Karlsruhe Institute of Technology

3D MATTER
MADE TO ORDER

UNIVERSITÄT
HEIDELBERG
ZUKUNFT
SEIT 1386

Future 3D Additive Manufacturing | The 3DMM2O Conference

3D Molecular Systems

Abstract Booklet

March 12 – 16, 2023

Schöntal Monastery, Germany

Content

Welcome

Dear Colleagues and Friends,

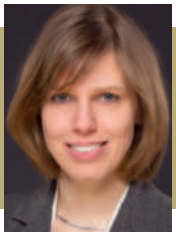
It is our great pleasure to welcome you to

The Future 3D Additive Manufacturing – The 3DMM2O Conference 2023: 3D Molecular Systems.

The annual conference on topics surrounding 3D Additive Manufacturing is organized by the Cluster of Excellence "3D Matter Made to Order" (3DMM2O), a joint Research Cluster of Karlsruhe Institute of Technology (KIT) and Heidelberg University (Uni HD).

The conference aims at linking Molecular Materials with 3D Hybrid Organotypic Systems.

Lectures by international speakers in the fields of materials, molecular self-assembly, and (bio)nanomaterials design and characterization, poster sessions and social networking events will give you an insight in alternating aspects of 3D Additive Manufacturing as well as the opportunity for inspiring and fruitful scientific discussions and exchange.



Franziska Thomas
Heidelberg University

Stefan Bräse
Karlsruhe Institute of Technology

Program

Monday, March 13

	Breakfast	
9:00 AM–9:15 AM	Opening & Welcome	
9:15 AM–10:00 AM	Aromatic Foldamers: Engineering Molecular Shape	**Ivan Huc**
10:00 AM–10:15 AM	Coffee Break	
10:15 AM–11:00 AM	Nitrogen-Doped Polycyclic Architectures of Different Dimensions: From Chemical Synthesis to Functional Materials	**Milan Kivala**
11:00 AM–11:45 AM	Bioactive Peptide Nanostructures in Three Dimensions	**Ian Hamley**
11:45 AM–12:00 PM	Group Picture	
12:00 PM–2:00 PM	Lunch	
2:00 PM–2:30 AM	Atomically Precise Assembly of Functional Molecular Solids from Building Blocks: The SURMOF Approach	**Christof Wöll**
2:30 PM–3:00 PM	Designing New Functional Polymers for 4D Microprinting	**Eva Blasco**
3:00 PM–3:20 PM	Laser-based Nano 3D Printing for Parallel Chemistry and Screening	**Felix Löffler**
3:20 PM–3:35 PM	Coffee Break	
3:35 PM–4:05 PM	Tools for Research Data Management, Digitalization and Automation as Important Pillars of Scientific Progress in Experimental Chemistry	**Nicole Jung**
4:05 PM–4:15 PM	Flashtalks	
4:15 PM–5:45 PM	Poster Session I & Drinks	
7:00 PM	Dinner	

Tuesday, March 14

	Breakfast	
9:00 AM–9:45 AM	Xolography for Volumetric 3D Printing	**Stefan Hecht**
9:45 AM–10:30 AM	Towards Living Synthetic Materials	**Sijbren Otto**
10:30 AM–10:45 AM	Coffee Break	
10:45 AM–11:15 AM	Near-Field Electrospinning, DLW, EBL: It's in the Inks	**Uwe Bunz**
11:15 AM–11:35 AM	Printability and Post-Processing Characteristics of Powder Bed Fusion Additive Manufacturing SS 17-4ph Fine Porous TPMS Cellular Structures	**Manjaiah Mallaiah**
11:35 AM–12:00 PM	Controlling Cell-Material Interactions through Responsive Peptide Nanostructures	**Christopher V. Synatschke**
12:00 PM–2:00 PM	Lunch	
2:00 PM–2:45 PM	Online: Mucin Mimics to Influence Microbial Function	**Laura Kiessling**
2:45 PM–3:15 PM	3D Structured Micro-Environments for Controlling Cells	**Christine Selhuber-Unkel**
3:15 PM–3:30 PM	Coffee Break	
3:30 PM–4:15 PM	Designing New Bioinspired 3D Hydrogels for Tissue Regeneration	**Lihi Adler-Abramovich**
4:15 PM–5:00 PM	Cluster–Support Interaction Dynamics	**Barbara Lechner**
5:00 PM–5:30 PM	Enhancing Biosynthetic Soft Materials for 3D Bioprinting of Tissues	**Ute Schepers**
5:30 PM–5:45 PM	Flashtalks	
5:45 PM–7:00 PM	Poster Session II & Drinks	
7:00 PM	Dinner	

Wednesday, March 15

	Breakfast	
9:00 AM–9:45 AM	Controlling Supramolecular Assemblies with Peptidic Scaffolds	**Helma Wennemers**
9:45 AM–10:15 AM	The Story of Photoinitiators: A Quantum Mechanical Perspective	**Mariana Kozlowska**
10:15 AM–10:30 AM	Coffee Break	
10:30 AM–11:15 AM	Repurposing the Chemistry of Life for Nanotechnology	**Rein Ulijn**
11:15 AM–12:00 PM	Microgel Particles as Stabilizers for Foams: A Multiscale Approach	**Regine von Klitzing**
12:00 PM–1:30 PM	Lunch	
1:45 PM–2:00 PM	Meet for Social Program (In the Foyer)	
2:00 PM–6:00 PM	Social Program (Guided Tour, Archery, Yoga)	
7:00 PM	Conference Dinner & Poster Award	

Thursday, March 16

	Breakfast	
9:00 AM–9:45 AM	Functional Materials from Protein Self-Assembly	**Tuomas Knowles**
9:45 AM–10:15 AM	Molecular Mechano-Sensing in Collagen	**Markus Kurth**
10:15 AM–10:45 AM	Coffee Break	
10:45 AM–11:30 AM	Synthetic Carbohydrate-Based Materials	**Martina Delbianco**
11:30 AM–11:50 AM	Phosphate-Driven Systems Chemistry	**Charalampos Pappas**
11:50 AM–1:30 PM	Lunch	
1:30 PM–2:15 PM	Self-Assembly of Gigantic Coordination Polyhedra: From Synthetic to Peptidic	**Makoto Fujita**
2:15 PM–2:35 PM	3D-Bioprinting Effects on Cell and Organoid Proliferation and Metabolism	**Erin Spiller**
2:35 PM–2:55 PM	Stimuli Responsive Hydrogel Actuators for Microfluidic Applications	**Tobias Spratte**
2:55 PM–3:10 PM	Coffee Break	
3:10 PM–3:55 PM	Online: Reticular Materials to Machines for Climate Change	**Omar Yaghi**
3:55 PM–4:40 PM	Online: One Ellipsoid to Rule them All – Cathelicidin-Mimicking Peptoids that are Antiviral, Antibacterial & Antifungal and Well-Tolerated in the Lung	**Annelise Barron**
4:40 PM	Farewell	
4:45 PM	Departure	

Speakers'

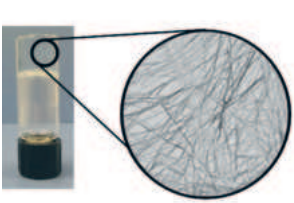
Tuesday, March 14
3:30 PM–4:15 PM

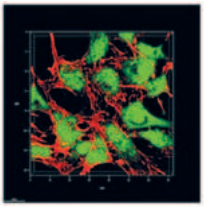
Lihi Adler-Abramovich

Tel Aviv University, Israel

DESIGNING NEW BIOINSPIRED 3D HYDROGELS FOR TISSUE REGENERATION

The emerging demand for tissue engineering scaffolds capable of inducing bone regeneration using minimally invasive techniques prompts the need for the development of new biomaterials. One promising route is molecular self-assembly, a key direction in current nanotechnology and material science. In this approach, the physical properties of the formed supramolecular assemblies are directed by the inherent characteristics of the specific building blocks. Molecular co-assembly at varied stoichiometry substantially increases the structural and functional diversity of the formed assemblies, thus allowing tuning of their architecture and physical properties.





Here, in line with polymer chemistry paradigms, we applied a co-assembly approach using hydrogel-forming peptides, resulting in a synergistic modulation of their mechanical properties to form extraordinarily rigid hydrogels which supported osteogenic differentiation based on cells-mechanosensing. Furthermore, we designed a multi-component scaffold composed of polysaccharides, short self-assembling peptides, and bone minerals.

Abstracts

In Alphabetical Order

We demonstrate the formation of a rigid, yet injectable and printable hydrogel without the addition of cross-linking agents. The formed composite hydrogel displays a nanofibrous structure, which mimics the extracellular matrix and exhibits thixotropic behavior and a high storage modulus. This composite scaffold can induce osteogenic differentiation and facilitate calcium mineralization.

This work provides a conceptual framework for the utilization of co-assembly strategies to push the limits of nanostructure physical properties obtained through self-assembly for the design of new biomaterials for tissue engineering and personalized medicine applications.

1. Ghosh, Ghosh, M., Bera, S., Schiffmann, S., Shimon, L.J.W., Adler-Abramovich, L.. ACS Nano 2020
2. Cohen-Gerassi, D.; Arnon, Z. A.; Guterman, T.; Levin, A.; Ghosh, M.; Aviv, M.; Levy, D.; Knowles, T. P. J.; Shacham-Diamand, Y.; Adler-Abramovich, L.. Chem. Mater. 2020
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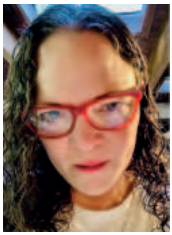
4. Aviv, M.; Halperin-Sternfeld, M.; Grigoriants, I.; Buzhansky, L.; Mironi-Harpaz, I.; Seliktar, D.; Einav, S.; Nevo, Z.; Adler-Abramovich, L. ACS Appl. Mater. Interfaces 2018
5. Netti, F., Aviv, M., Dan, Y., Rudnick-Glick, S., Halperin-Sternfeld, M., Adler-Abramovich, L. Nanoscale; 2022 14, 8525-8533.

Speakers'

Thursday, March 16
3:55 PM–4:40 PM



Annelise E. Barron

School of Medicine, Stanford University, USA

ONE ELLIPSOID TO RULE THEM ALL – CATHELICIDIN-MIMICKING PEPTOIDS THAT ARE ANTIVIRAL, ANTIBACTERIAL & ANTIFUNGAL AND WELL-TOLERATED IN THE LUNG

Viral infections, such as those caused by SARS-CoV-2 and Influenza A, affect millions of people each year. Few antiviral drugs can effectively treat these infections. The standard approach in the development of antiviral drugs involves the identification of a unique viral target, followed by the design of an agent that addresses that target.

Antimicrobial peptides (AMPs) represent a novel source of potential antiviral drugs. AMPs can inactivate numerous different enveloped viruses through disruption of their viral envelopes. Yet the clinical development of AMPs as antimicrobial therapeutics has been hampered by a number of factors, especially their enzymatically labile structure as peptides.

We report the antiviral potential of peptoid mimics of AMPs (sequence-specific N-substituted glycine oligomers). These peptoids have the advantage of being insensitive to proteases, and exhibit increased bioavailability. Our results demonstrate that several peptoids exhibit potent in vitro antiviral activity against SARS-CoV-2 and Influenza virus when incubated prior to infection. Thus, they have direct effects on the viral structures that render the viral particles non-infective. Visualization by cryo-EM shows viral envelope disruption similar to what is observed in AMP activity against these viruses. Even at 50X we observe no cytotoxicity against primary cultures of epithelial cells. Results suggest a biomimetic mechanism, likely due to the differences between the phospholipid head group makeup of viral envelopes and host cell membranes, thus underscoring the potential of this class of molecules as safe and effective broad-spectrum antiviral agents.

Furthermore, in recent work we have found some of the same peptoids are effective in killing both bacterial and fungal pathogens that commonly co-occur in pneumonia in ICU patients, and to sterilize biofilms. We discuss how and why differing molecular features between ten different peptoid candidates may affect both antimicrobial activity and selectivity, specifically, the self-assembly of the most effective peptoids into discrete micellar structures such as ellipsoidal micelles comprising ~100 peptoid molecules per micelle.

Remarkably, some of these same peptoids with broad-spectrum activity against respiratory viruses are also active against a broad array of pathogenic bacterial and fungal organisms, offering the possibility of a truly novel therapeutic approach to treating polymicrobial lung infections.

Eva Blasco

Heidelberg University, Germany

DESIGNING NEW FUNCTIONAL POLYMERS FOR 4D MICROPRINTING

4D microprinting has become a promising tool for the fabrication of dynamic microstructures opening new opportunities for the additive manufacturing of functional devices with high precision.

During the last years, promising examples of defined 4D microstructures employing stimuli-responsive polymers have been shown using two-photon laser printing.

Herein, we present our recent work on the field with emphasis on new printable polymeric materials.

In particular, shape memory polymers as well as dynamic covalent polymer networks have been demonstrated to be excellent candidates for the preparation of “living” 4D microstructures with potential applications in micro and nanorobotics or biomedicine.

Tuesday, March 14
10:45 AM–11:15 AM

Uwe Bunz

Heidelberg University, Germany

NEAR-FIELD ELECTROSPINNING, DLW, EBL: ITS IN THE INKS

Additive manufacturing (AM) reaching from the nano- to the macroscopic-regime is fundamentally a domain of physicists, mechanical engineers and coders, who provide the tools that transform CAD data of an imagined structure into reality.

The progress in disparate fields like micromachining, photolithography, DLW, 3D-printing, electrospinning, origami-type folding etc. has been achieved with a handful of commercially available elastomers, thermoplastic polymers and thermosets in addition to simple monomers monomers and photo initiators.

Yet, a multitude of properties other than mechanical ones are difficult to realize for objects made by AM, but bespoke inks (single or multicomponent) revolutionizes AM to give microscopic to macroscopic "plastic objects" with properties as disparate as (semi) conductivity, ultra-low shrinkage, displaying functional gradients of mechanical and optical properties, bio compatibility, and much more.

The creation of bespoke inks is the domain of synthetic chemistry. The inks have to play to the AM method used to deliver the exact function in fields ranging from inorganic and organic electronics, photonics, etc. to biological applications. Together with the Korvink group we develop inks for near field electrospinning.

Fairly conventional parameters such as viscosity, solubility and solvent choice already create a large parameter set of variables, the introduction of specific functional groups adds a layer of complexity together with the desired resolution and chemical composition but promises to deliver materials with outstanding properties with respect to mechanical, optical, sensory and biological applications.

