**Project Description – Project Proposal within the Priority Programme**
**"Dynamic Wetting of Flexible, Adaptive and Switchable Surfaces" (SPP 2171)**

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# Bioinspired composite materials with aligned cellulose fibers as adaptive substrates with dynamic surface functionalities

## Project Description

## 1 State of the art and preliminary work

The surface of a material is of fundamental importance, because it determines its function and properties for the respective application regarding a potential interaction with its environment (Zollfrank 2014). The two-dimensional planar or non-planar surface delimits a material from a given environment and represents the boundary for any interaction with other materials, fluids (liquids or gases) or complex objects. In engineering applications, the surface of the material is often designed to exert a specific function (directional interaction) or property (mechanical resistance), which is chemically and physically predetermined once the material is fabricated. This predetermination is not subject to change, which means, that the material surface undergoes no or only a limited amount of variation during its lifetime. If an artificial material does change its surface characteristic due to an altered environmental influence, this will lead to eventual loss of function or entail properties leading to failure of the material. Contrary to that, biological materials are able to change and develop as an inherent capability in order to restore or maintain the original functionality within certain limits.

Natural materials and processes offer a tremendous pool of solutions to tailor and design a novel class of materials and surfaces also known as bioinspired materials, which have the potential to conquer complex multi-variant environments and applications. The characteristic properties of natural materials and their surfaces result from a complex relationship between the surface morphology and physical and chemical properties. As a consequence, the hierarchical construction of biological materials leads to a combination of multiple characteristics including failure tolerance, adaptation, and multifunctionality. Biological materials and their construction processes are interesting and important models for research and development of bioinspired materials. Manifold materials based on a bioinspired approach have been developed for various applications including adhesion (hydrophobicity, self-cleaning, drag reduction in fluid flow, antifouling), optics (structural coloration, energy conversion, antireflection), mechanics (materials and fibers combining stiffness and high mechanical strength), structure formation (self-assembly), and adaptation (reversible adhesion, self-healing, sensory orientation, response).

During the past two decades, numerous publications have demonstrated that biomimetics is a very powerful approach for the development of surfaces with novel functional properties (e.g., superhydrophobicity and self-cleaning, drag reduction, physical coloration pattern; Barthlott and Neinhuis, 1997; Bechert et al., 2000; Gorb, 2006; Yu et al., 2013, Grumbein et al. 2016). Also biological attachment devices may represent an important source of information for the development of novel adhesives (Creton and Gorb, 2007). However, to understand the functional principles of animal attachment pads, having information about the external morphology of structures is not sufficient. An integrative approach is necessary to combine data on the ultrastructure and mechanical properties of biological materials, muscle arrangement, joint design, movements during making and breaking contact (motor control), the sensory systems involved in pad positioning, forces and their directionality, contact mechanics at the micro- and nanoscale levels, potential substrates (e.g., surface profile and surface energy), and the presence and properties of fluid in contact between the attachment pad and substrate. Recently, numerous studies have attempted to understand the functional principles underlying the performance of biological attachment systems of insects, spiders, and geckos (Gorb, 2001; 2011; Federle, 2006; Autumn, 2007; Kamperman et al., 2010; Jagota and Hui, 2011). In reality, the so-called gecko effect is the result of several mechanisms identified from studies of various biological attachment devices, not just those of the gecko. It has been demonstrated that the geometry of micro- and nanostructures plays a fundamental role in biological attachment systems. One can roughly classify such systems into (1) those that have smooth adhesive organs and (2) those that have evolved numerous hair-like adhesive setae, such as setae found in some insects, spiders, and geckos (Beutel and Gorb, 2001). This second, fibrillar type - in contrast to the smooth one - consists of many smaller subcontacts. This principle of contact splitting has been the subject of many theoretical and experimental works (Jagota and Bennison, 2002; Arzt et al., 2003; Peressadko and Gorb, 2004; Crosby et al., 2005; Varenberg et al., 2010; 2011).

Several advantages of such hairy adhesive systems have been proposed. For example, in a smooth, continuous adhesive contact, once a crack is initiated at the adhesive interface, the crack may easily propagate over the entire contact area until complete detachment occurs. By contrast, in a fibrillar system, the crack leads initially to the detachment of one seta, and the elastically stored energy in the seta is released and can no longer contribute to the propagation of the crack (Jagota and Bennison, 2002; Hui et al., 2004; Chung and Chaudhury, 2005; Tang and Hui, 2005). This principle is known as crack trapping. Thus, the crack has to be reinitiated at each individual subcontact. In addition, fibrillar systems adapt better to uneven and rough surfaces (Persson, 2003; Persson and Gorb, 2003; Kim and Bhushan, 2007; Filippov et al., 2011). Because each seta is virtually independent of other neighboring setae, a seta can contact the asperities and valleys of a rough surface without being mechanically influenced by neighboring setae (Figure 1). In contrast, in a smooth system, the region around the contact with a surface asperity can be prevented from forming contact. Moreover, the effective stiffness of a fibrillar adhesive system is strongly reduced compared with the stiffness of the bulk material of setae. Therefore, the fibrillar system is very compliant also to rough surfaces (Persson, 2003).

*Gorb group, A: Functional morphology and biomechanics*

We (Gorb group, Kiel) have an expertise in characterization of adhesive forces on local (nanoindentation and Atomic Force Microscopy) and global (Centrifugal Force Tester and Microtribotester Basalt-BT01) scales as well as in a broad range of microscopy techniques. Some limitations of commercial systems were recently removed in homemade microtribometers by using a self-aligning system of specimen holders and an improved force sensor based on a symmetric design. Previous comparison of a wide variety of animal groups using microscopy techniques and tribological experiments revealed that the size of single contacting points gets smaller and their density increases as the body mass increases. The effective elastic modulus of the fiber arrays is very small, which is of fundamental importance for adhesion on smooth and rough substrates.

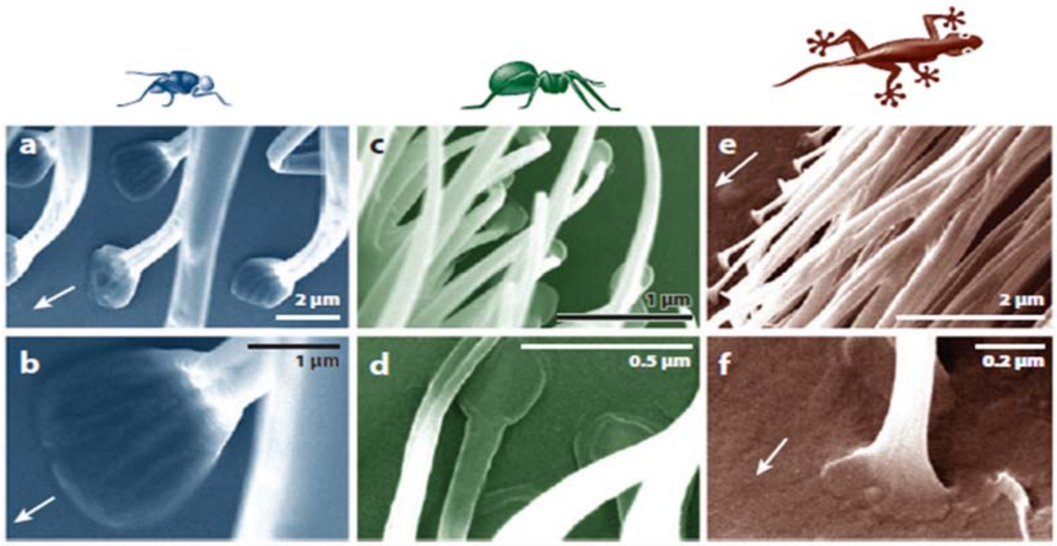


***Figure 1.*** *Cryo-scanning electron micrographs of hairy structures with spatula-shaped terminal contact elements, in contact with smooth glass, as found in the hairy attachment pads of the (a,b) fly (Calliphora vicina), (c,d ) spider (Cupiennius salei), and (e,f ) tokay gecko (Gekko gecko). Arrows point in the distal direction. From Heepe and Gorb (2014).*

