**Project Description – Project Proposals**

Prof. Dr. Jürgen Rühe, Freiburg

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

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Project Description

1   State of the art and preliminary work

In the past years several different strategies have been developed to generate surfaces whose properties can be switched by applying an outside stimulus such as light or mechanical deformation. Surface layers containing photochromic groups like spiropyrane and azobenzene can be reversibly switched from a polar into a less polar state by illumination with light in the UV and visible range.[1-7] An example taken from ref. [5] is shown in Figure 1. For such systems where the wetting properties change due a photoisomerization process, a number of possible applications mostly in the biomedical field have been suggested, including release surfaces and nanovalves.[8-11]
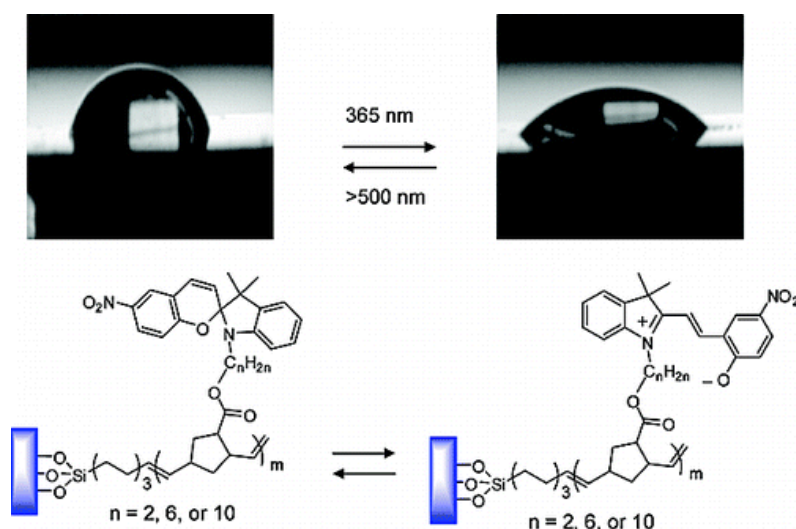
Figure 1: *Example of a switchable spiropyrane surface. The open charged form is more hydrophilic and leads to lower water contact angles. The picture is taken from ref. [5].*

However, as far as flat surfaces are concerned, all compounds which undergo reversible photoisomerization exhibit generally only small changes of the wetting properties upon switching. The reason for this is that the energy input for the isomerization reaction must be quite limited to avoid irreversible side reactions. For azobenzenes typical values for the water contact angle (CA) changes caused by the photoisomerization are on the order of 10 to 15° at maximum when a planar, flat substrate is taken.[12,13] The changes which can be observed are, however, largely empirical and no deeper understanding of the connection between energy input, isomerization and change in wetting properties has been achieved.

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In many cases the wetting contrast could be enhanced by applying the photoisomerizable units onto rough surfaces.[3,4,7,14-17] Examples are spiropyran containing monolayers on a silicon nanowire structure which showed a CA difference of $\Delta\theta = 37°$ upon isomerization[9] and spiropyrane chromophores on porous and flat silicon wafers with CA difference from $\Delta\theta = 3$ to $12°$.[11] Jiang et.al. have shown that the geometric properties of the surface is very important as they were able to generate a maximum $\Delta\theta = 3$ to $12°$ only for one specific post geometry on microstructured model surfaces.[3]

We have shown in previous work, that strong changes in the wetting behavior can be triggered on nanostructured surfaces even if the change in polarity of surface-anchored groups are rather small. In some cases the receding contact angle could be reversibly switched between >175° and 0°, i.e. from a fully superhydrophobic to a superhydrophilic surface.[18]

One of the key requirements was to have a very strongly nanostructured surface, as all microstructures lead to a pinning of the contact line. We modify these nanostructures using surface-attached polymer films. When wetting properties are studied a covalent attachment of the molecules to the underlying substrate is crucial because whenever then low surface energy coatings have a damage there is a high possibility that a polar liquid will creep under the coating and alter the behavior, eventually leading to delamination and complete loss of the coating layer. The use of polymer coatings has the advantage, that the coatings can become somewhat thicker and more robust compared to thin self-assembled monomolecular layers.

In this example the roughness of the silicon nanograss[18-20] surface (Figure 2a) with its very small spikes played an important role to enable the observed dramatic changes in the wetting behavior. Surfaces with wetting properties, which show superwetting behavior and a roll-off angle of <1° have been generated.[18] Thus a key feature for all studies on surfaces with attractive wetting properties relies on the presence of such nanoscale structures. Such structures can be obtained by deep reactive ion etching in silicon when after the structure formation the obtained surfaces are coated with thin polymer layers, which allow to tailor the surface composition and thus wetting behavior. When the surface energy is varied distinct wetting transitions can be observed, where at a certain value of the surface energy very strong changes in the wetting behavior can be observed. Clear transitions between superwetting, a Wenzel regime and a superhydrophobic regime can be observed.[18]

However, the process is not limited to thin coatings on silicon substrates. We were also able to show that a double replication process can be used to generate nanograss surface structures in various polymers with very different polarity such that all states of wetting can be realized. Figures 2b-c show the PDMS master replicated from the nanograss sample along with two examples of polymer nanograss surfaces replicated from the PDMS master. One is generated from PMMA, the other one from a perfluourinated acrylate (PFA). Depending on the material used superhydrophilic surfaces but also sticky Wenzel-type wetting and true superhydrophobicity was observed on these samples.[21] As nanostructures are inherently mechanically fragile, an improvement of the mechanical properties seed favorable. The nanoscale structures can be mechanically stabilized by in interdispersed cone structures, where the cones had a size of a few micrometers and which reduced any possible mechanical load to which the samples maybe exposed. Even more stable structures are found if the process is adapted such that metallic nanostructures are formed.[22]
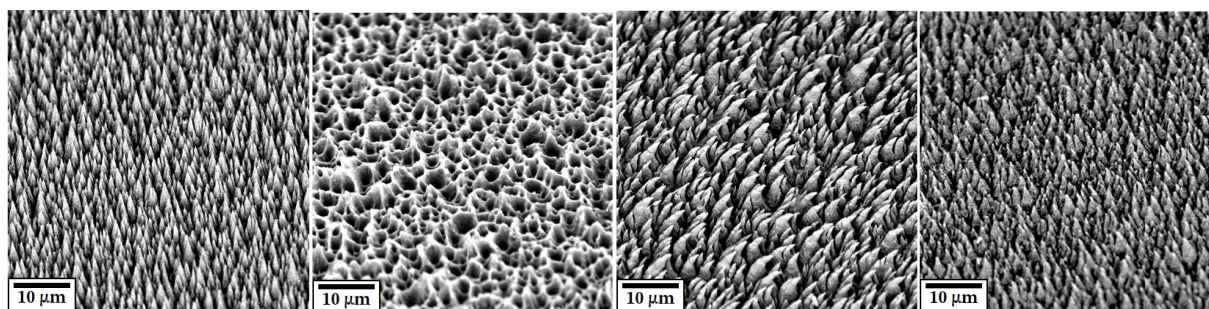
Figure 2: *SEM micrographs of a) silicon nanograss generated by Deep Reactive Ion Etching (DRIE), b) PDMS master replicated from the nanograss, c) PMMA replica from the PDMS master and d) PFA (fluorinated polyacrylate) replica from the PDMS master.*

