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

FIT

Report 2020

UNI FREIBURG

REPORT

2020

FIT

FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

FIT

FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

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FOREWORD

FIT—EXCITING RESEARCH IN DIFFICULT TIMES

After an exciting, but somewhat unspectacular start into the new decade, which I referred to as the "roaring twenties" in the foreword to last year's FIT report, the COVID pandemic reached Freiburg in March and kept us at FIT on our toes for the rest of the year. The pandemic presented our FIT community with numerous challenges to ensure the health and safety of our employees and prevent the further spread of viral infections. Extensive work succeeded in implementing an office and laboratory occupancy plan that ensured work at FIT was compliant and safe for all employees and guests. As far as possible, home office workplaces have been set up to reduce the number of staff present at the same time, but also to meet administrative and scientific challenges. Many event formats were converted to virtual formats. For the first time, the Advisory Board meeting was also held in a digital format and the General Assembly in a hybrid format. These formats have worked very well over time. Even though they cannot replace personal and direct contact, they allow a very good continuation of the scientific discourse in FIT.

Despite the difficulties caused by the pandemic, there were again many exciting new activities in 2021. The *liv*MatS research cluster, which is the largest activity in FIT, continued to gain momentum in 2020. At the end of 2020, the cluster for the first time included over 100 people working in science and administration. This group consists of PhD students, postdocs and young independent researcher groups who are either directly employed in the *liv*MatS cluster or in associated projects. In addition, from September to December, another 16 staff members initiated important new research questions or completed research projects in short projects. Furthermore, the Master Lab was held for the second time, introducing advanced students to cluster research. A new activity, the Writer's Studio, was established to support the rapid publication of research results in high quality publications.

At the end of the year, two new independent junior research groups started their activities. Dr. Pappas will work on adaptive systems by chemical self-assembly and Dr. Slesarenko on adaptive metamaterials. In the first days of 2021, the junior research groups were complemented by Dr. Calvino, who is establishing an Agnes-Pockels junior research group in *liv*MatS to address questions on how specially designed polymer materials can be degraded by photochemical processes. All three groups were selected in a highly competitive selection process involving leading international reviewers. The excellent groups complement the cluster profile in an outstanding way and allow the junior research group leaders an early scientific independence.

In addition to building up the cluster in terms of personnel, the expansion of the infrastructure has also made great progress. In October, the shared laboratories of ideasFactory@FIT were officially opened in the presence of the new rector of the University of Freiburg, Professor Dr. Kerstin Krieglstein. Furthermore, towards the end of the year, a large investment package from *liv*MatS and IPROM funds was initiated to expand the infrastructure in the FIT building with equipment worth several million euros. Some of the procurements are still ongoing and will be reported on in more detail in the next annual report. For the coming year, we are looking forward to continuing the planning for an additional pavilion at the FIT, the so-called sea urchin pavilion, for which a building application was submitted shortly before Christmas 2020.

Further highlights of the year - and here I would like to mention only 4 important awards - were the Helmholtz Award for Prof. Peter Woais in the category "Applications" and the Cross of Merit of the Federal Republic of Germany to Prof. Rainer Grießhammer for his outstanding service on behalf of the community and his achievements on behalf of the

Federal State. Prof. Dr. Ingo Krossing was elected a new member of the National Academy of Sciences Leopoldina in recognition of his scientific achievements and Dr Linnea Hesse has been selected for the "Margarete von Wrangell Program" of the state of Baden-Württemberg.

In addition to the larger (joint) research projects described above, many attractive individual projects have also been acquired or continued, as in previous years. With 33 projects (outside of the 21 projects in *liv*MatS), a new all-time record (!) has been reached. It is very pleasing that the FIT has developed very well in the last years. The description of a number of research projects carried out in the FIT can be found in this report.

We would like to express our sincere thanks to all employees for their outstanding achievements and merits, which have made the excellent development of our FIT possible. Without the everlasting commitment of many hands, we would not be able to deliver an outstanding scientific performance. Our thanks go to all administrative and technical staff, FIT members, in-house scientific staff, our scientific advisory board, and a wide variety of supporters and funders both inside and outside the university.

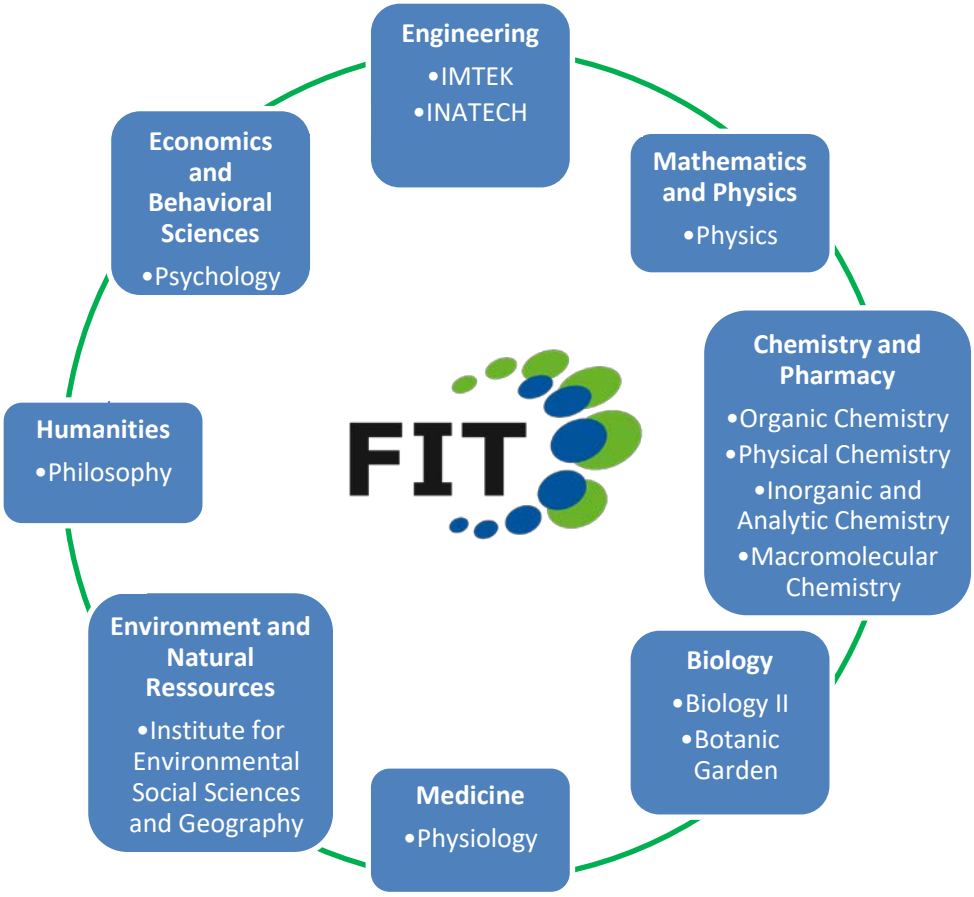
We look forward to a challenging 2021 and hope that the Corona pandemic can be contained and that our FIT team remains healthy. At the same time, of course, we also hope that the pandemic will not delay our research too much true to the motto: 365 new days, 365 new opportunities, 365 new possibilities for FIT, 365 great new deeds. I hope you enjoy reading our annual report.

Jürgen Rühe

(Executive Director FIT)

THE CENTER

STRUCTURE

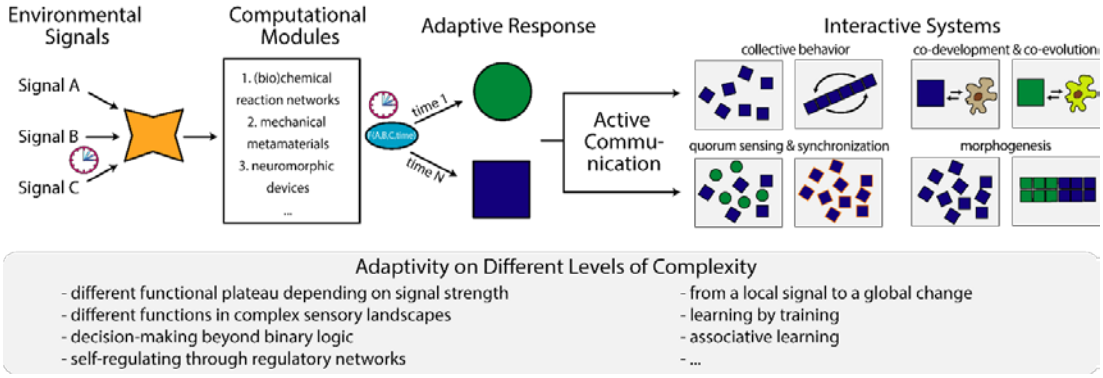


Overview of the various faculties and institutes that carry out disciplinary and interdisciplinary projects within the framework of basic research at FIT. A list of current and completed projects is available on the FIT website.

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, cephalopods 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.

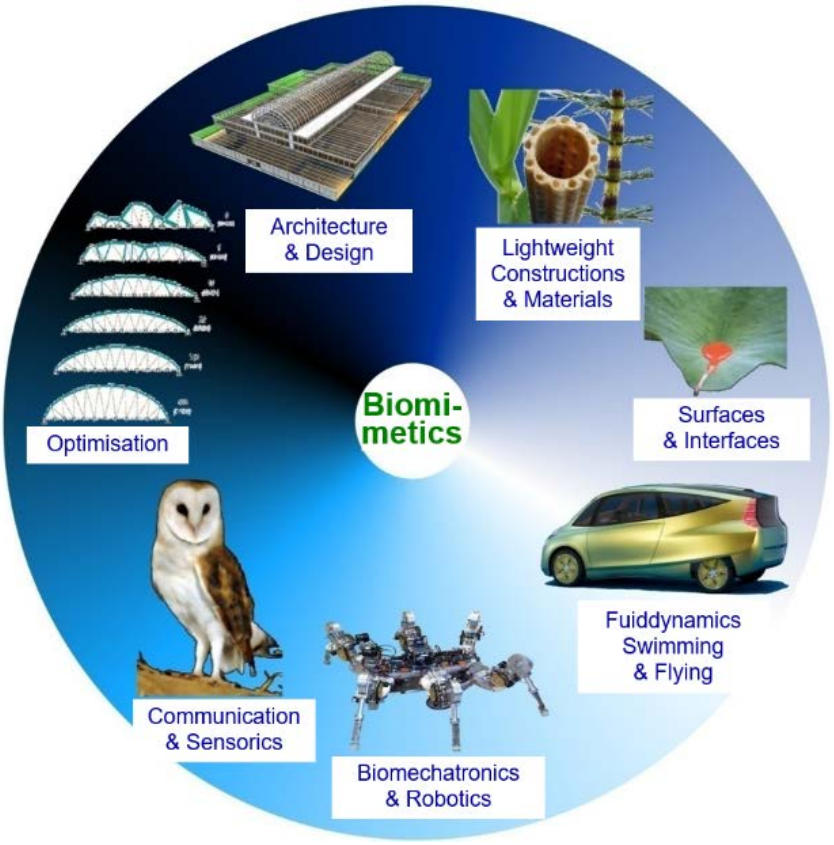
FIT targets such disruptive concepts and the new *liv*MatS Cluster and the ETN Creanet Project are important project lines in this context.

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



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.

Lignin-based ink

Inspired from the morphogenesis of the wood cell wall, the FIT project *Lignosit* aimed at developing high-value materials from organosolv lignin through its mixing and processing within a liquid crystalline cellulosic mesophase. Lignosit resulted in new fundamental knowledge on the liquid crystalline phase behavior of lignin/ liquid crystalline cellulosics. Building on this fundamental understanding, new lignin-based inks for 3D printing have been recently developed within the *Pilot Project Lignin* at the Sustainability Center Freiburg and Freiburg Materials Research Center (FMF) by blending organosolv lignin with a liquid crystalline cellulose derivative. This fully bio-based and bioinspired ink for direct ink writing (DIW) has been recently highlighted by the Leichtbau BW in the “Thinking November 2020”.

Thomas Speck & Marie-Pierre Laborie

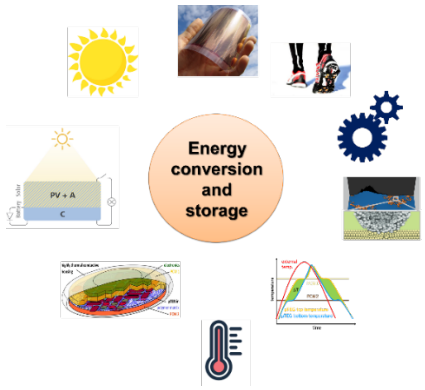
(Micro)Systems for Energy Conversion, Storage and Energy-autonomy

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.



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 *liv*MatS, 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

The Core Facility represents a specialized laboratory for microscopy and tomography, with 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 material science as well as in biological systems as role models for new technological developments.

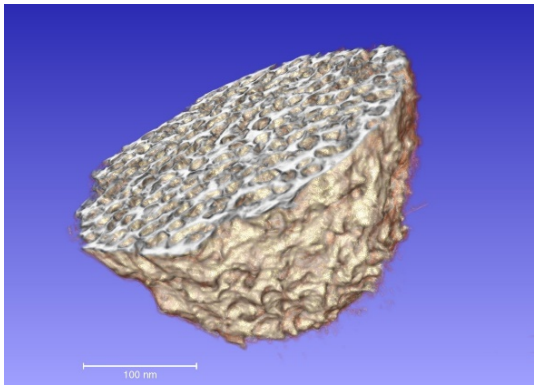


Fig. 1: 3D TEM tilt series tomography of N-doped carbon nanoballs with 12nm pore diameter. (IMOD/Avizo reconstruction) © Thomann, Fischer, Berestok

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

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

Some highlights of research works accomplished in the core facility in the year of 2020:

1) 3D tomographical investigation of mesoporous N-doped carbon nanoballs (AK Anna Fischer, FIT) - see Fig. 1
2) Host-guest mediated self-assembly of 3D DNA Origami cuboids (Andreas Walther, FIT)
3) Structural imaging of wood samples (Thomann, Mülhaupt, FIT)
4) Investigation of porous structured within 3d-printed polymer structures (Thomann, Schirmeister, Mülhaupt, FIT/FMF) - see Fig. 2
5) FIB/SEM Tomography of bariumtitanate composites as flexible piezo elements (Yuan, Thomann, Mülhaupt, FIT/FMF)
6) HR-TEM/STEM investigation on SnO2 nanowires (Bürger, Gutsch, Zaccharias, Thomann) - see Fig. 3

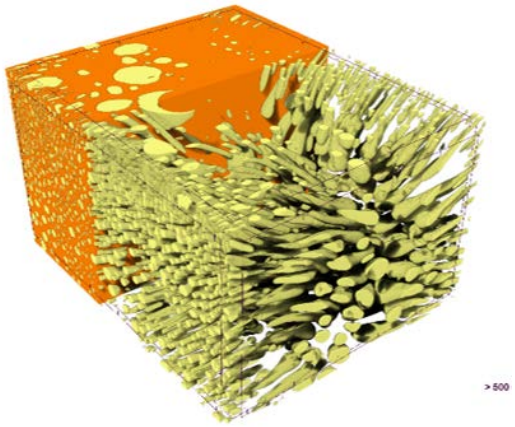


Fig. 2: µ-CT tomography of the pore structure (yellow) in a 3D-printed polymer sample © Thomann

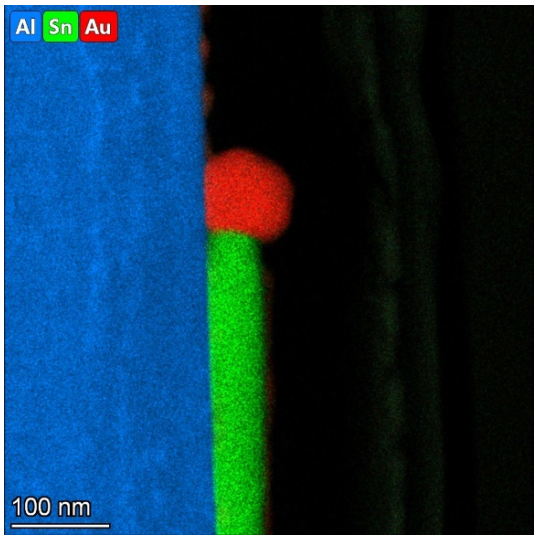


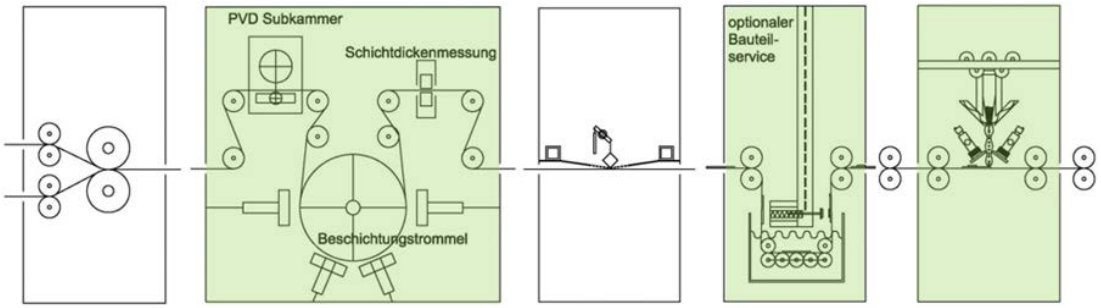
Fig. 3: STEM EDS map of a laterally aligned SnO2 nanowire on sapphire. TEM lamella prepared by FIB/SEM © Thomann

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



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.

Two project proposals have been prepared and submitted to Deutsche Forschungsgemeinschaft in year 2020. These planned research projects are listed below:

1. Fabrication of a polymer-based, localized SPR sensor platform
2. Fabrication of bio functional multilayers by electrophoretic deposition "BioEPD"

During 2020, 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:

Marko Čehovski, Jing Becker, Ouacef Charfi, Hans-Hermann Johannes, Claas Mueller, Wolfgang Kowalsky: Single-mode Polymer Ridge Waveguide Integration of Organic Thin-Film Laser, Appl. Sci. 2020, 10(8), 2805; DOI: 10.3390/app10082805

Marko Čehovski, Jing Becker, Ouacef Charfi, Hans-Hermann Johannes, Claas Mueller, Wolfgang Kowalsky: Single-mode Polymer Ridge Waveguide Integration of Organic Thin-Film Laser, Appl. Sci., Special Issue “Modern Applications in Optics and Photonics: From Sensing and Analytics to Communication"

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.

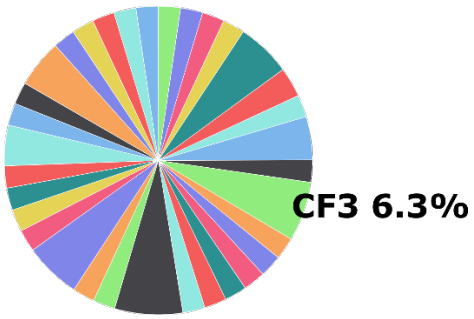


Fig. 1: Partition of computational time used on the full NEMO-cluster in the year 2019. The fraction used by CF3 is highlighted. © RZ University of Freiburg

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.

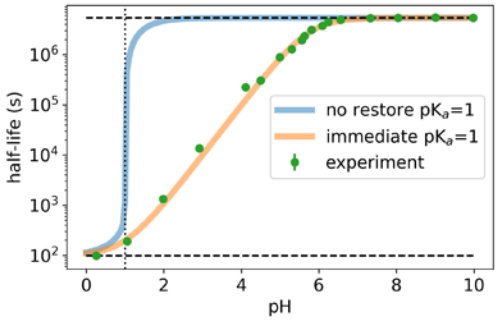


Fig. 2: Comparison of the modeled and measured half-lifes for the thermal spontaneous transition back-transition of AAP (see text) from the Z-form to the E-form. The model uses the experimental half-lives $\tau_{1/2}$ (pH > 7) = 5.40 · 10^6 s (upper dashed line) and $\tau_{1/2}$ (pH 0.3) = 98.5 s (lower 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 2020, 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. Bastian E. Rapp
(Managing director of the FMF)
Faculty of Engineering

Dr. Severein Vierrath / Dr. Can Dincer
(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 2020, the members included (in alphabetical order):

Dr. Maria Asplund (Faculty of Engineering)

Prof. Dr. Jan C. Behrends (Faculty of Medicine, until 31.12.2020)

Dr. Witali Beichel (Faculty of Engineering, until 31.12.2020)

Ludmila Cojocaru, PhD (Faculty of Engineering, until 01.02.2020)

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)

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Dr. Dorothea Helmer (Faculty of Engineering)

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Dr. Olga Speck (Faculty of Biology)

Prof. Dr. Thomas Speck (Faculty of Biology)

Dr. Severin Vierrath (Faculty of Engineering)

PD Dr. Michael Walter (Faculty of Mathematics and Physics)

Prof. Dr. Andreas Walther (Faculty of Chemistry and Pharmacy, until 30.09.2020)

Prof. Dr. Peter Woias (Faculty of Engineering)

Dr. Uli Würfel (Faculty of Mathematics and Physics)

Prof. Dr. Roland Zengerle (Faculty of Engineering)

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. The following professors belonged to the Scientific Advisory Board:

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

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

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

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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 2020 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. Heiner Schanz (Dean of the Faculty of Environmental and Natural Resources)

Prof. Dr. Dierk Reiff (Dean of the Faculty of Biology)

Prof. Dr. Wolfgang Soergel (Dean of the Faculty of Mathematics and Physics)

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

Prof. Dr. Rolf Backofen (Dean of the Faculty of Engineering)

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

Prof. Dr. Bastian Rapp (Management Director of the Freiburg Materials Center) / Prof. Dr. Eberhard Schockenhoff (Management Director of the Interdisziplinäres Ethikzentrum)

Dr. Bruno Ehmann (Management Freiburg Research Services)

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

Dr. Stefanie Meisen (Administrative Management of FIT)

Figures and Finances

Despite the departure of five members and despite the Corona pandemic, we were able to successfully carry out 33 projects in FIT 2020 and again increase the total budget. A total of 2.7 million Euros was available for research. In this context, 82% of the funds were spent on personnel. The number of staff working in FIT increased again: in 2020, 295 staff were active in FIT, including 31 postdocs, 117 PhD students, 52 master students and 22 bachelor students.

They all mastered the exceptional situation and were absolutely successful regardless of it. This is also reflected in the available budget. 14% of the budget was spent on materials and 4% on investments. In order to be able to understand the figures accordingly, please refer to the following graphs and tables for further details.

The *liv*MatS cluster of the Excellence Initiative, which is associated with us, started its second year. In 2020, the cluster spent 2,367 k€ for direct project costs, 300 k€ for the expansion of shared laboratories and 1,452 k€ for strategic measures and administration. At the same time, large-scale equipment worth 2,003 k€ was purchased together with the DFG. 23 projects and 13 short projects started in 2020 within the cluster with 105 scientists of all career levels.

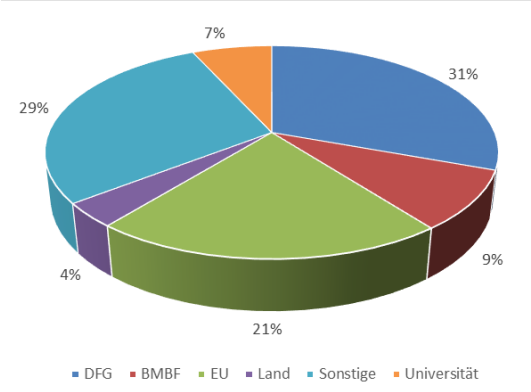

Fig 1: Percentages participation of the FIT-budget 2020

Tab. 1 Budget from 2017 until today in €

	2017	2018	2019	2020
DFG	986.267	1.055.197	1.062.597	828.882
Land	4.048.018	928.292	0	98.857
BMBF	69.121	409.381	407.970	243.345
EU	288.415	355.219	518.315	576.875
Other	62.672	189.235	270.947	777.965
University	75.200	75.200	82.000	183.964
Total	5.529.693	3.012.525	2.341.829	2.709.888

Tab. 2: Projects in 2020

Leader of the project	Project	Overall project	Spent 2020
Dincer	DFG miPAT	366.549	72.391
	DFG miRNAs	369.904	81.048
Fischer	Vectorstiftung AlkaCell	201.644	80.858
	BMBF TEMCat3D	106.334	70.484
Goldschmidtböing	DFG Adaptive Linsen	157.400	75.581
Helmer	DFG Schaltbare Oberflächen	234.200	30.104
Koltay	MWK DINAMIK	299.987	23.485
	DFG 4D-Bioprinting	204.000	39.835
Krossing	EU ERC UnipHied	270.000	50.562
Lienkamp	BMBF ANTIBUG	1.408.848	136.068
	BMBF BioMAMPs	379.680	32.852
	EU ERC Regenerate	1.498.987	116.319
Müller	DFG Polymerbasierte	181.830	89.065
Pelz	DFG MiTEG	321.649	61.853
Rapp	EU ERC CaLa	1.999.750	100.530
Rühe	DFG Modifizierte Papiere	211.400	43.814
	DFG PAK	165.800	48.690
	DFG Dynamisches	202.500	44.853
	DFG KOMMA	246.250	28.921
	Carl-Zeiss IPROM	4.500.000	361.959
Rühe, Speck, Reiter	EU Marie Curie PlaMatSu	747.649	43.609
Speck, T.	EU ERC GrowBot	696.166	80.712

Vierrath	Vectorstiftung AlkaCell	259.778	202.327
	Vectorstiftung CO2-to-X	1.000.000	202.327
	Alexander von Humbold	63.600	2.396
	BMBF FC CAT	330.000	3.941
Walter	DFG Donor Akzepter	162.950	27.726
	DFG HYBRIDS	159.850	36.941
	DFG Synthese , X-ray	169.550	2.093
Walther	DFG Chemo-mechanische	427.140	106.414
	EU ERC CReaNet	505.577	48.996
	EU ERC TimePROSAMAT	1.499.813	136.148
Woias	DFG NiLax	150.500	39.552

Tab. 3 Budgets of project groups from 2017 until 2020 in €

Project group	**2017**	**2018**	**2019**	**2020**
Dincer	0	30.727	93.407	153.439
Fischer	0	71.540	65.373	151.342
Gold-schmidtböing	0	0	19.138	75.581
Helmer	0	0	0	30.104
Koltay	0	0	0	138.692
Krossing	0	0	47.578	50.562
Lienkamp	357.536	665.109	507.898	285.240
Müller	0	0	82.220	89.065
Pelz	0	0	0	61.853
Rapp	0	0	39.077	100.530
Reiter	194.042	212.350	110.428	4.404
Rühe	93.852	174.286	234.350	550.142
Speck, T.	212.547	186.637	126.483	98.011
Vierrath	0	0	31.703	339.089
Walter	44.047	56.464	84.064	66.759
Walther	121.500	174.062	284.013	291.558
Woias	0	0	51.887	39.552

HIGHLIGHTS

FUTURE FIELD "ADAPTIVE AND ACTIVE POLYMER MATERIALS"

Evaluation of droplet shape and three phase contact line movement on dynamically switchable spiropyran gels

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[2]Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

Project funding: German Research Foundation (DFG)

Surface-bound or material-integrated molecular switches are capable of changing the surface energy of substrates. Photoswitches such as spiropyrans (SP) are especially interesting, because the switch can be spatially controlled by the controlled exposure to light and it is a visible reversible switch between colourless, hydrophobic SP and hydrophilic, magenta merocyanine form (MC), (Fig. 1). Also, acidic conditions lead to a third, protonated SP state which has an intense green colour.

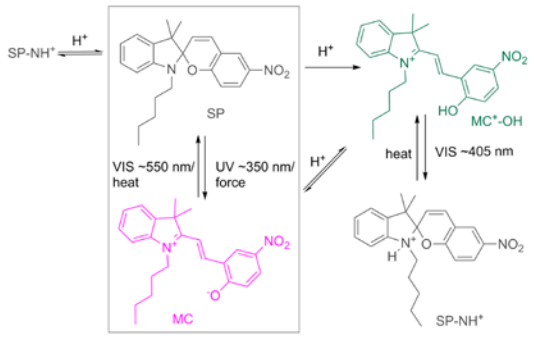

Fig. 1: Reversible photoswitching and acidoswitching of SP (© NeptunLab, IMTEK)

SP can also be used to generate photorheological gels, which change their rheological properties such as viscosity upon photoswitching. There are several types of physical gels such as wormlike (reversed) micelles, molecular gels (supramolecular self-assembly of an organogelator in a solvent). Photorhelogical gels have shown the rheology of the permanent gel with a wormlike micellar structure and the rheological switch is because of the long wormlike micelles transition to smaller vesicle micelles induced by photo-triggers [1].