It has been previously demonstrated that carbon nanotubes (CNTs) are promising material for the fabrication of biomimetic dry adhesives inspired by the abovementioned studies. The dimensions of single CNTs are in the range of those of terminal elements of biological dry hairy adhesion systems. The densely packed arrays of vertically aligned and up to 1.1 mm long multi-walled CNTs synthesized by chemical vapor deposition previously demonstrated excellent adhesive and frictional properties. The coefficient of friction can be as high as 5–6. Such high values can only be explained by the strong contribution of adhesion induced by applied shear force to CNTs (Schaber et al., 2015). However, the use of CNTs in a wide variety of applications is restricted due to their high costs, as well as to some medical and environmental issues. That is why parallel-aligned high aspect ratio nanofibers made of biological materials, such as cellulose, might be an interesting alternative for development of biologically-inspired fibrillar adhesives (Kreitschitz et al., 2015; 2016; Schaber et al., 2018).

*Zollfrank group, B: Biogenic materials processing*

The fabrication and processing of structural and functional materials using biological templates and structural materials such as natural plant tissue, fibers, and (pre-)processed lignocellulosic preforms is a major part of the research activities of the Zollfrank group for more than 15 years. One major research focus is the multiscale (hierarchical) design of functional materials using organized or structured and patterned biomacromolecular architectures from polysaccharides (e.g. (ligno)celluloses, chitin), biological templates (e.g. wood, algae; Poppinga et al. 2018) as well as processed biological materials (e.g. paper, cardboard). The research of the Zollfrank group is devoted to the development of novel concepts and strategies for the sustainable use and application of biomacromolecules from renewable, secondary and waste sources in materials science and engineering. We are currently developing tailor-made cellulose materials for actuation device through parchmentizing paper sheets and subsequent calandering (Scholz et al. 2018). Recently, a photo-crosslinkable cellulose derivative was developed, which can be applied in e.g. direct laser writing (DLW) techniques. It enables the generation of two- and three-dimensional hierarchical structures with a feature size of less than 500 nm via two-photon absorption. This new photoresist paves the way towards designing and fabricating biomimetic architectures solely made from biopolymers (Rothammer et al. 2018).

*Lieleg group, C: Biopolymers and biointerfaces*

The Lieleg group has expertise both with the macrotribological response of biological systems (Crouzier et al., 2015, Biegler et al. 2016, Boettcher et al., 2016), as well as with the characterization of the wetting resistance and topography of material surfaces (Fig. 2; Grumbein et al., 2016, Kesel et al., 2016). For biotribological experiments, two different setups are available which offer measurements over a broad range of sliding speeds and normal forces as well as in both, constant and migrating contact geometry (Boettcher et al. 2014, Winkeljann et al., 2018).

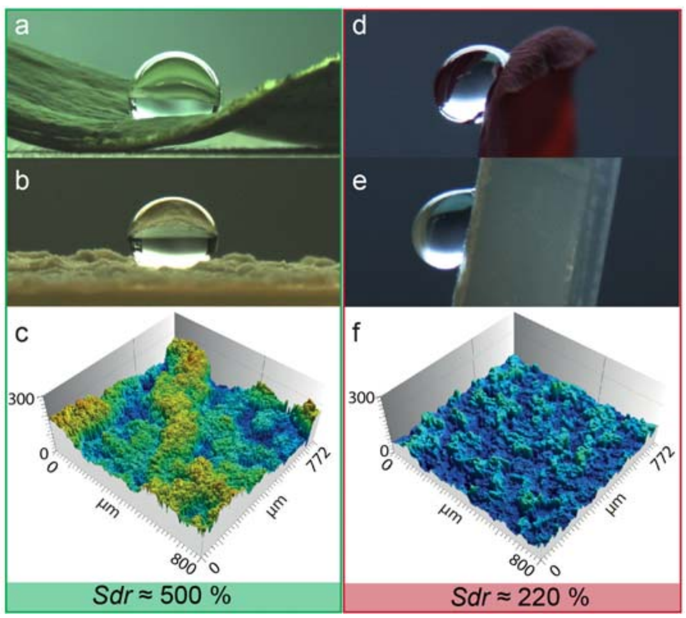


***Figure 2.*** *Wetting and topography of plant leaves and bacterial biofilms. Both, plant leaves (lotus: a; rose: d) and bacterial biofilms (b,e) can exhibit two different types of hydrophobic behavior. In the first case, the droplet rolls off easily as observed on lotus leaves whereas, in the second case, the droplet remains attached when the surface is tilted. Topographical images of biofilm surfaces obtained by light profilometry (c,f) can be quantified by the ISO parameter Sdr and return higher roughness values for lotus-like hydrophobicity than for rose-like hydrophobicity (Figure adapted from Werb et al. 2017).*

Surface characterization on the micro-scale is conducted using SEM and white light profilometry, the latter is a variant of confocal microscopy and offers a spatial resolution in z-direction in the range of a few nm. With this imaging technique, we have recently demonstrated the close relation between the different modes of hydrophobicity occurring both on plant leaves (lotus leaf, rose petal) and bacterial biofilms (Fig. 2; Werb et al., 2017, Dragos et al. 2018). We were also able to quantify different variants of surface damage by using metrological parameters (Boettcher et al., 2017, Winkeljann et al., 2017). In this project, we will contribute our experience in those fields to characterize the friction properties and microtopography of artificial cellulose-based surfaces as well as their durability.

*Project delineation*

Our project is inspired by biological role models, which exhibit adaptive and dynamic surface properties. The focus of the proposed research lies in the development and characterization of flexible, adaptive and switchable functional substrates for liquid interaction. E.g., the peristome of the pitcher plant (genus *Nepenthes*) exhibits a distinct microstructure designed to trap insects (Bohn and Federle, 2004). This surface is completely wettable by nectar secreted at the inner margin of the peristome and by rain water, so that homogenous liquid films cover the surface under humid weather conditions. Only when wet, the peristome surface is slippery for insects, so that most visitors become trapped. A smart fluid-controlled surface has been recently proposed, via the rational integration of the unique properties of three natural examples, i.e., the unidirectional wetting behaviors of butterfly's wing, liquid-infused "slippery" surface of the pitcher plant, and the motile microcilia of micro-organisms. However, the fabrication of an adaptive surface with switchable properties for mechanical or liquid interaction using aligned natural fibers such as cellulose has to our knowledge not been attempted so far. The biological role model will be used a source of inspiration for the development of engineering materials applying biological principles. Additionally, our envisioned materials are based on renewable resources and are environmentally benign, which fits well to the biological transformation in industry and society.

