck, O.	SFB TRR 141 A03	158.900	22.766
Speck, T.	SFB TRR 141 A02	173.000	27.604
	SFB TRR 141 A04	200.900	47.504
	EU ERC GrowBot	696.166	51.375
Vierrath	Vectorstiftung AlkaCell	259.778	31.704
Walter	DFG Kraftbereich	129.300	37.913
	DFG HYBRIDS	159.850	46.151
Walther	DFG Chemo-mechanisch	355.950	23.341
	EU ERC CReaNet	505.577	22.327
	EU ERC TimePROSAMAT	1.499.813	147.747
Woias	DFG NiLax	150.500	51.887

Tab. 3 Budgets of project groups from 2016 until 2019 in €

Projektgruppe	2016	2017	2018	2019
Behrends	20.548	46.054	93.150	59.576
Beichel	0	0	0	94.923
Dincer	0	0	30.727	93.407
Fischer	0	0	71.540	65.373
Glunz	0	18.490	69.746	54.468
Goldschmidtböing	0	0	0	19.138
Krossing	0	0	0	47.578
Lienkamp	202.420	357.536	665.109	507.898
Masselter	67.780	90.000	79.748	35.522
Mülhaupt	745.017	4.054.850	1.044.537	35.247
Müller	0	0	0	82.220
Rapp	0	0	0	39.077
Reiter	136.307	194.042	212.350	110.428
Römer	72.859	100.797	133.308	45.197
Rühe	86.074	93.852	174.286	234.350
Speck, O.	50.992	47.187	53.139	22.766
Speck, T.	158.847	212.547	186.637	126.483
Vierrath	0	0	0	31.703
Walter	38.157	44.047	56.464	84.064
Walther	0	121.500	174.062	284.013
Woias	0	0	0	51.887

HIGHLIGHTS

FUTURE FIELD “ADAPTIVE AND ACTIVE POLYMER MATERIALS”

Polymer ionic liquids based upon Polyisobutylene-*b*-poly(2-ethyl-2-oxazoline) Diblock Co-polymers as thermoresponsive micelles and nanostructured hydrogels

Benjamin Kerscher[1], Tobias M. Trötschler[1,2], Balázs Pásztói[3,4], Saskia Gröer[1,2], Ákos Szabó[3], Béla Iván[3], Rolf Mülhaupt[1,2]

[1]Freiburg Material Research Center (FMF) and Institute for Macromolecular Chemistry, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg; [3]Polymer Chemistry Research Group, Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Budapest; [4]George Hevesy PhD School of Chemistry, Faculty of Science, Eötvös Loránd University, Budapest

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Owing to their expected use in highly diversified applications, the development of functional stimulus-responsive polymer nanosystems is in the focus of current research. Key issues in designing such advanced materials are precise tailoring of polymeric building blocks, incorporation of responsive macromolecules, and sophisticated choice and balance of hydrophilic and hydrophobic segments in order to control functions via nanostructure formation. Obviously, the combination of nonpolar polyisobutylene (PIB) and polar poly(2-oxazoline)s (POXs) represents a highly promising approach for the creation of amphiphilic diblock copolymers which self-assemble to afford thermoresponsive micellar nanostructures. PIB is liquid and characterized by a very low glass transition temperature, the absence of crystallization in conjunction with high thermal and chemical stability, excellent solubility in non-polar solvents, and biocompatibility. POXs with short alkyl substituents, which typically are biocompatible as well, display lower critical solution temperature (LCST) behavior in aqueous solution, i.e. they enable thermal switching between water-soluble and water-insoluble. However, only few examples of PIB-*b*-POX diblock copolymers have been reported [1-4], and neither expected self-assembly into micelles nor possible thermoresponsive properties have been investigated.

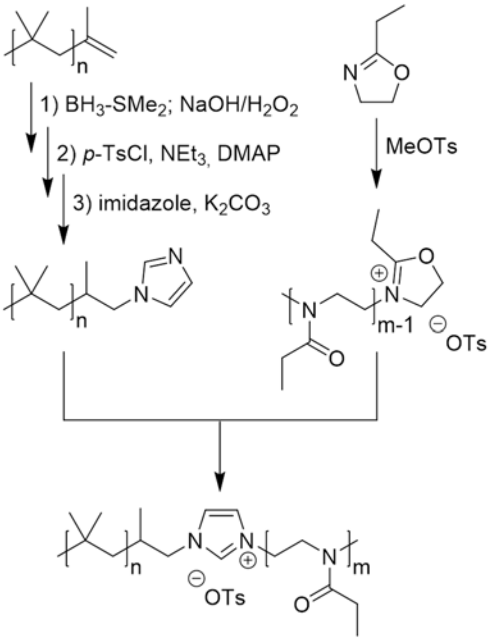

Fig. 1: Synthesis pathway toward amphiphilic PIB-IL-PetOx diblock copolymers. © FMF, University of Freiburg.

Aiming at novel functional and thermoresponsive micellar polymer ionic liquids (PILs), a unique class of PIB-*b*-POX diblock copolymers has been developed at FIT and FMF [5]. In these copolymers the hydrophobic PIB block and a hydrophilic poly(2-ethyl-2-oxazoline) (PEtOx) block are covalently coupled via an imidazolium cation as an ionic liquid (IL) moiety. The straightforward synthetic approach toward the PIB-IL-PEtOx copolymers is illustrated in Fig. 1. Key step is the termination of the cationic ring-opening 2-ethyl-2-oxazoline (EtOx) polymerization with imidazole-functionalized PIB derived from commercial PIB Glissopal®1000 (BASF SE).

By systematic variation of the molar ratio of EtOx monomer and the PIB macro-terminating agent, a series of four PIB$_{23}$-IL-PEtOx$_m$ diblock copolymers with the same PIB chain length (23 isobutylene units) and variable degree of polymerization (DP) of the PEtOx block (m = 10, 20, 30, 40) was synthesized. Highly efficient purification procedures based on either liquid-liquid extraction or hot filtration removed any PEtOx homopolymer impurities and afforded the products in good to excellent yields. As evidenced by ^{1}H NMR spectroscopy, the block lengths were in good accordance with the expected values and SEC analysis unveiled very low dispersities < 1.2, which proves the feasibility of the synthesis route for the precise and highly controlled production of well-defined diblock copolymers. The SEC elugrams of the amphiphilic PILs, nicely illustrating the differences in molar masses owing to the different lengths of the PEtOx segment, are depicted in Fig. 2.

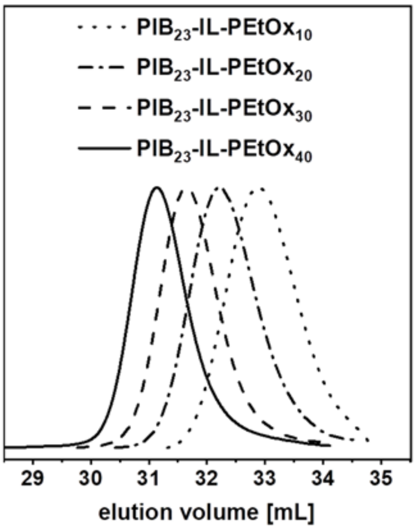

Fig. 2: SEC elugrams of the series of PIB-IL-PEtOx diblock copolymers. Adapted with permission from ref. 5. © 2019 American Chemical Society.

Manipulation of the block length ratio and thus the hydrophilic/hydrophobic balance enables the controlled adjustment of the properties of PIB-IL-PEtOx, in particular solubility behavior both in organic solvents and water as well as nanostructure formation. Notably, PIB$_{23}$-IL-PEtOx$_m$ with a DP of the PEtOx segment of 20, 30 and 40 readily dissolve in water under formation of low-viscosity solutions. In contrast, more hydrophobic PIB$_{23}$-IL-PEtOx$_{10}$ forms hydrogels already at moderate concentrations. Investigation by means of a dye absorption method evidences that all four amphiphilic block copolymers form micellar aggregates in water, as anticipated, with critical micelle concentration (CMC) values in the order of magnitude of 10^{-4} mol/L. However, a closer inspection by means of transmission electron microscopy (TEM) unveils distinct differences in the morphology of the PIL assemblies (Fig. 3). PIB$_{23}$-IL-PEtOx$_{40}$ exclusively forms spherical micelles. Reduction of the PEtOx segment length to a DP of 30 and 20 gradually changes the morphology of the micelles to elongated. In contrast, PIB$_{23}$-IL-PEtOx$_{10}$ self-assembles into ultra-long worm-like micelles, which are capable of entangling and thus account for the emergence of network nanostructures, resulting in the observed hydrogel formation.

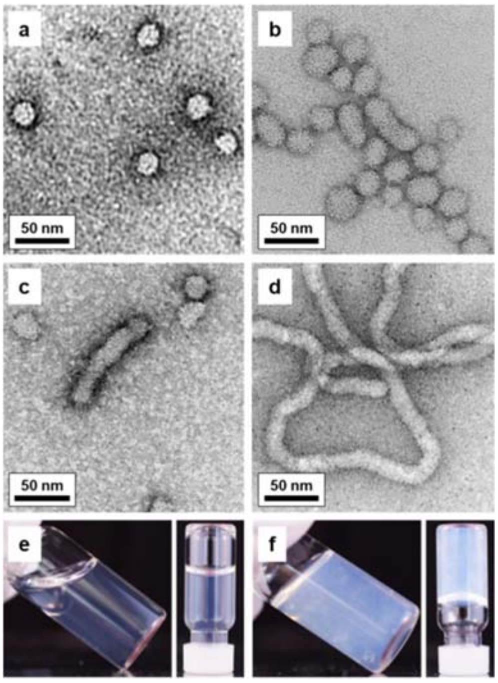

Fig. 3: TEM images of micellar assemblies of PIB-IL-PEtOx copolymers in water: PIB23-IL-PEtOx40 (a), PIB23-IL-PEtOx30 (b), PIB23-IL-PEtOx20 (c), and PIB23-IL-PEtOx10 (d). Photographs of low-viscosity aqueous solution of PIB23-IL-PEtOx30 (e) and PIB23-IL-PEtOx10 hydrogel (f) in tilted and inverted tube. Adapted with permission from ref. 5. © 2019 American Chemical Society.

The highly water-soluble PIB$_{23}$-IL-PEtOx$_m$ copolymers (with m ≥ 20) display thermoresponsive LCST behavior, which enables thermal switching between colloidal solution and polymer dispersion. As illustrated in Fig. 4, heating above the critical solution temperature induces hydrophobization of the PEtOx segment, which results in massive aggregation of the PIL micelles under formation of turbid dispersions. Upon cooling, the original clear solution is obtained. Photometric transmission measurements reveal composition- and concentration-dependent cloud points (T_{CP}) in the range from 72 °C to 90 °C and clearly prove the reversibility of the phase transition. The PIB$_{23}$-IL-PEtOx$_{10}$ hydrogels show thermoresponsive properties as well. By changing the temperature, they can be switched between a macroscopically homogeneous gel and a two-phase system consisting of a polymer phase and a water phase.

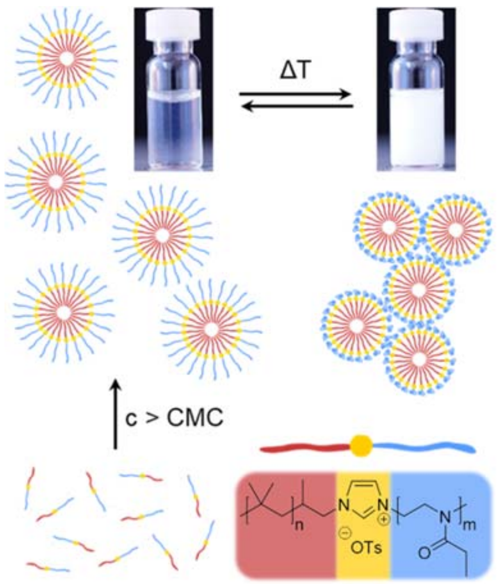

Fig. 4: Schematic illustration of micellar self-assembly of PIB-IL-PEtOx diblock copolymers and temperature-induced hydrophobization/collapse of the PEtOx block resulting in aggregation of the PIL micelles. The photographs show an aqueous solution of PIB$_{23}$-IL-PEtOx$_{40}$ at room temperature (left) and on a heating plate set to 100 °C (right). Adapted with permission from ref. 5. © 2019 American Chemical Society.

First trials underline the potential of both the water-soluble block copolymers and the nanoworm-type hydrogels for use in advanced applications. The water-soluble PILs turned out to function as thermoresponsive solubilization and dispersing agents. Experiments with Sudan Red III not only demonstrate the capability of the PIL micelles for encapsulation and thereby efficient solubilization of hydrophobic molecules in aqueous media but unveil the possibility of temperature-triggered reversible switching between colloidal solution of encapsulated dye and precipitated aggregates of dye-loaded micelles (Fig. 5a). Furthermore, PIB-IL-PEtOx diblock copolymers serve as highly efficient thermorepsonsive dispersing agents for nanomaterials such as functionalized graphene. At temperatures below T_{CP}, the amphiphilic PILs account for the formation of long-term stable aqueous graphene dispersions, which are reversibly transformed into a biphasic water – graphene/polymer/water system by heating above T_{CP} (Fig. 5b). In collaboration with Prof. Rolauffs at the G.E.R.N. Research Center of the Freiburg University Medical Center we exploit nanostructured PIB-IL-PEtOx hydrogels in tissue engineering. In conclusion, a novel family of well-defined amphiphilic PIB-IL-PEtOx diblock copolymers has been tailored as thermoresponsive and functional micellar PIL nanosystems, which hold great prospect to be applied in temperature-controlled reversible transport and separation of molecules and nanomaterials, catalytic processes with facile recovery and reuse of catalysts, and biomedical applications.

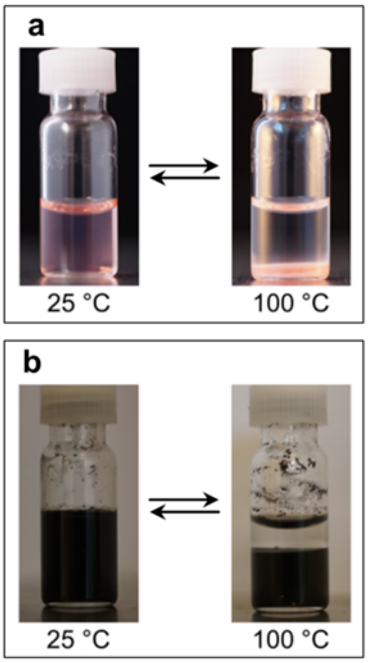

Fig. 5: PIB-IL-PEtOx diblock copolymers as thermoresponsive solubilization and dispersing agents: Thermal switching of aqueous PIB$_{23}$-IL-PEtOx$_{30}$/Sudan Red III colloidal solution (a) and aqueous PIB$_{23}$-IL-PEtOx$_{30}$/graphene dispersion (b). Adapted with permission from ref. 5. © 2019 American Chemical Society.

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New crosslinker-systems for CHic-based wet-strengthening application

Simon Schölch[1,2], Thomas Brandstetter[1,2], Jürgen Rühe[1,2]

[1]Chemistry and Physics of Interfaces, Department of Microsystems Engineering of the University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

Project funding: German Research Foundation (DFG) – PAK 962 – Project A3 “Thermische und photochemische Vernetzung von Papierfasern zur Erzeugung von nassfesten und multifunktionalen Papieren“

Polymer-modification of cellulosic material plays a key role in nearly all application areas for cellulose, including wet-strengthening applications of paper. Modification via CH-insertion reaction through photo- or thermally activated functional groups offers an interesting alternative to commercially available polymer agents[1]. In former work[2] it was shown that cellulose-modification via CH-insertion with benzophenone moieties is an attractive route for the design and modification of paper devices. Our work in the last year tried to extend the spectrum of functional monomers which can be used for this modification process and which can be activated thermally or more efficiently at longer wavelength compared to the so far used benzophenones. Additionally we are very much interested in a better understanding about the whole modification process itself, concerning questions like polymer distribution inside the paper and the dependency of the modification process on copolymer properties like crosslinker content or molecular weight.

Two new functional comonomers have been applied successfully for the modification of paper. A diazomalonic ester monomer[3] (MAz, Fig. 1) was synthesized and copolymerized with *N,N*-dimethylacrylamide and a fluorescence marker for analytical purposes to demonstrate successful attachment via fluorescence microscopy.

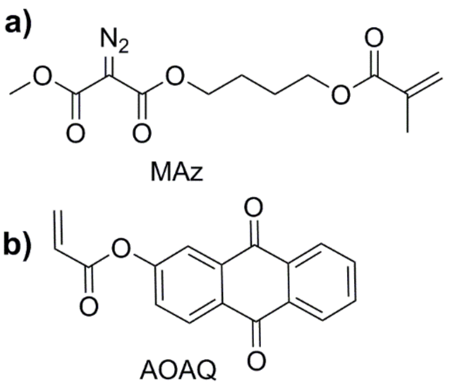

Fig. 1: Chemical structures of a) Diazomalonic ester monomer (MAz) and b) Acryloxyantraquinone (AOAQ). © chair Rühe

Comparing fluorescence intensity before and after washing the samples provides information of how much polymer is bound throughout the crosslinking process. In Fig. 2 it can be seen that polymer attachment to the cellulose fibers is efficient from 150°C upward.

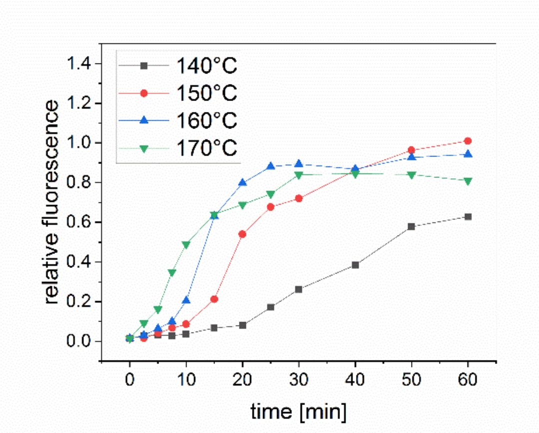

Fig. 2: Relative fluorescence (fluorescence after washing / fluorescence before washing) of PDMAA-5%MAz-RhoB copolymer which was crosslinked in the oven at different temperatures. © chair Rühe

Analogue experiments carried out with an anthraquinone-containing monomer (AOAQ, Fig. 1) as crosslinker demonstrate its viability for use in paper-modification processes as well. As the CH-insertion reaction at 365 nm is very efficient for Antraquinones, the required energy dose can be significantly lower compared to so far applied crosslinkers. It is important to mention, that the molecular weight of the copolymer used in this experiment was very low (M_n = 10 k). As soon as higher molecular weights can be achieved for the copolymers, this class of crosslinker is very promising for a fast polymer attachment to the cellulose fibers in paper substrates at 365 nm.

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Polymer modification by CHic reactions to reduce sensitivity loss in paper-based analytical devices

Anna Luongo[1,2], Alexander von Stockert[3], Thomas Brandstetter[1,2], Markus Biesalski[3], Jürgen Rühe[1,2]

[1]Chemistry and Physics of Interfaces, Department of Microsystems Engineering of the University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [3]Ernst-Berl-Institute for Technical and Macromolecular Chemistry of the Technical University of Darmstadt

Project funding: German Research Foundation (DFG) - “Polymer-modifizierte Papiere - Vermeidung von Sensitivitätsverlusten in papierbasierten analytischen Verfahren“

The fibrous structure of paper allows for the transport of aqueous solutions through capillary action. Thus, paper makes the generation of microfluidic devices possible, which do not require any pumps for fluid movement. However, despite huge efforts, as of today only rather simple diagnostic devices based on paper strips have been realized. A main reason for this is that for paper-based diagnostics even today many fundamental problems remain unsolved and strong losses of the sensitivity are observed when standard immunodiagnostic processes are transferred to paper-based devices. These sensitivity losses are mainly caused by light scattering during optical detection and unspecific adsorption of analytes to the highly polar paper fibers. The last year, the project focused on modification of paper fibers with polymers, which are covalently attached to the fiber surface by C,H-insertion reactions, with the aim of obtaining an (almost) isorefractive material, where light scattering is strongly attenuated and sensor sensitivity is enhanced compared to read-out of standard paper-based analytical processes.

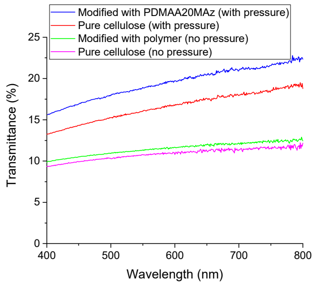

Fig. 1: Transmittance in visible light wavelengths region of pure cellulose and modified cellulose with PDMAA20MAz (without mechanical loading) and pure cellulose and modified cellulose with PDMAA20MAz (with mechanical loading). All results are in wet state. © chair Rühe

Multi-layers of PDMAA-*co*-MAz, copolymer of *N,N*-dimethylacrylamide and diazomalonic ester[1], have been applied successfully for the modification of paper, through dip coating and UV crosslinking processes preceded by mechanical loading of pure cellulose, in order to reduce the amount of air inside, since the refractive index of air is far from the refractive index of cellulose (air has n~1, cellulose and PDMAA have n~1.47). Therefore, the choice of the hydrogel has been led by the search for the best refractive index matching between cellulose and copolymer.[2] Besides, we are interested in the study of the wet state, since the final application is the analysis of analytes transported through the capillaries of the cellulose. In this first approach it has been chosen to focus on *transmittance*, with the aim of optimizing transparency and therefore the amount of visible light able to pass through the sample. In Fig. 1 it can be seen that the modification of cellulose with a copolymer doesn't show a real improvement in the transmittance. However, it can be seen that the mechanical loading, and more precisely a sample pressure, leads to a real improvement in the transmittance of pure cellulose and even higher of cellulose coated with copolymer.

A different approach has been applied successfully for the modification of paper too. Primarily, the cellulose has been modified with the same copolymer used in the previous experiments (PDMAA-*co*-MAz) by dip coating process, to provide it mechanical strength for the further step, and successively the sample has been coated with very high polymer concentration (300 mg/ml) by drop coating process. With this method, a greater amount of polymer inside the cellulose is obtained, leading towards isorefractivity and therefore to higher transparency. In Fig. 2, it can be seen that, with this new approach too, higher transmittance value than pure cellulose is obtained, in both dry and wet states.

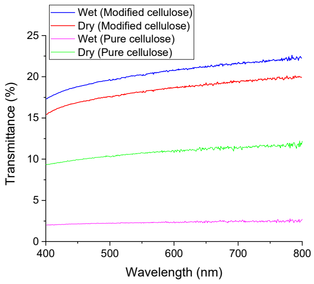

Fig. 2: Transmittance in visible light wavelengths region of pure cellulose and modified cellulose with very high concentration polymer solution, in wet and dry state. © chair Rühe

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Lubrication Mechanism of Surface-attached hydrogels

Maryam Bahrami[1,2,3,] Vincent Le Houérou[3,4,] Jürgen Rühe[1,2]

[1]Laboratory for Chemistry and Physics of Interfaces, Department of Microsystems Engineering, University of Freiburg, Georges Koehler Allee 103, 79110 Freiburg, Germany; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges Koehler Allee 105, 79110 Freiburg, Germany; [3]Institut Charles Sadron - CNRS UPR 022, University of Strasbourg, 23 Rue du Loess, 67034 Strasbourg, France; [4]ICube, University of Strasbourg, CNRS UMR 7357, 300 boulevard Sébastien Brant, 67412 Illkirch cedex, Strasbourg, France

Project funding: IRTG “Soft Matter Science” – Project A06

In this project, we are inspired by the lubrication occurring in synovial joints. Synovial joints exhibit low friction under varying load conditions and can undergo millions of loading cycles without wear and failure [1,2]. The spectacular frictional properties are due to an interplay between the cartilage and the synovial fluid. Articular cartilage, although complicated in its structure, is a biphasic material made of a soft matrix and interstitial fluid (mainly composed of water). In joints, both countersurfaces (i.e., bones) sliding against each other are covered by cartilage, which is a soft cushion-like tissue [2–4].

Previous studies on lubrication of surfaces bearing charged brushes show that these surfaces can provide extremely low friction [5]; however, charged brushes are susceptible to fragmentation of the chains through “entropic death” [6,7], so that they can be detached from the substrate [4]. Additionally, thicknesses of brushes are rather small compared to the size of typical roughness features which results in limitations in the application of brushes as lubricants.

Hydrogels are composed of a flexible polymer matrix and a high percentage of water which is very similar to articular cartilage. In many studies, it has been shown that swollen hydrogels with high water content can result in well lubricated surfaces. In spite of the many studies on the tribology of hydrogels, the lubrication mechanism is not currently fully understood. The lubrication of hydrogels cannot be explained by the conventional Stribeck curve [8] due to their biphasic nature [9]. Influence of load and sliding speed has been investigated extensively, although leading to considerable discrepancy [10–12]

One of the resources for such inconsistency is that most of the previous studies have been done between a hydrogel sample and a solid impermeable slider [9,13–17]. In such a case, the interaction between the two opposing surfaces and chain entanglement between subchains of the swollen polymer networks should play a significant role. Therefore, it is expected that the friction behavior of two identical hydrogel surfaces sliding against each other will differ from that of a solid slider sliding on a swollen gel. In more recent cases, friction systems have been studied, where the surfaces sliding against each other are both covered with hydrogels [8,18–21]. It has been shown that friction is significantly lower when identical permeable counter-surfaces are in contact [18].

Furthermore, the frictional properties of free hydrogels cannot be compared with the constrained surface-attached ones. One of the difficulties associated with soft hydrogels is their handling and stability. These problems can be eliminated by covalent bonding of the gel to a stiff substrate. This can prevent delamination of the strongly swollen layers, especially during compression and shearing. The difference between the bulk hydrogel and surface-attached ones arises from the difference in their swelling behavior [22]. Similar to brushes, surface-attached layers can extend only in a direction (i.e., away from the surface) normal to the substrate. Stretching away from the surfaces influences different properties of the polymer networks such as swelling behavior, mechanical properties, and to whether they can be penetrated by large molecules in a contacting environment [18]. Strong configurational entropy effect prevents the interpenetration of the chains of two contacting hydrogel surfaces. Frictional properties of such layers need further investigations specifically under strong compression as the layers show extensive deswelling and the transport of water within the network during the deswelling/swelling processes plays important role in lubrication of such a system.