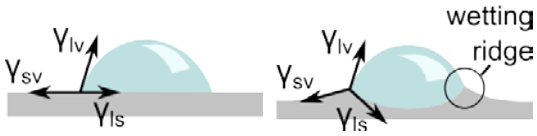

Fig. 2: Wetting ridge that forms on soft surfaces. (© NeptunLab, IMTEK)

Physical gels are well-known because of their easy reversible transit between sol and gel states which makes them advantageous for switchable materials studies compared to chemical gels. The aim of this project is to evaluate the water droplet shape on dynamically switchable spiropyran-containing photorheological gels. Such soft gel surfaces induce a different wetting state, which depends on the softness of the material. The wetting ridge that forms between the substrate and the droplet exerts a force on the droplet and can induce droplet movement upon modulus changes of the surface gels (Fig. 2).

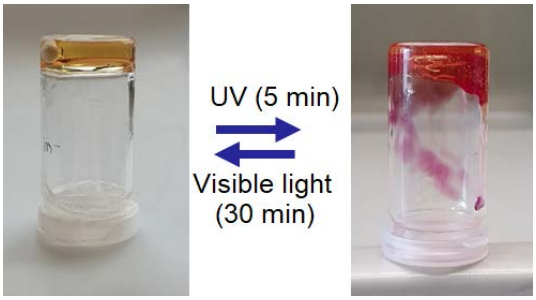

Fig. 3: Bulk-functionalized SP organogel (© NeptunLab, IMTEK)

Mono-functional SP was successfully synthesized according to the previously reported synthesis route by Fissi et al. [2]. Synthesized SP was incorporated into the fabricated non-

aqueous gels to induce the switch upon UV irradiation. Physical organogels were fabricated with different compositions to serve as a flexible surface. Lecithin-based photorhelogical gels reported by Lee et al. [3] were fabricated straightforward by mixing commercial components including cyclohexane, lecithin, sodium deoxycholate (SDC) (or P-coumaric acid, Kumer et al. [4]). As can be observed in (Fig. 3). Rheological properties, i.e. viscosity was altered after UV exposure accompanied by colour change due to the SP to MC switch. If an inverted vial can hold the gel for a long period, it is representative of a gel because of the finite yield stress [1].

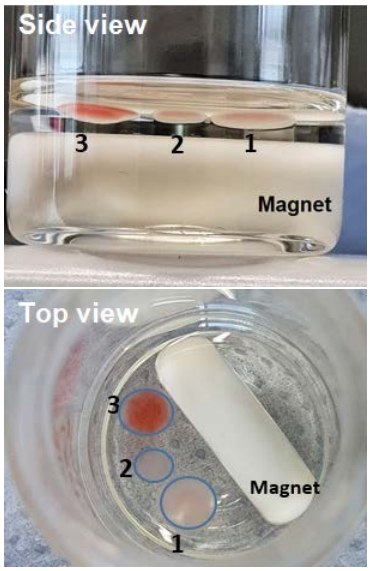

Fig. 4: Water droplets with dye that were placed on top of the fabricated lecithin-based organogel. (© NeptunLab, IMTEK)

Upon placement of water droplets on the gel surface, the softness of the gel can be observed by the droplets sinking into the gel structure, inducing a large deformation of the gel (Fig. 4). To further observe the droplet behaviour on switchable gels, an imaging platform was built based on two high-speed cameras. A monochrome camera (Baumer VCXU-15M) was installed to analyze the droplet from the side view. The ability of the camera to record a high number of frames per second provides the chance to record the very small changes in droplet upon switching of the surface and to analyze the static contact angle of the droplet on the surface.

A colour camera (Baumer VCXU-15C) was installed above the setup to detect the droplet movement and the colour change upon switching (Fig. 5). With a DMD-based lithography machine, the SP switch and switching patterns can be induced from below the sample, and precisely controlled.

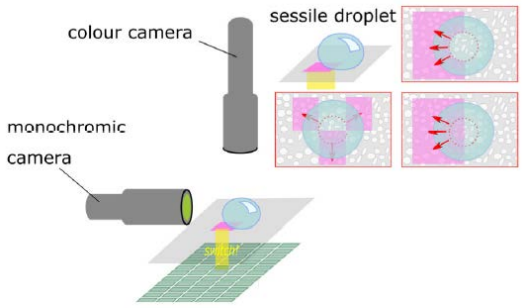

Fig. 5: Imaging platform consisting of two high speed cameras. (© NeptunLab, IMTEK)

Utilizing the monochrome camera, the droplet shape on the surface can be observed as shown in (Fig. 6).

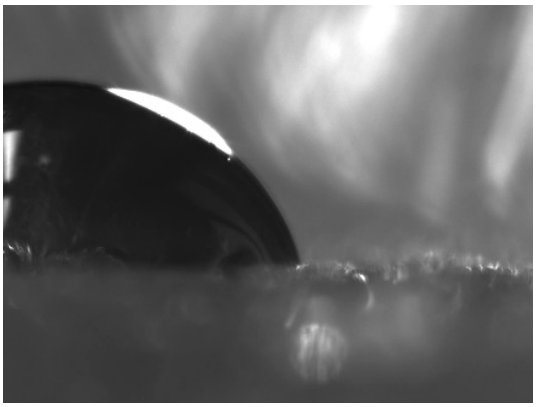

Fig. 6: Imaging platform consisting of two high speed cameras. (© NeptunLab, IMTEK)

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Reducing sensitivity loss in paper-based analytical devices

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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.[1] A main reason for this is that for microfluidic paper-based analytical devices (µPADs) 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 strong light scattering process among the paper fibers depends on how thick the paper sample is, because the thicker the paper, the greater the chance that light will be scattered. Indeed, different paper samples have a different appearance, which means that a different amount of light is able to be transmitted and a different amount of light is scattered.[2] Therefore, the interaction of the light with the paper itself is crucial for the optical read-out: a different amount of scattered light means different detected background signal. In Figure 1 it can be seen that the diffuse reflection, which is the light scattered back towards the detector in all directions, increases as paper thickness increases. This experiment shows that paper thickness is a critical parameter for diagnostics and therefore it needs to be strongly taken in account. With increasing thickness, paper cellulose samples appear whiter and more opaque, light transmittance decreases and scattered light increases.

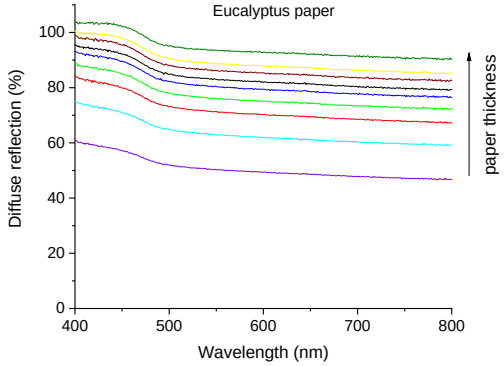

Fig. 1: Diffuse reflection in visible light wavelengths region of Eucalyptus paper cellulose © CPI, IMTEK Univ. of Freiburg.

Thus, the reflection mode approach has been studied for fluorescent read-out on paper cellulose: Cy5-conjugated bovine serum albumin (BSA) was investigated. In Figure 2 it can be seen that the droplet size depends on the thickness of the cellulose, even though the concentration and volume of solution used are the same.

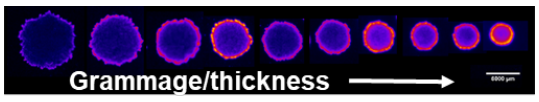

Fig. 2: Fluorescence images of cellulose samples with different thicknesses after spreading a solution with BSA conjugated with Cy5 © CPI, IMTEK Univ. of Freiburg.

The results indicate that as thickness increases, solution penetrates deeper into the thickness and there is more diffusion into the thickness than along the surface. In Figure 3,

the plot shows that the mean gray value increases too as the paper thickness increases. This confirms that solution penetrates more into thicker samples, meaning that the number of voxel layers behind a surface pixel increases and therefore mean gray value increases too.

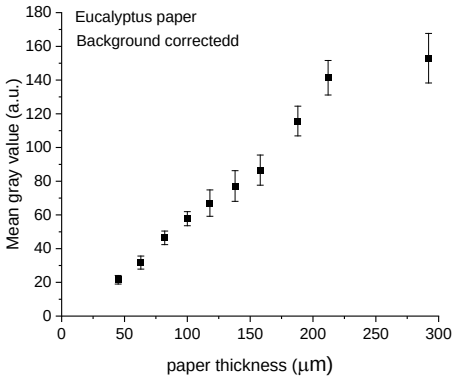

Fig. 3: Mean gray values after background correction evaluated from fluorescence images. The values are plotted against Eucalyptus paper cellulose thickness. Samples were analyzed after spreading a solution with BSA-Cy5 conjugate © CPI, IMTEK Univ. of Freiburg.

The mean gray value is the average gray value within the selected area. Since the area of droplet spreading is different depending on paper thickness, integrated values have been also evaluated, resulting in a similar increasing trend, meaning that a higher thickness provides a higher fluorescence signal intensity. In many cases the goal of analytical devices is to lower the limit of detection as much as possible and in the case of fluorescence detection, sensitivity can be increased by enhancing the performance of the fluorescence system.[3] According to the results obtained, a better detection can be achieved because, as seen in Figure 1, paper cellulose is able to reflect visible light efficiently and suspend it among the fibers: a reflection of the non-absorbed excitation light is back into the fluorophore. In this way a higher fluorescence efficiency can be successfully gained.

In Figure 4, µPADs have been performed. Each device is made of a sample pad, a waste pad and a detection pad in between. The detection pad is the only one of interest for this experiment, thus it has been made using a different Eucalyptus paper thickness for each device. The capture molecule used is bovine serum albumin−biotin conjugate (BSA-biotin) and Streptavidin conjugated with Cy5 in PBS has been used as target molecule.

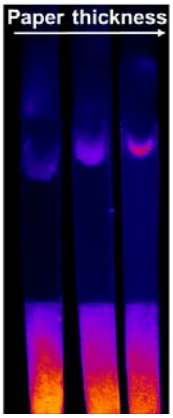

Fig. 4: Fluorescence images of paper-based analytical devices made by sample pad (bottom part), detection pad (middle part) and waste pad (upper part). 3 different thicknesses of Eucalyptus paper cellulose have been used as detection pads. BSA-biotin was the capture molecule spread on the device and let it dry. Streptavidin-Cy5 was the target molecule let flow for about 10 minutes and afterwards the device was analyzed © CPI, IMTEK Univ. of Freiburg.

It can be clearly seen that the signal obtained from the sample performed with the thicker cellulose is stronger due to its stronger ability to reflect light, as expected from the previous shown results.

Hence, paper cellulose represents a promising material for the development of analytical devices for fluorescence analysis with enhanced sensitivity.

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– Push, Push, Push – Cooperative actuators and actuators fields by direct writing processes

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Project funding: Deutsche Forschungsgemeinschaft (DFG)

The generation of microactuators is of great interest, especially in the fields of soft robotics[1] and lab-on-chip applications[2].

In a previous work, our group already fabricated magnetic microactuators to produce fluid transport without external pumps. These so called artificial cilia were produced with a mask based photolithographic process out of prepolymeres.[3,4] A reactive group in the prepolymer can be activated by UV light and a C,H-insertion reaction leads to crosslinking into neighboring chains as well as covalent attachment to the surface (Figure 1). This entire process takes place in the glass-like state of a polymer coating.[5]

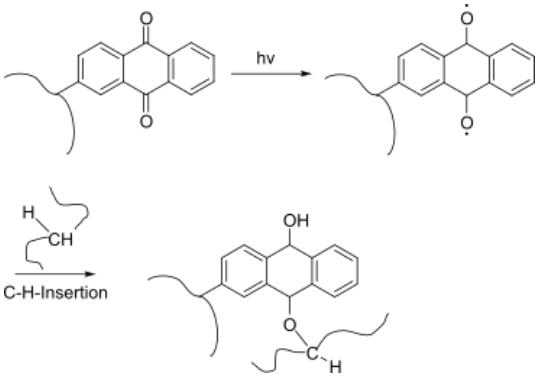

Fig.1: Schematic representation of the C,H-insertion reaction of a reactive group (anthraquinone derivate) via a biradical transition state. © CPI, IMTEK Univ. of Freiburg.

With a direct writing process, the flexibility for designing microactuators in any desired shape could be heavily increased. Two photon crosslinking (2PC) based on two photon lithography and the C,H-insertion crosslinking (Chic) is a powerful tool for direct writing of polymeric structures (Figure 2). In another work, our group already showed, that 2PC of prepolymers based on anthraquinones leads to well defined microstructures.[6]

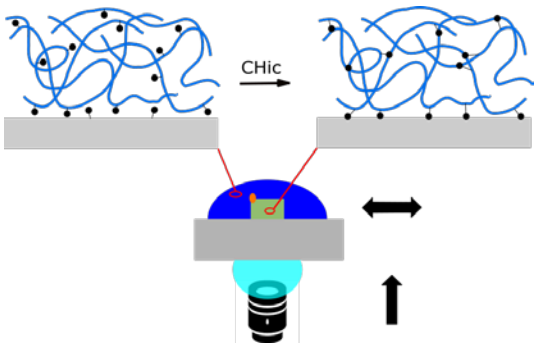

Fig. *2*: Schematic illustration of two photon crosslinking (2PC) using the C,H insertion reaction, where voxel (volumetric pixel) after voxel is written first in the x- and y-directions and then in the z-direction. © CPI, IMTEK Univ. of Freiburg.

Using the same prepolymers combined with superparamagnetic nanoparticles, it is possible to print microactuators out of a polymer-nanoparticle composite in one step. These microactuators can then be moved by a rotating external magnetic field (Figure 3). Parameters for printing (to example energy dose) and for the composite composition (nanoparticle content, crosslinker content in the polymer, molecular weight) need to be investigated in consideration of the resulting mobility of the microactuators in a magnetic field. Major goals are to design microactuators with any desired shape and adjustable properties and fields of micro actuators to enable cooperative interactions.

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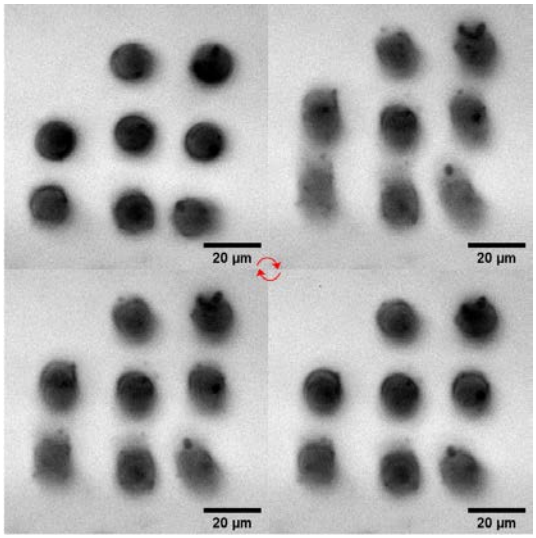

Fig.3: Light microscopy images of cylindrical microactuators, which are moving in a rotating external magnetic field. © CPI, IMTEK Univ. of Freiburg.

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

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Project funding: *Deutsche Forschungsgemeinschaft,* DFG (*liv*MatS)

Surface-attached polymer networks are a powerful and durable surface architecture to tailor surface properties. For the synthesis of these polymer networks there are various methods, e.g. the network can be formed during the polymerization by adding multifunctional monomers. By the incorporation of reactive species it is also possible to crosslink existing polymer chains (e.g. by vulcanization or the click-reaction of azides and alkines). These methods have some drawbacks like the challenge to removing residual monomer in the polymer network or the problem that the reactive groups have to come into contact to perform the crosslinking.[1-3]

In our group we incorporate dormant crosslinker molecules in copolymers that can be activated on demand by photochemical or thermal stimulation. Reactive species are formed that do not require a specific reaction partner for the crosslinking reaction but rather bind to C-H-bonds in their vicinity. Examples for the crosslinker molecules are diazo-compounds, benzophenones or anthraquinones. For all of them the crosslinking occurs through a C-H insertion based crosslinking (CHic), which makes it a powerful and universal method. The reaction mechanism is shown for an anthraquinone based crosslinker in Fig. 1 [4-8]

The activation parameters for the CHic process depend on the chemical environment of the anthraquinone group. Anthraquinones with electron-donor substituents have an increased probability for two-photon absorption (2PA) which enables the use for a process called two-photon crosslinking (2PC), a 3D-printing technique to generate free standing microstructures with a resolution <1 µm.[9-10]

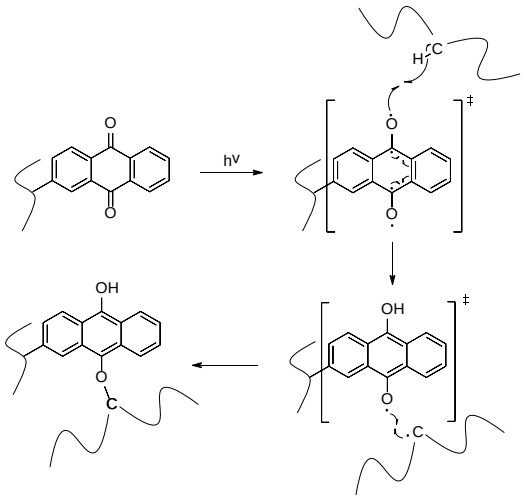

Fig. 1: Mechanism of the photochemical induced CHic-reaction of an anthraquinone via a biradical transition state. © CPI, IMTEK Univ. of Freiburg.

Our goal is to synthesize novel crosslinker molecules, characterize their crosslinking behavior and therefore improve the 2PC process and the resolution of the printed microstructures.

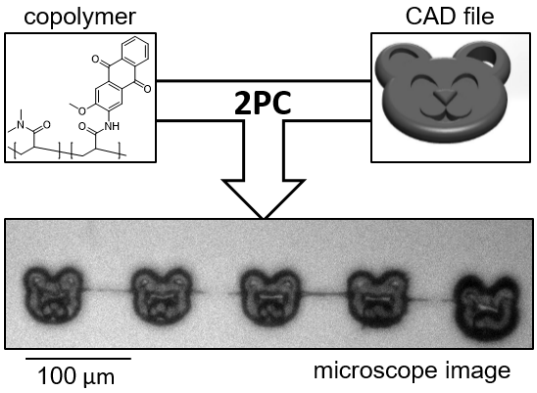

Fig. 2: 2PC process with the anthraquinone based copolymer P(DMAA-co-AAMAQ5%) to generate free standing 3D-microstructures (microscope images). © CPI, IMTEK Univ. of Freiburg.

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Revelation of polymer distribution in modified paper substrates by confocal laser scanning microscopy

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

Paper as a versatile and interesting material is increasingly moving back into focus as a sustainable alternative in many application areas. However, only the addition of additives allows paper to be applied in our everyday lives to the extent we are used to.

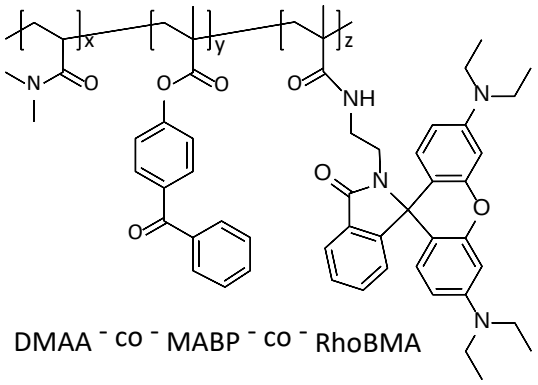

Fig. 1. Structural formula of p(DMAA-co-MABP-co-RhoBMA) © CPI, IMTEK Univ. of Freiburg.

Among these additives is a group of mainly polymer-based agents that prevent the paper from disintegrating upon contact with water, the so-called wet strength resins. Modification via C,H-insertion crosslinking through photochemically 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.

The spatial distribution of these applied wet strength resins in the cellulose network and the influencing parameters are still unknown. To tackle this question, a copolymer was synthesized from the hydrophilic matrix monomer N,N-dimethylacrylamide (DMAA) and a benzophenone based crosslinker MABP (Figure 1), together with a rhodamine B methacrylate (RhoBMA) to be able to perform confocal laser scanning microscopy (CLSM).

Our fluorescent copolymer was applied to a lab-made eucalyptus sulfate paper sample through a simple impregnation process from water or isopropanol. After impregnation, samples were dried, crosslinked with UV-light (254 nm, 2 J/cm^2) and unbound polymer was removed by Soxhlet extraction in ethanol over night. The paper samples were pre-treated with Calcofluor White, which is a fluorescence marker known to well-bind to hydrocarbon, especially to cellulose. This way, the cellulose fibers can be visualized with fluorescence microscopy at 405 nm excitation, while the rhodamine B carrying polymer can be visualized at 561 nm excitation.

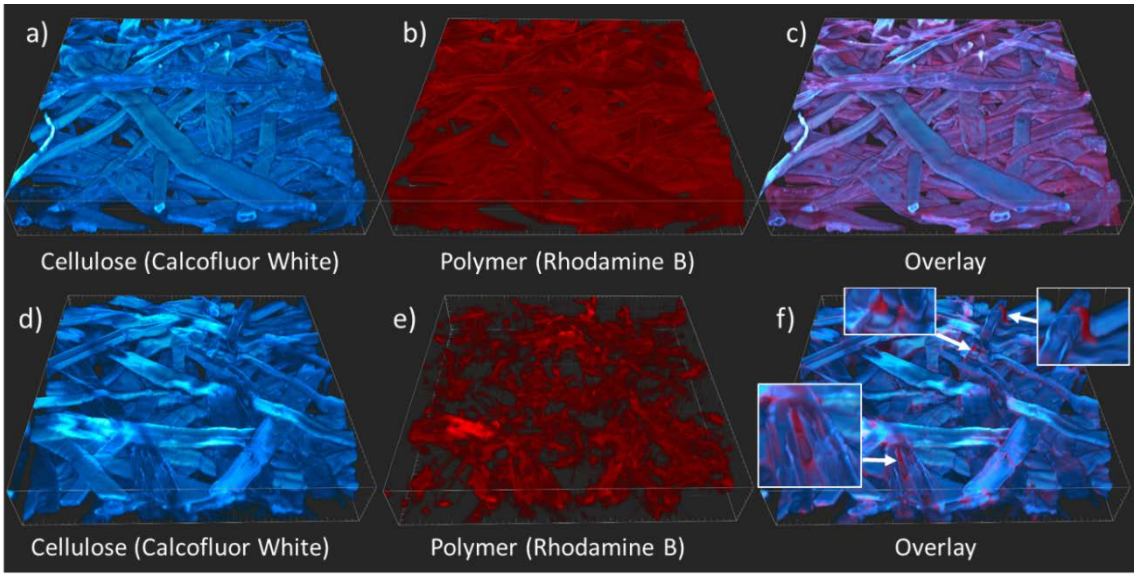

Fig. 2. CLSM image of a Calcofluor White stained paper sample modified with p(DMAA-2%-MABP-0.25%-RhoBMA). From an aqueous (a-c) and from isopropanol (d-f))((c = 30 mg·mL^{-1}). a+d) 405 nm channel (Calcofluor White M2R); b+e) 561 nm channel (rhodamine B); c+f) overlay. © CPI, IMTEK Univ. of Freiburg.

The Calcofluor White stain is homogeneously distributed over the cellulose fibers (Figure 2a+d). This way, the location of the polymer can be located in relation to the fiber. When polymer is applied from water the resulting distribution is highly homogeneous and covers the whole surface of the cellulose fibers (Figure 2b). The overlay from the cellulose fiber channel and the polymer channel (Figure 2c) underlines that there is no polymer in the free space between the fibers but that the polymer is directly adsorbed to the fiber surface. When the polymer is applied from isopropanol, the CLSM images reveal a different outcome (Figure 2e). Here, the polymer is not homogeneously distributed over the cellulose fibers but is rather accumulated in patches. The

overlay shows that the polymer of these polymer accumulations is located in the free space between the fibers, often at fiber-fiber crossings (Figure 2f).

The exact reasons for the observed behavior are still under ongoing research. We believe that the ability of the solvent to swell the cellulose fibers has a strong impact as swelling highly increases the fiber surface. While H_2O is known to swell the cellulose fibers to a high degree, isopropanol does not swell the fibers properly. [3] There may be other parameters involved like vapor pressure of the solvent and polarity of the applied polymer. These parameters are still investigated to for a more complete understanding on how the polymer distribution is influence.

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Thermal and photochemical activation of diazo groups containing Polymers for the generation of Polymer networks through C-H-insertion crosslinking (CHic)

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Funding: Deutsche Forschungsgemeinschaft, DFG

Interfaces determine the interactions between a material and the contacting environment. Polymer coatings enable targeted modification of these surface properties across a broad spectrum of chemical resistance, adhesion, wettability and biocompatibility. For almost all practical applications, permanent attachment and longevity of the coating is an essential requirement. One way to achieve sufficient coating durability even under adverse conditions is to attach chemically polymer networks.[1–6] C,H-insertion based crosslinking offers a simple method to make this possible. In this process, dormant groups are integrated into the polymers, which can be activated on demand and react with the backbone or other groups of neighboring chains by insertion into C-H bonds.[7] To date we have developed crosslinker systems that allow photochemical (benzophenone or anthraquinone, forming ketyl biradicals) or thermal and photochemical (diazocompounds, forming carbenes, Fig. 1) activation in prepolymers.[5,6,8–10]

Thermal crosslinking is advantageous if a layer is opaque to UV light. To prevent any degradation and deformation of the substrate and/or the layer it is advantageous to perform the crosslinking with mild temperatures. This can be tuned by designing the molecular structure around the diazo-group. In general, an acceptor group next to the diazo group enhances its stability while a donor group facilitates the decomposition to a carbene.[11]

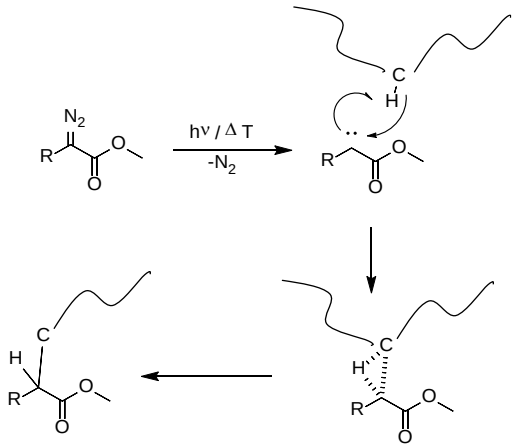

Fig. 1: Mechanism of the CHic-reaction. Photochemical or thermal crosslinking of a diazo.compound in a concerted reaction. © CPI, IMTEK Univ. of Freiburg.

We therefore took one of our efficient crosslinker PEDAz12 (Fig. 2) and added a donor group (here a methyl group in para position) to decrease the stability of the diazo-group. Fig. 2 shows the gel-content experiments of the two different crosslinker systems. The donor-functionalized crosslinker has a lower percolation point and takes less time to reach sufficient crosslinking throughout the film.

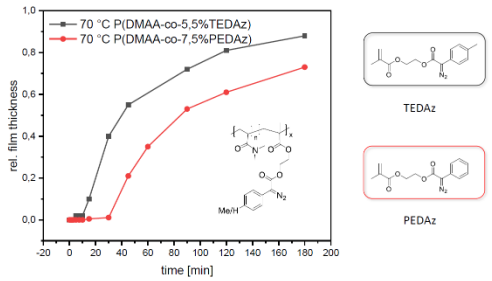

Fig. 2: Gel-content measurement of our established PEDAz crosslinker and of the donor-functionalized crosslinker TEDAz. © CPI, IMTEK Univ. of Freiburg.

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Autonomous light-responsive LCE actuators

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

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) (Figure 1a). Possible triggers include for example temperature, pH or light.

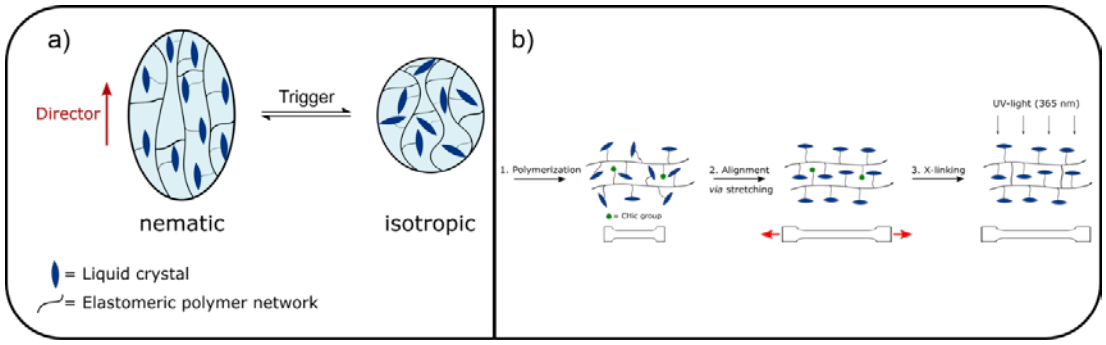

Fig. 1: Schematic representation of an LCE and of the concept of stretch-alignment. a) The order-disorder transition from the nematic to the isotropic state can be triggered, e.g. by temperature, pH or light, and leads to a contraction of the LCE. b) By applying a stretching force in one direction, the liquid crystals can be aligned into a monodomain and crosslinked in that state to form an LCE. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg.