## 1.1 Project-related publications

### 1.1.1 Articles published by outlets with scientific quality assurance, book publications, and works accepted for publication but not yet published.


Crouzier, T., Boettcher, K., Geonnotti, A.R., Kavanaugh, N.L., Hirsch, J.B., Ribbeck, K., **Lieleg, O**. (2015). Modulating Mucin Hydration and Lubrication by Deglycosilation and Polyethylene Glycol Binding, *Advanced Materials Interfaces*, (2) 18: 1500308.

Grumbein, S., Minev, D., Tallawi, M., Boettcher, K., Prade, F., Pfeiffer, F., Große, C.U., **Lieleg, O.** (2016) Hydrophobic properties of biofilm-enriched hybrid mortar. *Advanced Materials*, 28 (37): 8138–8143.

Kreitschitz, A., Kovalev, A., **Gorb, S. N.** (2015) Slipping vs sticking: water-dependent adhesive and frictional properties of *Linum usitatissimum* L. seed mucilaginous envelope and its biological significance. *Acta Biomaterialia*, 17: 152–159.

Kreitschitz, A., Kovalev, A., **Gorb, S. N.** (2016) "Sticky invasion" – the physical properties of *Plantago lanceolata* L. seed mucilage. *Beilstein Journal of Nanotechnology*, 7: 1918–1927.

Peisker, H., Michels, J., **Gorb, S. N.** (2013) Evidence for a material gradient in the adhesive tarsal setae of the ladybird beetle *Coccinella septempunctata*. *Nature Communications*, 4 (1661): 1-7.

Rothammer, M., Heep, M. C., v. Freymann, G., **Zollfrank, C.** (2018) Enabling direct laser writing of cellulose-based submicron architectures. *Cellulose*, 25: 6031-6039.

Schaber, C. F., Kreitschitz, A., **Gorb, S. N.** (2018) Friction-active surfaces based on free-standing anchored cellulose nanofibrils. *ACS Applied Materials & Interfaces*, DOI:10.1021/acsami.8b05972.

Scholz, R., Langhansl, M., **Zollfrank, C.**, Walther, F. (2018) Experimental study on the actuation and fatigue behavior of the biopolymeric material Cottonid. *Materials Today Proceedings*, accepted

Winkeljann, B., Boettcher, K., Balzer, B., **Lieleg, O.** (2017). Mucin coatings prevent tissue damage at the cornea-contact lens-interface, *Advanced Materials Interfaces*, (4) 19: 1700186

Winkeljann, B., Bussmann, A., Bauer, M.G., **Lieleg, O.** (2018). Oscillatory tribology performed with a commercial shear rheometer, *Biotribology*, 14: 11-18.

## 2 Objectives and work programme

### 2.1 Anticipated total duration of the project

Three years (36 months)

Proposed starting date: 01.10.2019

### 2.2 Objectives

A specific feature of fibrous surfaces is the dependence of their mechanical properties on the alignment of the fibers. Vertically aligned fibers enhance friction and adhesion, whereas horizontal fibers are known to act as lubricants reducing friction. Many plants form a specific fibrous mucilage cover around their seeds upon hydration. This mucilage consists of cellulose, hemicelluloses, and strongly hydrophilic pectins. In this project we aim at fabricating arrays of high-aspect ratio free standing cellulose nanofibers, which can generate high friction and adhesion arising from bending of the single cellulose fibers and their alignment with the counterpart surface in close contact. We suggest that surfaces covered with free-standing cellulose nanofibrils as a biosourced material have the potential to be a natural and environmentally benign material where high contact forces to surfaces in dry environments are desired. Additionally, the aligned free-standing cellulose nanofibrils will be functionalized with magnetic particles or photo-stimulated switches to generate an anisotropic adaptive surface tailored for specific interactions with fluids and solids.

In this project, we will follow three directions: i) exploration of natural vertically-aligned cellulose nanofibre arrays from mucilaginous plant seeds, ii) fabrication of similar cellulose nanofibre arrays following various synthetic routes based on biogenic material choices, i.e. cellulose nanofibers and iii) combining both microscopy techniques and tribological methods to characterize properties of biological systems and biologically-inspired artificial materials with enhanced adhesive, frictional and functional properties. The following work hypotheses H1-H3 are therefore postulated for the present proposal:

H1) Biological vertically-aligned cellulose nanofiber arrays, depending on their geometrical parameters (length, aspect ratio, density, coiling, etc.), may enhance contact with smooth and rough surfaces and by this generate strong adhesion and friction in contact, an effect similar to attachment devices of geckos, spiders and insects.

H2) Bioinspired network structures with a tailored disorder artificially fabricated from biogenic polymers via patterning or directed writing techniques will mechanically perform similar or with enhanced characteristics compared to the biological role model.

H3) Responsive surface structures with adaptive characteristics can be generated from aligned cellulose nanofibers via a tailored functionalization with e.g. magnetic particles or photo-switchable groups.

For work hypotheses H1, it will be necessary to study a variety of plant seeds to explore the range of geometrical parameters present in biological systems. This will be addressed in WP 1.1 along with a tribological characterization of these nanofibre arrays. Work hypotheses H2 will be studied in WP 1.2, where the development and fabrication of such networks and their performance from cellulose templates will be envisioned. The modification of the aligned cellulose fiber networks and architectures in order to achieve adaptive and responsive surface structures will be developed in order to verify work hypotheses H3. This objective will be addressed in WP 2. All materials synthesized and fabricated in WP 1 as well as the structures generated in WP 2 require detailed experimental characterization, which is integrated into work package WP 3.

To achieve the above objectives, the project is organized along the following work program.

## 2.3 Work program incl. proposed research methods

Some of the work packages (WPs) are operated by the applicant groups individually, whereas others will be conducted in close cooperation between the three groups.

### WP 1 Studies of structure-function relationships in biological prototypes

*WP 1.1 (A/C) Properties of vertically aligned cellulose fibrils in mucilaginous seeds*

We will use controlled critical point drying of hydrated seed mucilage of several seed mucilage-rich plant species (Fig. 3) to expose free-standing cellulose nanofibers with very high aspect ratios. The structural dimensions of the cellulose nanofibers (CNFs), which are anchored to the seed surface, are similar to vertically aligned carbon nanotubes and resemble the contact elements in the adhesion system of the gecko, which show outstanding high dry friction and adhesion. The array of nanotubes will be analyzed using the variety of microscopy techniques, such as white light profilometry, CLSM, SEM, TEM and AFM. Tribological experiments using the microtribotester Tetra Basalt-01 will be performed to reveal adhesive properties and friction coefficients of vertical aligned cellulose fibrils, when sliding a smooth stiff probe over the surface of such arrays of dry free-standing cellulose nanofibrils. We will select plant species with straight cellulose fibrils of various aspect ratios, and plant species with coiled fibrils, to reveal different tribological properties in contact. The microtopography of the different plant seed surfaces will be quantified by a set of metrological parameters including traditional roughness values described in ISO 25178 (*Sq, Sdr*) as well as more complex hybrid parameters (*Str, Sdq*), the latter of which take into account additional features such as anisotropy effects. Mechanical properties (effective elasticity modulus) of the natural nanofibre arrays will be also measured using the microindentation mode of the microtribotester.