In this project, we examine different properties of surface-attached hydrogels that can influence frictional properties such as elasticity, permeability and adhesion. Moreover, the friction properties of two hydrogel coated surfaces immersed in water are investigated. The lubrication mechanism of surface-attached hydrogel pairs is explained in terms of the forces contributing to friction.

According to our experimental results, the friction reduces by increasing the sliding speed, then, it reaches a minimum value and rises after the minimum. In our previous report, different components of the friction force have been discussed. The friction force consists of components due to elastic stresses and fluid pressure. It was also shown that compared to the friction force, the adhesion is negligible between the surface-attached hydrogel pairs. Thus, the main forces are the forces due to the deformation of the polymer network and the water that has to be displaced.

The lubrication mechanism can be explained in light of these two forces. When the sliding is slow, or the permeability is high, or the sample thickness is small, the water in the network can be displaced easily, so there is not a significant resistance of water against sliding. Therefore, the main force at low sliding speed is the polymer deformation. Polymer deformation force depends on the penetration depth and apparent elastic modulus. As the sliding speed increases, the penetration depth becomes smaller and after a specific sliding speed, it does not change considerably. This reduction in penetration depth leads to smaller friction force (Fig. 1) and thus smaller coefficient of friction. Penetration depth and thickness of the sample directly affect the contact stiffness or effective elastic modulus of the system. As it was evidenced by our elastic modulus measurements, the contact becomes progressively stiffer as the penetration depth to thickness ratio gets larger. Drag force starts to add up to the polymer deformation force as the slider slides faster than the relaxation time of the compressed zone. So the water cannot squeeze out of the network completely. The remaining water in the network imposes a resistance against sliding which results in a higher friction force at higher sliding speed

(Fig. 1). In this regime, presumably, there is no water layer separating the two countersurfaces completely like in hydrodynamic lubrication. Instead, water exists in the interfaces as the hydrogel itself has water inside the network (including the interface) which has not yet squeezed out. This results in a similar effect as hydrodynamic lubrication, although COF does not follow exactly the same power as in hydrodynamic lubrication [8].

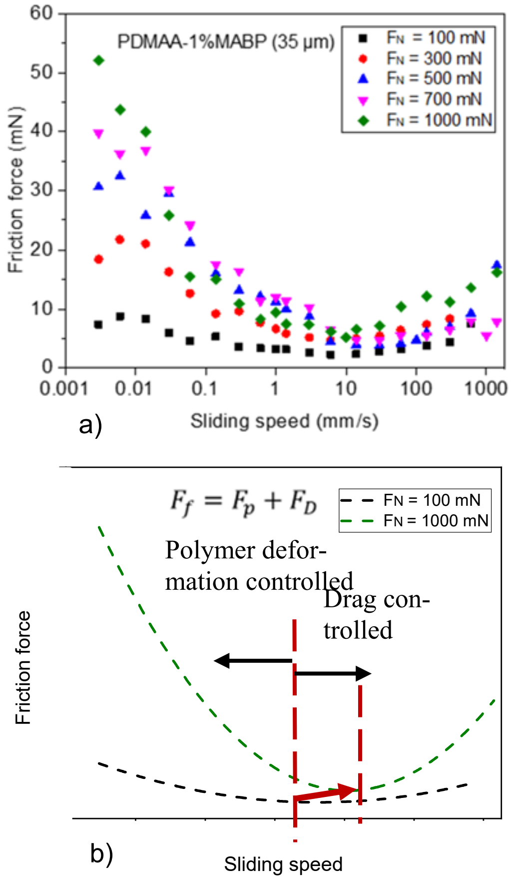

Fig. 1: a) Friction force obtained from scratch tests at different sliding speeds b) Different lubrication regimes controlled by the two main forces (Polymer deformation force and Drag force). The red arrow shows the shift in minimum by changing the normal load. © CPI, IMTEK Univ. of Freiburg

The lubrication of surface-attached hydrogels occurs in two main regimes that we called polymer deformation controlled regime and drag controlled regime. These two regimes are illustrated in **Fehler! Verweisquelle konnte nicht gefunden werden.**b. The minimum is shifted as the applied force is increased. The minimum happens at different sliding speeds depending on the permeability and confinement of the system.

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Dynamic behavior of water droplets on flexible, adaptive and switchable surfaces generated using surface attached polymer networks and brushes

Anil Kumar Rajak[1], Jürgen Rühe[1]

[1]Chemistry and Physics of Interfaces (CPI)
Freiburg

Project funding: Deutsche Forschungsgemeinschaft (DFG)

Light responsive surfaces are of great interest for multiple applications from microfluidics to sensors [1,2]. Spiropyran and azobenzene molecules can be used as photochromic groups to generate reversibly switchable surfaces [3,4]. The illumination on such surfaces with light in the UV and the visible range changes the polarity of the surface and, hence, the wettability also changes. However, flat surfaces do not show big changes in the contact angle (CA) before and after illumination and remain within the range of 10-15° [5,6]. This CA difference can be increased by introducing rough surfaces with the combination of photochromic groups [7]. Figure 1 shows dynamic contact angles and roll off angles of water on silicon nanograss with such coating upon illumination. It is an indication of wetting transition between Wenzel wetting and Cassie-Bexter wetting.

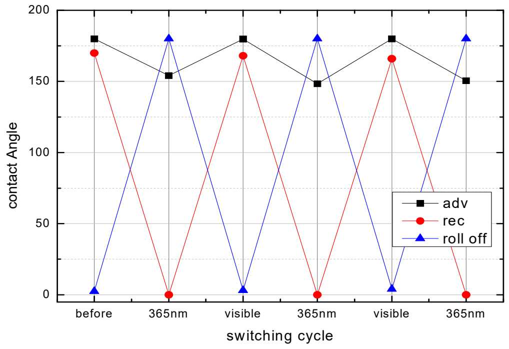


Fig. 1: Dynamic contact angles on nanograss coated with photoisomerizable azobenzene groups [7]. © CPI, IMTEK Univ. of Freiburg.

Additionally, these wetting transitions can be controlled by controlling the amount of photoisomerizable moieties on the surface. Groten et al. [7] have shown that by controlling the azobenzene groups on the surfaces, the three wetting transition states can be achieved. Figure 2 shows the dynamic contact angles measured on silicon nanograss as a function of the angles measured on flat silicon surface for different coatings.

The aim of this project is to realize surfaces with such light responsive wetting properties. The nanostructured surfaces will be generated and will be decorated with photoisomerizable groups, which will allow to reversibly change the surface polarity of the coated substrate through irradiation of light with an appropriate wavelength. The variation in the surface chemistry will be achieved by coupling thin conformal surface-attached polymer networks to the nanoscale structures. The conformal coating of the nano-sized features will be achieved by the immobilization and crosslinking of polymer layers through the CHic process (C,H-insertion crosslinking).

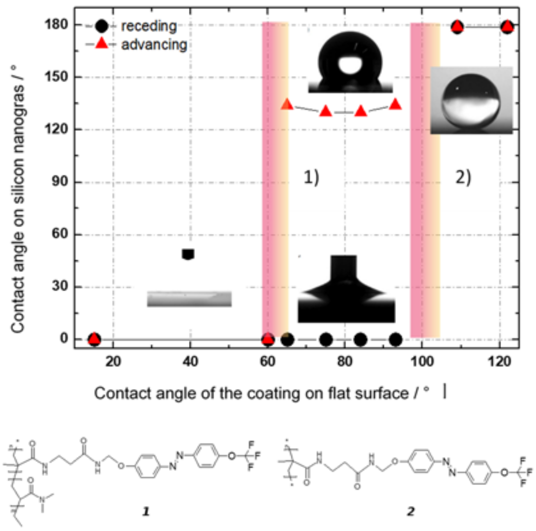
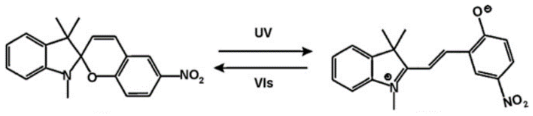


Fig. 2: Dynamic contact angles on coated silicon nanograss as a function of contact angles on coated flat silicon surface. The polymers used for coatings are given below [7]. © CPI, IMTEK Univ. of Freiburg

Using polymers instead of the commonly used self-assembled monolayers has the advantage that the system can be precisely tuned by generating copolymers of a desired composition and then immobilizing them. So far, the polymers containing azobenzene groups were used, which contained both hydrophilic groups and fluorinated groups to shift the value of the surface energy of the coating exactly to the surface energy of the wetting transition.



1 2

Fig. 3: Structures of Spiropyran form 1 and merocyanin form 2. © CPI, IMTEK Univ. of Freiburg

In the proposed project a different system for the isomerization, the well-known spiropyran – merocyanin system will be investigated. It can be expected that the system will exhibit a stronger change in the polarity compared to the azobenzene counterparts as in the spiropyran form 1 it is a rather non-polar compound, whereas the merocyanin 2 form is zwitterionic in nature (Figure 3).

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Progress in Self-Shedding Polymer Surfaces

Esther K. Riga,[1] and Karen Lienkamp[1]

[1] Bioactive Polymer Synthesis and Surface Engineering Group, Department of Microsystems Engineering (IMTEK) and Freiburg Centre for Interactive Materials and Bioinspired Technologies (FIT)

Project funding: European Research Council (ERC) Starting Grant, Project Acronym: REGENERATE

As reported previously,[1] the aim of the REGENERATE project is to make functional materials consisting of polymer multilayer stacks that can (self-)regenerate their top functional layer by shedding, for example when that layer becomes damaged or contaminated. The key solution strategy to achieve this is to break the adhesive forces between these layers and thus enable their dissociation.

In technical systems consisting of a polymer coating on a hard substrate (e.g. a metal or a rigid piece of plastic), layer shedding or delamination is a well-known phenomenon and is rather fought than sought. In such systems, layer shedding is typically the result of mechanical stresses at the interface between the polymer coating and the substrate. This explains why layer shedding is much more difficult to achieve at the interface of two rather soft polymer layers: they are much more compliant to mechanical deformation, which prevents build-up of stresses at their interface.

Therefore, the multi-stacks used in this project contain separation layers (or sacrificial layers) between the actual functional layers. Removing these sacrificial layers is thus turning the event of layer shedding into a case of “cohesive failure” rather than “adhesive failure”. So far, we have investigated three mechanisms to induce cohesive failure of the sacrificial layers: hydrolysis,[2] depolymerization,[3] and dissolution.[3] Notably, we found that the shedding process depends substantially on the disintegration kinetics of the sacrificial layers. This means that the mass loss of the sacrificial layer has to proceed at a certain rate. If the mass loss rate is sufficient, enough medium can enter the forming gap between the top functional layer and the next one. If the mass loss is too slow, the top functional layer will close that forming void and re-attached to the next functional layer, so that shedding is prevented.

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Antimicrobial Copolymers Made From Itaconic Acid

Alexandra Schneider-Chaabane[1,2] and
Karen Lienkamp[1,2]

[1] Polymer Synthesis and Surface Engineering Group, Department of Microsystems Engineering (IMTEK), University of Freiburg; [2] Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg

Project funding: Federal Ministry of Education and Research (BMBF), "Materialinnovationen für gesundes Leben: ProMatLeben – Polymere", Project BioSMAMPs

The aim of the BioSMAMPs project is to develop synthetic mimics of antimicrobial peptides (SMAMPs) based on the building block itaconic acid, which can be obtained from renewable resources. These BioSMAMPs would then be available as an alternative to traditional antibiotics, both as drugs with low resistance formation potential, and as antimicrobial surface coating. The key point in the design of SMAMPs is that they need to maintain facial amphiphilicity, i.e. a locally balanced distribution of hydrophobic and cationic groups along the polymer chain. This design feature is also found in their natural archetype, antimicrobial peptides (AMPs), which are the first line of defense against microbial pathogens in most organisms. Additionally, the BioSMAMPs project aims at developing polymer structures that are optimized for stability under conditions of use, so they could eventually become parts of real-life products.

Itaconic acid is on the one hand an ideal starting material for SMAMPs because it can carry two functional groups. This allows attaching one hydrophobic group and one cationic group to each itaconic acid unit, which enables the desired amphiphilic balance. On the other hand, itaconic acid and its derivatives are notorious for their poor homopolymerization performance. This is why BioSMAMPs also contain other comonomers an addition to the itaconic acid-based ones. In this context, much effort was put into understanding the kinetics of these polymerizations, and optimizing the reaction parameters. Thus we determined the copolymerization parameters of the reversible addition fragmentation chain transfer polymerization (RAFT) for the model system 1-((N-tertbutoxycarbonyl)-2-aminoethyl)-4-propyl diitaconate (PrIA) and N,N-dimethylacrylamide (DMAA), which were r_{DMAA} = 0.49 and r_{PrIA} = 0.17, compared to r_{DMAA} = 0.52 and r_{PrIA} = 0.54 obtained by free radical copolymerization (FRP).[1] It seems that the RAFT process leads to a larger fraction of alternating repeat units than the FRP process. The polydispersity index (PDI) of the RAFT copolymers was 1.2-1.8, compared to 2.8-2.9 for the FRP copolymers. Obtaining lower PDIs is critical for the applications of BioSMAMPs as drugs, as their bioactivity is strongly molecular weight dependent and as such not only affected by the number average molecular weight of a polymer batch, but also its PDI. After activation with HCl (Figure 1), the thus obtained BioSMAMPs had an increasing activity against *Escherichia coli* and *Staphylococcus aureus* with increasing molar mass. Due to their lower PDI, the RAFT copolymers were less toxic than comparable FRP polymers.

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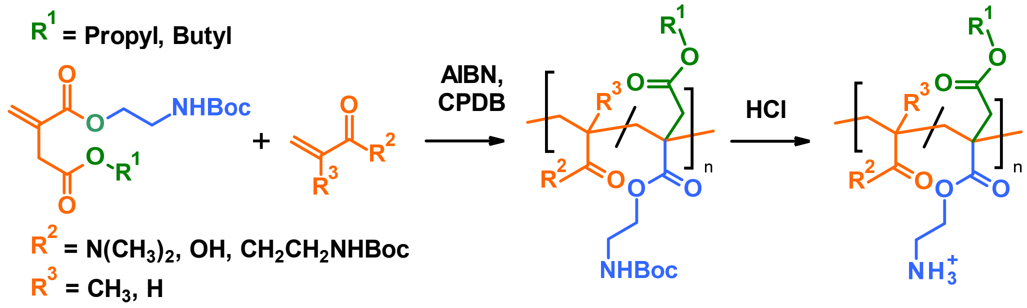

Fig. 1: Synthesis of antimicrobially active BioSMAMPs. The asymmetrically substituted 1-(N-Boc-2-aminoethyl)-4-propyl or butyl diitaconate was copolymerized with a comonomer (N,N-dimethylacrylamide (DMAA), acrylic acid (AA), or N-Boc-2-aminoethyl methacrylate (AEMA)) by RAFT polymerization using the initiator azobisisobutyronitrile (AIBN) and the RAFT agent 2-cyano-2-propyl benzodithioat (CPDB). To remove the Boc protective group and obtain the activated BioSMAMP, the polymers were treated with HCl in dioxane. Image from [1], Copyright: Creative Commons Attribution License (CC BY).

Synthesis of novel crosslinker molecules for polymer network building through C,H-insertion based crosslinking (CHic)

Patrick Huber, Dennis Rusitov, Jürgen Rühe

Chemistry and Physics of Interfaces, Department of Microsystems Engineering, University of Freiburg, Georges Koehler Allee 103, 79110 Freiburg, Germany

Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany’s Excellence Strategy – EXC-2193/1 – 390951807.

Surface-attached polymer networks are an effective method to modify surface properties. Network layers are formed either during the polymerization process by using bifunctional monomers or through incorporating dormant crosslinker molecules, which enable the crosslinking after polymer deposition on demand through an external stimulus [1-6]. In the past we have developed crosslinker systems that allow photochemical (benzophenone or anthraquinone, Fig. 1a) or thermal and photochemical (diazo-compounds, Fig. 1b)) activation in prepolymers. The crosslinking reaction occurs in all cases through a C-H insertion based crosslinking reaction (CHic). This approach has the advantage over other methods that the crosslinking agent only needs a C-H-group in its to form a crosslink. The mechanisms typically proceed via radicals, carbenes of nitrenes which abstract a hydrogen from the reaction partner followed be recombination reactions as shown for several examples in Figure 1 [6-10].

These general structures can be tuned on a molecular level to a adjust activation parameters such as wavelength or temperature. The anthraquinones for example can be used for two-photon crosslinking (2PC) to manufacture free standing microstructures. The resolution of these microstructures depends on the two-photon absorption, which was adjusted through the molecular structure of the anthraquinone. For the diazo-compounds used in our studies, the molecular structure mainly influences the thermal stability and hence the crosslinking temperature. Therefore, our goal is to modify and synthesize novel crosslinker molecules and characterize their crosslinking behavior [11-14].

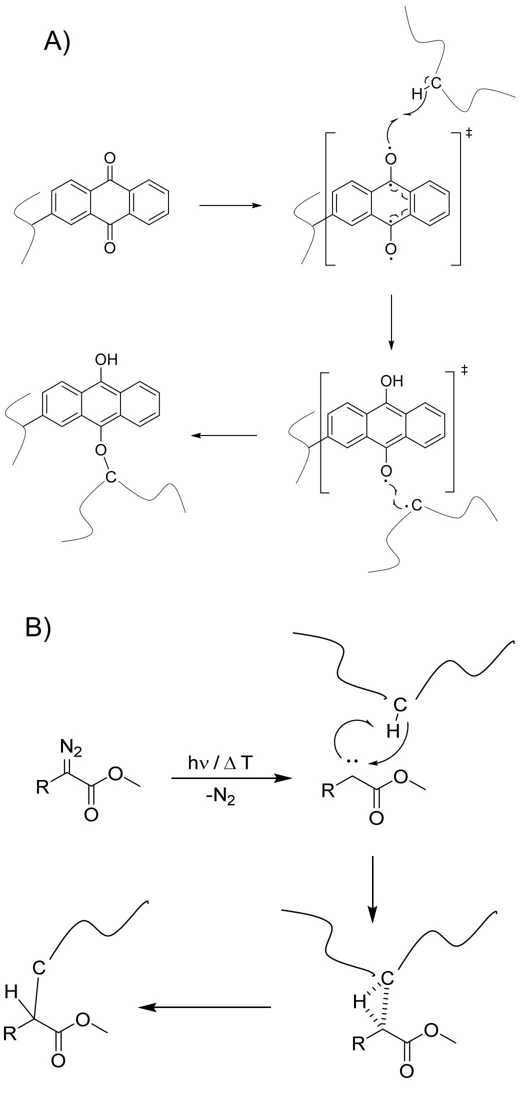

Fig. 3: Mechanism of the CHic-reaction. A) Photochemical crosslinking of an anthraquinone via a bi-radical transition state. B) Photochemical or thermal crosslinking of a diazo.compound in a concerted reaction. © CPI, IMTEK Univ. of Freiburg.

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Autonomous light-responsive LCE actuators

Paula Straub[1,2], Jürgen Rühe[1,2]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [2]Laboratory for Chemistry and Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg

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This project focuses on the improvement of liquid crystalline elastomers from a chemical point of view as well as on the incorporation of the elastomeric material into microelectromechanical systems (MEMS). The research is conducted by a collaborating team of chemists and engineers from IMTEK and is part of the *liv*MatS cluster of excellence.

Liquid crystalline elastomers (LCEs) are often referred to as artificial muscles as they respond to external stimuli with a strong anisotropic deformation [1]. The fundamental principle is that there is a reversible order-disorder-transition from the nematic (= ordered) to the isotropic (= disordered) state which can be induced using external triggers, as depicted schematically in Fig. 1. Possible triggers include for example temperature, pH or light.

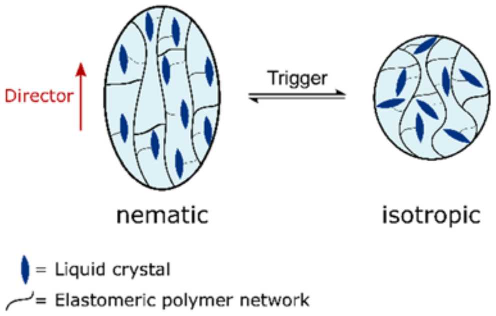

Fig. 1: Schematic representation of an LCE. The order-disorder transition from the nematic to the isotropic state can be triggered, e.g. by temperature or light, and leads to a contraction of the LCE. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg

Light is a particularly favorable trigger as it is non-invasive and easy to control. Light-responsive LCEs have gained much attention recently. Azobenzene (AB) as a photostable compound is frequently incorporated into the LCE. The photoisomerization of AB (Fig. 2a, left) from the thermodynamically more stable *trans* to the *cis* state induces the order-disorder transition. However, AB faces many challenges such as low photostationary states (PSS) of only about 80% [2] and short thermal half-lives of the *cis*-isomer [3]. For LCEs this means that the disordered material does not retain its shape permanently but slowly undergoes a thermal relaxation towards its original shape containing the *trans*-isomer [4].

To address the above mentioned challenges we investigate arylazopyrazoles (AAPs, Fig. 2b) as molecular switches. AAPs have photostationary states with higher percentages and faster switching kinetics compared to their azobenzene analogues [3]. This is, in part, due to a larger separation in the absorption bands, as the UV/Vis spectra in Fig. 2a and b demonstrate. We synthesize AAPs which are similar in molecular structure to common AB-based liquid crystals and incorporate them into liquid crystalline polymers. In order to monitor improvements we study energy consumption and shape retention of the light responsive liquid crystalline elastomers.

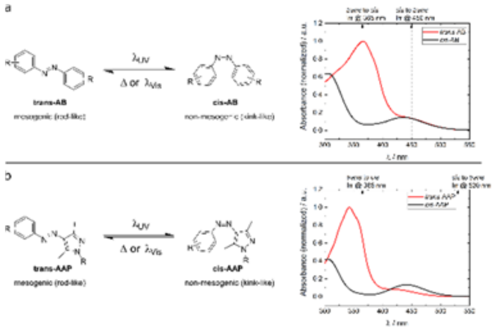

Fig. 2: Photoisomerization and corresponding UV/Vis spectra of different azo-compounds. a) AB. The spectra show a strong overlap in absorption between 420-500 nm, leading to lower PSS. b) AAP. The spectra show the separation of the absorption bands which allows for more efficient photoswitching.. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg.

Another aspect of generating photoactuators is the crosslinking of liquid crystalline polymers. Hence, we investigate the incorporation of CHic-able units into the polymer chain. The CHic reaction (C,H-insertion based crosslinking) [5] is a facile way of network formation when starting from a pre-polymer. By simply copolymerizing CHic monomers, for example benzophenone derivatives as shown in Fig. 3a, with the desired matrix polymer we obtain clean pre-polymers which can then be processed and crosslinked without any additives and hence without laborious post-processing purification steps.

We successfully copolymerize benzophenone derivatives with a frequently used thermo-responsive LCE monomer, namely 4-ADBB (molecular structure shown in Fig. 3a). We then align the liquid crystalline copolymer using common techniques and induce network formation through activation with light. The alignment is not disturbed by the crosslinking process as Fig. 3b demonstrates. Furthermore, the transition temperatures of the copolymer are comparable to those of the homopolymer [6].

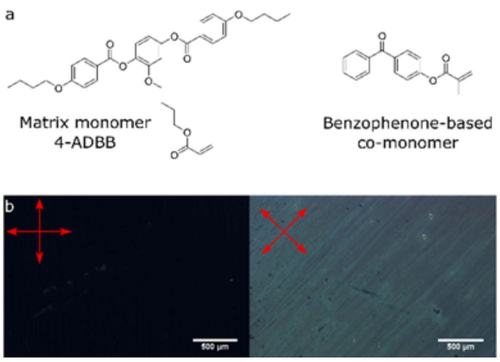

Fig. 3: Molecular structure of the monomers and POM images of aligned LCE. a) Molecular structure of the matrix monomer 4-ADBB and the comonomer based on benzophenone. The benzophenone moiety allows crosslinking in the aligned state in the polymer. b) POM images of the copolymer aligned via a rubbed PVA layer. Left: 0°, Right: 45°. The contrast between the two images demonstrates that the alignment of the pre-polymer is successful and unharmed by the crosslinking process. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg.

One large advantage of the use of our pre-polymer is that it allows for a more flexible fabrication process. Rather than producing only thin films on wafer level, our polymer can be brought into virtually any shape through polymer processing and then crosslinked. We currently investigate 3D printing of these polymers.

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Ordering of PEO-PLLA Block Copolymer at the Air-Water Interface

E. Khechine[1,2], R. Reiter[1,2] & G. Reiter[1,2,3]

[1]Experimental Polymer Physics, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bio-inspired Technologies (FIT); [3]Freiburg Materials Research Center (FMF)

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Amphiphilic block copolymers have achieved great scientific interest due to their capacity to form well defined structures. The possibility to tune properties of these molecules as for example the hydrophobic-hydrophilic balance, the differences in steric requirements of the building blocks or differences in their crystallization behavior offers a unique playground to tailor structure formation processes. Here we focus on their ability to form monolayers at the air/water interface [1] and investigate the structure formation in confined geometry. Langmuir studies on amphiphilic di-block copolymer have shown that several systems organize into surface patterns at the air-water interface [2]. However, the basic laws of 2D pattern formation are still not well understood compared to the 3D block copolymer morphologies [3]. This study focuses on the investigation of morphologies of Langmuir films of the di-block co-polymer system of PEO-PLLA.