Previous results within this project show that the copolymerization of the CHic-able unit MABP (Figure 2a, top row) with the thermo-responsive LC monomer 4-ADBB (Figure 2a, left) leads to a pre-polymer that can easily be aligned on wafer-level and post-crosslinked with UV-light. The CHic reaction (C,H-insertion based crosslinking)[2] serves as a facile way of network formation when starting from the pre-polymer. We are now extending the scope to thicker, free-standing films. To achieve this, we apply stretch-alignment. Figure 1b schematically shows the principle of this technique. The films are pre-crosslinked to a certain degree in the isotropic phase and then stretched at elevated temperature ($T > T_{NI}$). Stretching induces the alignment of the liquid crystals, allowing them to form a monodomain in the direction of the applied force. The polymers are then post-crosslinked to form an elastomeric network and can alternate between the original and the stretched shape when the nematic-to-isotropic phase transition is induced.

Since the polymer P1 (Figure 2a, top row) is brittle and therefore hard to handle at RT, we introduce a different crosslinker, namely C4OBP (Figure 2a, bottom row), which holds the same functionality as MABP in P1 but contains a C4-chain as a short spacer. Even though the DSC results in Figure 2b show that the transitions temperatures (T_g and T_{NI}) are comparable to those of P1, P2 is much softer and hence easier to handle and process. Stretch-alignment of P2 produces well-aligned films (Figure 2c) that are able to change repeatedly between the two states upon heating/cooling, as Figure 2d demonstrates.

This technique is not limited to rectangular shapes but rather allows for a manifold of printed (original) and programmed (stretched/deformed) shapes. A good example for the versatility of this method is a paper recently published by Barnes and Verduzco.[3] Since part of this project is the fabrication of light-responsive LCE, we currently work on further extending the scope of pre-polymers to light-responsive systems. Light is a particularly favorable trigger as it is non-invasive and easy to control. There are two main mechanisms to incorporate light-responsiveness into LCE. One is photothermal heating. In this case, a photothermal dye is incorporated into the LCE, Disperse Red 1 (DR1, Figure 3a) being a prominent example. Irradiation with a specific wavelength triggers the isomerization of DR1. Since the half-life of the thermodynamically less stable *cis*-isomer is on the timescale of seconds, the isomerization is triggered continuously, producing heat through vibrational relaxation. This heat in turn triggers the transition from the nematic to the isotropic phase. The second mechanism is also based on the photoisomerization of azo-compounds, here however the thermal half-life of the *cis*-isomer in on the timescale of hours to days. Switching from the *trans*- to the *cis*-isomer reduces the order of the LC phase and hence significantly reduces the transition temperature of the LCE. For the second mechanism, unsubstituted azobenzenes (AB, Figure 3b) are frequently applied

in literature. However, AB faces many challenges such as low photostationary states of only about 80%[4] and short thermal half-lives of the *cis*-isomer.[5] 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.[6]

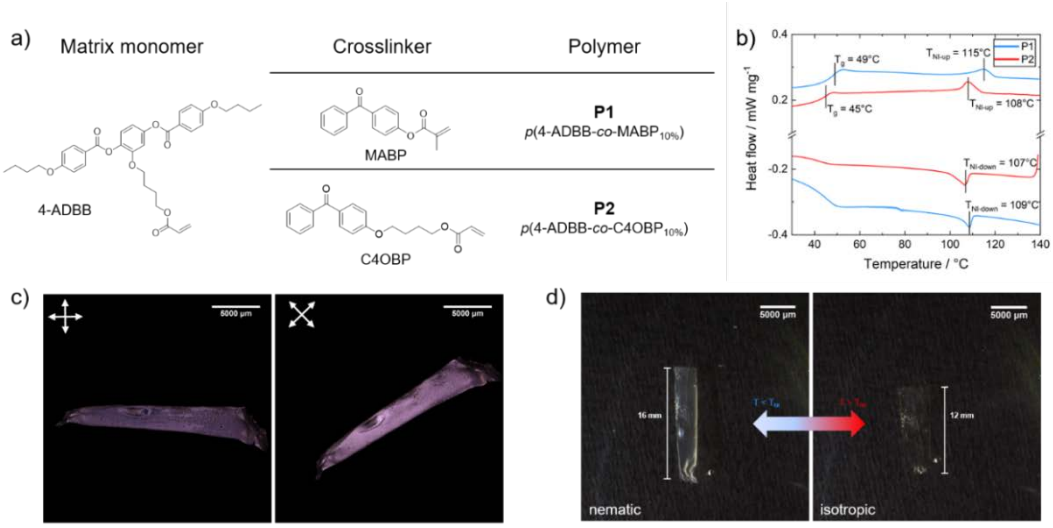

Fig. 2: Polymer compositions of CHic-able LC pre-polymers with corresponding DSC data and microscopy images of the aligned films of P2 a) Polymer compositions of P1 and P2. Both polymers contain 10 mol-% of a crosslinker based on benzophenone and 4-ADBB as the temperature-responsive LC monomer. b) DSC data from P1 and P2. P1 (blue) has slightly higher transition temperatures than P2 (red). c) Polarized optical microscopy images of an LCE consisting of P2. Alignment is visible by the change in birefringence between 0° and 45°. d) Microscopy images of the film in the nematic (RT, left) and the isotropic (120°C, right) to demonstrate the reversible contraction. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg.

To address these limitations we investigate arylazopyrazoles (AAPs, Figure 3c) as molecular switches. AAPs have photostationary states with higher percentages and faster switching kinetics compared to their AB analogues.[5]

One current challenge in the project is the combination of the stretch-alignment of CHic-able pre-polymers these with light-responsive motifs, as the azo-compounds cannot be irradiated with UV-light or heated to induce the crosslinking step since they would lose their orientation and reduce the order of the LC-phase in either case. Hence, we work on developing and incorporating new CHic-able crosslinkers suitable for these motifs as part of a joint project within the FIT.

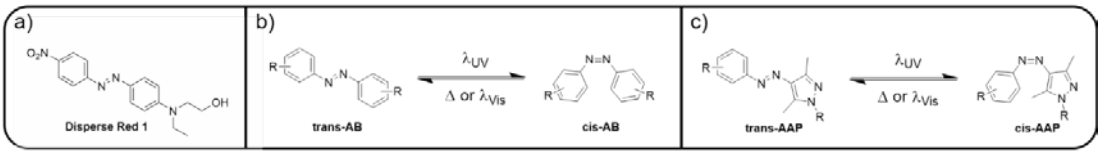

Fig. 3: Different motifs for light-responsive LCE a) Disperse Red 1 as a photothermal dopant. Due to the push-pull-system thermal relaxation is on the timescale of seconds. b) Photoisomerization of AB. c) Photoisomerization of AAP. © Chemistry and Physics of Interfaces, IMTEK, University of Freiburg.

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Heterogeneous mechanical metamaterials: towards adaptivity and learning

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This project focuses on the development of adaptive heterogeneous mechanical metamaterials capable of altering their internal architecture. To acquire mechanical properties appropriate for the specific conditions, mechanical metamaterials have to sense the environment, process received information, and then change their internal architecture accordingly. The ability to store the history of previous external stimuli using the local reconfiguration paves the way towards learning behaviour.

A key goal of the subproject that has been initiated last year is to design mechanical metamaterials containing multistable cells and understand how these cells can interact with each other through the architecture. Such metamaterials will be able to store "digital" data and perform basic logical computations. Experimental and numerical studies reveal the feasibility of shaping the local energy landscape using the involved interplay between elastic and magnetic energies (Fig. 1) [1]. Depending on the arrangement and orientation of magnetic inclusions, developed mechanical metamaterials can exist in multiple stable states and switch between these states when subjected to external stimuli.

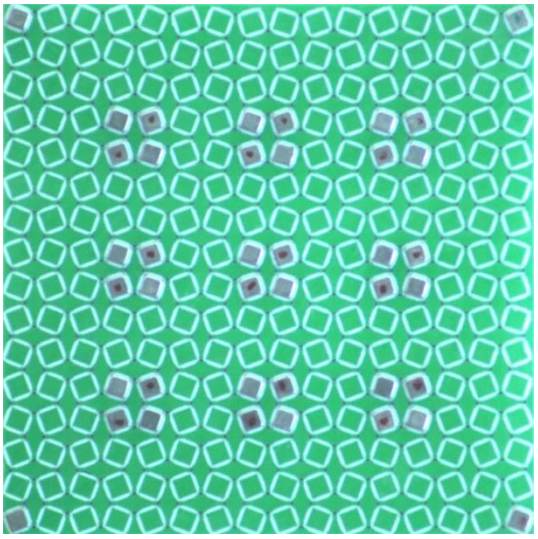

Fig. 1: Multistable mechanical metamaterial with embedded magnets © Viacheslav Slesarenko

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Dynamic chemical networks: steps towards living materials

Charalampos G. Pappas

Cluster of Excellence *liv*MatS; Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

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

The project focuses on the use of a systems chemistry approach towards the discovery of materials that are capable of altering their structures and properties in response to changing situations. This research programme will be conducted by chemist Dr. Charalampos Pappas (recently appointed as a Junior Research Group Leader) from the University of Freiburg and his research team.

Systems chemistry focusses on mixtures of interacting molecules that continuously exchange chemical information, leading to emergent properties, properties that cannot be attributed to the individuals of the system. This network concept contrasts with the analytic or reductionist approach – a traditional chemical route in synthesis and analysis of isolated compounds, in which parts themselves cannot be analysed any further. The construction of dynamic chemical networks, in which molecules can interconvert by exchanging subunits through reversible covalent bond formation has already paved the way towards highly ordered self-assembling structures and materials.

Synthetic mimics of biology's active self-assembly systems, which combine chemical conversions with self-assembly to achieve non-equilibrium functions, have been the focus of considerable research efforts in recent years. Active molecular systems and interactive materials are of interest as they may give rise to new features that are normally not associated with synthetic systems, in that they may be reconfigurable, externally fuelled, self-healing, or even self-replicating. Peptides and peptide derivatives are particularly attractive building blocks for the construction of supramolecular materials. This has resulted in the growing field of peptide nanotechnology, showing a variety of current and potential applications, *e.g.* emulsifiers and gelators for food ingredients, biomaterials, soft robotics and energy harvesting.

Particular to the project, the research team will investigate in detail the mechanisms and pathways that allow the discovery of functional materials by engineering and furthermore mimicking the way that living systems employ both covalent chemistry and physical assembly to achieve complex behaviours. By merging a chemically activated approach (peptide esters) and catalytic self-assembly (aminolytic reactions), the spontaneous formation of peptide chemical networks will be targeted. We will investigate in parallel, the construction of metabolic (promiscuous assemblies that move towards their own food and save energy), behavioural (assemblies that are trained to have specific functions) and ''energized'' materials (programmable assemblies that only exist under the influence of chemical fuels). Chemical messengers (external templates) and physical stimuli (audible sound waves) will be used to install into these networks energy and furthermore investigate the pathways that allow fully synthetic chemical systems and biological entities to co-emerge and actively reconfigure (Fig. 1).

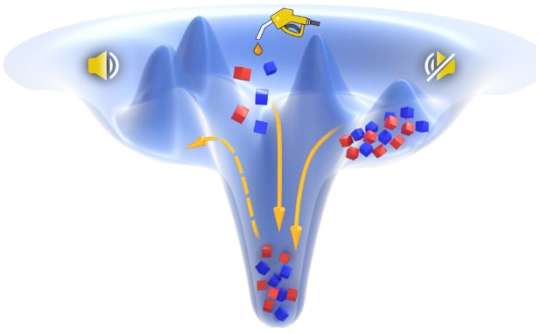

Fig. 1: Schematic representation of a complex energy landscape, highlighting the effect of chemical (fuels) and mechanical (audible sound waves) energy towards dissipative adaptation and active communication. Cubes represent building blocks and assemblies produced from amino acids. © Charalampos G. Pappas

Adaptive lenses based on conductive and optically transparent silver nanowire networks

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Department for Microsystems Technology, Laboratory for Design of Microsystems

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

Soft electronics have shown to be evident for monitoring (soft) robotic and human motion. Within the work of this project, we have been developing a highly flexible resistive strain gauge prototype that facilitates a measurement of elongations of over 10%. Our system is based on a layer of silver nanowires that changes its electrical resistance in response to a stretching deformation.

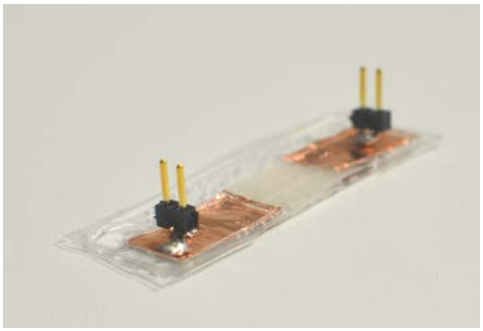

Fig. 1: Silver nanowire-based Strain gauge. The nanowire layer is located between the copper stripes and protected by a PDMS layer. (© Laboratory for the Design of Microsystems, IMTEK)

For the fabrication of a highly flexible strain gauge, PDMS (Sylgard 184, Dow Chemicals) was chosen as a substrate. The PDMS was spin coated onto a glass wafer and the nanowires were applied with a doctor blading step on top of this PDMS layer. To improve the electrical conductivity, the nanowire network undergoes a thermal treatment in which the nanowires are welded together. For protecting the nanowire layer from physical damage, a stripe of the PDMS-nanowire compound was encapsulated by casting a further layer of PDMS onto it. The electrical contact to the nanowire layer was provided by applying an adhesive copper tape (1181/9.5, 3M) on the nanowires before the encapsulation step. After encapsulating the whole device in PDMS, a window was cut into the encapsulation layer to access the copper contacts. A fully prepared strain gauge can be seen in Fig. 1. Solder pins were attached on the connector areas in this case.

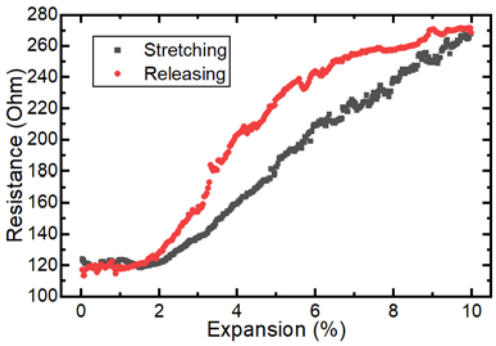

Fig. 2: Resistance response of the strain gauge to a stretching of up to 10%. (© Laboratory for the Design of Microsystems, IMTEK)

The fabricated strain gauges were mounted on a linear motor stage with mechanical clamps on the fixed and moving part of the apparatus. The measured resistance to expansion behaviour is shown in fig. 2.

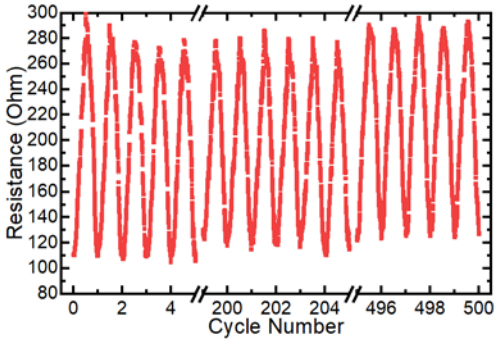

Fig. 3: Resistance plotted over the number of stretch and release cycles with a strain from 0% to 10%. (© Laboratory for the Design of Microsystems, IMTEK)

The resistance response to the expansion can be considered linear for the stretching. The flat onset is caused by the improper clamping. The nonlinear response in the releasing can be attributed to the viscoelastic properties of the PDMS. The whole system shows a stable operation even after 500 cycles, as can be seen in fig. 3. The results of this

sensor design can be compared to the recently reported sensor of Choi *et al.* [1], showing an almost identical behaviour.

This sensor design, for example, facilitates the measurement of human motion, if attached to a joint. The PDMS type can be changed to a more rigid or soft material to adapt to almost any use case.

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FUTURE FIELD "BIOMIMETIC, BIOBASED AND BIOACTIVE MATERIALS SYSTEMS"

Damage management in cacti

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The interdisciplinary project "Abscission and self-repair in biological and artificial materials systems" is part of the Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems" (*liv*MatS) and is assigned to Research Area C, which deals with ensuring and promoting the functionality of materials systems for their defined lifetime. The aim of the biological subproject is to identify and analyse concepts found in the plant kingdom that show to potential for transferring to technical applications.

An important field of longevity is damage control. This includes the two major fields of damage prevention and damage management. In living nature, damage prevention is often achieved by gradient structures, which can particularly be found in areas of high mechanical stress, such as the transition from rod-shaped to planar structures [1]. Materials systems that respond or adapt to (changing) environmental conditions can also make an essential contribution to prevent damage. These two aspects are investigated in the Plant Biomechanics Group using herbaceous model plants in the *liv*MatS associated project BioElast.

During biological evolution, however, a plethora of functional principles have been developed that enable plants to manage damage by means of self-repair and/or abscission. On the one hand, wounds can be repaired by self-sealing and self-healing processes. On the other hand, plant organs that are no longer needed (as can be seen every autumn in the deciduous leaves) can be shed (so-called "abscission"). A plant family perfectly suited for the analysis of both of these processes are the cacti, or more precisely their subfamily Opuntioideae (see Fig. 1). Their adaptations to (semi-)arid habitats and the accompanying water storage are associated with the importance of sealing wounds in case of injury, to prevent the plants from losing a great amount of water. This presumption was confirmed by the anatomical examination of our two test species, *Opuntia ficus-indica* and *Cylindropuntia bigelovii*, during a 21-day healing period, after artificially wounding the branches. A peridermal wound tissue had completely covered the wound in both examined species and thereby limited the loss of water after damage to the outer protective layers. However, mechanical bending tests showed that this repair of the wound was not, or only to a very limited extent, accompanied by a recovery of the mechanical stability of the branch. Since the cross-sectional area is reduced considerably in the branch-branch junctions of Opuntioideaea, and these are commonly the locations where the greatest mechanical stresses occur, it can be assumed that the selective pressure for branch injuries is mostly on sealing to prevent excessive water loss and less on mechanical stability for which the principle "sufficient is good enough" applies [2].

These very branching junctions are what make the Opuntioideae also fascinating research objects for abscission processes: Some species have quite stable connections that rarely fail, while other species have unstable connections and use branch shedding to reproduce vegetatively via offshoots [3]. In order to investigate the different mechanical behaviour of the junctions, comparative morphological, anatomical and mechanical experiments are carried out. Stained microscopic sections show at (sub-)cellular level which tissues are present in the attachment zones of the different species. MRI scans are used as modern analytical methods for 3D imaging of these tissues involved. Micro-tensile tests of fresh, isolated dermal tissues and fibres allow to quantify their mechanical properties. Furthermore, tensile tests with 3D-scanned and 3D-printed, individualised clamping jaws are used to analyse the mechanical behaviour of the entire materials systems. This is supplemented by the digital image correlation to determine the local strains of the surface under tensile load [4].

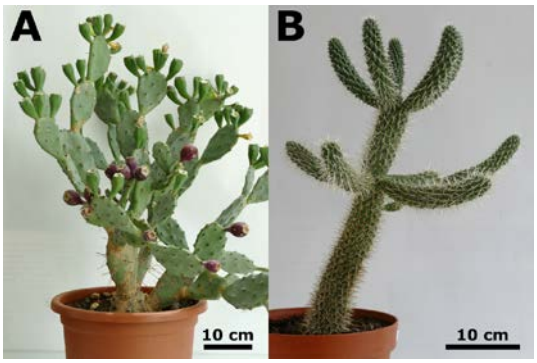

Fig. 2: Selected experimental species of the cactus subfamily of Opuntioideae. A: *Opuntia ficus-indica*. B: *Cylindropuntia bigelovii.* © Plant Biomechanics Group Freiburg.

With the findings from all these experiments, we are confident to achieve a deeper understanding of damage management in Opuntioideae and in cacti in general. Moreover, in the context of an interdisciplinary cooperation within the *liv*MatS cluster, we are aiming to make a valuable contribution to the Sustainable Development Goal 12 'Responsible consumption and production patterns' through the efficient use of resources and the reduction of waste generation [5].

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Physics and mechanics of plant surfaces with cuticular folds and other microstructures

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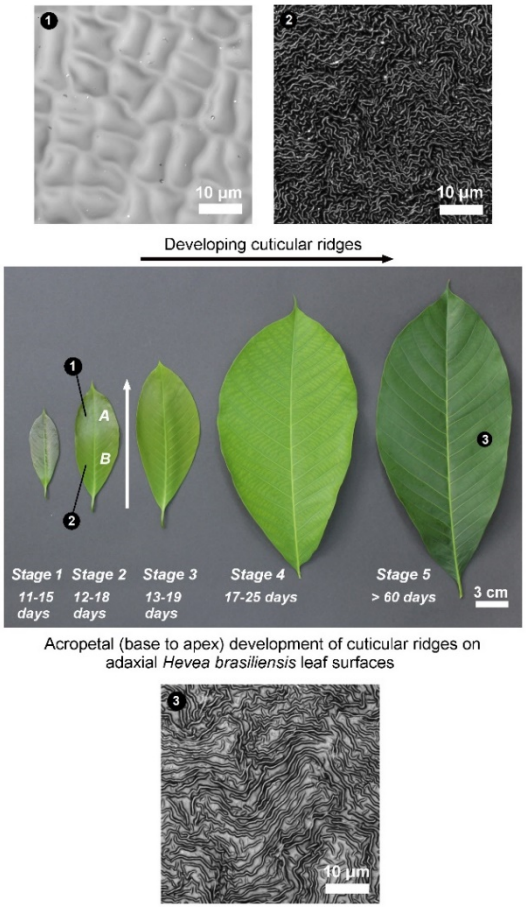
PlaMatSu - Plant-Inspired Materials and Surfaces (www.plamatsu.eu)

The PhD-project "Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures" was one of the nine PhD projects carried out under Plant-Inspired Materials and Surfaces (PlaMatSu) at four leading European universities in the field of bio-inspired materials including: University of

Strathclyde (Prof. Bruns), Glasgow, UK, Adolphe Merkle Insitute/Université de Fribourg, Switzerland (Prof. Steiner, Prof. Weder), Universität Freiburg, Germany (Prof. Reiter, Prof. Rühe, Prof. Speck), and University of Cambridge, UK (Prof. Glover, Prof. Vignolini). PlaMatSu aimed for a better understanding of the structure-function relationships at the plant cuticle and to develop new functional materials and interfaces that mimic multifunctional plant surfaces.



Acropetal (base to apex) development of cuticular ridges on adaxial *Hevea brasiliensis* leaf surfaces

Fig. 1. The ontogenetic development of cuticular ridges on the adaxial leaf surfaces of *Hevea brasiliensis*. The leaf surfaces were composed of smooth epidermal cells at stage 1 (young); the cuticular ridges developed rapidly on the leaf surfaces at stages 2 to 3, and the adult leaf stages (stage 4 and 5) were characterized by fully developed cuticular ridges. The colour changes on the leaves also coincided with the ridge development. (adapted from [4])

The research topic of the PhD-project "Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures" was a better understanding of growth-induced variations in plant leaf surfaces having wrinkled cuticles and to estimate corresponding changes in the walking frictional forces of insects [1,2]. For this study, the model plants *Hevea brasiliensis* (Rubber tree) and *Schismatoglottis calyptrata* cultivated in green houses of the Botanic Garden, University of Freiburg were selected. The microscale morphology of leaf surfaces of *Schismatoglottis calyptrata* and other model plants *Calathea zebrina* and *Ludicia discolor* grown under different environmental conditions in the Botanic Garden was also compared.

Confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) techniques were used to carry out microstructural investigations of the surface structures. For insect attachment experiments, we used the model species – Colorado potato beetle (*Leptinotarsa decemlineata*) having hairy tarsal attachment systems. One end of a human hair was attached to the elytra (back) of the beetle using molten beeswax and the other end was connected to a highly sensitive force transducer. A small light source was used to guide insects to walk straight during the experiments and the median values of the maximum traction forces obtained from the traction experiments were measured. To avoid artefacts due to ontogenetic changes in surface chemistry and dehydration of the leaves during microscopic analyses and insect walking experiments, polymer replicas [3] of the whole leaf surfaces of *Hevea brasiliensis* and *Schismatoglottis calyptrata* were used for CLSM observations and traction force measurements.

CLSM measurements showed direction-dependent formation and development of cuticular ridges (or folds) on the adaxial leaf surfaces of *Hevea brasiliensis* and *Schismatoglottis calyptrata*. The cuticular ridges developed acropetally (from base to apex of the leaves) on *Hevea brasiliensis* leaves (Fig. 1) and basipetally (from apex to base of the leaves) on *Schismatoglottis calyptrata* leaves. The ridge development also coincided with the visible colour changes on the leaf surfaces during growth. In both species, three distinct levels of morphology were identified - (i) smooth epidermal cells on young leaf surfaces, (ii) high aspect ratio cuticular ridges on the leaf surfaces at an in-

termediate growth stage, and (iii) fully developed (stretched and thickened) cuticular ridges on adult leaf surfaces.

The insect traction experiments also showed significant differences in the walking frictional (traction) forces with leaf ontogeny. The insect traction forces were highest on replicates of young leaf stages and decreased significantly for walking experiments performed on replicates of adult leaf stages. The forces correlated strongly with the dimensions of the cuticular ridges [4]. Comparison of the leaf surfaces of plants grown under different environmental conditions showed that the analysed growth conditions did not markedly affect the microscale morphology in the model species selected.

In order to obtain a detailed understanding of the influence of morphology and dimensions of cuticular ridges on the insect traction forces, additionally a theoretical approach was taken. Assuming that attachment and detachment of the hairy structures of the insect tarsea, i.e. the seta tips, on respectively from cuticular ridge-like wrinkled morphologies are governed by elasto-capillarity, different parameters like the interfacial contact area fraction, the optimal wrinkle spacing and the peeling forces were estimated. In collaboration with Prof. Steiner and his Group at the University of Fribourg, insect traction experiments were performed on artificial polymer-based rough surfaces that mimic the natural leaf surfaces with cuticular ridges. The biomimetic surfaces produced resulted in reduced insect walking frictional forces [5], and thus proved their high potential for the development of chemical-free insect repellents

Our results provided crucial information on how the functional properties such as insect attachment change with leave surfaces micromorphology during the growth of the leaves. In addition, the experimental and theoretical results also serve as a basis for the development of adaptive bioinspired technical surfaces.

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The plant role models: A spring-damped adhesive system and self-stiffening braided support structures

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GrowBot - Towards a new generation of plant-inspired growing artefacts (www.growbot.eu)

The project "GrowBot - Towards a new generation of plant-inspired growing artefacts" aims to develop new, low-mass and low-volume bio-inspired robots, able to navigate environments not accessible to conventional robots equipped with wheels, legs or other types of animal inspired climbing devices. To that end it proposes a disruptively new paradigm of

movements in robotics based on the inspiration from plant role models. Plant movements are relatively unexplored as concept generators for movements in (soft-)robots. In addition, they fundamentally differ from animal movements, since plants move from one point to another mainly using growth and thereby continuously and adaptively changing their size and shape. These movements are particularly apparent and fast in climbing plants.