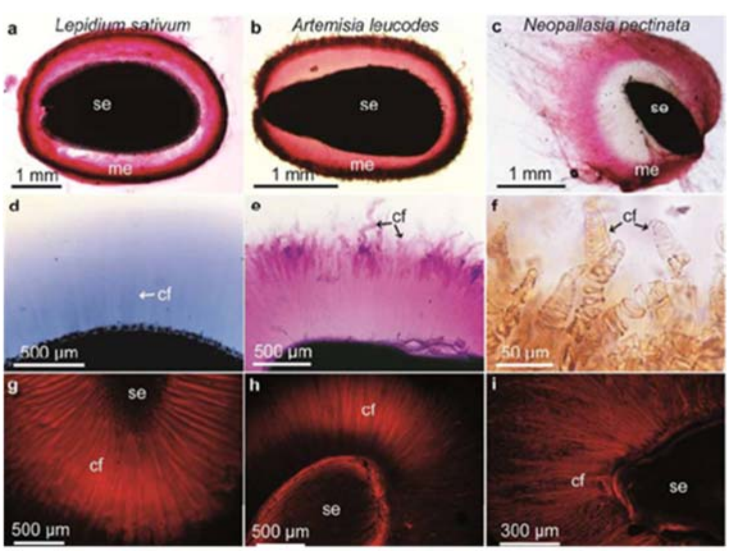


***Figure 3.*** *Identification of mucilage components in hydrated seeds. (a) Ruthenium red staining of seeds of L. sativum, (b) A. leucodes, and (c) N. pectinata demonstrates the presence of pectins (reddish color) forming the main mass of the mucilage envelopes (me) around the seed (se). The dark "shells" in (a) and (b) indicate increased mucilage material density due to coiling of fibrils resulting in dye accumulation, whereas in (c) N.pectinata a copious mucilage envelope of long, outreaching, and at "low magnification apparently uncoiled fibrils is visible. (d) Delicate cellulose fibrils (c,f) stretch radially from the seed surface in the mucilage of L. sativum (methylene blue staining). (e) Slightly coiled cellulose fibrils (c,f) in A. leucodes (crystal violet staining). (f) In N. pectinata the cellulose fibrils (c,f) formed thick and strongly coiled fibers (safranin staining). (g–i) CLSM optical sections show the cellulose fibrils (c,f), identified by their fluorescence after staining with Direct Red 23, embedded in the mucilage and stretching from the seed surface (se). From Schaber et al. 2018.*

*WP 1.2 (B/C) Properties of aligned fibres from lignocellulosic templates*

Lignocellulosics (i.e. wood) is a porous and fibrous structural lignified tissue found of higher plants. The wood cell wall is basically a biopolymeric nanocomposite composed of cellulose fibers embedded in a matrix of lignin. In the secondary cell wall 2 (S2) – the most prominent cell wall compartment in wood – the cellulose is arranged in elementary fibrils forming fibers which run at a microfibril angle of 5° almost in the growth direction of the wood fiber. Our approach is to selectively liberate the cellulose fibers from axial wood sections through a careful delignification process reported in our recent work (Paris et al. 2013, Van Opdenbosch et al. 2016). This is intended to result into a modified surface where the cellulose fibers stick out according to their unidirectional alignment from their respective wood cell wall (Figure 4). The delignification process will be carried out in such a way that the cellulose fibers are still embedded in the lignin matrix at the lower plane of the substrate. The tribological properties of the aligned cellulose fiber covered surfaces will be determined by the Lieleg group in both, constant and migrating contact geometries, at different normal loads and over a broad range of sliding speeds. A parchmentizing process developed in the Zollfrank group will be applied to partly dissolve the cellulose fibers to produce a surface with a hydrogel character. These new materials will be thoroughly characterized by spectroscopic and microscopic (profilometry) techniques. Furthermore, their wetting properties will be assessed by a combination of static and dynamic contact angle measurements. Contact angle hysteresis will be used to distinguish between different modes of hydrophobicity – if observable.

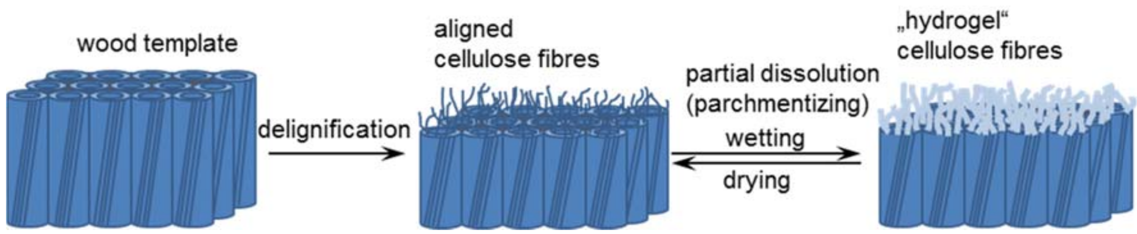


***Figure 4**. Process scheme for the generation of aligned cellulose fiber from a lignocellulosic (wood) template and subsequent modification of the fibers (parchmentizing)*

Alternatively, paper materials can be used as a source for aligned cellulose fiber materials. Machine fabricated papers from cellulose fibers usually exhibit a preferential orientation of the cellulose fibers. The orientation of the fibers results from the directed withdrawal from paper machine. We plan to fabricate fiber sheets with an oriented alignment from bacterial cellulose and/or commercially available nanofibrillated cellulose (both cellulose fibers have a high aspect ratio) using a custom-made tape casting equipment. The fibers will hydrodynamically align within the sheet according to the withdrawal direction. The fabricated sheets will be subsequently parchmentized using a 70 wt% zinc dichloride solution at elevated temperatures and calandered (pressing between two heated cylinders) into multiple sheets. The layered sheets will be cut to attain a surface with the cellulose fibers aligned perpendicular to the sectioned surface.

**WP 2 Generation of functionalized aligned cellulose fiber surfaces**

*WP 2.1 (B) Stabilization of the aligned cellulose fiber determined surface*

The unidirectional aligned cellulose fiber arrays can be stabilized by chemical modification. Two possible routes to alter the surface chemical and physical properties will be evaluated: i) reaction of the cellulose hydroxyl groups with fatty acids (stearic acid, oleic acid), ii) modification with photo-curable groups according to our developed protocols (Rothammer et al. 2018), iii) derivatization of the cellulose fibrils using standard paper modifying compounds such as alkyl ketene dimers (AKD, Yutao et al. 2016). Using these methods, the physical properties (wetting behavior) and the chemical structural characteristics (stabilization of alignment) of the lignocellulosic or paper sheet derived aligned fibers will be custom-designed.