For our study, we chose a block copolymer (BCP) with a low molecular weight of 3690 g/mol. The total length of the BCP, if a helical crystalline morphology for both blocks is assumed, is around 20 nm. The molecular weights of both blocks are balanced. However, the extended length of the helical PLLA block is around 7 nm while the corresponding length of the PEO block is around 13 nm [4], [5].

An important step in the characterization of a Langmuir monolayer is the measurement of the isotherm. Such a measurement records the surface pressure as a function of the mean surface area occupied per molecule during the compression with a constant rate and a constant temperature.

Figure 1 shows the surface pressure-area isotherm of a Langmuir film of PEO-PLLA (BCP) (red curve) and the surface pressure-area isotherm of a Langmuir film of a PLLA homopolymer (black curve) as a reference. For the BCP, the surface pressure gradually increased upon compression already at relatively low surface densities. This behavior of the monolayer is called expanded type. A region of decreasing surface pressure with decreasing area per molecule, a so-called depression, appeared at values around 300 – 350 Å^2 /molecule. Upon further compression the surface pressure increased steeply reaching higher values. The PLLA isotherm showed rather a condensed monolayer type characterized by the presence of a pseudo plateau at small areas starting from 320 Å²/molecule. The changes in the slopes of the isotherms are indicative for phase transitions. However they are difficult to identify from the isotherms and therefore the derivative of the Π-A curves with respect to A have been determined according to reference [6]. These curves show the static elastic modulus E_s as a function of A. Compared to the small inflections observed in Π-A isotherms, the peaks in elastic modulus - area (E_s-A) curves are easily detected. Indeed, an (E_s-A) curve is another form to express the changes of the surface pressure during the compression and can be regarded as a 2D analogue of the 3D bulk compression modulus. As shown in figure 1, the BCP has a maximum of the elastic modulus at an area of 500 Å²/molecule. The homopolymer has a maximum at 426 Å²/molecule. Those maxima are indicative of a maximum molecular packing and the corresponding areas per molecule are compatible with models of crystallized PLLA.

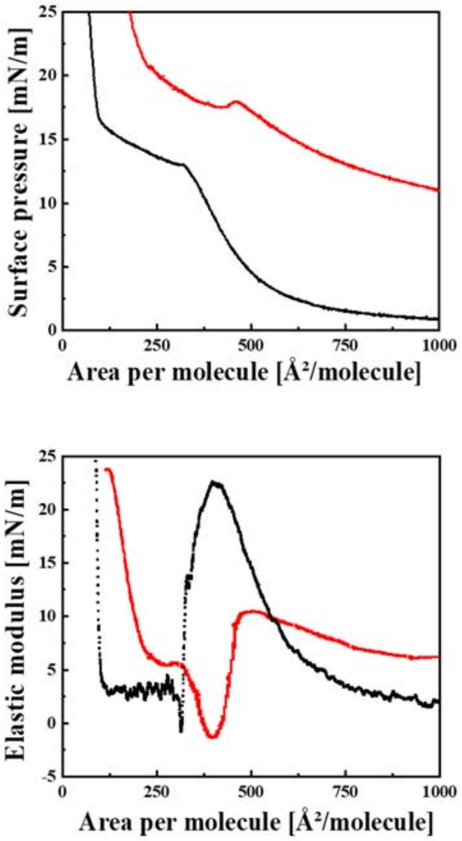

Fig. 1: Isotherms of PEO-PLLA block copolymer (red curve) and PLLA homopolymer (black curve) at the air/water interface, compressed at a constant temperature of 20°C and their corresponding elastic modulus. © Experimental Polymer Physics, Freiburg

Previous studies of a PLLA homopolymer by Das et al. [7] have shown the formation of a 2D matrix coexisting with nanoscopic aggregates when films were transferred at the area corresponding to the maximum of elastic modulus. In our study, we wanted to see the effect of the addition of a hydrophilic PEO block on the structure formation of PLLA.

Here we report on two experimental routs to form monolayers of the PEO-PLLA block copolymer.

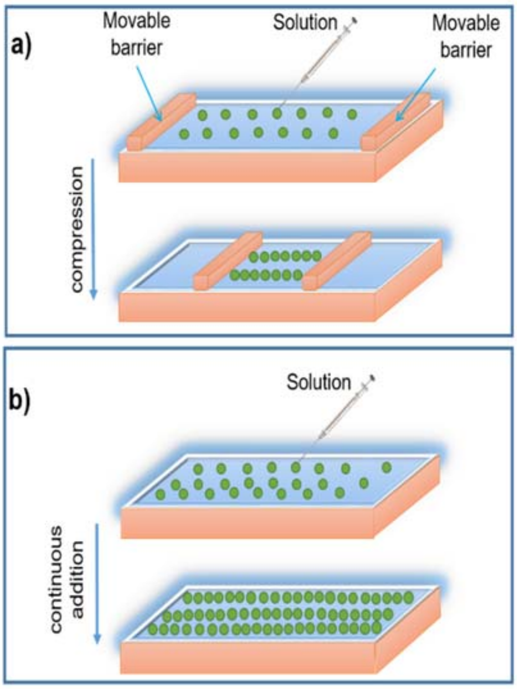

Fig. 2: a) The film was compressed at a constant rate of compression to obtain the surface density of interest. b) The trough area was kept constant and the final surface concentration was achieved by continuous dropwise additions of the volume of the spreading solution corresponding to the surface pressure of interest. © Experimental Polymer Physics, Freiburg

In the first experiment, we spread the block copolymer solution on the water surface, waited for 30 minutes until the solvent evaporated and then we compressed the film by means of two movable barriers. We stopped the compression when we reached the surface density of interest, in our case the area per molecule which corresponds to the maximum of the elastic modulus and a surface pressure of 17 mN/m. This procedure is shown in cartoon (a) in figure 2. The resulting film was transferred to a solid substrate by Langmuir Schäfer (also known as horizontal lifting) method for further characterization by AFM.

Atomic force microscopy (AFM) images of the transferred films, which are shown in figure 3, revealed a homogeneous phase of circular fibers characterized by a minimal radius of curvature of around 1.5 µm. The fibers showed a variance in terms of height and width as shown in the small scale image. The average width of one fiber was around 20 nm and the average height was around 3 nm.

The surface coverage of the circular fibers was around 47% from the whole surface. The surface coverage was determined by using the software packet provided by ImageJ. First the color-coded image was converted to grayscale. Then an appropriate threshold was determined to convert the image into a binary map. And finally the area of the circles portion was calculated.

Figure 3B shows an enlarged region of 3A. In this image the color code was modified to get a better representation of the height variations. From this image one can clearly see that there is a blue layer underneath the circular fibers which is approximately 1 nm high.

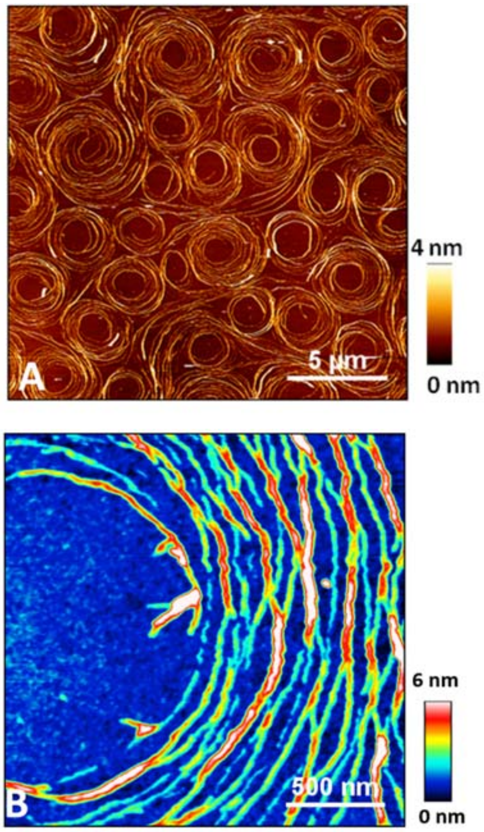

Fig. 3: AFM measurements of PEO-PLLA (BCP) Langmuir films transferred at the maximum of the elastic modulus, where the surface pressure was 17 mN/m in the isotherm. Scale bars: 5 µm for image A) and 500 nm for image B). © Experimental Polymer Physics, Freiburg

In the second experiment, we kept the trough area constant and we reached the targeted surface concentration by dropwise additions of the spreading solution. The volume of the spreading solution allowed us to reach the surface pressure corresponding to the maximum of elastic modulus. 800 µl were used to reach the surface pressure of 17 mN/m, corresponding to the maximum of E_s as determined in the first experiment. This procedure is shown in cartoon (b) in figure 2. After 30 minutes of evaporation time, we transferred the film to a solid substrate.

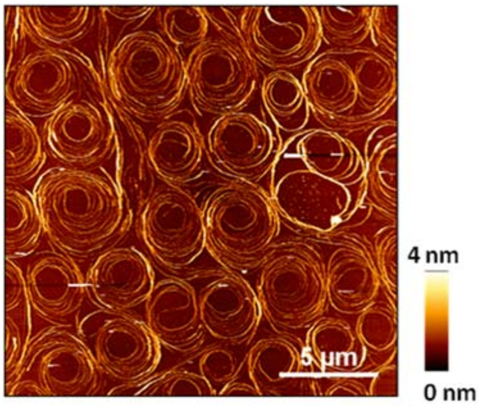

Fig. 4: AFM measurements of PEO-PLLA (BCP) Langmuir films transferred after dropwise additions of spreading solution at a pressure value of 17 mN/m in the isotherm. © Experimental Polymer Physics, Freiburg

As a result we found similar circular structures to the ones obtained in the first experiment. (Figure 4). This shows that the formation of circular fibers is independent of the compression induced by the barriers. The process behind the formation of these regular patterns is still under investigation and we cannot give a detailed explanation at present. It is however obvious that intrinsic properties of the BCP trigger the transition once the critical 2D density was reached. If both blocks of the BCP would crystallize, a geometrical mismatch of these units would result. Based on this idea we are currently working on a model to explain the curvature of the fibers which might be crystalline.

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Future Field “Biomimetic, Biobased and Bioactive Materials Systems”

Adaptive actuator systems for biomimetic snap-trap demonstrators

Falk Esser[1,2], Thomas Speck[1,2,3]

[1]Plant Biomechanics Group (PBG) Freiburg, Botanic Garden of the University of Freiburg; [2]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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The Cluster of Excellence “Living, adaptive and energy-autonomous Materials Systems (*liv*MatS)” at the University of Freiburg aims at developing novel materials systems that show dynamic, life-like and non-equilibrium (energy-autonomous) features. Within the *liv*MatS research area “Demonstrators” technical demonstrators like an artificial Venus flytrap are envisaged, which will demonstrate the feasibility of the developed materials systems. Such demonstrators will be the first step towards future implementation of novel technologies into industrial products and everyday life applications. Here, we present a first set of bio-inspired demonstrators which not only incorporate and combine the snap-trap movement principles of two carnivorous plant species (Venus flytrap and waterwheel plant [1,2]), but also show adaptive responses to different environmental triggers [3]. The presented actuator systems are the first to successfully implement several plant movement actuation and deformation systems into one versatile adaptive technical compliant mechanism, and can serve as a basis for the further developments within *liv*MatS.

Living organisms like plants and animals have evolved a multitude of mechanisms for sensing, reacting and adapting to the environment, e.g. by harvesting and storing energy, which can be used to power movement. Such adaptability is based on the respective structure’s material building blocks, i.e. multifunctional biological composites. Plants in particular are well-suited role models for adaptive material systems, consisting of material systems that are hierarchical structured spanning several orders of magnitude. Because plants are habitat-bound sessile organisms, they have to adapt to the conditions of the (micro)environment and harvest energy from it.

The biological role models, the Venus flytrap (*Dionaea muscipula*) and the waterwheel plant (*Aldrovanda vesiculosa*), are two closely related carnivorous plants, which are able to sense prey and perform very fast catching movements upon triggering of sensitive hairs on the trap lobes [1,2,4]. In both species, the traps are modified leaves consisting of two lobes connected via a midrib. Novel actuator systems were developed implementing and combining the movement principles of the Venus flytrap (snap buckling) and the waterwheel plant (kinematic coupling with motion amplification). We abstracted the basic snap-trap form of the plants into a foil model, which is able to perform a closure movement of its “lobes” via kinematic coupling and motion amplification by curved folds (inspired by *Aldrovanda*) and an inverse snap-buckling movement for opening (inspired by *Dionaea*) (Fig. 1).

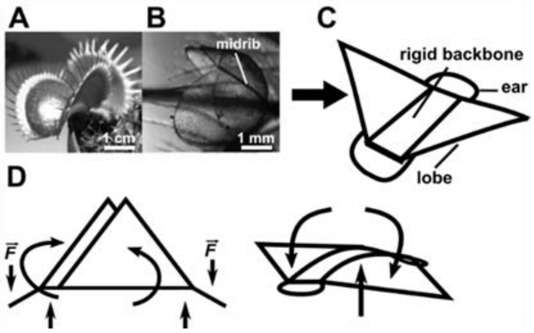

Fig. 1: Foil based artificial Venus flytrap model. Movement principles of biological role models Venus flytrap (*Dionaea muscipula*) (A) and the waterwheel plant (*Aldrovanda vesiculosa*) (B) were abstracted and incorporated into foil model (C) with closure through kinematic coupling and motion amplification by curved folds (D, left) and snap-buckling of the backbone for opening (D, right). © Plant Biomechanics Group Freiburg

To drive these movements’ four different actuator systems were developed [2]. The first used pneumatic cushion to close and snap open the artificial Venus flytrap (Fig. 2A). In a second system, a contactless actuation took place through magnetic displacement of attached magnets (Fig. 2B) and the third type of actuation was achieved via thermally driven shape memory alloy springs (Fig. 2C). The fourth system showed the possibility of energy storage and movement locking via hydrogel based actuators in combination with a 3D printed backbone with a low T_g (glass transition temperature, $T_g = 50°C$). Additionally, this system utilizes a stimulus combination to initializes the model for movement. Only the combination of heat and moisture within steam initializes the system. Heating up the backbone over its T_g and moisturizing the hydrogel, which then expands and straightens the backbone.

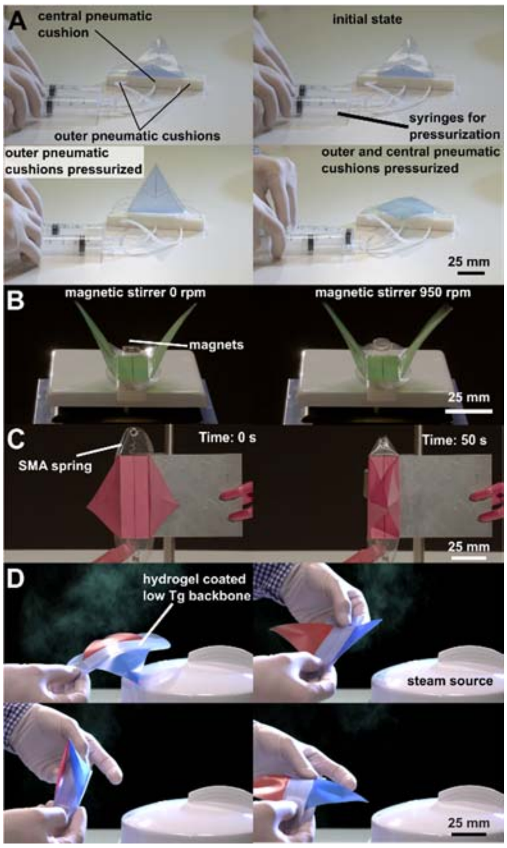

Fig. 2: Actuator systems of the foil based artificial Venus flytrap. The first system utilizes pneumatic cushions to move the backbone (A). Actuation through changing magnetic fields with magnets attached to the model (B) or thermally driven SMA springs (C). Stimulus combination to initializes movement (D). © Plant Biomechanics Group Freiburg

By further characterizing the system with regard to movement speed, exerted force during closing and energy consumption, a basis for the development of more advanced demonstrators is created. On this basis, boundary conditions, energy requirements and efficiencies can be determined. These will be regarded as guideline values for future materials systems developed within *liv*MatS.

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Biomechanics and functional morphology of citrus fruit peel as inspiration for auxetic logic self-reporting metamaterials

Maximilian Jentzsch[1,2,3], Sarah Becker[1],
Thomas Speck[1,2,3]

[1]Plant Biomechanics Group (PBG) Freiburg, Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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In this subproject of *liv*MatS Research Area B we quantitatively analyze on a micro-, meso- and macroscopic level ontogenetic variations, adaptivity and the structural basis of auxetic behaviour in hierarchically structured plant tissues.

Auxetic materials and structures that contract orthogonal to the direction of the compression load as soon as they experience an impact show improved damping characteristics, react load adaptive and can attenuate impacts. Auxetic materials systems can be used for applications such as protection vests or helmets. As a consequence, objects or persons can be markedly better protected by such auxetic materials systems than by standard (non-auxetic) materials like styrofoam. Models for such adaptive damping structures can be found in nature. So far, these properties have been demonstrated in the foamy middle part (albedo) of the pomelo fruit peel (*Citrus maxima*) [1-3]. In this project, the fruit peels of different *Citrus* species will be examined, characterized and compared as to their damping properties and the development of the underlying structures during ontogeny in order to abstract the properties and the development of these properties during their ontogeny.

Focus of this part of the subproject is the analysis of citrus fruit peels as an inspiration for the transfer into technical auxetic materials systems. Today, technical auxetic structures are very regularly structured, consist of re-entrant cells and are mostly only working in one direction in a 2-dimensional demonstrator. 3-dimensional auxetic structures are rather complicated to construct (today still mostly via 3D-printing) and even to simulate. One of the main aims is to create a simple 3-dimensional structure with auxetic properties without a highly regular structuring as found in the biological role models which show a kind of “ordered-disorder”.

At first sight, it appears that the cells in the flavedo and albedo of *Citrus limon* (lemon) are in a random order but at a more detailed second view, a gradient in the cells density becomes apparent (Fig. 1). The density decreases from the flavedo to the middle of the albedo, similar as shown for the pomelo [2,3]. On basis of the results of *Citrus maxima* with its promising damping behaviour and its auxetic properties, other citrus fruit peels are currently characterized and will be compared to the pomelo.

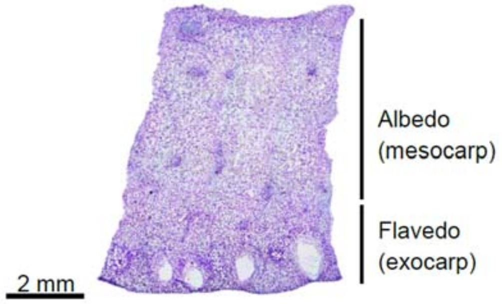

Fig. 1: Radial-section of the peel (exocarp and mesocarp) of *Citrus limon*, stained with Toluidinblue. © Plant Biomechanics Group Freiburg

Energy dissipation behaviour can be analysed with impact tests, a method that was established for pomelo in the Plant Biomechanics Group Freiburg [1-3]. A high-speed camera records the impact. The dissipated kinetic energy can be calculated from the velocity before and after the impact (Fig. 2).

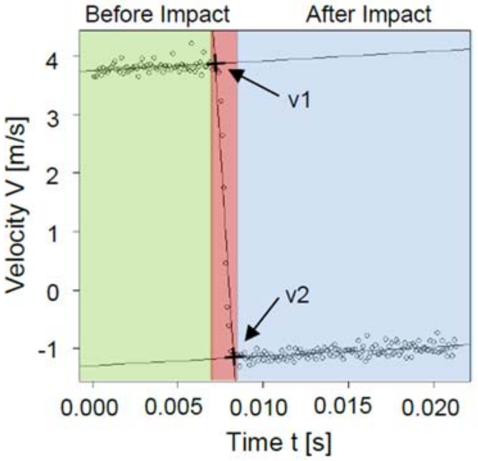

Fig. 2: Velocity-time diagram of a characteristic impact test of *Citrus limon*. The impact process can be divided in three phases: before impact (green), impact (red) and after impact (blue). The three linear regression lines characterize the velocity and velocity change of the impactor before, during and after the impact. The velocities V1 and V2 are defined at the crossings of the two regression lines. (© Plant Biomechanics Group)

The relation between the velocity before and after the impact is known as the coefficient of restitution (COR). The COR-value describes the elasticity of the impact. A COR-value of 1 means that all the energy returns to the impactor (elastic impact). Whereas a COR-value of 0 means that all the energy is dissipated by the impacted sample (plastic impact) [1].

First results of the impact tests show that the *Citrus limon* dissipates about 90% of the kinetic energy, which is very similar to the pomelo that dissipates up to 95% of the kinetic energy. Although the dissipated energy is very similar, the peel of *Citrus limon* is approximately only half as thick as the peel of *Citrus maxima* [1,3].

Considering these results, further investigations on various citrus fruit peel as an inspiration for biomimetic transfer into polymer-based materials systems are highly promising.

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Self-healing in cacti branches: a morphological, anatomical and biomechanical analysis

Max D. Mylo[1,2], Friederike Krüger[1],
Thomas Speck[1,2], Olga Speck[1,2]

[1]Plant Biomechanics Group (PBG) Freiburg, Botanic Garden of the University of Freiburg, Germany; [2]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, D-79110 Freiburg, Germany

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Research area C of the Cluster of Excellence *liv*MatS deals with concepts for increasing the longevity of artificial materials systems inspired by natural role models. The key elements of longevity include damage management such as sealing and healing of wounds. Since the last decades have proven that functional principles in plants can be a real treasure trove for biomimetic inspirations, a literature research for suitable plant models was carried out. It was shown that the family of Cactaceae (and especially the subfamily of Opuntioideae) can serve as appropriate role model for self-sealing and self-healing functions, since this is a particularly important ability in water-storing plants [1,2].

Within a comparative study, morphological, anatomical, and biomechanical analyses with focus on self-repair were performed on the selected plants *Opuntia ficus-indica* and *Cylindropuntia bigelovii* [3-5]. By means of artificial ring incisions lateral branches of both species were wounded in a comparable manner (Fig. 1A). Over a repair phase of 21 days, a rolling-in of the wound edges was detected. This enables the plant to avoid evaporation of water and protects it from pathogen infection. On an anatomical level, the formation of wound periderm and division of parenchymatous cells could be observed (Fig. 1B). This ligno-suberized coverage of the wound protects the stems from greater water loss, which is crucial for succulent plants growing in (semi-)arid habitats. Repeated bending tests on the same branches in intact, freshly wounded and healed states after 21 days were conducted to quantify the biomechanical performance. In order to provide an optimal form fit between the samples and the mounts during the biomechanical tests and thus make the measurements as repeatable as possible, individually constructed clamps (3D printed after 3D-scanning the plant branches) were used for each sample. Bending stiffness and work necessary for bending were selected as mechanical parameters to calculate the self-healing efficiency. In contrast to *O. ficus-indica*, a significant mechanical healing effect could be observed for the bending stiffness of *C. bigelovii*. In both plant species, anatomical studies show during self-repair the formation of a peripheral protective layer that reduces water loss. These results indicate that in *O. ficus-indica* the avoidance of water loss is most probably the driving factor for self-healing, while the statement "sufficient is good enough" seems to apply to the mechanical stability of this plant species. Further research on the experimental plants should provide more insight into the mechanical nature of their branch-branch connections and of individual tissues involved.

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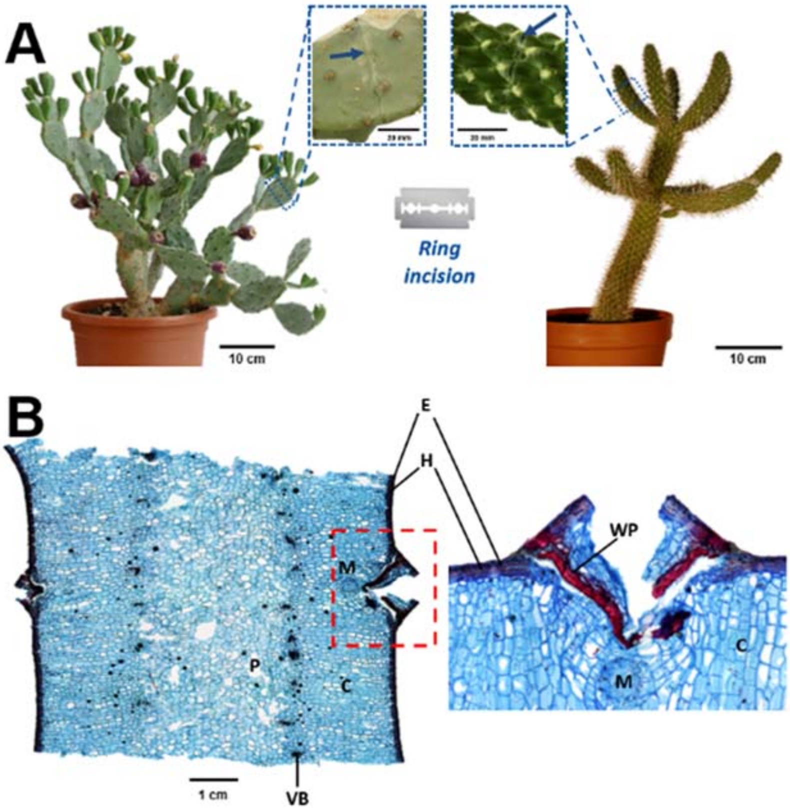

Fig. 1: Self-repair analyses in cacti branches. A: Ring incision of lateral branches in plants of *Opuntia ficus-indica* (left) and *Cylindropuntia bigelovii* (right). B: Longitudinal sections of healed branch of *O. ficus-indica* after a healing phase of 21 days, stained with Safranin O & Astra Blue. (C): cortex, (E): epidermis (covered by a cuticle layer), (H): hypodermal layers, (P): pith (water-storing cells), (M): mucilage cell, (VB): vascular bundle, (WP): wound periderm. (© Plant Biomechanics Group Freiburg)

Multi-material 3D-printer for rapid prototyping of bio-inspired demonstrators

Stefan Conrad[1,2], Falk Esser[1,2],
Thomas Speck[1,2,3]

[1]Plant Biomechanics Group (PBG) Freiburg, Botanic Garden of the University of Freiburg; [2]Cluster of Excellence livMatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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The Cluster of Excellence "Living, adaptive and energy-autonomous Materials Systems (*liv*MatS)" at the University of Freiburg aims at developing novel materials systems that show dynamic, life-like and non-equilibrium (energy-autonomous) features. Within the *liv*MatS research area "Demonstrators" technical demonstrators like an artificial Venus flytrap [1-4] are envisaged, which will demonstrate the feasibility of the developed materials systems.