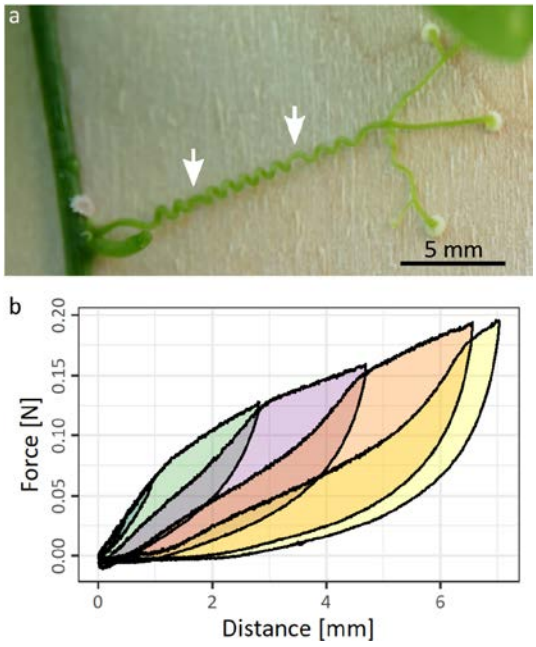

Fig. 1: Spring-like spiralized tendril of *Passiflora discophora* featuring 2 perversions (white arrows) (a), and incremental hysteresis test performed on the main axis of a tendril with elongation cycles of 5%, 10% (not discernible in the figure), 30% (green), 50% (purple), 70% (orange) and 75% (yellow) strain (b). (© Plant Biomechanics Group)

Twining vines, climbers with adventitious roots and tendril climbers with or without adhesive pads use various methods to ascend with the help of support structures. The passion-flower *Passiflora discophora* for instance forms complex, branched tendrils carrying several adhesive pads at their tips that anchor safely the plant to its substrate. Once the ends are fixed, the tendril coils, forming at least one point of inversion in the handedness of the helices, a so-called perversion. Morphometric analysis of the tendril main axes showed that other than the minimal number of one, also two or three perversions are relatively common in this species (> 10%, n = 127, Fig. 1a), and, although rarer, as much as four or five perversions can occur. Preliminary analyses of the tendril anatomy at different stages of the coiling process have been carried out, to continue these investigations assessing the coiling mechanism itself and the underlying structural changes.

The damping properties of the delicate, spring-like, coiled tendril axis have been quantified, by submitting the axes to cycles of incrementally increased elongation (Fig. 1b) and – finally – loading up to failure. Hysteresis tests showed that the tendril axis has viscoelastic properties, shows pronounced energy dissipation and high strains at failure. Therefore, the attachment system consisting of the branched sprialized tendrils and the safely attached adhesive pads can be viewed as a fail-safe system, as shown before for the much less spiralized tendrils of Boston Ivy (*Parthenocissus tricuspidata*) [1,2].

Besides anchoring to the substrate or winding around supports, the mere reaching of the supporting structures is often a major challenge. Just as for plants, technical *GrowBots* often have to bridge void spaces to the next anchorage point in a self-supporting way. We were able to show that plants often have several young searcher shoots winding around each other and that this braid-like intertwining is a very effective method of increasing stiffness with relatively little weight gain, and thus ultimately allows for increasing the possible reach at little material and energy invest [3]. At present, we are conducting experiments to quantify the increase in range resulting from intertwining of shoots *in situ*, inter alia on the Dutchman's pipe (*Aristolochia macrophylla*) and other plant species as *Dipladenia* sp. and *Wisteria* sp..

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Artificial Venus flytraps as adaptive actuator systems for biomimetic snap-trap demonstrators

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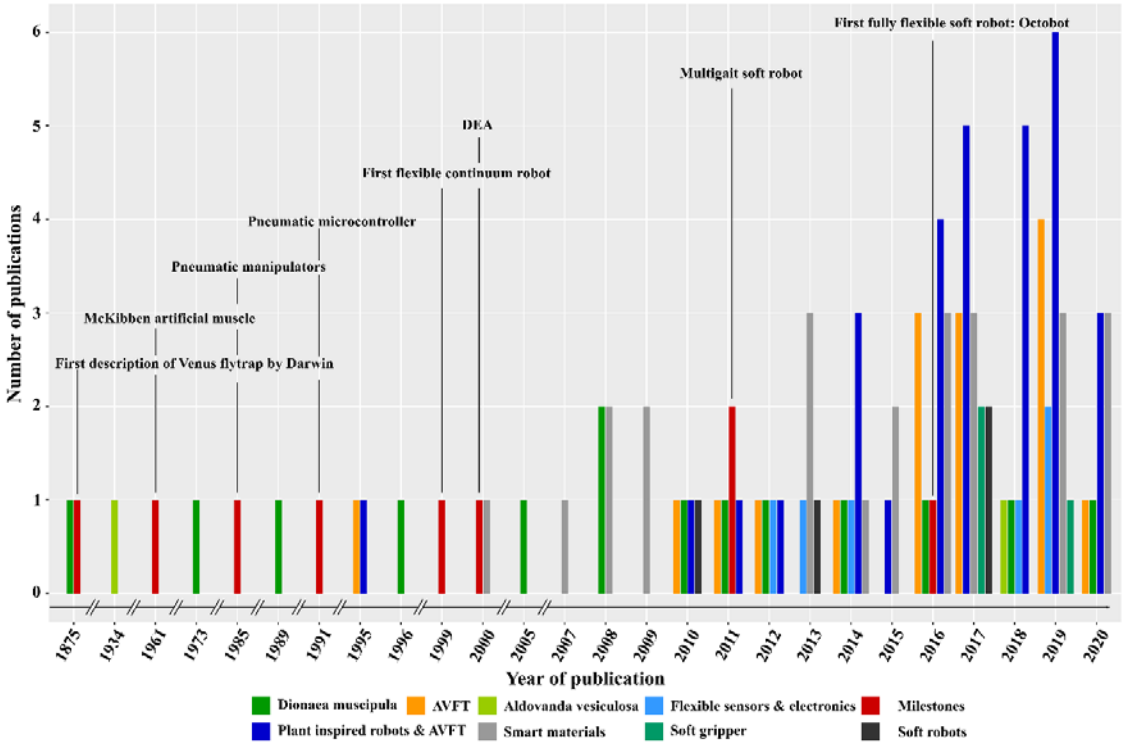
Project funding: Funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under Germany's Excellence Strategy – EXC-2193/1 – 390951807

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 give a short overview about artificial Venus flytrap systems [1] and present the results characterizing our first set of bio-inspired demonstrators, which not only incorporate and combine the snap-trap movement principles of two carnivorous plant species (Venus flytrap (*Dionaea muscipula*) and waterwheel plant (*Aldrovanda vesiculosa*) [2-5]), but also show adaptive responses to different environmental triggers [6]. 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.



Within the last the decade the research interest in artificial motile living systems using plant as role models has risen, seen in an incline of publications concerning plant inspired robots and especially artificial Venus Flytrap systems (AVFT) (Fig. 1). Over the last 25 years over a dozen different AVFT systems were developed. In 1995, Shahinpoor and Thompson were the first to consider theoretically, how to develop an AVFT based on ionic polymer–metal composites (IPMC) [7], and in 2011, Shahinpoor published a paper on an actual IPMC-based AVFT [8]. Within the last decade,

publication numbers have risen from one in 2010 to five in 2019, highlighting the growing interest in AVFT systems as platforms or showcases for novel materials developments. None of the developed systems incorporates all Venus flytrap functions (i.e. prey detection, trapping and digestion; decision making; energy harvesting; self-healing), and only the system of Shahinpoor has sensing capabilities [8].

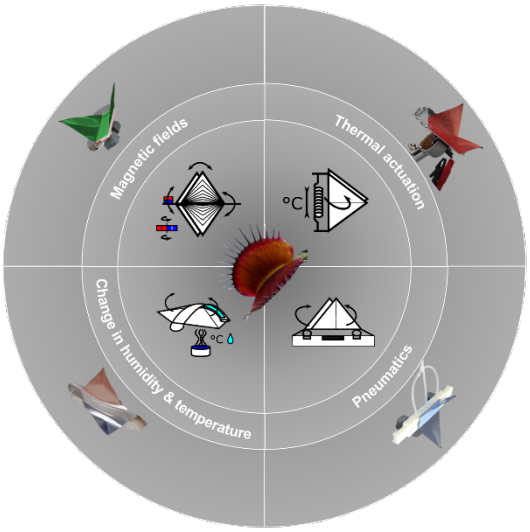


Fig. 2: Actuator systems of the foil based artificial Venus flytrap developed in *liv*MatS. The system utilizes actuation either through changing magnetic fields with magnets attached to the model or through thermally driven SMA springs or through pneumatic cushions that move the backbone closing and opening the systems. Also, a stimulus combination of change in relative humidity and temperature can be used to initializes movement in the fourth system utilizing a SMP backbone coated with hydrogel. © Plant Biomechanics Group Freiburg

Within the current project, we aim for replicating and further developing AVFT systems using novel *liv*MatS materials systems to set a new state-of-the-art integrating sensing, decision-making and energy harvesting and storing within one system

For the first *liv*MatS AVFTs, the snap trap foil demonstrators, the basic snap-trap form of the plants was abstracted 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 vesiculosa*) and an inverse snap-buckling movement for opening (inspired by *Dionaea muscipula*) [2-6]. The system is driven by four different actuators: pneumatic cushions (closing and opening the system), magnetic (via magnet attachment), thermal actuation (via shape memory alloy springs) and combining temperature and humidity changes by using shape memory polymer (SMP) backbones coated with hydrogel [1,6] (Fig. 2).

The systems were characterized in terms of opening and closing speeds, input requirements (force and energy) and reversibility of movement (see Table 1). Within the characterization of the various systems and in direct comparison with the biological role model *Dionaea muscipula*, the pneumatic driven system achieved the highest closing and opening speed. It is even faster than the biological role model with a closure time under 500 ms. For the characterization a high speed video tracking system was developed with which the kinematics of the demonstrator movement could be analyzed. The energy needed to actuate the systems were in all cases lower than the energy necessary for movement of *Dionaea muscipula.* The pneumatic and SMP/hydrogel systems are the most sophisticated of the four systems, as they both incorporate snap-buckling. The pneumatic system allows for opening and closing faster than the biological role model and the SMP/hydrogel system is environmentally triggerable by the combination of the two stimuli.

In identifying and analysing the systems energy requirements and kinematics concerning movement speed, force necessary for closing and energy consumption, a basis for the development of more advanced demonstrators is given. These are regarded as guideline values for future materials systems and AVFT based gripper systems currently under development within *liv*MatS.

Table 1: Comparison of the results characterizing the snap trap foil demonstrator to the biological role model *Dionaea muscipula.*

Type	Actuation	Sensing	Snap-buckling	Speed / Closing time	Energy input for actuation	Reversible
Venus flytrap and *Dionaea muscipula*	Prey/ATP consumption	Touch sensitive trigger hairs	**Yes**	**100 – 500 ms**	**9.66 J**	**Yes**
Magnetic demonstrator	Rotating magnetic field	No sensor / manually actuated	**No**	**Faster**	**less**	**Yes**
Thermal SMA spring demonstrator		Sensing of temperature change	**No**	**Slower**	**less**	**Yes**
Pneumatic demonstrator	Pressurized air	No sensor / manually actuated	**Yes**	**Faster**	**less**	**Yes**
System intialization demonstrator	Change in humidity and temperature	Acuated via environmential changes	**Yes**	**Slower** **No opening or closing**	**less**	**Yes**

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Biomechanics and functional morphology of citrus fruit peel as inspiration for highly damping materials systems

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In this project of *liv*MatS Research Area B ontogenetic variations, adaptivity and the structural basis of impact dissipation and auxetic behaviour in hierarchically structured plant tissues are quantified on a micro-, meso- and macroscopic level. Focus of this part of the project is the analysis of citrus fruit peels, being used as an inspiration from nature for innovative technical materials systems with pronounced energy dissipation and high damping capacity.

There exists a wide variety of citrus fruits and their differentiation into species and hybrids is controversial [1]. A citrus fruit in general can be divided into seed, pulp and peel. The latter consists of the inner albedo (mesocarp) and the outer flavedo (exocarp). There is a smooth transition from albedo to flavedo and a clear border between the two tissue types cannot be determined.

By scanning the peel of lemon (*Citrus limon*), citron (*Citrus medica*) and pomelo (*Citrus maxima*) in micro computed tomography µCT (Bruker Skyscan 1272, Belgium) we characterized their peel (micro-)structure (Fig. 1). The peel consists for the most part of parenchymatous albedo and flavedo cells forming a spongy structure with varying density from the outside to the inside of the peel. Additionally, mainly radial running vascular bundles appear within the whole peel and oil glands in the flavedo. We measured the area of vascular bundles in different distances to the pulp. Our analysis proves that the number of vascular bundles increases with the distance to the pulp, while the average area of each vascular bundle decreases. Both processes effect that the total area of vascular bundles remains (nearly) constant in each layer. Furthermore, no significant difference was found between the three species as to the amount of oil glands per area.

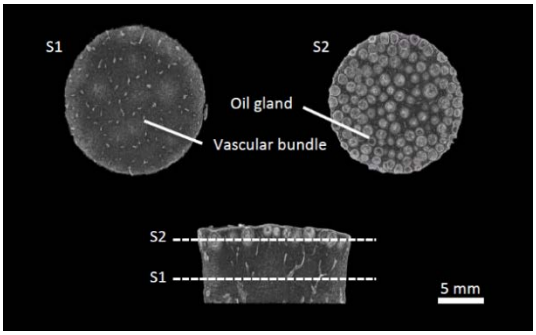

Fig. 1: Horizontal-section of a µCT scan of a cylindric peel sample of *Citrus limon*. The radial sections show the distribution of vascular bundles (S1) and oil glands (S2) in the peel structure. (© Plant Biomechanics Group)

A comparison of the parenchymatous albedo and flavedo cells shows that the albedo cells are smaller and less densely arranged than the flavedo cells. To quantify the differences in the cell arrangement we determined the gradient of cell distribution by analysing thin sections stained with toluidine blue by light microscopy. To quantify the cell distribution of the peel tissues, pictures of the sections we taken in which we marked the borders of the peel to pulp and epidermis by lines. The peel area was then subdivided by 20 lines and the cells that crossed these 20 interpolation lines were counted to determine the cell distribution in the different regions of the peel.

The results show that the cells in the fruit peel of all three species are arranged in a density gradient (Fig. 2). Overall, the cells are closer together with increasing distance to the pulp causing a higher density of the spongy peel tissue. However, there are differences between the tested *Citrus* species. *Citrus medica* has a significantly lower cell density in the albedo region (inner part of the peel) than the other two species. The cell density in the middle region of the peel is highest in *Citrus limon*, whereas *Citrus maxima* and *Citrus medica* have lower cell densities within this middle

area which are similar for these two species. In the flavedo region (outer part of the peel) again *Citrus limon* shows the highest cell density, followed by *Citrus medica* while the cell density is lowest in *Citrus maxima*.

The µCT images and the differences in the cell arrangement gradients found for the various citrus species show that the peel structure, although similar in many aspects, still have differences which might be of functional importance. In addition to the macroscopic differences in, for example, size and relative proportion of peel in the fruit, there are also microscopic differences in cell arrangement. A cell arrangement gradient is found in all three species, but the cells number per millimeter differ significantly from between the three *Citrus* species, especially in the outer flavedo region. Based on this anatomic analysis of the fruit peel, potential ideas for bioinspired materials systems can be derived.

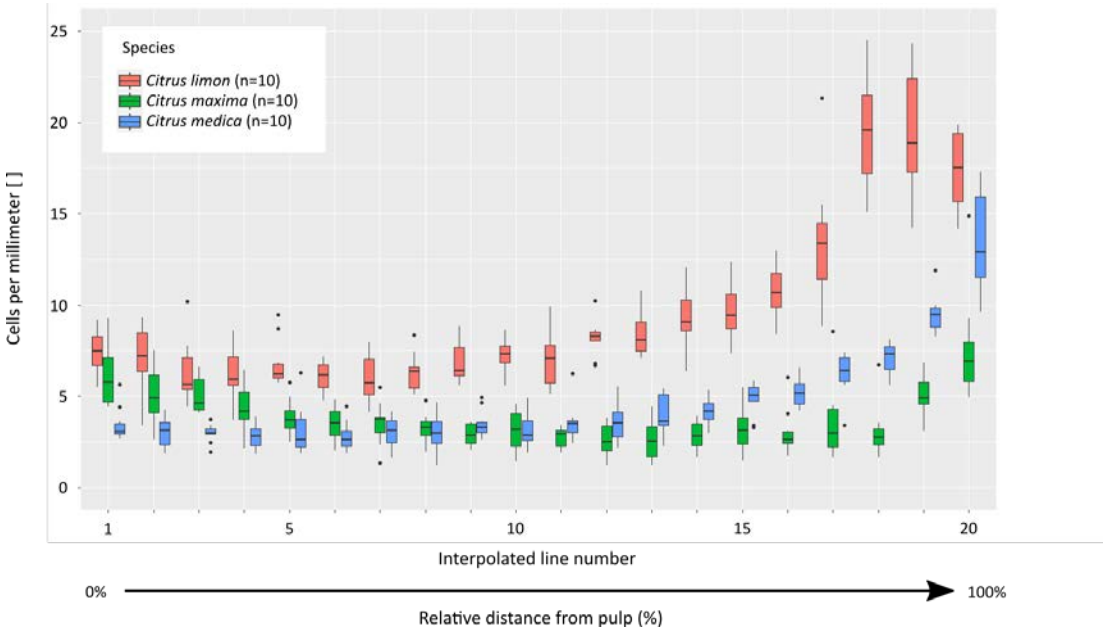

Fig. 2: Cell density gradient of the peel of lemon (*Citrus limon*), pomelo (*Citrus maxima*) and citron (*Citrus medica*). The 20 lines at which cells were counted were interpolated from the boundary lines of the epidermis and endodermis. (© Plant Biomechanics Group)

While the compression behavior [2], the viscoelastic properties [3] and the impact behavior [4] of the peel of *Citrus maxima* have been studied in detail, there are fewer biomechanical studies on *Citrus limon* and *Citrus medica*. Therefore, the next step within this project will be the mechanical characterization of the fruit peels of the latter two species and the comparison with data found for *Citrus maxima*. Due to the anatomical differences of the fruit peels shown above, it is highly promising to generate a deeper understanding of these natural damping structures by identifying their main structural principles as basis for a transfer into novel materials systems.

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4D-Bioprinting of vascularized bone tissue and evaluation of blood vessel and bone formation in an orthotopic bone defect model

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Project funding: German Research Foundation (DFG FKZ KO 3910/1-2)

In recent years, 3D bioprinting processes have increasingly entered the research areas of regenerative medicine and the development of microfluidic organ-on-a-chip systems. In 3D bioprinting cells are arranged for the first time in an exactly defined and reproducible spatial configuration using additive manufacturing processes. This opens up the possibility of reproducing the architecture of native tissues in a targeted, automated manner and with high resolution [1].

A 3D bioprinter was established at IMTEK which combines Drop-on-Demand (DoD) and extrusion printing technologies on a common platform. This 3D bioprinter enables the production of 3D constructs with varying spatial resolution of the cells using a large spectrum of bioinks with different rheological properties.

The Cell Printing Group carried out systematic studies about the physicochemical properties of a variety of hydrogels with regard to 3D bioprinting of relevant cell types prospectively for a vascularized bone replacement [2, 3]. In particular, endothelial cells such as HUVECs were investigated as building blocks for vascularization processes [4]. In this context, a sophisticated workflow was established for the large-scale fabrication of endothelial cell spheroids by a DoD approach [5]. Furthermore, mesenchymal stem cells from adipose tissue (ASCs) were identified as a potent cell source for bioprinting of 3D artificial bone tissue [6].

In a hybrid bioprinting process larger 3D cubes comprising of ASCs and HUVECs were fabricated and characterized *in vitro* and *in vivo* (Fig. 1). Such 3D constructs are able to form a calcified bone matrix while HUVECs printed by means of DoD are able to form perfused blood vessels upon subcutaneous implantation in immunocompromised mice *in vivo* [7].

In a BMBF-funded 3D-Bio-Net project a generic 3D bioprinter with extended functionality (including FDM printing for thermoplastics) was established, for which the Cell Printing Group developed generic 3D bioprinting processes [8]. Innovative biofabrication concepts, as described above for endothelial cells for regenerative medicine approaches, are also being pursued by the Cell Printing Group for renal epithelial cells to realize perfusible microtubules for organ-on-a-chip approaches [9]. 3D bioprinting activities in the field of regenerative medicine are performed in collaboration with Prof. Dr. Günter Finkenzeller (Department of Plastic Surgery, University Hospital Freiburg).

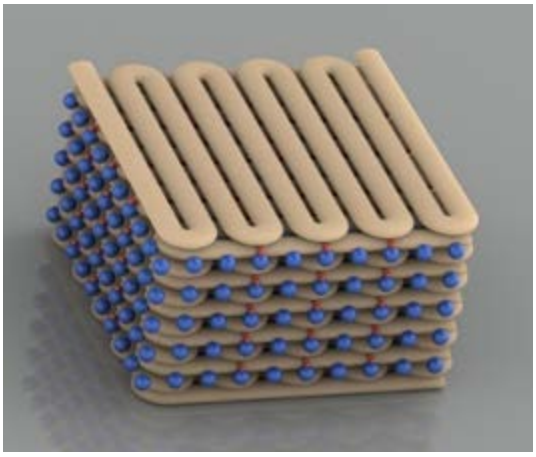

Fig. 1: Template for a hybrid bioprinting process featuring extruded ASCs (beige) and DoD-printed HUVECs (red) and thrombin (blue) for a vascularized bone tissue model characterized *in vitro* and *in vivo*. (© Cell Printing Group)

As seen in our previous DFG-funded project 3D Bioprinting, the stiffness of the 3D-bioprinted constructs is approximately equivalent to that of native human soft tissue (approx. 1 kPa), that of native bone tissue is approx. 100,000 times higher (approx. $1 \cdot 10^5$ kPa). Therefore, one of the main goals of this follow-up project 4D Bioprinting is the development of a combined printing process for printing cell-containing hydrogels and stability generating thermoplastics and calcium phosphate cements (CPC) in order to print vascularized

bone replacement tissue with a stiffness equivalent to that of native bone tissue.

The second goal is the implementation of the so-called 4D-printing ('time' as fourth dimension), where the temporal and spatial maturation of the constructs will be controlled by the additional spatially resolved printing of growth factors, differentiation factors and additional cell entities.

The third goal of this project is the *in vivo* validation of the printed 4D combination constructs in a physiologically relevant orthotopic bone healing model of the rat with respect to vascularization and bone formation. In particular, it will be investigated whether the quantity and/or quality of bone and blood vessel formation can be controlled by modulating the E-moduli of the printed constructs.

In connection with the first goal, the Cell Printing Group has upgraded an open-source FDM 3D printer (i3 MK3, Prusa Research, Prague, Czech Republic) for the combined printing of thermoplastics via FDM and hydrogels via extrusion. For this printing system an extensive and systematic characterization was started.

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FUTURE FIELD "(MICRO)SYSTEMS FOR ENERGY CONVERSION, STORAGE AND ENERGY-AUTONOMY"

Understanding the platinum carbon-support interaction for improved catalysis in hydrogen fuel cells

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As part of Europe's and Germany's ambition to create a hydrogen-based ecosystem to meet the EU's climate neutrality and zero pollution goal, the development of mature and cost-effective fuel cell technology remains a key objective for zero-emission mobility.[1,2] Although in recent years the efficiency of fuel cells have been greatly improved, the optimization of platinum-based catalysts remains a fundamental challenge.[3]

In cooperation with the Fraunhofer Institute for Solar Energy Systems (ISE) and AVL Deutschland GmbH, the project "FC-CAT" aims to develop a comprehensive simulation model for the performance of state-of-the-art materials used in Polymer Exchange Membrane Fuel Cells (PEMFCs), based on numerous ex-situ and in-situ experiments of fuel cell components. Especially the role of the carbon support as a carrier material for platinum nanoparticles (NPs) and the fundamental interaction between catalyst, carbon support, and the polymeric binder is not yet sufficiently understood. A better comprehension may lead to lower platinum loading especially on the cathode side, which currently requires much higher loadings compared to the anodic side because of the sluggish kinetics of the oxygen reduction reaction.

Within the framework of this project, the anchoring and localization of the nanoparticles on (doped) porous carbon supports are investigated using macroscopic (e.g. Raman spectroscopy) and nanoscopic methods (e.g. Transmission Electron Microscopy, TEM), which were established in the first year. Carbon black are suitable catalyst supports not only because of their high surface area, porosity and excellent electrical conductivity, but also because they facilitate electron transfer.[4] By targeted synthesis of different Pt/C catalysts, the importance of location, shape and size of the platinum particles on their resulting electrochemical performance can be explored.

For this study, two synthesis routes described by Harzer *et al.* were established on the same high surface area Ketjenblack (KB) carbon support.[5] Although both synthesis routes use hexachloroplatinic acid H_2PtCl_6 as a precursor, the type of particle deposition is different depending on the synthesis protocol. It is hypothesized that the route known as "polyol reduction process" (PO) leads to Pt nanoparticles deposited preferentially on the outside of the carbon support while using the "incipient wetness impregnation" (IWI) leads to a preferred deposition inside the pores of the carbon support (Fig. 1).

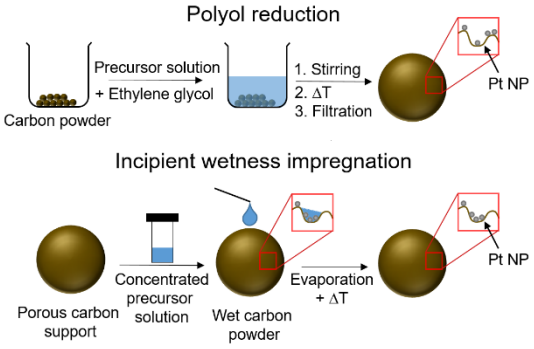

Fig. 1: Synthesis techniques for a controlled deposition of platinum nanoparticles on porous carbon support. (© Electrochemical Energy Systems Group)

Furthermore, the surfaces of the carbon supports can be doped with nitrogen in a preparational step. Applying these synthesis protocols, finely distributed platinum nanoparticles with a narrow size distribution can be obtained (Fig. 2). Different Pt sizes and shapes can be

set by varying heating rate, precursor concentration and pre-treatment. Smaller platinum particles have a higher surface to mass ratio and thus lead to higher catalytic activity in the fuel cell at constant loading, while large platinum particles are beneficial for long-term stability. The analysis and optimization of this trade-off between activity and stability can therefore help to achieve equally efficient catalyst materials with significantly less platinum content.

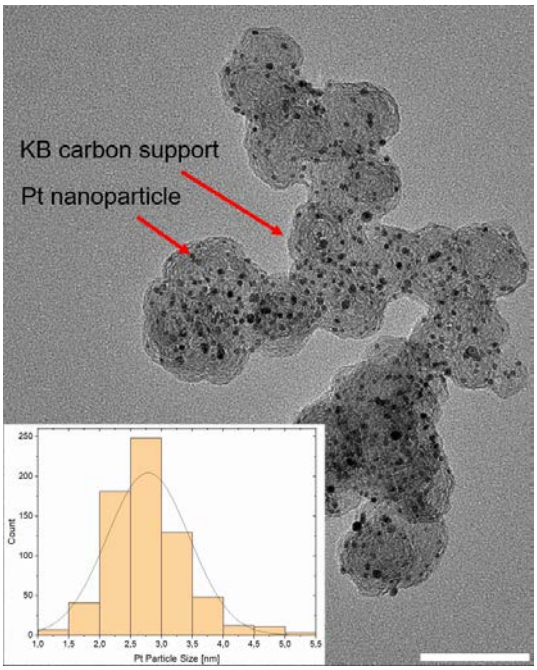

Fig. 2: TEM image of 40 wt% Platinum on N-doped Ketjenblack, with 20 wt% Pt deposited by IW and 20 wt% Pt deposited by PO. The scale bar represents 50 nm. Inset: Platinum particle size distribution. (© Electrochemical Energy Systems Group)

Applying the in-house synthesized Pt/C catalysts in membrane electrode assemblies (MEAs) resulted in significantly different fuel cell power densities between ~480 mW/cm^2 and ~540 mW/cm^2 at 0.6 V cell voltage, which proves the importance of the localization and interaction of Pt nanoparticles on/with the carbon support (Fig. 3).

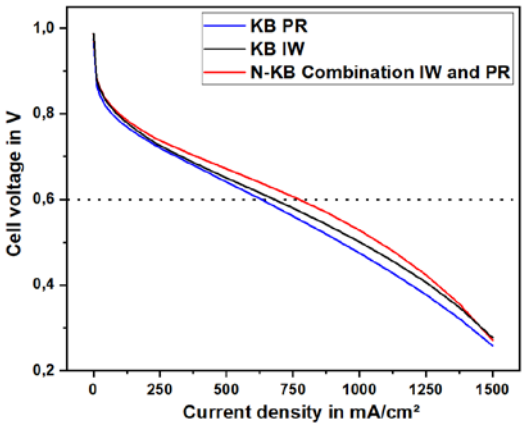

Fig. 3: H_2-air fuel cell polarization plots of MEAs with similar Pt-loading fabricated using the in-house synthesized Pt/C catalysts. (© Electrochemical Energy Systems Group)

Although a relationship between Pt nanoparticle properties and corresponding electrochemical performance of the MEA can already be established by analysing 2D-TEM images, the exact localization of the NPs (inside or outside the carbon support pores) cannot be determined in this way. Therefore, it is a goal of this work to obtain 3D reconstructions of Pt/C particles by TEM tomography. Further, XPS experiments shall be carried out in the future to gain insight into the specific chemical connection of the Pt particles to the (doped) carbon support.