*WP 2.2 (B) Generation of photo-switchable surfaces*

To generate an adaptive photoswitchable surface, azobenzene Schiff bases with photochromic or thermochromic properties will be used (Hou et al. 2012). The action of this molecular switch is based on intermolecular proton transfer or cis-trans isomerization resulting in contraction upon light irradiation. This isomerization reaction can be reversed either by irradiation or heat treatment. The aligned cellulose fibres on the surface will be reacted with an azobenzene Schiff base, e.g. N,N-bis{p-[(2′-sulphatoethyl)sulphonyl phenylazo] salicylidene}-1,2-ethylenediamine, after prior periodate oxidation of the cellulose (aldehyde formation). After modification, the chemical and physical surface properties can be altering during irradiation heat cycles. This would open the option to generate material surfaces with designed characteristics which follow the diurnal cycle.

*WP 2.3 (B) Introducing functional particles into the aligned fiber network for adaptive structures*

Another approach to achieve an adaptive surface is the modification of the aligned cellulose fibre networks with magnetic particles. In our approach, we envision to functionalize the free standing cellulose fibres from biological templates or the sectioned paper sheets with magnetic particles, such as cobalt micron-sized particles (Cao et al. 2017). The cobalt particles will be covalently attached to the cellulose moiety using capping agents based on our previous work (Gruber et al. 2011, Gruber et al. 2012). Incorporating magnetoresponsive particles should promote the smart manipulation of surface properties towards its wetting behavior. Functional particles might be also introduced in the hydrogel cellulose fiber network during the parchmentizing process either on the lignocellulosic templates (Fig. 5), or during paper sheet calandering. The fiber alignment can be varied according to the applied magnetic field. In WP 3, the tribological properties and the wetting behavior of those surfaces will be investigated as a function of the fiber alignment and orientation. It is expected that the mechanical and physico-chemical properties for a flat fiber orientation will significantly differ from an askew or perpendicular fiber alignment and orientation.

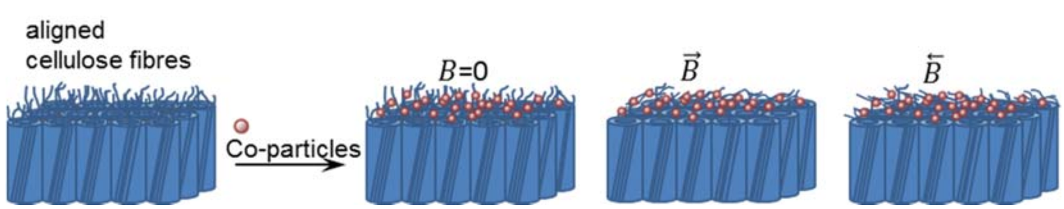


***Figure 5****. Modification of aligned cellulose fibres with magnetic particles; fibre alignment changes as function of magnetic field* B

*WP 2.4 (B/C) Chemically modified cellulose fiber architectures*

To optimize their interaction with both, magnetic particles and wetting fluids, the cellulose fibers can be either modified with anionic groups (-COOH through TEMPO-oxidation) or cationic groups such as amino functions. The latter can be readily obtained by aminoethylation of the cellulose fibers. As a result, the surface should become selectively responsive towards the respective wetting fluid and might possibly change its characteristics when the fluid is applied. Alternatively, the cellulose fibers can be also modified with a hydrophobic side chain (by esterification with, e.g., fatty acids) to further adjust the surface properties. To verify successful generation of such variants of synthetic cellulosic fiber architectures, the surfaces will be studied by scanning electrochemical microscopy (SECM), which will return information on the spatial heterogeneity/homogeneity of the modification process. Wetting tests and imaging of the surfaces before and after a secondary modification of the surfaces with magnetic particles will complement this set of quality control tests before a detailed, in-depth analysis of the surface properties will be conducted in WP 3.

### WP 3 Material properties of the (semi-)synthetic, adaptive surfaces

*WP 3.1 (B) Compound characterization*

All fabricated compounds will be investigated by Fourier transform infrared spectroscopy (FTIR) to validate success of the performed conversions and reactions. FTIR will be also used to monitor the photo-induced curing of our polysaccharide derivatives and the photo-switches. The fibers alignments and hydrogels are further spectroscopically characterized by UV-Vis Microscopic characterization by light microscopy using polarized light will be used to study light interaction and optical properties of the fiber alignments. Scanning electron microscopy (SEM) will be used to investigate the surface topographies of the prepared samples. Insights into the ultrastructure of the aligned fiber system will be obtained by transmission electron microscopy (TEM) on cross sections. The fiber alignment and the orientation changes can be analyzed by small-angle light scattering (SALS). The difference in the relative orientation of the cellulose fibrils as a function of fluid interaction or adaptive alignment (photo-switches, magnetic) the will be measured through changes in the spatial distribution of the SALS signal.

*WP 3.2 (A/C) Structural, mechanical and adhesive properties of the materials*

Here we will analyze the bioinspired synthetic surfaces using different microscopy techniques (light profilometry, CLSM, SEM, TEM, AFM) and run adhesion tests with synthetic vertically aligned cellulose nanofibers in accordance to the methods mentioned in WP 1.1 or following established ISO protocols for synthetic glues using standard equipment (employing a research-grade shear rheometer as the experimental platform). We also plan to run a kind of combined test, where the synthetic surface will be brought into contact and, after reaching certain normal load, will be laterally sheared. Then after reaching a certain shear distance, the pull-off force will be measured. The samples will be tested in dry condition and in flooded condition under water. During adhesion and friction tests of artificial samples, the contact behavior will be visualized with the use of reflection contrast microscopy (example: Fig. 6).

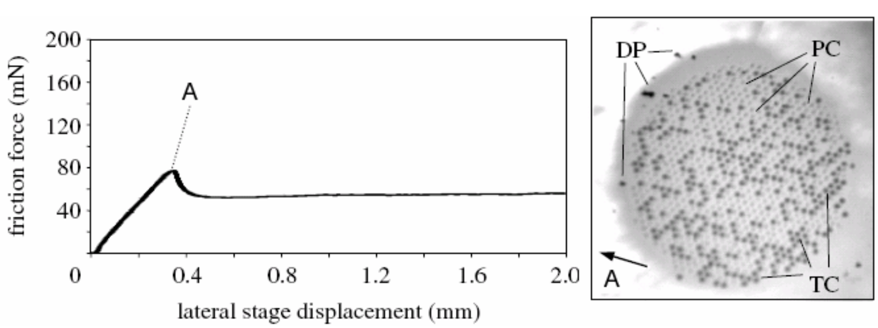


***Figure 6.*** *Characterization of frictional properties with direct visualization of contact. Left: Friction force of a pillar-structured surface measured as a function of lateral stage displacement under an applied load of 40 mN. A, Static friction. Right: Contact area of the sample during force measurement. A indicates direction of sliding. DP, dirt particles; PC, buckled pillars in contact; TC, straight pillars in contact.*

The viscoelastic behavior will be evaluated by microindentation and QCM-D (quartz crystal microbalance with dissipation monitoring). The latter technique measures the shift in resonance frequency of an oscillating crystal as a function of its molecular coating and allows for estimating both, the elastic and viscous properties of surface coatings using the Sauerbrey equation (Dunér et al., 2013). For those QCM-D experiments, the cellulose surfaces will be generated either on gold-sputtered crystals or on PDMS-coated crystals.

