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

FIT

Report
2018

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REPORT

2018

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FREIBURG CENTER FOR INTERACTIVE MATERIALS AND BIOINSPIRED TECHNOLOGIES

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FOREWORD

At a time when many developments in global and national politics and in our society have to be viewed with some concern, the view back onto the year 2018 is extremely gratifying for our Freiburg Institute for Interactive Materials and Bioinspired Technologies, the FIT. In 2018 we have initiated numerous new projects and greatly expanded the number of FIT members. In a variety of joint efforts, we have consistently pushed ahead with the development of the FIT idea that began to really pick up speed with the opening of the FIT building about two years ago. In the past year we have started very attractive research projects in many different areas of basic research ranging from energy-autonomous to adaptive systems and bio-inspired new technologies. Many examples of these fascinating projects can be found in this annual report.

2018 was definitively a year in motion. On the one hand, this is seen in the changes in our Board of Directors. Professor Rolf Mülhaupt, the Executive Director of FIT for many years, who has shown tireless commitment to FIT right from the beginning, passed the baton on to me in order to be able to allow himself to spend more time in research again in the coming years. He was a key player starting from the state-wide competition to establish a center dedicated to fundamental materials research in Freiburg, all through the construction work of the building and the start-up phase of the institute. Rolf Mülhaupt deserves our great gratitude for the fact that he has always been committed to the interests of FIT beyond all measure and that he has promoted the FIT idea with great personal commitment. Without him, FIT would not exist in this form. In addition, in a rotational movement, two colleagues, Professor Marie-Pierre Laborie, and Professor Günter Reiter, have resigned from the FIT Executive Board and have been replaced by Profs. Andreas Walther and Jürgen Rühe. We are also grateful for Marie-Pierre's and Günter's commitment.

In addition to these personnel changes in the FIT board and the admission of a total of five members and one associate members, which almost doubled the number of FIT members within one year, a single event kept the FIT on it’s toes: winning the cluster competition in the framework of the Excellence Strategy by the Federal and State Governments. The concept "Living, Adaptive and Energy-autonomous Materials Systems", short *liv*MatS, convinced the expert commission evaluating the proposal and is one of the very few material science clusters selected in Germany. The cluster's vision is to create new materials systems that are energy-autonomous and can adapt to a changing environment. Such systems, inspired by living nature, will harvest the energy from their environment and show complex adaptive behavior – through interactions across all size scales from the molecule to the macroscopic overall structure. This approach brings together the research of six faculties of our university and three non-university institutions and takes a holistic view – from fundamental natural sciences to the engineering system design to the social implications that such new systems will bring along. In the acquisition of the cluster, the groundwork of the State of Baden-Württemberg and the university in building and setting up the FIT has really paid off. The *liv*MatS project will certainly be profile-building for the FIT in the coming years and with the numerous planned scientific events and the establishment of ideasFactory@FIT will give our center numerous new impulses. We are very much looking forward to the results of this visionary research.

We would like express our sincere thanks our staff for all their achievements, also those not explicitly mentioned here. In particular, we would like to thank Dr. Stefanie Meisen and her team, our FIT members, the members of our Scientific Advisory Boards, and various supporters and sponsors, both inside and outside the university.

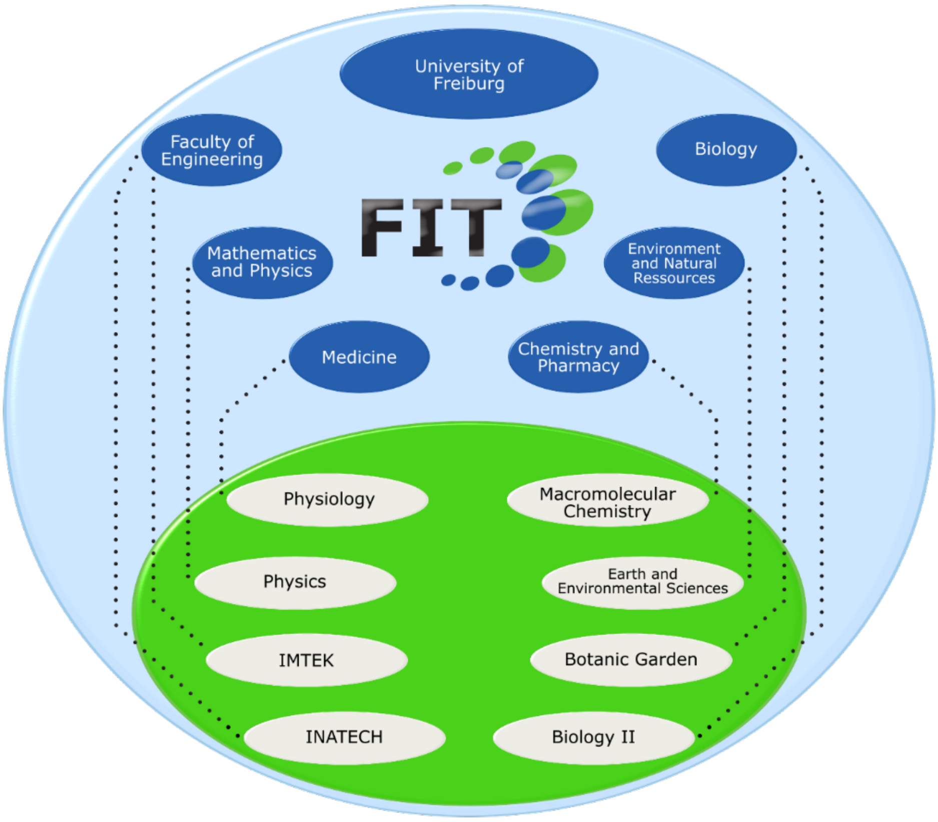
In order to satisfy the growing demand for information from non-German-speaking countries, the annual report is now only available in English, both in printed form and online. I hope you enjoy reading it.

J. Rühe

Jürgen Rühe
(Executive Director FIT)

THE CENTER

STRUCTURE



FUTURE AREAS

- **Adaptive and Active Polymer Materials**
  Development of interactive and intelligent functional materials, foils and surfaces, as well as material-integrated (micro)systems

- **Biomimetic, Biobased and Bioactive Materials Systems**
  Bioinspired and biomimetic construction of materials systems. Development of new active hybrids by integration of synthetic and biological components. Bioactive functionalization of materials and (micro)systems to enable them to interact with proteins, cells and tissues.

- **(Micro)Systems for Energy Conversion, Storage and Energy-autonomy**
  Development of materials and (micro)systems for energy conversion and storage as well as development of energy autonomous embedded (micro)systems using bioinspired approaches

CORE FACILITIES

- **Imaging of Materials Systems**
  Specialized laboratory for microscopy and tomography, establishment of a competence network 3D visualization

- **Functional Processing**
  Manufacturing technique for bioinspired materials with focus on nanolithography, film technology, and generative processes

- **Modelling and Simulation of Materials Systems**
  Concept development, modelling and simulation of interactive materials systems

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 2018, 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 Walter
Faculty of Chemistry and Pharmacy

Prof. Dr. Peter Woias
Faculty of Engineering

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

Dr. Can Dincer
(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 2018, the members included (in alphabetical order):

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

Ludmila Cojocaru, PhD (Faculty of Engineering)

Dr. Can Dincer (Faculty of Engineering)

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

Prof. Dr. Stefan Glunz (Faculty of Engineering)

Dr. Peter Koltay (Faculty of Engineering)

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

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

PD Dr. Karen Lienkamp (Faculty of Engineering)

Dr. Tom Masselter (Faculty of Biology)

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

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

Prof. Dr. Claas Müller (Faculty of Engineering)

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

Prof. Dr. Ralf Reski (Faculty of Biology)

Prof. Dr. Winfried Römer (Faculty of Biology)

Prof. Dr. Jürgen Rühe (Faculty of Engineering)

Dr. Olga Speck (Faculty of Biology)

Prof. Dr. Thomas Speck (Faculty of Biology)

Dr. Simon Thiele (Faculty of Engineering)

Dr. Severin Vierrath (Faculty of Engineering)

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

Prof. Dr. Peter Woias (Faculty of Engineering)

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

ADVISORY BOARD

The 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. In 2018, the following professors belonged to the Advisory Board:

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

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

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

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

Prof. Dr. Christoph Neinhuis (TU Dresden, Germany)

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

Prof. Dr. Thomas Scheibel (University of Bayreuth, Germany)

INTEGRATIVE BOARD 2018

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 2018 the following persons were members of the Integrative Board, with the deans always changing to the winter semester and a new Managing Director being elected in the course of 2018.

Prof. Dr. Rolf Mülhaupt / Prof. Dr. Jürgen Rühe (Managing Director of FIT)

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

Prof. Dr. Tim Freytag (Dean of the Faculty of Environmental and Natural Resources)

Prof. Dr. Bettina Warscheid (Dean of Biology)

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

Prof. Dr. Manfred Jung (Dean of Faculty of Chemistry and Pharmacy)

Prof. Dr. Oliver Paul (Dean of Faculty of Engineering)

Prof. Dr. Kerstin Krieglstein (Dean of Faculty of Medicine)

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

Dr. Bruno Ehmann (Management Freiburg Research Services)

Dr. Stefanie Meisen (Administrative Management of FIT)

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

FIGURES AND FINANCES

Due to the requirements resulting from the non-profit status of the building financed by the BW Foundation and the existing objectives for research in the building, only appropriate projects can be acquired. Nevertheless, we have managed to increase the number of projects compared to the previous year. From 31 projects, 3.0 million euros were made available for research. If we compare this budget with 2017 without including the investments in large-scale equipment, this is an increase of 5 projects and 1.0 million euros. After the basic equipment and the purchases of large equipment had been completed, the budget was solely available for the projects in FIT. 62 % of the funds were spent on personnel, 10 % on material resources and still 29 % on investments in the partly still new laboratories. The FIT has only two budgeted positions: The administrative management with 25 % and an assistant with 100 %.

In 2018, 190 employees, including 27 postdocs, 80 doctoral students, 23 master students and 7 bachelor students, were supervised with this financial basis. All of them were able to take a look beyond the faculties and experience a culture of togetherness at FIT.

The graphs and tables will help to understand the figures a bit better.

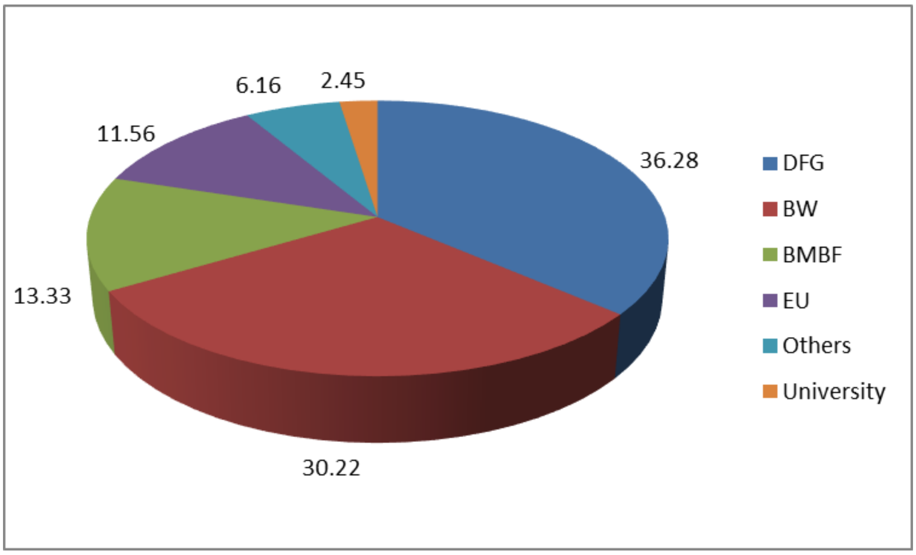


Fig. 1: Percentage share by funding agencies of the total FIT budget in 2018

Tab. 1: Absolute figures in Euro by funding agency from 2015 to 2018

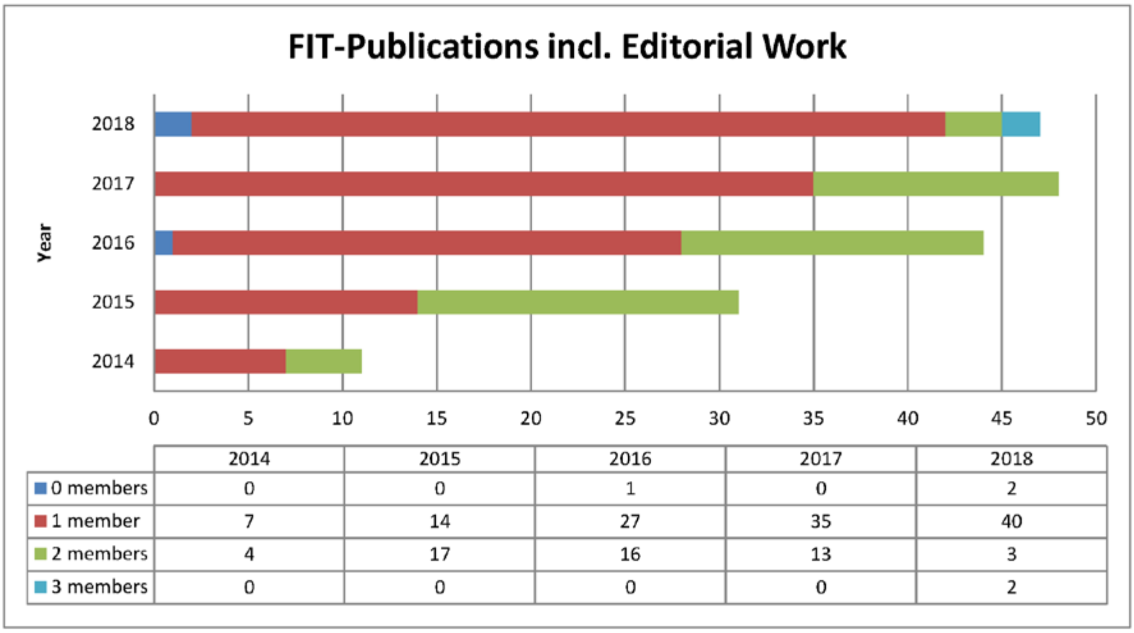
	2015	2016	2017	2018
DFG	714.700	874.430	986.267	1.055.197
BW	1.437.617	2.468.606	4.048.018	928.292
BMBF	0	0	69.121	409.381
EU	470.058	202.420	288.415	355.219
Others	0	0	62.672	189.235
University	0	93.657	75.200	75.200
Total	**2.6222.374**	**3.639.113**	**5.529.693**	**3.012.525**

Tab. 2: Projects and active members in 2018

Project leader	**Project**	**Total (€)**	**Issued in 2018 (€)**
Behrends	IRTG-SoMaS	131.100	93.150
Dincer	DFG-miPAT	300.450	30.727
Fischer	DFG-SPP 1613	155.200	71.540
Glunz	DFG OPoSiT	142.400	69.746
Lienkamp	BMBF –ANTIBUG	1.174.040	82.956
	BMBF-BioMAMPs	316.400	57.334
	EU-ERC-Regenerate	1.498.987	163.277
Masselter	SFB TRR 141 A06	239.300	79.747
Mülhaupt	IRTG-SoMaS	204.925	116.244
Mülhaupt/Behrends/Moseler/Müller	BW-Stiftung BITS	5.295.000	928.292
Reiter	SFB TRR 141 A08	163.365	4.448
	IRTG-SoMaS	3.722.074	186,409
Reski	SFB TRR 141 A09	219.200	70.891
Römer	IRTG-SoMaS	57.600	53.624
	DFG Energetisch	168.155	77.986
Rühe	IRTG-SoMaS	120.000	114.934
	DFG PAK	165.800	18.133
Rühe, Speck, Reiter	EU-Marie Curie	747.649	41.220
Speck, O.	SFB TRR 141 A03	158.900	53.139
Speck, T.	IRTG SoMaS	57.600	10.629
	SFB TRR 141 A02	173.000	57.956
	SFB TRR 141 A04	200.900	92.133
	SFB TRR 141 B01	150.100	25.919
Thiele	BLBT	131.000	80.158
	AvH	67.200	54.238
Walter	DFG Kraftbereich	129.300	52.136
	DFG HYBRIDS	159.850	4.328
Walther	DFG Chemo-mechanisch	355.950	23.341
	ERC Grant	1.499.813	150.722

Tab. 3: Budgets of project groups from 2015 until 2018 in €

Project group	**2015**	**2016**	**2017**	**2018**
Behrends	31.340	20.548	46.054	93.150
Dincer	0	0	0	30.727
Fischer	0	0	0	71.540
Glunz	0	0	18.490	69.746
Lienkamp	470.058	202.420	357.536	665.109
Masselter	73.640	67.780	90.000	79.748
Mülhaupt	92.007	745.017	4.054.850	1.044.537
Reiter	142.233	136.307	194.042	212.350
Reski	0	0	59.990	70.891
Römer	13.303	72.859	100.797	133.308
Rühe	73.585	86.074	93.852	174.286
Speck, O.	44.972	50.992	47.187	53.139
Speck, T.	139.608	158.847	212.547	186.637
Thiele	0	18.457	62.672	134.396
Walter	4.160	38.157	44.047	56.464
Walther	0	0	121.500	174.062



	2014	2015	2016	2017	2018
🟦 0 members	0	0	1	0	2
🟥 1 member	7	14	27	35	40
🟩 2 members	4	17	16	13	3
🟦 3 members	0	0	0	0	2

Fig. 2: FIT-publications incl. editorial work from 2014 until 2018. Detailed information can be found in the chapter “Publications”.

HIGHLIGHTS

ADAPTIVE AND ACTIVE POLYMER MATERIALS

Antimicrobial copolymers made from itaconic acid – teaching an old monomer new tricks

Alexandra Schneider-Chaabane[1,2], Ali Al-Ahmad[3], Karen Lienkamp[1,2]

[1] Polymer Synthesis and Surface Engineering Group, Department of Microsystems Engineering (IMTEK), University of Freiburg; [2] Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT), University of Freiburg; 3 Department of Operative Dentistry and Periodontology, Center for Dental Medicine, University Hospital, University of Freiburg

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

Diseases related to antibiotics-resistant bacteria have been on the rise for the past decades. If current trends continue, infections caused by these bacteria are estimated to become the number one lethal disease worldwide by 2050, with up to 10 million deaths annually.[1] Thus, alternatives for antibiotics are urgently needed. The aim of this project is to develop a new class of antimicrobial polymers with low resistance formation potential based on itaconic acid. These polymers were inspired by natural antimicrobial peptides (AMPs, Figure 1a), a class of facially amphiphilic molecules found in virtually every organism. AMPs selectively kill bacteria but have a very low resistance formation potential.[2] It has been previously shown that their properties can be emulated by oligomers and polymers called synthetic mimics of antimicrobial peptides (SMAMPs, Figure 1b) that are also facially amphiphilic,[3, 4] yet so far SMAMPs have not been successfully applied as drugs or in biomedical materials at the clinical level. Among many reasons for this, synthesis costs and molecular stability play a big role. Thus, this project aims at developing a synthetic platform for itaconic acid-based SMAMPs, which should be accessible in few synthetic steps, and will be optimized for stability under conditions of use.

Itaconic acid is an old, but increasingly interesting monomer because it is cheap and can be produced biotechnologically from renewable resources.[5] Since the homopolymerization of itaconic acid and itaconates is rather slow, these monomers are typically used as comonomers, e.g. with acrylics.[5, 6] To obtain SMAMPs based on itaconic acid, we first synthesized asymmetrically functionalized diitaconates that imitate the facial amphiphilicity of natural AMPs (Figure 1). Starting from itaconic anhydride, these monomers can be obtained in two synthetic steps (Figure 1).[7] As shown by 2D-NMR techniques, when ring-opening itaconic anhydride, the first substituent is introduced exclusively at the carbonyl group in β-position to the double bond. The facially amphiphilic diitaconate monomers were copolymerized with *N,N*-dimethylacrylamide, a bio-inert monomer. The copolymerization parameters of these two monomers indicate that the reaction yields statistical to alternating copolymers. This is of interest when making functional polymers that require a perfectly regular distribution of two functional groups along the backbone, which is required for SMAMPs with well-defined bioactivity profile. The here presented facially amphiphilic diitaconate copolymers showed promising antimicrobial activity and could be useful as antimicrobial agents with low resistance development potential [7] – thus demonstrating that it is never too late to teach an old monomer class new tricks.

Within the BioSMAMPs project, the next steps will be to replace the itaconate ester groups by amide groups to improve the hydrolytic stability of the polymers, and to surface-immobilize them so that simultaneously antimicrobial, protein-repellent and cell-compatible polymer surfaces are obtained.

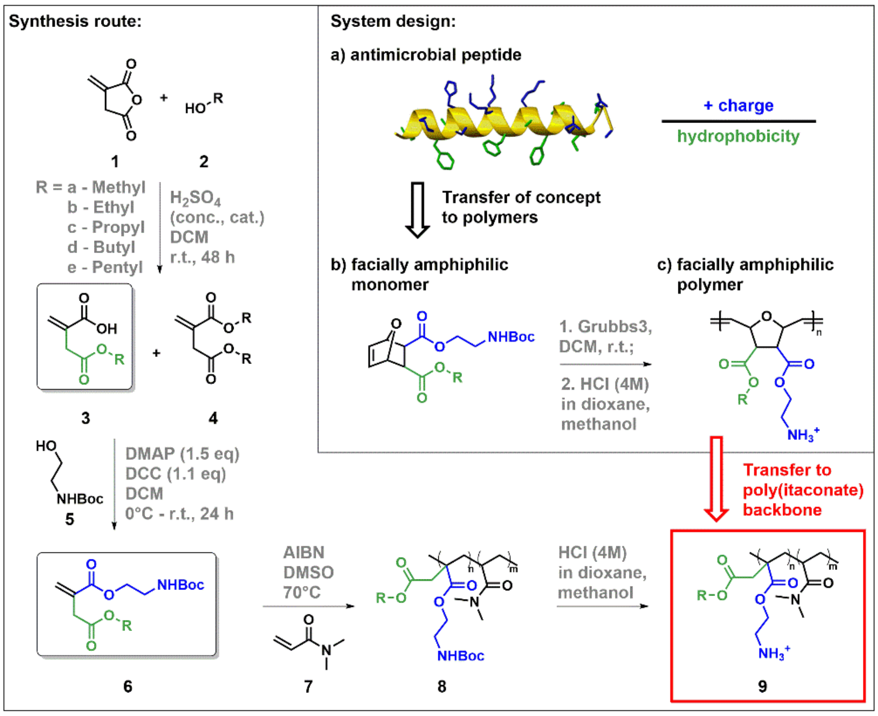


Fig. 1. System Design and Synthesis: a) The natural antimicrobial peptide (AMP) magainin illustrates the blueprint of AMPs: they are facially amphiphilic, with hydrophobic groups (green) on one side and cationic, hydrophilic groups (blue) on the other side of the molecule. This enables selective interaction with the negative cell envelope of bacteria. b) Facially amphiphilic polymers like functional poly(oxanorbornenes) (SMAMPs) can emulate the bioactivity of AMPs. By translating this concept to poly(itaconic acid derivatives), SMAMPs with enhanced stability should be obtained. © 2018, John Wiley and Sons. Reproduced with permission.

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Towards medical products with simultaneous antimicrobial activity, protein-repellency and cell-compatibility

Esther K. Riga[1,2], Vera Bleicher[1,2], Stefan Paschke[1,2], Alice Eickenscheidt[1,2], and Karen Lienkamp[1,2]

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

Project funding: Federal Ministry of Education and Research (BMBF), Fördermaßnahme "Validierung des technologischen und gesellschaftlichen Innovationspotenzials wissenschaftlicher Forschung – VIP+", Project acronym: AntiBug

Bacterial biofilms on medical devices can cause severe infections that may end lethally. In addition to the patients' suffering involved, this causes enormous additional heathcare costs. Thus, materials that reduce the spreading of resistant bacteria and biofilm formation on medical materials and are urgently needed. We have previously reported a number of bioinspired polymeric materials that were designed to prevent the proliferation of bacteria. Among these were antimicrobial, polycationic synthetic mimics of antimicrobial peptides (SMAMPs),[1, 2] protein-repellent and antimicrobial polyzwitterions,[3, 4] and materials made from combinations of protein-repellent and antimicrobial components.[5-7] While we demonstrated for each of these materials that they can effectively kill bacteria when immobilized on model surfaces, none of them was so far shown to be stable and effective under actual conditions of use that would be expected in practical applications, for example a urinary catheter or a wound dressing.