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Highly efficient all-solid-state CO_2 electrolysis

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Project funding: Vector Foundation,
Project: CO_2-to-X

For the transformation to a CO_2-neutral society, new technologies are needed to replace fossil feedstocks of the chemical industry with regenerative carbon sources. One key technology here is CO_2 electrolysis, in which renewable energy can be used to convert captured CO_2 into feedstocks for valuable products, e.g. for synthetic fuels for aviation or synthetic materials. Membrane-based CO_2 electrolysis promises high efficiency and low costs and is therefore the focus of current research [1].

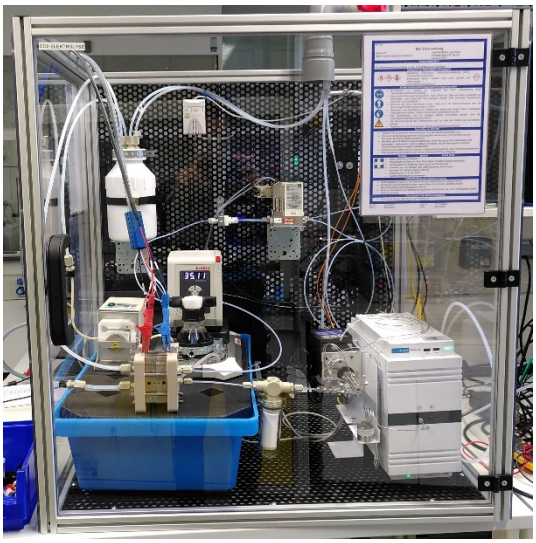

Fig. 1: Custom-built CO_2-electrolysis test bench. (© Electrochemical Energy Systems Group)

With the project CO_2-to-X the Vector Foundation awarded Severin Vierrath a research grant to build up an independent junior research group tackling efficiency and cost barriers in CO_2 electrolysis. While the product of CO_2 electrolysis can be chosen through the catalyst, a first literature review and brief techno-economic calculation lead to the focus of carbon monoxide (CO) as desired product. While the CO demand by the chemical industry will possibly see a constant rise in the future, its current production is fully based on fossil resources [2].

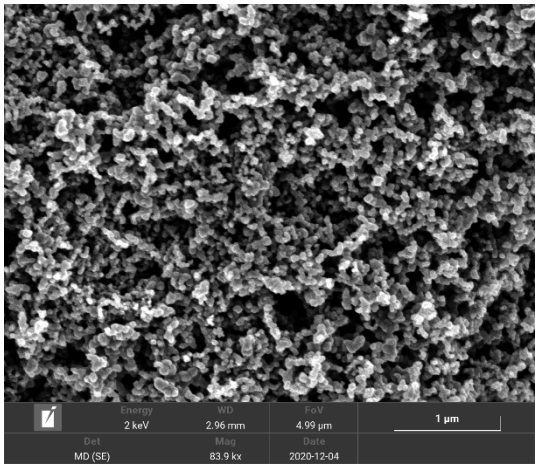

Fig. 2: Electron micrograph of silver nanoparticles deposited on a carbon gas diffusion layer. (© Electrochemical Energy Systems Group)

The electrolyzer design selected in CO_2-to-X, consists of two half-cell compartments, which are divided by an anion exchange membrane. The cathode compartment is fed with gaseous CO_2, whereas the anode is fed with a liquid alkaline/water solution. By applying a potential to the cell, CO_2 is reduced to CO at the cathode and oxygen evolves at the anode.

Since the start of the project in March 2020, a custom test bench and test cell have been designed and built (Figure 1). The whole setup is equipped with several safety features, such as a CO detector, which automatically shuts down the power supply, in case a critical concentration of CO in the surrounding air is reached. With the help of an online gas chromatograph (Figure 1, device on the bottom right) the gas composition of the products are analyzed to ensure that the measured current correlates with the CO_2 reduction and not with undesired reactions like hydrogen evolution (so-called Faradaic efficiency).

Key components of the electrolyzer cell are the electrodes and membranes. For the first tests, several gas diffusion electrodes with silver nanoparticles as CO_2 reduction catalyst and different ion conductive polymers were fabricated. Figure 2 shows a scanning electron micrograph of silver nanoparticles on the

surface of a carbon electrode. The silver nanoparticles were deposited with a spray coater on top of a carbon based gas diffusion layer, resulting in a porous structure.

First measurements were conducted with the test setup and different electrodes were electrochemically characterized. The graphs in Figure 3 show linear sweep voltammograms of an electrolysis cell, with such a silver-coated electrode at different operating temperatures. At 3,0 V cell voltage and 60°C, a total current density of 845 mA cm^{-2} could be reached, which is comparable to state-of-the-art performance.

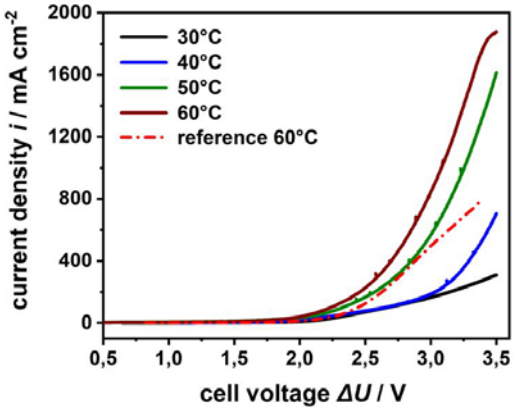

Fig. 3: Linear sweep voltammetry of a custom-built CO_2 electrolyzer at different operation temperatures. Anode: nickel foam electrode and 20 mL min^{-1} of 0,85 M potassium hydroxide. Cathode: 0,7 mg cm^{-2} silver nanoparticles on carbon gas diffusion layer and 95 mL min^{-1} CO_2, fully humidified. The red dotted line shows values of a reference currently published by Endrődi et al. [3]. (© Electrochemical Energy Systems Group)

First online GC measurements proved the evolution of carbon monoxide. However, the gas composition needs to be more precisely determined to fully evaluate the efficiency of the electrolyzer.

One unsolved challenge remaining in CO_2 electrolysis, is the CO_2-crossover from the cathode to the anode half-cell [4]. In presence of hydroxide ions, CO_2 forms carbonate and bicarbonate ions, which can pass the anion exchange membrane resulting in lower efficiency and reduction of the membrane conductivity. The employment of bipolar membranes instead of monolithic anion exchange membranes has the potential to solve this issue as carbonate ions cannot pass the cation exchange part of the membrane [5]. Therefore, the focus of the next phase of the project is set on the development of novel bipolar membranes designed for CO_2-electrolysis.

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Photocatalytic fiber mats of Fe-based metal-organic framework for energy and environmental applications

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Project funding: Alexander von Humboldt-Stiftung / Foundation

Solar energy is a clean, vast, and renewable energy source, which can be exploited by photocatalysis to facilitate energy conversion and counter environmental pollution. In photocatalysis, the solar radiation is absorbed by a light-harvesting photocatalyst and used to drive a chemical reaction, for example decomposition of water for hydrogen production or degradation of pollutants in wastewater. As photocatalysts are the heart of photocatalytic systems, extensive research has been directed toward

the development of photocatalysts with desirable physicochemical and photocatalytic properties [1]. Among the photocatalytic materials explored so far, Fe-based metal-organic frameworks (MOFs) have recently received special attention because of their high potential in the field of photocatalysis. This includes their properties, such as porous structures, high surface area, adequate physicochemical stability, intensive absorption of light in the visible region and (Fig. 1) and also their low material cost. However, due to some deficiencies, the solar energy conversion efficiency of this new class of photocatalysts is still not satisfactory for use in practical applications [2].

Our aim in this Alexander-von-Humboldt funded research is to provide a cost-effective and environmentally friendly approach to address the issue of low photocatalytic efficiency of Fe-based MOFs. To achieve this goal, electrospinning is employed to engineer Fe-based MOFs as fibrous macrostructures for photocatalytic purposes. The unique structure and morphology of such fibrous designs can provide a large surface area-to-volume ratio and a short pathway for charges to reach the photocatalyst surface, leading to the high photocatalytic activity. Besides, fabrication of Fe-based MOFs as fibrous macrostructures is an effective approach to easily stabilize the photocatalysts and thus separate them from the reaction mixtures, as required for their recovery and reuse in practical applications.

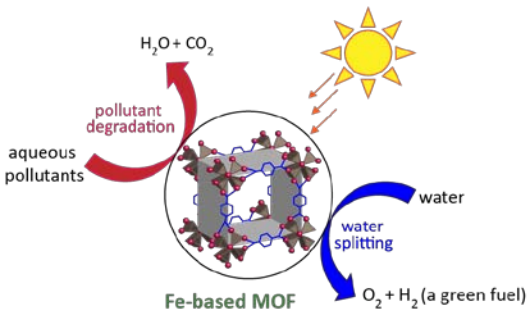

Fig. 1: The current state of the utilization of Fe-based MOFs for energy and environmental applications under solar radiation. Inside of the central circle shows the unit cell of a typical Fe-based MOF consisting of iron nodes (red spheres) and organic linkers (blue and gray structures). (© Electrochemical Energy System Group)

The work in this project includes the fabrication of fibrous mats by electrospinning of various polymers (e.g. PAN and PVA) followed by growing Fe-based MOFs (e.g., MIL-101 (Fe)) on the electrospun fibers. Fig. 2 shows a photograph and micrographs of the produced fiber macrostructures as a mat. In the next step, other characterization techniques such as X-ray diffraction, Brunauer–Emmett–Teller surface area and infrared spectroscopy will be employed to further investigate the chemophysical properties of the mats. Finally the photocatalytic activity of the Fe-based MOF mats toward: (1) the degradation of pollutants in wastewaters, and (2) the water splitting reaction will be investigated using a solar simulator.

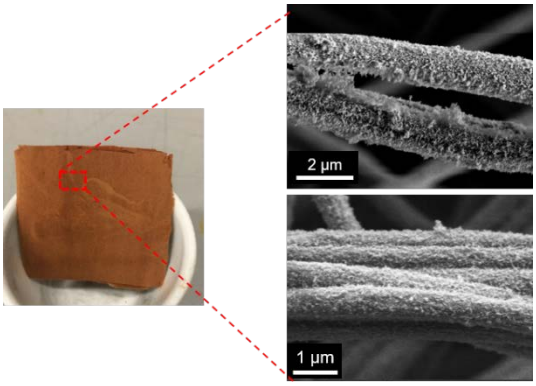

Fig. 2: A digital photograph (left side) and SEM images (right side) of the electrospun fiber mat. (© Electrochemical Energy System Group)

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Development of SolStore devices to harvest and store electrical energy

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The cooperative project *SolStore* aims at the development of highly integrated solar-charging energy devices, such as solar batteries and solar capacitors, able to harvest, convert and store solar energy from their surroundings. To realize such self-charging electrochemical devices with high level of integration, different modes of integration (mode II and mode III) involving either three or two electrodes, respectively, will be tackled. In all cases photo-charging electrodes combining the function of energy harvesting and storing in one device (mode II) or material system (mode III) will be explored. The *SolStore* project combines advanced material development (simulation and synthesis), characterisation and testing along with device fabrication, simulation and optimization; tasks achieved in cooperation in a large team of experts with complementary expertise.

In terms of mode II, two types of devices are possible: mode II photobatteries and mode II photosupercapacitors, integrating advanced PV with electrochemical storage technology.

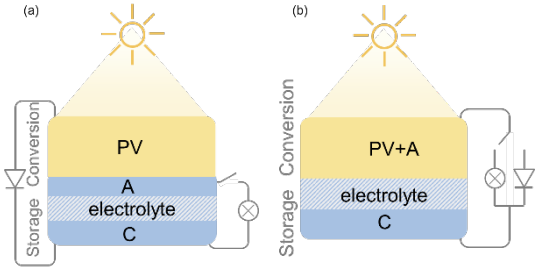

Fig. 1: Schematic diagram of the Mode II (a) and Mode III (b) photostorage devices. © livMatS/Daniel Hellweg

For mode III, two types of self-charging photoelectrode 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 1.

Organic photo-charging batteries – Organic SolStore

Aim of the *Organic SolStore* project is to develop integrated photo-charging organic batteries. In a mode III configuration, charge generation and storage occur in the same material, while in a mode II configuration these processes are refined to separate layers. In our design the organic solar cell part is based on the so-called bulk-hetero-junction (BHJ) configuration, where an organic donor and an acceptor material form an interpenetrating network. Upon photoexcitation, charge separation occurs at their interface, after which the holes/electrons are transported through the

donor/acceptor phase to the two electrodes. In the organic battery part, redox-active polymers are used as electrode-active materials that can store either holes or electrons.

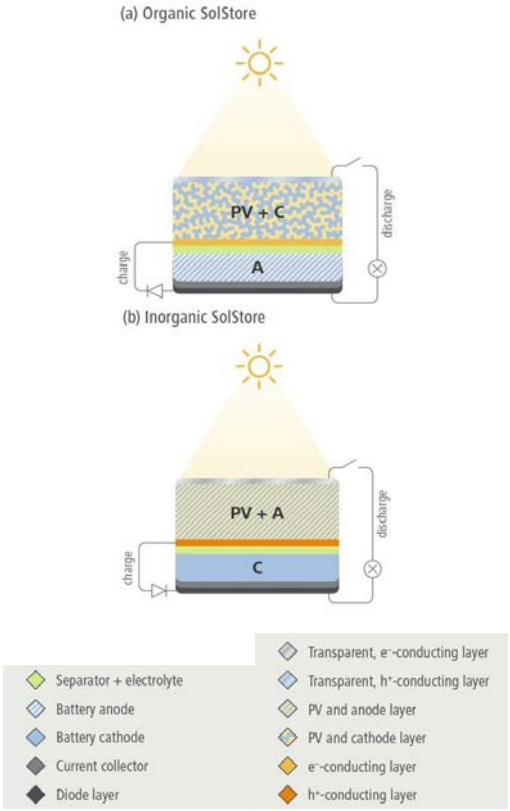

Fig. 2: Schematic of solar batteries at the highest level of integration, with energy conversion and storage in the same material (mode III). (a) Organic SolStore, (b) Inorganic SolStore. © IivMatS/Daniel Hellweg

First attempts went into developing a fully integrated photo-charging organic battery operating in mode III, as shown in Fig. 1a (PIs: Esser, Würfel). For this, novel donor-acceptor polymers were synthesized that show both broad visible light absorption and reversible electrochemistry. Phenothiazine as donor was combined with diketopyrrolopyrrol as well as benzothiadiazole as acceptors in conjugated co-polymers. Alkyl chains of different lengths and at different positions were attached to obtain soluble materials. Phenothiazine can reversibly store holes at a relatively high potential of 3.6 V vs. Li/Li^+. This property was maintained in these co-polymers, resulting in a high cycling stability, as battery half-cell measurements showed (cyclic voltammetry and galvanostatic charge/discharge experiments). Investigations in integrated photo-storage devices are currently in process. Future efforts will focus on improving the mode III cell configuration. Modelling of electronic (redox-) and optical properties of the organic materials used can provide insight into the working principles of the device (PIs: Moseler, Walter). Furthermore it is envisioned to develop porous and electrolyte-permeable layers, both the BHJ layer as well as the electron/hole-conducting layers for these photobatteries (PI: Fischer) and identify suitable electrolytes with high stability in light (PI: Krossing). Lastly, porous anode materials with a suitable reduction potential will be required able to store electrons (PIs: Esser, Hillebrecht, Fischer). Furthermore, we aim at developing a mode II organic photo-battery, which is as of yet unknown in the literature. For this a BHJ solar cell will be combined with electrodes for storing holes and electrons, using organic redox polymers for the charge storage.

Inorganic photo-charging batteries and supercapacitors – Inorganic SolStore

The project *Inorganic SolStore* tackles the coupling of a perovskite solar cell (PSC) to an internal electrochemical storage unit (battery or capacitor) in integration modes II and/or III (Fig. 1b). Lead halide perovskites (ABX_3, e.g. with A = methylammonium, B = Pb and X = halides as I or Br) are known for their high optical absorption and excellent carrier transport properties allowing PSCs to reach conversion efficiencies of more than 20%. Hereby, design of selective electrodes and lead substitution by less toxic elements are ongoing challenges (Research Area D, sustainability and societal acceptance). Despite these challenges, simple processing out of precursor solutions makes PSCs excellent candidates for integrated multifunctional systems to be assembled by printing or other industrially feasible technologies. In addition, $APbX_3$ perovskite materials have been demonstrated to exhibit certain Li^+-storage capacities, dependent on the type of perovskite and the cut-off voltages used. However, at the beginning of the project it was not clear, whether and to what extent the storage results from a reversible ion intercalation or from a conversion process to a

lead-containing intermetallic compound. Also, recently published research demonstrated, that a 2D perovskite material may act as true bifunctional electrode/material, combining the function of (i) photogeneration of charge carriers and (ii) storage of one of these charge carriers in one single active layer.

The tasks and aims of the *Inorganic SolStore* project are the combination, optimization and integration of (as a starting point) novel perovskite materials for both solar energy conversion and electrochemical storage into various new devices (realized either in mode II or mode III) to obtain energy-autonomous systems.

Regarding mode II, the *Inorganic SolStore* project aims at developing integrated photosupercapacitors based on the coupling of perovskites solar cells (PSCs) and suitable supercapacitors (PIs: Glunz, Fischer) through one shared bifunctional electrode in a monolithic fashion.

A novel perovskite solar cell design with an optimized layer sequence suitable for the integration was developed (PI: Glunz). A shared electrode, acting simultaneously as a charge acceptor electrode in the solar cell, and as a charge storing electrode in the supercapacitor, was designed (PI: Fischer). The supercapacitor module was assembled in a symmetrical configuration using a semi-solid electrolyte, thereby simplifying device packaging, addressing perovskite instabilities and allowing a free-standing architecture. Suitable high-surface area supercapacitor electrodes with tuned porosity and outstanding supercapacitive behaviour were designed and studied. The photovoltaic and supercapacitor units were (photo)-electrochemically characterized before and after assembly (as an integrated photosupercapacitor) in order to identify the device performance (PIs: Fischer, Glunz). The integrated devices featured large energy and power densities and outstanding overall photo-electrochemical conversion efficiencies; results, which are currently summarized in a publication.

Regarding mode III, the *Inorganic SolStore* project aims at developing photobatteries with truly bifunctional photoelectrodes. Theoretical modelling and computational simulation of properties of ions and electrons at the atomic scale has been 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 have been synthesized (PI: Hillebrecht), and absorber layers have been deposited based on solution processing and evaporation, together with a characterization of their structural, optical, electrical (PIs: Glunz, Fischer) and photoelectrochemical properties (PI: Fischer), pointing to certain challenges and limitations in the systems so far overlooked in literature. A variety of 2D and 3D perovskite materials were investigated which showed differences in their charge storage capabilities and stability. Additionally, lead-free perovskites and promising multifunctional metal oxides were screened for their potential as photo-harvesting charge storage materials (PIs: Fischer, Krossing, Hillebrecht). In addition, suitable counter electrodes with adjusted potentials for charge storage are under investigation (PIs: Fischer, Hillebrecht, Krossing, Esser) as well as electrolyte development to achieve a better property fit with the cathode and photoelectrode materials (PI: Krossing). Overall device fabrication is tackled but challenging due to intrinsic material limitations and will in future (for suitable materials) rely on – and expand – existing processing technologies located at the 2D- and 3D-printing and processing core facility @FIT as well as in the *liv*MatS shared laboratories.

Development of integrated and flexible manufacturing process for micro-Thermoelectric generators – MiTEG

Negin Sherkat, Uwe Pelz, Peter Woias

Laboratory for the Design of Microsystems, Department of Microsystems Engineering (IMTEK), University of Freiburg

Project funding: German Research Foundation (DFG)

The main gaol of this project is developing novel manufacturing technologies and materials for micro thermoelectric generators (µTEGs). This project is collaborated between the Departments of Microsystems Engineering (Prof: Dr. Peter Woias, Dr. Uwe Pelz) and [2]Leibniz Institute for Solid State and Materials Research (Dr. Heiko Reith). Two PhD students are working on this project (Negin Sherkat from IMTEK and Nithin Bharadwaj Pulumati from IFW).

Several different fabrication processes for µTEGs have been presented in the literature. Most of the employed methods rely on cleanroom micro-fabrication processes. However, they are complex and costly [1]. In order to achieve maximum design flexibility and increase the application of thermoelectric generators (µTEGs), two different manufacturing processes are being investigated and optimized. One process is electrodeposition of metallic thermoelectric materials with high power factor. The other process is paste dispersion and sintering of high efficiency thermoelectric semiconductor materials from powder precursors into the thermolegs.

Currently, the first part of the fabrication process of µTEGs which is manufacturing of µTEGs substrates is being developed. In order to reduce processing times, steps, temperature and adapting to the low-cost production processes, printed circuit board (PCB) based substrate is used for structuring. There are two different fabrication processes for creating the µTEGs substrates which are one-sided process and double-sided process for paste and dispensing of thermoelectric materials. Figure 1 shows a double-sided process that holes are alternately created on the both sides of the substrate, each of which expand to the opposite metal surface. This can be done by laser processing or by a drilling and milling machine at high speed and with high reproducibility. When the substrate is structured the n-type and p-type thermoelectric materials are successively deposited in the respective holes. By lithography or milling electrical contacts are created between thermolegs. Subsequently, electrical insulation is created between the two peers of thermocouples.

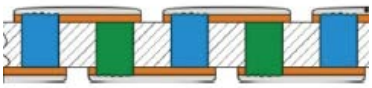

Fig. 1: Double-sided electroplating µTEG-PCB- based consisting holes, nonconductive thermal and electrical substrate material (beige), contact pads (orange), TE material (blue and green). © IMTEK/Laboratory for Design of Microsystems

Figure 2 shows a one-sided process which uses the same substrate. The production of the holes is done from one side, and at the same time, a layer with filter is created at the bottom of the holes. After forming the cavities, they are filled by a thermo-electric ink. Next, the solvent is removed from the pastes by applying a vacuum to the underside of the substrate. For creating the electrical conductivity between the thermolegs and electrical isolation between the thermocouples, the same procedure as double-sided process is used.

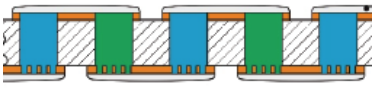

Fig. 2: One-sided electroplating µTEG-PCB- based consisting holes and a filter layer at bottom, nonconductive thermal and electrical substrate material (beige), contact pads (orange), TE material (blue and green). © IMTEK/Laboratory for Design of Microsystems

Simulation study of µTEGs is being performed in order to optimize the final µTEG design in terms of geometric parameters as well as material properties. Future work will focus on developing, characterizing and evaluation of our manufactured µTEGs.

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Novel cell concepts and PGM-free catalysts for anion exchange membrane fuel cells

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Project funding: Vector Foundation, project “AlkaCell”

Fuel cells are a key technology for emission-free mobility, and also, besides batteries, a way to provide energy for adaptive material systems. Proton exchange membrane fuel cells are the most widespread fuel cell technology due to their beneficial characteristics like low-temperature operation, high power density, and compactness. One of the biggest hurdles for their widespread application though is the high material cost (e.g. for platinum catalysts). Anion Exchange Membrane Fuel Cells (AEMFCs) have gained increasing interest in recent years as they offer the possibility to use abundant platinum-group-metal (PGM) free catalysts and potentially cheaper polymers and can thus significantly reduce the capital costs. [1]

The joint project “AlkaCell” between the Inorganic Functional Materials and Nanomaterials Group (*Prof. Dr. Anna Fischer)* and the “Electrochemical Energy Systems” Junior Research Group (Dr. *Severin Vierrath)* focuses on two of the most important remaining challenges in AEMFC development: (1) developing PGM-free catalysts for the hydrogen oxidation reaction (HOR) and the oxygen reduction reaction (ORR) and (2) achieving comparable performance and stability to PEMFC. [1]

Hydrogen oxidation and oxygen reduction electrocatalysts (Patrick Elsässer, Jan Oechsler, and Anna Fischer)

In the first year of the project, NiMo-containing HOR and Fe-N-containing ORR catalysts based on pyrolyzed metal-polymer precursors were developed, achieving some promising HOR and ORR activities. Additional investigations however pointed to the fact, that the accessibility of the active species (NiMo nanoparticles, Fe-N-C active sites) in these catalysts was insufficient to provide high activity.

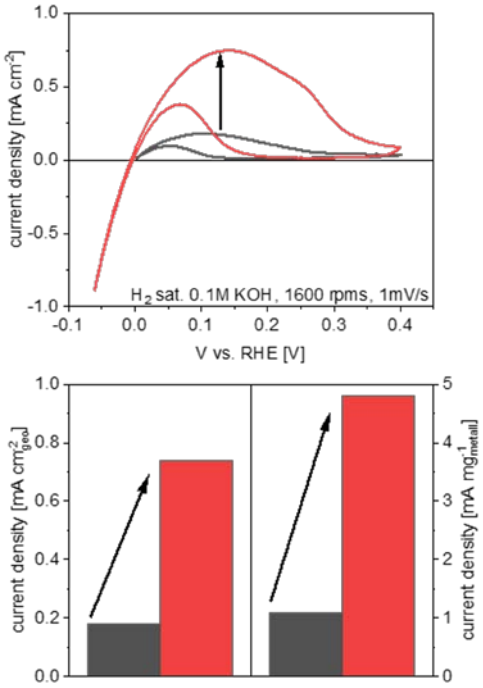

Fig. 1: Cyclic voltammetry curves and maximum current densities of polymer-derived NiMo@N-C (black) and NiMo@N-C (red) (© Fischer group)

In order to improve the accessibility of the NiMo-species, a novel NiMo-based HOR electrocatalyst (NiMo@N-C) was developed based on mesoporous N-doped carbon particles as support. The advantage of using a mesoporous N-doped carbon support instead of a polymeric carbon and nitrogen precursors are the high surface area, defined pore sizes, smaller particle sizes, and higher accessibility, yielding NiMo@N-C catalysts with highly distributed NiMo alloy NP. As a result, a 4.4 times higher HOR activity, when compared to the

polymer-derived NiMo@N-C catalyst, was achieved (Fig. 1).

To further increase the catalytic activity towards HOR, the next steps are variation of the Ni:Mo ratio, alloying of Ni with other metals, and further optimization of the particle distribution and size on the carbon support.

The activity of the iron- and nitrogen-doped carbon catalysts (Fe-N-C) synthesized in the first year of the project were improved by using metal-organic-frameworks (MOF) as carbon and nitrogen source instead of the initially chosen polyformamidine polymer. Due to the high distribution of Fe atoms in the MOF precursor, less catalytically inactive Fe and Fe-carbide NPs were formed during carbonization.

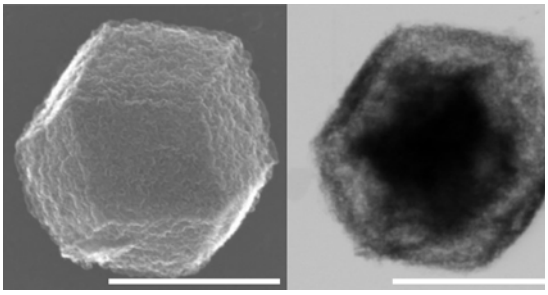

Fig. 2: SEM and STEM images of the upscaled MOF-derived Fe-N-C catalyst (scale bar 100 nm). (© Fischer group)

The MOF-derived Fe-N-C catalysts showed particle sizes between 0.5 and 1.0 µm (Fig. 2) and high surface areas (S_{BET} ~400 m²/g) with large fractions of micropores. The MOF-derived Fe-N-C catalyst (small scale synthesis) showed a significant improvement in ORR activity compared to the polymer-derived Fe-N-C catalyst (Fig. 3). The ORR activity of upscaled MOF-catalysts, required for fuel cell incorporation in the Vierrath group, was however slightly lower.

Since MOF-derived Fe-N-C catalysts contain a large fraction of micropores, restricting accessibility, the next steps will involve porosity tuning as well as optimization of Fe content.