Martina Delbianco

Max Planck Institute of Colloids and Interfaces, Germany

SYNTHETIC CARBOHYDRATE-BASED MATERIALS

Polysaccharides are the most abundant organic materials in nature, yet correlations between their three-dimensional structures and macroscopic properties have not been established. With automated glycan assembly (AGA), we prepared well-defined oligo- and polysaccharides resembling natural as well as unnatural structures.[1]

These synthetic glycans are ideal probes for the fundamental study of polysaccharides, shedding light on how the primary sequence affects the polysaccharide properties (i.e. solubility and crystallinity). Molecular dynamics simulations, NMR spectroscopy, and single molecule imaging allowed for the visualization of polysaccharides' conformation and revealed that some polymers form helices while others adopt rod-like structures.[2]

Modifications in specific positions of the oligosaccharide chains permitted to tune the three-dimensional structures and solubility of such compounds.[3] These synthetic oligosaccharides self-assembled into nanostructures of varying morphologies.[4]

Differences in chain length, monomer modification, and aggregation methods yielded glycomaterials with distinct shapes and chirality, offering valuable models to study the aggregation of natural polysaccharides.[5]

1. M. Delbianco, A. Kononov, A. Poveda, Y. Yu, T. Diercks, J. Jiménez-Barbero, P. H. Seeberger, J. Am. Chem. Soc. 2018, 140, 5421-5426.
2. X. Wu, M. Delbianco, K. Anggara, T. Michnowicz, A. Pardo-Vargas, P. Bharate, S. Sen, M. Pristl, S. Rauschenbach, U. Schlickum, S. Abb, P. H. Seeberger, K. Kern, Nature 2020, 582, 375-378.
3. Y. Yu, T. Tyrikos-Ergas, Y. Zhu, G. Fittolani, V. Bordoni, A. Singhal, R. J. Fair, A. Grafmüller, P. H. Seeberger, M. Delbianco, Angew. Chem., Int. Ed. 2019, 58, 1433-7851.
4. S. Gim, G. Fittolani, Y. Nishiyama, P. H. Seeberger, Y. Ogawa, M. Delbianco, Angew. Chem., Int. Ed. 2020, 59, 22577-22583.
5. G. Fittolani, D. Vargová, P. H. Seeberger, Y. Ogawa, M. Delbianco, J. Am. Chem. Soc. 2022, 144, 12469-12475.

Speakers'

Thursday, March 16
1:30 PM–2:15 PM

Makoto Fujita

University of Tokyo, Japan

SELF-ASSEMBLY OF GIGANTIC COORDINATION POLYHEDRA: FROM SYNTHETIC TO PEPTIDIC

Self-assembly of gigantic polyhedral complexes from a number of metal ions and small organic molecules will be discussed.

The organic components can be either simple and rigid bridging ligands or oligopeptides that adopt fixed conformation when folded.

Ian Hamley

University of Reading, UK

BIOACTIVE PEPTIDE NANOSTRUCTURES IN THREE DIMENSIONS

Peptides offer outstanding potential as bioactive and biocompatible nanomaterials that can be programmed with unique properties.

I will review work from our group on peptides, lipopeptides (peptide amphiphiles) and polymer-peptide conjugates. This includes a diversity of designed or bio-inspired or bio-derived systems that self-assemble into micelles, vesicles, fibrils, nanotapes, and other nanostructures in solution and as hydro- or organo-gels.

A remarkable range of biofunctionality has been demonstrated, including use as antimicrobial materials, scaffolds for regenerative medicine and tissue engineering, as amyloid functional materials and potential therapeutics, in gene delivery, and in other biomedical applications.

Tuesday, March 14
9:00 AM–9:45 AM

Stefan Hecht

Humboldt University of Berlin, Germany

XOLOGRAPHY FOR VOLUMETRIC 3D PRINTING

The presentation will highlight xolography as a new and powerful volumetric 3D printing technique. It is based on the use of dual color photoinitiators that enable the precise confinement of the polymerization process into regions defined by two different light sources consisting of an UV/blue light sheet and an orthogonal visible light projector. The linear nature of the process in combination with the high-definition of the projection allow for rapid printing of homogeneous materials and complex multicomponent objects in high resolution without the need for support structures. Advantages and disadvantages as well as opportunities will be discussed.

Light-based additive manufacturing techniques offer various advantages based on their superior speed and resolution. Until now this great potential has not fully been harnessed due slow build rates and material inhomogeneities caused by point-wise or layered object generation common for methods including stereolithography and digital light processing. Volumetric 3D printing is the next evolutionary step to realize a fast and continuous printing process. However, both currently established methods, two-photon photopolymerization and computed axial lithography, suffer from low volume generation rates and limited resolution, respectively.

To overcome this limitation, we have developed xolography as a new and powerful volumetric 3D printing technique. It is based on the use of photoswitchable photoinitiators that require a sequence of two one-photon processes taking place at distinctly different wavelengths. Therefore, these dual color photoinitiators enable the precise confinement of the polymerization into regions defined by two different light sources consisting of an activating UV/blue light sheet and an orthogonal visible light projector. Since the crossing (x) light beams generate an entire (holos) object by this printing process, we refer to it as xolography. The linear nature of the process in combination with the high-definition of the projection allow for rapid printing of homogeneous materials and complex multicomponent objects in high resolution and without the need for support structures.

The presentation will highlight the action principle of xolography and discuss advantages and disadvantages with regard to build speed and resolution, object dimensions and complexity, as well as employable materials.

Nature 588, 620-624 (2020). DOI: 10.1038/s41586-020-3029-7

Ivan Huc

Ludwig-Maximilians-University, Germany

AROMATIC FOLDAMERS: ENGINEERING MOLECULAR SHAPE

Aromatic oligoamides constitute a distinct and promising class of synthetic foldamers – oligomers that adopt stable folded conformations. Single helical structures are predictable, show unprecedented conformational stability, and constitute convenient building blocks to elaborate synthetic, very large (protein-sized) abiotic architectures[1] and peptide-foldamer hybrid structures.[2]

They possess a high propensity to assemble into double, triple and quadruple helices, or to fold into sheet-like structures.[3] Cavities can be designed within such synthetic molecules that enable them to act as artificial receptors[4] and molecular motors.[5] Water soluble analogues of these foldamers show promise in protein recognition.[6]

This lecture will give an overview of the design principles of these functional molecular architectures it will highlight recent developments and emphasize key methodologies.

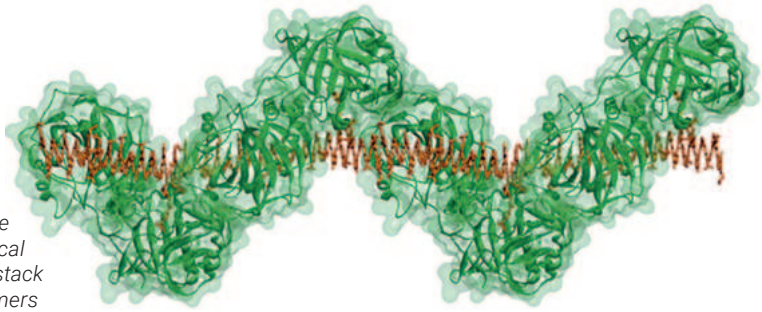


Figure 1: Crystal structure of a protein helical array around a stack of helical foldamers

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2. J. M. Rogers, S. Kwon, S. J. Dawson, P. K. Mandal, H. Suga, I. Huc., Nat. Chem., 2018, 10, 405
3. B. Gole, B. Kauffmann, A. Tron, V. Maurizot, N. McClenaghan, I. Huc, Y. Ferrand, J. Am. Chem. Soc. 2022, 144, 6894.
4. P. Mateus, N. Chandramouli, C. D. Mackereth, B. Kauffmann, Y. Ferrand, I. Huc, Angew. Chem. Int. Ed. 2020, 59, 5797.
5. V. Koehler, A. Roy, I. Huc, Y. Ferrand, Acc. Chem. Res. 2022, 55, 1074.
6. K. Ziach, C. Chollet, V. Parissi, P. Prabhakaran, M. Marchivie, V. Corvaglia, P. Pratim Bose, K. Laxmi-Reddy, F. Godde, J.-M. Schmitter, S. Chaignepain, P. Pourquier, I. Huc, Nat. Chem., 2018, 10, 251.

Monday, March 13
3:35 PM–4:05 PM

Nicole Jung

Karlsruhe Institute of Technology (KIT), Germany

TOOLS FOR RESEARCH DATA MANAGEMENT, DIGITALIZATION AND AUTOMATION AS IMPORTANT PILLARS OF SCIENTIFIC PROGRESS IN EXPERIMENTAL CHEMISTRY

In the last decade, important progress was made with respect to scientific infrastructure, software tools, and methods that may change and improve the way scientists work in academia. While progress which depends on technical developments (in terms of software and hardware) was formerly reserved mostly to the chemistry industry, new developments based open source software, open hardware projects and open science in general are available to the whole community.

In this talk, examples for synergistic effects of systematic research data management, digitalization and automation in synthetic chemistry projects will be presented. It will be shown how the adaptation of currently manual processes to digital workflows can improve and accelerate scientific work, enabling the use of robotic systems in the end. Another focus will lie on the challenges of the community to use the potential of the new methods efficiently and in a sustainable way.

Laura Kiessling

Massachusetts Institute of Technology, USA

MUCIN MIMICS TO INFLUENCE MICROBIAL FUNCTION

Antibiotic resistance is a global health emergency that demands new solutions. Especially valuable are innovative anti-infection strategies that do not drive the emergence of resistance.

Mucus, which is composed of highly glycosylated proteins called mucins, is a natural barrier that can tame bacterial virulence. Mucins reside at the barrier between animal tissues and the microbiome. They resemble block copolymers, with domains that engage in protein – protein interactions and others that present glycan epitopes that can be recognized by bacteria.

Understanding the attributes of mucins responsible for taming pathogens could lead to fundamentally new strategies to regulate pathogenic bacteria. We are generating materials that mimic mucin structure and capture critical anti-virulence properties. This seminar will describe our latest advances on this front.

Monday, March 13
10:15 AM–11:00 AM

Milan Kivala

Heidelberg University, Germany

NITROGEN-DOPED POLYCYCLIC ARCHITECTURES OF DIFFERENT DIMENSIONS: FROM CHEMICAL SYNTHESIS TO FUNCTIONAL MATERIALS

Triarylamines have in the meanwhile become ubiquitous in the area of organic electronics owing to their appreciable electron donor and hole transport properties.

In our research we employ various structurally relatively simple triarylamines for the construction of unprecedented nitrogen-doped π-conjugated scaffolds upon introduction of different bridging moieties.

In these compounds the nitrogen atom readily adopts a planar sp^2-hybridized geometry to provide for efficient electronic communication with the surrounding π system. The resulting electron-rich compounds are highly attractive both as objects for fundamental studies and functional materials for diverse applications.

Our recent achievements in this area will be presented herein.

1. M. Krug, M. Wagner, T. A. Schaub, W.-S. Zhang, C. M. Schüßelbauer, J. D. R. Ascherl, P. M. Münich, R. R. Schröder, F. Gröhn, P. O. Dral, M. Barbatti, D. M. Guldi, M. Kivala, Angew. Chem. Int. Ed. 2020, 59, 16233.
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3. I. Michalsky, V. Gensch, C. Walla, M. Hoffmann, F. Rominger, T. Oeser, P. Tegeder, A. Dreuw, M. Kivala, Chem. Eur. J. 2022, 28, e202200326.
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Regine von Klitzing

Technical University of Darmstadt, Germany

MICROGEL PARTICLES AS STABILIZERS FOR FOAMS: A MULTISCALE APPROACH

Foams appear in many applications such as in personal care products, firefighting and food technology. An elegant tool to tune the foam stability is the addition of polymers of different charge, amphiphilicity or molecular architecture. An example, which will be addressed here are foams which are stabilized by stimuli-responsive microgels.

For understanding macroscopic foam properties, it is important to get deeper insight into the different length scales, i.e. the structuring of microgels at the *air/water interface*, in *foam films*, which separate the *air bubbles* from each other and (macroscopic) *foams*.

The presentation will focus on microgels based on Poly-N-isopropylacrylamid (PNIPAM). Their stiffness and deformation at the air/liquid interface is controlled by the amount of cross-linker content which dominates the lateral pattern formation at the liquid interface. A challenge for studies of microgel-stabilized foam films are their massive inhomogeneities, which makes it difficult to measure the respective foam film thickness.

To get insight into foam film properties, we use a camera based thin film pressure balance to study microgel-stabilized foam films in terms of disjoining pressure inside the foam films, drainage kinetics, and foam film stability. Film thickness profiles give insights into particle bridging, agglomeration and network formation in the foam films.

For a complete picture, small angle neutron scattering (SANS) measurements on macroscopic foams provide additional insights into the link between foams and single foam films.

M. Kühnhammer, K. Gräff, E. Loran, O. Soltwedel, O. Löhmann, H. Frielinghaus, R. von Klitzing,
"Structure formation of PNIPAM microgels in foams and foam films", Soft Matter, 2022, doi:10.1039/d2SM01021F.

Speakers'

Thursday, March 16
9:00 AM–9:45 AM

Tuomas Knowles

University of Cambridge, UK

FUNCTIONAL MATERIALS FROM PROTEIN SELF-ASSEMBLY

This talk describes our research on exploring new types of artificial functional materials formed from the assembly of natural proteins.

The use of microscale engineering approaches, including droplet microfluidics, allows the formation of materials with multiscale structure, with the molecular scale structure from self-assembly and microscale structure from microfluidic processing.

I will highlight applications in different areas of interest, ranging from molecular encapsulation to hydrogels.

Mariana Kozlowska

Karlsruhe Institute of Technology (KIT), Germany

THE STORY OF PHOTOINITIATORS: A QUANTUM MECHANICAL PERSPECTIVE

Polymerization of photoresists in 3D laser nanoprinting is triggered by the formation of radicals upon light activation of the photoinitiator with a specific wavelength.

This process depends on a cascade of diverse preceding processes, such as multiphoton absorption, excited state absorption, internal conversion, radiative decay, nonradiative processes, e.g., intersystem crossing, etc.

They often also compete with each other. Moreover, highly reactive excited states may induce diverse intermolecular reactions with photoresist components, demonstrating different 3D laser nanoprinting resolution and speed.

Such processes cannot be fully understood by experiments alone. In my talk, I will reveal the molecular basis of the photoactivation and deactivation of photoinitiators from first principles calculations.

I will explain key processes that control the reactivity of the photoresists and their mutual dependence, discuss mechanisms of radical formation, and demonstrate the efficiency of polymerization initiation by 7-diethylamino-3-thenoylcoumarin (DETC) photoinitiator.

Thursday, March 16
9:45 AM–10:15 AM

Markus Kurth

Heidelberg University, Germany

MOLECULAR MECHANO-SENSING IN COLLAGEN

Nature has evolved sophisticated molecular systems that sense mechanical force. They do so by specifically responding to the external force by a structural change or mechanochemical reaction. Here, we will showcase collagen proteins as a model to study basic principles of molecular mechano-sensing and how to engineer or mimic such systems. Both by computational and experimental methods, we investigate how the proteins respond to force, and deal with radical migration after bond rupture and degradation. With these insights, for instance, we aim to design mimetic peptides that imitate the redox chemistry of collagen.

Barbara Lechner

Technical University of Munich, Germany

CLUSTER–SUPPORT INTERACTION DYNAMICS

Sub-nanometer metal clusters exhibit particular chemical and physical properties which often change non-monotonically with cluster size. Such clusters are used in heterogeneous catalysis, plasmonic devices, biosensors or coatings, to name just a few examples.

We produce size-selected clusters and soft-land them on oxide supports to investigate the dynamics inherent to such systems experimentally and correlate functionality with structural dynamics. Pt clusters, for example, typically become encapsulated by reducible supports such as Fe_3O_4 or TiO_2, altering the available active sites for catalytic reactions. Moreover, the cluster sinter by atom or cluster diffusion, depending on initial cluster size.

By combining atomically resolved movie-rate scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy in pressures from ultra-high vacuum to near-ambient conditions, we investigate dynamic phenomena including cluster fluxionality, diffusion and sintering as well as support etching and growth, cation dynamics, and adsorbate spillover on a fundamental level.