The aim of this project is to close this "technology validation gap" for our recently reported simultaneously antimicrobial, protein-repellent and cell-compatible poly(oxanorbornene)-based polyzwitterion (PZI).[3, 4] This material could be a promising candidate for many medical applications due to its multifunctionality and because it can be surface-attached to many medically relevant materials (other polymers, metals, ceramics) in a simple process. We have already demonstrated that PZI coatings significantly reduce the formation of bacterial biofilms in vitro.[3] In the AntiBug project, we looked more closely at the stability of PZI under conditions used for storage, long-term use and sterilizing of medical devices. Inertness under these conditions is prerequisite for any medical application. The current data shows that PZI can be stored for several weeks without loss of activity, however the stability in solution is compromised within a few days if the pH is higher than 5.5. The compound could also be sterilized with ethylene oxide, after which it had 98% of the antimicrobial activity of freshly prepared PZI reference surfaces. Chemical analysis indicates that the activity loss is related to intramolecular amide formation. To avoid this, other structures with less sensitive functional groups are currently investigated.

References:

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Progress in self-shedding polymer surfaces

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

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

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

As reported in previous FIT-Reports,[1] the aim of the REGENERATE project is to design systems consisting of discrete, sufficiently thick functional polymer layers assembled into polymer multilayer stacks which can (self-)regenerate (Figure 1). When such a material sheds its top layer upon damage or contamination, the original surface activity is regenerated. Antimicrobial activity is one example of an activity that could thus be regenerated; another one is the activity of an electrochemical sensor. In advanced systems, the shedding process should be autonomously or triggered by an external stimulus.

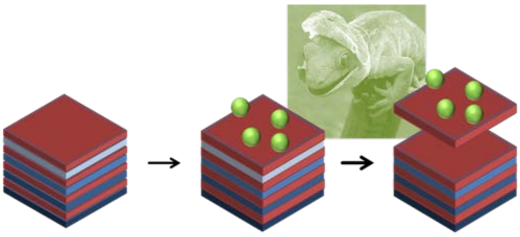

Fig. 1: Project concept. The target material is a polymer layer multi-stack consisting of alternating degradable and functional (e.g. antimicrobial) layers. Like a reptile shedding its skin, the top antimicrobial layer (red) can be removed when it is contaminated. This is possible by degradation of the polymer layer underneath (light blue). The shedding event removes the contamination and reveals a fresh functional polymer layer underneath. (© Karen Lienkamp)

So far, we have realized four different polymer multilayer designs for the regeneration of antimicrobial surfaces by layer shedding. These multilayer architectures consisted of 100-200 nm thick, discrete polymer layers. They were made from poly(guanidinium oxanorbornene) networks as the antimicrobial component, and different interlayers made from degradable poly(adipic anhydrides), depolymerizable poly(ethyl glyoxylate) (PEtG), or water-soluble poly(acrylamide). In each case, the multilayer fabrication and disassembly was monitored by fluorescence microscopy, ellipsometry FT-IR spectroscopy and atomic force microscopy. By testing the antimicrobial activity of the restored surfaces, their functional integrity after layer shedding was confirmed.

In the case of the polyanhydrides, shedding was initiated by anhydride hydrolysis. This however only worked under strongly acidic conditions because of undesired side reactions between the layers when slowly degrading the system under physiological conditions. Using PEtG, the shedding process could be triggered by UV irradiation. The resulting depolymerization was fast, and neutral depolymerization products were released. The freshly revealed antimicrobial surface was antimicrobially active, indicating full removal of the PEtG layer. Finally, by exploiting the solubility of poly(acrylamide), a material which could regenerate its surface activity twice was realized.

When disassembling a polymer multilayer stack made from discrete layers, one has to consider how to break the adhesive forces between these layers. With the above described model systems, we are just beginning to understand the factors required to achieve this process.

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Interaction of a 3arm star-shaped poly(ethylene glycol) with two biological nanopores

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Poly(ethylene glycol) (PEG) is an amphiphilic polymer with low toxicity and a broad variety of uses from industrial applications to biomedical drug delivery systems.[1,2] This polymer is known to enter and interact with protein nanopores.[3] Early studies by Krasilnikov and colleagues [4-6] showed that partitioning of PEG into the alpha-hemolysin (aHL) protein pore - as detected by the concomitant reduction in pore conductance- is a steep function of molecular weight. This effect was, in fact, used to infer pore size and geometry, all the while assuming that interaction of polymer with the pore interior was negligible at low ionic strength (100 mM salt). However, in a more concentrated ionic environment (1 M salt), clear evidence was found that PEG molecules can interact with the pore [7] (but see [8]) and at near-saturating salt concentration (4 M), individual events of binding in the pore were detected as clearly resolvable pulse-shaped reductions in pore conductance (resistive pulses).[9] It was also shown, in that work, that in a mass range 800 to 3500 g/mol the mean depth of block as well as the mean duration of resistive pulses increased with the number average molecular weight of the polydisperse PEG preparations used. Subsequently, the groups of Kasianowicz and Krasilnikov jointly demonstrated that collecting the averaged residual current during a large number of individual resistive pulses into a histogram resulted in a multimodal distribution, in which every maximum corresponds to one molecular species of specific chain length in a polydisperse mixture, thus in essence realizing single-molecule size spectrometry with monomer resolution.[10] It was then also shown that this interaction strongly depended on the ionic conditions as well as on the driving potential applied.[11] Since then, these findings have been reproduced with remarkable agreement of results from recordings in different labs.[12-15] While all of the above results were achieved with the aHL pore, it was recently found that another bacterial pore forming toxin, aerolysin (AeL), showed even stronger interaction with PEG with correspondingly enhanced resolution, albeit, interestingly, with a maximum sensitivity at a very different driving force (-120 mV *trans*-side) compared to aHL (+40 mV *trans*-side).[16]

While a numerical model has been formulated that reproduces important aspects of the apparent sensitivity of this polymer-pore interaction to the degree of polymerization (d.p.) [17,18], a full physical explanation of the exquisite dependence of the residual pore current on d.p. of the blocking polymer is still lacking. In particular, it is still not clear which molecular properties, i.e. mass itself, physical length of the chain, monomer number, cross-sectional area, hydrodynamic volume or particular – e.g. helical – conformations, density or hydrophobicity are dominant or at least important in determining the depth of block or the dwell time of resistive pulses. In order to obtain more insight into the relative importance of molecular shape vs. monomer number, we decided to study a possible interaction of star-shaped PEGs with aHL and AL pores. Star polymers comprise at least three polymer chains/arms joined together by a central core and star-shaped variants of PEG are of considerable interest in biomedicine and pharmacy.[19,20] Because of the centrally linked arms, a star-shaped polymer is conformationally more restricted than a linear one of the same degree of polymerization. Early theoretical work suggests that a p-armed branched polymer has a mean radius of gyration or hydrodynamic radius that is lower by a factor of $p^2/(3p-2)$ with respect to a linear polymer of the same mass [21] and this prediction was borne out by measurement.[22]. If, therefore, the radius of gyration (or the hydrodynamic radius) or, indeed, the ability of the polymer to assume some well-defined conformational state were important for determining the depth of block or the dwell time of the interaction, one would predict that for stars these values would be strongly different from the corresponding values of a linear PEG of the same mass. We, therefore, conducted high-resolution voltage clamp measurements to compare the interaction of 3-arm PEG oligomers of 1 kDa and linear PEG of the same average mass with two types of biological nanopores, aHL and AeL. Our results show that the star-shape does not preclude interaction and size discrimination which therefore does not appear to require a particular ordered conformation of the polymer. Also, despite some uncertainty regarding the estimation of the true molecular mass distribution of the 3-arm PEG sample, the depth of bock as a function of d.p. is very similar for both polymers, suggesting that hydrodynamic volume of the random coil is not a dominant factor in determining the resistance of the blocked pore.

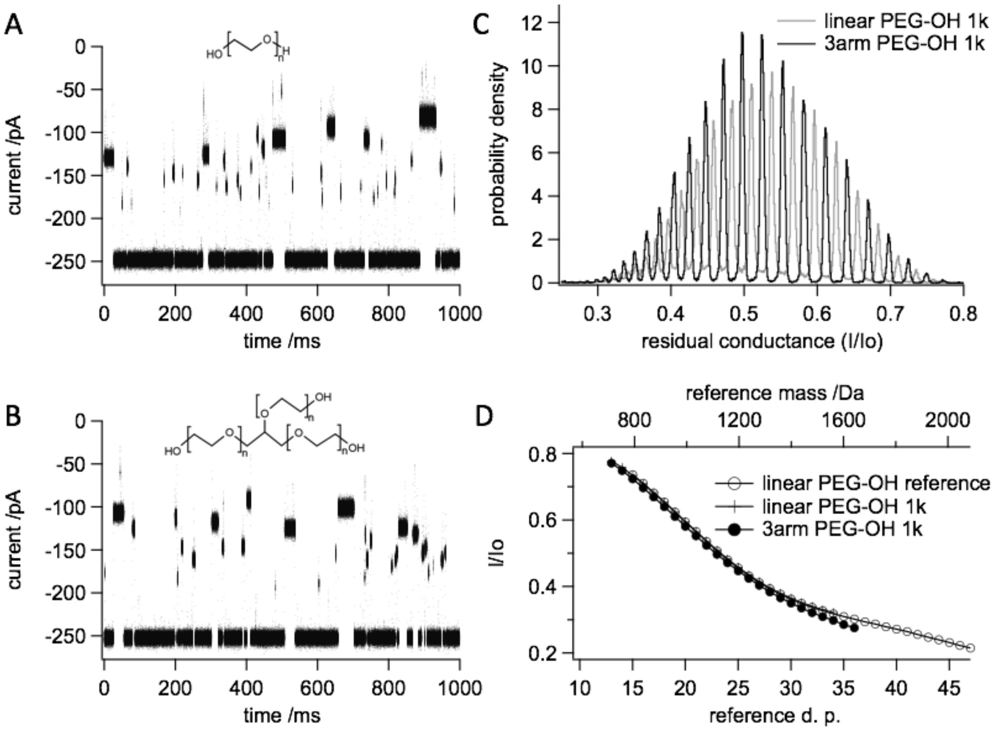

Fig. 1: Interaction of 3-arm (A1,2) and linear (B1,2) PEG-OH 1k with the aerolysin pore. A, B: current versus time traces (1 s duration). C: Superimposed histograms (averages of 4 and 3 experiments, respectively, of I/Io for 3 arm (black) and linear PEG-OH 1k (grey). D: Plot of calibrated reference values of I/Io-maxima for linear PEG of d.p. 15-47 with aligned values for maxima obtained from B vs. reference degree of polymerization (d.p.) and mass resulting in the assignment of d.p. 13-32 to the species producing the maxima for PEG-OH 1k and of d.p. 13-36 for 3arm PEG-OH.

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Lubrication of surfaces covered by surface-attached hydrogel layers

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Synovial joints serve as an attractive inspiration for the generation of low wear surfaces as they exhibit low friction under quite strongly varying load conditions and can undergo millions of loading cycles during a human lifespan without failure [1]. The impressive frictional properties are due an intricate interplay between the cartilage forming the joint and the synovial fluid between the sliding surfaces. The synovial fluid is a thixotropic fluid that facilitates a uniform distribution of the applied pressure [1,2]. Articular cartilage is a highly specialized tissue, which is attached to the bone underneath. It is composed essentially of a dense extracellular matrix and has a high water content.

Hydrogels show some resemblance to the articular cartilage as they constitute also of a polymer matrix with a high water content. Covalent binding of hydrogels to a solid substrate provides layers, which are stable against both compression and shearing. One of the most important properties of surface-attached hydrogels is their anisotropic swelling which is due to the fact that such layers can extend only in one direction (ie. away from the surface). This stretching of the polymer (sub-)chains away from the surfaces influences the properties of the polymer networks in respect to their mechanical properties and often such surface architectures can no longer be penetrated by other large molecules either through entropic shielding or size exclusion [3,4]. This feature renders surface attached polymer hydrogels rather biocompatible [4,5] and makes them interesting candidates for low friction surfaces [3-8].

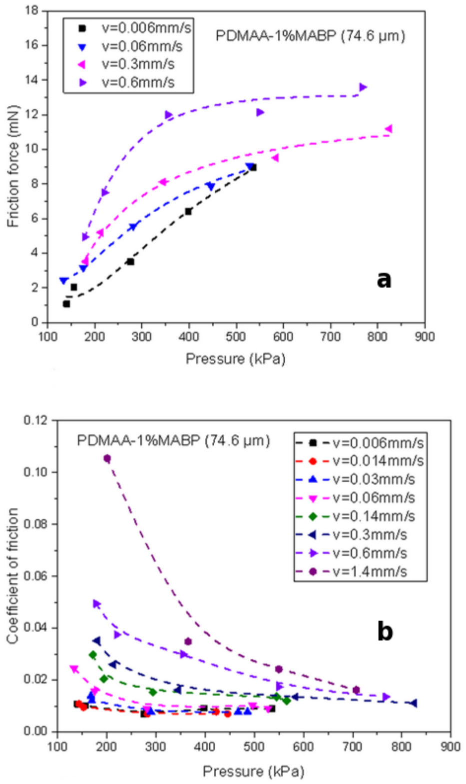

Fig. 1: a) Friction force versus pressure b) Coefficient of friction as a function of applied pressure at different sliding speeds for a sample with wet thickness of 74.6 µm. © Chemistry and Physics of Interfaces, IMTEK, Uni Freiburg.

We now examined the friction properties of surface-attached hydrogel layers coated onto two sliding surfaces in contact with water. We have found a very rich behavior as the friction coefficient was studied as a function of parameters like the sliding speed and the normal force. As an example the friction force and the coefficient of friction are plotted as a function of the pressure between a sliding hydrogel coated cylinder and a flat hydrogel layer. Quite against intuition the coefficient of friction decrease quite strongly to very small values for most sliding speeds as the pressure increases (Figure 1).

Based on a comprehensive study of such parameters we have developed a model to describe these fundamentally interesting friction phenomena. As two hydrogel-coated surfaces slide against each other, one needs to consider several different forces that influence the friction force (Fig. 2). The adhesion forces (F_A) originate from van der Waals forces and entanglement of polymer chains with chains contained in the opposite surface layer. Adhesion dominates the frictional properties only when the applied load and penetration depth are very small. Polymer deformation force (F_p): This component is a function of the penetration depth and assumed to be independent of the sliding and thus compression velocity. This contribution is determined by the difference between the osmotic pressure and the applied pressure. It is (as well as the penetration depth) influenced by the (apparent) elastic modulus which itself depends on the confinement and crosslinker density. Drag force (F_D): The water displacement induces a force that resists sliding. With increasing sliding speed the resistance of water to flow will become stronger. The resistive force depends on the geometry of the slider, the penetration depth and the viscosity of the water inside of the hydrogel.

In our experiments, it was shown that the adhesion between the sliding surfaces is very small and cannot contribute much to the friction behavior so that at low normal load and low sliding speed, extremely small adhesion between the hydrogel-coated surfaces is observed. This is due to fact that the surface-attached hydrogel layers cannot interpenetrate each other and two strongly hydrated layers show only rather weak attractive interactions. Consequently, the force to separate the two surfaces required for sliding and accordingly the friction is extremely low.

Thus, the polymer deformation and drag forces are the main components of the friction force in sliding experiments at higher loads and higher velocities. Therefore, the two main factors that govern the friction force are volume of the zone affected by the indentation and the sliding speed. The very thin polymer layer becomes almost incompressible at high applied pressures so that the friction force assumes an almost constant value. As a consequence, the COF decreases with increasing the normal load and becomes independent of the sliding speed.

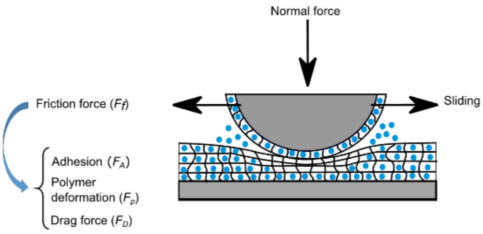

Fig. 2: Influential forces on friction during sliding of the hydrogel coated slider on a surface-attached hydrogel. © Chemistry and Physics of Interfaces, IMTEK, Uni Freiburg.

When looking at higher sliding speeds we need to consider the rate of polymer network compression or in other words the water displacement. The flow of water through the swollen hydrogel, which on a molecular scale resembles a rather concentrated (i.e. 20%) polymer solution, causes a drag force F_D. As the Reynolds number for the system in this regime is extremely small, the drag force will depend on the apparent viscosity of the water inside of the gel and on the volume of water which needs to be displaced, which is hidden in the form factor c. The drag force depends strongly on the sliding velocity. The force induced by water displacement at low speeds (ie. low Reynolds numbers), is proportional to the velocity, however, when the velocity is high, the drag force becomes nonlinearly dependent on the sliding speed.

Two surfaces covered with identical surface-attached hydrogel layers in the presence of water show a rich friction behavior as a function of the applied load and the sliding speed. To describe the frictional properties of surface-attached hydrogels, two parameters must be considered: the adhesion between the sliding layers and the drag induced by the compression of the gel through the applied normal force under sliding conditions, which depends on the amount of water to be displaced during shearing and the rate of the displacement. As surface-attached hydrogel are almost impenetrable for other polymer chains, the adhesion between the strongly water-swollen layers is extremely low and superlubricious behavior is observed at very low normal forces. When a strong force is applied and the film is strongly sheared, the gels become compressed. The extent of the compression determines how much water is displaced and determines the drag force stemming from the flow during squeezing out of the water. The limited compressibility of the layers leads to a strong reduction of the coefficient of friction with increasing force so that coefficients of friction of < 0.01 are observed even at rather high loads. In follow-up experiments we will study the influence of layer confinement and of the water viscosity inside of the gel onto the frictional properties of such surface-attached hydrogel layers and compare them to those of free gels.

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Thermo-responsive micelle-inspired polymeric ionic liquids as molecular shuttles and thermally switchable nanostructures

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Micelles and micelle-like nanostructures are the basis of innumerable biological processes and functions. For example, micellar lipid structures enable storage and transport of molecules and provide compartments for essential biochemical reactions [1,2]. Therefore, one objective of bio-inspired research consists in the design of sophisticated micellar systems and their use as functional nano-compartments and transporters. Typically, amphiphilic block copolymers are synthesized, which self-assemble into micelles. However, such multi-molecular micelles may disintegrate upon changes of conditions such as pH or shear. This risk is avoided by creating “unimolecular micelles”, in which core and shell of the micelle are part of one single macromolecule. This is achieved by utilization of highly branched polymers as core molecule and appropriate modification of the shell-forming peripheral functional groups.

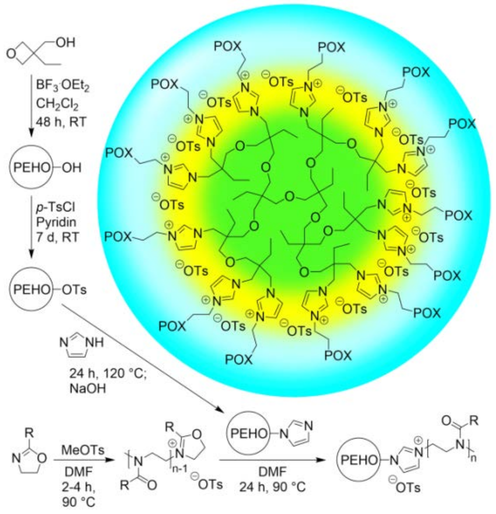

Fig. 1: Synthesis of thermo-responsive core/shell PILs and illustration of the micelle-like topology (the PILs of the first generation mentioned in the text have an analogous structure but bear an outer shell of alkyl chains instead of POX segments). (© FMF, University of Freiburg)

Some time ago, micelle-like polyelectrolytes with an onion-type compartmentalized topology have been developed, which are equipped with ions from the class of ionic liquids (ILs) [3,4]. These polymeric ionic liquids (PILs) have been presented in the FIT Report 2016. They are composed of a hyperbranched poly(3-ethyl-3-hydroxymethyloxetane) (PEHO) core, a polar inner shell of covalently attached imidazolium cations and low-molecular-weight anions, and a non-polar outer shell of alkyl chains. Owing to their chemical structure, these amphiphilic PILs show excellent performance as emulsifiers, dispersants, polymer additives, and transporters [3-6]. They enable transportation of molecules and nanoparticles from aqueous phase into non-polar solvents. However, this transport is unidirectional. The PIL-micelles do not allow for the desirable re-transport in response to a stimulus. In order to enable re-transportation and thermally switchable change of the transporter (“molecular shuttle“) between two phases, a second generation of these polyelectrolytes, which bear an outer shell of thermo-responsive poly(2-oxazoline)s (POX) instead of alkyl chains, was tailored at FIT and FMF (Fig. 1).

As illustrated in Figure 1, synthesis of the micelle-like PILs is based on the use of imidazole-functionalized PEHO for termination of the cationic ring-opening polymerization of 2-oxazolines. By this means, POX chains and PEHO core are covalently coupled via imidazolium cations in an efficient way. Owing to the POX shell, the hyperbranched PILs display thermo-responsive lower critical solution temperature (LCST) behavior and can be switched between water-soluble and water-insoluble by changing the temperature. Upon heating aqueous solutions above the critical solution temperature, the POX chains dehydrate and collapse, resulting in aggregation and precipitation of the PIL micelles, observable from blurring of the solution. This process is fully reversible. Upon cooling, the same clear solution as before is obtained (Fig. 2).

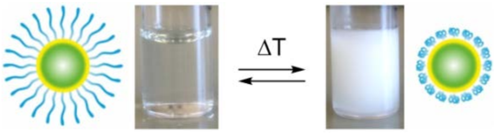

Fig. 2: Schematic drawings and photographs illustrating thermal switching of aqueous solutions of the micelle-like PILs. (© FMF, University of Freiburg)

In the course of synthesis, the shell of the PILs can be easily modified by the choice of the monomer employed (2-ethyl-2-oxazoline, 2-*n*-propyl-2-oxazoline), copolymerization, and variation of the POX chain length. Thus, the critical solution temperatures can be adjusted in a broad temperature range in a controlled manner (Fig. 3).

Owing to the switchability of polarity between hydrophilic and hydrophobic, the micelle-like PILs reversibly travel between water and water-immiscible ethyl acetate, depending on the temperature, and thus enable the envisioned temperature-triggered phase transfer of molecules. In the system water/ethyl acetate, the PIL micelles accomplish efficient transport of the water-soluble dye Congo red from aqueous phase into the organic phase upon increasing the temperature above the critical solution temperature. By simple cooling, the dye is re-transferred into the aqueous phase (Fig. 4). Several heating-cooling cycles prove repeatability of the dye transport.

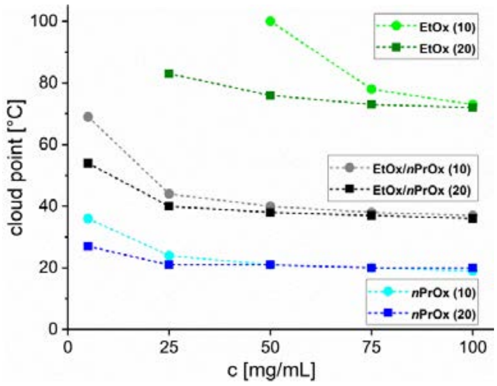

Fig. 3: Cloud points of PILs with different POX shell as a function of concentration (EtOx = 2-ethyl-2-oxazoline, *n*PrOx = 2-*n*-propyl-2-oxazoline; values in brackets specify the degree of polymerization of the POX chains). (© FMF, University of Freiburg)

These results unveil the potential of the micelle-like PILs as intelligent transporters in diverse specialty applications. First trials confirm excellent suitability of the responsive polyelectrolytes for use as stabilizers in the synthesis of metal nanoparticles. Therefore, in view of possible applications in catalysis, ongoing research at FIT and FMF aims at utilization of the novel hyperbranched PILs for preparation of thermally switchable colloid systems. Main focus is placed on the thermally triggered controlled and reversible transport of catalytically active nanoparticles and metal complexes.