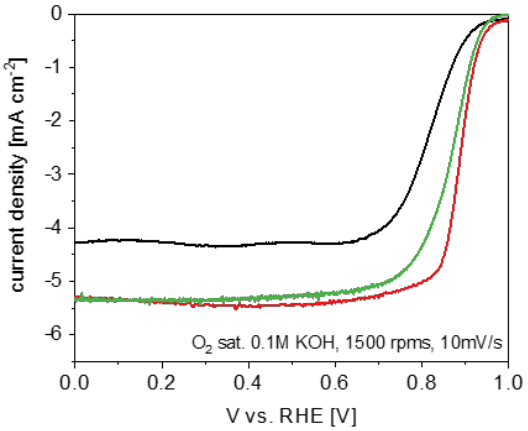

Fig. 3: LSV curves of polymer-derived Fe-N-C (black), small scale (red), and upscaled (green) MOF-derived Fe-N-C catalysts. (© Fischer group)

Membrane electrode assemblies with high power density (Philipp Veh, Matthias Breitwieser and Severin Vierrath)

In the first year of the project, a highly reproducible fabrication process for membrane-electrode-assemblies was established, the direct membrane deposition. The deposition allows to fabricate ultra-thin polymeric anion-exchange membranes below 5 µm, which lead to the most robust water management reported to date. The effective water removal in the anode thus enabled state-of-the-art power densities beyond 1 W/cm². These results have been published in the peer-reviewed journal *RSC Advances* in February this year. [2]

Based on this work, further experiments regarding the optimization of water management, cell performance and stability were conducted: The application of new polymers (Aemion⁺ instead of HMT-PmBI [3]) as an ion conducting membrane and electrode ionomer significantly improved the stability of the fuel cells and reduced the voltage loss over time from 7.5 mV/h to 6.1 mV/h. Additionally, variations of the electrode composition, especially the ratio between anion conducting polymer and catalyst particles, further decreased the voltage reduction over time to 3.7 mV/h (Fig. 4).

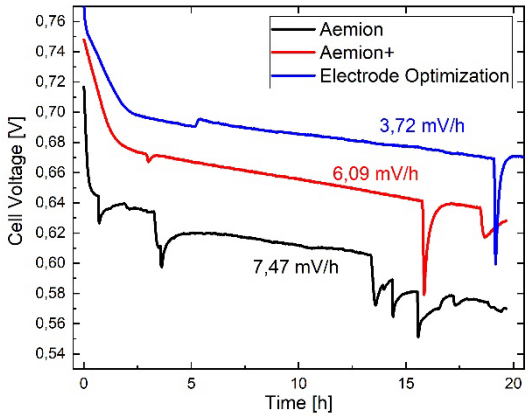

Fig. 4: Voltage reduction over time of different AEMFCs (© Vierrath group)

Besides the reduction of the voltage degradation, the overall AEMFC performance was significantly improved, achieving maximum power densities beyond 1.8 W/cm^2. Therefore, different ionomer and catalyst materials as well as operation conditions and novel fabrication approaches were applied and optimized accordingly (Fig. 5).

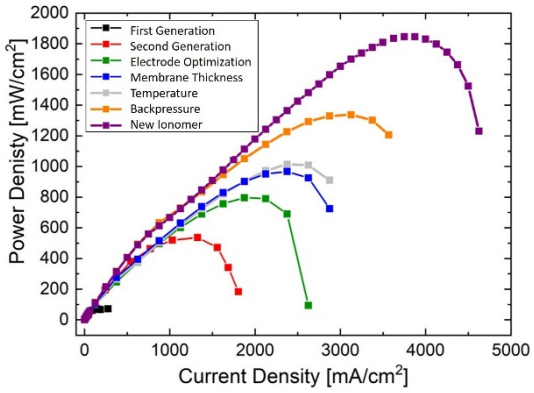

Fig. 5: Power density data, depicting the main optimization steps of the AEMFC development (© Vierrath group)

Furthermore, first fuel cells were tested applying the platinum-group-metal free catalysts synthesized by the *Anna Fischer Research Group* for the oxygen reduction reaction in the cathode. The results show a high catalytic activity achieving power densities beyond 300 mW/cm^2 (Fig. 6) and thereby indicate the productive cooperation between the two involved research groups.

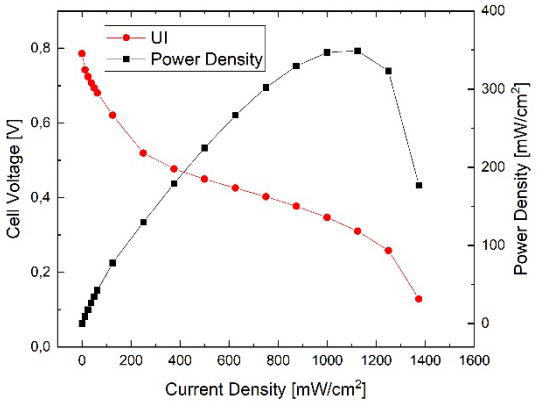

Fig. 6: AEMFC performance with Fe-N-C catalyst instead of Pt catalyst on cathode (© Vierrath group)

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2D and 3D Investigations of Porous Fuel Cell Catalysts by Transmission Electron Microscopy

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The project TEMCat3D aimed at the in-depth understanding by advanced electron microscopic characterizations of the 2D- and 3D-structure of porous Pt/C fuel cell catalysts developed in the Fischer group. Both newly designed porous carbon supports as well as porous Pt/C catalysts, were systematically investigated by 2D- and 3D- transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) as well as energy dispersive X-ray spectroscopy (STEM-EDX) in terms of structure, composition and porosity. The resulting 2D and 3D structural findings were on the one hand used to optimize synthesis conditions, and on the other hand, used to determine structure-activity and structure-stability correlations and thereby contribute to elaborate knowledge-based optimization pathways for catalyst activities and stabilities. In addition, identical location (IL) TEM studies allowed the analysis of catalyst degradation mechanisms.

2D (HR-)TEM investigations

By TEM and high resolution (HR) TEM both the morphology and structure of the carbon supports as well as the Pt nanoparticle (NP) size distribution, dispersion and crystallinity were obtained. For example, as seen in Fig.1, HR-TEM analysis of carbon support materials pyrolyzed at increasing temperatures revealed an increasing graphitization of the carbon structure. Such differences in graphitization could be correlated by us with changes in wettability and conductivity of similar carbon supports [1]; changes, which, in addition to the Pt deposition method, influence the Pt NP size distribution and dispersion. As seen in Fig. 2, a Pt/C catalyst (Pt40wt%/HTC-P900), based on a carbon support pyrolyzed at only 900°C with low graphitization, exhibits a much narrower particle size distribution than a Pt/C catalyst (Pt40wt% / HTC-P1500), based on a carbon support with similar morphology but pyrolyzed at 1500°C and hence higher graphitization. These differences in Pt NP size distributions could be correlated with differences in terms of surface functionalities for different pyrolysis temperatures.

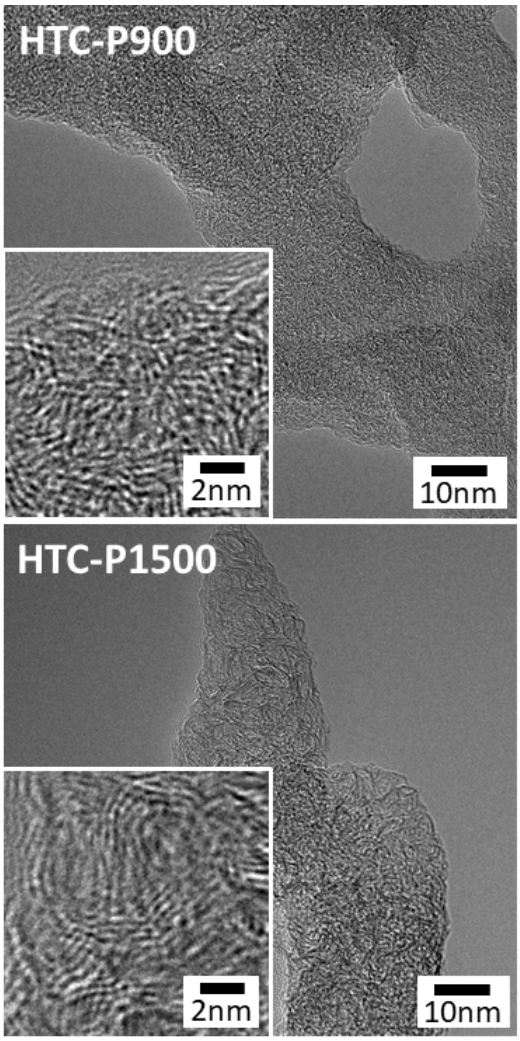

Fig. 1. HR-TEM images of carbon support materials (HTC-P-*T*) prepared by hydrothermal carbonization and subsequent pyrolysis at different temperatures *T*, with *T* = 900° C and 1500°C. (© Fischer Group, Inorganic Functional Materials and Nanomaterials)

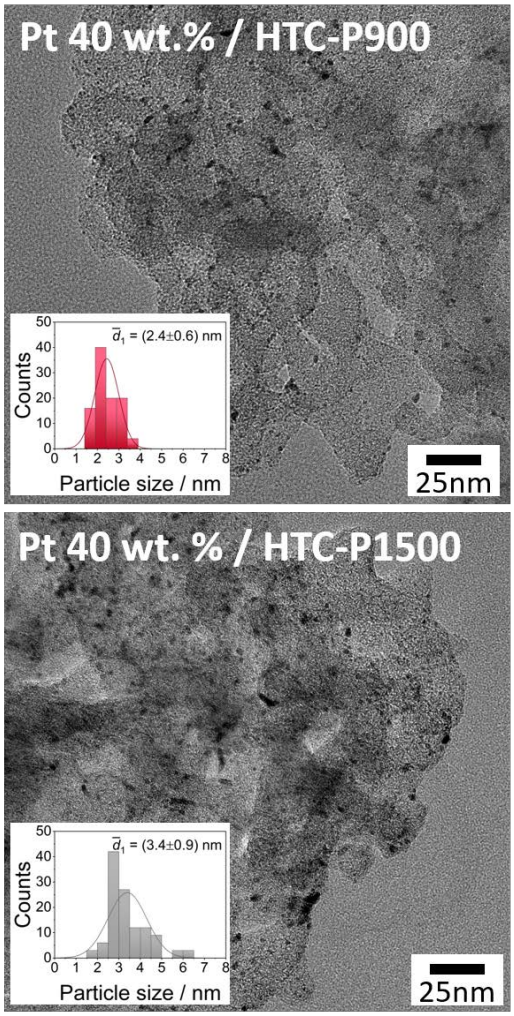

Fig. 2. TEM images of HTC-P900 and HTC-P1500 with 40 wt.% of Pt loading (obtained via carbon support impregnation by H_2PtCl_6, subsequent freeze drying and reduction in N_2/H_2 at 100°C). (© Fischer Group, Inorganic Functional Materials and Nanomaterials)

2D STEM-EDX investigations

By STEM-EDX measurements spatially-resolved elemental compositions of the support material were investigated and related to the Pt nanoparticle (size) distribution.

For example, one of the Pt/C reference catalysts within the project showed an inhomogeneous Pt NP distribution. In this case, the occurrence of Pt correlated with the presence of sulphur, which might indicate that sulphur-groups could act as anchor points for Pt NP (data not shown).

For the mesoporous N-doped carbon materials (MPNC), previously developed by the Fischer group [1, 2], a very homogeneous distribution of N was found by STEM-EDX measurements (Fig. 3) and in agreement a homogeneous Pt NP dispersion was obtained for MPNC based Pt/MPNC catalysts prepared by incipient wetness impregnation. For both reference and MPNC catalysts a correlation between the Pt and O EDX cartographies were found, indicating the surface oxidation of the Pt NP.

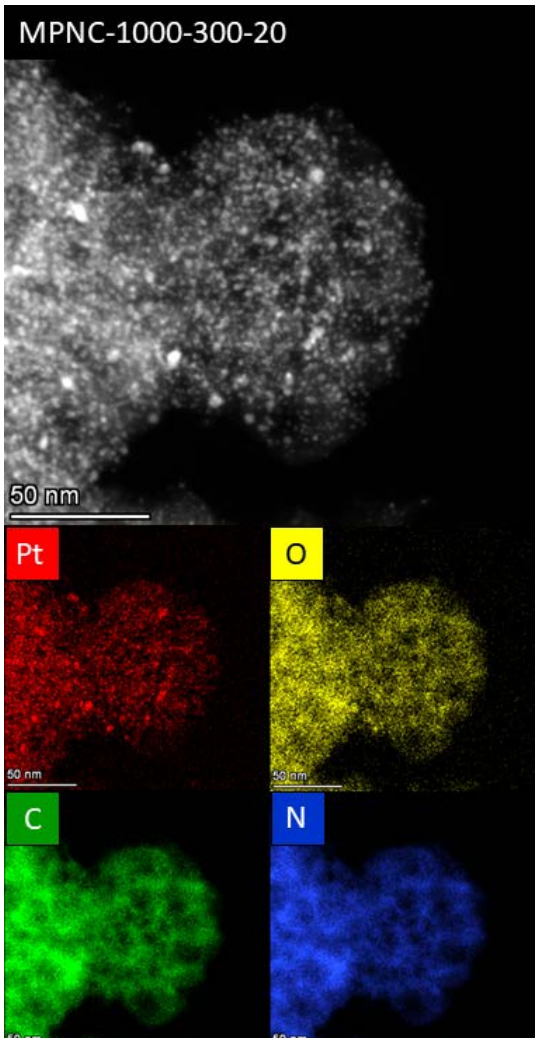

Fig. 3. STEM-EDX measurements for a Pt/MPNC catalyst prepared by incipient wetness impregnation using H_2PtCl_6 as precursor and subsequent reduction in Ar/H_2 at 300°C. (© Fischer Group, Inorganic Functional Materials and Nanomaterials)

3D STEM tomography

For the Pt/MPNC catalysts the homogenous distribution of Pt NP within the pores of the MPNC support was further investigated/visualized by 3D STEM tomography (Fig. 4). Besides the Pt NP dispersion, the pore size distribution, pore wall thickness and pore connectivity was characterized by TEM and STEM tomography, showing a very homogenous distribution of the Pt NP throughout the entire MPNC particles; distribution, which was found to be beneficial for high electrochemical surface areas (ECSA).

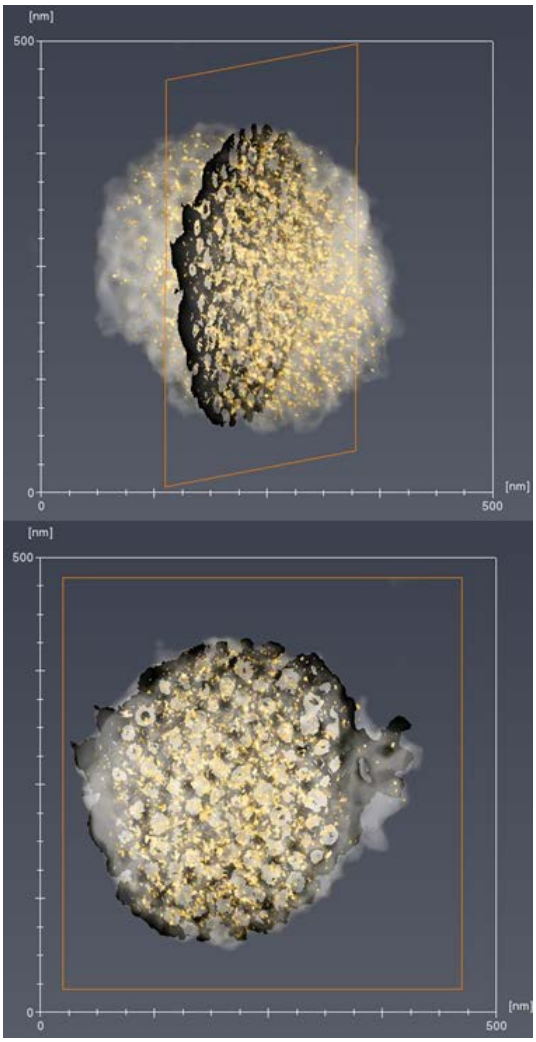

Fig. 4. 3D reconstruction of a Pt/MPNC catalyst, obtained by STEM tilt series measured at different tilt angles (± 70°). (© Fischer Group, Inorganic Functional Materials and Nanomaterials)

IL-TEM investigations

In order to analyse the degradation mechanisms of Pt/C electrocatalysts, an IL-TEM (*IL = identical location*) set-up and measurement protocol was developed within the project. To validate the set-up and method, IL-TEM images of a reference Pt/C catalyst (20 wt.% Pt) distributed on a conductive TEM finder grid were taken before and after an electrochemical accelerated stress test (AST, s. Fig. 5). After the AST, TEM analysis of the electrocatalyst particles at identical location were undertaken showing specific differences such as particle detachment, migration and growth. Such analysis were also performed on Pt/MPNC catalysts (data not shown).

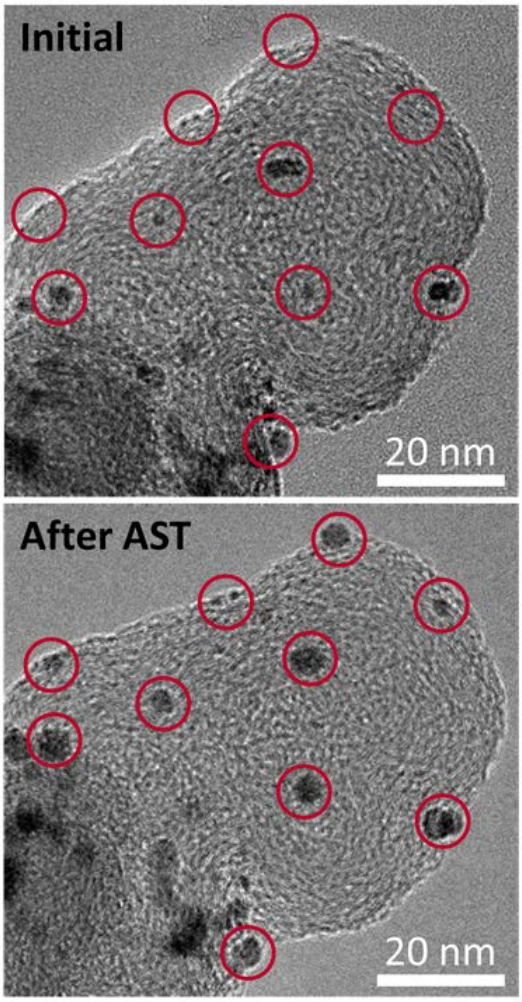

Fig. 5. IL-TEM images of a commercial Pt/C 20 wt.% catalyst before and after an accelerated stress test (AST, 10 000 cycles, 1 – 1.5 V vs. RHE, 500 mV/s, 0.1 $HClO_4$, N_2 saturated). (© Fischer Group, Inorganic Functional Materials and Nanomaterials)

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The responsibility for the content of this publication lies with the authors.

Demonstrator for soft autonomous machines - soft robotic low energy gripper systems based on *liv*MatS materials with sensing capabilities

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The cooperation project focuses on the research of designing and prototyping a soft robot which is equipped with sensing modules and is able to grab items and crawl on surfaces, while requiring a low amount of energy. The attachment mechanism is inspired by the cups in the nature like on the tentacles of an octopus. (Fig. 1)

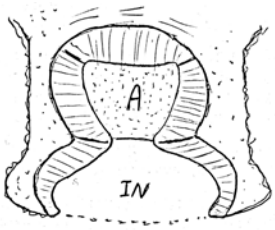

Fig. 1: Anatomical structure of the suction cup of an octopus. IN: the infundibulum, A: the acetabulum (© Laboratory for the Design of Microsystems, IMTEK)

When the suction cup comes in contact with the surface, the outer rings form a seal and trap the fluid inside the cup. Meanwhile, the muscles surrounding the lower chamber (infundibulum) contract and send the fluid to the upper chamber (acetabulum) while flattening the suction cup over the substratum. Next, the contraction of the radial muscles surrounding the acetabulum increases the inner surface and therefore the volume of the acetabulum, which decreases the pressure of the trapped fluid. The pressure difference between inside and outside of the suction cup results in the attachment force until either the muscles are relaxed, or the attachment seal is broken. For the fluids with a higher bulk modulus (indicating how a material is resistant to compression or expansion) the smallest volume change of the suction cup ends up in a significant pressure difference and adhesion force. However, the pressure drop is limited to the cohesiveness of the molecules in a liquid. [1]

For the actuation, electro active polymers like the dielectric elastomer actuators (DEAs) are built and used. A DEA consists of a thin layer of dielectric elastomer material sandwiched between the compliant electrodes on either side as shown in Fig. 2. When the material is subjected to voltage, equal and opposite charges spread on either side of the dielectric elastomer and an electric field is formed between the two electrodes. Due to the mutual attraction of the charges on the electrodes, the elastomer experiences Maxwell stress, which expands the elastomer's area and decrease its thickness. DEAs are a promising candidate for soft robots owing to their large deformation, high energy density, fast response, lightweight and compact structure. [2]

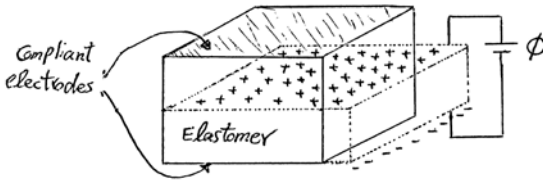

Fig. 2: Schematic of the principle of dielectric elastomer actuator (© Laboratory for the Design of Microsystems, IMTEK)

In this project, we are aiming first to produce artificial suction cups by using molding techniques and later to attach them to the robot's arm and control the motion and adhesion. The molds were 3D printed (Fig. 3), and several cups with different materials and dimensions were parametrized and prototyped. The stiffness of each part of the suction cup plays an important role in the adhesion process. In reality, the octopus implements several muscles in a complex procedure. One big challenge of this project is to simplify the mechanism and imitate the nature with a smaller number of actuators. On the other hand, a smart design may even overcome some limitations of the natural suction cups. Therefore, in parallel to the mold design, it is planned to make a finite element model of the suction cup to and optimize the abovementioned design parameters.

Fig. 3: The mold prototyped for molding the suction cups (© Laboratory for the Design of Microsystems, IMTEK)

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ThermoBatS – Thermoelectric battery systems

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

The livMatS project ThermoBatS is part of the thermal energy thrust in research area A and aims at harvesting this abundant and easily accessible form of energy by developing a micro-thermoelectric generator (µTEG) with two different phase change materials (PCM) on both sides, acting as heat reservoirs. This package will be capable of powering e.g. a small sensor or being used as a sensor itself. Thermoelectric generators (TEG) 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 amount of time, making time dependent temperature fluctuations (e.g. by the daylight cycle) accessible for the harvester.

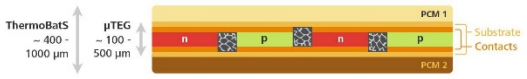

Fig. 1: ThermoBatS µTEG-PCM stack consisting of PCM reservoirs on top (light beige) and bottom (brown), thermally conductive substrate material (beige), contact pads (orange), TE material (red and green) and a thermally insulating polymer foam (gray) (© livMatS/Daniel Hellweg)

The ThermoBatS project has four main parts. The first part is focused on developing high quality nano-structured thermoelectric materials. The second part is the formulation of printable n- and p-type thermoelectric (TE) inks by means of sonication or high energy ball milling. In the third part, the fabrication of µTEGs in pre-defined microstructures, based on the

TE inks as well as the integration of commercial PCM materials is in focus. In Fig. 1 a sketch of the envisioned µTEG-PCM stack is shown. The fourth phase is dedicated towards demonstration of a self-sustained Thermo-BatS with additional functionalities.

Presently, the first three phases of the project are running in parallel. Currently two type 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. Both are produced by mechanical alloying the elements using high energy ball milling. In Fig. 2 the morphology of the resulting coarse agglomerates of the nano-material is shown. The correct phase composition is confirmed using powder-XRD and SEM-EDX. The produced nano-powders are reproducible and scalable.

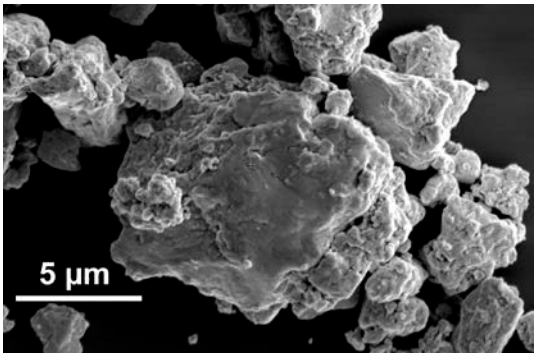

Fig. 2: SEM image of $Bi_{0.5}Sb_{1.5}Te_3$ heavily agglomerated nano-powder after ball milling. © IMTEK/Laboratory for Design of Microsystems

A dispensable TE ink is formed from nano-powders dispersed in a mixture of terpineol (solvent) and PVP (additive). The ink shows the desired thixotropic behaviour and is stable for up to 3 weeks. Ultrasonic treatment of the ink removed the coarse aggregates and improved the stability. The µTEGs are currently fabricated on PCB-based substrates (FR4+Cu) with laser machined holes, but will likely be changed to more suitable substrates like 3D printed hollow structures or polymer foams with low thermal conductivity. In our current µTEG design, the FR4 layer creates the support structure for the TE legs and top and bottom copper layers act as electrical contacts. The TE ink is manually dispensed into the holes and the solvent removed via vacuum filtration. A subsequent hot pressing ensures good electrical contact and high density within the TE materials. Automated ink dispensing as well as alternative sintering methods like electro-sintering are topics of future investigations. The next steps: electrical contact structuring and integration of PCM materials (both printing methods) have been started by the end of the year.

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.

Tiered approach for prospective assessment of benefits and challenges (TAPAS)

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Project funding: German Research Foundation (DFG) – Cluster of Excellence "*liv*MatS"

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 op-

tions. 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.

After having completed the review of existing assessment systems regarding sustainability issues of technology / product development, current work within the project aims to outline the fundamentals of the TAPAS framework. Covering sustainability, ethics and consumer issues, this framework encourages and enables innovators to carry out assessments that are embedded in the innovation process as early as possible. Guiding principles, as well as appropriate early engagement tools to help enable developmentally integrated assessments, have been described and published in the journal "TATuP" with several co-authors from the *liv*MatS cluster [3].

In addition, responses to the challenges of the Anthropocene were highlighted from the perspective of sustainability research for a publication in the journal "Elementa" [4]. Within the framework of a transdisciplinary approach, the prospective assessment of substances of very high concern was described, inter alia.

In the upcoming iterative steps, the TAPAS framework will be implemented and tested on the basis of concrete *liv*MatS developments and demonstrators.

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The concept of life in *liv*MatS and the Anthropocene: a multi-layered analysis of life

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The term 'life' is not a neutral concept, but is linked to various contexts with different intentions and interests. Making this clear is relevant if one intends to promote a definition of 'life' and, expanding on this definition, the development of 'life-like technologies' that are to be generally accepted.

This is the task addressed by the cooperation project between philosophy and psychology, which is carried out as part of Research Area D "Societal Challenges and Sustainability" of the Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems" (*liv*MatS). It seeks to clarify the prerequisites for a contemporary definition of the term 'life', both with regard to the life-like materials systems in the cluster of excellence *liv*MatS and in view of the blurring boundaries between the naturally living and the artificial in the Anthropocene, the new geological age proposed by the natural scientists Crutzen and Stoermer in 2000 [1, 2, 3]. The project thus contributes to elucidating one of *liv*MatS' basic concepts, insofar as a definition of 'life-like' can only be applied against the background of a definition of the concept of 'life'. Before that, however, we must first establish the different levels and contexts that are important when talking about the phenomenon of 'life'.

For this purpose, on the one hand, the method of cognitive-affective mapping, developed by the philosopher and cognitive scientist Paul Thagard, is used [4]. Cognitive-affective maps (CAMs) represent a kind of mind maps that not only capture concepts but also their affective evaluation, which are of importance when talking about the phenomenon of 'life'. These CAMs are drawn by experts from different scientific fields, especially within the cluster of excellence *liv*MatS. On the other hand, we review and systematize current philosophical theories of life [5, 6] in order to evaluate them in the context of the CAMs on the concept of life. At the same time, the concepts of life of the various scientists who draw the CAMs can be examined in this way with regard to their background in the history of ideas.