Tuesday, March 14
9:45 AM–10:30 AM

Sijbren Otto

University of Groningen, Netherlands

TOWARDS LIVING SYNTHETIC MATERIALS

How the immense complexity of living organisms has arisen is one of the most intriguing questions in contemporary science. We have started to explore experimentally how organization and function can emerge from complex molecular networks in aqueous solution.[1]

We focus on networks of molecules that can interconvert, to give mixtures that can change their composition in response to external or internal stimuli or internal processes. Noncovalent interactions within molecules in such mixtures can lead to the formation of foldamers.[2,3]

Molecular recognition between molecules in such mixtures leads to their mutual stabilization, which drives the synthesis of more of the privileged structures (Figure 1), giving rise to self-assembled materials. As the assembly process drives the synthesis of the very molecules that assemble, the resulting materials are self-synthesizing. Intriguingly, in this process the assembling molecules are replicating themselves, where replication is driven by self-recognition of these molecules in the dynamic network.[4] The selection rules that dictate which (if any) replicator will emerge from such networks are starting to become clear.[5] We have also witnessed spontaneous differentiation (a process akin to speciation as it occurs in biology) in a system made from a mixture of two building blocks.[6] When such systems are operated under far-from-equilibrium flow conditions, adaptation of the materials to a changing environment can occur.

Materials that are able to catalyse reactions other than their own formation have also been obtained, representing a first step towards metabolism.[7,8] Thus, the prospect of Darwinian evolution of purely synthetic molecules and materials is tantalizingly close and the prospect of synthesizing life *de-novo* is becoming increasingly realistic.[9,10]

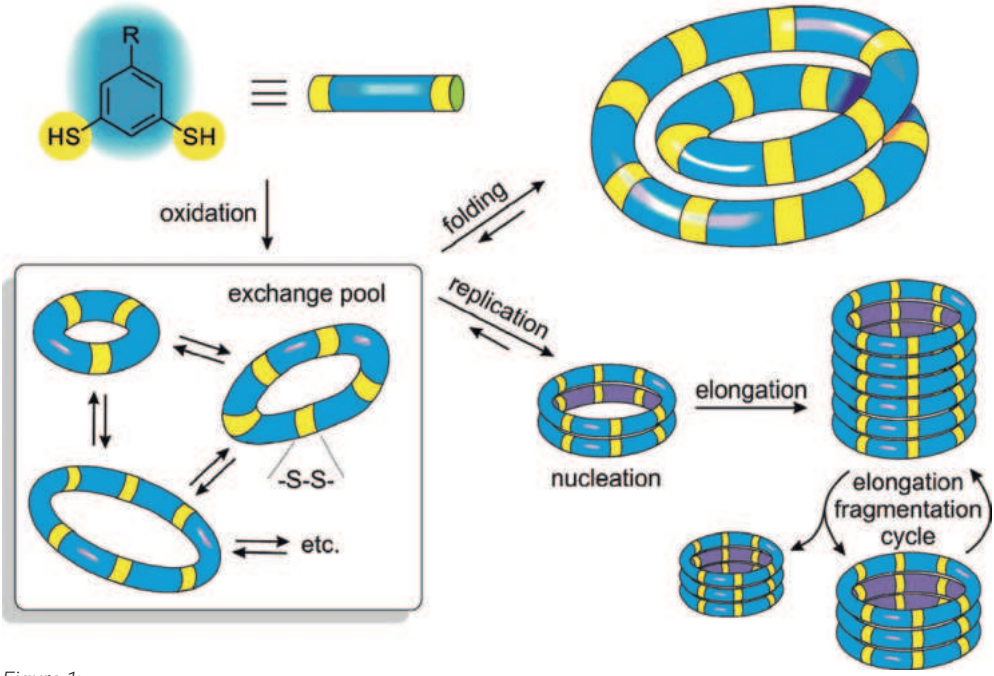

Figure 1:
Molecular recognition between molecules in a dynamic molecular network can lead to self-synthesizing materials, build up from self-replicating molecules, while non-covalent interactions within a molecule lead to self-synthesizing foldamers.

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Tuesday, March 14
5:00 PM–5:30 PM

Ute Schepers

Karlsruhe Institute of Technology (KIT), Germany

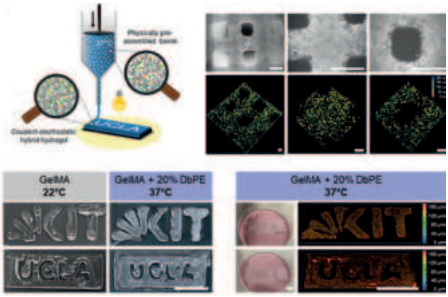
ENHANCING BIOSYNTHETIC SOFT MATERIALS FOR 3D BIOPRINTING OF TISSUES

Despite a remarkable progress of biofabrication techniques in tissue engineering, the development of extrudable bioinks that perform optimally at physiological temperatures remains a major challenge. Technologies such as light based printing technologies such as two photon based direct laser writing and DLP circumvent the problem. However, these technologies usually need sophisticated photoinitiators and are limited to their printing size. In order to enhance the survival of cells in 3D bioprinted objects functionalized biopolymers often based on extracellular matrix components are used.

The majority of these biopolymers and photocurable precursor solutions exhibit low viscosities at 37 °C, resulting in undesirable flows and loss of form prior to chemical crosslinking. Temperature-sensitive bioinks, such as gelatin methacryloyl (GelMA) or other gelatin and collagen based bioinks, can be deposited near their gelling point, but suffer from suboptimal temperature-induced pre-gelation, poor cell viability emerging from long holding times in the cooled cartridges, inefficient temperature transfer from the print bed, and discontinuous layer-by-layer fabrication.

Recently we have developed block polyelectrolyte additives serve as effective viscosity enhancers when added to non-extrudable precursor solutions. Rapid, electrostatic self-assembly of block polyelectrolytes into either micelles or interconnected networks provides a hydrogel scaffolding that forms nearly instantly, lends initial structural robustness upon deposition, and enhances shear and tensile strength of the deposited bioinks.

Moreover, our approach enables continuous extrusion without the need of chemical crosslinking between individual layers, paving the way for fast biomanufacturing of human-scale tissue constructs with improved inter-layer bonding. In order to enhance vialbility of cells we also are heavily involved in the synthesis of novel cell friendly photoinitiators.



Christine Selhuber-Unkel

Heidelberg University, Germany

3D STRUCTURED MICRO-ENVIRONMENTS FOR CONTROLLING CELLS

Tissue cells encounter complex, microstructured 3D environments in their *in vivo* surroundings. These environments can have tiny pores, various mechanical properties and they are also actively deformed and shaped by the cells themselves.

To mimic such extracellular microenvironments and to systematically study their effects on the cells, we are working on methods to dynamically and structurally control cellular microenvironments. Examples include processes using two-photon direct laser for controlling single cells and multicellular systems, but also dynamic and reversible changes of the mechanical properties of hydrogels by transiently changing polymer entanglement, as well as scaffolds that are actively deformed by the cellular systems.

We will here show both the methods to achieve these effects, but also results on cell adhesion and cell migration, thus providing prospects for shaping dynamic, structured microenvironments in biomaterial applications.

Wednesday, March 15
10:30 AM–11:15 AM

Rein Ulijn

Advanced Science Research Center, City University of New York, USA

REPURPOSING THE CHEMISTRY OF LIFE FOR NANOTECHNOLOGY

We are interested in how functionality emerges from interactions and reactions between biomolecules, and subsequently how these functions can be incorporated into materials.

Instead of using sequences known in biological systems, we use unbiased computational and experimental approaches to search and map the peptide sequence space for specific interactions and functions, with a focus on side chain, instead of backbone interactions.

The talk will explore how to program molecular order and disorder through side chain interactions in short peptides, and how the conformations adopted by these peptides can be exploited to regulate interfacial assembly properties, and liquid-liquid phase separation. We will discuss chemo-mechanical peptide-crystals with connected soft and stiff domains, that change their properties upon changes in hydration states. The last part of the talk will focus on our progress in holistic study of mixtures of molecules that individually are simple and non-functional, but as components of complex interacting systems, however, they give rise to self-organization patterns that are dictated by the environmental conditions.

Collectively, we expect to identify insights that allow the repurposing of nature's molecules to design new materials beyond those available through biology.

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Helma Wennemers

ETH Zürich, Switzerland

CONTROLLING SUPRAMOLECULAR ASSEMBLIES WITH PEPTIDIC SCAFFOLDS

Self-assembly and selective recognition events involving proteins are critical in nature for the function of numerous different processes, for example, catalysis, signal transduction or the controlled formation of structural components such as bones.

My group is intrigued by the question whether also peptides with significantly lower molecular weights compared to proteins can fulfill functions for which nature evolved large macromolecules. Specifically, we ask whether peptides can serve as effective asymmetric catalysts, templates for the controlled formation of metal nanoparticles,[1] hierarchical supramolecular assemblies,[2,3] and synthetic collagen-based assemblies.[4,5]

The lecture will focus on our research interests in supramolecular assemblies and their application in chemical biology and material sciences.

Monday, March 13
2:00 PM–2:30 AM

Christof Wöll

Karlsruhe Institute of Technology (KIT), Germany

ATOMICALLY PRECISE ASSEMBLY OF FUNCTIONAL MOLECULAR SOLIDS FROM BUILDING BLOCKS: THE SURMOF APPROACH

Realizing molecular "Designer Solids" by programmed assembly of building units taken from libraries is a very appealing objective. Recently, metal-organic frameworks (MOFs) have attracted a huge interest in this context. Here, we will focus on MOF-based electrochemical, photoelectro-chemical, photovoltaic, and sensor devices. Internal interfaces in MOF heterostructures are also of interest with regard to photon-upconversion and the fabrication of diodes.

Since the fabrication of reliable and reproducible contacts to MOF-materials represent a major challenge, we have developed a layer-by-layer (lbl) deposition method to produce well-defined, highly oriented and monolithic MOF thin films on appropriately functionalized substrates. The resulting films are referred to as SURMOFs[1,2] and have very appealing properties in particular with regard to optical applications[3]. The fabrication of hetero-multilayers is rather straightforward with this lbl method.

In this talk, we will describe the principles of SURMOF fabrication as well as the results of systematic investigations of electrical and photophysical properties exhibited by empty MOFs and after loading their pores with functional guests. We will close with discussing further applications[4] realized by loading MOFs with nanoparticles or quantum dots and by creating molecular solids lacking inversion symmetry for second harmonic generation (SHG).[5]

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Omar Yaghi

University of California, USA

RETICULAR MATERIALS TO MACHINES FOR CLIMATE CHANGE

Reticular chemistry, linking of molecular building blocks by strong bonds to make crystalline extended structures, has led to ultra-porous metal-organic frameworks (MOFs) and covalent organic frameworks (COFs).

Here, organic and inorganic (for MOFs), as well as just organic molecules are stitched together with covalent bonds (for COFs) to make crystalline, porous frameworks of high architectural and chemical robustness. This opened the way to carrying out chemistry on frameworks and chemically functionalizing the pores for water harvesting from air and carbon capture from air and flue gas.

The chemistry to make these frameworks and their integration into machines capable of producing clean water and clean air will be presented.

Selected Talks

Sorted by Date

A Selected Talk consists of a 15-minute talk and a 5-minute Q&A session.

Monday, March 13 3:00 PM–3:20 PM	Laser-Based Nano 3D Printing for Parallel Chemistry and Screening	**Felix Loeffler**
Tuesday, March 14 11:15 AM–11:35 AM	Printability and Post-Processing Characteristics of Powder Bed Fusion Additive Manufacturing SS 17-4ph Fine Porous TPMS Cellular Structures	**Manjaiah Mallaiah**
Tuesday, March 14 11:35 AM–11:55 AM	Controlling Cell-Material Interactions through Responsive Peptide Nanostructures	**Christopher V. Synatschke**
Thursday, March 16 11:30 AM–11:50 AM	Phosphate-Driven Systems Chemistry	**Charalampos Pappas**
Thursday, March 16 2:15 PM–2:35 PM	3D-Bioprinting Effects on Cell and Organoid Proliferation and Metabolism	**Erin Spiller**
Thursday, March 16 2:35 PM–2:55 PM	Stimuli Responsive Hydrogel Actuators for Microfluidic Applications	**Tobias Spratte**

Monday, March 13
3:00 PM–3:20 PM

LASER-BASED NANO 3D PRINTING FOR PARALLEL CHEMISTRY AND SCREENING

Felix F. Loeffler

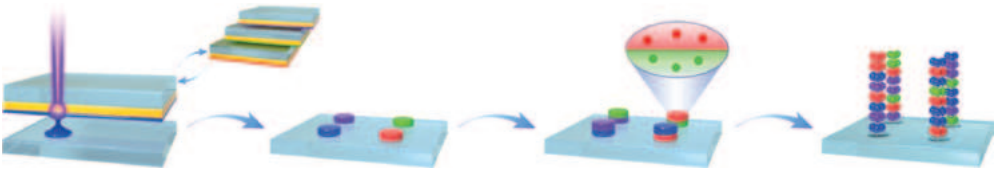
Max Planck Institute of Colloids and Interfaces, Germany

The screening of large and diverse chemical or materials libraries promises the discovery of new biomedical compounds or catalysts. However, the lack of flexible and cost-efficient synthesis technologies for complex substance libraries prevents many research applications. By employing solid polymers instead of liquid solvents as a medium for delivery of chemicals and reaction control, we can rapidly synthesize large libraries of different biomolecules and nanomaterials.

Chemical reactions and syntheses typically proceed in liquid solvents. Yet, once the reaction partners are added to the liquid, diffusion governs the process, making it difficult to control. Especially when performing many reactions in parallel, this severely hampers reproducibility and efficiency.

Instead of solvents, polymers can be an ideal alternative. Solid and stable at room temperature, they can be triggered by heating above the glass transition temperature. This switches on diffusion inside the polymer, without losing its shape and position, enabling well-controlled parallel reactions in polymer reactors.

With our laser-based polymer patterning technologies[1–3], we can synthesize biomolecules in parallel, such as peptides for vaccine development[4]. In combination with our novel vapor-based synthesis approach [5], other reactions, such as chemical glycosylation can be explored in parallel. Recently, we developed a high-speed approach for printing and driving chemical reactions at the same time with the laser[2]. Thereby, we can synthesize defined nanoparticles[6] or generate fluorescent material libraries within milliseconds for high-throughput materials screening[7]. Currently, we strive to revolutionize nano 3d printing of polymers, enabling nanometer layer resolution for e.g. device and sensor fabrication[8].



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6. Zhang et al., Nat. Commun. 2021, 12, 3224
7. Zhang et al., under review
8. Reonneberger et al., in preparation

PRINTABILITY AND POST-PROCESSING CHARACTERISTICS OF POWDER BED FUSION ADDITIVE MANUFACTURING SS 17-4PH FINE POROUS TPMS CELLULAR STRUCTURES

Manjaiah Mallaiah,
Shivank Tyagi

National Institute of Technology Warangal, India

Triply periodic minimal surfaces (TPMS) are emerging as an excellent solution in the manufacturing of porous structures due to their smooth surface and mathematically controllable design features. The laser powder bed fusion (LPBF) additive manufacturing technique is the most preferable method for the development of such complex lattice structures.

However, this technology can't be employed directly in medical implant applications due to poor surface integrity. It requires post-processing to overcome such limitations in the surface integrity of AM. The post-processing methods like sandblasting, electro-discharge machining, laser polishing, chemical polishing, and traditional machining is often used.

All these methods are not suitable for intricate complex structures as well as lattice structures. On the other hand, methods like blasting and electrochemical anodizing are most suitable for intricate geometries and lattice structures.