Based on these observations, the nanograss features were combined with isomerizable groups contained in the side chain, along the lines as described above.[23] Polymers with azobenzene units were chemically anchored on nanograss surfaces using C,H insertion chemistries (CHic). The resulting surface is shown in Figure 3. Through photoisomerization the azobenzene units shuttle between the trans- and the cis-form. As these forms have a slightly different dipole moment they exhibit also a difference in the polarity.
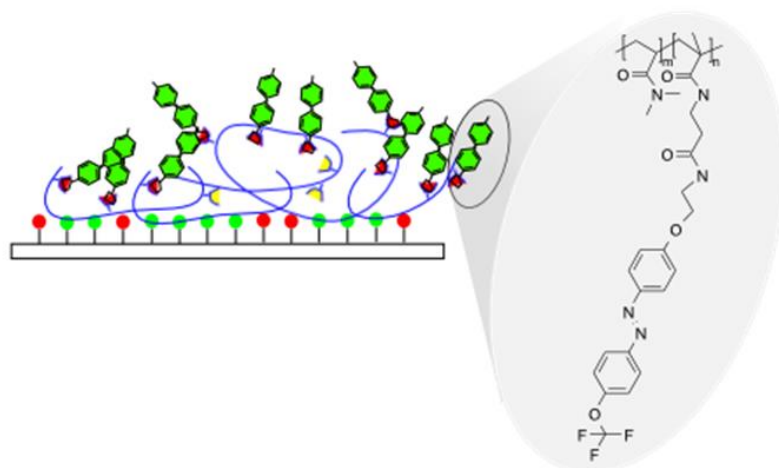

Figure 3: *Surface-attached polymer containing azobenzene units which can be used to switch wetting behavior.*

Such polymer layers, when deposited on a flat substrate exhibit a change in the water contact angle of around 10° when switched between cis and trans states. This change is amplified by either exposing or hiding the CF_3 groups which are present as substituents at the azo group at the surface. Following up on this, Groten and Rühe have shown recently that extremely large changes in the wetting behavior can be achieved when the isomerization process is coupled to such a wetting transition.[2]

If now in one state one is at a surface energy slightly below a wetting transition, in the other state slightly above, very strong changes in the wetting behavior should be observed. This is indeed the case. Figure 4 shows the dynamic contact angles and the roll off angles of water on these surfaces upon isomerization. The strong effect especially on the receding angle and the roll off angle are very obvious. The advancing contact angle is less strongly influenced and values of 150° in one case and 180° in the other are observed. These values mark a transition from the superhydrophobic Cassie-Baxter wetting to a sticky Wenzel wetting. Accordingly, vast differences are found for the receding angle and the roll off angle. The first one is rather high in the Wenzel state and vanishes for the superhydrophobic state. Vice versa the drop rolls off the surface at a very small angle for this state and simply sticks to the surface for Wenzel wetting. Similar

transitions have also been found for PEL brushes on rough surfaces through the exchange of the counterions.[24]
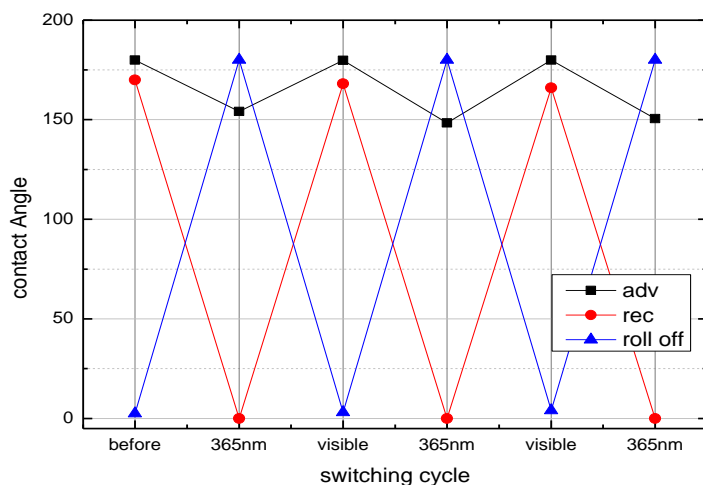
Figure 4: Dynamic contact angles on switchable azobenzene coatings on nanograss. The wetting behavior cycles between Wenzel wetting and Cassie-Baxter wetting.[6]