*WP 3.3 (C) Characterization of the dynamic friction behavior and durability of the surfaces*

In this working package, we will analyze the friction response of the generated surfaces both in dry and wet conditions. We expect different behavior as a function of hydration state, sliding speed, treatment time and as a function of the measurement type (stationary vs migrating contact mode). For example, we anticipate to experience stick-slip events to occur more frequently in migrating contact mode since, here, the oscillating motion of the probing head will induce short phases of arrest (at the turning points) where strong adhesion may kick in. In addition to probing their friction properties, we will inspect the surfaces (using light profilometry) after the tribological treatment for damage. Here, similar metrological parameters as employed in WP 1.1 will allow us to sensitively detect and quantify different variants of surface alterations.

In addition, we will expose the artificial surfaces to different environmental/chemical challenges. For instance, we will incubate samples at room temperature and elevated temperatures (40 °C, 70 °C) for different incubation times (a few hours, days and weeks) prior to tribological treatment to assess the thermal stability of the surfaces. Moreover, we will expose samples to acidic and basic conditions, aqueous solutions, organic solvents (ethanol, isopropanol) and selected oils (hexane, dodecane) and then test their friction properties and surfaces structure. This set of experiments will allow us to obtain a first idea of chemical conditions the surfaces can survive without losing their functionality, so we can pinpoint suitable scenarios where the artificial surfaces could be used in biomedical or technical applications later on.

*WP 3.4 (A/B/C) Responsiveness of cellulosic fiber architectures*

Here, we will test the properties of selected aligned cellulose fiber networks as a function of the pH-values and the ionic strengths of the wetting solutions. The pH-value and the ionic strength will be systematically varied, to determine ‘pivot points’ at which the surface properties switch, and/or to test if some of those chemical conditions interfere with the functionality of the surfaces. As the mapping of the surface properties of both, pH-value and ionic strength, is time consuming, those cellulose fiber architectures will be chosen that performed well in the previous tests conducted in WP 3.2 and WP 3.3. The goal of this final working package is to identify parameter ranges for bioinspired cellulosic surfaces that could be interesting for biomedical and/or technical applications of the synthetic surfaces.

Furthermore, the photo-induced cis-/trans-isomerization of the azobenzene-modified cellulose and the accompanying change of the surface wettability will be studied, as well as its effect on the tribological behavior of the surfaces. For the trans-to-cis isomerization, the fluid contacted surface will be illuminated with UV-light (280 nm), and the dynamic behavior of the fluid will be evaluated. The cis-to-trans back-conversion will be accomplished by blue-light illumination (340 nm). The surface characteristics of cellulose fibrils with this less distorted and more stable trans-configuration should lead to an altered surface architecture of the cellulose fibrils. Alternatively, the UV-induced cis-azobenzene cellulose might relax back in the dark to the trans-isomer, which happens slowly at room temperature. This provides the opportunity to study the dynamic surface behavior during the thermally induced back-conversion after UV illumination.

Third, the magnetoresponsive surface with the incorporated cobalt particles can be altered by the variation of the fiber alignment as a function of the applied magnetic field. Therefore, the arrangement of the magnetoresponsive modified cellulose materials will be aligned and altered under a vertical magnetic field with a superficial intensity of ≈0.5 Tesla (Cao et al. 2018). Through adjusting the inclination angle $\alpha$ of the magnetic field, the cellulose fibrils can be tilted. The reorientation will be assessed by SALS (see WP 3.1), and the dynamic properties with respect to liquid interaction and the mechanical characteristics investigated.

### *Time schedule*

***Table 1.*** *Quarterly graphical depiction of the work program.*

| **Working package** | **groups** | **Q1** | **Q2** | **Q3** | **Q4** | **Q5** | **Q6** | **Q7** | **Q8** | **Q9** | **Q10** | **Q11** | **Q12** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **WP 1 Studies of structure-function relationships in biological prototypes** | | | | | | | | | | | | | |
| *WP 1.1* | AC | | | | | | | | | | | | |
| *WP 1.2* | BC | | | | | | | | | | | | |
| **WP 2 Generation of functionalized aligned cellulose fiber surfaces** | | | | | | | | | | | | | |
| *WP 2.1* | B | | | | | | | | | | | | |
| *WP 2.2* | B | | | | | | | | | | | | |
| *WP 2.3* | B | | | | | | | | | | | | |
| *WP 2.4* | BC | | | | | | | | | | | | |
| **WP 3 Material properties of the (semi-)synthetic, adaptive surfaces** | | | | | | | | | | | | | |
| *WP 3.1* | B | | | | | | | | | | | | |
| *WP 3.2* | AC | | | | | | | | | | | | |
| *WP 3.3* | C | | | | | | | | | | | | |
| *WP 3.4* | ABC | | | | | | | | | | | | |

## 2.4 Data handling

Data produced by all participants is stored on their respective network servers which are running regular backups. All data is stored in formats that are in compliance with either open source standards or are compatible to products offered by the Microsoft Corporation, allowing for a good accessibility. Hand written laboratory journals are compulsory for scientific co-workers. They will be stored at the respective institutions.

## 2.8 Information on scientific cooperation within SPP 2171

In this priority program, we plan cooperations with the following projects:

The proposed project from **H. Stark (TU Berlin)** also deals also photo-switchable substrates. There, photo-stimulated switches are used in order to generate an anisotropic adaptive surface. The project wants implement a boundary element method (BEM), which is capable to simulate the dynamics of a droplet on a switchable substrate. We agreed to cooperate in the course of the ongoing work within in the SPP to explore this method for our systems.

A cooperation is planned between the project of **K. Harth (U Twente, NL)** and our project to investigate the contact line dynamics during drop impact and drop spreading on the aligned cellulose fibers and responsive surfaces.

The imbibition of fluids into a deformable and porous media, where the interaction of parallel aligned fibres is an integral part of the model as in our aligned cellulose fiber materials, will be described in cooperation with **T. Gambaryan-Roisman (TU Darmstadt)**.

In a cooperation with the project proposed by **J. Hussong and E. Gurevich (U Bochum)** we will investigate the applicability of their developed rapid 2PP method for our aligned cellulose arrays.

Furthermore, we anticipate that the specific characterization techniques involved in our project will beneficial for a variety of other projects of the SPP.

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# 4 Requested modules/funds

## A 4.1 Basic Module [Gorb group, Kiel]

### A 4.1.1 Funding for Staff

One TV-L 13 (75%) position, **doctoral researcher** for 36 months: **€ 145,125**

The personnel funds are intended for exploration of aligned cellulose fibre arrays in biological systems (mucilaginous seeds of plants). The candidate is responsible for the seed collection, materials preparation, and characterization using microscopy and mechanical characterization techniques. Extensive experience in biology and materials science as well as mechanical characterization techniques are required. Apart from standard microscopy techniques, such as LM, CLSM, SEM excellent scientific abilities in advanced microscopy techniques, such as Cryo-SEM, TEM and AFM are required. The materials characterization includes microindentation, adhesion and friction characterization. Finally, he/she will be responsible for the documentation and publication of the achieved results.

**Student assistants** working 8 hours per week for 36 months: **€ 15,000**

The student co-workers will support the doctoral researcher in routine sample preparation and characterization. Simple documentation and evaluation of the experiments will also be part of the duties.