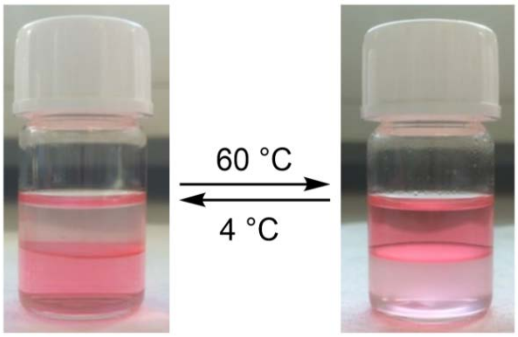

Fig. 4: Thermally switchable reversible phase transfer of Congo red between water and ethyl acetate by thermo-responsive micelle-like PILs. (© FMF, University of Freiburg)

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Controlling nucleation in quasi-two-dimensional systems by the rate of compression

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The Langmuir technique has been used to study the chain conformation [1-2], visco-elastic properties [3-4], and crystallization [5-7] of polymers in quasi-2D systems. Phase transitions in Langmuir films can be induced by varying distance between the polymer molecules at the air/water interface [5-7]. Structural transitions associated with different phase transitions, in particular first order phase transitions, are an integral step to get an insight in the ordering process of polymer thin films under confinement. In this context, our work aims to identify first order phase transitions in Langmuir polymer films and the morphological changes associated with such transitions. Intriguingly, although it is known that the compression kinetics has a significant influence on the structure formation processes in quasi 2-dimensions [4, 7], detailed studies to address this issue are still missing. Therefore, the influence of compression kinetics on the nucleation process (associated with the phase transitions) is investigated and quantified in this work. Our results suggest that the probability of nucleation in quasi 2-dimensional systems can be controlled directly by the rate of compression.

Using the Langmuir technique, we studied the morphological evolution (correlated with phase transitions) of a mono-molecular layer of poly L-lactic acid (PLLA) with increasing surface density (or with decreasing distance between the molecules). The morphological studies of the Langmuir polymer films were performed ex-situ by Atomic Force Microscopy (AFM) after transferring the films onto silicon substrates using the Langmuir-Schaefer method. In this work, we have used PLLA because it can crystallize and it can also form a monolayer at the air/water interface [5]. PLLA with a molecular weight of 1800 g/mol (24 monomer units) was used in this study.

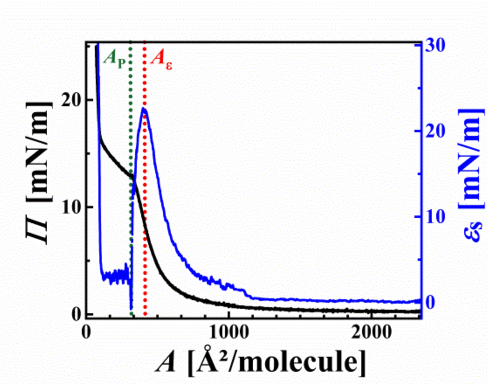

Fig. 1: $\Pi-A$ isotherm of PLLA at the air/water interface, compressed at a rate (C_R) of 36 Å^2/(molecule·min) at a fixed temperature of 20 °C. The elastic modulus (ε_S) is plotted on the right y-axis (blue curve). The green dashed line in the plot indicates the area per molecule at the onset of the apparent plateau (A_P) and the red dashed line shows the area at which the maximal value of the elastic modulus (A_ε). © Experimental Polymer Physics Group.

An isotherm of a PLLA monolayer (two dimensional phase diagram) at the air/water interface, compressed at a rate of 36 Å^2/(molecule·min), was obtained by plotting the surface pressure (Π) as a function of area occupied by each molecule (A) (see Figure 1). This Π–A isotherm shows five distinct regions, characterized by different slopes. At the large areas per molecule (> 1000 Å^2/molecule, region 1) Π remained almost zero upon compression, followed by a shallow increase of Π (at areas between 1000 Å^2/molecule and 700 Å^2/molecule, region 2). Upon further compression (320 Å^2/molecule < A < 700 Å^2/molecule, region 3),

Π began to increase rapidly before a weakly increasing “apparent plateau” (100 $Å^2$/molecule < A < 320 $Å^2$/molecule, region 4) region. A second steep increase of Π (at A < 100 $Å^2$/molecule, region 5) was observed after this “apparent plateau”.

The changes in slope in the isotherm can be associated with phase transitions occurring in the system. Slopes can be quantified by taking the derivative of this curve according to equation below.

$$\varepsilon_S = C^{-1} = -A\frac{\partial \Pi}{\partial A}$$

ε_S can be considered as the 2D analog of the bulk elastic modulus. C is analogous to the bulk compressibility. Thus, a closely packed monolayer would correspond to the maximum value of ε_S. After the maximum value a sudden drop in elastic modulus (coupled with the onset of the apparent plateau) is observed, which is indicative of a first order phase transition.

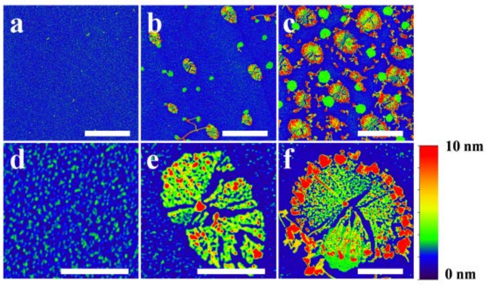

Fig. 2: Nucleation and growth of large meso-scopic clusters (*MC*s) during the compression of the PLLA monolayer. AFM images ((a) – (f)) obtained at an area per molecule, *A* of: (a), (d) 360 $Å^2$/molecule, (b), (e) 288 $Å^2$/molecule, and (c), (f) 190$Å^2$/molecule respectively. The rate of compression (C_R) and temperature for all these experiments were 36 $Å^2$/(molecule·min) and 20 °C, respectively. The scale bar of images (a) – (c) is 5 µm, and the scale bar for the images (d) – (f) is 1 µm. © Experimental Polymer Physics Group.

We were able to identify the nucleation and growth of meso-scopic clusters (*MC*s) associated with the apparent plateau (Figure 2).AFM images of the films transferred at an area before the apparent plateau showed a film consisting of aggregates of sizes 40 ± 10 nm (see Figure 2d). Interestingly, the films transferred within the plateau region showed the presence of two morphological features: (i) large meso-scopic clusters (*MC*s) with thickened boundaries and (ii) aggregates surrounding the *MC*s, indicating the possibility of phase co-existence within the plateau (shown in Figure 2).

The formation of *MC*s may be discussed in the context of phase diagrams predicted by the van der Waals equation of state [8]. In Langmuir films, at low surface density and weak polymer-polymer interactions, polymers are widely separated and can be dispersed evenly at the water surface. Upon compression, polymer molecules come closer and polymer-polymer interactions start to become relevant, leading at a certain surface density to the formation of domains of molecular aggregates. Further compression of the monolayer leads to an increase of the size of these domains and most likely to a metastable “over-compressed” regime. There, analogous to passing the binodal line in a 3Dphase diagram, nucleation of a new phase is expected, which is consistent with the observation of *MC*s [8].

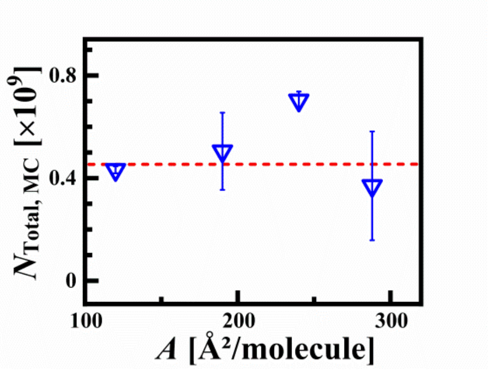

Fig. 3: Total number of meso-scopic clusters ($N_{\text{Total,MC}}$ = N_{MC} (number density of *MC*s, averaged over ten regions in the transferred films) × A_{trough} (area between the barriers at the time of transfer)) is represented as a function of *A*. The compression rate and the temperature for all these experiments are 36 $Å^2$/(molecule·min) and 20 °C, respectively. © Experimental Polymer Physics Group.

In order to determine the surface density where nucleation of the *MC*s is initiated, we calculated the total number of *MC*s ($N_{\text{Total,MC}}$) on the whole Langmuir trough with decreasing *A*. $N_{\text{Total,MC}}$ was obtained by multiplying the measured nucleation density (N_{MC}) observed in transferred films by the area between the barriers (A_{trough}) at the time of transfer. Interestingly, within the apparent plateau $N_{\text{Total, MC}}$ remained constant with decreasing *A* (Figure 3), indicating that the *MC*s might have nucleated at an area before reaching the onset of the plateau. Thus, we assume that the *MC*s were nucleated at an area between the inflection point (A_ε) and the onset of the plateau (A_P) (indicated in Figure 1).

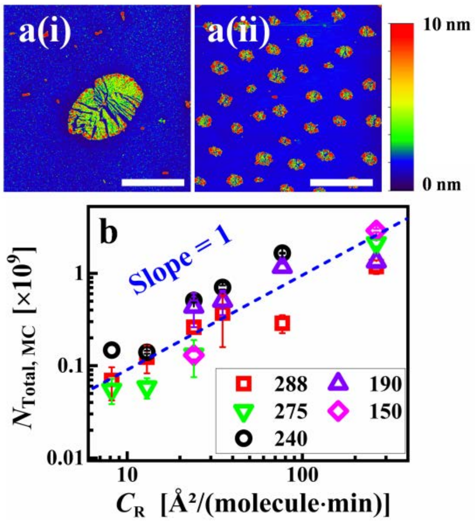

Fig. 4: Compression rate determines the nucleation probability in Langmuir films of PLLA. (a) AFM images of the films transferred at A = 240 Å^2/molecule for the compression rates (C_R) of (i) 8 Å^2/(molecule·min), (ii) 77 Å^2/(molecule·min). The experiments were carried out at a temperature of 20 °C. The value of the scale bars shown in the images is 5 μm. (b) Total number of nuclei of the clusters ($N_{\mathrm{Total,\,MC}}$) as a function of the rate of compression (C_R) for various areas per molecule (A). The error bars of $N_{\mathrm{Total,MC}}$ resulted from averaging over five different measurements of the same sample, representing the variance in the *MC*s in the transferred films. All experiments were carried out at a temperature of 20 °C. The different symbols in the plots indicate different values of A as indicated in the figure legend. © Experimental Polymer Physics Group.

Our experimental results indicate that the rate of compression has a significant impact on the total number of *MC*s observed in the Langmuir films. Intriguingly, at a constant surface density and temperature, while the total number of *MC*s increased linearly with increasing rate of compression, the morphological analysis of the transferred film indicated a decrease in their lateral size (Figure 4). Under isothermal conditions, such observations elucidate a correlation between nucleation probability and compression kinetics, thus opening an effective and precise route to control nucleation in quasi two-dimensions.

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Surface-attached polymer networks from thioxanthone group containing polymers

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Crosslinking is an effective way to modify the properties of polymer materials and therefore various methods to form well-defined polymer networks have been developed over the last decades.[1–4] One strategy, which has been explored more recently, is to use reactive moieties that lay dormant in the polymer material and can be activated on demand, either thermally or under light exposure. Three classes of crosslinkers have been described in this context which form different reactive species – azides, diazo compounds and aromatic ketones.[5-8] After activation, these groups can react with nearly any kind of CH-Bond in direct vicinity by abstracting a hydrogen atom, followed by a covalent attachment to the respective carbon atom. This crosslinking method is called CHic as it includes a formal C,H-insertion mechanism. It has been shown, that crosslinking can be achieved in a variety of different materials, making it a versatile way to form crosslinked networks in solid polymer films.

For delicate applications, it is desirable to investigate photoreactive substances that can be activated at longer wavelength, preferably close to the visible region. We have chosen thioxanthones in this regard as they show a strong absorbance at λ = 365 nm and are well known as potent photoinitiators.[10] Hence, we designed such a derivative and incorporated it into a PDMAA matrix to generate hydrogel layers which may be interesting for biomedical purposes. The copolymer also contains tertiary amin residues as they strongly enhance the photoreactivity of thioxanthones. Figure 1 shows the synthesis of the polymer and its crosslinking reaction.

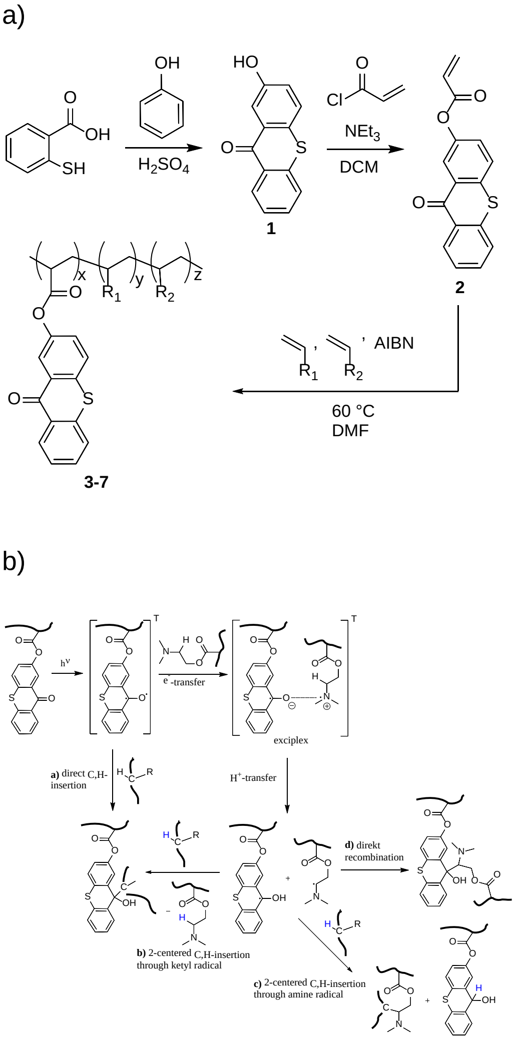

Fig. 1: a) Synthesis and copolymerization of TXAO. The Thioxanthone ring system was synthesized after S. Smiles and H. Gilman41,42 followed by esterification. Various copolymers with MMA, DMAMA and DMAA were produced by free radical polymerization with AIBN as initiator. b) Scheme 2: Excitation and possible reactions of TXAO 2 incorporated into a polymer chain that lead to crosslinking. a) Direct CH-insertion crosslinking (CHic) into the polymer chain; b) reactions involving tertiary amines. © Chemistry and Physics of Interfaces, IMTEK, Uni Freiburg.

Ilumination experiments have then shown, that these copolymers that can be crosslinked very effectively with low energetic UV light (λ = 365 nm). Figure 2 shows the gel content of the layers as a function of irradiation time and energy. Fully crosslinked films are typically obtained as long as the thioxanthone content is sufficiently high. Typically all material is incorporated into the film. This enables the formation of well-defined polymer networks under mild conditions, while simultaneously inducing surface attachment. The addition of a tertiary amine as comonomer increases the reactivity of the used thioxanthone derivative drastically and improves the solubility in aqueous solvents for PDMAA based copolymers. This enables environmentally friendly processing and makes the described system a promising candidate for biomedical applications.

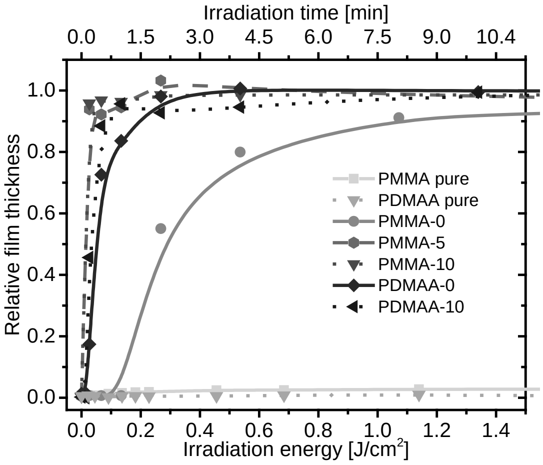

Fig. 2: Gel contents of the synthesized copolymers with varied activator and crosslinker contents after different irradiation times at λ = 365 nm (Ī = 2.23 mW/cm2). Reference experiments with the same polymers containing no crosslinker showed no gel formation at all. © Chemistry and Physics of Interfaces, IMTEK, Uni Freiburg.

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BIOMIMETIC, BIOBASED AND BIOACTIVE MATERIALS SYSTEMS

Unraveling the sequence-specific thermoresponsive behavior of polynucleotides: a new concept to structure programmable all-DNA materials

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The acute understanding of the organization of individual molecules into the self-assembled architectures with specific properties at nano- meso-, and macroscopic length scales is an important area of current science and represents a vital contribution of chemistry to the general understanding of the development of emergent complexity. The crucial challenge of tailoring hierarchical architectures with emergent properties in an energy-efficient bottom-up pathway lies in the notion of using simple enough building-blocks and simultaneously increasing the complexity and functionality of self-assembling superstructures which eventually relies on a shift towards multicomponent systems that intertwine with non-trivial interactions. Ultimately, choosing simple constituents, orchestrating kinetic pathway guidance strategy and balancing between synergistic and competing interactions are the fundamental pillars for a rational design to build hierarchical architectures with emergent properties.[1]

The programmability of supramolecular DNA duplexes has made DNA a powerful tool for self-assembled materials and molecular computation in DNA nanoscience.[2] In the realm of DNA-based assemblies, there have been exciting developments towards highly defined nanoscale structures (e.g., DNA origami).[3] However, since the construction of such materials is based only on nanoscale building blocks relying on the classical supramolecular duplex formation, the overall superstructures are limited in their dimensions to the nanoscale. On the other hand, In the world of synthetic polymers, self-assembly into ordered morphologies and switchability of properties counts heavily on phase-separation (a macromolecular property). Despite extensive progress to, e.g., design switchable block copolymer self-assemblies and microgels using thermoresponsive polymers, programmability down to a sequence level or similar structural complexity as in DNA, have not been reached in polymer science.

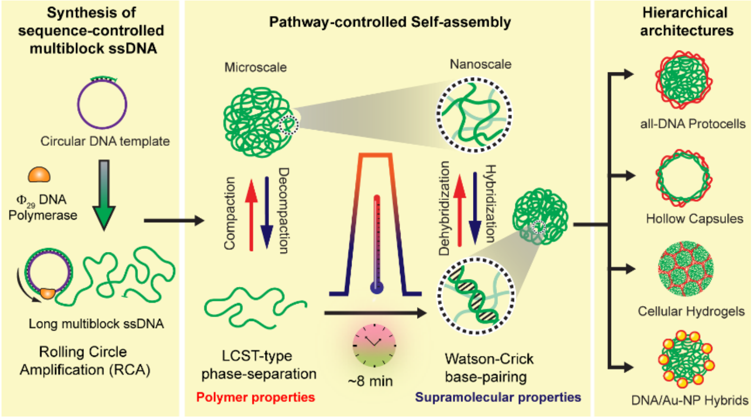

Fig. 1: Schematic representation of the long multiblock ssDNA synthesis, antagonistic phase separation (polymer character) along with DNA duplex hybridization (supramolecular character) during heating ramp and the formation of complex hierarchical self-assembled microstructures. © Walther Lab

Complementary to this nanoscale realm of supramolecular structuring (duplex) based on DNA, we have recently discovered that the polymer character of single-stranded DNA (ssDNA) can also be activated for the self-assembled structuration on the mesoscale level. In this context, a sequence-specific (purine-rich) ssDNA undergoes a reversible phase-separation upon elevation of temperature, resembling the LCST-type synthetic polymer, e.g., poly(N-isopropyl acrylamide) (PNIPAM, possibly the best known thermoresponsive polymer till date).[4] The physical origin of this phenomena resides in a thermoresponsive desolvation of the DNA strands which is specific to selected nucleobases and thus can be easily programmed via sequence coding. It has been evident that a series of hierarchical all-DNA mesoscale self-assembled structures can be fabricated by using the kinetic control in single-step heating ramp balancing between the cloud point temperature (T_{cp}) (desolvation point) and the melting temperature (T_m) of the complementary sequences of the ssDNA multiblock polymers (Fig. 1). The most important contribution to the success of this project was the clean synthesis of sequence-controlled DNA multiblock copolymers (via rolling circle amplification, RCA) and the exact study of their thermoresponsive behaviors. We have managed to balance these two antagonistic behaviors to construct a landscape of morphologies, such as protocell-like DNA microparticles (with liquid DNA encapsulated in a DNA hydrogel shell), hollow microcapsules and DNA/Au-NP hybrids (Fig. 2).

To investigate the phase-separation of ssDNA, a group of multiblock ssDNAs each containing a repeating unit of twenty adenosine (A) or thymine (T) along with a barcode sequence for the post-functionalization were synthesized by rolling circle amplification (RCA). The adenosine-rich ssDNAs, phase-separate at high temperature in the presence of Mg^{2+} while the thymine-rich ssDNAs do not exhibit such kind of behavior. This phase-separation behavior or the cloud point (T_{cp}) depends on the molecular weight of the ssDNA and the concentration of divalent ions. The key to the achievement of the self-assembling systems lies in the control of the energy landscapes to capture defined metastable states via kinetic pathway guidance. Two antagonistic effects are operating: at the one hand, classical duplex formation occurs between the complementary DNA strands rapidly on the nanoscale and upon cooling, whereas, on the other hand, the LCST-type phase-segregation proceeds slowly on the microscale during heating (**Fig. 1**). A particular highlight of this kinetic pathway controlled self-assembly process is the DNA protocells (built from two different sequence-defined DNA multiblock copolymers), which emerged at the end of the heating ramps leading to a compartmentalized structure entrapping a liquid ssDNA solution (genetic information) under the high osmotic pressure in a hydrogel shell of dsDNA (Fig. 2b).

The entire process of their formation takes less than 10 minutes, and a variety of post-functionalizations are possible since the specific barcode-sequences were embedded in DNA building-blocks. For instance, the incorporation of thermoplasmonic gold nanoparticles allows spatiotemporally controlled selective heating of the protocell shells in order to release DNA information from the core (Fig. 2f). By adjusting sequences, we also designed systems in which the T_{cp} is only slightly greater than the T_m, putting the hybridization and phase-separation processes in direct competition, to produce hollow capsules (Fig. 2e). In addition, cellular hydrogels can be created that show interesting mechano-adaptive behavior (Fig. 2c). Lately, we have been using these DNA protocells to study several catalytic reactions (e.g., metathesis, ROMP and DNAzyme-based bond cleavage) in confined space to comprehend the crowding effects on ther rates as it would transcend the understanding of the numerous biochemical reactions inside the cellular matrix.

In summary, this project bridges concepts of pathway-controlled DNA programmable assembly, fundamental chemistry, materials science, and polymer science, underlining the overarching importance of interdisciplinary science in driving new discoveries. In this project, we have elucidated a novel phase-transition behavior in a complex DNA-based system and used a simple and versatile pathway to access a landscape of all-DNA morphologies in different physical states. Lastly, a further thrilling question is whether such thermoinduced compartmentalization could have played a role in the selection of genetic information in later processes at the origin-of-life.

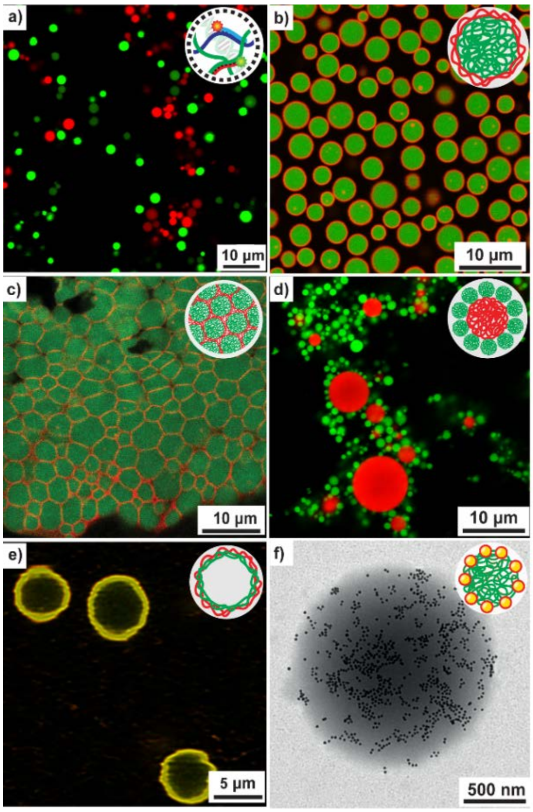

Fig. 2: Pathway-controlled formation of tunable and addressable metastable all-DNA microgel architectures and their superstructures. CLSM images of a) crosslinked microspheres, b) protocell like core-shell microcompartments, c) patterned hydrogels, d) hierarchical self-assembly of microspheres, e) hollow capsules; and f) TEM image of DNA/Au-NP hybrids. The schematic representations are shown at the right corner of every images. CLSM images were recorded after staining the structures with DNA-dye conjugates. © Nature Nanotechnology and Walther Lab.