Apparently, rather strong wetting transitions could be triggered even though the change in surface polarity upon irradiation of the azobenzene groups is rather limited. The reason for this observation is that the overall wetting properties of the surface used here is close to the transition point from Wenzel to Cassie-Baxter wetting. This is shown in Figure 5 that plots the dynamic contact angles as measured on nanograss surfaces as a function of the angles as measured on flat surfaces for different coatings. The coating chosen for the above mentioned surfaces shows contact angles just before and after the transition between two wetting states and, hence, even small polarity changes are sufficient to trigger huge differences in wetting.
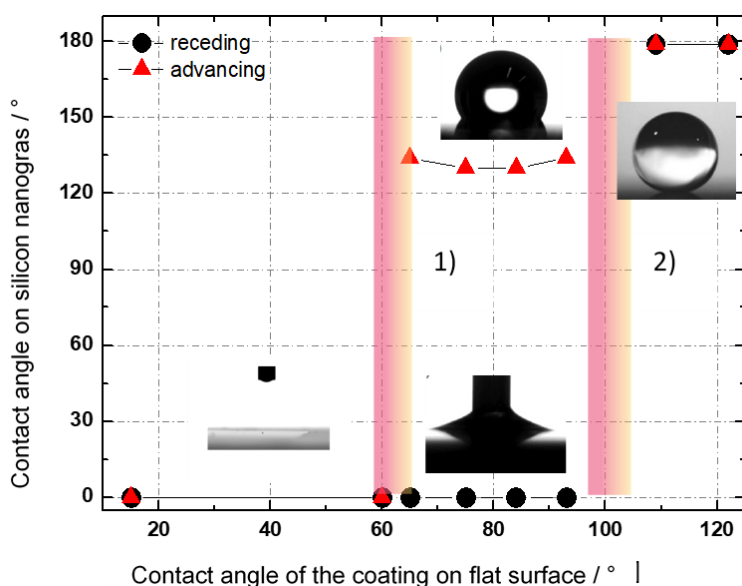
Figure 5: Dynamic contact angles of coated nanograss surfaces as a function of the contact angles on flat coatings. Clear transitions between different wetting types are visible. The chemical structure of the employed polymers is given below. For more details see Groten et al.[6]
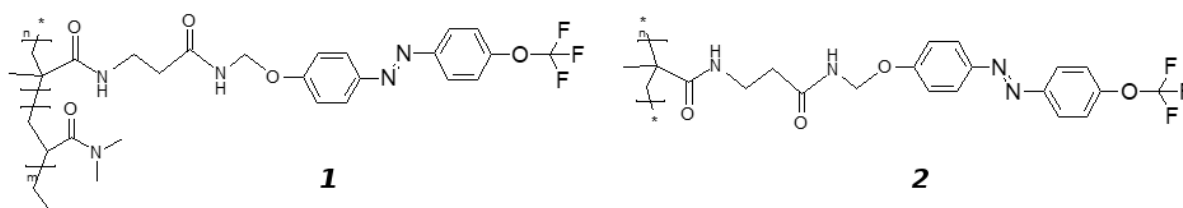
However, there are still many open questions concerning the exact surface energy at which the transition occurs and how this is influenced by the details of the surface topography.

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.

1. Christian Dorrer, Jürgen Rühe; Condensation and wetting transitions on microstructured ultrahydrophobic surfaces, Langmuir, Vol. 23 (7), 2007, 3820-3824. DOI: 10.1021/la063130f.
2. Christian Dorrer, Jürgen Rühe, Contact line shape on ultrahydrophobic post surfaces Langmuir, Vol. 23 (6), 2007, 3179-3183. DOI: 10.1021/la062596v.
3. Christian Dorrer, Jürgen Rühe; Wetting of Silicon Nanograss: From Superhydrophilic to Superhydrophobic Surfaces, Advanced Materials, Vol 20, 2008, 159-163. DOI: 10.1002/adma.200701140.
4. Christian Dorrer and Jürgen Rühe; Some thoughts on superhydrophobic wetting, Soft Matter, Vol 5, 51-61, 2009, 51-61. DOI: 10.1039/B811945G.
5. Christian Dorrer and Jürgen Rühe: Micro to nano: Surface size scale and superhydrophobicity, Beilstein J. Nanotechnol., Vol 2, 2011, 327-332-1. DOI: 10.3762/bjnano.2.38.
6. Jonas Groten, Chrstine Bunte, Jürgen Rühe; Light induced switching of surfaces at wetting transitions through photoisomerization of polymer monolayers, Langmuir, 2012; 28: 15038-15046. DOI: 10.1021/la302764k.
7. Vitaliy Kondrashov, Jürgen Rühe; Microcones and Nanograss: towards mechanically robust superhydrophobic surfaces, Langmuir, 2014,30, 4342-4350. DOI: 10.1021/la500395e.
8. Srinivas Bengaluru Subramanyam, Vitaliy Kondrashov, Jürgen Rühe, and Kripa K. Varanasi, Low Ice Adhesion on Nano-Textured Superhydrophobic Surfaces under Supersaturated Conditions; ACS Applied Materials & Interfaces 2016, 8, 12583–12587. DOI: 10.1021/acsami.6b01133.
9. Roland Hönes, Vitaliy Kondrashov, Haosu Huai, and Jürgen Rühe; Wetting Transitions in Polymer Nanograss Generated by Nanoimprinting, Macromolecular Chemistry and Physics 2017, 218, 1700056. DOI: 10.1002/macp.201700056.
10. Roland Hönes, Vitaliy Kondrashov, and Jürgen Rühe; Molting materials: Restoring Superhydrophobicity after Severe Damage via Snakeskin-like Shedding, Langmuir 2017, 33, 4833–4839. DOI: 10.1021/acs.langmuir.7b00814.

1.1.2   Other publications

1.1.3   Patents

1.1.3.1   Pending

None.

1.1.3.2   Issued

None.

2   Objectives and work programme

2.1   Anticipated total duration of the project

The project is designed for 36 months. After that we plan a continuation of the project during the second funding period of the priority program.

2.2   Objectives

The overarching goal of the research project within the SPP2171 is to generate substrate surfaces with tailor-made chemistry and topography which can respond dynamically to changes in the environment and to study the wetting behavior of simple liquids on such reconfigurable surfaces. We will aim to obtain a deeper insight into dynamics of wetting as well as dewetting of such liquids on switchable/ substrates. We will focus primarily on experimental work but combine this in collaborations with theoretical analyses.

We will follow essentially two concept lines which will be brought together in the course of the project. We will

1) generate substrates where a specific surface topography is chosen and the surface chemistry is adjusted to allow dynamic changes through e.g. isomerization reactions which allow to change the wetting behavior in a dynamic way.
2) generate substrates, where a certain surface chemistry is chosen and the surface is made reconfigurable through microengineering tools, eg. the surface topography is systematically switched from smooth to rough or where the surface is exposed to a stimulus or becoming deformed in the course of liquid contact. In some cases the switching process will be induced by the wetting liquid itself so that responsive/adaptive surfaces are obtained.

In orienting experiments towards the end of the funding period the two lines will be brought together either by

3a) generating multiple-stimulus responsive surface, where one stimulus acts on the surface chemistry/ surface polarity and one on the topography.
3b) In other cases it is envisioned to use the developed technologies as a toolbox, where features of the surfaces in the two project lines (stimulus responsive surface chemistry and stimulus responsive topography) are combined to generate dynamically reconfigurable surfaces, where the dynamic changes have a very strong impact on the wetting behavior.

The core objectives of the project can be broken down into the following sub-objectives which leads to the subsequent development of the work packages:

Objective 1):
To realize surfaces with stimulus responsive wetting properties we will continue earlier work published by us[9] where we generate nanostructured surfaces and decorate them with photoisomerizable groups, which allow to reversibly change the surface polarity of the coated substrate through irradiation of light with an appropriate wavelength. Key concept is here to couple the reconfiguration of the surface chemistry to a wetting transition. Such a wetting transition occurs when nanoscale structures experience variations in the surface polarity (see chapter 1) and very small changes in the surface polarity lead to strong changes in the wetting behavior.