Hence, in the present study blast finishing and electrochemical anodizing have been employed to achieve the desired surface finish and integrity of very fine pore sized (100~200 µm) SS17-4ph-based TPMS structures. Three different lattice structures such as gyroid, diamond, and Schwarz were considered for printing using the LPBF technique.

A significant reduction in surface roughness has attained a maximum of 85% in electrochemical anodizing and 50% in blast finishing post-processing even inside the intricate surfaces. In addition, the cell size and morphology were studied to correlate the designed and post-processed lattice structures. Also, an increase in surface hardness properties was observed in both post-processed samples.

Based on the results, electrochemical anodizing showed excellent capability in improving surface integrity, especially for lattice structures that may be used in biomedical implants.

Tuesday, March 14
11:35 AM–11:55 AM

CONTROLLING CELL-MATERIAL INTERACTIONS THROUGH RESPONSIVE PEPTIDE NANOSTRUCTURES

Christopher Synatschke,
Kübra Kaygisiz, Adriana Ender, Jasmina Gačanin, Luisa Wiechmann, Tanja Weil

Max-Planck-Institute for Polymer Research, Germany

Short, self-assembling peptides (SAPs) are emerging as functional biomaterials, due to their ability to mimic naturally occurring structures. Using tailor-made SAPs, we study cell-material interactions and develop novel biomaterials.

Short peptides with an optimized sequence were able to support the growth of neuronal cells and enhance nerve regeneration *in vivo*. A library of peptides was used to identify structure-activity correlations for enhancing viral transduction efficiency. Data mining identified critical structural parameters for bioactivity and enabled the prediction of highly efficient sequences. By introducing pH- and light-responsive groups, we gain control over the assembly and disassembly behavior of SAPs as well as their ability to present epitopes to cells (Figure 1a). We can create bioactive gradients on surfaces, which precisely control the number of cells that attach to the coated surface.[1] Using photolithography to destroy pre-assembled photoreactive SAPs, patterns of cell-adhesive and cell-repulsive regions are created with high spatial precision (Figure 1b, c).[2] Finally, hydrogels with novel properties are obtained when SAPs are connected to polymer backbones: By conjugating pH-responsive depsi-peptides to biopolymers, we can create injectable and thixotropic hydrogels, where the SAPs act as supramolecular crosslinkers (Figure 1d).[3] These gels show ultrafast and quantitative recovery of their mechanical properties after experiencing liquifying shear.

Figure 1: *a) Bioactive gradient of RGD-presenting peptides measured in MALDI-MSI.* *b) Minerva pattern (Proteostat staining) and c) MPIP logo from A549 cells (calceine staining) obtained through photolithography of photocleavable peptide.* *d) Injectable hydrogel from peptide grafted biopolymer.*

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PHOSPHATE-DRIVEN SYSTEMS CHEMISTRY

Charalampos G. Pappas,
Kun Dai, Mahesh Pol

Cluster of Excellence livMatS, University of Freiburg, Germany

Phosphates and phosphate esters regulate and enable functions[1]: from encoding genetic information and directing temporal protein functions to signaling transduction mechanisms. Despite the multifaceted role of phosphates in biology, their use in supramolecular systems chemistry remains largely uninvestigated.

Our group focusses on developing roles for phosphates outside of biology and researches on the idea of providing chemical information within abiotic phosphate fuels to control selectivity and reactivity in the context of phosphate-driven structure formation. The information is provided by chemical functionalization of energy-rich molecules, whereby the information encode structural assembly of phosphate precursors prior to their consumption, or transfer large chemical groups onto self-assembling species during energy transfer. Herein, we utilize aminoacyl phosphates, which contain enough chemical information to trigger dynamic phase changes during spontaneous peptide oligomerisation. This strategy leads to the formation of a pool of oligomers, where aqueous phase peptide synthesis occurs, in which short oligomers are prevalent in the solution phase, while more hydrophobic residues are self-protected in the aggregated phase. By continuous addition of activated monomers, oligomers of different length and composition were self-selected, capable of forming highly ordered supramolecular structures. Moreover, the presence of less reactive nucleophiles in the networks drives dynamic phase separation, where the local microenvironment dictates the self-assembling pathway. The approach taken here enables access to materials that respond to chemical energy and displaying mnemonic effects.

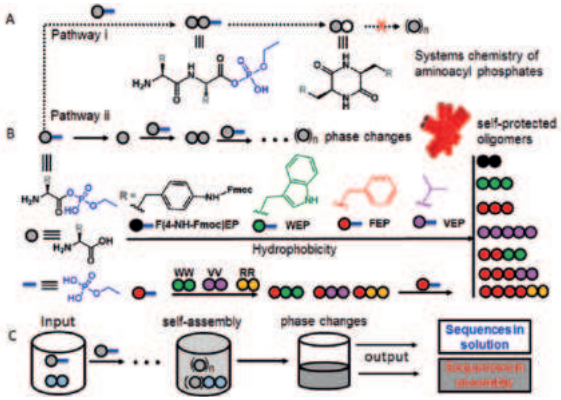

Figure 1:

Systems chemistry of aminoacyl phosphates:

(a) Pathway-dependent oligomerisation.

(b) Chemical structure of aminoacyl phosphates and

(c) Aqueous peptide synthesis, emerging from spontaneous phase changes.

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3D-BIOPRINTING EFFECTS ON CELL AND ORGANOID PROLIFERATION AND METABOLISM

Erin Spiller[1,2],
Ivan Bagaric[1], Daniela Duarte Campos[1,2]

1 Bioprinting Group, Center for Molecular Biology (ZMBH), Heidelberg University, Germany
2 3DMM2O - Cluster of Excellence (EXC-2082/1 – 390761711), Heidelberg University, Germany

Introduction: 3D bioprinting is becoming more common within the bioengineering field and with it bringing many benefits, however more understanding of the effect on the cells is needed. In traditional 2D cell culture common assays used to characterize cells include vital dyes, metabolic assays, and morphological analysis. Often these characterizations are relatively straight forward as cells are grown in a single layer. The addition of a 3rd dimension adds challenges to these traditional characterizations.

Objectives: Using patient derived organoids, we want to examine the effect of bioprinting on cells, specifically investigating metabolic states and viability over time.

Materials and Methods: Patient derived colon organoids were grown in organoid growth media, harvested from basement membrane extract (BME) and directly printed or digested to single cell. Cells were encapsulated in hydrogels at 5x105 cells/ml, then casted (controls) or printed with a drop-on-demand bioprinter (BlackDrop). Viability was measured at multiple time points using vital dyes. Metabolism via ATP was measured using a luminescent assay. Organoid formation and morphology was imaged and tracked over time using brightfield and fluorescent microscopy.

Results: We compared cell viability in printed and casted organoids using vital dyes and image analysis. We tracked the proportion of live/dead cells over time (up to one week) to examine the percentage of cells that survive the printing process as well as proliferation over time. Metabolic changes between printed and unprinted cells were also examined. Organoid formation, size and growth were tracked to determine recovery after the 3D printing process.

Conclusion: Using tools adapted from traditional 2D cell culture methods we were able to characterize 3D printed and non-printed organoid cells. This is a pilot study showing the impact of bioprinting technologies on the functionality of cells at the organelle and molecular level over time.

STIMULI RESPONSIVE HYDROGEL ACTUATORS FOR MICROFLUIDIC APPLICATIONS

Tobias Spratte,
S. Geiger, F. Colombo, A. Leal-Egaña, L-Y. Hsu, E. Blasco and C. Selhuber-Unkel

Institute for Molecular Systems Engineering and Advanced Materials (IMSEAM),
Heidelberg University, Germany

Stimuli responsive hydrogels are ideal materials for the design of soft actuators, due to their deformable and soft nature and their capability of exerting forces to external objects. These materials change their properties as a response to environmental changes. Thermoresponsive poly(N-isopropylacrylamide) (pNIPAM) hydrogels, for example, can undergo a volume change by controlling the environmental temperature and therefore actuate soft robots. We recently discovered the potential of integrating interconnected microchannels into the pNIPAM hydrogels to increase their responsivity, response rate and the mechanical forces exerted by the material.[1]

In addition, high-resolution fabrication methods such as two-photon direct laser writing, allow for precise control about the microstructure shapes. In our previous work, we observed that controlling the surface-to-volume ratios of pNIPAM hydrogel micropillars influences the material shrinkage significantly and improves the actuation function of the micropillars.[2]

In our project, we focus on the fabrication of a dynamically adjustable microfluidic chip made of pNIPAM hydrogel pillars, which are arranged in a densely packed array. Stimulation of the hydrogel pillars causes a volume change, that can lead to a channel formation. Such a dynamic actuator system could be highly beneficial in dynamic microfluidic systems, where the function of currently used devices is limited by predefined geometries.

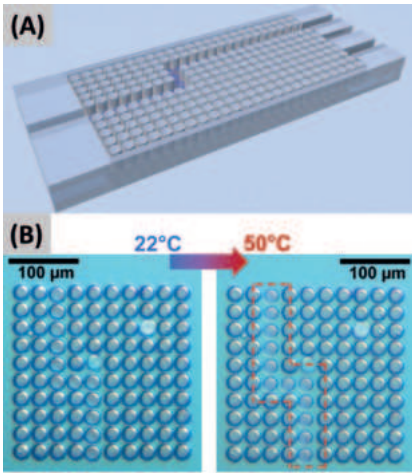

Figure 1: (A) Sketch and

(B) real structure of the soft and dynamic microfluidic chip forming a channel upon stimulation.

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2. T. Spratte, S. Geiger, F. Colombo, A. Mishra, M. Taale, L-Y. Hsu, E. Blasco, C. Selhuber-Unkel, "Increasing the Efficiency of Thermoresponsive Actuation at the Microscale by Direct Laser Writing of pNIPAM". Adv. Mater. Technol., 2022, 2200714

Flash Talks

Monday, March 13

4:05 PM–4:07 PM	Infrared Scanning Near-Field Spectroscopic Studies of Bulk and 3D Laser Printed P(MMA-co-HEMA)-PS Block Copolymer	**Nadine von Coelln**
4:07 PM–4:09 PM	Two-Photon Laser Printing of Peptide-Functionalized Hydrogels	**Niklas Simon Schwegler**
4:09 PM–4:11 PM	Constructing Photoresponsive MOFs Containing Azoheteroarenes as Light-Switchable Ligands	**Jonas Christian Rickhoff**
4:11 PM–4:13 PM	Earth-Abundant Transition Metal Complexes in Two-Step Absorption for 3D Printing	**Aleksandra Vranic**
4:13 PM–4:15 PM	Optical Properties of Metal-Organic Frameworks and Devices Thereof	**Marjan Krstić**

Sorted by Date

Tuesday, March 14

5:30 PM–5:32 PM	Photoresponsive Hybrid Hydrogel with a Self-Assembling Peptide which Switches in the NIR Range Due to the Addition of UCNPs	**Ivo Rosenbusch**
5:32 PM–5:34 PM	Dynamical Consistent Anisotropic Coarse Grained Simulation and Application to Polymer Additive Manufacturing	**Ka Chun Chan**
5:34 PM–5:36 PM	Cell-Mimics Continuously Communicate in 2D, Supported by 3D Microfluidic Perfusion	**Imre Banlaki**
5:36 PM–5:38 PM	Chemical Functionalization and Actuation of Microprinted DNA-Hydrogels	**Brigitta Dúzs**
5:38 PM–5:40 PM	3D Macro and Micro Printing of Semiconductor Based Photoresins and Their Optoelectronic Applications	**Ozan Karakaya**
5:40 PM–5:42 PM	Bioprinting of Synthetic Vesicles for Tissue Engineering Applications	**Ole Thaden**
5:42 PM–5:44 PM	Isolation of Cell Clusters in Spheroid by 2PP 3D Printing	**Barbara Schamberger**
5:44 PM–5:46 PM	Push-Pull Chromophores for Electro-Optical Materials	**Patrick Kern**

Monday, March 13
4:05 PM–4:07 PM
Poster Presentation:
Monday, 4:15 – 4:45 PM

INFRARED SCANNING NEAR-FIELD SPECTROSCOPIC STUDIES OF BULK AND 3D LASER PRINTED P(MMA-CO-HEMA)-PS BLOCK COPOLYMER

Nadine von Coelln[1]

Britta Weidinger[2,3], Tanja Schmitt[1], Christian Huck[1], Irene Wacker[3], Rasmus Schröder[3], Eva Blasco[2,3] and Petra Tegeder[1]

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2 Institute of Organic Chemistry, Heidelberg, Germany
3 Institute for Molecular Systems Engineering and Advanced Materials, Heidelberg, Germany

Block copolymers consist of chemically distinct polymer blocks which are covalently bond to each other. In the bulk, P(MMA-co-HEMA)-polystyrene block copolymer spontaneously separates in microphases due to the block segments being thermodynamically incompatible.[1] For 3D laser printing on the nanoscale, however, self-assembly of block copolymers has not been reported yet.

Scattering-type infrared scanning near-field optical microscopy (IR-SNOM) and atomic force microscopy-infrared spectroscopy (AFM-IR) offer the possibility of infrared imaging and spectroscopy at 10 nm spatial resolution.[2] When irradiating P(MMA-co-HEMA)-polystyrene block copolymer at independent absorption bands corresponding to either P(MMA-co-HEMA) or polystyrene, chemical imaging of the components' spatial arrangement is possible.[3]

Here, for bulk P(MMA-co-HEMA)-polystyrene block copolymer samples a strong self-assembly of the block segments is shown using IR-SNOM and AFM-IR. Nanoscale investigations of the 3D laser printed samples demonstrate the need for optimization of the printing process. These studies allow to gain insights into the printing process and provide guidelines for its optimization approaching the aim of the formation of microstructures with controlled nanoscale periodic porosity.

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3. W. Lee et al., Polym. Test. 2021, 104, 107409.

Monday, March 13
4:07 PM-4:09 PM
Poster Presentation:
Monday, 4:15 – 4:45 PM

TWO-PHOTON LASER PRINTING OF PEPTIDE-FUNCTIONALIZED HYDROGELS

Niklas Simon Schwegler

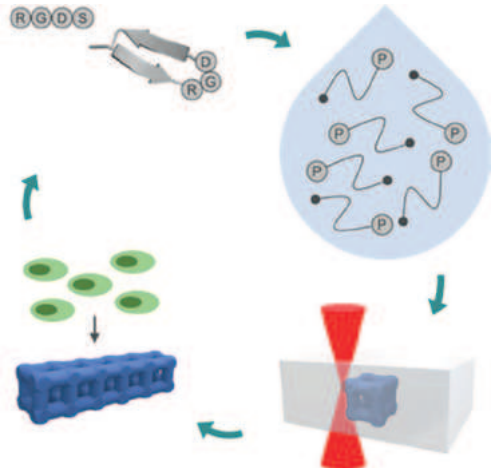
Eva Blasco, Franziska Thomas

Institute of Organic Chemistry, Institute for Molecular Systems Engineering and Advanced Materials, Heidelberg University

The extracellular matrix regulates and initiates cell migration, differentiation, and morphogenesis. It is thus an irreplaceable mediator of processes like tissue growth, wound healing, and fibrosis. Consequently, artificial matrix models are of high scientific interest for the creation of customizable, functional 3D environments for cell experiments.

We propose the development of such materials in a bottom-up approach. Peptide scaffolds are redesigned to mimic components of natural extracellular matrix. Starting from simple models of matrix proteins such as fibronectin, increasingly complex and similar-to-native peptides are developed. These peptidic models are synthesized via solid-phase synthesis. They are functionalized with printable moieties such as acrylates. The resultant monomers are processed via two-photon laser printing to produce hydrogels of predefined shapes and architectures at the microscale. The cell-responsive properties of the printed structures are being evaluated in proof-of-concept cell adhesion studies.