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Personalized antibiotherapy: development and evaluation of a microfluidic biosensor platform for non-invasive, multianalyte on-site diagnostics – miPAT

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German Research Foundation (DFG)

Antibiotherapy has become a central issue of human medicine in the recent years. Herein, a personalized antibiotherapy, covering the antibiotic dosage and the dosing interval and the treatment duration, plays a crucial role in the efficacy of the anti-infective therapy [1, 2]. Due to the lack of the bedside testing systems, antibiotic doses are, if at all, adapted only to the body weight of the patient. In this context, a major problem is the in-hospital development of multidrug resistance as a consequence of suboptimal antibiotic use.

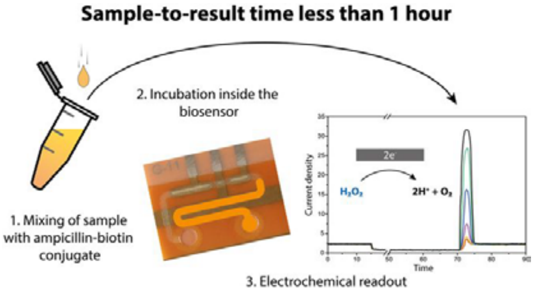

Fig. 1: Illustration of the bedside monitoring scenario in the case of antibiotic concentrations. After the sample is collected from the patient, it is mixed with the ampicillin-biotin conjugate (1.) and incubated in the immobilization section of the biosensor (2.). After applying the avidin-glucose oxidase enzyme, the electrochemical readout of the sensor completes the measurement (3.), resulting in a sample-to-result time of less than 1 hour. Reproduced with permission. [4] Copyright 2017, Nature Publishing Group.

A non-invasive approach, enabling such diagnostics in various body fluids like exhaled breath condensate (EBC), urine and saliva, would be highly desirable for an individualized antibiotherapy [3]. In this regard, microfluidic lab-on-a-chip platforms enables the point-of-care testing of different analytes along with a low sample consumption, faster sample-to-result times and an easy integration of complex laboratory functions. Such a microfluidic lab-on-a-chip device in combination with a performant biomolecular sensing system could assure an adequate and non-invasive profiling of physiological antibiotic levels and the inflammation progress, and thus, tailor a personalized anti-infective therapy.

The goal of this project is the design, development and pre-clinical evaluation of a microfluidic multiplexed biosensor platform for the non-invasive, on-site quantification of a panel of parameters, including various ß-lactam antibiotics, as well as renal and inflammation biomarkers. Herein, different endogenous biomarkers (such as cystatin C) for renal function, and acute phase proteins (for example, procalcitonin) for bacterial inflammation will be evaluated regarding their sensitivity and selectivity. Additionally, in large animal experiments, investigating various antibiotic doses, the quasi real-time surveillance of inflammation markers and antibiotic pharmacokinetics will be performed in blood, tissue and non-invasively collected EBC specimen. Hence, this project includes the implementation of an exhaled breath condensate sampling device for rapid and non-invasive sample collection.

A successful realization of the planned microfluidic lab-on-a-chip device for non-invasive on-site testing of inflammation progress and antibiotic pharmacokinetics could pave the way to an individualized antibiotherapy. It would consequently improve patient's outcome as well as further development of drug-resistant bacteria. Therefore, the outcome of this project could be a significant landmark on the global combat against the antibiotic resistance.

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Physics and mechanics of plant surfaces with cuticular folds and other microstructures – ontogenetic development of the microstructures

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The PhD project “Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures” is carried out under Plant-Inspired Materials and Surfaces (PlaMatSu), an *Innovative Training Network* (ITN), funded by the European Commission’s Marie Skłodowska-Curie Actions. This project is one of the nine PhD projects carried out at four leading European universities in the field of bio-inspired materials: Adolphe Merkle Insitute/Université de Fribourg, Switzerland (PIs: Prof. Steiner, Prof. Weder), Universität Freiburg, Germany (PIs: Prof. Reiter, Prof. Rühe, Prof. Speck), University of Cambridge, UK (PIs: Prof. Glover, Prof. Vignolini) and since summer 2018 University of Strathclyde, Glasgow (PI: Prof. Bruns). PlaMatSu aims to understand the structure-function relationships of plant cuticles and other surface microstructures and to develop new functional materials or surfaces/interfaces that mimic the multifunctional plant surfaces.

The Freiburg project (Prof. Speck) aims at understanding ontogenetic variations in plant leaf surfaces having wrinkled cuticles and to quantify corresponding changes in their functional properties like promotion or prevention of insect adhesion [1] and water contact angle. For this study, several model plant species are currently being grown under different environmental conditions in six experimental greenhouses at the Botanic Garden, University of Freiburg. Observations of ontogenetic structural changes in leaf surface microstructures are being carried out using confocal laser scanning microscopy (CLSM) and scanning electron microscopy measurements (SEM).

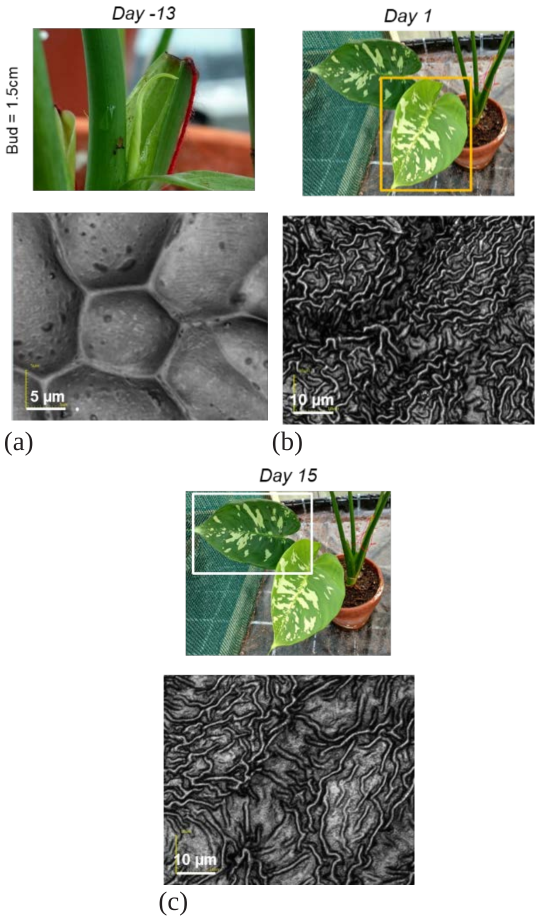

Fig. 1: Confocal laser scanning microscopy images of developing cuticular wrinkles on a young leaf of *Schismattoglottis calyptrata*. The images were taken on 13th day before unfolding (a), 1st day after unfolding (b) and 15th day after unfolding (c). © Plant Biomechanics Group Freiburg

Using confocal laser scanning microscopy measurements, we identified different stages of cuticular folds development on the leaf surfaces of the two model plants *Schismattoglottis calyptrata* and *Hevea brasiliensis*. On the leaf surfaces of both the species, we find gradual development of cuticular folds, with no folds during the early ontogenetic stages, then gradual formation of the cuticular folds and finally completely developed cuticular folds in the final stages of leaf development. Confocal laser scanning microscopy images of the leaf surface structures at different stages are shown in fig. 1.

From our observations done so far, on *Schismattoglottis calyptrata*, the wavelength of cuticular folds (measured by Rsm) reached up to 5 µm and fold height (mesured by Rc) reached up to 1 µm, and on *Hevea brasiliensis* the values of up to 3 µm and 1 µm, respectively, are found.

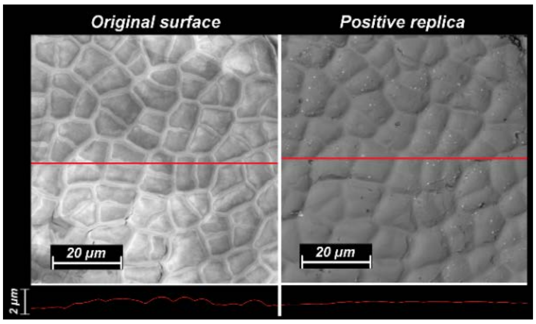

Fig. 2: CLSM images (Olympus LEXT OLS 4000). Comparison of topography of original and positive replicas of young leaves of *Hevea brasiliensis* replicated by Epoxy/PDMS replication method. © Plant Biomechanics Group Freiburg

Surface chemistry is an important parameter affecting water contact angle, however for insect attachment, it has been reported that surface roughness has a higher influence than surface chemistry [2, 3]. This is particularly interesting for example, to understand the changes in insect attachment due to changes in surface roughness or chemistry during the ontogeny of leaf surfaces. However, studying the effect of both parameters on insect attachment is quite difficult, notably because of the complex changes that occur on leaf surfaces during development. To overcome this, we plan to use surface replicas of leaves for microscopic and traction force measurements of insects walking on the surfaces.

We produced thin surface replicas of young leaves of *Hevea brasiliensis* using an epoxy negative and a PDMS positive, and quantified the replication quality. We used the two parameters cross-covariance ratio (ACCFMAX) and relative topography difference (Ds) to compare the height differences at the same spots (fig. 2) on PDMS positives and the original young leaves. The replicas from young leaves showed a replication quality with values ACCFMAX = 84.2% and 1−Ds = 57.4% compared to ACCFMAX =79.3 %, 1−Ds = 60.7 % found for adult leaves [4]. This project part was carried out in collaboration with Prof. Tim Higham, University of California Riverside and Prof. Vincent Le Houérou, University of Strasbourg. In forthcoming studies we intend to use the results from this study to analyze surface replicas of leaf surfaces at different stages of ontogeny. Importantly, we also will use replicas of whole leaf laminas to study spatial variations, which help us eliminate the effect of leaf drying while studying original leaves.

Following a necessary surface analysis, insect walking frictional force measurements and contact angle measurements will be carried out on the surface replicas taken at different stages. For insect attachment experiments, we make use of different insect model species such as e.g. *Coccinella septumpunctuata* and *Leptinotarsa decemlineata*. These measurements will be then analyzed for possible correlations with changes in microscale geometry of the cuticular folds on the leaf surfaces.

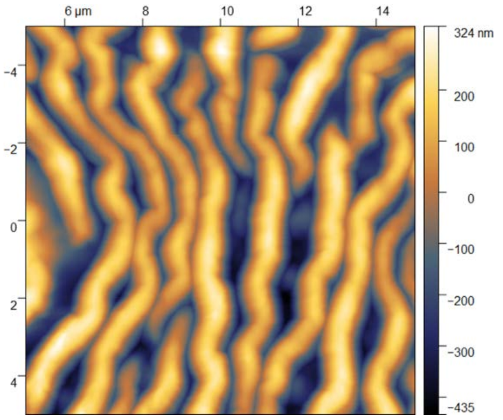

Fig. 3: Atomic force microscopy image of cuticular wrinkles on the leaves of *Hevea brasiliensis* (JPK NanoWizard II). © Plant Biomechanics Group Freiburg

In addition to the above described studies, genetic transformations of the model plant *Nicotiana tabacum* to induce cuticular ridges on the leaf surfaces have been carried out at Prof. Glover’s lab, University of Cambridge. Currently the transformed plants are being grown at the green houses of Botanic Garden of the University of Cambridge. Further studies to analyze the ontogenetic development of wrinkled cuticular structures on the leaf surfaces of the transformed plants will be carried out during the next research stay in Cambridge.

Training on atomic force microscopy measurements on JPK NanoWizard II (Fig. 3) was also taken up during one month visit to Prof. Nico Bruns lab at the Université de Fribourg. During the period, surface chemistry analysis using “Attenuated Total Reflectance – Infrared Spectroscopy” (Prof. Christof Weder’s Lab) was also carried on the surfaces of plant leaves at different growth stages. Changes in surface chemistry between the leaf stages quantified by the methodological approach will be analysed in detail within the next months.

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Energetic investigations of induced particle uptake into functionalized synthetic membrane systems

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Project funding: German Research Foundation (DFG RO 4341/3-1)

The study represents an interdisciplinary research project based on the collaboration of biologists/biophysicists of the Synthetic Biology of Signalling Processes Group from the Faculty of Biology, University of Freiburg (PI: Prof. Dr. Winfried Römer) with physicists from the Bio- and Nano-Photonics Research Group from the Department of Microsystems Engineering (IMTEK), University of Freiburg (PI: Prof. Dr. Alexander Rohrbach).

Pathogenic bacteria like Pseudomonas aeruginosa (PA) can cause infections and diseases especially in immunocompromised patients (1). Binding of pathogens to specific host cells is the first step of the infection mechanism. Thereafter, the cell membrane is deformed in a way to first wrap and further absorb the bacterium into its cellular cytoplasm. Cell membrane deformation for particle-induced invagination is also crucial in other biological phenomena such as viral infection or micro drug careers (2).

In case of PA, it has been demonstrated that bacterium engulfment is mostly initiated by specific ligand-receptor interactions followed by membrane deformation and subsequent reorganization of intracellular constituents e.g. actin cortex (2). PA bacteria implement their lectin molecules at the outer bacterial surface as ligands to bind to glycosphingolipid receptors on the cell surfaces (3). Glycosphingolipids are mainly found together with sphingomyelin and cholesterol in distinct lipid domains (termed lipid rafts) of the exoplasmic leaflet of the cell membrane. These domains are believed to play a vital role in cell signaling involved in endocytosis processes (4).

Giant unilamellar vesicles (GUVs), spherical compartments with a single lipid bilayer and sizes ranging from 5 to 50 µm, represent the most popular biomimetic systems that resemble mammalian cells. Due to the several advantages such as variation of membrane composition, encapsulation of proteins or genomic factors (e.g. DNA or RNA), incorporation of transmembrane proteins, they have been extensively used to rebuild cellular processes.

The previous work of our lab could interestingly show that specific binding of the bacterial lectin LecA with the glycosphingolipid globotriaosylceramide (Gb3) is fully sufficient to induce bacterial engulfment into Giant Unilamellar Vesicles (GUVs) as a minimal model of the cell membrane. It indicates the importance of ligand-receptor interaction that can lead to engulfment even in a synthetic system having neither actin cortex nor other active endocytic cell machineries (5). Due to the importance of specific ligand-receptor for proper engulfment, we decided to investigate the physical interaction of a ligand-coated particle resembling the polar region of the PA bacterium and receptor-containing synthetic lipid bilayer system.

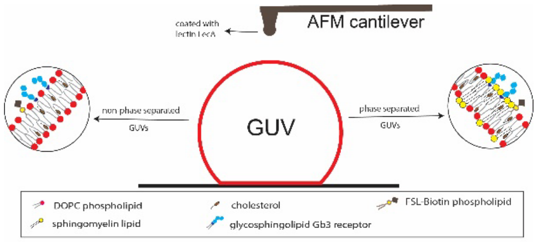

Fig. 1: Two different groups of GUVs (non-phase separated and phase separated GUVs) containing the Gb3 receptor interact with a LecA-functionalized AFM probe mimicking the bacterium. Membrane components of GUVs are depicted in the box. © Synthetic Biology of Signalling Processes Group, Faculty of Biology, Freiburg.

To quantify the physical interactions, we use Atomic Force Microscopy (AFM) technique to measure the interaction forces between LecA-coated spherical probes and Gb3-containging GUVs. AFM has shown its great power for measuring the forces in various biological applications e.g. protein domains unfolding (6), single ligand-receptor bond unbinding (7) and detachment of single cells from another cell (8) or from a substrate (9). A micro -beam called cantilever is positioned over the sample far from the surface and moved downward until it touches the sample surface at one point and pushes the point downward. The probe can be immediately or after a particular time retracted from the surface till complete separation from the surface occurs again. During this cycle, the vertical deflection of the cantilever is recorded precisely via a laser detection system and thereafter converted to the force using Hooke’s law. Figure 1 shows a schematic view of a GUV underneath an AFM cantilever (coated with the lectin LecA).

As mentioned earlier, glycosphingolipids like Gb3 molecules are mainly located in lipid raft domains of cell membranes. In GUVs, the demixing of membrane components in more ordered (liquid-ordered, Lo) and less ordered (liquid-disordered, Ld) domains has been reported about two decades ago (10). Liquid-ordered domains are artificial structures that resemble lipid raft domains of cell membranes and can be reconstituted in GUVs by mixing different lipid components, a low melting temperature lipid (e.g. dipalmitoylphosphatidylcholine; DOPC), cholesterol, and sphingomyelin (SM) as high melting temperature lipid.

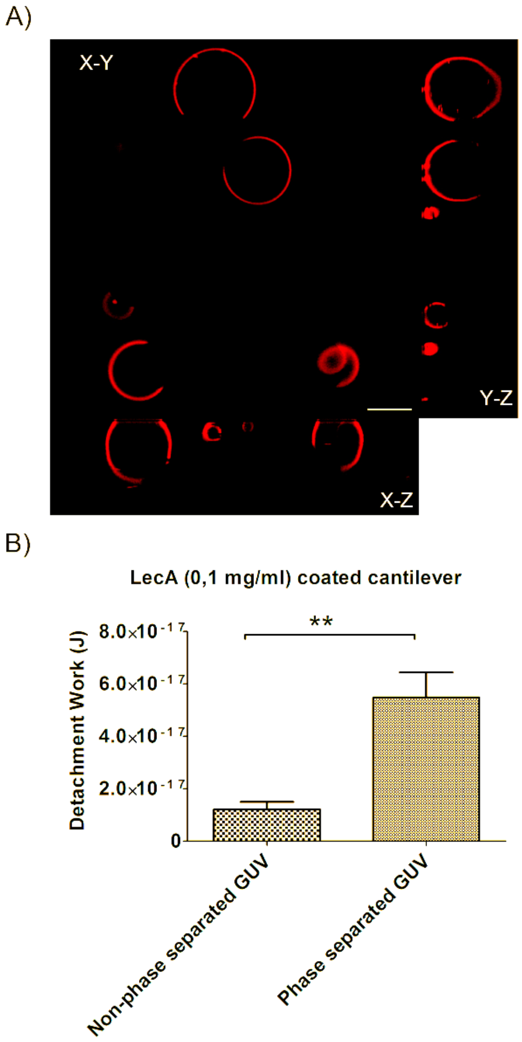

Fig. 2: (A) Confocal microscopy image of phase-separated GUVs attached to the streptavidin-coated substrate. Black areas represent the liquid-ordered domains enriched in sphingomyelin lipids and cholesterol. The equatorial xy plane and the two cross sections (yz) and xz) are shown. (scale bar 10 µm) (B) Comparison of the work of detachment (WD) between vesicles containing Gb3 without or with phase separation interacted with lectin-coated cantilevers. Asterisks show the significant difference (T-test; p-value < 0.05). © Synthetic Biology of Signalling Processes Group, Faculty of Biology, Freiburg.

In this study, we prepared two types of GUVs (Figure 1) that contained Gb3 receptors. One type were GUVs (called non-phase separated GUVs) with only low melting temperature lipids (DOPC) and cholesterol. Additionally, GUVs contained small portions of a fluorescently labeled lipid (TR-DHPE lipid) and a biotinylated lipid (FSL-biotin lipid). As second type of GUVs we produced GUVs with the coexistence of liquid-ordered and liquid-disordered domains. These so called phase-separated GUVs were prepared by mixing DOPC, SM, Gb3, and cholesterol, TR-DHPE and FSL-biotin lipids. The GUV preparation was conducted using the electroformation method as comprehensively described in this protocol (11). FSL-biotin lipid had been added to the membrane composition in order to immobilize the vesicles on a streptavidin-functionalized substrate. Due to preferential partitioning of TR-DHPE lipid in liquid-disordered domains (i.e. DOPC domains in our samples), phase-separated GUVs don't show full coverage of fluorescence signal as shown in Figure 2A.

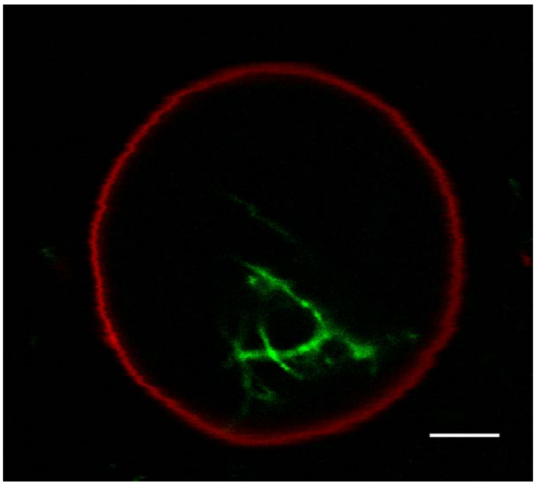

Fig. 3: Confocal microscopy image of an actin-encapsulated GUV (scale bar 5 µm). © Synthetic Biology of Signalling Processes Group, Faculty of Biology, Freiburg.

Cantilevers were cleaned by plasma cleaning treatment and then incubated in a 50 µl droplet of lectin LecA solution (0.1 mg/ml) at 37°C for 30 minutes. The JPK Nanowizard3 and Cellhesion200 systems were used to apply low force values (about 100 pN) and slightly indent vesicles. Vertical deflection (or force) versus indentation depth curves were recorded and the retract part of the curves were analysed to compute the work of detachment (i.e. hatched area enclosed by the retract section of force-indentation curve (12). It indirectly indicates level of adhesion strength between coated cantilevers and the membrane). Calculating the work of detachment (WD) for these two types of vesicles showed a significant increase for phase-separated GUVs compared to non-phase separated GUVs. It can be described by pre-clustering of Gb3 receptors in the liquid-ordered domains (black domains in Figure 2A) as is expected from glycosphingolipids.

We have started to study another complex synthetic system (i.e. actin-encapsulated GUVs) that can better elucidate the biophysical mechanism underlying lectin-driven phagocytosis. Figure 3 depicts an image of actin filaments encapsulated in a GUV. As next step, we will apply AFM force measurements on this type of GUVs.

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Bioinspired energy dissipation in civil engineering, and scaling of properties of highly porous biological and biomimetic constructions

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Project funding: German Research Foundation (DFG) – Collaborative Research Center SFB-TRR 141 „Biological Design and Integrative Structures - Analysis, Simulation and Implementation in Architecture“ – Projects A02 and B01

The two sub-projects presented here (project A02: “Plants and animals as source of inspiration for energy dissipation in load bearing systems and facades”, and project B01: “Scaling of properties of highly porous biological and biomimetic constructions”) are part of the interdisciplinary Collaborative Research Center Transregio (CRC) 141 “Biological Design and Integrative Structures – Analysis, Simulation and Implementation in Architecture”. Central aim of this CRC, is the optimization of specific properties of buildings or building components in terms of their mechanical resistance based on the inspiration from construction principles in biology. Inherent properties of the biological role models such as an efficient use of resources and a closed material cycle may additionally contribute to an increased sustainability in civil engineering and architecture.