Open questions which remain after the publication of the first work in this area and which will addressed in the proposed project are:

1) How can the topography be correlated to the exact location of wetting transitions? So far both the surface chemistry and the topography were empirically chosen and a prediction of the switching of the wetting properties has not been possible.
2) What is the importance of irregularities in the surface topography of the substrate (ie. variations in spacing, height and shape of the nanoscale features) on the stimulus responsiveness of the wetting behavior?
3) Under what conditions is a switching of the wetting properties back and forth possible **in contact** with the liquid placed on top. So far switching back was only possible on dry samples.
4) Can the surface chemistry/surface topography be chosen such that an isomerization reaction allows a direct switching from a superhydrophobic state to a superwetting state? This requires a slightly larger change in the surface polarity during (photo)isomerization and a smaller differences of the surface polarities of the wetting transitions..
5) Can a thermal stimulus be used to achieve a change in the surface polarity through phase separation rather than photoisomerization?
6) Under what conditions is switching from a kinetically trapped Wenzel state back into the superhydrophobic state possible?
7) What is the kinetics of the switching of the wetting properties? How fast can the process be made?

The general structure of the systems to be investigated is shown in Figure 6. The variation in the surface chemistry will be achieved by coupling thin conformal surface-attached polymer networks to the nanoscale structures. As nano rough surfaces silicon nanograss will be chosen. The conformal coating of the nanosized features will be achieved by the immobilization and crosslinking of polymer layers through the CHic process (C,H-insertion crosslinking) developed recently by us.[25-28] Such a process has the advantage that extremely robust and conformal coatings can be obtained. Using polymers instead of the commonly used self-assembled monolayers has the advantage that the system can be very easily and very precisely tuned by generating copolymers of a desired composition and then immobilizing them. This way many different surface chemistries can be obtained through only one type of surface reaction. When self-assembled monolayers are generated and it is desired to vary the surface chemistry for every single surface chemistry the self-assembly process has to be studied anew. By varying the conditions of the silicon nanograss generation (input power, relation between passivation and etching) different size and distances of the surface features will be obtained. Through appropriate lithographic process also regular nano-needle arrays will be generated.
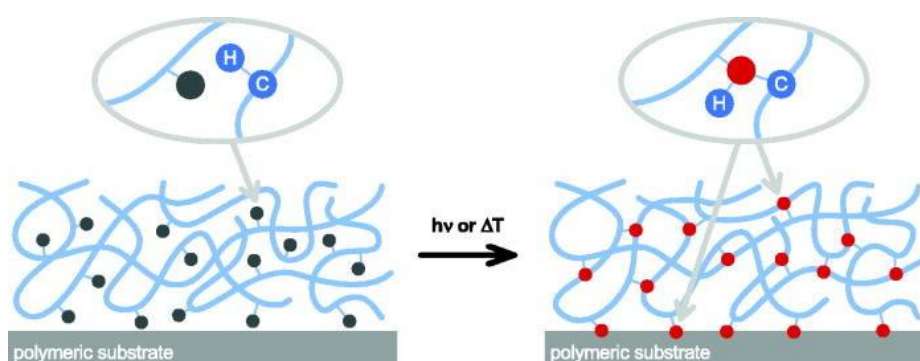

Figure 6: Schematic description of the C,H insertion crosslinking (CHic) for the generation of surface attached polymer networks on polymeric supports. Similar groups must be depositied as self-assembled monolayers on substrates like silicon.

Similar surface chemistries can be also achieved by generating polymer brushes through surface-initiated polymerization. The Rühe group has a longstanding experience on the generation of brush structures. The brushes will be generated through self-assembled monolayers of initiators and growth of polymer chains in situ by free radical polymerization. As initiators for the generation of the SAM layers azosilanes will be used as published in a larger series of publications.[29-31] This, however, will be only an application of already developed knowledge. No synthetic processes will be developed here in the course of the project.

To enhance the change in the polarity of the surface-attached coating not only the composition of the copolymer will be varied, but also different isomerization reactions will be employed. So far polymers containing azobenzene groups were used, which contained both hydrophilic groups and fluorinated groups to shift the value of the surface energy of the coating exactly to the surface energy of the wetting transition. The composition of the copolymers was so far quite empirically chosen, by varying of the hydrophilic/hydrophobic balance larger effects seem to be feasible. In the proposed project a different system for the isomerization, the well-known spiropyran – merocyanin system will be investigated. The isomerization of spiropyrans have been well studied and there is a large spectrum of publications on this topic available. Furthermore, also the isomerization in thin films has been reported.[32] However, no studies have been performed so far to couple the isomerization process to a wetting transition on a nanostructured surface close to a wetting transition. Surfaces of varying roughness have been employed, but the results by our group show clearly that this is a necessary, but not sufficient condition. The spiropyran groups need to be incorporated into photocrosslinkable polymers which have exactly the right hydrophilic/hydrophobic balance to couple to wetting transition. It can be expected that the system will exhibit a stronger change in the polarity compared to the azobenzene counterparts as in the spiropyran form 1 it is a rather non-polar compound, whereas the merocyanin 2 form is zwitterionic in nature (Figure 7). Although the spiropyran system requires from a synthetic point of view more effort, this might be justified by having a larger polarity change during isomerization.

To generate surfaces which respond to a thermal stimulus surface-attached, ultrathin polymer networks consisting of a thermoresponsive polymer will be studied as well. While the polymer layer at low temperature is highly swollen in the aqueous medium and has a high polarity, at high temperatures the water is expelled as polymer-polymer interactions dominate over the polymer-solvent interactions. Here essentially all the processes described before can be employed, just the polymer is exchanged for a thermoresponsive unit.

We will perform both experimental studies and simple FEM calculations (surface evolver, Comsol). For more detailed studies we will cooperate with theoretical scientists in the SPP (eg. Prof. Holm, Stuttgart).
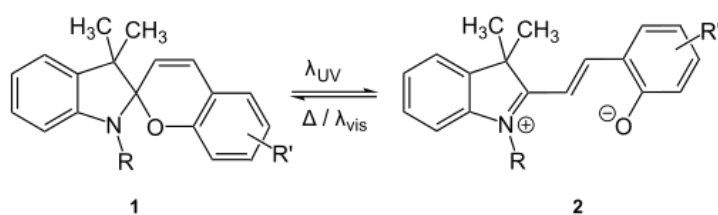
Figure 7: Switching behavior of spiropyrane compound switching between a less polar cyclic configuration *1* and an ionic, open configuration *2*; R=H,Alkyl R' represents the polymer

Objective 2:

In the second part of the project we will use engineering tools to generate surfaces where the surface topography can be altered by an external stimulus. In this line of work and the

corresponding work packages we will benefit from the possibilities given by the equipment and processes established at the department of microsystems engineering (IMTEK) at the University of Freiburg, where we can make easily use of advanced cleanroom, micro- and nanoprinting technologies and the appropriate tool making for such purposes.