This approach allows for the creation of extracellular microenvironments, e.g. for interaction assays of immune cells and malignant cells. While past models in this research area were mainly based on 2D matrices, these novel materials will provide two important additional aspects to the experiments: The influence of the extracellular matrix as biochemically active 3D scaffold for cells. And, through precise printing of precursors at the microscale, the production of materials with micro-architectures, customized for each application purpose.



Monday, March 13
4:09 PM–4:11 PM
Poster Presentation:
Monday, 4:15 – 4:45 PM

CONSTRUCTING PHOTORESPONSIVE MOFS CONTAINING AZOHETEROARENES AS LIGHT-SWITCHABLE LIGANDS

Jonas Christian Rickhoff[1]

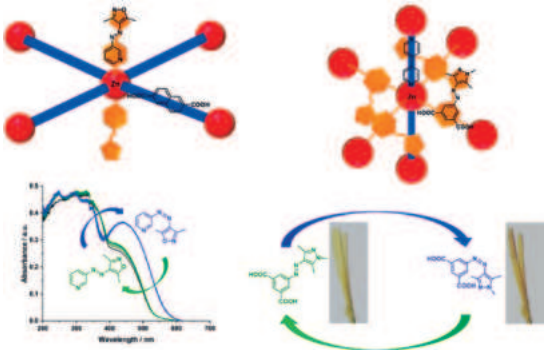
Misaki Nakagawa[2], Bart Jan Ravoo[1], Ryotaro Matsuda[2]

1 University of Münster, Germany
2 Nagoya University

Metal-organic frameworks (MOFs) are promising materials for various applications such as gas storage, or catalysis. Being able to address these compounds with light to alter macroscopic behavior is a feasible way to obtain responsive materials.[1] A series of MOFs have been synthesized using Zn as metal node and arylazopyrazoles or -isoxazoles as well as different dummy ligands under solvothermal conditions. These materials were characterized using single crystal- and powder X-ray diffraction, UV- and NMR spectroscopy.

The reversible E- to Z-isomerization of the photoswitches was used to control different properties of the crystals using UV- and green light in MOFs containing pyridine based azoisoxazoles. Under UV irradiation (365 nm), a photostationary state of up to 76% Z-isomer could be achieved while full back conversion to 100% E-isomer occurred at irradiation with green light (510 nm). At the PSS365, a reversible increase in CO2 sorption of 76% compared to the non-irradiated material was observed.

Furthermore, a MOF that undergoes photoinduced macroscopic changes could be obtained using isophthalate derivatives of arylazopyrazoles. Thin crystal sheets of this system twist under UV irradiation and flatten out upon irradiation with green light. Interestingly, a plethora of different ligand systems have been tested of which many showed the ability to crystallize into MOFs. This work can be used as a toolbox for constructing photoresponsive MOFs and may serve as a guide towards fabrication and application of such.



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Monday, March 13
4:11 PM–4:13 PM
Poster Presentation:
Monday, 4:15 – 4:45 PM

EARTH-ABUNDANT TRANSITION METAL COMPLEXES IN TWO-STEP ABSORPTION FOR 3D PRINTING

Aleksandra Vranić[1]

Valentina Ferraro[1], Martin Wegener[2], Stefan Bräse[1]

1 Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Germany
2 Institute of Applied Physics and Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany

Photopolymerization reactions require photoinitiators able to absorb light and transfer it to form free radicals. UV light is commonly applied to initiate photopolymerizations although longer wavelengths should be preferred due to their higher depth of penetration and less-energetic demands. The resulting polymer can be used for a wide variety of applications that include 3D printing.[1]

Differently from common one-photon processes, two-step absorption is an emerging alternative that allows to exploit NIR irradiation and that can be applied for 3D laser nanoprinting due to its nonlinearity. Organic fluorophores were recently exploited for such purpose,[2] but transition metal complexes represent possible candidates thanks to their redox potentials and long photoluminescent lifetimes.

Transition metal-based photoinitiators have been widely investigated in two- or three-component systems together with onium salts as co-initiators and additives for the free-radical polymerization of trimethylolpropane triacrylate (TMPTA).[3] In this context, earth-abundant complexes should be preferred with respect to photoinitiators based on precious and rare metals such as Ru(II) and Ir(III), thanks to their lower toxicity and cost, as well as their higher abundance. Between them, Cu(I) complexes represent a valid choice due to the versatility of the photophysical properties that can be directly tuned in terms of emission maxima, lifetimes and quantum yields by performing small modifications on the ligands skeleton.[4]

1. A. Bagheri, J. Jin, ACS Appl. Polym. Mater. 1 (2019) 593.
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Monday, March 13
4:13 PM–4:15 PM
Poster Presentation:
Monday, 4:15 – 4:45 PM

OPTICAL PROPERTIES OF METAL-ORGANIC FRAMEWORKS AND DEVICES THEREOF

Marjan Krstić[1]

B. Zerulla[2], C. Holzer[1], D. Beutel[1], A. Fingolo[3],
L. Heinke[3], I. Fernandez-Corbaton[2], C.Wöll[3], and C. Rockstuhl[1,2]

1 Institute of Theoretical Solid State Physics, Karlsruhe Institute of Technology (KIT), Germany
2 Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany
3 Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), Germany

Designing hybrid organic-inorganic optical devices requires understanding and methodology from multiple scientific domains, i.e., chemistry, optics, material science, and engineering. Recently, a novel multi-scale modeling approach, connecting quantum simulations of individual molecules to optical simulations of entire devices, was developed to serve precisely that need.[1, 2]

To demonstrate the application of such a multi-scale modeling scheme, we explore here the optical properties of crystalline metal-organic frameworks (MOFs) and devices thereof. MOFs are materials made by the additive arrangement of metal and organic building blocks in periodic scaffolds. MOFs with a tailored optical response are obtained by selecting optically active linkers that connect metallic centers. By integrating MOFs into structured photonic devices, advanced structure-property relations emerge that we explore by computational means. In our contribution, the optical response of these systems that can be probed with different spectroscopic techniques is analyzed, e.g., UV-VIS,[1] ECD, IR, VCD, Raman, etc. Examples of such analysis are shown in Fig. 1.

Our results show an excellent agreement between simulations and experiments for chosen MOFs, opening a promising route for designing novel optical devices based on new molecular materials with unprecedented performance.

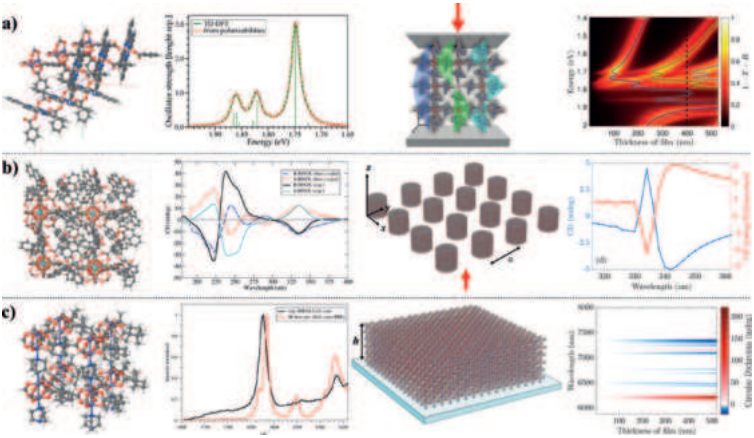

Fig. 1:

a) TDDFT absorption of Zn-SiPc-MOF and Fabry-Perot cavity filled with it. Optical response shows light-matter interaction in the cavity.

b) A model of chiral UiO-67-BINOL MOF with ECD spectra. Metasurface made of MOF cylinders shows enhancement of the ECD.

c) The chiral camphoric acid MOF and IR spectrum. The VCD response of the MOF thin film on the surface.

1. B. Zerulla, M. Krsti´c, D. Beutel, C. Holzer, C.W¨oll, C. Rockstuhl, I. Fernandez-Corbaton, Adv. Mater. 34 2200350, 2022
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Tuesday, March 14
5:30 PM–5:32 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

PHOTORESPONSIVE HYBRID HYDROGEL WITH A SELF-ASSEMBLING PEPTIDE WHICH SWITCHES IN THE NIR RANGE DUE TO THE ADDITION OF UCNPS

Ivo Rosenbusch

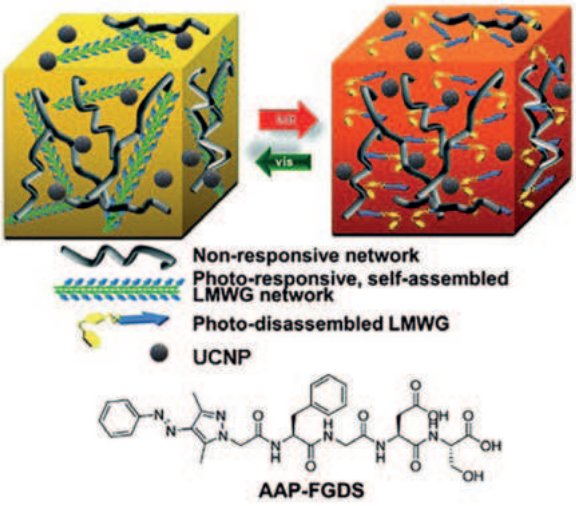
Prof. Dr. Bart Jan Ravoo

University of Münster, Germany

Self-assembled low molecular weight hydrogels are of particular interest for smart nanomaterials because they have special mechanical properties and are easy to prepare.

Here, we prepare the gel by adding AAP-FGDS to a covalent non-reactive agarose network. The photoresponsive peptide hydrogel exhibits excellent reversible properties. The photochemical properties are triggered by upconversion nanoparticles (UCNPs) located in the gel. These nanoparticles can convert photons in the NIR range into photons of higher energy through the process of upconversion. Irradiation with an NIR laser dissolves the self-assembled three-dimensional structure, resulting in a softer hydrogel. When irradiated with visible light, the gel returns to its original shape.

The hydrogel and its various characteristic properties were studied by Uv-vis-, NMR spectroscopy and rheometric measurements. The properties of UCNPs were investigated by DLS, TEM and emission spectroscopy and adapted to the requirements of the photosensitive hybrid hydrogel. The obtained gel can be used for future *in vivo* applications (e.g. targeted delivery of drugs in the human body) due to its non-toxic properties and the fact that NIR light is tissue-permeable.



Tuesday, March 14
5:32 PM–5:34 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

DYNAMICAL CONSISTENT ANISOTROPIC COARSE GRAINED SIMULATION AND APPLICATION TO POLYMER ADDITIVE MANUFACTURING

Ka Chun Chan

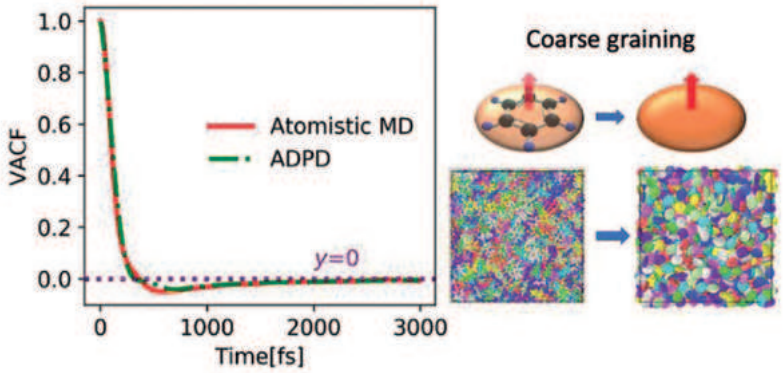
Wolfgang Wenzel

Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany

Coarse grained (CG) molecular dynamics simulations are widely used to accelerate atomistic simulations, but generally lack a formalism to preserve the dynamics of the system. For spherical particles the Mori-Zwanzig approach has ameliorated this problem. Here we present an anisotropic dissipative particle dynamics (ADPD) model as an extension of this approach, which accounts for the anisotropy for both conservative and non-conservative interactions.

For a simple anisotropic system we employ ellipsoidal CG particles to represent benzene molecules. To represent the anisotropy of the system, the conservative and dissipative term are approximated using Gay-Berne functional forms via a force-matching approach. We compare our model with other CG models and demonstrate that it yields better results in both static and dynamical properties. The inclusion of the anisotropic non-conservative force preserves the microscopic dynamical details and hence the dynamical properties, such as diffusivity, can be better reproduced by the aspherical model. By generalizing the isotropic DPD model, this framework is effective and promising for the development of CG model for polymers, macromolecules and biological system.

One of the application is to simulate polymer additive manufacturing, i.e. direct laser writing. Due to the length scale and aromatic rings of the polymer molecules, ADPD model is able to capture the dynamical properties of the macromolecular system in long time scale by preseving the molecular structural details at CG level. Herein we extend our model from simple organic molecules application to complex macromolecules. Based on the ADPD model, we vary the relative concentration of photoresist reactions to calculate the degree of conversion and the relative mechanical strength of the printed structures.



Tuesday, March 14
5:34 PM–5:36 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

CELL-MIMICS CONTINUOUSLY COMMUNICATE IN 2D, SUPPORTED BY 3D MICROFLUIDIC PERFUSION

Imre Banlaki

Henrike Niederholtmeyer

Max Planck Institute for Terrestrial Microbiology, Marburg, Germany

Cell free transcription and translation provides a well-controlled environment to test gene regulatory networks and their products ex vivo. Gene regulatory networks distributed in communities of cell-mimics could lead to the formation of self-organized patterns in gene expression. To achieve this goal, it is necessary to increase the life-likeness of the cell free *in vitro* system using a continuous perfusion setup maintaining the reaction far from equilibrium.

However, perturbations, from the feeding of fresh reagents, mix establishing concentration gradients in an unprotected reaction space. We present a multilayer, microfluidic chip separating the feeding flow from the protected, 2D reaction chamber. As cell-mimics, we use porous capsules, with immobilized DNA cargo in an internal, primary hydrogel, to distribute gene regulatory networks in a discrete 2D array. An external hydrogel immobilizes the capsules after arrangement and constitutes the reaction space. Overflowing the gel pad with reagents, creates a two-layer system with separated feeding and reaction spaces.

This setup allows us to model communication between synthetic cells in two dimensions, a prerequisite for multicellular organization. Using this device, we aim to characterize increasingly complex gene regulatory networks, leading to dynamic and static self-organizing patterns.

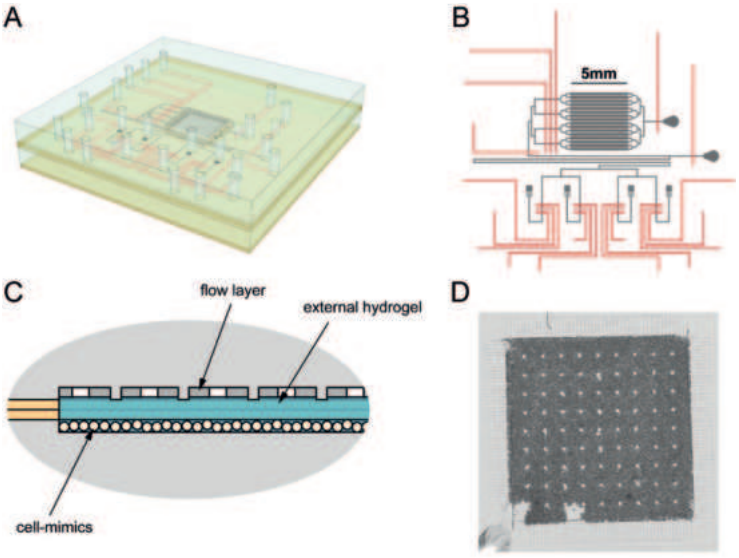


Figure 1:

A) 3D rendering of microfluidic chip. Membrane-thickness (yellow) is exaggerated for visualization.