The biological role models examined in the two projects A02 and B01 are the fibrous bark of the giant redwood (*Sequoiadendron giganteum*) and the triple-layered fruit wall of the coconut palm (*Cocos nucifera*) which are being investigated by botanists and biomechanicists of the University of Freiburg, PI: Prof. Thomas Speck as well as sea urchin spines (studied by mineralogists and materials scientists of the University of Tübingen, PI: Prof. Klaus Nickel). Thereby, the bark of the giant redwood and the brittle and highly porous sea urchin spines are capable of dissipating high amounts of impact energy, whereas the innermost fruit wall layer (the endocarp) of the coconut is additionally characterized by a high puncture resistance. The insights gained during the investigation of the functional anatomy and biomechanics of these biological role models are abstracted with the aid of computer simulations carried out by material scientists and mathematicians from the University of Stuttgart (PI: Prof. Siegfried Schmauder). Finally, the implementation into building components with an increased energy dissipation capability and impact resistance is conducted by civil engineers and architects of the University of Stuttgart (PI: Prof. Werner Sobek). One major challenge during this process is the scaling from the biological role models to the building components. While the biological structures of interest are usually in the order of a few micrometres up to a few centimetres, the technical building components reach up to several (tenth of) meters in size. When simply scaling up the biological structures, the bioinspired technical building components would be more prone to failure compared to their biological counterparts. Therefore, a mathematical description of the changes in mechanical properties during the scaling up process is necessary in order to properly predict the failure limits of the bioinspired building components. For homogeneous, isotropic and brittle materials, such descriptions are already known from the literature [1, 2]. However, they need yet to be developed and/or adapted for non-brittle or quasi-brittle materials, respectively, such as the coconut endocarp.

In the following, the results of research on the two biological models investigated in the Plant Biomechanics Group Freiburg (i.e. the bark of the giant redwood and of the coconut fruit wall) will be presented. The bark of the giant redwood needs to fulfil a multitude of functions. For example, it protects the inlying tissues from high temperatures during forest fires or from mechanical damages during regularly occurring rock fall events. Thereby, especially the protection from mechanical damage during rock fall events is of interest for the research within the CRC 141 since the underlying principles of impact protection of the bark during rock fall events can be transferred into impact protection and energy dissipation of building components [3]. The thick bark of the giant redwood is mainly composed of lignified, long, interconnected fibres and fibre bundles that are arranged in interwoven layers. The suitability of this composition for impact protection has been proven during dynamic impact tests and quasi-static compression tests [4]. Thereby, the bark shows a non-uniform compaction behaviour and protects the inlying (living) tissues very efficiently by dissipating high amounts of impact energy and markedly decreasing the magnitude of force peaks. A mixture of elastic, viscoelastic and plastic functional components during deformation could be verified. Due to these properties of the giant redwood bark, its composition serves as a role model for a transfer into biomimetic concrete based construction elements. These will benefit from an improved energy dissipation capability, which is relevant e.g. for protection against damage by earthquakes or impacts from rock falls, cars, airplanes or derailed trains.

For the scaling analysis of the coconut endocarp, cylindrical samples with two different volumes were prepared and tested in uniaxial compression. The small samples had an average volume of 30 mm³ and the large ones a volume of 205 mm³. Fig. 1 shows the results of the uniaxial compression tests. The tests clearly proved a size effect (Fig. 1A) as small samples had significantly higher compressive strength than large samples (Wilcoxon Rank Sum Test, W = 493, ***: $p < 0.001$; [5]).

The generated model, following an approach developed by Weibull [6], proved to be very accurate (Fig. 1B): small samples had a coefficient of determination of 0.94 and large samples had a coefficient of determination of 0.95. The analysis resulted in a Weibull modulus of 16.5 (small samples) and 14.1 (large samples) and a characteristic strength of 225 MPa (small samples) and 205 MPa (large samples), respectively. As stated above, the Weibull analysis also allows for predicting a scaling effect of materials [2]. The predicted scaling effect for the coconut endocarp was thus slightly reduced compared to the observed size effect [6]. Since such a minimized size effect has also been observed in other plant materials [7], it is possible that the hierarchical structuring existing in plant materials minimizes the scaling effect. However, in order to evaluate the principles of this minimized size effect in more detail, future studies are necessary.

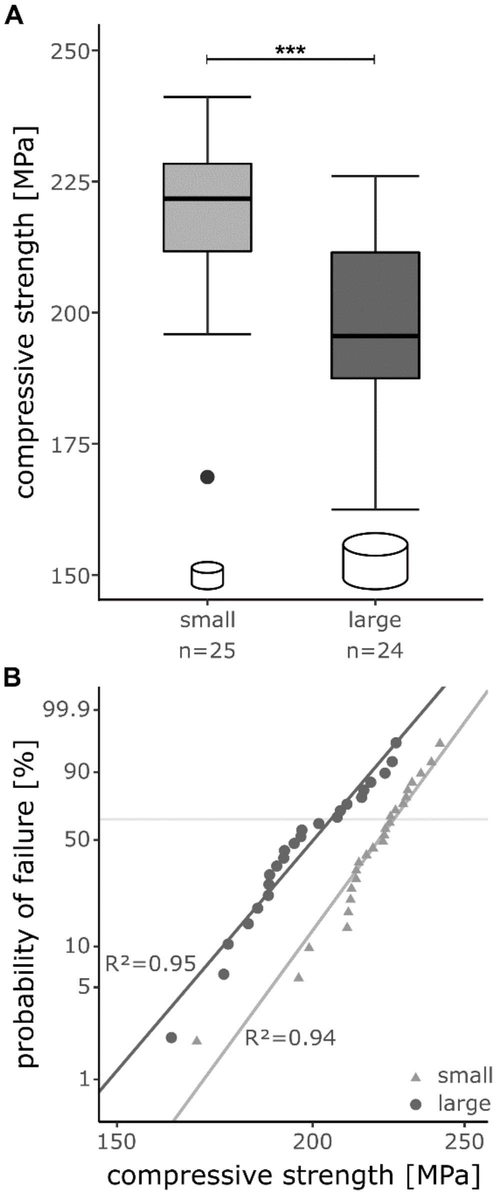

Fig. 1: Compressive strengths for small and large cylindrical endocarp specimens determined in uniaxial compression tests. (A) A size effect for the coconut endocarp could be demonstrated. A Wilcoxon rank sum test revealed a significantly higher compressive strength for small samples than for large ones. (B) The Weibull analysis yielded a Weibull modulus of 16.5 and a characteristic strength of 225 MPa for the small samples. For the large samples a Weibull modulus of 14.1 and a characteristic strength of 205 MPa was found (Figure adapted from [5]). (© Plant Biomechanics Group)

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Smooth transition from rod-shaped to planar elements: leaves as concept generators for technical solutions in architecture

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Project funding: German Research Foundation (DFG) – Cooperative Research Centre 141 „Biological Design and Integrative Structures - Analysis, Simulation and Implementation in Architecture“ – Project A03

In classical civil engineering and architecture, connections between individual elements with various geometries often represent weak points, since the use of additional parts to connect the individual components, (e.g., bolts and nuts) results in regions of high stress and strain. In the framework of subproject A03 we focus on the investigation of transition zones between rod-shaped and planar elements in various plant models. During biological evolution, a variety of solutions for the smooth transition between rod-shaped and planar elements developed in terms of gradient structures at different hierarchy levels [1] that may serve as concept generators for technical applications in general and in particular in architecture.

Foliage leaves have emerged as very suitable biological role models, because of their general composition of a rod-shaped petiole and a planar lamina. In contrast to the aforementioned technical connections, these two elements are interconnected without intermediate pieces via a smooth and robust transition zone. In a first approach, the morphology and anatomy of the transition zone in leaves of *Caladium bicolor* were investigated to gain insights into the change of shape and internal structuring of such a biological connection (Fig. 1).

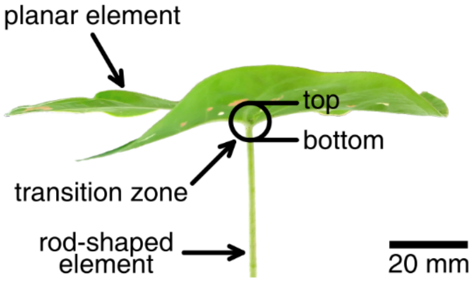

Fig. 1: Side view of a leaf of *Caladium bicolor*. The leaf consists of a planar lamina, which smoothly transitions into the rod-shaped petiole. The labels top and bottom correspond to the cross-sections in Fig. 2. (© Plant Biomechanics Group)

Looking at serial cross-sections along this transition zone, the gradual change in shape between the individual sections is evident (Fig. 2). The cross-sectional shapes in the transition zone change from almost round in the petiole to a three-lobed star at the transition to the lamina. This morphological change gives first indications on the relevance of gradient structures for the connection of rod-shaped and planar elements. This morphological gradient becomes even more relevant when the typical type of mechanical load acting on a plant leaf is taken into account, i.e., high dynamic wind loads [2].

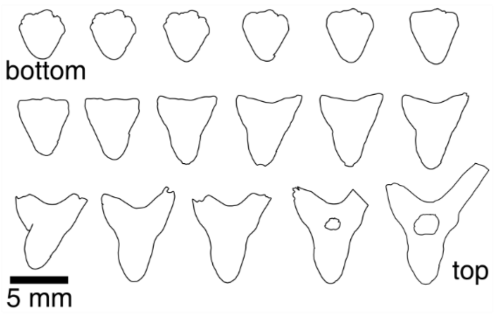

Fig. 2: The outlines of cross-sections through the petiole-lamina transition zone of a leaf of *Caladium bicolor* (Fig. 1) display the smooth shape gradient between petiole (bottom) and lamina (top). (© Plant Biomechanics Group)

In this regard, the arrangement of the vascular bundles on an anatomical level is also of great importance for the functionality and stability of the transition zone. On the one hand, the bundles are necessary for the transport of water and assimilate between the lamina, the petiole and the main plant body. On the other hand, the vascular system can also be considered as a fiber-reinforcement both in the lamina and in the petiole that serves biomechanical purposes [3]. The latter is particularly important, especially in the case of additional wind loading, for the transmission of force from the large-surface lamina via the petiole into the main plant body, i.e., stem or roots. In addition, for the genus *Caladium* fiber caps around the vascular bundles are described [4], which represent a further structural gradient at tissue level and thereby support the mechanical role of the vascular bundles.

Consequently, future work will focus on the histological quantification of the various tissues along the transition zone and on the biomechanical investigation of the transition zone under torsional and bending stresses. Moreover, the influence of mechanical environmental factors (in particular wind) on the morphology, anatomy and biomechanics of the transition zone will be investigated in a special setup in one of the phytochambers of the Botanic Garden Freiburg which allows for cultivating plants under controlled windy conditions.

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Full-field 3D deformation and displacement analyses on plant surfaces

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Within the framework of the CRC 141, the research projects A04 and A06 investigate how principles of plant movements and of plant stem-branch attachments can be abstracted and transferred to adaptive and/or light-weight biomimetic components for application in architecture. They are based on the interdisciplinary co-operation of biologists from the Plant Biomechanics Group from the University of Freiburg (PBG, PI: Prof. T. Speck, T. Masselter) and construction engineers and architects from the Institute of Building Structures and Structural Design (ITKE, PI: Prof. J. Knippers), the Institute for Structural Mechanics (IBB, PI: Prof. M. Bischoff), and the Institute for Textile and Fiber Technologies (ITFT, PI: Prof. G. T. Gresser) of the University of Stuttgart.

Moving plant structures, their structural basis and the biomechanical principles involved are of increasing interest for researchers in the context of biomimetic applications. Up to now, measuring continuous 3D displacement and deformation is methodically very complex.

Furthermore, plant movements often complicate respective analyses because of the temporal, dimensional and physical ranges in which they operate [1].

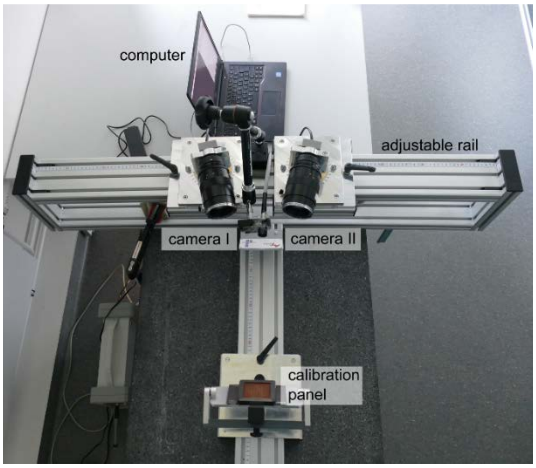

Fig. 1: Top view on the adjustable camera rail with time-lapse cameras mounted © Plant Biomechanics Group Freiburg

In principal, full-field deformation and displacement measurements of the surface of the study object (i.e., the motile plant structure) can be obtained by digital image correlation (DIC) [2]. Compared to 2D single camera recordings, a stereo-camera based method is more robust as it enables for valid out-of-plane analyses in a three-dimensional measuring volume. The commercially available GOM Aramis evaluation software allows for 3D analyses of entire surfaces. The major fields of application for this measuring system are automotive crash tests, the analyses of biological tissues for biomedical research as well as the quantification of technical materials during crack or tensile tests [3]. Aramis applies DIC algorithms onto imported stereo image stacks from two stereo-coupled cameras. An artificial speckle pattern on the specimen surface provides a bimodal distribution of the image pixels' grey-values which are used for the correlation algorithms. As a result, the region of interest is divided into smaller sub-areas (facets) which can then be tracked over time. The quality of the 3D surface reconstruction and the spatial measurement accuracy strongly depend on the surface contrast.

To test the method's applicability for a broad range of plant movements, different plant motions were analyzed. The desiccation-driven movements of pine cone scales (within 20 hours) and thereof inspired 3D printed replicas which mimic the bilayer structure of the biological role model [4] were investigated and compared, as well as the fast trap closure of active carnivorous Venus flytrap snap-traps (within 100-300 ms) which relies on a combination of hydraulic actuation and passive snap-buckling [5]. Additionally, tests with the branching regions tree-dimensionally deforming under bending loads were started as an example of externally induced plant movements.

Using an adjustable rail (custom-made by the Bio II/III workshop, University of Freiburg), two cameras were mounted at 25° with respect to each other facing the specimen. We used time-lapse cameras for recording the motions of the pine cone scale and its replica, and high-speed cameras for recording Venus flytrap closure. For bending tests high-speed and conventional cameras are used. To minimize perturbations of the cameras which result in measurement inaccuracies, tight mounting of the cameras onto the rail system and frame capture synchronization are required. The measuring volume is defined by a calibration process that transfers the axes of both 2D camera sensors into a 3D coordinate system [6].

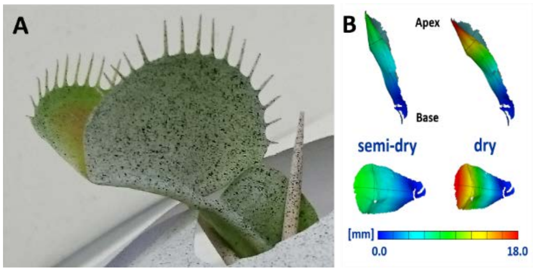

Fig. 2: A) Venus flytrap snap-trap prepared for analyses with sprayed on speckle pattern, B) displacement pattern during desiccation-driven motion of pine scale (upper images: lateral view; lower images: bottom view) © Plant Biomechanics Group Freiburg

The results of these comparative experiments are currently evaluated. To summarize, the presented method was successfully used to investigate biological movements over time in very high spatial resolution. Displacement as well as deformation and therefore strains can be measured over the entire scale surfaces, single points on the surface, or planes through the surface. The resulting data can also be used to create a 3D model of the specimen which can be merged and combined with other data sets (e.g. CAD data). The possibility to study and compare not just movement but also deformation, demonstrates its value for plant movement analyses and future developments of smart bio-inspired materials and materials systems.

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Morphological changes in Langmuir films of a crystallizable diblock copolymer with increasing surface density

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Films of a thickness of one molecule formed at interfaces have been used as models for the study of biomembranes and biological interactions [1]. Among the most widely investigated monomolecular systems, we find the amphiphilic compounds which provide a means to control structure formation at the air/water interface [2]. One expects that phase transitions like crystallization in quasi-2D and 3D lead to differences in morphologies. Therefore, we have investigated Langmuir films of a crystallizable diblock copolymer of poly-ethylene-oxide (PEO) and poly-L-lactic-acid (PLLA). In the bulk, the melting temperature of PEO and PLLA are distinctly different. However, due to the influence of the second block and confinement effects in quasi-2D we anticipate observing deviations from bulk values. Furthermore, the two blocks have different affinities to water and correspondingly different surface mobilities. Thus, even at temperatures below the lowest melting point of the two blocks, we are not certain that both blocks crystallize at the same time. Alternatively, crystallization of one block may drive crystallization of the second one. Accordingly, we aim to identify crucial parameters of crystal nucleation and growth.

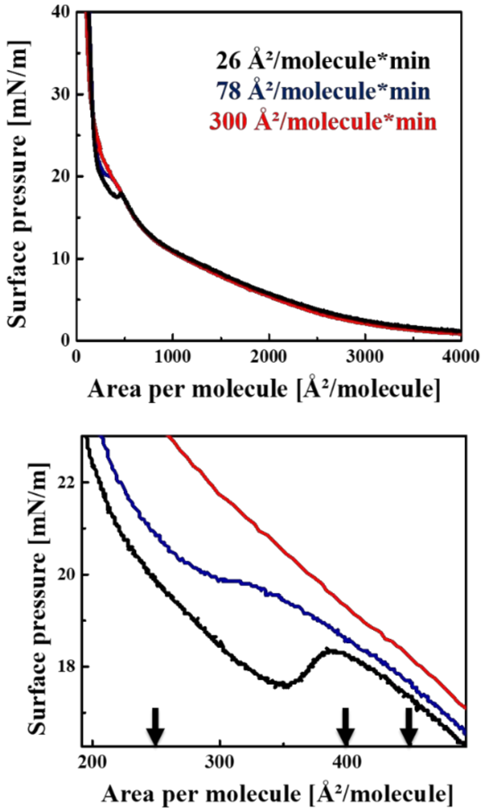

Fig. 1: Isotherms of PEO-PLLA measured at 20°C for different compression rates. At areas per molecules marked by the black arrows we have transferred the Langmuir film and investigated the resulting morphologies. © Experimental Polymer Physics, Freiburg.

For our study, we chose a block copolymer (BCP) with a low molecular weight of 3690 g/mol in order to enable fast kinetics of microstructure formation. The total length of the BCP in its crystalline state is around 20 nm. The molecular weights of both blocks are similar. However, the maximum length of the crystalline PLLA block is around 7 nm while the corresponding length of the PEO block is around 13 nm [3], [4].

Characterization of a Langmuir monolayer is provided through the measurement of the isotherm. Such a measurement records the surface pressure as a function of the mean surface area occupied per molecule during the compression with a constant rate and a constant temperature.

When Langmuir films of PEO-PLLA diblock copolymer were compressed at a high compression rate of 300 Å^2 /molecule*min, a smooth and monotonic increase in surface pressure was observed. At a moderate compression rate of 78 Å^2 /molecule*min, the isotherm showed a presence of a pseudo plateau region at values around 300 – 350 Å^2 /molecule. However, at a slower compression rate of 26 Å^2 /molecule*min, a decreasing surface pressure with decreasing area per molecule, a so-called depression appeared instead of the pseudo plateau. The dependence of the isotherms on the compression rate is depicted in Figure 1.

To explore the origin of the compression rate dependence, we examined the resulting morphological features and tried to relate them to the area per molecule at which the depression was observed. To visualize the corresponding morphologies by means of atomic force microscopy (AFM), we transferred the films onto a solid substrate, using the Langmuir-Schäfer technique. The arrows in Figure 1, indicate the positions where the films were transferred. The corresponding AFM images are shown in Figure 2.

Atomic force microscopy (AFM) images of the films transferred at an areal density of 450 Å^2 /molecule (before the area of the depression in surface pressure) revealed the presence of circular structures of bundles of fibers. The width of the individual fiber was observed to be around 7 nm, which is comparable with the maximum length of the PLLA block in its extended crystalline state. This suggests that these structures might consist of crystalline lamellae. The films transferred at an areal density of 225 Å^2 /molecule (after the area of depression in surface pressure) revealed areas consisting of a large number of parallel arranged fiber-like structures with a width of 7 nm as well. These results show that fibers are present before and after the area of depression, characterized by a similar width but a different geometrical organization. The fibers present a thermodynamically stable structure which might be crystalline. Here we can address the following question: how can we go from a circular arrangement to a parallel arrangement in a relatively small interval of surface density? Therefore, we investigated the morphology of the BCP Langmuir films at the area of 400 Å^2 /molecule between the areas of the two states. Our results (Figure 2) suggest that the transformation from circular to parallel arranged structures is indeed related to the breaking of the circles by increasing the surface density upon compression. Consequently, the surface pressure change, observed in the area of depression in the isotherm is related to a geometrical rearrangement of the structures after breaking.

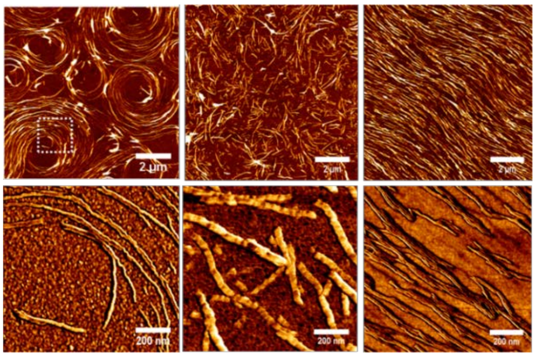

Fig. 2: AFM height images from left to right taken from a film transferred at areas 450,400 and 225 Å^2 /molecule as indicated in Figure 1 and their corresponding phase images from a small area. © Experimental Polymer Physics, Freiburg.

Further systematic studies are in progress which exploit additional in situ Brewster angle microscopy measurements, and focus on the structure formation at different compression rates.

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Analysis of *Physcomitrella* chloroplasts to reveal adaptation principles leading to structural stability at the nano-scale

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The cooperation project focuses on research of the plastoskeleton in the moss *Physcomitrella patens*. This adaptive structure is built by five different FtsZ (Filamentous temperature sensitive Z)-proteins, which are evolutionary ancestors of the eukaryotic cytoskeleton protein tubulin. These proteins assemble into microfilaments *in vivo* and *in vitro*, and are GTPases. These highly dynamic filaments can branch and can form homo- and hetero-filaments. Collectively, they provide stability to the photosynthetic organelles of this moss. Aim of this cooperation project is to describe and to model the dynamic adaptation of these filaments, to identify their principles and to transfer these across scales to building blocks in mechanics and in architecture. This wide-ranging interdisciplinary research programme is conducted by plant biologists of the University of Freiburg (PI: Prof. Dr. Ralf Reski) and engineers/mathematicians (PI: Prof. Oliver Röhrle) of the University of Stuttgart.

In 2018, we developed a method to reliably visualise FtsZ-based microfilaments in living moss cells, to obtain high-resolution 3D images of these structures, to extract physical features from these images, and to compute their characteristics [1]. This newly developed pipeline was used for a structural quantification of two of these networks [2], for the first time quantitatively discriminating between cellular microfilaments of similar phenotypical characteristics. To further enhance the utility, speed and accuracy of our pipeline, we subsequently employed machine learning, an automated method exploiting a random forest model [3].

First attempts to derive physical constraints of these networks via Atomic Force Microscopy with isolated single moss chloroplasts were successful.

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

The role of synthesis conditions for structural defects and lattice strain in *β*-TaON and their effect on photo- and photoelectron-catalysis

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Project funding: German Research Foundation (DFG) – Priority Programm 1613: “Fuels Produced Regeneratively Through Light-Driven Water Splitting: Clarification of the Elemental Processes Involved and Prospects for Implementation in Technological Concepts”, Project number: FI 1885/1-2

In consideration of the rising global energy demand and the environmental concerns raised by fossil fuels combustion, the production of clean and renewable fuels has become increasingly essential. [1] Because of its high energy density (142 MJ/kg [2]) and emission free combustion, hydrogen is one of the most promising alternatives to fossil fuels. In the context of establishing a sustainable hydrogen economy, emission free hydrogen production is crucial.

Photoelectrochemical (PEC) water splitting is considered to be one of the most elegant ways for sustainable hydrogen production. Sunlight, the most abundant renewable energy source, is converted by semiconductor electrodes into electric voltage which is used to electrolyze water into oxygen and hydrogen. Semiconductor materials that absorb a sufficient portion of solar light ($E_g \approx 2.1$ eV), separate and transport the charge carriers efficiently, thereby favoring the water splitting half-reactions at their surfaces, and that are stable in aqueous media under illumination are desired for the development of efficient PEC water splitting devices. In this context, especially the development of a well-performing photoanode for the water oxidation half reaction is an extensively investigated research subject.