Line 1:

In one set of experiments we will start from the expertise we have developed on the generation of magnetically actuable rubber (poly-n-butylacrylate) or hydrogel networks, again crosslinked by the CHic process. To this the microstructured networks will be generated in the presence of supra- or ferromagnetic nanoparticles. The networks are quite flexible and upon application of a magnetic field the magnetic microstructures will be lifted up from a resting position, so that a previously more or less flat substrate becomes quite rough and in some cases a previously hidden surface becomes exposed. This is especially the case when the movable flaps are hydrophobic, the substrate below hydrophilic.

When the flaps, which are also shown in Figure 8, are closed, the surface will be quite strongly hydrophobic. As the areas between the flaps form essentially a hydrophobic pore no water will penetrate into the voids. The flaps, which serve as a gate to the substrate will be lifted up and lowered by magnetic forces induced by a turning permanent magnet. When they are lifted up the hydrophilic substrate, which was hidden before, becomes available to the liquid and thus it can be wetted by the contacting water. In consequence, in situation 1 in Figure 8 the surface will be (super-) hydrophobic, in situation 2 the surface will be hydrophilic. A major challenge will be to prevent ground collapse and bunching of the flaps, especially when the sample is drying out. Ground collapse might be prevented by the use of a suitable support structure on which the flap can rest and an antiadhesive surface modification of the flaps. An important question will be what happens when the gate is closed in the presence of water and the surface becomes hydrophobic again. In between the hydrophobic plates will be now a little bit of water, which will prevent a drop roll-off. However, the smaller the water droplet in the pore between the structures, the smaller the pinning force.
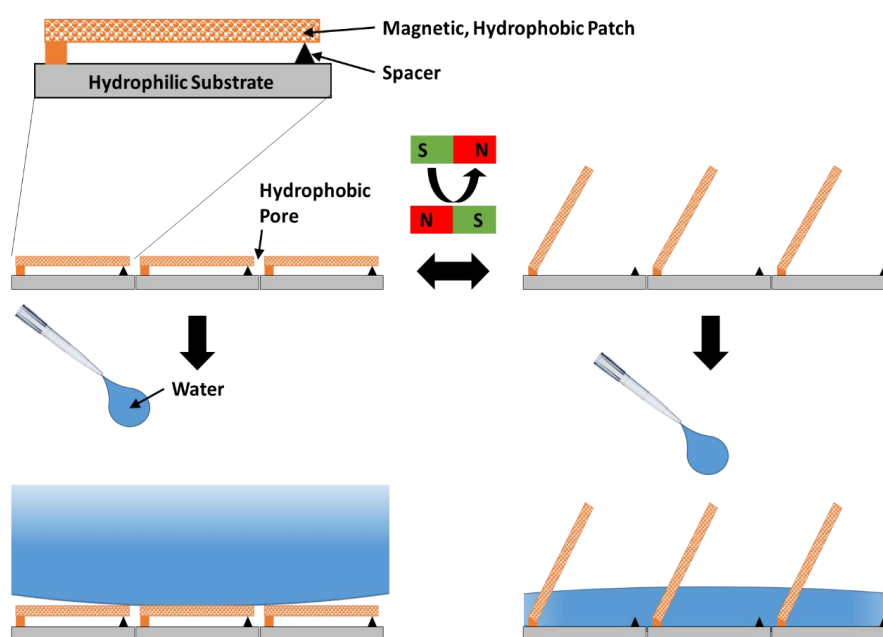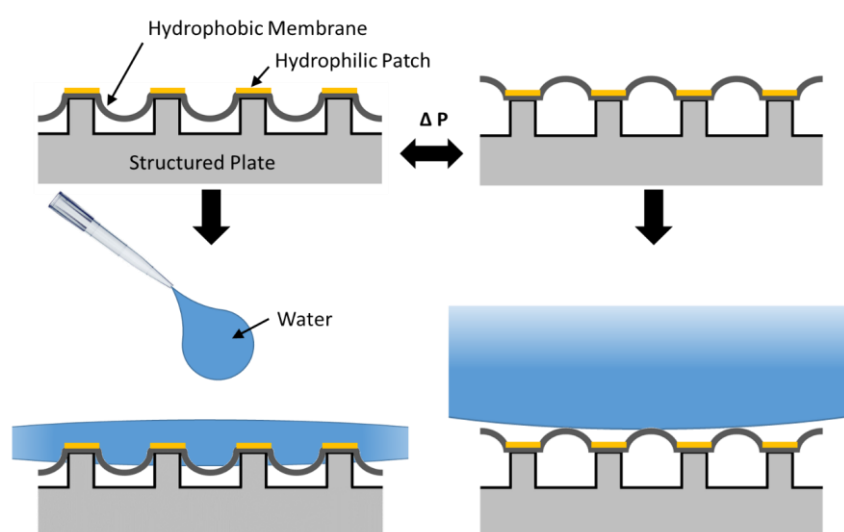

Figure 8: Schematic depiction of the realization of a surface with a topography switched by magnetic actuation.

Line 2:

In an alternative approach a stimulus will be used to vary the topography of the substrate eg. from -flat to a strongly corrugated surface and back in a dynamic way. In this concept which is shown

as a first example schematically in Figure 9, a thin membrane will be generated, which will look somewhat like an array of flat suspension bridges. If now pneumatically a small pressure from below through the trenches is applied, the membrane will buckle between the support posts and switch from a flat to a corrugated surface. To generate such a structure a membrane is microstructured so that it consists of an array of trenches, which have a periodicity of 1 μm or several μm, generating a corrugated surface. Onto this substrate a thin sheet of polymer is deposited as schematically shown in Figure 9. To this a thin layer of a rubberelastic polymer (e.g. poly-n-butylacrylate) is generated on a stiff (e.g. glass substrate) covered by a sacrificial layer (glucose or a water soluble polymer). This sheet can be nanostructured through a nanoimprinting process similar to previous work.[13] This sheet of polymers is covalently linked to the corrugated surface and the sacrificial layer dissolved leading to the release of the mechanical support. When now a (positive or negative) pressure is applied this will strongly change the topography of the substrate, not quite unlike this is done in a blister test.

Figure 9: Schematic depiction of the realization of a surface with a stimulus depended topography based on an actuatable membrane.