Just like the originals, these bio-inspired constructs are intended to show complex, reacting behaviour to changing in environmental conditions. These reactions in form of motion or shape changes will not be initiated via a central control unit but plant-like through decentralized stimulus-response systems using embedded intelligence and embedded energy. Depending on the nature of the stimulus and the intended response, this requires the integration of diverse materials and mechanisms. Especially in case of materials composition in complex patterns a specific method of fabrication is required, that offers rapid prototyping and a high degree of automation.

For this purpose, a novel multi-material 3D-printer with on demand tool changing properties is currently under development. It is based on a commercial FDM-printer that extrudes molten thermoplastics through a thin nozzle layer by layer. The project aims at extending the range of printable substances including high and low viscous fluids and conductive materials for low cost rapid prototyping applications. When finished the device will be able to process up to eight substances within one printing process. This is achieved by an X/Y-axes geometry combined with a coupling mechanism that allows switching the tool on demand. The different materials will be loaded in individual printheads all equipped with an extruder motor and temperature control. The different tools are hold in standby on a docking position at the front and back side of the 3D-printer frame. When needed during the fabrication the carriage moving on the axes-system picks it up, initializes the print head and prints the specified part of the currently printed layer. After use it is placed back in its docking position and the next tool is selected. In contrast to other printers with multiple nozzles on the same tool, this setup avoids any kind of unwanted interaction between the printheads, since at every time only one head is moving above the build platform.

Up to date the acquired commercial device (Fig. 1) has been upgraded with a 32-bit controller board and a new hotend, which is especially suitable for flexible filaments. In combination with an additional cooling system and the connecting parts for coupling and docking, this hotend forms the first of the newly developed filament printheads (Fig. 1 B). The core element of the printer is the currently developed kinematic coupling. It is based on the Maxwell-design which uses six edges on one surface and three spheres on the counter part to eliminate all six degrees of freedom when both sides are pulled together [5]. Within the printer this is realized using parallel rods on the carriage side (Fig. 1 C) and ball screws on the back side of the tool (Fig. 1 D). The attraction is achieved by an electromagnet located in the centre of the interface and a corresponding iron plate. This design allows a highly repeatable positioning of the printheads. The relative deviations of their nozzle positions can be compensated by using individual coordinate systems for each tool, which are shifted relative to the absolute workspace. To calibrate a new printhead the user manually positions the nozzle tip above the hair cross of a USB microscope once after adding the new printhead and then triggers a procedure in the printer firmware to measure the offset (Fig. 1 E). After calibration, the system will be ready for printing and tool changing. On the software side the printer has been equipped with a self-programmed management system for single and multiple extrusion and a coupe of additional features that simplify calibration and fine tuning. Using a laser diode, the starting point of the print can be defined very precisely, what is mandatory when it comes to printing additional parts on a given object like a foil. For making the prototyping even more flexible the firmware has a mode to stop on a given height so non-printable objects can be inserted into the demonstrator. Parts of the tool change procedure are already implemented as well and are currently under testing.

When finished this will form a suitable platform for the evaluation of a wide range of substances. In a close cooperation with other groups of the Cluster of Excellence additional printheads will be designed specifically adapted to the needs of their newly developed materials. This will provide high flexibility and response speed for the prototyping within the area “Demonstrators” and within the other *liv*MatS research areas.

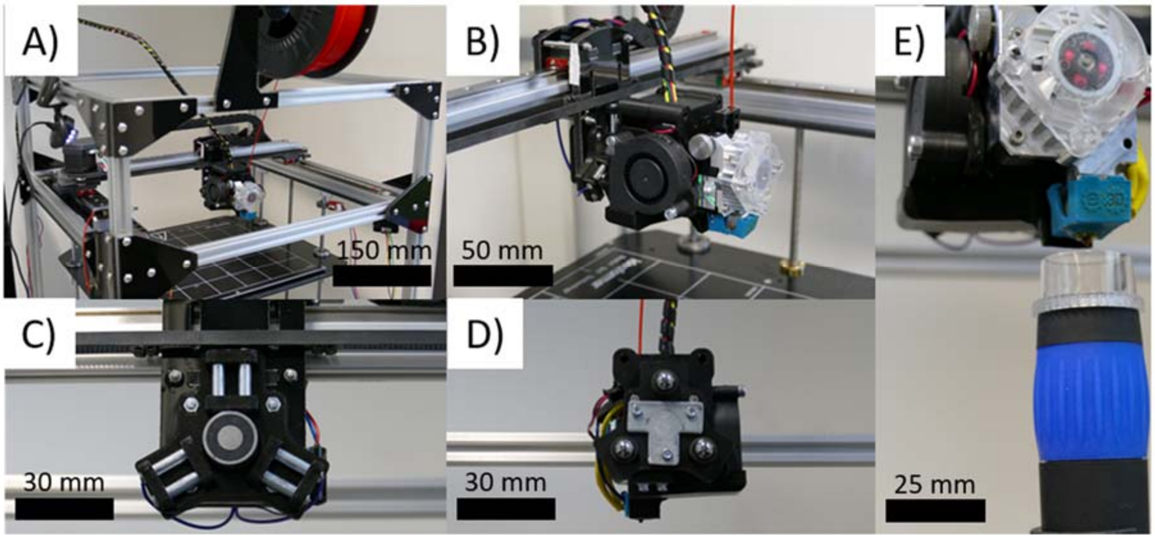

Fig. 1: Multi-material 3D-printer with on demand tool changing. The total setup consists of the printer frame and its axis system (A) and the newly developed filament printhead attached to the X-carriage (B). The carriage side provides the "female part" of the Maxwell coupling with an electromagnet in its centre (C), which attracts an iron surface on the "male side" of the Maxwell coupling forming the back side of the printhead (D). To calibrate the tools offset its nozzle is manually positioned above a USB microscope (E). © Plant Biomechanics Group Freiburg

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Multiplexed point-of-care testing for inflammatory miRNA and neurotransmitter profiling in Alzheimer's disease diagnostics – NeuroSENS

Can Dincer[1,2], Michael Heneka[3,4]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies – FIT, University of Freiburg; [2]Department of Microsystems Engineering – IMTEK, University of Freiburg; [3]Department of Neurodegenerative Diseases and Geriatric Psychiatry, University Hospital of Bonn; [4]German Center for Neurodegenerative Diseases – DZNE

Project funding: German Research Foundation (DFG)

Alzheimer's disease (AD) is the most frequent type of dementia affecting about 10% of the world population older than 65 years [1]. The pathological mechanisms behind AD are still not completely understood. This again results in a lack of practical treatments and of sufficient diagnostic and prognostic biomarkers. In the clinical AD diagnostics, extracellular plaques of amyloid beta and intracellular fibrillar aggregates of hyperphosphorylated tau protein are currently two major hallmarks. They can be monitored either by imaging or by the measurement of cerebrospinal fluid (CSF) protein biomarkers. Yet, these biomarkers still require further standardization [2]. Another issue is that they get significant only after beginning of the disease and do not allow to track other key pathological processes, including neuroinflammation. As a result, there is a great and urgent demand for novel and complementary biomarkers, and also for validation and clinical translation of previously reported biomarker candidates. MicroRNAs (miRNAs), small non-coding RNA molecules, play an important role in the regulation of gene expression in humans. The presence or a dysregulation of miRNAs is related to many diseases and thus, they have recently become more and more important as potential biomarkers. There are numerous miRNA screening studies targeting to identify new biomarker candidates for cancer, cardiovascular disease, dementias such as AD and neuroinflammation. However, only the detection of single miRNA is not sufficient for the appropriate diagnosis since a panel of different miRNAs (so-called a cluster family) is usually up- or downregulated in patients, suffering from a certain disease. Therefore, it is highly desirable to measure different miRNAs simultaneously along with a rapid, low-cost and reliable system. This project is dedicated to implement a novel detection strategy based on the CRISPR/Cas technology (Fig. 1) for a 4-plex panel of miRNAs associated with neuroinflammation, using an electrochemical biosensor with multiplexed microfluidics for point-of-care testing (POCT) [3].

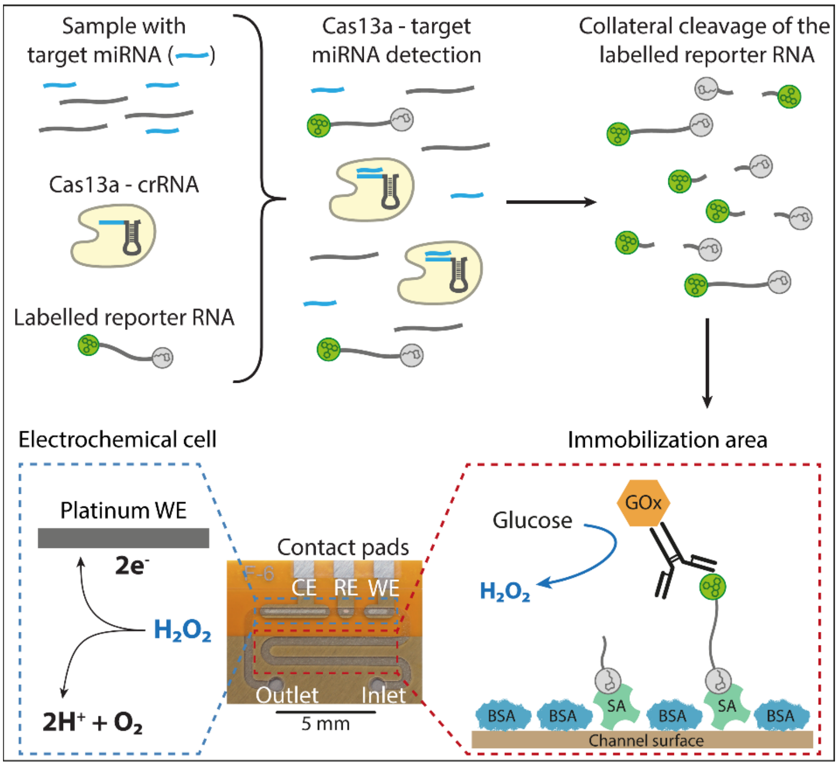

Fig. 1: **Top:** Illustration of the CRISPR-powered miRNA detection, including the enzyme Cas13a, the target RNA, the target-specific guide RNA (crRNA) and the biotin and 6-FAM labelled reporter RNA. The reporter RNA is immobilized after the cleavage process onto the channel surface, coated with streptavidin (SA) and subsequently blocked with bovine serum albumin (BSA). **Bottom:** Working principle of the electrochemical microfluidic biosensor. **Right:** Schematics of the employed CRISPR/Cas13a assay. **Middle:** Image of the biosensor, highlighting the working (WE), counter (CE) and reference (RE) electrodes, and the hydrophobic stopping barrier (SB). The immobilization capillary and the measurement cell are highlighted in red and blue, respectively. **Left:** The subsequent electrochemical measurement of the hydrogen peroxide, which is produced by the enzyme glucose oxidase (GOx) in the immobilization area. Reproduced with permission. [3] Copyright 2019, John Wiley & Sons, Inc.

Neurotransmitters are not only a neuronal signal transmitter, but also act as an inflammatory mediator as they expressed by immune cells of both peripheral and central nervous system [4]. Although there is a large amount of research on the role of neurotransmitters in the Alzheimer's disease, it has not yet been sufficiently clarified if these multifunctional transmitters involve in the disease pathology and if they can be used as a clinical biomarker. Hence, this project will deal with the question about the applicability of neurotransmitters (such as substance P) as a biomarker in the AD diagnostics.

To summarize, the main goal of this project will be the design and development of an electrochemical microfluidic multiplexed biosensor for the highly selective, sensitive and on-site detection of a 4-plex panel of potential AD biomarkers in human body fluids. For this purpose, different neuroinflammatory biomarkers, such as neurotransmitters and miRNAs, will be measured and validated for their applicability in the clinical diagnostics of Alzheimer's disease. Herein, the implemented POCT platform will be applied for the analysis of relevant biospecimen of Alzheimer patients, primarily human cerebrospinal fluid (CSF) and peripheral blood.

The successful realization of such an electrochemical microfluidic multiplexed POCT device along with a performant biomolecular sensing system will enable the direct, low-cost, rapid and easily scalable detection of neurotransmitters and miRNAs without any prior target amplification. This would be a major milestone on neuroinflammation analysis in the AD research and beyond since the proposed biosensing platform could be implemented on many different areas of application.

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Future Field “(Micro)Systems for Energy Conversion, Storage and Energy-autonomy”

Non-noble catalysts and novel cell concepts for anion exchange polymer fuel cells

Patrick Elsässer[1,2], Phililpp Veh[2,3], Severin Vierrath[2,3], Anna Fischer[1,2,4]

[1]Inorganic Functional Materials, Institute for Inorganic and Analytical Chemistry, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg; [3]Electrochemical Energy Systems Group, IMTEK - Department of Microsystems Engineering, University of Freiburg and [4]Freiburger Materialforschungszentrum (FMF), University of Freiburg

Project funding: Vector Foundation, project “AlkaCell”

Fuel cells are a key technology for emission-free mobility but also, once integrated, to provide energy for adaptive materials systems. High costs of the platinum catalyst and membrane polymer are the biggest hurdle for their breakthrough. In "AlkaCell" a membrane-based alkaline fuel cell is developed, which work without these costly materials. The main challenges, activity of non-noble catalyst and stable cell operation, are addressed in a joint consortium of catalyst and fuel cell developers. The aim is to significantly increase performance and lifetime and also to investigate the hybrid use of alcohol as a fuel. In the first year of the project, it was planned to establish a catalyst system for the hydrogen oxidation reaction (anode) and build a stable reference fuel cell with commercial noble catalysts.

Catalyst development (Patrick Elsässer, Anna Fischer)

Polymer-based catalysts for hydrogen oxidation (HOR) with nickel (Ni) and nickel-molybdenum (Ni-Mo) nanoparticles were synthesized by modification of an earlier reported synthesis route for Fe-N-C catalysts for oxygen reduction (ORR).[1] The carbonization of polyform-amidine in the presence of a Ni salt resulted in the formation of Ni nanoparticles in a porous N-doped carbon support. Increasing Ni loading resulted in the formation of Ni nanoparticles with broad particle size distribution. While the smaller nanoparticles (~10 nm) were embed-ded in amorphous carbon, the main fraction of the nanoparticles was significantly larger (30-40 nm) and the particles were covered by a graphitic shell consisting of up to 30 layers of graphene (Fig. 1).

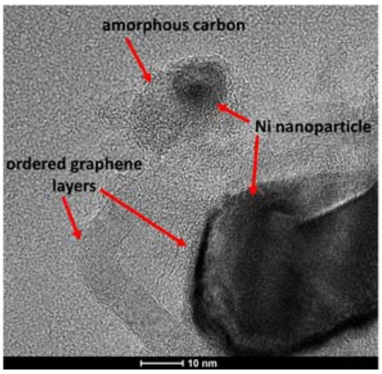

Fig. 1: TEM image of PFA-Ni20-800 depicting the Ni nanoparticles embedded in layers of graphene and amorphous carbon. (© Fischer group)

These materials showed activity for the HOR in alkaline electrolyte (Fig. 2) as demonstrated by rotating disc electrode measurements. Higher carbonization temperatures resulted in a strong sintering of the Ni nanoparticle and a decreased hydrogen oxidation activity. To improve the catalytic activity towards hydrogen oxidation, an additional Mo precursor was added to the synthesis. The presence of Mo during carbonization resulted in the formation of significantly smaller nanoparticles (~20 nm). X-ray diffraction and EDX analysis revealed the formation of a Ni-Mo alloy and a small amount of MoO_2. Additionally, the nanoparticles were stable against sintering at higher carbonization temperatures and the activity towards hydrogen oxidation improved (Fig. 2).

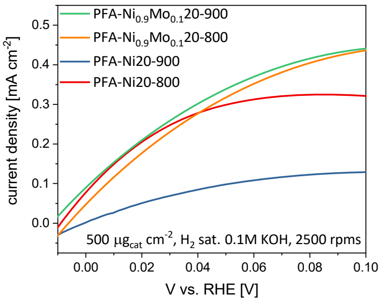

Fig. 2: Linear sweep voltammograms in H_2 sat. 0.1 M KOH depicting the activity towards hydrogen oxidation. (© Fischer group)

However, the activity is still too low and needs to be further improved. Improving the catalytic activity by optimization of the Ni to Mo ratio and the carbonization parameters for the HOR side, and the scale-up of the previously reported iron-based catalysts on the ORR side (Fig. 3) are the next steps in this project regarding catalyst development.

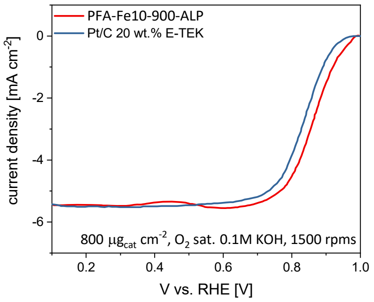

Fig. 3: Linear sweep voltammogram in O_2 sat. 0.1 M KOH depicting the activity towards oxygen reduction. (© Fischer group)

Fuel Cell development (Phililpp Veh, Severin Vierrath)

In the first year of the project, anion exchange membrane fuel cells (AEMFCs) were fabricated via a novel fabrication process for AEMFCs based on direct deposition of ionomer (ion conducting polymer) onto gas diffusion electrodes. This enabled the deposition of unprecedented thin membranes of only 3 – 10 µm thickness, which led to the most robust water management in AEMFCs reported until today. The developed membrane electrode assemblies featuring a platinum-ruthenium anode, a platinum cathode and a HMT-PmBI based membrane achieve maximum power densities beyond 1 W/cm^2 in H_2/O_2 atmosphere (Fig 4). These results have been submitted in form of a publication and are currently in peer review.

Besides the general optimization of the fuel cells, further experiments were conducted: In order to simulate more real application oriented operation conditions, the AEMFCs were operated with ambient air instead of pure oxygen as oxidizing agent, which led to maximum power densities of 288 mW/cm^2. By comparing the performance of the cells operated with ambient air and pure oxygen, the carbonation caused by CO_2 in ambient air became visible in the strong reduction in cell performance. Additionally, a platinum group metal-free cathode was fabricated using silver as catalyst. Even though the power density was significantly reduced to 133 mW/cm^2, this experiment was a promising proof-of-principle investigation for further research in PGM-free AEMFCs. Finally, as AEM fuel cells suffer from rapid power decay over time. This issue was thoroughly investigated and alleviated during the first year of the project by carefully tuning the operation conditions and the water management in the cells [2,3].

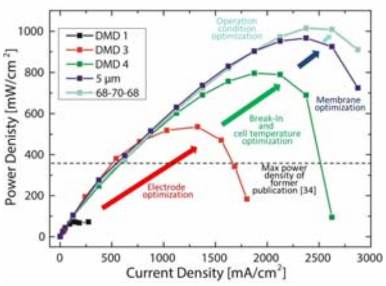

Fig. 4: Power density data, depicting the main optimization steps of the anion exchange membrane fuel cells fabricated via the direct membrane deposition approach. (© Vierrath group)

In the upcoming steps of the project, the experience of both research groups will be combined by integrating the novel catalysts developed by the group of Anna Fischer into the presented AEMFC system. This collaboration aims at the ultimate goal of the project, building low-cost fuel cells with high performance, stability and without platinum-group metal catalysts.

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Pan-European Network of Fundamental pH Research: UnipHied

V. Radtke[1,2], D. Priester[1,2], M. Bäuerle[1,2],
N. Gebel[1,2], I. Krossing[1,2,3]

[1]Institut für Anorganische und Analytische Chemie,
[2]Freiburger Materialforschungszentrum (FMF) and
[3]Freiburger Zentrum für interaktive Werkstoffe und bioinspirierte Technologien (FIT)

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Research Objectives:

- Development and Validation of a reliable and universally applicable measurement procedure for the determination of $\mathrm{pH_{abs}}$ expressed relative to the aqueous scale ($\mathrm{pH}_{\mathrm{abs}}^{\mathrm{H_2O}}$-values) in non-aqueous and mixed solvents, colloids, etc. This enables the comparison of their acidities to the conventional aqueous pH-scale.
- Creation of a reliable method for the evaluation of the liquid junction potential between aqueous and non-aqueous solutions.
- Development of a coherent and validated suite of calibration standards for standardizing routine measurements systems in terms of $\mathrm{pH_{abs}}$ values for a variety of media.

Summary:

The cooperation project aims to overcome the situation that it is impossible to compare pH values of solutions made in different solvents. This is done by putting the new theoretical concept of a unified $\mathrm{pH_{abs}}$ scale on a metrologically well-founded basis into practice. Thus, the availability for accurate pH testing in a wide variety of media will be provided to industry and academia.

Since the pH of solutions is a widely used concept in many areas outside the field of chemistry, e.g. medicine and life science, biology, environmental science, agrology, material sciences, energy related sciences, etc. valid comparability of pH values in different media is essential. Material related processes, e.g. processing metals papers, plastics, glasses, etc. as well as their reprocessing (wastewater, extraction of solid wastes, etc.) demand accurate analysis and monitoring of pH values in a variety of media in which these processes occur. As a result of the impossibility of valid comparability of pH values in different media, several pH scales were introduced in the past, which are loosely correlated to each other. Since conversion of these scales is difficult and not possible with the necessary level of accuracy, the unified acidity concept ($\mathrm{pH_{abs}}$) was introduced in 2010 [1]. Although even pH values between different phases (gaseous, liquid and solid) can be compared, putting this concept into practical use has not yet been fully achieved. Physicochemical quantities, in the first place Gibbs free energies of solvation, $\Delta_{\mathrm{solv}}G°$, as well as suitable measurement and calibration procedures are required, which still need to be developed.

Progress was made by establishing a measurement setup for the determination of Gibbs free energies of transfer of $\mathrm{Ag^+}$ between various solvents [2, 3]. The latter can be converted to Gibbs free energies of solvation of $\mathrm{Ag^+}$ – a procedure which can be adopted to proton measurements. The setup consists of two half-cells with the redox active species dissolved in the relevant solvent and electrodes immersed in the solutions. The half-cells are connected by a salt bridge, which is filled with an Ionic Liquid, the diffusion coefficients of which are identical. In 2019 a hydrogen line was set up and initial experiments with an adjusted measurement setup for the determination of Gibbs free energies of protons between water, organic solvents (acetonitrile, propylene carbonate, dimethylformamide, ethanol and methanol) and even highly concentrated sulfuric acid seem very promising.

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Development of safe and long-lived rechargeable lithium metal based batteries for electromobility

Witali Beichel[1,2], Stephan Burger[3], Petra Klose[3], Julian Skrotzki[1,2], Lili Liu[1,2], Simon Thiele [4,5], Ingo Krossing[2,3]

[1]Laboratory for MEMS Applications, Department of Microsystems Engineering – IMTEK; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), [3]Freiburger Materials Research Center (FMF), [4]Forschungszentrum Jülich GmbH, Helmholtz-Institute Erlangen-Nürnberg for Renewable Energy (HI-ERN), [5]Department of Chemical and Biological Engineering, Friedrich-Alexander-Universität Erlangen-Nürnberg

Project funding: Vector Stiftung „ LIM-MOBIL - Entwicklung von sicheren und zyklenfesten Lithium-Metall basierten Batterien für den Einsatz in der Elektromobilität“

Rechargeable lithium metal based batteries (LMBs) are highly promising future battery cell technologies, in particular in the context of automotive applications. LMBs can achieve gravimetric and volumetric energies in the range of 400-500 Wh/kg and 800-1000 Wh/L, which is substantially higher than that of state-of-the art Lithium ion batteries (LIBs). However, the lithium metal anode is a huge obstacle for the broad commercialization of LMBs. In contrast to LIBs no stable solid electrolyte interphase (SEI) is formed during the operation of LMBs. Continuous electrolyte decomposition, low coulombic efficiencies and the formation of dendrites prevent a long-term and stable cycling behaviour of LMBs.[1-3]

Among the various approaches to stabilize the lithium metal anode, the artificial SEI concept is quite promising. Instead of the in situ SEI formation out of the electrolyte like in LIBs, the SEI is preformed ex situ prior to battery operation. The ex situ SEI formation is achieved via the application of reagents with a deposition method (DM) on the lithium metal surface. The advantage of the artificial SEI approach is the possibility to control and regulate the SEI composition via the choice of the used reagents and the process technology.[1-3]

In LIM-MOBIL a special type of a reagent is applied to the lithium metal surface by immersion of lithium coins in a diluted solution of **1** in dimethoxyethan (DME). Compound **1** is a phosphate based coordination polymer (Fig. 1).[4] As a weak acid it reacts with the native oxide layer of the lithium metal surface, removes it and forms the corresponding Li-salt (**Li-1**). The Li-salt itself is also a “breathable” and Li-ion conducting coordination polymer and is solely held by ionic interactions. In that way **Li-1** acts as a protective layer on lithium, thus enabling a reversible lithium metal anode operation. Apart from that, **Li-1** gelifies in contact with a standard electrolyte forming a so-called gel-type polymer electrolyte (GPE). The use of such an electrolyte in a battery replaces the separator, contributes to the flexibility of the cell, reduces the flammability and prevents leakage or drying out of the cell. Thus, the combination of a protective layer on lithium and the use of **Li-1** based GPE both contribute to the realization of long-term safe operation of LMBs.