B) Double layer chip design with flow layer (grey) and pneumatic valves (red) for on chip flow control.

C) Cross-section of device layers at relative scale.
D) Microscopy image of cell-mimic array in fully assembled chip.

Tuesday, March 14
5:36 PM–5:38 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

CHEMICAL FUNCTIONALIZATION AND ACTUATION OF MICROPRINTED DNA-HYDROGELS

Brigitta Dúzs[1]

Philipp Mainik[2,3], Christoph Alexander Spiegel[2,3], Eva Blasco[2,3], Andreas Walther[1]

1 Life-Like Materials and Systems Lab, Department of Chemistry, Johannes Gutenberg University of Mainz, Germany
2 Organic Chemistry Institute, Heidelberg University, Germany
3 Institute for Molecular Systems Engineering and Advanced Materials, Heidelberg University, Germany

The realization of biomimetic functions in synthetic materials is a long-term challenge that requires the integration of bio-physico-chemical dynamics with materials science strategies. Our approach targets DNA-containing mechanomaterials that contain functional DNA units and thus can be actuated by external chemical signals. Our long-term goal is to go beyond simple responsiveness and design more autonomous smart materials, embedding DNA-based nonlinear chemical reaction networks. These units can have applications in soft robotics and neuromorphic computing.

The miniaturization of the DNA-based devices is beneficial because less chemical is needed, and quicker total device operation can be achieved on a total system level in smaller volumes. Thus, we developed new techniques to microfabricate custom-made multimaterial hydrogel objects with versatile chemical compositions. Two-photon lithography and microscale one-photon optical printing are excellent tools for creating micron-sized objects with nanometer resolution and different material properties.

We successfully incorporated single-stranded and double-stranded DNA in the printed gel blocks and verified the stability of the structures in our working conditions. We optimized the chemical composition of the hydrogel network and the structural design of the printed objects for efficient chemical actuation. After printing, we added fluorophore-labeled DNA strands that can react with the DNA units incorporated in the microstructures, and we followed the induced chemical and mechanical changes (diffusion, binding, swelling) with a confocal laser scanning microscope.

These results will help design more sophisticated miniaturized actuators for complex signaling and soft robotic applications.

Tuesday, March 14
5:38 PM–5:40 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

3D MACRO AND MICRO PRINTING OF SEMICONDUCTOR BASED PHOTORESINS AND THEIR OPTOELECTRONIC APPLICATIONS

Ozan Karakaya[1,2]

Luis Arturo Ruiz-Preciado[1,2], Peter Krebsbach[1,2], Kai Xai[1,2], Gerardo Hernandez-Sosa[1,2,3]

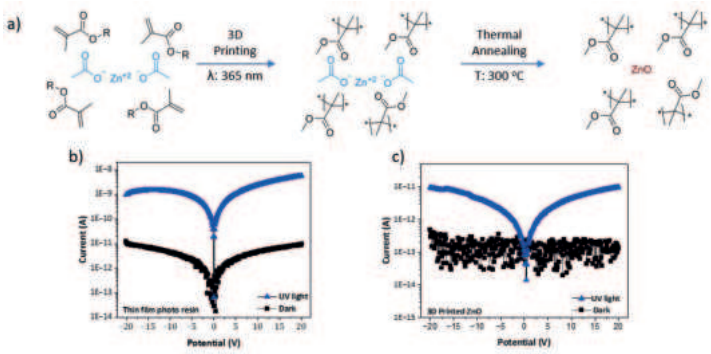
1. Light Technology Institute, Karlsruhe Institute of Technology (KIT), Germany
2. InnovationLab, Heidelberg, Germany
3. Institute of Microstructure Technology, Karlsruhe Institute of Technology (KIT), Germany

The interest in 3D-printed functional microstructures has significantly increased over the past decade due to their potential utilization in microelectronics, photonics, optoelectronics and biological applications.[1] To date, mainly 3D structures based on organic polymers have been assembled due to the absence of multifunctional (e.g. conducting, semiconducting, etc.) photoresins. One of the main challenges that have been encountered when designing functional photoresins is the undesired light absorption of the ink, which leads to relatively low spatial resolution or crosslinking efficiency.[2]

Here we use an approach for designing a multifunctional photoresin to fabricate 3D-printed ZnO microstructures by mixing a commercial photoresin with a Zinc-based metal complex. This ZnO precursor material doesn't have any optical absorption that interferes with photoresin crosslinking process (Fig 1a). After the printing process the 3D structure is thermally annealed to transform into a Polymer/ZnO composite.

Material characterization experiments performed by depositing the photoresin onto glass and subsequently UV-curing and thermally annealing demonstrated that the composite is photoconductive (Fig 1b). The ZnO based UV-photodetector exhibited a current on/off ratio of 600 (@ 395 nm). Printing the photoresin by Direct Laser Processing (DLP) yielded 3D Zinc based structure which also exhibited photoconductive properties under UV light (Fig 1c).

In the future, we plan to extend the obtained results towards its use in the Direct Laser Writing (DLW) process to obtain micro-architected 3D ZnO structures which will be potentially used in optoelectronic and bioelectronic devices.



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2. Liu, et al. Adv. Mater. Technol., 2022, 7, 1–8.

Tuesday, March 14
5:40 PM–5:42 PM
Poster Presentation:
Tuesday, 5:45 - 7:00 PM

BIOPRINTING OF SYNTHETIC VESICLES FOR TISSUE ENGINEERING APPLICATIONS

Ole Thaden[1,3]

Nicole Schneider[1], Tobias Walther[2,3], Kerstin Göpfrich[2,3], Daniela Duarte Campos[1,3]

1 Center for Molecular Biology (ZMBH), Heidelberg University, Germany
2 Max-Planck-Institute for Medical Research, Germany
3 3DMM2O – Cluster of Excellence (EXC-2082/1 – 390761711), Heidelberg University

Introduction: Over the past years, bottom-up synthetic biology has allowed for the incorporation of tailored biological functions into synthetic vesicles. Utilizing synthetic vesicles in combination with bioprinting technologies is a new approach to create 3D artificial tissues with higher complexities and enhanced functionality. Giant unilamellar vesicles (GUVs) are synthetic vesicles that form a micron-sized biomimetic compartment and are used to demonstrate the feasibility of synthetic cells in bioprinting.

Objectives: The present study aims to investigate the printability and usability of synthetic vesicles for bioprinting. Requirements for these synthetic vesicles in the bioprinting process include, but are not limited to, the need for encapsulation of a target material as well as the long-term stability of the synthetic vesicles incorporated in hydrogels to be cultured *in vitro*. Here we investigate the structural integrity of GUVs before and after the printing process.

Materials & Methods: A protocol for printing GUVs was developed consisting of production, filtering (to exclude GUVs smaller than 10 µm), and printing with a bioprinter. This is the equivalent process to printing mammalian cells, but using GUVs instead. After bioprinting, the number and size of the GUVs were determined by fluorescence microscopy.

Results: Initial experiments showed that up to 70% of the GUVs maintain their structural integrity when printing with pressures between 0.2 and 1 bar. This is an encouraging demonstration that GUVs can be printed via drop-on-demand and extrusion methods.

Conclusion: The use of synthetic vesicles can become a powerful tool in the field of bioprinting, as it allows the integration of additional biological function and supports the creation of more complex artificial tissues. As the research in the field of synthetic biology advances, the use of synthetic cells will become more relevant in the fields of tissue and organ engineering.

Tuesday, March 14
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Poster Presentation:
Tuesday, 5:45 - 7:00 PM

ISOLATION OF CELL CLUSTERS IN SPHEROID BY 2PP 3D PRINTING

Barbara Schamberger

Mohammadreza Taale, Aldo Leal Egaña, Yasmin Antonelli, Fereydoon Taheri, Federico Colombo, Christine Selhuber-Unkel

Institute for Molecular Systems Engineering and Advanced Materials (IMSEAM), Heidelberg University, Germany

Three-dimensional cell cultures (e.g. spheroids) are widely used in cancer research due to their capability to resemble the three-dimensionality of the malignant milieu. However, the ability to alter the microenvironment or even isolate parts of the spheroid in an *in vivo* setup is technically challenging. 2PP 3D printing is emerging as a promising technique for bioprinting. Currently, the difficulty lies in printing in the presents of cells due to the limited number of suitable biocompatible inks.

This project aims to separate single cells from the surrounding tissue by a physical barrier in form of a ring using the 2PP 3D printing technique and, in a next step, to isolate the encapsulated cells for downstream analysis or cell culture. For this purpose, MCF7 breast cancer spheroids were mounted on glass-clover slides.

In the next step, individual cell clusters were isolated from surrounding cells using HYDROBIO INX X100 cross-linked by Nanoscribe Photonic Professional GT2 with a hydrogel barrier. Cell viability after printing was tested using calcein/PI staining. The use of the ink in combination with the printing process resulted in isolation of the cells from their environment. The cells in direct contact or in close proximity to the exposure area were dead after 24 hours, while the remaining cells were viable. This leads to a separation of the cells within the printed ring from the rest of the spheroid.

The next steps will be to remove the isolated cells from the culture for further cell culture or molecular biology analysis. The presented technique currently being developed could be used, for example, in organoid or organ-on-a-chip research to spatially and temporally isolate cells from culture.

Tuesday, March 14
5:44 PM–5:46 PM
Poster Presentation:
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PUSH-PULL CHROMOPHORES FOR ELECTRO-OPTICAL MATERIALS

Patrick Kern[1]

Sidra Sarwar[1], Ali Acan[1], Carsten Eschenbaum[2], Peter Erk[2], Christian Koos[2], Stefan Bräse[1]

1 Institute of Organic Chemistry, Karlsruhe Institute of Technology (KIT), Germany
2 Institute of Photonics and Quantum Electronics, Karlsruhe Institute of Technology (KIT), Germany

To handle the increasing volume of global data traffic, telecommunication technologies need further developments such as larger bandwidths, higher power efficiencies and lower drive voltages.[1] High-performance electro-optical (EO) modulators are key components to push the boundaries of optical communications, computing, sensor technology and ultra-wideband signaling.[2]

Over the past decades, significant developments have been made by silicon-organic-hybrid modulators that integrate organic EO materials with silicon photonics. Organic EO materials deliver very large EO activity which is derived from second-order nonlinear hyperpolarizability.[2]

The last few years of research led to chromophores with impressive EO activities and device characteristics such as JRD1 and HLD.[3] Nevertheless, the commercial realization of these materials requires EO chromophores combining large hyperpolarizability, good optical transparency at telecommunications wavelength, long-term acentrical alignment, excellent thermal- and photostability to ensure the longevity of the device.

Strategies to improve their stability involve the covalent attachment of dyes with high glass transition polymers or the incorporation of cross-linkable groups on the chromophore. Herein, we will use different donors and acceptors to target chromophores with large hyperpolarizability and improved stability.

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Poster Presen

Monday, March 13 — 5:45 - 7:00 PM

Infrared Scanning Near-Field Spectroscopic Studies of Bulk and 3D Laser Printed P(MMA-co-HEMA)-PS Block Copolymer	**Nadine von Coelln**
Two-Photon Laser Printing of Peptide-Functionalized Hydrogels	**Niklas Simon Schwegler**
Constructing Photoresponsive MOFs Containing Azoheteroarenes as Light-Switchable Ligands	**Jonas Christian Rickhoff**
Earth-Abundant Transition Metal Complexes in Two-Step Absorption for 3D Printing	**Aleksandra Vranic / Valentina Ferraro**
Optical Properties of Metal-Organic Frameworks and Devices Thereof	**Marjan Krstić**
Manufacturing "Living" 3D Structures	**Hoang Bao Duc Tran**
Peptide Membranes From *de novo* Designed Helix-Loop-Helix Peptides	**Thomas Heim**
Microscaffolds for Studying 3D Cell Migration	**Maria Villiou**
Designing Self-Assembled 3D Structures Based on Photo-Crosslinkable Block Copolymers	**Britta Weidinger**
2D and 3D Multimaterial Nano-Printing Via Laser-Induced Forward Transfer of Solid Ink	**Sebastian Ronneberger**
Synthesis of Adamantane-Based Organo-Group 14 Chalcogenide Clusters Used For 3D Printing Materials	**Jie Wang**
Calcium-Binding Miniproteins for Tissue Engineering	**Florian Raphael Häge**
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Miniature Tensile Tests – An Introduction to New Concepts for Accessing Mechanical Data of 3D Printed Structures	**Malin Schmidt**
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tation

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MANUFACTURING "LIVING" 3D STRUCTURES

Hoang Bao Duc Tran[1,2]

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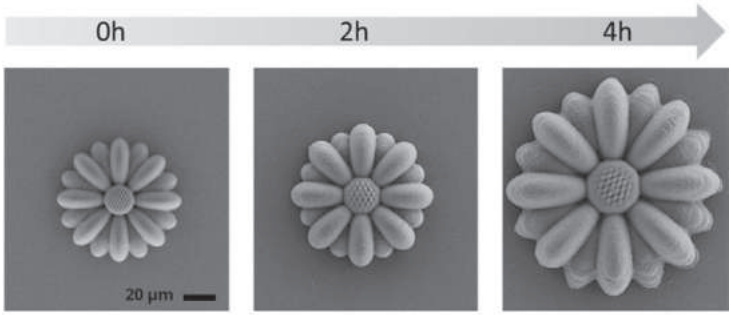
4 Institute of Nanotechnology, Karlsruhe Institute of Technology (KIT), Germany

Manufacturing 3D complex structures able to adapt on-demand – similarly to systems in Nature – is highly desired for many applications. Such features can be obtained by the introduction of dynamic chemistry in printable materials. Dynamic bonds can be broken and reformed under certain conditions and can provide unprecedent "livingness" to the printed structures.

Recently, we have exploited alkoxyamine chemistry in light-based 3D printing to enable the fabrication of 3D structures with dynamically tunable size and mechanical properties using 2-photon laser printing.[1] The alkoxyamine bond is a particularly interesting example of dynamic covalent chemistry. It offers the opportunity for nitroxide exchange reaction (NER), but also can be used to initiate nitroxide mediated polymerization (NMP).

Herein, by post-printing modification via NER and NMP, the mechanical properties as well as the size were fine-tuned on demand. For example, chain extension via NMP resulted not only in an increase of two order of magnitude in Young Modulus but also in an impressive size increase (8-fold), while preserving the initial 3D shape (see figure). We believe that this approach will open new pathways for applications where tailored structures are of highest necessity.