When a slight underpressure is applied the membrane will sag through between the "bridge heads". Now a similar sheet consisting of a thin polymer layer, a sacrificial layer and a solid support are added, only that this time the polymer will consist of a hydrophilic polymer. The tops of the "bridge heads" of the suspension bridge will now contact the polymer sheet on top. When now the assembly is irradiated with UV light residual photoactive moieties in the rubber layer will bind a monomolecular layer at exactly these positions. This way a substrate with nanostructured hydrophilic posts and hydrophobic "suspension bridges" will be generated. When now the pressure is modulated, a liquid placed on top will contact either the nanostructured hydrophilic parts of the substrate or the nanostructured hydrophobic parts of the substrate, which might allow to have very strong dynamic control over the wetting properties in a wide range.

Line 3:
For an interesting new approach two components will be prepared as shown in Figure 10. As one component a substrate will be generated, which is composed of an array of posts, which are superhydrophobic. The second component is a foil/membrane containing holes which is hydrophilic. The posts and the holes are generated by photolithography so that they can perfectly fit to each other. The two substrates are then brought together while the upper foil is fixed. The lower substrate, which is connected to a solid support is then lifted up and down through a piezodrive such that the posts/pins pass through the hole. When now a drop is placed on the assembly, depending on the position of the piezo, it will be either exclusive in contact with the superhydrophobic posts or with the hydrophilic foil. The behavior of the drop will also crucially

depend on the size and the distance of the movable pins. When they are too far apart sagging through of the drop will occur. One major challenges which needs to be addressed is the alignment of the two components. This will depend crucially on the size of the holes and the pins. While for larger holes and pins this will be a smaller challenge, with decreasing size of the structures it will become more and more of an issue. A second challenge will be to prevent sagging through of the foil on a larger scale. This problem can be addressed by employing instead of a flexible foil a rather stiff membrane or by mechanically stretching the foil.
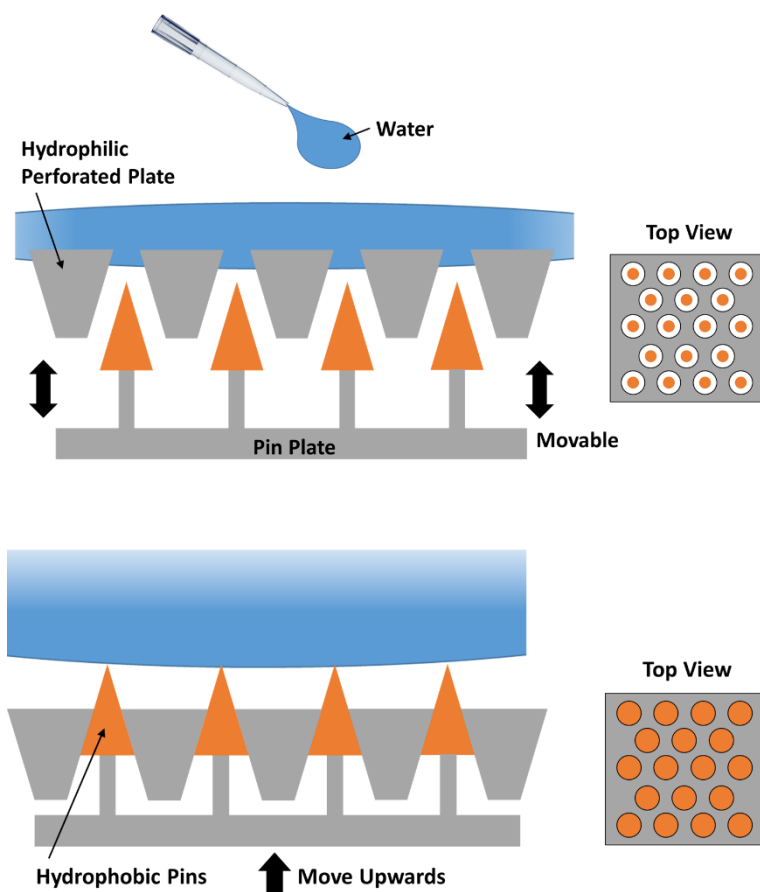
Figure 10: *Schematic depiction of the realization of a surface with a stimulus depended topography through actuation through a grid.*

2.3   Work programme incl. proposed research methods

Work package 1:

Work package 1 comprises the synthesis of the precursor polymers containing the photoisomerable groups (ie. azobenzene or spiropyrane group containing polymers) and the crosslinker groups. For the generation of the monomers literature procedure will be employed. In some cases slight adaptations of the chemical structure and thus the synthesis process will be required to adjust the polarity of the switchable units. The synthetic procedures will require 3-5 reaction steps. Concerning the crosslinker units standard procedures which have been developed in our research group will be employed. This will typically employ 2-3 reaction steps. Depending on the required film thickness the crosslinker groups will be either incorporated into the polymer or attached to the surface in form of a selfassembled monolayer. In the latter case no crosslinker units need to be incorporated into the polymer itself.

In addition to the polymers containing the photoisomerizable groups also groups with a thermally responsive unit (based the well studied N-isopropyacryamide (NIPAM) or polymers containing ethyleneoxide units in the side chain having a well defined length of the side chains will be employed. To this appropriate knowledge is present in group through a recently completed PhD thesis.[33]

The obtained monomers will be copolymerized with appropriate comonomers, which allow to tailor the polarity of the polymers exactly that the surface-attached polymer layers generated in WP 3 have the right hydrophilic/hydrophobic balance for the wetting transitions. This will allow the generation of a toolbox of polymers with tailored polarity. All monomers and polymers will be characterized concerning composition and molecular weight

Work package 2:

In work package 2 various micro- and nanostructured surfaces will be generated. Here we will rely on the equipment available in IMTEK-cleanroom. We will generate silicon nanograss and by double replication also polymer nanograss and other nanoscale structures (eg hairy surfaces). Here we will employ established DRIE etching process and polymer microprocessing procedures (for example for the generation of hairy structures). All structured substrates will be characterized by SEM/optical profilometry and AFM.

Work package 3:

In work package 3 the materials generated in WP 1 and 2 will be combined. We will generate and characterize surface-attached polymer networks from the precursor polymers on the micro- and nanostructured surfaces. We will study the crosslinking behavior of the films by SPR and ellipsometry. The surface roughness of the substrates will be determined by AFM and/or optical profilometry, The chemical composition of the surface-attached layers will be generated by XPS and infrared spectroscopy. For the latter different approaches will be used depending on the layer thickness transmission (using a double side polished silicon wafer) or ATR/GIR configurations.