Tantalum-based nitrides and oxide nitrides have been studied for many years due to their interesting defect chemistry and optical properties. Recently, they have also gained a lot of attention due to their potential application in visible light photocatalysis and photoelectrochemistry. [3-5] *β*-TaON turned out to be the most promising tantalum-based compound for PEC water splitting because of its band gap of 2.5 eV allowing a theoretical solar-to-hydrogen efficiency of about 10% [6], its band edge positions straddling the OER and HER redox potentials which principally enables overall water splitting, its stability in aqueous media, and its moderate cost and acceptable earth abundance.

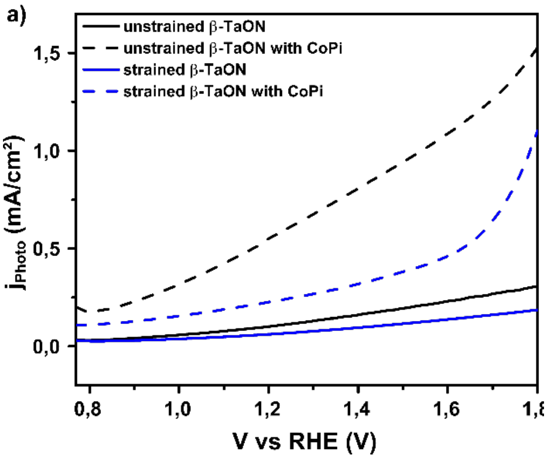

Fig. 1: PEC water oxidation experiments. a) j-V curves for water oxidation for strained and unstrained *β*-TaON with and without surface functionalization with CoPi water oxidation catalyst. b) photocurrent transients for strained and unstrained *β*-TaON samples without surface functionalization or c) with surface functionalization with CoPi catalyst.

In accordance, substantial progress has been made regarding the application of *β*-TaON for water splitting. [7-9] However, comparison of catalysts’ perfomances prepared in different laboratories is often critical. There is a great consensus that synthesis conditions play a crucial role in this context. [10-12] However, detailed analyses of the real structure of the products gained from different synthesis methods which might help to understand observed differences in photochemical activity is only rarely provided.

In the present work [13], synthesis conditions of β-TaON are related with its structural properties. Two different solid-state synthesis routes are used to prepare the nominally same phase-pure β-TaON material as revealed by x-ray diffraction measurements. However, as revealed by Rietveld analysis, neutron diffraction measurements and transmission electron microscopy (TEM) analysis, one synthesis route leads to a β-TaON modification which structurally is in good agreement with theory, whereas the other synthesis route leads to a β-TaON modification which is strongly affected by anisotropic microstrain. TEM investigations further revealed that the origin of the strain is due to lattice defects such as stacking faults.

The influence of the anisotropic microstrain in β-TaON on its photocatalytic activity regarding water oxidation was investigated by photocatalytic water oxidation measurements using $AgNO_3$ as sacrificial agent and measuring the amount of evolved oxygen by mass spectrometry. Additionally, PEC water oxidation experiments were carried out using electrodes prepared out of both powdered β-TaON compounds by an electrophoretic deposition method followed by a certain post-treatment (post-necking). [7] Both, photo- and photoelectrocatalytic water oxidation experiments revealed less water oxidation performance for the strained β-TaON samples. As can be seen in Figure 1a, PEC water oxidation performance expressed by photocurrents is significantly lower for the strained TaON electrodes before and after surface functionalization with CoPi water oxidation catalyst. [14] Hence, stacking faults/ anisotropic strain is highly detrimental regarding photochemical water oxidation. Furthermore, analysis of the photocurrent transients shown in Figure 1b and c revealed that the stacking faults most likely act as charge carrier traps hindering the photo-generated holes to diffuse to the reaction sites at the surface.

As such, this work highlights the importance of high crystallinity and defect minimization for semiconductors in the field of photo(electro)catalysis. In addition, detailed investigations of the semiconductors' microstructure is crucial in order to fully understand differences in photocatalytic and photoelectrochemical performance between samples of the same compound.

This work was published in "M. Rohloff, S. Cosgun, C. Massué, T. Lunkenbein, A. Senyshyn, M. Lerch*, A. Fischer*, M. Behrens*, *Z. Naturforsch. B.*, **2018**, *74(1)*, 71-83".

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High-quality perovskite absorber and hole transport layer for efficient perovskite solar cells

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Project funding: German Research Foundation (DFG) – Cooperative Research Centre – Advanced Optics for Perovskite-Silicon-Tandem Solar Cells“ (Oposit)

Perovskite solar cells (PSCs) based on $CH_3NH_3PbI_3$ have shown impressive power conversion efficiencies (PSCs) of over 23% in a single junction and over 27% in tandem configurations. In a typical single junction cell structure the $CH_3NH_3PbI_3$ absorber is sandwiched between an electron and a hole transport layer (ETL and HTL). When the device is irradiated, electron-hole-pairs are created in the absorber and then extracted by the ETL and HTL, respectively. For efficient carrier extraction which strongly affects the PSCs performance both the $CH_3NH_3PbI_3$ film quality and the contact layers (ETLs and HTLs) are important.

In order to control the $CH_3NH_3PbI_3$ film formation, several methods like anti-solvent dripping, solvent assisted annealing, etc. have been developed over the last few years to fabricate pin-hole free, flat films for high efficiencies. However, as these methods are applied only for small scale cells in laboratories, the challenge of making high-quality perovskite films in large scale still remains. Although vapor deposition and spray coating methods are two easily scalable methods, little effort has been invested in developing these methods for perovskites. Therefore, we have recently developed a co-evaporation and a hybrid evaporation-spray method in our lab for high-efficiency PSCs [1,2].

The HTL plays also an important role in preventing the direct contact of the perovskite absober with the metal contact and extracts successfully the positive charge (holes) from the perovskite absorber. In order to obtain high-performance solar cells the HTL should have a HOMO level above the valence band of perovskite. This configuration determines the open-circuit voltage of the solar cells. A good hole mobility, transparency, and stability are also required characteristics of HTLs. The most widely used HTL is spiro-OMeTAD (2,2,7,7-Tetrakis[N;N-di(4-methoxy-phenyl)amino]-9,9 spirobifluorene) which is applied in many perovskite works leading for the best PCE devices. Nevertheless, there are several drawbacks of spiro-OMeTAD such as high costs, modest hole mobility and conductivity. Thus dopants are always required. By adding dopants into the spiro-MeTAD strong optical absorption can be observed at around 520 nm which would limit the current of a tandem device.

In this work we have focused on the fabrication of high quality $CH_3NH_3PbI_3$ layers and an investigation of a HTL based on terthiophene using evaporation technique.

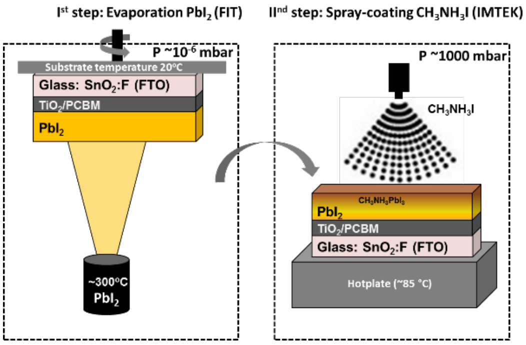


Fig. 1: Schematic diagram of the process for fabrication of perovskite based on $CH_3NH_3PbI_3$ absorber. © Laboratory for Photovoltaic Energy Conversion

(a) Fabrication of perovskite ($CH_3NH_3PbI_3$) absorber using evaporation/spray method

For the hybrid method a $CH_3NH_3PbI_3$ layer was obtained by the combination of evaporation of PbI_2 and spray-coating a solution of

CH_3NH_3I in isoproponal (IPA) (Fig. 1). The spray process has been performed in the junior research group of Severin Vierrath and Matthias Breitwieser at FIT and the Laboratory for MEMS Applications which has experience in the spraying of materials for different applications for electro-chemical energy conversion and storage.

The evaporated PbI_2 film with a thickness of about 264 nm (controlled by a quartz crystal microbalance) has a porous morphology with the material uniformly distributed on the whole surface of the substrate. Many of the particles of PbI_2 have a well-defined nanoplate shape (Fig. 2a), which is beneficial for the interpenetration of the sprayed MAI into the layer and thereby facilitating the complete conversion of PbI_2 into $CH_3NH_3PbI_3$ (Fig. 2b). The thickness of the absorber increased during the conversion from 264 nm (just PbI_2) to about 320 nm ($CH_3NH_3PbI_3$).

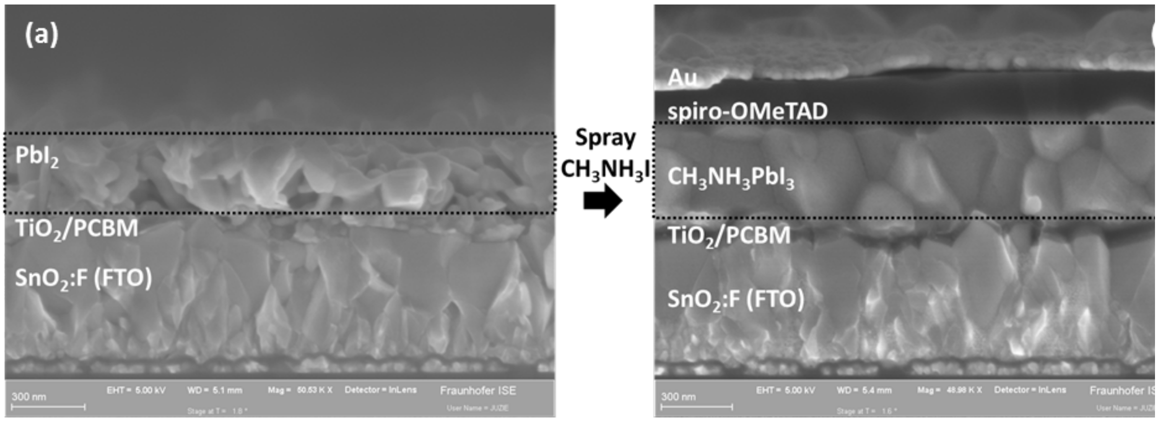


Fig. 2: Cross-sectional SEM images of (a) a stocked PbI_2 on ETL (TiO_2/PCBM) and (b) complete perovskite solar cell (*n-i-p* structure) prepared by evaporation/spray method. © Laboratory for Photovoltaic Energy Conversion

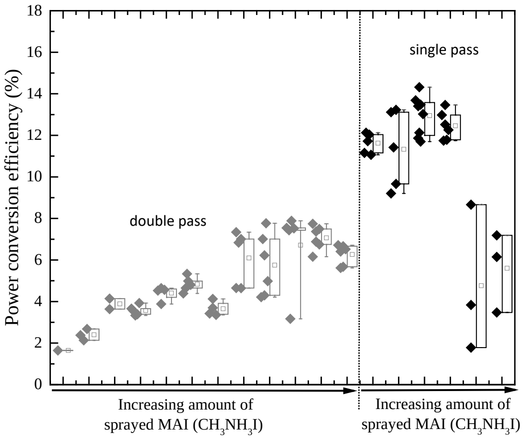


Fig. 3: Statistics of PCEs vs amount of sprayed MAI of perovskite solar cells prepared by evaporation/spray method. © Laboratory for Photovoltaic Energy Conversion

Figure 3 represents the PCEs of perovskite solar cells versus the sprayed amount of MAI using double and single spray passes. After the optimization process and a selection of the best conditions, a maximum PCE of 14.3% has been obtained for devices with a single spray pass.

All results of section (a) are preliminary results for joint research activities of Ludmila Cojocaru, Stefan Glunz, Severin Vierrath and Matthias Breitwieser. A joint DFG proposal and a joint journal publication [2] was submitted at the end of 2018.

(b) Synthesis of a poly(terthiophene) thin film on conductive substrates using an evaporation method

The work in this part has been performed by a visitor PhD student Koki Suwa (supervisor Professor Hiroyuki Nishide) from Waseda University, Japan, who has joined the group of Professor Stefan Glunz for a period of three months. The aim of this work is to apply poly(terthiophene) process already developed by the group of Professor Nishide [3] to prepare p-type electrode for perovskite solar cells using our own co-evaporated perovskite absorber [1].

The first step to the synthesis of the terthiophene polymer involved in this study is illustrated in Figure 4. Monomer films were prepared by sublimation of terthiophene at different temperatures for 1 h, followed by the oxidation of the monomer layers by Iodide (I_2) to form the final terthiophene polymer layers on top of ITO substrates.

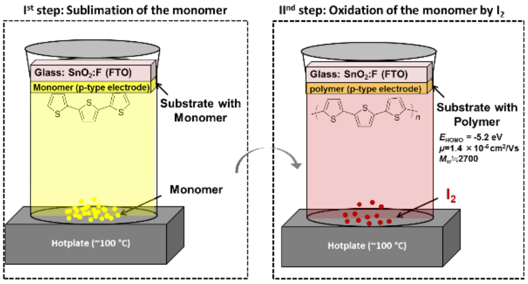


Fig. 4: Sublimation-polymerization process for fabrication of poly(terthiophene) layers. © Laboratory for Photovoltaic Energy Conversion

We have seen that the thickness of the poly(terthiophene) film on ITO depends as well on the time the sample was exposed as on the temperature of sublimation. Figure 5 shows AFM images of the terthiophene polymers deposited at 90 °C, 110 °C, 130 °C, and 145 °C for 1 h on ITO substrates.

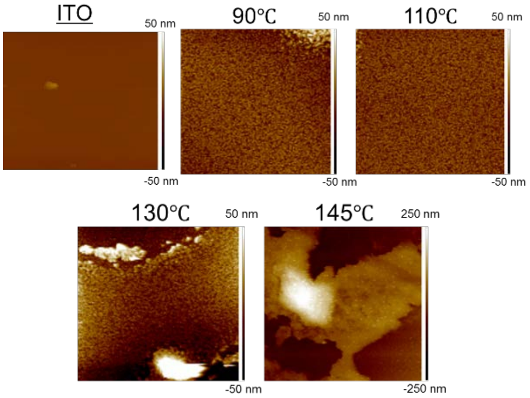


Fig. 5: AFM images of the poly(terthiophene) hole transport layers prepared on ITO at different sublimation temperatures. © Laboratory for Photovoltaic Energy Conversion

The films are uniform and densely packed when the sublimation temperatures are 90 °C and 110 °C. AFM images also show that the films became inhomogeneous when the temperature increases (130 °C and 145 °C). That is probably due to the concentrated amount of evaporated monomer on the beaker and the thickness of the film which dramatically increases at temperatures of 130 and 145 °C. After the experiment the film can be easy peeled off the ITO substrates. This confirms that the film thickness was too high. In order to decrease the thickness of the monomer the sublimation time was reduced from 1 h to 30 min at a temperature of 130 °C. The effect of the thickness variation was clearly observed in the photovoltaic response of the devices, by decreasing the thickness from 100 nm to 30 nm an increase in PCEs from 2.4 % to 3.3% was achieved, respectively.

After adopting this process of sublimation at a simple setup we moved on to a controllable process using an evaporation chamber (Fig. 6). The evaporation chamber was operated under a vacuum pressure of about 10^{-5} mbar. At the beginning of the controllable process the first run of terthiophene monomer was evaporated on the substrates at around 30 °C and a rate of 1 Å s^{-1}. Finally the film was reabsorbed from the surface of the substrates and no film was formed. In a next step the temperature was increased to about 60 °C where a higher rate was observed and a layer of terthiophene monomer of ~30 nm was successfully deposited within 15 s. Subsequently the layer was oxidized by I_2.

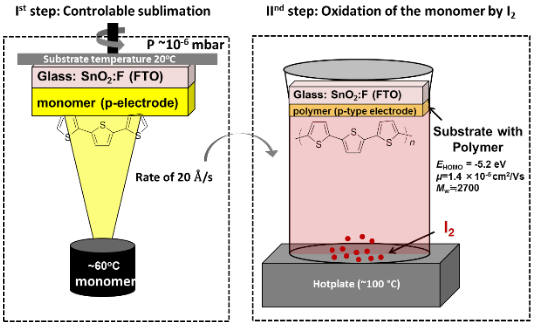


Fig. 6: Sublimation of terthiophene monomer in a controlled setup. © Laboratory for Photovoltaic Energy Conversion

To demonstrate the compatibility of the poly(terthiophene) as hole transport films with co-evaporated perovskite, devices with a configuration of ITO/ poly(terthiophene)/$CH_3NH_3PbI_3$/PCBM(AZO)/Au were fabricated using monomer layers prepared by the simple and the controllable setup. Figure 7 shows a typical cross-sectional SEM image of a complete device using poly(terthiophene) as

HTL. The thickness of the HTL was calculated to be around 20 nm and 30 nm for the simple and the controllable process, respectively. The $CH_3NH_3PbI_3$ perovskite film is shown to be uniform, fully covering the poly(terthiophene) layer with an optimized thickness of around 320 nm. On top of perovskite a layer of 20 nm PCBM (AZO) was spin-coated.

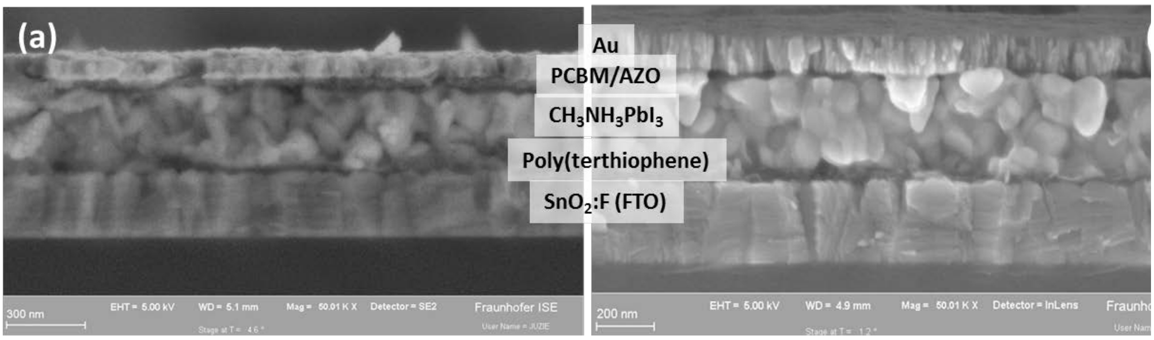


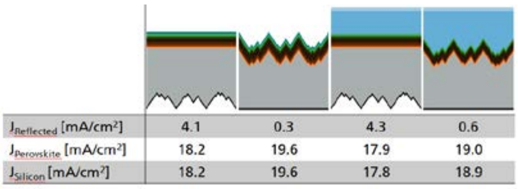
Fig. 7: Cross-sectional SEM images of perovskite solar cells (*p-i-n* structure) prepared by co-evaporation using poly(terthiophene) as HTL, terthiophene layer prepared using (a) uncontrolled and (b) controlled setup. © Laboratory for Photovoltaic Energy Conversion

The best-performing cell for the uncontrollable poly(terthiophene) layer device exhibits a PCE of 3.31% with an open-circuit voltage (V_{OC}) of 0.952 V, a short-circuit current density (J_{SC}) of 5.6 mA cm^{-2}, and a fill factor (FF) of 62.2%. For the controlled evaporated poly(terthiophene) films, the best cell exhibits a V_{OC} of 0.951 V, a higher J_{SC} of 9.1 mA cm^{-2}, and a FF of 44.4, resulting in a PCE of 3.84 %.

At this stage the PCEs of cells are low but further optimization of deposition processes here including the doping of HTL and thickness may help to enhance the PCEs of perovskite solar cells and then application for tandem solar cells configuration.

(c) Optical simulation of perovskite-silicon tandem solar cells

A very relevant question for the fabrication of perovskite-silicon tandem solar cells is whether a textured silicon front interface is required to reach high short circuit current densities. This was investigated using optical simulation, namely the OPTOS formalism, which was successfully applied to single-junction solar cells in the last years and has been extended to tandem solar cell within this year [4]. Fig. 8 gives a short summary of the results, comparing the photocurrent densities of tandem cell and module configurations with textured silicon front or rear side [4,5]. For the investigated case, the random pyramid structure at the front side results in a significant reduction of the reflectance and thereby leads to a higher photocurrent in the perovskite as well as the silicon absorber.



$J_{Reflected}$ [mA/cm²]	4.1	0.3	4.3	0.6
$J_{Perovskite}$ [mA/cm²]	18.2	19.6	17.9	19.0
$J_{Silicon}$ [mA/cm²]	18.2	19.6	17.8	18.9

Fig. 8: Summary of the simulation based performance between perovskite-silicon tandem solar cells textured silicon front or rear side. © Laboratory for Photovoltaic Energy Conversion

(d) Summary

In summary, we present a novel production route for perovskite solar cells, based on a hybrid deposition using evaporation of PbI_2 and spray-coating of MAI. With this method we could obtain high quality perovskite absorber and in the optimal conditions a maximum PCE of 14.3% was achieved.

We have also demonstrated an effective low-temperature vacuum deposition process for poly(terthiophene) as HTL for perovskite solar cells via reaction of sublimation/oxidation of a terthiophene monomer layer. Device characterization shows that efficiencies are slightly higher for a controlled process which takes extremely short time of about 15 s to obtain a layer of 30 nm. Along with these advantages, the evaporated monomer approach is a low-temperature process with prospects for large area deposition, as it supports features that are highly advantageous for tandem solar cell applications. Also the simulations show that the ability to prepare perovskite solar cells on textured interfaces is optically superior and therefore highly relevant.

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Quantitative synchrotron X-ray tomography of the material-tissue interface in rat cortex implanted with neural probes

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In neuroscience, gathering functional information of brain tissue is required in order to improve the understanding of neural circuits and interactions between neurons and glial cells. In order to investigate brain function on the level of single unit activity, implantable neural probes are used. While this type of probes provides outstanding possibilities regarding recording functional data of single neurons compared to non-invasive measurement techniques, brain tissue damage upon the trauma of probe insertion as well as long-term effects facilitated by the host's immune system, the so-called foreign body response, impair signal quality and long-term stability. For example, histological changes in the form of a glial scar occur upon implantation, accompanied by neuronal cell death in close proximity of the implanted probe.

Thus, neural probes need to be optimized towards high biocompatibility, suppressing immune responses and tissue damage as much as possible. The project CAPRI (characterization of probe interactions with host tissue) focused on the interplay between brain tissue and implanted neural probes. Since elucidating the local effect of neural probes on brain tissue requires sophisticated imaging approaches capable of investigating probe and tissue simultaneously, a novel tomographic approach was developed. Using synchrotron X-ray tomography, 3D imaging of a neural probe and the surrounding brain tissue is possible. Technically similar to computed tomography (CT) in clinical applications, yet with a substantially higher spatial resolution of < 1 µm³ and with remarkably higher contrast from soft tissue, resin-embedded brain cortex tissue of rats implanted with flexible neural probes was investigated.

Synchrotron X-ray tomography allowed the distinction of cells, blood vessels, and electrode sites on the probe (see Fig. 1a and b). Compared to standard methods such as immunohistochemistry followed by light microscopic imaging or electron microscopy on heavy metal stained tissue, this approach can be performed without the requirement of physical sectioning or tissue contrasting. In addition, this tomographic imaging approach gathers 3D data in the surrounding of a neural probe whereas the aforementioned techniques are typically only employed on single 2D tissue sections or very small sample volumes for imaging. Thus, synchrotron X-ray tomography reduces time required for sample preparation and increases imaging speed significantly when volume information is requested. Further, artefacts from probe removal prior to physical sectioning of the tissue or artefacts from sectioning of a neural probe incorporated in brain tissue are avoided. Besides qualitative information from the tissue, synchrotron X-ray tomography also allows quantification of tissue characteristics. For example, the distance between tissue and blood vessels increased in rat brain cortex upon probe implantation (Fig. 1c). This first-time study demonstrates a way for simultaneous 3D investigation of brain tissue with implanted probe, providing information beyond what was hitherto possible.