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March 13, 2023
4:15 – 4:45 PM

PEPTIDE MEMBRANES FROM *DE NOVO* DESIGNED HELIX-LOOP-HELIX PEPTIDES

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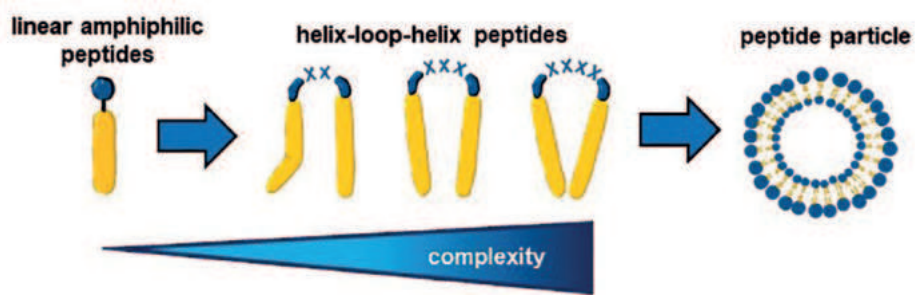
The amphiphilic nature of lipids allows self-assembly into structurally variable bi-layers with various functions. *In vitro* self-assembly of amphiphilic moieties is of high interest for the synthesis of biomembrane mimetics, microreactors, and drug delivery systems in medical applications. To avoid complicated *in vitro* lipid synthesis, amphiphilic peptides are designed to mimic lipid membranes. Compared to lipid membranes, amphiphilic peptides are easily accessible through solid-phase peptide synthesis (SPPS) and also show improved stability as well as great functionalisation potential. The sub-class of surfactant-like amphiphilic peptides is currently based on small linear peptide molecules with hydrophobic tails and hydrophilic headgroups.[1-5]

It is believed that a precise adjustability of peptide characteristics is crucial for controlling shape and properties of the resulting membranes. To overcome design limitations of the recent linear, amphiphilic peptides, a new design approach is studied in this project, using amphiphilic helix-loop-helix motifs as building blocks. This motif comprises a hydrophilic loop section that connects two hydrophobic helical regions, resulting in greater structural complexity and allowing more fine-tuning options for precise control of the shape and properties of the resulting membrane.

This project combines monomer synthesis *via* solid-phase peptide synthesis with biophysical analysis, and different microscopy techniques to characterise the assembled entities. It is aimed to investigate applications of these peptide vesicles as carrier systems or biomimetic membranes, in which *de novo* designed transmembrane proteins could be inserted to test potential signalling through the membrane.



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MICROSCAFFOLDS FOR STUDYING 3D CELL MIGRATION

Maria Villiou

Mohammadreza Taale, Celine Marie Kesenheimer, Federico Colombo, Tobias Spratte, Fereydoon Taheri, Christine Selhuber-Unkel

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Minimalistic 3D models are great tools to study cellular processes, such as differentiation, proliferation, and motility in a more realistic setting *in-vitro*.

Two-photon polymerization method provides a unique possibility to fabricate tunable microstructures with known mechanical properties.

Here we simplified the complex microstructure of biological environments to 3D microscaffolds from different materials (collagen-based, hydrogel-based) employing this technique.

As a result, the effect of physical parameters, e.g., thickness and distance between the columns, their curvature on biological processes from the proliferation to the migration of fibroblasts can be investigated systematically. We vary the structural material features (e.g. columns) of scaffolds by two-photon polymerization in a micrometer scale.

A particularly challenging aspect is to reproducibly fabricate these scaffolds at total scaffold sizes in the mm range, which are necessary for large-scale cell cultures.

DESIGNING SELF-ASSEMBLED 3D STRUCTURES BASED ON PHOTO-CROSSLINKABLE BLOCK COPOLYMERS

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Block copolymers can self-assemble into a variety of morphologies on the nm scale. The self-assembly is dependent of both the block lengths and the incompatibility between the blocks, described by Flory-Huggins parameter χ. This makes them promising candidates for multiple applications, ranging from membranes and drug delivery to templating for nanofabrication. For the latter, the limits of conventional top-down techniques are being reached, whereas bottom-up self-assembled nanostructures could play an important role in the future.

Recently, the self-assembly has thoroughly been investigated especially for thin films, while less attention has been brought to the bulk morphologies.

In this work, block copolymers (poly(styrene)-*b*-poly(methylmethacrylate-*co*-hydroxyethylmethacrylate)) of different compositions and molecular weights were synthesized using sequential RAFT polymerization and characterized by NMR and GPC. The investigation and confirmation of their bulk morphology was performed using both SEM and IR-SNOM as well as SAXS after assembling the films by solvent casting from chloroform.

Consecutively, a methacrylate group was introduced via post-functionalization. This not only opens the possibility for (photo)-crosslinking, but it also enables the fabrication of highly nano-ordered structures using light-based 3D printing such as two-photon laser printing.

2D AND 3D MULTIMATERIAL NANO-PRINTING VIA LASER-INDUCED FORWARD TRANSFER OF SOLID INK

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Junfang Zhang[1], Yuxin Liu[1], Felix F. Loeffler[1]

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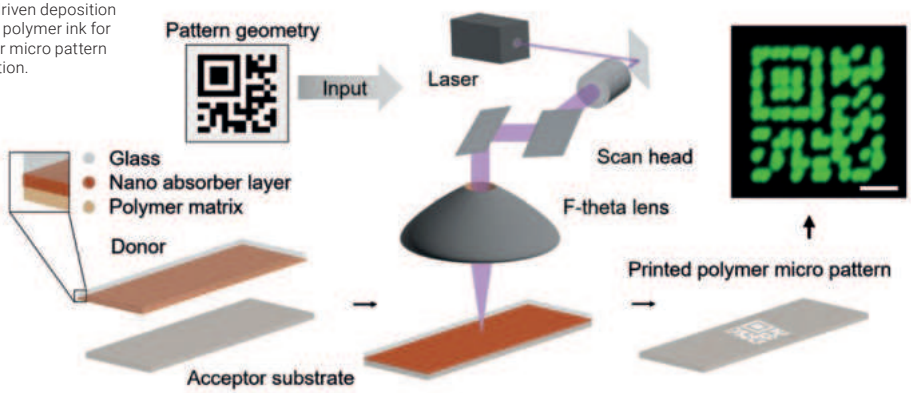
2 Institute of Physics and Astronomy, University Potsdam, Germany

Tagging, tracking, or validation of products is often facilitated by inkjet-printed optical information labels. However, this requires thorough substrate pretreatment, ink optimization, and typically lacks in printing precision and resolution. Here, we demonstrate a printing method based on laser transfer printing of solid polymer ink on various substrates without pretreatment.[1] During the process, the solid ink is transferred by focused laser irradiation from a donor onto an acceptor substrate with a lateral precision of <1 µm. This high positioning precision allows for the introduction of a new sub-positioning concept: Well-defined overlapping polymer spot geometries encode information in high-resolution fluorescent labels with spot-to-spot distances of down to 15 µm (444,444 spots/cm²). This also enables rapid machine learning-supported readout with simple and low-cost fluorescence imaging. Finally, the thickness of the printed polymer layer can be adjusted in the nanometer range, facilitating a hidden information layer within the topography.

More recently, we used this approach to print multiple different polymers in 3d.[2] Combined with post-processing techniques, solvent resistant polymer micropatterns can be printed with nanometer thickness control. Exploiting polymer specific properties, such as specific solubility and refractive indices, our method enables applications in the field of sensors and 4d printing with a z-resolution exceeding the state-of-the art.

Figure 1:

Laser-driven deposition of solid polymer ink for polymer micro pattern fabrication.



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SYNTHESIS OF ADAMANTANE-BASED ORGANO-GROUP 14 CHALCOGENIDE CLUSTERS USED FOR 3D PRINTING MATERIALS

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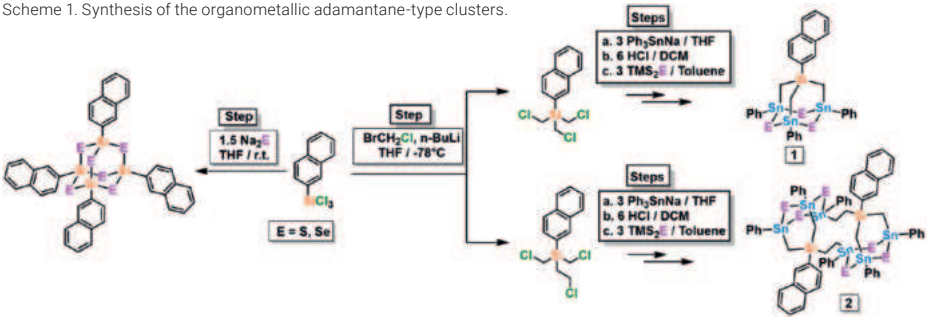
Tetrel chalcogenide clusters with organic substituents have been widely investigated regarding their structural, chemical, and physical properties in the past.[1] A very prominent class of compounds in this field possesses the formula $[(RT)_4E_6]$ (R: organic substituent, T: Si, Ge, Sn, E: S, Se, Te),[2,3] with four organometallic groups linked by six chalcogenide ligands to produce an adamantane-type cluster core.[4,5]

We report our strategy to expand the library of known adamantane-type clusters by adding further examples of the still rare silicon-based species, and also towards species with a quaternary cluster core. In this work, we report on syntheses starting from $NpSiCl_3$ (Np: naphthyl) to form adamantane-type clusters, with the general formula $[(NpSi)_4E_6]$ (E = S, Se), and compounds 1 and 2 (scheme 1), in which the organometallic-core was obtained by reaction of $NpSiCl_3$ with different relative amounts of $BrCH_2Cl$.

As a consequence, a monomeric or a dimeric cluster core were obtained. With the advantage of super-melting, the products have the potential to be three-dimensional (3D) printed, the 3D printed items feature nonlinear properties.

Scheme 1. Synthesis of the organometallic adamantane-type clusters.



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CALCIUM-BINDING MINIPROTEINS FOR TISSUE ENGINEERING

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Tissue Engineering requires artificial constructs to support the formation of tissue from cells. These scaffolds consist of microporous material that binds the cells of interest.

There are two common strategies to functionalize materials for cell responsiveness: the immobilization of cell adhesion motifs, which bind to a cell receptor,[1] or of entire domains of cell binding proteins. However, the small motifs lack a defined three-dimensional structure and thus bioactivity and the large protein fragments are difficult to immobilize and often denature in the attempt.[2]

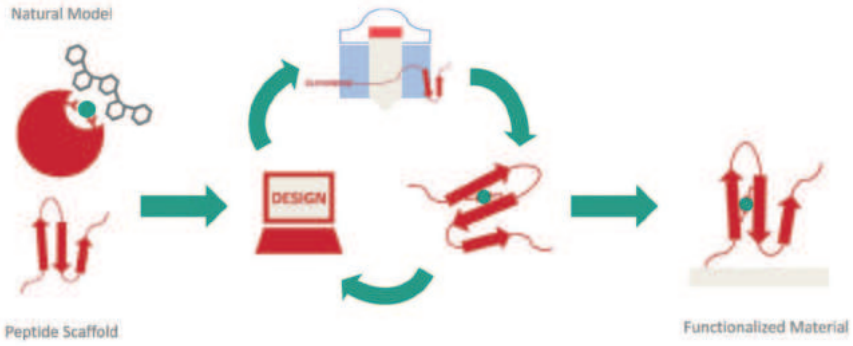
We aim to unify the bioactivity of a cell binding protein with the chemical modifiability of cell adhesion motifs: the design of adhesion miniproteins based on independently folding peptide scaffolds with a cell binding active site.

Many protein-carbohydrate binding sites in extracellular matrix proteins are mediated by calcium ions.[3] We therefore based our designs on the active site of the calcium-binding regulatory protein Calmodulin.

The natural model is incorporated into the sequence of the WW domain, a short β-sheet peptide scaffold, using intuitive Design and computational modeling with Rosetta to ensure similar-to-native folding.

We designed and synthesized a series of calcium-binding miniproteins that fold independently and will soon be tested for their carbohydrate binding activity.

Our goal is to design a biomimetic, easy to immobilize miniprotein that adds cell responsiveness to a microporous material and thus generate a functionalized material for retina tissue engineering.



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SOLUBILIZATION OF ORGANOTIN(IV)CHALCOGENIDE CLUSTERS

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Stefanie Dehnen

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Adamantane-type sulfide clusters of group 14 (semi)metals, $[(RT)_4S_6]$ (T= group 14 atom; R= organic group), have been investigated with regard to their strong non-linear optical (NLO) response upon irradiation with infrared laser light.[1,2] They can be obtained either as crystalline or amorphous materials, which differ in the type of their NLO behavior. While crystalline compounds show second harmonic generation (SHG), amorphous samples can exhibit white light generation (WLG). The nature of the NLO property seems to be closely tied to the adamantane-type cage and the amorphous habitus as various examples showed.[3–5]

So far mostly all investigated compounds have poor till medium solubility. To use them as ink the solubility needed to be increased. By partially replacing sulfur with selenium atoms hetero-chalcogenide clusters are accessible. The presence of multiple hetero-chalcogenide cluster in one solution increases the overall concentration of cluster, as first solubility experiments showed. Here we report on the synthetic approach and compositional analysis of the obtained mixtures of discrete hetero-chalcogenide clusters in solution and as solid solutions.

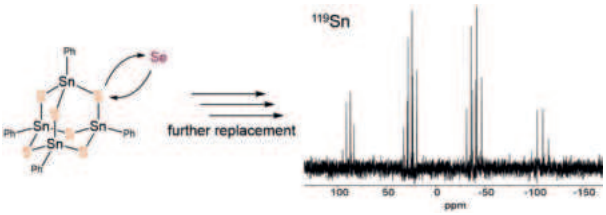

Figure 1 shows the replacement of chalcogenide atoms to form hetero-chalcogenide organotin(IV) chalcogenide cluster.
In the ^{119}Sn NMR spectrum these clusters can be distinguished.

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MINIATURE TENSILE TESTS - AN INTRODUCTION TO NEW CONCEPTS FOR ACCESSING MECHANICAL DATA OF 3D PRINTED STRUCTURES

Malin Schmidt

S. Geiger, M. Taale, T. Kalkus, G. Dave, C. Selhuber-Unkel

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The diversity of resins available for 3D nano- and microprinting, which include acrylate-based inks and hydrogel inks, enable a wide variety of applications, ranging from electronic systems and metamaterials to the production of cell scaffolds and responsive microrobots.

Accessing mechanical data on a micron level is of high interest, especially for the study of mechanical metamaterials as well as complex lattices and substrates for cells. Unlike macroscale samples, tensile tests have not been standardized on the microscale. To address miniature tensile tests, scientists created creative methods like a "push-to-pull" mechanism using indentation on a frame with an integrated test specimen,[1] nanomechanical testing setups under SEM/FIB[2] or nanoindentation setups in SEM.[3] However, none of these existing methods investigated microscale samples from 2PP DLW in liquid. A method for tensile testing complex geometries like strain-stiffening or Kirigami structures or for testing hydrogels in an interchangeable fluid permitting pH or temperature changes would benefit the thorough characterization of these materials.

We aim to mechanically investigate the properties of the 3D printed structures using new methods, like FluidFM or sensor/actuator-based measurements, and to study widely applicable methods for comprehensively testing the mechanical properties of the variety of different 2PP resins, including hydrogels and elastic materials. Using the reference geometry common in macroscale tensile tests, dogbone specimens are produced by two-photon polymerization subjected to these new miniature tests.

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PROTEIN-MOF BINDING MECHANISM

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Cell-free application of proteins has received a lot of attention in biotechnology. However due to their environmental sensitivity, it is important that a suitable framework such as MOFs encapsulates the structure to protect the protein from damage. The successful inclusion of a protein into the desired MOF is essential to exploit its properties in a specific need.

Experiments show that very low loading takes place for the inclusion of a specific peroxygenas (Direct-evolutioned unspecific peroxygenase from Agrocybe aegerita) into the MOF NU-1000. Here we want to study the binding mechanism of proteins to predict whether the protein can bind.

Although there are many approaches for calculating binding energy, we will use the Molecular Mechanics/ Poisson Boltzmann Surface Area (MM/PBSA) as it can be used for different systems from small size to the large one. Also, this method is a compromise between accuracy and speed.