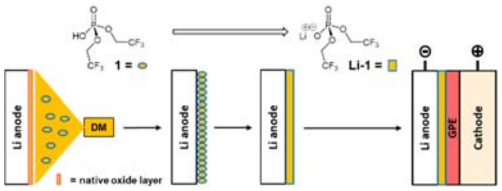

Fig. 1: Schematic approach followed in LIM-MOBIL to realize rechargeable LMBs. (© Witali Beichel)

Fig. 2 shows the positive effect of the artificial SEI layer in Li-Li symmetrical model coin cell tests in a voltage-time (*U*-*t*) diagram. These cell experiments simulate the plating and stripping behaviour of lithium during battery operation. The increase of the voltage indicates electrolyte decomposition and in the long term battery failure. While pristine lithium cells already fail after 74 cycles, lithium coins treated with **1** show a significant prolongation of the cells' lifetime.

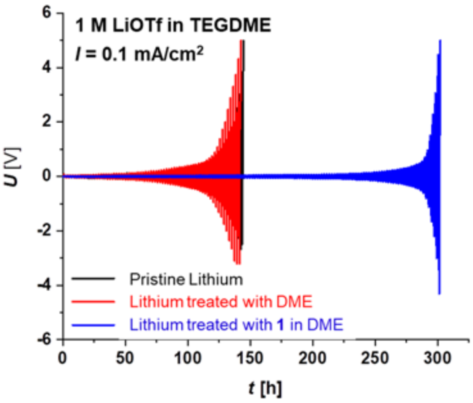

Fig. 2: Voltage-time diagram of Li-Li symmetrical model cell tests of pristine and treated Li coins. (© Witali Beichel)

A close inspection of the surface of treated Li coins via scanning electron microscopy (SEM) shows a porous layer (Fig. 3). The porous layer has a thickness of a few micrometers and contains the elements P and F, which is seen in the corresponding EDX element mapping analysis. Additional ATR-IR measurements confirm the presence of **Li-1** on top of the lithium metal surface (not shown).

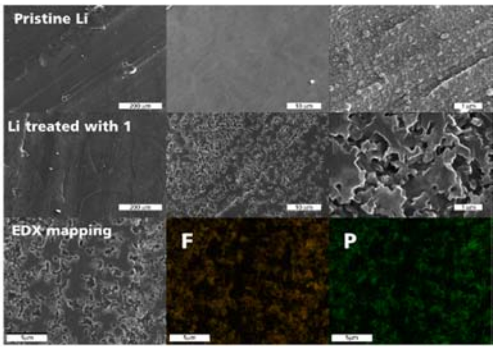

Fig. 3: SEM pictures of pristine (top) and treated Li coins (middle) with different magnifications. EDX mapping (bottom) shows the elemental distribution of P and F on top of the treated Li coin. (© Witali Beichel) Electron microscopical characterization was performed by R. and Y. Thomann (Core facility 1, FIT).

In future work optimization of the deposition method with regard to the cells' lifetime will be performed. The effect of the deposition parameters on the metal surface composition will be thoroughly investigated by XPS, SEM and surface sensitive IR measurements. Finally, the protected lithium metal coins will be combined with the GPE and cathode materials to form LMBs.

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ThermoBatS – Thermoelectric Battery Systems

Swathi Krishna Subhash[1,3], Uwe Pelz[1,3],
Harald Hillebrecht[2,3], Peter Woias[1,3]

[1]Laboratory for the Design of Microsystems, Department of Microsystems Engineering (IMTEK), University of Freiburg, [2]Laboratory for Solid State Chemistry, Faculty of Chemistry and Pharmacy, University of Freiburg; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg

Project funding: German Research Foundation (DFG) – Cooperative Research Centre 141 „Thermal energy harvesting "– Project A2

The ThermoBatS project, as a part of the thermal energy thrust in research area A, aims at harvesting this abundant and easily accessible form of energy. The final goal of the project is to develop a micro-thermoelectric generator (μTEG), capable of powering a small sensor or providing sensor signals or small amounts of continuous power to other livMatS projects. The interdisciplinary project consortium is formed from the Departments of Microsystems Engineering (Prof: Dr. Peter Woias, Dr. Uwe Pelz) and Chemistry & Pharmacy (Prof. Dr. Harald Hillebrecht). Currently one livMatS PhD student (Swathi Krishna Subhash) is working on the project since July 2019.

Within the ThermoBats project an efficient and scalable µTEG will be developed, with two different phase change materials (PCM) on both sides, acting as heat reservoirs. Thermoelectric generators (TEGs) in general are, based on the Seebeck effect, able to generate an electric voltage when subjected to a temperature difference. The integration of the µTEG together with PCMs in a µTEG-PCM stack enables the µTEG to create its own temperature difference for a short period of time, making time-dependent temperature fluctuations (e.g. by the daylight cycle) accessible for the harvester.

The first part of the project is dedicated to the development of high-quality nanostructured thermoelectric materials. As extensive studies in this area have been published in literature during the last decade, the project is focused on identifying and using recipes from existing literature on larger scale chemical synthesis and mechanical alloying to produce nanomaterials. Two different materials will be evaluated during the project, BiSb-based alloys and Bi_2Te_3-type alloys.

The second part of the project involves formulation of printable inks and dispersions using sonication or high energy ball milling to be able to print n- and p- type thermoelectric (TE) materials and later PCMs and electrical contacts. Additives and solvents added during ink fabrication have to be removed after printing in order to regain the materials electrical conductivity. This requires precise process control and the development of a multi-step cleaning process.

The fabrication of µTEGs (part three) will involve forming the functional structures out of TE material as well as PCM deposition and formation of electrical contacts. For TE-structure formation, suitable substrates like 3D-printed hollow structures or polymer foam with low thermal conductivity will be evaluated. PCB-based substrates with laser machined holes are currently investigated in a parallel project. After the printing process, hot pressing or electro sintering will be employed to increase the density of the TE structures and to reduce their electrical resistance. The contact structuring and PCM addition will be done by different printing methods like screen printing or dispenser printing. Figure 1 shows the sketch of the envisioned µTEG-PCM stack with substrate and electrical contacts. The final structure will be packed in an insulated polymer foam to reduce parasitic thermal conduction.

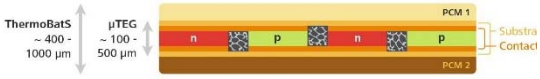

Fig. 1: ThermoBatS µTEG-PCM stack consisting of PCM reservoirs on top (light beige) and bottom (brown), thermally conductive substrate material (beige), contact pads (orange), TE material (red and green) and a thermally insulating polymer foam (gray). © IMTEK/Laboratory for Design of Microsystems

The fourth part of the project is dedicated to the development and demonstration of ThermoBatS as self-sustained assemblies with advanced functionalities. For this process we use low power step-up and power management electronics already developed by the Woias group [1] as well as low energy communication in combination with small energy storage devices. The potential applications include auto-triggered short wireless operation, triggered operation via mechanical or electrical impact and actuator operations.

Presently, the first part of production of thermoelectric nanomaterials and the second part involving the development of ink dispersion is being investigated. Two types of materials are being investigated: $Bi_{0.5}Sb_{1.5}Te_3$ as p-type and $Bi_2Te_{2.7}Se_{0.3}$ as n-type TE material. The provision of these materials in nanosized form is of prime importance as this does not only improve the material quality but is also a requirement for stable and printable dispersions. For the fabrication of the TE materials in a nanosized form, mechanical alloying by high energy ball milling is employed. This method uses friction and impact between steel balls, container wall and elemental powder to fabricate TE alloys from the respective elements. The produced TE nanopowders shows a homogenous dispersion and is reproducible and scalable.

For the formulation of printable TE inks two methods are evaluated. Again, high energy ball milling was used for mixing TE material with ethylene glycol as a solvent without any additives. The solvents have to be carefully selected in order to be easily removed after the printing process. Most additives operate on two principles: steric stabilization or charge stabilisation. Our focus will be small molecule additives with charge stabilisation, so that they can be easily removed from the system. The ink produced by this process showed a homogenous dispersion and was found to be stable for about one week. Further studies showed that sonication can help to remove aggregation and improves the quality of the ink. However, stability has still to be further improved so that an ink can be stored and reused within a required period of time.

Alternative preparation methods like bath sonication, magnetic agitation and ultra-sonication are being researched, together with studies on the stability and viscosity of different ink preparations.

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Adaptive lenses based on conductive and optically transparent silver nanowire networks

Stefan Schierle, Peter Woias,
Frank Goldschmidtboeing

University of Freiburg, Department for
Microsystems Technology, Laboratory for
Design of Microsystems

Project funding: German Research Foundation (DFG) – GO 1686/4-2

The project aims to develop a technology for depositing and structuring transparent, electrically conductive and optically transparent silver nanowire networks on thin silicone sheets by lithographic means. This novel technology will be used for fabricating electrostatically actuated adaptive lenses.

The silver nanowires are homogenously spread on thin silicone sheets by doctor blading that allows the alignment of the wires in two perpendicular directions as shown in Fig. 1.

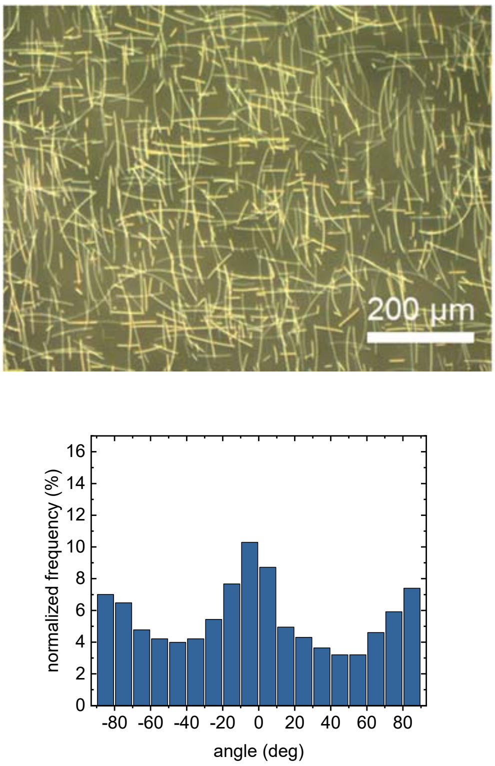

Fig. 1: Photograph and histogram of wire directions of a silver nanowire network. © IMTEK/Laboratory for Design of Microsystems

These networks show a high optical transparency, while still having a reasonably high electrical conductivity, i.e a sheet resistivity of less than 30 Ω/sq can be achieved while having an optical transparency of more than 90% at a wavelength of 550 nm [1]. Fig. 2 demonstrates this feature.

While similar results for aligned nanowire networks have been achieved by different groups all over the world [2-4], the patterning of the conductive layer with critical dimensions in the sub millimetre range on silicone substrates is still an open question. The most promising method developed during this project consists of (1) spinning a photo resist onto the silver nanowire network, (2) patterning the resist by photo lithography, (3) etching the nanowires in the open areas by Fe_2O_3 and (4) removing the resist. A U-turn of a 500 µm wide meander is shown in Fig. 3. A further reduction in critical dimension ca be achieved by optimizing the lithography step.

Fig. 2: Photograph of the FIT logo through a silicon foil with a structured nanowire network. © IMTEK/Laboratory for Design of Microsystems

Future work will focus on developing and characterizing sensor and actuator [5,6] functions realized by using this novel technology, with the finial goal of incorporating these elements into an electrostatically actuated adaptive lens.

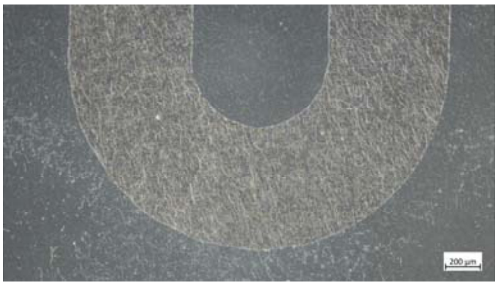

Fig. 3: Micrograph of a structured silver nanowire sheet. © IMTEK/Laboratory for Design of Microsystems

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Development of SolStore devices to harvest and store electrical energy

Birgit Esser,[1,2,3] Robin Weßling,[1,3] Anna Fischer,[2,3,4] Jan Büttner,[3,4] Taissia Berestok,[3,4] Uli Würfel,[2,3,5] Rodrigo Delgado,[2,3] Stefan Glunz,[3,6] Christian Diestel,[3,6] Harald Hillebrecht,[2,3,4] Ines Ketterer,[3,4] Ingo Krossing,[2,3,4] Christian Elsässer,[2,3,7] Wei Wei,[3,7] Julian Gebhardt,[7] Michael Moseler,[7] Michael Walter[3,7] Mejdeddine Mokhtar[3]

[1]Institute for Organic Chemistry, University of Freiburg; [2]Freiburg Materials Research Center (FMF), University of Freiburg; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [4]Institute for Inorganic and Analytical Chemistry, University of Freiburg; [5]Fraunhofer ISE, Freiburg; [6]Department of Sustainable Systems Engineering (INATECH), University of Freiburg; [7]Fraunhofer IWM, Freiburg

Project funding: German Research Foundation (DFG) – livMatS Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems" – Project A-1

This cooperative project tackles the development of highly integrated solar-charging energy devices, including solar batteries and solar capacitors, which are able to harvest and store solar energy from their surroundings. To realize such self-charging electrochemical devices at high levels of integration (mode II or mode III with three or two electrodes, respectively), photo-charging electrodes will be developed, which combine the function of energy harvesting and storing in one material system. As such, this project will combine intensive material development (simulation and synthesis), material characterisation and testing as well as device fabrication, simulation and optimization and require a large team of experts with complementary expertise.

Fig. 1: Interplay of Research Areas in *liv*MatS. © *liv*MatS/ Daniel Hellweg

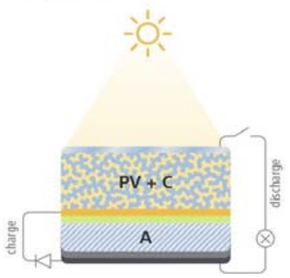
Two types of photocharging electrode systems have been identified: a) donor-acceptor bulk-heterojunctions of tailored conjugated polymers (organic Solstore – oSolstore) and b) inorganic semiconductors with suitable hole- and electron-extraction layers (inorganic Solstore - iSolstore). The working principles of both systems are depicted in Figure 2.

Organic photo-charging batteries – Organic SolStore

The goal of this research project is to develop an integrated photo-charged organic battery, where charge generation and storage occur in the same material. Organic solar cells (OSCs) are based on so-called bulk-hetero-junctions (BHJs), where a donor and an acceptor material form an interpenetrating network. Upon photoexcitation, a fast electron transfer occurs at their interface, after which the hole (electron) is transported through the donor (acceptor) phase to the respective electrode. In an organic battery, p- or n-type redox-active polymers are typically employed as electrode-active material. To achieve a fully integrated photo-charging organic battery, the combination of a BHJ solar cell and an organic battery is targeted in this project (Fig. 2a). The organic BHJ layer will both efficiently generate charge carriers as well as store the photo-generated holes in the donor material. We aim at developing organic polymers, which can function both as a donor material in a solar cell and store charge after oxidation (PI: Esser). Modelling of electronic (redox-) and optical properties will aid the design of novel organic absorber materials (PIs: Moseler, Walter). These will be used to fabricate organic solar batteries incorporating an electrolyte layer (PI: Würfel). To ensure both efficient charging as well as power output to an external consumer, the absorber layer will be contacted on both sides. The porous and permeable electron-conducting layer at the bottom side serves for charging, i.e. to extract photo-generated electrons (PI: Fischer). When the stored energy is required by an external circuit, photo-generated holes will be extracted at the top contact, while electrons are extracted from the battery anode. Suitable electrolytes with high stability in light will be developed (PI: Krossing). The BHJ layer will be equipped with a continuous porous structure to allow for permeation with electrolyte solution for charge balancing (PI: Fischer). To store electrons, porous anode materials with a suitable reduction potential will be developed (PIs: Hillebrecht, Fischer).

Inorganic photo-charging battery – Inorganic SolStore

This project aims at coupling a perovskite solar cell (PSC) to an internal electrochemical storage unit (battery or capacitor) in integration modes II and III (Fig. 2b). Lead halide perovskites (ABX_3, e.g. with A = methylammonium, B = Pb and X = halides as I or Br) exhibit high optical absorption and excellent carrier transport properties with conversion efficiencies of more than 20%. The choice of the hole-conducting electrode and substitution of the toxic lead by less toxic elements are ongoing challenges (Research Area D, sustainability). Yet, simple solvent-based processing makes PSCs an excellent candidate for integrated multifunctional systems to be assembled by printing technologies. In addition, $APbX_3$ perovskites can store charges reversibly in a battery by Li^+-incorporation, dependent on the type of perovskite and the cut-off voltages used. It is not clear, however, whether and to what extent the storage results from a reversible intercalation of Li^+/Na^+ or from a conversion to a lead-containing intermetallic compound. Recently published research demonstrates, however, that a perovskite material may be conceived as true bifunctional material, combining the function of photogeneration of charge carriers and charge storage in one single active layer.


(a) Organic SolStore

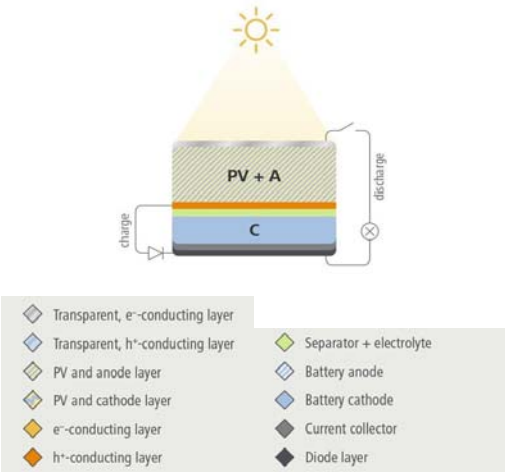

(b) Inorganic SolStore

Fig. 2: Schematic of solar batteries at the highest integration level, with energy conversion and storage in the same material. (a) Organic SolStore, (b) Inorganic SolStore. © livMatS/Daniel Hellweg

The tasks and aims of this project are the combination, optimization and integration of novel perovskite materials for both solar-energy conversion and electrochemical storage into various new devices (mode II or mode III) to obtain energy-autonomous systems. Regarding mode II, the projects aims at developing solar capacitors based on the coupling of perovskites solar cells and suitable (pseudo)supercapacitors (PIs: Glunz, Fischer) in a monolithic fashion. Regarding mode III, the goal of the project is to develop solar batteries with truly bifunctional photoelectrodes. Theoretical modelling and computational simulation of properties of ions and electrons at the atomic scale will be performed in order to identify and understand suitable bifunctional perovskite absorber and intercalation materials as well as their interphases and interfaces to electrolytes (PIs: Elsässer, Walter, Moseler). Structurally promising phases will be synthesized (PI: Hillebrecht) and characterized photoelectrochemically (PI: Fischer), and perovskite absorbers will be realized based on solution processing and evaporation, together with a characterization of their optical and electrical properties (PI: Prof. Stefan Glunz). Suitable counter electrodes with adjusted potentials for charge storage will be developed (PIs: Fischer, Hillebrecht, Krossing). Electrolytes will be tailored in order to adjust the battery cathode materials (PI: Krossing). Overall device fabrication will rely on – and expand – existing fabrication know-how (PI: Glunz) using, for example, supply electrode configurations based on sputtered or evaporated layers. Final print processed device fabrication will be realized in cooperation with all groups at the 2D- and 3D-printing core facility located at FIT.

Fluorine Doping – A Tool to boost the PEC Water Oxidation Performance of $BiVO_4$ and $Mo:BiVO_4$ Thin Film Photoanodes

Martin Rohloff[1,2,3], Björn Anked[4], Olga Kasiane[5], Siyuan Zhange[5], Martin Lerch[4], Christina Scheue[5], Anna Fischer*[1,2,3]

1 Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg; 2 Institute of Inorganic and Analytical Chemistry (IAAC), University of Freiburg; 3 Freiburger Materialforschungszentrum (FMF), University of Freiburg; 4 Institute of Chemistry, Technical University Berlin; 5 Max-Planck-Institut für Eisenforschung GmbH

Project funding: German Research Foundation (DFG) – Priority Program 1613: “Fuels Produced Regeneratively Through Light-Driven Water Splitting: Clarification of the Elemental Processes Involved and Prospects for Implementation in Technological Concepts”

In consideration of the rising global energy demand and the environmental concerns raised by fossil fuels combustion, the production of clean and renewable fuels has become increasingly essential. Because of its high energy density (142 MJ/kg) and emission free combustion, hydrogen is one of the most promising alternatives to fossil fuels and hence, in the context of a sustainable hydrogen economy, its CO_2-emission free production is crucial.

In that context, photoelectrochemical (PEC) water splitting represents one elegant way for sustainable hydrogen production. One way to achieve photoelectrochemical water splitting is to couple a semiconductor photoanode with a suitable counter electrode. Sunlight, the most abundant renewable energy source, is thereby absorbed by the semiconductor photoanode yielding a photovoltage, which allows the oxidation of water at the semiconductor electrolyte interface, while hydrogen is produced at the counter electrode. Semiconductor materials that absorb a sufficient portion of solar light ($E_g \approx 2.1$ eV), separate and transport light-induced charge carriers efficiently, have suitable valence band and conduction band positions with respect to the water oxidation and proton reduction reactions, and that are stable in aqueous media under illumination are highly desired for the development of efficient PEC water splitting devices. In this context, especially the development of well-performing photoanodes for the water oxidation half reaction is an extensively investigated research subject.

Since Kudo et al. discovered the ability of $BiVO_4$ to oxidize water under illumination with visible light [1], $BiVO_4$ has become one of the most investigated photoanode materials for PEC water oxidation because of its manifold beneficial materials properties as well as for its economic characteristics like its high earth-abundance and its reasonable price. [2,3]

Low conductivity has been identified as the main PEC limiting factor for $BiVO_4$. [4] This problem can be overcome by doping $BiVO_4$ for instances with molybdenum thereby increasing the amount of free charge carriers within the material. [5] While cation doping has been widely explored for $BiVO_4$, anion doping / substitution is by far less explored.

In the present cooperative project, we have investigated different synthesis and doping strategies to improve the photoelectrochemical water oxidation activity of $BiVO_4$ photoanodes, as summarized in our recent review paper. [6]

Amongst others, we have investigated the effect of fluorine incorporation on the PEC water oxidation performance of $BiVO_4$ and $Mo:BiVO_4$ thin film photoanodes. In a first step, $BiVO_4$ and $Mo:BiVO_4$ thin films were prepared according to our recently developed molecular precursor approach. [5] In a second step, fluorine was incorporated into the $BiVO_4$ and $Mo:BiVO_4$ thin films using of our recently developed solid-vapor approach for the F-doping of $BiVO_4$ powders [7] with adjusted fluorination conditions to thin films.

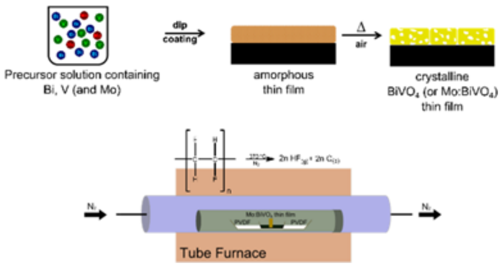


Fig. 1: Synthesis scheme for $BiVO_4$, Mo:$BiVO_4$ thin films with subsequent fluorination procedure. (Reprinted with permission ACS Appl. Mater. Interfaces 2019, 11, 18, 16430-16442, Copyright 2020 American Chemical Society)

The obtained fluorine-containing $BiVO_4$ and Mo:$BiVO_4$ thin film photoanodes (F:$BiVO_4$ and F/Mo:$BiVO_4$) were characterized extensively by different characterization methods. X-ray diffraction in grazing incidence mode (GI-XRD) proved the monoclinic scheelite crystal structure to remain unchanged upon fluorination, while x-ray photoelectron spectroscopy (XPS) revealed the presence of fluorine in both Mo-free and Mo-doped $BiVO_4$ thin film photoanodes. UV/Vis spectroscopy demonstrated a slight shift of the light absorption onset to larger wavelengths induced by fluorination indicating a slight decrease of the optical band gap. Investigations of the photoanodes morphologies by scanning electron microscopy revealed a slight sintering of the photoanodes nanostructures, resulting from the additional heat treatments coming along with the fluorination procedure.

To investigate the effect of fluorine incorporation on the photoelectrochemical properties for water oxidation, the pristine and fluorinated $BiVO_4$ and Mo:$BiVO_4$ thin film photoanodes were investigated regarding their PEC performance. Our measurements revealed that F-modification had a positive effect on the PEC water oxidation performance before (Figure 1a and b) and after surface functionalization of the photoanodes with CoPi, a water oxidation catalyst [8] (Figure 1c and d).

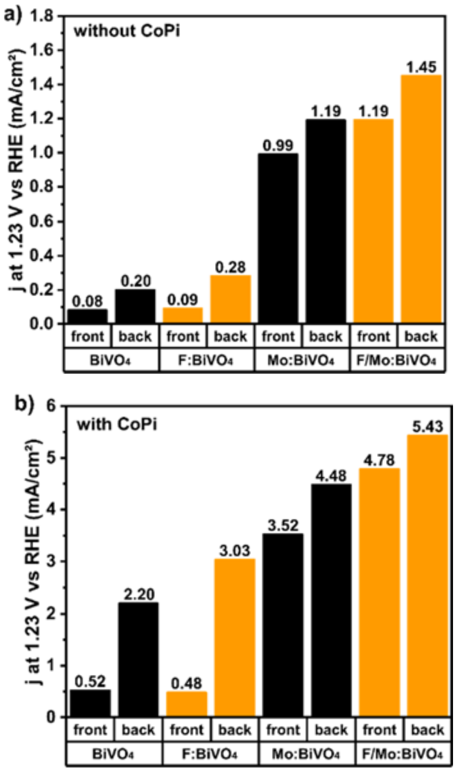


Fig. 2: Overview of photocurrent densities @ 1.23 V vs RHE in frontside and backside illumination for BiVO4, Mo:BiVO4 thin film photoanodes and their fluorinated counterparts without (a) and with (b) CoPi surface modification (Adapted with permission ACS Appl. Mater. Interfaces 2019, 11, 18, 16430-16442, Copyright 2020 American Chemical Society).