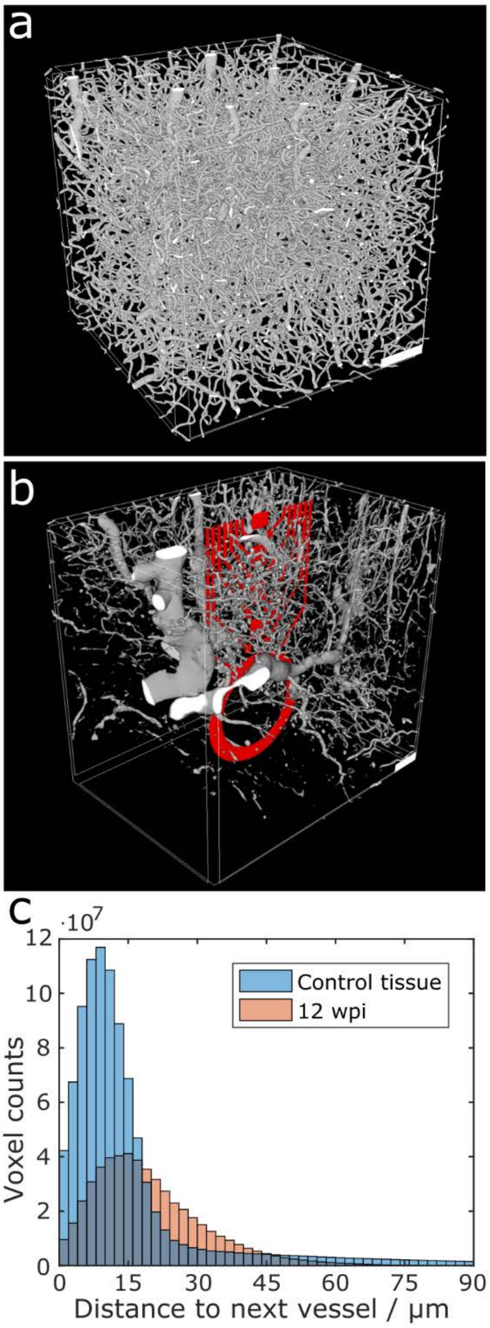

Fig. 1: Blood vessels in rat cortex tissue and quantification of vessel distances. **a)** Vasculature in rat brain cortex and **b)** vasculature in rat brain cortex 12 weeks post implantation of a neural probe (12 wpi). Electrode sites of the neural probe are represented in red. Scale bars in both images equal 100 µm. **c)** Quantification of distances from within the tissue towards the next blood vessel. (© Electrochemical Energy Systems Group)

Micro tomographic investigation on Li-Air (Li-O_2) batteries

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Project funding: Humboldt Research Fellowship for Postdoctoral Researchers, Alexander von Humboldt (AvH) Foundation

This project intends to investigate lithium-air (Li-O_2) batteries by tomography. With this 3D technique, we will develop an understanding of the relation between electrode morphology and mass transportation processes in Li-air batteries upon cycling to understand degradation mechanisms.

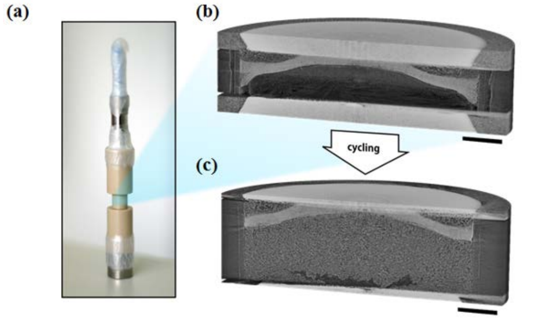

Fig. 1. (a) Digital image of a homemade Li-air battery for tomography analysis, (b) three-dimensional representation of a fresh Li-air cell. The scale bar represents 500 µm, and (c) three-dimensional representation of a Li-air cell after 5 cycles. The scale bar represents 500 µm. (© Electrochemical Energy Systems (EES) Group)

The rechargeable non-aqueous lithium-oxygen (Li-O_2) battery expanded rapid interest in recent years due to its intrinsically very high theoretical gravimetric energy that far exceeds that of Li-ion batteries [1]. During battery discharge, the Li-metal anode is oxidized, releasing Li^+ into electrolyte. O_2 from the air enters the porous cathode and reacts with Li^+ to form lithium peroxide (Li_2O_2). The process is reversed during charging [2]. The micro structure of the cathode and especially the morphology evolution of the discharge product (usually Li_2O_2) during the battery operation have a pronounced influence on the Li-O_2 battery performance [3]. Traditional 2D measurements e.g. by SEM or TEM only provide limited morphological information on the cathode surface. To date, there have been rather few studies of 3D investigations on electrodes for aprotic Li-O_2 battery. This project aims to use quantitative three-dimensional (3D) tomography analysis to "see through" the whole cathode upon battery aging.

Tomography is an effective method for the reconstruction of three dimensional (3D) structures from the nanometer scale to the centimeter scale. It provides quantitative analysis of morphology and morphological changes (including volume change, feature size, porosity, specific surface area). Also, it allows to access transport parameters, such as electrical conductivity and ionic diffusivity or morphological changes during battery operation [4].

Li-air cell that is suitable for tomography measurement was made (Fig. 1a). First, tomography on a fresh Li-air battery was performed. The three-dimensional (3D) represented result is shown in Fig. 1b, with the porous cathode, separator, and metallic lithium anode in the pristine state (without cycling). Meanwhile, another Li-air battery was cycled with a voltage range of 2.35-4.5 V (vs. Li^+/Li) at a current density of 0.1mA cm^{-2}. Then tomography was performed after 5 cycles. The 3D result is shown in Fig. 1c. Fig. 2 provides the discharge and charge curves that corresponded to Fig. 1c.

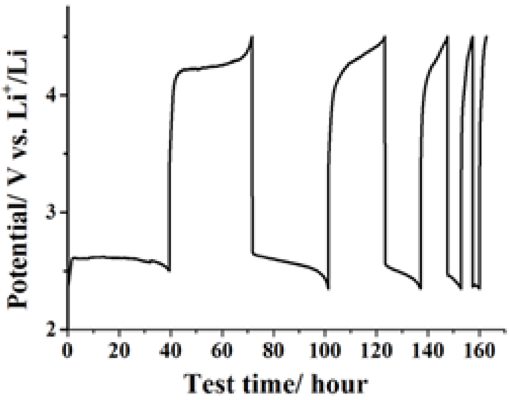

Fig. 2. Cycling curves of a Li-air cell with a voltage range 2.35-4.5 V (vs. Li^+/Li) at a current density of 0.1mA cm^{-2}. (© Electrochemical Energy Systems (EES) Group)

Morphological change in cathode part is impossible to observe clearly due to limited resolution of the machine. However, metallic dense Li anode almost changed into microporous structure, with the thickness becoming approximately twice. Another interesting point is that the Li microstructure formation starts from the edge to the center of the Li anode, with some dense Li left after cycling. Further investigation is still in progress.

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CORE FACILITY "IMAGING OF MATERIALS SYSTEMS"

Core Facility 1: specialized laboratory for microscopy and tomography

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[1]FIT Freiburg Center for Interactive Materials and Bioinspired Technologies, [2]Institute for Macromolecular Chemistry, [3]Institute of Inorganic and Analytical Chemistry

1. Work focus

Material science microscopy with focus on tomography

- High Resolution Transmission Electron Microscopy
- Cryo Electron Microscopy
- Scanning Electron Microscopy
- FIB/SEM
- Atomic Force Microscopy
- µ-CT
- Light Microscopy

The seven new research microscopes and periphery devices (see equipment details) are already demonstrating their potential and are building an important research infrastructure for both, current and future FIT research works. The special lab can now deliver competent works in the modern electron microscopy area.

2. Equipment and research examples:

The 200 kV TEM / STEM instrument, Talos F200X, is an atomically resolving, state-of-the-art high-performance system. With X-FEG emitter, Super-X EDX system, TEM and STEM with extensive detector equipment, a high-performance camera, different sample holders for different applications and tomography equipment, it is ideally suited for all high resolution (2D and 3D) and / or analytic needs.

The smaller Talos L120C is a practical 120 kV TEM device with LaB6 emitter. In addition to standard measurements, it has a Cryo equipment with special sample holder and Vitrobot preparation device and it is fully equipped for the TEM Tilt Series Tomography. The high-quality Ceta camera allows both high-quality images and high throughput with low electron doses, and makes tilt (and cryo-tilt) series for tomography possible.

The FIB/SEM system Scios 2 is a high-performance SEM device combined with a Focused Ion Beam column and therefore particularly well suited for slice serial tomography and for the production of TEM lamellae. The powerful EDX system allows analytics as well as element-specific tomography.

The Leica ICE high-pressure freezer with EM AFS2 and EM FSP is an important peripheral device for the non-destructive preservation and preparation of aqueous samples, in a way that their structure can be investigated in the as-native, aqueous state by means of electron microscopy. Compared to the atmospheric pressure Vitrobot, the high-pressure technique (200 MPa) allows vitrification of water-containing samples with larger volumes (up to a thickness of about 150 µm). This allows in particular the study of a) biological samples and b) technically functional materials such as e.g. from a polymer electrolyte fuel cell. After the subsequent semi-automatic dyeing and embedding, the sample is in a microtomable form. It can be measured directly as well as form the basis for tomography.

200 kV TEM/STEM: Talos F200X:

- X-FEG High-brightness Emitter
- Super-X Super Fast EDX System
- HR-STEM (HAADF, BF, DF)
- Tomography for TEM, STEM und EDX
- Cryo-Tomography
- idpc, ddpc
- Piezo-Stage 20pm
- Low-Dose
- Double Tilt Holder
- Resolution < 0.1 nm
- Ceta 16 Megapixel Digital Camera

Fig. 1: The Talos F200X HR-TEM in the FIT (© Thomann)

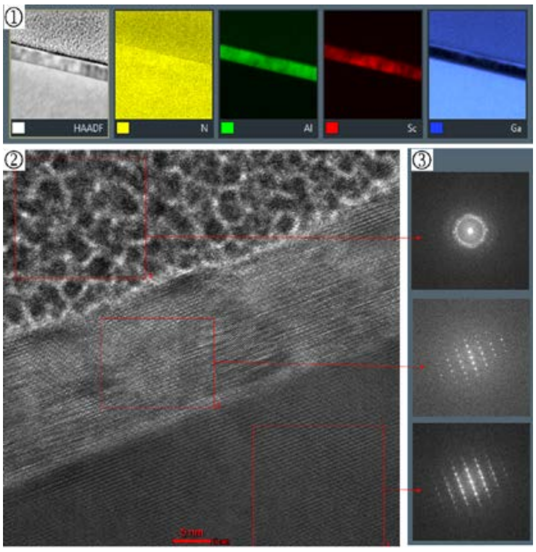

Fig. 2: HR-TEM (Talos F200X) image, (Sc,Al)N / GaN multilayer – sample AK Fiederle (© Thomann)

120 kV TEM: Talos L120C G2:

- LaB6 cathode
- tomography equipment
- cryo TEM
- cryo-tomography
- Low-Dose

Fig. 3: The TEM Talos L120C in the FIT (© Thomann)

FIB/SEM Anlage - Scios2:

- 30 kV
- Gallium-ion-column
- SE, T1, T2 and DBS Detectors
- C and Platin deposition
- Tomography equipment
- 70mm2 EDX System
- EDX
- Micromanipulator
- Preparation of TEM Lamella

Fig. 4: FIB / SEM system Scios 2 in the FIT (© Thomann)

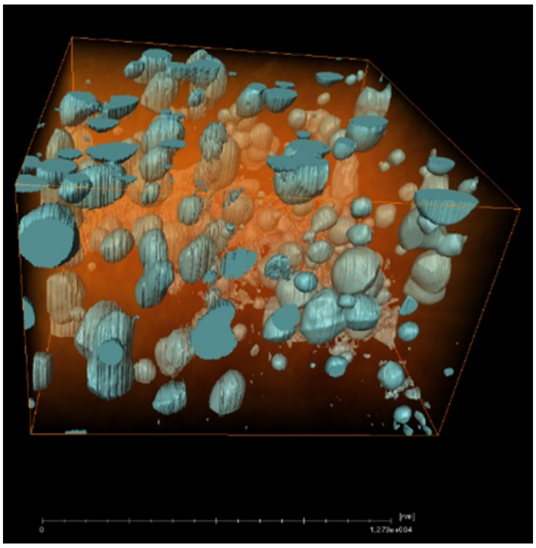

Fig. 5: 3D reconstruction (tomography) of a FIB / SEM section series of a stainless steel (alloy), created at the Scios 2 in the FIT (© Thomann)

µ-ct instrument (X-ray Tomography): Sky-Scan 1272:

- X-ray source: 20-100kV,10W,<5 µm spot size @ 4W
- X-ray detector: 16Mp, 14-bit cooled CCD fiber-optically coupled to scintillator

- Maximum object size 75mm in diameter using offset scan (27mm in fast single scan)
- Detail detectability 0.35 µm (16Mp) at highest magnification

AFM MultiMode Nanoscope 8:

- Contact Mode
- Tapping Mode
- Nano indentation
- Nano scratch test
- PeakForce Tapping
- PeakForce QNM
- vertical resolution of less than 0.05 nm possible,
- lateral resolution of less than 5 angstroms possible
- lateral scan width up to 170µm possible

Confocal 3D-single-photon-fluorescence microscope LSM: MicroTime 200

- FLIM, FRET, FCS. etc.
- Single Photon Counting Modi (SPAD); 50 µm, 100 µm
- TTTR data aquisition

High Pressure Freezer - LEICA ICE AFS2 FSP:

- Vitrification of aqueous samples at a pressure of 200 MPa
- Automatic process
- Freeze substitution
- Automatic dosing and embedding
- Light stimulation

3. Activities:

In 2018, all the major research electron microscopes were integrated in the special laboratory and successfully used for and by different research groups within the FIT research networks. Expertise works were offered by the Core Facility staff, which was followed by giving regular trainings to PhD students and others, focused on their respective individual requirements.

CORE FACILITY "FUNCTIONAL PROCESSING"

Polymer-based optical sensor platform with integrated light source

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Project funding: German Research Foundation (DFG)

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. Optical sensors based on evanescent field sensing provide very high selectivity and sensitivity for the detection of chemical and biological substances distributed in liquids or gases. By simply replacing the sensing layer, different kinds of substances could be detected by using the same sensor platform. Unfortunately, till now, such kind of sensor platforms are mainly fabricated on rigid substrates, such as glass or semiconductor materials with relatively high fabrication cost and complicated manufacturing processes. In the last couple of decades, polymer based optical devices are drawing more and more attentions due to its low cost, simple processing abilities and reliability for mass production. Besides of that, polymeric materials possess lots of unique properties such as wide spectral transparent window, high flexibility and good biocompatibility. They could be easily processed by conventional and unconventional fabrication methods and their properties could be tuned even during the manufacturing processes.

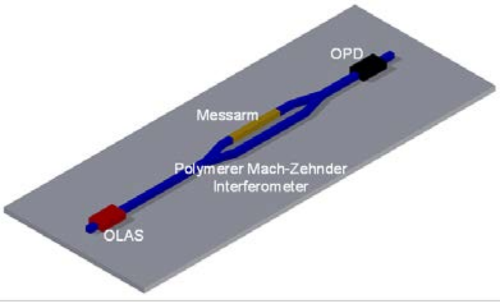

Fig. 1: Schematic view of Mach-Zehnder interferometer.
© Core Facility 2, FIT, Freiburg

In this DFG project, a planar optical sensor platform (Fig. 1) 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. In order to realize such kind of polymer based sensor platform, various technologies and processes have to be developed and optimised in Core Facility 2.

In order to realize the integration purpose, a straightforward Combined Nanoimprint and Photolithography (CNP) replication technique with extremely high reproducibility and high resolution will be developed and optimized. By using the CNP process, laser structures, in the dimension of nano- (DFB gratings) and micrometer (waveguides), will be fabricated in one step with high precision and low cost.

In this project, the possibility to produce the polymer based OLAS and OPDs by means of aerosol printing technology will be also thoroughly investigated. In the fabrication process, the pinholes and other defects which may affect the functionality of the devices have to be avoid.

A major challenge for the use of polymer lasers is their sensitivity to the various harsh environments such as oxygen and humidity. A proper encapsulation of the polymer laser is essential to extend the sensor lifetime. In this project, a novel reactive laminating process would be developed to produce a functionalized encapsulation layer.

Another focus of the project is the investigation of final functionality of the sensor platform. The sensor platform depends on detecting the shift of the Bragg wavelength due to the change of the effective refractive index on the sensing area. Therefore, any variation that affects the refractive index would results in a signal change in the spectrum. By encoded directly the measurement results, the refractive index change could be measured precisely.

A team of experts in polymer technology and polymer processing (Core Facility 2, FIT, and University of Freiburg) and experts in organic optoelectronics (TU Braunschweig) will work together in this project.

CORE FACILITY "MODELLING AND SIMULATION OF MATERIALS SYSTEMS"

Simulation of bond breaking induced by molecule stretching with constant velocity

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Project funding: German research foundation (DFG) WA1687/9-1.

Since the end of the last century, more and more experimental results have been published where single molecules were stretched up to bond breaking to measure the rupture force [1-3]. One end of the molecule is often attached to a fixed substrate while the other end is hold for instance with the tip of an atomic force microscopy (AFM) and pulled with constant velocity. The aim of the present study is the simulation of these experiments and the calculation of the rupture force.

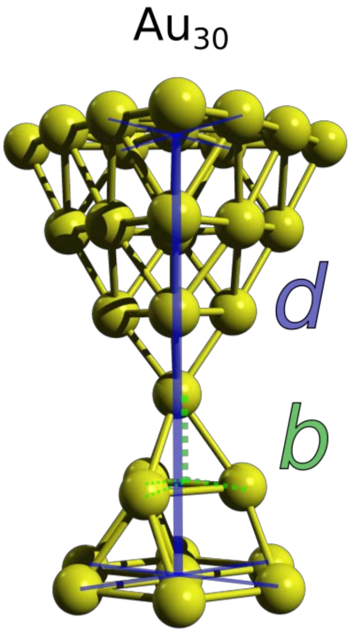

Fig. 1: Molecule structure of Au_{30} with definitions of end-to-end distance d and bond length b. The lowest layer was always fixed and the highest layer was parallel shifted when d was changed and was also fixed during all structure optimizations. © Functional Nanosystems Group, Freiburg.

We start with breaking gold bonds. We describe thin gold chains by the model “molecule” of length d similar to the model applied in Pobelov et al. [3]. The Au_{30} structure is fused from tetrahedral Au_{20} and Au_{10} as depicted in Fig. 1. The bond indicated with length b is the weakest bond which breaks first. The force-free energy landscape $U(d,b)$ with all other degrees of freedom energetically optimized is deformed by the potential $U_{\text{ext}}(d;t)$ created by the external force at time t, hence the total potential is

$$U_{\text{tot}}(d,b;t) = U(d,b) + U_{\text{ext}}(d;t).$$

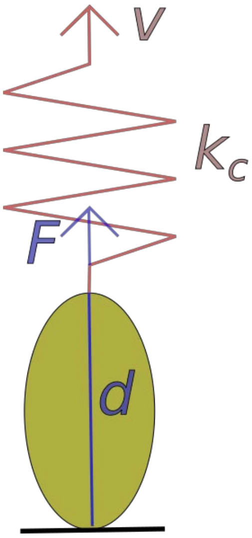

Fig. 2: Schema of the spring model. The molecule with end-to-end distance d (yellow area) connected to a fixed wall and a spring (red zigzag line). The spring with spring constant k_c represents the cantilever moving with constant velocity v at the open end and transferring force F to the molecule. © Functional Nanosystems Group, Freiburg.

The force is transferred from the AFM cantilever tip to the molecule. We model the cantilever as a spring with spring constant k_c, as depicted in Fig. 2. This leads to a quadratic dependence of the external potential on the molecular extension $\Delta d = d - d_0$ relative to its equilibrium length d_0. The minimum of the quadratic potential moves with the velocity v of the cantilever base to larger Δd as described by the potential

$$U_{\text{ext}}(d;t) = \frac{1}{2} k_c \Delta d^2 - k_c v t \Delta d$$

and the corresponding external force is

$$F(d;t) = k_c(vt - \Delta d).$$

We obtained time-dependent activation energies in $U_{\mathrm{tot}}(d,b;t)$ with the *three-segments COGEF* (3S-COGEF) method where a universal path through the force-deformed energy landscape is obtained [4] containing reactant, transition and product states for all t, see FIT report 2016.

We used the Eyring equation to obtain time-dependent rate constants for the bond breaking and the reverse reaction. The rate constants define the probability flux from the intact to the broken configuration, so that the probability $P(t)$ of the broken form can be calculated numerically. $P(t)$ is zero initially and goes to unity for large t. The states of the molecule (intact and broken) correspond to different molecular lengths d and therefore lead to different external forces $F(d;t)$ at a given t. We calculated $F(t)$ as the average $F(d;t)$ weighted by the probabilities of the intact (1-$P(t)$) and the broken configuration $P(t)$. $F(t)$ increases first due to molecular stretching, but goes to zero for large t after bond breaking. The maximum of $F(t)$ is here referred to as the measured rupture force F_{rup}.

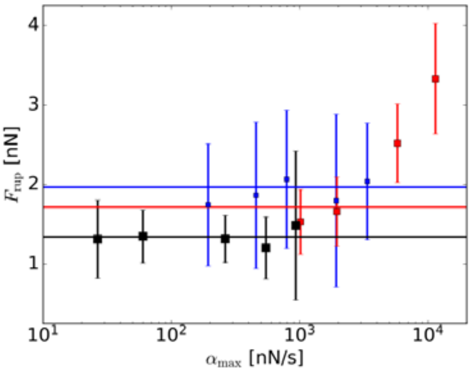

Fig. 3: Calculated rupture force of Au_{30} (solid lines)at room temperature in dependence of the maximum force loading rate $\alpha_{\max} = k_c v$ and spring constant k_c = 5 N/m (black), 10 N/m (red) and 40 N/m (blue). These are compared to corresponding experimental results (squares with error bars) adapted from Pobelov et al. [3]. © Functional Nanosystems Group, Freiburg.

Fig. 3 shows the excellent agreement between calculated and experimental F_{rup} up to $\alpha_{\max} = k_c v$ =5000 nN/s where an increase was assumed experimentally for a single spring constant only. Our calculation shows also an increase of F_{rup} for this spring constant, however at the much higher value of $\alpha_{\max} = 10^{10}$ nN/s (not shown).

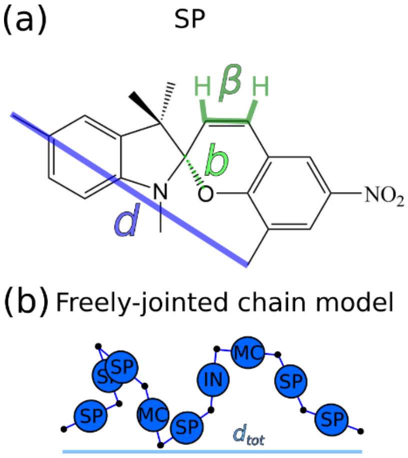

Fig. 4: (a) SP structure with definition of distance d, bond length b and dihedral angle β. (b) Schema of the freely-jointed chain model where the effect of the entropic force is approximately included. © Functional Nanosystems Group, Freiburg.

Next, we consider a polymer chain with spiropyran (SP) monomers as investigated in the experiment of Gossweiler et al. [2]. We have shown earlier that two energy barriers must be overcome that SP reaches the broken and planar merocyanine form (MC) induced by external forces, see FIT reports 2016 and 2017. As above, activation energies were obtained with the 3S-COGEF method in the energy landscapes $U_{\mathrm{tot}}(d,b;t)$ [first barrier] and U_{tot}(d,β;t) (second barrier) [definitions in Fig. 4(a)], where $U_{\mathrm{ext}}(d;t) = -F(t)\Delta d$ is used for simplicity as the effective spring constant is influenced by the polymer itself. SP, MC and intermediate (IN) forms, as well as two co-monomers are taken into account in the simulated polymer, see Fig. 4(b) which shows only SP, IN and MC monomers for simplicity. Application of the freely-jointed chain model adds the effect of the entropic force and, together with the spring model (Fig. 2), allows to obtain the external force $F(t)$ for given velocity and spring constant iteratively of the cantilever known for this experiment. $F(t)$ depends on the number of monomers N which we obtain from the experimental force-extension curve ($\mathrm{N} = 137$).