Work package 4:

In work package four the dynamics of the wetting behavior of simple liquid, in most cases water, in some cases also other simple solvents, will be studied. The questions listed above under "objectives" will be addressed. Imaging of the droplets will be carried by using confocal fluorescence microscopy after adding simple fluorescence dyes to the liquid. The experiments will be carried out partly at the Life Imaging Center of the University of Freiburg, partly in collaboration with the group of Hans-Jürgen Butt/Doris Vollmer (Max-Planck-Institute for Polymer Research, Mainz). The influence of both photochemical as well as thermal stimuli, which induce structural changes in the substrate, onto the wetting behavior of liquids on such substrates will be studied.

We will perform both experimental studies and simple FEM calculations using Surface Evolver or COMSOL as software packages. Extensive experience in working with Surface Evolver is available, local collaborations with the Laboratory for Simulation at the Department of Microsystems Engineering (IMTEK) will supplement this. We will start with simple regular arrangements of the nanostructures and study the influence of size, acuteness, surface energy and other parameter onto the static wetting behavior and then change the surface energy and re-perform the calculation. These simple simulations are not meant to solve all the theoretical questions listed under "objectives", but they will allow go get into a more qualified discussion with the theoreticians. For more detailed studies we will cooperate with theoretical scientists in the SPP (eg. Prof. Holm, Stuttgart).

Work package 5:

In the fifth work package we will address the generation of substrates with responsive and/or adaptive topographies. While for the substrates in work package 4 the topography is given, here the topography will be changed systematically by using magnetical or mechanical stimuli as lined out in the lines 1-3 laid down in the previous paragraph. While changes in the surface chemistry lead often to an abrupt change in the wetting properties at a certain threshold (wetting transition) which will switch the system, the surface designs studied in work package 5 will allow a more gradual change of the topography (which still might lead to abrupt changes in the wetting properties). We will use typical engineering tools to generate micro- and nanostructured surfaces. The surface we envision are hierarchical, i.e. there is a microstructure which is changed by the stimulus. But at the same time the microstructured surfaces carry nanoscale structures to allow to obtain less strongly pinned surfaces.

In contrast to the materials generated by work package 1/3, where the changes in the surface chemistry will have a rather slow kinetics, here also rather fast changes in the topography should be feasible. If for example a magnetic field is reversed, a small pressure is built up or a piezo lifts a part of the substrate up and down, in all these cases rather fast processes can be envisioned. In experiments on magnetic cilia for example frequencies of the beating of the magnetic flaps on the order of several Hertz (actually up to 100 Hz) have been employed.

Work package 6:

In work package 6 we envisage to combine the structures and chemistries of the work packages to generate surfaces where in dynamic way both parameters can changes, this way generating of multi-stimulus responsive substrates. This will open up an interesting perspective, which will be explored more extensively in the second funding period. Here only some orienting experiments are planned. It will interesting to explore how the wetting properties change, when two stimuli (light, mechanical energy) are imparted onto the substrate at the same time acting synergistic or antagonistic.

Work package 7:

Towards the end of the funding period the documentation of the results obtained in the project will be finalized and publication of the project results will be prepared. An application for the second funding period will be prepared.

The time sequence in the implementation of the project is outlined in the following table (Gantt chart).

Work packages	Year 1				Year 2				Year 3			
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
WP1	▓	▓	▓				▓			▓		
WP2	▓	▓	▓	▓				▓			▓	
WP3			▓	▓	▓	▓	▓	▓	▓			
WP4			▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
WP5			▓	▓	▓	▓	▓	▓	▓	▓	▓	▓
WP6											▓	▓
WP7											▓	▓

2.4 Data handling

The data generated in the project is backed up several times electronically and is available to the staff of the group directly and at all times (read access). This is realized through an electronic laboratory journal which has to be kept by all scientific and technical employees. The laboratory journal consists of a data repository (Tortoise SVN) with which the relevant documents (descriptions of experiments, spectra, data tables, graphical material, etc.) are synchronized from the employee's work computer against a server. The document history is automatically tracked ac-cording to the philosophy of such repositories. The server is operated at the Computer Center of Freiburg University and the data of the server is permanently mirrored redundantly on several hard disks following state of the art protocols.

2.5 Other information

Not applicable.

2.6 Descriptions of proposed investigations involving experiments on humans, human materials or animals as well as dual use research of concern

None.

2.7 Information on scientific and financial involvement of international cooperation partners

None.

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4   Requested modules/funds

4.1   Basic Module

4.1.1   Funding for Staff

We request for the duration of the project positions for two PhD students (2x0.67xTVL13).

One of the doctoral researchers (0.67xTVL13) should have a strong background in chemistry/polymer science for the performance of the synthetic work and more physicochemical tasks. This doctoral researcher will generate the light-switchable or thermally switchable monomers and crosslinkers. She/he will perform the polymerization reactions and characterize all the low and high molecular weight compounds. She/he will generate surface attached polymer networks or brushes from the precursor layers and study the layer formation process in detail. This will also include the generation of magnetic compounds and photostructurable rubber precursors used for the microengineering approaches. He/She will characterize the obtained surface-attached polymer layers by using a broad spectrum of surface-analytical tools.

Additionally, we request for the duration of the project the position of a PhD student with a strong background in microengineering for the generation of micro- and nanostructures. To this she /he will employ diverse engineering tools such as deep reactive ion etching and microreplication. He/She will focus very strongly on the generation of surfaces, whose topography can be switched as a function of an external stimulus such as described under objectives line 1-3. He/she will generate the surfaces and characterize them by using a broad range of microscopy tools and surface analytical tools. Additionally the engineering oriented PhD student will perform the FEM simulations using COMSOL and surface evolver. (Note: in Engineering the positions of PhD students are frequently compensated differently compared to chemistry or physics students). In case this should be necessary to move to a higher salary to be competitive we will complement this difference from other financial sources).

The two doctoral researchers will collaborate very strongly on the generation of micro- and nanostructured surfaces with tailor-made chemistries. It will be very beneficial to bring in the different expertise to generate completely novel systems. They will also collaborate on a day-to-day basis on the study of the wetting properties of the obtained systems and on the study of the dynamic behavior of the films as described in the work packages 4-6. They will collaborate also with other members of the SPP on the more sophisticated theories. We had in the past extremely positive experiences with such a pairing of two students with very different areas of expertise. The outcome of such pair formation has been extremely productive.