In addition to the mentioned protein, we will compute the binding energy between esterase AaEST2 and MOF NU-1000 which has been known that could be able to enter into the desired MOF.

HIGHLY SOLUBLE ORGANOTETRELCHALCOGENIDE CLUSTERS AS FUNCTIONAL MATERIAL FOR 2D INKJET PRINTING

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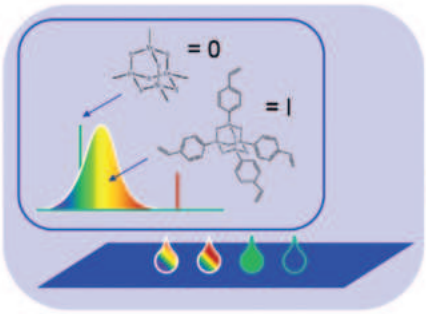
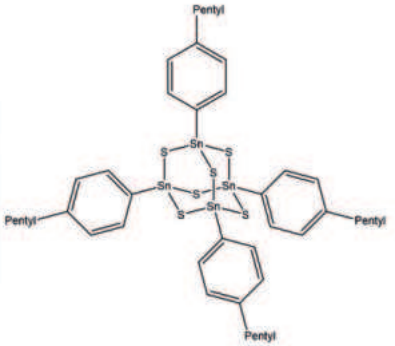
Standard data storage mediums are reaching the limits of their longevity and the loss of data is with present mediums unavoidable.[1] To prevent a digital "dark age", where a substantial amount of digital data would be lost it is necessary to develop new single molecule-based concepts for data storage.

In 2016, extremely non-linear optical properties of certain organotetrel chalcogenide clusters were reported for the first time, and in the following years these properties were extensively investigated. When cluster compounds with the general formular $[(RT)_4E_6]$ (T = tetrel atom, E = chalcogen atom) are irradiated by a continously emitting infrared laser diode, either frequency doubling (second-harmonic generation, SHG) or white-light emission (white-light generation, WLG) phenomena can be detected, depending on the organic substituent that controls the crystalline versus amorphous habitus of the compound.[2-5]

In order to achieve the highest possible data density in an optical storage medium, the cluster compounds are to be deposited via an inkjet printer in the form of small "dots" on a carrier material to which values of "0" and "1" are assigned. The novel cluster $[(pPh)_4S_6]$ shows high solubility in organic solvents compared to other related adamantane-type compounds and was used for coating experiments.





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SNAKESKIN KIRIGAMI-INSPIRED SCAFFOLD AS A CANDIDATE FOR STUDYING CELL-MECHANICS

Gaurav Dave

Tobias Spratte, Malin Schmidt, Florine Sessler, Mohammedreza Taale, Christine Selhuber-Unkel

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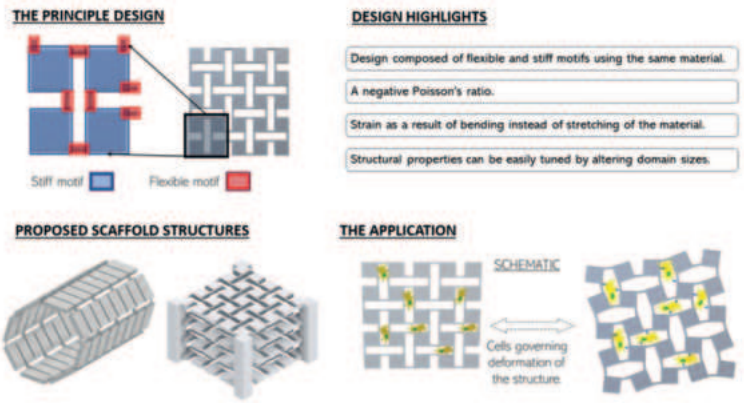
It has been established that cells have a two-way interaction with their surroundings. Biomechanical and biochemical cues are exchanged that impact not only cell behaviours such as shape, proliferation and migration, but also the scaffold/ECM(extra-cellular matrix) properties. The aim of this project is to design and fabricate such structures via the help of two-photon polymerization based 3D printing and further apply them to study cell mechanics and cell migration.

In the current work, a scaffold design inspired from snakeskin Kirigami based meta-material has been showcased to have unique mechanical behavior in comparison to traditionally designed scaffolds. Similar to how a snakeskin is flexible, yet it protects the creature on multiple harsh terrains, the current scaffold is made of basic stiff and flexible motifs, 3D printed of the same material. The structure is composed of stiff tiles, that provide surface area and flexible connectors, that provide flexibility for deformation.

It is known that cells actively participate in shaping of the ECM *in vivo*. Majority of the approaches include changes/modification in material to alter the scaffold properties. The goal of the project is to design a scaffold that can actively respond to the mechanical cues provided by cells. A bio-inspired design has been proposed to achieve a mechanically adaptive scaffold for cells. The current Kirigami design, without any alteration to material chemistry, showcases a negligible stress to strain response up to 15% elongation in comparison to the bulk material. The scaffold also showcases a negative Poisson's ratio.

Such a 3D structure can provide cells with an active environment to study how cells respond to different structural stiffness by studying the structural deformation during expansion/contraction as well as traction forces exerted during migration.



GLASS FORMATION OF ADAMANTANE-TYPE MATERIALS AND OPTO-ELECTRONIC PROPERTIES (WLG)

Irán Rojas-León

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Materials capable of non-linear optical (NLO) properties, in particular second harmonic generation (SHG) or white-light generation (WLG),[1] have been investigated with great activity in recent times.[2] Applications of such materials have always been very important, so scientists of the last generations have been searching hard for new materials with these properties for consumption in everyday life.[3]

Recently, a class of amorphous molecular materials have been shown to convert infrared light of an inexpensive CW laser diode into highly directed white light. These materials comprise organic adamantane derivatives or inorganic adamantane-type compounds that share the general formula $[(RT)_4E_6]$, in which R is an organic substituent, T represents a group 14 atom (C, Si, Ge, Sn), and E represents a chalcogenide atom (S, Se, Te) or CH2.[4]

Here we present our strategy to reach this goal by the formation of hybrid adamantane-type clusters of the type $[(R^1T^1)(CH_2)_3(R^2T^2)E_3]$, based on so far unprecedented quaternary adamantane-type cages $\{T^1(CH_2)_3T^2E_3\}$ with two different group 14 atoms, T^1 and T^2, and two types of bridging units, CH_2 and E.

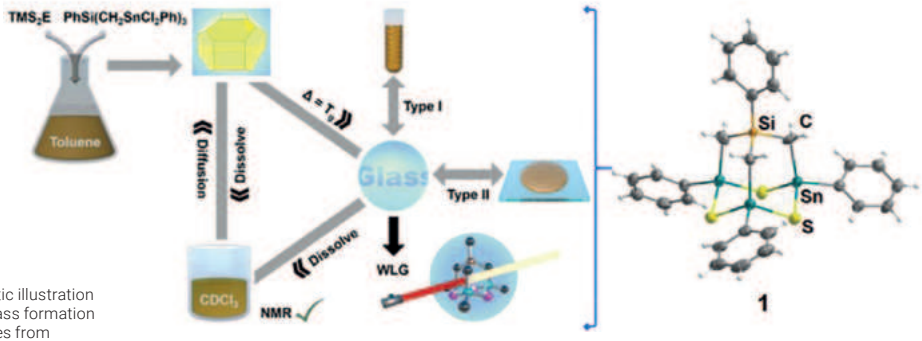

Figure 1: Schematic illustration of the glass formation processes from crystalline powders of hybrid adamantane-type clusters and molecular structure 1.

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POLYMER-BASED STRATEGIES TO CULTURE CANCER CELLS IN MECHANICALLY TUNABLE 4D MATRICES

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Most semisolid tumors are characterized by their gradually increasing matrix stiffness, which is mediated by the deposition of collagen, the upregulated expression of crosslinking enzymes (i.e., lysyl oxidase), and the secretion of inhibitors of metalloproteinases in the tumor microenvironment. For example, in the case of breast tumors, elasticities of up to 100 kPa (Lekka, *BioNanoScience*, 2016) are found in advanced phases of cancer progression, that are comparatively higher than those found in healthy tissues. These modifications in their mechanical properties are known to promote cancer progression and malignancy.

Since most *in vitro* cancer studies have been carried out with scaffolds of constant elasticity, this work focused on developing 4D scaffolds, and in particular, those exhibiting dynamic and controllable mechanical properties over time. Therefore, photoresponsive anthracene moieties were linked to PEG-based hydrogel systems, offering tunable crosslinking and hydrogel stiffness by [4+4]-cycloaddition. Additionally, to enhance the biocompatibility of the hydrogels and provide cell-matrix adhesion, PEG-anthracene was blended with gelatin.

After the mechanical characterization by rheological measurements upon irradiation at λ_{ex} = 405 nm, cancer cell line MDA MB 231 was immobilized in the PEG-anth/gelatin hydrogels at different stiffnesses. Preliminary results reveal, that polyploid giant cancer cells, a subtype of cancer cells involved in drug resistance and metastasis, were formed inside the confined hydrogels. In the future, the described system may act as promising *in vitro* cancer model mimicking primary tumors more accurately than traditional 3D scaffolds and may be applied as ink for 3D printing methods.

3D-PRINTED SINGLE WALLED CARBON NANOTUBES FOR OPTOELECTRONICS APPLICATIONS

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Single-walled carbon nanotubes (SWNTs) show outstanding mechanical, optical and electronic properties, such as huge charge carrier mobilities (μ), excellent chemical and photo-stability, large surface area,exceptional mechanical strength combined with flexibility, and very high intrinsic charge carrier mobilities (>1000 cm2V-1s-1) Moreover, they show strong tuneable absorption and emission in the near-infrared (NIR) region, which is highly interesting for both biological applications (imaging in the second biological window) and telecommunication (C-band). However, for applications such as supercapacitors or electrochemical transistors the volumetric capacitance is the other crucial performance parameter, and this is low for a 2D nanotube network.

As such, we decided to transition to a 3D-SWNTs-based network with superior mechanical properties and enhanced conductivity of both electrons and ions for applications in superior performing devices. The 3D printing of SWNTs is performed by 3D direct-laser printing, which results in sub-micrometer resolution, and allows for tailoring shape and corresponding properties with regard to the intended application.

The so-obtained 3D-SWNTs were characterized via Raman mapping and photoluminescence assays. They showed no significant increase in the sp3/sp2 carbon ratio (D/ G+ peak ratio), which highlights that the SWNTs excellently survive the printing process. This was also reflected in the maintained photoluminescence properties, as the composites still show SWNTs photoluminescence centered at λmax ~ 1010 nm. Future work involves i) the use of biocompatible (PNIPAM or hydrogel-based) 3D-printed (6,5)-SWNTs for near-infrared emitting scaffolds for *in situ*-monitoring of cell growth and activity, and ii) the fabrication of 3D printed SWNTs-based organic electrochemical transistors.

IN-DEPTH INVESTIGATION OF THE POLYMERIZATION MECHANISMS FOR HIGH RESOLUTION 3D PRINTING

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The control of the resolution and speed of 3D laser nanoprinting is subjected to the efficiency of the photoinitiators (PIs). Upon light absorption, several competing excited states and complex photoreactions are responsible for the radical formation that leads to the activation of radical polymerization.

Here I focus on the investigation of Norrish type I and II PIs, i.e. Irgacure 369, DETC* and BBK**, which show a well known radical photoinitiation mechanism, proceeding via the lowest triplet excited state, but using different radical formation channels (see Figure 1). Among all, particular attention is paid to DETC. Depending on the presence of a co-initiator, it activates radical generation either with common two photon or with a unique three-photon excitation. Both mechanisms were not well understood for several years.[1]

Employing quantum-mechanical calculations, we show that the three-photon based mechanism results from the excitation of special highly excited triplet states followed by multiple bond scission possibilities for the radicals generation, i.e. hydrogen atom transfer, photolysis and reaction with the monomer. Moreover, with the model proposed, the uncommon depletion mechanism,[2] shown also by DETC, can finally be enlightened. Through our investigation, based on the simulation multiphoton absorption spectra, optimization of excited states and calculations of reaction rates, an extensive merged computational and experimental study is presented for the first time.

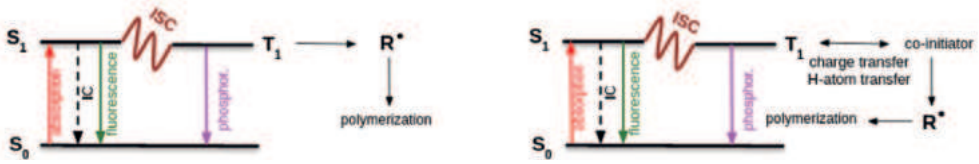

Figure 1: Polymerization mechanism for Norrish type I (left) and II (right) PIs.

* DETC: 7-diethylamino-3-thenoylcoumarin
** BBK: ((2E,6E)-2,6-bis(4-(dimethylamino)benzylidene)-4-methylcyclohexanone

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ELECTROHYDRODYNAMIC JETTING: IMPORTANT TOOL FOR PARTICLE & SURFACE ENGINEERING TO CREATE 3D SCAFFOLD MATERIAL

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Electrohydrodynamic jetting (E-jetting) is an additive manufacturing process used to fabricate structures in the nano to micron ranges. A polymer solution is subjected to electrical & mechanical forces resulting into the formation of a liquid jet, which upon solidification yields polymeric nano/microstructures. During the jetting process, up to a certain polymer concentration the jet disintegrates into finer droplets giving particles upon solidification. This is then termed as electrospraying. For higher polymer concentration, the jet elongates instead of disintegration, and yields into micro/nano fibres. This is termed as electrospinning.

E-jetting has been conventionally used to create particles and fibres to be used for various biomedical applications. The main objective of current work is to further exploit this technique & create three-dimensional scaffold materials. This can be done by engineering of the resulting materials either in-situ or post jetting. Obtained particles or fibres can be used as base template to create 3D structures. Biodegradable electrospun fibres are used as sacrificial template to create porous 3D scaffold structures having continuous microchannels. These channels can serve as a reservoir for drug release, or can be simply used as scaffolds for 3D cell culture.

Exploring the particle fabrication via electrospraying, in this work we also tried to encapsulate various cargos inside these particles such as drugs, dyes, peptides, living cells. Cell encapsulation is used for applications such as cell therapy, drug screening & cancer research. Encapsulating living cells inside a hydrogel particle is carried out using this technique. Breast cancer cells were used for the encapsulation into alginate-based matrix. The overall idea of this work is to expand the boundaries of E-jetting method which has been used mostly for fabricating fibres & particles till now and how it can be utilized to engineer 3D structures and bioactive scaffold materials.

Tuesday

March 14, 2023
5:45 - 7:00 PM

Thank You

Dear Colleagues and Friends,

We want to take this opportunity to thank everyone involved in this conference: the invited speakers as well as the participants with or without oral and poster presentations.

Futhermore, the conference would not have been possible without the funding by the Deutsche Forschungsgemeinschaft (DFG) within the Excellence Strategy as well as the Carl Zeiss Foundation.

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Franziska Thomas
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Stefan Bräse
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We hope to see you again at

Future 3D Additive Manufacturing | The 3DMM2O Conference

April 7-11, 2024 | Schöntal Monastery

Save the Date

3D Cellular Systems: Synthetic Environments, Mechanobiology and Organoids

Kerstin Göpfrich
Heidelberg University

Martin Bastmeyer
Karlsruhe Institute of Technology

3D Matter Made to Order (3DMM2O)

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