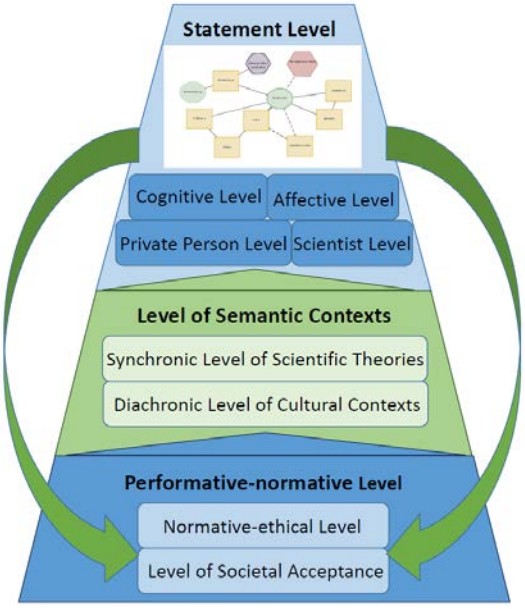

Fig. 1: Presentation of the multi-layered way of talking about the concept of 'life'. The statement level is captured by the CAMs (above), this is shaped by the semantic contexts and the normative-performative level and vice versa (below). (© Cluster of Excellence "Living, Adaptive and Energy-autonomous Materials Systems" (*liv*MatS))

Using this method, three main levels and different sub-levels can be made visible, which are in play and must be taken into account when speaking about the phenomenon of 'life' (Fig. 1). The distinction between three main levels is based on John Austin's three-level distinction for all speech acts, namely between locutionary, illocutionary and perlocutionary speech acts [7]. This is further differentiated and specified here using a three-layer division into the statement level, the level of the semantic context and the performative-normative level:

(1) First of all, we have to mention the pure statement level or the direct communicative level with which someone indicates what he or she understands by life. In the project, this level is investigated by having scientists from different disciplines draw CAMs on the concept of life. These are scientists from the fields of micro- and materials mechanics, neurology, neuro-ethics and AI ethics, sustainability research, bionic chemistry, biology with a focus on biomechanics and biomimetics, as well as theology, media studies and philosophy, i.e. especially from subjects that are also represented in *liv*MatS. The CAMs integrate four sub-levels: (a) On the one hand, they reflect the concepts used to define life in a purely cognitive way. (b) The fact that the CAMs also allow for a graduated affective evaluation reflects another level of communication. For example, in individual CAMs, a term such as death was assessed as affectively negative or a term such as artificial intelligence (AI) as affectively ambivalent. (c) Furthermore, the CAMs do not only show what individual private persons understand by life. (d) At the same time, the test persons were also addressed as representatives of the sciences they study respectively, so that the CAMs ultimately also represent an understanding of life that transcends the individual.

(2) The concepts of life articulated in each case, however, are not to be taken in isolation. Rather, they stand in a semantic context in two senses. (a) This connotative aspect refers, on the one hand, to the synchronic level: the CAMs on the concept of life drawn by scientists are to be contextualised with regard to the scientific theories they represent, which we make recognisable in the project through subsequent interviews with these scientists. (b) On the other hand, a diachronic-historical level must be taken into account: the articulated concepts of life show explicit or implicit connections to concepts of life that shape the history of ideas and culture. What is understood and articulated as life has, in other words, a cultural, social and historical background. Where the boundary between living and non-living is set, for example, has to do with the cultural background. The project will reflect on this by confronting and comparing CAMs with different concepts of life that are tangible in the mainly philosophical research literature.

(3) When concepts of life are articulated, this ultimately also aims, explicitly or not, to produce an effect on those to whom they are represented. (a) This performative level can be expressed on the one hand as a normative level. Thus, concepts of life represented by certain disciplines have consequences for the approach of the respective disciplines. In a broader sense, however, certain concepts of life can also give rise to demands for action on the part of society. If something is regarded as alive and an inherent value is attributed to it, it goes hand in hand with normative demands. (b) Conversely, certain concepts of life also evoke certain reactions in society, both positive and negative, which must be taken into account by science in the course of society's acceptance of new research and especially life-like technologies. For example, in the field of AI, not every abolition of the boundary between natural and artificial is accepted. Robots that are too human-like, for instance, can also appear uncanny.

In this way, the project seeks to highlight the multi-layered nature of life. To a certain extent, this can serve as a yardstick to prevent the assertion of a one-sided definition of life. But this meta-analysis of the concept of life is not only a prerequisite for any reflection on the content of what life is. At the same time, this level distinction regarding the concept of life is also indispensable for acceptance research. In particular, research projects that, like *liv*MatS, aim to develop life-like technologies can only ensure the acceptance of their research if they keep in mind the diverse disciplinary and social-cultural connotations of life and especially the performative-normative level that usually accompanies discussions about life.

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Cognitive-Affective Mapping (CAM): An Innovative Method to Visualize Belief Systems

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In this project, we explore and advance the method of Cognitive-Affective Mapping [1]. A Cognitive-Affective Map (CAM) is a graphical representation of interacting concepts, similar to a cognitive map. It visualizes an individual's or a group's belief system including cognitive and affective aspects towards a given topic (see Figure 1 for an example). As an extension to cognitive maps or even more simple mind maps, concepts and connections carry certain weights, which are interpreted as valence values. We explore this method as a tool for data collection, data analyses and supporting communication processes. With regard to new technology developments, CAMs are able to foster an inter- and transdisciplinary exchange on *liv*MatS' new materials systems and to establish a bridge between science and society. As a first step, we explore the CAM method and its properties in different contexts, e.g. (1) the perception of the coronavirus pandemic in different countries; (2) the effect of walking on the perception of the pandemic; (3) the evaluation of certain property terms depending on the context; (4) the perception of abstract concepts like "life" in different scientific disciplines; (5) the perception of expenses for car versus public transport, and (6) the mediating effect of CAMs on the evaluation of controversial technology. In addition, we are working on extending the usage of the method by developing a software package supporting the creation of individual CAMs, *Valence* [2]. Whereas to date researchers used CAMs mainly to draw CAMs on the basis of other, already collected data like questionnaires and qualitative interviews, we showed how it is possible to instruct participants to draw CAMs on their own in order to collect large datasets online. The software can be configured to allow participants to graphically arrange pre-defined concepts in the CAM for comparison analyses. For more open examinations of a topic and to gain impressions researchers might not have considered yet, CAMs can be drawn freely, without content constraints. Thus, the CAM method can serve as a tool for quantitative as well as qualitative research. We also showed that CAMs can be used in an experimental setting [3] to explore the influence of different conditions or to compare attitudes of different samples [4]. Examples of typical structural CAM measures for analyses are (1) Number of concepts (nodes) and connections (edges); (2) Connectedness: Existence of paths from one concept to another; sub-CAMs; (3) Number and share of different types of concepts and connections; (4) Valence values: Average valence of a CAM or valences of single concepts; (5) Density: Number of links in a network divided by the number of all possible links in a network; (6) Diameter: Maximum distance from one concept to another, i.e. number of "hops".

Besides exploring CAMs as a method in general, we also apply CAMs in the *liv*MatS context to examine societal acceptance in particular towards new materials systems. In an empirical study, we explored the effect of different scenarios on the respective CAMs drawn. Here, we instructed participants to arrange

pre-defined attributes in a CAM [5]. The attributes were taken from a list containing potential basal attributes of *liv*MatS' materials systems, based on qualitative interviews with *liv*MatS researchers [6]. Before drawing their CAMs, participants were randomly assigned to one of two scenarios, which contained the same 32 attributes, but described different technological applications. We analyzed whether the scenarios influenced the drawing of the CAMs. As a result, we found that only few attributes were rated significantly different, implying that many attributes are rated independently of the context and might therefore be rather normatively evaluated. Future studies have to validate these findings. We use CAMs in *liv*MatS also to foster the exchange between varied scientific disciplines, by revealing different perspectives on the concept of "life". In an empirical investigation we instruct researchers to draw a CAM about the concept of "life" in their discipline. The resulting CAMs show that the understanding of "life" differs considerably between disciplines like biology, pyhsics, theology and others. These findings are an important step for the interdisciplinary communication in *liv*MatS. We now focus on the analysis of CAM networks. We expect purely quantitative analysis helpful only in scenarios, where the number and types of concepts and their connections are almost identical. Qualitative analysis comes into play in scenarios where the context is important. In this regard, we develop categorization options for the CAMs. We also plan to validate the CAM method with other established measurement tools, such as questionnaires.

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). Testing the CAM software Valence is free: https://cam1.psychologie.uni-freiburg.de/users/loginpage?next=/

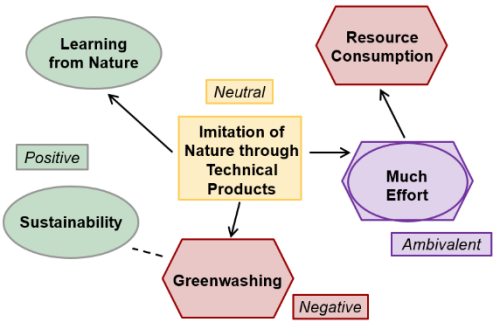

Fig. 1. Exemplary CAM on the Topic of Nature Imitation in Technology Development. *Note.* Each concept is evaluated as neutral (yellow rectangle), positive (green oval), negative (red rectangle) or ambivalent (purple oval + rectangle). Concepts can be connected with different kinds of links: solid (supporting influence) or dashed (inhibiting influence). Links without arrows imply mutual interactions while arrows imply causality. © Area D of the *liv*MatS Cluster

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CORE FACILITY "FUNCTIONAL PROCESSING"

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

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A central goal of the Cluster of Excellence "Living, adaptive and energy-autonomous Materials Systems (*liv*MatS)" at the University of Freiburg is the development of novel materials systems with dynamic, life-like and non-equilibrium (energy-autonomous) features. A target within the *liv*MatS research area "Demonstrators" are technical demonstrators like an artificial Venus flytrap [1-5], which will demonstrate the feasibility of the developed materials systems. Like their biological role models, these bio-inspired constructs will show complex behaviour in reaction to changing environmental conditions, whereby these reactions in form of motion or shape changes will not be initiated via a central control unit but in a plant-like manner 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 the material composition in complex systems requires special manufacturing methods that offer rapid prototyping and a high degree of automation.

For this purpose, a novel multi-material 3D-printer with on demand tool changing properties (Fig. 1 A), is being developed with a motion system based on a commercial filament-printer that extrudes molten thermoplastics through a thin nozzle layer by layer. Unlike a commercial printer, the new device does not have a directly mounted extruder but holds different tools in standby on a docking position. Using a carriage with a specifically developed adaptive coupling mechanism the motion system picks up the required print head, initializes it and prints the specified part of the currently printed layer. After use, the tool is returned to 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 nozzles, loaded filaments or printheads, since at every time only one head is moving above the build platform [6].

The core element of the pick-up mechanism is a kinematic coupling based on the Maxwell-design, which uses three groves arranged in a triangle on one surface and three corresponding balls on the counterpart. When pressed together this eliminates all six degrees of physical freedom, what results in a very precise and repeatable positioning [7]. Within our 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 between both sides is realised by a key-lock principle. A T-shaped key, located in the centre of the coupling, is inserted into a lock on the tool side, rotated and then retracted until the tool attaches to the carriage.

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. So far, the printer is equipped with two filament print heads (Fig. 1 B), and an additional wax extruder is under construction. The directly driven FFF-heads have proofed their reliability in handling even the most flexible materials, which are currently commercially available as filaments. To characterize the tool and materials several pneumatic actuators were printed and tested (see P. Kappel et al. this report for details). Using a dynamic variation of the extrusion factor it was possible to form pneumatic chambers and bending fingers (Fig. 1 E) with air tight walls and a high surface quality. To test the tool change procedure, a series of

multi-color and multi-material objects were printed. The first functional multi-material structure was a pneumatic actuator with a stiff body and a flexible membrane (Fig. 1 F). In order to compensate the lack of chemical bonding between both materials, the membrane was physically embedded by directly printing it into the surrounding body.

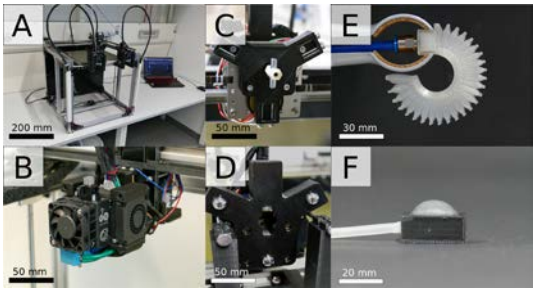

Fig. 1: Novel multi-material 3D-printer with on demand tool changing. The entire setup consists of the printer frame and its axis system (A), and the newly developed filament printhead attached to the X-carriage (B). The carriage side provides the grooves of the Maxwell coupling with a T-shaped key in its centre (C), which is inserted into a lock on the back side of the printhead (D). The system is able to print pneumatic actuators like bending fingers (E) and multi-material chambers (F). © Plant Biomechanics Group Freiburg.

The described manufacturing platform allows higher flexibility in the development of *liv*MatS demonstrators and enables the integration of 3D printable materials developed in *liv*MatS into complex 3D multi materials systems. Additional tools will be designed in a close cooperation with other groups of the cluster and can be fitted to the requirements of specific materials and materials combinations. Based on the tests with ultra-flexible filament the printer has a high potential for further research on actuators and complex pneumatic systems. This is especially beneficial for the gripper development of line 2 in the *liv*MatS area “Demonstrators”.

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Development of a baseline bioinspired macroscopic gripper system within *liv*MatS

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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. Devices suitable to envisage the feasibility of novel materials systems as aimed for in *liv*MatS are developed within the research area “Demonstrators”. As example for such a device, we develop a demonstrator based on principles of elastic

movements found, for example, in many soft motile plant and animal organs.

With the evolution of thumbs, grasping became a fundamental movement and a cornerstone of development of the great apes (Hominidae), and opposable thumbs with their complex musculature often discussed as contributing to the dominance of humans (genus Homo) and their direct precursors. The unconscious movement during grasping, which is an everyday occurrence for people, requires in technical systems an immense amount of computing power, especially in the technical implementation of grippers for fine and adaptive movements. In order to reduce the required computing power or make it obsolete, we want to develop a bioinspired gripper in *liv*MatS that is based on the multi-material systems developed by *liv*MatS. The gripper should be capable of adapting to the object to be grabbed and this adaptation should take place through a decentralized material-immanent processing, so to speak, material based embodied intelligence. As an artificial device, the gripper can be optimized by the combination of several principles from various biological role models to gain a system, which autonomously identifies, grasps and adapts to versatile objects. The aim of this project is the development of a bioinspired gripper, with the ability to sense qualities of an object like shape, size, weight and fragility and adapt its grasping in an adequate way and with appropriate force.

Especially a gripper with dimension in a centimeter scale has a high potential as a palpable showcase for public communication about the potential benefit of novel bioinspired materials systems developed in the *liv*MatS cluster and represents an innovative device for future industrial and medical applications where robots grasp very variable objects or directly interact with humans. To achieve this, we choose the approach of constructing a soft autonomous machine as it shows for our purpose suitable characteristics like softness, flexibility and adaptability. The construction of a modular gripper platform will enable the integration of e.g. various materials and sensors of other *liv*MatS projects in the future.

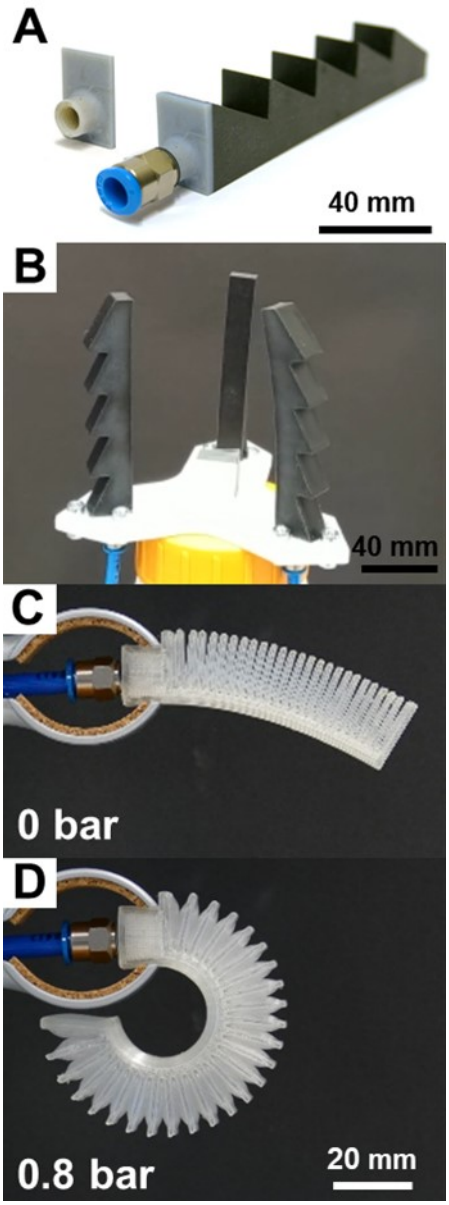

Fig. 1: 3D-printed pneumatic finger actuator and gripper concepts. A: Pneumatic actuator with uniform wall thickness printed as a combination of two materials (bright grey: rigid, black: flexible) B: Assembled demonstrator of a basic multi-material gripper using actuators shown in A. C and D: Demonstrator of a basic pneumatic actuator printed from flexible material (TPU, Shore A70) with a wall thickness reduced to 0.5 mm for reduced energy consumption during actuation. (© Plant Biomechanics Group)

As a first step, we build a baseline gripper platform by state-of-the-art 3D multi-material-printing as starting point for further development. The feasibility to print all parts of a gripper system from a multi-materials combination in one printing process enables us to quickly and easily create and test new gripper geometries. Our first successful system was printed with the inkjet printer available at the FIT

(Fig. 1 A, B). Whereas the parts had to be cleaned from supporting material and assembled post-printing to obtain a working gripper, a future aim is the production of a complete multi-material system ready to use when removed from the printer. The basic gripper platform consists of a solid base plate with coupling structures for the fingers and the fingers themselves. The fingers (Fig. 1 A) made up from flexible materials, consist of the actuators, and will include flexible sensor elements. In the first phase of the project, the sensor elements will sense actuator bending, while later improvements will aim for material embodied sensors for object recognition to trigger a change of the gripper's material properties.

For actuation, pneumatic actuators are used, that directly move the fingers by changes in applied air pressure. While the pressure comes from an external pressure source, the grasping characteristics are determined by the material and design of the fingers.

Today's 3D-printed pneumatic actuators are manufactured typically with a wall thickness, which is a multiple of the nozzle diameter of the printer to obtain airtight pressure chambers. [1]. With the newly developed *liv*MatS multi-material printer [2] we were able to 3D-print basic airtight pneumatic bending actuators from flexible TPU (Recreus, Filaflex, shore hardness A70) with a wall thickness of 0.5 mm (Fig. 1 C, D). The reduction in the wall thickness of the expanding pressure cushions correlates with a reduction in necessary air-pressure and overall power consumption for actuation. These results open up novel possibilities for future designs of low energy bioinspired actuators and gripper systems within our project.

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Single-mode polymer waveguide integration of organic laser

Jing Becker, Claas Müller

Core Facility 2, Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT)

Project funding: German Research Foundation (DFG) – "Polymer-based optical sensor platform with integrated light source"

Nowadays, we live in a world which is becoming more digital-driven and automated. Sensors, especially optical sensors are playing a more and more important role due to their various application possibilities in the bio-detection, drug development as well as chemical analysis. In this DFG 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. Novel manufacturing processes will be developed and optimized in this project. By applying such kind of manufacturing methods, optical sensor platforms could be fabricated cost effectively with high precision. A team of experts in polymer technology and polymer processing (AG Müller, University of Freiburg) and experts in organic optoelectronics (AG Kowalsky, TU Braunschweig) will work together in this project.

Organic thin-film lasers (OLAS) are promising optical sources when it comes to flexibility and small-scale manufacturing. These properties are required especially for integrating organic thin-film lasers into single-mode waveguides. Optical sensors based on single-mode ridge waveguide systems, especially for Lab-on-a-chip (LoC) applications, usually need external laser sources, free-space optics and coupling structures, which suffer from coupling losses and mechanical stabilization problems [1]. In this project, we have successfully integrated the organic thin-film lasers directly into polymeric single-mode ridge waveguides forming a monolithically laser device for LoC applications.

The schematic sketch of the OLAS integrated polymeric single-mode waveguide (1.0 µm in width and 1.0 µm in height) is shown in Figure 1. The integrated waveguide laser is

achieved by three production steps: nanoimprint of Bragg gratings onto the waveguide cladding material EpoClad, UV-Lithography of the waveguide core material EpoCore and finally thermal evaporation of the OLAS material Alq3:DCM2 on top of the single-mode waveguides and the Bragg grating area.

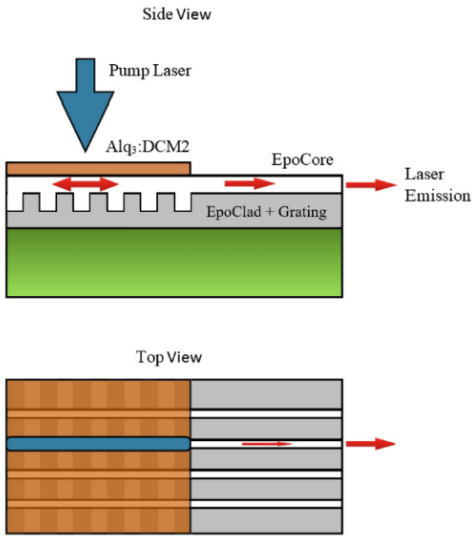

Fig. 1. Schematic sketch of the OLAS integrated into the polymeric single-mode waveguide. (© Core Facility 2)

Before the thermal evaporation of the OLAS material, the device structure is, first of all, investigated by SEM method. Figure 2 presents the SEM images of the EpoCore waveguide on top of the DFB gratings.

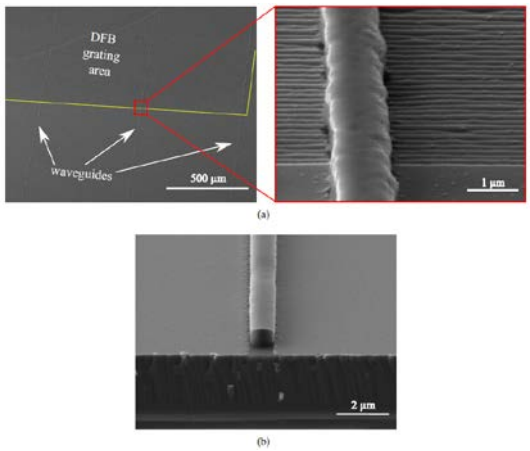

Fig. 2. SEM overview image of the whole waveguide and grating structure and a detailed view on the waveguides on top of the DFB grating and (b) the waveguide end facet. (© Core Facility 2)

The figures show a good waveguide integration on top of the DFB gratings as well as a satisfying waveguide end facet for the optical analysis of the integrated waveguide laser. Figure 2(a) gives also a detailed look on the waveguide. The waveguides outside this grating area show good optical quality and a smooth surface (cf. Figure 2(b)). After the fabrication of the DFB gratings and the waveguides, 200 nm of the guest-host laser active material system Alq3:DCM2 with a DCM2 doping concentration of 6% was co-evaporated in an ultrahigh vacuum chamber with $p < 10^{-8}$ mbar by organic molecular beam deposition method.

The samples were measured and characterized by the optical set-up schematically shown in Figure 3.

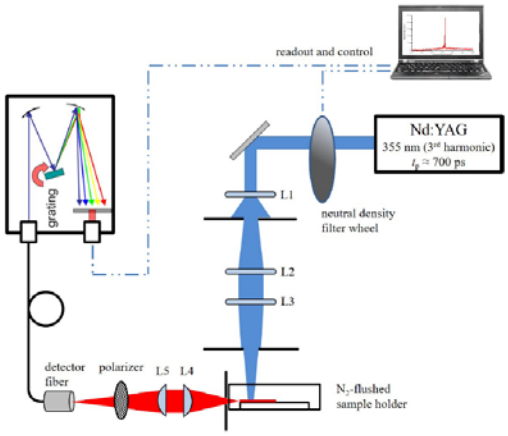

Fig. 3. Optical set-up for laser performance measurements of the integrated OLAS. The laser emission was measured orthogonal to the pump beam. (© Core Facility 2)

In this work, the laser light is analysed out of the waveguide facet with optical spectroscopy presenting single-mode characteristics even with high pump energy densities (Figure 4). The laser emission could be measured at 642.03 nm with a FWHM of 200 pm. No other higher modes could be observed even with excitation energy densities up to 173 µJ/cm^2.

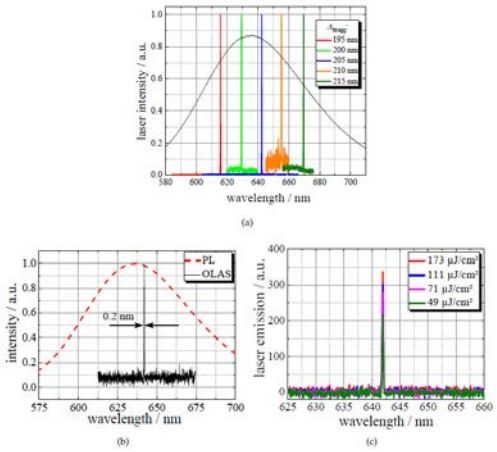

Fig. 4. (a) Lasing lines out of the integrated OLAS with different DFB grating periods and (b) the spectral response of the integrated OLAS with (c) increasing excitation energy density. (© Core Facility 2)

The LoC application ability for photonic or interferometric based sensors could be supported by the polarization extinction ratio of 15.5:1 (Figure 5), which indicts a linear polarization.

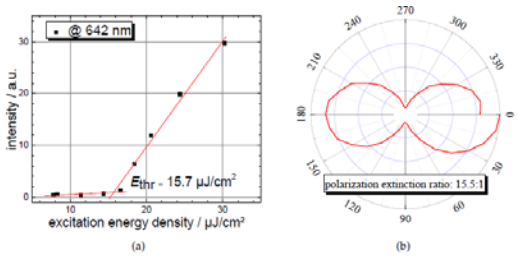

Fig. 5. (a) Laser threshold of the waveguide integrated OLAS and (b) the polar plot of the polarization properties. (© Core Facility 2)

By using this type of laser with the described integration, light can be easily coupled into the single-mode waveguide. This type of laser integration allows an uncomplicated light coupling into a single-mode waveguide. With this work a milestone towards the monolithically integration of organic lasers are achieved. Especially, optical sensor systems based on single-mode waveguides and, in particular, LoC systems could benefit from this work.

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CORE FACILITY "MODELLING AND SIMULATION OF MATERIALS SYSTEMS"

Twisted intramolecular charge transfer (TICT) fluoroscence in 1-trimethyl-ammonium-6-pentafluorstyryl-pyrene (qStyPy)

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Intermolecular charge transfer (ICT) processes play the fundamental role in various applications connected to the conversion of light such as photosynthesis in plants, artificial light harvesting systems, and in numerous existing or conceived molecular photonic applications [1–3]. A prototypical system to investigate ICT is a molecule with an electron donor (D) and an electron acceptor (A) moiety linked by a single bond. Upon electronic excitation, internal rotation around the central bond is a possible relaxation mechanism in such systems [4,5]. The fundamental understanding of the structure and dynamics of the ICT process in the excited states has been of remarkable interest, and hence, numerous donor (D) and acceptor (A) substituted aromatic have been studied extensively [4, 6].

The concept of relaxation of the excited state via twisting of a single bond has mainly evolved from the observations of dual fluorescence of 4-dimethylaminobenzonitrile (DMABN) and related molecules [5,7]. Recently similar molecules called 1-trimethyl-ammonium-6-pentafluorstyryl-pyrene (StyPy) were reported by the Walther group [8,9]. This molecule is modularly applicable, features a desired fluorescence in the infrared regime.

StyPy is a compound in which the electron donor N,N-dimethylaniline and pentafluorstyrene (PFS) is covalently linked to the electron acceptor pyrene. Because of the lack of an extended bridge between the donor and acceptor in StyPy, the physical characteristics of

these groups themselves significantly influence the electron-transfer mechanism. This leads to very unusual absorption and emission spectra in the optical regime, and because of this, related structures are considered to be a molecular diode where electron donor and electron acceptor moieties are twisted against each other modulating the electron charge-transfer processes [10].

In this report, we investigated electronic and optical spectra StyPy. The potential curve of ground state (S0) and excited state (S1) value as a function of the torsion angle between possible donor group and acceptor groups are analysed ans fluorescence spectra as a function of relative permittivity are described

We model the structures within density functional theory (DFT) as implemented in the GPAW package [11], where the exchange correlation potential is modeled as devised by Perdew, Burke and Ernzerhof [12].