In order to gain more insights into the effect of fluorination on the PEC performance, the surface catalysis efficiency (or charge injection efficiency) η_{cat} as well as the charge separation efficiency η_{sep} have been determined for $BiVO_4$, F:$BiVO_4$, Mo:$BiVO_4$ and F/Mo:$BiVO_4$ photoanodes. Our results reveal that fluorine incorporation predominantly enhances the surface catalysis, i.e. the aptitude of the fluorinated semiconductor surface to oxidize water, while the charge separation efficiencies remain nearly unchanged by fluorine incorporation.

In summary, the improvement by fluorine incorporation of the PEC performance of both $BiVO_4$ and Mo:$BiVO_4$ photoanodes could be ascribed to an improvement of the catalytic efficiency for water oxidation as well as to a slight decrease of the optical band gap, i.e. a slightly improved light harvesting. Additionally, as demonstrated by us previously, [7] Mo-doping in $BiVO_4$ results in an improved conductivity, a slight band gap decrease and, in turn, in an improved charge separation.

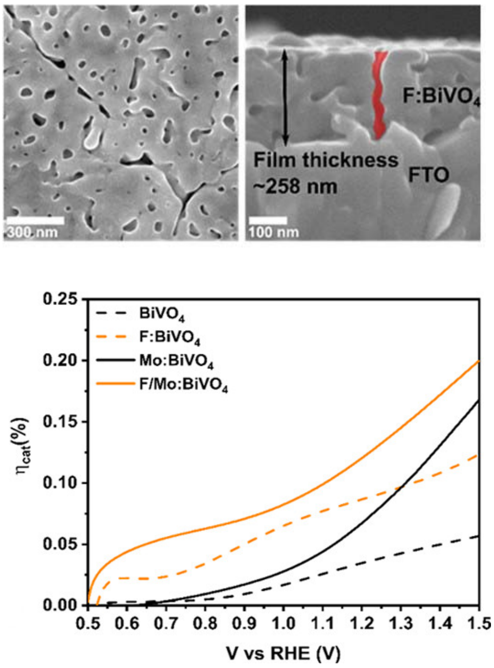


Fig. 3: SEM image (top view and cross-section) of $F:BiVO_4$ (top) and plots of charge injections efficiencies versus applied potential (bottom) for $BiVO_4$, $Mo:BiVO_4$ and their F-modified counterparts. (Adapted with permission ACS Appl. Mater. Interfaces 2019, 11, 18, 16430-16442, Copyright 2020 American Chemical Society)

Combining both cationic (molybdenum) and anionic (fluorine) dopants in this study, we could reveal that anion and cation co-doping in $BiVO_4$ allows combining the PEC relevant benefits associated to each type of dopant, making anion and cation co-doping a promising strategy to improve the PEC performance of ternary photoanodes in general.

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Future Topic “Societal Challenges“

The development of materials systems with life-like functions and properties is scientifically accompanied within the cluster of excellence “Living, Adaptive and Energy-autonomous Materials Systems“ (*liv*MatS) with regard to its social implications. Philosophy, psychology and sustainability assessment play a crucial role in this context.

Cognitive-Affective Mapping (CAM): Predicting Acceptance and Bridging the Gap between Science and Society

Sabrina Livanec[1,2], Lisa Reuter[1,2], Oliver Müller[1,3], Michael Stumpf[1,2], Andrea Kiesel[1,2]

[1]Cluster of Excellence *liv*MatS, University of Freiburg; [2]Institute of Psychology, University of Freiburg; [3]Department of Philosophy, University of Freiburg

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In this project we develop a new method that 1) allows to predict the acceptance of not yet existing technologies and 2) can be used as a communication tool to foster mutual exchange between scientific and non-scientific stakeholders. This new method will be derived from the concept of Cognitive-Affective Mapping (CAM) [1].

The project is carried out as part of Research Area D “Sustainability and Societal Implications” of the Cluster of Excellence “Living, Adaptive and Energy-autonomous Materials Systems” (*liv*MatS). The materials systems to be developed in *liv*MatS will have lifelike properties. For example, they will be able to adapt to changes in their environment, protect or repair themselves, be durable and mobile, and supply themselves with energy autonomously. The novel technologies envisaged by *liv*MatS can help to identify solution approaches to urgent issues of the present, such as climate change and the question of how people can live more sustainably. But these approaches can only show their full potential if they are accepted by society. An early acceptance prediction is needed.

Classical acceptance research only applies at a rather late stage of the research and development process, when a prototype already exists or can at least be simulated. Here, we develop a method that will allow an acceptance estimation and initiate a societal and ethical reflection already at an early stage of the research process.

Our work builds upon the concept of CAM. Originally, CAM is a method to visualize an individual’s or a group’s belief system towards a given topic as a network of interacting concepts. CAM depicts not only the cognitive representations underlying a belief system. It also provides insights into the affective connotation associated with each concept. Furthermore, CAM shows the influence of different concepts on one another.

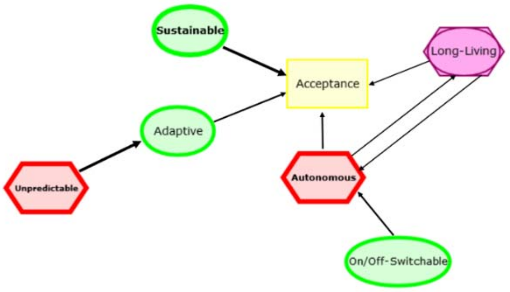

Fig. 1: With the adapted and refined CAM method, interactions and interdependencies between attributes can be considered. Example: The attribute “autonomous” can have a strongly negative connotation, e.g. in the case of autonomous façade shading. However, people might assess the attribute “autonomous” less negative, if there is a master switch, i.e. if people feel they keep control of the technical system. © Cluster of Excellence “Living, Adaptive and Energy-autonomous Materials Systems (livMatS)

We want to use CAM as a means to predict societal acceptance towards new materials systems. Our research is based on two assumptions: First, we assume that novel lifelike materials systems can be characterized by basal attributes. Basal attributes are adjectives describing the properties of the materials systems. Second, it is possible to predict acceptance on the basis of a cognitive-affective assessment of these basal attributes.

We generate a list of adequate basal attributes using qualitative interviews with *liv*MatS researchers and quantitative online questionnaires with experts and laypeople. The basal attributes obtained in this way, serve as building blocks for the cognitive-affective maps. In empirical studies we instruct people to create their individual CAM with prescribed basal attributes against the background of an exemplary scenario with a new living materials system. We also investigate instruction and aggregation methods for this.

With our studies we expand the spectrum of methodological instruments in the field of acceptance research. Moreover, we propose to use the CAM method as a tool to mediate between scientific and non-scientific stakeholders. CAM can help stakeholders to exchange information about the background, hopes, concerns, opportunities, and risks of new, potentially disruptive technologies. The CAM method can also support science communicators with pre- and post-processing of multidirectional communication interventions.

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Tiered Approach for Prospective Assessment of Benefits and Challenges (TAPAS)

Rainer Grießhammer[1,2],
Martin Möller[2,3]

[1] Faculty of Environment and Natural Resources of the University of Freiburg; [2] Cluster of Excellence *liv*MatS @ FIT Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg and [3] Öko-Institut e.V. – Institute for Applied Ecology, Freiburg

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The ultimate goal of the project is the design of a new interdisciplinary development-accompanying sustainability assessment method. It can be characterized as a heuristic-systematic approach that aims to pose the “right” questions at early stages of technology development and to develop recommendations in order to challenge, substantiate and further develop the sustainability claims of *liv*MatS.

TAPAS will act as a strategic radar and assessment methodology within *liv*MatS for the cross-cutting topic of “Resilience and Sustainability”, which will show guiding boundaries and recommend shifts to more sustainable options. Regarding the methodology’s key aspects and functionalities, TAPAS will detect existing chances and opportunities as well as challenges and possible threats that may be associated with novel living materials systems. Thus, the method serves both as an “early warning system” for less sustainable options and as an “early encouraging system” for favourable paths of innovation.

As part of the overall approach TAPAS will identify and operationalize relevant normative settings for the sustainability assessment. In particular, this refers to the 2030 Agenda with its 17 Sustainable Development Goals [1] and the concept of Planetary Boundaries [2]. Furthermore, TAPAS will also mirror ongoing transformation processes in major areas of need and identify their implications with regard to the research activities in *liv*MatS.

From the methodological point of view, TAPAS will integrate and further develop existing interdisciplinary approaches of sustainability assessments for the purpose of *liv*MatS. One of the key challenges in this context will be to develop a workable assessment framework for the new concepts, which are characterized by a low Technology Readiness Level. Therefore, an iterative approach to sustainability assessment is followed, considering e.g. toxicology and the availability of resources. The assessment begins with a qualitative investigation that is gradually refined with semi-quantitative and quantitative data in iteration steps.

Current work within the project aims to investigate which explicit and implicit assessment systems regarding sustainability issues of technology or product development processes already exist at various levels. This analysis covers general methods like PROSA – Product Sustainability Assessment – developed by the Öko-Institut [3], the SEEBalance® put forward by BASF [4] and BiSA – the Bioinspired Sustainability Assessment [5]. Furthermore, also technology-related tools like the Nano SustainabilityCheck [6] are part of the current review process.

As a first iteration step within the outlined iterative approach, the substances used in the laboratories were subjected to a hot spot analysis. It was examined whether the toxicological properties of the identified substances could lead to future restrictions on use under the European chemicals legislation REACH.

Prospectively, the methodology development will also be inspired by lessons learnt from biological evolution and fitness, and tested by existing biomimetic products, with learning from ex-post assessment improving the exante method TAPAS.

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*liv*MatS as part of and reaction to the Anthropocene: Ethical and philosophical implications of living materials systems

Philipp Höfele[1,2], Oliver Müller[1,2] and Lore Hühn[1,2,3]

[1]Department of Philosophy, University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT University of Freiburg, Germany; [3]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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The present age is increasingly characterized by terms such as the Anthropocene and the technosphere, as man and technology dominate and irrevocably permeate the entire biosphere of our planet, and thus living as well as inanimate nature [5]. At the same time, more and more technical artefacts are being produced that blur the traditional oppositions between the natural and the artificial. For example, the notion of "biofacts", coined by Nicole Karafyllis, draws attention to phenomena that no longer have a clearly recognizable boundary between the natural and the artificial [14]. Furthermore, the orientation to the natural strategies in biomimetics, and particularly in the development of "living materials systems", raises the question of the distinction between natural and artificial properties. Against this background, the philosophical-ethical project of Area D within the Cluster of Excellence *liv*MatS re-examines the relationship between nature and technology in the present age. In order to sharpen the conceptual apparatus, we first go back to the history of the philosophy of nature (a), before in a second step an evaluation of current developments in the philosophy of technology (b) and in particular the bioinspired materials systems of *liv*MatS (c) can be made. Finally, the ethical consequences and even opportunities of these developments have to be asked (d).

(a) The project first elucidates the mostly neglected prehistory of the concept of "nature" around 1800 with regard to basic natural-phil osophical concepts such as “matter”, “system”, “organism”, “function”, “adaptability”, and “autonomy” [2, 9, 8, 10]. In contrast to the bioinspired materials systems targeted by *liv*MatS, technique/technology and its artefacts are usually seen in strict opposition to nature and natural products in current philosophical debates. The use of the term technique/technology around 1800 shows, however, that the concepts of technology and technical artefacts are initially not understood in sharp contrast to the natural [12, 13]. Thus, this project re-modernizes these traditions since they can help to understand a central aim of *liv*MatS, the transfer of properties of natural entities to artificial ones.

(b) In a second step, the insights gained in the first step are confronted with current concepts in the philosophy of technology in order to supplement them with a view to properly understanding of the materials systems to be developed by *liv*MatS. The numerous approaches from the philosophy of technology [e.g. 11, 19, 1, 16, 4] are tested for their appropriateness in understanding these technical systems. They should help to understand the specific materiality and the “agency” status of life-like materials systems. In addition, the debate on process philosophy is taken up in this project [17]. On the one hand, process philosophy offers organological, holistic models that touch on current problems of part/whole relationships as well as the interaction of open systems, rejecting dichotomous positions [6, 3]. On the other hand, process philosophical approaches turn against a static concept of substance, which must be regarded as inappropriate in view of new technical materials and systems with dynamic properties [17].

(c) As a central step, the project will undertake a philosophical analysis of the bio-inspired materials systems of *liv*MatS. The aim here is to clarify the conceptual foundations with regard to a common basis of the whole *liv*MatS Cluster as well as a widespread, multi-perspective assessment of the demonstrators in terms of functionality, sustainability and societal acceptability. The properties of bio-inspired materials systems and their functions will not only change the perception of the boundaries between nature and technology, but will also influence society’s relationship to technology, as life-like technical systems will adapt to the natural and societal environment in novel ways (Fig. 1).

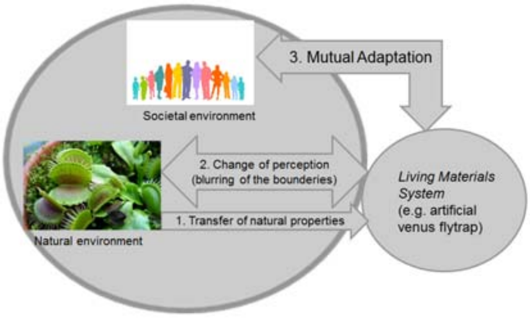

Fig. 1: Process-ontological understanding of natural and technical entities. © Department of Philosophy, Freiburg / Plant Biomechanics Group Freiburg

This aims at classifying the materials systems to be developed by *liv*MatS into the current societal discourse as well as into the present age, understood as “Anthropocene”, an epoch of the Earth, in which man is the dominant factor and integral, all-passing component of the Earth system [18, 15].

(d) The life-like materials systems should not only be understood as examples of the “Anthropocene” insofar as they stand for the biomorphic nature of technology. Rather, the materials systems should also be understood as “actors” within the “Anthropocene” insofar as they already represent a “re-action” to the “Anthropocene” and can thus provide answers to (environmental-)ethical problems of the present age. The ethical evaluation must be based on the approach of technological assessment [7]. In light of the research initiated by *liv*MatS, preference needs to be given to models that demand a new orientation of the interplay between nature and technology. Nature should not only be seen as something that must be overcome by technology. Rather, technology should be understood as an opportunity for sustainability and the preservation of nature.

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CORE FACILITY "FUNCTIONAL PROCESSING"

Polymer-based optical sensor platform with integrated light source

Jing Becker[1,2], Claas Müller[1,2]

[1]FIT Core Facility "Functional Processing", [2]IMTEK Department of Microsystems Engineering, Servicecenter Mechanische Mikrofertigung (MSC)

Project funding: Deutsche Forschungsgemeinschaft DFG (Project-ID: KO1040/22-1)

At the beginning of year 2018, a research project with the title of "Polymer-based optical sensor platform with integrated light source" has been submitted to Deutsche Forschungsgemeinschaft (DFG) and got selected at the end of the year. In this project, a planar optical sensor platform with integrated organic laser as optical light source, single-mode waveguide structures, sensor systems and organic photodiodes will be fabricated on a flexible polymer foil. A novel electrically tuned laser concept will be developed for the optically pumped organic laser source which is very important for the polymer sensor systems. In this project, in order to realize the integration purpose, novel manufacturing processes will be developed and optimized in Core Facility 2, in FIT. By applying such kind of manufacturing methods, polymer-based optical sensor platforms could be fabricated cost effectively with high precision. In this project, Core Facility "Functional Processing" will cooperate with research group Prof. Dr. Wolfgang Kowalsky (Technische Universität Braunschweig) on the topic of fabrication and investigation of polymer-based optical sensor platform with integrated light source from January, 2019.

Integrated Waveguide Structures Fabricated By CNP Process

Jing Becker[1,2], Claas Müller[1,2]

[1]FIT Core Facility "Functional Processing"; [2]IMTEK Department of Microsystems Engineering, Servicecenter Mechanische Mikrofertigung (MSC)

Project funding: Deutsche Forschungsgemeinschaft DFG (Project-ID: KO1040/22-1)

Currently, polymer based optical devices are drawing more and more attentions due to its low cost, simple processing abilities and reliability for mass production. Besides of that, polymeric materials possess a lot of unique properties such as wide spectral transparent window, high flexibility and good bio-compatibility. They can be easily processed by conventional and unconventional fabrication methods and their properties could be tuned even during the manufacturing processes. OrmoCer®s (ORganically MOdified CERamics) are inorganic-organic hybrid polymers, which are fabricated and commercially available by micro resist technology GmbH in Germany. The UV cross-linked OrmoCer®s shows very low absorption across the visible and infrared spectrum, excellent mechanical properties as well as very high chemical and thermal stabilities [1-5]. In this DFG project, one type of commercial OrmoCer® materials, OrmoCore® (refractive index = 1.539 @589 nm), was used as the core material to fabricate the ridge-type Bragg grating waveguide structures on the Cyclic Olefin Copolymer (COC) foils and silicon based rigid wafers. Such kind of Bragg grating waveguide structures can be applied in the area of optical sensing or chip integrated laser systems.

The mostly used techniques to fabricate the Bragg gratings integrated waveguide structures are two-step processes [6-9]. Such kind of two-step processes are complicated and time consuming due to the extra precise alignment demands in the second manufacturing step. Therefore, they are not suitable for mass-production with high reproducibility applications.

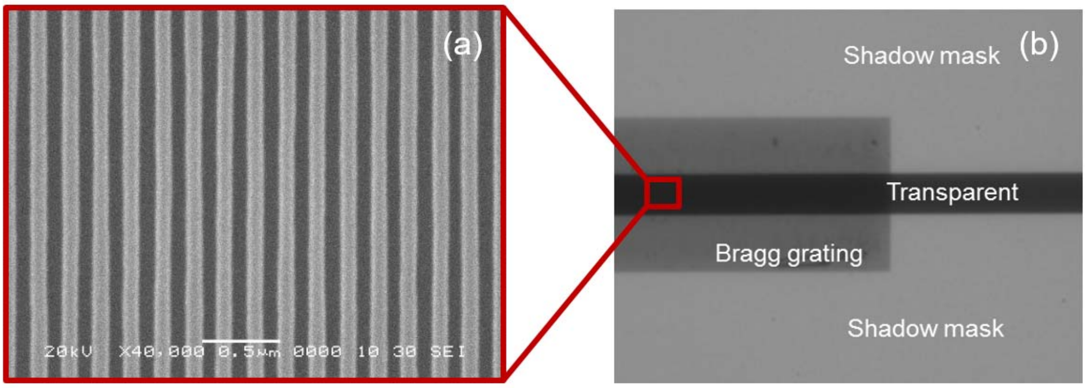

Fig. 1 (a) SEM image of stamp-mask: Bragg gratings with Λ = 205 nm and 1:1 line to space ratio, and (b) Optical micrograph of the mask-stamp structure. © Core Facility 2, FIT, Freiburg

In this project, a one-step, straightforward CNP replication process with extremely high reproducibility and high resolution was applied to fabricate OrmoCer®s based Bragg grating integrated waveguide structures on COC foils and silicon based substrates. CNP technique is a hybrid replication method. By using a UV transparent nanoimprint stamp with an integrated shadow mask, CNP process combines the benefits of the high resolution of nanoimprint and the flexibility of photolithography simultaneously. It could realize the nanometer features precisely by nanoimprint, while larger structures can be defined by the following photolithography process [10]. CNP technique is also a parallel wafer scale method where the whole wafer could be patterned simultaneously. By using this duplication method, Bragg grating integrated waveguide devices could be fabricated with high simplicity and reproducibility.

The optical micrograph of the fabricated prestructured Bragg grating with defined shadow mask is illustrated in Fig. 1. As shown in Fig. 1(b), the contour line of the shadow mask, which defined the waveguide structure formed by the deposited Cr layer had very sharp edges. The etched Bragg grating structure outside the waveguide range was completely overlapped by the Cr layer. In this way, during the CNP process, the OrmoCore® material shadowed by the Cr layer would be not crosslinked during the UV exposure and therefore could be removed during the following developing process.

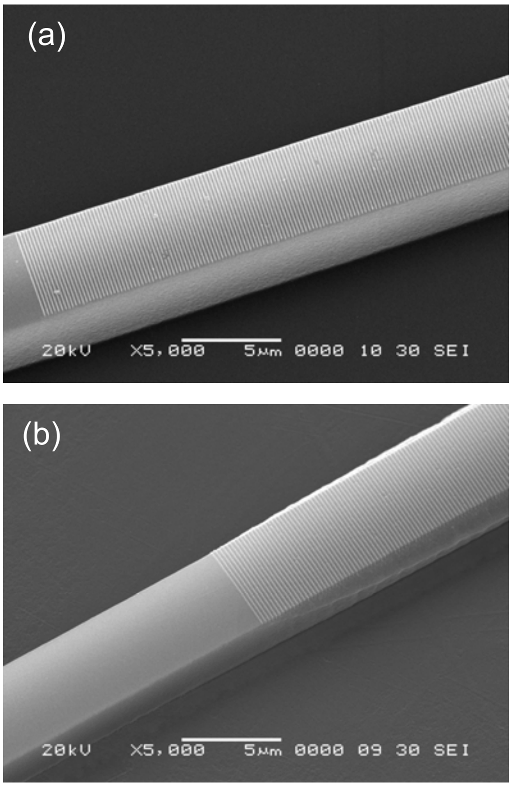

Fig. 2. SEM images of Bragg grating integrated structure structures on (a) silicon based wafer and (b) Topas® COC foil (waveguide: 5.0 μm in width and 2.5 μm in height). © Core Facility 2, FIT, Freiburg

After the fabrication of the high quality mask-stamp structures, Bragg grating integrated waveguide structures were successfully fabricated by one-step CNP process. As shown in

Fig. 2, ridge-type Bragg grating integrated waveguide structures with 5.0 µm ridge width and 2.5 µm ridge height are generated on both of the flexible COC foil and rigid silicon based wafer. As shown in the figure, due to the existence of shadow mask, no residual layer could be found outside the waveguide structures. As could be seen in the image, Bragg gratings with sharp contours were uniformly achieved on the surface of the polymer waveguide on both substrates. As explained above, during the entire imprinting process, the substrate/mask-stamp couple was kept at room temperature. This will eliminate the typical problems (such as pattern distortions or stress buildup) due to the thermal expansion mismatch of the two materials in the nanoimprint process. Therefore, independently on the substrate materials, the CNP replicated structures matched the CNP mask-stamp dimension very precisely.

Besides the SEM investigation, waveguide integrated laser source was built up by deposition of the guest-host laser active material system Alq3:DCM2 (4-(dicyanomethylene)-2-methyl-6-(julolidin-4-ylvinyl)-4H-pyran) on the top of the Bragg grating area by organic molecular beam deposition method on the silicon based wafer. The spectroscopic characterization of the DFB ridge waveguide laser is shown in Fig. 3. As shown in the figure, lasing occurred at 653.6 nm, which is in good agreement with the Bragg condition for the mode m = 1. The full width at half maximum (FWHM) of the emission peak is 180 pm @ 653.6 nm. Fig. 3 (b) summarizes the emission intensity of the organic DFB laser as a function of the pumped energy density. As shown in the figure, a clear threshold behavior can be seen with a laser threshold around 20.5 µJ/cm2.

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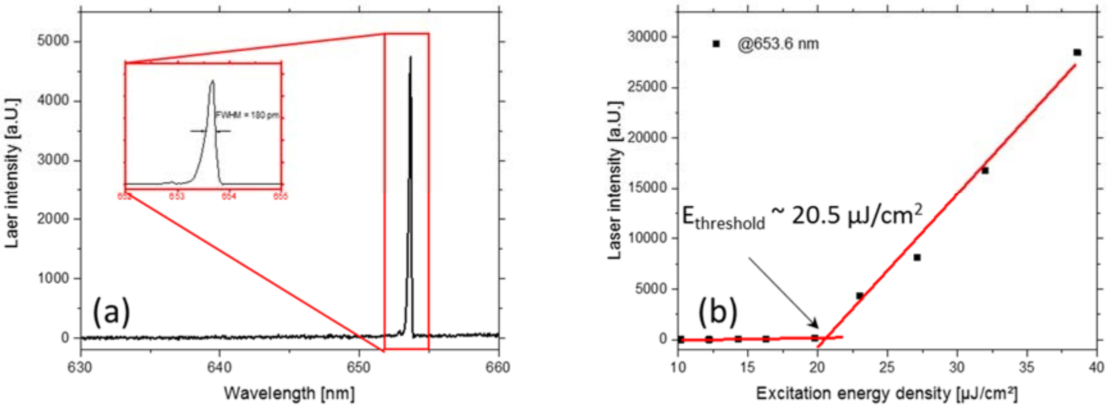

Fig. 3. (a) Laser spectrum, and (b) Lasing threshold of the waveguide type of organic DFB laser (Λ = 205 nm). © Core Facility 2, FIT, Freiburg

Core Facility "Modelling and Simulation of Materials Systems"

Dispersion forces inside the medium and vdW correction method based on self-consistent screening calculation

Shubham Sharma[1], Michael Walter[1,2,3]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [2]Fraunhofer IWM, Wöhlerstraße 11, D-79108 Freiburg; [3]Living, Adaptive and Energy-autonomous Materials Systems (*liv*MATS)

Project funding: German Research Foundation (DFG) - WA 1687/10-1

Van der Waals (vdW) interactions are ubiquitous in nature. They play a vital role in defining the structure, stability, and function for a wide range of molecules. Thus, the accurate description of vdW interactions is essential in understanding of many biological, chemical, and (hard & soft) condensed matter. Long range vdW interactions also play a major role in case of large polymer units and in macromolecular protein units.