Total staff requested: 2 TVL13 67% positions for the whole project time frame.
Total costs as calculated by ELAN: **259.290 €**

4.1.2   Direct Project Costs

4.1.2.1   Equipment up to Euro 10,000, Software and Consumables

We request funding for consumables of € 20.000 per year. The amount is needed for chemicals, glassware, lab supplies, substrates, GPC columns and other consumables and represents an average value for the consumables per student of the research group in the past years.

Substrates and model substrates	EUR	5.000
GPC columns for MW determination	EUR	2.000
AFM supplies (AFM tips of various kinds)	EUR	4.000
Replacement bulbs for UV setups	EUR	3.000
Chemicals (monomers, reagents), solvents, lab supplies, glassware, liquid nitrogen and helium, technology cost in the clean room	EUR	6.000
Total costs per year	**EUR**	**20.000**

Total costs for consumables for the entire project duration: 60.000 €

4.1.2.2   Travel Expenses

We request travel expenses of € 1.500 per year. These costs may be used by the student, the applicant and Dr. Oswald Prucker as senior research fellow. The funds will be used for participation at international conference and visits at the lab of the cooperation partners within the priority program.

Total travel costs for the entire project duration: 4.500 €

4.1.2.3   Visiting Researchers (excluding Mercator Fellows)

None.

4.1.2.4   Expenses for Laboratory Animals

None.

4.1.2.5   Other Costs

None.

4.1.2.6   Project-related publication expenses

We apply for funds for project-related publication expenses of **2.250 Euro (750 Euro per year)**. These funds will be used for color figures and open access costs.

4.1.3   Instrumentation

4.1.3.1   Equipment exceeding Euro 10,000

None.

4.1.3.2   Major Instrumentation exceeding Euro 50,000

None.

4.2   Module Temporary Position for Principle Investigator

None.

4.3   Module Replacement Funding

None.

4.4   Module Temporary Clinician Substitute

Not applicable.

4.5   Module Mercator Fellows

None.

4.6   Module Workshop Funding

None.

4.7   Module Public Relations Funding

None.

5   Project requirements

5.1   Employment status information

Prof. Dr. Jürgen Rühe, Chair – permanent position.

5.2   First-time proposal data

Not applicable.

5.3   Composition of the project group

Our group at the IMTEK currently employs about 40 people plus an independent subgroup (Karen Lienkamp). In the following, only those members of staff are listed who have direct ties to the proposed project.

Permanent staff:
- Dr. Oswald Prucker, Senior Scientist (Akademischer Oberrat)
- Natalia Schatz, Technical Assistant
- Daniela Mössner, Technical Assistant

Staff employed from third party funding:
- Dr. Thomas Brandstetter, Project leader for Biointerfaces
- Stefan Müllers, PhD student, Functional surfaces
- Jonas Kost, PhD student, CHic chemistries

5.4   Cooperation with other researchers

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

Collaborations within the SPP 2171 are planned with the groups of

- **Hans Jürgen Butt / Doris Vollmer** (Max-Planck-Institute for Polymer Research, Mainz) – in situ characterization of droplets by in-situ fluorescence imaging,
- **Christian Holm** (Universiry of Stuttgart) – theoretical description of the dynamical wetting properties of droplets on complex nanostructured surfaces

- **Thomas Pfohl / Günter Reiter** (University of Freiburg, German) – physical description of fluidics on nanostructured surfaces
- **Egbert Oesterschulze** (TU Kaiserslautern) – we will provide micro- and nanostructured surfaces decorated with surface-attached networks with tailormade surface chemistries

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

Within the DFG project "Molecular Analysis of Mechanobiological Reactions of Human Mesenchymal Stem Cells to Biomechanical Environmental Stimulation induced by Magnetically Actuatable Microstructures - µMSC", the Rühe group cooperates with Prof. Pascal Tomakidi (Dentistry Department, University of Freiburg). Further collaborations with Prof. Tom Seery (University of Connecticut, Storrs, USA), Prof. William Brittain (Texas State University, San Marco, USA), Prof. Christopher K. Ober (Cornell Univ., Ithaca, USA) Prof. Dr. Kwan-Sup Lee, Hannamm University, Daejeon, Korea during their sabbatical stays in the Rühe group in Freiburg have been established. Other partners, with whom a direct project cooperation has been established are:

- Prof. Dr. Markus Biesalski, Darmstadt
- Prof. Dr. Kripa Varanasi, MIT, Boston, USA
- Dr. Jörg Hohe, Fraunhofer Institute for Mechanics of Materials
- Dr. Tobias Amann, Fraunhofer Institute for Mechanics of Materials
- Prof. Karine Anselme, CNRS, Mulhouse, France
- Prof. Joan-Francois Lutz, Institute Charles Sadron, CNRS, Strasbourg, France
- Prof. Vincent de Houerou, Universite de Strasbourg, France

Rühe also collaborates with professors inside and outside the University of Freiburg within the framework of the International Research Training Group (IRTG) Soft Matter of the Universities of Freiburg, Basel, Mulhouse and Strasbourg as well as the EU-funded research association PlaMatSu of the Universities of Freiburg, Fribourg (CH) and Cambridge.

5.5 Scientific equipment

All equipment necessary for the experimental implementation of the project is available:

- Laboratories for the synthesis of polymers and low molecular weight compounds like monomers, initiators, photoreactive substances and molecules for self-assembled monolayers; Hoods, inert gas lines
- Access to the IMTEK Clean Room Facilities (600 m2, Class 100) providing general microstructuring technologies and nanoimprint facilities
- X-Ray Photoelectron Spectrometer (XPS, Physical Electronics 5600 ci)
- Fourier transform infrared spectrometer (FTIR, Bio-rad Exalibur)
- NMR Spectroscopy (Bruker Avance, 250MHz)
- UV Spectroscopy (Cary50 Bio, Varian)
- Gel permeation chromatography (GPC, Fa. PSS and Agilent)
- Light scattering equipment (static & dynamic; ALV Laservertriebs GmbH)
- Atomic Force Microscope (AFM, Two setups from Digital Instruments & JPK)
- Imaging Ellipsometry (EP3 SE, Nanofilm Technology)
- Laser Ellipsometer (SenTech)

- FTIR microscope (Varian UMA600)
- Surface plasmon and optical waveguide spectroscopy (Res-Tec GmbH, two instruments)
- X-ray reflectometer (Siemens/Bruker D5000)
- Video-based instrument for measuring contact angles (Dataphysics OCA20)
- Mechanical Testing (Z2.5, Fa. Zwick GmbH & Co)

Also see www.imtek.de/cpi.

5.6   Project-relevant cooperation with commercial enterprises

None.

5.7   Project-relevant participation in commercial enterprises

None.

6   Additional information

None.