### A 4.1.2 Direct Project Costs

#### A 4.1.2.1 Equipment up to € 10,000, Software and Consumables

| Position | Cost (€) |
|---|---|
| Chemicals (solvents, silicones, liquid nitrogen, EM chemicals: OsO4, uranyl acetate, lead citrate, dyes for staining, embedding media, etc.), preparation tools (forceps, micro-scissors, blade holders), glassware, EM-targets | 5,000 |
| Force sensors (for AFM, microtribometers, etc.) | 4,000 |
| Sum consumables per year | 9,000 |
| **Sum consumables for 36 months** | **27,000** |

#### A 4.1.2.2 Travel expenses

| Position | Cost (€) |
|---|---|
| 1st year SPP workshop (employed researcher and PI); 4 days | 1,040 |
| 1st year Advanced School (employed researcher); 5 days | 600 |
| 2nd year SPP workshop (employed researcher and PI); 4 days | 1,040 |
| 2nd year PhD-candidate workshop (employed researcher); 4 days | 520 |
| 3rd year international conference (employed researcher and PI); 5 days | 1,200 |
| Annual visit of an International and national conferences (Society of Experimental Biology (SEB), Materials Research Society (MRS)) | 7,500 |
| Visit to cooperation partners (Munich groups) | 500 |
| **Sum travel expenses for 36 months** | **12,400** |

#### A 4.1.2.3 Other Costs

| Position | Cost (€) |
|---|---|
| Use of the clean-room facility and SEM EDX at the Technical Faculty of Kiel | |

| | |
|---|---|
| University (50 €/ month) | |
| Annual expenses | 600 |
| **Sum other costs for 36 months** | **1,200** |

### A 4.1.2.4 Project-related publication expenses

| Position | Cost (€) |
|---|---|
| Annual publication expenses | 750 |
| **Publication expenses for 36 months** | **2,250** |

## B 4.1 Basic Module [Zollfrank group, TUM/Straubing]

### B 4.1.1 Funding for Staff

One TV-L 13 (75%) position, **doctoral researcher** for 36 months: **€ 145,125**

The candidate is responsible for the chemistry synthesis, materials preparation and characterization. He or she should therefore hold a degree on the master level in Chemistry, Material Science or Renewable Resources. Experience in bio- and general materials processing as well as soft-chemical synthesis techniques are beneficial. Experimental work covers synthesis routes using advanced chemical techniques on a molecular and nanoscale. Apart from standard analytical measurements such as NMR, FT-IR, UV-Vis, DSC, TGA the materials characterization includes the advanced high level electron microscopy techniques SEM and TEM and molecular analytical techniques for which excellent scientific abilities are required. Processing also includes engineering techniques such as calandering. Finally, he or she will be responsible for the documentation and publication of the achieved results.

**Student assistants** working 8 hours per week for 36 months, in total: **€ 15,000**

The student co-workers will support the research associate in routine materials preparation and characterization. Simple documentation and evaluation of the experimental will also be part of the duties.

### B 4.1.2 Direct Project Costs

### B 4.1.2.1 Equipment up to €10,000, Software and Consumables

| Position | Cost (€) |
|---|---|
| Fine chemicals (biopolymers, functionalization reagents, pure solvents) and laboratory glass ware | 6,000 |
| Sample preparation equipment (electron, light and scanning electrochemical microscopy (SEM, TEM, LM and SECM)) | 4,000 |
| Processing aids for parchmentizing and calandering (baths and washing units) | 2,000 |
| Sum consumables per year | 12,000 |
| **Sum consumables for 36 months** | **36,000** |

### B 4.1.2.2 Travel expenses

| Position | Cost (€) |
|---|---|
| 1st year SPP workshop (employed researcher and PI); 4 days | 1,040 |
| 1st year Advanced School (employed researcher); 5 days | 600 |

| | |
|---|---|
| 2nd year SPP workshop (employed researcher and PI); 4 days | 1,040 |
| 2nd year PhD-candidate workshop (employed researcher); 4 days | 520 |
| 3rd year international conference (employed researcher and PI); 5 days | 1,200 |
| Annual visit of international conferences (2019 MRS Fall Meeting, 2020 MSE Darmstadt, 2021 MRS Fall Meeting) | 7,500 |
| Visit to cooperation partners (Kiel group) | 500 |
| **Sum travel expenses for 36 months** | **12,400** |

### B 4.1.2.4 Project-related publication expenses

| Position | Cost (€) |
|---|---|
| Annual publication expenses | 750 |
| **Publication expenses for 36 months** | **2,250** |

## C 4.1 Basic Module [Lieleg group, TUM/Garching]

### C 4.1.1 Funding for Staff

One TV-L 13 (75%) position, **doctoral researcher** for 36 months: **€ 145,125**

The candidate will be responsible for performing various characterization experiments of both, biological and bio-inspired samples. He/she will conduct macroscopic friction and adhesion experiments, static and dynamic wetting experiments and perform profilometric analyses of various samples. He/she will therefore require a strong experimental background and hold a degree on the master level in Mechanical Engineering or Material Science. Finally, he/she will be responsible for the documentation and publication of the achieved results.

**Student assistants** working 8 hours per week for 36 months, in total: **€ 15,000**

The student lab assistants will support the research associate by performing routine characterization experiments following procedures that the research associate has established. Simple documentation and evaluation of the experimental will also be part of the duties.

### C 4.1.2 Direct Project Costs

### C 4.1.2.1 Equipment up to €10,000, Software and Consumables

| Position | Cost (€) |
|---|---|
| Chemicals (reagents, solvents, biopolymers) and lab consumables | 6,000 |
| Quartz crystals for QCM-D | 1,500 |
| Consumables for tribology and adhesion tests (disposable sample holders and single-use measuring heads) | 2,500 |
| Sum consumables per year | 10,000 |
| **Sum consumables for 36 months** | **30,000** |

### C 4.1.2.2 Travel expenses

| Position | Cost (€) |
|---|---|
| 1st year SPP workshop (employed researcher and PI); 4 days | 1,040 |

| | |
|---|---:|
| 1st year Advanced School (employed researcher); 5 days | 600 |
| 2nd year SPP workshop (employed researcher and PI); 4 days | 1,040 |
| 2nd year PhD-candidate workshop (employed researcher); 4 days | 520 |
| 3rd year international conference (employed researcher and PI); 5 days | 1,200 |
| Annual visit of an international conference (2019 MRS Fall Meeting, 2020 ICoBT Biotribology congress, 2021 MRS Fall Meeting) | 7,500 |
| Visit to cooperation partners (Kiel group) | 500 |
| **Sum travel expenses for 36 months** | **12,400** |

**C 4.1.2.4 Project-related publication expenses**

| Position | Cost (€) |
|---|---:|
| Annual publication expenses | 750 |
| **Publication expenses for 36 months** | **2,250** |

## 5 Project requirements

### 5.1 Employment status information

Prof. Dr. rer. nat. habil. Gorb, Stanislav N., permanent position

Prof. Dr. rer. silv. habil. Zollfrank, Cordt, permanent position

Prof. Dr. rer. nat. Lieleg, Oliver, permanent position

### 5.3 Composition of the project group

[Uni Kiel / Gorb group]

Dr. Clemens Schaber, scientific co-worker, fixed-term position, state funded
Dr. Alexander Kovalev, engineer, permanent position, state funded
Esther Appel, technician, permanent position, state funded

[TUM Straubing / Zollfrank Group]

M.Sc. Matthias Langhansl, scientific co-worker, fixed-term position
M.Sc. Maximilian Rothammer, scientific co-worker, fixed-term position
Sabine Witzel, technician, permanent position, state funded

[TUM Garching / Lieleg group]
M.Sc. Benjamin Winkeljann, scientific co-worker, fixed-term position
NN, scientific co-worker, fixed-term position
Christine Braig, technician, permanent position, state funded

### 5.4 Cooperation with other researchers

#### 5.4.1 Researchers with whom you have agreed to cooperate on this project

See 2.5. Depending on the success of the proposals of these groups, we will continue existing and start new cooperations.