Common approximations within density functional theory (DFT) miss these interactions, however. To describe the vdW interactions correctly Tkatschenko and Scheffler proposed a TS-vdW Method (TS09) in 2009 [1]. This method computes the vdW energy of atoms in molecules using the self-consistent ground-state electron density and thus takes changes in the atoms due to chemical interactions into account.

The TS approximation assumes that dispersive contributions are absent in the exchange-correlation functional approximation (here PBE [2]), such that these can be applied as a correction. The total energy is written as

$$E = E_{\mathrm{PBE}} + w_s E_{\mathrm{vdW}} \qquad (1)$$

where E_{PBE} is the PBE energy and E_{vdW} is the TS correction. We have introduced an additional weight factor w_S that will allow to incorporate electrolyte effects into the dispersive contributions as discussed below ($w_s = 1$ for interactions in vacuum).

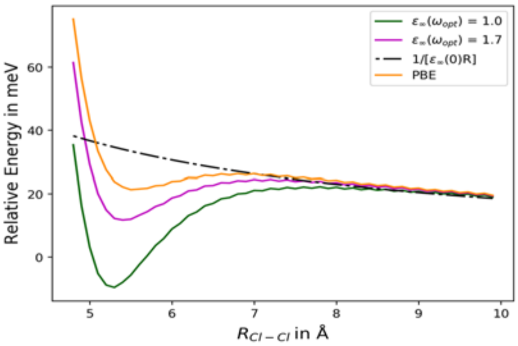

Fig. 1: The relative energy of two ClO-4 anions as a function of the distance between their chlorine atoms, RCl-Cl, where the separated anions define the energy reference; ε(ωopt) = 1 with full van der Waals (vdW) corrections and ε(ωopt) = 1.7 with scaled vdW corrections. (© Functional Nanosystem, Freiburg)

We have studied self-organization of molecular ions on gold surfaces in collaboration with our experimental collaborators from the University of Leuven/Belgium [3]. We continue this work in collaboration with the modelling group of G. Kahl/Vienna [4].

During these studies, we observed an unexpected effect in the interaction of two perchlorate anions (used as counter-ions in the experiment). We model the presence of the aqueous environment by our continuum solvent model [5]. The potential energy in dependence of their distance as shown in Fig. 1 for different approximations for the total energy in Eq. (1). As expected, the potentials follow the screened electrostatic repulsion $[\varepsilon_\infty(0)R_{Cl\text{-}Cl}]^{-1}$ for large distances $R_{Cl\text{-}Cl}$, where $\varepsilon_\infty(0) = \varepsilon_r$ is the static relative permittivity of water. There is a slight attractive part in the potential around $R_{Cl\text{-}Cl} \cong 5.2$ in the PBE potential that leads to a very shallow local minimum. Including the full dispersion contribution [w_s= 1] this local minimum substantially deepens and even becomes the total minimum of the potential. An attractive contribution to the potential is not to be expected for the interaction of two anions and needs further discussion. We suspect an overestimation of dispersion interactions by treating them as in vacuum without considering screening through the electrolyte.

We determine an approximation of the missing screening effect by the electrolyte by considering the Casimir Polder integral determining the coefficient for vdW energy calculation. This is defined as

$$C_6 = \frac{3}{8\pi^2\varepsilon_0}\int_0^\infty \alpha_A(i\xi)\alpha_A(i\xi)\phi(i\xi)d\xi \qquad (2)$$

where $\alpha_{A,B}(i\xi)$ are the frequency-dependent polarizability of the interacting molecules or atoms A and and ϕ is determined by propagation of the electric field through the embedding medium (with ϕ = 1 in vacuum). In the simplest model [] we may write $\phi(i\xi) = \varepsilon^{-2}(i\xi)$ with the frequency dependent relative permittivity of the electrolyte ε. The effects of the electrolyte on the polarizabilities $\alpha_{A,B}(i\xi)$ should, at least partly, already be included in the TS09 description through the effective atomic polarizabilities derived from the self-consistent electron density calculated within the electrolyte. What is left is the effect of the permittivity entering through the function $\phi(i\xi)$ in Eq. (2). We assume that the main contribution is at the resonance frequencies of $\alpha_{A,B}$, which are in the optical region for usual molecules. We further assume that $\varepsilon(\omega_{\mathrm{opt}})$ is approximately constant in this frequency region, such that we may pull $\phi = \varepsilon^{-2}(\omega_{\mathrm{opt}})$ out of the integral. This factor scales the C_6 coefficient and therefore the vdW contribution. This approach reduces considerably the depth of the suspiciously deep minimum as seen in Fig. 1 such that only a shallow local minimum remains similar as with the PBE potential as expected.α

molecule	Literature value	Our TS12 calculation
N_2	$\alpha_{\parallel} = 16.1$, $\alpha_{\perp} = 9.8$ ($\alpha_{\mathrm{iso}} = 11.9$)	$\alpha_{\parallel} = 16.37$, $\alpha_{\perp} = 8.95$ ($\alpha_{\mathrm{iso}} = 11.43$)
O_2	$\alpha_{\parallel} = 15.45$, $\alpha_{\perp} = 8.16$ ($\alpha_{\mathrm{iso}} = 10.59$)	$\alpha_{\parallel} = 14.33$, $\alpha_{\perp} = 7.59$ ($\alpha_{\mathrm{iso}} = 9.84$)
H_2	$\alpha_{\parallel} = 6.28$, $\alpha_{\perp} = 4.86$ ($\alpha_{\mathrm{iso}} = 5.33$)	$\alpha_{\parallel} = 5.93$, $\alpha_{\perp} = 3.35$ ($\alpha_{\mathrm{iso}} = 4.21$)
F_2	$\alpha_{\mathrm{iso}} = 7.83$	$\alpha_{\mathrm{iso}} = 7.59$
CO	$\alpha_{\mathrm{iso}} = 13.18$	$\alpha_{\mathrm{iso}} = 13.21$
NH_3	$\alpha_{\mathrm{iso}} = 14.19$	$\alpha_{\mathrm{iso}} = 13.85$
C_6H_6	$\alpha_{\mathrm{iso}} = 67.21$	$\alpha_{\mathrm{iso}} = 67.20$

Table 1: Polarizabilities along the molecular axis $\alpha_{\parallel}$, perpendicular $\alpha_{\perp}$and averaged α_{iso} as calculated with self-consistent screening Method (TS12) compared to the literature. All values in atomic units.

The TS09 method lacks the long-range electrostatic screening, which would be influential in long chain polymers and large protein units. Improving on TS09, Tkatschenko and Scheffler proposed the self-consistent screening method (TS12) in order to include the long-range screening effect [6]. The polarizabilities entering Eq. (2) are determined though the self-consistent screening equation

$$\alpha_A = \alpha_A^{\mathrm{TS09}} + \alpha_A^{\mathrm{TS09}} \sum_{B \neq A} \tau_{AB}\alpha_A \qquad (3)$$

where τ_{AB} is the dipole interaction tensor between atoms A and B, and α_A^{TS09} is the polarizability from the TS09 approximation. The self-consistent polarizabilities computed with TS12 method (Eq. 3) become anisotropic and are in good agreement to reference values from the literature as compared in table 1.

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DFT Study: Donor-Acceptor (D-A) Torsional Springs on DPP for Force Sensing and Stress Imaging

Wafa Maftuhin[1], Michael Walter[1,2,3]

[1]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [2]Cluster of Excellence livMatS @ FIT; [3]Fraunhofer IWM, Wöhlerstraße 11, D-79108 Freiburg

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Smart materials, which transform their properties due to an external stimulus in a selective and predictable way, are currently attracting interest because of their broad potential application in information technology, optoelectronic, sensing and energy-related topics [1]. Mechano-responsive polymers transform their properties drastically upon exposure to mechanical stress, which can be used to image stress or strain [2], switch reactivity [3] or to bias distinct reaction pathways [4] that are otherwise difficult to access.

One of the most prevalent mechanochromic system is the spiropyran/merocyanine system (SP/MC) [2] as documented in FIT reports 2016 and 2017. This system relies on homogeneous or heterogeneous bond scission and therefore shows intrinsic limitations that are typically related to their two-state nature and the associate barrier between the two forms [2,5]. Explicitly, SP derivatives experience further disadvantages of being temperature-labile, which disallows melt processing and therefore broad applicability. SP derivatives also show photo bleaching which generally limits long-term stability. For many applications related to biological systems, robotics, the development of high-performance materials or fundamental investigations, a barrierless mechanochromic system with fast and direct response and full reversibility would grasp significant advantages. For mechanochromic systems that rely on bond breaking, forces on the order of several hundred pN to a few nN are frequently needed. To this end, strain induced conformational changes of single conjugated polymer chains keep an intriguing concept that has been shown to amplify emission for extremely weak strains and forces as low as 300 fN [6].

The present study is concerned with the development of the concept of donor-acceptor (D-A) torsional springs for force sensing and stress imaging. The central component of such a spring is a covalently linked donor-acceptor dyad exhibiting a large dihedral angle in its equilibrium geometry. The application of force by appropriate covalent linkage to a polymer chain/matrix, then allows force-induced planarization of the D-A system, leading to increased electronic interaction that is expected to lead to a change in the visible spectrum.

Our experimental collaborators, the group of Prof. Michael Sommer in Chemnitz, designed a suitable covalent D/A system with diketopyrrolopyrole (DPP) as the acceptor and two phenyl groups as donor groups. We consider the case that the external force acts at two configurations, one with ortho-ortho pulling direction (o-DPP) and one with meta-meta pulling direction (m-DPP) as depicted in Fig. 1.

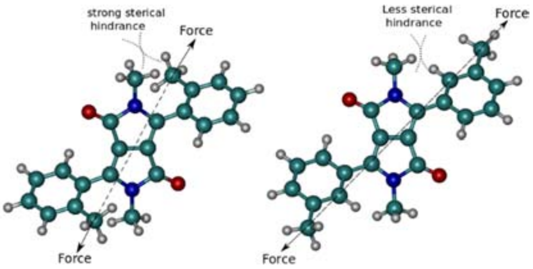

Fig. 1. Structures of diketopyrrolopyrole (DPP) by pulling ortho-ortho direction (left) and meta-meta direction (right) (© Functional Nanosystems Group).

We model the structures within density functional theory (DFT) as implemented in the GPAW package [7], where the exchange correlation potential is modeled as devised by

Perdew, Burke and Ernzerhof [8]. Our DFT calculations show that the lowest energy structures of ortho (o-DPP) and meta DPP (m-DPP) are different due to the steric hindrance between the methyl group in case of o-DPP (see figure 1). This leads to an o-DPP equilibrium geometry with a large dihedral angle (~59°) while m-DPP has less steric hindrance leading to a lower dihedral angle (~31°).

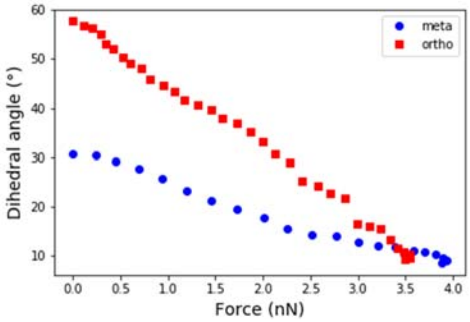

Fig. 2. Change of dihedral angle by external force for m-DPP (blue circle) and o-DPP(red square) (© Functional Nanosystems Group).

In order to explore the action and effects of an external force on the molecules, we use the method of constrained geometries to simulated external force (COGEF), where the energy path $U(d)$ that depends on the external parameter d appears. This potential is universal in the external force F and is obtained via relaxation of all degrees of freedom except one [5,9]. The parameter d is chosen as the distance between the two atoms in the structure where the external force is thought to act. The parameter d is then stepwise increased until the weakest bond breaks. There is a unique external force $F(d)$ associated to each length d, which can be determined from the derivative $\delta U/\delta d$ or from the forces acting on the constrained atoms. See also FIT reports from O. Brügner and M. Walter in 2016, 2017 and 2018.

As the external force increases, the distance between the methyl-group and the central part of the molecule increases also, which results in diminishing steric hindrance. This causes the dihedral angles of o-DPP and m-DPP to decrease as shown in Fig. 2. This effect is stronger for o-DPP, which had the larger initial dihedral angle. Both isomers decrease their dihedral angle until the molecule eventually reaches a nearly planar structure and one of the weakest bonds (the bond between phenyl and methyl group always breaks first) breaks at forces around 3.5-4 nN.

As we are interested in detectable signals for the force acting on the molecular scale, we have to investigate the optical properties. These are calculated within time dependent DFT (TDDFT) [10] in Casidas linear response formalism [11]. The number of additional unoccupied orbitals needed for TDDFT calculations is chosen to almost double the number of occupied orbitals. Transitions between Kohn-Sham orbitals within an energy range of 8 eV are considered in the linear response calculations, which is checked for convergence.

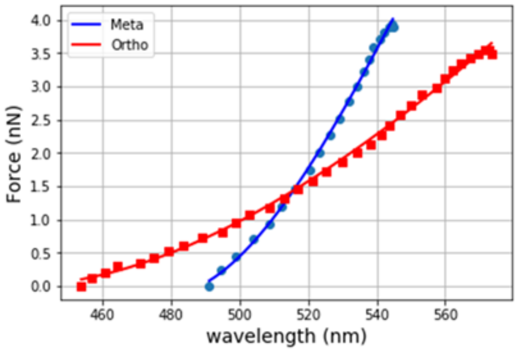

Fig. 3. Relation between external force and wavelength of the main optical absorption for both DPP variants. The polynomial fit line is added as guide to the eye (© Functional Nanosystems Group).

The TDDFT calculation reveals a clear effect of the external force on the optical absorption spectra. Here we can observe a shift of the main peak in the absorption spectrum with increasing external force (see figure 3). Larger forces lead to an increase of the wavelength. Similar as in changes in dihedral angle, o-DPP displays a larger range of this absorption shift from 454 nm to 573 nm (119 nm) with force up to 3.5 nN, while m-DPP has smaller of range absorption shifts from 491 nm to 545 nm (54 nm) up to slightly larger force of 3.9 nN. The wavelength change is slightly stronger in the small force range for both m-DPP and o-DPP, which means that shift absorption spectra us more effective there.

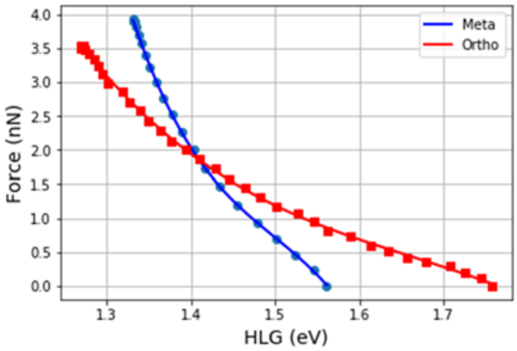

Fig. 4. Relation between external force and HOMO-LUMO gap (© Functional Nanosystems Group).

The changes in optical spectra are reflected within single particle picture in the separation between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies, the HOMO-LUMO gap (HLG). The transition between these orbitals is the main contribution to the strongest optical peak. Fig. 4 shows that there is stronger dependence of the HLG on force in o-DPP than in m-DPP in agreement with Fig. 3. Similarly, the effect is strongest for small forces.

In conclusion, we have investigated the force dependent donor-acceptor (D/A) properties two variants of the DPP polymer with DFT and TDDFT. We have found that these molecules should indeed be usable for force sensing and stress imaging in that their optical absorption properties change reversibly under the application of force. This can be traced back to change in the electronic properties due to changes in the dihedral angle and therefore in the coupling between the donor acceptor parts in the molecules. Application of external forces on m-DPP and o-DPP leads to force-induce planarization and a resulting shift of the optical spectra to longer wavelengths. Increased steric hindrance in o-DPP leads to a larger dihedral angle of this conformer as compared to m-DPP. This leads also to larger optical shifts in o-DPP making this conformer a more effective force sensor. First results of our experimental collaborators indicate the validation of our theoretical results, as will be reported in the literature in near future.

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PROJECTS

*LIV*MATS

Living, Adaptive and Energy-autonomous Materials Systems (*liv*MatS)

Jürgen Rühe[1,2], Anna Fischer[1,3],
Thomas Speck[1,4]

[1]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technologies, University of Freiburg, Georges-Köhler-Allee 105, D-79110 Freiburg, Germany; [2]Laboratory for Chemistry and Physics of Interfaces, Department of Microsystems Engineering (IMTEK), University of Freiburg, Georges-Koehler-Allee 103, D-79110, Freiburg, Germany; [3]Institut für Anorganische und Analytische Chemie, Albert-Ludwigs-Universität Freiburg, Albertstraße 21, 79104 Freiburg, Germany; [4]Plant Biomechanics Group (PBG) Freiburg and Botanic Garden of the University of Freiburg

www.livmats.uni-freiburg.de

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The Cluster of Excellence "Living, Adaptive, and Energy-autonomous Materials Systems" (*liv*MatS) has received funding from the German Research Foundation (DFG) under Germany's Excellency Strategy – EXC-2193/1 39051807 since January 2019. *liv*MatS develops bioinspired materials systems that adapt autonomously to various environments and harvest clean energy from their surroundings. The intention of these purely technical – yet in a behavioral sense quasi-living – materials systems is to meet the demands of humans with regard to pioneering environmental and energy technologies. The societal relevance of autonomous systems and their sustainability thus plays a crucial role in their development.

Bioinspired materials, efficient energy systems, and reactive, self-repairing materials with different and often even contradictory properties and functional conditions all meet in a quasi-living materials system. Energy autonomy, adaptivity, longevity, and sustainability are the core properties of the materials systems to be developed in *liv*MatS. They are investigated and combined with each other in four research areas: A – Energy Autonomy, B – Adaptivity, C – Longevity, and D – Sustainability (cf. Fig. 1). Research from all four areas feeds into demonstrator projects.

Fig. 1: Interplay of Research Areas in *liv*MatS. © *liv*MatS/ Daniel Hellweg

Research area A – Energy Autonomy studies novel methods of energy harvesting and energy storage within a single highly integrated system. Light, temperature differences, and vibrations are taken as potential sources of energy. Once harvested, the energy is either consumed directly or stored for later use. Another important factor is the transformation of energy to make it available in mechanical, chemical, or thermal form or as light energy for adaptive processes within a materials system.

Research area B – Adaptivity develops new concepts for adaptive materials systems with complex energy landscapes that recognize and can react to sensory input from their environment. The recognition of the sensory input and the reaction to it are not performed by a pre-programmed chip but directly by the material or the materials system, using energy harvested from the environment. The goal is to develop a materials system with a "memory" that can adapt to its environment and improve itself.

Research area C – Longevity develops strategies that focus on the longevity of complex materials systems, drawing inspiration from living nature, particularly plant life. Mechanisms for self-repair, the shedding and replacement of damaged parts, or also a training-based strengthening of system parts under special stress help to prevent minor damages from leading to a loss of functioning of the entire system.

Research area D – Sustainability considers the societal dimension of autonomous, quasi-living materials systems and their sustainability. A societal discourse on disruptive technologies, such as autonomous driving or expert systems, is often conducted only after the development and introduction of these technologies. In *liv*MatS, this discourse will be initiated even as the technologies are being developed. The goal is to strengthen the development of the materials systems by means of concurrent sustainability analyses and to actively explore their societal dimension by engaging in critical philosophical reflection and conducting psychological studies.

There are myriad potential applications for these materials systems. One example is "soft" machines that can recognize and grasp objects by feeling them, without the help of a computer. The capability of a materials system to adapt itself to temperatures, lighting conditions, or pressure opens up perspectives in a wide range of areas, such as protective clothing like helmets and back protectors or prostheses that can adjust themselves to fit the wearer automatically autonomously and without needing batteries – for instance through the use of body heat. Other ideas include packaging materials that grow stronger automatically when placed under stress and building envelopes that level out temperature differences, for example to prevent overheating.

*liv*MatS is based at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT) and unites researchers from the Faculty of Engineering, the Faculty of Chemistry and Pharmacy, the Faculty of Biology, the Faculty of Mathematics and Physics, the Faculty of Economics and Behavioral Sciences, and the Faculty of Humanities. Our institutional composition reinforces the university's strategic alliance with Freiburg's Fraunhofer Institutes, with the Fraunhofer Institute for Solar Energy Systems (ISE) and the Fraunhofer Institute for Mechanics of Materials (IWM) as partner institutions within the Cluster, and is complemented by the Institute for Applied Ecology (Öko-Institut e.V.).

*liv*MatS uses the ideas factory IDEASfactory@FIT to implement new forms of scientific exchange and interdisciplinary cooperation. Three Shared Laboratories, one for the Research Areas A, B and C each, foster close collaboration between researchers within and across Research Areas.

In 2019, this scientific exchange was also encouraged by various events, which *liv*MatS initiated. The cluster's kick-off workshop brought renowned international guest speakers to Freiburg to discuss the key lines of the Research Areas with the *liv*MatS members and the public. A workshop by Research Area D took a similar approach, discussing *liv*MatS' position in the Anthropocene. At the first bootcamp, the cluster's early career researchers were able to talk about their projects and thus lay the foundation for future interdisciplinary cooperation. Just like the *liv*MatS Colloquium, started in 2019 as a regular event, the bootcamp format will be continued in 2020.

The communication concept "learning from nature in nature" conveys the scientific content at the interface between nature, technology, and society to the general public. As a first measure within this context, *liv*MatS contributed to the exhibition "Baubionik – Biologie beflügelt Architektur" in the WaldHaus Freiburg. Visitors could learn more about the ***liv***MatS objectives, about the interdisciplinary cooperation in the cluster and about the role biological models play in achieving the overall vision.

The interdisciplinary team of spokespersons includes Prof. Dr. Jürgen Rühe (Faculty of Engineering), Prof. Dr. Anna Fischer (Faculty of Chemistry and Pharmacy), and Prof. Dr. Thomas Speck (Faculty of Biology).

PLAMATSU

Physics and mechanics of plant surfaces with cuticular folds and other microstructures—characterization and quantification of the ontogenetic development

Venkata A. Surapaneni[1,2], Tobias Aust[1],
Georg Bold[1,2], Thomas Speck[1,2,3],
Marc Thielen[1,2]

[1]Plant Biomechanics Group Freiburg, Botanic Garden, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [3]Cluster of Excellence livMatS – Living, Adaptive and Energy-autonomous Materials Systems

www.plamatsu.eu

Project funding: This project is funded within the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 722842

The PhD project "Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures" is carried out under Plant-Inspired Materials and Surfaces (PlaMatSu), an Innovative Training Network (ITN), funded by the European Commission's Marie Skłodowska-Curie Actions. This project is one of the nine PhD projects carried out at four leading European universities in the field of bio-inspired materials: University of Strathclyde, Glasgow, UK, Adolphe Merkle Insitute/Université of Fribourg, Switzerland (Prof. Bruns, Prof. Steiner, Prof. Weder), Universität Freiburg, Germany (Prof. Reiter, Prof. Rühe, Prof. Speck) and University of Cambridge, UK (Prof. Glover, Prof. Vignolini). PlaMatSu aims to understand the structure-function relationships at the plant cuticle and to develop new functional materials and interfaces that mimic the multifunctional plant surfaces.

The project "Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures" aims at understanding ontogenetic variations in plant leaf surfaces having wrinkled cuticles and to estimate corresponding changes in their functional properties, e.g. as to insect adhesion [1, 2] and water contact angle. For this study, the model plants *Hevea brasiliensis* (Rubber tree) and *Schismattoglottis calyptrata* cultivated in the Botanic Garden, University of Freiburg were selected. Observations of ontogenetic structural changes in leaf surface microstructures were carried out using confocal laser scanning microscopy (CLSM) and scanning electron microscopy techniques (SEM).

Studying the effect of both surface chemistry and structural dimensions on insect attachment is difficult, noting the complex changes that occur on leaf surfaces during development. In addition, during microscopic observations and insect walking experiments, the leaves may already start to dehydrate which could influence the measurements. To overcome these problems, we used polymer replicas [3] of whole leaf surfaces for microscopic observations using CLSM and traction force measurements.

Confocal laser scanning microscopy measurements were carried out at different locations on the leaf replicas to study ontogenetic and spatial differences. The results showed different stages of cuticular wrinkle development on the leaf surfaces of the two model plants - *Schismattoglottis calyptrata* and *Hevea brasiliensis*. On both leaf surfaces, we find gradual development of wrinkles with no surface wrinkles during the early ontogenetic stages and completely developed wrinkled cuticles in the final stages of leaf development. In addition, we also find spatial changes in wrinkle development in specific ontogenetic stages (Fig. 1). The cuticular wrinkles showed complex orientations with a wrinkle height up to 1 µm and a spacing of 3-4 µm. Wrinkles in these size scales were shown to have diminishing influence on the traction forces of insects [1][4] walking on those surfaces.