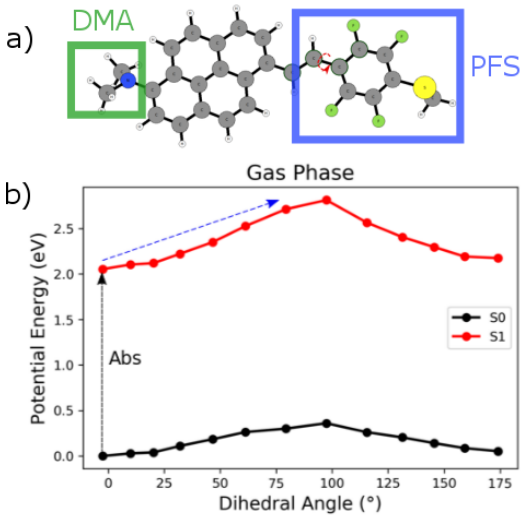

Fig. 1: a) Optimized structure of the StyPy in its electronic ground state. DMA and PFS groups are indicated. b) Energetics of StyPy depending on the dihedral angle of the PFS group in the electronic ground state S0 and the first excited state S1 in the gas-phase (© Functional Nanosystems Group)

The DFT optimized structure of StyPy in its electronic ground state is shown in Figure 1a. The PFS ring is found to be nearly planar respected to the pyrine part of the molecule. The DMA group is slightly twisted with the C-N-C-C dihedral angle at 21°. This result is in close in agreement to the experimental crystal structure, where this angle is 26° [9].

We consider two distinct mechanisms of twisted groups in StyPy. First the rotation of the PFS group and the second the rotation of the dimethylamine (DMA).

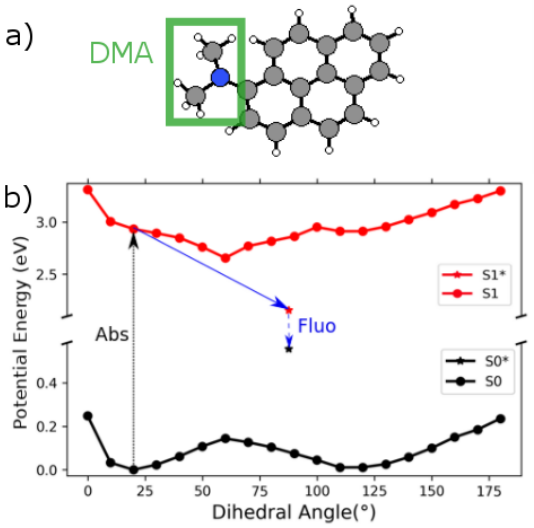

Fig. 2: a) Ground state structures of the PyDMA molecule. b) Energetics of the PyDMA depending on the dihedral angle of the DMA group. The circle and star symbol represent relaxation in ground (S0) and excited states (S1), respectively. Black and red colors represent energies of S0 state and S1 states, respectively. The blue dashed line represents the resulting fluorescence (© Functional Nanosystems Group)

To analyze the effect of rotation of the PFS group, the dihedral angle of C-C-C-C (Fig. 1) was stepwise varied starting from ground state structure from ~0° to ~180°. The molecule was re-optimized in the electronic ground state at each fixed value of the dihedral angle. The optical properties were then calculated within time dependent DFT (TDDFT) [13] in Casidas linear response formalism [14]. The resulting energies of electronic ground state (S0) and first optically active excited state (S1) are depicted in Fig. 1b). The S0 state shows a rotational barrier of ~0.4 eV with its maximum at ~90°, i.e. when the PFS is perpendicular. Similarly, the energy of the S1 state energy increases when the dihedral angle rotated until ~90° with an energy barrier even ~0.8 eV. The lowest energy of the S1 state is thus still at ~0° indicating no sensitivity of the transition to S1 on this dihedral angle.

The second possibility for excited state relaxation is rotation of the DMA group. We modeled this by following the same strategy as

above. We removed the PFS group in our model for sake of computational simplicity. The effect of the torsion of the DMA group is shown in Fig 2 and is quite different to the case above. The minimal energy in the electronic ground state S0 is found for the torsion angle of 21°. There are two distinct rotational barriers of 0.2 and 0.3 eV, respectively. The initial torsional angle as well as the appearance of two rotational barriers is a consequence of the asymmetry of the DMA group.

The potential of the excited state S1 is quite different. Here, stabilization is achieved through rotation around the single bond between the Pyrene and the DMA group. Explicit relaxation in the excited state results in a twisted state showing a dihedral angle of about 90°. Similar effects have been observed in related molecules [15]. There are two unpaired electrons in the frontier orbitals: one is located in the acceptor unit (Pyrene) and the other one of the nitrogen atom (donor unit). The rotation around the single bond between these units minimizes the repulsive interaction between the unpaired electrons and results in a full charge separation and enhancement of the dipole moment. Fluorescence spectra of this molecule also observed in the experiment [16].

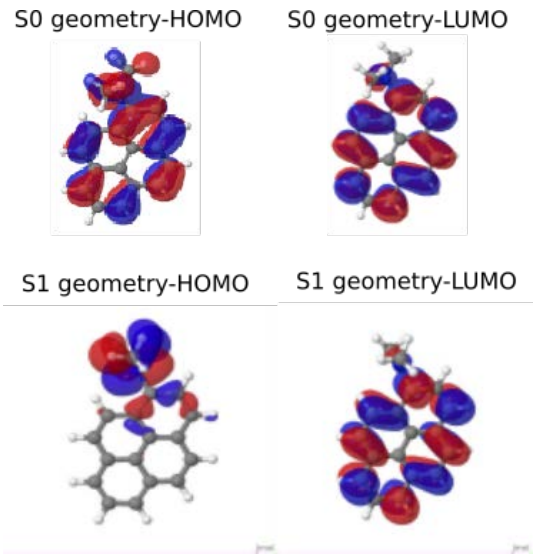

Fig. 3: Optimize equilibrium geometry of PyDMA in the ground state (S0) and excited state (S1) (© Functional Nanosystems Group)

The main single-particle contribution to S1 is the transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The 3D plot frontier MOs can be seen in the fig 3. In the S0 geometry, the orbitals of the HOMO are mainly distributed over the whole molecule while the LUMO located on the Pyrine part. In the S1 geometry, the HOMO is dominated by contributions from the DMA group, while the LUMO orbital is still located at Pyrine molecule. The energy value of HOMO and LUMO levels for the ground state of the PyDMA are computed to be -4.57 eV and -2.33 eV respectively, and the energy different is 2.24 eV. In the S1 geometry the HOMO energy increases to -4.22 eV and the LUMO energy decreases -2.62 eV. The high energy of HOMO means that it is easy for HOMO to donate electrons whereas the low energy of LUMO means that is easy for LUMO to accept electrons. The change in HOMO and LUMO energy cause the energy gap decrease to 1.6 eV.

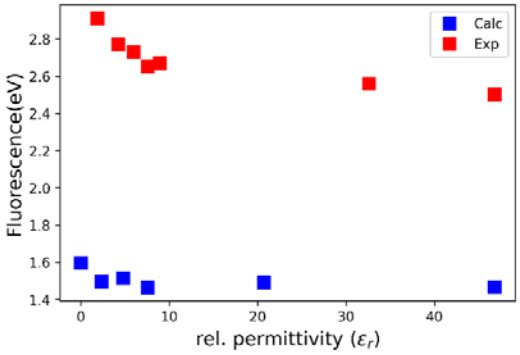

Fig. 4: Calculated fluorescence energy (Calc) as function of relative permittivity. Experimental values (Exp) are adapted from [14]. (© Functional Nanosystems Group)

Finally, we address the effect of solvation. Solvent effects were described by continuum solvent model (CSM) [17]. Starting with the rotational optimized structure of the S0 state as the initial guess, geometry relaxation for the S1 state of the PyDMA by using the TDDFT method leads to a structure of the lowest energy, in which the dihedral angle of the DMA group is twisted by ~90° with respect to the rest of the molecular plane. The absorption energies of the PyDMA were calculated in various solvents. There is a single optically active $S_0 \rightarrow S_1$ transition at 2.93 eV (423 nm) that

does practically not change by changing the solvent permittivity. The transition can be described as a nearly pure HOMO-LUMO transition with a theoretical oscillator strength of 0.18.

For the fluorescence spectra, the solvents give a slight bathochromic shift according to our calculations. From fig 4 we can see the fluorescence energy lowers with an increasing of relative permittivity. For high relative permittivity like DMSO ($\varepsilon_r = 46.8$) the dipole moment change drastically after excitation, the solvents rearrange so the highly polar excited state stabilizes. The higher relative permittivity or polar solvents lead to better stabilized excited state, which explains the bathochromic shift effect for this molecule. This effect is much stronger in the experiment, but the fluorescence energy is found to be much higher also.

In summary, we have investigated the TICT of StyPy in the gas phase and various solvents based on their relative permittivity. In the excited state (S1) the stabilization is achieved through rotation between the Pyrene and the dimethylamino group with dihedral angle about 90°. This relaxation causes a significant redshift of spectra. In contrast, no TICT or redshift can be observed under rotation of the PSF group. The absorption spectra of PyDMA show only small changes under variations of the solvent permittivity resulting in a small shift of fluorescence energy with increasing relative permittivity.

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PROJECTS

*liv*MATS—LIVING, ADAPTIVE AND ENERGY-AUTONOMOUS MATERIALS SYSTEMS

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www.livmats.uni-freiburg.de

The Cluster of Excellence "Living, Adaptive, and Energy-autonomous Materials Systems" (*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 within the framework of *liv*MatS. The cluster receives funding from the German Research Foundation (DFG) under Germany's Excellency Strategy – EXC-2193/1 39051807 since January 2019.

Goal of the Cluster is that bioinspired materials, efficient energy materials systems (harvesting, conversion and storage), and interactive, self-repairing materials with different and often even contradictory properties and functional conditions all meet to form 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. These challenging topics 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 the closely interconnected Research Areas in *liv*MatS (A – Energy Autonomy, B – Adaptivity, C – Sustainability, D – Sustainability and Societal Implications). © *liv*MatS / Daniel Hellweg.

Research area A – Energy Autonomy studies novel methods of energy harvesting and/or energy storage within a single highly integrated system, i.e. aims for the development of materials systems with embedded energy and energy management. Light, temperature differences, and vibrations are used 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 har-

vested from the environment. The goal of research in area B 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 and “self-control” of complex materials systems, drawing inspiration from living nature, particularly plant life, i.e. aims for the development of materials systems with embedded intelligence. 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 the materials systems developed in *liv*MatS. One example are “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 application 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 external energy supply – 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. Shared Lab A provides equipment for synthesis, modification and processing (2D and 3D) of energy materials as well as advanced photo-, electrochemical and microscopic characterization. Shared Lab B focuses on Microscopy, Spectroscopy and Rheology, with additional equipment for wet lab chemistry and sample preparation. Shared lab C provides additional options for microscopy and imaging but has its main focus on materials testing from macro- to microscale, 3D printing and sample preparation. The Shared Labs were officially inaugurated with a Lab Warming Party on October 20th 2020, after a continuous build-up period of 1 ½ years.

Since 2019, the Cluster has implemented a total of 21 projects within and across its four Research Areas and the Demonstrator Area. Projects within the Cluster are collaborative, combining the expertise of several PIs, RIs, Postdocs and PhD researchers and also include master candidates in the framework of science based learning. A third call for projects will be published in fall 2021. Over the past two years, the Cluster has been able to recruit excellent early career researchers for these projects.

Currently, a total of 105 researchers at all levels from young doctoral researchers to experienced principal investigators are working in projects directly funded by the Cluster or associated to it. In addition to the 58 PhD and Postdoc researchers working in these projects (some of them currently joining), 14 PhD researchers and 2 Postdocs have contributed to *liv*MatS research in short impulse projects running from September 2020 to December 2020. In 2020, the Cluster has also hired two Junior Research Group Leaders within the *liv*MatS Junior Research Group Program and one Junior Research Group Leader within the Agnes Pockels Junior Research Group Program in a highly competitive selection process including leading international reviewers. Junior Research Groups are funded for five years. These excellent young groups add to the Cluster's research profile and provide attractive career opportunities and early academic independence.

A special building block of the Cluster's early career advancement objectives includes a Doctoral Fellowship program, where candidates are invited to apply with a project pitch and chose a PI within the Cluster to work with. Within the Doctoral Fellowship Program, the Cluster has hired an equal number of male and female researchers in its Hermann Staudinger Doctoral Fellowship Program and its Agnes Pockels Doctoral Fellowship program, and is thus combining its objectives in early career advancement and gender equality. To further promote writing and presentation skills of early career researchers the Cluster hired a Writer's Studio Trainer in autumn 2020.

Given the pandemic-related constraints in 2020, *liv*MatS has made a major effort to promote scientific exchange and interaction with the public in virtual formats.

This also affected the cluster's first international conference from 28th – 30th July 2020, which was switched to a virtual format – with great success. More than 120 participants attended the individual sessions of the "Living Machines. 9th International Conference on Biomimetic and Biohybrid Systems". 12 lectures and 29 posters dealt with topics from biomimetics, robotics, neuro- and material science as well as architecture. Workshops and plenary lectures completed the program.

The cluster was also able to promote the expansion of the "Convergence Center for Living Multifunctional Material Systems" (LiMC^2) founded in 2019 in several webinars. Researchers from the two sites united in the Center, the Penn State University and the University of Freiburg, exchanged views on the key questions of their research in these webinars. The goal was to identify challenges, sharpen the focus for joint activities and thus provide the Center with a guideline for transnational research in the coming years.

In 2020, internal exchange in *liv*MatS was again of central importance. The regularly held *liv*MatS Colloquium contributed to this. As an online format, it offered all *liv*MatS members the opportunity to discuss current developments in their field with renowned international researchers, with the Colloquium covering a wide range of disciplines. Another component of knowledge dissemination within *liv*MatS was a Boot Camp and Fall School for PhD and Postdoc researchers. The Boot Camp from 15th – 16th January 2020 covered overarching soft-skill topics such as good scientific practice, scientific writing, and diversity in research whereas the Fall School from 16th – 17th November 2020 addressed hard science topics such as simulation, surface analysis techniques, 3D printing, and sustainability aspects in additive manufacturing. All *liv*MatS members came together for the first Scientific Advisory Board meeting on November 18th 2020 and the cluster's annual retreat from 19th – 20th November 2020 and discussed challenges, interfaces, and goals of collaborative research. The cluster also received input and support for its further development from the members of its Scientific Advisory Board.

To support the next generation of young scientists, the cluster implemented the Master Lab Program in summer 2020. In the winter semester 2020/21, the next group of Master students will work independently on research ideas in the fields of chemistry, microsystems technology, sustainable materials, philosophy and psychology under the supervision of a researcher from the cluster. This second round of the *liv*MatS Master Lab started with a kick-

off event, where the students presented their projects and gained insights into the interdisciplinary research of the cluster.

As an outreach measure of the cluster, *liv*MatS participated in this year's digital "Science Days". As Germany's oldest science festival, the Science Days annually present hands-on activities and workshops for children, young people and adults. In an experiment and a series of videos offered by *liv*MatS, children were invited to understand how the scales of pine cones react to moisture and why scientists want to understand the mechanism behind it.

The interdisciplinary team of spokespersons of *liv*MatS 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).

IPROM—Interactive and Programmable Materials

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Project Funding: Carl Zeiss Foundation

www.fit.uni-freiburg.de/iprom

One of the core principles in the design of technical objects is the static nature of the materials: They have more or less unchangeable properties. In nature, on the other hand, the (bio-)materials used by living systems are geared towards enabling the best possible adaptation to the respective environmental conditions in order to be best react to changes in the surrounding. The aim of the Research Cluster "Interactive and Programmable Materials (IPROM)" funded by the Carl Zeiss Foundation is the development of innovative technical materials that respond to changing environmental conditions with a response, which is preprogrammed into the material and thus triggers a material adaptation to changes in the surrounding and the load conditions. In order to do so, they have to be able to change their internal structure and/or their external shape as a consequence of an external stimulus, e.g. by adapting the adhesion, wettability or mechanical properties of the materials. This concept opens up new opportunities for the production of complex objects in many areas such as optics, medical technology or architecture.

Fig. 1: IPROM – Interactive and Programmable Materials (www.fit.uni-freiburg.de/iprom)

“The IPROM cluster will bring forth a paradigm shift in materials research from static to dynamic materials. The novel materials generated will dynamically adapt their properties to the constantly changing conditions of their environment in a previously programmed manner.”

IPROM projects include the following topics:

TP 1: Bio-inspired programmable material systems (PI: Thomas Speck)
TP 2: Multiparameter / Multimaterial 4D Printing (PI: Bastian E. Rapp)
TP 3: Light-responsive surfaces (PIs: Jürgen Rühe & Bastian E. Rapp)
TP 4: Nonlinear micromechanics of programmable materials (PIs: Christoph Eberl & Lars Pastewka)
TP 5: Sustainable materials for 4D printing (PI: Dorothea Helmer)
TP 6: Programmable Tribology (PIs: Jürgen Rühe & Lars Pastewka)
TP 7: Biocompatible, programmable materials for soft micro-robots (PI: Karen Lienkamp)

TP 8: Bioelectroactive Interfaces for dynamic interaction with biology (PI: Maria Asplund)
TP 9: Autonomous and reconfigurable metamaterials and soft robots (PI: Andreas Walther)
TP 10: Digitized dynamic illumination (PI: Hans Zappe)

PLAMATSU—PLANT-INSPIRED MATERIALS AND SURFACES

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www.plamatsu.eu

Plant-Inspired Materials and Surfaces (PlaMatSu) aimed for creating new functional polymeric materials and surfaces inspired by structure formation and function-property relationships of plant cuticles.

The Innovative Training Network (ITN) "PlaMatSu" was funded by the European Commission's Marie Skłodowska-Curie Actions from 2016 to 2020. In this ITN nine PhD projects were carried out at four leading European universities in the field of bio-inspired materials: Adolphe Merkle Insitute/Université de Fribourg, Switzerland (PIs: Prof. U. Steiner, Prof. C. Weder), University of Freiburg, Germany (PIs: Prof. G. Reiter, Prof. J. Rühe, Prof. T. Speck), University of Cambridge, UK (PIs: Prof. B. Glover, Prof. S. Vignolini) and since summer 2018 University of Strathclyde, Glasgow (PI: Prof. N. Bruns). This academic network of excellence was strengthened by the industrial partners BASF SE (Germany), fischerwerke GmbH & Co. KG (Germany), Dr. Tillwich GmbH Werner Stehr (Germany), E.G.O. (Germany), L'Oréal (France) as well as by the communication partners VDI - The Association of German Engineers and Wikimedia CH.

Fig. 1: PlaMatSu – I Plant-inspired materials and surfaces (www.plamatsu.eu)

PlaMatSu brought together distinguished plant biologists, polymer chemists and soft matter physicists to study the development, morphology and properties of multifunctional plant cuticles on a fundamental level with the aim to create novel materials and surfaces based on the working principles of cuticles. This external layer of bio-polymers and wax protects leaves and flowers and serves many functions for the plant. It can, for example, use its pores to adjust water permeability and thus regulate water evaporation, the absorption of carbon dioxide, and the release of oxygen. Moreover, its complex surface structure is responsible for a number of other functions determined at the micrometer and sub-micrometer level, such as self-cleaning, the formation of structural color and the regulation of insect-adhesion. Understanding the formation of these surfaces lead to the development of functional materials such as structurally colored surfaces, surfaces with tailored wetting properties for lubrication, materials that can repel insects or membranes that can control moisture permeability.

One Freiburg PhD-project, carried out by V. A. Surapaneni (supervisors: Prof. T. Speck & Dr. M. Thielen) dealt with physics and mechanics of plant Surfaces with cuticular folds and other microstructures. This PhD-project aimed at understanding ontogenetic variations in plant leaf surfaces having wrinkled cuticles and at quantifying corresponding changes in their functional properties like promotion or prevention of insect adhesion and water contact angle. In the second Freiburg PhD-project Ha-Neul Chae (supervisor Prof. J. Rühe) worked on hairy surfaces and aimed at a transfer from plants to novel technical materials. The third

Freiburg PhD-project, carried out by Konstantinos Roumpos (supervisor: Prof. G. Reiter), concentrated on the development of plant-inspired surface patterns by tuning hierarchical topographical and chemical patterns in thin polymer films.

GROWBOT—TOWARDS A NEW GENERATION OF PLANT-INSPIRED GROWING ARTEFACTS

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www.growbot.eu

GrowBot proposes a disruptively new paradigm of movement in robotics inspired by the moving-by-growing abilities of climbing plants.

Fig. 1: GrowBot - Towards a new generation of plant-inspired growing artefacts (www.growbot.eu)

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 greatly, on a different time scale, purposively, effectively and efficiently. To move from one point to another, plants must grow and continuously adapt their body to the external environmental conditions. This continuous growth is particularly evident in climbing plants.

Fig. 2: The three Freiburg GrowBot researchers in the greenhouse of the Botanic Garden of the University of Freiburg studying a searcher twig. © University of Freiburg, Photo: Klaus Polkowski

By imitating them, the GrowBot objective is to develop low-mass and low-volume robots capable of anchoring themselves, negotiating voids, and more generally climbing, where current climbing robots based on wheels, legs, or rails would get stuck or fall. Specifically, the ability to grow will be translated by additive manufacturing processes inside the robot, which creates its body by depositing new materials with multi-functional properties, on the basis of the perceived external stimuli (without a pre-defined design). Perception and behaviour will be based on the adaptive strategies that allow climbing plants to explore the environment. GrowBot is based on a strongly interdisciplinary character and can open the way for a new technological paradigm around the concept of growing robots, fostering a European innovation eco-system for several high-tech sectors [1].

The Plant Biomechanics Group Freiburg will contribute to this task based on their long experience on eco-biomechanics, stem structure and mechanics of climbing plants and on the various attachment systems existing in climbing plants. The main focus will be on elucidating the form-structure-function relationship of (1) the tendrils of various passion flower species (*Passiflora* spp.) - especially with regard to the force they are able to generate while spiralising - and (2) on searcher shoots of selected plant species. Of particular interest with the latter is the fact that they intertwine to form long, cantilevered structures [2].

Fig. 3: GrowBot Kick-off meeting in Pisa © IIT-CMBR

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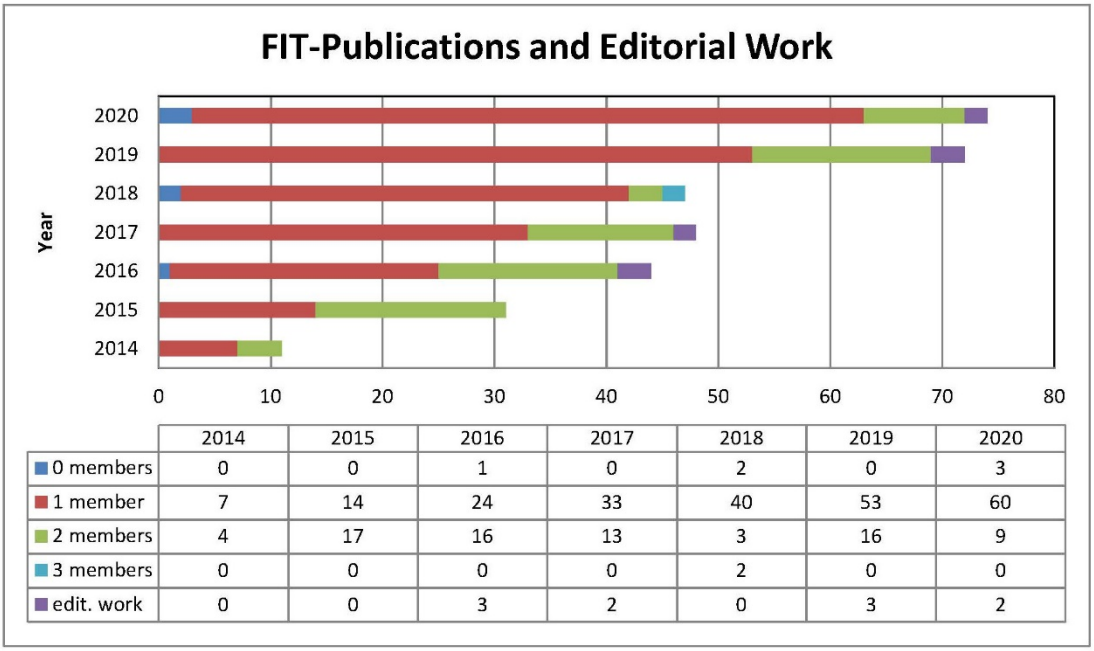

	2014	2015	2016	2017	2018	2019	2020
0 members	0	0	1	0	2	0	3
1 member	7	14	24	33	40	53	60
2 members	4	17	16	13	3	16	9
3 members	0	0	0	0	2	0	0
edit. work	0	0	3	2	0	3	2

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Hofmann, Mara: Host-parasite interaction of European mistletoe—An anatomical, morphological and biomechanical study. — Master thesis, University of Freiburg; supervisors: Speck O, Mylo, M, Speck T; completed on: 24.11.2020.

Kimme, Luca: *Handlungstheorie und Moralphilosophie bei Nietzsche*. — Master thesis, University of Freiburg; supervisor: Hühn L; completed in 2020.

Koloczek, Niklas: *Förderung der Benutzerfreundlichkeit für die Methode „Cognitive-Affective-Mapping".* — Master thesis. University of Freiburg; supervisors: Kiesel A, Reuter L; completed on: 04.08.2020

Mathorne, William: *Reflexion und Versöhnung*. — Master thesis, University of Freiburg; supervisor: Hühn L; completed in 2020.

May, Moritz: *Marx. Die Kritik der bürgerlichen Gesellschaft*. — Bachelor thesis, University of Freiburg; supervisor: Hühn L; completed in 2020.

Modert, Michelle: *Free coiling in climbing plants—examination of form-structure-function relationship with special focus on the Passifora genus*. — Master thesis, University of Freiburg; supervisors: Thielen M, Klimm F, Speck T; completed on: 11.11.2020.

Ricken, David: *A step towards sustainable development: predicting the acceptance of life-like materials systems with cognitive-affective mapping.* — Master thesis. University of Freiburg; supervisors: Kiesel A, Reuter L; completed on: 04.08.2020

Riechert, Laura: Charakterisierung von geometrischen Aktorsystemen für eine bionische künstliche Venusfliegenfalle. — Bachelor thesis, University of Freiburg; supervisors: Tauber F (né Esser), Speck T; completed on: 01.09.2020.

Teichmann, Joscha: *Charakterisierung von formgedächtnislegierungs- und hydrogelbasierten Aktuatoren für bionische Demonstratoren von künstlichen Venusfliegenfallen.* — Bachelor thesis, Westfälische Hochschule Bocholt, supervisor: Beismann H; University of Freiburg; supervisors: Jentzsch M, Speck T; completed on: 21.09.2020.

Umlas, Franziska: *Quasistatische Charakterisierung der Querkontraktionszahl der Schale von Citrus limon 'Verna' und Citrus mediva 'Nasone'.* — Bachelor thesis, University of Freiburg; supervisors: Jentzsch M, Speck T; completed on: 18.09.2020.

AWARDS

The International Society for Bionic Engineering (ISBE) has granted Prof. Dr. Thomas Speck the honorary title of an Excellent Member for his academic achievements on bionic engineering and contributions to the International Society for Bionic Engineering. (https://www.livmats.uni-freiburg.de/en/news-press/thomas-speck-elected-excellent-member-of-the-isbe)

Dr. Philipp Höfele received the "MTZ-Preis für Bioethik" ("MTZ Award for Bioethics") (https://www.livmats.uni-freiburg.de/en/news-press/scientific-achievements-social-responsibility).

Dr. Falk Tauber (né Esser) has won second place in the International Bionic Award 2020, which is awarded by the Schauenburg Foundation and the Association of German Engineers (VDI). (https://www.livmats.uni-freiburg.de/en/news-press/the-human-esophagus-as-a-model)

Prof. Dr. Ingo Krossing was elected a new member of the National Academy of Sciences Leopoldina in recognition of his scientific achievements. (https://www.livmats.uni-freiburg.de/en/news-press/krossing-elected-member-leopoldina)

Dr. Linnea Hesse has been selected this year to receive funding for her post-doctoral qualifications from the "Margarete von Wrangell Habilitation Programme for Women". (https://www.livmats.uni-freiburg.de/en/news-press/a-boost-for-post-doctoral-qualification)

A research team led by Prof. Dr. Peter Woias, microsystems engineer and member of the cluster of excellence livMatS at the University of Freiburg, and the physicist Prof. Dr. Saskia F. Fischer from the Humboldt University of Berlin have been awarded the Helmholtz Prize 2020 in the "Applications" category. (http://www.fit.uni-freiburg.de/news/helmholtz_2020-en)

Prof. Dr. Rainer Grießhammer was awarded the Cross of Merit of the Federal Republic of Germany for his outstanding service on behalf of the community, his achievements on behalf of the Federal State, and his voluntary work. (http://www.fit.uni-freiburg.de/news/Griesshammer-Verdienstkreuz-en)

IMPRESSUM

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