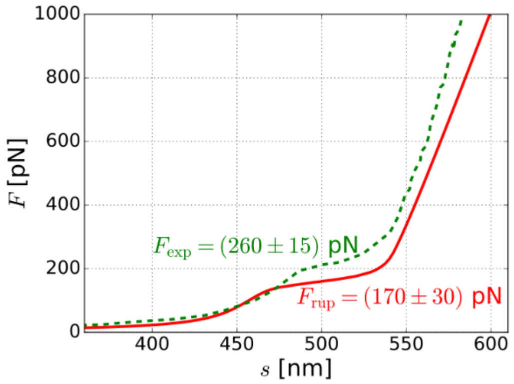

Fig. 5: External force F over length of polymer plus cantilever $s = vt$. The rupture force F_{rup} is indicated. The calculated force (red solid line) is compared to the experimental force (green dashed line) adapted from Gossweiler et al. [2]. © Functional Nanosystems Group, Freiburg.

Calculated and experimental force-extension curves are compared in Fig. 5. These curves qualitatively agree and our model can clearly explain their shape. The slight increase for small extensions s results from the entropic force due to polymer unfolding and gets more energetic for larger s due to SP stretching. The plateau is caused by successive bond breakings b and the transition from SP to MC. The final increase describes pure MC stretching. The width of the plateau is very similar between experiment and calculation. The calculated rupture force defined by the height of the plateau is slightly smaller compared to experimental value but is much more accurate compared to the result from simpler models [4].

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PROJECTS

GROWBOT

Towards a new generation of plant-inspired growing artefacts

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

Plants are still a quite unexplored model in robotics and ICT technologies, as their sessile nature leads to think that they do not move. Instead, they move 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.

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). Energy efficiency will be intrinsic to such approach, but novel bio-hybrid energy harvesting solutions will be also implemented to generate energy by interfacing soft technologies with real plants. Perception and behaviour will be based on the adaptive strategies that allow climbing plants to explore the environment, described mathematically after experimental observations.

GrowBot would contribute to consolidate this ground-breaking and pioneering research area on plant-inspired robotics that, although still in its infancy, can represent a revolutionary approach in robotics, as it has already happened with plant-inspired solutions in material science. 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.

The Plant Biomechanics Group 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 studies on climbing plants as concept generators for a new paradigm of movement in robotics will be carried out in close collaboration with the working group of Nick Rowe from the institute “Botanique et bioinformatique de l’architecture des plantes, UMR – AMAP” in Montpellier, France.

GROWBOT

www.growbot.eu

SFB-TRR 141

„SFB-Transregio 141: Biological Design and Integrative Structures - Analysis, Simulation and Implementation in Architecture” – year 4

T. Speck

Plant Biomechanics Group Freiburg, Botanic Garden of the University of Freiburg and Freiburg Centre for Interactive Materials and Bioinspired Technologies (FIT)

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

As in the years before also in year four of the SFB Transregio 141 (TRR 141), eight of the eleven projects at the University of Freiburg were successfully carried out at the Freiburg Center for Interactive Materials and Bioinspired Technologies (FIT).

Fig. 1: Entrance hall allowing a first glance in the exhibition of the TRR 141 "Baubionik - Biologie beflügelt Architektur", at Schloss Rosenstein of the State Museum of Natural History in Stuttgart. © PBG & SMNS

On May 6th 2018 the exhibition "Biomimetics of Building - Biology inspires Architecture’ (Baubionik - Biologie beflügelt Architektur) im Schloss Rosenstein of the State Museum of Natural History in Stuttgart (SMNS) closed its doors after nearly seven very successful months (Figs. 1 & 2). The Exhibition (coordinated by Jan Knippers Univ. Stuttgart, Thomas Speck, FIT/Univ. Freiburg and Ulrich Schmid, SMNS) was visited by ca. 60.000 persons, and offered special guided tours for pupils and school classes with specifically developed hands-on-experiments.

Fig. 2: Impression of the 6x6m large demonstrator of the Flectofold façade shading system inspired by the closing mechanism of the waterwheel plant and developed in the A04-project at the TRR 141 exhibition in the State Museum of Natural History in Stuttgart. © PBG & SMNS

Additionally more than 100 guided tours for over 1500 visitors were offered by PhD-students and scientists involved in the TRR 141, and the popular scientific lecture series (7 lectures, one by T. Speck) was visited by over 600 listeners (many of them undergraduate and graduate students).

The popular scientific exhibition guide edited by J. Knippers, U. Schmid and T. Speck (152 pp.) [1] was sold out after two thirds of the exhibition will be published in an extended version in German and English by Birkhäuser Publishers in July 2019 [2 & 3]. A virtual tour the exhibition can be found under: https://www.trr141.de/

The exhibition was also used as platform for the evaluation of the SFB-Transregio 141 by an international reviewing panel on 1st and 2nd of February 2018. Unfortunately, in spite of a for most of the projects (very) favorable scientific evaluation by the reviewers, the SFB-Transregio 141 was not selected for a further funding period and ends in June 30th 2019 after one year of bridging financing from the DFG for the positively evaluated projects.

Further highlights from the Freiburg perspective were various awards and grants awarded to employees of the TRR 141:

Linnea Hesse (project A06) who finished as first doctoral researcher of the TRR 141 her PhD in December 2018 (title of the thesis: Qualitative and quantitative analysis of plant branchings and their biomimetic potential using the example of *Dracaena marginata* / supervised by TRR 141 PIs Tom Masselter and Thomas Speck). Her PhD-thesis was awarded with the renowned “Camillo-Schneider-Preis” of the Deutschen Dendrologischen Gesellschaft (DDG). This annual prize is awarded to the best PhD-thesis in the field of dendrology in the German speaking area. She was invited to present her research in an invited talk at the DDG annual meeting in Ahrensburg and and to write an article, summarizing her PhD-thesis, in the “Mitteilungen der Deutschen Dendrologischen Gesellschaft” [4].

Anna Westermeier (project A04) was invited by the award committee of the Society of Integrative and Comparative Biology (SICB) for the “Rising Star Symposium” as one of the most promising graduate students in field of organismal botany. She presented her research at the annual SICB Annual Meeting in Tampa (Florida, USA) where she gave a very well appreciated talk with the title “Biology, biomechanics and biomimetic potential of *Aldrovanda vesiculosa* underwater snap-traps”.

In addition to the work published in the cited books of the TRR 141, numerous publications in peer reviewed journals and books as well as several contributions to conference proceedings volumes and further short communication (miscellaneous) were published. They are compiled on the webpage of the TRR 141 and can be found under:
http://www.trr141.de/index.php/publications/s

Here also a list of interviews can be found given by scientists of the TRR 141 in 2018 for various print-media and electronic media as well as on air or in TV. Additionally, media coverage on projects of the TRR 141 and the most important oral presentations given by TRR 141 scientists are complied, and a detailed description of the structure of TRR 141, the topics of the various projects and the portraits of the scientists involved is given.

Fig. 3: Branched supporting column with braided textile hull consisting of carbon and glass fibers inspired by the outer form and structure of the branching regions of *Dracaena marginata* and *Schefflera arboricola* and developed in the A06-project at the TRR 141 exhibition in the State Museum of Natural History in Stuttgart. This demonstrator will find its final home in the entrance hall of the FIT building in Freiburg. © PBG & SMNS

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IRTG 1642

International Research Training Group (IRTG) “Soft Matter Science: Concepts for the Design of Functional Materials”

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A. Joers, A. Link

between the universities of Freiburg and Strasbourg with the participation of scientists from Basel and Mulhouse

IRTG SoMaS
Soft Matter Science

Fig. 1: IRTG SoMas Logo. Photo: IRTG SoMaS

Attracting equal attention from chemists, physicists, biologists, and engineers, soft matter science is without any doubt a growing and interdisciplinary field of research. In part, this appeal comes from the astounding properties of “soft materials”, e.g., from their unique capacity to respond to external stimuli. Even weak stimuli may induce significant changes in behaviour due to the “softness” and mesoscopic structuring of the material. While the softness results from weak interactions – comparable in strength to the thermal energy – between the constituents, mesoscopic structuring is often a consequence of self-assembly, i.e., of the spontaneous organization of matter into ordered arrangements much larger in size than the constituent molecules. Modern materials science increasingly exploits these distinctive features for the design of new materials. Many of today's interesting systems have multiple components, various interfaces, and complex effective interactions. Understanding the synergy of these factors and their impact on materials properties presents a great scientific challenge. Advances in this respect hold the promise of creating novel materials with a level of functionality similar to that existing in nature.

The International Research Training Group (IRTG) “Soft Matter Science: Concepts for the Design of Functional Materials” is a research training programme between the universities of Freiburg and Strasbourg with the participation of scientists from Basel and Mulhouse. The objective of the IRTG “Soft Matter Science” is to promote graduate education and scientific exchange in this modern field of research on soft matter materials.

The first funding period of the IRTG Soft Matter Science started in October 2010 and ended in March 2015. The research programme of the second funding period (April 2015 to September 2019) consists of three interconnected themes with currently 20 PhD projects in total, representing a large spectrum of diverse aspects of soft matter science. All PhD projects are bilateral, having a German and a French supervisor. Stays at the partner laboratories, facilitated by the geographic proximity of the involved sites, are an integral part of the PhD training programme. Training through research is complemented by a qualification programme consisting of internal workshops, summer schools, and seminars given by experts from outside the IRTG. In 2018, the IRTG successfully organized its 8th SoMas Summer School with the topic “Non-Equilibrium Phenomena In “Soft Matter Science”, which took place from July 8-13, 2018 in Mittelwihr, Alsace. Amongst other events, the IRTG also organized a scientific workshop on “Soft Matter Science" in November 2018. Two field trips to Bayer and Merck were organized by the PhD students themselves.

Fig. 2: SoMas Summer School 2018 in Mittelwihr. Photo: Birgitta Zovko

The research programme of the second funding period has been designed by drawing on the experience gained during the first funding period. It follows the same interdisciplinary strategy as before, but consists of PhD projects that are more strongly interlinked to enhance collaborations. Even though the programme is mainly engaged in basic research (“Concepts”), it has a clear focus to contribute to the development of functional materials for future applications. In order to realize this core research idea, the research programme is structured around three thematic areas:

A Soft Matter Interfaces: From Membranes to Tribology

B From Design to Multifunctional Materials and Devices

C From Physical Concepts to Material Properties

These thematic areas constitute the pillars of a coherent research programme due to the following reasons: The investigation of advanced functional materials based on soft matter systems involves an understanding of (self-) assembly processes and of the impact of interfaces. Typically, the studied materials consist of specifically designed molecules, often with multiple functional features and programmed to assemble into hierarchical structures. The properties of many soft matter systems are not only dictated by thermal equilibrium, but often depend on preparation or processing history. Thus, physical pathways exist which allow to tune properties by directing assembly processes, for example, via the control of interfacial structures or formulations.

The scientific questions of all three thematic areas are thus closely linked and have multiple methodological overlap. Success of the IRTG Soft Matter Science rests upon an interconnected and interdisciplinary research programme which requires and brings together complementary knowledge from physics, chemistry, materials science, engineering, and biology. In this way, the IRTG Soft Matter Science contributes to developing concepts for the design of advanced soft matter materials.

PUBLICATIONS

PEER-REVIEWED PUBLICATIONS

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Kutluk H, Bruch R, Meirich M, Partel S, Urban G, Dincer C (2018): Microfluidic biosensor for the electrochemical on-site detection of microRNAs. *MicroTAS* 2018, Kaohsiung, Taiwan.

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BOOK CHAPTERS

Masselter T, Bold G, Thielen M, Speck O, Speck T (2018): Bio-inspired materials and structures: a case study based on selected examples. In: Yang G, Xiao L, Lamboni L (eds.), *Bioinspired Materials Science and Engineering*, 253–266. John Wiley & Sons.

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MISCELLANEOUS

Poppinga S, Westermeier A, Speck T, Fleischmann A (2018): Differenze strutturali e funzionali nelle trapopole delle utricolarie. *AIPC Magazine* **50**, 4–17. (Associazione Italiana Plante Carnivore).

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THESES/AWARDS

PHD THESES

Bunk, Katharina: Branchings and axes in selected plant species as concept generators for high load-bearing joints of branched building structures. [Promotion im Rahmen des SFB/TRR 141 “Biological Design and Integrative Structures – Analysis, Simulation and Implementation in Architecture” – Förderung durch DFG / Promotion, Universität Freiburg, Supervisor: T. Masselter; expected completion SS 2019]

Eichhorn, Melanie: 3D-microstructures with designed surface chemistry for the study of cell adhesion and deformation (IRTG)

Erath, Roman: Synthese und Charakterisierung von degradierbaren antimikrobiellen Polymernetzwerken. – Dissertation, Universität Freiburg, 2018. [Supervisor: K. Lienkamp]

Kumar, Charchit: Inspiration from insect-plant interactions: Adhesion and friction on micro-textured bioimimetic surfaces. [Promotion im des Internationalen Graduiertenkollegs IRTG 1642 „SoftMatterScience“ – Förderung durch DFG / Promotion, Universität Freiburg; Supervisor: T. Speck; expected completion: WS 2018/19]

Riga, Esther Karolin: Selbstregenerierende antimikrobielle Oberflächen durch Multilagendesign. – Dissertation, Universität Freiburg, 2018. [Supervisor: K. Lienkamp]

Scheibelein, Christoph: Mechanical Activation of Polymer Brushes and the Evolution of Stable Brush Architectures (IRTG)

Schmier, Stefanie: Plants as source of inspiration for energy dissipation in load bearing systems and facades. [Promotion im Rahmen des SFB/TRR 141 “Biological Design and Integrative Structures – Analysis, Simulation and Implementation in Architecture” – Förderung durch DFG / Promotion, Universität Freiburg, Supervisor: T. Speck; expected completion WS 2018/2019]

Schuler, Anne-Katrin: Entwicklung photoreaktiver Polymersysteme zur Adhäsionsverbesserung an Grenzflächen inkompatibler Polymermaterialien (TRR123)

Surapaneni, Venkata Amarnadh: Physics and Mechanics of Plant Surfaces with Cuticular Folds and Other Microstructures. [Promotion im Rahmen von "Plant-Inspired Materials and Surfaces (PlaMatSu)" - Förderung durch das Forschungs- und Innovationsprogramm Horizon 2020 der Europäischen Union im Rahmen der Marie Skłodowska-Curie-Maßnahme Nr. 722842 / Promotion, Universität Freiburg, Supervisors: T. Speck & M. Thielen; expected completion SS 2020].

Westermeier, Anna: Kinematik planarer, gekrümmter und gewellter Pflanzenstrukturen als Ideengeber für bewegliche Strukturen in der Architektur. [Promotion im Rahmen des SFB/TRR 141 “Biological Design and Integrative Structures – Analysis, Simulation and Implementation in Architecture” – Förderung durch DFG / Promotion, Universität Freiburg, Supervisors: T. Speck & S. Poppinga; expected completion SS 2019].

DIPLOMA, MASTER AND STATE EXAMINATION THESES

Marx, Franziska: Synthese und Charakterisierung von Oberflächengebundenen Zwitterionischen Polymernetzwerken. – Master thesis, Universität Freiburg. [Supervisors: R. Mülhaupt & K. Lienkamp]

Moosmann, Natalie: Probenpräparation für die Visualisierung nicht-verholzter Pflanzen mittels Mikro-Computertomographie. – Bachelor thesis, Universität Freiburg [Supervisors: T. Speck & A. Westermeier; completed SS 2018]

Schweigert, Alexander: Herstellung und Untersuchung des Abbaus von salicylsäurehaltigen Poly(anhydrid estern) mittels gravimetrischer und chromatographischer Methoden. – Master thesis, Universität Freiburg. [Supervisors: R. Mülhaupt & K. Lienkamp]

Isaza, Sebastian Montoya: Photoelectrochemical water splitting performance of tantalum and niobium doped BiVO4. – Master thesis, Universität Freiburg [Arbeitskreis Prof. Anna Fischer]

AWARDS

Walther, Andreas: The 2018 Hanwha-Total IUPAC Young Scientist Award presented at the IUPAC World Polymer Congress

Hesse, Linnea: “Camillo-Schneider-Preis” of the Deutschen Dendrologischen Gesellschaft (DDG)

FIT-KOLLOQUIUM 2018

Programm
6. FIT-Kolloquium am 08.03.2018

ab 09:00 Empfang

9:20 Jing Becker (Core Facility 2) Manufacturing technique

9:35 Oliver Brügner (Core Facility 3)
Spiropyran ring opening reactions to measure forces on the molecular scale

9:50 Maria Zober / Esther Riga (Lienkamp)
Projekt Regenerate - Self-regenerating Functional Surfaces – Towards a Technology Platform for New Materials and Devices

10:05 Lili Liu (Thiele)
Nanotomographic investigation of Lithium-Air (Li-O2) battery

10:20 Thomas Speck
How the carnivorous waterwheel plant (*Aldrovanda vesiculosa*) snaps

10:35 Raisa Kociurzynski (Römer)
Binding of viral capsid protein VP1 to its glycosphingolipid receptor GM1; a molecular dynamics study

10:50 – 11:10 Kaffeepause

11:10 Karen Lienkamp (Lienkamp)
ANTIBUG - Validation of Simultaneously Antimicrobial and Protein-repellent Polymer Coatings for Medical Applications

11:25 Maryam Bahrami (Rühe)
Lubrication of surfaces through surface-attached hydrogels – Slippery when wet

11:40 Thomas Böhm (Thiele)
X-ray tomographic 3D reconstruction of the brain-probe-interface in rat cortex

11:55 Farzad Ramezani (Reiter)
Negative Creep in Polymer Melts

12:10 Linnea Hesse (T. Speck)
High-resolution MRI reveals the functional morphology, biomechanics and development of the branch-attachments in *Dracaena marginata*

12:25 – 13:25 Mittagspause (Buffet)

13:25 Marco Caliaro (O. Speck)
From plant models to computer simulations

13:40 Taras Sych (Römer)
Investigation of plasma membrane order modifications induced by lectins

13:55 Nico Tucher (Glunz)
Advanced optics of perovskit silicon tandem solar cells

14:10 Constanze Lamprecht (Römer/Reiter)
Exploration of protein-lipid interactions on the molecular level by Atomic Force microscopy

14:25 Stefan Müllers (Rühe)
Bioinspired hairy surfaces

14:40 – 15:00 Kaffeepause

15:00 Can Dincer
Smart and biodegradable wearables for real-time monitoring and therapy

15:15 Peter Koltay
3d-Bio-Printing of artificial vascularized bone tissue

15:30 Severin Vierrath
Tomography-based material development for energy autonomous systems

15:45 Ludmila Cojocaru (Glunz)
Novel absorber materials based on Pb-free evaporated perovskites for efficient and environmentally friendly solar cells

16:00 Anna Fischer
Entwicklung von BiVO4 Photoanoden für die Licht-induzierte Wasserspaltung

16:15 Ende für das Auditorium (kurze Kaffee- und Umbaupause)

16:30 Mitgliederversammlung

MEETING OF THE ADVISORY BOARD 2018

Agenda für das 3. Treffen des Wissenschaftlichen Beirats des FIT
Agenda for the third meeting of the Advisory Board of FIT

Donnerstag, den 12. April 2018 um 12:00 – 17:10 Uhr
Thursday, 12th of April 2018 from 12:00 to 5:10 pm

Ort / Venue: FIT, Georges-Köhler-Allee 105, Seminarraum EG

12:00 Empfang und Lunch im Foyer / Lunch at the foyer

13:00 Beginn öffentlicher Teil / Start of the public session

13:00 Begrüßung durch den Geschäftsführenden Direktor des FIT (Jürgen Rühe)
Welcome by the executive director of the FIT (Jürgen Rühe)

13:05 Begrüßung durch Ingo Burgert, Vorsitzender des Advisory Boards
Welcome by Ingo Burgert, chairman of the Advisory Board

Kooperationsprojekte / Cooperation Projects

13:10 **Jürgen Rühe**
(Kurz-Bericht des Geschäftsführenden Direktors / short report by the executive director)
"FIT for the future – the future of the FIT"

13:25 **Thomas Speck**
***"**Bio-inspired architecture – Plants as role models"*
SFB/TRR 141

13:40 **Jürgen Rühe**
"**Living, Adaptive and Energy-autonomous Materials Sytems (livMatS)**"
Cluster Initiative *liv*MatS

Wissenschaftliche Vorträge / Scientific Presentations: Core Facilities

13:55 **Stefanie Schmier**
"Three-dimensional visualization of the microstructure of the coconut endocarp using the µCT"
Core facility "Bildgebung von Materialsystemen" / Core facility „Imaging of Materials Systems"

14:10 **Claas Müller**
"The partner to realize new ideas"
Core facility „Fertigungstechnik" / Core facility „Functional Processing"

14:25 **Michael Walter**
"**Modelling and Simulation of complex experiments by ab-initio methods**"
Core Facility „Modellierung und Simulation von Materialsystemen" / Core facility "Modelling and Simulation of Materials Systems"

14:40 **Kaffeepause mit Posterpräsentationen / Coffee break and poster session**

Posters:

Core facility „Fertigungstechnik"/Core facility „Functional Processing"

- Georg Bold *"FIT 3D Lab - New 3D printers for diverse applications"*

Zukunftsfeld „Adaptive polymere Werkstoffe" / Future Field "Adaptive Polymer Materials"

- Esther Riga *"Self-regenerating antimicrobial surfaces via multilayer design"*
- M. Bahrami *"Lubrication of surfaces through surface-attached hydrogels: Slippery when wet"*
- D. Schwärzle *"Two-photon crosslinking f photoactive polymers – A new method for the two-photon lithography"*

Zukunftsfeld "Energieautarke (Mikro)Systeme" / Future Field "Energy-Autonomous Microsystems"

- Severin Vierrath *„FIB-SEM tomography for polymer electrolyte fuel cells: chances and challenges"*
- Stefan Schierle *"High aspect ratio silver nanowires for flexible conductive networks with high optical transparency as electrodes for mechanical actuators"*

Zukunftsfeld "Biomimetische und biobasierte Materialien" / Future Field "Biomimetic and Bio-based Materials"

- Stefanie Schmier *"Plants and animals as source of inspiration for increased energy dissipation, residual strength and improved insulation – theoretical background and application in load-bearing building components"*
- Max Langer *"Force transmission and actuation in the transition zone between rod-shaped and planar elements"*
- Anna Westermeier *"Kinematic principles and motion design in shape shifting plant structures"*
- Tom Masselter "*Stem and root branching types of selected plant species as concept generators for supporting and anchoring structures"*
- Simon Poppinga *"Responsive autonomous surface structures inspired by passive multi-phase plant movements"*
- Olga Speck *"Public relations"*
- D. Hoenders, A. Walther *"Photoactive Cellulose Nanofibrils as a Versatile Platform for Functional Materials"*
- Taras Sych *„Investigation of the membrane reorganization during uptake processes"*

Wissenschaftliche Vorträge/Scientific Presentations: Forschungsfelder/Future Fields

Zukunftsfeld „Adaptive polymere Werkstoffe" / Future Field "Adaptive Polymer Materials"

15:30 Jan Behrends
"Polymers in pores: from single molecule analytics to stochastic exploration of energy landscapes"

15:45 Karen Lienkamp
"The Quest for the Holy Grail in Anti-Infective Materials: From Self-regenerating Multilayers to Simultaneously Antimicrobial and Protein-repellent One-layer Coatings"

Zukunftsfeld "Biomimetische und biobasierte Materialien" / Future Field "Biomimetic and Bio-based Materials"

16:00 **Andreas Walther**
"Autonomous Self-Assemblies Inspired From Living Systems"

16:15 **Tom Masselter**
"Stems and root branching types of selected plant species as concept generators for supporting and anchoring structures"

Zukunftsfeld "Energieautarke (Mikro)Systeme" / Future Field "Energy-Autonomous Microsystems"

16:30 **Peter Woias**
"Characterization platforms for single thermoelectric nanowires"

16:45 **Anna Fischer**
"BiVO4 thin films for solar water splitting"

17:00 Schlussworte / Closing remarks

17:10 Ende des öffentlichen Teils / End of the public part of the meeting

IMPRESSUM

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