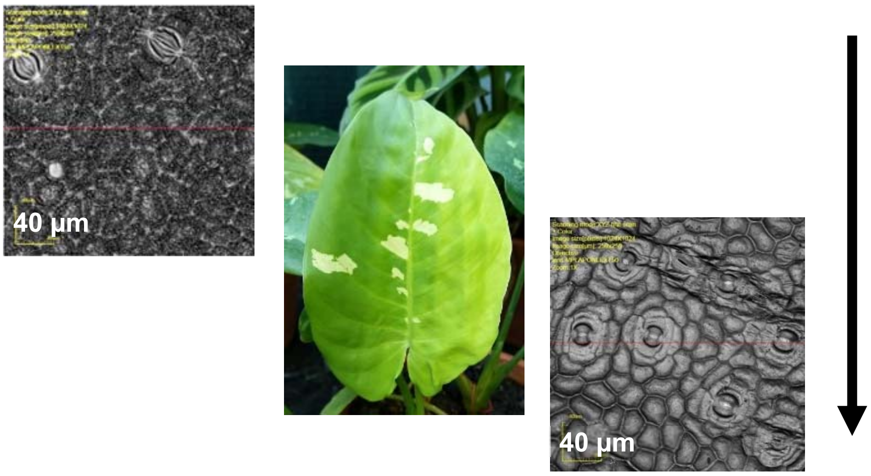

Fig. 1. Development of wrinkles from apex to base on *Schismattoglottis calyptrata* leaves. © PBG Freiburg

For insect attachment experiments, we used the model species – Colorado potato beetle (*Leptinotarsa decemlineata*) having hairy tarsal attachment systems. One end of a straight human hair is attached to the back (elytra) of the beetle using molten bees wax and the other end is attached to a highly sensitive force transducer. Guided by a small light source, the insects were made to walk straight on polymer replicas of leaf samples, glass and other smooth samples. The mean values of the maximum traction forces obtained from the experiments were measured and compared. The results showed significant differences in traction forces for replicas of leaves compared with glass and other smooth samples. The differences in traction forces were also significant when the results on different ontogenetic stages were compared.

Attempts are also being made for a theoretical understanding of the traction forces in relation to the dimensions of the wrinkles. Such a study would be of importance in providing a reference to biomimetic applications for chemical resistant anti-insect attachment systems. Collaborative work was also taken up with Prof. Ulrich Steiner, University of Fribourg, Switzerland to understand the reduction in traction forces of Colorado potato beetles on artificially produced wrinkled surfaces that mimic the wrinkled leaf surfaces.

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GrowBot

Towards a new generation of plant-inspired growing artefacts: The plant role models

Frederike Klimm[1,2],Thomas Speck[1,2,3],
Marc Thielen[1,2]

[1]Plant Biomechanics Group Freiburg, Botanic Garden, University of Freiburg; [2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT); [3]Cluster of Excellence *liv*MatS – Living, Adaptive and Energy-autonomous Materials Systems

www.growbot.eu

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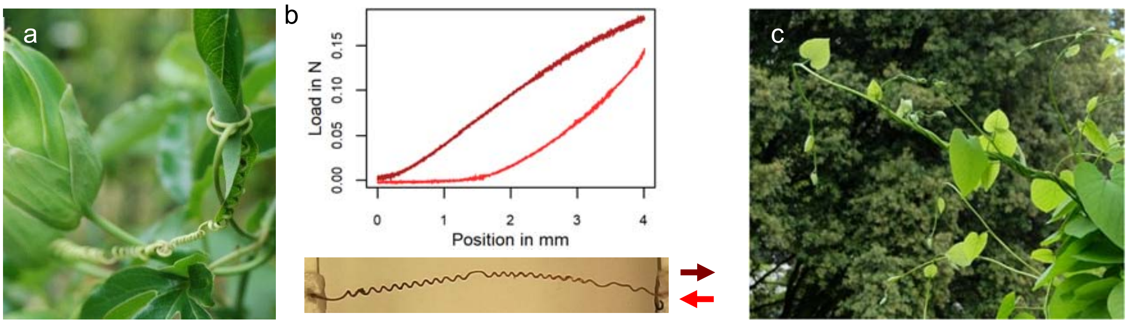

Fig. 1: Tendril climbers and twining vines. a: Coiled tendril of *Passiflora caerulea*. b: Mechanical test of a senescent tendril of *Passiflora discophora* (sample length 4 cm), showing force and displacement during 4 mm elongation (dark red) and subsequent release (light red) which clearly proves the visco-elastic behaviour of the system. c: Intertwined searcher shoots of *Aristolochia macrophylla* in the Botanic Garden Freiburg. © Plant Biomechanics Group Freiburg.

GrowBot proposes a disruptively new paradigm of movement in robotics inspired by the moving-by-growing abilities of climbing plants. Plants are still a quite unexplored model in robotics and ICT technologies, as their sessile nature leads to think that they do not move. Instead, they move markedly, effectively and efficiently, however, on a different time scale. To move from one point to another, plants must grow and continuously adapt their body shape and structure to the external environmental conditions. This continuous growth is particularly evident and fast in climbing plants.

To study climbing plants as concept generator for a new paradigm of movement in robotics, several climbers growing in the Botanic Garden Freiburg have been selected, representing various climbing and attachment modes, respectively (twining, tendrils with adhesive pads and tendrils using contact coiling, for example *Passiflora caerulea*, depicted in figure 1a) [1]. Understanding of the form-structure-function relationships and of how the movements involved in climbing are achieved, requires not only extensive anatomical and morphological analyses, to be carried out, but also a detailed biomechanical examination of the respective role model.

In case of the passion flower *Passiflora discophora* - a tendril climber with adhesive pads - the initial focus was put on testing the mechanical properties of the spring-like connections the tendril is forming between the plant's stem and the attachment pads providing a firm connection to the substrate. Once their distal end developed into adhesive pads, the initially straight tendrils start coiling, eventually forming a spring with at least one perversion resulting from the inversion of coiling handedness. Hysteresis tests on these structures are currently being carried out (see figure 1b) in order to quantify – in addition to the force measurements ("spring constant") – the damping properties and failure behaviours of the tendrils. When elongating the tendril, the so called "overwinding" can be observed in some cases.

This is a mechanically very interesting phenomenon where during the beginning of the elongation, the tendril is coiling further instead of unwinding. This effect is additionally addressed during the mechanical testing.

Twining vines such as *Aristolochia macrophylla* on the other hand use a different method to climb. Its stems twine around a support. In order to get hold of a support in the first place, young searcher shoots often have to bridge more or less large gaps between host trees. By intertwining, these searchers can increase their reach by providing mutual support. Mechanical testing aiming at assessing inter alia the bending stiffness of individual and intertwined shoots is ongoing and will be complemented by morphological and anatomical studies.

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SFB-TRR 141

Biological Design and Integrative Structures - Analysis, Simulation and Implementation in Architecture” – Year 5

Georg Bold[1], Linnea Hesse[1], Olga Speck[1,2,3], Thomas Speck[1,2,3]

[1]Plant Biomechanics Group Freiburg, Botanic Garden of the University of Freiburg; [2]Cluster of Excellence *liv*MatS @ FIT – Freiburg Center for Interactive Materials and Bioinspired Technology, [3]Freiburg Centre for Interactive Materials and Bioinspired Technologies (FIT)

www.trr141.de

Project funding: German Research Foundation (DFG) – Cooperative Research Center 141 „Biological Design and Integrative Structures – Analysis, Simulation and Implementation in Architecture“

In the final half year of funding of the SFB Transregio 141 (TRR 141), which ended end of June 2019, eight of the eleven projects at the University of Freiburg were carried out at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT). For the scientific results in these projects we refer to two recently published books, which summarize as well the basic research done in the TRR 141 as the successful transfer to architectural demonstrators and built reality [1,2].

A prominent outreach activity of the SFB Transregio 141 (TRR 141) in 2019 and 2020, which extends significantly beyond the eligibility period, is the exhibition on biomimetics in architecture ‘Baubionik – Biologie beflügelt Architektur’ (Fig. 1) in the WaldHaus Freiburg. This exhibition was organized in cooperation with the Plant Biomechanics Group & the Botanic Garden of the University of Freiburg, the Stuttgart State Museum of Natural History and the WaldHaus Freiburg. It is open to the public from October 10th 2019 until March 22nd 2020 (www.waldhaus-freiburg.de/kontakt-und-besuch/ausstellungen).

Fig. 1: Announcement flyer of the exhibition on biomimetics in architecture in the WaldHaus Freiburg. © SMNS & WaldHaus

For this exhibition, various contents of the same-titled past exhibition in the Stuttgart State Museum of Natural History (19.10.2017 – 06.05.2018) were transferred to the WaldHaus Freiburg, adapted and partially extended. Besides introductory exhibits on the question ‘What is biomimetics?’ (Fig. 2) and several examples of biomimetic products, the visitors may expect wall charts, video contents and interactive exhibits on the following topics: plants in action (‘Pflanzen in Aktion’; Figs. 3 & 4) as role model for turgor inspired actuators, planar movements in plants (‘Pflanzliche Flächenbewegungen’) and the bioinspired façade-shading systems Flectofin/Flectofold, from plant branchings to technical support structures (‘Vom Ast zum Palast’), the plastid skeleton (‘Zellskelett’) as role model for evolutionary architecture, controlled failure (‘Kontrolliertes Versagen’) and impact protection (‘Aufpralldämpfung’) for better earthquake protection in buildings, and lightweight shell constructions (‘Schalenbau – leicht gemacht’).

Fig. 2: Showcase with examples of biomimetic everyday products such as Velcro® or the pneumatic muscle. © Plant Biomechanics Group

Furthermore, the Cluster of Excellence ‘Living, Adaptive and Energy-autonomous Materials Systems’ (*liv*MatS) is on display in this exhibition with several projects which will render new materials systems also applicable in bio-inspired architecture. In *liv*MatS projects, parts of topics dealt within the TRR141 were taken up and are currently carried forward in further research projects (some of them funded by the Ministerium für Wissenschaft, Forschung und Kunst Baden-Württemberg in the project Bioinspirierte elastische Materialsysteme und Verbundkomponenten für nachhaltiges Bauen im 21ten Jahrhundert - BioElast).

Fig. 3: Jan Knippers at the interactive binocular while observing various cross-sections of plants. © Plant Biomechanics Group

The exhibition is accompanied by further events, such as four lectures in the WaldHaus (each of them followed by a guided tour through the exhibition) and two guided tours through the Botanic Garden, all of these events related to the topic of biomimetics in architecture. Listed in chronological order, these events include: opening of the exhibition accompanied by an introductory lecture by Prof. Dr. Thomas Speck, Botanic Garden of the University of Freiburg (10.10.2019, WaldHaus Freiburg), guided tour ‘Pflanzen als Inspiration für bionische Architektur’ by Prof. Dr. Thomas Speck (12.10.2019, Botanic Garden Freiburg), lecture ‘Wie Pflanzen sich bewegen und die Architektur inspirieren’ by Dr. Simon Poppinga, Botanic Garden of the University of Freiburg (17.10.2019, WaldHaus Freiburg), lecture ‘Warum Bionik?’ by Prof. Dr. Jan Knippers, Institute of Building Structures and Structural Design of the University of Stuttgart (07.11.2019, WaldHaus Freiburg), guided tour ‘Bionik im Botanischen Garten’ by Dr. Olga Speck & Dr. Georg Bold, Botanic Garden of the University of Freiburg (08.02.2020, 2 pm, Botanic Garden Freiburg), lecture ‘Bionische Nachhaltigkeit’ by Dr. Olga Speck, Botanic Garden of the University of Freiburg (13.02.2020, 5 pm, WaldHaus Freiburg).

Fig. 4: Wall chart to the topic: plants in action (‘Pflanzen in Aktion’) presented in the exhibition on biomimetics in architecture in the WaldHaus Freiburg. © Plant Biomechanics Group

Both the exhibitions in WaldHaus Freiburg and the Stuttgart State Museum of Natural History, which summarize in a visualized manner the results of the TRR 141 projects, let to the publication of the books “Biomimetics for Architecture: Learning from Nature” and “Bionisch Bauen: Von der Natur Lernen”, which not only addresses scientists but also the general public [1,2].

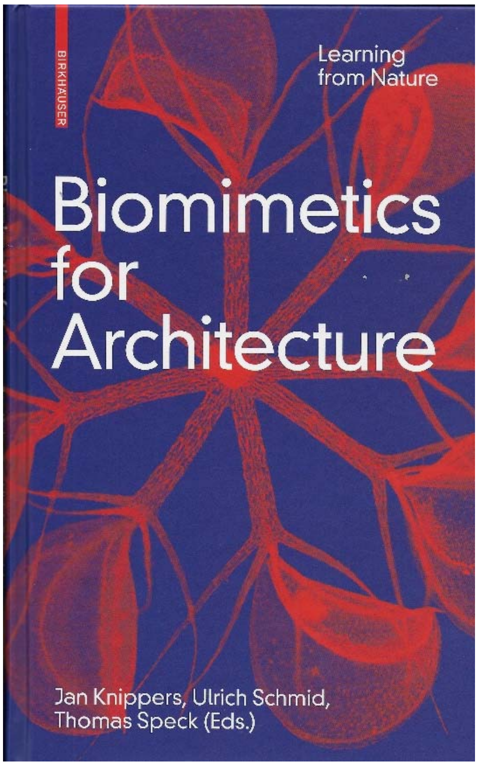

Fig. 5: Book cover “Biomimetics for Architecture: Learning from Nature”. © Plant Biomechanics Group

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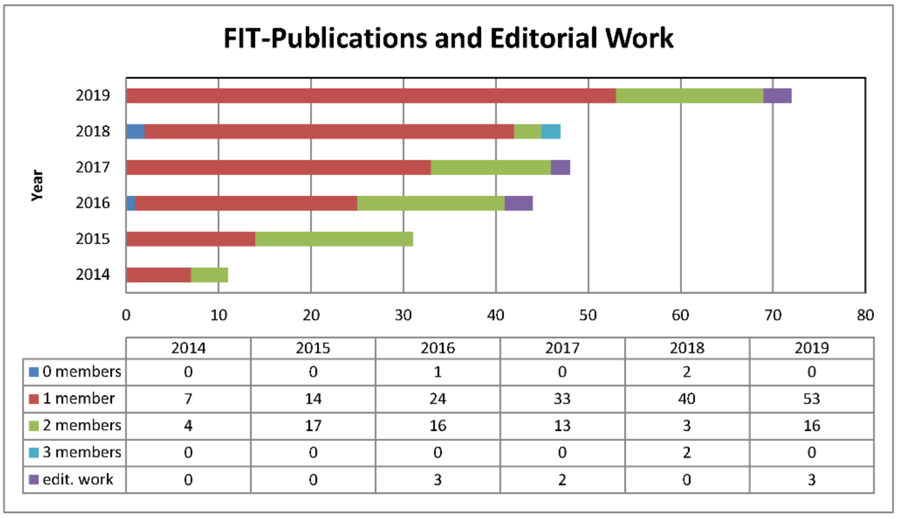
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	2014	2015	2016	2017	2018	2019
🟦 0 members	0	0	1	0	2	0
🟥 1 member	7	14	24	33	40	53
🟩 2 members	4	17	16	13	3	16
🟦 3 members	0	0	0	0	2	0
🟪 edit. work	0	0	3	2	0	3

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Editorial Work

Geitmann A, Niklas KJ, Speck T (eds.) (2019): Plant Biomechanics. *J Exp Bot* **70**(14). DOI: 10.1093/jxb/erz280

Knippers J, Schmid U, Speck T (eds.) (2019): Biomimetics for Architecture: Learning from Nature, 208 pp. Birkhäuser Verlag, Basel. (ISBN 978-3-0356-1785-6)

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Miscellaneous

Speck T & Plant Biomechanics Group (2019): Attachment and anti-attachment structures in plants as concept generators for bioinspired technical materials systems. Technical Digest of the 6th International Workshop on Low Temperature Bonding for 3D Integration 2019, Kanazawa, Wafer Bond East, 177–185.

Speck T (2019): Baubionik – Ist die Natur ein Vorbild beim Bauen? Tagungsbeiträge 10. Baden-Württembergischer Tragwerkplaner Tag. Messe Stuttgart, 27.11.2019, 17pp. Ingenieurkammer Baden-Württemberg, Leichtbau BW GmbH & InformationsZentrum Beton GmbH.

THESES

PHD THESES

Bunk, Katharina: Branchings and axes in selected plant species as concept generators for high load-bearing joints of branched building structures. — PhD thesis, Universitity of Freiburg; supervisors: Speck T, Masselter T; completed on: 09.08.2019

Kumar, Charchit: Quantitative and qualitative investigation of adhesion and friction on textured surfaces: inspiration from insect-plant interactions. — Thèse en Cotutelle Universität Freiburg und Université de Strasbourg; supervisors: Speck T (University of Freiburg), Le Houérou V (Université de Strasbourg); completed on: 28.05.2019

Schmier, Stefanie: Funktionelle Morphologie und mechanische Eigenschaften des Endokarps von *Cocos nucifera* und deren Skalierbarkeit. — PhD thesis, Universitity of Freiburg; supervisor: Speck T; completed on: 05.03.2019

Widyaya, Vania: Three-Dimensional, Bioactive Microstructured Surface-Attached Polymer Networks by Microcontact Printing – Simultaneous Antimicrobial Activity, Protein Repellency, and Cell Compatibility. — PhD thesis, Universitity of Freiburg; supervisor: Lienkamp K; completed in 2018

Zou, Peng: Poly(oxonorbornene-diester) Based SMAMPs as Antimicrobial Drugs and Coating Materials. — PhD thesis, Universitity of Freiburg; supervisor: Lienkamp K

DIPLOMA, MASTER, BACHELOR AND STATE EXAMINATION THESES

Aust, Tobias: Ontogenic changes and distribution of cuticular structures of Schismatoglottis calyptrata leaves. — Bachelor thesis, University of Freiburg; supervisors: Speck T, Thielen M; completed on: 08.05.2019

Bräuer, Marcel: Der Einfluss verschiedener Reize auf die Verengungsbewegung der Schnappfallen der karnivoren Wasserfalle (Aldrovanda vesiculosa). — Bachelor thesis, University of Freiburg; supervisors: Speck T, Poppinga S; completed on: 06.08.2019

Elsäßer, Patrick: Polyformamidine-derived Ni/C catalysts for hydrogen oxidation in alkaline media. — Master thesis, University of Freiburg; supervisor: Fischer, A

Katzmaier, Moritz: An investigation on the charge density dependent tribology of surface-attached hydrogels. — Master thesis, University of Freiburg; supervisors: Mülhaupt R, Lienkamp K; 4.2019-10.2019

Kelbel , Mark Cedric: Vergleichende Analyse stabförmiger biologischer Strukturen – Morphologie, Anatomie und Mechanik. — Bachelor thesis, University of Freiburg; supervisors: Müller C, Speck O, Speck T; completed on: 02.10.2019).

Krüger, Friederike: Interrelation of morphology, anatomy and biomechanical parameters of cacti branches under cyclic bending: an analysis of self-repair in Opuntia ficus-indica and Cylindropuntia bigelovii. — Master thesis, University of Freiburg; supervisors: Speck T, Speck O; completed on: 06.11.2019)

Liao, Peikun: Controlled Delamination of Polymer Multilayer System. — Master thesis, University of Freiburg; supervisors: Mülhaupt R, Lienkamp K

Martin, Johannes: Synthese, Charakterisierung und Oberflächenvernetzung von Oxanorbornenbasierten Polyzwitterionen für antimikrobielle Beschichtungen. — Master thesis, University of Freiburg; supervisors: Mülhaupt R, Lienkamp K

Shi, Yue: Synthesis and Properties of Aliphatic-aromatic Block Copolymers. Liao, Peikun: Controlled Delamination of Polymer Multilayer System — Master thesis, University of Freiburg; supervisors: Mülhaupt R, Lienkamp K

MISSION STATEMENT

Since the beginning of mankind, the development and use of innovative materials as well as the construction of complex systems based on these materials have been key technologies. This has not changed to this day, because new materials and materials systems promote technological progress and contribute to innovative solutions to social problems.

We pursue the development of new, bioinspired and interactive materials and material systems and the basic research for the generation of such systems with commitment, motivation and passion. By developing new technologies, we make a significant contribution to the technical and social challenges of the present and the future.

VISION

The Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT) is a research institution of national and international importance for the development of future-oriented, innovative materials and materials systems. Special focus is placed on materials systems that react to changes in the environment and thus, inspired by plants and animals, have life-like functions. Following the model of living nature, these "vital" materials systems are interactive, adaptive, energy-autonomous, self-repairing, self-improving or even learning. These extraordinary properties and functions make them a decisive advance in the sustainable development of technology and society.

MISSION

The FIT is committed to increasing and disseminating knowledge in the field of research on interactive and bioinspired materials and materials systems and to making it available to science and the public. The FIT stands for basic research that lays the basis for the development of new materials and technologies. The projects handled by FIT consist of individual research projects and long-term collaborative research projects and are supported by interdisciplinary cooperation between scientists from chemistry, physics, engineering, biology, materials sciences and medicine. An important aspect here is learning from living nature and transferring functional principles to technical systems. The common goal of all FIT employees is to facilitate and conduct groundbreaking basic research that is oriented towards solving important social challenges. This research can position itself at the top of the global scientific competition and plays an important role in the international scientific discourse in the most important profile areas.

FIT deals with the development of interactive and intelligent functional materials, foils and surfaces as well as material-integrated (micro)systems in order to create novel adaptive and active (polymer-based) materials. Furthermore, inspired by nature, new materials for energy conversion and energy storage are developed and coupled with system functions. Furthermore, energy-autonomous embedded (micro)systems are being developed that generate energy directly from their environment. Another central focus is research on biomimetic, biobased and bioactive material systems. This includes the bioinspired and biomimetic construction of materials systems and the development of new active hybrids of synthetic and biological components as well as the bioactive functionalization of materials and (micro)systems to enable them to interact with proteins, cells and tissues.

GUIDING PRINCIPLES: INTERDISCIPLINARY–COOPERATIVE–SUPPORTIVE–COMMUNICATIVE

- We work in an interdisciplinary, transparent and constructive manner in basic research-oriented collaborative projects. We are constantly striving to opening up new fields of research and building up or expanding competencies.
- We are well embedded in the organization and research of the University of Freiburg. As a central scientific institution of the University of Freiburg, we are committed to the mission statement of our university.
- We cooperate to a high degree with regional, national and international research institutions and maintain close relationships with partners from science, industry and society.
- Our work is characterized by synergy-oriented cooperation based on a culture of creativity, scientific honesty and the pursuit of excellence.
- Our scientists are supported in their quest for excellent research by outstanding core facilities and a modern infrastructure.
- The cooperation of the members of the FIT is characterized by mutual respect and trust and cooperation across professional, organizational and hierarchical levels. We value team spirit and good cooperation and promote partnership. We involve our employees in the planning and design of research topics and objectives and give them a great deal of freedom in carrying out their research work.
- We support and promote scientists in all stages of their academic careers. All members of the FIT are given equal opportunities and conditions and the performance of each individual is appreciated. Equal opportunities and diversity are the cornerstones of our actions.
- We are committed to supporting the compatibility of family and career irrespective of lifestyle and situation—from childcare to eldercare.
- We communicate the contents and results of our work to the scientific community and the general public.
- Our research contributes to the sustainable development of society. Our actions are based on social, ecological and ethical standards. We are committed to the responsible use of natural resources.

FIT Colloquium 2019

Program for the 7th FIT Colloquium

on Friday, 18.01.2019

„FIT meets *liv*MatS 2019“

09:00 Reception

9:30 **Welcome by the Managing Director Prof. Rühe**
Presentation of the Cluster of Excellence livMatS (Prof. Dr. Jürgen Rühe)
10:15 *“Slender structures in nature and architecture“* (Prof. Dr. Thomas Speck)
10:45 *“BiVO4 photoanodes for light-induced water splitting”* (Prof. Dr. Anna Fischer)

11:15 – 11:45 Coffee break (Poster session)

11:45 *„Hierarchical programmable mechanical metamaterials“* (Prof. Dr. Christoph Eberl)
12:15 *„Predicting acceptance for not-yet existing living materials systems“* (Prof. Dr. Andrea Kiesel)

12:45 – 13:45 Lunch break (Poster session)

13:45 “The UnipHied Project – How unified acidity and redox scales may help to understand interactive materials” (Prof. Dr. Ingo Krossing)
14:00 *"MiTEG – Development of Integrated and? Flexible Thermoelectric Micro Generators"* (Dr. Uwe Pelz)
14:15 “How materials science might contribute to the next generation of neural interfaces” (Dr. Maria Asplund)

14:45 – 15:15 Coffee break (Poster session)

15:15 Presentation for admission as a member (junior research group)
"Tailor-made multifunctional interphases enabling dendrite free rechargeable Lithium metal batteries“ (Dr. Witali Beichel)
15:30 *“Adaptive lenses based on conductive, stretchable and optically transparent silver nanowire networks”* (Dr. Frank Goldschmidtböing)

15:45 Short coffee break

16:00 General meeting (only for FIT members)

MEETING OF THE SCIENTIFIC ADVISORY BOARD 2019

AGENDA FOR THE FOURTH MEETING OF THE ADVISORY BOARD OF THE FIT

PUBLIC EVENT

Thursday, 11th of April 2019
Venue: FIT, Georges-Köhler-Allee 105, seminar room ground floor

12:00 Reception and lunch in the foyer

Words of welcome (start of the public session) (Chairperson: Thomas Speck)

13:00 Welcome by **Jürgen Rühe**, Managing Director of the FIT
13:05 Welcome by **Ingo Burgert**, Chairperson of the Advisory Board
13:15 *"Status report of FIT"* (Jürgen Rühe)

New Projects in FIT (I) * (Chairperson: Peter Woias)

13:30 ***"**FIT for livMatS**"*** (Jürgen Rühe)
14:00 *"Antimicrobial copolymers made from itaconic acid – teaching an old monomer new tricks (BioSMAMPs)"* (Karen Lienkamp)
14:30 *"Lessons from Nature: Transition zones and abscission zones in plant organs"* (Olga Speck)

15:00 – 16:00 Poster session and coffee break

New Projects in FIT (II) * (Chairperson: Karen Lienkamp)

16:00 *„HYBRIDIS – Dispersion interaction in the presence of environments"* (Michael Walter)
16:30 *"PDMS-based microsensors and microactuators"* (Peter Woias)
17:00 *"PlaMatSu - Plant-inspired Materials and Surfaces"* (Thomas Speck)

17:30 **Closing remarks** (Jürgen Rühe)
17:40 End of the public part

** Please note: all presentations should be held in English and should be divided into 25 minutes talk and 5 minutes discussion.*

IMPRESSUM

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