### 5.4.2 Researchers with whom you have collaborated scientifically within the past three years

[Gorb group, Kiel]

Prof. Rainer Adelung: Materials Science, Kiel University, D; Prof. Anne Staubitz: Organic Chemistry, Kiel University, D; Prof. Ruth Schmitz-Streit: Microbiology, Kiel University, D; Dr. Bo N.J. Persson: Forschungszentrum Jülich GmbH, Jülich, D; Prof. Jörg J. Schneider: TU Darmstadt, D; Prof. Thomas Speck: Botany, University of Freiburg, D; Prof. Rolf G. Beutel: Zoology, University of Jena, D; Prof. Vladimir Katanaev: Biology, University of Lausanne, CH; Prof. Alexander Filippov: Theoretical Physics, Donetsk, UA; Prof. Jürgen Blum: Astrophysics, TU Braunschweig, D; Dr. Gianandrea Salerno: Plant Protection, University of Perugia, IT; Dr. Manuela Rebora: Entomology, University of Perugia, IT

[Zollfrank group, München/Straubing]

Prof. Claudio Conti: Random lasing, Uni Rome, Italy; Prof. Michael Bartl: Photonic materials, Uni Utah, USA; Prof. Rainer Adelung: Self-reporting materials, Uni Kiel, D; Prof. Wolfgang Gindl-Altmutter, BOKU, Wien, A; Prof. Werner Kunz: Ionic liquids, Uni Regensburg, D; Prof. Frank Müller: Nanoparticle fabrication, Uni Jena, D; Prof. Oskar Paris: Biotemplating SAXS, Montanuniversität Leoben, A; Prof. Alain Celzard: Biocarbon materials, Uni Epinal, F; Prof. Dr. Nahum Travitzky: Additive manufacturing, Uni Erlangen, D; Prof. Robin Klupp Taylor: Cellulosic functional materials, Uni Erlangen, D; Prof. Johann Plank: Bioinspired concrete, TUM, D; Prof. Thomas Scheibel: Bioinspired materials, U Bayreuth, D; Prof. Volker Sieber: Bioengineering, TUM, D; Prof. Thomas Speck: Bioinspired actuators, U Freiburg, D

[Lieleg group, München/Garching]

Prof. Akos Kovács: Biofilms, DTU, Denmark; Dr. Bizan Balzer: Contact lens coatings, U Freiburg, D; Prof. Thomas Crouzier: Mucins, KTH Stockholm, Sweden; Prof. Tannin Schmidt: Cartilage, UConn, USA; Dr. Madeleine Opitz: Biofilms, LMU, D; Prof. Andreas Bausch: Self-assembly, TUM, D; Prof. Peter Müller-Buschbaum: Self-assembly, TUM, D; Prof. Job Boekhoven: Self-assembly, TUM, D; Prof. Stephan Sieber: Biofilms, TUM, D; Prof. Paul Janmey: Neurofilament gels, UPenn, USA; Prof. Mireille Claessens: Neurofilament gels, U Twente, Netherlands; Prof. Franz Pfeiffer: Hybrid-Mortar, TUM, D; Prof. Christian Große: Hybrid-Mortar, TUM, D; Prof. Sonja Berensmeier: Protein Purification, TUM, D; Prof. Thomas Hofmann: Saliva/astrigency, TUM, D; Prof. Thorsten Hugel: Cartilage, U Freiburg, D; Prof. Thomas Bein: Hydrogels, LMU, D; Prof. Daniel Huster: Hydrogels, U Leipzig, D

### 5.5 Scientific equipment

[Gorb group, Kiel]

Scanning electron microscope Hitachi S-4800 (equipped with cryo-system Gatan ALTO2500); Sputter coating system Leica EM SCD500; Critical point dryer Polaron E3000; Transmission electron microscope FEI Tecnai G2 Spirit BT; Ultramicrotome Leica EM UC7; Confocal laser scanning microscope ZEISS LSM 700; Nanoindenter MTS SA2; Microtribometers Tetra Basalt 01 and Tetra MUST; High-speed videocameras Photron Ultima and Olympus; Atomic Force Microscope JPK Nanowizard; White Light Interferometer Zygo New View 6000; Macroscope Keyence, MicroCT Sky-Scan; Contact Angle Measurement Device Dataphysics OCA 2000.

[Zollfrank group, TUM/Straubing]

Standard laboratory equipment for chemical synthesis including high vacuum Schlenk line; Berghof autoclave with 300 ml volume in PTFE-lined stainless, with 200 bar max.pressure, 230 °C max. temperature, stirring rate of 2000 max. rpm and safety rupture disc; Linseis STA PT 1600, TGA/HDSC high vacuum with maximum heating system of 1600 °C, Mettler Toledo differential scanning calorimety (DSC), scanning electron microscope (SEM) Zeiss DSM 940 A; High temperature furnace LM-312.27 Linn High Term with control unit Gefram 880P (in air and under inert atmosphere); Element analysis CHNS/O Hekatech; Thermogravimetric analysis Linseis; Diamond Wire precision saw Well; Microtome unit; Melt flow index testing machine Karg; Mechanical testing machine Karg; Light microsope with attached UV-Vis spectroscopic unit Mikroskopwerke Rathenau; Microcontact printer/nanoimprint lithography/ microfluidic device GeSim µCP 4.0; Permanent access to transmission electron microscopy (at TUM and U Regensburg). Scanning Electrochemical Microscope (SECM) CHI920D; low-voltage transmission electron microscope TEM LVEM5 Delong; Scanning Electrochemical Microscopy/CH Instruments. Calander (Sumet).The spectroscopic and chemical equipment, e.g. NMR (JEOL ECS 400 MHZ liquid NMR spectrometer), HPLC (Seric Prominence 20A, Shimadzu) and GC (Trace 1300 Thermo fisher Science Autosamples RSH, AS TRIPLUS RSH liquid headspace SPME) and Fourier-transform infrared spectroscopy (FT-IR) present at the Science Centre in Straubing can be used on a cooperative base.

[Lieleg group, TUM/Garching]

Shear rheometers with tribological extension equipment for rotational and oscillatory tribology (Anton Paar MCR 302); Optical Profilometer (µSurf, Nanofocus); FPLC (Äkta Purifier, GE), QCM-D (q Cell TQ2, 3t-analytik), fluorescence microscope (DMi8, Leica). Additional equipment available in the Munich School of Bioengineering if needed.